Studies of the Reactions of Perfluoroarylborane Lewis Acids with Transition Metal Compounds

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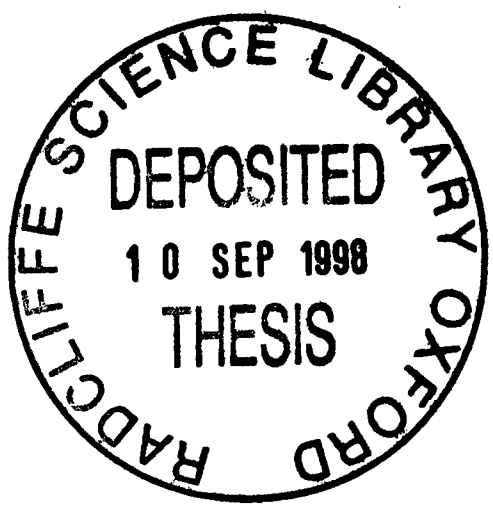
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A thesis submitted in part-fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Oxford

April 1998



Abstract:

Studies of the Reactions of Perfluoroarylborane Lewis Acids with Transition Metal Compounds

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Submitted for D.Phil.
Trinity Term, 1998

This thesis describes the preparation of strongly electrophilic boranes and their reactivity with transition metal compounds.

Chapter One presents an overview of the reactivity of boron-containing Lewis acids as found in the literature focusing primarily on reactions of electrophiles containing a boron-perfluoroaryl bond that are of synthetic rather than catalytic interest.

Chapter Two presents studies into the reactivity of boranes of the general formula $RB(C_6F_5)_2$ [R = (C_6F_5), Ph, H or Cl] with some metallocene hydrides. The previously synthesised adduct $[(\eta^5\text{-}C_5H_5)_2Mo(H)(\eta^1\text{-}HB(C_6F_5)_3)]$ has been further investigated and the analogous adduct of $HB(C_6F_5)_2$ is also reported. The zwitterionic compounds $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2R)(\eta^5\text{-}C_5H_5)WH_3]$ {R = (C_6F_5), Ph, H or Cl*} and $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)ReH_2]$ are described and have been fully characterised (* indicates that an X-ray crystal structure was obtained). Investigations into the reactivity of these compounds towards competing Lewis bases have been undertaken and reveal that the rhenium zwitterion is considerably more stable than the tungsten analogues.

Chapter Three presents reactions between $B(C_6F_5)_3$ and transition metal nitrido complexes. $B(C_6F_5)_3$ reacts directly with a number of nitrido compounds; $[\{(C_6F_5)_3BN\}Re(PR_3)(S_2CNR'_2)_2]$ (R_3 = $MePh_2$ and R' = Et*; R_3 = Me_2Ph and R' = Me*), $[\{(C_6F_5)_3BN\}ReCl(PMePh_2)_2(S_2CNMe_2)]$, $[\{(C_6F_5)_3BN\}Mo(S_2CNR_2)_3]$ (R = Me or Et) and $[\{(C_6F_5)_3BN\}Os(1,2\text{-}S_2C_6H_4)_2][^nBu_4N]$ have all been prepared (* indicates that an X-ray crystal structure has been obtained). The reactivity of these adducts towards competing Lewis bases has been probed revealing a range of stabilities over the three metals considered. The adduct of an osmium nitrido compound has also been reacted with competing Lewis acids and the compound $[\{(C_6F_5)_3BN\}Os(1,2\text{-}(S)(SMe)C_6H_4)(1,2\text{-}S_2C_6H_4)]$ has been made and characterised by NMR spectroscopy.

Chapter Four describes the synthesis of Lewis acids containing a boron-perfluoroaryl bond. Firstly, modified literature preparations of $RB(C_6F_5)_2$ [R = (C_6F_5), Cl or H] are reviewed. Attempts to prepare the new Lewis acid BAr'_3 [Ar' = $(3,5\text{-}C_6H_3(CF_3)_2)$] are described, including the synthesis and characterisation of the new tin reagent $^nBu_3SnAr'$. Additionally, the new electrophile $B(C_6H_5)(C_6F_5)_2$ has been prepared using either $^nBu_3Sn(C_6F_5)$ or $[LiC_6F_5]$ as the source of (C_6F_5).

Chapter Five contains experimental details for the thesis, characterising data for new compounds are presented in **Chapter Six** and details of the X-ray crystal structures may be found in the **Appendices**.

The work described in this thesis was carried out in the Inorganic Chemistry Laboratory, Oxford between October 1994 and March 1998 under the supervision of Professor M. L. H. Green F.R.S. All the work is my own unless stated to the contrary and has not been submitted for a degree at this, or any other, university.

Dedicated to my parents for all their support

during my eight years in Oxford

Acknowledgements

The time comes at last to thank all the people who have helped in the sometimes painful genesis of this thesis over the last three and a half years. The list is quite long, so I hope that nobody who is inadvertently omitted feels too aggrieved- just blame it on my advancing years.

Firstly, many thanks must go to my supervisor, Prof. Malcolm Green, FRS for being a constant supply of ideas and enthusiasm throughout the time I have worked for him. Even if being in Malcolm's office while he was in full flow sometimes led to severe mental exhaustion whilst trying to catch just some of the thoughts bouncing from the walls, enough pearls could be plucked from such encounters to make it all worthwhile. Thanks must also be due to the EPSRC and Malcolm for their generous funding of my endeavours.

Among the Green group, my hearty thanks go firstly to Dr. Nils Metzler and Dr. Jane Galsworthy who successively occupied the same bench in T15 and very patiently put up with my constant badgering. They both proved to be a continual source of enthusiasm, encouragement and ideas and I owe a great deal to both of them. Dr. Christian Mehnert also considerably eased my progress by his novel and effective glassware design.

Dr. Linda Doerrer was kind enough to solve two crystal structures for me while this thesis was being written and I would like to thank her for not only making the appendices look rather less undernourished but also for putting up with my almost total lack of crystallography knowledge without so much as a murmur of complaint. Thanks also to Mike Leach who solved the other structure without too many moans about the disordered solvent molecules.

Although most of the NMR spectra were obtained on the neolithic Bruker AM300, I would like to thank those who have given up their time to run things for me on the Varian. These are (in no particular order) Nils, Nigel Bailey, Cliff Williams and Martin Humphries.

Of course, much less would have been accomplished had it not been for the technical staff of the lab. I would like to thank in particular the analysts Jim and Ann (especially for her unusual technique of dropping my Schlenks which always seemed to yield the best results), the glassblowers Martyn and Terri (who very creditably concealed their expressions of dread every time I took down the Barf apparatus to be repaired), Chris Botham who gave the antediluvian Mass Spec. a good kicking when required, Keith and Nenad from electronics for responding to my ever-increasing requests to fix the NMR machine with speed and good grace and lastly to Dave from the workshop for sharpening my darts for me on several occasions. The boys from stores- Steve, Keith,

Ken, Tony and Bill- have all been good for a gossip from time to time so thanks to them too.

I'm sure proof-reading the first draft of every chapter wasn't much fun, but many thanks to Jane for doing so and providing so many helpful comments (including the odd 'gibberish'). Further checking was done by Linda and Martin for which I am very grateful.

On a more general note, the various members of the Greater Green Group have all, in their various ways, been helpful (or at the very least a source of amusement) over the past few years. I would like to single out my partners in crime in T17 and especially Dr. Adam Stephens (an ever-willing (if not ever-present!) source of advice), Dr. Tom James (who introduced me to the twin dubious delights of the Mass Spec. machine and Bulgarian wedding bands (and it **is** curry-house music whatever you may say to the contrary, Tom!)), Dr. Wolf Spaether (for his novel ideas on glassware ownership) and Ronan Bellabarba (who put up with wall-to-wall Shostakovich in return for my tolerance of the sound of snapping TLC plates and Italian curses).

And so we come to all those people outside the lab who have made Oxford such a memorable place for me over the last 8 years. Nigel Bailey and Nick Woodruff (possessor of the silliest sideburns ever to grace the set of University Challenge) have been there throughout, generally round the same table in a pub. We even managed to live together for a year without falling out which probably says something... Before I wind up (lest the acknowledgements rival the length of the rest of the thesis) I would like to register my thanks to all the people who I have rung bells, sung or played darts with during my time in Oxford.

"Always remember that I have taken more

out of alcohol than alcohol has taken out of me."

Winston Churchill

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List of Abbreviations

General:

Me	methyl, $-CH_3$
Et	ethyl, $-CH_2CH_3$
^{i}Pr	*iso*-propyl, $-CH(CH_3)_2$
^{n}Bu	butyl, $-CH_2(CH_2)_2CH_3$
^{t}Bu	*tert*-butyl, $-C(CH_3)_3$
Ph	phenyl, $-C_6H_5$
R	general alkyl group
Ar	general aryl group
Ar'	3,5-$C_6H_3(CF_3)_2$
Cp	general cyclopentadienyl group, (η^5-C_5R_5)
Cp*	pentamethylcyclopentadienyl group, (η^5-C_5Me_5)
thf	tetrahydrofuran, C_8H_8O
dme	dimethoxyethane, $H_3CO(CH_2)_2OCH_3$
acac	acetylacetonate, $[H_3CC(O)CHC(O)CH_3]^-$
bipy	2,2'-bipyridine, $(C_5H_4N)_2$
TMEDA	tetramethylethylenediamine, $(H_3C)_2N(CH_2)_2N(CH_3)_2$
μ	bridging moiety
η^n	n-hapto ligand
b.p.	boiling point
NMR	nuclear magnetic resonance
IR	infrared
UV	ultraviolet
ν(X-Y)	infrared X-Y stretch

Nuclear Magnetic Resonance Spectroscopy:

δ	chemical shift
ppm	parts per million
Hz	Hertz (s^{-1})
$^{n}J_{XY}$	n bond coupling constant between X and Y
$\{^{1}H\}$	proton decoupled
fwhh	full width at half height

Multiplicities:

s	singlet
d	doublet
t	triplet
q	quartet
dd	doublet of doublets
m	unresolved multiplet
br	broad

Infrared Spectroscopy:

cm^{-1}	wavenumbers
br	broad
s	strong
m	medium
w	weak

Mass Spectrometry:

m/z	mass to charge ratio
$[M]^{+}$	parent ion

Chapter One

An Introduction to the Chemistry of Strong Boron-Containing Electrophiles

1.1 Introduction

This thesis is concerned with the synthesis and reactivity of strongly electrophilic, boron-containing, Lewis acids. Such compounds are of considerable interest not just for their wide-ranging and often unexpected reactivity, but also because of their utility in organic synthesis as alkyl and aryl transfer reagents, as organic catalysts and as co-catalysts with transition metal complexes.

For example, trialkyl- and triaryl-boranes are used as synthons in the alkylation of α-halo carbonyl compounds and also for the addition of alkyl groups to a carbonyl-activated double-bond; much work in this area has been undertaken by Brown.[1-3] In these cases, only one alkyl group is transferred from boron to the substrate; norbornadiene is a convenient choice for the two remaining groups since it displays low migratory aptitude and is easily recovered after the reaction. Another highly important use of these compounds is in their reaction with CO to form $R_2BC(O)R$; this intermediate is then conveniently converted to an aldehyde (with $LiAlH(OMe)_3$ then H_2O then H_2O_2/NaOH), a ketone (with H_2O then H_2O_2/NaOH) or a tertiary alcohol (with ethylene glycol then H_2O_2/NaOH). These reactions are summarised in Fig. 1.1.

In the field of organic catalysis, boron-containing reagents find even greater utility for instance in the hydrosilation of aromatic carbonyl compounds,[4] the Oppenauer oxidation of secondary alcohols to ketones,[5] the catalytic de-hydrocoupling of phenylsilanes[6] and the Aldol and Michael reactions between silyl enol ethers and electrophiles such as carbonyl compounds.[7]

Most important is the role of strong triarylborane Lewis acids as co-catalysts with group 4 transition metal complexes in the production and stabilisation of the cationic "14-electron" metallocene species implicated in Ziegler-Natta olefin polymerisation. This topic will be covered more fully in section 1.3 below.

The main thrust of the work in this thesis has been directed towards the synthesis of boranes containing the pentafluorophenyl moiety, C_6F_5- and a study of their reactivity. In general, perfluoroalkyl boranes have been found to be highly unstable since alkyl groups of this type are unable to relieve the electron-deficiency of the boron centre

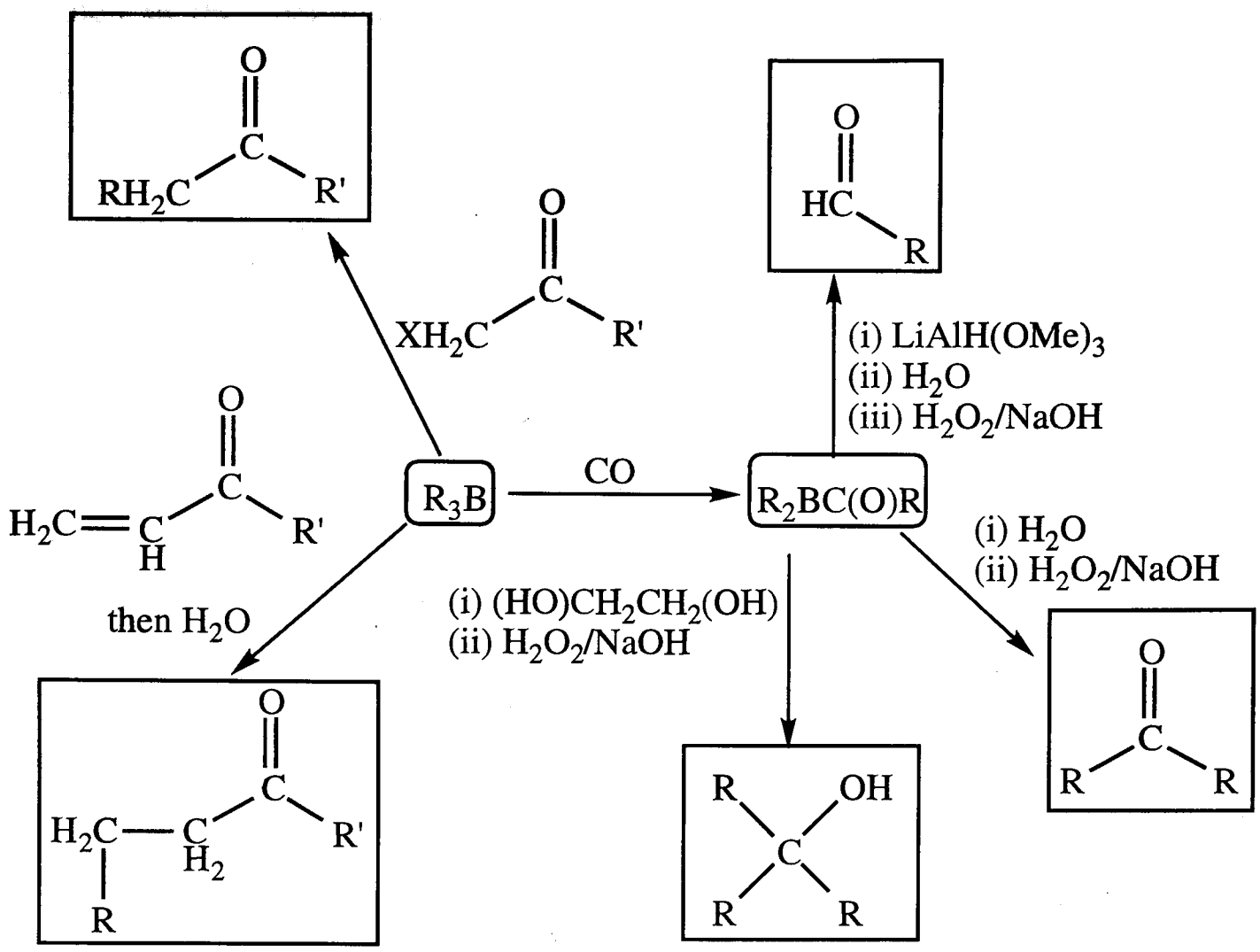


Fig. 1.1: The uses of BR_3 in organic synthesis.

by π-bonding.[8] Among the only known compounds of this type are F_3CBF_2[9] and $F_2C{=}C(F)BF_2$[10] which relieve the electron-deficiency, caused by the σ-withdrawing fluoroalkyl group, by π-donation from fluorine. In contrast, the pentafluorophenyl group, although inductively electron-withdrawing through its fluorine substituents, can provide mesomeric electron donation *via* its π-system. However, compounds containing more than one aryl group are significantly non-planar about boron and so electron donation is not usually large enough to compromise acidity.[11] Thus, compounds containing the B-C_6F_5 moiety are predicted to be powerful electrophiles and synthetically accessible. The synthesis of a range of such compounds is reviewed in the introduction to Chapter Four of this thesis.

The remainder of this chapter will discuss the relative strengths of boron-containing Lewis acids and then provide a review of the reactivity of such compounds as

described in the chemical literature. A further review on this topic has recently appeared.[12]

1.2 The Comparative Strengths of Boron-Containing Lewis Acids

The boron-containing Lewis acids that appear in the work in this thesis are all considered to be 'strong' electrophilic compounds. The strength of a Lewis acid is a somewhat nebulous concept since any value obtained depends quite strongly on the method used to obtain the data. For instance simple measurements on the strength of acid-base adducts, by studying exchange reactions, can yield very different results depending on the base used. The Lewis acidity of boron trihalides has been thoroughly studied since they offer a variety of useful synthetic and catalytic applications.

On electronegativity considerations alone, one would expect the inductive electron-withdrawing effect of the halogen, and hence the electron-deficiency at B, to decrease in the order F>Cl>Br>I. This order is not observed experimentally except in certain situations under thermodynamic control *e.g.* $BF_3{\cdot}Et_2O$ can be distilled without decomposition whereas the other BX_3 etherates dissociate on heating. Methods which measure ΔH values for association or dissociation of a series of adducts generally produce the reverse order of Lewis acid strength, *i.e.* $BF_3<BCl_3<BBr_3<BI_3$. The work of Brown and Holmes[13] further explains this observation by noting that the most important stage in adduct formation is initial distortion of BX_3 from planar to pyramidal geometry prior to attack of the Lewis base, which is most unfavourable for BF_3 where large π-overlap between the fluorine lone-pairs and the empty 2p orbital on boron occurs.

The relative acidity of $B(C_6F_5)_3$ was studied extensively soon after its initial synthesis.[14] Attempts to study exchange reactions of the type:

$$\mathbf{BX_3 + BY_3{:}D \longrightarrow BX_3{:}D + BY_3}$$

are futile for $B(C_6F_5)_3$ since the adducts tend to lose pentafluorobenzene rather than the donor molecule, D. The method of Milner and Onyszchuk,[15] which utilises NMR spectroscopy, was more fruitful. $^{19}F\{^1H\}$ NMR spectroscopic studies indicate that the

para-fluorine resonance in the C_6F_5- moiety is shifted significantly upfield on adduct formation, indicative of an interaction between the π-system and the empty 2p orbital on boron. ^1H NMR spectrosocopic studies of NMe_3 adducts of several Lewis acids reveal a decrease in chemical shift in the order $BI_3>BBr_3>BCl_3>B(C_6F_5)_3\approx BF_3\approx BH_3>BAr_3>BMe_3$ and this is also assigned as the order of Lewis acidity by Massey and Park since proton deshielding is expected to occur when electron density is removed from the donor molecule on adduct formation.[14]

It can be seen that strongly π-interacting groups, such as (C_6F_5), impart a strongly electrophilic character to boron-containing Lewis acids. This factor, in addition to the sheer bulk of such groups, gives rise to varied and novel chemistry. The wide reactivity of such strong Lewis acids as found in the literature is reviewed below.

1.3 Electrophilic Addition to Neutral Metal-Carbon Bonds

1.3.1 Attack at a Methyl Group Bound to a Group 4 Metal

1.3.1.1 Reaction with Complexes of the Type $[Cp_2M(R)(Me)]$

The vast majority of reactions of $B(C_6F_5)_3$ found in the literature involve its interaction with a Group 4 metallocene dimethyl complex. These frequently produce a cationic 14-electron metal species which may or may not be bound in some way to the borate anion that also forms in the reaction. The earliest example of the structural elucidation of such an ion pair was published by Marks who obtained the crystal structure of the product from the reaction between $[(\eta^5\text{-}C_5H_5)_2ZrMe_2]$ and $B(C_6F_5)_3$ (Fig. 1.2).[16]

This compound contains a nonlinear (Zr-C-B = 161.8 °), highly unsymmetrical (Zr-C = 2.549 Å, C-B = 1.662 Å) Zr-(μ-CH_3)-B bridge containing a formally pentavalent carbon atom. Two of the C-H bonds are bent away from B and towards Zr, although the shortest Zr-H distance is still longer than a typical Zr...$H_{agostic}$ distance.[17] As expected, this compound is an active catalyst for the polymerisation of olefins with activity comparable to typical zirconocene/alumoxane systems. Marks has subsequently

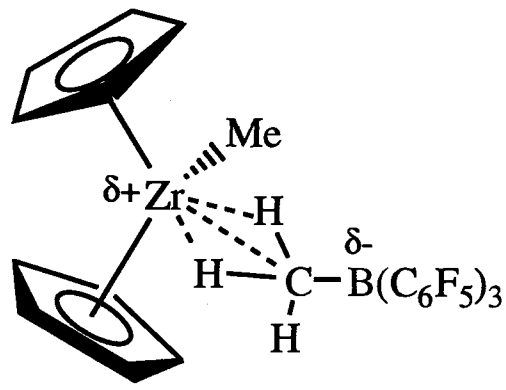


Fig. 1.2: The ion-pair formed in the reaction [(η^5-C_5H_5)$_2$$ZrMe_2$] + $B(C_6F_5)_3$.

published a more comprehensive catalytic study of such complexes investigating the effects of changing the ligand environment around the zirconium centre and the substrate upon activity.[18]

Modifications have been made to this system in an attempt to lessen the degree of association between the cation and anion components and thus improve the efficiency of the catalytic system. Bochmann reacted both [*rac*-$Me_2Si(\eta^5$-Indenyl$)_2ZrMe_2$] and [(η^5-1,3-$C_5H_3(SiMe_3)_2)_2ZrMe_2$] with $B(C_6F_5)_3$ to produce the expected Zr-(μ-Me)-B bridged complexes.[19] The molecular structure of the latter complex shows a rather more linear bridge (170.5 ° *vs.* 161.8 °) and a slightly longer Zr-C bond (2.667 Å *vs.* 2.549 Å) than the case above[16] but is otherwise unremarkable. This may be attributable to steric crowding caused by the bulky groups on the Cp ligands. A study on the thermodynamics and kinetics of the dissociation of the [(η^5-$C_5H_5)_2Zr(Me)(\mu$-Me)$(B(C_6F_5)_3)$] ion pair has been published.[20]

In the continuing search for a one-component catalyst system with a non-coordinating anion, Marks has reported the synthesis of the new acid *tris*(perfluorobiphenyl)borane, B(*para*-C_6F_4-$C_6F_5)_3$, and used this reagent to abstract methyl groups from complexes of the type [Cp_2MMe_2] (M = Zr, Hf).[21] His attempts to synthesise binuclear acids by double hydroboration of alkynes followed by reaction with [$Li(C_6F_5)$] have, however, only achieved limited success due to the tendency of the products to redistribute and form $B(C_6F_5)_3$.[22]

Green has investigated analogous benzamidinato systems, $[Cp^*\{\eta^3\text{-}CPh(N(SiMe_3))_2\}ZrCl_2]$ and $[(\eta^5\text{-}C_5H_5)\{\eta^3\text{-}CPh(N(SiMe_3))_2\}ZrMe_2]$, in which the benzamidinato ligand is formally equivalent to a cyclopentadienyl moiety.[23] These compounds are not active catalysts for olefin polymerisation in conjunction with $B(C_6F_5)_3$ since the Zr-(μ-CH_3) interaction with the Lewis acid is found to be too strong.

Other reactions between $[Cp_2MMe_2]$ (M = Ti, Zr, Hf) species and strong electrophiles are more directed towards synthetic interest rather than polymerisation activity. Erker has reacted $[(\eta^5\text{-}C_5H_5)_2ZrMe_2]$ with the imidazole·$B(C_6F_5)_3$ adduct eliminating methane and producing a binuclear compound (Fig. 1.3(a)) after aqueous work-up.[24] This is analogous to the compound formed from the reaction of $[(\eta^5\text{-}C_5H_5)_2ZrCl_2]$ with $Na[BPh_4]$ in water with subsequent addition of a nitrile (Fig. 1.3(b)).[25]

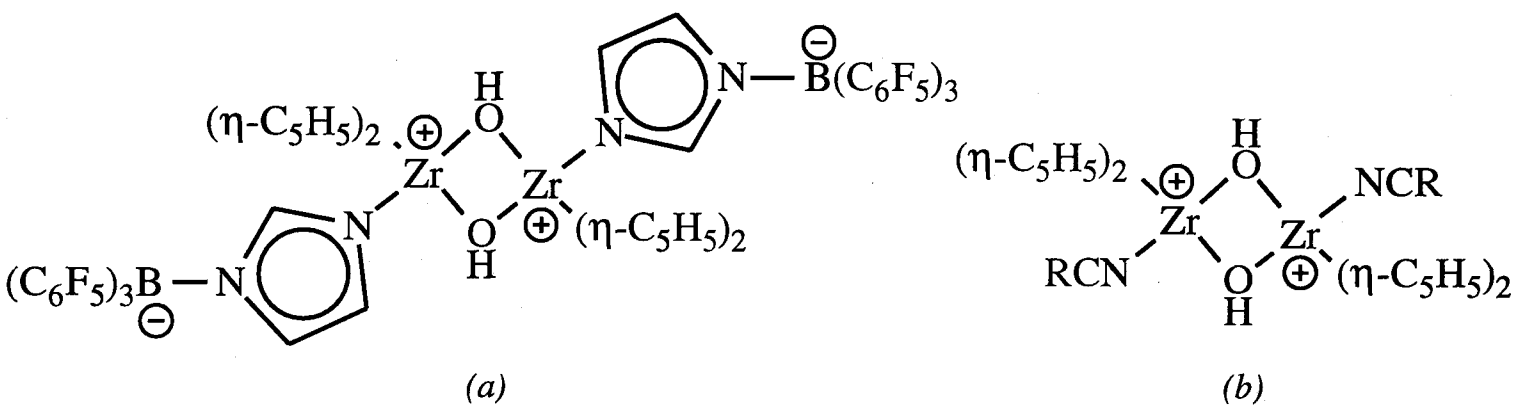


Fig. 1.3: Dimers formed in the reactions (a) $[(\eta^5\text{-}C_5H_5)_2ZrMe_2]$ + imidazole·$B(C_6F_5)_3$ with aqueous work-up and (b) $[(\eta^5\text{-}C_5H_5)_2ZrCl_2]$ + $Na[BPh_4]$ in H_2O with addition of RCN.

Piers has explored the reaction of $[(\eta^5\text{-}C_5H_5)_2ZrMe_2]$ with the Lewis acid $HB(C_6F_5)_2$ to produce a series of borohydride complexes, one of which contains a formally pentavalent carbon atom (Fig. 1.4).[26] The electronic structure of this intriguing compound has been investigated by extended Hückel and *ab initio* Molecular Orbital calculations.[27]

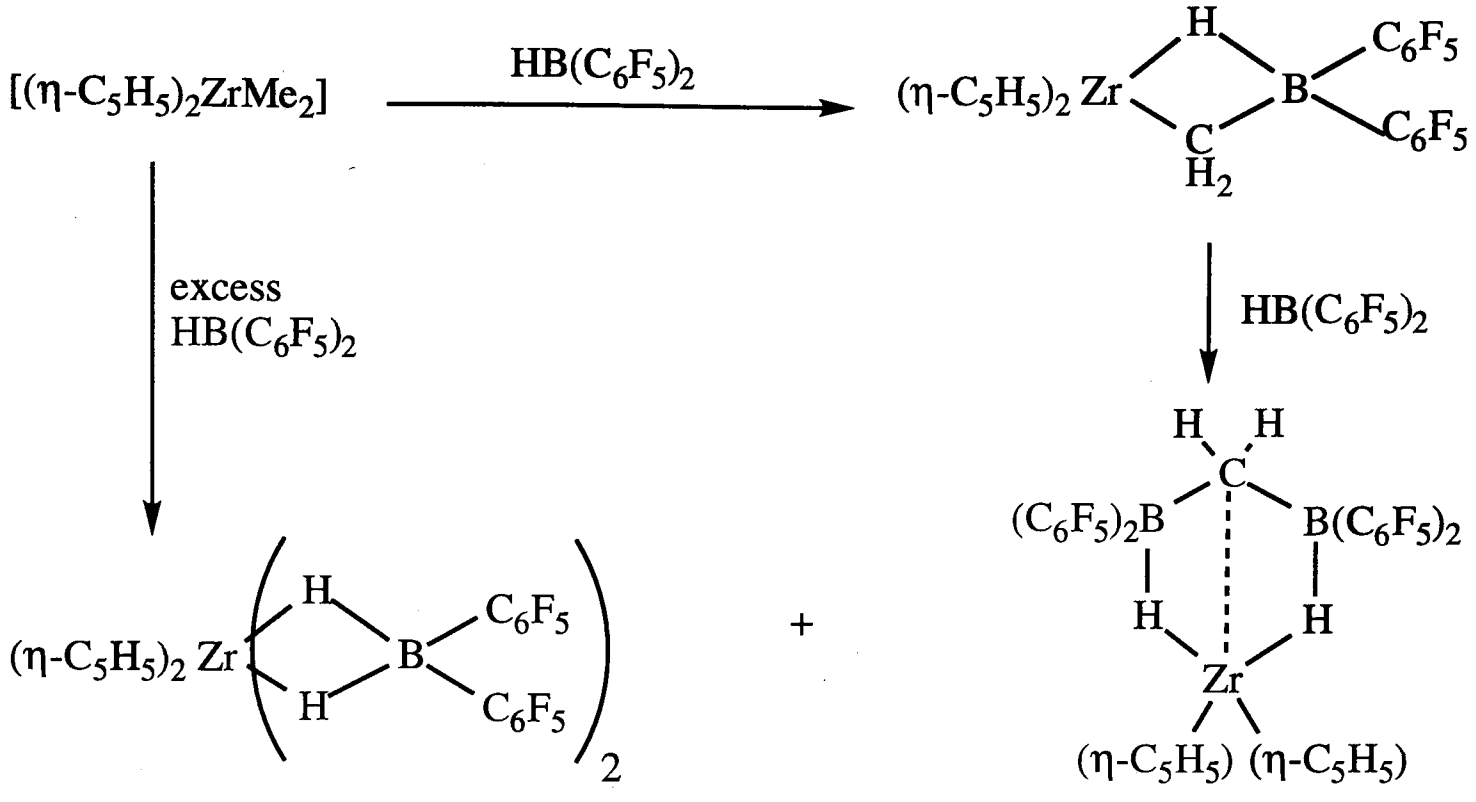


Fig. 1.4: The unexpected reaction between [(η^5-C_5H_5)$_2$ZrMe$_2$] and HB(C_6F_5)$_2$.

The [Cp^*_2Zr(Me)(μ-Me)(B(C_6F_5)$_3$)] system, formed analogously to the ion-pair in Fig. 1.2, is found to react with two equivalents of CO to form [Cp^*_2Zr(COMe)(CO)][MeB(C_6F_5)$_3$].[28] Contrasting reactivity is observed for the complexes [Cp_2Zr(Me)(CH_2CMe_3)] (Cp = (η^5-C_5H_5) or (η^5-C_5Me_5)) which react with B(C_6F_5)$_3$ and, in the case of the crowded Cp* analogue, eliminates *iso*butene spontaneously even at -75 °C to yield [Cp^*_2Zr(Me)(μ-Me)(B(C_6F_5)$_3$)] whereas the less crowded [(η^5-C_5H_5)$_2$Zr(CH_2CMe_3)(μ-Me)(B(C_6F_5)$_3$)] is stable in solution at 0 °C but undergoes reversible β-elimination at 25 °C.[29]

1.3.1.2 Reaction with Complexes of the Type [CpM(R)$_2$Me]

Complete abstraction of Me^- is observed when [Cp^*MMe_3], (M = Hf, Zr) react with B(C_6F_5)$_3$ in a mixture of toluene/hexanes (1:10) to form the separated ions [Cp^*M(Me)$_2$(η^6-PhMe)][MeB(C_6F_5)$_3$] which have been structurally characterised (Fig. 1.5).[30] In contrast, the analogous titanium complex formed [Cp^*TiMe_2(μ-Me)B(C_6F_5)$_3$].[31] Although no molecular structure of this complex was obtained, variable temperature NMR spectroscopic studies of isotopically enhanced samples have

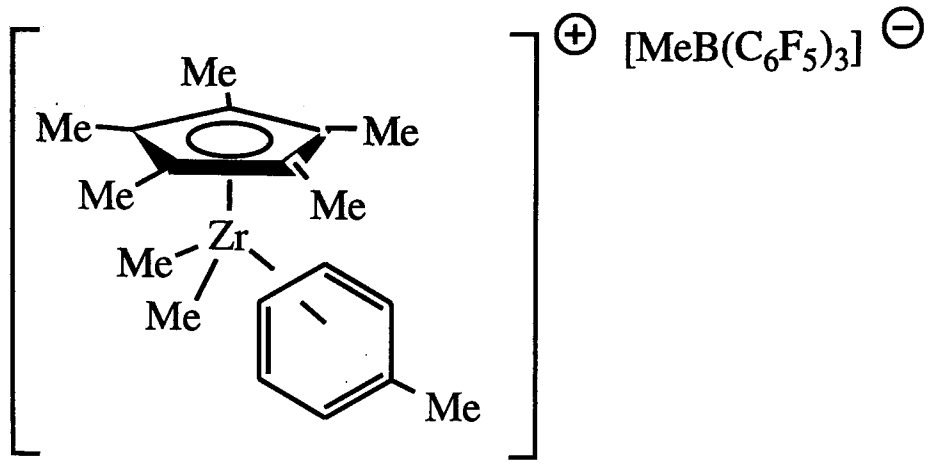


*Fig. 1.5: The product formed in the reaction [Cp*ZrMe3] + B(C6F5)3.*

shown that the borane is bound to one methyl group and shows no signs of 'hopping' from one to another. Further work by the same authors has studied the systems $[Cp^*Ti(Me)(E)(\mu\text{-}Me)(B(C_6F_5)_3)]$ (observed for E = C_6F_5 or OC_6F_5) and $[Cp^*Ti(OC_6F_5)_2][MeB(C_6F_5)_3]$.[32]

These results have been compared to those of the analogous zirconium and hafnium compounds. When M = Zr or Hf, the product exists as separate ions, $[Cp^*M(Me)_2(\eta^6\text{-}PhMe)][MeB(C_6F_5)_3]$, in which the cation is stabilised by solvent coordination. When M = Ti, the product may be a μ-methyl species, $[Cp^*Ti(Me)(E)(\mu\text{-}Me)(B(C_6F_5)_3)]$ (E = Me, (C_6F_5) or (OC_6F_5)), or distinct ions in which the cation is believed to be naked in solution, $[Cp^*Ti(OC_6F_5)_2][MeB(C_6F_5)_3]$.

1.3.1.3 Reaction with Complexes of the Type [Cp3MMe]

Erker has studied the compound $[(\eta^5\text{-}C_5H_5)_3ZrMe]$ which readily undergoes methide abstraction by $B(C_6F_5)_3$ to form a cation which is associated with a $[MeB(C_6F_5)_3]^-$ counterion.[33] The cation-anion interaction is disrupted by donors such as MeCN, PhCN, ^{t}BuNC or CO. The crystal structures of three of these complexes have been published.[34]

1.3.1.4 Reaction with Metallocenes with Donor Substituted Cyclopentadienyl Rings

Erker has also studied the reaction between $B(C_6F_5)_3$ and $[(\eta^5\text{-}C_5H_4(C(R)_2NMe_2))_2ZrMe_2]$.[35] In this system, the cation formed after abstraction of the methyl group by $B(C_6F_5)_3$ is stabilised by the amine substituents 'tucking in' to bind to the metal centre (Fig. 1.6). The resulting complex is chiral but rapidly racemizes at

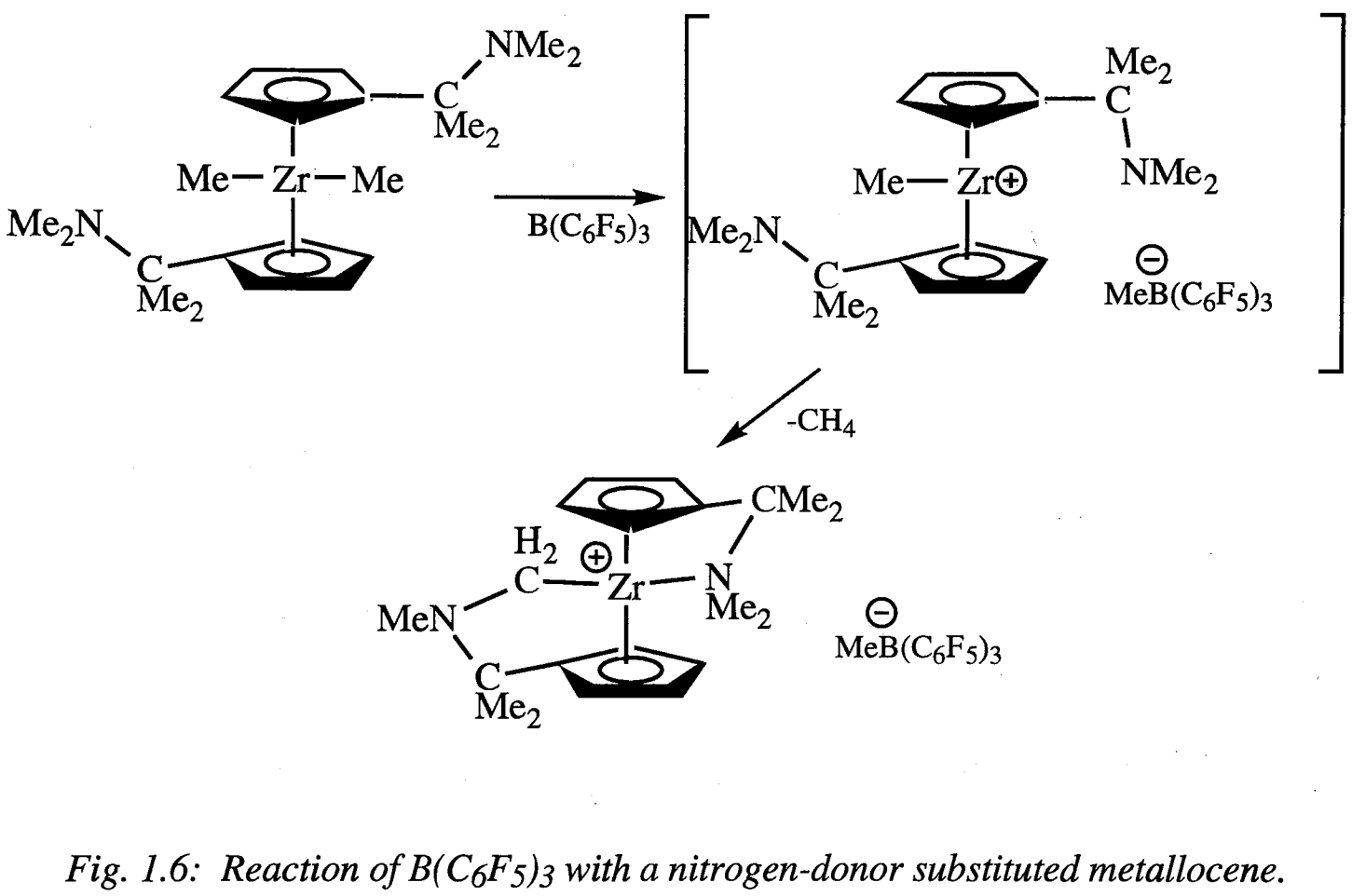


Fig. 1.6: Reaction of $B(C_6F_5)_3$ with a nitrogen-donor substituted metallocene.

ambient temperatures. Following this work, Erker succeeded in sequentially abstracting two methyl groups by reacting $B(C_6F_5)_3$ with $[\{\eta^5\text{-}C_5H_4(C(Me)_2PAr_2)\}_2ZrMe_2]$ (Ar = *p*-tolyl) and described consequent coordination of the two phosphine ligands to the metal.[36] The dication product formed is unstable in CH_2Cl_2 solution and decomposes to a chloride as shown in Fig. 1.7. The same cation is also produced when $[\{\eta^5\text{-}C_5H_4(C(Me)_2PAr_2)\}_2ZrCl_2]$ is treated with $B(C_6F_5)_3$.

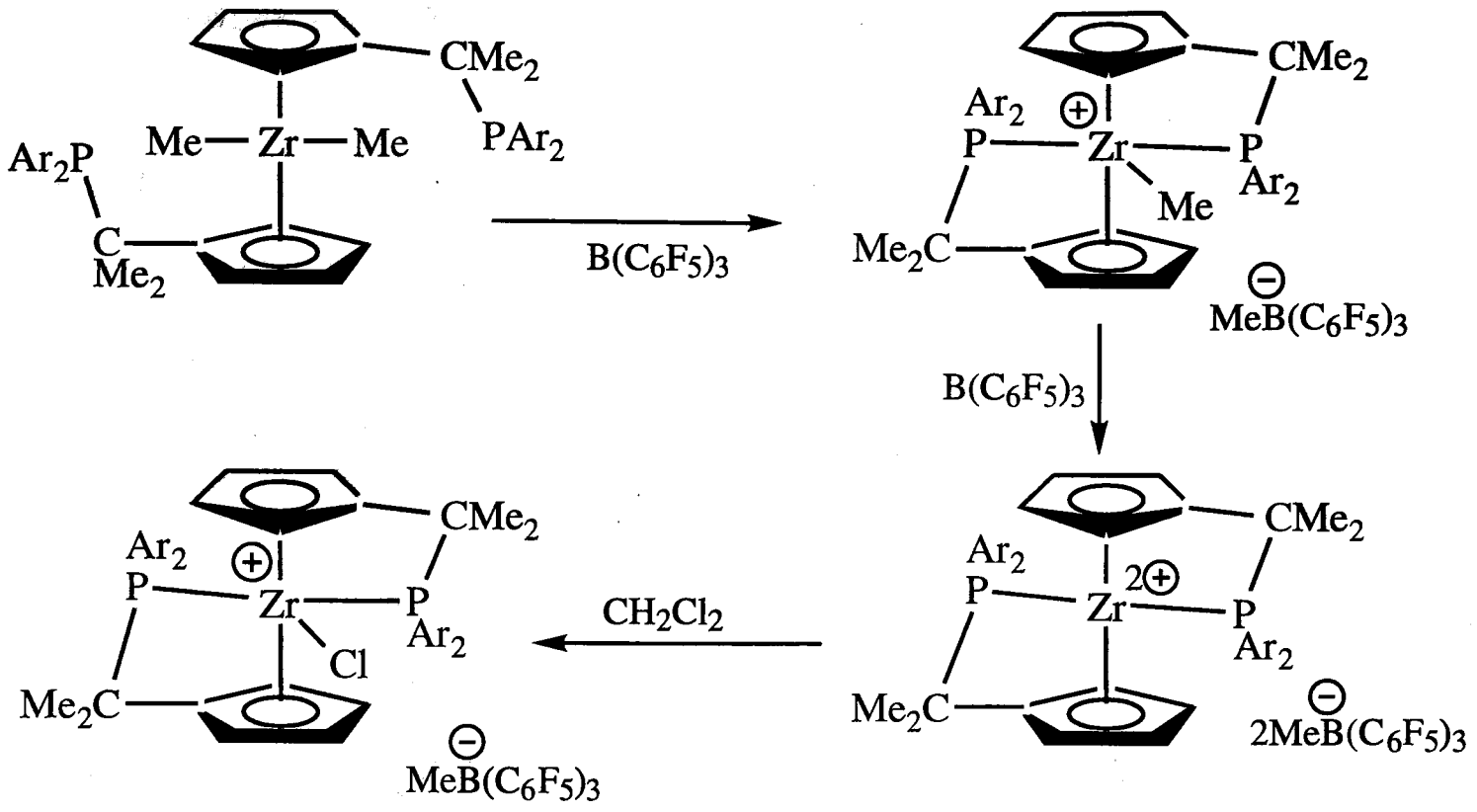


Fig. 1.7: Reaction of $B(C_6F_5)_3$ with a phosphine-donor substituted metallocene.

1.3.1.5 Reaction with Non-Cyclopentadienyl Supported Methyl Complexes

A chelating *bis*-amide complex of titanium, $[(ArN(CH_2)_3NAr)TiMe_2]$ has been shown to form an active polymerisation catalyst, $[(ArN(CH_2)_3NAr)Ti(Me)(\mu\text{-}Me)(B(C_6F_5)_3)]$, on treatment with $B(C_6F_5)_3$.[37] The catalyst becomes deactivated *via* elimination of methane and unexpected cleavage of a B-(C_6F_5) bond to yield $[(ArN(CH_2)_3NAr)Ti(CH_2B(C_6F_5)_2)(C_6F_5)]$.

Other amide complexes, $[((Me_3Si)_2N)_3MMe]$ (M=Zr or Hf), have been shown to react with $B(C_6F_5)_3$, removing the methide group entirely and forming $[((Me_3Si)_2N)_3M][MeB(C_6F_5)_3]$ in which the cation is stabilised by M-C and M-Si interactions.[38]

1.3.2 Attack on a Non-Methyl Alkyl Complex of a Group 4 Metal

1.3.2.1 Reaction with Benzyl Complexes

Reaction between dibenzyl complexes of the type $[(\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2)_2Zr(CH_2Ph)_2]$ and $B(C_6F_5)_3$ leads to an non-associated ion pair of the form $[(\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2)_2Zr(\eta^2\text{-}CH_2Ph)][PhCH_2B(C_6F_5)_3]$.[19] Cation-anion non-association persists in solution even at temperatures up to 60 °C and partly explains the utility of these compounds as alkene polymerisation catalysts.

A further example of attack by $B(C_6F_5)_3$ at a metal-benzyl bond is reported by Pellecchia who published the molecular structure of the novel complex formed by the reaction of $[Zr(CH_2Ph)_4]$ with $B(C_6F_5)_3$ (Fig. 1.8).[39]

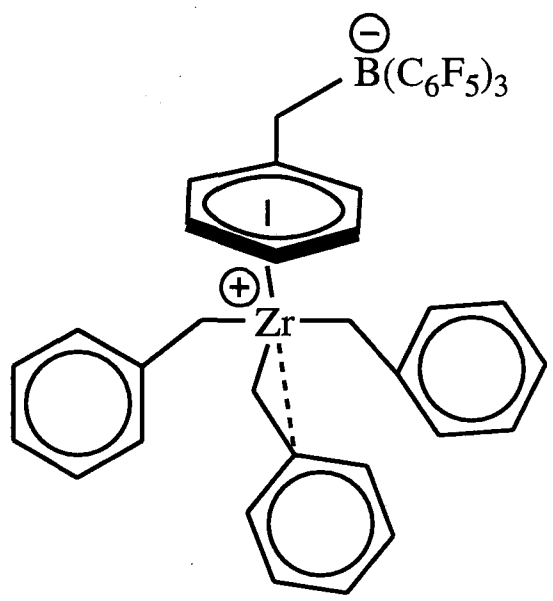


Fig. 1.8: The product formed in the reaction $[Zr(CH_2Ph)_4] + B(C_6F_5)_3$.

As previously observed, the Lewis acid pulls one alkyl group away from the metal centre to create an electron-deficient cation which is stabilised both by one of the remaining benzyl groups adopting an η^2-coordination mode and also by coordination of the $(PhCH_2B(C_6F_5)_3)^-$ fragment in an η^6 fashion. This mode of arene coordination, although common for low-valent metals *e.g.* $[(\eta^6\text{-arene})_2Ti]$ (arene = (C_6H_6), $(C_6H_5CH_3)$ or $(1,3,5\text{-}C_6H_3(CH_3)_3)$)[40] or $[(\eta^6\text{-}C_6H_5CH_3)_2M(PMe_3)]$ (M = Zr, Hf),[41] is rare for a d^0 tetravalent metal and had previously only been found for $[(\eta^6\text{-}$

$C_6H_5BPh_3)Zr(CH_2Ph)_3]$, described by Bochmann.[42] More recent work has shown that $B(C_6F_5)_3$ can cause such a coordination in a wide variety of systems (*vide supra*).[30] This non-metallocene system is moderately active for alkene polymerisation.[43]

A further non-cyclopentadienyl supported benzyl complex, namely $[(^tBuNSi(Me)_2N^tBu)Zr(CH_2Ph)_2]$, was reported to react with $B(C_6F_5)_3$.[44] The displaced benzyl ligand, coordinated to boron, binds to the metal *via* η^6-arene coordination as previously observed which may be subsequently displaced by two molecules of thf. In contrast, the same reaction with the neopentyl analogue, $[(^tBuNSi(Me)_2N^tBu)Zr(CH_2CMe_3)_2]$, forms a separate ion pair, although it is believed that the cation is stabilised by weak solvent coordination.

1.3.2.2 Reaction with "Tucked-In" Metallocene Complexes

Reactions of complexes of the type $[Cp^*(\eta^5\text{-}\eta^1\text{-}C_5Me_4CH_2)ZrR]$ (R = Cl, Me, Ph) with $B(C_6F_5)_3$[45] and $HB(C_6F_5)_2$[46] have been studied. In both cases, insertion of the borane into the CH_2-Zr bond is observed, and the metal centre stabilised by a variety of interactions from the groups around boron (Fig. 1.9).

1.3.3 Attack at an Alkene, Alkyne or Butadiene Coordinated to a Group 4 Metal

Piers *et al.* have published papers on the reaction of zirconocene phosphine olefin complexes of with $HB(C_6F_5)_2$ (Fig. 1.10)[47, 48] where attack takes place at the alkene after the phosphine ligand has been removed by an additional molecule of $HB(C_6F_5)_2$. The cationic zirconium centre thus formed is stabilised both by the bridging hydrogen and the β-carbon atoms attached to the anionic borate counterion.

Dienes coordinated to metal centres will also react with strong Lewis acids; for instance, treatment of $[(\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2)Zr(\eta^3\text{-}C_3H_5)(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)]$ with $B(C_6F_5)_3$ results in the conversion of the η^4-dienyl ligand to an η^3-dienyl and stabilisation of the cationic metal centre by C-H...Zr bonding (Fig. 1.11).[49]

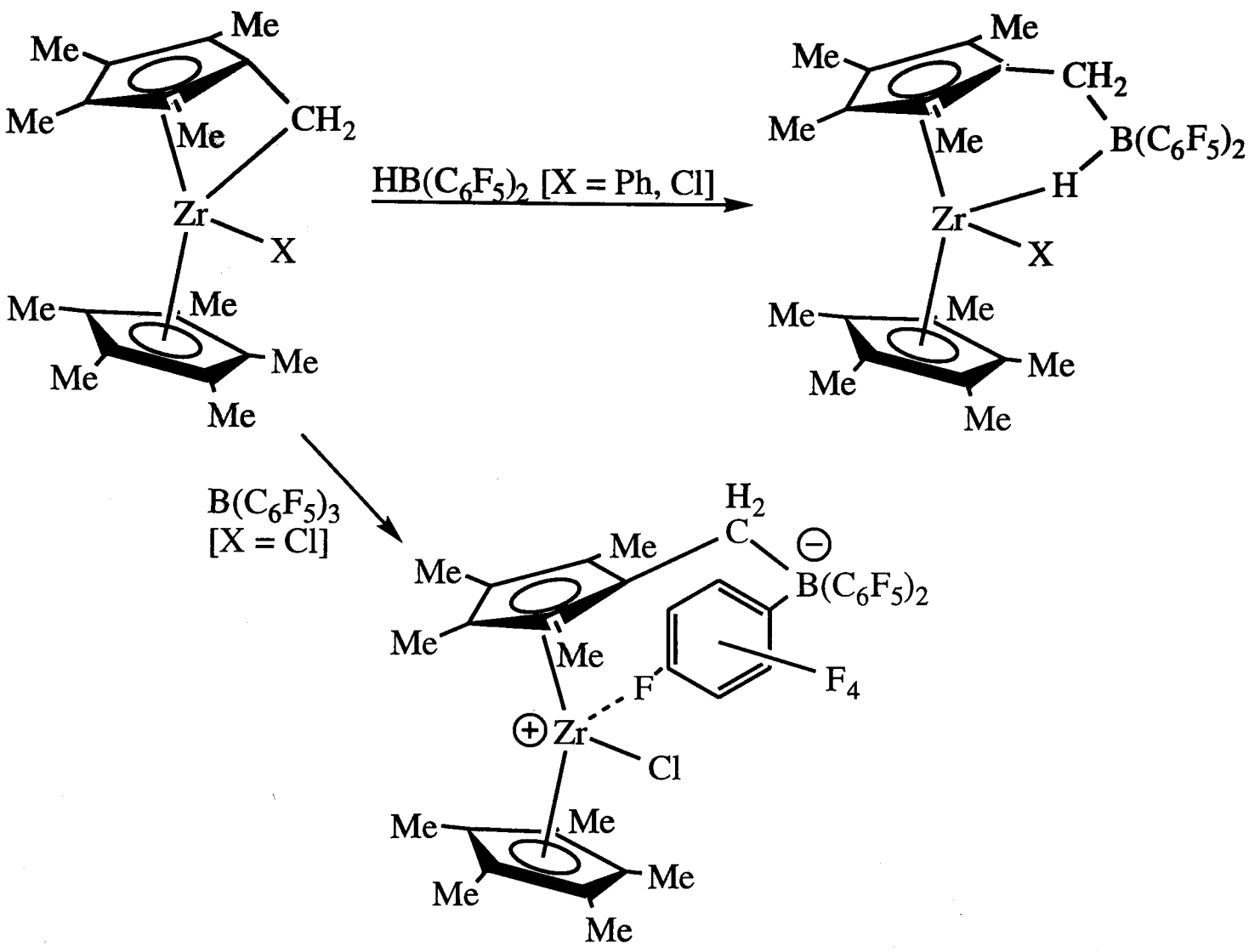


Fig. 1.9: Reactions of $B(C_6F_5)_3$ with 'tucked-in' metallocene complexes.

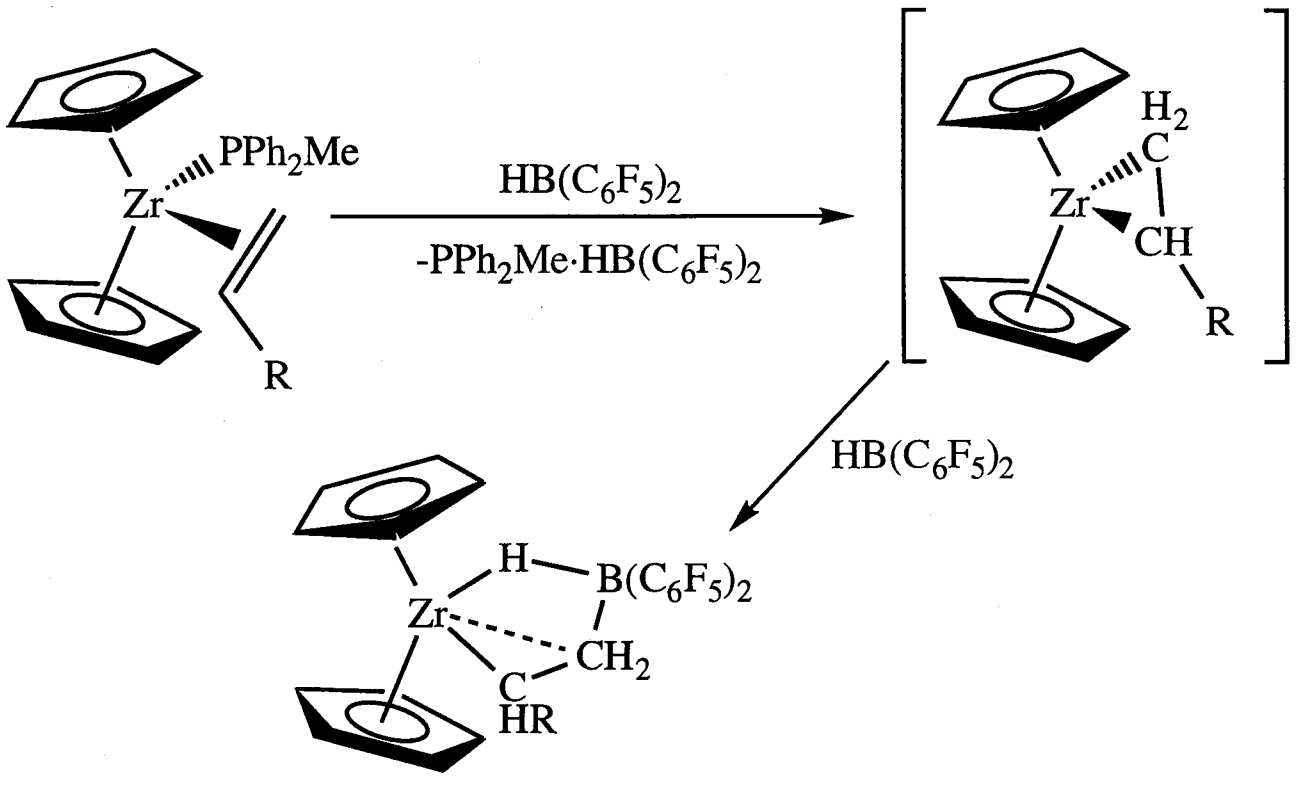
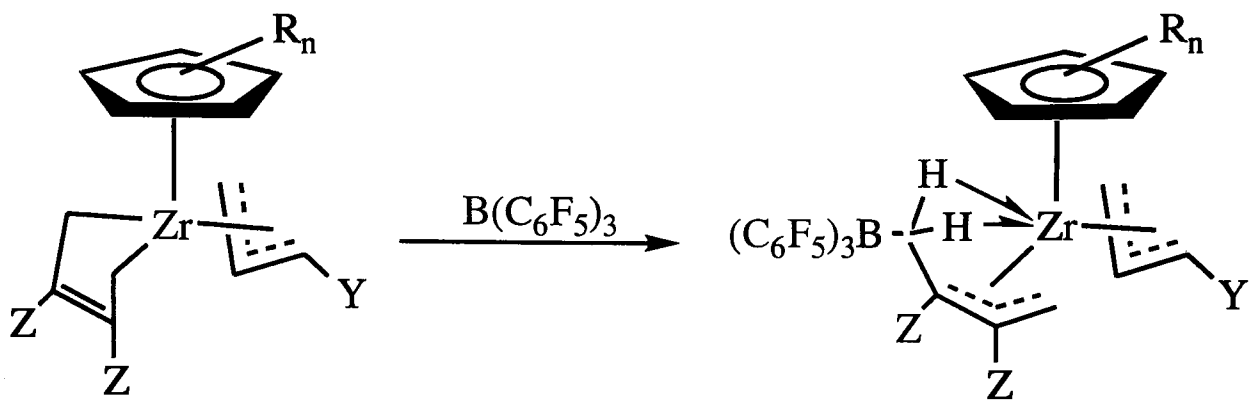


Fig. 1.10: Reaction of $HB(C_6F_5)_2$ with a phosphine olefin complex of zirconium.



[R_n = 1,3-$(SiMe_3)_2$, Y = H, Z = Me;
R_n = 1,3-$(SiMe_3)_2$, Y = Me, Z = H;
R_n = Me_5, Y = Me, Z = H]

Fig. 1.11: Unusual stabilisation of a cationic zirconium centre.

This unexpected multicentre interaction was confirmed by the unusually high-field ^1H NMR spectroscopic shift of these protons. Earlier studies[50-54] of reactions between the compounds $[Cp_2Zr(CH_2{=}CHCH{=}CH_2)]$ and $B(C_6F_5)_3$ show that simple addition products form where a distorted π-allyl moiety coordinates to a bent metallocene unit. The metal centre in the (η^5-C_5H_5) case achieves steric saturation by coordination of one of the *ortho*-fluorines from the borate moiety, whereas in the complex $[Cp^*_2Zr(\eta^3\text{-}CH_2CHCHCH_2B(C_6F_5)_3)]$, the borate 'dangles' loose and a vacant coordination site is found on the metal centre (Fig. 1.12). Both complexes catalyse alkene polymerisation.

Recent work has attempted to elucidate the nature of the intermediate species formed by insertion of active olefins into the catalyst system[53] and studied the nature of the protecting interaction between the fluorine and metal centre.[54]

Cyclopropenylioborate betaine complexes may be formed when *bis*(propynyl)zirconocene is reacted with $B(C_6F_5)_3$ followed by treatment with ^{t}BuNC.[55] The reaction appears to proceed *via* a zwitterionic complex formed by the coupling of the propynyl ligands and subsequent coordination of $B(C_6F_5)_3$ (Fig. 1.13). The reactivity of this complex with isonitriles has been probed.[56]

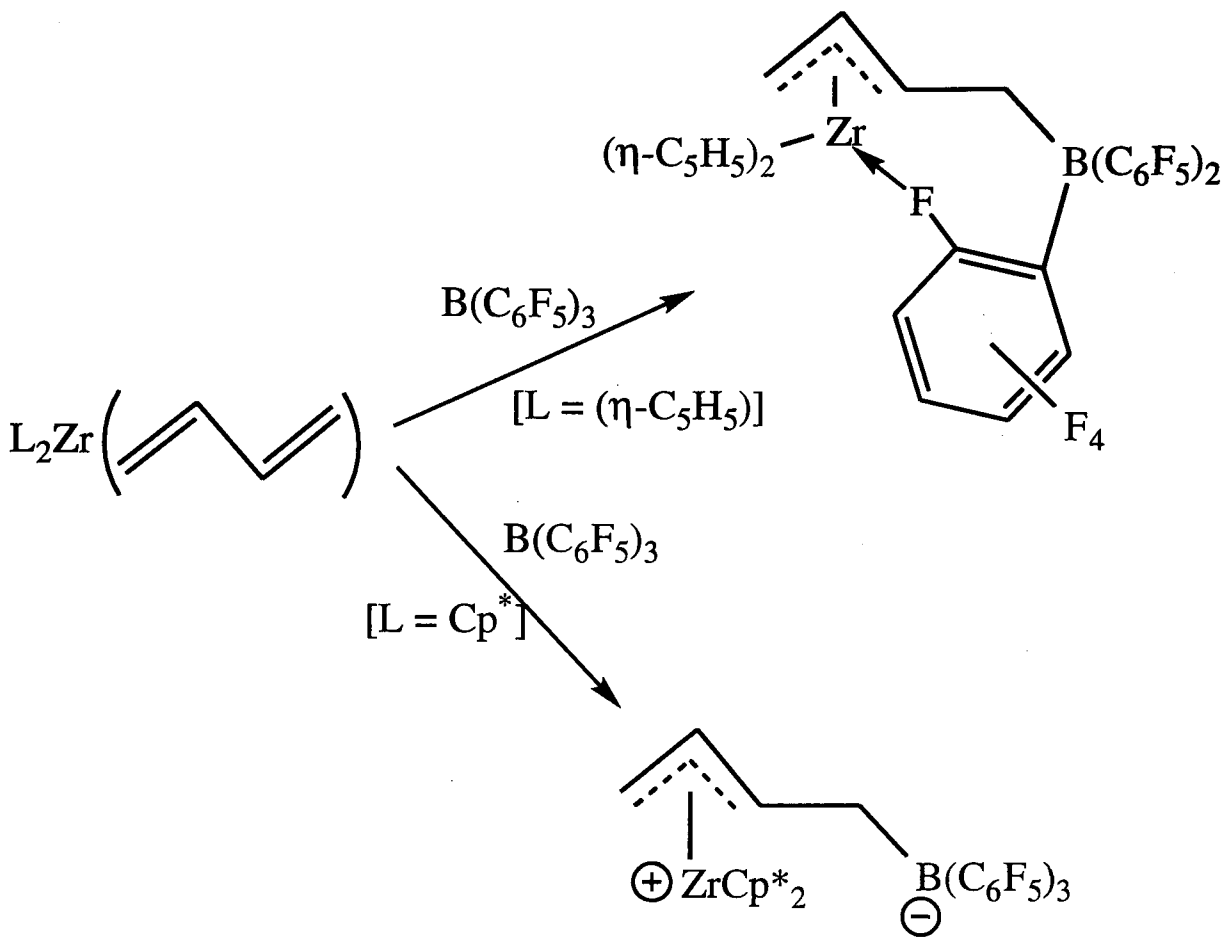


Fig. 1.12: Reaction between $B(C_6F_5)_3$ and butadiene-zirconocene complexes.

1.3.4 Catalytic Studies Using Organoboranes as Co-Catalysts

As has been noted in the above text, many of the novel compounds resulting from the interaction of group 4 metallocene complexes and $B(C_6F_5)_3$ are active as polymerisation catalysts for olefins. This is unsurprising given that Ziegler-Natta polymerisation is believed to occur *via* an active "14 electron" species and many of these complexes contain such a metal centre, stabilised to some degree by a weak interaction with a large, weakly coordinating anion or the solvent, but nevertheless easily attacked by an alkene to form a polymer chain. The area of Ziegler-Natta olefin polymerisation catalysis by cationic "14 electron" species of group 4 has been reviewed in 1996 by Bochmann.[57]

As well as the work cited above mainly for its synthetic interest, there have been many studies in the field of catalytic systems produced by strong boron-containing Lewis acids. As might be expected, most are based on metallocene systems of group 4 including Cp_2MMe_2,[58-61] $Cp_2M(CH_2Ph)_2$,[62] $CpMMe_3$,[63, 64] $CpM(CH_2Ph)_3$[65, 66] and $CpM(L)Me_2$.[67] Marks has also investigated the use of actinide metallocene methyl

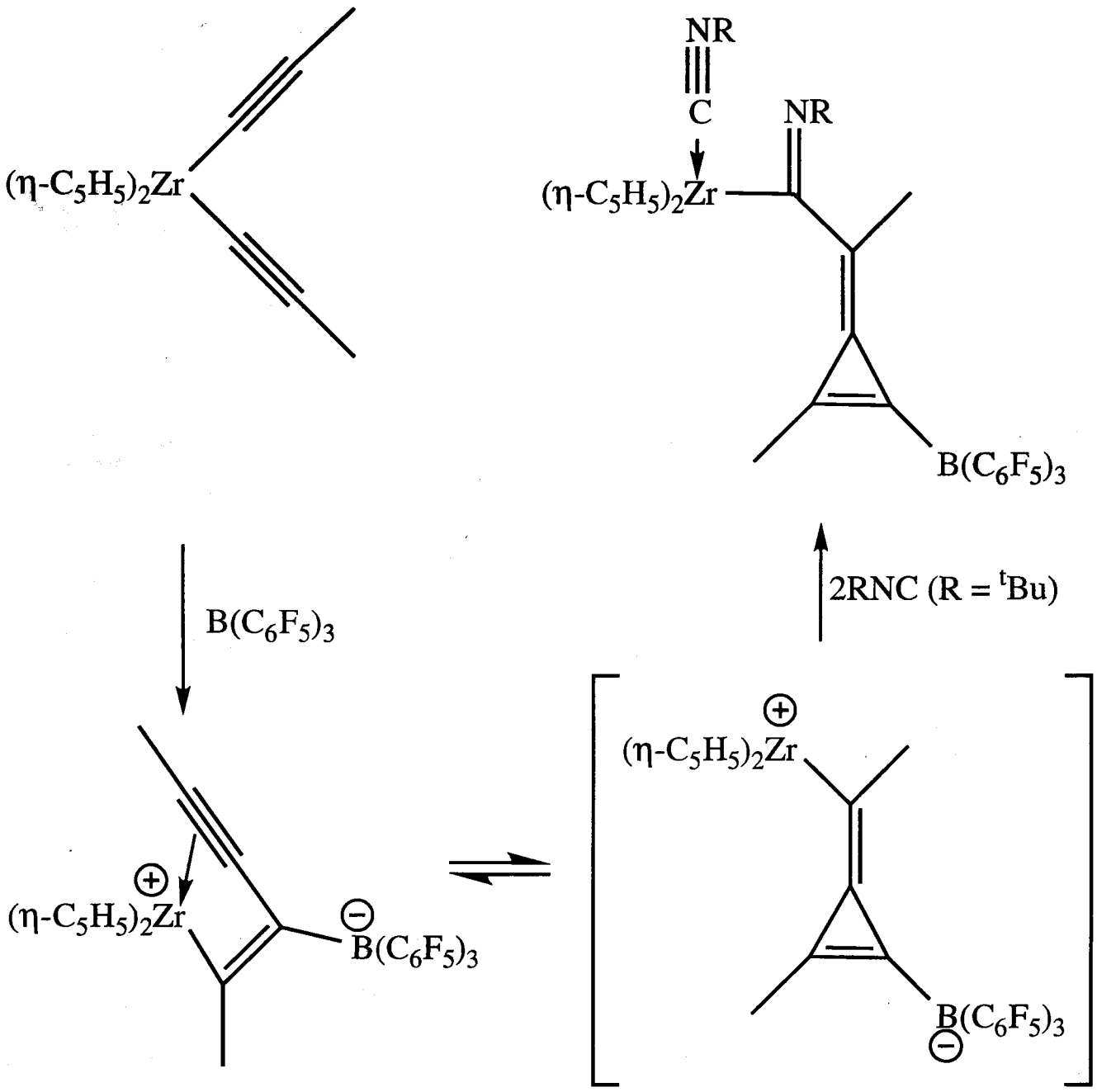


Fig. 1.13: Reaction between $B(C_6F_5)_3$ and bis-propynyl zirconocene.

complexes as catalyst precursors.[68] Other work has attempted to form a one-component catalysis system by appending $B(C_6F_5)_n$ groups to a cyclopentadienyl ligand *e.g.* Bochmann has published the syntheses of $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2)HfMe_2][NEt_4]$ and $[(PhCH_2)_3Zr(\eta^5\text{-}C_5H_4\text{-}B(C_6F_5)_2\text{-}\eta^5\text{-}C_5H_4)Zr(CH_2Ph)_3][Li(thf_4)]$.[69] Piers has produced several metallocene-based catalysts with pendant $B(C_6F_5)_2$ groups using a hydroboration technique with $HB(C_6F_5)_2$ (Fig. 1.14).[70]

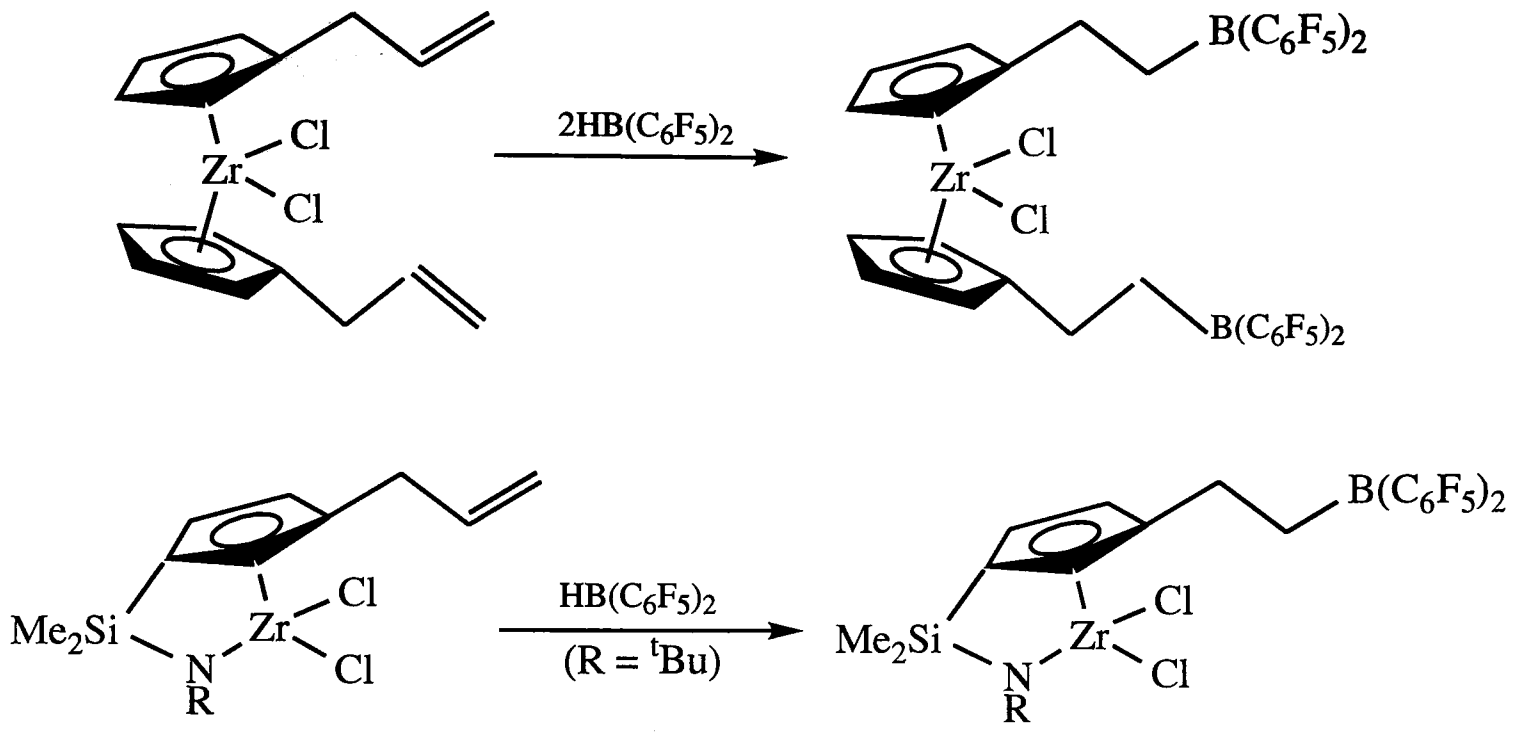


Fig. 1.14: Formation of intramolecular one-component Ziegler-Natta catalysts by hydroboration.

Other workers have concentrated on the role of the anion in determining the polymer structure,[71, 72] the development of bulkier and thus more weakly coordinating anions[73-75] and the use of chiral metallocenes to produce stereospecific polymerisation.[6, 76-78] Very few reports of catalysis using non-group 4 compounds exist; one example is the imide complex $[Cp^*Ta(N(2,6\text{-}C_6H_3{}^iPr_2))(\eta^3\text{-}C_3H_5)(CH{=}CH\text{-}CH{=}CH_2)]$.[79]

1.3.5 Reaction with Complexes of Other Metals

Work in this laboratory discovered a novel and unexpected reaction between $[(\eta^5\text{-}C_5H_5)M(CO)_nMe]$ and $B(C_6F_5)_3$ (M = Fe, n = 2; M = Mo or W, n = 3) (Fig. 1.15).[80-84] The preferred site of attack in this case appears to be at one of the carbonyl ligands followed by migration of the methyl group and insertion of a C_6F_4- moiety into the metal-acyl bond with consequent elimination of various fluoro(pentafluorophenyl)borane species, $BF_x(C_6F_5)_{3-x}$ (x = 1-3). This is a further example of the cleavage of a B-C_6F_5 bond as described above;[37] yet another is reported by Metzler and Denk in the slow decomposition of a silylene-$B(C_6F_5)_3$ adduct.[85]

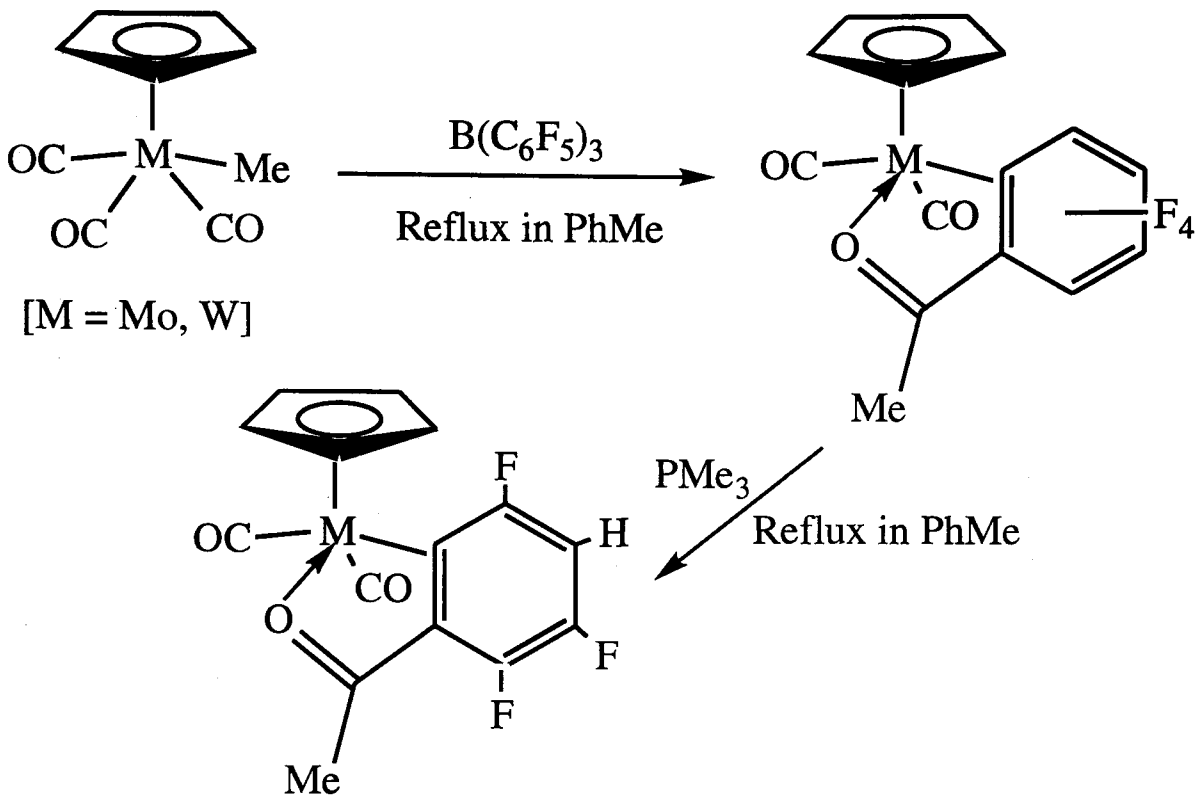


Fig. 1.15: The unexpected reaction between [(η^5-C_5H_5)M(CO)$_3$Me] and B(C_6F_5)$_3$ [M = Mo or W].

Puddephatt has studied the reactivity of methyl complexes of platinum with B(C_6F_5)$_3$.[86, 87] Reaction of either [(bipy')Pt(Cl)Me] or [(bipy')PtMe$_2$] (bipy' = 4,4'-di-*tert*-butyl-2,2'-bipyridine) occurs *via* abstraction of a methyl group to yield a vacant site on platinum which is readily filled by a nucleophile such as ethene, CO or PPh_3. Additionally, in the presence of water, B(C_6F_5)$_3$ is believed not to attack a methyl group directly but rather to form an adduct which acts as a strong acid, H[HOB(C_6F_5)$_3$], protonating off a methyl group as methane and either coordinating in the vacant site itself to yield [(bipy')Pt(Me)(O(H)B(C_6F_5)$_3$)] or opening the way for attack by a nucleophile as already outlined. This chemistry is summarised below (Fig. 1.16).

Lastly, Bochmann observed a remarkable reaction between [(η^5-C_5H_5)$_2$AlMe] and B(C_6F_5)$_3$ which yields [(η^5-C_5H_5)$_2$Al]$^+$[MeB(C_6F_5)$_3$]$^-$ implying, most unexpectedly, that the borane is a stronger Lewis acid than the aluminocenium cation.[88] This ion pair is active as an initiator for the carbocationic polymerisation of isobutene and improves on the typical industrial catalyst, $AlCl_3$, by operating closer to ambient temperatures and in non-chlorinated solvents.

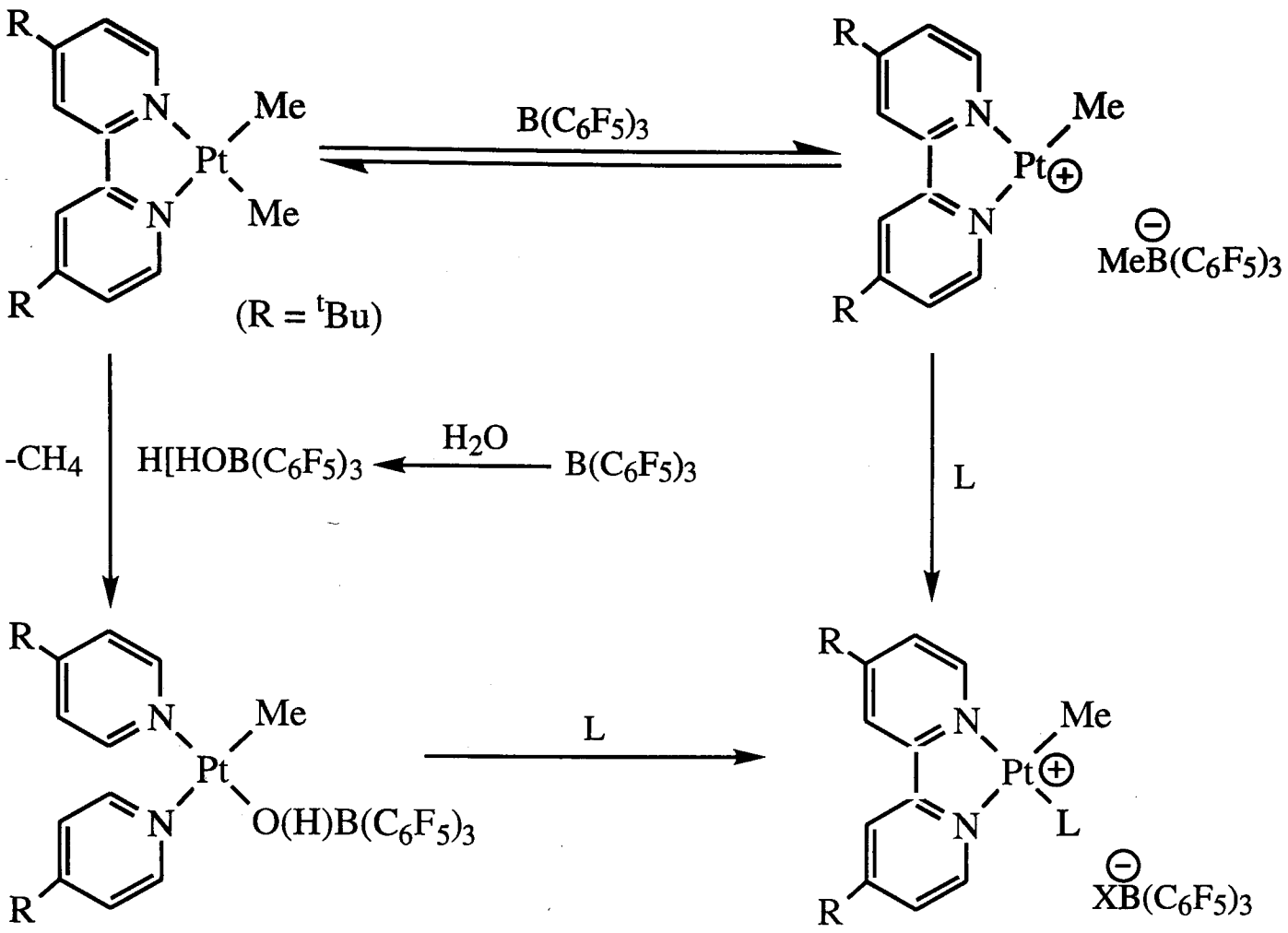


Fig. 1.16: Reactions between a bipyridyl dimethyl complex of platinum and $B(C_6F_5)_3$.

1.4 Electrophilic Addition to Neutral Metal-Hydrogen and Metal-Nitrogen Single Bonds

As expected, $B(C_6F_5)_3$ abstracts hydride from the complex $[(\eta^5\text{-}C_5H_5)_2ZrH_2]$.[89] However, the mode of binding between the metallocene cation and the $[HB(C_6F_5)_3]^-$ anion is somewhat unexpected since it is *via* two fluorines (*ortho* and *meta*) on one of the C_6F_5- moieties and the hydride is held well away from the metal centre (Fig. 1.17).

A second example of hydride abstraction is reported following the reaction of $B(C_6F_5)_3$ with the dimer $[(\eta^5\text{-}C_5H_5)_2ZrC(H)(Me)O]_2$, opening one of the metallaoxirane groups (Fig. 1.18).[90]

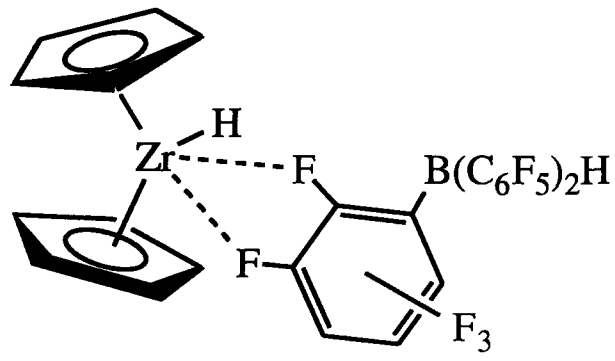


Fig. 1.17: Product formed in the reaction [(η-^{5}C$_5$H$_5$)$_2$ZrH$_2$] + B(C$_6$F$_5$)$_3$.

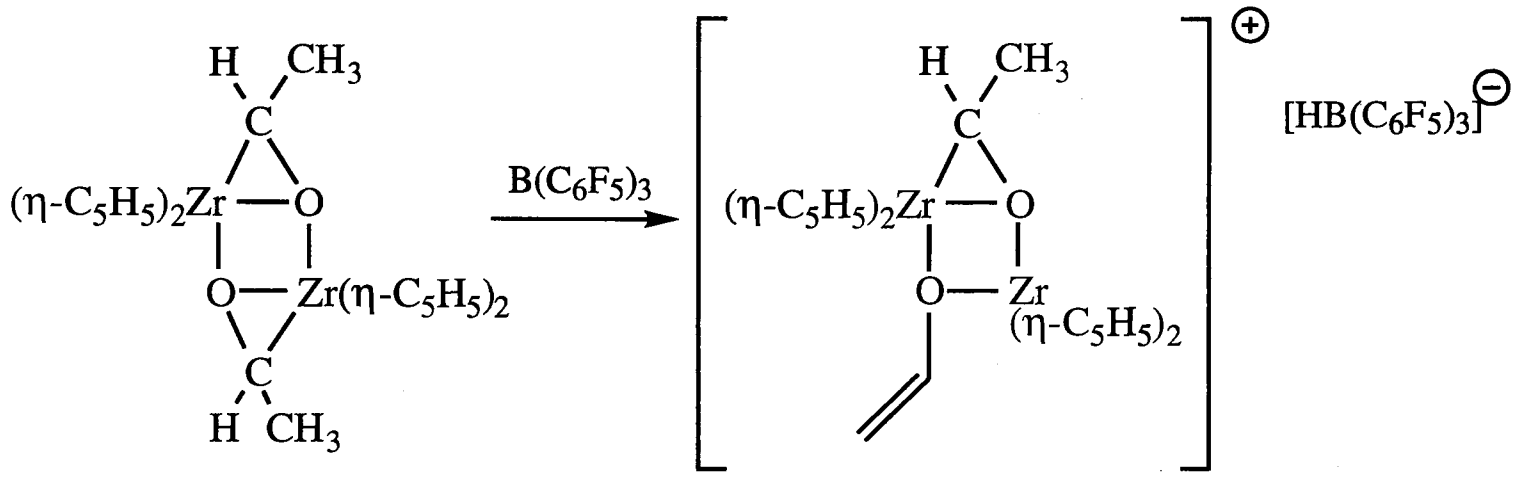


Fig. 1.18: Hydride abstraction by B(C$_6$F$_5$)$_3$ from a metallaoxirane dimer.

Metal-nitrogen single bonds are also susceptible to attack by B(C$_6$F$_5$)$_3$ as demonstrated in the removal of the pyrrolyl ligand from [(η^5-C$_5$H$_5$)$_2$Zr(Me)(N-pyrrolyl)] as a borane adduct, thus freeing a coordination site on the cationic zirconium centre.[91] However, the borane reacted with both [(η^5-C$_5$H$_5$)$_2$Zr(Me)(N-piperidyl)] and [(η^5-C$_5$H$_5$)$_2$Zr(Me)(NEt$_2$)], to remove the methyl group rather than the amide. In both of these cases, the product is thermally unstable and eliminates methane (Fig. 1.19).

1.5 Electrophilic Attack at a Metal-Coordinated Cyclopentadienyl Ring or at a Metal Centre

Two reports of attack at a metal-coordinated cyclopentadienyl ring by strong boron-containing Lewis acids have been published recently. The first is the reaction of dichloroalkylboranes, RBCl$_2$ (where R = ^{i}Pr or ^{t}Bu), with [(η^5-C$_5$H$_5$)$_2$WH$_2$] causing

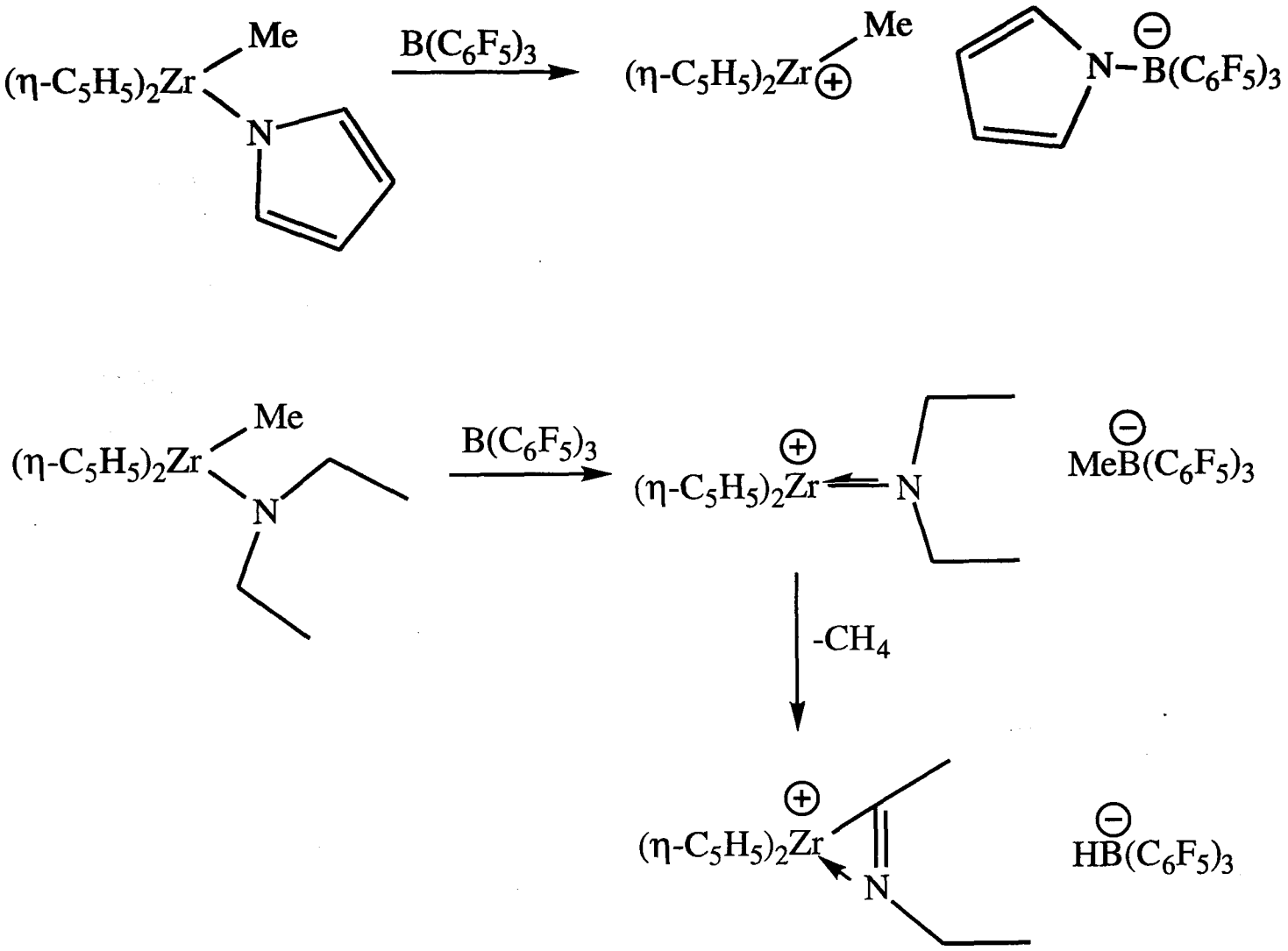


Fig. 1.19: Reactions of $B(C_6F_5)_3$ with some amide methyl zirconocenes.

displacement of a proton from one of the Cp rings and formation of a zwitterionic trihydride cation (Fig. 1.20).[92]

Similarly, $B(C_6F_5)_3$ attacks a Cp ring in 1,1-*bis*(cyclopentadienyl)-2,3,4,5-tetramethylzirconacyclopentadiene to form a zirconocene-betaine system (Fig. 1.21).[93]

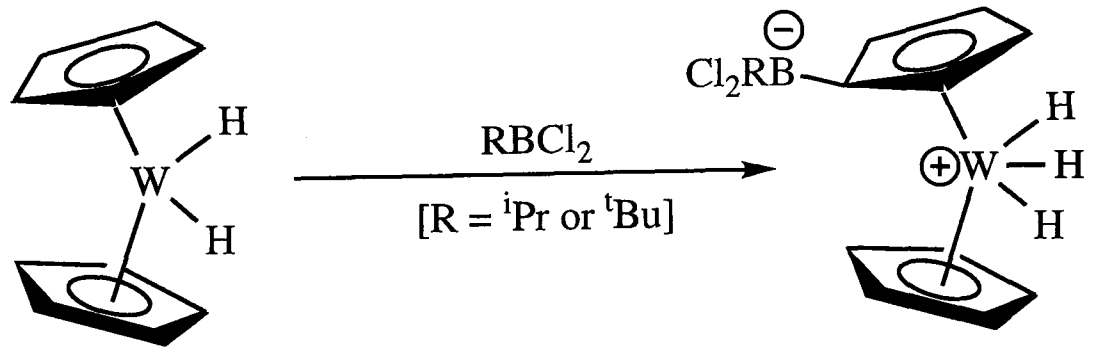


Fig. 1.20: Reaction between $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and dichloroalkylboranes.

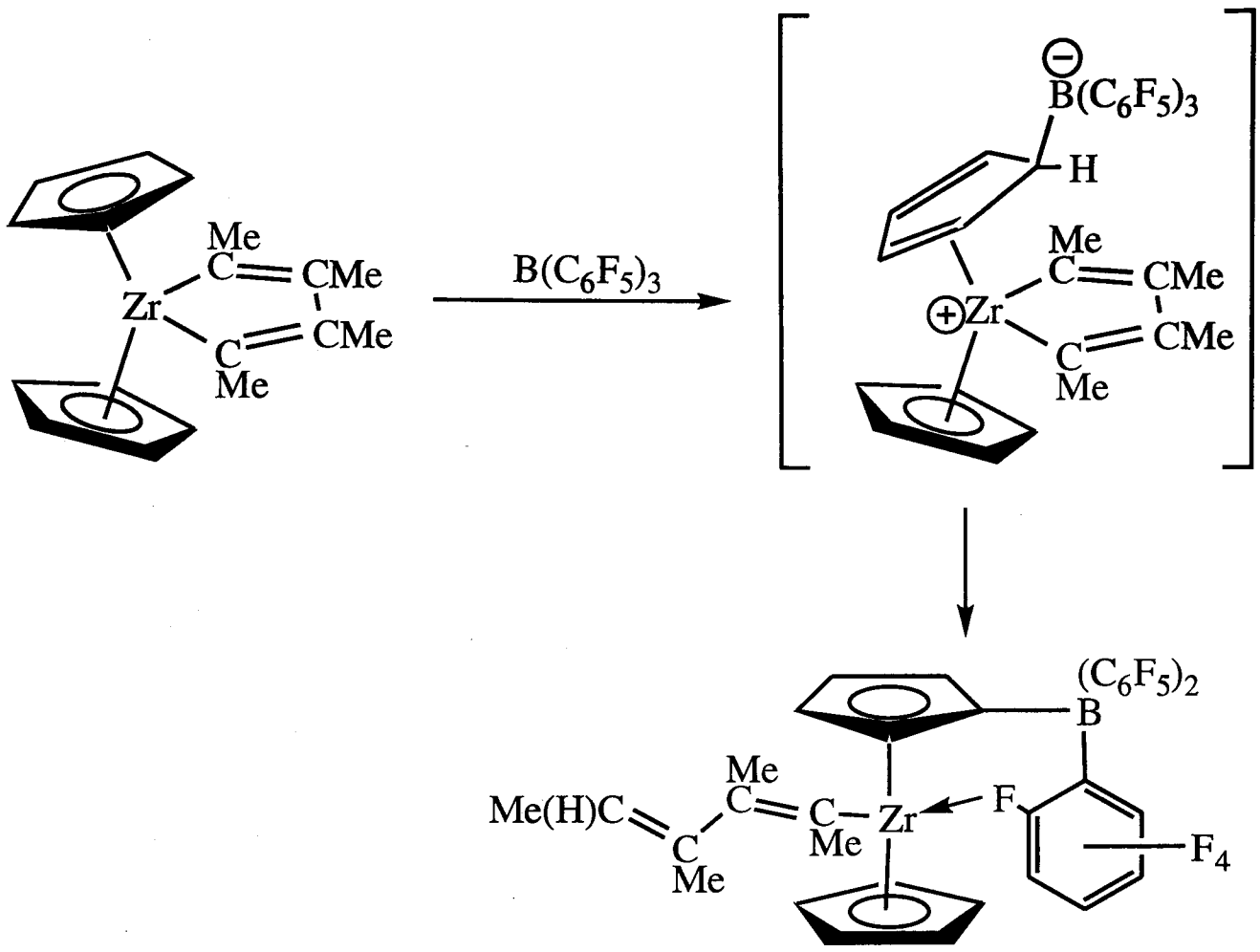


Fig. 1.21: Formation of a zirconocene-betaine system.

Attack by boron compounds at metal centres has been described by Shriver[94, 95] who reports that BF_3 and BCl_3 coordinate to the metal lone pair present in the hydride complexes $[(\eta^5\text{-}C_5H_5)_2WH_2]$, $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ and $[(\eta^5\text{-}C_5H_5)_2ReH]$. Characterisation was by means of infrared spectroscopy and tensiometric titrations and it was observed that B_2H_6 did not react similarly.

Although not strictly speaking attack at a metal, one unexpected reaction of $B(C_6F_5)_3$ that should be mentioned is its use as a C_6F_5-transfer reagent in the synthesis of pentafluorophenyl-xenon compounds:[96, 97]

$$\mathbf{XeF_2 + B(C_6F_5)_3 \longrightarrow [Xe(C_6F_5)][F_2B(C_6F_5)_2]}$$

1.6 Electrophilic Attack at M-E Multiple Bonds (E = O or N)

Multiply-bonded M=O and M≡N units are electron-rich and fairly common in the literature so it is unsurprising that there exist several known examples in which these

groups coordinate to strong boron-containing electrophiles. Lewis acid metal-oxo adducts are formed between $[MO_n(acac)_2]$ (M = V or Ti, n = 1; M = Mo, n = 2) and $B(C_6F_5)_3$.[98] Structural characterisation of these complexes has revealed an almost linear M-O-B linkage (angle between 165.8 ° and 171.2 °) and a slight lengthening of the M=O bond distance. Cyclopentadienyl-supported metal-oxo complexes have also been shown to form adducts with $B(C_6F_5)_3$ (Fig. 1.22).[99]

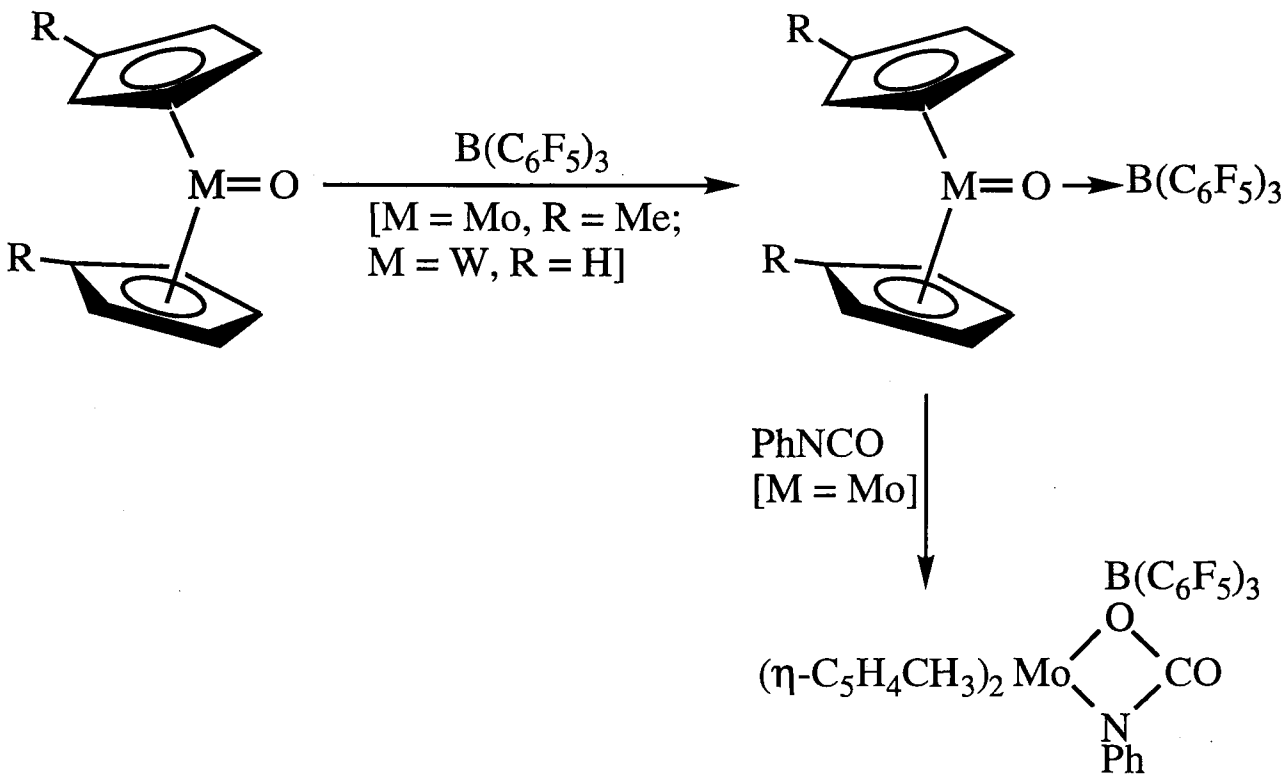


Fig. 1.22: Reaction of cyclopentadienyl group 6 oxo compounds with $B(C_6F_5)_3$.

In the case of further reaction with phenylisocyanate, the site of the borane is suggested by NMR spectroscopy and confirmed by Density Functional Theory calculations.

A further example of $B(C_6F_5)_3$ bonding to an oxygen lone-pair is reported by Otero who reacted $[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(R)(\eta^2\text{-}CO_2)]$ (R = Et or CH_2CH_2Ph) with $B(C_6F_5)_3$ to give initially simple, isolable, adducts with reaction occurring at the C=O moiety.[100] These species lose CO to yield the complexes $[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(R)(OB(C_6F_5)_3)]$. One example where the B-O bond is not actually formed in the reaction is the formation of $[(\eta^5\text{-}C_5H_5)_2Zr(Me)(OB(C_6F_5)_3)]$ in the reaction of $[(\eta^5\text{-}C_5H_5)_2ZrMe_2]$ with $[Et_3NH][(C_6F_5)_3BOH]$,[101] but elimination of

methane and formation of a zirconoxyborane, $[(\eta^5\text{-}C_5H_5)_2Zr(OB(C_6F_5)_3)]$, which is stabilised by a short (2.346 Å) Zr-F interaction, occurs.

The reactivity of boron compounds with metal-nitrido complexes has a much longer history which began with Chatt who isolated the adducts between BX_3 (X = F, Cl or Br) and *mer*-$[NReX'_2(PEt_2Ph)_3]$ (X' = Cl or Br).[102] These compounds were characterised by microanalysis and infrared spectroscopy and their stability was found to decrease in the order $BBr_3>BCl_3>BF_3$, consistent with the predicted order for Lewis acidity of these boranes.[13]

This work has been extended by Abram to include the BCl_3 adduct of the complex $[NRe(PMe_2Ph)(Et_2NCS_2)_2]$[103] and also the BPh_3 adduct of the same complex.[104] The latter species was not synthesised by direct reaction, but rather by addition of acetone and concentrated HCl to the parent nitrido compound followed by reaction with $Na[BPh_4]$. Of less relevance to this work is Abram's synthesis of the trichlorogallane adducts $[Cl_3GaNReCl_2(PMe_2Ph)_3]$ and $[Cl_3GaNReCl(PMe_2Ph)_3(NCMe)][GaCl_4]$.[105] A reaction is also observed between BF_3 and $[(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2]$.[106]

1.7 Conclusions

This chapter has provided an overview of the chemistry of strongly electrophilic Lewis acids containing boron. The emphasis has been placed on synthetic routes although the utility of these compounds in Ziegler-Natta olefin polymerisation has also been touched upon. The reactivity of boron Lewis acids with a range of organometallic compounds, both metallocenes and metals supported by other ligands, has been reviewed and illustrates the importance and interest of these compounds in the context of synthetic chemistry.

The work in this thesis attempts to extend this chemistry in two directions- the reaction of strong Lewis acids of the form $RB(C_6F_5)_2$ (R = (C_6F_5), Ph, H, Cl) with *bis*-cyclopentadienyl hydrides of the metals of groups 5, 6 and 7 and also reactions of *tris*(pentafluorophenyl)borane with nitrido complexes of group 6, 7 and 8 metals.

Chapter Two presents the reactivity of some Lewis acids containing a boron-pentafluorophenyl group with metallocene hydride compounds and Chapter Three describes the reactions of *tris*(pentafluorophenyl)borane with nitrido complexes of molybdenum, rhenium and osmium. Chapter Four presents an overview of the range of strong Lewis acids available and synthetic routes to new boron-containing electrophiles. Experimental details for the thesis are presented in Chapter Five and characterising data for previously unpublished compounds are given in Chapter Six.

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Chapter Two

Reactions Between Strongly Electrophilic Boranes and Metallocene Hydride Compounds

2.1 Introduction

This chapter describes reactions between Lewis acids containing a boron-perfluoraryl linkage and *bis*(cyclopentadienyl) hydrides of groups 5, 6 and 7 metals. There are prior reports in the literature of work describing the interactions of these metallocenes with other boranes. Early work explored the reactivity of $[(\eta^5\text{-}C_5H_5)_2MoH_2]$, $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and $[(\eta^5\text{-}C_5H_5)_2ReH]$ towards gaseous BF_3 and BCl_3[1, 2] and the formation of various molybdaborane and molybdacarbaborane species on the reaction of $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ with BH_3·thf under UV light.[3] The work by Shriver and Johnson has, to some extent, been cast into doubt by that of Braunschweig who has observed the contrasting reactivity of $[(\eta^5\text{-}C_5H_5)_2WH_2]$ towards $RBCl_2$ [R = ^{i}Pr or ^{t}Bu][4] and R_2BCl [R = ^{i}Pr or Cl] or BF_3·Et_2O in CH_2Cl_2[5] (Fig. 2.1). In the latter cases, more than one equivalent of the borane is consumed per molecule of dihydride, hence the formation of a $[R_2BCl_2]^-$ or $[BF_4]^-$ counterion. Additionally, as has been described in Chapter One, the product of the reaction between $[Cp^*_2ZrH_2]$ and $B(C_6F_5)_3$ has been characterised.[6]

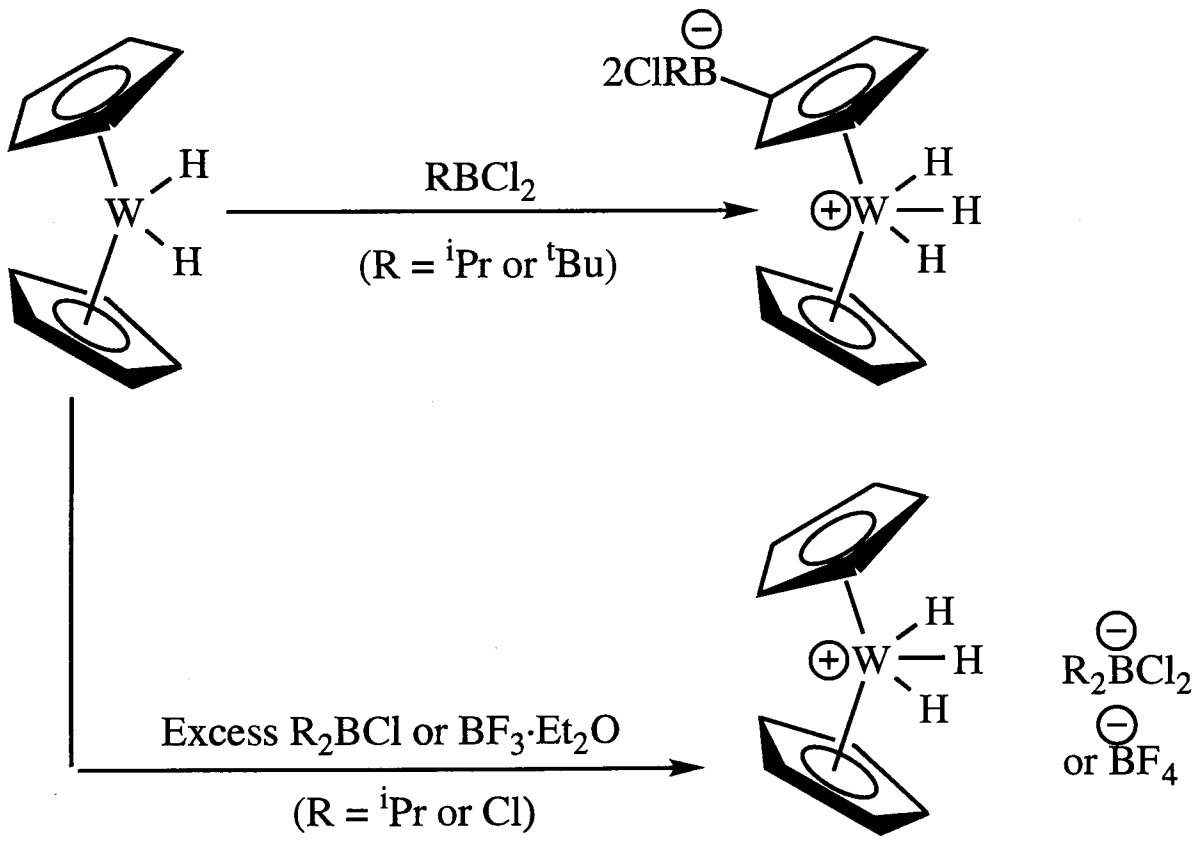


Fig. 2.1: Contrasting reactivity of $[(\eta\text{-}^5C_5H_5)_2WH_2]$ with R_2BCl and $RBCl_2$.

In the present work, the aim was to investigate the reactivity of $RB(C_6F_5)_2$ [R = (C_6F_5), Ph, H or Cl] towards metallocene hydrides of groups 5,6 and 7. It was hoped that, since these metals are more electron-rich than those of group 4, new and interesting reactivity with perfluoroarylborane Lewis acids would be observed. These metallocene hydrides offer several potential sites for electrophilic attack including the lone pair on the metal centre, the cyclopentadienyl rings as well as the metal-bound hydrogen so it was clear that the field was ripe for further study.

2.2 Reactions of Lewis Acids with $[(\eta^5\text{-}C_5H_5)_2WH_2]$

Previous work has described the interaction between $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and $B(C_6F_5)_3$ in the aromatic solvent toluene at -78 °C.[7] A deep purple solution forms immediately but on warming towards room temperature, the colour gradually changes to pale yellow at approximately -50 °C. This final product does not appear to be pure, containing substantial quantities of starting dihydride as well as several other species.

A similar reaction is observed between $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and $B(C_6H_5)(C_6F_5)_2$ (the preparation of this new Lewis acid is described in Chapter Four). However, if the pale yellow solution is allowed to stir overnight it darkens to orange in colour and a white solid precipitates; this further reaction is not observed in the reaction with $B(C_6F_5)_3$. The orange solution was determined to contain only unreacted $[(\eta^5\text{-}C_5H_5)_2WH_2]$ (by ^1H NMR spectroscopy) and the white precipitate was found to be a complex and impure mixture after microanalysis and ^1H NMR spectroscopy in CD_2Cl_2.

No reaction was observed between $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and $B(C_6H_5)_3$ even on prolonged stirring at room temperature; both starting materials were recovered unchanged.

The reaction between $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and $B(C_6F_5)_3$ was investigated using the competing Lewis base NEt_3 (4-picoline, as used to investigate the analogous reaction with $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ (*vide infra*), was unsuitable since it freezes at 2 °C). Excess NEt_3 was added to the purple reaction mixture at -78 °C and also, in a separate experiment, to the pale-yellow room-temperature product. The experiment is summarised

below in Fig. 2.2. In both cases, the final product was a pale yellow solution which, after removal of volatiles *in vacuo* proved to consist of $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and $(C_6F_5)_3B{\cdot}NEt_3$ when analysed by ^1H and $^{11}B\{^1H\}$ NMR spectroscopy.

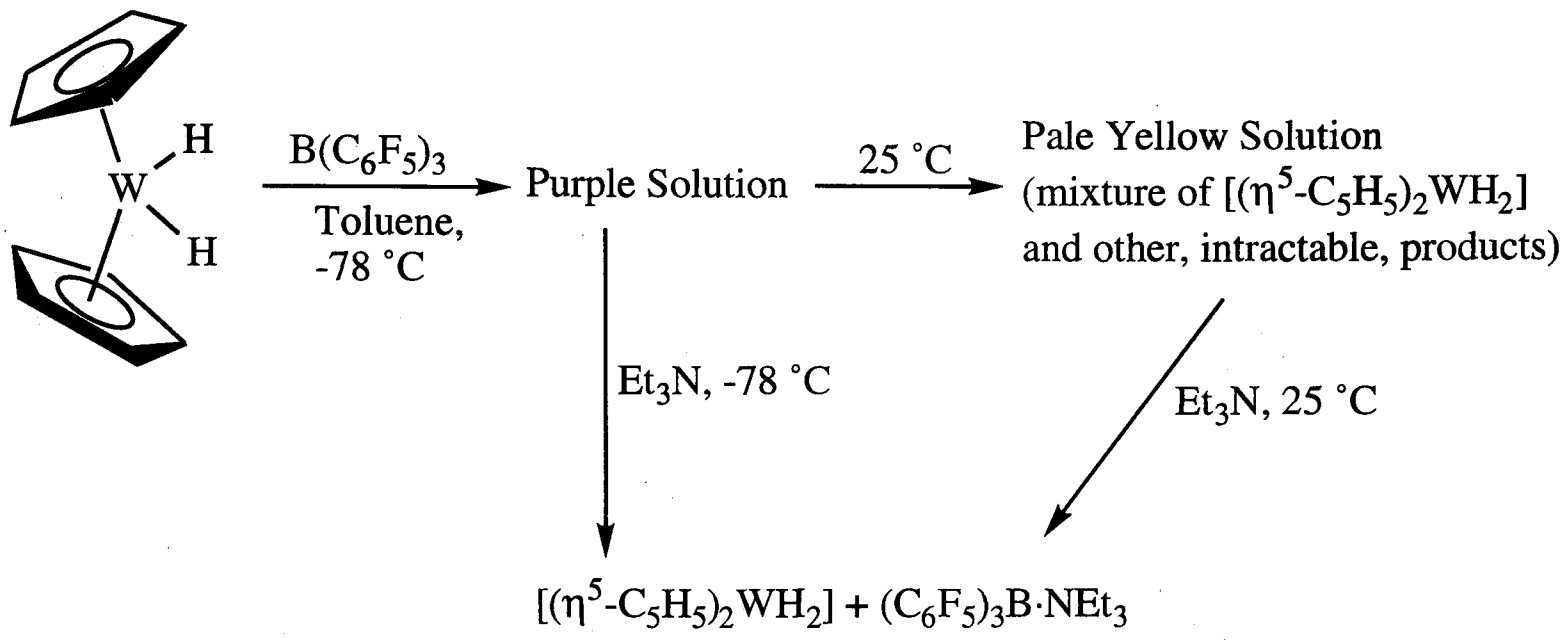


Fig. 2.2: Investigation into the reaction between $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and $B(C_6F_5)_3$ using NEt_3.

These experiments strongly indicate that the purple solution formed initially has a similar structure to the blue product formed by reacting $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ with $B(C_6F_5)_3$[7] and that, in this case, it is still more loosely held together since it decomposes well below ambient temperature. The yellow decomposition product appears to consist of dihydride plus other products which are readily attacked by the competing Lewis base NEt_3.

2.2.1 Formation of the Zwitterionic Complexes $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2R)(\eta^5\text{-}C_5H_5)WH_3]$ {R = (C_6F_5), (C_6H_5), H or Cl} (1, 2, 3 and 4)

The reaction between *bis*(cyclopentadienyl)dihydridotungsten and boranes of the form $RB(C_6F_5)_2$ [R = (C_6F_5), (C_6H_5), H or Cl] performed in an aliphatic solvent at ambient temperature follows an entirely different course. On addition of a solution of $B(C_6F_5)_3$ to $[(\eta^5\text{-}C_5H_5)_2WH_2]$, with both compounds in petroleum ether (b.p. 100-120 °C), a white flocculent precipitate was observed to form instantly. After stirring for one

hour, the product was isolated by filtration and washed thoroughly with hexanes to remove all remaining traces of $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and $B(C_6F_5)_3$. After drying under vacuum overnight, the product (**1**) was obtained analytically pure in 91 % yield, and was found by NMR spectroscopy (see below) to be the zwitterionic compound $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)WH_3]$.

The complexes $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2(C_6H_5))(\eta^5\text{-}C_5H_5)WH_3]$ (**2**), $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2H)(\eta^5\text{-}C_5H_5)WH_3]$ (**3**) and $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2Cl)(\eta^5\text{-}C_5H_5)WH_3]$ (**4**) were obtained in analogous syntheses from $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and the appropriate boranes in yields of 75 %, 72 % and 65 % respectively (Fig. 2.3).

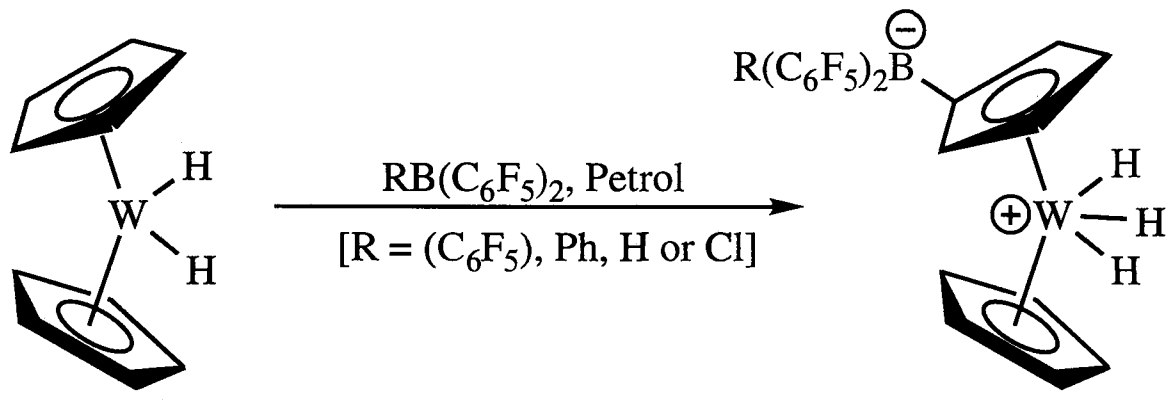


Fig. 2.3: Reactions between $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and the boranes $RB(C_6F_5)_2$ [R = (C_6F_5), (C_6H_5), Cl or H].

2.2.2 Characterisation of the Zwitterionic Complexes $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2R)(\eta^5\text{-}C_5H_5)WH_3]$ {R = (C_6F_5), (C_6H_5), H or Cl} (1, 2, 3 and 4)

All four compounds, **1-4**, yielded satisfactory microanalytical data. The compounds are all white or off-white powdery solids which are moderately soluble in aromatic solvents and reasonably soluble in polar solvents such as dichloromethane. Donating solvents are found to cause decomposition (see Section 2.2.3 below). They are found to be air- and moisture-sensitive but not excessively so in the solid state. Compound **4** is the most air- and moisture-sensitive of the four presumably due to the presence of a boron-chlorine bond. Prolonged storage, even under nitrogen, appeared to

cause some discolouration presumably due to decomposition, although this was only found to be to a small degree.

The compounds can be crystallised by slow evaporation of a dilute benzene solution although the crystals produced by this method were often either too small for X-ray ray diffraction or needles. Needles were also obtained by slow cooling of toluene or dichloromethane solutions to -30 °C.

2.2.2.1 ^{1}H NMR Spectroscopy

^{1}H NMR spectra were obtained of compounds **1-4** in both C_6D_6 and CD_2Cl_2 (the exception being compound **3** where spectra were recorded in d_8-toluene and CD_2Cl_2). It was noted that in all cases, small traces (*ca.* 5%) of starting [$(\eta^5$-$C_5H_5)_2WH_2$] could be observed in the spectra. This is believed to be due to decomposition of the product in solution rather than impurities in the solid since the product was washed thoroughly with petroleum ether and showed no trace of yellow colouring and the amount of dihydride in the NMR sample was found to increase slightly with time.

The characterisation of compounds **1-4** as zwitterionic trihydride cations was made primarily on examination of the hydride regions of the ^{1}H NMR spectra where the resonance of the starting material (at δ = -12.36 ppm in C_6D_6[8]) was replaced by two new signals in the region δ = -6.5 to -7.0 ppm. These are found to be a doublet and a triplet (with integrals in the ratio 1:2) with additional ^{183}W satellite peaks, a typical pattern for an AB_2X spin system. The H-H coupling constants in compounds **1** to **3** are found to be in the region 8-9 Hz, consistent with data reported for [$(\eta^5$-$C_5H_5)_2WH_3$]Cl.[9] The value for compound **4** in CD_2Cl_2 is surprisingly low (4.8 Hz), more in the range for compounds such as [$Cp^*_2WH_3$][BPh_4].[10] The one bond ^{183}W-H coupling constant (where it could be determined) is of a similar magnitude to that found in the compounds cited above[4,5,9,10] with coupling to the central hydride being greater than that to the outer ones.

This product is not without precedent in the literature; Braunschweig has obtained a zwitterionic trihydride cation from the reaction of $[(\eta^5\text{-}C_5H_5)_2WH_2]$ with $RBCl_2$ (R = ^{i}Pr or ^{t}Bu) (Fig. 2.1),[4] although he obtains a different product when using a borane of the type R_2BCl[5] and has not reported reactions with trialkylboranes. The ^{1}H NMR data and coupling constants obtained for the four compounds under discussion are entirely consistent with those obtained for Braunschweig's complexes.

The cyclopentadienyl regions of the spectra typically show three resonances as well as a small signal for the residual $[(\eta^5\text{-}C_5H_5)_2WH_2]$ caused by decomposition (δ = 4.24 ppm in C_6D_6[8]). A resonance of relative intensity 5 is assigned as the cyclopentadienyl ring that is not attacked and two signals each of relative intensity 2 as the two sets of equivalent protons on the borane substituted ring. These two signals should be split by coupling to one another but it is generally not observable; in some cases it is visible but insufficiently well-defined to calculate coupling constants, in others it is clearly so small that it merely causes broadening of the signals.

The principal ^{1}H NMR spectral data including coupling constants for all four complexes, as obtained in CD_2Cl_2, are given below in Table 2.1. The remaining data, including that obtained in C_6D_6, are given in Chapter Six. The ^{1}H NMR spectrum of compound **3**, obtained in CD_2Cl_2, is shown in Fig. 2.4, along with an expansion of the upfield region of the spectrum showing the AB_2 spin system and ^{183}W satellite peaks.

2.2.2.2 $^{11}B\{^1H\}$ and $^{13}C\{^1H\}$ NMR Spectroscopy

$^{11}B\{^1H\}$ NMR spectra were obtained for all four compounds and confirmed that in each case the boron was fourfold coordinated since the spectra consisted of single sharp resonances in the range δ = *ca.* -7 to -25 ppm. The values obtained do not correlate in any obvious way with the differing group, R, on the boron centre. Proton-coupled ^{11}B NMR spectra were also obtained to confirm that there was no coordination of the boranes to a hydride moiety. For compounds **1**, **2** and **4** there was found to be no splitting; compound **3** yielded a doublet with $^1J_{BH}$ = 86 Hz (CD_2Cl_2) or 98 Hz (d_8-toluene) since boron is bound directly to a proton in the parent borane.

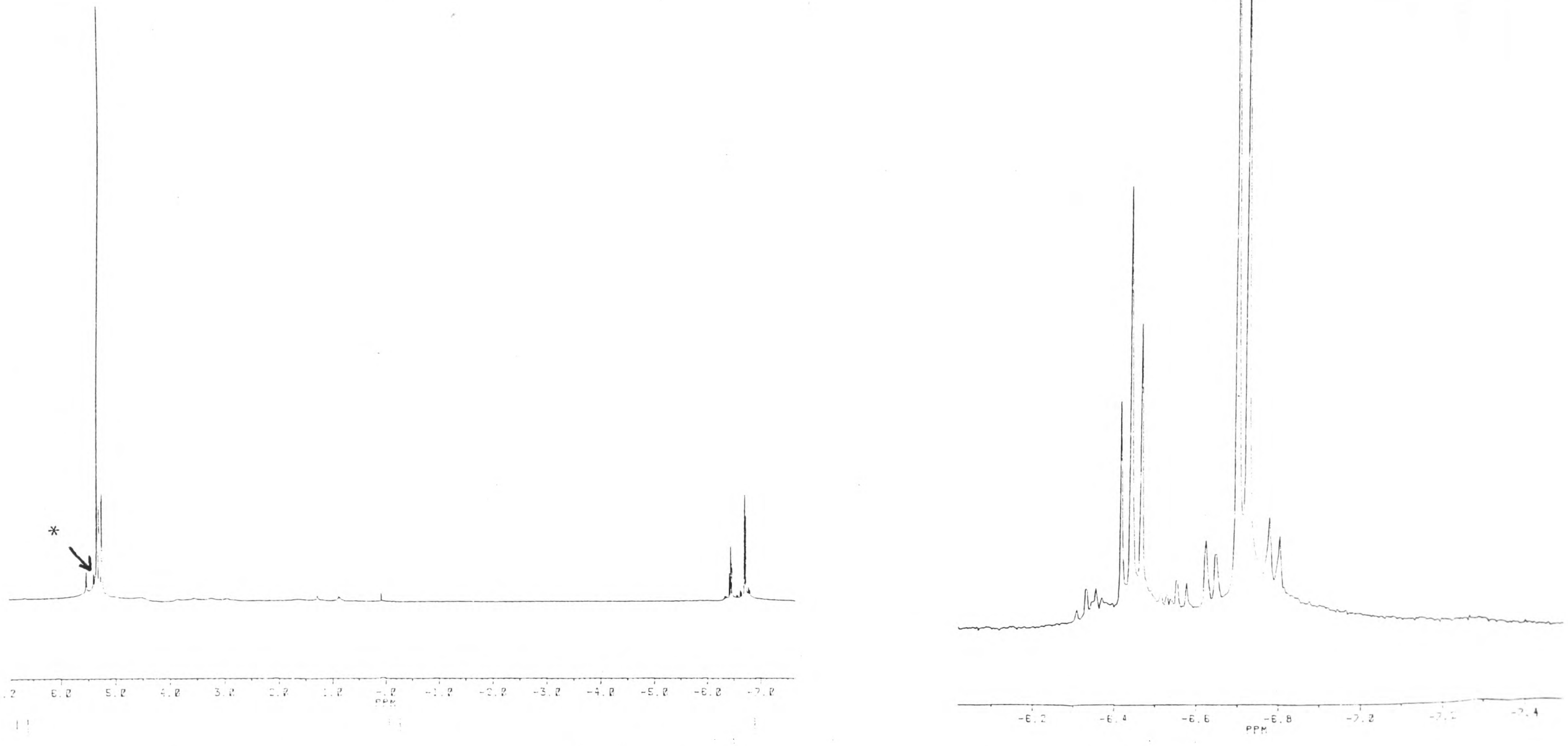


*Fig. 2.4: ^{1}H NMR spectrum of **3** obtained at 300.13 MHz in CD_2Cl_2, including expansion of high-field region.*

[indicates residual protio-solvent, $CDHCl_2$].*

Compound	**1**	**2**	**3**	**4**
^{1}H NMR				
$R_3BC_5H_4$	5.56	5.38	5.29	5.52
	5.52	4.94	5.25	5.20
C_5H_5	5.23	5.10	5.33	5.40
W-$H_{central}$	-6.27	-6.38	-6.44	-6.26
W-H_{outer}	-6.90	-6.48	-6.71	-6.37
$^{2}J_{HH}$ (WH_3)	9.6	4.8	7.6	7.8
$^{1}J_{WH}$ (Central)	*a*	*a*	66.6	66.2
$^{1}J_{WH}$ (Outer)	*a*	*a*	46.0	46.2
^{11}B NMR				
$R_3BC_5H_4$	-15.6	-13.1	-23.4	-6.7
^{13}C NMR				
ortho-C_6F_5	148.46	148.21	148.24	147.54
para-C_6F_5	137.60	138.46	138.55	139.26
meta-C_6F_5	130.46	137.16	136.88	137.16
ipso-C_6F_5	*b*	112.6	*b*	123.0
ipso-$R_3BC_5H_4$	87.11	87.24	89.50	87.70
$R_3BC_5H_4$	84.18	84.03	82.67	84.66
	83.30	71.60	71.77	(coincident)
C_5H_5	96.93	83.42	84.71	83.71
$^{1}J_{CF}$ (*ortho*)	249	220	293	239
$^{1}J_{CF}$ (*para*)	253	239	242	269
$^{1}J_{CF}$ (*meta*)	251	258	242	264

a = ^{183}W satellites not resolved, b = resonance not observed.

*Table 2.1: NMR spectroscopic data for compounds **1**, **2**, **3** and **4**. Shifts given as δ in ppm and coupling constants given in Hz. All NMR data obtained in CD_2Cl_2.*

$^{13}C\{^{1}H\}$ NMR spectroscopic analysis was also undertaken in CD_2Cl_2 (the complexes were found to be insufficiently soluble in C_6D_6 for all the expected resonances to be detected). Assignment is straightforward with four peaks in the cyclopentadienyl region; a strong resonance attributable to the (η^5-C_5H_5) ring, two weaker signals in the same area assigned to the substituted (η^5-$C_5H_4BR_3$) ring and a broader resonance, usually appreciably downfield from the others, due to the *ipso*-cyclopentadienyl carbon bound to boron. This pattern is consistent with data for the published complex [(η^5-$C_5H_4B(C_6F_5)_3$)(η^5-C_5H_5)$ZrMe_2$][$Li(thf)_4$] where the $^{13}C\{^{1}H\}$ NMR spectroscopic signals for the substituted cyclopentadienyl moiety are found at δ = 112.61 ppm, 117.45 ppm and 135.20 ppm (*ipso*) and the (η^5-C_5H_5) ring at δ = 116.15 ppm in CD_2Cl_2.[11]

As in all compounds containing a B-C_6F_5 group, there are resonances in the range δ = *ca.* 130 to 150 ppm assigned in the order *meta*, *para*, *ortho* on moving downfield. These resonances are very weak as they are split into doublets with $^{1}J_{CF}$ = *ca.* 240 Hz and further complicated by 3-bond C-F coupling although this is not resolvable and merely smears the signals out to widths of 75-100 Hz. This line width means that accurate $^{1}J_{CF}$ values are difficult to calculate and so any observed trends in the four compounds should be treated with caution. The *ipso*-C_6F_5 signal is extremely broad (typically fwhh = 150 Hz) and frequently only barely observable above the baseline. The observability of all these resonances is improved by the use of long relaxation delays, typically of the order of 4-5 seconds, when obtaining NMR spectra.

The principal $^{11}B\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR data obtained are summarised in Table 2.1; other data may be found in Chapter Six.

2.2.2.3 Infrared Spectroscopy

Infrared spectra were obtained of the four complexes as Nujol mulls; selected data are shown in Table 2.2 with equivalent absorptions aligned for comparison. The four spectra share many common features since they are dominated by stretches associated with C_6F_5- moieties in the regions 1500-1600 cm^{-1} and 800-1100 cm^{-1}. Compound **2** also has an absorption at *ca.* 3550 cm^{-1} attributed to C-H stretches of the

phenyl group. All four complexes display a weak, fairly broad band at *ca.* 1950 cm^{-1} assigned as the W-H stretch. This is in line with the values for $[(\eta^5\text{-}C_5H_4B(R)Cl_2)(\eta^5\text{-}C_5H_5)WH_3]$ (R = ^{i}Pr, ν(W-H) = 1947 cm^{-1}; R = ^{t}Bu, ν(W-H) = 1952 cm^{-1})[4] and $[(\eta^5\text{-}C_5H_5)_2WH_3][^{i}Pr_2BCl_2]$ and $[(\eta^5\text{-}C_5H_5)_2WH_3][BCl_4]$ (ν(W-H) = 1947 cm^{-1} and 1956 cm^{-1} respectively).[5] No band unambiguously assignable as ν(B-H) was observed in the spectrum of compound **3**.

1	**2**	**3**	**4**
	3551m		
1939w	1951w	1991w	1941w
1768w			
1645m	1645m	1636w	1645m
1516m	1518m	1510m	1516m
1262s		1275m	1280m
	1103m	1108m	
1089 s br		1087m	1089s br
	1052s	1073m	
		1023w	1019w
	981s	964s br	974s
	811s br		

*Table 2.2: Comparison of selected infrared data obtained for compounds **1**, **2**, **3** and **4** as Nujol mulls.*

2.2.2.4 Mass Spectrometry

Fast Atom Bombardment mass spectra were obtained for compounds **1** and **2**. In the former case, peaks due to the parent ion and the parent complex + Na^+ are visible albeit weakly. Stronger peaks are observed at m/z = 660 and 316 corresponding to loss of (C_6F_5) and $B(C_6F_5)_3$ respectively. The only assignable peak observed for **2** occurs at

m/z = 316 which again is assigned as the parent ion minus the borane. No data were obtained for the other two compounds and in general these species ran poorly and produced weak ions.

2.2.2.5 X-Ray Crystallography

Single crystals of **4** suitable for analysis by X-ray crystallography were grown by slow evaporation of a solution in benzene at ambient temperature. A crystal of dimensions 0.35 x 0.20 x 0.15 mm was selected for diffraction, covered with paratone-N oil under an inert atmosphere and mounted on the end of a glass fibre. Data were collected at 125 K on an Enraf-Nonius DIP2000 image plate diffractometer with graphite monochromated Mo K_α radiation (λ = 0.71073 Å) and indexed as triclinic with space group P-1. The images were processed with the DENZO and SCALEPACK programs.[12]

All solution, refinement and graphical calculations were performed using the CRYSTALS[13] and CAMERON[14] software packages. The structure was solved by direct methods using the SIR92 program[15] and refined by a full-matrix least squares procedure on F. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters. The three hydrides bound to tungsten were located in the final difference map and their positions refined with isotropic thermal parameters. A Chebychev weighting scheme with the parameters 2.84, 0.362 and 2.06 was applied as well as an empirical absorption correction.[16] This yielded a final R value of 2.7 %. Data collection and structure solution were performed by Dr. Linda Doerrer of this laboratory. Full details of the structure determination may be found in Appendix One.

The molecular structure of compound **4** is given in Fig. 2.5; selected bond angles and distances are summarised in Table 2.3. The structure is similar to that of the compound $[(\eta^5\text{-}C_5H_4B^iPrCl_2)(\eta^5\text{-}C_5H_5)WH_3]$,[4] although some of the details differ.

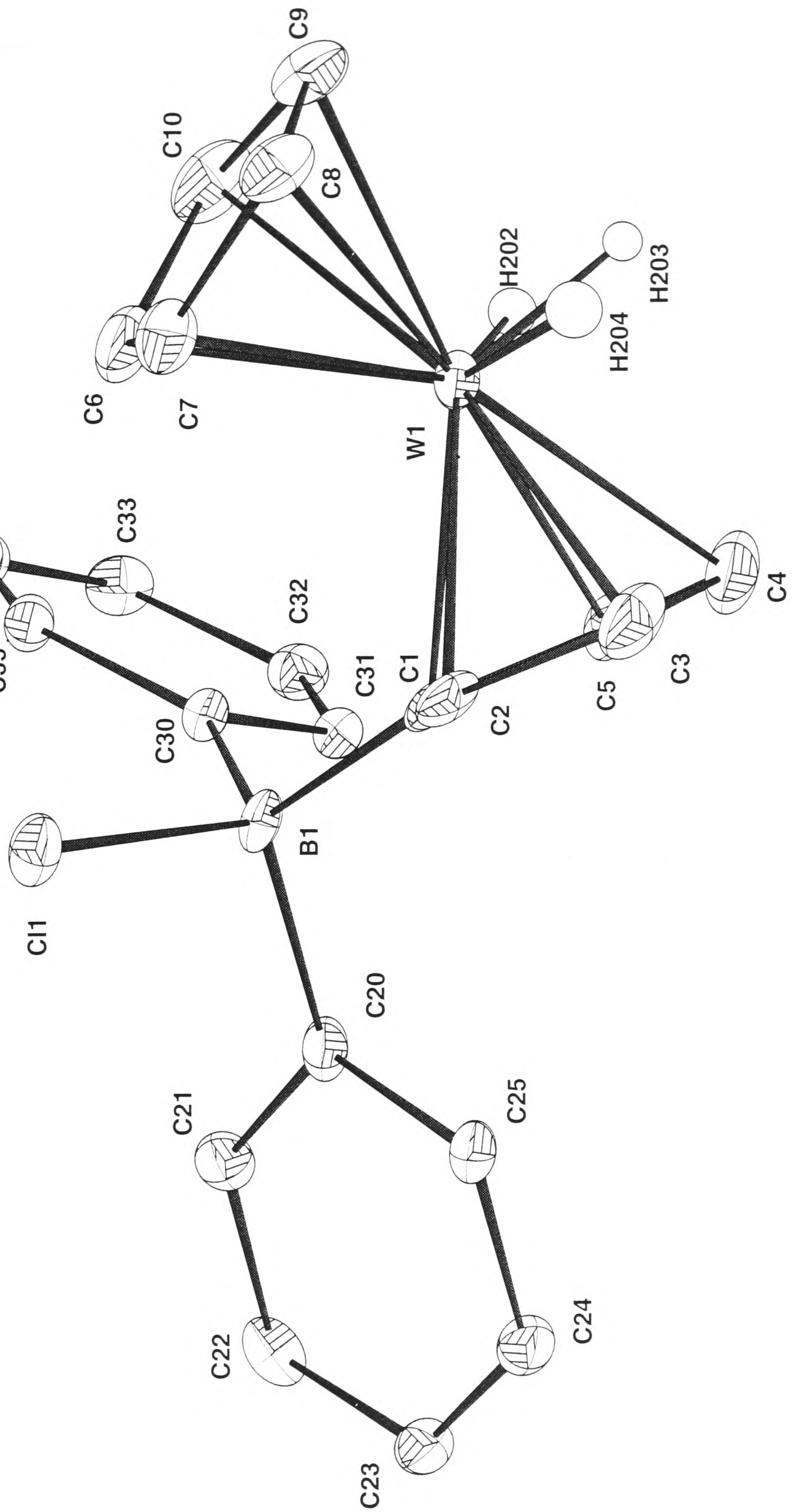


Fig. 2.5: Molecular structure of compound **4**. *Fluorine atoms and hydrogen atoms bound to carbon are omitted for clarity.*

Bond	**Distance (Å)**		**Angle (°)**
W(1) - H(202)	1.49(5)	Cp_{cent}-W-Cp'_{cent}	145.89
W(1) - H(203)	1.52(5)	H(202)-W-H(203)	54.8(27)
W(1) - H(204)	1.41(6)	H(203)-W-H(204)	60.8(30)
Cp_{cent} - W(1)	1.9780	H(202)-W-H(204)	115.6(33)
Cp'_{cent} - W(1)	1.9723		
B(1) - Cl(1)	1.915(5)		
B(1) - C(20)	1.652(6)		
B(1) - C(30)	1.648(5)		
B(1) - C(1)	1.637(6)		

(Cp_{cent} = centroid of (η^5-C_5H_5) ring; Cp'_{cent} = centroid of (η^5-$C_5H_4B(C_6F_5)_2Cl$) ring)

*Table 2.3: Selected bond distances and angles for compound **4**.*

The W-H bonds in compound **4** are slightly shorter (1.41-1.52 Å) than those of the $^iPrBCl_2$ analogue (1.51-1.58 Å) and the H_{outer}-W-H_{outer} angle much tighter (115.6 ° *vs.* 141.0 °). There does not seem to be any obvious explanation for this given the minimal effect the borane has on the tungsten centre, although bearing in mind the difficulties involved in accurately locating hydrogen atoms so close to a heavy metal atom, this large discrepancy can perhaps be viewed with some caution. In both compounds, the substituted and non-substituted cyclopentadienyl rings are at almost the same distance from the metal and this distance differs little between the two compounds where the borane is either $ClB(C_6F_5)_2$ or $^iPrBCl_2$ (*ca.* 1.95-1.97 Å in both cases).

When comparing the immediate coordination sphere of the boron atom with that of the free borane,[17] one finds, as expected, an increase of *ca.* 0.1-0.15 Å in the B-Cl and B-C distances on moving from approximately trigonal to tetrahedral geometry. The B-C_5H_4 distance is in line with that found in [(η^5-$C_5H_4B^iPrCl_2$)(η^5-C_5H_5)WH_3].

2.2.3 Reactions of $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)WH_3]$

The instability of compounds **1** to **4** in solution is believed to be due to a slowly achieved equilibrium rather than actual decomposition, since examination of ^1H NMR spectra show that the amount of $[(\eta^5\text{-}C_5H_5)_2WH_2]$ in a given sample increases overnight and is constant thereafter. Hence compound **1** was reacted with a series of competing Lewis bases in the hope that they would attack the free borane, trapping it out, and force the equilibrium to the right hand side (Fig. 2.5).

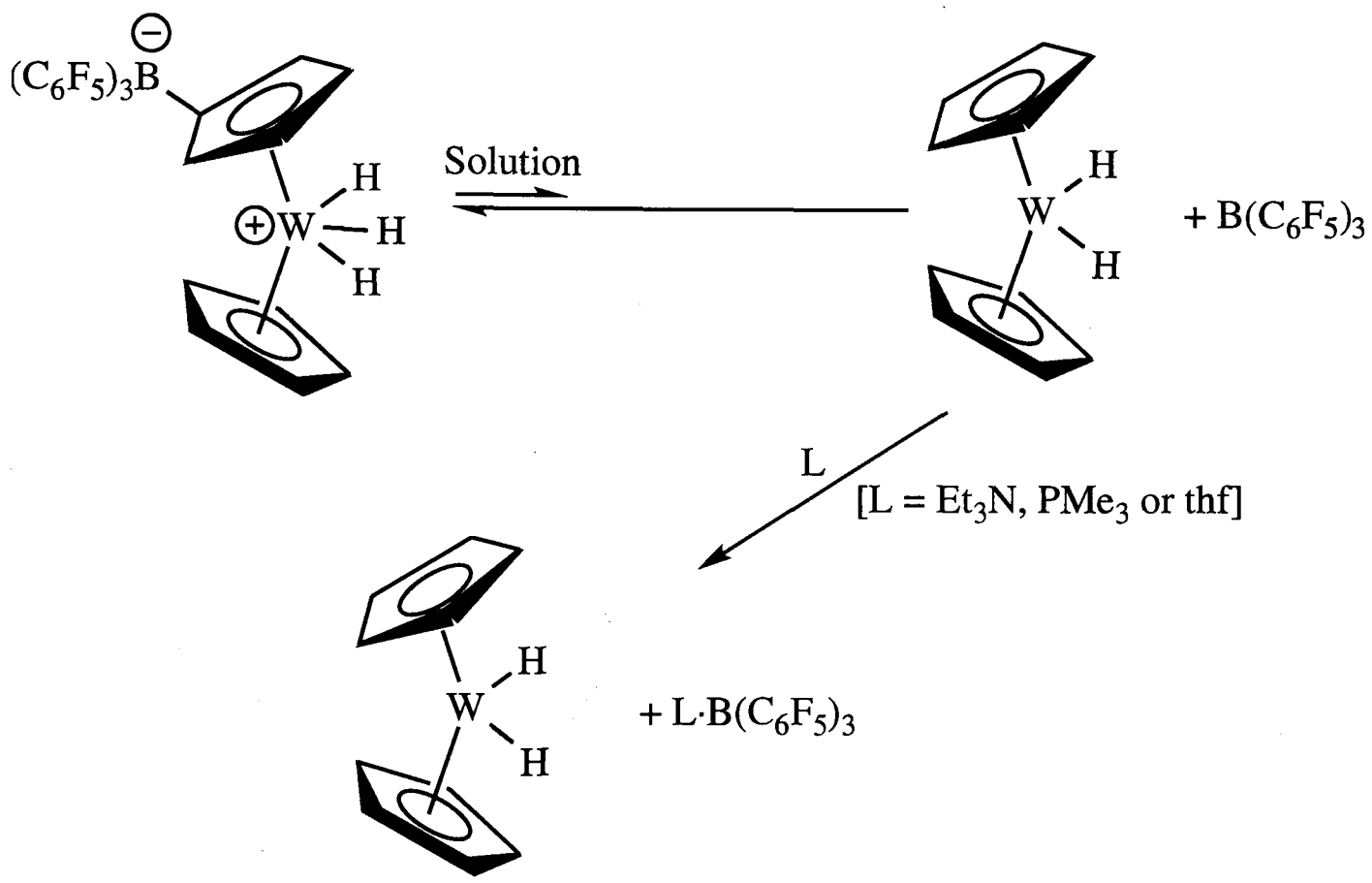


*Fig. 2.5: Investigation into the instability of compound **1** using a series of Lewis bases.*

In a typical experiment, *ca.* 20 mg of **1** was dissolved in toluene and excess Lewis base added either neat (thf or NEt_3) or as a solution in hexanes (PMe_3). In all three cases, the solution quickly became yellow and in the case of the Lewis base PMe_3, precipitation was observed (this was expected since $(C_6F_5)_3B{\cdot}PMe_3$ is known to be virtually insoluble in toluene). After 1 hour stirring, volatiles, including excess Lewis base, were removed under vacuum and the reaction residues dissolved in C_6D_6 for analysis by ^1H and $^{11}B\{^1H\}$ NMR spectroscopies.

For all three bases, almost total reaction of **1** to $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and $L{\cdot}B(C_6F_5)_3$ (L = Lewis base) had occurred (the adducts have been independently synthesised from $B(C_6F_5)_3$ and L to confirm this). The exception occurred with thf where residual **1** remained but only in a ratio of *ca.* 1:10 with respect to $[(\eta^5\text{-}C_5H_5)_2WH_2]$ (by integration of the ^1H NMR spectrum). $^{11}B\{^1H\}$ NMR spectroscopy confirmed these observations, with disappearance of the peak due to **1** at δ = -15.5 ppm and appearance of a new resonance at δ = -3.7 ppm (thf) or δ = -3.9 ppm (Et_3N). No $^{11}B\{^1H\}$ NMR spectral peak was obtained in the case of L being PMe_3 since, as has already been pointed out, this adduct is virtually insoluble in aromatic solvents.

These experiments indicate that compound **1** (and, by extension, compounds **2**, **3** and **4**) exists in solution in equilibrium with the parent dihydridotungstenocene and borane, and that the equilibrium can easily be disturbed by introduction of a rival strong Lewis base. This situation may also explain why attempted deprotonation of **1** using $K[N(SiMe_3)_2]$ failed since this amide can act as a Lewis base as well as a proton abstractor. A similar experiment, using a rhenium hydride species, is described below in Section 2.4.2 and these results are further discussed there.

2.2.4 Summary

Four zwitterionic compounds formed in reactions between $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and various boranes of the form $RB(C_6F_5)_3$ have been synthesised and characterised by NMR and infrared spectroscopies, mass spectrometry and microanalysis. The compounds are formulated as $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2R)(\eta^5\text{-}C_5H_5)WH_3]$ {R = (C_6F_5) (**1**), (C_6H_5) (**2**), H (**3**) or Cl (**4**)} and are found to exist in solution in equilibrium with the starting materials. This equilibrium is easily displaced by addition of a Lewis base. Compound **4** has also been characterised by means of X-ray crystallography.

2.3 Reactions of Lewis Acids with $[Cp_2MoH_2]$

2.3.1 The Reaction of $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ with $B(C_6F_5)_3$

2.3.1.1 Introduction

The reaction between $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ and $B(C_6F_5)_3$ has previously been described.[7] A blue solid forms rapidly on the addition of the borane to the dihydride, even at -78 °C, in either toluene or petroleum ether. The product (designated hereafter as **a**) is difficult to investigate owing to its extreme insolubility in common organic solvents such as toluene and petroleum ether. Dichloromethane causes fairly rapid decomposition of the product to an intractable green solution although NMR spectra were obtained before this occurred. These suggested strongly that **a** could be formulated as an adduct of the form $[(\eta^5\text{-}C_5H_5)_2Mo(H)(\eta^1\text{-}HB(C_6F_5)_3)]$, since two resonances were observed in the hydride region of the ^1H NMR spectrum; a sharp peak at δ = -6.21 ppm in the area expected for molybdenum-bound hydrides and a very broad signal at δ = -17.5 ppm. The latter signal is assigned to a Mo-H-B bridging hydride rather than an abstracted $[HB(C_6F_5)_3]^-$ since the ^1H NMR spectral shift of this anion is found to be δ = 3.98 ppm.[6] The proton-coupled ^{11}B NMR spectrum also shows a doublet with $^1J_{BH}$ = 87 Hz, consistent with other reported M-H-B bridging units.[18] Infrared spectroscopic and microanalytical data for **a** are also consistent with the proposed formulation.[7]

2.3.1.2 Solubility Studies

Further work on this system has attempted to find a suitable solvent for **a** in order to confirm its structure by growing crystals suitable for X-ray diffraction. Donor solvents such as diethylether and thf are unsuitable owing to the reaction of the complex with Lewis bases (*vide infra*). More reactive solvents such as chlorobenzene, acetone and nitromethane, are found to cause rapid decomposition. Fluorinated solvents were also tried following the 'like dissolves like' principle; however the solubility of the complex in hexafluorobenzene and perfluorohexane was found to be negligible and

although a solution was obtained in α,α,α-trifluorotoluene, it decomposed slowly at room temperature and failed to form crystals on cooling to -20 °C.

2.3.1.3 Reaction with a Lewis Base

A Lewis base was added to **a** in order to confirm that it was a simple adduct (Fig. 2.6). 4-Picoline was chosen since the $(C_6F_5)_3B{\cdot}NC_5H_4(CH_3)$ adduct had already been independently synthesised and characterised.[7] Excess 4-picoline was added to a suspension of the blue adduct in toluene and, over the course of two days, the solid

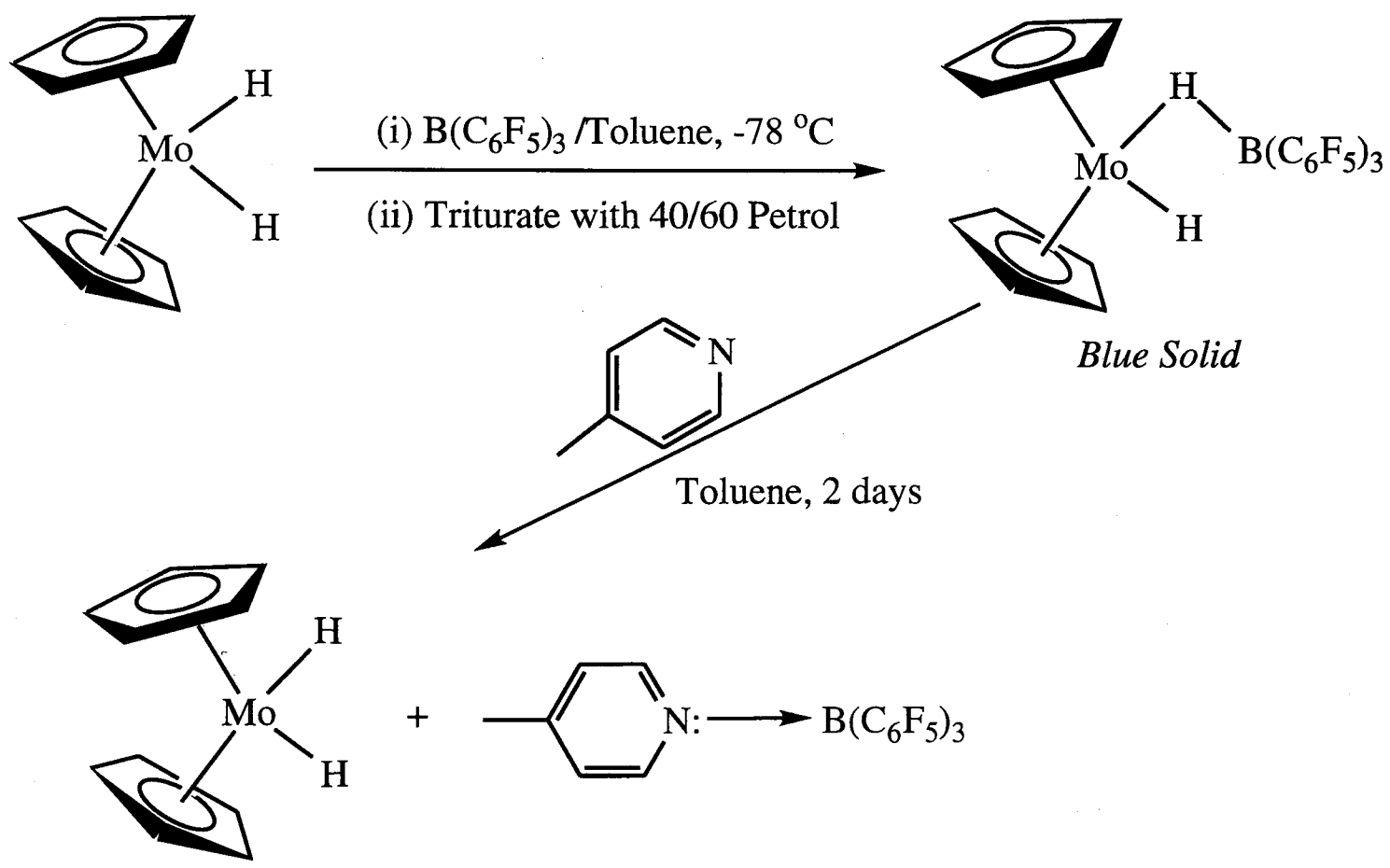


Fig. 2.6: The reaction between $[(\eta\text{-}^5C_5H_5)_2MoH_2]$ and $B(C_6F_5)_3$ and the subsequent reaction of the product with 4-picoline.

vanished and the solution phase became golden yellow. NMR spectroscopic analysis of this solution revealed it to be a mixture of $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ and $(C_6F_5)_3B{\cdot}NC_5H_4(CH_3)$. The reaction is believed to be slow owing to the extremely low solubility of compound **a** in toluene. This clean cleavage reaction suggests that the complex is a simple Lewis acid-base adduct, although since similar results were obtained

in the case of the more complex $[(\eta^5\text{-}C_5H_5)_2WH_2]/B(C_6F_5)_3$ system (*vide supra*), some caution should be exercised over this assumption.

2.3.1.4 Conclusions

Although the additional data obtained has still failed to confirm absolutely the structure of the blue adduct formed in the reaction between $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ and $B(C_6F_5)_3$, progress has been made in that several possibilities can be ruled out. Abstraction of the hydride as found for $[Cp^*_2ZrH_2]$[6] is precluded by the NMR spectra obtained. Attack at a cyclopentadienyl ring with displacement of a proton onto the metal lone pair is also inconsistent with the NMR spectroscopic data obtained, since only one cyclopentadienyl resonance is observed. In addition, the broad hydride signal obtained for molybdenum trihydride cations (assigned as being due to fast exchange at room temperature) typically occurs at δ = *ca.* -7 ppm[9] rather than δ = -17.5 ppm as found in the present case. Clean displacement of the borane by the strong Lewis base 4-picoline provides strong evidence that **a** can be formulated as a simple adduct.

2.3.2 The Reaction of $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ with $HB(C_6F_5)_2$

The reaction between $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ and *bis*(pentafluorophenyl)borane was performed in a similar fashion to that with $B(C_6F_5)_3$. Thus, the borane was added to the dihydride in toluene at -78 °C and an immediate colour change from yellow to red *via* orange was observed. Upon warming to ambient temperature and removal of volatiles *in vacuo*, an olive-green oily solid was obtained which, after washing thoroughly with petroleum ether (b.p. 40-60 °C), afforded the product (**5**) as a blue powder in 35 % yield. Compound **5** could be crystallised from toluene at -80 °C as needles which were not suitable for X-ray diffraction.

2.3.2.1 Characterisation of $[(\eta^5\text{-}C_5H_5)_2Mo(H)(\eta^1\text{-}H_2B(C_6F_5)_2)]$, (5)

Blue compound **5** shared many characteristics with the product formed from $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ and $B(C_6F_5)_3$, (**a**), being unstable both to air and heat. The high air-

sensitivity precluded obtaining entirely satisfactory microanalytical or mass spectral data. The solubility of **5** was somewhat greater than that of compound **a** and so NMR spectra were obtained in d_8-toluene. A single (C_5H_5) resonance was observed in both the ^1H and $^{13}C\{^1H\}$ NMR spectra, indicating that the Lewis acid had not attacked the cyclopentadienyl rings. Two ^1H NMR spectroscopic resonances appeared in the high field region of the spectrum, a sharp signal at δ = -13.56 ppm,which was assigned to a Mo-H moiety, and a broad resonance at δ = -18.2 ppm attributed to a bridging Mo-H-B unit. The other proton bound to boron is observed at δ = 4.59 ppm, close to its position in the free borane (δ = 4.5 ppm, fwhh = 25 Hz[19]) but a sharper resonance.

The $^{11}B\{^1H\}$ NMR spectrum shows a single peak at δ = -12.1 ppm in the region assigned to fourfold coordination of boron. No splitting ascribable to protons appears on removal of proton-decoupling; although it may be that the relatively large line width of the signal precludes its observation. Unfortunately, the solubility of **5** was too low to permit the weak (C_6F_5) resonances to be observed in the $^{13}C\{^1H\}$ NMR spectrum and a sample in CD_2Cl_2 decomposed before spectra could be acquired.

An infrared spectrum of **5** was obtained as a KBr disc. As is expected for compounds containing pentafluorophenyl groups, there are several strong absorptions in the range 950-1500 cm^{-1}. An Mo-H stretch is observed at 1724 cm^{-1} which is broad, as predicted for such monodentate borohydride complexes.[18] The $B\text{-}H_{bridge}$ stretch is predicted to appear at around 2000 cm^{-1}, however no peak is observed in this region- it is possibly broadened into the baseline. A weak absorption at 2390 cm^{-1} can be assigned to the $B\text{-}H_{terminal}$ stretch.

2.3.3 The Reaction of Other Compounds of the Form $[Cp_2MoH_2]$ with $B(C_6F_5)_3$

The insolubility of both compounds **a** and **5** suggested that the incorporation of alkyl substituents onto the cyclopentadienyl rings might be favourable. Such groups are lipophilic and improve solubility in most common organic solvents. Additionally mono-

substituted cyclopentadienyl rings are believed to provide a crystallographic 'lock' by preventing ring-spinning and thus improve crystallinity.[20, 21]

The reaction between $[(\eta^5\text{-}C_5H_4Me)_2MoH_2]$ and $B(C_6F_5)_3$ has already been discussed.[7] As expected, the blue product obtained is considerably more soluble in benzene than is **a**; however the improvement in solubility was insufficient to obtain meaningful $^{13}C\{^1H\}$ NMR spectral data. The *iso*propyl derivative, $[(\eta^5\text{-}C_5H_4{}^iPr)_2MoH_2]$, was therefore synthesised from $[MoCl_4\cdot dme]$, $Na[C_5H_4{}^iPr]$ and $LiAlH_4$ following the method of Persson and Anderssen.[22] This complex was isolated in 61 % yield as a yellow-brown oil and reacted with $B(C_6F_5)_3$ in toluene at -78 °C. No immediate reaction was observed so the reaction mixture was first allowed to reach ambient temperature and then warmed to 60 °C for 12 hours. This induced a colour change to green and the solvent was removed from the reaction mixture to yield an olive-green oily solid which, although exhibiting some evidence of being the desired product *e.g.* the presence of hydride signals in the ^1H NMR spectrum at δ = *ca.* -6 ppm rather than δ = *ca.* -9 ppm as found in the starting material, could not be purified.

The reaction between $[(\eta^5\text{-}C_5H_4{}^nBu)_2MoH_2]$ (prepared by Dr. John F. C. Turner of this laboratory) and $B(C_6F_5)_3$ was also attempted but no colour change was observed even on warming. It is clear that adding longer chain alkyl substituents to the cyclopentadienyl rings, although improving the solubility of the adduct, also hinders the reaction considerably and increases the oiliness of the products, so this approach was abandoned.

2.4 The Reaction of $[(\eta^5\text{-}C_5H_5)_2ReH]$ with $B(C_6F_5)_3$

After $B(C_6F_5)_3$ had been shown to react with $[(\eta^5\text{-}C_5H_5)_2MH_2]$ (M = Mo or W), other metallocene hydrides were synthesised and reacted with the borane in the hope of observing reactivity. One such is $[(\eta^5\text{-}C_5H_5)_2ReH]$ which is available in a simple reaction from a high-valent metal halide. The preparation used was from $ReCl_5$, excess $Na[C_5H_5]$ and $NaBH_4$ in dme[23] which gives the dihydride in a yield of *ca.* 20 % after sublimation at 80 °C (0.01 mbar) or extraction into benzene followed by crystallisation

from hexanes (-80 °C). This system is predicted to react readily with $B(C_6F_5)_3$ since there are many potential sites of attack- the hydride, the metal lone pairs or the cyclopentadienyl rings. Characterised Lewis acid adducts of $[(\eta^5\text{-}C_5H_5)_2ReH]$ such as that with BF_3[2] and with AlX_3 (X = Cl or Br) or $AlHCl_2$[24] have usually assigned the site of attack as being at one of the metal's lone pairs; however, in view of the reactivity of $[(\eta^5\text{-}C_5H_5)_2WH_2]$ with $B(C_6F_5)_3$ (*vide supra*), attack at a cyclopentadienyl ring was anticipated.

The hydride was dissolved in petroleum ether (b.p. 100-120 °C) and one equivalent of $B(C_6F_5)_3$ in the same solvent added. A light brown precipitate formed immediately and was isolated by filtration after one hour of stirring. Washing with hexanes to remove excess starting materials failed to render the product entirely pure so it was crystallised from toluene by slow cooling to -80 °C which yielded the product, **6**, as brown microcrystals in 65 % yield. Subsequent analysis by NMR spectroscopy amd microanalysis revealed **6** to be formulated as $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)ReH_2]\cdot 0.5PhMe$ (Fig. 2.7).

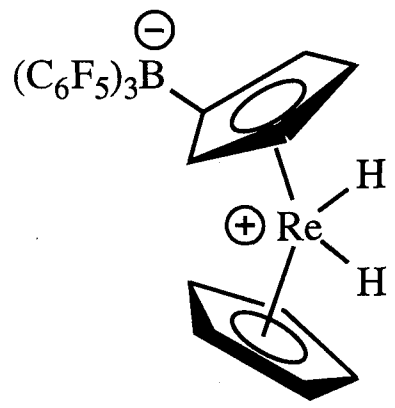


Fig. 2.7: Structure of the product formed in the reaction between $[(\eta^5\text{-}C_5H_5)_2ReH]$ and $B(C_6F_5)_3$.

2.4.1 Characterisation of $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)ReH_2]$ (6)

Microanalytical data were obtained for **6** and were satisfactory for its proposed formulation with half an equivalent of co-crystallised toluene.

2.4.1.1 NMR Spectroscopy

^1H NMR spectroscopy in CD_2Cl_2 showed a typical pattern in the cyclopentadienyl region for such complexes (*vide supra*) with a sharp resonance of relative intensity 5 at $\delta = 4.98$ ppm, ascribable to the unsubstituted (η^5-C_5H_5) moiety, and two broader signals, each of intensity 2, downfield of this which are assigned to the (η^5-$C_5H_4B(C_6F_5)_3$) ligand. As the two hydrides are equivalent, only one upfield resonance is observed, at $\delta = -13.87$ ppm, and this peak has relative intensity 2. Unlike the analogous tungsten complex, **1**, compound **6** is stable in solution, and thus no hydride resonance due to the starting material at $\delta = -12.90$ ppm is observed. Note that in the report of the $[(\eta^5\text{-}C_5H_5)_2ReH_2]^+$ cation in the literature,[23] the hydride also moves upfield when compared to the starting monohydride, although not to such a great an extent as is observed here. Toluene is also observed in the spectrum and integration of both the methyl peak and the phenyl region indicates that there is one half an equivalent of solvent present, a figure that is confirmed by the microanalytical data.

$^{11}B\{^1H\}$ NMR spectroscopy showed a single sharp peak at $\delta = -15.8$ ppm which does not split when the proton decoupler is turned off, providing further evidence that the borane does not attack the hydride.

The expected resonances were all observed in the $^{13}C\{^1H\}$ NMR spectrum except that of the *ipso*-C_6F_5 signal which was too weak and broad to be located. As is the case with compounds **1** to **4**, assignment is straightforward with similar patterns being observed in both the cyclopentadienyl and pentafluorophenyl regions in all five complexes.

2.4.1.2 Infrared Spectroscopy

Infrared spectroscopic analysis of compound **6** as a Nujol mull showed the expected bands assignable to C_6F_5 groups but no significant absorptions between 1650 cm^{-1} and 2400 cm^{-1}. This is unsurprising since the original characterisation of the $[(\eta^5\text{-}C_5H_5)_2ReH_2]^+$ cation reported only weak bands around 2000 cm^{-1} for the Re-H stretch[23]

and later solution and matrix isolation studies found no infrared-active Re-H stretch.[25] The infrared spectrum was thus of little use for the characterisation of **6**.

2.4.1.3 Mass Spectrometry

A Fast Atom Bombardment mass spectrum was obtained and showed several peaks assignable to expected fragments of **6**. A weak peak for the parent ion was visible at m/z = 830 as well as stronger ones for the parent ion plus sodium and the parent ion minus one and two protons. Other fragments observed included the parent ion minus (C_6F_5) at m/z = 663, $[B(C_6F_5)]^+$ at m/z = 512, $[(\eta^5\text{-}C_5H_5)_2ReH]^+$ and $[(\eta^5\text{-}C_5H_5)_2ReH_2]^+$ at m/z = 318 and 319 and $[C_6F_5]^+$ at m/z = 167. This supported the structure proposed for **6** although it is not conclusive since a simple adduct *via* a hydride bridge or lone pair might be expected to give a similar spectrum. The spectrum is shown in Fig. 2.8.

2.4.2 Reaction of $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)ReH_2]$ with a Competing Lewis Base

Since the ^1H NMR spectrum of compound **6** showed no traces of the parent hydride, it was postulated that this species was not in equilibrium with its constituents, unlike the tungsten analogues, **1** to **4**. To test this assumption, *ca.* 20 mg of **6** was reacted with an excess of PMe_3 in toluene as described in Section 2.2.3 above. No immediate colour change was observed and, after allowing one hour reaction time, the volatiles were removed *in vacuo* and the sticky brown residues analysed by ^1H and $^{11}B\{^1H\}$ NMR spectroscopy. This revealed that, as indicated by the lack of colour change or precipitation, **6** remained substantially unaltered with no trace of a hydride resonance characteristic of $[(\eta^5\text{-}C_5H_5)_2ReH]$ at δ = -12.90 ppm in the ^1H NMR spectrum. The $^{11}B\{^1H\}$ NMR spectrum showed a strong resonance for **6** at δ = -15.6 ppm and only an extremely small peak at δ = -3.9 ppm due to $(C_6F_5)_3B{\cdot}PMe_3$ (although since this species has low solubility in C_6D_6, the relative intensities of these two signals may not reflect the composition of the reaction mixture as a whole).

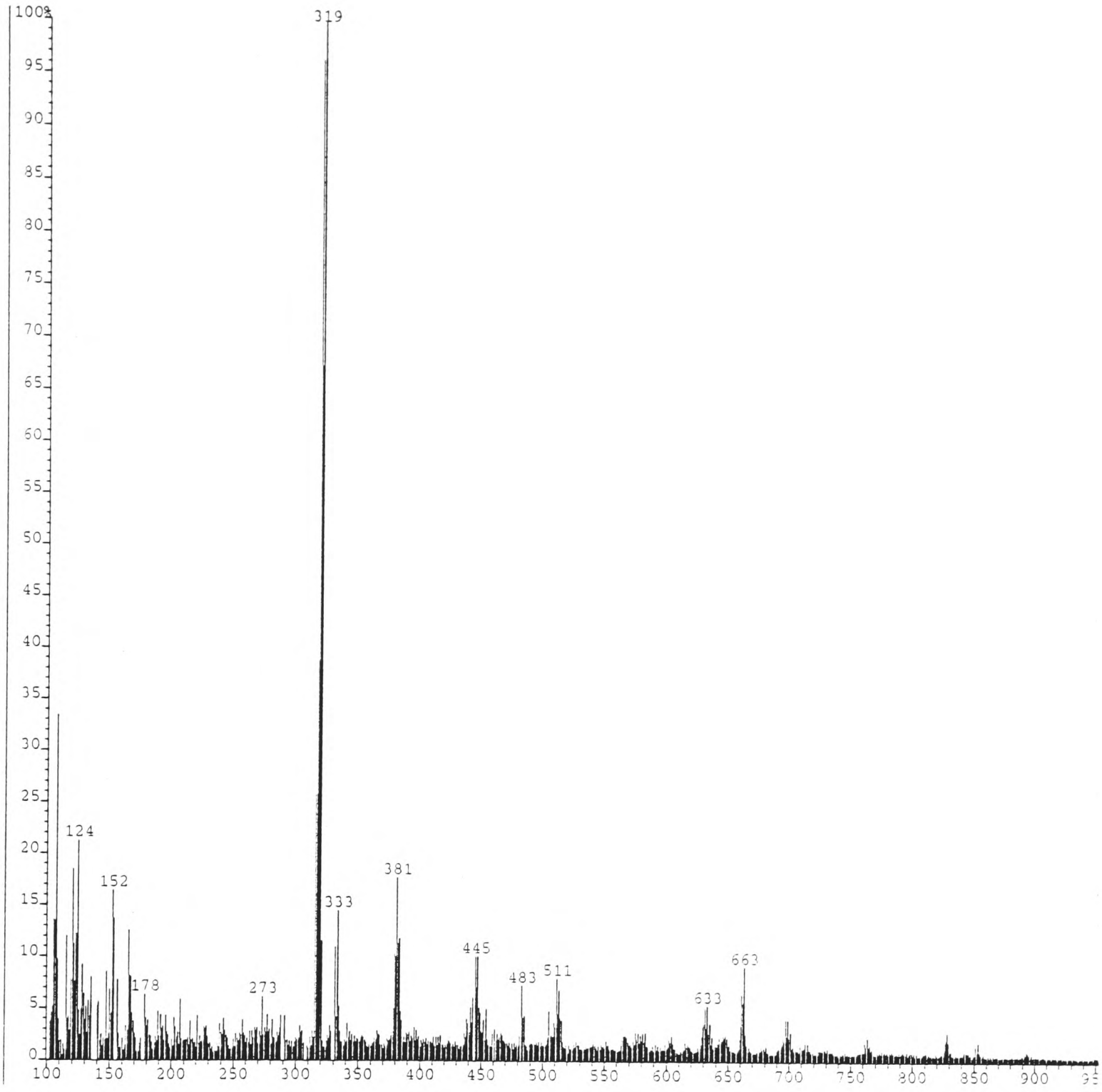


Fig. 2.8: Fast Atom Bombardment mass spectrum of compound ***6****.*

Comparison of the results of the two experiments is instructive since they reveal differences in the solution stability of the otherwise similar complexes $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)WH_3]$ (**1**) and $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)ReH_2]$ (**6**). The former appears to be a kinetically formed product that is trapped out by its formation in, and subsequent precipitation from, petroleum ether. Under thermodynamic conditions of formation, such as those found in toluene where the products are soluble, other

compounds are formed and the reaction does not run to completion. When the kinetic product, **1**, is placed under conditions of thermodynamic control *i.e.* in solution overnight, it is found to exist in equilibrium with its two constituent parts. By contrast, compound **6** can be described as a thermodynamic product, even though it forms under conditions of kinetic control, since it does not exhibit this dissociation in solution.

2.5 The Reaction of $[(\eta^5\text{-}C_5H_5)_2TaH_3]$ with $B(C_6F_5)_3$

The metallocene trihydride, $[(\eta^5\text{-}C_5H_5)_2TaH_3]$, is synthetically available from $[TaCl_5]$, $Na[C_5H_5]$ and $Na[BH_4]$ in thf using a modification by Jones and Eisenberg[26] of the original procedure.[8] The yield from this procedure is low (30 % or less), but sufficient quantity of $[(\eta^5\text{-}C_5H_5)_2TaH_3]$ was prepared to study its reaction with *tris*(pentafluorophenyl)borane.

One equivalent of the borane was added to the trihydride, both as toluene solutions at room temperature. A slow colour change from pale yellow to dark orange was observed over three hours and then the volatiles were removed under vacuum to yield an orange oil. Sonication in hexanes for 15 minutes rendered the product as a light-orange powder. This product analysed correctly for a 1:1 adduct (C: found 40.68 % (calculated 40.71 %), H: 1.66 (1.59), B: 1.52 (1.31)); unfortunately NMR spectroscopy failed to confirm that adduct formation had occurred. The $^{11}B\{^1H\}$ NMR spectrum showed a fairly sharp resonance at δ = -0.2 ppm in the region expected for four-coordinate boron, however there was no splitting visible on removal of decoupling and the line width was of a sufficiently low magnitude to lead one to expect that proton-coupling should be observable if a B-H unit existed.

Attack on the cyclopentadienyl ring, as seen in the reaction with $[(\eta^5\text{-}C_5H_5)_2WH_2]$, is not thought likely to occur in this system since there is no lone pair on the metal centre to accept the displaced proton. Published reactions of $[(\eta^5\text{-}C_5H_5)_2TaH_3]$ with Lewis acids have found attack occurs at the central hydride ligand *e.g.* the reaction with triethylaluminium described by Tebbe.[27] In accord with this, one might therefore expect the ^1H NMR spectrum of the product of the reaction with $B(C_6F_5)_3$ to show a

more or less unaltered B_2 component and a shifted and broadened A component in the hydride region of the spectrum. In actual fact, the only observed upfield resonance is an extremely broad (fwhh = *ca.* 200 Hz), very weak signal centered at δ = -4.1 ppm which could possibly correspond to the borane rapidly hopping between all three hydrides (Fig. 2.9).

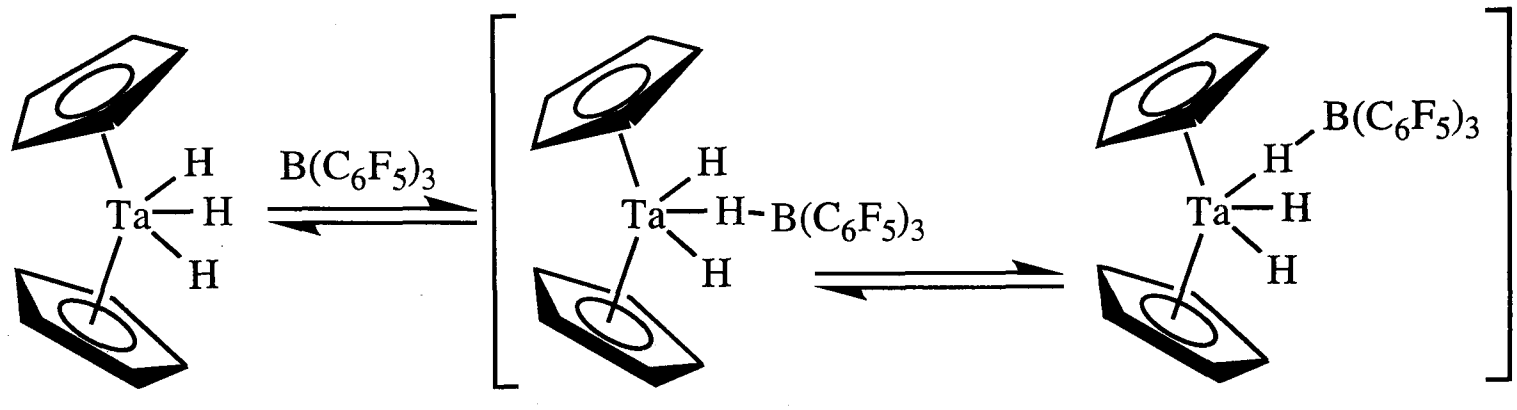


Fig. 2.9: Possible reaction between [(η^5-C_5H_5)$_2$$TaH_3$] and $B(C_6F_5)_3$.

The cyclopentadienyl region of the spectrum displayed more than one resonance despite the accurate analytical data obtained. Recrystallisation from toluene did not improve the situation so the system was not further investigated.

2.6 Summary and Conclusions

This chapter has described several reactions between Lewis acids of the form $RB(C_6F_5)_2$ [R = (C_6F_5), (C_6H_5), H or Cl] and metal complexes of the form [Cp_2MH_n] where Cp is a generalised (η^5-C_5H_4R) ligand [R = H, Me, ^{i}Pr or ^{n}Bu], M is Mo, W, Ta or Re and n = 1, 2 or 3. Two types of reactivity are found to occur- attack at a hydride moiety or attack at a cyclopentadienyl ring with displacement of a proton which subsequently coordinates to a lone pair on the metal centre.

The reaction between [(η^5-C_5H_5)$_2$$WH_2$] and $B(C_6F_5)_3$ is found to depend upon the reaction solvent. In toluene, a purple, thermally unstable species forms which is believed to be analogous to the product formed in the reaction between [(η^5-C_5H_5)$_2$$MoH_2$] and $B(C_6F_5)_3$.[7] In aliphatic solvents, the zwitterionic product [(η^5-

$C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)WH_3]$ (**1**) forms rapidly. This compound, along with the analogous $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2(C_6H_5))(\eta^5\text{-}C_5H_5)WH_3]$ (**2**) $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2H)(\eta^5\text{-}C_5H_5)WH_3]$ (**3**) and $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2Cl)(\eta^5\text{-}C_5H_5)WH_3]$ (**4**), have been synthesised and fully characterised by means of multinuclear NMR spectroscopy, infrared spectroscopy, microanalysis and Fast Atom Bombardment mass spectrometry. An X-ray crystal structure of compound **4** has also been obtained. The instability of these complexes in solution has been investigated through reactions of **1** towards competing Lewis bases.

Reaction between $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ and $B(C_6F_5)_3$ yields a blue product (**a**) that has been previously described[7] and is believed to be a simple 1:1 adduct bound *via* a single Mo-H-B bridge. The present work describes some further characterisation of this system and reports the analogous complex $[(\eta^5\text{-}C_5H_5)_2Mo(H)(\eta^1\text{-}H_2B(C_6F_5)_2)]$ (**5**).

The zwitterion $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)ReH_2]$ (**6**) is formed when $[(\eta^5\text{-}C_5H_5)_2ReH]$ reacts with $B(C_6F_5)_3$ in petroleum ether and this complex has been characterised by NMR and infrared spectroscopies, microanalysis and Fast Atom Bombardment mass spectrometry. The compound was found to be only minimally reactive towards the competing Lewis base trimethylphosphine.

The reaction between $[(\eta^5\text{-}C_5H_5)_2TaH_3]$ and $B(C_6F_5)_3$ has been studied and although the product could not be fully purified or characterised is believed to be a simple adduct, containing a Ta-H-B unit, in which the borane hops between the three hydride ligands.

The aim of this work was to investigate the wide variety of reactivity between metallocene hydride complexes and strong Lewis acids with a boron-pentafluorophenyl linkage. Contrasting modes of attack have been observed depending not only on whether there are lone pairs of electrons on the metal but also on the actual identity of the metal centre (*e.g.* the contrast between molybdenum and tungsten).

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Chapter Three

Reactions Between $B(C_6F_5)_3$ and Transition Metal Nitrido Compounds

3.1 Introduction

This chapter describes studies into the reactivity of the strong Lewis acid *tris*(pentafluorophenyl)borane with some nitrido complexes of rhenium, molybdenum and osmium. These compounds contain a metal-nitrogen triple bond and a comprehensive review of their synthesis, bonding and reactivity can be found in Nugent and Mayer's text on metal-ligand multiple bonds.[1] Other substantial reviews are those by Griffith[2] and Dehnicke.[3, 4]

The nitrido ligand is predicted to be a sufficiently strong Lewis base to bind the strong electrophiles under consideration in this work; reactions between $[NReCl_2(PR_3)_3]$ or $[NRe(PR_3)(S_2CNR_2)_2]$ and trihaloboranes have already been surveyed in Section 1.6. Reactions with non-boron-containing electrophiles have also been reported such as those of $[NOsO_3][^nBu_4N]$ with the Lewis acidic metal complexes $[Au(PPh_3)(F_3CSO_3)]$ and *cis*-$[Pt(PMe_3)_2(F_3CSO_3)_2]$ (Fig. 3.1).[5]

Other reactions of interest include the alkylation of $[NM(1,2\text{-}S_2C_6H_4)_2][^nBu_4N]$ (M = Ru, Os),[6] which is discussed in Section 3.4 below and the reactions of $[NMo(S_2CNR_2)_3]$ (R = Me or Et) with the electrophilic species R'X (R' = PhCO, $PhSO_2$, Ph_3C or Me; X = Cl, I or BF_4) to form $[(R'N)Mo(S_2CNR_2)_3]^+$.[7] Therefore, following the recent demonstration in this laboratory that nucleophilic metal oxo compounds readily form adducts with $B(C_6F_5)_3$,[8, 9] it was decided to extend this to study the reactions of this Lewis acid with metal nitrido complexes.

The reactivity of $B(C_6F_5)_3$ towards nitrido complexes of rhenium(V), molybdenum(VI) and osmium(VI) will be examined in turn, followed by a brief investigation of related reactions with metal sulphido and thionitrosyl complexes.

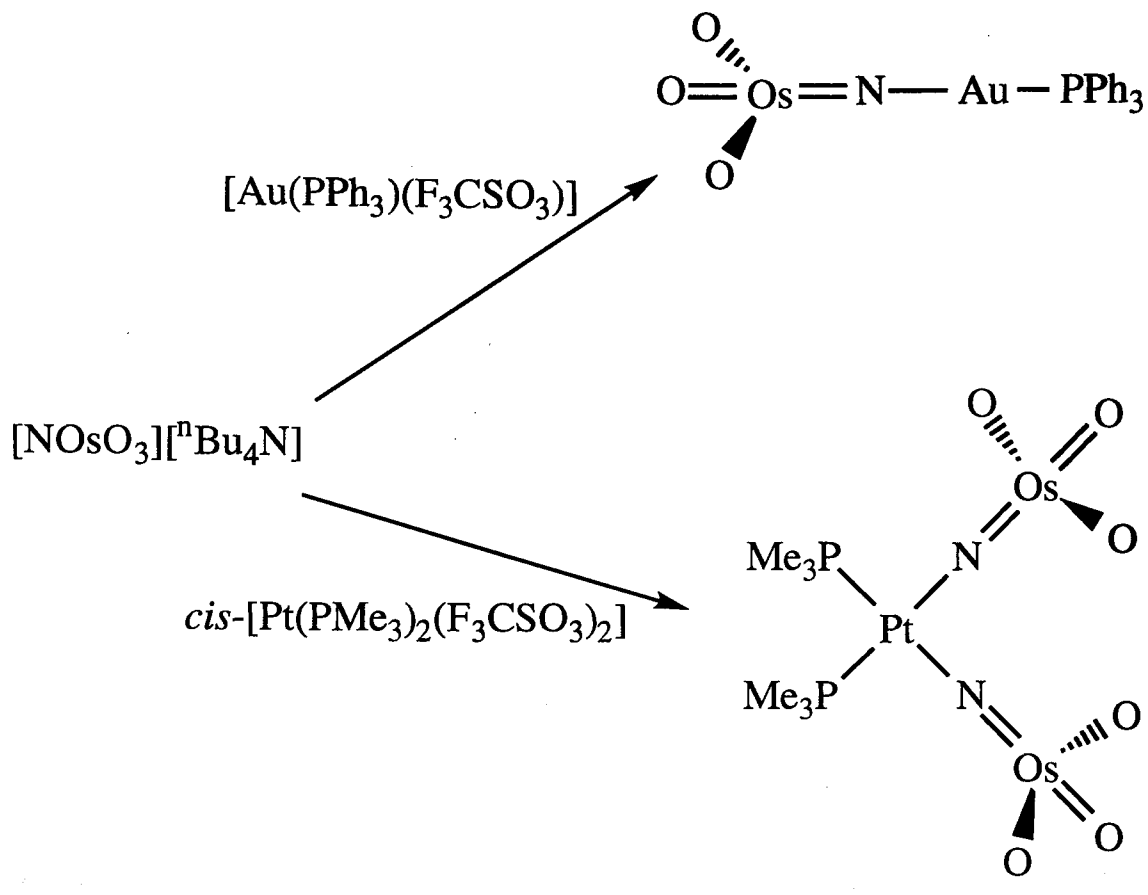


Fig. 3.1: Reactions of $[NOsO_3]^-$ with Lewis acidic metal complexes.

3.2 Reactions Between Nitrido Complexes of Rhenium (V) and $B(C_6F_5)_3$

3.2.1 Synthesis of Rhenium Nitrido Complexes

The rhenium nitrido complexes studied in this work all derive from the compounds $[NReCl_2(PR_3)_3]$ (where $PR_3 = PMe_2Ph$ or $PMePh_2$). The synthesis of these complexes has been described by Chatt and involves reaction of a perrhenate (in the present work, the source of this was perrhenic acid pentahydrate) with hydrazine hydrochloride in the presence of an excess of the tertiary phosphine in ethanol.[10] The reaction is believed to proceed *via* the formation of $[ORe(OEt)Cl_2(PR_3)_2]$ and to require the presence of trace amounts of water. The compounds $[NReCl_2(PMe_2Ph)_3]$ and $[NReCl_2(PMePh_2)_3]$ are formed by this methodology in yields of 41 % and 38 % respectively.

$[NReCl_2(PMe_2Ph)_3]$ has been found by Abram and co-workers to provide a useful entry-point into various dithiocarbamate complexes containing a $\{NRe(PMe_2Ph)\}$

core.[11] Substitution of either one chloride and one phosphine or both chlorides and two phosphines occurs when the parent complex is treated with one or two equivalents of $Na[S_2CNR_2]$ (R = Me or Et) respectively. Thus the complexes $[NReCl(PMe_2Ph)_2(S_2CNR_2)]$ and $[NRe(PMe_2Ph)(S_2CNR_2)_2]$ can be synthesised easily in good (61-77 %) yield. Structural characterisation of these complexes reveals a considerably lengthened *trans* Re-X bond (X = Cl or S respectively) which has been discussed in terms of a considerable *trans*-influence of the nitrido ligand. This influence appears to diminish when electrophiles such as BCl_3 coordinate to the nitrido ligand, as indicated by a reduction in the *trans* Re-X bond length.[12]

3.2.2 Synthesis of Some New Nitrido Complexes of Rhenium

Following Abram's work on the synthesis of dithiocarbamate complexes of rhenium, the related new complexes $[NRe(PMePh_2)(S_2CNEt_2)_2]$ and $[NReCl(PMePh_2)_2(S_2CNMe_2)]$ were synthesised, starting from $[NReCl_2(PMePh_2)_3]$ using analogous preparations to those found in the literature.[11]

3.2.2.1 Synthesis and Characterisation of $[NRe(PMePh_2)(S_2CNEt_2)_2]$ (7)

Reaction of $[NReCl_2(PMePh_2)_3]$ with two equivalents of the sodium salt of diethyldithiocarbamic acid, $Na[S_2CNEt_2]$, in refluxing methanol gave the compound $[NRe(PMePh_2)(S_2CNEt_2)_2]$ (**7**). Removal of volatiles *in vacuo*, washing with *iso*propanol and recrystallisation from a 1:1 mixture of *iso*propanol and dichloromethane at -80 °C yielded the product analytically pure in 48 % yield.

Characterisation was achieved by means of microanalysis (which confirmed the proposed formulation of the product) and infrared and NMR spectroscopies. The value for the metal-nitrogen stretch was found to be 1054 cm^{-1}; this band was selected from several other bands in the region 900-1100 cm^{-1} by analogy with the assignment of ν(Re-N) at 1055 cm^{-1} for $[NRe(PMe_2Ph)(S_2CNEt_2)_2]$.[11]

The NMR spectra, obtained in CD_2Cl_2, were easy to assign. $^{13}C\{^1H\}$ NMR spectroscopy indicates that there are two pairs of ethyl groups in the molecule since there

are two resonances in both the methylene and the methyl regions of the spectrum. The presence of two quaternary signals for the dithiocarbamate ligand indicate that the two ligands are inequivalent corresponding to the expected structure in which one is coordinated in an axial-axial fashion and the other axial-equatorial. The presence of a single set of phenyl signals indicates that rotation about the Re-P bond is fast on the NMR timescale.

The ^1H NMR spectrum confirms that there are two distinct pairs of ethyl groups present since the methylene region shows four signals which are complex multiplets, probably doublets of quartets. This is expected since any given methylene group should display two ^1H NMR spectral resonances as the two protons are diastereotopic and hence magnetically distinguishable. Coupling between the two methylene protons as well as to the three protons on the adjacent methyl group should be observed. As there are two types of methylene carbon in the molecule, four separate multiplets are visible. The methyl region of the spectrum is simpler since the two types of methyl group each show a single resonance, both being a doublet of doublets through coupling to the two adjacent methylene protons.

The structure proposed for compound **7** is given below in Fig. 3.2 with protons labelled to show which are found to be magnetically equivalent.

3.2.2.2 Synthesis and Characterisation of $[NReCl(PMePh_2)_2(S_2CNMe_2)]$ (**8**)

The compound $[NReCl_2(PMePh_2)_3]$ was also reacted with one equivalent of $Na[S_2CNMe_2]$. Once again, the desired product formed after 1 hour of reflux in methanol, however the work-up procedure was slightly different. Concentration of the volume of the reaction mixture to one-half, filtration and washing with *iso*propanol gave $[NReCl(PMePh_2)_2(S_2CNMe_2)]$ (**8**) analytically pure in 53 % yield.

Satisfactory microanalytical data were obtained for compound **8** and the Re≡N stretch was located at 1060 cm^{-1} in the infrared spectrum (compare with 1058 cm^{-1} for the

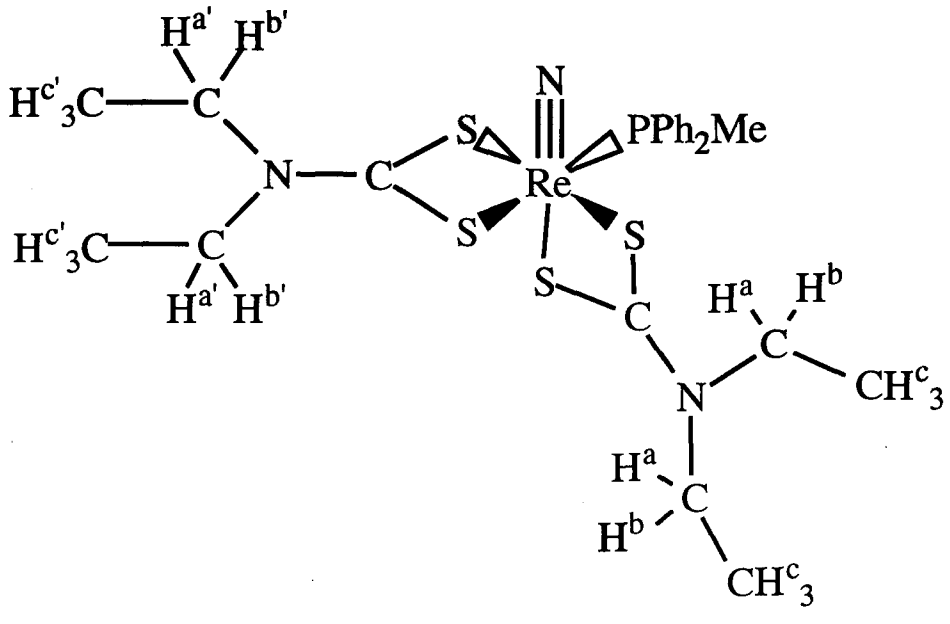


Fig. 3.2: Structure of compound 7 indicating protons shown to be equivalent by NMR spectroscopy.

similar complex $[NReCl(PMe_2Ph)_2(S_2CNMe_2)]$[11]). NMR spectroscopic studies in CD_2Cl_2 gave simpler spectra in comparison to those obtained for compound **7** since there is only one dithiocarbamate group, and the substitution of methyl for ethyl further clarifies the spectra. There is one ^1H NMR spectroscopic signal attributable to the dithiocarbamate ligand, located at $\delta = 3.24$ ppm. Both the tertiary phosphines are found to be equivalent since there is a single resonance in the $^{31}P\{^1H\}$ NMR spectrum, consistent with the presence of one doublet in the region of the ^1H NMR spectrum expected for P-Me groups. These data indicate that the structure of **8** is octahedral with the chloride *trans* to the nitrido ligand; as the phosphines are equivalent they must both be *cis*. This is entirely in accord with the published structure of $[NReCl(PMe_2Ph)_2(S_2CNMe_2)]$.[11]

3.2.3 Synthesis and Characterisation of $[\{(C_6F_5)_3BN\}Re(PMePh_2)(S_2CNEt_2)_2]$ (9)

Compound **7** was reacted with $B(C_6F_5)_3$ in dichloromethane at ambient temperature. An immediate colour change in the solution was observed from dark yellow to violet. After one hour of stirring, petroleum ether (b.p. 40-60 °C) was added, but no precipitation of the product was observed. Hence the volatiles were removed *in vacuo*

and the resulting oily solid triturated with hexanes to yield the product (**9**) as a lavender powder in 65 % yield. Slow evaporation of a solution of **9** in a 1:1 mixture of *iso*propanol and dichloromethane yielded purple single crystals which were found to be partially suitable for X-ray diffraction (*vide infra*).

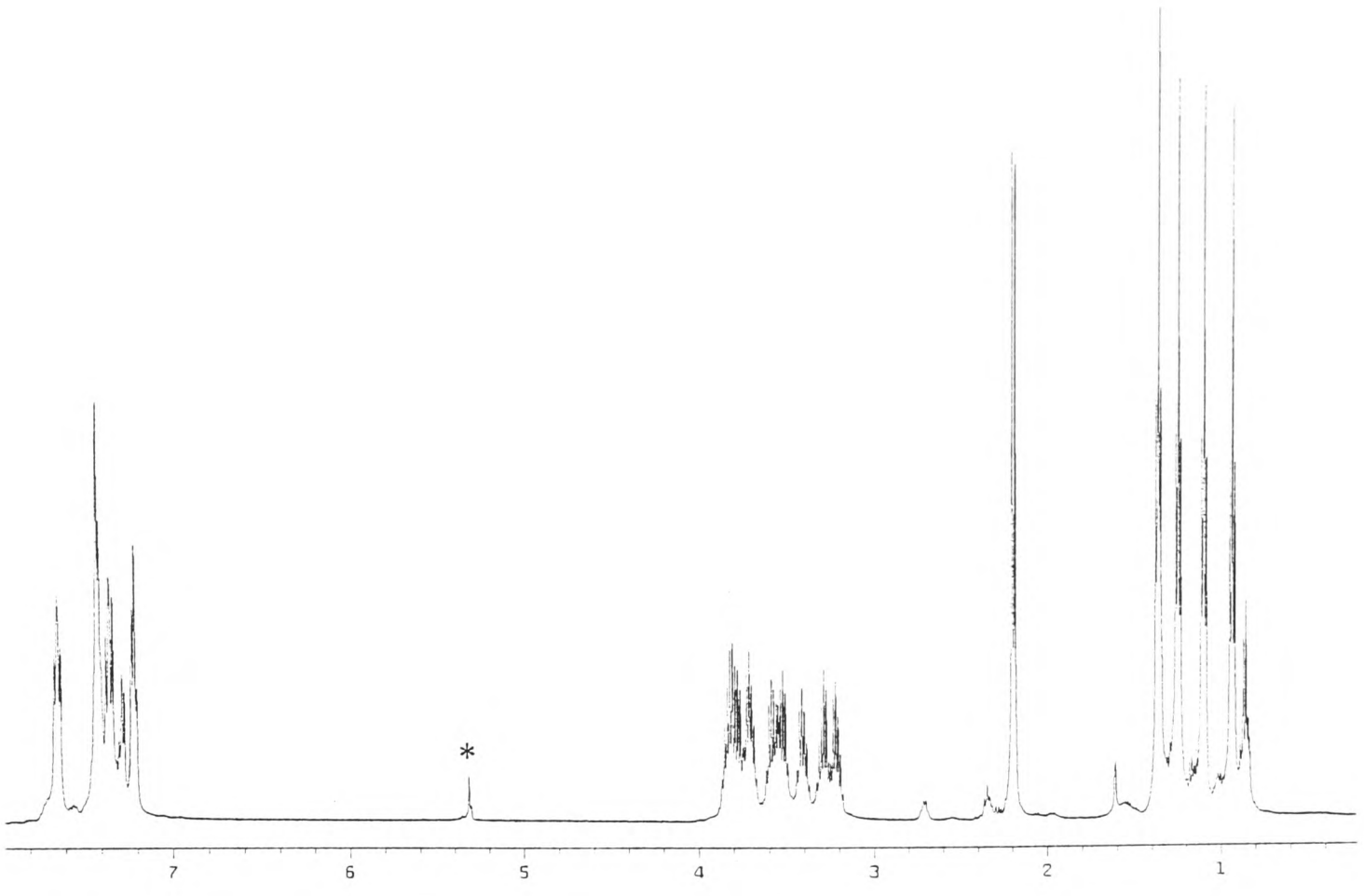
Microanalytical data were obtained for the crystals and indicated that compound **9** was formulated as $[\{(C_6F_5)_3BN\}Re(PMePh_2)(S_2CNEt_2)_2]\cdot 0.5^iPrOH$.

3.2.3.1 Characterisation by ^1H NMR Spectroscopy

Full NMR spectroscopic studies were carried out in CD_2Cl_2. The ^1H NMR spectrum showed that compound **9** exhibited lower symmetry than **7**. Five methyl signals are observable each with relative intensity three, one for each methyl group in the molecule. The four methyl groups assignable as dithiocarbamate ligands appear as virtual triplets in the range δ = 0.9-1.4 ppm due to coupling to the two adjacent methylene protons with identical coupling constants. The methylene region is highly complex since all eight protons appearing here are inequivalent and all are coupled not only to the other proton on the appropriate methylene carbon but also to protons in the adjacent methyl group. No coupling constants could be calculated but the central positions of the eight complex resonances were determined. Close examination of the spectrum also reveals two extra resonances attributable to *iso*propanol at δ = 0.86 ppm (doublet) and 3.73 ppm (multiplet). The integrals of these regions confirm the presence of approximately one half an equivalent of ^iPrOH in the crystals. The phenyl region of the ^1H NMR spectrum is complex, indicating that the two phenyl groups on the phosphine are magnetically inequivalent. The ^1H NMR spectrum of compound **9** is given in Fig. 3.3 together with an expansion of the methylene and methyl regions.

3.2.3.2 Characterisation by $^{11}B\{^1H\}$, $^{13}C\{^1H\}$, ^{19}F and $^{31}P\{^1H\}$ NMR Spectroscopy

$^{11}B\{^1H\}$ NMR spectroscopic analysis showed a single sharp resonance at δ = -3.4 ppm characteristic of fourfold coordinated boron. The $^{13}C\{^1H\}$ NMR spectrum



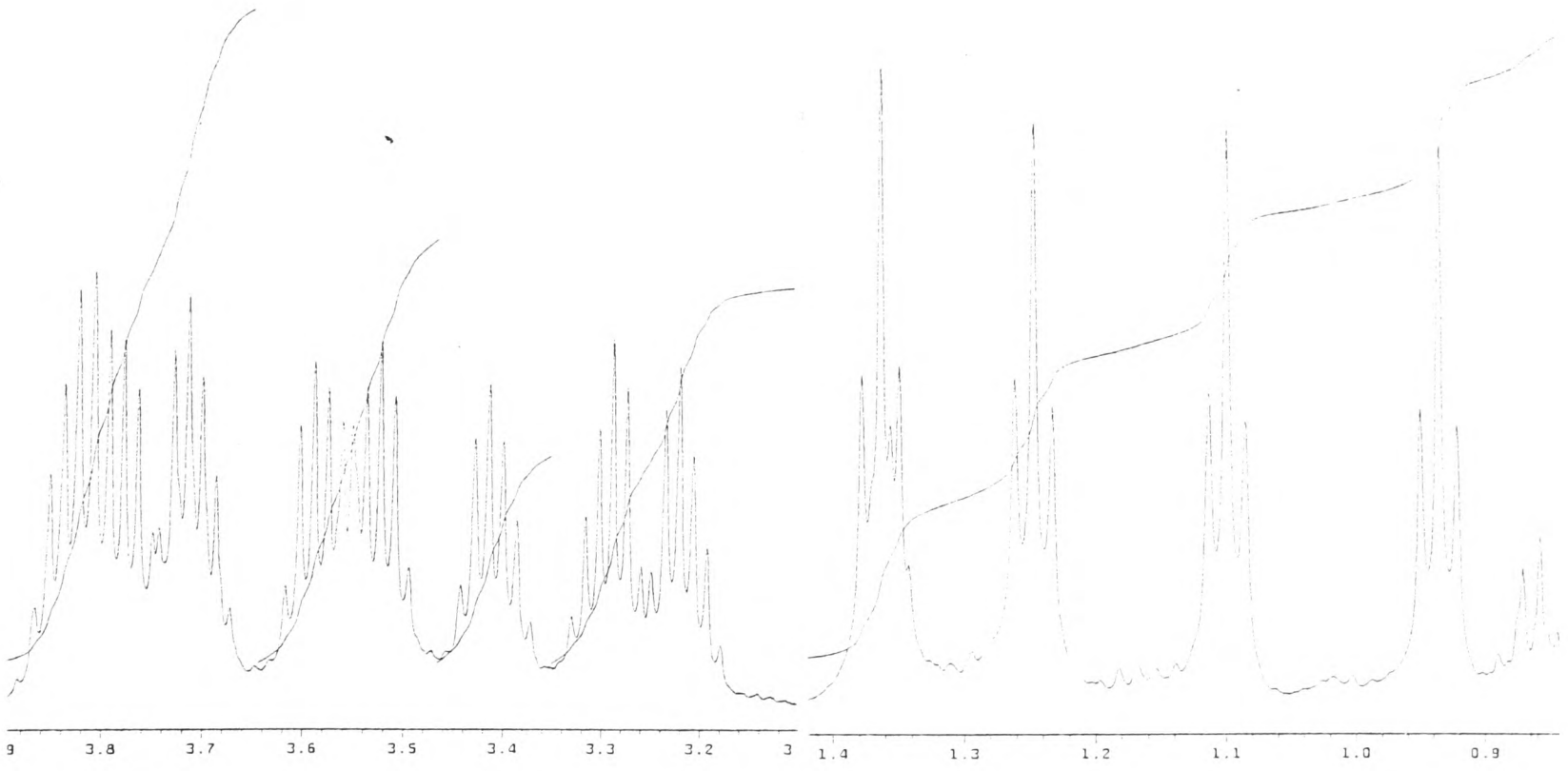


*Fig. 3.3: ^1H NMR spectrum of compound **9** obtained at 499.99 MHz in CD_2Cl_2, together with expansions of the methylene and methyl regions. [* indicates residual protio solvent, $CDHCl_2$].*

confirmed the findings of the ^{1}H spectrum in that there were four each of methyl and methylene resonances visible and a doublet at δ = 17.2 ppm assigned as the P-Me carbon. Two signals were observed at very low field (δ = 229.78 and 199.95 ppm); these were assigned as the quaternary carbons of the two dithiocarbamate ligands. The C_6F_5 carbon atoms give rise to signals found between δ = 136 and 148 ppm which is typical for complexes containing $B(C_6F_5)_3$. Two non-equivalent phenyl groups are visible, as indicated by the ^{1}H NMR spectrum; these results imply that coordination of the bulky $B(C_6F_5)_3$ group to the nitrido ligand restricts rotation about the Re-P bond, thus rendering the two phenyl groups magnetically inequivalant. The individual *ipso*, *ortho*, *meta* and *para* resonances could be assigned on the basis of the magnitude of the phosphorous-carbon coupling constant. A ^{13}C-^{1}H correlation experiment was also performed on the phenyl regions of the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra and this enabled assignment of the phenyl resonances in the ^{1}H NMR spectrum as well as the determination of some coupling constants. The low field (δ = 110-160 ppm) region of the $^{13}C\{^{1}H\}$ NMR spectrum is shown in Fig. 3.4 and the ^{13}C-^{1}H correlation experiment is depicted in Fig. 3.5

^{19}F NMR spectroscopy studies showed the expected three signals assigned as the *ortho* (d), *para* (t) and *meta* (dd) C_6F_5 fluorines on moving from low (δ = -133.8 ppm) to high (δ = -168.8 ppm) field. The $^{31}P\{^{1}H\}$ NMR spectrum is also as predicted, revealing a single resonance shifted somewhat upfield from the spectrum of the uncomplexed nitrido complex, **7**.

3.2.3.3 Characterisation by Infrared Spectroscopy and Mass Spectrometry

An infrared spectrum of compound **9** was obtained as a Nujol mull. Unfortunately, this means of characterisation was not wholly informative since the position of the rhenium-nitrogen stretch is unclear for two reasons. One is the partial obscurement of the 900-1100 cm^{-1} region by absorptions attributable to the C_6F_5-groups. The other reason is that it is not altogether certain which way the position of

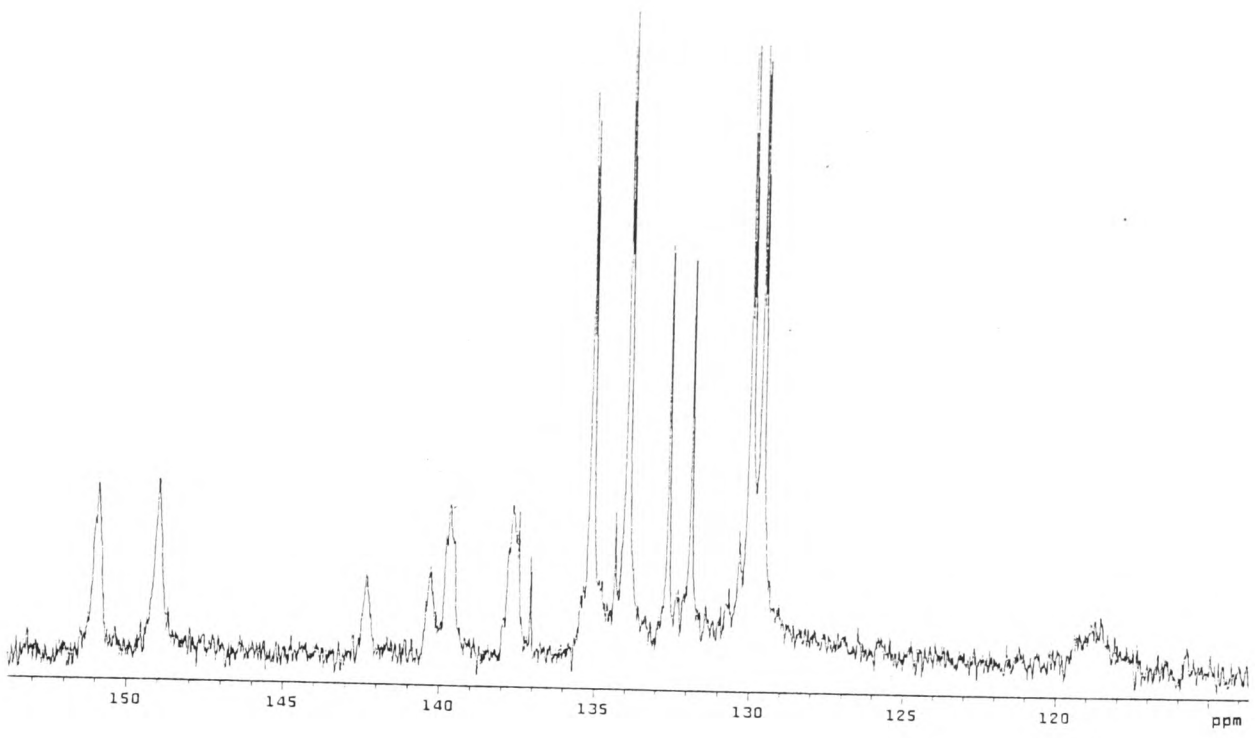


Fig. 3.4: Low-field region of the $^{13}C\{^1H\}$ NMR spectrum of compound **9** *recorded in CD_2Cl_2 at 123.70 MHz.*

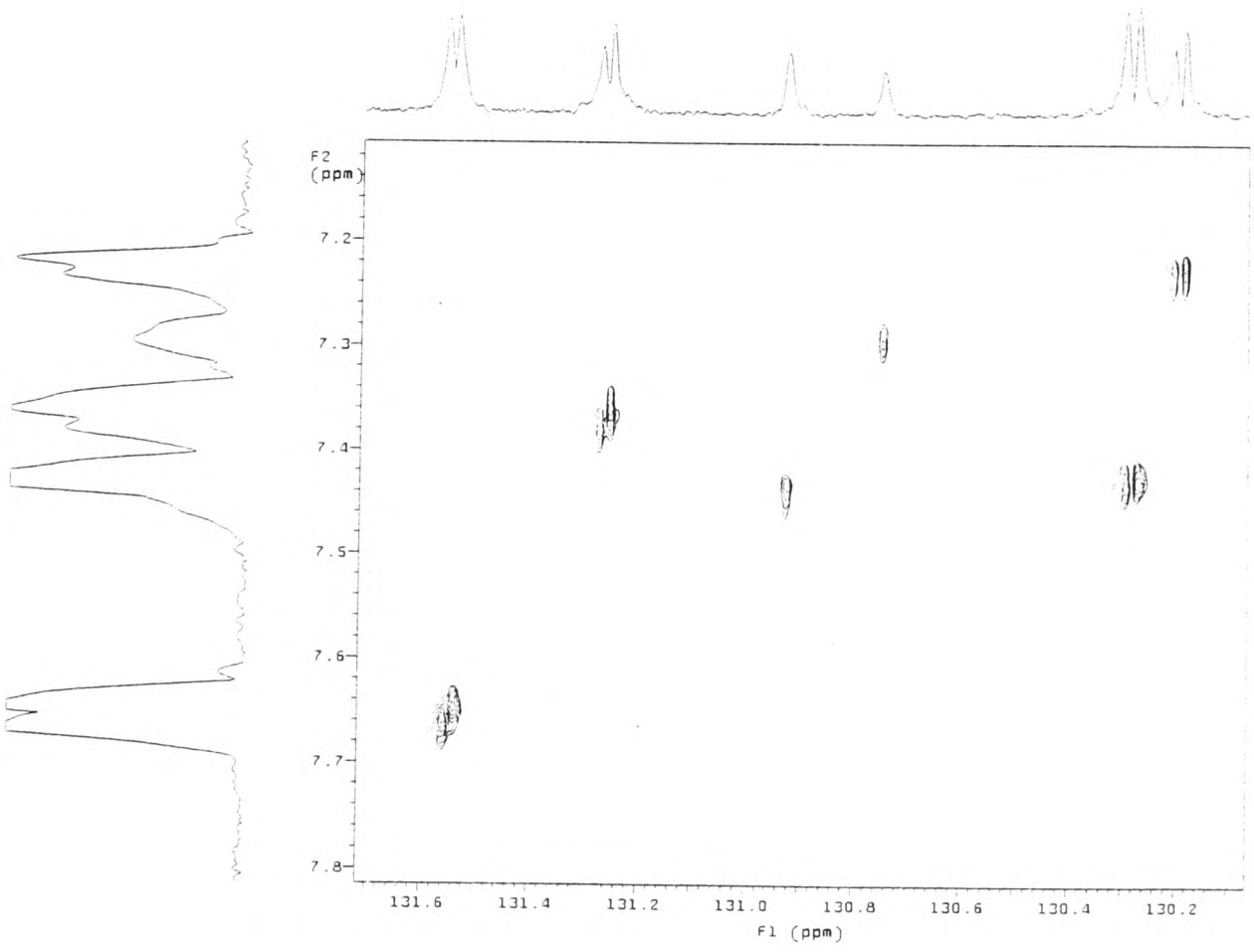


Fig. 3.5: ^{13}C-^1H correlation NMR spectrum of the phenyl region of compound **9**.

ν(M-N) in a metal-nitrido complex will move upon Lewis acid coordination. A weakening in the M≡N bond should occur leading to a shift to lower wavenumber. However, in practice, a shift to higher wavenumber is frequently observed due to resonance between the M≡N stretch and the B-N stretch. For instance the Re≡N stretch in $[NReBr_4][AsPh_4]$ is observed to move from 1099 cm^{-1} to 1170 cm^{-1} on addition of BBr_3.[13] A band does appear in a suitable position in compound **9**, namely 1089 cm^{-1}, but stretches assignable to C_6F_5 groups also appear in this region so at best this can be only very tentatively ascribed to the Re≡N stretch.

A Fast Atom Bombardment mass spectrum of compound **9** was also obtained. Although only very weak peaks assignable as the parent ion, $[M]^+$, and $[M\text{-}C_6F_5]^+$ were observed, several strong signals were observed at other assignable values of m/z. These included 697 $[M\text{-}B(C_6F_5)_3]^+$, 549 $[M\text{-}B(C_6F_5)_3\text{-}(S_2CNEt_2)]^+$, 497 $[M\text{-}B(C_6F_5)_3\text{-}PMePh_2]^+$ and 399 $[M\text{-}B(C_6F_5)_3\text{-}2(S_2CNEt_2)]^+$.

3.2.3.4 X-Ray Crystal Structure

Single crystals of **9** suitable for analysis by X-ray crystallography were grown by slow evaporation of a solution in *iso*propanol and dichloromethane (1:1 mixture) at ambient temperature. A crystal of dimensions 0.30 x 0.25 x 0.20 mm was selected for diffraction, covered with paratone-N oil under an inert atmosphere and mounted on the end of a glass fibre. Data were collected at 125 K on an Enraf-Nonius DIP2000 image plate diffractometer with graphite monochromated Mo K_α radiation ($\lambda = 0.71069$ Å) and indexed as triclinic with space group P-1. The images were processed with the DENZO and SCALEPACK programs.[14]

All solution, refinement and graphical calculations were performed using the CRYSTALS[15] and CAMERON[16] software packages. The structure was solved by direct methods using the SIR92 program[17] and refined by a full-matrix least squares procedure on F. Unfortunately, the crystal quality was very poor and full refinement was not possible; however, the connectivity between atoms is certain. All non-hydrogen atoms were refined with anisotropic displacement parameters except carbon atoms which were

refined isotropically. All hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters. Two solvent molecules were found in the lattice, one of CH_2Cl_2 and one of ^iPrOH. The hydroxyl hydrogen atom was not located and no solvent atoms were refined. A Chebychev weighting scheme with the parameters 8.29, -6.35 and 4.72 was applied. This yielded a final R value of 12.9 %. Data collection and structure solution were performed by Mr. Michael Leech of the Chemical Crystallography Laboratory, Oxford; further refinement was carried out by Dr. Linda Doerrer of this laboratory. Details of the structure determination may be found in Appendix Two.

The molecular structure of compound **9** is shown in Fig. 3.6 and selected bond distances and angles are given in Table 3.1. The packing diagram (Fig. 3.7) shows the channels that run through the crystal containing solvent molecules. The structure shows the expected, approximately octahedral, coordination environment around the rhenium atom and an almost linear (172.9(18) °) Re-N-B moiety.

Unfortunately, no crystal structure of the parent nitrido complex, **7**, was obtained. However a structure of $[NRe(PMe_2Ph)(S_2CNEt_2)_2]$, which differs from **7** only in the nature of the tertiary phosphine ligand, has been published.[11] The main structural features found in adducts of metal nitrido compounds are attributable to a slight lengthening of the Re≡N bond on coordination with consequent weakening of this moiety's *trans* influence. For compound **9**, a Re-N bond distance of 1.67(2) Å is found, slightly longer, but not significantly so, than the distance of 1.666(6) Å reported for $[NRe(PMe_2Ph)(S_2CNEt_2)_2]$.[11] Additionally, the Re-S(2) (*trans*) distance is now only *ca.* 0.15-0.25 Å longer than the other Re-S distances, a much smaller difference than that found in the previously reported structure (*ca.* 0.35-0.40 Å). This indicates a substantial lessening of the *trans* influence of the nitrido ligand upon Lewis acid coordination. The structure is otherwise unremarkable with approximately tetrahedral coordination around the boron atom and the two phenyl rings on the tertiary phosphine found in locations that minimise steric interference with the bulky pentafluorophenyl groups.

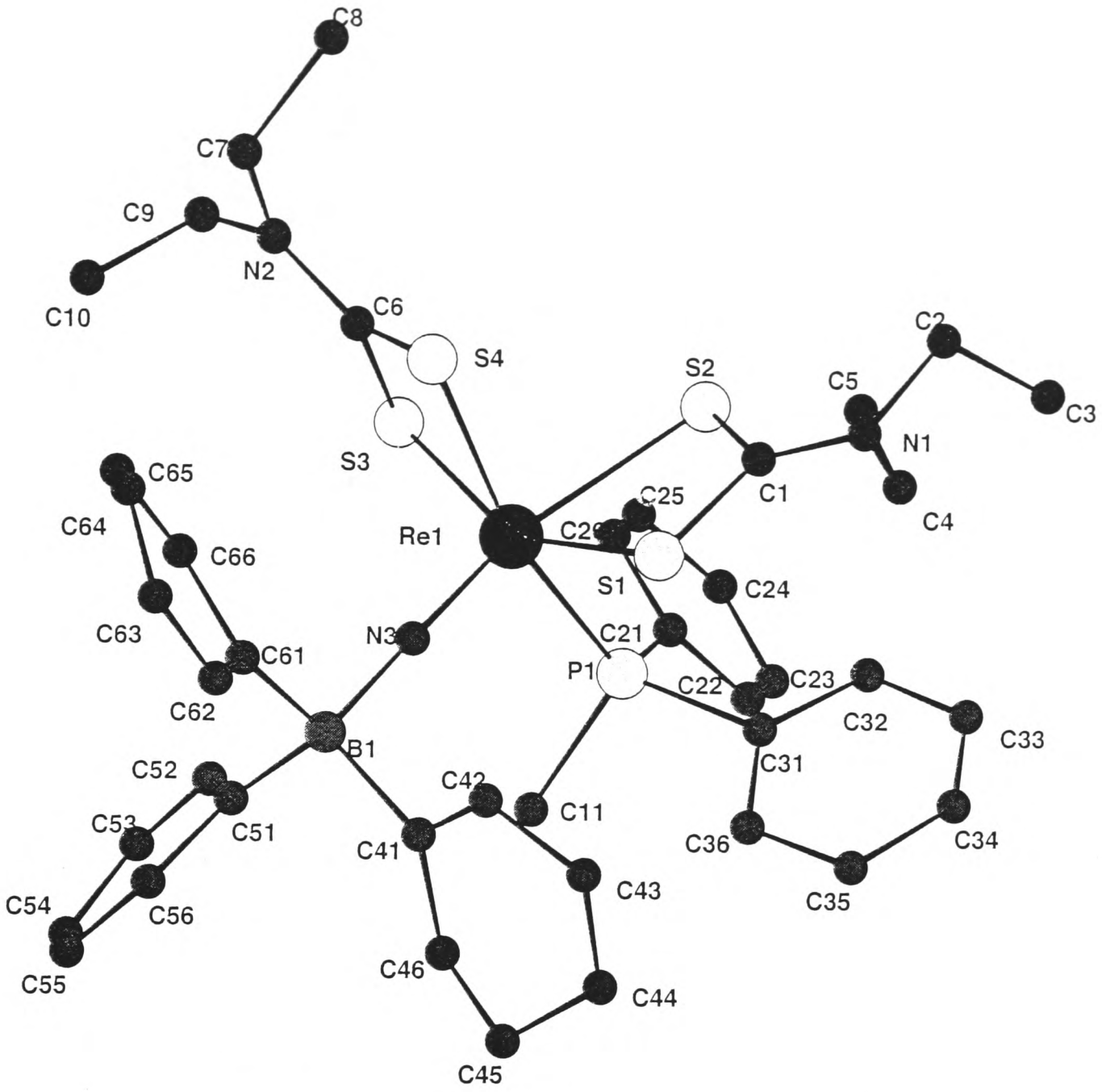


Fig. 3.6: Molecular structure of compound ***9****.*

[Hydrogen and fluorine atoms are omitted for clarity].

Bond	**Distance (Å)**		**Angle (°)**
B(1) - N(3)	1.58(4)	B(1) - N(1) - Re(1)	172.9(18)
Re(1) - N(3)	1.67(2)	C(41) - B(1) - C(51)	110.4(21)
Re(1) - S(1)	2.449(7)	C(51) - B(1) - C(61)	106.6(23)
Re(1) - S(2)	2.631(8)	C(41) - B(1) - C(61)	116.7(23)
Re(1) - S(3)	2.389(6)	C(41) - B(1) - N(3)	103.7(22)
Re(1) - S(4)	2.421(8)	C(51) - B(1) - N(3)	113.7(22)
Re(1) - P(1)	2.435(8)	C(61) - B(1) - N(3)	105.9(22)

Table 3.1: Selected bond distances and angles for compound ***9****.*

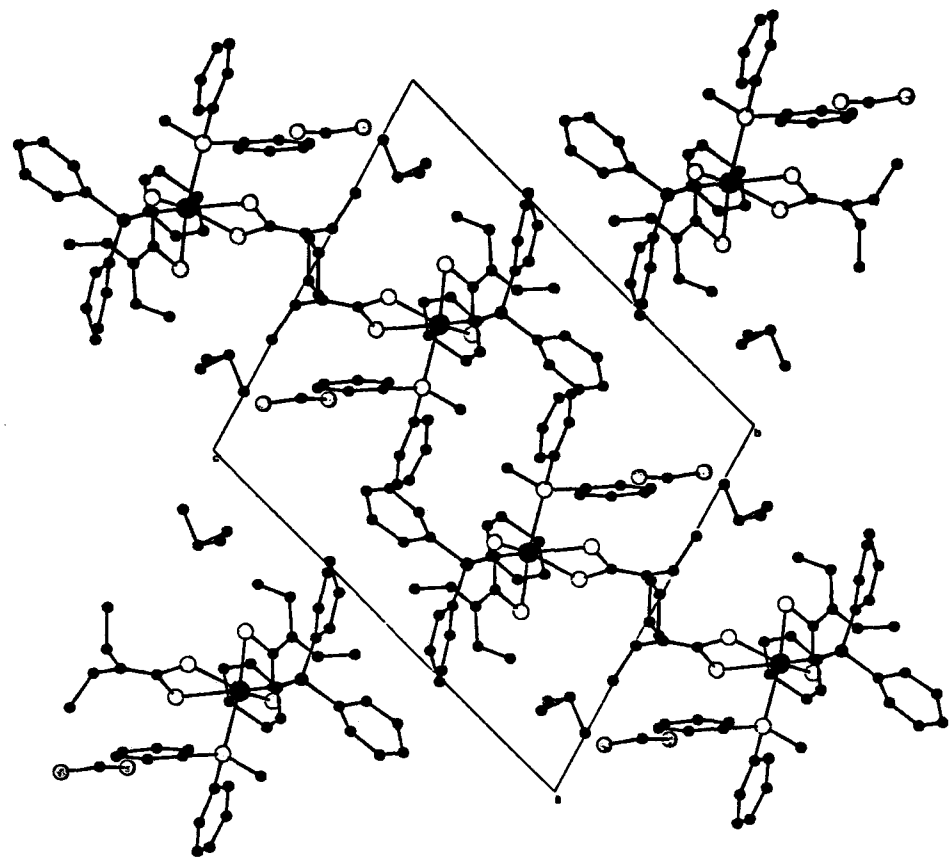


*Fig. 3.7: Crystal packing diagram for compound **9**, viewed along the a axis.*

[Hydrogen and fluorine atoms are omitted for clarity].

The crystal structures of compounds **9** and **10** are compared with those of the published complexes [{X_3MN}Re(PMe_2Ph)(S_2CNEt_2)$_2$] (MX_3 = BCl_3, $GaCl_3$[12] or BPh_3[19]) in Section 3.2.4.2 below.

3.2.4 Synthesis and Characterisation of [{$(C_6F_5)_3BN$}Re(PMe_2Ph)(S_2CNMe_2)$_2$] (10)

The Lewis acid $B(C_6F_5)_3$ was also reacted with [NRe(PMe_2Ph)(S_2CNMe_2)$_2$], synthesised according to the method of Abram.[11] The borane was added to the nitrido complex, with both reactants in CH_2Cl_2, and a fairly slow colour change from orange to dark red was observed. After removal of volatiles *in vacuo*, a grey oily solid resulted which was rendered as a lavender powder (**10**) in 55 % yield by trituration with pentane. Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a dichloromethane solution of **10**.

3.2.4.1 Characterisation

Full characterising data were obtained and supported the proposed formulation of **10** as $[\{(C_6F_5)_3BN\}Re(PMe_2Ph)(S_2CNMe_2)_2]$. Satisfactory microanalytical results were obtained and NMR spectroscopic studies indicated that, like compound **9**, **10** had lower symmetry than the parent nitrido complex. The ^1H NMR spectrum displays two doublets, assigned to the two P-Me groups, and four signals attributable to N-Me moieties in contrast to the starting material where there is just one P-Me signal.[11] The $^{13}C\{^1H\}$ NMR spectrum is easily assigned and once again displays many similarities with that of **9**. Two of the N-Me peaks are assigned as being coincident in the $^{13}C\{^1H\}$ NMR spectrum since there are just three resonances between δ = 39 and 40 ppm, one with approximately double the intensity of the others.

The $^{11}B\{^1H\}$ NMR spectrum shows a single sharp peak in the region expected for fourfold coordinated boron and $^{31}P\{^1H\}$ NMR spectral analysis reveals a single peak at δ = -26.6 ppm, shifted from the resonance of the starting material which was found to occur at δ = -23.8 ppm.

For reasons explained in Section 3.2.3.3 above, the infrared spectrum (obtained in Nujol) is not terribly informative, although a very tentative assignment of ν(Re-N) at 1092 cm^{-1} can be made (*cf.* 1055 cm^{-1} in the starting material[11]). The Fast Atom Bombardment mass spectrum obtained showed only a peak due to the parent nitride complex (although this is expected to occur in a mass spectrum of the adduct).

3.2.4.2 X-Ray Crystal Structure

Single crystals of **10** suitable for analysis by X-ray crystallography were grown by slow vapour diffusion of pentane into a solution of **10** in dichloromethane. A plate-shaped crystal of dimensions 0.25 x 0.05 x 0.05 mm was selected for diffraction, covered with paratone-N oil under an inert atmosphere and mounted on the end of a glass fibre. Data were collected at 125 K on an Enraf-Nonius DIP2000 image plate diffractometer with graphite monochromated Mo K_α radiation (λ = 0.71069 Å) and

indexed as triclinic with space group P-1. The images were processed with the DENZO and SCALEPACK programs.[14]

All solution, refinement and graphical calculations were performed using the CRYSTALS[15] and CAMERON[16] software packages. The structure was solved by direct methods using the SIR92 program[17] and refined by a full-matrix least squares procedure on F. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters. A Chebychev weighting scheme with the parameters 2.84, 0.362 and 2.06 was applied as well as an empirical absorption correction.[18] This yielded a final R value of 4.2 %. Data collection and structure solution were performed by Dr. Linda Doerrer of this laboratory. Full details of the structure determination may be found in Appendix Three.

The molecular structure of compound **10** is shown in Fig. 3.8; selected bond-lengths and bond-angles are given in Table 3.2. No crystal structure of the parent nitrido compound is found in the literature, although structural similarities with the closely related complex $[NRe(PMe_2Ph)(S_2CNEt_2)_2]$[11] are apparent. Features corresponding to those found in the structure of compound **9** are also observed here, namely a Re-N bond length slightly longer than typically found for uncomplexed nitrido compounds and a less pronounced *trans* influence.

Table 3.3 presents a comparison of important bond distances and the Re-N-B bond angle of compounds **9** and **10** with several known Lewis acid adducts of rhenium nitrido compounds. The important features of the new compounds described in this work are seen to be in accord with those previously reported. In general, the Re-N bond lengthens on coordination of a Lewis acid, but only slightly. One exception is the triphenylborane adduct of **w**, compound **z**, where the Re-N distance actually decreases slightly on coordination. The other major trend that is observed is the reduction in *trans* influence. This has already been noted for compounds **9** and **10** as compared to a free nitrido complex, **w**. Examination of the difference in bond distances between Re-S_{trans} and Re-S_{cis} for compounds **x**, **y** and **z** as compared to nitrido complex **w** shows a

significant diminishing of the *trans* influence on coordination of an electrophile to the nitrido unit. Lastly, it can be observed that all the structurally characterised adducts with boranes have nearly linear (*ca.* 170 °) Re-N-B bridges. Note that the trichlorogallane adduct, **y**, stands out somewhat in its longer Ga-N distance and non-linear Re-N-Ga linkage, but it does follow the observed trend of reduction in the *trans* influence of the nitrido ligand upon electrophile coordination.

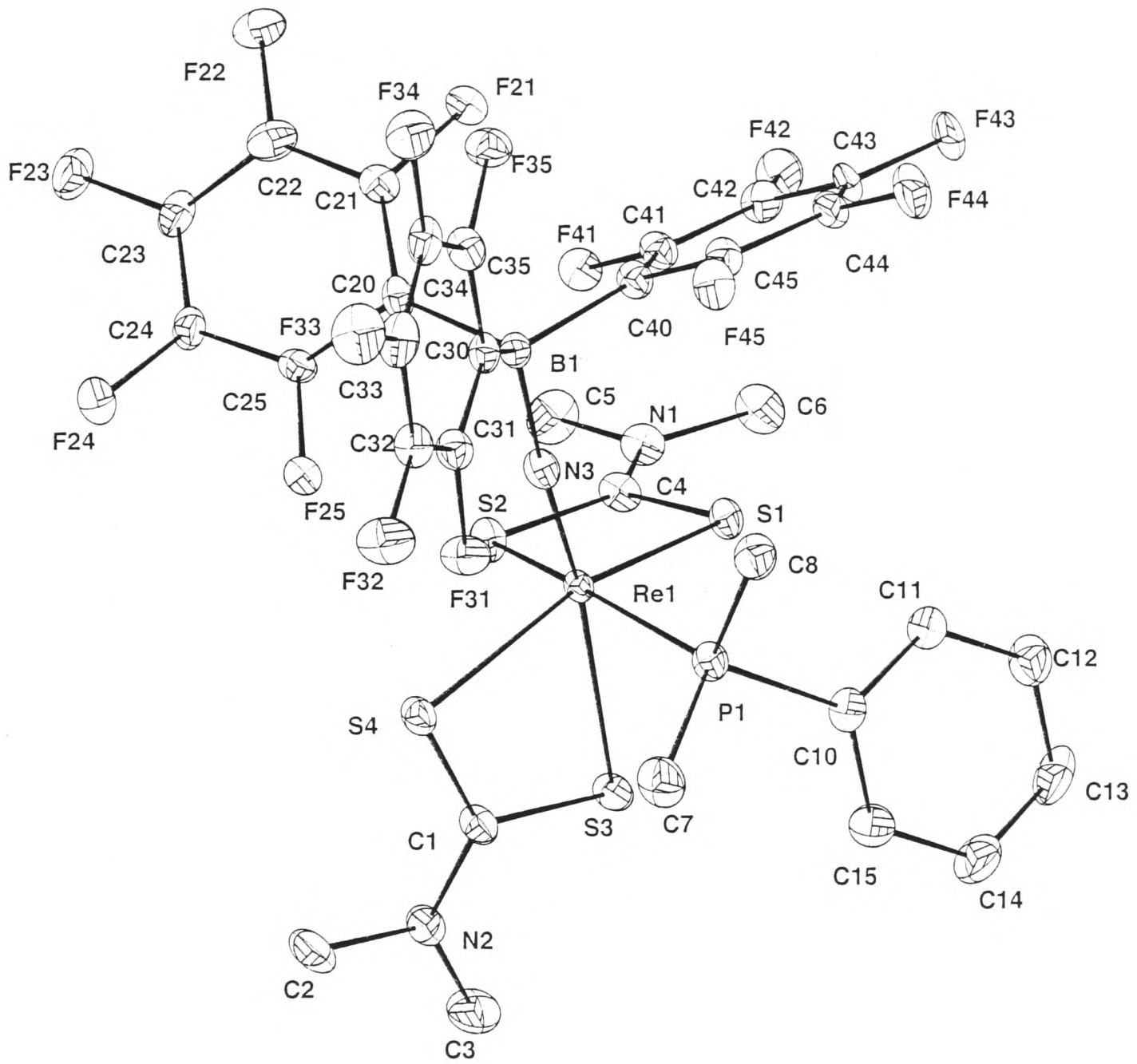


Fig. 3.8: Molecular structure of compound ***10****.*

[Hydrogen atoms are omitted for clarity].

Bond	**Distance (Å)**		**Angle (°)**
B(1) - N(3)	1.548(7)	B(1) - N(3) - Re(1)	170.9(3)
Re(1) - N(3)	1.700(4)	C(20) - B(1) - C(30)	103.3(4)
Re(1) - S(1)	2.3769(12)	C(30) - B(1) - C(40)	114.5(4)
Re(1) - S(2)	2.4350(15)	C(20) - B(1) - C(40)	114.7(4)
Re(1) - S(3)	2.6090(12)	C(20) - B(1) - N(3)	109.0(4)
Re(1) - S(4)	2.4608(13)	C(30) - B(1) - N(3)	115.2(4)
Re(1) - P(1)	2.4154(15)	C(40) - B(1) - N(3)	100.4(4)

Table. 3.2: Selected bond distances and angles for compound ***10****.*

	N-Re	Y-N	Re-S_{trans}	Re-S_{cis}	Y-N-Re
[{$(C_6F_5)_3$BN}Re(PMePh_2)(S_2CNEt_2)$_2$] (**9**)	1.67(2)	1.58(4)	2.631(8)	2.389(6)-2.449(7)	172.9(18)
[{$(C_6F_5)_3$BN}Re(PMe_2Ph)(S_2CNMe_2)$_2$] (**10**)	1.700(4)	1.548(7)	2.6090(12)	2.3769(12)-2.4608(13)	170.9(3)
[NRe(PMe_2Ph)(S_2CNEt_2)$_2$][11] (**w**)	1.666(6)	n/a	2.793(2)	2.396(1)-2.449(1)	n/a
[{Cl_3BN}Re(PMe_2Ph)(S_2CNEt_2)$_2$][12] (**x**)	1.704(3)	1.518(5)	2.565(2)	2.376(2)-2.455(2)	170.5(3)
[{Cl_3GaN}Re(PMe_2Ph)(S_2CNEt_2)$_2$][12] (**y**)	1.695(6)	1.916(6)	2.581(2)	2.377(2)-2.430(2)	154.5(4)
[{Ph_3BN}Re(PMe_2Ph)(S_2CNEt_2)$_2$][19] (**z**)	1.653(12)	1.64(3)	2.579(4)	2.362(4)-2.431(3)	170.9(9)

[Y = B or Ga]

Table 3.3: Comparison of selected bond distances (in Å) and angles (in °) for compounds ***9****,* ***10*** *and related complexes.*

3.2.4.3 Reactions of Compound 10 with Lewis Bases

In order to test the strength of the interaction between *tris*(pentafluorophenyl)borane and the Re≡N moiety, reactions between compound **10** and a series of competing Lewis bases were examined. The bases used were the same as those used to test the stability of $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)WH_3]$ (*vide supra*) *i.e.* thf, NEt_3 and PMe_3. The reaction used was also analogous, with the base being added to a solution of *ca.* 20 mg of **10** in dichloromethane. After the reaction had been allowed to proceed for one hour, the volatiles were removed under vacuum and the residues analysed by ^1H and $^{11}B\{^1H\}$ NMR spectroscopy in $CDCl_3$.

In all three cases, the only observed resonances were those attributable to compound **10** and the appropriate, free, Lewis base. It may be concluded that this complex, and by extension the whole series of complexes **9** to **11**, exhibit a quite unexpected stability towards attack by competing Lewis bases. Since these bases are almost certainly more electron-rich than the coordinated nitrido ligand, it is postulated that the stability is mainly kinetic rather than thermodynamic since the bulky pentafluorophenyl and *cis*-tertiary phosphine groups shield the boron-nitrogen bond to some extent (see Fig. 3.6 and Fig. 3.8). This stability extends to atmospheric oxygen (the adducts were not observed to be particularly air-sensitive) and to traces of water, since the NMR spectroscopic analysis was carried out in wet deuterochloroform and compound **9** could be crystallised from (undried) Analar *iso*propanol.

3.2.5 Synthesis and Characterisation of $[\{(C_6F_5)_3BN\}ReCl(PMePh_2)_2(S_2CNMe_2)]$ (11)

The complex $[NReCl(PMePh_2)_2(S_2CNMe_2)]$ (**8**) is readily available from $[NReCl_2(PMePh_2)_3]$ and one equivalent of $Na[S_2CNMe_2]$ (*vide supra*). Once again, the reaction with the borane was performed in CH_2Cl_2 and an immediate colour change from yellow to red/orange was observed. The solvent was removed *in vacuo* and the oily solid thus produced triturated with pentane to yield **11** as an orange powder in 66 % yield.

Microanalytical data were obtained which supported the formulation of **11** as a simple adduct of the borane and the rhenium nitrido complex.

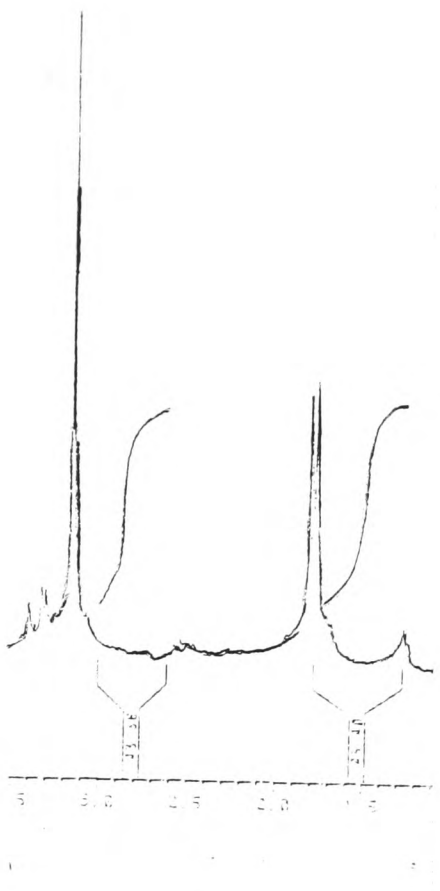
3.2.5.1 Characterisation of Compound 11

NMR spectroscopic data were obtained in CD_2Cl_2 and, as with compounds **9** and **10**, showed some reduction in symmetry on coordination of the borane. The ^1H and $^{31}P\{^1H\}$ NMR spectroscopic data indicated that the two phosphines were equivalent as were the two methyl groups of the dithiocarbamate ligand. However the $^{13}C\{^1H\}$ NMR spectral data indicated that both phosphines were distinct as were the methyl groups on the dithiocarbamate and even both phenyls on each phosphine. Hence there appeared to be four sets of phosphorous-phenyl signals in the $^{13}C\{^1H\}$ NMR spectrum (although their complex overlap meant total assignment was impossible), two doublets due to P-CH_3 and two singlets assignable as N-CH_3. By contrast, the ^1H NMR spectrum exhibited only two methyl signals and the $^{31}P\{^1H\}$ NMR spectrum displayed a single resonance. The δ = 1.5-3.5 ppm region of the ^1H NMR spectrum, the $^{31}P\{^1H\}$ NMR spectrum and the $^{13}C\{^1H\}$ NMR spectrum are shown in Fig. 3.9.

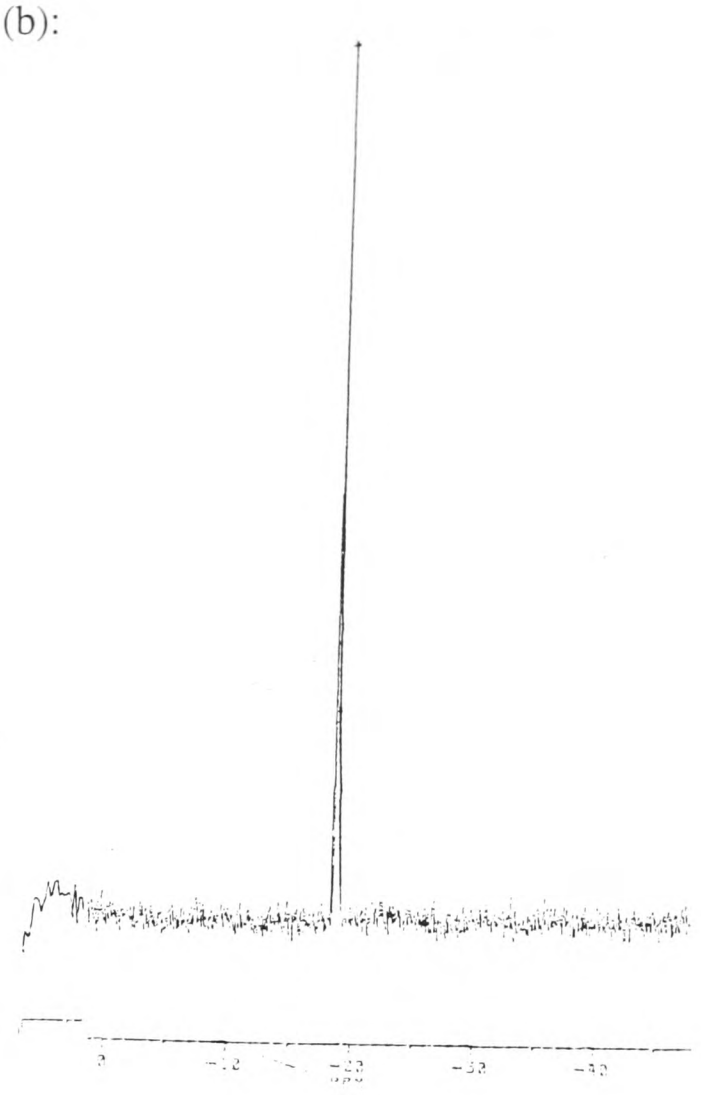
There are two possible explanations for these data. One is that some signals in the ^1H and $^{31}P\{^1H\}$ NMR spectra are coincident; however this would mean that the two N-Me signals and the two P-Me signals *and* the two $^{31}P\{^1H\}$ signals would have to be exactly coincident which seems unlikely. The other postulated reason is that the methyl groups are equivalent on timescales up to that of $^{31}P\{^1H\}$ NMR spectroscopy but become distinguishable on the longer timescales found in $^{13}C\{^1H\}$ NMR spectroscopy. It is possible that the actual reason is a compromise between the two explanations *i.e.* that the signals are distinguishable in the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra and not on the fast ^1H NMR spectroscopic timescale, but that the two $^{31}P\{^1H\}$ NMR spectroscopic signals are so close in chemical shift that they are apparently isochronous.

Infrared spectroscopy and mass spectrometry were less informative since the former yielded only the possible position of the rhenium-nitrogen stretch as being 1099

(a):



(b):



(c):

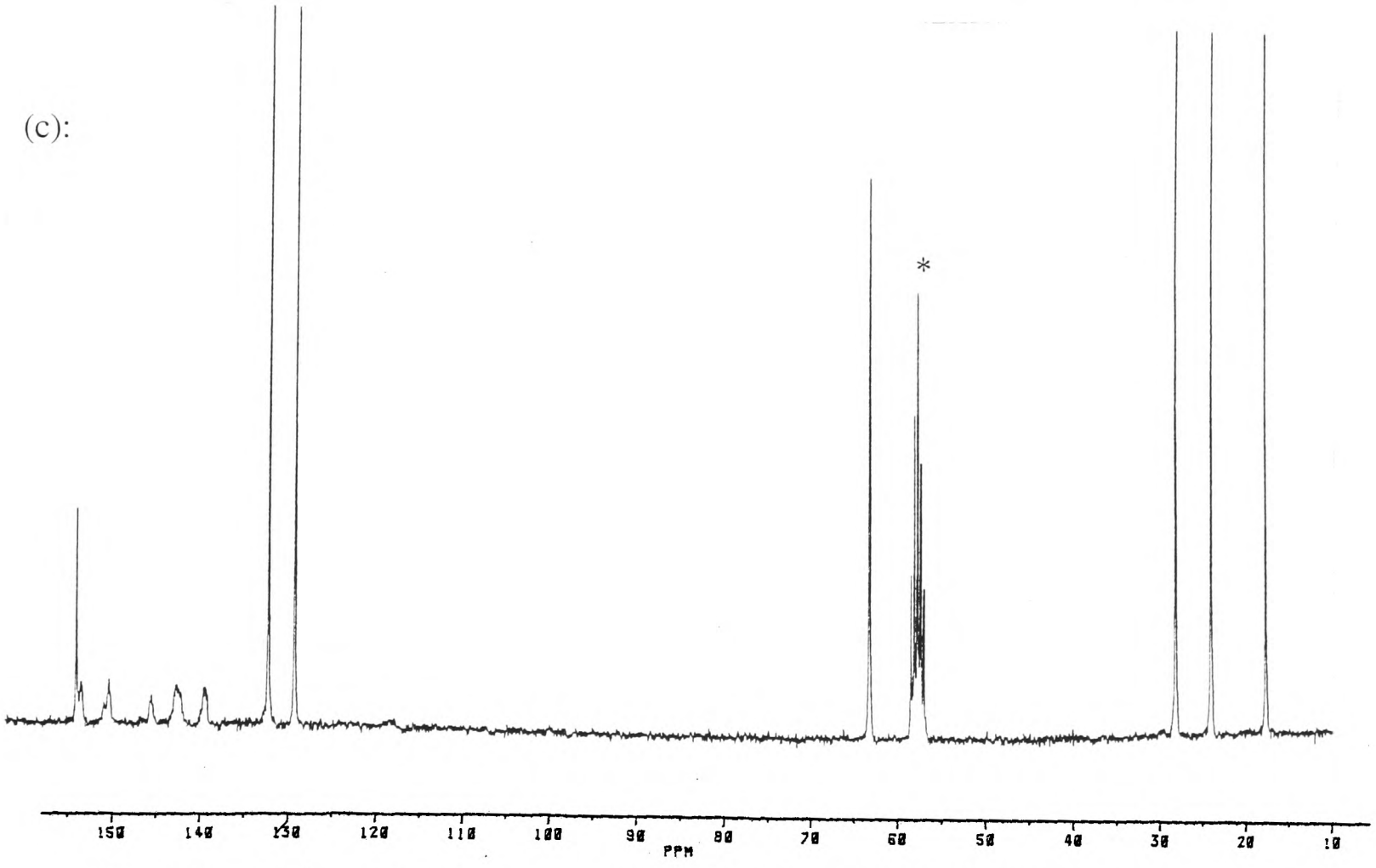


*Fig. 3.9: (a) ^{1}H, (high field region) (b) $^{31}P\{^{1}H\}$ and (c) $^{13}C\{^{1}H\}$ NMR spectra of compound **11** recorded in CD_2Cl_2 at 300.13, 121.6 and 75.5 MHz respectively. [* indicates resonance att ributable to CD_2Cl_2].*

cm^{-1} and in the latter technique, compound **11** ran poorly and produced no assignable ion fragments.

3.2.6 Reaction Between $[NReCl_2(PMePh_2)_3]$ and $B(C_6F_5)_3$

Reactions between boranes and nitrido complexes of the form $[NReCl_2(PR_3)_3]$ have appeared in the literature.[20, 21] Accordingly, $B(C_6F_5)_3$ was reacted with a complex of this type, namely $[NReCl_2(PMePh_2)_3]$, in dichloromethane at ambient temperature. After stirring overnight, the solution colour had changed from yellow to red/brown. Removal of solvent and trituration with petroleum ether (b.p. 40-60 °C) yielded a brown powder. This analysed well as a 1:1 adduct of $[NReCl_2(PMePh_2)_3]$ and $B(C_6F_5)_3$ *i.e.* C: found 49.65 % (calculated 49.48), H: 3.08 (2.84), N: 1.10 (1.01), B: 0.76 (0.78) and Cl: 5.44 (5.12). Unfortunately, NMR spectroscopy showed the product to be a mixture of at least two products. Crystallisation by slow cooling of a solution in a 1:4 mixture of CH_2Cl_2 and petroleum ether (b.p. 100-120 °C) to -80 °C yielded the product as a mixture of two distinct microcrystalline solids. Total separation by eye was not feasible, but it was possible to obtain a sample containing predominantly purple solid and one consisting mostly of a red/orange compound.

NMR spectroscopic analysis of these two partially separated products was carried out in CD_2Cl_2. The ^1H NMR spectra were generally rather uninformative since there were several overlapping resonances in both phenyl and methyl regions. The $^{11}B\{^1H\}$ spectra showed two signals- in the case of the purple fraction, the predominant product gave a signal at δ = -9.9 ppm and the red-orange fraction displayed a strong resonance at δ = -3.9 ppm. $^{31}P\{^1H\}$ NMR spectroscopy showed a similar pattern with the purple product characterised by a signal at δ = 7.34 ppm and the red/orange product by one at δ = 47.58 ppm. Unfortunately, these compounds were too water-sensitive to permit column chromatography so complete separation could not be achieved.

The formation of two products has been observed to occur in similar reactions by other workers.[22] It is believed that the problem may lie in the presence of a chloride ligand in a *trans* position to the nitrido ligand. Owing to the large *trans* influence of the

M≡N unit, the metal-chlorine bond is sufficiently weakened to labilise the chloride ligand and provide an alternative site for electrophilic attack. This would lead to the formation of two competing products as observed, and indeed this alternative form of attack may have occurred in the literature report of the X-ray crystal structure of $[\{Cl_3BN\}ReCl_2(PMe_2Ph)_3]$.[20] Here the single crystals are described as being violet and the rest of the reaction product is found to be red microcrystals. This explanation, however, must be treated with a degree of caution as similar side-reactions are not observed in the formation of compound **11** above, where the parent nitride complex also has a *trans* Re-Cl bond and yet clean attack at the nitrido ligand is observed.

The reaction was repeated in a sealed NMR tube and warming to 40 °C over a period of 6 days appeared to afford mainly the purple product, since the main peaks in the $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were at δ = -9.9 and 7.5 ppm respectively. However, there were clearly still two species present and the ^{19}F NMR spectrum after 6 days showed not only two distinct C_6F_5-containing products but also that some decomposition had occurred. With regret, further attempts to isolate clean products from this reaction had to be abandoned.

3.2.7 Summary and Conclusions

The strong electrophile $B(C_6F_5)_3$ has been shown to react cleanly with a range of rhenium nitrido complexes. Previous reactions with BBr_3, BCl_3 and BF_3 have observed direct attack by boranes on such species, but an adduct of BPh_3 was only reported to be synthesised by indirect attack by $Na[BPh_4]$ after treatment with HCl and acetone.[19] *Tris*(pentafluorophenyl)borane attacks species of the form $[NReCl_x(PR_3)_y(S_2CNR_2)_z]$ (x = 0,1; y = 1,2; z = 1,2) directly and with the formation of adducts which are remarkably stable to attack by competing Lewis bases. In general, the symmetry of these adducts, as observed in their NMR spectra, is lower than that of the parent nitrido complexes.

The reaction between $B(C_6F_5)_3$ and $[NReCl_2(PMePh_2)_3]$ produces two inseparable products one of which is believed to result from attack at the labilised *trans*-chloride ligand.

3.3 Reactions Between Nitrido Complexes of Molybdenum (VI) and $B(C_6F_5)_3$

The alkylation of nitrido complexes of molybdenum has already been touched upon above (Section 3.1). It was felt that, since complexes of the form $[NMo(S_2CNR_2)_3]$ are readily alkylated by $[Ph_3C]BF_4$,[7] reactions with the sterically and electronically similar $B(C_6F_5)_3$ would be worth investigating.

3.3.1 Synthesis of Nitrido Complexes of Molybdenum

The starting point for all the molybdenum nitrido complexes discussed here is the molybdenum (IV) complex $MoCl_4$·dme, synthesised by the method of Persson and Andersson.[23] Reaction with trimethylsilylazide, causing elimination of Me_3SiCl and dinitrogen, produces a red-orange highly sensitive solution believed to contain the species $[NMoCl_3]$.[24, 25] This solution can then be reacted with $(Me_3Si)SC(S)NR_2$, an anhydrous source of dithiocarbamate, to yield the pentagonal bipyramidal complexes $[NMo(S_2CNR_2)_3]$. Reaction of the intermediate with tertiary phosphines generally yields molybdenum(V) species formulated as $[NMoCl_2(PR_3)_2]$ and reaction with 2,2'-bipyridyl yields $[NMoCl_3(bipy)]$.

3.3.2 Synthesis and Characterisation of $[\{(C_6F_5)_3BN\}Mo(S_2CNMe_2)_3]$ (12) and $[\{(C_6F_5)_3BN\}Mo(S_2CNEt_2)_3]$ (13)

The *tris*(dithiocarbamate)nitrido complexes of molybdenum(VI), $[NMo(S_2CNR_2)_3]$ (R = Me or Et), were found to have low solubility; however they were sufficiently soluble in dichloromethane to permit reaction with $B(C_6F_5)_3$ over the course of two days. In both cases the reaction mixture darkened slightly in colour and yielded an oily solid after removal of volatiles. The products were rendered as solids after trituration

with pentane and recrystallisation from CH_2Cl_2 at -80 °C was then attempted. In the case where R = Me, this resulted in yellow microcrystals (60 %) which were found to be formulated as $[\{(C_6F_5)_3BN\}Mo(S_2CNMe_2)_3]$ (**12**) by microanalysis. Where R = Et, crystallisation did not occur, even from a very concentrated solution, so the product, $[\{(C_6F_5)_3BN\}Mo(S_2CNEt_2)_3]$ (**13**), could only be obtained as a red/brown foamy solid in 21 % yield.

Other attempts to crystallise these compounds *e.g.* by layering a CH_2Cl_2 solution with pentane, produced only oily material.

3.3.2.1 Characterisation by NMR Spectroscopy

Complexes of the type $[YMo(S_2CNR_2)_3]$ (Y = Cl, N, N_2Ph, N_2COPh, NS or NO) display a low degree of symmetry and have prexiously been shown to exhibit interesting NMR spectroscopic behaviour.[26] The ^1H NMR spectrum of the parent nitrido compound $[NMo(S_2CNMe_2)_3]$ displays four signals assignable to methyl groups at δ = 3.36, 3.35, 3.33 and 3.21 ppm in ratios 2:1:2:1 whereas the methylene region of the ^1H NMR spectrum of $[NMo(S_2CNEt_2)_3]$ displays three overlapping quartets. It is found that in many of these complexes, the NMR spectroscopic resonances collapse to a singlet on warming.[26] This is presumably due to scrambling of the dithiocarbamate ligands possibly by a de-coordination of one sulphur moiety followed by re-coordination at a different site (Fig. 3.10).

In the case of the adducts **12** and **13**, four distinct alkyl groups are visible in both ^1H and $^{13}C\{^1H\}$ NMR spectra with intensities in the ratio 1:2:2:1; this is consistent with data reported for the literature compound $[\{Ph_3CN\}Mo(S_2CNMe_2)_3][BF_4]$.[7] Two of the quaternary carbons of the dithiocarbamate ligands are also found to be magnetically equivalent (or coincident) as there are only two low-field peaks in both $^{13}C\{^1H\}$ NMR spectra. Investigation of the high-temperature NMR spectroscopic behaviour of this system was not possible as the only suitable solvent was dichloromethane. An NMR sample of **12** was cooled to -80 °C in the hope of freezing out all six possible methyl

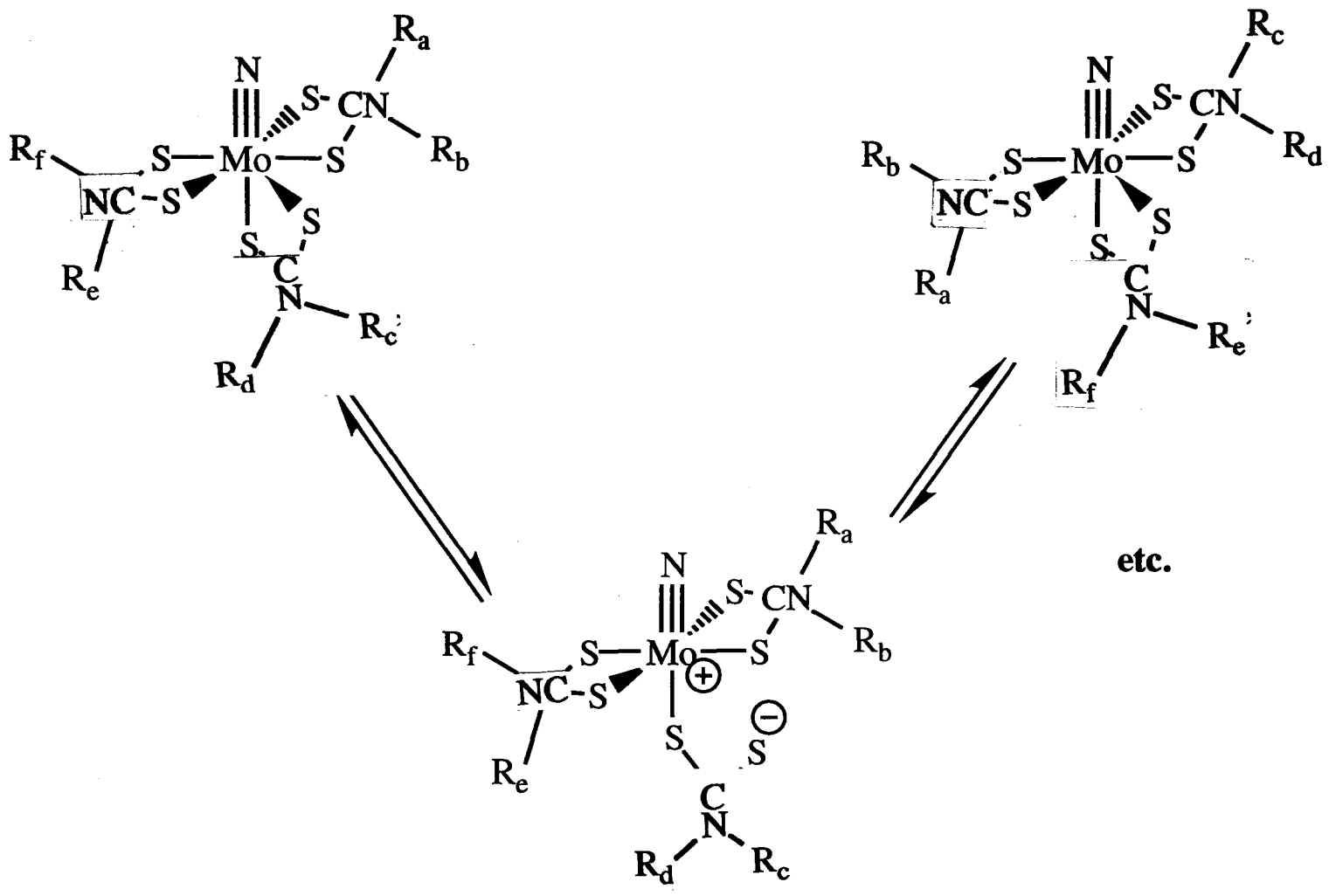


Fig. 3.10: Possible mechanism for the scrambling of the dithiocarbamate ligands in the complexes [NMo(S_2CNR_2)$_3$].

environments, however the cooling had no effect other than to slightly broaden the resonances.

Other NMR spectroscopic resonances were easily assigned and are not discussed further here.

3.3.2.2 Characterisation by Infrared Spectroscopy and Mass Spectrometry

Infrared spectra of both adducts were obtained as Nujol mulls. Again, the position of the metal-nitrogen stretch after adduct formation was not clear. Suitable bands appeared at 1082 and 979 cm^{-1} for the methyl derivative, **12**, and 1089 and 976 cm^{-1} for the ethyl derivative, **13**. The Mo≡N stretch for [NMo(S_2CNMe_2)$_3$] is reported as 1019 cm^{-1} and that of [NMo(S_2CNEt_2)$_3$] as 1015 cm^{-1}.[25] Once again (see Section 3.2.3.3), it is not clear which way the position of ν(Mo-N) will move upon adduct formation and, still more importantly, this region is once again obscured by bands caused by the C_6F_5-

moieties. The assignment of the absorptions at 1082 cm^{-1} and 1089 cm^{-1} for **12** and **13** respectively as the metal-nitrogen stretch can be nothing more than tentative.

A Fast Atom Bombardment mass spectrum of compound **12** was obtained and showed several ions expected from the proposed formulation, although the peak due to the parent ion was very weak. Peaks corresponding to loss of one pentafluorophenyl and one dithiocarbamate ligand (m/z = 697), loss of the borane (m/z = 472) and loss of the borane and a dithiocarbamate ligand (m/z = 352) were among those assigned.

3.3.2.3 Reactions of Compound 12 with Lewis Bases

As with compound **10** (*vide supra*), reactions of one of these adducts with competing Lewis bases was attempted. Hence the interaction of compound **12** with thf, NEt_3 and PMe_3 was examined as previously described and the reaction residues analysed by ^1H and $^{11}B\{^1H\}$ NMR spectroscopy in $CDCl_3$. Addition of tetrahydrofuran produced no alteration whatsoever in the $^{11}B\{^1H\}$ NMR spectrum of **12** and only signals due to uncomplexed thf could be seen in the ^1H NMR spectrum. By contrast, PMe_3 and NEt_3 (both in excess) appeared to cause *ca.* 50 % decomposition of the adduct over the course of one hour since an extra peak in the $^{11}B\{^1H\}$ NMR spectrum appeared at δ = -4.4 ppm and δ = -4.2 ppm respectively. Additionally, both free and bound Lewis base could be observed by ^1H NMR spectroscopy. One may conclude that, although lacking the high stability of $B(C_6F_5)_3$ adducts of rhenium nitrido complexes, these adducts of molybdenum nitride compounds are relatively inert towards competing Lewis bases over short periods of time.

3.3.3 Reactions between Other Nitrido Complexes of Molybdenum and $B(C_6F_5)_3$

Two other nitrido complexes were reacted with *tris*(pentafluorophenyl)borane, namely $[NMoCl_3(bipy)]$ (prepared as described by Chatt and Dilworth[25]) and $[NMo(O^tBu)_3]$ (prepared by Chris Jardine of this laboratory[27]). Unfortunately, both these nitrido complexes are extremely insoluble, even in dichloromethane, and the

attempted reactions had to take place with the nitride compounds as suspensions. It was hoped that the borane would coordinate to the small amounts of the metal complex in the CH_2Cl_2 and form a soluble adduct. This was not observed even upon prolonged stirring (several weeks) and warming, so no products were isolated from these reactions.

3.3.4 Summary and Conclusions

Tris(dialkyldithiocarbamate)nitrido complexes of molybdenum(VI) have been shown to form easily isolable and relatively stable adducts with the strong electrophile *tris*(pentafluorophenyl)borane. The fluxional processes believed to occur in compounds of this type could not be investigated by variable temperature NMR spectroscopy owing to the lack of a suitable high-temperature solvent.

3.4 Reactions Between Nitrido Complexes of Osmium (VI) and $B(C_6F_5)_3$

The reaction of $[NOs(1,2\text{-}S_2C_6H_4)_2][^nBu_4N]$ with various electrophiles has been described by Sellmann *et al.*[6] Of the two potential donor sites in this molecule, S and N, the lone pair on sulphur is found to be most nucleophilic since methylation using $[Me_3O]BF_4$ occurs at this site. When the electrophile is bulky, such as the reaction with $[Ph_3C]PF_6$, attack occurs at the less hindered nitrido site (Fig. 3.11). Given the large size of $B(C_6F_5)_3$, electrophilic attack at nitrogen atom was expected to occur in this system.

3.4.1 Synthesis of Nitrido Complexes of Osmium

The starting point for syntheses of osmium nitrido complexes in this study was commercially available osmate(VI) anion, $K_2[OsO_4]\cdot 2H_2O$. Griffith has described the use of this reagent, in conjunction with sodium azide, concentrated hydrochloric acid and *tetra*-n-butylammonium hydroxide, to prepare the species $[NOsCl_4][^nBu_4N]$ in virtually quantitative yield.[28] The chloride ligands in this species are labile to substitution by other

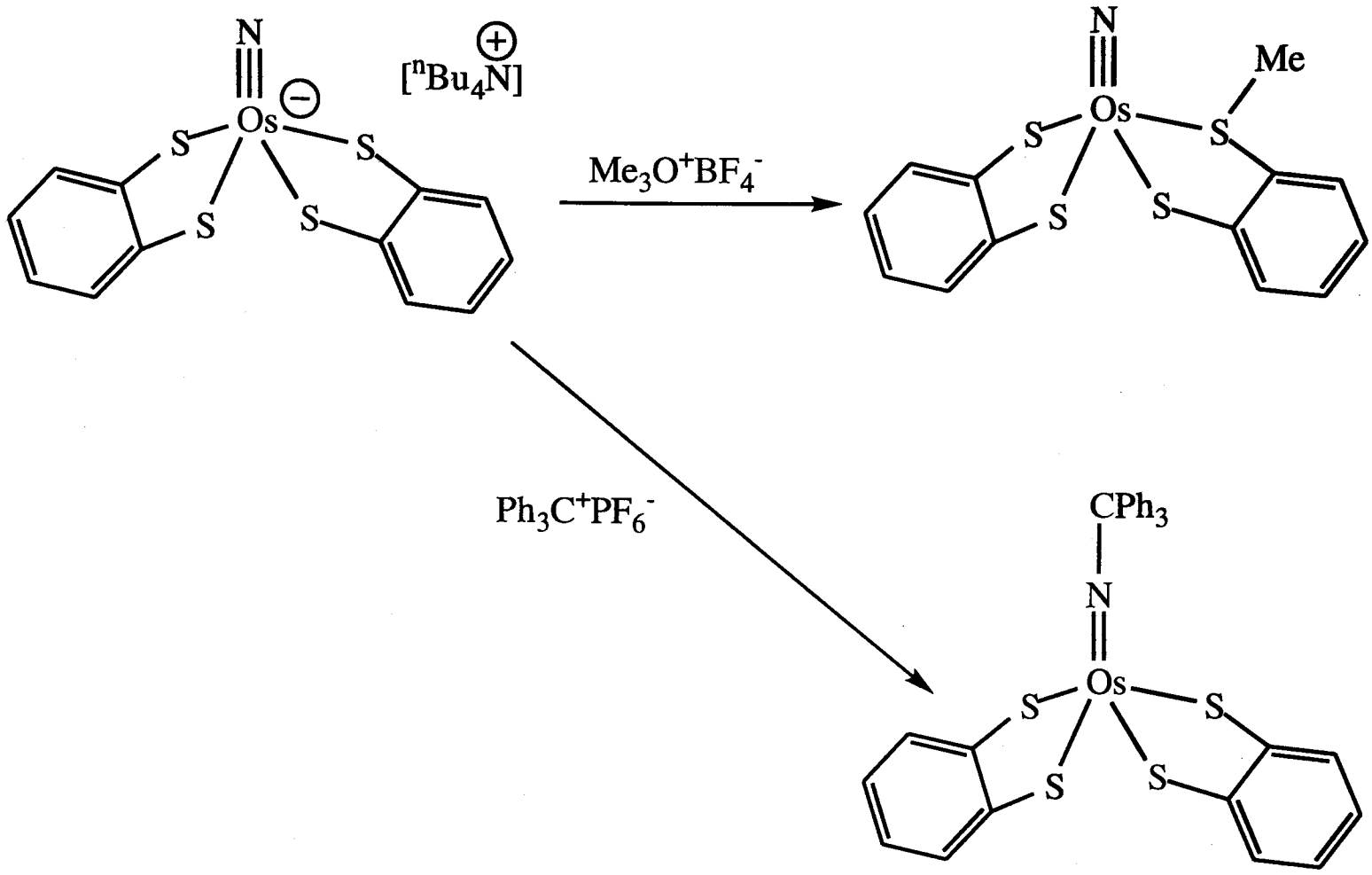


Fig. 3.11: Alkylation of [NOs(1,2-$S_2C_6H_4)_2$][$^nBu_4N$].

ligands, for instance (CH_2SiMe_3),[29] (η^5-C_5H_5)[30] or 1,2-benzenedithiolate.[6] The latter complex is of interest in the present work.

3.4.2 Synthesis and Characterisation of [{$(C_6F_5)_3BN$}Os(1,2-$S_2C_6H_4)_2$] [$^nBu_4N$] (14)

The compound $B(C_6F_5)_3$ was added to [NOs(1,2-$S_2C_6H_4)_2$][$^nBu_4N$] in dichloromethane at ambient temperature causing an immediate colour change from yellow to deep red. The reaction was allowed to proceed for one hour and then the volatiles were removed to yield a green oily solid. Stirring with pentane for 48 hours afforded the product as an olive-green powder (**14**) which was shown by microanalysis to be formulated as [{$(C_6F_5)_3BN$}Os(1,2-$S_2C_6H_4)_2$][$^nBu_4N$]. Cooling to -80 °C of even a very concentrated solution of **14** in CH_2Cl_2 failed to produce crystals, as did various solvent diffusion and layering experiments.

3.4.2.1 Characterisation

Full NMR and infrared spectroscopic data were obtained for compound **14**. ^{1}H NMR spectroscopy afforded results very much in accord with those obtained for $[\{Ph_3CN\}Os(1,2\text{-}S_2C_6H_4)_2]$.[6] Resonances for the $^{n}Bu_4N$ cation were visible and little shifted from those of the starting material and the benzenedithiolate ligands appeared as two multiplets in the range δ = 7.0-7.7 ppm as is expected for such AA'BB' spin systems. $^{11}B\{^{1}H\}$ NMR spectroscopy showed a sharp resonance at δ = -3.7 ppm in agreement with known compounds where $B(C_6F_5)_3$ is coordinated to a nucleophile and results consistent with this were obtained by ^{19}F NMR spectroscopy.

A $^{13}C\{^{1}H\}$ NMR spectrum was also obtained and was easily assigned, with the *ipso*-$S_2C_6H_4$ resonance being appreciably downfield (and with half the intensity) of the other two signals attributed to this moiety. The spectrum is shown in Fig. 3.12.

An infrared spectrum was obtained in Nujol and the osmium-nitrogen stretch assigned as 1097 cm^{-1}, slightly higher than that in the starting material of 1063 cm^{-1} for reasons already discussed above.

A Fast Atom Bombardment mass spectrum failed to show any assignable peaks other than one at m/z = 242 corresponding to $[^{n}Bu_4N]^{+}$.

3.4.3 Reactions of Compound 14

The reaction of several of the metal complex-$B(C_6F_5)_3$ adducts with competing Lewis bases had been investigated (*vide supra*). It was decided to repeat these reactions with compound **14** to gain further insight into the strength of the B-N≡M interaction. Reactions with competing Lewis acids were also performed; the species chosen were Ph_3C^{+} to see if this electrophile would displace the borane or be forced to attack the more electron-rich, but more sterically crowded sulphur site and "Me^{+}" to see if a compound with different electrophiles coordinated at the two sites could be isolated.

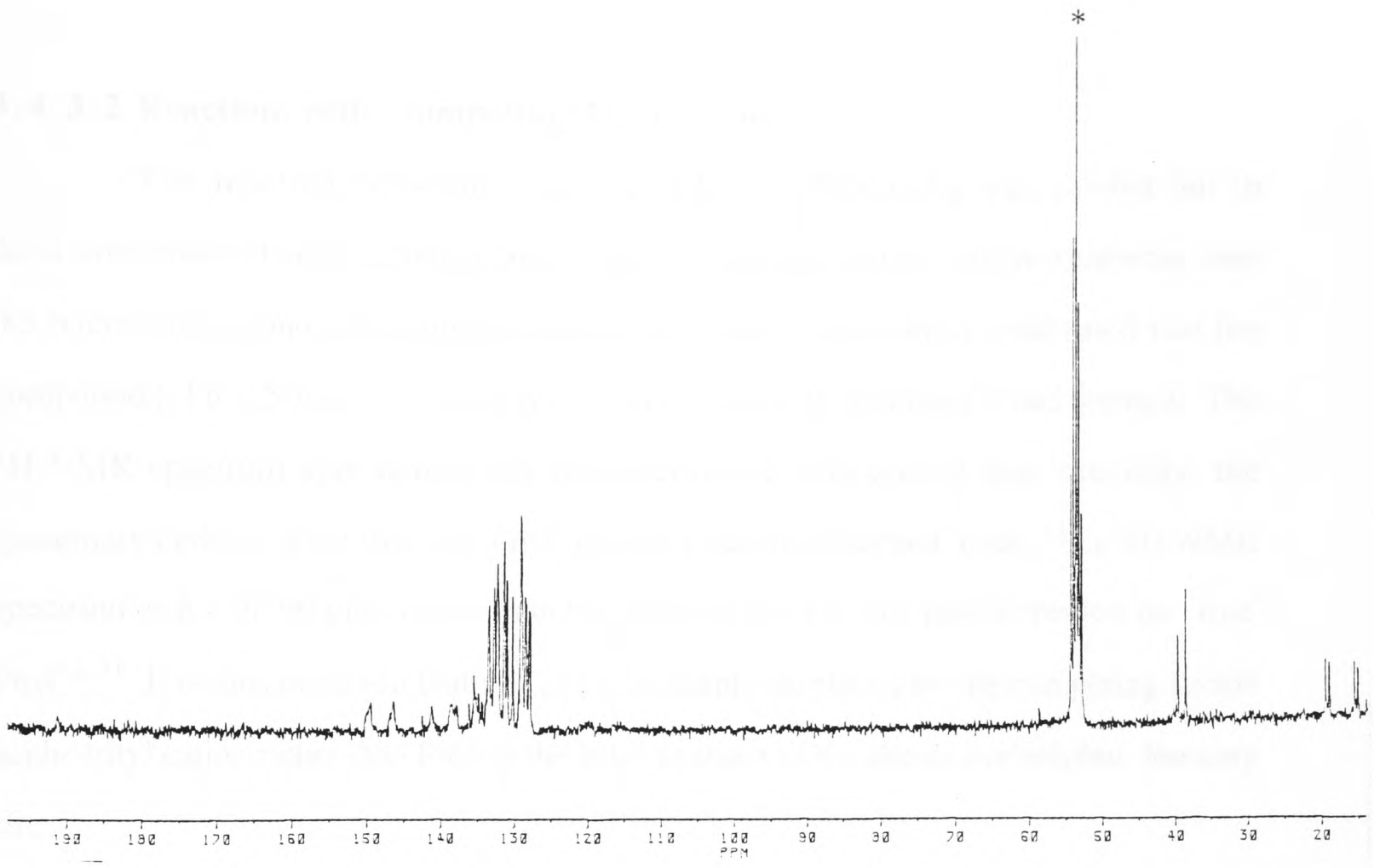


*Fig. 3.12: $^{13}C\{^1H\}$ NMR spectrum of compound **14**, obtained at 75.5 MHz in CD_2Cl_2. (* indicates resonance attributable to CD_2Cl_2).*

3.4.3.1 Reaction with Lewis Bases

The same selection of Lewis bases as previously examined was reacted with compound **14** in dichloromethane and the results analysed by NMR spectroscopy in $CDCl_3$. No displacement whatsoever by thf was observed since the $^{11}B\{^1H\}$ NMR spectrum of **14** remained unchanged and only free thf was observed in the ^1H NMR spectrum. By contrast, both PMe_3 and NEt_3 were found to cause total decomposition of

14 to $[NOs(1,2\text{-}S_2C_6H_4)_2][^nBu_4N]$ and $(C_6F_5)_3B{\cdot}L$ [L = NEt_3 or PMe_3]. This was clear from the $^{11}B\{^1H\}$ NMR spectra (resonances at δ = -4.2 and -4.4 respectively) and also by ^1H NMR spectroscopic analysis where signals due to complexed Lewis base and free nitrido complex could be observed.

3.4.3.2 Reaction with Competing Lewis Acids

The reaction between compound **14** and $[Ph_3C]BF_4$ was carried out in dichloromethane at ambient temperature. The colour appeared to darken somewhat over 0.5 hours stirring and after removal of solvent, NMR spectroscopy confirmed that the compound $[\{Ph_3CN\}Os(1,2\text{-}S_2C_6H_4)_2]$ (as synthesised by Sellmann[6]) had formed. The ^1H NMR spectrum appeared nearly identical to the data quoted and, crucially, the quaternary carbon signal from the Ph_3C moiety could be observed in the $^{13}C\{^1H\}$ NMR spectrum at δ = 95.90 ppm rather than the value of δ = *ca.* 214 ppm expected for 'free' Ph_3C^+.[31] It is thus observed that $B(C_6F_5)_3$ is cleanly displaced by the competing Lewis acidic trityl cation rather than forcing the latter to attack at the alternative sulphur donating site.

The reaction between compound **14** and methyl triflate, $Me(O_3SCF_3)$, was carried out similarly. No obvious colour change occurred, but upon removal of volatiles and extraction into toluene, a green solution was obtained with some oily insoluble residues (assumed to be $[^nBu_4N][O_3SCF_3]$). The product from this extraction proved to be a dark green highly air-sensitive oil which could not be rendered as a solid even on vigorous trituration with hexanes. ^1H and $^{11}B\{^1H\}$ NMR spectroscopy suggested that the methyl cation had added to a sulphur moiety without disturbing coordination of the borane. As well as the presence of residual $[^nBu_4N]$ groups in the ^1H NMR spectrum, a fairly broad peak appeared at δ = 3.06 ppm, assigned as an S-Me group (*c.f.* δ = 3.05 ppm for the literature compound $[NOs(1,2\text{-}(S)(SMe)C_6H_4)(1,2\text{-}S_2C_6H_4)]$[6]). The peaks in the phenyl region also became very broad, indicative of the lowering of symmetry and perhaps also that the methyl group was 'hopping' from one sulphur atom to another. The $^{11}B\{^1H\}$ NMR spectrum indicated that the borane was still coordinated (δ = -2.3 ppm)

and coordination to triflate anion was ruled out by mixing $B(C_6F_5)_3$ and $Me(O_3SCF_3)$ in an NMR tube and finding no evidence of reaction.

The formation of $[\{(C_6F_5)_3BN\}Os(1,2\text{-}(S)(SMe)C_6H_4)(1,2\text{-}S_2C_6H_4)]$ (**15**) is thus postulated and a $^{13}C\{^1H\}$ NMR spectrum was also obtained where the broadened signals in the phenyl region and of the Me-S group both support the theory that the methyl group was mobile. Also, the lack of a signal attributable to the CF_3 moiety of triflate confirms that the borane has not coordinated to O_3SCF_3. Unfortunately, compound **15** was too oily and sensitive to permit microanalytical data to be obtained and was available in too small quantities for further investigation of its spectroscopic properties.

The chemistry explored in this section is summarised in Fig. 3.13.

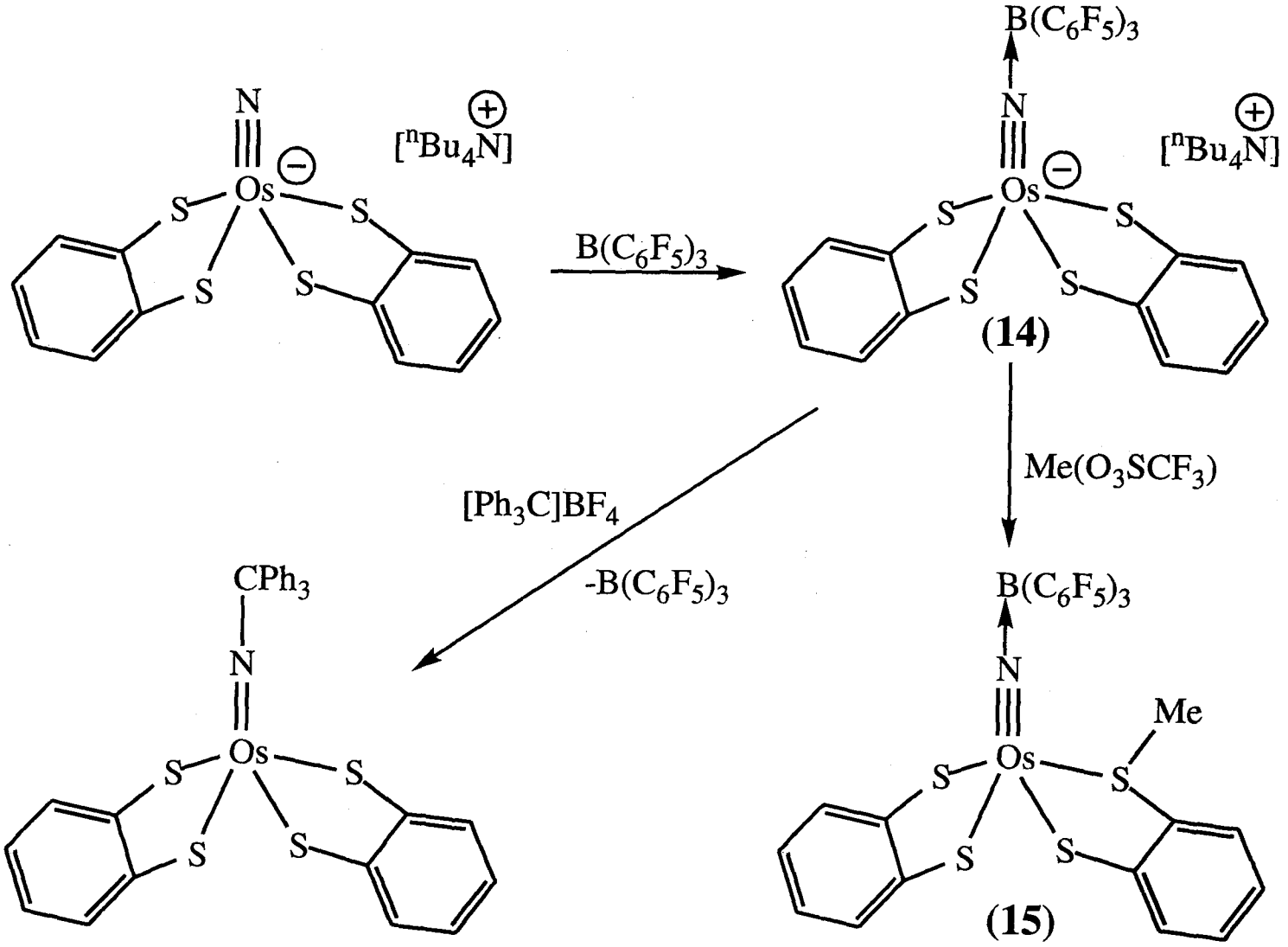


*Fig. 3.13: Formation of $[\{(C_6F_5)_3BN\}Os(1,2\text{-}S_2C_6H_4)_2][^nBu_4N]$ (**14**) and its reactions with competing Lewis acids; formation of $[\{(C_6F_5)_3BN\}Os(1,2\text{-}(S)(SMe)C_6H_4)(1,2\text{-}S_2C_6H_4)]$ (**15**).*

3.4.4 Summary and Conclusions

Tris(pentafluorophenyl)borane has been shown to form an adduct with an osmium nitrido complex although this compound, **14**, is significantly less stable than those formed with rhenium and molybdenum nitride compounds. For instance, rapid displacement of the borane by the competing Lewis bases NEt_3 and PMe_3 was observed and the N-B interaction is not sufficiently strong to prevent the trityl cation attacking there rather than at the more hindered sulpur site. Methyl cation, however, attacks the sulphur site to form a compound with electrophiles coordinated to both nitrogen and sulphur, **15**. This complex is a highly sensitive oil so could not be completely purified and was characterised only by NMR spectroscopy.

3.5 Reactions Between Some Sulphur Donors and $B(C_6F_5)_3$

Having achieved considerable success in extending the known number of adducts between metal nitrido complexes and boron-containing electrophiles, it was decided to investigate some complexes containing sulphur ligands. Thionitrosyl compounds of rhenium are available by sulphur atom transfer to the appropriate nitrido complex[26] so $[(SN)ReCl_2(PMePh_2)_3]$ was synthesised from $[NReCl_2(PMePh_2)_3]$ and 0.5 equivalents of S_2Cl_2 and reacted with $B(C_6F_5)_3$. No obvious colour change of the purple solution was observed upon addition of the borane but after the solvent had been removed and the product washed with pentane, $^{11}B\{^1H\}$ NMR spectroscopic analysis implied that a reaction had taken place (δ = -9.9 ppm). Unfortunately, the ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were obviously not clean (though the latter did confirm that there was only one type of C_6F_5 group in the product) and no pure product could be isolated. The similar $^{11}B\{^1H\}$ NMR shift obtained in the case of the reaction between $B(C_6F_5)_3$ and $[NReCl_2(PMePh_2)_3]$ (Section 3.2.6) might lead one to suppose that some species such as $[ClB(C_6F_5)_3]^-$ has been formed. The nitrido and thionitrosyl ligands both exert a significant *trans* influence and are thus expected to labilise the *trans* chloride moiety.

A similar result was obtained on reaction of $B(C_6F_5)_3$ with a metal sulphido complex, $[SWCl_2(PMePh_2)_3]$ (available from $[WCl_2(PMePh_2)_4]$ and $S{=}PMePh_2$[32]). The $^{11}B\{^1H\}$ NMR spectrum showed a single peak implying fourfold coordinated boron (this time at δ = -10.2 ppm), but other NMR spectroscopic analysis was complex and no clean product could be isolated.

It seems reasonable to assume that some interaction between S and B is occurring, given the $^{11}B\{^1H\}$ NMR spectroscopic evidence, however this interaction may well be very weak and preclude isolation of the adduct in a pure form.

3.6 Summary and Conclusions

Several adducts between the strong electrophile, *tris*(pentafluorophenyl)borane, and metal nitrido complexes have been synthesised and characterised by standard methods including microanalysis, multinuclear NMR spectroscopy, infrared spectroscopy and Fast Atom Bombardment mass spectrometry. Two of the adducts have also been structurally characterised by X-ray crystallography.

Two new rhenium nitrido compounds were synthesised by modifications to standard preparations, $[NRe(PMePh_2)(S_2CNEt_2)_2]$ (**7**) and $[NReCl(PMePh_2)_2(S_2CNMe_2)]$ (**8**). Three new adducts between $B(C_6F_5)_3$ and rhenium nitrido complexes have been synthesised, namely $[\{(C_6F_5)_3BN\}Re(PMePh_2)(S_2CNEt_2)_2]$ (**9**), $[\{(C_6F_5)_3BN\}Re(PMe_2Ph)(S_2CNMe_2)_2]$ (**10**) and $[\{(C_6F_5)_3BN\}ReCl(PMePh_2)_2(S_2CNMe_2)]$ (**11**). All have been fully characterised, and X-ray crystal structures have been determined for compound **9** and **10**. This work substantially increases the number of known borane adducts of rhenium nitrido complexes and represents the first time that triarylboranes have been shown to attack directly a Re≡N moiety. The reaction between $B(C_6F_5)_3$ and $[NReCl_2(PMePh_2)_3]$ yields two main products which appear to be inseparable by crystallisation. It is believed that one may result from attack at the labilised *trans* chlorine ligand.

Two adducts of molybdenum nitrido complexes and $B(C_6F_5)_3$ have also been prepared. These are formulated as $[\{(C_6F_5)_3BN\}Mo(S_2CNR_2)_3]$ (R = Me (**12**) and R =

Et (**13**)). These complexes represent the first borane adducts of such systems and also the first non-carbocationic electrophilic attack at a Mo≡N group.

The osmium nitrido complex $[NOs(1,2\text{-}S_2C_6H_4)_2][^nBu_4N]$ has been previously shown to have two potential sites of attack for electrophiles. It is found that $B(C_6F_5)_3$, like Ph_3C^+, attacks the less hindered site to yield $[\{(C_6F_5)_3BN\}Os(1,2\text{-}S_2C_6H_4)_2][^nBu_4N]$ (**14**). The borane is displaced on reaction with $[Ph_3C]BF_4$, but Me^+ is shown to attack at a sulphide moiety of **14** to yield $[\{(C_6F_5)_3BN\}Os(1,2\text{-}(S)(SMe)C_6H_4)(1,2\text{-}S_2C_6H_4)]$ (**15**).

The reactions of compounds **10**, **12** and **14** with various competing Lewis bases have also been studied. All three complexes are stable to thf and are affected to varying degrees by PMe_3 and NEt_3, the stability decreasing with the metal centre in the order Re (unaffected) > Mo > Os (total displacement observed). Although it may be tempting to ascribe some electronic effect to this order, it is more likely to be a function of kinetic stability given that the thermodynamic driving force for displacement is formation of the strong $(C_6F_5)_3B{\cdot}L$ (L = PMe_3 or NEt_3) complex and thus independent of the metal centre. In the rhenium complex studied, the Re-N-B linkage is protected to a great extent by the *cis* tertiary phosphine whereas in the osmium compound, **14**, the Os≡N-B moiety is exposed due to the 'tied back' dithiolate ligands. The molybdenum compound displays intermediate steric hindrance and so shows intermediate reactivity.

Lastly, $B(C_6F_5)_3$ has been shown to interact to some extent with sulphur-containing Lewis basic ligands, namely $[(SN)ReCl_2(PMePh_2)_3]$ and $[SWCl_2(PMePh_2)_3]$; however no clean products could be isolated from these reactions and it was clear that the interaction was weak. It is possible that, certainly in the former case, attack at a labile *trans* chloride ligand is favoured over attack at sulphur.

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Chapter Four

The Synthesis of Strong Boron-Containing Lewis Acids

4.1 Introduction

This chapter describes a variety of strong Lewis acid compounds containing a boron-perfluoroaryl group. These compounds are not only strongly electrophilic (*vide supra*) but are also relatively air- and water-stable crystalline solids. This makes them facile to handle using standard inert-atmosphere and Schlenk-line techniques. By contrast, the more widely used trihaloborane Lewis acids are highly volatile and reactive substances which are hard to purify, difficult to handle and tend to be more indiscriminate in their reactivity, for instance reacting with silicone vacuum grease. It was thought advantageous to synthesise a range of perfluoroaryl-boron compounds in order to study trends in reactivity as well as increasing the scope for new and interesting chemistry.

After surveying the synthetic routes to a range of such compounds as reported in the literature, an account of attempts to synthesise new Lewis acids in this general class follows, including partially successful attempts to synthesise boranes containing the (3,5-$C_6H_3(CF_3)_2$) moiety, two synthetic routes to $B(C_6H_5)(C_6F_5)_2$ and some reactions directed to the formation of compounds containing two $\{B(C_6F_5)_2\}$ moieties. The synthetic strategies employed for these new Lewis acids are summarised in Fig. 4.1.

4.2 The Synthesis of Strong Lewis Acids Containing a Boron-Perfluoroaryl Bond

This section will summarise the preparations, as given in the literature, of a variety of Lewis acids as well as discussing modifications to these procedures.

4.2.1 Synthesis of *Tris*(pentafluorophenyl)borane

The borane $B(C_6F_5)_3$ is the archetype of this class and was first reported by Massey and Park in 1963.[1] The published synthesis[2] involves formation of a suspension of $[LiC_6F_5]$, from ^nBuLi and BrC_6F_5 at -78 °C in pentane, followed by the addition of a solution of BCl_3 and warming slowly to ambient temperature over several

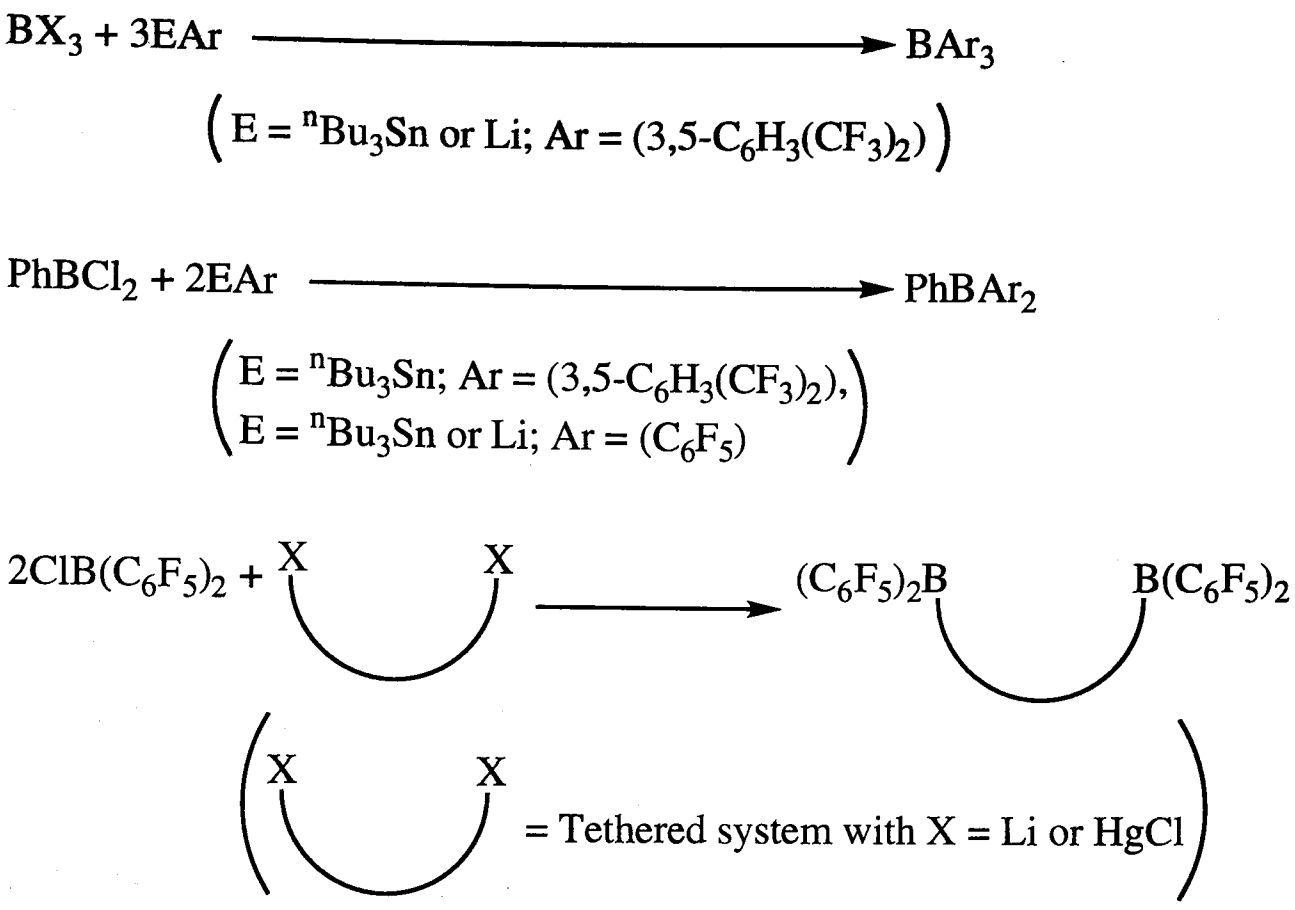


Fig. 4.1: Synthetic strategies to new Lewis acids.

hours. Yields of 30-50 % of white, needle-like crystals are reported and the compound is found to be reasonably oxygen- and water-tolerant.[3]

The reaction temperature is crucial since [LiC_6F_5] is known to decompose explosively at temperatures above *ca.* -40 °C, forming LiF and tetrafluorobenzyne (this decomposition is also true of the aluminium analogue, $Al(C_6F_5)_3$, which "tends to explode under circumstances not exactly determined"[4]). This temperature consideration is the reason why the BCl_3 solution should be added to the stirred pentafluorophenyllithium suspension and not *vice versa*, since efficient cooling of the suspension while it is being transferred is not readily achieved.

4.2.1.1 Synthesis *via* a Modified Method

Addition of [$Li(C_6F_5)$] to BCl_3 should be favourable since keeping an excess of trihaloborane should minimise formation of the by-product $Li[B(C_6F_5)_4]$; hence a modified version of the synthesis has been developed in this laboratory and reported in the literature.[5] The borane is prepared in a specially designed apparatus that not only

enables thorough cooling of all reagents to -78 °C, but also allows the suspension of $[LiC_6F_5]$ to be added slowly to the trihaloborane thus maximising yield by maintaining BX_3 in local excess. A further modification is the use of BBr_3 for the synthesis instead of BCl_3 and this has been found to improve yields by a factor of *ca.* 1/3. It has been found that using a small (*ca.* 5 %) excess of BrC_6F_5 is favourable since this prevents there being any ^nBuLi remaining in the suspension when it is added to the BBr_3 and thus minimises the formation of side products containing B-^{n}Bu bonds; the extra bromopentafluorobenzene is easily removed at the purification stage.

Subsequent modifications of the apparatus include replacement of teflon taps by ground glass ones, since they have less tendency to shrink at low temperature and thereby to leak reactants, a reduction in the diameter of the central vessel in which $[LiC_6F_5]$ is formed in order to increase its surface to volume ratio and improve cooling efficiency and use of a Teflon tube to direct the $[LiC_6F_5]$ suspension into the BBr_3 solution rather than running down the walls of the lower reaction vessel. It should be noted that a large quantity of solvent must be used for this preparation since yields are found to be significantly reduced if the final $[LiC_6F_5]/BBr_3$ mixture is too viscous for efficient magnetic stirring.

Purification by crystallisation from pentane or hexanes at -80 °C gives the product sufficiently pure for use; however, in order to obtain $B(C_6F_5)_3$ completely free of solvent, vacuum sublimation (100 °C, 0.1 mbar) is required. This modified method provides a reliable route to large amounts (up to 30 g) of pure *tris*(pentafluorophenyl)borane in yields of up to 60 %.

4.2.1.2 Preparation of $B(C_6F_5)_3$ Using a Grignard Reagent

Due to the safety considerations inherent in the use of $[LiC_6F_5]$ as a reagent, an alternative synthesis has been developed by Pohlmann and Brinckmann.[6] This involves reaction of $BF_3{\cdot}Et_2O$ with $[(C_6F_5)MgBr]$, easily prepared from BrC_6F_5 and magnesium metal, in diethylether. The reaction proceeds smoothly and in high yield (85-90 %), however the product initially formed is the etherate, $B(C_6F_5)_3{\cdot}Et_2O$, from which it is

found to be difficult to remove all the diethylether. The literature method involves addition of toluene to the reaction mixture and slow removal of the ether as an azeotrope; this has been found to be an unsatisfactory and unreliable way of obtaining the borane ether-free since more than one distillation is frequently required and leads to considerable decomposition of the product. Recent work in this laboratory has shown that slow sublimation of $B(C_6F_5)_3 \cdot Et_2O$ under dynamic vacuum will yield the uncomplexed borane if it is carried out twice.[7] In view of these problems, the favoured method of synthesis of $B(C_6F_5)_3$ has been *via* the lithium salt with appropriate safety precautions.

4.2.2 Synthesis of Chloro*bis*(pentafluorophenyl)borane

The compound $ClB(C_6F_5)_2$ was first reported by Chambers and Chivers in 1965 from the reaction of gaseous BCl_3 and $Me_2Sn(C_6F_5)_2$ in a sealed tube in the absence of solvent.[8] The Me_2SnCl_2 by-product is removed from the reaction mixture by sublimation and the $ClB(C_6F_5)_2$ product was obtained pure in 36 % yield by distillation (70 °C, 0.02 mmHg). The same reaction was also used to prepare the dichloride, $Cl_2B(C_6F_5)$, using the appropriate ratio of reactants. This preparation has been modified and improved by Piers.[9]

4.2.2.1 Preparation of $ClB(C_6F_5)_2$ by a Modified Method

The modified route utilises $Me_2Sn(C_6F_5)_2$ (synthetically available from Me_2SnCl_2 and $[(C_6F_5)MgBr]$) and BCl_3 in 1:1 ratio in a solution-phase reaction. A high-pressure ampoule is used to heat a mixture of the reagents in an aliphatic solvent such as hexanes to 120 °C for 48 hours. The amount of solvent used is found to be critical and the components are required to be in a concentration of *ca.* 0.3 mol dm^{-3} in the reactor vessel. Upon cooling the reaction mixture to room temperature, a large proportion of the Me_2SnCl_2 by-product crystallises out and the filtrate, which contains the product, can be easily isolated. Unfortunately, complete removal of Me_2SnCl_2 is non-trivial despite its almost total insolubility in petroleum ether. It was found that repeated extraction of the product into hexanes followed by removal of solvent eradicated all but traces of

Me_2SnCl_2 and final purification could be achieved by vacuum sublimation (80 °C, 0.1 mbar), although this method reduced the yield to 65-75 % from the reported 80-90 %.

The compound $ClB(C_6F_5)_2$ is a white crystalline solid whose structure has been determined by X-ray crystallography and shown the molecule to be significantly non-planar.[10] Its tolerance towards moisture and air is markedly less than *tris*(pentafluorophenyl)borane owing to the presence of a boron-chlorine bond but it can still be easily handled using standard inert-atmosphere techniques.

4.2.3 Synthesis of *Bis*(pentafluorophenyl)borane

Piers has reported the versatile and highly reactive hydroborating agent $HB(C_6F_5)_2$ which is synthesised *via* the reduction of $ClB(C_6F_5)_2$.[11] Donating solvents must be avoided in this preparation since they are found to react with *bis*(pentafluorophenyl)borane; Piers in a recent review described several such borane-solvent reactions.[12] Suitable reducing agents include $[(\eta^5\text{-}C_5H_5)_2Zr(Cl)H]_n$, Bu_3SnH and $Me_2Si(Cl)H$; the latter is found to be the most convenient since it acts as a solvent for the reaction and may be readily removed, along with the Me_2SiCl_2 by-product, from the $HB(C_6F_5)_2$ precipitate. This reduction is found to proceed smoothly on warming from -78 °C to ambient temperature in yields ranging from 75 % to virtually quantitative.

In both the solid state and in solution, the borane is predominently dimeric; the infrared spectrum shows a band at 1550 cm^{-1}, characteristic of ν_{asym} for a B-(μ-H)$_2$-B unit and no terminal B-H stretch. Additionally, the $^{11}B\{^1H\}$ NMR spectrum shows a peak at δ = 18.0 ppm characteristic of four-coordinate boron species and a minor resonance at δ = 60.1 ppm indicative of monomeric $HB(C_6F_5)_2$. The borane is an extremely useful hydroborating agent for both organic[11] and metallocene[13] substrates (see Fig. 1.13). Its use as a precursor to other boranes containing one or more $\{B(C_6F_5)_2\}$ moieties is summarised in Fig. 4.2.

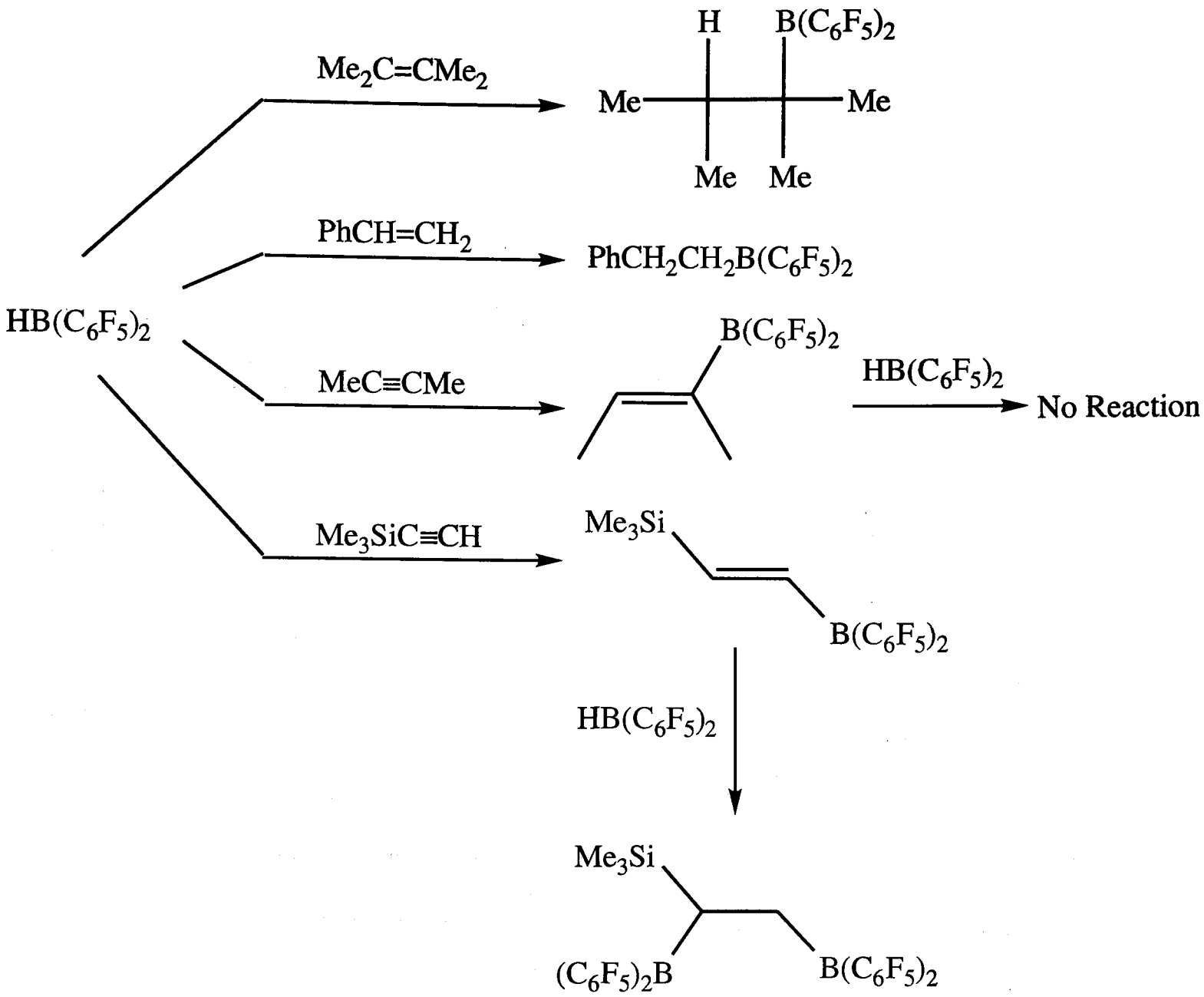


Fig. 4.2: The utility of $HB(C_6F_5)_2$ as a hydroborating agent.

4.2.4 *Tris*(perfluorobiphenyl)borane

Recently, Marks has described the preparation and reactivity of B(*para*-C_6F_4-$C_6F_5)_3$ which undergoes many analogous reactions to $B(C_6F_5)_3$.[14] Reactions with metallocene methyl complexes form ion pairs which are still more loosely bound than those formed by *tris*(pentafluorophenyl)borane or even entirely separate ions. For instance $[(\eta^5\text{-}C_5H_5)_2ZrMe_2]$ reacts with $B(C_6F_5)_3$ to yield $[(\eta^5\text{-}C_5H_5)_2ZrMe(\mu\text{-}Me)(B(C_6F_5)_3)]$[15] but with B(*para*-$C_6F_4$-$C_6F_5)_3$, the remarkable complex $[(\eta^5\text{-}C_5H_5)_2Zr(Me)(\mu\text{-}Me)Zr(Me)(\eta^5\text{-}C_5H_5)_2][MeB(C_{12}F_9)_3]$ (Fig. 4.3) is formed. This implies that $[(\eta^5\text{-}C_5H_5)_2ZrMe_2]$ has a greater affinity for the $[(\eta^5\text{-}C_5H_5)_2ZrMe]^+$ cation than does the $[MeB(C_{12}F_9)_3]^-$ anion.

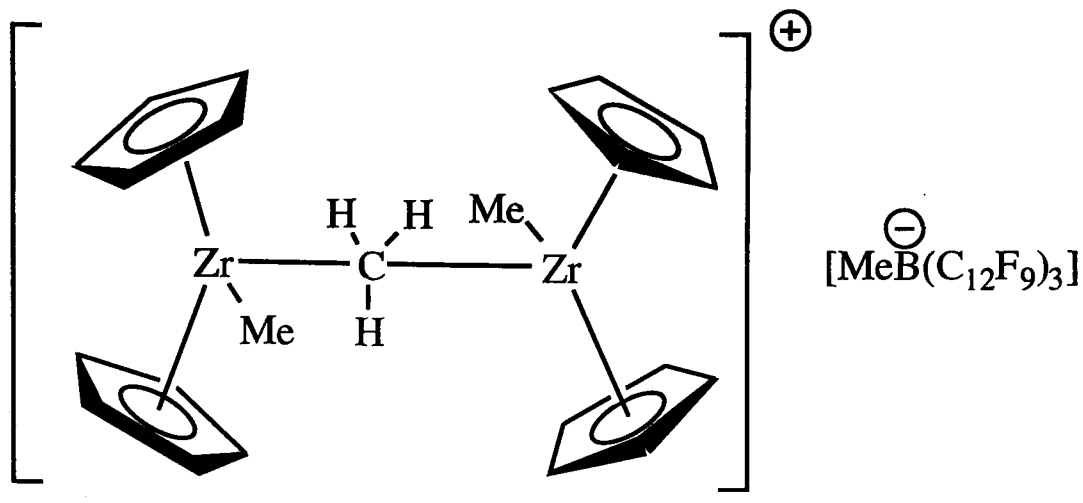


Fig. 4.3: The product of the reaction between [(η^5-C_5H_5)$_2$$ZrMe_2$] and B(para-$C_6F_4$-$C_6F_5$)$_3$.

4.2.5 Summary

A wide variety of boranes containing one or more perfluoroaryl group are found in the literature; in some cases more than one synthesis exists. The routes used to synthesise them in this work are summarised in Fig. 4.4.

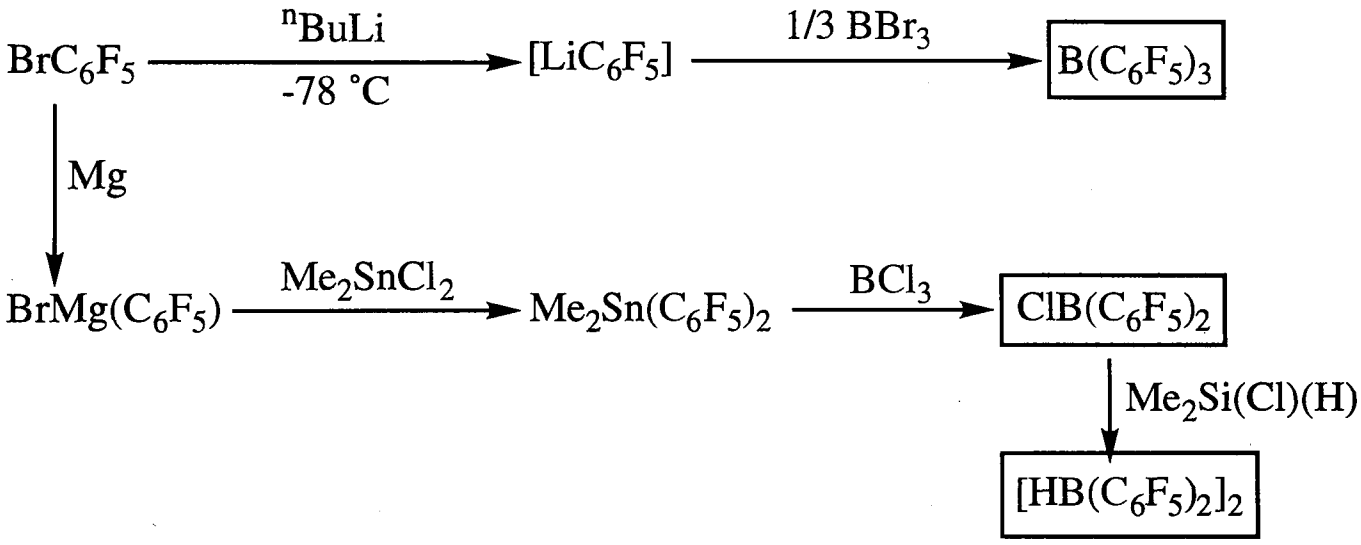


Fig. 4.4: Summary of synthetic routes to strong Lewis acids.

4.3 Attempts to Synthesise BAr'$_3$ [Ar' = (3,5-$C_6H_3(CF_3)_2$)]

The [BAr'$_4$]$^-$ anion has featured prominently in the literature as a highly non-nucleophilic non-coordinating ion since its initial synthesis in 1984.[16] The synthesis of the three-coordinate borane, BAr'$_3$, was attempted in the hope that this compound, with

its strongly withdrawing phenyl groups, would display interesting and novel reactivity and provide a contrast with $B(C_6F_5)_3$. The literature synthesis of $Na[BAr'_4]$ involves reaction between $BF_3{\cdot}Et_2O$ and excess Ar'MgI in diethyl ether; in view of the problems associated with preparation of $B(C_6F_5)_3$ in donor solvents, the reaction of BBr_3 with LiAr' was attempted.

4.3.1 Attempted Synthesis *via* [LiAr']

Treatment of BrAr' with one equivalent of ^{n}BuLi in hexanes at -78 °C appeared to produce no reaction. Upon warming to room temperature, the solution gradually darkened from yellow to orange and a white precipitate (presumed to be the desired lithium salt) formed. This suspension was re-cooled to -78 °C and added to a solution of 1/3 equivalent of BBr_3 in hexanes. After warming to ambient temperatures and work-up analogous to that used in the preparation of $B(C_6F_5)_3$, a brown oil was isolated.

$^{11}B\{^{1}H\}$ NMR spectroscopy indicated the presence of at least three boron-containing species (δ = 86.4, 79.3, 46.6 ppm), all in the region expected for threefold boron coordination. The ^{1}H NMR spectrum showed significant resonances attributable to butyl groups so it was postulated that the formation of the lithium salt was incomplete thus leaving residual ^{n}BuLi to attack the BBr_3; however repetition of the experiment with longer reaction times did not afford a tractable product.

4.3.2 Synthesis and Characterisation of $^{n}Bu_3SnAr'$ (16)

As an alternative aryl transfer reagent, $^{n}Bu_3SnAr'$ was chosen since its purity could be confirmed before reaction with the trihaloborane and its reactivity should be slightly less aggressive. It proved to be readily available from the reaction of $^{n}Bu_3SnCl$ with Ar'MgBr in diethylether. Surplus $^{n}Bu_3SnCl$ is undesirable as it is hard to remove owing to its high boiling point (171 °C at 25 mmHg), so a *ca.* 10 % excess of Grignard reagent was used. The reaction was monitored by $^{119}Sn\{^{1}H\}$ NMR spectroscopy and was deemed to be complete after four hours when the resonance attributable to $^{n}Bu_3SnCl$ (δ = 120 ppm)[17] had vanished. After removal of solvent, the clear, viscous liquid

product (**16**) was distilled from the sticky brown reaction residues at 150 °C under high vacuum (0.01 mbar). The isolated pure yield was 56 % with respect to $^{n}Bu_3SnCl$.

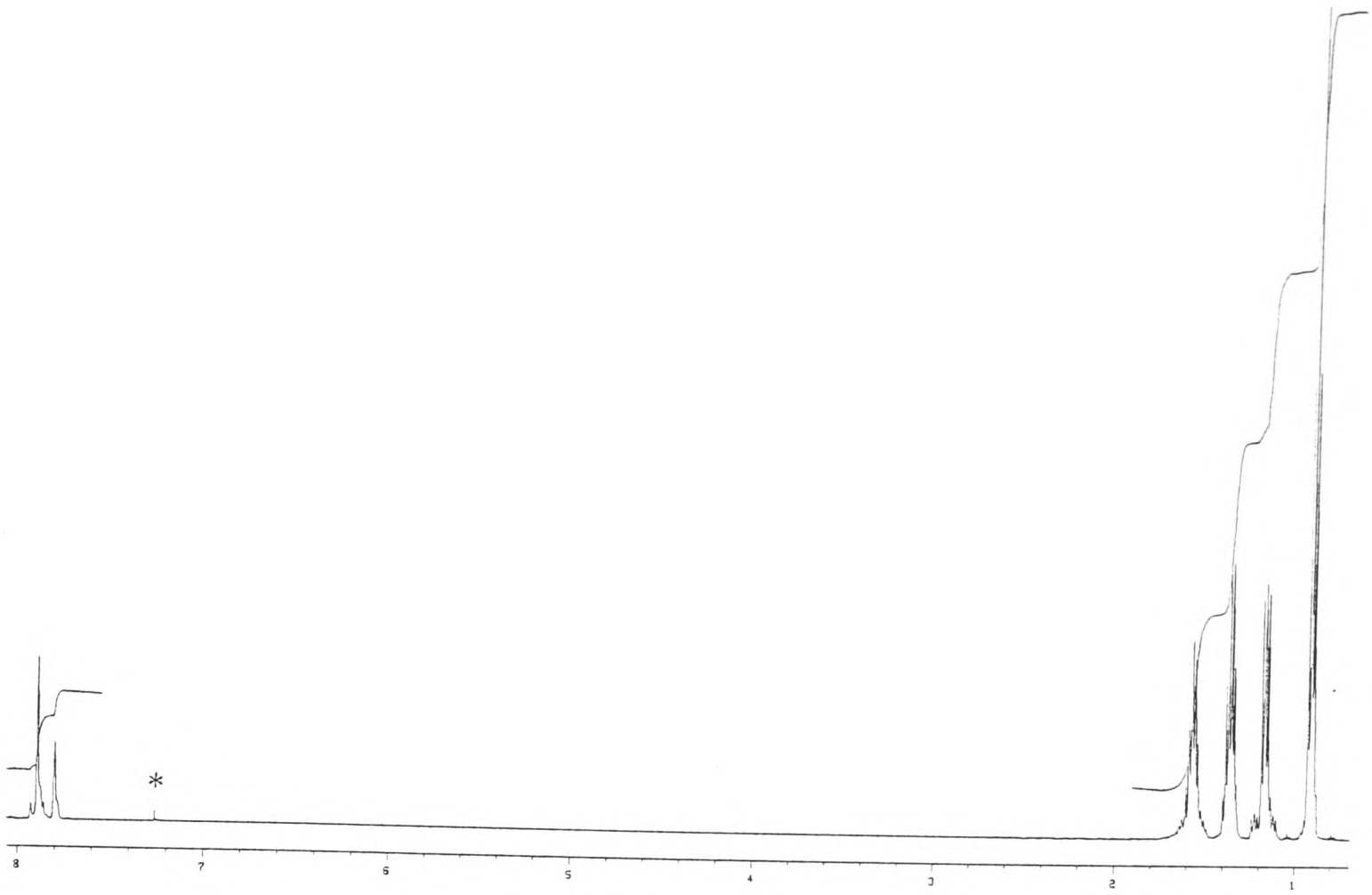
4.3.2.1 Characterisation

Microanalytical and Electron Impact mass spectral data were obtained and supported the formation of the expected product. The latter shows the parent ion as well as sequential loss of all three n-butyl groups, the aryl group or aryl plus one and two butyl groups. For all the major peaks in the spectrum, the expected isotopic pattern for tin was observed (masses 112, 114, 116, 117, 118, 119, 120, 122 and 124 in the ratios 3:2:45:24:75:27:100:14:17).

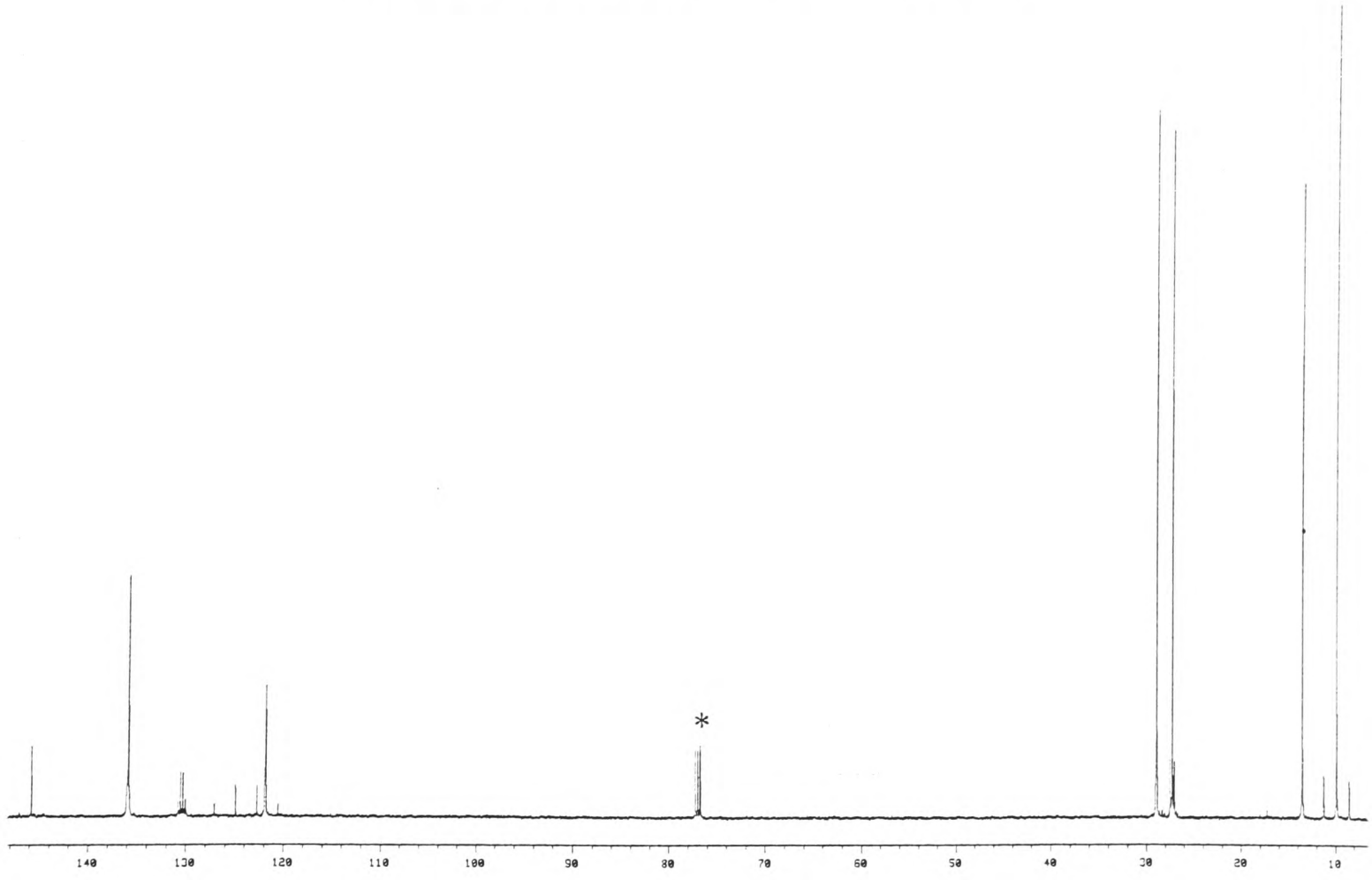
^{1}H NMR spectroscopic data was completely assigned- the *ortho*- and *para*-aryl resonances are distinguished by the presence of ^{119}Sn satellite peaks in the former case; similarly, the appearance of the α-protons of the butyl groups in a position between the methyl resonance and the γ-protons was confirmed by the presence of tin satellites. The $^{13}C\{^{1}H\}$ NMR spectroscopic data was fully assigned using the presence and magnitude of C-F and C-^{119}Sn coupling. $^{119}Sn\{^{1}H\}$ NMR spectroscopic data showed a resonance at δ=-33.8 ppm, consistent with other $^{n}Bu_3SnAr$ compounds (*e.g.* $^{n}Bu_3SnPh$ δ = -41.7 ppm,[17] $^{n}Bu_3Sn(C_6F_5)$ δ = -25.0 ppm[18]). The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, obtained in $CDCl_3$, are shown in Fig. 4.5.

4.3.3 Reaction between $^{n}Bu_3SnAr'$ and BBr_3

The tin reagent was added to 1/3 equivalent of BBr_3 in toluene in the hope of inducing threefold substitution to yield the target borane BAr'_3. After 3 hours at ambient temperature, an aliquot was withdrawn from the reaction mixture for NMR spectroscopic analysis. The $^{11}B\{^{1}H\}$ NMR spectrum revealed no BBr_3 present (δ = *ca.* 38 ppm[19]), and a new resonance at δ = 68.8 ppm. However, the $^{119}Sn\{^{1}H\}$ NMR spectral data indicated the presence of two tin-containing species, a new resonance at δ = 60.0 ppm (tentatively assigned to $^{n}Bu_3SnBr$) and a signal due to the starting material in a 1:2 ratio. It was concluded that mono-substitution had taken place and the ^{11}B NMR spectroscopic



(a) [indicates residual protio-solvent, $CHCl_3$]*



(b) [indicates solvent, $CDCl_3$]*

Fig. 4.5: (a) ^1H and (b) $^{13}C\{^1H\}$ NMR spectra of compound 16 obtained at 300.13 and 75.5 MHz respectively in $CDCl_3$.

signal was indicative of the presence of BBr_2Ar' (note also that the $^{11}B\{^1H\}$ NMR spectroscopic shift of the similar borane BBr_2Ph is given in the literature as *ca.* $\delta = 60$ ppm[19]).

The reaction mixture was heated to reflux for 8 hours in an attempt to induce further substitution although this only introduced several further peaks into both $^{119}Sn\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra and no tractable product could be isolated. The reaction was repeated with just one equivalent of $^nBu_3SnAr'$ and a product believed to be BBr_2Ar' isolated as a grey liquid. This compound proved to be too sensitive to air and moisture to handle with Schlenk-line techniques and was not investigated further. $^nBu_3SnAr'$ also did not react with $PhBCl_2$, even after prolonged reflux in toluene, confirming that it was an insufficiently nucleophilic source of aryl groups to substitute more than once at a boron centre.

4.4 Synthesis and Reactivity of $B(C_6H_5)(C_6F_5)_2$ (17)

$PhBCl_2$ is commercially available and was investigated as a starting material for the synthesis of the mixed fluorinated/non-fluorinated Lewis acid $BPh(C_6F_5)_2$. The desired compound is formed by interaction of $PhBCl_2$ with either $^nBu_3Sn(C_6F_5)$ (prepared by Dr. Nils Metzler of this laboratory) or $[Li(C_6F_5)]$.

4.4.1 Synthesis of $B(C_6H_5)(C_6F_5)_2$ Using $^nBu_3Sn(C_6F_5)$

In contrast to $^nBu_3SnAr'$, $^nBu_3Sn(C_6F_5)$ was found to react cleanly with $BPhCl_2$ after 12 hours reflux in toluene. After the solvent was removed, a white solid (presumed to be the desired product) and a clear liquid (presumed to be $^nBu_3SnCl$) remained. Crystallisation from 40/60 petroleum ether at -80 °C followed by thorough washing with cold petrol failed to remove traces of residual $^nBu_3Sn(C_6F_5)$ as confirmed by $^{119}Sn\{^1H\}$ and ^1H NMR spectroscopy and Electron Impact mass spectrometry. Even vacuum sublimation (100 °C, 0.1 mbar) failed to render the product more than 98 % pure, so an alternative synthetic route was attempted *via* the lithium salt, $[Li(C_6F_5)]$.

4.4.2 Synthesis of $B(C_6H_5)(C_6F_5)_2$ Using $[Li(C_6F_5)]$

The synthesis was carried out in the same manner as that of $B(C_6F_5)_3$- initially on a small scale following the method of Massey and Park[2] and secondly on a larger (*ca.* 20 mmol) scale using the modified methodology.[5] Half an equivalent of $BPhCl_2$ was used in place of one third of an equivalent of BBr_3 and the white microcrystalline product formed (**17**) could be isolated analytically pure by cooling a concentrated hexanes solution to -80 °C and washing the precipitate with pentane at -40 °C. ^1H NMR spectroscopy showed that **17** could be obtained virtually solvent-free by drying *in vacuo* for 12 hours. The yield obtained was 36 %, slightly lower than that normally achieved in the preparation of $B(C_6F_5)_3$.

4.4.2.1 Characterisation

Satisfactory elemental analyses were obtained for the borane and also an Electron Impact mass spectrum. The latter showed a peak due to the parent ion as well as peaks corresponding to loss of Ph, C_6F_5 and both of these moieties. **17** is found to be soluble in all common organic solvents to a slightly greater degree than $B(C_6F_5)_3$ and sublimes easily (100 °C, 0.1 mbar). Full NMR spectroscopic studies were carried out in C_6D_6 and these spectra were fully assigned. The pentafluorophenyl region in both $^{13}C\{^1H\}$ and ^{19}F NMR spectra was assigned by comparison with the spectra obtained for $B(C_6F_5)_3$;[3, 20] the order *ortho*, *para*, *meta* on moving from low field to high field is a characteristic feature of the resonances of the C and F nuclei in the $-C_6F_5$ group. A similar order of resonances is observed in the NMR spectra of the $-C_6H_5$ group in which the ^1H NMR spectrum was assigned using the multiplicities and intensities of the signals and the $^{13}C\{^1H\}$ NMR spectrum assigned by analogy with this.

Infrared spectra of **17** and $B(C_6F_5)_3$ were obtained as Nujol mulls and comparison is instructive, revealing the similarity between the two compounds leaving aside the aromatic C-H stretches, typically found somewhere over 3000 cm^{-1} (Table 4.1).

$BPh(C_6F_5)_2$	$B(C_6F_5)_3$
3566m	
3353m br	
1651s	1651s
1598m	1607m
1520s	1524s
1315m	1321s
1289m	1292m
1094m br	1161s br
976s	977s

Table 4.1: Comparison of the infrared spectra of $BPh(C_6F_5)_2$ and $B(C_6F_5)_3$ obtained as Nujol mulls.

4.4.3 Reactivity of $B(C_6H_5)(C_6F_5)_2$

4.4.3.1 Reactions with $[(\eta^5\text{-}C_5H_5)M(CO)_3Me]$ (M = Mo or W)

The unexpected reaction observed between $[(\eta^5\text{-}C_5H_5)M(CO)_3Me]$ (M = Mo or W) and $B(C_6F_5)_3$ has already been described (Section 1.3.5).[5] It was of interest whether **17** would also undergo this transformation and whether, owing to its predicted lower Lewis acidity, the proposed intermediates involved in the reaction could be isolated. The reactants were mixed in toluene and the extent of reactivity monitored by infrared spectroscopic analysis of aliquots withdrawn from the reaction mixture. Although immediate colour changes were observed in both cases, virtually no product had formed after 24 hours (compare with the reaction with $B(C_6F_5)_3$ where reaction is nearly complete after this time). Product did form after the solution was heated to reflux, but even after heating for 2 weeks, the reaction was only 50 % (M = W) to 75 % (M = Mo) complete (these figures were obtained approximately from the infrared data and

confirmed by integration of the ^{19}F NMR spectra of the final products). Addition of excess **17** at this point failed to force the reaction to go to completion.

These experiments serve to confirm the lowering of Lewis acidity on replacement of a pentafluorophenyl ring by a phenyl ring which does not possess electron-withdrawing substituents. They would also seem to indicate that the reaction is rate-limited by initial attack of the Lewis acid (probably at a carbonyl moiety) followed by rapid elimination of fluoroborane species since, even though the reaction clearly proceeded much more slowly when the borane was **17**, no species other than the starting material and product were observed at any time during the reaction (Fig. 4.6).

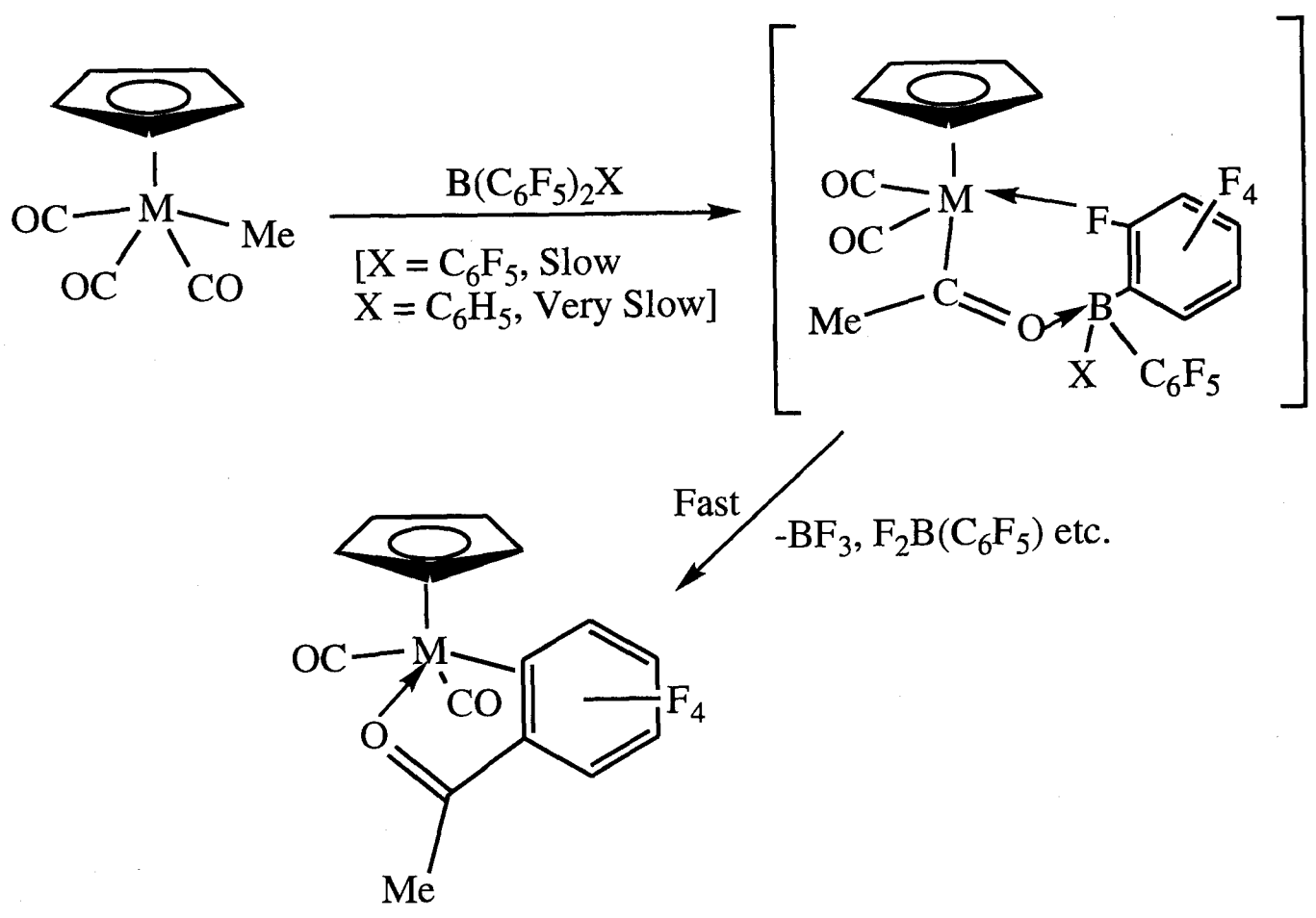


Fig. 4.6: The reaction between [(η^5-C_5H_5)M(CO)$_3$Me] (M = Mo or W) and perfluoroarylboranes.

4.4.3.2 Other reactivity

Other reactions involving **17** have confirmed its weaker Lewis acidity as compared to $B(C_6F_5)_3$. A relatively stable adduct of *tris*(pentafluorophenyl)borane with a *bis*(amino)silylene ligand is reported, but the corresponding adduct of **17** can only be characterised at -60 °C and the two components are totally dissociated at room

temperature.[21] The reaction between $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ and $B(C_6F_5)_3$ proceeds instantaneously to a blue adduct even at -78 °C,[20] whereas using **17** leads to a slow and ultimately incomplete reaction which did not yield a tractable product. $B(C_6H_5)(C_6F_5)_2$ has been found to react cleanly with $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and this reaction is covered in Chapter Two of this thesis.

4.5 Attempts to Synthesise Bidentate Lewis Acids

The synthesis of bidentate strong Lewis acids has been sparked by the interest in Ziegler-Natta catalysis since such species should abstract methide groups better than monodentate boranes by more effectively dispersing the negative charge thus produced. Marks[22] and Piers[11] have both produced such species by double hydroboration of alkynes although catalytic studies are still in their infancy. This family of compounds are also of synthetic interest since they may form, for example, adducts with two hydride ligands simultaneously. It was hoped to use $ClB(C_6F_5)_2$ as a synthon for the introduction of a $B(C_6F_5)_2$ moiety.

4.5.1 Attempted syntheses of *ortho*-$C_6H_4\{B(C_6F_5)_2\}_2$, 1,8-$C_{10}H_6\{B(C_6F_5)_2\}_2$ and $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2)_2Fe]$

Kaufmann has demonstrated the reaction of BX_3 (X = Cl or Br) with $C_6H_4(SiMe_3)_2$ (*ortho, meta* or *para*) which yields, after elimination of $SiMe_3X$, firstly $C_6H_4(SiMe_3)(BX_2)$ and then $C_6H_4(BX_2)_2$.[23] The analogous reaction, between *ortho*-$C_6H_4(SiMe_3)_2$ and two equivalents of $ClB(C_6F_5)_2$ failed to produce even mono-substitution at the phenyl ring of $-B(C_6F_5)_2$ for $-SiMe_3$. The reasons for this are unclear since $ClB(C_6F_5)_2$ was expected to be of comparable Lewis acidity to BCl_3. Similar difficulties have been encountered in the substitution of four (C_6F_5) moieties onto *ortho*-$C_6H_4(BCl_2)_2$.[18] Both problems may have their origin in steric factors since the (C_6F_5) group is considerably larger than a chloride moiety.

Similarly, the chelating 1,8-naphthalenediyl*bis*(dichloroborane) has also been reported.[24] Attempts in this laboratory to substitute the chloride moieties by

pentafluorophenyl groups were unsuccessful, so $ClB(C_6F_5)_2$ was reacted with both [1,8-$C_{10}H_6$][Li_2·TMEDA] (TMEDA = tetramethylethylenediamine) and [1,8-$C_{10}H_6(HgCl)_2$]. Substitution of neither -Li nor -HgCl by $-B(C_6F_5)_2$ was found to occur although the presence of the chelating diamine, TMEDA, in the dilithio-salt was likely to be undesirable in the presence of Lewis acids.

The same problem was observed in the reaction between [(η^5-$C_5H_4Li)_2Fe$.TMEDA][25] and two equivalents of $ClB(C_6F_5)_2$. Although an orange product was obtained it was not tractable.

4.5.2 Attempted Synthesis of [(^{t}BuN)$_2$W{N(^{t}Bu)B(C_6F_5)$_2$}$_2$]

The homoleptic dilithium salt $Li_2[(^tBuN)_4W]$ is readily available[26] from the mixed diamide-diimide $[(^tBuN)_2W(^tBuNH)_2]$[27] and is synthesised base-free. Thus in the reaction with $ClB(C_6F_5)_2$ it was hoped to avoid some of the problems previously encountered in the preparation of bidentate Lewis acids. Reaction between two equivalents of $ClB(C_6F_5)_2$ and the dilithium salt was performed in toluene at -78 °C followed by warming to ambient temperature. A colour change from pale yellow to blue-green was observed after one hour although examination of the $^{11}B\{^1H\}$ NMR spectrum of the reaction mixture revealed significant residual $ClB(C_6F_5)_2$ in addition to a new peak at δ=31 ppm. Extended reaction times did not yield a single product, so the reaction was repeated in a sealed NMR-tube in d_8-toluene.

The reaction mixture was monitored frequently by NMR spectroscopy over the course of five days' heating at 50 °C, with the $^{11}B\{^1H\}$ NMR spectrum found to be much more informative than the crowded ^1H NMR spectrum. After one day, although substantial quantities of $ClB(C_6F_5)_2$ remained, there were two product peaks in the $^{11}B\{^1H\}$ NMR spectrum at δ = 38 ppm and δ = 32 ppm. These were tentatively assigned as being due to mono- and di-substitution respectively, a suspicion that was supported by the fact that, over the following two days, the $ClB(C_6F_5)_2$ peak disappeared and the peak at δ = 32 ppm increased in intensity at the expense of the peak at δ = 38 ppm. However, before the disubstituted product had completely formed, a further peak

with an $^{11}B\{^1H\}$ NMR spectroscopic shift of $\delta = -17$ ppm appeared- this was assumed to be a decomposition product since the shift is indicative of a 4-coordinate boron environment.

Examination of the ^1H NMR spectra indicated that there were two *tert*-butyl environments associated with both of the three-coordinate $^{11}B\{^1H\}$ NMR spectroscopic peaks. ^1H NMR spectroscopic resonances at $\delta = 1.34$ and 1.30 ppm grew in and were thus assigned to the disubstituted product whilst signals at $\delta = 1.26$ and 0.92 ppm shrank and were believed to be attributable to the monosubstituted product. Once the 4-coordinate $^{11}B\{^1H\}$ NMR spectroscopic resonance had appeared, the ^1H NMR spectrum was an unassignable forest of peaks so the experiment was stopped after 5 days.

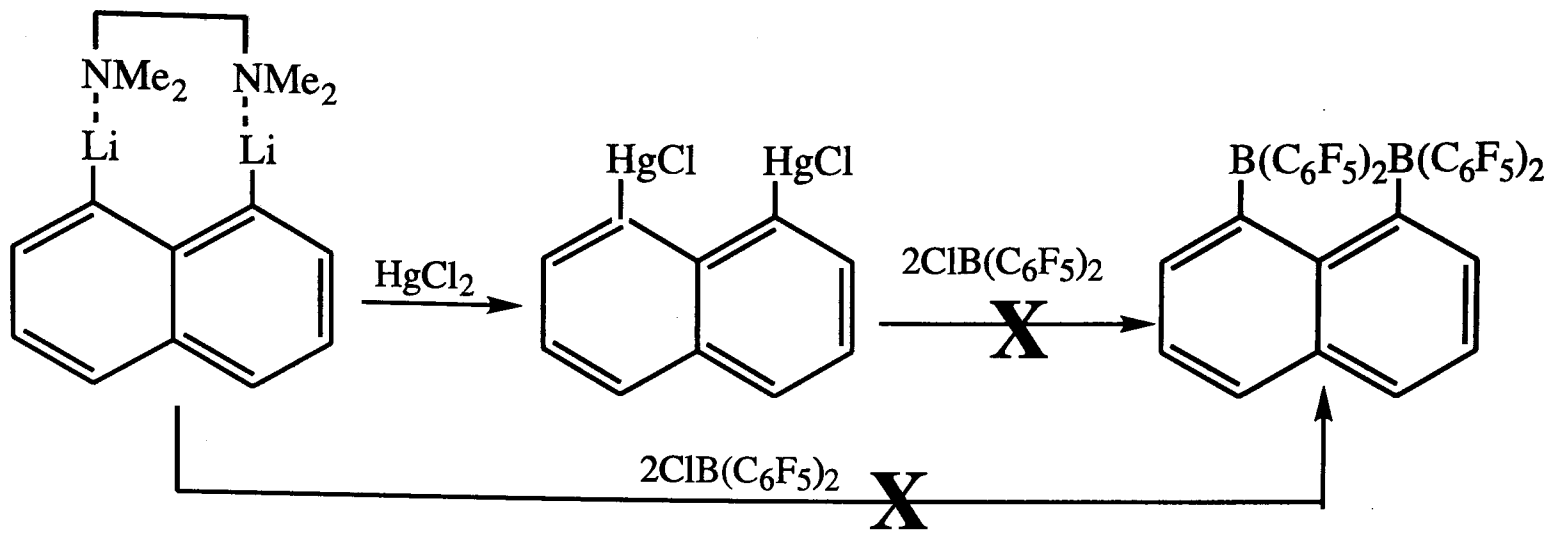
4.5.3 Summary

Attempts to synthesise bidentate Lewis acids (summarised below in Fig. 4.7) met with little success. This was for several reasons, notably because the lithium salts used were frequently not base-free and thus there was competition for the boron reagent. $ClB(C_6F_5)_2$ is also likely to be less reactive than BCl_3, even though their Lewis acidities are similar,[3] on simple grounds of bulk. It is entirely possible, as postulated in Section 4.5.2, that the desired products form but simply not fast enough for the reactions to reach completion before decomposition occurs. Work in this laboratory has found that hydroboration using $HB(C_6F_5)_2$ is generally a more reliable route to bidentate boranes.[28]

4.6 Summary and Conclusions

This chapter firstly reviewed the syntheses of a range of highly electrophilic Lewis acids containing a boron-perfluoroaryl linkage. In some cases, the published procedures have been modified to optimise yield and/or purity.

Two attempted preparations of BAr'_3 [Ar' = $(3,5\text{-}C_6H_3(CF_3)_2)$] are then described utilising [LiAr'] or $^nBu_3SnAr'$ (**16**). The latter tin reagent, new to the literature, has been fully characterised by microanalysis, NMR spectroscopy and mass spectrometry.



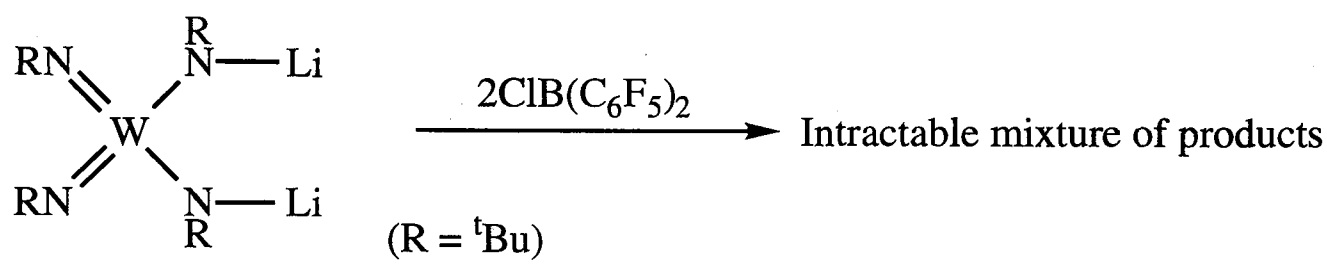


Fig. 4.7 Scheme showing attempted synthetic routes to a range of bidentate Lewis acids.

Two preparations of the new Lewis acid $B(C_6H_5)(C_6F_5)_2$ (**17**) are described, *via* $^nBu_3Sn(C_6F_5)$ or $[Li(C_6F_5)]$. Compound **17** has been fully characterised by microanalysis, NMR and infrared spectroscopies and mass spectrometry. Its reactivity is shown to be similar to $B(C_6F_5)_3$ although it exhibits weaker Lewis acidity.

Lastly, several attempts to make bidentate Lewis acids using $ClB(C_6F_5)_2$ as a synthon for the $B(C_6F_5)_2$ moiety are described. These routes have met with very limited success although there was evidence for the formation of $[(^tBuN)_2W\{N(^tBu)B(C_6F_5)_2\}_2]$. In this case, the desired product appeared to form too slowly to prevent it decomposing before the reaction was complete.

4.7 References for Chapter Four

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Chapter Five

Experimental Details

5.1 General Experimental Details

All preparations and manipulations of air and/or moisture sensitive materials were carried out under an atmosphere of dinitrogen using standard Schlenk line techniques or in an inert-atmosphere glove-box containing dinitrogen.[1] Dinitrogen was purified before use by passage through a drying column filled with activated molecular sieves (4Å) and a de-oxygenating column filled with either manganese (II) oxide suspended on vermiculite (Schlenk line) or BASF catalyst (glove-box). Solvents and solutions were transferred through stainless steel cannulae using a positive pressure of inert gas. Filtrations were performed using modified cannulae which could be fitted with glass fibre filter discs. All glassware and cannulae were dried overnight at 150 °C before use, as was Celite filtration aid (purchased from Fluka).

All solvents were thoroughly de-oxygenated before use either by bubbling dinitrogen through them for 15 minutes or by repeated evacuation followed by admission of dinitrogen. Solvents were pre-dried over activated 4Å molecular sieves and then distilled from sodium (petroleum ether (b.p. 100-120 °C) and toluene), sodium/potassium alloy (diethyl ether, dme, pentane and petroleum ether (b.p. 40-60 °C)), potassium (benzene and thf) or calcium hydride (dichloromethane, hexafluorobenzene, perfluorohexane and α,α,α-trifluorotoluene) under a slow continuous stream of dinitrogen. The Analar solvents methanol, ethanol and *iso*propanol were used as supplied without drying and degassed by bubbling dinitrogen through them for 15 minutes. Deuterated solvents for NMR spectroscopy were dried over potassium (benzene and toluene) or calcium hydride (dichloromethane) and de-oxygenated by three freeze-pump-thaw cycles. Deuterochloroform was used as supplied.

NMR spectra were recorded on either a Varian UnityPlus 500 spectrometer (^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{31}P and ^{119}Sn NMR spectra were recorded at 499.87, 160.38, 123.70, 470.28, 202.35 and 186.42 MHz respectively) or a Bruker AM300 spectrometer (^{1}H, ^{11}B, ^{13}C and ^{31}P NMR spectra were recorded at 300.13, 96.25, 75.5 and 121.6 MHz respectively). The spectra were referenced internally using the residual protio-solvent (^{1}H) and solvent (^{13}C) resonances and measured relative to tetramethylsilane (δ =

0 ppm); or referenced externally to $BF_3{\cdot}Et_2O$ (^{11}B, $\delta = 0$ ppm), $CFCl_3$ (^{19}F, $\delta = 0$ ppm), 85 % H_3PO_4 (^{31}P, $\delta = 0$ ppm) or $SnMe_4$ (^{119}Sn, $\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants given in Hertz.

Electron Impact mass spectra were recorded on an AEL MS 302 mass spectrometer, updated by a data-handling system supplied by Mass Spectrometry Services Ltd. Fast Atom Bombardment mass spectra were obtained by the EPSRC Mass Spectrometry Service at the University College of Swansea under the supervision of Dr. J. A. Ballantine.

Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer in the range 400 to 4000 cm^{-1}. Samples were prepared either as Nujol mulls between NaCl plates, as KBr discs or as dilute solutions in a solution cell with KBr windows. Solution spectra were referenced to a blank cell containing only the solvent. All data are given in wavenumbers (cm^{-1}).

Elemental analyses were obtained by the microanalytical department of the Inorganic Chemistry Laboratory.

5.1.1 Reagents and Starting Materials

$NaS_2CNMe_2{\cdot}H_2O$ (98 %), $NaS_2CNEt_2{\cdot}3H_2O$ (99 %), $[Ph_3C]BF_4$, MeO_3SCF_3 (99 %), ^nBuLi (2.5 M solution in hexanes), $PhBCl_2$ (97 %), Mg turnings, BBr_3 (1.0 M solution in heptane), BCl_3 (1.0 M solution in heptane), $BF_3{\cdot}Et_2O$ (redistilled) and $Me_2Si(Cl)H$ (98 %) were purchased from Aldrich and used as supplied. $^nBu_3SnCl$ (96 %), 3,5-$BrC_6H_3(CF_3)_2$ (98 %) and *ortho*-$C_6H_4(SiMe_3)_2$ were purchased from Aldrich and de-oxygenated before use by three freeze-pump-thaw cycles. 4-picoline (99 %) and NEt_3 (99 %) were purchased from Aldrich and pre-dried before use over activated 4 Å molecular sieves. BrC_6F_5 (99 %) was purchased from Fluorochem and de-oxygenated before use by three freeze-pump-thaw cycles. Me_2SnCl_2 (technical grade) was purchased from Fluka and used as supplied.

$[(\eta^5\text{-}C_5H_5)_2WH_2]$,[2] PMe_3,[3] $[(\eta^5\text{-}C_5H_5)_2MoH_2]$,[4] $[(\eta^5\text{-}C_5H_5)_2TaH_3]$,[5] $[(\eta^5\text{-}C_5H_5)_2ReH]$,[6] $[NReCl_2(PMePh_2)_3]$,[7] $[NRe(PMe_2Ph)(S_2CNMe_2)_2]$,[8] $[NMo(S_2CNR_2)_3]$ (R=Me or Et),[9] $[NMoCl_3(bipy)]$,[9], $[NMo(O^tBu)_3]$,[10] $[NOs(1,2\text{-}S_2C_6H_4)_2][^nBu_4N]$,[11] $[(SN)ReCl_2(PMePh_2)_3]$,[12] $[SWCl_2(PMePh_2)_3]$,[13] $[1,8\text{-}C_{10}H_6][Li_2\cdot TMEDA]$,[14] $[1,8\text{-}C_{10}H_6(HgCl)_2]$,[15] $[(\eta^5\text{-}C_5H_4Li)_2Fe]\cdot TMEDA$[16] and $[(^tBuN)_2W(N^tBu(Li))_2]$[17] were prepared by literature methods. $B(C_6F_5)_3$,[18, 19] $ClB(C_6F_5)_2$[20] and $HB(C_6F_5)_2$[21] were prepared by literature methods modified as described in Chapter Four. $[(\eta^5\text{-}C_5H_4{}^iPr)_2MoH_2]$ was prepared by a modification of a literature method for the preparation of $[(\eta^5\text{-}C_5H_5)_2WH_2]$, using $[MoCl_4\cdot dme]$ and $Na[C_5H_4{}^iPr]$ in place of $[WCl_4\cdot dme]$ and $Li[C_5H_5]$ respectively.[2] $[(\eta^5\text{-}C_5H_4{}^nBu)_2MoH_2]$[22] and $^nBu_3Sn(C_6F_5)$ were prepared by Dr. J. F. C. Turner and Dr. N. Metzler respectively of this laboratory.

5.2 Experimental Details for Chapter Two

5.2.1 Reaction of the Adduct of $B(C_6F_5)_3$ and $[(\eta^5\text{-}C_5H_5)_2WH_2]$ with NEt_3

(The formation of the adduct has been described previously).[23]

To a cold (-78 °C) solution of $[(\eta^5\text{-}C_5H_5)_2WH_2]$ (56 mg, 0.175 mmol) in toluene (10 cm^3) was added dropwise $B(C_6F_5)_3$ (1 cm^3 of a standard 0.175 M solution in toluene, 0.175 mmol) with stirring. An immediate colour change from yellow to deep purple was observed. To this solution at -78 °C, excess NEt_3 (3 drops) was added and the purple colour was observed to disappear over the course of 10 minutes. After this time, a pale yellow solution with a white precipitate had resulted. Volatiles were removed *in vacuo* at -78 °C and the residues dried under vacuum overnight before analysis by NMR spectroscopy. This showed the reaction products to be $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and $(C_6F_5)_3B{\cdot}NEt_3$.

^{1}H NMR Data *(300.13 MHz, C_6D_6)*: 4.24 (s, 5H, C_5H_5), 1.62 (m, 6H, NCH_2CH_3 (adduct)), 0.51 (m, 9H, NCH_2CH_3 (adduct)), -12.26 (s, 2H, WH_2)

$^{11}B\{^1H\}$ NMR Data *(96.25 MHz, C_6D_6)*: -3.9 (s)

In a parallel experiment, the purple solution was formed in an identical fashion from identical quantities of starting materials. This time, the solution was allowed to reach ambient temperature, at which point it had become very pale yellow in colour, before addition of a few drops of NEt_3. A colour change to darker yellow was observed and after 10 minutes stirring, the solvent was removed *in vacuo* and the residues dried overnight before NMR spectroscopic analysis. This showed that the products consisted solely of $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and $(C_6F_5)_3B{\cdot}NEt_3$ (NMR spectroscopic data as above).

5.2.2 Synthesis of $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)WH_3]$ (1)

To a stirred solution of $[(\eta^5\text{-}C_5H_5)_2WH_2]$ (0.316 g, 1.00 mmol) in petroleum ether (b.p. 100-120 °C) (40 cm^3) a solution of $B(C_6F_5)_3$ (0.530 g, 1.04 mmol) in

petroleum ether (b.p. 100-120 °C) (10 cm^3) was added dropwise. Immediate precipitation of a flocculent white solid was observed and the solution rapidly lost its yellow colour. Stirring was maintained for one hour after which time the product was isolated by filtration, washed with petroleum ether (b.p. 40-60 °C) (2x20 cm^3) and dried *in vacuo* overnight. It was shown to be pure by microanalysis.

Yield 0.750 g (91 %).

5.2.3 Synthesis of $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2(C_6H_5))(\eta^5\text{-}C_5H_5)WH_3]$ (2)

To a stirred solution of $[(\eta^5\text{-}C_5H_5)_2WH_2]$ (0.316 g, 1.00 mmol) in petroleum ether (b.p. 100-120 °C) (30 cm^3) was added dropwise a solution of $B(C_6F_5)_2(C_6H_5)$ (0.430 g, 1.02 mmol) in petroleum ether (b.p. 100-120 °C) (15 cm^3). Immediate precipitation of a flocculent off-white solid was observed and the solution rapidly lost its yellow colour. Stirring was maintained for thirty minutes after which time the product was isolated by filtration, washed with petroleum ether (b.p. 100-120 °C) (2x20 cm^3) and dried *in vacuo* overnight. It was shown to be pure by microanalysis.

Yield 0.550 g (75 %).

5.2.4 Synthesis of $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2H)(\eta^5\text{-}C_5H_5)WH_3]$ (3)

To a stirred solution of $[(\eta^5\text{-}C_5H_5)_2WH_2]$ (0.316 g, 1.00 mmol) in petroleum ether (b.p. 100-120 °C) (40 cm^3) was added dropwise a solution of $HB(C_6F_5)_2$ (0.355 g, 1.03 mmol) in petroleum ether (b.p. 100-120 °C) (20 cm^3). Rapid precipitation of a flocculent off-white solid was observed and the solution lost its yellow colour. After stirring for one hour, the product was isolated by filtration, washed with petroleum ether (b.p. 100-120 °C) (30 cm^3) then petroleum ether (b.p. 40-60 °C) (2x30 cm^3) and dried *in vacuo* overnight. It was shown to be pure by microanalysis.

Yield 0.470 g (72 %).

5.2.5 Synthesis of $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2Cl)(\eta^5\text{-}C_5H_5)WH_3]$ (4)

To a stirred solution of $[(\eta^5\text{-}C_5H_5)_2WH_2]$ (0.316 g, 1.00 mmol) in petroleum ether (b.p. 100-120 °C) (20 cm^3) was added dropwise a solution of $ClB(C_6F_5)_2$ (0.400 g, 1.05 mmol) in petroleum ether (b.p. 100-120 °C) (10 cm^3). Immediate precipitation of a floccu lent grey-white solid was observed and the solution rapidly lost its yellow colour. Stirring was maintained for one hour after which time the product was isolated by filtration, washed with petroleum ether (b.p. 100-120 °C) (3x10 cm^3) and dried *in vacuo* overnight. Single crystals suitable for X-ray diffraction were grown by slow evaporation at room temperature of a solution of **4** (20 mg) in benzene (15 cm^3) under a flow of dinitrogen.

Yield 0.450 g (65 %).

5.2.6 Reaction Between $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)WH_3]$ and L [L = thf, NEt_3 or PMe_3]

To a solution of $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)WH_3]$ (20 mg, 0.024 mmol) in toluene (10 cm^3) was added excess Lewis base; either thf (3 drops), NEt_3 (3 drops) or PMe_3 (1 cm^3 of a 0.105 M solution in petroleum ether (b.p. 40-60 °C)). The solution rapidly became yellow in colour and after the reaction had been allowed to proceed for 1 hour, the volatiles were removed *in vacuo* and the residues dried for a further 2 hours. The products were analysed by ^1H and $^{11}B\{^1H\}$ NMR spectroscopy and showed that in all three experiments, virtually quantitative formation of $[(\eta^5\text{-}C_5H_5)_2WH_2]$ and $(C_6F_5)_3B{\cdot}L$ [L = thf, NEt_3 or PMe_3] had occurred. In the case where L = thf, a small amount (*ca.* 10 %) of $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)WH_3]$ also remained. Where L = PMe_3, some of the residue proved to be insoluble in C_6D_6 and this was identified as being $(C_6F_5)_3B{\cdot}PMe_3$ since an independent synthesis of this adduct confirmed its insolubility in benzene.

^1H NMR Data *(300.13 MHz, C_6D_6)*

L = thf: 4.23 (s, 5H, C_5H_5), 3.55 (m, 4H, C_4H_8O (adduct)), 1.42 (m, 4H, C_4H_8O (adduct)), -12.26 (s, 2H, WH_2). Also small peaks at 4.42, 3.86 and -6.90 attributable to residual $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)WH_3]$ (See Section 6.2.1).

L = NEt3: 4.24 (s, 5H, C_5H_5), 1.62 (m, 6H, NCH_2CH_3 (adduct)), 0.51 (m, 9H, NCH_2CH_3) (adduct), -12.26 (s, 2H, WH_2).

L = PMe3: 4.24 (s, 5H, C_5H_5), -12.25 (s, 2H, WH_2)

$^{11}B\{^1H\}$ NMR Data *(96.25 MHz, C_6D_6)*

L = thf: -3.7 (s). Also small peak at -15.5 attributable to residual $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)WH_3]$ (See Section 6.2.1).

L = NEt3: -3.9 (s)

L = PMe3: No signal observed (*vide supra*).

5.2.7 Reaction Between $[(\eta^5\text{-}C_5H_5)_2Mo(H)(\eta^1\text{-}HB(C_6F_5)_3)]$ and 4-picoline

To a suspension of $[(\eta\text{-}C_5H_5)_2Mo(H)(\eta^1\text{-}HB(C_6F_5)_3)]$[23] (45 mg, 0.061 mmol) in toluene (5 cm^3), excess 4-picoline (3 drops) was added. Over the course of 2 days stirring, the blue solid disappeared and the solution phase became golden yellow. The volatiles were removed, the residue dried overnight *in vacuo* and analysis by ^1H NMR spectroscopy in C_6D_6 was undertaken. This allowed the products to be identified as $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ and $(C_6F_5)_3B{\cdot}4\text{-picoline}$.[23]

^1H NMR Data *(300.13 MHz, C_6D_6)*: 7.89 (br m, 2H, *ortho*-$NC_5H_4CH_3$ (adduct)), 6.14 (br m, 2H, *meta*-$NC_5H_4CH_3$ (adduct)), 4.36 (s, 5H, C_5H_5), 1.39 (br s, 3H, $NC_5H_4CH_3$ (adduct)), -8.77 (s, 2H, MoH_2)

5.2.8 Synthesis of $[(\eta^5\text{-}C_5H_5)_2Mo(H)(\eta^1\text{-}H_2B(C_6F_5)_2)]$ (5)

To a cold (-78 °C) solution of $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ (0.228 g, 1.00 mmol) in toluene (25 cm^3) a solution of $HB(C_6F_5)_2$ (0.346 g, 1.00 mmol) in toluene (30 cm^3) was slowly added with stirring. The solution gradually darkened from yellow through orange to red and was allowed to reach ambient temperature. Removal of volatiles under vacuum

yielded an olive-green oily solid which was afforded as a blue powder by trituration with petroleum ether (b.p. 40-60 °C) (30 cm^3). The product was crystallised from toluene (-80 °C) as blue needles.

Yield 0.201 g (35 %).

5.2.9 Reaction between $[(\eta^5\text{-}C_5H_4{}^iPr)_2MoH_2]$ and $B(C_6F_5)_3$

To a stirred cold (-78 °C) solution of $[(\eta^5\text{-}C_5H_4{}^iPr)_2MoH_2]$ (10 cm^3 of a standard 0.1 M solution in toluene, 1.00 mmol) diluted further with toluene (30 cm^3), $B(C_6F_5)_3$ (0.512g, 1.00 mmol) dissolved in toluene (10 cm^3) was added dropwise with stirring. No immediate colour change from brown-yellow was observed so the mixture was allowed to reach ambient temperature and stirred for 12 hours. There was still no colour change so the reaction mixture was warmed to 60 °C for 12 hours after which it had become green in colour. The solvent was removed *in vacuo* and the resulting oily green-black product washed with petroleum ether (b.p. 40-60 °C) (30 cm^3) and analysed by ^1H NMR spectroscopy. No starting materials were observed but the products were an intractable mixture which could not be further purified.

5.2.10 Reaction between $[(\eta^5\text{-}C_5H_4{}^nBu)_2MoH_2]$ and $B(C_6F_5)_3$

To $[(\eta^5\text{-}C_5H_4{}^nBu)_2MoH_2]$ (3 cm^3 of a 0.085 M solution in toluene, 0.255 mmol) was added $B(C_6F_5)_3$ (0.131g, 0.256 mmol) dissolved in toluene (10 cm^3). Stirring this mixture produced no colour change over the course of 12 hours, so the reaction mixture was warmed to 60 °C for 12 hours but still no reaction occurred.

5.2.11 Synthesis of $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)ReH_2]$ (6)

To a stirred solution of $[(\eta^5\text{-}C_5H_5)_2ReH]$ (0.317 g, 1.00 mmol) in petroleum ether (b.p. 100-120 °C) (40 cm^3) was slowly added a solution of $B(C_6F_5)_3$ (0.530 g, 1.04 mmol) in petroleum ether (b.p. 100-120 °C) (10 cm^3). Immediate formation of a light-brown precipitate was observed and after 1 hour stirring this was isolated by filtration. The product was washed with petroleum ether (b.p. 40-60 °C) (3x20 cm^3) and

recrystallised from toluene as a brown micro-crystalline solid at -80 °C. Its purity as **6**·0.5 PhMe was confirmed by microanalysis and NMR spectroscopy.

Yield: 0.529 g (65 %).

5.2.12 Reaction Between $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)ReH_2]$ and PMe_3

$[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)ReH_2]$ (20 mg, 0.024 mmol) was dissolved in toluene and PMe_3 (1 cm^3 of a 0.105 M solution in petroleum ether (b.p. 40-60 °C), 0.105 mmol) was added with stirring. No immediate colour change was evident and, after 1 hour, volatiles were removed under vacuum and the residues examined by ^1H and $^{11}B\{^1H\}$ NMR spectroscopy. This revealed that compound **6** was present unaltered.

5.2.13 Reaction Between $[(\eta^5\text{-}C_5H_5)_2TaH_3]$ and $B(C_6F_5)_3$

To a stirred solution of $[(\eta^5\text{-}C_5H_5)_2TaH_3]$ (0.314 g, 1.00 mmol) in toluene (20 cm^3) was added $B(C_6F_5)_3$ (0.512 g, 1.00 mmol) in toluene (15 cm^3). Over the course of 3 hours stirring, a slow colour change from pale yellow to dark orange was observed. After this time, volatiles were removed *in vacuo* to yield an orange oil. Sonication of this product in petroleum ether (b.p. 40-60 °C) (20 cm^3) for 15 minutes rendered it as a light orange powder which was isolated by filtration and dried under vacuum overnight. Microanalytical data confirmed the product's formulation as a 1:1 adduct between the reactants, however ^1H NMR spectroscopy revealed that the compound was not pure. No further purification could be achieved by crystallisation from toluene (-80 °C).

Microanalytical Data *(% Found (Calculated for $C_{28}H_{13}BF_{15}Ta$))*: C: 40.68 (40.71); H: 1.66 (1.59); B: 1.52 (1.31)

^1H NMR Data *(300.13 MHz, C_6D_6)*: 5.08 (s, 23 H, C_5H_5), 4.65 (s, 9H, C_5H_5), -4.1 (br s, fwhh *ca.* 200 Hz, TaH_3)

$^{11}B\{^1H\}$ NMR Data *(96.25 MHz, C_6D_6)*: -0.2 (s)

Selected $^{13}C\{^1H\}$ NMR Data *(75.5 MHz, C_6D_6)*: 106.44 (s, C_5H_5), 91.60 (s, C_5H_5) [Peaks in *ca.* 3:1 ratio]

5.3 Experimental Details for Chapter Three

5.3.1 Synthesis of [NRe(PMePh$_2$)(S$_2$CNEt$_2$)$_2$] (7)

To a stirred solution of [NReCl$_2$(PMePh$_2$)$_3$] (0.300 g, 0.34 mmol) in methanol (30 cm^3), NaS$_2$CNEt$_2$·3H$_2$O (0.233 g, 1.03 mmol) in methanol (15 cm^3) was added. The reaction mixture, which immediately changed colour from yellow to orange, was heated to reflux for 1 hour before being allowed to cool to room temperature. The solvent was removed *in vacuo* and the resulting, rather oily, orange solid washed with *iso*propanol (20 cm^3). Recrystallisation from *iso*propanol and dichloromethane (15 cm^3 of a 1:1 mixture) at -80 °C afforded compound **7** analytically pure.

Yield: 0.116g (48 %)

5.3.2 Synthesis of [NReCl(PMePh$_2$)$_2$(S$_2$CNMe$_2$)] (8)

[NReCl$_2$(PMePh$_2$)$_3$] (0.436 g, 0.500 mmol) was dissolved in methanol (20 cm^3) and a solution of NaS$_2$CNMe$_2$·H$_2$O (72 mg, 0.500 mmol) in methanol (15 cm^3) was added causing some immediate darkening of the reaction mixture. The mixture was heated to reflux for 1 hour after which time it was cooled to ambient temperature and concentrated to half volume. This led to precipitation of the product which was isolated analytically pure by filtration and washing with *iso*propanol (2x10 cm^3).

Yield: 0.201 g (53 %)

5.3.3 Synthesis of [{(C$_6$F$_5$)$_3$BN}Re(PMePh$_2$)(S$_2$CNEt$_2$)$_2$] (9)

To a stirred solution of compound **7** (90 mg, 0.129 mmol) in dichloromethane (15 cm^3), B(C$_6$F$_5$)$_3$ (72 mg, 0.140 mmol) in dichloromethane (5 cm^3) was added. An immediate colour change from yellow to violet was observed. After 1 hour stirring, petroleum ether (b.p. 40-60 °C) (30 cm^3) was added but no solid precipitated overnight. Hence the volatiles were removed under vacuum and the resulting oily solid triturated with petroleum ether (b.p. 40-60 °C) (20 cm^3) to yield the product as a lavender powder. Crystallisation by slow evaporation of a solution of the product in *iso*propanol and

dichloromethane (10 cm^3 of a 1:1 mixture) led to its isolation as purple single crystals suitable for X-ray diffraction. Microanalysis and NMR spectroscopy identified this product as pure **9**·0.5 ^iPrOH.

Yield: 0.104 g (65 %).

5.3.4 Synthesis of [{$(C_6F_5)_3BN$}Re(PMe_2Ph)(S_2CNMe_2)$_2$] (10)

To a stirred solution of [NRe(PMe_2Ph)(S_2CNMe_2)$_2$] (0.289 g, 0.500 mmol) in dichloromethane (20 cm^3) was added $B(C_6F_5)_3$ (0.280 g, 0.547 mmol) in dichloromethane (15 cm^3). Upon stirring overnight, the solution had darkened somewhat and the solvent was removed under vacuum to yield a grey oily solid. The product was afforded analytically pure as a lavender powder by trituration with pentane (2x15 cm^3) and drying overnight *in vacuo*. Single crystals suitable for analysis by X-ray diffraction were grown by slow vapour diffusion of pentane into a dichloromethane (20 cm^3) solution of **10** (*ca.* 20 mg).

Yield: 0.300 g (55 %)

5.3.5 Reaction Between [{$(C_6F_5)_3BN$}Re(PMe_2Ph)(S_2CNMe_2)$_2$] and L [L = thf, NEt_3 or PMe_3]

To a solution of [{$(C_6F_5)_3BN$}Re(PMe_2Ph)(S_2CNMe_2)$_2$] (20 mg, 0.018 mmol) in dichloromethane (10 cm^3) was added excess Lewis base; either thf (3 drops), NEt_3 (3 drops) or PMe_3 (1 cm^3 of a 0.105 M solution in petroleum ether (b.p. 40-60 °C), 0.105 mmol). No immediate colour change was observed and the reactions were allowed to proceed for 1 hour. Volatiles were then removed *in vacuo* and the residues dried for a further 2 hours. The products were analysed by ^1H and $^{11}B\{^1H\}$ NMR spectroscopy in $CDCl_3$ and this showed that in all three experiments no reaction of compound **10** had occurred.

5.3.6 Synthesis of [{$(C_6F_5)_3BN$}$ReCl(PMePh_2)_2(S_2CNMe_2)$] (11)

To a stirred solution of compound **8** (0.180 g, 0.238 mmol) in dichloromethane (15 cm^3) a solution of $B(C_6F_5)_3$ (0.144 g, 0.281 mmol) in dichloromethane (5 cm^3) was added dropwise. An immediate colour change from yellow to orange/red was observed. Stirring was maintained for 3 hours after which time the solvent was removed under vacuum and the resulting red oily solid triturated with pentane (20 cm^3). This afforded the product as a dark orange powder which was dried *in vacuo* overnight and shown to be pure by microanalysis.

Yield: 0.199 g (66 %)

5.3.7 Reaction Between $[NReCl_2(PMePh_2)_3]$ and $B(C_6F_5)_3$

A solution of $B(C_6F_5)_3$ (0.530 g, 1.04 mmol) in dichloromethane (15 cm^3) was added slowly to a stirred solution of $[NReCl_2(PMePh_2)_3]$ (0.872 g, 1.00 mmol) in dichloromethane (20 cm^3). An immediate colour change from yellow to deep red was observed and stirring was maintained overnight. After this time, volatiles were removed *in vacuo* and the resulting red/brown oily solid triturated with petroleum ether (b.p. 40-60 °C) (3x10 cm^3). The brown powder thus obtained was crystallised by slow cooling to -80 °C of a solution in dichloromethane/petroleum ether (b.p. 100-120 °C) (50 cm^3 of a 1:4 mixture). Two distinctly coloured microcrystalline products were obtained and partial separation by eye was achieved leading to mostly purple and mostly red/brown fractions. No further purification was possible either by chromatography or crystallisation.

Microanalytical Data *(% Found (Calculated for $C_{57}H_{39}BCl_2F_{15}NP_3Re$))*: C: 49.65 (49.48); H: 3.08 (2.84); N: 1.10 (1.01); B: 0.76 (0.78); Cl: 5.44 (5.12)

$^{11}B\{^1H\}$ NMR Data *(96.25 MHz, CD_2Cl_2)*

Mostly purple fraction: -3.9 (s), -9.9 (s) [Peaks in *ca.* 1:3 ratio]

Mostly red/orange fraction: -3.9 (s), -9.9 (s) [Peaks in *ca.* 2:1 ratio]

$^{31}P\{^1H\}$ NMR Data *(121.6 MHz, CD_2Cl_2)*

Mostly purple fraction: 47.58 (s, 1P), 7.34 (s, 4P)

Mostly red/orange fraction: 47.58 (s, 3P), 7.34 (s, 2P)

$[NReCl_2(PMePh_2)_3]$ (50 mg, 0.057 mmol) and $B(C_6F_5)_3$ (30 mg, 0.060 mmol) were combined in an NMR tube fitted with a teflon tap and dissolved in perdeuterodichloromethane (0.8 cm^3). The tube was warmed to 40 °C in an oil-bath over a period of 6 days and the progress of the reaction monitored by NMR spectroscopy.

Selected data for final product:

^{1}H NMR Data *(499.99 MHz, CD_2Cl_2)*: 7.2-7.8 (m, 30H, C_6H_5), 2.25 (dd, 6H, J_{HP} = 4.8, 4.8, PCH_3), 1.97 (d, 3H, J_{HP} = 11.0, PCH_3)

^{11}B{^{1}H} NMR Data *(160.38 MHz, CD_2Cl_2)*: -3.4 (s), -9.9 (s) [Peaks in *ca.* 1:10 ratio]

^{13}C{^{1}H} NMR Data *(75.5 MHz, CD_2Cl_2)*: 148.51 (d, $^1J_{CF}$ = 243, *ortho*-C_6F_5), 140.15 (d, $^1J_{CF}$ = 272, *para*-C_6F_5), 137.31 (d, $^1J_{CF}$ = 222, *meta*-C_6F_5), 133.32, 132.73, 132.63, 131.90, 131.49, 129.49, 128.72 (C_6H_5), 115.1 (br s, *ipso*-C_6F_5), 11.16 (d, J_{CP} = 35.2, PCH_3), 9.43 (t, J_{CP} = 17.6, PCH_3)

^{19}F NMR Data *(470.28 MHz, CD_2Cl_2)*: -130.56 (d, $^3J_{FF}$ = 20.7, *ortho*-C_6F_5), -134.07 (d, $^3J_{FF}$ = 20.7, *ortho*-C_6F_5), -160.97 (t, $^3J_{FF}$ = 20.7, *para*-C_6F_5), -162.61 (t, $^3J_{FF}$ = 20.7, *para*-C_6F_5), -168.85 (dd, $^3J_{FF}$ = 20.7, 20.7, *meta*-C_6F_5), -169.10 (dd, $^3J_{FF}$ = 20.7, 20.7, *meta*-C_6F_5) [2 sets of signals in *ca.* 1:1 ratio]

^{31}P{^{1}H} NMR Data *(121.6 MHz, CD_2Cl_2)*: 7.46 (s)

5.3.8 Synthesis of $[\{(C_6F_5)_3BN\}Mo(S_2CNMe_2)_3]$ (12)

To a stirred suspension of $[NMo(S_2CNMe_2)_3]$ (0.200 g, 0.425 mmol) in dichloromethane (30 cm^3) a solution of $B(C_6F_5)_3$ (0.250 g, 0.488 mmol) in dichloromethane (15 cm^3) was slowly added. Stirring was maintained for 48 hours after which time all solid material had dissolved and the solution colour had changed from orange to red. Volatiles were removed *in vacuo* to yield a brown oily solid which was rendered as an orange powder by trituration with pentane (40 cm^3). The yellow microcrystalline solid was obtained analytically pure by cooling a solution in dichloromethane (15 cm^3) to -80 °C.

Yield: 0.251 g (60 %).

5.3.9 Synthesis of $[\{(C_6F_5)_3BN\}Mo(S_2CNEt_2)_3]$ (13)

To a stirred suspension of $[NMo(S_2CNEt_2)_3]$ (0.250 g, 0.451 mmol) in dichloromethane (30 cm^3) a solution of $B(C_6F_5)_3$ (0.245 g, 0.479 mmol) in dichloromethane (15 cm^3) was slowly added. Stirring was maintained for 48 hours after which time all solid material had dissolved and the solution colour had changed from brown to red. Volatiles were removed *in vacuo* to yield a brown/red oil. This failed to crystallise from a solution in dichloromethane/pentane (30 cm^3 of a 1:4 mixture) and was rendered as a solid by sonication for 15 minutes in pentane (30 cm^3). The red/brown foamy solid product was isolated by filtration and dried overnight *in vacuo*.

Yield: 0.101 g (21 %).

5.3.10 Reaction Between $[\{(C_6F_5)_3BN\}Mo(S_2CNMe_2)_3]$ and L [L = thf, NEt_3 or PMe_3]

To a solution of $[\{(C_6F_5)_3BN\}Mo(S_2CNMe_2)_3]$ (20 mg, 0.020 mmol) in dichloromethane (10 cm^3) excess Lewis base was added; either thf (3 drops), NEt_3 (3 drops) or PMe_3 (1 cm^3 of a 0.105 M solution in petroleum ether (b.p. 40-60 °C), 0.105 mmol). Little immediate colour change was observed and the reactions were allowed to proceed for 1 hour. Volatiles were then removed *in vacuo* and the residues dried for a further 2 hours. The products were analysed by ^1H and $^{11}B\{^1H\}$ NMR spectroscopy and showed that in the case where L = thf, no decomposition of compound **12** had occurred whereas when L = NEt_3 or L = PMe_3, the residue consisted of *ca.* 50 % **12** and 50 % $[NMo(S_2CNMe_2)_3]$ plus $(C_6F_5)_3B{\cdot}L$.

^1H NMR Data *(300.13 MHz, $CDCl_3$)*

L = thf: Only resonances assignable to compound **12** (see Section 6.3.6) and free thf were observed.

L = NEt_3: 3.60 (m, 6H, NCH_2CH_3 (adduct)), 3.2-3.4 (m, NCH_3 from **12** and $[NMo(S_2CNMe_2)_3]$, overlapping), 1.46 (m, 9H, NCH_2CH_3 (adduct))

L = PMe_3: 3.2-3.4 (m, NCH_3 from **12** and $[NMo(S_2CNMe_2)_3]$, overlapping), 1.79 (d, $^2J_{PH}$ = 13.1, PCH_3 (adduct))

$^{11}B\{^1H\}$ NMR Data *(96.25 MHz, $CDCl_3$)*

L = thf: -6.3 (s)

L = NEt_3: -4.2 (s), -6.3 (s) [Peaks in *ca.* 1:1 ratio]

L = PMe_3: -4.4 (s), -6.3 (s) [Peaks in *ca.* 1:1 ratio]

5.3.11 Reaction Between [$NMoCl_3$(bipy)] and $B(C_6F_5)_3$

To a suspension of [$NMoCl_3$(bipy)] (0.100 g, 0.268 mmol) in dichloromethane (20 cm^3) a solution of $B(C_6F_5)_3$ (0.137 g, 0.268 mmol) in dichloromethane (10 cm^3) was added. Stirring for 3 days did not cause any colour to appear in the supernatant so the mixture was gently warmed to 40 °C for 8 hours. This had no effect and $^{11}B\{^1H\}$ NMR spectroscopic analysis of the solution confirmed that no reaction had taken place. Maintenance of stirring for 3 weeks did not cause any reaction to occur.

5.3.12 Reaction Between [$NMo(O^tBu)_3$] and $B(C_6F_5)_3$

To a suspension of [$NMo(O^tBu)_3$] (0.100 g, 0.304 mmol) in dichloromethane (20 cm^3) was added a solution of $B(C_6F_5)_3$ (0.155 g, 0.304 mmol) in dichloromethane (10 cm^3). Stirring for 3 days did not cause any colour to appear in the supernatant so the mixture was gently warmed to 40 °C for 8 hours. This had no effect and $^{11}B\{^1H\}$ NMR spectroscopic analysis of the solution confirmed that no reaction had taken place. Maintenance of stirring for 3 weeks did not cause any reaction to occur.

5.3.13 Synthesis of [{$(C_6F_5)_3BN$}$Os(1,2\text{-}S_2C_6H_4)_2$][$^nBu_4N$] (14)

To a stirred solution of [$NOs(1,2\text{-}S_2C_6H_4)_2$][$^nBu_4N$] (0.450 g, 0.619 mmol) in dichloromethane (40 cm^3), $B(C_6F_5)_3$ (0.450 g, 0.879 mmol) in dichloromethane (20 cm^3) was added. An immediate colour change from yellow to deep red was observed and after 1 hour stirring, the volatiles were removed under vacuum. The resulting oily green solid was triturated with pentane (20 cm^3) over a period of 48 hours to yield the product.

It was isolated analytically pure as an olive-green powder by filtration and drying under vacuum.

Yield: 0.675 g (88 %).

5.3.14 Reaction Between $[\{(C_6F_5)_3BN\}Os(1,2\text{-}S_2C_6H_4)_2][^nBu_4N]$ and L [L = thf, NEt_3 or PMe_3]

To a solution of $[\{(C_6F_5)_3BN\}Os(1,2\text{-}S_2C_6H_4)_2][^nBu_4N]$ (20 mg, 0.016 mmol) in dichloromethane (10 cm^3) excess Lewis base was added; either thf (3 drops), NEt_3 (3 drops) or PMe_3 (1 cm^3 of a 0.105 M solution in petroleum ether (b.p. 40-60 °C), 0.105 mmol). Little immediate colour change was observed and the reactions were allowed to proceed for 1 hour. Volatiles were then removed *in vacuo* and the residues dried for a further 2 hours. The products were analysed by ^1H and $^{11}B\{^1H\}$ NMR spectroscopy and showed that in the case where L = thf, no decomposition of compound **14** had occurred whereas when L = NEt_3 or L = PMe_3, the residue consisted entirely of $[NOs(1,2\text{-}S_2C_6H_4)_2][^nBu_4N]$[11] and $(C_6F_5)_3B{\cdot}L$.

[For ^1H and $^{11}B\{^1H\}$ NMR data for $(C_6F_5)_3B{\cdot}L$ (L = NEt_3 or PMe_3), see Sections 5.2.6 and 5.3.10 above.]

5.3.15 Reaction Between $[\{(C_6F_5)_3BN\}Os(1,2\text{-}S_2C_6H_4)_2][^nBu_4N]$ and $[Ph_3C]BF_4$

$[\{(C_6F_5)_3BN\}Os(1,2\text{-}S_2C_6H_4)_2][^nBu_4N]$ (50 mg, 0.040 mmol) and $[Ph_3C]BF_4$ (50 mg, 0.151 mmol) were combined as solids and dissolved in dichloromethane (15 cm^3). The mixture was stirred for 30 minutes after which its colour appeared to have darkened slightly. The volatiles were removed *in vacuo* and the whole of the reaction residues analysed by ^1H, $^{11}B\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy. This confirmed the formation of the known compound $[\{Ph_3CN\}Os(1,2\text{-}S_2C_6H_4)_2]$,[11] $B(C_6F_5)_3$ and $[^nBu_4N]BF_4$.

^1H NMR Data *(300.13 MHz, CD_2Cl_2)*: 7.82 (m, 4H, $S_2C_6H_4$), 7.22 (m, 3H, *para*-C_6H_5), 7.11-7.15 (m, 10H, $S_2C_6H_4$ and *meta*-C_6H_5), 6.78 (d, 6H, $^3J_{HH}$ =

7.3, *ortho*-C_6H_5), 3.07 (m, 6H, $NCH_2(CH_2)_2CH_3$), 1.56 (m, 6H, $NCH_2CH_2CH_2CH_3$), 1.37, (m, 6H, $N(CH_2)_2CH_2CH_3$), 0.99 (t, 9H, $^3J_{HH}$ = 7.3, $N(CH_2)_3CH_3$)

$^{11}B\{^1H\}$ NMR Data *(96.25 MHz, CD_2Cl_2)*: 58.0 (br s, $B(C_6F_5)_3$), -1.3 (s, BF_4)

$^{13}C\{^1H\}$ NMR Data *(75.5 MHz, CD_2Cl_2)*: 151.01, 137.76, 128.71, 128.52, 128.20, 128.04, 126.02 ($S_2C_6H_4$ and C_6H_5), 148.16 (d, $^1J_{CF}$ = 243 *ortho*-C_6F_5), 139.20 (d, $^1J_{CF}$ = 249, *para*-C_6F_5), 136.90 (d, $^1J_{CF}$ = 256, *meta*-C_6F_5), 95.90 (s, CPh_3), 59.02 (s, $NCH_2(CH_2)_2CH_3$), 23.91 (s, $NCH_2CH_2CH_2CH_3$), 19.74 (s, $N(CH_2)_2CH_2CH_3$), 13.30 (s, $N(CH_2)_3CH_3$)

5.3.16 Synthesis of [{$(C_6F_5)_3BN$}Os(1,2-(S)(SMe)C_6H_4)(1,2-$S_2C_6H_4$)] (15)

[{$(C_6F_5)_3BN$}Os(1,2-$S_2C_6H_4)_2$][$^nBu_4N$] (200 mg, 0.160 mmol) and MeO_3SCF_3 (50 mg, 0.305 mmol) were combined in a dry-box and dissolved in dichloromethane (15 cm^3). The reaction mixture was stirred for 1 hour without any obvious colour change and then the volatiles were removed under vacuum. Extraction of the oily residues with toluene yielded a red solution. Removal of the solvent from this afforded the product as an olive green oil. Vigorous washing with pentane (30 cm^3) failed to yield a solid so the product was characterised by NMR spectroscopy. It was too air-sensitive to allow satisfactory microanalytical data to be obtained.

5.3.17 Reaction Between [(SN)$ReCl_2(PMePh_2)_3$] and $B(C_6F_5)_3$

To a stirred solution of [(SN)$ReCl_2(PMePh_2)_3$] (0.200 g, 0.221 mmol) in dichloromethane (15 cm^3), $B(C_6F_5)_3$ (0.113 g, 0.221 mmol) in dichloromethane (10 cm^3) was slowly added. Over the course of 2 weeks stirring, the reaction mixture changed colour from purple to red/purple. After this time, the volatiles were removed *in vacuo* to afford a red oily residue. This was rendered as a red-purple powder by

trituration with pentane (20 cm^3) and analysed by NMR spectroscopy. This gave complex spectra which could not be assigned. No further purification was possible.

$^{11}B\{^1H\}$ NMR Data *(96.25 MHz, CD_2Cl_2)*: -9.9 (s)

5.3.18 Reaction Between $[SWCl_2(PMePh_2)_3]$ and $B(C_6F_5)_3$

To a stirred solution of $[SWCl_2(PMePh_2)_3]$ (0.150 g, 0.169 mmol) in dichloromethane (15 cm^3), $B(C_6F_5)_3$ (0.130 g, 0.254 mmol) in dichloromethane (10 cm^3) was added dropwise. Over the course of 2 days, a colour change from green to orange/brown was observed. Removal of volatiles *in vacuo* and trituration with pentane (30 cm^3) yielded an orange solid but it proved to be intractable.

$^{11}B\{^1H\}$ NMR Data *(96.25 MHz, CD_2Cl_2)*: -10.2 (s)

5.4 Experimental Details for Chapter Four

5.4.1 Reaction Between [Li(3,5-$C_6H_3(CF_3)_2$)] and BBr_3

To a cold (-78 °C) solution of 3,5-$BrC_6H_3(CF_3)_2$ (2.93 g, 10.0 mmol) in petroleum ether (b.p. 40-60 °C) (20 cm^3), ^nBuLi (4 cm^3 of a 2.5 M solution in hexanes, 10.0 mmol) diluted with petroleum ether (b.p. 40-60 °C) (10 cm^3) was added dropwise. No reaction was observed after 15 minutes stirring so the reaction mixture was allowed to reach ambient temperature. After 20 minutes at room temperature, the solution had become orange in colour and a white precipitate had formed. This suspension was recooled to -78 °C and added slowly through a wide-bored cannula to a stirred, cold (-78 °C) solution of BBr_3 (3.3 cm^3 of a 1.0 M solution in heptane, 3.3 mmol) diluted with petroleum ether (b.p. 40-60 °C) (10 cm^3). This reaction mixture was allowed to warm slowly to ambient temperature overnight. The resulting yellow solution was filtered and the brown precipitate washed with petroleum ether (b.p. 40-60 °C) (3x20 cm^3). The volatiles of the combined filtrates were removed under vacuum to yield a brown oil which proved to be an intractable mixture of products.

^1H NMR Data *(300.13 MHz, C_6D_6)*: 7.0-8.2 (m, $C_6H_3(CF_3)_2$), 0.7-1.3 (m, ^nBu)

$^{11}B\{^1H\}$ NMR Data *(96.25 MHz, C_6D_6)*: 86.4 (s), 79.3 (s), 46.6 (s)

5.4.2 Synthesis of $^nBu_3Sn(3,5\text{-}C_6H_3(CF_3)_2)$ (16)

A 500 cm^3 round-bottomed flask was charged with Mg turnings (0.416 g, 17.1 mmol), covered with diethylether (75 cm^3) and fitted with a reflux condenser and a gas inlet. A solution of 3,5-$BrC_6H_3(CF_3)_2$ (5.00 g, 17.1 mmol) in diethylether (25 cm^3) was added dropwise causing the reaction mixture to reflux on its own. Reflux was maintained for 2 hours by means of a water bath and then $^nBu_3SnCl$ (5.00 g, 15.4 mmol) was added dropwise. Immediate precipitation was observed and the mixture was stirred for a further 4 hours after which $^{119}Sn\{^1H\}$ NMR spectroscopy showed that the reaction was complete. The precipitated magnesium salts were removed by filtration and washed

with diethylether (20 cm^3). The volatiles of the combined filtrates were removed under vacuum to yield a brown oil. This was extracted with petroleum ether (b.p. 40-60 °C) (3x30 cm^3) and the volatiles of this fraction removed under vacuum to afford a red/brown oil. This was distilled under high vacuum (180 °C, 0.01 mbar) to yield the product as a clear viscous liquid.

Yield 4.323 g (56 % with respect to $^nBu_3SnCl$).

5.4.3 Reaction Between $^nBu_3Sn(3,5\text{-}C_6H_3(CF_3)_2)$ and BBr_3: Synthesis of $Br_2B(3,5\text{-}C_6H_3(CF_3)_2)$

To a solution of BBr_3 (0.90 cm^3 of a 1.0 M solution in hexanes, 0.90 mmol) in toluene (10 cm^3), $^nBu_3Sn(3,5\text{-}C_6H_3(CF_3)_2)$ (1.366 g, 2.71 mmol) dissolved in toluene (10 cm^3) was added. After 3.5 hours vigorous stirring, an aliquot was withdrawn for $^{11}B\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR spectroscopic analysis. This implied formation of $Br_2B(3,5\text{-}C_6H_3(CF_3)_2)$ so the mixture was heated to reflux for 8 hours but this only served to cause decomposition.

$^{11}B\{^1H\}$ NMR Data *(160.38 MHz, Toluene)*: 68.8 (s)

$^{119}Sn\{^1H\}$ NMR Data *(186.42 MHz, Toluene)*: 60.0 (s, $^nBu_3SnBr$), -31.4 (s, $^nBu_3Sn(3,5\text{-}C_6H_3(CF_3)_2)$) [Peaks in *ca.* 1:2 ratio]

The experiment was repeated using BBr_3 (1.0 cm^3 of a 1.0 M solution in hexanes, 1.00 mmol) and $^nBu_3Sn(3,5\text{-}C_6H_3(CF_3)_2)$ (0.503 g, 1.00 mmol) and an identical methodology. After 6 hours stirring at ambient temperature, the solvent was removed carefully under vacuum to yield an involatile black liquid product, believed to be $Br_2B(3,5\text{-}C_6H_3(CF_3)_2)$, which was too sensitive to isolate and characterise.

5.4.4 Reaction Between $^nBu_3Sn(3,5\text{-}C_6H_3(CF_3)_2)$ and $PhBCl_2$

To a solution of $PhBCl_2$ (0.159 g, 1.00 mmol) in toluene (10 cm^3) was slowly added a solution of $^nBu_3Sn(3,5\text{-}C_6H_3(CF_3)_2)$ (1.06 g, 2.00 mmol) in toluene (10 cm^3). The mixture was stirred and the progress of the reaction monitored by $^{119}Sn\{^1H\}$ and

$^{11}B\{^1H\}$ NMR spectroscopic analysis of aliquots withdrawn from the reaction vessel. After 72 hours at ambient temperature, no reaction had occurred so the mixture was heated to reflux for 12 hours. This failed to induce any reaction whatsoever and the starting materials were recovered unchanged

5.4.5 Reaction Between $^nBu_3Sn(C_6F_5)$ and $PhBCl_2$: Synthesis of $PhB(C_6F_5)_2$ (17)

To a solution of $PhBCl_2$ (0.477 g, 3.00 mmol) in toluene (10 cm^3) was slowly added a solution of $^nBu_3Sn(C_6F_5)$ (2.743 g, 6.00 mmol) in toluene (10 cm^3). The mixture was stirred and the progress of the reaction monitored by $^{119}Sn\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectroscopic analysis of aliquots withdrawn from the reaction vessel. No reaction was observed at ambient temperature so the mixture was heated to reflux for 12 hours. After this time, the reaction mixture was cooled to room temperature and the volatiles removed *in vacuo* to yield a white solid and an involatile clear liquid (*ca.* 2 cm^3). The product was crystallised from petroleum ether (b.p. 40-60 °C) (20 cm^3) at -80 °C, isolated by filtration, washed with cold (-78 °C) petroleum ether (b.p. 40-60 °C) (3x10 cm^3) and sublimed under vacuum (100 °C, 0.1 mbar). This afforded the product *ca.* 98 % pure but the final traces of $^nBu_3Sn(C_6F_5)$ could not be removed.

Yield 0.350g (28 %)

5.4.6 Synthesis of $PhB(C_6F_5)_2$ (17)

To a cold (-78 °C) solution of BrC_6F_5 (6.530 g, 26.40 mmol) in petroleum ether (b.p. 40-60 °C) (100 cm^3) was added dropwise ^nBuLi (10.6 cm^3 of a 2.5 M solution in hexanes, 26.50 mmol) diluted with pentane (10 cm^3). Instant formation of a white suspension was observed which was stirred for 1 hour at -78 °C. $PhBCl_2$ (2.100 g, 13.20 mmol) dissolved in petroleum ether (b.p. 40-60 °C) (40 cm^3) was added in one portion and the reaction mixture allowed to warm to ambient temperature overnight. The precipitated lithium salts were removed by filtration and washed with petroleum ether (b.p. 40-60 °C) (3x25 cm^3). The petrol fractions were combined and the volatiles

removed *in vacuo* to yield the product as a white solid. It was obtained as analytically pure white needles by crystallisation at -80 °C from petroleum ether (b.p. 40-60 °C) (50 cm^3), which were washed with cold (-40 °C) pentane (2x20 cm^3) and dried overnight under vacuum. Alternatively, the product could also be purified by vacuum sublimation (100 °C, 0.1 mbar).

Yield 1.70 g (36 %)

5.4.7 Reaction Between *ortho*-$C_6H_4(SiMe_3)_2$ and $ClB(C_6F_5)_2$

To a cold (-78 °C) stirred solution of *ortho*-$C_6H_4(SiMe_3)_2$ (0.233 g, 1.00 mmol) in dichloromethane (20 cm^3), $ClB(C_6F_5)_2$ (0.760 g, 2.00 mmol) in dichloromethane (10 cm^3) was slowly added. The temperature was maintained for 2 hours before being allowed to rise to ambient conditions. Removal of volatiles under vacuum yielded only the starting materials.

5.4.8 Reaction Between [1,8-$C_{10}H_6$][Li_2·TMEDA] and $ClB(C_6F_5)_2$

To a cold (-78 °C) stirred suspension of [1,8-$C_{10}H_6$][Li_2·TMEDA] (69 mg, 0.269 mmol) in petroleum ether (b.p. 40-60 °C) (15 cm^3) a solution of $ClB(C_6F_5)_2$ (0.205 g, 0.539 mmol) in petroleum ether (b.p. 40-60 °C) (10 cm^3) was added dropwise. The reaction mixture was allowed to reach ambient temperature overnight. The solution was filtered from the precipitated salts which were washed with petroleum ether (b.p. 40-60 °C) (2x20 cm^3). The solvent was removed from the combined filtrates *in vacuo* to yield an intractable off-white solid.

5.4.9 Reaction Between [1,8-$C_{10}H_6(HgCl)_2$] and $ClB(C_6F_5)_2$

To a stirred suspension of [1,8-$C_{10}H_6(HgCl)_2$] (1.270 g, 2.12 mmol) in toluene (30 cm^3) was added $ClB(C_6F_5)_2$ (1.613 g, 4.25 mmol) in toluene (10 cm^3). No change was apparent on stirring at ambient temperature for 3 hours, so the mixture was heated to reflux for 3 hours. No tractable product could be isolated from the reaction mixture.

5.4.10 Reaction between $[(\eta^5\text{-}C_5H_4Li)_2Fe]\cdot$TMEDA and $ClB(C_6F_5)_2$

To a cold (-78 °C) stirred suspension of $[(\eta^5\text{-}C_5H_4Li)_2Fe]\cdot$TMEDA (0.314 g, 1.00 mmol) in petroleum ether (b.p. 40-60 °C) (20 cm^3) a solution of $ClB(C_6F_5)_2$ (0.760 g, 2.00 mmol) in petroleum ether (b.p. 40-60 °C) (15 cm^3) was slowly added. The mixture was allowed to warm to ambient temperature over the course of 3 hours after which time a red solution and some red precipitate had formed. The solution phase was removed by filtration and the precipitate washed with petroleum ether (b.p. 40-60 °C) (2x30 cm^3). The volatiles were removed from the petrol fraction and NMR analysis of the orange residue showed that it was predominantly unreacted $ClB(C_6F_5)_2$. The orange residual solid proved to be toluene-soluble but NMR spectra obtained of it were complex and unassignable.

5.4.11 Reaction Between $Li_2[(^tBuN)_4W]$ and $ClB(C_6F_5)_2$

To a stirred cold (-78 °C) solution of $Li_2[(^tBuN)_4W]$ (0.253 g, 0.530 mmol) in toluene (20 cm^3) was added dropwise $ClB(C_6F_5)_2$ (0.400 g, 1.050 mmol). The mixture was allowed to attain ambient temperature and stirred for a further hour. After this time a blue-green solution and a small amount of precipitated solid had formed. NMR spectroscopic analysis of an aliquot showed significant quantities of the two starting materials were still present so the reaction mixture was stirred for a further 48 hours. After this time, the green-yellow solution was filtered and the solvent removed under vacuum to yield a yellow oily solid. $^{11}B\{^1H\}$ NMR spectroscopy showed that there was more than one product present as well as residual $ClB(C_6F_5)_2$.

$^{11}B\{^1H\}$ NMR Data *(96.25 MHz, C_6D_6)*: 57.6 (s, $ClB(C_6F_5)_2$), 32.5 (s), -2.4 (s)

In a separate experiment, $Li_2[(^tBuN)_4W]$ (35 mg, 0.073 mmol) was combined with $ClB(C_6F_5)_2$ (53 mg, 0.139 mmol) in an NMR tube fitted with a teflon tap and dissolved in perdeuterotoluene (0.8 cm^3). The reaction was allowed to proceed over 5 days and monitored by means of ^1H and $^{11}B\{^1H\}$ NMR spectroscopy. The results are discussed in Section 4.5.2

5.5 References for Chapter Five

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Chapter Six

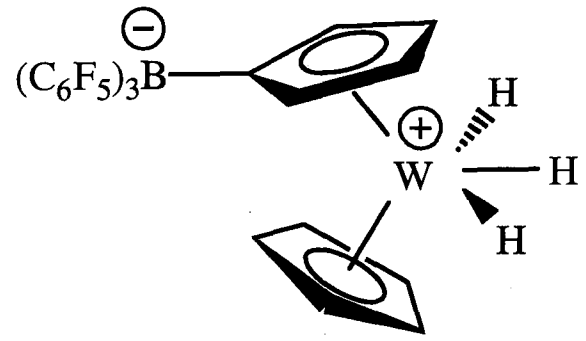
Characterising Data

6.1 Characterising Data- General

All NMR spectroscopic chemical shifts are quoted as δ (ppm) and coupling constants are given in Hertz (Hz). Infrared data are given in wavenumbers (cm^{-1}). Mass spectral data are quoted for the most common isotopic form *i.e.* ^{11}B, ^{32}S, ^{35}Cl, ^{98}Mo, ^{120}Sn, ^{184}W and ^{187}Re. $[M]^+$ refers to the parent ion Note that the calibration of the Electron Impact mass spectrometer is only accurate to +/- 1%.

6.2 Characterising Data for Chapter Two

6.2.1 Data Characterising $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)WH_3]$ (1)



Molecular Formula	$C_{28}H_{12}BF_{15}W$
Formula Weight	828.04
	White powder, 91 %
Microanalytical Data	*% Found (Calculated)*
	C: 40.7 (40.6); H: 1.1 (1.5); B: 1.05 (1.3)
^{1}H NMR Data	*[300.13 MHz, C_6D_6]*
	4.42 (m, 2H, $(C_6F_5)_3BC_5H_4$)
	4.16 (m, 2H, $(C_6F_5)_3BC_5H_4$)
	3.86 (s, 5H, C_5H_5)
	-6.67 (t, 1H, $^2J_{HH}$ = 7.8, Central W-*H*)
	-6.90 (d, 2H, $^2J_{HH}$ = 7.8, $^1J_{WH}$ = 45.0, Outer W-*H*)

[300.13 MHz, CD_2Cl_2]

5.56 (s, 2H, $(C_6F_5)_3BC_5H_4$)

5.52 (s, 2H, $(C_6F_5)_3BC_5H_4$)

5.23 (s, 5H, C_5H_5)

-6.27 (t, 1H, $^2J_{HH}$ = 9.6, Central W-*H*)

-6.38 (d, 2H, $^2J_{HH}$ = 9.6, Outer W-*H*)

$^{11}B\{^1H\}$ NMR Data *[96.25 MHz, C_6D_6]*

-15.4 (s)

[96.25 MHz, CD_2Cl_2]

-15.6 (s)

$^{13}C\{^1H\}$ NMR Data *[75.5 MHz, C_6D_6]*

149.02 (d, $^1J_{CF}$ = 245, *ortho*-C_6F_5)

139.52 (d, $^1J_{CF}$ = 256, *para*-C_6F_5)

137.31 (d, $^1J_{CF}$ = 254, *meta*-C_6F_5)

123.0 (br s, *ipso*-C_6F_5)

87.00 (br s, *ipso*-$(C_6F_5)_3BC_5H_4$)

82.96 (s, $(C_6F_5)_3BC_5H_4$)

82.35 (s, C_5H_5)

71.51 (s, $(C_6F_5)_3BC_5H_4$)

[75.5 MHz, CD_2Cl_2]

148.46 (d, $^1J_{CF}$ = 249, *ortho*-C_6F_5)

137.60 (d, $^1J_{CF}$ = 253, *para*-C_6F_5)

130.46 (d, $^1J_{CF}$ = 251, *meta*-C_6F_5)

96.93 (s, C_5H_5)

87.11 (br s, *ipso*-$(C_6F_5)_3BC_5H_4$)

84.18 (s, $(C_6F_5)_3BC_5H_4$)

83.30 (s, $(C_6F_5)_3BC_5H_4$)

The *ipso*-C_6F_5 resonance was not detected.

Selected Infrared Data *[Nujol Mull]*

1939w (ν(W-H)), 1768w, 1645w, 1516m, 1262s, 1089s,

975m, 833m, 800s

Mass Spectral Data *[Fast Atom Bombardment]*

851: $[M+Na]^+$

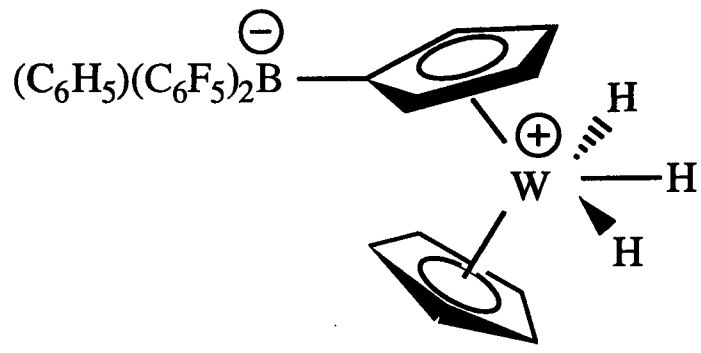
828: $[M]^+$

826: $[M]^+$ for ^{182}W

660: $[M-(C_6F_5)-H]^+$

316: $[M-B(C_6F_5)_3]^+$

6.2.2 Data Characterising $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2(C_6H_5))(\eta^5\text{-}C_5H_5)WH_3]$ (2)



Molecular Formula	$C_{28}H_{17}BF_{10}W$
Formula Weight	738.09
	Off-white powder, 75 %
Microanalytical Data	*% Found (Calculated)*
	C: 45.6 (45.6); H: 2.1 (2.3); B: 1.7 (1.5)
^{1}H NMR Data	*[300.13 MHz, C_6D_6]*
	7.1-7.6 (m, 5H, C_6H_5)
	4.55 (s, 2H, $(C_6H_5)(C_6F_5)_2BC_5H_4$)
	4.16 (s, 2H, $(C_6H_5)(C_6F_5)_2BC_5H_4$)
	3.67 (s, 5H, C_5H_5)
	-6.64 (t, 1H, $^2J_{HH}$ = 7.1, Central W-*H*)
	-7.00 (d, 2H, $^2J_{HH}$ = 7.1, Outer W-*H*)
	[300.13 MHz, CD_2Cl_2]
	7.1-7.3 (m, 5H, C_6H_5)
	5.38 (s, 2H, $(C_6H_5)(C_6F_5)_2BC_5H_4$)
	5.10 (s, 5H, C_5H_5)
	4.94 (s, 2H, $(C_6H_5)(C_6F_5)_2BC_5H_4$)
	-6.38 (t, 1H, $^2J_{HH}$ = 4.8, Central W-*H*)
	-6.48 (d, 2H, $^2J_{HH}$ = 4.8, Outer W-*H*)
$^{11}B\{^1H\}$ NMR Data	*[96.25 MHz, C_6D_6]*
	-13.0 (s)

[96.25 MHz, CD_2Cl_2]

-13.1 (s)

$^{13}C\{^1H\}$ NMR Data

[75.5 MHz, C_6D_6]

87.63 (br s, *ipso*-$(C_6H_5)(C_6F_5)_2BC_5H_4$)

83.17 (s, $(C_6H_5)(C_6F_5)_2BC_5H_4$)

82.27 (s, $(C_6H_5)(C_6F_5)_2BC_5H_4$)

71.51 (s, C_5H_5)

The remaining resonances were not observed.

[75.5 MHz, CD_2Cl_2]

148.21 (d, $^1J_{CF} = 220$, *ortho*-C_6F_5)

138.46 (d, $^1J_{CF} = 239$, *para*-C_6F_5)

137.16 (d, $^1J_{CF} = 258$, *meta*-C_6F_5)

133.91 (s, *ortho*-C_6H_5)

126.41 (s, *para*-C_6H_5)

124.80 (s, *meta*-C_6H_5)

112.60 (br s, *ipso*-C_6F_5)

96.91 (br s, *ipso*-C_6H_5)

87.24 (br s, *ipso*-$(C_6H_5)(C_6F_5)_2BC_5H_4$)

84.03 (s, $(C_6H_5)(C_6F_5)_2BC_5H_4$)

83.42 (s, C_5H_5)

71.60 (s, $(C_6H_5)(C_6F_5)_2BC_5H_4$)

Selected Infrared Data

[Nujol Mull]

3551m (aromatic ν(C-H)) , 1951w (ν(W-H)), 1645m,

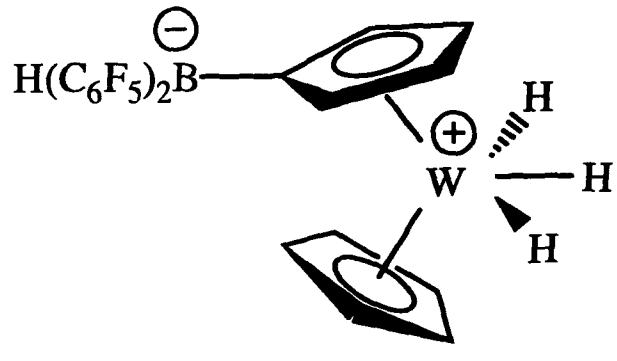
1518m, 1103m, 1082s, 981s, 811s br

Mass Spectral Data

[Fast Atom Bombardment]

316: $[M\text{-}B(C_6H_5)(C_6F_5)_2]^+$

6.2.3 Data Characterising $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2H)(\eta^5\text{-}C_5H_5)WH_3]$ (3)



Molecular Formula	$C_{22}H_{13}BF_{10}W$
Formula Weight	661.99
	Off-white powder, 72 %
Microanalytical Data	*% Found (Calculated)*
	C: 39.9 (39.9); H: 1.7 (2.0); B: 1.6 (1.6)
^{1}H NMR Data	*[300.13 MHz, $D_3CC_6D_5$]*
	4.73 (m, 2H, $H(C_6F_5)_2BC_5H_4$)
	4.3 (br s, 1H, $H(C_6F_5)_2BC_5H_4$)
	4.21 (s, 5H, C_5H_5)
	4.20 (m, 2H, $H(C_6F_5)_2BC_5H_4$)
	-7.04 (t, 1H, $^2J_{HH}$ = 7.3, $^1J_{WH}$ = 66.4, Central W-*H*)
	-7.39 (d, 2H, $^2J_{HH}$ = 7.3, $^1J_{WH}$ = 46.2, Outer W-*H*)
	[300.13 MHz, CD_2Cl_2]
	5.33 (s, 5H, C_5H_5)
	5.29 (m, 2H, $H(C_6F_5)_2BC_5H_4$)
	5.25 (m, 2H, $H(C_6F_5)_2BC_5H_4$)
	4.5 (br s, $H(C_6F_5)_2BC_5H_4$)
	-6.44 (t, 1H, $^2J_{HH}$ = 7.6, $^1J_{WH}$ = 66.6, Central W-*H*)
	-6.71 (d, 2H, $^2J_{HH}$ = 7.6, $^1J_{WH}$ = 46.0, Outer W-*H*)
$^{11}B\{^1H\}$ NMR Data	*[96.25 MHz, $D_3CC_6D_5$]*
	-23.2 (s)
	[96.25 MHz, CD_2Cl_2]
	-23.4 (s)

^{11}B NMR Data *[96.25 MHz, $D_3CC_6D_5$]*

-23.2 (d, $^1J_{BH}$ = 98)

[96.25 MHz, CD_2Cl_2]

-23.4 (d, $^1J_{BH}$ = 86)

^{13}C{^{1}H} NMR Data *[75.5 MHz, $D_3CC_6D_5$]*

89.66 (br s, *ipso*-H$(C_6F_5)_2BC_5H_4$)

84.25 (s, C_5H_5)

81.90 (s, H$(C_6F_5)_2BC_5H_4$)

71.51 (s, H$(C_6F_5)_2BC_5H_4$)

The (C_6F_5) resonances were not located.

[75.5 MHz, CD_2Cl_2]

148.24 (d, $^1J_{CF}$ = 293, *ortho*-C_6F_5)

138.55 (d, $^1J_{CF}$ = 242, *para*-C_6F_5)

136.88 (d, $^1J_{CF}$ = 242, *meta*-C_6F_5)

89.50 (br s, *ipso*-H$(C_6F_5)_2BC_5H_4$)

84.71 (s, C_5H_5)

82.67 (s, H$(C_6F_5)_2BC_5H_4$)

71.77 (s, H$(C_6F_5)_2BC_5H_4$)

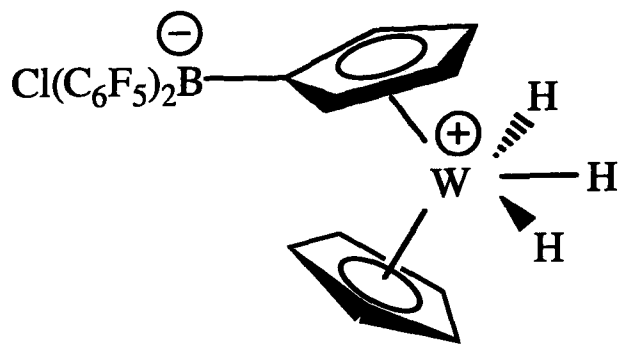
The *ipso*-C_6F_5 resonance was not located.

Selected Infrared Data *[Nujol Mull]*

1991w (ν(W-H)), 1636w, 1510m, 1275m, 1108m,

1087m, 1073 m, 1023w, 964s br

6.2.4 Data Characterising $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2Cl)(\eta^5\text{-}C_5H_5)WH_3]$ (4)



Molecular Formula	$C_{22}H_{12}BClF_{10}W$
Formula Weight	696.43
	Grey-white powder (clear single crystals), 65 %
Microanalytical Data	*% Found (Calculated)*
	C: 39.25 (37.9); H: 2.5 (1.7); B: 1.2 (1.55);
	Cl: 5.5 (5.1)
^{1}H NMR Data	*[300.13 MHz, C_6D_6]*
	4.62 (s, 2H, $Cl(C_6F_5)_2BC_5H_4$)
	4.37 (s, 2H, $Cl(C_6F_5)_2BC_5H_4$)
	4.28 (s, 5H, C_5H_5)
	-6.70 (t, 1H, $^2J_{HH}$ = 7.7, $^1J_{HH}$ = 67.4, Central W-*H*)
	-6.87 (d, 2H, $^2J_{HH}$ = 7.7, $^1J_{HH}$ = 45.6, Outer W-*H*)
	[300.13 MHz, CD_2Cl_2]
	5.52 (s, 2H, $Cl(C_6F_5)_2BC_5H_4$)
	5.40 (s, C_5H_5)
	5.20 (s, 2H, $Cl(C_6F_5)_2BC_5H_4$)
	-6.26 (t, 1H, $^2J_{HH}$ = 7.8, $^1J_{HH}$ = 66.2, Central W-*H*)
	-6.37 (d, 2H, $^2J_{HH}$ = 7.8, $^1J_{WH}$ = 46.2, Outer W-*H*)
$^{11}B\{^1H\}$ NMR Data	*[96.25 MHz, C_6D_6]*
	-6.7 (s)
	[96.25 MHz, CD_2Cl_2]
	-6.7 (s)

$^{13}C\{^{1}H\}$ NMR Data *[75.5 MHz, CD_2Cl_2]*

147.54 (d, $^{1}J_{CF}$ = 239, *ortho*-C_6F_5)

139.26 (d, $^{1}J_{CF}$ = 269, *para*-C_6F_5)

137.16 (d, $^{1}J_{CF}$ = 264, *meta*-C_6F_5)

123.0 (br s, *ipso*-C_6F_5)

87.70 (br s, *ipso*-$Cl(C_6F_5)_2BC_5H_4$)

84.66 (s, $Cl(C_6F_5)_2BC_5H_4$). Two coincident peaks.

83.71 (s, C_5H_5)

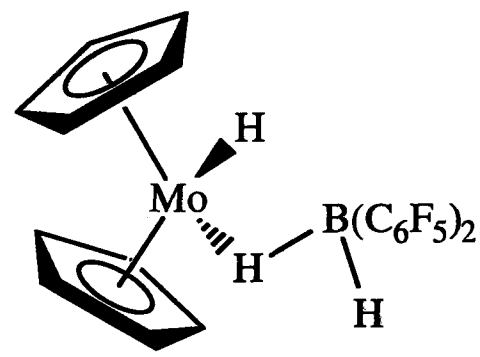
Selected Infrared Data *[Nujol Mull]*

1941w (ν(W-H)), 1645m, 1516m, 1280m, 1089s br,

1019w, 974s

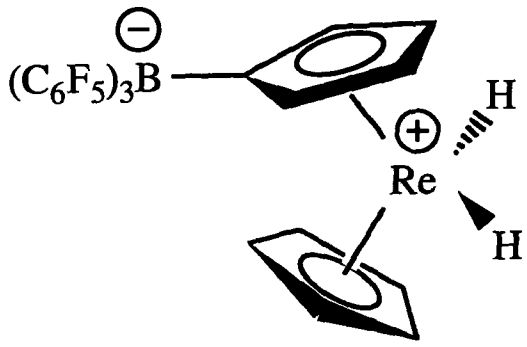
Other Data See Appendix One for X-Ray crystal structure.

6.2.5 Data Characterising $[(\eta^5\text{-}C_5H_5)_2Mo(H)(\eta^1\text{-}H_2B(C_6F_5)_2)]$ (5)



Molecular Formula	$C_{22}H_{13}BF_{10}Mo$
Formula Weight	574.08
	Dark-blue needles, 35 %
Microanalytical Data	*% Found (Calculated)*
	C: 44.5 (46.0); H: 1.75 (2.3); B: 1.6 (1.9)
^{1}H NMR Data	*[300.13 MHz, $D_3CC_6D_5$]*
	4.6 (br s, 1H, B-*H*)
	4.18 (s, 10H, C_5H_5)
	-13.56 (s, 1H, Mo-*H*)
	-18.2 (br s, 1H, Mo-*H*-B)
^{11}B{^{1}H} NMR Data	*[96.25 MHz, $D_3CC_6D_5$]*
	-12.1 (s)
^{13}C{^{1}H} NMR Data	*[75.5 MHz, $D_3CC_6D_5$]*
	63.1 (s, C_5H_5)
	The compound was insufficiently soluble for the (C_6F_5)
	resonances to be detected.
Selected Infrared Data	*[KBr Disc]*
	3600w, 3130w, 2964w, 2930w, 2866w, 2390w, 1724w,
	1645m, 1516s, 1470s, 1405m, 1340m, 1308m, 1102s,
	984s

6.2.6 Data Characterising $[(\eta^5\text{-}C_5H_4B(C_6F_5)_3)(\eta^5\text{-}C_5H_5)ReH_2]$ (6)



Molecular Formula	$C_{28}H_{11}BF_{15}Re$
Formula Weight	829.39
	Light-brown microcrystals, 65 %
Microanalytical Data	*% Found (Calculated for 6·0.5 Toluene)*
	C: 43.4 (43.2); H: 2.0 (1.7); B: 0.9 (1.2)
^{1}H NMR Data	*[300.13 MHz, CD_2Cl_2]*
	{7.3-7.0 (m, 2.5H, $H_3CC_6H_5$)}
	5.16 (br s, 2H, $(C_6F_5)_3BC_5H_4$)
	5.07 (br s, 2H, $(C_6F_5)_3BC_5H_4$)
	4.98 (s, 5H, C_5H_5)
	{2.34 (s, 1.5H, $H_3CC_6H_5$)}
	-13.87 (s, 2H, ReH_2)
^{11}B{^{1}H} NMR Data	*[96.25 MHz, CD_2Cl_2]*
	-15.8 (s)
^{13}C{^{1}H} NMR Data	*[75.5 MHz, CD_2Cl_2]*
	148.30 (d, $^1J_{CF}$ = 222, *ortho*-C_6F_5)
	136.76 (d, $^1J_{CF}$ = 243, *para*-C_6F_5)
	134.71 (d, $^1J_{CF}$ = 232, *meta*-C_6F_5)
	84.10 (br s, *ipso*-$(C_6F_5)_3BC_5H_4$)
	77.60 (s, $(C_6F_5)_3BC_5H_4$)
	76.63 (s, C_5H_5)
	74.63 (s, $(C_6F_5)_3BC_5H_4$)
	The *ipso*-C_6F_5 resonance was not located.

Selected Infrared Data *[Nujol Mull]*

2727m, 1644s, 1515s, 1456s, 1273s, 1089s, 967s, 858m

Mass Spectral Data *[Fast Atom Bombardment]*

852 : $[M+Na]^+$

829: $[M]^+$

828: $[M-H]^+$

662: $[M-(C_6F_5)]^+$

512: $[B(C_6F_5)_3]^+$

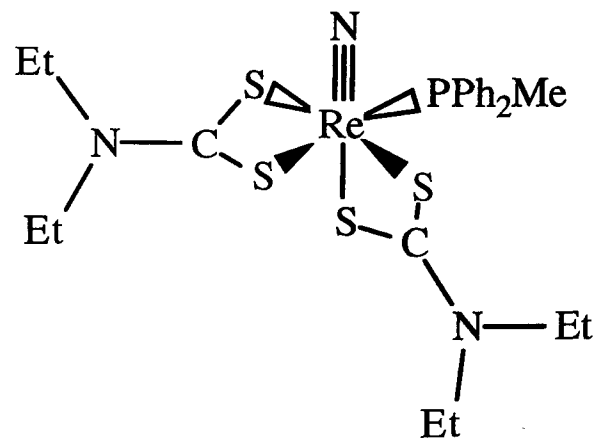
318: $[M+H-B(C_6F_5)_3]^+$

317: $[M-B(C_6F_5)_3]^+$

167: $[(C_6F_5)]^+$

6.3 Characterising Data for Chapter Three

6.3.1 Data Characterising $[NRe(PMePh_2)(S_2CNEt_2)_2]$ (7)



Molecular Formula	$C_{23}H_{33}N_3PReS_4$
Formula Weight	696.95
	Orange / brown microcrystalline solid, 48 %
Microanalytical Data	*% Found (Calculated)*
	C: 40.2 (39.6); H: 4.7 (4.8); N: 5.8 (6.0);
	P: 4.6 (4.4)
^{1}H NMR Data	*[300.13 MHz, CD_2Cl_2]*
	7.3-7.8 (m, 10H, $P(C_6H_5)_2$)
	3.87, 3.71, 3.58, 3.36 (m, 2H each, NCH_2CH_3)
	2.31 (d, 3H, $^2J_{PH}$ = 8.8, PCH_3)
	1.36 (dd, 6H, $^3J_{HH}$ = 7.2, 7.2, NCH_2CH_3)
	1.04 (dd, 6H, $^3J_{HH}$ = 7.1, 7.2, NCH_2CH_3)
$^{31}P\{^1H\}$ NMR Data	*[121.6 MHz, CD_2Cl_2]*
	-5.05 (s)
$^{13}C\{^1H\}$ NMR Data	*[75.5 MHz, CD_2Cl_2]*
	223.87 (s, S_2CNEt_2)
	202.66 (s, S_2CNEt_2)
	135.17 (d, $^3J_{CP}$ = 8.9, *meta*-PC_6H_5)
	134.04 (d, $^1J_{CP}$ = 48.5, *ipso*-PC_6H_5)
	131.56 (s, *para*-PC_6H_5)

128.38 (s, $^2J_{CP}$ = 11.2, *ortho*-PC_6H_5)

46.03, 45.14 (s, NCH_2CH_3)

18.02 (d, $^1J_{CP}$ = 36.7, PCH_3)

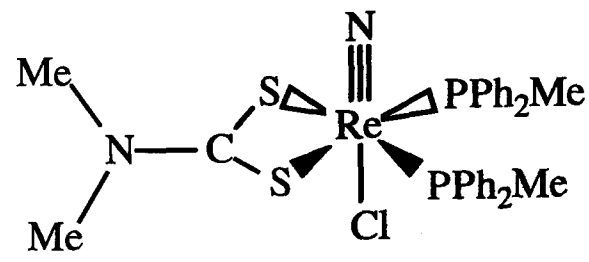
12.84, 12.45, (s, NCH_2CH_3)

Selected Infrared Data *[Nujol Mull]*

1358s, 1302s, 1273s, 1212s, 1146s, 1096s, 1076s,

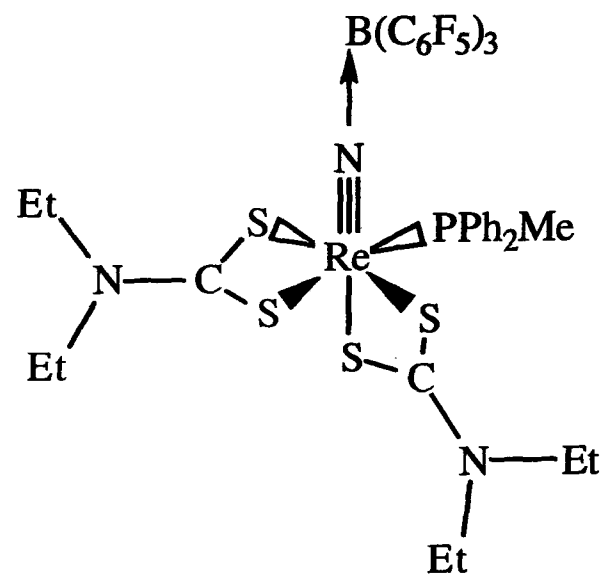
1054s (ν(Re-N)), 914s, 888s

6.3.2 Data Characterising [NReCl(PMePh$_2$)$_2$(S$_2$CNMe$_2$)] (8)



Molecular Formula	$C_{29}H_{32}ClN_2P_2ReS_2$
Formula Weight	756.32
	Yellow-brown microcrystals, 53 %
Microanalytical Data	*% Found (Calculated)*
	C: 46.5 (46.1); H: 4.1 (4.3); N: 4.0 (3.7)
^{1}H NMR Data	*[300.13 MHz, $CDCl_3$]*
	7.1-7.7 (m, 20H, P(C_6H_5)$_2$)
	3.24 (s, 6H, NCH_3)
	2.13 (d, 6H, $^2J_{PH}$ = 8.9, PCH_3)
^{31}P{^{1}H} NMR Data	*[121.6 MHz, $CDCl_3$]*
	-10.77 (s)
Selected Infrared Data	*[Nujol Mull]*
	1261s, 1094s, 1060s (ν(Re-N)), 1020s, 800s

6.3.3 Data Characterising [{$(C_6F_5)_3BN$}Re($PMePh_2$)(S_2CNEt_2)$_2$] (9)



Molecular Formula	$C_{41}H_{33}BF_{15}N_3PReS_4$
Formula Weight	1208.93
	Purple single crystals, 65 %
Microanalytical Data	*% Found (Calculated for 9·0.5 ^iPrOH)*
	C: 41.3 (41.2); H: 3.05 (3.0); N: 3.4 (3.4);
	B: 0.85 (0.9); P: 2.6 (2.5)
^{1}H NMR Data	*[499.9 MHz, CD_2Cl_2]*
	7.65 (dd, 2H, $^3J_{HH}$ = 8.5, 8.5, *meta*-P(C_6H_5))
	7.43 (m, 1H, *para*-P(C_6H_5))
	7.42 (m, 2H, *ortho*-P(C_6H_5))
	7.36 (dd, 2H, $^3J_{HH}$ = 8.5, 8.5, *meta*-P(C_6H_5))
	7.29 (t, 1H, $^3J_{HH}$ = 8.5, *para*-P(C_6H_5))
	7.22 (dd, 2H, $^3J_{PH}$ = 8.5, $^3J_{HH}$ = 8.5, *ortho*-P(C_6H_5))
	3.81, 3.78, 3.72, 3.59, 3.52, 3.42, 3.29, 3.22 (m, 1H each, NCH_2CH$_3$)
	{3.73 (m, 0.5H, $(CH_3)_2CH$OH)}
	2.20 (d, 3H, $^2J_{PH}$ = 9, PCH_3)
	1.37, 1.25, 1.10, 0.94 (dd, 3H each, $^3J_{HH}$ = 7.0, 7.0, NCH$_2$CH_3)
	{0.86 (d, 3H, $^3J_{HH}$ = 6.5, $(CH_3)_2$CHOH)}

$^{11}B\{^1H\}$ NMR Data *[160.38 MHz, CD_2Cl_2]*

-3.4 (s)

$^{31}P\{^1H\}$ NMR Data *[202.35 MHz, CD_2Cl_2]*

-12.86 (s)

^{19}F NMR Data *[470.28 MHz, CD_2Cl_2]*]

-133.80 (d, 6F, $^3J_{FF}$ = 22.6, *ortho*-B(C_6F_5)$_3$)

-163.90 (t, 3F, $^3J_{FF}$ = 20.7, *para*-B(C_6F_5)$_3$)

-168.79 (dd, 6F, $^3J_{FF}$ = 22.6, 20.7, *meta*-B(C_6F_5)$_3$)

$^{13}C\{^1H\}$ NMR Data *[123.70 MHz, CD_2Cl_2]*

229.78 (s, NCS_2)

199.95 (s, NCS_2)

148.02 (d, $^1J_{CF}$ = 241, *ortho*-C_6F_5)

139.52 (d, $^1J_{CF}$ = 245, *para*-C_6F_5)

136.88 (d, $^1J_{CP}$ = 49.2, *ipso*-P(C_6H_5)$_2$)

136.81 (d, $^1J_{CF}$ = 271, *meta*-C_6F_5)

133.77 (d, $^1J_{CP}$ = 49.2, *ipso*-P(C_6H_5)$_2$)

133.40 (d, $^3J_{CP}$ = 9.2, *meta*-P(C_6H_5)$_2$)

132.28 (d, $^3J_{CP}$ = 9.2, *meta*-P(C_6H_5)$_2$)

130.93 (s, *para*-P(C_6H_5)$_2$)

130.23 (s, *para*-P(C_6H_5)$_2$)

128.38 (d, $^2J_{CP}$ = 11.0, *ortho*-P(C_6H_5)$_2$)

128.02 (d, $^2J_{CP}$ = 11.0, *ortho*-P(C_6H_5)$_2$)

119.0 (br s, *ipso*-C_6F_5)

45.98, 45.00, 44.96, 44.72 (s, NCH_2CH_3)

{22.68 (s, $(CH_3)_2$*C*HOH)}

17.22 (d, $^1J_{CP}$ = 36.8, PCH_3)

12.67, 12.58, 12.43, 12.01 (s, NCH_2CH_3)

{1.10 (s, $(CH_3)_2$CHOH)}

Selected Infrared Data *[Nujol Mull]*

1303m, 1276m, 1147m, 1089m (ν(Re-N)?), 978s

Mass Spectral Data *[Fast Atom Bombardment]*

1209: $[M]^+$ (very weak)

1042: $[M-(C_6F_5)]^+$ (very weak)

842: $[M-(PPh_2Me)-(C_6F_5)]^+$

697: $[M-B(C_6F_5)_3]^+$

581: $[M-B(C_6F_5)_3-4Et]^+$

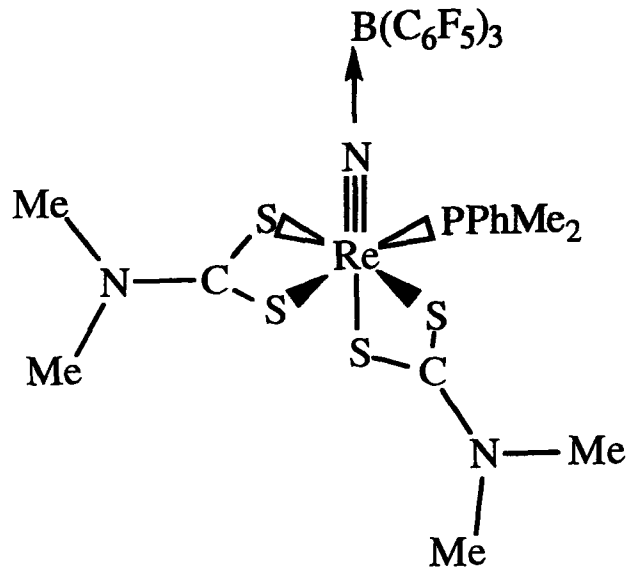
549: $[M-B(C_6F_5)_3-(S_2CNEt_2)]^+$

497: $[M-B(C_6F_5)_3-(PPh_2Me)]^+$

399: $[M-B(C_6F_5)_3-2(S_2CNEt_2)]^+$

Other Data See Appendix Two for X-Ray crystal structure.

4.3.4 Data Characterising [{$(C_6F_5)_3BN$}Re(PMe_2Ph)(S_2CNMe_2)] (10)



Molecular Formula	$C_{32}H_{23}BF_{15}N_3PReS_4$
Formula Weight	1090.75
	Lavender microcrystalline solid, 55 %
Microanalytical Data	*% Found (Calculated)*
	C: 35.4 (35.2); H: 2.1 (2.1); N: 3.2 (3.85);
	B: 0.7 (1.0)
^{1}H NMR Data	*[300.13 MHz, CD_2Cl_2]*
	7.3-7.4 (m, 5H, PC_6H_5)
	3.35, 3.28, 2.98, 2.67 (s, 3H each, NCH_3)
	1.97 (d, 3H, $^2J_{PH}$ = 9.6, PCH_3)
	1.81 (d, 3H, $^2J_{PH}$ = 9.6, PCH_3)
^{11}B{^{1}H} NMR Data	*[96.25 MHz, CD_2Cl_2]*
	-3.9 (s)
^{31}P{^{1}H} NMR Data	*[121.6 MHz, CD_2Cl_2]*
	-26.57 (s)
^{13}C{^{1}H} NMR Data	*[75.5 MHz, CD_2Cl_2]*
	228.20 (s, S_2CNMe_2)
	201.75 (s, S_2CNMe_2)
	147.77 (d, $^1J_{CF}$ = 241, *ortho*-C_6F_5)
	139.42 (d, $^1J_{CF}$ = 247, *para*-C_6F_5)

136.89 (d, $^1J_{CF}$ = 257, *meta*-C_6F_5)

134.28 (d, $^1J_{CP}$ = 53.1, *ipso*-P(C_6H_5)$_2$)

131.37 (d, $^3J_{CP}$ = 8.3, *meta*-P(C_6H_5)$_2$)

130.03 (s, *para*-P(C_6H_5)$_2$)

127.32 (d, $^2J_{CP}$ = 9.7, *ortho*-P(C_6H_5)$_2$)

117.5 (br s, *ipso*-C_6F_5)

39.71 (s, NCH_3)

39.17 (s, NCH_3)

39.07 (s, NCH_3). Two coincident resonances.

16.04 (d, $^1J_{CP}$ = 39.3, PCH_3)

15.82 (d, $^1J_{CP}$ = 33.6, PCH_3)

Selected Infrared Data *[Nujol Mull]*

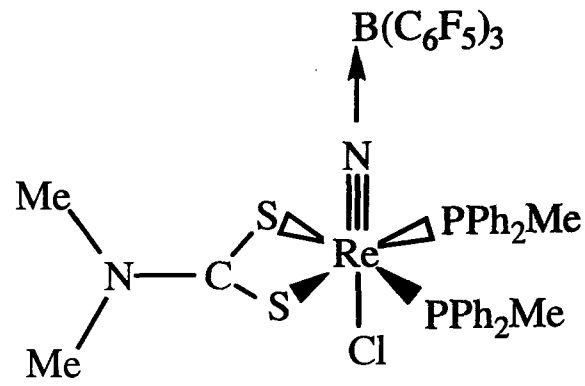
2727s, 1304s, 1281s, 1156s, 1092s (ν(Re-N)?), 980m

Mass Spectral Data *[Fast Atom Bombardment]*

579: $[M\text{-}B(C_6F_5)_3]^+$

Other Data See Appendix Three for X-Ray crystal structure.

6.3.5 Data Characterising [{$(C_6F_5)_3BN$}ReCl$(PMePh_2)_2(S_2CNMe_2)$] (11)



Molecular Formula	$C_{47}H_{32}BClF_{15}N_2P_2ReS_2$
Formula Weight	1268.31
	Orange powder, 66 %
Microanalytical Data	*% Found (Calculated)*
	C: 44.5 (44.5); H: 3.3 (2.5); N: 1.9 (2.2)
	Accurate boron and phosphorous analyses were not obtained owing to the insolubility of the compound in concentrated HNO_3 and *aqua regia*.
^{1}H NMR Data	*[300.13 MHz, CD_2Cl_2]*
	7.0-7.8 (m, 20H, P(C_6H_5)$_2$)
	3.16 (s, 6H, N(CH_3)$_2$)
	1.79 (d, 6H, $^2J_{PH}$ = 9.5, PCH_3)
^{11}B{^{1}H} NMR Data	*[96.25 MHz, CD_2Cl_2]*
	-2.7 (s)
^{31}P{^{1}H} NMR Data	*[121.6 MHz, CD_2Cl_2]*
	-16.73 (s)
^{13}C{^{1}H} NMR Data	*[75.5 MHz, CD_2Cl_2]*
	191.15 (s, S_2CNMe$_2$)
	148.03 (d, $^1J_{CF}$ = 253, *ortho*-C_6F_5)
	139.27 (d, $^1J_{CF}$ = 263, *para*-C_6F_5)
	136.68 (d, $^1J_{CF}$ = 252, *meta*-C_6F_5)
	135.82 (d, $^1J_{CP}$ = 58.9, *ipso*-P(C_6H_5)$_2$)

134.37 (d, $^1J_{CP}$ = 59.6, *ipso*-P(C_6H_5)$_2$)

133.32, 132.62, 132.18, 131.28, 130.92, 130.17,

129.01, 128.39, 127.84 (P(C_6H_5)$_2$)

120.1 (br s, *ipso*-C_6F_5)

39.65, 38.58 (s, N(CH_3)$_2$)

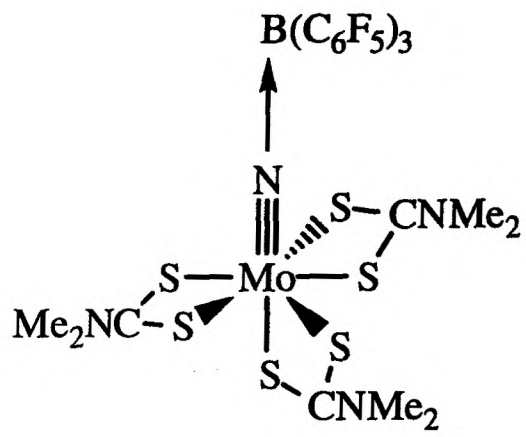
19.17 (d, $^1J_{CP}$ = 38.3, PCH_3)

15.31 (d, $^1J_{CP}$ = 36.6, PCH_3)

Selected Infrared Data *[Nujol Mull]*

1099w (ν(Re-N)?), 970w, 895m, 722m

6.3.6 Data Characterising [{$(C_6F_5)_3BN$}Mo$(S_2NMe_2)_3$] (12)



Molecular Formula $C_{27}H_{18}BF_{15}MoN_4S_6$

Formula Weight 982.55

Cream coloured microcrystalline solid, 60 %

Microanalytical Data *% Found (Calculated)*

C: 33.6 (33.0); H: 1.9 (1.85); N: 4.9 (5.7);

B: 1.0 (1.1); S: 16.0 (19.6)

^{1}H NMR Data *[300.13 MHz, CD_2Cl_2]*

3.38 (s, 3H, NCH_3)

3.34 (s, 6H, NCH_3)

3.25 (s, 6H, NCH_3)

3.19 (s, 3H, NCH_3)

^{11}B{^{1}H} NMR Data *[96.25 MHz, CD_2Cl_2]*

-6.5 (s)

^{19}F NMR Data *[470.28 MHz, CD_2Cl_2]*

-134.17 (d, 6F, $^3J_{FF}$ = 18.8, *ortho*-C_6F_5)

-163.87 (t, 3F, $^3J_{FF}$ = 26.3, *para*-C_6F_5)

-168.98 (m, 6F, *meta*-C_6F_5)

^{13}C{^{1}H} NMR Data *[75.5 MHz, CD_2Cl_2]*

203.62, 200.78 (s, S_2CNMe_2, 1:2 Intensity Ratio)

147.81 (d, $^1J_{CF}$ = 239, *ortho*-C_6F_5)

139.28 (d, $^1J_{CF}$ = 247, *para*-C_6F_5)

136.86 (d, $^1J_{CF}$ = 241, *meta*-C_6F_5)

119.0 (br s, *ipso*-C_6F_5)

41.40, 40.68, 37.36, 35.63 (s, NCH_3, 1:1:2:2 Intensity Ratio)

Selected Infrared Data *[Nujol Mull]*

1645w, 1559m, 1514m, 1305m, 1156m, 1082m br (ν(Mo-N)?), 979m br

Mass Spectral Data *[Fast Atom Bombardment]*

984: $[M]^+$

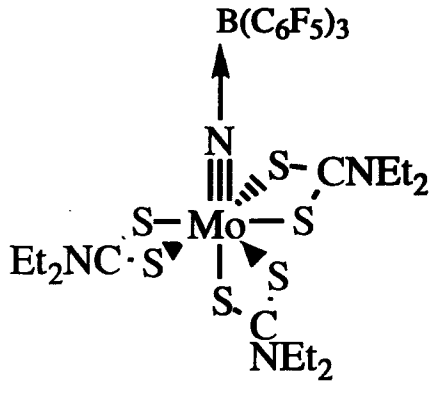
773: $[M-(C_6F_5)-N(CH_3)_2]^+$

697: $[M-(C_6F_5)-(S_2CNMe_2)]^+$

72: $[M-B(C_6F_5)_3]^+$

52: $[M-B(C_6F_5)_3-(S_2CNMe_2)]^+$

6.3.7 Data Characterising [{$(C_6F_5)_3BN$}Mo$(S_2CNEt_2)_3$] (13)



Molecular Formula $C_{33}H_{30}BF_{15}MoN_4S_6$

Formula Weight 1066.71

Red-brown foamy solid, 21 %

Microanalytical Data *% Found (Calculated)*

C: 38.7 (37.2); H: 3.1 (2.8); N: 4.6 (5.25);

B: 1.0 (1.0)

^{1}H NMR Data *[300.13 MHz, CD_2Cl_2]*

3.61-3.81 (m, 12H, NCH_2CH_3)

1.11-1.46 (m, 18H, NCH_2CH_3)

$^{11}B\{^1H\}$ NMR Data *[96.25 MHz, CD_2Cl_2]*

-6.6 (s)

$^{13}C\{^1H\}$ NMR Data *[75.5 MHz, CD_2Cl_2]*

202.38, 199.39 (s, S_2CNEt_2, 1:2 Intensity Ratio)

147.81 (d, $^1J_{CF}$ = 240, *ortho*-C_6F_5)

139.24 (d, $^1J_{CF}$ = 248, *para*-C_6F_5)

136.87 (d, $^1J_{CF}$ = 255, *meta*-C_6F_5)

119.8 (br s, *ipso*-C_6F_5)

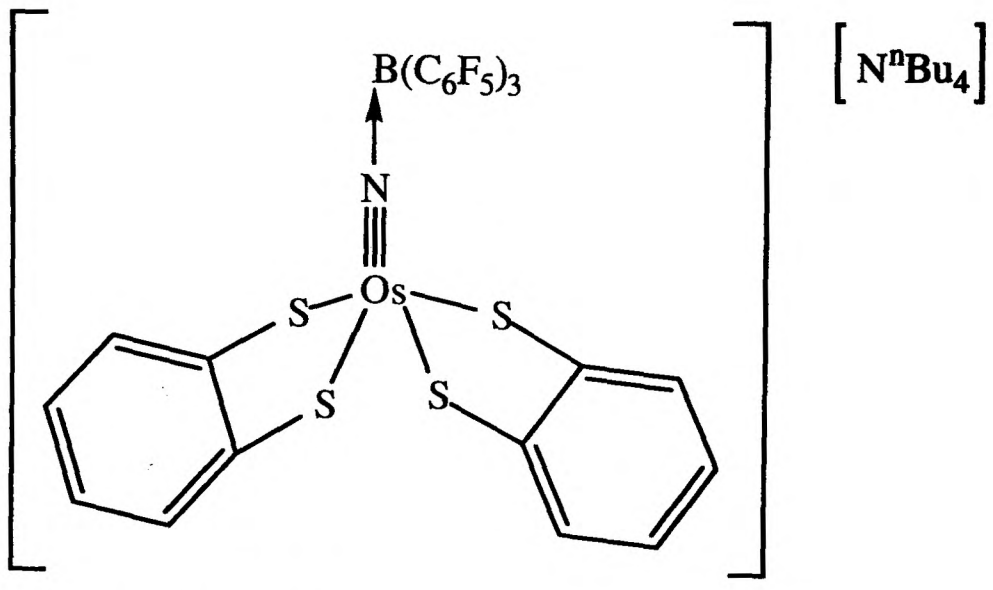
46.64, 45.58, 44.46, 43.31 (s, NCH_2CH_3, 1:1:2:2 Intensity Ratio)

12.48, 12.36, 12.23, 11.77 (s, NCH_2CH_3, 1:1:2:2 Intensity Ratio)

Selected Infrared Data *[Nujol Mull]*

1302s, 1262s, 1209m, 1152m, 1089m (ν(Mo-N)?), 976s

6.3.8 Data Characterising [{$(C_6F_5)_3BN$}Os(1,2-$S_2C_6H_4)_2$][$^nBu_4N$] (14)



Molecular Formula $C_{46}H_{44}BF_{15}N_2OsS_4$

Formula Weight 1239.09

Olive-green microcrystals / red solution in CH_2Cl_2, 88 %

Microanalytical Data *% Found (Calculated)*

C: 44.9 (44.6); H: 3.25 (3.6); N: 2.0 (2.3);

B: 1.2 (0.9)

^{1}H NMR Data *[300.13 MHz, CD_2Cl_2]*

7.68, 7.03, (AA'BB' Spin System, 8H, $S_2C_6H_4$)

2.63 (m, 8H, $NCH_2(CH_2)_2CH_3$)

1.37 (m,8H, $NCH_2CH_2CH_2CH_3$)

1.26 (m, 8H, $N(CH_2)_2CH_2CH_3$)

0.90 (t, $^3J_{HH}$ = 7.1, $N(CH_2)_3CH_3$)

^{11}B{^{1}H} NMR Data *[96.25 MHz, CD_2Cl_2]*

-3.7 (s)

^{19}F NMR Data *[470.28 MHz, CD_2Cl_2]*

-134.72 (d, 6F, $^3J_{FF}$ = 24.0, *ortho*-C_6F_5)

-162.99 (t, 3F, $^3J_{FF}$ = 20.7, *para*-C_6F_5)

-168.80 (m, 6F, *meta*-C_6F_5)

$^{13}C\{^1H\}$ NMR Data *[75.5 MHz, CD_2Cl_2]*

149.77 (s, *ipso*-$S_2C_6H_4$)

147.56 (d, $^1J_{CF}$ = 246, *ortho*-C_6F_5)

139.56 (d, $^1J_{CF}$ = 228, *para*-C_6F_5)

136.67 (d, $^1J_{CF}$ = 238, *meta*-C_6F_5)

127.90, 124.69 (s, $S_2C_6H_4$)

114.0 (br s, *ipso*-C_6F_5)

58.98 (s, $NCH_2(CH_2)_2CH_3$)

23.68 (s, $NCH_2CH_2CH_2CH_3$)

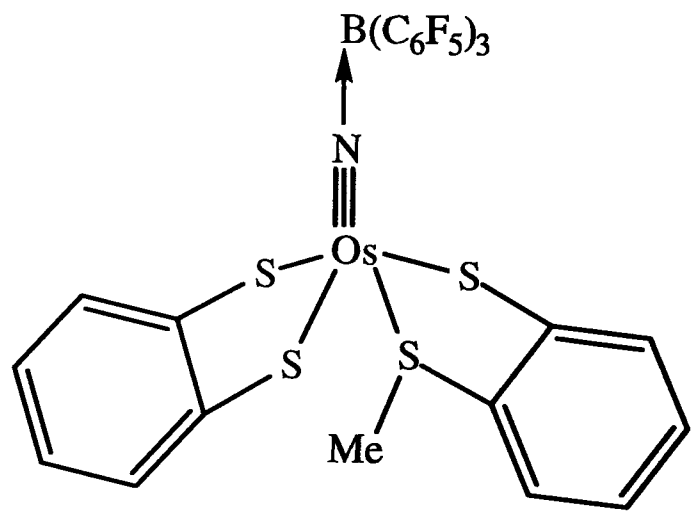
19.72 (s, $N(CH_2)_2CH_2CH_3$)

13.32 (s, $N(CH_2)_3CH_3$)

Selected Infrared Data *[Nujol Mull]*

1644m, 1515s, 1283m, 1275m, 1097s (ν(Os-N)?), 979s, 794m

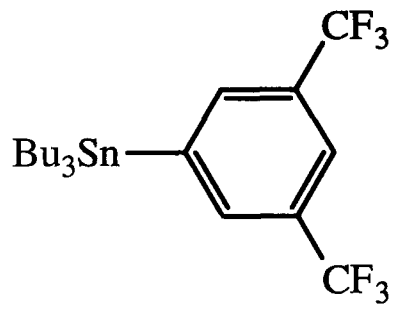
6.3.9 Data Characterising [{$(C_6F_5)_3BN$}Os(1,2-(S)(SMe)C_6H_4)(1,2-$S_2C_6H_4$)] (15)



Molecular Formula	$C_{31}H_{11}BF_{15}NOsS_4$
Formula Weight	1011.67
	Dark green oil
^{1}H NMR Data	*[300.13 MHz, CD_2Cl_2]*
	7.0-7.8 (br, C_6H_4)
	3.06 (s, SCH_3)
^{11}B{^{1}H} NMR Data	*[96.25 MHz, CD_2Cl_2]*
	-2.3 (s)
^{13}C{^{1}H} NMR Data	*[75.5 MHz, CD_2Cl_2]*
	148.12 (d, $^1J_{CF}$ = 240, *ortho*-C_6F_5)
	140.30 (d, $^1J_{CF}$ = 267, *para*-C_6F_5)
	136.90 (d, $^1J_{CF}$ = 246, *meta*-C_6F_5)
	132.27, 130.47, 128.97, 128.36, 127.01, 122.17 (br s, $S_2C_6H_4$ and (S)(SMe)C_6H_4)
	118.7 (br s, *ipso*-C_6F_5)
	33.5 (br s, SCH_3)

6.4 Characterising Data for Chapter Four

6.4.1 Data Characterising $(C_4H_9)_3Sn(3,5\text{-}C_6H_3(CF_3)_2)$ (16)



Molecular Formula	$C_{20}H_{30}F_6Sn$
Formula Weight	503.14
	Colourless, viscous liquid, 56 %
Boiling Point	150°C at 0.01 mbar
Density	1.366 gcm^{-3} at 298K
Microanalytical Data	*% Found (Calculated)*
	C: 47.7 (47.7); H: 5.95 (6.0); Sn: 22.7 (23.6)
^{1}H NMR Data	*[499.9 MHz, $CDCl_3$]*
	7.90 (s, 2H, $^3J_{SnH}$ = 17.0, *ortho*-$C_6H_3(CF_3)_2$)
	7.80 (s, 1H, *para*-$C_6H_3(CF_3)_2$)
	1.57 (m, 6H, $SnCH_2CH_2CH_2CH_3$)
	1.37 (m, 6H, $Sn(CH_2)_2CH_2CH_3$)
	1.17 (t, 6H, $^3J_{HH}$ = 8.2,$^2J_{SnH}$ = 26.1,
	$SnCH_2(CH_2)_2CH_3$)
	0.92 (t, 9H, $^3J_{HH}$ = 7.3, $Sn(CH_2)_3CH_3$)
^{119}Sn{^{1}H} NMR Data	*[186.42 MHz, $(C_2H_5)_2O$]*
	-33.75 (s)
^{13}C{^{1}H} NMR Data	*[123.7 MHz, $CDCl_3$]*
	145.82 (s, *ortho*-$C_6H_3(CF_3)_2$)
	135.90 (s,$^1J_{CSn}$ = 32, *ipso*-$C_6H_3(CF_3)_2$)
	130.42 (q, $^2J_{CF}$ = 32, *meta*-$C_6H_3(CF_3)_2$)

123.83 (q, $^{1}J_{CF}$ = 273, $C_6H_3(CF_3)_2$)

121.88 (m, *para*-$C_6H_3(CF_3)_2$)

28.95 (s, $^{2}J_{CSn}$ = 10.7, $SnCH_2CH_2CH_2CH_3$)

27.28 (s, $^{1}J_{CSn}$ = 28.4, $SnCH_2CH_2CH_2CH_3$)

13.54 (s, $SnCH_2CH_2CH_2CH_3$)

9.89 (s, $SnCH_2CH_2CH_2CH_3$)

Mass Spectral Data

[Electron Impact]

508: $[M]^+$

451: $[M-(C_4H_9)]^+$

294: $[M-2(C_4H_9)]^+$

337: $[M-3(C_4H_9)]^+$

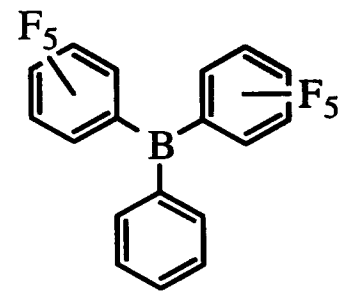
271: $[M-(C_6H_3(CF_3)_2)]^+$

235: $[M-(C_6H_3(CF_3)_2)-(C_4H_9)]^+$

176: $[M-(C_6H_3(CF_3)_2)-2(C_4H_9)]^+$

The correct tin isotope pattern was observed.

6.4.2 Data Characterising $B(C_6H_5)(C_6F_5)_2$ (17)



Molecular Formula	$C_{18}H_5BF_{10}$
Formula Weight	422.04
	White needles, 36 %
Sublimation Point	100 °C at 0.1 mbar
Microanalytical Data	*% Found (Calculated)*
	C: 51.2 (51.2); H: 1.55 (1.2); B: 2.6 (2.6)
^{1}H NMR Data	*[300.13 MHz, C_6D_6]*
	7.55 (d, 2H, $^3J_{HH}$ = 7.4, *ortho*-C_6H_5)
	7.26 (t, 1H, $^3J_{HH}$ = 7.3, *para*-C_6H_5)
	7.15 (m, 2H, *meta*-C_6H_5)
^{11}B{^{1}H} NMR Data	*[96.25 MHz, C_6D_6]*
	64.5 (s)
^{13}C{^{1}H} NMR Data	*[75.5 MHz, C_6D_6]*
	146.63 (d, $^1J_{CF}$ = 246, *ortho*-C_6F_5)
	143.23 (d, $^1J_{CF}$ = 267, *para*-C_6F_5)
	139.45 (s, *ortho*-C_6H_5)
	137.98 (d, $^1J_{CF}$ = 222, *meta*-C_6F_5)
	136.51 (s, *para*-C_6H_5)
	136.0 (br s, *ipso*-C_6H_5)
	128.51 (s, *meta*-C_6H_5)
	114.0 (br s, *ipso*-C_6F_5)
^{19}F NMR Data	*[470.28 MHz, $D_3CC_6D_5$]*
	-132.48 (d, 2F, $^3J_{FF}$ = 18.9, *ortho*-C_6F_5)
	-151.63 (t, 1F, $^3J_{FF}$ = 14.2, *para*-C_6F_5)

-164.05 (dd, 2F, $^3J_{FF}$ = 14.2, 18.9, *meta*-C_6F_5)

Selected Infrared Data *[Nujol Mull]*

3566s, 3353m br, 1651s, 1598m, 1520s, 1315m, 1289m, 1094m br, 976s

Mass Spectral Data *[Electron Impact]*

419: $[M]^+$

346: $[M-(C_6H_5)]^+$

254: $[M-(C_6F_5)]^+$

181: $[M-(C_6H_5)-(C_6F_5)]^+$

168: $[C_6F_5]^+$

78: $[C_6H_5]^+$

Appendix One

X-Ray Structural Data for [(η^5-$C_5H_4B(C_6F_5)_2Cl$)(η^5-C_5H_5)WH_3] (4)

X-Ray Structural Data for $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2Cl)(\eta^5\text{-}C_5H_5)WH_3]$ (4)

Formula	$C_{22}H_{12}BClF_{10}W$
Formula Weight	696.43
Crystal System	Triclinic
a (Å)	8.470(4)
b (Å)	10.106(4)
c (Å)	13.403(3)
α (°)	80.26(3)
β (°)	74.88 (3)
γ (°)	67.53(2)
Unit-cell Volume (Å^3)	1322.9
Space Group	P-1
ρ_{calc} (gcm^{-3})	2.01
μ (mm^{-1})	0.601
Crystal Size (mm)	0.35 x 0.20 x 0.15
Radiation	Mo K_α (λ=0.71073 Å)
Transmission Coefficient	0.84 - 1.00
2 Θ Limits	2 - 53
Total Data Collected	5082
Unique Data	3795
Data Observed[a]	3539
Parameters Refined	364
Weighting Scheme	Chebychev
Weighting Parameters	2.84, 0.362, 2.06
R[b]	0.027
R_w[c]	0.032
Largest Final Shift	0.0789
Largest Peak, (eÅ^{-3})	1.76
Temperature (K)	125

a: Criterion for observation $I > 3\sigma(I)$

b: $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$

c: $R_w = [w\Sigma(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$

(i) Bond Distances in [(η^5-$C_5H_4B(C_6F_5)_2Cl$)(η^5-C_5H_5)WH_3], Å

W(1) - C(1)	2.352(4)	C(1) - C(5)	1.420(6)
W(1) - C(2)	2.309(4)	C(1) - B(1)	1.637(6)
W(1) - C(3)	2.310(4)	C(2) - C(3)	1.414(6)
W(1) - C(4)	2.300(5)	C(3) - C(4)	1.430(8)
W(1) - C(5)	2.330(4)	C(4) - C(5)	1.427(6)
W(1) - C(6)	2.290(5)	C(6) - C(7)	1.417(7)
W(1) - C(7)	2.291(4)	C(6) - C(10)	1.401(7)
W(1) - C(8)	2.329(4)	C(7) - C(8)	1.400(7)
W(1) - C(9)	2.314(4)	C(8) - C(9)	1.420(6)
W(1) - C(10)	2.320(4)	C(9) - C(10)	1.414(7)
W(1) - H(202)	1.49(5)	C(20) - C(21)	1.397(6)
W(1) - H(203)	1.52(5)	C(20) - C(25)	1.386(6)
W(1) - H(204)	1.41(6)	C(20) - B(1)	1.652(6)
Cl(1) - B(1)	1.915(5)	C(21) - C(22)	1.380(6)
F(21) - C(21)	1.350(5)	C(22) - C(23)	1.370(6)
F(22) - C(22)	1.347(5)	C(23) - C(24)	1.396(6)
F(23) - C(23)	1.344(5)	C(24) - C(25)	1.385(6)
F(24) - C(24)	1.330(5)	C(30) - C(31)	1.406(5)
F(25) - C(25)	1.354(5)	C(30) - C(35)	1.389(6)
F(31) - C(31)	1.345(5)	C(30) - B(1)	1.648(5)
F(32) - C(32)	1.340(5)	C(31) - C(32)	1.392(5)
F(33) - C(33)	1.341(4)	C(32) . C(33)	1.376(6)
F(34) - C(34)	1.341(5)	C(33) - C(34)	1.373(6)
F(35) - C(35)	1.347(5)	C(34) - C(35)	1.396(5)
C(1) - C(2)	1.439(5)		

(ii) Bond Angles in $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2Cl)(\eta^5\text{-}C_5H_5)WH_3]$,

C(1) - W(1) - C(2)	35.95(13)	C(2) - W(1) - H(202)	126.4(21)
C(1) - W(1) - C(3)	59.92(14)	C(3) - W(1) - H(202)	121.5(21)
C(2) - W(1) - C(3)	35.64(16)	C(4) - W(1) - H(202)	85.5(21)
C(1) - W(1) - C(4)	59.90(15)	C(5) - W(1) - H(202)	68.8(21)
C(2) - W(1) - C(4)	59.69(17)	C(1) - W(1) - H(203)	126.5(19)
C(3) - W(1) - C(4)	36.15(19)	C(2) - W(1) - H(203)	133.3(19)
C(1) - W(1) - C(5)	35.31(14)	C(3) - W(1) - H(203)	99.4(19)
C(2) - W(1) - C(5)	59.04(15)	C(4) - W(1) - H(203)	75.0(19)
C(3) - W(1) - C(5)	59.56(16)	C(5) - W(1) - H(203)	91.2(19)
C(4) - W(1) - C(5)	35.89(16)	C(1) - W(1) - H(204)	126.7(25)
C(1) - W(1) - C(6)	89.15(15)	C(2) - W(1) - H(204)	96.3(25)
C(2) - W(1) - C(6)	96.03(16)	C(3) - W(1) - H(204)	66.7(25)
C(3) - W(1) - C(6)	129.66(18)	C(4) - W(1) - H(204)	77.2(26)
C(4) - W(1) - C(6)	149.06(17)	C(5) - W(1) - H(204)	113.0(26)
C(5) - W(1) - C(6)	116.72(16)	C(6) - W(1) - C(7)	36.03(17)
C(1) - W(1) - C(7)	101.47(15)	C(6) - W(1) - C(8)	59.00(17)
C(2) - W(1) - C(7)	86.56(16)	C(7) - W(1) - C(8)	35.27(17)
C(3) - W(1) - C(7)	107.91(18)	C(6) - W(1) - C(9)	59.14(18)
C(4) - W(1) - C(7)	143.55(19)	C(7) - W(1) - C(9)	59.44(17)
C(5) - W(1) - C(7)	136.72(16)	C(8) - W(1) - C(9)	35.63(16)
C(1) - W(1) - C(8)	136.33(15)	C(6) - W(1) - C(10)	35.39(18)
C(2) - W(1) - C(8)	112.94(15)	C(7) - W(1) - C(10)	59.56(18)
C(3) - W(1) - C(8)	116.38(16)	C(8) - W(1) - C(10)	59.07(16)
C(4) - W(1) - C(8)	145.04(17)	C(9) - W(1) - C(10)	35.53(17)
C(5) - W(1) - C(8)	171.37(16)	C(6) - W(1) - H(202)	96.3(22)
C(1) - W(1) - C(9)	146.81(16)	C(7) - W(1) - H(202)	128.7(22)
C(2) - W(1) - C(9)	145.83(16)	C(8) - W(1) - H(202)	118.1(21)
C(3) - W(1) - C(9)	147.92(16)	C(9) - W(1) - H(202)	82.5(21)
C(4) - W(1) - C(9)	150.87(19)	C(10) - W(1) - H(202)	69.5(21)
C(5) - W(1) - C(9)	150.68(16)	C(6) - W(1) - H(203)	130.5(19)
C(1) - W(1) - C(10)	112.24(16)	C(7) - W(1) - H(203)	131.9(19)
C(2) - W(1) - C(10)	130.43(17)	C(8) - W(1) - H(203)	97.1(19)
C(3) - W(1) - C(10)	165.0(2)	C(9) - W(1) - H(203)	76.4(19)
C(4) - W(1) - C(10)	153.91(19)	C(10) - W(1) - H(203)	95.4(19)
C(5) - W(1) - C(10)	122.62(16)	C(6) - W(1) - H(204)	127.8(26)
C(1) - W(1) - H(202)	92.4(21)	C(7) - W(1) - H(204)	94.7(26)

C(8) - W(1) - H(204)	69.5(26)	C(21) - C(20) - C(25)	113.3(4)
C(9) - W(1) - H(204)	84.2(25)	C(21) - C(20) - B(1)	120.8(3)
C(10) - W(1) - H(204)	119.7(25)	C(25) - C(20) - B(1)	125.9(3)
H(202) - W(1) - H(203)	54.8(27)	F(21) - C(21) - C(20)	120.2(3)
H(202) - W(1) - H(204)	115.6(33)	F(21) - C(21) - C(22)	115.7(4)
H(203) - W(1) - H(204)	60.8(30)	C(20) - C(21)- C(22)	124.1(4)
W(1) - C(1) - C(2)	70.4(2)	F(22) - C(22) - C(21)	120.2(4)
W(1) - C(1) - C(5)	71.5(2)	F(22) - C(22) - C(23)	119.6(4)
C(2) - C(1) - C(5)	106.2(4)	C(21) - C(22) - C(23)	120.2(4)
W(1) - C(1) - B(1)	132.2(2)	F(23) - C(23) - C(22)	121.7(4)
C(2) - C(1) - B(1)	125.3(4)	F(23) - C(23) - C(24)	119.7(4)
C(5) - C(1) - B(1)	127.4(3)	C(22) - C(23) - C(24)	118.6(4)
W(1) - C(2) - C(1)	73.6(2)	F(24) - C(24) - C(23)	120.1(4)
W(1) - C(2) - C(3)	72.2(2)	F(24) - C(24) - C(25)	121.1(4)
C(1) - C(2) - C(3)	109.4(4)	C(23) - C(24) - C(25)	118.8(4)
W(1) - C(3) - C(2)	72.1(2)	F(25) - C(25) - C(20)	120.7(3)
W(1) - C(3) - C(4)	71.5(3)	F(25) - C(25) - C(24)	114.4(4)
C(2) - C(3) - C(4)	107.5(4)	C(20) - C(25) - C(24)	124.9(4)
W(1) - C(4) - C(3)	72.3(3)	C(31) - C(30) - C(35)	113.4(3)
W(1) - C(4) - C(5)	73.2(3)	C(31) - C(30) - B(1)	118.5(3)
C(3) - C(4) - C(5)	107.5(4)	C(35) - C(30) - B(1)	127.8(3)
W(1) - C(5) - C(1)	73.2(2)	F(31) - C(31) - C(30)	120.1(3)
W(1) - C(5) - C(4)	70.9(3)	F(31) - C(31) - C(32)	115.9(3)
C(1) - C(5) - C(4)	109.4(4)	C(30) - C(31) - C(32)	123.9(4)
W(1) - C(6) - C(7)	72.0(3)	F(32) - C(32) - C(31)	120.3(4)
W(1) - C(6) - C(10)	73.5(3)	F(32) - C(32) - C(33)	120.2(3)
C(7) - C(6) - C(10)	108.7(4)	C(31) - C(32) - C(33)	119.5(4)
W(1) - C(7) - C(6)	72.0(3)	F(33) - C(33) - C(32)	120.1(4)
W(1) - C(7) - C(8)	73.8(3)	F(33) - C(33) - C(34)	120.6(4)
C(6) - C(7) - C(8)	107.7(4)	C(32) - C(33) - C(34)	119.3(4)
W(1) - C(8) -C(7)	70.9(2)	F(34) - C(34) - C(33)	120.0(3)
W(1) - C(8) - C(9)	71.6(2)	F(34) - C(34) - C(35)	120.3(4)
C(7) - C(8) - C(9)	108.1(4)	C(33) - C(34) - C(35)	119.7(4)
W(1) - C(9) - C(8)	72.8(2)	F(35) - C(35) - C(30)	121.8(3)
W(1) - C(9) - C(10)	72.5(3)	F(35) - C(35) - C(34)	114.1(3)
C(8) - C(9) - C(10)	107.9(4)	C(30) - C(35) - C(34)	124.1(4)
W(1) - C(10) - C(6)	71.1(3)	Cl(1) - B(1) - C(1)	107.9(3)
W(1) - C(10) - C(9)	72.0(3)	Cl(1) - B(1) - C(20)	103.1(3)
C(6) - C(10) - C(9)	107.6(4)	C(1) - B(1) - C(20)	111.5(3)

Cl(1) - B(1) - C(30)	112.8(3)	C(20) - B(1) - C(30)	108.4(3)
C(1) - B(1) - C(30)	112.7(3)		

(iii) Fractional Atomic Coordinates and Isotropic Thermal Parameters for $[(\eta^5\text{-}C_5H_4B(C_6F_5)_2Cl)(\eta^5\text{-}C_5H_5)WH_3]$

Atom	*x/a*	*y/b*	*z/c*	*U(iso) or U(eq)**
W(1)	1.728677(19)	0.062356(15)	0.215607(12)	0.0147
Cl(1)	1.18944(13)	0.1754(1)	0.38426(8)	0.0200
F(21)	0.9475(3)	0.5378(3)	0.3386(2)	0.0243
F(22)	0.6797(3)	0.6659(3)	0.2473(2)	0.0310
F(23)	0.6650(3)	0.5615(3)	0.0753(2)	0.0313
F(24)	0.9361(4)	0.3261(3)	-0.0033(2)	0.0280
F(25)	1.2104(3)	0.2014(3)	0.0815(2)	0.0265
F(31)	1.3065(3)	0.5405(2)	0.13736(19)	0.0200
F(32)	1.3251(4)	0.7756(3)	0.1893(2)	0.0246
F(33)	1.3310(4)	0.7987(3)	0.3877(2)	0.0264
F(34)	1.3192(3)	0.5773(3)	0.5336(2)	0.0230
F(35)	1.3041(3)	0.3417(2)	0.48581(19)	0.0215
C(1)	1.4402(5)	0.1902(4)	0.1950(3)	0.0159
C(2)	1.4823(5)	0.0394(4)	0.1886(3)	0.0189
C(3)	1.6189(6)	-0.0080(5)	0.1012(4)	0.0276
C(4)	1.6679(7)	0.1122(6)	0.0529(4)	0.0320
C(5)	1.5561(5)	0.2332(5)	0.1103(3)	0.0209
C(6)	1.6320(7)	0.0800(5)	0.3908(4)	0.0268
C(7)	1.6828(6)	-0.0658(5)	0.3717(4)	0.0259
C(8)	1.8637(6)	-0.1170(5)	0.3321(4)	0.0238
C(9)	1.9245(6)	-0.0016(5)	0.3230(4)	0.0269
C(10)	1.7803(7)	0.1194(5)	0.3617(4)	0.0302
C(20)	1.0996(5)	0.3654(4)	0.2131(3)	0.0168
C(21)	0.9539(5)	0.4821(4)	0.2523(3)	0.0176
C(22)	0.8112(5)	0.5494(4)	0.2071(4)	0.0217
C(23)	0.8026(5)	0.4987(5)	0.1209(3)	0.0199
C(24)	0.9412(5)	0.3789(5)	0.0798(3)	0.0198
C(25)	1.0832(5)	0.3173(4)	0.1267(3)	0.0171
C(30)	1.3032(5)	0.4254(4)	0.3080(3)	0.0137
C(31)	1.3127(5)	0.5424(4)	0.2363(3)	0.0149

C(32)	1.3202(5)	0.6674(4)	0.2619(3)	0.0173
C(33)	1.3208(5)	0.6798(4)	0.3624(3)	0.0180
C(34)	1.3151(5)	0.5680(4)	0.4357(3)	0.0168
C(35)	1.3082(5)	0.4439(4)	0.4074(3)	0.0152
B(1)	1.2674(6)	0.2942(4)	0.2704(3)	0.0141
H(21)	1.433(8)	-0.040(7)	0.244(5)	0.042(17)
H(31)	1.666(8)	-0.108(7)	0.079(5)	0.037(16)
H(41)	1.776(9)	0.096(7)	-0.003(5)	0.045(17)
H(51)	1.560(7)	0.333(6)	0.086(4)	0.019(12)
H(61)	1.54(1)	0.124(9)	0.414(6)	0.06(2)
H(71)	1.611(8)	-0.119(7)	0.388(5)	0.038(16)
H(81)	1.942(9)	-0.213(8)	0.336(6)	0.05(2)
H(91)	2.060(9)	-0.021(7)	0.300(5)	0.046(18)
H(101)	1.79(1)	0.216(8)	0.361(6)	0.06(2)
H(202)	1.774(7)	0.195(6)	0.192(4)	0.028(13)
H(203)	1.894(6)	0.075(5)	0.144(4)	0.019(12)
H(204)	1.850(8)	-0.058(7)	0.163(5)	0.038(16)

* U(eq) = one third of the trace of the orthogonalised U_{ij} tensor.

(iv) Anisotropic Thermal Parameters for [(η^5-C_5H_4B(C_6F_5)$_2$Cl)(η^5-C_5H_5)WH_3]

Atom	*U(11)*	*U(22)*	*U(33)*	*U(23)*	*U(13)*	*U(12)*
W(1)	0.0168(1)	0.0154(1)	0.01046(12)	-0.00102(6)	-0.00172(6)	-0.00499(7)
Cl(1)	0.0284(5)	0.0225(4)	0.0128(5)	0.0009(3)	-0.0031(4)	-0.0149(4)
F(21)	0.0210(12)	0.0302(13)	0.0233(15)	-0.016(1)	0.000(1)	-0.008(1)
F(22)	0.0180(12)	0.0275(13)	0.0449(19)	-0.0134(12)	-0.0038(11)	-0.003(1)
F(23)	0.0218(12)	0.0425(16)	0.0304(17)	0.0051(12)	-0.0132(11)	-0.0106(11)
F(24)	0.0316(13)	0.0440(15)	0.0153(14)	-0.004(1)	-0.0104(11)	-0.0169(12)
F(25)	0.0261(12)	0.0318(13)	0.0207(15)	-0.016(1)	-0.007(1)	-0.0026(11)
F(31)	0.0291(12)	0.0238(12)	0.0120(13)	0.0022(9)	-0.008(1)	-0.014(1)
F(32)	0.0347(13)	0.0195(12)	0.0225(15)	0.0054(9)	-0.0101(11)	-0.013(1)
F(33)	0.0371(14)	0.0213(12)	0.0285(16)	-0.007(1)	-0.0079(11)	-0.0163(11)
F(34)	0.0324(13)	0.0258(12)	0.0148(14)	-0.0075(9)	-0.007(1)	-0.011(1)
F(35)	0.0362(14)	0.0185(11)	0.0104(13)	-0.0005(8)	-0.006(1)	-0.010(1)
C(1)	0.0190(17)	0.0188(18)	0.011(2)	0.0003(14)	-0.0089(15)	-0.0048(15)

C(2)	0.0221(19)	0.0213(19)	0.017(2)	-0.0081(15)	-0.0104(16)	-0.0049(15)
C(3)	0.032(2)	0.028(2)	0.019(3)	-0.0104(17)	-0.0100(19)	-0.0002(18)
C(4)	0.032(2)	0.040(3)	0.013(3)	-0.0045(18)	-0.0036(19)	-0.001(2)
C(5)	0.0211(19)	0.023(2)	0.011(2)	0.0038(15)	-0.0042(16)	-0.0015(16)
C(6)	0.029(2)	0.032(2)	0.014(2)	-0.0077(17)	-0.0056(18)	-0.0018(19)
C(7)	0.030(2)	0.029(2)	0.017(2)	0.0076(17)	-0.0072(18)	-0.0123(19)
C(8)	0.030(2)	0.0184(19)	0.024(3)	0.0002(16)	-0.0145(19)	-0.0044(17)
C(9)	0.031(2)	0.032(2)	0.025(3)	-0.0019(17)	-0.0153(19)	-0.0132(19)
C(10)	0.043(3)	0.027(2)	0.027(3)	-0.0092(18)	-0.016(2)	-0.010(2)
C(20)	0.0203(18)	0.0215(19)	0.010(2)	-0.0026(14)	-0.0005(15)	-0.0107(15)
C(21)	0.0172(18)	0.0200(18)	0.018(2)	-0.0045(15)	-0.0021(15)	-0.0095(15)
C(22)	0.0177(19)	0.0216(19)	0.023(2)	-0.0042(16)	0.0022(16)	-0.0069(16)
C(23)	0.0184(18)	0.027(2)	0.016(2)	0.0033(15)	-0.0062(16)	-0.0103(16)
C(24)	0.0217(19)	0.028(2)	0.015(2)	0.0014(15)	-0.0053(16)	-0.0153(17)
C(25)	0.0189(18)	0.0209(18)	0.011(2)	-0.0026(14)	-0.0018(15)	-0.0065(15)
C(30)	0.0147(16)	0.0163(17)	0.010(2)	-0.0020(13)	-0.0028(14)	-0.0053(14)
C(31)	0.0143(16)	0.0191(18)	0.012(2)	-0.0020(14)	-0.0033(14)	-0.0065(14)
C(32)	0.0165(17)	0.0166(17)	0.018(2)	0.0005(14)	-0.0048(15)	-0.0054(14)
C(33)	0.0193(18)	0.0149(17)	0.022(2)	-0.0044(15)	-0.0056(16)	-0.0062(14)
C(34)	0.0161(17)	0.0213(18)	0.014(2)	-0.0075(14)	-0.0025(14)	-0.0054(14)
C(35)	0.0158(17)	0.0165(17)	0.012(2)	-0.0008(14)	-0.0027(14)	-0.0039(14)
B(1)	0.022(2)	0.0142(18)	0.008(2)	-0.0021(14)	-0.0034(16)	-0.0075(16)

Appendix Two

X-Ray Structural Data for
$[\{(C_6F_5)_3BN\}Re(PMePh_2)(S_2CNEt_2)_2]$ (9)

X-Ray Structural Data for $[\{(C_6F_5)_3BN\}Re(PMePh_2)(S_2CNEt_2)_2]\cdot{}^{i}PrOH\cdot CH_2Cl_2$ (9)

Formula	$C_{45}H_{43}BCl_2F_{15}N_3OPReS_4$
Formula Weight	1353.96
Crystal System	Triclinic
a (Å)	11.301(5)
b (Å)	16.173(5)
c (Å)	17.520(5)
α (°)	72.58(2)
β (°)	83.16(2)
γ (°)	69.47(2)
Unit-cell Volume (Å^3)	2860.90
Space Group	P-1
ρ_{calc} (gcm^{-3})	1.57
μ (mm^{-1})	2.5
Crystal Size (mm)	0.30 x 0.25 x 0.20
Radiation	Mo K_α (λ = 0.71069 Å)
2 Θ Limits	2 - 52
Total Data Collected	10997
Unique Data	6792
Data Observed[a]	4322
Parameters Refined	390
Weighting Scheme	Chebychev
Weighting Parameters	8.29, -6.35, 4.72
R[b]	0.129
R_w[c]	0.127
Largest Final Shift	0.302
Temperature (K)	125

a: Criterion for observation $I > 3\sigma(I)$

b: $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$

c: $R_w = [w\Sigma(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$

(i) Bond Distances in $[\{(C_6F_5)_3BN\}Re(PMePh_2)(S_2CNEt_2)_2]\cdot{}^{i}PrOH\cdot CH_2Cl_2$, Å

Re(1) - S(1)	2.449(7)	C(2) - C(3)	1.52(6)
Re(1) - S(2)	2.631(8)	C(4) - C(5)	1.50(5)
Re(1) - S(3)	2.389(6)	C(7) - C(8)	1.54(5)
Re(1) - S(4)	2.421(8)	C(9) - C(10)	1.41(5)
Re(1) - P(1)	2.435(8)	C(21) - C(22)	1.36(4)
Re(1) - N(3)	1.67(2)	C(21) - C(26)	1.41(4)
S(1) - C(1)	1.72(3)	C(22) - C(23)	1.34(4)
S(2) - C(1)	1.73(3)	C(23) - C(24)	1.36(4)
S(3) - C(6)	1.74(3)	C(24) - C(25)	1.34(5)
S(4) - C(6)	1.73(3)	C(25) - C(26)	1.41(5)
P(1) - C(11)	1.84(3)	C(31) - C(32)	1.30(4)
P(1) - C(21)	1.81(3)	C(31) - C(36)	1.44(5)
P(1) - C(31)	1.83(3)	C(32) - C(33)	1.42(5)
F(42) - C(42)	1.36(3)	C(33) - C(34)	1.27(5)
F(43) - C(43)	1.33(4)	C(34) - C(35)	1.33(6)
F(44) - C(44)	1.33(4)	C(35) - C(36)	1.43(5)
F(45) - C(45)	1.26(7)	C(41) - C(42)	1.33(4)
F(46) - C(46)	1.34(3)	C(41) - C(46)	1.41(4)
F(52) - C(52)	1.41(3)	C(41) - B(1)	1.66(4)
F(53) - C(53)	1.41(4)	C(42) - C(43)	1.48(4)
F(54) - C(54)	1.30(4)	C(43) - C(44)	1.40(5)
F(55) - C(55)	1.34(4)	C(44) - C(45)	1.63(7)
F(56) - C(56)	1.42(3)	C(45) - C(46)	1.24(7)
F(62) - C(62)	1.34(3)	C(51) - C(52)	1.33(4)
F(63) - C(63)	1.32(4)	C(51) - C(56)	1.35(4)
F(64) - C(64)	1.27(4)	C(51) - B(1)	1.67(4)
F(65) - C(65)	1.32(3)	C(52) - C(53)	1.36(4)
F(66) - C(66)	1.33(3)	C(53) - C(54)	1.34(4)
N(1) - C(1)	1.29(4)	C(54) - C(55)	1.38(4)
N(1) - C(2)	1.46(5)	C(55) - C(56)	1.40(4)
N(1) - C(4)	1.50(4)	C(61) - C(62)	1.38(4)
N(2) - C(6)	1.30(4)	C(61) - C(66)	1.44(4)
N(2) - C(7)	1.49(4)	C(61) - B(1)	1.61(4)
N(2) - C(9)	1.49(4)	C(62) - C(63)	1.38(4)
N(3) - B(1)	1.58(4)	C(63) - C(64)	1.36(5)

C(64) - C(65)	1.46(5)	C(103) - C(101)	1.4357(4)
C(65) - C(66)	1.37(4)	C(100) - Cl(2)	1.8255(8)
Cl(1) - C(100)	1.7536(5)	O(1) - C(101)	1.5637(5)
C(102) - C(101)	1.3291(5)		

(ii) Bond Angles in $[\{(C_6F_5)_3BN\}Re(PMePh_2)(S_2CNEt_2)_2]\cdot{}^{i}PrOH\cdot CH_2Cl_2$, °

S(1) - Re(1) - S(2)	68.6(2)	C(6) - N(2) - C(9)	125.1(26)
S(1) - Re(1) - S(3)	153.0(3)	C(7) - N(2) - C(9)	113.9(23)
S(2) - Re(1) - S(3)	90.9(2)	Re(1) - N(3) - B(1)	172.9(18)
S(1) - Re(1) - S(4)	88.2(3)	S(1) - C(1) - S(2)	112.3(17)
S(2) - Re(1) - S(4)	86.7(3)	S(1) - C(1) - N(1)	122.8(23)
S(3) - Re(1) - S(4)	72.8(2)	S(2) - C(1) - N(1)	124.9(23)
S(1) - Re(1) - P(1)	92.6(3)	N(1) - C(2) - C(3)	112.7(31)
S(2) - Re(1) - P(1)	79.6(3)	N(1) - C(4) - C(5)	112.4(27)
S(3) - Re(1) - P(1)	101.1(3)	S(3) - C(6) - S(4)	111.1(17)
S(4) - Re(1) - P(1)	165.0(2)	S(3) - C(6) - N(2)	123.4(24)
S(1) - Re(1) - N(3)	98.6(7)	S(4) - C(6) - N(2)	125.4(25)
S(2) - Re(1) - N(3)	165.7(7)	N(2) - C(7) - C(8)	113.3(26)
S(3) - Re(1) - N(3)	103.2(7)	N(2) - C(9) - C(10)	111.4(29)
S(4) - Re(1) - N(3)	99.4(7)	P(1) - C(21) - C(22)	121.3(21)
P(1) - Re(1) - N(3)	95.3(7)	P(1) - C(21) - C(26)	122.5(22)
Re(1) - S(1) - C(1)	92.7(10)	C(22) - C(21) - C(26)	115.1(26)
Re(1) - S(2) - C(1)	86.4(11)	C(21) - C(22) - C(23)	124.3(28)
Re(1) - S(3) - C(6)	88.2(10)	C(22) - C(23) - C(24)	118.3(28)
Re(1) - S(4) - C(6)	87.4(11)	C(23) - C(24) - C(25)	123.4(32)
Re(1) - P(1) - C(11)	110.2(11)	C(24) - C(25) - C(26)	116.7(31)
Re(1) - P(1) - C(21)	121.6(9)	C(21) - C(26) - C(25)	122.2(30)
C(11) - P(1) - C(21)	102.2(14)	P(1) - C(31) - C(32)	124.4(23)
Re(1) - P(1) - C(31)	112.9(10)	P(1) - C(31) - C(36)	115.0(23)
C(11) - P(1) - C(31)	105.4(14)	C(32) - C(31) - C(36)	120.2(28)
C(21) - P(1) - C(31)	102.9(13)	C(31) - C(32) - C(33)	120.4(29)
C(1) - N(1) - C(2)	123.2(27)	C(32) - C(33) - C(34)	119.1(36)
C(1) - N(1) - C(4)	119.6(25)	C(33) - C(34) - C(35)	126.0(41)
C(2) - N(1) - C(4)	116.7(26)	C(34) - C(35) - C(36)	117.4(34)
C(6) - N(2) - C(7)	121.0(25)	C(31) - C(36) - C(35)	116.8(31)

C(42) - C(41) - C(46)	114.1(24)	C(54) - C(55) - C(56)	117.3(27)
C(42) - C(41) - B(1)	118.1(23)	F(56) - C(56) - C(51)	119.5(24)
C(46) - C(41) - B(1)	127.5(22)	F(56) - C(56) - C(55)	113.2(24)
F(42) - C(42) - C(41)	122.2(25)	C(51) - C(56) - C(55)	126.4(27)
F(42) - C(42) - C(43)	113.0(25)	C(62) - C(61) - C(66)	112.3(25)
C(41) - C(42) - C(43)	124.7(27)	C(62) - C(61) - B(1)	130.5(24)
F(43) - C(43) - C(42)	119.6(26)	C(66) - C(61) - B(1)	117.1(24)
F(43) - C(43) - C(44)	124.1(28)	F(62) - C(62) - C(61)	118.9(23)
C(42) - C(43) - C(44)	115.7(28)	F(62) - C(62) - C(63)	115.4(24)
F(44) - C(44) - C(43)	115.6(27)	C(61) - C(62) - C(63)	124.6(26)
F(44) - C(44) - C(45)	124.4(33)	F(63) - C(63) - C(62)	119.8(26)
C(43) - C(44) - C(45)	119.0(34)	F(63) - C(63) - C(64)	116.6(30)
F(45) - C(45) - C(44)	103.9(45)	C(62) - C(63) - C(64)	123.4(31)
F(45) - C(45) - C(46)	140.6(59)	F(64) - C(64) - C(63)	126.8(36)
C(44) - C(45) - C(46)	109.1(48)	F(64) - C(64) - C(65)	118.4(33)
F(46) - C(46) - C(41)	120.1(23)	C(63) - C(64) - C(65)	114.6(33)
F(46) - C(46) - C(45)	104.7(37)	F(65) - C(65) - C(64)	117.8(26)
C(41) - C(46) - C(45)	134.7(40)	F(65) - C(65) - C(66)	121.4(25)
C(52) - C(51) - C(56)	111.1(26)	C(64) - C(65) - C(66)	120.5(27)
C(52) - C(51) - B(1)	130.1(25)	F(66) - C(66) - C(61)	119.0(25)
C(56) - C(51) - B(1)	118.5(24)	F(66) - C(66) - C(65)	117.4(25)
F(52) - C(52) - C(51)	119.3(25)	C(61) - C(66) - C(65)	123.6(26)
F(52) - C(52) - C(53)	113.8(25)	N(3) - B(1) - C(41)	103.7(22)
C(51) - C(52) - C(53)	126.5(28)	N(3) - B(1) - C(51)	113.7(22)
F(53) - C(53) - C(52)	120.0(27)	C(41) - B(1) - C(51)	110.4(21)
F(53) - C(53) - C(54)	119.6(27)	N(3) - B(1) - C(61)	105.9(22)
C(52) - C(53) - C(54)	120.2(30)	C(41) - B(1) - C(61)	116.7(23)
F(54) - C(54) - C(53)	120.3(28)	C(51) - B(1) - C(61)	106.6(23)
F(54) - C(54) - C(55)	121.7(27)	Cl(1) - C(100) - Cl(2)	84.58(4)
C(53) - C(54) - C(55)	117.3(29)	C(102) - C(101) - C(103)	80.28(3)
F(55) - C(55) - C(54)	120.5(27)	C(102) - C(101) - O(1)	89.80(4)
F(55) - C(55) - C(56)	122.0(26)	C(103) - C(101) - O(1)	106.64(3)

(iii) Fractional Atomic Coordinates and Isotropic Thermal Parameters for $[\{(C_6F_5)_3BN\}Re(PMePh_2)(S_2CNEt_2)_2]\cdot{}^{i}PrOH\cdot CH_2Cl_2$

Atom	*x/a*	*y/b*	*z/c*	*U(iso) or U(eq)**
Re(1)	0.35592(11)	0.37693(9)	0.29701(8)	0.0182
S(1)	0.2427(7)	0.4199(5)	0.1727(4)	0.0312
S(2)	0.4284(7)	0.4991(5)	0.1836(4)	0.0319
S(3)	0.5419(6)	0.3363(5)	0.3711(4)	0.0285
S(4)	0.5203(7)	0.2609(6)	0.2476(5)	0.0321
P(1)	0.2259(7)	0.5176(6)	0.3306(5)	0.0288
F(42)	0.1328(14)	0.2722(11)	0.2427(9)	0.0315
F(43)	-0.0841(17)	0.3745(15)	0.167(1)	0.0494
F(44)	-0.2852(14)	0.4662(13)	0.2470(11)	0.0440
F(45)	-0.2641(15)	0.4520(13)	0.4032(12)	0.0462
F(46)	-0.0499(15)	0.3514(12)	0.479(1)	0.0382
F(52)	0.3324(15)	0.3065(12)	0.510(1)	0.0369
F(53)	0.3012(18)	0.2791(15)	0.6668(11)	0.0525
F(54)	0.155(2)	0.1795(15)	0.7471(12)	0.0596
F(55)	0.0351(18)	0.1078(13)	0.6684(11)	0.0483
F(56)	0.0560(16)	0.1431(12)	0.509(1)	0.0379
F(62)	0.1028(14)	0.1218(12)	0.343(1)	0.0354
F(63)	0.2464(17)	-0.0315(14)	0.3132(13)	0.0499
F(64)	0.4987(19)	-0.0976(15)	0.3402(13)	0.0586
F(65)	0.6003(16)	-0.0057(13)	0.4026(12)	0.0501
F(66)	0.4573(14)	0.1508(12)	0.435(1)	0.0341
N(1)	0.299(3)	0.543(2)	0.0496(14)	0.0399
N(2)	0.725(2)	0.1895(18)	0.3418(16)	0.0339
N(3)	0.2767(19)	0.3114(13)	0.3562(12)	0.0163
C(1)	0.322(3)	0.494(2)	0.1229(18)	0.033(7)
C(2)	0.375(4)	0.599(3)	0.004(2)	0.06(1)
C(3)	0.309(3)	0.701(3)	-0.004(2)	0.053(9)
C(4)	0.203(3)	0.534(2)	0.0041(19)	0.039(7)
C(5)	0.258(3)	0.458(2)	-0.036(2)	0.048(8)
C(6)	0.615(3)	0.253(2)	0.3217(18)	0.036(7)
C(7)	0.785(3)	0.122(2)	0.2951(18)	0.034(7)
C(8)	0.860(4)	0.158(3)	0.221(2)	0.056(9)
C(9)	0.800(3)	0.177(2)	0.4113(19)	0.039(7)
C(10)	0.777(3)	0.111(3)	0.479(2)	0.054(9)

C(11)	0.136(3)	0.490(2)	0.424(2)	0.043(8)
C(21)	0.295(2)	0.5950(19)	0.3491(16)	0.026(6)
C(22)	0.222(3)	0.679(2)	0.3565(19)	0.038(7)
C(23)	0.264(3)	0.735(2)	0.3807(18)	0.032(7)
C(24)	0.388(3)	0.705(2)	0.4012(19)	0.041(7)
C(25)	0.469(3)	0.622(3)	0.399(2)	0.049(9)
C(26)	0.422(3)	0.566(2)	0.372(2)	0.045(8)
C(31)	0.107(3)	0.593(2)	0.2550(17)	0.030(6)
C(32)	0.126(3)	0.657(2)	0.1937(17)	0.031(6)
C(33)	0.034(3)	0.706(3)	0.133(2)	0.048(8)
C(34)	-0.068(4)	0.688(3)	0.140(3)	0.068(11)
C(35)	-0.097(3)	0.623(2)	0.199(2)	0.047(8)
C(36)	-0.006(3)	0.570(3)	0.261(2)	0.044(8)
C(41)	0.054(2)	0.3038(17)	0.3651(14)	0.017(5)
C(42)	0.037(3)	0.311(2)	0.2892(19)	0.036(7)
C(43)	-0.081(3)	0.366(2)	0.2450(19)	0.037(7)
C(44)	-0.179(3)	0.416(2)	0.2873(19)	0.039(7)
C(45)	-0.167(6)	0.394(5)	0.384(4)	0.107(19)
C(46)	-0.054(3)	0.353(2)	0.4024(17)	0.029(6)
C(51)	0.193(2)	0.2300(18)	0.5014(15)	0.022(6)
C(52)	0.252(3)	0.255(2)	0.5468(17)	0.031(6)
C(53)	0.235(3)	0.245(2)	0.6271(19)	0.037(7)
C(54)	0.161(3)	0.197(2)	0.6697(18)	0.034(7)
C(55)	0.110(3)	0.157(2)	0.6296(18)	0.033(7)
C(56)	0.129(3)	0.175(2)	0.5467(17)	0.031(7)
C(61)	0.270(3)	0.149(2)	0.3862(17)	0.029(6)
C(62)	0.225(2)	0.0927(19)	0.3616(16)	0.024(6)
C(63)	0.299(3)	0.015(2)	0.3402(19)	0.038(7)
C(64)	0.426(4)	-0.022(3)	0.351(3)	0.06(1)
C(65)	0.479(2)	0.0302(19)	0.3840(16)	0.026(6)
C(66)	0.403(3)	0.109(2)	0.4027(18)	0.033(7)
B(1)	0.197(3)	0.248(2)	0.402(2)	0.0282
Cl(1)	0.4597	0.8296	0.0461	0.0500
C(102)	0.3364	0.1202	0.1084	0.0500
C(103)	0.3064	0.1571	0.0038	0.0500
C(100)	0.3903	0.7533	0.1116	0.0500
Cl(2)	0.5392	0.7067	0.1648	0.0500
O(1)	0.1453	0.1481	0.1059	0.0500
C(101)	0.2469	0.1946	0.0688	0.0500

H(111)	0.0831	0.5532	0.4343	0.0600
H(112)	0.1922	0.4555	0.4678	0.0600
H(113)	0.0777	0.4621	0.4166	0.0600
H(21)	0.4550	0.5808	0.0348	0.0460
H(22)	0.3953	0.5900	-0.0489	0.0460
H(31)	0.3628	0.7363	-0.0346	0.0559
H(32)	0.2870	0.7118	0.0498	0.0559
H(33)	0.2273	0.7210	-0.0339	0.0559
H(41)	0.1685	0.5953	-0.0360	0.0487
H(42)	0.1358	0.5221	0.0433	0.0487
H(51)	0.1885	0.4572	-0.0664	0.0554
H(52)	0.3258	0.4719	-0.0756	0.0554
H(53)	0.2931	0.3987	0.0037	0.0554
H(71)	0.8439	0.0652	0.3289	0.0386
H(72)	0.7174	0.1070	0.2747	0.0386
H(81)	0.8970	0.1117	0.1922	0.0661
H(82)	0.9274	0.1740	0.2404	0.0661
H(83)	0.8008	0.2158	0.1862	0.0661
H(91)	0.8898	0.1651	0.3960	0.0427
H(92)	0.7667	0.2403	0.4243	0.0427
H(101)	0.8271	0.1018	0.5269	0.0585
H(102)	0.8099	0.0469	0.4667	0.0585
H(103)	0.6869	0.1220	0.4950	0.0585
H(221)	0.1286	0.7026	0.3437	0.0474
H(231)	0.2076	0.7986	0.3830	0.0416
H(241)	0.4200	0.7461	0.4188	0.0484
H(251)	0.5571	0.6021	0.4112	0.0595
H(261)	0.4799	0.5023	0.3699	0.0567
H(321)	0.2059	0.6754	0.1888	0.0422
H(331)	0.0517	0.7568	0.0891	0.0501
H(341)	-0.1392	0.7305	0.0963	0.0702
H(351)	-0.1780	0.6091	0.2027	0.0612
H(361)	-0.0193	0.5198	0.3058	0.0470
H(101)	0.3149	0.7819	0.1417	0.0600
H(102)	0.3721	0.7107	0.0879	0.0600
H(1021)	0.3301	0.1175	0.1659	0.0600
H(1022)	0.4205	0.1230	0.0870	0.0600
H(1023)	0.3252	0.0647	0.1018	0.0600
H(1031)	0.2629	0.1974	-0.0467	0.0600

H(1032)	0.3962	0.1532	-0.0009	0.0600
H(1033)	0.3010	0.0949	0.0140	0.0600
H(1)	0.2210	0.2611	0.0638	0.0600

* U(eq) = one third of the trace of the orthogonalised U_{ij} tensor.

(iv) Anisotropic Thermal Parameters for $[\{(C_6F_5)_3BN\}Re(PMePh_2)(S_2CNEt_2)_2]\cdot{}^{i}PrOH\cdot CH_2Cl_2$

Atom	*U(11)*	*U(22)*	*U(33)*	*U(23)*	*U(13)*	*U(12)*
Re(1)	0.0084(5)	0.0216(6)	0.0256(6)	-0.0102(4)	-0.0035(4)	-0.0020(4)
S(1)	0.031(4)	0.037(4)	0.029(4)	-0.007(3)	-0.008(3)	-0.015(3)
S(2)	0.029(4)	0.037(4)	0.030(4)	-0.006(3)	-0.001(3)	-0.013(3)
S(3)	0.022(3)	0.035(4)	0.030(4)	-0.008(3)	-0.010(3)	-0.010(3)
S(4)	0.030(4)	0.037(5)	0.036(4)	-0.016(3)	0.000(3)	-0.014(3)
P(1)	0.026(4)	0.032(4)	0.036(5)	-0.014(3)	0.001(3)	-0.015(3)
F(42)	0.026(8)	0.032(9)	0.034(9)	-0.017(7)	-0.002(7)	0.001(7)
F(43)	0.04(1)	0.082(15)	0.022(9)	0.006(9)	-0.005(8)	-0.03(1)
F(44)	0.010(7)	0.057(12)	0.048(11)	-0.003(9)	-0.019(7)	0.005(7)
F(45)	0.019(8)	0.044(11)	0.068(13)	-0.018(9)	-0.006(8)	0.002(8)
F(46)	0.04(1)	0.045(11)	0.03(1)	-0.020(8)	-0.003(8)	-0.005(8)
F(52)	0.038(9)	0.04(1)	0.04(1)	-0.015(8)	-0.007(8)	-0.014(8)
F(53)	0.055(12)	0.074(15)	0.041(11)	-0.02(1)	-0.007(9)	-0.027(11)
F(54)	0.076(15)	0.063(14)	0.038(12)	-0.02(1)	0.00(1)	-0.018(11)
F(55)	0.057(12)	0.042(11)	0.03(1)	0.002(8)	0.006(9)	-0.014(9)
F(56)	0.05(1)	0.03(1)	0.03(1)	-0.000(7)	-0.001(8)	-0.024(8)
F(62)	0.034(9)	0.04(1)	0.05(1)	-0.022(8)	-0.006(8)	-0.011(7)
F(63)	0.04(1)	0.052(12)	0.075(14)	-0.045(11)	-0.00(1)	-0.018(9)
F(64)	0.054(12)	0.053(13)	0.070(15)	-0.028(11)	-0.01(1)	-0.01(1)
F(65)	0.028(9)	0.039(11)	0.066(13)	-0.007(9)	-0.006(9)	0.005(8)
F(66)	0.030(9)	0.04(1)	0.04(1)	-0.017(8)	-0.007(7)	-0.015(7)
N(1)	0.058(17)	0.053(18)	0.014(13)	-0.001(11)	-0.006(12)	-0.031(14)
N(2)	0.018(12)	0.041(16)	0.039(15)	-0.016(12)	-0.01(1)	0.000(11)
N(3)	0.031(11)	-0.000(9)	0.025(12)	-0.008(8)	-0.004(9)	-0.009(8)
B(1)	0.018(15)	0.036(19)	0.028(18)	-0.010(14)	-0.005(13)	-0.003(13)

Appendix Three

X-Ray Structural Data for
[{$(C_6F_5)_3BN$}Re(PMe_2Ph)(S_2CNMe_2)$_2$] (10)

X-Ray Structural Data for [{$(C_6F_5)_3BN$}Re(PMe_2Ph)(S_2CNMe_2)$_2$] (10)

Formula	$C_{32}H_{23}BF_{15}N_3PReS_4$
Formula Weight	1090.75
Crystal System	Triclinic
a (Å)	8.871(5)
b (Å)	13.23(10)
c (Å)	16.72(13)
α (°)	80.73(4)
β (°)	77.13(5)
γ (°)	86.05(5)
Unit-cell Volume (Å^3)	1887.6
Space Group	P-1
ρ_{calc} (gcm^{-3})	1.92
μ (mm^{-1})	3.62
Crystal Size (mm)	0.25 x 0.05 x 0.05
Radiation	Mo K_α (λ = 0.71069 Å)
Transmission Coefficient	0.85 - 1.00
2 Θ Limits	2 - 53
Total Data Collected	11663
Unique Data	6103
Data Observed[a]	5408
Parameters Refined	514
Weighting Scheme	Chebychev
Weighting Parameters	2.84, 0.362, 2.06
R[b]	0.042
R_w[c]	0.051
Largest Final Shift	0.0004
Largest Peak, (eÅ^{-3})	1.61
Temperature (K)	125

a: Criterion for observation $I > 3\sigma(I)$

b: $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$

c: $R_w = [w\Sigma(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$

(i) Bond Distances in [{$(C_6F_5)_3BN$}Re(PMe_2Ph)(S_2CNMe_2)$_2$], Å

Re(1) - S(1)	2.3769(12)	N(2) - C(1)	1.323(7)
Re(1) - S(2)	2.4350(15)	N(2) - C(2)	1.462(8)
Re(1) - S(3)	2.6090(12)	N(2) - C(3)	1.463(7)
Re(1) - S(4)	2.4608(13)	N(3) - B(1)	1.548(7)
Re(1) - P(1)	2.4154(15)	C(10) - C(11)	1.392(8)
Re(1) - N(3)	1.700(4)	C(10) - C(15)	1.383(8)
S(1) - C(4)	1.746(6)	C(11) - C(12)	1.385(9)
S(2) - C(4)	1.721(6)	C(12) - C(13)	1.377(9)
S(3) - C(1)	1.719(6)	C(13) - C(14)	1.372(11)
S(4) - C(1)	1.715(5)	C(14) - C(15)	1.408(9)
P(1) - C(7)	1.830(6)	C(20) - C(21)	1.388(7)
P(1) - C(8)	1.817(6)	C(20) - C(25)	1.398(7)
P(1) - C(10)	1.825(6)	C(20) - B(1)	1.635(8)
F(21) - C(21)	1.351(6)	C(21) - C(22)	1.389(9)
F(22) - C(22)	1.342(6)	C(22) - C(23)	1.377(9)
F(23) - C(23)	1.334(7)	C(23) - C(24)	1.382(8)
F(24) - C(24)	1.341(7)	C(24) - C(25)	1.378(8)
F(25) - C(25)	1.362(6)	C(30) - C(31)	1.392(7)
F(31) - C(31)	1.345(6)	C(30) - C(35)	1.394(7)
F(32) - C(32)	1.347(6)	C(30) - B(1)	1.635(7)
F(33) - C(33)	1.341(6)	C(31) - C(32)	1.375(7)
F(34) - C(34)	1.350(6)	C(32) - C(33)	1.389(8)
F(35) - C(35)	1.357(6)	C(33) - C(34)	1.365(9)
F(41) - C(41)	1.329(7)	C(34) - C(35)	1.381(7)
F(42) - C(42)	1.348(6)	C(40) - C(41)	1.410(7)
F(43) - C(43)	1.351(6)	C(40) - C(45)	1.373(9)
F(44) - C(44)	1.330(8)	C(40) - B(1)	1.650(8)
F(45) - C(45)	1.357(6)	C(41) - C(42)	1.383(8)
N(1) - C(4)	1.315(7)	C(42) - C(43)	1.37(1)
N(1) - C(5)	1.448(9)	C(43) - C(44)	1.384(9)
N(1) - C(6)	1.461(8)	C(44) - C(45)	1.406(8)

(ii) Bond Angles in [{$(C_6F_5)_3BN$}Re(PMe_2Ph)(S_2CNMe_2)$_2$], °

S(1) - Re(1) - S(2)	72.74(5)	S(1) - C(4) - N(1)	123.2(5)
S(1) - Re(1) - S(3)	88.02(4)	S(2) - C(4) - N(1)	126.0(5)
S(2) - Re(1) - S(3)	86.81(5)	P(1) - C(10) - C(11)	118.6(4)
S(1) - Re(1) - S(4)	152.79(4)	P(1) - C(10) - C(15)	121.9(5)
S(2) - Re(1) - S(4)	90.94(5)	C(11) - C(10) - C(15)	119.4(5)
S(3) - Re(1) - S(4)	69.04(4)	C(10) - C(11) - C(12)	120.5(5)
S(1) - Re(1) - P(1)	95.28(5)	C(11) - C(12) - C(13)	119.6(6)
S(2) - Re(1) - P(1)	162.55(5)	C(12) - C(13) - C(14)	121.1(6)
S(3) - Re(1) - P(1)	80.01(5)	C(13) - C(14) - C(15)	119.4(6)
S(4) - Re(1) - P(1)	94.91(5)	C(10) - C(15) - C(14)	120.0(6)
S(1) - Re(1) - N(3)	104.07(14)	C(21) - C(20) - C(25)	113.2(5)
S(2) - Re(1) - N(3)	100.14(16)	C(21) - C(20) - B(1)	127.1(5)
S(3) - Re(1) - N(3)	167.36(14)	C(25) - C(20) - B(1)	119.1(5)
S(4) - Re(1) - N(3)	100.08(15)	F(21) - C(21) - C(20)	121.0(5)
P(1) - Re(1) - N(3)	95.01(16)	F(21) - C(21) - C(22)	115.0(5)
Re(1) - S(1) - C(4)	88.75(18)	C(20) - C(21) - C(22)	124.0(5)
Re(1) - S(2) - C(4)	87.4(2)	F(22) - C(22) - C(21)	121.0(6)
Re(1) - S(3) - C(1)	85.92(18)	F(22) - C(22) - C(23)	119.2(6)
Re(1) - S(4) - C(1)	90.84(18)	C(21) - C(22) - C(23)	119.7(5)
Re(1) - P(1) - C(7)	118.2(2)	F(23) - C(23) - C(22)	120.2(5)
Re(1) - P(1) - C(8)	114.0(2)	F(23) - C(23) - C(24)	120.5(5)
C(7) - P(1) - C(8)	102.3(3)	C(22) - C(23) - C(24)	119.2(6)
Re(1) - P(1) - C(10)	113.88(19)	F(24) - C(24) - C(23)	120.4(5)
C(7) - P(1) - C(10)	104.2(3)	F(24) - C(24) - C(25)	120.8(5)
C(8) - P(1) - C(10)	102.3(3)	C(23) - C(24) - C(25)	118.8(5)
C(4) - N(1) - C(5)	122.3(5)	F(25) - C(25) - C(20)	118.8(5)
C(4) - N(1) - C(6)	119.9(5)	F(25) - C(25) - C(24)	116.0(5)
C(5) - N(1) - C(6)	117.6(5)	C(20) - C(25) - C(24)	125.0(5)
C(1) - N(2) - C(2)	120.7(5)	C(31) - C(30) - C(35)	113.6(5)
C(1) - N(2) - C(3)	121.8(5)	C(31) - C(30) - B(1)	126.2(5)
C(2) - N(2) - C(3)	117.4(5)	C(35) - C(30) - B(1)	119.4(4)
Re(1) - N(3) - B(1)	170.9(3)	F(31) - C(31) - C(30)	121.0(5)
S(3) - C(1) - S(4)	113.7(3)	F(31) - C(31) - C(32)	115.3(5)
S(3) - C(1) - N(2)	122.9(4)	C(30) - C(31) - C(32)	123.7(5)
S(4) - C(1) - N(2)	123.3(4)	F(32) - C(32) - C(31)	121.4(5)
S(1) - C(4) - S(2)	110.8(3)	F(32) - C(32) - C(33)	118.5(5)

C(31) - C(32) - C(33)	120.0(5)	F(42) - C(42) - C(43)	119.5(5)
F(33) - C(33) - C(32)	120.5(5)	C(41) - C(42) - C(43)	120.3(5)
F(33) - C(33) - C(34)	120.8(5)	F(43) - C(43) - C(42)	120.5(5)
C(32) - C(33) - C(34)	118.8(5)	F(43) - C(43) - C(44)	119.4(6)
F(34) - C(34) - C(33)	120.2(5)	C(42) - C(43) - C(44)	120.2(5)
F(34) - C(34) - C(35)	120.2(5)	F(44) - C(44) - C(43)	121.0(5)
C(33) - C(34) - C(35)	119.6(5)	F(44) - C(44) - C(45)	121.6(5)
F(35) - C(35) - C(30)	118.7(4)	C(43) - C(44) - C(45)	117.4(6)
F(35) - C(35) - C(34)	117.0(5)	F(45) - C(45) - C(40)	120.6(5)
C(30) - C(35) - C(34)	124.3(5)	F(45) - C(45) - C(44)	114.2(5)
C(41) - C(40) - C(45)	114.2(5)	C(40) - C(45) - C(44)	125.2(5)
C(41) - C(40) - B(1)	119.9(5)	N(3) - B(1) - C(20)	109.0(4)
C(45) - C(40) - B(1)	125.4(5)	N(3) - B(1) - C(30)	115.2(4)
F(41) - C(41) - C(40)	120.5(5)	C(20) - B(1) - C(30)	103.3(4)
F(41) - C(41) - C(42)	116.8(5)	N(3) - B(1) - C(40)	100.4(4)
C(40) - C(41) - C(42)	122.7(6)	C(20) - B(1) - C(40)	114.7(4)
F(42) - C(42) - C(41)	120.2(6)	C(30) - B(1) - C(40)	114.5(4)

(iii) Fractional Atomic Coordinates and Isotropic Thermal Parameters for [{$(C_6F_5)_3BN$}Re(PMe_2Ph)(S_2CNMe_2)$_2$]

Atom	*x/a*	*y/b*	*z/c*	*U(iso) or U(eq)**
Re(1)	-0.25156(2)	-0.101639(13)	-0.25044(1)	0.0142
S(1)	-0.26486(17)	-0.1016(1)	-0.10690(7)	0.0198
S(2)	-0.51872(17)	-0.1318(1)	-0.17848(8)	0.0230
S(3)	-0.32732(18)	0.09340(9)	-0.26264(8)	0.0231
S(4)	-0.33329(18)	-0.0400(1)	-0.38165(7)	0.0214
P(1)	0.00223(18)	-0.0305(1)	-0.29636(8)	0.0199
F(21)	-0.2715(4)	-0.5373(2)	-0.1554(2)	0.0280
F(22)	-0.5029(5)	-0.6386(2)	-0.1779(2)	0.0333
F(23)	-0.6632(4)	-0.5630(3)	-0.2956(2)	0.0326
F(24)	-0.5817(5)	-0.3816(3)	-0.3960(2)	0.0329
F(25)	-0.3453(4)	-0.2802(2)	-0.37797(19)	0.0248
F(31)	-0.0288(4)	-0.2036(2)	-0.43135(19)	0.0279
F(32)	0.1389(5)	-0.2710(3)	-0.5658(2)	0.0361
F(33)	0.2419(5)	-0.4693(3)	-0.5608(2)	0.0373
F(34)	0.1687(5)	-0.6021(3)	-0.4161(2)	0.0337

F(35)	-0.0025(4)	-0.5370(2)	-0.2797(2)	0.0270
F(41)	-0.3343(4)	-0.3515(2)	-0.09634(19)	0.0248
F(42)	-0.2377(5)	-0.3722(3)	0.04525(19)	0.0315
F(43)	0.0702(5)	-0.3890(3)	0.0450(2)	0.0334
F(44)	0.2803(5)	-0.3900(3)	-0.1018(2)	0.0337
F(45)	0.1861(4)	-0.3715(3)	-0.2440(2)	0.0276
N(1)	-0.5463(6)	-0.1503(4)	-0.0120(3)	0.0241
N(2)	-0.4485(7)	0.1531(4)	-0.3965(3)	0.0266
N(3)	-0.1898(6)	-0.2230(3)	-0.2656(2)	0.0192
C(1)	-0.3795(7)	0.0790(4)	-0.3531(3)	0.0220
C(2)	-0.484(1)	0.1382(5)	-0.4749(4)	0.0382
C(3)	-0.5019(9)	0.2496(5)	-0.3656(4)	0.0361
C(4)	-0.4593(7)	-0.1323(4)	-0.0872(3)	0.0208
C(5)	-0.7047(8)	-0.1816(5)	0.0033(4)	0.0368
C(6)	-0.4801(8)	-0.1469(5)	0.0600(3)	0.0303
C(7)	0.0512(8)	0.0436(5)	-0.4004(3)	0.0327
C(8)	0.1604(8)	-0.1256(4)	-0.2983(4)	0.0276
C(10)	0.0459(7)	0.0537(4)	-0.2287(3)	0.0241
C(11)	0.0776(8)	0.0101(4)	-0.1525(4)	0.0269
C(12)	0.1092(9)	0.0713(5)	-0.0988(4)	0.0333
C(13)	0.1064(9)	0.1762(5)	-0.1205(5)	0.0385
C(14)	0.074(1)	0.2213(5)	-0.1950(5)	0.0422
C(15)	0.0425(8)	0.1592(5)	-0.2497(4)	0.0322
C(20)	-0.2984(7)	-0.4005(4)	-0.2636(3)	0.0189
C(21)	-0.3452(7)	-0.4930(4)	-0.2154(3)	0.0202
C(22)	-0.4657(8)	-0.5482(4)	-0.2253(3)	0.0263
C(23)	-0.5471(7)	-0.5107(4)	-0.2856(3)	0.0243
C(24)	-0.5068(7)	-0.4186(4)	-0.3355(3)	0.0224
C(25)	-0.3856(7)	-0.3672(4)	-0.3236(3)	0.0193
C(30)	-0.0223(6)	-0.3666(4)	-0.3471(3)	0.0181
C(31)	0.0168(7)	-0.3032(4)	-0.4231(3)	0.0210
C(32)	0.1040(7)	-0.3355(4)	-0.4938(3)	0.0230
C(33)	0.1576(8)	-0.4368(5)	-0.4920(3)	0.0287
C(34)	0.1201(7)	-0.5029(4)	-0.4196(4)	0.0243
C(35)	0.0328(7)	-0.4676(4)	-0.3497(3)	0.0229
C(40)	-0.0795(7)	-0.3630(4)	-0.1783(3)	0.0194
C(41)	-0.1827(7)	-0.3623(4)	-0.1009(3)	0.0205
C(42)	-0.1336(8)	-0.3720(4)	-0.0271(3)	0.0258
C(43)	0.0216(8)	-0.3806(4)	-0.0270(3)	0.0239

C(44)	0.1297(8)	-0.3812(4)	-0.1007(4)	0.0264
C(45)	0.0738(7)	-0.3725(4)	-0.1740(3)	0.0208
B(1)	-0.1450(7)	-0.3382(4)	-0.2646(3)	0.0166
H(21)	-0.5361	0.2019	-0.4988	0.0600
H(22)	-0.5551	0.0796	-0.4648	0.0600
H(23)	-0.3866	0.1228	-0.5147	0.0600
H(31)	-0.5506	0.2952	-0.4074	0.0600
H(32)	-0.5796	0.2354	-0.3121	0.0600
H(33)	-0.4119	0.2843	-0.3564	0.0600
H(51)	-0.7497	-0.1912	0.0643	0.0600
H(52)	-0.7069	-0.2476	-0.0183	0.0600
H(53)	-0.7667	-0.1276	-0.0256	0.0600
H(61)	-0.5616	-0.1623	0.1119	0.0600
H(62)	-0.3931	-0.1990	0.0608	0.0600
H(63)	-0.4405	-0.0772	0.0568	0.0600
H(71)	0.1579	0.0679	-0.4109	0.0600
H(72)	-0.0220	0.1032	-0.4045	0.0600
H(73)	0.0442	-0.0002	-0.4420	0.0600
H(81)	0.2602	-0.0909	-0.3177	0.0600
H(82)	0.1549	-0.1638	-0.2418	0.0600
H(83)	0.1521	-0.1738	-0.3366	0.0600
H(111)	0.0775	-0.0661	-0.1364	0.0600
H(121)	0.1338	0.0394	-0.0446	0.0600
H(131)	0.1283	0.2202	-0.0814	0.0600
H(141)	0.0735	0.2976	-0.2103	0.0600
H(151)	0.0175	0.1913	-0.3038	0.0600

* U(eq) = one third of the trace of the orthogonalised U_{ij} tensor.

(iv) Anisotropic Thermal Parameters for [{$(C_6F_5)_3BN$}Re $(PMe_2Ph)(S_2CNMe_2)_2$]

Atom	*U(11)*	*U(22)*	*U(33)*	*U(23)*	*U(13)*	*U(12)*
Re(1)	0.01692(15)	0.01501(12)	0.01175(12)	-0.00458(7)	-0.00468(8)	0.00292(8)
S(1)	0.0215(8)	0.0245(6)	0.0145(5)	-0.0060(4)	-0.0047(5)	0.0008(5)
S(2)	0.0189(8)	0.0293(6)	0.0218(6)	-0.0074(5)	-0.0046(5)	0.0011(5)
S(3)	0.0346(9)	0.0190(6)	0.0182(6)	-0.0074(4)	-0.0099(5)	0.0077(5)
S(4)	0.0283(8)	0.0212(6)	0.0177(6)	-0.0061(4)	-0.0103(5)	0.0039(5)
P(1)	0.0216(8)	0.0224(6)	0.0162(6)	-0.0051(5)	-0.0039(5)	0.0001(5)
F(21)	0.035(2)	0.0246(16)	0.0259(16)	0.0015(12)	-0.0131(14)	-0.0016(14)
F(22)	0.040(2)	0.0214(16)	0.0361(18)	-0.0007(13)	-0.0053(16)	-0.0050(14)
F(23)	0.023(2)	0.0297(17)	0.051(2)	-0.0120(15)	-0.0138(16)	-0.0027(14)
F(24)	0.037(2)	0.0330(18)	0.0347(18)	-0.0051(14)	-0.0201(16)	-0.0005(15)
F(25)	0.029(2)	0.0238(15)	0.0230(15)	-0.0003(12)	-0.0114(13)	-0.0023(13)
F(31)	0.038(2)	0.0229(15)	0.0199(14)	-0.0036(12)	-0.0018(14)	0.0023(13)
F(32)	0.048(3)	0.0346(18)	0.0196(15)	-0.0036(13)	0.0037(15)	-0.0007(16)
F(33)	0.036(2)	0.046(2)	0.0304(18)	-0.0226(15)	0.0014(16)	0.0087(16)
F(34)	0.038(2)	0.0260(17)	0.0417(19)	-0.0191(14)	-0.0116(16)	0.0132(15)
F(35)	0.031(2)	0.0209(15)	0.0278(16)	-0.0040(12)	-0.0063(14)	0.0048(13)
F(41)	0.025(2)	0.0263(15)	0.0227(15)	-0.0044(12)	-0.0033(13)	0.0017(12)
F(42)	0.041(2)	0.0362(18)	0.0165(14)	-0.0068(13)	-0.0022(14)	-0.0040(15)
F(43)	0.050(3)	0.0340(18)	0.0248(16)	-0.0074(13)	-0.0255(16)	0.0008(16)
F(44)	0.024(2)	0.043(2)	0.0395(19)	-0.0114(15)	-0.0184(16)	0.0069(15)
F(45)	0.021(2)	0.0356(17)	0.0269(16)	-0.0119(13)	-0.0041(13)	0.0051(13
N(1)	0.022(3)	0.026(2)	0.023(2)	-0.0043(17)	-0.0022(19)	0.0017(18)
N(2)	0.032(3)	0.023(2)	0.028(2)	-0.0050(18)	-0.015(2)	0.0045(19)
N(3)	0.020(3)	0.025(2)	0.0128(18)	-0.0045(15)	-0.0021(16)	0.0006(17)
C(1)	0.024(3)	0.024(2)	0.018(2)	-0.0024(19)	-0.007(2)	0.002(2)
C(2)	0.058(5)	0.032(3)	0.030(3)	-0.001(2)	-0.027(3)	0.007(3)
C(3)	0.039(4)	0.027(3)	0.043(3)	-0.007(2)	-0.013(3)	0.012(3)
C(4)	0.020(3)	0.023(2)	0.018(2)	-0.0041(18)	-0.001(2)	0.0047(19
C(5)	0.024(4)	0.042(3)	0.042(3)	-0.008(3)	0.000(3)	-0.004(3)
C(6)	0.031(4)	0.039(3)	0.018(2)	-0.006(2)	0.000(2)	0.002(2)
C(7)	0.036(4)	0.041(3)	0.019(3)	-0.002(2)	-0.003(2)	-0.005(3)
C(8)	0.029(4)	0.027(3)	0.030(3)	-0.012(2)	-0.008(2)	0.005(2)
C(10)	0.023(3)	0.028(3)	0.023(2)	-0.006(2)	-0.005(2)	-0.003(2)
C(11)	0.030(4)	0.025(3)	0.028(3)	-0.005(2)	0.010(2)	-0.003(2)
C(12)	0.036(4)	0.034(3)	0.034(3)	-0.014(2)	-0.012(3)	0.005(3)

C(13)	0.034(4)	0.036(3)	0.054(4)	-0.027(3)	-0.014(3)	-0.000(3)
C(14)	0.044(5)	0.023(3)	0.067(5)	-0.015(3)	-0.026(4)	0.003(3)
C(15)	0.035(4)	0.025(3)	0.039(3)	-0.005(2)	-0.013(3)	0.003(2)
C(20)	0.014(3)	0.026(3)	0.019(2)	-0.0085(18)	-0.006(2)	0.0033(19)
C(21)	0.020(3)	0.021(2)	0.019(2)	-0.0063(18)	-0.003(2)	0.0064(19
C(22)	0.030(3)	0.020(2)	0.027(3)	-0.006(2)	0.002(2)	0.001(2)
C(23)	0.021(3)	0.023(3)	0.032(3)	-0.013(2)	-0.006(2)	-0.001(2)
C(24)	0.024(3)	0.023(3)	0.024(2)	-0.0097(19)	-0.010(2)	0.001(2)
C(25)	0.024(3)	0.018(2)	0.016(2)	-0.0013(17)	-0.0051(19)	0.0018(19)
C(30)	0.014(3)	0.022(2)	0.020(2)	-0.0074(18)	-0.0054(19)	0.0010(18)
C(31)	0.019(3)	0.023(2)	0.022(2)	-0.0061(19)	-0.006(2)	0.002(2)
C(32)	0.020(3)	0.029(3)	0.019(2)	-0.006(2)	-0.002(2)	-0.002(2)
C(33)	0.026(3)	0.039(3)	0.022(3)	-0.018(2)	-0.001(2)	0.000(2)
C(34)	0.015(3)	0.027(3)	0.035(3)	-0.016(2)	-0.010(2)	0.006(2)
C(35)	0.024(3)	0.025(3)	0.021(2)	-0.0096(19)	-0.007(2)	0.006(2)
C(40)	0.021(3)	0.020(2)	0.018(2)	-0.0057(17)	-0.006(2)	0.0025(19)
C(41)	0.021(3)	0.021(2)	0.021(2)	-0.0038(18)	-0.007(2)	0.0043(19)
C(42)	0.040(4)	0.023(3)	0.015(2)	-0.0076(18)	-0.006(2)	-0.001(2)
C(43)	0.033(4)	0.024(3)	0.020(2)	-0.0016(19)	-0.019(2)	0.001(2)
C(44)	0.036(4)	0.018(2)	0.031(3)	-0.005(2)	-0.020(2)	0.005(2)
C(45)	0.018(3)	0.022(2)	0.024(2)	-0.0066(19)	-0.006(2)	0.0042(19)
B(1)	0.016(3)	0.018(2)	0.018(2)	-0.0041(19)	-0.006(2)	0.000(2)