BODLEIAN LIBRARY OXFORD
DEPOSITED
THESIS
2·5·73

THE CHEMISTRY OF TITANIUM

AND RELATED STUDIES

by

C. R. LUCAS

Thesis submitted in part fulfilment of the
requirements for the degree of
Doctor of Philosophy
at the
University of Oxford

Balliol College,
Oxford.

November,
1972.

The work described in this thesis was carried out in the Inorganic Chemistry Laboratory, South Parks Road, Oxford, from October 1969 to September 1972, under the supervision of Dr. M.L.H. Green. All the work is my own unless stated to the contrary, and it has not been submitted for any degree in this or any other university.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor, Dr. M. L. H. Green, for his constant good humour and enthusiasm and for his patience on those occasions when the work was not proceeding rapidly. I should also like to thank all my laboratory colleagues for their co-operation, but in particular I am grateful to Mr. L.C. Mitchard and Mr. F.W.S. Benfield who from time to time ran n.m.r. spectra for me and at all times provided light entertainment in the laboratory. My thanks are due as well to Drs. J. Knight, W.E. Silverthorn, J.S. Poland, and B.R. Francis for helpful discussions and advice and to Dr. R. Forder for the structure determination reported in Chapter III. I wish also to acknowledge Titanium Intermediates Limited who provided the money for this project. Finally, I am most grateful to my wife who has not only typed portions of this thesis but who has also cheerfully borne the vicissitudes of the last three years and without whose help and encouragement this thesis would never have been completed.

ABSTRACT

This thesis describes some studies of mono- and bis(π-cyclopentadienyl)titanium and bis(π-cyclopentadienyl)-niobium systems. In Chapter I, publications which are relevant to work discussed later in the text and which have appeared in the literature since 1967 are reviewed. At the end of the chapter, a formal method for the classification of covalent compounds of an element in terms of electron number, valence number, and ligand bond number is described and its usefulness illustrated.

In Chapter II, the preparation and some properties of several complexes of trivalent titanium with nitrogen- and phosphorus-donor ligands are described, as well as two new preparations of $[(\pi\text{-}C_5H_5)_2TiCl]_2$ and a preparation of $[(\pi\text{-}C_5H_5)TiCl_2]_n$. The new complexes are of the form: $(\pi\text{-}C_5H_5)_2TiCl\cdot L$ (L = a monodentate ligand), $[(\pi\text{-}C_5H_5)_2Ti\cdot L_2']A$ (L_2' = a chelating bidentate ligand; A = Cl or PF_6), $[(\pi\text{-}C_5H_5)_2TiCl]_2\cdot L_2''$ (L_2'' = a bridging bidentate ligand), $(\pi\text{-}C_5H_5)TiCl_2\cdot 2L$ and $(\pi\text{-}C_5H_5)TiCl_2\cdot L_2'$. These compounds were characterized by analysis, i.r. and in some cases e.s.r. spectroscopy. In some cases, cryoscopic molecular weight determinations and solution conductivity studies were made. From the occurrence of these compounds, certain conclusions about the electronic and steric environments of π-cyclopentadienyltitanium species are drawn and the

implications of these conclusions, concerning the ability of such systems to function as nitrogen fixation catalysts, are discussed.

In Chapter III, several attempts to prepare trivalent organo-titanium compounds, $(\pi\text{-}C_5H_5)_2TiR$ or $(\pi\text{-}C_5H_5)TiR_2$, that contain the metal bonded only to carbon are described. It seems that such compounds are unstable with respect to disproportionation and as a result, certain conclusions are drawn concerning the structure of the compound currently formulated as $(\pi\text{-}C_5H_5)_2TiPh$. The divalent and tetravalent titanium-containing products of several disproportionation reactions have been examined and the tetravalent ones of general formula $(\pi\text{-}C_5H_5)_2TiR_2$ or $(\pi\text{-}C_5H_5)TiR_3$ have been identified. A mechanism is proposed for the disproportionation reactions and some studies in support of the proposed mechanism are reported. The reversible fixation of molecular nitrogen by a system similar to that described by Vol'pin and Shilov is also described briefly.

As a result of the conclusions reached in Chapter III concerning the instability with respect to disproportionation of trivalent organo-titanium compounds, an attempt was made to obtain information concerning the structure of the stable trivalent titanium compound, $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)$. This initially involved oxidation of that compound with ferric chloride, silver hexafluorophosphate and silver

tetrafluoroborate, in hopes of obtaining the cation $\left[(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)\right]^+$. The product of these reactions was, however, $(\pi\text{-}C_5H_5)_2TiX_2$, X having been derived from the anionic part of the oxidizing agent. The structure of tris(cyclopentadienyl)titanium was therefore determined and a unique type of bonding between the metal and only two carbon atoms of one of the three planar cyclopentadienyl rings was discovered.

In Chapter IV, new preparations of $(\pi\text{-}C_5H_5)_2NbCl_2$, $(\pi\text{-}C_5H_5)_2NbBH_4$, and $(\pi\text{-}C_5H_5)_2Nb(H)PR_3$ in high yield are described. The properties of the hydrides as Lewis bases have been examined and as a result, the dihydride cation, $\left[(\pi\text{-}C_5H_5)_2Nb(H)_2PMe_2Ph\right]^+$, has been isolated and characterized. Investigation of phosphine exchange is reported as is the preparation of a highly reactive substance believed to be $(\pi\text{-}C_5H_5)_2Nb(CN)TCNE$. Exchange of the hydride ligand for a halogen to give $(\pi\text{-}C_5H_5)_2Nb(Br)PMe_2Ph$ is reported, as well as the ease with which the phosphine hydrides are oxidized to the corresponding dihalides, $(\pi\text{-}C_5H_5)_2NbX_2$, by substances containing halogen atoms or pseudohalogen functional groups. This property has led to the preparation, inter alia, of $(\pi\text{-}C_5H_5)_2NbBr_2$ and $(\pi\text{-}C_5H_5)_2Nb(NCS)_2$. Finally, brief comparison between niobium, molybdenum, and titanium chemistry relevant to the work in this thesis is made.

In Chapter V, details of instrumentation and experimental

procedure are given while in the Appendix tables of analytical, molecular weight, conductivity, i.r.,and decomposition point data are presented, as well as the preparation and a few reactions of $\{[(\pi\text{-}C_6Me_6)TiCl_2]_3\}Cl$.

LIST OF ABBREVIATIONS

petroleum ether = a mixture of aliphatic hydrocarbons, boiling range 30°-40°.

ether = diethyl ether

diphos = bis(1,2-diphenylphosphino)ethane

DMPE = bis(1,2-dimethylphosphino)ethane

en = ethylenediamine

Me en = sym-dimethylethylenediamine

dipy = 2,2′-dipyridyl

py = pyridine

TCNE = tetracyanoethylene

Cp = π-cyclopentadienyl

CONTENTS

CHAPTER I: Introduction 1

A. Titanium in Nitrogen Fixation 1

1. Reversibly Formed Complexes of Molecular Nitrogen 3

2. Nitride-Like Substances 9

3. Mixtures Yielding Organic Nitrogen Compounds 13

B. Other Organo-Titanium Compounds 15

1. Titanocene and the Titanium Hydrides 16

2. Other Cyclopentadienyl and Alkyl Compounds 26

3. Bonding in Bent Bis(π-cyclopentadienyl)metal Compounds 32

C. A Classification Scheme for Compounds of Niobium and Other Elements 36

D. References 45

CHAPTER II: Some d^1 Mono- and Bis(π-cyclopentadienyl)-titanium Compounds with Nitrogen and Phosphorus Donor Ligands 52

A. Introduction 52

B. Chemical Studies 56

1. Preparation of $[(\pi\text{-}C_5H_5)_2TiCl]_2$ 56

2. Preparation of $(\pi\text{-}C_5H_5)_2TiCl\cdot NH_2R$ and $(\pi\text{-}C_5H_5)_2TiCl\cdot py$ 59

3. Preparation of $(\pi\text{-}C_5H_5)_2TiCl\cdot PR_3$ and $[(\pi\text{-}C_5H_5)_2TiCl]_2\cdot diphos$ 61

4. Preparation of $\left[(\pi\text{-}C_5H_5)_2Ti\cdot L'_2\right]A$ 63

5. Preparation of $(\pi\text{-}C_5H_5)TiCl_2\cdot 2L$ 64

6. Characterization of the New Compounds 66

7. Properties of the New Compounds 74

8. Reactions of the New Compounds 76

C. Discussion 79

1. Stereochemical Considerations 80

2. Electronic Considerations 83

3. Conclusion 84

D. References 87

CHAPTER III: Some Reactions and Properties of d^1 Cyclopentadienyl Titanium Species with Metal-Carbon σ-Bonds 91

A. Introduction 91

B. Chemical Studies 92

1. Disproportionation Reactions: Mono-π—cyclopentadienyl Systems 92

2. Disproportionation Reactions: Bis-π-cyclopentadienyl Systems 96

3. The Divalent Titanium-Containing Residues 99

4. Reactions and Structural Features of $(\pi\text{-}C_5H_5)_nTiR_{3-n}$ 102

5. The Structure of Tris(cyclopentadienyl)titanium 105

C. Discussion 108

D. References 115

CHAPTER IV: Some Features of the Chemistry of Lower-Valent Bis(π-cyclopentadienyl)niobium Compounds 118

A. Introduction 118

B. Chemical Studies 119

1. Preparation of $(\pi\text{-}C_5H_5)_2NbCl_2$ 119

2. Preparation of $(\pi\text{-}C_5H_5)_2NbBH_4$ 121

3. Reactions of $(\pi\text{-}C_5H_5)_2NbBH_4$ with Donor Ligands 123

4. Reactions of $(\pi\text{-}C_5H_5)_2Nb(H)PR_3$; Basic Character 125

5. Reactions of $(\pi\text{-}C_5H_5)_2Nb(H)PR_3$; Ligand Exchange 133

6. Reactions of $(\pi\text{-}C_5H_5)_2Nb(H)PR_3$; Hydride Reactivity 135

7. Reactions of $(\pi\text{-}C_5H_5)_2Nb(H)PR_3$; Nature of the Nb-H Bond 139

C. Discussion 142

D. References 146

CHAPTER V: Experimental 149

A. Introduction 149

1. Instrumentation 149

2. Techniques 151

B. Details from Chapter II 152

C. Details from Chapter III 156

D. Details from Chapter IV 163

E. References 169

APPENDIX 170

A. Table of Analytical Data, Melting Points and Colours of Compounds 170

B. Data from Conductance Measurements 173

C. Infrared Spectra 174

D. Cryoscopic Molecular Weights 180

E. Studies on $\left\{\left[(\pi\text{-}C_6Me_6)TiCl_2\right]_3\right\}Cl$ 180

LIST OF TABLES

II.I	New Compounds Reported in Chapter II	57
II.II	Conductivity Studies of $\left[(\pi\text{-}C_5H_5)_2Ti\cdot en\right]PF_6$	71
II.III	Trends in Thermal Stability of Phosphine Adducts	82
III.I	Bond Lengths in Tris(cyclopentadienyl)titanium	107
IV.I	Ionization Potentials of Titanium and Niobium	119
IV.II	Some I.r. and N.m.r. Data for New Bis(π-cyclopentadienyl)-niobium Compounds	126
IV.III	Trends in Thermal Stabilities of Bis(π-cyclopentadienyl)-metal Hydrides	145

LIST OF FIGURES

I.I A Proposed Structure of a Titanocene-Nitrogen Complex 8

I.II A Catalytic System for Converting Nitrogen into Ammonia 10

I.III Illustration of the Equatorial Plane in Bis(π-cyclopentadienyl)titanium Compounds 16

I.IV A Possible Structure of Thermally Stable Titanocene 19

I.V A Possible Structure of Thermally Stable Titanocene 19

I.VI Structure of the Reaction Product of Titanocene and $AlEt_3$ 22

I.VII Proposed Structure of $(\pi\text{-}C_5Me_5)(\pi\text{-}C_5Me_4\text{-}\sigma\text{-}CH_2\text{-})TiMe$ 25

I.VIII Proposed Structure of $(\pi\text{-}C_5Me_5)_2TiH_2$ 26

I.IX Structure of $(\pi\text{-}C_5H_5)_2Ti(OOCC_6H_4)$ 30

I.X Ballhausen-Dahl Bonding Model for Bent Bis-π-cyclopentadienyl Systems 32

I.XI Alcock Bonding Model for Bent Bis-π-cyclopentadienyl Systems 33

I.XII Partial M.O. Diagram for Bent Bis-π-cyclopentadienyl Systems 33

I.XIII Classification Chart for Covalent Compounds of Molybdenum 40

I.XIV Classification Chart for Covalent Compounds of Niobium 40

I.XV Classification Chart for Covalent Compounds of Titanium 40

I.XVI A Pictorial Representation of Various Types of Reactions 42

II.I A Possible Mechanism of Nitrogen Fixation by Bis(π-cyclopentadienyl)titanium Compounds 53

II.II	Proposed Structure of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2ZnCl_2$	59
II.III	Proposed Structure of $(\pi\text{-}C_5H_5)_2TiCl\cdot L$	67
II.IV	Proposed Structure of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2\cdot$diphos	68
II.V	Proposed Structure of $\left[(\pi\text{-}C_5H_5)_2TiL'_2\right]^+$	69
II.VI	Proposed Structure of $(\pi\text{-}C_5H_5)TiCl_2\cdot 2L$	72
III.I	Structure of Tris(cyclopentadienyl)titanium	107
III.II	Projection of Tris(cyclopentadienyl)titanium on the Ti-C31-C32 Plane	107
IV.I	Some Features of Bis(π-cyclopentadienyl)niobium Chemistry	119
IV.II	A Possible Structure of $\left[(\pi\text{-}C_5H_5)_2Nb(H)_2PR_3\right]$	127
IV.III	A Possible Structure of $\left[(\pi\text{-}C_5H_5)_2Nb(H)_2PR_3\right]$	127
IV.IV	Proposed Mechanism for the Reaction Between $(\pi\text{-}C_5H_5)_2MoH_2$ and HCl	131
IV.V	Proposed Mechanism for the Reaction Between $(\pi\text{-}C_5H_5)_2Nb(H)PR_3$ and HCl	132
V.I	A Conductance Cell for Air-Sensitive Solutions	150
V.II	Device for Measurement of Cryoscopic Molecular Weights of Air-Sensitive Compounds	150
APPENDIX	Device for Preparation of $\left\{\left[(\pi\text{-}C_6Me_6)TiCl_2\right]_3\right\}Cl$	181

CHAPTER I

Introduction

This thesis describes certain aspects of the chemistry of lower valent titanium and niobium compounds. Some recent developments in the chemistry of such systems is presented in this introductory chapter but it is not intended to be a comprehensive survey and therefore covers only those publications that have a bearing on work appearing later in the thesis.

A number of useful books and reviews of both the academic and industrial literature are available(A1-A5) for the period up to 1968 and so this chapter will be concerned primarily with reports which have appeared subsequently. These reports and other material are discussed under the headings: A. Titanium in nitrogen fixation; B. Other organo-titanium compounds; C. A classification scheme for covalent compounds of niobium and other elements.

A. Titanium in Nitrogen Fixation

Titanium has figured prominently in the quest for a non-biological nitrogen fixation catalyst for several reasons. The reaction of nitrogen gas with titanium metal is very exothermic, being -80 kcal/mol (A6) and the resulting nitride liberates ammonia (A2) when treated with alkalis. It is therefore tempting to anticipate the occurrence of nitride-like species in a process employing a titanium

catalyst.

Organic diazo compounds can be thought of as complexes between molecular nitrogen and carbenes and this analogy has been shown (A7) to have some basis in fact by the demonstration that decomposition of diazomethane is reversible in the gas phase, involving methylene and molecular nitrogen.

$$CH_2N_2 \rightleftharpoons CH_2: + N_2 \qquad (1)$$

Titanium in the divalent state should have two electrons in its valence shell which are not associated with bonding and its compounds should therefore behave in a manner analogous to methylene in the presence of molecular nitrogen.

$$R_2Ti: + N_2 \rightleftharpoons R_2TiN_2 \qquad (2)$$

These theoretical considerations were supported in early studies by Vol'pin and Shur (A8) of a variety of transition metal compounds with nitrogen gas and reducing agents. Titanium compounds reduced more nitrogen per metal atom than any other system (A9). They were relatively unaffected by variations in temperature or pressure, being nearly as active at room temperature and atmospheric pressure as they were under more severe conditions (A10). Furthermore, titanium showed retention of activity in a wide range of ligand environments (A11-A13) where other metals had shown requirements for rather specific ligands in order to attain activity (A14). Rather more attention has been devoted, therefore, to the chemistry of titanium in the attempt to achieve isolation of a metal-nitrogen complex and subsequent

reduction of the bound nitrogen. Nevertheless, several complexes of molecular nitrogen with other transition metals have been isolated (A15) but only one (A16) of these undergoes oxidation or reduction of the bound nitrogen.

The several compounds and mixtures containing titanium which have been reported to reduce nitrogen fall conveniently into three categories: 1. Reversibly formed complexes of molecular nitrogen; 2. Nitride-like substances; 3. Mixtures yielding organic nitrogen compounds.

1. Reversibly Formed Complexes of Molecular Nitrogen.

Since all biological and other systems that reduce nitrogen are inhibited by the presence of agents such as carbon monoxide, olefins, and acetylenes (A17) which are known to complex with transition metals, a complex of molecular nitrogen related to those found with the inhibiting ligands might be expected as an intermediate in nitrogen reduction (A18). Furthermore, since several stable complexes of molecular nitrogen are known (A15) in only one of which (A16) the nitrogen can be reduced, it might be inferred that instability of the complex is associated with reducibility of the nitrogen. Thermodynamic arguments in support of such a conclusion have been presented recently in a review (A19). On the basis of these considerations, workers in three laboratories have carried out successful searches at low temperatures for complexes of molecular nitrogen with bis(π-cyclopentadienyl)titanium systems. All the resulting

complexes are closely related as is evident from their spectral and chemical properties as well as their methods of preparation.

Shilov has prepared a deep blue compound (A20) as a powder from ether solutions of bis(π-cyclopentadienyl)titanium dichloride and two moles of isopropylmagnesium chloride under nitrogen gas at -100°. The resulting blue solutions discharge their colour with loss of one mole of nitrogen gas per two atoms of titanium in vacuo or upon warming to -60°. No blue colour is formed if argon is present instead of nitrogen.

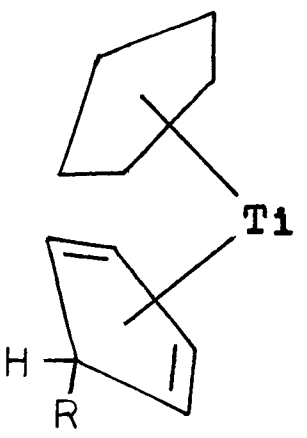
It has been reported (A19) that the heat of formation of the blue complex is 5 kcal/mol, that its absorption maximum, λ_{max} , occurs at 610 nm and that no i.r. absorptions between 2200 and 1900 cm^{-1} attributable to an N-N stretching frequency are seen. It has also been reported (A21) that at constant concentration of nitrogen, the concentration of the blue species is proportional to the square of the titanium concentration and the rate of nitrogen reduction is also proportional to the square of the titanium concentration.

From these results, there is little doubt that the complex is a bimetallic compound containing reversibly co-ordinated molecular nitrogen. The results also suggest, as do the kinetic studies of Maskill and Pratt (A10) on the same system, that it is the nitrogen complex which may be reduced further to a species releasing ammonia upon hydrolysis.

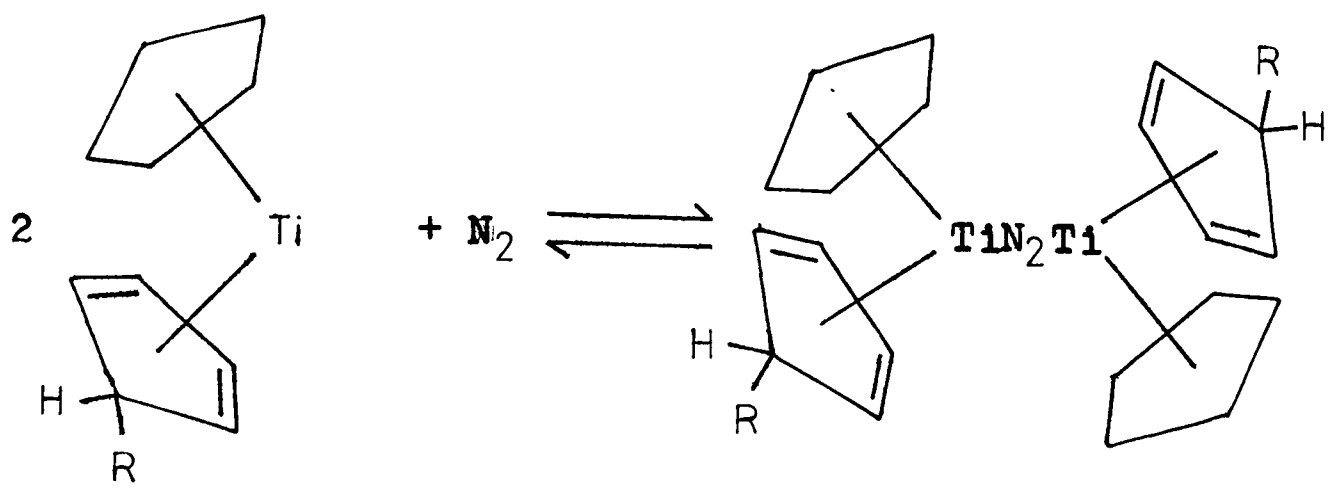
Shilov has carried out chemical studies (A20, A21) of the blue complex and has shown that the nitrogen in it is unreduced. Hydrolysis quantitatively liberates only molecular nitrogen. The action of deuterium chloride at -80° upon the blue complex derived from isopropylmagnesium chloride liberates nitrogen gas and C_3H_7D in the ratio $Ti:N_2:C_3H_7D = 1:0.5:1$. On the basis of these observations, he has speculated that the sequence of events in equations 3 to 5 leads to the formation of the blue complex, although no definitive evidence for the substituted cyclopentadiene structure he has proposed is available.

$$(\pi\text{-}C_5H_5)_2TiCl_2 + RMgCl \longrightarrow (\pi\text{-}C_5H_5)_2TiCl + MgCl_2 \quad (3)$$

$$(\pi\text{-}C_5H_5)_2TiCl + RMgCl \longrightarrow MgCl_2 +$$



(4)



(5)

Upon addition to the blue complex at low temperature of further Grignard reagent followed by a proton source, hydrazine is liberated. If a greater excess of Grignard is used and hydrolysis is carried out at 0°, ammonia is the product. These observations clearly indicate the role of the Grignard as reducing agent.

A similar series of blue powders were obtained by de Liefde Meijer (A22) using $[(\pi\text{-}C_5H_5)_2TiCl]_2$ and aryl Grignard reagents. In this case, however, a compound of proposed formula $(\pi\text{-}C_5H_5)_2TiPh$ was first isolated as green leaflets and then reacted reversibly with molecular nitrogen in toluene at -80° to give a blue powder.

$$[(\pi\text{-}C_5H_5)_2TiCl]_2 + 2PhMgCl \longrightarrow 2(\pi\text{-}C_5H_5)_2TiPh + 2MgCl_2 \quad (6)$$

$$2\,(\pi\text{-}C_5H_5)_2TiPh + N_2 \rightleftharpoons [(\pi\text{-}C_5H_5)_2TiPh]_2N_2 \quad (7)$$

This blue substance has an absorption maximum, λ_{max}, in toluene of 616 nm; exhibits no i.r. absorptions between 2200 and 1900 cm^{-1} attributable to an N-N stretching frequency; is too highly coloured to give a Raman spectrum; has an analysis consistent with the proposed formulation, $[(\pi\text{-}C_5H_5)_2TiPh]_2N_2$, and behaves chemically in a manner identical to Shilov's complex when decomposed thermally, with water or with hydrogen chloride. Treatment of this compound with excess sodium naphthalide followed by hydrolysis yields ammonia.

$$[(\pi\text{-}C_5H_5)_2TiPh]_2N_2 \xrightarrow{>-60^\circ} 2(\pi\text{-}C_5H_5)_2TiPh + N_2 \quad (8)$$

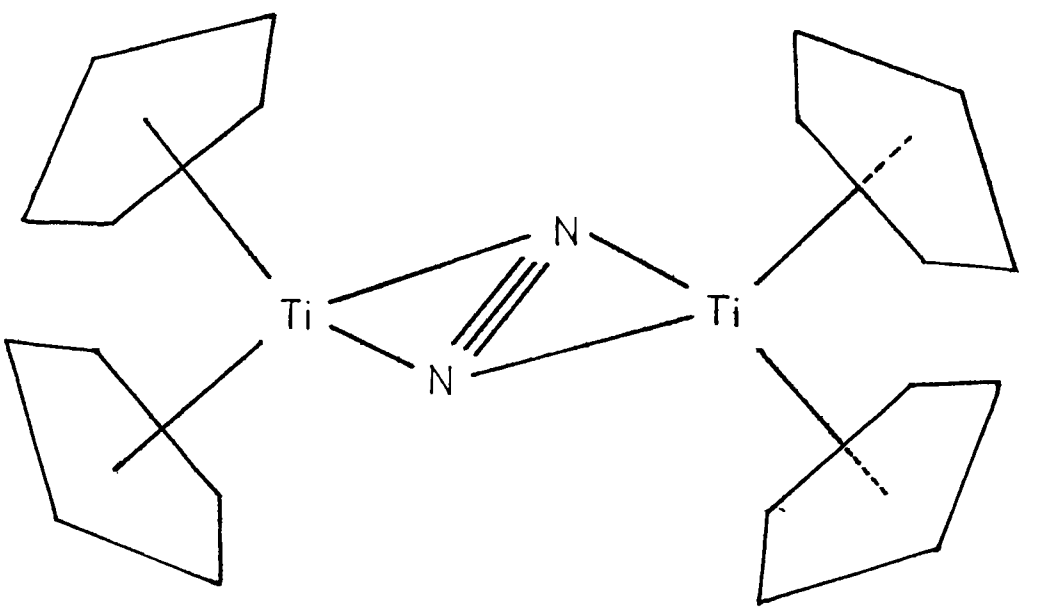
$$[(\pi\text{-}C_5H_5)_2TiPh]_2N_2 + HCl \longrightarrow [(\pi\text{-}C_5H_5)_2TiCl]_2 + 2PhH + N_2 \quad (9)$$

It is clear that this material is closely related to Shilov's compound but neither worker has reported n.m.r. or magnetic susceptibility studies which might clarify the structure of the hydrocarbon parts of the molecules.

De Liefde Meijer did conduct some physical and chemical studies (A22) on the green leaflets of proposed formula $(\pi\text{-}C_5H_5)_2TiPh$ but these do not conclusively prove the way in which the five-membered rings are attached to the metal, and in any event, those studies would apply only to the compound $(\pi\text{-}C_5H_5)_2TiPh$ and not to its complex with molecular nitrogen.

Brintzinger has also prepared blue compounds of formulae $[(\pi\text{-}C_5Me_5)_2Ti]_2N_2$ and $[(\pi\text{-}C_5H_5)_2Ti]_2N_2$ containing reversibly co-ordinated nitrogen (A23). These were obtained by chilling pentane solutions of $[(\pi\text{-}C_5Me_5)_2Ti]_2$ or $[(\pi\text{-}C_5H_5)_2Ti]_2$, which exist in equilibrium with their monomers, to -100° or -80°, respectively, under nitrogen gas. Solutions of the blue compounds have absorption maxima, λ_{max}, at 568 and 597 nm, respectively, and behave in an identical fashion to the compounds prepared by Shilov (A20) and de Liefde Meijer (A22) as far as their i.r. and Raman spectra between 2200 and 1900 cm^{-1} are concerned. The main difference between these and the compounds reported by Shilov or de Liefde Meijer is the absence of alkyl or aryl groups in addition to π-cyclopentadienyl rings, so that treatment of Brintzinger's compounds with hydrogen chloride, while

liberating nitrogen (A23), gives no hydrocarbons such as are released in reactions 8 and 9. It is probable that these substances are all closely related but not identical. Brintzinger has suggested (A23) that molecular nitrogen may be co-ordinated sideways to the metal as shown in Figure I.



I. A Proposed Structure of a Titanocene-Nitrogen Complex

He favours such a configuration because there are no bis(π-cyclopentadienyl)titanium species known for which it has been proved that less than two co-ordination sites are occupied in the equatorial plane as would be the case if nitrogen were co-ordinated end-on.

Van Tamelen has claimed (A24) that treatment of $[(\pi\text{-}C_5H_5)(C_5H_4)TiH]_2$ with nitrogen gas at room temperature for three weeks results in reversible absorption of one molecule of nitrogen per atom of titanium although the evidence for reversibility is not conclusive.

$$2\,[(\pi\text{-}C_5H_5)(C_5H_4)TiH]_2 + 2N_2 \rightleftharpoons (\pi\text{-}C_5H_5)_2Ti(N_2)_2Ti(\pi\text{-}C_5H_5)_2 \quad (10)$$

On the basis of reaction stoicheiometry and an osmometric molecular weight, the product has been formulated as $(\pi\text{-}C_5H_5)_2Ti(N_2)_2Ti(\pi\text{-}C_5H_5)_2$. An i.r. band at 1960 cm^{-1} was assigned to the N-N stretching frequency but this assignment was not confirmed by ^{15}N labelling or other means. When the material is treated first with sodium naphthalide and then with water high yields of ammonia are obtained (A24). This substance is clearly different from others mentioned in this section and may in fact be more closely related to the compounds discussed in the next section.

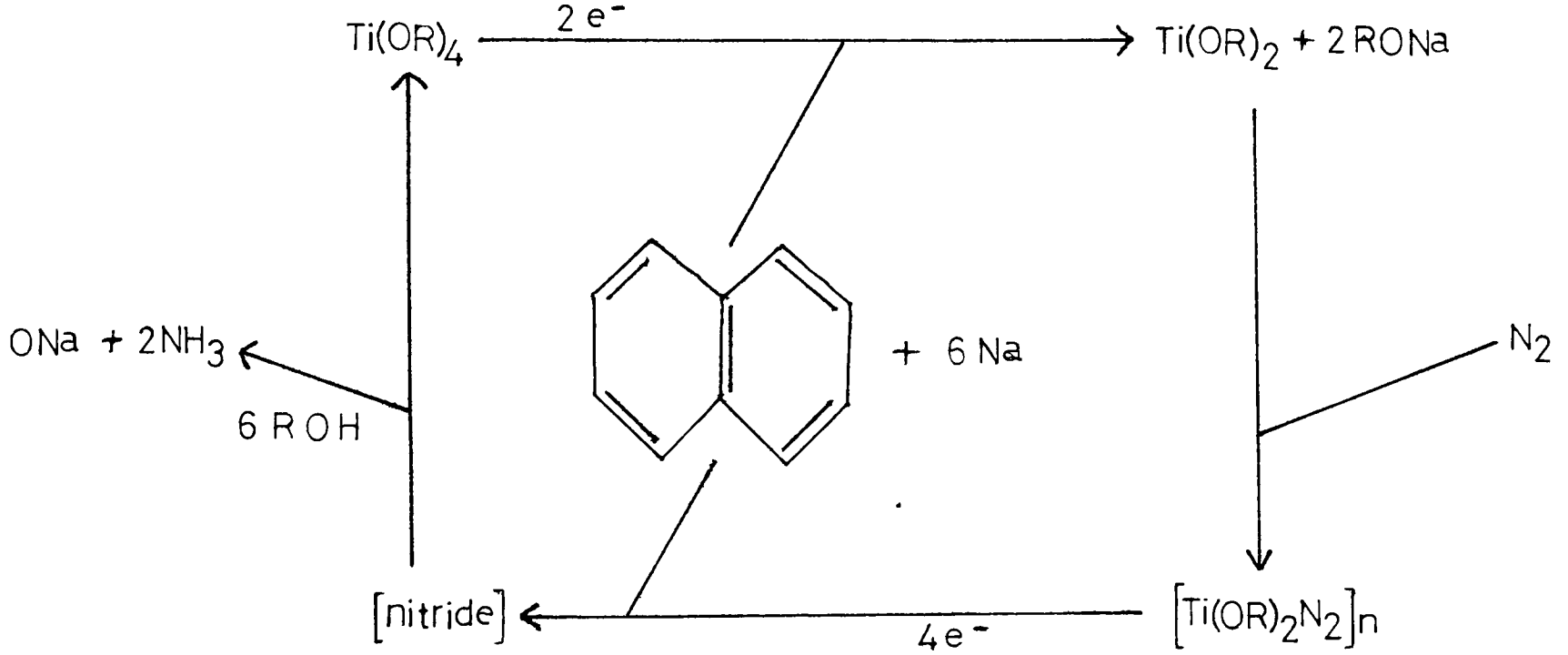
2. Nitride-Like Substances

Several laboratories have reported preparations of materials which liberate ammonia or hydrazine directly upon hydrolysis. Unlike compounds discussed in Section 1, these do not contain co-ordinated molecular nitrogen and do not require treatment with reducing agents prior to hydrolysis in order to liberate reduced nitrogen-containing species.

Van Tamelen has investigated the production of ammonia and hydrazine using titanium tetrachloride (A13) or titanium tetra-alkoxides (A25) and various reducing agents. In addition to chemical reducing agents, such as potassium metal (A13) or sodium naphthalide (A26), he has also employed electrolytic reduction (A27) and in all cases the stoicheiometry has indicated that divalent titanium is the active species. His reactions result in a nitride-like material which on

addition of a proton source yields ammonia. Van Tamelen has succeeded in operating one of these systems in a cyclic fixation-reduction scheme involving a nitride-like derivative of divalent titanium (A25). Using titanium tetraisopropoxide as the catalyst precursor, isopropanol as the proton source and sodium naphthalide as the reducing agent, after five cycles of careful addition of sodium followed by isopropanol as shown in Figure II, an ammonia yield of 340% based on titanium had been realised in a process which overall can be represented (A25) as:

$$N_2 + 6H^+ + 6e^- \longrightarrow 2NH_3 \qquad (11)$$



II. A Catalytic System for Converting Nitrogen into Ammonia

The great disadvantage of any nitride system is that a proton source must be added at some point to free ammonia from titanium and this usually destroys the catalyst as well (A28).

Several approaches have been tried to circumvent this particular problem.

Mixtures of aluminium and aluminium trichloride with titanium tetrachloride are known (A29) to produce divalent titanium in the form of a complex whose empirical formula is $C_6H_6 \cdot TiCl_2 \cdot 2AlCl_3$. Vol'pin (A28) found that from these mixtures prepared under nitrogen a substance with an empirical formula of $C_6H_6(TiCl_2 \cdot 2AlCl_3)_3N$ can be isolated which upon hydrolysis yields ammonia. Addition of catalytic amounts of this material to large quantities of aluminium trichloride and aluminium powder permitted preparation of up to 115 molecules of ammonia per atom of titanium (A28). This suggested that the trivalent aluminium was acting as a carrier to which the reduced nitrogen might be transferred, thereby freeing the titanium to fix and reduce more nitrogen. A similar conclusion had also been reached by van Tamelen (A30) who found that addition of aluminium compounds (usually alkoxides) improved his yields of ammonia. In one such case involving an electrolytic cell with an aluminium anode, titanium isopropoxide and aluminium isopropoxide he achieved an ammonia yield of 610% after hydrolysis (A30).

In a different study, Japanese workers (A12) showed that magnesium can be used as well as aluminium in the role of reducing agent. From a mixture of $TiCl_3 \cdot 3THF$ and magnesium powder in tetrahydrofuran at room temperature and atmospheric pressure, they isolated a black powder of empirical formula

$TiNMg_2Cl_2THF$ which gives ammonia upon hydrolysis.

Brintzinger and Shilov have prepared a number of compounds which react directly with nitrogen gas forming nitrides, all of which contain the π-cyclopentadienyl function. Brintzinger (A23) obtained $\left[(\pi\text{-}C_5H_5)_2TiEt\right]_2 \cdot 6MgCl_2 \cdot 7Et_2O$ as a yellow precipitate from ethereal solutions of bis(π-cyclopentadienyl)titanium dichloride at room temperature to which had been added large excesses of ethylmagnesium chloride. Reaction in an ethereal solvent of this yellow compound with nitrogen under pressure at room temperature gives $\left[(\pi\text{-}C_5H_5)_2Ti^{2+}\right]_3\left[N^{3-}\right]_2$, a black solid containing some magnesium chloride and co-ordinated ethers. It liberates ammonia upon hydrolysis or nitrogen upon treatment with chlorine.

Brintzinger and Shilov have independently prepared nitrides which appear to be closely related compounds, both of which contain π-cyclopentadienyl and triphenylphosphine ligands. Shilov (A21) added triphenylphosphine at low temperatures to his blue ethereal solutions of bis(π-cyclopentadienyl)-titanium dichloride, isopropylmagnesium chloride and nitrogen, thereby obtaining another blue compound which upon hydrolysis yields ammonia. This new compound's absorption maximum, λ_{max}, occurs at 510 nm. Brintzinger (A23) prepared and identified $\left[C_{10}H_{10}TiPPh_3\right]_2$ and showed that it reacts irreversibly with nitrogen to give a substance similar to Shilov's. Brintzinger's product is also reported to have λ_{max} = 512 nm and to hydrolyze giving ammonia.

It is obvious that two distinct reactions between reduced titanium species and molecular nitrogen can occur. The problem this presents, however, is to discover why in some cases, reduction of nitrogen to a nitride occurs without addition of further reducing agents whereas in other cases the reduction is either incomplete yielding hydrazine or altogether absent yielding unchanged nitrogen.

3. Mixtures Yielding Organic Nitrogen Compounds

The opinion has been expressed (A31) that it is unlikely, in view of the cheapness of ammonia produced by the Haber process and the extent of investment in plant for this process by large chemical firms, that ammonia production based on organo-titanium compounds will replace the Haber process in the near future. However, ammonia is merely the starting point for the commercial synthesis of a host of organic and inorganic nitrogen compounds which might very well be made more cheaply from molecular nitrogen by an organo-titanium catalyzed process.

Van Tamelen has reported a means (A32) by which the oxygen atom of certain organic carbonyl compounds may be replaced by a nitrogen atom from molecular nitrogen. A tetrahydrofuran solution of bis(π-cyclopentadienyl)titanium dichloride is added dropwise to magnesium powder under nitrogen at room temperature, producing a black solution. To this is added excess carbonyl compound and high yields of amines are obtained subsequently if the carbonyl compound was a ketone

or aldehyde, while nitriles are obtained from acid chlorides. Esters are unreactive.

Vol'pin has shown (A23) that solutions of bis(π-cyclopentadienyl)titanium dichloride with large excesses of phenyllithium form, after hydrolysis, some aniline as well as ammonia. It has been demonstrated in another study that mixtures of bis(π-cyclopentadienyl)titanium dichloride and excess phenyllithium give what is presumed to be diphenyl titanium (A34) and it has therefore been postulated (A33) that the observed aniline formation occurs <u>via</u> co-ordination of nitrogen to diphenyltitanium followed by its insertion into a phenyl-titanium bond.

$$Ph_2Ti + N_2 \longrightarrow Ph_2TiN{\equiv}N \qquad (12)$$

$$PhTi\begin{matrix}/ \\ \\ \backslash\end{matrix}\begin{matrix}N{\equiv}N \\ \\ Ph\end{matrix} \longrightarrow PhTiN{=}NPh \qquad (13)$$

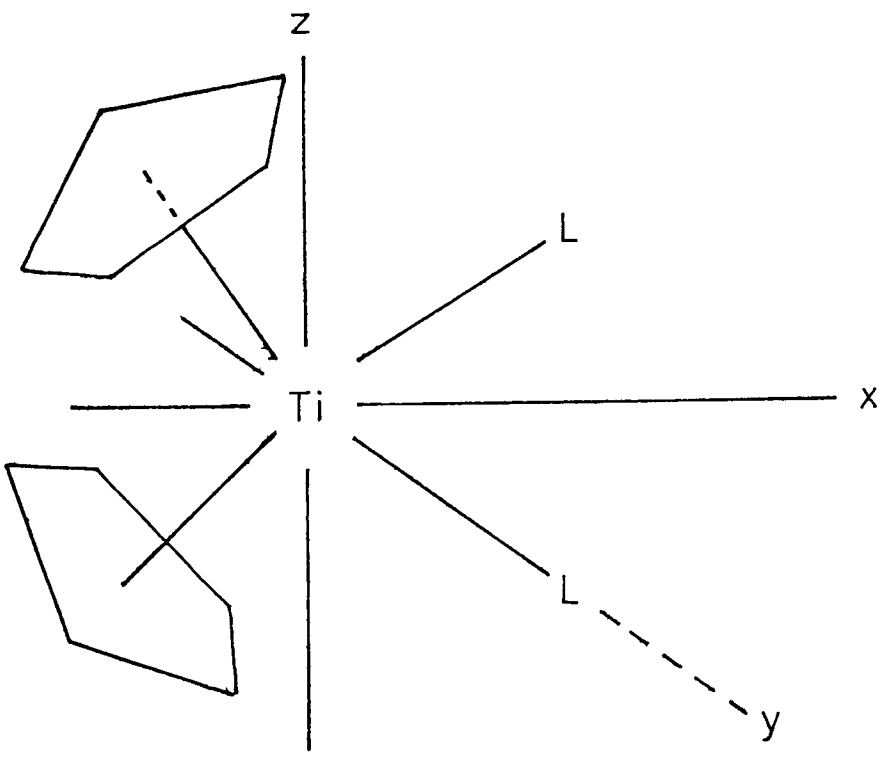
Such an arylazo derivative of titanium would be similar to $PhN{=}NPtCl(PEt_3)_2$ or $PhN{=}NMo(CO)_2(\pi\text{-}C_5H_5)$. Both of these undergo reductive cleavage (A35, A36) to form N-metal substituted amines and they in turn yield free amines upon hydrolysis as is observed in the titanium system. Amine formation by the same method but starting from alkyllithium is, however, not observed and this has been explained (A33) on the grounds of the greater stability of the titanium-aryl bond compared to the titanium-alkyl bond. The implication is that the life time of the dialkyltitanium

species is too short for nitrogen insertion to occur.

A system by which nitrogen from the gas phase may be used to prepare various naphthylamines has been reported (A37). This employs a tetrahydrofuran solution of titanium tetrachloride and sodium naphthalide under nitrogen. It has been pointed out by the authors, however, that a solution of lithium (but not sodium) naphthalide treated similarly but containing no titanium gives nearly as good yields of the same products.

B. Other Organo—Titanium Compounds

A review (A38) of lower valent organo-titanium complexes is available which lists such compounds discovered prior to 1970. The majority are derived from $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ by replacement of the halogen atoms with pseudohalides, alkoxides, mercaptides, carboxylates, simple inorganic anions such as carbonate or sulphate or in a few cases with organic groups. Perhaps the most striking feature displayed by all these derivatives, whether obtained from aqueous or anhydrous media, is the filling of both co-ordination positions in the equatorial plane (Figure III). This is found in all compounds for which structures are known from X-ray diffraction studies and it is achieved by chelation where possible such as in the carboxylates, $(\pi\text{-}C_5H_5)_2Ti(OOCR)$, or by dimerization as in the phosphides, $\left[(\pi\text{-}C_5H_5)_2Ti(PR_2)\right]_2$. In addition to the compounds mentioned in that review, however, a series of studies of more reactive species has recently been reported.



III. Illustration of the Equatorial Plane, L—Ti—L , in Bis(π-cyclopentadienyl)titanium Compounds

1. Titanocene and the Titanium Hydrides

Elegant work by Brintzinger has recently resolved many earlier questions concerning the existence of compounds containing titanium-hydrogen bonds and the nature of so-called "titanocene". His first reports described the preparation of a titanium hydride by treating solid $(\pi\text{-}C_5H_5)_2TiMe_2$ with hydrogen gas (A39).

$$2(\pi\text{-}C_5H_5)_2TiMe_2 + 2H_2 \longrightarrow \left[(\pi\text{-}C_5H_5)_2TiH\right]_2 + 4MeH \qquad (14)$$

This yields a purple diamagnetic solid (equation 14) which was shown, as discussed below, to be the dimeric hydride, $\left[(\pi\text{-}C_5H_5)_2TiH\right]_2$, containing two hydrogens bridging between the metal atoms.

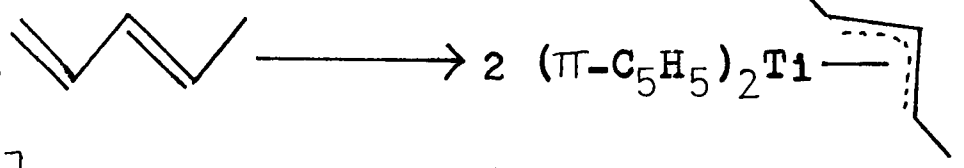
This substance is stable as a solid at room temperature under argon, but on heating to about 150° it loses hydrogen

to give the deep green form of titanocene $\left[(\pi\text{-}C_5H_5)(C_5H_4)TiH\right]_2$, (see below).

$$\left[(\pi\text{-}C_5H_5)_2TiH\right]_2 \xrightarrow{150^\circ} H_2 + \left[(\pi\text{-}C_5H_5)(C_5H_4)TiH\right]_2 \qquad (15)$$

The presence of a metal-hydrogen system in the purple compound is suggested by a number of observations, especially equation 18.

$$\left[(\pi\text{-}C_5H_5)_2TiH\right]_2 + 2 \longrightarrow 2\ (\pi\text{-}C_5H_5)_2Ti \qquad (16)$$



$$\left[(\pi\text{-}C_5H_5)_2TiH\right]_2 + B_2H_6 \longrightarrow 2(\pi\text{-}C_5H_5)_2TiBH_4 \qquad (17)$$

$$\left[(\pi\text{-}C_5H_5)_2TiH\right]_2 + DCl \longrightarrow \left[(\pi\text{-}C_5H_5)_2TiCl\right]_2 + 2HD \qquad (18)$$

The i.r. spectrum of $\left[(\pi\text{-}C_5H_5)_2TiH\right]_2$ exhibits a strong broad absorption at 1450 cm^{-1} which disappears upon air-oxidation of the sample or when the material is prepared using deuterium gas. That absorption has been assigned to the antisymmetric hydrogen bridge stretching frequency. The electronic spectrum of the purple compound is virtually indistinguishable from that of $(\pi\text{-}C_5H_5)_2TiBH_4$ as might be expected since the local ligand environment of titanium is very similar in both compounds. Unfortunately, the ^1H n.m.r. spectrum of $\left[(\pi\text{-}C_5H_5)_2TiH\right]_2$ was not obtained due to paramagnetism of the solution. Purple $\left[(\pi\text{-}C_5H_5)_2TiH\right]_2$, when treated with triphenylphosphine at low temperatures (ca. -60°), gives a solution having an e.s.r. spectrum interpreted by Brintzinger as indicating the presence of a phosphine hydride monomer, $(\pi\text{-}C_5H_5)_2Ti(H)PPh_3$. These solutions are not, however, thermally stable and the phosphine

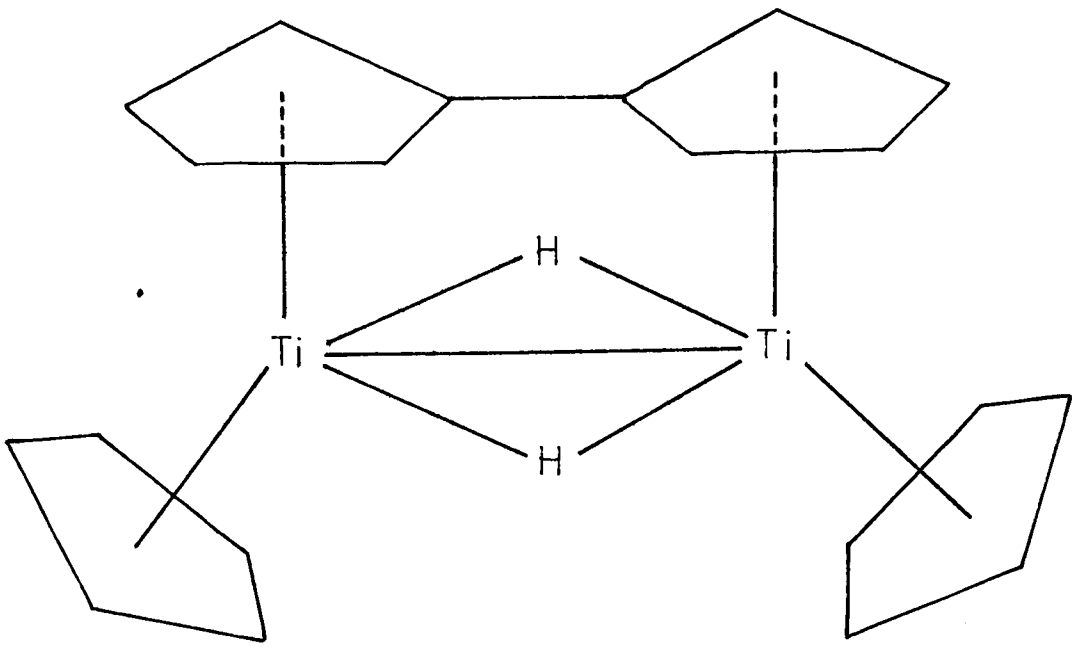
hydride was not isolated. Ethereal solutions of $[(\pi\text{-}C_5H_5)_2TiH]_2$ also react with nitrogen gas and hydrolysis of the product gives ammonia, suggesting that a nitride-like species had been formed.

In addition to preparing the purple hydride $[(\pi\text{-}C_5H_5)_2TiH]_2$, Brintzinger has resolved some of the questions concerning the structure of so-called "titanocene". Before his studies, seriously conflicting reports (A40-A45, A58) existed as to the physical and chemical properties of the substance supposed to have the empirical formula $C_{10}H_{10}Ti$. Its behaviour appeared to be a function of its method of preparation of which there were two main ones reported in the literature, namely:

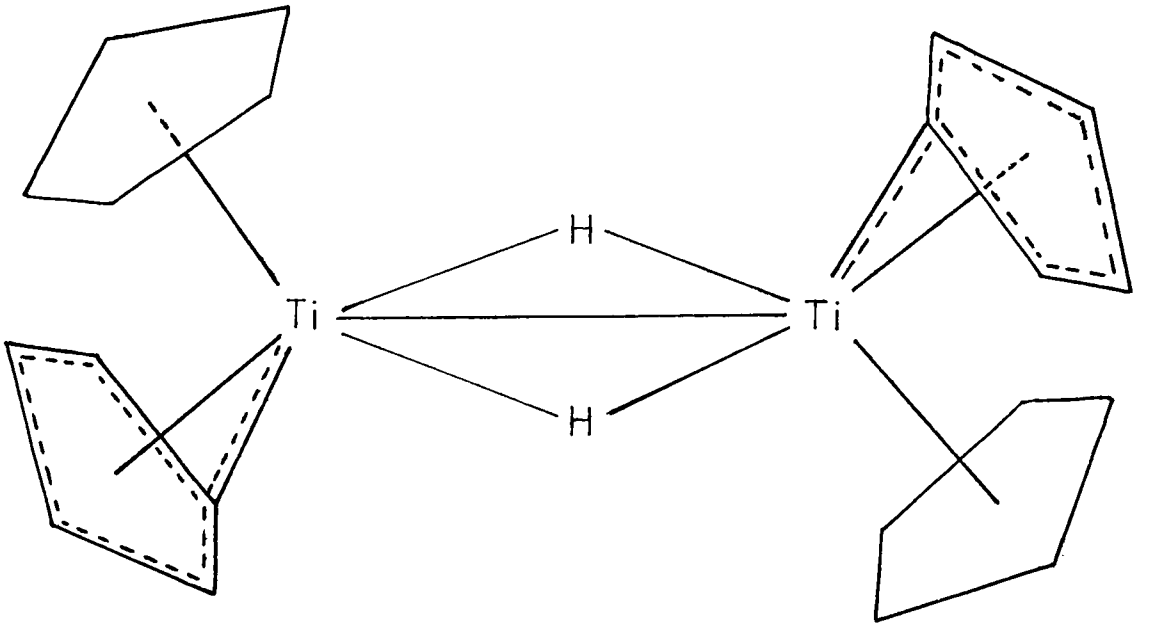
$$(\pi\text{-}C_5H_5)_2TiMe_2 + H_2 \xrightarrow{\text{cold}} C_{10}H_{10}Ti + 2MeH \qquad (19)$$

$$(\pi\text{-}C_5H_5)_2TiCl_2 + 2NaC_{10}H_8 \xrightarrow{\text{warm}} C_{10}H_{10}Ti + 2C_{10}H_8 + 2NaCl \qquad (20)$$

Brintzinger has shown that there are, in fact, at least three green substances all having empirical formulae approximating to $C_{10}H_{10}Ti$. Of these, a deep green, diamagnetic compound, $[(\pi\text{-}C_5H_5)(C_5H_4)\ TiH]_2$, which is probably the substance originally prepared by Wilkinson (A40) and named titanocene, is the most thermally stable and is the compound eventually obtained from the others or the purple hydride $[(\pi\text{-}C_5H_5)_2TiH]_2$ upon their thermal decomposition. On the basis of spectroscopic and chemical evidence, two alternative structures (Figures IV and V) have been proposed (A46) for this green compound.



IV. A Possible Structure of Thermally Stable Titanocene



V. A Possible Structure of Thermally Stable Titanocene

Both mass spectral and cryoscopic molecular weight studies suggest a dimeric formulation for this deep green titanocene. A strong band at 1230 cm^{-1} in the compound's i.r. spectrum has been assigned to the antisymmetric

stretching frequency of a hydrogen bridging system and the diamagnetism of the compound is interpreted as indicating the presence of a metal-metal bond.

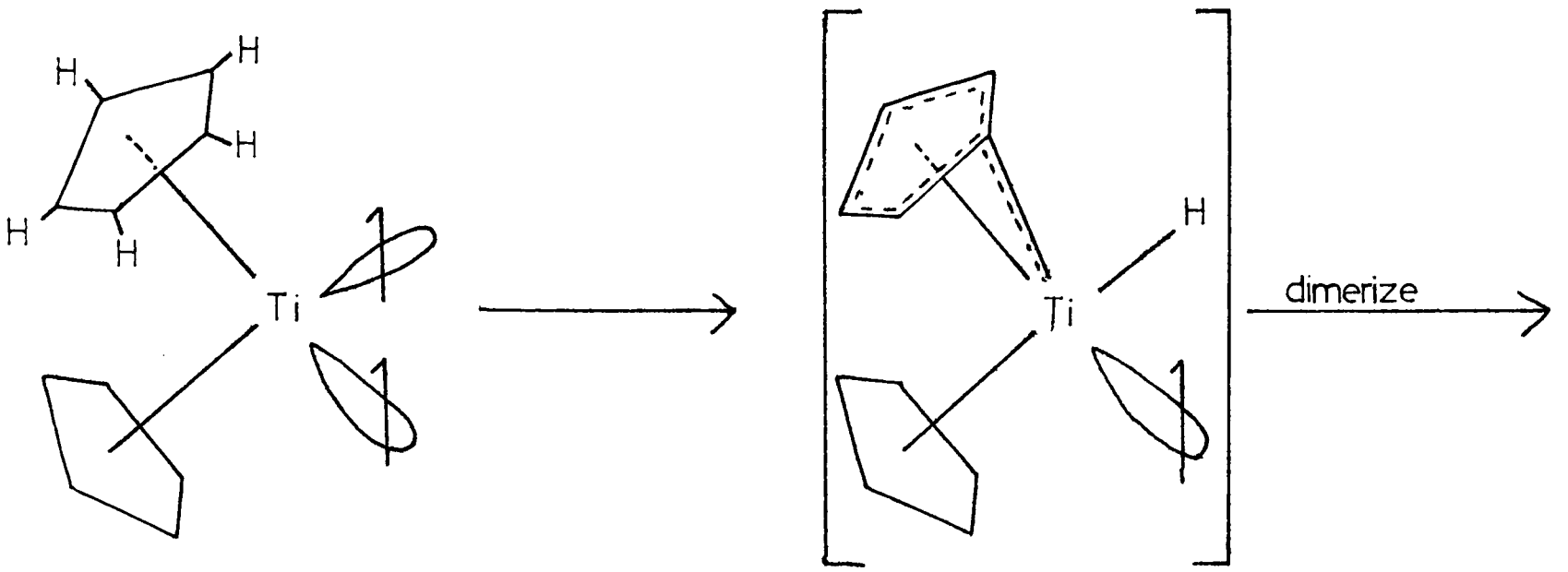
Treatment of $\left[(\pi\text{-}C_5H_5)(C_5H_4)TiH\right]_2$ with deuterium chloride gives a purple chloride, $\left[(\pi\text{-}C_5H_5)(C_5H_4)TiCl\right]_2$, which is different from both red $(\pi\text{-}C_5H_5)_2TiCl_2$ and green $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$.

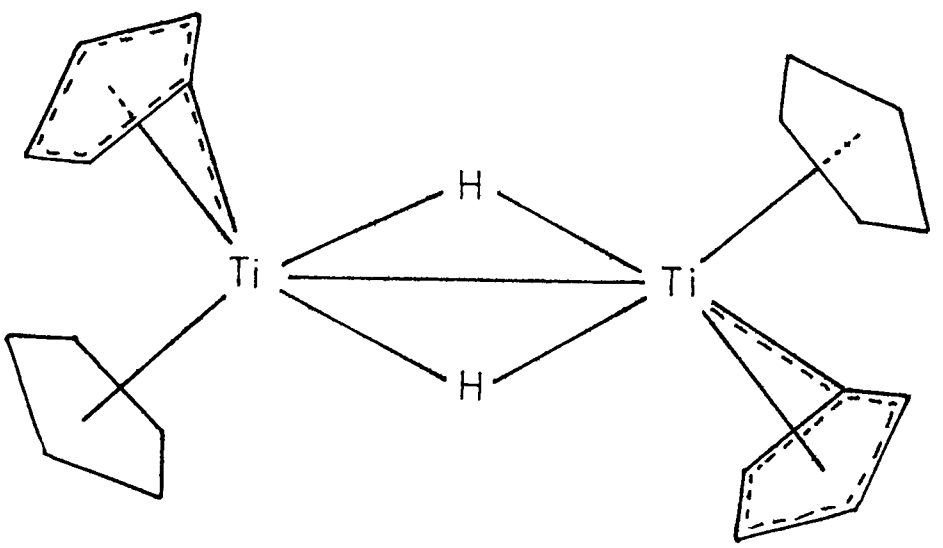
$$\left[(\pi\text{-}C_5H_5)(C_5H_4)TiH\right]_2 + 2DCl \longrightarrow \left[(\pi\text{-}C_5H_5)(C_5H_4)TiCl\right]_2 + 2HD \quad (21)$$

The i.r. spectrum of the purple chloride is almost identical to that of the green hydride except for absence of the band at 1230 cm^{-1}, thus supporting its assignment to a hydrogen-bridge vibration.

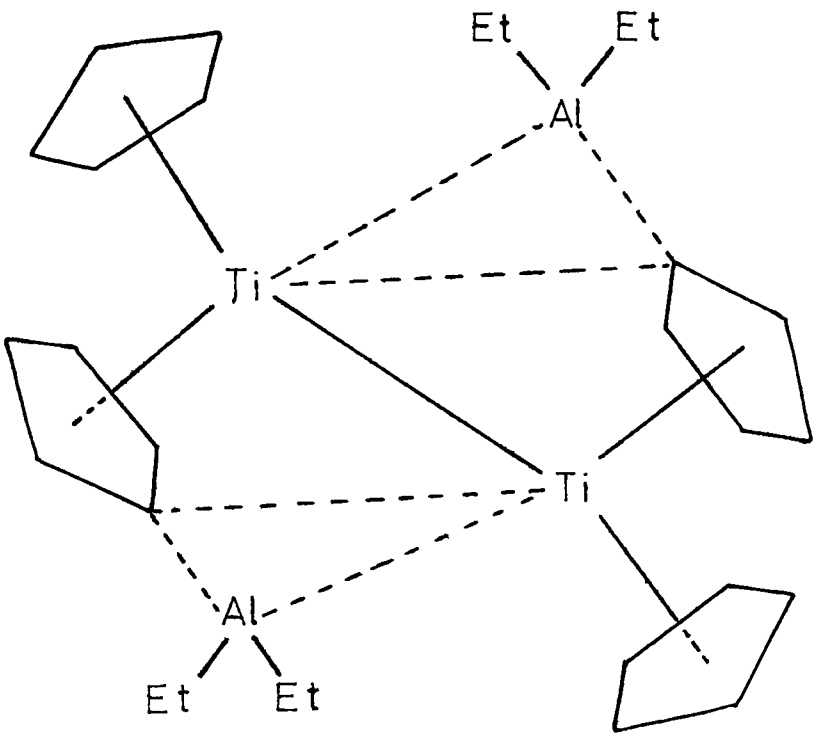
It has been proposed (A46) that the hydride ligand in $\left[(\pi\text{-}C_5H_5)(C_5H_4)TiH\right]_2$ is derived from one of the cyclopentadienyl rings of the compound's precursor. The exchange of ring-hydrogens with deuterium gas has been observed (A45, A23) in bis(π-cyclopentadienyl)titanium and related systems (A54) and this provides evidence (A55) for a facile ring-to-metal hydrogen shift in these species. A mechanism for the hydrogen-deuterium exchange reaction involving carbene-like reactivity for bis(π-cyclopentadienyl)titanium has been proposed (A23) and has been supported by theoretical considerations (A47).. In this particular respect, organo-carbenes are known to rearrange by abstraction of α-hydrogens, thus forming olefins (A48) and therefore, the observed formation of a molecule having the structure shown in Figure V could conceivably proceed in an analogous fashion,

as indicated.





An argument in support of the alternative structure (A46) for $[(\pi\text{-}C_5H_5)(C_5H_4)TiH]_2$ shown in Figure IV is the relatively high abundance of the ion $C_{10}H_8^+$ in the mass spectra of both $[(\pi\text{-}C_5H_5)(C_5H_4)TiH]_2$ and $[(\pi\text{-}C_5H_5)(C_5H_4)TiCl]_2$ compared to the abundance of this ion in mass spectra of other metallocene derivatives. On the other hand, however, it is known that $[(\pi\text{-}C_5H_5)(C_5H_4)TiH]_2$ reacts with triethylaluminium with evolution of ethane (A49) and the molecular structure of the organometallic product of that reaction (A50) has been determined (Figure VI).



VI. Structure of the Reaction Product of Titanocene and AlEt

In such reactions a carbon-carbon bond would be expected to survive. The absence of such a ring-ring bond in Figure VI suggests the structure for $\left[(\pi\text{-}C_5H_5)(C_5H_4)TiH\right]_2$ shown in Figure V is to be preferred to that of Figure VI. It can be argued, in fact, that occurrence of the ion $C_{10}H_8^+$ in the mass spectra is not inconsistent with the structure of Figure V. The C_5H_5 ring in that structure would be expected to be more labile than the π-cyclopentadienyl rings found in other metallocenes and furthermore, it would contain a relatively more reactive carbon atom. The greater occurrence of C_{10} species in the mass spectra may, therefore, simply reflect this situation.

Unlike $\left[(\pi\text{-}C_5H_5)(C_5H_4)TiH\right]_2$ which is the product (A43) of reaction 20, the "titanocene" obtained by reaction 19

from $(\pi\text{-}C_5H_5)_2TiMe_2$ and hydrogen in cooled solutions (A47) is a grey-green <u>insoluble</u> solid whose known reactions are otherwise identical to those of purple $\left[(\pi\text{-}C_5H_5)_2TiH\right]_2$. Brintzinger has suggested (A47) that the grey-green substance is $\left[(\pi\text{-}C_5H_5)_2TiH\right]_x$, a polymeric form of $\left[(\pi\text{-}C_5H_5)_2TiH\right]_2$ and i.r. data are consistent with a formulation involving bridging hydrogens. Equation 19 should therefore be rewritten in the form of equation 23.

$$X(\pi\text{-}C_5H_5)_2TiMe_2 + \frac{3x}{2}H_2 \xrightarrow{\text{cold}} \left[(\pi\text{-}C_5H_5)_2TiH\right]_x + 2XMeH \qquad (23)$$

This grey-green solid which is stable at room temperature under argon slowly decomposes and loses 0.5 moles of hydrogen per atom of titanium when suspended in ether at the same temperature (A51). It has been demonstrated (A23, A51) that the product of this reaction is a green paramagnetic monomer, bis(π-cyclopentadienyl)titanium, which is in equilibrium with its diamagnetic dimer.

$$2\left[(\pi\text{-}C_5H_5)_2TiH\right]_x \longrightarrow X\left[(\pi\text{-}C_5H_5)_2Ti\right]_2 + XH_2 \qquad (24)$$

$$2(\pi\text{-}C_5H_5)_2Ti \rightleftharpoons \left[(\pi\text{-}C_5H_5)_2Ti\right]_2 \qquad (25)$$

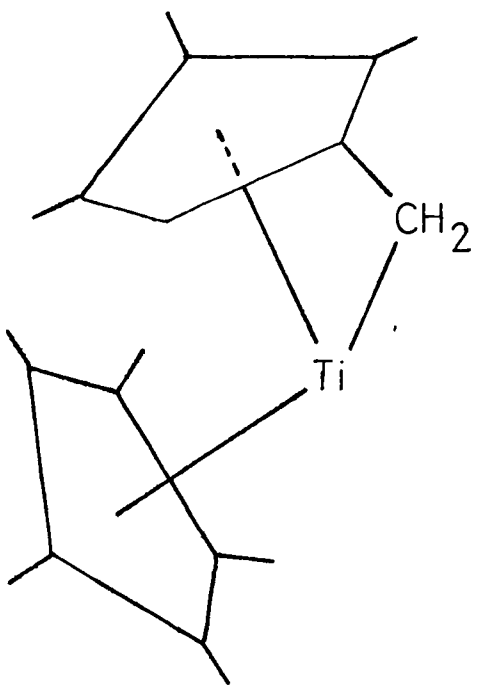
Solutions in which this equilibrium occurs can be stored at room temperature for a few days under argon but upon warming a rearrangement takes place (A23) giving the bright green and relatively more stable $\left[(\pi\text{-}C_5H_5)(C_5H_4)TiH\right]_2$. These solutions of bis(π-cyclopentadienyl)titanium react instantly and irreversibly with carbon monoxide (A51) to give brown $(\pi\text{-}C_5H_5)_2Ti(CO)_2$ and with hydrogen chloride (A51) to form green $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$. They undergo a reversible

reaction (A23) with nitrogen gas, as discussed in Part A of this chapter, and they also undergo a reversible reaction with hydrogen gas (A23, A51) but the products of that reaction have not been identified. The reaction is, however, presumed to be similar to that of $\left[(\pi\text{-}C_5Me_5)_2Ti\right]_2$ with hydrogen gas (A23, A52) (see below) but to include formation of some other species as well. With deuterium gas, complete exchange of all ring hydrogens for deuteriums occurs (A23), which has been discussed earlier, while with triphenylphosphine, the purple complex, $\left[C_{10}H_{10}TiPPh_3\right]_2$, mentioned in Part A is formed (A23).

Since in the above work, Brintzinger noted that reaction and decomposition frequently seemed to involve ring-to-metal hydrogen transfer steps, he also studied the pentamethylcyclopentadienyl systems, $(\pi\text{-}C_5Me_5)_2Ti$, in which analogous hydrogen transfer steps are precluded. The pentamethylcyclopentadienyl compounds are relatively more stable than their unsubstituted analogues with two exceptions.(A23, A52). The compound, $(\pi\text{-}C_5Me_5)_2TiMe_2$, when warmed in solution, decomposes to a diamagnetic, turquoise compound which sublimes at about 75° <u>in vacuo</u>.

$$(\pi\text{-}C_5Me_5)_2TiMe_2 \xrightarrow{110^\circ} (\pi\text{-}C_5Me_5)(\pi\text{-}C_5Me_4\text{-}\sigma\text{-}CH_2\text{-})TiMe + MeH \qquad (26)$$

On the basis of stoicheiometry, i.r., n.m.r., and mass spectral evidence the structure shown in Figure VII has been proposed (A23).

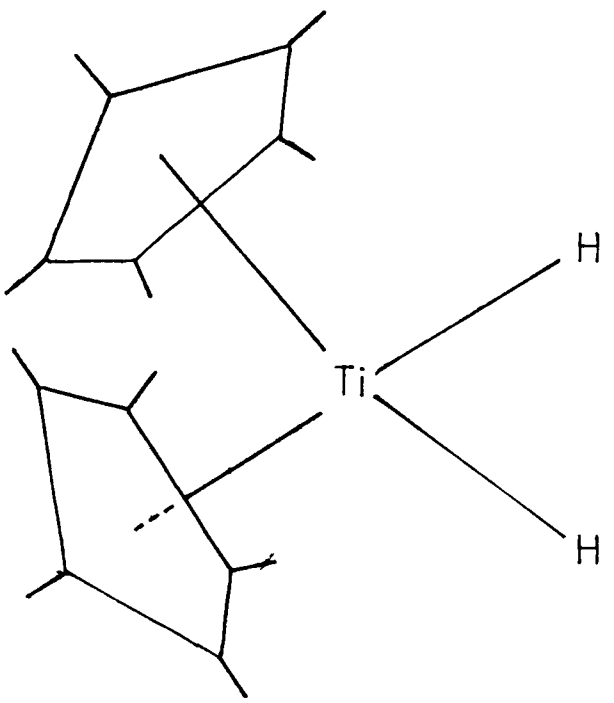


VII, Proposed Structure of $(\pi\text{-}C_5Me_5)(\pi\text{-}C_5Me_4\text{-}\sigma\text{-}CH_2\text{-})TiMe$

The turquoise substance readily reacts with hydrogen gas (A23) in pentane at 0° in a manner analogous to that of $(\pi\text{-}C_5H_5)_2TiMe_2$.

$$2(\pi\text{-}C_5Me_5)(\pi\text{-}C_5Me_4\text{-}\sigma\text{-}CH_2\text{-})TiMe + 2H_2 \longrightarrow [(\pi\text{-}C_5Me_5)_2Ti]_2 + 2MeH \qquad (27)$$

solutions of decamethyltitanocene, react reversibly with hydrogen gas giving an orange product (A23) which is stable in the solid state at room temperature under argon. A structure, shown in Figure VIII, has been suggested for that product. The compound's n.m.r. spectrum consists of two singlets at 8.05 and 9.72 τ in the ratio of 30:2, assigned, respectively, to methyl and hydride hydrogens while a strong, broad i.r. absorption at 1560 cm^{-1} has been assigned to the titanium-hydrogen stretching mode (A23).



VIII. Proposed Structure of $(\pi\text{-}C_5Me_5)_2TiH_2$

The striking work by Brintzinger described in this section shows clearly that whereas in most bis(π-cyclopentadienyl)-metal compounds the π-cyclopentadienyl ring may safely be reagrded as inert, with titanium a much greater subtlety and complexity of chemistry arises from active participation of the π-cyclopentadienyl system in various ways.

2. Other Cyclopentadienyl and Alkyl Compounds of Titanium

Apart from the above, there have been only a few unrelated studies involving low valent titanium systems. A new and more convenient preparation of $(\pi\text{-}C_5H_5)_2Ti(CO)_2$ has been described (A53). This involves treatment of $(\pi\text{-}C_5H_5)_2Ti(CH_2C_6H_5)_2$ with carbon monoxide at room temperature and atmospheric pressure. The reaction is believed to proceed via carbonyl insertion into the metal-carbon σ-bond.

$$(\pi\text{-}C_5H_5)_2Ti(CH_2C_6H_5)_2 + 3CO \longrightarrow (\pi\text{-}C_5H_5)_2Ti(CO)_2 + (C_6H_5CH_2)_2CO \quad (28)$$

The dicarbonyl itself reacts with acyl chlorides (A56) to undergo oxidative replacement together with elimination.

$$(\pi\text{-}C_5H_5)_2Ti(CO)_2 + RCOCl \longrightarrow (\pi\text{-}C_5H_5)_2Ti(COR)Cl + 2CO \quad (29)$$

The ability of low valent nitride-like titanium compounds to transfer their nitrogen to aluminium or magnesium (Part A, Section 2) has been observed by several workers and it seems that this phenomenon is not restricted to nitrogen. Saito (A57) has described a catalytic method for the preparation of bis(cyclopentadienyl)magnesium from cyclopentadiene and magnesium powder in tetrahydrofuran at room temperature. For this process, he uses π-cyclopentadienyl-titanium trichloride as catalyst precursor although bis(π-cyclopentadienyl)titanium dichloride and $TiCl_4 \cdot 2THF$ are also effective. He has isolated a dark solid having an empirical formula, $(C_5H_5)_2Ti_2Mg_2Cl_3 \cdot 2THF$, from the reaction mixture and this material is also effective as a catalyst precursor.

A similar transfer reaction has been described by Bayer and Schurig (A59) who observed formation of sodium hydride by sodium metal and hydrogen gas in the presence of catalytic quantities of bis(π-cyclopentadienyl)titanium dichloride.

The question of the occurrence and stability of trivalent titanium compounds containing the metal bonded

only to carbon has been raised by recent reports (A60, A61) concerning species of this kind. In general, compounds of the form $[R_3Ti]_n$ are thermally unstable and disproportionate to the corresponding tetravalent compound and a divalent titanium-containing residue. In ethers, splitting of a carbon-oxygen bond may occur to give a tetravalent diethoxide (A60). These reactions have been demonstrated most convincingly (A60) for R = $CH_2C_6H_5$.

$$TiCl_3 + 3C_6H_5CH_2MgCl \xrightarrow[-78^\circ]{Et_2O} Ti(CH_2C_6H_5)_3 + 3MgCl_2 \qquad (30)$$

$$2Ti(CH_2C_6H_5)_3 + 6(C_2H_5)_2O \xrightarrow{0^\circ} Ti(CH_2C_6H_5)_4 \cdot 2(C_2H_5)_2O + \text{divalent Ti-containing residue} + Ti(CH_2C_6H_5)_2(OC_2H_5)_2 \cdot 2(C_2H_5)_2O \qquad (31)$$

In contrast to that behaviour, a substance of proposed formula $(\pi\text{-}C_5H_5)_2TiPh$ has been isolated (A22) in 50% yield by de Liefde Meijer as green leaflets from petrol at -20°. This material has an effective magnetic moment of ca. 1.50 BM and is reported to have an i.r. spectrum consisting only of the expected π-cyclopentadienyl and σ-phenyl absorptions. Its treatment with hydrogen chloride and bromine gives the expected reactions (32 and 33) and it fixes nitrogen (see Part A).

$$2(\pi\text{-}C_5H_5)_2TiPh + 2HCl \longrightarrow [(\pi\text{-}C_5H_5)_2TiCl]_2 + 2PhH \qquad (32)$$

$$(\pi\text{-}C_5H_5)_2TiPh + \tfrac{3}{2}Br_2 \longrightarrow (\pi\text{-}C_5H_5)_2TiBr_2 + PhBr \qquad (33)$$

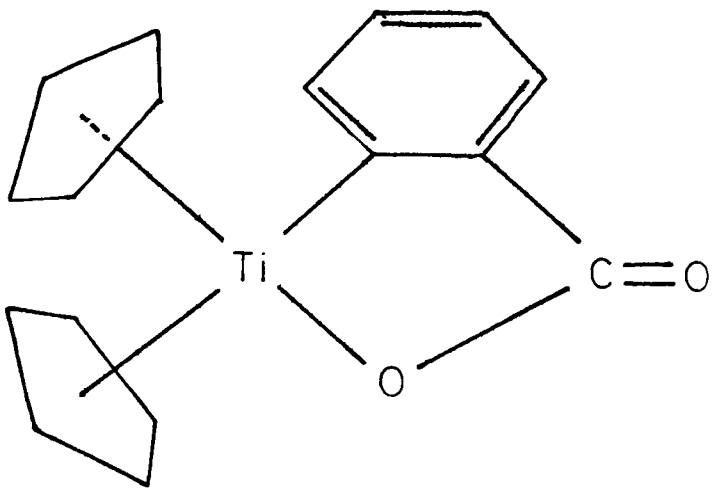
An apparently related material, tris(cyclopentadienyl)-titanium, which was originally believed (A62) to have a symmetrically π-bonded structure has been examined by

de Liefde Meijer (A63). On the basis of i.r. studies and by comparison with $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)_2$, he proposed the formula, $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)$. It seems likely, however, that this compound and the related $(\pi\text{-}C_5H_5)_2TiPh$ are in fact dimers or else have unconventional geometries like that proposed by Shilov (A20) for a $(\pi\text{-}C_5H_5)_2Ti(\underline{iso}\text{-}C_3H_7)$ species (equation 3) or that found (A 64, A65) in $(\pi\text{-}C_5H_5)_3MoNO$.

The compound $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)_2$ has been shown by Cotton (A66, A67) to display a type of stereochemical non-rigidity which at this time is unique. The σ-bonded rings exhibit conventional fluxional behaviour detected by the appearance of a single absorption in the n.m.r. at 4.17 τ which does not collapse to a more complex absorption until a temperature of -138° has been reached. In addition, however, a rapid interconversion of both π- and σ-bonded rings is indicated by the fact that only a single absorption at 4.4 τ is observed which persists down to -30° before it collapses to two singlets at 4.8 and 4.1 τ, corresponding to the hydrogens of the π-cyclopentadienyl rings and the fluxional σ-cyclopentadienyl rings, respectively. The structure of the molecule in the solid state was shown (A68) to be $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)_2$.

The behaviour of $(\pi\text{-}C_5H_5)_2TiPh_2$ has been examined under a variety of conditions by Vol'pin. It reacts with carbon dioxide (A69) at 90° to give a red, diamagnetic product in 35% yield for which the molecular structure

shown in Figure IX has been determined.



IX. Structure of $(\pi\text{-}C_5H_5)_2Ti(OOCC_6H_4)$

Orange $(\pi\text{-}C_5H_5)_2TiPh_2$ also acts as a catalyst precursor (A34) for the conversion of phenyllithium into lithium metal and phenyl radicals. A mechanism has been proposed which involves conversion of $(\pi\text{-}C_5H_5)_2TiPh_2$ to diphenyltitanium by loss of lithium cyclopentadienide in presence of excess phenyllithium. The occurrence of lithium cyclopentadienide in the solutions has been confirmed but the precise identity of the species described as diphenyltitanium is as yet uncertain.

Little progress has been made recently towards the understanding of the mechanism of olefin polymerization by Ziegler catalysts except for a few papers (A70-A73) by Henrici-Olive and Olive. It has been recently demonstrated by Clark during his studies of methyltitanium trichloride and its derivatives (A74-A76) that the preparation of

anionic organo-titanium species is possible. He has isolated three series of anions (A77) from mixtures containing various mole ratios of tetraethylammonium halide and methyltitanium trichloride. The products are $Me_2Ti_2X_7^-$, $Me_2Ti_2X_8^{2-}$ and $MeTiX_5^{2-}$ and they have been shown by comparison of their i.r. spectra with the spectra of the known ions $Ti_2Cl_9^-$, $Ti_2Cl_{10}^{2-}$ and $TiCl_6^{2-}$ to have the same essential geometries as these ions but with terminal methyl groups.

The mono-π-cyclopentadienyl compound, $\left[(\pi\text{-}C_5H_5)TiCl_2\right]_n$, has been prepared (A78) by reduction of π-cyclopentadienyltitanium trichloride with zinc dust and its electronic spectrum and magnetic properties have been examined but the nature of its structure is still unclear.

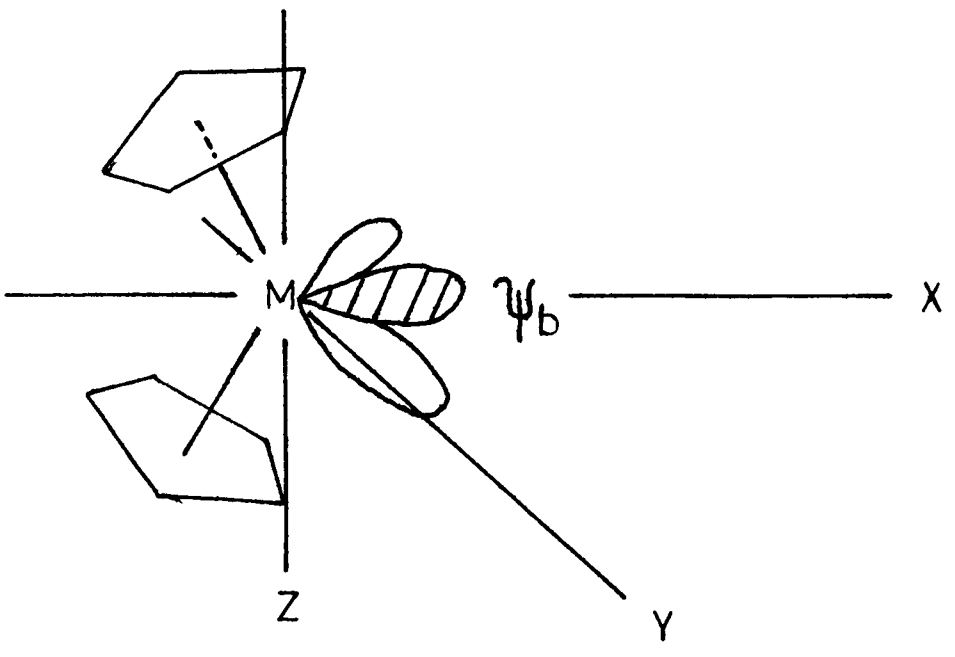
E.s.r. spectra and magnetic properties of $\left[(\pi\text{-}C_5H_5)Ti(OOCC_6H_5)_2\right]_2$ have been measured (A79) and it was deduced from these studies that the molecule was a dimer with bridging carboxyl groups. This was confirmed by subsequent i.r. studies (A84, A85). The i.r. spectra between 60 and 500 cm^{-1} of π-cyclopentadienyltitanium trichloride and $(\pi\text{-}C_5Me_5)TiX_3$, (X = Cl and Br) have been recorded and the Ti-X and Ti-ring absorptions assigned (A80, A81).

Other recent studies of mono-π-cyclopentadienyl systems include the preparation (A82) and characterization by X-ray techniques (A83) of chloro(π-cyclopentadienyl)-bis(8-quinolinolato)titanium(IV), the preparation and characterization (A84, A85) of $(\pi\text{-}C_5H_5)Ti(OOCC_6H_5)_3$,

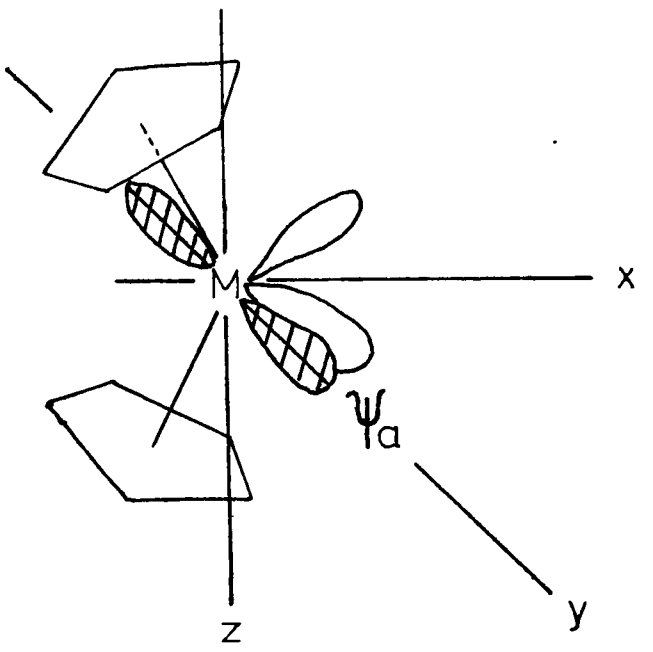
the preparation and characterization by X-ray techniques (A86) of cyclotetra[μ-oxochloro-π-cyclopentadienyltitanium(IV)] and the investigation (A87) of activity as an isomerization catalyst of a mixture of π-cyclopentadienyltitanium trichloride and butyllithium.

3. Bonding in Bent Bis(π-cyclopentadienyl)metal Compounds

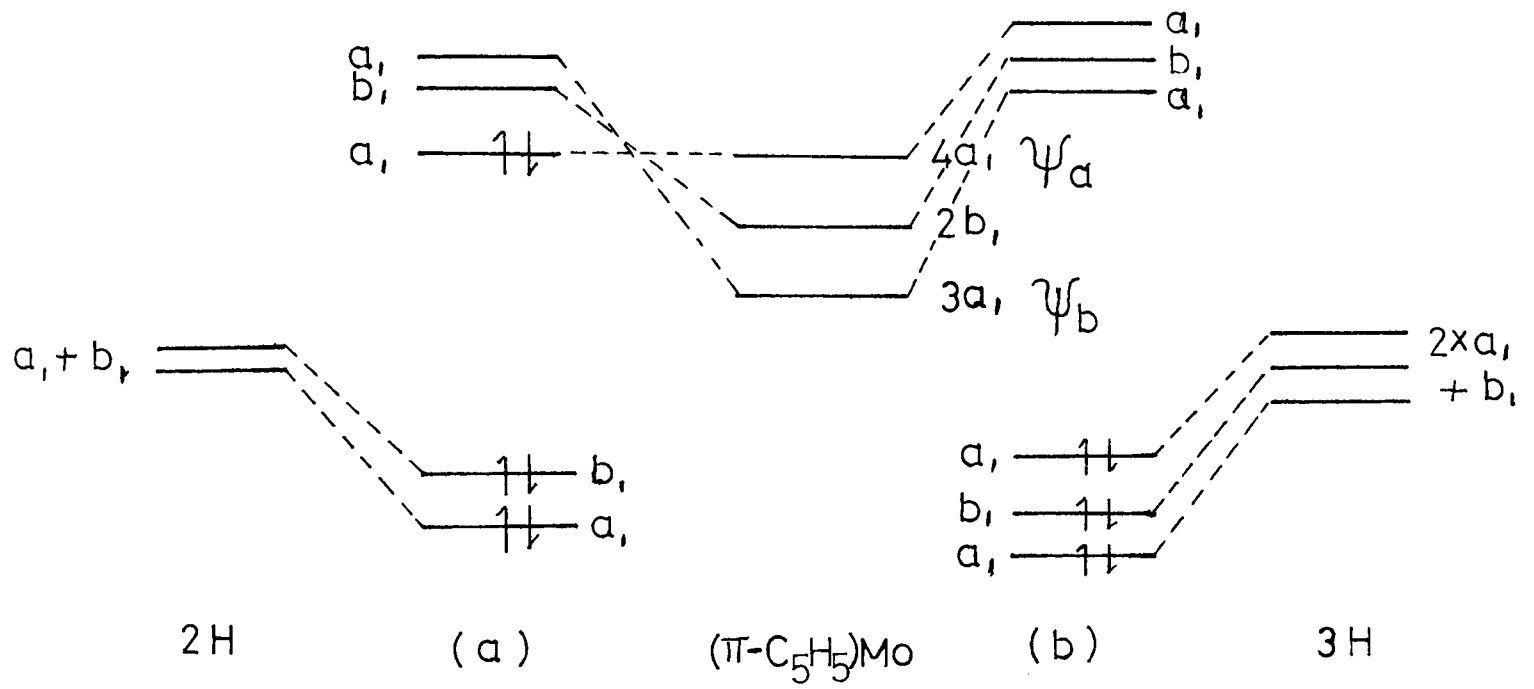
Two descriptions of the bonding in bent bis(π-cyclopentadienyl)metal compounds have been proposed. Ballhausen (A88) has suggested that the non-bonding electron pair in $(\pi\text{-}C_5H_5)_2MoH_2$ lies in an orbital located between the two hydrogen atoms (Figure X). Alcock (A89), however, observed that the Me-Re-Me angle of 76° in $(\pi\text{-}C_5H_5)(C_5H_5Me)ReMe_2$ was too narrow to accomodate a non-bonding pair of electrons and he suggested that the lone pair of electrons lies in an orbital outside the X-M-X system (Figure XI).



X. Ballhausen-Dahl Bonding Model for Bent Bis(π-cyclopentadienyl)metal Systems



XI. Alcock Bonding Model for Bent Bis-π-cyclopentadienyl Systems



XII. Partial M.O. Diagram for Bent Bis-π-cyclopentadienyl Systems (a) M.O.s resulting from interaction between the $(\pi\text{-}C_5H_5)_2Mo$ system and two hydrogen ligands, showing the "lone pair" in the Alcock orbital. (b) M.O.s resulting from interaction between the $(\pi\text{-}C_5H_5)_2Mo$ system and three hydrogen ligands.

Independently, it has been observed (A90) that the X-M-X angles in $(\pi\text{-}C_5H_5)_2MX_2$ systems decrease upon going from a d^0 to a d^1 to a d^2 system which strongly supports the Alcock proposal.

A solution to this apparent conflict between the two theories has been proposed (A90) by Green. It involves generating the M.O. diagram for the bent bis-π-cyclopentadienyl systems by "bending" the ferrocene system to C_{2v} symmetry. From this, two orbitals, ψ_a and ψ_b, which correspond to Alcock's and Ballhausen's models, respectively, are obtained. When the bent bis(π-cyclopentadienyl)metal system interacts with two ligands as in $(\pi\text{-}C_5H_5)_2MX_2$ the highest filled orbital is ψ_a but when it interacts with three ligands, as in $\left[(\pi\text{-}C_5H_5)_2MoH_3\right]$, there are three bonding M.O.'s and no lone pair (Figure XII) so that it appears as if the lone pair had been located between the two hydrogens of $(\pi\text{-}C_5H_5)_2MoH_2$ in a ψ_b or Ballhausen orbital.

Further evidence in support of this interpretation has been found in some recent e.s.r. studies (A31, A91-A93) of substances of the form $\left[M^+\right]\left[(\pi\text{-}C_5H_5)_2TiH_2^-\right]$. In these, it has been shown (A92) that the unpaired electron is confined to an orbital on titanium which is largely metal 3d in character and is directed along an axis between the two hydrogen atoms, as is ψ_b or the Ballhausen orbital. This result seems to be in contrast to the findings of earlier (A90) X-ray diffraction studies on $(\pi\text{-}C_5H_5)_2MX_2$ systems which

show that the d^1 electron resides in a ψ_a orbital. However, unlike the X-ray diffraction study which examined neutral species, in the present case, the species under examination are all anions and evidence of interaction between the unpaired electron of the anion and the counter-cation has been obtained (A31, A91, A92). Since that interaction is occurring, the electronic structure in these anionic titanium complexes is actually an approximation to that found in $\left[(\pi\text{-}C_5H_5)_2MoH_3\right]^+$, as illustrated in Figure XII, and there is no longer a conflict between these results and the earlier ones from the X-ray diffraction study.

In agreement with this interpretation, the same authors have shown (A94) that the unpaired electron in bis(π-cyclopentadienyl)vanadium dichloride and bis(π-cyclopentadienyl)niobium dichloride does not reside in the ψ_b orbital between the chlorine atoms. Unfortunately, the e.s.r. technique does not show that the electron resides in a ψ_a orbital, it only shows that it does not lie in a ψ_b orbital. If the reasonable assumption is made, however, that when the electron is not in ψ_b then it must be in ψ_a, it is gratifying to note that both the e.s.r. and X-ray diffraction examinations of bis(π-cyclopentadienyl)niobium dichloride (the only compound common to both studies) give the same result and place the non-bonding d^1 electron in the ψ_a or Alcock orbital.

C. A Classification Scheme for Covalent Compounds of Niobium and Other Elements

The chemistry of niobium is still largely unexplored. Difficulties in obtaining the element in a pure state, difficulties with its analytical chemistry and difficulties in the handling of some of its compounds have all contributed to this situation. Nonetheless, in addition to its more traditional compounds of oxygen, the halogens, etc., some four dozen or so organometallic compounds of niobium are now known.

While attempting to correlate the known chemistry of this element and to compare it with that of other elements, a formal method for the display and correlation of the covalent compounds of any element has been developed. Although this method is a formalism and empirical in its approach, it is useful for visualizing the probable reactivity of a complex and for gauging the likelihood of existence of presently unknown compounds. It can be used as well, to assist in the prediction of reasonable structures for substances for which only empirical formulae are available. It can also be used as an aid in developing experiments intended to expand the chemistry of an element through preparation of new compounds or through elucidation of a known compound's structure.

The justification for description of a new formalism lies partly in the benefits to be gained from it, some of

which have just been mentioned and partly in the fact that earlier classifications in terms of oxidation state are not entirely satisfactory for description of many recently discovered covalent compounds. The formalism of oxidation state developed from and is very useful for the description of the aqueous, ionic chemistry of the commoner elements. However, that concept has become increasingly difficult to apply as more unusual, covalent compounds of less common elements are discovered. To illustrate the problem, consider the oxidation states of the metals in WCl_6 and ReH_9^{2-}. It would be generally agreed that the oxidation state of tungsten in WCl_6 is +6, however, it is rather more difficult to say whether rhenium is in oxidation state +7 or -11. Consideration of the Pauling Electroneutrality Principle (A95) makes it clear that none of these descriptions of the oxidation states of rhenium and tungsten relate to real charges on the atoms. The justification for the new system, therefore, is that it carries out (at least for covalent compounds) the functions of the formalism it replaces; it removes difficulties caused by failings in the earlier systems and in addition, it provides some benefits not previously available.

Classification of a particular covalent compound in the new formalism is done in terms of valence number, (VN), electron number, (EN), and ligand bond number, (LBN) which are closely related to but not necessarily synonymous with the conventional ideas of valence, number of electrons in

the valence shell of a central atom and co-ordination number, respectively.

The presentation of definitions for these new concepts implies a previous understanding of the behaviour of ligands and central atoms. In the new approach, central atoms and ligands are considered to behave in a manner consistent with the Pauling Electroneutrality Principle (A95) or in other words, that, formally, compounds may be thought of as being derived from uncharged central atoms and uncharged ligand-donor-atoms. In this way, the accepted behaviour and notation for ligands as defined for co-ordination compounds (A96) is not contradicted in the new formalism. Specifically, ligands formally donating two electrons to a central atom such as amines, phosphines or carbon monoxide are designated L and the number of such ligands as n. Ligands formally donating one electron towards the formation of a covalent bond to a central atom such as halogens or alkyls are designated X and the number of such ligands as x. A ligand which formally accepts an electron pair from the central atom such as boron trifluoride is designated Z and the number of such ligands as z. The notation used for the central atom is M.

Thus, any uncharged, covalent species can be represented by the general formula $ML_nX_xZ_z$. For the purposes of this formalism, charged complexes are also written in the above form by employing the following equivalences which are

based on accepted chemical behaviour of the various classes of ligands.

$X^- = L$ e.g., Cl^- = L as in $[CoCl_4]^{2-}$

$L^+ = X$ e.g., NH_3^+ = X as in $[Co(NH_3)_5Cl]^{2+}$

$X^+ = Z$ e.g., Cl^+ = Z as in $[PCl_4]^+$

$L^- = LX$ e.g., CO^- = LX as in $[Co(CO)_4]^-$

Having written a compound in the $ML_nX_xZ_z$ notation, certain definitions of it can be made as follows:

Electron Number (EN) = $m+2n+x$ where m is the number of electrons in the isolated central atom's valence shell.

Valence Number (VN) = x or the number of odd electron ligands. VN bears some relationship to the former concept of oxidation state but unlike it, cannot be negative.

Ligand Bond Number (LBN) = $x+n+z$ LBN is closely related to co-ordination number.

Having reduced the covalent compounds of an element to the $ML_nX_xZ_z$ notation and having determined EN and VN for each compound, a chart may be constructed on which the abscissa represents EN and the ordinate represents VN. As a consequence of this construction, the prime diagonals represent LBN. Examples of these charts are given in Figures XIII, XIV and XV for molybdenum, niobium and titanium and have been prepared from lists of covalent compounds of known structures found in the literature. It

should be emphasized that before a compound can be correctly placed on one of these charts, its structure must be known with certainty, otherwise incorrect values for EN and VN may be ascertained resulting in misplacement of the compound.

Inspection of the chart for a particular element readily exposes general trends in the chemistry. The chart of molybdenum compounds, for example, reveals that the chemistry of that element is dominated by the occurrence of substances with LBN = 6 or EN = 18. The reasons for relatively greater stability of compounds obeying these two rules are subtle combinations of kinetic and thermodynamic factors; for example, the shielding of an atom by a spherical distribution of ligands or the complete filling of a valence shell of an atom. Compounds of molybdenum not following one of these rules usually have some atypical feature such as bulky or highly electronegative ligands to which may be attributed their anomalous stability and hence occurrence.

In contrast to the behaviour of molybdenum, there is no clustering of titanium compounds along any particular column or diagonal although a preponderance of compounds with high valence numbers (VN) may be noted. This preponderance of titanium compounds with high VN is probably a reflection of the high energies of titanium's orbitals (low ionization potentials) relative to those of other transition elements.

VN↓ EN→	11	12	13	14	15	16	17	18
0								ML_6 $Mo(CO)_nL_{6-n}$ Arene-MoL_3 $(\pi\text{-}C_6H_6)_2Mo$ $[Mo(CO)_3(CN)_3]^{3-}$
1	LBN → 3						ML_5X $CpMo(\pi\text{-}C_6H_6)$ $(\pi\text{-}C_6H_6)_2Mo^+$	
2		Boxes surrounded by thick lines are relatively more densely populated than others.				ML_4X_2 $Mo(diars)_2X_2$ $Mo(CN)_6^{4-}$		ML_5X_2 $Mo(CO)_5^{2-}$ $CpMo(CO)_3X$ $MoL_2(CO)_3X_2$ $\pi\text{-}BzMoC_3H_5LX$
3	LBN → 4				ML_3X_3 MoX_6^{3-} $Mo(acac)_3$ $MoX_3(THF)_3$			
4				ML_2X_4 MoX_6^{2-} $MoCl_4(RCN)_2$				ML_4X_4 Cp_2MoX_2 $MoH_4(PR_3)_4$ $Mo(NO)_2Cl_2L_2$
5	LBN → 5		MLX_5 MoF_6^- $MoOCl_4^-$ Mo_2Cl_{10}				ML_3X_5 $Mo(CN)_8^{3-}$ $Cp_2MoCl_2^+$	
6		MX_6 MoX_6 MoO_2Cl_2 MoO_4^{2-}				ML_2X_6 MoF_8^{2-} $CpMoO_2Cl$		ML_3X_6 $Cp_2MoH_3^+$

XIII. Classification Chart for Covalent Compounds of Molybdenum

VN↓ / EN→	10	11	12	13	14	15	16	17	18
0								ML_6 $Nb(dipy)_3$	
1	LBN 3		Boxes surrounded by thick lines are relatively more densely populated than others.				MXL_5 $CpNb(CO)(Ph_2C_2)_2$ $CpNb(CO)_2(Ph_2C_2)$?		MXL_6 $CpNb(CO)(C_8H_8)$ $Nb(CO)_6^-$ $CpNb(CO)_3AsR_3$ $CpNb(CO)_2(PPh_3)_2$
2									
3	LBN 4						MX_3L_4 $CpNb(CO)_2(Ph_2C_2)$ Cp_2NbBH_4		MX_3L_5 $Cp_2Nb(X)L$ $Cp_2Nb(\pi\text{-}C_3H_5)$ $[CpNb(CO)(Ph_2C_2)]_2$
4				MX_4L_2 $NbCl_4\cdot 2py$ $[Nb(OEt)Cl_5]^{2-}$ $CpNb(NMe_2)_3$				MX_4L_4 Cp_2NbPh_2 Cp_2NbCl_2 $NbCl_4\cdot 2diars$ $Cp_2Nb(SR)_2Mo(CO)_4$	
5	MX_5 NbO_2F Me_3NbCl_2		MX_5L $[NbX_5]_2$ NbX_6^- $NbOCl_3$ $NbCl_5\cdot R_3P$		MX_5L_2 NbF_7^{2-} NbO_2 NbI_4 $NbCl_5\cdot 2PR_3$		MX_5L_3 $(NbOF_6)^{3-}$ $[Cp_2Nb(SR)_2]^+$ $[(Cp_2NbCl)_2O]^{2+}$		MX_5L_4 niobocene Cp_2NbH_3 NbF_8^{3-} $[Cp_2Nb(H)_2PR_3]^+$

XIV. Classification Chart for Covalent Compounds of Niobium

VN↓	EN → 10	11	12	13	14	15	16	17	18
0	LBN ↗ 3						ML_6 $Ti(dipy)_3$ $(C_8H_8)_2Ti$		
1		Boxes surrounded by thick lines are more densely populated than others.				ML_5X $(C_8H_8TiCl)_2$ $C_8H_8TiCl\cdot py$ $(C_8H_8)_3Ti_2$		ML_6X $CpTiC_8H_8$ $Ti(dipy)_3^-$	
2	LBN ↗ 4				MX_2L_4 $TiCl_6^{4-}$ $TiX_2\cdot 4NH_3$ $CpTiPh\cdot 2NH_3$ Cp_2Ti		ML_5X_2 $C_7H_7TiC_7H_9$ $CpTiC_7H_7$		ML_6X_2 $Cp_2Ti(CO)_2$ $Cp_2Tidipy$
3		MX_3L_2 $TiCl_3\cdot 2THF$ $TiCl_3\cdot 2NMe_3$		MX_3L_3 TiX_6^{3-} $TiCl_3\cdot 3THF$ $[TiBr_2\cdot dipy]_2$		ML_4X_3 Cp_2TiBH_4 $CpTiCl_2\cdot 2py$		ML_5X_3 Cp_3Ti $Cp_2TiL_2^+$ $Cp_2Ti(Cl)L$ $Cp_2TiCl_2AlEt_2$ $Cp_2Ti(\pi\text{-}C_3H_5)$	
4	MX_4L $R_4Ti\cdot L$ $RTiX_3L$ TiX_4NR_3		MX_4L_2 TiO_2 $[Ti(OR)_4]_4$ $CpTiX_3$				ML_4X_4 $(Cp_2Ti)_2$ $Ti(NO_3)_4$ Cp_2TiR_2 $(Cp_2TiH)_2$		ML_5X_4 $(Cp_2TiSR)_2$ $(Cp_2TiCl)_2$

XV. Classification Chart for Covalent Compounds of Titanium

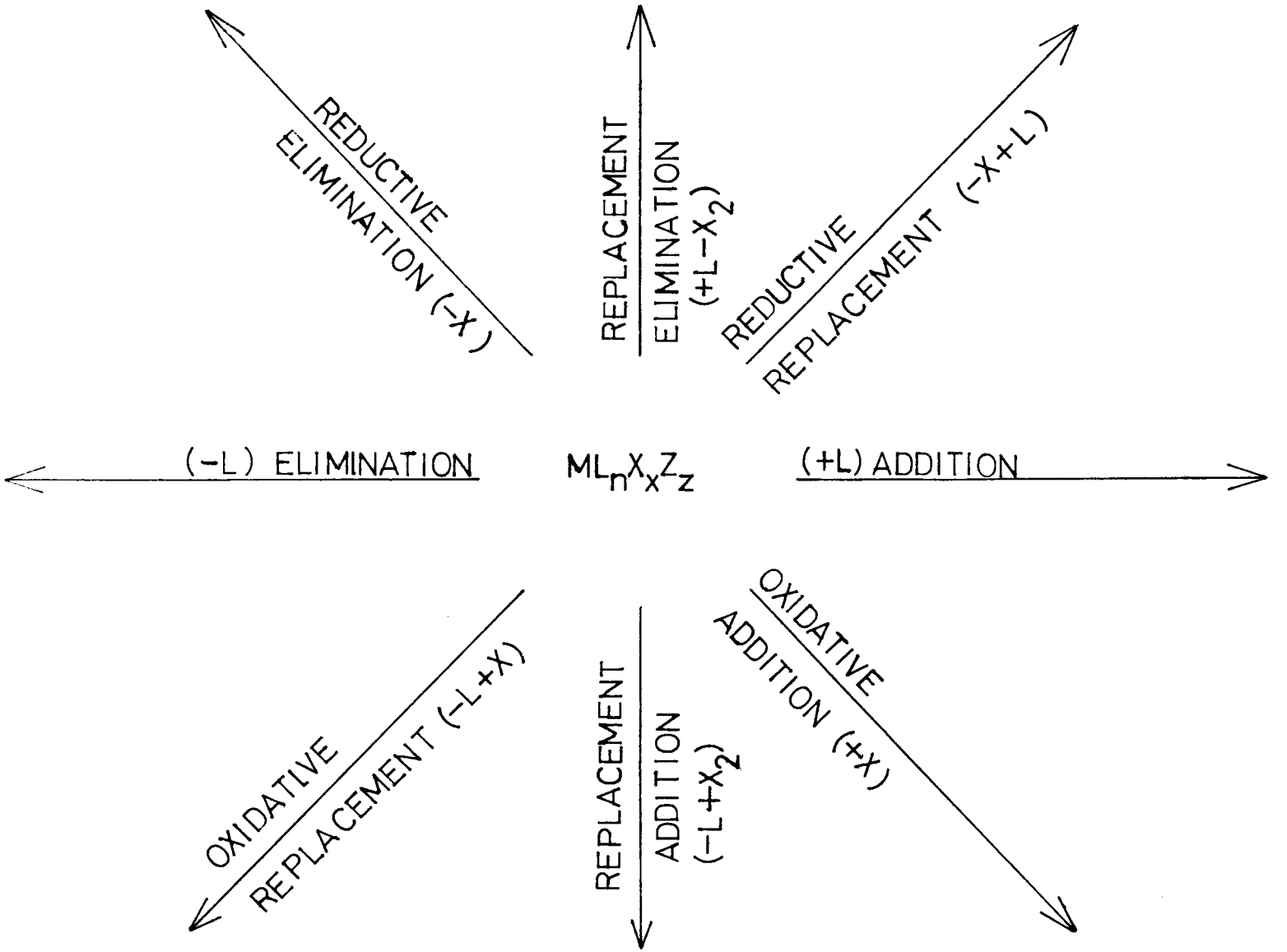
In spite of the relatively unexplored nature of the chemistry of niobium, the developing trends for its compounds seem to be to cluster in the EN = 18 column and along the diagonals corresponding to LBN = 6, 7 or 8. The apparent increase in occurrence of 18 electron compounds of niobium relative to titanium is probably a consequence of an electronic effect such as the lower energies of niobium's orbitals rather than a steric effect since the two atoms are nearly the same size. From the foregoing discussion, it may be seen that occurrence trends for compounds of a particular element can be ascertained from a chart constructed in the manner described and that these trends as well as their variations from those of other elements can be correlated with physical or other properties of the element.

The charts can also be useful for making certain predictions concerning the probable reactivity of compounds. Bearing in mind that preparation of a compound not falling in a well populated chart area often requires a special ligand property which confers stability on the otherwise unusual species, it is logical to expect that reactions of such a compound would yield products appearing in a more densely populated chart area. It is also logical to anticipate that reactions of compounds already in favoured areas would yield products also appearing in these areas unless some very different or unusual ligand were introduced in the reaction.

The stabilization by special ligands of an otherwise unusual compound appearing in a relatively unpopulated chart area is exemplified by tetranorbornyltitanium which is air stable at room temperature (A97) or tetrakis(pentafluorophenyl)titanium which decomposes at 119° in vacuo (A98). These stabilities may be contrasted with that of tetramethyltitanium (A99) which decomposes at -80° under argon.

One of the few reactions other than decomposition undergone by $(\pi\text{-}C_5H_5)_2Ti(CO)_2$ is that with acyl chlorides (A56) to yield $(\pi\text{-}C_5H_5)$ Ti(Cl)OCR. This reaction, which has been described in the literature as an oxidative addition, can be seen by reference to the titanium chart (Figure XV) and Figure XVI to be better classified as elimination with oxidative replacement. Furthermore, it illustrates the argument concerning reactions of a compound in a relatively unpopulated box leading to a product appearing in a relatively more densely populated one.

Finally, examination of a chart shows that specific kinds of reactions correspond to a specific movement on the chart. Thus, an addition reaction (+L) is represented by horizontal movement to the right while elimination (-L) is indicated by movement horizontally to the left. Oxidative addition (+X) corresponds to movement diagonally downwards to the right. Simple reduction (+L-X) is indicated by a movement diagonally upward and to the right while oxidation



XVI. Movements on Classification Charts Corresponding to Various Types of Reactions

(-L+X) is in the opposite direction. These reactions, as well as some others, and the corresponding movements on the charts are summarized in Figure XVI.

Reference to the chart of niobium compounds (Figure XIV) was made while designing some of the experiments reported later in Chapter IV. This made it possible not only to design reactions which were likely to give tractable products but also to obtain an idea of what the alternative types of products from these reactions might be. For example, treatment of $(\pi\text{-}C_5H_5)_2NbBH_4$ with excess ligand, L, might be expected to give rise to products appearing in the EN = 18, VN = 3 or the EN = 18, VN = 1 or, less likely, the EN = 16, VN = 1 box. All these reactions (equations 34 to 36) are possible and plausible mechanisms can be written for each but the first two are more probable, according to the chart, and it is in fact one of these which actually occurs.

$$(\pi\text{-}C_5H_5)_2NbBH_4 + 2PR_3 \rightarrow (\pi\text{-}C_5H_5)_2Nb(H)PR_3 + H_3BPR_3 \quad (34)$$

$$(\pi\text{-}C_5H_5)_2NbBH_4 + 3PR_3 \rightarrow (\pi\text{-}C_5H_5)(C_5H_6)Nb(PR_3)_2 + H_3BPR_3 \quad (35)$$

$$(\pi\text{-}C_5H_5)_2NbBH_4 + 4PR_3 \rightarrow (\pi\text{-}C_5H_5)Nb(PR_3)_3 + C_5H_6 + H_3BPR_3 \quad (36)$$

As a further example of the use of the charts, it will be shown later in Chapter IV, that the compounds $(\pi\text{-}C_5H_5)_2Nb(H)PR_3$ and $(\pi\text{-}C_5H_5)_2Nb(Br)PR_3$ are very readily oxidized to $(\pi\text{-}C_5H_5)_2NbBr_2$. A glance at the chart shows this to be hardly surprising since bis(π-cyclopentadienyl)-niobium compounds appearing in the EN = 17, VN = 4 box tend to have ligands attached to the metal which are relatively

more electronegative than those in EN = 18, VN = 3. One might expect, therefore, that a substance in EN = 18, VN = 3 would have some considerable tendency to undergo oxidation in the presence of species which are potentially electronegative ligands and thus shift itself to EN = 17, VN = 4. There would be expected to be an even greater tendency for this to occur if the substance already has an electronegative ligand on the metal such as does $(\pi\text{-}C_5H_5)_2Nb(Br)PR_3$.

D. References

A1 R. Feld and P.L. Cowe, The Organic Chemistry of Titanium, Butterworth and Co. Ltd., London, 1965.

A2 R.J.H. Clark, The Chemistry of Titanium and Vanadium, Elsevier Publishing Co. Ltd., London, 1968.

A3 F. Fairbrother, The Chemistry of Niobium and Tantalum, Elsevier Publishing Co. Ltd., London, 1967.

A4 R.H. Stanley, Encyclopedia of Chemical Technology, Vol. 20, 2nd ed., John wiley and Sons, Inc., New York, 1969, pp.424-503.

A5 G.A Razuvaev and V.N. Latyaeva, Organomet. Chem. Rev., 1967, 2, 349.

A6 R. Juza, Adv. Inorg. Chem. Radiochem., 1966, 9, 81.

A7 Yu.G. Borodko, A.E Shilov, and A.A. Shteinman, Dokl. Akad. Nauk SSSR, 1966, 168, 581.

A8 M.E. Vol'pin and V.B. Shur, Dokl. Akad. Nauk SSSR, 1964, 156, 1102.

A9 M.E. Vol'pin and V.B. Shur, Nature, 1966, 209, 1236.

A10 R. Maskill and J.M. Pratt, J. Chem. Soc. (A), 1968, 1914.

A11 M.E. Vol'pin, V.B. Shur, M.A. Ilatovskaya, Izvest. Akad. Nauk SSSR, Ser. Khim., 1964, 1728.

A12 A. Yamamoto, M. Ookawa, and S.Ikeda, Chem. Comm., 1969, 841.

A13 E.E. van Tamelen, G. Boche, S.W. Ela, and R.B. Fechter, J. Amer. Chem. Soc., 1967, 89, 5707.

A14 L.G. Bell and H.H. Brintzinger, J. Amer. Chem. Soc., 1970, 92, 4465.

A15 G.J. Leigh, Preparative Inorganic Reactions, 1971, 7, 165.

A16 J. Chatt, G.A. Heath, and R.L. Richards, Chem. Comm., 1972, 1010.

A17 R.W.F. Hardy and R.C. Burns, Annual Review of Biochemistry, 1968, 37, 671.

A18 G.N. Schrauzer and G. Schlesinger, J. Amer. Chem. Soc., 1970, 92, 1808.

A19 A.E. Shilov and G.I. Likhtenshtein, Izvest. Akad. Nauk SSSR., Ser. Biol., 1971, 4, 518.

A20 A.E. Shilov, A.K. Shilova, E.F. Kvashina, and T.A. Vorontsova, Chem. Comm., 1971, 1590.

A21 A.E. Shilov, A.K. Shilova, and E.F. Kvashina, Kinet. Katal., 1969, 10, 1402.

A22 J.H. Teuben, and H.J. de Liefde Meijer, Rec. Trav. Chim., 1971, 90, 360.

A23 J.E. Bercaw, R.H. Marvich, L.G. Bell, and H.H. Brintzinger, J. Amer. Chem. Soc., 1972, 94, 1219.

A24 E.E. van Tamelen, R.B. Fechter, S.W. Schneller, G. Boche, R.H. Greeley, and B. Akermark, J. Amer. Chem. Soc., 1969, 91, 1551.

A25 E.E. van Tamelen, G. Boche, and R. greeley, J. Amer. Chem. Soc., 1968, 90, 1677.

A26 E.E. van Tamelen, R.B. Fechter, and S.W. Schneller, J. Amer. Chem. Soc., 1969, 91, 7196.

A27.E.E. van Tamelen, and B. Akermark, J. Amer. Chem. Soc., 1968, 90, 4492.

A28 M.E. Vol'pin, M.A. Ilatovskaya, L.V. Kosyakova, and V.B. Shur, Chem. Comm., 1968, 1074.

A29 G. Natta, G. Mazzanti, and G. Pregaglia, Gazetta, 1959, 89, 2065.

A30 E.E. van Tamelen and D.A. Seeley, J. Amer. Chem. Soc., 1969, 91, 5194.

A31 G. Henrici-Olive and S. Olive, Angew. Chem. Int Ed., 1969, 8, 650.

A32 E.E. van Tamelen and H. Rudler, J. Amer. Chem. Soc., 1970, 92, 5253.

A33 M.E. Vol'pin, V.B. Shur, R.V. Kudryavtsev, and L.A. Prodayko, Chem. Comm., 1969, 1038.

A34 V.N. Latyaeva, L.I. Vishinskaya, V.B. Shur, L.A. Fyodorov, and M.E. Vol'pin, J. Organomet. Chem., 1969, 16, 103.

A35 G.W. Parshall, J. Amer. Chem. Soc., 1967, 89, 1822.

A36 R.B. King and M.B. Bisnette, Inorg. Chem., 1966, 5, 300.

A37 M.E. Vol'pin, A.A. Belyi, V.B. Shur, N.A. Katkov, I.M. Nekaeva, and R.V. Kudryavtsev, Chem. Comm., 1971, 246.

A38 R.S.P. Coutts and P.C. Wailes, Adv. Organomet. Chem., 1970, 9, 136.

A39 J.E. Bercaw and H.H. Brintzinger, J. Amer. Chem. Soc., 1969, 91, 7301.

A40 A.K. Fischer and G. Wilkinson, J. Inorg. Nucl. Chem., 1956, 2, 149.

A41 K. Clauss and H. Bestian, Ann. Chem., 1962, 654, 8.

A42 K. Yokokawa and K. Azuma, Bull. Chem. Soc. Japan, 1965, 38, 859.

A43 G.W. Watt, L.J. Baye, and F.O. Drummond, Jr., J. Amer. Chem. Soc., 1960, 88, 1138.

A44 Y. Takegami, T. Ueno, T. Suzuki, and Y. Fuchizaki, Bull. Chem. Soc. Japan, 1968, 41, 2637.

A45 H.O. Martin and R.O. de Jongh, Chem. Comm., 1969, 1366.

A46 H.H. Brintzinger and J.E. Bercaw, J. Amer. Chem. Soc., 1970, 92, 6182.

A47 H.H. Brintzinger and L.S. Bartell, J. Amer. Chem. Soc., 1970, 92, 1105.

A 48 W. Kirmse, Carbene Chemistry, Academic Press, New York, 1964.

A49 P.C. Wailes and H. Weigold, J.Organomet. Chem., 1970, 24, 713.

A50 P. Corradini and A. Sirigu, Inorg. Chem., 1967, 6, 601.

A51 R.H. Marvich and H.H. Brintzinger, J. Amer. Chem. Soc., 1971, 93, 2046.

A52 J.E. Bercaw and H.H. Brintzinger, J. Amer. Chem. Soc., 1971, 93, 2045.

A53 G. Fachinetti and C Floriani, Chem. Comm., 1972, 654.

A54 H.A. Martin, M. van Gorkom, and R.O. de Jongh, J. Organomet. Chem., 1972, 36, 93.

A55 M.E. Vol'pin, A.A. Belyi, V.B. Shur, Yu. I. Lyakhovetsky, R.V. Kudryavtsev, and N.N. Bubnov, J. Organomet. Chem., 1971, 27, C5.

A56 C. Floriani and G. Fachinetti, Chem. Comm., 1972, 790.

A57 T. Saito, Chem. Comm., 1971, 1422.

A58 J.J. Salzmann and P. Masemann, Helv. Chim. Acta, 1967, 50, 1831.

A59E. Bayer and V. Schurig, Chem. Ber., 1969, 102, 3378.

A60 K.H. Thiele and W. Schafer, Z. Anorg. Allg. Chem., 1970, 379, 63.

A61 W. Schafer and K.H. Thiele, Z. Anorg Allg. Chem., 1971, 381, 205.

A62 E.O. Fischer and A. Lochner, Z. Naturforsch., 1960, 15b, 266.

A63 F.W. Siegert and H.J. de Liefde Meijer, J. Organomet. Chem., 1969, 20, 141.

A64 J.L. Calderon, F.A. Cotton, and P. Legzdins, J. Amer. Chem. Soc., 1969, 91, 2528.

A65 F.A. Cotton and P. Legzdins, J. Amer. Chem. Soc., 1968, 90, 6232.

A66 J.L. Calderon, F.A. Cotton, B.G. de Boer, and J. Takata, J. Amer. Chem. Soc., 1970, 92, 3801.

A67 J.L. Calderon, F.A. Cotton and J. Takata, J. Amer. Chem. Soc., 1971, 93, 3587.

A68 J.L. Calderon, F.A. Cotton, B.G. de Boer and J. Takata, J. Amer. Chem. Soc., 1971, 93, 3592.

A69 I.S. Kolomnikov, T.S. Lobeeva, V.V. Gorbachevskaya, G.G. Aleksandrov, Yu.T. Struchkov and M.E. Vol'pin, Chem. Comm., 1971, 972.

A70 G. Henrici-Olive and S. Olive, J. Organomet. Chem., 1969, 16, 339.

A71 G. Henrici-Olive and S. Olive, J. Organomet. Chem., 1969, 19, 309.

A72 G. Henrici-Olive and S. Olive, Makromol. Chem., 1969, 121, 70.

A73 G. Henrici-Olive and S. Olive, J. Polymer Sci., (13), 1970, 8, 271.

A74 R.J.H. Clark and A.J. McAlees, J. Chem. Soc., (A), 1970, 2026.

A75 R.J.H. Clark and A.J. McAlees, Inorg. Chem., 1972, 11, 342.

A76 R.J.H. Clark and A.J. McAlees, J. Chem. Soc., (Dalt. Trans), 1972, 640.

A77 R.J.H. Clark and M. Coles, Chem. Comm., 1971, 1587.

A78 R.S.P. Coutts, R.L. Martin, and P.C. Wailes, Aust. J. Chem., 1971, 24, 1533.

A79 V.T. Kalinnikov, G.M. Larin, O.D. Ubozhenko, A.A. Zharkikh, V.N. Latyaeva and A.N. Lineva, Dokl. Akad. Nauk SSSR., 1971, 199, 95.

A80 E. Maslowsky, Jr. and K. Nakamoto, Appl. Spectrosc., 1971, 25, 187.

A81 O.S. Roschupkina, V.A. Dubovitskii and Yu.G. Borodko, Zh. Strukt. Khim., 1971, 12, 1007.

A82 J. Charalambous, M.J. Frazer, and W.E. Newton, J. Chem. Soc., (A), 1971, 2487.

A83 J.D. Mathews, N. Singer and A.G. Swallow, J. Chem. Soc. (A), 1970, 2545.

A84 V.N. Vyshinskii, T.I. Ermolaeva, V.N. Latyaeva, A.N. Lineva, and N.E. Lukhton, Dokl. Akad. Nauk SSSR, 1971, 198, 487.

A85 G.A. Razuvaev, V.N. Latyaeva and A.N. Lineva, Zh. Obsch. Khim., 1970, 40, 1804.

A86 A. Skapski and P.G.H. Troughton, Acta Crystallogr., (B), 1970, 26, 716.

A87 W. Schneider, (B.F. Goodrich Co. Ltd.) U.S. Pat. 3,535,396, 1970.

A88 C.J. Ballhausen and J.P. Dahl, Acta Chem. Scand., 1961, 15, 1333.

A89 N.W. Alcock, J. Chem. Soc. (A), 1967, 2001.

A90 J.C. Green, M.L.H. Green, and C.K. Prout, Chem. Comm., 1972, 421.

A91 G. Henrici-Olive and S. Olive, J. Organomet. Chem., 1969, 19, 309.

A92 J.G. Kenworthy, J. Myatt, and M.C.R. Symons, J. Chem. Soc, (A), 1971, 1020.

A93 J.G. Kenworthy, J. Myatt and M.C.R. Symons, J. Chem. Soc. (A), 1971, 3428.

A94 M.C.R. Symons, private communication.

A95 L. Pauling, The Nature of the Chemical Bond, cornell University Press, Ithaca, New York, 1939.

A96 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, third ed., Interscience Publishers, London, 1972, pp.23.

A97 B.K. Bower and H.G. Tennent, J. Amer. Chem. Soc., 1972, 94, 2512.

A98 G.A. Razuvaev, V.N. Latyaeva, G.A. Kilyakova, and G.Ya. Mal'kova, Dokl. Akad. Nauk SSSR., 1970, 191, 620.

A99 F.S. D'yachkovskii and N.E. Krushch, Zh. Obshch. Khim., 1971, 41, 1779.

CHAPTER II

Some d^1 Mono- and Bis(π-cyclopentadienyl)titanium Compounds with Nitrogen and Phosphorus Donor Ligands

A. Introduction

As discussed in Chapter I, it is only recently that a complex between molecular nitrogen and a titanium compound has been isolated in which the nitrogen may subsequently be reduced to ammonia (B1-B3). In contrast, several non-reducible nitrogen complexes of other metals have been known for some time (B4) and it is, therefore, of interest to try to discover how nitrogen in the titanium complex is reduced to ammonia and what distinguishes this system from those in which molecular nitrogen is bound to other metals.

A mechanism for the reduction has been proposed by Brintzinger (B5) on the basis of e.s.r. and other studies which involves a titanium hydride as the nitrogen fixing centre. His later work has shown (B3) that such a hydride is unlikely to be directly involved in the reduction but that a similar mechanism involving bis(π-cyclopentadienyl)-titanium instead of $\left[(\pi\text{-}C_5H_5)_2TiH\right]_2$ is also consistent with the data. A revised mechanism based on his earlier proposals is shown in Figure I. A five-line e.s.r. signal which may be interpreted in terms of the presence of the species (a) in Figure I has been detected (B5) which vanishes upon addition of hydrogen chloride or Grignard reagent.

I. A Possible Mechanism for Nitrogen Fixation by Bis(π-cyclopentadienyl)titanium Compounds

Some recent observations concerning edge-on bonding to metal atoms by pairs of multiply bonded nitrogen atoms may also be interpreted as supporting the mechanism in Figure I. Thus, edge-on bonding of azobenzene to a nickel atom has been observed in bis(<u>tert</u>-butylisocyanide)(azobenzene)nickel and bis(triphenylphosphine)(azobenzene)nickel (B6, B7) and has been observed to have a remarkable effect on both the chemistry

of azobenzene (B7) and upon the N-N bond length (B6). In the isocyanide complex (B6) the N-N length is 1.385 Å or about that of an N-N single bond (average 1.44 Å) (B8) and considerably longer than an N-N double bond (average 1.24 Å) (B8). This lengthening upon edge-on bonding is in contrast to the lengthening achieved by end-on bonding of molecular nitrogen. For example, the N-N length in $\left[Ru(en)_2(N_2)(N_3)\right] PF_6$ is 1.106 Å (B9) which may be compared with an N-N triple bond length of 1.098 Å (B8).

These variations in the extent of bond lengthening achieved upon co-ordination would be expected to be reflected in the chemistry of the two types of system. In this regard, it is notable that whereas many complexes of end-on bonded molecular nitrogen are known, in none can the nitrogen be reduced. On the other hand, the edge-on bonded azobenzene mentioned earlier (B7) reacts readily with water and is reduced to sym-diphenylhydrazine.

Recently, Chatt (B10, B11) has observed reduction of the nitrogen in trans-$\left[M(N_2)_2(diphos)_2\right]$ (M = Mo or W) but since one of the co-ordinated molecules of nitrogen is lost as the other is being reduced, the structure of the species actually undergoing reduction is not known. It has, however, been proposed that the nitrogen molecule which is being reduced may be bonded edge-on to the metal in these systems.

Further indirect evidence supporting some aspects of the mechanism shown in Figure I may also be found in

Armor and Taube's examination of the kinetics of reaction 1 (B12).

$$\left[Ru(NH_3)_5{}^{15}NN\right]^{2+} \rightleftharpoons \left[Ru(NH_3)_5N^{15}N\right]^{2+} \qquad (1)$$

They concluded that the isomerization is an intramolecular process and that the transition state corresponds to edge-on bonding of the nitrogen molecule. They also concluded that in the transition state the energy of the bond between the nitrogen molecule and the metal atom is about 7kcal/mol or close to the value of 5 kcal/mol found by Shilov (B13) to be the heat of formation of his titanium-nitrogen complex. Shilov's complex (B1, B14) is postulated to be similar to Brintzinger's intermediate (B3) and to have the nitrogen bonded edge-on.

Although, in the light of the above discussion, Brintzinger's proposed mechanism (Figure I) for nitrogen reduction (B5) appears plausible, only tenuous evidence for two of the proposed intermediates is available. It therefore seemed desirable, when commencing the present project, to attempt preparation of these or related systems.

As a suitable starting material for the proposed preparations, the dimer (B15) with two chlorine bridges, $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$, was selected. In addition to two cyclopentadienyl rings attached to a low valent metal atom, it also contains two halogen bridges which, if cleaved, would leave a vacant co-ordination position on each metal atom which might be filled by a nucleophilic ligand. The cleavage of halogen bridges by nucleophilic reagents such

as amines or phosphines is a well documented phenomenon (B16).

Following such a route, one would anticipate the preparation of monomeric complexes having, in addition to the two cyclopentadienyl rings, one halogen atom and one nucleophilic ligand attached to the metal. These substances would be expected to undergo reduction to still lower valent species or be convertible to hydrides or alkyls, all of which have been suggested, at one time or another, to be important in nitrogen fixation or olefin isomerization and polymerization.

A search for suitable preparations of the dimer, $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$, revealed only methods acceptable for producing small amounts of pure compound. Concerning larger scale preparations, the literature was discovered to be confused and incomplete. Accordingly, it was first necessary to devise a satisfactory synthesis of relatively large quantities of the dimer, $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$, before examining its properties with donor ligands.

B. Chemical Studies

A list of all new compounds discussed in this chapter is given in Table I.

1. Preparation of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$

Reaction 2 was discovered to be a new, rapid synthesis for small amounts of pure $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$.

$$2(\pi\text{-}C_5H_5)_2TiCl_2 + 2(\pi\text{-}C_5H_5)_2TiBH_4 \longrightarrow 2\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2 + B_2H_6 + H_2 \qquad (2)$$

The reaction was carried out in tetrahydrofuran and the

Table I

New Compounds Reported in Chapter II		
Compound	Colour	Decomp. Pt. (°C)
$[(\pi\text{-}C_5H_5)_2TiCl]_2$	green	-
$(\pi\text{-}C_5H_5)_2TiCl\cdot NH_3$	green	191
$(\pi\text{-}C_5H_5)_2TiCl\cdot NH_2Me$	green	154
$(\pi\text{-}C_5H_5)_2TiCl\cdot NH_2Et$	green	155
$(\pi\text{-}C_5H_5)_2TiCl\cdot NH_2C_3H_5$	green	154
$(\pi\text{-}C_5H_5)_2TiCl\cdot NH_2Ph$	green	168
$(\pi\text{-}C_5H_5)_2TiCl\cdot py$	brown	148
$(\pi\text{-}C_5H_5)_2TiCl\cdot PMe_2Ph$	green	135
$(\pi\text{-}C_5H_5)_2TiCl\cdot PMePh_2$	green	130
$[(\pi\text{-}C_5H_5)_2TiCl]_2\cdot$diphos	green	222
$[(\pi\text{-}C_5H_5)_2Ti\cdot en]Cl$	blue	265
$[(\pi\text{-}C_5H_5)_2Ti\cdot en]PF_6$	blue	197
$[(\pi\text{-}C_5H_5)_2Ti\cdot Me_2en]PF_6$	blue	176
$[(\pi\text{-}C_5H_5)_2Ti\cdot dipy]PF_6$	purple	262
$(\pi\text{-}C_5H_5)TiCl_2\cdot PMe_2Ph$	green	134
$(\pi\text{-}C_5H_5)TiCl_2\cdot PMePh_2$	green	125
$(\pi\text{-}C_5H_5)TiCl_2\cdot$diphos	green	143
$(\pi\text{-}C_5H_5)TiCl_2\cdot$DMPE	green	205

product purified by subliming the excess $(\pi\text{-}C_5H_5)_2TiBH_4$ used to drive the reaction to completion, followed by recrystallization of the residue from a tetrahydrofuran-ether mixture. Green $[(\pi\text{-}C_5H_5)_2TiCl]_2$ prepared in this way was

identified by elemental analysis and comparison of its i.r. spectrum with that of an authentic sample prepared by a published method.

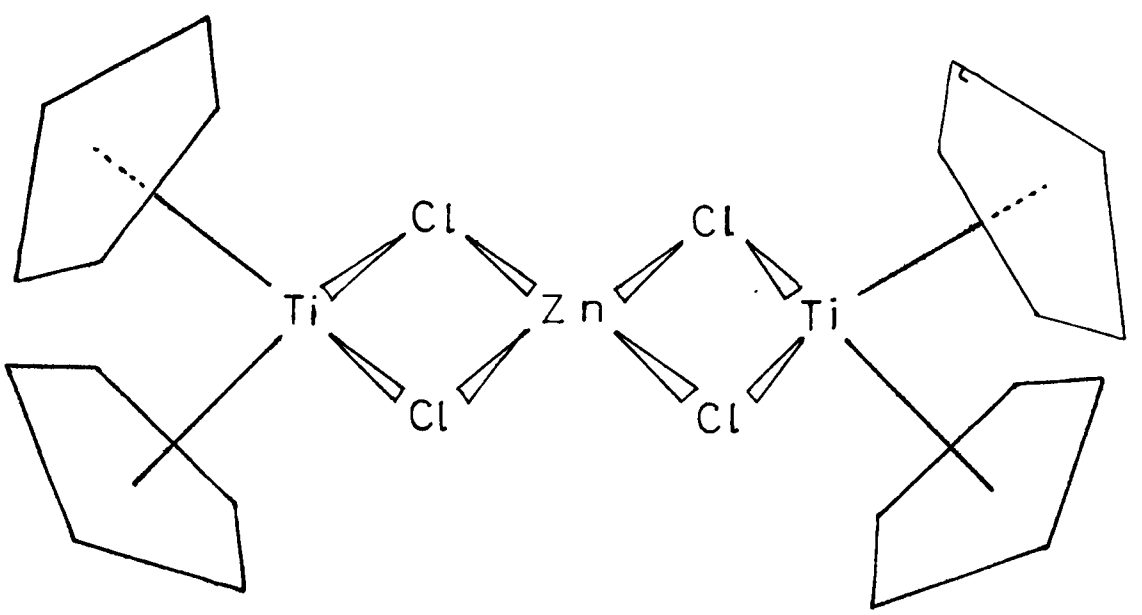
A serious disadvantage to using reaction 2 as a source of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ is the requirement for pure $(\pi\text{-}C_5H_5)_2TiBH_4$ as a reagent. The published synthesis (B17) of $(\pi\text{-}C_5H_5)_2TiBH_4$ calls for reduction of $(\pi\text{-}C_5H_5)_2TiCl_2$ with sodium borohydride in tetrahydrofuran followed by removal of the solvent and sublimation of $(\pi\text{-}C_5H_5)_2TiBH_4$ from the residue. Only moderate yields, usually less than 50%, are obtained by this procedure but it was discovered that changing the solvent to 1,2-dimethoxyethane permits isolation of the compound in greater than 80% yield. Even with the improved yield, however, preparation of pure $(\pi\text{-}C_5H_5)_2TiBH_4$ in sufficient quantities for the purposes of this study proved tedious and time-consuming.

It was finally determined that the best method for large-scale preparations of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ is by zinc reduction of bis(π-cyclopentadienyl)titanium dichloride (B18).

$$2(\pi\text{-}C_5H_5)_2TiCl_2 + Zn \longrightarrow \left[(\pi\text{-}C_5H_5)_2TiCl\right]_2 + ZnCl_2 \qquad (3)$$

Removal of zinc chloride from the product, however, has always been a problem (B19) and its presence has led to a general reluctance (B15) to use this relatively simple method of preparation. The zinc chloride-containing substance, shown by Salzmann (B20) to have the structure

indicated in Figure II, which is isolated as pale green needles when the reduction is carried out in non-polar solvents, is apparently decomposed by polar ones.



II. Proposed Structure of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2ZnCl_2$

Thus, from a mixture of tetrahydrofuran and ether, the compound, $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$, free from zinc chloride may be crystallized as dark green cubes. The two compounds, one zinc-containing and one zinc-free, are readily distinguishable by colour, crystal shape and i.r. spectrum. Samples of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ used in the studies reported in the remainder of this chapter were shown to be zinc-free by the dithizone spot-test.

2. <u>Preparation of $(\pi\text{-}C_5H_5)_2TiCl\cdot NH_2R$ and $(\pi\text{-}C_5H_5)_2TiCl\cdot py$</u>

Green $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ is cleaved smoothly in the presence or absence of solvents adding one molecule of primary amine to each metal atom of the dimer according to equation 4. A concomitant colour change from dark to light green is observed

except when pyridine is present in which case the colour changes to brown.

$$\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2 + 2RNH_2 \longrightarrow 2(\pi\text{-}C_5H_5)_2TiCl\ NH_2R \qquad (4)$$

$$R = H,\ Me,\ Et,\ C_3H_5,\ Ph,\ Cy;\ NH_2R = py$$

The reaction was demonstrated with pyridine, ammonia, methylamine, ethylamine, allylamine, aniline and cyclohexylamine although in the last case no attempt was made to identify the product which has the same appearance and behaviour as the other primary amine adducts. The characterization of the compounds, their properties and some further reactions involving them will be discussed later in sections B6, B7 and B8 of this chapter.

Various methods for preparing secondary and tertiary amine homologues of the compounds formed by the primary amines were tried using dimethylamine, diethylamine, dicyclohexylamine, diphenylamine, trimethylamine, tributylamine, hexamethylenetetramine, piperidine and azobenzene. In the absence of solvents, $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ is usually unaffected by the secondary or tertiary amines although it shows some tendency to dissolve in those of higher molecular weight. Refluxing toluene solutions of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ containing the amines also failed to cause any reaction other than decomposition after several hours. Likewise, addition of the amines to solutions of the primary amine adducts fails to cause displacement of the primary amines and the reactants may be recovered unchanged except when prolonged refluxing

causes general decomposition. When hydrazine hydrate is added to $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ at room temperature in the absence of solvent, almost instantaneous deposition of Ti_2O_3 is the sole result observed.

In contrast to its inertness in the presence of piperidine and other secondary or tertiary amines, $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ dissolves readily in pyridine giving a red-brown solution from which similar-coloured needle-like crystals may be obtained. Compound formation between $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ and pyridine or 4,4′-dipyridyl was mentioned recently in a review by Coutts and Wailes (B21) as unpublished work. The former compound is undoubtedly identical to the substance described in this work while the latter might be expected, on the basis of its colour and solubility properties, to have a structure analogous to that of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$·diphos, discussed in the next section.

3. <u>Preparation of $(\pi\text{-}C_5H_5)_2TiCl\cdot PR_3$ and $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$·diphos</u>

The apparent dependence of amine-reactivity on the extent of substitution at the nitrogen atom prompted an investigation into the behaviour of substituted phosphines under similar conditions. It was hoped, thereby, to gain insight into the factors by which secondary and tertiary amines are prevented from reacting.

The tertiary phosphines, dimethylphenylphosphine, and methyldiphenylphosphine react with $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ in the presence or absence of solvent according to equation 5

with liberation of heat and a colour change from dark to light green. The amount of heat liberated in the reaction of methyldiphenylphosphine seems markedly less than that which is liberated when dimethylphenylphosphine is used.

$$\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2 + 2PR_3 \longrightarrow 2(\pi\text{-}C_5H_5)_2TiCl\cdot PR_3 \qquad (5)$$

$$R = Me_2Ph \text{ or } MePh_2$$

The two phosphine-containing complexes were also prepared by replacement of pyridine, as indicated in equation 6.

$$(\pi\text{-}C_5H_5)_2TiCl\cdot py + R_3P \longrightarrow (\pi\text{-}C_5H_5)_2TiCl\cdot PR_3 + py \qquad (6)$$

Treating $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ with triphenylphosphine or tricyclohexylphosphine in melts of those phosphines or in benzene solutions at room temperature or under reflux fails to cause any reaction and the unchanged starting materials may be recovered. Similarly, neither trimethylphosphite nor triphenylphosphite causes any permanent change although both dissolve $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ which can subsequently be recovered from them. The pyridine displacement reaction (equation 6) was attempted with both phosphines and phosphites as well as with carbon monoxide and no reactions were observed. Even when methyl iodide was added to the solutions in order to encourage pyridine replacement by precipitation of N-methylpyridinium iodide according to equation 7, no reactions occurred.

$$(\pi\text{-}C_5H_5)_2TiCl\cdot py + L + MeI \not\longrightarrow (\pi\text{-}C_5H_5)_2TiCl\cdot L + \left[pyMe\right]I \qquad (7)$$

As the first stage in an investigation of the effects on $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ of bidentate ligands related to the

monodentate ones already examined, 1,2-bis(diphenylphosphino)-ethane was added to a solution of the dimer, $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$. In benzene, a product is formed as shown in equation 8 with the usual colour change from dark to light green, but in ethanol no reaction at all is observed. The stoicheiometry of equation 8 suggests that the 1,2-bis(diphenylphosphino)-ethane may be bridging between two titanium atoms.

$$\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2 + \text{diphos} \longrightarrow \left[(\pi\text{-}C_5H_5)_2TiCl\right]_2\cdot\text{diphos} \qquad (8)$$

Characterization and properties of all the compounds whose preparations have been described here will be discussed later in sections B6, B7 and B8.

4. Preparation of $\left[(\pi\text{-}C_5H_5)_2Ti\cdot L'_2\right]A$

In spite of the moderately vigorous conditions employed in some of the reactions discussed so far, no evidence had been found to suggest the existence of cationic species which would be formed upon co-ordination of more than one ligand molecule to the metal and simultaneous displacement of chlorine as the anion. Bearing this in mind, as well as the probable structures of both the 4,4′-dipyridyl derivative (B21), $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2\cdot$4,4′-dipy, and the compound $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2\cdot$diphos described in section B3 of this chapter, it seemed plausible that in the bis(π-cyclopentadienyl)titanium systems, bidentate ligands of the type being examined might form bridges between two metals rather than chelates with one. To test that hypothesis, or in the event of the occurrence of chelates, to investigate the extent to which the "chelate effect" (B32) might assist reaction of other than primary

amines, an examination of some bidentate amines in the presence of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ was carried out.

Benzene or tetrahydrofuran solutions of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ containing ethylenediamine, sym-dimethylethylenediamine or 2,2′-dipyridyl rapidly precipitate blue or purple ionic substances at room temperature according to equation 9.

$$\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2 + 2N\text{—}N \longrightarrow 2\left[(\pi\text{-}C_5H_5)_2Ti\begin{smallmatrix}N\\N\end{smallmatrix}\right]Cl \qquad (9)$$

$$N\text{—}N = en,\ Me_2en \text{ or dipy}$$

These cationic species, which may be isolated initially as their chlorides, dissolve in water with which they react, forming Ti_2O_3. By working quickly, however, it is possible to re-precipitate them as their hexafluorophosphates and these salts can in turn be separated from any Ti_2O_3 by extraction with organic solvents. A related reaction employing N,N,N′,N′-tetramethylethylenediamine at room temperature or in refluxing benzene yielded only starting materials.

5. Preparation of $(\pi\text{-}C_5H_5)TiCl_2\cdot 2L$

The bis-π-cyclopentadienyl systems of titanium have been moderately extensively studied in comparison to the (B21) mono-π-cyclopentadienyl ones. Bearing this in mind and in view of the behaviour of systems with two cyclopentadienyl rings reported earlier in this chapter, it was decided to try to extend that sort of chemistry to the less well studied mono-π-cyclopentadienyl systems.

For this aspect of the work, the dimeric or polymeric compound of unknown structure, $\left[(\pi\text{-}C_5H_5)TiCl_2\right]_n$, was used as the starting material (B23). It was prepared by zinc reduction of π-cyclopentadienyltitanium trichloride, itself obtained by Gorsich's method (B24) from $(\pi\text{-}C_5H_5)_2TiCl_2$ and titanium tetrachloride and purified by sublimation. Samples used in the study were shown to be zinc-free by the dithizone spot-test.

Subsequent to the present study, compounds of the form $(\pi\text{-}C_5H_5)TiX_2\cdot 2L$ where L is tetrahydrofuran or pyridine have been briefly mentioned by Coutts and Wailes (B25, B26) and Russian workers have reported (B27, B28) dimeric carboxylates, $\left[(\pi\text{-}C_5H_5)Ti(OOCR)_2\right]_2$, which may be thought of as having the form $(\pi\text{-}C_5H_5)TiX_2\cdot 2L$. This work confirms the existence of such compounds and extends the series to include phosphorus-donor ligands.

Smooth reactions of dimethylphenylphosphine, methyldiphenylphosphine, 1,2-bis(diphenylphosphino)ethane and 1,2-bis(dimethylphosphino)ethane occur at room temperature, as indicated in equation 10, in the presence of a suitable solvent such as tetrahydrofuran. When dimethylphenylphosphine or methyldiphenylphosphine are used, the reaction occurs even in the absence of solvents.

$$\left[(\pi\text{-}C_5H_5)TiCl_2\right]_n + 2nL \longrightarrow n(\pi\text{-}C_5H_5)TiCl_2\cdot 2L \qquad (10)$$

$$L = Me_2PhP,\ MePh_2P;\ 2L = \text{diphos, DMPE}$$

Formation of the product is accompanied by a colour change

from purple to green. Care must be exercised when isolating the 1,2-bis(diphenylphosphino)ethane- and methydiphenylphosphine-containing substances that solution temperatures do not rise above 40° at which point decomposition commences.

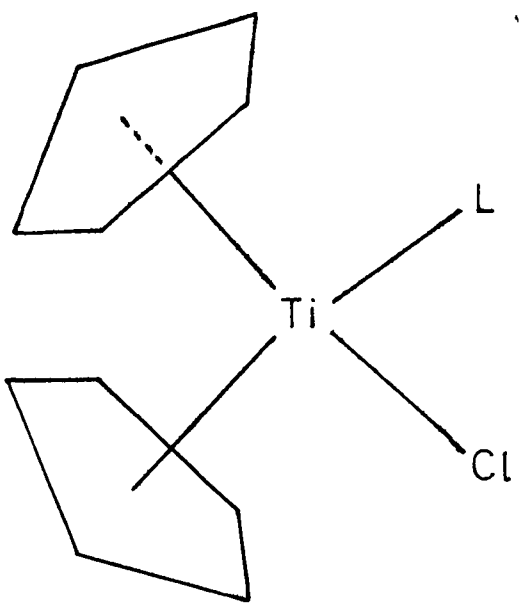
In accord with the greater thermal instability of complexes derived from bulkier phosphines, it was found impossible to prepare derivatives of triphenylphosphine or tricyclohexylphosphine. Treatment of $\left[(\pi\text{-}C_5H_5)TiCl_2\right]_n$ with molten ligand for twenty-four hours resulted only in recovery of the starting materials as did similar reactions in benzene at room temperature or under reflux. The characterization and some properties of these compounds are discussed later in sections B6, B7 and B8.

6. Characterization

All the new compounds mentioned in this chapter have been characterized by elemental analysis, i.r. spectroscopy, conductivity measurements, melting points and in some instances by cryoscopic molecular weight determinations in benzene, e.s.r. and mass spectroscopy. In a number of cases, the stoicheiometry of the reactions has been established by gravimetric methods. Tables of the relevant physical data may be found in the Appendix.

All the monodentate ligands form adducts having the structure shown in Figure III as may be deduced from the evidence that follows. The stoicheiometry of the reactions and the elemental analyses indicate an empirical formula in accord with the structure of Figure III. For example, reaction

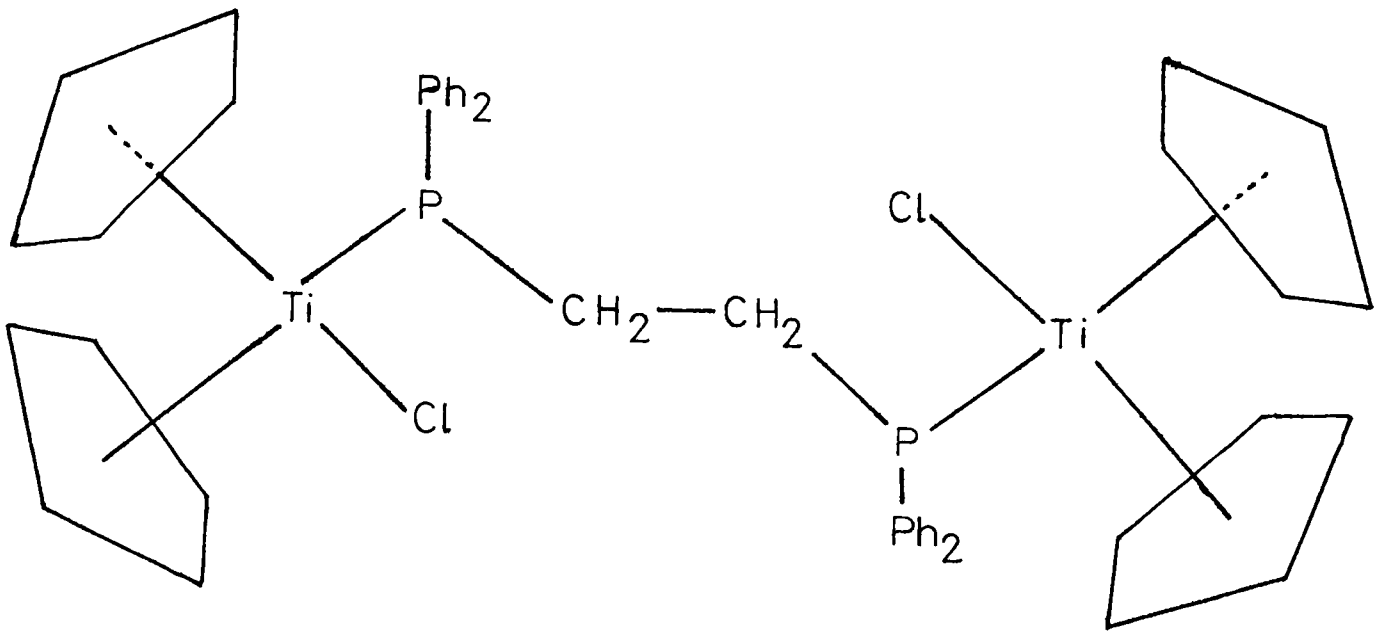
of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ (0.500 g, 1.19 mmol) with pyridine (0.530 g, 6.50 mmol) was followed by isolation of 0.662 g of product. This suggests combination of 0.162 g (or 2.05 mmol) of pyridine with the $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ since no other products were formed in significant amounts. The stoicheiometry of the reaction is thus established as involving combination of one mole of pyridine with one gram-atom of titanium. Cryoscopic molecular weight determinations in benzene of the substance in which the ligand was ethylamine or methyldiphenylphosphine agree within 6% and 13%, respectively, with the values expected for monomers. Conductivities of the compounds in dilute (ca. 10^{-3}M) acetone solutions are less than $10^{-6}\,\Omega^{-1}cm^{-1}$, indicating an essentially non-ionic nature for these materials. Mass spectra of the compounds do not show parent ion peaks although ions of relatively great abundance with mass to charge ratios corresponding to $\left[(\pi\text{-}C_5H_5)_2TiCl\right]^+$, $\left[(\pi\text{-}C_5H_5)_2Ti\right]^+$ and $\left[L\right]^+$ are seen.



III. Proposed Structure of $(\pi\text{-}C_5H_5)_2TiCl\cdot L$

The absence of parent ion peaks is not surprising since, for example, the complex $(\pi\text{-}C_5H_5)_2TiCl\cdot PPhMe_2$ readily decomposes *in vacuo* at 130° giving dimethylphenylphosphine and $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$.

The compound formed by 1,2-bis(diphenylphosphino)ethane probably has the structure shown in Figure IV.



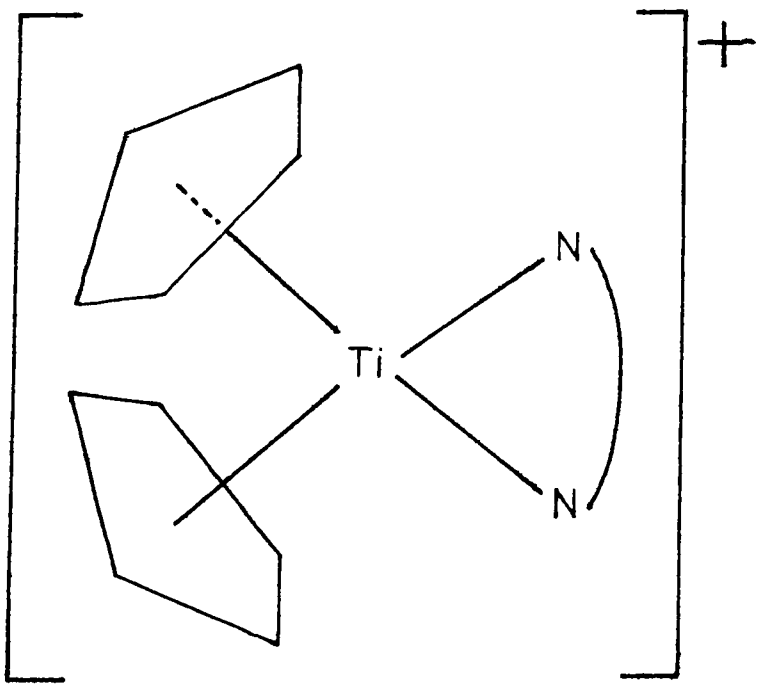
IV. Proposed Structure of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2\cdot$diphos

The stoicheiometry of its formation was established by treating 1.88 mmol of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ with 3.84 mmol of 1,2-bis(diphenylphosphino)ethane. From the reaction, was recovered 2.00 mmol of 1,2-bis(diphenylphosphino)ethane and a single product whose weight indicated combination of 1.79 mmol of 1,2-bis(diphenylphosphino)ethane with the starting material. Thus, one molecule of ligand combines with two atoms of titanium in the reaction. Elemental analyses agree well with data expected from a compound with the structure shown in Figure IV and the conductivity of a dilute solution (*ca.* 10^{-3}M) in acetone is less than

$10^{-6}\Omega^{-1}cm^{-1}$ showing the substance to be non-ionic.

The e.s.r. spectra of the compounds $(\pi\text{-}C_5H_5)_2TiCl\cdot L$ (L = py, $EtNH_2$, Me_2PhP) and $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2\cdot$diphos were recorded in tetrahydrofuran solutions (ca. 10^{-3}M) over the temperature range -60° to +20° and all were found to consist of singlets about 25 gauss wide. The g_{iso} value for each of the complexes fell within the range 1.980 ± 0.005 and may be compared to that of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ which is also 1.980 (B20). Thus, the presence of an unpaired electron usually associated with titanium in formal oxidation state three is confirmed and the absence of interaction between the unpaired spins on the two metal atoms in $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2\cdot$diphos is indicated.

With the exception of 1,2-bis(diphenylphosphino)ethane, all the bidentate ligands gave compounds probably having the structure shown in Figure V. Elemental analyses agree with values expected for compounds of this nature.



V. Proposed Structure of $\left[(\pi\text{-}C_5H_5)_2Ti\cdot L'_2\right]^+$

As an example of the formation of this class of compound, the stoicheiometry of the reaction between $[(\pi\text{-}C_5H_5)_2TiCl]_2$ and 2,2′-dipyridyl was examined in detail. Particular interest was focussed on the examination since Coutts and Wailes have reported the preparation of a compound of formula $(\pi\text{-}C_5H_5)_2TiCl\cdot 1.5$dipy by an identical method (B29). Their compound was, however, poorly characterized and the postulated structure is improbable. In contrast to their report, $[(\pi\text{-}C_5H_5)_2Ti\cdot dipy]Cl$ is formed virtually quantitatively under their conditions or in presence of large excesses of 2,2′-dipyridyl. Thus, $[(\pi\text{-}C_5H_5)_2TiCl]_2$ (0.513 g, 1.20 mmol) and 2,2′-dipyridyl (0.760 g, 7.19 mmol) were mixed in tetrahydrofuran, resulting in recovery of 0.508 g of unreacted 2,2′-dipyridyl and the isolation of a single product weighing 0.750 g. These figures indicate use of 0.273 g or 2.24 mmol of ligand, thereby establishing the stoicheiometry of the reaction as involving combination of one molecule of ligand with one atom of titanium.

That all the substances having the structure shown in Figure V are ionic is shown by their solubilities in water and insolubility in organic solvents, the conversion of their chlorides to hexafluorophosphates and the electrical conductivity of their acetone solutions. The slope of plots of $\Lambda_o - \Lambda_m$ versus $\sqrt{c}$ made from conductivity data obtained at about 20° over the concentration range 6×10^{-3}M to 1×10^{-3}M agree well with slopes calculated from

the Onsager Equation (B30) for 1:1 electrolytes. Table II gives an example of the conductivity data and their treatment. Similar data for other compounds may be found in the Appendix.

Table II

Conductivity Studies of $(\pi\text{-}C_5H_5)_2Ti\cdot en\ PF_6$ in Acetone at 22.0°

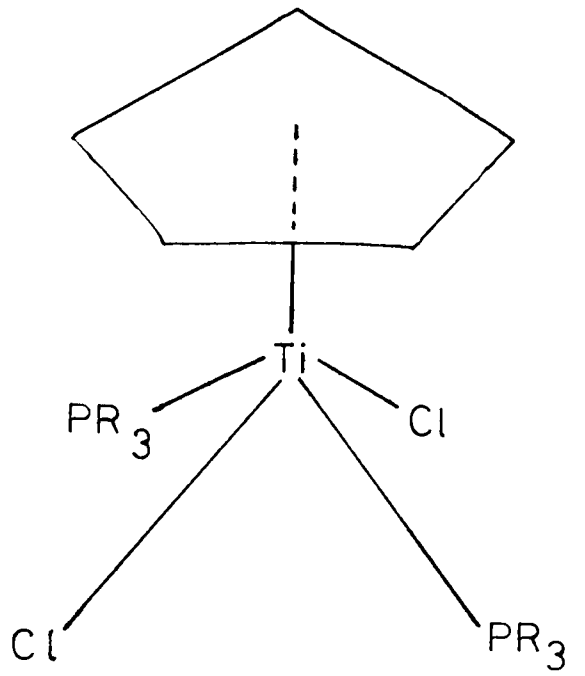
Vol(ml)	Cond($\mu\upsilon$)	Sp Cond(υcm^{-1})	Conc(M)	$\sqrt{c}$	Λ_M($\upsilon cm^2 eq^{-1}$)
10.00	440.0	607.2×10^{-6}	5.693×10^{-3}	7.551×10^{-2}	106.7
20.00	244.4	337.3×10^{-6}	2.841×10^{-3}	5.343×10^{-2}	118.8
30.00	170.9	235.8×10^{-6}	1.894×10^{-3}	4.352×10^{-2}	124.8
40.00	131.4	181.3×10^{-6}	1.420×10^{-3}	3.772×10^{-2}	127.7
47.80	112.2	154.8×10^{-6}	1.195×10^{-3}	3.451×10^{-2}	130.1

Λ_o = 150.5 Slope of Λ_M versus $\sqrt{c}$ = 587

Calculated Onsager slope for a 1:1 electrolyte = 586

The new compounds derived from $\left[(\pi\text{-}C_5H_5)TiCl_2\right]_n$ probably have the structure shown in Figure VI. It was shown by successive additions of aliquots of methyldiphenylphosphine to a benzene suspension of $\left[(\pi\text{-}C_5H_5)TiCl_2\right]_n$ that only one compound is formed in the ensuing reaction and that its formation requires two molecules of ligand per atom of titanium. Elemental analyses of the new substances agree with the data calculated for compounds having the structure shown in Figure VI and in the case of the substance derived from dimethylphenylphosphine, the cryoscopic molecular

weight determined in benzene was within 13% of the expected value.



VI. Proposed Structure of $(\pi\text{-}C_5H_5)TiCl_2 \cdot 2L$

Mass spectra of these compounds exhibit no parent ion peaks. At source temperatures below 300°, ions derived from L are seen but above 300° ions derived from pyrolysis products of the $(\pi\text{-}C_5H_5)TiCl_2$ unit begin to appear. This is consistent with the behaviour of these compounds in melting point tubes where ligand is thermally displaced and appears in the cooler part of the tube at the same time as purple $[(\pi\text{-}C_5H_5)TiCl_2]_n$ appears in the hotter part.

On the basis of the available data, it is impossible to distinguish between <u>cis</u> and <u>trans</u> isomers of the derivatives of $[(\pi\text{-}C_5H_5)TiCl_2]_n$. It is also impossible to distinguish between a chelated structure for the bidentate ligands and a less likely one involving two ligands bridging between two metals. The low energy region of the

i.r. spectra are not informative in this regard since bands due to metal-ring stretch,ring tilt, metal-chlorine stretches and possibly also metal-phosphorus stretches are all clustered below 400 cm^{-1} and cannot readily be distinguished (B 27, B31-B33).

In general, the i.r. spectrum of each of the compounds is essentially what would arise if spectra of $\left[(\pi\text{-}C_5H_5)TiCl_2\right]_n$ or $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ and the ligands were superimposed, except in the region below 400 cm^{-1} where distinct changes occur. In the bis-π-cyclopentadienyl compounds, III, IV and V, a weak band at 3080 cm^{-1} is associated with a C-H stretching vibration of the cyclopentadienyl rings (B34). Strong bands at 1010 and 795 cm^{-1} are thought to be due, respectively, to the in-plane and out-of-plane C-H bends of the cyclopentadienyl ligands and a strong band at 1440 cm^{-1} has been assigned to a ring torsion vibration (B34). A medium intensity band at 380 cm^{-1} is also characteristic of the π-cyclopentadienyl system but has not been assigned to a specific vibration.

The primary amine adducts, (Figure II), have three N-H stretching bands in the regions 3310-3270, 3240-3210 and 3150-3125 cm^{-1} and also an N-H deformation band between 1588 and 1600 cm^{-1}, as would be expected for compounds of this sort (B35). The absorption at 1640 cm^{-1} due to a C=C stretching vibration in free allylamine is unchanged in the spectrum of its complex, indicating the absence of an interaction between the double bond and metal. Intense

absorptions characteristic of P-F vibrations (B36) at 830 and 558 cm^{-1} were found in the spectra of the cations, (Figure V), isolated as their hexafluorophosphate salts.

Between 4000 and 400 cm^{-1}, the spectra of compounds containing only one cyclopentadienyl ring are very similar to those of related compounds with two rings; exhibiting bands at 3100 (weak, ring C-H stretch), 1440 (strong, ring torsion), 1010 (strong, in-plane C-H bend) and 810 cm^{-1} (strong, out-of-plane C-H bend) (B37). Two further strong absorptions occurring at 360 and 270 cm^{-1} in all the spectra are unassigned. The other absorptions in the spectra of the mono-π-cyclopentadienyl compounds correspond closely to those seen in spectra of the free ligands.

7. <u>Properties</u>

The non-ionic compounds of formula $(\pi\text{-}C_5H_5)_2TiCl\cdot L$ and $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2\cdot$diphos are all green, crystalline solids except when pyridine is a ligand in which case the colour is brown. Crystals of these compounds are essentially cubic except for the pyridine adduct which occurs as needles. They are all moderately soluble in aromatic hydrocarbons, tetrahydrofuran, dichloromethane, 1,2-dimethoxyethane and acetonitrile, but insoluble in petroleum ether and only sparingly soluble in ether. All these non-ionic compounds decompose at their melting points and with the exception of those containing volatile phosphines as ligands, no identifiable products were obtained upon pyrolysis. When

the volatile phosphines, dimethylphenylphosphine and methyldiphenylphosphine are present as ligands, pyrolysis of the compounds **in vacuo** causes the free ligand to distil into the cooler regions of the reaction vessel and large crystals of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ to grow in the hotter part.

$$2(\pi\text{-}C_5H_5)_2TiCl\cdot PR_3 \longrightarrow \left[(\pi\text{-}C_5H_5)_2TiCl\right]_2 + 2PR_3 \qquad (11)$$

The cationic substances of general formula $\left[(\pi\text{-}C_5H_5)_2Ti\cdot L_2'\right]A$ are found as blue essentially cubic crystals except for the derivative of 2,2′-dipyridyl which occurs as purple needles. The chloride salts are insoluble in tetrahydrofuran and acetone but are soluble in ethanol and water although they are rapidly decomposed by the latter. The hexafluorophosphate salts, on the other hand, are soluble in acetone but insoluble in ethanol and ether.

All the compounds, both ionic and neutral, oxidize very rapidly in air forming free ligand or ligand oxide and either orange $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2O$, in the case of chlorine-containing materials or in the case of the hexafluorophosphates which do not contain chlorine, a red unidentified compound. On the whole, the ionic substances are more stable to oxidation both as solids and in solution than are the non-ionic ones and among the non-ionic compounds the phosphine adducts are more oxidatively stable than are those of primary amines. All the compounds hydrolyze (most of them very rapidly) with formation of Ti_2O_3.

The mono-π-cyclopentadienyl derivatives are green,

crystalline solids which oxidize readily in air to yellow titanium-containing compounds and free ligand or ligand oxide. They react with hydroxylic solvents to give blue solutions which slowly deposit Ti_2O_3 and they dissolve in ethers or aromatic hydrocarbons giving solutions from which the compounds may be recovered. The solubilities of the complexes derived from bidentate ligands are very considerably lower than those of related complexes derived from monodentate ligands. All the compounds are virtually insoluble in petroleum ether. Solutions of the 1,2-bis(diphenylphosphino)-ethane and methyldiphenylphosphine complexes dissociate above about 40°, as mentioned earlier, although in the solid state they are both thermally stable to much higher temperatures.

8. Reactions of the Adducts

As mentioned in the introduction to this chapter, it was hoped that the new compounds could be converted to lower valent species, hydrides or alkyls and that study of these compounds would shed some light on the mechanisms of nitrogen fixation, olefin polymerization or isomerization. With this in mind, the non-ionic compounds were dissolved in 1,2-dimethoxyethane and treated with sodium borohydride. Those compounds having two cyclopentadienyl rings on each metal react according to equation 12 to form $(\pi\text{-}C_5H_5)_2TiBH_4$.

$$(\pi\text{-}C_5H_5)_2TiCl\cdot L + NaBH_4 \longrightarrow (\pi\text{-}C_5H_5)_2TiBH_4 + L + NaCl \quad (12)$$

In order to avoid the evident disadvantage of having borohydride present in the mixture, the attempted

preparation of $(\pi\text{-}C_5H_5)_2Ti(H)L$ was repeated using sodium trimethylboronhydride as a potential source of the hydride ligand. This yielded an intractable blue oil. When these reactions were repeated at -55° or under argon instead of nitrogen, the observations were the same.

Compounds of the form $(\pi\text{-}C_5H_5)_2Zr(BH_4)_2$ have been shown (B38) to react with certain amines and phosphines according to equation 13 to form, inter alia, hydrides and the corresponding amine- or phosphine-borane. At the time the reaction was demonstrated using $(\pi\text{-}C_5H_5)_2Zr(BH_4)_2$, it was also attempted for $(\pi\text{-}C_5H_5)_2TiBH_4$.

$$(\pi\text{-}C_5H_5)_2Zr(BH_4)_2 + R_3N \longrightarrow (\pi\text{-}C_5H_5)_2Zr(H)BH_4 + R_3NBH_3 \quad (13)$$

Not surprisingly, no success was obtained, for in that attempt ligands such as tertiary amines and bulky tertiary phosphines which, as a result of this work, are now known to be usually unreactive with the bis(π-cyclopentadienyl)titanium system were employed. It seemed worthwhile, therefore, to repeat that work with more suitable ligands in hopes that by such a route the amine- or phosphine-hydrides, $(\pi\text{-}C_5H_5)_2Ti(H)L$, might be prepared.

Treatment of $(\pi\text{-}C_5H_5)_2TiBH_4$ in benzene with either dimethylphenylphosphine or ethylamine at room temperature or under reflux, however, causes no reaction except the eventual decomposition of $(\pi\text{-}C_5H_5)_2TiBH_4$ which occurs in hot benzene solutions even in the absence of any potential ligand. This result is in contrast to the behaviour of

$(\pi\text{-}C_5H_5)_2NbBH_4$ which has been found to react readily with phosphines to give stable compounds of the form $(\pi\text{-}C_5H_5)_2Nb(H)PR_3$, as discussed in Chapter IV.

The compounds $(\pi\text{-}C_5H_5)TiCl_2 \cdot 2L$ react with sodium borohydride to evolve a gas and after passing through a blue intermediate which could not be isolated to deposit a black residue from which no identifiable products except the ligands, L, could be obtained. Similarly, when the compounds were treated with methylmagnesium bromide, allylmagnesium chloride or trimethylsilylmethyllithium in ether, toluene or petroleum ether at room temperature or -90°, under nitrogen or argon, a series of colour changes from green through red to yellow-brown were observed in all cases. From the yellow-brown mixtures, the various phosphine ligands were extracted but no other tractable products could be found.

The compounds of the form $(\pi\text{-}C_5H_5)_2TiCl \cdot L$ were subjected to the action of an assortment of alkylating and reducing agents such as methylmagnesium chloride, butyllithium, lithium phenylacetylide and sodium amalgam. These reactions were carried out in ethereal and hydrocarbon solvents, under atmospheres of nitrogen and argon and at temperatures ranging from -90° to room temperature. Despite the considerable variety of these conditions, the reactions were similar in each case and gave blue or purple solutions which deposited intractable tars of the same colours upon standing.

No attempt was made to reduce the ionic materials, $[(\pi\text{-}C_5H_5)_2Ti\cdot L_2']A$, although it is probable that at least $[(\pi\text{-}C_5H_5)_2Ti\cdot dipy]Cl$ is reducible since the compound $(\pi\text{-}C_5H_5)_2Ti\cdot dipy$ is already known (B49, B51).

C. Discussion

Theories which account for the behaviour of nitrogen fixation and reduction catalysts abound and have been reviewed by several authors (B13, B39, B40). They generally are based either on electronic arguments concerning the oxidation state changes of titanium during the reaction or, less frequently, they are based on stereochemical considerations. As an example of the latter, it has been proposed (B13) that nitrogenase enzymes are able to conduct in an aqueous environment what appears to be a reaction with which water interferes because of extensive folding by the organic parts of the enzyme. This creates an unusual shielded "hole" in the co-ordination sphere of a metal atom which is part of the enzyme. This results in a stereochemical situation such that only slim molecules like molecular nitrogen or the nitrogenase inhibitors, carbon monoxide, hydrogen or acetylene can pass through the "hole" to the metal, whereas bulkier substances which might destroy the active site are excluded. Some experimental support for this hypothesis has been obtained from recent studies of arene-molybdenum species (B41) which indicate that, in addition to electron-rich substances (B42) with relatively high energy orbitals (B43), a stereochemical "hole" of about the correct dimensions is

desirable to exclude molecules which might compete with nitrogen for the site.

Despite an abundance of such theories, however, the only facts which have been firmly established concerning the titanium-containing nitrogen-fixing systems are that the metal must be in formal oxidation state three or lower and that the catalytically active substance is extremely reactive towards a number of reagents other than nitrogen and, therefore, exceedingly difficult to handle. It is clear from this discussion that any information concerning the electronic environment of low valent bis(π-cyclopentadienyl)titanium species or their stereochemical situations is potentially of some considerable value for the understanding of nitrogen fixation catalysts.

It is usually difficult and often injudicious to attempt a separation of steric and electronic effects in discussions of experimental observations in which both effects are apparently operating. However, consideration of the occurrence of the new cyclopentadienyl complexes described in this chapter makes certain conclusions seem justifiable.

1. Stereochemical Considerations

De Liefde Meijer has noted certain variations in the chemistry of the bent bis-π-cyclopentadienyl systems of metals occurring early in the transition series and he has accounted for some of these irregularities on the basis

of stereochemical arguments (B44, B45). For example, $(\pi\text{-}C_5H_5)_2MPh_2$ can be prepared when M is niobium or titanium but not when M is vanadium. De Liefde Meijer has suggested that some form of steric interaction between the phenyl and cyclopentadienyl ligands is preventing formation of the bis-phenyl complex of the relatively small vanadium atom, whereas, that interaction is not taking place in the corresponding compounds of the relatively larger atoms niobium and titanium.

In addition to this type of steric effect, however, there is another type which de Liefde Meijer did not consider. It arises from the stereochemical significance of the non-bonding electrons in d^1 or d^2 bis(π-cyclopentadienyl)metal systems. Recent X-ray crystallographic studies have shown (B46) that the X-M-X angle in $(\pi\text{-}C_5H_5)_2MX_2$ species is a function of the number of non-bonding electrons in an orbital lying in the X-M-X plane (Chapter I, Part B, Section 3). In these $(\pi\text{-}C_5H_5)_2MX_2$ systems, the X-M-X angle can vary by as much as 15° upon going from a d^o to a d^2 situation, thereby clearly indicating that the non-bonding electrons are stereochemically significant. An alternative, therefore, to de Liefde Meijer's proposal which takes into account the stereochemical significance of the non-bonding electrons is that steric interaction between the d^1 non-bonding electron in the Alcock orbital on vanadium and the phenyl ligands may be the cause of the non-existence of $(\pi\text{-}C_5H_5)_2VPh_2$.

This explanation is consistent with the inability to prepare the analogous compound $(\pi\text{-}C_5H_5)_2MoPh_2$ which would have two electrons in the Alcock orbital resulting in an even greater steric interaction between it and the phenyl groups.

It is apparent that some form of steric interaction, probably of the types just discussed, is operating in all the systems described in this chapter. This is indicated by the non-occurrence of triphenylphosphine or tricyclohexylphosphine complexes of the form $(\pi\text{-}C_5H_5)_2TiCl\cdot L$ or $(\pi\text{-}C_5H_5)TiCl_2\cdot 2L$ analogous to those which occur when L is methyldiphenylphosphine or dimethylphenylphosphine. The trend of decreasing thermal stability with increasing ligand size, illustrated in Table III, may be a reflection of the increasing steric interactions.

Table III

Trends in Thermal Stability of Phosphine Adducts	
Compound	Decomp Pt (°C)
$(\pi\text{-}C_5H_5)_2TiCl\cdot PMe_2Ph$	135
$(\pi\text{-}C_5H_5)_2TiCl\cdot PMePh_2$	130
$(\pi\text{-}C_5H_5)TiCl_2\cdot 2PMe_2Ph$	134
$(\pi\text{-}C_5H_5)TiCl_2\cdot 2PMePh_2$	125
$(\pi\text{-}C_5H_5)TiCl_2\cdot$DMPE	205
$(\pi\text{-}C_5H_5)TiCl_2\cdot$diphos	143

The absence of secondary or tertiary amine adducts of the type $(\pi\text{-}C_5H_5)_2TiCl\cdot L$ might at first sight also seem to be steric in origin, however, their occurrence is influenced

by electronic factors as well as steric ones. This is clearly indicated if one contrasts the non-existence of the cation $\left[(\pi\text{-}C_5H_5)_2Ti\cdot L_2'\right]^+$ derived from two methylamine ligands with the existence of such a cation derived from sym-dimethylethylenediamine, even though the bidentate ligand is more sterically demanding than two molecules of methylamine. It is further indicated by the observation that functional group size in the primary amines has no apparent effect on the occurrence of adducts. The desired product is always obtained even when the hydrocarbon group attached to nitrogen is the bulky cyclohexyl group. In contrast, even with the relatively small secondary amine, dimethylamine, no adduct would form. These observations suggest that the behavioural differences between primary and secondary amines in these reactions are not exclusively steric in origin.

2. Electronic Considerations

Photoelectron spectroscopy has clearly shown that the effect of increasing ligand basicity in a series of metal complexes is to raise the energy of the valence electrons associated with the metal atom (B47). Titanium has the highest orbital energies (lowest ionization potentials) of any first row transition element except scandium and it has been suggested that its orbitals are just inside the upper limit of the so-called "valence band" (B48). Given these observations, it is possible to offer a rationalization of the occurrence of the amine adducts.

It may be that the increased basicity of secondary and tertiary amines relative to primary ones is such that the already high energy titanium orbitals would be sufficiently raised in energy in a secondary or tertiary amine adduct that no stable bond could be formed between ligand and metal. Consistent with this explanation is the existence of the ionic species $\left[(\pi\text{-}C_5H_5)_2Ti\cdot L_2'\right]X$. The positive charge on these ions may be thought of as "pulling down" titanium's orbital energies sufficiently so that, together with the "chelate effect", it becomes energetically favourable for compounds to be formed, not only by the bidentate primary amine, ethylenediamine, but also by the bidentate secondary amine, sym-dimethylethylenediamine. In contrast, however, not even the operation of both the positive charge and the "chelate effect" is enough to create a favourable situation for formation of a compound by N,N,N',N'-tetramethylethylenediamine, thereby indicating the fine balance of factors influencing the stability of bis(π-cyclopentadienyl)titanium compounds.

3. Conclusions

It seems that a satisfactory explanation for the behaviour of the bis(π-cyclopentadienyl)titanium system must include, not only steric considerations, but also and probably with greater emphasis, a recognition of an unusual electronic situation involving very high energy metal orbitals, only barely within the upper limits of the so-called "valence shell". Such a condition of the system accounts for

the observation that relatively minor influences like the "chelate effect" can make the difference between existence or non-existence of compounds. It also accounts for the experimental observation of a situation particularly unfavourable to the bonding of very bulky or strongly electron-donating ligands but rather more favourable to the bonding of electron-withdrawing ones of moderate size.

The inability to isolate any products from reduction of the compounds $(\pi\text{-}C_5H_5)_2TiCl\cdot L$ is consistent with either an electronic or steric argument. Reduction would involve addition of an electron to the already very high energy orbitals and it may be argued that this would be sufficient to raise orbital energies beyond the point where stable bonds exist, therefore causing the compounds to decompose. Alternatively, addition of a further electron to the orbital containing the d^1 electron may expand that orbital sufficiently for steric interactions to occur between it and the ligands, causing the ligand to dissociate. The occurrence (B49, B51) of the reduction product, $(\pi\text{-}C_5H_5)_2Ti\cdot$dipy, can be cited as support for either point of view since the extra electron can be delocalized into the aromatic system of 2,2′-dipyridyl, which would not only reduce steric requirements of the lone-pair orbital but also lower the energies of the titanium orbitals.

From the results of this study, certain conclusions concerning the use of bis(π-cyclopentadienyl)titanium

catalysts for nitrogen fixation may be drawn. The steric requirements imposed on potential ligands by the "hole" in the co-ordination sphere of the metal are relatively modest and, therefore, use of these systems as catalysts will always require the greatest handling care. In other words, the metal atoms which are sufficiently reactive to reduce nitrogen are not adequately protected by their shrouds of ligands from attack by species such as water or oxygen or reactive solvents which eliminate their ability to react with nitrogen. Although handling problems can be overcome, it should be noted that the kinetic stability of the simple ammonia adduct, $(\pi\text{-}C_5H_5)_2TiCl\cdot NH_3$, is such as to make ammonia production from nitrogen gas using these systems as catalysts seem unlikely. As already suggested by Vol'pin (B50), the conditions required to liberate ammonia from the complex are also sufficiently violent to destroy the catalyst. The alternative, however, which is suggested by the results of this work would seem to be to attempt formation of secondary or tertiary amines from the reduced nitrogen as these would probably dissociate from the metal, thereby regenerating the catalyst or a precursor.

D. References

B1 A.E. Shilov, A.K. Shilova, E.F. Kvashina and T.A. Vorontsova, Chem. Comm., 1971,1590.

B2 J.H. Teuben and H.J. de Liefde Meijer, Rec. Trav. Chim., 197, 90, 360.

B3 J.E. Bercaw, R.H. Marvich, L.G. Bell and H.H. Brintzinger, J. Amer. Chem. Soc., 1972, 94, 1219.

B4 G.J. Leigh, Preparative Inorganic Reactions, 1971, 7, 165.

B5 H.H. Brintzinger, J. Amer. Chem. Soc., 1966, 88, 4307.

B6 R.S. Dickson and J.A. Ibers, J. Amer. Chem. Soc., 1972, 94, 2988.

B7 H.F. Klein and J.F. Nixon, Chem. Comm., 1971, 42.

B8 International Tables for X-Ray Crystallography, The Kynoch Press, Birmingham, England, 1962.

B9 B.R. Davis and J.A. Ibers, Inorg. Chem., 1970, 9, 2768.

B10 J. Chatt, GA. Heath, and R.L. Richards, Chem, Comm., 1972, 1010.

B11 J. Chatt, G.A. Heath and G.J. Leigh, Chem. Comm., 1972, 444.

B12 J.N. Armor and H. Taube, J. Amer. Chem. Soc., 1970, 92, 2560.

B13 A.E. Shilov and G.I. Likhtenshtein, Izvest. Akad. Nauk SSSR., Ser. Biol., 1971, 4, 518.

B14 A.E. Shilov, A.K. Shilova and E.F. Kvashina, Kinet. Katal., 1969, 10, 1402.

B15 R.L. Martin and G. Winter, J. Chem. Soc., 1965, 4709.

B16 J.P. Candlin, K.A. Taylor and D.T. Thompson, Reactions of Transition Metal Complexes, Elsevier Publishing Co., London, 1968.

B17 H. Noth and R. Hartwinner, Chem. Ber., 1960, 93, 2238.

B18 J.M. Birmingham, A.K. Fischer and G. Wilkinson, Naturwiss., 1955, 42, 96.

B19 H.A. Martin and F. Jellinek, J. Organomet. Chem., 1967, 8, 115.

B20 J.J. Salzmann, Helv. Chim. Acta, 1968, 51, 526.

B21 R.S.P. Coutts and P.C. Wailes, Adv. Organomet. Chem., 1970, 9, 136.

B22 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, third ed., Interscience Publishers, London, 1972, pp. 650.

B23 P.D. Bartlett and B. Seidel, J. Amer. Chem. Soc., 1961, 83, 581.

B24 R.D. Gorsich, J. Amer. Chem. Soc., 1960, 82, 4211.

B25 R.S.P. Coutts, R.L. Martin and P.C. Wailes, Aust. J. Chem., 1971, 24, 1079.

B26 R.S.P. Coutts, R.L. Martin and P.C. Wailes, Aust, J. Chem., 1971, 24, 2533.

B27 V.N. Vyshinskii, T.I. Ermolaeva, V.N. Latyaeva, A.N. Lineva and N.E. Lukhton, Dokl. Chem., Eng. Trans., 1971, 198, 487.

B28 V.T. Kalinnikov, G.M. Larin, O.D. Ubozhenko, A.A. Zharkikh, V.N. Latyaeva and A.N. Lineva, Dokl. Akad. Nauk SSSR., 1971, 199, 95.

B29 R.S.P. Coutts and P.C. Wailes, Aust. J. Chem., 1968, 21, 2199.

B30 R.D. Feltham and R.G. Hayter, J. Chem. Soc., 1964, 4587.

B31 O.S. Roshchupkina, V.A. Dubovitskii and Yu.G. Borod'ko, Zh. Strukt. Khim., 1971, 12, 1007.

B32 E. Maslowsky, Jr., and K. Nakamoto, Appl. Spectrosc., 1971, 25, 187.

B33 J.A. Waters and G.A. Mortimer, J. Organomet. Chem., 1970, 22, 417.

B34 P.M. Druce, B.M. Kingston, M.F. Lappert, T.R. Spalding, and R.C. Srivastava, J. Chem. Soc., (A), 1969, 2106.

B35 J. Chatt, L.A. Duncanson and L.M. Venanzi, J. Chem. Soc., 1956, 2712.

B36 H.G. Mayfield, Jr. and W.E. Bull, J. Chem. Soc., (A), 1971, 2279.

B37 D.J. Parker and M.H.B. Stiddard, J. Chem. Soc., (A), 1970, 480.

B38 B.D. James, R.K. Nanda and M.G.H. Wallbridge, Inorg, Chem., 1967, 6, 1979.

B39 G. Henrici-Olive and S. Olive, Angew. Chem., Int. Ed., 1969, 8, 650.

B40 R. Murray and D.C. Smith, Coord. Chem. Rev., 1968, 3, 429.

B41 M.L.H. Green and W.E. Silverthorn, Chem. Comm., 1971, 557.

B42 M.L.H. Green, J. Knight, L.C. Mitchard, G.G. Roberts and W.E. Silverthorn, Chem. Comm., 1971, 1619.

B43 S.E. Jackson, private communication.

B44 H.J. de Liefde Meijer and F. Jellinek, Inorg. Chim. Acta, 1970, 4, 651.

B45 J.H. Teuben and H.J. de Liefde Meijer, J. Organomet. Chem., 1969, 17, 87.

B46 J.C. Green, M.L.H. Green and C.K. Prout, Chem. Comm., 1972, 421.

B47 S. Evans, M.L.H. Green, J.C. Green, A.F. Orchard and D.W. Turner, Disc. Farad. Soc,, 1969, 112.

B48 C.S.G. Phillips and R.J.P. Williams, Inorganic Chemistry,

Clarendon Press, Oxford, 1965.

B49 E.O. Fischer and R. Amtmann, J. Organomet, Chem., 1967, 9, P15.

B50 M.E. Vol'pin, M.A. Ilatovskaya, L.V. Kosyakova and V.B. Shur, Chem. Comm., 1968, 1074.

B51 F. Calderazzo, J.J. Salzmann and P. Mosimann, Inorg. Chim. Acta, 1967, 1, 65.

CHAPTER III

Some Reactions and Properties of d^1 Cyclopentadienyl Titanium Species with Metal-Carbon σ-Bonds

A. Introduction

The success of de Liefde Meijer (C1) and Shilov (C2) in forming complexes of molecular nitrogen with organo-titanium compounds which appear to contain the metal in formal oxidation state three, focuses attention, with respect to nitrogen fixation, on that oxidation state. Unfortunately, there remains considerable doubt about the exact structural details of these and related complexes since, for various reasons, pertinent and informative physical data have not been obtained. This chapter describes attempts to isolate and characterize compounds of trivalent titanium containing the metal bonded only to carbon.

A general absence from the literature of reports concerning such compounds may be noted. In fact, only the species formulated as $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)$ (C3), $(\pi\text{-}C_5H_5)_2TiPh$ (C1), $\left[(\pi\text{-}C_5H_5)_2Ti(C{\equiv}CPh)\right]_n$ (C5) and $(\pi\text{-}C_5H_5)_2Ti(\pi\text{-}C_3H_5)$ (C4) are known which have been reasonably well identified. The structural feature of the elusive $(\pi\text{-}C_5H_5)_2TiR$ compounds which is attractive from the point of view of nitrogen fixation is the possibility of a formally vacant co-ordination position on the metal to which nitrogen might bond. In the compounds $\left[(\pi\text{-}C_5H_5)_2Ti(C{\equiv}CPh)\right]_n$ and $(\pi\text{-}C_5H_5)_2Ti(\pi\text{-}C_3H_5)$,

however, no such vacant position occurs. In the former case, some form of polymerization, possibly by co-ordination of the triple bond of one unit to the metal in another, is indicated (C5), although the exact scheme of bonding is unclear. In the latter case, the vacant co-ordination site is presumably occupied by the π-bonded allyl group. Of the two remaining compounds, the former $(\pi\text{-}C_5H_5)_2TiPh$, fixes nitrogen (C1) and the latter, $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)$, had unexplored chemical properties and an unknown structure before the present study was carried out. Certainly, therefore, a study of these and related compounds is justifiable.

B. Chemical Studies

1. Disproportionation Reactions: Mono-π-cyclopentadienyl Systems

It has become clear that decomposition of organo-titanium compounds proceeds by pathways involving homolytic (C7) or heterolytic (C8) bond rupture, cyclopentadienyl ring-to-metal hydrogen shift (C9), β-elimination (C10, C11) or associative mechanisms (C7). In principle, therefore, it should be possible to isolate trivalent titanium compounds containing the metal bonded only to carbon in which these pathways have been blocked. With this in mind, the trimethylsilylmethyl functional group was selected as an appropriate ligand because in it, β-eliminations cannot occur. This ligand has two further desirable properties. Firstly, it often confers solubility in hydrocarbons and secondly, its bulkiness confers a certain degree of inertness, with respect to decomposition

by associative mechanisms, upon its compounds (C10). A plausible way, therefore, to attempt isolation of a trivalent titanium species containing the metal bonded only to carbon seemed to be *via* introduction of this group at low temperatures into mono-π-cyclopentadienyl systems in which there is, as yet, no evidence of ring-to-metal hydrogen shift mechanisms.

Trimethylsilylmethyllithium in petroleum ether was accordingly added to a petroleum ether suspension of purple $[(\pi\text{-}C_5H_5)TiCl_2]_n$ at -90° in 2:1 molar ratio, as in equation 1.

$$[(\pi\text{-}C_5H_5)TiCl_2]_n + 2nMe_3SiCH_2Li \longrightarrow (\pi\text{-}C_5H_5)Ti(CH_2SiMe_3)_3 + \text{black residue} \qquad (1)$$

No reaction occurred at first. The mixture was gradually warmed to -35° when the solution slowly turned yellow, the purple solid disappeared and a black residue formed. From the solution, yellow crystals were obtained in *ca.* 50% yield. These crystals sublime *in vacuo* at 60° and are soluble in all the common organic solvents. When finely divided, the substance reacts with air during the course of several minutes forming a yellow oil.

The compound's i.r. spectrum has bands at 3100, 1010 and 810 cm^{-1} characteristic of a π-cyclopentadienyl system (C12) and has strong bands at 1250 and 850 cm^{-1} found in spectra of substances containing the trimethylsilylmethyl ligand (see Appendix). An n.m.r. spectrum of the compound dissolved in $[^2H_6]$benzene consists of three singlets at 4.18, 8.17 and 9.97 τ. The ratio of the intensities of these peaks is 5:6:27

and the resonances may be assigned to cyclopentadienyl, methylene and methyl hydrogens, respectively. The spectroscopic and analytical data (see Appendix) are, therefore, consistent with the formulation of the yellow compound as $(\pi\text{-}C_5H_5)Ti(CH_2SiMe_3)_3$.

The preparation was repeated under argon and all observations were the same. It was also repeated in ether using trimethylsilylmethylmagnesium chloride under atmospheres of nitrogen or argon. In both cases, $(\pi\text{-}C_5H_5)Ti(CH_2SiMe_3)_3$ and a <u>white</u> precipitate were formed.

$$\left[(\pi\text{-}C_5H_5)TiCl_2\right]_n + 2nMe_3SiCH_2MgCl \longrightarrow (\pi\text{-}C_5H_5)Ti(CH_2SiMe_3)_3 + \text{white residue} \qquad (2)$$

Isolation of formally tetravalent titanium-containing compounds from trivalent starting materials in the presence of Grignard reagents or other metal alkyls suggests that a rapid disproportionation of any initially formed trivalent organo-titanium compound is taking place. In order to try to determine whether disproportionation under these conditions is a general rule or whether such a reaction is peculiar to the ligand already selected, a series of experiments employing other ligands which cannot undergo β-elimination were commenced.

An ether suspension of $\left[(\pi\text{-}C_5H_5)TiCl_2\right]_n$ under argon or nitrogen was treated with a 2:1 molar ratio of methylmagnesium bromide or methyllithium at room temperature. A gas was vigorously evolved which was collected and shown by i.r.

spectroscopy to be methane.

$$\left[(\pi\text{-}C_5H_5)TiCl_2\right]_n + 2nMeMgBr \longrightarrow CH_4 + \frac{n}{2}(\pi\text{-}C_5H_5)TiMe_3 + \text{black residue} \quad (3)$$

$$\left[(\pi\text{-}C_5H_5)TiCl_2\right]_n + 2nMeLi \longrightarrow CH_4 + \frac{n}{2}(\pi\text{-}C_5H_5)TiMe_3 + \text{black residue} \quad (4)$$

During the course of the reaction, the purple suspension slowly changed to a black one and simultaneously, the solution became yellow. The solvent was removed and the residue was extracted with petroleum ether. The yellow extract was taken to dryness and the residue from this operation was sublimed *in vacuo* at room temperature onto a probe cooled to -78°. The yellow sublimate, obtained in *ca.* 50% yield and subsequently shown to be $(\pi\text{-}C_5H_5)TiMe_3$ is soluble in all common organic solvents and is oxidized rapidly in air to a product of the same colour.

A sample of $(\pi\text{-}C_5H_5)TiMe_3$, prepared from π-cyclopentadienyltitanium trichloride and methyllithium (C13), has an n.m.r. spectrum in $\left[^2H_6\right]$benzene which is identical to that of the yellow sublimates obtained from reactions 3 and 4. These spectra all consist of two singlets at 4.13 and 8.86 τ which have an intensity ratio of 5:9. These resonances may be assigned to cyclopentadienyl and methyl hydrogens, respectively. Analytical data (see Appendix) also support the formulation of the yellow compound as $(\pi\text{-}C_5H_5)TiMe_3$.

Treatment of $\left[(\pi\text{-}C_5H_5)TiCl_2\right]_n$ with phenylmagnesium bromide in ether at -95° caused no reaction but on warming

to -30° a black solid was deposited and an orange-brown colour developed in the solution. No tractable products could be obtained from either of these phases. Similar treatment of $[(\pi\text{-}C_5H_5)TiCl_2]_n$ with allylmagnesium chloride causes the appearance of a scarlet colour which persists upon warming to room temperature. The solvent may be removed at this temperature and the red substance extracted from the residue with petroleum ether. Alternatively, the red substance may be sublimed from the residue <u>in vacuo</u> at 40° onto a probe cooled to -78°. This red substance is, however, too unstable to characterize. It turns brown upon standing <u>in vacuo</u> at room temperature within half an hour.

2. <u>Disproportionation Reactions: Bis-π-cyclopentadienyl Systems</u>

A further investigation into the generality of the disproportionation reaction was carried out using bis(π-cyclopentadienyl)titanium species. The green dimer, $[(\pi\text{-}C_5H_5)_2TiCl]_2$, was treated with trimethylsilylmethyllithium in toluene at -95° under atmospheres of nitrogen or argon.

$$[(\pi\text{-}C_5H_5)_2TiCl]_2 + 2Me_3SiCH_2Li \longrightarrow (\pi\text{-}C_5H_5)_2Ti(CH_2SiMe_3)_2 + \text{black residue} \qquad (5)$$

The solution turned red-brown and upon warming to -90° a dark green colour developed which was stable at this temperature and was unaffected by replacement of the nitrogen atmosphere with argon or vice versa. Upon warming to -84°, a colour change to yellow-brown occurred and after a few minutes black insoluble material was deposited. From the liquid phase a yellow substance, which sublimes <u>in vacuo</u> at 100° and is

soluble in common organic solvents, was isolated in 43% yield. The compound was also prepared in ether using trimethylsilylmethylmagnesium chloride. Well crystallized samples of the material do not appear to be particularly air sensitive but solutions are. This is indicated by the marked warming of these solutions when oxygen is bubbled through them, even though there is no apparent colour change.

The i.r. spectrum of the substance, sublimed at 100°, has bands at 3080, 1010 and 795 cm^{-1} associated with the π-cyclopentadienyl ligand (C12) and further bands at 1250 and 850 cm^{-1} attributable to the trimethylsilylmethyl functional group (see Appendix). The n.m.r. spectrum of the substance in $[^2H_6]$benzene consists of three singlets at 4.25, 9.17 and 10.00 τ. The ratio of intensities of these peaks is 10:4:18 and the resonances may be assigned to the π-cyclopentadienyl, methylene and methyl hydrogens, respectively. The formulation of the yellow compound as $(\pi\text{-}C_5H_5)_2Ti(CH_2SiMe_3)_2$ is consistent with the data given above and is supported by the analytical results (see Appendix).

In view of the high reactivity of some titanium-carbon σ-bonds with respect to insertion by oxygen (C14), ethylene (C15), carbon dioxide (C14, C16) and carbon monoxide (C17), several experiments were carried out to try to discover whether comparable reactivity of such bonds in $(\pi\text{-}C_5H_5)_2Ti(CH_2SiMe_3)_2$ exists. Toluene solutions of that compound at room temperature and 60° were, therefore, tested with ethylene, carbon monoxide,

carbon dioxide and 100 atmospheres of nitrogen.

$$(\pi\text{-}C_5H_5)_2Ti(CH_2SiMe_3)_2 + C_2H_4 \longrightarrow \text{N.R.} \quad (6)$$

$$(\pi\text{-}C_5H_5)_2Ti(CH_2SiMe_3)_2 + CO_2 \longrightarrow \text{N.R.} \quad (7)$$

$$(\pi\text{-}C_5H_5)_2Ti(CH_2SiMe_3)_2 + CO \longrightarrow \text{N.R.} \quad (8)$$

$$(\pi\text{-}C_5H_5)_2Ti(CH_2SiMe_3)_2 + N_2 \longrightarrow \text{N.R.} \quad (9)$$

No reactions (N.R.) were observed except at higher temperatures when general decomposition occurred.

Attempts, analogous to equation 5, to prepare $(\pi\text{-}C_5H_5)_2TiMe_2$ by reactions between $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ and methyllithium or the Grignard reagent did not succeed and other products were obtained. Stirring suspensions of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ in ether with methyllithium or methylmagnesium bromide for several minutes at 0° and again for several minutes at room temperature gives yellow solutions and dark coloured precipitates. These yellow solutions react reversibly with molecular nitrogen and irreversibly with carbon monoxide. Bubbling carbon monoxide through the yellow solutions results in the instant formation of $(\pi\text{-}C_5H_5)_2Ti(CO)_2$ which was isolated and identified by comparison of the i.r. spectrum with that of an authentic sample (C18). Passing nitrogen gas through the solutions has no apparent effect until the temperature of the solutions is lowered to about -50° when an ink-blue colour develops. Warming the solutions to about 0° discharges the blue colour. If nitrogen gas is replaced by argon or if the solutions are degassed before chilling, no colour change occurs. In both cases, however,

admission of nitrogen gas to the cold yellow solutions turns them instantly blue. If the solvent is removed at room temperature from the yellow ethereal solutions, a yellow solid remains which dissolves in petroleum ether to give a solution behaving in the same manner as do the ethereal ones in the presence of nitrogen or carbon monoxide. In the solid state, the yellow residue from the ethereal solutions decomposes after several minutes at room temperature under argon or instantly in air forming a black residue. It appears possible to sublime the yellow solid in vacuo at about 40° onto a probe cooled to -78° but the sublimate is no longer active towards nitrogen or carbon monoxide.

3. The Divalent Titanium-Containing Residues

The isolation of organometallic compounds of tetravalent titanium in about 50% yield from reactions of trivalent titanium species strongly suggests disproportionation is taking place. The residues also formed in the reactions were, therefore, examined for the presence of divalent titanium.

In all cases where a tetravalent titanium-containing substance was identified, a black residue was also formed, except when trimethylsilylmethylmagnesium chloride was employed as reagent. Instead of black residues, its reactions with $\left[(\pi\text{-}C_5H_5)TiCl_2\right]_n$ and $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ lead to the formation of white residues. These white residues appear to be dissolved by water to the accompaniment of considerable frothing and the deposition of titanium dioxide. If they are suspended in ether and hydrogen chloride is bubbled through

the mixture, no obvious change occurs. The nature of these white residues is at present unknown. All the corresponding black residues partially dissolve in water with violent frothing and precipitation of Ti_2O_3. All are soluble in toluene but no crystalline material could be obtained from any of these solutions.

In spite of being unable to grow crystals of these black substances, an examination of the product obtained from the reaction of methylmagnesium bromide with $[(\pi\text{-}C_5H_5)TiCl_2]_n$ (equation 3) was carried out. Treatment of the black powder with hydrochloric acid causes violent effervescence and a colour change to yellow. If ether is then added to the mixture, the yellow colour is extracted into the organic layer. Removal of the ether from this extract and sublimation of the residue *in vacuo* at 110° gives a yellow sublimate which was shown by its i.r. spectrum (C19) to be π-cyclopentadienyltitanium trichloride. A similar reaction was carried out by suspending the black powder in ether and bubbling hydrogen chloride through the mixture. This causes a smooth reaction to occur, marked by the deposition of a white residue, subsequently shown to be magnesium halide, and the appearance of π-cyclopentadienyltitanium trichloride in the liquid phase. Pyrolysis of the black powder *in vacuo* at temperatures below 325° yields only ether. At temperatures greater than 325° unidentified organic substances were formed.

A sample of the gas evolved when the powder is treated

with water was collected and its i.r. spectrum obtained. This suggests that the gas is primarily one which is not i.r. active, contaminated with small amounts of methane and ether vapour. It may be concluded from these results that the black powder consists mainly of magnesium halide, co-ordinated ether, a five-membered ring and divalent titanium which reacts with water to evolve hydrogen.

$$\text{black powder} + H_2O \xrightarrow{HCl} H_2 + Et_2O + MgCl_2 + (\pi\text{-}C_5H_5)TiCl_3 + Ti_2O_3 + \text{other products} \qquad (10)$$

The i.r. spectrum of the black powder is complex and yields little useful information. It is perhaps noteworthy, though, that the bands at 3100, 1010 and 810 cm^{-1}, usually found in π-cyclopentadienyl species (C12), are not immediately obvious in the spectrum although they may be shifted slightly and, therefore, obscured by neighbouring bands. The n.m.r. spectrum of the substance in $[^2H_6]$benzene consists of a triplet and a quartet centred, respectively, at 8.85 and 6.26 τ, probably arising from the presence of ether. In addition to these bands, there is a complex band centred at 5.98 τ which partially overlaps the previously mentioned triplet. No other absorptions between 0 and 10 τ were observed.

These black powders, like so many of the compounds of so-called divalent titanium and even titanium dichloride itself, appear to be of complex structure (C20). Often compounds of divalent titanium are highly associated in

rather poorly understood polymeric structures, in some of which, there is evidence for metal-metal interactions and halogen bridges (C21). It is not inconceivable that some such interactions exist in the black powders encountered in the present study, however, with the information currently available, it is impossible to propose any meaningful structure for these substances.

4. Reactions and Structural Features of $(\pi\text{-}C_5H_5)_nTiR_{3-n}$

Having ascertained the occurrence of disproportionation in the systems described earlier in this chapter, it seemed plausible that one of the steps leading to the observed products might involve dimerization. In order to test this hypothesis, several reactions were carried out using species similar to those previously examined but with their vacant co-ordination positions or potential dimerization sites filled by bulky ligands.

$$(\pi\text{-}C_5H_5)_2TiCl\cdot PMe_2Ph + Me_3SiCH_2Li \longrightarrow PMe_2Ph + \text{residue} \quad (11)$$

$$(\pi\text{-}C_5H_5)TiCl_2\cdot 2PMe_2Ph + 2Me_3SiCH_2Li \longrightarrow 2PMe_2Ph + \text{residue} \quad (12)$$

$$(\pi\text{-}C_5H_5)TiCl_2\cdot \text{diphos} + 2MeMgBr \longrightarrow \text{diphos} + \text{residue} \quad (13)$$

$$(\pi\text{-}C_5H_5)TiCl_2\cdot 2PMePh_2 + 2C_3H_5MgCl \longrightarrow 2PMePh_2 + \text{residue} \quad (14)$$

The reactions were carried out at low (ca. -80°) temperatures in ether, petroleum ether or toluene and in all cases a rapid colour change to brown or red-brown was observed. From the solutions, the phosphine ligands were isolated but no other tractable products were found. These results are consistent with those reported in Chapter II for the attempted reductions of compounds of the form $(\pi\text{-}C_5H_5)_2TiCl\cdot L$, using

metal alkyls. It seems, however, that blocking the potential dimerization sites has, in fact, stopped disproportionation from occurring in reactions 11 to 14. It may be assumed, therefore, that at least one reason for the stability of the trivalent titanium compounds $(\pi\text{-}C_5H_5)_2Ti(\pi\text{-}C_3H_5)$ (C4) and $[(\pi\text{-}C_5H_5)_2Ti(C{\equiv}CPh)]_n$ (C5) is that their dimerization and subsequent disproportionation is prevented by there being no vacant co-ordination sites on the metal. If that is true, the need is immediately raised to account for the existence of the compounds formulated as $(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)$ (C3) and $(\pi\text{-}C_5H_5)_2TiPh$ (C1). It has been observed that the latter reacts with molecular nitrogen (C1) and on the assumption that their structures are similar, as is implicit in their usual formulations, it would seem logical to expect tris(cyclopentadienyl)titanium to do so as well.

Therefore, a green toluene solution of that compound was slowly chilled to -95° while a stream of nitrogen was passed through it. No change was detected. This observation suggests that there is a difference between the stereochemistry about titanium in $(\pi\text{-}C_5H_5)_2TiPh$ and in tris(cyclopentadienyl)-titanium and more specifically, that in the latter there is no vacant co-ordination site to which the nitrogen molecule may bond. In support of this, it was observed that tris(cyclopentadienyl)titanium does not react with pyridine in toluene until warmed to 80° when decomposition begins.

$$(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5) + py \longrightarrow N.R. \qquad (15)$$

In order to acquire further information on the structure

of tris(cyclopentadienyl)titanium, an attempt was made to oxidize the compound under mild conditions. It was hoped that the diamagnetic ion, $\left[(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)\right]^+$, could thus be obtained which might have a similar stereochemistry about the metal atom as exists in paramagnetic tris(cyclopentadienyl)-titanium.

Selection of a series of oxidizing agents for the proposed preparations was made by reference to procedures in analytical chemistry. One method for the determination of titanium (C22) involves reduction of ferric iron to the ferrous state using a solution of a titanous salt. Following this analogy, ether solutions of anhydrous ferric chloride and tris(cyclopentadienyl)-titanium were mixed, resulting in an immediate colour change to red and formation of a precipitate.

$$2(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5) + 2FeCl_3 \longrightarrow 2(\pi\text{-}C_5H_5)_2TiCl_2 + (\pi\text{-}C_5H_5)_2Fe + FeCl_2 \qquad (16)$$

After removal of the solvent, an orange solid which may be shown to be ferrocene sublimes from the residue at 100° <u>in vacuo</u> and a red substance which may be demonstrated to be bis(π-cyclopentadienyl)titanium dichloride is washed from the residue with ether. The off-white solid which remains when the other two products have been removed is water soluble, giving a solution whose pale green colour is typical of the ferrous ion in aqueous solution.

Related attempts to oxidize tris(cyclopentadienyl)-titanium using silver hexafluorophosphate and silver tetrafluoroborate were carried out in benzene. On mixing

solutions of the reactants, a black precipitate appeared and at the same time a yellow colour developed in the liquid phase. After removal of the liquid, the residue was extracted with acetone, the extract concentrated and yellow platelets of bis(π-cyclopentadienyl)titanium difluoride obtained by chilling the concentrated extract to -78°.

$$(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5) + AgPF_6 \longrightarrow (\pi\text{-}C_5H_5)_2TiF_2 + \text{Other Prod.} \quad (17)$$

$$(\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5) + AgBF_4 \longrightarrow (\pi\text{-}C_5H_5)_2TiF_2 + \text{Other Prod.} \quad (18)$$

Yellow bis(π-cyclopentadienyl)titanium difluoride was identified by spectroscopic techniques. Its mass spectrum has a parent ion peak at m/e = 216 and relatively intense peaks due to ions with mass to charge ratios corresponding to $\left[(\pi\text{-}C_5H_5)_2TiF\right]^+$ and $\left[(\pi\text{-}C_5H_5)_2Ti\right]^+$. The n.m.r. spectrum of the substance dissolved in $\left[^2H_6\right]$ dimethylsulphoxide consists of a narrow triplet centred at 3.56 τ with coupling J(H-F) = 1.6 Hz. The i.r. spectrum has bands at 3080, 1440, 1010 and 825 cm^{-1} associated with the π-cyclopentadienyl ligand (C12) but bands at 3065, 1420, 1410, 1395, 1005, 755 and 725 cm^{-1} seen in the spectrum of tris(cyclopentadienyl)-titanium (see Appendix), and attributable to vibrations associated with the σ-cyclopentadienyl ring are absent, thus supporting the other evidence which indicates loss of the so-called σ-cyclopentadienyl ring. The analytical results (see Appendix) are consistent with the formulation of the yellow compound as $(\pi\text{-}C_5H_5)_2TiF_2$.

5. <u>The Structure of Tris(cyclopentadienyl)titanium</u>

Failure to obtain the desired cationic oxidation product

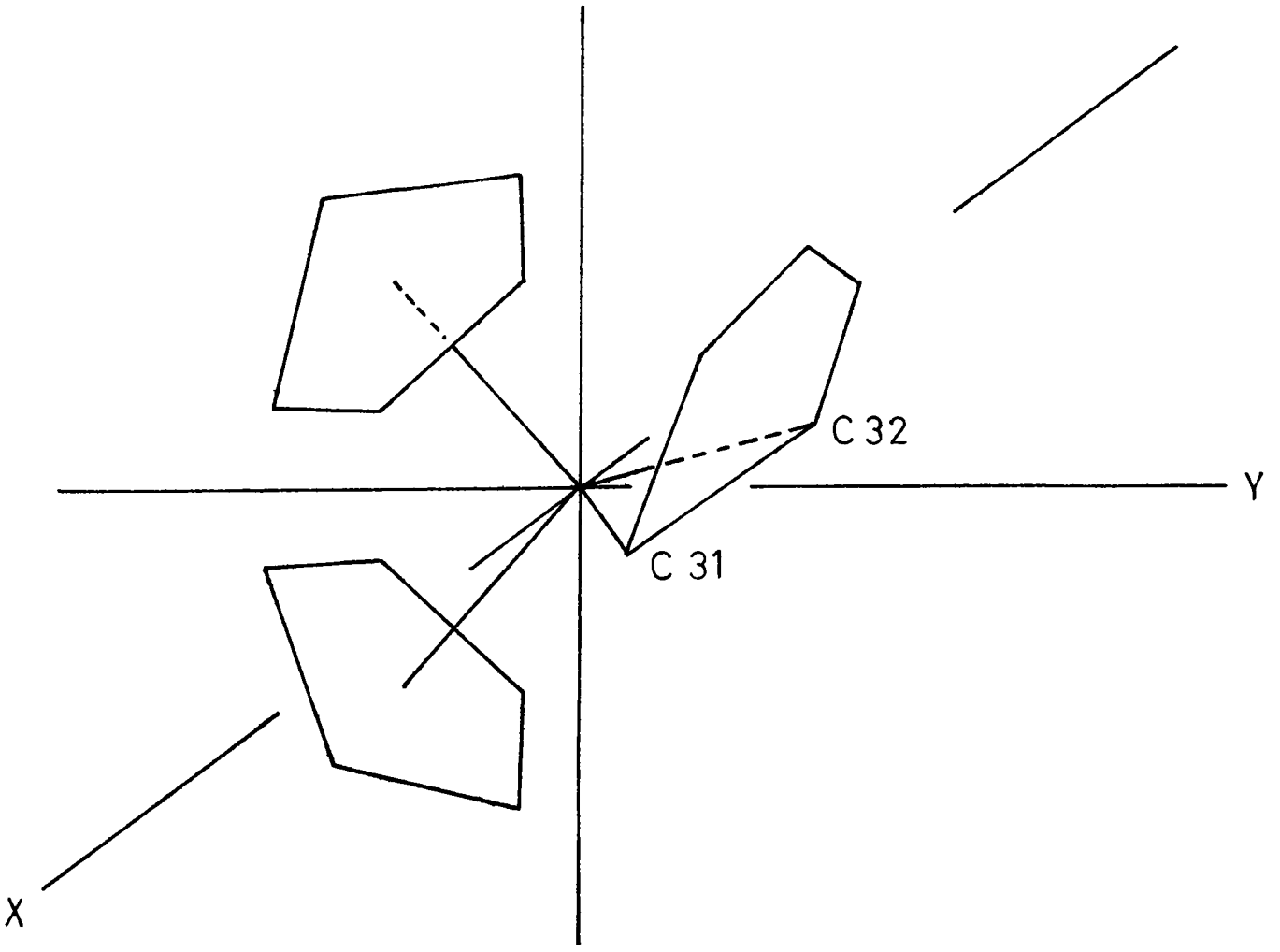
of tris(cyclopentadienyl)titanium made it impossible to obtain structural information on the unoxidized material by the proposed route and therefore, it was necessary to carry out a more detailed examination of tris(cyclopentadienyl)-titanium, itself. Fischer (C6) showed that the compound is paramagnetic in the solid state, a fact which he presented as evidence for its monomeric nature. A mass spectrum of the substance obtained during the course of the present study by a route differing from Fischer's, supports his interpretation since it has a parent ion peak at m/e = 243, corresponding to $\left[(C_5H_5)_3Ti\right]^+$. Other ions of high abundance in the spectrum are those with mass to charge ratios which suggest that they arise from successive loss of C_5H_5 units from the parent ion.

The molecular structure of the compound was determined and is shown in Figures I and II. Two of the rings in this molecule are exemplary π-cyclopentadienyl ligands while the third ring is novel if not unique in its method of attachment to the metal by only two carbon atoms. The three rings are all essentially planar and have more or less constant carbon-carbon distances within a given ring. The bisector of the angle between the perpendiculars from the π-bonded rings to the metal passes through the middle of the carbon-carbon bond which is closest to the metal in the third ring. Some bond lengths determined when the R value was 8% are given in Table I. The angle

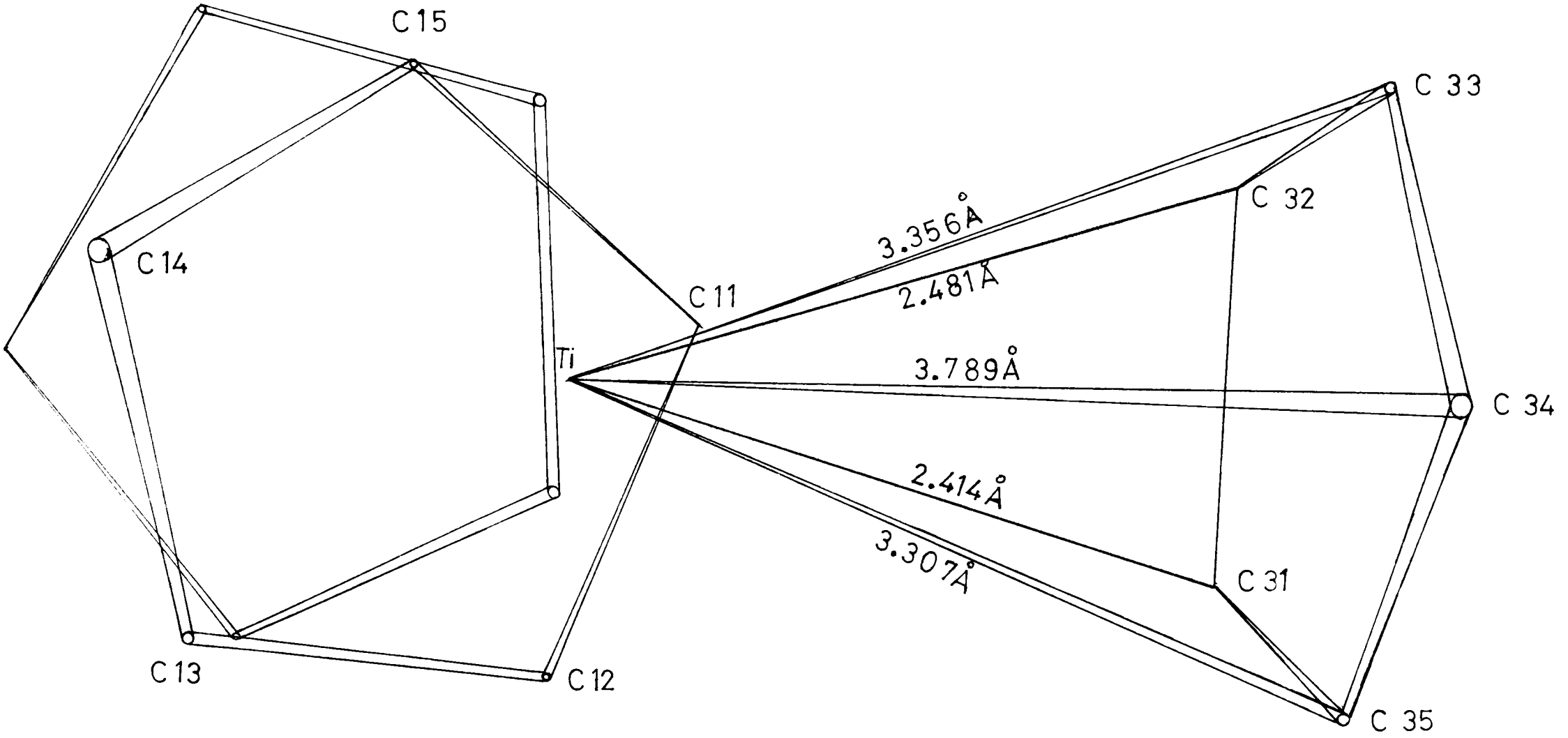
defined by the titanium atom and the centres of the two π-bonded rings is 133.72° and the perpendicular distances from the metal to the planes of those rings are 2.039 and 2.070 Å.

Table I

Bond Lengths (in Angstroms) in Tris(cyclopentadienyl)titanium			
Ti-C11 2.417	Ti-C21 2.365	Ti-C31 2.414	C31-C32 1.413
Ti-C12 2.405	Ti-C22 2.370	Ti-C32 2.481	C32-C33 1.415
Ti-C13 2.400	Ti-C23 2.383	Ti-C33 3.356	C33-C34 1.418
Ti-C14 2.391	Ti-C24 2.359	Ti-C34 3.789	C34-C35 1.435
Ti-C15 2.369	Ti-C25 2.375	Ti-C35 3.307	C35-C31 1.460



I. The Molecular Structure of Tris(cyclopentadienyl)titanium



II. Projection of Tris(cyclopentadienyl)titanium on the Ti-C31-C32 Plane

C. Discussion

This work contributes to the growing body of evidence which suggests that the preparation of isolable compounds of trivalent titanium containing the metal bonded only to carbon may be accomplished only under special conditions (C5). Disproportionation is the usual behaviour of these substances (C23, C24) and when that behaviour is viewed against the rest of the chemistry of trivalent titanium, it does not appear unusual. For example, titanium trichloride disproportionates at 450° (C20) and the complex $TiCl_3 \cdot 3THF$, when heated to just over 100°, loses part of its tetrahydrofuran and then disproportionates (C20) to an involatile low valent titanium-containing residue and a yellow sublimate of $TiCl_4 \cdot 2THF$. Likewise, the complex $[Ti(NMe_2)_3]_2$, disproportionates (C25) at 55° according to equation 19.

$$[Ti(NMe_2)_3]_2 \rightleftharpoons Ti(NMe_2)_2 + Ti(NMe_2)_4 \qquad (19)$$

It seems probable that all these disproportionation reactions proceed <u>via</u> a dimerization step, since it has been shown that many of those derivatives of trivalent titanium which disproportionate readily are associated in some manner. For example, titanium trichloride is a polymer (C20); so is the complex $TiCl_3 \cdot THF$ (C26) and tris(dimethylamido)-titanium is a dimer (C25). Consistent with this hypothesis, is the observation that the five-co-ordinated monomeric (C27) complex, $TiBr_3 \cdot 2NMe_3$, does not disproportionate when

heated to its melting point (C28), nor does tris(cyclopentadienyl)-titanium which is shown in this study to be a monomer.

In the present study, a green coloured solution which was stable at -90° was observed upon mixing solutions of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ and trimethylsilymethyllithium (equation 5). That green colour may have been due to a trivalent titanium species which disproportionates to give the observed products upon warming to -84°. It would seem possible that the green substance is dimeric with a metal-metal bond since no reaction with nitrogen gas at low temperatures, analogous to the reaction of $(\pi\text{-}C_5H_5)_2TiPh$, was observed. Furthermore, no additional colour change was observed before the yellow colour of the product appeared at -84° which suggests that it was the green species which disproportionated and would therefore already have been dimeric.

Additional evidence in support of the hypothesis that dimerization occurs prior to disproportionation may be found in the fact that disproportionation is prevented in those species such as $(\pi\text{-}C_5H_5)TiCl_2\cdot 2L$ and $(\pi\text{-}C_5H_5)_2TiCl\cdot L$ in which the potential dimerization site is blocked. The fact that no products are isolated from these reactions, with the exception of the liberated ligands, L, has been discussed in Chapter II in connection with attempts to reduce species of the form $(\pi\text{-}C_5H_5)_2TiCl\cdot L$. The structure and reactivity of tris(cyclopentadienyl)titanium, determined during the course of this study, are also consistent with

the hypothesis that dimerization preceeds disproportionation. It is impossible for that compound to dimerize and it is found to be stable at its melting point. The question remains, however, why the compound formulated (C1) as $(\pi\text{-}C_5H_5)_2TiPh$ does not disproportionate and what differences exist between its structure and that of tris(cyclopentadienyl)titanium that might account for the striking differences in their chemistry.

Until the determination of the structure of tris(cyclopentadienyl)titanium, only three types of covalent bonding between cyclopentadienyl rings and metal atoms were recognized (C34). Rings which are π- or σ-bonded are frequently encountered and well known. A more unusual type of bonding was shown (C35) to exist in $(C_5H_5)_3MoNO$. Two of the rings in this molecule do not have constant metal-carbon distances, although all ten carbon atoms in the two rings are close enough to the metal to be considered to be involved in bonding to it. The possibility of trihapto-bonding of a regular pentagonal cyclopentadienyl ring to a metal has been discussed and has been shown on geometric grounds (C36) to be indistinguishable by structural studies from a pentahapto-ring. Thus, the type of bonding seen in tris(cyclopentadienyl)titanium is highly unusual.

The type of bond between titanium and the bihapto-ring is difficult to understand in valence bond terms but may be considered to be an approximation to a metallocyclic form of Dewar benzene. Alternatively, the bonding may be

considered to arise from interaction of the two highest filled M.O.s of the cyclopentadienyl radical and the three equatorial M.O.s proposed by Ballhausen (C37) on the $(\pi\text{-}C_5H_5)_2M$ systems. This would result in formation of one three centre, two electron bond of sigma symmetry involving Ballhausen's empty ψ_0 orbital and the filled cyclopentadienyl orbital which has the same sign to its wave function over only two carbon atoms. This could be regarded formally as donation of two electrons to titanium by the cyclopentadienyl ligand. Overlap of Ballhausen's ψ_{-y} and ψ_{+y} orbitals, in each of which there is one electron, with the orbital of the cyclopentadienyl radical containing one electron whose wave function changes sign between the two carbon atoms in question would give rise to a three centre, two electron bond of pi symmetry and a non-bonding orbital containing one electron. Formally, this may be thought of as donation of one electron to titanium by the cyclopentadienyl ligand. In this way, the paramagnetism of the complex and the unique attachment of the cyclopentadienyl ring to the metal by only two carbon atoms may be appreciated. Presumably, it is for steric reasons that one ring is bonded to titanium by only two carbon atoms in this molecule rather than in some other more conventional fashion.

In the light of the molecule's structure, much of its chemistry becomes more readily understood. Both of its equatorial co-ordination positions are filled, as is true

in all bis-π-cyclopentadienyl systems of titanium for which structures are known. The absence of an empty co-ordination position prevents dimerization and subsequent disproportionation and it also accounts for the lack of reactivity of the molecule with molecular nitrogen or pyridine.

It is interesting that bis(π-cyclopentadienyl)titanium difluoride is obtained in good yield from the reactions of tris(cyclopentadienyl)titanium with silver tetrafluoroborate and silver hexafluorophosphate. The high yield of difluoride from these reactions indicates that the product cannot be arising simply from traces of hydrogen fluoride in the solutions of the silver salts. It is possible, however, that the oxidation of tris(cyclopentadienyl)titanium proceeds <u>via</u> species with double fluorine bridges between titanium and boron or phosphorus. In support of such a hypothesis, may be cited the existence of the compound $(\pi\text{-}C_5H_5)_2TiBF_4$ in which such a bridge occurs (C29). This shows that with titanium, even though tetrafluoroborate and hexafluorophosphate anions are generally considered to be non-co-ordinating, such species are plausible.

The nature of the black disproportionation products containing divalent titanium encountered in this study is ill-understood compared to the tetravalent compounds. Certain useful comparisons between properties of the black powders and properties of divalent titanium, in general, may be made, however, which shed some light on the former's

possible structures. Association into polymers or clusters with metal-metal interactions or ligand bridges between metal atoms, such as is found in titanium dichloride seems to be a general feature of the chemistry of divalent titanium (C20, C21), as mentioned earlier. Some properties of the black powders prepared during this work are consistent with their being such clusters composed of π-cyclopentadienyl-titanium and magnesium halide units with co-ordinated solvent molecules. It would also seem likely that the hydrocarbon ligands, other than cyclopentadienyl, have been lost. This may be deduced from the fact that methane was vigorously evolved in the reactions of $\left[(\pi\text{-}C_5H_5)TiCl_2\right]_n$ with methyl-lithium and methylmagnesium bromide and is supported by the fact that hydrolysis of these black powders does not result in the evolution of significant quantities of methane. The exact nature of these black powders is obscure but they may be related to those with somewhat similar properties obtained by Saito (C30) from π-cyclopentadienyltitanium trichloride and magnesium powder, discussed in Chapter I. They may also be similar, in some respects, to substances which have bonds between transition metals and Main Group I, II or III metals that have recently been encountered. Compounds with bonds between nickel and magnesium and behaving like Grignard reagents have been reported (C31) while crystalline substances, possibly of a polymeric nature, formed by reactions between bis(π-cyclopentadienyl)molybdenum or tungsten

dihydrides and trimethylaluminium, dimethylmagnesium or methyllithium with evolution of methane are currently under investigation (C32).

The reversible absorption of molecular nitrogen by mixtures of $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ and methylmagnesium bromide or methyllithium, observed during this study, seems to be similar to that occurring in mixtures of isopropylmagnesium bromide and bis(π-cyclopentadienyl)titanium dichloride (C2), mentioned in Chapter I. The structure of the species fixing nitrogen in the present study is probably, therefore, related to that of the active species in the isopropylmagnesium bromide mixture. It seems unlikely that the active material is bis(π-cyclopentadienyl)titanium which Brintzinger (C9) has shown reacts with nitrogen and might be expected to be formed in small quantities under the experimental conditions employed in this work. Had that substance been the major constituent of the yellow solution, the sublimation of the residue, after removal of the solvent, should have yielded deep green $\left[(\pi\text{-}C_5H_5)(C_5H_4)TiH\right]_2$ as the sublimate (C33), instead of the yellow highly reactive one actually obtained. Therefore, as in the studies by de Liefde Meijer (C1) and Shilov (C2), the exact nature of the nitrogen fixing entity remains obscure. As a result of this study, however, it is possible to state that the attempted preparation of compounds containing titanium formally in oxidation state three is not sufficient, by itself, to ensure nitrogen

fixing ability. Compounds of that kind will either dimerize or the ligands will be distorted in such a way as to block the site for nitrogen co-ordination. In those cases where dimerization occurs instead of nitrogen fixation or ligand distortion, subsequent disproportionation can be expected.

D. References

C1 J.H. Teuben and H.J. de Liefde Meijer, Rec. Trav. Chim., 1971, 90, 360.

C2 A.E. Shilov, A.K. Shilova, E.F. Kvashina and T.A. Vorontsova, Chem. Comm., 1971, 1590.

C3 F.W. Siegert and H.J. de Liefde Meijer, J. Organomet. Chem., 1969, 20, 141.

C4 H.A. Martin and F. Jellinek, J. Organomet. Chem., 1968, 12, 149.

C5 J.H. Teuben and H.J. de Liefde Meijer, J. Organomet. Chem., 1969, 17, 87.

C6 E.O. Fischer and A. Lochner, Z. Naturforsch., 1960, 15b, 266.

C7 J.A. Waters, V.V. Vickroy and G.A. Mortimer, J. Organomet. Chem., 1971, 33, 41.

C8 H. Burger and H.J. Neese, J. Organomet. Chem., 1970, 21, 381.

C9 J.E. Bercaw, R.H. Marvich, L.G. Bell and H.H. Brintzinger, J. Amer. Chem. Soc., 1972, 94, 1219.

C10 M.R. Collier, M.F. Lappert and M.M. Truelock, J. Organomet. Chem., 1970, 25, C36.

C11 G. Yagupsky, W. Mowat, A Shortland and G. Wilkinson, Chem. Comm., 1970, 1369.

C12 P.M. Druce, B.M. Kingston, M.F. Lappert, T.R. Spalding and R.C. Srivastava, J. Chem. Soc., (A), 1969, 2106.

C13 U. Giannini and S. Cesca, Tet. Lett., 1960, 14, 19.

C14 U. Zucchini, E. Albizzati and U. Giannini, J. Organomet. Chem., 1971, 26, 357.

C15 R.J.H. Clark and A.J. McAlees, J. Chem. Soc., (A), 1970, 2026.

C16 I.S. Kolomnikov, T.S. Lobeeva, V.V. Gorbachevskaya, G.G. Aleksandrov, Yu.T. Struchkov and M.E. Vol'pin, Chem. Comm., 1971, 972.

C17 G. Fachinetti and C. Floriani, Chem. Comm., 1972, 654.

C18 F. Calderazzo, J.J. Salzmann and P. Mosimann, Inorg. Chim. Acta, 1967, 1, 65.

C19 R.D. Gorsich, J. Amer. Chem. Soc., 1960, 82, 4211.

C20 R.J.H. Clark, The Chemistry of Titanium and Vanadium, Elsevier Publishing Company, London, 1968.

C21 G.W.A. Fowles, T.E. Lester and R.A. Walton, J. Chem. Soc., (A), 1968, 1801.

C22 A.I. Vogel, Quantitative Inorganic Analysis, Longmans Green and Co., Ltd., London, 1959.

C23 K.H. Thiele and W. Schafer, Z.Anorg. Allg. Chem., 1970, 379, 63.

C24 F.S. D'yachkovskii and N.E. Khrushch, Zh. Obshch. Khim., 1971, 41, 1779.

C25 M.F. Lappert and A.R. Sanger, J. Chem. Soc. (A), 1971, 874.

C26 M. Zikmund and L. Stepnickova, Chem. Zvesti, 1969, 23, 850.

C27 P.T. Greene, B.J. Russ and J.S. Wood, J. Chem. Soc. (A),

1971, 3636.

C28 M. Antler and W. Laubengayer, J. Amer. Chem. Soc., 1955, 77, 5250.

C29 H. Noth and R. Hartwinner, Chem. Ber., 1960, 93, 2246.

C30 T. Saito, Chem. Comm., 1971, 1422.

C31 H. Felkin and P.J. Knowles, J. Organomet. Chem., 1972, 37, C14.

C32 J.S. Poland, private communication.

C33 R.H. Marvich and H. H. Brintzinger, J. Amer. Chem. Soc., 1971, 93, 2046.

C34 F.A. Cotton and P. Legzdins, J. Amer. Chem. Soc., 1968, 90, 6232.

C35 J.L. Calderon, F.A. Cotton and P. Legzdins, J. Amer. Chem. Soc., 1969, 91, 2528.

C36 F.A. Cotton, Discuss. Farad. Soc., 1969, 47, 79.

C37 C.J. Ballhaysen and J.P. Dahl, Acta Chem. Scand., 1961, 15, 1333.

CHAPTER IV

Some Features of the Chemistry of Lower Valent Bis(π-cyclopentadienyl)niobium Compounds

A. Introduction

The organic chemistry of titanium appears to differ substantially from that of most other transition metals and various explanations may be put forward to account for this. Comparisons between the chemistry of titanium and other transition elements must, however, involve those elements which occur much later in the transition series due to the fact that the organic chemistry of titanium's nearest neighbours, zirconium, hafnium, niobium and tantalum is, as yet, largely unexplored. It would, therefore, seem desirable to acquire further insight into the organic chemistry of these elements and in this chapter are described some attempts to expand the organic chemistry of niobium.

There is some justification, from a stereochemical point of view, for anticipating certain similarities between the chemistry of niobium (atomic radius 1.47 Å) and that of titanium (atomic radius 1.46 Å) since atoms of the two elements are of approximately the same size (D1). Arguments based on this fact have been developed by de Liefde Meijer (D2) and are referred to in Chapter II. Some interesting differences between the behaviour of the two elements may also be expected. These would arise from the lower energies of niobium's orbitals, relative to those

of titanium, as is reflected in their respective ionization potentials (D3) (Table I).

Table I

Ionization Potentials of Titanium and Niobium					
Element	Ionization Potentials in Volts				
titanium	6.82	13.57	27.47	43.24	99.80
niobium	6.88	14.32	25.04	38.3	50

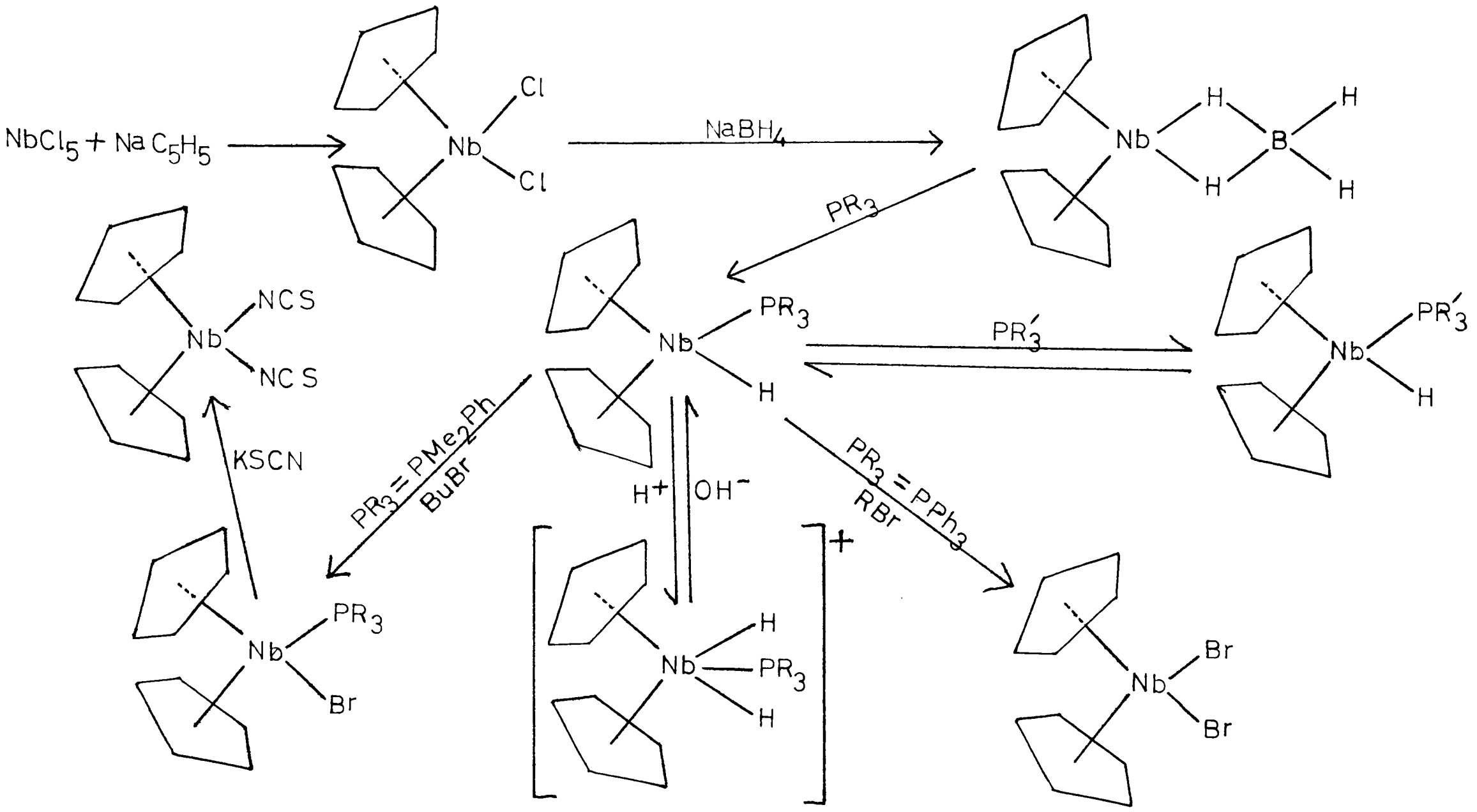
The remainder of this chapter is, therefore, devoted to exploring these similarities and differences and hopefully gaining not only new knowledge of the chemical properties of niobium but also further understanding of the chemistry of titanium. Some of the results are presented for convenience in Figure I.

B. Chemical Studies

1. Preparation of $(\pi\text{-}C_5H_5)_2NbCl_2$

Although preparations of bis(π-cyclopentadienyl)niobium dichloride are reported in the literature (D2, D5), they involve procedures which are prolonged or tedious and give only modest yields (*ca.* 35%). The first step in this project, therefore, involved development of a satisfactory large-scale preparation of that compound.

Following Fischer's procedure (D4), niobium pentachloride was treated in benzene with dry sodium cyclopentadienide to obtain tetrakis(cyclopentadienyl)niobium. The benzene solution of this compound was then poured onto concentrated



I. Some Features of Bis(π-cyclopentadienyl)niobium Chemistry

hydrochloric acid and the suspension boiled until all organic liquids were evaporated. To the remaining suspension, bromine was added to destroy excess sodium cyclopentadienide and to ensure that oxidation to the +5 state was complete. When excess bromine had been removed by boiling, the hot suspension was filtered and to the filtrate excess stannous chloride in hydrochloric acid was added which causes the precipitation of brown, tabular crystals of bis(π-cyclopentadienyl)niobium dichloride in 75% yield.

$$NbCl_5 + 6NaC_5H_5 \longrightarrow 5NaCl + (C_5H_5)_4Nb + \text{organic products} \quad (1)$$

$$2(C_5H_5)_4Nb + 4HCl + [O] \xrightarrow{Br_2/O_2} \left\{\left[(\pi\text{-}C_5H_5)_2NbCl\right]_2O\right\}Cl_2 + 2C_5H_6 \quad (2)$$

$$5Cl^- + \left\{\left[(\pi\text{-}C_5H_5)_2NbCl\right]_2O\right\}^{2+} + SnCl_3^- + 2H^+ \longrightarrow 2(\pi\text{-}C_5H_5)_2NbCl_2 + SnCl_6^{2-} + H_2O \quad (3)$$

This method has the obvious advantage over previous ones that large quantities (ca. 35 g) of $(\pi\text{-}C_5H_5)_2NbCl_2$ can be prepared with ease in one day, starting from solid sodium cyclopentadienide and niobium pentachloride. Furthermore, this procedure does not involve any exceptionally difficult or tedious processes and the product is obtained in good yield and high purity. The compound, which is essentially air-stable in the solid state, was identified by analysis (see Appendix) and comparison of its i.r. spectrum with that of an authentic sample of the compound, prepared by a previously reported method (D5).

The i.r. spectrum consists of bands at 3080 (weak, C-H stretch), 1012 (medium, in-plane C-H bend) and 825 cm^{-1}

(strong, out-of-plane C-H bend) arising from vibrations of the π-cyclopentadienyl ligands (D6), as well as bands at 728, 380, 308, 290 and 268 cm^{-1} which are unassigned.

It is vital for the success of this preparation that the sodium cyclopentadienide be free of tetrahydrofuran. It has been shown (D7) that niobium pentachloride and tetrahydrofuran react via ring opening and formation of an alkoxide followed by thermal decomposition of this species to Nb_2O_5 and organic products. Therefore, following preparation of sodium cyclopentadienide in tetrahydrofuran (D8), the bulk of that solvent must be removed and the white residue maintained in vacuo at 100° until no further solvent distils (ca. three days) before it can be used in the preparation of bis(π-cyclopentadienyl)niobium dichloride.

The identity of the red ion which is reduced by stannous chloride to bis(π-cyclopentadienyl)niobium dichloride (equation 3) has not been directly established but it is likely to be $\{[(\pi\text{-}C_5H_5)_2NbCl]_2O\}^{2+}$. This red cation is formed when bis(π-cyclopentadienyl)niobium dichloride is dissolved in concentrated hydrochloric acid in air. It has been isolated as the tetrafluoroborate salt from these solutions and its molecular structure determined (D5).

2. Preparation of $(\pi\text{-}C_5H_5)_2NbBH_4$

The chemistry of bis(π-cyclopentadienyl)niobium dichloride is somewhat restricted by its low solubility in common solvents but it reacts smoothly with sodium borohydride

in 1,2-dimethoxyethane to give green $(\pi\text{-}C_5H_5)_2NbBH_4$. This compound has been very briefly reported previously but was obtained in less than 50% yield and its properties were not examined except for characterization (D9).

If the crude product from the reaction with sodium borohydride (equation 4) is extracted with toluene, filtered and an equal volume of petroleum ether added, green crystals of $(\pi\text{-}C_5H_5)_2NbBH_4$ are obtained in 84% yield upon chilling the solution to -78° overnight.

$$2(\pi\text{-}C_5H_5)_2NbCl_2 + 4NaBH_4 \longrightarrow 2(\pi\text{-}C_5H_5)_2NbBH_4 + 4NaCl + B_2H_6 + H_2 \qquad (4)$$

This compound sublimes <u>in vacuo</u> at 80° and dissolves in ethers or aromatic hydrocarbons. It is pyrophoric in air but is stable indefinitely at room temperature under an inert atmosphere. The i.r. spectrum of the substance consists of bands at 3080, 1010 and 800 cm^{-1} arising from vibrations associated with the π-cyclopentadienyl group (D6). Further bands at 2420 (strong, terminal B-H stretch), 2310 (weak, out-of-plane bridge expansion), 1720 (medium, symmetrical bridge stretch) and 1160 cm^{-1} (strong, terminal B-H bend) are associated with the borohydrido ligand, (D10). Comparison of this spectrum with those of other borohydrido-metal species (D10, D11) suggests that the ligand is attached to niobium by a double hydrogen bridge similar to that in $(\pi\text{-}C_5H_5)_2TiBH_4$ (D12).

The n.m.r. spectrum of a solution of the compound in

$[^2H_6]$ benzene consists of a single resonance at 5.00 τ which may be assigned to the cyclopentadienyl hydrogens. The fact that no resonance due to the borohydride hydrogens was detected is not unusual (D11, D13) and is probably due to line-broadening by the ^{11}B and ^{10}B quadrupole moments and by ^{93}Nb (I = 9/2; 100% abundance). The compound's mass spectrum has a parent ion peak at m/e = 238.

3. Reaction of $(\pi\text{-}C_5H_5)_2NbBH_4$ with Donor Ligands

Some borohydrido-metal species react with ligands which can form complexes with borane (D14). Thus, tris(borohydrido)-aluminium and bis(borohydrido)bis(π-cyclopentadienyl)zirconium react with amines to form an amineborane and substances containing co-ordinated amine as well as a metal-hydrogen bond. In contrast, purple $(\pi\text{-}C_5H_5)_2TiBH_4$ is inert to both phosphines and amines, as discussed in Chapter II, so it is of interest to see which sort of behaviour is exhibited by bis(π-cyclopentadienyl)niobium borohydride.

Toluene solutions of the niobium borohydride were treated with several donor ligands at low (ca. -80°) temperatures. With dimethylsulphide, no reaction occurs even after warming to 60° for several hours. With methylamine and butylamine, no reactions occur until the solutions have been warmed to room temperature when a green precipitate forms. Although that precipitate is soluble in water to give a solution from which a green hexafluorophosphate may be precipitated, it is otherwise too reactive to characterize.

When the reaction is carried out with pyridine at -65°, a red solution is obtained but the colour is discharged at about -20° and only a brown intractable oil was isolated.

If the green niobium borohydride is dissolved in benzene and dimethylphenylphosphine or triphenylphosphine added, a deep red colour develops after a few minutes. This colour is stable up to about 40° and from these solutions may be isolated dark red needle-like crystals of the appropriate phosphine hydrides, $(\pi\text{-}C_5H_5)_2Nb(H)PR_3$.

$$(\pi\text{-}C_5H_5)_2NbBH_4 + 2R_3P \longrightarrow (\pi\text{-}C_5H_5)_2Nb(H)PR_3 + R_3PBH_3 \quad (5)$$

These hydrides tend to be thermally unstable in solution, particularly the one derived from dimethylphenylphosphine, and it is necessary to keep temperatures of their solutions below about 50° during their isolation and subsequent handling. They are soluble in hydrocarbon solvents, ethers, alcohols and acetone.

The i.r. spectra of these compounds consist of bands at 3095, 1010 and 805 cm^{-1} which arise from vibrations of the π-cyclopentadienyl group (D6), while bands characteristic of the phosphine ligands are seen at 3045, 1580, 1180, 1100, 750, 700 and 510 cm^{-1}. There is, in addition to these bands, a strong broad absorption which may be assigned to the metal-hydrogen stretching frequency occurring at 1630 cm^{-1} in the dimethylphenylphosphine hydride and at 1625 cm^{-1} in the compound containing triphenylphosphine. N.m.r. spectra of the two compounds were recorded in $[^2H_6]$ benzene and

$[^2H_6]$acetone and were observed to be unaffected by this change of solvent. The spectrum of $(\pi\text{-}C_5H_5)_2Nb(H)PMe_2Ph$ consists of a complex band centred at 2.65τ, a doublet with splitting J(P-H) = 2.0 Hz centred at 5.34τ, a doublet with splitting J(P-H) =6.8 Hz centred at 8.53τ and a doublet with splitting J(P-H) = 28.6 Hz centred at 17.53τ. Integration of the spectrum gives an intensity ratio of 5:10:6:1 for these peaks and the signals have accordingly been assigned to resonances of the phenyl, cyclopentadienyl, methyl and hydride hydrogens, respectively. The spectrum of $(\pi\text{-}C_5H_5)_2Nb(H)PPh_3$ is similar and consists of a complex band centred at 2.8τ, a doublet with splitting J(P-H) = 1.9 Hz centred at 5.43τ and a doublet with splitting J(P-H) = 27.0 Hz centred at 16.65τ. Integration of the spectrum gives an intensity ratio for the peaks of 18:10:1 and the resonances have, therefore, been assigned to the phenyl, cyclopentadienyl and hydride hydrogens, respectively. Some of the pertinent data for characterization of these and several other compounds discussed in this chapter are summarized in Table II for convenience. Analytical data (see Appendix) are consistent with the proposed formulations of these compounds.

4. <u>Reactions of $(\pi\text{-}C_5H_5)_2Nb(H)PR_3$; Basic Character</u>

The new phosphine hydrides of trivalent niobium would be expected to behave like Lewis bases because they have a non-bonding electron pair occupying either an Alcock or Ballhausen orbital (see Chapter I), lying in the P-Nb-H plane.

Table II

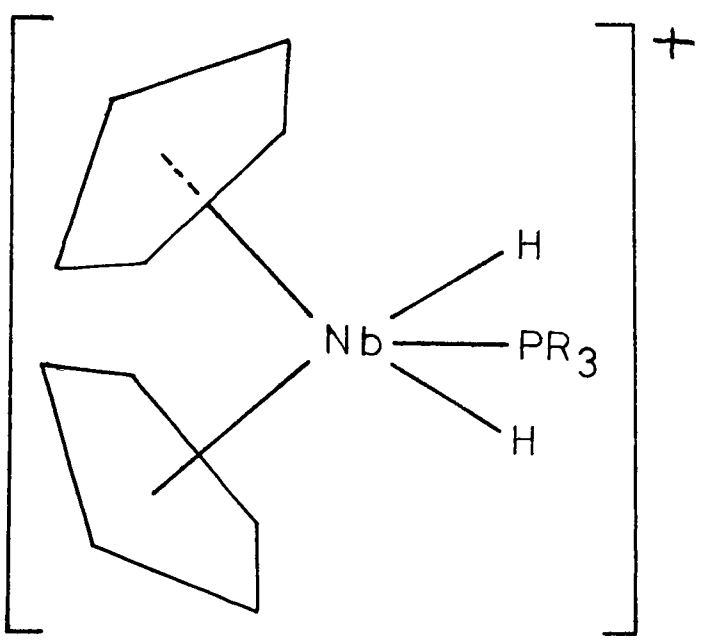
Some I.r. and N.m.r. Data from new Bis(π-cyclopentadienyl)niobium Compounds

Compound	i.r.[a]	n.m.r.[b]			
		Ph	π-C_5H_5	Me	H
$(\pi\text{-}C_5H_5)_2NbBH_4$	νB-H 2420	-	5.00(s)	-	not detected
	δB-H 1160				
$(\pi\text{-}C_5H_5)_2Nb(H)PMe_2Ph$	νM-H 1630	2.65(m)	5.34(d), 2.0	8.53(d), 6.8	17.53(d), 28.6
$(\pi\text{-}C_5H_5)_2Nb(H)PPh_3$	νM-H 1625	2.80(m)	5.43(d), 1.9	-	16.65(d), 27.0
$[(\pi\text{-}C_5H_5)_2Nb(H)_2PMe_2Ph]^+$	νM-H 1740	2.40(m)	4.42(d), 2.0	8.52(d). 7.1	13.96(d), 31.5
$(\pi\text{-}C_5H_5)_2Nb(Br)PMe_2Ph$	-	2.70(m)	5.21(d), 2.1	8.50(d), 7.5	-
$(\pi\text{-}C_5H_5)_2Nb(NCS)_2$	νC-N 2068	-	paramagnetic	-	-
	2040				
	νC-S -				
	δNCS 468				

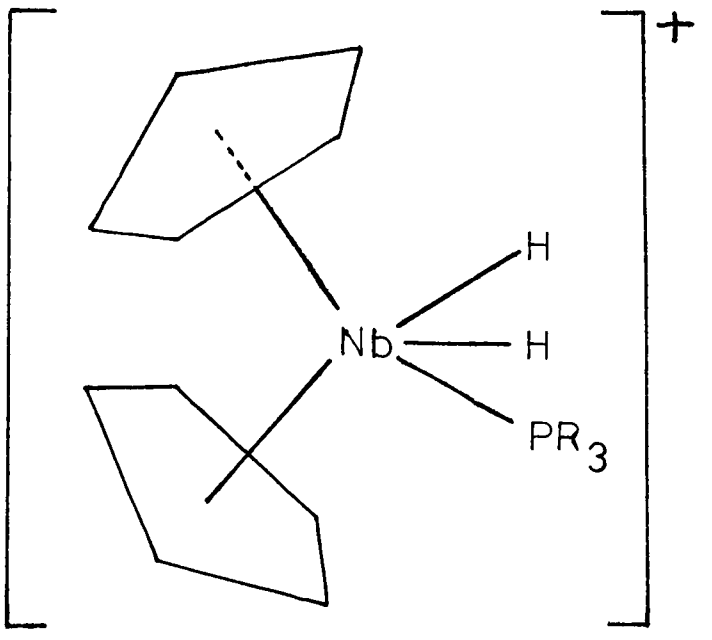
a. in cm^{-1}

b. chemical shifts in τ, multiplicity and coupling constants in Hz.

It should, therefore, be possible to protonate the phosphine hydrides and the resulting dihydride cations would be expected to have one of the structures indicated in Figures II and III.



II. A Possible Structure of $\left[(\pi\text{-}C_5H_5)_2Nb(H)_2PR_3\right]^+$



III. A Possible Structure of $\left[(\pi\text{-}C_5H_5)_2Nb(H)_2PR_3\right]^+$

In principle it ought to be possible to determine which of the two structures the product actually has from its n.m.r. spectrum.

That it is indeed possible to protonate red $(\pi\text{-}C_5H_5)_2Nb(H)PMe_2Ph$, as expected, is shown by the fact that the red solid dissolves in cold dilute hydrochloric acid to give a clear green-yellow solution from which precipitates the red phosphine hydride upon addition of aqueous sodium hydroxide.

$$(\pi\text{-}C_5H_5)_2Nb(H)PMe_2Ph + H^+ \longrightarrow \left[(\pi\text{-}C_5H_5)_2Nb(H)_2PMe_2Ph\right]^+ \quad (6)$$

$$\left[(\pi\text{-}C_5H_5)_2Nb(H)_2PMe_2Ph\right]^+ + OH^- \longrightarrow (\pi\text{-}C_5H_5)_2Nb(H)PMe_2Ph + H_2O \quad (7)$$

The cationic dimethylphenylphosphine dihydride may be isolated as its tetrafluoroborate and hexafluorophosphate salts by addition of aqueous hexafluorophosphoric or tetrafluoroboric acids to a cold (ca. -30°) ethereal solution of the red phosphine hydride. This causes disappearance of the red colour and formation of a white precipitate which has been shown to be $\left[(\pi\text{-}C_5H_5)_2Nb(H)_2PMe_2Ph\right]A$. In the solid state, the cation is only stable at room temperature for about an hour but it can be stored indefinitely at -20°. In acetone solutions, both the hexafluorophosphate and tetrafluoroborate salts are stable at -20° but they are rapidly decomposed at room temperature. The i.r. spectrum of the tetrafluoroborate salt has bands at 3120, 1010 and 815 cm^{-1} arising from vibrations of the π-cyclopentadienyl

ligands (D6) and bands at 3060,1580, 1195, 1100, 750, 700 and 490 cm^{-1} due to vibrations of co-ordinated dimethylphenylphosphine. Absorptions at 1050 and 530 cm^{-1} characteristic of the tetrafluoroborate anion (D15) are also present and a strong band at 1740 cm^{-1} may be assigned to the niobium-hydrogen stretching vibration.

The n.m.r. spectrum at -36° of an acetone solution of the hexafluorophosphate salt consists of a complex band centred at 2.4 τ, a doublet with J(P-H) = 2.0 Hz centred at 4.42 τ, a doublet with J(P-H) = 7.1 Hz centred at 8.52 τ and a doublet with J(P-H) = 31.5 Hz centred at 13.96 τ. Integration of the spectrum shows that the relative intensities of the peaks are in the ratio 5:10:6:2 and the absorptions have, therefore, been assigned to the phenyl, cyclopentadienyl, methyl and hydride hydrogens, respectively. Analytical data (see Appendix) are consistent with the proposed formulation of this compound.

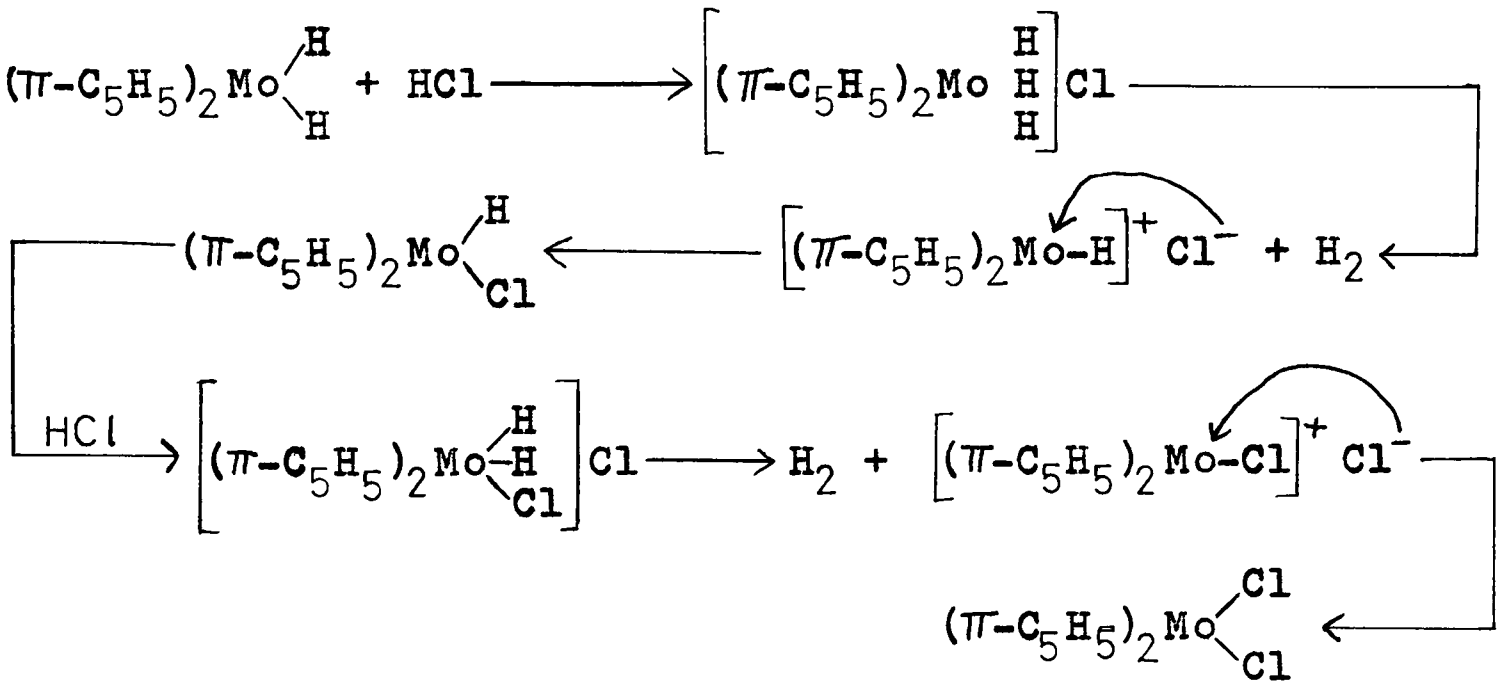
The fact that the hydride resonance in the spectrum of the dihydride cation appears as a well resolved doublet may be interpreted as suggesting that the cation has the symmetrical structure shown in Figure II. A species like that in Figure III, with asymmetrical bonding of the two hydrogens, should give rise to a considerably more complex hydride resonance. Alternatively, if the two hydride ligands were exhibiting fluxional behaviour or if the hydrides and the phosphine were all involved in a fluxional process such

as has been observed for several other tertiary phosphine hydrides (D16), the same sort of signal as was observed would be expected.

Similar experiments were carried out with the triphenylphosphine hydride $(\pi\text{-}C_5H_5)_2Nb(H)PPh_3$, but the resulting dihydride cation is highly reactive and rapidly decomposes to other products. Treatment of the triphenylphosphine hydride in tetrahydrofuran with a few drops of hydrobromic acid at room temperature causes initial precipitation of a white product, presumably the dihydride cation, which quickly decomposes with evolution of a gas to give the isolated product, bis(π-cyclopentadienyl)niobium dibromide. Such an oxidation also occurs as a result of bubbling hydrogen chloride through a benzene solution of the triphenylphosphine hydride at room temperature. Initially, the formation of an intractable green gum is observed, followed eventually by formation of bis(π-cyclopentadienyl)-niobium dichloride.

It is interesting to compare this reaction with the behaviour of $(\pi\text{-}C_5H_5)_2MoH_2$ in hydrochloric acid (D19). The molybdenum compound is also protonated under these conditions to give initially a trihydride cation $\left[(\pi\text{-}C_5H_5)_2MoH_3\right]^+$, which is stable at room temperature in the acid solution. Upon heating the solution, however, gas evolution occurs and crystals of $(\pi\text{-}C_5H_5)_2MoCl_2$ are formed. It is probable that this reaction proceeds by a mechanism

(Figure IV) essentially the same as that by which $(\pi\text{-}C_5H_5)_2Nb(H)PR_3$ is oxidized to $(\pi\text{-}C_5H_5)_2NbX_2$ (Figure V); the major difference between the two systems being the far greater stability of the molybdenum trihydride cation.



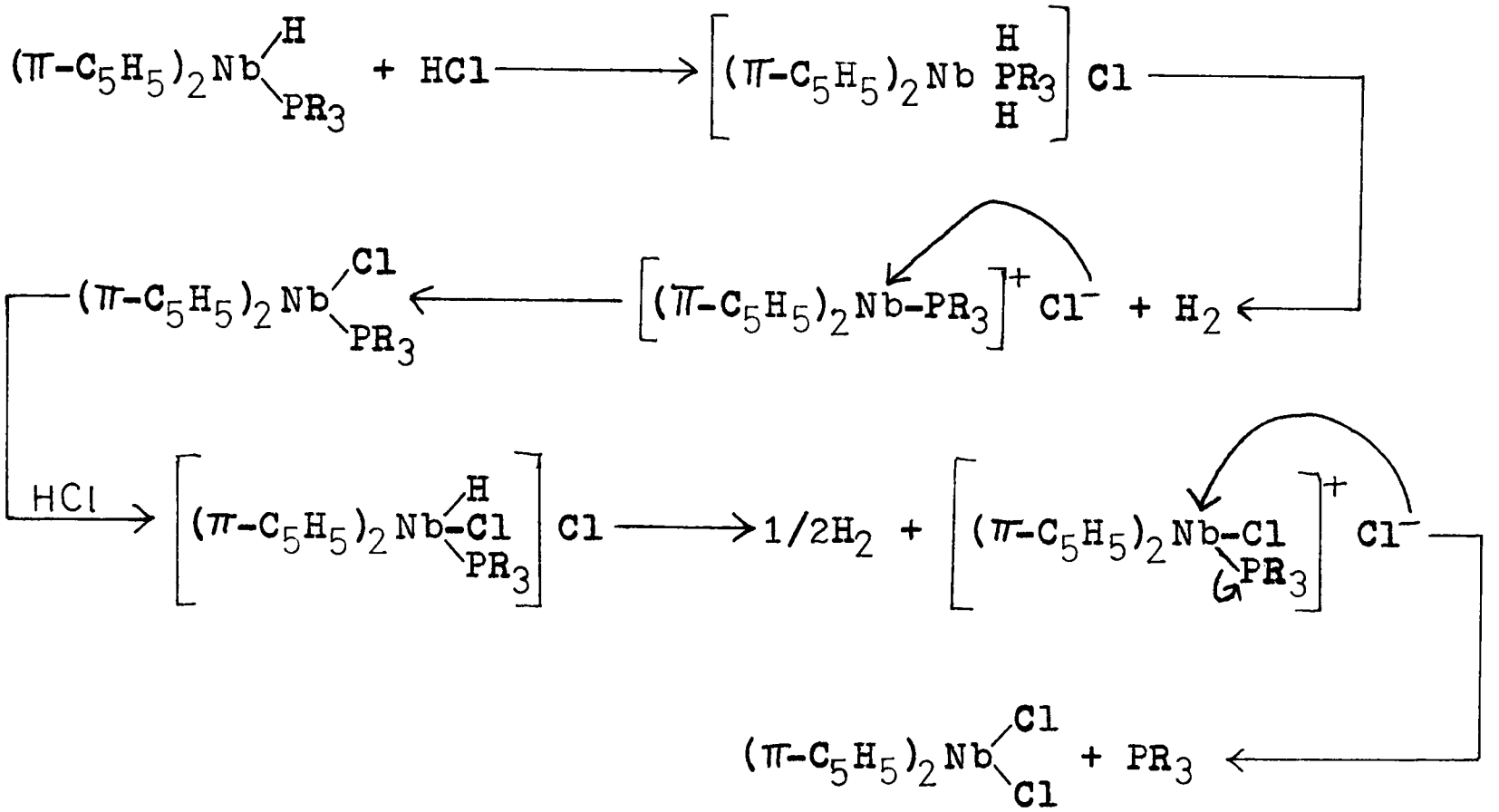
$$(\pi\text{-}C_5H_5)_2MoH_2 + 2HCl \longrightarrow (\pi\text{-}C_5H_5)_2MoCl_2 + 2H_2$$

IV. Proposed Mechanism for the Reaction Between $(\pi\text{-}C_5H_5)_2MoH_2$ and HCl

Attempts to protonate the triphenylphosphine hydride, $(\pi\text{-}C_5H_5)_2Nb(H)PPh_3$, by dissolving it in glacial acetic acid at room temperature resulted in decomposition of the compound.

From these results, it seems that the hydrides are susceptible to further reaction with the acids used to protonate them. Some attempts were, therefore, made to demonstrate further the basic character of the phosphine hydrides using Lewis acids. Benzene solutions of the phosphine

hydrides were treated with gaseous boron trifluoride and toluene solutions of trimethylaluminium. When boron



$$2(\pi\text{-}C_5H_5)_2Nb(H)PR_3 + 4HCl \longrightarrow 2(\pi\text{-}C_5H_5)_2NbCl_2 + 2PR_3 + 3H_2$$

V. Proposed Mechanism for the Reaction Between $(\pi\text{-}C_5H_5)_2Nb(H)PR_3$ and HCl

trifluoride was bubbled through the solutions at room temperature, immediate precipitation of an unidentified black oil occurred, while the addition of trimethylaluminium to the solutions caused no obvious reaction, even when the solutions were warmed gently to about 50°.

The ease with which these trivalent niobium compounds

are oxidized by acids, organic or inorganic halides or pseudohalides is discussed later in this chapter.

5. Reactions of $(\pi\text{-}C_5H_5)_2Nb(H)PR_3$: Ligand Exchange

Although n.m.r. spectra of the phosphine hydrides do not contain peaks attributable to free phosphine, thereby indicating a labile phosphorus-niobium bond, attempts were nevertheless made to exchange phosphine ligands. A $[^2H_6]$benzene solution of the dimethylphenylphosphine hydride and an equimolar quantity of triphenylphosphine has an n.m.r. spectrum consistent with the presence of both phosphine hydrides as well as both free phosphines. The phenyl resonance of this solution is a broad band extending from 1.75 to 3.05 τ while near 5.4 τ there is a pair of doublets due to the cyclopentadienyl hydrogens of the two different phosphine hydrides. Near 8.5 τ, a pair of doublets is also seen, the lower field pair arising from the methyl hydrogens in the dimethylphenylphosphine hydride and the pair to higher field, with splitting J(P-H) = 4.0 Hz, arising from the methyl hydrogens of free dimethylphenylphosphine. In the region of 15 τ, another pair of doublets is seen due to the presence of the two different types of hydride. These hydride resonances were examined as a function of temperature over the range 5° to 52° and growth of the peaks due to the triphenylphosphine hydride at the expense of those due to the dimethylphenylphosphine hydride noted with increasing temperature.

$$(\pi\text{-}C_5H_5)_2Nb(H)PMe_2Ph + Ph_3P \longrightarrow (\pi\text{-}C_5H_5)_2Nb(H)PPh_3 + Me_2PhP \quad (8)$$

Similar ligand exchange reactions were attempted with acetonitrile and pyridine at room temperature but no reactions occurred. When the phosphine hydrides are treated with carbon monoxide, however, a reaction does occur which liberates the phosphine ligands and gives a dark coloured oil, having an i.r. absorption at 1925 cm^{-1}, consistent with the presence of a Nb-C=O system (D15). This oil, however, could not be purified and was not further identified.

Benzene solutions of the triphenylphosphine hydride and freshly sublimed tetracyanoethylene react at room temperature to form a green precipitate and a colourless solution containing liberated triphenylphosphine. This precipitate is soluble in acetone, tetrahydrofuran, dichloromethane and dimethylsulphoxide, with all of which it reacts rapidly. It is insoluble in ether and petroleum ether. The mass spectrum of this substance has what appears to be a parent ion peak at m/e = 301 which could be due to the ion $\left[(\pi\text{-}C_5H_5)_2Nb(CN)_3\right]^+$. The analytical data, however, (see Appendix) correspond approximately to $(\pi\text{-}C_5H_5)_2Nb(CN)TCNE$ and the substance's i.r. spectrum supports this formulation. Attempts to replace tetracyanoethylene with carbon monoxide in the complex and thus obtain a characterizable derivative of this compound gave only decomposition products and the n.m.r. spectrum of the green material could not be obtained due to its instability in solution.

6. Reactions of $(\pi\text{-}C_5H_5)_2NbPR_3$; Hydride Reactivity

Treatment of the dimethylphenylphosphine hydride in petroleum ether with excess 1-bromobutane causes the slow formation of green needles which may be recrystallized from mixtures of tetrahydrofuran and ether. This green substance was identified as the phosphine bromide, $(\pi\text{-}C_5H_5)_2Nb(Br)PMe_2Ph$, from its i.r. and n.m.r. spectra and elemental analysis (see Appendix).

$$(\pi\text{-}C_5H_5)_2Nb(H)PMe_2Ph + BuBr \longrightarrow (\pi\text{-}C_5H_5)_2Nb(Br)PMe_2Ph + BuH \quad (9)$$

The i.r. spectrum is essentially the same as that of the parent phosphine hydride except for the absence of the band at 1630 cm^{-1} in that compound which has been assigned to a metal-hydrogen stretching frequency. The n.m.r. spectrum of the green phosphine bromide dissolved in $[^2H_6]$benzene consists of a complex band centred at 2.7 τ, a doublet with splitting J(P-H) = 2.1 Hz centred at 5.21τ and a doublet with splitting J(P-H) = 7.5 Hz centred at 8.50τ. There are no peaks in the region 10 to 30τ. Integration of the spectrum shows the relative intensities of the observed peaks to be in the ratio 5:10:6 and the resonances have, therefore, been assigned to the phenyl, cyclopentadienyl and methyl hydrogens, respectively.

The phosphine bromide is soluble in tetrahydrofuran, acetone and benzene and is insoluble in petroleum ether. It dissolves in chloroform but is oxidized by that solvent to a paramagnetic species, as was shown by the absence of

any detectable n.m.r. signals from solutions prepared by dissolving the phosphine bromide in chloroform.

Passing carbon monoxide through a green benzene solution of the phosphine bromide caused no reaction until the solution had been warmed to 60°. The solution then turned mauve and the phosphine ligand was released. The niobium-containing product was isolated from this solution as an unidentified, insoluble grey powder which has an i.r. absorption at 1900 cm^{-1}, consistent with the presence of an Nb-C=O system (D15).

Surprisingly, solutions of the phosphine bromide in tetrahydrofuran do not appear to react at room temperature with methylmagnesium bromide.

Attempts to prepare the analogous triphenylphosphine bromide by this route failed and rapid precipitation of bis(π-cyclopentadienyl)niobium dibromide was the only result. The brown crystals of this compound were identified by analysis (see Appendix) and comparison of their i.r. spectrum with that of the analogous dichloride. The two spectra are similar except in the region below 300 cm^{-1}.

$$(\pi\text{-}C_5H_5)_2Nb(H)PPh_3 + 2BuBr \longrightarrow (\pi\text{-}C_5H_5)_2NbBr_2 + PPh_3 + \text{organic products} \qquad (10)$$

Oxidation of the phosphine hydrides to the corresponding dihalides by species containing halogen atoms occurs readily and was demonstrated using chlorotriphenyltin, N-bromosuccinimide, hydrobromic acid and 1-chloro-1,1,2-trifluoroethylene. In the last case, the dichloride is

formed, not the difluoride.

Oxidation in the presence of pseudohalides can also occur, as was discovered when an attempt was made to convert the phosphine bromide to the corresponding phosphine thiocyanate. Acetone solutions of potassium thiocyanate and the phosphine bromide were mixed and a white precipitate slowly formed while the solution took on a deeper green colour. From this solution, was isolated a green solid which is only sparingly soluble in tetrahydrofuran and is insoluble in benzene or petroleum ether. The substance is paramagnetic, as shown by the absence of any detectable n.m.r. signals from acetone solutions of it. The analysis (see Appendix) is consistent with formulation of the compound as $(\pi\text{-}C_5H_5)_2Nb(NCS)_2$ and its i.r. spectrum supports that formulation.

$$(\pi\text{-}C_5H_5)_2Nb(Br)PMe_2Ph + KSCN \longrightarrow (\pi\text{-}C_5H_5)_2Nb(NCS)_2 + KBr + PMe_2Ph + \text{other products} \qquad (11)$$

The spectrum consists of bands at 3080, 1005 and 825 cm^{-1}, characteristic of the π-cyclopentadienyl ligand (D6). There are also two extremely intense bands at 2068 and 2040 cm^{-1} due to C=N stretching vibrations of the isothiocyanate ligands (D22), as well as weak bands at 468 and 385 cm^{-1} which are probably due, respectively, to the N-C-S bending frequency (D23) and some unspecified vibration of the π-cyclopentadienyl ligand. There are no bands attributable to the phosphine ligand which the

analytical results suggest has been lost.

Although i.r. data alone cannot prove whether the SCN group is N-bonded or S-bonded to the metal, they can give strong indications as to the mode of bonding (D22). In the present case, the indications are that the ligand is N-bonded and such bonding would be in accord with the expected behaviour. X-ray studies have shown that metals of the first transition series and first half of the second and third series tend to form M-N bonds, whereas those of the latter half of the second and third series tend to form M-S bonds (D15, D23). It has been shown that isothiocyanates tend to give extremely intense doublets in the region 2084 to 2106 cm^{-1}, where an intense doublet is seen in the spectrum of the compound under discussion, whereas thiocyanates give relatively weak (for C=N frequencies) singlets in the region 2137 to 2156 cm^{-1} (D22). The C-S frequency which appears near 700 cm^{-1} in S-bonded compounds or 820 cm^{-1} in N-bonded ones (D15, D22, D23) is not seen in this spectrum. Although potentially diagnostic for the bonding mode of SCN, it is usually a weak absorption and often is not seen. The region around 820 cm^{-1}, where the band would be expected in the spectrum of $(\pi\text{-}C_5H_5)_2Nb(NCS)_2$, is obscured by the strong C-H out-of-plane bending vibration at 825 cm^{-1} of the π-cyclopentadienyl system. Thus, although this part of the spectrum does not offer positive evidence for N- or S-bonding, it is, at least, not

inconsistent with N-bonding.

The S-C-N bending vibration has also been used to distinguish between the two bonding modes of the SCN ligand (D23). This absorption tends to be in the region 450 to 490 cm^{-1} for N-bonded compounds (D15, D23, D24), where, in fact, an absorption is observed in the spectrum of $(\pi\text{-}C_5H_5)_2Nb(NCS)_2$. In S-bonded complexes, it tends to appear in the region 410 to 440 cm^{-1} (D15, D23, D24), where there are no absorptions in the spectrum under discussion. The possibility that this substance is a polymer with bridging thiocyanate ligands can be ruled out on the basis of i.r. evidence as well. Such bridging ligands absorb between 2182 and 2150 cm^{-1} (D15, D22), which is well outside the region in which absorptions are seen in the spectrum of the niobium compound. It would seem, therefore, that i.r. evidence suggests the product of reaction 11 is N-bonded $(\pi\text{-}C_5H_5)_2Nb(NCS)_2$.

7. <u>Reactions of $(\pi\text{-}C_5H_5)_2Nb(H)PR_3$; Nature of the Nb-H Bond</u>

In an attempt to ascertain whether the hydrogen attached to niobium in the phosphine hydrides is protonic or hydridic, the compounds were treated with N-bromosuccinimide, as discussed earlier, and with triphenylcarbenium hexafluorophosphate. In the former case, oxidation took place and in the latter no reaction (N.R.) was detected.

$$(\pi\text{-}C_5H_5)_2Nb(H)PR_3 + 2(CH_2CO)_2NBr \longrightarrow (\pi\text{-}C_5H_5)_2NbBr_2 + PR_3 + \text{organic products} \quad (12)$$

$$(\pi\text{-}C_5H_5)_2Nb(H)PR_3 + \left[Ph_3C\right]PF_6 \longrightarrow \text{N.R.} \qquad (13)$$

The hydrides were also treated with trimethylaluminium, as mentioned earlier, with trimethylsilylmethylmagnesium chloride and with butyllithium in various solvents at room temperature and no obvious changes in the reaction mixtures were observed.

Mixing the hydrides with phenol in benzene or tetrahydrofuran at room temperature causes no observable change but in the same solvents benzoic acid causes a rapid decomposition of the red hydrides to brown, unidentified oils, the i.r. and n.m.r. spectra of which suggest the absence of π-cyclopentadienyl and phosphine ligands.

Since these reactions failed to yield the desired information about the niobium-hydrogen bond, an attempt was made to react the hydrides with an unsymmetrical alkene. The possibility of observing either Markownikoff or anti-Markownikoff addition to the double bond should, in principle, yield information concerning the nature of the niobium-hydrogen bond. By analogy to such a reaction (D25) of π-cyclopentadienyliron dicarbonyl hydride, acrylonitrile and the phosphine hydrides were mixed in petroleum ether. This resulted in precipitation of a fluffy, yellow solid which was identified by analysis (see Appendix) and its i.r. and n.m.r. spectra as polyacrylonitrile. The n.m.r. spectrum of the substance was obtained in $\left[^2H_6\right]$dimethylsulphoxide and consists of two broad peaks in intensity ratio 1:2 centred

at 6.2 and 7.3τ, respectively. The i.r. spectrum is given in the Appendix.

Treatment of the phosphine hydrides with 1,3-butadiene in benzene at room temperature resulted in no change. Likewise, treatment with diethyl maleate at room temperature for a week, analogous to that of bis(π-cyclopentadienyl)-molybdenum dihydride (D26), also causes no change while refluxing ether solutions of the phosphine hydrides and diethyl maleate causes decomposition.

Since the niobium-hydrogen bond in the phosphine hydrides appears to be moderately inert, it was treated with some more reactive substances. Addition of carbon disulphide to benzene solutions of the hydrides causes immediate precipitation of a black unmanageable oil. In contrast, passage of a stream of carbon dioxide through petroleum ether solutions of the phosphine hydrides at room temperature causes no detectable reaction. Nitric Oxide passed through similar solutions precipitates an orange, insoluble, unidentified solid.

A final attempt to obtain an indication of the state of the niobium-hydrogen bond was made by treatment of petroleum ether solutions of the triphenylphosphine hydride with ethyl diazoacetate at 0°. It has been suggested (D27) that only acidic organometallic hydrides react with diazoalkanes and that they do so, either by loss of nitrogen followed by insertion of the carbene into the metal-hydrogen

bond, or by 1,3-dipolar addition of the metal-hydrogen system across the N-N-C system. No evolution of gas was observed when the niobium triphenylphosphine hydride was treated with ethyl diazoacetate. After an hour and a half, the solution, which was shown to contain all the phosphine ligand, was colourless and a yellow precipitate had formed which is photochemically, thermally and air unstable and was, therefore, not fully characterized. This highly reactive precipitate is sparingly soluble in ether, freely soluble in acetone, benzene or tetrahydrofuran and insoluble in petroleum ether. It reacts rapidly in the presence of dilute hydrochloric acid and slowly in the presence of water, with evolution of a gas, to give yellow solutions from which no precipitate is obtained upon addition of ammonium hexafluorophosphate or silicotungstic acid.

It is impossible to propose a structure for this compound based upon the available evidence, but it may be related to the molybdenum and tungsten complexes, $(\pi\text{-}C_5H_5)(CO)_2\overline{M:N\cdot NH\cdot C(CO_2Et)\cdot C}\cdot OH$, to which it bears a superficial resemblance as far as its spectroscopic properties and reactivity are concerned (D28).

C. Discussion

This chapter has described the preparation and properties of some tetra- and trivalent niobium compounds. Tetravalent organo-niobium species seem to be readily prepared, both by reduction of pentavalent substances and by oxidation of

trivalent ones and they appear to have considerable stability with respect to both thermal and oxidative decomposition.

Trivalent niobium compounds are relatively rare and those reported in this chapter, together with those recently described by Parshall (D30) represent most of the known examples. As a result of the preparation of these compounds, it is now clear that trivalent organo-niobium species, unlike their inorganic counterparts, are not only discrete molecular entities but also are thermally and hydrolytically stable enough to be isolated.

The indications of the results reported here and elsewhere (D2, D5, D30-D34) are that an extensive organic chemistry of niobium in formal oxidation states III, IV and V is yet to be discovered and that the chemistry of the lower states is likely to include some useful or interesting catalytic reactions. In this particular regard, the observations by Parshall concerning reduction of ethylene to ethane by hydrogen at room temperature and atmospheric pressure using $(\pi\text{-}C_5H_5)_2NbH_3$ as catalyst precursor (D30) are especially relevant, as are reports of activation of the carbon-hydrogen bond in benzene by a similar system (D35).

It would seem that the kinetic and thermal stability, often found in other bent bis(π-cyclopentadienyl)metal systems and now shown to exist here also, (for example, boiling in concentrated hydrochloric acid and bromine does not destroy these compounds) may prove particularly useful

during development of niobium chemistry.

In general, the chemistry of niobium, as anticipated, exhibits features which lie partway between those of titanium and molybdenum or tungsten. The features of niobium's behaviour which differ from those of earlier and later elements of the transition series are, in most cases, however, largely differences of degree rather than kind. This is well illustrated by comparison of the reactions between hydrogen chloride and $(\pi\text{-}C_5H_5)_2MoH_2$, $(\pi\text{-}C_5H_5)_2Nb(H)PR_3$ and $(\pi\text{-}C_5H_5)_2Ti(H)PR_3$, some of which have been discussed earlier (Figures IV and V).

The molybdenum compound protonates in acid solutions to give a relatively stable trihydride cation which can, however, be converted to the corresponding dihalide (Figure IV) by boiling the solution (D19). The niobium hydride undergoes the same reaction (Figure V) but the order of stability of the protonated species is much lower and it requires delicate manipulation of experimental conditions in order to stop the reaction at the protonation stage and isolate the highly reactive cationic intermediate. The compound $(\pi\text{-}C_5H_5)_2Ti(H)PR_3$ is so unstable that it has never been isolated and has only been detected in cold solutions by e.s.r. techniques (D36). Treatment of these solutions with hydrogen chloride, however, gives $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$, analogous to the products obtained from similar reactions of the niobium and molybdenum hydrides.

It should be noted, however, that in this particular case, the absence of a non-bonding electron pair in an orbital on the metal precludes protonation as the first step in the formation of the chloride. Thus, differences in this particular aspect of the three elements' chemistry seem to arise mainly from differences in the stability of the respective metal-hydrogen bonds or differences in the ability of the various hydrides to be protonated, since, in general, the same kind of reaction occurs in all cases.

A further example of the variation in a particular property of a compound as the metal is changed from molybdenum to niobium or titanium may be seen in the thermal stabilities of the hydrides, illustrated in Table III.

Table III

Trends in Thermal Stabilities of $(\pi\text{-}C_5H_5)_2M$ Hydrides		
Mo	Nb	Ti
$(\pi\text{-}C_5H_5)_2MoH_2$	$(\pi\text{-}C_5H_5)_2Nb(H)PR_3$	$(\pi\text{-}C_5H_5)_2Ti(H)PR_3$*
>170°d	>40°d	>-60°d
$[(\pi\text{-}C_5H_5)_2MoH_3]^+$	$[(\pi\text{-}C_5H_5)_2Nb(H)_2PR_3]^+$	-
>100°d	>-20°d	

* This species is not isoelectronic with other members of its series but it is the only known example of a terminal Ti-H bond in the $(\pi\text{-}C_5H_5)$ Ti system and is therefore included for comparison.

A general trend in thermal stabilities of hydrides of early transition metals may now be noted as a result of the work reported in this chapter and this trend draws attention to the highly unstable nature of substances containing a titanium-hydrogen bond and thereby accounts in some degree for the general lack of success encountered in attempted preparations of compounds containing such bonds.

Because of similarities between the chemistry of molybdenum, niobium and titanium, such as those just discussed, there is some justification for saying that trivalent niobium compounds might serve as models for investigating types of reactions to be expected from divalent titanium species.

D. References

D1 International Tables for X-Ray Crystallography, The Kynoch Press, Birmingham, England, 1962.

D2 F.W. Siegert and H.J. de Liefde Meijer, J. Organomet. Chem., 1970, 23, 177.

D3 C.S.G. Phillips and R.J.P. Williams, Inorganic Chemistry, Clarendon Press, Oxford, 1965.

D4 E.O. Fischer and A. Treiber, Chem. Ber., 1961, 94, 2193.

D5 W.E. Douglas and M.L.H. Green, J. Chem. Soc., Dalt. Trans., 1972, 1796.

D6 P.M. Druce, B.M. Kingston, M.F. Lappert, T.R. Spalding and R.C. Srivastava, J. Chem. Soc. (A), 1969, 2106.

D7 F. Fairbrother, The Chemistry of Niobium and Tantalum, Elsevier Publishing Company, London, 1967.

D8 R.B. King, Organometallic Syntheses, Vol. I, Academic Press, London, 1965

D9 C.H. Campbell, D. Phil. Thesis, Oxford, 1970.

D10 B.D. James and M.G.H. Wallbridge, Progr. Inorg. Chem., 1970, 11, 99.

D11 M.L.H. Green, H. Munakata and T. Saito, J. Chem. Soc. (A), 1971, 469.

D12 H. Noth and R. Hartwinner, Chem. Ber., 1960, 93, 2238.

D13 M. Grace, H. Beall and C.H. Bushweller, Chem. Comm., 1970, 701.

D14 B.D. James, R.K. Nanda and M.G.H. Wallbridge, Inorg. Chem., 1967, 6, 1979.

D15 K. Nakamoto, Infrared Spectra of Inorganic and Co-ordination Compounds, John Wiley and Sons, Inc., London, 1963.

D16 P.G. Douglas and B.L. Shaw, J. Chem. Soc. (A), 1970, 334.

D17 J.C. Green, M.L.H. Green and C.K. Prout, Chem. Comm., 1972, 421.

D18 M.C.R. Symons, private communication.

D19 M.L.H. Green, private communication.

D20 W.H. Baddley and L.M. Venanzi, Inorg. Chem., 1966,5, 33.

D21 W.H. Baddley, J. Amer. Chem. Soc., 1966, 88, 4545.

D22 L.J. Bellamy, Advances in Infrared Group Frequencies, Methuen and Co., Ltd., London, 1968.

D23 J.L. Burmeister, E.A. Deardorff, A. Jensen and V.H. Christiansen, Inorg. Chem., 1970, 9, 58.

D24 J.S. Thayer and R. West, Adv. Organomet. Chem., 1967, 5, 171.

D25 J.K.P. Ariyaratne and M.L.H. Green, J. Chem. Soc., 1963, 2976.

D26 B.R. Francis, M.L.H. Green and G.G. Roberts, Chem. Comm., 1971, 1290.

D27 M.F. Lappert and J.S. Poland, Adv. Organomet. Chem., 1970, 9, 424.

D28 M.L.H. Green and J.R. Sanders, J. Chem. Soc. (A), 1971, 1947.

D29 L.J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen and Co., Ltd., London, 1954.

D30 F.N. Tebbe and G.W. Parshall, J. Amer. Chem. Soc., 1971, 93, 3793.

D31 P.M. Treichel and G.P. Werber, J. Amer. Chem. Soc., 1968, 90, 1753.

D32 L.J. Guggenberger and F.N. Tebbe, J. Amer. Chem. Soc., 1971, 93, 5924.

D33 H.J. de Liefde Meijer and F. Jellinek, Inorg. Chim. Acta, 1970, 4, 651.

D34 F. Huq, N. Mowat, A.A. Skapski and G. Wilkinson, Chem. Comm., 1971, 1477.

D35 E.K. Barefield, G.W. Parshall and F.N. Tebbe, J. Amer. Chem. Soc., 1970, 92, 5234.

D36 J.E. Bercaw, R.H. Marvich, L.G. Bell and H.H. Brintzinger, J. Amer. Chem. Soc., 1972, 94, 1219.

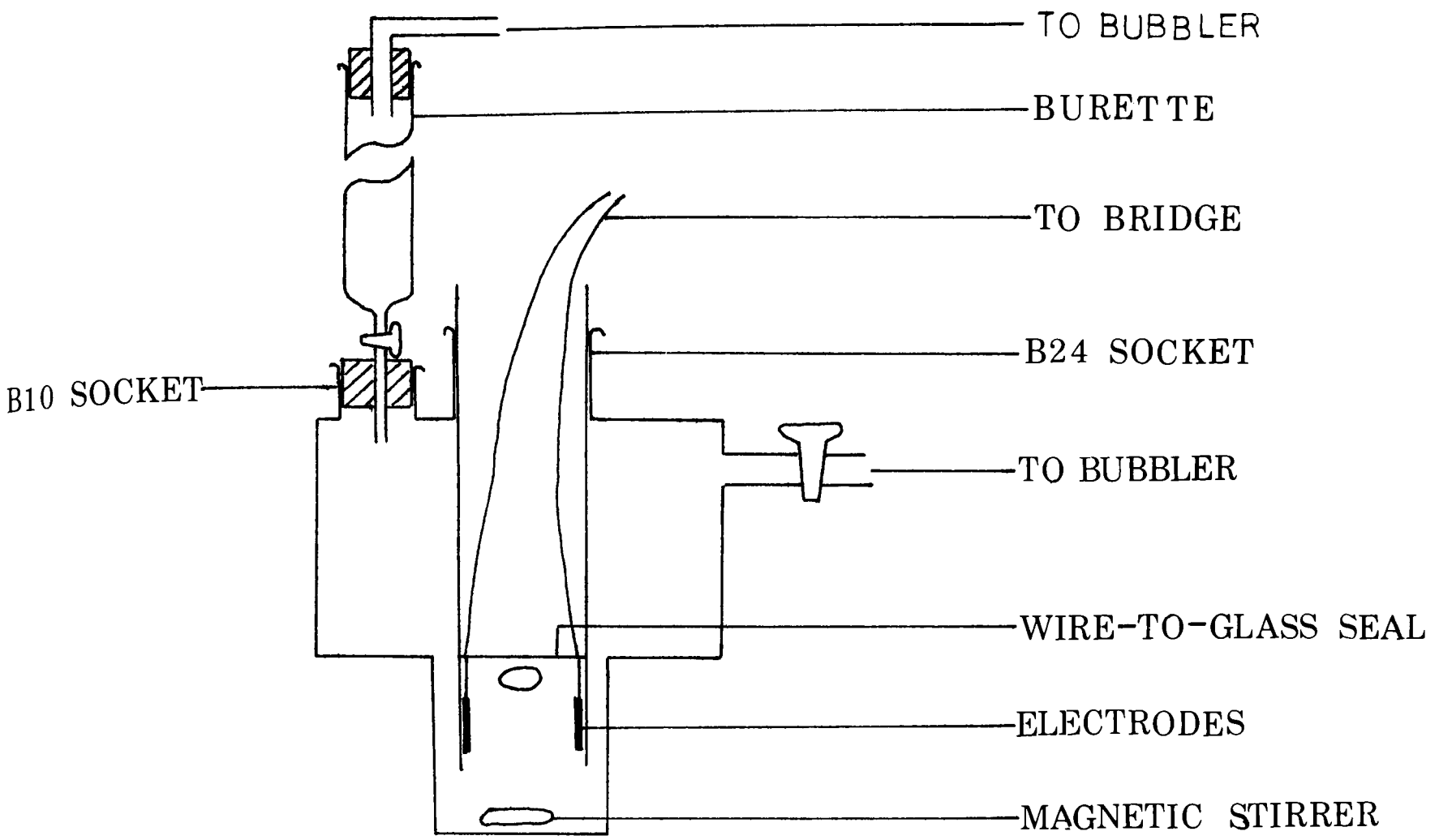
CHAPTER V

Experimental

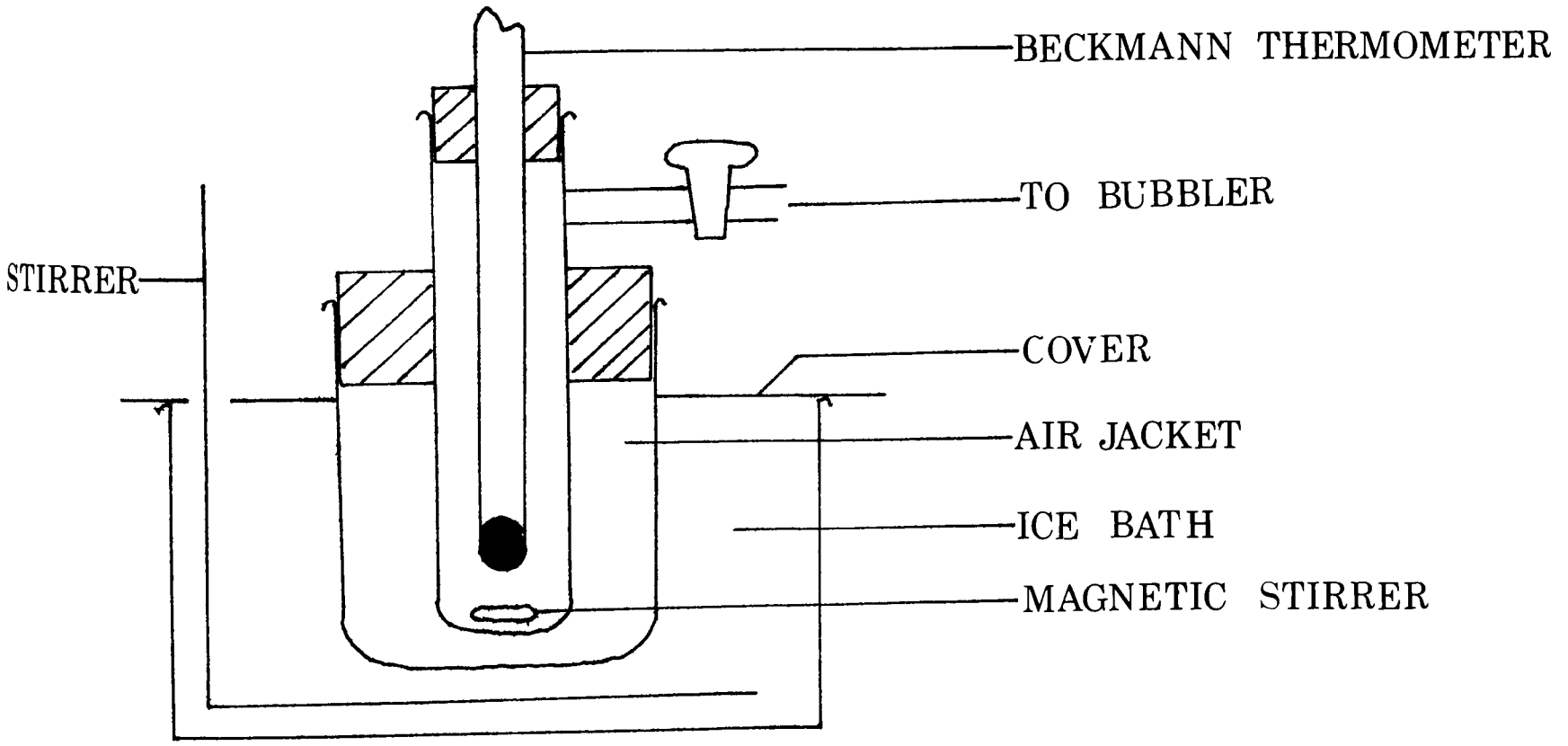
A. Introduction

1. Instrumentation

I.r. spectra of compounds discussed in this thesis are listed in the Appendix and were recorded as potassium bromide discs or mulls in either Nujol or hexachlorobutadiene using a Perkin-Elmer Model 457 spectrophotometer. Magnetic resonance spectra were recorded on a Japan Electron Optics Limited C60HL n.m.r. spectrometer operating at 60 MHz and a Japan Electron Optics Limited JES-3BX e.s.r. spectrometer operating at 9.4 GHz. The former were calibrated versus tetramethylsilane and the latter versus diphenylpicrylhydrazyl radical ($\langle g \rangle$ = 2.0036). Mass spectra were obtained using a Varian CH7 mass spectrometer. Conductivities were measured at ca. 20° using a Wayne-Kerr Laboratories Universal Bridge B221A and the cell shown in Figure I which was calibrated with standard potassium chloride solution. The data resulting from these measurements are given in the Appendix. Molecular weights were determined cryoscopically in benzene using the apparatus shown in Figure II and are also to be found listed in the Appendix. Determinations of carbon, hydrogen and nitrogen were carried out by the Inorganic Chemistry Laboratory Analytical Service while other elements were determined by Bernhardt Microanalytical Laboratories, Germany. Analytical results are listed in the Appendix.



I. A Conductance Cell for Air-Sensitive Solutions



II. Device for Measurement of Cryoscopic Molecular Weights of Air-Sensitive Compounds

2. Techniques

All procedures were carried out in vacuo or under an inert atmosphere and anhydrous conditions unless otherwise specified. The inert gases used at various times during these studies were argon or "white spot" nitrogen supplied by British Oxygen Co., Ltd., and "high purity" nitrogen supplied by Air Products Co., Ltd. The gases were led directly from the cylinders to the reaction vessels without further purification. For the preparation of even the most hydrolytically and oxidatively unstable substances described in this thesis, a vacuum/nitrogen line was used in conjunction with Schlenk tubes. Procedures, some of which have been previously described (E1, E2) were devised which eliminate the necessity of blowing large quantities of nitrogen through solutions of the compounds or over the solids. It was therefore possible, by keeping the volume of gas over the reactive substances small (<500 ml) and the quantity of solids relatively large in molar terms (>250 mg), to use commercially available inert gases without their further purification.

Solvents were dried by refluxing for several hours over calcium hydride, from which they were distilled immediately before use. Throughout this thesis, the words ether and petroleum ether are used, respectively, to describe diethyl ether and a mixture of aliphatic hydrocarbons having a boiling range of 30° to 40°. All temperatures are quoted in Centigrade degrees.

B. Details from Chapter II

All the liquid amines were distilled from potassium hydroxide pellets before use; ammonia and methylamine were passed through a column of freshly activated 3 Å molecular sieves. The alkyl- and arylphosphines were used as obtained from the various suppliers.

1. $[(\pi\text{-}C_5H_5)_2TiCl]_2$ from $(\pi\text{-}C_5H_5)_2TiBH_4$

Purple $(\pi\text{-}C_5H_5)_2TiBH_4$ (0.5 g, 2.6 mmol) and $(\pi\text{-}C_5H_5)_2TiCl_2$ (0.5 g, 2.0 mmol) were each dissolved in tetrahydrofuran (75 ml). The solutions were mixed and refluxed for four hours and evolution of a gas was noted. The solution was filtered and the solvent removed at 50° under reduced pressure. Excess $(\pi\text{-}C_5H_5)_2TiBH_4$ was sublimed from the product in vacuo at 70° and the residue was recrystallized from a 1:1 tetrahydrofuran-ether mixture giving dark green cubic crystals which were dried in vacuo at room temperature. Yield 86%.

2. $[(\pi\text{-}C_5H_5)_2TiCl]_2$ by Reduction of $(\pi\text{-}C_5H_5)_2TiCl_2$ with Zinc

Red $(\pi\text{-}C_5H_5)_2TiCl_2$ (16.6 g, 67 mmol) was stirred in tetrahydrofuran (400 ml) with zinc dust (2.3 g, 35 g-atom) for four hours at room temperature. The mixture was filtered and the green solution concentrated to 125 ml by distillation of the solvent in vacuo at 80°. Ether (125 ml) was added and the solution allowed to stand overnight. Filtration removed dark green cubic crystals which were dried in vacuo at room temperature. Yield 40%.

3. $(\pi\text{-}C_5H_5)_2TiCl\cdot NH_2R$, (R = H, Me, Et, Allyl, Ph)

Green $[(\pi\text{-}C_5H_5)_2TiCl]_2$ was either dissolved in benzene and excess (ca. 10%) ligand added or it was treated with the ligand in the absence of solvent. The solutions were stirred for two hours at room temperature and then the solvent and other volatile substances were evaporated in vacuo at 50°. The residues were dissolved at room temperature in a minimum of tetrahydrofuran, the solutions filtered and ether added until precipitation began. After standing for several hours, green crystals were separated and dried in vacuo at room temperature. Yields ca. 80%.

4. $(\pi\text{-}C_5H_5)_2TiCl\cdot L$, (L = py, PMe_2Ph, $PMePh_2$)

Green $[(\pi\text{-}C_5H_5)_2TiCl]_2$ was either dissolved in benzene and excess (ca. 10%) ligand added or it was treated with the ligand in the absence of solvent. The solutions were stirred overnight and all the volatile substances were removed in vacuo at 50°. The residues were washed several times with petroleum ether and then dissolved in a minimum amount of tetrahydrofuran at room temperature. An equal volume of ether was then added to precipitate crystals which were separated and dried in vacuo at room temperature. Yields ca. 90%.

5. $[(\pi\text{-}C_5H_5)_2Ti\cdot L'_2]X$, ($L'_2$ = en, Me en; X = Cl, PF_6)

Green $[(\pi\text{-}C_5H_5)_2TiCl]_2$ was dissolved in benzene and a 10% excess of ligand added. The solution was stirred for half an hour at room temperature when the colourless supernatant liquid was removed. The residue was washed with petroleum

ether and dried *in vacuo* at room temperature. Yields 96%.

The solid was dissolved in water and aqueous ammonium hexafluorophosphate quickly added, giving a blue precipitate. This was washed with water, dried, dissolved in acetone and filtered. Ether was added until blue crystals formed which were removed and dried *in vacuo* at room temperature. Yields 70%.

6. $\underline{\left[(\pi\text{-}C_5H_5)_2Ti\cdot dipy\right]X,\ (X = Cl,\ PF_6)}$

The method was the same as for $\left[(\pi\text{-}C_5H_5)_2Ti\cdot L_2'\right]X$ except that the reaction solvent was tetrahydrofuran. Yield 98%.

7. $\underline{\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2\ diphos}$

Green $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ (0.800 g, 1.88 mmol) and diphos (1.51g, 3.84 mmol) were each dissolved in benzene (100 ml) and the solutions mixed. After half an hour of stirring at room temperature the colourless supernatant liquid was removed. The precipitate was dissolved in tetrahydrofuran at room temperature, an equal volume of ether added and the solution chilled in an ice-bath overnight. Green crystals were obtained which were separated and dried *in vacuo* at room temperature. Yield 95%.

8. $\underline{(\pi\text{-}C_5H_5)TiCl_3}$

Red $(\pi\text{-}C_5H_5)_2TiCl_2$ (12.5 g, 50 mmol) and titanium tetrachloride (11.2 ml, 100 mmol) were placed in a glass tube and sealed *in vacuo*. The tube was heated to 120° for sixty hours After cooling to room temperature, the tube was opened and the orange-brown contents were removed and washed three times with petroleum ether (50 ml) and the

washings discarded. The solid was dissolved in benzene, filtered and the solvent removed *in vacuo* at 80°. The residue was sublimed *in vacuo* at 150° into a large-bore air-cooled glass tube to give large orange crystals. Yield 80%.

9. $[(\pi\text{-}C_5H_5)TiCl_2]_n$

Orange $(\pi\text{-}C_5H_5)TiCl_3$ (6.00 g, 2.75 mmol) and zinc dust (1.00 g, 1.52 g-atom) were suspended in tetrahydrofuran (350 ml) at room temperature and stirred for three hours. The green solution was filtered to remove unreacted zinc and its volume was reduced *in vacuo* on a hot water bath to 80 ml. Upon cooling, crystals of $(\pi\text{-}C_5H_5)TiCl_2 \cdot 2THF$ formed. Heating the crystals at 100° *in vacuo* for two hours causes loss of terahydrofuran accompanied by a colour change from blue-green to purple. Yield 70%.

10. $(\pi\text{-}C_5H_5)TiCl_2 \cdot 2L$, (L = PMe_2Ph, $PMePh_2$)

Purple $[(\pi\text{-}C_5H_5)TiCl_2]_n$ was washed with toluene to remove oxidized material until the washings were colourless. It was then suspended in toluene and stoicheiometric amounts of the ligands added. After stirring at room temperature overnight, volatile substances were removed *in vacuo* at 50°. The residue was washed several times with petroleum ether and was recrystallized from ether. Yield 85%.

11. $(\pi\text{-}C_5H_5)TiCl_2 \cdot$ diphos

Purple $[(\pi\text{-}C_5H_5)TiCl_2]_n$ (0.380 g, 2.06 mmol) was washed with toluene until the washings were colourless. It was then dissolved in tetrahydrofuran (60 ml) to which was added a solution of 1,2-bis(diphenylphosphino)ethane (0.830 g,

2.21 mmol) in tetrahydrofuran (50 ml). The mixture was stirred at room temperature for two hours before the solvent was removed *in vacuo* at 35°. A saturated toluene solution of the residue was prepared at room temperature and crystals were grown in this solution by slowly distilling half the solvent *in vacuo* at 35°. Yield 60%.

12. $(\pi\text{-}C_5H_5)TiCl_2 \cdot DMPE$

Purple $\left[(\pi\text{-}C_5H_5)TiCl_2\right]_n$ (0.40 g, 1.08 mmol) was washed with ether to remove oxidation products until the washings were colourless. It was then dissolved in tetrahydrofuran (50 ml) and 1,2-bis(dimethylphosphino)ethane was added and the solution left standing at room temperature overnight. Concentration of the solution *in vacuo* caused formation of green crystals. Yield 93%.

13. Dithizone Test for Zinc

Diphenylthiocarbazone was dissolved in acetone. A piece of filter paper was soaked in this solution and then dried. A sample of the substance to be tested was digested in boiling concentrated aqueous sodium hydroxide until all the titanium was precipitated as its dioxide. On the prepared filter paper was placed a drop of the supernatant liquid. If the $\left[Zn(OH)_4\right]^{2-}$ ion was present a purple colour was observed but in its absence only an orange colour was obtained.

C. Details from Chapter III

1. $(\pi\text{-}C_5H_5)_2Ti(CH_2SiMe_3)_2$

Green $\left[(\pi\text{-}C_5H_5)_2TiCl\right]_2$ (1.68 g, 7.9 mmol) was suspended

in ether (100 ml) at -40° and trimethylsilylmethylmagnesium chloride (7.9 mmol) in ether (19.8 ml) was slowly added. After stirring for three hours, the solvent was removed *in vacuo* at 0°. The residue was extracted with petroleum ether at 0° and the extract chilled to -78° to obtain yellow crystals which were separated and dried *in vacuo* at 0°. Yield 48%.

The reaction was repeated in toluene at -80° with a 0.5M petroleum ether solution of trimethylsilylmethyllithium. The mixture was stirred for two hours and then was allowed to warm to room temperature and the solvent was removed *in vacuo*. The product was isolated from the residue in the same manner as previously described. Yield 37%.

2. $(\pi\text{-}C_5H_5)Ti(CH_2SiMe_3)_3$

Purple $[(\pi\text{-}C_5H_5)TiCl_2]_n$ (1.30 g, 7.1 mmol) was washed with ether to remove oxidation products until the washings were colourless. It was then suspended in ether (100 ml) at -35°, and trimethylsilylmethylmagnesium chloride (14.2 mmol) in ether (35.4 ml) was slowly added. After stirring for three hours, the ether was removed *in vacuo* at -35°.The residue was extracted with petroleum ether at -35° and the extract chilled to -78° to obtain yellow crystals. These were separated and dried *in vacuo* at 0°. Yield 45%.

The reaction was repeated in petroleum ether at -35° with a 0.5M petroleum ether solution of trimethylsilylmethyllithium. The mixture was stirred for three hours, the solvent removed

and the product isolated from the residue as described above. Yield 43%.

3. $(\pi\text{-}C_5H_5)TiMe_3$

Purple $[(\pi\text{-}C_5H_5)TiCl_2]_n$ (2.95 g, 16 mmol) was washed with ether until the washings were colourless and then suspended in ether (150 ml) at room temperature. Methylmagnesium bromide (32 mmol) in ether (16 ml) was slowly added, causing evolution of a gas and formation of a black precipitate. Some of the evolved gas was led into an i.r. gas sample cell and its spectrum subsequently obtained. After stirring for two hours, the ether was removed *in vacuo* at room temperature. The residue was extracted with petroleum ether at room temperature and the extract chilled to -78° to obtain yellow crystals. These were separated and dried *in vacuo* at 0°. Yield 47%.

The reaction was repeated in ether at room temperature with a 1.3M solution of methyllithium in ether. The mixture was stirred for two hours and then the solvent was removed. The product was isolated from the residue in the manner previously described. Yield 44%.

4. A Nitrogen Fixing System

Green $[(\pi\text{-}C_5H_5)_2TiCl]_2$ (0.253 g, 0.592 mmol) was suspended in ether (25 ml) at 0°. Methylmagnesium bromide or methyllithium (1.18 mmol) in ether was added and the suspension stirred for five minutes. After warming to room temperature, the suspension was stirred for another

five minutes and then allowed to settle. The yellow solution was decanted and chilled under an atmosphere of nitrogen to about -50° when a deep blue colour developed. The solution turned yellow when it was warmed to about 0°.

The nitrogen atmosphere over the solution was replaced by argon which was also bubbled through the solution for two minutes. The solution was then chilled to -100° but no colour change occurred. Nitrogen gas was then bubbled through the yellow solution which immediately turned dark blue as before. The system was degassed by freezing the solution, evacuating the vessel and then thawing the solution. During each of these freeze-pump-thaw cycles the blue colour of the cold solutions became paler, until, after three cycles, the solution was yellow even at its freezing point. Admission of nitrogen to this solution turned it immediately blue while argon similarly admitted had no effect.

5. Reactions of the Black Residue

The black residue (1.00 g) formed in the reaction of $[(\pi\text{-}C_5H_5)TiCl_2]_n$ with methylmagnesium bromide (Part B3 of this chapter) and which remains after $(\pi\text{-}C_5H_5)TiMe_3$ has been separated from the crude product, was extracted with toluene (30 ml) and the extract filtered. Addition of an equal volume of petroleum ether to the extract and chilling of the resulting solution to -78° gave a black powder.

A sample of the black powder was treated with concentrated hydrochloric acid which caused violent effervescence and

the development of a yellow colour in the suspension. The vessel in which this reaction was carried out was connected to an i.r. gas sample cell which was filled to a pressure of ca. 300 mm of mercury with the gaseous reaction products. The spectrum of this sample was then recorded. Ether was added to the yellow suspension after gas evolution was complete and the yellow colour was extracted into the organic layer which was then separated from the aqueous one. The ether was removed *in vacuo* at 50° and the yellow residue sublimed *in vacuo* at 110° to give a dark yellow sublimate of $(\pi\text{-}C_5H_5)TiCl_3$ which was identified from its i.r. spectrum.

A sample of the black powder was suspended in ether at room temperature and hydrogen chloride was bubbled through the suspension. This caused the gradual formation of a white precipitate and a yellow colour in the solution. The solution was filtered and the yellow substance was isolated and shown to be $(\pi\text{-}C_5H_5)TiCl_3$ as previously described. The white precipitate was washed several times with ether and dried *in vacuo* at room temperature. It was identified as a magnesium halide by the following tests. It dissolves in water. Addition of aqueous silver nitrate to a solution of the white solid gives a white precipitate which dissolves in aqueous ammonia, confirming the presence of halide in the white solid. Addition of aqueous ammonia to a solution of the white solid causes formation of a gelatinous precipitate which redissolves upon addition of ammonium chloride

solution thus suggesting the presence of magnesium in the white solid. Addition of monobasic sodium phosphate to this solution causes formation of a white crystalline precipitate which is soluble in concentrated hydrochloric acid, thus confirming the presence of magnesium in the white solid.

A sample of the black powder, covered by a plug of glass wool, was sealed in vacuo in one arm of a U-shaped tube. This arm was heated in an oil bath or a gas flame while the other was chilled in liquid nitrogen. In this way, pyrolysis products were collected. They were identified from their i.r. spectra as discussed in Chapter III.

6. Tris(cyclopentadienyl)titanium

Green $[(\pi\text{-}C_5H_5)_2TiCl]_2$ (5.0 g, 11.7 mmol) was dissolved in toluene (125 ml) and the solution chilled to -78°. A concentrated solution of sodium cyclopentadienide (1.1 g, 12.5 mmol) in tetrahydrofuran (15 ml) was added and the mixture stirred for fifteen minutes at -78°. It was then warmed to room temperature and stirred for one hour. The red solution was filtered and concentrated in vacuo at 50° to 50 ml. An equal volume of petroleum ether was added and the solution chilled to -78° overnight to obtain green needle-like crystals. Yield 60%.

Crystals of tris(cyclopentadienyl)titanium suitable for examination by X-ray techniques were grown by placing a sample of recrystallized material in a copper-jacketed glass tube

about 0.5 meters long. The sample was maintained in vacuo and the lower tip of the copper jacket was heated to 110°, thus providing a gentle thermal gradient along the glass tube. Overnight, suitable crystals grew at a point about 3 centimeters above the hot end of the tube.

7. $(\pi\text{-}C_5H_5)_2TiCl_2$ from $FeCl_3$ and Tris(cyclopentadienyl)titanium

To tris(cyclopentadienyl)titanium (0.522 g, 2.15 mmol) in ether (100 ml) was added a solution of ferric chloride (0.348 g, 2.15 mmol) also in ether (50 ml). An immediate colour change to red occurred and a precipitate was formed. The solvent was removed in vacuo on a warm water bath and the residue was sublimed in vacuo at 100°. An orange sublimate (0.185 g) was obtained which was shown by its i.r. spectrum to be ferrocene. The residue from the sublimation was washed repeatedly with small amounts of ether (10 ml) until the washings were colourless. The ether was removed from the washings and the red residue was shown by its i.r. spectrum to be bis(π-cyclopentadienyl)titanium dichloride. The off-white residue which remains after removal of the red titanium compound was dissolved in water to give a pale green solution. A precipitate of the same colour is obtained upon addition of aqueous ammonia but this turns red-brown upon standing in air, thus indicating the presence of ferrous iron in the off-white residue. Yield 93%.

8. $(\pi\text{-}C_5H_5)_2TiF_2$ from Tris(cyclopentadienyl)titanium

To a green solution of tris(cyclopentadienyl)titanium

(0.537 g, 2.21 mmol) in benzene (40 ml) was added at room temperature a solution of silver hexafluorophosphate (0.559 g, 2.21 mmol) in benzene (50 ml). Instant formation of a black precipitate and a yellow solution occurred and the mixture was stirred for one hour. After settling, the precipitate was separated and the supernatant liquid discarded. The precipitate was extracted with acetone (50 ml) at room temperature, the extract concentrated in vacuo at room temperature to 10 ml and yellow platelets obtained by chilling the concentrate to -78°. Further extractions of the precipitate gave more of the yellow difluoride. It was recrystallized from benzene to obtain samples for elemental and spectroscopic analysis. Yield 70%.

A reaction between silver tetrafluoroborate and tris(cyclopentadienyl)titanium was carried out in the same way and bis(π-cyclopentadienyl)titanium difluoride was isolated in 75% yield.

D. Details from Chapter IV

1. $(\pi\text{-}C_5H_5)_2NbCl_2$

A solution of sodium cyclopentadienide in tetrahydrofuran was prepared from sodium sand and cyclopentadiene according to a published method (E2). The solvent was removed from this solution and the residue was heated in vacuo to 100° for seventy-two hours in order to remove all the tetrahydrofuran from the residue.

Dry sodium cyclopentadienide (100 g, 1.14 mol) was

suspended in benzene (400 ml) at room temperature. With vigorous mechanical stirring, niobium pentachloride (57 g, 0.21 mol) was added in small portions, care being taken to prevent the reaction temperature from exceeding ca. 70° after each addition. After about one hour, the suspension had returned to room temperature and was a uniform purple-brown colour. It was stirred for another half hour and then poured in air onto concentrated hydrochloric acid (1 l). The resulting mixture was heated with occasional swirling until all the benzene had been evaporated. To the boiling brown suspension were then added small quantities of bromine (ca. 60 ml in all) until the solid phase had been pulverized and no longer behaved as a solid sticky lump. When all the excess bromine had been boiled away, the hot mixture was filtered and the residue then extracted repeatedly with hot concentrated hydrochloric acid and bromine, making sure each time that all the bromine had been removed from the extracts before they were filtered. After about nine extractions the collected filtrates were brought to the boiling point and placed under an inert atmosphere. To the hot, red solution was added a hot solution of stannous chloride dihydrate (47.5 g, 0.21 mol) in concentrated hydrochloric acid (200 ml). The solution was left standing overnight and was then filtered to remove brown tabular crystals of bis(π-cyclopentadienyl)niobium dichloride. The product was washed with water to remove excess stannous

chloride and once with a small amount (50 ml) of acetone before being dried *in vacuo* at room temperature. Yield 75%.

2. $(\pi\text{-}C_5H_5)_2NbBH_4$

A mixture of bis(π-cyclopentadienyl)niobium dichloride (12.0 g, 40.8 mmol) and sodium borohydride (4.60 g, 121 mmol) was suspended in 1,2-dimethoxyethane (250 ml) at room temperature. Vigorous effervescence occurred; the solution turned dark green and the brown crystals disappeared. After one and a half hours, the mixture was filtered and the residue washed with 1,2-dimethoxyethane (60 ml). The solvent was removed *in vacuo* on a hot water bath from the combined filtrates and the resulting residue was extracted with benzene at room temperature until the extracts were only a pale green colour. The collected extracts were filtered and the solvent removed *in vacuo* on a hot water bath to give green tabular crystals of $(\pi\text{-}C_5H_5)_2NbBH_4$. The substance was recrystallized from a mixed toluene-petroleum ether solvent at -78°. Yield 85%.

3. $(\pi\text{-}C_5H_5)_2Nb(H)PMe_2Ph$

To a green solution of $(\pi\text{-}C_5H_5)_2NbBH_4$ (1.07 g, 4.54 mmol) in benzene (50 ml) at room temperature was added dimethylphenylphosphine (1.28 ml, 9.08 mmol) which caused an immediate colour change to dark red. The solution was stirred for fifteen minutes and the solvent removed *in vacuo* at room temperature. The residue was dissolved in ether (50 ml) and the solution chilled to -50°. Hydrogen chloride

was passed through the solution causing formation of a white precipitate and the disappearance of the red colour. The supernatant liquid was discarded and the white precipitate washed twice with ether (25 ml) and then vigorously stirred at room temperature with 3N aqueous sodium hydroxide solution (50 ml) and ether (50 ml). The white precipitate changed to a red one and slowly dissolved in the ether layer which was then separated from the aqueous phase. The ether was removed in vacuo at room temperature and the residue recrystallized from petroleum ether at -78°. Yield 70%.

4. $(\pi\text{-}C_5H_5)_2Nb(H)PPh_3$

To a green solution of $(\pi\text{-}C_5H_5)_2NbBH_4$ (1.10 g, 4.62 mmol) in benzene (50 ml) at room temperature was added a solution of triphenylphosphine (2.42 g, 9.24 mmol) in benzene (30 ml). The mixed solutions rapidly turned red and after stirring for fifteen minutes, the solvent was removed in vacuo at 50°. Working as fast as possible since the crude product seemed to react with ether, the residue was extracted twice at room temperature with ether (50 ml), the extracts filtered and the solvent removed from the combined filtrates in vacuo at room temperature. The residue from this operation was extracted with benzene (50 ml), the extract filtered and the solvent removed from the filtrate in vacuo at 50°. The red solid was then recrystallized from petroleum ether at -78°. Yield 85%.

5. $\underline{[(\pi\text{-}C_5H_5)_2Nb(H)_2PMe_2Ph]A,\ (A = PF_6 \text{ or } BF_4)}$

To a red solution of $(\pi\text{-}C_5H_5)_2Nb(H)PMe_2Ph$ (0.522 g, 1.44 mmol) in ether (30 ml) at -78° was added five drops of 60% aqueous tetrafluoroboric or hexafluorophosphoric acid. After standing one hour, the solution was colourless and a white precipitate had formed. The solution was separated and discarded while the white precipitate of $[(\pi\text{-}C_5H_5)_2Nb(H)_2PMe_2Ph]A$ was dried *in vacuo* at -20°. Yield 100%.

6. <u>A Reaction Between Tetracyanoethylene and $(\pi\text{-}C_5H_5)_2Nb(H)PPh_3$</u>

Tetracyanoethylene (0.579 g, 4.52 mmol), sublimed *in vacuo* at 80° immediately before use, was dissolved in benzene (50 ml) and added at room temperature to a red solution of $(\pi\text{-}C_5H_5)_2Nb(H)PPh_3$ (1.10 g, 2.26 mmol) in benzene (50 ml). Within a few seconds of mixing, a dark green precipitate formed and after stirring the suspension for an hour, the pink solution was separated from the precipitate. The filtrate was concentrated *in vacuo* at 80° and crystals of triphenylphosphine (0.600 g, 2.29 mmol) were obtained upon cooling the concentrate to room temperature. The green precipitate was washed twice with benzene (50 ml) and dried *in vacuo* at 60°. The weight of the product was 0.815 g which represents a 96% yield if the product is $(\pi\text{-}C_5H_5)_2Nb(CN)TCNE$ as discussed earlier.

7. <u>$(\pi\text{-}C_5H_5)_2Nb(Br)PMe_2Ph$</u>

To a red solution of $(\pi\text{-}C_5H_5)_2Nb(H)PMe_2Ph$ (0.247 g,

0.682 mmol) in petroleum ether (125 ml) was added 1-bromobutane (0.2 ml, 1.13 mmol) and the solution stirred briefly. After standing overnight, green needle-like crystals of $(\pi\text{-}C_5H_5)_2Nb(Br)PMe_2Ph$ had formed and the solution was colourless. The supernatant liquid was decanted and discarded and the precipitate was recrystallized at room temperature by addition of ether to a solution of it in tetrahydrofuran. The green crystals were dried in vacuo at room temperature. Yield 90%.

8. $(\pi\text{-}C_5H_5)_2NbBr_2$ from $(\pi\text{-}C_5H_5)_2Nb(H)PPh_3$

To a red solution of $(\pi\text{-}C_5H_5)_2Nb(H)PPh_3$ (0.522 g, 1.07 mmol) in petroleum ether (125 ml) was added 1-brombutane (0.45 ml, 4.24 mmol) and the solution stirred briefly. After standing overnight, the solution was almost colourless and a green-brown precipitate had formed. The solution was filtered and the filtrate taken to dryness in vacuo at 80° to obtain crystals of triphenylphosphine (0.262 g, 1.00 mmol). The green-brown precipitate was washed once with tetrahydrofuran (5 ml) and dried in vacuo at room temperature. Yield 70%.

9. A Reaction Between Ethyl Diazoacetate and $(\pi\text{-}C_5H_5)_2Nb(H)PPh_3$

To a red solution of $(\pi\text{-}C_5H_5)_2Nb(H)PPh_3$ (1.531 g, 3.15 mmol) in ether (125 ml) at 0° in a flask wrapped with aluminium foil to exclude light was added ethyl diazoacetate (0.34 ml, 3.22 mmol). The solution was stirred briefly and let stand for one and a half hours at 0°. It was then

filtered to separate the yellow precipitate from the almost colourless supernatant liquid and the filtrate was taken to dryness *in vacuo* at 70° to yield a residue of triphenylphosphine (0.844 g, 3.22 mmol).

The yellow precipitate was examined, as discussed in Chapter IV, after drying *in vacuo* at 0°. The dry solid was stored in the dark at -20°.

10. $(\pi\text{-}C_5H_5)_2Nb(NCS)_2$

To a green solution of $(\pi\text{-}C_5H_5)_2Nb(Br)PMe_2Ph$ (1.602 g, 3.62 mmol) in acetone (100 ml) was added potassium thiocyanate (0.352 g, 3.62 mmol) in acetone (70 ml). The resulting solution was stirred briefly and then let stand for three hours at room temperature. During this time, the colour darkened to a more intense green and a white precipitate formed. The solution was filtered and the filtrate taken to dryness *in vacuo* at 60°. The sticky residue was washed twice with tetrahydrofuran (40 ml) and dried *in vacuo* at room temperature. Yield 38%

E. References

E1 M. Ishaq, D. Phil. Thesis, Oxford, 1967.

E2 R.B. King, Organometallic Syntheses, Vol. I, Academic Press, London, 1965.

APPENDIX

A. Analytical Data, Colour and Decomposition Points

Compound[a]	Colour	mp*	Analytical Data, % Found(Calc)				
			C	H	N or P	M	Cl
$(Cp_2TiCl)_2$ (B1)[b]	green	-	56.02(56.24)	4.58(4.72)	-	-	-
$(Cp_2TiCl)_2$ (B2)	green	-	55.97(56.24)	4.47(4.72)	-	-	-
$Cp_2TiCl\cdot NH_3$	green	191d	51.64(52.09)	6.01(5.68)	6.02(6.08)	-	-
$Cp_2TiCl\cdot NH_2Me$	green	154d	53.32(54.01)	6.11(6.18)	5.51(5.73)	-	-
$Cp_2TiCl\cdot NH_2Et$	green	155d	55.38(55.73)	6.65(6.63)	5.37(5.42)	18.67(18.52)	13.80(13.71)
$Cp_2TiCl\cdot NH_2C_3H_5$	green	154d	57.10(57.69)	6.32(6.33)	5.07(5.18)	-	-
$Cp_2TiCl\cdot NH_2Ph$	green	168d	60.90(62.67)	5.47(5.59)	4.23(4.57)	16.25(15.62)	-
$Cp_2TiCl\cdot py$	brown	148d	61.05(61.57)	5.22(5.17)	4.39(4.79)	-	12.42(12.11)
$Cp_2TiCl\cdot PPhMe_2$	green	130d	61.06(61.30)	5.93(6.00)	-	-	-
$Cp_2TiCl\cdot PPh_2Me$	green	135d	66.01(66.77)	5.49(5.60)	7.72(7.48)	11.94(11.58)	8.68(8.57)
$(Cp_2TiCl)_2\cdot$diphos	green	222d	66.36(66.93)	5.24(5.37)	-	-	-
$(Cp_2Ti\cdot en)Cl$	blue	265d	51.73(52.67)	7.23(6.63)	10.16(10.24)	-	-
$(Cp_2Ti\cdot en)PF_6$	blue	197d	37.35(37.61)	4.89(4.73)	7.00(7.31)	-	-

Compound	Colour	mp	Analytical Data, % Found(Calc)				
			C	H	N or P	M	Cl
$(Cp_2Ti\cdot Me_2en)PF_6$	blue	176d	40.43(40.90)	5.42(5.39)	6.47(6.81)	-	-
$(Cp_2Ti\cdot dipy)PF_6$	purple	262d	49.51(50.12)	4.12(3.79)	5.81(5.85)	-	-
$(CpTiCl_2)_n$	purple	300	32.58(32.66)	2.87(2.78)	-	26.32(26.05)	-
$CpTiCl_2\cdot 2PPhMe_2$	green	134d	54.61(54.80)	6.05(5.92)	13.65(13.46)	10.77(10.41)	15.84(15.41)
$CpTiCl_2\cdot 2PPh_2Me$	green	125d	63.27(63.72)	5.40(5.35)	-	-	-
$CpTiCl_2\cdot$ diphos	green	143d	63.77(63.94)	4.93(5.04)	10.58(10.64)	-	-
$CpTiCl_2\cdot$ DMPE	green	209d	39.66(39.55)	6.76(6.34)	18.36(18.55)	14.11(14.34)	21.13(21.23)
$CpTi(CH_2SiMe_3)_3$	yellow	60s	54.41(54.50)	10.34(10.22)	-	-	-
$CpTiMe_3$	yellow	20s	60.51(60.78)	9.47(8.92)	-	-	-
$Cp_2Ti(CH_2SiMe_3)_2$	yellow	100s	61.17(61.33)	9.04(9.15)	-	-	-
Cp_3Ti	green	120s	73.87(74.09)	6.50(6.22)	-	-	-
Cp_2TiF_2	yellow	230s	55.14(55.58)	4.66(4.66)	-	-	-
Cp_2NbCl_2	brown	-	40.79(40.85)	3.50(3.43)	-	-	-
$Cp_2Nb(H)PMe_2Ph$	red	94d	58.80(59.68)	6.09(6.12)	-	-	-
$Cp_2Nb(H)PPh_3$	red	144d	69.13(69.14)	5.56(5.39)	-	-	-

Compound	Colour	mp	Analytical Data, % Found(Calc)				
			C	H	N or P	M	Cl
$[Cp_2Nb(H)_2PMe_2Ph]BF_4$	white	20d	47.58(48.04)	4.92(5.15)	-	-	-
$Cp_2Nb(CN)TCNE$	green	260d	54.61(54.13)	3.09(2.67)	17.23(18.56)	25.07(24.63)	-
$Cp_2Nb(Br)PMe_2Ph$	green	185d	49.90(49.01)	4.93(4.80)	-	-	-
Cp_2NbBr_2	brown	-	31.28(31.37)	2.50(2.63)	-	-	-
polyacrylonitrile product of ethyl diazoacetate	yellow	-	68.25(67.89)	5.35(5.70)	27.00(26.40)	-	-
and $Cp_2Nb(H)PPh_3$	yellow	20d	40.50	4.75	5.90	-	-
$Cp_2Nb(NCS)_2$	green	-	42.03(42.47)	3.00(2.97)	7.93(8.26)	-	-

* m.p. in °C. were carried out in capillaries sealed under vacuum and are uncorrected.

d = decomposes

s = sublimes

a. Cp = π-cyclopentadienyl, $(\pi\text{-}C_5H_5)$

b. prepared by method described in these sections of Chapter V.

B. Conductance Measurements

Cell constant = 1.38

$[(\pi\text{-}C_5H_5)_2Ti\cdot Me_2en]PF_6$ in acetone at 21.0°					
Vol(ml)	Cond($\mu\upsilon$)	Sp Cond(υcm^{-1})	Conc(M)	$\sqrt{c}$	$\Lambda_m(\upsilon cm^2 eq^{-1})$
10.00	516.8	713.2×10^{-6}	6.181×10^{-3}	7.862×10^{-2}	115.4
20.00	282.6	390.0×10^{-6}	3.094×10^{-3}	5.564×10^{-2}	126.2
30.00	197.4	272.4×10^{-6}	2.063×10^{-3}	4.541×10^{-2}	132.2
40.00	153.0	211.1×10^{-6}	1.555×10^{-3}	3.941×10^{-2}	136.2
50.00	124.9	172.4×10^{-6}	1.244×10^{-3}	3.521×10^{-2}	139.0

Λ_o = 157.9 Slope of Λ_m versus $\sqrt{c}$ = 546

Calculated Onsager slope for a 1:1 electrolyte = 598

$[(\pi\text{-}C_5H_5)_2Ti\cdot dipy]PF_6$ in acetone at 21.0°					
Vol(ml)	Cond($\mu\upsilon$)	Sp Cond(υcm^{-1})	Conc(M)	$\sqrt{c}$	$\Lambda_m(\upsilon cm^2 eq^{-1})$
10.00	496.8	685.6×10^{-6}	5.303×10^{-3}	7.295×10^{-2}	129.4
20.00	270.6	373.4×10^{-6}	2.651×10^{-3}	5.153×10^{-2}	140.9
30.00	188.3	259.8×10^{-6}	1.774×10^{-3}	4.212×10^{-2}	146.8
40.00	145.2	200.4×10^{-6}	1.332×10^{-3}	3.654×10^{-2}	150.7
50.00	119.2	164.5×10^{-6}	1.063×10^{-3}	3.254×10^{-2}	155.2

Λ_o = 173.0 Slope of Λ_m versus $\sqrt{c}$ = 598

Calculated Onsager slope for a 1:1 electrolyte = 624

C. Infrared Spectra* in cm^{-1}

$[(\pi\text{-}C_5H_5)_2TiCl]_2$

3080w, 1800vw, 1700vw, 1620vw, 1442s, 1438s, 1260vw,1060w, 1009s, 890m, 840m, 810s, 790vs, 779vs, 382m.

$(\pi\text{-}C_5H_5)_2TiCl\cdot NH_3$

3310m, 3240m, 3150w, 3080w, 1725vw, 1600m, 1480s, 1258w, 1225s, 1119vw, 1060vw, 1010s, 799vs, 718m, 652m, 600w, 378m

$(\pi\text{-}C_5H_5)_2TiCl\cdot NH_2Me$

3339w, 3270w, 3235m, 3140w, 3080w, 1730vw, 1592m, 1580m, 1420m, 1300w, 1258m, 1225m, 1204m, 1120w, 1035m, 1005s, 930w, 902vw, 830m, 803vs, 788s, 719m, 630w, 610w, 592w, 405m, 378s

$(\pi\text{-}C_5H_5)_2TiCl\cdot NH_2Et$

3300w, 3218m, 3135m, 3080w, 1722vw, 1588m, 1350m, 1260w, 1178m, 1120w, 1038s, 1003s, 914w, 882w, 799vs, 610m, 380m

$(\pi\text{-}C_5H_5)_2TiCl\cdot NH_2C_3H_5$

3280s, 3220s, 3140m, 3080w, 1735vw, 1638w, 1589m, 1420m, 1330w, 1270w, 1220m, 1158m, 1135w, 1120w, 1079w, 1019w, 1010s, 995s, 935s, 925m, 838s, 810vs, 100s, 720vw, 650vw, 591w, 420w, 378s

$(\pi\text{-}C_5H_5)_2TiCl\cdot NH_2Ph$

3309m, 3215m, 3123w, 3080w, 1735vw, 1600m, 1575m, 1491s, 1340w, 1230m, 1155w, 1120w, 1071s, 1055s, 1010s, 910w, 900w, 840w, 828m, 800s, 790s, 760s, 698s, 608w, 540m, 528m, 400m, 385s

$(\pi\text{-}C_5H_5)_2TiCl\cdot py$

3080w, 1600m, 1582m, 1440s, 1300vw, 1258vw, 1218m, 1148m, 1065m, 1035w, 1015sh, 1006s, 840m, 828s, 813s, 794vs, 785sh, 758s, 702s. 628w, 554vw, 539w, 380m

$(\pi\text{-}C_5H_5)_2TiCl\cdot PPhMe_2$

3080w, 3050w, 1445s, 1431s, 1420m, 1300w, 1280m, 1268w, 1140w, 1100w, 1070w, 1025m, 1009s, 948s, 900s, 870w, 845w, 815m, 795vs, 785vs, 745vs, 733mm 695vs, 671w, 600w, 495m, 390m

$(\pi\text{-}C_5H_5)_2TiCl\cdot PPh_2Me$

3080w, 3040w, 1310vw, 1280w, 1260w, 1160w, 1122w, 1090m, 1009s, 930w, 885s, 842w, 828sh, 800vs, 745s, 719m, 700m, 692m, 507s, 492m, 440m, 392m

$[(\pi\text{-}C_5H_5)_2Ti\cdot en]Cl$

3240sh, 3190m, 3119m, 3080w, 1586m, 1330m, 1290w, 1270w, 1145m, 1100m, 1060w, 1030m, 999s, 870w, 838m, 810vs, 690m, 600w, 520m, 420w, 395m

$[(\pi\text{-}C_5H_5)_2Ti\cdot en]PF_6$

3355s, 3310s, 3160w, 3080w, 1620w, 1589s, 1445s, 1320m, 1285m, 1260w, 1145m, 1105m, 1060w, 1030s, 1020s, 1005s, 975w, 830s,br, 630m, 600w, 555s, 505m, 382m

$[(\pi\text{-}C_5H_5)_2Ti\cdot Me_2en]PF_6$

3300s, 3100s, 3080w, 1675w, 1625w, 1590w, 1475s, 1435s, 1289s, 1279m, 1240m, 1150m, 1120w, 1060m, 1010s, 970s, 930m, 830s,br, 615m, 553s, 415m, 395m

$[(\pi\text{-}C_5H_5)_2Ti\cdot dipy]PF_6$

3110w, 3080w, 1600s, 1560w, 1495m, 1445s, 1315m, 1260w, 1230w, 1175m, 1159m, 1122w, 1103w, 1070m, 1045w, 1025s, 1015s, 1010sh, 900s, 830s,br, 767s, 748m, 737s, 652m, 560s, 452m, 430m, 410m, 390w

$[(\pi\text{-}C_5H_5)_2TiCl]_2\cdot diphos$

3100w, 3080w, 1580w, 1430s, 1308w, 1200w, 1190s, 1180s, 1158m, 1110w, 1088w, 1062w, 1010s, 995m, 910w, 850w, 840w, 812s, 800vs,

783vs, 750vs, 710s, 700vs, 520vs, 490m, 440m, 420m, 390m, 362w, 349w

$\underline{[(\pi\text{-}C_5H_5)TiCl_2]_n}$

3110m, 1830vw, 1740vw, 1650vw, 1440s, 1260w, 1110w, 1063w, 1016s, 822vs, 725w, 690w, 560vw, 530vw, 395s, 360s, 330vs, 300vs

$\underline{(\pi\text{-}C_5H_5)TiCl_2 \cdot 2PPhMe_2}$

3105vw, 3070vw, 1580vw, 1435s, 1418m, 1328w, 1310w, 1290w, 1278s, 1160w,1115w, 1100w, 1074w, 1018m, 1009m, 999m, 945s, 904s, 868m, 804s, 750vs, 733s, 709m, 699s, 671w, 560w, 492s, 402m, 390m, 350s, 330m, 305m, 265s

$\underline{(\pi\text{-}C_5H_5)TiCl_2 \cdot 2PPh_2Me}$

3110vw, 3040vw, 1568vw, 1438vs, 1330w, 1310m, 1280m, 1190m, 1160m, 1120w, 1098s, 1070m, 1020s, 1000m, 969w, 900vs, 840m, 810vs, 748vs, 722s, 698vs, 516vs, 484s, 440s, 422m, 396m, 360s, 340m, 320w, 270s

$\underline{(\pi\text{-}C_5H_5)TiCl_2 \cdot \text{diphos}}$

3095vw, 1600vw, 1585vw, 1430vs, 1310w, 1260w, 1180s, 1155w, 1110m, 1088s, 1063m, 1010s, 960w, 900w, 809vs, 738vs, 728vs, 710s, 690vs, 510vs, 485s, 465w, 440m, 425w, 395m, 360s, 345m, 320w, 270s

$\underline{(\pi\text{-}C_5H_5)TiCl_2 \cdot DMPE}$

3090w, 1800vw, 1710vw, 1620vw, 1438s, 1422s, 1410m, 1298s, 1284s, 1265s, 1197s, 1122s, 1020s, 1015s, 948vs, 918s, 905s, 873m, 818vs, 803vs, 740s, 730m, 722s, 701m, 402sh, 395m, 388m, 360s, 338w, 310w, 275s

$\underline{(\pi\text{-}C_5H_5)_2Ti(CH_2SiMe_3)_2}$

3095vw, 1840w, 1740w, 1620w, 1390m, 1280m, 1245vs, 1070vw,

1015vs, 935m, 905s, 838s, 810vs, 738s, 710m, 672s, 625w, 600w, 450vs, 413w, 390s, 333w,

$(\pi\text{-}C_5H_5)Ti(CH_2SiMe_3)_3$

3130vw, 1310s, 1260vs, 1245vs, 1134w, 1018vs, 930m, 910s, 840s, 805vs, 740s, 700m, 685s, 620m, 540s, 510m, 430vs, 350w, 300s, 275s,

$(\pi\text{-}C_5H_5)TiMe_3$

3115w, 1835vw, 1740vw, 1630vw, 1450vs, 1320m, 1260w, 1115w, 1025s, 815vs, 710w, 690w, 625m, 510s, 360m, 290m

Black Residue

1380s, 1350w, 1328w, 1290m, 1210m, 1195m, 1155s, 1125w, 1095s, 1040s,br, 1020sh, 1005sh, 960vw, 925m, 900s, 875s, 835s, 800sh, 785s, 730w,br, 685w,br, 605w,br, 550s,br, 470w, 320s

Gas Samples from Reactions Involving Black Residue

3100w, 3000s, 2880s, 1450m, 1390s, 1360s, 1310vs, 1140vs,br, 1080m, 940w, 900w, 850w, 670m

$(C_5H_5)_3Ti$

3100w, 3070w, 1450s, 1370s, 1360m, 1345w, 1300vw, 1265m, 1120w, 1070w, 1022s, 1002s, 915w, 892w, 850m, 828s, 800vs, 752s, 722s, 670s, 618m, 578w, 490w, 420m, 380w

$(\pi\text{-}C_5H_5)_2TiF_2$

3100s, 1900vw, 1790vw, 1700vw, 1440s, 1360w, 1260w, 1128w, 1070w,1015s, 952w, 872m, 825vs, 610m, 568vs, 543vs, 420s, 351w, 290w

$(\pi\text{-}C_5H_5)_2NbCl_2$

3090m, 1310w, 1260w, 1170w, 1105w, 1120w, 1075w, 1011m, 970w, 870w, 822s, 725m, 380w, 308m, 290s, 268s

$(\pi\text{-}C_5H_5)_2NbBr_2$

3085m, 1310w, 1260w, 1170w, 1105w, 1120w, 1075w, 1010m, 970w, 870w, 828s, 726m, 380w, 300m

$(\pi\text{-}C_5H_5)_2Nb(H)PMe_2Ph$

3100w, 3070w, 1630s,br, 1440s, 1420m, 1409w, 1380s, 1325w, 1308w, 1295m, 1281m, 1260sh, 1240w, 1180m, 1120sh, 1108s, 1075w, 1010s, 990s, 940s, 918sh, 905s, 872m, 838m, 805s, 780sh, 748s, 715m, 700s, 675m, 608w, 530w, 508s, 440w, 421m, 399w, 370vw, 335m

$(\pi\text{-}C_5H_5)_2Nb(H)PPh_3$

3095vw, 3050w, 1625s,br, 1580w, 1435s, 1340w, 1310w, 1260w, 1180w, 1168vw, 1158vw, 1100m, 1090s, 1070m, 1030w, 1010m, 999s, 970w, 878w, 840s, 810w, 795w, 780m, 760s, 748s, 700vs, 682m, 620vw, 605vw, 535vs, 515s, 495m, 458m, 425m, 365w, 330vw

$[(\pi\text{-}C_5H_5)_2Nb(H)_2PMe_2Ph]BF_4$

3100m, 3090w, 1740m, 1590vw, 1580w, 1440s, 1370sh, 1318m, 1299m, 1262vw, 1198vw, 1160m,sh, 1100s,br, 1050s,br, 1010s, 960s, 940sh, 920s, 870m, 850s, 840s, 815s, 752s, 738s, 719m, 699s, 660vw, 618vw, 610vw,528s, 490s, 430m, 395w, 379w, 360w, 330w, 310w

$(\pi\text{-}C_5H_5)_2Nb(CN)TCNE$

3110m, 2210s, 2162s, 2140s, 1590m, 1515m, 1450s, 1420m, 1328sh, 1320vw, 1270vw, 1195vw, 1118m, 1078w, 1030m, 848s,br, 732s, 700m, 535m,

$(\pi\text{-}C_5H_5)_2Nb(Br)PMe_2Ph$

3100vw, 3050w, 1440s, 1420s, 1405m, 1390m, 1315w, 1295m,1280m, 1182vw, 1155w, 1100m, 1070m, 1040w, 1005sh, 990s, 945s, 928m,

910s, 870vw, 850w, 838sh, 828s, 805s, 750vs, 728s, 700vs, 670m, 600w, 505vs, 420s, 390m, 360sh, 338w, 268s

Polyacrylonitrile

2258vs, 2190w, 1310vw, 1268w, 1170vw, 1080w,br, 1020w,sh, 972m, 820w,br, 725m, 550w,br, 420w,br

$(\pi\text{-}C_5H_5)_2Nb(H)PPh_3 + N_2CHCOOEt$

3285s, 3150w, 3120s, 3100sh, 3040vw, 3015sh, 2980s, 2940w, 2920w, 2880vw, 1700vs, 1550vs, 1490sh, 1460vs,br, 1370m, 1328s, 1270w, 1215w, 1170vs,br, 1175vs,br, 1090sh, 1070sh, 1045m, 1030s, 970w, 885w, 875w, 865m, 840s, 830s, 820s, 785m, 770m, 740m, 625vw, 605w, 575m, 550vw, 528w, 470w, 430w, 390m, 372m, 330w, 300w

$(\pi\text{-}C_5H_5)_2Nb(NCS)_2$

3070m, 2065vs, 2040vs, 1440s, 1310w, 1260w, 1150w, 1052w, 1002m, 895m, 828s, 720m, 690vw, 610vw, 490vw, 458w, 386w

$(\pi\text{-}C_5H_5)_2NbBH_4$

3100w, 2470sh, 2420s,br, 2310m, 1720m,br, 1440s, 1295w, 1280m, 1265sh, 1160s, 1110w, 1080w, 1058w, 1010m, 885m, 870m, 850m, 838m, 800s, 730w, 695w, 648m, 605w, 480vw, 440vw, 380sh, 370m, 360sh

*vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad and sh = shoulder

D. Cryoscopic Molecular Weights

Compound	Molecular Weight	
	Found	Calculated
$(\pi\text{-}C_5H_5)_2TiCl\cdot NH_2Et$	275	259
$(\pi\text{-}C_5H_5)_2TiCl\cdot PPh_2Me$	492	414
$(\pi\text{-}C_5H_5)TiCl_2\cdot 2PPhMe_2$	399	460

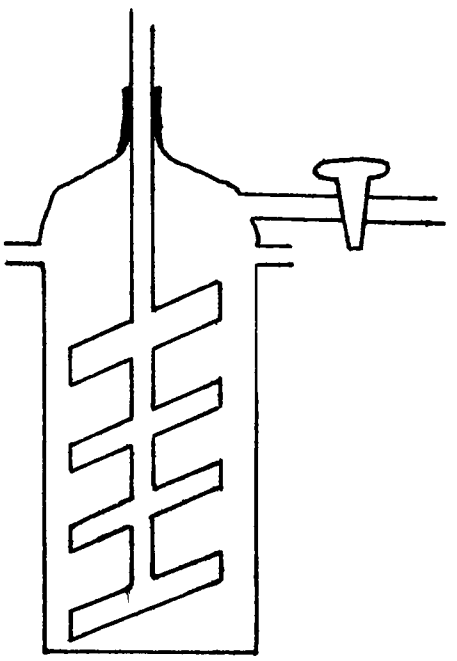
E. Studies on $\{[(\pi\text{-}C_6Me_6)TiCl_2]_3\}Cl$

Considerable time was spent attempting to prepare the π-arene title compound in order to investigate its properties and compare them with those of some π-arene compounds of molybdenum and tungsten which have been recently reported (F1-F3). Initially, it was found impossible to repeat the preparation described in the literature (F4), in spite of correspondence with both Dr. F. Rohrscheid and Professor E.O. Fischer, the co-authors of the paper in which the synthesis of the compound is reported. Eventually, however, a successful method was developed which is given below and a few test reactions which are also reported, were carried out on the product. This compound, however, seems to have a rather limited chemistry and is also rather unstable with respect to thermal decomposition and hydrolysis and so the project was abandonned at this stage.

1. Experimental

An apparatus, shown in the diagram, was built from a

carpenter's auger with the tip removed and a special flanged Schlenk tube. The tube can be split into two parts, the upper one of which contains a stirrer bearing and a side-arm with tap.



Device for Preparation of $\{[(\pi\text{-}C_6Me_6)TiCl_2]_3\}Cl$

A powerful electric motor was used to turn the auger slowly in a direction such that the material at the centre of the vessel would be forced to the bottom of the tube and up again at the outside. In the tube were placed aluminium powder (0.973 g, 0.036 g-atom), freshly sublimed and powdered aluminium trichloride (25.0 g, 188 mmol), hexamethylbenzene (5.0 g, 31 mmol) and titanium tetrachloride (5.1 ml, 46 mmol). The viscous mixture was stirred and heated in an oil bath at 130° for six hours. Initially, the mixture melted but after about an hour it turned to a brown solid which eventually broke into small lumps with constant stirring. After cooling to room temperature, the solid was removed from

the vessel and ground to a fine powder.

A dispersion of ice crystals in dichloromethane was prepared by placing water (250 ml) in a flask containing dichloromethane (250 ml) and stirring the mixture vigorously while chilling it in a liquid nitrogen bath. To this dispersion of ice in dichloromethane, small quantities of the brown powdered solid were added at -35° with vigorous stirring until after about one hour all the solid had been added and had reacted with the ice. The two layers were then allowed to separate; the purple organic layer was removed and filtered at 0° and the solvent removed from the filtrate <u>in vacuo</u> at room temperature. The purple residue from this operation was recrystallized from dichloromethane by adding petroleum ether until precipitation commenced and then allowing the mixture to stand for one hour, filtering and drying the purple precipitate <u>in vacuo</u> at room temperature. Yield 60%.

A sample of purple $\{[(\pi\text{-}C_6Me_6)TiCl_2]_3\}Cl$ was treated with trimethylphosphite and no reaction was observed until the suspension was warmed slightly, when decomposition occurred. Similar observations were made during a reaction between triphenylphosphine and the purple π-arene compound.

A sample of the purple π-arene compound was dissolved in 95% ethanol and sodium borohydride added to the solution. Effervescence occurred and the solution darkened in colour but no tractable products were obtained.

F. References

F1 M.L.H. Green and W.E. Silverthorn, Chem. Comm., 1971, 557.

F2 M.L.H. Green, L.C. Mitchard and W.E. Silverthorn, J. Chem. Soc. (A), 1971, 2929.

F3 M.L.H. Green, J. Knight, L.C. Mitchard, G.G. Roberts and W.E. Silverthorn, Chem. Comm., 1971, 1619.

F4 E.O. Fischer and F. Rohrscheid, J. Organomet. Chem., 1966, 6, 53.