

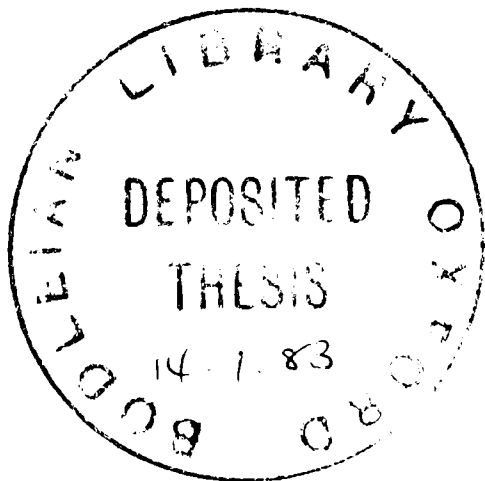
ORGANOMETALLIC CHEMISTRY
Structural, Synthetic, and Theoretical Studies

by

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Abstract

Organometallic Chemistry

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Transition metal organometallic chemistry is a rapidly expanding field, which has an important relationship to industrial problems of petrochemical catalysis. This thesis describes studies of fundamental organometallic reaction processes, such as C-H and C-C bond formation and cleavage, and investigations of the structure and bonding of organometallic compounds. A number of techniques were used to pursue these studies, including synthesis, X-ray crystallography, and semi-empirical molecular orbital calculations.

Chapter 2 reports synthetic and structural studies of a number of new molybdenocene dimers. The crystal structures of seven dimers are described, including that of 'black molybdenocene', the fourth isomer of $\text{Mo}_2\text{C}_{20}\text{H}_{20}$ to be isolated. The interrelationships linking molybdenocene dimers are discussed from structural, thermodynamic, and kinetic points of view, and a critical comparison is made with the related chemistry of other transition metals. A classification scheme for metallocene dimers is introduced to aid the discussion.

Chapter 3 describes structural studies of the half-sandwich compounds $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{O})\text{dmpe}]\text{PF}_6$ and $\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{dppe})\text{Br}_3$. Isomerism and bonding of CpML_5 derivatives is discussed. Reductive elimination of methane from the sandwich compounds $(\eta\text{-C}_5\text{H}_5)_2\text{WRR}'$ is also investigated, and the synthesis of

$(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{Me})\text{D}$ is described.

Chapter 4 reports theoretical and structural studies of low-valent transition metal compounds with arene and phosphine ligands. Extended Huckel theory is used to explore the bonding and conformational preferences of the new class of molecule, bent bis(arene) MX_n , and the crystal structure of the first $\text{M}(\text{arene})_2\text{X}_2$ derivative, $\text{Hf}(\eta\text{-MePh})_2(\text{SnMe}_3)_2$, is described. The crystal structure of $\text{Mo}(\text{PMe}_3)_6$ is reported, and the structure and bonding of related low-valent species are discussed; some interesting points of metal-butadiene bonding are noted.

Chapter 5 contains the experimental details of the work described in this thesis.

The work described in this thesis was carried out in the Inorganic Chemistry and Chemical Crystallography Laboratories, Oxford, from October 1977 to September 1982, under the supervision of Dr. M.L.H. Green. All work is my own, unless stated to the contrary, and it has not been previously submitted for a degree in this or any other University.

James K. Bashkin

For my parents

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Abbreviations

nmr	nuclear magnetic resonance
ir	infra-red
uv	ultra-violet
PES	photoelectron spectroscopy
EHT	extended Hückel theory
MVS	metal vapour synthesis
Ph	phenyl
Me	methyl
Et	ethyl
Bu ⁿ	n-butyl
Cp	η -cyclopentadienyl
dppe	bis(diphenylphosphino)ethane
dmpe	bis(dimethylphosphino)ethane

Chapter 1 Introduction

Chapter 1. Introduction.

Organometallic chemistry is one of the fastest growing areas of chemical research, and is intimately linked with problems of major social and industrial importance, such as petrochemical and energy conservation. This thesis describes studies in the area of transition-metal organometallic chemistry, and the main interest has been in certain fundamental principles governing the reactivity, structure, and bonding of organometallic molecules. In the course of these studies, a number of different techniques have been employed, including synthesis, X-ray crystallography, and semi-empirical molecular orbital calculations. Chapters 2, 3, and 4 contain the results and discussion, as well as detailed accounts of the relevant chemical literature. Because of the diversity of subjects investigated, this approach was thought to be more appropriate than the traditional practice of including a single introductory chapter; a brief introduction to the results is given below. The experimental details are reported in Chapter 5.

Chapter 2. Molybdenocene Dimer Chemistry.

Molybdenocene, which has been isolated only in low-temperature matrices¹, has the formula $(\eta\text{-C}_5\text{H}_5)_2\text{Mo}$; when generated in solution as a reaction intermediate, it can dimerize in a number of different ways². These dimerizations,

and various subsequent reactions of their binuclear products, have provided examples of metal-assisted C-H and C-C bond cleavage and formation. Such reactions are currently of great interest, because of their occurrence in many industrially important, metal-catalyzed processes³. Chapter 2 reports synthetic and structural studies of the molybdenocene dimer system, including the crystal structure of the fourth isomer of $\text{Mo}_2\text{C}_{10}\text{H}_{10}$ to be isolated (the 'black dimer'). This compound, $\text{Mo}(\eta\text{-C}_5\text{H}_5)(\sigma\text{:}\eta\text{-C}_5\text{H}_4)\text{Mo}(\text{H})(\text{C}_5\text{H}_5)_2$, provides convenient routes to $(\text{C}_5\text{H}_5)_2\text{MoCl}_2$ and to a number of new and known dimeric species. The crystal structures of six related compounds are reported, and the structural, thermodynamic, and kinetic properties of these compounds are compared with the those of other metallocene dimers. A scheme for the classification of metallocene dimers is introduced in order to aid the discussion.

Chapter 3. Structure and Bonding of Half-Sandwich Compounds.

In Chapter 3, the crystal structures of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{dmpe})\text{O}]\text{PF}_6$ and $\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{dppe})\text{Br}_3$ are reported; they are discussed in relation to the current theories of bonding in CpML_n derivatives, with particular attention being given to isomerism in CpML_5 species, and to an unusual property of the 'Cp-capped square pyramidal' geometry. This property is that the axial M-L bond, which is trans to the $\eta\text{-C}_5\text{H}_5$ ring, is much longer than might be expected.

Chapter 3. Reductive Elimination from the $W(\eta-C_5H_5)_2RR'$ System.

The synthesis of $W(\eta-C_5H_5)_2(CD_3)_2$ and $W(\eta-C_5H_5)_2(Me)D$ are reported; these compounds and their protio analogues decompose thermally to give methane (CH_nD_{4-n}). The possible mechanisms of such reductive eliminations are discussed, and the results of some labelling studies are presented in relation to matrix-isolation experiments, and to alkyl titanocene chemistry. The attempted vacuum uv photolysis of $W(\eta-C_5H_5)Me_2$, under matrix isolation conditions, is also reported.

Chapter 4. Structure and Bonding of Bent Bis(arene) Derivatives of the Transition Metals.

The first examples of bent bis(arene) compounds, analogous to the well-known bent bis(cyclopentadienyl)M series⁴, were prepared in Oxford⁵. With the help of the extended Hückel method, some principles of bonding in bent bis(arene) derivatives are introduced, and these principles are then applied to a study of the conformational preferences of $W(\eta-C_6H_5Me)_2H^+$ and $W(\eta-C_6H_5F)_2H^+$. In addition, the crystal structure of $Hf(\eta-C_6H_5Me)_2(SnMe_3)_2$, the first $M(\eta\text{-arene})_2X_2$ derivative, is reported, and its structural properties are discussed. Some attention is given to the reasons why complexed arene rings may be nonplanar.

Chapter 4. Low-valent Molybdenum Derivatives.

The crystal structure of a new, homoleptic Mo(0) compound, $\text{Mo}(\text{PMe}_3)_6$, is reported, and its high lability is interpreted in terms of the steric crowding that the structure exhibits. Metal-phosphorus bond lengths are compared for several group VI derivatives, and the structure of $\text{Mo}(\text{PMe}_3)(\text{C}_4\text{H}_6)$ is described briefly, with reference to some intriguing questions about metal-butadiene bonding.

General.

In order to aid comparison of the present work with published crystal structures, extensive use has been made of the Cambridge Crystallographic Data Centre data bank⁶, and of the Crystal Structure Search and Retrieval (CSSR) program⁷. The ready availability of atomic coordinates was particularly powerful when combined with the CHEMGRAF suite of molecular modelling and display programs⁸, written by E.K. Davies of the Chemical Crystallography Laboratory, Oxford. In the following discussion, $(\eta\text{-C}_5\text{H}_5)$ is referred to as Cp for brevity.

Chapter 1. References.

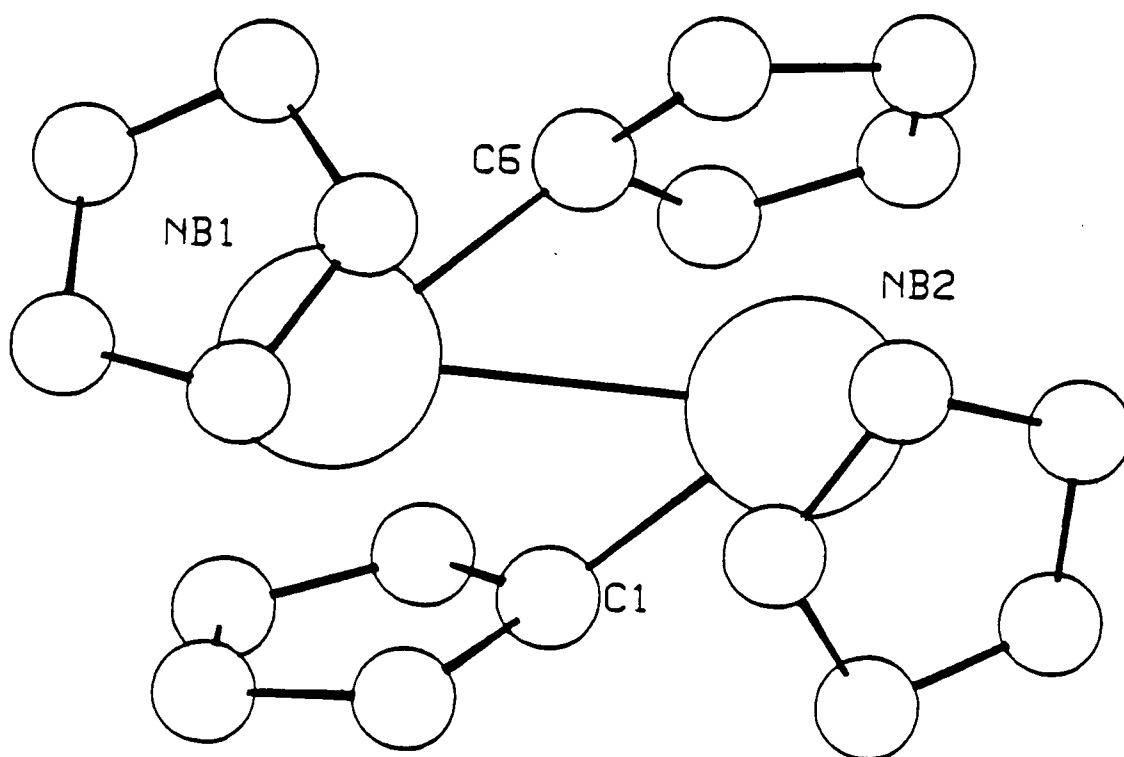
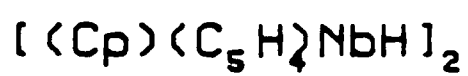
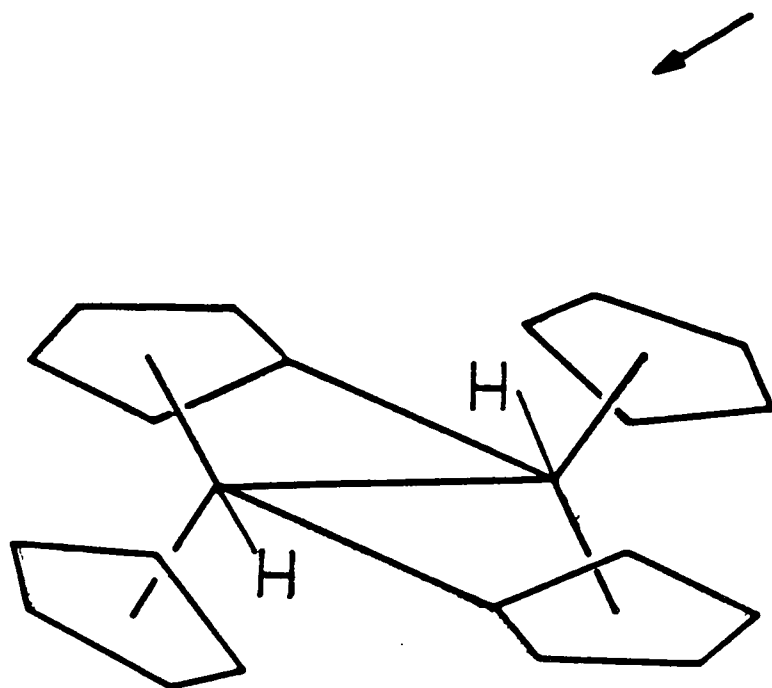
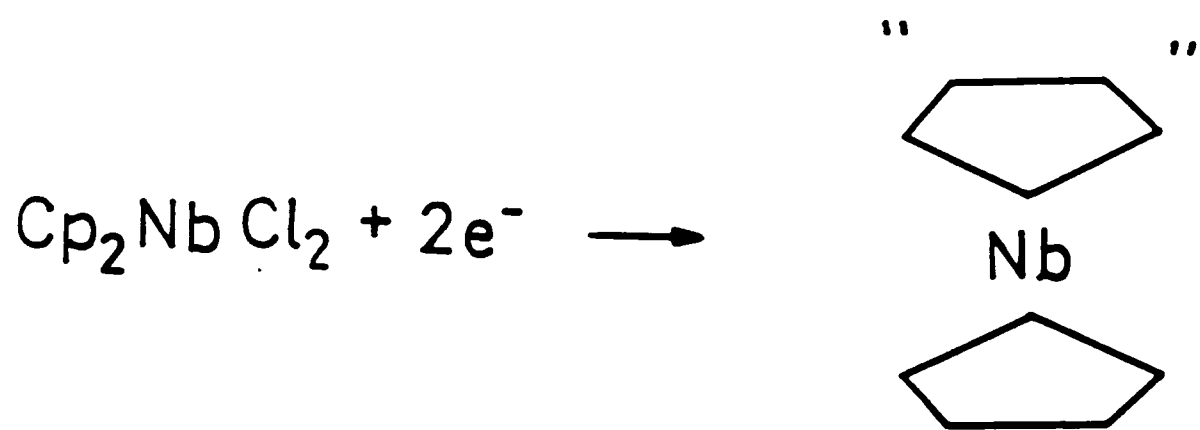
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Chapter 2 Molybdenocene Dimers

In this chapter I present a systematic study of molybdenocene dimers. Before describing my own research, I propose a scheme for the classification of metallocene dimers according to structural type, and then use the scheme to introduce relevant chemical properties of the dimers.

2.0 METALLOCENE DIMERS

As is common practice¹, a metallocene is defined here to be an organometallic sandwich compound with molecular formula $C_{10}H_{10}M$, that contains two $\eta-C_5H_5$ rings. The archetypal metallocene is ferrocene. A metallocene dimer may then be defined to have the molecular formula $C_{20}H_{20}M_2$, with five-membered carbocyclic rings arranged in a sandwich fashion about the two metals. These dimers are found with metals early in the transition series, whose metallocene monomers are too electronically unsaturated to be isolated. For example, the niobocene^{2,3,4,81} monomer Cp_2Nb is a 15-electron, Nb(II) species, which needs three electrons to reach a stable, 18-electron configuration. This requirement is satisfied by dimerization, which involves the formation of Nb-H, Nb-C, and Nb-Nb bonds, as shown in Fig. 2-1 (see also Fig. 2-6). It will be seen that the majority of characterised metallocene dimers do attain 16- or 18-electron environments, and that the need for a metal to utilize fully its valence orbitals and electrons often appears to be the driving force for dimerization. The most obvious exceptions to this generalization are the antiferromagnetic, 17-electron, Ti(III)



Synthesis and structure of the niobocene dimer.

Fig. 2-1

dimers^{5,6}, such as those which are shown in Fig. 2-2. Furthermore, a number of organometallic compounds with low electron-counts, usually containing phosphine, halide, and perhaps carbene ligands, are now appearing in the literature⁷, and such species may become more important in metallocene dimer chemistry.

In addition to the compounds which may be regarded as 'parent' metallocene dimers, I consider derivatives which are formed by chemical processes such as protonation, halogenation, alkylation, and oxidation, in which the metallocene framework is left largely intact, together with bimetallic compounds, including heterobimetallic species, in which perhaps only a few Cp-rings are present, but whose properties are relevant to the discussion.

Before presenting a critical analysis of molybdenocene chemistry, the following classification scheme for metallocene dimers is proposed. There are six major structural isomers of the metallocenes and their derivatives that have been reported to date. They are labelled I to VI in Fig 2-3, where their metal-carbon skeletons are sketched. The disposition of hydrido ligands and the M-M bond-order depend on the particular transition-metal involved. The isomers can also accomodate a number of bridging or terminal ligands of various types. Each class of the scheme is subdivided depending on the presence or absence of a direct M-M bond. Thus, molecules classified as Ia to VIa lack metal-metal bonds; those classified as Ib to VIb are proposed to contain M-M bonds; and those molecules for which there is some ambiguity in the

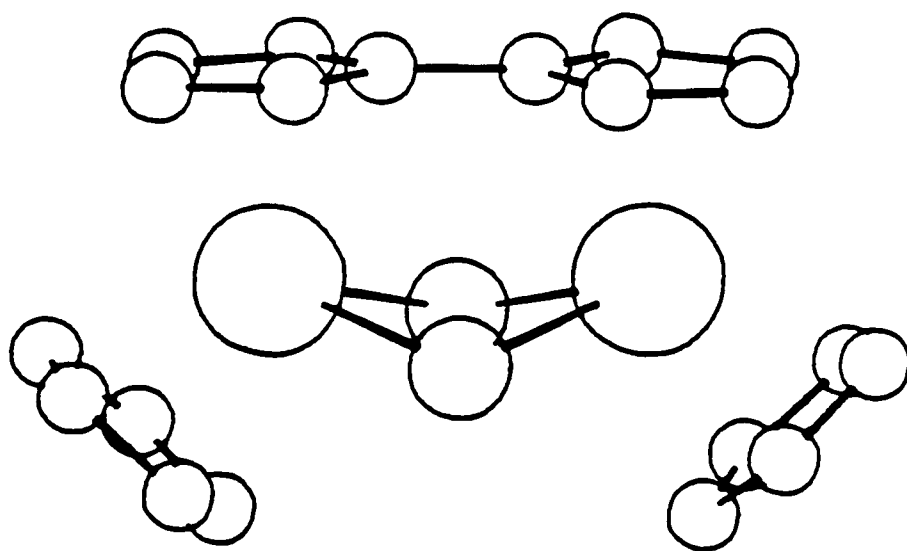
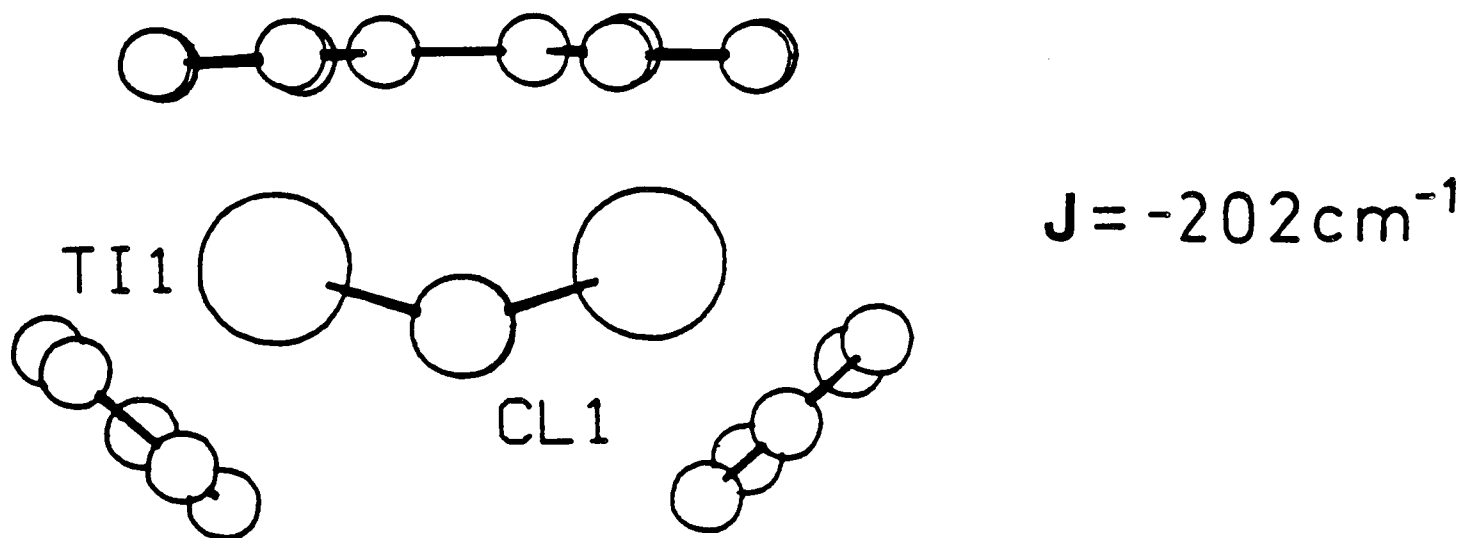
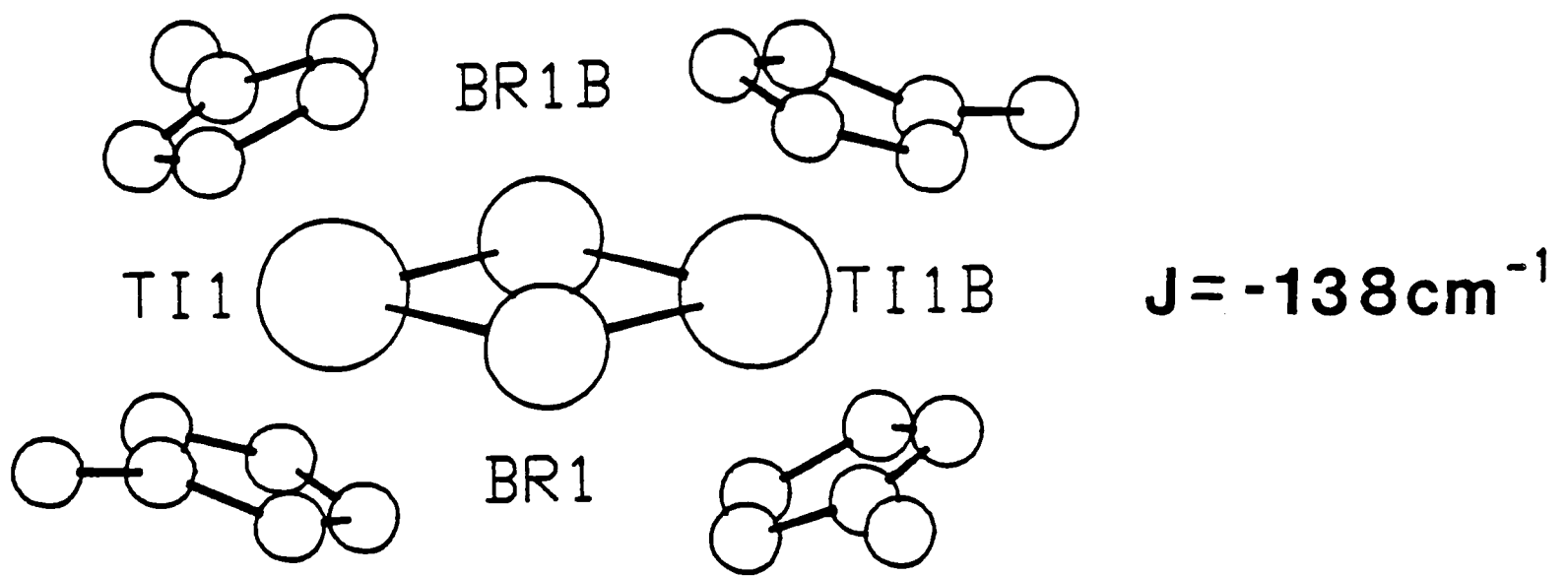
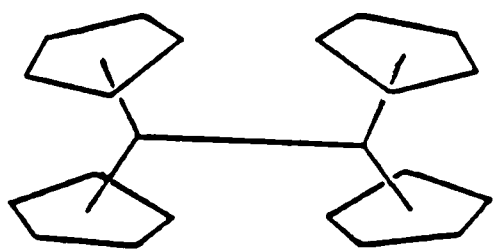
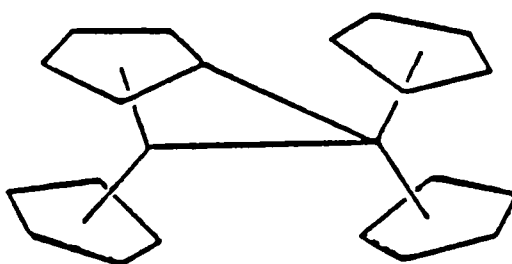


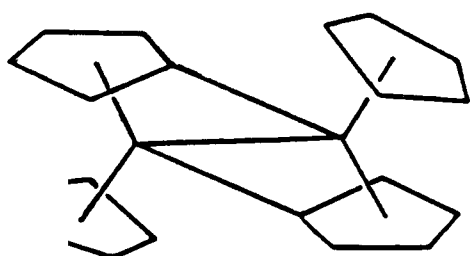
Fig. 2-2. The antiferromagnetic dimers $[\text{Cp}_2\text{TiBr}]_2$ and $(\text{CpTiCl})_2(\text{C}_{10}\text{H}_8)$.



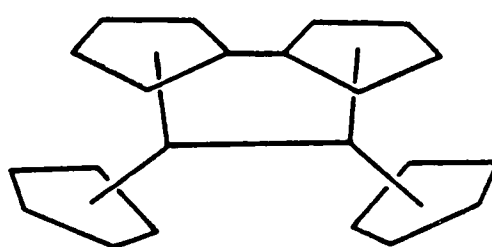
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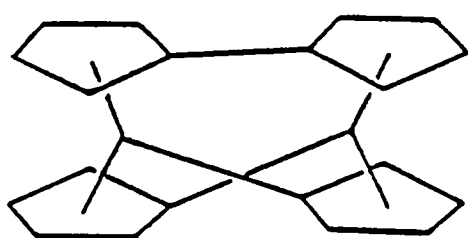
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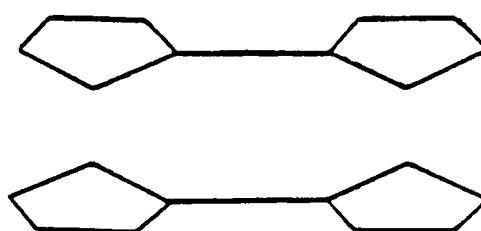
III



IV



V



VI

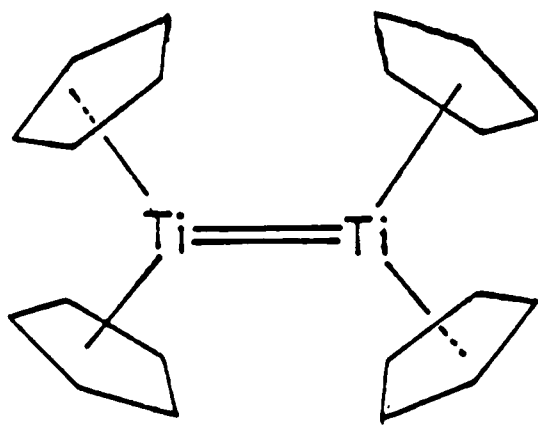
Classes I–VI

Fig. 2-3

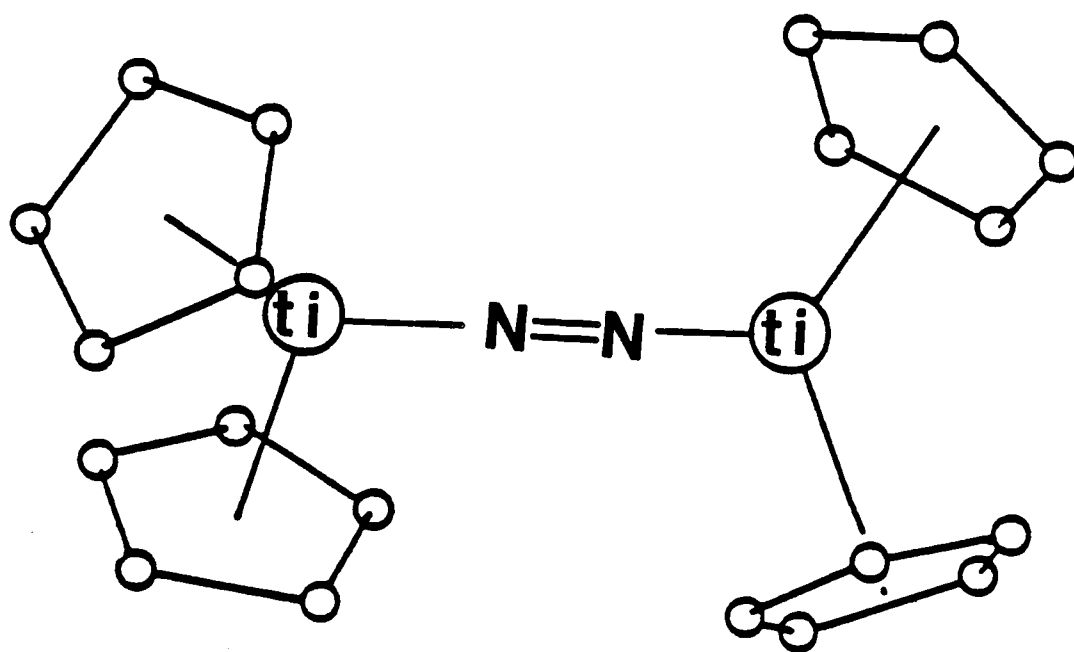
assignment of M-M bonding are not given a division.

Class I. Although a Class Ib structure has been proposed⁸ for 'metastable titanocene', there appears to be no example in the literature of a fully characterised Class I dimer whose metal centres are linked only by a direct metal-metal bond. However, some of the most important metallocenes fall into the category of bridged-Class I compounds (Fig. 2-4). Many different atomic and molecular species can bridge the metal centres of a Class I dimer, but there are only two common modes of bridging: the single bridge and the bent, double bridge. A linear, single bridge is found in the dinitrogen derivatives of titanocene⁹ and zirconocene¹⁰, which also illustrate the preference of Ti for a 16-electron environment when the analogous Zr centre attains an 18-electron count. A linear oxygen bridge is found¹¹ in $(\text{Cp}_2\text{HfMe})_2\text{O}$, which is formed by oxidation of Cp_2HfMe_2 . This rare example of a hafnocene dimer has a Hf-O-Hf angle of 173.5° ; the oxygen may donate a lone pair of electrons to each hafnium centre in order to satisfy their electron counting requirements.

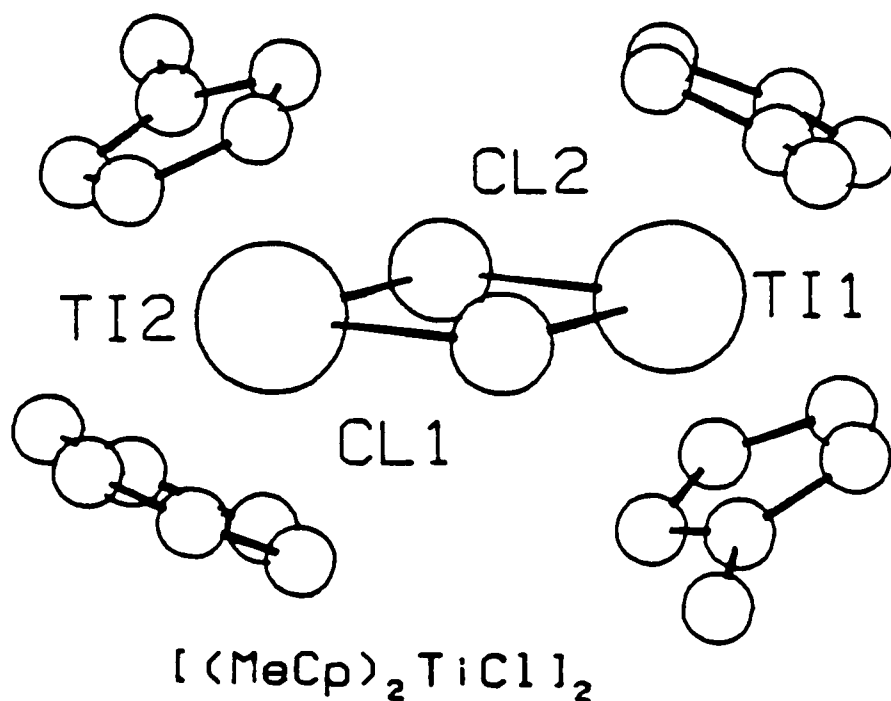
A combination of non-bonded contacts between Cp-rings and the symmetry requirements of the bridging ligand usually results in a perpendicular disposition of the two Cp_2M units of a singly-bridged, Class I dimer. However, as the crystal structure⁵ of $(\text{Cp}_2\text{TiCl})_2$ demonstrates (Fig. 2-4), the presence of two bridging ligands in a Class I dimer forces the Cp_2M units to face each other. This geometry is adopted¹² by $[(\text{MeCp})_2\text{ZrH}_2]_2$, and presumably by the purple form of



'metastable titanocene'



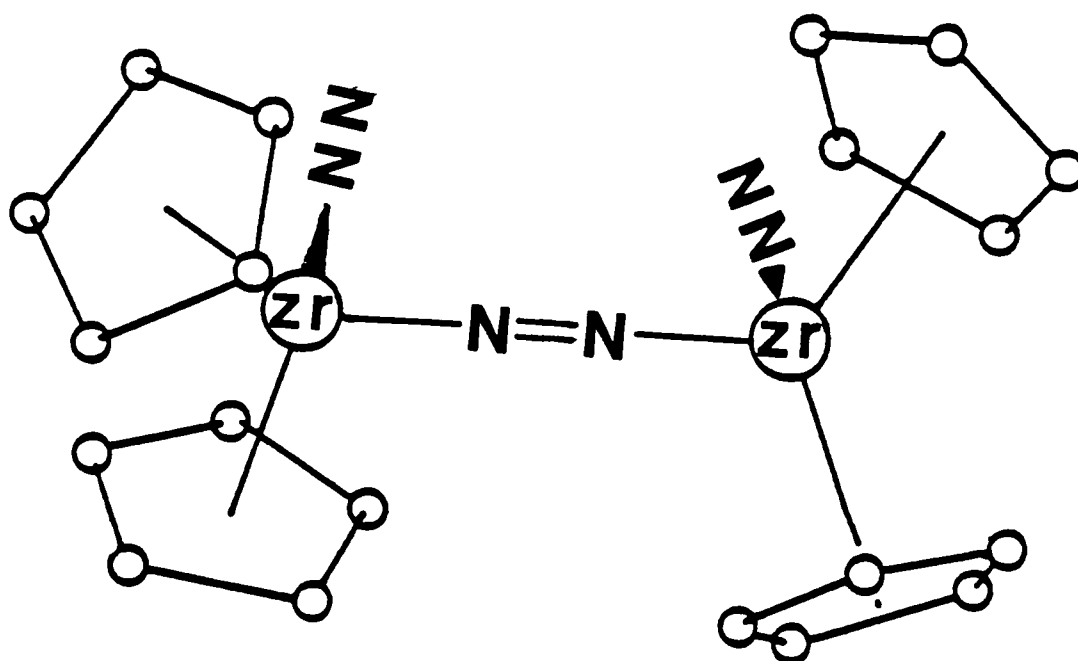
$[(\text{Me}_5\text{Cp})_2\text{Ti}_2]_2\text{N}_2$ with methyls excluded for clarity



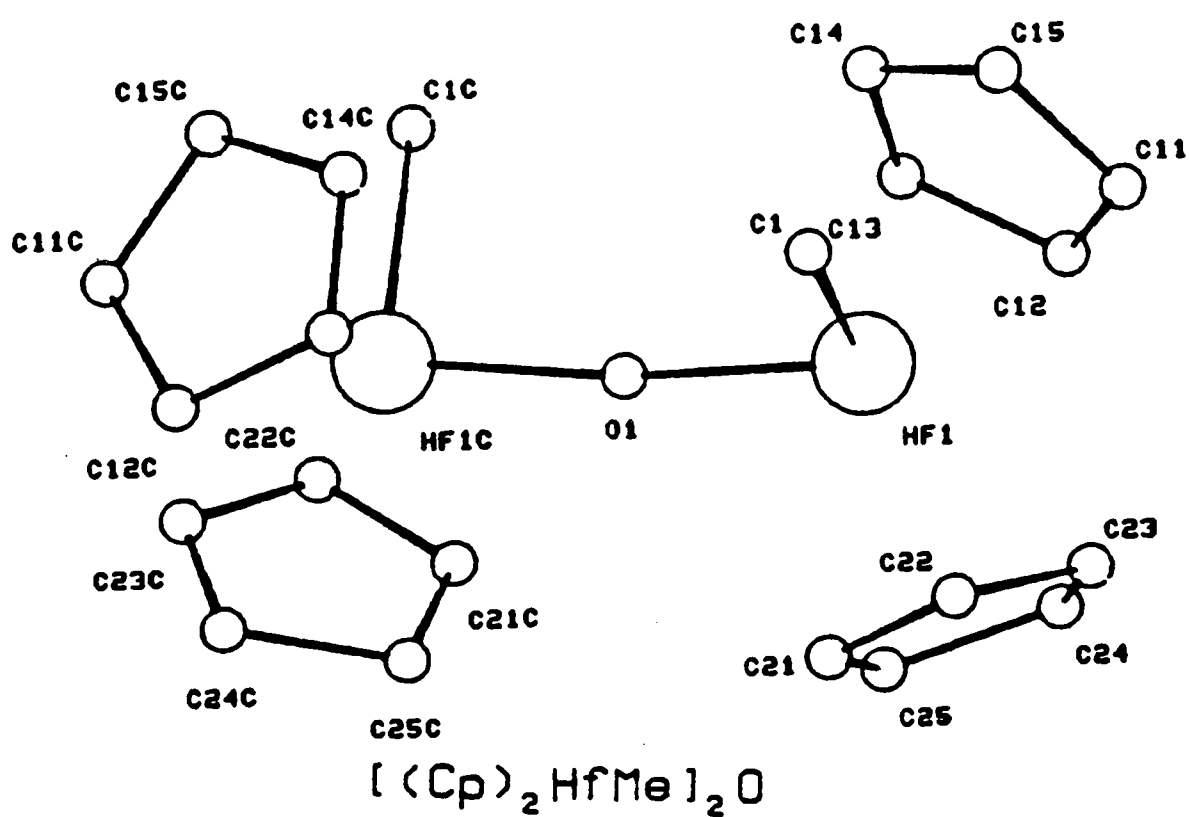
$[(\text{MeCp})_2\text{TiCl}]_2$

Class I dimers.

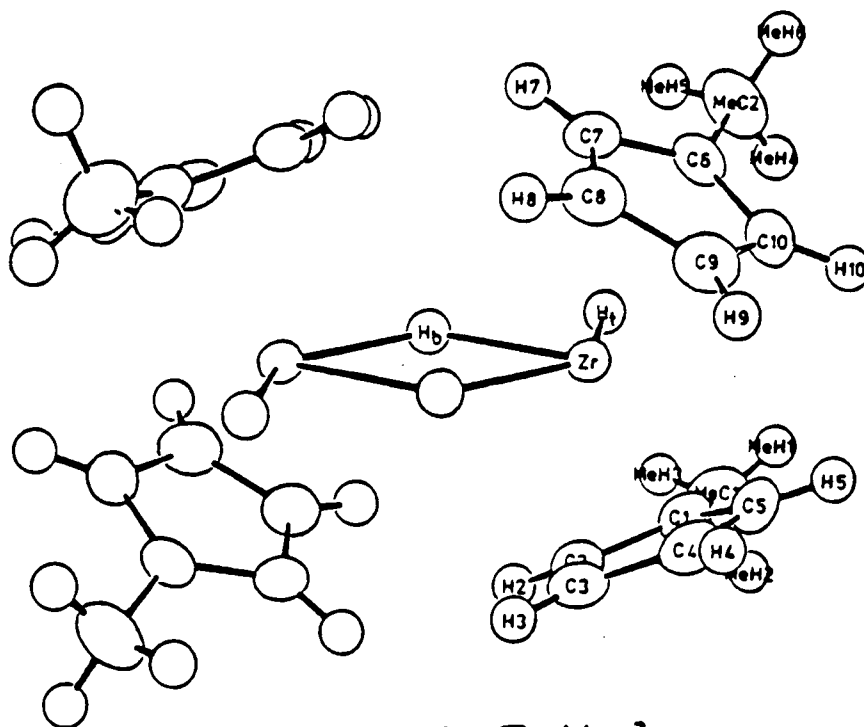
Fig. 2-4



$[(\text{Me}_5\text{Cp})_2\text{ZrN}_2]_2\text{N}_2$ with methyls excluded for clarity



$[(\text{Cp})_2\text{HfMe}]_2\text{O}$

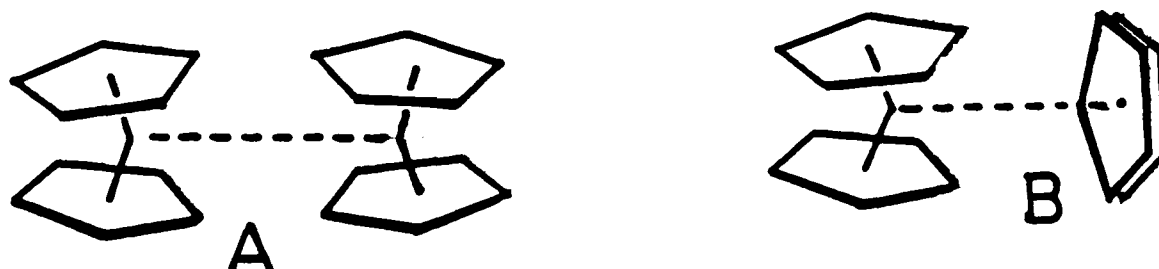


$[(\text{MeCp})_2\text{ZrH}_2]_2$

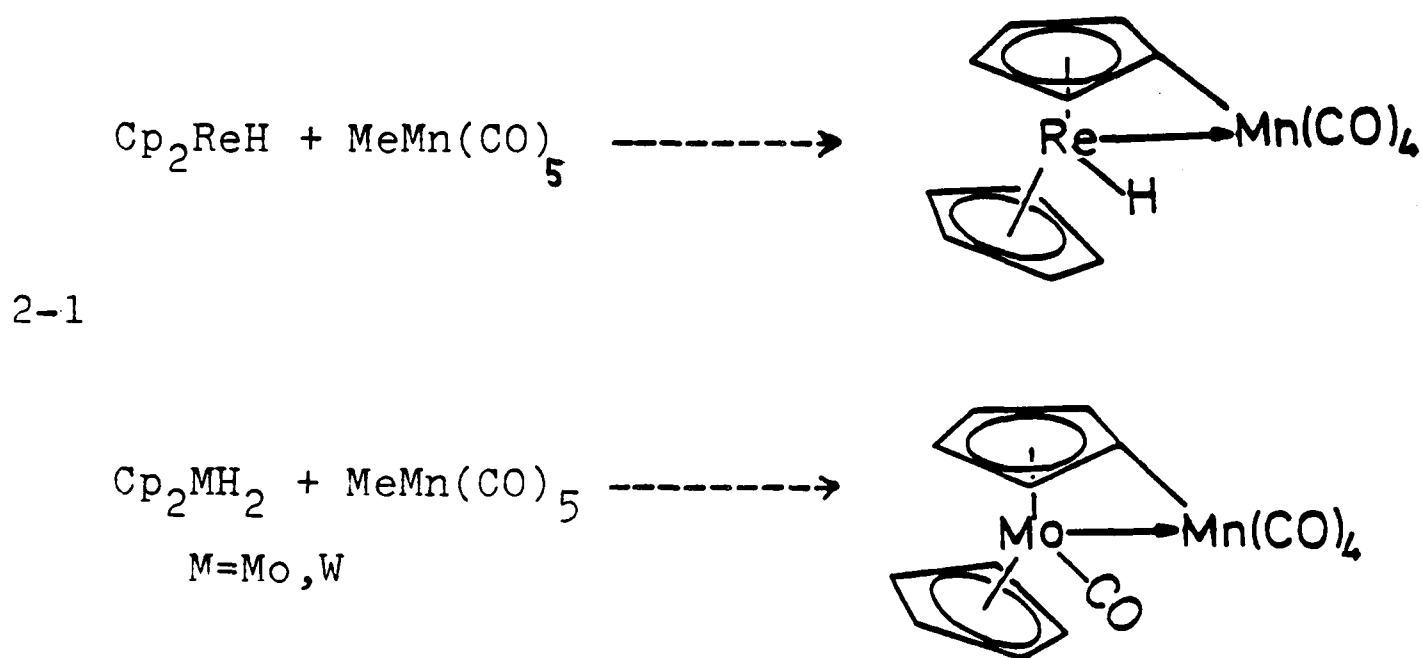
Class I dimers (cont.)

Fig. 2-4 (cont.)

titanocene, $[\text{Cp}_2\text{TiH}]_2$, which is synthesized¹³ by the solid-state reaction of Cp_2TiMe_2 with H_2 . Schematic representations of the parallel (A) and perpendicular (B) conformations are given here:



Class II. The ability of reactive transition-metal centres to insert into C-H bonds via oxidative addition is well known¹⁴. This process leads to the functionalized C_5H_n -rings found in Classes II to VI. The prototype Class II dimers were synthesized¹⁵ by Kaesz, as shown in Eq. 2-1.

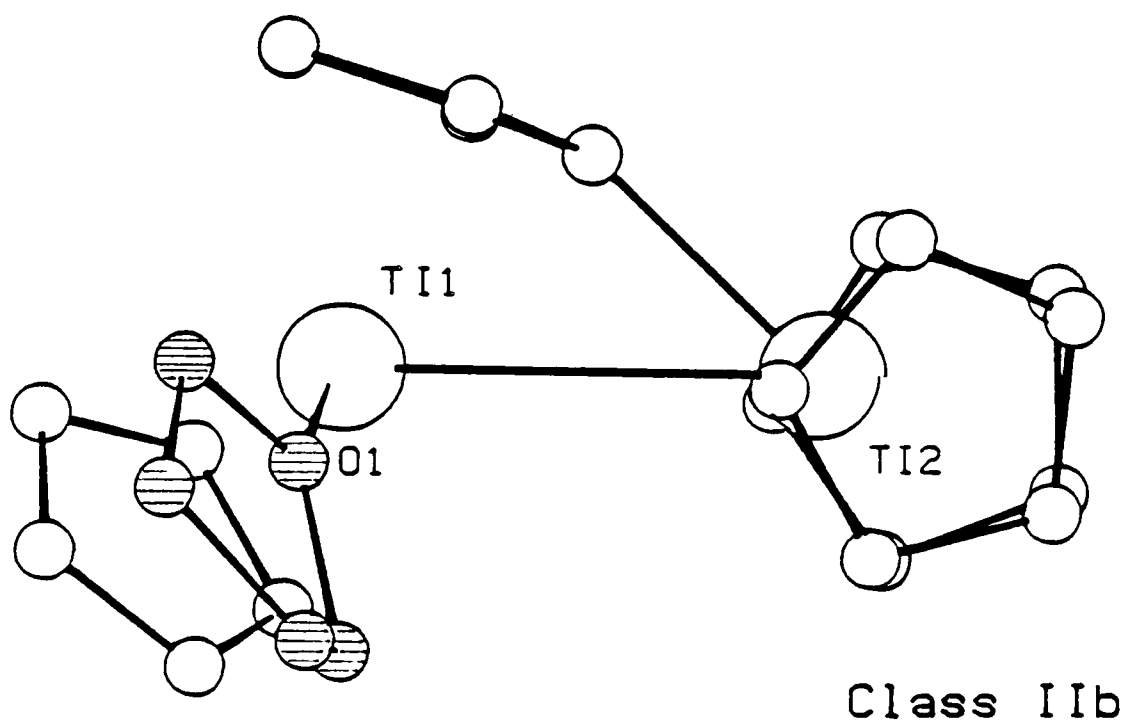
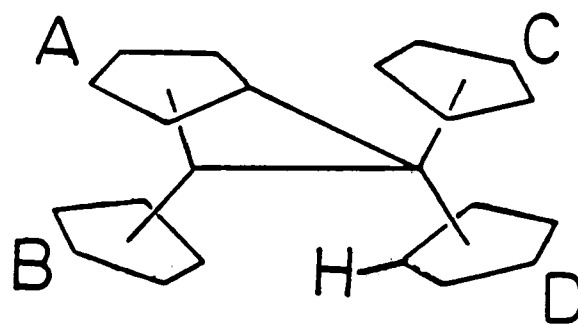
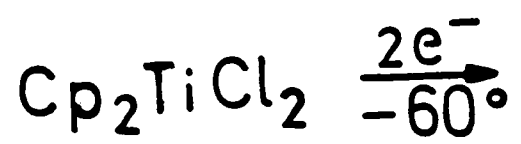


The metal-metal linkages in these heterobimetallic derivatives possessed two novel features which have since become building blocks of metallocene chemistry: the $\eta^1:\eta^5\text{-C}_5\text{H}_4$ bridging ligand and the donor-acceptor metal-metal bond.

Kaesz reported the synthesis of his dimers (and the crystal structure of the Mo/Mn compound) in 1971, but it was

not until five years later that Pez reported¹⁶ the synthesis of the next Class II dimers, his titanocene and its THF adduct. The two Cp_2M units of these molecules are perpendicularly disposed, as was found for singly-bridged Class I dimers (Fig. 2-5). In the mean time, a number of other metallocene dimers had been made, including the (Class III) niobocene dimer mentioned above². The relative scarceness of Class II dimers can be rationalized with reference to the labelling scheme in Fig. 2-5. In the case of Pez's titanocene, Ti1 is highly exposed to attack by any incoming ligand, and does, in fact, coordinate a THF molecule. However, ring D is held in a good position for one of its C-H bonds to attack the sterically unsaturated titanium. Because of this proximity, the second oxidative addition of a C-H bond can take place soon after the first under the normal conditions for metallocene dimer formation (see Fig. 2-6). For Nb, Ta², Mo^{17,18}, and W¹⁸, a Class III dimer is isolated, but, for Ti and also one interesting Mo case²⁰, a Class IV species is the stable product. Only when special experimental measures are taken, such as reaction at low temperature, can the intermediate Class II compound be isolated.

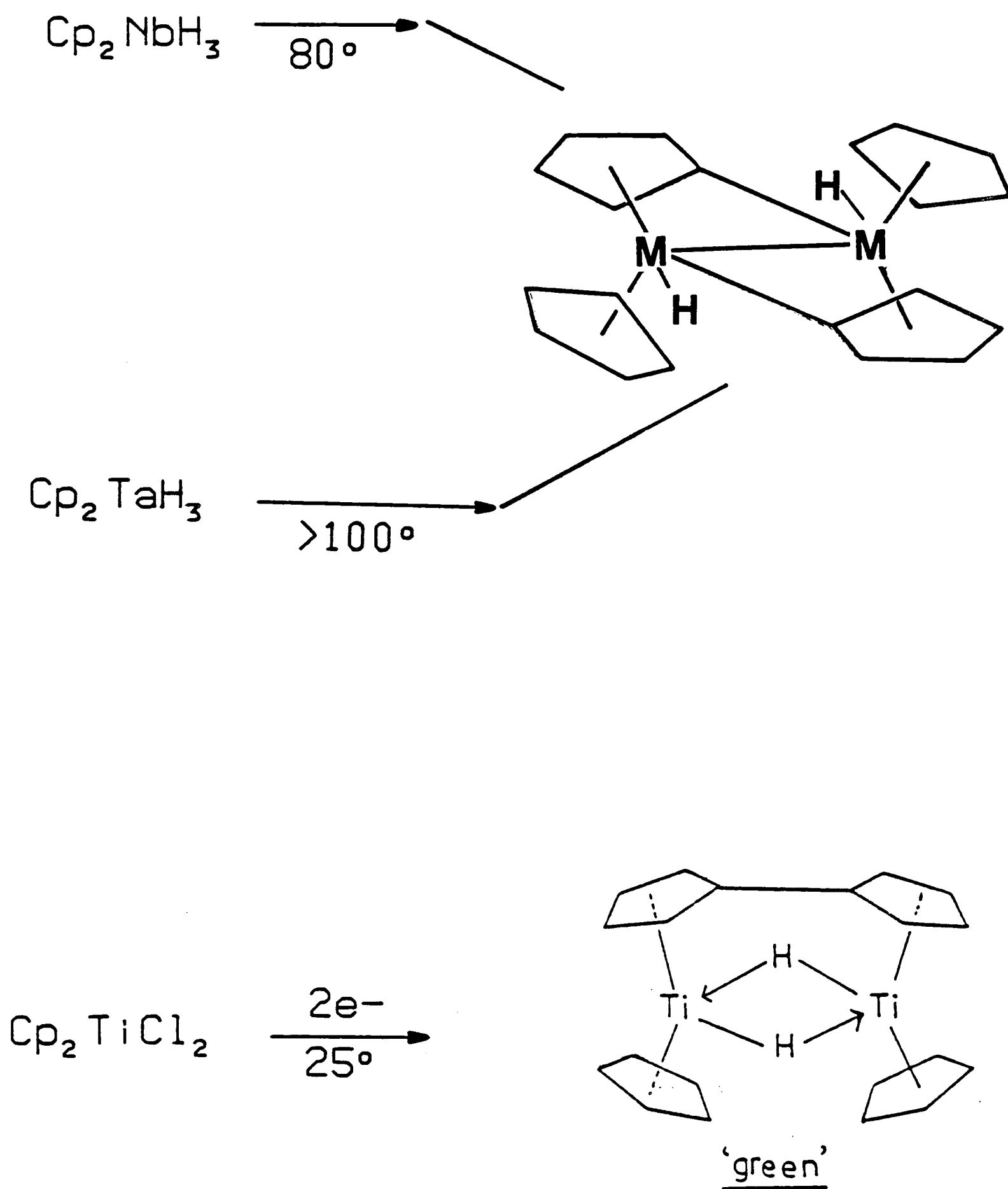
Class III. There are numerous examples of Class III dimers in the literature, more than ten of which have been characterized crystallographically (see section 2-6). It is particularly instructive to look at a group of compounds which illustrates the differences between Class IIIa and Class IIIb (see Fig. 2-7, and also Class IIIb niobocene, in Fig. 2-1). The yellow tungstenocene¹⁷ and molybdenocene¹⁸ dimers fall into Class IIIa: they lack metal-metal bonds, and the valency



Synthesis and structure of $\text{Cp}_3\text{Ti}_2(\text{C}_5\text{H}_4)(\text{THF})$

The THF ligand is shaded.

Fig. 2-5



Typical metallocene dimer syntheses.

Fig. 2-6

requirements of the Group VI metals are met by two $\eta^5\text{-C}_5\text{H}_n$ rings, one M-C σ -bond, and one hydrido ligand. The crystal structure²¹ of the trans-tungsten derivative shows the $(\text{C}_5\text{H}_n)_2\text{M}$ units to be parallel, the W-W distance to be 3.811(1) Å, and the W-C σ -bond to bend only 10° out of the plane of the C_5H_4 ring'. However, on photolysis, yellow molybdenocene evolves H_2 to form 'dehydromolybdenocene', a Class IIIb dimer¹⁷. The crystal structure²² of dehydromolybdenocene shows the Mo-Mo bond length to be 2.886(1) Å, and the angle of bend of the Mo-C σ -bond vector out of the C_5H_4 -ring plane to be 38°. The $(\text{C}_5\text{H}_n)_2\text{M}$ moieties now have a perpendicular disposition. The value 2.886(1) Å is short for Mo-Mo single bonds, which can be as long as 3.235(1) Å (in $[\text{CpMo}(\text{CO})_3]_2$ ²³). Therefore, contrary to an early rationalization for the Nb-Nb bond length in the niobocene dimer⁴, two $\mu\text{-}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4$ rings do not prevent the formation of a strong, short metal-metal bond. Furthermore, the bridges are willing to distort to a considerable degree to accommodate such a bond.

A similar IIIa/IIIb system has recently been developed for niobocene. Lemenovskii et al have reported⁸¹ the synthesis of the IIIa niobocene dianion. Two electrons presumably populate a metal-metal antibonding orbital, and the crystal structure of a derivative of this dianion shows that it closely resembles yellow tungstenocene, as expected.

The labels cis and trans, when applied to compounds such as yellow tungstenocene and the niobocene dimer, refer to the disposition of M-C(σ) and M-H bonds about the metal-metal

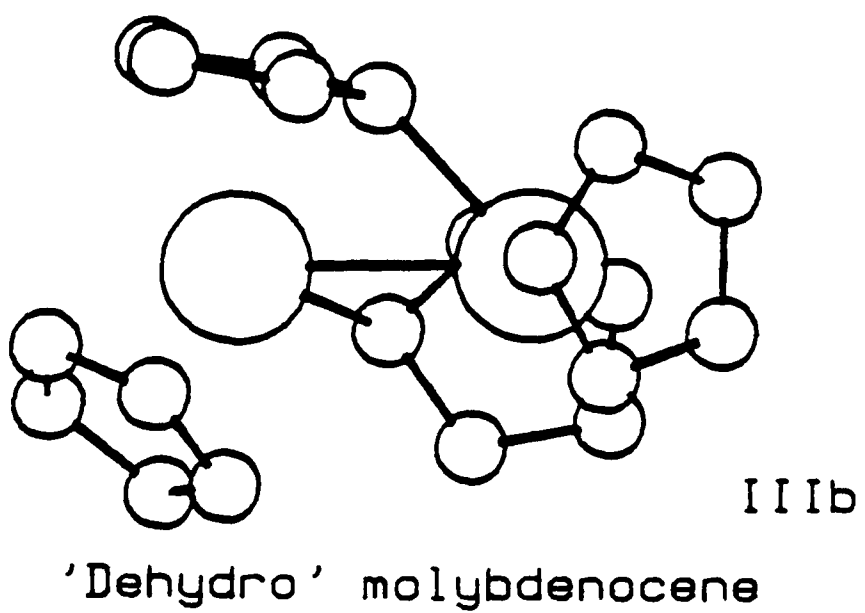
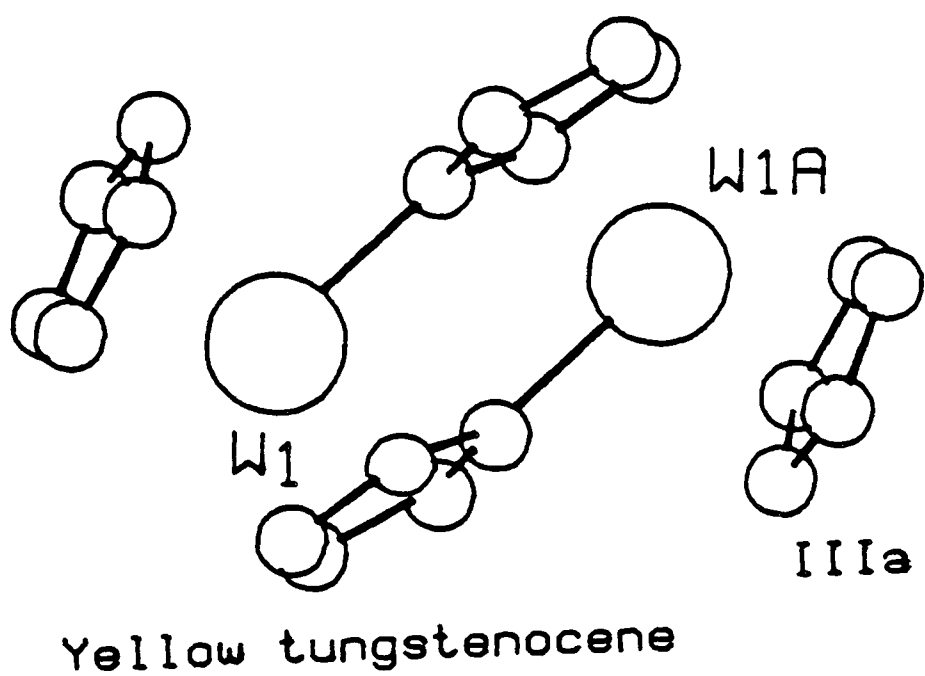
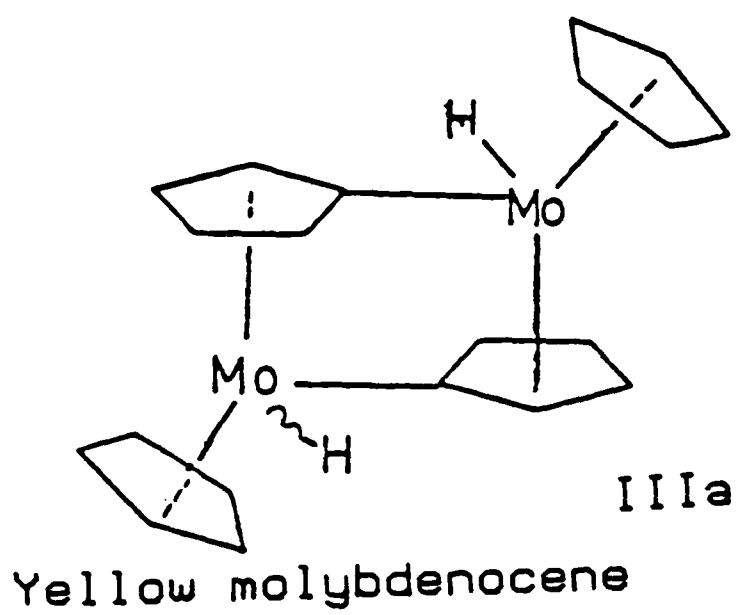


Fig. 2-7 Class III

vector. A schematic representation of the two isomers is given here:



Class IV. For dimeric titanocene and molybdenocene¹⁸, the Class IV structure seems to be the most thermodynamically stable one. Thus, yellow molybdenocene will rearrange at 70° in toluene to green molybdenocene, which has a IVb structure²⁴. It is interesting that this rearrangement does not occur, even at high temperature, for the yellow tungstenocene dimer, and a neutral Class IV tungstenocene has not been prepared²⁵. The thermodynamics of this situation are discussed in section 2.5, after my own results have been presented. The room-temperature preparation of titanocene gives¹⁹ a green, Class IV product (Fig. 2-6); its bridging hydrido ligands were characterised by ir spectroscopy, and the fulvalene ligand was identified²⁶ by careful ¹H and ¹³C nmr studies. Crystals of the green dimers of both molybdenocene²⁷ and titanocene²⁴ are unsuitable for X-ray studies, and it is the hydrolysis products of these dimers that were subjected to single-crystal analysis. The μ -hydroxo- μ -hydrido molybdenocene^{17,28} and di- μ -hydroxo titanocene²⁹ structures are shown in Fig. 2-8; these were reasonably expected to reflect the geometry of their parent metallocenes. However, it has recently been shown that a reaction as simple as protonation can radically alter a dimer framework. Thus, the elusive tungsten Class IV dimer was formed²⁵ under mild

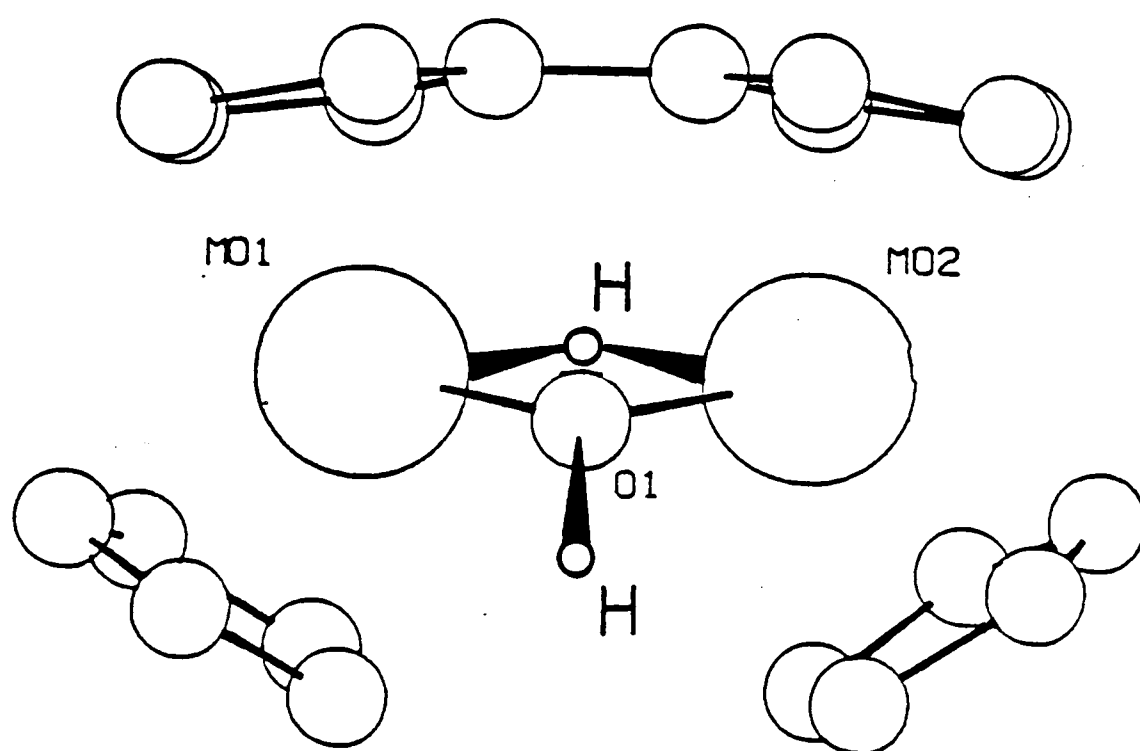
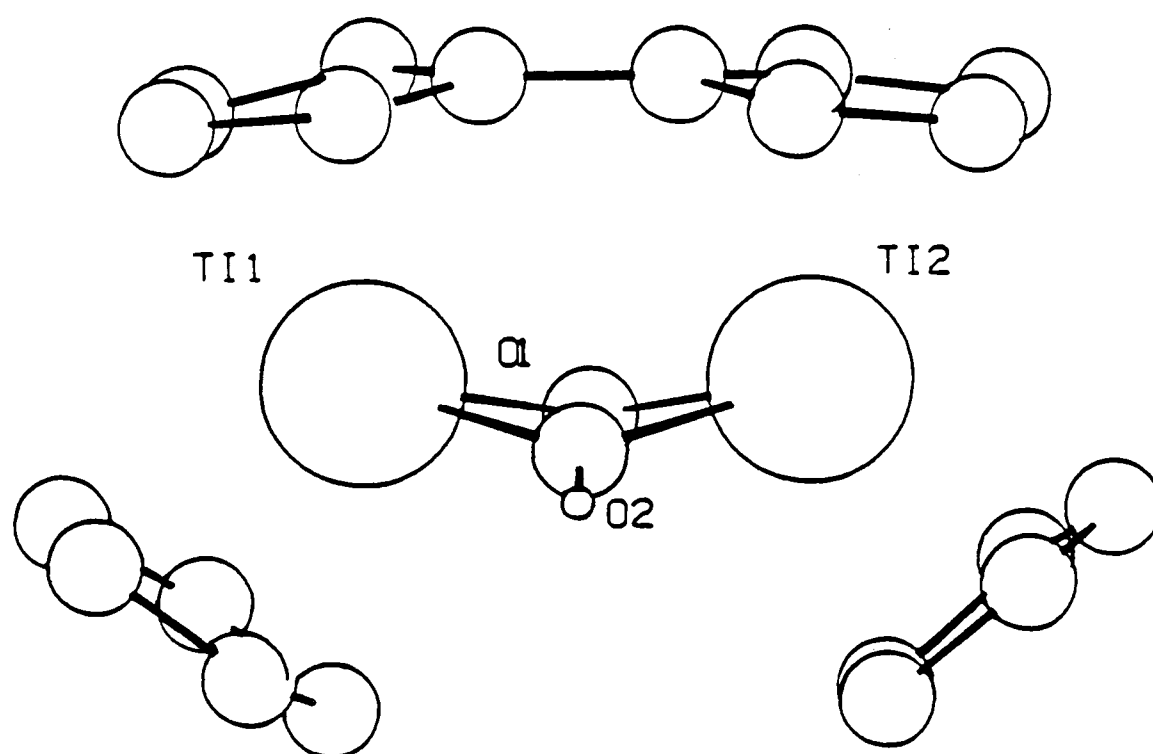


Fig. 2-8. The hydrolysis products of green titanocene and molybdenocene.

conditions on reaction of yellow tungstenocene with HBF_4 , and the product trihydride cation has been investigated by X-ray crystallography³⁰. This result, and some molybdenocene reactions that are discussed below, suggest that it is not always appropriate to assign a metallocene dimer to a particular class on the basis of a structural characterization of its derivatives. An X-ray structure determination is always desirable for unambiguous characterisation, and this is especially the case for the Group VI system, where low solubility hampers nmr studies^{18,31}.

Class V. Among the first derivatives of titanocene to be prepared and characterized was $[(\text{C}_5\text{H}_4)\text{TiH}(\text{AlEt}_2)]_2(\text{C}_{10}\text{H}_8)$, reported by Guggenberger and Tebbe³². This compound, shown in Fig. 2-9, is one of several metallocene dimers which contain alkylaluminium moieties, but it is distinguished by being the only known member of Class V. I introduce this

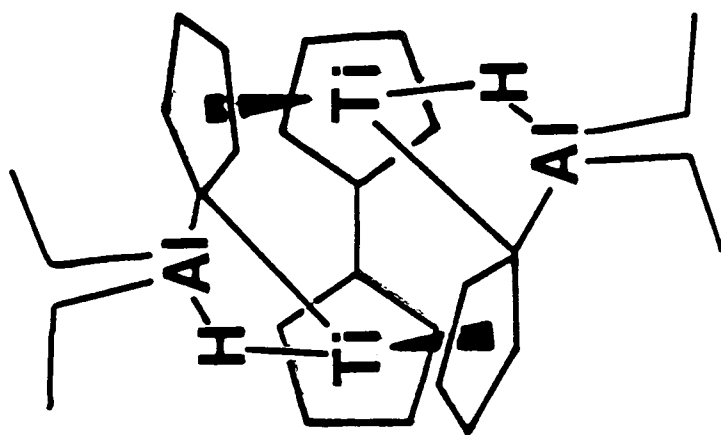


Fig. 2-9

rather limited class to illustrate the versatility of the $\text{C}_5\text{H}_n\text{M}$ units, but also because it provides the opportunity to emphasize an important structural point which is exemplified by its member compound. First of all, the compound contains,

of course, a fulvalene unit. However, the metal-metal distance is quite short, 2.910 Å, and the dihedral angle between the five-membered rings of the fulvalene is 25.8°. These dimensions show what extreme distortions the fulvalene ligand can undergo in order to accomodate a metal-metal bond, and advise against invoking the 'rigidity' of the C₁₀H₈ ligand to rationalize a long metal-metal bond. The range of M-M distances and dihedral angles for metallofulvalene derivatives is tabulated and discussed below, in section 2.5.

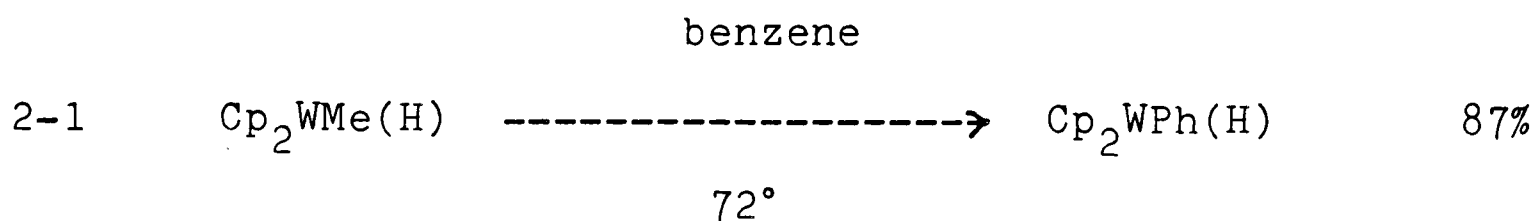
Class VI. Smart^{33,34,35} and others^{36,37,38} have synthesized bis(fulvalene) derivatives of a number of transition metals, including vanadium³⁵, chromium³⁵, iron^{36,37,38}, cobalt³⁵, and nickel^{33,39}. Their reaction chemistry tends to be limited in comparison with Classes I to V, because the two fulvalene ligands provide both steric and electronic saturation. Many class VI dimers have interesting electrochemical and magnetic properties, however, and most can be prepared in several oxidation states. The electronic structure of bis(fulvalene) dinickel will be discussed in a later section.

2.1 PRELUDE

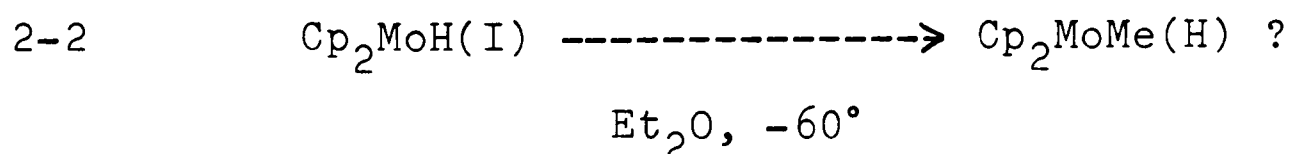
The purpose of this historical prelude is to explain how I became involved in molybdenocene chemistry, and to sketch briefly the extent of my research in this area. In the remainder of the chapter I present further results, followed by a systematic analysis of the chemistry of Group VI

metallocene dimers, in the context of the large body of related work on metallocenes of Groups IV and V. Chapter VI, the experimental chapter, will detail the experiments and calculations that I have carried out. Throughout the chapter, crystal structures determined as part of my postgraduate research will be identified by an asterisk,*.

The chemistry of $\text{Cp}_2\text{WMe(H)}$ is dominated by the thermal or photochemical loss of CH_4 to produce tungstenocene, and the subsequent attack of a substrate by the highly labile tungstenocene^{18,40}. The substrate is commonly the reaction solvent, or when the solvent is inert, another molecule of $\text{Cp}_2\text{WMe(H)}$. This reaction⁴¹ has provided examples of the oxidative addition of C-H bonds, as shown in Eq. 2-1.



In order to develop a similar chemistry of molybdenum, with particular regard to studying reductive elimination, I attempted the synthesis of $\text{Cp}_2\text{MoMe(H)}$, which had not previously been prepared. Since molybdenum-carbon and molybdenum-hydrogen bonds are often weaker than their tungsten analogues⁴², and since $\text{Cp}_2\text{WMe(H)}$ undergoes slow thermal decomposition even at room temperature, it was anticipated that $\text{Cp}_2\text{MoMe(H)}$ would need to be synthesized at low temperature, and that it might not be stable at all. The first route to be tried was that shown in Eq. 2-2.

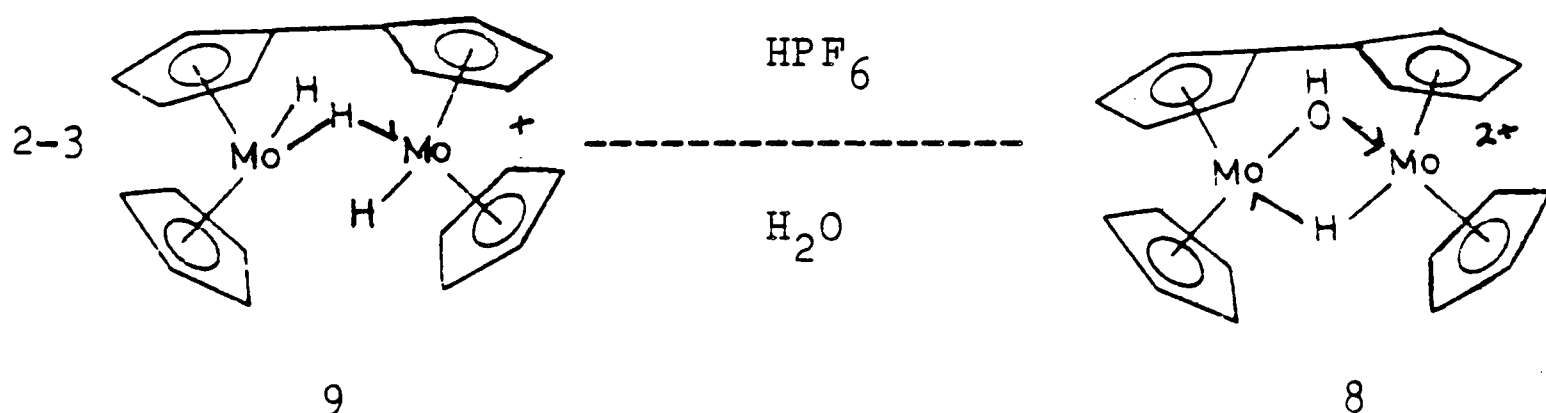


Synthesis of the Dark-Red Crystals, A.

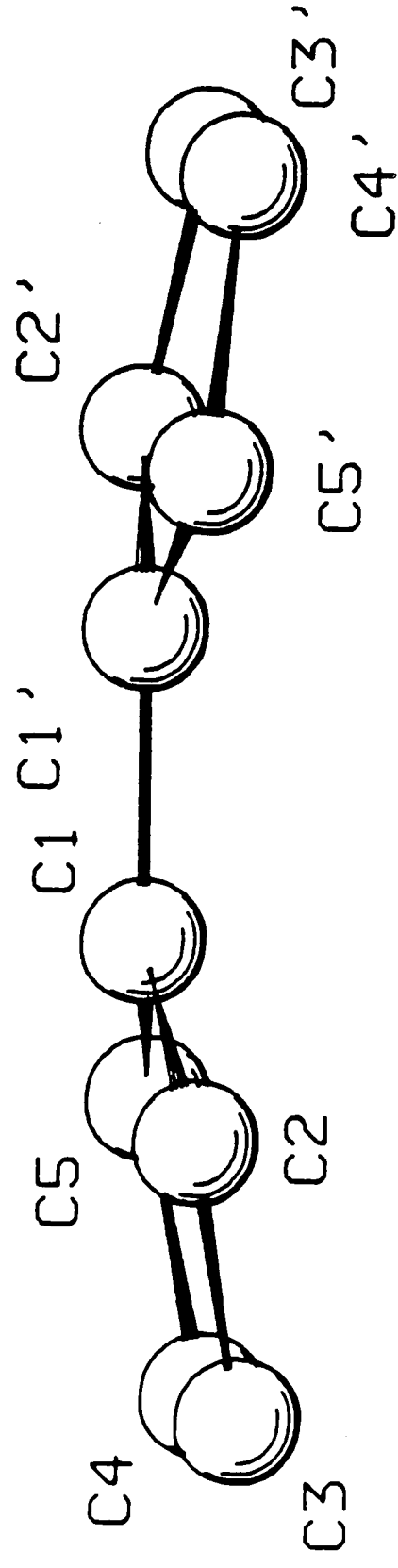
The dihydride Cp_2MoH_2 was dissolved in Et_2O , and an equimolar amount of MeI was added by syringe. After 12 h, a copious deposit of dark crystals had appeared. These were collected, and an ir spectrum showed them to be pure $\text{Cp}_2\text{MoH(I)}$ ⁴³. The hydrido-iodide was suspended in Et_2O at -60° , and a slight excess of MeMgBr was added. The solution slowly took on an orange colour, and was allowed to warm up to RT over a period of hours. At this point, a red precipitate had been deposited. When the solid was dissolved in H_2O , and, the solution treated with silicotungstic acid, a heavy off-white precipitate appeared, suggesting the presence of a large cation. Nmr spectra in $(\text{CD}_3)_2\text{CO}$ further suggested that a mixture of products containing Cp-rings and hydrides had been formed. The red solid was recrystallized from $(\text{CH}_3)_2\text{CO}/\text{H}_2\text{O}$ several times, NH_4PF_6 was added, and a final crystallization from hot acetone gave dark, octahedrally-shaped crystals A, which formed a red powder on grinding. The nmr and ir spectral data were consistent with a dimeric structure that contained a fulvalene bridge.

Crystal Structure Determination of the Dark Red Crystals, A.

At that time, only one fulvalene-bridged derivative of molybdenocene had been characterized by X-ray structure analysis, although two research groups had synthesized a number of such compounds^{18,20}. Some of these³¹ are shown in Fig. 2-10. Cooper synthesized¹⁷ the hydroxy-hydride derivative 8 by the hydrolysis of 9, and Prout and Couldwell determined²¹ its structure. The compound numbers refer to Fig. 2-22, a scheme which summarizes the dimer chemistry presented here.



I undertook the crystal structure determination of the dark crystals in order to unambiguously identify them, and to obtain structural information about the fulvalene bridge, which is an important feature of metallocene chemistry. The result is shown in Fig. 2-11, along with the crystallographic numbering scheme; when combined with nmr and ir data, it shows the molecule to be the hexafluorophosphate salt of compound 9. The dimeric units of this trihydride cation possess crystallographic two-fold symmetry. The metal-metal separation is 3.227(1) Å, significantly longer than the 3.053(3) Å separation found²¹ in 8 (which is obtained on hydrolysis of 9). The hydride ligands of 9 were not unambiguously located,



M01'

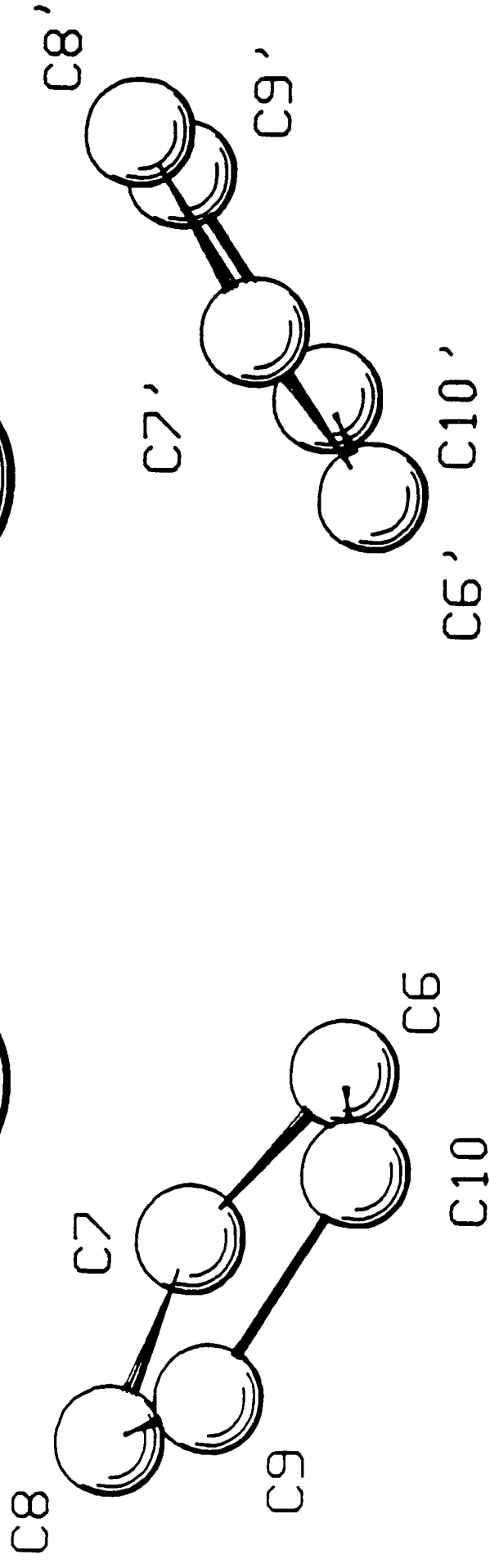
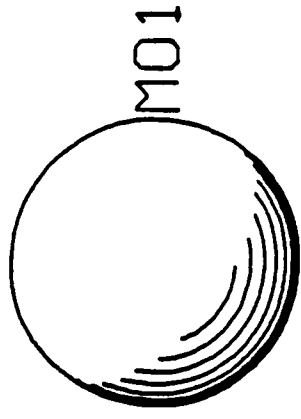


Fig. 2-11 Molecular structure of the cation 9.

but comparison with the related molecules^{6,44,45} depicted in Fig. 2-12 suggests that the hydrides may occur in either of the three arrangements shown in Fig. 2-13. The cis isomer, 9B, would have to be disordered to retain crystallographic C_2 symmetry. The final difference-Fourier suggests that isomer 9A, with three terminal hydrides, one of which is disordered over two sites, is the true structure, but the ir spectrum¹⁸ implicates a bridging hydride ($\nu_{\text{Mo-H-Mo}}=1262\text{ cm}^{-1}$). There are, in fact, a number of electron-density peaks in the inter-metal region, and I do not feel justified in proposing a model which gives great significance to a few of those peaks while ignoring the others. Azimuthal scans indicated that absorption was insignificant for the nearly spherical crystals of 9, so that inadequate absorption correction, which often causes small features to appear in final difference-Fourier maps, is not a factor here.

The bonding in isomers 9B and 9C is essentially the same. Apart from the conventional metal-Cp⁴⁶ interactions, it involves two terminal hydrido ligands and one bridging, three-centre, two-electron Mo-H-Mo interaction. Isomer 9A is different, however, in that it retains a direct Mo-Mo bond, and avoids a bridging hydride; a nonbonded pair of electrons localized on a single metal centre has been attacked by a proton. The mechanism of formation of 9 is discussed below, after some relevant results have been presented.

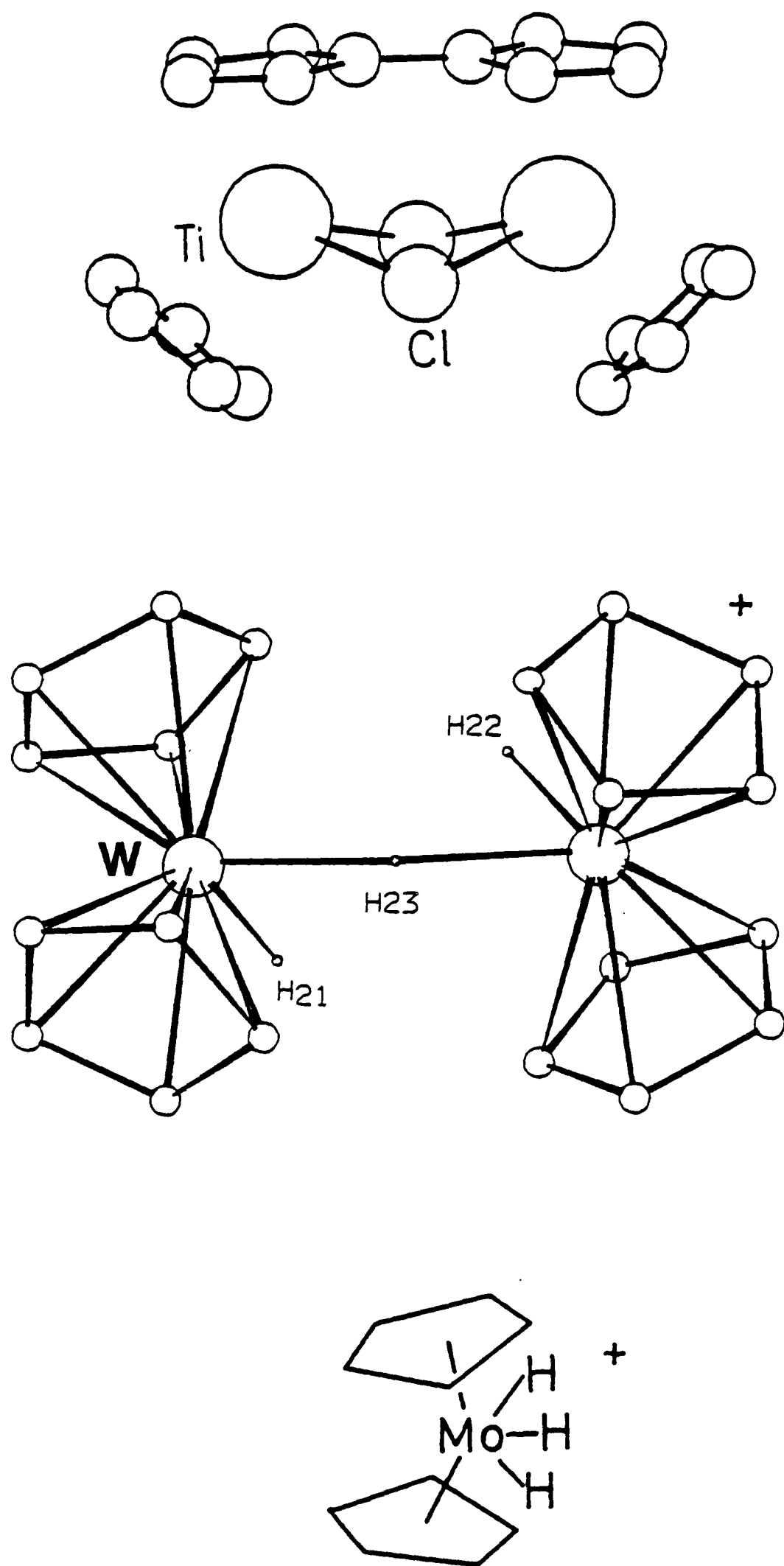


Fig. 2-12 Structures related to 9.

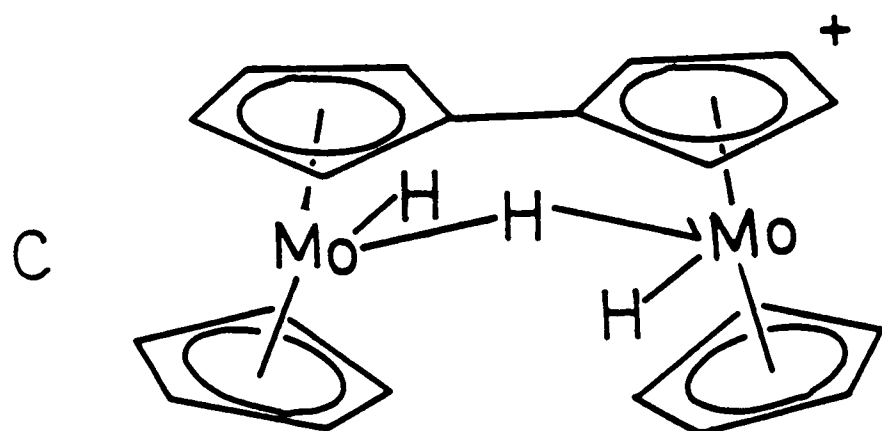
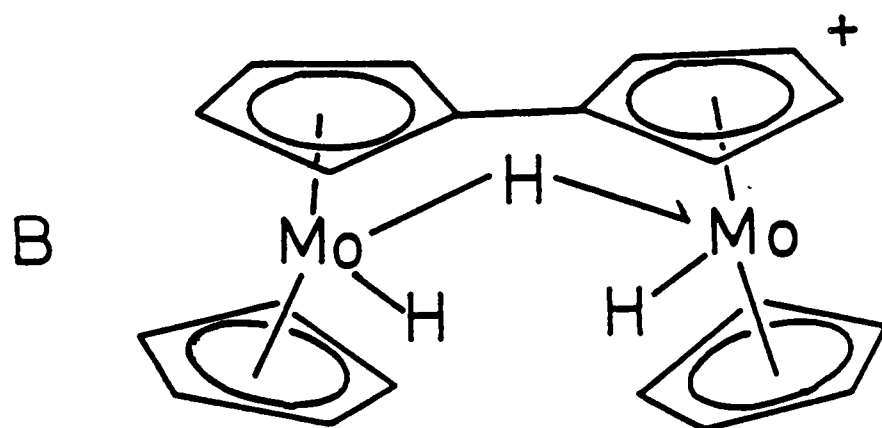
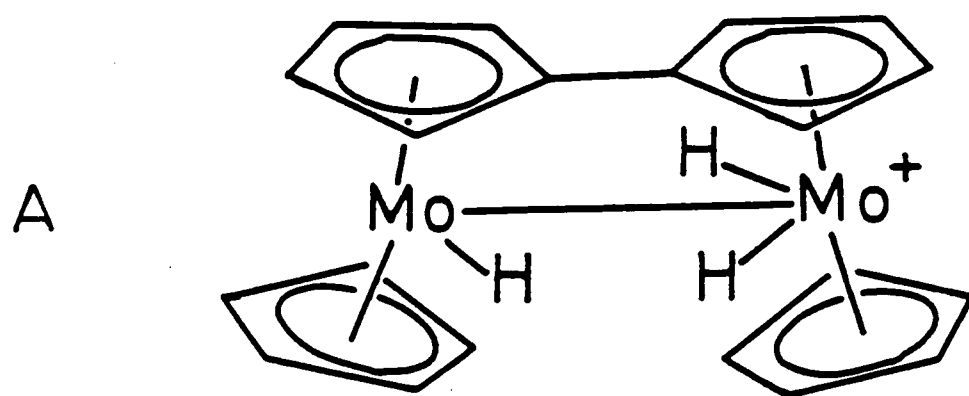
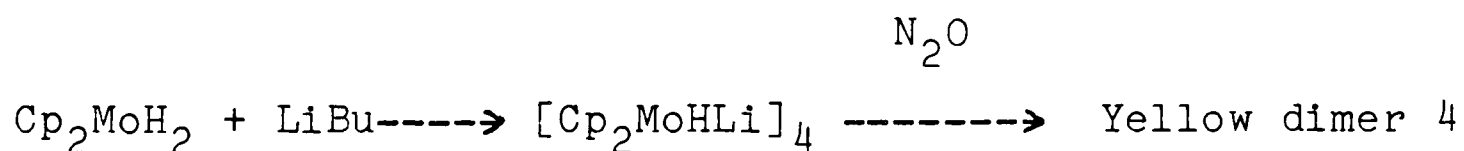
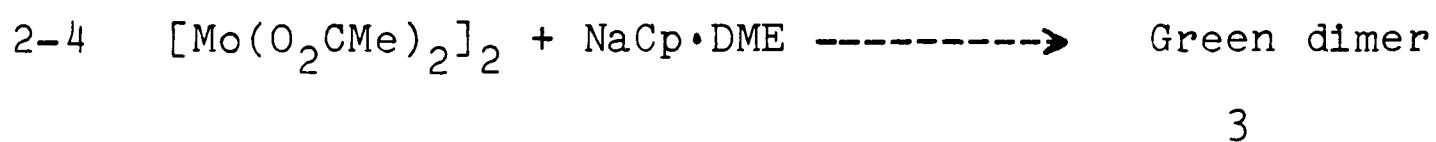


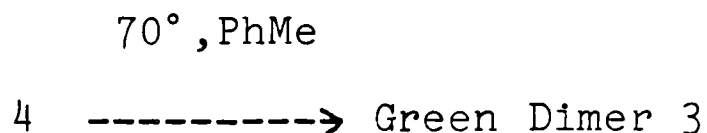
Fig. 2-13 Possible arrangements of the hydrides in 9.

Investigation of the Black Dimer.

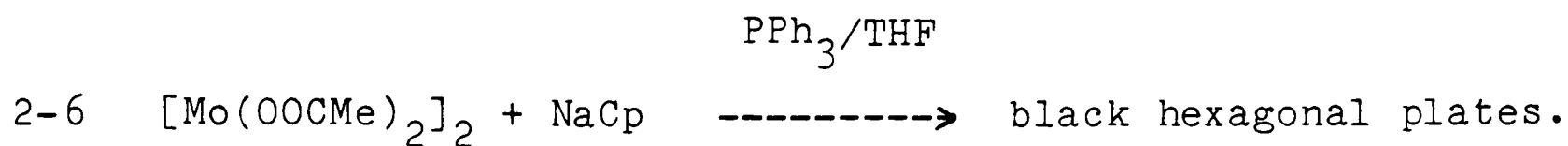
Shortly after I completed the crystal structure of 9, Dr. Manuel Lopez Poveda arrived in the Inorganic Chemistry Laboratory to carry out post-doctoral research with my supervisor, Dr. M.L.H. Green. Dr. Poveda's project was to study Smart's direct synthesis²⁰ of the green dimer 3, the fulvalene-bridged molybdenocene which is related to 9 by removal of a proton. Smart's synthesis is shown in Eq. 2-4; it is experimentally simpler than the original route¹⁵ shown in Eq. 2-5, but its mechanism is obscure (see also Fig. 2-17 and Fig. 2-22).



2-5



In an attempt to isolate some intermediate in reaction 2-4, Dr. Poveda carried out the reaction in the presence of PPh_3 , with the following result (Eq. 2-6):



2

The nmr spectrum (THF-d^8) showed 2 to be unstable in solution, converting into the known dimers 3 and 4 as well as new species which contained metal-hydrides. The ir spectrum of 2 showed a peak assignable to $\nu\text{Mo-H}$ at 1900 cm^{-1} , and elemental analysis gave a poor fit to the stoichiometry $\text{C}_{10}\text{H}_{10}\text{Mo}$ (the percentage carbon was systematically two percent high). Figure 2-14 shows the molecular structure of 2, the black isomer of molybdenocene, which I determined by single-crystal, X-ray methods^{47,48}.

Black molybdenocene consists of one $(\eta\text{-C}_5\text{H}_4)\text{CpMo}$ unit which is linked by a C-Mo σ -bond to a Cp_2MoH moiety. The metal-metal bond length is rather long, at $3.189(2) \text{ \AA}$, but the $\eta^1\text{-C-Mo}$ vector is bent 30° out of the C_5H_4 -ring plane, as is normal for Class IIb and Class IIIb dimers. A long metal-metal bond was also found¹⁶ by Pez in his Class II titanocene. Thus, compound 2 is the first Class II molybdenocene, although Kaesz¹⁵ set a precedent for such molecules in 1971, as discussed above. In fact, 2 is the first true Class II metallocene, with molecular formula $\text{C}_{20}\text{H}_{20}\text{M}_2$, since Pez could find no evidence for a twentieth hydrogen in his titanocene.

The final structure of 2 is quite acceptable by modern

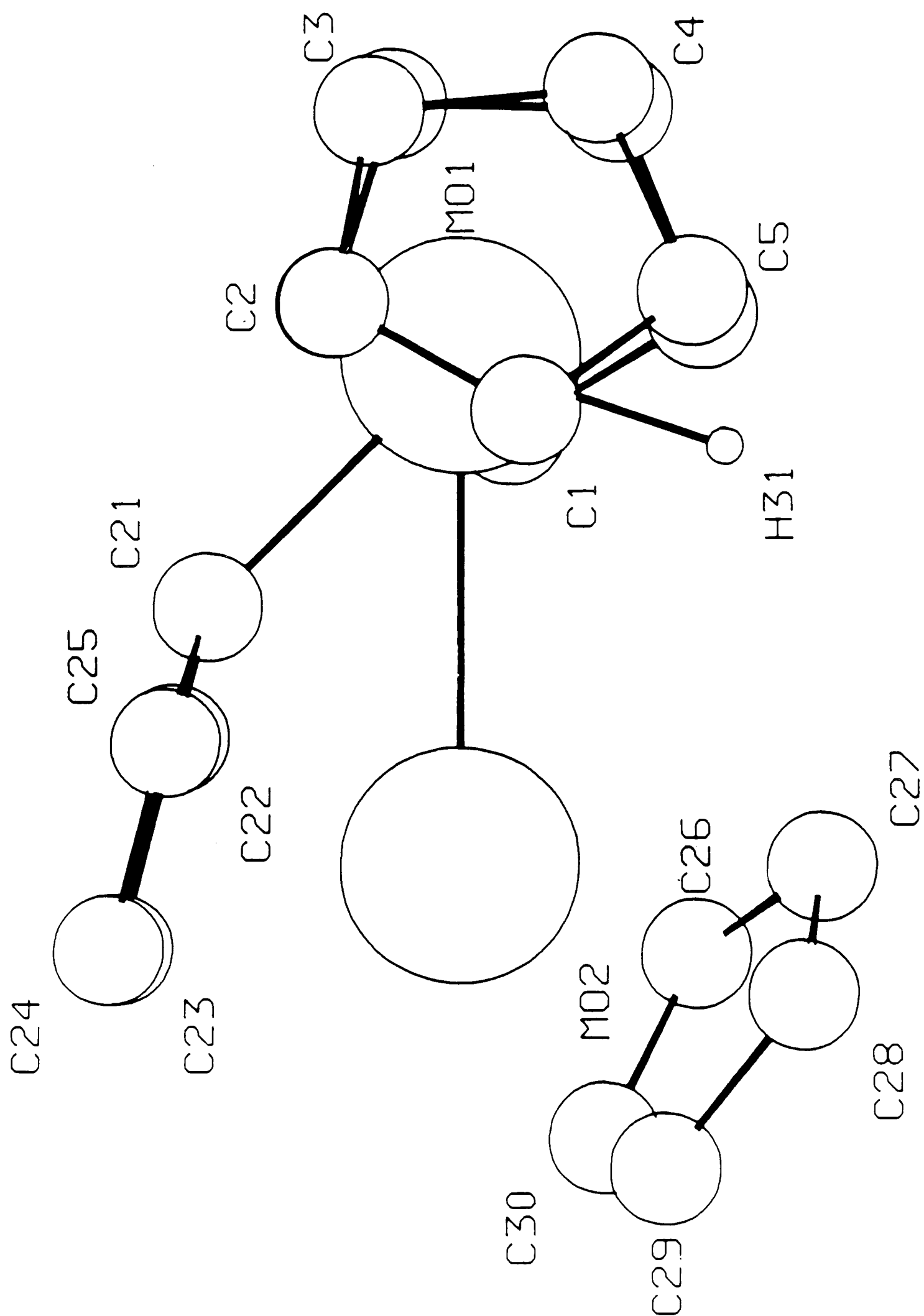


Fig. 2-14 The molecular structure of the black dimer, 2.

standards ($R(\text{final})=0.062, R_w=0.090$), and there is no ambiguity in the disposition of the heavy atoms or the C_5H_n rings, in spite of rather poor crystal quality. The hexagonal plates separate at their edges, giving the crystals a flake-like appearance, and of the several hundred crystals examined, only one was judged suitable for single-crystal X-ray studies. A large data set was collected, giving an observation to parameter ratio of greater than 10:1, but even the best crystal was badly split, and the atomic parameters were not determined to high precision. There was no crystallographic or spectroscopic evidence for any solvent in the crystals, so the 2% high carbon analysis has not been explained. There may be a systematic error in the combustion analyses.

There is some uncertainty in the location of the hydrido ligand. The presence of a terminal hydrido ligand is clearly indicated by nmr and ir, and is wholly consistent with reaction 2-6, but there is no spectroscopic evidence suggesting which molybdenum centre the hydride bonds to. The structural isomers depicted in Fig. 2-15 are both consistent with the data presented so far, and are equally possible on bonding and mechanistic grounds. In isomer 2a, the environment of Mo1 is similar to that of the Nb^{49} in $Cp_2NbH(\mu-\eta^1:\eta^5-C_5H_4)Fe(CO)_2$ (see Fig. 2-15). Furthermore, the angle $\emptyset$ between the ring normals at Mo1 is 134° , the same as that reported for the Nb-Fe dimer. The Cp rings about Mo2 are, in contrast, considerably more parallel, with a $\emptyset$ -angle of 154° that is considerably larger than the 145.8° found⁵⁰ for Cp_2MoH_2 . However, the construction of molecular models and the $\emptyset$ -value of 148° reported⁵¹ for $[Cp_2WH_3]Cl$ suggest that the

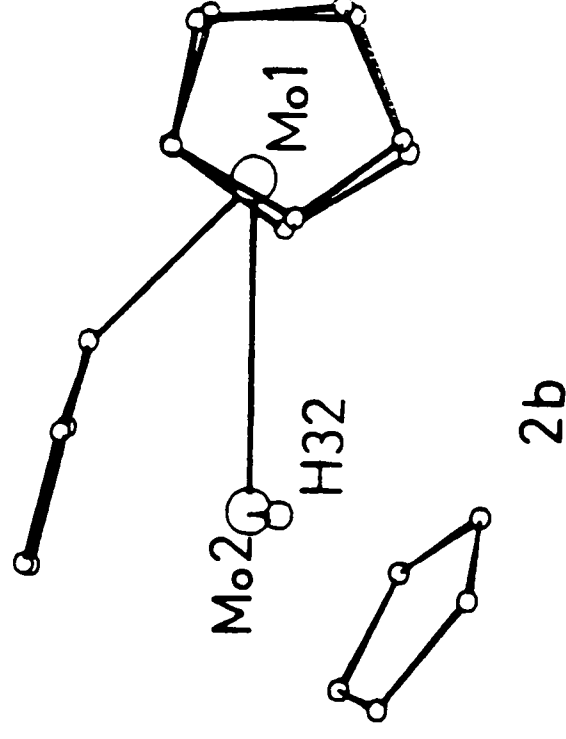
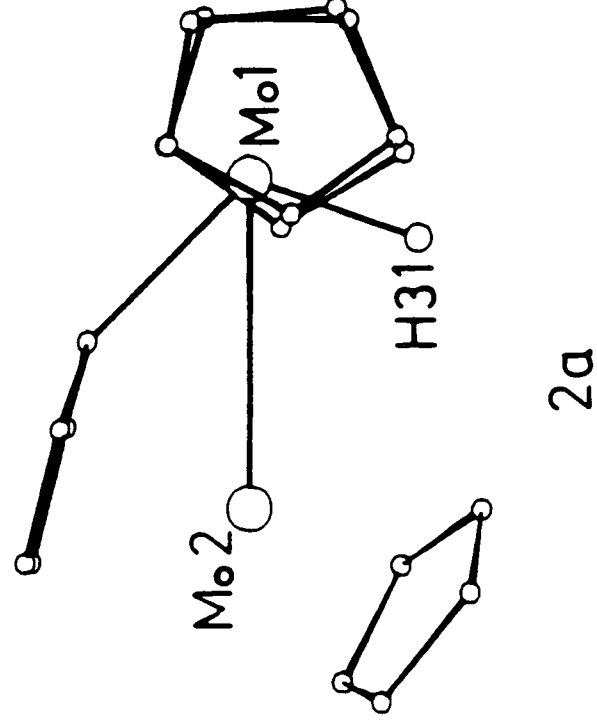
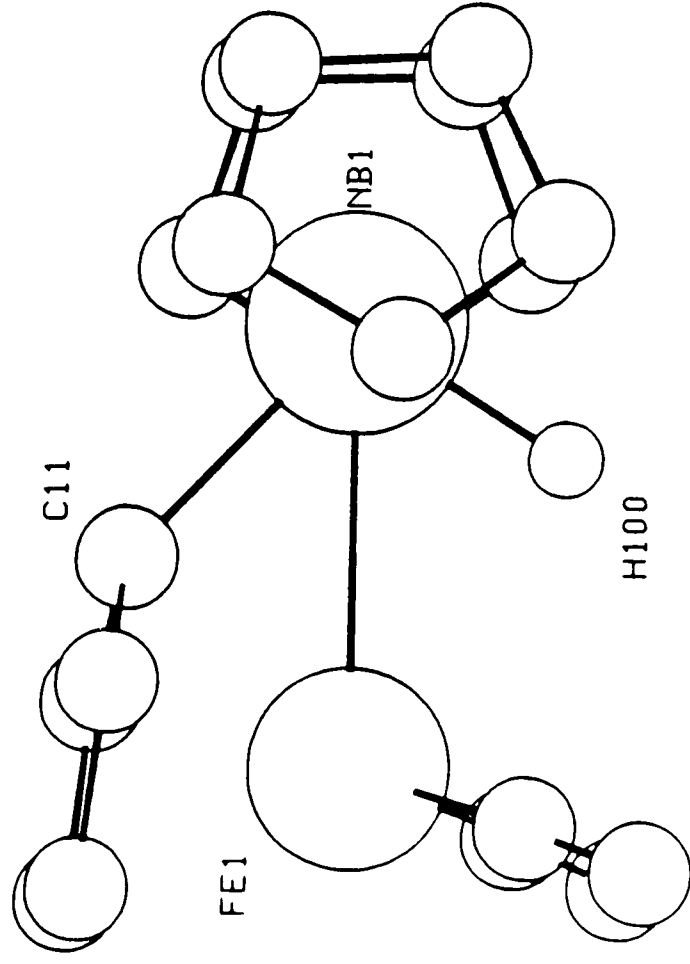


Fig. 2-15 Isomers 2a and 2b, and
a related niobium compound.

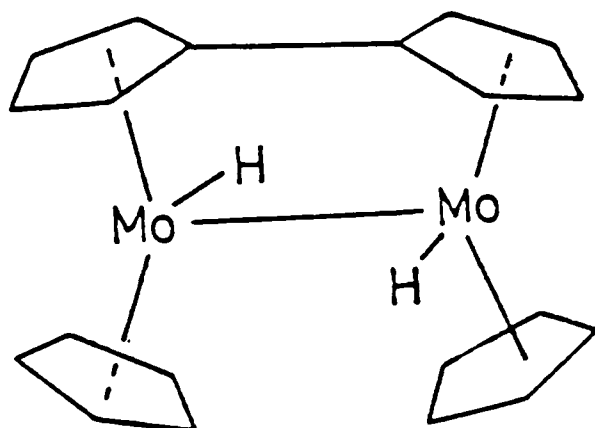
environment of Mo₂ can accomodate a hydride. The final difference-Fourier shows several peaks at a distance of 1 Å from each Mo, but only one peak in a position suitable for a molybdenum hydride⁵². This peak, labelled H31, is 1.7 Å from Mo₁, and lies in the plane defined by Mo₁, Mo₂, and C21. The angle C21-Mo₁-H31 is 115°, which is intermediate between the outer H-Nb-H angle of 120° and the (η^1 -C)-Nb-H angle of 100° in Cp₂NbH(η^1 : η^5 -C₅H₄)Fe(CO)₂. The location of a metal hydride by difference-Fourier techniques is not definitive⁵², and I conclude that the data are most consistent with isomer 2a but do not rule out isomer 2b. The low solubility and instability of 2 in solution in THF precluded detailed nmr studies which might be envisaged to distinguish between 2a and 2b.

The bonding in 2a may be described in terms of an electron-pair donation from the 18-electron Cp₂MoH(η^1 -C₅H₄) moiety to the 16-electron Cp(η -C₅H₄) Mo unit. This bonding mode is not unprecedented, since Cp₂MoH₂ is known to act as a Lewis base, e.g.⁵³ towards BF₃, and it is easily protonated⁴⁵. Similar metal-metal donor-acceptor bonds have been found in Cp₂(CO)Nb(μ -H)Fe(CO)₄⁵⁴ and Cp(CO)Mo(μ - η^1 : η^5 -C₅H₄)Mn(CO)₄¹⁵.

The identification of black molybdenocene brings to four the characterised^{17,18,21} isomers of C₂₀H₂₀Mo₂; Classes II, III and IV are represented, as shown in Fig. 2-16. The colours of these isomers are yellow, green, and black. The black colour of compound 2 may result from the mixed-valence, Mo(IV)-Mo(II) situation that is found in isomer 2a, and lends further support to the assignment of 2a instead of 2b as the correct structure.

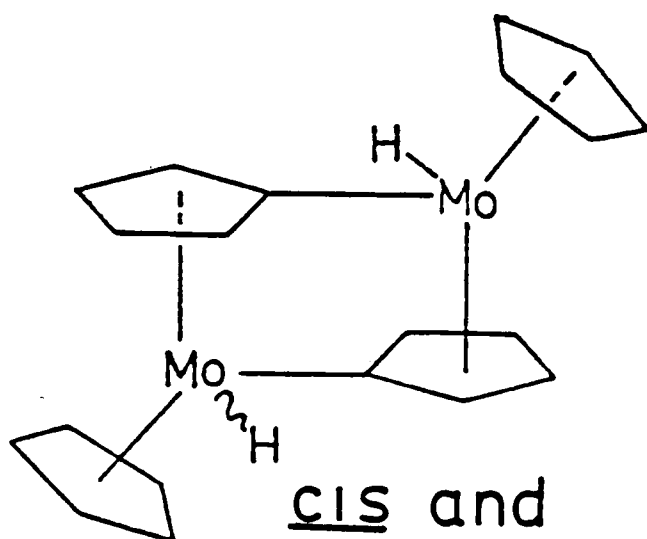
Colour

Class



Green

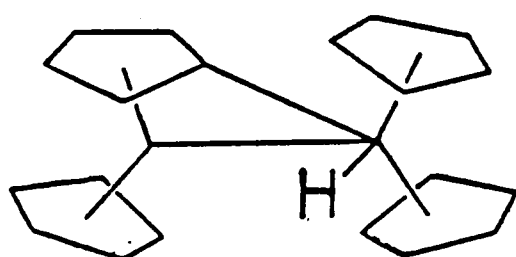
IVb



Yellow

IIIa

cis and
trans



Black

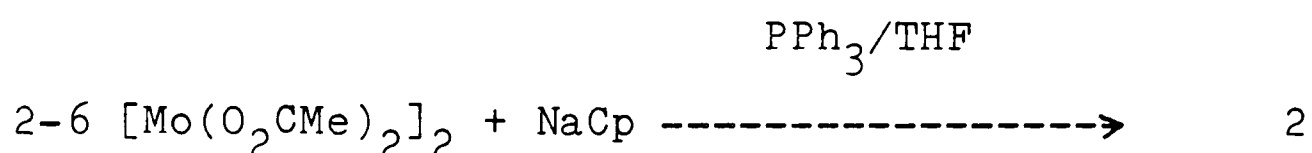
IIb

Fig. 2-16 The isomers of molybdenocene.

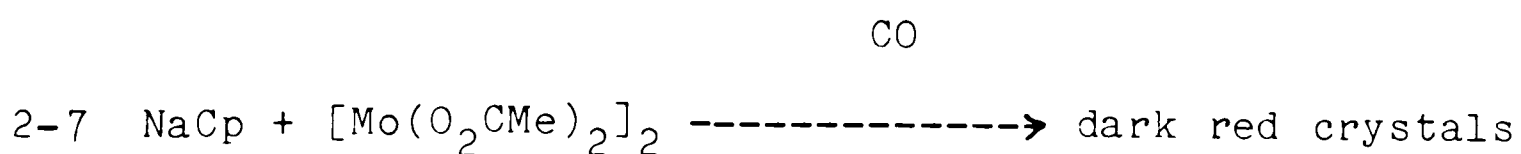
My investigation of the crystal structure of the black crystals was the start of a long collaboration with Dr. Poveda. The black dimer was found to be a convenient source of Cp_2MoCl_2 (obtained by reaction with HCl), as well as being a good precursor for dimer chemistry. Dr. Poveda synthesized a number of new molybdenocene derivatives, many of which could not be fully characterized by the techniques of nmr, ir, mass spectroscopy, and elemental analysis; I combined an analysis of the spectroscopic and analytical data with single crystal X-ray studies to determine the molecular structures of the compounds. In the course of this collaboration, a number of new reaction pathways were discovered, and I determined five crystal structures. One additional crystal structure⁵⁵, of a compound made by Mr. G. Parkin, is reported in this chapter because of its relevance to the mechanisms of reactions 2-4 and 2-6.

2.2 The Mechanism of Formation of 2.

Although the black dimer, 2, may be formally regarded as an intermediate in the reaction of molybdenocene with itself to give the yellow dimer, 4, it is unlikely that reaction 2-6 involves the production of monomeric molybdenocene.



The starting material, molybdenum acetate, is a dimeric, quadruply metal-metal bonded species, and the integrity of the dimeric unit may well be maintained during the course of the reaction, which reduces the Mo-Mo bond-order to one. The role of the triphenylphosphine in reaction 2-6 is unknown, but it may be weakly associated with Mo₂ when 2 is formed in solution, thus preventing Mo₂ from attacking the C-H bond of a Cp ring. The reaction was tried in the presence of several other phosphines, such as PMe₃ and PEt₃, but 2 could not be isolated under those conditions. It was thought that the course of the reaction might be elucidated by adding NaCp to [Mo(O₂CMe)₂]₂ in the presence of carbon monoxide (Eq. 2-7). The sterically undemanding nature of the CO ligand, and its strong pi-acidity, might render isolable a reaction intermediate that has only a transient association with the bulky triphenyl phosphine.



Reaction 2-7 was carried out by Dr. Poveda; it yielded dark-red hexagonal plates that are soluble in polar solvents. The nmr of this compound, 5, shows peaks attributable to two terminal Cp ligands, and an ABCD pattern in the cyclopentadienyl region which suggests an $(\eta^1:\eta^5\text{-C}_5\text{H}_4)$ group. The ir spectrum has three very intense features, at 1945, 1870, and 1765 cm^{-1} , the first two of which can be assigned to terminal metal-carbonyl stretches. The third, very low-frequency band, strongly suggests a semi-bridging carbonyl group⁵⁶, which commonly absorb⁵⁷ in the region **1700 to 1860** cm^{-1} . The structure of 5 could not be unambiguously determined on the basis of spectroscopic and analytical data, so I undertook an X-ray structure investigation.

The molecular structure of 5 is shown in Fig. 2-17, along with the atom labelling scheme. The molecule is dimeric, and consists of an $(\eta\text{-C}_5\text{H}_4)\text{CpMo(CO)}$ unit joined by C-Mo and Mo-Mo bonds to a CpMo(CO)_2 moiety. The metal-metal bond length is 3.081(1) Å, and the compound is reminiscent of Kaesz's original Class II dimer¹⁵, $\text{Cp(CO)Mo}(\eta^5:\eta^1\text{-C}_5\text{H}_4)\text{Mn(CO)}_4$.

Compound 5 has a number of unusual structural features which, together with the Mo-Mo separation, suggest the two valence-bond representations that are shown in Fig. 2-18. Structure 5a has a donor-acceptor Mo-Mo bond, and a conventional $(\eta^1:\eta^5\text{-C}_5\text{H}_4)$ bridging ligand, while 5b has a single bond between the Mo-centres and a carbene-diene bridge which is analogous to fulvene. For 5a there would be a large build-up of negative charge on Mo1 caused by the dative bond

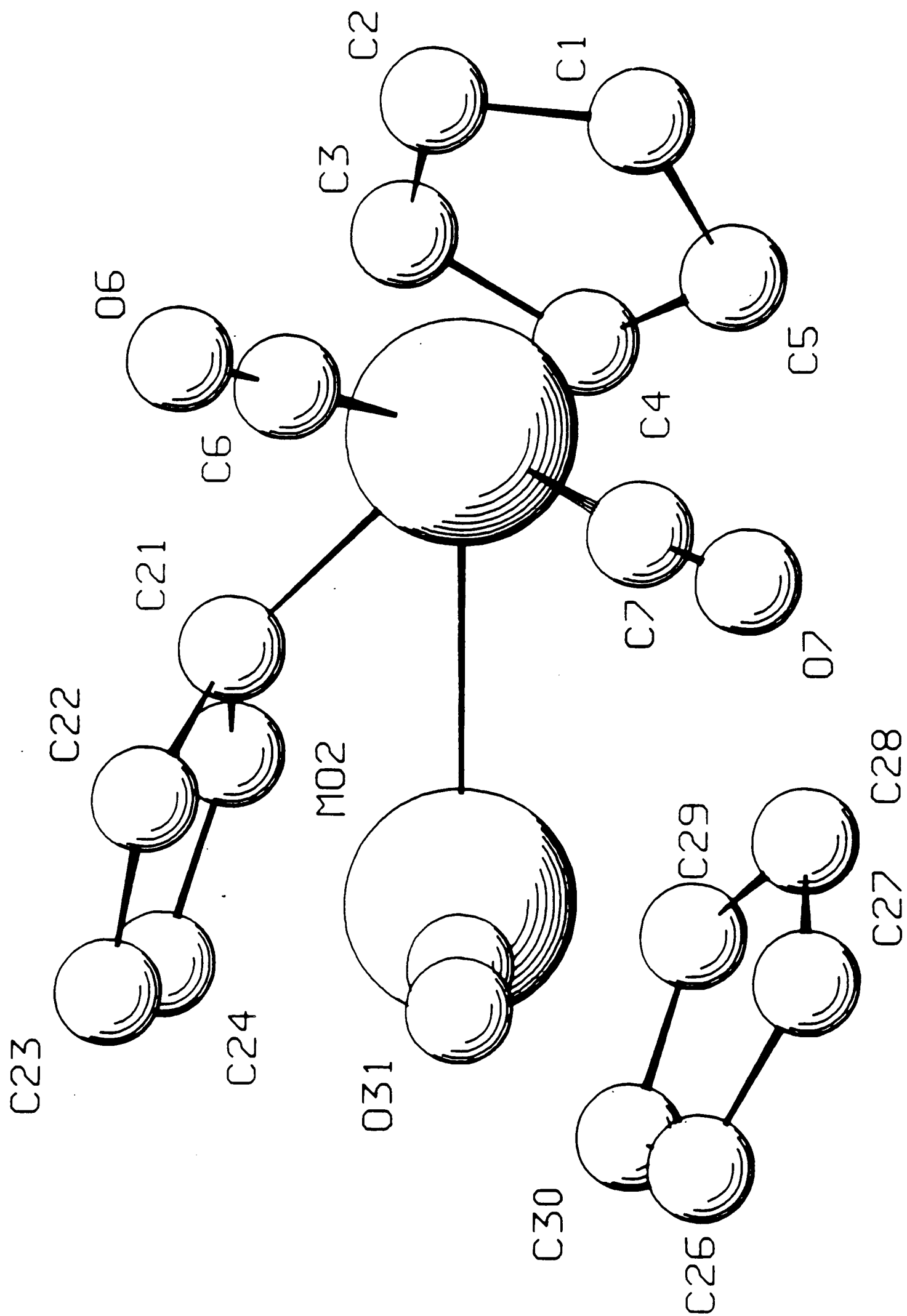


Fig. 2-17 The molecular structure of 5.

from Mol and the donor properties of the cyclopentadienyl ligand. A similar situation is found⁵⁸ in the anion $[\text{CpMo}(\text{CO})_3]^-$, which delocalizes its excess charge onto the carbonyl ligands, resulting in one very low terminal carbonyl stretching frequency at 1763cm^{-1} . Model 5a seems particularly

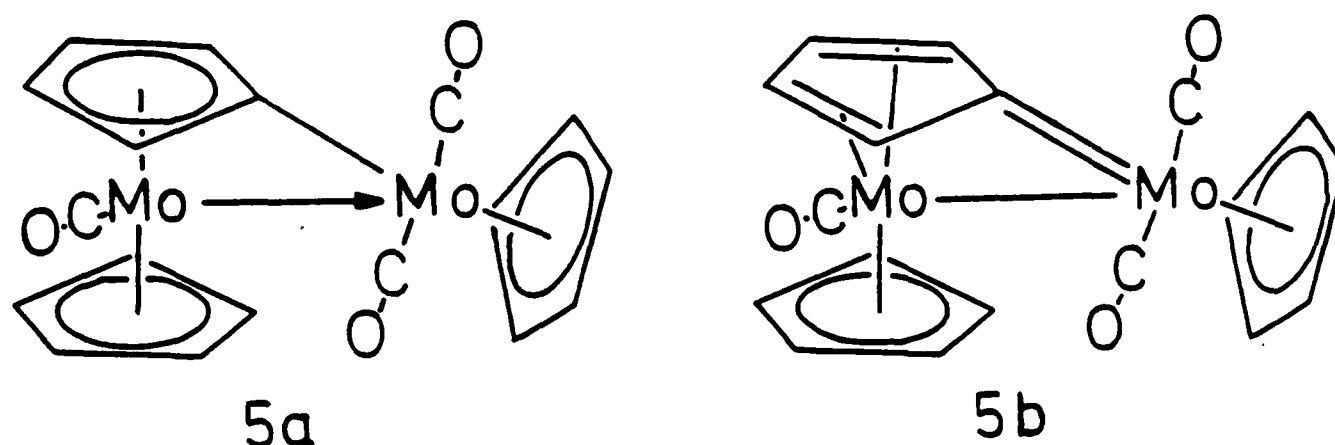


Fig. 2-18 Valence-bond representations of 5.

relevant since 5 has a carbonyl absorption at 1765cm^{-1} , and this can be assigned to a terminal carbonyl stretch. This low-frequency band may be thought of as the asymmetric stretch of an $\text{L}_n\text{M}(\text{CO})_2$ fragment, the higher (symmetric) stretch of which occurs at 1870cm^{-1} . There may be only a small coupling between the ' $\text{L}_n\text{M}(\text{CO})_2$ ' and the ' $\text{Cp}_2\text{M}(\text{CO})$ ' fragments of 5, because a rather high-frequency band at 1945cm^{-1} may be assigned to the latter, relatively electron-poor, moiety. In fact, compound 5 has one of the lowest terminal carbonyl stretches known⁵⁷: cis- $[\text{Mo}(\text{CO})_3(\text{bipy})(\text{PPh}_3)]$ absorbs at 1913, 1820, and 1792cm^{-1} , and cis- $[\text{Mo}(\text{CO})_3(\text{dien})]$ has C-O stretches at 1898 and 1758cm^{-1} . To check that the low-frequency band of 5 did not result from the compound being dissolved in Nujol, yielding a solution structure containing bridging carbonyls, the ir spectrum was recorded in a KBr disc. The Nujol mull and KBr disc spectra have differences in detail (several

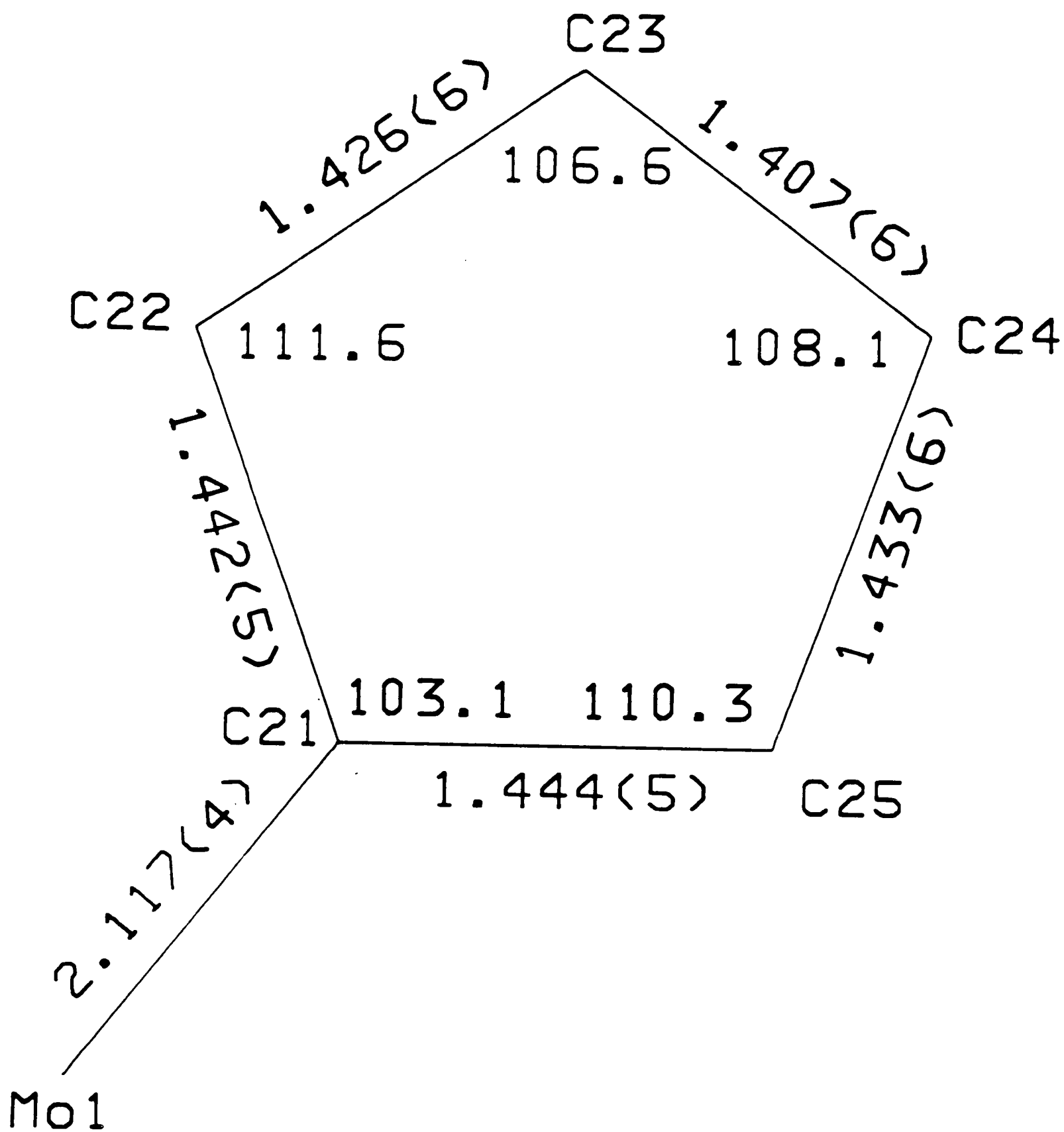
wavenumbers or more), but they are qualitatively identical.

The M-C and C-O bond lengths of metal carbonyls are usually poor indicators of the nature of the M-(CO) bond; C-O stretching frequencies are a much more sensitive probe of carbonyl bonding. However, for 5, a rather localized, strong back-bonding from Mo1 to C6-O6 is suggested by the very short Mo1-C6 distance of 1.914(4) Å and the long C6-O6 bond of 1.174(5) Å. The group Mo1-C7-O7 exhibits more typical dimensions for a molybdenum carbonyl, with Mo-C and C-O distances of 1.949(4) and 1.159(6) Å, respectively. For comparison, the Mo-C(carbonyl) and C-O bond lengths of dicarbonyl(Cp)((3-dimethylarsino)propyl)molybdenum⁵⁹ and [CpMo(CO)₃]₂²³ are given in Table 2-1. Any semi-bridging interaction between C7-O7 and Mo2 is unlikely, since the group Mo1-C7-O7 is nearly linear, with an angle of 175.6(4)°, and the distance Mo2-C7 is long (3.240(4) Å).

TABLE 2-1. Dimensions of Metal-carbonyl Groups.

<u>Compound</u>	<u>M-C(Å)</u>	<u>C-O(Å)</u>
5 Mo1-C6-C7	1.914(4)	1.174(5)
Mo1-C7-O7	1.949(4)	1.159(6)
Mo2-C31-O31	1.986(4)	1.142(5)
[CpMo(CO) ₃] ₂	1.984	1.149
	1.964	1.150
	1.983	1.144
CpMo(CO) ₂ (CH ₂) ₃ AsMe ₂	1.94	1.15
	1.95	1.16

A contribution to the bonding in 5 from structure 5b would result in a shortening of the η^1 -bond and a systematic variation in the C-C distances of the bridging ring. The relevant dimensions of the Mol-C₅H₄ group are shown in Fig. 2-19, and some dimensions of other dimers are given in Table 2-2 for comparison (see section 2-6 for further discussion and explanation of Table 2-2). For compound 5, the bond Mol-C21 is found to be 2.117(4) Å, very significantly shorter than the average of 2.18 Å found for the Group VI dimers listed in Table 2-2; the C-C bond lengths of the bridging ligand follow the pattern found⁴ in Nb(Cp)($\eta^1:\eta^5$ -C₅H₄)]₂ of two long bonds, two intermediate bonds, and one short bond. The dimensions of 5 are therefore consistent with a significant contribution from resonance form 5b, by analogy with the central C-C bond of complexed butadiene, which is the usually same length or shorter than the outer bonds, from population of ψ_3 by metal-to-ligand back bonding. The endocyclic angle of 103.1° at C21 exemplifies a common feature of Class II and Class III dimers: as Table 2-2 shows, substitution of a Cp-ring hydrogen by a transition metal can cause a large decrease in the endocyclic angle at the site of substitution. A study of ring angles in Cp compounds might provide useful information about their bonding, because angles are less prone than distances to distortion by the large thermal motion that Cp rings often undergo. A study⁶⁰ of substituted benzene rings has shown that σ -releasing and both pi-accepting and pi-donating substituents cause a decrease in the endocyclic angle at the substituted carbon. Therefore, the ($\eta^1:\eta^5$) linkage may be involved in either the donation of electron density from Mo2 to Mol or the redistribution of excess electron density away from Mol.

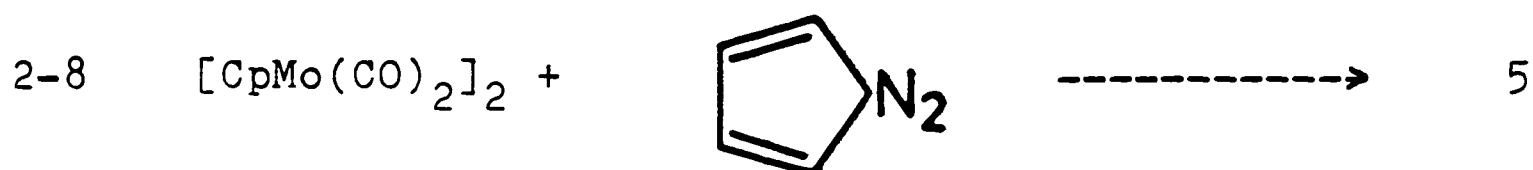


The C_5H_4 unit of compound 5.

Fig. 2-19

One further interesting feature of the bridging geometry in 5 is the 2.218(3) Å bond length of C21-Mo2, which, like C21-Mo1, is unusually short. The effect of this short bond on the C₅H₄-ring is a 4.2° bend of the ring towards Mo2 about the C22-C25 vector. A similar departure from planarity was found¹⁵ in the C₅H₄ ring of CpMo(CO)(μ-η¹:η⁵-C₅H₄)Mn(CO)₄.

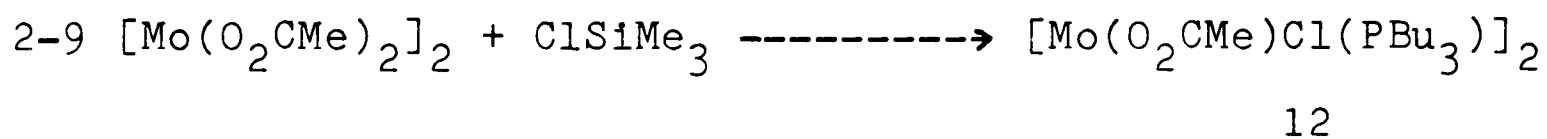
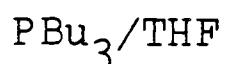
At the time that we were preparing a preliminary communication⁶¹ describing the synthesis, structure, and reactivity of 2 and 5, a communication appeared from the laboratory of Professor W.A. Herrman, describing a different synthesis of 5 (Eq. 2-8) and its crystal structure.



This independent synthesis used diazocyclopentadiene to attack the metal-metal triple bond; the intention had been to introduce a bridging-carbene ligand. The spectroscopic and X-ray crystallographic results are in agreement with those reported here.

At the same time that Dr. Poveda was carrying out reaction 2-6, Mr. G. Parkin was investigating some related chemistry of molybdenum acetate. McCarley had reported⁶² that ClSiMe₃ could be used as a reagent for the removal of ligated acetato groups, the driving force being the formation of a strong Si-O bond. Mr. Parkin found⁵⁵ that, by varying the stoichiometry of the reaction, he could remove two or all four

acetato groups from $[\text{Mo}(\text{O}_2\text{CMe})_2]_2$, and, if the reaction were carried out in the presence of donor ligands, compounds of the type $\text{Mo}_2\text{Cl}_2(\text{O}_2\text{CMe})_2\text{L}_2$ and $\text{Mo}_2\text{Cl}_4\text{L}_4$ could be isolated. There are a number of possible isomers for such compounds, as shown in Fig. 2-20, and complete assignment of stereochemistry was not always possible on the basis of ir and nmr alone. It was thought, however, that these phosphine derivatives of molybdenum acetate might resemble some intermediate in reaction 2-6, so Mr Parkin tried the reaction of 12, $[\text{MoCl}(\text{PBU}_3)(\text{O}_2\text{CMe})]_2$, with NaCp, as shown in Eq. 2-9. The reaction did produce some 2, although in low yield.



Since 12 was found to be a precursor of the dimer 2, I decided to investigate its crystal structure. As well as clarifying the structure of Mr. Parkin's new dimer, I thought that some insight might be gained into the role of the phosphine in reaction 2-6.

The molecule $[\text{Mo}(\text{PBU}_3)\text{Cl}(\text{O}_2\text{CMe})]_2$, 12, is dimeric, with a crystallographic inversion centre lying between the two Mo atoms; these metal centres are separated by 2.099(1) Å, and are linked by two coplanar, bridging acetato ligands (see Fig. 2-21). Perpendicular to the acetato plane is the $\text{Mo}_2\text{P}_2\text{Cl}_2$ plane, which has a trans disposition of ligands as required by the site symmetry. The Mo1-P1 distance is 2.501(3) Å and the

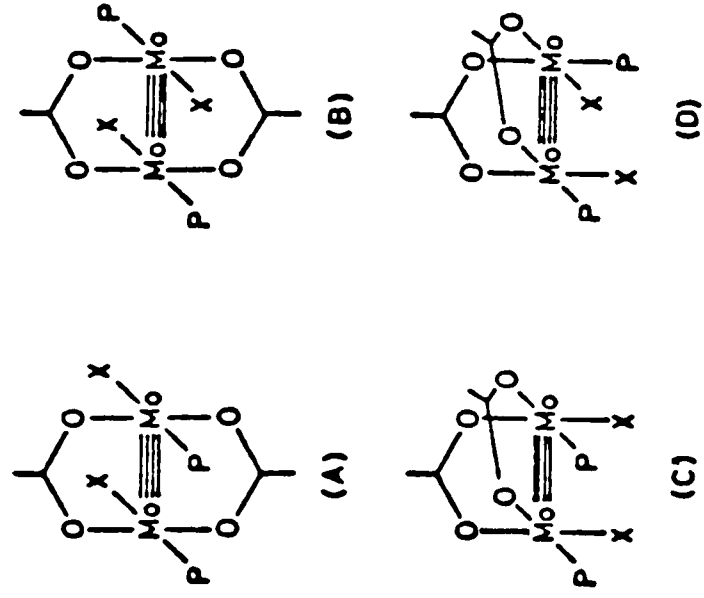


Fig. 2-20

Possible isomers of $[(\text{MoX}(\text{PR}_3)_2(\mu\text{-OCOMe}))_2]$

Selected bond lengths (Å) and angles (°) for compound		times refer to the symmetry operation $1 - x, -y, -z$	
$\text{Mo}(1) - \text{Mo}(1')$	2.099(1)	$\text{C}(11) - \text{C}(12)$	1.500(15)
$\text{Mo}(1) - \text{Cl}(1)$	2.427(2)	$\text{C}(12) - \text{C}(13)$	1.550(15)
$\text{Mo}(1) - \text{O}(1)$	2.109(5)	$\text{C}(13) - \text{C}(14)$	1.513(19)
$\text{Mo}(1) - \text{O}(2')$	2.100(6)	$\text{C}(21) - \text{C}(22)$	1.506(19)
$\text{Mo}(1) - \text{P}(1)$	2.501(3)	$\text{C}(121) - \text{C}(22)$	1.453(17)
$\text{O}(1) - \text{C}(1)$	1.282(10)	$\text{C}(22) - \text{C}(23)$	1.556(16)
$\text{O}(2) - \text{C}(1)$	1.269(11)	$\text{C}(23) - \text{C}(24)$	1.482(16)
$\text{P}(1) - \text{C}(11)$	1.855(10)	$\text{C}(31) - \text{C}(32)$	1.563(16)
$\text{P}(1) - \text{C}(21)$	1.813(15)	$\text{C}(131) - \text{C}(132)$	1.574(17)
$\text{P}(1) - \text{C}(121)$	1.850(17)	$\text{C}(32) - \text{C}(33)$	1.546(16)
$\text{P}(1) - \text{C}(31)$	1.847(14)	$\text{C}(132) - \text{C}(33)$	1.520(18)
$\text{P}(1) - \text{C}(131)$	1.882(17)	$\text{C}(33) - \text{C}(34)$	1.508(15)
$\text{C}(1) - \text{C}(2)$	1.531(12)		
$\text{Mo}(1') - \text{Mo}(1) - \text{Cl}(1)$	119.00(8)	$\text{O}(1) - \text{C}(1) - \text{O}(2)$	121.4(8)
$\text{Mo}(1') - \text{Mo}(1) - \text{P}(1)$	101.21(8)	$\text{O}(1) - \text{C}(1) - \text{C}(2)$	118.6(9)
$\text{Cl}(1) - \text{Mo}(1) - \text{P}(1)$	139.8(1)	$\text{O}(2) - \text{C}(1) - \text{C}(2)$	120.0(9)
$\text{O}(1) - \text{Mo}(1) - \text{O}(2')$	176.2(2)		

Figure. Crystal structure of compound (5) showing only one configuration of the disordered n-butyl chains and with the principal atoms labelled

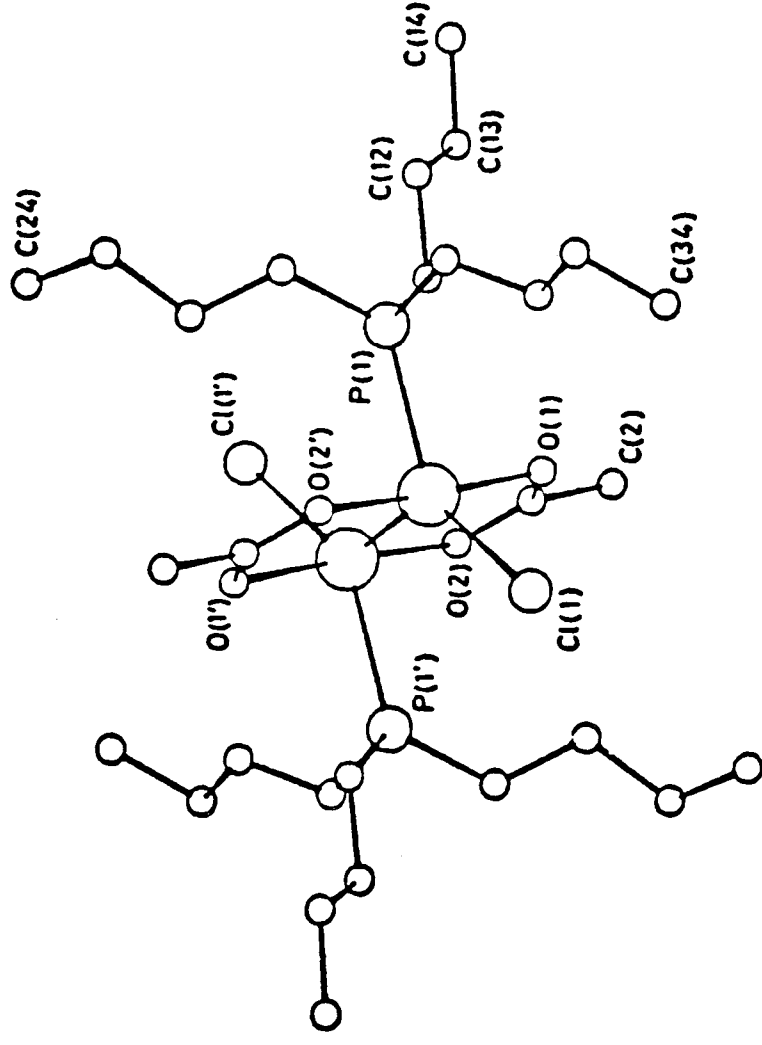
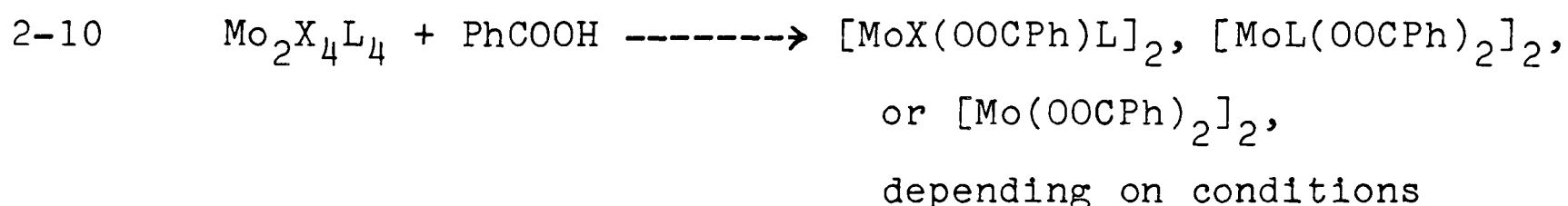


Fig. 2-21

Mo1-Cl1 bond length is 2.427(2) Å. The Mo-Mo separation is consistent with a Mo-Mo quadruple bond, whose distances fall in the range 2.06 to 2.18 Å. Compound 12 is very similar to $[\text{MoBr}(\text{O}_2\text{CPh})(\text{P}^i\text{Bu}_3)]_2$, which was prepared and structurally characterized⁶³ by San Filippo's group; its metal-metal bond length is 2.091(3) Å. However, the Mo-P bond of the benzoate derivative is 2.526(5) Å, which is significantly longer than the corresponding distance in 12. The reason for this difference may be steric interaction between the phenyl groups and the phosphine ligands. The method of preparation of the benzoate derivative, shown in Eq. 2-10, was not successful for the preparation of acetato derivatives.



2.3 The mechanism of formation of 2. Conclusions.

Although reaction 2-6 resulted in the formation of a new, dimeric molybdenocene, there is no evidence for the appearance of monomeric molybdenocene, even as a transient, during the course of the reaction. This would require the complete cleavage of the dimolybdenum unit of $[\text{Mo}(\text{O}_2\text{CMe})_2]_2$, followed by the recombination of the monomeric subunits. However, the fact that 2, the black dimer, can be synthesized from 12 suggests that reaction 2-6 may involve phosphine coordination at an early stage, perhaps initially in the axial

site of molybdenum acetate. Subsequent attack by cyclopentadienide on the metal centres would be somewhat hindered by the bulky phosphine, which could eventually dissociate. The relevance of these reaction steps, especially the early coordination and subsequent loss of phosphine, is supported by Hermann's synthesis⁶¹ of 5 from the carbonylated dimer, $[\text{CpMo}(\text{CO})_2]_2$, from which a CO ligand is lost under the action of a source of C_5H_4 . The insolubility of 2 and the bulk of the phosphine result in an unusual kinetic trap for the Class II, dimeric product, although increased temperature will cause further C-H bond insertion, as discussed below.

2.4 Further Molybdenocene Chemistry.

Since the black dimer 2 can be prepared on a 5-10g scale, it is a convenient precursor for new and known molybdenocene dimers. The results of most of our studies^{47,48} are shown in Fig. 2-22, and the crystallographic identification of some of the reaction products is discussed in the next sections. The molecules to be discussed are all Class IV derivatives of molybdenocene.

The Molybdato-bridged Dimer, 11.

When a DMSO solution of the yellow dimer, 4, was left standing for several weeks under dinitrogen, small crystals appeared on the Schlenk-tube walls. This reaction was repeated by Dr. Poveda, and subsequently by me, and the product

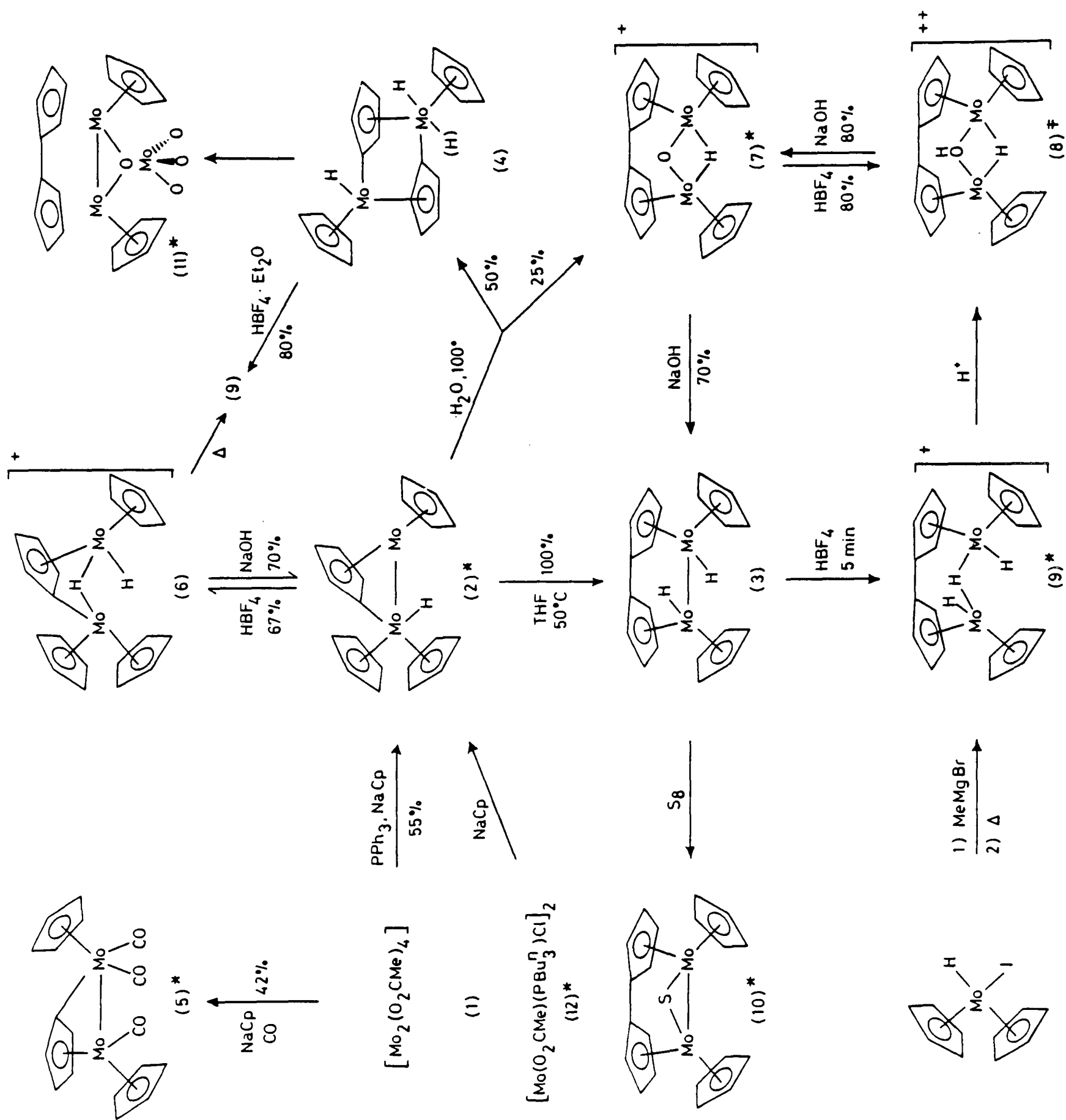


Fig. 2-22 A summary of the results presented in Chapter 2. * refers to a crystal structure reported here; † refers to the work of Prout and Couldwell.

crystals were obtained reproducibly, although in low yield. The crystals, 11, appeared to originate from the reaction of 4 with DMSO. It is not uncommon for Cp_2Mo derivatives to 'decompose' in DMSO, but no product of such a decomposition had been characterized. I solved the crystal structure of 11 to provide such a characterization.

After some initial problems caused by the presence of an extra, unsuspected heavy atom, the structure of 11 was solved by Patterson and direct methods, to give the result shown in Fig. 2-23. The Class IIIa structure of the starting dimer 4 has been transformed under mild conditions into a Class IVb framework, which has a metal-metal bond length of $3.076(1) \text{ \AA}$. Most striking about 11 is the bridging molybdate group, which is linked by one oxygen to the two molybdenum centres of a $[\text{CpMo}]_2(\text{C}_{10}\text{H}_8)$ moiety. The triply-bridging oxygen has a nearly trigonal-planar geometry, which may reflect delocalization of the oxygen lone-pairs, or the steric constraints of the dimer framework. The average terminal Mo-O bond length in 11 is $1.723(3) \text{ \AA}$, which is the same as that found⁶⁴ in $[\text{CpMo}(\mu\text{-O})_2\text{MoO}_2]_2$ (Fig. 2-24). The triply-bridging oxygen participates in much longer Mo-O bonds, of 2.085, 2.093, and $1.910(6) \text{ \AA}$ to Mo1, Mo2, and Mo3, respectively. The triply-bridging oxygen in $[\text{CpMo}(\mu\text{-O})_2\text{MoO}_2]_2$ bonds somewhat more symmetrically to the three metals, with bond lengths of 2.09, 2.10, and $1.98 \text{ \AA}$. The bonding in 11 may be described by the valence-bond representation, Fig. 2-25, which shows that 11 is closely related to the hydroxy-hydride dimer characterized^{17,18,21} by Cooper and Couldwell (see Fig. 2-8). In fact, the Mo-O-Mo geometry of these two compounds is

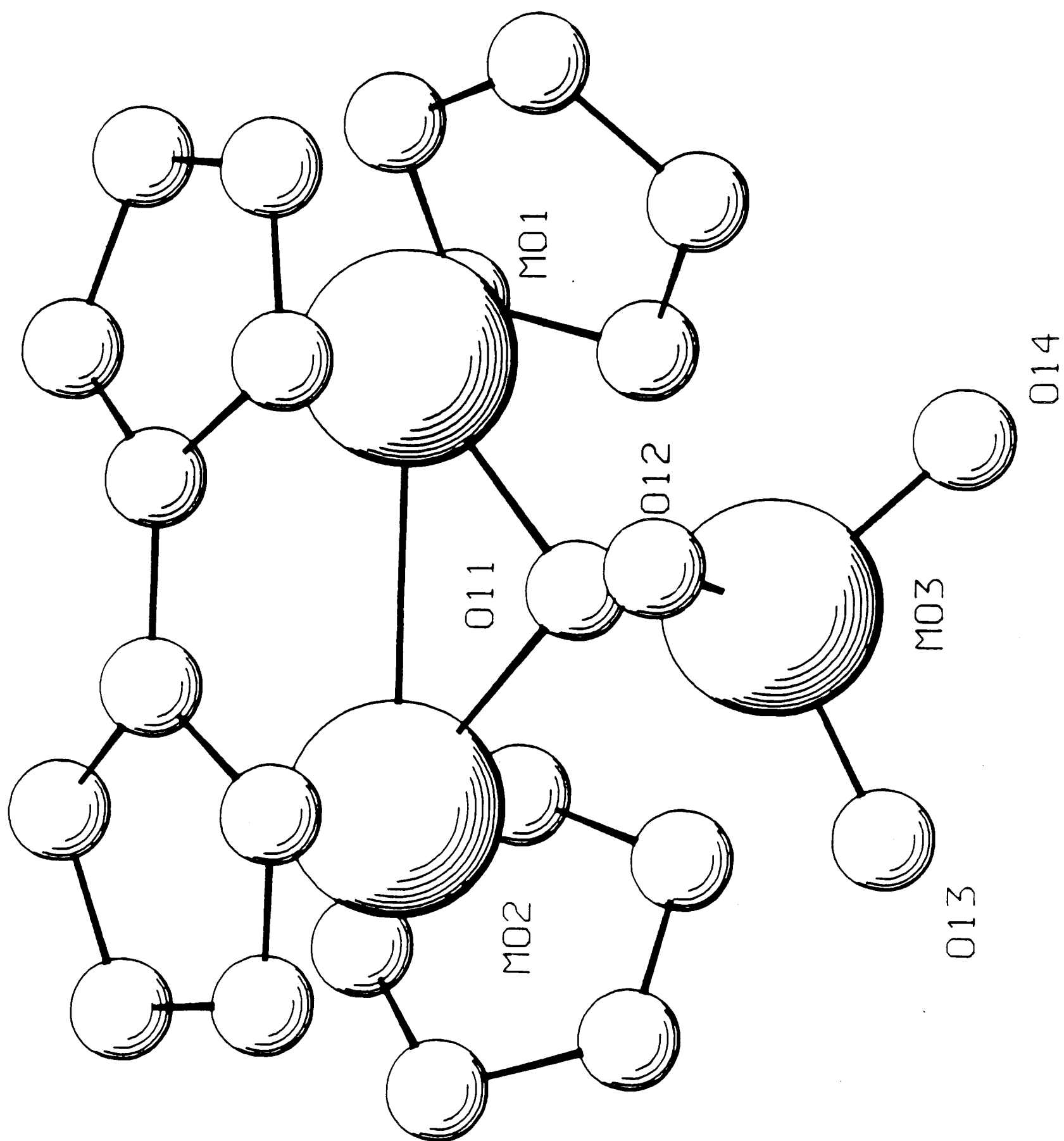
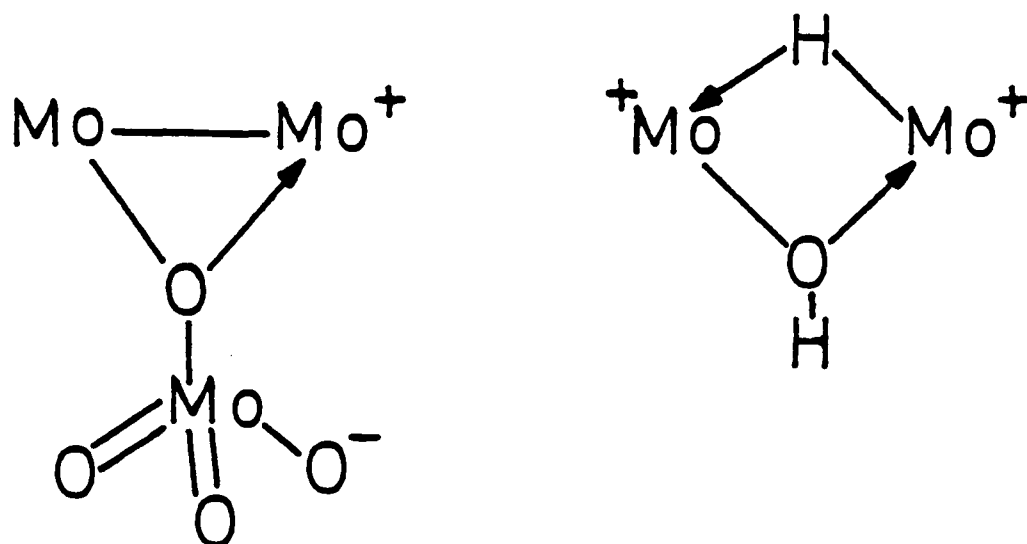


Fig. 2-23 The molecular structure of 11.

indistinguishable within experimental error.



The presence of the molybdate group was a surprise, and it is thought to originate from hydrolysis of the starting dimer by the small amount of water usually present in DMSO. The production of molybdate under such mild conditions has important implications for some of the reactions in Fig. 2-22 which seem to involve disproportionation. For example, the formation of 3 in 70% yield by reaction of 7 with NaOH is formally a reduction. The conjugate oxidation may well be formation of molybdate.

The molybdate group and its thiomolybdate analogues have been found to act as ligands to transition metals in a number of systems, and some examples are shown in Fig. 2-24. In all these examples, the molybdate group coordinates via at least two bridging oxygens, i.e. forming $M(\mu-O)_2MoO_2$ systems. Compound 11, which has only one bridging oxygen, may be thought of as a model intermediate in the formation of the doubly-bridged systems, which also occur in the well known⁶⁵ in iso- and heteropoly molybdates (see Fig. 2-24). A planar, triply-bridging molybdate-oxygen was recently found⁶² by

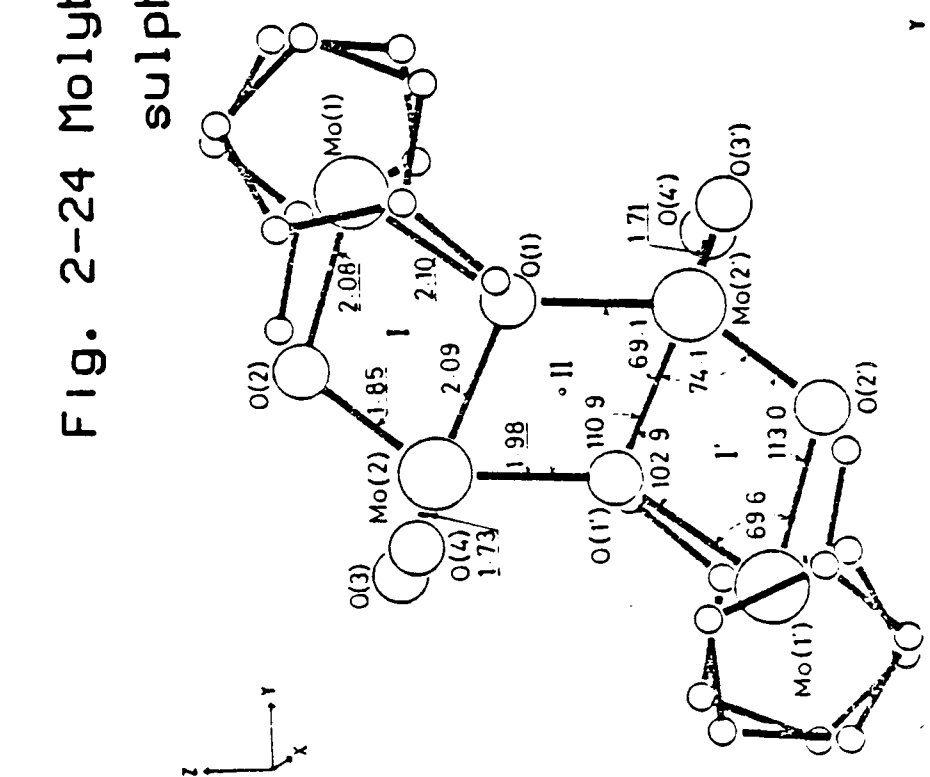
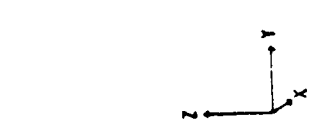
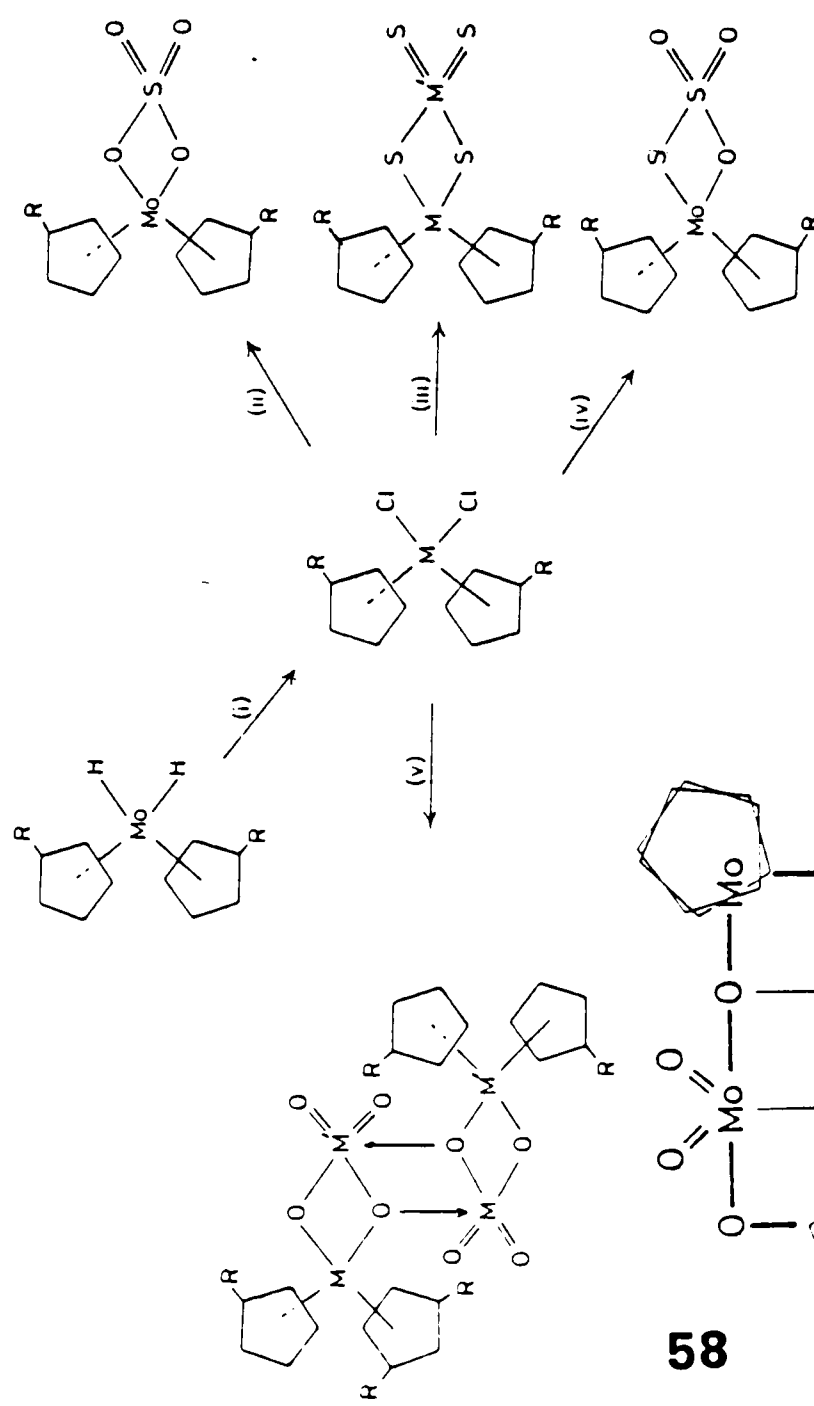
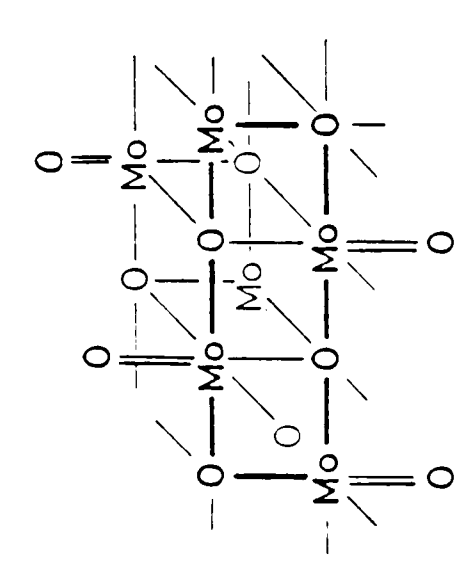
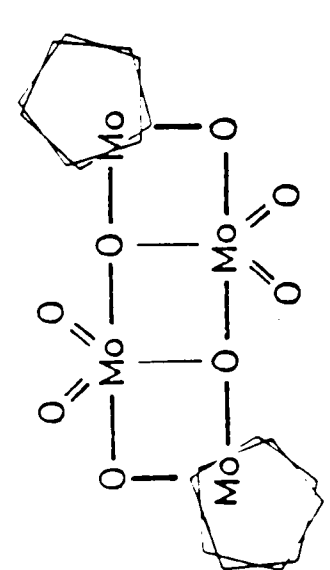
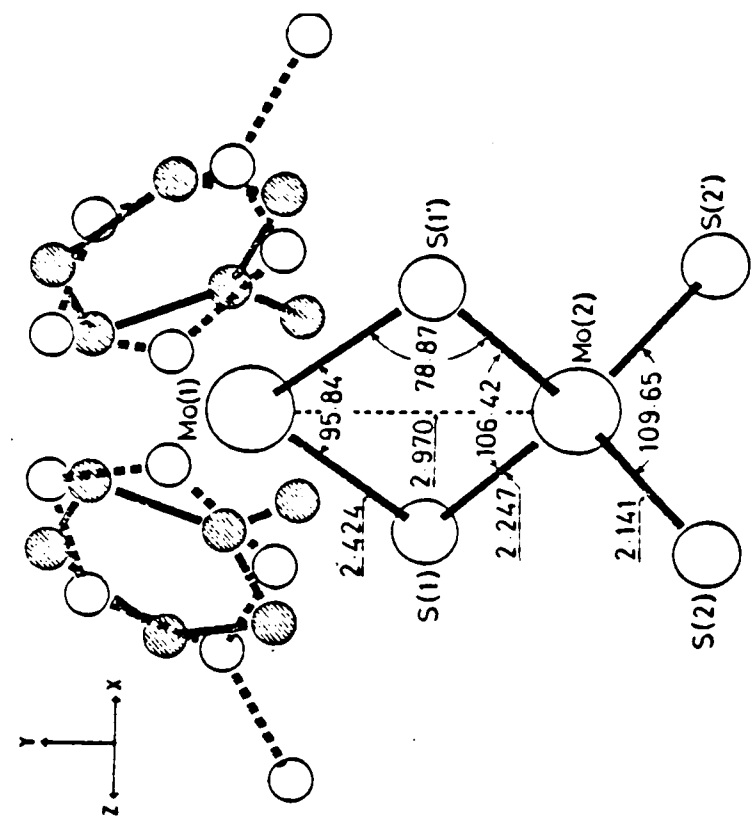
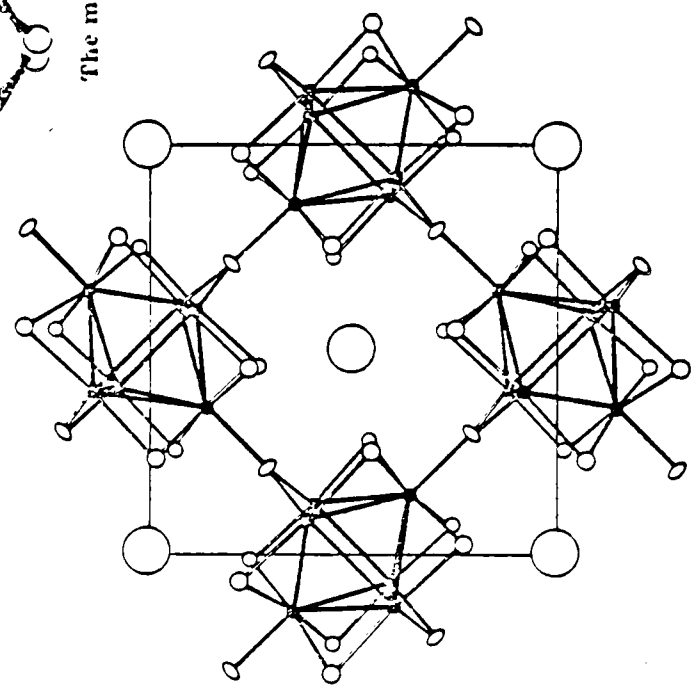
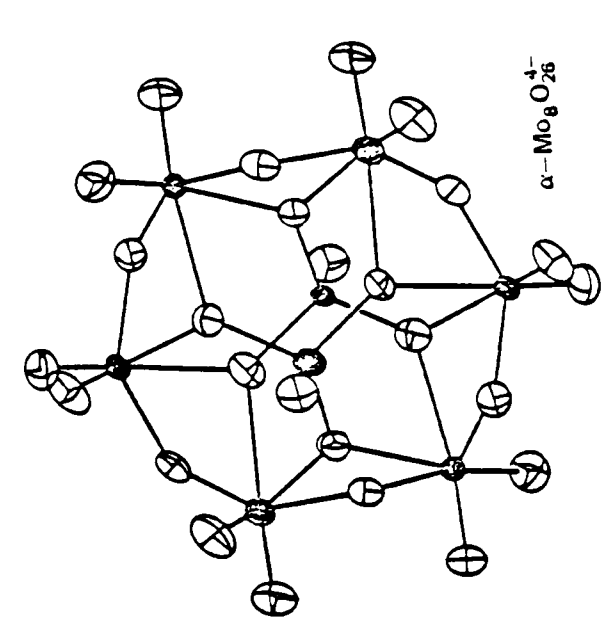


Fig. 2-24 Molybdenum oxide and sulphide derivatives.



(a) Structure of $(\eta\text{-C}_3\text{H}_4\text{CH}_3)_4\text{Mo}_4\text{O}_8$

(b) a fragment of the MoO_3 structure.

McCarley in his reduced molybdenum oxide, NaMo_4O_6 .

Compound 7, the Oxo-hydride.

When the black dimer, 5, was heated in water at 100° , two products were obtained. One product, produced in 50% yield, was spectroscopically identified as the yellow dimer, 4. The second product, isolated in 25% yield, was cationic, and an initial examination of its nmr and ir spectra suggested that one bridging hydrido ligand, two Cp rings, and two $\eta^1:\eta^5\text{-C}_5\text{H}_4$ ligands were present. The structure proposed on the basis of spectroscopic evidence was that of 'dehydro' molybdenocene with a protonated metal-metal bond (Fig. 2-7), and elemental analysis was in agreement with this. Crystals of the tetrafluoroborate salt of 7 were grown by Dr. Poveda, and I began an X-ray investigation.

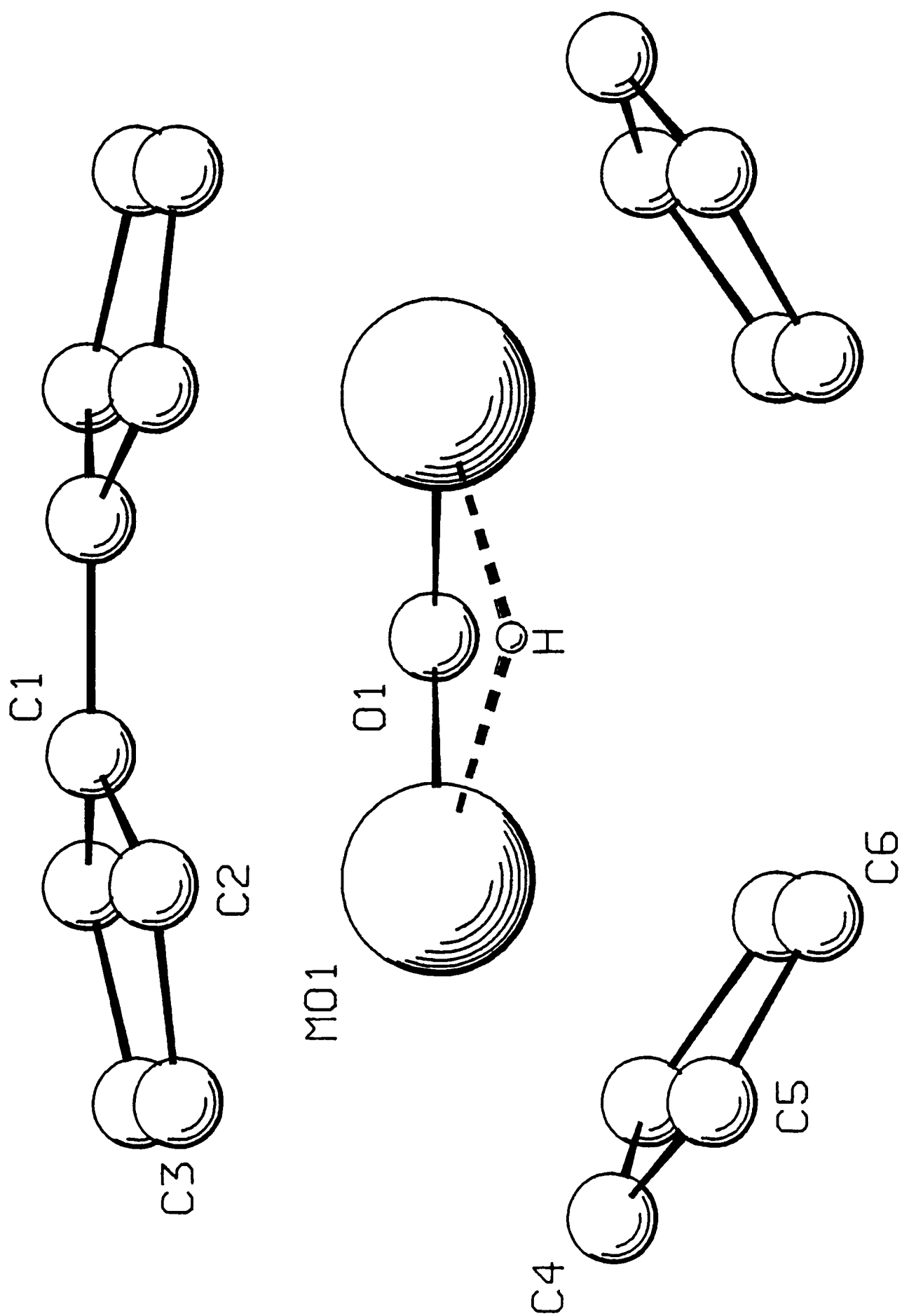
The systematic absences, as determined with the diffractometer, correspond to space groups Bbmm , $\text{Bb2}_1\text{m}$, and Bbm2 , which are nonstandard settings of Cmcm , Cmc2_1 , and Ama2 , respectively. The two latter space groups are obtained by removal of one mirror plane from the centrosymmetric space group Bbmm . The Patterson was solved for one heavy atom lying on a mirror in Bbmm , and successive difference Fouriers revealed a dimeric, Class IVa structure, with two terminal Cp rings and a fulvalene bridge, not the $\eta^1:\eta^5\text{-C}_5\text{H}_4$ rings that were expected. Furthermore, a bridging oxygen was found disordered on either side of the Mo-Mo vector. With this characterization, Dr. Poveda was able to confirm, by

reversible protonation to give the hydroxy-hydrido dimer 8, that compound 7 is the oxo-hydride shown in Fig. 2-26 (note that the oxygen is disordered over two sites, O1 and O1B, as discussed below). An appropriate elemental analysis was also obtained. Although no hydride was located in the X-ray study, a hydride is seen in the nmr spectrum of 7, thus eliminating the isomer with a metal-metal bond and a bridging hydroxy group, in spite of its apparently greater thermodynamic stability (O-H bonds are very strong, a typical bond enthalpy being 111 kcal/mol).



The oxo-hydride structure refined to an R of 9.7% ($R_w=11.9\%$) with isotropic temperature factors for the bridging oxygen and BF_4^- counterion, and anisotropic temperature factors for the carbons and molybdenum. The boron is located at (0,0,1/2), a site of 2/m symmetry, and the tetrahedral BF_4^- is correspondingly disordered. A model of four superimposed anions was refined, and the final dimensions are good, but the temperature factors are large. Such disorder is to be expected for highly symmetrical ions, but there also appears to be disorder in the organometallic cation. The temperature factors of the terminal Cp carbons are large and $U[22]$ of the molybdenum is surprisingly large, as well. A comparison (Fig. 2-27A) with the structure of the molybdato-bridged dimer shows the cause of this disorder. When the bridging oxygen is on one side of the M-M vector, the five-membered rings bend away to

Fig. 2-26 Compound 7.



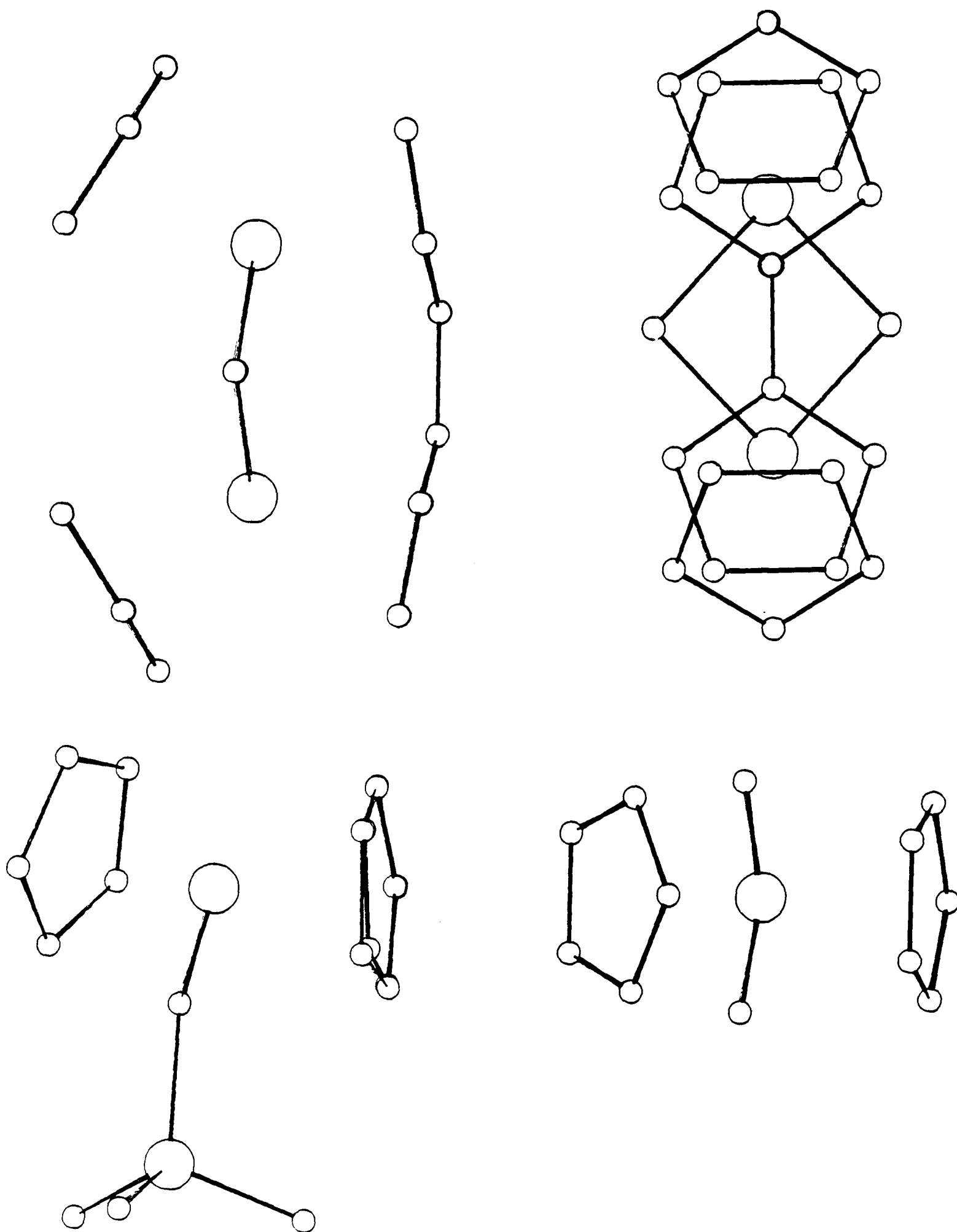


Fig. 2-27A A comparison of 7 and 11.

avoid unfavorable contacts. Since the oxygen is disordered over both sides of the metal-metal bond, the Cp-rings will be tilted both ways in the crystal. It also seems, from the large $U[22]$ of the molybdenum, that the true position of Mo(1) in each molecule is displaced slightly from the mirror plane, and this displacement is also disordered. The thermal ellipsoids are shown in Fig. 2-27B.

It can be extremely difficult to distinguish between a disordered structure that possesses a mirror plane, and an ordered structure with only approximate mirror symmetry. On removal of the mirror plane containing the molybdenum, the space group becomes $Bb2_1m$. The structure was refined in this space group, and refinement converged at $R=11\%$ with all atoms isotropic except the molybdenum. However, all attempts to refine the carbons anisotropically resulted in physically unreasonable temperature factors for at least one atom (the thermal ellipsoids had negative volumes). The entire structure was highly unstable towards least-squares refinement, and only converged with the extensive use of dimensional constraints of the Waser-Rollet^{66,67} type. No set of constraints could be found to keep all the temperature factors positive, and $U[22]$ of Mo(1) did not take on a reasonable value.

In conclusion, it must first be said that the crystal did not diffract well, and only 488 unique reflections were observed. The structure would not be determined to high precision with such a small data set, even if no disorder had been present. On the basis of the unsuccessful refinement in $Bb2_1m$, and the rather poor refinement in $Bbmm$, the latter

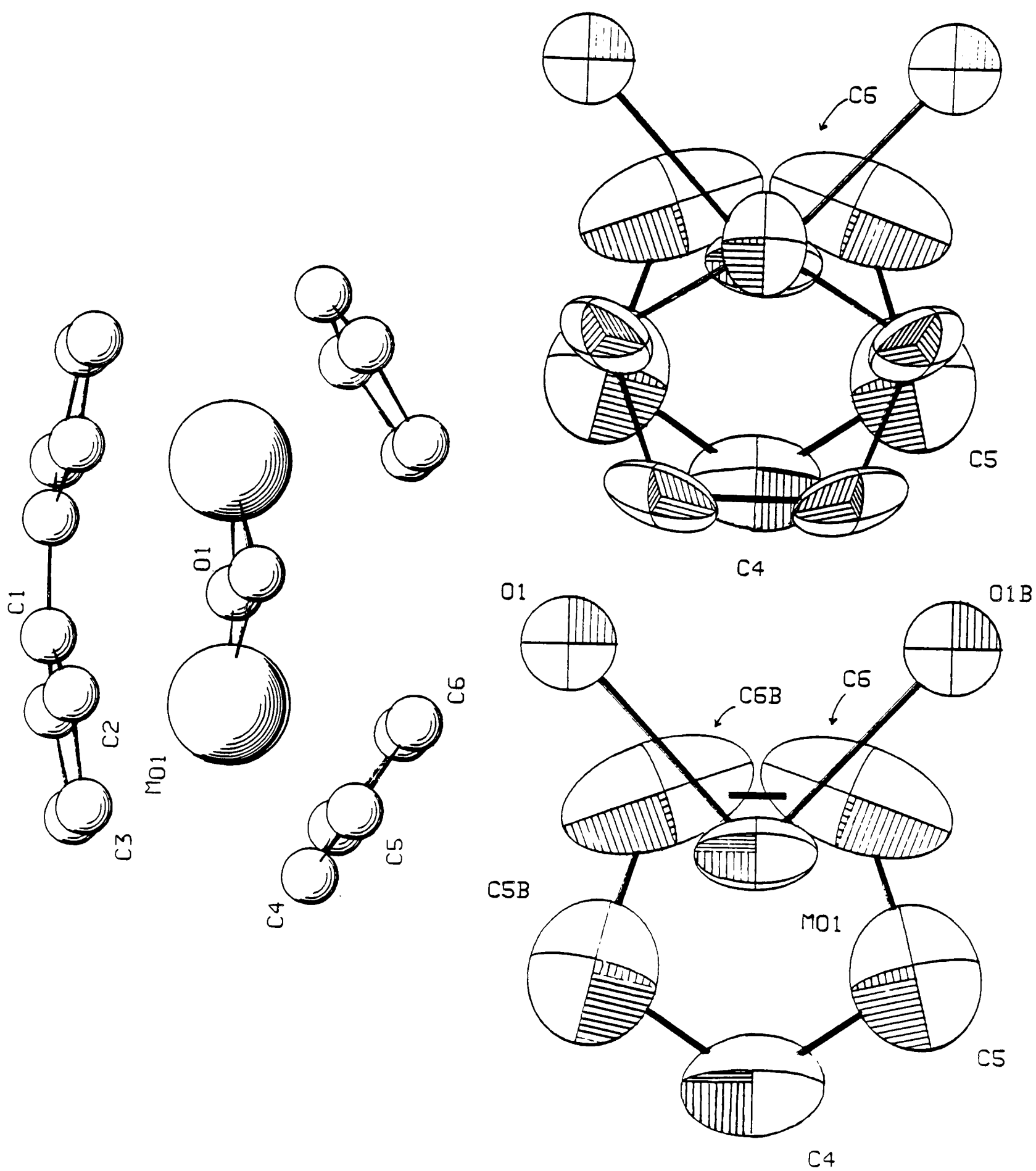


Fig. 2-27B Thermal ellipsoid plots of 7, showing the disorder.

space group does seem more acceptable. It may be that long-range ordering of the different molecular orientations prevents the assignment of a true space group, or requires a super-lattice description, but the data are not of sufficient quality to permit a detailed analysis. It has been possible, however, to identify the molecular structure with some confidence, and to obtain approximate molecular dimensions.

The sulfur-bridged dimer, 10.

When the green dimer 3 was reacted with elemental sulfur in toluene, a low yield of dark-red crystals was obtained. The mass spectrum of these crystals shows a characteristic molybdenum dimer envelope at $m/e=480$, corresponding to the formula $\text{Mo}_2\text{C}_{20}\text{H}_{18}\text{S}$. The data suggested that compound 10 was a neutral, sulfur-bridged analogue of the oxygen-bridged dimers 7 and 11, and I began an X-ray diffraction study.

The space group of 10 is $\text{P}2_1/a$, and the unit-cell volume is $3148 \text{ \AA}^3$. Using the approximate figure of $20 \text{ \AA}^3$ per nonhydrogen atom, there should be eight molecules in the unit cell, which means two molecules in the asymmetric unit. Asymmetric units of metallocene dimers have been found to contain half, one, two²², and three^{3,4} molecules, so the present case is not unique. However, the Patterson becomes increasingly difficult to solve with large numbers of heavy atoms, and Guggenberger had to use Patterson supersition techniques to solve the structure of $[\text{Nb}(\text{Cp})(\text{C}_5\text{H}_4)\text{H}]_2$, which is a six-heavy-atom problem. The striking feature of the

Patterson of 10 is a peak at $(1/2, 0, 1/2)$, which almost corresponds to the nonprimitive lattice translation of a B-centred cell, but is only 75% as large as the origin at $(0, 0, 0)$. This 'pseudo-B-centering' suggests that a large proportion of the scattering matter of one molecule is related to that of the second molecule by a translation of $(1/2, 0, 1/2)$, but that the relationship does not hold for all atoms. A solution for the Patterson was obtained by assuming that the $(1/2, 0, 1/2)$ peak corresponded to intermolecular Mo-Mo cross-vectors, and successive Fourier maps revealed the Cp rings, bridging sulfur, and fulvalene ligands of a Class IVb species, as shown in Fig. 2-28. The final R-value is 3.8%, $R_w = 4.2\%$.

The average Mo-S bond length in 10 is $2.419(6) \text{ \AA}$, similar to the distance of $2.424 \text{ \AA}$ found⁶⁴ for $\text{Cp}_2\text{Mo}(\mu\text{-S})_2\text{MoS}_2$ (see Fig. 2-24), but this thiomolybdate derivative has Mo-S-Mo angles of 78.9° , somewhat more acute than the 83° angle of 10. The Mo-S-Mo bond angle can be as acute as 64° , when the Mo-Mo interaction is strong⁹². The metal-metal bond lengths in the two independent molecules of 10 are $3.202(1)$ and $3.214(1) \text{ \AA}$, very significantly longer than those found in the three oxygen-bridged dimers 7, 8, and 11, and approaching that of the trihydride cation 9. This long distance lead me to question the presence of a direct Mo-Mo bond in 10, and I examined the final difference-Fourier for signs of hydrido ligands. There is a peak at a height of one electron, $1.8 \text{ \AA}$ from one molybdenum of each independent dimer unit, so that structures B and C had to be considered as well as A. All of

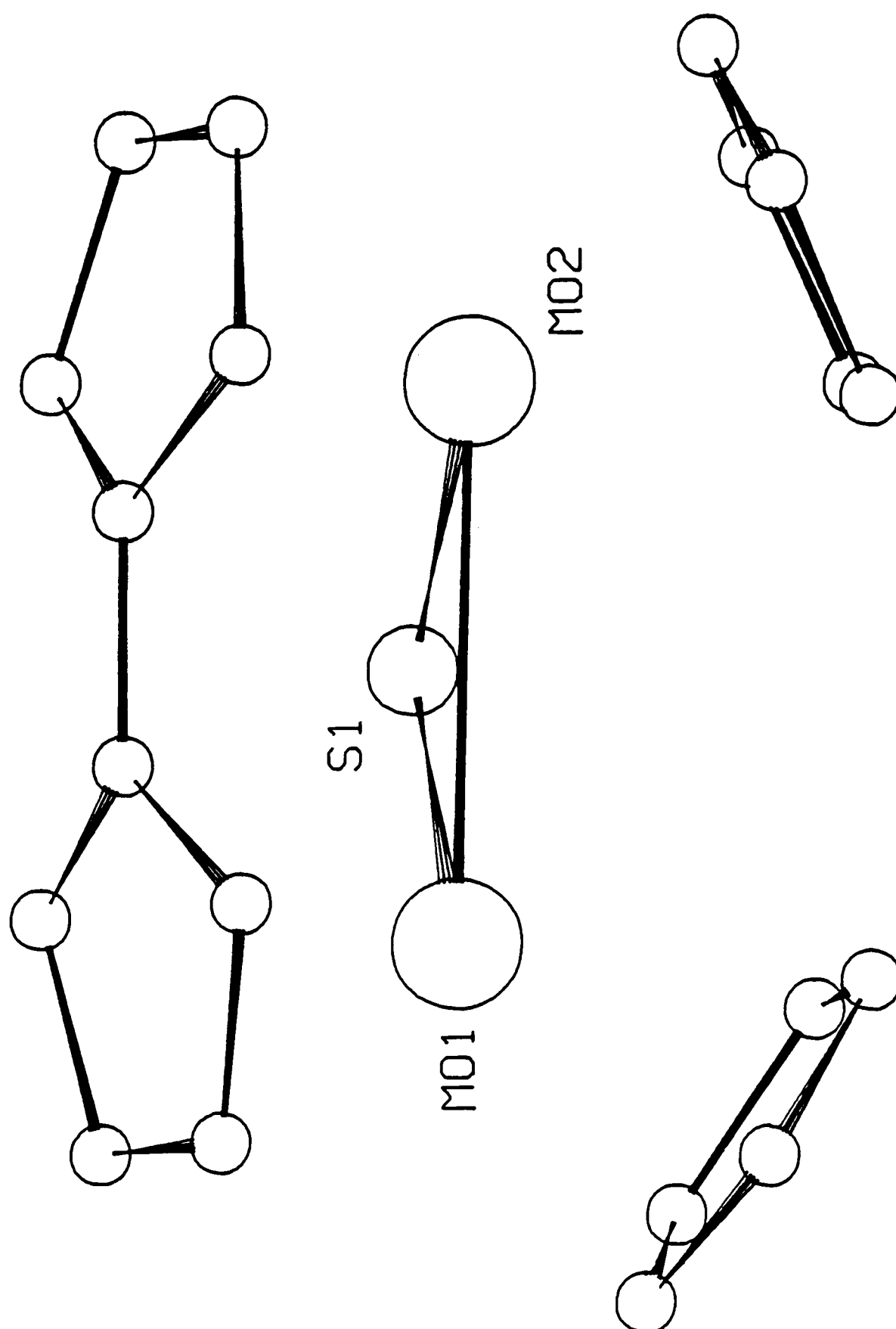
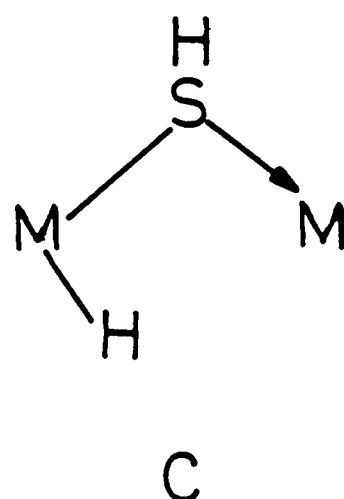
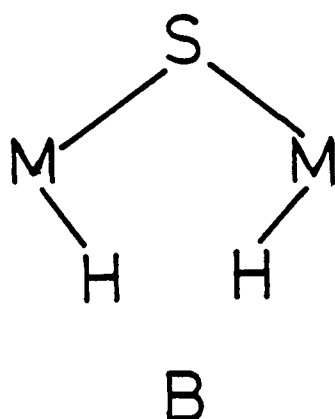
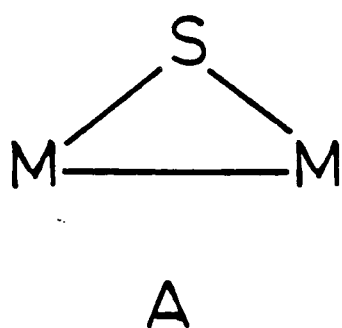


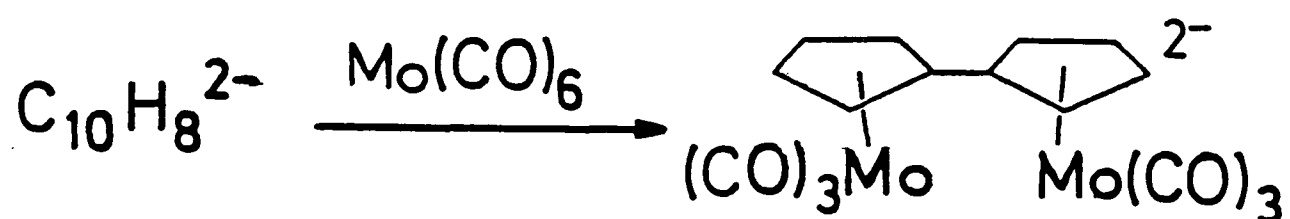
Fig. 2-28. Compound 10, molecule 1.

these structures could be distinguished by ir and nmr spectroscopy, but 10 had not been synthesized by Dr. Poveda in sufficient quantity to permit spectroscopic characterisation. I therefore repeated the synthesis of 10 on a 100mg scale, having first made the green dimer 3 by heating the black dimer 2 in toluene, at 80°, overnight. On addition of a slight excess of elemental sulfur (S_8) to a stirred, toluene solution of 3 at room temperature, there was an immediate reaction and formation of a red precipitate. The sulfur was added under a gentle flow of argon, and, within seconds, the distinctive odor of H_2S could be detected. The reaction was found to give a mixture of products, and characterisation is not yet complete.

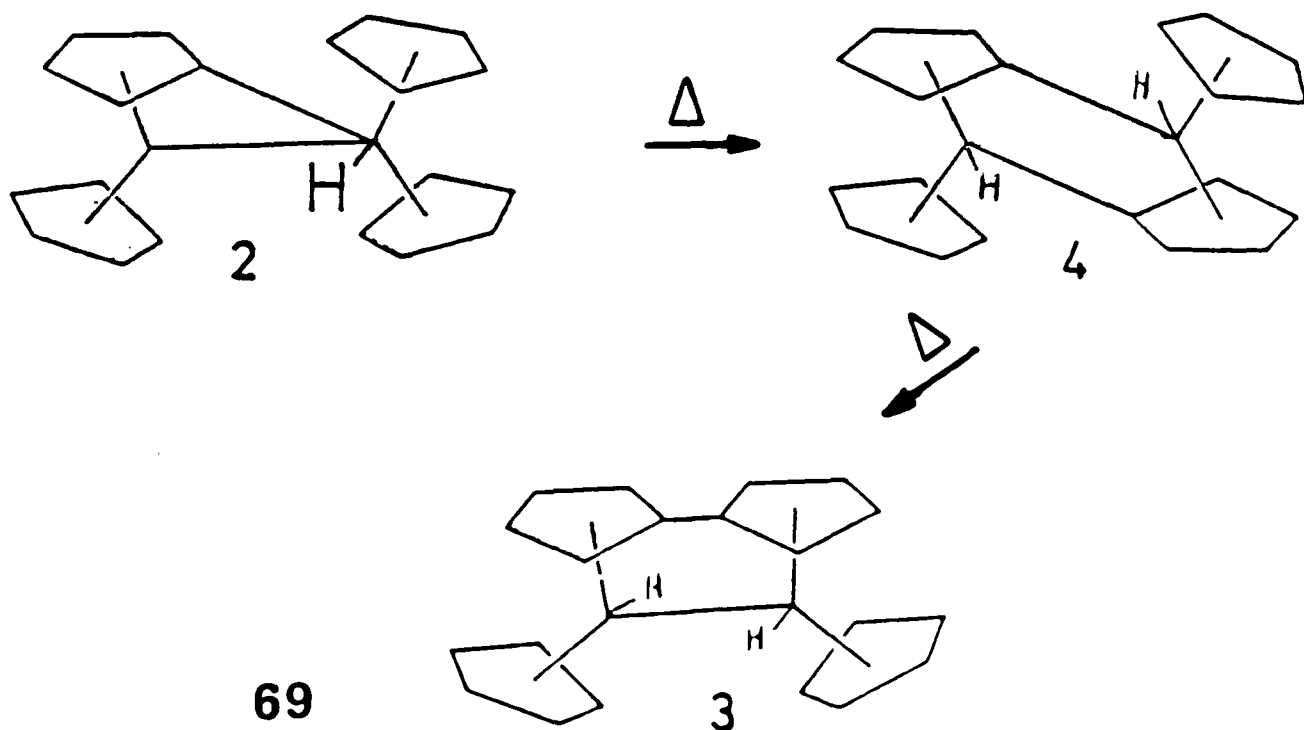


2.5 Fulvalene Dimers: Their formation, structure, and rearrangement to give Class III products.

The preparation of fulvalene complexes from the dianion $C_{10}H_8^{2-}$ has been investigated by Smart^{20,33}, and he has isolated mono- and bis(fulvalene) metal derivatives. For example³⁴,

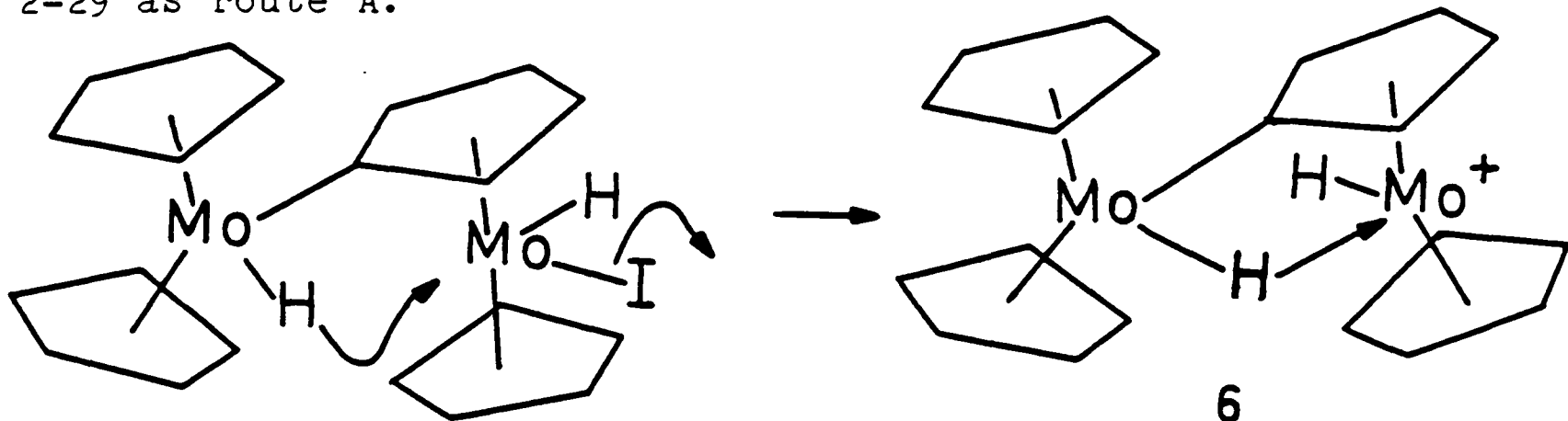


However, many metallofulvalenes have been made by the reaction of cyclopentadienide with suitable metal substrates, followed by a process of metal-assisted carbon-carbon bond formation. This process involves more than one step, and some reaction intermediates have been isolated under the proper conditions. Equation 2-11 shows such a process for molybdenocene, invoking the now familiar, fully characterised, black, yellow, and green dimers (Fig. 2-7).



2-11

There are even more ways to form a fulvalene ligand with Group VI metals, as shown in Fig. 2-29. Dr. Poveda's discovery of route B led me to propose the following mechanism to explain the formation of 9 from $\text{Cp}_2\text{Mo}(\text{H})\text{I}$ and MeMgBr , shown in Fig. 2-29 as route A.



The first step is the reaction of methyl Grignard with $\text{Cp}_2\text{Mo}(\text{H})\text{I}$ to form $\text{Cp}_2\text{Mo}(\text{Me})\text{H}$. This thermally unstable alkyl hydride then eliminates methane to form molybdenocene, which can attack a C-H bond of another $\text{Cp}_2\text{MoH}(\text{I})$ molecule. The result is a Class II, dihydrido-iodide species. The formation of a 3-centre, 2-electron Mo-H-Mo bond then accompanies loss of iodide, yielding the known cation, 6. The final reaction step is recrystallization from hot acetone, which, in light of Dr. Poveda's results, we would expect to isomerize 6 to 9. This mechanism is meant to sketch the overall course of the reaction; 6 was not actually isolated under the conditions of route A, and may only appear transiently, during the heating process.

In the next sections, I discuss the relationship between bonding, structure and reactivity of fulvalene derivatives, drawing on my own results and on the literature. The bonding in metallofulvalene derivatives may be described with reference to three valence-bond representations of the ligand.

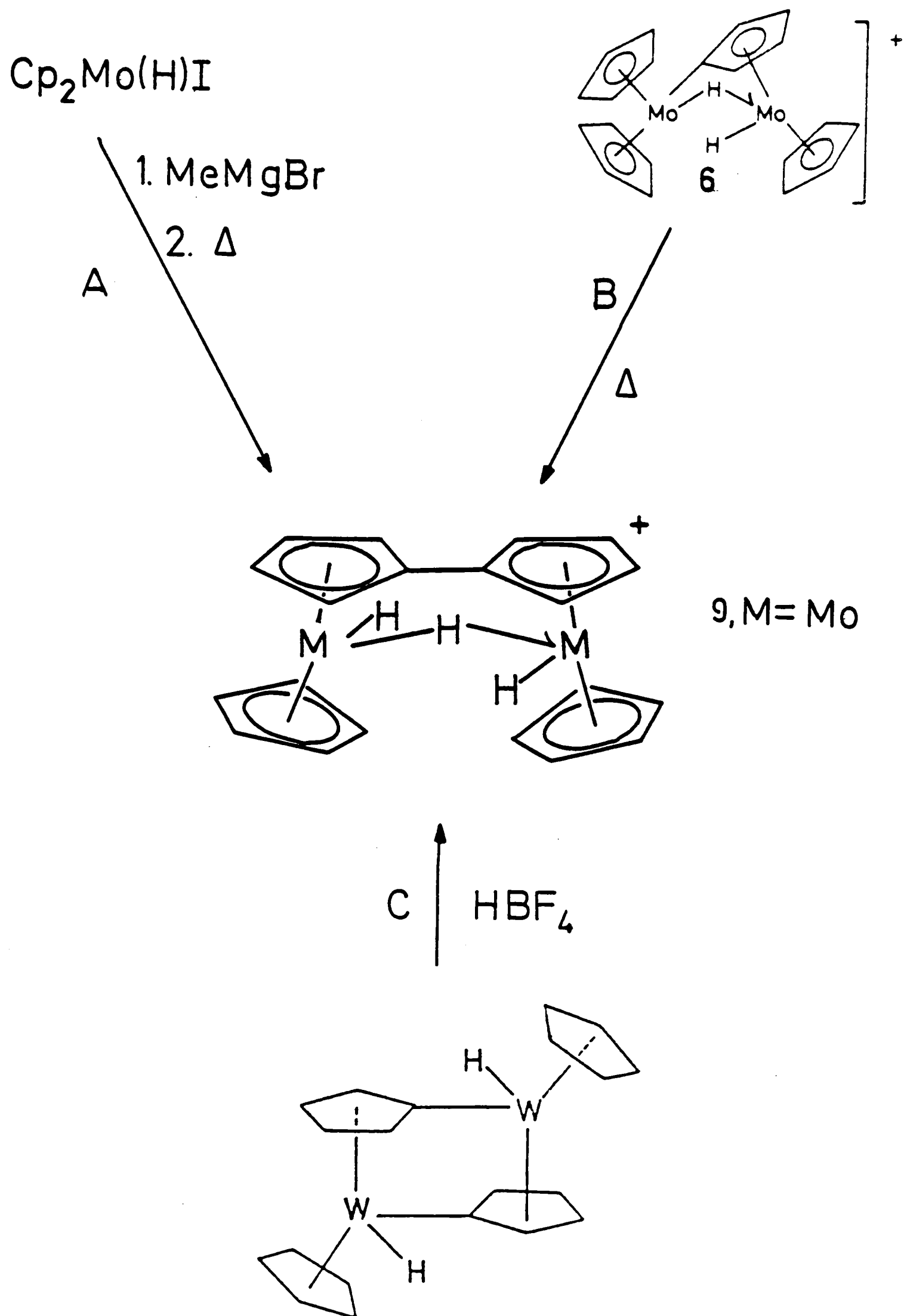
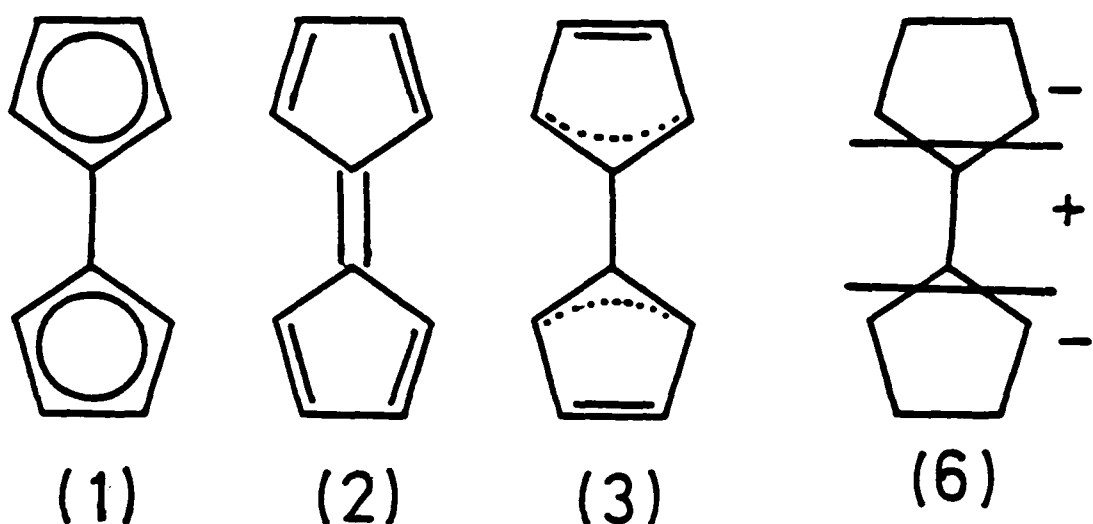
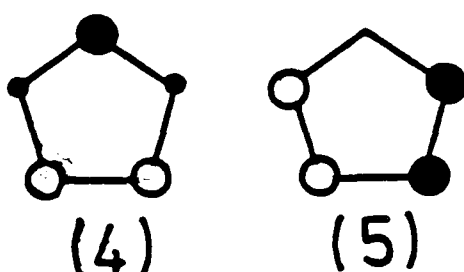


Fig. 2-29 Formation of the fulvalene ligand.

Resonance form (1) is of major importance when the two halves of the fulvalene ligand do not perturb each other significantly.

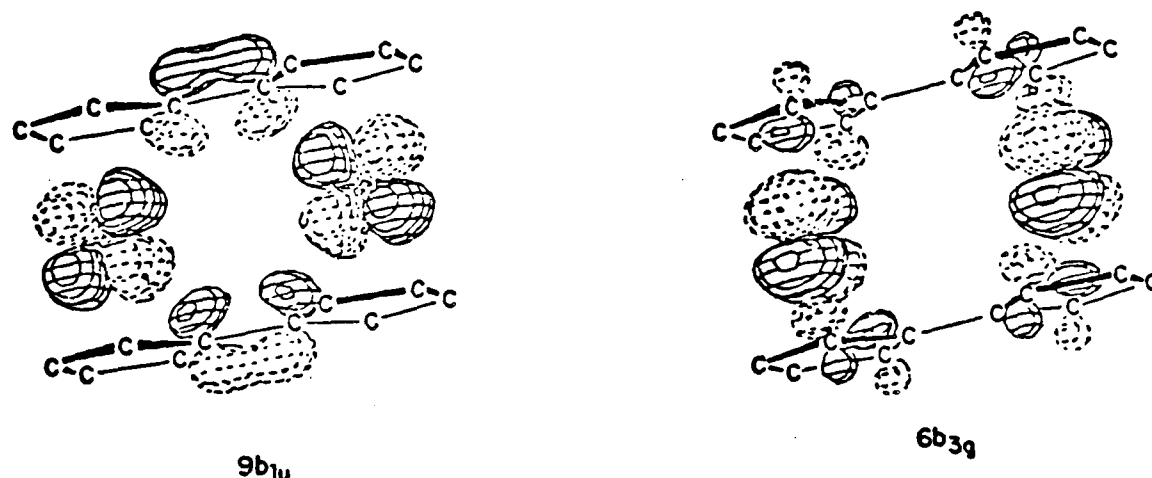


There will be unequal contributions from (2) and (3) in compounds where the degeneracy of the e_1 orbital [(4) and (5)] is lifted. Resonance form (2) has been proposed as a major contributor to two structures, $[\text{TiCpCl}]_2(\text{C}_{10}\text{H}_8)$ ⁶ and $[\text{Ni}(\text{C}_{10}\text{H}_8)]_2$ ³⁹.



The Class VI Ni compound is diamagnetic, unlike monomeric nickelocene, and has³⁹ an M-M separation of 4.163 Å. A direct metal-metal bond is therefore unlikely. The bridging C-C bond length, D, is 1.433 Å, and these dimensions are consistent with its formulation as two independent, bis(diene)Ni(0) units, joined by carbon-carbon double bonds. The same systematic variation in the C-C bond lengths of the fulvalene rings was found in both $[\text{TiCpCl}]_2(\text{C}_{10}\text{H}_8)$ and $[\text{Ni}(\text{C}_{10}\text{H}_8)]_2$. Two long bonds (1.433 Å), two short bonds (1.403 Å), and one medium bond are disposed about a noncrystallographic mirror plane that contains the bridging C-C bond and the metals; the long bond is adjacent to the bridge. These dimensions were cited by Olthof⁶ and Sharp *et al*³⁹ as further support for the

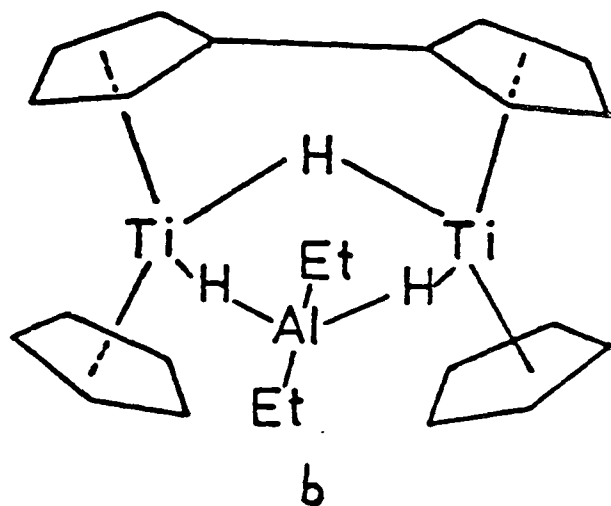
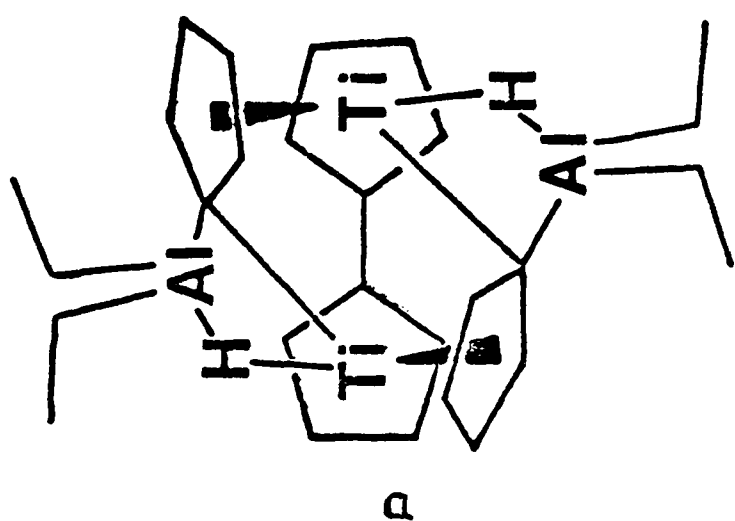
importance of valence bond description (2), although the latter group used extended Hückel theory to provide a more satisfactory description of bis(fulvalene) M_2 compounds. When all the intra-ring C-C bonds were set to 1.44 Å, the calculations yielded overlap populations in agreement with the observed bond length variations, and also predicted that the analogous cobalt compound would have an even shorter bridging distance, D. The combination of two 20-electron, D_{5h} Cp_2Ni fragments led to the frontier orbitals shown here, which are antibonding with respect to metal-ligand interactions.



The interpretation of the bond length variations in $[Ni(C_{10}H_8)]_2$ in terms of resonance form (2) is an oversimplification that can be misleading, since the C-C bonds in 'bis(butadiene)Ni(0)' should be nearly the same length⁶⁸, as a result of back-bonding from the zero-valent metal centre to the ligand π^* orbitals. If the nickels preferentially accept from a ligand orbital resembling (3), then the resulting ligand dimensions will resemble (2). This certainly does not imply that the metals are zero-valent. In fact, Sharp's calculations showed that (3), a (4)+(4) combination, can mix with higher-lying δ^* orbitals, resulting in a shift of the nodal planes as shown in (6). Occupation of the HOMO's derived from (6) and the (5)+(5) combination then

accounts for the structure of $[\text{Ni}(\text{C}_{10}\text{H}_8)]_2$, but not its diamagnetism. Sharp et al suggested that configuration interaction could stabilize the spin-paired ground state.

Figure 2-30 shows representations of eleven Class IV dimers which have been characterized crystallographically. The fulvalene and Cp ligands have been omitted for clarity. Fig. 2-30 serves as a key to Table 2-3, where some important dimensions of the compounds are listed. Two additional compounds, a and b, are included in Table 2-3; both are alkyl-aluminium derivatives of titanocene, whose structures do not fit into the simple MM'AB labelling scheme of Fig. 2-30.



Several points of structure and bonding are clarified by Table 2-3 and Fig. 2-30. First of all, the metal centres are linked by single bonds, partial bonds, or no direct bond at all, but no Class IV or V compound with a metal-metal double bond has been isolated. The reason for the reluctance of Class IV dimers to form metal-metal double bonds must lie in the strain that such bonds would cause in the fulvalene ligand. Although I have stressed the flexibility of the C_{10}H_8 ligand, there must be a limit to the amount of distortion that it can undergo. Table 2-3 shows that, for an M-M distance of $2.834 \text{ \AA}$ (quite a short single bond compared to $2.86 \text{ \AA}$ in Nb metal)

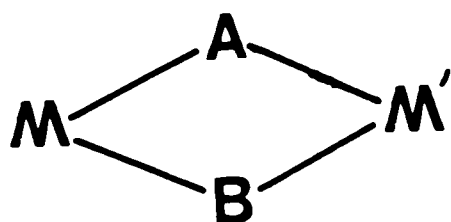
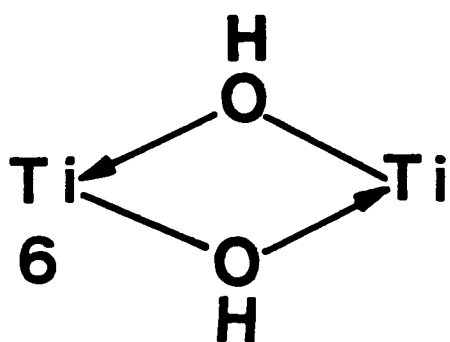
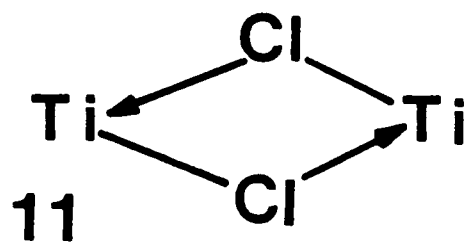
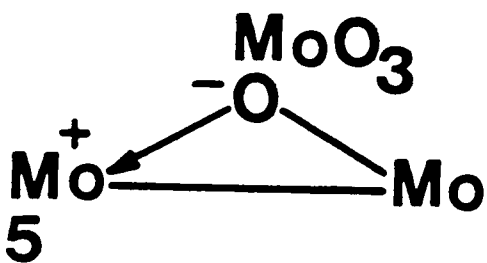
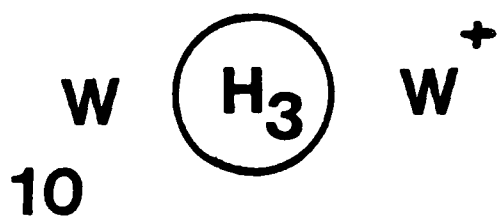
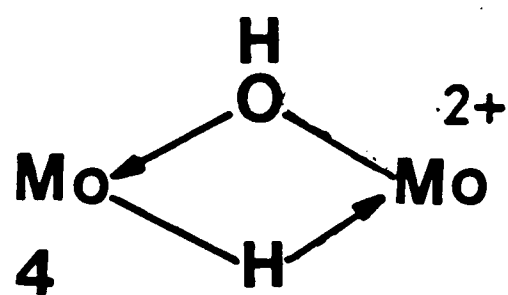
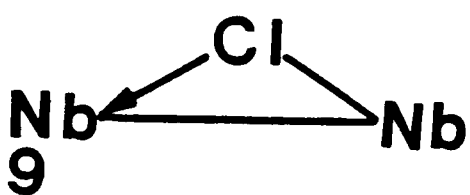
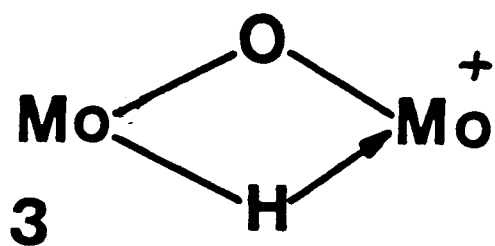
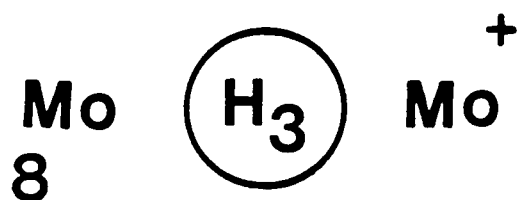
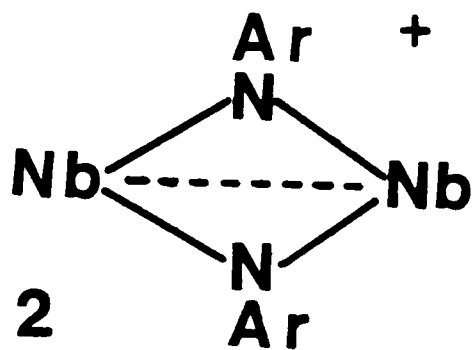
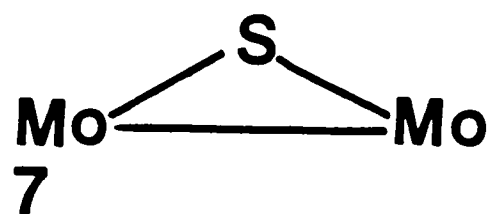
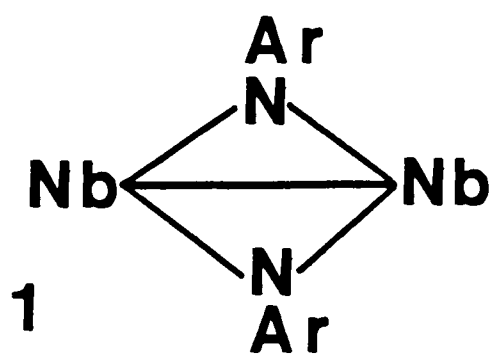


Figure 2-30. Fulvalene dimers;
Key to Table 2-3.

	<u>M-M'</u>	<u>M-A</u>	<u>M-B</u>	<u>M'-A</u>	<u>M'-B</u>	<u>AMB</u>	<u>MAM'</u>	<u>AM'B</u>	<u>MBM'</u>	<u>w</u>	<u>D</u>	<u>REF</u>
1	2.834	2.01	2.10	1.96	2.08	95	87	88	89	32	1.53	69
a	2.910	2.46								25.8	1.45	32
2	2.921	2.048	2.031	2.035	2.055	87.7	91.3	87.4	91.3	24.5	1.46	69
3	2.982	2.03		2.03			94			21.6	1.45	*
4	3.053	2.07		2.09			94.3			18.1	1.42	28
5	3.076	2.085		2.093			94.9			19.3	1.42	*
6	3.195	2.10	2.05	2.10	2.05	76.0	98.8	74.8	102.7	15.1	1.43	29
7	3.202	2.413		2.419			83.0			17.7	1.45	*
	3.214	2.426		2.416			83.2			16.6	1.44	*
8	3.229	The hydrido ligands were not located								17.5	1.45	*
9	3.270									15.1	1.46	70
10	3.359	The hydrido ligands were not located								16.6	1.41	30
b	3.374	1.80	1.69	1.80	1.69		138			12.5	1.45	71
11	3.638	2.514	2.524	2.524	2.514	81.29	92.47	81.29	91.47	5.3	1.455	6

Table 2-3. Important dimensions of Class IV and V dimers. Distances are in Å and angles in (°). The angle w is the dihedral angle between five-membered rings of the fulvalene and D is the length of the C-C bond joining them. For compounds 1 to 11, see Fig. 2-30; for compounds A and B, see the text.

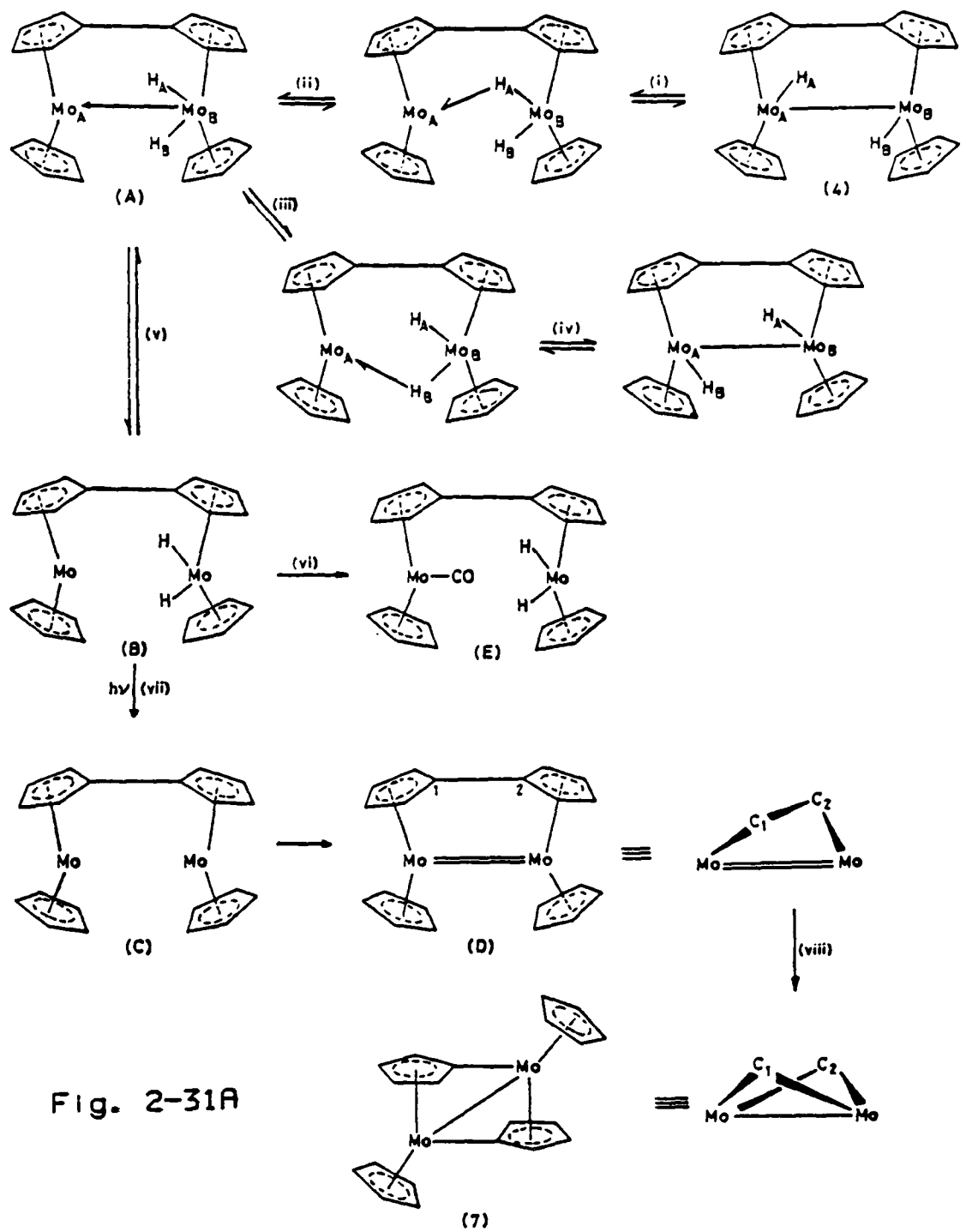
the dihedral angle w between the C_5 rings of the fulvalene is 32° . The effect of this large angle can be seen in the length, D , of the C-C bond that joins the two halves of the fulvalene: for examples 2 to 11 in Table 2-3, $D_{ave} = 1.44(2) \text{ \AA}$, indicative of nearly the same double-bond character as is commonly found in Cp rings. However, in ex. 1, D is $1.53 \text{ \AA}$, a true single-bond length. Thus, it seems that, up to $w=26^\circ$, some stabilizing conjugation can be retained across the fulvalene ligand, but it is lost very rapidly as w increases just a few degrees more. The robust nitrene bridges in ex. 1 may be the key to its stability; they hold the niobium centres close together even in ex. 3, which has had a bonding electron oxidized away. The electron may have been involved in 4-centre, Nb_2N_2 bonding, because the planarity of the M_2N_2 unit is lost on oxidation.

A rational synthesis of a Class IV dimer with metal-metal double bond would be, for example, photolysis of the green molybdenocene dimer. However, the product of this reaction was found¹⁸ to be 'dehydro' molybdenocene, 15, a Class IIIb dimer (Fig. 2-7). Typically, 15 is formed in 80% yield after 20h photolysis in pyrex apparatus with a medium-pressure, mercury lamp. This system was studied recently⁷² by Barral, Green, and Jimenez, who prepared their starting materials via the black dimer. They observed that photolysis of 3 in the presence of PPr^n_3 gave an 80% yield of cis and trans 4, with no evidence for the formation of the red dimer, 15. Prolonged photolysis of a toluene solution of 4 and $PPrn_3$ slowly produced 15, which was isolated in 30% yield after 72 h. This same behavior was found for toluene solutions

of the black dimer 2 and PPr^{n}_3 , and uv/visible spectra of the reaction mixtures confirmed that (green) 3 forms (yellow) 4 first, which then loses dihydrogen to give (red) 15.

The original mechanism¹⁸ for the formation of 15 from 3 and 4 is shown in Fig. 2-31A. Although Barral et al were able to rationalize their results in terms of a more complicated version of this mechanism, I proposed (Fig. 2-31B) the following, simpler scheme, which they subsequently adopted. I believe that the Class IIIb molecule 15 is formed by loss of H_2 from the Class IIIa dimer, 4, and that the conversion of 3 to 4 is the photochemical reverse of the thermal Class IIIa to Class IVb isomerization that I have mentioned above. This process could be observed experimentally because of the mechanism of H_2 -loss from 4. As Fig. 2-31 shows, I propose that both hydrido ligands bond to the same metal centre before they reductively eliminate, and they are able to do so because a vacant coordination site is created photochemically. The n^5 to η^3 ring-slip, which provides coordinative unsaturation, has been observed and studied in a number of systems^{73,83}, and seems a likely candidate here. When phosphine is present in solution, it readily coordinates to any available site on molybdenum, preventing the transfer of hydride via a bridging position. Thus, elimination of dihydrogen is blocked.

Since the thermal and photochemical interconversion of Class IIIa and IVb dimers involves the metal-assisted making and breaking of carbon-carbon bonds, a comparison of these processes for molybdenum and tungsten dimers might provide useful thermodynamic information about the relative M-C, M-M,



(i)–(iv) Proposed mechanism for the sequential equilibration of Mo–H in (4); (i), (ii), (v), (vi) proposed mechanism for formation of carbonyl (E); (i), (ii), (v), (vii), (viii) proposed mechanism for photochemical formation of (7) from (4)

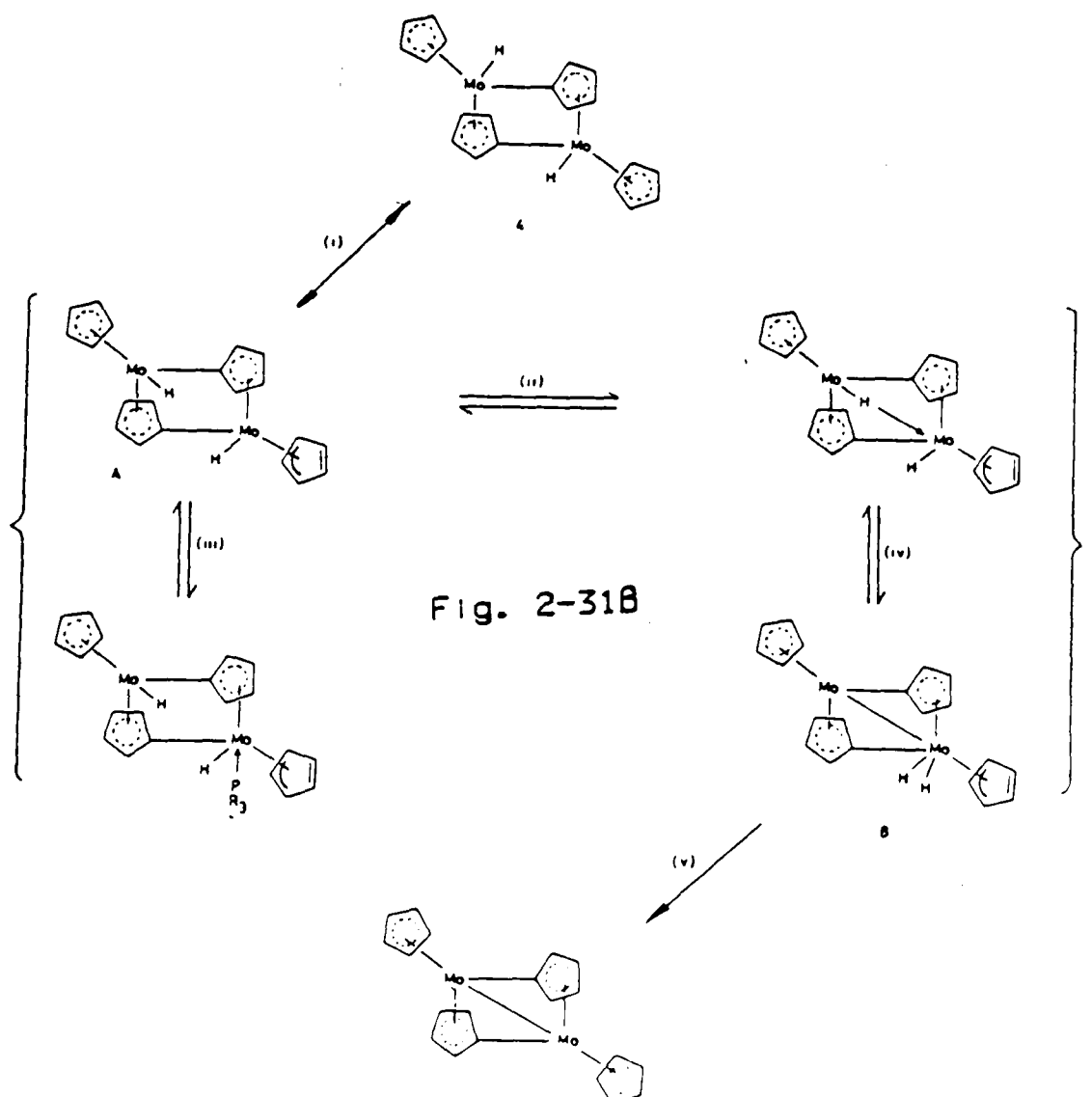


Fig. 2-31 Early and revised mechanisms for the conversion of Class IVb molybdenocene to Class IIIb 'dehydro' molybdenocene.

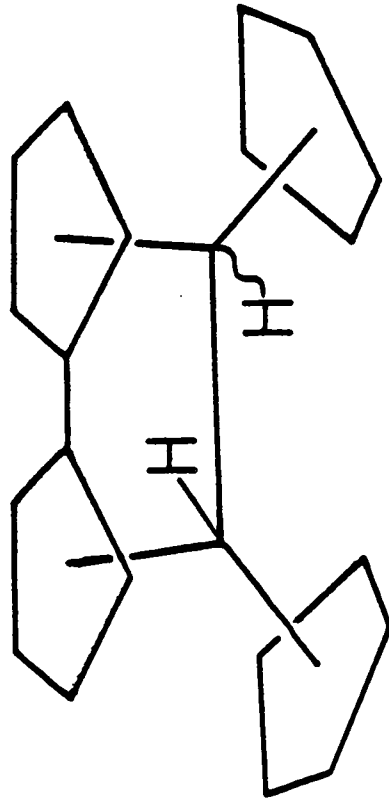
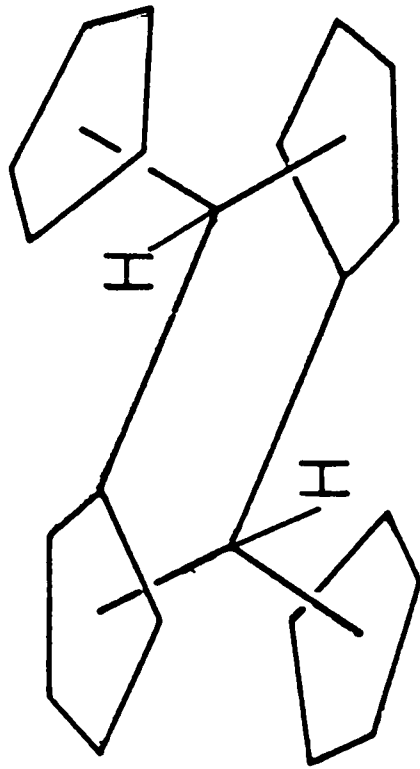
and C-C bond enthalpies for second and third-row transition metal compounds. In contrast to the behavior of yellow molybdenocene, Class IIIa tungstenocene does not thermally rearrange to a Class IVb dimer. The differences between the Class IIIa and Class IVb structures are simple: a Class IIIa dimer has two M-C sigma bonds, while the corresponding Class IVb structure has one C-C bond and one M-M bond. The stability of the Class IIIa tungsten compound may be either kinetic or thermodynamic, perhaps arising from the increase in M-C bond strength on changing from a 4d to a 5d transition metal. This increase has recently⁷⁴ been found to be 48 kJmol^{-1} , on the basis of thermochemical studies of Cp_2MMe_2 and Cp_2MCl_2 (the M-C bond enthalpies are 149.5 and 197.8 kJmol^{-1} for Mo and W, respectively). The bond enthalpy of the bridging C-C bond of the fulvalene ligand, which has partial double-bond character, should be on the order of 400 kJmol^{-1} . Finally, the Mo-Mo bond enthalpy can be estimated⁷⁵ from the following empirical formula (Eq. 2-12), where $r(\text{Mo-Mo})$ is the distance in pm, and E is in kJmol^{-1} .

$$2-12 \quad E(\text{Mo-Mo}) = 4.42 \times 10^{12} [r(\text{Mo-Mo})]^{-4.29}$$

A typical Mo-Mo separation of $3 \text{ \AA}$, 300 pm, gives a bond enthalpy of 100 kJmol^{-1} . This approximate thermochemistry is summarized in Table 2-4, which clearly suggests that the strength of C-C bonds relative to Mo-C bonds favors the Class IVb structure, even if the metal-metal bond is very weak. Furthermore, it seems that the greater strength of W-C bonds is not sufficient to reverse the situation and favor the Class

Table 2-4. Bond-enthalpy Differences Between IIIa and IVb Dimers.

<u>Metal</u>	Class IIIa	Class IVb	IVb-IIIa
	$\frac{2 \times \text{M-C}}{\text{kJ mol}^{-1}}$	$\frac{1 \times \text{C-C}; 1 \times \text{M-M}}{\text{kJ mol}^{-1}}$	kJ mol^{-1}
Mo	$2 \times 150 = 300$	$400 + 100 = 500$	$500 - 300 = 200$
W	$2 \times 198 = 396$	$400 + 100 = 500$	$500 - 396 = 104$



IIIa structure. There may, however, be an increased activation energy for this rearrangement associated with the larger W-C bond strength.

We may now ask why the tungsten and molybdenum Class IIIa dimers rearrange to Class IV structures on protonation? The answer may be found in the recent uv-PES work of Dr. J.C. Green and co-workers, who found⁷⁶ that the ionization energy of metal-centred valence orbitals is greatly increased, i.e. the orbitals are stabilized, when a bridging hydride is present. Thus, the 3-centre, 2-electron M-H-M bond is much more energetically favorable than the 2-centre, 2-electron M-M bond. In the yellow dimer, 4, no electrons are involved in direct Mo-Mo bonding, so an incoming proton does not have the opportunity to form an M-H-M bridge. It would be a 3-centre, 0-electron bridge. The proton can only attack a lone-pair of the d^2 metal centres. However, rearrangement to a Class IV structure has all the thermodynamic advantages discussed above, plus the possibility of forming a hydrido bridge. Of course, kinetics may still present a problem. However, the hydrido ligands of 9 were found^{17,18} to be fluxional by Cooper and Green, and this molecular flexibility may help overcome kinetic barriers to isomerization.

One interesting fulvalene derivative, which was reported⁷⁷ in a note, may have an M-M double bond; it is bis(fulvalene)dimolybdenum. Smart, who synthesized this Class VI dimer from molybdenum acetate and fulvalene dianion, commented on the strain that it would suffer from, and suggested various structures to explain the observed

diamagnetism. However, nmr data were reported only briefly, and low solubility required the use of a solvent (THF d^8) with complex bands (6.5 τ) in the rather wide 'Cp' region (ca. 4 τ to nearly 7 τ). Furthermore, no mass spectrum was reported in spite of the fact that sublimation was used to purify the compound. It seems possible, until further evidence is reported, that the highly strained bis(fulvalene)dimolybdenum may have broken two C-C bonds and scavenged H_2 from the solvent to form, after rearrangement, dehydro molybdenocene. Both compounds are red. Such a rearrangement would have been unexpected in the early days of metallocene dimer chemistry. A more complete characterisation of this interesting compound is eagerly awaited.

2.6 The $\eta^1:\eta^5-C_5H_4$ Bridging Ligand.

There are a number of transition-metal species which have the ability to insert into carbon-hydrogen bonds (e.g. tungstenocene¹⁷; see also Chapter 4). As measured by force-constant and bond-enthalpy criteria, aromatic C-H bonds are stronger than their aliphatic counterparts⁷⁸. However, aromatic C-H bonds often react more readily with transition-metal centres than aliphatic bonds, and they are referred to by organometallic chemists as 'activated'. The reasons for this high reactivity may be kinetic and thermodynamic:

1. The pi-system of the aromatic molecule can complex with a coordinatively unsaturated metal centre, either on a surface

or in a molecule, and can hold the C-H bonds in close proximity to the reactive site.

2. The C-H bonds of aromatic rings are more exposed to attack than those bonded to tetrahedral carbon.

3. The resultant M-C sigma bonds can be supplemented, in the case of aromatic ligands, by stabilizing pi-interactions.

Perhaps for these reasons, when tungstenocene is formed⁷⁹ by photolysis of Cp_2WH_2 in Et_2O , the product is the (cis and trans) yellow dimer, $[\text{CpW}(\text{C}_5\text{H}_4)]_2$. The abundant ethyl groups of the solvent seem to have been ignored by the transient tungstenocene, which inserted into the activated C-H bond of a Cp ring to give a Class IIIa dimer. One important characteristic of photochemical reactions should be remembered, however. The products isolated from photochemical reactions must photochemically stable. Tungstenocene may insert into a C-H bond of Et_2O , but, if the product is unstable with respect to photoregeneration of Cp_2W and Et_2O , then Cp_2W will be free to react again until a photostable species is formed. The delocalized aromatic systems may have available relaxation pathways other than M-C bond cleavage.

Because of the preference of transition metals for aromatic C-H bonds, a number of $\eta^1:\eta^5\text{-C}_5\text{H}_4$ derivatives have been isolated. Furthermore, the crystal structures of more than ten compounds containing $\eta^1:\eta^5\text{-C}_5\text{H}_4$ ligands have been determined. The molecules result from the activation of Cp rings by transition metals, and their structures provide an opportunity to study the nature of the bridging ligand, its interaction with metal centres, and the way that its structure

is affected by that interaction. Some important dimensions of the molecules are given in Table 2-2, the key to which is as follows:

M-C(σ) is the η^1 bond length .

C-C(σ)-C is the endocyclic angle at the η^1 carbon.

σ -bond is the angle between the η^1 -bond vector and the C_5 -ring plane.

a Average of two chemically equivalent molecules.

b Dimension not available.

c Average of three chemically equivalent molecules.

d Two chemically non-equivalent sites.

* This work.

There are a number of compounds (1. to 9.) in Table 2-2 whose metal centres do not attain 18-electron configurations unless a metal-metal bond is postulated. However, examples (3.) to (9.) have M-M distances that significantly longer than the sum of the appropriate metallic radii. Bonds of 2.80, 2.82, and 2.97 Å would be expected for dimers of Mo, W, and Ti, respectively. It is, therefore, questionable whether direct M-M bonding occurs in these molecules to any significant degree. It has been generally known since the early work of Mason and Mingos⁸² that bridged metal-metal 'bonds' are found over a wide range of distances for compounds with the same formal bond order, but different molecular environments. We must find more reliable criteria than length to assess the bonding in the present series of dimers.

Table 2-2. Important dimensions of transition-metal dimers containing the $(\eta^1:\eta^5\text{-C}_5\text{H}_4)$ group.

Compound	M-M (Å)	M-C(σ) (Å)	C-C(σ)-C (°)	σ-bend (°)	ref.
1. $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\eta^1:\eta^5\text{-C}_5\text{H}_4)]_2$ ^a	2.886(1)	2.21(1)	105(1)	38	22
2. $[\text{Ti}(\eta^1:\eta^5\text{-C}_5\text{H}_4)(\text{HAlet}_2)]_2(\text{C}_{10}\text{H}_8)$	2.910	2.46	b	b	32
3. $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_4$	2.961	2.00	103.0	40	15
4. $\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2(\text{H})(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2$	2.968(1)	2.189(5)	102.9(4)	34	49
5. $\text{W}(\eta^5\text{-C}_5\text{H}_5)(\eta^1:\eta^5\text{-C}_5\text{H}_4)(\mu\text{-H})_2\text{Ir}(\text{H})(\text{PEt}_3)_2$	3.0771(7)	2.073(8)	106.5	33	80
6. $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\eta^5:\eta^1\text{-C}_5\text{H}_4)\text{Mo}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$	3.098(1)	2.117(4)	103.1(3)	30	*
7. $[\text{Nb}(\text{H})(\eta^5\text{-C}_5\text{H}_5)(\eta^1:\eta^5\text{-C}_5\text{H}_4)]_2$ ^c	3.105(5)	2.23(2)	102(2)	32	4
8. $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{H})\text{Mo}(\eta^1:\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)$	3.189(2)	2.21(1)	106(1)	30	*
9. $\text{Ti}_2(\eta^5\text{-C}_5\text{H}_5)_3(\eta^1:\eta^5\text{-C}_5\text{H}_4)(\text{C}_4\text{H}_8\text{O})\bullet(\text{C}_4\text{H}_8\text{O})$	3.336(4)	2.19(2)	103(1)	25	16
10. $[\text{W}(\text{H})(\eta^5\text{-C}_5\text{H}_5)(\eta^1:\eta^5\text{-C}_5\text{H}_4)]_2$	3.811(1)	2.19(1)	107	11	21
11. $\overline{\text{cis-}}[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CH}_2\text{SiMe}_3)(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{W}(\text{H})-(\eta^5\text{-C}_5\text{H}_5)(\eta^1:\eta^5\text{-C}_5\text{H}_4)]^{\text{d}}$	3.816(1)	2.15(2)	101(2)	10	21
12. $\overline{\text{trans-}}[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CH}_2\text{SiMe}_3)\text{W}(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{W}(\text{H})-(\eta^5\text{-C}_5\text{H}_5)(\eta^1:\eta^5\text{-C}_5\text{H}_4)]^{\text{d}}$	3.859(1)	2.18(1)	104(1)	11	21
13. $[\text{Nb}_2(\text{H})_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{OSiMe}_2-\eta^5:\eta^1\text{-C}_5\text{H}_3)_2]-[\text{Na}(\text{OEt})_2]_2$	3.932(1)	2.311(7)	105.2(6)	12.3	81

We may consider by what mechanism the metals achieve their close approach, which is certainly closer than the nonbonded contacts found in ex. (10.) to (13.). In no case does a metal 'slip' significantly away from the position above the centroid of a C_5 ring, although this slip has been well documented in other electronic situations⁸³. In no case does the angle between the ring-normals at one metal centre decrease significantly below the typical value of 130° found in monomeric Cp_2MX_n derivatives, to allow the approach of a second organometallic group. The most striking feature of the $\eta^1:\eta^5-C_5H_4$ dimers, whose appearance is correlated with possible M-M bonding, is the angle (σ -bend) between the η^1 -bond vector and the C_5 -ring plane. This distortion was so surprising that it led Corradini and Sirigu⁸⁴, in 1967, incorrectly to formulate $[Ti(\eta^1:\eta^5-C_5H_4)(HAlEt_2)]_2(C_{10}H_8)$ as $[Ti(\eta^1:\eta^5-C_5H_5)(HAlEt_2)_2](C_{10}H_8)$. However, Tebbe and Guggenberger realized⁸⁵ the mistake after niobocene² (4.) and Kaesz's $\eta^1:\eta^5-C_5H_4$ Mo-Mn dimer¹⁵ (3.) were characterized by a combination of X-ray and nmr studies. This bending angle is clearly related to the presence of a metal-metal bond. For compounds (10.) to (13.) in Table 2-2, electron counting and M-M distance discount the presence of an M-M bond, and σ -bend is correspondingly on the order of 11° . The angle increases to a maximum of 40° in Kaesz's compound (3.), and since the overlap between the substituted carbon and the σ -bound metal is a function of the cosine of σ -bend, the extreme of 40° results in a 23% reduction in overlap. Out-of-plane bending is energetically easier than bond stretching, the appropriate ir frequencies being 3100 and 1000 cm^{-1} (ave) respectively for C-H bond stretching and deformations in ferrocene⁸⁶, but a large

value of σ -bond does seem to indicate a stronger M-M interaction than the bond lengths suggest.

Having discussed the angle of the η^1 bond, we now investigate its length. The η^1 C-M bond is shorter than normal M-C sigma bonds in every case except the Class V titanium dimer 2., in which the M-C bond is bridged by a diethylaluminiumhydrido moiety. Some related M-C bond lengths are given here for comparison.

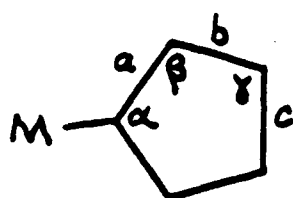
Compound	M-C(σ) Å	ref
$(C_5H_5)_2Ti(\eta^1-C_5H_5)_2$	2.332(2)	87
$(C_5H_5)_3Zr(\eta^1-C_5H_5)$	2.447(6)	88
$(C_5H_5)_2Hf(\eta^1-C_5H_5)_2$	2.38(2)	89
$(C_5H_5)_2Mo(\eta^1-C_5H_5)(NO)$	2.29	90
$(C_5H_5)_2W(Me)(CH_2PMe_2Ph)$	2.26(1)	91

If we suppose that the bond shortening may be attributed to a pi-interaction, then we might expect the dimensions of the $\eta^1:\eta^5-C_5H_4$ ring to reflect this. In terms of Valence Shell Electron Pair Repulsion theory, the endocyclic angle at the substituted carbon would be expected to decrease if electron density is brought from the adjacent C-C bonds into the M-C(σ) region. The same change in angle would be expected if electron density was donated from the metal into the M-C(σ) region. Table 2-2 shows that this decrease in endocyclic angle, which was particularly marked in compound 5, is a general structural feature of the $\eta^1:\eta^5-C_5H_4$ moiety.

In order to determine if any other systematic distortions occur in $\eta^1:\eta^5-C_5H_4$ -ligands, I calculated the

average dimensions of the ligand as follows. First, I assumed a mirror plane passing through the sigma-bound metal, perpendicular to the C_5 -ring plane. The ring can then be defined in terms of three independent lengths and three independent angles. The labelling scheme is shown below, along with the resultant averages (in Å and °), which were obtained from the 38 separate measurements for a, b, β , and γ , and 19 measurements of c and α that were reported for the crystal structures in Table 2-2.

$$a=1.45(3); \alpha=104(2)^\circ; b=1.43(3); \beta=110(2)^\circ; c=1.41(3); \gamma=108(2)^\circ$$

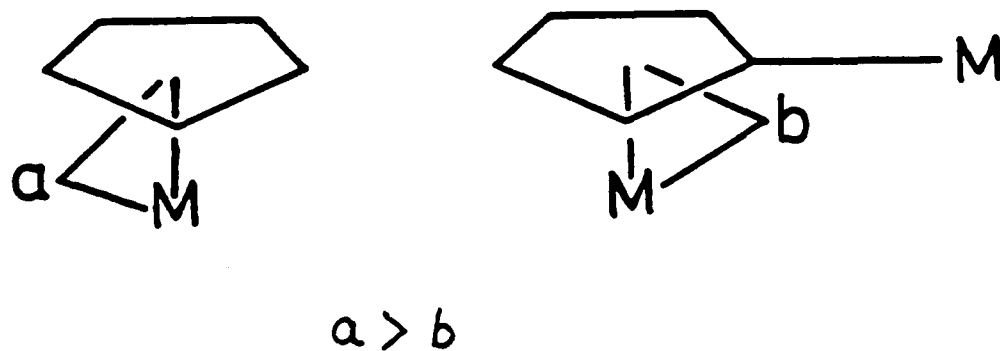


The C-C bond-length variation is different than that of fulvalene ligands in bis(fulvalene)dinickel³⁹: it is the bond furthest away from the substituted carbon that tends to be short for $\eta^1:\eta^5-C_5H_4$ ligands. Once again, the degeneracy of the ring e-levels has been lifted. Recalling the discussion of fulvalene dimers, it appears that the allyl-olefin component is favored here.

There is another systematic feature of compounds containing the $\eta^1:\eta^5-C_5H_4$ bridge: the distance between the metal and a pi-bound C_5 -ring is shorter to an $\eta^1:\eta^5-C_5H_4$ ring than to an $\eta-C_5H_5$ ring. This difference is reflected in the M-C bond lengths, but is more clear, and more statistically significant, when the perpendicular ring-to-metal distance M-R is considered.

Metal	M-R(ave)		M-C(ave)	
	$\eta^1:\eta^5\text{-C}_5\text{H}_4$	$\eta^5\text{-C}_5\text{H}_5$	$\eta^1:\eta^5\text{-C}_5\text{H}_4$	$\eta^5\text{-C}_5\text{H}_5$
Ti		2.08	2.34(3)	2.39(1)
Nb	2.00	2.07(4)	2.35(1)	2.38(3)
Mo	1.903(6)	1.97(1)	2.266(8)	2.30(1)
W	1.93(1)	1.95(1)	2.29(4)	2.31(6)

The scatter in M-C is especially large for tungsten, which may be caused by inaccuracy in the location of light atoms such as carbon near very heavy atoms. The closer approach of the $\eta^1:\eta^5\text{-C}_5\text{H}_4$ ligand can be attributed either to increased donor ability or increased acceptor ability of the C_5H_4 ring, as a result of its η^1 interaction.



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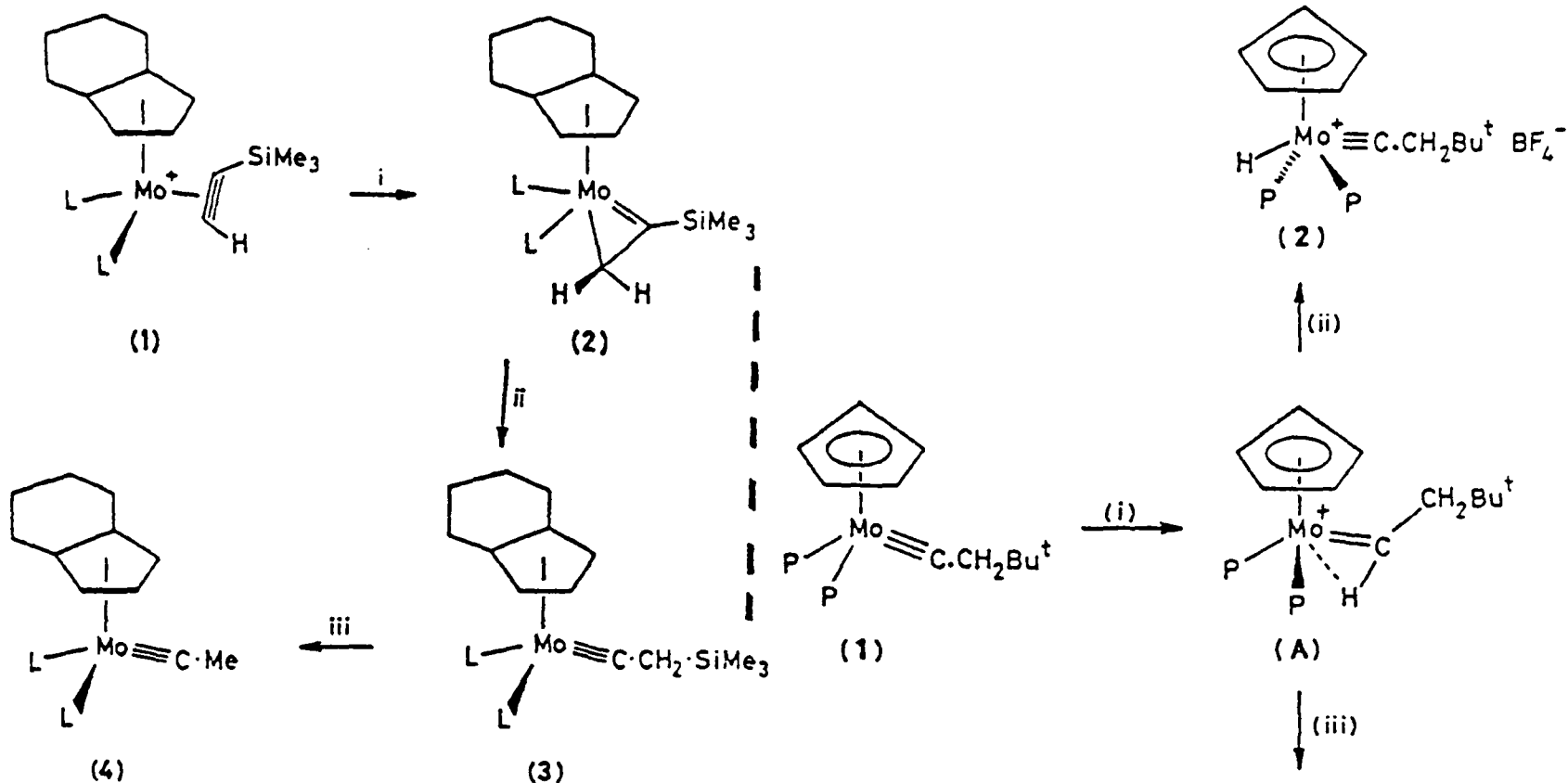
Chapter 3 Structural Studies of Half-sandwich Compounds;
Mechanistic Studies of Sandwich Compounds

3.0 Introduction.

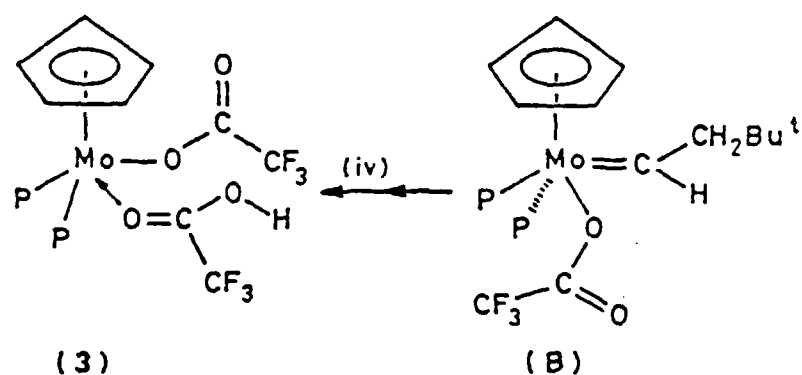
This chapter describes crystallographic and mechanistic studies of cyclopentadienyl derivatives of Groups IV, V, and VI. In the first section, which deals with half-sandwich compounds, the molecular structures of $[\text{CpMo}(\text{dmpe})\text{O}]\text{PF}_6$ and $\text{CpNb}(\text{dppe})\text{Br}_3$ are described. Their properties are discussed in relation to the theory of CpML_n compounds, and, in particular, an unusual property of the class CpML_5 is mentioned. The second part of the chapter is concerned with 'full-sandwich' compounds; it reports a study of the reductive elimination of methane from Cp_2WMe_2 (see section 2.2), the synthesis of $\text{Cp}_2\text{W}(\text{Me})\text{D}$, and, finally, the molecular structure of $(\text{EtCp})_2\text{TiBr}_2$.

3.1 Crystallographic Studies of Half-Sandwich Compounds.

The study of half-sandwich transition-metal compounds, i.e. those with only one η -bound ring, has been a fruitful area of organometallic chemistry, and many such compounds have been prepared. These compounds tend to have a rich substitution chemistry, relative to 'full-sandwich' molecules such as ferrocene, because half-sandwich derivatives have fewer coordination sites taken up by essentially inert, ring ligands. The versatility of mono-Cp chemistry (and related η^5 -indenyl systems) is illustrated in Fig. 3-1 by some recent



Scheme 1. L = P(OMe)₃. Reagents and conditions: i, K[BHBU₃], tetrahydrofuran (THF), -78 °C; ii, 25 °C, toluene; iii, NaF, aqueous MeCN, 25 °C.



Scheme 1. P = P(OMe)₃; (i) H⁺, (ii) BF₄⁻, (iii) CF₃CO₂⁻, (iv) CF₃CO₂H.

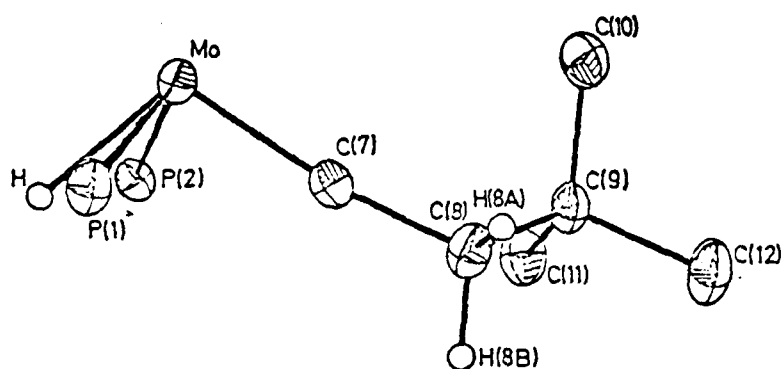
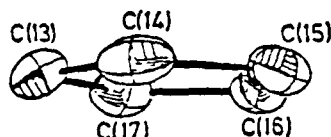
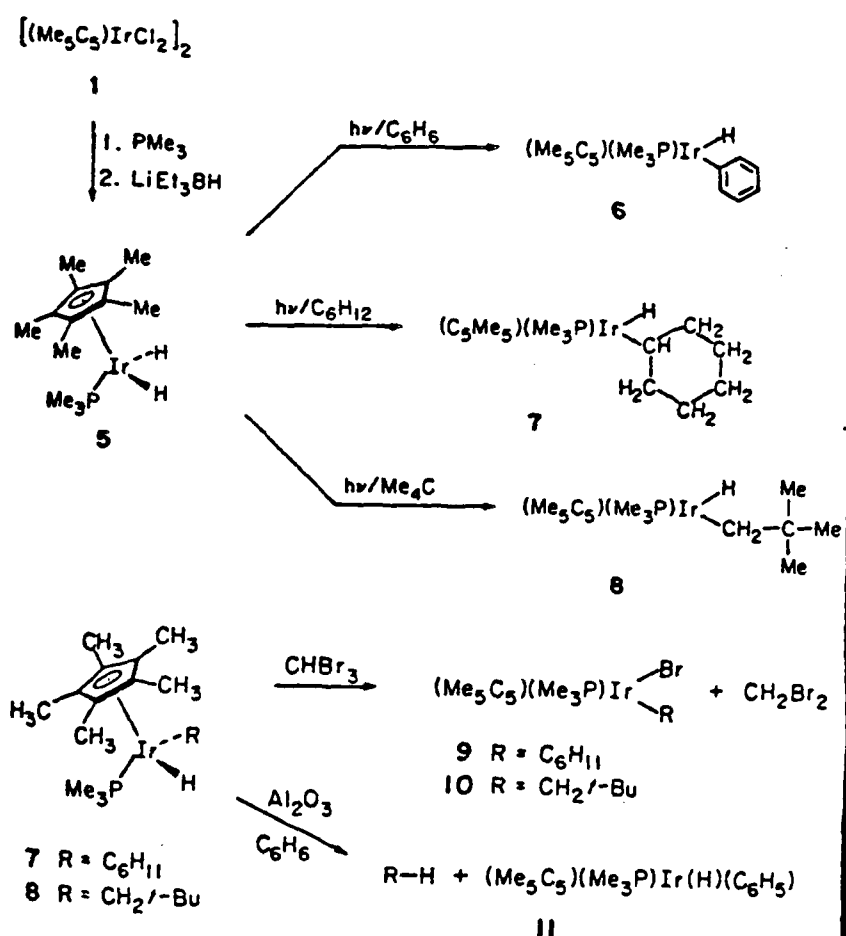


Figure 1. Molecular structure of (2) [HMo(CCH₂Bu^t)(P(OMe)₃)₂-(η-C₅H₅)] [BF₄]⁻ with methoxy groups, methyl and cyclopentadienyl hydrogen atoms omitted for clarity. Important geometrical parameters: Mo-H 1.74(3), Mo≡C 1.798(2), mean Mo-P 2.390 Å (individual e.s.d. 0.001 Å); angles, mean P-Mo-H 62.6, mean P-Mo-C 88.8, (individual e.s.d. <0.07°), H-Mo-C 106.0(8), P-Mo-P 121.9(1)°.

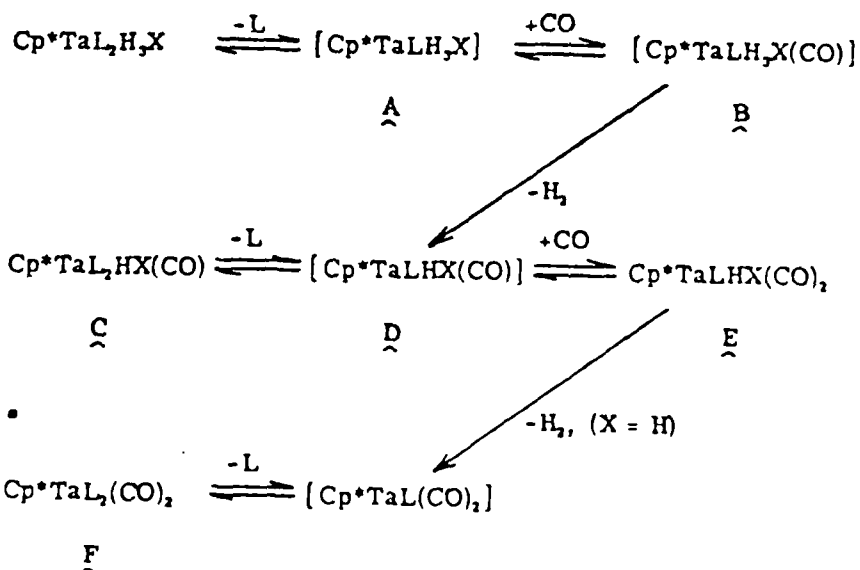
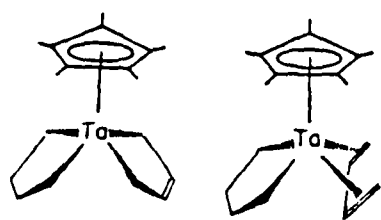


Fig. 3-1 Mono-Cp chemistry.

results from the laboratories of M. Green¹, J. Bercaw², and R.G. Bergman³.

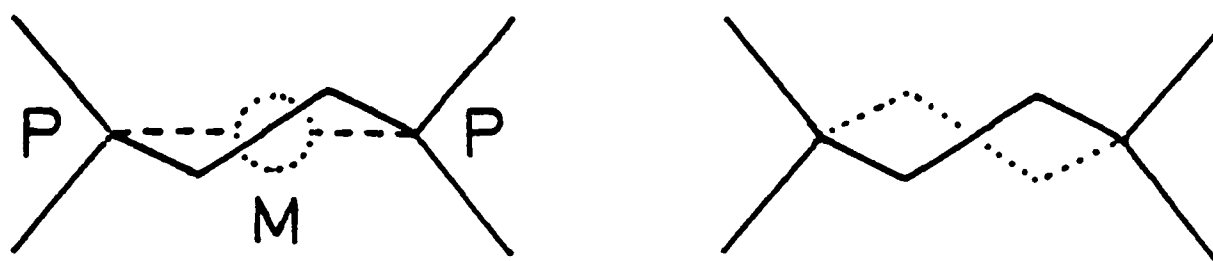
[CpMo(dmpe)O]PF₆ The catalytic deuteration of organic compounds by CpMo(dmpe)H₃ has been investigated with considerable success by A. Izquierdo⁴. The initial development of the CpMo(dmpe) system was done by G.S.B. Adams⁵, who prepared a number of derivatives of the CpMo(dmpe) fragment (Fig. 3-2). These compounds proved to be more labile than the analogous dppe derivatives⁶, which presumably have lower-energy metal electrons due to the relatively poor donor properties of arylphosphine ligands. One of Dr. Adams' compounds, labelled 3-8 in Fig. 3-2, is formed by hydrolysis of either CpMo(dmpe)Cl₃ or CpMo(dmpe)H₃, and it could not be fully characterized by wet-chemical methods. I therefore undertook a crystal structure analysis to complete the characterization.

The space group of 3-8 was determined on the diffractometer, and by successful refinement, to be P2₁/m; the data were collected in the first setting of this space group, with c-unique. Patterson methods were used to locate the molybdenum, which lies on a crystallographic mirror plane, and two phosphorus atoms, one of which corresponds to the PF₆, and lies on an inversion centre. Fourier maps revealed the oxygen and carbon atoms of the molybdenum coordination sphere, and showed the cation to be [CpMo(dmpe)O]⁺, a CpML₃ 'piano-stool' species (Fig. 3-2 and 3-3). The cation has mirror symmetry, with Mo1, O1, and Cl lying in the crystallographic symmetry

plane.

Fourier maps also showed that the PF_6^- is highly disordered. A (stick and ball) model of the electron density around P2 was constructed, and this allowed three distinct PF_6 octahedra to be identified. Each octahedron was given an occupancy of one third, soft constraints were applied to all PF_6^- dimensions, and the anion was refined anisotropically to absorb additional disorder into the temperature factors. In the final stages of refinement the PF_6^- constraints were removed, and the dimensions remained chemically reasonable.

The temperature factors of the dmpe carbons revealed that the ligand suffers from conformational disorder, which is especially apparent in the CH_2CH_2 chain. Chelating phosphines are often, although not always, disordered³⁵. The conformation found in 8, and the superposition of its mirror image, are shown below.



Two sites (C4 and C140) were resolved for the unique methylene carbon, and each was given an occupancy of 0.5. One of the two ligand conformations is shown in Fig. 3-3; it is the result of anisotropic refinement in which the C-C (C4-C140) and P-C distances were constrained. Alternative sites for the methyl carbons, C5 and C6, were not resolved, and their temperature factors are correspondingly somewhat high. The Cp hydrogens were located in a difference-Fourier map, and were then placed

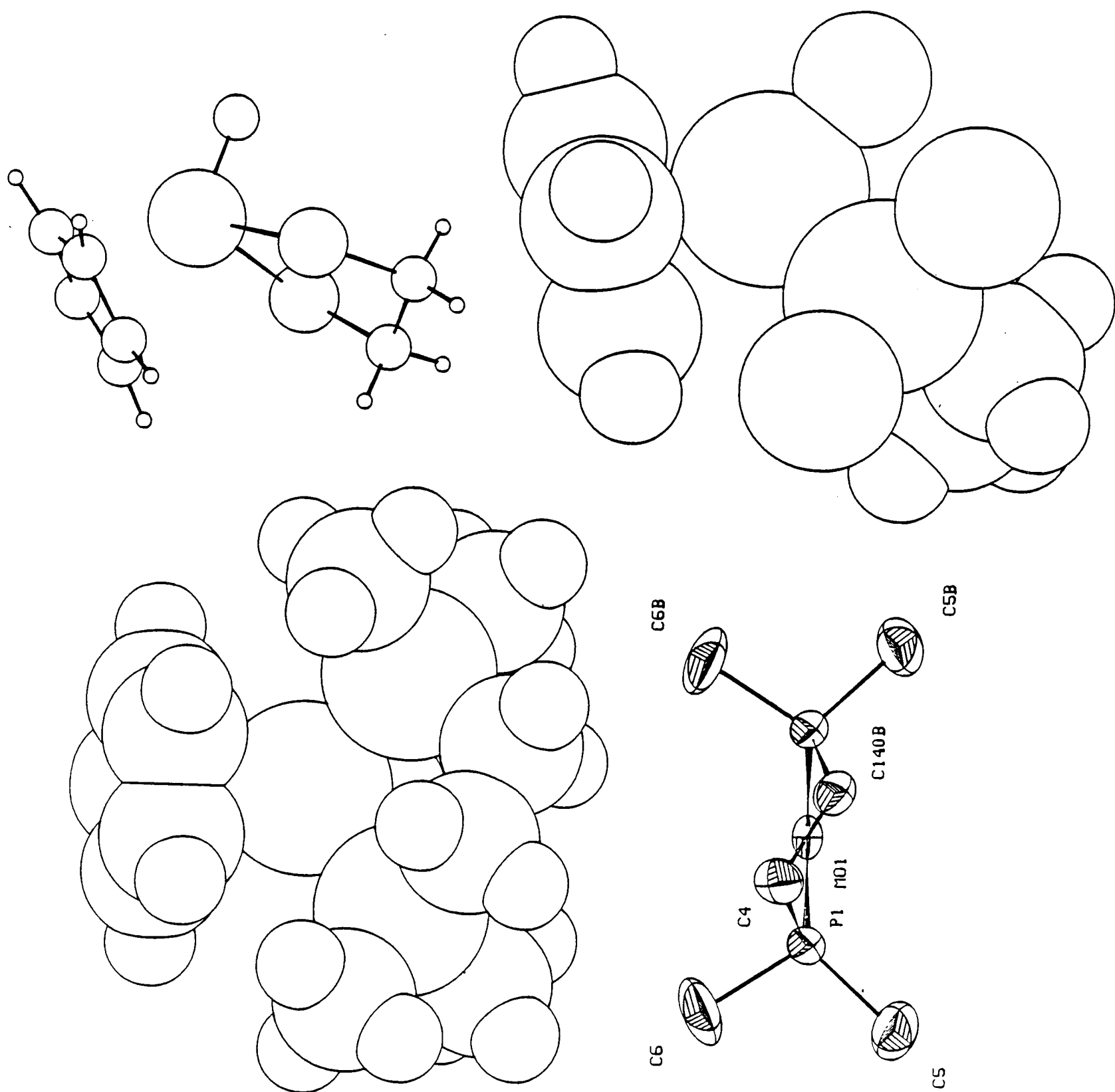
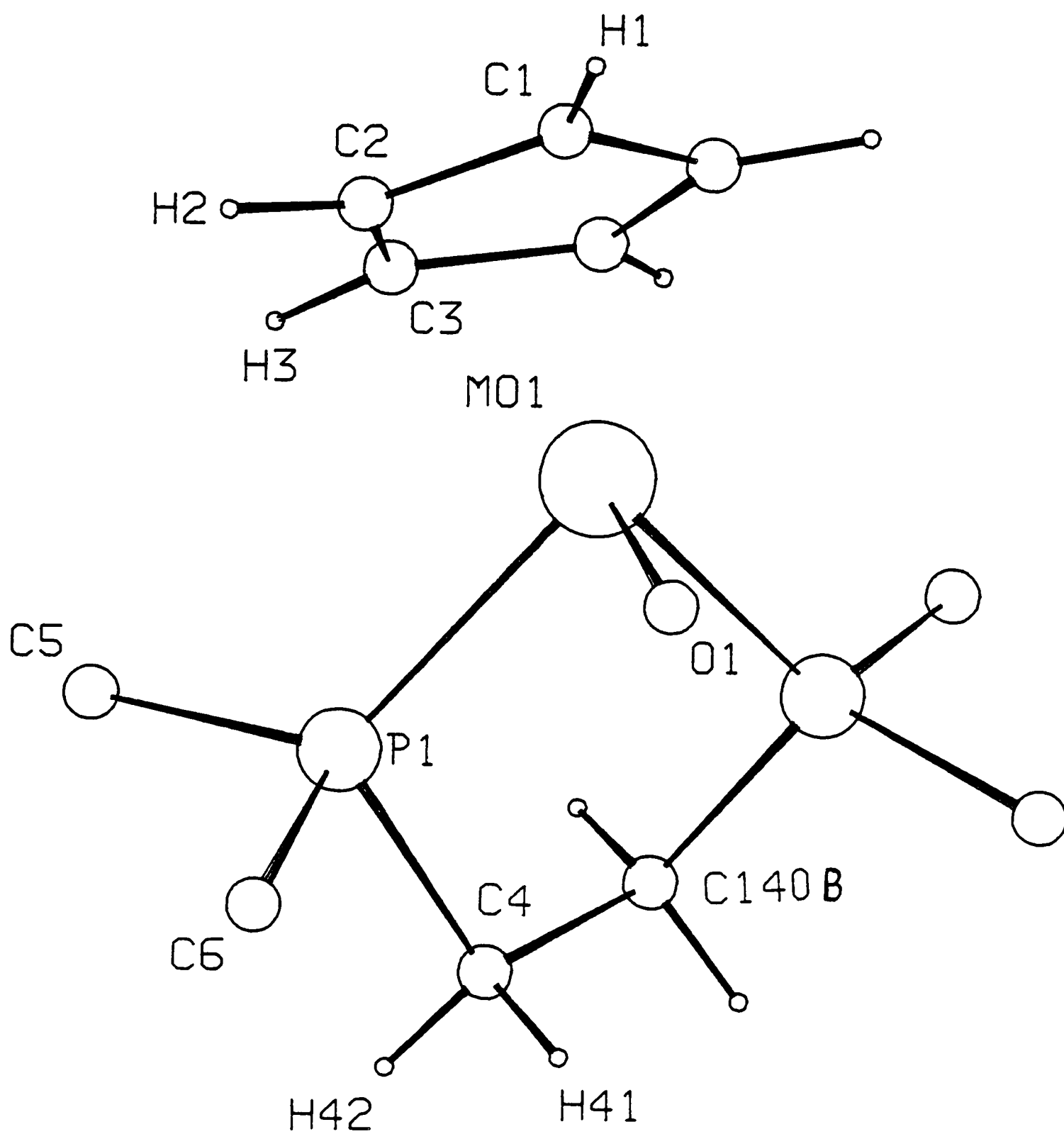


Fig. 3-3 The molecular structure of 38; some views have hydrogens or methyls omitted for clarity.

Fig. 3-3 (cont.)



along with the dmpe-methylene hydrogens, the positions being adjusted after each refinement cycle. The final R-value is 3.80%, $R_w=4.58\%$, for 1125 observations and 170 parameters. Some important dimensions of compound 3-8, $[\text{MoCp}(\text{dmpe})\text{O}]\text{PF}_6$, are:

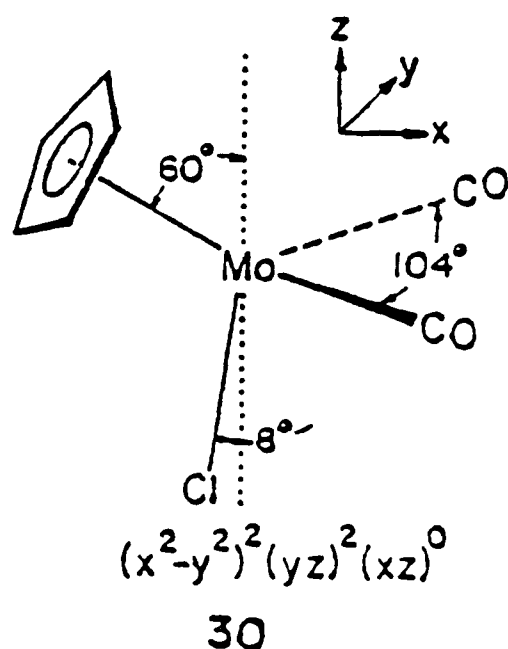
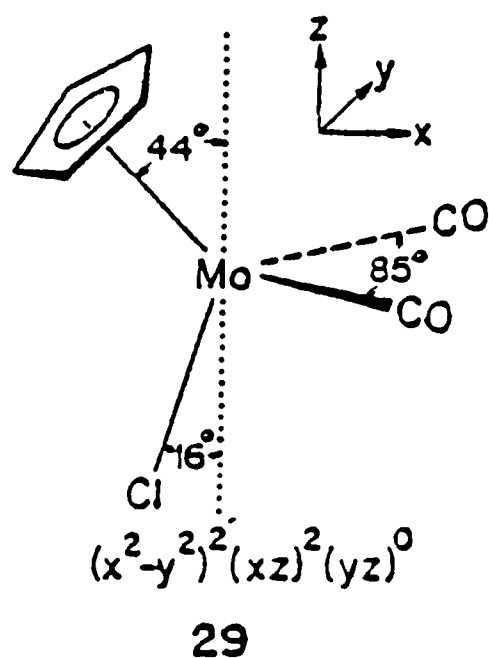
Bond lengths ($\text{\AA}$) and angles ($^\circ$)

Mol-P1 2.442(2) Mol-O1 1.700(7)
 Mol-C1 2.21(1) Mol-C2 2.300(7)
 Mol-C3 2.499(7) Mol-(ring plane) 2.015
 P1-Mol-P1B 81.09(9)

The Mo-Cp group is rather asymmetric, as judged by the 0.28 $\text{\AA}$ spread of Mo-C bond lengths (note that Mol-C3 is extremely long). This asymmetry is also reflected in the projection of Mol onto the least-squares best ring plane; in projection, a metal usually falls within 0.1 $\text{\AA}$ of the ring centroid, but in compound 3-8, there is a 0.34 $\text{\AA}$ slip of the metal towards C1. Although delta-bonding effects may determine the ring-slip in compounds such as $\text{CpV}(\text{CO})_4$ ⁷, steric effects must be the driving force here. The H3-C5(methyl) distance is only 2.71 $\text{\AA}$, while Pauling's van der Waals contact distance⁸ between CH_3 and H is 3.2 $\text{\AA}$. The close contact between the dmpe and Cp ligands is shown in the van der Waals diagrams of Fig. 3-3, to which methyl hydrogens were added using the CHEMGRAF graphics program MODEL, which was written by E.K. Davies⁹. It should be mentioned that the long Mo-C3 bond is trans to the oxo ligand.

Compound 3-8 is formally a d^2 , Mo(IV) species, and might be thought to have only 16 valence electrons. However, it seems more reasonable to regard both 3-8 and the analogous

acetylene derivative 6 (Fig. 3-2) formally as 18-electron compounds, although this requires both the oxo and acetylene ligands to contribute four electrons to the metal's valence shell. A simple, two-electron bond between O^{2-} (or $RC=CR$) and a metal centre may be more common, but both oxo and acetylene ligands have a pi-symmetry orbital which can donate a further two electrons into an unfilled metal d-orbital. The distance $Mo-O$ is similar to that found in other oxo derivatives of molybdenum which would be electronically unsaturated if a four-electron $Mo-O$ bond were not postulated. In the $Mo(PR_3)_3Cl_2O$ derivatives prepared by Chatt and Butcher¹⁰, and studied crystallographically by Manojlovic-Muir and Muir¹¹, there may even be an isomerism in which the relative pi-donor interaction from chlorine and oxygen is varied (see Fig. 3-4, in one isomer $Mo-Cl$ is short, in the other isomer, $Mo-O$ is short). The difference in $Mo-O$ bond lengths is more than 0.1 Å for Chatt's two isomers. Hoffmann has recently⁷ investigated the closely related molecule, $CpMo(CO)_2Cl$, using the extended-Hückel technique and symmetry principles. He found two minima on the conformational energy surface of this molecule, and they are shown here as 29 and 30.

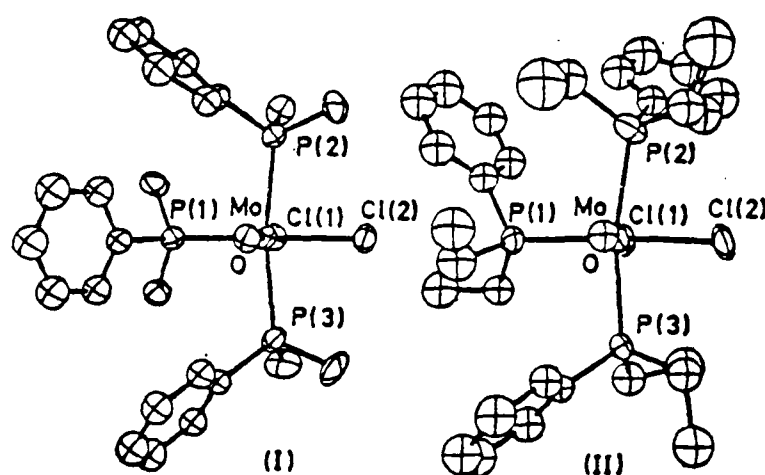


Hoffmann does not mention the possibility (and he therefore

X-Ray Determination of Molecular Structures of Molybdenum(IV) Oxo-complexes. The Possibility of a New Type of Isomerism

By J. CHATT, LJUBICA MANOJLOVIĆ-MUIR,* and K. W. MUIR
(School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ)

Summary Notable differences between corresponding bond lengths and interbond angles in the complexes blue *cis-mer*-[MoOCl₂(PMe₂(Ph)₃)] and green *cis-mer*-[MoOCl₂(PEt₂Ph)₃] are caused by ligand repulsions; an explanation of the isomerism of *mer*-[MoOCl₂(PMe₂Ph)₃] is suggested in terms of the structures of the above complexes.



Molecular structures of *cis-mer*-[MoOCl₂(PR₂Ph)₃] (I; R = Me; II; R = Et) viewed along the normal to the plane Mo, Cl(2), P(2)

Selected intramolecular distances (Å) and angles (°) in (I) and (II)

	(I)	(II)		(I)	(II)
Mo—O	1.678(7)	1.803(11)	Mo—P(1)	2.500(3)	2.521(5)
Mo—Cl(1)	2.551(3)	2.426(6)	Mo—P(2)	2.541(3)	2.582(6)
Mo—Cl(2)	2.464(3)	2.479(5)	Mo—P(3)	2.558(3)	2.556(6)
O—Cl(2)	3.333(8)	3.280(12)	Cl(1)—Cl(2)	3.405(4)	3.353(8)
O—P(1)	3.058(8)	3.185(12)	Cl(1)—P(1)	3.141(4)	3.233(6)
O—P(2)	3.086(8)	3.142(12)	Cl(1)—P(2)	3.581(4)	3.567(8)
O—P(3)	3.087(8)	3.117(14)	Cl(1)—P(3)	3.594(4)	3.549(8)
P(1)—P(2)	3.700(5)	3.856(6)	Cl(2)—P(2)	3.421(4)	3.407(9)
P(1)—P(3)	3.694(4)	3.666(8)	Cl(2)—P(3)	3.393(5)	3.403(5)
	(I)	(II)		(I)	(II)
Cl(1)—Mo—P(1)	76.9(1)	81.6(2)	P(1)—Mo—P(3)	93.8(1)	92.4(2)
P(1)—Mo—O	91.9(3)	93.4(4)	P(3)—Mo—Cl(2)	85.0(1)	85.0(2)
O—Mo—Cl(2)	105.7(3)	98.8(4)	P(2)—Mo—P(3)	171.2(1)	169.4(2)
Cl(2)—Mo—Cl(1)	85.5(1)	86.2(2)	O—Mo—P(2)	91.7(3)	89.7(4)
Cl(1)—Mo—O	168.8(3)	175.0(4)	P(2)—Mo—Cl(1)	89.4(1)	90.8(2)
Cl(2)—Mo—P(1)	162.4(1)	167.5(2)	Cl(1)—Mo—P(3)	89.4(1)	90.8(2)
Cl(2)—Mo—P(2)	86.2(1)	84.6(2)	P(3)—Mo—O	91.2(3)	89.6(4)
P(2)—Mo—P(1)	94.4(1)	98.2(2)			

Fig. 3-4

classifies the molecule as 16-electron), but, on symmetry principles, an unfilled metal orbital can accept a lone pair of electrons from the chlorine, thereby raising the formal valence-electron count at molybdenum from 16 to 18. The appropriate metal orbital would be d_{xz} in 30 or d_{yz} in 29. Of course, a typical Mo-Cl bond length is 2.5 Å, which is much longer than Mo1-O1 in compound 3-8, so the Mo-Cl pi overlap will not be as effective as Mo-O overlap, and the corresponding Mo-Cl pi-bond energy may be low. It is instructive to compare the structural parameters of 3-8 with those calculated by Hoffmann for structures 29 and 30. In 3-8, the L-M-L angle is fixed to near 80° by the bite-angle of dmpe, so we might expect 8 to resemble 29. Indeed, the angle between the normal to the Cp-ring and the z-axis is 36°, which is closer to the 44° angle of 29 than the 60° angle of 30, and is quite a good fit considering the differences between $(CO)_2$ and dmpe. However, the Mo1-O1 vector makes a 4.8° angle with -z, which resembles the angle of structure 30. This difference between 8 and 29 probably arises from the fact that both 29 and 30 are d^4 , while 3-8 is d^2 . Thus, in 8, there is no lone pair of electrons in either the xz or the yz plane, and O1 can move close to the z-axis in order to maximize the overlap between its p-pi levels and the unfilled metal (xz and yz) orbitals.

[NbCp(dppe)Br₃] $\cdot$ 2MePh. The reaction of trialkyltin Cp reagents with niobium and tantalum halides to give the oligomeric compounds $[CpNbX_4]_x$ 50 was pioneered by Bunker, Green, and co-workers as a route to mono- and bis(Cp) derivatives of Group V¹²; this route was developed simultaneously by Professor

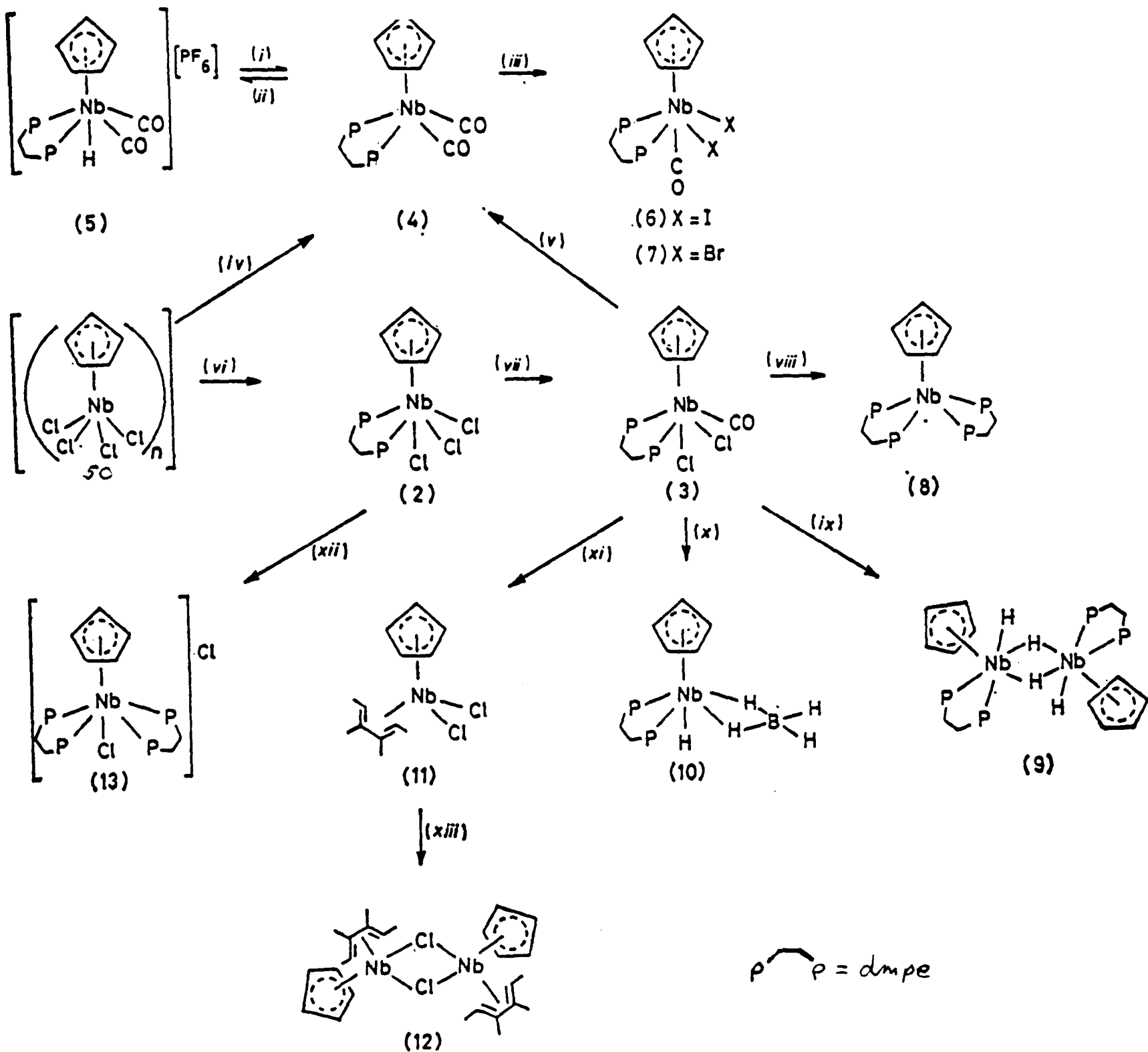
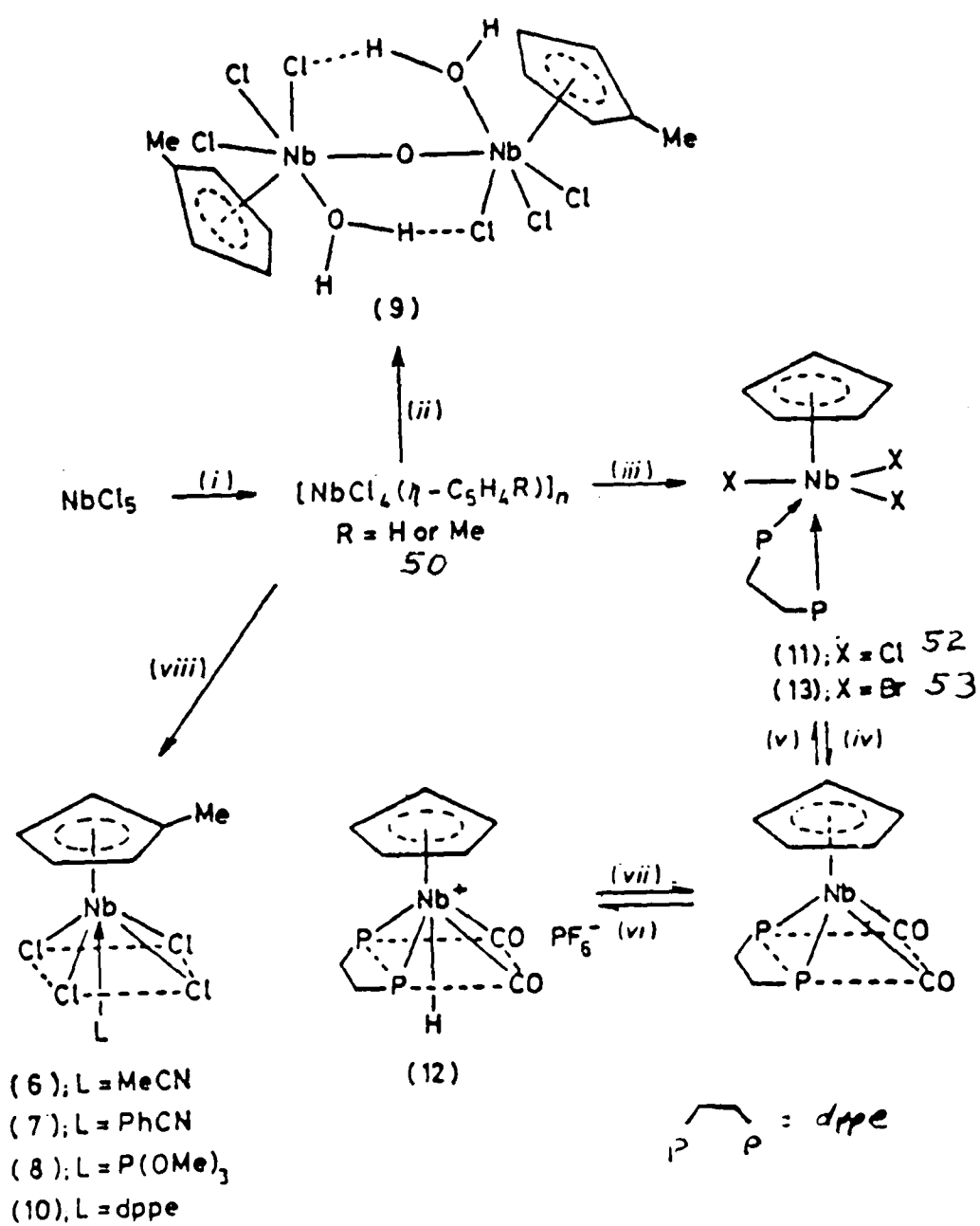


Fig. 3-5 CpNb derivatives with dppe and dmpe ligands.



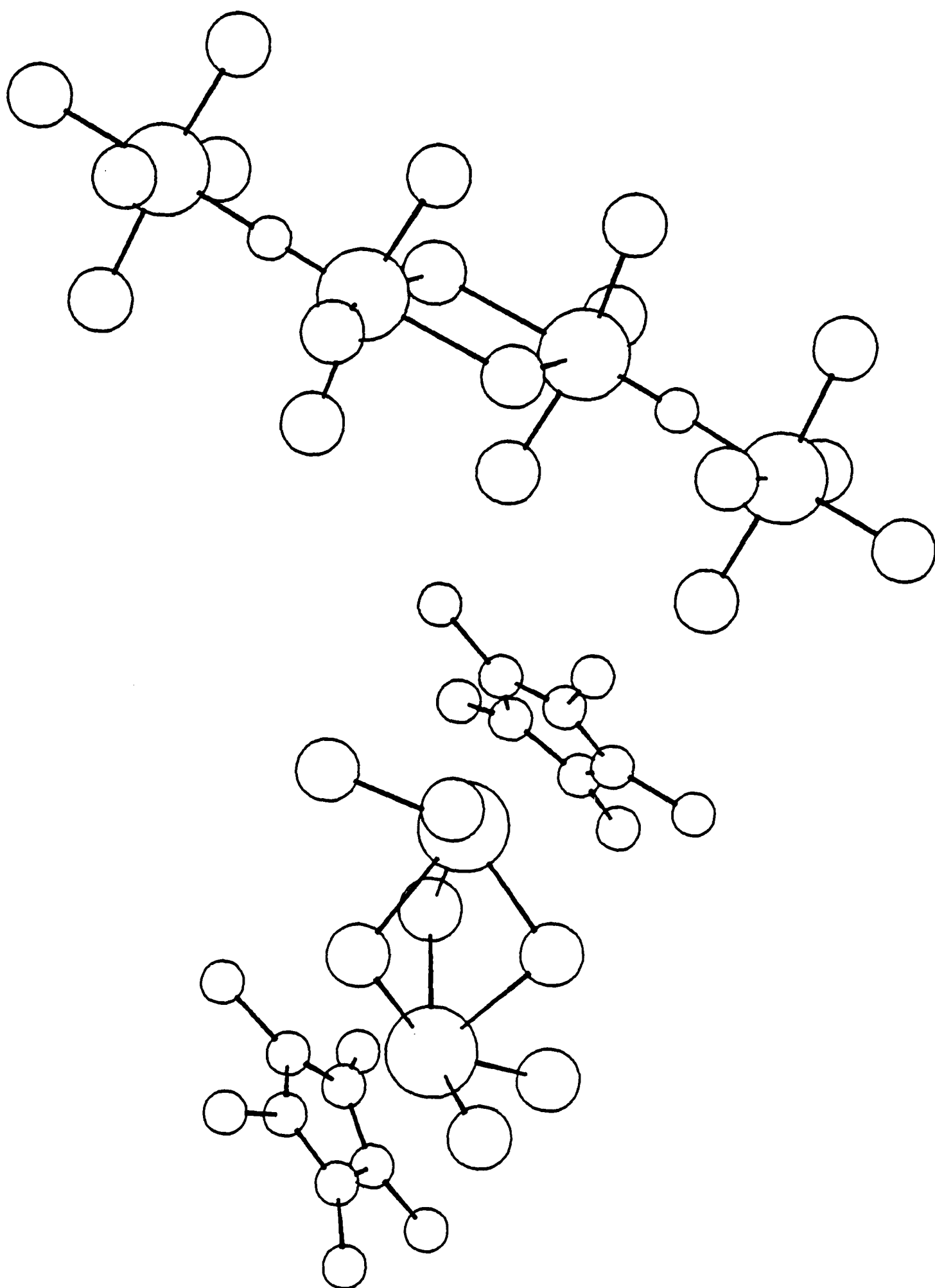


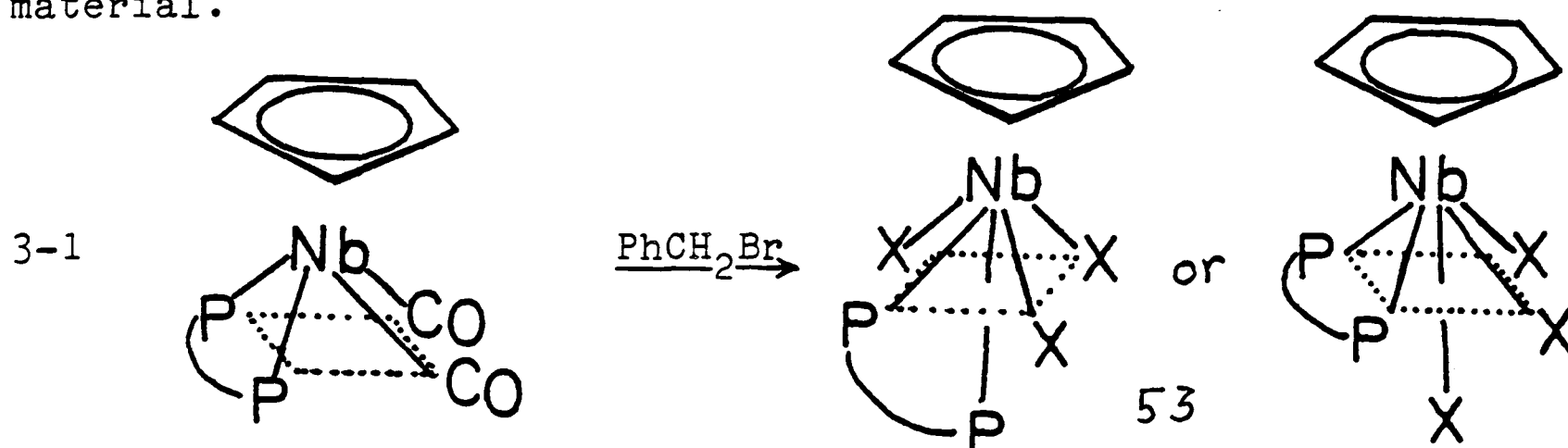
Fig. 3-5 (cont.) The novel tantalum chloride derivative of J.C. Green and coworkers, 51.

Chatt's group¹⁷. The route was found to be successful for alkyl-substituted Cp as well as C₅H₅ itself, and a variety of compounds was prepared (see Fig. 3-5). The structure of the precursor compounds 50 is unknown. However, the related compound $\{[(\text{Me}_5\text{Cp})\text{TaCl}_2]_2(\mu\text{-Cl})_3^+\}_2\{\text{Cl}_5\text{TaOTaCl}_3)_2(\mu\text{-Cl})_2^{2-}\}$ 41 was recently prepared by J.C. Green and C.P. Overton, and structurally characterized by J.M. Marin¹³ (Fig. 3-5). Compound 51, which was found to contain numerous bridging chlorines, is a side-product of the reaction between (Me₅Cp)SnBu₃ and TaCl₅; its cationic component may closely resemble $[(\text{Me}_5\text{Cp})\text{TaCl}_4]_x$.

The compound CpNb(dppe)Cl₃ 52 can be made¹⁴ by treating 50, X=Cl, with dppe under reducing conditions, and a sample of 52 prepared in this way was characterized crystallographically by Daran and Prout (see the schematic representation in Fig. 3-5)¹⁵. The molecule crystallizes as the bis(toluene) solvate, in space group P $\bar{1}$. As shown in Fig. 3-5, CpNb(dppe)Cl₃ can be converted into CpNb(dppe)(CO)₂, which has the CpML₄ piano-stool structure. Thus, the dppe chelating ligand has moved from an equatorial-axial to an equatorial-equatorial coordination geometry. Hoffmann has recently⁷ investigated alternative geometries for the CpML₄ compounds, and has found that a Cp-capped trigonal pyramid is unfavourable on steric grounds, but gains in importance with small axial ligands which are both good sigma and pi donors. The structure of 42 may be described as a Cp-capped square pyramid.

The dicarbonyl CpNb(dppe)(CO)₂ reacts with PhCH₂Br at 70° in toluene to give CpNb(dppe)Br₃ 53 in what must be a

multi-step process (Eq. 3-1). In contrast, the reaction of CpNb(dppe)(CO)_2 with HCl results in a simple protonation (Fig. 3-5). We were interested in determining whether the dppe changes its coordination geometry during the course of reaction 3-1 to become equatorial-axial, or whether it remains in the equatorial-equatorial arrangement of the starting material.



We were also interested in finding another example of an unusual structural feature that seems characteristic of CpMl_5 species: the axial bond trans to the Cp ring is very long. Thus, in 52, the axial Nb-P bond is $2.787(1) \text{ \AA}$, while the equatorial bond is $2.678(1) \text{ \AA}$. Furthermore, in the compound $[\text{CpNb(dmpe)}_2\text{Cl}]\text{Cl}$ (see Fig. 3-5¹⁶), the axial chlorine is $2.557(4) \text{ \AA}$ from Nb1, which may be compared to the equatorial Nb-Cl bonds of $2.481(1)$, $2.463(1)$, and $2.475(1) \text{ \AA}$ in 52. It is interesting that this structural property of Cp-capped square pyramidal compounds is also found for "oxo-capped" square pyramids such as $\text{NbOCl}_3(\text{NCMe})_2$, where the MeCN ligands occupy axial and equatorial sites analogous to the dppe of 52, and the axial Nb-N bond is unusually long, perhaps due to a combination of the trans influence of the oxo ligand and steric repulsion³⁶.

Crystals of 53 were grown from toluene solution by Dr.

M.J. Bunker. Preliminary photographs and diffractometer data indicated that 53 crystallizes in a triclinic space group, with a volume similar to that of its chloride analogue, 52. This suggested, in agreement with elemental analysis, that 53 also crystallizes with two toluene molecules per asymmetric unit. Inspection of the Patterson function yielded the niobium and three bromine positions, and, after an absorption correction was applied, successive Fourier maps revealed the positions of all nonhydrogen atoms except those of the (disordered) solvent molecules. Anisotropic refinement with extensive dimensional constraints on the phenyl groups allowed the solvent molecules to be located in a difference-Fourier (as well as many of the hydrogens), and the toluene carbons were refined isotropically. Hydrogens were placed geometrically on all carbons except those of the solvent, and their positions were adjusted after each refinement cycle. The final R-value is 4.89%, $R_w=6.44\%$, for 375 parameters, 2851 reflections, and 136 constraints.

The structure of 53 is shown in Fig. 3-6; it is the same as that found for the chloride analogue by Daran and Prout¹⁵, and further demonstrates the preference of dppe for axial-equatorial ligation in these $CpML_5$ compounds. Van der Waals and stick diagrams of 53 are given in Fig. 3-7, to illustrate the steric crowding and molecular connectivity. The elongation of the axial Nb-P bond is particularly pronounced in 53: Nb-P1 is $2.664(3) \text{ \AA}$, while Nb-P2 is $2.800(3) \text{ \AA}$. The increased axial-equatorial bond-length differential on changing Cl for Br is consistent with the differential being a steric effect (the van der Waals radii of Cl, Br, and P are

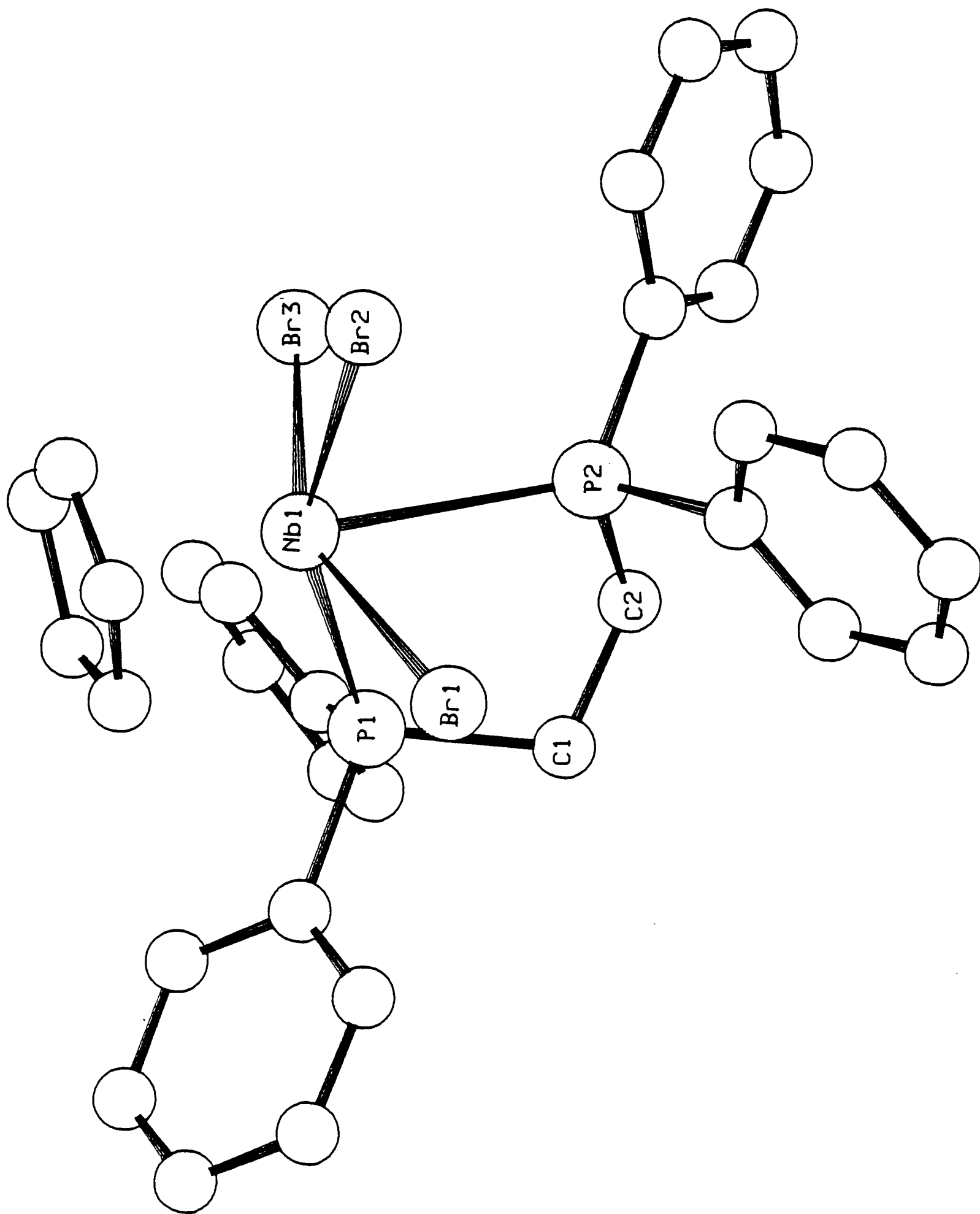


Fig. 3-6 The molecular structure of 53.

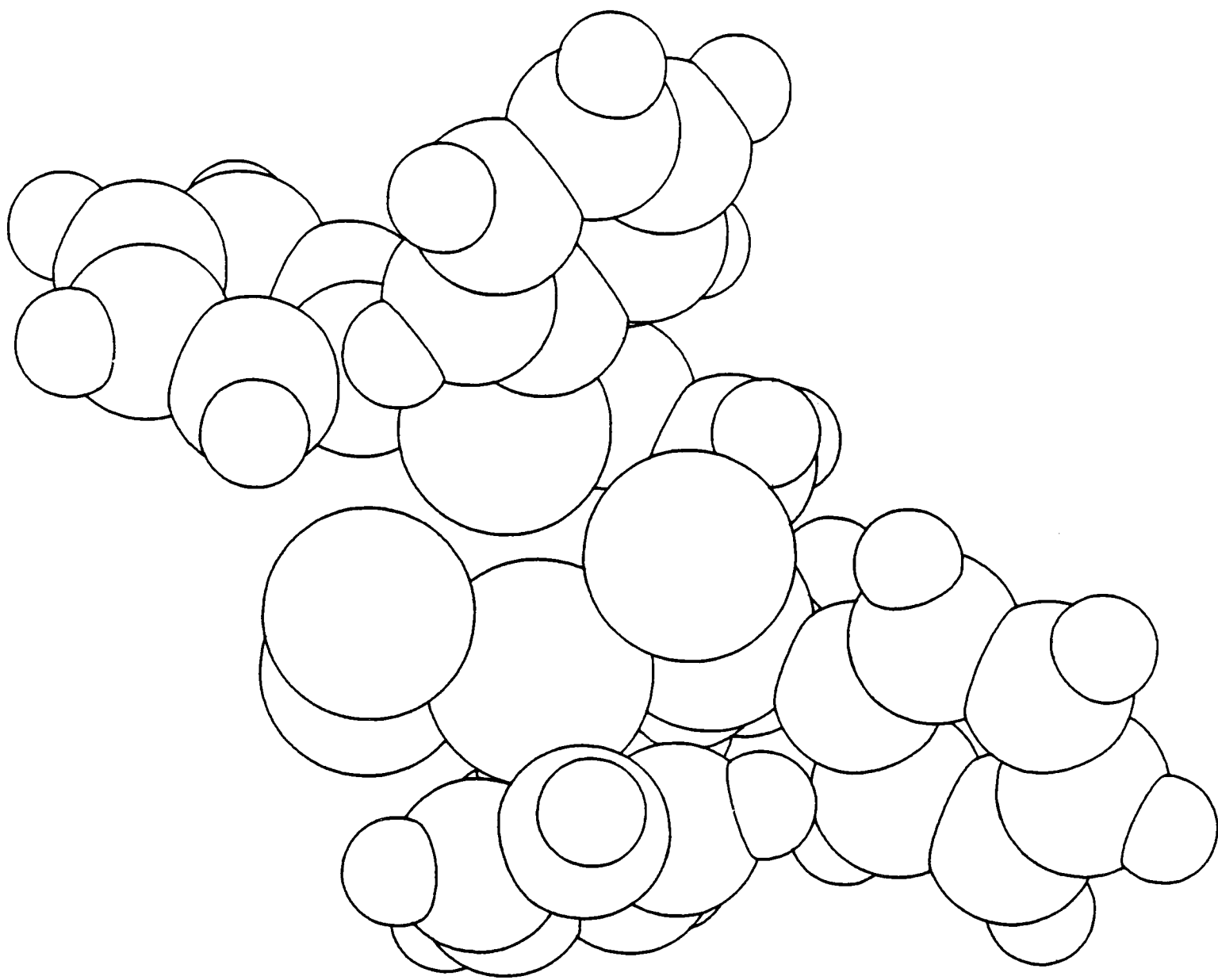
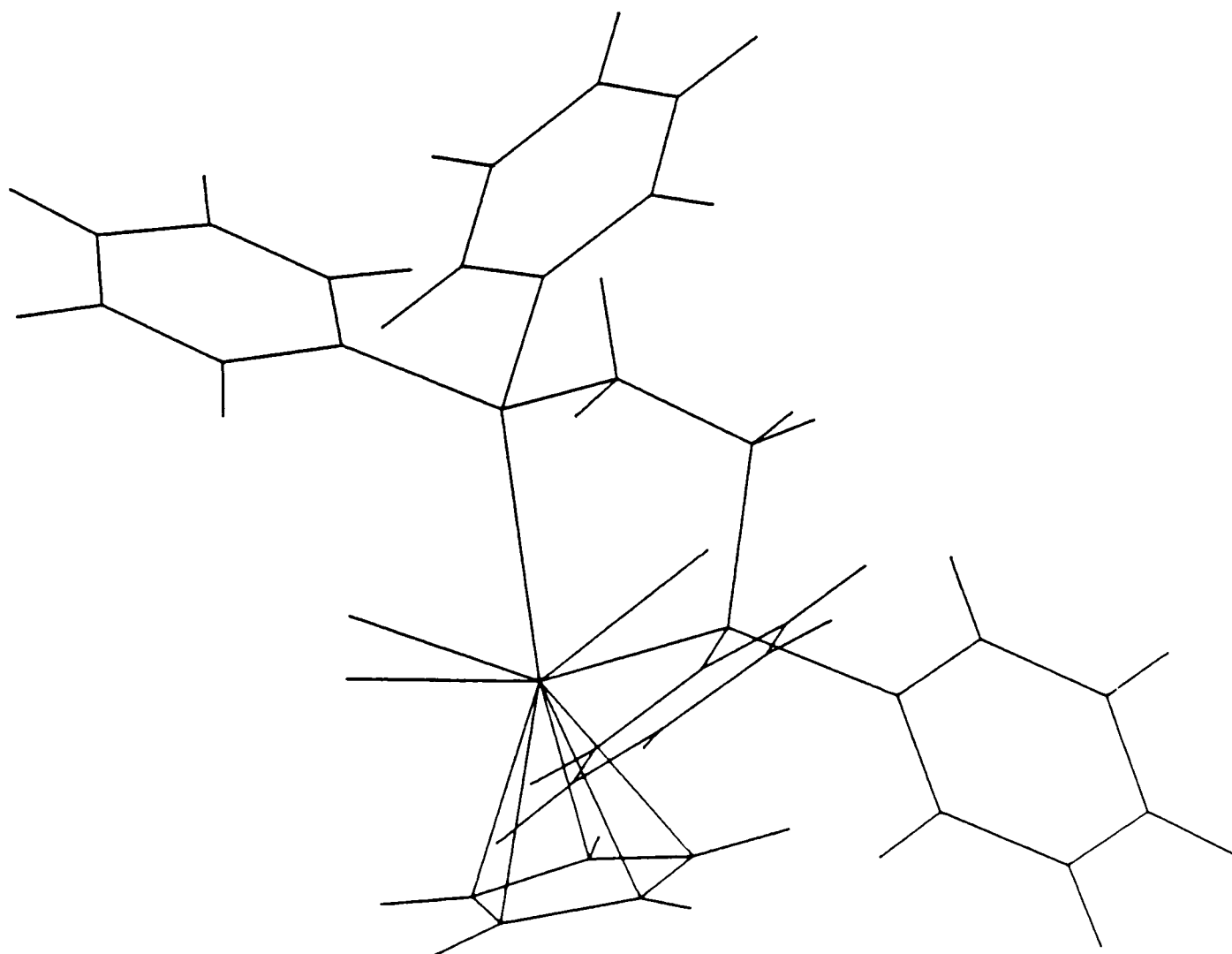


Fig. 3-7 Two representations of 53.



1.8, 1.95, and 1.9 Å, respectively). However, the preference of P for an axial site does not seem to be entirely steric in origin, since P is larger than Cl. Furthermore, in $[\text{CpNb}(\text{dmpe})_2\text{Cl}]\text{Cl}$, it is the chlorine that takes up the axial position.

The key to this isomerism may be related to the formal occupation of the d-orbitals of the central metal. Thus, when Hoffmann predicted⁷ that a pi-donor ligand would prefer the axial position in a Cp-capped trigonal pyramid CpML_4 derivative, he used $d^4 \text{CpNb}(\text{CO})_4$ as his reference point. For this class of molecule, the pi-donor ligand moves to an axial position to avoid antibonding, pi-symmetry interactions with the filled metal orbitals, d_z^2 and d_{xy} . However, for the 17-electron compounds $\text{CpNb}(\text{dppe})\text{X}_3$, the metal is in a formal +4 oxidation state, and the d-orbitals are not so highly occupied. Thus, a stabilizing pi-donation from equatorial halogen lone-pairs to empty d-orbitals can take place, and this seems to override the delicate steric preference for axial chloride instead of phosphorus. The compound $[\text{CpNb}(\text{dmpe})_2\text{Cl}]\text{Cl}$ has formally a d^2 , 3+ metal centre, and the desirability of halogen-to-metal lone-pair donation is diminished. The resulting structure is in agreement with predictions on steric grounds.

3.2 Sandwich Compounds.

The chemistry of organometallic 'sandwich' molecules is extensive¹⁸, and the literature of dimeric sandwich compounds

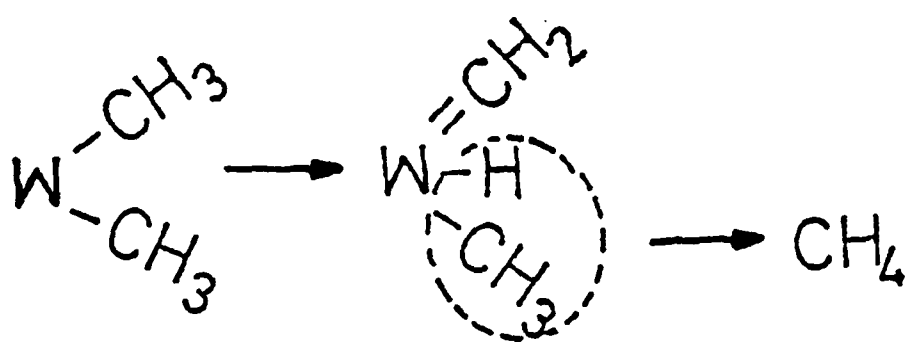
is discussed in Chapter 2. From a mechanistic point of view, one useful characteristic of metallocenes, the cyclopentadienyl sandwiches, is that there are relatively few coordination sites available once the Cp ligands are in place. Therefore, for a particular metallocene reaction, the number of reaction pathways may be limited, and experiments may be devised to determine, or at least suggest, the reaction mechanism. We were particularly interested in the mechanism of reductive elimination of alkanes from transition-metal centres, because this process is fundamental to many catalytic organometallic reactions, and it is at present only poorly understood. In fact, there seem to be number of different fundamental reaction types which are loosely referred to as 'reductive eliminations', including homolytic M-C bond cleavage, concerted C-H elimination, and intimate radical mechanisms¹⁹. Metal-assisted formation of C-H bonds can also be complicated by binuclear processes, although this may be limited to carbonyl derivatives such as those studied by Norton²⁰, where the bridging of two metals by CO ligands aids in dimer formation.

The $\text{Cp}_2\text{MRR}'$ system, $\text{M}=\text{Mo}, \text{W}$, is particularly suited to mechanistic studies of alkane reductive elimination because the complete series of compounds Cp_2MH_2 , Cp_2MMe_2 , and $\text{Cp}_2\text{W}(\text{Me})\text{H}$, is available. The photochemical reductive elimination of H_2 from Cp_2MH_2 has been studied both in solution^{21,24} and in low-temperature matrices²², and was found to be a concerted process; the product was identified by Grebenik and Perutz to be the parent molybdenocene or tungstenocene²³. The methyl hydride, $\text{Cp}_2\text{W}(\text{Me})\text{H}$, was found to

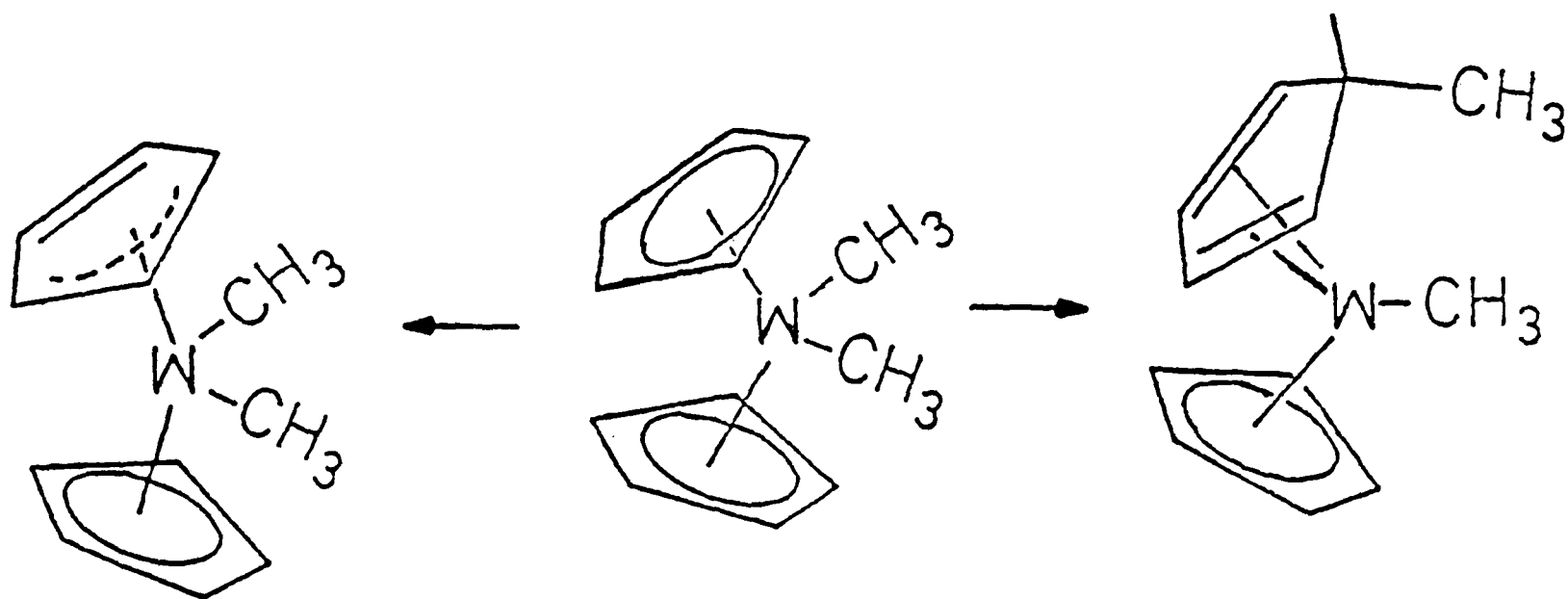
yield tungstenocene under both thermal²⁵ (solution) and photochemical (matrix-isolated) conditions; on the basis of matrix-isolation results, the production of CH₄ is thought to be an example of concerted reductive elimination²³, because methyl radicals were not detected. The dimethyl derivative, Cp₂WMe₂, was known to have a high thermal stability²⁶, and to produce methane (and only small amounts of C₂ products) under forcing thermolysis conditions (160° or more)²⁶, and we wished to study this reaction in ^{order} to distinguish among the various possible mechanisms, which are shown in Fig. 3-8. We were also interested in synthesizing Cp₂W(Me)D to look for the production of CH₃D under thermolysis conditions, and in attempting the synthesis of Cp₂Mo(Me)H, which had not previously been prepared. The latter synthetic project led to my involvement with molybdenocene dimers, as described in section 2.1, and, in the pursuit of their chemistry, the reductive elimination studies were somewhat curtailed. I am grateful to Dr. P.D. Grebenik for running the mass spectra that were essential to the results presented below.

We first carried out a repetition of Benfield's decomposition²⁶ of Cp₂WMe₂ 50, to confirm his conclusion that methane is the major product of this reaction, with ethane and ethylene being formed in yields of only a few percent. The compound 50 was heated to 160° in vacuo, and to 180° in decalin solution, and the atmosphere above the reactant was introduced into a gas chromatograph. Both thermolyses produced largely methane, and less than 5% each of C₂H₄ and C₂H₆. It is interesting that, even at high temperatures, the solution decomposition of 50 is slow. Thus, a decalin solution of 50

1. Homolytic cleavage of a W-C bond can occur resulting in a methyl radical which can abstract H• from the solvent.
2. Creation of a vacant coordination site on W may occur, followed by α -elimination and then reductive elimination.



Coordinative unsaturation can be generated by an $\eta^5\text{-}\eta^3$ slip of a Cp ring, or by migration of a methyl group to a ring to form an endo- η^4 -methylcyclopentadiene moiety.



3. A departing methyl group can abstract H• from a Cp ring or another methyl group.

Fig. 3-8 Reductive elimination.

was heated to 170° for 9 days, and the resulting volume of noncondensable gas was measured with a Toepler pump; only 85% of one equivalent of CH₄ was produced in that time (the content was checked by mass spectroscopy). The following Table shows the results of several isotopic labelling studies of the formation of methane from Cp₂WMe₂ and Cp₂W(Me)H.

Table of Reductive Elimination Results

<u>Compound</u>	<u>Solvent; conditions</u>	<u>Products</u>
1. Cp ₂ WMe ₂	C ₆ D ₆ ; 170°, 5 days	85% CH ₄ , 6% CH ₃ D
2. Cp ₂ WMe ₂	recovered from 1.	no incorporation of D .
3. Cp ₂ WMe ₂	C ₆ H ₆ ; 170°, 5 days	CH ₄
4. Cp ₂ W(CD ₃) ₂	C ₆ D ₆ ; 170°, 14 days	80% CD ₃ H, 20% CD ₄
5. Cp ₂ (Me)H	C ₆ D ₆ ; 80°, 2 days	95 % CH ₄ , less than 5% CH ₃ D

The experiment labelled 4., in which the only source of H is the Cp-rings of the organometallic dialkyl, suggests that most of the CH₄ formed by heating Cp₂WMe₂ is the result of the capture of H• from a Cp ring, in what may be an intimate radical process. There is also evidence for approximately 10% of the methane being formed by free methyl radicals scavenging H• (or D•) from the solvent, and for a similar amount of H-capture from other methyl groups, so the reaction is not 'clean' in the sense of proceeding via only one pathway. These results show that the production of methane from Cp₂W(Me)₂ is similar to its formation from Cp₂Ti(Me)₂^{27,28} and Cp₂TiMe²⁹, whose thermal and photochemical decompositions have been elegantly studied in the laboratories of Rausch²⁷, Teuben²⁹, McCowan²⁸. These workers deuteriated the Cp rings as well as

the methyl groups of their compounds, and found the major process to be intermolecular H-abstraction from Cp rings, which accompanies some intramolecular alpha-elimination³⁰.

Experiment 5. demonstrates that free methyl radicals are not important in the thermal decomposition of $\text{Cp}_2\text{W}(\text{Me})\text{H}$ in benzene, but does not rule out hydrogen abstraction from the Cp rings. However, the product of this decomposition is known²⁵ to be $\text{Cp}_2\text{W}(\text{Ph})\text{H}$, so the scavenging of hydrogen from the rings seems unlikely here. The preparation of isotopically pure $\text{Cp}_2\text{W}(\text{Me})\text{D}$ is described briefly below. The original, lengthy route to $\text{Cp}_2\text{W}(\text{Me})\text{H}$ ²⁵ was shortened by Mahtab, who found that one equivalent of benzoic acid reacts with Cp_2WMe_2 to give $\text{Cp}_2\text{W}(\text{Me})(\text{OOCPh})$, which can be reduced with $\text{Na}[\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})_2\text{H}_2]$, Redal, to give the desired product. The particular reducing agent was found to be critical, since NaBH_4 , LiAlH_4 , and other hydrides were not suitable. Since Redal is produced by the autoclave reaction of aluminium, glyme (2-methoxy ethanol), and sodium in benzene at elevated temperature and pressure, the synthesis of deuteriated Redal was envisioned as an expensive process; Aldrich Chemical Company was unwilling to undertake such a synthesis, and we decided to seek an alternative route to the desired compound. A number of reducing agents, including $\text{NaBH}_4/\text{cyclohexyl-18-crown-6}$ and $\text{Li}(\text{Et}_3\text{BH})$, were reacted with both $\text{Cp}_2\text{WMe}(\text{OOCPh})$ and $\text{Cp}_2\text{WMe}(\text{I})$, and the reaction of $\text{Cp}_2\text{W}(\text{Me})\text{I}$ with $\text{Li}(\text{Et}_3\text{BH})$ successfully yielded $\text{Cp}_2\text{W}(\text{Me})\text{H}$. The reaction was then repeated with commercial $\text{Li}(\text{Et}_3\text{BD})$, and the nmr of the purified product showed $85\pm 10\%$ deuteration of the hydrido position. The ir spectrum showed a peak at 1350cm^{-1}

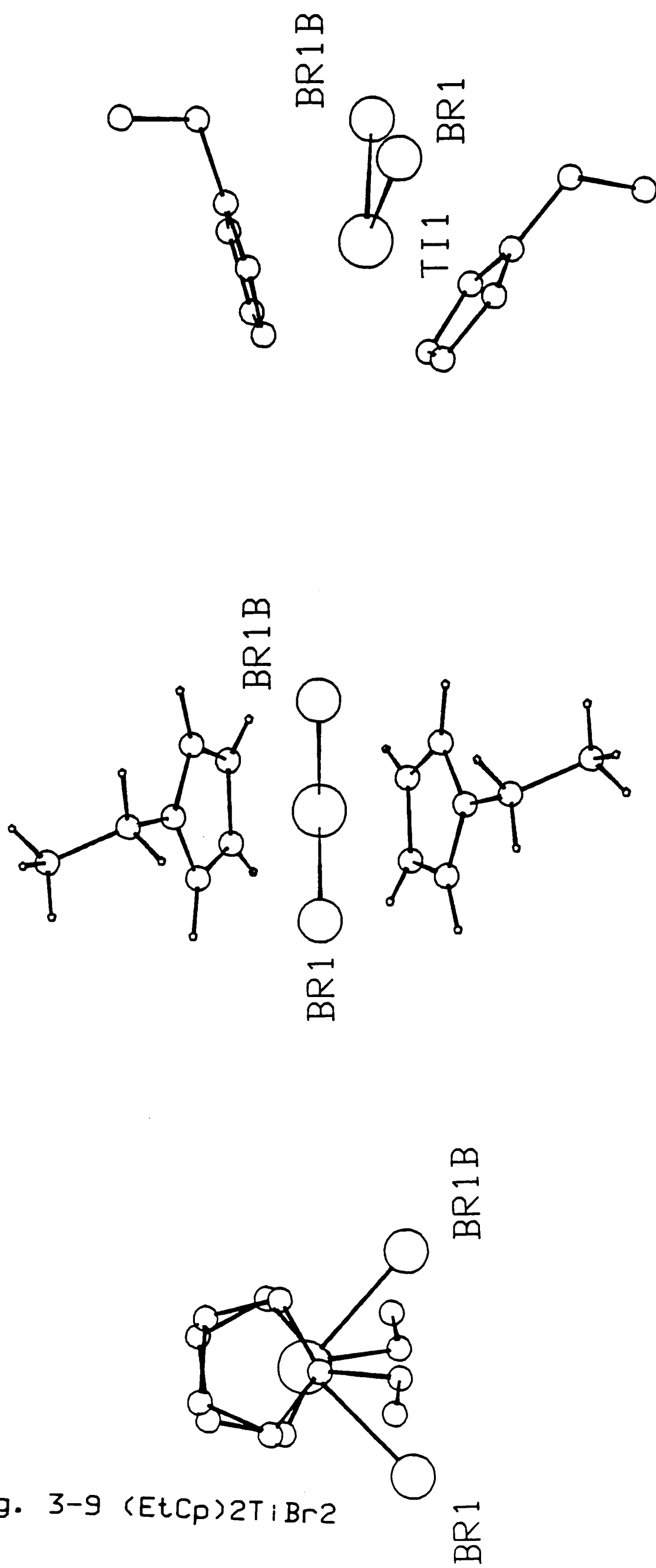
assignable to $\nu_{\text{W-D}}$ ($\nu_{\text{W-H}}=1868\text{cm}^{-1}$). Samples of the deuteriated methyl(hydride) were then thermolysed in cyclohexane and C_6D_6 , and mass spectra of the resulting gasses were kindly run by Dr. R. Aplin of the Dyson Perrins Laboratory. The cyclohexane experiment yielded a CH_4 to CH_3D ratio of 3.5:1, while the C_6D_6 experiment gave a value of 2:1 for this ratio. These results, which were corrected for the overlap of CH_2D^+ and CH_4^+ peaks, were not in accord with our intuitive expectations or with matrix-isolation studies²³ (which suggest that a concerted reductive elimination takes place), and we began to doubt the accuracy of the nmr integration. Since we had no regular access to mass spectrometry facilities at that time, these studies were not pursued further. When mass spectrometry facilities became available, and the experiments detailed in the Table above were carried out, it became apparent that the resolution of peaks due to CH_4^+ and O^+ is a delicate matter. The exact mass of O is 15.99491, and the mass of CH_4 is 16.03130 amu, so the difference is only 0.2% of the total mass. The oxygen arises from trace quantities of water in the mass spectrometer, and, since the resolution problem had not been appreciated during the early studies of $\text{Cp}_2\text{W}(\text{Me})\text{D}$, it may have influenced the confusing $\text{CH}_4:\text{CH}_3\text{D}$ ratios. Unfortunately, time has prevented my preparing $\text{Cp}_2\text{W}(\text{Me})\text{D}$ again, and, with the benefit of experience, the reductive elimination study is being continued by other students.

In view of the instability of Cp_2NbMe_2 to room-light³¹, a final experiment was conducted to probe the photochemical reactivity of Cp_2WMe_2 . Under the supervision of Dr. R.N. Perutz, and with the assistance of C.J. Nunn, 50 was

irradiated under matrix-isolation conditions with vacuum uv radiation, and the ir spectrum was inspected for signs of new compounds. The ir spectrum was unchanged by the irradiation and no reaction products were detected. Recent work by Dias³² has shown that the 17-electron cation $\text{Cp}_2\text{WMe}_2^+$ is photolabile, perhaps because oxidation of a nonbonding electron allows excitation of an M-C bonding electron into the unoccupied orbital. Furthermore, oxidation of a molecule often makes reductive elimination easier¹⁹.

(EtCp)₂TiBr₂. The crystal and molecular structure of this bent metallocene derivative was determined because the compound was thought to be a titanocene dimer which was formed by the co-condensation of titanium atoms with spiro[2.4]hepta-4,6-diene (see Chapter 4 for a discussion of the metal vapour synthesis technique). The Patterson function shows a triangular arrangement of three heavy atoms, and these were initially assigned to be titanium centres. However, the Fourier-map peak heights were consistent with a TiBr_2 moiety, and this structure refined in a satisfactory manner. The remaining carbons and hydrogens were readily located, and the resulting molecular structure is shown in Fig. 3-9. $(\text{EtCp})_2\text{TiBr}_2$ has crystallographic two-fold symmetry, with the C_2 axis passing through Ti1. The final R-value is 5.08%, $\text{Rw}=6.15\%$, with all atoms anisotropic except hydrogens, which were placed geometrically. The temperature factors of the ethyl carbons reveal fairly high thermal motion, or slight disorder; some important dimensions³³ of the compound (in Å and °) are:

Fig. 3-9 (EtCp)₂TiBr₂



Ti1-Br1 2.334(1)

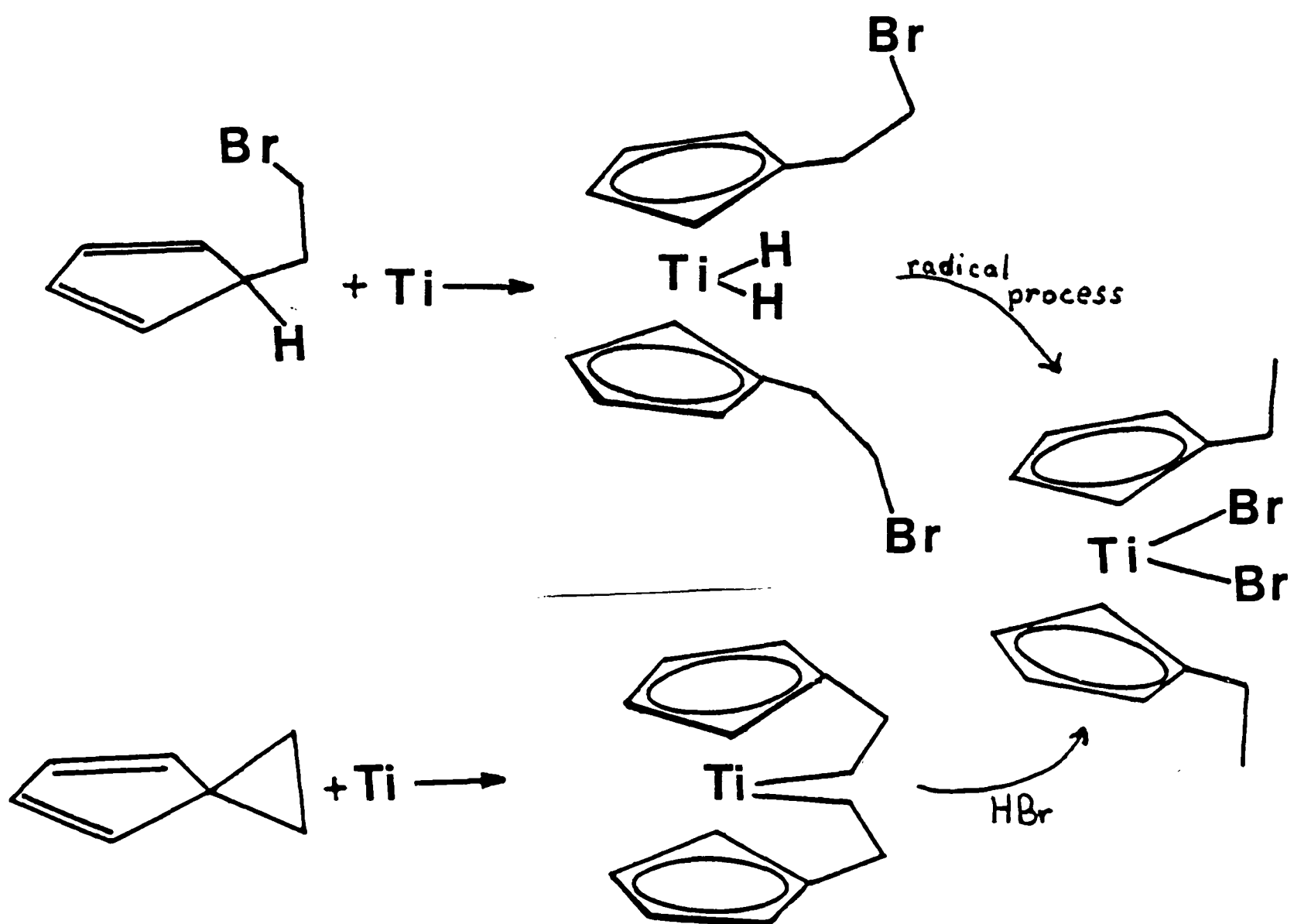
Br1-Ti-Br1B 93.7(1)

Ti1-C(pi) 2.334(1)- 2.428(8)

Ti-ring plane 2.063

angle between ring normals 128.3

In retrospect, it was found that the mass spectrum of the crystals was in perfect agreement with the crystal structure analysis. The synthesis, which was performed by Dr. A. Barretta, has not proved reproducible, and there is some doubt about the purity of the spirodiene co-condensate. Several possible synthetic routes to $(\text{EtCp})_2\text{TiBr}_2$ are illustrated below. The first is based on the preparation of the spirodiene ligand, and the second, which is an analogy to known Group VI chemistry³⁴, postulates the presence of HBr as an impurity in the reaction mixture (hydrolysis of alkyl halides commonly leads to acid impurities).



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Chapter 4 Low-valent Phosphine and Arene Derivatives
of the Early Transition Metals

4.0 Low-valent Derivatives of the Early Transition Metals

This chapter describes extended-Hückel calculations on bis(arene)molybdenum hydrides, the crystal structure of $\text{Hf}(\eta\text{-MePh})_2(\text{SnMe}_3)_2$ ¹, and the structures of two molybdenum trimethylphosphine derivatives², $\text{Mo}(\text{PMe}_3)_6$ and $\text{Mo}(\text{PMe}_3)_2(\text{C}_4\text{H}_6)_2$; all of these compounds have either been made by the metal vapour synthesis (MVS) technique^{3,5,6}, or by further reaction of an MVS-derived product.

High reactivity with organic substrates and dinitrogen is often found for transition-metal derivatives which may be described as 'electron-rich', or, alternatively, 'high-energy'. The important general characteristic of these species is the ready availability of their electrons, which allows them to be oxidized by such mild oxidants as a C-H bond. The 'availability of electrons', a rather imprecise phrase, can be quantified with the help of UV-photoelectron spectroscopy, which explores the valence levels of a molecule. Ionization potentials and band assignments for organometallic compounds have been thoroughly discussed in a recent review by Dr. J.C. Green⁴. Molecules with very low first I.P.'s, less than 5.5 eV, usually have phosphine and arene ligands, and a metal centre in a low formal oxidation state. The preparation of such compounds, and the investigation of their reactions, is of considerable interest to organometallic chemists.

Metal vapour synthesis was pioneered by Skell⁵ and Timms⁶, who co-condensed metal atoms with substrates which were typically organic liquids or solutions. The first machines used resistance-heated furnaces and hot filaments as their sources of metal atoms, and were used to synthesize a number of new and known compounds, especially with metals of the first transition series. The MVS technique allows direct reaction between transition metal and substrate without the high temperature that is usually required for acceptable kinetics. A large-scale, electron-gun metal vapour synthesis machine was recently developed in Oxford by Dr. F.G.N. Cloke, making possible a systematic study of low-valent compounds of even the most refractory metals. This MVS machine, which has been described in detail elsewhere^{3,7}, operates on a several gram scale, and was the source of the compounds described below, or their precursors.

4.1 Bent Bis(arene) Tungsten Derivatives.

Among the low-valent compounds that have been prepared via the MVS method are the bis(arene) tungsten(0) derivatives, whose chemistry has been explored by F.G.N. Cloke, G.E. Morris, P.R. Brown, and N.J. Hazel, in the laboratories of Dr. M.L.H. Green^{3,8}. It was found that several bis(arene) tungsten compounds, including $(\text{PhF})_2\text{W}$ and $(\text{PhMe})_2\text{W}$, could be protonated, giving the first arene analogues of bent bis(Cp)M derivatives. A chloride analogue, $(\text{PhMe})_2\text{WCl}^+$, was also prepared⁹. In competition with the protonation of $(\text{arene})_2\text{M}(0)$ is a one-electron oxidation, which yields the 17-electron

cation, $(\text{arene})_2\text{M}^+$. In contrast to the tungsten chemistry, for $(\text{arene})_2\text{Mo}$, when the arene is a common ligand such as PhMe, the one-electron oxidation is dominant, and the bent $(\text{arene})_2\text{MoH}^+$ species has not been isolated. Recently, however, I. Treurnicht has successfully protonated (silylarene) $_2\text{Mo}$ compounds such as $(\text{C}_6\text{H}_5\text{SiMe}_3)_2\text{Mo}$ and $(\text{C}_6\text{H}_5\text{SiMe}_2(\text{vinyl}))_2\text{Mo}^{3,10}$.

Gourdon and Prout determined the crystal and molecular structures of $(\text{arene})_2\text{WH}^+$, arene=FPh 20, MePh 21, in order to characterise the structural features of this new class of molecule¹¹. The hydrido ligands were not located, but there is clear evidence for them in ir and nmr spectra, and they are assumed to lie in the plane that bisects the angle between the C_6 rings, 1.85 Å from W. As shown in Fig. 4-1, 20 and 21 have different arene-ring conformations: the fluorines of 20 form an eclipsed F-H-F arrangement, while the toluene methyl groups point away from the hydrido ligand. It was initially thought that F-H hydrogen bonding stabilized the eclipsed conformation of 20, and P.R. Brown examined its ir spectrum, and the ir of $(\text{FPh})_2\text{WD}^+$, for the vibrational consequences of such bonding⁹. The W-H stretch was assigned to a band at 1898 cm^{-1} , which shifted to 1375 cm^{-1} for the deuteride. The value of $\nu(\text{W-H})/\nu(\text{W-D})$ is 1.38, which corresponds to the theoretical (anharmonic) value for a 'pure' M-H vibration. The W-H stretch is to higher frequency than that found for 21, 1859 cm^{-1} , but it is not exceptional for a tungsten hydride. However, the postulated hydrogen bond is nearly orthogonal to the M-H vector, and might be expected to have a greater effect on the M-H bending modes, which occur at low frequency (approximately

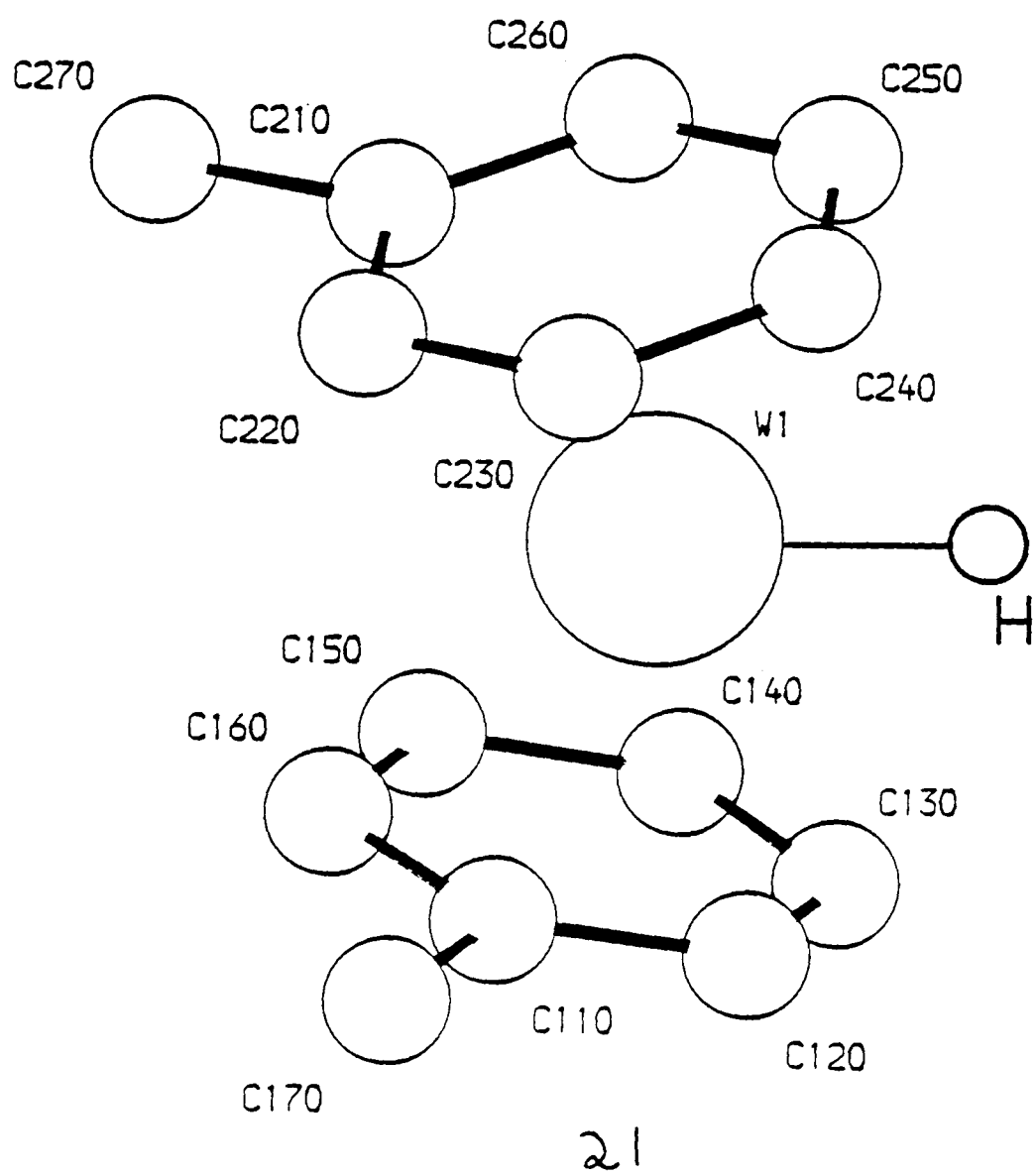
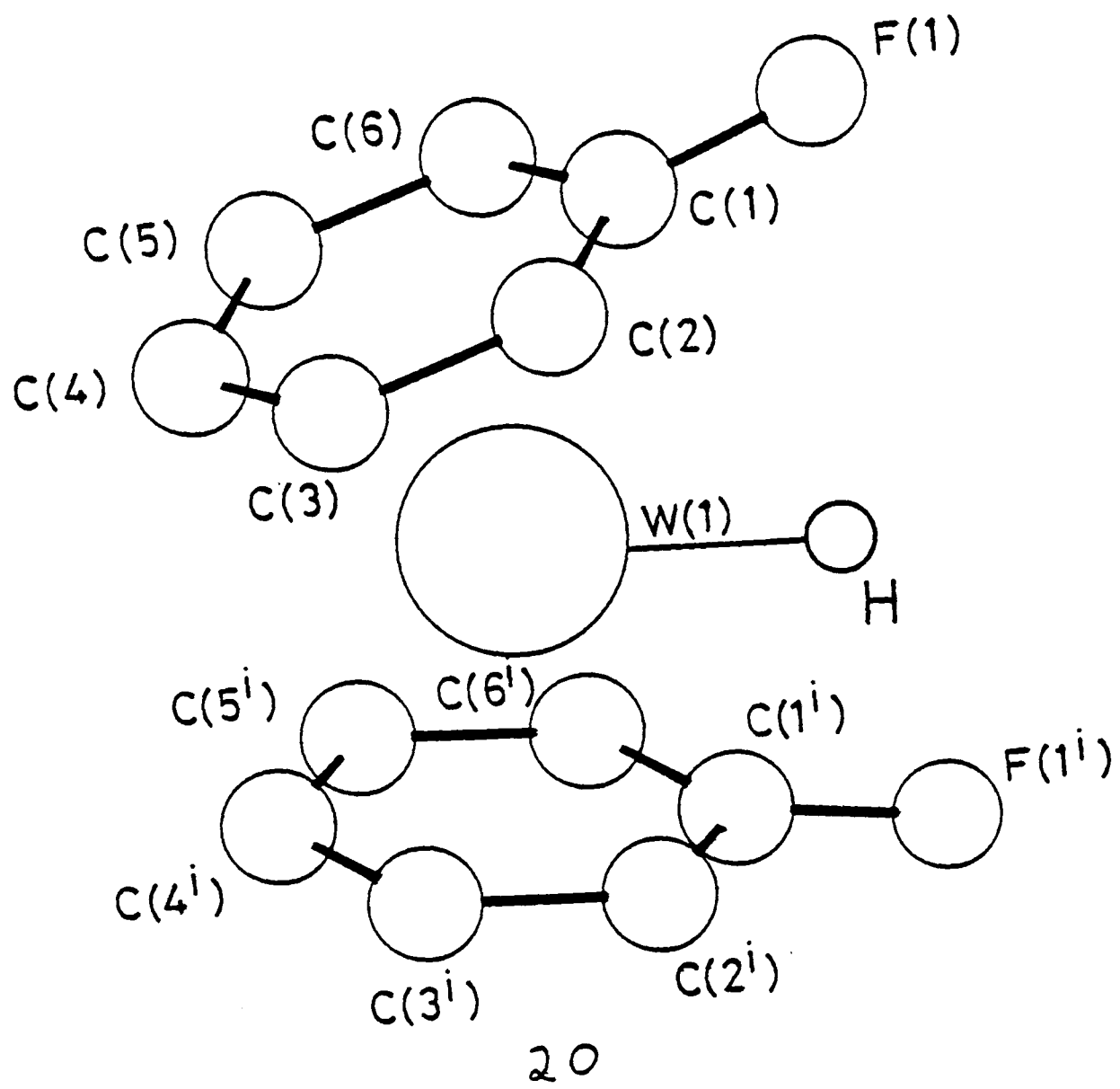


Fig. 4-1 Bent bis(arene) hydrides.

700 cm^{-1}), and usually mix with other bands in complex molecules¹². There are some unusual features in the spectrum of 20: a number of weak bands occur in the M-H region of 1800-2000 cm^{-1} . However, these absorptions do not undergo any clear changes on deuteration, and the bands were not assigned.

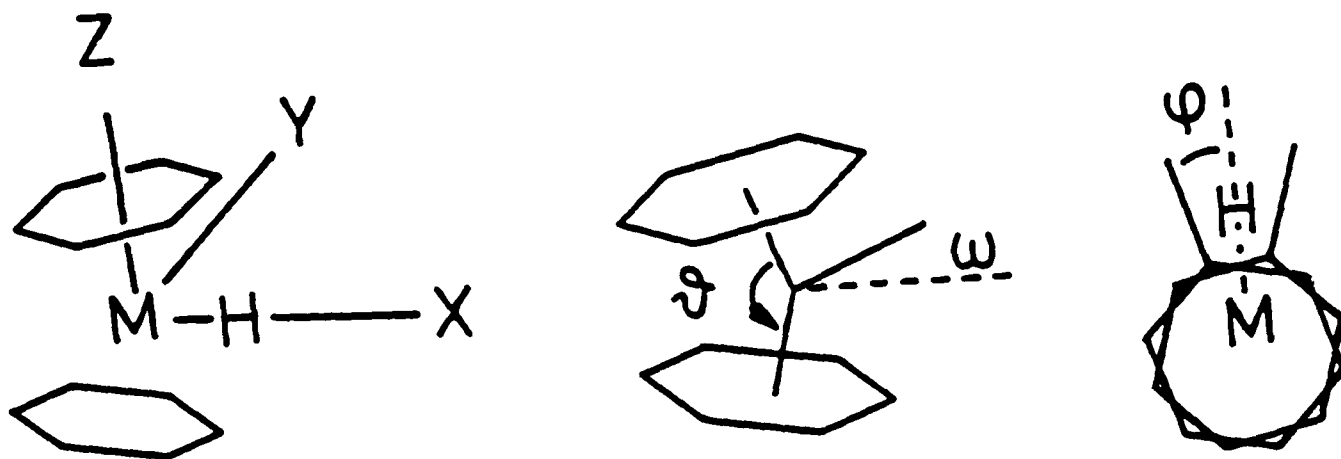
Since there was no spectroscopic evidence for an F-H hydrogen bond, it seemed that there might be another reason for the observed conformations of 20 and 21: fluorine and methyl, with very different electronegativities, split the degeneracy of benzene's MO's in different ways, and might therefore impose strong orientational preferences on any arene-metal interactions. If this were the case, then simple perturbation-theory arguments might form an adequate basis for the predication of conformations of ring-substituted sandwich compounds. I decided, therefore, to test this hypothesis by investigating the electronic structures and conformational preferences of 20 and 21, using qualitative and semi-quantitative techniques. Different calculational procedures have recently been critically reviewed by Mingos, who singled out the extended Hückel (EH) method as being particularly appropriate for geometrical problems in organometallic chemistry¹³. For such problems, it is sufficient to calculate the relative energies of different angular dispositions of ligands about a metal centre, and these relative energies are determined largely by changes in overlap. More sophisticated calculations are necessary only when absolute energies and precise bond lengths are required. The relative economy of EHT is also an important advantage. The programs used for this study include COORDINATE, GENERATE,

and ICON8, which were written by Professor Hoffmann's group at Cornell, and were kindly supplied along with advice by Dr. D.M.P. Mingos and his students¹⁴.

4.2 Structure and Bonding of Bent Bis(arene) Compounds.

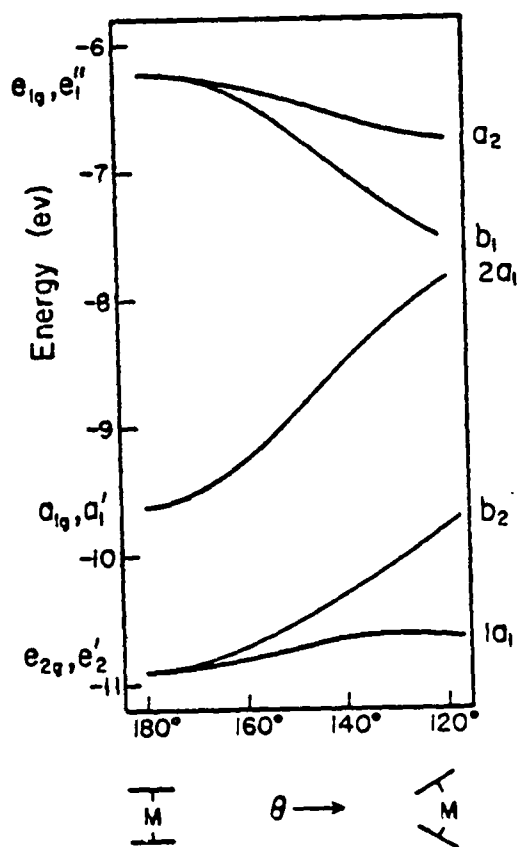
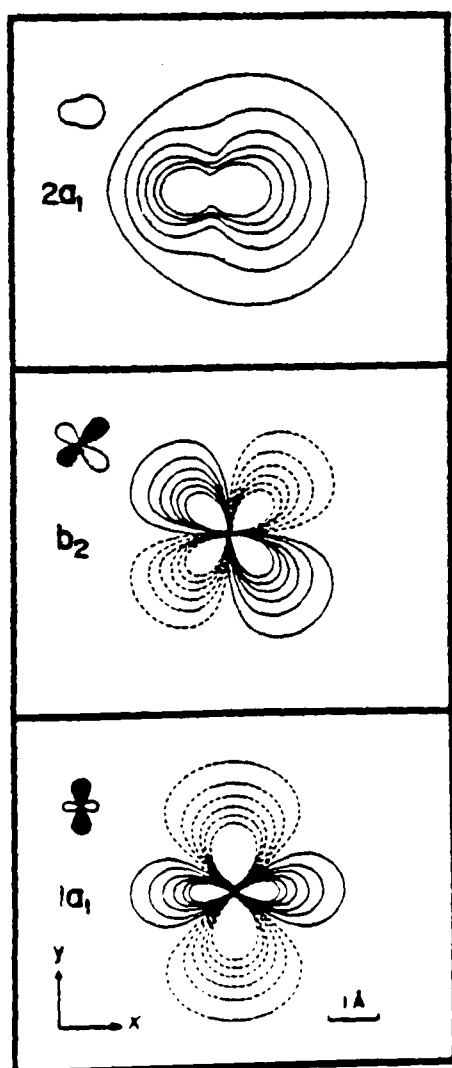
The bonding studies reported here are in two parts. The first section deals with the relationship between $(\text{arene})_2\text{M}$ and Cp_2M systems, with the parent, parallel sandwich compound $(\text{C}_6\text{H}_6)_2\text{Mo}^{2+}$ 22, the effect of bending back the rings on its frontier orbitals, and the interaction between these orbitals and a hydride ligand. The dication 22 was studied for consistency: both it and $(\text{C}_6\text{H}_6)_2\text{MoH}^+$ are d^4 species. It was necessary to study bent 22, because, in spite of the great number of experimental⁴ and theoretical^{15,16} studies of Cp_2MX_n and parallel bis(arene) derivatives, to my knowledge no calculations had been performed to investigate the structure and bonding of a bent bis(arene) molecule. After establishing some general principles governing bent $(\text{arene})_2\text{M}$ fragments, I address the conformational preferences of 20 and 21. For computational expediency, all EH calculations were carried out on molybdenum derivatives, and, to make full use of symmetry, the molecular dimensions were idealized, with all C-C bonds set to 1.41 Å, all C-H bonds 1.09 Å, the Mo-H bond 1.78 Å, and the Mo to ring-centroid distance set to 1.82 Å.

To avoid confusion in the discussion of bonding in parallel and bent sandwich compounds, I define in Fig. 4-2 a standard coordinate system. I prefer not to relabel the axes



C_{2v}	
A_1	x, x^2, y^2, z^2
A_2	R_x, yz
E_1	z, R_y, xz
E_2	y, R_z, xy

Fig. 4-2 Definitions.



Molecular orbitals of $M(\eta-C_3H_5)_2$ as a function of the bonding angle θ .

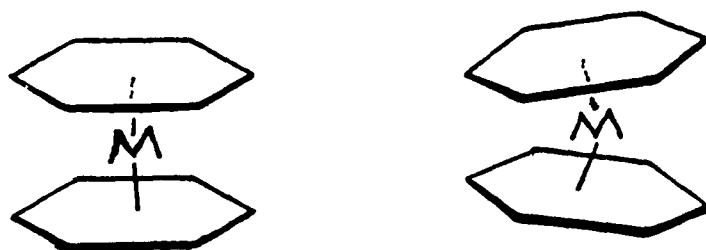
Electron density contour maps of the three frontier orbitals of electron-deficient $M(\eta-C_3H_5)_2$ fragments. The plots represent a section through the plane.

on bending from a D_{6h} (or D_{5h}) sandwich compound to a C_{2v} structure, although this results in a nonstandard setting of the C_{2v} point group (x is the C_2 axis, not z). The transformation properties of the metal orbitals are given in Fig. 4-2 for this coordinate system, and all literature results that are discussed below have been transformed to be consistent with this standard. I also define three geometry variables in Fig. 4-2: θ , ϕ , and w . The angle between the ring normals is θ , whose value is 180° for a parallel sandwich compound such as bis(benzene)Mo. The angle ϕ is the torsion angle R-C-M-H which, for substituted arene derivatives, describes the rotation away from an eclipsed R-H-R arrangement, about the M-ring-centroid vector. Finally, w is the angle that the M-H bond makes with the x-axis, which is zero for most of the cases to be discussed.

The frontier orbitals of Cp_2M derivatives form a good starting point for discussing the bent bis(arene) system, because there is a great similarity between the two types of compound: the Cp ligand may be considered an aromatic anion, with six pi electrons available for donation to a metal. Of course, arene is a less oxidizing ligand than Cp, so that bis(arene)W is zero-valent, while Cp_2W is formally divalent.

The current bonding model for bent Cp_2MX_2 systems evolved from the work of many researchers. The most recent major alteration to the theory was made by Alcock¹⁷, and later Green, Green, and Prout¹⁸, who removed the nonbonding a_1 orbital from between the M-X bonds and placed it, still in the MX_2 plane, outside of the M-X vectors. This proposal was

confirmed by the elegant crystallographic studies of Prout¹⁹, who correlated many structural properties of the Cp_2MX_2 series with the number of d-electrons at the metal. It was shown, for example, that X-M-X angles fall into three distinct, nonintersecting groups: $94-97^\circ$ for d^0 compounds, $85-88^\circ$ for d^1 compounds, and $76-82^\circ$ for d^2 derivatives. Lauher and Hoffmann²⁰ subsequently explained the effect of bending back the rings on a metallocene's frontier orbitals, as part of a comprehensive extended-Hückel study of bent metallocenes. In idealized forms, both bent Cp_2M and $(\text{arene})_2\text{M}$ fragments have C_{2v} symmetry, and the effect of bending the arene fragment may be described with the help of Lauher and Hoffmann's correlation diagram for the analogous metallocene process (Fig. 4-2).



The HOMO's are destabilized, although $1a_1$ manages to remain at nearly the same energy as the e_{2g} level, because it mixes with the higher lying $2a_1$. The antibonding e_{1g}^* descendents are stabilized as θ becomes smaller, because the (antibonding) overlap with the filled ligand ' e_{1g} ' level is decreased, and because they mix with empty ligand π^* levels, an interaction which had been symmetry-forbidden in the unbent state. The

contour diagrams in Fig. 4-2 are from Lauher and Hoffmann's²⁰ calculation on Cp_2Ti with $\theta=136^\circ$; they show the extent of mixing between d_z^2 and $d_{x^2-y^2}$, and we might expect them to adequately describe the directional properties of the frontier orbitals of a bent $(\text{arene})_2\text{M}$ fragment. However, this is not quite the case, as my calculations on $(\text{benzene})_2\text{Mo}^{2+}$ 22 have shown. Since θ was found by Gourdon and Prout¹¹ to be 156° for both 20 and 21, and since Lauher and Hoffmann's calculations refer to Cp_2Ti with $\theta=136$, I carried out EH calculations on 22 with $\theta=180, 156$, and 136° .

$(\text{C}_6\text{H}_6)_2\text{Mo}^{2+}$, $\theta=180^\circ$. The EH calculations on this dication give the same MO scheme as they would for the neutral sandwich compound, but only four metal electrons are included when the orbitals are filled according to the aufbau principle. The true effect of the charge is not seen, because charge iteration (see below) was not carried out. The orbital compositions for the HOMO's a_{1g} and e_{2g} are given in Table 4-1, which includes the results of Clack and Warren's INDO calculations on bis(benzene) chromium and ferrocene for comparison¹⁶. The EH calculation on 22, $\theta=180^\circ$, accurately reproduces the well-known bis(arene)M HOMO's, but places e_{1g}^* above the virtual ring π^* orbitals, e_{2u} and e_{2g} , in disagreement with more sophisticated calculations. The same result was found by Anderson and Drago²¹, who very successfully predicted nmr contact shifts of a large series of 3d sandwich compounds with EHT calculations which were empirically corrected for electron-electron repulsion. They stressed that such an MO scheme, with $e_{1g}^* > e_{2g}^* > e_{2u} > a_{1g}$

$\rangle e_{2g}$, does not imply that the first excited state of the sandwich compounds is metal-to-ligand charge transfer in nature, because electronic transitions cannot be predicted from the energies of empty orbitals of a ground-state wave function. Furthermore, on moving to the right in the Periodic Table, self-consistent-charge EH calculations showed the e_{1g}^* to drop in energy relative to e_{2u} and e_{2g}^* , so that the correct ground states for Cp_2Co and Cp_2Ni , with e_{1g}^* occupied, were predicted²¹. The ground states of these metallocenes, which have 19 and 20 electrons, respectively, are known with some accuracy from esr and other experimental measurements.

For parallel sandwich compounds, with either Cp or arene ligands, there is no mixing of the d_z^2 and $d_{x^2-y^2}$ orbitals, because they are a_{1g} and e_{2g} symmetry, respectively. There is, however, an important difference^{4,15,16} in the frontier orbitals of metallocenes and bis(arene) compounds, which depends on the nature of the rings, and which Table 4-1 emphasizes. Ferrocene's e_{2g} is only 9% ligand in character, while the e_{2g} 's of bis(benzene) molybdenum and chromium have approximately 40% ligand character. The backbonding e_{2g} interaction, which is almost negligible for metallocenes, is a major contributor to bonding in arene derivatives. This backbonding results in a relatively large energy gap between a_{1g} and e_{2g} for $(\text{arene})_2\text{M}$ compounds, which is reflected in the following ionization energies⁴:

Compound	Ionization Energy (eV)		Difference ${}^2E_g - {}^2A_1$
	${}^2A_1$	${}^2E_g$	
$\text{Fe}(\text{Cp})_2$	7.23	6.88	-0.35
$\text{Mo}(\text{benzene})_2$	5.52	6.59	1.07

Table 4-1 (Cont.). A Comparison of Frontier Orbital Compositions.

Composition, %		Composition, %	
<u>Orbital</u>	<u>Ligands</u>	<u>Orbital</u>	<u>Ligands</u>
Metal		Metal	
g) Mo(C ₆ H ₆) ₂ H ⁺ , θ=136°		h) Mo(MeC ₆ H ₅) ₂ H ⁺ , θ=156°	
a ₁	30 34x ² -y ² , 33z ² , 3s	a ₁	30 35x ² -y ² , 32z ² , 3s
b ₂	37 62xy, 1y	b ₂	37 62xy, 1y
i) Mo(FC ₆ H ₅) ₂ ²⁺ , θ=156°		j) Mo(FC ₆ H ₅) ₂ H ⁺ , θ=156°	
2a ₁	26 48z ² , 13s, 7x, 6x ² -y ²	a ₁	26 37z ² , 35x ² -y ² , 2s
a ₁	48 39x ² -y ² , 8z ² , 4x, 1s	b ₂	36 62xy, 2y
b ₂	58 38xy, 4y		

The cause of the large e_{2g} interaction in bis(arene) species is that, as the ring size increases, the e levels drop in energy, and the e_{2g} ligand-metal energy match is much closer for arenes than for Cp^{4,15,16}.

$(C_6H_6)_2Mo^{2+}$, $\theta=156, 136^\circ$. As expected, the degeneracy of d_{xy} and $d_{x^2-y^2}$ is lifted for θ less than 180° , but for 22, unlike the Cp_2M case, $1a_1$ and $2a_1$ do not mix much with each other, and $2a_1$ hardly mixes with the ligands at all, even when $\theta=136^\circ$ (Table 4-1). It is quite confusing to compare the compositions of Lauher and Hoffmann's Cp_2Ti frontier orbitals²⁰ with my own results, because of the different coordinate systems; my coordinate system was chosen for a simple correspondence between the unbent and bent bis(arene)M MO schemes. However, Calhorda and Mingos²² chose the present standard coordinate system for their EHT investigation of ferrocene, $\theta=136^\circ$, which was part of a study of ferrocene-based metallocarboranes, so it is convenient to compare their frontier-orbitals compositions (Table 4-1) with my results. The reason why d_z^2 mixes so little with $d_{x^2-y^2}$ and the ligands is that the ligand a_1 is far above $2a_1$, while $1a_1$ is far below, as a result of the strong backbonding interaction which is discussed above. Thus, $2a_1$ remains almost pure d_z^2 in bent bis(benzene)Mo, and is not highly oriented along x as in the Cp_2M case.

The formation of a bond between bent bis(benzene)Mo ($\theta=156^\circ$) and a single hydrido ligand situated on the x-axis is similar to the formation of d^4 Cp_2ReH , which is described by Lauher and Hoffmann's²⁰ interaction diagram (Fig. 4-3). The resemblance is quite close, in spite of the rather weak directional properties of the bent bis(arene)M fragment MO's, because the hydride helps to mix d_z^2 and $d_{x^2-y^2}$, thus improving the sigma-bonding capability of the organometallic fragment. The $(2a_1 + \text{H } 1s)$ combination must be close in energy to $1a_1$, so that d_z^2 and $d_{x^2-y^2}$, which had been separated in energy by the backbonding e_{2g} interaction, can finally combine effectively. The resulting a_1 nonbonding level is very similar in composition to that found for Cp_2M systems (see Table 4-1), but it has been destabilized above b_2 by mixing with the lower Mo-H bonding orbital. Thus, $(\text{C}_6\text{H}_6)_2\text{MoH}^+$ has a HOMO of a_1 symmetry, while Cp_2ReH has b_2 as its HOMO, which is consistent with the well-documented increase in back-bonding on changing Cp for arene in sandwich compounds^{4,15,16}. The b_2 is quite similar in composition to the bent Cp_2M b_2 level (Table 4-1), and a compound such as bis(arene)Mo halide cation would be stabilized by donation to this pi-type orbital from a halide lone pair.

4.3 Ring-substituted Bis(arene)M Derivatives. Before discussing the effects of ring-substitution on the MO's of

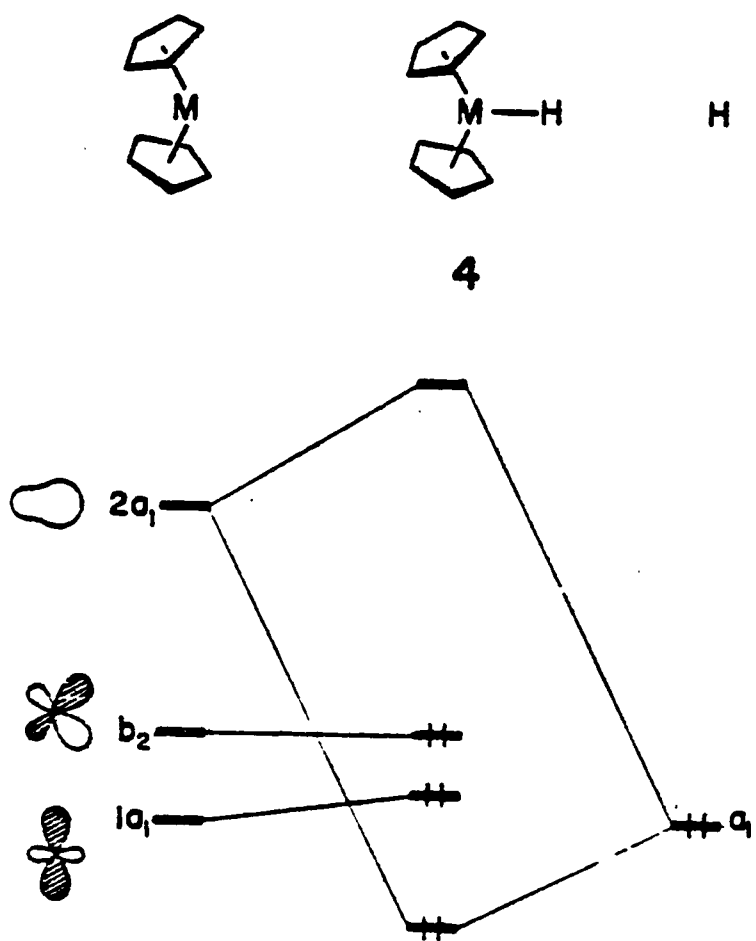
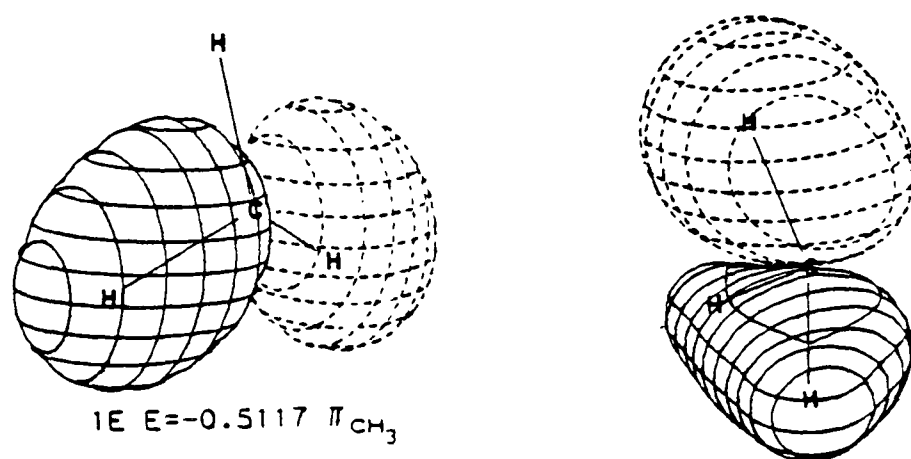
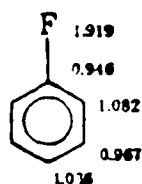
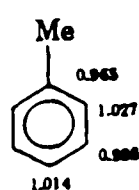


Fig. 4-3 Cp_2ReH

(PhR)₂M, it is helpful to review the pi-MO's of benzene (Fig. 4-4), and to see how they are perturbed by different substituents. In order to model the ground state of alkyl-substituted benzenes, Fleming (and others) use the MO's of the benzyl anion, which are reproduced in Fig. 4-5 from Fleming's book on frontier orbitals²³. For toluene, this model overestimates the mesomeric effect of hyperconjugation, which involves overlap between the pi-type methyl orbital⁵⁰ shown below and the arene pi system, but it has proved useful, for example in rationalizing electrophilic substitution rates.

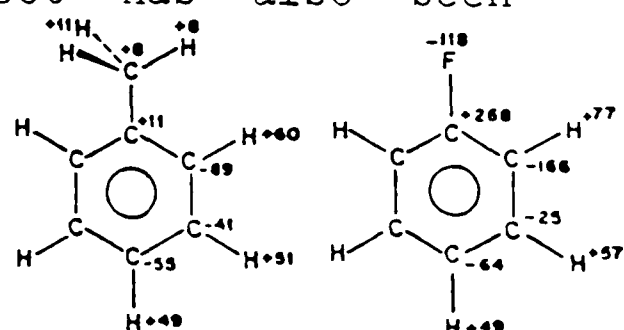


The HOMO of the benzyl anion is destabilized with respect to benzene, and this is reflected in the first ionization potentials (IP's) of 9.40 eV and 8.9 eV for benzene and MePh, respectively (the first IP of FPh is 9.5 eV). Since the D_{6h} symmetry has decreased to C_{2v} on substitution, the e levels are split; the bonding e_1 yields an a_1 , which has been stabilized, and a b_2 , which remains at the same energy as benzene's e_1 , -beta. Although the methyl group causes little flow of electron density onto the ring, and does not alter the orbital energies much, it does have an important polarizing effect on the ring's pi-density. Hehre and Pople's²⁴ ab initio calculations, the results of which are given here, show the magnitude of this polarization. This effect has also been studied with EHT, by Libit and Hoffmann²⁵.

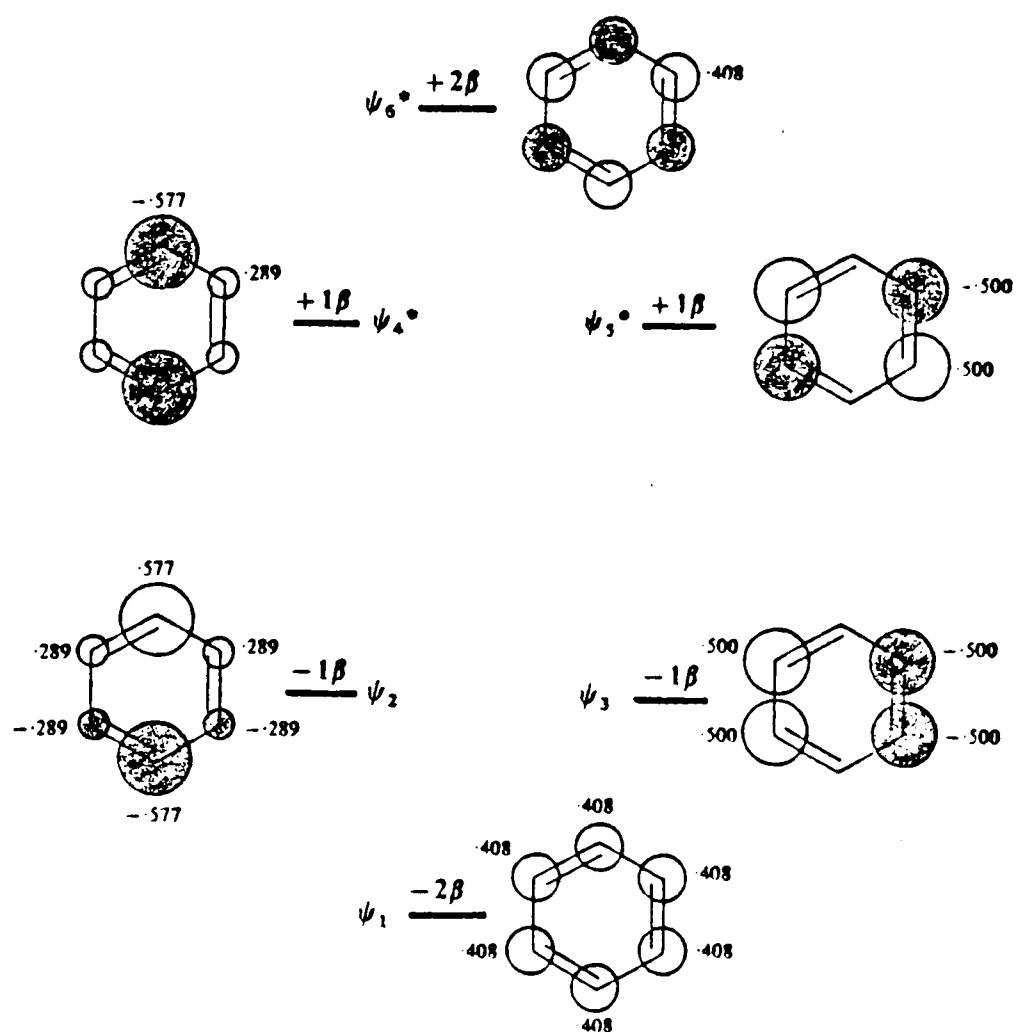


pi-charges

144



electron populations
(10^{-3} electrons)



π -Molecular orbitals on benzene

Fig. 4-4

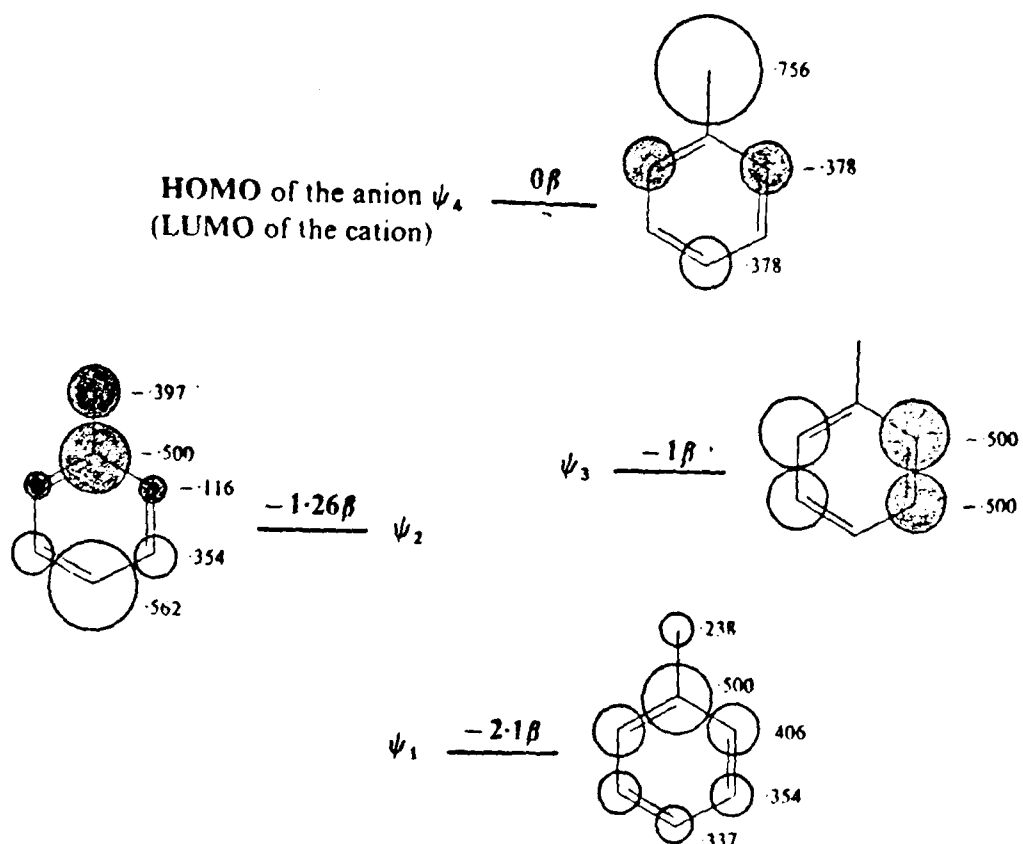
As dipole moment measurements have shown, a strongly electronegative arene substituent such as chlorine does not act merely as an electron sink^{23,24,25,26}. In addition to its sigma inductive properties, chlorine makes use of a lone pair and interacts with the aromatic pi-system in a mesomeric manner. This 'back-donation' of electron density to the ring causes a decrease in dipole moment relative to the value calculated from sigma-inductive effects alone. Fleming²³ models such a system with the pi-MO's of anisole, and his diagrams are reproduced in Fig. 4-5. Since ψ_1 is largely the heteroatom lone pair, the main a_1 ring-metal interaction of chlorobenzene would involve ψ_2 . Fluorobenzene is a different, somewhat special case, however^{24,25,26}. The pi-type lone pair of fluorine is very tightly bound, and does not overlap much with the ring pi-system, so the mesomeric interaction is similar in magnitude to the hyperconjugation in toluene, and polarization of the ring pi-orbitals is again more important than (pi) charge flow. Hehre and Pople's ab initio calculations²⁴ (see above) show FPh to be polarized in the same direction as MePh, although fluorine's sigma-inductive power does cause a more substantial positive charge on the substituted carbon than is found in MePh.

Of course, FPh and MePh have different shapes and sizes, and, since these differences may be important, the relevant van der Waals radii are given here²⁷.

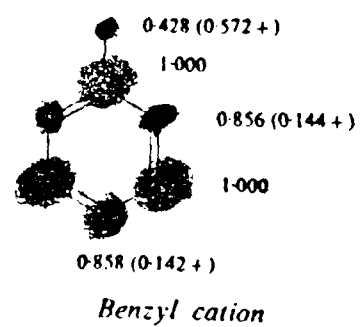
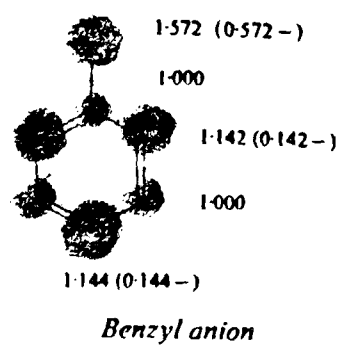
van der Waals Radius, Å

H 1.2 F 1.35 Me 2.0

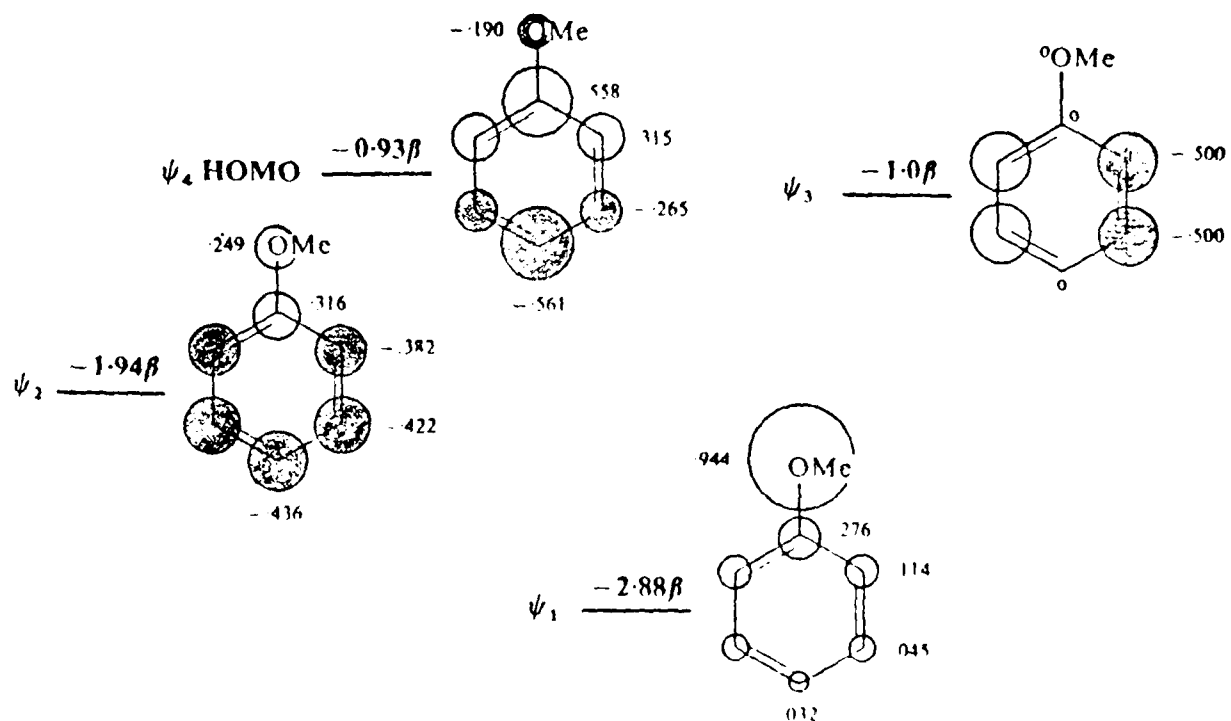
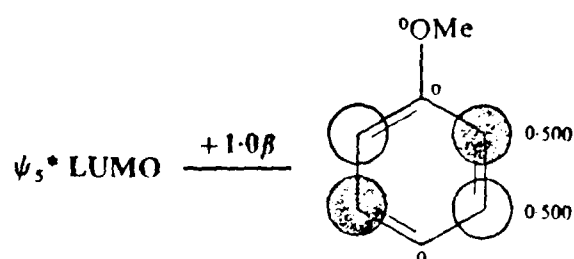
half-thickness of aromatic molecule 1.85



The occupied π -orbitals of the benzyl anion⁷



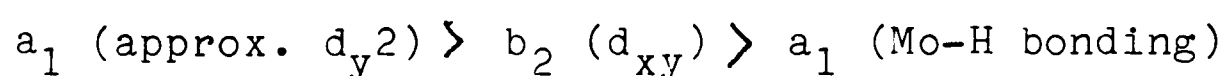
Total π -electron population (and excess-charge distribution) in the benzyl anion and the benzyl cation



Filled and LU π -molecular orbitals calculated for anisole

Fig. 4-5

In idealized, eclipsed forms, both $(\text{FPh})_2\text{Mo}$ and $(\text{MePh})_2\text{Mo}$ have C_{2v} symmetry, so that d_z^2 and $d_{x^2-y^2}$ can mix even before the rings are bent back. When the bending perturbation is switched on, the resulting frontier orbitals of $(\text{FPh})_2\text{Mo}^{2+}$ are very similar in composition to the Cp_2M fragment orbitals, whose directionality could not be matched by the orbitals of unsubstituted, bent $(\text{C}_6\text{H}_6)_2\text{Mo}^{2+}$ (Table 4-1). The combination of two perturbations, substitution and bending, both of which lower the symmetry of the ligand fragment orbitals, thoroughly mixes the metal levels of a_1 symmetry. One result of this mixing is that the relative energies of the bent bis(fluorobenzene) Mo^{2+} frontier orbitals follow the same trend as those of $(\text{C}_6\text{H}_6)_2\text{MoH}^+$; the nonbonding $1a_1$ has again been destabilized above b_2 . Since a similar MO scheme is found for eclipsed $(\text{MePh})_2\text{Mo}^{2+}$, $\theta=156^\circ$, all three hydride cations studied here, $(\text{RPh})_2\text{MoH}^+$ ($\text{R}=\text{H}, \text{F}, \text{Me}$), have the same order of frontier MO's:



Now that the MO scheme of the bent bis(arene)MH cations has been developed, we may again address the question of conformational preferences, with particular reference to 20 and 21. Such preferences may be determined by several factors which are mentioned above: polarization of the arene a_1 level, polarization and splitting of the arene e levels, and steric repulsion (four-electron destabilizing interactions). It should be noted that the e-levels are not split much, even in the benzyl radical and anisole (Fig. 4-5), and, to find a substantially noncylindrical metal-ring interaction, it may be

more effective to perturb the metal with other ligands than to perturb the ring. This will be discussed somewhat more specifically in section 4-4.

$(FPh)_2Mo^{2+}$, $\theta=156^\circ$. The rotational energy barrier of this fragment was investigated by changing the torsion angle ϕ from 0 to 180° (retaining C_2 symmetry), and calculating the total energy every 10° . The energy surface is quite flat, with a maximum at $\phi=40^\circ$, a shallow minimum at $\phi=160^\circ$, and an energy gap of 3.06 kcal/mol between these conformations which is close to the rotation barrier of ethane. The energy minimum, at $\phi=160^\circ$, is in the same region as the observed solid-state structure of 21, for which $\phi=140^\circ$.

$(MePh)_2MoH^+$, $\theta=156^\circ$. Calculations on the cation 21, $\phi=0$ to 180° , show that the eclipsed configuration ($\phi=0^\circ$) is 3.19 kcal/mol less stable than when $\phi=100^\circ$. The methyl carbon is only 2.5 Å away from the hydrido ligand when $\phi=0^\circ$, so that a destabilizing interaction is expected. Furthermore, the methyl-substituted carbon is only 2.19 Å away from the hydride in this eclipsed conformation, which is well within Pauling's value of 3.05 Å for an arene-ring to hydrogen nonbonded contact²⁷, so we should expect any conformation (of any arene) which places a ring carbon directly above the hydride to involve considerable H-C(ring) interaction (see Fig. 4-6).

Calculations on the fragment $(FPh)_2Mo^{2+}$ and on 21 show that both steric and electronic effects destabilize the $\phi=0^\circ$ conformation of a bent bis(arene)M derivative. However, the formation of 20 by addition of a hydride to $(FPh)_2Mo^{2+}$ stabilizes the $\phi=0^\circ$ conformation by 3 kcal/mol relative to the $\phi=40^\circ$ conformation, and the EH calculations show $\phi=0^\circ$ to

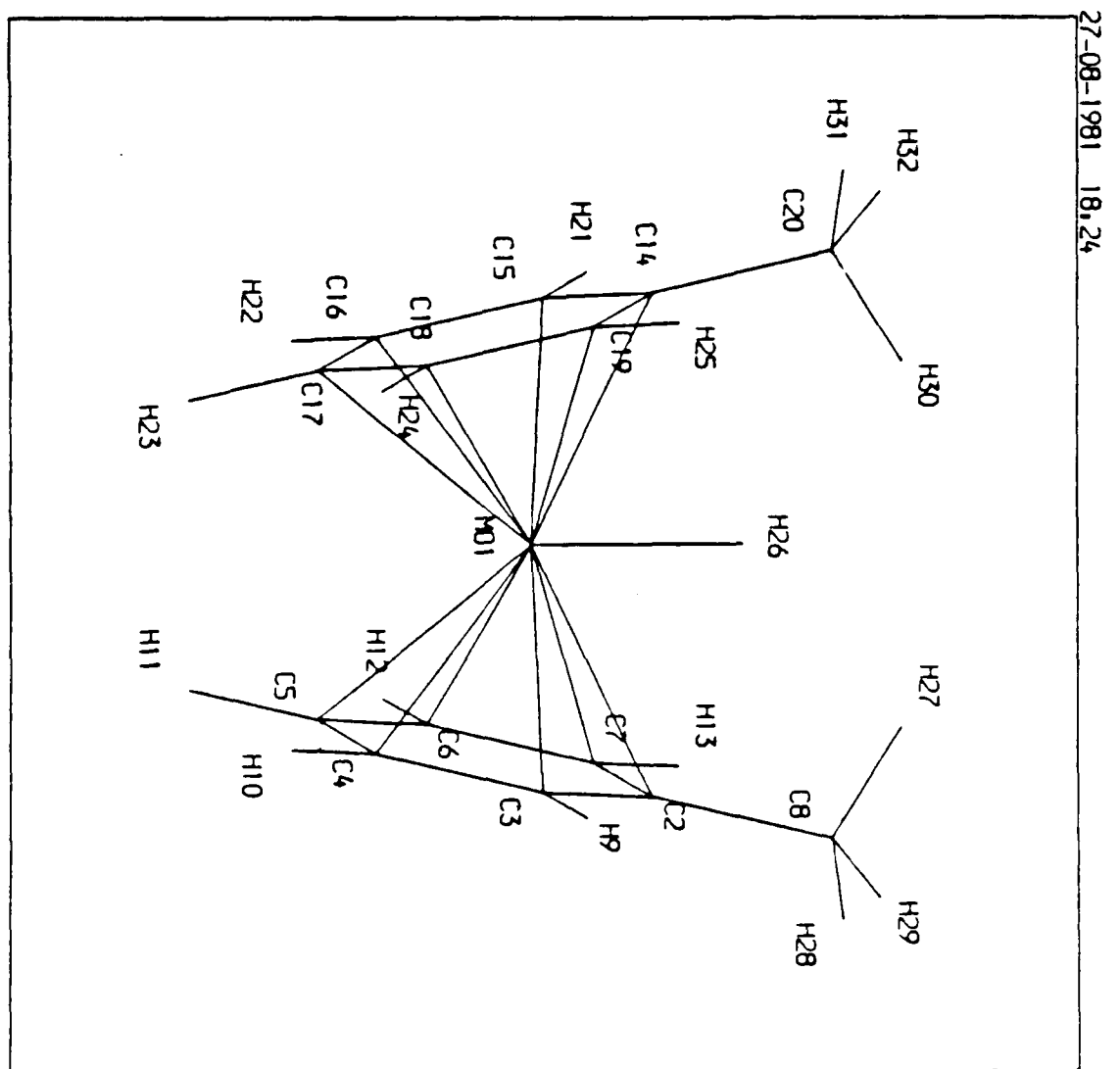
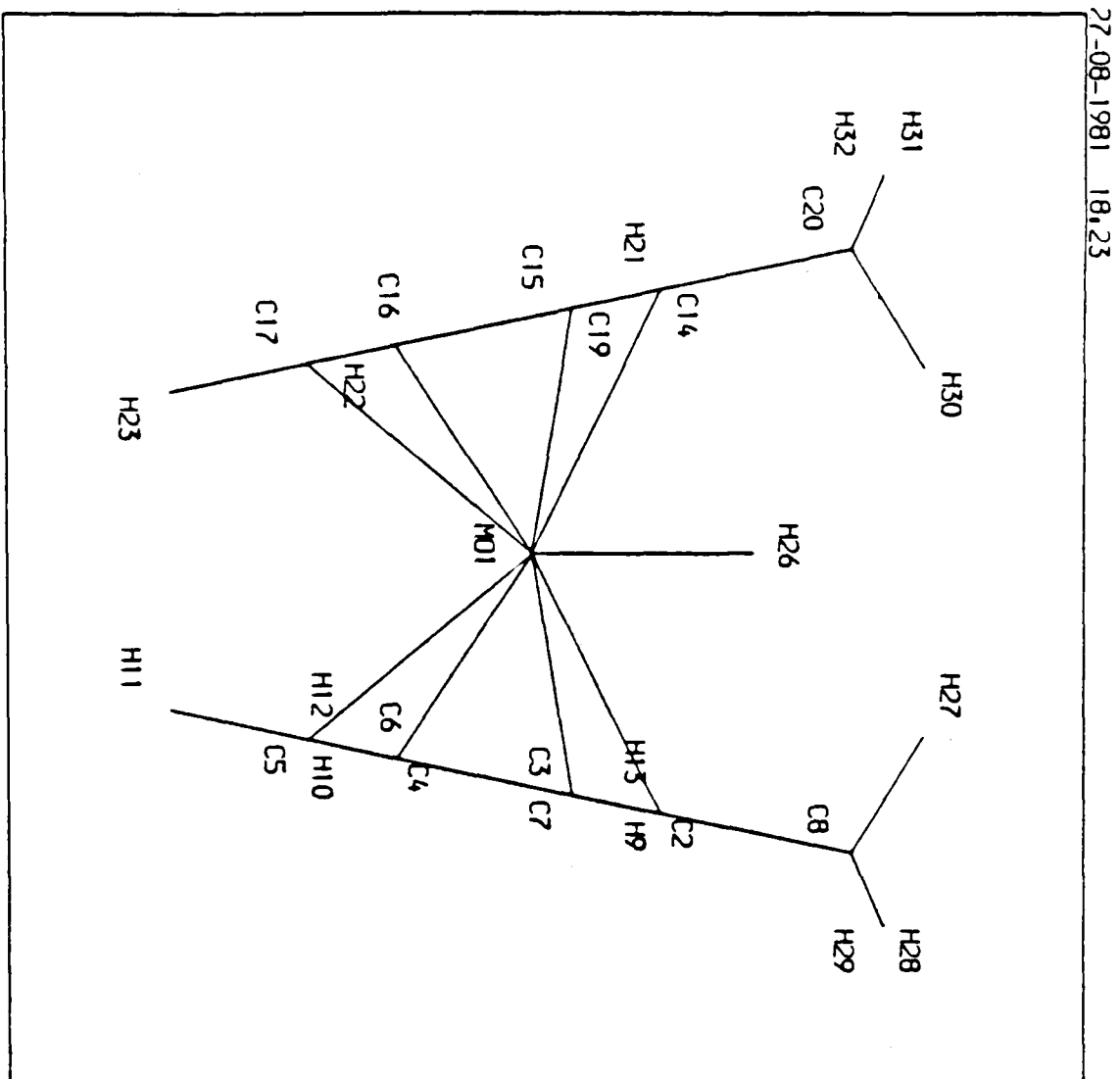


Fig. 4-6 An unfavourable conformation of 21.

be the most stable conformation of 20, in agreement with the crystal structure. So, it is the hydride itself that stabilizes this conformation, which brings to mind the original idea of F-H bonding (see Fig. 4-4). The F-H distance (for the geometrically placed hydride, Mo-H=1.7 Å), is 2.39 Å, well within the van der Waals contact distance, but examination of the reduced overlap population matrix shows the F-H Mulliken overlap population²⁸ to be small and negative (-0.0051). Furthermore, fluorine has a net atomic charge of -0.52, and the hydride is hydridic, with a charge of -0.40 (Table 4-3). Although charge-iteration, to obtain a self-consistent charge (SCC) model, was not carried out, these results may be reliably interpreted as suggesting a substantial coulombic repulsion between the fluorine and the hydride, which should destabilize the $\theta=0^\circ$ configuration.

Thus, the eclipsed F-H-F conformation is stabilized in spite of any repulsion between F and H. It is mentioned above that the substituted carbon is considerably closer (0.2 Å) to the hydride than its substituent is (see Fig. 4-4); a 2.19 Å C-H contact is really very short, so the key to the stability of 20, $\theta=0^\circ$, may be a C(ring)-H interaction. For 20, the Mulliken overlap population between the substituted carbon and the hydride is 0.0097, compared to 0.0011 for the eclipsed conformation of 21. Furthermore, an examination of the net atomic charges (Table 4-3) reveals a rather unusual situation: the substituted carbon has a high positive charge (0.72) due to the inductive effect of fluorine, so there should be an electrostatic attraction between a negatively charged hydrogen and a positively charged carbon. The actual magnitude of this interaction cannot be determined from the present

ATOM	NET CHG.	ATOMIC ORBITAL OCCUPATION FOR GIVEN MO OCCUPATION					
		S	X	Y	Z	X ² -Y ²	XY
MO 1	1.29757	0.13720	0.14761	0.11880	-0.11303	1.15710	0.99135
C 2	0.71783	1.01365	0.52207	0.90539	0.84106		
C 3	-0.11215	1.18351	0.94658	0.91816	1.06391		
C 4	-0.00291	1.18238	0.92254	0.91464	0.98336		
C 5	-0.03125	1.18231	0.89782	0.93720	1.01371		
C 6	-0.00291	1.18238	0.92254	0.91464	0.98336		
C 7	-0.11215	1.18351	0.94658	0.91816	1.06391		
F 8	-0.51785	1.76802	1.81766	1.98697	1.94519		
H 9	0.02423	0.97577					
H 10	0.02070	0.97930					
H 11	0.02141	0.97859					
H 12	0.02070	0.97930					
H 13	0.02423	0.97577					
C 14	0.71783	1.01365	0.52207	0.90539	0.84106		
C 15	-0.11215	1.18351	0.94658	0.91816	1.06391		
C 16	-0.00291	1.18238	0.92254	0.91464	0.98336		
C 17	-0.03125	1.18231	0.89782	0.93720	1.01371		
C 18	-0.00291	1.18238	0.92254	0.91464	0.98336		
C 19	-0.11215	1.18351	0.94658	0.91816	1.06391		
F 20	-0.51785	1.76802	1.81766	1.98697	1.94519		
H 21	0.02423	0.97577					
H 22	0.02070	0.97930					
H 23	0.02141	0.97859					
H 24	0.02070	0.97930					
H 25	0.02423	0.97577					
H 26	-0.39734	1.39734					

hydride

ATOM	NET CHG.	ATOMIC ORBITAL OCCUPATION FOR GIVEN MO OCCUPATION					
		S	X	Y	Z	X ² -Y ²	XY
MO 1	1.38654	0.14297	0.15141	0.11831	-0.11123	1.15283	0.90758
C 2	0.08791	1.15775	0.91120	0.92110	0.92204		
C 3	-0.07342	1.18257	0.93714	0.91591	1.03680		
C 4	-0.00727	1.18256	0.92390	0.91476	0.98605		
C 5	-0.02621	1.18237	0.89823	0.91686	1.00875		
C 6	-0.00727	1.18256	0.92390	0.91476	0.98605		
C 7	-0.07342	1.18357	0.93714	0.91591	1.03680		
C 8	-0.08469	1.20343	0.97284	0.95161	0.95700		
H 9	0.02008	0.97592					
H 10	0.02109	0.97891					
H 11	0.02171	0.97829					
H 12	0.02109	0.97891					
H 13	0.02008	0.97992					
C 14	0.08791	1.15775	0.91120	0.92110	0.92204		
C 15	-0.07342	1.18257	0.93714	0.91591	1.03680		
C 16	-0.00727	1.18256	0.92390	0.91476	0.98605		
C 17	-0.02621	1.18237	0.89823	0.91686	1.00875		
C 18	-0.00727	1.18256	0.92390	0.91476	0.98605		
C 19	-0.07342	1.18357	0.93714	0.91591	1.03680		
C 20	-0.08469	1.20343	0.97284	0.95161	0.95700		
H 21	0.02008	0.97592					
H 22	0.02109	0.97891					
H 23	0.02171	0.97829					
H 24	0.02109	0.97891					
H 25	0.02008	0.97992					
H 26	-0.39141	1.39141					
H 27	0.03420	0.96580					
H 28	0.02437	0.97563					
H 29	0.02437	0.97563					
H 30	0.03420	0.96580					
H 31	0.02437	0.97563					

(TOLY)2 MOH PLUS

Table 4-3 Net atomic charges for (FPh)2MoH +
and (MePh)2MoH +, theta=156°.

calculations, because the net atomic charges are not accurate. The EH method uses as H_{ii} 's the Valence Shell Ionization Energies (VSIE's)²⁹ of neutral atoms, and an accurate account of highly polar molecules can only be obtained by charge iteration, which adjusts the H_{ii} 's of each atom according to its calculated net charge, and then recalculates the net charge until self-consistency is reached. Since this investigation was intended to explore the qualitative influences of symmetry and electronegativity, the more elaborate SCC calculations were not carried out.

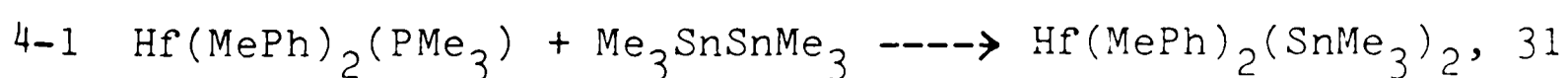
A final geometry optimization for $(FPh)_2MoH^+$ was performed by varying w , the angle between the x-axis and the Mo-H bond vector, between 0 and 10° in 1° steps. The purpose of these calculations was to determine whether the hydride might be expected to bend towards one of the positively charged carbons of the ring, and the results show that a steady destabilization occurs when this bending takes place. The $w=10^\circ$ structure is 2.2 eV less stable than $w=0^\circ$, indicating that $(FPh)_2MoH^+$ prefers a symmetrical arrangement of ligands.

4.4 Arene Hafnium Derivatives.

The zero-valent hafnium compound, bis(toluene)(trimethylphosphine)hafnium 30, was made by Dr. F.G.N. Cloke, who co-condensed hafnium atoms with a toluene solution of PMe_3 ^{7,30}. This highly reactive compound joined the bis(arene)tungsten(X) cations discussed above as the first

arene analogues of bent bis(cyclopentadienyl) derivatives, and we wished to compare the structural properties of 30 with those of the Group VI compounds, 20 and 21. Another zero-valent hafnium compound, (butadiene)₂Hf(dmpe), was reported³¹ by Wreford's group at du Pont at about the same time as 30. Wreford's compound and some related molecules will be discussed in section 4.5, which reports the crystal structures of some low-valent phosphine and butadiene derivatives of molybdenum.

Unfortunately, crystals of 30 suitable for crystal structure determination could not be grown, and crystals of the related dimer, [Hf(toluene)₂]₂dmpe, synthesized and grown by K.P. Cox, also proved unsuitable for X-ray studies. It was recognized, however, that the zero-valent hafnium compound should easily undergo oxidative addition. In fact, the problem was to find an oxidizing agent mild enough to prevent complete oxidation to a Hf(IV) species. For this reason, K.P. Cox reacted 30 with the ethane-like Me₃SnSnMe₃. The bulk of the trimethyltin groups was expected to lead to steric saturation, which is normally associated with thermal stability. The electropositive Me₃Sn ligand, was also chosen to encourage back-donation from the d² metal centre to the arene rings. Reaction 4-1 was carried out by Mr. Cox, and spectroscopic data suggested that the product was, indeed, bis(n-toluene)hafniumbis(trimethyltin) 31. Air and moisture sensitive crystals were obtained and were mounted in glass capillaries using an argon dry-box.



Examination of the diffractometer data showed the space group of 31 to be C2/c, and solution of the Patterson showed the hafnium to lie on a two-fold axis. The position of the independent tin atom was also obtained from the Patterson, but difficulties were experienced in finding the light atoms from difference-Fourier maps phased only on the two heavy atoms. The carbons could be located by successive difference-Fouriers only after an empirical absorption correction had been applied, and the heavy atoms had been refined anisotropically. The final R-value is 2.98%, $R_w=3.88\%$ for 1738 observed reflections and 106 parameters. The aromatic hydrogens were located, and included in the model without refinement, but the methyl hydrogens were not well resolved in Fourier maps, and were not included.

The molecular structure and labelling scheme of 31 are shown in Fig. 4-7. The arrangement of ligands about Hf1 is pseudotetrahedral, with the two toluene rings and the trimethyltin ligands comprising the coordination sphere. The methyl groups are all arranged to avoid each other, and the overall geometry of the molecule seems to be governed by the bulk of the ligands. The Hf1-Sn1 bond length is 2.952(1) Å, which, when compared with the 2.69 Å bond found³² in $\text{Cp}_2\text{Mo}(\text{SnBr}_3)\text{Br}$, reflects the large covalent radius of the Hf(II) centre. The arene ligand is η^6 -bonded to hafnium, with Hf-C bond lengths ranging from 2.418(8) to 2.519(8) Å, the average of which is 2.47(4) Å, comparable to the average Hf-C(pi) length of 2.50(4) Å in $\text{Cp}_2\text{Hf}(\text{o-Cp})_2$ ³³. Hf1 is 2.038

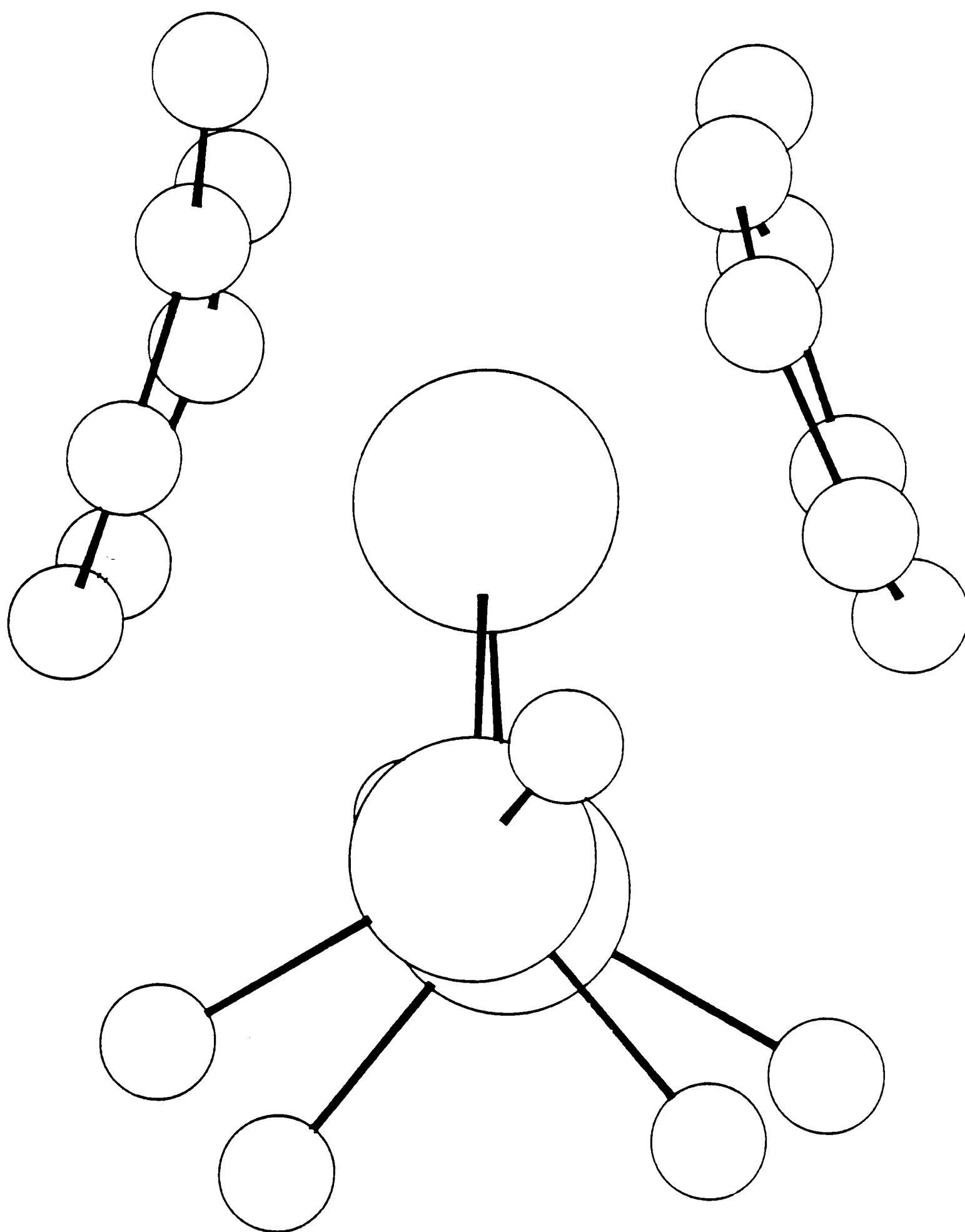
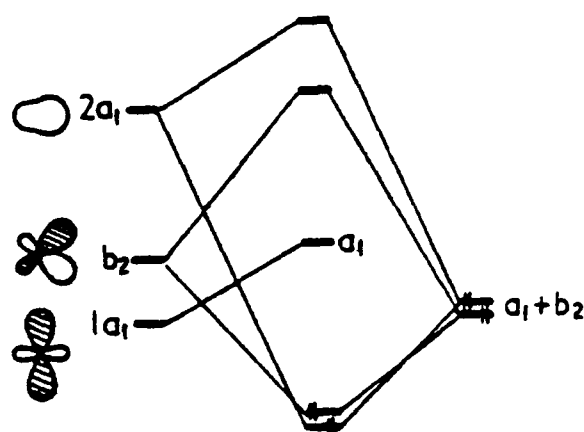


Fig. 4-7 Compound 31

Å from the least-squares best plane of the C_6 -ring, and it projects onto the plane 0.09 Å from the ring centroid. The angle between the ring-normals is 138.8° .

The electronic structure of 31 can be described with the now familiar extension of the molecular orbital scheme of Cp_2MX_2 compounds. Hoffmann's²⁰ $Cp_2M + X_2$ interaction diagram is shown here for convenience.



By analogy with the d^2 compound Cp_2MoCl_2 ¹⁹, we would expect the (a_1) lone-pair to constrain the Sn-Hf-Sn angle by electron-electron repulsion to between 76 and 82° . The observed angle is $81.14(2)^\circ$, in extremely good agreement with the predicted value, and in support of the Cp-arene analogies of sections 4.1-4.3.

Complexed arene rings sometimes exhibit a significant degree of nonplanarity, and distortion is found with the arene rings of 31: the two groups of carbons, C1, C2, C3, C4 and C4, C5, C6, C1, are noncoplanar, and the angle between the planes C6 C1 C2 and C3 C4 C5 is quite large, 8.6° . The deviations from the least-squares best plane of the C_6 ring are as follows:

Atom	Deviation($\overset{\circ}{\text{\AA}}$)	Atom	Deviation($\overset{\circ}{\text{\AA}}$)	Atom	Deviation($\overset{\circ}{\text{\AA}}$)
C1	0.036	C4	0.031	C7(Me)	0.183
C2	-0.038	C5	-0.032		
C3	0.004	C6	-0.002		

Arene rings, whether complexed or not, are usually planar within experimental error, which is commonly $0.004 \overset{\circ}{\text{\AA}}$. The nonplanarity of a complexed ring results from noncylindrical ring-metal interactions, and there are several factors, both bonding and nonbonding, which can contribute to the breakdown of cylindrical symmetry:

- 1 The nonbonded, steric contacts may be of low symmetry.
- 2 The ring e-levels are split by substitution.
- 3 The metal e-levels are split by low molecular symmetry.

The effects of arene-ring substitution are discussed above, in section 4.3, and the ring pi-MO's are shown in Fig. 4-5. With reference to labelling for the benzyl anion in Fig. 4-5, the metal-ring pi interaction can be qualitatively described as follows:

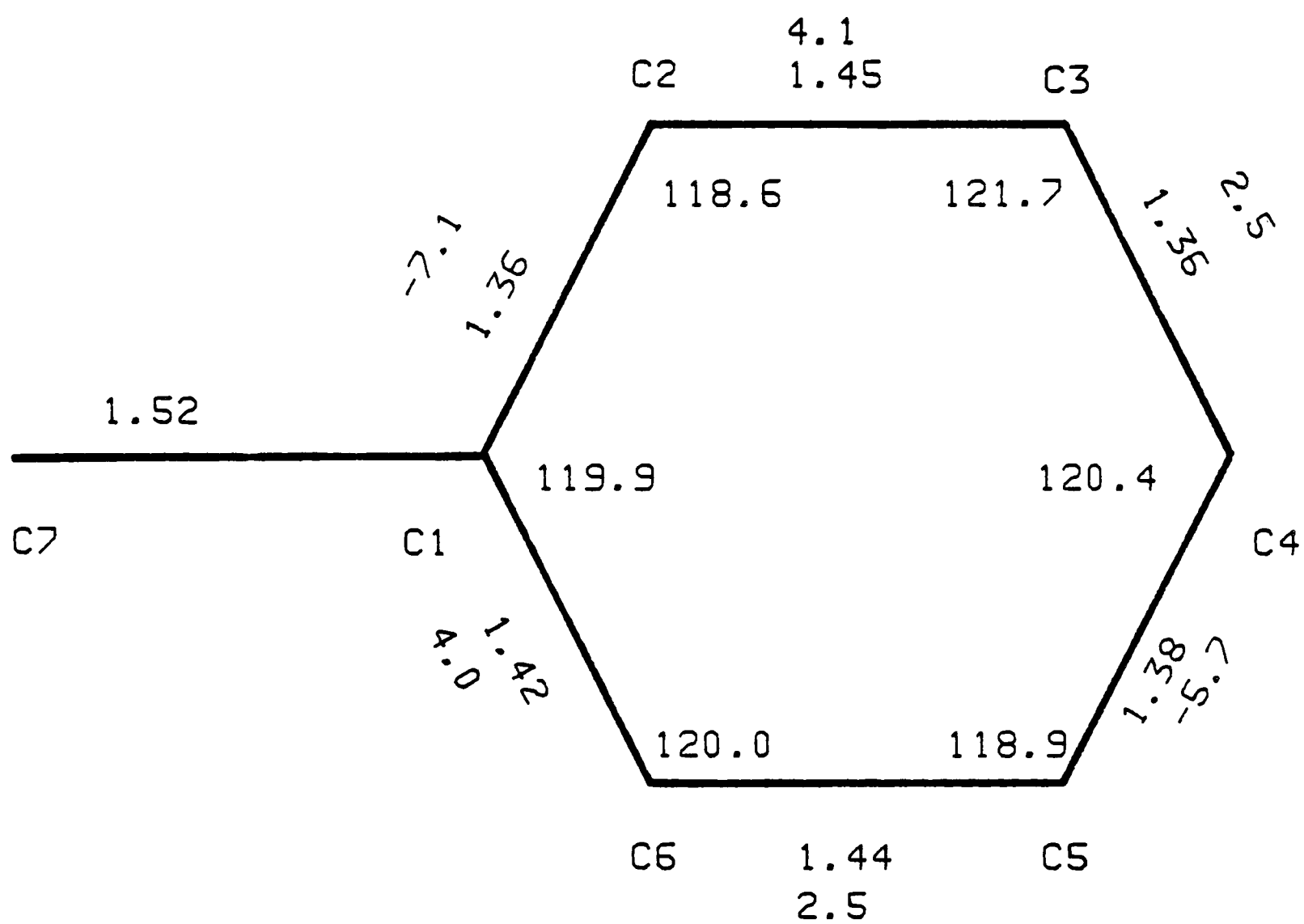
$$4-2 \quad \phi_{\text{pi}, \text{M-ring}} = (c_2 \psi_2 + c_4 d_{xz}) + (c_3 \psi_3 + c_5 d_{yz})$$

Ring distortions can be quantitatively described using the 'asymmetry paramters' which have been developed by steroid chemists³⁴, and which are based on the intra-ring torsion angles. The parameters of 31 show the absence of a mirror plane in the toluene ring, and that the best C_2 axis bisects the two bonds, C1-C2 and C4-C5. A second, less exact, C_2 axis passes through C3 and C6, and the ring may be described as having a twist conformation. The distortion axes do not

correspond to the local symmetry axes of the toluene ligand, in agreement with evidence presented below, which suggests that effect 2 is minor in comparison with effects 1 and 3. Certainly, the steric effect 1 must contribute to the dimensions of 31, which is a crowded molecule. Only 2.82 Å separate H3 from one of the trimethyltin carbons, C10, and such a van der Waals contact may push C3 and C4 out of the C₆ plane: both participate in the longest Hf-C bonds of 2.512(7) and 2.519(8) Å, respectively.

Of course, some of the ring distortions may be caused by backbonding from the metal into arene pi* orbitals. This is probably not important for the cationic molybdenum dimers 32 and 33 discussed below, but it could play a significant role in low-valent compounds. Backbonding could, for example, be the cause of the highly significant differences in ring C-C bond lengths found in 31, (see Fig. 4-6, note that the internal angles do not vary much). However, the variation in bond length does not follow a simple pattern which may be explained by symmetry arguments alone, and the correlation of C-C with Hf-C distances might best be ascribed to steric effects. C5 and C6 have the shortest M-C bonds of 2.420(8) and 2.218(8) Å respectively, and they are involved in long C-C bonds. The converse is true for C3 and C4.

It should be noted that the ring pi* orbitals have delta symmetry with respect to metal-ligand interactions. The two d-electrons of 31 are in a 'd_y²' orbital which does not extend far toward the arene rings, and is of a₁ symmetry (refer to Fig. 4-2 for the coordinate system). Any 'backbonding' from a



Bis(toluene)hafniumbis(trimethyltin),
bond lengths, angles, and torsion angles.
The e.s.d's are 0.01 Å, 0.8°.

Fig. 4-8

d^2 (arene) $_2MX_2$ system should occur by mixing of the ring π^* orbitals with the bonding b_2 orbital, which has some d_{xy} character, but also has a considerable amount of X-ligand character (see Table 4-1). For a d^4 system such as arene $_2WH^+$, the b_2 orbital is nonbonding with respect to W-H interactions, and its d_{xy} character is of the correct symmetry to mix with the arene rings (see Fig. 4-2).

Nonplanar arene rings were found by Couldwell³⁵ for the two dications 32 and 33, where the the rings fold about the C3-C6 vector by 7.7 and 9.6°, respectively (see Fig. 4-9, note the unconventional labelling scheme). These molecules have high local symmetry, but their four-fold $Mo(SR)_4$ fragments are joined to arene rings, so that the overall molecular symmetry is low, and a noncylindrical M-ring interaction is not surprising.

A dramatic example of arene-ring folding is found in the work of Atwood³⁶, who reported the structures of (arene) $MoMe_2(PMe_2Ph)_2$, arene=toluene, benzene. These compounds, 34 and 35 respectively, exhibit extremely nonplanar rings, with deviations from the plane of up to 0.09 Å in each case (see Fig. 4-10). The folding axis of 34 does not include the substituted carbon, and, of course, 35 has an unsubstituted arene ring, demonstrating that the remaining coordination environment of a metal can lift the cylindrical degeneracy of the ring-metal interaction much more effectively than ring-substitution. The resulting distortions may be qualitatively explained within the molecular orbital approximation with the help of Eq. 4-2 (effect 3), with terms

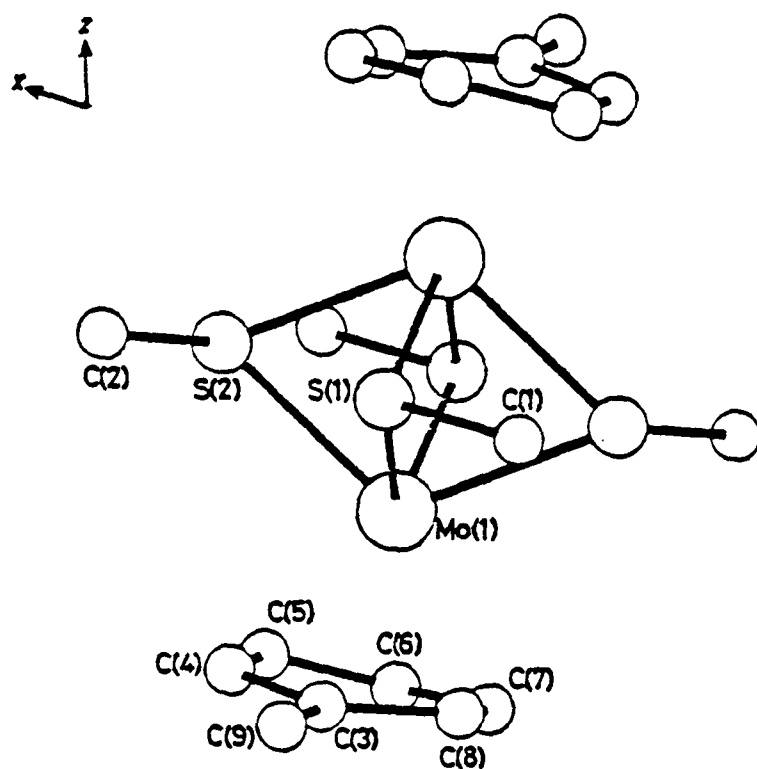


FIGURE. Structure of $[(\eta\text{-MePh})\text{Mo}(\mu\text{-SMe})_4\text{Mo}(\eta\text{-MePh})]^{2+}$.

32

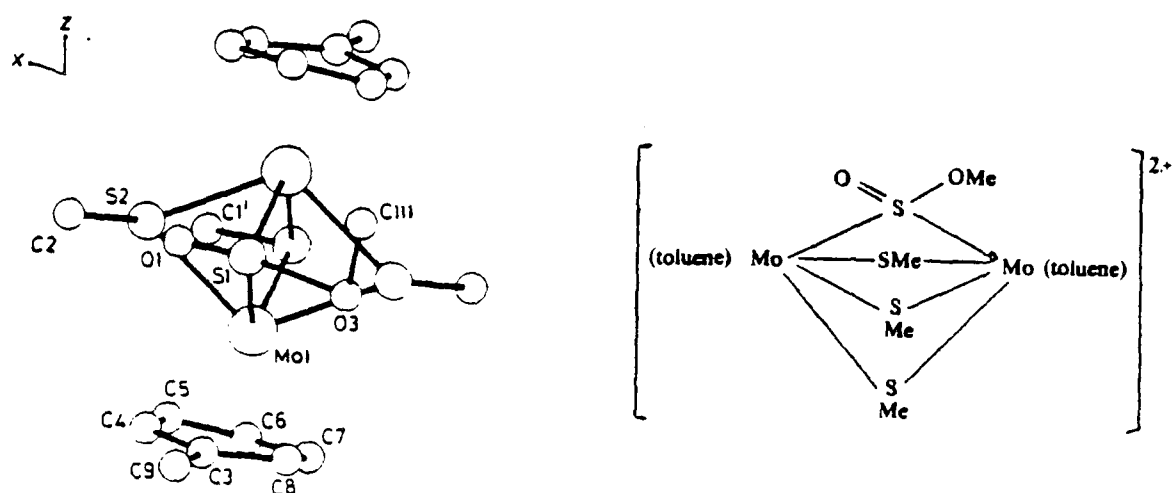
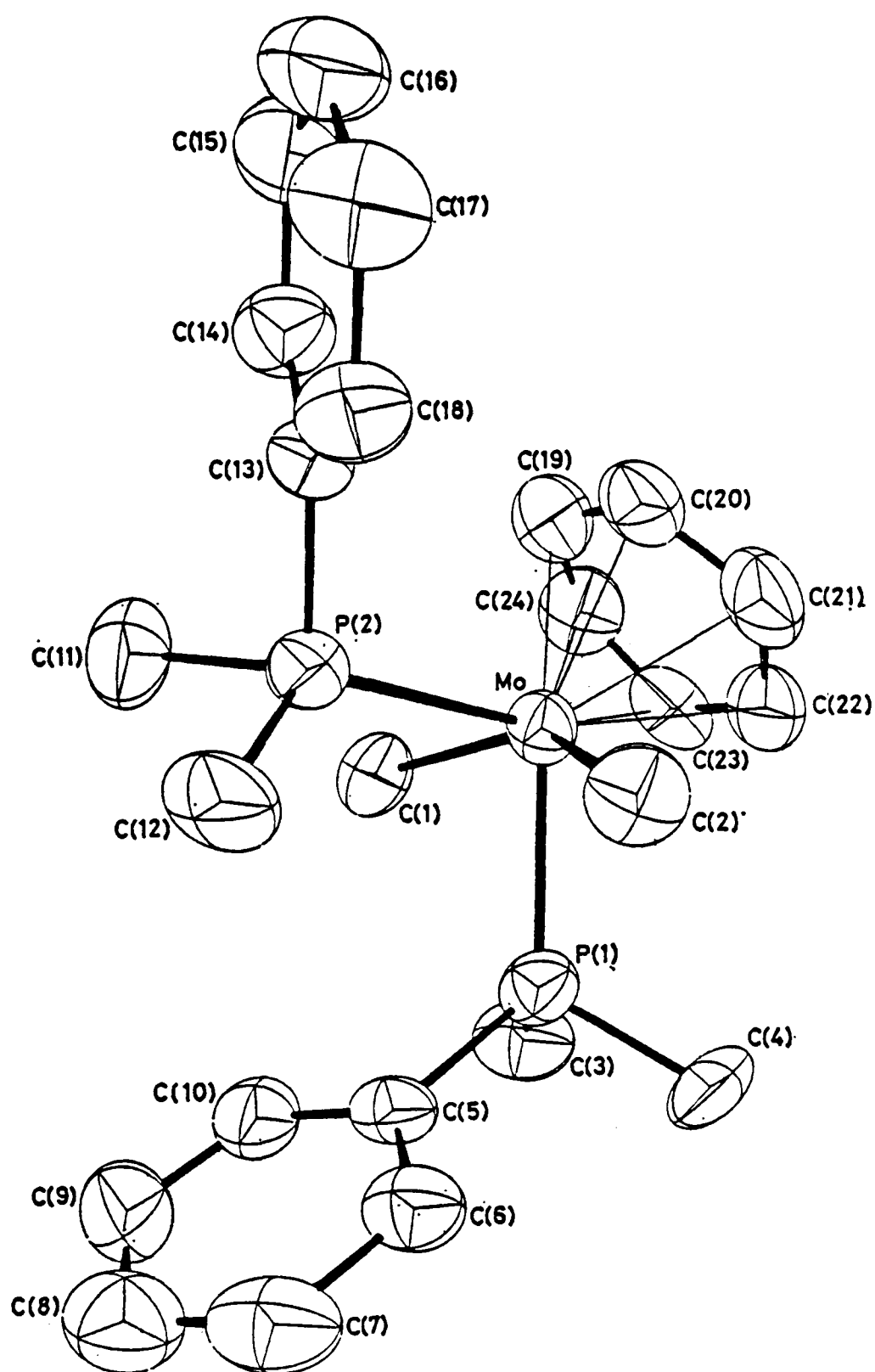


Fig. 3. The $[(\text{toluene})\text{Mo}(\mu\text{-SCH}_3)_3\{\mu\text{-SO}(\text{OCH}_3)\}\text{Mo}(\text{toluene})]^{2+}$ cation, showing one of the orientations of the disordered ion.

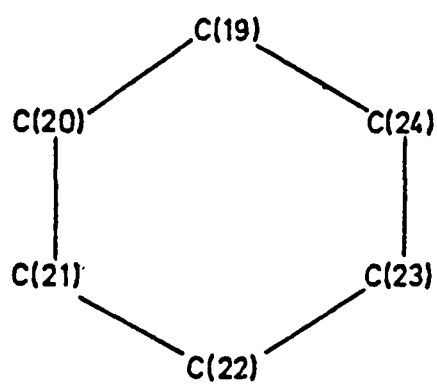
33

Fig. 4-9

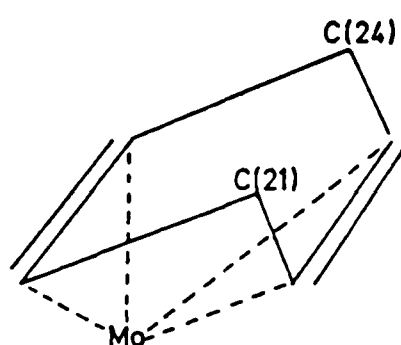


35

Molecular structure of $\text{MoMe}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PPhMe}_2)_2$ with the atoms represented by their 40% probability ellipsoids for thermal motion



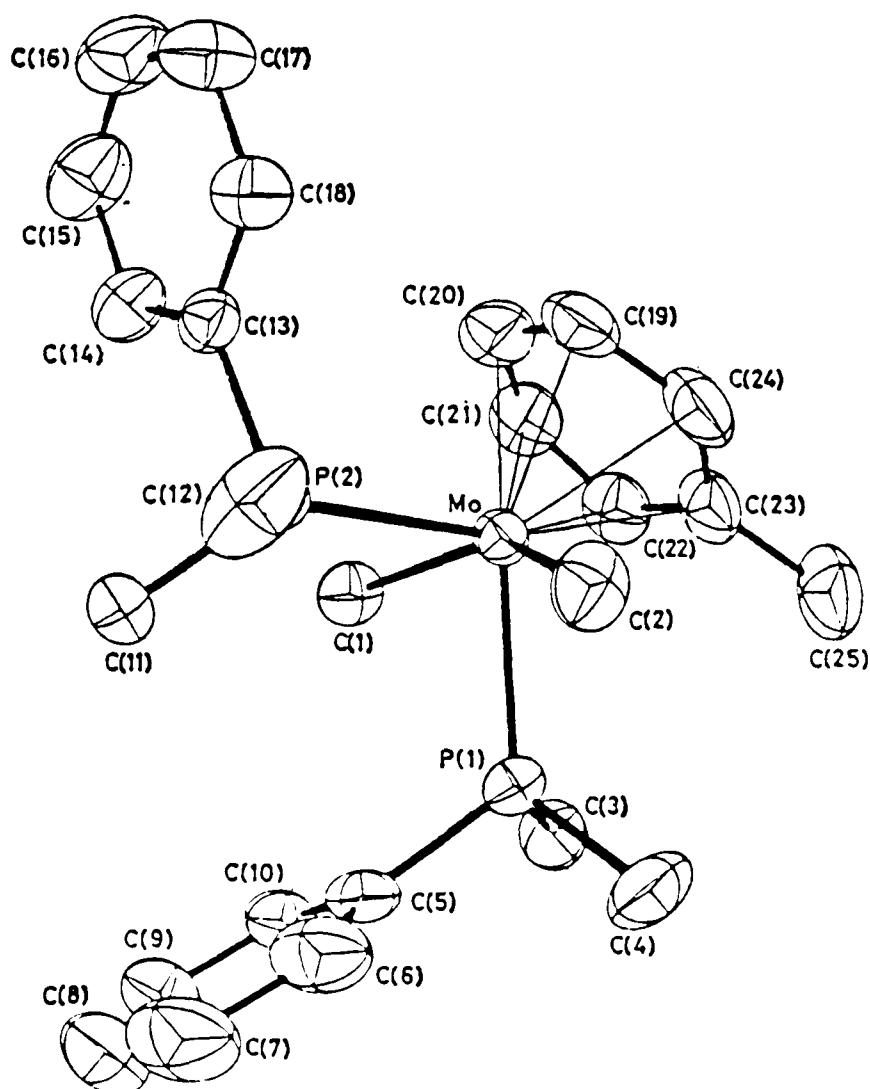
(I)



(II)

Fig. 4-10

-A-



Molecular structure of $\text{MoMe}_2(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{PPhMe}_2)_2$ 34

added to account for nonbonded interactions (effect 1), and it is not necessary to postulate, as Atwood does, that the arene is 'acting as a diene'. For 34 and 35, non-bonded interactions seem especially important, because the two ring carbons furthest from Mol both suffer from contact with a methyl group at the Van der Waals limit of 2.4 Å.

A ring distortion similar to those of 34 and 35 might be expected for the closely related compound 36, [(toluene)WCl₂(PMe₃)₂H]PF₆, since the Van der Waals radius of Cl (1.80 Å) is nearly that of methyl (2.0 Å). In addition, with reference to Fig.'s 4-10A and B, the hydride might be expected to increase the Cl-W-Cl angle of 36 above the Me-M-Me angle of 142.4(1)° found for 34. However, as Gourdon's crystal structure shows¹¹, none of these predictions is realized. The tungsten arene derivative 36 has a planar C₆ ring, and the Cl-W-Cl angle is 123.8(2)°. A close relationship is found between this angle and the P-M-P angle, because the latter angle has increased to 124.9(2)° from the 100.1(2)° angle in 34. The Me-Mo-Me angle of 34 is likely to be governed by the location of the lone pairs in this d⁴ molecule (see Fig. 4-11). It is difficult at present to predict the structural details of these low symmetry molecules; a systematic crystallographic study of the Group VI (arene)ML₂X₂ derivatives would provide more guidelines for such predictions (there are a large number of molybdenum compounds in this class which have been not investigated crystallographically³⁷.) Hoffmann and his co-workers have used EHT to study several classes of half-sandwich Cp-derivative³⁸, and an extension of their results to arene half-sandwich compounds would be of some interest.

4.5 Trimethylphosphine Molybdenum Derivatives.

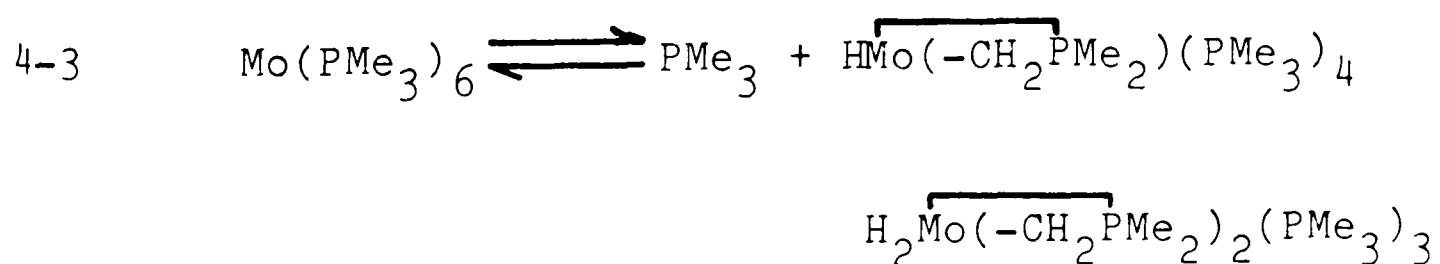
Trimethylphosphine, amongst the tertiary phosphines, acts as a relatively strongly electron-releasing and compact ligand towards transition metal centres. These properties, combined with its availability, have led to increasing usage of PMe_3 in the study of organometallic compounds, for example in the chemistry of carbene and carbyne derivatives of Ta, W, and other metals developed by R.R. Schrock³⁹.

Molybdenum atoms were condensed with PMe_3 by F.G.N. Cloke and K.P. Cox, in an attempt to synthesize $\text{Mo}(\text{PMe}_3)_n$. Such a molecule would be expected to have 'high-energy' metal electrons, and possibly steric crowding which might favour dissociative processes, and for these reasons a high reactivity was anticipated for the system. It was also hoped that structural comparisons could be made between $\text{Mo}(\text{PMe}_3)_n$ and the series $\text{M}(\text{dmpe})_3$, $\text{M}=\text{Cr}, \text{Mo}, \text{W}, \text{V}, \text{Nb}, \text{Ta}$, which had been studied crystallographically by A. Gourdon and K. Prout⁴⁰. One characteristic of the Group VI compounds $\text{M}(\text{dmpe})_3$, is that they are white, air-stable materials, and nonlabile to substitution^{40,41}.

The product isolated by Cox and Cloke from the MVS reaction of Mo and PMe_3 was an orange solid⁴⁰, whose ^1H nmr spectrum showed small concentrations of free PMe_3 and two hydrido species, as well as the major component, $\text{Mo}(\text{PMe}_3)_n$.

The sensitivity of the compound 40 delayed the determination of 'n', although the reactions which are shown in Fig. 4-11 suggested that n was at least 5, and probably 6. A number of the compounds in Fig. 4-11 were first prepared by Professor Carmona's group in Seville, who very kindly provided us with data prior to publication^{42,43}. It was shown by Cox and Cloke that 40 readily loses PMe_3 in solution or under vacuum, and a peak corresponding to $\text{Mo}(\text{PMe}_3)_5^+$ was observed in the mass spectrum. Satisfactory elemental analysis could not be obtained at first, and a crystal structure analysis was undertaken in order to further characterise 40, and to determine its structural properties.

The space group of 40 was determined by zero- and upper-layer precession photography to be Im3m. This body-centred cubic space group is the same as that found by Gourdon for the $M(dmpe)_3$ series⁴⁰, the molecular structures of which proved to be highly disordered. The disorder in the compounds $M(dmpe)_3$ results from the low-symmetry molecules being placed on sites of octahedral (m3m) point symmetry. The space group of 40 strongly suggested that the compound was $Mo(PMe_3)_6$, and any lingering doubt was dispelled during the refinement process, when the MoP_6 fragment was found to be a well-ordered octahedron. A satisfactory elemental analysis was eventually obtained, and the nmr spectrum of 40 could be explained in terms of the following equilibria:



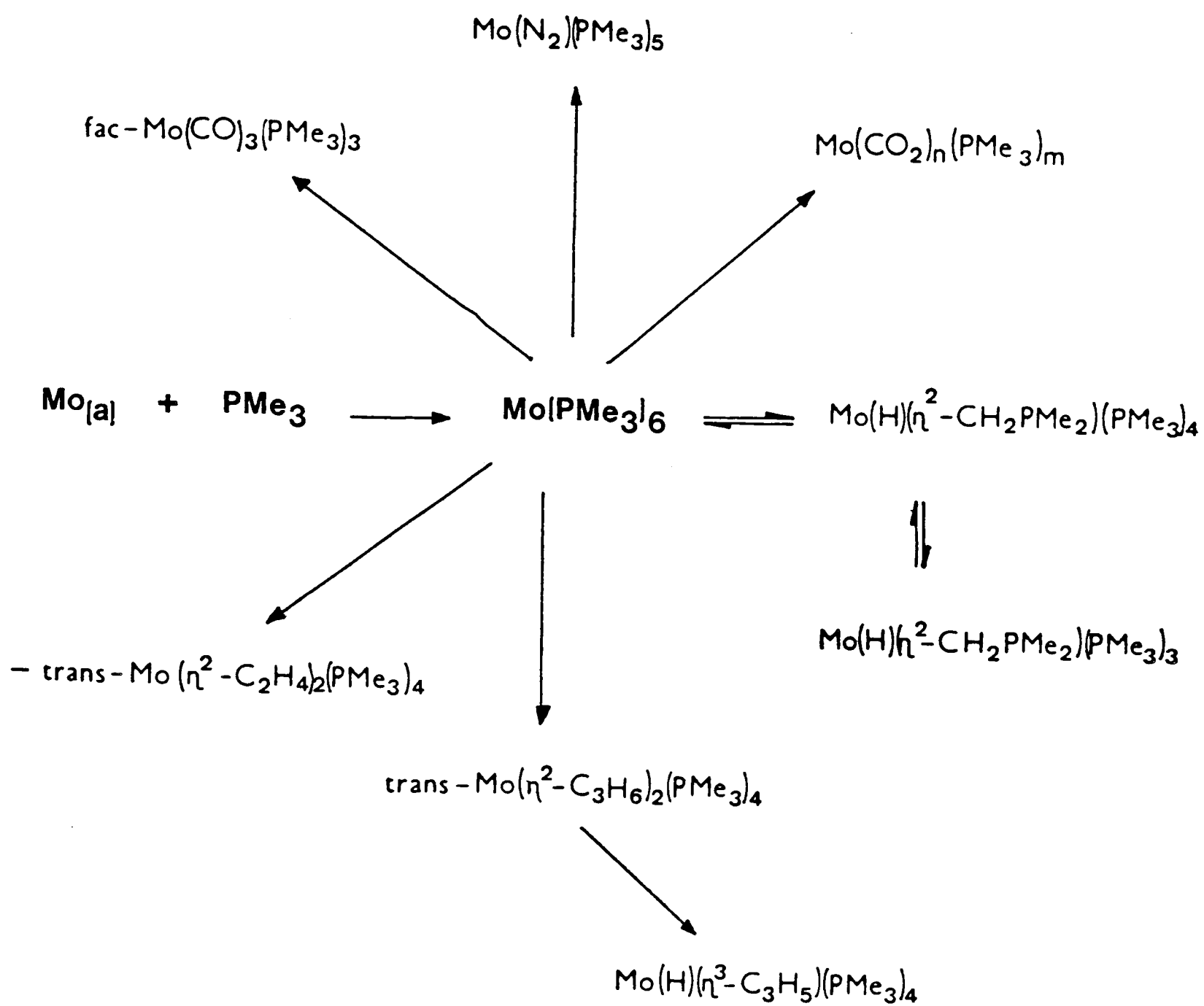


Fig. 4-11 Reactions of $\text{Mo(PMe}_3)_6$.

Although $\text{Mo}(\text{PMe}_3)_6$ certainly has a higher symmetry than $\text{M}(\text{dmpe})_3$, it is not a true octahedral molecule, because the PMe_3 groups have only three-fold symmetry. The phosphorus atoms of $\text{Mo}(\text{PMe}_3)_6$ lie on the four-fold axes of the crystallographic octahedron, on sites of $4mm$ symmetry, which requires the PMe_3 to be disordered over at least four positions (twelve is the least common multiple of three and four, and the disorder must result in the presence of both the three-fold symmetry of PMe_3 and the four-fold crystallographic symmetry). A difference-Fourier map phased on Mo1 and P1, whose positions and temperature factors had been refined with as much freedom as site symmetry would allow, showed a torus of electron density at a reasonable P-C distance of $1.88 \text{ \AA}$. This torus has a radius of $1.63 \text{ \AA}$, so that, if the twelve expected carbons were placed around it, they would be $0.85 \text{ \AA}$ apart [circumference = $2(\pi)r = 10.24 \text{ \AA}$, and $(10.24 \text{ \AA}/12) = 0.85 \text{ \AA}$]. The twelve carbons would therefore overlap, especially when thermal motion is taken into account, which explains the lack of any prominent features in the torus. There are, however, two small peaks where the torus intersects the two independent mirror planes, the peak at $(-0.296, 0, 0)$ being twice the height of that at $(-0.316, 0.134, 0)$. Numerous attempts were made to use these peaks as the starting point in the construction of the four PMe_3 positions, and dimensional constraints were applied to the P-C distances and Mo-P-C and C-P-C angles. However, all such models investigated were highly unstable to least-squares refinement, and no model comprised of twelve

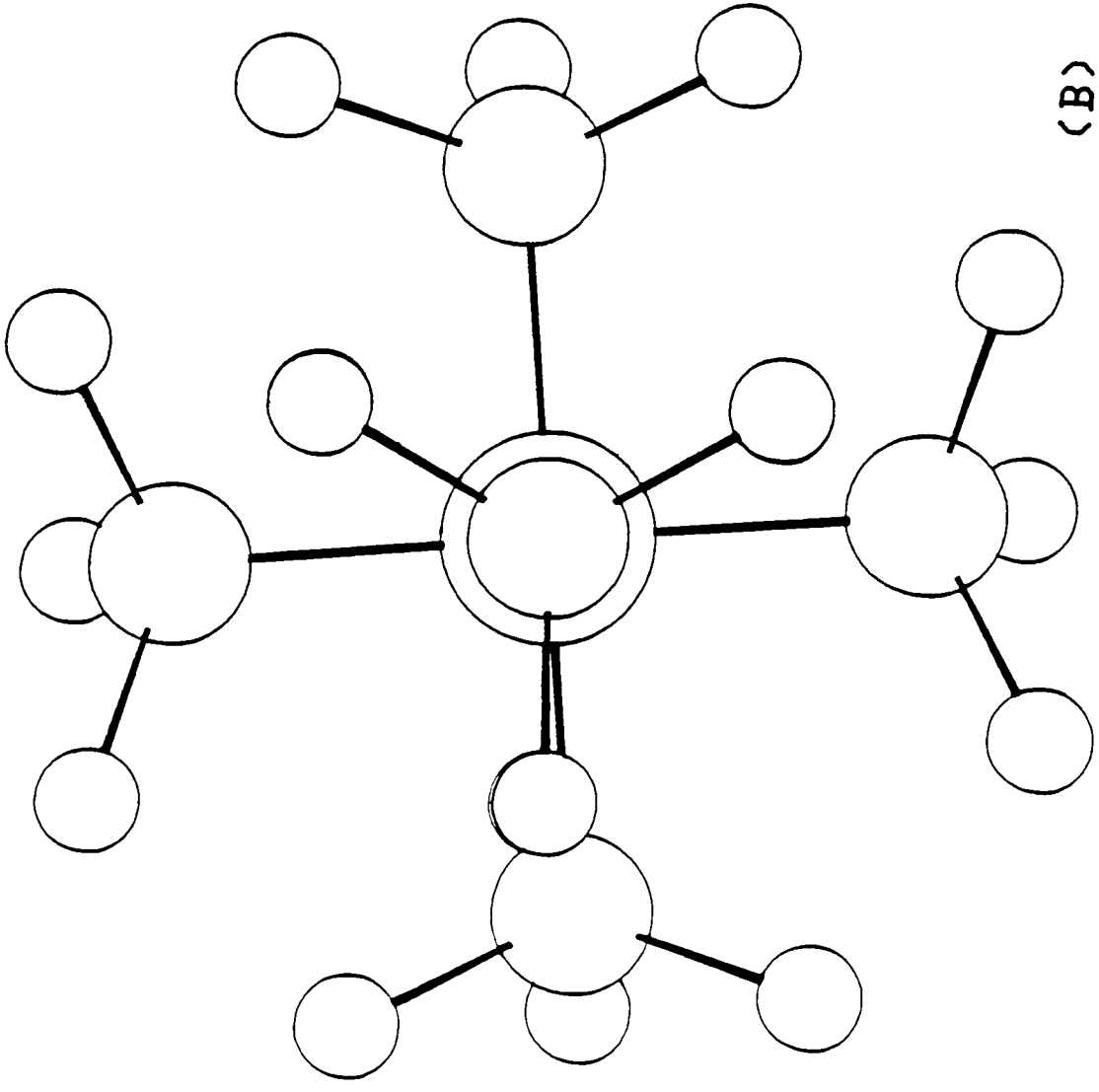
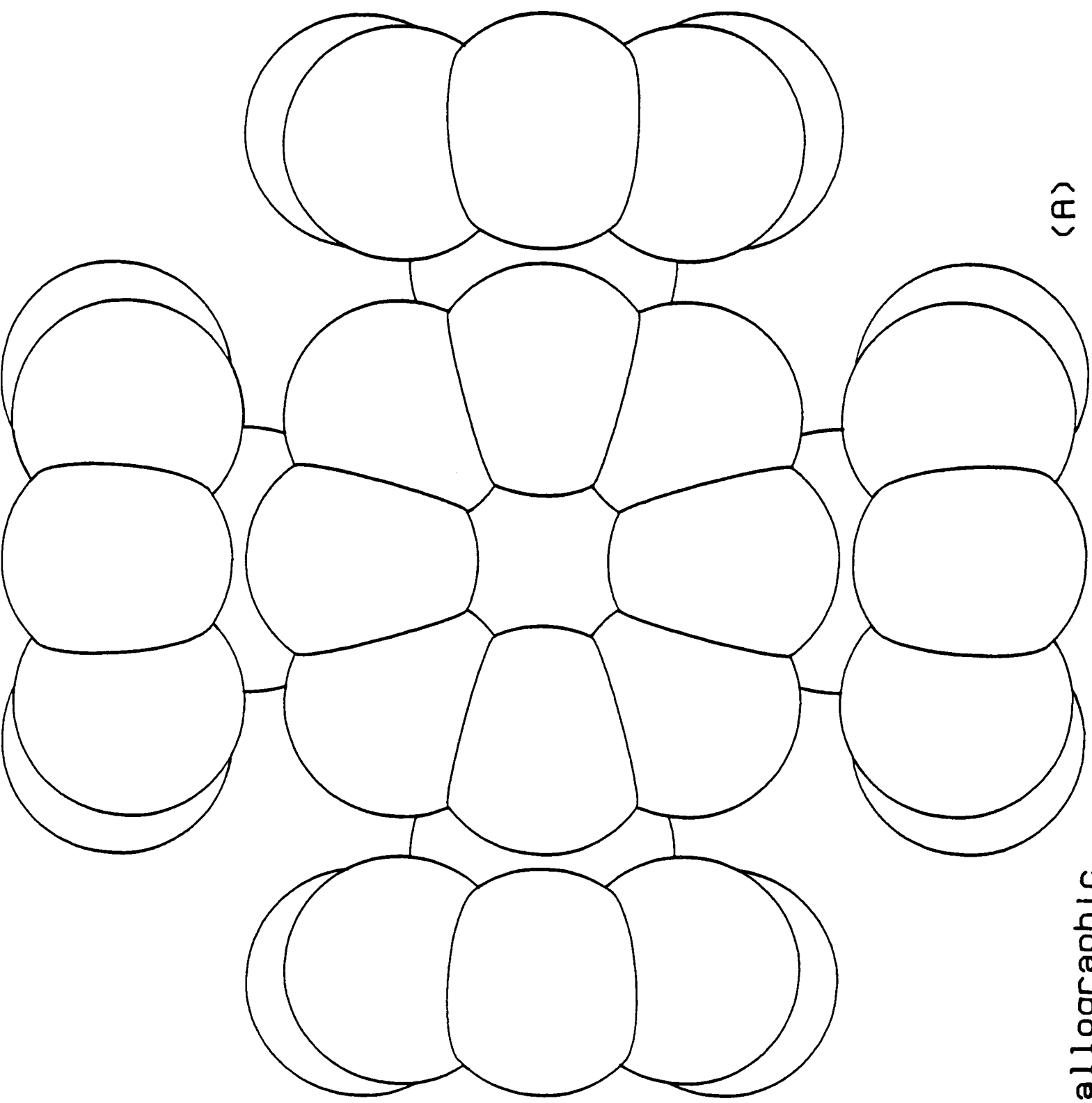


Fig. 4-12 Compound 40; the crystallographic model (A) and the 'true' molecule (B).

carbons could be satisfactorily refined. The main problem was caused by the close proximity of the 'carbon positions' to the mirror planes which pass through P1, resulting in a collapse of the atoms onto the symmetry element, in spite of the use of dimensional constraints. Faced with these refinement troubles, I wondered how well the torus could be described by simply fixing one carbon on each independent mirror plane, resulting in eight carbons which are disposed about P1 in agreement with its 4mm symmetry, whose occupation numbers have been adjusted to give the correct C to P ratio of 3:1. This model was refined with a high degree of success, when constraints were applied to the dimensions involving C1 and C2. The final R-value is 5.18%, and R_w is 6.90%, for twelve parameters (Mo1, C1, and C2 isotropic; P1 anisotropic) and 228 observations. Since, in addition, the final difference-Fourier map is featureless and the carbon temperature factors are reasonable, the approximations in the model are justified. A van der Waals sphere diagram of the crystallographic model of 40 is shown in Fig. 4-12, along with a diagram of $\text{Mo}(\text{PMe}_3)_6$ constructed with the molecular modelling program, MODEL⁴⁴.

Although it was necessary to model the torus of electron density instead of individual methyl groups, the derived parameters of the structure are quite precise. Those dimensions of 40 which are not fixed by symmetry are given in Table 4-2, along with the relevant dimensions of several other Group VI compounds. I am grateful to Dr. J.M. Marin-Elena for providing me with structural information prior to publication^{42,43} for the trans dichloro and

Table 4-2. Important Dimensions of Mo and W Phosphine Derivatives.

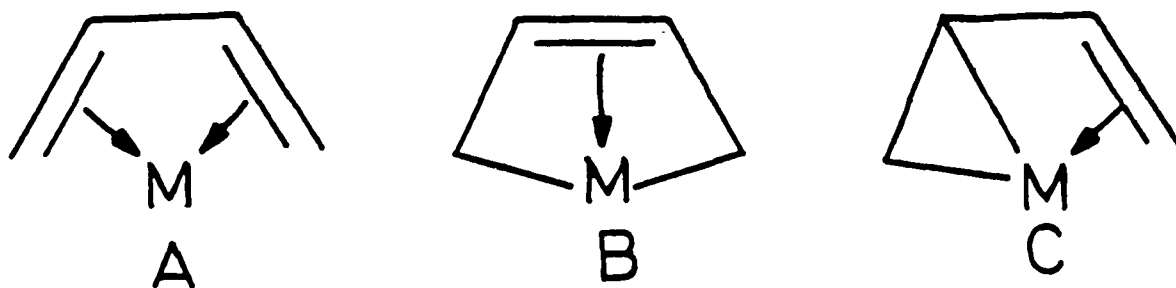
<u>Compound</u>	<u>M-P (Å)</u>	<u>P-C (Å)</u>	<u>M-P-C (°)</u>	<u>P-Mo-P(°)</u>	<u>ref.</u>
Mo(PMe ₃) ₆ 40	2.467(2)	1.884(4)	118.1(8)	90, 180	
		1.880(4)	126(1)		
<u>trans</u> -MoCl ₂ (PMe ₃) ₄	2.496(3)ave				43
<u>trans</u> -Mo(C ₂ H ₄) ₂ (PMe ₃) ₄	2.49(1)ave				42,43
<u>trans</u> , <u>mer</u> -Mo(C ₂ H ₄) ₂ (CO)(PMe ₃) ₃	2.486(3)ave				43
	P <u>trans</u> to CO	2.561(1)			
Mo(C ₄ H ₆) ₂ (PMe ₃) ₂ 42	2.456(1), 2.465(1)			97.96(2)	
[MoH(μ -H)(PMe ₃) ₃] ₂	2.42(1)ave	1.83(1)ave	104.6(3)-129.0(4)		45
Mo(dmpe) ₃	2.421(3)				40
[Mo(P(OMe) ₃) ₅ (P(OMe) ₂)]PF ₆	2.248				46
	P <u>trans</u> to P(OMe) ₂	2.488			
Mo(CO) ₄ (PMe ₃) ₂	2.522(1)		114-123	97.5	51
Mo(CO) ₄ (PEt ₃) ₂	2.544(4)		112-118	100.3	51
Mo(CO) ₄ (PBu ⁿ) ₃ 2	2.552(8)		110-122	99.3	51
W(CO) ₅ (PMe ₃)	2.516(2)	1.85(2)ave	115.6(2)		52
W ₂ H ₅ (μ -PMe ₂)(PMe ₃) ₅	2.46(3)	1.80-1.89	112.2(6)-128.1(1)		45
	(μ -PMe ₂)	2.352(5), 2.446(5)			

bis(ethylene) $\text{Mo}(\text{PMe}_3)_n$ derivatives ($n=3,4$; $m=1,0$). The M-P bond length in 40 is $2.467(2) \text{ \AA}$, $0.047 \text{ \AA}$ longer than the $2.42(1) \text{ \AA}$ M-P bonds of $\text{Mo}(\text{dmpe})_3$ and $[\text{Mo}(\text{H})(\eta\text{-H})(\text{PMe}_3)_3]_2$ ⁴⁵, which is consistent with the facile dissociation of PMe_3 from $\text{Mo}(\text{PMe}_3)_6$. The compound trans- $\text{Mo}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)_4$ also loses phosphine easily⁴², and its (average) M-P bond is even longer, $2.49(1) \text{ \AA}$. However, ground-state bond strengths are not the only factor governing reactivity, as emphasized by the $2.496(3) \text{ \AA}$ M-P average for trans- $\text{MoCl}_2(\text{PMe}_3)_2$, and the exceptionally long Mo-P bond which is trans to CO in trans, mer- $\text{Mo}(\text{C}_2\text{H}_4)_2(\text{CO})(\text{PMe}_3)_3$; neither of these latter two compounds has labile phosphines^{42,43}. The large Mo1-P1-C2 angle ($126(1)^\circ$) that occurs in 40 is not unprecedented, as Table 4-2 shows, and it probably results from steric crowding. The P-Mo-P angles of 40 are constrained to be 90° (and 180°) by site symmetry, and this seems to be sterically undesirable, because the P-Mo-P angle increases to 98° when steric constraints are removed (e.g. in $\text{Mo}(\text{PMe}_3)_2(\text{C}_4\text{H}_6)_2$ and $\text{Mo}(\text{CO})_4(\text{PMe}_3)_2$).

It is interesting to compare a number of formally zero-valent molybdenum compounds, which have very different properties. The homoleptic molecules $\text{Mo}(\text{CO})_6$ and $\text{Mo}(\text{P}(\text{OMe})_3)_6$ ⁴⁶ are both air-stable, kinetically rather inert molecules, which may result from the electron-withdrawing properties of their ligands, and the fact that the relatively small cone angles of CO and $\text{P}(\text{OMe})_3$ do not favour ligand dissociation. The compounds $\text{Mo}(\text{dmpe})_3$, $\text{Mo}(\text{PMe}_3)_6$ 40, and $\text{Mo}(\text{C}_6\text{H}_6)_2$ are all readily oxidized, having electron-rich metal centres, but of this group only 40 is

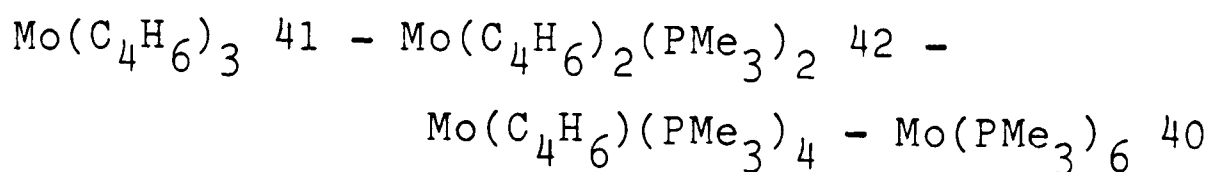
substitutionally labile^{40,41}. An intuitive association of butadiene with ligands such as benzene would place $\text{Mo}(\text{C}_4\text{H}_6)_3$ 41 in the (latter) group of easily oxidized molecules, with its substitutional lability probably low, as a result of the chelate effect. Compound 41 has been found, however, to belong to the former group, being air stable as well as nonlabile.

Tris(butadiene)molybdenum 41 has an unusual, trigonal structure, and appears to have the only coordinated butadiene ligands whose C-C bond length alternation resembles that of free butadiene, i.e. short, long, short⁴⁸. Coordinated butadiene usually has nearly equal C-C bond lengths, or a somewhat shorter central bond, and this is thought to arise from population of ψ_3 by metal to ligand back-bonding. The electronic structure of 41 has been discussed⁴⁹ by J.C Green, D.M.P. Mingos, and co-workers. Their uv-PE spectra show no metal-based lone pairs of electrons, suggesting that an Mo(VI) description was more appropriate than Mo(0); i.e. with the ligands acting formally in an $\eta^1:\eta^2:\eta^1$ (A)sense rather than as $\eta^2:\eta^2$ (B). This description does not seem to be consistent with the C-C bond lengths of 41, but it does agree with the stability of 41 to oxidation. Perhaps⁵³ a more appropriate description of the metal-butadiene bonding is given by (C), $\eta^1:\eta^1:\eta^2$.



When K.P. Cox synthesized $\text{Mo}(\text{PMe}_3)_2(\text{C}_4\text{H}_6)_2$ 42 by reaction of

40 with butadiene, the following series of compounds was envisaged (a sequential transition from one homoleptic compound to another):



It was hoped that, by changing the phosphine to butadiene ratio and solving the crystal structure at each step, more insight could be gained into the apparently unique bonding in 41. Furthermore, since there is some crystallographic uncertainty in the dimensions of 41 (in spite of similar results from two independent structure investigations^{47,48}), it was thought that the other members of the series might provide firmer evidence for the unusual butadiene-metal bonding. The uncertainty is caused by somewhat unusual thermal parameters for the butadiene carbons, which suggests that some subtle disorder may occur in the crystals.

Unfortunately, $\text{Mo}(\text{C}_4\text{H}_6)(\text{PMe}_3)_4$ has not yet been prepared. However, Cox grew crystals of 42 which were excellent for structure analysis, and the crystal structure was solved and refined by Dr. P.D. Grebenik under my supervision; the results are briefly mentioned here. Since the structure of 42 was investigated to provide accurate dimensions, a large data set was collected. This, and the high crystal quality, allowed all hydrogens to be located and refined, and resulted in a high precision for the final atomic parameters. The final R-value is 2.38%, $R_w = 3.04\%$. The butadiene ligands of 42 are not unusual, the central bond being somewhat shorter than the outer C-C bonds (see Fig.

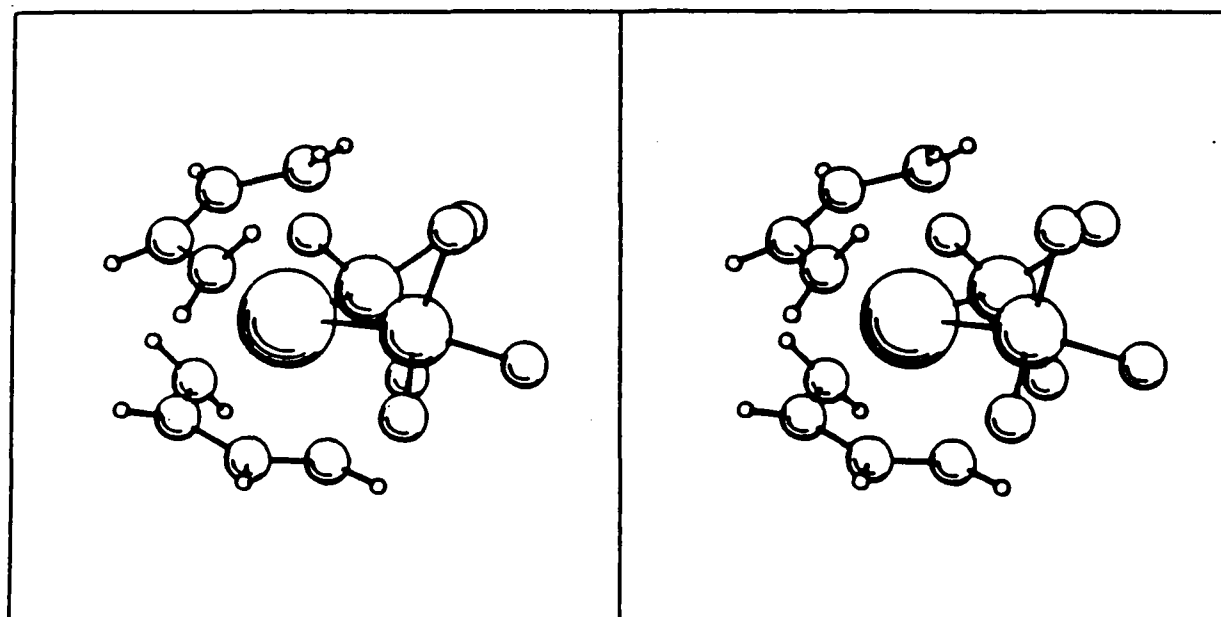
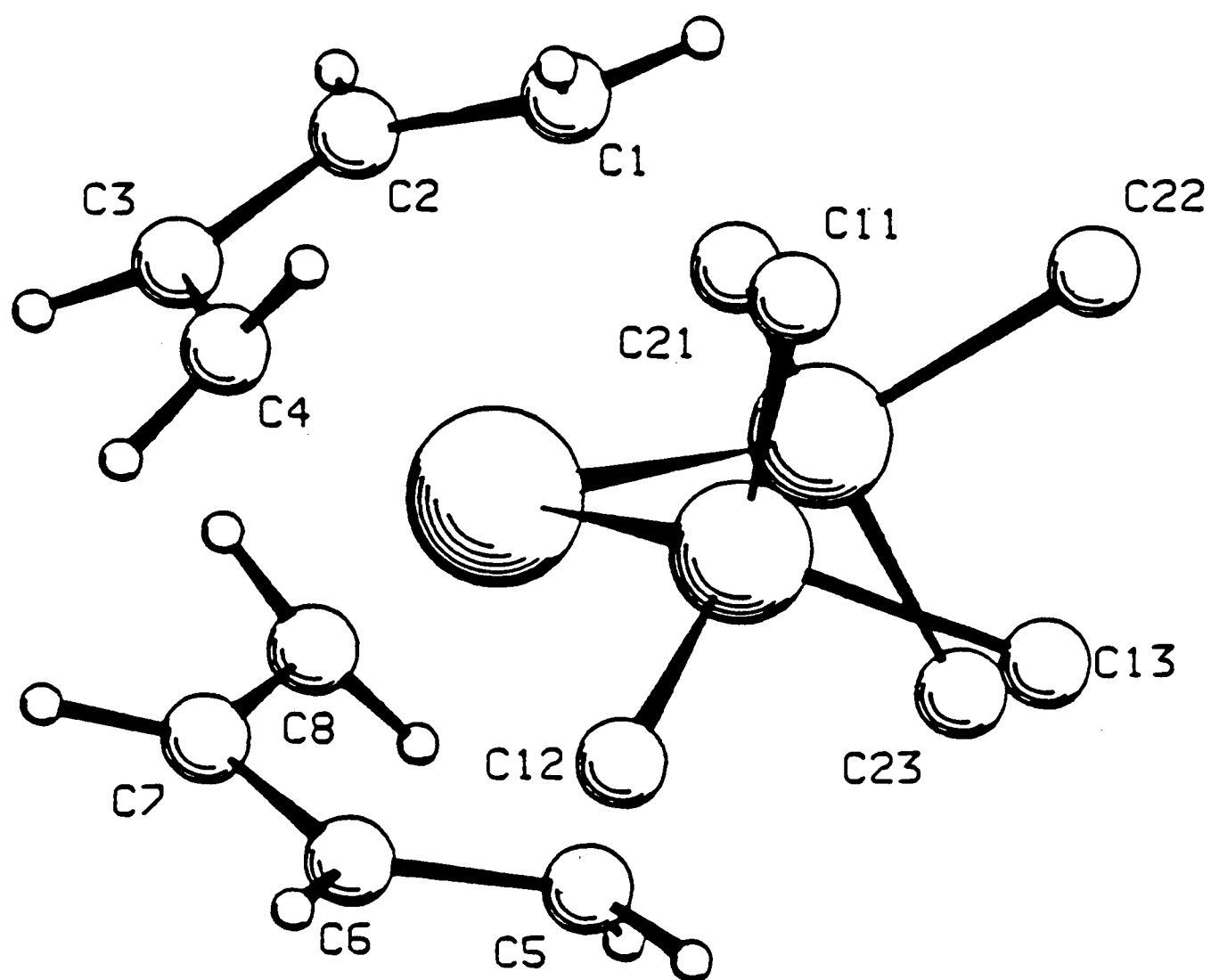


Fig. 4-13 Compound 42

4-13). There is a striking resemblance between 42 and $\text{Hf}(\text{C}_4\text{H}_6)_2(\text{dmpe})^{31}$ 43, which was mentioned in section 4.4 as being, along with $\text{Hf}(\text{MePh})_2(\text{PMe}_3)$, the first zero-valent hafnium compound. Figure 4-14 shows several views of a least-squares best fit of 43 onto 42, which was carried out with a BASIC program written by Dr. Grebenik; the dmpe phosphorus atoms of 43 are shaded. The common model of butadiene-metal bonding, which is the $\eta^2:\eta^2$ interaction mentioned and illustrated above, leads here to the unusual conclusion that there is greater backbonding to ψ_3 in the d^4 compound 43 than in the d^6 species, 42. (In contrast to the dimensions of 42, the internal C-C bonds of the butadienes in 43 are exceptionally short.) Thus, in agreement with the PES study on $\text{Mo}(\text{C}_4\text{H}_6)_3$, these results stress the oxidizing nature of the butadiene ligand, and the importance of considering its (less well-known) bonding modes, $\eta^1:\eta^2:\eta^1$ and $\eta^1:\eta^1:\eta^2$.

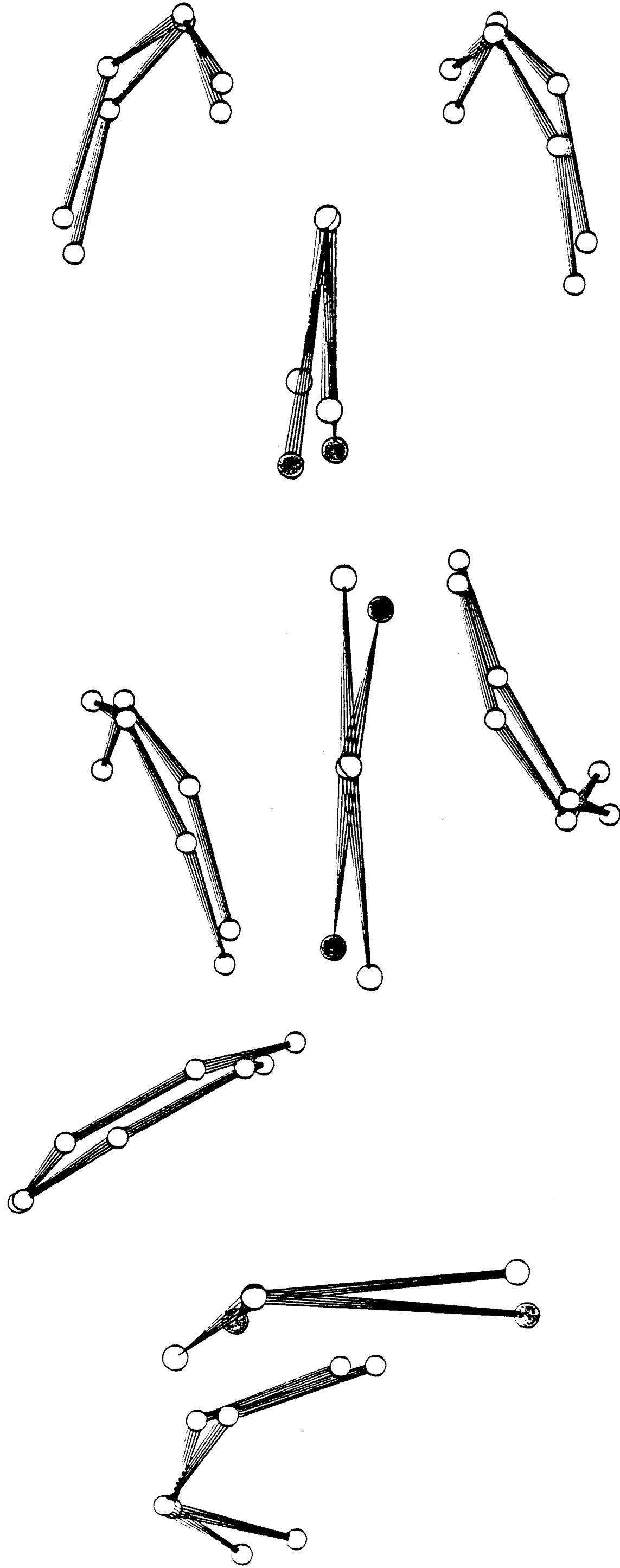


Fig. 4-14 Several views of the least-squares fit of 43 onto 42, the dmpe is shaded and only butadiene carbons and P atoms are shown around the metal centre.

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Chapter 5 Experimental

Chapter 5. Experimental.

5.0 General. A number of different techniques were employed for the studies reported in this thesis, including the synthesis of air-sensitive compounds, the characterization of such compounds by various spectroscopies and X-ray crystallography, and the investigation of their bonding properties with Extended Huckel Theory. All of these techniques have been described in detail elsewhere, and they will only be outlined in this chapter unless there are points of particular interest to discuss.

Synthesis. All manipulations were carried out under dinitrogen or vacuum unless otherwise stated. Vacuum-line practices were standard, and "White spot" or "High Purity" dinitrogen was used as supplied by BOC or Air Products Ltd., respectively. Benzene, toluene, and diethyl ether were distilled from sodium benzophenone ketyl under dinitrogen. Benzene-d⁶ was dried over activated molecular sieves, and alkyl halides were dried by passing them through activated alumina (100-120 mesh).

Spectra. Infra-red spectra were recorded as Nujol mulls between KBr or CsI plates on Perkin Elmer 457 or Pye SP2000 instruments, the former being calibrated with polystyrene film. ¹H nmr spectra were recorded at 60 MHz on a JEOL PMX60 and at 90 MHz on a Perkin Elmer R14 spectrometer. Calibration of spectra was done with respect to internal solvent peaks. Unless otherwise stated, mass spectra were run by Dr. P.D. Grebenik on an AEI MS9,

Table 5-0 Selected Dimensions Involving Molecular Planes; A Tabulation for all Crystal Structures Reported in this Thesis. Phi is the angle between the normals to the planes defined on the preceding and following lines; omega is the dihedral angle between the C5 rings of a fulvalene ligand.

Chapter	Compound	Plane	M-plane(Å)	phi(°)	omega(°)
2	2, Black Dimer	C1-C5	1.98		
		C6-C10	1.98	134	
		C21-C25	1.91		
		C26-C30	1.95	154	
2	5, Carbonyl Dimer	C1-C5	2.039		
		C21-C25	1.916		
		C26-C30	1.962	148.2	
2	7, Oxo-hydride	C1,C2,C3,C2',C3'	1.95		22
		C4,C5,C6,C5',C6'	1.99	137	
2	9, Trihydride Cation	C1-C5	1.941		17.5
		C6-C10	1.957	140	
2	10, Sulfur-bridged	C10-C14	1.971		17.4
		C15-C19	1.995	136.5	
		C20-C24	1.957		
		C25-C29	1.979	137.2	
	10, Molecule 2	C30-C34	1.968		16.5
		C35-C39	1.989	136.5	
		C40-C44	1.969		
		C45-C49	1.986	136.4	
2	11, Molybdate-bridged	C10-C14	1.954		19.3
		C15-C19	1.973	136.4	
		C20-C24	1.941		
		C25-C30	1.958	134.5	
3	8, Oxo-Cation	C1,C2,C3,C2',C3'	2.015		
		O1,P1,P1'	1.201	4.75	
3	42, NbCp(dppe)-Br3	C11-C15	2.089		
		Br1,Br2,Br3,P1	0.634	3.11	
3	(EtCp)2TiBr2	C1-C5	2.063	128.3	
4	Hf(MePh)2(SnMe3)2	C1-C6	2.038	138.8	
		C7(Me)-plane	=0.183		

reconditioned by MSS. Gas chromatography was carried out on a Pye 104 chromatograph using a 10% KCl on alumina column.

Crystallography

Data Collection. Two Enraf Nonius CAD4 diffractometers were used for data collection; one diffractometer is controlled by a PDP-8A minicomputer, and the other by PDP 11/34 and LSI minicomputers. The CAD4 diffractometer has kappa geometry, in which the kappa axis is not orthogonal to the omega axis; this configuration is more mechanically robust than traditional chi-circle designs. Crystals were irradiated with graphite-monochromated molybdenum K-alpha radiation, which has a wavelength of $0.710685 \text{ \AA}$, and X-rays were detected with a thallium-doped NaI crystal which was coupled to a photomultiplier and pulse-height discriminator.

A standard routine was followed for the determination of orientation matrices and data collection parameters¹. First, a polaroid photograph is taken, and then 25 reflections are chosen either from the photograph or by an automatic search routine. The search routine is used when the photographic information cannot be successfully indexed. The chosen reflections are centred to improve the values of their setting angles, and a preliminary orientation matrix, Niggli matrix, and cell dimensions are calculated using an indexing routine, which produces a "reduced" cell. Transformation to a nonprimitive, conventional cell may be done at this time. A final orientation matrix is obtained by least-squares refinement using the setting angles of 25 reflections (including symmetry equivalents), which usually lie in the region $10 < \theta < 15^\circ$. Strong reflections in this range may be found with a rapid data collection (prescan), from the

polaroid photograph or search routine, or from preliminary photographic data. The reflections are chosen to describe a wide range of reciprocal space, in order to give the highest precision for lattice parameters.

The data collection parameters such as scan angle and aperture are optimised for a few strong reflections, whose net intensities are maximised for each parameter. All data sets were collected with ω - 2θ scans. Reflections are measured for a fixed time, after which the ratio of intensity to standard deviation is used to decide whether the measurement is sufficiently precise, whether it should be repeated for a longer time, or whether the reflection is too weak to be measured with sufficient precision within the permitted time (usually 90 seconds). Sufficient precision is taken to be an intensity three or more times the standard deviation based on counting statistics. During the course of data collection, several intensity standards and orientation controls are periodically measured in order to monitor possible crystal decomposition and to insure that the orientation matrix is redetermined if movement of the crystal occurs.

For each crystal, the importance of absorption was determined by measuring ϕ scans of several reflections whose scattering vectors are approximately parallel to the diffractometer ϕ axis. When significant variations in intensity were found, the semi-empirical absorption correction of North, Phillips, and Mathews² was applied. For plate-like crystals, the "plate-mode" of data collection was employed; this allows each reflection to be measured at the minimum absorption position, with some constraints imposed by machine geometry. Data reduction (correction for Lorentz and polarization effects, checking of systematic absences, and merging of equivalent reflections) was performed with the Oxford CRYSTALS program³.

Structure Determination and Refinement. Only those reflections with $I \geq 3\sigma(I)$ were used in the refinement process. All structures were solved by Patterson methods, and all crystallographic calculations were performed with the Oxford CRYSTALS system, using ICL 1906, ICL 2980, and VAX 11/750 computers. Least-squares refinement was usually carried out with a large-block approximation to the normal matrix, the blocks consisting of x, y, z ; scale, U_{II} 's; and U_{IJ} 's. Extinction parameters, when refined, were added to the block containing the scale factor. For large structures, a further blocking of the normal matrix was sometimes carried out, so that discrete molecular fragments such as cyclopentadienyl rings were refined in their own blocks. Full-matrix refinement was carried out whenever practical; when this was impractical, highly correlated parameters were blocked together. Extensive use was made of 'slack' constraints, especially to help describe the (frequently encountered) disorder of nearly spherical anions such as BF_4^- and PF_6^- . This method of constrained refinement adds observations to the set of normal equations, and does not decrease the number of parameters in the way that the use of 'hard' constraints does^{3,4}. A separate R-value and minimisation function is evaluated for the constraints, so that their validity may be ascertained, and the constraining observations are given weights (e.s.d.'s) which reflect the expected parameter distribution. Thus, an F-P-F angle of a PF_6^- may be constrained to $90 \pm 2.0^\circ$. The weights (w) of reflections for least-squares refinement were determined so that $w(\Delta)^2 = w(|F_o| - |F_c|)^2$ would be constant⁵ for any systematic analysis of the structure. Chebyshev polynomials⁶, truncated usually to three terms, were used to calculate these weights; the polynomial coefficients were determined by a least-squares calculation which minimised the variation in $w(\Delta)^2$ with $|F_o|$. Scattering factors for nonhydrogen atoms were taken from Los Alamos publication⁷ LA-3816; the International Tables for Crystallography⁸ were used as a source for anomalous dispersion corrections, and for the hydrogen scattering factor. Hydrogens were usually

located in difference-Fourier maps, and then placed geometrically with $U[ISO]=0.05 \text{ \AA}^2$, their positions being adjusted after each cycle of refinement. Final atomic positional and thermal parameters are tabulated after each CRYSTAL DATA section, along with important molecular dimensions. Observed and calculated structure factors are included on microfiche.

5.1 Experimental Details for Chapter 2: Synthesis.

The Preparation of $Cp_2MoH(I)$ The compound $Cp_2MoH(I)$ was prepared several times; the following conditions are typical. Cp_2MoH_2 (0.39 g, 1.7 mmol) was dissolved in 50cm^3 Et_2O , and MeI (0.24g, 1.7mmol) was added via a syringe. The solution was left to stand for 12h, after which time dark crystals had appeared in the Schlenk tube. The product was identified from its mass spectrum and by comparing its ir spectrum with that of an authentic sample⁹. The yield was 0.52g, 87%.

The Reaction of $Cp_2MoH(I)$ and MeMgBr. This reaction was carried out several times, under various conditions. When the reaction was carried out at room temperature, a red precipitate appeared within seconds of adding the Grignard reagent to a stirred, Et_2O suspension of $Cp_2MoH(I)$. The conditions for reaction at low temperature are given here. $Cp_2MoH(I)$ (0.59g, 1.67mmol) was suspended in 50cm^3 Et_2O , and the suspension was cooled to -60° with a dry-ice/acetone bath. MeMgBr (1.2cm^3 of a 2M solution in Et_2O) was added via a syringe, while the solution was stirred. After 2h, the solution had taken on a faint yellow-orange colour. The stirring was continued, and the reaction mixture was allowed to warm up over a 12h period, when a red ppt. was present in the reaction vessel. The Et_2O was filtered off, and the red

solid was recrystallized from acetone/H₂O, to which NH₄PF₆ had been added. The ¹H nmr spectrum of this product was recorded in acetone-d⁶ and acetonitrile-d³, and it suggested a mixture of products, because there were a number of peaks in the Cp-region, and the relative intensities of these peaks changed with further recrystallization. Four more recrystallizations were performed, the final one involving the slow cooling of a saturated acetone/H₂O solution from 80° to room temperature. This last step produced dark, octahedrally shaped crystals, whose spectral properties corresponded to those of 9, [(MoCp)₂(μ-fulvalene)H₃]PF₆, which was first prepared by Cooper¹⁰. The crystal structure of 9 was then performed.

5.2 Chapter 2. Crystallographic Studies.

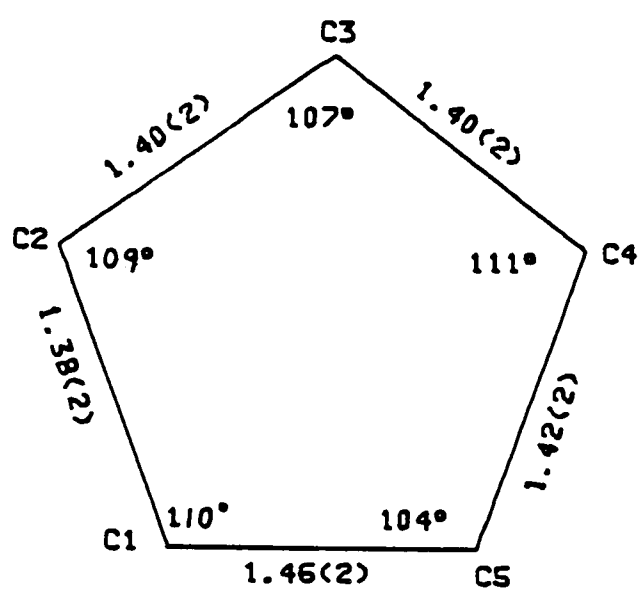
The experimental details of the seven crystal structures reported in Chapter 2 are given below, along with tables of atomic parameters and molecular dimensions.

Crystal structure of 2, Mo(η -C₅H₅)(σ : η -C₅H₄)Mo(η -C₅H₅)₂H

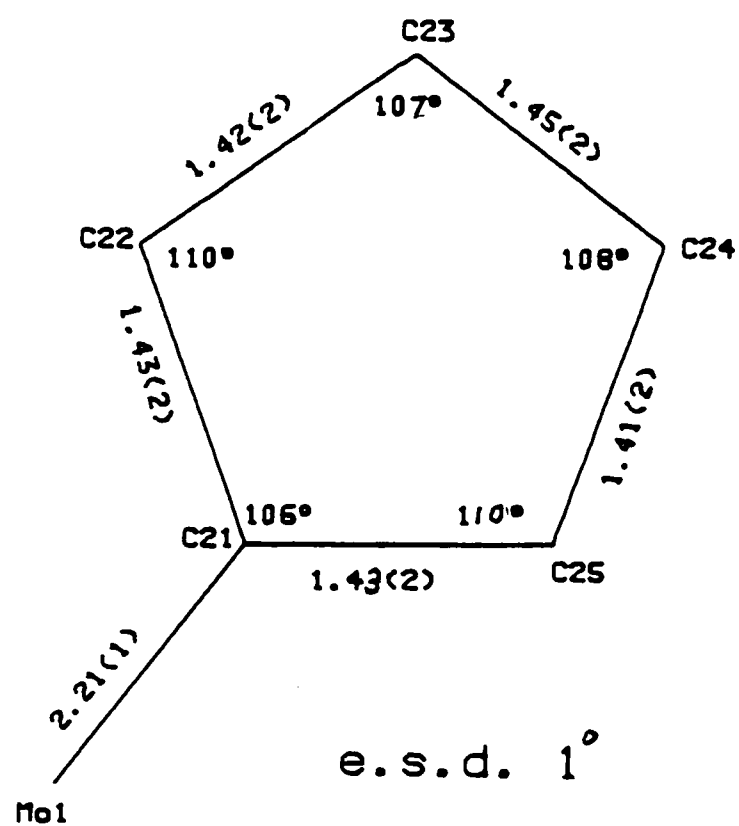
CRYSTAL DATA: C₂₀ H₂₀ Mo₂, M 452.10, monoclinic, $P2_1/c$, $a=13.674(7)$, $b=8.012(7)$, $c=13.37(1)$ Å, $\beta=108.69(6)^\circ$, $U=1595$ Å³, $Z=4$, $D_c=1.88\text{g/cm}^3$. A black crystal (hexagonal plate) was mounted on the end of a glass fiber, and intensities of 5865 reflections were measured on a CAD-4 diffractometer using graphite-monochromated Mo-Kalpha radiation. 2149 independent reflections $[I \geq 3\sigma(I)]$, corrected for extinction and absorption $[\mu(\text{Mo-Kalpha})=15.30\text{cm}^{-1}]$, were used in the refinement procedure. The structure was solved by heavy-atom and Fourier methods and refined by least squares with a large block approximation to the normal matrix. Non-hydrogen atoms were refined anisotropically. Ring hydrogens were located in difference maps and then placed geometrically (C-H=1.0 Å, $U[\text{ISO}]=0.05$), their positions being adjusted after each cycle. The hydride was located in a difference map and included in the model, but, as with the other hydrogens, its parameters were not refined. The R-value is 0.062 ($R_w=0.090$). Weights were calculated from a Chebyshev polynomial with coefficients of 81.84, 104.88, and 33.71.

Table 5-1. Selected interatomic distances (Å) and angles ($^\circ$) for 2

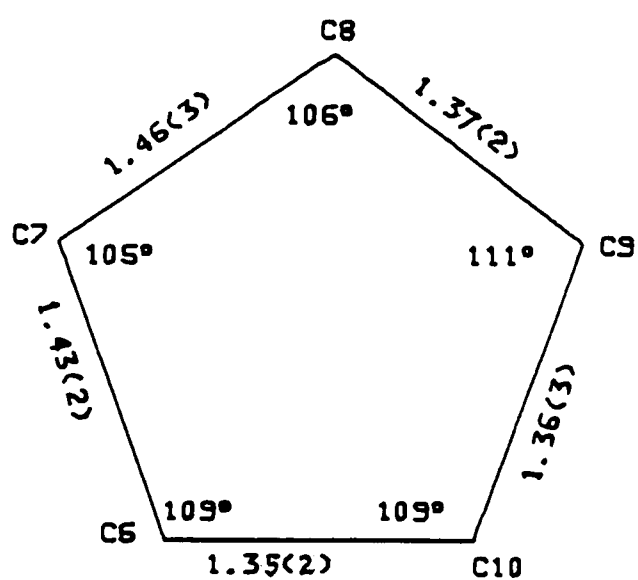
Mo(1)-H(31)	1.7 (not refined)	Mo(2)-C(21)	2.23(2)
Mo(1)-C(1)	2.33(1)	Mo(2)-C(22)	2.24(2)
Mo(1)-C(2)	2.32(2)	Mo(2)-C(23)	2.27(2)
Mo(1)-C(3)	2.31(2)	Mo(2)-C(24)	2.31(2)
Mo(1)-C(4)	2.31(2)	Mo(2)-C(25)	2.27(2)
Mo(1)-C(5)	2.30(2)	Mo(2)-C(26)	2.28(2)
Mo(1)-C(6)	2.30(2)	Mo(2)-C(27)	2.32(2)
Mo(1)-C(7)	2.30(2)	Mo(2)-C(28)	2.31(2)
Mo(1)-C(8)	2.28(2)	Mo(2)-C(29)	2.27(2)
Mo(1)-C(9)	2.32(2)	Mo(2)-C(30)	2.25(2)
Mo(1)-C(10)	2.32(2)	H(31)-Mo(1)-Mo(2)	71
Mo(1)-Mo(2)	3.189(1)	H(31)-Mo(1)-C(21)	115
Mo(1)-C(21)	2.21(2)		



e.s.d. 2°



e.s.d. 1°



e.s.d. 2°

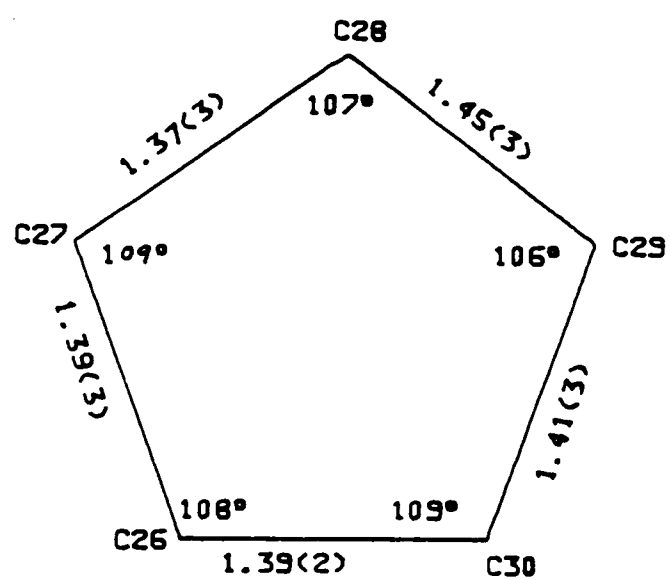


Fig. 5-1 The black dimer
2, dimensions

Table 5-2 Fractional coordinates for 2.

ATOM	X/A	Y/B	Z/C	U(ISO)
MO(1)	0.29663(8)	0.1378(1)	0.42456(7)	0.0241
MO(2)	0.23638(8)	-0.0646(1)	0.23600(7)	0.0264
C(1)	0.247(1)	-0.119(2)	0.468(1)	0.0352
C(2)	0.346(1)	-0.088(2)	0.524(1)	0.0454
C(3)	0.347(1)	0.055(2)	0.5763(9)	0.0397
C(4)	0.244(1)	0.111(2)	0.553(1)	0.0407
C(5)	0.179(1)	0.011(2)	0.481(1)	0.0428
C(6)	0.380(1)	0.388(2)	0.468(1)	0.0446
C(7)	0.277(1)	0.405(2)	0.470(1)	0.0416
C(8)	0.211(1)	0.384(2)	0.375(1)	0.0427
C(9)	0.278(1)	0.362(2)	0.3257(9)	0.0337
C(10)	0.378(1)	0.363(2)	0.381(1)	0.0491
C(21)	0.382(1)	-0.004(2)	0.3483(9)	0.0315
C(22)	0.373(1)	-0.182(2)	0.3400(9)	0.0296
C(23)	0.375(1)	-0.232(2)	0.252(1)	0.0405
C(24)	0.391(1)	-0.083(2)	0.2053(9)	0.0379
C(25)	0.394(1)	0.054(2)	0.264(1)	0.0359
C(26)	0.103(1)	-0.229(2)	0.243(1)	0.0459
C(27)	0.065(1)	-0.067(2)	0.232(1)	0.0443
C(28)	0.068(1)	-0.004(2)	0.150(1)	0.0548
C(29)	0.108(1)	-0.133(3)	0.106(1)	0.0466
C(30)	0.129(1)	-0.271(2)	0.165(1)	0.0499
H(1)	0.2252	-0.2157	0.4251	0.0500
H(2)	0.4084	-0.1565	0.5264	0.0500
H(3)	0.4080	0.1076	0.6221	0.0500
H(4)	0.2211	0.2079	0.5822	0.0500
H(5)	0.1032	0.0265	0.4483	0.0500
H(6)	0.4439	0.3949	0.5231	0.0500
H(7)	0.2539	0.4270	0.5247	0.0500
H(8)	0.1341	0.3846	0.3513	0.0500
H(9)	0.2553	0.3482	0.2575	0.0500
H(10)	0.4396	0.3465	0.3608	0.0500
H(22)	0.3654	-0.2595	0.3888	0.0500
H(23)	0.3676	-0.3484	0.2272	0.0500
H(24)	0.3975	-0.0776	0.1426	0.0500
H(25)	0.4038	0.1732	0.2494	0.0500
H(26)	0.1109	-0.3025	0.2972	0.0500
H(27)	0.0396	-0.0052	0.2772	0.0500
H(28)	0.0457	0.1106	0.1257	0.0500
H(29)	0.1194	-0.1259	0.0442	0.0500
H(30)	0.1574	-0.3806	0.1540	0.0500
H(31)	0.1652	0.1421	0.3737	0.0500

Table 5--3 Anisotropic temperature factors for 2.

ATOM	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
MO(1)	0.0285(9)	0.0239(9)	0.0211(9)	0.0022(4)	0.0087(5)	0.0003(5)
MO(2)	0.0292(9)	0.0305(9)	0.0221(9)	0.0007(5)	0.0101(5)	0.0016(5)
C(1)	0.078(8)	0.026(7)	0.041(8)	0.006(6)	0.032(6)	-0.014(6)
C(2)	0.078(9)	0.035(7)	0.041(8)	0.015(5)	0.016(7)	0.008(8)
C(3)	0.067(8)	0.046(8)	0.022(6)	0.010(5)	0.009(6)	-0.003(7)
C(4)	0.067(8)	0.06(1)	0.024(6)	0.007(6)	0.021(6)	-0.002(7)
C(5)	0.058(9)	0.042(8)	0.055(8)	0.002(7)	0.033(7)	-0.017(6)
C(6)	0.047(7)	0.030(8)	0.076(9)	0.001(7)	0.028(8)	-0.007(7)
C(7)	0.048(7)	0.036(8)	0.063(8)	-0.020(7)	0.028(6)	-0.013(7)
C(8)	0.026(7)	0.042(9)	0.078(9)	-0.001(8)	0.002(5)	0.014(6)
C(9)	0.084(8)	0.021(6)	0.035(7)	0.015(6)	0.019(6)	-0.001(7)
C(10)	0.062(7)	0.040(8)	0.082(9)	0.002(9)	0.041(7)	-0.018(8)
C(21)	0.030(6)	0.036(5)	0.035(6)	0.011(6)	0.013(5)	0.001(6)
C(22)	0.030(6)	0.035(5)	0.032(6)	0.000(5)	0.008(5)	0.016(5)
C(23)	0.042(8)	0.055(8)	0.033(6)	-0.007(6)	0.007(6)	0.019(7)
C(24)	0.026(6)	0.079(8)	0.027(6)	0.001(5)	0.007(5)	0.011(7)
C(25)	0.037(7)	0.048(8)	0.046(7)	0.015(5)	0.027(6)	0.012(7)
C(26)	0.045(9)	0.055(8)	0.044(8)	0.010(7)	0.011(7)	-0.015(7)
C(27)	0.030(7)	0.068(8)	0.058(8)	-0.015(7)	0.022(7)	-0.002(7)
C(28)	0.045(9)	0.06(1)	0.060(9)	0.012(7)	0.001(7)	0.011(8)
C(29)	0.040(8)	0.09(1)	0.026(7)	-0.004(6)	-0.003(6)	-0.002(8)
C(30)	0.05(1)	0.049(9)	0.053(8)	-0.019(6)	0.008(7)	-0.015(8)

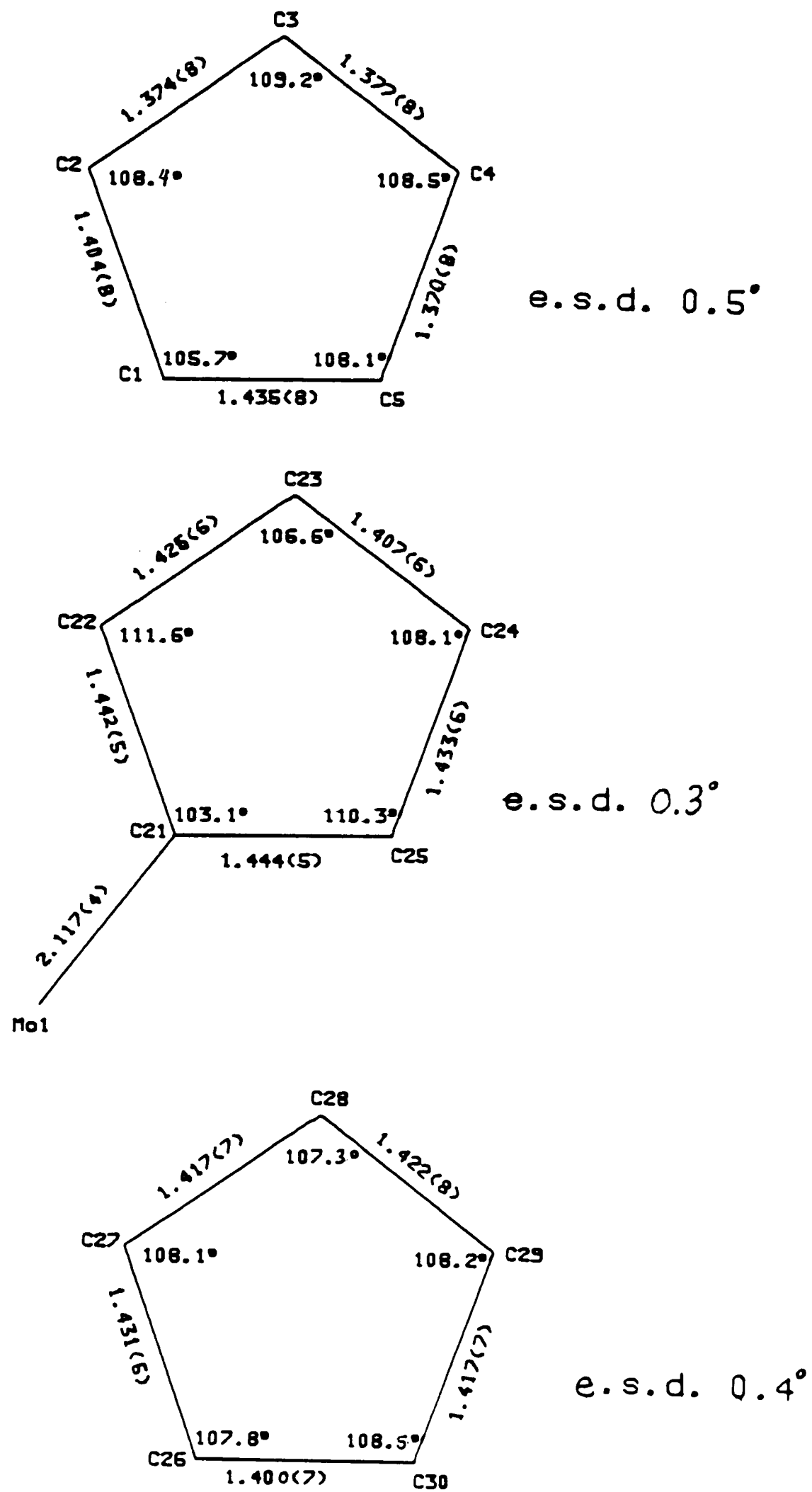
The crystal structure of the carbonyl dimer 5,
Mo(CO)(η -C₅H₅)(σ : η -C₅H₄)Mo(η -C₅H₅)(CO)₂

CRYSTAL DATA: C₁₈ H₁₄ Mo₂ O₃, M 407.08, monoclinic, $P2_1/n$, $a=8.644(2)$, $b=15.336(2)$, $c=12.203(6)$ Å, $\beta=92.59(3)^\circ$, $U=1616$ Å³, $Z=4$, $D_c=1.67$ g/cm³. A dark red hexagonal plate was mounted on the end of a glass fiber and intensities of 6699 reflections were measured ($2\theta_{\max}=60^\circ$) on a CAD-4 diffractometer using graphite-monochromated Mo-Kalpha radiation. 3575 Independent reflections with $I \geq 3\sigma(I)$, corrected for extinction and absorption [$\mu(\text{Mo-Kalpha})=15.3\text{cm}^{-1}$], were used in the refinement procedure, but towards the end of refinement the 200 reflection was discarded due to a suspected deadtime error. The structure was solved by heavy-atom and Fourier methods and refined by least squares with a large-block approximation to the normal matrix. All atoms were refined anisotropically except for the hydrogens, which were placed geometrically (C-H=1.0 Å, $U[\text{ISO}]=0.05$) after being located in a difference map. The final R-value is 0.033 ($R_w=0.045$). The Chebyshev coefficients for the weighting scheme are 54.62, 75.08, and 22.07.

Table 5-4 Selected interatomic distances (Å) and angles ($^\circ$) for compound 5

Mo(1)-Mo(2)	3.089(1)	C(6)-O(6)	1.174(5)
Mo(1)-C(1)	2.345(4)	C(7)-O(7)	1.159(6)
Mo(1)-C(2)	2.339(4)	C(31)-O(31)	1.142(5)
Mo(1)-C(3)	2.372(4)	C(21)-C(22)	1.442(5)
Mo(1)-C(4)	2.383(4)	C(22)-C(23)	1.426(6)
Mo(1)-C(5)	2.356(4)	C(23)-C(24)	1.407(6)
Mo(1)-C(6)	1.914(4)	C(24)-C(25)	1.433(6)
Mo(1)-C(7)	1.949(4)	C(25)-C(21)	1.444(5)
Mo(1)-C(21)	2.117(4)	C(6)-Mo(1)-C(7)	79.0(2)
Mo(2)-C(21)	2.218(3)	Mo(1)-C(6)-O(6)	179.7(4)
Mo(2)-C(22)	2.250(4)	Mo(1)-C(7)-O(7)	175.6(4)
Mo(2)-C(23)	2.314(4)	Mo(2)-C(31)-O(31)	177.9(4)
Mo(2)-C(24)	2.313(4)	Mo(1)-Mo(2)-C(31)	94.0(1)
Mo(2)-C(25)	2.266(4)		
Mo(2)-C(26)	2.297(4)		
Mo(2)-C(27)	2.295(4)		
Mo(2)-C(28)	2.331(4)		
Mo(2)-C(29)	2.308(4)		
Mo(2)-C(30)	2.286(4)		
Mo(2)-C(31)	1.986(4)		

Fig. 5-2 The carbonyl dimer 5, dimensions



Fractional coordinates for 5.

ATOM	X/A	Y/B	Z/C	U(ISO)
MO(1)	-0.00785(3)	0.16496(2)	-0.20083(2)	0.0302
MO(2)	-0.12655(3)	0.35115(2)	-0.25237(2)	0.0286
C(1)	0.0979(6)	0.0378(3)	-0.2736(5)	0.0560
C(2)	0.1989(6)	0.0666(4)	-0.1877(4)	0.0556
C(3)	0.2621(5)	0.1447(4)	-0.2177(4)	0.0534
C(4)	0.2027(7)	0.1678(3)	-0.3203(5)	0.0531
C(5)	0.1019(6)	0.1040(4)	-0.3566(4)	0.0560
C(6)	-0.0960(4)	0.1339(2)	-0.0651(3)	0.0371
O(6)	-0.1505(4)	0.1146(2)	0.0179(3)	0.0515
C(7)	-0.2238(5)	0.1472(3)	-0.2484(4)	0.0463
O(7)	-0.3504(4)	0.1309(3)	-0.2767(4)	0.0691
C(21)	0.0307(4)	0.2885(3)	-0.1271(3)	0.0336
C(22)	-0.0874(5)	0.3342(3)	-0.0701(3)	0.0389
C(23)	-0.0817(6)	0.4258(3)	-0.0892(3)	0.0472
C(24)	0.0454(5)	0.4406(3)	-0.1549(4)	0.0453
C(25)	0.1168(4)	0.3582(3)	-0.1755(3)	0.0393
C(26)	-0.2714(5)	0.4201(3)	-0.3890(3)	0.0470
C(27)	-0.2747(6)	0.3284(3)	-0.4106(4)	0.0487
C(28)	-0.1225(7)	0.3014(3)	-0.4327(3)	0.0483
C(29)	-0.0250(6)	0.3759(4)	-0.4213(4)	0.0505
C(30)	-0.1177(6)	0.4483(3)	-0.3940(4)	0.0507
C(31)	-0.3352(5)	0.3289(3)	-0.1965(4)	0.0451
O(31)	-0.4562(4)	0.3188(3)	-0.1648(4)	0.0670
H(1)	0.0361	-0.0173	-0.2763	0.0500
H(2)	0.2211	0.0354	-0.1167	0.0500
H(3)	0.3391	0.1794	-0.1723	0.0500
H(4)	0.2287	0.2219	-0.3613	0.0500
H(5)	0.0416	0.1036	-0.4285	0.0500
H(22)	-0.1637	0.3051	-0.0229	0.0500
H(23)	-0.1540	0.4707	-0.0615	0.0500
H(24)	0.0800	0.4986	-0.1823	0.0500
H(25)	0.2125	0.3502	-0.2175	0.0500
H(26)	-0.3625	0.4575	-0.3731	0.0500
H(27)	-0.3682	0.2900	-0.4101	0.0500
H(28)	-0.0897	0.2412	-0.4528	0.0500
H(29)	0.0893	0.3770	-0.4307	0.0500
H(30)	-0.0799	0.5091	-0.3807	0.0500

Table 5-6 Anisotropic temperature factors for 5.

ATOM	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
MO(1)	0.0285(2)	0.0337(2)	0.0302(2)	0.0023(1)	0.0063(1)	0.0003(1)
MO(2)	0.0290(2)	0.0312(2)	0.0267(2)	0.00084(9)	0.0045(1)	-0.0021(1)
C(1)	0.060(3)	0.042(2)	0.097(3)	-0.017(2)	0.033(2)	0.006(2)
C(2)	0.061(3)	0.079(3)	0.056(2)	0.015(2)	0.022(2)	0.036(2)
C(3)	0.035(2)	0.081(3)	0.067(3)	-0.018(2)	0.015(2)	0.009(2)
C(4)	0.063(3)	0.060(3)	0.064(2)	0.008(2)	0.038(2)	0.009(2)
C(5)	0.068(3)	0.081(3)	0.043(2)	-0.019(2)	0.007(2)	0.024(2)
C(6)	0.033(2)	0.038(2)	0.043(2)	0.006(1)	0.007(1)	-0.002(1)
O(6)	0.055(2)	0.069(2)	0.046(2)	0.014(2)	0.019(1)	-0.006(2)
C(7)	0.044(2)	0.038(2)	0.060(2)	-0.001(2)	-0.001(2)	-0.003(2)
O(7)	0.046(2)	0.060(2)	0.135(4)	0.003(2)	-0.022(2)	-0.011(2)
C(21)	0.031(2)	0.047(2)	0.027(1)	0.003(1)	-0.002(1)	-0.006(1)
C(22)	0.048(2)	0.050(2)	0.025(1)	-0.003(1)	0.004(1)	-0.005(2)
C(23)	0.061(2)	0.045(2)	0.042(2)	-0.013(2)	0.002(2)	-0.004(2)
C(24)	0.051(2)	0.038(2)	0.056(2)	-0.006(2)	-0.002(2)	-0.015(1)
C(25)	0.034(2)	0.041(2)	0.047(2)	0.002(1)	-0.001(1)	-0.011(1)
C(26)	0.055(2)	0.054(2)	0.042(2)	0.013(2)	-0.003(2)	0.015(2)
C(27)	0.059(2)	0.058(2)	0.038(2)	0.003(2)	-0.015(2)	-0.000(2)
C(28)	0.083(3)	0.062(2)	0.025(2)	-0.001(2)	0.001(2)	0.023(2)
C(29)	0.057(3)	0.084(3)	0.036(2)	0.019(2)	0.017(2)	0.012(2)
C(30)	0.067(2)	0.053(2)	0.042(2)	0.016(2)	0.008(2)	-0.002(2)
C(31)	0.038(2)	0.049(2)	0.053(2)	0.004(2)	0.012(2)	0.000(2)
O(31)	0.043(2)	0.087(3)	0.099(3)	0.011(2)	0.027(2)	-0.002(2)

Compound 7, $[(\text{Mo}(\eta\text{-C}_5\text{H}_5))_2(\mu\text{-O})(\mu\text{-H})(\mu\text{-C}_{10}\text{H}_8)]\text{BF}_4$

CRYSTAL DATA: $\text{C}_{20}\text{H}_{19}\text{OMo}_2\text{BF}_4$, M 553.88, orthorhombic, $Bbmm$ (No. 63, nonstandard setting, x,y,z ; $-x,-y,z$; $x,-y+1/2,z$; $-x,y+1/2,z$), $a=13.38(1)$, $b=11.153(3)$, $c=12.584 \text{ \AA}$, $U=1877 \text{ \AA}^3$, $Z=4$, $D_c=1.96 \text{ g/cm}^3$. A dark-red crystal was sealed in a glass capillary under N_2 , and the intensities of 2601 reflections were measured ($2\theta_{\text{max}}=50^\circ$); 488 independent, observed reflections were used for the structure solution and refinement. The data were not corrected for extinction or absorption [$\mu(\text{Mo-K}\alpha)=13.50\text{cm}^{-1}$]. The independent molybdenum position was determined by Patterson methods, and the remaining nonhydrogen atoms were found, with extreme difficulty, using Fourier and least-squares procedures. The BF_4^- ion lies on a site of $2/m$ symmetry, and is therefore required to be disordered. Although Fourier maps did not reveal reasonable tetrahedra, dimensional constraints were applied to the anion, and chemically reasonable bond lengths and angles were obtained after isotropic refinement. The anion was not refined anisotropically, nor was the bridging oxygen (which lies on a mirror plane), but anisotropic refinement was carried out for the remaining nonhydrogen atoms. Hydrogens were not included in the model. As discussed in Chapter 2, there are two other space groups which have the same systematic absences as $Bbmm$, namely $Bb2_1m$ and $Bbm2$. However, refinement in these space groups was not successful. The $\eta\text{-C}_5\text{H}_5$ ring is disordered, as is apparent from its temperature factors; the molybdenum is also disordered. The final R-value is 9.85%, $R_w=12.46\%$, for 488 reflections, 30 constraints, and 70 parameters. Weights were calculated from a Chebyshev polynomial with the following coefficients: 47.5, 65.6, 25.4, and 4.8. I would like to thank Dr F.M. Miao for helpful discussions of the refinement.

Table 5-7 Atomic and molecular parameters for compound 7.

The ' refers to operation x,y,-z

Distances and e.s.d's (Å) from the refinement in 8bmm.

Fractional coordinates

ATOM	X/A	Y/B	Z/C	U(100)
MO(1)	688(2)	2500	1185(2)	398
C(1)	-921(20)	2500	576(18)	433
C(2)	-783(15)	3539(12)	1217(13)	412
C(3)	-607(17)	3137(8)	2275(13)	392
C(4)	1492(25)	2500	2826(21)	490
C(5)	1801(19)	3529(12)	2264(19)	699
C(6)	2349(16)	3136(8)	1362(19)	624
O(1)	848(30)	1277(39)	0	407(107)
B(1)	0	0	5000	1908(595)
F(1)	0	284(132)	3845(15)	2278(352)
F(2)	1001(34)	-1218(38)	5418(32)	2278(352)
F(3)	-276(112)	889(99)	5361(33)	2278(352)
F(4)	-716(81)		5406(32)	2278(352)

PIVOT ATOM	MO	1.	2.983	0.006
	C	1.	2.284	0.025
	C	2.	2.284	0.018
	C	3.	2.321	0.020
	C	4.	2.327	0.030
	C	5.	2.319	0.023
	C	6.	2.343	0.020
	O	1.	2.032	0.030

PIVOT ATOM	C,	1.	1.450	0.044
	C	2.	1.424	0.015

PIVOT ATOM	C	2.	1.424	0.016
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PIVOT ATOM	C	3.	3.	
	C	3.	1.421	0.018

PIVOT ATOM	C	4.	1.410	0.015
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PIVOT ATOM	C	5.	5.	
	C	6.	1.420	0.017

PIVOT ATOM	C	6.	6.	
	C	6.	1.419	0.018

PIVOT ATOM	B	1.	1.453	0.019
	F	2.	1.473	0.020
	F	3.	1.479	0.020
	F	4.	1.470	0.020

Mo1-O1-Mo1' 94(2)°

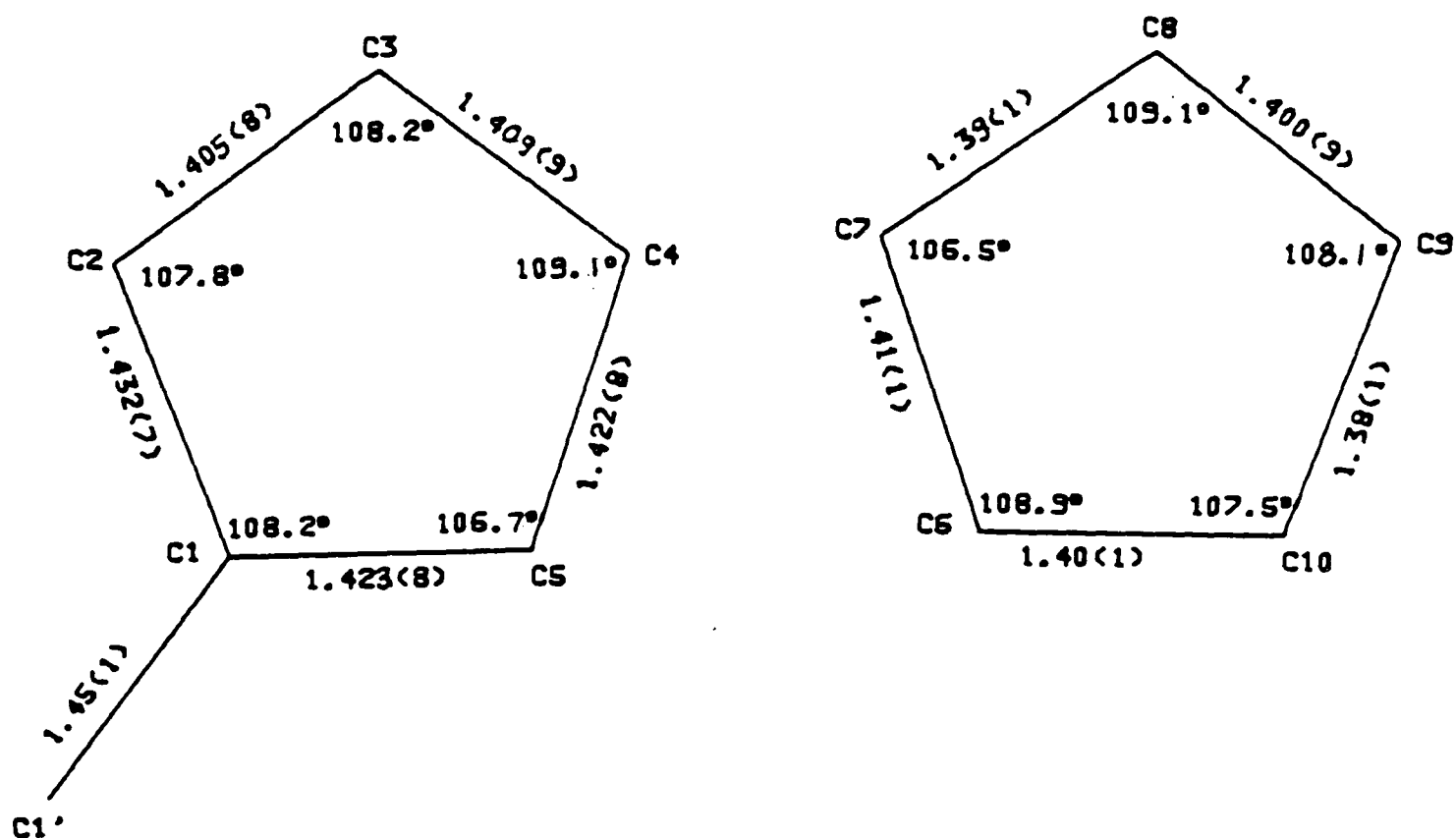
Anisotropic temperature factors

ATOM	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
MO(1)	285(13)	817(23)	273(13)	0	-27(20)	0
C(1)	367(106)	422(163)	595(210)	0	-163(159)	0
C(2)	494(112)	516(125)	411(89)	-98(107)	117(144)	210(121)
C(3)	398(120)	778(169)	373(93)	-120(109)	133(116)	270(141)
C(4)	507(242)	1111(288)	354(205)	0	-330(186)	0
C(5)	694(186)	920(230)	918(207)	43(169)	-510(139)	-94(180)
C(6)	467(138)	1971(449)	653(171)	319(198)	-296(124)	-625(177)

Crystal structure of 9, [(Mo(η -C₅H₅))₂(μ -C₁₀H₈)H₃]PF₆

CRYSTAL DATA: C₂₀H₂₁Mo₂PF₆, M 598.07, orthorhombic, Pbcn, a=13.030(1), b=13.302(3), c=11.446(2) Å, U=1984 Å³, Z=4, D_c=2.00g/cm³. A black crystal of octahedral shape was sealed in a glass capillary under N₂ and the intensities of 3461 reflections were measured ($2\theta_{\text{max}}=54^\circ$) on a CAD-4 diffractometer using graphite-monochromated Mo-Kalpha radiation. 1285 Independent reflections with $I \geq 3\sigma(I)$, corrected for extinction but not absorption [$\mu(\text{Mo-Kalpha})=12.9\text{cm}^{-1}$], were used in the refinement procedure. In the final stages of refinement reflection 200 was removed because it was measured at a count-rate for which deadtime was significant. The structure was solved by heavy-atom and Fourier methods and refined by least squares with a large-block approximation to the normal matrix. All nonhydrogen atoms were refined anisotropically, the fluorine temperature factors being used to accomodate some of the disorder found in the anion. Ring-hydrogens were located in difference maps and then placed geometrically (C-H=1.0 Å). A final difference map showed a peak near the Mo (Mo-peak=1.98 Å). The peak was quite broad, and may correspond to the expected disorder of the three hydrides (see the discussion in Section 2.2). Since we could not be sure of the arrangement of the hydrides, they were not included in the model. The final R-value is 0.034, R_w=0.037. During the final stages of refinement, weights were calculated from a three-term Chebyshev polynomial with coefficients 33.42, 45.57, and 17.66.

e.s.d. 0.6°

Fig. 5-3 Compound 9
dimensionsTable 5-8 Average dimensions for the C₅-rings of 2, 5, and 9.

a) Compound 2.

Ring	C-C (Å)	C-C-C (°)	Mo-ring plane (Å)	ϕ (°)
C(1) TO C(5)	1.41(3)	108(3)	1.98	134
C(6) TO C(10)	1.39(5)	108(3)	1.98	
C(21) TO C(25)	1.43(1)	108(2)	1.91	154
C(26) TO C(30)	1.40(3)	108(1)	1.95	

b) Compound 5.

Ring	C-C (Å)	C-C-C (°)	Mo-ring plane (Å)	ϕ (°)
C(1) TO C(5)	1.39(3)	108(1)	2.039	148.2
C(21) TO C(25)	1.43(1)	108(3)	1.916	
C(26) TO C(30)	1.42(1)	108.0(4)	1.962	

c) Compound 9.

Ring	C-C (Å)	C-C-C (°)	Mo-ring plane (Å)	ϕ (°)	ω (°)
C(1) TO C(5)	1.42(1)	108.0(9)	1.941	140.4	17.5
C(6) TO C(10)	1.40(1)	108(1)	1.957		

ϕ is the angle between the ring normals and ω is the dihedral angle between five-membered rings of the fulvalene.

Table 5-9 Fractional coordinates for 9.

ATOM	X/A	Y/B	Z/C	U(ISO)
MO(1)	0.12156(3)	0.07214(3)	-0.22312(4)	0.0327
P(1)	0.5000	0.0000	0.0000	0.0418
C(1)	0.0549(4)	-0.0857(3)	-0.2390(5)	0.0315
C(2)	0.1000(4)	-0.0777(5)	-0.1253(5)	0.0427
C(3)	0.2057(5)	-0.0608(5)	-0.1400(6)	0.0484
C(4)	0.2272(4)	-0.0609(4)	-0.2606(6)	0.0434
C(5)	0.1342(4)	-0.0748(4)	-0.3236(5)	0.0431
C(6)	0.1285(5)	0.2394(4)	-0.2740(8)	0.0501
C(7)	0.2120(6)	0.1904(6)	-0.3273(7)	0.0607
C(8)	0.2735(5)	0.1551(5)	-0.2375(7)	0.0513
C(9)	0.2287(5)	0.1803(5)	-0.1303(6)	0.0534
C(10)	0.1395(5)	0.2333(5)	-0.1528(8)	0.0566
F(10)	0.4576(4)	-0.0226(5)	-0.1260(4)	0.0841
F(21)	0.465(2)	0.109(1)	-0.016(2)	0.1231
F(22)	0.6058(7)	0.028(2)	-0.048(1)	0.0676
F(31)	0.414(1)	0.075(1)	0.023(1)	0.1048
F(32)	0.429(1)	-0.083(1)	0.049(1)	0.1088
H(2)	0.0631	-0.0831	-0.0492	0.0550
H(3)	0.2567	-0.0508	-0.0757	0.0550
H(4)	0.2967	-0.0522	-0.2963	0.0550
H(5)	0.1260	-0.0769	-0.4105	0.0550
H(6)	0.0708	0.2735	-0.3157	0.0690
H(7)	0.2243	0.1824	-0.4132	0.0690
H(8)	0.3392	0.1179	-0.2482	0.0690
H(9)	0.2571	0.1629	-0.0516	0.0690
H(10)	0.0918	0.2616	-0.0925	0.0690

Table 5-10. Selected bond lengths for compound 9 (Å).

Mo(1)-Mo(1)'	3.227 (1)
Mo(1)-C(1)	2.279(4)
Mo(1)-C(2)	2.303(6)
Mo(1)-C(3)	2.288(6)
Mo(1)-C(4)	2.283(5)
Mo(1)-C(5)	2.274(6)
Mo(1)-C(6)	2.302(5)
Mo(1)-C(7)	2.299(7)
Mo(1)-C(8)	2.273(6)
Mo(1)-C(9)	2.269(6)
Mo(1)-C(10)	2.302(6)
C(1)-C(1)'	1.45(1)
P(1)-F(ave)	1.54(2)

The ' refers to an atom related by the symmetry operation $-x, y, -1/2-z$

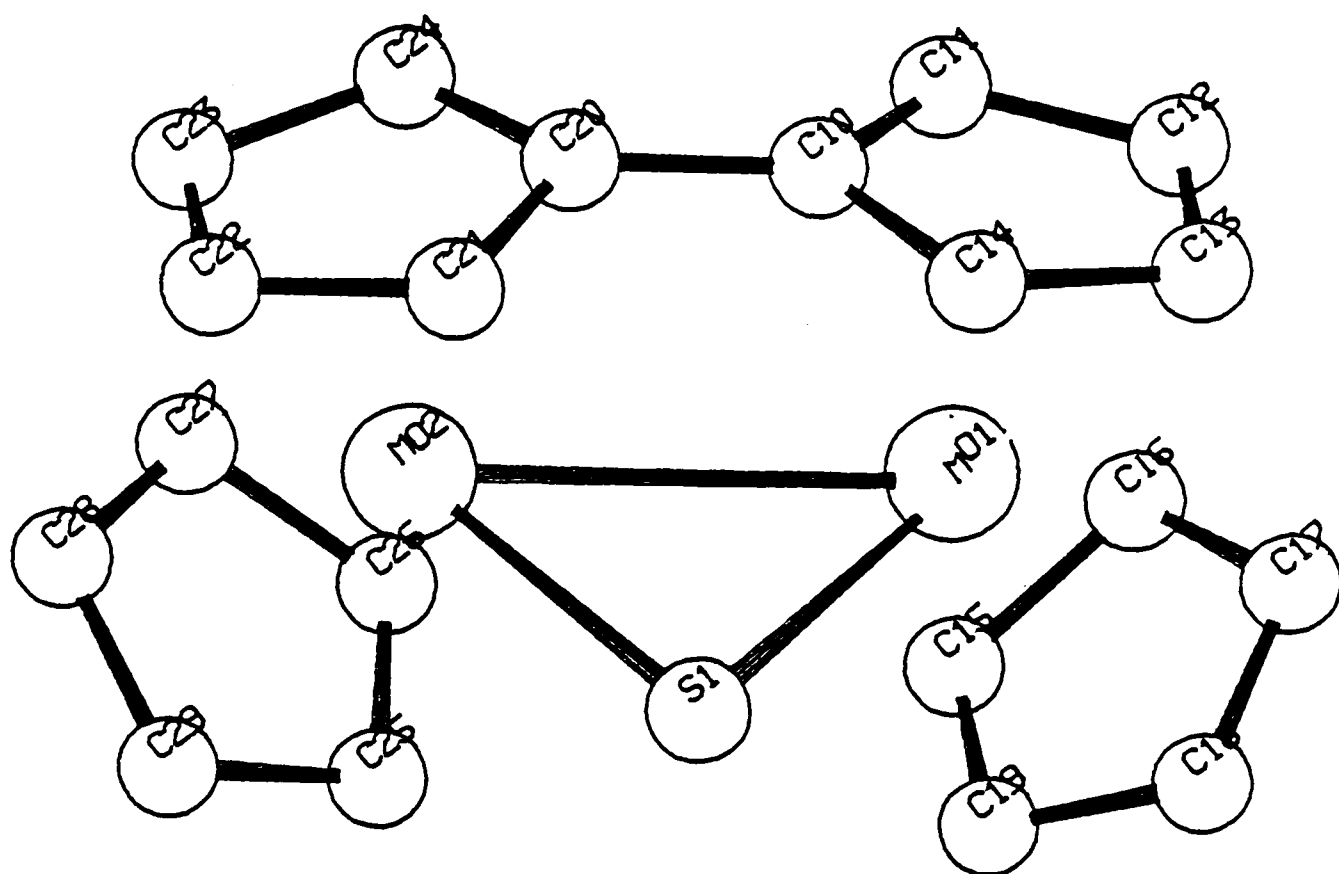
Table 5-11 Anisotropic temperature factors for 9.

ATOM	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
MO(1)	0.0310(2)	0.0231(2)	0.0508(3)	0.0025(2)	0.0072(3)	-0.0000(2)
P(1)	0.0277(9)	0.069(1)	0.042(1)	-0.015(1)	-0.0001(9)	-0.0005(1)
C(1)	0.038(3)	0.020(2)	0.044(3)	0.004(2)	-0.005(2)	0.003(2)
C(2)	0.046(3)	0.041(3)	0.046(3)	0.012(3)	-0.007(2)	-0.001(3)
C(3)	0.041(3)	0.044(3)	0.076(4)	0.010(4)	-0.019(3)	0.006(3)
C(4)	0.032(2)	0.032(3)	0.088(4)	-0.004(3)	0.008(2)	0.009(2)
C(5)	0.044(3)	0.036(3)	0.055(3)	-0.006(3)	0.007(2)	0.008(3)
C(6)	0.057(3)	0.026(3)	0.131(5)	0.017(4)	-0.031(5)	-0.019(3)
C(7)	0.095(5)	0.060(4)	0.058(4)	0.015(4)	0.009(3)	-0.035(4)
C(8)	0.039(3)	0.047(3)	0.091(4)	-0.004(3)	0.010(3)	-0.018(3)
C(9)	0.066(4)	0.044(4)	0.070(4)	-0.014(4)	-0.016(3)	-0.018(3)
C(10)	0.057(4)	0.038(3)	0.115(4)	-0.030(4)	0.023(4)	-0.011(3)
F(10)	0.083(3)	0.175(6)	0.050(2)	-0.023(3)	-0.014(2)	-0.029(4)
F(21)	0.19(2)	0.065(7)	0.22(2)	-0.01(1)	-0.12(2)	0.02(1)
F(22)	0.038(5)	0.37(3)	0.056(8)	-0.01(1)	0.010(5)	-0.09(1)
F(31)	0.098(9)	0.16(2)	0.125(9)	-0.02(1)	0.021(8)	0.07(1)
F(32)	0.16(1)	0.12(1)	0.11(1)	0.021(7)	0.012(9)	-0.08(1)

Compound 10, [Mo(η -C₅H₅)]₂(η -C₁₀H₈)(μ -S)

CRYSTAL DATA: C₂₀H₁₈Mo₂S, M 481.88, monoclinic, P2₁/a, a=15.93(1), b=11.284(1), c=18.849(4) Å, U=3148 Å³, Z=8, D_c=2.04. A crystal was sealed in a glass capillary under N₂, and the intensities of 7787 reflections were measured (2 θ _{max}=54°). The data were corrected for extinction but not absorption [μ (Mo-K α)=16.80cm⁻¹], and 2941 independent, observed reflections were used for structure solution and refinement. The structure has a pseudo B-centred cell, which shows up in the Patterson as a peak at 0,1/2,0 with a height 3/4 that of the origin; the positions of four Mo and two S atoms were determined from the Patterson, and the remaining nonhydrogen atoms were located in successive Fourier syntheses. There are two discrete, independent dimers in the asymmetric unit. After the anisotropic refinement of all nonhydrogens had converged (and hydrogens had been placed on the Cp and fulvalene ligands), a difference Fourier map showed what appeared to be two hydrido ligands, one at a distance of 1.8 Å from Mo2, the other 1.8 Å from Mo4. In addition, the highest and fourth-highest peaks in the difference map were 1.3 Å from S1 and S2, respectively, corresponding to typical S-H moieties. The pairs of Mo-H and S-H bonds were constrained (e.s.d.=0.005 Å) to their respective means, an equivalent temperature factor was refined for the two hydrido ligands, and the U[ISO]'s of the two thiol hydrogens were equivalenced. After further refinement had converged, with reasonable hydrogen temperature factors, it was realized that the four 'hydrogens' found in the difference map were in physically unreasonable positions. Slant-difference Fourier maps were calculated in the Mo₂S plane of each molecule, and they showed a number of well-resolved features in appropriate positions for hydrido ligands. The fact that four misplaced hydrogens refined to convergence, and the resulting bond lengths (if not angles) were reasonable, suggests that considerable scepticism is in order when one surveys the large number of

hydrides in the literature that have been refined with X-ray data¹². The subsequent confirmation of X-ray structures with neutron diffraction experiments does not validate the least-squares and Fourier calculations based on X-ray data, it merely pays tribute to the crystallographers' stereochemical intuition. When intuition is not sufficient to place hydrido ligands, X-ray structure determinations must be interpreted with caution. There are many systematic errors that can affect the model or the data, such as anisotropic extinction, absorption, and inadequate scattering factors, and all of these errors are common for structures which contain transition-metals. An attempt to refine hydrides may simply take into account certain inadequacies in the structure determination, and may have no relation to any "true" hydride position. It does seem that low-temperature data collections decrease the importance of many systematic errors that might otherwise interfere with hydride location¹³.



DISTANCES ABOUT ATOM MO 1.

ATOM	SERIAL	S(I)	L	T(X)	T(Y)	T(Z)		
S	1.	1	1	0	0	0	2.413	0.003
C	10.	1	1	0	0	0	2.306	0.008
C	11.	1	1	0	0	0	2.283	0.010
C	12.	1	1	0	0	0	2.306	0.009
C	13.	1	1	0	0	0	2.327	0.009
C	14.	1	1	0	0	0	2.338	0.008
C	15.	1	1	0	0	0	2.354	0.010
C	16.	1	1	0	0	0	2.339	0.010
C	17.	1	1	0	0	0	2.283	0.009
C	18.	1	1	0	0	0	2.301	0.012
C	19.	1	1	0	0	0	2.294	0.010

DISTANCES ABOUT ATOM MO 2.

ATOM	SERIAL	S(I)	L	T(X)	T(Y)	T(Z)		
S	1.	1	1	0	0	0	2.419	0.003
C	20.	1	1	0	0	0	2.221	0.008
C	21.	1	1	0	0	0	2.348	0.008
C	22.	1	1	0	0	0	2.332	0.008
C	23.	1	1	0	0	0	2.277	0.010
C	24.	1	1	0	0	0	2.264	0.011
C	25.	1	1	0	0	0	2.283	0.009
C	26.	1	1	0	0	0	2.327	0.010
C	27.	1	1	0	0	0	2.351	0.012
C	28.	1	1	0	0	0	2.319	0.011
C	29.	1	1	0	0	0	2.294	0.009

ANGLES ABOUT ATOM S 1.

KEY	ATOM	SERIAL	S(I)	L	T(X)	T(Y)	T(Z)		
1	MO	1.	1	1	0	0	0		
2	MO	2.	1	1	0	0	0	83.00	0.10

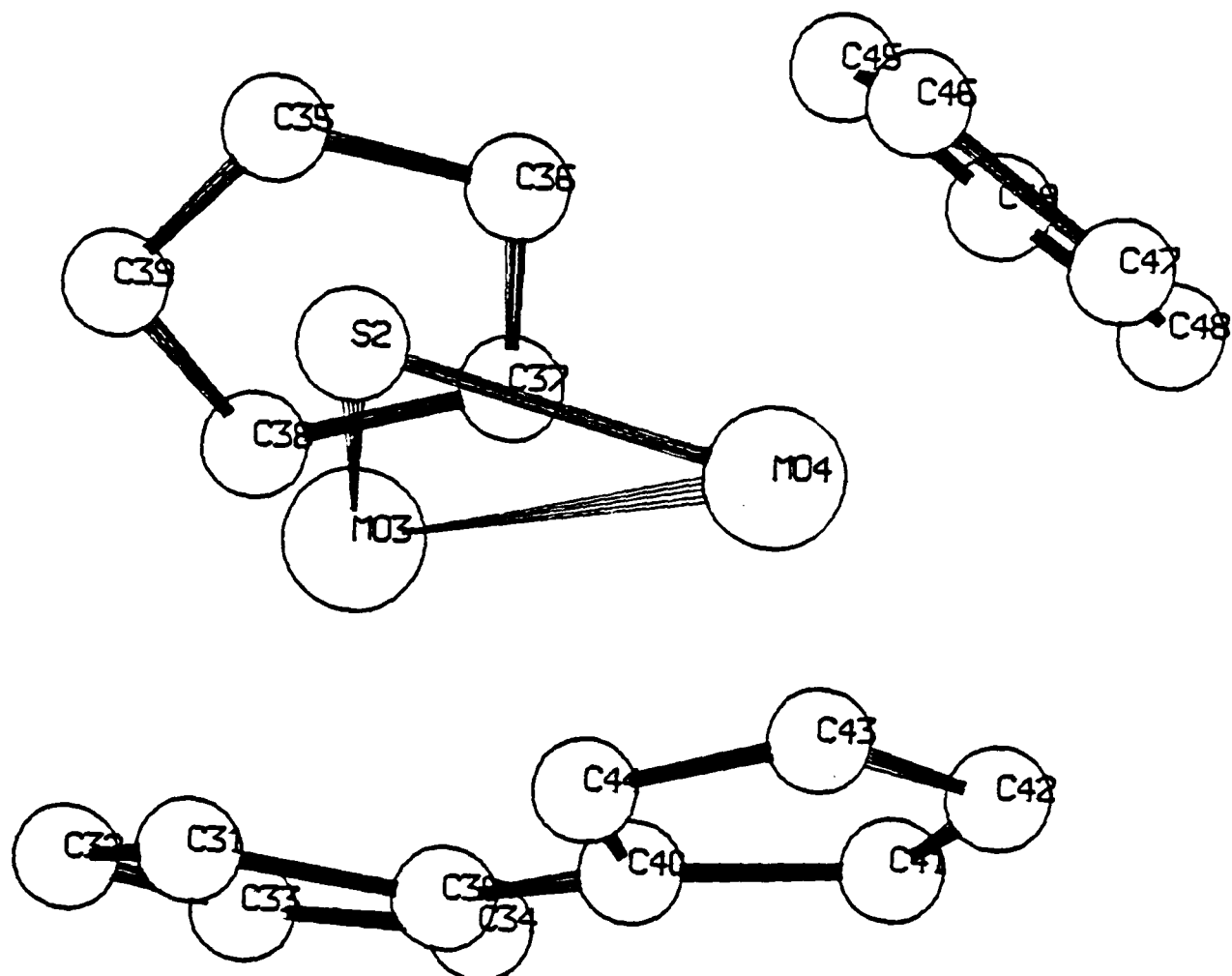
KEY

Table S-12 Dimensions of Molecule 1, Compound 10.

1

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PIVOT ATOM MO      1.
                MO      2. 3.202 0.001
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207



DISTANCES ABOUT ATOM MO 3.

ATOM	SERIAL	S(I)	L	T(X)	T(Y)	T(Z)		
S	2.	1	1	0	0	0	2.426	0.003
C	30.	1	1	0	0	0	2.293	0.008
C	31.	1	1	0	0	0	2.343	0.009
C	32.	1	1	0	0	0	2.327	0.009
C	33.	1	1	0	0	0	2.306	0.011
C	34.	1	1	0	0	0	2.264	0.011
C	35.	1	1	0	0	0	2.326	0.010
C	36.	1	1	0	0	0	2.359	0.009
C	37.	1	1	0	0	0	2.330	0.011
C	38.	1	1	0	0	0	2.289	0.010
C	39.	1	1	0	0	0	2.295	0.010

DISTANCES ABOUT ATOM MO 4.

ATOM	SERIAL	S(I)	L	T(X)	T(Y)	T(Z)		
S	2.	1	1	0	0	0	2.416	0.003
C	40.	1	1	0	0	0	2.299	0.008
C	41.	1	1	0	0	0	2.278	0.010
C	42.	1	1	0	0	0	2.304	0.009
C	43.	1	1	0	0	0	2.331	0.009
C	44.	1	1	0	0	0	2.353	0.008
C	45.	1	1	0	0	0	2.304	0.009
C	46.	1	1	0	0	0	2.322	0.010
C	47.	1	1	0	0	0	2.305	0.009
C	48.	1	1	0	0	0	2.339	0.009
C	49.	1	1	0	0	0	2.348	0.009

ANGLES ABOUT ATOM S 2.

KEY	ATOM	SERIAL	S(I)	L	T(X)	T(Y)	T(Z)		
1	MO	3.	1	1	0	0	0		
2	MO	4.	1	1	0	0	0	83.16	0.10

KEY

Table 5-13 Dimensions of Molecule 2, Compound 10. 1

Table 5-13 (cont.)

PIVOT ATOM		MO	3.	4.	3.214	0.001				
							PIVOT ATOM	C	30.	
							1	C	31.	
							2	C	34.	108.16 0.87
							3	C	40.	125.48 1.00 125.62 0.97
							PIVOT ATOM	C	31.	
							1	C	30.	
							2	C	32.	108.33 1.05
							PIVOT ATOM	C	32.	
							1	C	31.	
							2	C	33.	108.04 1.01
							PIVOT ATOM	C	33.	
							1	C	32.	
							2	C	34.	109.45 1.06
							PIVOT ATOM	C	34.	
							1	C	30.	
							2	C	33.	105.92 1.14
							PIVOT ATOM	C	35.	
							1	C	36.	
							2	C	39.	110.05 1.18
							PIVOT ATOM	C	36.	
							1	C	35.	
							2	C	37.	107.67 0.93
							PIVOT ATOM	C	37.	
							1	C	36.	
							2	C	38.	105.96 1.03
							PIVOT ATOM	C	38.	
							1	C	37.	
							2	C	39.	107.51 1.09
							PIVOT ATOM	C	39.	
							1	C	35.	
							2	C	38.	108.79 1.14
							PIVOT ATOM	C	40.	
							1	C	30.	
							2	C	41.	126.75 0.92
							3	C	44.	123.56 0.91 108.64 0.79
							PIVOT ATOM	C	41.	
							1	C	40.	
							2	C	42.	107.02 0.88
							PIVOT ATOM	C	42.	
							1	C	41.	
							2	C	43.	109.72 0.83
							PIVOT ATOM	C	43.	
							1	C	42.	
							2	C	44.	106.81 0.90
							PIVOT ATOM	C	44.	
							1	C	40.	
							2	C	43.	107.73 0.90
							PIVOT ATOM	C	45.	
							1	C	46.	
							2	C	49.	109.50 0.92
							PIVOT ATOM	C	46.	
							1	C	45.	
							2	C	47.	103.80 1.02
							PIVOT ATOM	C	47.	
							1	C	46.	
							2	C	48.	111.31 0.91
							PIVOT ATOM	C	48.	
							1	C	47.	
							2	C	49.	107.13 1.02
							PIVOT ATOM	C	49.	
							1	C	45.	
							2	C	48.	108.24 1.00

Table 5-14 Fractional Coordinates for 10 (x1000)

ATOM	X/A	Y/B	Z/C	U (ISO)
MO(1)	4828.7(5)	-1222(1)	2244.6(4)	218
MO(2)	3254.3(5)	-1880.2(9)	685.8(4)	214
MO(3)	8362.4(5)	-1841(1)	5673.8(4)	232
MO(4)	9719.7(5)	-1224.1(9)	7353.1(4)	203
S(1)	3842(2)	10(3)	1251(1)	245
S(2)	8795(2)	30(3)	6338(1)	253
C(10)	5332(5)	-1986(11)	1333(5)	232
C(11)	5616(6)	-2746(10)	1984(5)	307
C(12)	6231(6)	-2077(11)	2579(5)	293
C(13)	6302(6)	-912(11)	2319(6)	351
C(14)	5757(6)	-872(10)	1544(5)	257
C(15)	3967(10)	-1719(18)	2990(7)	460
C(16)	4847(10)	-2024(13)	3395(6)	385
C(17)	5347(7)	-969(13)	3529(5)	394
C(18)	4791(9)	-9(14)	3214(6)	453
C(19)	3929(8)	-486(17)	2859(6)	451
C(20)	4630(6)	-2251(10)	615(5)	243
C(21)	4224(6)	-1380(12)	41(5)	321
C(22)	3435(6)	-1896(12)	-489(5)	263
C(23)	3371(7)	-3060(12)	-255(6)	343
C(24)	4106(7)	-3313(11)	436(6)	329
C(25)	2186(6)	-1501(13)	1204(7)	309
C(26)	2455(7)	-2687(15)	1391(7)	433
C(27)	2201(7)	-3322(12)	715(9)	440
C(28)	1801(7)	-2585(12)	126(7)	422
C(29)	1763(6)	-1432(13)	384(7)	396
C(30)	7811(6)	-2347(10)	6603(5)	282
C(31)	7178(6)	-1545(12)	6118(6)	345
C(32)	6825(7)	-2056(14)	5389(6)	393
C(33)	7206(9)	-3190(15)	5423(6)	417
C(34)	7847(7)	-3389(12)	6167(6)	373
C(35)	9043(9)	-982(13)	4893(7)	433
C(36)	9615(6)	-1866(14)	5283(6)	370
C(37)	9150(10)	-2966(13)	5081(7)	395
C(38)	8283(8)	-2685(12)	4548(6)	402
C(39)	8245(8)	-1458(13)	4446(6)	445
C(40)	8414(5)	-2085(10)	7359(5)	226
C(41)	9159(7)	-2787(10)	7809(5)	235
C(42)	9649(7)	-2098(10)	8435(6)	261
C(43)	9245(7)	-944(11)	8377(5)	329
C(44)	8463(6)	-953(10)	7715(5)	294
C(45)	10831(6)	-563(12)	6934(6)	325
C(46)	10961(7)	14(12)	7651(7)	345
C(47)	11168(6)	-934(11)	8180(6)	331
C(48)	11166(6)	-2026(12)	7822(6)	323
C(49)	10971(7)	-1793(13)	7051(6)	389
H(11)	5418	-3579	2014	500
H(12)	6564	-2379	3102	500
H(13)	6666	-244	2625	500
H(14)	5682	-173	1201	500
H(15)	3445	-2268	2817	500

Table 5-14 (cont.)

ATOM	X/A	Y/B	Z/C	U(ISO)
H(16)	5078	-2842	3562	500
H(17)	6009	-912	3813	500
H(18)	4970	846	3232	500
H(19)	3380	-21	2563	500
H(21)	4454	-561	19	500
H(22)	3007	-1500	-948.	500
H(23)	2886	-3641	-525	500
H(24)	4224	-4069	732	500
H(25)	2269	-833	1570	500
H(26)	2770	-3011	1914	500
H(27)	2304	-4192	670	500
H(28)	1564	-2833	-418	500
H(29)	1503	-718	71	500
H(31)	7011	-751	6268	500
H(32)	6380	-1684	4927	500
H(33)	7059	-3773	4996	500
H(34)	8238	-4098	6347	500
H(35)	9186	-113	4928	500
H(36)	10245	-1752	5645	500
H(37)	9383	-3772	5275	500
H(38)	7794	-3266	4295	500
H(39)	7721	-1007	4101	500
H(41)	9306	-3612	7696	500
H(42)	10191	-2368	8861	500
H(43)	9476	-266	8736	500
H(44)	8024	-284	7530	500
H(45)	10667	-158	6430	500
H(46)	10915	879	7749	500
H(47)	11301	-836	8735	500
H(48)	11281	-2825	8070	500
H(49)	10933	-2393	6651	500

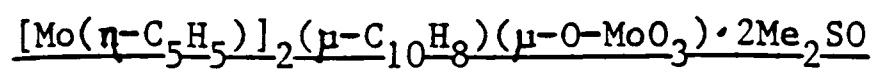
Table 5-15 Thermal Parameters for 10 (x1000).

ATOM	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
MO(1)	227(3)	258(7)	184(3)	-16(4)	80(2)	11(4)
MO(2)	197(3)	257(7)	194(3)	-0(4)	69(2)	-3(4)
MO(3)	234(3)	323(7)	166(3)	-9(4)	67(2)	-45(4)
MO(4)	193(3)	224(7)	187(3)	7(4)	56(2)	-4(4)
S(1)	261(10)	196(20)	263(10)	12(12)	48(7)	27(12)
S(2)	296(10)	211(20)	260(10)	40(12)	87(7)	28(13)
C(10)	157(31)	516(86)	245(35)	-52(46)	115(21)	65(44)
C(11)	241(38)	362(94)	352(44)	-59(46)	109(27)	18(43)
C(12)	218(38)	384(93)	317(44)	43(47)	44(28)	111(45)
C(13)	275(40)	430(100)	387(46)	-66(51)	127(29)	-30(48)
C(14)	202(34)	318(85)	307(39)	-61(43)	114(24)	-51(41)
C(15)	798(62)	1501(148)	296(43)	-274(70)	374(32)	-689(76)
C(16)	1020(78)	406(105)	260(40)	20(55)	353(33)	-135(78)
C(17)	490(56)	747(120)	155(39)	67(52)	35(33)	-15(65)
C(18)	806(77)	488(103)	252(45)	-42(56)	150(40)	123(75)
C(19)	397(48)	1457(155)	240(42)	32(69)	179(30)	248(76)
C(20)	243(36)	314(87)	239(36)	-72(40)	113(23)	21(41)
C(21)	328(40)	559(97)	211(37)	-16(47)	126(24)	-69(51)
C(22)	320(39)	597(91)	121(32)	-54(46)	105(23)	-18(54)
C(23)	411(46)	431(90)	329(42)	-167(51)	166(29)	-9(57)
C(24)	442(48)	244(89)	418(47)	-106(49)	187(31)	13(50)
C(25)	216(36)	809(111)	557(49)	-501(51)	218(27)	-222(49)
C(26)	200(40)	1026(129)	536(58)	234(69)	135(33)	-86(59)
C(27)	346(47)	307(103)	945(82)	123(72)	265(40)	24(55)
C(28)	403(49)	415(98)	499(55)	-116(61)	176(35)	-26(58)
C(29)	177(40)	657(115)	548(62)	136(63)	47(35)	103(51)
C(30)	326(40)	355(86)	234(37)	-23(43)	120(25)	-111(45)
C(31)	174(37)	622(110)	386(47)	57(54)	92(28)	-9(48)
C(32)	254(41)	819(124)	414(51)	-20(65)	116(31)	-237(54)
C(33)	702(63)	694(111)	305(48)	-132(60)	151(40)	-503(59)
C(34)	437(48)	539(104)	337(46)	-73(52)	118(33)	-295(49)
C(35)	653(52)	526(110)	550(48)	-76(64)	452(28)	-187(67)
C(36)	268(39)	809(108)	308(42)	-97(57)	157(25)	-0(59)

Table 5-15 (cont.)

ATOM	U(11)	L(22)	U(33)	U(23)	U(13)	U(12)
C(37)	930(68)	376(101)	460(49)	154(56)	420(35)	386(66)
C(38)	586(57)	461(105)	333(44)	-142(53)	227(32)	-143(61)
C(39)	549(56)	725(123)	286(43)	44(57)	222(30)	-3(66)
C(40)	198(33)	329(84)	242(35)	26(41)	124(21)	-35(40)
C(41)	383(43)	144(84)	312(40)	22(41)	146(27)	-81(42)
C(42)	367(42)	252(90)	374(42)	196(45)	173(28)	55(47)
C(43)	459(48)	462(98)	208(37)	-48(46)	132(28)	-169(53)
C(44)	316(38)	354(93)	351(39)	-25(47)	219(23)	-5(46)
C(45)	228(38)	577(97)	349(44)	203(50)	117(28)	56(50)
C(46)	260(41)	311(90)	703(66)	-5(65)	168(35)	-133(49)
C(47)	204(40)	477(104)	338(49)	-3(51)	-52(32)	-8(47)
C(48)	187(38)	401(97)	419(52)	70(52)	27(31)	50(46)
C(49)	261(40)	584(102)	490(53)	-66(63)	163(31)	99(55)

The Crystal Structure of Compound 11, the molybdato-bridged dimer,



CRYSTAL DATA: $\text{C}_{20}\text{H}_{18}\text{O}_4\text{Mo}_3 \cdot \text{C}_4\text{H}_{12}\text{O}_2\text{S}_2$, M 593.8156, orthorhombic, $P2_12_12_1$, $a=10.819(7)$, $b=14.667(2)$, $c=16.579(3)$ Å, $U=2631$ Å³, $Z=4$, $D_c=1.89$ g/cm³. A dark-coloured crystal was sealed in a glass capillary under N_2 , and the intensities of 5461 reflections were measured ($2\theta_{\text{max}}=60^\circ$). For the structure solution and refinement, 2872 independent, observed [$I \geq 3\sigma(I)$] reflections were used; Friedel pairs were not merged, and the data were corrected for extinction but not absorption [$\mu(\text{Mo-K}\alpha)=14.2\text{cm}^{-1}$]. The structure was solved by a combination of Patterson, direct, and Fourier methods, and was refined by least squares. The two DMSO solvent molecules are highly disordered, and they were refined isotropically with dimensional constraints imposed. All other non-hydrogen atoms were refined anisotropically, and the "polarity"¹¹ was refined to check the hand of this noncentrosymmetric structure. The final R-value is 4.13%, $R_w=4.60\%$, for 2872 reflections, 20 constraints, and 325 parameters. The Chebyshev coefficients for the weighting scheme are 12.06, 16.30, and 6.38.

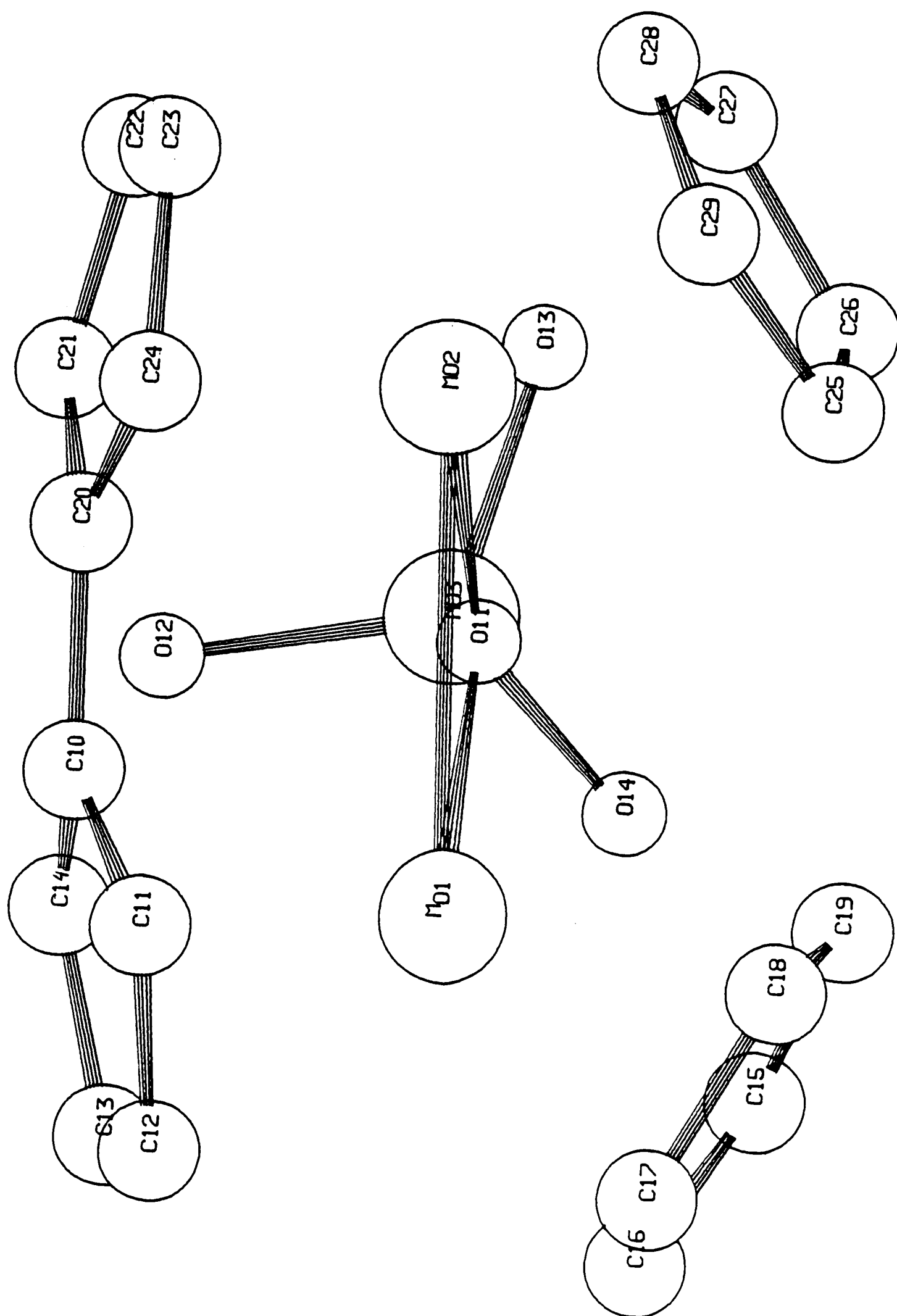


Fig. 5-4 Compound 11.

Fig. 5-5 Compound 11, Selected Dimensions.

THE MOLYBDATE TRIMER

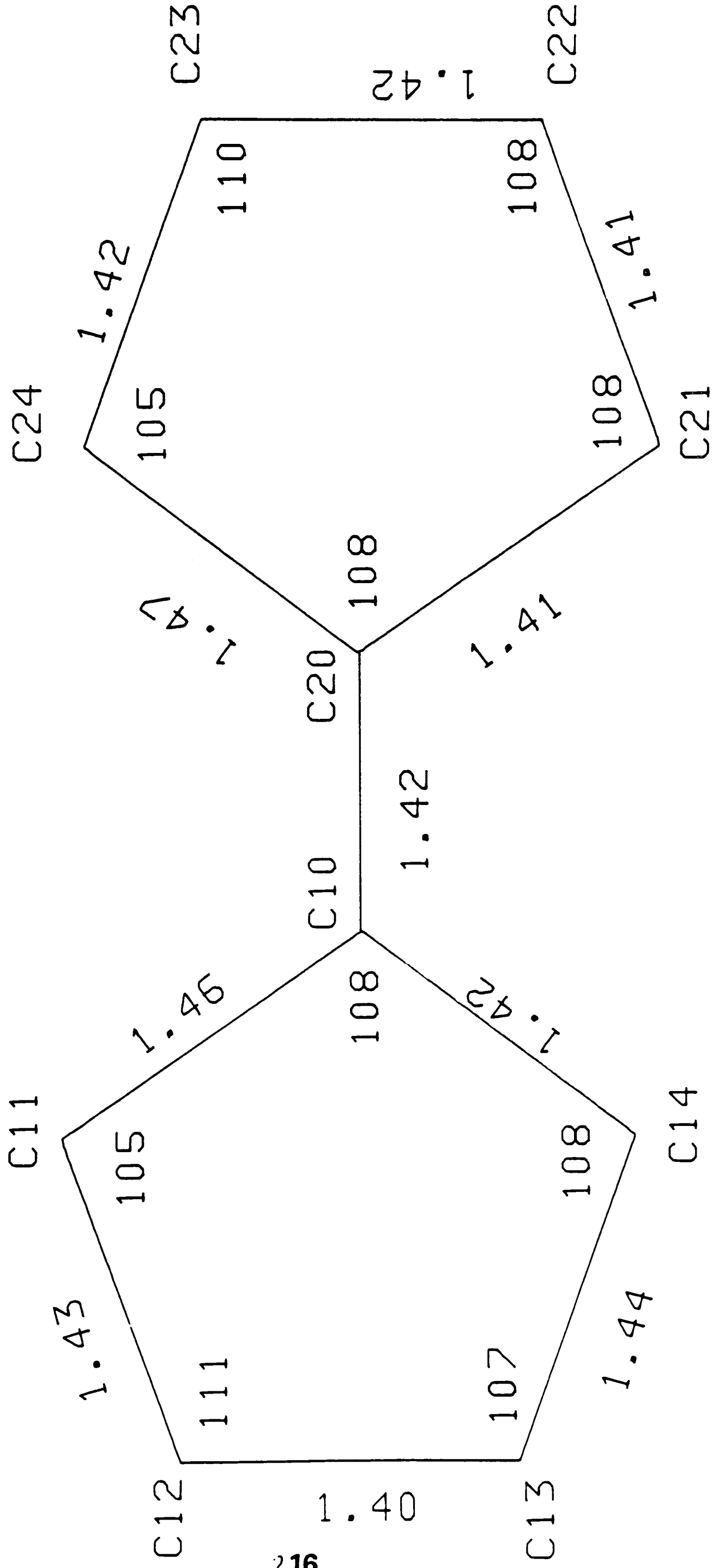


Table 5-16 Compound 11, Selected Dimensions.

PIVOT ATOM MO 1.				PIVOT ATOM C 15.			
MO	2.	3.075	0.001	C	16.	1.404	0.020
O	11.	2.085	0.006	C	19.	1.410	0.018
C	10.	2.275	0.010	PIVOT ATOM C 16.			
C	11.	2.253	0.011	C	17.	1.376	0.022
C	12.	2.302	0.011	PIVOT ATOM C 17.			
C	13.	2.343	0.012	C	18.	1.352	0.020
C	14.	2.335	0.011	PIVOT ATOM C 18.			
C	15.	2.295	0.011	C	19.	1.419	0.017
C	16.	2.277	0.012	PIVOT ATOM C 19.			
C	17.	2.304	0.015	PIVOT ATOM C 20.			
C	18.	2.334	0.011	C	21.	1.411	0.016
C	19.	2.278	0.011	C	24.	1.468	0.016
C	20.	3.101	0.011	PIVOT ATOM C 21.			
PIVOT ATOM MO 2.				C	22.	1.410	0.018
O	11.	2.093	0.006	PIVOT ATOM C 22.			
C	10.	3.078	0.011	C	23.	1.405	0.017
C	20.	2.273	0.011	PIVOT ATOM C 23.			
C	21.	2.340	0.012	C	24.	1.421	0.016
C	22.	2.284	0.012	PIVOT ATOM C 24.			
C	23.	2.307	0.011	PIVOT ATOM C 25.			
C	24.	2.239	0.011	C	26.	1.459	0.019
C	25.	2.326	0.013	C	29.	1.402	0.019
C	26.	2.342	0.012	PIVOT ATOM C 26.			
C	27.	2.263	0.012	C	27.	1.393	0.017
C	28.	2.258	0.012	PIVOT ATOM C 27.			
C	29.	2.314	0.013	C	28.	1.410	0.019
PIVOT ATOM MO 3.				PIVOT ATOM C 28.			
O	11.	1.910	0.006	C	29.	1.422	0.019
O	12.	1.725	0.008	O11-Mo1-Mo2 42.7(8)			
O	13.	1.724	0.009	O11-Mo2-Mo1 42.5(2)			
O	14.	1.719	0.009	Mo1-O11-Mo2 94.9(2)			
PIVOT ATOM O 11.				Mo1-O11-Mo3 133.1(4)			
O	12.	2.955	0.009	Mo2-O11-Mo4 129.4(4)			
O	13.	2.991	0.010	O11-Mo3-O12 108.7(3)			
O	14.	3.000	0.010	O11-Mo3-O13 109.1(6)			
C	10.	2.949	0.012	O11-Mo3-O14 107.3(6)			
C	14.	2.881	0.012	O12-Mo3-O13 109.6(6)			
C	15.	3.116	0.014	O12-Mo3-O14 109.6(5)			
C	19.	2.931	0.013	O13-Mo3-O14 107.3(6)			
C	20.	2.960	0.011				
C	21.	2.886	0.013				
C	26.	2.898	0.014				
PIVOT ATOM O 12.							
O	13.	2.808	0.014				
O	14.	2.814	0.012				
C	14.	3.232	0.014				
C	202.	3.279	0.058				
H	14.	2.359	0.008				
H	21.	2.592	0.009				
PIVOT ATOM O 13.							
O	14.	2.773	0.015				
C	23.	3.242	0.018				
C	29.	3.139	0.015				
C	202.	3.128	0.061				
H	29.	2.419	0.009				
PIVOT ATOM O 14.							
C	12.	3.241	0.015				
H	12.	2.341	0.009				
PIVOT ATOM C 10.							
C	11.	1.461	0.015				
C	14.	1.415	0.015				
C	20.	1.422	0.016				
PIVOT ATOM C 11.							
C	12.	1.431	0.016				
PIVOT ATOM C 12.							
C	13.	1.399	0.018				
PIVOT ATOM C 13.							
C	14.	1.437	0.018				

5-17 Compound 11, Fractional Coordinates.

ATOM	X/A	Y/B	Z/C	U(ISO)
MO(1)	0.87747(6)	0.47712(5)	0.25314(6)	0.0237
MO(2)	0.59370(6)	0.46468(5)	0.25060(7)	0.0249
MO(3)	0.71684(9)	0.66648(5)	0.15402(5)	0.0298
O(11)	0.7276(6)	0.5601(4)	0.2199(4)	0.0259
O(12)	0.747(1)	0.6365(5)	0.0554(5)	0.0541
O(13)	0.5701(9)	0.7124(6)	0.1598(8)	0.0571
O(14)	0.819(1)	0.7495(6)	0.1843(6)	0.0608
C(10)	0.802(1)	0.3832(7)	0.1534(7)	0.0305
C(11)	0.890(1)	0.3323(7)	0.2077(7)	0.0301
C(12)	1.010(1)	0.3719(8)	0.1972(8)	0.0377
C(13)	1.006(1)	0.4448(8)	0.1429(9)	0.0344
C(14)	0.881(1)	0.4509(7)	0.1142(7)	0.0319
C(15)	0.967(1)	0.5963(9)	0.3209(8)	0.0411
C(16)	1.057(1)	0.527(1)	0.3127(8)	0.0467
C(17)	1.018(1)	0.452(1)	0.3552(9)	0.0508
C(18)	0.909(1)	0.4698(9)	0.3922(7)	0.0404
C(19)	0.873(1)	0.5593(8)	0.3697(7)	0.0384
C(20)	0.678(1)	0.3775(7)	0.1516(8)	0.0339
C(21)	0.600(1)	0.4396(8)	0.1113(7)	0.0387
C(22)	0.479(1)	0.4271(9)	0.1400(8)	0.0413
C(23)	0.479(1)	0.3507(8)	0.1911(8)	0.0411
C(24)	0.602(1)	0.3211(7)	0.2051(7)	0.0361
C(25)	0.593(1)	0.488(1)	0.3894(8)	0.0467
C(26)	0.554(1)	0.5725(8)	0.3514(8)	0.0425
C(27)	0.447(1)	0.554(1)	0.3074(8)	0.0436
C(28)	0.416(1)	0.4622(9)	0.3222(9)	0.0456
C(29)	0.507(1)	0.4192(9)	0.3716(8)	0.0475
S(1)	0.2226(4)	0.3118(2)	0.0477(2)	0.035(1)
S(2)	0.7530(8)	0.1862(4)	0.3859(5)	0.046(2)
S(101)	0.234(2)	0.266(1)	0.0117(9)	0.057(4)
S(201)	0.766(2)	0.217(1)	0.393(1)	0.041(5)
S(301)	0.759(2)	0.153(1)	0.384(1)	0.050(5)
O(1)	0.298(1)	0.2267(9)	0.0553(8)	0.066(3)
O(2)	0.757(3)	0.106(2)	0.332(1)	0.048(7)
O(101)	0.266(4)	0.263(2)	0.095(2)	0.053(7)
O(201)	0.891(4)	0.219(3)	0.432(3)	0.048(8)
O(202)	0.785(7)	0.140(6)	0.319(6)	0.050(9)
O(301)	0.763(3)	0.070(2)	0.356(2)	0.037(7)
C(1)	0.273(2)	0.369(1)	-0.0387(9)	0.068(4)
C(2)	0.072(1)	0.2739(9)	0.0062(8)	0.050(3)
C(3)	0.903(2)	0.187(1)	0.438(2)	0.060(6)
C(4)	0.663(2)	0.150(1)	0.470(1)	0.060(6)
C(201)	0.765(6)	0.154(4)	0.324(4)	0.051(8)
C(202)	0.651(6)	0.184(4)	0.458(4)	0.053(9)
H(11)	0.8699	0.2822	0.2451	0.0500
H(12)	1.0859	0.3501	0.2254	0.0500
H(13)	1.0728	0.4820	0.1237	0.0500
H(14)	0.8524	0.4976	0.0761	0.0500
H(15)	0.9684	0.6579	0.2967	0.0500
H(16)	1.1345	0.5349	0.2798	0.0500
H(17)	1.0714	0.3952	0.3578	0.0500

ATOM	X/A	Y/B	Z/C	U(ISO)
H(18)	0.8634	0.4257	0.4269	0.0500
H(19)	0.7971	0.5913	0.3877	0.0500
H(21)	0.6254	0.4851	0.0697	0.0500
H(22)	0.4093	0.4649	0.1281	0.0500
H(23)	0.4023	0.3213	0.2146	0.0500
H(24)	0.6292	0.2725	0.2433	0.0500
H(25)	0.6722	0.4791	0.4204	0.0500
H(26)	0.5942	0.6517	0.3571	0.0500
H(27)	0.3988	0.5960	0.2712	0.0500
H(28)	0.3439	0.4293	0.3015	0.0500
H(29)	0.5035	0.3564	0.3925	0.0500

Table 5-18 Compound 11, Thermal Parameters.

ATOM	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
MO(1)	0.0266(3)	0.0239(3)	0.0219(4)	-0.0016(5)	-0.0002(5)	0.0049(3)
MO(2)	0.0280(4)	0.0227(3)	0.0253(4)	-0.0028(5)	-0.0040(5)	-0.0008(3)
MO(3)	0.0405(5)	0.0204(3)	0.0329(4)	0.0032(3)	-0.0039(4)	0.0010(4)
O(11)	0.031(3)	0.020(3)	0.028(3)	0.002(2)	-0.001(3)	0.001(3)
O(12)	0.093(8)	0.047(4)	0.041(4)	0.014(3)	-0.002(5)	0.007(5)
O(13)	0.066(6)	0.043(5)	0.107(8)	0.015(6)	0.001(7)	0.036(4)
O(14)	0.115(8)	0.046(5)	0.076(6)	0.012(5)	-0.036(6)	-0.042(5)
C(10)	0.056(7)	0.031(5)	0.017(4)	-0.002(4)	-0.001(5)	0.003(5)
C(11)	0.041(6)	0.027(4)	0.034(6)	0.005(5)	0.002(5)	0.017(5)
C(12)	0.037(6)	0.044(6)	0.040(7)	-0.005(5)	0.005(5)	0.016(5)
C(13)	0.040(6)	0.041(6)	0.041(7)	-0.008(6)	0.020(5)	0.010(5)
C(14)	0.052(7)	0.035(5)	0.027(6)	-0.002(4)	0.015(5)	0.016(5)
C(15)	0.062(8)	0.043(6)	0.047(7)	-0.004(6)	-0.024(6)	-0.024(6)
C(16)	0.022(5)	0.13(1)	0.043(7)	-0.025(9)	-0.002(5)	-0.013(8)
C(17)	0.074(9)	0.072(9)	0.030(7)	-0.010(8)	-0.005(7)	0.025(8)
C(18)	0.062(7)	0.055(7)	0.024(6)	0.006(5)	-0.010(5)	-0.023(7)
C(19)	0.037(6)	0.048(6)	0.040(6)	-0.018(5)	-0.006(5)	0.002(5)
C(20)	0.048(6)	0.027(5)	0.033(6)	-0.008(5)	-0.003(6)	0.003(5)
C(21)	0.060(8)	0.038(6)	0.028(6)	-0.008(5)	-0.009(6)	-0.001(6)
C(22)	0.049(7)	0.047(7)	0.034(7)	-0.008(6)	-0.009(5)	-0.001(6)
C(23)	0.038(6)	0.041(6)	0.054(8)	-0.009(6)	-0.013(6)	-0.006(5)
C(24)	0.061(7)	0.034(5)	0.026(6)	-0.006(5)	-0.010(5)	-0.004(6)
C(25)	0.044(7)	0.08(1)	0.035(7)	-0.005(7)	0.017(5)	-0.011(7)
C(26)	0.047(7)	0.046(6)	0.041(6)	-0.011(6)	0.012(6)	-0.004(5)
C(27)	0.044(6)	0.059(7)	0.039(7)	-0.011(6)	0.001(5)	0.018(6)
C(28)	0.038(6)	0.059(7)	0.070(8)	-0.038(6)	0.009(6)	0.002(6)
C(29)	0.063(8)	0.042(7)	0.046(8)	0.002(6)	0.017(6)	0.002(7)

The Crystal Structure of Compound 12, [Mo(O₂CMe)(PBuⁿ₃)Cl]₂.

CRYSTAL DATA: C₂₈H₆₀Cl₂Mo₂O₄P₂, M 785.52, monoclinic, P2₁/n (No. 14, nonstandard setting; x,y,z; 1/2+x,1/2-y,1/2+z), a=14.969(2), b=15.146(2), c=8.920(2) Å, Beta=105.14(1)°, U=1952 Å³, Z=2, D_c=1.34 g/cm³. Intensities of 5417 reflections were measured (2θ_{max}=52°); the data were not corrected for extinction or absorption [μ(Mo-Kα)=8.7 cm⁻¹], and 1762 independent, observed reflection were used for structure solution and refinement. The structure was solved by heavy-atom and Fourier methods, and all nonhydrogen atoms were refined with anisotropic temperature factors; no hydrogens were included in the model. During the final stages of refinement, weights were calculated from a three-term Chebyshev series, with parameters 21.3, 29.0, and 8.7. The final R-value is 0.048, R_w=0.063, for 1776 observations including 14 constraints, and 199 parameters. Dimensional constraints were applied to the butyl groups, which are highly disordered. Alternative sites were resolved for carbons C21, C31, and C32, labelled C121, C131, and C132, respectively. All other disorder of the C₄ chains was absorbed into the thermal parameters.

Selected bond-lengths (Å) and angles (°) for

compound 12; the ' refers to symmetry operation 1-x,-y,-z.

Table 5-19

MO(1)-MO(1')	2.099(1)	C(121)-C(22)	1.453(17)
MO(1)-CL(1)	2.427(2)	C(22)-C(23)	1.556(16)
MO(1)-O(1)	2.109(5)	C(23)-C(24)	1.482(16)
MO(1)-O(2')	2.100(6)	C(31)-C(32)	1.563(16)
MO(1)-P(1)	2.501(3)	C(131)-C(132)	1.574(17)
O(1)-C(1)	1.292(10)	C(32)-C(33)	1.546(16)
O(2)-C(1)	1.269(11)	C(132)-C(33)	1.520(18)
P(1)-C(11)	1.855(10)	C(33)-C(34)	1.508(15)
P(1)-C(21)	1.813(15)		
P(1)-C(121)	1.850(17)	MO(1')-MO(1)-CL(1)	119.00(8)
P(1)-C(31)	1.847(14)	MO(1')-MO(1)-P(1)	101.21(8)
P(1)-C(131)	1.882(17)	CL(1)-MO(1)-P(1)	139.8(1)
C(1)-C(2)	1.531(12)	O(1)-MO(1)-O(2')	176.2(2)
C(11)-C(12)	1.500(15)	O(1)-C(1)-O(2)	121.4(8)
C(12)-C(13)	1.550(15)	O(1)-C(1)-C(2)	118.6(9)
C(13)-C(14)	1.513(19)	O(2)-C(1)-C(2)	120.0(9)
C(21)-C(22)	1.506(19)		

Table S-20

Fractional atomic coordinates ($\times 10^4$) and equivalent* isotropic temperature factors ($\text{\AA}^2$, $\times 10^4$) for compound 12.

ATOM	Fractional occupancy	X/A	Y/B	Z/C	U(eq)
MO(1)		4918.5(5)	648.8(5)	355.6(8)	546
CL(1)		6208(2)	1364(2)	2170(3)	749
O(1)		5344(4)	1168(4)	-1540(6)	654
O(2)		5554(4)	-209(4)	-2246(6)	653
P(1)		3302(2)	981(2)	-1184(3)	781
C(1)		5570(7)	618(7)	-2470(10)	697
C(2)		5879(9)	976(8)	-3858(11)	829
C(11)		3172(8)	997(9)	-3309(11)	987
C(12)		2248(9)	1313(9)	-4265(13)	1053
C(13)		2257(11)	1326(11)	-5999(14)	1226
C(14)		1347(12)	1683(12)	-6977(17)	1438
C(21)	0.427	2274(14)	687(18)	-583(33)	781
C(121)	0.573	2301(14)	225(17)	-1456(31)	1316
C(22)		2220(13)	-259(13)	-92(32)	2000
C(23)		1210(13)	-482(13)	-65(27)	1811
C(24)		1114(15)	-1446(13)	-346(23)	1827
C(31)	0.644	2922(12)	1984(11)	-349(27)	1143
C(131)	0.356	3337(23)	2218(12)	-982(23)	708
C(32)	0.665	3733(15)	2644(11)	-289(29)	1272
C(132)	0.335	3435(23)	2511(15)	746(24)	615
C(33)		3581(12)	3495(12)	569(22)	1779
C(34)		4500(14)	3959(15)	826(25)	1843

* $U(\text{eq}) = (U_1 U_2 U_3)^{1/3}$ where U_1, U_2, U_3 are the mean-square displacements ($\text{\AA}^2$) along the principal axes of the thermal ellipsoid.

ATOM	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
NO(1)	583(4)	573(4)	480(4)	-32(4)	115(3)	-42(4)
CL(1)	808(15)	772(15)	700(14)	-137(12)	66(12)	-213(13)
O(1)	814(42)	645(37)	554(34)	-55(29)	185(31)	-104(31)
O(2)	719(38)	808(43)	507(33)	-50(34)	133(29)	-97(23)
F(1)	690(17)	807(20)	650(16)	-53(14)	72(13)	38(14)
O(3)	694(60)	869(64)	524(49)	-70(53)	191(43)	170(59)
O(11)	1490(106)	1067(82)	653(66)	-79(58)	233(71)	-132(55)
O(12)	936(66)	1062(97)	652(72)	-33(67)	-52(61)	-138(74)
O(13)	1264(105)	1194(101)	753(75)	-36(70)	-59(69)	130(93)
O(14)	1747(140)	1470(129)	763(103)	-72(81)	125(82)	30(115)
O(15)	1691(150)	1757(132)	708(109)	134(101)	147(100)	59(119)
O(16)	665(182)	1340(780)	1058(109)	1323(330)	377(120)	33(119)
O(17)	529(183)	3340(344)	1017(103)	1329(213)	374(125)	62(119)
O(18)	524(202)	2203(104)	1272(103)	-35(216)	1320(127)	33(119)
O(19)	1339(170)	1742(105)	3203(206)	-94(170)	1329(129)	33(119)
O(20)	2300(220)	1538(165)	1672(176)	-36(143)	339(141)	-211(157)
O(21)	3956(135)	1203(157)	1543(113)	-11(154)	335(136)	-314(142)
O(22)	1234(232)	1010(217)	1549(168)	-46(166)	330(173)	-240(144)
O(23)	1435(202)	785(137)	1931(100)	9(153)	599(170)	520(119)
O(24)	1227(267)	833(214)	506(163)	-40(156)	599(165)	179(136)
O(25)	1523(161)	2025(204)	1775(177)	-120(133)	435(165)	-277(193)
O(26)	1914(195)	2110(212)	2217(217)	-665(177)	212(131)	-123(160)
					932(180)	-806(167)

Table S-21 Compound 12, Thermal Parameters.

5.3 Experimental Details for Chapter 3: Crystallography.

Compound 38, $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{O})(\text{dmpe})]\text{PF}_6$.

CRYSTAL DATA: $\text{C}_{11}\text{H}_{21}\text{F}_6\text{MoOP}_3$, M 471.85, monoclinic, $\text{P2}_1/\text{m}$, $a=6.301(3)$, $b=7.989(5)$, $c=17.936(9)$ Å, $\gamma=76.93(5)^\circ$, $U=879$ Å³, $Z=4$, $D_c=1.78$ g/cm³.

A red, needle-like crystal was sealed under N_2 in a glass capillary, and the intensities of 3332 reflections were recorded ($2\theta_{\text{max}}=50^\circ$). The data were corrected for extinction but not absorption [$\mu(\text{Mo-K}\alpha)=10.49\text{cm}^{-1}$], and 1120 independent, observed reflections were used for the structure solution and refinement. The structure was solved by heavy-atom and Fourier methods, and all non-hydrogen atoms were refined with anisotropic temperature factors. The PF_6^- ion is highly disordered (three superimposed octahedra were used in the model), and the dmpe ligand is also disordered, especially in the CH_2CH_2 chain. Satisfactory models were achieved for both the anion and the dmpe with the help of soft, dimensional constraints. Hydrogens were located and then placed on all carbons, their positions being adjusted after each cycle of refinement. The final R-value is 3.8%, $R_w=4.6\%$, for 1120 reflections, 5 constraints, and 170 parameters. Unit weights were found to be appropriate in this case.

Table 5-22 Fractional coordinates for [MoCp(O)dmpe]PF₆, 3-8.

ATOM	X/A	Y/B	Z/C	U (Iso)
MO(1)	1027(1)	2260(1)	2500	331
P(1)	-1064(3)	4911(2)	1615(1)	331
P(2)	5000	0	0	400
O(1)	3179(11)	3914(10)	2500	331
O(1)	1793(18)	18(13)	2500	331
O(2)	444(15)	507(10)	1962(5)	331
O(3)	-1664(13)	-1137(9)	2120(4)	331
O(4)	-2324(26)	6867(13)	2132(7)	331
O(140)	-3254(18)	6338(15)	2132(6)	331
O(5)	-2898(15)	4350(12)	927(5)	331
O(6)	694(14)	5903(12)	1069(6)	331
F(11)	3244(38)	1641(33)	257(16)	331
F(12)	6187(95)	27(21)	760(19)	1011
F(13)	3609(36)	-1223(26)	337(15)	331
F(21)	3970(50)	1854(24)	151(25)	1011
F(22)	2740(32)	-372(40)	-83(17)	331
F(23)	3296(49)	-603(46)	812(12)	331
F(31)	2622(46)	313(45)	-293(21)	331
F(32)	4179(52)	1314(35)	609(14)	331
F(33)	4567(40)	-1403(33)	323(18)	331
H(1)	3368	-561	2500	500
H(2)	936	404	1331	500
H(3)	-2975	1557	1796	500
H(41)	-1201	7540	2242	500
H(42)	-3522	7581	1829	500
H(141)	-3841	7413	1828	500
H(142)	-4455	5761	2239	500

Table 5-23 Dimensions of [Mo(Cp)(O)dmpe]PF₆, in Å and (°).

Mo1-P1	2.442(2)	P1-C4	1.835(8)
Mo1-O1	1.700(7)	P1-C140	1.838(8)
Mo1-C1	2.21(1)	P1-C5	1.814(7)
Mo1-C2	2.300(7)	P1-C6	1.817(6)
Mo1-C3	2.499(7)	P-F(ave)	1.55(2)
C1-C2	1.42(1)	C3-C3'	1.36(2)
C2-C3	1.39(1)	C4-C140'	1.535(9)
C1-C2-C3	107.0(8)	C2-C3-C3'	109.4(5)
C2-C1-C2'	107(1)	Mo1-P1-C4	107.8(4)
P1-Mo1-P1'	81.09(9)	Mo1-P1-C140	108.0(4)
P1-Mo1-O1	93.6(2)	Mo1-P1-C5	123.6(3)
C4-P1-C5	112.1(6)	Mo1-P1-C6	111.5(3)
C4-P1-C6	94.2(6)	C140-P1-C5	94.0(6)
C140-P1-C6	115.6(6)	C5-P1-C6	103.6(5)

The ' refers to symmetry operation x,y,1/2-z.

ATOM	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
MO(1)	291(4)	259(4)	441(5)	0	0	-64(3)
F(1)	485(10)	334(9)	324(10)	18(7)	9(8)	-90(7)
F(2)	551(17)	456(15)	437(16)	22(13)	-123(14)	-156(12)
O(1)	398(36)	604(44)	792(56)	0	0	-217(28)
O(1)	446(64)	264(52)	1489(136)	0	0	24(45)
O(2)	894(57)	433(39)	709(56)	-162(40)	170(49)	-318(32)
O(3)	676(42)	373(34)	695(48)	-8(35)	-110(40)	-316(25)
O(4)	735(113)	265(69)	465(92)	95(64)	47(83)	4(65)
O(140)	134(83)	419(75)	469(79)	166(27)	49(38)	-62(59)
O(5)	959(60)	852(59)	744(59)	250(51)	-431(49)	-409(42)
O(5)	794(55)	759(52)	1008(70)	436(48)	10(58)	-571(32)
F(11)	1161(142)	1001(136)	943(169)	91(141)	375(119)	229(120)
F(12)	3594(293)	1413(174)	867(145)	200(139)	-1353(133)	-1199(175)
F(13)	745(99)	680(98)	1398(163)	-73(112)	177(109)	-445(52)
F(21)	1267(192)	378(102)	2041(360)	-372(162)	-390(202)	104(106)
F(22)	443(92)	1493(161)	1657(182)	-465(149)	-281(113)	-289(91)
F(23)	1565(194)	1769(216)	433(109)	416(113)	-221(120)	-180(173)
F(31)	1003(156)	2252(288)	1289(187)	31(207)	-792(104)	207(180)
F(32)	1537(178)	1142(131)	1061(136)	-525(114)	468(131)	-799(98)
F(33)	984(134)	1124(137)	1559(176)	818(111)	-259(130)	-501(90)

Table 5-24 Compound 38, Thermal Parameters.

Compound 52, Nb(η -C₅H₅)(dppe)Br₃.

CRYSTAL DATA: C₃₁H₂₉Br₃NbP₂·2C₇H₈, M 980, triclinic, $P\bar{1}$, $a=9.186(2)$, $b=12.120(3)$, $c=17.224(6)$ Å, $\alpha=71.72(3)$, $\beta=87.30(3)$, $\gamma=79.77(2)^\circ$, $U=1792$ Å³, $Z=2$, $D_c=1.82$ g/cm³. A black crystal was mounted in a capillary under N₂, and 7398 intensities were measured ($2\theta_{\max}=50^\circ$). The data were corrected for extinction but not absorption [$\mu(\text{Mo-K}\alpha)=37.9\text{cm}^{-1}$], and 2851 independent, observed reflections were used for structure solution and refinement. The structure was solved by Patterson and Fourier methods, and refined by least squares. The two toluene solvent molecules, which are disordered about inversion centres, were heavily constrained, their carbons were refined isotropically, and their hydrogens were not included in the model. All other nonhydrogen atoms were refined with anisotropic temperature factors, and hydrogens were placed on the dppe and Cp carbons. Slack constraints were imposed on all phenyl dimensions, resulting in 136 constraints and 2851 reflections for 375 parameters. The final R-value is 4.9%, $R_w=6.4\%$. The weighting scheme used Chebyshev parameters 42.62, 55.60, and 24.01.

Table 5-25

Selected molecular dimensions (Å and °)
for NbCp(Br)₃(dppe).

Nb1-BR1	2.611(2)	C1-C2	1.51(2)
Nb1-BR2	2.637(2)	C11-C12	1.37(2)
Nb1-BR3	2.600(2)	C12-C13	1.38(2)
Nb1-P1	2.644(3)	C13-C14	1.40(2)
Nb1-P2	2.800(3)	C14-C15	1.39(2)
Nb1-C11	2.36(1)	C15-C11	1.37(2)
Nb1-C12	2.39(1)	BR1-Nb1-BR2	86.40(6)
Nb1-C13	2.45(1)	BR1-Nb1-BR3	149.50(7)
Nb1-C14	2.44(1)	BR1-Nb1-P1	82.21(7)
Nb1-C15	2.36(1)	BR1-Nb1-P2	75.72(7)
P1-C1	1.824(8)	BR2-Nb1-BR3	85.79(6)
P1-C111	1.829(6)	BR2-Nb1-P1	154.12(8)
P1-C121	1.828(6)	BR2-Nb1-P2	80.23(7)
P2-C2	1.825(7)	BR3-Nb1-P1	93.32(8)
P2-C211	1.832(6)	BR3-Nb1-P2	73.92(7)
P2-C221	1.833(6)	P1-Nb1-P2	74.47(9)

NbCp(dppe)Br₃

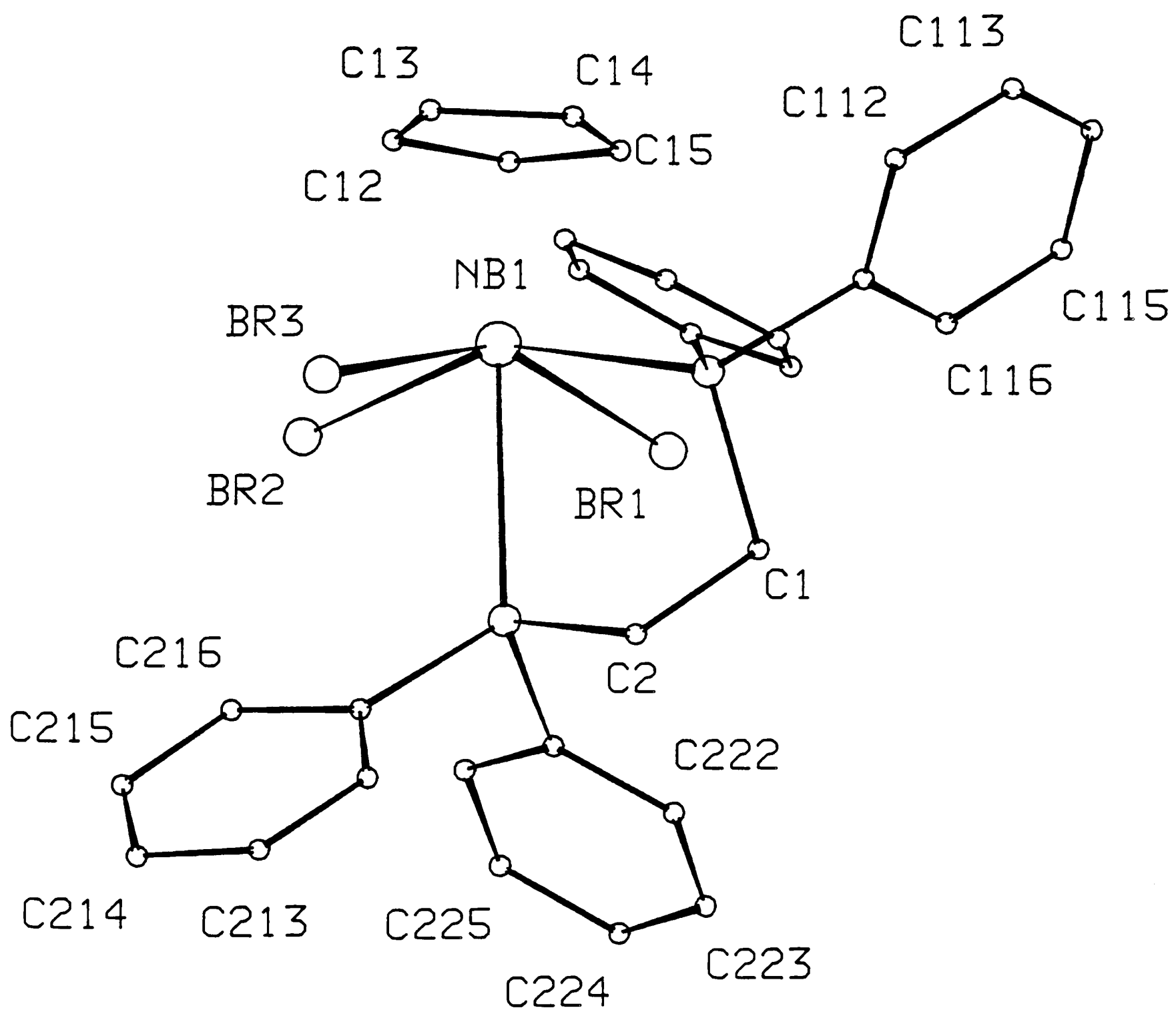


Table 5-26 Fractional Coordinates for 52 (x1000).

ATOM	X/A	Y/B	Z/C	U(ISO)
NR(1)	403(1)	1240.1(9)	2749.1(6)	275
BR(1)	-35(2)	2315(1)	1182.3(8)	475
BR(2)	-457(2)	-585(1)	2488(1)	503
BR(3)	2014(2)	-319(1)	3925.5(8)	542
P(1)	2205(3)	2807(2)	2569(2)	273
P(2)	2963(3)	378(2)	2019(2)	279
C(1)	3552(11)	2633(10)	1783(6)	383
C(2)	4280(10)	1352(9)	2014(7)	294
C(11)	-2166(14)	1959(13)	2786(11)	529
C(12)	-1845(17)	1077(13)	3511(12)	500
C(13)	-950(17)	1440(13)	3974(10)	370
C(14)	-685(14)	2570(11)	3512(8)	399
C(15)	-1433(14)	2877(11)	2766(9)	429
C(111)	1344(8)	4368(5)	2214(5)	323
C(112)	1050(9)	5000(7)	2770(5)	399
C(113)	351(9)	6175(8)	2509(6)	515
C(114)	-69(9)	6719(7)	1699(7)	544
C(115)	223(9)	6091(8)	1144(6)	512
C(116)	923(9)	4916(8)	1401(5)	454
C(121)	3375(8)	2745(7)	3420(5)	371
C(122)	4481(9)	3430(7)	3285(5)	432
C(123)	5383(9)	3380(9)	3925(7)	572
C(124)	5183(11)	2643(9)	4705(7)	620
C(125)	4071(12)	1963(8)	4848(6)	682
C(126)	3170(10)	2016(8)	4204(6)	591
C(211)	4053(9)	-1097(6)	2488(5)	357
C(212)	5558(9)	-1247(7)	2646(5)	421
C(213)	6384(9)	-2375(8)	2944(5)	494
C(214)	5714(12)	-3359(8)	3088(5)	627
C(215)	4216(12)	-3217(8)	2946(6)	538
C(216)	3382(10)	-2090(8)	2652(5)	562
C(221)	2861(9)	394(7)	954(4)	317
C(222)	3532(9)	1162(8)	327(6)	475
C(223)	3425(10)	1145(9)	-472(5)	370
C(224)	2642(11)	367(10)	-647(6)	448
C(225)	1971(10)	-399(9)	-18(7)	545
C(226)	2079(9)	-384(8)	784(6)	543
C(61)	-1088(13)	-4280(13)	4817(6)	253(46)
C(62)	-239(19)	-3380(11)	4592(6)	945(119)
C(63)	1306(19)	-3631(13)	4645(6)	376(57)
C(64)	1965(15)	-4840(15)	4931(7)	1042(133)
C(65)	455(13)	-4576(18)	4877(7)	954(121)
C(71)	3926(17)	5678(12)	-86(8)	450(63)
C(72)	4342(26)	6151(12)	496(9)	948(119)
C(73)	5718(28)	5681(18)	886(7)	950(119)
C(74)	6586(20)	4761(18)	661(8)	1274(163)
C(75)	5306(18)	5206(15)	301(9)	1098(141)
H(1)	4319	3141	1748	500
H(2)	3038	2867	1239	500
H(3)	4729	1117	2574	500
H(4)	5078	1260	1610	500
H(11)	-2825	1046	2342	500
H(12)	-2199	299	3672	500
H(13)	-560	979	4539	500
H(14)	-75	3062	3625	500
H(15)	-1438	3624	2301	500
H(111)	1343	4608	3659	500
H(112)	131	6629	2910	500
H(113)	-582	7567	1314	500
H(114)	-74	6438	586	500
H(115)	1125	4465	998	500
H(116)	4630	3065	2721	500
H(122)	6177	3878	3623	500
H(123)	3842	2599	5166	500
H(124)	3917	1436	5313	500
H(125)	2370	1522	4207	500
H(126)	6052	-640	2843	500
H(212)	7470	-2479	3093	500
H(213)	6316	-4172	3095	500
H(214)	3725	-3928	3037	500
H(215)	2290	-1992	2556	500
H(222)	4094	1728	449	500
H(223)	3918	1997	-925	500
H(224)	2564	361	-1224	500
H(225)	1406	-861	-140	500
H(226)	1589	-935	1227	500

Table 5-27 Thermal Parameters for 52.

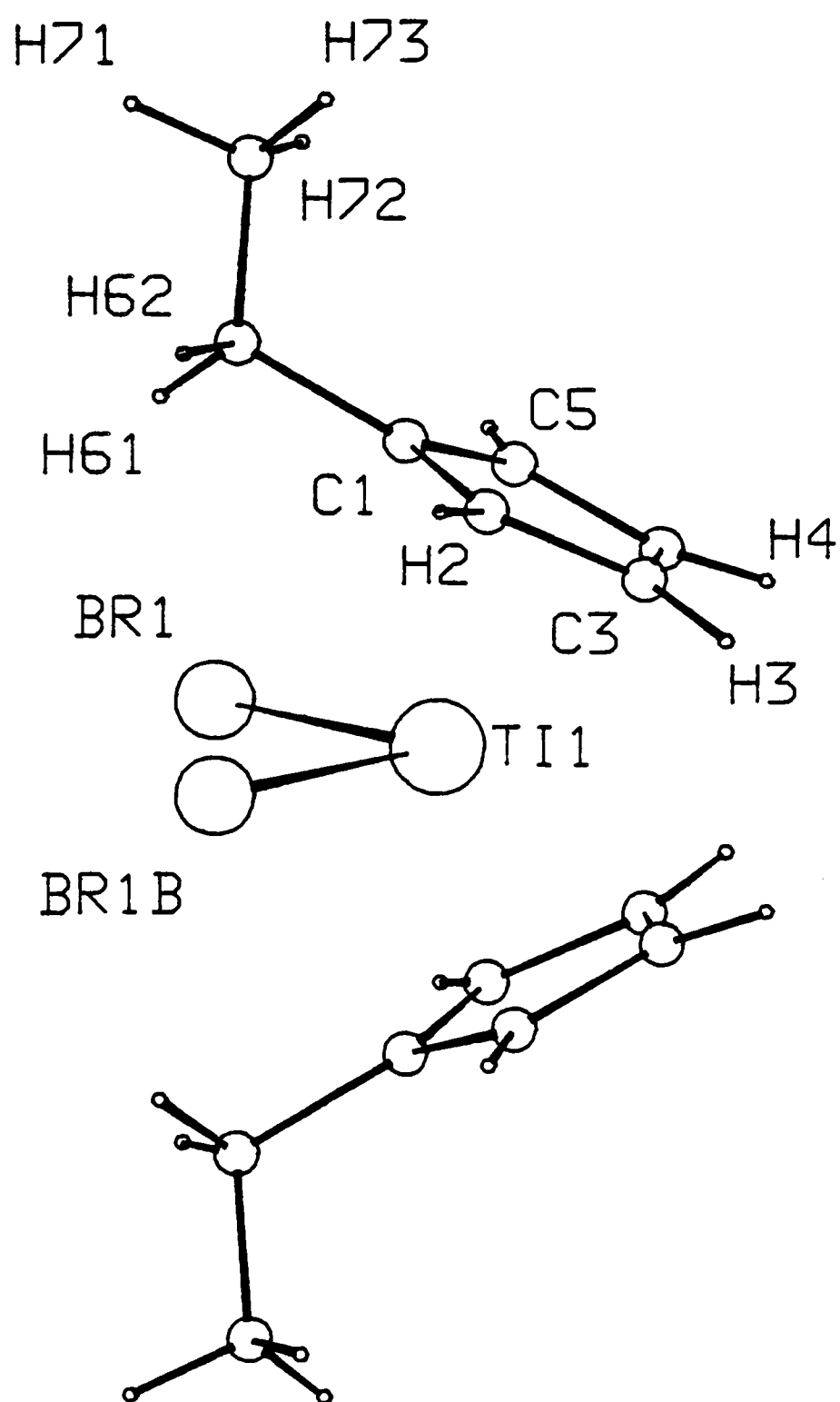
ATOM	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
N8(1)	255(6)	286(5)	273(6)	-71(4)	7(4)	-47(4)
BR(1)	557(9)	538(8)	368(7)	-117(5)	-134(6)	43(7)
BR(2)	461(8)	492(7)	762(9)	-285(6)	-27(7)	-168(6)
BR(3)	717(10)	532(9)	374(8)	-46(6)	-52(7)	21(7)
F(1)	330(16)	258(14)	253(14)	-73(10)	-12(13)	-54(12)
F(2)	275(16)	293(14)	287(14)	-115(10)	-14(13)	-35(12)
O(1)	406(68)	378(62)	407(67)	-139(46)	-0(57)	-118(52)
O(2)	230(57)	349(57)	343(60)	-133(41)	44(48)	-61(45)
C(11)	280(71)	618(23)	1051(110)	-430(61)	-31(75)	12(66)
C(12)	576(84)	517(78)	1232(125)	-406(68)	569(78)	-364(59)
C(13)	610(97)	614(90)	641(92)	-237(64)	223(77)	81(79)
C(14)	415(73)	485(71)	373(66)	-167(48)	135(57)	-18(58)
C(15)	423(76)	402(68)	600(81)	-213(50)	102(61)	96(61)
C(111)	394(67)	245(54)	313(52)	-44(36)	7(50)	-10(48)
C(112)	392(69)	419(57)	488(63)	-228(38)	-114(57)	39(54)
C(113)	509(81)	457(62)	833(77)	-349(54)	-192(70)	111(62)
C(114)	602(91)	324(66)	866(77)	-178(47)	-182(75)	103(63)
C(115)	785(102)	439(68)	428(73)	28(48)	-241(70)	78(69)
C(116)	765(97)	367(61)	295(57)	-83(47)	-33(62)	16(63)
C(121)	344(61)	344(60)	568(65)	-218(44)	-134(56)	45(45)
C(122)	408(67)	386(65)	554(71)	-200(49)	-34(55)	-2(43)
C(123)	387(75)	716(86)	1025(86)	-433(62)	-232(67)	-39(68)
C(124)	827(91)	659(86)	881(83)	-392(61)	-497(76)	38(65)
C(125)	1118(106)	698(95)	559(76)	-150(70)	-390(71)	-161(69)
C(126)	749(97)	596(86)	562(74)	-78(64)	-225(68)	-221(72)
C(211)	368(55)	370(54)	354(58)	-148(42)	-11(51)	-22(45)
C(212)	320(56)	397(60)	568(80)	-101(53)	18(59)	-53(49)
C(213)	310(72)	523(65)	687(95)	-52(66)	-42(66)	81(51)
C(214)	600(76)	409(70)	914(121)	21(77)	-41(85)	93(59)
C(215)	632(75)	180(60)	1599(122)	-81(80)	-11(100)	-121(55)
C(216)	428(80)	357(59)	1114(123)	-82(72)	-153(78)	-48(49)
C(221)	374(66)	451(60)	251(55)	-188(39)	-57(48)	16(46)
C(222)	582(85)	563(74)	500(60)	-339(44)	97(61)	-87(61)
C(223)	744(104)	813(95)	317(59)	-157(52)	57(70)	140(73)
C(224)	470(83)	1318(102)	381(65)	-558(49)	-109(58)	277(68)
C(225)	508(89)	1494(119)	845(71)	-930(52)	55(72)	-251(79)
C(226)	613(85)	818(77)	527(62)	-371(51)	29(71)	-295(62)

Bis(ethylCp)titanium dibromide, $\text{Ti}(\eta\text{-EtC}_5\text{H}_4)_2\text{Br}_2$.

CRYSTAL DATA: $\text{C}_{14}\text{H}_{14}\text{Br}_2\text{Ti}$, M 389.70, monoclinic, C2/c , $a=14.529(3)$, $b=6.883(5)$, $c=14.617(4)$, $\beta=95.32^\circ$, $U=1456 \text{ \AA}^3$, $D_c=1.78 \text{ g/cm}^3$, $Z=8$. The intensities of 1822 reflections were measured ($2\theta_{\text{max}}=50^\circ$), and, after data reduction, 548 independent reflections were available for structure solution and refinement; the data were corrected for extinction but not absorption [$\mu(\text{Mo-K}\alpha)=59.96\text{cm}^{-1}$]. The structure was solved by Patterson and Fourier methods, and refined by full-matrix least squares to an R of 5.08%, $R_w=6.19\%$. The least-squares process varied 79 parameters, and weights were calculated from a Chebyshev series with coefficients 18.37, 23.88, and 10.28.

Table 5-28 Selected Bond Lengths (Å) and Angles (°) for $(\text{EtCp})_2\text{TiBr}_2$.

Ti1-Br1	2.533(2)	C1-C2	1.395(9)	C6-C7	1.47(2)
Ti1-C1	2.428(8)	C2-C3	1.392(9)		
Ti1-C2	2.408(9)	C3-C4	1.393(9)		
Ti1-C3	2.36(1)	C4-C5	1.401(9)		
Ti1-C4	2.33(1)	C5-C1	1.395(9)		
Ti1-C5	2.381(9)	C1-C6	1.522(2)		
Br1-Ti1-Br1'	93.9(1)				
C1-C6-C7	115(1)				



ATOM	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
TI(1)	471(19)	213(14)	454(18)	0	-42(14)	0
BR(1)	316(11)	451(8)	643(9)	36(8)	99(6)	-171(8)
C(1)	700(96)	332(73)	553(32)	-177(65)	-220(71)	138(70)
C(2)	667(92)	776(101)	463(77)	136(75)	-145(68)	157(84)
C(3)	973(120)	447(83)	706(94)	234(85)	-271(91)	-41(86)
C(4)	952(115)	391(75)	830(106)	-152(83)	-443(96)	244(89)
C(5)	495(80)	643(89)	687(88)	8(78)	-227(68)	187(73)
C(6)	1131(137)	463(85)	850(111)	69(78)	-363(98)	-115(83)
C(7)	593(99)	714(113)	1583(179)	-7(107)	-313(104)	-100(78)

Table S-29 Atomic Parameters for (EtCP)2TiBr2 (x1000).

ATOM	X/A	Y/B	Z/C	U(ISO)
TI(1)	0	-2017(4)	2500	357
BR(1)	273(1)	496(2)	1655(1)	597
C(1)	1259(7)	-1655(14)	3701(6)	451
C(2)	532(8)	-2570(18)	4088(7)	580
C(3)	356(9)	-4354(17)	3659(8)	610
C(4)	992(9)	-4545(17)	3003(9)	580
C(5)	1547(7)	-2379(16)	3022(7)	546
C(6)	1712(12)	252(21)	4010(12)	722
C(7)	2607(10)	103(23)	4430(15)	537
H(2)	196	-2047	4597	760
H(3)	-145	-5272	3797	780
H(4)	1041	-5719	2599	750
H(5)	2054	-2591	2619	700
H(61)	1711	1116	3463	920
H(62)	1331	851	4473	920
H(71)	2901	1430	4612	1000
H(72)	3055	-475	3931	1000
H(73)	2685	-739	4991	1000

5.4 Chapter 3: Synthesis and Mechanistic Studies.

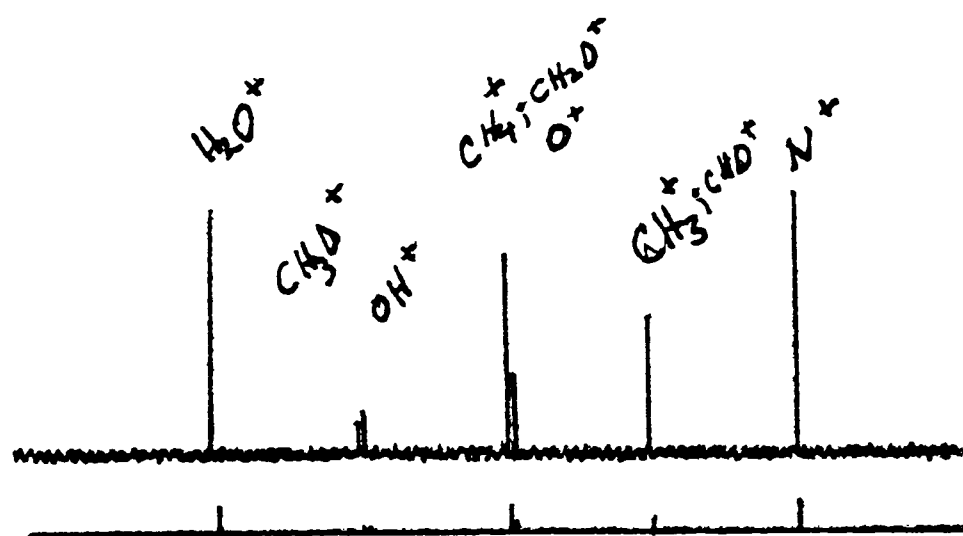
$\text{Cp}_2\text{W}(\text{CD}_3)_2$. This compound was made by the standard route to Cp_2WMe_2 ¹⁴, the only change being the use of CD_3MgI as the Grignard reagent with which Cp_2WCl_2 was reacted. Commercial CD_3I (Aldrich) was used to prepare the CD_3MgI . The red, air-sensitive product was characterized by nmr, ir, and mass spectroscopies, using the authentic spectra of Cp_2WMe_2 as standards. The mass spectrum gives the following parent envelope (reported as m/e, relative intensity): 353, 11; 352, 86; 351, 23; 350, 100; 349, 66; 348, 89; 347, 11. There are peaks in the mass spectrum which correspond to P^+ , 350; $(\text{P-CD}_3)^+$, 332; $(\text{P-CD}_3\text{H})^+$, 331; and $(\text{P-CD}_4)^+$, 330.

$\text{Cp}_2\text{W}(\text{Me})\text{D}$. The compound $\text{Cp}_2\text{W}(\text{Me})(\text{O}_2\text{CPh})$ was prepared in the standard manner¹⁵, by reacting Cp_2WMe_2 with one equivalent of benzoic acid, and $\text{Cp}_2\text{W}(\text{Me})\text{I}$ was prepared by reaction of the benzoate derivative with NaI ¹⁶. Both the methyl-benzoate and methyl-iodide derivatives were reacted with a number of reducing agents, including NaBH_4 , $\text{NaBH}_4/\text{dicyclohexyl-18-crown-6}$, LiAlH_4 , Redal (Aldrich, $\text{Na}[\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})_2\text{H}_2]$), and Super Hydride (Aldrich, $\text{Li}(\text{Et}_3\text{BH})$). In most cases, no reaction occurred unless elevated temperatures were employed, and then the product was largely Cp_2WH_2 . The Redal and Super Hydride reactions were successful, and, of these two reagents, only Super Hydride can readily be obtained in deuteriated form (Super Deuteride, Aldrich). Typical reaction conditions were as follows: $\text{Cp}_2\text{W}(\text{Me})\text{I}$ (0.03g, 0.07 mmol) was dissolved in THF (50 cm^3), and the solution was cooled to -78° . LiEt_3BD (0.1 cm^3 of a 1M solution) was added while the solution was stirred, and stirring was continued over 10 h, while the reaction mixture slowly warmed to room temperature. The solution, which had initially been green, was yellow-orange at this point. The THF was

evaporated, giving a yellow oil, and the oil was carefully hydrolysed near 0° with 2 cm^3 of D_2O . The D_2O was then frozen, and extraction with light petroleum ($40-60^{\circ}$) gave the extremely air-sensitive product, which was recrystallized twice from light petroleum ($30-40^{\circ}$). The nmr, ir, and mass spectra were recorded, and compared with those¹⁵ of $\text{Cp}_2\text{W}(\text{Me})\text{H}$. The ir shows a peak at 1350 cm^{-1} which may be assigned to $\nu\text{W-D}$ (the ratio $\nu\text{W-H}/\nu\text{W-D}$ is 1.38). The ^1H nmr shows the compound to be $85\pm 10\%$ deuteriated at the hydrido position. The mass spectrum gives a complicated parent envelope, whose most intense peak of $m/e=329$ corresponds to Cp_2WMe^+ . The envelope does not correspond to a simple tungsten isotope pattern (whose isotopes 182, 184, and 186 all have approximately 30% natural abundance), and extensive loss of both H and D seems to occur. The mass spectrum of $\text{Cp}_2\text{W}(\text{Me})\text{H}$ is similar, and this behaviour is consistent with the known thermal instability of the compound. The peak at $m/e=314$, due to Cp_2W^+ , is the most intense peak in the spectrum.

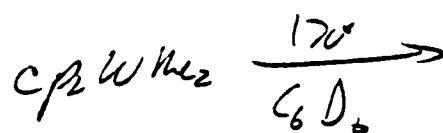
Mass Spectra These experiments were carried out with the help of Dr. P.D. Grebenik. When a sample of $\text{Cp}_2\text{WRR}'$ was thermally decomposed in solution, the mass spectrum was run after freezing the solvent with liquid nitrogen, by pumping the gas into the spectrometer with the standard gas inlet. Spectra of all samples were run four or five times, to check for statistical fluctuations in intensities. Since methane loses hydrogen in the mass spectrometer, the spectra had to be corrected for the superposition of peaks, e.g. CH_2D^+ (P-H^+ for CH_3D) overlaps with CH_4^+ , m/e being 16.0297 and 16.0313, respectively. The difference of 0.01% in m/e was not resolved. An empirical correction to the intensities was performed, which was based on the observed cracking pattern of CH_4 , and which neglected isotope effects in the cracking process. The spectrum included below shows how the peak assignable to CH_3^+ has 66% the intensity of the

CH_4^+ peak. Only a small amount (5%) of CH_3D is present. Attempts to develop a more rigorously quantitative method of analysis were hampered by a very high rate of equipment failure, and computer data fitting (by least squares) was not carried out.



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 Jim Baslin I-⑥
 run ⑥

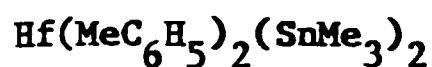
Complete run small scale



Matrix Isolation and Attempted Photolysis of Cp_2WMe_2 . The technique of matrix isolation has been described in detail elsewhere¹⁷. The experiments reported here, which were carried out under the supervision of Dr. R.N. Perutz, with the assistance of C.J. Nunn, involved the deposition of matrices onto a CsBr window which was cooled by a Displex refrigerator (Air Products) to approximately 10K. A 4 inch diffusion pump maintained a pressure of 10^{-6} to 10^{-7} mmHg inside the apparatus. Cp_2WMe_2 was sublimed onto the window, and spectroscopic grade Ar and CO were admitted via a needle valve at a rate of 1-2 cmHg per hour from a 1.0 l bulb. A Perkin Elmer 580 ir spectrometer was used to monitor the experiments, in which both Ar and 10% CO/Ar matrices were used. Vacuum uv photolysis was carried out first with a Xe lamp, and then with a 1% CH_4/He lamp, using an apparatus with a LiF window to prevent the radiation from being absorbed before it reached the sample. After 19 h photolysis of Cp_2WMe_2 in a 10% CO/Ar matrix, using the Xe lamp, the only noticeable changes in the spectrum were the appearance of small peaks at 1700 and 660 cm^{-1} . Annealing at 25 K for 10 min, followed by a further 5 h photolysis with the 1% CH_4/He lamp, produced no further change, except for the growth of a band at 2350

cm^{-1} , assignable to CO_2 , and a small increase in intensity of a band at 740 cm^{-1} , which had been present before photolysis. Although acetyl radicals might be formed by the homolytic cleavage of W-C bonds, and the reaction of the resulting methyl radicals with CO, the product CH_3CO would probably photodecompose under the reaction conditions. The new bands could not be assigned to any known species, and, since their intensities were always low, they are thought to arise from a very minor process.

5.5 Experimental Details for Chapter 4: Crystallography



CRYSTAL DATA: $\text{C}_{20}\text{H}_{34}\text{HfSn}_2$, M 690.09, monoclinic, C2/c, $a=14.027(3)$, $b=9.714(3)$, $c=17.946(8)$ Å, $\beta=111.11(4)^\circ$, $U=2281$ Å³, $Z=8$, $D_c=2.01$ g/cm³. Intensities of 3326 reflections were measured ($2\theta_{\text{max}}=52^\circ$), and the data were corrected for both extinction and absorption [$\mu(\text{Mo-K}\alpha)=66.8\text{cm}^{-1}$]. The structure was solved by heavy atom and Fourier methods, and refined by least squares in two blocks, with all nonhydrogen atoms anisotropic. Hydrogens were located and then placed geometrically on the phenyl ring, but were not included for the methyl groups. The final R-value is 2.98%, $R_w=3.88\%$, for 1738 reflections and 106 parameters. Weights were calculated from a Chebyshev polynomial with coefficients 13.56, 17.97, and 6.27.

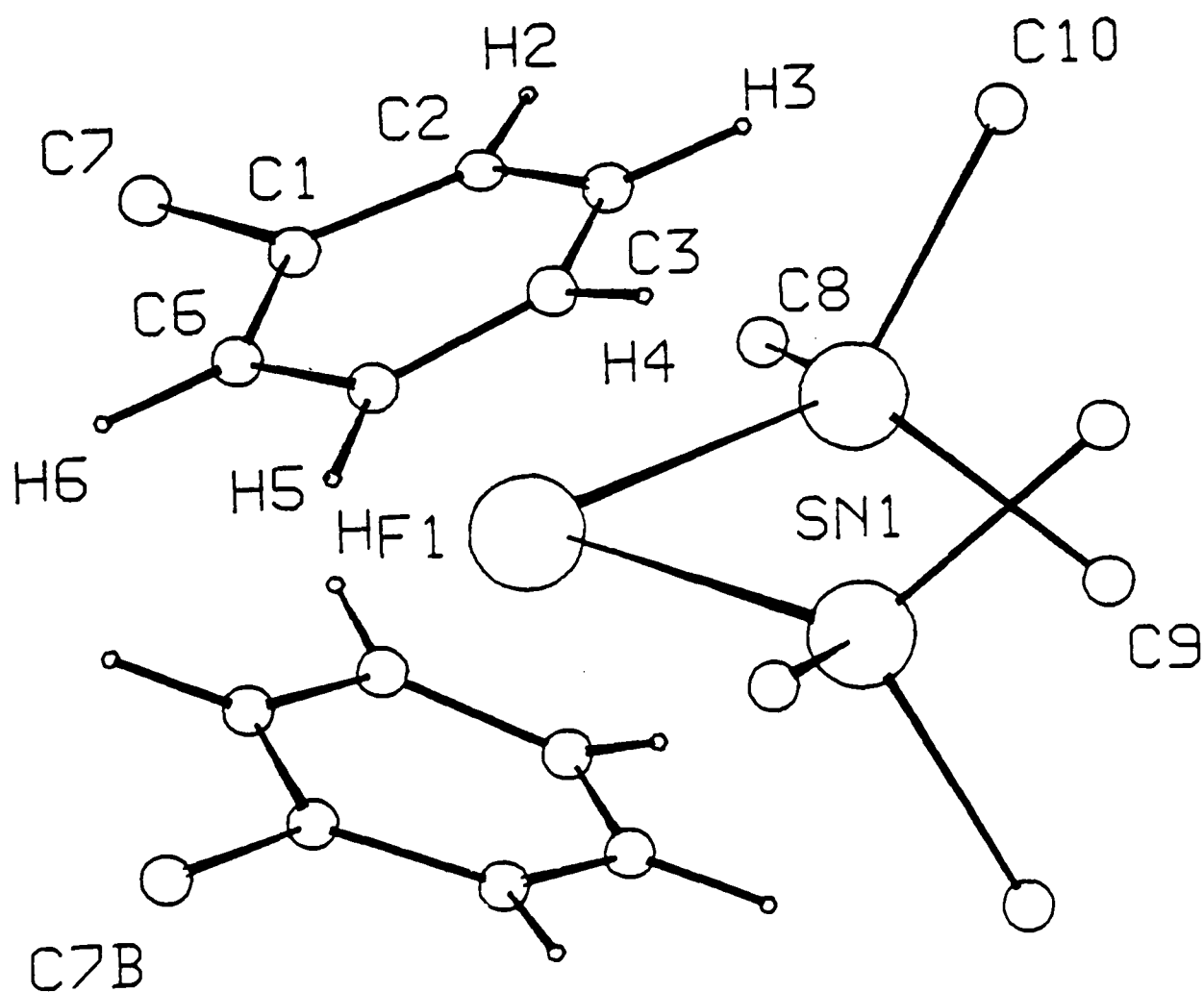


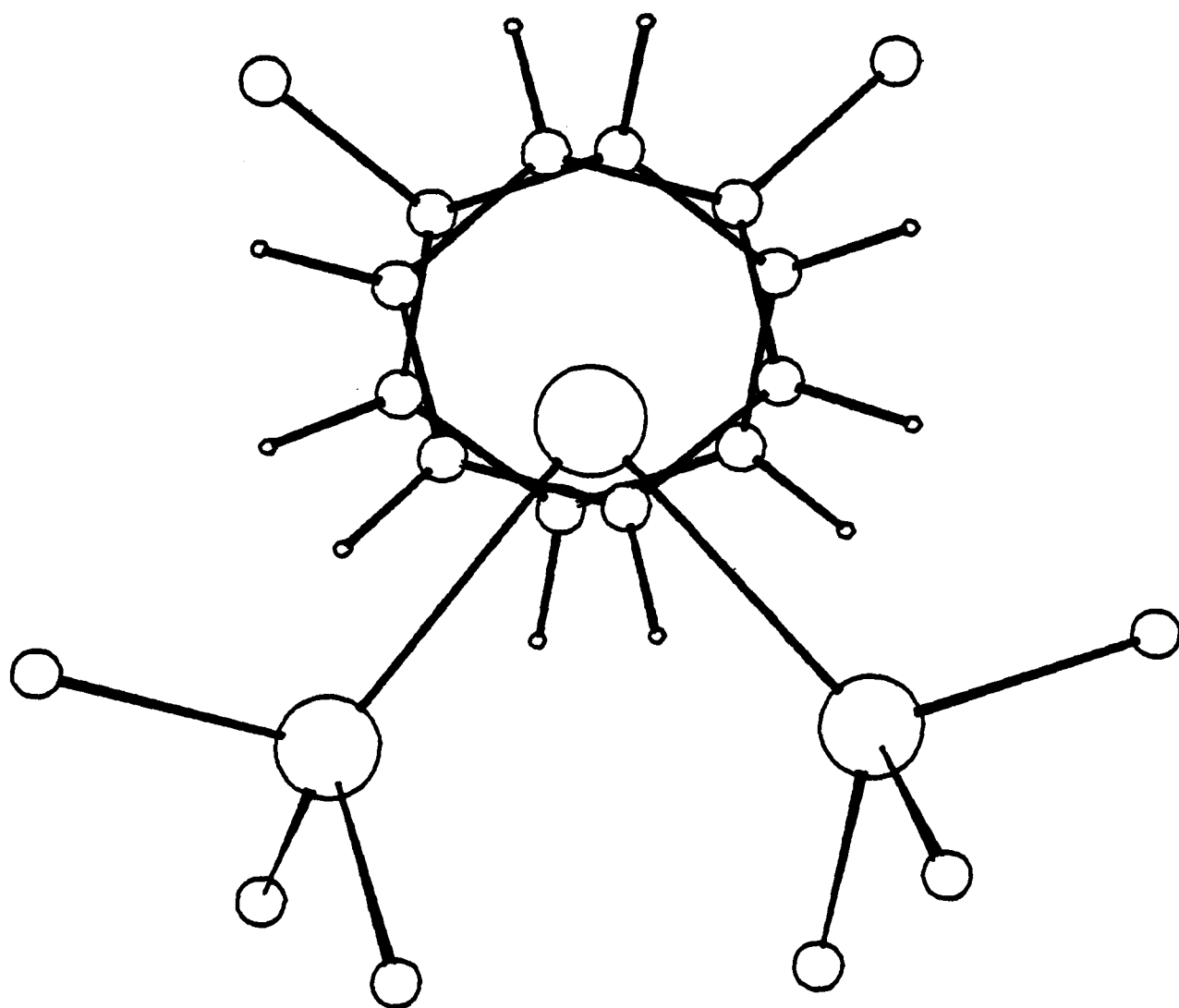
Fig. 5-6 $\text{Hf}(\text{MePh})_2(\text{SnMe}_3)_2$

TABLE 5-30 Dimensions of $\text{Hf}(\text{MePh})_2(\text{SnMe}_3)_2$ in (Å) and (°).

Hf1-Sn1	2.952(1)	Sn1-Hf1-Sn1'	81.14(2)
Hf1-C1	2.495(8)	Hf1-Sn1-C3	112.8(4)
Hf1-C2	2.461(8)	Hf1-Sn1-C9	117.3(3)
Hf1-C3	2.512(7)	Hf1-Sn1-C10	121.2(3)
Hf1-C4	2.519(8)	C8-Sn1-C9	102.7(6)
Hf1-C5	2.420(8)	C8-Sn1-C10	99.5(3)
Hf1-C6	2.418(8)	C9-Sn1-C10	100.4(4)
Sn1-C8	2.199(10)		
Sn1-C9	1.196(10)		
Sn1-C10	2.188(9)		

The ' refers to symmetry operation $x, -y, 1/2+z$

Fig. 5-6 A projection onto the Sn1-Hf1-Sn1' plane.



ATOM	X/A	Y/B	Z/C	U(ISO)
Hf(1)	0	792.1(4)	2500	311
Sn(1)	-337.7(4)	3100.3(5)	1363.9(3)	398
C(1)	-1431(7)	-762(8)	1726(6)	525
C(2)	-1778(6)	548(9)	1537(5)	491
C(3)	-1642(6)	1435(9)	2166(6)	488
C(4)	-1508(6)	1023(10)	2939(5)	510
C(5)	-1057(7)	-250(12)	3154(5)	577
C(6)	-1033(7)	-1162(9)	2536(6)	575
C(7)	-1488(10)	-1776(12)	1064(8)	866
C(8)	-228(11)	2477(16)	220(6)	826
C(9)	723(8)	4835(12)	1724(8)	731
C(10)	-1798(7)	4197(11)	919(6)	656
F(2)	-1995	895	980	500
H(3)	-2127	2384	2027	500
H(4)	-1600	1658	3345	500
H(5)	-735	-552	3735	500
H(6)	-751	-2120	2687	500

Table S-31 Hf(MePh)2(SnMe3)2, Atomic Parameters (x1000).

ATOM	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Hf(1)	338(2)	207(2)	316(2)	0	148(2)	0
Sn(1)	414(3)	437(3)	361(3)	-122(39)	124(2)	-20(2)
C(1)	568(47)	446(43)	635(52)	18(36)	191(41)	-171(37)
C(2)	435(40)	590(52)	473(43)	-75(43)	122(34)	-136(34)
C(3)	350(35)	481(42)	840(62)	-145(44)	244(38)	-69(33)
C(4)	446(41)	849(66)	510(48)	102(49)	277(38)	-192(41)
C(5)	600(55)	1025(78)	431(45)	195(45)	236(41)	-322(55)
C(6)	646(54)	441(47)	893(71)	-403(67)	296(51)	-116(39)
C(7)	1006(90)	849(82)	908(88)	147(66)	264(71)	-146(55)
C(8)	1428(116)	1277(115)	485(60)	350(64)	538(70)	270(93)
C(9)	690(64)	747(71)	1075(87)	134(50)	81(60)	-316(55)
C(10)	498(49)	714(61)	744(64)		-6(45)	112(44)

Hexakis(trimethylphosphine)molybdenum, Mo(PMe₃)₆.

CRYSTAL DATA: C₁₈H₅₄MoP₆, M 551.97, cubic, Im3m, a=11.319(2) Å, U=1450 Å³, Z=2, D_c=1.26 g/cm³. The intensities of 1622 reflections were measured (2θ_{max}=60°), and the data were corrected for extinction but not absorption [μ(Mo-Kα)=7.3 cm⁻¹]. A total of 224 independent, observed reflections was used for structure solution and refinement; the structure was solved by Patterson and Fourier methods, and refined by full-matrix least squares. The methyl carbons are highly disordered, resulting in a torus of electron density at approximately 1.85 Å from the phosphorus. After several models for the methyl disorder had been investigated unsuccessfully, it was decided to fix one carbon on each of the two independent mirrors that pass through P1. The occupancies were set to Mol 0.02083, P1 0.125, C1 0.25, C2 0.125, and refinement converged with R=5.18%, R_w=6.90%, for 12 parameters, 224 reflections, and 4 constraints. A 5-term Chebyshev series was used to calculate the weights; the coefficients are 13.46, 3.30, -5.73, 2.21, and 10.41. The final difference Fourier map is featureless.

Table 5-32 Atomic and Molecular Parameters for Mo(PMe₃)₆.

ATOM	X/A	Y/B	Z/C	U(ISO)
MO(1)	0.0000	0.0000	0.0000	0.0272(5)
P(1)	-0.2180(2)	0.0000	0.0000	0.0593
C(1)	-0.296(2)	0.1038(8)	0.1038(8)	0.126(9)
C(2)	-0.316(3)	0.134(2)	0.0000	0.13(1)

ATOM	U(11)	U(22)	U(33)	U(23)
P(1)	0.029(1)	0.085(1)	0.085(1)	0.0000

	U(13)	U(12)
	0.0000	0.0000

	Å		°
Mo1-P1	2.467(2)	Mo1-P1-C1	118.1(8)
P1-C1	1.880(4)	Mo1-P1-C2	126(1)
P1-C2	1.884(4)		

5.6 Chapter 4: Extended Huckel Calculations.

The Huckel¹⁸ and extended Huckel¹⁹ methods have been described in detail elsewhere. For this study, the computer programs written by Hoffmann and his group were used²⁰. These programs, ICON8, COORDINATE, and GENERATE, were implemented in Oxford by Dr. D.M.P. Mingos and his group on an ICL 2980, and I am grateful for the opportunity to use them. Slater atomic orbitals were used for all s and p functions, and a linear combination of two Slater orbitals was used for d-orbitals, to account better for their radial properties. A weighted H_{ij} formula (B) was used in the calculations instead of the traditional Wolfsberg-Helmholz formula (A).

$$(A) \quad H_{ij} = k S_{ij} (H_{ii} + H_{jj}) / 2$$

$$(B) \quad H_{ij} = k' (S_{ij} / 2) (H_{ii} + H_{jj})$$

where $k' = k + d^2 + d^4(1 - k)$
and $d = (H_{ii} - H_{jj}) / (H_{ii} + H_{jj})$

This formula was proposed²¹ to decrease the effects of Counter-intuitive Orbital Mixing (COM), which commonly results in large negative occupancies of virtual orbitals. COM is thought to arise at least partially from the inadequacy of the Wolfsberg-Helmholz formula in describing the interaction between orbitals of differing diffuseness. The constant k was taken to be 1.75. The atomic orbital parameters^{20,22} that were used are given below, as well as the coordinates of some important conformations of the bis(arene)Mo species, and relevant numerical results of the calculations.

EXTENDED HUCKEL CALCULATION.
WEIGHTED HIJ FORMULA USED.

5-30 Mo(C6H6)2H PLUS, THETA=156°,
Orthogonal Coordinates and Orbital Parameters.

ATOM	X	Y	Z	N	S EXP	COUL N	EXP	COUL N	D EXP1	COUL	C1 CONTRACTED D C2	EXP2			
MO 1	0.000000	0.000000	0.000000	5	1.960	-8.340	5	1.960	-5.240	4	4.540	-10.500	0.59881	0.59881	1.800
C 2	1.002868	0.000000	2.063603	2	1.625	-21.400	2	1.625	-11.400						
C 3	0.313274	1.221096	1.917025	2	1.625	-21.400	2	1.625	-11.400						
C 4	-1.065914	1.221096	1.623869	2	1.625	-21.400	2	1.625	-11.400						
C 5	-1.755508	0.000000	1.477292	2	1.625	-21.400	2	1.625	-11.400						
C 6	-1.065914	-1.221096	1.623869	2	1.625	-21.400	2	1.625	-11.400						
C 7	0.313274	-1.221096	1.917025	2	1.625	-21.400	2	1.625	-11.400						
H 8	2.069049	0.000000	2.290226	1	1.300	-13.600									
H 9	0.846364	2.165064	2.030337	1	1.300	-13.600									
H 10	-1.599005	2.165064	1.510558	1	1.300	-13.600									
H 11	-2.821609	0.000000	1.250668	1	1.300	-13.600									
H 12	-1.599005	-2.165064	1.510558	1	1.300	-13.600									
H 13	0.846364	-2.165064	2.030337	1	1.300	-13.600									
C 14	1.002868	0.000000	-2.063603	2	1.625	-21.400	2	1.625	-11.400						
C 15	0.313274	-1.221096	-1.917025	2	1.625	-21.400	2	1.625	-11.400						
C 16	-1.065914	-1.221096	-1.623869	2	1.625	-21.400	2	1.625	-11.400						
C 17	-1.755508	0.000000	-1.477292	2	1.625	-21.400	2	1.625	-11.400						
C 18	-1.065914	1.221096	-1.623869	2	1.625	-21.400	2	1.625	-11.400						
C 19	0.313274	1.221096	-1.917025	2	1.625	-21.400	2	1.625	-11.400						
H 20	2.069049	0.000000	-2.290226	1	1.300	-13.600									
H 21	0.846364	-2.165064	-2.030337	1	1.300	-13.600									
H 22	-1.599005	-2.165064	-1.510558	1	1.300	-13.600									
H 23	-2.821609	0.000000	-1.250668	1	1.300	-13.600									
H 24	-1.599005	2.165064	-1.510558	1	1.300	-13.600									
H 25	0.846364	2.165064	-2.030337	1	1.300	-13.600									
H 26	1.728000	0.000000	0.000000	1	1.300	-13.600									

5-31 Mo(C6H6)2H PLUS, THETA=156°,
Reduced Overlap Population Matrix.

REDUCED OVERLAP POPULATION MATRIX, ATOM BY ATOM

bony2 m0 m+

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	3.7425	0.0662	0.1185	0.1248	0.0914	0.1248	0.1185	-0.0131	-0.0120	-0.0114	-0.0103	-0.0114	-0.0120	0.0662
2	0.0662	2.6711	1.0263	-0.0702	-0.0247	-0.0702	1.0263	0.8018	-0.0603	0.0021	0.0000	0.0021	-0.0603	0.0006
3	0.1185	1.0263	2.7189	1.0191	-0.0692	-0.0252	-0.0724	-0.0600	0.7991	-0.0605	0.0021	0.0000	0.0021	-0.0005
4	0.1248	-0.0702	1.0191	2.6642	1.0229	-0.0197	-0.0252	0.0021	-0.0603	0.7994	-0.0606	0.0021	0.0000	-0.0003
5	0.0914	-0.0247	-0.0692	1.0229	2.6869	1.0229	-0.0692	0.0000	0.0021	-0.0605	0.8001	-0.0605	0.0021	-0.0000
6	0.1248	-0.0702	-0.0252	-0.0692	1.0229	2.6642	1.0191	0.0021	0.0000	0.0021	-0.0606	0.7994	-0.0603	-0.0003
7	0.1185	1.0263	-0.0724	-0.0252	-0.0692	1.0191	2.7189	-0.0600	0.0021	0.0000	0.0021	-0.0605	0.7991	-0.0005
8	-0.0131	0.8018	-0.0600	0.0021	0.0000	0.0021	-0.0600	0.6562	-0.0070	0.0000	0.0000	-0.0000	-0.0070	0.0000
9	-0.0120	-0.0603	0.7991	-0.0605	0.0021	0.0000	0.0021	-0.0070	0.6512	-0.0071	0.0000	0.0000	-0.0000	0.0000
10	-0.0114	0.0021	-0.0605	0.7994	-0.0605	0.0021	0.0000	-0.0071	-0.0071	0.6510	-0.0071	-0.0000	0.0000	0.0000
11	-0.0103	0.0000	0.0021	-0.0606	0.8001	-0.0606	0.0021	0.0000	-0.0000	-0.0071	0.6507	-0.0071	-0.0000	0.0000
12	-0.0114	0.0021	0.0000	0.0021	-0.0605	0.7994	-0.0605	-0.0000	0.0000	-0.0000	-0.0071	0.6510	-0.0000	0.0000
13	-0.0120	-0.0603	0.0021	0.0000	0.0021	-0.0603	0.7991	-0.0070	0.0000	0.0000	-0.0071	0.6512	0.0000	0.0000
14	0.0662	0.0006	-0.0005	-0.0003	-0.0000	-0.0003	-0.0005	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	2.6711
15	0.1185	-0.0005	-0.0004	-0.0000	-0.0005	-0.0013	0.0029	0.0000	0.0000	0.0000	0.0000	-0.0001	-0.0001	1.0263
16	0.1248	-0.0703	-0.0000	-0.0008	-0.0043	0.0067	-0.0013	-0.0006	-0.0000	-0.0000	-0.0004	-0.0008	-0.0001	-0.0702
17	0.0914	-0.0000	-0.0005	-0.0043	0.0166	-0.0043	-0.0005	0.0000	0.0000	-0.0002	-0.0023	-0.0002	0.0000	-0.0247
18	0.1248	-0.0003	-0.0013	0.0067	-0.0043	-0.0008	-0.0000	-0.0000	-0.0001	-0.0008	-0.0004	-0.0000	-0.0000	-0.0702
19	0.1185	-0.0005	0.0029	-0.0013	-0.0035	-0.0000	-0.0004	0.0000	-0.0001	0.0000	0.0000	0.0000	0.0000	1.0263
20	-0.0131	0.8000	0.0000	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.8018
21	-0.0120	0.0000	0.0000	-0.0000	0.0000	-0.0001	-0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0603
22	-0.0114	0.0000	0.0000	-0.0000	-0.0002	-0.0008	-0.0001	0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	0.0021
23	-0.0103	0.0000	0.0000	-0.0004	-0.0023	-0.0004	0.0000	0.0000	0.0000	0.0000	-0.0007	0.0000	0.0000	0.0000
24	-0.0114	0.0000	-0.0001	-0.0008	-0.0002	-0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0021
25	-0.0120	0.0000	-0.0001	-0.0001	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0603
26	0.5373	0.0053	-0.0073	-0.0005	-0.0005	-0.0005	-0.0073	-0.0085	-0.0011	-0.0001	-0.0000	-0.0001	-0.0011	0.0053

15 16 17 18 19 20 21 22 23 24 25 26

1	0.1185	0.1248	0.0914	0.1248	0.1185	-0.0131	-0.0120	-0.0114	-0.0103	-0.0114	-0.0120	0.5373
2	-0.0005	-0.0003	-0.0000	-0.0003	-0.0005	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0053
3	-0.0004	-0.0000	-0.0005	-0.0013	0.0029	0.0000	0.0000	0.0000	0.0000	-0.0001	-0.0001	-0.0073
4	-0.0000	-0.0006	-0.0043	0.0067	-0.0013	-0.0000	-0.0000	-0.0000	-0.0004	-0.0008	-0.0001	-0.0005
5	-0.0005	-0.0043	0.0166	-0.0043	-0.0005	0.0000	0.0000	-0.0002	-0.0023	-0.0002	0.0000	-0.0005
6	-0.0013	0.0067	-0.0043	-0.0008	-0.0003	-0.0000	-0.0001	-0.0008	-0.0004	-0.0000	-0.0000	-0.0005
7	0.0029	-0.0013	-0.0005	-0.0000	-0.0004	0.0000	-0.0001	0.0000	0.0000	0.0000	0.0000	-0.0073
8	0.0000	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0085
9	0.0000	-0.0000	0.0000	-0.0001	-0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0011
10	0.0000	-0.0000	-0.0002	-0.0008	-0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0001
11	0.0000	-0.0004	-0.0023	-0.0004	0.0000	0.0000	0.0000	0.0000	-0.0007	0.0000	0.0000	0.0000
12	-0.0001	-0.0008	-0.0002	-0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000
13	-0.0001	-0.0001	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001
14	1.0263	-0.0702	-0.0247	-0.0702	1.0263	0.8018	-0.0603	0.0021	0.0000	0.0021	-0.0603	0.0053
15	2.7189	1.0191	-0.0692	-0.0252	-0.0724	-0.0600	0.7991	-0.0605	0.0021	0.0000	0.0021	-0.0073
16	1.0191	2.6642	1.0229	-0.0697	-0.0252	0.0021	-0.0603	0.7994	-0.0606	0.0021	0.0000	-0.0073
17	-0.0692	1.0229	2.6869	1.0229	-0.0692	0.0000	0.0021	-0.0605	0.8001	-0.0605	0.0021	-0.0005
18	-0.0252	-0.0697	1.0229	2.6642	1.0191	0.0021	0.0000	0.0021	-0.0606	0.7994	-0.0603	-0.0005
19	-0.0724	-0.0252	-0.0692	1.0191	2.7189	-0.0600	0.0021	0.0000	0.0021	-0.0605	0.7991	-0.0073
20	-0.0600	0.0021	0.0000	0.0021	-0.0600	0.6562	-0.0070	0.0000	0.0000	-0.0000	-0.0070	-0.0085
21	0.7991	-0.0603	0.0021	0.0000	0.0021	-0.0070	0.6512	-0.0071	0.0000	0.0000	-0.0070	-0.0011
22	-0.0605	0.7994	-0.0605	0.0021	0.0000	-0.0071	0.6510	-0.0071	0.0000	0.0000	-0.0071	-0.0001
23	0.0021	-0.0606	0.8001	-0.0606	0.0021	0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0000	-0.0001
24	0.0000	0.0021	-0.0605	0.7994	-0.0605	-0.0000	0.0000	-0.0000	0.0000	0.0000	-0.0000	-0.0000
25	0.0021	0.0000	0.0021	-0.0603	0.7991	-0.0070	0.6507	-0.0071	0.0000	0.0000	-0.0071	-0.0001
26	-0.0073	-0.0005	-0.0005	-0.0005	-0.0073	-0.0085	-0.0011	-0.0001	-0.0000	-0.0001	-0.0001	1.1490

5-32 MO(C6H6)2H PLUS, THETA=156°,
Net Charges and Total Atomic Orbital Occupations.

ATOM	NET CHG.	S	X	Y	Z	M.O. OCCUPATION X ² -Y ²	ZZ	XY	XZ	YZ
MO 1	1.41402	0.14107	0.14409	0.11840	-0.11165	1.12881	0.91889	1.36021	0.44034	0.44502
C 2	0.0702	1.18134	0.92401	0.93234	0.95529					
C 3	-0.05522	1.18254	0.93711	0.91469	1.02088					
C 4	-0.00556	1.18237	0.92256	0.91470	0.98595					
C 5	-0.01968	1.18236	0.89815	0.93691	1.00224					
C 6	-0.00556	1.18237	0.92256	0.91470	0.98595					
C 7	-0.05522	1.18254	0.93711	0.91469	1.02088					
H 8	0.01849	0.98151								
H 9	0.02113	0.97867								
H 10	0.02113	0.97867								
H 11	0.02105	0.97815								
H 12	0.02113	0.97887								
H 13	0.02113	0.97887								
C 14	0.00702	1.18134	0.92401	0.93234	0.95529					
C 15	-0.05522	1.18254	0.93711	0.91469	1.02088					
C 16	-0.00558	1.18237	0.92256	0.91470	0.98595					
C 17	-0.01968	1.18236	0.89815	0.93691	1.00224					
C 18	-0.00558	1.18237	0.92256	0.91470	0.98595					
C 19	-0.05522	1.18254	0.93711	0.91469	1.02088					
H 20	0.01849	0.98151								
H 21	0.02113	0.97867								
H 22	0.02113	0.97867								
H 23	0.02185	0.97815								
H 24	0.02113	0.97867								
H 25	0.02113	0.97887								
H 26	-0.039601	1.39601								

(benzene M₀H + O = 156)

1(TITLE)2 FROM PLUS		ROTATING KINGS U-80		0.0		0.01328261389525200											
ATOM	X	Y	Z	M	S	COUL N	EXP	COUL N	EXP	COUL N	EXP	COUL N	EXP	COUL N	EXP	COUL N	EXP
M0	1	0.000000	0.000000	0.000000	5	1.960	-6.340	5	1.960	-5.240	4	4.540	-10.500	0.59881	0.59881	1.800	1.800
C	2	1.002868	0.000000	2.063603	2	1.625	-21.400	2	1.625	-11.400							
C	3	0.313274	1.221096	1.917025	2	1.625	-21.400	2	1.625	-11.400							
C	4	-1.065914	1.221096	1.623869	2	1.625	-21.400	2	1.625	-11.400							
C	5	-1.755508	0.000000	1.477292	2	1.625	-21.400	2	1.625	-11.400							
C	6	-1.065914	-1.221096	1.623869	2	1.625	-21.400	2	1.625	-11.400							
C	7	0.313274	-1.221096	1.917025	2	1.625	-21.400	2	1.625	-11.400							
C	8	2.499434	0.000000	2.381708	2	1.625	-21.400	2	1.625	-11.400							
H	9	0.846364	2.165064	2.030337	1	1.300	-13.600										
H	10	-1.599005	2.165064	1.510558	1	1.300	-13.600										
H	11	-2.821689	0.000000	1.250668	1	1.300	-13.600										
H	12	-1.599005	-2.165064	1.510558	1	1.300	-13.600										
H	13	0.846364	-2.165064	2.030337	1	1.300	-13.600										
C	14	1.002868	0.000000	-2.063603	2	1.625	-21.400	2	1.625	-11.400							
C	15	0.313274	-1.221096	-1.917025	2	1.625	-21.400	2	1.625	-11.400							
C	16	-1.065914	-1.221096	-1.623869	2	1.625	-21.400	2	1.625	-11.400							
C	17	-1.755508	0.000000	-1.477292	2	1.625	-21.400	2	1.625	-11.400							
C	18	-1.065914	1.221096	-1.623869	2	1.625	-21.400	2	1.625	-11.400							
C	19	0.313274	1.221096	-1.917025	2	1.625	-21.400	2	1.625	-11.400							
C	20	2.499434	0.000000	-2.381708	2	1.625	-21.400	2	1.625	-11.400							
H	21	0.846364	-2.165064	-2.030337	1	1.300	-13.600										
H	22	-1.599005	-2.165064	-1.510558	1	1.300	-13.600										
H	23	-2.821689	0.000000	-1.250668	1	1.300	-13.600										
H	24	-1.599005	2.165064	-1.510558	1	1.300	-13.600										
H	25	0.846364	2.165064	-2.030337	1	1.300	-13.600										
H	26	1.728000	0.000000	0.000000	1	1.300	-13.600										
H	27	3.068957	0.000000	1.452330	1	1.300	-13.600										
H	28	2.748520	0.689823	2.959869	1	1.300	-13.600										
H	29	2.748520	-0.689823	2.959869	1	1.300	-13.600										
H	30	3.068957	0.000000	-1.452330	1	1.300	-13.600										
H	31	2.748520	-0.689823	-2.959869	1	1.300	-13.600										
H	32	2.748520	0.689823	-2.959869	1	1.300	-13.600										

5-33 Mo(MePh)2H PLUS, THETA=156°, PHI=0°,

Orthogonal Coordinates and Orbital Parameters.

5-33 Mo(MePh)2H PLUS, THETA=156°, PHI=0°,
Orthogonal Coordinates and Orbital Parameters.

SUM OF ONE-ELECTRON ENERGIES * -1360.786839 EV.

72.42/14.11 d=0°
0.156°

REDUCED OVERLAP POPULATION MATRIX, ATOM BY ATOM

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	3.7745	0.0671	0.1208	0.1247	0.0923	0.1247	0.1208	-0.0234	-0.0122	-0.0114	-0.0103	-0.0114	-0.0122	0.0671
2	0.0671	2.6686	1.0337	-0.0715	-0.0249	-0.0715	1.0337	0.7748	-0.0598	0.0021	0.0000	0.0021	-0.0598	0.0008
3	0.1208	1.0337	2.7438	1.0186	-0.0698	-0.0251	-0.0734	-0.0701	0.8007	-0.0605	0.0021	0.0000	0.0021	-0.0005
4	0.1247	-0.0715	1.0186	2.6671	1.0233	-0.0695	-0.0251	0.0020	-0.0610	0.7993	-0.0607	0.0021	0.0000	-0.0003
5	0.0923	-0.0249	-0.0698	1.0233	2.6957	1.0233	-0.0698	0.0001	0.0021	-0.0606	0.8000	-0.0606	0.0021	-0.0000
6	0.1247	-0.0715	-0.0251	-0.0695	1.0233	2.6671	1.0186	0.0020	0.0000	0.0021	-0.0607	0.7993	-0.0610	-0.0003
7	0.1208	1.0337	-0.0734	-0.0251	-0.0698	1.0186	2.7438	-0.0701	0.0021	0.0000	0.0021	-0.0605	0.8007	-0.0005
8	-0.0234	0.7748	-0.0701	0.0020	0.0001	0.0020	-0.0701	2.6100	-0.0092	-0.0000	0.0000	-0.0000	-0.0092	0.0000
9	-0.0122	-0.0598	0.8007	-0.0610	0.0021	0.0000	0.0021	-0.0092	0.6529	-0.0071	-0.0000	0.0000	-0.0000	0.0000
10	-0.0114	0.0021	-0.0605	0.7993	-0.0606	0.0021	0.0000	-0.0000	-0.0071	0.6511	-0.0072	-0.0000	0.0000	0.0000
11	-0.0103	0.0000	0.0021	-0.0607	0.8000	-0.0607	0.0021	0.0000	-0.0000	-0.0072	0.6510	-0.0072	-0.0000	0.0000
12	-0.0114	0.0021	0.0000	0.0021	-0.0606	0.7993	-0.0605	-0.0000	0.0000	-0.0072	0.6511	-0.0071	0.0000	0.0000
13	-0.0122	-0.0598	0.0021	0.0000	0.0021	-0.0610	0.8007	-0.0092	-0.0000	0.0000	-0.0000	-0.0071	0.6529	0.0000
14	0.0671	0.0008	-0.0005	-0.0003	-0.0000	-0.0003	-0.0005	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	2.6686
15	0.1208	-0.0005	-0.0005	-0.0000	-0.0000	-0.0004	0.0014	0.0027	0.0000	0.0000	0.0000	-0.0001	-0.0001	1.0337
16	0.1247	-0.0003	-0.0000	-0.0008	-0.0042	0.0067	-0.0014	-0.0000	-0.0000	-0.0000	-0.0004	-0.0008	-0.0001	-0.0715
17	0.0923	-0.0000	-0.0004	-0.0042	0.0159	-0.0042	-0.0004	0.0000	0.0000	-0.0002	-0.0023	-0.0002	0.0000	-0.0249
18	0.1247	-0.0003	-0.0014	0.0067	-0.0042	-0.0008	-0.0000	-0.0000	-0.0001	-0.0008	-0.0004	-0.0000	-0.0000	-0.0715
19	0.1208	-0.0005	0.0027	-0.0014	-0.0004	-0.0000	-0.0000	-0.0000	-0.0001	-0.0001	0.0000	0.0000	0.0000	1.0337
20	-0.0234	0.0000	0.0000	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.7748
21	-0.0122	0.0000	0.0000	-0.0000	0.0000	-0.0001	-0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0598
22	-0.0114	0.0000	0.0000	-0.0000	-0.0002	-0.0008	-0.0001	0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	0.0021
23	-0.0103	0.0000	0.0000	-0.0004	-0.0023	-0.0004	0.0000	0.0000	0.0000	0.0000	-0.0007	0.0000	0.0000	0.0000
24	-0.0114	0.0000	-0.0001	-0.0008	-0.0002	-0.0008	0.0000	0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0021
25	-0.0122	0.0000	-0.0001	-0.0001	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0598
26	0.5349	0.0011	-0.0063	-0.0006	-0.0005	-0.0006	-0.0063	-0.0177	-0.0011	-0.0001	-0.0000	-0.0001	-0.0011	0.0011
27	-0.0095	-0.0453	-0.0022	0.0000	-0.0000	0.0000	-0.0022	0.7864	-0.0000	-0.0000	0.0000	-0.0000	-0.0000	-0.0002
28	0.0007	-0.0469	-0.0124	0.0001	-0.0000	-0.0000	0.0012	0.7921	-0.0004	-0.0000	0.0000	0.0000	0.0001	0.0000
29	0.0007	-0.0469	0.0012	-0.0000	-0.0000	0.0001	-0.0124	0.7921	0.0001	0.0000	0.0000	-0.0000	-0.0004	0.0000
30	-0.0095	-0.0002	0.0000	0.0000	-0.0000	0.0000	0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0453
31	0.0007	0.0000	-0.0000	0.0000	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0469
32	0.0007	0.0000	-0.0000	-0.0000	0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0469
	15	16	17	18	19	20	21	22	23	24	25	26	27	28
1	0.1208	0.1247	0.0923	0.1247	0.1208	-0.0234	-0.0122	-0.0114	-0.0103	-0.0114	-0.0122	0.5549	-0.0095	0.0007
2	-0.0005	-0.0003	-0.0000	-0.0003	-0.0005	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0011	-0.0453	-0.0469
3	-0.0005	-0.0000	-0.0004	-0.0014	0.0027	0.0000	0.0000	0.0000	0.0000	-0.0001	-0.0001	-0.0063	-0.0022	-0.0124
4	-0.0000	-0.0008	-0.0042	0.0067	-0.0014	-0.0000	-0.0000	-0.0000	-0.0004	-0.0008	-0.0001	-0.0006	0.0000	0.0001
5	-0.0004	-0.0042	0.0159	-0.0042	-0.0004	0.0000	0.0000	-0.0002	-0.0023	-0.0002	0.0000	-0.0005	-0.0000	-0.0000
6	-0.0014	0.0067	-0.0042	-0.0008	-0.0000	-0.0000	-0.0001	-0.0008	-0.0034	-0.0000	-0.0000	-0.0006	0.0000	-0.0000
7	0.0027	-0.0014	-0.0004	-0.0000	-0.0005	0.0000	-0.0001	-0.0001	0.0000	0.0000	0.0000	-0.0063	-0.0022	0.0012
8	0.0000	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0177	0.7864	0.7921
9	0.0000	-0.0000	0.0000	-0.0001	-0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0011	-0.0000	-0.0004
10	0.0000	-0.0000	-0.0002	-0.0008	-0.0001	0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	-0.0001	-0.0000	-0.0000
11	0.0000	-0.0004	-0.0023	-0.0004	0.0000	0.0000	0.0000	0.0000	-0.0007	0.0000	0.0000	-0.0000	0.0000	0.0000
12	-0.0001	-0.0008	-0.0002	-0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0001	-0.0000	0.0000
13	-0.0001	-0.0001	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0011	-0.0000	0.0001
14	1.0337	-0.0715	-0.0249	-0.0715	1.0337	0.7748	-0.0598	0.0021	0.0000	0.0021	-0.0598	0.0011	-0.0002	0.0000
15	2.7438	1.0186	-0.0698	-0.0251	-0.0734	-0.0701	0.8007	-0.0605	0.0021	0.0000	0.0021	-0.0063	0.0000	-0.0000
16	1.0186	2.6671	1.0233	-0.0695	-0.0251	0.0020	-0.0610	0.7993	-0.0607	0.0021	0.0000	-0.0006	0.0000	0.0000
17	-0.0698	1.0233	2.6957	1.0233	-0.0698	0.0001	0.0021	-0.0606	0.8000	-0.0606	0.0021	-0.0005	-0.0000	0.0000
18	-0.0251	-0.0695	1.0233	2.6671	1.0186	0.0020	0.0000	0.0021	-0.0607	0.7993	-0.0610	-0.0006	0.0000	-0.0000
19	-0.0734	-0.0251	-0.0698	1.0186	2.7438	-0.0701	0.0021	0.0000	0.0021	-0.0605	0.8007	-0.0063	0.0000	-0.0000
20	-0.0701	0.0020	0.0001	0.0020	-0.0701	2.6100	-0.0092	-0.0000	0.0000	-0.0000	-0.0092	-0.0177	-0.0000	0.0000
21	0.8007	-0.0610	0.0021	0.0000	0.0021	-0.0092	0.6529	-0.0071	-0.0000	0.0000	-0.0000	-0.0011	-0.0000	0.0000
22	-0.0605	0.7993	-0.0606	0.0021	0.0000	-0.0000	-0.0071	0.6511	-0.0072	-0.0000	0.0000	-0.0001	-0.0000	0.0000
23	0.0021	-0.0607	0.8000	-0.0607	0.0021	0.0000	-0.0000	-0.0072	0.6510	-0.0072	-0.0000	-0.0000	-0.0000	0.0000
24	0.0000	0.0021	-0.0606	0.7993	-0.0605	-0.0000	0.0000	-0.0000	-0.0072	0.6511	-0.0071	-0.0001	-0.0000	0.0000
25	0.0021	0.0000	0.0021	-0.0610	0.8007	-0.0092	-0.0000	0.0000	-0.0000	-0.0071	0.6529	-0.0011	-0.0000	0.0000
26	-0.0063	-0.0006	-0.0005	-0.0006	-0.0063	-0.0177	-0.0011	-0.0001	-0.0000	-0.0000	-0.0000	-0.0030	0.6441	-0.0405
27	0.0000	0.0000	-0.0000	0.0000	0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0002	-0.0405	0.6506
28	-0.0000	0.0000	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0002	-0.0405	-0.0437
29	-0.0000	-0.0000	0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0030	0.0003	-0.0000
30	-0.0022	0.0000	-0.0000	0.0000	-0.0022	0.7864	-0.0000	-0.0000	0.0000	-0.0000	-0.0000	-0.0030	0.0003	-0.0000
31	-0.0124	0.0001	-0.0000	-0.0000	0.0012	0.7921	-0.0004	-0.0000	0.0000	0.0000	0.0001	-0.0002	-0.0000	0.0000
32	0.0012	-0.0000	-0.0000	0.0001	-0.0124	0.7921	0.0001	0.0000	0.0000	-0.0000	-0.0004	-0.0002	-0.0000	0.0000
	29	30	31	32										
1	0.0007	-0.0095	0.0007	0.0007										
2	-0.0469	-0.0002	0.0000	0.0000										
3	0.0012	0.0000	-0.0000	-0.0000										
4	-0.0000	0.0000	0.0000	-0.0000										
5	-0.0000	-0.0000	0.0000	0.0000										
6	0.0001	0.0000	-0.0000	0.0000										
7	-0.0124	0.0000	-0.0000	-0.0000										
8	0.7921	-0.0000	0.0000	0.0000										
9	0.0001	-0.0000	0.0000	0.0000										
10	0.0000	-0.0000	0.0000	0.0000										
11	0.0000	-0.0000	0.0000	0.0000										
12	-0.0000	-0.0000	0.0000	0.0000										
13	-0.0004	-0.0000	0.0000	0.0000										
14	0.0000	-0.0453	-0.0469	-0.0469										
15	-0.0000	-0.0022	-0.0124	0.0012										
16	-0.0000	0.0000	0.0001	-0.0000										
17	0.0000	-0.0000	-0.0000	-0.0000										
18	0.0000	0.0000	-0.0000	0.0001										
19	-0.0000	-0.0022	0.0012	-0.0124										
20	0.0000	0.7864	0.7921	0.7921										
21	0.0000	-0.0000	-0.0004	0.0001										
22	0.0000	-0.0000	-0.0000	0.0000										
23	0.0000	0.0000	0.0000	0.0000										
24	0.0000	-0.0000	0.0000	-0.0000										
25	0.0000	-0.0000	0.0001	-0.0004										
26	-0.0002	-0.0030	-0.0002	-0.0002										

ATOM	X	Y	Z	N	EXP	COUL	M	EXP	COUL	N	EXP	COUL	C1	C2	EXP	D
MO 1	0.000000	0.000000	0.000000	5	1.960	-8.340	5	1.960	-5.240	4	4.540	-10.500	0.59481	0.59481	1.800	
C 2	-0.615614	1.386579	1.719541	2	1.625	-21.400	2	1.625	-11.400							
C 3	-1.672335	0.482248	1.494971	2	1.625	-21.400	2	1.625	-11.400							
C 4	-1.432840	-0.906331	1.545877	2	1.625	-21.400	2	1.625	-11.400							
C 5	-0.136627	-1.388579	1.821353	2	1.625	-21.400	2	1.625	-11.400							
C 6	0.919693	-0.482248	2.045923	2	1.625	-21.400	2	1.625	-11.400							
C 7	0.680199	0.906331	1.995017	2	1.625	-21.400	2	1.625	-11.400							
C 8	-0.875690	2.895335	1.664303	2	1.625	-21.400	2	1.625	-11.400							
H 9	-2.674215	0.855050	1.282014	1	1.300	-13.600										
H 10	-2.249581	-1.606949	1.572273	1	1.300	-13.600										
H 11	0.048314	-2.462019	1.840706	1	1.300	-13.600										
H 12	1.921575	-0.855050	2.258880	1	1.300	-13.600										
H 13	1.496941	1.606949	2.168621	1	1.300	-13.600										
C 14	-0.615614	-1.388579	-1.719541	2	1.625	-21.400	2	1.625	-11.400							
C 15	-1.672335	-0.482248	-1.494971	2	1.625	-21.400	2	1.625	-11.400							
C 16	-1.432840	0.906331	-1.545877	2	1.625	-21.400	2	1.625	-11.400							
C 17	-0.136627	1.388579	-1.821353	2	1.625	-21.400	2	1.625	-11.400							
C 18	0.919693	0.482248	-2.045923	2	1.625	-21.400	2	1.625	-11.400							
C 19	0.680199	-0.906331	-1.995017	2	1.625	-21.400	2	1.625	-11.400							
C 20	-0.875690	-2.895335	-1.664303	2	1.625	-21.400	2	1.625	-11.400							
H 21	-2.674215	-0.855050	-1.282014	1	1.300	-13.600										
H 22	-2.249581	1.606949	-1.572273	1	1.300	-13.600										
H 23	0.048314	2.462019	-1.840706	1	1.300	-13.600										
H 24	1.921575	0.855050	-2.258880	1	1.300	-13.600										
H 25	1.496941	-1.606949	-2.168621	1	1.300	-13.600										
H 26	1.726000	0.000000	0.000000	1	1.300	-13.600										
H 27	-0.723866	3.253657	0.646140	1	1.300	-13.600										
H 28	-1.901459	3.099140	1.971666	1	1.300	-13.600										
H 29	-0.167148	3.408173	2.335874	1	1.300	-13.600										
H 30	-0.723866	-3.253657	-0.646140	1	1.300	-13.600										
H 31	-1.901459	-3.099140	-1.971666	1	1.300	-13.600										
H 32	-0.167148	-3.408173	-2.335874	1	1.300	-13.600										

5-35 Mo(MePh)2H PLUS, THETA=156°, PHI=100°,
The Most Favourable Conformation,
Orthogonal Coordinates and Orbital Parameters.

5-36 MoH⁺

Theta = 156° Phi = 100°

REDUCED OVERLAP POPULATION MATRIX, ATOM BY ATOM

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	3.7210	0.1212	0.1010	0.1156	0.1238	0.0794	0.1041	-0.0188	-0.0106	-0.0107	-0.0122	-0.0124	-0.0120	0.1212
2	0.1212	2.6528	1.0204	-0.0705	-0.0260	-0.0718	1.0363	0.7688	-0.0607	0.0021	0.0000	0.0021	-0.0599	-0.0001
3	0.1010	1.0204	2.7087	1.0229	-0.0695	-0.0246	-0.0709	-0.0706	0.8016	-0.0607	0.0021	0.0000	0.0021	-0.0017
4	0.1156	-0.0705	1.0229	2.6752	1.0185	-0.0703	-0.0247	0.0019	-0.0614	0.7995	-0.0604	0.0021	0.0000	-0.0004
5	0.1238	-0.0260	-0.0695	1.0185	2.7004	1.0321	-0.0723	0.0001	0.0021	-0.0605	0.7989	-0.0604	0.0021	0.0026
6	0.0794	-0.0718	-0.0246	-0.0703	1.0321	2.6932	1.0150	0.0020	0.0000	0.0021	-0.0606	0.8011	-0.0608	-0.0007
7	0.1041	1.0363	-0.0607	-0.0247	-0.0723	1.0150	2.7466	-0.0709	0.0021	0.0000	0.0021	-0.0599	0.8015	-0.0002
8	-0.0188	0.7688	-0.0607	0.0019	0.0001	0.0020	-0.0709	2.5997	-0.0093	-0.0000	0.0000	-0.0000	-0.0000	-0.0000
9	-0.0106	-0.0607	0.8016	-0.0614	0.0021	0.0000	0.0021	-0.0093	0.6527	-0.0071	-0.0000	0.0000	-0.0000	-0.0000
10	-0.0107	0.0021	-0.0607	0.7995	-0.0605	0.0021	0.0000	-0.0000	-0.0071	0.6508	-0.0072	-0.0000	0.0000	-0.0005
11	-0.0122	0.0000	0.0021	-0.0604	0.7989	-0.0606	0.0021	0.0000	-0.0000	-0.0072	0.6514	-0.0070	-0.0000	-0.0003
12	-0.0124	0.0021	0.0000	0.0021	-0.0604	0.8011	-0.0599	-0.0000	0.0000	-0.0070	0.6548	-0.0069	-0.0000	-0.0000
13	-0.0120	-0.0599	0.0021	0.0000	0.0021	-0.0599	0.8015	-0.0093	-0.0000	-0.0000	-0.0000	-0.0000	0.6540	-0.0000
14	0.1212	-0.0001	-0.0017	-0.0004	0.0026	-0.0007	-0.0002	-0.0000	-0.0000	-0.0005	-0.0003	-0.0000	-0.0000	2.6528
15	0.1012	-0.0017	-0.0013	0.0083	-0.0023	-0.0001	-0.0000	0.0000	-0.0010	-0.0012	0.0000	0.0000	-0.0000	1.0304
16	0.1156	-0.0006	0.0083	-0.0042	-0.0002	-0.0000	-0.0000	-0.0005	-0.0015	-0.0001	-0.0000	-0.0000	-0.0000	-0.0705
17	0.1238	0.0026	-0.0023	-0.0002	-0.0002	0.0006	0.0008	-0.0009	-0.0001	-0.0000	-0.0000	-0.0000	-0.0001	-0.0260
18	0.0794	-0.0007	-0.0001	-0.0000	-0.0006	-0.0003	0.0009	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0718
19	0.1041	-0.0002	-0.0000	-0.0000	0.0008	0.0009	-0.0008	0.0000	0.0000	0.0000	-0.0000	0.0000	0.0000	1.0363
20	-0.0188	-0.0000	0.0000	-0.0005	-0.0009	0.0000	0.0000	0.0000	0.0000	-0.0000	-0.0002	0.0000	0.0000	0.7688
21	-0.0106	-0.0000	-0.0010	-0.0019	-0.0001	0.0000	0.0000	0.0000	-0.0000	-0.0002	0.0000	0.0000	0.0000	-0.0600
22	-0.0107	-0.0005	-0.0012	-0.0001	-0.0000	0.0000	0.0000	-0.0000	-0.0002	0.0000	0.0000	0.0000	0.0000	0.0021
23	-0.0122	-0.0003	-0.0000	-0.0000	-0.0000	0.0000	0.0000	-0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
24	-0.0124	-0.0000	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0021
25	-0.0120	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0599
26	0.5398	-0.0012	-0.0005	-0.0004	-0.0035	-0.0008	-0.0004	-0.0001	-0.0000	-0.0000	-0.0003	-0.0006	-0.0031	-0.0012
27	-0.0097	-0.0440	-0.0023	0.0000	-0.0000	0.0000	-0.0023	0.7861	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0000
28	0.0007	-0.0470	-0.0123	0.0001	-0.0000	-0.0000	0.0012	0.7922	-0.0005	-0.0000	-0.0000	0.0000	0.0000	-0.0000
29	0.0007	-0.0471	0.0012	-0.0000	-0.0000	0.0001	-0.0124	0.7923	0.0000	0.0000	-0.0000	0.0000	0.0000	-0.0440
30	-0.0097	-0.0000	0.0000	-0.0003	-0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.0000	0.0000	-0.0470
31	0.0007	-0.0000	-0.0000	0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0470
32	0.0007	0.0000	-0.0000	-0.0000	0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0471

	15	16	17	18	19	20	21	22	23	24	25	26	27	28
1	0.1012	0.1156	0.1238	0.0794	0.1041	-0.0188	-0.0106	-0.0107	-0.0122	-0.0124	-0.0120	0.5398	-0.0097	0.0007
2	-0.0017	-0.0006	0.0026	-0.0007	-0.0002	-0.0000	-0.0000	-0.0005	-0.0003	-0.0000	-0.0000	-0.0012	-0.0440	-0.0470
3	-0.0013	0.0083	-0.0023	-0.0001	-0.0000	0.0000	-0.0010	-0.0012	0.0000	0.0000	-0.0000	-0.0005	-0.0023	-0.0123
4	0.0003	-0.0042	-0.0002	-0.0000	-0.0000	-0.0005	-0.0015	-0.0001	-0.0000	-0.0000	-0.0000	-0.0004	0.0000	0.0001
5	-0.0023	-0.0002	-0.0002	-0.0002	0.0009	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0001	-0.0023	-0.0000
6	-0.0001	-0.0000	-0.0000	-0.0000	0.0009	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0001	0.0000	-0.0000
7	-0.0000	-0.0006	0.0003	0.0009	-0.0009	0.0000	0.0000	0.0000	-0.0000	-0.0000	0.0000	-0.0001	0.0000	-0.0000
8	0.0000	-0.0005	-0.0009	0.0000	0.0000	0.0000	0.0000	-0.0002	0.0000	0.0000	0.0000	-0.0000	0.0000	-0.0005
9	-0.0010	-0.0015	-0.0021	0.0000	0.0000	0.0000	0.0000	-0.0002	0.0000	0.0000	0.0000	-0.0000	0.0000	-0.0000
10	-0.0012	-0.0001	-0.0000	0.0000	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	-0.0000
11	0.0000	-0.0000	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	-0.0000
12	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	-0.0000
13	-0.0000	-0.0000	-0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0001	0.0000	0.0000
14	1.0304	-0.0705	-0.0260	-0.0718	1.0363	0.7688	-0.0607	-0.0607	-0.0604	0.0021	-0.0599	-0.0012	-0.0000	-0.0000
15	2.6752	1.0185	-0.0695	-0.0703	-0.0247	0.0019	-0.0614	0.7995	-0.0604	0.0021	-0.0606	0.8011	-0.0608	-0.0007
16	1.0229	2.6752	1.0185	-0.0703	-0.0247	0.0019	-0.0614	0.7995	-0.0604	0.0021	-0.0606	0.8011	-0.0608	-0.0007
17	-0.0695	1.0185	2.7004	1.0321	-0.0723	0.0001	0.0021	-0.0605	0.7989	-0.0604	0.0021	-0.0606	0.8011	-0.0608
18	-0.0246	-0.0703	-0.0247	-0.0723	1.0150	2.7466	-0.0709	0.0021	0.0000	0.0021	-0.0599	0.8015	-0.0002	-0.0000
19	-0.0709	-0.0247	-0.0723	1.0150	2.7466	-0.0709	0.0021	0.0000	0.0021	-0.0599	0.8015	-0.0002	-0.0000	-0.0000
20	-0.0706	0.0019	0.0001	0.0020	-0.0709	2.5997	-0.0093	-0.0000	0.0000	-0.0000	-0.0000	-0.0000	0.0000	0.0000
21	0.8016	-0.0614	0.0021	0.0000	0.0021	-0.0093	-0.0071	-0.0000	0.0000	-0.0000	-0.0000	-0.0000	0.0000	0.0000
22	-0.0607	0.7995	-0.0605	0.0021	0.0000	-0.0000	-0.0071	0.6527	-0.0071	-0.0000	-0.0000	-0.0000	0.0000	-0.0000
23	0.0021	-0.0604	0.7989	-0.0606	0.0021	0.0000	-0.0000	-0.0072	0.6514	-0.0070	-0.0000	-0.0000	0.0000	-0.0000
24	0.0000	0.0021	-0.0604	0.8011	-0.0599	-0.0000	-0.0000	-0.0070	0.6548	-0.0069	-0.0000	-0.0000	0.0000	-0.0000
25	0.0021	0.0000	0.0021	-0.0608	0.8015	-0.0093	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	-0.0000
26	-0.0005	-0.0004	-0.0035	-0.0008	-0.0004	-0.0001	-0.0000	-0.0000	-0.0003	-0.0006	-0.0031	1.1567	0.0000	-0.0000
27	0.0000	-0.0003	-0.0008	0.0000	-0.0000	0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	-0.0440	0.6508
28	-0.0000	-0.0000	0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0407	-0.0437
29	-0.0000	-0.0000	0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000
30	-0.0023	0.0000	-0.0000	0.0000	-0.0023	0.7861	0.0000	-0.0000	-0.0000	0.0000	0.0000	-0.0000	-0.0000	-0.0000
31	-0.0123	0.0001	-0.0000	0.0000	0.0012	0.7922	-0.0005	-0.0000	-0.0000	0.0000	0.0000	-0.0000	-0.0000	-0.0000
32	0.0012	-0.0000	-0.0000	0.0001	-0.0124	0.7923	0.0000	-0.0000	-0.0000	-0.0000	-0.0005	-0.0000	-0.0000	0.0000

	29	30	31	32
1	0.0007	-0.0097	0.0007	0.0007
2	-0.0471	-0.0000	-0.0000	0.0000
3	0.0012	0.0000	-0.0000	-0.0000
4	-0.0006	-0.0003	0.0000	-0.0000
5	-0.0000	-0.0008	0.0000	0.0000
6	0.0001	0.0000	-0.0000	-0.0000
7	-0.0124	-0.0000	0.0000	-0.0000
8	0.7923	0.0000	0.0000	-0.0000
9	0.0000	0.0000	0.0000	-0.0000
10	0.0000	0.0000	-0.0000	-0.0000
11	-0.0000	0.0002	-0.0000	-0.0000
12	-0.0000	0.0000	-0.0000	-0.0000
13	-0.0005	0.0000	-0.0000	-0.0000
14	0.0000	-0.0440	-0.0470	-0.0471
15	-0.0000	-0.0023	-0.0123	0.0012
16	-0.0000	0.0000	0.0001	-0.0000
17	0.0000	-0.0000	-0.0000	-0.0000
18	-0.0000	0.0000	-0.0000	0.0001
19	-0.0000	-0.0023	0.0012	-0.0124
20	-0.0000	0.7861	0.7922	0.7923
21	-0.0000	0.0000	-0.0005	0.0000

1 (C6H5F)2 MOH PLUS
ROTATING RINGS 0-80
0.0
0.0
0.0618431247

EXTENDED HUCKEL CALCULATION.
WEIGHTED HIJ FORMULA USED.

5-37 Mo(FPh)2H PLUS, THETA=156°, PHI=0°,
Orthogonal Coordinates and Orbital Parameters.

ATOM	X	Y	Z	N	S		COUL	N	EXP	COUL	N	D		CONTRACTED D	
					EXP							EXP01		C1	EXP02
MO 1	0.000000	0.000000	0.000000	5	1.960	-8.340	5	1.960	-5.240	4	4.540	-10.500	0.59881	0.59881	1.800
C 2	1.002868	0.000000	2.063603	2	1.625	-21.400	2	1.625	-11.400						
C 3	0.313274	1.221096	1.917025	2	1.625	-21.400	2	1.625	-11.400						
C 4	-1.065914	1.221096	1.623869	2	1.625	-21.400	2	1.625	-11.400						
C 5	-1.755508	0.000000	1.477292	2	1.625	-21.400	2	1.625	-11.400						
C 6	-1.065914	-1.221096	1.623869	2	1.625	-21.400	2	1.625	-11.400						
C 7	0.313274	-1.221096	1.917025	2	1.625	-21.400	2	1.625	-11.400						
F 8	2.254897	0.000000	2.329730	2	2.425	-40.000	2	2.425	-18.100						
H 9	0.846364	2.165064	2.030337	1	1.300	-13.600									
H 10	-1.599005	2.165064	1.510558	1	1.300	-13.600									
H 11	-2.821689	0.000000	1.250668	1	1.300	-13.600									
H 12	-1.599005	-2.165064	1.510558	1	1.300	-13.600									
H 13	0.846364	-2.165064	2.030337	1	1.300	-13.600									
C 14	1.002868	0.000000	-2.063603	2	1.625	-21.400	2	1.625	-11.400						
C 15	0.313274	-1.221096	-1.917025	2	1.625	-21.400	2	1.625	-11.400						
C 16	-1.065914	-1.221096	-1.623869	2	1.625	-21.400	2	1.625	-11.400						
C 17	-1.755508	0.000000	-1.477292	2	1.625	-21.400	2	1.625	-11.400						
C 18	-1.065914	1.221096	-1.623869	2	1.625	-21.400	2	1.625	-11.400						
C 19	0.313274	1.221096	-1.917025	2	1.625	-21.400	2	1.625	-11.400						
F 20	2.254897	0.000000	-2.329730	2	2.425	-40.000	2	2.425	-18.100						
H 21	0.846364	-2.165064	-2.030337	1	1.300	-13.600									
H 22	-1.599005	-2.165064	-1.510558	1	1.300	-13.600									
H 23	-2.821689	0.000000	-1.250668	1	1.300	-13.600									
H 24	-1.599005	2.165064	-1.510558	1	1.300	-13.600									
H 25	0.846364	2.165064	-2.030337	1	1.300	-13.600									
H 26	1.728000	0.000000	0.000000	1	1.300	-13.600									

SUM OF ONE-ELECTRON ENERGIES = -1459.090325 EV. S-38 Mo(FPh)2H PLUS, THETA=156°, PHI=0°,
 Reduced Overlap Population Matrix.

REDUCED OVERLAP POPULATION MATRIX, ATOM BY ATOM

$\langle F^{\mu} \rangle_{\lambda} m_{\mu} H^{\mu}$

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	3.8741	0.0617	0.1159	0.1247	0.0916	0.1247	0.1159	-0.0133	-0.0132	-0.0113	-0.0104	-0.0113	-0.0132	0.0617
2	0.0617	2.0647	1.0322	-0.0675	-0.0218	-0.0675	1.0322	0.5637	-0.0566	0.0020	0.0000	0.0020	-0.0566	0.0004
3	0.1159	1.0322	2.7795	1.0185	-0.0704	-0.0238	-0.0835	-0.0543	0.7955	-0.0609	0.0021	-0.0000	0.0017	-0.0004
4	0.1247	-0.0675	1.0185	2.6600	1.0236	-0.0699	-0.0238	0.0005	-0.0592	0.7993	-0.0606	0.0021	0.0001	-0.0003
5	0.0916	-0.0218	-0.0704	1.0236	2.7000	1.0236	-0.0704	0.0000	0.0021	-0.0607	0.8005	-0.0607	0.0021	-0.0000
6	0.1247	-0.0675	-0.0238	-0.0699	1.0236	2.6600	1.0185	0.0005	0.0001	0.0021	-0.0606	0.7993	-0.0592	-0.0003
7	0.1159	1.0322	-0.0835	-0.0238	-0.0704	1.0185	2.7795	-0.0543	0.0017	-0.0000	0.0000	-0.0609	0.7955	-0.0004
8	-0.0133	0.5637	-0.0543	0.0005	0.0000	0.0005	-0.0543	7.2997	-0.0018	-0.0000	0.0000	0.0000	-0.0018	-0.0000
9	-0.0132	-0.0566	0.7955	-0.0592	0.0021	0.0001	0.0017	-0.0018	0.6457	-0.0072	-0.0000	0.0000	-0.0001	0.0000
10	-0.0113	0.0020	-0.0609	0.7993	-0.0607	0.0021	-0.0000	-0.0000	-0.0072	0.6517	-0.0071	-0.0000	0.0000	0.0000
11	-0.0104	0.0000	0.0021	-0.0606	0.8005	-0.0606	0.0021	0.0000	-0.0000	-0.0071	0.6511	-0.0071	-0.0000	0.0000
12	-0.0113	0.0020	-0.0000	0.0021	-0.0607	0.7993	-0.0609	-0.0001	0.0000	-0.0000	-0.0000	0.6517	-0.0072	0.0000
13	-0.0132	-0.0566	0.0017	0.0001	0.0021	-0.0592	0.0017	-0.0018	0.0001	0.0000	-0.0000	-0.0072	0.6457	0.0000
14	0.0617	0.0004	-0.0004	-0.0003	-0.0000	-0.0003	-0.0004	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	2.0647
15	0.1159	-0.0004	-0.0003	-0.0001	-0.0004	-0.0014	0.0027	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0001	1.0322
16	0.1247	-0.0003	-0.0001	-0.0008	-0.0040	-0.0066	-0.0014	-0.0000	-0.0000	-0.0000	-0.0004	-0.0008	-0.0001	-0.0675
17	0.0916	-0.0000	-0.0004	-0.0040	-0.0040	-0.0049	-0.0004	-0.0000	-0.0001	-0.0008	-0.0004	-0.0000	-0.0000	-0.0218
18	0.1247	-0.0003	-0.0014	0.0066	-0.0040	-0.0008	-0.0001	0.0000	-0.0001	-0.0000	-0.0004	-0.0000	-0.0000	-0.0675
19	0.1159	-0.0004	0.0027	-0.0014	-0.0004	-0.0001	-0.0005	0.0000	-0.0001	-0.0000	-0.0000	-0.0000	-0.0000	1.0322
20	-0.0133	0.0000	0.0000	0.0000	-0.0000	-0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0000	-0.5637
21	-0.0132	0.0000	-0.0000	-0.0000	-0.0002	-0.0008	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0020
22	-0.0113	0.0000	0.0000	-0.0000	-0.0000	-0.0004	-0.0000	-0.0000	0.0000	0.0000	-0.0007	0.0000	0.0000	0.0000
23	-0.0104	0.0000	-0.0000	-0.0004	-0.0002	-0.0004	0.0000	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0020
24	-0.0113	0.0000	-0.0000	-0.0008	-0.0002	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0566
25	-0.0132	0.0000	-0.0001	-0.0001	0.0000	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0097
26	0.5330	0.0097	-0.0074	-0.0005	-0.0005	-0.0005	-0.0074	-0.0051	-0.0012	-0.0001	-0.0000	-0.0001	-0.0012	0.0097

15 16 17 18 19 20 21 22 23 24 25 26

1	0.1159	0.1247	0.0916	0.1247	0.1159	-0.0133	-0.0132	-0.0113	-0.0104	-0.0113	-0.0132	0.5330
2	-0.0004	-0.0003	-0.0000	-0.0003	-0.0004	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0097
3	-0.0005	-0.0001	-0.0004	-0.0014	0.0027	0.0000	0.0000	0.0000	0.0000	-0.0000	-0.0001	-0.0074
4	-0.0001	-0.0008	-0.0040	-0.0066	-0.0014	0.0000	-0.0000	-0.0000	-0.0004	-0.0008	-0.0001	-0.0005
5	-0.0004	-0.0040	0.0149	-0.0040	-0.0004	-0.0000	0.0000	-0.0002	-0.0024	-0.0002	0.0000	-0.0005
6	-0.0014	0.0066	-0.0040	-0.0008	-0.0001	0.0000	-0.0001	-0.0008	-0.0004	-0.0000	-0.0000	-0.0005
7	0.0027	-0.0014	-0.0004	-0.0001	-0.0005	0.0000	-0.0001	-0.0000	-0.0000	0.0000	-0.0000	-0.0074
8	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	0.0000	-0.0000	-0.0000	-0.0051
9	0.0000	-0.0000	0.0000	-0.0000	-0.0001	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0012
10	0.0000	-0.0000	-0.0002	-0.0008	-0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	-0.0001
11	0.0000	-0.0004	-0.0024	-0.0004	0.0000	0.0000	0.0000	0.0000	-0.0007	0.0000	0.0000	0.0000
12	-0.0000	-0.0008	-0.0002	-0.0000	0.0000	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0012
13	-0.0001	-0.0001	0.0000	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0097
14	1.0322	-0.0675	-0.0218	-0.0675	1.0322	0.5637	-0.0566	0.0020	0.0021	-0.0000	-0.0566	0.0097
15	2.7795	1.0185	-0.0704	-0.0238	-0.0835	-0.0543	0.7955	-0.0609	0.0017	-0.0000	0.0017	-0.0074
16	1.0185	2.6600	1.0236	-0.0699	-0.0238	0.0005	-0.0592	0.7993	-0.0606	0.0021	0.0001	-0.0005
17	-0.0704	1.0236	2.7000	1.0236	-0.0704	0.0000	0.0021	-0.0607	0.8005	-0.0607	0.0021	-0.0005
18	-0.0238	-0.0699	1.0236	2.6600	1.0185	0.0005	0.0001	-0.0021	-0.0606	0.7993	-0.0592	-0.0005
19	-0.0835	-0.0238	-0.0704	1.0185	2.7795	-0.0543	0.0017	-0.0000	0.0021	-0.0609	0.7955	-0.0074
20	-0.0543	0.0005	0.0000	-0.0543	7.2997	-0.0018	-0.0000	-0.0000	0.0021	-0.0000	-0.0018	-0.0031
21	0.7955	-0.0592	0.0021	0.0001	0.0017	-0.0018	0.6457	-0.0072	-0.0000	0.0000	-0.0001	-0.0012
22	-0.0609	0.7993	-0.0607	0.0021	-0.0000	-0.0000	-0.0072	0.6517	-0.0071	-0.0000	0.0000	-0.0001
23	0.0021	-0.0606	0.8005	-0.0606	0.0021	0.0000	-0.0000	-0.0071	0.6511	-0.0071	-0.0000	-0.0001
24	-0.0000	0.0021	-0.0607	0.7993	-0.0609	0.0000	-0.0000	-0.0071	-0.0071	0.6517	-0.0072	-0.0001
25	0.0017	0.0001	0.0021	-0.0592	0.7955	-0.0018	-0.0001	-0.0000	-0.0000	-0.0072	0.6457	-0.0012
26	-0.0074	-0.0005	-0.0005	-0.0005	-0.0074	-0.0051	-0.0012	-0.0001	-0.0000	-0.0001	-0.0012	1.1450

5-39 Mo(MePh)2H PLUS, THETA=156°, PHI=50°,
 Orthogonal Coordinates and Orbital Parameters.

EXTENDED HUCKEL CALCULATION.
 WEIGHTED HIJ FORMULA USED.

ATOM	X	Y	Z	N	S	EXP	COUL	M	EXP	COUL	M	D	EXPD1	COUL	C1	CONTRACTED D	C2	EXPD2
MO 1	0.000000	0.000000	0.000000	5	1.960	-8.340	5	1.960	-5.240	4	4.540	-10.500	0.59881	0.59881	1.800			
C 2	0.510205	1.080123	1.958884	2	1.625	-21.400	2	1.625	-11.400									
C 3	-0.842030	1.324967	1.670182	2	1.625	-21.400	2	1.625	-11.400									
C 4	-1.734555	0.244844	1.481745	2	1.625	-21.400	2	1.625	-11.400									
C 5	-1.262845	-1.080123	1.582010	2	1.625	-21.400	2	1.625	-11.400									
C 6	0.095390	-1.324967	1.870712	2	1.625	-21.400	2	1.625	-11.400									
C 7	0.981915	-0.244844	2.059149	2	1.625	-21.400	2	1.625	-11.400									
F 8	1.314994	2.060660	2.129947	2	2.425	-40.000	2	2.425	-18.100									
H 9	-1.212686	2.349232	1.592672	1	1.300	-13.600												
H 10	-2.784539	0.434120	1.258565	1	1.300	-13.600												
H 11	-1.948173	-1.915111	1.436340	1	1.300	-13.600												
H 12	0.460045	-2.349232	1.948222	1	1.300	-13.600												
H 13	2.031698	-0.434120	2.282330	1	1.300	-13.600												
C 14	0.510205	-1.080123	-1.958884	2	1.625	-21.400	2	1.625	-11.400									
C 15	-0.848030	-1.324967	-1.670182	2	1.625	-21.400	2	1.625	-11.400									
C 16	-1.734555	-0.244844	-1.481745	2	1.625	-21.400	2	1.625	-11.400									
C 17	-1.262845	1.080123	-1.582010	2	1.625	-21.400	2	1.625	-11.400									
C 18	0.095390	1.324967	-1.870712	2	1.625	-21.400	2	1.625	-11.400									
C 19	0.981915	0.244844	-2.059149	2	1.625	-21.400	2	1.625	-11.400									
F 20	1.314994	-2.060660	-2.129947	2	2.425	-40.000	2	2.425	-18.100									
H 21	-1.212686	-2.349232	-1.592672	1	1.300	-13.600												
H 22	-2.784539	-0.434120	-1.258565	1	1.300	-13.600												
H 23	-1.948173	1.915111	-1.436340	1	1.300	-13.600												
H 24	0.460045	2.349232	-1.948222	1	1.300	-13.600												
H 25	2.031698	0.434120	-2.282330	1	1.300	-13.600												
H 26	1.728000	0.000000	0.000000	1	1.300	-13.600												

5-40 Mo(MoPh)2H PLUS, THETA=156°, PHI=50°,
Reduced Overlap Population Matrix.

SUM OF ONE-ELECTRON ENERGIES = -1458.924051 EV.

$\phi = 50^\circ$

REDUCED OVERLAP POPULATION MATRIX, ATOM BY ATOM

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	3.8696	0.1040	0.1243	0.0926	0.1207	0.1240	0.0678	-0.0147	-0.0126	-0.0099	-0.0111	-0.0119	-0.0137	0.1040
2	0.1040	2.1178	1.0304	-0.0667	-0.0219	-0.0498	1.0316	0.5584	-0.0567	0.0020	0.0000	0.0020	-0.0560	-0.0006
3	0.1243	1.0304	2.7297	1.0212	-0.0709	-0.0242	-0.0818	-0.0545	0.7956	-0.0610	0.0021	-0.0000	0.0017	-0.0001
4	0.0926	-0.0667	1.0212	2.6806	1.0262	-0.0694	-0.0235	0.0005	-0.0594	0.7999	-0.0607	0.0021	0.0001	-0.0001
5	0.1207	-0.0219	-0.0709	1.0262	2.6773	1.0168	-0.0710	0.0000	0.0021	-0.0609	0.7998	-0.0604	0.0022	-0.0012
6	0.1240	-0.0498	-0.0242	-0.0694	1.0168	2.7108	1.0265	-0.0543	0.0001	0.0021	-0.0605	0.7990	-0.0591	0.0021
7	0.0678	1.0316	-0.0818	-0.0235	-0.0710	1.0265	2.7294	-0.0543	0.0017	-0.0000	0.0021	-0.0608	0.7981	-0.0001
8	-0.0147	0.5584	-0.0545	0.0005	0.0000	0.0001	-0.0017	7.3037	-0.0018	-0.0000	0.0000	-0.0000	-0.0018	0.0000
9	-0.0126	-0.0567	0.7956	-0.0594	0.0021	0.0001	0.0017	-0.0018	0.6454	0.0073	-0.0000	-0.0000	-0.0000	0.0000
10	-0.0099	0.0020	-0.0610	0.7999	-0.0609	0.0021	-0.0000	-0.0000	-0.0000	0.6514	-0.0071	-0.0000	0.0000	0.0000
11	-0.0111	0.0000	0.0021	-0.0607	0.7998	-0.0605	0.0021	0.0000	-0.0000	-0.0071	0.6510	-0.0000	0.0000	0.0000
12	-0.0119	0.0020	-0.0000	0.0021	-0.0604	0.7990	-0.0602	-0.0000	0.0000	-0.0071	0.6510	-0.0071	-0.0000	-0.0000
13	-0.0137	-0.0560	0.0017	0.0001	0.0022	-0.0591	0.7981	-0.0018	-0.0000	-0.0000	-0.0000	-0.0071	-0.0071	0.0000
14	0.1040	-0.0006	-0.0001	-0.0001	-0.0012	0.0021	-0.0001	0.0000	0.0000	0.0000	-0.0000	-0.0000	0.6502	0.0000
15	0.1243	-0.0001	-0.0002	-0.0036	0.0029	0.0005	-0.0005	-0.0000	-0.0000	-0.0001	-0.0008	-0.0000	-0.0000	2.1178
16	0.0926	-0.0001	-0.0036	0.0106	-0.0003	-0.0012	-0.0000	-0.0000	-0.0000	-0.0017	-0.0006	0.0000	0.0000	1.0304
17	0.1207	-0.0012	0.0029	-0.0003	-0.0020	-0.0000	-0.0002	0.0000	-0.0006	-0.0010	-0.0000	-0.0000	-0.0000	-0.0667
18	0.1240	-0.0021	0.0005	-0.0012	-0.0000	-0.0003	-0.0006	-0.0001	-0.0002	-0.0010	-0.0000	-0.0000	-0.0000	-0.0219
19	0.0678	-0.0001	-0.0005	-0.0000	-0.0002	-0.0006	0.0004	-0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0698
20	-0.0147	0.0000	-0.0000	-0.0000	0.0000	-0.0001	0.0000	-0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	1.0316
21	-0.0126	0.0000	-0.0000	-0.0000	-0.0006	-0.0002	0.0000	-0.0000	-0.0000	-0.0004	0.0000	0.0000	0.0000	-0.5584
22	-0.0099	0.0000	-0.0000	-0.0000	-0.0017	-0.0000	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0020
23	-0.0111	-0.0000	-0.0001	-0.0006	-0.0008	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
24	-0.0119	-0.0000	-0.0002	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0020
25	-0.0137	0.0000	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0560
26	-0.5354	-0.0071	-0.0009	-0.0005	-0.0004	-0.0053	0.0037	-0.0004	-0.0001	-0.0000	-0.0000	-0.0006	-0.0083	-0.0071

	15	16	17	18	19	20	21	22	23	24	25	26
1	0.1243	0.0926	0.1207	0.1240	0.0678	-0.0147	-0.0126	-0.0099	-0.0111	-0.0119	-0.0137	0.5354
2	-0.0001	-0.0001	-0.0012	0.0021	-0.0001	0.0000	0.0000	0.0000	-0.0000	-0.0000	0.0000	-0.0071
3	-0.0002	-0.0036	0.0029	0.0005	-0.0003	-0.0000	-0.0000	-0.0001	-0.0008	-0.0002	-0.0000	-0.0009
4	-0.0036	0.0106	-0.0003	-0.0012	-0.0000	-0.0000	-0.0000	-0.0017	-0.0006	0.0000	0.0000	-0.0005
5	0.0029	-0.0003	-0.0020	-0.0000	-0.0002	-0.0000	-0.0002	-0.0000	0.0000	-0.0000	-0.0000	-0.0004
6	0.0005	-0.0012	-0.0000	-0.0003	-0.0006	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0053
7	-0.0005	-0.0000	-0.0002	-0.0006	0.0004	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0037
8	-0.0000	-0.0000	0.0000	-0.0001	0.0000	-0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0004
9	-0.0000	-0.0000	-0.0006	-0.0002	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0001
10	-0.0001	-0.0017	-0.0010	-0.0000	0.0000	-0.0000	-0.0000	-0.0004	0.0000	0.0000	0.0000	-0.0000
11	-0.0006	-0.0006	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0000
12	-0.0002	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0006
13	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0083
14	1.0304	-0.0667	-0.0219	-0.0698	1.0316	0.5584	-0.0567	0.0020	0.0000	0.0020	-0.0560	-0.0071
15	2.7297	1.0212	-0.0709	-0.0242	-0.0818	-0.0545	0.7956	-0.0610	0.0021	-0.0000	0.0001	-0.0009
16	1.0212	2.6806	1.0262	-0.0694	-0.0235	0.0005	-0.0594	0.7999	-0.0607	0.0021	0.0001	-0.0005
17	-0.0709	1.0262	2.6773	1.0166	-0.0710	0.0000	0.0021	-0.0609	0.7998	-0.0604	-0.0004	0.0004
18	-0.0242	-0.0694	1.0168	2.7108	1.0265	0.0005	0.0001	0.0021	-0.0605	0.7990	-0.0591	-0.0053
19	-0.0818	-0.0235	-0.0710	1.0265	-0.0543	7.3037	-0.0017	-0.0000	0.0021	-0.0608	0.7981	0.0037
20	-0.0345	0.0005	0.0000	0.0000	-0.0543	-0.0000	0.0016	-0.0000	0.0000	-0.0000	-0.0018	-0.0004
21	0.7956	-0.0594	0.0021	0.0001	-0.0017	-0.0018	0.6454	-0.0000	-0.0000	-0.0000	-0.0001	0.0001
22	-0.0610	0.7999	-0.0609	0.0021	-0.0000	-0.0000	-0.0073	0.6514	-0.0071	-0.0000	0.0000	-0.0000
23	0.0021	-0.0607	0.7998	-0.0605	0.0021	0.0000	-0.0000	-0.0071	0.6510	-0.0071	-0.0000	-0.0000
24	-0.0000	0.0021	-0.0604	0.7990	-0.0608	-0.0000	-0.0000	-0.0000	-0.0071	0.6517	-0.0071	-0.0006
25	0.0017	0.0001	0.0022	-0.0591	0.7981	-0.0000	-0.0000	0.0000	-0.0000	0.6502	-0.0071	-0.0083
26	-0.0009	-0.0005	-0.0004	-0.0053	0.0037	-0.0004	-0.0001	-0.0000	-0.0000	-0.0006	-0.0083	1.1468

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**Bis(trimethyltin)bis-(η -toluene)-hafnium and -zirconium; X-Ray
Crystal Structure of the Hafnium Compound**

By F. GEOFFREY N. CLOKE, KEVIN P. COX, and MALCOLM L. H. GREEN
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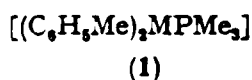
Bis(trimethyltin)bis-(η -toluene)-hafnium and -zirconium; X-Ray Crystal Structure of the Hafnium Compound

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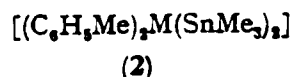
and JIM BASHKIN and KEITH PROUT
(*Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD*)

Summary Treatment of the compound $[\text{Hf}(\eta\text{-C}_6\text{H}_5\text{Me})_2\text{PMe}_3]$ with hexamethylditin gives the compound $[\text{Hf}(\eta\text{-C}_6\text{H}_5\text{Me})_2(\text{SnMe}_3)_2]$, a d^2 , bent bis-arene derivative, the crystal structure of which has been determined; the analogous zirconium compound is similarly prepared.

RECENT reports of the compounds $\{[\text{W}(\text{arene})_2\text{H}]\text{PF}_6\}^1$ and $[(\text{C}_6\text{H}_5\text{Me})_2\text{MPMe}_3]$ (1)² suggested that the chemistry of the bent bis-arene compounds of the transition metals might parallel the extensive and interesting chemistry of their bent bis-(η -cyclopentadienyl) metal analogues. Hence, we have further investigated the bis-arene derivatives.



a; M = Hf
b; M = Zr



Treatment of the compounds (1) with hexamethylditin at 45 °C gave a smooth reaction and, from the resulting deep red-purple solutions, black crystals of the compounds $[\text{M}(\text{C}_6\text{H}_5\text{Me})_2(\text{SnMe}_3)_2]$ (2), were isolated; ^1H n.m.r. (C_6H_6):

(2a) τ 4.47, 5.27, and 6.02 {[2H, t, J (H-H) 6.9 Hz], [4H, d, J (H-H) 6.0 Hz], and [4H, t, J (H-H) 6.9 Hz], respectively, all $2 \times \text{Ph}$ }, 8.49 [6H, t, J (Sn-H) 10 Hz, $2 \times \text{CMe}$], and 9.42 [18H, t, J (Sn-H) 29 Hz, $6 \times \text{SnMe}$]; (2b) 4.46, 5.29, and 6.03 {[2H, t, J (H-H) 6.9 Hz], [4H, d, J (H-H) 6.0 Hz], and [4H, t, J (H-H) 6.9 Hz], respectively, all $2 \times \text{Ph}$ }, 8.74 [6H, t, J (Sn-H) 8 Hz, $2 \times \text{CMe}$], and 9.44 [18H, t, J (Sn-H) 29 Hz, $6 \times \text{Me}$].

Solutions of the compounds (2) are very sensitive to oxygen and are slowly hydrolysed. Crystals of the compounds (2) are only slowly decomposed in air (hours). The mass spectrum of (2a)[†] shows a parent-ion centred at m/e 690, with the expected isotope-distribution pattern.

The crystal structure of (2a) has been determined.

Crystal structure: $\text{C}_{20}\text{H}_{14}\text{HfSn}_2$, M 690.09, monoclinic, space group $C_{2/c}$, $a = 14.027(3)$, $b = 9.714(3)$, $c = 17.946(8)$ Å, $\beta = 111.11(4)^\circ$, $U = 2281$ Å³, $Z = 4$, $F(000) = 1304$, $D_c = 2.01$ g cm⁻³. Intensities of 3326 independent reflections were measured ($2\theta_{\text{max}} = 52^\circ$) on a CAD-4 diffractometer using graphite-monochromated Mo- K_α radiation. 1737 Reflections with $I > 3\sigma(I)$, corrected for absorption [$\mu(\text{Mo-}K_\alpha) = 66.8$ cm⁻¹], were used in the refinement

[†] Satisfactory microanalyses have been obtained.

procedure. The structure was solved by heavy-atom and difference-Fourier methods and refined by full-matrix least-squares methods, using anisotropic temperature factors. The current R value is 0.031.[†] Each hafnium atom is located on a two-fold axis (Figure). The molecular configuration adopted is analogous to that of the d^2 , 18-electron $\{[\eta\text{-C}_6\text{H}_5)_2\text{MX}_2]\}$ compounds; the Sn(1)–Hf–Sn(1B) angle is less than 90° and the angle between the normal and the least-squares best-plane of the arene rings is 138.9° (c.f. the corresponding angles for $[\text{Mo}(\eta\text{-C}_6\text{H}_5)_2\text{Br}(\text{SnBr}_3)]$ which are 80.2 and 128.3° , respectively³).

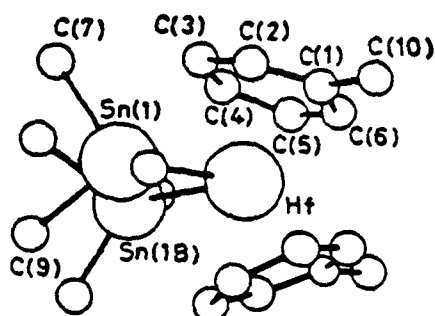


FIGURE. Molecular structure of (2a). Bond distances to the Hf atom are Sn(1) 2.953(1), C(1) 2.496(9), C(2) 2.491(9), C(3) 2.517(9), C(4) 2.523(9), C(5) 2.43(1), and C(6) 2.43(1) Å. The angle Sn(1)–Hf–Sn(1B) is $81.14(3)^\circ$.

The trimethyltin ligand was chosen because of its bulk which would give a sterically saturated molecule, which normally leads to thermal stability. In fact, compound (2a) has a slight curvature of the normally planar C_6 -ring which may reflect steric strain. Further, the trimethyltin group is electropositive relative to other common ligands. We wished to avoid a build-up of positive charge on the transition metal centres and thereby encourage back-donation from the d^2 metal electrons. Hexamethylditin may be regarded as 'bulky dihydrogen.'

The compounds (1) are clearly analogues of the d^4 compounds $[(\eta\text{-C}_6\text{H}_5)_2\text{ML}]$, $\text{M} = \text{Mo}$ or W and $\text{L} = \text{R}_2\text{P}$ or CO .⁴ Correspondingly, the compounds (2) are the first bis- η -arene analogues of the d^2 compounds $[(\eta\text{-C}_6\text{H}_5)_2\text{MR}_2]$, $\text{M} = \text{Mo}$ or W and $\text{R} = \text{alkyl}$.⁵

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[†] Atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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Inter-relationships in Molybdenocene Dimer Chemistry: a Convenient Synthesis of Bis- η -cyclopentadienyldichloromolybdenum

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The dimers $[(\eta\text{-C}_5\text{H}_5)_2\text{HMo}\{\mu\text{-}(\eta^1:\eta^5\text{-C}_5\text{H}_4)\}\text{Mo}(\eta\text{-C}_5\text{H}_5)]$ and $[(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{Mo}\text{-}\mu\text{-}(\eta^5:\eta^1\text{-C}_5\text{H}_4)\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ have been prepared from $[\text{Mo}_2(\text{O}_2\text{CMe})_4]$ and characterised by crystal structure determination; the former dimer reacts readily with aqueous hydrochloric acid forming the dichloro-monomer $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$.

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The dimers $[(\eta\text{-C}_5\text{H}_5)_2\text{HMo}(\mu\text{-}(\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4))\text{Mo}(\eta\text{-C}_5\text{H}_5)]$ and $[(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{Mo}\text{-}\mu\text{-}(\eta^5\text{:}\eta^1\text{-C}_5\text{H}_4)\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ have been prepared from $[\text{Mo}_2(\text{O}_2\text{CMe})_4]$ and characterised by crystal structure determination; the former dimer reacts readily with aqueous hydrochloric acid forming the dichloro-monomer $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$.

Treatment of the dimer $[\text{Mo}_2(\text{O}_2\text{CMe})_4]$ (1) in tetrahydrofuran (THF) with triphenylphosphine (2 mol) and sodium cyclopentadienide (5 mol) at room temperature causes a smooth reaction. After 20 min slightly soluble black hexagonal plates of the binuclear molybdenocene dimer $[(\eta\text{-C}_5\text{H}_5)_2\text{HMo}(\mu\text{-}(\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4))\text{Mo}(\eta\text{-C}_5\text{H}_5)]$ (2) are deposited in 55% yield. In a typical reaction 12 g of (2) were prepared and isolated in

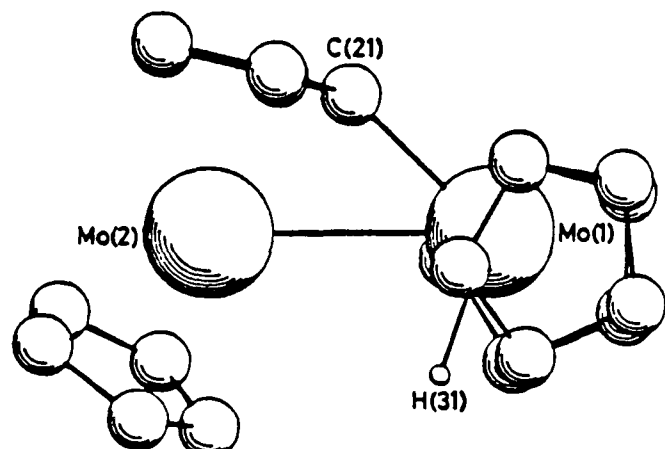


Figure 1. Molecular structure of (2). The nearly eclipsed configuration of the rings about Mo(1) is shown, as is the perpendicularity of the two $(\eta\text{-C}_5\text{H}_5)_2\text{Mo}$ units. Ring hydrogens are omitted for clarity. Key parameters are: Mo(1)–Mo(2) 3.189(1), Mo(1)–H(31) 1.72, Mo(1)–C(21) 2.21(1), Mo(2)–C(21) 2.23(1) Å; C(21)–Mo(1)–H(31) 115.0(4), C(21)–Mo(1)–Mo(2) 44.4(3)°. The angle between the ring-normals about Mo(1) is 134° and about Mo(2) is 154°.

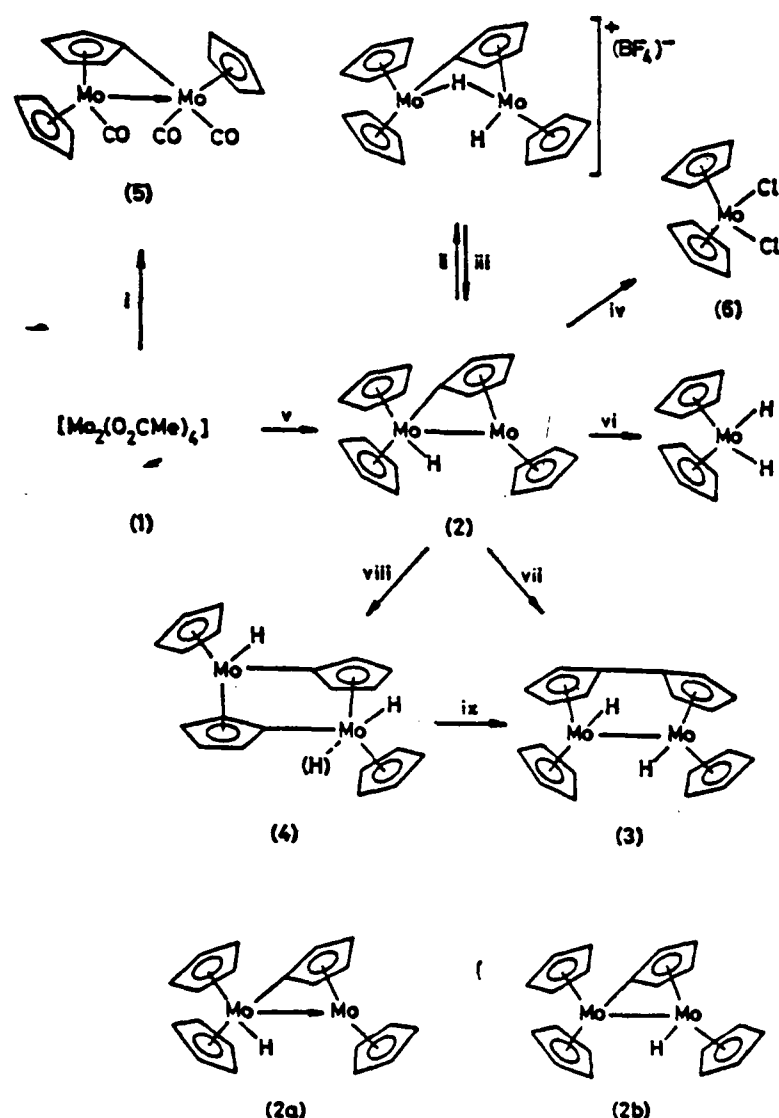
a day. If triphenylphosphine is absent then the green dimer $[(\text{Mo}(\eta\text{-C}_5\text{H}_5)\text{H})_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]$ (3) is formed.¹

The crystal structure of (2) has been determined and the structure is shown in Figure 1.

Crystal data for (2): $\text{C}_{20}\text{H}_{20}\text{Mo}_2$, M 452.10, monoclinic, space group $P2_1/c$, $a = 13.674(7)$, $b = 8.012(7)$, $c = 13.37(1)$ Å, $\beta = 108.69(6)^\circ$, $U = 1595$ Å³, $Z = 4$, $D_{\text{calc}} = 1.88$ g cm⁻³. Intensities of 5865 reflections were measured ($2\theta_{\text{max}} = 52^\circ$) on a CAD-4 diffractometer using graphite-monochromated Mo- K_α radiation. 2149 independent reflections [$I \geq 3\sigma(I)$], corrected for absorption [$\mu(\text{Mo-}K_\alpha) = 15.30$ cm⁻¹], were used in the refinement. The structure was solved by heavy-atom and Fourier methods and refined by least squares with a large-block approximation to the normal matrix. Non-hydrogen atoms were refined anisotropically. Ring hydrogens were located in difference maps and then placed geometrically ($\text{C-H} = 1.0$ Å), their positions being adjusted after each cycle. The hydride was located in a difference map and included in the model, but, as with the other hydrogens, its parameters were not refined. The current R -value is 0.062 ($R_w = 0.088$).†

A difference-Fourier map shows a peak near Mo(1) in a position appropriate for a Mo-hydride. This location for the

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Scheme 1. i, NaC_5H_5 , THF, CO (1 atm), room temp., 15 min, 42%; ii, aq. tetrafluoroboric acid, room temp. 67%; iii, aq. NaOH, 70%; iv, excess of aq. HCl (6 M) at room temp., 5 min, 78%; v, NaC_5H_5 , THF, PPh_3 , room temp. for 20 min, 55%; vi, excess of aq. NaOH, 100 °C for 5 h, 60%; vii, warm in THF 45 °C for 5 h, 100%; viii, suspension in water at 100 °C, 5 h, 50%; ix, toluene, 70 °C.

hydrogen is supported by comparison with the molecular geometry of the compound $[(\eta\text{-C}_5\text{H}_5)_2\text{NbH}(\mu\text{-}(\eta^1\text{-}\eta^5\text{-C}_5\text{H}_5))\text{-Fe}(\text{CO})_2]$.² The i.r. spectrum of (2) shows a band at 1900 cm^{-1} assignable to a Mo–H stretching mode. The ^1H n.m.r. spectrum of very dilute solutions of (2) in $[\text{D}_6]\text{THF}$ shows a single band at high field (τ 21.99) assignable to a Mo–hydride resonance. However, there are also bands at τ 18.75 and 19.04 assignable to other hydrido-derivatives and after a few hours the spectrum showed the appearance of bands due to the previously described³ dimers (3) and (4). We conclude that the data are consistent with the isomer (2a) shown in Scheme 1 but do not conclusively eliminate isomer (2b).

The role of triphenylphosphine in the synthesis of (2) is unknown but it is likely that it acts to stabilise some intermediate in the reaction. For example, the black dimer (2) is formed⁴ in small yield by treatment of the compounds $[\text{Mo}_2\text{Cl}_2(\text{OAc})_2(\text{PR}_3)_2]$ ($\text{R} = \text{Ph}$ or Bu^n) with sodium cyclopentadienide in THF. Further, treatment of (1) with sodium cyclopentadienide in the presence of carbon monoxide rather than Ph_3P gives the binuclear carbonyl derivative $[(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{Mo}-\mu\text{-}(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (5).

The i.r. spectrum of (5) shows bands at 1945, 1870, and 1765 cm^{-1} (KBr) assignable to terminal carbonyl groups and possibly a semi-bridging CO group. The crystal structure of (5), given in Figure 2, shows that the Mo(2)–C(7) distance is

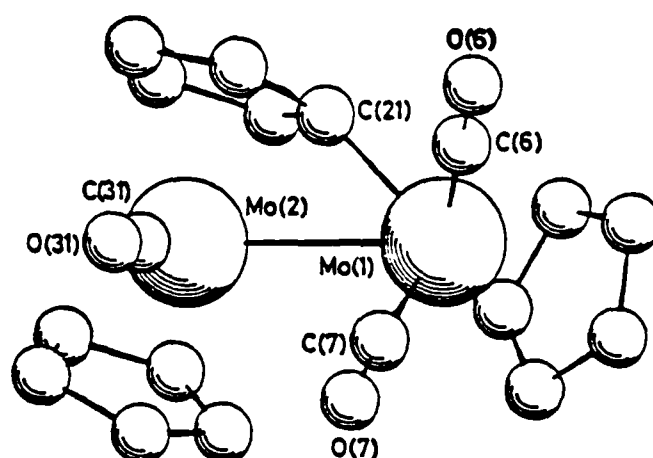


Figure 2. Molecular structure of (5). Hydrogens are omitted for clarity. Key parameters are: Mo(1)–Mo(2) 3.089(1), Mo(1)–C(6) 1.914(4), Mo(1)–C(7) 1.949(4), Mo(1)–C(21) 2.117(4), C(6)–O(6) 1.174(5), C(7)–O(7) 1.160(6), Mo(2)–C(21) 2.218(3), Mo(2)–C(7) 3.240(4), C(31)–O(31) 1.142(5) Å; C(6)–Mo(1)–C(7) 79.0(2), Mo(1)–Mo(2)–C(31) 94.77(8), Mo(1)–C(6)–O(6) 179.4(4), Mo(1)–C(7)–O(7) 175.6(4), Mo(2)–C(31)–O(31) 177.9(4)°. The angle between ring-normals about Mo(2) is 148.2°.

3.240(4) Å. A donor–acceptor metal–metal bond is proposed to attain an 18-electron environment at Mo(1).

Crystal data for (5): $\text{C}_{18}\text{H}_{14}\text{Mo}_2\text{O}_3$, M 470.08, monoclinic, space group $P2_1/n$, $a = 8.644(2)$, $b = 15.336(2)$, $c = 12.203(6)$ Å, $\beta = 92.59(3)^\circ$, $U = 1616\text{ Å}^3$, $Z = 4$, $D_{\text{calc}} = 1.93\text{ g cm}^{-3}$. Intensities of 6699 reflections were measured ($2\theta_{\text{max}} = 60^\circ$) as above. 3575 independent reflections with $I \geq 3\sigma(I)$, corrected for absorption [$\mu(\text{Mo-K}\alpha) = 15.3\text{ cm}^{-1}$], were used in the refinement. The structure was solved by heavy-atom and Fourier methods and refined by least squares with a large-block approximation to the normal matrix. All atoms were refined anisotropically except for the hydrogens, which were placed ($\text{C-H} = 1.0\text{ Å}$) geometrically after being located in a difference map. The current R -value is 0.033 ($R_w = 0.045$).

Treatment of (2) with hydrochloric acid gives the compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ (6) in 78% yield. The compound (6) is well known but the normal synthesis is tedious.^{5,6} Using the reactions described here it is possible to convert (1) into (6) in ca. 43% yield on a 10–12 g scale in two days. This represents a very convenient laboratory synthesis for (6).

Finally, Scheme 1 shows the reactions, structures, and interrelationships of the new and known molybdenocene dimers and some of their derivatives. The black dimer (2) can be seen to be the precursor for the yellow dimer (4) which, in turn, is thermally converted in toluene solution at 70 °C into the green isomer (3). The dimer (3) appears therefore to be the thermodynamically stable isomer but, nonetheless, (2) is partially converted into (4) in the presence of water at 100 °C; surprisingly, under these conditions no (3) is formed.

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Synthesis of Hexakis(trimethylphosphine)molybdenum using Molybdenum Atoms and its X-Ray Crystal Structure

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Co-condensation of molybdenum atoms with an excess of trimethylphosphine gives hexakis(trimethylphosphine)molybdenum which crystal structure studies show to have an octahedral MoP₆ unit; it is highly reactive to substitution by dinitrogen, olefins, and dihydrogen, forming a variety of derivatives.

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Transition metal compounds which have high energy (electron-rich) centres frequently are reactive towards normally inert systems such as carbon-hydrogen bonds and dinitrogen.

Amongst the monodentate tertiary phosphines, trimethylphosphine combines strongly electron-releasing properties with relative compactness of size. We set out to synthesise a

compound of the type $\text{Mo}(\text{PMe}_3)_n$ using the method of metal vapour synthesis.

In a typical experiment, molybdenum atoms (1 g) were co-condensed with an excess of trimethylphosphine (50 cm³) using the apparatus recently described.¹ After removal of the volatile trimethylphosphine and recrystallisation of the red-orange residue from cyclohexane, orange crystals of $\text{Mo}(\text{PMe}_3)_6$ (1) were obtained in ca. 55% yield.

The compound (1) has been characterised by crystal structure determination and microanalysis [Found Mo: 17.6%; (1) requires 17.4%]. The mass spectrum shows a highest band assignable to the cation $[\text{Mo}(\text{PMe}_3)_6]^+$.

Crystal data: $\text{C}_{18}\text{H}_{54}\text{MoP}_6$, $M = 551.97$, cubic, space group $Im\bar{3}m$, $a = 11.319(2)$ Å, $U = 1450$ Å³, $Z = 2$, $D_c = 1.26$ g cm⁻³. Intensities of 1622 reflections were measured ($2\theta_{\text{max}} 60^\circ$) on a CAD-4 diffractometer using Mo- K_α radiation. The structure was solved by Patterson and difference-Fourier methods, and refined by full-matrix least squares using 224 independent reflections [$I > 3\sigma(I)$], not corrected for absorption [$\mu(\text{Mo-}K_\alpha) 7.3$ cm⁻¹].†

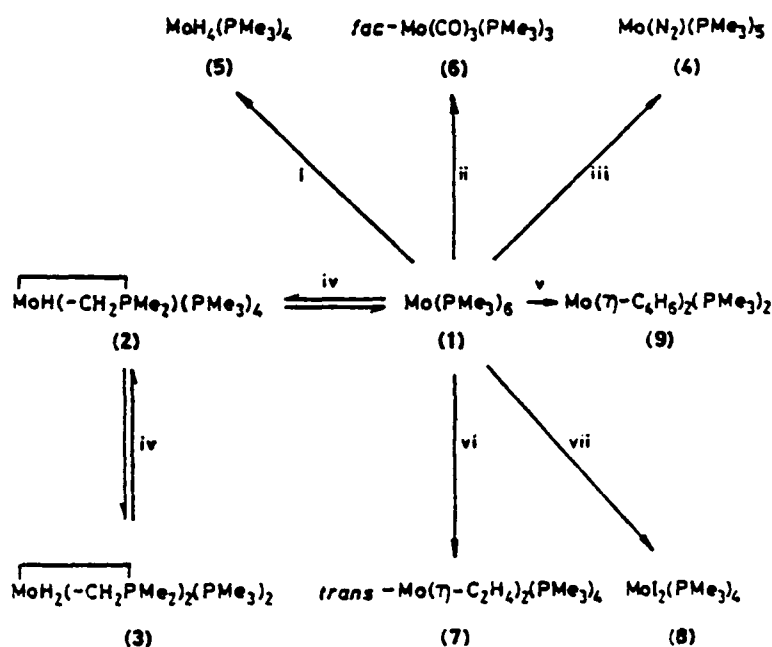
The P atoms lie on sites of crystallographic $4mm$ symmetry, requiring at least four-fold disorder for the methyl groups. The disorder was modelled by placing two independent carbons on the mirror-planes at (x, y, y) and $(x, y, 0)$. C(1) and C(2) were given a relative occupancy of 2:1 in accord with difference-Fourier peak heights and cell symmetry, and were refined with isotropic temperature factors. Symmetry requires that Mo(1) be refined isotropically as well, but P(1) was allowed anisotropic temperature factors. The R -value is 0.052, and R_w is 0.069.

The molecule has an octahedral arrangement of the six phosphorus atoms about the central Mo, with a separation Mo(1)–P(1) of 2.467(2) Å. This is considerably longer than the Mo–P bond-length of 2.421(3) found in another zero-valent Mo–phosphine compound, $\text{Mo}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_3$,² and may reflect steric pressure caused by the bulky PMe_3 ligands. The angles Mo(1)–P(1)–C(1) and Mo(1)–P(1)–C(2) are 118.1(8) and 126(1)°, respectively; the P(1)–C(1) bond length is 1.884(4) Å, and the distance P(1)–C(2) is 1.880(4) Å.

The ¹H and ³¹P n.m.r. spectra of solutions of (1) in C_6H_6 show that partial dissociation of trimethylphosphine has occurred and that (1) is in equilibrium with small quantities of two hydrido-compounds. The spectra may be interpreted in terms of an equilibrium between the compounds (2) and (3) shown in Scheme 1; for both molecules the phosphorus nuclei are made equivalent by a rapid fluxional process involving reversible C–H addition of a methyl group to the molybdenum centres. (Partial ¹H n.m.r. data (C_6D_6) are for (1) 8.64 τ (s, no P–H coupling owing to rapid exchange of PMe_3 groups); for (2) 15.67 τ [sext., $J(\text{P–H})$ 40.5 Hz, MoH]; for (3) 14.0 τ [quint., $J(\text{P–H})$ 45.2 Hz, MoH₂].)

In accord with the long Mo–P distances, the trimethylphosphine ligands of (1) are highly labile and (1) very readily undergoes ligand substitutions.

Treatment of solutions of (1) in light petroleum with dinitrogen at 15 atm forms the compound $\text{Mo}(\text{PMe}_3)_4\text{N}_2$ (4). Similarly, treatment of (1) with hydrogen, carbon monoxide, ethylene, or butadiene causes in each case a smooth displacement of two or more trimethylphosphine ligands and the reactions and structure proposed for the products, namely (5)–(7), (9), respectively, are shown in Scheme 1. Treatment of (1) with methyl iodide gives the di-iodo-compound (8). The



Scheme 1. Conditions and yields: i, hydrogen at 2 atm and 20 °C in light petroleum, >60%; ii, CO at 2 atm and 20 °C in light petroleum, >90%; iii, dinitrogen at 15 atm and 20 °C in light petroleum, $\nu(\text{N}_2)$ 1950 cm⁻¹ (mull), >90%; iv, solution in benzene at 20 °C, reversible dissociation of a PMe_3 group, followed by C–H metallation; v, excess of butadiene at 20 °C in light petroleum, >60%; vi, ethylene at 2 atm and 20 °C in light petroleum, >60%; vii, excess of methyl iodide at 20 °C in light petroleum, >60%.

compounds (4), (6), (7), and (8) have been independently prepared and characterised.^{3,6} The compounds (4)–(9) have been characterised by microanalysis, mass spectra, and by n.m.r. spectroscopy.

There is a very marked difference between the reactivity of (1) and that of the previously described analogue containing the bis(1,2-dimethylphosphino)ethane ligand, namely $\text{Mo}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_3$,^{2,4} which is very inert to substitution and, for example, protonates with hydrogen chloride forming the dihydrido-derivative $[\text{MoH}_2(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_3]^{2+}$.⁶ Further, the compound $\text{Mo}[\text{P}(\text{OMe})_3]_6$ is inert to substitution except when photolysed.⁷

The molybdenum centre in (1) is probably highly electron-rich and this, together with the steric overcrowding, can account for the exceptional lability and ease of substitution of the PMe_3 ligands. The compound (1) is clearly a useful precursor to a wide variety of low valent derivatives.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

