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STUDIES IN GROUP VIII METAL-PHOSPHINE -TETRAHYDROBORATE CHEMISTRY

BY

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ABSTRACT

Co(I) and nickel(I) complexes containing both bidentate and monodentate tetrahydroborate have been prepared from the reductions of divalent metal compounds in the presence of triphenylphosphine with ethanolic sodium tetrahydroborate. These complexes, $Co(BH_4)(PPh_3)_3$, $Co(BH_4)(PPh_3)_2$, $[Ni(BH_4)(PPh_3)_3]_2$ and $Ni_2(BH_4)_2(PPh_3)_3$ have been characterised by chemical analyses and a variety of physical methods which were made very difficult by the pyrophoric nature of the Ni complexes. Two derivatives of $[Ni(BH_4)(PPh_3))_2$, the dimeric $[Ni_2(PPh_3)_6][PF_6]_2$ and the monomeric $[Ni(PPh_3)_3(CH_3CN)][PF_6]$ have also been obtained. Reaction mechanisms for these reductions are proposed.

As part of a study of the catalytic activity of group VIII metal tetrahydroborate complexes, the use of hydridotetrahydroboratotris(triphenylphosphine)-ruthenium(II), $HRu(BH_4)(PPh_3)_3$, in the homogeneous hydrogenation of 1-hexene at 20°C and 1 atmosphere pressure is reported. The dependence of rates of hydrogenation on catalyst and substrate concentrations, partial pressure of hydrogen and triphenylphosphine concentration are described and the suggested mechanism is discussed in the light of these results.

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ABBREVIATIONS

Bu^n	n-butyl
Bu^t	tert-butyl
Cy	cyclohexyl
DBP	5-phenyl-5H-dibenzophosphole
DMA	dimethylacetamide
DMF, (dmf)	dimethylformamide
DMGH	dimethylglyoxime
dppe	1,2-bis(diphenylphosphino)ethane
en	ethylenediamine
Et	ethyl
Me	methyl
NP_3	tris(2-diphenylphosphinoethyl)amine
Ph	phenyl
Phen	1,10-phenanthroline
PP	1,2-bis(dicyclohexylphosphino)ethane
PP_3	tris(2-diphenylphosphinoethyl)phosphine
Py	pyridine
Siphos	tris(trimethylsilylmethyl)phosphine
THF	tetrahydrofuran

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I. INTRODUCTION

Very little work has been done on the uses of sodium tetrahydroborate in organometallic chemistry compared with its wide application in organic synthesis although its importance is now beginning to be realized. This is particularly apparent in the area of metal recovery (1,2), homogeneous and heterogeneous catalysis (3) and synthesis. For example, one of the most useful methods for the preparation of transition metal hydride complexes involves reactions between $NaBH_4$ and metal halides or their complexes (4). Before the formation of metal hydrides or metal(0) complexes in such reactions, intermediate complexes involving coordinated BH_4 are formed and have been isolated (5,6).

In general then, several types of products may be formed during the reactions of $NaBH_4$ with metal complexes (particularly phosphine complexes). The formation of different types of complexes depends upon a number of factors (to be discussed later) but for phoshorus containing ligands, several schemes are possible which may be summarised by one of the following reaction outlines (7), (where P represents a phosphine ligand):

1)

$$\begin{tikzcd}
 & \mathrm{M(II,\ III\ or\ IV)Cl/P} \arrow[r] & \mathrm{MClP_x/P} \arrow[r] & \mathrm{M(BH_4)P_x} \arrow[d] & \\
\mathrm{MH_5P_x} \arrow[r, shift left] & \mathrm{MH_3P_x} \arrow[l, shift left] \arrow[r, shift left] & \mathrm{MHP_x} \arrow[l, shift left] & \mathrm{MHP_x} \arrow[r, shift left] & \mathrm{MP_x} \arrow[l, shift left]
\end{tikzcd}$$

2) $MCl_2P_x \longrightarrow MHClP_x \longrightarrow MH(BH_4)P_x \longrightarrow MH_2P_x \longrightarrow MH_4P_x$

3) $MHCl_2P_x \longrightarrow MH_2(BH_4)P_x \longrightarrow MH_3P_x \longrightarrow MH_5P_x$

4) $MX(CO)P_x \longrightarrow M(BH_4)(CO)P_x \longrightarrow MH(CO)P_x$

These schemes, of course, lack detail and concern only phosphine-metal systems. They are included here simply to illustrate the types of products which may be obtained by tetrahydroborate reduction of metal complexes. What follows, therefore, is a detailed survey of the variety of metal complexes which are formed when $NaBH_4$ is reacted with metal salts in the presence of different ligands. The reactions, for convenience, are grouped according to product type.

I.1. Formation of Hydride Complexes from Metal Salts by the Use of Sodium Tetrahydroborate in the Presence of Ligands other than Phosphines.

Transition metal hydrides can be stabilised in the presence of certain ligands other than phosphines which will be discussed in detail later. Examples of such ligands are cyclopentadiene, carbon monoxide various nitriles etc. The formation of a hydride complex is facilitated by the presence of an electron donating ligand which can stabilize a lower than usual oxidation state of the metal if a change of oxidation state occurs (8). Since the formation of these hydride complexes is not readily systematized according to the reactants and products, the following sections are classified by metal.

I.1.1. Titanium, Zirconium and Hafnium.

There are only a few reports of complex hydrides for members of the titanium triad. Thus, reactions of $MCl_2(\pi\text{-}C_5H_5)_2$ (M=Zr or Hf) with $LiBH_4$ in diethyl ether gives $M(BH_4)_2(\pi\text{-}C_5H_5)_2$ which will react further with trimethylamine to give the volatile complexes $HM(BH_4)(\pi\text{-}C_5H_5)_2$ (9).

I.1.2. Vanadium, Niobium, and Tantalum.

Treatment of $VI(CO)_3(\pi\text{-mesitylene})$ with $NaBH_4$ gives $HV(CO)_3(\pi\text{-mesitylene})$ (10). The tantalum complex $H_3Ta(\pi\text{-}C_5H_5)$ is formed when $TaCl_5$ is treated with $Na(C_5H_5)$ and $NaBH_4$ in tetrahydrofuran(11) and the niobium analog is prepared similarly(12).

I.1.3. Chromium, Molybdenum and Tungsten.

Hydrides of the type $H_2M(\pi\text{-}C_5H_5)$ (M=Mo and W) can be formed from the reaction of MCl_5, $Na(C_5H_5)$ and $NaBH_4$ in tetrahydrofuran(12). The binuclear hydrido anions $[HM_2(CO)_{10}]^-$ (M=Cr, Mo and W) are formed from reactions between $M(CO)_6$ and $NaBH_4$ in THF(13).

I.1.4. Manganese, Technetium and Rhenium.

$HM(\pi\text{-}C_5H_5)_2$ (M=Re and Tc) can be formed from the reaction of $NaBH_4$ and $Na(C_5H_5)$ with the corresponding chloride salts in THF(14,15). When $Re_2(CO)_{10}$ and $NaBH_4$ are heated together under reflux in THF and then stirred at 25° for several days, salts of the $[H_6Re(CO)_{12}]^{2-}$ anion can be isolated. The same anion is obtained when $H_4Re(CO)_{12}$ reacts with $NaBH_4$ in cyclohexane (17).

I.1.5. Iron, Ruthenium and Osmium.

The reaction of $RuI(\pi\text{-}C_5H_5)(CO)_2$ with $NaBH_4$ gives $HRu(\pi\text{-}C_5H_5)(CO)_2$ and the corresponding iron hydride is prepared in the same way(18). The reaction of $Ru_3(CO)_{12}$ with $NaBH_4$ in THF gives a mixture of $H_2Ru_4(CO)_{12}$ and $\beta\text{-}H_4Ru_4(CO)_{12}$ (19). No osmium hydrides, other than those containing phosphines, have been reported from the reactions of $NaBH_4$ with osmium salts.

I.1.6. Cobalt, Rhodium and Iridium.

When CsCl is added to a mixture of $[Co(CN)_5H_2O]^{3-}$ and $NaBH_4$ in H_2O, $NaCs_2[HCo(CN)_5]$(20) precipitates out from solution. With $NaBH_4$ in H_2O at 0°C, $RhCl_2(en)_2^+$ gives $[H_2Rh(en)_2]^+$ which can be isolated as the tetraphenylborate salt. No hydride complex of iridium, except those containing phosphines, have been reported.

I.1.7. Nickel, Palladium and Platinum.

No hydride complexes of these elements have been isolated from reactions between M(II) compounds (M=Ni, Pd and Pt) and $NaBH_4$ except when, as will be discussed later, phosphorus-containing ligands are present.

I.1.8. Copper, Silver and Gold.

Again, no hydride complexes, without phosphorus-containing ligands, of these metals have yet been reported from reactions involving $NaBH_4$.

I.2. Formation of Hydride Complexes from Metal Salts by the Use of Sodium Tetrahydroborate in the Presence of Phosphorus Containing Ligands.

It is apparent from the preceding sections that reactions of $NaBH_4$ with metal complexes of tertiary phosphines have received considerably more attention. In general, these reactions give three different types of product, which depend mainly upon the nature of the ligand, the metal ion and the experimental conditions. These are metal(O)-phosphine (21), metal hydride (4), and metal tetrahydroborate complexes (4). The following discussion presents a summary of these reactions which lead to the formation of hydride complexes, and, as in section 1, the discussion is arranged according to groups of metals.

I.2.1. From Group IV B to VII B.

There are no reports in the literature on the preparation of complexes in the Ti, Zr, Hf and the V, Nb, Ta group of metals from tetrahydroborate reactions, while in group VI B, only two hydride phosphine complexes have been made using $NaBH_4$. These are the dimethylphenylphosphine (L) complexes H_6WL_3 (22) and cis-$HMo(\pi\text{-}C_5H_5)(CO)_2(PPh_3)$ (23), prepared by the reaction of $NaBH_4$ with the corresponding halogen complexes. In the Mn, Tc, Re group, there are many examples of hydrido-phosphine complexes. However, most of them do not arise from $NaBH_4$ reductions, but by ligand exchange reactions, and this is particularly true for manganese (24,25). There are two hydride complexes of rhenium, H_5ReL_3 (26, 27) (see Table 1) obtained from reactions involving $NaBH_4$.

I.2.2. Iron, Ruthenium and Osmium.

The use of $NaBH_4$ in the preparation of hydride-complexes of the Fe, Ru, Os group has been more extensive and Table 2 presents a summary of reactions which have been studied and the complexes obtained. Thus, iron(II) chloride reacts with triethylphosphite and sodium tetrahydroborate in methanol at -78° to give $H_2Fe[P(OC_2H_5)_3]_3$ (28). With ethyldiphenylphosphine or butyldiphenylphosphine, $NaBH_4$ and iron(II), H_2FeL_3 is formed under hydrogen or argon, while $H_2Fe(N_2)L_3$ is formed under nitrogen (29).

The reaction of $RuCl_2(PPh_3)_3$ with $NaBH_4$ and H_2 in a benzene/ethanol mixture gives $RuCl_2(CO)(PPh_3)_3$, where the carbonyl ligand is apparently abstracted from the solvent (32). This compound may also be formed from the reaction of Ru(III) chloride, triphenylphosphine, aqueous formaldehyde and $NaBH_4$ in EtOH, but in the absence of formaldehyde, $H_2Ru(PPh_3)_4$ is obtained (33). The reaction of $RuCl_2(PPh_3)_3$ with $NaBH_4$ in a benzene/water mixture gives $HRuCl(PPh_3)_3{\cdot}C_6H_6$ (32), while with $RuCl_3$, PPh_3 and $NaBH_4$ in EtOH, $H_4Ru(PPh_3)_3$ is formed (34). These reactions serve to illustrate the fact,

Table 1.

Hydrido-phosphine complexes of W, Mo and Re

Complexes	Reagents	Reference
$H_6W(PMe_2Ph)_3$	$NaBH_4 + t\text{-}[WCl_4(PMe_2Ph)_2]$	22
cis-$HMo(\pi\text{-}C_5H_5)(CO)_2(PPh_3)_2$	$NaBH_4 +$ cis$MoCl(\pi\text{-}C_5H_5)(CO)_2(PPh_3)$	23
$H_5Re(PPh_3)_3$	$NaBH_4 + K_2ReI_6 + PPh_3$	26
H_5ReL_3 (L=tri-p-tolylphosphine)	$NaBH_4 + ReI_2(O)(OC_2H_5)L_2 + L$	27

Table 2.

Hydrido-phosphine complexes of Fe, Ru and Os.

Complexes	Reagents	Reference
$H_2Fe[P(OC_2H_5)_3]_4$	$NaBH_4 + FeCl_2 + P(OC_2H_5)_3$	28
$H_2Fe(PPh_2C_2H_5)_3$	$NaBH_4 + FeCl_2 + PPh_2C_2H_5$	29
$H_2Fe(PPh_2C_4H_9)_3$	$NaBH_4 + FeCl_2 + PPh_2C_4H_9$	29
$H_2Fe(N_2)(PPh_2C_2H_5)_3$	$NaBH_4 + FeCl_2 + PPh_2C_2H_5 + N_2$	29
$H_2Fe(N_2)(PPh_2C_4H_9)_3$	$NaBH_4 + FeCl_2 + PPh_2C_4H_9 + N_2$	29
$[Fe_2H_3L_2]^+$	$NaBH_4/EtOH + L/CH_2Cl_2 + FeCl_2/BuOH$	30
L=1,1,1-tris(diphenylphosphinomethyl)ethane		
HFeCl(dppe)	$NaBH_4 + FeCl_2 \cdot 2H_2O$ + dppe	31
H_2Fe(dppe)	$NaBH_4 + FeCl_2 \cdot 2H_2O$ + dppe	31
$H_4Fe(PBuPh_2)_3$	$NaBH_4 + FeCl_2 \cdot 2H_2O + PBuPh_2$	31
$HRuCl(PPh_3)_3 \cdot C_6H_6$	$NaBH_4/H_2O + RuCl_2(PPh_3)_3/C_6H_6$	32

Table 2, cont'd

Complexes	Reagents	Reference
$H_2Ru(PPh_3)_4$	$NaBH_4 + RuCl_3 + PPh_3$	33
$H_2Ru(CO)(PPh_3)_3$	$NaBH_4 + RuCl_3 + PPh_3 + H_2CO/H_2O$	33
	$NaBH_4/EtOH + RuCl_2(PPh_3)_3/C_6H_6 + H_2$	32
$H_2Ru(DBP)_3$	$NaBH_4/EtOH + RuCl_3(DBP)_3/C_6H_6$	6
$H_2Ru(CO)(DBP)_2$	$NaBH_4$ + Ru(II)-CO + DBP	6
$H_2Ru(CO)(PEtPh_2)_3$	$NaBH_4$ + Ru(II)-CO + $PEtPh_2$	6
$H_2Ru(CO)_2(dppe)$	$NaBH_4 + RuCl_2(CO)_2(dppe)$	6
$H_4Ru(PPh_3)_4$	$NaBH_4 + RuCl_3 + PPh_3$	34
H_4OsL_3 (L=tertiary phosphine)	$NaBH_4$ + mer-$OsCl_3L_3$	35
H_4OsL_2L' (L=tertiary phosphine)	$NaBH_4 + OsCl_4L_2 + L'$	35
$H_4Os(PPh_3)_3$	$NaBH_4 + Na_2OsCl_6 + PPh_3$	33
H_6OsL_2 (L=tertiary phosphine)	$NaBH_4 + OsCl_4L_2$	35

which will become increasingly apparent in this thesis, that quite different compounds may be formed from reactions involving $NaBH_4$ when only minor changes are made in the experimental conditions.

H_4OsL_3 is usually made from the reaction of mer-$OsCl_3L_3$ (L=tertiary phosphine) with $NaBH_4$ in ethanol (35), but when Na_2OsCl_6 is used in a similar reaction, $H_2Os(PPh_3)_3$ is formed (33). When $OsCl_4L_2$ (L=tertiary phosphine) is treated with $NaBH_4$ in ethanol, it gives the hexahydride complex, H_6OsL_2, but in the presence of other tertiary phosphines, arsines or phosphites, tetrahydride complexes of the type H_4OsL_2L' are produced (35).

I.2.3. Cobalt, Rhodium and Iridium.

The reactions between $NaBH_4$ and this group of metals have also been well investigated and the many resulting hydride complexes are listed in Table 3. Thus, Cobalt(II) chloride can be reduced by $NaBH_4$ in ethanol in the presence of triphenylphosphite to give $HCo[P(OPh)_3]_4$ (36). This is also true for the triethylphosphite analog (37). The reaction of Cobalt(II) chloride with $NaBH_4$ in the presence of PPh_3 under nitrogen yields $HCo(N_2)(PPh_3)_3$ (38), which, in H_2, readily undergoes reversible displacement of coordinated N_2 to give $H_3Co(PPh_3)_3$ (52,53,54).

Table 3.

Hydrido-phosphine complexes of Co, Rh and Ir.

Complexes	Reagents	Reference
$HCo[P(OPh)_3]_4$	$NaBH_4 + CoCl_2 + P(OPh)_3$	36
$HCo[P(OEt)_3]_4$	$NaBH_4 + CoCl_2 + P(OEt)_3$	37
$HCo(N_2)(PPh_3)_3$	$NaBH_4 + CoCl_2 + PPh_3 + N_2$	38
$HCo(dppe)_2$	$NaBH_4 + CoBr_2(dppe)_2$	39
$HCoL \cdot \frac{1}{2}DMF$	$NaBH_4 + CoCl_2 + L$ in DMF/BuOH	40
$HCoL \cdot \frac{1}{2}(Me_2CO)$	$NaBH_4 + Co(BF_4)_2 + L$ in Acetone/EtOH	40
L=tris(2-diphenylphosphinoethyl)phosphine		
$(H_3Co_2L_2)^+$	$NaBH_4 + Co(BF_4)_2 + L$	41
L=1,1,1-tris(diphenylphosphinomethyl)ethane		
$H_3Co(PPh_3)_3$	$NaBH_4 + CoCl_2 + PPh_3$	43
$H_3Co(PEt_3)_3$	$NaBH_4 + CoCl_2 + PEt_3$	43,42,44
$HRh(CO(PPh_3)_3$	$NaBH_4 + RhCl_3 + PPh_3 + H_2CO/H_2O$	33,45
$HRh(PPh_3)_4$	$NaBH_4 + RHCl_3 + PPh_3$	33,45

Table 3, cont'd

Complexes	Reagents	Reference
$HRh(PPh_3)_3$	$NaBH_4 + RhCl(PPh_3)_3$	46
$HRh(DBP)_4$	$NaBH_4 + RhCl_3 + DBP$	47
$HRh(DMGH)_2(PPh_3)$	$NaBH_4 + RhCl(DMGH)_2(PPh_3)$	48
$HIr(CO)(PPh_3)_3$	$NaBH_4 + IrCl(CO)(PPh_3)_3$	49
	$NaBH_4 + Na_3IrCl_6 \cdot 2H_2O + PPh_3 + H_2CO/H_2O$	33
$HIr(CO)_2(PPh_3)_2$	$NaBH_4 + IrCl(CO)(PPh_3) + CO$	49
mer-$H_3Ir(PPh_3)_3$	$NaBH_4 + Na_3IrCl_6 + PPh_3$	33
mer-$H_3Ir(CO)(PPh_3)_2$	$NaBH_4 + IrCl(CO)(PPh_3)_2$	50
$H_5Ir(PPh_3)_2$	$NaBH_4 + Na_3IrCl_6 + PPh_3$	33
$H_5Ir(PBu_2{}^tMe)_2$	$NaBH_4 + HIrCl_2(PBu_2{}^tMe)_2$	51
$H_5Ir(PBu_3{}^t)_2$	$NaBH_4 + HIrCl_2(PBu_3{}^t)$	51

The latter can also be made by the reaction of $CoCl_2$, PPh_3 and $NaBH_4$ in EtOH under either argon or hydrogen (42,43). The diethylphenylphosphine analogue can also be formed under similar conditions (42,43,44). The complex $CoBr_2(dppe)_2$ reacts with $NaBH_4$ in EtOH to give $HCo(dppe)_2$ (39). With 1,1,1-tris(diphenylphosphinomethyl)ethane, as the corresponding ligand, $NaBH_4$ reacts with $Co(BF_4)_2 \cdot 6H_2O$ in EtOH at 0°C to give $(H_3Co_2L_2)^+$ (40).

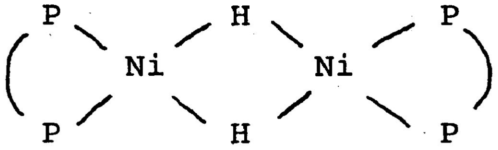
When rhodium(III) reacts with $NaBH_4$ in the presence of PPh_3 and aqueous formaldehyde in ethanol, the catalytically important complex $HRh(CO)(PPh_3)_3$ is formed (33,45). In the absence of aqueous formaldehyde, however, only $HRh(PPh_3)_4$ is produced (33,45). Starting with Rh(I), further Rh(I) monohydride complexes may be produced; for example, the reaction of $RhCl(PPh_3)_3$ and $NaBH_4$ in ethanol gives $HRh(PPh_3)_3$ (46), and, under analogous conditions, the corresponding DBP complex (47). In cold aqueous solution, $RhCl(DMGH)_2(PPh_3)$ reacts with $NaBH_4$ to give $HRh(DMGH)_2(PPh_3)$ (48).

There are many iridium hydride complexes formed from reactions involving a variety of Ir(I), (III) and (IV) compounds with sodium tetrahydroborate. For example, $HIr(CO)(PPh_3)_3$ is formed from the reaction of $NaBH_4$ with $IrCl(CO)(PPh_3)_2$ in ethanol (49). This same compound can also be made from the reaction of

$NaBH_4$ with $Na_3IrCl_6 \cdot 2H_2O$ in the presence of PPh_3 and aqueous formaldehyde in 2-methoxyethanol (33). When an ethanol solution of Na_3IrCl_6, PPh_3 and $NaBH_4$ is heated under reflux, mer-$H_3Ir(PPh_3)_3$ is obtained (33). In contrast, a similar reaction involving Na_3IrCl_6 produces the penta-hydride $H_5Ir(PPh_3)$ (55). Under an atmosphere of carbon monoxide, $IrCl(CO)(PPh_3)_3$ reacts with $NaBH_4$ in EtOH to give $HIr(CO)_2(PPh_3)_2$ (49).

I.2.4. Nickel, Palladium and Platinum.

There is only one example of the formation of a Ni(I) hydride complex from the reactions related to these $NaBH_4$ reductions. This involves (Table 4) the $NaBH_4$ derivative, $NaBHMe_3$, which reacts with $NiCl_2(PP)$ to produce $[HNi(PP)]_2$ (56). The proposed structure, as shown below, is consistent with the fact that the complex is diamagnetic and that it shows



a proton signal at τ=21.4 in the n.m.r. spectrum due to the bridging hydrogens.

There are a number of $NaBH_4$ produced Ni(II) hydrides known. For example, $NaBH_4$ reacts in

Table 4.

Hydrido-phosphine complexes of Ni, Pd and Pt.

Complexes	Reagents	Reference
$[HNi(PP)]_2$	$NaBHMe_3 + NiCl_2(PP)$	56
$[HNi(PP_3)]^+$	$NaBH_4 + NiX(PP)_3$	40
$[HNi(NP_3)]^+$	$NaBH_4 + Ni(NO_3)_2 + NP_3$	57
$HNiCl(PCy)_2$	$NaBH_4 + NiCl_2(PCy_3)_2$	58
$HNiCl(PPr_3^i)_2$	$NaBH_4 + NiCl_2(PPr_3^i)_2$	58
$HNi(\pi\text{-allyl})PPh_3$	$NaBHMe_3 + NiBr(\pi\text{-allyl})PPh_3$	59
$HNi(\pi\text{-allyl})PF_3$	$NaBHMe_3 + NiBr(\pi\text{-allyl})PF_3$	59
$HPdCl(PCy_3)_2$	$NaBH_4 + PdCl_2(PCy_3)_2$	60
$HPdCl(PPr_3^i)_2$	$NaBH_4 + PdCl_2(PPr_3^i)_2$	60
H_2PtL_2	$NaBH_4 + PtCl_2L_2$	61
(L=bulky tertiary phosphine)	$NaBH_4 + HPtClL_2$	61

THF/EtOH with $NiCl_2L_2$($L=PCy_3$ or PPr^i_3) to give trans-$HNiClL_2$ (58). π-Allyl complexes of Ni(II) also react with the $NaBH_4$ derivative, $NaBHMe_3$ (59) to give Ni(II) hydrides as listed in Table 4.

The only $NaBH_4$ produced palladium hydrides known are the two complexes of palladium(II) $HPdClL_2$ ($L=PCy_3$, PPr^i_3) made from reactions of $NaBH_4$ with the corresponding chloride complexes (60). For platinum, the dihydride complexes, H_2PtL_2 have been made from the reaction of $NaBH_4$ with either $PtCl_2L_2$ or $HPtClL_2$ (61), (L=bulky tertiary phosphine).

I.2.5. Copper, Silver and Gold .

There is one well characterized complex reported in this group. Thus the reaction of $[CuCl(PPh_3)]_4$ with the $NaBH_4$ derivative, $Na[HB(OMe)_3]$, yields the interesting metal cluster $H_6Cu_6(PPh_3)_6$ (62). This compound was shown by X-ray crystallography to have an octahedral arrangement of Cu atoms and apical phosphines. The hydrogens were not located, but it is thought that they bridge six equivalent, slightly longer Cu-Cu bonds of the octahedron.

I.3. Formation of Tetrahydroborate Complexes.

As well as being a powerful reducing agent and an excellent source of hydride ions in the synthesis of metal hydrides, the BH_4 group will also coordinate to metals to form essentially covalent complexes such as $M(BH_4)_n$ (63), e.g. $Zr(BH_4)_4$. It is also likely that in the reaction of metal salts with $NaBH_4$ in water in the absence of other ligands, intermediate compounds containing coordinated tetrahydroborate are involved, e.g. $Ti(BH_4)_3$ (64) or $Ni(BH_4)_2$ (65) which then undergo further rapid decomposition by water to give the metal boride. These intermediate BH_4^- complexes can be stabilized by carrying out the metal reductions in the presence of certain ligands, and, for example, complexes such as $Ti(BH_4)(\pi\text{-}C_5H_5)_2$, $Zr(BH_4)(\pi\text{-}C_5H_5)$ (9), $Ni(BH_4)_2(A)$ (A=cyclic tetramine) (66), $RuCl_2(BH_4)(Py)_2(dmf)$ (Py=pyridine) (67), and a number of complexes involving phosphines, e.g. $HCo(BH_4)(PCy_3)_2$ (68), $HNi(BH_4)(PPr^i_3)_2$ (69). This section is a detailed survey of metal-BH_4-ligand systems and is divided into two parts. The first concerns the synthesis of tetrahydroborate complexes and the second part discusses the various ways in which the BH_4 group can coordinate to metals.

I.3.1. Synthesis of Tetrahydroborate Complexes.

The tetrahydroborate complexes are of particular interest because of their potential as homogeneous catalysts. These complexes range from well characterized species such as $HCo(BH_4)(PCy_3)_2$ (68) and $HNi(BH_4)(PCy_3)_2$ (69) to compounds which have not been isolated but which are thought to be the catalytically active intermediates in certain reactions. An example of such a postulated intermediate is $NiCl(BH_4)(dmf)_3$ (70).

This thesis is particularly concerned with the conditions under which these intermediate complexes containing coordinated BH_4 are formed in reductions by $NaBH_4$ both of metal salts (particularly group VIII B) in the presence of various ligands and also of metal complexes. The isolation of unstable, low valent intermediates should mainly depend upon three factors (5).

i) Ease of reduction of metal ions: For example, the stability of M(I) is in the order $Cu > Co > Ni \gg Pd$ and Pt (5).

ii) Nature of the ligand: It appears, for example, that triphenylphosphine can stabilize Co(I) and Ni(I) tetrahydroborate complexes (5), while with other phosphines (e.g. tricyclohexylphosphine, triisopropylphosphine) only Co(II) and Ni(II) tetrahydroborate complexes are produced (68,69).

(iii) Experimental conditions: It is well established that divalent metal halides in the presence of phosphines are reduced by $NaBH_4$ under reflux producing, generally, metal(O) complexes, e.g. $M(PPh_3)_4$ (M=Ni, Pd, Pt) (71). By carefully controlling reaction conditions, such as temperature, time and molar ratio of reactants, a number of intermediate products have already been isolated (5).

This section of the introduction to this thesis gives an account of the variety of known BH_4 complexes and also of the factors which control their formation. As in the previous section, the BH_4 conplexes are classified by the group of the metals.

I.3.1.1. Iron, Ruthenium and Osmium.

In this group, ruthenium is the only metal for which tetrahydroborate complexes have so far been isolated (see Table 5). It is interesting that in reactions between Ru(II) and $NaBH_4$ in the presence of PPh_3, no BH_4 complex has been isolated under conditions analogous to those used in Co(II) and Ni(II) reactions where univalent metal BH_4 complexes are formed (5) (see later). In fact, no Ru(I)-BH_4

Table 5.

Hydrido-tetrahydroborate complexes of Ru.

Complexes	Reagents	Reference
$HRu(BH_4)(PPh_3)_3$	$NaBH_4 + RuCl_3 + PPh_3$	6
	$NaBH_4 + RuCl_2(PPh_3)_3 + PPh_3$	6
	$NaBH_4$ + blue Ru(II) chloride + PPh_3	6
$HRu(BH_4)(CO)(PPh_3)_3$	$NaBH_4$ + Ru(II) - carbonyl + PPh_3	6
$HRu(BH_4)(CO)_2(PCy_3)_2$	$NaBH_4$ + Ru(II)-carbonyl + PCy_3	6

complex has yet been identified. Thus, $NaBH_4$ reacts with the blue Ru(II) chloride solutions (72) (1:1 mole ratio) in the presence of a six-fold excess of PPh_3, and produces $HRuCl(PPh_3)_3$ as the sole product (32). However, when much more $NaBH_4$ is used ($Ru:NaBH_4 \sim 1:10$) the yellow diamagnetic complex, $HRu(BH_4)(PPh_3)_3$ (6) is formed. The same product can also be synthesized from the reaction of $NaBH_4$ with Ru(II) chloride hydrate ($\sim$10:1) in ethanol in the presence of a 6 molar excess of PPh_3 and from the reaction between $NaBH_4$ and $RuCl_2(PPh_3)_2$ in the presence of PPh_3 in EtOH. The other two known Ru(II)-BH_4 complexes, $HRu(BH_4)(CO)L_3$ (L=PPh_3, PCy_3) (6), are formed from reactions between $NaBH_4$ and the red Ru(II) carbonyl ethanolic solutions (73) in the presence of an excess of the appropriate phosphine (6).

I.3.1.2. Cobalt, Rhodium and Iridium.

Table 6 lists a variety of BH_4 complexes formed by these three elements. For example, the reaction of $NaBH_4$ with Co(II) chloride in the presence of PPh_3 in ethanol produces the yellow, paramagnetic $Co(BH_4)(PPh_3)_3$ (5) which on recrystallization from nitrogen saturated benzene and n-hexane resulted in the uptake of varying amounts of dinitrogen and the formation of what is presumably $Co(BH_4)(N_2)(PPh_3)_3$.

Table 6.

Tetrahydroborate complexes of Co, Rh and Ir.

Complexes	Reagents	Reference
$Co(BH_4)(PPh_3)_3$	$NaBH_4 + CoCl_2 + PPh_3$	5
$HCo(BH_4)(PCy_3)_2$	$NaBH_4 + CoCl_2 + PCy_3$	68
$Rh(BH_4)(PPh_3)_3$	$NaBH_4 + RhCl(PPh_3)_3$	46
$Rh(BH_4)(CO)(PPh_3)_2$	$NaBH_4 + Rh(ClO_4)(CO)(PPh_3)_2$	74
$Rh(BH_4)(CO)(PCy_3)_2$	$NaBH_4 + RhCl(CO)(PCy_3)_2$	74
$Rh(BH_4)(CO)(Siphos)_2$	$NaBH_4 + RhCl(CO)(Siphos)_2$	75
$HRh(BH_4)(\underline{o}\text{-tolyl}_3P)$	$NaBH_4 + RhCl_2(\underline{o}\text{-tolyl}_3P) + \underline{o}\text{-tolyl}_3P$	46
$H_2Rh(BH_4)L_2$	$NaBH_4 + HRhCl_2L_2$	76
(L=tertiary bulky phosphine).		
$Rh(BH_4)Cl_2(dmf)(Py)_2$	$NaBH_4 + RhCl_3(Py)_3 + dmf$	77
$Rh(BH_4)Cl_2(Py)_2(C_5H_{12}NCl)$	$Rh(BH_4)Cl(Py)_2(dmf) + H_2 + CHCl_3$	77

Table 6, cont'd.

Complexes	Reagents	Reference
$Ir(BH_4)(CO)(PCy_3)_2$	$NaBH_4 + Ir(ClO_4)(CO)(PCy_3)_2$	74
$Ir(BH_4)(CO)(Siphos)_2$	$NaBH_4 + IrCl(CO)(Siphos)_2$	75
$H_2Ir(BH_4)(PR_3)_2$	$NaBH_4 + HIrCl_2(PR_3)_2$	76

The reflectance spectrum of $Co(BH_4)(PPh_3)_3$ is consistent with a d^8 tetrahedral system. It is very interesting that, when the above reaction is carried out in the presence of PCy_3 in a mixture of toluene and ethanol, no reduction of the Co(II) occurs, the only product being $HCo(BH_4)(PCy_3)_2$ (60).

Rhodium complexes of BH_4^- have been characterized in oxidation states III, II and I, (Table 6). Thus, treatment of $HRhCl_2L_2$ (L=bulky tertiary phosphine) with $NaBH_4$ gives (76) $H_2Rh(BH_4)L_2$. Addition of $NaBH_4$ to a solution of $RhCl_3(Py)_3$ in dimethylformamide or in dimethylformamide-chloroform gives a tetrahydroborate complex of composition $Rh(BH_4)Cl_2$-(dmf)$(Py)_2$ (77). In dmf, this complex absorbs hydrogen and produces $Rh(BH_4)Cl_2(Py)_2(C_5H_5NCl)$, containing piperidine hydrochloride (77).

The Rh(II) complex, $HRh(BH_4)L$ (L=o-tolyl$_3$P) is made by the reaction of an excess of $NaBH_4$ with a mixture of $RhCl_2L_2$ and L in EtOH (46). Some air-stable Rh(I)-BH_4 complexes have been reported by Vaska and coworkers (74). These are trans-$Rh(BH_4)$-$(CO)L_2$ (L=PPh_3, PCy_3) and they are made from the reaction of $NaBH_4$ with trans-$[Rh(A)(CO)L_2]$ (A=ClO_4^-,Cl^-) in a benzene\ EtOH mixture. A highly unstable Rh(I) complex $Rh(BH_4)(PPh_3)_3$ has been made from the reaction between $NaBH_4$ and $RhCl(PPh_3)_3$ in a mixture of benzene and EtOH (46). The preparation of this complex is very susceptible to slight variations in experimental conditions, and when the reaction time is extended slightly, $HRh(PPh_3)_3$ is formed. Another example of the way different ligands affect the final reaction product is illustrated by reactions between $NaBH_4$ and trans-$RhCl(CO)(PPh_3)_2$ in ethanol which gives $HRh(CO)(PPh_3)_3$ in the presence of PPh_3 (45), while the tris-(trimethylsilylmethyl)phosphine, (siphos), yields, under similar conditions, $Rh(BH_4)(CO)(Siphos)_2$ (75).

The Ir(III) complex, $H_2Ir(BH_4)L_2$ (L=bulkyl tertiary phosphine) is made in the same manner as its rhodium analog discussed above (76). Finally, two Ir(I) complexes, $Ir(BH_4)(CO)L_2$ (L=PCy_3 (74) and siphos (75)) have been made from similar reactions.

I.3.1.3. Nickel, Palladium and Platinum.

The BH_4 complexes of the Ni group metals are listed in Table 7 and , to give a complete picture, this table includes some compounds with non-phosphine ligands. The two compounds trans-$HNi(BH_4)L_2$ (L=PCy_3, PPr^i_3), are made from similar reactions involving $NaBH_4$ and trans $HNiClL_2$ (69). The very interesting diamagnetic Ni(I) complex, $Ni(BH_4)(PPh_3)_3$, is formed

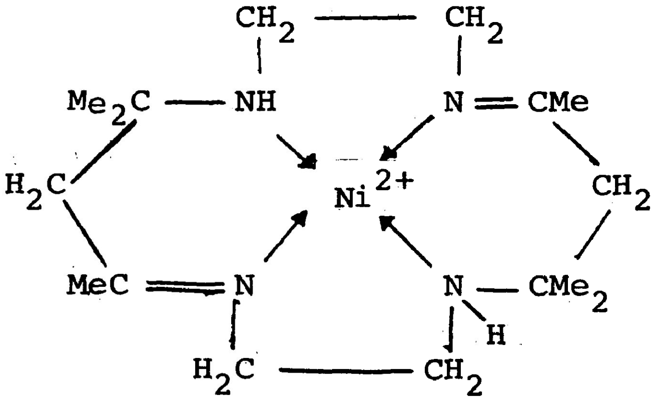
Table 7.

Tetrahydroborate complexes of Ni, Pd and Pt.

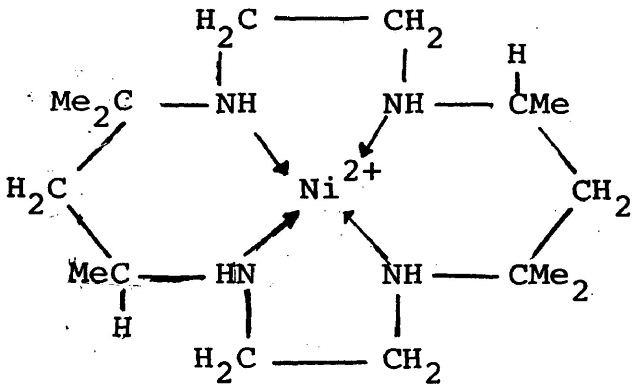
Complexes	Reagents	Reference
$HNi(BH_4)(PCy_3)_2$	$NaBH_4 + HNiCl(PCy_3)_2$	69
$HNi(BH_4)(PPr^i_3)_2$	$NaBH_4 + HNiCl(PPr^i_3)_2$	69
$(II_b)(BH_4)(ClO_4)$	$NaBH_4 + (II_a)(ClO_4)_2$	78
$(III)(BH_4)(ClO_4)$	$NaBH_4 + (III)(ClO_4)_2$	78
$(II_b)(BH_4)_2$	$NaBH_4 + (II_b)Cl_2$	78
$(II_a)(BH_4)_2$	$NaBH_4 + (II_a)Cl_2$	78
$Ni(BH_4)(PPh_3)_3$	$NaBH_4 + NiCl(PPh_3)_3$	5
$HPd(BH_4)(PCy_3)_2$	$NaBH_4 + HPdCl(PCy_3)_2$	69
$HPd(BH_4)(PPr^i_3)_2$	$NaBH_4 + HPdCl(PPr^i_3)_2$	69

when $NaBH_4$(6-10M excess) is added to $NiCl(PPh_3)$ in ethanol (5).

Besides tertiary phosphines, $Ni-BH_4$ complexes may be stabilized in the presence of various tetradentate amines (78). For example, a bis-tetrahydroborate compound is formed when $NaBH_4$ is added to an aqueous solution of the perchlorate of the nickel complex(I).

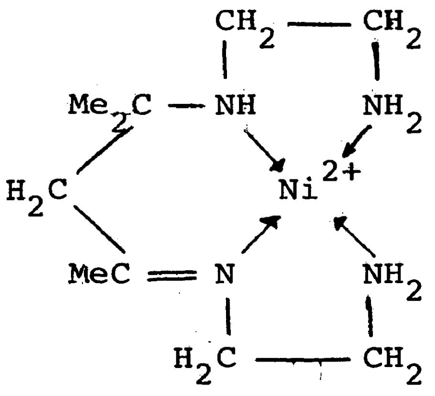


(I)



(IIa) and (IIb)

(IIa is an isomer of IIb)



(III)

Various other BH_4-amine complexes are listed in Table 7 and these are derived from the above structural units. There appears to be no reduction of Ni(II) to lower valent states in these systems.

There are no Pt-BH_4 complexes reported, and the two known Pd-BH_4 complexes, trans-$HPd(BH_4)L_2$ ($L=PCy_3$, PPr^i_3) are formed (69) in reactions totally analogous to those of the corresponding Ni systems discussed above.

I.3.1.4. Copper, Silver and Gold.

The first Cu-BH_4 complex was prepared by Cariati and Naldini (79) and, using similar methods, the range of complexes, with composition $Cu(BH_4)L_2$ (L=tertiary phosphine), has been recently extended by S.J. Lippard and D.A.Ucko (80). These and certain other related compounds are listed in Table 8 and all contain Cu(I). In each case the complexes are made by reactions between $NaBH_4$ and Cu(I) chloride in the presence of the appropriate phosphine. Similar reactions with Cu(II) lead also to Cu(I) complexes. Uncomplexed silver(I) tetrahydroborate is only stable below-30° C, but stabilization may be achieved by addition of triphenylphosphine yielding $Ag(BH_4)(PPh_3)_2$ (82).

I.3.1.5. Other Transition Elements.

Tetrahydroborate complexes of metals other than group VIII B and group I B have also been reported. They are listed in Table 9.

I.3.2. Structural Analysis of Tetrahydroborate Complexes.

I.3.2.1. X-ray, Electron and Neutron Diffraction.

There are four obvious types of MBH_4 geometries shown below, and the existence of all except type V, the monodentate case, has been established by either X-ray, electron or neutron diffraction methods.
The ionic structure IV is known for a number of alkali metal tetrahydroborates (63,88) and it is reasonable

Table 8.

Tetrahydroborate complexes of Cu and Ag.

Complexes	Reagents	Reference
$Cu(BH_4)(PPh_3)_2$	$NaBH_4 + CuCl + PPh_3$	80
	$NaBH_4 + CuCl_2 \cdot 2H_2O + PPh_3$	5
$Cu(BH_4)[P(\underline{p}\text{-}MeOC_6H_4)_3]_2$	$NaBH_4 + CuCl + P(\underline{p}\text{-}MeOC_6H_4)_3$	80
$Cu(BH_4)[P(\underline{p}\text{-}MeC_6H_4)_3]_2$	$NaBH_4 + CuCl + P(\underline{p}\text{-}MeC_6H_4)_3$	80
$Cu(BH_4)[P(\underline{m}\text{-}MeC_6H_4)_3]_2$	$NaBH_4 + CuCl + P(\underline{m}\text{-}MeC_6H_4)_3$	80
$Cu(BH_4)(dppe)$	$NaBH_4 + CuCl + dppe$	80
$Cu(BH_4)(DBP)_2$	$NaBH_4 + CuCl_2 + DBP$	5
$Cu(BH_4)(PPh_3)(Phen)$		79
$[Cu_2(BH_4)(PPh_3)_4]^+$	$Cu(BH_4)(PPh_3)_2 + HClO_4$	81
$Ag(BH_4)(PPh_3)_2$	$NaBH_4 + AgCl(PPh_3)_3 + PPh_3$	82

Table 9.

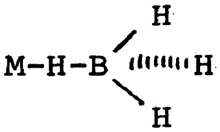
Tetrahydroborate complexes of the early transition metals.

Complexes	Reagents	Reference
$Ti(BH_4)_2(C_4H_9O) \cdot THF$	$B_2H_6 + Ti(OC_4H_9)_4 + THF$	83
$Ti(BH_4)(\pi\text{-}C_5H_5)_2$	$LiBH_4 + TiCl_2(\pi\text{-}C_5H_5)_2$	84
$Ti(BH_4)_2(\pi\text{-}C_5H_5)$	$LiBH_4 + TiCl_3(\pi\text{-}C_5H_5)$	9
$\left[HTi(BH_4)(\pi\text{-}C_5H_5)\right]_x$	$Ti(BH_4)_2(\pi\text{-}C_5H_5) + Me_3N$	9
$Zr(BH_4)_2(\pi\text{-}C_5H_5)_2$	$Li(BH_4) + ZrCl_2(\pi\text{-}C_5H_5)_2$	85
$\left[HZr(BH_4)(\pi\text{-}C_5H_5)\right]_x$	$Zr(BH_4)_2(\pi\text{-}C_5H_5)_2 + Me_3N$	9
$Zr(BH_4)Cl(\pi\text{-}C_5H_5)_2$	$Li(BH_4) + ZrCl_2(\pi\text{-}C_5H_5)_2$	85
$Hf(BH_4)_2(\pi\text{-}C_5H_5)_2$	$Li(BH_4) + HfCl_2(\pi\text{-}C_5H_5)_2$	86
$Nb(BH_4)Cl(\pi\text{-}C_5H_5)_2$	$Li(BH_4) + NbCl_5 + Na(C_5H_5)$	87

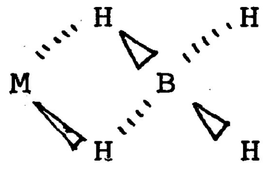
to presume that in the ammonia complexes such as $Cr(NH_3)_6(BH_4)_3$, $Co(NH_3)_4(CO_3)(BH_4)$, $Ni(NH_3)_6(BH_4)_2$, $Zn(NH_3)_4(BH_4)_2$ (89), the BH_4 is also ionic.

$M^+BH_4^-$

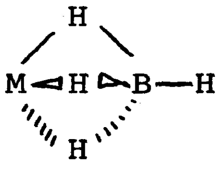
(IV)



(V)

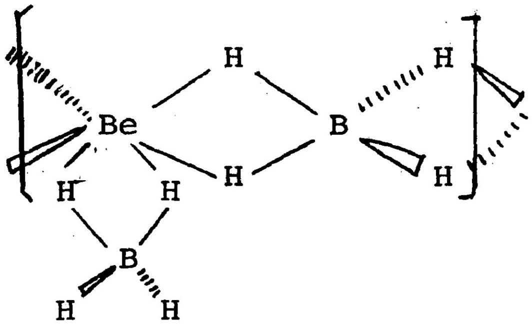


(VI)



(VII)

There are a number of transition metal tetrahydroborate complexes where the presence of bidentate BH_4 groups(structure VI) has been confirmed, examples being $Zr(BH_4)_2(\pi-C_5H_5)_2$ (9), $HCo(BH_4)(PCy_3)_2$ (68) and $Cu(BH_4)(PPh_3)_2$ (90) as well as uncomplexed $Al(BH_4)_3$ (88). The tridentate structure VII is mostly found with large metal ions, such as in uncomplexed $Zr(BH_4)_4$ (91) and $U(BH_4)(\pi-C_5H_5)$ (92). In addition to these four basic structures, the existence of tetradentate BH_4 groups has now been established (93) in the molecule $Be(BH_4)_2$, the structure of which is shown below:

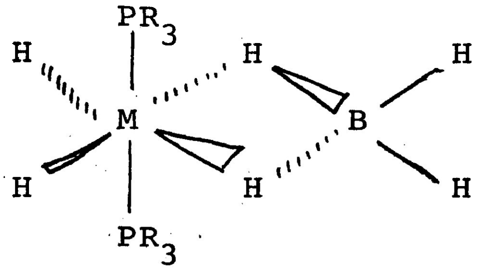


(VIII)

These compounds, where the mode of coordination of the BH_4 groups has been established, become important model systems so that, by comparisons of their physical properties, (particularly infrared spectra, see later) with the physical properties of other complexes, the structures of the latter may be deduced.

I.3.2.2. Nuclear Magnetic Resonance Spectra

The proton n.m.r. of the BH_4^- ion consists of four peaks of equal intensity due to the coupling between the protons and the ^{11}B nucleus (63). In the proton n.m.r. of diborane, the terminal protons and the bridging protons appear as two separate signals (94,95), but this is not, unfortunately, generally true for metal complexes of BH_4^-. Thus the proton n.m.r. spectra of many metal BH_4 complexes show magnetically equivalent hydrogens due to fluxional behavior, ie. rapid internal exchange of the BH_4 protons. Attempts to resolve the proton signals by running the spectra at low temperatures have not led to significant improvements (96,97) in terms of structural elucidations. In other cases, e.g. the nickel and palladium complexes $HM(BH_4)(PR_3)_2$ ($R=Pr^i$ or Cy) (69) the resonance of the BH_4 protons could not be observed because of the quadrupole broadening by boron. For $Cu(BH_4)(PPh_3)_2$ (98), the hydrogens of the BH_4 group appear as one extremely broad signal at 298° K but at low temperatures a broad singlet was observed due to thermal decoupling of the boron quadrupole nucleus. However, some nonfluxional tetrahydroborate complexes have been reported (76) where the signals for the bridge and terminal hydrogens of BH_4^- are resolved. At 300° K, the iridium complex $H_2Ir(BH_4)$-$(PR_3)_2$, (PR_3=bulky tertiary phosphine) gives a broad singlet at $\delta=-6.87$. With $^1H-{}^{11}B$ double resonance, the peak at $\delta=-6.87$ is sharpened and a new singlet appears at $\delta=6.86$. At 222° K the singlet at $\delta=-6.79$ (previously ca.-6.87 above) sharpens as does the peak at $\delta=7.05$ (previously ca.6.86 above and not observed at 300° K without ^{11}B coupling). The signal at $\delta=-6.87$ is thought to be the resonance of the bridging protons of IrH_2B and the peak at $\delta=6.86$ is for terminal B-H. The Rhodium analog shows a similar spectrum with bridging RhH_2B protons at $\delta=-4.53$ and terminal BH protons at $\delta=3.9$. This indicates that the tetrahydroborate complexes of $H_2M(BH_4)L_2$ (M=Rh or Ir, L=bulky tertiary phosphine) have a static structure as shown below.



(IX)

In general however, proton n.m.r. spectra have given only very limited information about the mode of coordination of the BH_4 group.

I.3.2.3. Vibrational Spectra.

In the absence of structural data from diffraction methods, infrared spectroscopy is the most useful technique for distinguishing between the different structures of tetrahydroborate complexes. The approximate frequency ranges expected for the infrared active bands of the structural types IV, V, VI and VII are shown in Table 10 (99).

A careful inspection of the data in Table 10 would suggest that it should not be too difficult to distinguish between the various structural types by infrared means. There are a number of reasons however why this is not always the case. For the ionic

Table 10. (99).

ir-Active Fundamental Vibrational Transitions for MBH_4 configurations.

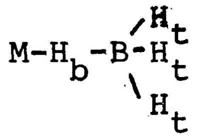
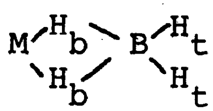
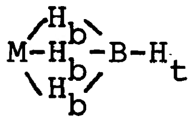
Structure	Approx. frequency	Type of internal Coordinate Change	Comment
IV $M^+BH_4^-$	2200-2300	$B\text{-}H_t$str.	broad, strong
	1050-1150	BH_2def.	broad, strong
V 	2300-2450	$B\text{-}H_t$str.	doublet, strong
	ca.2000	$B\text{-}H_b$str.	strong
	1000-1150	BH_3def.	strong
VI 	2400-2600	$B\text{-}H_t$str.	strong doublet
	1650-2150	$B\text{-}H_b$str.	strong, possibly shoulder
	1300-1500	bridge str.	broad, strong
	1100-1200	BH_2def.	strong

Table 10, cont'd.

	Structure	Approx. frequency	Type of internal Coordinate Change	Comment
VI		2450-2600	BH_t str.	strong
		2100-2200	B-H_b str.	doublet
		1150-1250	bridge def.	strong

structure (IV), usually 2 strong bands are observed in the infrared spectrum. The triply degenerate antisymmetric B-H stretching frequency appears as a broad band at $\sim 2250\text{cm}^{-1}$, and the sharper antisymmetric BH_2 bending frequency at $\sim 1100\text{cm}^{-1}$. For example, the infrared spectrum of sodium tetrahydroborate shows these two absorptions at 2270 and 1080cm^{-1} (100). For $Tl(BH_4)$ the antisymmetric B-H stretching frequency occurs at 2180cm^{-1}, the lower valuve probably arising from hindered rotation of the hydroborate ion in the crystal lattice (101). Transition metal complexes such as $Ni(NH_3)_6(BH_4)_2$ and $Nien_3(BH_4)_2$ show the ionic νBH_4^- at $\sim 2250\text{cm}^{-1}$ (7).

The infrared spectra of the proposed monodentate BH_4 complexes are shown in Table 11. When these data are compared with the expected monodentate frequencies, type V in Table 10, it is apparent that none of the compounds listed show the expected $B\text{-}H_b$ stretching frequency in the 2000cm^{-1} region. In the cases of $HRu(BH_4)(CO)L_3$, it is possible that this band may be coincident with the Ru-H or the Ru-CO stretching frequencies, and its absence from the other complexes will be discussed in detail later.

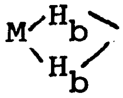
From the data on the bidentate structure VI, Table 10, it could be concluded that, since the expected strong broad absorption in the $1300\text{-}1500\text{cm}^{-1}$ range, due to the  $M\overset{H_b}{\underset{H_b}{\rightleftarrows}}B$ group, is unique to structure VI,

Table 11.

Infrared Spectra of Monodentate BH_4 Complexes.

Complexes	ν_{B-H_t}	ν_{B-H_b}	δ_{B-H}	Reference
$HRu(BH_4)(PPh_3)_3$	2382(s)	-	1119(m)	6
	2340(sh)			
$HRu(BH_4)(CO)(PPh_3)_3$	2382(s)	-	1119(m)	6
	2350(w)			
$HRu(BH_4)(CO)_2(PCy_3)_2$	2480(m)	-	—	6
	2430(m)			
$Co(BH_4)(PPh_3)_3$	2390(s)	-	1105(m)	5
	2340(sh)			
$Ni(BH_4)(PPh_3)_3$	2388(s)	-	1120(m)	5
	2350(sh)			

this absorption could be used to assign unequivocally this mode of coordination of the BH_4 group. The infrared spectra of the bidentate BH_4 complexes are listed in Table 12. All these complexes show the expected symmetric and antisymmetric $\nu B\text{-}H_t$ at 2400-2600cm^{-1} and the symmetric and antisymmetric $\nu B\text{-}H_b$ (which sometimes overlap) at 1650-2150cm^{-1}, but the frequency associated with the bridging unit is conspicuous by its absence.

Of the complexes listed in Table 12, only $Al(BH_4)_3$ and $HCo(BH_4)(PCy_3)_2$ show this band in the 1300-1500cm^{-1} region. Even $Cu(BH_4)(PPh_3)_2$, for which the structure has also been confirmed as having bidentate BH_4, does not show the bridging stretching frequency. A possible reason for the apparent absence of this band is that it occurs in a region of the spectrum which is either obscured by ligand vibrations or where assigment is made difficult because of the number and complexity of ligand vibrations (80).

Apart from the absence of the frequency associated with $M{<}^{H_b}_{H_b}{>}B$ group, the infrared spectra of the tridentate structure (type VII, Table 10) are quite similar to those of the bidentate structure VI. The spectra of the tridentate species show a single sharp $B\text{-}H_t$ stretching vibration at ~2560cm^{-1} compared with a doublet in the bidentate case. Thei.r.spectra of some known tridentate

Table 12.

Infrared spectra of bidentate BH_4 complexes.

Complexes	ν B-H_t	ν B-H_b	Bridge Stretch	δ B-H	Reference
*$Al(BH_4)_3$	2559	2050	1480	1175	102
	2493			1118	
*$HCo(BH_4)(PCy_3)_2$	2390	1958	1379		68
	2368				
$HNi(BH_4)(PCy_3)_2$	2340	2050	-	1140	69
		2020			
		1868			
$HNi(BH_4)(PPr^i_3)_2$	2360	2060	-	1130	69
		1860			
$HRh(BH_4)(o\text{-}tolyl_3P)$	2425	1966	-	1148	46
	2380	1850			
$Rh(BH_4)(CO)(PPh_3)_2$	2452			1149	74
	2416				

Table 12, cont'd.

Complexes	ν_{B-H_t}	ν_{B-H_b}	Bridge Stretch	δ_{B-H}	Reference
$Rh(BH_4)(CO)(PCy_3)_2$	2460	—	–	1174	74
	2402				
$Rh(BH_4)(CO)(Siphos)_2$	2385	–	—		75
	2370				
$Ir(BH_4)(CO)(PCy_3)_2$	2485	—	–		74
	2425				
$HPd(BH_4)(PCy_3)_2$	2330	1980	–	1070	69
	2260	1800			
$HPd(BH_4)(PPr^i_3)_2$	2363	1833	–		69
*$Cu(BH_4)(PPh_3)_2$	2392	1984			80
	2350	1924	–		
$Cu(BH_4)[P(p\text{-}MeOC_6H_4)_3]_2$	2385	2005	–		80
	2350	1961			

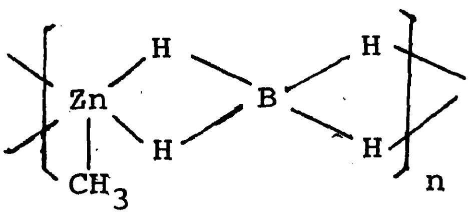
Table 12, cont'd.

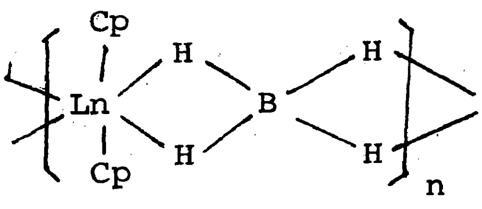
Complexes	ν_{B-H_t}	ν_{B-H_b}	Bridge Stretch	δ_{B-H}	Reference
$Cu(BH_4)[P(p-MeC_6H_4)_3]_2$	2382	1990	-		80
	2343	1930			
$Cu(BH_4)[P(m-MeC_6H_4)_3]_2$	2380	2010	-		80
	2343	1944			
$Cu(BH_4)(DBP)_2$	2340	2030	-	1065	5

*Bidentate BH_4 confirmed by diffraction methods.

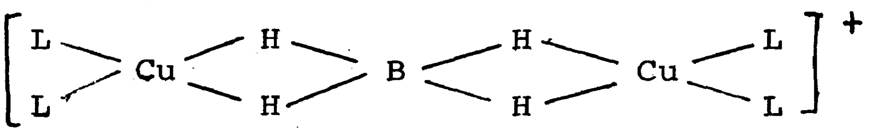
tetrahydroborate compounds are listed in Table 13.

As mentioned previously, polymeric tetradentate BH_4^- coordination has been reported in $Be(BH_4)_2$ (104). The major infrared difference between a tetradentate, bridging BH_4^- group and a bidentate BH_4^- is clearly that the former would have no $B-H_t$ frequency. Thus the spectrum of $Be(BH_4)_2$ shows bands at 2350 and 2330 cm^{-1} ($\nu B-H_b$), 1320 cm^{-1} (bridging stretching) and 1130 cm^{-1} ($\delta B-H$). Infrared spectral evidence has also led to the following structures being proposed.





Another exmple for the tetradentate bridging BH_4^- complex is the cationic $Cu(I)-BH_4$ complex, $[(Ph_3P_2Cu-(BH_4)Cu(PPh_3)_2]^+$, which only shows the bridging $B-H_b$ stretching frequency at 2140 cm^{-1} (128).



It is therefore clear from this discussion that a very careful assessment of infrared spectral data is necessary before structural assignments can be made and even then unambiguous conclusions are often not possible.

Table 13.

Infrared Spectra of Tridentate BH_4 Complexes.

Complexes	$\nu\,\text{B-H}_t$	$\nu\,\text{B-H}_b$	δ B-H	Reference
$Zr(BH_4)_4$	2560	2179	1210	99
	2472	2117		
$Hf(BH_4)_4$	2570	2197	1218	99
	2490	2128		
$U(BH_4)(\pi\text{-}C_5H_5)_3$	2480	2220	1160	103
		2160		

I.4. Homogeneous Hydrogenation.

Since the first homogeneously catalysed hydrogenation reaction was observed by Calvin in 1938, (105) and particularly since the Rh and Ru work of the 1960's (106,107) this field has undergone very rapid expansion. Numerous reactions have been studied , and for comprehensive surveys of homogeneous hydrogenation, the reader is referred to those written by Halpern (108), Harmon (109), Volpin (110) and James (111). The following is a very brief summary of the features of homogeneous catalytic hydrogenations relevant to this thesis.

I.4.1. Mechanism of Homogeneous Hydrogenation.

In hydrogenations, it is possible to distinguish between reactions where the sequence of activation of hydrogen, activation of substrate and transfer of hydrogen to the substrate are different. For example, in Scheme I,

$$M + H_2 \rightleftarrows M\cdot H_2$$

$$M\cdot H_2 + S \rightleftarrows S\cdot M\cdot H_2$$

$$S\cdot M\cdot H_2 \longrightarrow SH_2 + M$$

the activation of hydrogen takes place first through the formation of a hydride which then reacts with the substrate before final transfer occurs.

In <u>Scheme II</u>,

$$M + S \rightleftharpoons M{\cdot}S$$

$$M{\cdot}S + H_2 \rightleftharpoons H_2{\cdot}M{\cdot}S$$

$$H_2{\cdot}M{\cdot}S \rightleftharpoons H_2S + M$$

the activation of hydrogen occurs after the activation of substrate, While in <u>Scheme III</u>,

$$M + S \rightleftharpoons M{\cdot}S$$

$$M + H_2 \rightleftharpoons M{\cdot}H_2$$

$$M{\cdot}S + M{\cdot}H_2 \longrightarrow M + SH_2 + M$$

the activation of hydrogen and substrate is effected separately . Irrespective of the sequence of reactions, however, it is clear that in the reduction of a substrate, three basic processes must occur: (i) activiation of hydrogen by formation of M-H bonds, (ii) activation of the substrate and (iii) hydrogen transfer. Generally these three processes occur on the same metal center.

I.4.1.1. Activation of Hydrogen.

In all cases of homogeneous hydrogenations catalysed by transition metals, molecular hydrogen is activated or split by the catalyst with the formation of intermediate metal hydride complexes (108-111). Four ways of hydrogen activation have been distinguished.

a) Heterolytic splitting to form a monohydride.

This process is illustrated by the following examples (112-115) where the molecular hydrogen is

$$\mathrm{Rh^{III} + H_2 \rightleftharpoons Rh^{III}H^- + H^+}$$

$$\mathrm{Cu^{II} + H_2 \rightleftharpoons Cu^{II}H^- + H^+}$$

$$\mathrm{Ru^{III} + H_2 \rightleftharpoons Ru^{III}H^- + H^+}$$

split into a negative hydride ion which bonds to the metal catalyst and a proton which becomes associated with a Lewis base. In this type of hydrogen activiation, no change in oxidation state of the metal ion occurs. Reactivity depends on the substitution lability of the complex, the stability of the hydride complex and the presence of a suitable Lewis base.

b) Homolytic splitting to form a monohydride.

In this case, both hydrogen atoms become incorporated equivalently into the catalyst molecule and as shown in the following example (20), where

$$2[Co^{II}(CN)_5]^{3-} + H_2 \rightleftharpoons 2[HCo^{III}(CN)_5]^{3-}$$

the formation of hydride complex occurs with the simultaneous oxidation of the metal. The reactivity therefore depends on the ease with which the metal is oxidized and its ability to expand its coordination number.

c) Formation of a dihydride.

In this case, the hydrogen molecule is added reversibly and oxidatively to, for example, a coordinatively unsaturated d^8 system, e.g. $RhCl(PPh_3)_3$ (107) or $IrCl(CO)(PPh_3)_2$ (116), where both the coordination number and the oxidation state of the

$$RhCl(PPh_3)_3 + H_2 \rightleftharpoons H_2RhCl(PPh_3)_3$$

$$IrCl(CO)(PPh_3) + H_2 \rightleftharpoons H_2IrCl(CO)(PPh_3)_2$$

metal increase by two units. The activation of molecular hydrogen can take place in two possible ways. The first considers the partial donation of the bonding electrons of the hydrogen molecule into suitable, low lying vacant orbitals on the metal ion to form a transition state which can be represented as $M\cdots\cdots H_2^+$. The second possibility involves the transfer of an electron from the metal to an anti-bonding orbital of the hydrogen molecule, which, therefore, in this case, acts as an electron acceptor. The formation of this dative $M\cdots\cdots H_2^-$ bond is favored when the metal has a minimal positive charge and in the presence of electron donating ligands.

d) Electron transfer.

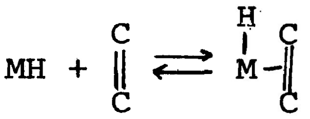
Finally, a simple redox process may occur without formation of a stable hydride intermediate e.g. (117)

$$Hg^{2+} + H_2 \longrightarrow Hg^o + 2H^+$$

I,4.1.2. Activation of Substrate.

In the homogeneous hydrogenation process, it is generally accepted that a vacant site on the transition metal complex is necessary. This coordination site may then be used to activate the substrate and place the substrate cis to the hydride.

Activation of organic substrates has been studied in detail for the hydrogenation of alkenes and alkynes (107). In most cases the hydrogenation occurs only when both the hydrogen (through a covalent ∡ bond) and the substrate are coordinated to the same metal M. It is generally accepted that the substrate is activated through the formation of a π-complex.

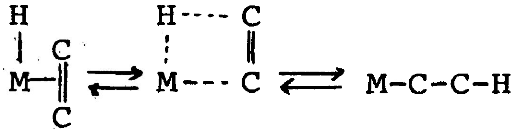


$$MH + \overset{C}{\underset{C}{\|}} \rightleftarrows \overset{H}{\overset{|}{M}}-\overset{C}{\underset{C}{\|}}$$

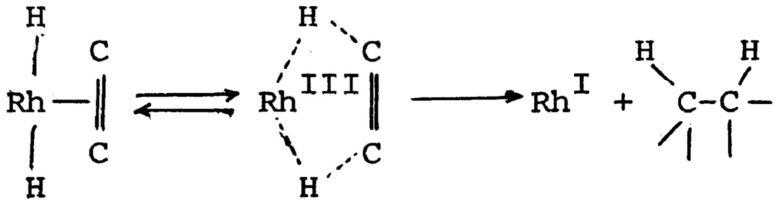
Although several π-olefin hydrido complexes have been isolated, there is little direct evidence for their formation in the activation process (118).

I.4.1.3. <u>Hydrogen Transfer</u>.

After the activation of hydrogen and substrate an insertion reaction then occurs. Usually the substrate is inserted between the metal and a hydrogen by a four-center reaction followed by formation of a σ-complex. However, formation of the latter is not always observed and during, for example, hydrogenation of alkenes by a complex rhodium hydride (46) no σ-C-Rh bonding has been detected by n.m.r. spectrometry. This hydrogenation process is thought to involve the simultaneous transfer of two hydrogens to the alkene through two three-center transition states.



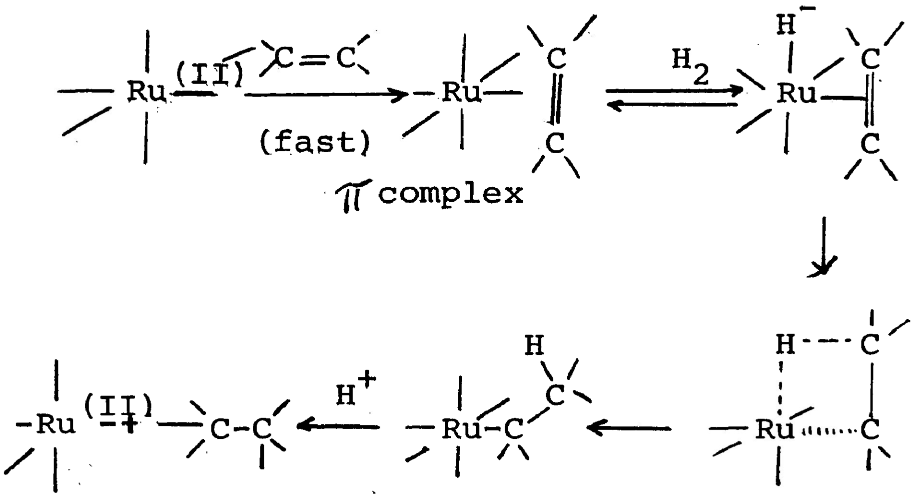
$$\overset{H}{\overset{|}{M}}-\overset{C}{\underset{C}{\|}} \rightleftarrows \begin{array}{ccc} H & \cdots & C \\ \vdots & & \| \\ M & \cdots & C \end{array} \rightleftarrows M-C-C-H$$



I.4.2. Examples of Homogeneous Hydrogenation.

I.4.2.1. Hydrogenation of Olefins by Ruthenium(II) Chloride Complexes.

In acid solutions, ruthenium(II) chloride complexes are active catalysts for the hydrogenation of certain substituted ethylenes (106) via the formation of monohydrides. This process is thought to occur through Scheme II, as discussed above. Thus, the substrate is activated by interaction with Ru(II)



to form a π complex. Heterolytic splitting of molecular hydrogen then occurs followed by the formation of a σ complex through a four center transition state.

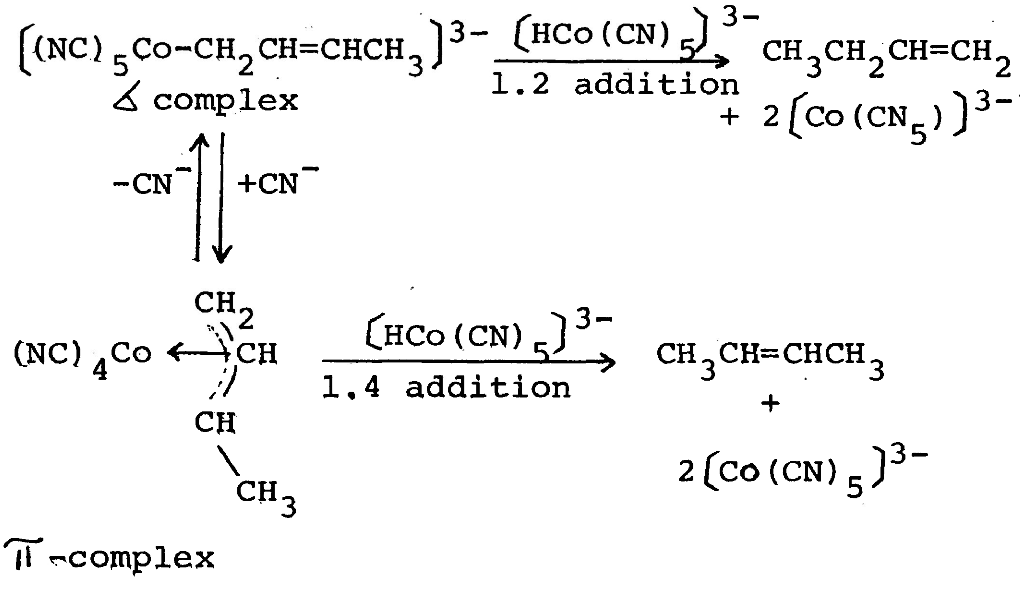
Electrophilic attack by a proton at the carbon attached to the metal liberates the reduced olefin and regenerates the ruthenium catalyst.

I.4.2.2. Hydrogenation of an Olefin by Pentacyanocobaltate(II).

The hydrogenation of butadiene in aqueous solutions of pentacyanocobaltate(II) (20) is an example of a reaction which proceeds according to Scheme I (above).

$$2\left[Co^{II}(CN)_5\right]^{3-} + H_2 \rightleftharpoons 2\left[HCo^{III}(CN)_5\right]^{3-}$$

$$\left[HCo^{III}(CN)_5\right]^{3-} + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \left[(NC)_5Co{-}CH_2{-}CH{=}CH{-}CH_3\right]^{3-}$$



The molecular hydrogen is activated by the catalyst through homolytic splitting followed by activation of the substrate. The σ-complex, formed by the reaction of the hydride with the substrate, is subsequently converted into a π-complex. The formation of the latter depends mainly upon the concentrations of CN^-. Thus at high concentrations formation of the π-complex is unfavorable and the main product is 1-butene, while at low cyanide concentrations, the π-complex can be formed easily and the main product is 2-butene.

I.4.2.3. Hydrogenation of an Olefin by a Rhodium(I) Chloride Complex.

The hydrogenation of ethylene and other olefins calalysed homogeneously by $RhCl(PPh_3)_3$ in benzene solution (119) involves the formation of a cis-dihydride intermediate, probably by the previously defined Scheme I mechanism, as illustrated below:

$$RhCl(PPh_3)_3 \underset{PPh_3}{\overset{solvent}{\rightleftharpoons}} RhCl(PPh_3)_2(S) + PPh_3$$

$$\begin{tikzcd}
RhCl(PPh_3)_2(S) + H_2 \arrow[r, shift left] \arrow[d, shift left, "olefin"] & H_2RhCl(PPh_3)_2(S) \arrow[l, shift left] \arrow[d, "olefin"] \\
RhCl(PPh_3)_2(olefin) \arrow[u, shift left] \arrow[r, "H_2"'] & RhCl(PPh_3)_2(S) + alkane
\end{tikzcd}$$

I.4.3. Literature Reports on the Catalytic Properties of Tetrahydroborate Complexes.

When compared with the other complexes (e.g. hydrides, halides, carbonyls, phosphines and various mixed ligand complexes) the catalytic properties of tetrahydroborate complexes have been relatively little studied. A number of tetrahydroborate complexes are active for a variety of catalytic reactions but the kinetics have not in general been studied in detail. The following is a summary of the available data on such systems.

Mixtures of Ni(II) chloride and $NaBH_4$ in dmf are effective in the hydrogenation of methyl linoleate at room temperature under hydrogen at atmospheric pressure (120), although the similar Rh(III) system is (~10 times) more active under comparable conditions. The former nickel system is also effective in the homogeneous hydrogenation of alkenes, cycloalkenes, conjugated dienes and polyunsaturated vegetable oil fatty acid components (121). Terminal alkenes are more readily hydrogenated than the internal alkenes and in both cases, the catalyst is selective and shows little tendency to cause positional isomerization. Although the active species has not been isolated, the color of the catalytic mixture (121) resembles that of soluble Ziegler-type catalysts, and on this basis, it was suggested that the catalyst is possibly $NiCl(BH_4)(dmf)_3$. This system has also been studied by Strohmeier and Steigerwald (122), who found that ethyl acrylate, 1,3-cyclohexene, 1,3-and 1,5-cyclooctadiene are hydrogenated to ethylpropionate, cyclohexane and cyclooctene respectively under mild conditions (0-100°C, 1 atm pressure).

The complex $RhCl_2(BH_4)(Py_2)(dmf)$, which is obtained from $RhCl_3Py_3$ and $NaBH_4$ in dmf, is also an active catalyst for homogeneous hydrogenations of both straight chain and cyclic alkenes (77). The hydrogenation rates of the terminal olefins, e.g., 1-pentene, 1-hexene, 1-heptene and 1-octene, are only marginally affected by variation in molecular size, but the cycloalkenes, e.g. Cyclopentene, cyclohexene, cycloheptene and cyclooctene, show very significant rate variations with structure. In addition to the hydrogenation of these olefins and of methylphenylbutenoate (120), various steroid 4-en-3-ones, as well as $-N=N-$, $-N=C<$ and NO_2 groups, have been successfully hydrogenated with this catalyst (123).

Finally, $HCo(BH_4)(PCy_3)_2$ is an active and selective catalyst for hydrogenation and isomerization at room temperature and less than atmospheric pressure (68). Initial rates are in the order of 1-olefin >

styrene>2-alkene>isoprene, butadiene. Isomerization causes a marked decrease in the hydrogenation rate.

I.5. Aim of Work.

It is clear from these introductory sections that reactions of $NaBH_4$ with transition metals lead to many different products depending on reaction conditions. While metal hydrides are the most widely studied group of products, there are a significant number of complexes involving coordinated BH_4^-, which may be stabilized by the presence of certain ligands, especially tertiary phosphines. Preliminary studies have suggested that coordinated BH_4 complexes are formed as intermediates in the reduction of transition metals by $NaBH_4$ in the presence of phosphines and indeed, a mechanism for such reductions has been proposed (5). Furthermore, a number of metal $-BH_4$ complexes have been shown to possess catalytic properties, especially in homogeneous hydrogenations, but little kinetic data are available.

The main objects of the work described in this thesis are to further investigate the reductions of some group VIII metals (especially Ni and Co) by $NaBH_4$ in the presence of phosphines. Of particular interest and importance are the conditions necessary for the preparation, isolation and characterization of low valent intermediates which, in turn, should lead to a better understanding of the detailed mechanism of the reduction of metal salts by $NaBH_4$. Furthermore, the potential catalytic properties of the reduction products are of great interest, and this thesis presents a preliminary study of this topic in the form of kinetic data on one transition metal $-BH_4$ complex.

II. EXPERIMENTAL

II. 1. Chemicals.

Sodium tetrahydroborate, hydrated cobalt(II) chloride, cobalt(II) perchlorate and nickel(II) chloride were obtained from British Drug Houses Ltd.. Hydrated ruthenium (III) chloride was obtained from Engelhard Industries and sodium hexafluorophosphate and sodium tetraphenylborate from Alfa products, Ventron Corporation. All the above chemicals were used without further purification. Triphenylphosphine was obtained from Aldrich Chemical Co. Ltd. and was recrystallized from hot ethanol before use.

The complexes $CoX_2(PPh_3)_2$ (X=Cl, Br or I) (124), $NiX_2(PPh_3)_2$ (X=Cl, Br or I) (125), and $RuCl_2(PPh_3)_2$ (107), were prepared by standard literature methods.

Due to the oxygen sensitivity of the complexes, all reactions were carried out in a glove box which was continuously flushed with dry, oxygen free nitrogen at a rate of 3 l. per min.. When not in use, the glove box was maintained at a positive pressure of nitrogen to minimize the inward diffusion of air.

Reagent grade benzene was heated under reflux with calcium hydride for three hours and then distilled. 1-Hexene was distilled after first stirring with iron(II) chloride for ~12 hours and then heating under reflux with calcium hydride for three hours. All other solvents were reagent grade. All solvents were degassed with oxygen free nitrogen and stored over type 4A molecular sieves in the glove box.

In the catalytic reactions, hydrogen gas (Matheson Gas Co.) was passed through a deoxocatalyst tube before admission to the vacuum system.

II.2. Instrumental Procedures.

All samples used for physical measurements were protected from atmospheric oxygen. Infrared studies were carried out on a Beckman IR12 infrared spectrophotometer. The samples were mounted as nujol mulls between polyethylene plates (200-650 cm^{-1}) and between sodium chloride plates (650-4000 cm^{-1}). The spectra were calibrated with a polystyrene reference film. Electronic (solution and reflectance) spectra were recorded on a Cary 14 spectrophotometer. Room temperature magnetic moments in the solid state were measured by the Gouy method in a double ended tube calibrated with $Nien_3(S_2O_3)$ or in solutions using the n.m.r. method described by Evans (126). N.M.R. data were obtained from a Varian Associates model A60-A spectrometer. Conductivity measurements were made on a YSI model 31 conductivity bridge. Samples for X-ray powder diffraction were sealed in Lindeman X-ray and photographs were recorded on Debye-Scherrer type cameras (114.6 mm dia.) using nickel filtered copper Kα radiation from a Phillips PW1130, 3KW X-ray generator.

Chemical analyses for nickel and cobalt were performed using standard volumetric procedures with E.D.T.A., after first degrading the metal complexes by prolonged treatment with concentrated HNO_3. Carbon, hydrogen and nitrogen analyses were carried out under nitrogen atmospheres on a Perkin-Elmer model 240 CHN analyser.

II.3. Synthesis.

II.3.1. Chlorotris(triphenylphosphine)cobalt(I), $CoCl(PPh_3)_3$.

The synthesis of $CoCl(PPh_3)_3$ was reported by Sacco who reacted a warm ethanolic solution of Co(II) chloride and triphenylphosphine with sodium tetrahydroborate (127). This reaction however does not lead to a pure compound, and only approximately 50% of the resulting yellow green product dissolved in benzene from which the green $CoCl(PPh_3)_3$ was precipitated by addition of ethanol.

Analysis: calc. for $CoCl(PPh_3)_3$		
	C 73.6	H 5.2%
found.	C 73.4	H 5.3%

d-spacings (relative intensities*):

9.60(5), 8.89(10), 5.40(2), 4.94(2), 4.35(2), 3.85(5), 3.57(5), 3.41(3), 2.86(1).

The yellow brown residue which was insoluble in benzene was not further investigated. In all subsequent reactions involving $CoCl(PPh_3)_3$, the pure recrystallized product was used otherwise more complex reactions occurred

II.3.2. Tetrahydroboratotris(triphenylphosphine)-cobalt(I) $Co(BH_4)(PPh_3)_3$.

II.3.2.1. $CoCl(PPh_3)_3/NaBH_4/PPh_3$.

A suspension of $NaBH_4$ (~0.2g) in ethanol (~10 ml) was added dropwise to a stirred suspension of $CoCl(PPh_3)_3$ (~0.4 g) and PPh_3 (~0.4 g) in ethanol (~15 ml). The resultant molar ratio of $CoCl(PPh_3)_3$:PPh_3:$NaBH_4$ was 1:3:10. After addition of all the $NaBH_4$ suspension, the mixture was stirred for four days.

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*Estimated intensities based on an arbitrary scale of 0-10.

The resulting yellow green precipitate was filtered off, washed with ethanol, water, ethanol and ether, and finally dried under high vacuum for three hours. Attempts to recrystallize this product, e.g. from benzene or THF, resulted in decomposition to $Co(BH_4)(PPh_3)_2$ (see later).

Analysis: calc. for $Co(BH_4)(PPh_3)_3$

C. 75.4, H. 5.7, Co 6.8 %

found, C. 73.1, H. 5.9, Co 7.3 %

d-spacings (relative intensities).

9.67(5), 8.99(10), 5.41(2), 4.91(2), 4.36(2)
3.85(5), 3.58(5), 3.42(2), 2.86(1).

II.3.2.2. $Co(BH_4)(PPh_3)_2/PPh_3$

PPh_3 (~0.3 g) was added to a suspension of $Co(BH_4)(PPh_3)_2$ (~0.3 g) in ethanol (~25 ml), giving a molar ratio of the reactants, $Co(BH_4)(PPh_3)_2 : PPh_3$ of 1:3. The mixture was stirred for four days during which time the color changed slowly from dark green to yellow green. The product, which was collected, washed and dried as described above was shown from its x-ray powder diffraction pattern, to be $Co(BH_4)(PPh_3)_3$.

Chemical analyses of different samples of $Co(BH_4)(PPh_3)_3$ were variable for reasons to be discussed later.

II.3.2.3. Co(II) chloride/$NaBH_4$/PPh_3.

As a potential route to Co-BH_4 complexes, reactions of $CoCl_2$, PPh_3 and $NaBH_4$ in ethanol were extensively investigated under conditions where the molar ratio of the reactants, reaction time and reaction conditions were systematically varied. Thus, although reactions were investigated where the molar ratios of Co : PPh_3: $NaBH_4$ were varied from 1:3:5 up to 1:10:20, it was found that the nature of the product(s) formed is more dependent on the rate of addition of $NaBH_4$ than on the ratio of reactants. For example, if the rate of addition of the $NaBH_4$ suspension is very slow (addition time longer than 30 minutes), only $CoCl(PPh_3)_3$ was produced even though the mixture was stirred for up to 3 or 4 days. If, on the other hand, the $NaBH_4$ suspension was added more rapidly (less than ~3 mins.), mixtures of $H_3Co(PPh_3)_3$ and $HCo(N_2)(PPh_3)_3$ were formed. In addition, varying amounts of Ph_3P-BH_3 were also produced in these reactions, apparently formed from the presence of small amounts of oxygen.

When the above reactions were carried out in air, large amounts of Ph_3P-BH_3, Ph_3P=0 and probably Co(II)-OH species were produced.

II.3.3. Tetrahydroboratobis(triphenylphosphine)-cobalt(I) $Co(BH_4)(PPh_3)_2$.

II.3.3.1. $CoCl(PPh_3)_3/NaBH_4$.

A suspension of $NaBH_4$ ($\sim$0.2 g) in ethanol ($\sim$10 ml) was added dropwise into a stirred solution of $CoCl(PPh_3)_3$ ($\sim$0.4 g), (molar ratio 10:1) in benzene ($\sim$15 ml). The green solution became brownish green and quickly precipitated dark green crystals. The product was filtered off, washed with ethanol, water, ethanol and ether, and then dried under high vacuum for three hours. Recrystallization from benzene or THF resulted in no change in the final compound.

Analysis: calc. for $Co(BH)_4(PPh_3)_2$

C. 72.3, H. 5.7, Co 8.8 %

found. C. 72.1, H. 6.0, Co 9.2 %

d-spacings (relative intensities):

13.52(8), 9.62(1), 8.70(10), 7.85(2), 6.30(1)
5.77(1), 4.95(1), 4.71(5), 4.37(7), 3.86(3)
3.35(1).

II.3.3.2 $CoCl_2(PPh_3)_2/NaBH_4/PPh_3$.

A suspension of $NaBH_4$ ($\sim$0.2 g) in ethanol ($\sim$10 ml) was added dropwise to a blue suspension of $CoCl_2(PPh_3)_2$ ($\sim$0.3 g) and PPh_3 ($\sim$0.3 g) in benzene (15 ml).

The resultant molar ratio of $CoCl_2(PPh_3)_2$: PPh_3 : $NaBH_4$ was 1:3:10. A gas, (presumably hydrogen), was generated during the initial stages of $NaBH_4$ addition and the blue solution changed immediately to green and then within ~10 mins., to brownish green. After the addition of all the $NaBH_4$ suspension, dark green crystals were produced. The product was then filtered off, washed, dried and recrystallized as described above and shown to be $Co(BH_4)(PPh_3)_2$ by its X-ray powder diffraction pattern.

II.3.3.3. $Co(BH_4)(PPh_3)_3/PPh_3$.

$Co(BH_4)(PPh_3)_3$ (~0.3 g) was dissolved in benzene (~30 ml) either in the absence of PPh_3 or with additional PPh_3 (Co:PPh_3 up to 1:10). The solution was then filtered and concentrated under vacuum at room temperature until the total volume was reduced to ~15 ml. The dark green product was precipitated by the addition of absolute ether (~20 ml), filtered off, washed with ether and dried under high vacuum for three hours and shown to be $Co(BH_4)(PPh_3)_2$.

II.3.3.4. Co(II) chloride/PPh_3/$NaBH_4$.

A suspension of $NaBH_4$ (~0.2 g) in ethanol (~10 ml) was added dropwise to the stirred suspension of $CoCl_2 \cdot 6H_2O$ (~0.15 g) and PPh_3 (~1 g) in benzene or toluene or benzene/ethanol (2:1) or toluene/ethanol (2:1) (~10 ml). A gas (presumably hydrogen) was generated during the initial stages of $NaBH_4$ addition and the blue suspension changed immediately to green and then brownish green (within 10 minutes). The dark green crystals were filtered off, washed, dried and recrystallized as described above. The product was shown to be $Co(BH_4)(PPh_3)_2$ by its x-ray powder diffraction pattern.

II.3.3.5. Co(II) perchlorate/$NaBH_4$/PPh_3.

A suspension of $NaBH_4$ (~0.2 g) in ethanol (~10 ml) was added dropwise to a suspension of $Co(ClO_4)_2$ (~0.15 g) and PPh_3 (~ 0.7 g) in ethanol (~15 ml). The resultant molar ratio of $Co(ClO_4)_2$: PPh_3 : $NaBH_4$ was 1:6:10. A gas (presumably hydrogen) was generated in the initial stages of the addition of the $NaBH_4$ suspension and the color of the solution turned from pink to greenish yellow. The mixture was stirred for three hours, after which the yellow green product was filtered off, washed and dried as described above, and then recrystallized from benzene or THF to give dark green crystals of $Co(BH_4)(PPh_3)_2$.

Chemical analyses of samples of $Co(BH_4)(PPh_3)_2$

made by the different reactions described above, and, in same cases, after repeated recrystallizations, were variable and will be discussed later.

II.3.2.6. Other Reactions.

The reactions of $CoX_2(PPh_3)_2$ (X=Cl or Br) and $NaBH_4$ in ethanol, both in the presence and absence of free PPh_3 were investigated as potential routes to $Co-BH_4$ complexes. No such pure complexes could be isolated from any of a large number of reactions where reaction times were varied from ~30 minutes up to 2 hours and where molar ratios of $Co:NaBH_4$ were varied between 1:2 and 1:20. The products from these reactions were shown to be mixtures of $CoCl_2(PPh_3)_2$ and $CoCl(PPh_3)_3$, in the absence of PPh_3. As reaction times were extended (up to ~5 hours), the presence of $Co(BH_4)(PPh_3)_3$ and $Co(BH_4)(PPh_3)_2$ was detected (from i.r. spectral data). Similar reactions in the presence of additional PPh_3, ($Co:PPh_3$ 1:3) and with various amounts of $NaBH_4$ yielded $CoCl(PPh_3)_3$ as the only product when the reaction time was less than 3 hours. Longer reactions, (up to ~15 hours) produced mixtures of $H_3Co(PPh_3)_3$, $HCo(N_2)(PPh_3)_3$ and $Co(BH_4)(PPh_3)_2$.

II.3.4. Tetrahydroboratotris(triphenylphosphine)-Nickel(I) $Ni(BH_4)(PPh_3)_3$.

This compound was synthesized in a way similar to that reported in the literature (5). A suspension of $NaBH_4$ (~0.2 g) in ethanol (~10 ml) was added dropwise to the stirred suspension of $NiCl_2$ (~0.1 g) and PPh_3 (~0.6 g) in ethanol (~25 ml). A gas (presumably hydrogen) was generated rapidly during the initial stages of the addition of the $NaBH_4$ suspension. The color of the solution changed from green to orange and then slowly to reddish brown. The mixture was stirred for three hours, when the yellow brown precipitate was filtered off, washed with ethanol, water, ethanol, and ether and then dried under vacuum for three hours. Attempts to recrystallize this compound from benzene or THF followed by addition of alcohol resulted in immediate decomposition to compounds containing no coordinated BH_4.

Analysis: calc. for $Ni(BH_4)(PPh_3)_3$

C. 75.4, H.5.7 Ni 6.8 %

found. C. 74.8, H.5.9 Ni 6.4 %

d-spacing (relative intensities):

9.63(7), 8.92(10), 7.48(2), 6.30(2), 5.42(2)
4.45(4), 4.34(4), 4.04(2), 3.88(5), 3.44(2).

This complex, $Ni(BH_4)(PPh_3)_3$, is pyrophoric. It turns black and burns instantly when exposed to air and therefore it is essential that great care be taken to exclude all traces of oxygen during its synthesis, otherwise products contaminated with varying amounts of $Ph_3P=O$, Ph_3P-BH_3 and Ni(O)-PPh_3 complexes will be obtained.

II.3.5. Bis(tetrahydroborato)tris(triphenylphosphine)-dinickel(I) $Ni_2(BH_4)_2(PPh_3)_3$.

A suspension of $NaBH_4$ (~0.2 g) in ethanol (~10 ml) was added to a stirred suspension of $NiI_2(PPh_3)_2$ (~0.4 g) in ethanol (~15 ml). The molar ratio of $NiI_2(PPh_3)_2$: $NaBH_4$ was 1:10. In the initial stages of addition of the $NaBH_4$ suspension, a gas was generated rapidly (presumably hydrogen). The dark brown solution was stirred for 15 mins. after the addition of all the $NaBH_4$, and then filtered. The dark brown solid was washed with ethanol, water and ethanol, and finally with ether until all the brown $NiI_2(PPh_3)_2$ was removed and the ether washings were colorless. The remaining green product was then recrystallized from benzene and ether.

Analysis: calc. for $Ni(BH_4)(PPh_3)_{1.5}$

C. 69.4, H. 5.7, Ni 12.6 %

found. C. 69.5, H. 5.6, Ni 12.6 %

d-spacings (relative intensities):

11.81(3), 9.24(10), 8.45(10), 6.96(1), 6.22(5),

4.94(1), 4.79(1), 4.61(1), 4.45(7), 4.10(6).
This green compound turns black and burns instantly when exposed to air.

II.3.6. Tris(triphenylphosphine)nickel(I)hexafluorophosphate $[Ni(PPh_3)_3][PF_6]$.

A solution of $NaPF_6$ (~0.2 g) in ethanol (~10 ml) was added to the stirred suspension of $Ni(BH_4)(PPh_3)_3$ (~0.2 g) and PPh_3 (~0.2 g) in ethanol (~15 ml).
A small amount of gas was generated during the initial stages of addition of the $NaPF_6$ solution. The color of the mixture changed slowly from reddish brown to yellow brown. After stirring for two hours, the pale yellow precipitate was filtered off, washed with ethanol, water, ethanol and ether, and finally recrystallized from THF.

Analysis: calc. for $[Ni(PPh_3)_3][PF_6]$.
C. 65.5, H.4.6, Ni. 5.9.%
found. C. 65.2, H.4.9, Ni. 6.1 %

d-spacings (relative intensities):
11.01 (3), 10.14(2), 8.95(10), 8.05(2), 7.40(5), 4.71(1), 4.41(10), 4.25(3), 3.98(4), 3.78(3).

II.3.7. Acetonitriletris(triphenylphosphine)nickel(I)-hexafluorophosphate $[Ni(PPh_3)_3(CH_3CN)][PF_6]$.

$[Ni(PPh_3)_3][PF_6]$ (~0.2 g) was dissolved in acetonitrile (~10 ml) in the presence of free PPh_3 (~0.1 g). A small amount of gas was generated as the $[Ni(PPh_3)_3][PF_6]$ dissolved in CH_3CN to form an orange colored solution. The solution was filtered to remove traces of a residue and then the filtrate was concentrated under vacuum to ~2 ml. Addition of ether (~5 ml) produced orange crystals which were filtered off, washed with ether and dried under high vacuum for three hours.

Analysis: calc. for $[Ni(PPh_3)_3(CH_3CN)][PF_6]$

C. 65.2, H. 4.7, N. 1.4, Ni. 5.7 %

found. C. 64.7, H. 4.8, N. 1.3, Ni. 6.1 %

d-spacings (relative intensities):

10.54(10), 9.35(6), 8.01(2), 7.55(8), 6.21(3)
5.42(5), 5.11(7), 4.44(8), 4.26(2), 3.05(1).

II.3.8. Hydridotetrahydroboratotris(triphenylphosphine)-ruthenium(II) $HRu(BH_4)(PPh_3)_3$.

A suspension of $NaBH_4$ (~0.23 g) in ethanol (~10 ml) was added dropwise to a supension of $RuCl_2(PPh_3)_3$ (~0.5 g) and PPh_3 (~0.4 g) in ethanol (~20 ml). The resultant molar ratio of $RuCl_2(PPh_3)_3$: PPh_3 : $NaBH_4$ was 1:3:10. The mixture was stirred for three hours during which the color of the mixture changed slowly from brown to yellow brown and then to yellow.

The product was filtered off, washed with ethanol, water, ethanol and ether, and finally recrystallized from benzene and dried under vacuum for three hours.

Analysis: calc. for $HRu(BH_4)(PPh_3)_3$

C. 72.1, H. 5.6.

found. C. 72.4, H. 5.3.

d-spacings (relative intensities):

10.36(8), 9.65(10), 4.68(3), 4.38(8), 3.75(1).

II.4. Apparatus for Catalysis Studies.

The apparatus for catalytic studies consists of a vacuum line as shown in Figure 1. The rate of hydrogenation was followed by measuring the drop in pressure within the system as the reaction progressed.

The reaction took place in a 100 ml three-necked round bottom flask. One neck was fitted with a burette which contained the liquid substrate. If a solid substrate was used, the flask was fitted with a rotating side arm from which a teflon bucket could be suspended. The other neck was fitted with a rotating side arm on which a teflon bucket containing the catalyst was suspended.

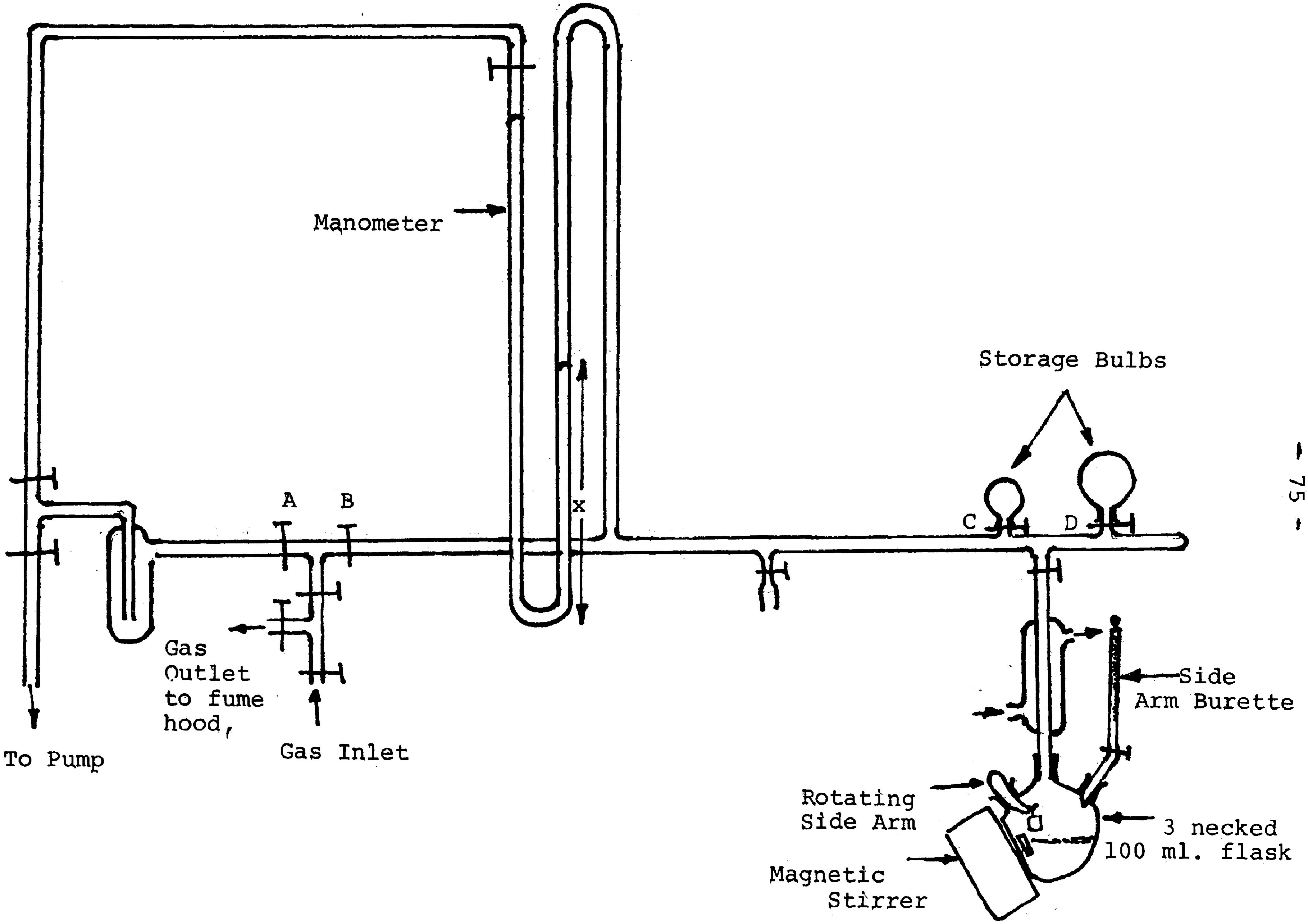


Figure 1. Apparatus for Catalytic Studies.

II.5. Procedure for Catalytic Studies.

Apiezon L grease was used on all stopcocks and joints. The substrate (liquid) was placed in the side-arm burette in the glove box and was stoppered before transfer to the vacuum line. The required amount of benzene was placed in the reaction vessel with a teflon-coated magnetic stirrer. The catalyst was weighed into the teflon bucket under a pure nitrogen atmosphere and then attached to the rotating side arm which was placed in the reaction vessel. The flask was then attached to the vacuum line via a condenser and the system evacuated. The benzene was then frozen with liquid nitrogen and the remaining air was removed by evacuating the flask. The whole system was flushed twice with hydrogen while the benzene was still frozen and then hydrogen was admitted until a reading of ~20 cm was obtained on the manometer. The benzene was allowed to warm up to room temperature in the presence of hydrogen and was then stirred for a few minutes in order to allow the hydrogen to exchange with any residual oxygen. The freezing, flushing and warming up procedure was repeated twice in order to ensure removal of all air. The catalyst was added by rotating the side-arm and the solution was stirred until all the catalyst was dissolved. The required amount of substrate was then added to the flask from the burette and the desired amount of hydrogen was allowed into the system. At this time, the stopcock to the storage bulbs (C and D) and the stopcock between the gas inlet and flask (B) were closed. When stirring commenced, the pressure drop of hydrogen within the system was recorded as a function of time.

After the run, the solution was frozen and the whole system was evacuated. Stopcock B was closed, the solution was warmed up to room temperature and the partial pressure of the solution was recorded.

II.6. Calculation of the Rate of Hydrogenation.

During the hydrogenation of the substrate, hydrogen uptake was measured from the manometer reading x. Since the total length of the mercury column was 92 cm, the total pressure P_T is given by

$$P_T = 92 - 2x \text{ cm.}$$

The partial pressure of hydrogen P_{H_2} is given by

$$P_{H_2} = P_T - P_{soln}$$

Where P_{soln} is equal to the vapor pressure of the solution which is assumed to be constant during the whole run. The rate of hydrogenation of the substrate (or the rate of hydrogen uptake) is calculated at a given pressure. The rate of hydrogen uptake is calculated in moles per minute, as follows:

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$\frac{dn}{dt} = \frac{dp/dt \times V}{RT}$$

Where P is equal to pressure in atmospheres, V is the volume of the system (mls), n is the number of moles of hydrogen taken up, R is the gas constant (8.025 × $\frac{\text{ml-atm}}{{}^\circ\text{K-mole}}$) and T is the temperature in degrees Kelvin.

The volume of the system was calculated to be 80 mls without the condenser and the empty flask was measured to be 149 mls. Thus the total volume is 80 + 149 - 25 (volume occupied by the solution) = 204 mls.

III, RESULTS AND DISCUSSION

III, 1, Reactions of Cobalt Complexes with Sodium Tetrahydroborate.

Addition of an ethanolic suspension of $NaBH_4$ (1M excess) to a warm (~30-40°C) ethanolic suspension of $CoCl_2 \cdot 6H_2O$ and PPh_3 ($Co:PPh_3=1:3$) gives the brownish-green compound reported to be $CoCl(PPh_3)_3$ (127). However, only approximately 50 % of this material is soluble in benzene from which the pure green $CoCl(PPh_3)_3$ can be obtained. The reflectance spectrum (Figure 3) and room temperature magnetic moment (3.05 B.M) are consistent with a tetrahedral d^8 structure as previously reported (127), and indeed, the complex appears to have properties very similar to those reported for the same Co(I) complex made by reductions involving zinc metal or electrolytic methods (127).

The yellow brown benzene insoluble residue has not been extensively investigated, but it does have a reflectance spectrum and infrared spectrum (νCo-Cl at 300 cm^{-1}) similar to those of the green $CoCl(PPh_3)_3$. Both materials react with ethanolic $NaBH_4$ when dissolved or suspended in benzene solution in the presence or absence of additional PPh_3; in all cases, the product is $Co(BH_4)(PPh_3)_2$. However, the benzene insoluble material does not react with $NaBH_4$ in ethanol alone in the presence of PPh_3, while the green $CoCl(PPh_3)_3$ does so readily.

These two compounds could be isomers of $CoCl(PPh_3)_3$, the yellow-brown material possibly being polymeric.

III.1.1. Formation of Tetrahydroborate Cobalt Complexes.

III.1.1.1. Tetrahydroboratotris(triphenylphosphine)-cobalt(I), $Co(BH_4)(PPh_3)_3$.

Many attempts have been made to prepare and further characterize the previously reported (5) monodentate complex, $Co(BH_4)(PPh_3)_3$. Reactions between $CoCl_2$ $6H_2O$, PPh_3 and $NaBH_4$ in molar ratios varying from 1:3:5 to 1:10:20 have been investigated under conditions similar to those reported previously (5), but the synthesis of $Co(BH_4)(PPh_3)_3$ could not be reproduced. The products from the above reactions mostly depend upon the rate of addition of the $NaBH_4$ suspension and less so on the reaction time and molar ratios of the reactants.

If all of the $NaBH_4$ suspension is added to the $Co(II)$-PPh_3 mixture within 3 minutes, essentially the same products are formed even though reaction times may vary from 30 minutes to 18 hours. These reactions produce mixtures of $H_3Co(PPh_3)_3$ (νCo-H=1745 and 1973 cm^{-1}), $HCo(N_2)(PPh_3)_3$ (νN_2 2040 cm^{-1}) and small amounts of Ph_3P-BH_3 (weak νB-H ~2380 cm^{-1}). The last product was positively identified from its X-ray powder diffraction pattern. The formation of these products may be rationalized as follows.

The solubility of PPh_3 in ethanol at room temperature is low compared with that of $CoCl_2 \cdot 6H_2O$ Therefore, if the $NaBH_4$ suspension is added too quickly not enough PPh_3 is in solution to coordinate to the cobalt(II) and thereby protect all of the Co(II)chloride from rapid reduction to cobalt boride. Metal borides are generally amorphous and the presence of cobalt boride would therefore not be revealed on x-ray patterns. Moreover, it is well known that small amounts of metal borides catalyse the rapid decomposition of $NaBH_4$ to release large amounts of H_2 (129). This would explain the formation of cobalt hydride complexes rather than tetrahydroborato complexes. Oxidation of $Co(I)\backslash PPh_3\backslash BH_4^-$ complexes, which may be present in small amounts as intermediates in these reactions, leads to the formation of Ph_3P-BH_3. This oxidation may occur because of the presence of trace amounts of oxygen in the system. In this connection, it has been observed that, in recording X-ray powder patterns of $Co(BH_4)(PPh_3)_3$, lines of the adduct Ph_3P-BH_3 appear if the capillary is improperly sealed or the tip broken during its mounting in the camera.

If the $NaBH_4$ suspension is added to the Co(II)-PPh_3 mixture more slowly, e.g. over a period of 30 minutes, or if 1 mole (per mole of Co(II)) of $NaBH_4$ is first added, followed by a large excess, then the sole product is the yellow brown $CoCl(PPh_3)_3$ (c.f. the yellow complex previously described). This compound does not undergo further reaction with $NaBH_4$ in ethanol even if the mixture is stirred for up to 3 days.

Similar reactions have been carried out in air. Thus, when an ethanolic $NaBH_4$ suspension is added to a stirred Co(II)chloride/PPh_3 mixture in ethanol a mixture of Ph_3P-BH_3, $Ph_3P=0$ and a cobalt complex containing no PPh_3, $[Co(OH)_2]$ (?) , is obtained.

From the similarity of the B-H stretching frequencies previously reported in the infrared spectrum of $Co(BH_4)(PPh_3)_3$ (5) and those of Ph_3P-BH_3, together with the absence of a frequency associated with the $B-H_b$ group in the former, it seems likely that the earlier description of $Co(BH_4)(PPh_3)_3$ is wrong. It is unfortunate that no X-ray powder data were recorded on this compound, which may have been a mixture of $CoCl(PPh_3)_3$, Ph_3P-BH_3 and possibly a Co(I) hydride/phosphine intermediate which would readily produce, as was reported, $HCo(N_2)(PPh_3)_3$ on recrystallisation from N_2 saturated solvents.

However, a green complex formulated as $Co(BH_4)(PPh_3)_3$, can be synthesised by alternative routes which will now be described. Addition of an ethanolic $NaBH_4$ suspension (10M excess) to a stirred suspension of the green $CoCl(PPh_3)_3$ and PPh_3 (3M excess) in ethanol at room temperature under nitrogen for 4 days gives a green, air sensitive, paramagnetic solid, with a magnetic moment of 3.25 BM based on the formulation $Co(BH_4)(PPh_3)_3$. It appears that a minimum of four days is required for completion of this reaction. For example, the infrared spectrum of the precipitate obtained after one hour showed a strong absorption at $\sim 300\ cm^{-1}$ due to the Co-Cl stretching frequency, and no B-H stretching frequency was observed. Precipitates taken after increased reaction times showed a steadily decreasing Co-Cl absorption and increasing B-H stretching frequencies until after 4 days the former had disappeared completely.

This same compound, $Co(BH_4)(PPh_3)_3$ can also be prepared by the addition of PPh_3 to the complex $Co(BH_4)(PPh_3)_2$ in which the BH_4^- group is bidentate (see later discussion). Thus, when $Co(BH_4)(PPh_3)_2$ is stirred with PPh_3 (3M excess) in ethanol solution at room temperature under N_2 for 4 days, $Co(BH_4)(PPh_3)_3$ is produced. This reaction too needs a minimum of

4 days for completion, otherwise mixtures of products are obtained.

Instead of ethanol as the solvent in the above reactions, the use of methanol has also been investigated. In both reactions the rate is faster and, after 24 hours, both give $Co(BH_4)(PPh_3)_3$ identified by X-ray powder diffraction.

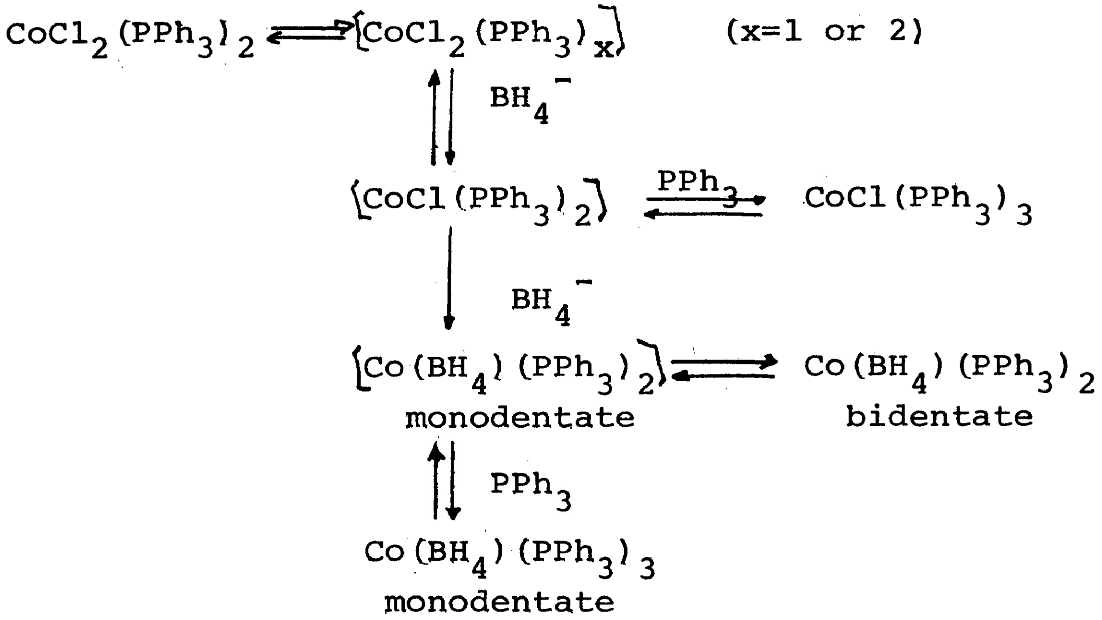
Unfortunately, repeated attempts to obtain good chemical analyses on these complexes have so far yielded results which are not entirely satisfactory. Analyses are particularly poor on the products from the methanol reactions which are probably contaminated by amorphous Co-borides, accounting for the abnormally high magnetic moments observed for these compounds. However, infrared spectra strongly support the presence of the monodentate BH_4^- group, electronic properties are consistent with the presence of Co(I) and the X-ray powder patterns of the above compounds are all the same. In fact it is the latter which provide the most convincing evidence for the existence of $Co(BH_4)(PPh_3)_3$ since they show the complex to be strictly isomorphous with the green $CoCl(PPh_3)_3$. This is particularly significant for the product from the $Co(BH_4)(PPh_3)_2 \setminus PPh_3$ reaction, in which no chloride ions are involved and therefore contamination of the product with $CoCl(PPh_3)_3$ is not possible. A further discussion of the physical properties and structure of this species will be presented later.

III.1.1.2. Tetrahydroboratobis(triphenylphosphine)-cobalt(I) $Co(BH_4)(PPh_3)_2$.

From the reaction of $NaBH_4$ with $CoCl_2 \cdot 6H_2O$ and PPh_3 in toluene-ethanol under nitrogen, a green crystalline solid, formulated as $Co(BH_4)(PPh_3)_2$ is produced. Infrared spectral data (to be discussed later) are consistent with the presence of a bidentate BH_4 group. It is interesting that, when PCy_3 is used instead of PPh_3 in analogous reactions, only the Co(II) complex $HCo(BH_4)(PCy_3)_2$ is formed (68). This is reasonable, since PPh_3 is a better π-acceptor than PCy_3 (135), and the bulky tertiary phosphines such as PCy_3, PPr^i_3, PBu^t_3 etc. have been shown to stabilize BH_4 complexes of transition metals in higher oxidation states (76).

The complex $Co(BH_4)(PPh_3)_2$ can also be made in a number of other ways. For example, addition of an ethanolic $NaBH_4$ (10M excess) suspension to suspensions of $CoCl(PPh_3)_3$ and PPh_3 (3M excess) in benzene produces the same green crystalline compound. Also, either the green recrystallised $CoCl(PPh_3)_3$ or the crude $CoCl(PPh_3)_3$ react in benzene with $NaBH_4$ (10 M excess, in ethanol) and $Co(BH_4)(PPh_3)_2$ is formed both from this reaction and from a similar reaction with additional free PPh_3 present. Furthermore, as has already been mentioned, this complex is also produced from attempts to recrystallize the previously discussed monodentate $Co(BH_4)(PPh_3)_3$ complex from benzene or THF, in the presence of free PPh_3. Finally, a convenient route to its preparation involves the reaction between hydrated cobalt(II) perchlorate, PPh_3(6M excess) and $NaBH_4$ (10M excess) in ethanol. The pure compound is obtained after recrystallization from benzene or THF. As has been described earlier, Co(II)chloride behaves quite differently under these conditions, producing a mixture of Co(I)chloride and hydride complexes.

A number of other reactions between $NaBH_4$ and a variety of Co complexes have been investigated. For example, addition of an ethanolic $NaBH_4$ (10M excess) suspension to a stirred suspension of $CoX_2(PPh_3)_2$, (X=Cl or Br, usually Cl) in ethanol gives a mixture of $Co(BH_4)(PPh_3)_2$ and $Co(BH_4)(PPh_3)_3$ in poor yields after 5 hours. If the reaction time is shorter than 2 hours, a mixture of $CoCl_2(PPh_3)_2$ and $CoCl(PPh_3)_3$ (identified by infrared spectroscopy) is obtained. The formation of these complexes may be rationalized by the following scheme:



Solvent; ethanol.

The formation of $Co(BH_4)(PPh_3)_3$ in this reaction (even though in small quantities) is much faster compared with its formation from the green $CoCl(PPh_3)_3$, PPh_3 and $NaBH_4$. One possible explanation is that the proposed 3-coordinated intermediate $\{CoCl(PPh_3)_2\}$ is very reactive towards substitution, forming the monodentate $\{Co(BH_4)(PPh_3)_2\}$ which can then either isomerise to form the bidentate $Co(BH_4)(PPh_3)_2$ or pick up PPh_3 to form $Co(BH_4)(PPh_3)_3$.

In the presence of free PPh_3 (3M excess), $NaBH_4$ reacts with $CoCl(PPh_3)_3$ in ethanol to give, after 15 hours, a mixture of $H_3Co(PPh_3)_3$, $HCo(N_2)(PPh_3)_2$ and a small amount of the bidentate $Co(BH_4)(PPh_3)_2$ (from infrared spectral data). Similar reactions between

Co(II)chloride, PPh_3 and $NaBH_4$ with a rapid rate of addition of the $NaBH_4$ (Section III.1.1.) yields only hydride complexes. The difference between these two reactions is that, in the latter case, a small amount of cobalt boride may be formed, which will catalyse the decomposition of the $NaBH_4$ to H_2, and therefore only the hydride complexes are formed.

Thus, $NaBH_4$ reacts with both Co(I) and Co(II) compounds under various conditions to produce $Co(BH_4)(PPh_3)_2$. Contamination of this complex by Co hydrides, produced via the formation of Co boride as described above, is minimized by reacting $NaBH_4$ with a Co(I) starting material.

In these reactions between $NaBH_4$ and various Co(II) or Co(I) complexes in the presence of PPh_3, it is apparent that the solvent plays a major role in determining the nature of the product(s). For example, the reaction of $CoCl(PPh_3)_3$ with $NaBH_4$ in ethanol, in the presence of free PPh_3 slowly gives the monodentate $Co(BH_4)(PPh_3)_3$ after 4 days. But, when the reaction is carried out in a benzene/ethanol mixture, the reaction proceeds much faster and in less than 30 minutes produces $Co(BH_4)(PPh_3)_2$. This can be explained if $CoCl(PPh_3)_3$ dissociates in benzene to give an intermediate complex $CoCl(PPh_3)_2$. No molecular weight data are available at this time, but the analgous $NiCl(PPh_3)_3$ has been found to dissociate extensively in benzene solution (130). As mentioned before, this proposed 3-coordinated species would be expected to be active towards substitution to give the monodentate $Co(BH_4)(PPh_3)_2$ intermediate, which subsequently isomerises to the bidentate $Co(BH_4)(PPh_3)_2$ complex, as summarised below:

$$\begin{tikzcd}
\mathrm{CoCl(PPh_3)_3} \arrow[r, shift left] & \underset{\text{3-coordinated}}{[\mathrm{CoCl(PPh_3)_2}]} \arrow[l, shift left] \arrow[d, "\mathrm{BH_4^-}"] & \\
& \underset{\text{monodentate}}{[\mathrm{Co(BH_4)(PPh_3)_2}]} \arrow[r, shift left, "K_1"] \arrow[d, shift left, "K_2"] & \underset{\text{bidentate}}{\mathrm{Co(BH_4)(PPh_3)_2}} \arrow[l, shift left] \\
& \underset{\text{monodentate}}{\mathrm{Co(BH_4)(PPh_3)_3}} \arrow[u, shift left] &
\end{tikzcd}$$

Solvent: benzene ethanol.

The fact that only the bidentate $Co(BH_4)(PPh_3)_2$ can be isolated, strongly suggests that $K_1 \gg K_2$ and that the equilibrium lies mostly to the right. That dissociation of $Co(BH_4)(PPh_3)_3$ must have occurred in benzene solution (even in the presence of added PPh_3) is supported by the fact that recrystallisation of the monodentate complex from benzene solution affords only $Co(BH_4)(PPh_3)_2$. K_2 therefore must be small. In ethanol solution, in which $CoCl(PPh_3)_3$ is only sparingly soluble, dissociation is suppressed by the presence of free ligand and therefore the formation of $Co(BH_4)(PPh_3)_3$ probably proceeds via a 5-coordinated intermediate by an S_N2 mechanism.

The reaction of $NaBH_4$ and Co(II)perchlorate/PPh_3 in ethanol results only in the formation of the bidentate $Co(BH_4)(PPh_3)_2$. This reaction must proceed via a different mechanism from that discussed above, and a cationic species, such as $[Co(PPh_3)_x]^+$ may be present as an intermediate. The PPh_3 concentration is relatively low compared to that of BH_4^- and this, together with the high affinity of a cationic cobalt intermediate towards the anionic BH_4^- ligand, makes it reasonable to suppose that the formation of the bidentate $Co(BH_4)(PPh_3)_2$ could be faster than the formation of the monodentate $Co(BH_4)(PPh_3)_3$ complex.

III.1.2. Structures of the Tetrahydroborato Cobalt Complexes.

III.1.2.1. Tetrahydroboratotris(triphenylphosphine)-cobalt(I) $Co(BH_4)(PPh_3)_3$.

The infrared spectrum of $Co(BH_4)(PPh_3)_3$ is shown in Figure 2 and the important frequencies are listed in Table 15. The two strong absorption bands at 2410 and 2320 cm^{-1} are assigned to the terminal $B\text{-}H_t$ stretching frequencies and the band at 2050 cm^{-1} to the bridging stretching frequency B-H_b. The expected strong BH_3 deformation mode is not observed, possibly because it is coincident with the absorption band of PPh_3 at 1090 cm^{-1}, but the expected weaker absorption band at slightly higher frequency appears at 1104 cm^{-1}. When compared with the bands expected for the various possible coordination modes of the BH_4^- group already discussed in the introduction to this thesis (Table 10), there seems little doubt that the complex $Co(BH_4)(PPh_3)_3$ has a monodentate BH_4 grouping.

In this connection, it should be mentioned that the infrared spectrum of the complex or mixture of complex as previously reported incorrectly to be $Co(BH_4)(PPh_3)_3$ (5) showed absorption bands at 2390(s), 2340(sh) and 1105 cm^{-1} which are remarkably similar to the νB-H and δB-H stretching frequencies of Ph_3P-BH_3 (see Table 15). No νB-H_b was observed and, as mentioned in the preceding discussion, the compound reported was probably a mixture of $CoCl(PPh_3)_3$, Ph_3P-BH_3 and a Co(I) hydride.

The electronic reflectance spectrum (Figure 4) of $Co(BH_4)(PPh_3)_3$ is quite similar to that of $CoCl(PPh_3)_3$ which has been interpreted (127) in terms of a d^8 tetrahedral system. The absorption bands are assigned as follows:

Table 14.

Electronic Reflectance Spectral Data of $Co(BH_4)(PPh_3)_3$ and $CoCl(PPh_3)_3$.

$Co(BH_4)(PPh_3)_3$ Abs. max. (cm^{-1})	Transition	$CoCl(PPh_3)_3$. (127) Abs. max. (cm^{-1})
6250	${}^3T_1(F) \rightarrow {}^3T_2$	5000
7407	${}^3T_1(F) \rightarrow {}^3A_2$	9090
16390	${}^3T_1(F) \rightarrow {}^3T_1(P)$	13420

The magnetic moment of $Co(BH_4)(PPh_3)_3$ at room temperature is 3.25 BM and this too is consistent with that expected for a tetrahedral high spin d^8 configuration. As mentioned previously, the X-ray powder pattern of $Co(BH_4)(PPh_3)_3$ is identical with that of $CoCl(PPh_3)_3$, indicating that the two compounds are probably isostructural. Thus, despite the rather poor chemical analyses, all the physical data are consistent with a tetrahedrally coordinated Co(I) with a monodentate BH_4 grouping.

III.1.2.2. Tetrahydroboratobis(triphenylphosphine)-cobalt(I) $Co(BH_4)(PPh_3)_2$.

The infrared spectrum of $Co(BH_4)(PPh_3)_2$ is shown in Figure 4 and the bands associated with the BH_4 group are tabulated in Table 15. These data should be compared with the assignments in Table 10 which considers the possible coordination modes of the BH_4 group. Thus the absorption bands at 2450 and 2390(sh) cm^{-1}, the terminal B-H_t stretches, and at 1970 and 2040 cm^{-1}, the symmetric and antisymmetric bridging stretches, fall within the range observed in other complexes containing the bidentate BH_4 grouping (see Table 12). The other two expected absorption bands (Table 10) at $\sim$1300-1500 cm^{-1}, $\nu\,\text{B-H}_b$, and

Table 15.

Infrared Spectral Data of $Co(BH_4)(PPh_3)_3$, $Co(BH_4)(PPh_3)_2$, and $Ph_3P\text{-}BH_3$.

	ν B-H_t (cm^{-1})	ν B-H_b (cm^{-1})	δ B-H (cm^{-1})
$Co(BH_4)(PPh_3)_3$	2410 (s)	2050 (m)	1104 (w)
	2320 (m)		
$Co(BH_4)(PPh_3)_2$	2450 (s)	2040 (m)	
	2390 (sh)	1970 (m)	
$Co(BD_4)(PPh_3)_2$	1830	-	-
$Ph_3P\text{-}BH_3$	2380 (s)		1105 (s)
	2340 (sh)		1060 (s)

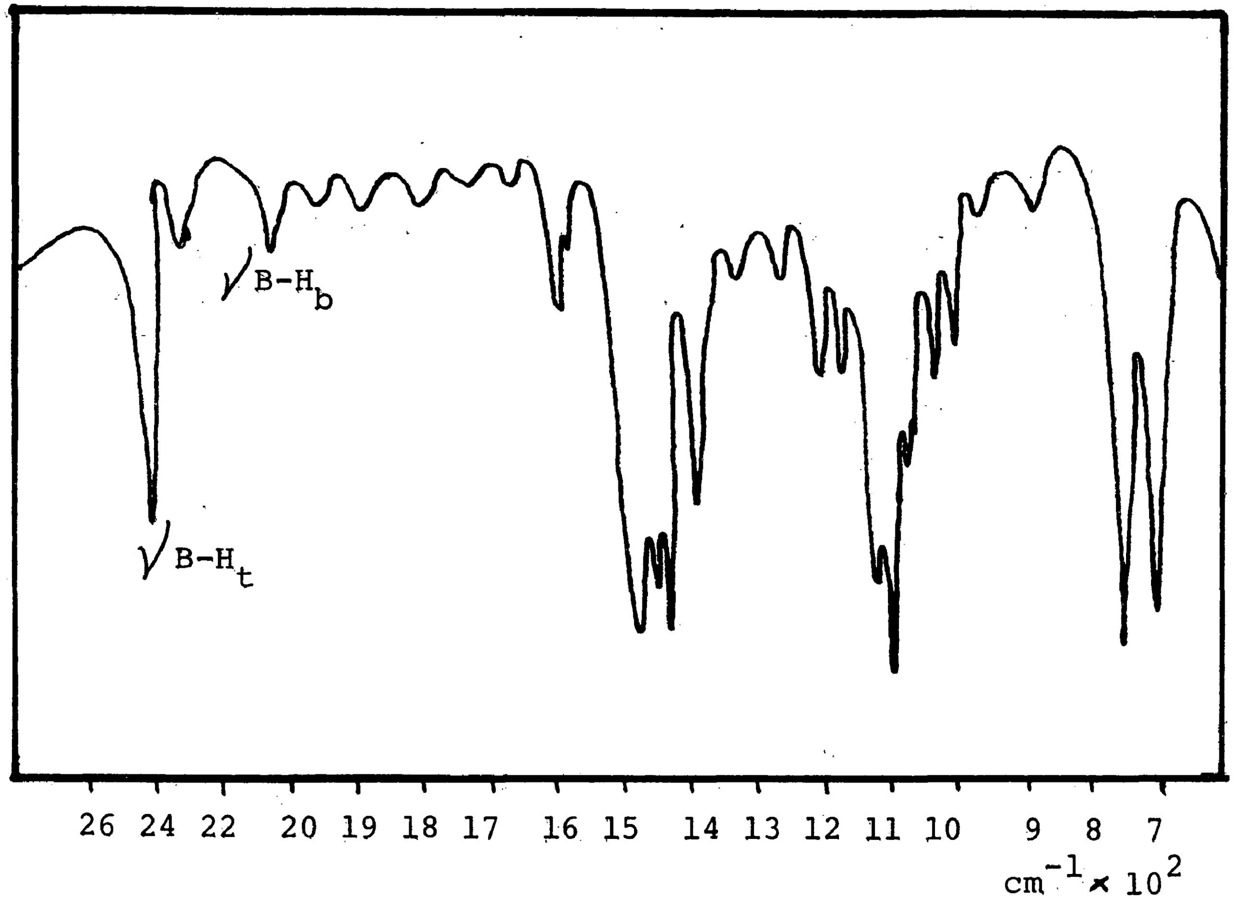


Figure 2. Infrared Spectrum of $Co(BH_4)(PPh_3)_3$ (Nujol Mull)

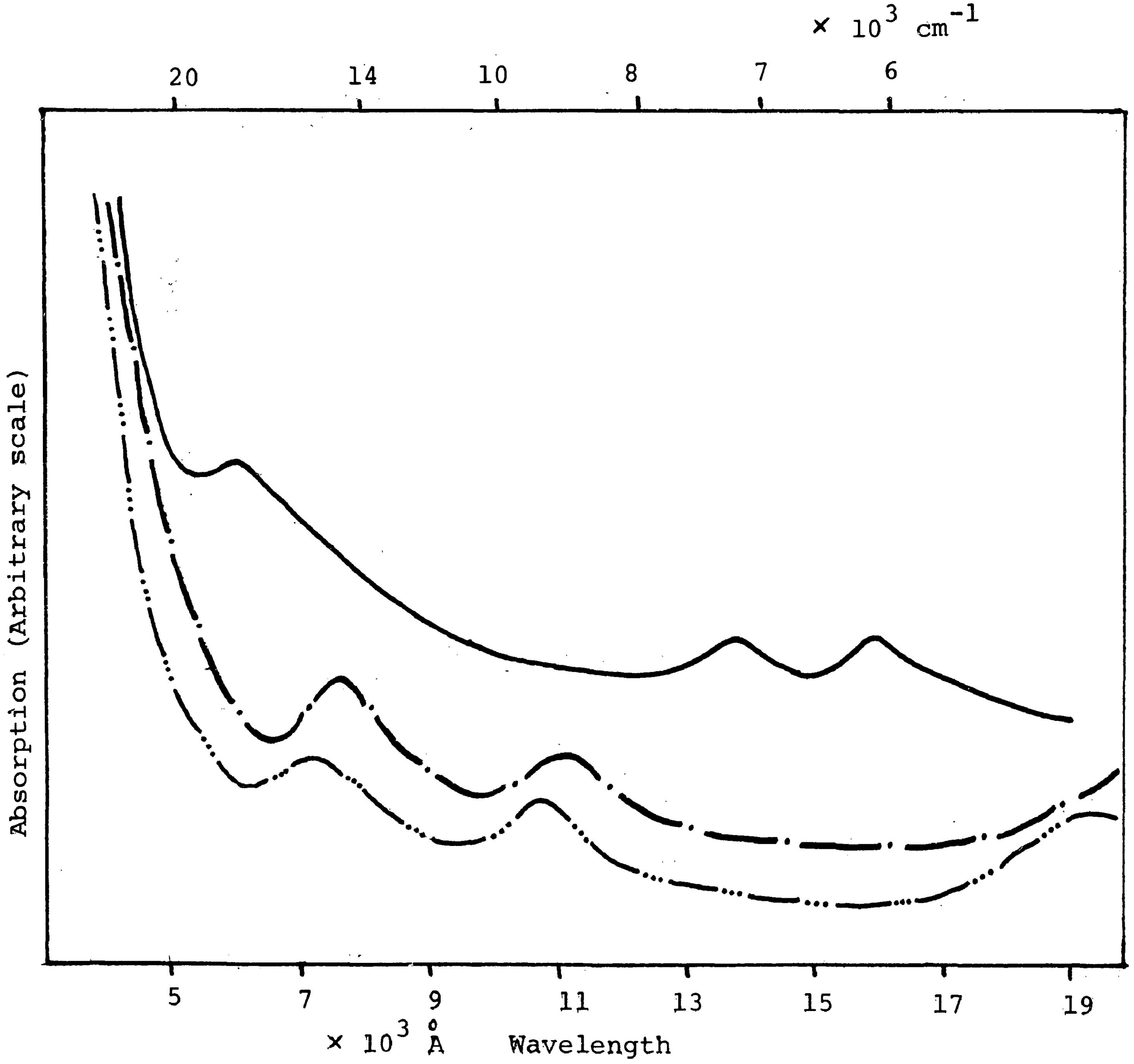


Figure 3. Electronic Reflectance Spectra of

—— $Co(BH_4)(PPh_3)_3$

—·— $CoCl(PPh_3)_3$

—···— $HCo(PPh_3)_3$ (?)

$\sim$1100-1200 cm^{-1}, δB-H, do not appear in the infrared spectrum of $Co(BH_4)(PPh_3)_2$, probably because they are hidden under the absorption bands of Nujol and ligand respectively (the complex is decomposed in hexachlorobutadiene). In an attempt to resolve this problem, the complex $Co(BD_4)(PPh_3)_2$ was made and its infrared spectrum shows the terminal νB-D$_t$ stretching frequency at 1830 cm^{-1}, but all other B-D vibrational modes appear to be hidden under the absorption bands of the ligand. The isotopic shift, $\nu(D)/\nu(H)$, of 0.747 is consistent with the value observed in the Co(II) complex, $HCo(BH_4)(PCy_3)_2$ (68). Therefore, on the basis of infrared spectral data, it is not unreasonable to suppose that $Co(BH_4)(PPh_3)_2$ contains a bidentate BH_4 group.

The electronic reflectance spectrum (Figure 5) of the $Co(BH_4)(PPh_3)_2$, unlike the spectra of $CoCl(PPh_3)_3$ and $Co(BH_4)(PPh_3)_3$, shows only a single low intensity absorption band at 14700 cm^{-1}, which shifts to 16600 cm^{-1} (ϵ=88) in benzene solution. The position and intensity of this single absorption band leaves little doubt that it is d-d in origin. Furthermore, its position and intensity are almost exactly what is expected for the electronic transition associated with a low spin square planar d^8 system. However, repeated magnetic moment determinations on different samples of $Co(BH_4)(PPh_3)_2$

in the solid state show that the complex is in fact high spin, with an average value of 2.98 BM. Moreover, magnetic moments measured in concentrated benzene solutions at room temperature by n.m.r. spectrometry (126) suggest that the paramagnetism of this complex is greatly reduced (~0.96 BM). There is no evidence of decomposition in solution. This apparent spin state change is not accompanied by any radical change in the electronic spectrum and an explanation of these observations is not obvious. The available evidence points to a square planar Co(I) system in solution, but in the solid state the structure will probably not be known until a single crystal X-ray study is undertaken.

A comparison was made of the X-ray powder patterns of $Co(BH_4)(PPh_3)_2$ and the potentially very closely related species $Cu(BH_4)(PPh_3)_2$. The latter is known from single crystal X-ray data (147), to have a tetrahedral structure with a bidentate BH_4 group. However, since the powder patterns of the two complexes, listed below, are radically different all that can be said with confidence is that the two complexes are not isostructural, although this does not exclude the possibility that the gross stereochemical arrangement about the two metal ions may be related.

d-spacing (relative intensities):

$Co(BH_4)(PPh_3)_2$

13.52(8), 9.62(1), 3.70(10), 7.85(2), 6.30(1), 5.77(1), 4.95(1), 4.71(5), 4.37(7), 3.86(3), 3.55(1).

$Cu(BH_4)(PPh_3)_2$

11.04(1), 7.55(8), 6.96(2), 5.84(4), 5.43(1), 4.32(10), 3.81(4), 3.24(1).

III.1.3. Stability and Reactivity.

Many metal-tetrahydroborate complexes are air sensitive, (particularly in solution), even those with metals in what are generally considered to be stable oxidation states like Ni(II) and Co(II), e.g. $HCu(BH_4)$-$(PCy_3)_2$ (68), $HNi(BH_4)(PCy_3)_2$ (69), etc. It is therefore not surprising that Co(I)-BH_4 complexes are even more air sensitive, and, for example, $Co(BH_4)(PPh_3)_3$ is rapidly oxidised in air in the solid state, producing Ph_3P-BH_3 and Ph_3P=0 (identified from i.r. spectral and X-ray powder data). However, when stored under a nitrogen atmosphere, the complex is quite stable over long periods of time. In spite of this, totally satisfactory chemical analyses for this compound have not yet been obtained. In this connection, it is interesting to note that the BH_4 complexes of aluminum, $Al(BH_4)(PPh_3)$ (131), and $Al(BH_4)(PMe_3)$ (132) decompose in the presence of an excess of the

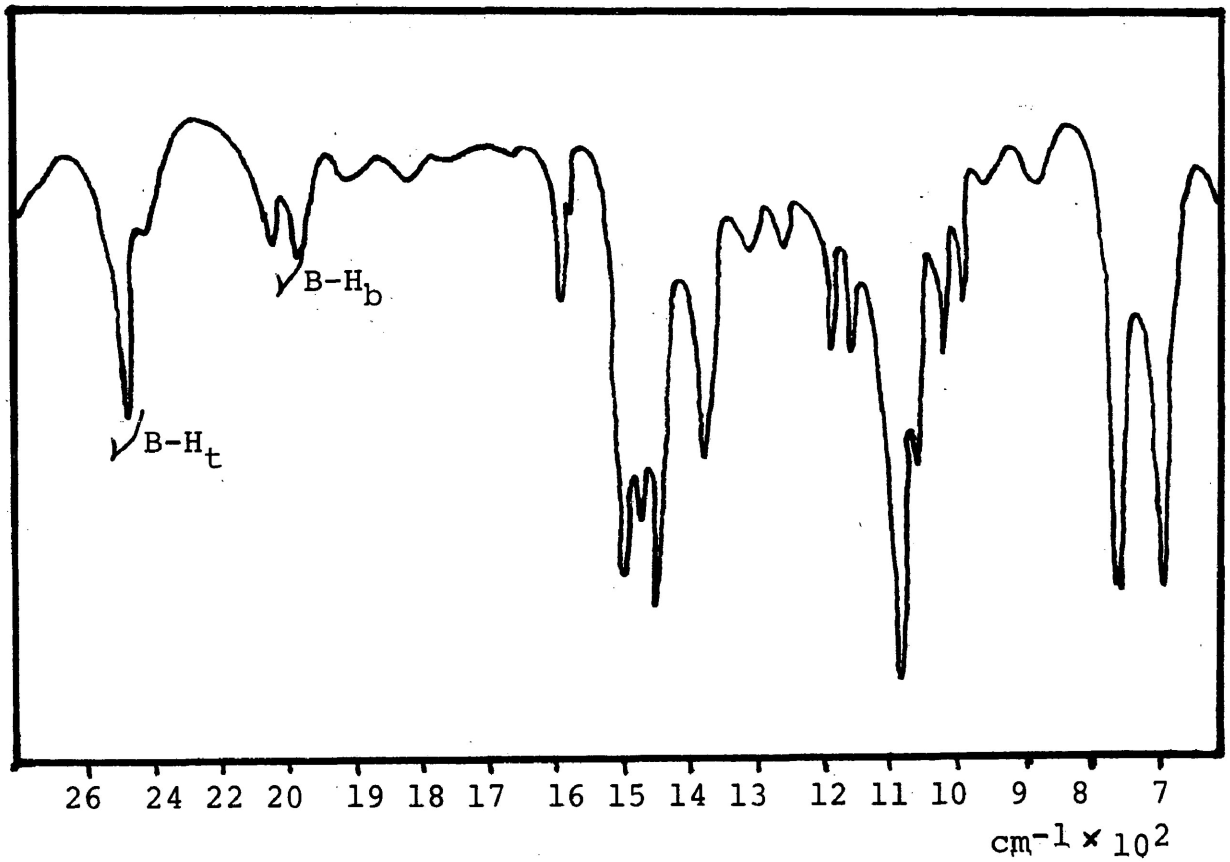


Figure 4. Infrared Spectrum of Co(BH$_4$)(PPh$_3$)$_2$ (Nujol Mull)

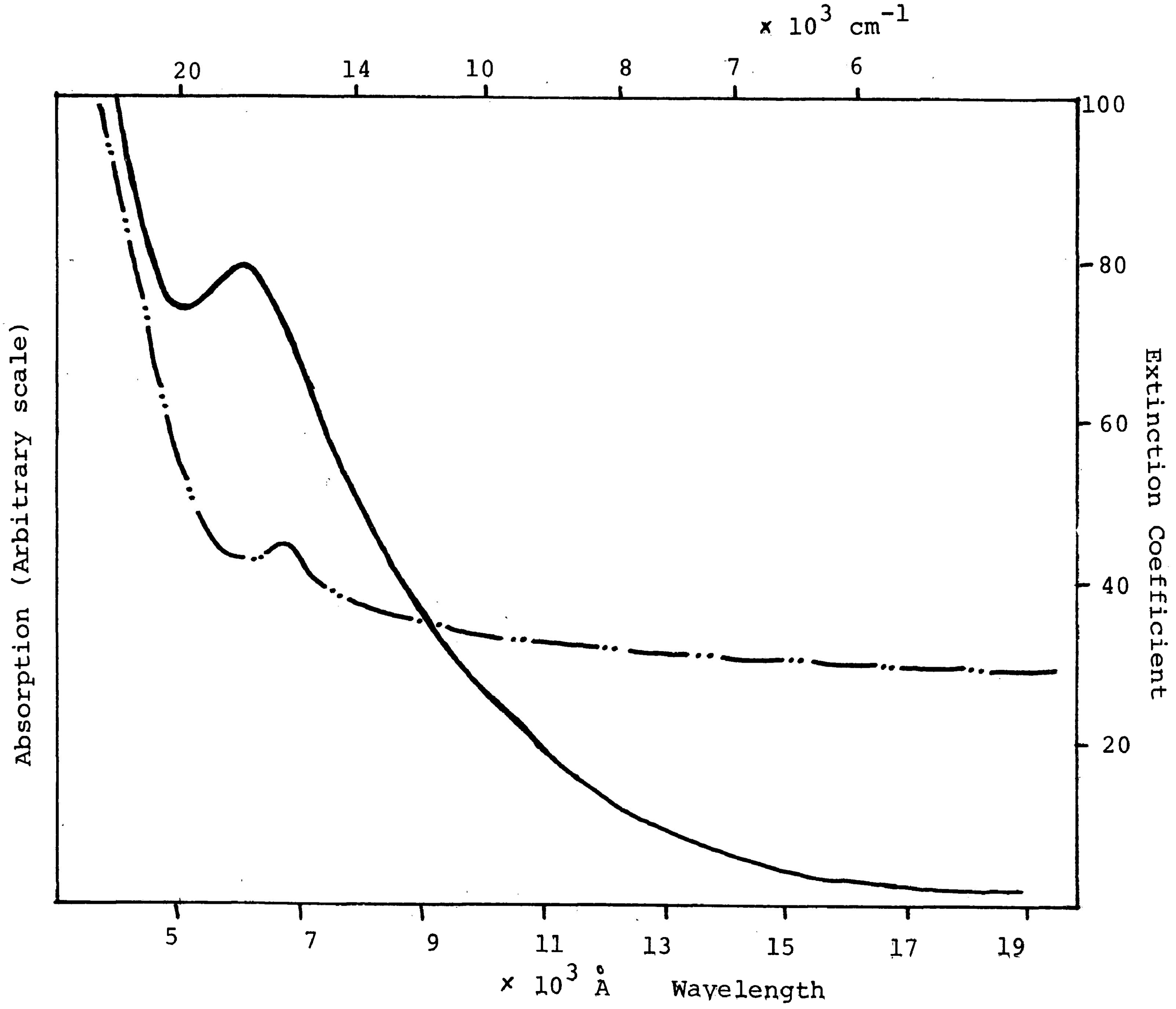


Figure 5. Electronic Spectra of $Co(BH_4)(PPh_3)_2$

—— Solution Spectrum (1.02 mM)

—··— Reflectance Spectrum

appropriate phosphine ligand. The preparation of $Co(BH_4)(PPh_3)_3$ involves a 4-day reaction in the presence of an excess of PPh_3 so that, by analogy, some decomposition may occur. This, coupled with the lack of a suitable method of recrystallizing the complex may account for the slight discrepancy in the analyses. When $Co(BH_4)(PPh_3)_3$ is heated under reflux with PPh_3 in ethanol, Ph_3P-BH_3 and an unidentified amorphous Co-(OH) complex which has a low carbon and hydrogen content, are produced. At room temperature, $Co(BH_4)(PPh_3)_3$ decomposes in ethanol over 24 hours to give a green precipitate in low yield. This green precipitate which has so far not been identified, appears to have a high spin d^8 tetrahedral system from its reflectance spectrum in Figure 3. The i.r. spectrum of this green precipitate shows no absorptions associated with the BH_4 group, and one possibility is that the complex may be a Co(I) hydride formed as shown below, although this clearly needs further investigation.

$$Co(BH_4)(PPh_3)_3 \longrightarrow HCo(PPh_3)_3 + \tfrac{1}{2}B_2H_6$$

When $Co(BH_4)(PPh_3)_3$ is stirred or heated under reflux for 3 hours in either CH_3CN or CH_3NO_2, a white precipitate of Ph_3P-BH_3 is produced (identified from i.r. spectral data).

When $Co(BH_4)(PPh_3)_3$ is dissolved in benzene or THF, decomposition to the bidentate $Co(BH_4)(PPh_3)_2$

occurs even in the presence of added PPh_3. This may be accounted for by a combination of the enhanced stability of a chelated BH_4^- group over a monodentate group, together with the known tendency of similar phosphine complexes to dissociate readily (e.g., $NiCl(PPh_3)_3$ (130), $RhCl(PPh_3)_3$ (107), $RuCl_2(PPh_3)_3$ (17)) possibly to relieve crowding about the metal center.

$Co(BH_4)(PPh_3)_2$ is also air sensitive and is rapidly converted into a Co(II)-complex (?), releasing $Ph_3P\text{-}BH_3$ and $Ph_3P{=}0$ at the same time. When it is stirred or heated under reflux in CH_3CN or CH_3NO_2, or heated under reflux with PPh_3 in ethanol, it produces, like $Co(BH_4)(PPh_3)_3$, the adduct $Ph_3P\text{-}BH_3$. In spite of its higher stability, $Co(BH_4)(PPh_3)_2$ can be converted to the monodentate $Co(BH_4)(PPh_3)_3$ in the presence of added PPh_3 in a solvent in which both complexes are only sparingly soluble (e.g. ethanol), (c.f. $Al(BH_4)(PMe_3)_2$ which can be formed by addition of one ligand to $Al(BH_4)(PMe_3)$ at low temperatures (132)). The complex, $Co(BH_4)(PPh_3)_3$, cannot convert back to the $Co(BH_4)(PPh_3)_2$ in ethanol probably due to the fact that the former, having a lower solubility, precipitates out from solution as soon as it is produced. The greater the excess of Ph_3P, the more easily the conversion to the monodentate complex occurs:

$$Co(BH_4)(PPh_3)_2 + PPh_3 \underset{}{\overset{EtOH}{\rightleftarrows}} Co(BH_4)(PPh_3)_3 \downarrow$$

Metal-BH_4 complexes have been shown to react with chloroform very rapidly (133). Both the bidentate and monodentate Co(I)-BH_4 complexes react, not only with chloroform, but also with methylene chloride, carbon tetrachloride and hexachlorobutadiene very rapidly to give $CoCl_2(PPh_3)_2$ (identified from i.r. spectral data). A similar result has been observed when $CoCl(PPh_3)_3$ is dissolved in CH_2Cl_2.

In view of the fact that certain Ni(I)-BH_4 complexes with nitrogen containing ligands e.g. $Ni(Phen)_2(BH_4)$ (7) react with $NaPF_6$ or $NaBPh_4$ in ethanol to produce the corresponding salts of PF_6^- and BPh_4^-, it was of interest to investigate similar reactions with the phosphine-BH_4 complexes. Reactions of $Co(BH_4)(PPh_3)_3$ and $Co(BH_4)(PPh_3)_2$ with both $NaPF_6$ and $NaBPh_4$ in the presence of PPh_3 in ethanol have been studied. $Co(BH_4)(PPh_3)_3$ is decomposed in ethanol within approximately 1 hour when stirred with either $NaPF_6$ or $NaBPh_4$ while, under similar conditions, some $Co(BH_4)(PPh_3)_2$ remains unreacted even after three hours. In all cases however, there appears to be general decomposition of the Co(I) complexes with the production of Ph_3P-BH_3 together with unidentified Co containing products.

III.1.4. Mechanism of the Reaction between Cobalt Complexes and Sodium Tetrahydroborate.

In the light of these studies, the earlier reported mechanism proposed for the reduction of transition metals by tetrahydroborate (5,134,6) can now be expanded. Figure 6 therefore presents a summary of the results obtained on Co(II)-$NaBH_4$ reductions in the presence of PPh_3 and shows the most probable mechanism for the reactions.

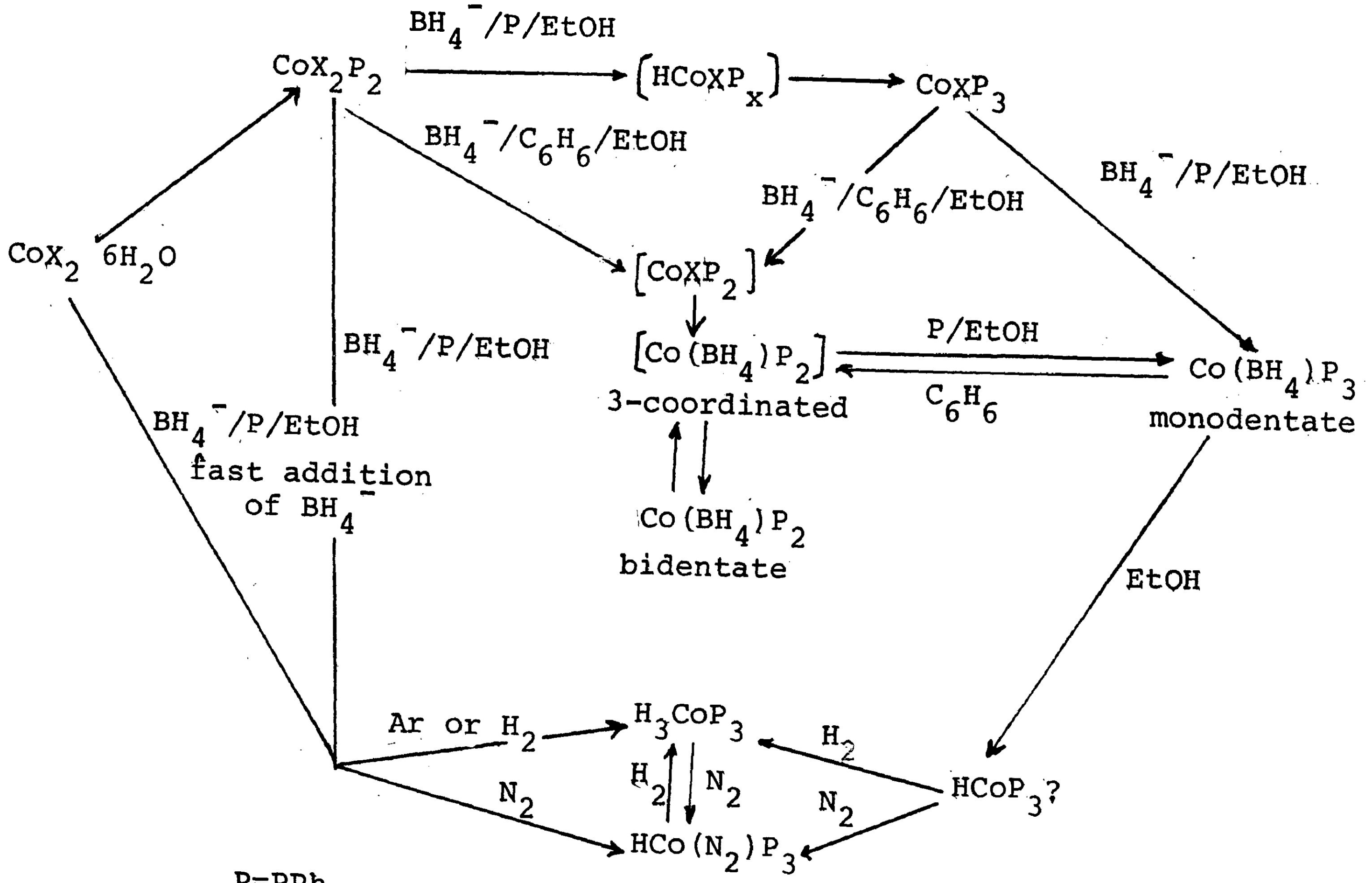
To summarize this section, it has been shown that the products formed from reactions of $NaBH_4$, Co(II) and PPh_3 depend essentially on three factors.

i). The rate of addition of $NaBH_4$.

If the rate of addition of $NaBH_4$ to the Co(II)/PPh_3 mixture is fast, then cobalt hydrides are the major products and the low valent Co-BH_4 complexes are not produced in any significant quantity. For the slow addition of $NaBH_4$, the unstable BH_4^- intermediate complexes can be intercepted and isolated.

ii). The presence of free ligand.

From reactions of $NaBH_4$ and $CoCl_2(PPh_3)_2$ in ethanol, Co(I)-BH_4 complexes are produced in the absence of free PPh_3. In the presence of free ligand,



P=PPh$_3$

Complexes within [ ] have not been isolated.

Figure 6. Possible mechanism for Co(II)-NaBH$_4$ reductions in the presence of PPh$_3$.

cobalt-hydrides are produced.

iii). The solvent.

While only two solvents have been used to any great extent in this work, clearly the solvent plays an important role in determining the final product of a reaction. If the proposed intermediate complex can dissociate, as apparently occurs in benzene, then $Co(BH_4)(PPh_3)_2$ is the main product. On the other hand, if dissociation of the intermediate is suppressed, as when ethanol is used, then the monodentate $Co(BH_4)(PPh_3)_3$ complex is the preferred product.

III.2. Reactions of Nickel Complexes with Sodium Tetrahydroborate.

III.2.1. Formation of Tetrahydroborato Nickel Complexes.

III.2.1.1. Tetrahydroboratotris(triphenylphosphine)-Nickel(I) $Ni(BH_4)(PPh_3)_3$.

It has been established that, while the previous report (5) of $Co(BH_4)(PPh_3)_3$ is wrong, this complex, and $Co(BH_4)(PPh_3)_2$ can be made by carefully controlled $NaBH_4$ reductions. It was therefore of considerable importance to reinvestigate the preparation (5) of the analogous Ni(I) complex, $Ni(BH_4)(PPh_3)_3$, and to reexamine its properties, especially its reported diamagnetism. A careful and systematic study of reactions between $NaBH_4$ and Ni compounds in the presence of PPh_3 was therefore undertaken.

In this work the complex $Ni(BH_4)(PPh_3)_3$ is made from the reaction between Ni(II) halides, PPh_3 and $NaBH_4$ (1:6:10 molar ratios) in ethanol at room temperature. It can also be made (136) by the reaction of $NiCl(PPh_3)_3$ with $NaBH_4$ in ethanol, like the corresponding Co complex. The reaction is complete in approximately 3 hours and is independent of the rate of addition of $NaBH_4$ (unlike the corresponding Co reaction).

The product is a pyrophoric solid with the same properties as reported (5) for $Ni(BH_4)(PPh_3)_3$. For example, the infrared spectrum shows 2 sets of absorption bands at 1060, 1105 and at 2390, 2340 cm^{-1} which were assigned (5) to δB-H and γB-H respectively of a monodentate BH_4 group, although it should be noted that the spectrum is very similar to that of Ph_3P-BH_3. The complex is diamagnetic and shows no d-d bands in its reflectance spectrum.

That the above product is not a mixture of Ph_3P-BH_3 and an air sensitive, diamagnetic Ni(0)-phosphine complex is shown by its unique X-ray powder pattern and by its chemical reactions. Thus, the complex reacts with $NaPF_6$ to give the pale yellow complex, $[Ni(PPh_3)_3][PF_6]$ which, on recrystallization from acetonitrile, gives $[Ni(PPh_3)_3(CH_3CN)][PF_6]$. These two PF_6^- salts will be discussed later, but the latter has electronic properties entirely consistent with the presence of Ni(I). These facts, together with consistent chemical analyses, support the formulation of the above complex as the Ni(I) species, $Ni(BH_4)(PPh_3)_3$.

However, unless oxygen is rigorously excluded from reactions of $NaBH_4$ with Ni(II) in the presence of PPh_3, mixtures of Ni(0)-PPh_3 complexes, $Ph_3P{=}O$ and Ph_3P-BH_3 are produced. These compounds are formed from the decomposition of $Ni(BH_4)(PPh_3)_3$.

The complex $Ni(BH_4)(PPh_3)_3$ is insoluble in ethanol, and attempts to recrystallize it from benzene result in decomposition and the formation of a mixture of the Ni(0) complex, $Ni(PPh_3)_2$, and $Ph_3P\text{-}BH_3$ (identified from i.r. spectral data and X-ray powder patterns). In fact, reactions between $NaBH_4$ and Ni(II) halides in the presence of PPh_3 in benzene lead to the same products.

Since the analogous chloro complex, $NiCl(PPh_3)_3$, dissociates in benzene to give $NiCl(PPh_3)_2$ (130), $Ni(BH_4)(PPh_3)_3$ may behave similarly in solution and decompose as follows:

$$\begin{tikzcd}
Ni(BH_4)(PPh_3)_3 \arrow[r] & \left[HNi(PPh_3)_2\right] \arrow[d] & + \; Ph_3P\text{-}BH_3 \\
 & Ni(PPh_3)_2 + \tfrac{1}{2}H_2 &
\end{tikzcd}$$

III.2.1.2. Bis(tetrahydroborato)tris(triphenylphospine)-dinickel(I), $Ni_2(BH_4)_2(PPh_3)_3$.

It is well known that reactions of $NaBH_4$ with nickel(II) hydrido complexes containing bulky phosphine ligands produce Ni(II)-BH_4 complexes, e.g. $HNi(BH_4)L_2$, ($L=PCy_3$ or PPr^i_3) (69). In this work, analogous reactions between $NaBH_4$ and the Ni(II)-halo complexes of PPh_3, $NiX_2(PPh_3)_2$ (X=Cl or I), in ethanol and benzene have been studied. These reactions (in ethanol) rapidly produce a pyrophoric diamagnetic tetrahydroborato-Ni complex in rather low yield (~30 %). Addition of small amounts of free PPh_3 and/or prolonging the reaction time (up to 1 hour) only leads to the coproduction of $Ph_3P\text{-}BH_3$ (identified from i.r. spectral and X-ray powder data). As the amount of free PPh_3 is increased, so $Ph_3P\text{-}BH_3$ becomes the major product. Similar reactions in benzene/ethanol mixtures lead to decomposition and to the production of $Ph_3P\text{-}BH_3$ and unidentified Ni complexes. The above Ni complex can be recrystallized readily from benzene or THF and appears as shiny dark green crystals. Excellent and consistently reproducible chemical analyses point to the empirical composition $Ni(BH_4)(PPh_3)_{1.5}$ or as a more reasonable molecular formula $Ni_2(BH_4)_2\text{-}(PPh_3)_3$.

Although all the $NiX_2(PPh_3)_2$, (X=Cl, Br, or I) complexes react with $NaBH_4$ in ethanol to give $Ni_2(BH_4)_2(PPh_3)_3$, it is convenient to use $NiI_2(PPh_3)_2$ for two reasons. First of all the iodide is more reactive than the chloride and bromide, and secondly, the iodide is more soluble in ether so that, after reaction, any unreacted starting material can be removed easily from the product by washing with ether.

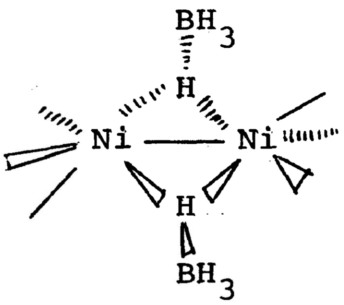
A catalytic system utilising $NiX_2(PPh_3)_2$ (X=Cl or Br) and $NaBH_4$ in C_6H_6/EtOH or THF/EtOH has been reported to be an effective polymerization catalyst (137) and it is thought that the active species is a Ni(0)-phosphine complex. If this is the case, then an intermediate Ni(I)-(BH_4) complex which would be soluble in this solvent system, must have reacted with PPh_3 instead of dimerizing to form the more stable $Ni_2(BH_4)_2(PPh_3)_3$.

III.2.2. Structures of the Tetrahydroborato Nickel Complexes.

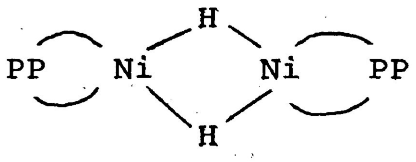
III.2.2.1. Tetrahydroboratotris(triphenylphosphine)-nickel(I) $Ni(BH_4)(PPh_3)_3$.

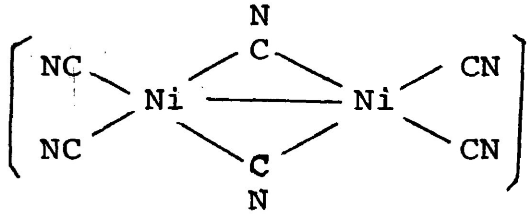
As reported in a previous section, the preparation of $Ni(BH_4)(PPh_3)$ has been successfully reproduced and the physical properties of this complex, which will be only briefly summarised here for the sake of completeness are as reported (5). Its infrared spectrum, with assignments, is recorded in Table 16 and is consistent with monodentate BH_4 coordination although its X-ray powder pattern is quite different from that of the corresponding Co(I) complex. The

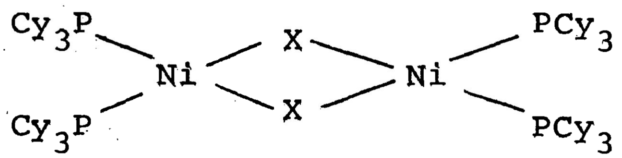
The diamagnetism and absence of d-d electronic bands are most reasonably explained by assuming that the complex is dimeric, with Ni-Ni bonding and bridging BH_4 groups as shown:



There are a number of other Ni(I) complexes which are suspected of having similar dimeric arrangements. For example, it has been proposed that the diamagnetic Ni(I) complexes of PP (56) and CN^- (138) have the structures shown below. Also, the complex $NiX(PCy_3)_2$, which is paramagnetic, is apparently dimeric in the solid state (as shown below) but monomeric in solution (139).







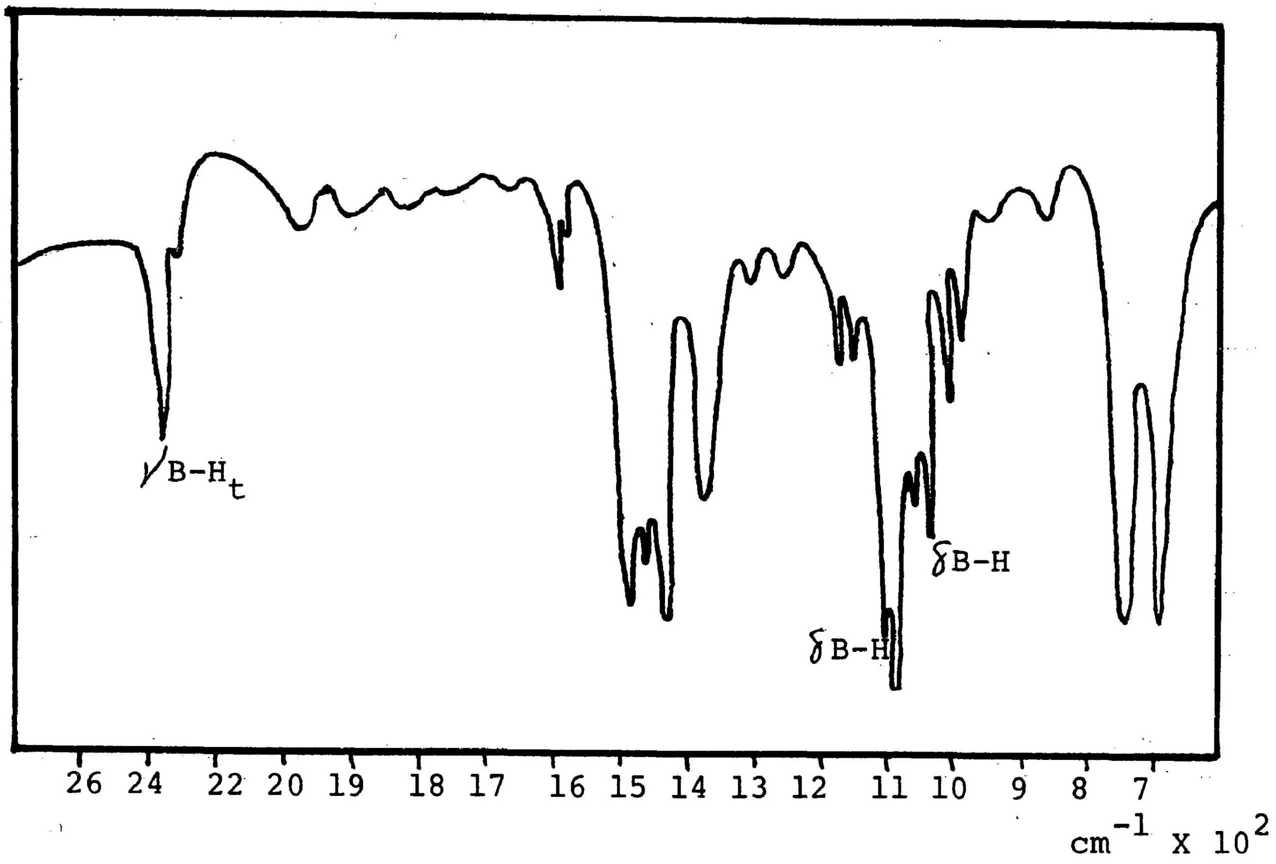


Figure 7. Infrared spectrum of $Ni(BH_4)(PPh_3)_3$ (Nujol mull)

There remains the possibility, however, that this complex should be formulated as the diamagnetic Ni(II) compound $HNi(BH_4)(PPh_3)_3$ and the arguments previously made against this (5) may be briefly summarised as follows.

i). It can be made from the reaction of $NaBH_4$ with Ni(I) in a similar way to that used for $Co(BH_4)(PPh_3)_3$.

ii). It would be unusual for a Ni(II) complex to be pyrophoric.

iii). A diamagnetic presumably 5-coordinated Ni(II) complex should have electronic absorptions below the charge transfer band at $\sim$16000 cm^{-1}.

iv). No Ni-H stretching frequency has been observed in the infrared spectrum (the complex decomposes so rapidly in solution that n.m.r. studies were not possible).

However, perhaps the most convincing evidence for the presence of Ni(I) in $Ni(BH_4)(PPh_3)_3$ arises from the work described in this thesis where cationic Ni(I) derivatives (to be discussed later) have been made in the absence of added reducing agent.

III.2.2.2. Bis(tetrahydroborato)tris(triphenylphosphine)-dinickel(I) $Ni_2(BH_4)_2(PPh_3)_3$.

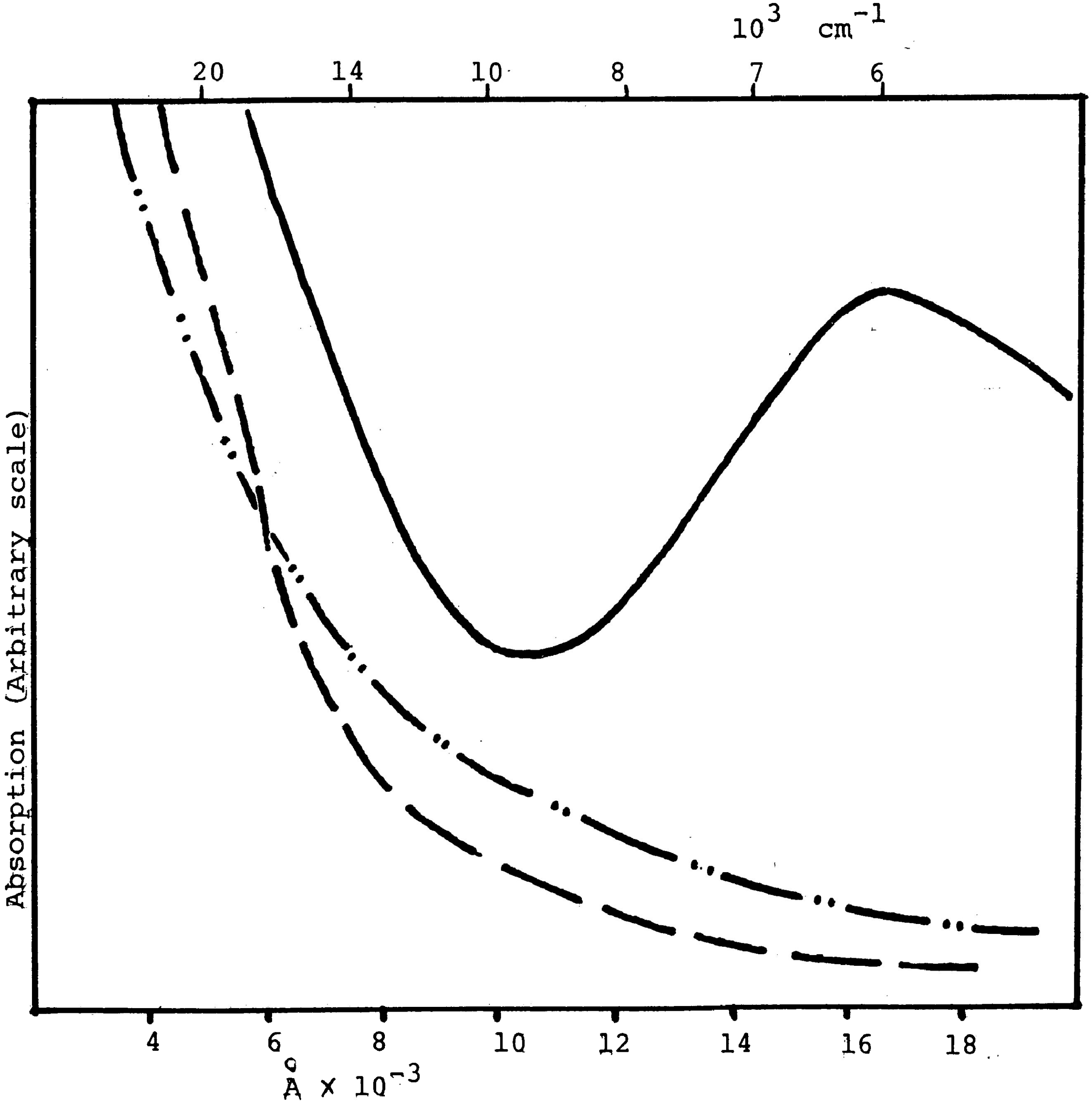


Figure 8. Reflectance Spectra of Ni Compounds.

- - - $[Ni_2(PPh_3)_6][PF_6]_2$

—— $[Ni(PPh_3)_3(CH_3CN)][PF_6]$

—··— $Ni(BH_4)(PPh_3)_3$

Table 16.

Infrared Spectral Data of $Ni(BH_4)(PPh_3)_3$, $Ni_2(BH_4)_2(PPh_3)_3$ and $Ni_2(BD_4)_2(PPh_3)_3$.

	ν_{B-H_t} cm^{-1}	ν_{B-H_b} cm^{-1}	δ_{B-H} cm^{-1}
$Ni(BH_4)(PPh_3)_3$	2380 (S)		1060 (M)
	2350 (Sh)		1105 (W)
$Ni_2(BH_4)_2(PPh_3)_3$	2440 (S)	1970 (M)	
	2380 (M)	1920 (W)	
$Ni_2(BD_4)_2(PPh_3)_3$	1840 (S)		

Infrared spectral data (Table 16 and Figure 9) on this complex provide excellent evidence for the presence of bidentate BH_4 coordination (c.f. Table 10). The 2440 and lower intensity 2380 cm^{-1} bands are assigned to the terminal $B-H_t$ stretching frequencies. Bands at 1970, 1920 and 1380 cm^{-1} are due to the bridging BH_4 modes. In fact, apart from $HCo(BH_4)(PCy_3)_2$ (68), this is the only complex which shows the bridging mode of a bidentate BH_4 group in the 1300-1500 cm^{-1} region. However, as with $Co(BH_4)(PPh_3)_2$, no δB-H was observed, probably because the band is obscured by ligand vibrations. On deuteration, the terminal νB-D shifts to 1840 cm^{-1} and the isotopic shift, (νD/νH), of 0.754 is consistent with the valves observed for $Co(BH_4)(PPh_3)_3$ and $HCo(BH_4)(PCy_3)_2$ (68).

The fact that this complex is diamagnetic raises the same questions as in the case of $Ni(BH_4)(PPh_3)_3$, namely is the complex a dimeric species containing two Ni(I) centers or a hydride complex of Ni(II). The latter is excluded for the same reasons as advanced before, and, in addition, a careful search of the ^{1}H n.m.r. spectrum (10-40τ) in both benzene and THF failed to reveal a hydride signal.

The reflectance spectrum, Figure 10, shows a band at 15380 cm^{-1} which shifts to 16670 cm^{-1} (ϵ max 1418)

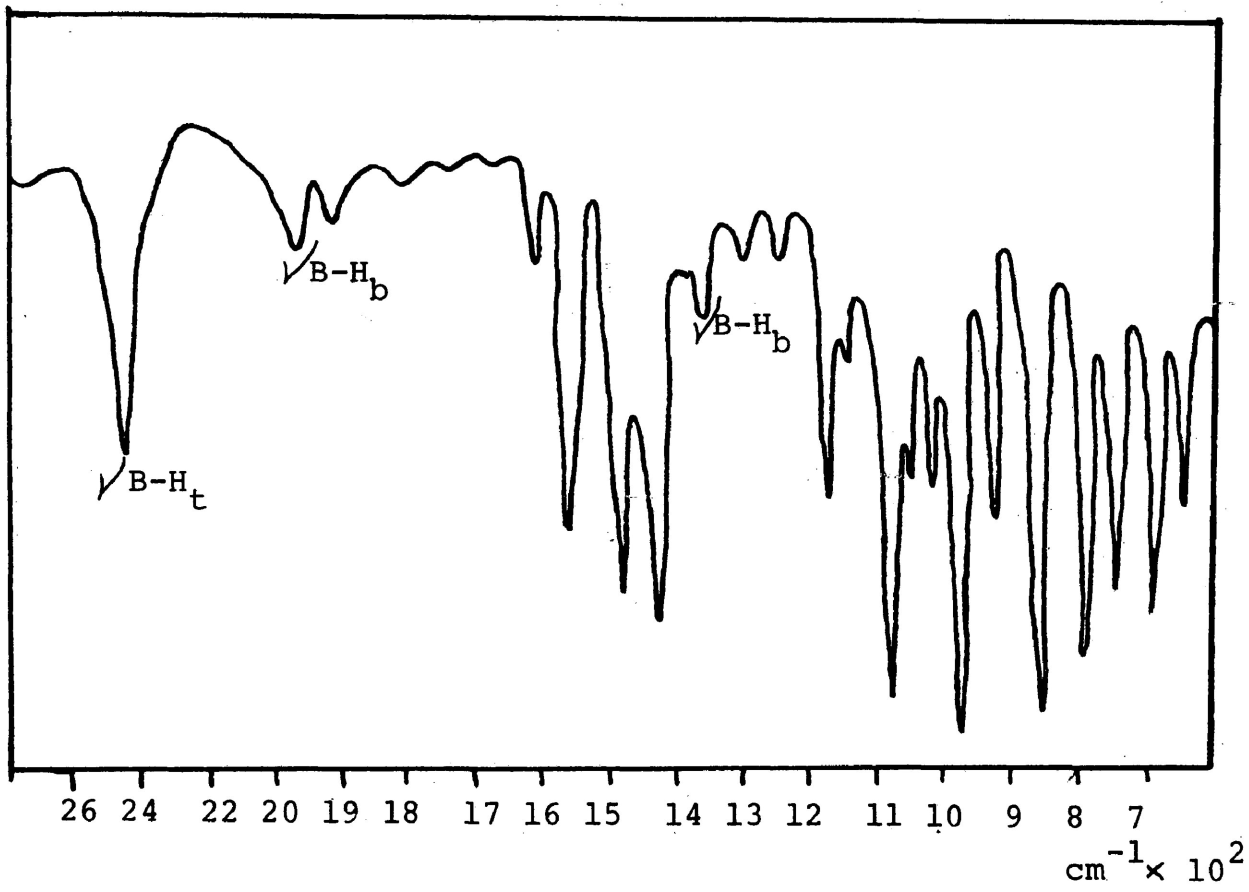


Figure 9. Infrared spectrum of $Ni_2(BH_4)_2(PPh_3)$.

(hexachlorobutadiene mull)

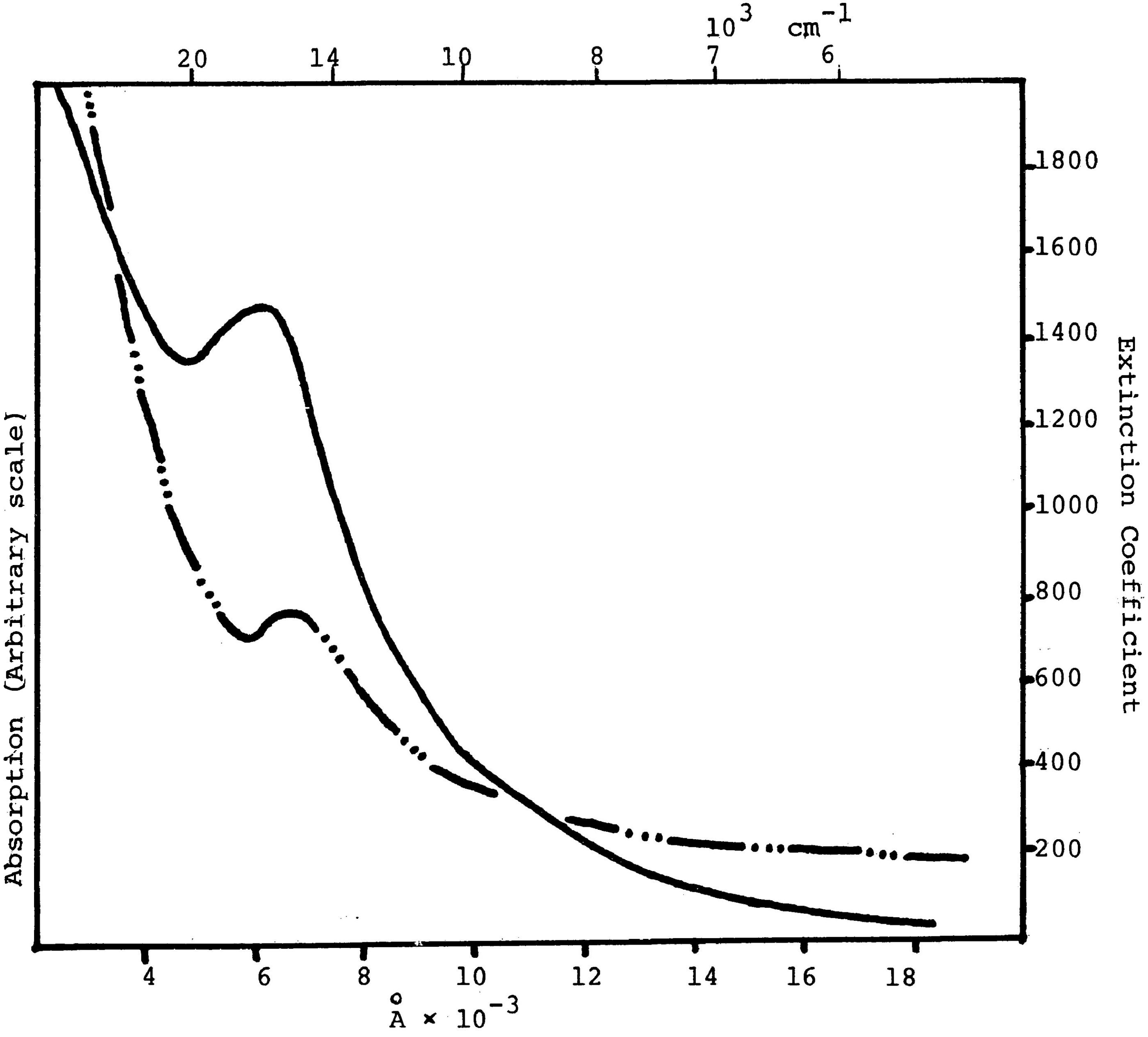


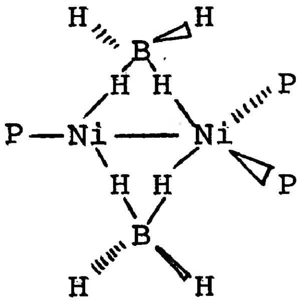
Figure 10. Electronic spectrum of $Ni_2(BH_4)_2(PPh_3)_3$

—— solution spectrum (benzene)

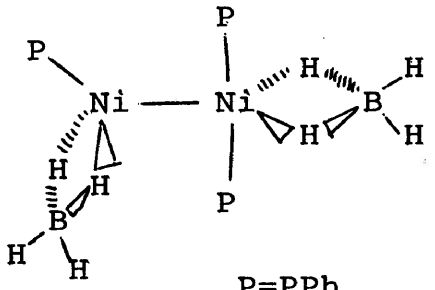
—·''·— reflectance spectrum

in solution. The origin of the transition is not understood but is probably not d-d in character. Solutions of the complex are so air sensitive that molecular weight data have not yet been obtained.

Thus, the most likely molecular structures for this complex are:



or



P=PPh_3

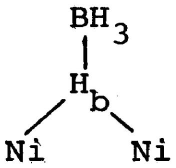
Alternatively a more symmetrical arrangement would be achieved if one of the phosphines was involved in bridging the two Ni atoms, but clearly a single crystal X-ray study is needed to resolve the issue.

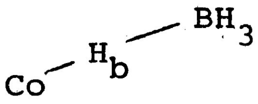
III.2.3. Stability and Reactivity.

The two Ni(I)-BH_4 complexes are much more air-sensitive than those of Co(I). Both complexes are pyrophoric, decomposing instantly in air to give black residues which, from infrared spectral data, contain both $Ph_3P\rightarrow BH_3$ and $Ph_3P=O$. The $Ni_2(BH_4)_2(PPh_3)_3$ complex is, like the Co(I)-BH_4 complexes, quite stable when stored under nitrogen atmospheres, but $Ni(BH_4)(PPh_3)_3$ decomposes under nitrogen within one week, to $Ni(PPh_3)_2$ and Ph_3P-BH_3 (identified from X-ray powder data).

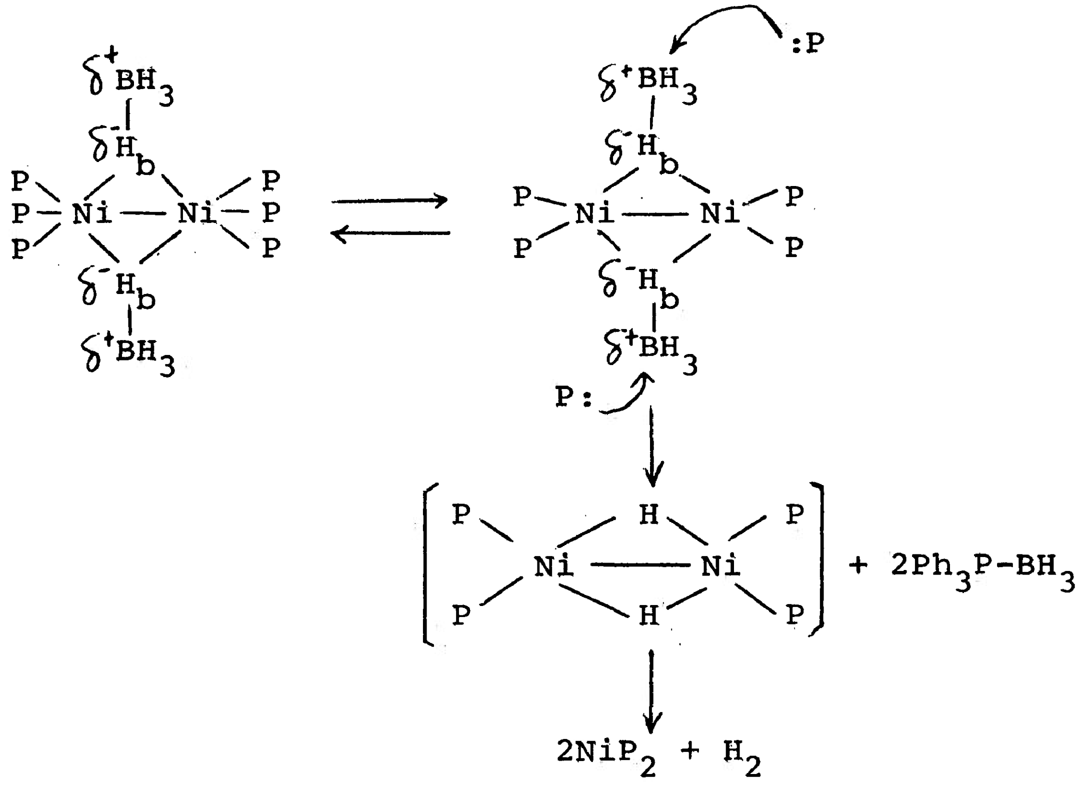
The complex $Ni_2(BH_4)_2(PPh_3)_3$ is recovered unchanged from benzene or THF solutions in the presence or absence of added PPh_3. When this compound is suspended and stirred in ethanol in the presence of PPh_3 for 24 hours, no BH_4 remained in the solid, but no Ph_3P-BH_3 was detected in the system. The fact that no Ph_3P-BH_3 was observed from these solutions would seem to indicate that the formation of Ph_3P-BH_3 in the reactions of NiX_2P_2, PPh_3 and $NaBH_4$ in ethanol (15 minutes to 1 hour) probably arises from the reaction of PPh_3 with an intermediate complex which must be present in the system prior to the formation of $Ni_2(BH_4)_2(PPh_3)_3$. This could be a monomeric, 3-coordinated intermediate $Ni(BH_4)(PPh_3)_2$. Unlike $Co(BH_4)(PPh_3)_3$, the monodentate $Ni(BH_4)(PPh_3)_3$ cannot be converted into a bidentate Ni(I)-BH_4 complex in benzene or THF solution, but decomposes to give $Ni(PPh_3)_2$ and Ph_3P-BH_3. This can be explained as follows:

The formation of the two Ni(I)-(BH_4) complexes occurs via two different mechanisms and no common intermediate, as occurs in the case of the Co(I)-BH_4 complexes, is involved. Also the coordination of the BH_4 group to the Ni(I) and Co(I) in the $M(BH_4)(PPh_3)_3$ complexes is different. In $Ni(BH_4)(PPh_3)_3$, the BH_4 group is probably coordinated to two Ni(I) centers, while the Co complex involves a simple monodentate BH_4 as shown below.





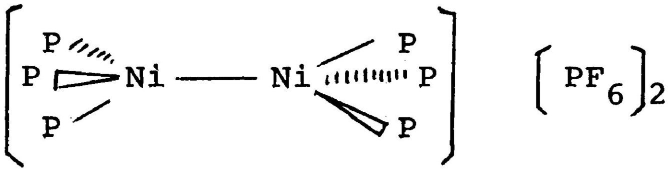
If this is the case, then it is reasonable to expect that the $B-H_b$ bond is weaker in the Ni complex than in both monodentate $Co(BH_4)(PPh_3)_3$ and the bidentate $Ni_2(BH_4)(PPh_3)_3$. The $Ni-H_b-Ni$ grouping involves a 2 electron 3-centered system, and therefore is electron deficient. Electron density could then be drawn from the $-BH_3$ group to the $Ni-H_b-Ni$, making the B atom slightly more positive. Then, as a phosphine dissociates from $Ni(BH_4)(PPh_3)_3$, it could attack the boron atom, producing, as shown below, Ph_3P-BH_3 and presumably a Ni(I)-H complex (?).



As with the Co(I)-BH_4 complexes, both Ni(I)-BH_4 complexes give, when stirred in solutions of acetonitrile or nitromethane at room temperature, a precipitate of Ph_3P-BH_3 and solutions of unidentified Ni complexes. When heated under reflux in CH_3CN, $Ni_2(BH_4)_2(PPh_3)_3$ gives the same products, while, $Ni(BH_4)(PPh_3)_3$ decomposes to Ni metal.

In view of the fact that $Ni(Phen)_2(BH_4)$ reacts with $NaPF_6$ or $NaBPh_4$ in ethanol to produce the cationic Ni(I) complexes Ni(Phen)X (X=PF_6 or BPh_4) (7), similar reactions of the Ni(I)/(BH_4)/(PPh_3) complexes were investigated especially since these may provide important corroborative evidence to support the Ni(I) formulations of the BH_4 complexes. Both of the $Ni-BH_4-PPh_3$ complexes were treated with $NaBPh_4$ and $NaPF_6$ in the presence of added PPh_3 in ethanol. In reactions with $NaBPh_4$, both of the Ni complexes are decomposed to Ph_3P-BH_3, as was observed with Co(I) complexes.

However, when an ethanolic solution of $NaPF_6$ ($\sim$10 M excess) is added to a stirred suspension of $Ni(BH_4)(PPh_3)_3$ and PPh_3 (3M excess), in ethanol, a cationic Ni(I) complex is formed. A small amount of gas is generated initially, (HF, B_2H_6 or PF_3?) and after stirring for 2 hours, a pale yellow diamagnetic solid is produced. This solid, which can be recrystallised from THF, analyses well for the formulation $[Ni(PPh_3)_3][PF_6]$. The presence of PF_6^- is confirmed by the absorption at 840 cm^{-1} in the infrared spectrum due to the P-F stretching frequency. No d-d absorption bands are visible in the reflectance spectrum (Figure 7) and the only resonable explanation of the properties of $[Ni(PPh_3)_3]$-$[PF_6]$ is to assume that the complex is dimeric with a Ni-Ni linkage, such as shown below.



In reactions between $Ni(BH_4)(PPh_3)_3$ and $NaPF_6$, the ratio of $Ni:NaPF_6$ has been varied between 1:1 and 1:10. The higher is this ratio, the greater is the yield of product. Since this is insoluble and precipitates out of solution immediately it is formed, together with the fact that other unidentified products are formed, these observations tend to rule out a simple substitution reaction based on the equation

$$Ni(BH_4)(PPh_3)_3 + NaPF_6 \rightleftarrows Ni(PPh_3)_3PF_6 + NaBH_4$$

Also, if the reaction were this simple, there is no apparent reason why $NaBPh_4$ should not produce similar compounds. The reactions of $Ni(Phen)_2(BH_4)$ with $NaPF_6$ and $NaBPh_4$ are probably simple substitutions, since the BH_4 is almost certainly ionic in this case.

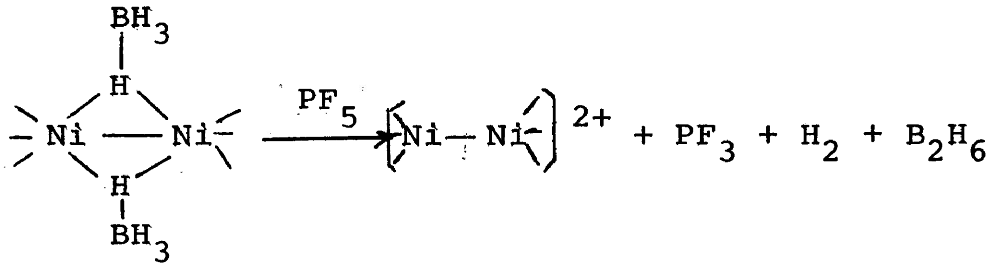
Although no direct evidence has been obtained for the mechanism of the formation of $[Ni_2(PPh_3)_6][PF_6]_2$, the following possibility is presented. $NaPF_6$ is a relatively inert compound at room temperature, but is susceptible to slow hydrolysis to give hydrogen fluoride (140). The presence of HF is apparent from the slight etching of the glassware during these ethanolic reactions, and its formation may occur as follows:

$$NaPF_6 + EtOH \longrightarrow NaPF_5(EtO) + HF$$

The organic complex, $PF_5(EtO)^-$ is itself unstable and rapidly decomposes in alcohol to form PF_5 (141).

$$NaPF_5(EtO) \xrightarrow[EtOH]{} PF_5 + NaOEt$$

It has been shown (142) that PCl_5 reacts with BH_4^- to generate PCl_3, B_2H_6 and H_2, and it is therefore possible that PF_5 could react with coordinated BH_4^- as follows:



Thus, of the Co(I) and Ni(I)-BH_4 complexes, only $Ni(BH_4)(PPh_3)_3$ reacts with $NaPF_6$ to produce an identifiable complex. This may be due to a weaker Ni-H_b bond in $Ni(BH_4)(PPh_3)_3$ compared with those in the other three complexes. The reason why no BPh_4^- complex could be formed is not fully understood, although $NaBPh_4$ is more stable and less susceptible to hydrolysis than is $NaPF_6$.

The pale yellow complex $[Ni_2(PPh_3)_6][PF_6]_2$ can be recrystallised from CH_3CN producing an orange crystalline solid. Chemical analyses (see Table 17) are consistent with the formulation $[Ni(PPh_3)_3(CH_3CN)][PF_6]$

and also with $[(PPh_3)_3Ni-N_2-Ni(PPh_3)_3][PF_6]_2$, (c.f. the Ni(O) complex $[(PCy_3)_2Ni-N_2-Ni(PCy_3)_2]$ (139)).

The reflectance spectrum of the complex is shown in Figure 7 and the absorption band at ~6370 cm^{-1} is the $^2T_2 \rightarrow {}^2E$ transition in a tetrahedral d^9 Ni(I) system. The complex is paramagnetic with one unpaired electron and has a magnetic moment of 1.88 BM based on the acteonitrile formula and 1.87 BM based on the dinitrogen structure. Conductivity measurements in acetonitrile solutions (Table 17) are also consistent with both formulations. The X-ray powder pattern is quite different from that of the $[Ni_2(PPh_3)_6][PF_6]_2$ complex.

It should be possible to distinguish clearly between these two formulas by an examination of spectroscopic data. Unfortunately the Raman spectrum is not available at this time, and no evidence of either the normally very strong $C\equiv N$ stretching frequency or the $\nu N\equiv N$ frequency could be seen in the infrared spectrum. Careful mass spectral studies showed no molecular nitrogen above background, but acetonitrile is consistently present, as shown by the peak at $m/e=41$. Finally, attempts to prepare the complex by bubbling N_2 into THF solutions of $[Ni_2(PPh_3)_6][PF_6]_2$ were not successful, and the starting material remained unchanged.

Table 17.

Analyses					Magnetic Moment (B M)	Conductivity* ohm^{-1} cm^{-1} (10^{-3}M, CH_3CN, 20°C)
	C	H	N	Ni		
Found	64.57	4.84	1.28	6.14		
Calc for $[Ni(PPh_3)_3(CH_3CN)][PF_6]$	65.20	4.69	1.36	5.69	1.88	151.3
Calc for $[(PPh_3)_3Ni{-}N_2{-}Ni(PPh_3)_3][PF_6]_2$	64.57	4.52	1.39	5.76	1.87 (per Ni)	294.6

* Typical valves for 1:1 and 1:2 elctrolytes in 10^{-3}M CH_3CN are:

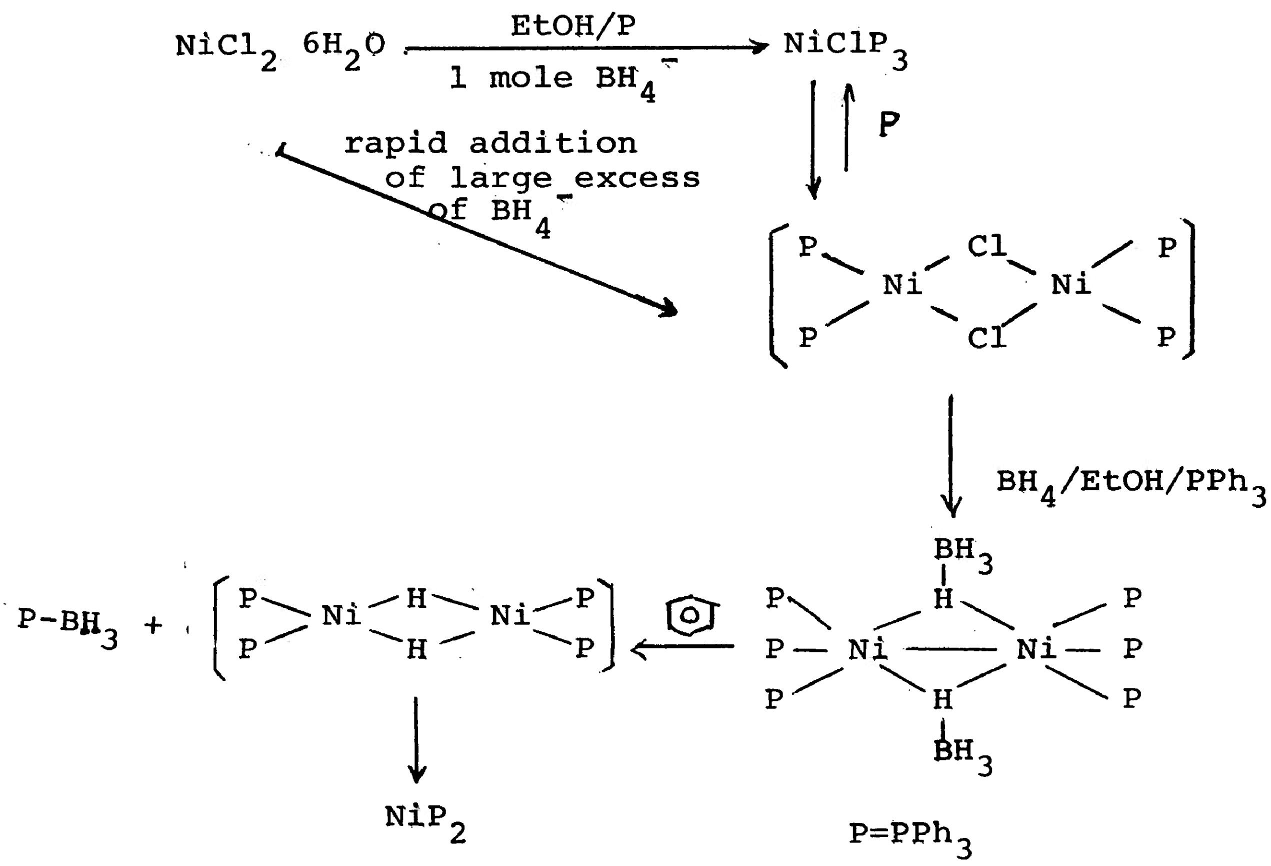
1:1, Ph_4PCl = 148.8 (7)

1:2, $(Ph_4P)_2C_8O_4S_3$ = 309 (143)

It therefore appears, on the available evidence, that the complex should be formulated as a tetrahedrally coordinated Ni(I) cation, $[Ni(PPh_3)_3(CH_3CN)]^+$ although it is not understood why, what is normally one of the strongest bands in the infrared (νCN), is not observed.

III.2.3. Mechanism of the Reaction between the Nickel Halide Complexes and Sodium Tetrahydroborate.

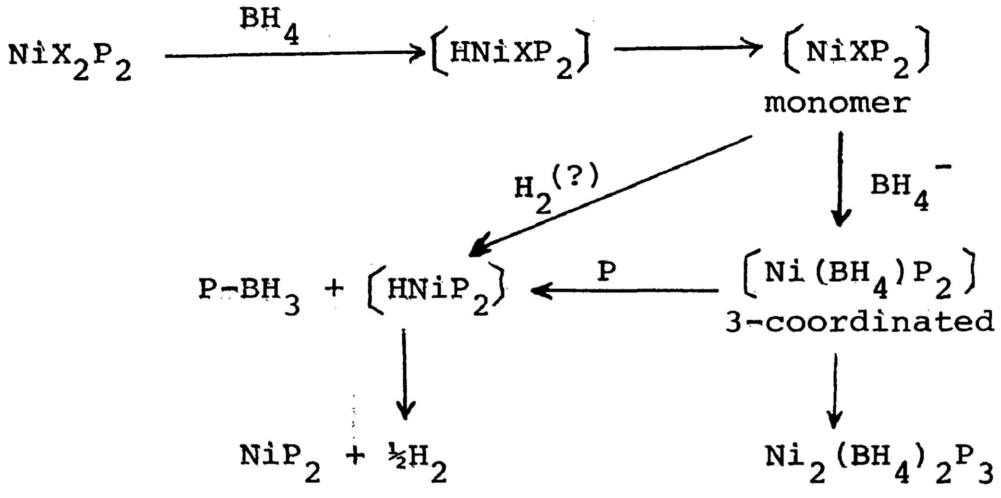
It has been established that $Ni(BH_4)(PPh_3)_3$ can be made from the reaction between Ni(II) chloride, PPh_3 and $NaBH_4$ in ethanol. The complex can also be made from the reaction of $NiCl(PPh_3)_3$ with $NaBH_4$ and PPh_3 (136) and also (5) from the Ni(II)/PPh_3/$NaBH_4$ reaction where $NiCl(PPh_3)_3$ is first made in situ, followed by the further addition of $NaBH_4$. Since $Ni(BH_4)(PPh_3)_3$ is dimeric, it is reasonable to assume that it is formed from a dimeric intermediate complex. Furthermore as the complex $NiCl(PCy_3)_2$ is dimeric (139) (at least in the solid state) and as it has been shown (130) that $NiCl(PPh_3)_3$ dissociates in solution to give $NiCl(PPh_3)_2$ it is possible that, by analogy, the latter may be the above mentioned dimeric intermediate. Therefore, the reaction between Ni(II) and $NaBH_4$ may proceed as follows:



Thus, addition of 1 mole of $NaBH_4$ to a mixture of Ni(II) and PPh_3 produces only $NiCl(PPh_3)_3$, but the dimeric intermediate could be formed by the rapid addition of a large excess of $NaBH_4$ due to unsufficient PPh_3 in solution.

In the reaction between $NaBH_4$ and Co complexes it has been shown that the main factors determining the nature of the final products are the rate of addition of $NaBH_4$, the presence of free PPh_3 and the solvent. With Ni, however, the nature of the starting Ni(II) compound is of much more importance, and it appears that a quite different reaction mechanism is followed depending on whether simple Ni(II) salts or the Ni(II) complexes $NiX_2(PPh_3)_2$ are used. In the Co system, the $CoX_2(PPh_3)_2$ complexes are formed very rapidly and are present as intermediates in the Co(II) halide-$NaBH_4$-PPh_3 reactions. The formation of $NiX_2(PPh_3)_2$, however, requires the heating under reflux of Ni(II)-halides with PPh_3 in ethanol and these complexes are therefore not formed as intermediate in the Ni(II)halide-$NaBH_4$-PPh_3 reactions at room temperature. This is supported by the fact that Ni(II)-halides-$NaBH_4$-PPh_3 in ethanol lead to $Ni(BH_4)(PPh_3)_3$ while $NiX_2(PPh_3)_2$ and $NaBH_4$ (no additional PPh_3) in ethanol gives $Ni_2(BH_4)_2(PPh_3)_3$. Since the $NiX_2(PPh_3)_2$ complexes are not present as intermediates, then intermediate complexes of the type $HNiX(PPh_3)_2$ (c.f. the Co system) cannot be present. Also, no conditions have been found which allow interconversions between $Ni(BH_4)(PPh_3)_3$ and $Ni_2(BH_4)_2(PPh_3)_3$ and therefore it is unlikely that a common intermediate is present in the formation of these two complexes.

Thus, considering these points, the following mechanism is proposed for the reaction of $NaBH_4$ with the $NiX_2(PPh_3)_2$ complexes in ethanol (no additional PPh_3).



P=PPh_3

Although no direct evidence is available to support the existence of a monomeric 3-coordinated $NiX(PPh_3)_2$ intermediate, other workers (139) have demonstrated the existence of such species in solutions of the analogous PCy_3 system—i.e. $NiX(PCy_3)_2$. Substitution of Cl^- by BH_4^- with retention of configuration would result in the 3-coordinated monodentate BH_4 complex from which the formation of the main reaction products can be rationalised. The complex $Ni_2(BH_4)_2(PPh_3)_3$ does not react with PPh_3 in benzene to produce Ph_3P-BH_3, nor is the latter apparently formed when PPh_3 is stirred with the Ni complex in ethanol for 24 hours. Therefore, formation of Ph_3P-BH_3 from the $NiX_2(PPh_3)_2-PPh_3-NaBH_4$ reaction takes place via an unstable intermediate, probably the monomeric $[Ni(BH_4)(PPh_3)_2]$. If this is present as the dimer, then $[Ni(BH_4)(PPh_3)_3]_3$ would be formed and none has been observed in these reactions. Furthermore, the proposed monomeric Ni-(BH_4) intermediate must have a monodentate BH_4 grouping, otherwise the stable analogue of $Co(BH_4)(PPh_3)_2$ would probably be produced rather than the dimeric $Ni_2(BH_4)_2(PPh_3)_3$.

The reductions of the $NiX_2(PPh_3)_2$ complexes by $NaBH_4$ are relatively fast (reactions complete within ~15 minutes), and large amounts of active hydrogen are generated during the reaction. This hydrogen may react with the $[NiCl(PPh_3)_2]$ intermediate to give an unstable hydrido complex, $[HNi(PPh_3)_2]$, which then undergoes further decomposition to give $Ni(PPh_3)_2$. This may, in fact, explain the relatively low yield of $[Ni_2(BH_4)_2(PPh_3)_3]$.

III.3. Homogeneous Hydrogenation of 1-Hexene Using Hydridotetrahydroboratotris(triphenylphosphine)-ruthenium(II) as Catalyst.

Dichlorotris(triphenylphosphine)ruthenium(II) has been found to be an effective catalyst for the homogeneous hydrogenation of some unsaturated organic substances (144). Wilkinson et. al. (32) later prepared the analogous hydrido complex, $HRuCl(PPh_3)_3$ and also found it to be extremely active in similar hydrogenations in benzene or toluene. However, a detailed kinetic study could not be made due to solubility problems, sensitivity towards oxygen and effects of catalyst poisoning.

Similarly, solutions of $HRuCl(PPh_3)_3$ in dimethylacetamide (145) are exceedingly effective in catalyzing the hydrogenation of maleic acid. It was suggested that the mechanism of the reaction involves dissociation of the catalyst to give a 4-coordinated monomer, $HRuCl(PPh_3)_2$, which then reacts with the substrate to form an alkyl complex followed by H_2 cleavage.

$$HRuCl(PPh_3)_3 \rightleftharpoons HRuCl(PPh_3)_2 + PPh_3$$

$$HRuCl(PPh_3)_2 + \text{olefin} \longrightarrow RuCl(PPh_3)_2(\text{alkyl})$$

$$RuCl(PPh_3)_2(\text{alkyl}) + H_2 \longrightarrow HRuCl(PPh_3)_2 + \text{alkane}$$

The complex $HRu(BH_4)(PPh_3)_3$, containing a monodentate BH_4 group, was first made in these laboratories (6), and is closely related to the above chloride complex. Also, as mentioned in the introduction, BH_4 complexes are known to be active hydrogenation catalysts, e.g. $Rh(BH_4)Cl_2(Py)_2(dmf)$ (120), and are thought to be the active species in mixtures of, for example, $NiCl_2/NaBH_4/Py$ (121), and $NiBr_2(PPh_3)_2/NaBH_4$ in THF-ethanol (137) or in ethanol (146).

However, no detailed kinetic study has been done on homogeneous hydrogenations where a BH_4 complex is the active species. This section of the thesis therefore presents as part of a general study of M/BH_4/phosphine reactions of which this thesis is one facet, kinetic data on the homogeneous hydrogenation of 1-hexene in benzene solution using $HRu(BH_4)(PPh_3)_3$ as catalyst, together with the most reasonable mechanism consistent with the kinetic data. From the work described in the preceding sections, it might seem more reasonable to use one or more of the Co(I) and Ni(I) tetrahydroborate complexes reported in this work,. However, these are extremely difficult to handle and it was felt that for a preliminary study, a more stable group VIII tetrahydroborate complex such as $HRu(BH_4)(PPh_3)_3$ should be used.

III.3.1. Catalytic Hydrogenation of 1-Hexene.

$HRu(BH_4)(PPh_3)_3$ was prepared as described in section II.3.8, and in benzene solution is effective in catalyzing the hydrogenation of 1-hexene at approximately one-fourth the rate observed with Wilkinson's catalyst, $RhCl(PPh_3)_3$, under similar conditions.

Graphs showing the hydrogen uptake for the hydrogenation of 1-hexene at 20°C for a variety of PPh_3, $HRu(BH_4)(PPh_3)_3$ and 1-hexene concentrations are shown in Figures 11 to 13. Solutions of the catalyst in benzene are reddish-brown, but change to yellow-brown on addition of 1-hexene when the catalyst concentration is low (less than $\sim 0.5 \times 10^{-3}$M). At higher catalyst concentrations, the color change is less apparent. Also the color of the $HRu(BH_4)(PPh_3)_3$ solution remains unchanged when it is stirred under hydrogen in the absence of added olefin. This indicates that the 1-hexene probably coordinates to the Ru^{II} species. No metal was visible in the reaction flask at the end of each experiment.

The initial rate of hydrogen uptake was obtained from the tangent to the plot of hydrogen uptake against time which is generally linear after the first 60 seconds. The dependence of these rates on PPh_3, 1-hexene, H_2 and $HRu(BH_4)(PPh_3)_3$ concentrations is shown in the following tables and figures.

Table 18.

$HRu(BH_4)(PPh_3)_3$ catalysed hydrogenation of 1-hexene in benzene. Dependence of initial rate on 1-hexene and hydrogen concentration at 20°C.

$[Ru^{II}]$ $\times 10^3$, M	$[PPh_3]$ $\times 10^3$ M	[1-hexene] M	H_2 mm	$[H_2]$ $\times 10^3$ M	Initial rate, $\times 10^5$ $MSec^{-1}$
1.00	3.00	0.32	655	4.48	3.61
1.00	3.00	0.50	650	4.48	4.59
1.00	3.00	0.85	655	4.48	8.99
1.00	3.00	0.94	655	4.48	10.25
1.00	3.00	1.25	655	4.48	12.28
1.00	3.00	1.57	655	4.48	14.81
1.00	3.00	0.50	290	1.925	2.28
1.00	3.00	0.50	349	2.25	2.86
1.00	3.00	0.50	415	2.68	3.45
1.00	3.00	0.50	607	3.93	4.78
1.00	3.00	0.50	680	4.68	5.49
1.00	3.00	0.50	766	4.95	5.95

Table 19.

$HRu(BH_4)(PPh_3)_3$ catalysed hydrogenation of 1-hexene in benzene. Dependence of initial rate on $HRu(BH_4)(PPh_3)_3$ and PPh_3 concentration at 20°C.

$[Ru^{II}]$ $\times 10^3$, M	$[PPh_3]$(total) $\times 10^3$, M	[1-hexene] M	H_2 mm	$[H_2]$ $\times 10^3$, M	Initial rate $\times 10^5$, $Msec^{-1}$
0.15	0.45	0.50	655	4.48	2.77
0.52	1.56	0.50	655	4.48	3.42
1.00	3.00	0.50	655	4.48	4.59
1.67	5.01	0.50	655	4.48	5.02
2.81	7.43	0.50	655	4.48	5.49
3.34	10.02	0.50	655	4.48	5.74
3.80	11.40	0.50	655	4.48	5.82
1.00	3.00	0.50	655	4.48	4.59
1.00	3.54	0.50	655	4.48	4.08
1.00	4.10	0.50	655	4.48	3.62
1.00	4.48	0.50	655	4.48	3.31
1.00	4.95	0.50	655	4.48	3.18

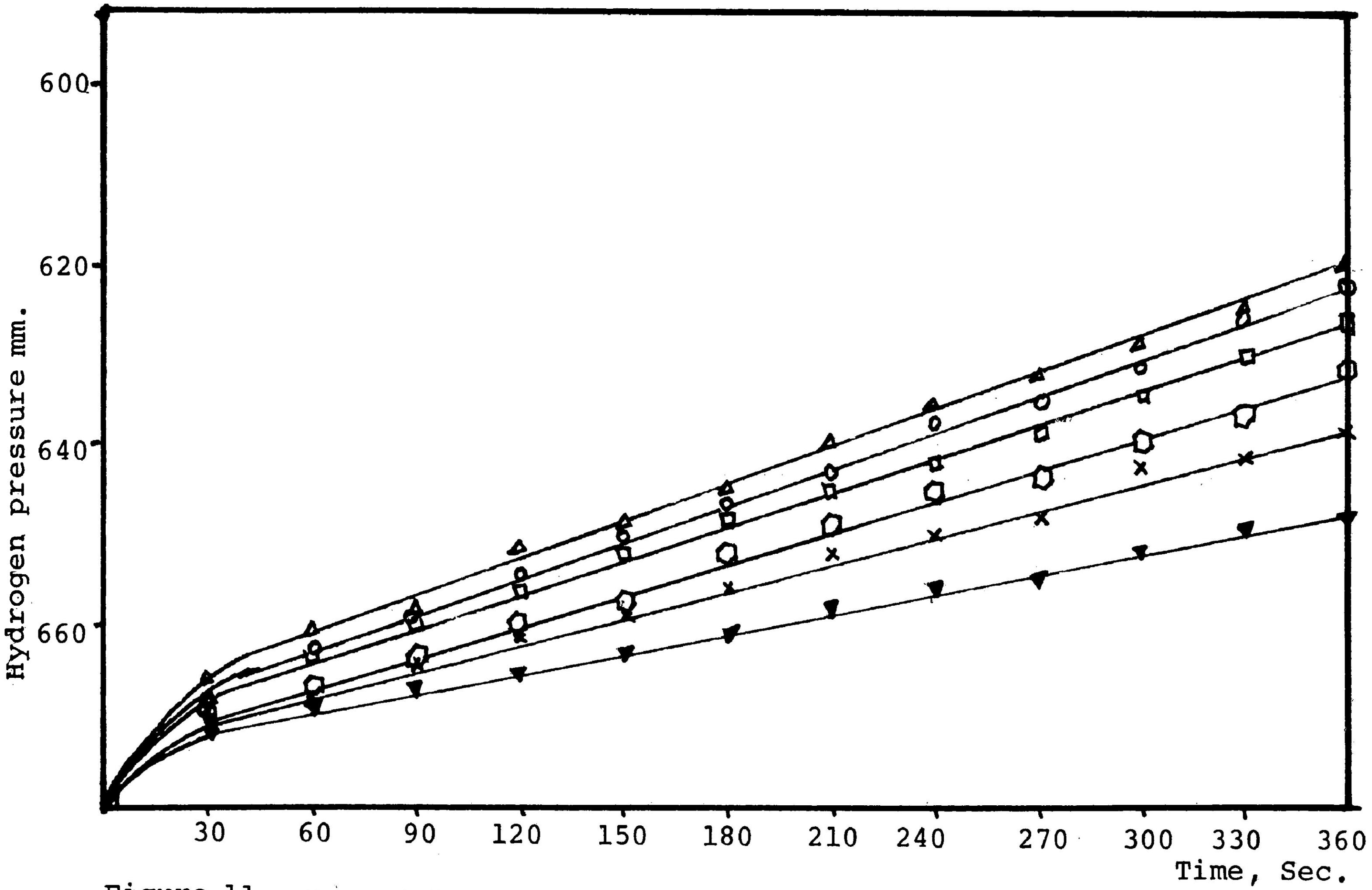


Figure 11 Rate plots for the $HRu(BH_4)(PPh_3)_3$ catalysed hydrogenation of 1-hexene in benzene at 20°C (680 mm H_2, 0.5 M 1-hexene, $[PPh_3]/[Ru^{II}]$ =3), $[Ru^{II}]$ (▼) 0.15×10^{-3} M, (×) 1.00×10^{-3} M, (⬠) 1.67×10^{-3} M, (□) 2.81×10^{-3} M, (o) 3.34×10^{-3} M, (△) 3.80×10^{-3} M.

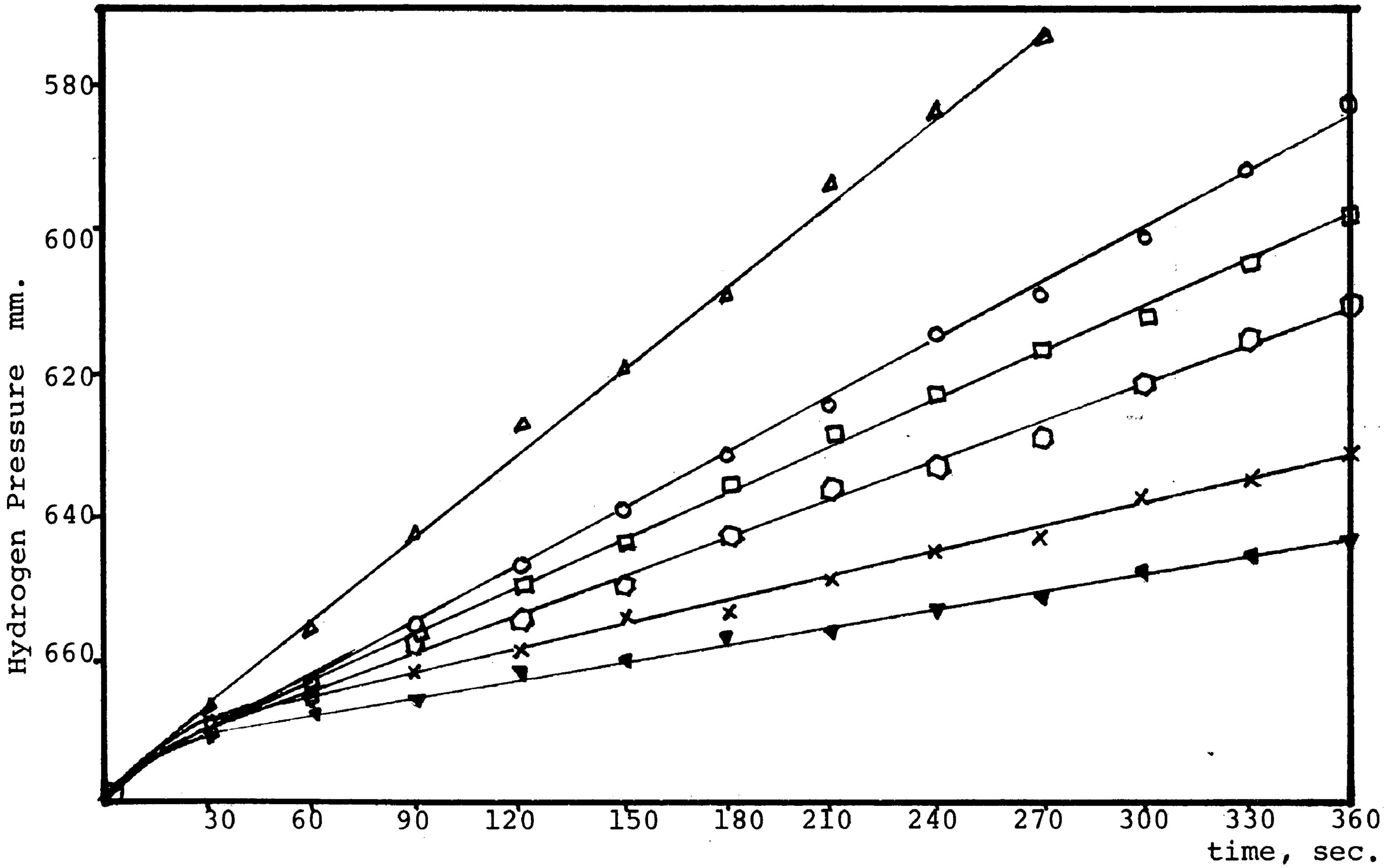


Figure 12. Rate plots for the $HRu(BH_4)(PPh_3)_3$ catalysed hydrogenation of 1-hexene in benzene at 20°C (680 mm H_2, 1.00 m, M $[Ru^{II}]$, $[PPh_3]/[Ru^{II}]=3$). 1-hexene (▼) 0.32 M, (×) 0.5 M, (⬡) 0.85 M (□) 0.94 M, (○) 1.25 M, (△) 1.57 M.

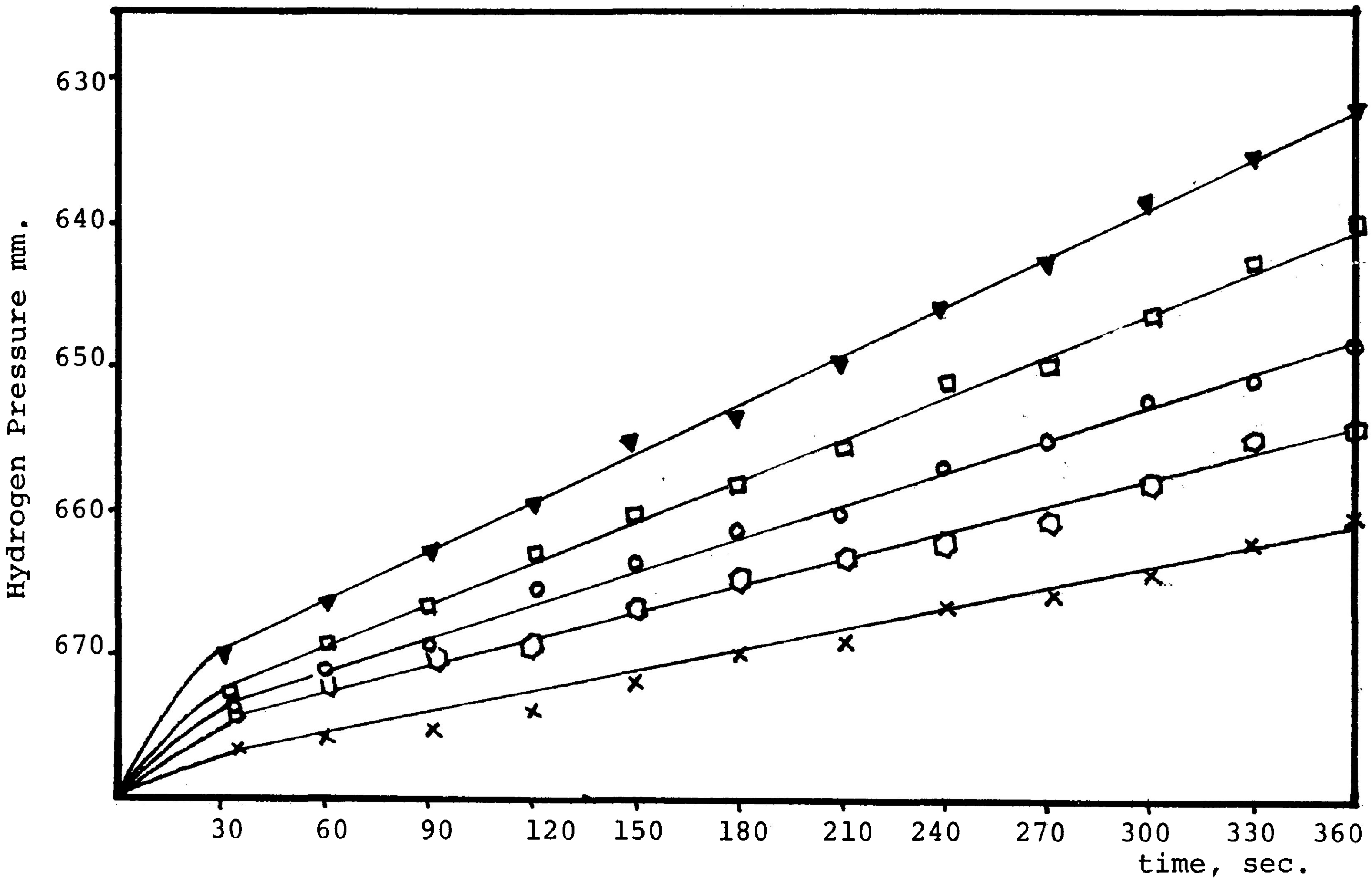


Figure 13. Rate plots for the $HRu(BH_4)(PPh_3)_3$ catalysed hydrogenation of 1-hexene in benzene at 20°C (680 mm H_2, 0.5 M 1-hexene, 1 mM $[Ru^{II}]$). $[PPh_3]$ added (×) 1.95×10^{-3} M, (⬡) 1.48×10^{-3} M, (○) 1.10×10^{-3} M, (□) 0.54×10^{-3} M, (▼) 0.00×10^{-3} M.

III.3.2. Discussion of Kinetic Results.

The transfer of hydrogen molecules to the olefin in solution via a catalyst complex may occur by either one or both of the following possible paths:

$$A + S \overset{K}{\rightleftarrows} AS \xrightarrow[\text{slow}]{H_2} \text{Products} \qquad (3.1)$$

$$A + H_2 \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} AH_2 \xrightarrow[\text{slow}]{S} \text{Products} \qquad (3.2)$$

where A is the catalyst and S the substrate. In this system, the rapid change in color of the catalyst solution when olefin is added probably indicates the formation of AS. No visible evidence for the formation of AH_2 was observed. As with the $HRuCl(PPh_3)_3$ system (145) therefore, the first step in the mechanism appears to be the formation of AS and the kinetic data can be explained satisfactorily on this basis.

The inverse dependence of the initial rate of hydrogenation on the concentration of phosphine is consistent with dissociation of the catalyst to give kinetically significant amounts of a square planar monomer, $HRu(BH_4)(PPh_3)_2$. This then reacts with and reduces the olefin according to the following scheme.

$$\underset{\text{I}}{\text{HRu(BH}_4\text{)(PPh}_3\text{)}_3} \overset{K_1}{\rightleftharpoons} \underset{\text{II}}{\text{HRu(BH}_4\text{)(PPh}_3\text{)}_2} + \text{PPh}_3 \qquad (3.3)$$

$$\underset{\text{II}}{\text{HRu(BH}_4\text{)(PPh}_3\text{)}_2} + \text{alkene} \overset{K_2}{\rightleftharpoons} \underset{\text{III}}{\text{Ru(BH}_4\text{)(PPh}_3\text{)}_2\text{(alkyl)}} \qquad (3.4)$$

$$\underset{\text{III}}{\text{Ru(BH}_4\text{)(PPh}_3\text{)}_2\text{(alkyl)}} + \text{H}_2 \xrightarrow{k} \underset{\text{II}}{\text{HRu(BH}_4\text{)(PPh}_3\text{)}_2} + \text{alkane} \qquad (3.5)$$

where K_1 is the dissociation constant of the complex $\text{HRu(BH}_4\text{)(PPh}_3\text{)}_3$, K_2 is the formation constant of the alkyl complex and k the rate constant for the rate determining step. This mechanism will lead from equation 3,5, to the following rate expression.

$$\text{Rate}=k[\text{H}_2][\text{III}] \qquad (3,6)$$

From equation (3,4)

$$K_2= \frac{[\text{III}]}{[\text{II}][\text{S}]} \qquad (3,7)$$

where [S] is the concentration of the substrate. Since the concentration of III will be considerably less than that of the substrate, the following approximation will apply, where $[\text{S}]_T$ represents the total free substrate concentration.

$$[\text{S}]_T \approx [\text{S}]$$

Then equation (3,6) becomes

$$\text{Rate} = kK_2[H_2][S][II] \qquad (3,8)$$

From equation (3,3)

$$K_1 = \frac{[II][P]}{[I]} \qquad (3,9)$$

where $[P] \equiv [PPh_3]$.

$$\begin{aligned} \text{Since } [Ru^{II}]_T &= [I] + [II] + [III] \\ &= \frac{[II][P]}{K_1} + [II] + K_2[II][S] \\ &= [II]\{1 + K_2[S] + [P]/K_1\} \end{aligned}$$

$$\text{then } [II] = \frac{[Ru^{II}]_T}{1 + K_2[S] + [P]/K_1} \qquad (3,10)$$

Equation (3,8) can now be expressed in terms of $[Ru^{II}]_T$ and becomes

$$\text{Rate} = \frac{kK_2[S][H_2][Ru^{II}]_T}{1 + K_2[S] + [P]/K_1} \qquad (3,11)$$

Evidence for this rate law, as expressed in equation (3,11), is obtained from data of rate dependence on concentrations of PPh_3, H_2, 1-hexene and $HRu(BH_4)(PPh_3)_3$ and will now be presented.

III.3.2.1. Dependence on Substrate Concentration.

The initial rate of hydrogenation of 1-hexene is not linearly dependent upon the concentration of

1-hexene. Figure 14 indicates that the dependence is between first and zero order, the order decreasing with increasing 1-hexene concentration. However, a plot of the reciprocal of the rate, 1/R, against the reciprocal of the alkene concentration is linear (Figure 15) and is in agreement with the rate law (3,11) since equation (3,11) can be rewritten as

$$\frac{1}{R} = \frac{1 + [P]/K_1}{kK_2[Ru_T][H_2]} \cdot \left\{\frac{1}{[S]}\right\} + \frac{1}{k[Ru]_T[H_2]} \qquad (3,12)$$

From the intercept of the straight line in Figure 15 the following relationship is obtained.

$$\text{Intercept} = \frac{1}{k[Ru^{II}]_T[H_2]} \qquad (3,13)$$

$$\text{then} \quad k = \frac{1}{1.6 \times 10^3 (M^{-1}\ sec) \times 1 \times 10^{-3}(M) \times 4.48 \times 10^{-3}(M)}$$

$$\simeq 139\ M^{-1}sec^{-1}$$

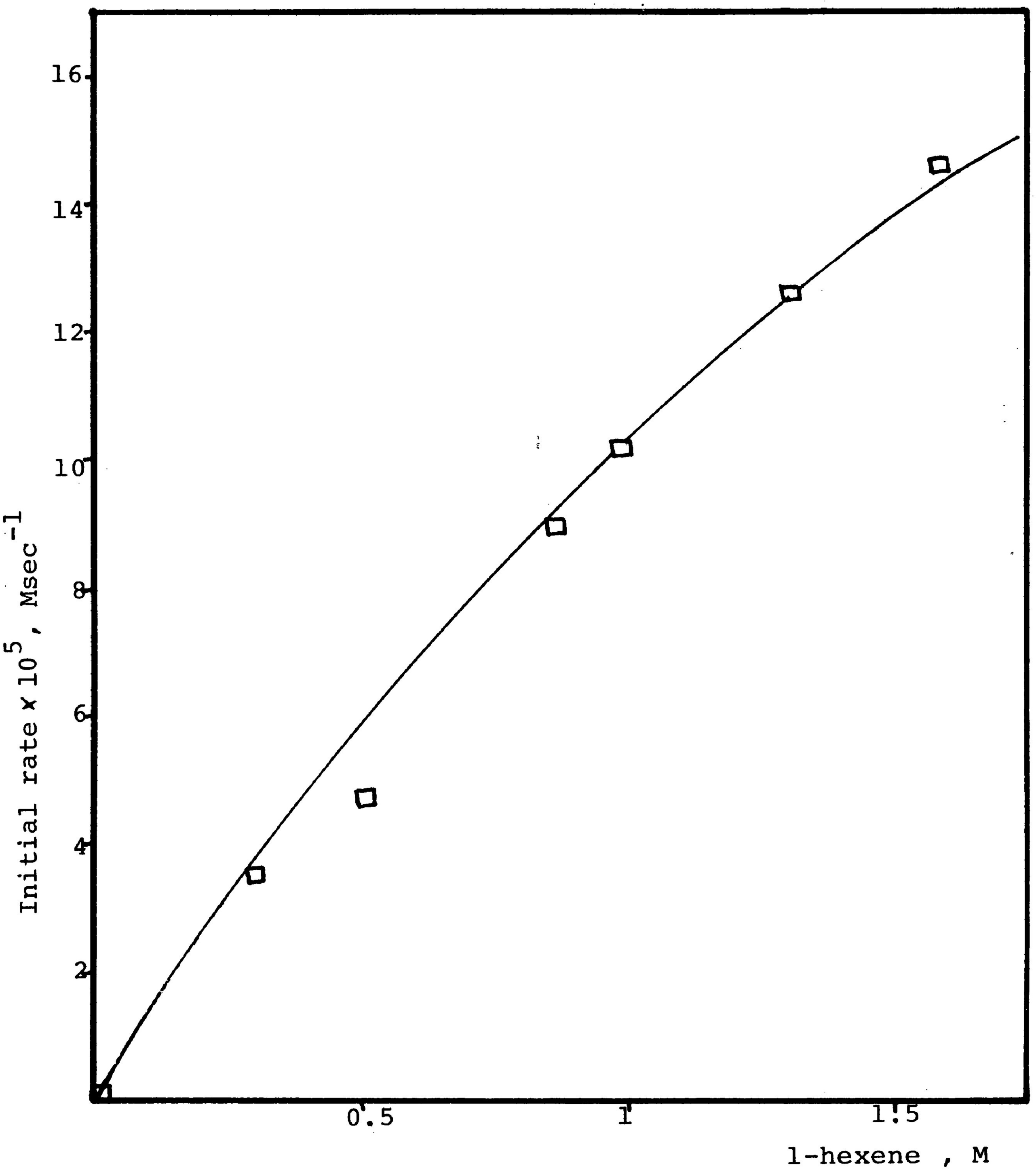


Figure 14. Dependence of initial rate of hydrogenation of 1-hexene in benzene at 20°C on [1-hexene] (655 mm H_2, 1mM[Ru^{II}])

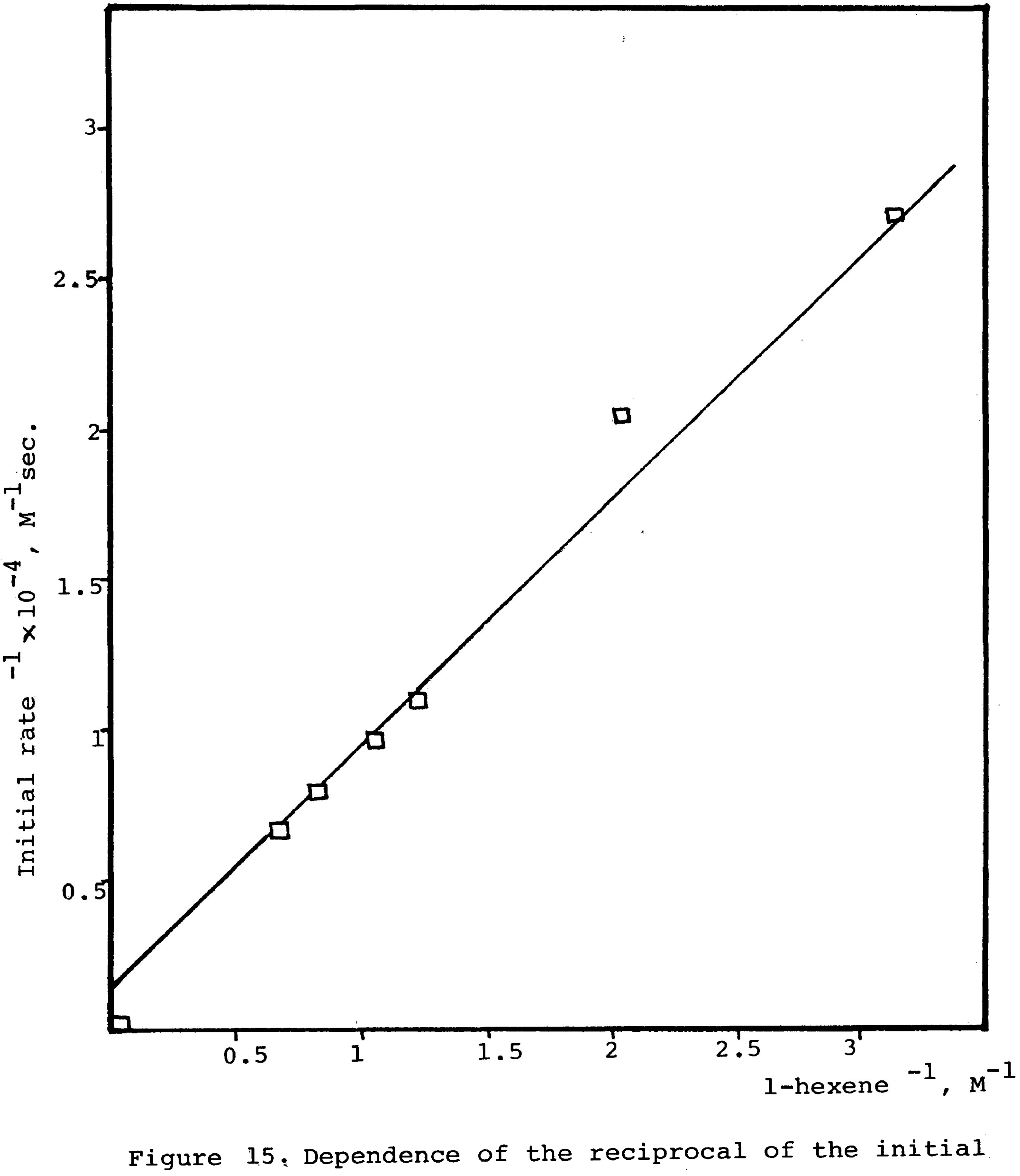


Figure 15. Dependence of the reciprocal of the initial rate on $[\text{1-hexene}]^{-1}$ at 20°C (655 mm H_2, 1mM $[Ru^{II}]_T$)

III.3.2.2. Dependence on Hydrogen Concentration.

Figure 16 shows that the plot of the initial rate against the hydrogen concentration is strictly linear with zero intercept. This indicates that the rate of hydrogenation is first order in the concentration of hydrogen, which is again consistent with equation (3,11).

III.3.2.3. Dependence on Triphenylphosphine Concentration.

A plot showing the initial rate of hydrogenation of 1-hexene against the concentration of added PPh_3 is shown in Figure 17. The reaction rate decreases as the concentration of PPh_3 increases. However, a plot of the reciprocal of the rate against the concentration of PPh_3 is linear with a positive intercept on the ordinate axis at zero $[PPh_3]$. This result provides additional evidence for the rate law based on the dissociation of $HRu(BH_4)(PPh_3)_3$ in benzene solution, since equation (3,11) can be rearranged to give:

$$\frac{1}{R} = \frac{[P]}{kK_1K_2[H_2][S][Ru^{II}]_T} + \frac{1 + K_2[S]}{kK_2[H_2][S][Ru^{II}]_T} \qquad (3,14)$$

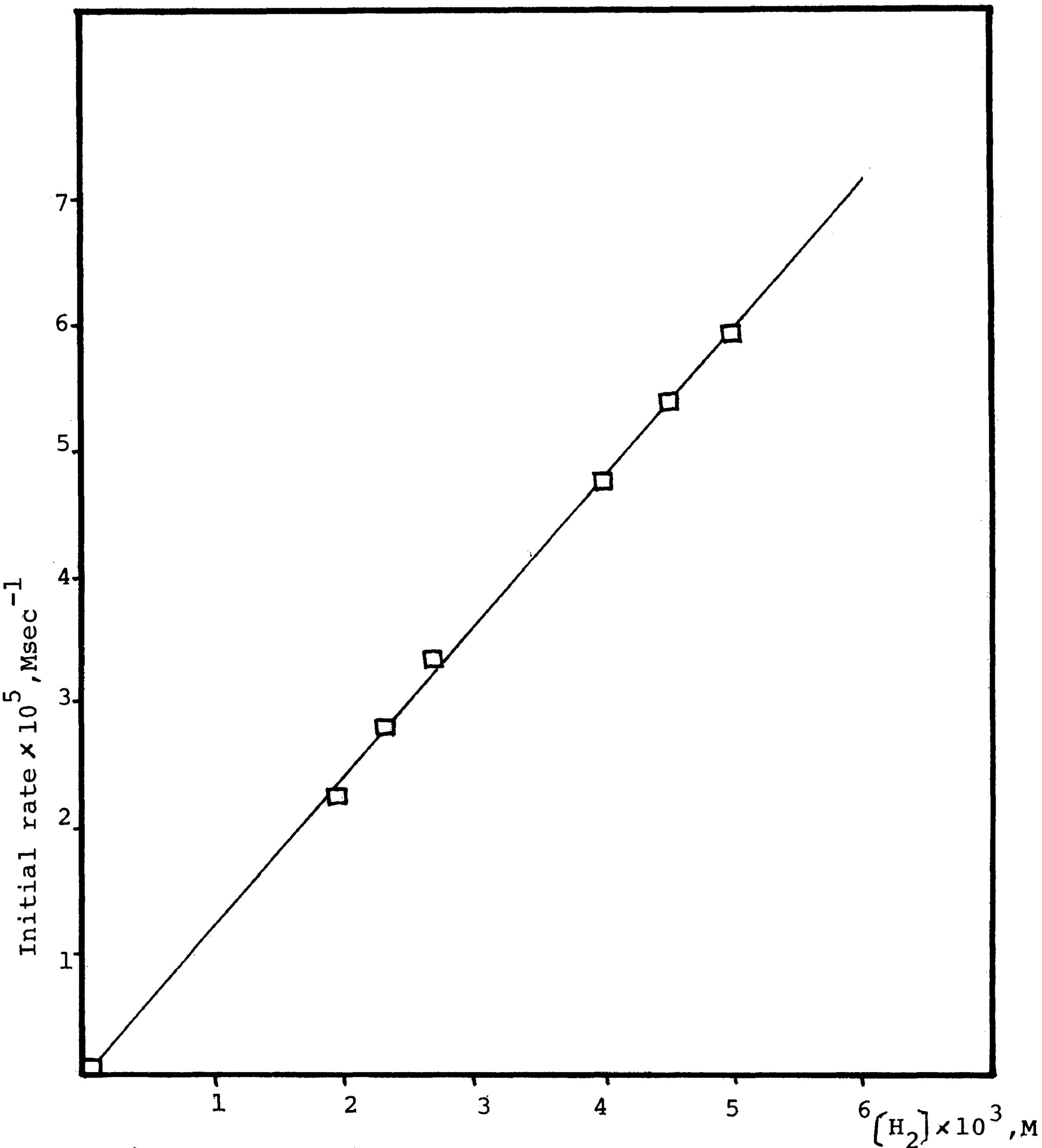


Figure 16. Dependence of initial rate of hydrogenation of 1-hexene in benzene at 20 C on $[H_2]$ (0.5 M 1-hexene, 1 mM $[Ru^{II}]$. $[PPh_3]/[Ru^{II}]$ =3)

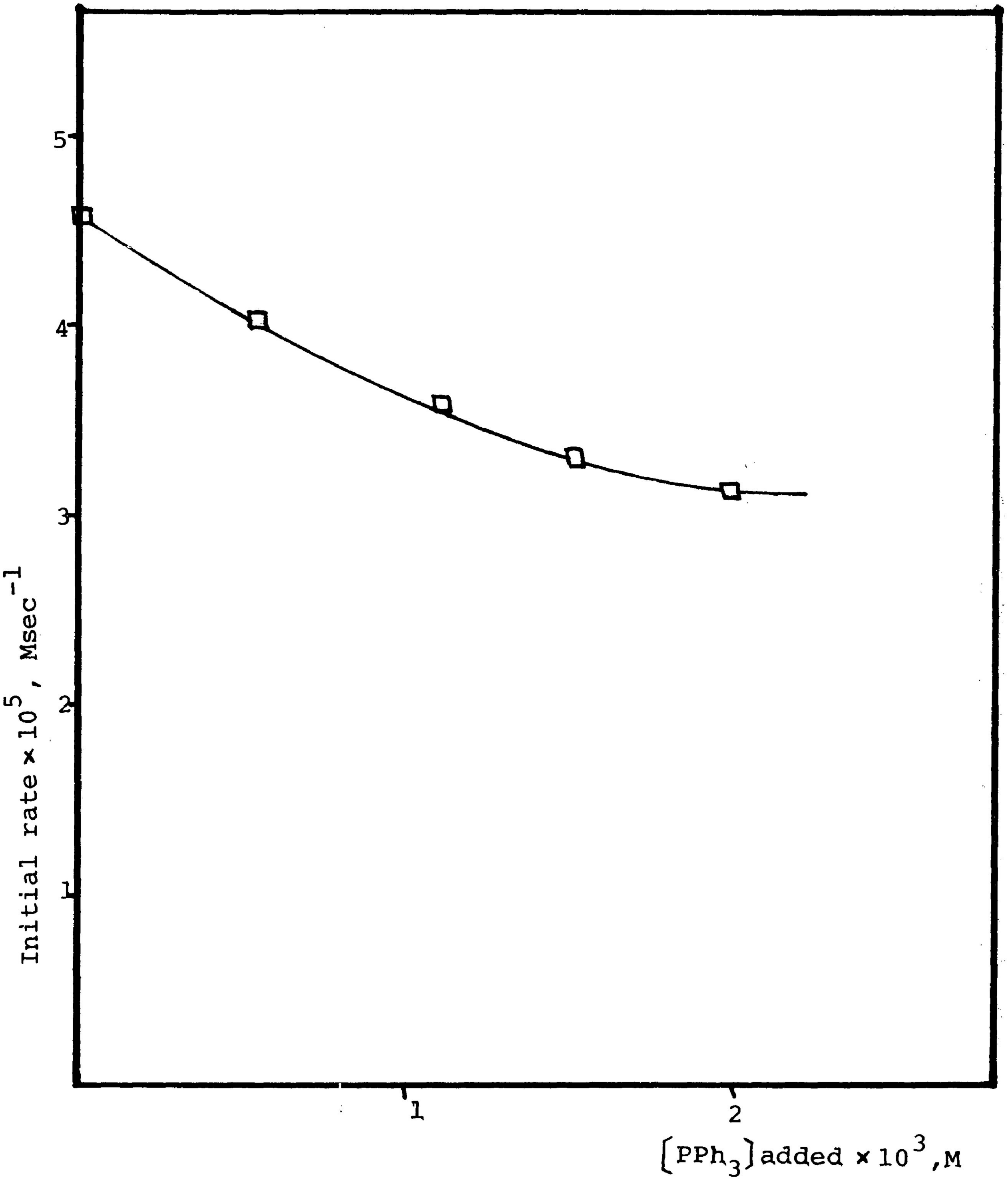


Figure 17. Dependence of initial rate of hydrogenation of 1-hexene in benzene at 20°C on [PPh$_3$] (655 mm H_2, 0.5 M 1-hexene, 1 mM [Ru^{II}])

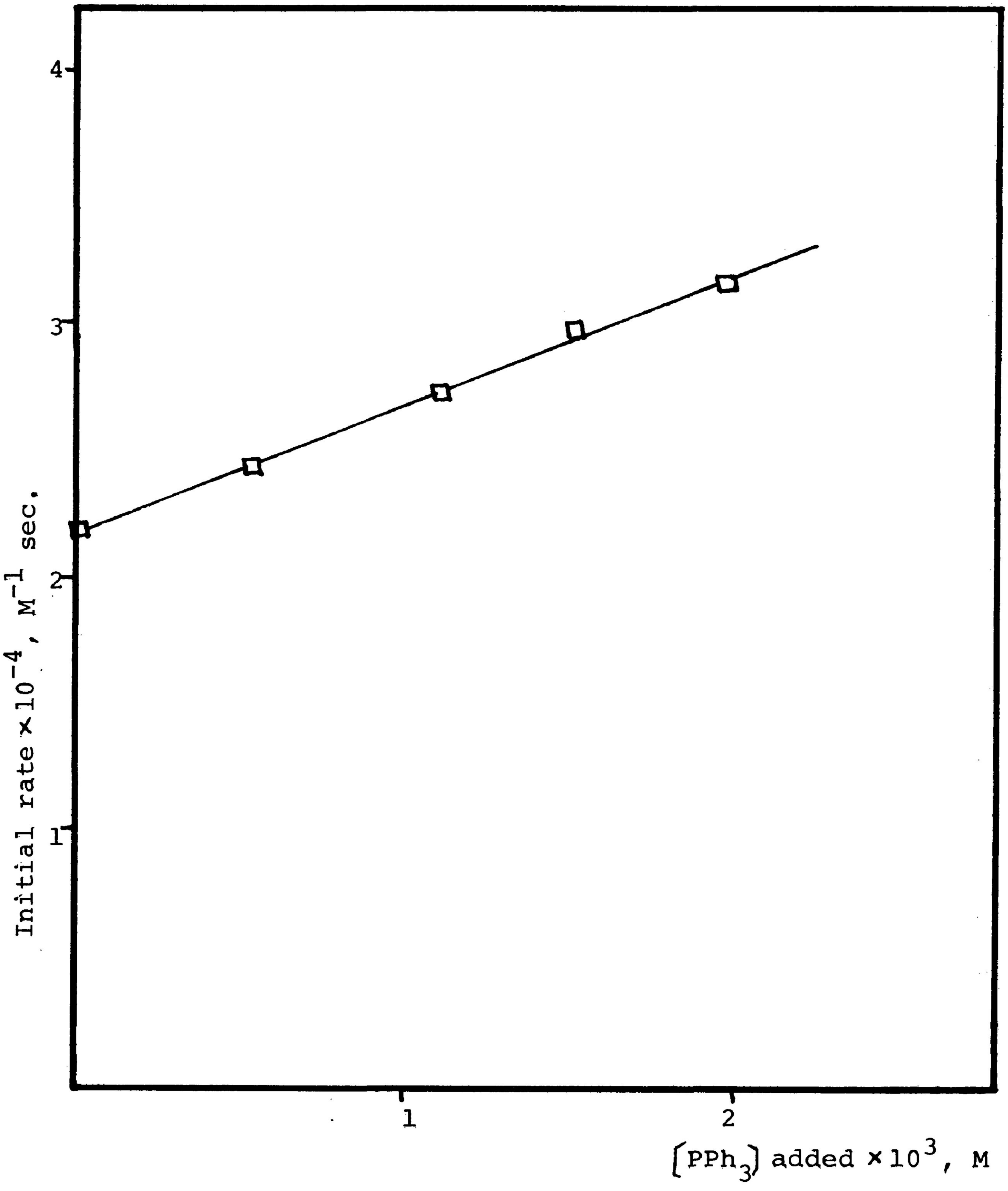


Figure 18. Inverse dependence of the initial rate of hydrogenation of 1-hexene in benzene at 20°C on [PPh_3] (655 mm H_2, 0.5 M 1-hexene, 1 mM [Ru^{II}])

From the slope and the intercept of the straight line obtined, the following relationships can be obtained.

$$kK_1K_2 = \{\text{slope} \times [H_2][S][Ru^{II}]_T\}^{-1} \qquad (3,15)$$

$$= \{4.4 \times 10^3 \times 4.48 \times 10^{-3} \times 0.5 \times 10^{-3}\}^{-1}$$

$$= 101\ M^{-1}S^{-1}$$

then $K_1K_2 = 101\ M^{-1}S^{-1}/k$

$$= 0.73$$

$$\text{Intercept} = \frac{1 + K_2[S]}{kK_2[H_2][S][Ru^{II}]_T} \qquad (3.16)$$

$$2.24\ 10^4 = \frac{1 + K_2 \times 0.5}{139 \times K_2 \times 4.48 \times 10^{-3} \times 0.5 \times 10^{-3}}$$

then $K_2 = 0.07\ M^{-1}$

Since the intercept is obtained from the plot of initial rate rate against the concentration of added PPh_3 (but not the free PPh_3), the K_2 value which is found from equation (3,15) is the minimum value. Also from the value of K_2, and the rate constant (calculated from equation 3,13), the maximum K value is approximately 10.4 M.

III.3.2.4. Dependence on Catalyst Concentration.

Figure 19 shows the dependence of the initial rate of hydrogenation of 1-hexene on the catalyst concentration. The rate is linearly dependent on the catalyst concentration above 0.5 mM and shows another linear relationship below ~0.5 mM. This indicates that there are two active species in the solution. When the catalyst concentration is higher than 0.5 mM the active species is the monomeric planar $HRu(BH_4)(PPh_3)_2$. In very low concentration the active species, $HRu(BH_4)(PPh_3)_2$ may undergo further dissociation to give $HRu(BH_4)(PPh_3)$ which is also active for the hydrogenation of 1-hexene. The observed catalyst concentration dependence at catalyst concentrations $\geqslant$ 1 mM is consistent with equation (3,11), which shows the initial rate of hydrogenation of 1-hexene is first order in catalyst concentration. From all the chemical and physical evidence, it appears that the principal catalyst is the square planar $HRu(BH_4)(PPh_3)_2$ produced by dissociation. Olefin activation is thought to take place before hydrogen transfer to the coordinated olefin, which probably occurs through a 4-centre transition state. The rate determining step is the hydrogenolysis of the Ru-C bond. This could take place either by reductive elimination of alkane by hydrogen transfer in this species or the oxidative addition of molecular hydrogen to alkyl to give a 6 coordinated Ru(IV) species. The former seems more likely.

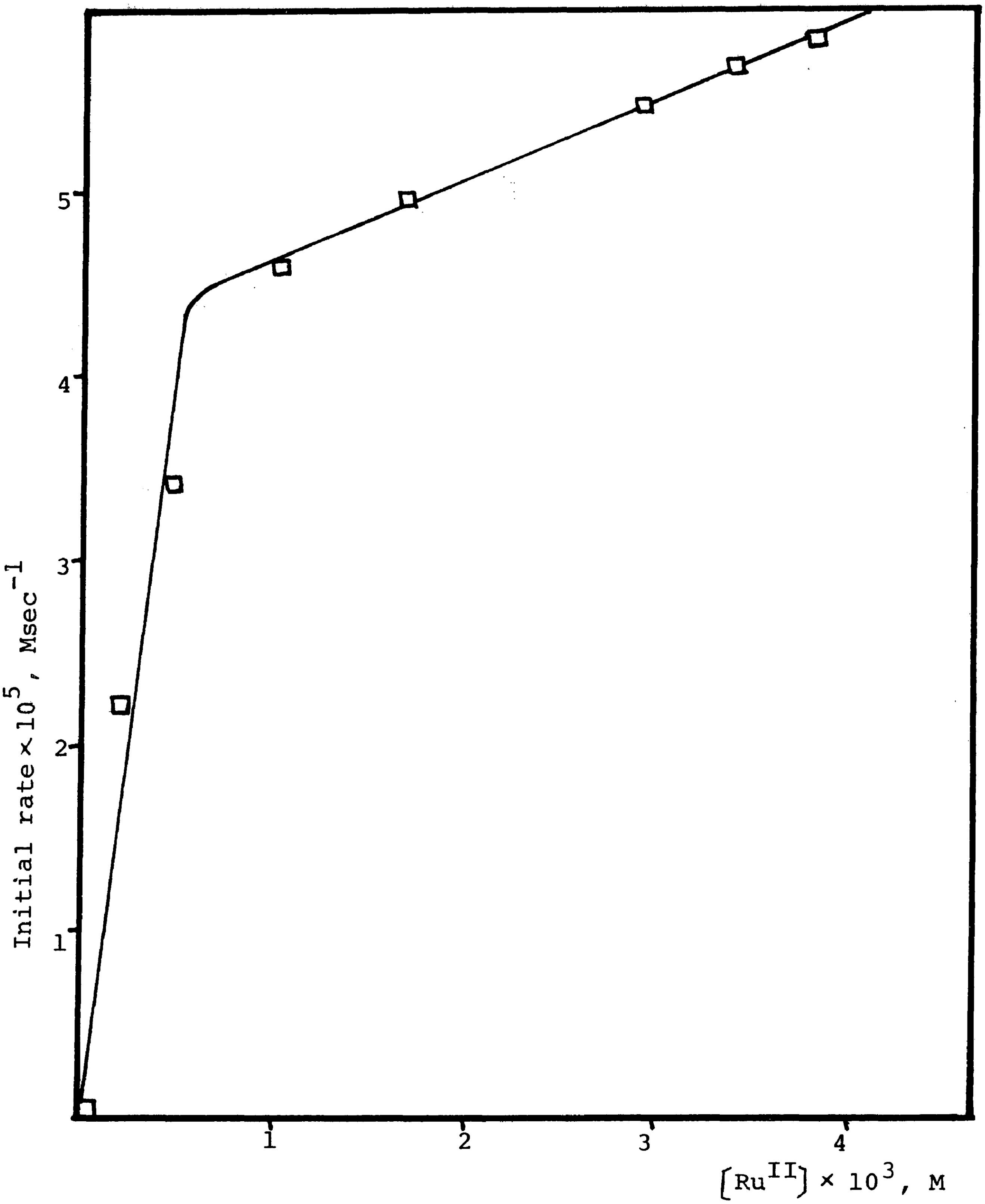


Figure 19. Dependence of initial rate of hydrogenation of 1-hexene in benzene at 20°C on [Ru^{II}] (655 mm H_2, o.5 M 1-hexene, [PPh_3]/[Ru^{II}] =3)

IV. SUMMARY AND SUGGESTIONS FOR FURTHER WORK.

The work described in this thesis has provided the author with experience in handling exceedingly air-sensitive materials and, more importantly, has added significantly to our understanding of the mechanism by which $NaBH_4$ reacts with Co and Ni compounds in the presence of triphenylphosphine. Furthermore, it is interesting to note the major differences in behavior between the two systems.

Until the work described in this thesis was done, there had been no reports of complexed metal systems where the same metal could form both monodentate or bidentate linkages with the tetrahydroborato grouping. However, this clearly is the case for the cobalt-triphenylphosphine system where complexes containing both monodentate and bidentate BH_4 groups have been synthesised. It has further been shown that interconversion between the two types of coordination is possible as follows:

$$Co(BH_4)(PPh_3)_3 \underset{+\,PPh_3}{\overset{-\,PPh_3}{\rightleftarrows}} Co(BH_4)(PPh_3)_2$$

The behavior of nickel(I) in this area of coordination chemistry appears to be dominated by the tendency to form low spin complexes. Although no direct evidence for the dimeric nature of $Ni(BH_4)(PPh_3)_3$,

$Ni(BH_4)(PPh_3)_{1.5}$ and $[Ni(PPh_3)_3][PF_6]$ has been presented, it does appear that this is a very reasonable explanation of their electronic properties. These complexes (especially the first two) are so exceedingly air-sensitive that molecular weight data proved quite impossible to obtain with the vapor pressure osmometric equipment in these laboratories.

The preliminary study of the homogeneous hydrogenation of 1-hexene using the group VIII $-BH_4$ complex $HRu(BH_4)(PPh_3)_3$ has been satisfactorily completed and the kinetic data accounted for by a reasonable rate law and mechanism.

However, there are a number of areas of weakness in the work described in this thesis which require further experimental work within the framework of available equipment. These are:

1) <u>The apparent spin-state change in $Co(BH_4)(PPh_3)_2$.</u>

While the magnetic moment of solid $Co(BH_4)(PPh_3)_2$ has been reproduced several times, the fact that a large reduction in paramagnetism occurs in solution must be reinvestigated. For example, the possibility that $Co(BH_4)(PPh_3)_2$ is contaminated by trace amounts of cobalt boride must be excluded. If cobalt boride were present, it would not be detected in X-ray powder patterns, but would result in $Co(BH_4)(PPh_3)_2$ showing paramagnetic properties, which in solution would be reduced because any boride would collect as an insoluble precipitate at the bottom of the n.m.r. tube.

2) The preparation and composition of $Ni(BH_4)(PPh_3)_{1.5}$

The yield of this complex, prepared from $NiI_2(PPh_3)_2/NaBH_4$ is, at best, 30 % and usually lower. Further reactions should be investigated, particularly in different solvents in an effort to improve the yield. Also, attempts should be made to purify the complex by chromatography in an attempt to establish beyond any doubt that the complex has indeed the above stoichiometry.

3) The composition of $[Ni(PPh_3)_3(CH_3CN)][PF_6]$.

The normally strong $\nu C\equiv N$ has not been observed in the infrared spectrum of this complex. While the presence of CH_3CN has been established by mass spectral studies, this was not on a quantitative basis and may have been simply small quantites of "lattice solvent". The proton signals in the n.m.r. spectrum of this complex would be shifted by the paramagnetic Ni(I), but it should be possible to observe and estimate the amount of CH_3CN present. Also, a Raman spectrum would be valuable in that it would provide evidence for or against the alternative N_2 bridged Ni(I) dimer formulation discussed earlier.

4) <u>Further catalysis work</u>.

Considerable experience has now been obtained in preparing and handling these Ni(I) and Co(I)-BH_4 complexes and the catalysis work already carried out on the Ru system must now be expanded to examine the catalytic potential of these low valent 3d metal systems.

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ADDENDUM

During the final proofreading of this thesis, certain references were found to have been duplicated, e.g. ref. 28 is the same as ref. 37, ref. 68 is the same as ref. 3, ref. 74 is the same as ref. 50, etc. Since these duplications create no ambiguity in the thesis, further correction has not been made since changing reference numbers in the body of the thesis could easily lead to the introduction of such ambiguities.