REACTIONS OF SODIUM TETRAHYDROBORATE WITH METAL IONS IN THE PRESENCE OF NITROGEN DONOR LIGANDS

BY

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ABSTRACT

The work described in this thesis is part of an on-going effort in these laboratories to determine in more detail how a variety of factors, particularly the nature of added ligands, affects the type of products and the overall mechanism of the reactions between transition metal salts and $NaBH_4$. This work specifically describes the results of the reactions between $NaBH_4$ and a number of II and III valent transition metal salts in the presence of the N-donor ligands ethylenediamine, 2, 2'-bipyridyl and 1, 10-phenanthroline. As well as the nature of the added ligand, variations in such factors as solvent (aqueous and ethanolic), molar ratios and rate of addition of reactants and time have also been studied.

In the case of reductions of Fe,Ru and Co in the presence of phen and bipy, univalent metal complexes of general formula $M(L\text{-}L)_2BH_4 \cdot xH_2O$ have been isolated. Reduction was also observed in the case of Cr(III) although no solids were isolated. With Zn(II) and Mn(II), no reduction occurred and simple hydrated metal(II)-ligand-tetrahydroborate complexes were obtained. Electrical conductivities, electronic spectra and magnetic moments on the above reduced metal complexes are reported and are consistent with the presence of the M(I) oxidation states which are unusual especially for Fe and Ru. Additional M(I) complexes of Fe and Ru with the anions PF_6^- and BPh_4^- have also been isolated.

On the other hand, reactions in the presence of ethylenediamine do not lead to the production of M(I) species and either metal reduction does not occur, when metal II or III complexes of the type $Men_3(BH_4)_x$ are obtained, or reduction directly to the boride or metal takes place.

The thesis contains a discussion of the π-bonding capabilities of bipy and phen which are believed to be responsible for their ability to stabilize the metal(I) complexes.

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ABBREVIATIONS

bipy	2,2'-bipyridyl
Bu^n	*n*-butyl
Bu^t	*tert*-butyl
Cy	cyclohexyl
DBP	5-phenyl-5*H*-dibenzophosphole
DMA	dimethylacetamide
DME	1,2-dimethoxyethane
DMF	dimethylformamide
DPPE	1,2-bis(diphenylphosphino)ethane
DMSO	dimethylsulfoxide
en	ethylenediamine
Et	ethyl
Me	methyl
Nas_3	tris(2-diphenylarsinoethyl)amine
Np_3	tris(2-diphenylphosphinoethyl)amine
Ph	phenyl
phen	1,10-phenanthroline
Pp_3	tris(2-diphenylphosphinoethyl)phosphine
Py	pyridine
Siphos	tris(trimethylsilylmethyl)phosphine
THF	tetrahydrofuran

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I. INTRODUCTION

The use of sodium tetrahydroborate in different areas of organometallic chemistry and industry, e.g. in metal recovery (1,2) generation of active catalysts (1,3) and in synthetic chemistry particularly regarding the preparation of transition metal hydrides, has made great strides in recent years. However, the mechanisms by which reductions of transition metal ions occur are poorly understood. The difficulties associated with such mechanistic studies are mainly due to the fast rates of reduction and also to the air sensitivity of many of the reaction products.

A wide variety of products has been isolated from reactions between $NaBH_4$ and transition metal halides and these fall into three main groups, (a) metals or borides (b) tetrahydroborates and (c) hydrides. These reactions depend upon experimental conditions, such as ratios of reactants, solvent, temperature and, to a very great extent, the presence or absence of certain ligands which may be able to stabilize one or other type of product. Since the experimental work to be described in this thesis concerns reactions between $NaBH_4$ and certain transition metal salts under various conditions, the following introduction will serve to familiarize the reader with the range of products already identified from related reactions.

A. Reactions of some transition metals and $NaBH_4$ in the absence of ligands.

1. Production of metals or borides.

Reduction of certain transition metal salts (e.g. those of Mn, Fe, Co, Ni and Cu) with sodium tetrahydroborate in aqueous solution was first reported by Schlesinger et al.(4). Cobalt and nickel salts were shown to give products containing both metal and boron in approximately a 2:1 ratio and were called, for the sake of convenience, metal borides although these products differ considerably from the true borides. It was also reported that these so-called metal borides greatly enhance the hydrolysis rate of $NaBH_4$ (4) as follows:

$$NaBH_4 + 2H_2O \xrightarrow{M_2B} NaBO_2 + 4H_2$$

Mal'tseva et al. (5) also reported similar results and suggested that the reactions of $NaBH_4$ with Ni(II) and Co(II) proceed as follows:

$$2NaBH_4 + MCl_2 + 4.5H_2O \longrightarrow 0.5M_2B + 1.5H_3BO_3 + 6.25H_2 + 2NaCl$$

M=Co or Ni

It was also suggested that $M(BH_4)_2$ complexes are formed as intermediates (5).

In contrast to the Ni(II) and Co(II) reductions, Brown and Brown (6) have studied the hydrolysis of sodium tetrahydroborate in the presence of some heavy metal compounds, e.g. $RuCl_3$, $RhCl_3$, $PdCl_2$, $IrCl_3$, H_2PtCl_4 and

OsO_4 and have found that each compound is instantly reduced with the formation of a black, finely divided solid. The black products were analyzed and found to be pure metals.

The formation of a product with the stoichiometry CrB_2 from the heterogeneous reaction of sodium tetrahydroborate with chromium(III) chloride at 380° to 420° C has also been reported (7).

Following Schlesinger's first study, numerous reports of the preparation of nickel and cobalt boron-containing products, called here borides, have been made. The actual composition and also the catalytic activities of these borides seems to vary when different reaction conditions are employed. For example, some of the properties of the products obtained by Schlesinger and co-workers (4) from the reactions of Ni(II) and Co(II) chlorides with $NaBH_4$ in an aqueous medium differ from those of the authentic borides obtained by fusion of the metals with boron. Thus the melting points of Co_2B and Ni_2B are 1265° and 1230° C respectively whereas products obtained by $NiCl_2/CoCl_2$ reactions with $NaBH_4$ in aqueous solution slowly decompose at 100° C liberating hydrogen (8).

Regarding reactions in ethanol under inert atmospheres, on the basis of the M:B ratio and the amount of hydrogen evolved, the formulas $(Ni_2B)_2H_3$ and $(Co_2B)_5H_3$ have very recently been assigned to the products obtained from the reaction of $NiCl_2/CoCl_2$ with a three fold excess of $NaBH_4$ in ethanol under nitrogen or hydrogen (8). These products slowly decompose at 100°C liberating hydrogen. When dry, these amorphous products are ferromagnetic, pyrophoric in air, very soluble in dilute mineral acids, almost insoluble in alkali (11), and are excellent heterogeneous hydrogenation catalysts (9).

On the other hand, Paul et al. in 1952 reported the preparation of nickel and cobalt borides from M(II) salts in aqueous solution in air by reduction with $NaBH_4$ (10). The voluminous black precipitates were neither ferromagnetic nor pyrophoric and less soluble in HCl and potassium triiodide than Raney nickel (10).

Much work has been done on these systems but a discussion in detail will not be made here since it has been recently reviewed thoroughly elsewhere (11). However, it is important to note that the products obtained under various conditions differ greatly, not only in their chemical and physical properties, but also in their catalytic activities in various reactions. For example, the nickel boride obtained by the reduction of nickel salts with $NaBH_4$ in air and in aqueous solution, has an activity inferior to that of Raney nickel for the hydrogenation of safrole, furfural and benzonitrile (10). However, more active metal boride catalysts can be prepared by addition of sodium tetrahydroborate to aqueous solutions of cobalt or nickel salts under nitrogen (12).

The resulting black granular precipitate is non-magnetic, non-pyrophoric and decomposes slowly in HCl (13). The amounts of Ni and B only account for 91% of the product and, for the product obtained from Ni(II) salts, the approximate formula Ni_2B and name P-1 Ni were assigned. Similar but much more active products designated P-2 Ni and P-3 Ni have been generated by modifications of this method and these have been reviewed (11).

It is difficult to establish the true composition of these metal borides as extensive washing with water leads to the formation of metal hydroxide, as identified by X-ray powder diffraction analysis, and less extensive washing leaves residual sodium salts (14). Hofer <u>et al.</u> (14) on the basis of chemical analysis of the various products obtained by reduction of Ni(II) salts with $NaBH_4$ suggested a different formula, $Ni_{2.5}B$, but the nickel and boron content accounts for only 89% of the precipitate. As indicated in Table 1, all the precipitates analyzed by X-ray powder diffraction are amorphous at room temperature while at 250° C the presence of both Ni_3B and Ni metal was observed. No <u>compound</u> of formula Ni_2B could be detected. The Ni_3B, which is prepared by fusion of nickel and boron at 900° C, is stable up to 750° C and is characteristic of the Rundquist and Fruchart structure (14). Other workers (15, 16, 17) obtained similar structural results. X-ray studies (18) of P-1 type Ni and Co

TABLE 1

X-ray powder diffraction analysis of nickel borides* (14)

Thermal treatment	X-ray powder diffraction analysis
a. Product of $NiCl_2/NaBH_4$	
1. Room temperature	Amorphous
11. 250° C	Ni, Ni_3B
111. 500° C	Ni, Ni_3B
1V. 750° C	Ni, Ni_3B
b. Product of $NiCl_2/NaBH_4$ after washing at 90° C	
1. Room temperature	Ni, amorphous
11. 250° C	Ni, Ni_3B
c. Product of nickel acetate/$NaBH_4$	
1. 100° C	Amorphous
11. 200° C	Amorphous
111. 260° C	Ni, Ni_3B
1V. 350° C	Ni, Ni_3B

* Nickel borides were made by adding 2.5M aqueous solutions of $NaBH_4$ to 0.5M aqueous solutions of nickel salts.

borides show that the products are amorphous at room temperature. At 300° to 500° C in *vacuo* X-ray diffraction patterns show the presence of Ni_3B sometimes as a mixture with Ni or Ni_2B. In contrast to the above reports, Sterlyadkina *et al.* (19) have reported that these 'so-called' nickel/cobalt borides, when heated at 400°C in argon show the presence of free metal and M_2B.

It can be seen from this brief discussion that the products obtained under various conditions are not strictly metal borides and the true nature of these products is as yet unknown. It should further be noted that these compounds are under intensive study by other workers in these laboratories.

2. Production of tetrahydroborates.

It is believed that metal tetrahydroborates are frequently formed as intermediates in the reduction of metal salts by $NaBH_4$ (5). The best known metal tetrahydroborates, which are stable at 25° C, are those of Zn(II), Ti(III), Zr(IV) and Hf(IV) (20,21,22j). Most of the other metal tetrahydroborates are much less stable and decompose above 0°C and a brief review of some of these is presented here. It is possible to stabilize metal tetrahydroborates by a variety of other ligands, but this will be discussed in a later section.

No simple tetrahydroborate of Cr is known, but it is reported that a solution of manganese(II) tetrahydroborate, $Mn(BH_4)_2$, may be obtained from manganese(II) chloride and $LiBH_4$ (22a). The reaction of manganese(III) alkoxide and diborane in THF has been claimed to produce the manganese(III) tetrahydroborate $Mn(BH_4)_3$ (22b). A complex formulated as $Li_2[Mn(BH_4)_2X_2]n(C_2H_5)_2O$ has been isolated as an oil-like etherate from the reaction of manganese(II) chloride or iodide with ethereal lithium tetrahydroborate (22c).

Iron(II) tetrahydroborate (22d), which is made from the reaction of iron(III) chloride and $LiBH_4$ in ether at -45° C, is a colourless solid, slightly soluble in ether and, while stable below -10° C, is rapidly decomposed above 0° C producing hydrogen, diborane and a black pyrophoric residue having a B/Fe ratio of 2:1. Such results may be interpreted in either of the two ways shown below (22d).

$$Fe(BH_4)_2 \longrightarrow Fe + H_2 + B_2H_6$$

$$Fe(BH_4)_2 \longrightarrow FeB_2 + 4H_2$$

Nöth reports that if $FeCl_2$ is used (instead of $FeCl_3$) in the above mentioned reaction, the oily compounds $Li[Fe(BH_4)_3]$ and $Li_2[Fe(BH_4)_4]$ are obtained at -30° C (22c). However $Fe(BH_4)_2$ can also be prepared from Li_2FeBr_4 and $LiBH_4$ in ether (22a). A monovalent iron complex has been recently claimed to be a product of a controlled reduction of $FeCl_3.6H_2O$ with $LiBH_4$ in THF (23), although further details were not given.

In the case of cobalt, it is reported that Co(II) bromide reacts with $LiBH_4$ in ether to form $Co(BH_4)_2$, although the grey-white solid was not fully characterized. The final product of the reaction is an insoluble compound or mixture having a cobalt to boron ratio of 1:2 (22c). Monnier reports that when lithium tetrahydroborate is added to the complex Li_2CoBr_4 in ether at -80° C, a colour change from blue-green to red occurs and at -20° C a black solid is precipitated (22a).

Nickel tetrahydroborate has been postulated as an intermediate in the preparation of nickel boride obtained by heating nickel chloride with sodium tetrahydroborate either in the solid state or in aqueous solution (22,f,g,h). The complex compounds $Li\left[Ni(BH_4)_3\right]n(C_2H_5)_2O$ and $Li_2\left[Ni(BH_4)_4\right]\ n(C_2H_5)_2O$ are obtained from the reaction of lithium tetrahydroborate and $NiCl_2$ in ether at -40° C (22c).

Zinc tetrahydroborate, $Zn(BH_4)_2$ is obtained from the metathetic reaction of $ZnCl_2.xH_2O$ with KBH_4 in ether. It is also obtained by using $LiBH_4$, and the white product decomposes above 50° C (22j). Various complex ions, <u>e.g.</u> $Li\left[Zn(BH_4)_2Cl\right]$ and $Li\left[Zn(BH_4)_3\right]$, are also obtained from the above mentioned metathetic reactions and similar sodium salts may also be obtained from this type of reaction (22c). The action of diborane on the alkoxide, $Na[Zn(OR)_3]$, in THF also leads to the formation of a sodium salt (22c).

B) Reactions of some transition metals and $NaBH_4$ in the presence of added ligands.

It is clear from the above discussion that reactions between transition metal salts and $NaBH_4$ lead to the production of either poorly defined and characterized metal borides (or metals or a mixture of the two) or to very unstable metal tetrahydroborates. This situation is radically changed when these reactions are carried out in the presence of certain ligands, the most widely studied being those containing phosphorus as the donor atom. The types of products formed from such reactions are summarized as follows (24), where P represents a tertiary phosphine.

i

$$\begin{tikzcd}
M(II,III,\text{ or }IV)Cl/P \arrow[r, "NaBH_4"] & MClP_x/P \arrow[r] & M(BH_4)P_x \arrow[d] & \\
MH_5P_x \arrow[r, shift left] & MH_3P_x \arrow[l, shift left] \arrow[r, shift left] & MHP_x \arrow[l, shift left] \arrow[r] & MP_x
\end{tikzcd}$$

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

iii $$MCl_2HP_x \longrightarrow MH_2(BH_4)P_x \longrightarrow MH_3P_x \longrightarrow MH_5P_x$$

iv $$M_x(CO)P_x \longrightarrow M(BH_4)(CO)P_x \longrightarrow MH(CO)P_x$$

Obviously these reactions produce a wide variety of products, including hydrides and tetrahydroborates (and mixed systems), in complexes where the metals are in unusually low, and often unstable, oxidation states. The following section is a summary of some of the more important complexes which have been isolated from these reactions.

1. Production of hydrides in the presence of ligands other than N donors.

In general, reduction of a transition metal compound in the presence of a π-bonding ligand is liable to give a hydride. In the earlier literature, many of these complexes were thought to involve low oxidation states of the metals and the presence of hydrogen was not suspected. However, the chemistry of metal hydrides is now extensive and the presence of the M-H bond is generally revealed by an infrared absorption in the region 1600 - 2200 cm^{-1}, and, more importantly, by a proton resonance signal at very high field, with τ values in the range 15 - 50 τ (25). Other hydrides such as organic compounds, water, ammonia and hydrides of the main group metals, have τ values from 0 to 10.

Reduction of metal complexes with $NaBH_4$ in the presence of a suitable ligand is one of the most useful methods of hydride preparation (26), and alcohols are generally suitable solvents for such reactions. Table 2 is an extensive listing of a wide variety of metal hydrides, arranged by groups

TABLE 2

Hydrido complexes of some transition metals

Complex	Mode of formation	Reference
$H_2Mo(\pi C_5H_5)_2$	$MoCl_5+Na(C_5H_5)+NaBH_4$	27
$H_2W(\pi C_5H_5)_2$	$WCl_6+Na(C_5H_5)+NaBH_4$	27
$[HM_2(CO)_{10}]^-$ M=Cr,Mo,W	$M(CO)_6+NaBH_4$	27
$H_6W(PMe_2Ph)_3$	t-$[WCl_4(PMe_2Ph)_2]+NaBH_4$	29
$HMo(\pi C_5H_5)(CO)_2PPh_3$	$MoCl(\pi C_5H_5)(CO)_2PPh_3+NaBH_4$	30
$H_3Mn_3(CO)_{12}$	$Mn_2(CO)_{10}/CH_3Mn(CO)_5+NaBH_4$	31
$HMn_3(CO)_{10}(BH_3)_2$	$Mn_2(CO)_{10}+NaBH_4$	32
$HMn(NO)_2(PPh_3)_2$	$MnBr(NO)_2(PPh_3)_2+NaBH_4$	
$HM(\pi C_5H_5)_2$ M=Re, Te	$Na(C_5H_5)+NaBH_4+ReCl_5/TeCl_4$	34,35
$[H_6Re_4(CO)_{12}]^{2-}$	$Re_2(CO)_{10}+NaBH_4$	36
$[HRe(CO)_4]_3$	$Re_2(CO)_{10}+NaBH_4$	37
$[H_3Re_3(CO)_{12}]^-$	$Re_2(CO)_{10}+NaBH_4$	39
$HRe_3(CO)_{14}$	$Re_2(CO)_{10}+NaBH_4$	38
$H_3Re(PPh_3)_2$	$ReI_2(PPh_3)_2+NaBH_4$	40
$H_3Re(PPh_3)_4$	$ReI_2(PPh_3)_2/PPh_3+NaBH_4$	40
$H_5Re(PPh_3)_2$	i, $K_2ReI_6+PPh_3+NaBH_4$	42
	ii, $ReI_2(PPh_3)_2+NaBH_4$	43

TABLE 2 --(continued)

Complex	Mode of formation	Reference
$HM(CO)_2(\pi C_5H_5)$ M= Ru, Fe	$MCl(CO)_2(\pi C_5H_5)+NaBH_4$	44
$H_2Fe[P(OC_2H_5)_3]$	$FeCl_2+[P(OC_2H_5)_3]+NaBH_4$	45
H_4FeL_3 $L= PEtPh_2, PBuPh_2$	$FeCl_2+L+NaBH_4$	47
H_2FeL_3 $L=PEtPh_2, C_2H_4(PPh_2)_2$	$FeCl_2+L+NaBH_4$	47
$[HFe(Pp_3)]BPh_4$	$FeX(Pp_3)\ BPh_4+NaBH_4$	49
$[H_3Fe(P_3)_2]^+$	$Fe(II)+P_3+NaBH_4$	50
$H_2Fe(CO)_4$	$Fe(CO)_4I_2+NaBH_4$	51
$H_2Ru(CO)_2(PPh_3)_2$	$RuCl_2(PPh_3)_3+NaBH_4$	52
$H_2Ru(PPh_3)_4$	$RuCl_3+PPh_3+NaBH_4$	53
$H_2Ru(CO)(PPh_3)_3$	$RuCl_3+PPh_3+NaBH_4+H_2CO/H_2O$	53
$H_4Ru(PPh_3)_3$	$RuCl_3+PPh_3+NaBH_4$	54
$H_2Ru(DBP)_3$	$RuCl_3(DBP)_3/C_6H_6+NaBH_4/EtOH$	57
$H_2Ru(CO)(DBP)_2$	$Ru(II)/CO+DBP+NaBH_4$	57
$H_2Ru(CO)(PEtPh_2)_3$	$Ru(II)/CO+PEtPh_2+NaBH_4$	57
$H_2Ru(CO)_2(DPPE)$	$RuCl_2(CO)_2(DPPE)+NaBH_4$	57
$H_2Os_3(CO)_{12}$	$Os_3Cl_2(CO)_{12}+NaBH_4$	55
H_4OsL_3 $L=PMe_2Ph$.	$OsCl_3L_3+NaBH_4$	56

TABLE 2 --(continued)

Complex	Mode of formation	Reference
$H_4Os(PPh_3)_3$	$Na_2OsCl_6+PPh_3+NaBH_4$	53
H_4OsL_2L'	$OsCl_4L_2+L'+NaBH_4$	56
$HCo\ P(OPh)_3\ {}_4$	$CoCl_2+P(OPh)_3+NaBH_4$	58
$H_3Co(PPh_3)_3$	$CoCl_2+PPh_3+NaBH_4$	59
$HCo(DPPE)_2$	$CoBr_2(DPPE)_2+NaBH_4$	61
$HCoL\cdot\frac{1}{2}DMF$	$CoCl_2+L+NaBH_4$ in DMF/BuOH $(L=Pp_3)$	62
$[H_3Co_2L_2]^+$	$Co(BF_4)_2\cdot 6H_2O+L+NaBH_4$ $(L=P_3)$	62
$HRh(CO)(PPh_3)_3$	$RhCl_3+PPh_3+NaBH_4+H_2CO/H_2O$	63
$HRh(PPh_3)_4$	$RhCl_3+PPh_3+NaBH_4$	64
$HRh(DBP)_4$	$RhCl_3+DBP+NaBH_4$	65
$HRh(PPh_3)_3$	$RhCl(PPh_3)_3+NaBH_4$	66
$HIr(CO)(PPh_3)_3$	$IrCl(CO)(PPh_3)_2+PPh_3+NaBH_4$	67
$HIr(CS)(PPh_3)_3$	$IrCl(CS)(PPh_3)_2+PPh_3+NaBH_3$	68
$H_3Ir(PPh_3)_3$	$Na_2IrCl_6+PPh_3+NaBH_4$	64
$H_5Ir(PPh_3)$	$Na_3IrCl_6+PPh_3+NaBH_4$	69
$HIr(CO)_2(PPh_3)_2$	$IrCl(CO)(PPh_3)_2+CO+NaBH_4$	67
H_3IrL_3	$HIrBr_2L_3+NaBH_4$ $(L=PMePh_2)$	70
$HNiCl(PCy_3)_2$	$NiCl_2(PCy_3)_2+NaBH_4$	71
$HNi(\pi\text{-allyl})PPh_3$	$NiBr(\pi\text{-allyl})PPh_3+NaBH(Me)_3$	72
$[HNi(PP)]_2$	$NiCl_2(PP)+NaBH(Me)_3$	73
$[HNi(Pp_3)]^+$	$Ni(II)+(Pp_3)+NaBH_4$	62

TABLE 2 --(continued)

Complex	Mode of formation	Reference
$HPdCl(PCy_3)_2$	$PdCl_2(PCy_3)_2 + NaBH_4$	74
$HPdCl(PPr^i_3)_2$	$PdCl_2(PPr^i_3)_2 + NaBH_4$	74
$HPtL_2$	$PtCl_2L_2/HPtClL_2 + NaBH_4$ L= bulky tertiary phosphine	75

of metals, formed from $NaBH_4$ reduction and should be referred to throughout the following discussion.

a. Chromium, Molybdenum and Tungsten.

The molecular hydrides $H_2Mo(\eta^5-C_5H_5)_2$ and $H_2W(\eta^5-C_5H_5)_2$ are formed by treating the metal chlorides ($MoCl_5$,WCl_6) with a THF solution of cyclopentadiene containing an excess of sodium tetrahydroborate (27). In related work, Hayter reported that the reactions of the group VI metal hexacarbonyls with $NaBH_4$ in THF yield the anionic complexes, $[M_2H(CO)_{10}]^-$ (M=Cr, Mo and W) as the major products (28).

Two hydridophosphine complexes, $H_6W(PMe_2Ph)_3$ (29) and $HMo(\eta^5-C_5H_5)(CO)_2PPh_3$ (30), are believed to result from the reaction of sodium tetrahydroborate with the corresponding halogen complexes.

b. Manganese, Technetium and Rhenium.

The polynuclear hydride, $H_3Mn_3(CO)_{12}$, is obtained from the reaction between $NaBH_4$ and either $Mn_2(CO)_{10}$ or $Mn(CH_3)(CO)_5$ (31). In addition, $HMn_3(CO)_{10}(BH_3)_2$, is also obtained from the reaction of $Mn_2(CO)_{10}$ with $NaBH_4$ (32). A nitrosyl hydride, $HMn(NO)_2(PPh_3)_2$, has been prepared from $MnBr(NO)_2(PPh_3)_2$ and sodium tetrahydroborate (33).

Dicyclopentadienyl technetium and rhenium hydrides are obtained from reactions between $NaBH_4$ and the appropriate metal chloride in the presence of sodium cyclopentadienylide (34,35). The reaction of $Re_2(CO)_{10}$ with $NaBH_4$ leads to different products depending upon the conditions and procedures employed. For example, the $[H_6Re_4(CO)_{12}]^{2-}$ anion is prepared by heating under reflux, and then stirring for several days, a mixture of $Re_2(CO)_{10}$ and $NaBH_4$ in THF (36). On the other hand, treatment of $Re_2(CO)_{10}$ with an excess of $NaBH_4$ in THF, with subsequent acidification in the presence of cyclohexane, results in the formation of the polynuclear complex $[HRe(CO)_4]_3$ (37). Other products are $HRe_3(CO)_{14}$ (38) and $[H_3Re_3(CO)_{12}]^-$ (39).

A variety of polyhydrido phosphine complexes of rhenium are obtained by the reaction of $NaBH_4$ with rhenium halide complexes (40,41). Thus, the reaction of sodium tetrahydroborate with $ReI_2(PPh_3)_2$ in ethanol gives $H_3Re(PPh_3)_2$, while the same reaction in the presence of an excess of triphenylphosphine is said to yield $H_3Re(PPh_3)_4$ almost quantitatively (40). A pentahydride complex $H_5Re(PPh_3)_2$, is obtained from the reaction of $NaBH_4$ with K_2ReI_6 in the presence of triphenylphosphine in ethanol (42) and the same compound is also produced from the reaction of $NaBH_4$ with $ReI_2(PPh_3)_2$ (43). The compound H_5ReL_3 (L=tri-p-tolylphosphine) is prepared by heating under reflux a mixture of $NaBH_4$ and $ReI_2O(OC_2H_5)L_2$, in ethanol, in the presence of an excess of tri-p-tolylphosphine (44).

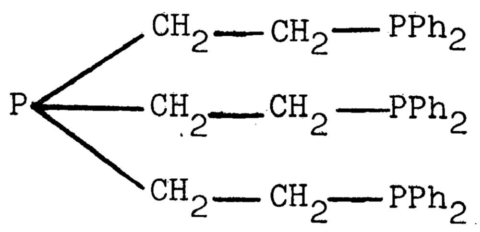
c. Iron, Ruthenium and Osmium.

Sodium tetrahydroborate has been extensively used in the synthesis of a variety of hydride complexes of iron, ruthenium and osmium. For example, $HFe(\eta^5-C_5H_5)(CO)_2$ is prepared by treating $FeCl(\eta^5-C_5H_5)(CO_2)$ with $NaBH_4$ in THF. The analogous ruthenium complex $HRu(\eta^5-C_5H_5)(CO)_2$ is also obtained in the same way (44).

The reaction of iron(II) chloride with triethylphosphite and $NaBH_4$ in methanol at -78° C produces $H_2Fe(P(OC_2H_5)_3)_4$ (45) while the complex H_2FeL_3 (L=ethyldiphenylphosphine or butyldiphenylphosphine) is formed from $FeCl_2.2H_2O$ and $NaBH_4$ in the presence of the phosphine under hydrogen or argon. Under a nitrogen atmosphere, $H_2Fe(N_2)L_3$ is obtained (46). Complexes of the type H_4FeL_3 (L=$PEtPh_2$,$PBuPh_2$), H_2FeL_3 (L=$PEtPh_2$ and $C_2H_4(PPh_2)_2$)and $HFeCl\left[C_2H_4(PPh_2)_2\right]$ are obtained from the reaction of $NaBH_4$ with $FeCl_2.2H_2O$ in the presence of the corresponding phosphine by changing the reaction conditions (47). It is possible that the above tetrahydride complexes, reported by Sacco et al., actually contain tetrahydroborate since they have an ir band at about 2400 cm^{-1} (48).

The reaction of $NaBH_4$ with $FeBr(Pp_3)BPh_4$ under argon gives a hydride compound of formula $[HFe(Pp_3)]BPh_4$, but if the reaction is carried out under nitrogen, $[HFe(N_2)(Pp_3)]BPh_4$ is obtained (49).

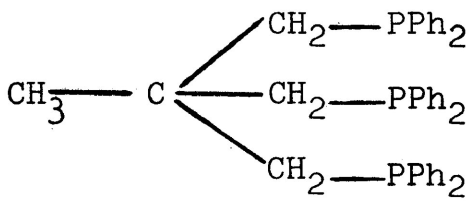
Pp_3 =



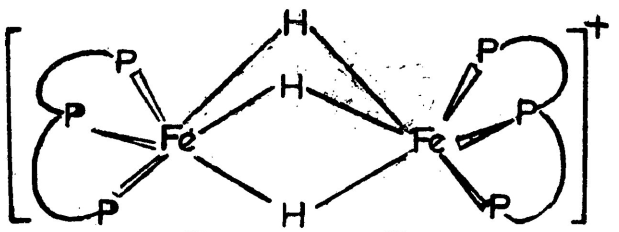
tris(2-diphenylphosphinoethyl)phosphine

Polynuclear complexes of the general formula $[H_3Fe_2(P_3)_2]Y$ ($Y=Br^-, I^-, ClO_4^-, PF_6^-$ and BPh_4^-) are formed when $NaBH_4$ is added to solutions of iron(II) salts and 1,1,1-tris(diphenylphosphinomethyl)ethane in ethanol (50), with a typical compound shown below:

P_3=



1,1,1-tris(diphenylphosphinomethyl)ethane



$[H_3Fe_2(P_3)_2]$

$H_2Fe(CO)_4$ is obtained by sodium tetrahydroborate reduction of $Fe(CO)_4I_2$ in THF (51).

The most convenient synthesis of $H_2Ru(CO)(PPh_3)_3$ is the reaction of ruthenium (III) chloride with triphenylphosphine, aqueous formaldehyde and $NaBH_4$ in boiling ethanol. However in the absence of formaldehyde, the complex $H_2Ru(PPh_3)_4$ is formed (53). The same product $[H_2Ru(CO)(PPh_3)_3]$ is also prepared by heating under reflux (1 hour) a mixture of $RuCl_2(PPh_3)_3$ and $NaBH_4$ in benzene/alcohol under hydrogen (52). When the reaction of $RuCl_2(PPh_3)_3$ with $NaBH_4$ is carried out in a benzene/water mixture, the product obtained is $HRuCl(PPh_3)_3.C_6H_6$ (52). Finally, $H_4Ru(PPh_3)_3$ is obtained from the reaction of $RuCl_3/PPh_3$ and $NaBH_4$ in ethanol (54). The important role of the solvent in determining the nature of the final product is evident from the above reactions.

In reactions with osmium compounds, $H_2Os_3(CO)_{12}$ is obtained, in low yield, from the reaction of $Os_3Cl_2(CO)_{12}$ with $NaBH_4$ in methanol (55). The reaction of mer-$OsCl_3L_3$ (L=PMe_2Ph) with $NaBH_4$ in ethanol gives H_4OsL_3 (56) and the analogous triphenylphosphine complex can be obtained from the reaction of Na_2OsCl_6 /PPh_3 and $NaBH_4$ in ethanol (53). Reactions of $OsCl_4L_2$ (L=$PMePh_2$) with $NaBH_4$ in ethanol give H_6OsL_2 but in the presence of other phosphines, phosphites or arsines (L'), the product is H_4OsL_2L' (56)

It is particularly interesting and relevant to point out at this stage that in all of the reactions described above, no metal complexes have been isolated where the metal has been reduced to an oxidation state below 2.

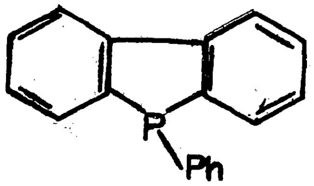
d. Cobalt, Rhodium and Iridium.

As is the case in the iron group, sodium tetrahydroborate is widely used in the synthesis of a variety of hydride complexes of these metals.

Reactions of alcoholic sodium tetrahydroborate with cobalt(II) salts in the presence of triphenylphosphite give, what is in this thesis, the first example of a metal(I) system, namely $HCo[P(OPh)_3]_4$ (58). On the other hand, $H_3Co(PPh_3)_3$ is obtained from the reaction of $CoCl_2$ with $NaBH_4$ in the presence of triphenylphosphine in ethanol under a hydrogen or argon atmosphere. However, in a nitrogen atmosphere the product is $HCo(N_2)(PPh_3)_3$ (59,60) which, on exposure to hydrogen, is readily converted to $H_3Co(PPh_3)_3$. The reaction of $CoBr_2(DPPE)_2$ (DPPE=1,2-bis(diphenylphosphino)ethane) with $NaBH_4$ in ethanol gives $HCo(DPPE)_2$ (61).

In the presence of 1,1,1-tris(diphenylphosphinomethyl) ethane, P_3, the reaction of $Co(BF_4)_2 6H_2O$ with $NaBH_4$ in ethanol yields the polynuclear hydride $[H_3Co_2(P_3)_2]^+$ (62). The cobalt(I) complex $HCo(Pp_3)\cdot0.5DMF$, is prepared by adding $NaBH_4$ to the solution of $CoCl_2$ (anydrous) and tris(2-diphenylphosphinoethyl)phosphine, Pp_3, in DMF(62).

Turning to Rh complexes, the complex $HRh(CO)(PPh_3)_3$, which is of catalytic importance, is obtained from the reaction of $RhCl_3 3H_2O$ with $NaBH_4$ in the presence of triphenylphosphine and formaldehyde in ethanol (63). However, in the absence of formaldehyde $HRh(PPh_3)_4$ is formed (64). The analogous DBP complex $HRh(DBP)_4$ is obtained in a similar fashion (65). DBP is the cyclic phosphine, 5-phenyl-5H-dibenzophosphole, shown below.



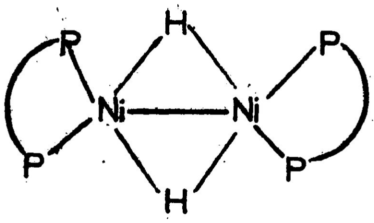
Regarding iridium systems, several iridium complexes react with $NaBH_4$ to form hydride complexes. Thus, the reaction of $IrCl(CO)(PPh_3)_2$ with PPh_3 and $NaBH_4$ in ethanol gives $HIr(CO)(PPh_3)_3$ (67), and the analogous thiocarbonyl complex $HIr(CS)(PPh_3)_3$, is formed in a similar way from $IrCl(CS)(PPh_3)_2$ (68). The complex $HIr(CO)(PPh_3)_3$ is also produced from the reaction of Na_2IrCl_6. xH_2O and triphenylphosphine with $NaBH_4$ in the presence of formaldehyde in 2-methoxyethanol (64). However, when a mixture of $Na_2IrCl_6.xH_2O$, triphenylphosphine and $NaBH_4$ in ethanol is heated under reflux, mer-$H_3Ir(PPh_3)$ is produced (64). Starting with Ir(III) (as Na_3IrCl_6) in similar reactions, the product is $H_5Ir(PPh_3)$.

Again it is apparent that varying the reaction conditions can drastically affect the nature of the final product.

The reaction of $IrCl(CO)(PPh_3)_2$ with $NaBH_4$ in a carbon monoxide atmosphere gives $HIr(CO)_2(PPh_3)_2$ (67). H_3IrL_3 (L=methyl diphenylphosphine) is claimed to be formed by heating under reflux a mixture of $HIrBr_2L_3$ and $NaBH_4$ in ethanol for several days (70).

e. Nickel, Palladium and Platinum.

The reaction of $NaBH_4$ with the complex $NiCl_2L_2$ (L=tricyclohexylphosphine) in THF/ethanol gives trans-$HNiClL_2$ (71). The sodium tetrahydroborate derivative $NaBHMe_3$ also reacts with Ni(II) complexes to produce both Ni(II) and Ni(I) hydrides depending on the ligand present. For example, the π-allyl complex of Ni(II) produce $HNi(\pi\text{-allyl})PPh_3$ (72), while the reaction between $NaBHMe_3$ and $NiCl_2(PP)$, ($PP=R_2P-(CH_2)n-PR_2$, $R=C_6H_{11}$, n=2,3 or 4), in toluene at room temperature gives the Ni(I) complex $(HNiPP)_2$. The diamagnetism of the latter and the presence of a proton signal at τ 21.4 in the nmr spectrum is consistent with the following dimeric structure (73).



Ni(II) complexes of the type $[HNi(Pp_3)]Y$, (Pp_3 = tris(2-diphenylphosphinoethyl)phosphine and $Y=I^-$, BF_4^-, NO_3^- and BPh_4^-), are prepared from the reaction of $NaBH_4$ with a mixture of a nickel(II) salt and Pp_3 in ethanol (62).

Only two palladium hydrides have been prepared using $NaBH_4$ namely $HPdClL_2$ ($L=PCy_3$ and PPr^i_3) which are obtained from the reaction of $NaBH_4$ with $PdCl_2L_2$ (74).

The dihydride complexes of platinum H_2PtL_2 (L= bulky tertiary phosphine e.g. PBu^tMe_2, PBu^tEt_2 and PCy_3) are prepared from the reaction of $NaBH_4$ with either $PtCl_2L_2$ or $HPtClL_2$ (75).

2. Production of hydrides in the presence of N-donor ligands.

It is clear that there is an extensive literature on the products from reactions of metal salts with $NaBH_4$ in the presence of phosphines and related ligands.

In contrast, there are only relatively few reports on similar reactions involving nitrogen donor ligands where hydrides are found.

Thus, addition of CsCl to a mixture of $[Co(CN)_5H_2O]^{3-}$ and $NaBH_4$ in water, precipitates $NaCs_2[HCo(CN)_5]$ (76).
$[CoH(np_3)]$ (np_3=$N(CH_2CH_2PPh_2)_3$, tris(2-diphenylphosphinoethyl) amine) is prepared by adding $NaBH_4$ to $Co(BF_4)_2 \cdot 6H_2O$ in the presence of the ligand at 50° C in acetone/ethanol. When carbon monoxide is passed through a solution of $HCo(np_3)$ in THF, $HCo(CO)(np_3)$ is obtained (77).

By adding cyanide ion to an aqueous solution of rhodium(III) chloride until the initial precipitate redissolves, and then reducing the solution with $NaBH_4$, a complex containing a Rh-H bond is formed, as shown by the appearance of a high field line in the nmr spectrum at τ=20.9. Attempts to isolate a solid compound containing this hydride species failed (78,79).

A number of cationic hydridoamine complexes of rhodium(III) are formed by the reaction of $NaBH_4$ with an aqueous solution of the corresponding chloroamine rhodium(III) cation (80). For example, the reaction of cis-$[RhCl_2trien]^+$ (trien=triethylenetetramine) with aqueous $NaBH_4$ affords a solution that displays two high field lines in the nmr spectrum, one at τ=28.5 and a much weaker one at τ=27.1.

The complexes are precipitated by using large anions, e.g. BPh_4^-. It has been suggested that the stronger high field line is due to a monohydridochloro complex, $[HRhCl(trien)]^+$ and the weaker line was attributed to a cis-dihydrido complex, formed in low concentration.

Both cis- and trans - $[RhCl_2en_2]^+$(en=ethylenediamine) yield the same hydrido species, $[H_2Rh\ en_2]^+$, on treatment with $NaBH_4$. The evidence for the hydride $[HRh(NH_3)_5]^{2+}$, obtained from the reaction of $[RhCl(NH_3)_5]^{2+}$ with $NaBH_4$ is an ir absorption at 2079 cm^{-1} observed on a tetraphenylborate salt. An aqueous solution of trans- $[RhCl_2Py_4]^+$ (Py=pyridine) on treatment with $NaBH_4$ deposits a brown solid which decomposed when attempts were made to isolate it. If the reaction is carried out in methanol, however, a product of unknown stoichiometery remains in solution, and shows a proton resonance at τ=28.6 in the nmr spectrum.

The brown intermediate from the reaction of the dichlorobis(bipyridyl) rhodium(III) cation, precipitated by adding $NaBPh_4$, shows an ir absorption at 2106 cm^{-1} which may be due to the Rh-H stretching frequency. This hydrido complex decomposes further to $[Rhbipy_2]^+$ (80).

Reactions of $NaBH_4$ with Ni(II) salts in the presence of np_3, $N(CH_2.CH_2.PPh_2)_3$, yield non-stoichiometric hydrido complexes of the general formula $[NiH_x(np_3)]Y$, which

$Y=BF_4$ $x=0.33$ to 0.98
$Y=ClO_4$ $x=0.34$ to 0.8
$Y=NO_3$ $x=0.18$ to 0.53

contain nickel in a range of formal oxidation states intermediate between +1 and +2 (81).

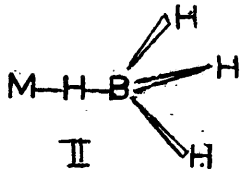
3. Production of tetrahydroborates in the presence of ligands other than N-donors

It is clear from the above discussions that metal hydrides are a major and important class of compounds obtained from the reduction of metal salts by $NaBH_4$. It has now been established (82) that under certain carefully controlled conditions, transition metal - BH_4 complexes can be isolated from such reactions prior to the formation of either hydrides or metal zero complexes. For example, the complexes $M(BH_4)(PPh_3)_n$ (M=Co,Ni; n=2,3) can be isolated from the reduction of M(II) compounds by $NaBH_4$ before the formation of $Ni(PPh_3)_n$ or $H_3Co(PPh_3)_3$ (82).

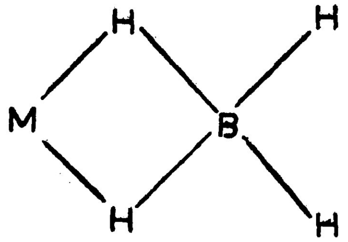
At this point it is appropriate to note that, at least in monomeric tetrahydroborate complexes, the BH_4 group can bind to metals in any of the four different ways shown below:

$\overset{+}{M}BH_4^-$

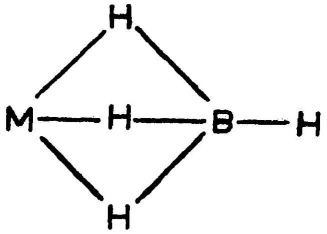
I



II



III



IV

Infrared spectroscopy has proved to be a very useful tool for distinguishing between these and, while the detailed assignments are fully discussed elsewhere (83), the following presents a brief summary of the essential points.

Structure I:- Usually two strong bands are observed in the ir spectrum at 2270 cm^{-1} and 1080 cm^{-1} assigned as the B-H stretching and BH_2 deformation modes respectively.

Structure II:- Molecules containing this grouping should exhibit terminal B-H stretches in the region 2300-2450 cm^{-1}, and one bridging stretch at about 2000 cm^{-1}.

Structure III:- For this structure, the characteristic symmetric and antisymmetric terminal $B-H_t$ stretches usually appear in the ir as a strong, sharp doublet at 2400-2600 cm^{-1}, together with the symmetric and antisymmetric bridging B-H_b as overlapping bands near 2000 cm^{-1}.

Structure IV:- This type of bonding can usually be distinguished from others by the presence of a single sharp B-H_t stretching vibration at 2450-2600 cm^{-1}, a doublet near 2100 cm^{-1} and an intense band near 1200 cm^{-1}.

As in previous sections, the tetrahydroborates obtained from reactions involving ligands other than those with N-donor atoms, are arranged in groups of metals as follows. The reader may find it convenient to refer to Table 3 which summarizes the results of this section.

a. Chromium, Molybdenum and Tungsten

Although no BH_4 complexes of these metals, other than with nitrogen donor ligands, have been reported, a compound of formula, $[C_5H_5Mo(CO)_2(CHNCH_3)_2BH_2]$ has been isolated from the reaction of the cationic species $[C_5H_5Mo(CO)_2(CNCH_3)_2]^+$ with $NaBH_4$ in THF at 0° C (84).

b. Manganese, Technetium and Rhenium

In this group, manganese is the only metal for

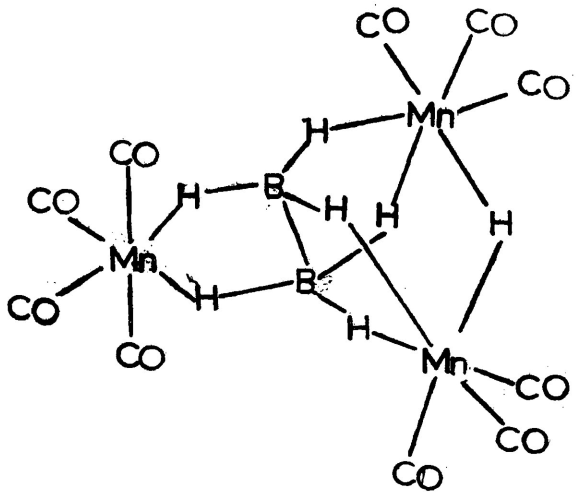
TABLE 3

Tetrahydroborate complexes of Co, Rh and Ir.

Complex	Mode of formation	Reference
$Co(BH_4)(PPh_3)_3$	$CoCl_2+PPh_3+NaBH_4$	82
$Co(BH_4)(PPh_3)_2$	$CoCl_2+PPh_3+NaBH_4$	88
$HCo(BH_4)(PCy_3)_2$	$CoCl_2+PCy_3+NaBH_4$	89
$Co(BH_3CN)(DBP)_4$	$CoCl_2+DBP+NaBH_3CN$	82
$Co(BH_4)(P_3)$	$Co(H_2O)_6(BF_4)_2+P_3+NaBH_4$	90
	P_3=1,1,1-tris(diphenylphosphinomethyl) ethane	
$Rh(BH_4)(PPh_3)_3$	$RhCl(PPh_3)_2+NaBH_4$	92
$Rh(BH_4)(CO)(PPh_3)_2$	$Rh(ClO_4)(CO)(PPh_3)_2+NaBH_4$	91
$Rh(BH_4)(CO)(PCy_3)_2$	$RhCl(CO)(PCy_3)_2+NaBH_4$	91
$HRh(BH_4)$(o-tolyl$_3$P)	$RhCl_2$(o-tolyl$_3$P)+o-tolyl$_3$P +$NaBH_4$	92
$H_2M(BH_4)L_2$ M=Rh,Ir	$MCl_2L_2+NaBH_4$ (L=bulky tertiary phosphine)	94
$Ir(BH_4)(CO)(PCy_3)_2$	$Ir(ClO_4)(PCy_3)_2+NaBH_4$	91

which tetrahydroborate complexes have been reported. Thus a pentacarbonyl tetrahydroborate of manganese is prepared from the reaction of manganese pentacarbonyl with $Al(BH_4)_3$ in mesitylene or isopentane at 20°C (85).

A polyborane-transition metal carbonyl complex, $HMn_3(CO)_{10}(BH_3)_2$, is obtained as a byproduct in the synthesis of $[HMn(CO)_4]_3$ from the reaction of $Mn_2(CO)_{10}$ with $NaBH_4$. This compound contains a $(BH_3)_2$ fragment with a B-B bond and with all three hydrogens of a BH_3 group coordinated to the other atoms <u>via</u> three centre bonds as shown below (86).

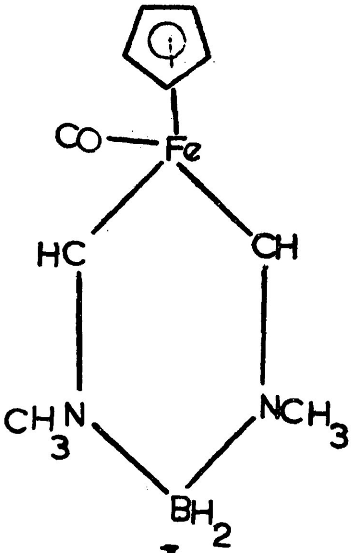


$HMn_3(CO)_{10}(BH_3)_2$

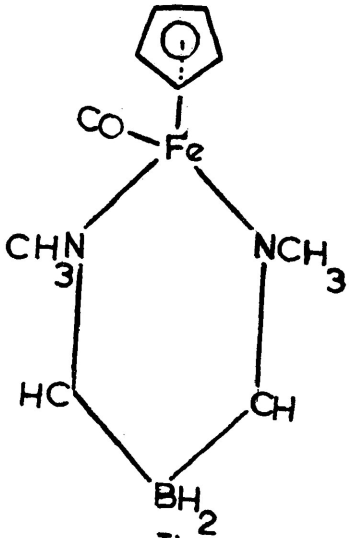
The reaction of sodium tetrahydroborate with the cationic complex $[C_5H_4CH_3Mn(NO)(CNCH_3)_2]^+$ in THF at 0°C yields the tetrahydroborate derivative $[C_5H_4CH_3Mn(NO)(CHNCH_3)_2BH_2]$ (84).

c. Iron, Ruthenium and Osmium.

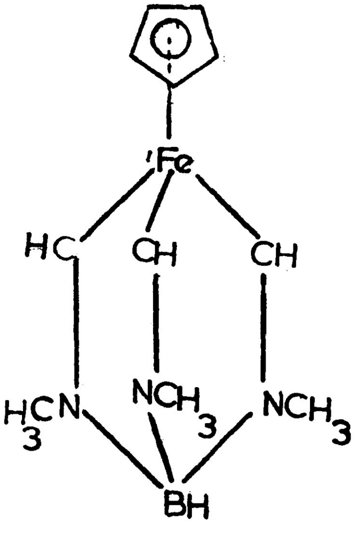
Complex compounds of tetrahydroborate derivatives have been prepared with iron. For example, reactions of sodium tetrahydroborate with the cationic complexes of iron, $\left[C_5H_5Fe(CO)(CNCH_3)_2\right]^+$ and $\left[C_5H_5Fe(CNCH_3)\right]^+$, in THF at 0°C give $\left[C_5H_5Fe(CO)(CHNCH_3)_2BH_2\right]$ and $\left[C_5H_5Fe(CHNCH_3)_3BH\right]$ respectively. The formation of these complexes proceeds apparently by the addition of BH units to C$\equiv$N bonds and the probable structures are as follows (84).



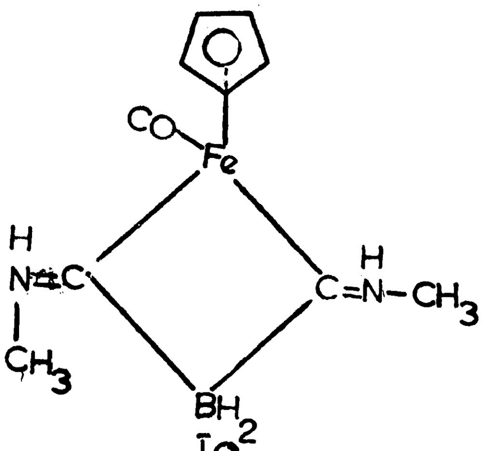
Ia



Ib

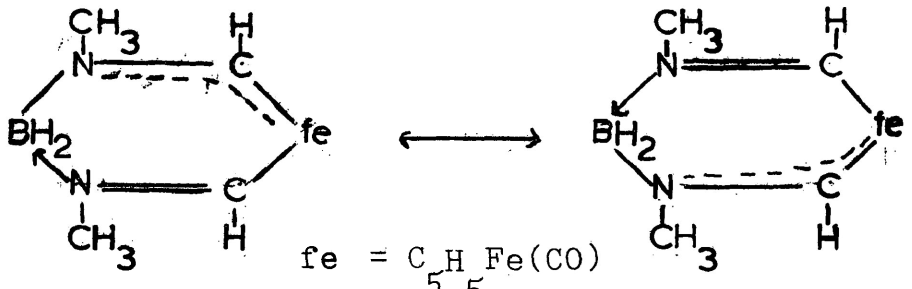


II



Ic

Assuming these structures, the bonding has been described in terms of canonical forms such as those shown below.



fe = $C_5H_5Fe(CO)$

In this group ruthenium is the only metal for which tetrahydroborate and cyanotrihydroborate complexes have been prepared and these are restricted to Ru(II). Thus, the addition of a large excess (over 10 times) of $NaBH_4$ to the blue ruthenium(II) chloride solution, containing the $[Ru_5Cl_{12}]^{2-}$ species, in the presence of triphenylphosphine gives a yellow diamagnetic complex, $HRu(BH_4)(PPh_3)_3$. This product is also obtained from the reaction of $NaBH_4$ with $RuCl_3 \cdot xH_2O$ (10:1) in ethanol in the presence of 6 molar excess of triphenylphosphine, and also by the addition of $NaBH_4$ to a mixture of $RuCl_2(PPh_3)_3$ and PPh_3 in ethanol (87).

The two other known tetrahydroborate complexes of ruthenium, $HRu(BH_4)(CO)L_3$ ($L=PPh_3,PGy_3$) have been isolated from the reaction of $NaBH_4$ and the red Ru(II) carbonyl ethanolic solution in the presence of an excess of the corresponding phosphine (87).

The reaction of a 6-fold excess of DBP with the red Ru(II) carbonyl ethanolic solution and $NaBH_3CN$ also yields a Ru(II) species, $HRu(BH_3CN)(CO)_2(DBP)_2$ (87). No tetrahydroborate complex of Ru(I) has yet been identified.

d. Cobalt, Rhodium and Iridium

Tetrahydroborate and cyanotrihydroborate complexes of this group of metals, especially cobalt, have been well characterized and are listed in Table 3. This also illustrates the importance of how small variations in the ligand can affect the ultimate product of the reaction. For example, the yellow-green paramagnetic $Co(BH_4)(PPh_3)_3$ and the green, diamagnetic $Co(BH_4)(PPh_3)_2$ (88), complexes can be synthesised by reactions of $NaBH_4$ with Co(II) starting materials, while only the Co(II) complex, $HCo(BH_4)(PCy_3)_2$, can be isolated when tricyclohexylphosphine is used as the added ligand (89).

Other Co(I) complexes, $Co(BH_3CN)(DPPE)_2$ (DPPE = 1,2-bis(diphenylphosphine)ethane) and $Co(BH_3CN)(DBP)_4$ can be isolated from the reaction of $CoCl_2 \cdot 6H_2O$ with $NaBH_3CN$ in the presence of the appropriate ligand (82). Also the reaction of $NaBH_4$ with $Co(H_2O)_6(BF_4)_2$ in the presence of P_3, (1,1,1 - tris(diphenylphosphinomethyl) ethane in ethanol/methylene chloride resulted in the formation of $Co(P_3)(BH_4)$ (90).

With rhodium systems, tetrahydroborate complexes have been prepared in which rhodium is mono, di and trivalent. For example, the crystalline, air-stable Rh(I) complexes trans- $[Rh(BH_4)(CO)L_2]$ (L=PPh_3, PCy_3) are reported to form from the metathetic reaction of $RhA(CO)L_2$ (A=Cl^-; ClO_4^-) with sodium tetrahydroborate in benzene/ethanol mixtures (91).
The analogous iridium complex, $Ir(BH_4)(CO)(PCy_3)_2$, is made in the same manner (91). Formation of a highly unstable complex $Rh(BH_4)(PPh_3)_2$ has been reported from the reaction of $NaBH_4$ with $RhCl(PPh_3)_3$ in a mixture of benzene and ethanol (92), but it is important to note that slight changes in the reaction conditions, such as prolonging the reaction time, produces $HRh(PPh_3)_3$(92). Yet another example of the way in which the ligand properties affect the reaction product is the fact that a hydride, $HRh(CO)(PPh_3)_3$, is formed from the addition of $NaBH_4$ to a mixture of $RhCl(CO)(PPh_3)_2/PPh_3$ in ethanol (91), but when PPh_3 is replaced with tris(trimethylsilylmethyl) phosphine (siphos), $Rh(BH_4)(CO)(siphos)_2$ is obtained. The analogous iridium complex, $Ir(BH_4)(CO)(siphos)_2$, is obtained by a similar route (93).

One Rh(II) complex, $HRh(BH_4)L$ (L=(o-tolyl)$_3$P), is obtained by the addition of an excess of $NaBH_4$ to a mixture of $RhCl_2L_2/L$ in ethanol (92).

The reactions of $NaBH_4$ with $HMCl_2L_2$ (M=Rh, Ir,L=bulky tertiary phosphine, e.g. PBu^t_2Me) in ethanol give the products $H_2M(BH_4)L_2$(94). The complex compounds of rhodium(I) and iridium(I), $Rh(BH_3CN)(CO)(PPh_3)_2$ and $Ir(BH_3CN)(CO)(PCy_3)_2$, have been prepared from the reactions of $NaBH_3CN$ with $Rh(CO)(PPh_3)_2ClO_4$ and $Ir(CO)(PCy_3)_2ClO_4$ respectively in benzene/ethanol mixtures (91).

e, Nickel, Palladium and Platinum

Nickel complexes of BH_4 have been characterized in oxidation states II and I. Thus, treatment of the stable nickel(II) hydride complexes $HNiClL_2$ ($L=PCy_3$ PPr^i_3) with sodium tetrahydroborate in a mixed solvent (acetone/ethanol) at room temperature under argon gives bright yellow, crystalline complexes which are formulated as trans-hydridotetrahydroboratobis(phosphine) nickel(II), $HNi(BH_4)L_2$ (95).

A diamagnetic, and presumably therefore dimeric, tetrahydroborate complex $[Ni(BH_4)(PPh_3)_3]_2$, in which the nickel is monovalent, has been prepared by the addition of a large excess of sodium tetrahydroborate (6-10M) to a $NiX(PPh_3)_3/PPh_3$ (X= Cl,Br,I) mixture in ethanol (82). A further dimeric, diamagnetic Ni(I) complex, $[Ni(BH_4)(PPh_3)_{1.5}]_2$ has also been synthesised from $NiX_2(PPh_3)_2$ (X=Cl,Br,I) and $NaBH_4$ in ethanol. The BH_4 unit is thought to be bidentate in this complex (88). When $NiCl(PPh_3)_3$ is treated with an excess of $NaBH_3CN$ the product obtained is the Ni(I) complex, $Ni(BH_3CN)(PPh_3)_2$. However, the nickel(II) complex, $HNi(BH_3CN)(DBP)_3$, is obtained from reactions of Ni(II)/$NaBH_3CN$ in the presence of the appropriate ligand (82).

Turning to palladium, the only known Pd-BH_4 complexes are _trans_-$HPd(BH_4)L_2$ (L=PPr^i_3, PCy_3) prepared in the same manner as their corresponding nickel complexes (95).

f. Zinc

The only known zinc tetrahydroborate complex is $Zn(NH_3)_4(BH_4)_2$ and this will be discussed later.

4. Production of tetrahydroborates in the presence of N-donor ligands

While most of the metal-BH_4 species have been isolated and stabilized in the presence of phosphine ligands, there are some interesting and, for the purpose of this thesis, significant metal-BH_4-N-donor ligand species which are discussed in this section.

a. Chromium, Molybdenum and Tungsten.

Chromium is the only metal of this group for which tetrahydroborate salts, containing nitrogen donor ligands, have been reported. Thus, the yellow hexamminechromium(III) tetrahydroborate $[Cr(NH_3)_6](BH_4)_3.0{\cdot}5NH_3$ is obtained by reacting $NaBH_4$ with $[Cr(NH_3)_6]F_3$ in liquid ammonia at low temperatures. The compound is stable at room temperature even under reduced pressure (96). According to a patent report, a complex formulated as $(Cren_2Cl_2)BH_4$ has been obtained from the reaction of $NaBH_4$ and Cr(III) salts in aqueous ammonia solution (100).

b. Manganese, Technetium and Rhenium.

No tetrahydroborates, or derivatives containing nitrogen donor ligands, of these elements have yet been reported.

c. Iron, Ruthenium and Osmium.

There are no reports in the literature, on tetrahydroborates or cyanotrihydroborates of iron and osmium but, cyanotrihydroborate derivatives of ruthenium, with nitrogen donor ligands have been prepared. Thus, the reaction between $NaBH_3CN$ and $[Ru(NH_3)_5H_2O]^{2+}$ gives a yellow-green solution from which a yellow green solid, formulated as $[Ru(NH_3)_5BH_3CN]Br$, is precipitated on addition of NaBr. When aqueous solutions of this compound are exposed to air, further addition of NaBr precipitates $[Ru(NH_3)_5(CNBH_3)]Br_2$ (97).

d. Cobalt, Rhodium and Iridium.

A yellow hexamminecobalt(III) tetrahydroborate, $[Co(NH_3)_6](BH_4)_3.NH_3$ has been prepared by Parry et al. (96) using a method similar to that used for the corresponding Cr(III) salt.

The syntheses of the red Co(II) hexammine tetrahydroborate and the blue ethylenediamine cobalt(II) tetrahydroborate, have also been reported (98,99). A patent (100) also claimed the formation of $Co(NH_3)_4(CO_3)(BH_4)$ and $[Coen_3](BH_4)_2Cl$ by tetrahydroborate reactions.

In the case of rhodium, a complex $[(Py)_2(dmf)RhCl(BH_4)]Cl$ (Py=Pyridine, dmf=dimethylformamide), is obtained from $(Py)_3RhCl_3$ and $NaBH_4$ in dmf solution. In solution, the pyridine ligands in the former complex undergo slow hydrogenation, and a complex containing piperidine has been isolated $[(Py)_2(C_5H_{12}NCl)RhCl(BH_4)]Cl$ (101).

No complex of iridium with tetrahydroborate, or its derivatives, with nitrogen donor ligands, has been reported so far.

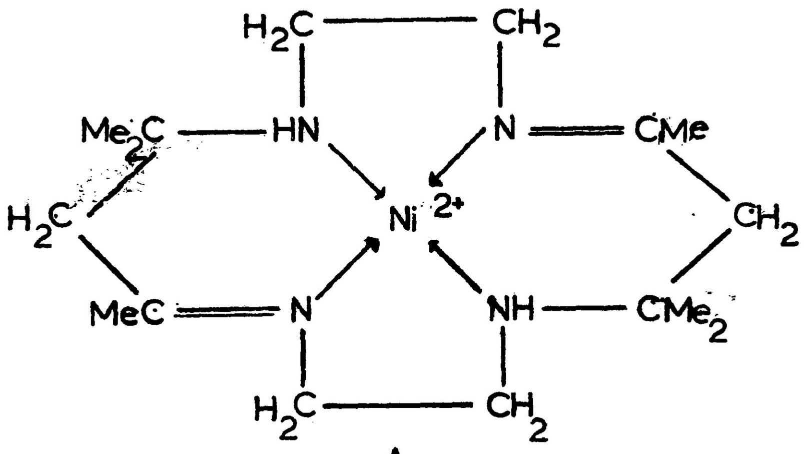
e. Nickel, Palladium and Platinum.

Nickel is the only member of this group for which tetrahydroborates containing nitrogen donor ligands are known. For example, violet crystals of the hexamminenickel(II) compound, $[Ni(NH_3)_6](BH_4)_2$, have been obtained from nickel sulphate and sodium tetrahydroborate in cold aqueous ammonia (98, 102). The complex $[Nien_3](BH_4)_2$ can be made in a similar way (98), and is also reported in a patent (103).

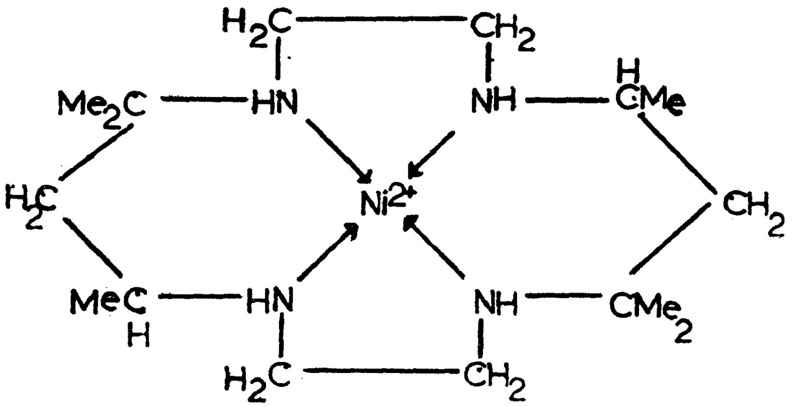
Stabilization of $Ni\text{-}BH_4$ species has been reported by the use of tetradentate amines, obtained by condensation of nickel ethylenediamine complexes with acetone (104) as shown in Fig. 1. A bis-tetrahydroborate compound of B is obtained when $NaBH_4$ is added to an aqueous solution of the perchlorate salt of the complex A. When $NaBH_4$ is added to a cold solution of the perchlorate of the complex C, also formed by condensation of the nickel ethylenediamine complex with acetone, the tetrahydroborate perchlorate of complex C is precipitated. Other tetrahydroborates of nickel amine systems are listed in Table 4 (104).

Tetrahydroborate complexes containing bipy and phen ligands, have been prepared recently, in which

Figure 1. Nickel(II) complexes of tetradentate amines.

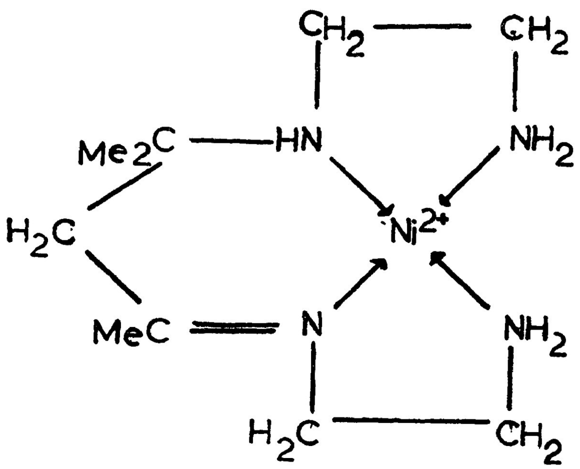


A



B

B_1 and B_2 are isomers



C

TABLE 4

Tetrahydroborate complexes of nickel

Complex	Mode of formation	Reference
$B_1(BH_4)(ClO_4)$	$B_1(ClO_4)_2+NaBH_4$	104
$C(BH_4)(ClO_4)$	$C(ClO_4)_2+NaBH_4$	104
$B_2(BH_4)_2$	$B_2Cl_2+NaBH_4$	104
$B_1(BH_4)_2$	$B_1Cl_2+NaBH_4$	104
$Ni(BH_4)(PPh_3)_3$	$NiCl(PPh_3)_3+NaBH_4$	82

nickel is monovalent, and these will be discussed later (105).

f. Zinc.

The only known zinc tetrahydroborate complex containing an N-donor ligand is $[Zn(NH_3)_4](BH_4)_2$, obtained by the addition of sodium tetrahydroborate to an ammoniacal solution of a zinc halide (107, 106).

5. Production of other complexes in the presence of phosphines.

This section of the introduction deals with the products other than hydrides and tetrahydroborates formed from reactions between $NaBH_4$ and transition metals in the presence of various ligands namely, metal(0) and other low-valent complexes. As before, the discussion is arranged by groups of metals in the presence of, firstly phosphines and related compounds and, secondly, nitrogen containing ligands. Because of the significance of the latter, to later work to be described in this thesis, the production of low-valent bipy and phen complexes by reducing agents other than $NaBH_4$ is included.

a. Chromium, Molybdenum and Tungsten.

The only report of this type of complex in this group of metals concerns the formation of $Na_2[Cr(CO)_{10}]$ from the reaction of $Cr(CO)_6$ with $NaBH_4$ (111).

b. Manganese, Technetium and Rhenium.

Sodium tetrahydroborate reduction of a $K_4ReO_2(CN)_6/KCN$ mixture gives the rhenium(I) complex $K_5Re(CN)_6$, as the main product. The same compound is also prepared from the $NaBH_4$ reduction of K_2ReCl_6/KCN (112). MnO_4^- is also reduced to MnO_2 by $NaBH_4$ (113).

c. Iron, Ruthenium and Osmium.

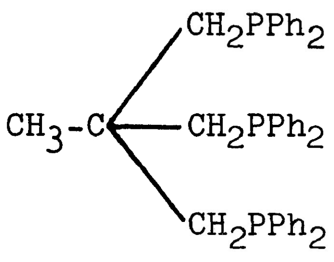
A kinetic study of the $NaBH_4$ reduction of $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ has been reported (114).

$RuCl_2[P(OC_2H_5)_3]_4$ is obtained from the reaction of sodium tetrahydroborate with a $RuCl_3/L$ mixture (115).

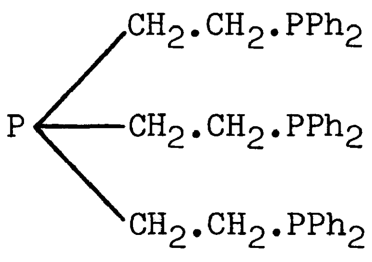
d. Cobalt, Rhodium and Iridium.

Some interesting low-valent cobalt complexes have been isolated from reactions involving $NaBH_4$. For example, the tetrahedral, paramagnetic Co(I) complexes $CoX(PPh_3)_3$ (X=Cl,Br,I) are formed from the reactions between $NaBH_4$ and CoX_2/PPh_3 mixtures in ethanol at 30-40°C (116). The related complex $CoCl(DBP)_3$ has been prepared by a similar route (82) although prolonged stirring of this reaction (up to 60 hours) with an excess of sodium tetrahydroborate results in further reduction and the formation of $Co(DBP)_4$. This compound is also obtained by heating under reflux an ethanol solution of a cobalt(II) halide and DBP in a 1:6 molar ratio with an excess of $NaBH_4$. When less ligand is used (1:3 molar ratio), the complex $Co(DBP)_2$ is obtained under similar conditions (82). Nothing is known about the structure of this last named complex.

Recently several unambiguously characterized five-coordinated Co(I) complexes have been obtained by the action of polydentate ligands, e.g. tris(2-diphenylphosphinoethyl)phosphine, Pp_3, on cobalt(II) salts in the presence of $NaBH_4$. The complexes have the general formula CoXL (X=Cl,Br, I,NCS and L is the polydentate ligand). For example, the addition of an ethanolic solution of $NaBH_4$ to a mixture of CoX_2 (X=Cl,Br,I) and the tripod ligand tris(o-diphenylphosphinophenyl)phosphine, QP, in ethanol/ethyleneglycolmonomethylether, results in the formation of (CoXQP) (117). The related complexes $Co(p_3)X$ (118) and $Co(Pp_3)$ (119) can be prepared similarly.



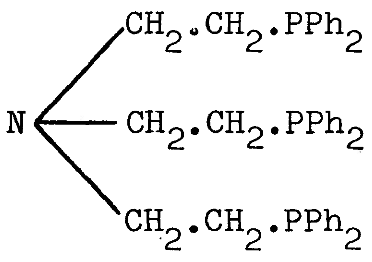
p_3



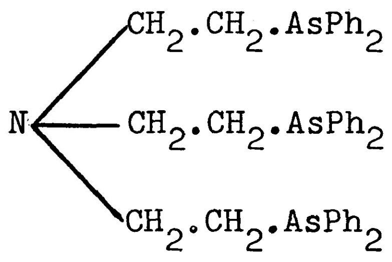
Pp_3

All of these complexes are diamagnetic, monomeric, and nonelectrolytes, and on the basis of their electronic spectra, a trigonal bipyramidal geometry has been assigned to the above Co(I) complexes.

It is interesting to note how the nature of the donor atoms influences the spin state of the metal. For example, when polydentate ligands containing nitrogen e.g. tris(2-diphenylarsinoethyl)amine, nas_3 reacts with Co(II) salts in the presence of $NaBH_4$, high spin complexes of Co(I), having a general formula CoXL (X=Cl,Br,I and L=np_3 or nas_3) are obtained (120, 147).



np_3



nas_3

It is evident from the above reactions that the tripod ligands have imposed trigonal bipyramidal geometry upon the metal ion in these complexes.

e. Nickel, Palladium and Platinum.

Sodium tetrahydroborate has been extensively used for the synthesis of zero-valent complexes of Ni, Pd and Pt containing phosphines, tertiary diphosphines and diarsines. Table 5 illustrates the variety of complexes so far obtained, and only brief additional comments are necessary. In general, reaction conditions are very mild, the reaction between $NaBH_4$ and Ni(II) in, for example, the presence of tri m-tolylphosphite proceeding at -60° C with the formation of $Ni\left[P(OC_6H_4Me\text{-}\underline{m})_3\right]_4$ (121). When the analogous reaction is carried out in anhydrous acetonitrile at room temperature, $Ni\left[P(OC_6H_4Me\text{-}\underline{m})_3\right]_3$ is obtained (122). As can be seen from Table 5, a number of nickel(0) complexes of the type ML_2, ML_4, ML'_2 and M(L-L') have been prepared by the reduction of the corresponding dipositive cationic complexes using $NaBH_4$. The various ligands are listed in Table 5 and it is claimed that $NaBH_4$ is at its most effective as a reducing agent when L and L' are aryl (108). Table 5 also lists a variety of similar Pd(0) and Pt(0) complexes which have been isolated from $NaBH_4$ reductions.

TABLE 5

Zero valent complexes of Ni, Pd and Pt.

Complex	Mode of formation	Reference
NiL_4 $L=P(OPh)_3$, $P(OC_6H_4Me\text{-}\underline{m})_3$ $P(OC_6H_4Me\text{-}\underline{p})_3$	$Ni(NO_3)_2+L+NaBH_4$	121
$Ni\left[P(OC_6H_4Me\text{-}\underline{o})_3\right]_3$	$Ni(NO_3)_2+L+NaBH_4$	122
$Ni\left[CH_3C(CH_2PPh_2)_3\right]_2$	$Ni(NO_3)_2+L+NaBH_4$	108
$Ni\left[C_2H_4(PPh_2)_2\right]_2$	$Ni\left[C_2H_4(PPh_2)_2\right]_2(NO_3)_2+NaBH_4$	108
$Ni\left[\underline{o}\text{-}C_6H_4(AsMe_2)_2\right]_2$	$\left[Ni(L\text{-}L)_2\right]Cl_2+NaBH_4$	108
$Pd(PPh_3)_4$	$K_2PdCl_4+L+NaBH_4$	108
$Pd(L)_2$ $L=C_2H_4(PPh_2)_2$, $CH_2(PPh_2)_2$, $C_3H_6(PPh_2)_2$, $\underline{o}\text{-}C_6H_4(PEt_2)_2$	$\left[Pd(L\text{-}L)_2\right]^{2+}+NaBH_4$ or $K_2PdCl_4+L\text{-}L+NaBH_4$	108
$Pd(L\text{-}L')$ $L\text{-}L'=\underline{o}\text{-}C_6H_4(PEt_2)_2$, $\underline{o}\text{-}C_6H_4(AsEt_2)_2$	$\left[Pd(L\text{-}L')_2\right]^{2+}+NaBH_4$	108

TABLE 5 --(continued)

Complex	Mode of formation	Reference
$Pt(L)_4$ L=PPh_3, $P(OPh)_3$, $P(OMe)_2Ph$, PMe_2Ph, $PMePh_2$, $AsPh_3$.	K_2PtCl_4+L+$NaBH_4$	123,125,126
$Pt[$trans$-C_2H_2(PPh_2)_2]_3$	K_2PtCl_4+L+$NaBH_4$	127
$Pt[C_2H_4(PPh_2)_2]_2$	K_2PtCl_4+L+$NaBH_4$	128
$Pt[$o$-C_6H_4(AsMe_2)_2]$	K_2PtCl_4+L+$NaBH_4$	127
$Pt_3[P(CH_2.Ch_2.PPh_2)_2Ph]_4$	K_2PtCl_4+L+$NaBH_4$	127

A series of Pt(0) complexes containing polytertiaryphosphines and phosphino-arsines, e.g. $(Pmt-Pf)_2$, 1-diphenylphosphino-2-di-m-tolyl-phosphino ethane and $(Asf-Pf)_2$, 1-diphenylphosphino-2-diphenylarsino ethane, are prepared by the reactions of $NaBH_4$ with mixtures of K_2PtCl_4 and the appropriate ligand in aqueous ethanol (127).

The addition of sodium tetrahydroborate to a solution of $(PPh_3)_2PtO_2$ saturated with ethylene results in the rapid and quantitative precipitation of $(PPh_3)_2Pt(CH_2{=}CH_2)$ (128).

As was the case with cobalt, the carefully controlled reactions of Ni(II) halides and $NaBH_4$ can lead to the isolation of Ni(I) complexes of the type $NiXL_3$ ($L{=}PPh_3$, X=Cl,Br and I and L=DBP, X=Cl) which have been prepared from ethanol solutions. These complexes are paramagnetic and have electronic spectra typical of that expected for a tetrahedral d^9 configuration. In general, longer reaction times lead to further reduction and, for example, $Ni(DBP)_4$ is formed on prolonged stirring (20-40 hours) with an excess of $NaBH_4$. The same complex can also be prepared by heating under reflux a mixture of NiX_2 and DBP in the ratio of 1:6 with $NaBH_4$ in ethanol, and, with less ligand (1:3), $Ni(DBP)_2$ is formed. The complexes. $Pd(DBP)_4$ and $Pt(DBP)_4$ are also obtained by a similar route (82).

As with cobalt, five-coordinate complexes of Ni(I) are also formed from the reactions of Ni(II) salts with various polydentate ligands, e.g. 1,1,1-tris(diphenylphosphinomethyl)ethane (p_3) in the presence of $NaBH_4$ (118). Thus, when an ethanolic solution of $NaBH_4$ is added to a solution of NiX_2 and ligand in methylene chloride/ethanol the paramagnetic compounds $NiX(p_3)$ (X=Cl,Br) (118), $NiX(np_3)$ (X= Cl,Br, and I) (120) and $NiX(nas_3)$ (X=Cl,Br,I,NCS or NO_3) (147) are obtained. Their electronic spectra are similar, and appear characteristic of d^9 ions in trigonal bipyramidal ligand fields. It is again obvious that the tripod shape of the ligand confers trigonal bipyramidal geometry to the metal ion in the complexes. The complexes $NiX(np_3)$ (X=Cl,Br,I) are further reduced to the nickel(0) complexes $Ni(np_3)$, which also have a trigonal pyramidal structure with the nitrogen atom at the apex of the pyramid and the metal atom in the plane of the three phosphorus atoms (120).

6. Production of other complexes in the presence of N-donor ligands.

Metal complexes of phen and bipy, where metals are in "normal" oxidation states, have been extensively investigated and reviewed (131,132). As has been seen, these ligands can also stabilize low valent states because the readily polarizable π-electronic system can adjust the electron density on the metal atom either by receiving electrons from it or giving electrons to it, the electron drift occurring through a π-molecular orbital covering the whole of the π-system of the ligands and metal (129, 130).

The preparation of many bipy complexes of metals in low oxidation states has been achieved by Herzog and his coworkers. The lithium salt of the bipyridyl anion, in THF, is the most commonly used reducing agent, but the use of the sodium salt of the bipyridyl anion or benzophenone is also reported. A typical reaction is as follows (131).

$$MX_y + YLi_2bipy + nbipy \longrightarrow Mbipy_n + YLiX + YLibipy$$

MX_y = transition metal salt or compound

Only a few examples are available of $NaBH_4$ being used as a reducing agent in the preparation of low-valent phen and bipy complexes.

a. Chromium, Molybdenum and Tungsten.

Treatment of $K_6[Cr(CN)_6]$ with phen and bipy in liquid ammonia at room temperature results in complete substitution to give $Crphen_3$ and $Crbipy_3$ (133). The former complex can also be obtained in good yield when $[Crphen_3]Br_2$ in THF, is treated with naphthalene dilithium or benzophenone dilithium. The chromium can be further reduced by shaking $Crbipy_3$ with an excess of Li in THF solution when $Li[Crbipy_3].4THF$ is produced. This and numerous other low valent complexes of Cr have been reported by Herzog and coworkers (134).

The $Mbipy_3$ complexes are also known for M= W and Mo. Thus, a suspension of $[Mobipy_3]Cl_3$ in THF is reduced when treated with 3 moles of Li_2bipy producing copper-coloured $Mobipy_3$ (135). Similarly, an ethanolic solution of WCl_6 and bipy in a 1:3 molar ratio is reduced by Li_2bipy in THF over a 6 hour period to produce the corresponding tungsten compound (136).

b. Manganese, Technetium and Rhenium.

The behaviour of manganese parallels that of the earlier transition metals in that the addition of an excess of Li_2bipy to $[Mnbipy_3]Br_2$ in THF produces $Mnbipy_3$ which can also be further reduced by Li in THF, in the absence of air to give $Li[Mnbipy_3]\cdot 4THF$ (137).

Reduction of $K_3[ReO_2(CN)_4]$with sodium amalgam in the presence of bipy in HCl, results in the formation of a dark purple solid, $[Rebipy_3]CN\cdot HCN$, and with phen in 4N HCl, a similar stable complex is obtained (138).

c. Iron, Ruthenium and Osmium.

The zero-valent iron complex, Febipy$_3$, is prepared by treating a solution of $[\text{Febipy}_3]I_2$ in THF with Li$_2$bipy (139). The compound is also obtained by adding Nabipy to anhydrous FeCl$_3$ in anhydrous 1,2-dimethoxyethane (DME) under moisture-free, oxygen-free conditions in an evacuated vessel (140). The blue-violet solution of Febipy$_3$ in DME, has absorption peaks at 525,502 and 357 nm, and it is reported that, except for a blue shift of approximately 30 nm, the spectrum of the Fe(0) complex resembles that of Na^+bipy^-, indicating the probable dissociation of Febipy$_3$. However, conductivity results show that the solution has a negligible amount of dissociation. esr studies of solid Febipy$_3$ gave an average 'g' value of 2.075 ±.003 which, when compared with values of 2.2125 ± .005 for Ni^{2+} and 2.1728 ± .0005 for Co^+, suggest that the iron atom in the complex has a d^8 configuration (140). Attempts to measure the magnetic susceptibility of the paramagnetic Febipy$_3$ failed due to metallic iron impurities (140). Further reduction of the iron can be achieved by the addition of a large excess of Nabipy to anhydrous $[\text{Febipy}_3]\text{Cl}_2$ in DME under oxygen-free conditions in an evacuated vessel to

give Na$[\text{Febipy}_3]$(141). The absorption spectrum of the salmon coloured solution of Na$[\text{Febipy}_3]$ in DME shows peaks at 352 (ϵ=33x10^3), 509 (ϵ=12 x 10^3), 535 (ϵ=12x10^3) and 700 nm (ϵ=5x10^3).
The esr spectrum of a solid sample gave g=2.0031, which is very close to the free electron value of 2.0023 and indicates that the unpaired electrons in Na$[\text{Febipy}_3]$ occupy molecular orbitals mainly of ligand character (141).

d. Cobalt, Rhodium and Iridium.

When the stoichiometric amount of Li_2bipy, in THF, is stirred with a mixture of CoCl_2/THF and bipy (1:3 molar ratio) for 6 hours in an oxygen-free atmosphere, Cobipy_3 is produced (142). The sodium tetrahydroborate reduction of bipy and phen complexes of Co(II) and Rh(III) has also been reported. For example, the paramagnetic (μ = 2.89B.M.) $[\text{Cobipy}_2]\text{ClO}_4$ is formed when $[\text{Cobipy}_3](\text{ClO}_4)_2$ is reduced by NaBH_4 (144, 146).

On the other hand, the hexacoordinated complex $[\text{Cophen}_3]\text{ClO}_4$ is obtained from the reduction of $[\text{Cophen}_3](\text{ClO}_4)_2$ by NaBH_4 (145).

With the rhodium system, the complexes $[\text{Rhbipy}_2]\text{ClO}_4\cdot3\text{H}_2\text{O}$ and $[\text{Rhbipy}_2]\text{NO}_3\cdot3\text{H}_2\text{O}$ have been prepared by adding NaBH_4 to aqueous solutions of

$[Rhbipy_3](ClO_4)_3$ and $[Rhbipy_3](NO_3)_3$ respectively (146). Conductivity results show that both of these complexes are 1:1 electrolytes in ethanol. It is interesting to note that $[Rhbipy_2]NO_3.3H_2O$ is paramagnetic (μ=1.86 B.M.), while $[Rhbipy_2]ClO_4$ is diamagnetic. To account for the difference in magnetic moments, several explanations have been given. For example, it is suggested that $[Rhbipy_2]NO_3$ is a mixture of Rh(0) and Rh(II) complexes or that the NO_3^- is coordinated through two oxygen atoms (146).

e. Nickel, Palladium and Platinum.

Addition of phen or bipy to $K_4[Ni(CN)_4]$ in liquid ammonia at above $-33^\circ C$ results in the formation of $Niphen_2$ and $Nibipy_2$ respectively (133).

A detailed study of the reactions of Ni(II) salts with $NaBH_4$ in the presence of bipy and phen ligands has been carried out very recently (105). For example, it has been shown that when $NaBH_4$ is added to aqueous solutions of $[NiL_3]Cl_2$ (L=bipy,phen) in <u>air</u>, compounds of the type $NiL_3(BH_4)_2 \cdot xH_2O$ are obtained. These compounds decompose to unidentified purple solids on crystallization or on drying under reduced pressure. On the other hand, from similar reactions under <u>nitrogen</u> atmospheres, Ni(I) complexes are obtained.

Thus $\mathrm{Niphen_2BH_4.H_2O}$ is formed when mixtures of $[\mathrm{Niphen_3}]\mathrm{Cl_2}$ or $\mathrm{Niphen_2Cl_2}$ and $\mathrm{NaBH_4}$ (1:5) are stirred in water for several hours. Similarly, $\mathrm{Nibipy_2BH_4.2H_2O}$ is formed from the reaction of $\mathrm{NaBH_4}$ with either Ni(II)/bipy (1:2) or $\mathrm{Nibipy_2Cl_2}$.

In these reactions, the quantity of ligand and the solvent are important factors in determining the nature of the product. For example, the reaction of $\mathrm{NaBH_4}$ with 1:3 metal:ligand mixtures in water (L=bipy) gives a mixture of Ni(I) and Ni(II) complexes. In the phen reactions, the presence of a large quantity of ligand (Ni:phen = 1:6) prevents reduction. On the other hand, reduction of Ni(II)is rapid in alcoholic solutions in the presence of a large excess of bipy and, from such reactions (Ni(II):bipy:$\mathrm{NaBH_4}$ = 1:6:5), blue solutions are produced from which $[\mathrm{Nibipy_2}]\mathrm{X}$ (X= $\mathrm{PF_6^-}$ and $\mathrm{BPh_4^-}$)are precipitated by adding the appropriate anions. The analogous complexes α-$\mathrm{Niphen_2PF_6}$ and $\mathrm{Niphen_2BPh_4}$ are obtained by similar routes and the former is converted to another form, β-$\mathrm{Niphen_2PF_6}$, when recrystallized from acetone.

All of the above complexes are paramagnetic with magnetic moments consistent with d^9 configurations. The ir spectrum of the $\mathrm{BH_4^-}$ complexes shows the presence of what are probably very weakly coordinated $\mathrm{BH_4^-}$ groups (absorptions at 1080 and 2150 Sh, 2230 and 2300 cm^{-1}, assigned as B-H deformation and stretching frequencies respectively). However, from conductivity results, all of these complexes are 1:1 electrolytes and this shows the dissociation of BH_4^- in solution. Thus, structural changes take place when some of these compounds are dissolved in organic solvents and these structural changes are confirmed by changes in electronic spectral properties in passing from the solid state to solution.

f. Zinc.

The reaction of $[Znbipy_3]I_2$ with Li_2bipy in liquid ammonia gives a violet-green product which analyzed correctly for $[Znbipy_2]\cdot 2NH_3$ (134).

c. Objectives of the Present Work.

It is obvious from the earlier sections that the use of sodium tetrahydroborate in synthetic organometallic chemistry is very extensive. Considerable progress has been made in our understanding of the complex reactions which take place between transition metal salts (particularly Co and Ni) and $NaBH_4$ in the presence of phosphine ligands (24). The conditions necessary for the formation of the various possible types of complex have been established and mechanisms for the reactions proposed.

It is equally apparent from the introduction that the use of $NaBH_4$ as a reducing agent for transition metal salts in the presence of N-donor ligands is much less studied and this forms the basis of the work to be described in this thesis. After exploratory reactions involving a number of transition metals, the main thrust of the work has centred on the following aspects of M/N-ligand/BH_4 systems:

i) Synthesis of low valent complexes of iron and ruthenium-e.g. M(I) complexes, rare oxidation states for these metals.

ii) Study of the effects of different bidentate N-ligands and of different solvents, since the results may help in understanding the mechanisms of $NaBH_4$ reductions of metal complexes.

iii) Synthesis of tetrahydroborate complexes of Fe, Co, Ru etc. since this forms a logical extension of the work already done in these laboratories on Ni(105).

Furthermore, it is already known that $Niphen_2BH_4.H_2O$ has catalytic potential and it would be desirable to explore the catalytic properties of M/N-ligand/BH_4 systems in general. This aspect of the topic, however, is outside the scope of this thesis which is concerned largely with synthetic aspects of the problem.

II. EXPERIMENTAL

A. Materials

The simple hydrated transition metal salts of Cr through Zn and $RuCl_3 \cdot 3H_2O$ and the ligands en, bipy and phen were obtained as reagent grade chemicals from standard suppliers and were used without further purification in all the syntheses. The complexes $[Fephen_3]Cl_2 \cdot 7H_2O$, $[Febipy_3]Cl_2 \cdot 5H_2O$ (148), $[Ruphen_3]Cl_2 \cdot 5H_2O$, $[Rubipy_3]Cl_2 \cdot 5H_2O$ (149), $[Ruen_3]Cl_2$ (150), $[Coen_3]Cl_3$ (151) and $[Cren_3]Cl_3 \cdot 3H_2O$ (152) were synthesized according to literature methods. Reagent grade solvents were degassed with oxygen-free nitrogen and stored over type 4A molecular sieves.

B. Physical Measurements.

All samples for physical measurements were suitably protected from atmospheric oxidation. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer, and were calibrated with polystyrene film.. Nujol mulls of the samples were spread beteeen potassium bromide plates for the 650 to 4000 cm^{-1} region and between polyethylene plates for the 200 to 650 cm^{-1} region.

Electronic spectra were recorded on a Cary-14 spectrophotometer. Magnetic susceptibilities were obtained at room temperature using the standard Gouy method in a double ended tube calibrated with $Nien_3S_2O_3$ or in solution using the nmr method described by Evans (153) on a Varian Associates model A60-A spectrometer. Electrical conductivites were measured on a YSI model 31 conductivity bridge. The cell was calibrated using a standard potassium iodide solution. Microanalyses for carbon, hydrogen and nitrogen were carried out under nitrogen atmospheres on a Perkin-Elmer model 240 CHN analyser by the staff of the Science Instrumentation Laboratory of this University.

C. Syntheses.

Due to the oxygen sensitivity of almost all of the complexes, all reactions (unless otherwise specified) were carried out in a glove box which was continuously flushed with dry, oxygen-free nitrogen at a rate of 3 l/min. Yields were in the 50-70% range except for $[Rubipy_3](BH_4)_2$, $[Coen_3](BH_4)_3$, $[Cren_3](BH_4)_3$ and $[Znen_3](BH_4)_2$ where yields of ~25% were obtained, probably due to the appreciable solubility of these complexes in water.

1. $Fephen_2BH_4 \cdot H_2O$.

$[Fephen_3]Cl_2 \cdot 7H_2O$ (0.8g,1mM) was dissolved in water (~15ml) to which a saturated solution of $NaBH_4$ (0.38g, 10mM) in water (5ml) was added dropwise. The initial red colour of the solution disappeared and a dark coloured product was precipitated. The mixture was left stirring for ~15 min. before the product was separated by filtration, washed with water (~5ml: the complex decomposes with extensive washing with water) and when almost dry washed with benzene (20 ml) and ether (until the washings were almost colourless) and dried under high vacuum for ~ 6 h.

The same product was also synthesized by adding a saturated solution of $NaBH_4$(0.285g, 7.5 mM) in water (5ml) to a mixture of $FeCl_3 \cdot 6H_2O$ (0.2g, 0.74 mM) and phen (0.44g, 2.2mM) in water (~15ml). The complex was isolated as described above.

Analyses: Calc. for $Fephen_2BH_4 \cdot H_2O$, C 64.13, H 4.89, N 12.46%

Found, C 65.4, H 5.0, N 12.7%.

2. $Fephen_2PF_6$

A mixture of $FeCl_3 \cdot 6H_2O$(0.2g, 0.74mM) and phen(0.73g, 3.7mM) was heated in ethanol (~25ml) and then cooled to room temperature. $NaBH_4$ (0.285g, 7.5mM) suspended in ethanol (~10ml) was then added dropwise to the red solution which slowly turned violet and which was then stirred for 1 h. After filtration, a solution of $NaPF_6$(0.14g, 0.8mM) in ethanol (~10ml) was added to the violet coloured filtrate, and the dark violet coloured product which precipitated out almost immediately was filtered off, washed liberally with water, ethanol and finally with ether. The product was recrystallized from an acetone/alcohol mixture (1:2) and then dried under reduced pressure.

Alternatively, when a suspension of $Fephen_2BH_4 \cdot H_2O$ (0.5g, 1.1mM) in ethanol (~15ml) was stirred with a solution of $NaPF_6$ (~0.19g, 1.13mM) in ethanol for 6 h. the same violet coloured product was obtained. This was purified as described above.

Analyses: Calc. for $Fephen_2PF_6$, C 51.3, H 2.85, N 9.77%

Found, C 52.1, H 2.9, N 9.8%

3. $Fephen_2BPh_4$.

This complex was prepared in the same way as described for Fephen$_2$PF$_6$, although satisfactory chemical analyses could not be obtained on this complex even after recrystallization from various solvent systems such as acetone/alcohol and acetone/ether. Recrystallization of the complex in the presence of phen did not lead to significant improvement in the analyses.

Analyses: Calc. for Fephen$_2$BPh$_4$.C$_2$H$_5$OH, C 76.77, H 5.37, N 7.16%

Found, C 72.2, H 5.0, N 7.5%

The instability of this complex made reproducible analyses difficult to obtain but the analyses obtained fitted the above formulation much better than any other reasonable alternative. Some doubt, however, must remain regarding the exact nature of the material although the manner of synthesis (similar to that of Fephen$_2$PF$_6$) would support the formulation proposed.

4. $[\text{Febipy}_3](BH_4)_2.6H_2O$

The addition of a saturated solution of NaBH$_4$ (0.38g, 10mM) in water (5ml) or solid NaBH$_4$ to a solution of $[\text{Febipy}_3]Cl_2.5H_2O$ (0.7g, 1mM) in water (~15ml) caused the immediate precipitation of a red coloured product, which after being stirred for ~15 min., was filtered off, washed with water (5 ml only as the complex is very soluble) and, when almost dry, with benzene and ether and finally dried under reduced pressure.

The same product was synthesized by the addition of NaBH$_4$ (0.285g, 7.5 mM) either in the solid state or as a saturated aqueous solution, to a mixture of $FeCl_3.6H_2O$ (0.2g, 0.74 mM) and bipy (0.35g, 2.2mM) in water (~15ml). The product was purified as described above.

Analyses: Calc. for $[Febipy_3](BH_4)_2.6H_2O$, C 54.38, H 6.64, N 12.68).

Found, C 54.7, H 5.5, N 12.7%.

5. $[Febipy_3](PF_6)_2.0.5C_2H_5OH$

A mixture of the above complex, $[Febipy_3](BH_4)_2.6H_2O$, (0.4g, 0.63mM) suspended in ethanol (~15ml), and an alcoholic solution of $NaPF_6$ (0.11g, 0.65mM) was stirred for about 1 h after which the resulting red solid was filtered off and liberally washed with water, ethanol and ether. The red coloured product was recrystallized from an acetone/alcohol (1:2) mixture.

Analyses: Calc. for $[Febipy_3](PF_6)_2.0.5C_2H_5OH$, C 44.4, H 3.32, N 10.04%

Found, C 44.2, H 3.3, N 10.12%.

6. $[Ruphen_2BH_4]_2.3H_2O$

A mixture of $[Ruphen_3]Cl_2$ $.5H_2O$ (0.4g, 0.5 mM) and phen (0.1g, 0.5mM) was heated in water (15ml) for 15 min. and then cooled to room temperature. A saturated solution of $NaBH_4$ (0.28g, 7.3mM) in water was added dropwise and the orange-red solution slowly turned dark. The mixture was left stirring for 6 h. after which an additional small amount of $NaBH_4$ (0.01g, 0.25mM) was then added. The mixture was stirred for a further ½ h. before the dark coloured product was separated by filtration, washed with water (~5ml) and, when almost dry, with benzene and finally with ether until the washings were almost colourless and dried under reduced pressure.

The same product was also synthesized by stirring $RuCl_3 \cdot 3H_2O$ (0.25g, 0.95 mM), phen (0.75g, 3.8mM) and an excess of $NaBH_4$ (0.54g, 14.2mM) in water (15ml) for about 6 h. The product was separated and purified as described above.

Analyses: Calc. for $[Ruphen_2BH_4]_2 \cdot 3H_2O$, C 57.22, H 4.57, N 11.12%

Found, C 57.3, H 4.3, N 10.8%.

7. $[Ruphen_2]_2(PF_6)_2$

This complex was prepared in a similar fashion to that already described for $[Fephen_2]PF_6$. Thus a mixture of $RuCl_3 \cdot 3H_2O$ (0.25g, 0.95 mM) and phen (0.95g, 4.7 mM) was heated in ethanol (25ml) and then cooled to room temperature. When a suspension of $NaBH_4$ (0.36g, 9.4 mM) in ethanol (15ml) was added dropwise to the above stirred mixture the initial brown precipitate slowly disappeared and after about 2 h. a deep violet coloured solution was obtained. This was filtered and a solution of $NaPF_6$ (0.17g, 1 mM) in ethanol (10ml) was added to the filtrate. The resulting violet coloured precipitate was separated, washed with water, ethanol and ether, and then recrystallized from an acetone/alcohol mixture (1:2) and finally dried under reduced pressure.

Analyses: Calc. for $[Ruphen_2]_2(PF_6)_2$, C 47.49,
H 2.63 N 9.23%
Found, C 47.2, H 2.5 N= 9.0%

8. $[Rubipy_3](BH_4)_2 \cdot 5H_2O$

The corresponding Ru(II) chloride complex $[Rubipy_3]Cl_2 \cdot 5H_2O$ (0.35g, 0.48 mM) was dissolved in water (~10ml) and solid $NaBH_4$ (0.36g, 9.5 mM) was added in small portions to the well stirred solution over a period of 15 min. The reddish coloured product, which started precipitating

9

immediately, was filtered off after the mixture was stirred for an additional ½ h., washed with the minimum amount of water (~3ml) and, when almost dry, with benzene and ether. The product was finally dried under reduced pressure.

Analyses: Calc. for $[\mathrm{Rubipy_3}](\mathrm{BH_4})_2\cdot 5\mathrm{H_2O}$, C 52.22, H 6.09, N 12.18%

Found, C 52.0, H 5.1, N 12.1%.

9. $\mathrm{Cophen_2BH_4\cdot H_2O}$

A solution of $NaBH_4$ (0.38g, 10 mM) in water (10ml) was added very slowly (over a period of 1½ h.) to a stirred solution of $CoCl_2\cdot 6H_2O$ (0.24g, 1mM) and phen (0.6g, 3 mM) in water (25ml) at room temperature. A large volume of gas was evolved and a green product was precipitated. The mixture was left stirring for an additional ½ h. before the product was filtered off, washed with water, and when almost dry, with benzene and ether before drying under reduced pressure.

The same product was also synthesized when a solution of $NaBH_4$ (0.18g, 4.7 mM) in water (10ml) was added to an aqueous solution of $\mathrm{Cophen_2Cl_2}$ (0.5g, 0.9 mM) at room temperature. The mixture was stirred for 15 min. before separation and purification of the complex as described above.

Analyses: Calc. for $Cophen_2BH_4 \cdot H_2O$ C 63.7, H 4.86, N 12.4%.
Found, C 63.0, H 4.6, N 12.3%.

10. $Cobipy_2BH_4 \cdot H_2O$

This complex was prepared by the slow addition of a solution of $NaBH_4$ (0.16g, 0.42 mM) in water (10ml) to a solution of $Cobipy_2Cl_2$ (0.4g, 0.83 mM) in water (20 ml). A large amount of gas was evolved as the dark blue product started to precipitate. The mixture was stirred for ½ h. after which the blue product was filtered off, washed with water and, when almost dry, with benzene and ether and finally dried under reduced pressure.

Alternatively the addition of a solution of $NaBH_4$ (0.38 g, 10 mM) in water (10ml) to a mixture of $CoCl_2 \cdot 6H_2O$ (0.24g, 1 mM) and bipy (0.47, 3mM) in water (20ml) yielded the same product, which was isolated as described above.

Analyses: Calc. for $Cobipy_2BH_4 \cdot H_2O$, C 59.38, H 5.44
N 13.86%.
Found, C 58.6 H 5.1 N 13.85%.

The following reactions were carried out in air.

11. $[\mathrm{Coen_3}](\mathrm{BH_4})_3\cdot 3\mathrm{H_2O}$.

A saturated solution of $\mathrm{NaBH_4}$ (1.5g, 40 mM) in concentrated ammonia (5ml) (or solid $\mathrm{NaBH_4}$) was added to a stirred solution of $[\mathrm{Coen_3}]\mathrm{Cl_3}$ (0.7g, 2mM) in concentrated ammonia solution (~10ml) at 0°C. The tetrahydroborate salt started to precipitate immediately from the solution which was stirred for ½ h. before the product was filtered off, washed with a minimum amount of a cold solution of concentrated ammonia, ethanol and ether, and then dried under reduced pressure.

Analyses: Calc. for $[\mathrm{Coen_3}](\mathrm{BH_4})_3\cdot 3\mathrm{H_2O}$ C 21.33, H 12.44, N 24.89%.

Found, C 20.9, H 11.55, N 24.62%.

12. $[\mathrm{Mnbipy_3}](\mathrm{BH_4})_2\cdot 3\mathrm{H_2O}$.

A mixture of $\mathrm{MnCl_2\cdot 4H_2O}$ (0.2g, 1.0 mM) and bipy (0.47g, 3.0 mM) in water (20ml) was heated until the solution became homogeneous and then cooled to room temperature. A solution of $\mathrm{NaBH_4}$ (0.38g, 10.0 mM) in water (10ml) was then added to the stirred solution. The tetrahydroborate salt started to precipitate almost immediately, and the mixture was stirred for ~15min. before being filtered. The yellow coloured solid was washed with water, ethanol and ether before being dried under reduced pressure.

The same product was obtained by adding $NaBH_4$ (0.19g, 5.0 mM) suspended in ethanol (5ml) to a mixture of $MnCl_2 \cdot 4H_2O$ (0.1g, 0.5 mM) and bipy (0.235g, 1.5 mM) in ethanol (15 ml). The solution was stirred for ½ h. and the product isolated as described above.

Analyses: Calc. for $[Mnbipy_3](BH_4)_2 \cdot 3H_2O$

C 59.28, H 6.25, N 13.83%.

Found, C 58.4, H 5.7, N 13.8%.

13. $[Znen_3](BH_4)_2 \cdot H_2O$.

The complex was prepared in the same way as described for $[Coen_3](BH_4)_3$. Thus $[Znen_3]Cl_2$ (1.85g, 5.0 mM) was dissolved in the minimum amount of concentrated ammonia solution (~10ml) at 0°C to which solid $NaBH_4$ (3.8g, 100 mM) was added slowly with stirring. The mixture was stirred for an additional 15 min. after which the white product was filtered off, washed with cold concentrated ammonia solution, alcohol and ether, and dried under reduced pressure.

Analyses: Calc. for $[Znen_3](BH_4)_2 \cdot H_2O$ C 24.56, H 11.6, N 28.66%.
Found, C 24.4, H 11.3, N 28.6%.

14. $[Znbipy_2BH_4](BH_4) \cdot 2H_2O$.

A mixture of $ZnCl_2$ (0.135g, 0.99 mM) and bipy (0.46g, 3.0 mM) was heated in water (20ml) until the solution became homogeneous and then cooled to room temperature. A solution of $NaBH_4$ (0.37g, 9.9 mM) in water (10 ml) was then added and precipitation of the yellow product started immediately. The mixture was stirred for 15 min. before the product was filtered off, washed with water and, when almost dry, with benzene and ether and then dried under reduced pressure.

Analyses: Calc. for $[Znbipy_2BH_4](BH_4) \cdot 2H_2O$
C 54.11, H 6.31, N 12.62%.
Found, C 53.1, H 5.8, N 12.4%.

15. $[Cren_3](BH_4)_3 \cdot 2H_2O$.

A concentrated solution of $NaBH_4$ (3.8g, 100 mM) in concentrated ammonia (~10ml) was added to a saturated solution of $Cren_3Cl_3$ (2.0g, 5.0 mM) in concentrated ammonia (~10ml) at 0°C. The mixture was stirred for 15 min. after which the yellow coloured product was filtered off, washed with cold ammonia, ethanol and ether and dried under reduced pressure.

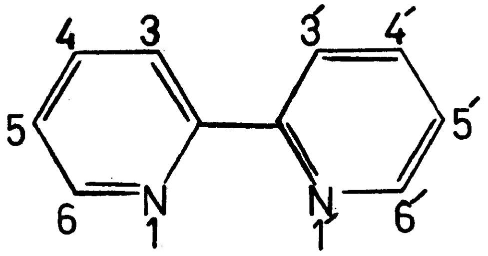
Analyses: Calc. for $[Cren_3](BH_4)_3.2H_2O$ C 23.03, H 12.79, N 26.87%.

Found, C 23.5, H 12.7, N 27.0%.

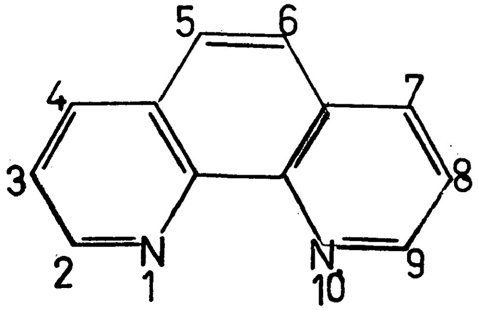
III. RESULTS AND DISCUSSION

A. Introduction

The bidentate heterocyclic diamines, 2, 2' - bipyridyl(bipy) and 1, 10-phenanthroline(phen), which are among the best coordinating agents known, were introduced by Blau in 1888 (154). Their structures and the numbering of the systems are shown below:



bipy



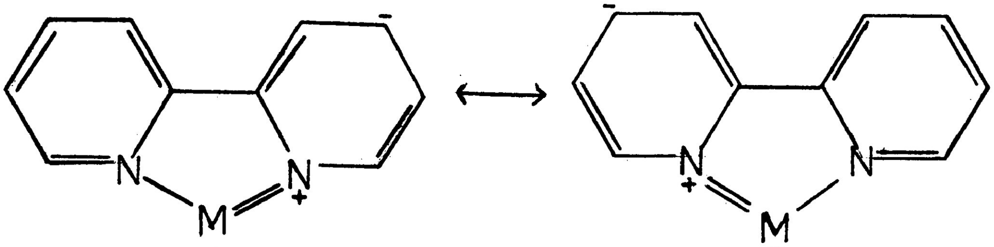
phen

Although bipy and phen are both relatively weak bases, (the highest of the two pK_a values ~ 5), they chelate with a wide variety of metal ions and the resulting complexes generally have large formation constants, e.g. The $\log \beta_3$ values for $[Febipy_3]^{2+}$, $[Cobipy_3]^{2+}$, $[Fephen_3]^{2+}$ and $[Cophen_3]^{2+}$ are 17.5,16.1,21.2 and 19.9 respectively (131). However, the formation constants of complexes of ethylenediamine (en) which is a much stronger base than either bipy or phen, but with the same basic atomic grouping (-N-C-C-N-), are considerably less than those of phen and bipy ($\log \beta_3$ values for

$[\mathrm{Feen}_3]^{2+}$ and $[\mathrm{Coen}_3]^{2+}$ are 9.55 and 13.76 respectively (167)).

It is evident therefore that in the interaction between metal ions and bipy and phen, much more is involved than the simple functional grouping. Thus it has been suggested that the unusual stability of metal complexes of bipy and phen is the result of π-bonding between the conjugated ligand and the unhybridized d- electron pairs of the metal atoms (156).

The bonding of bipy with certain transition metal ions has also been discussed in terms of the valence bond approach. Nyholm (157) has proposed that the major factor responsible for the unusual stabilization of complexes of this ligand is the formation of double bonds and he suggested that structures A and B contribute to the resonance hybrid.



A B

Similar structures can be written for the phen complexes.

Observations on the effect of substitution on the reactions of phen and bipy with Fe(II) provide support for this proposed mode of bonding (158).

For example, it was suggested that substitution of electron donating groups in the 4- and 7-positions of phen lead to an increase in the stability of the complexes formed, since substitution in these positions leads to an increase in the electron density on the nitrogen atoms. This has been verified experimentally (159).

The preparations of many complexes of bipy containing metals in low oxidation states have been achieved by Herzog and coworkers (131), although the similar use of phen is less well established. It is generally accepted (131) that the electron acceptor as well as the electron donor properties of the ligands is responsible for the stabilization of the low valent oxidation states.

Thus, the characteristic feature of phen and bipy in coordination chemistry is the stabilization of both low and high valent states, and this may be interpreted as due to the strong π- bonding between the metal atom and the ligand molecules. This is not possible with a ligand like en.

Since, because of the characteristics outlined above, bipy and phen would possibly stabilize low oxidation states of metals,generated by tetrahydroborate reductions of metal ions in conventional oxidation states, such reductions of a variety of transition metal ions in the presence of these ligands have been attempted. The results of these studies are summarized in the following sections.

B. Iron.

In view of the recent work in these laboratories concerning reactions between $NaBH_4$ and Ni(II) in the presence of phen and bipy from which a number of interesting Ni(I) species have been isolated (105), it seemed appropriate to extend this work to other group V111 metals. This section presents the results of similar reactions carried out with both iron(II) and iron(III).

Thus, the addition of a 10 molar excess of $NaBH_4$ to an aqueous solution of Fe^{3+}/phen in a 1:3 molar ratio, causes the precipitation of a very dark coloured air sensitive tetrahydroborate complex which analyses well for $Fephen_2BH_4 \cdot H_2O$ and which appears to be analogous to the Ni(I) complex with the same empirical formula (105). Similarly, the addition of a large excess of $NaBH_4$ to aqueous solutions of Fe(II) salts (*e.g.* $FeSO_4 \cdot 7H_2O$) in the presence of phen (1:3) gives the same product. Alternatively, the Fe(II) complex, $Fephen_3Cl_2$, can be used as the starting material. Reduction also occurs when a 10 molar excess of $NaBH_4$ is added to a Fe^{3+}/phen (1:3) mixture in ethanol solution but in this case, the yield of the product is low. As in the reduction of Ni(II), the ratio of the reactants plays an important role in determining the extent of the reduction and, for example, when a 1:6:10 molar ratio of Fe^{2+}:phen:$NaBH_4$ is used, no reduction apparently occurs as indicated by the absence of any colour change in the reaction vessel. However, when a very large excess of $NaBH_4$ is used, sufficient to give a Fe^{2+}:phen:$NaBH_4$ molar ratio of 1:6:20, reduction takes place and $Fephen_2BH_4 \cdot H_2O$ is produced.

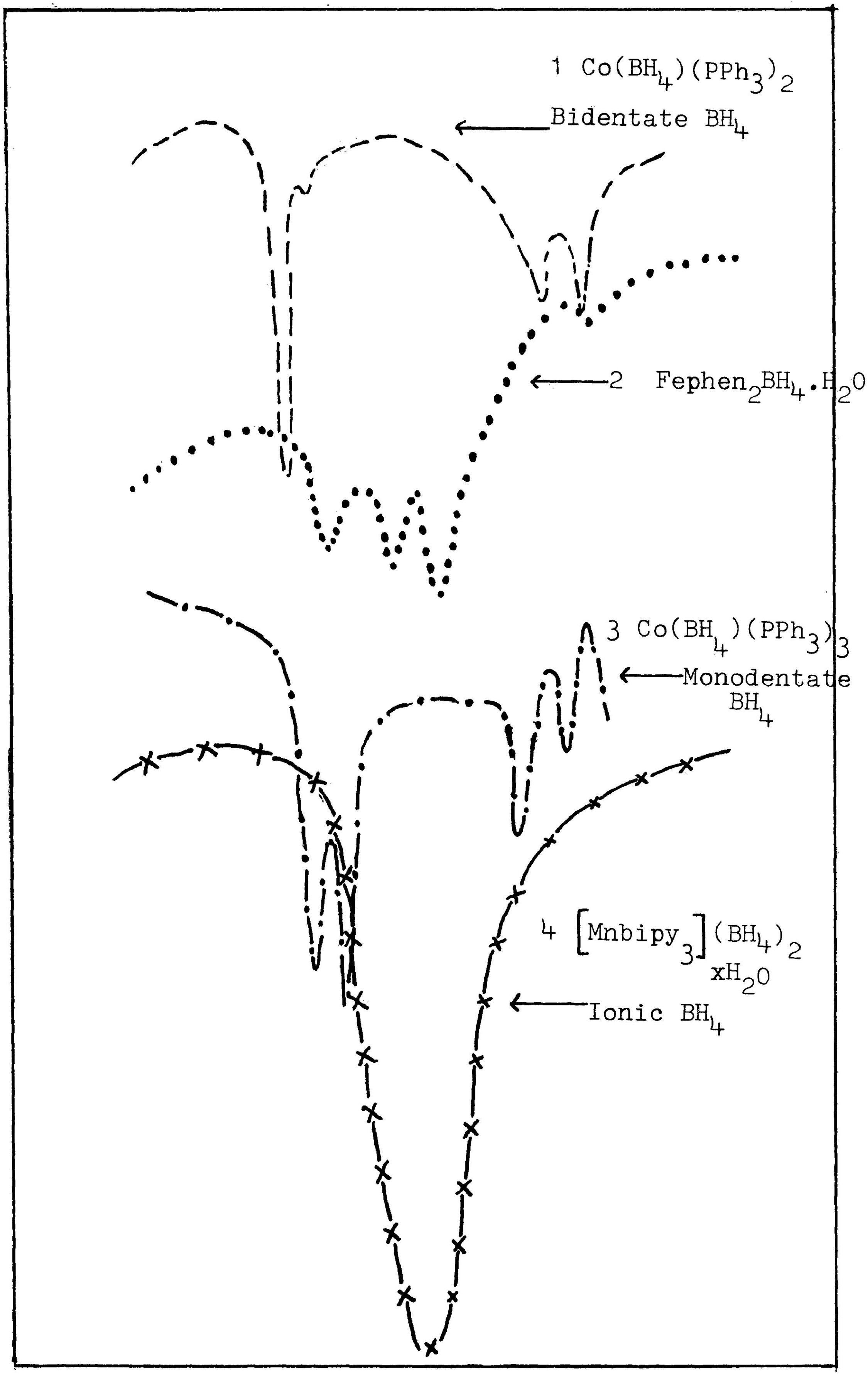
The dark-coloured complex, $Fephen_2BH_4 \cdot H_2O$, is insoluble in ether, hexane and benzene, is slowly oxidized by water, is sparingly soluble in ethanol and is soluble in DMSO, although all attempts at recrystallization resulted in the loss of the BH_4 group. Purification of the compound therefore had to be effected by successive washings with benzene and ether. The magnetic moment in the solid state is 2.2 B.M. indicating an iron(I), d^7 low spin system. This value of the magnetic moment is not only consistent with the presence of one unpaired electron, but also rules out the possibility that the complex should be formulated as an Fe(II) complex, such as $FeH(BH_4)phen_2$, since most of the bis(phenanthroline) complexes of Fe(II), e.g. $Fephen_2Cl_2$, $Fephen_2Br_2$, are high spin with four unpaired electrons. Only when stronger ligands such as CN^- are incorporated, as in $Fephen_2(CN)_2$ does the iron become diamagnetic (132).

The magnetic moment of 2.2 B.M. for $Fephen_2.BH_4.H_2O$ are also reproducible which tends to rule out the possibility that the paramagnetism is due to traces of boride or metal impurities (see also page 92).

The ir spectrum of the complex shows weak absorptions at 1080 and at 1975 sh, 2220, 2290 and 2380 cm^{-1} which can be assigned to the deformation and stretching frequencies of the BH_4 grouping respectively. This spectrum, in the B-H stretching region is shown in Fig. 2 and, for comparison, spectra are shown where the BH_4 group is monodentate, bidentate and ionic. It is clear that on the basis of the ir data the BH_4 group in this complex cannot be accurately described in terms of any of these coordination modes and, like $Niphen_2BH_4.H_2O$, the spectrum of which is very similar, the best that can be said is that the spectrum probably indicates some form of unspecified weakly interacting BH_4 group.

Bands at 1635 cm^{-1} and a broad band centred at 3400 cm^{-1} can be assigned to the bending and stretching frequencies of water respectively although whether the water is coordinated or not is not clear since the spectra of this and other hydrated metal complexes described in this thesis are poorly resolved. This point is discussed in the appendix concerning infrared spectral data.

Figure 2. Infrared spectrum of some BH_4 complexes in the BH_4 stretching frequency region



The electronic spectra of this compound are shown in Figures 3 and 4 and will be discussed shortly. The electrical conductivity (Table 6) of a freshly prepared DMSO solution ($\sim 10^{-3}$M) gave a value of 7.6 which is considerably lower than that expected for a 1:1 electrolyte. Whether this is due to partial dissociation or decomposition is not clear and this will be considered again later.

The BH_4 group can be replaced in this complex and this has led to the isolation of additional Fe(I) species. Thus, when $NaPF_6$ or $NaBPh_4$ are stirred for about 10 hours with an alcoholic suspension of $Fephen_2BH_4 \cdot H_2O$, complexes of formula $Fephen_2X$ ($X=PF_6$ or BPh_4) are obtained, although similar reactions in aqueous media lead to oxidized products. Also, when a 10 molar excess of sodium tetrahydroborate, suspended in ethanol or even in the solid state, is added to an alcoholic solution of Fe^{2+} or Fe^{3+} and phen, in the ratio of 1:3, the characteristic red colour of $[Fephen_3]^{2+}$ changes to dark violet, and upon addition of the large anions, the same compounds $Fephen_2X$ ($X=PF_6$ or BPh_4) are obtained. Finally these complexes are obtained when a 5 molar excess of $NaBH_4$, in the solid state or suspended in ethanol, is added to an alcoholic solution of Fe^{2+} or Fe^{3+}/phen in the ratio of 1:2.

The violet coloured complexes $Fephen_2X$ ($X=PF_6$, BPh_4)

Figure 3 Reflectance spectra of the iron-phen complexes.

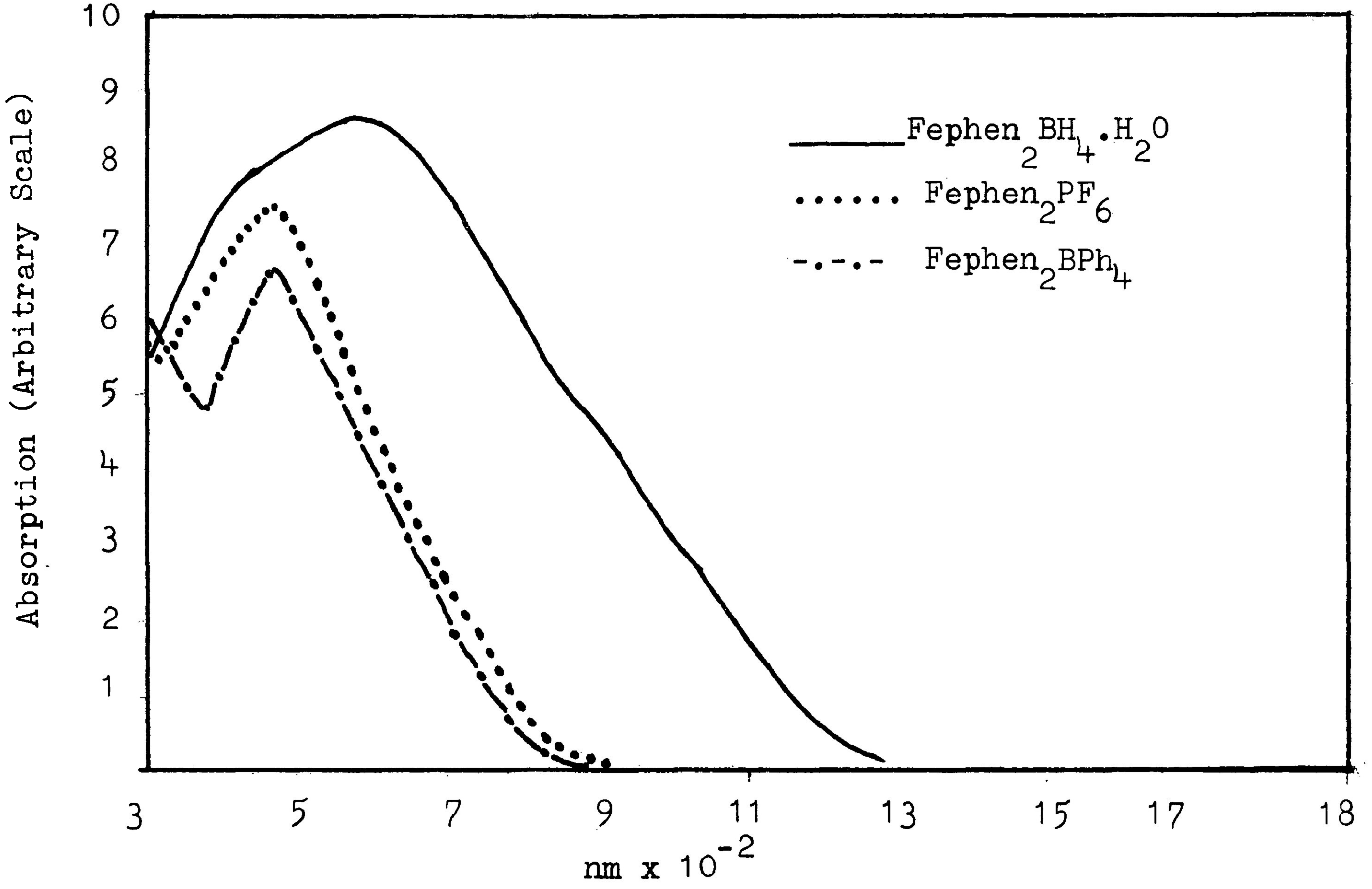
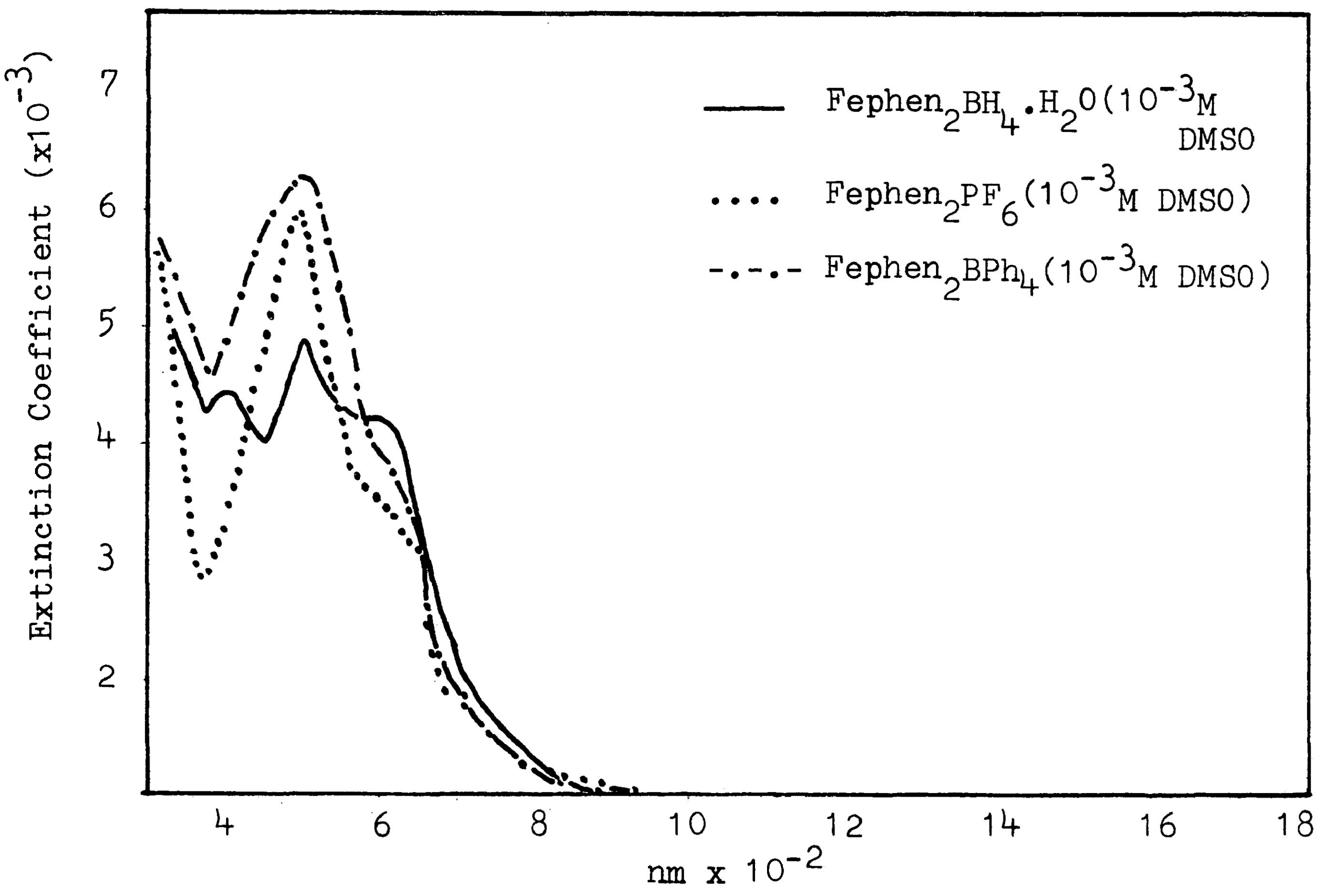


Figure 4 Solution spectra of the iron-phen complexes.



are very air sensitive, but are more stable in solution than the BH_4 complex and can be recrystallized from acetone/alcohol. These Fe(I) complexes are insoluble in water, alcohol and ether and are soluble in acetone and DMSO. Unlike the Ni(I) system, where one form, α-$Niphen_2PF_6$ is converted into a second form, β-$Niphen_2PF_6$ on recrystallization, the corresponding Fe(I) complex is unchanged on recrystallization. Even after recrystallization, totally satisfactory chemical analyses on the BPh_4 complex could not be obtained, although the following physical properties leave little doubt that the complex is as formulated.

The ir spectra show no absorptions in the region of 1650 to 2400 cm^{-1}, and this rules out the possibility that the complexes contain hydride or tetrahydroborate groupings. A very intense band in the PF_6^- complex at 850 cm^{-1} is due to the presence of the PF_6 grouping.

Reproducible magnetic moments (Table 6) of the two complexes are 1.9 B.M.(PF_6) and 2.1 B.M. (BPh_4), again indicating that the Fe(I) is in the low spin configuration. In 10^{-3}M DMSO solution the electrical conductance (Table 6) indicates that the complexes are 1:1 electrolytes so that presumably in solution, the complexes exist as the 4-coordinate $[Fephen_2]^+$ species, assuming no DMSO interaction.

Electronic spectral data for these Fe(I) complexes are shown in Figures 3 and 4 and in Table 6 and a number of points must be made regarding these spectra. The solution and reflectance spectra (Figures3 and 4) of the

Table 6. Some physical properties of the iron complexes.

Compound	Electronic spectra * cm^{-1}	μ eff B. M.	Conductivity of 10^{-3}M DMSO solution at 25° C ** Ohm^{-1} Cm^{2}mole^{-1}
Fephen$_2$BH$_4$.H$_2$0	Solid: ~16600 (v.b) Solution: 16400 (4.0x10^3),19500(4.7x10^3) 25000 (4.2x10^3)	2.2	7.6
Fephen$_2$PF$_6$	Solid: ~ 22200 vb Solution: 16300 (3.2x10^3), 19600(6.1x10^3)	1.9	27.7
Fephen$_2$BPh$_4$	Solid: 22200 vb Solution: 16000 (3.0x10^3), 19600(6.2x10^3)	2.1	29.2
[Febipy$_3$](BH$_4$)$_2$ .6H$_2$0	Solid: 18180 Solution: 18200(~3.5x10^3),	2.5-5.6	68.01
[Febipy$_3$](PF$_6$)$_2$	Solid: 18200 Solution: 18200 (~3.9x10^3)	Diamagnetic	70.1

* Molar Extinction coefficients in parentheses: All solution spectra were measured in 10^{-3}M DMSO Solution.

** For reference electrolytes, see Table 8.

[Fephen$_2$]X (X=PF$_6$,BPh$_4$) are very similar, considering the general observation that spectra measured in the solid state are less well resolved than when measured in solution. However, the solid state and solution spectra of Fephen$_2$BH$_4$·H$_2$O are significantly different, the solution spectrum showing, with the exception of an additional peak at $\sim$25000 cm^{-1}, marked similarities with the solution spectra of [Fephen$_2$]X (X=PF$_6$,BPh$_4$). It is tempting to suggest that all three solution spectra are characteristic of the [Fephen$_2$]$^+$ species but if this is the case, it is difficult to account for the very low value of the conductivity of the Fephen$_2$BH$_4$·H$_2$O complex in the same concentration range as used for the spectroscopic determination. Exactly what happens to this compound in solution is not clear, except that it should be stressed that it cannot be recovered from DMSO solution. One additional point about the spectra is the very high values of the extinction coefficients. If these bands are d-d in origin, they clearly cannot arise from a centrosymmetric molecule but, considering ϵ values of 6000, the transitions are probably charge-transfer in origin.

It is relevant here to point out that most of the low valent metal complexes of bipy and phen are intensely coloured and it has been suggested (135) that symmetry allowed transitions of the type $t_{2g} \rightarrow \pi^*$ are responsible for the intense colours. If the BH_4 group in $Fephen_2BH_4 \cdot H_2O$ is coordinated, then it is interesting to compare the observed spectra with those of other low spin, 5-coordinated d^7 systems. For example, the spectrum of the Co(II) complex $[Co(NP_3)I]I$ ($NP_3 = N(CH_2 \cdot CH_2 \cdot PPh_2)_3$ has bands at 6700 and 10600 cm^{-1} (160) quite different from those observed here in the Fe(I) complexes. There are no examples of low spin tetrahedral d^7 systems known but low spin square planar complexes are known and the spectrum of such a complex, $[Coen_2](AgI_2)_2$, shows only a shoulder at 22700 cm^{-1} (161). The presence of the intense band in this region in the spectra of $[Fephen_2]^+$ would obscure such a d-d band if present.

While these spectra do not give evidence for a specific geometry nor indeed for the iron(I) formulation, they are useful in providing further evidence against the Fe(II) hydride possibility. For example, the spectrum of the high spin

$Fephen_2Cl_2$ has d-d bands at 8470 and 10510 cm^{-1} and change transfer bands at 16670 and 18700 cm^{-1} (162), and the diamagnetic $Fephen_2(CN)_2$ complex has a d-d band at 12500 cm^{-1} and change transfer bands at 16670, 17850, 18850 and 27000 cm^{-1}. Again, these are quite different from the spectrum of $Fephen_2BH_4{\cdot}H_2O$.

Thus, while it is therefore very difficult to draw any definite conclusion about the geometry of these Fe(I) complexes on the basis of the spectroscopic results alone, when taken with other physical data, i.e. conductivity, magnetic moments and elemental analyses, it does appear reasonable that the $Fephen_2X$ ($X=PF_6$, BPh_4) complexes contain the four coordinated $[Fephen_2]^+$ moiety. Since it would be most unlikely for a 4-coordinated tetrahedral structure to be low spin, the most reasonable geometry for these complexes appears to be square-planar.

A structural assignment for $Fephen_2BH_4{\cdot}H_2O$ is more difficult. The ir data suggest that, at least in the solid state, the BH_4 group is weakly coordinated and, for that matter, the water molecule could also occupy a coordination site of the iron. There are electronic spectral changes in going from the solid state to solution and the latter has a low conductivity, which may or may not be reliable given the fact that the complex is decomposed in DMSO, although both the conductivity and solution spectrum are reproducible. However, it is known that low spin square planar complexes, $[ML_2]^{2+}$ where L is a bidentate ligand, can form five and six coordinate species in non aqueous solvents as follows:

$$[ML_2]X_2 \rightleftharpoons [ML_2X]X \rightleftharpoons [ML_2X_2]$$

For example, on the basis of electrical conductivity and spectrophotometric results in nitromethane solutions, the following equilibria have been proposed (163) for the behaviour in solution of $[Pdbipy_2]X_2$ (X=Cl,Br or I)

$$[Pdbipy_2]X_2 \rightleftharpoons [Pdbipy_2\ X]X \rightleftharpoons [Pdbipy_2X_2]$$

It is possible, therefore, that similar equilibria are established in DMSO solutions of the BH_4 complex,

$$[Fephen_2]BH_4 \rightleftharpoons Fephen_2BH_4$$

and this may account for the spectroscopic changes and the low conductivity value.

It therefore seems most likely that in the solid state $Fephen_2BH_4.H_2O$ is 5-coordinated (with lattice water). If the water molecule occupies a sixth coordination site making the iron octahedral, then the molecule would be expected to be high spin like the $\mathrm{Fephen_2Cl_2}$ species. It appears that, in solution at least, partial dissociation to $[\mathrm{Fephen_2}]^+$ occurs.

In view of the preceding discussion on the reduction by $\mathrm{NaBH_4}$ of Fe(II) and Fe(III) in the presence of phen, it was surprising to find that all attempts to reduce mixtures of $\mathrm{Fe^{2+}}$ and bipy with $\mathrm{NaBH_4}$ in aqueous solutions were unsuccessful. Thus, the addition of a large excess of $\mathrm{NaBH_4}$ ($\sim$10M) to either $[\mathrm{Febipy_3}]\mathrm{Cl_2}$ or $\mathrm{Fe^{3+}}$/bipy in a molar ratio of 1:3, gives the characteristic redish colour of the iron(II) complex, $[\mathrm{Febipy_3}](\mathrm{BH_4})_2\cdot 6\mathrm{H_2O}$. Surprisingly, no reduction was observed even when a large excess of $\mathrm{NaBH_4}$ ($\sim$20M) was added to an aqueous solution of $\mathrm{Fe^{2+}}$ and bipy (1:2 molar ratio) in reactions where the time was varied between $\frac{1}{2}$ hour and 20 hours. Changes in the molar ratios of M:L:$\mathrm{BH_4}$ from 1:2:10 to 1:6:20 also failed to produce any reduced species. However, in those reactions where large amounts ($\sim$20M) of $\mathrm{NaBH_4}$ were used, or where long reaction times ($>$3 hours) were involved, varying amounts of black precipitates were obtained. These precipitates are insoluble in water, ethanol and benzene but react with dilute acids and are almost certainly metal borides. Because of the occurrence of these metal borides from room temperature reactions, the reduction of Fe(II) by $NaBH_4$ in the presence of bipy was not attempted at higher temperatures since these would obviously lead to more boride production.

Similar reactions of Fe(II), bipy and $NaBH_4$ were studied in alcoholic solutions. Thus, the deep red colour of an alcoholic solution containing a 1:3 molar ratio of Fe(II) to bipy remained unchanged even when a 10 molar excess of $NaBH_4$ was added. No reduced species were obtained when the molar ratios of reactants were varied from 1:2:10 to 1:6:20 or when reaction times were varied from ½ hour to 48 hours.

The dark red coloured complex, $[Febipy_3](BH_4)_2 \cdot 6H_2O$ is air stable and insoluble in benzene, ether and hexane. As with other tetrahydroborate complexes, attempts to recrystallize the compound from organic solvents such as DMSO or nitromethane resulted in the loss of the BH_4 group. Again, therefore, purification of the complex was effected by repeated washings with water, benzene and ether. The ir spectrum shows bands typical of ionic BH_4

groups with maxima at 1075 cm^{-1} and a very broad band at 2250 cm^{-1} which are assigned as the B-H deformation and stretching modes respectively (see Fig. 2 for representative spectra).
As expected (Table 6), the complex is a 1:2 electrolyte in a freshly prepared DMSO solution. However, magnetic moment measurements gave extremely variable results with values ranging from 2.5 B.M. to a maximum on one sample of 5.6 B.M. These variations are almost certainly due to the presence of trace amounts of the ferromagnetic boride (or metal) and contamination of the reduced metal -BH_4 complex by such species, which affect only magnetic properties and not, for example, chemical analyses, has been observed a number of times in these laboratories.

When $NaPF_6$ is added to an ethanolic suspension of $[Febipy_3](BH_4)_2.6H_2O$, a complex which analyses well for $[Febipy_3](PF_6)_2$ results. The red coloured complex is air stable, soluble in acetone, slightly soluble in DMSO, but insoluble in ethanol, benzene, water and ether. As expected, the electrical conductivity (Table 6) indicates that the complex is a 1:2 electrolyte. The complex is diamagnetic (Table 6) as is typical of other tris(bipyridyl)iron(II) complexes (132) and this is strong evidence that the paramagnetism in the analogous BH_4 complex is indeed due to boride impurities.

Thus in contrast to the reduction by $NaBH_4$ of M/bipy systems ($M=Co^{2+}$(144), Ni^{2+}(105)) to univalent complexes and the reduction of Fe^{2+}/bipy by other methods, such as polarography (164), mixtures of Fe^{2+} and bipy cannot apparently be reduced by $NaBH_4$ in spite of the fact that $[Fephen_3]^{2+}$ and $[Febipy_3]^{2+}$ have almost the same redox potential. One possible explanation for the fact that Fe(I)-phen but not Fe(I)-bipy complexes can be made from sodiumtetrahydroborate reduction may be associated with the reactions

$$[Febipy_3]^{2+} \longrightarrow [Febipy_3]^{+} \longrightarrow [Febipy_2]^{+} + bipy$$

followed by the reoxidation of

$[Febipy_2]^{+}$ to $[Febipy_3]^{2+}$-probably by water.

The greater instability of the M-bipy system (compared with that of M-phen) has already been reported for Ni(I) (105) and has also been observed for other metals (to be discussed later).

The greater stability of the M-phen systems has been attributed to the greater resonance possibilities of the highly conjugated ring system derived from phen (201 and 156).

It has been shown that $NaBH_4$ reduces Fe(II) and (III) in the presence of phen and a number of iron (I) complexes have been characterized. At this point it is appropriate to stress the importance and significance of this work since iron(I) is an extremely uncommon oxidation state and there are very few genuine complexes known, even though considerable effort has been made to synthesize and study such species.

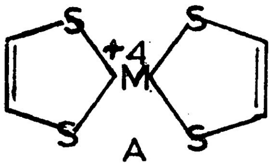
For example, compounds alleged to contain Fe(I) have been the subject of chemical and spectroscopic studies since 1940 (168). A number of these studies have involved ligands such as NO, with the inherent difficulty of deciding whether this behaves as NO^+, NO^- or neutral NO which in turn makes it difficult to assign formally an oxidation state to the metal ion involved. Thus, complexes of formula $Fe(NO)_{1 or 2}L_n$,(L is an anionic ligand, e.g. phosphate, arsenate, molybdate, benzoate) have been prepared by McDonald and coworkers (169). These complexes are paramagnetic and it is reported from esr studies that the formal oxidation state of iron in all of these species appears to be Fe(I). Considerable attention has also been paid to the species formed by the reduction of sodium nitroprusside, $Na_2[Fe(CN)_5NO]$ (generally considered to be best described in terms of neutral NO and Fe(III) (170)), by either chemical, electrical or γ irradiation methods, and in all cases the same paramagnetic species, $[Fe(CN)_5NO]^{3-}$, is produced (171a, b,c). In related work, the reduction of methanol solutions of $Na_2[Fe(CN)_5NO]$ with metallic sodium gives rise to the formation of $Na_5[Fe(CN)_5NO_2]$ and $Na_4[Fe(CN)_5NO(OCH_3)]$. All of these reduction products of the $[Fe(CN)_5NO]^{2-}$ ion are paramagnetic, the magnetic moments corresponding to one unpaired electron (171a, b,c).

The esr spectra have been recorded for $[Fe(NO)(H_2O)_5]$ in sodium sulphide and sodium hydroxide solution (172) and for $[Fe(CN)_5NO]^{3-}$ prepared by reductions by sodium dithionate and sodium sulphied (173). In all cases it is claimed that the iron occurs as a d^7 ion with the unpaired electron largely localized on the iron (172, 173).

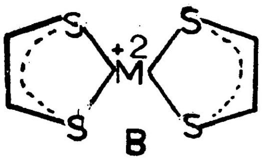
In contrast to the above studies there are reports which claim that the unpaired electron in the $[Fe(CN)_5NO]^{3-}$ system is mainly localized on the π^* orbital of NO. For example, from a detailed esr study of the above species, prepared from the reduction of $[Fe(CN)_5NO]^{2-}$ by RS^-(R is alkyl or H), $S_2O_4^{2-}$ or BH_4^- in aqueous, nonaqueous and aprotic solutions at different pH values, Van Voorst et al. (174) concluded that the unpaired electron is almost entirely localized on the nitrosyl ligand. Similar results have been reported by others (175), and in the molecular orbital scheme proposed by Fetham (170), for complexes of the type $[FeL_5NO]^z$ (L= variety of ligands), the unpaired electron is also localized on the NO molecule. If this is the case, then clearly the iron in $[Fe(CN)_5NO]^{3-}$ is best described in terms of Fe(II) rather than Fe(I).

Additional Fe-NO complexes have been obtained from iron complexes of 1,2- and 1,1-dithiolates. In general, the iron 1,2-dithiolate systems $[Fe(S_2C_2R_2)_2]^z$ (z = 0, R = Ph and z = -2, R=CN) and $[Fe(TDT)_2]^{2-}$ (TDT = toluene-3,4-dithiol), readily absorb NO in solution, and crystalline solids such as $[Fe(NO)(TDT)_2]^{2-}$ and $[Fe(NO)(S_2C_2Ph_2)_2]$ have been reported (176). These and several other five-coordinated nitrosyl complexes, such as $Fe(NO)(S_2CNMe_2)_2$ (177) are claimed to be best represented as containing Fe(I). Thus it is reported that results of an esr study of the $Fe(NO)(S_2CNMe_2)_2$ complex are best accommodated by considering the unpaired electron to be in the iron d_{z^2} orbital <u>i.e.</u> the NO is represented by NO^+ (177). On the other hand, Gibson (178) from an esr study of the same $Fe(NO)(S_2CNMe_2)_2$ complex, concluded that the unpaired electron is localized on <u>NO</u> so that again there is doubt as to the formulation of these complexes as formally containing Fe(I).

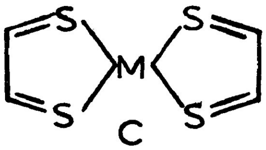
Gray <u>et al.</u>(179) claimed the formation of the first high spin Fe(I) complex from the reaction between Fe(II) and toluene-3-4-dithiol (TDT) which gives the paramagnetic (μ=4.38 B.M.) complex, $[Fe(TDT)_2]$. It was proposed that the complex is planar and consists of Fe^+ with two ligand radical anions whose unpaired electrons are paired in the molecule. However, like the nitrosyl complexes, it is difficult to assign a definite formal oxidation state to metal ions in certain dithiolate complexes because it is possible to represent these structures in different ways as shown below.



A

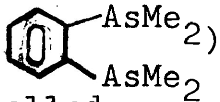


B



C

Thus, in the planar complex $MS_4C_4R_4$, M could be in the oxidation states + IV, + II or 0, as shown in formulas A, B and C with C being the least probable. It has been concluded from esr studies on various dithiolate systems (180) that the electronic charge is largely (75%) localized on the ligand in all cases studied. Thus, on the basis of these observations, the idea that $[Fe(TDT)_2]^-$ contains Fe(I) could reasonably be challenged.

Iron(I) complexes appear to be better characterized in carbonyl containing species. For example, $Fe(CO)_2I$ has been obtained by heating $Fe(CO)_4I_2$ in carbon monoxide, although its purity was poor owing to its instability (168). $Fe(CO)_2$(di-arsine)I, (di-arsine = ) has been isolated under carefully controlled conditions from the treatment of one equivalent of iodine with $Fe(CO)_3$(di-arsine). The compound is a nonelectrolyte in nitrobenzene and has a magnetic moment of 2.1 B.M. (175). Cotton et al. (182) obtained $Fe_2(CO)_8I_2$, by the reaction of iodine with $Fe_3(CO)_{12}$, as a white crystalline solid which melts at -5°C to a red liquid. The compound is air sensitive, diamagnetic and soluble in a variety of organic solvents to give pale red solutions, the red coloration being attributed to the formation of $Fe(CO)_4I$ by reversible dissociation of $Fe_2(CO)_8I_2$.

Iron pentacarbonyl reacts with cyclopentadiene at 135°C in an autoclave to give the binuclear complex, $[(\pi C_5H_5)Fe(CO)_2]_2$ as reddish-purple diamagnetic crystals which are air stable (183).

Perhaps the work which is most significant in terms of the results presented here is the recent report by Sacco and coworkers (184a, b) of the isolation of hydrido and chloro complexes of Fe(I). Reduction of $[FeHClL_2]$ or $[FeHL_2][BPh_4]$ ($L=Ph_2P.CH_2.CH_2.PPh_2$) with powdered sodium metal (1:1 molar ratio) in toluene or benzene under a nitrogen atmosphere at room temperature gives red, crystalline $FeHL_2$. The compound is stable in air for some hours, soluble in non-polar solvents (e.g. benzene and toluene) and insoluble in pentane and ethanol. The ir spectrum of the compound has a band at 1790(VS) cm^{-1} which has been assigned as the Fe-H mode. Furthermore, the compound is paramagnetic (μ = 1.8 B.M.), both in the solid state and in solution. The analogous compound $FeClL_2$ has been isolated from the reaction of $FeCl_2L$ with the stoichiometric amount of sodium in the presence of the ligand. This red chloro complex is unstable in air, soluble in non-polar organic solvents and is paramagnetic (μ = 2.11 B. M.).

Finally, it should be mentioned that, as in the case of metal complexes of NO and sulphur donor ligands, problems in the assignment of metal oxidation states also exist for bipy and phen systems, especially for zero valent complexes. For example, in a recent study (185), it was concluded, on the basis of ir spectra, that the ligand is negatively charged in the $Crbipy_3$ complex and that Cr exists as Cr(III). If this is the case here, namely that the ligand is behaving as a radical anion $L^{\bar{\cdot}}$, then in for example, $FeL_2BH_4.H_2O$, the formal oxidation of iron would be Fe(III), an unreasonable situation considering that in most reactions, the complex is made from an iron(II) starting material in the presence of a large excess of $NaBH_4$ under a nitrogen atmosphere. However, the neutral nature of the ligands, bipy and phen, is <u>generally accepted</u> (131). Thus, considering phen as a neutral ligand, we can speculate that $Fephen_2PF_6$, and most probably $Fephen_2.BH_4.H_2O$ also, are complexes containing iron in a formal oxidation state of +1.

C. Ruthenium.

In view of the success achieved in isolating and characterizing the Fe(I) complexes which have already been described, it was considered important to extend the study to similar reactions on ruthenium. While ruthenium(II) and (III) form a large variety of complexes with en, bipy and phen (186), the Ru(I) state is very poorly characterized and it seemed reasonable that reductions by $NaBH_4$ of Ru(III) and Ru(II) in the presence of the N-donor ligands may lead to the formation of Ru(I) complexes.

Thus, when a 10 molar excess of an aqueous solution of $NaBH_4$ is added to a mixture of $RuCl_3$ and phen (1:3 molar ratio) in water a dark coloured complex is obtained which analyses well for $Ruphen_2BH_4.1.5H_2O$. Also when a 10 molar excess of $NaBH_4$ is added to a concentrated aqueous solution of $[Ruphen_3]Cl_2$, the characteristic orange-red colour of the latter disappears slowly and the same dark coloured reduced Ru complex is precipitated after 2 hours stirring. However, better yields are obtained when a mixture of $[Ruphen_3]Cl_2$, phen and $NaBH_4$ in the molar ratio of 1:1:15 in water is stirred for 10 hours or when a 15 fold molar excess of $NaBH_4$ is added to a mixture of $RuCl_3$ and phen in the ratio of 1:4. It is important to note that the use of less than a 10 molar excess of $NaBH_4$ in these reactions leads to a marked reduction in yields.

It therefore appears that, as with Ni and Fe, a Ru(I) complex has been isolated and, in view of the extreme rarity of such complexes, it is even more surprising to note that the same complex, $Ruphen_2BH_4 \cdot 1{\cdot}5H_2O$ is air stable and can be prepared from the above reactions in air. The complex is insoluble in hexane, benzene and ether and slightly soluble in alcohol and DMSO, although like other tetrahydroborate complexes, the BH_4^- group is lost on recrystallization. The ir spectrum (Table 7) is illustrated in Fig. 5 and is extremely similar to those of the analogous Fe and Ni complexes, although the resolution is poor, suggesting the presence of a weakly interacting BH_4^- group. A band at $\sim 1640\ cm^{-1}$ and a broad absorption centred at $\sim 3400\ cm^{-1}$ are due to the presence of water.

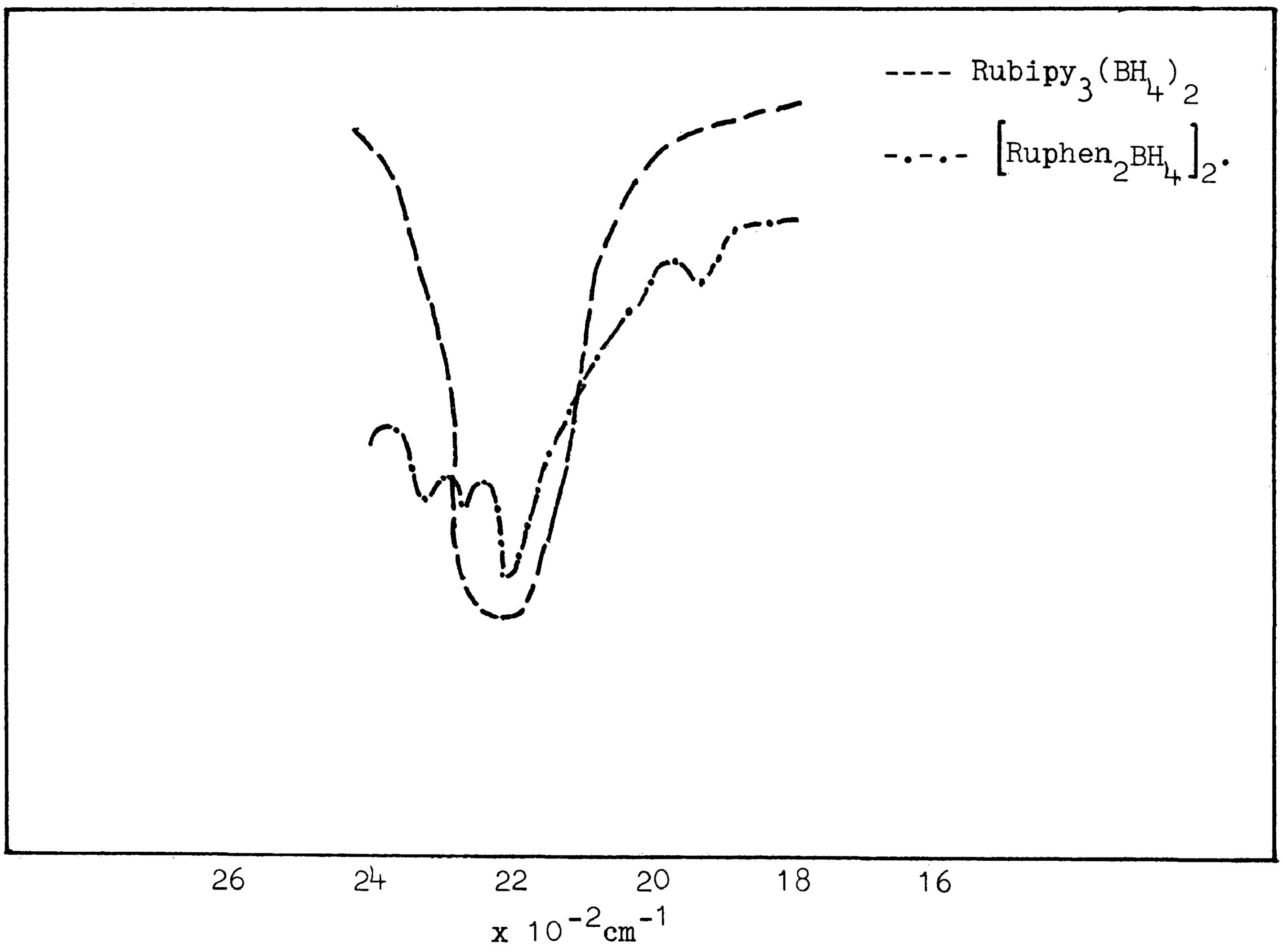
Table 7. Some physical properties of the ruthenium complexes.

Compound	Electronic spectra* cm^{-1}	ir absorptions due to BH_4 group cm^{-1}	μeff B. M.	Conductivity** of 10^{-3} solution at 25°C $Ohm^{-1} cm^2 mole^{-1}$
$[Ruphen_2BH_4]_2 3H_2O$	Solid: 22200(v.b) Solution: 22200 ($6.0x10^3$)	1080,1950(Sh), 222(M) 2290(W),2350(W)	Diamagnetic in solid state and in solution	14 (DMSO)
$[Ruphen_2]_2(PF_6)_2$	Solid: 22200(v.b) Solution: 22200($5.6x10^3$)		Diamagnetic in solid state and in solution	64.8 (DMSO) 210 (Acetone).
$[Rubipy_3](BH_4).5H_2O$	Solid: 22000(v.b) 17000(Sh) Solution: 22000($4.8x10^3$) 16500 Sh($2x10^3$).	1085,2220 (v.b)	Diamagnetic	56.9 (DMSO)

* Molar extinction Coefficients in parentheses, solution spectra in 10^{-3} DMSO Solution

** For reference electrolytes, see Table 8.

<u>Figure 5.</u> <u>I. R. Spectra of Ru complexes in the BH_4 stretching frequency region.</u>



When the above reactions are carried out in alcohol, reduction again takes place but most of the product stays in solution. For example, when a 10 molar excess of $NaBH_4$, suspended in ethanol, is added dropwise to a stirred alcoholic mixture of $RuCl_3.3H_2O$/phen in the molar ratio of 1:3 a violet coloured solution is produced within 1 hour and a violet solid shown to be $Ruphen_2PF_6$ precipitates from solution on addition of $NaPF_6$. Unlike reactions in aqueous media, the same product is obtained even when only a 5 molar excess of $NaBH_4$, suspended in ethanol, is added to a mixture of $RuCl_3.3H_2O$ and phen (in the ratio of 1:3) in alcohol. The ligand concentration at least between the limits Ru:phen of 1:3 to 1:6 has no effect on the nature of the product or on the rate of reaction. The complex $Ruphen_2PF_6$ like the analogous BH_4 complex, is air stable, insoluble in water, alcohol, benzene and ether and soluble in acetone and DMSO. Like its Fe(I) analogue it can easily be recrystallized from acetone/alcohol.

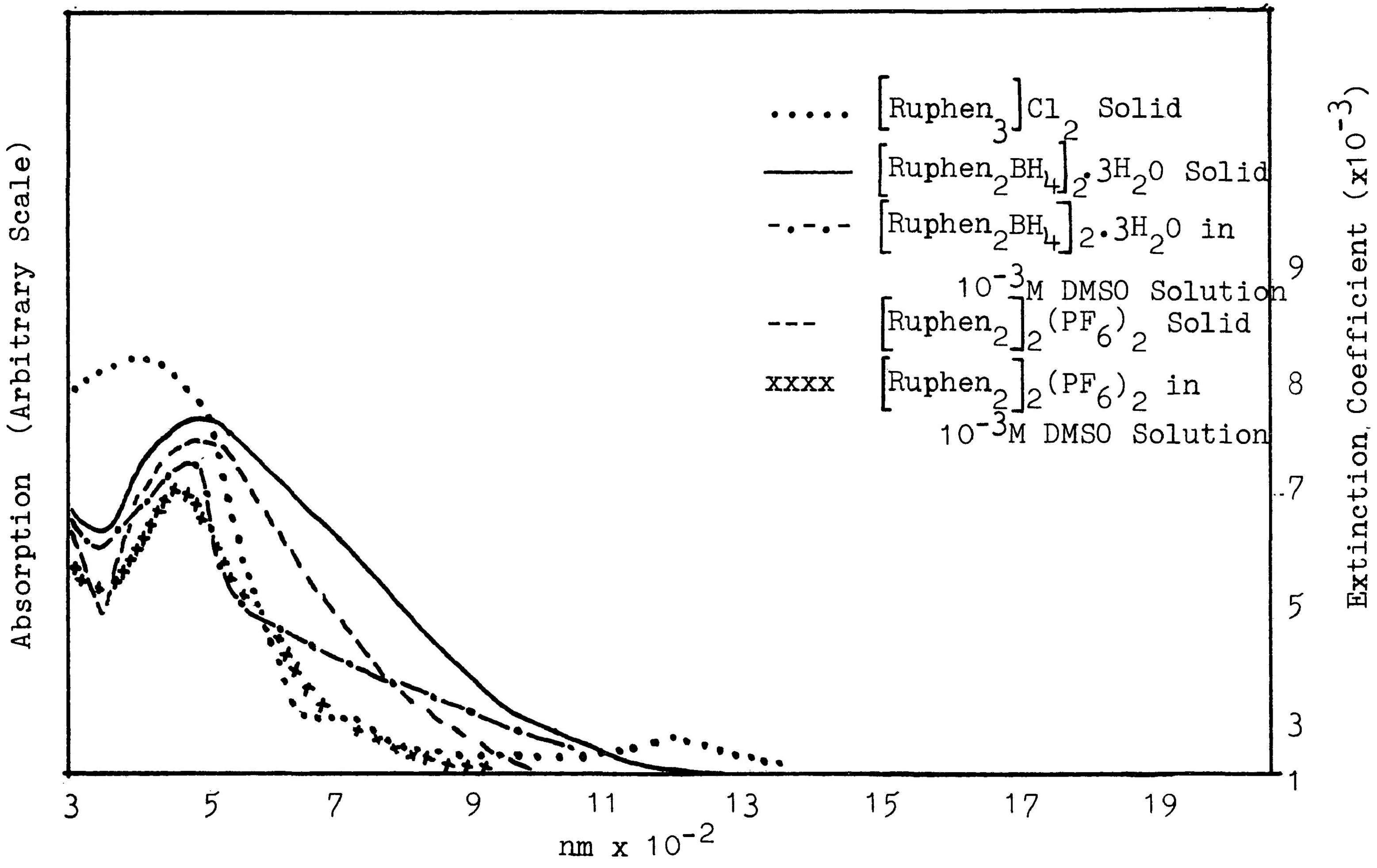
The ir spectrum, tabulated on page 160, is similar to that of the corresponding iron complex. In particular, it shows no absorption from 1650 to 2400 cm^{-1}, and has a very intense band at 850 cm^{-1} due to the presence of the PF_6 grouping.

Both the BH_4^- and PF_6^- complexes are diamagnetic in the solid state and in DMSO solution. These data can only be rationalized if the two complexes exist as dimers such that the unpaired electrons on the d^7, Ru(I) ions are paired. Alternatively the complexes may be formulated as hydrido-Ru(II) species, such as $HRu(BH_4)phen_2$ in which case the expected chemical analysis would remain essentially unchanged and the diamagnetism would be as expected for a low spin d^6 configuration. However, such a possibility is considered unlikely in view of the absence of any evidence for the presence of a hydride ion in the complex. Further arguments against such a possibility have been discussed (88) in the case of Ni-phosphine-BH_4 complexes, and the same arguments are considered to be valid here.

Electronic reflectance and solution spectra of the BH_4 and PF_6 complexes are shown in Fig. 6 and the maxima recorded in Table 7. It is clear that the four spectra are very similar with a high intensity band in the 20-25000 cm^{-1} region. This is unlikely to be associated with a d-d transition and in fact is quite similar in position to the band in the Ru(II) complex $[Ruphen_3]Cl_2$, the spectrum of which is also shown in Fig. 6. Thus the band is assigned to a charge transfer transition involving metal d and ligand π^* orbitals, and little can be said about the stereochemistry of the metal ions from these data.

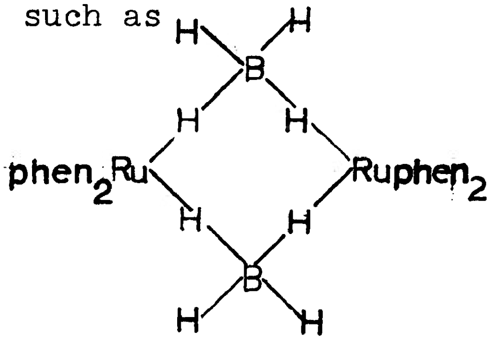
Table 7 reveals the only difference observed

Figure 6 Electronic spectra of the ruthenium-phen complexes



in the properties of the BH_4^- and PF_6^- complexes, namely the electrical conductivity. That of the PF_6^- complex is reasonably accounted for on the basis of the 1:2 electrolyte $[\text{phen}_2\text{Ru-Ruphen}_2]^{2+} (PF_6)_2^{2-}$ in both acetone and DMSO solutions, consistent with the diamagnetic nature of the complex.

The conductivity of the BH_4^- complex is much lower but is reproducible in freshly prepared DMSO solutions. Considering the fact that decomposition occurs in DMSO the question again arises as to the validity of this result for structural diagnostic purposes. It may indicate that the complex should be formulated as a non electrolyte with coordinated BH_4 groups, such as



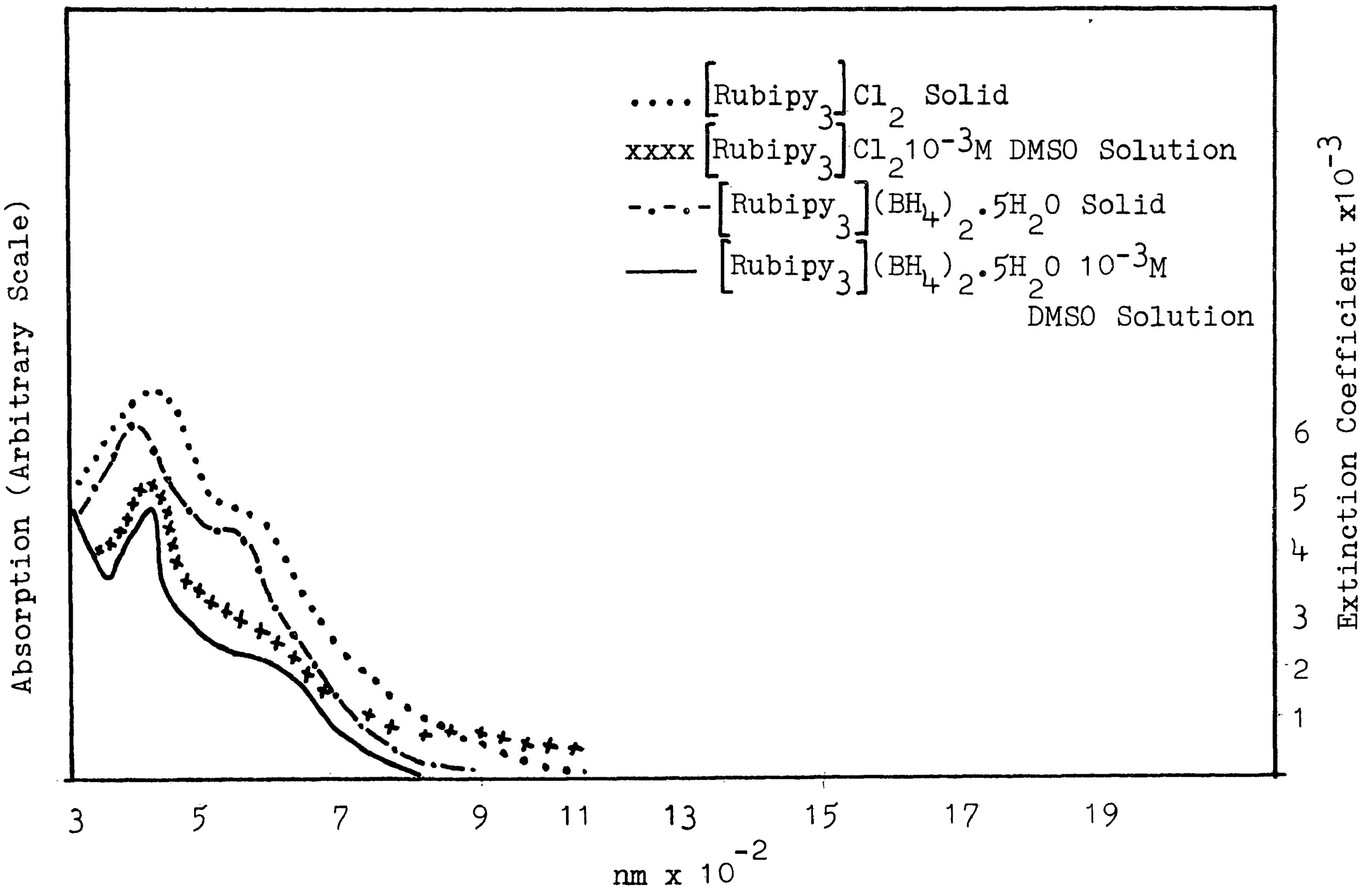
or it may simply reflect the decomposition which occurs in solution.

It is not surprising in view of the results obtained for the iron systems and also in view of the extraordinary inertness of $[\text{Rubipy}_3]^{2+}$ (187), (the red complex $\text{Rubipy}_3\text{Cl}_2$ is neither affected by heating at 300°C nor boiling with HCl or 5M KOH), that no reduction of this species was observed even when a 20 molar excess of $NaBH_4$ was added to an aqueous solution of $Rubipy_3Cl_2$. (The latter is made by heating under reflux for long periods of time a mixture of $RuCl_3.3H_2O$ and bipy in ethanol solution (149). This is consistent with the observation that no chemical method of reduction of the $[Rubipy_3]^{2+}$ ion has yet been effected (188), although it has been reduced by electrochemical, radiolysis and by flash photolysis methods to $[Rubipy_3]^{+}$. In fact, the above reaction between Ru(II) and $NaBH_4$ in water causes the precipitation of a red coloured solid which analyses well for the ruthenium(II) complex, $[Rubipy_3](BH_4)_2.5H_2O$. In ethanol, the orange-red color of $[Rubipy_3]^{2+}$ does not change even when a 30 molar excess of $NaBH_4$ is added, although no solid could be isolated.

The reaction between $NaBH_4$ and Ru(III) in ethanol has also been studied and in this case some evidence for reduction was observed. Thus the addition of a 10 molar excess of $NaBH_4$, suspended in ethanol, to an alcoholic mixture of $RuCl_3$/bipy in the ratio of 1:6 at room temperature causes a change of colour from green to deep blue over a period of $\sim$1 hour. No solid could be precipitated from this solution, but on the addition of $NaPF_6$ or $NaBPh_4$ yellowish-green solids were obtained which, even after recrystallization, never gave consistent or reproducible chemical analyses and it may be that these solids are mixtures of Ru(II) and Ru(I) species. What possibly happens is that the initially formed $[Rubipy_3]^{3+}$/$[Rubipy_2(H_2O)_2]^{3+}$ (both green (210)) dissociate to form some $[Rubipy_2]^{3+}$ (also green (210)) allowing attack by BH_4^- on a vacant coordination site of the Ru(III) system (105). In this way, the formation of significant amounts of the stable $[Rubipy_3]^{2+}$ (orange-red (149)) species would not occur. It is important to note that not even a trace of orange/red colour was observed during the reaction and this strongly indicates that if any $[Rubipy_3]^{2+}$ at all is formed under these conditions, the amount is insignificant.

The complex $[Rubipy_3](BH_4)_2.5H_2O$ is air stable, diamagnetic, soluble in water, alcohol and DMSO, and insoluble in benzene and ether. As expected the complex is a 1:2 electrolyte in 10^{-3} molar solution in DMSO (Table 7) and its ir spectrum (Table 7) has intense absorption at 1085 cm^{-1} and at 2220 cm^{-1} (broad), attributed to the deformation and stretching frequencies respectively of purely ionic BH_4^- groups. The solid state and solution spectra are illustrated in Fig. 7 and resemble those of $[Rubipy_3]Cl_2$ which have bands at 25000 cm^{-1} and a shoulder at 14300 cm^{-1} due to change-transfer transitions.

Figure 7 Electronic spectra of the Ru-bipy complexes



Further evidence for the extreme stability of the Ru(II) ammines is obtained from the reaction of $[\mathrm{Ruen}_3]^{2+}$ with $NaBH_4$. Thus when a 15 molar excess of $NaBH_4$ (solid) is added to an aqueous solution of $[\mathrm{Ruen}_3]^{2+}$, no change in colour is observed. Similarly, no reduced product could be isolated when a 20 molar excess of $NaBH_4$ is added to a solution of $[\mathrm{Ruen}_3]^{2+}$ in aqueous ammonia at 0° C.

It is relevant at this stage to emphasize the significance of the Ru(I)-phen complexes formed by tetrahydroborate reductions since, like iron(I), ruthenium(I) is rare in the chemistry of ruthenium. Other than in complexes with metal-metal bonds, good evidence has not been reported for the univalent state. For example, Manchot <u>et al.</u>(189) claimed the formation of RuX (X=Cl,Br,I) in aqueous solution by the action of hypophosphorous acid on the corresponding ruthenium(III) halides, but it is also possible that those solutions contain hydridohalo ruthenium(II) or even ruthenium(III) species. The same authors also reported that $[\mathrm{Ru(NO)X_2}]_n$ (X=Cl,Br,I) can be obtained from the reaction of nitric oxide with $[\mathrm{RuX_2(CO)_2}]_n$ at 230° C (190) and in related work, the formation of $[\mathrm{Ru(NO)I_2L_2}]_2$ L=Py,½bipy,Ph_2MeAs) have also been reported from the reactions of $[Ru(NO)I_2]_n$ with the appropriate ligand (191). However, as already discussed in the iron system, the assignment of formal oxidation states in metal nitrosyl complexes is a controversial matter. The monovalent state of ruthenium is better represented by the small number of complexes which are indicated below. It is important to note that all these well characterized Ru(I) complexes are <u>diamagnetic</u> and necessarily <u>dimeric</u> <u>or</u> <u>polymeric</u> in nature. For example, when mixtures of $Ru_3(CO)_{12}$ and certain carboxylic acids, RCOOH (R=H,Me,Et or <u>n</u>-C_9H_{19}), are heated under reflux for 10 hours orange coloured diamagnetic compounds $[Ru(CO)_2(RCO_2)]_n$ are produced (192). Further Ru(I) carbonyl complexes have been prepared by Shaw <u>et</u> <u>al.</u>(193) by the addition of bulky phosphines to yellow solutions obtained after prolonged treatment of $RuCl_3$ with CO in boiling 2-methoxyethanol. The resulting orange, binuclear, diamagnetic complexes were formulated as $[Ru_2Cl_2(CO)_4L_2]$ (L=PBu^t_2Ph,PBu^t_2-<u>p</u>-tol). In addition to these carbonyl complexes, the hydrogenation of $RuCl_3$ at 1 atmosphere pressure in DMA (N,N'-dimethylacetamide) at 85°C for 2 hours is also reported (194) to produce the dark brown diamagnetic complex formulated as Ru_2Cl_3(HDMA).

It is clear from these reports that relatively harsh conditions were employed for the preparation of the Ru(I) complexes mentioned above and these should be contrasted with the work reported in this thesis where very mild conditions were needed to synthesize air stable Ru(I) complexes.

D. Cobalt

Cobalt is the only metal for which reactions of its salts with $NaBH_4$ in the presence of en,bipy and phen have already been studied (100, 144, 145, 146). It has been reported (144) that the addition of $NaBH_4$ to the perchlorate salt of tris(bipyridyl)cobalt(III or II) in aqueous ethanol at room temperature results in the formation of a paramagnetic (μ =2.89 B.M.) complex, $Cobipy_2(ClO_4)$ in which the possibility of a coordinated ClO_4 group has been suggested. On the other hand $[Cophen_3](ClO_4)$ has been isolated (145) from the reaction of $NaBH_4$ and $[Cophen_3](ClO_4)_3$ in a molar ratio of 20:1, in aqueous ethanol at $-5^{\circ}C$ under reduced pressure. In addition to these complexes, a patent reported (100) the preparation of $[Coen_3](BH_4)_2Cl$ from the reaction of $[Coen_3]Cl_3$ with $NaBH_4$ in ammonia solution.

In view of what has been reported for the nickel (105), iron and ruthenium systems, namely the formation of tetrahydroborate complexes from reactions where the solvent plays an important role in determining the nature of product, the cobalt-ligand - $NaBH_4$ (Ligand=en,phen and bipy) reactions have been reexamined under different conditions from those already reported.

Thus, the addition of a very large excess (~20 molar) of solid $NaBH_4$ to a concentrated solution of $[Coen_3]Cl_3$ in aqueous ammonia solution at 0°C, causes the precipitation of a golden yellow complex which analyses reasonably well for $[Coen_3](BH_4)_3\cdot 3H_2O$. This complex is stable in air and also under reduced pressure, is soluble in water and DMSO but like other tetrahydroborate complexes, it decomposes upon attempted recrystallization. This means that the complex must be purified by repeated washings with alcohol. Even then the compound always gave a positive test for chloride ions, although the quantitative determination of Cl^- by a potentiometric titration gave inconsistent results, but always a Cl^- concentration of less than 2%. Thus, this Cl^- appears to be a persistent impurity since formulation of the product as $[Coen_3](BH_4)Cl$ (100) would require a Cl^- analysis of 11.64%.

The complex appears to be a typical Co(III) salt and, as shown in Table 8, has an electrical conductivity of a typical 1:3 electrolyte in a freshly prepared 10^{-3}M solution in DMSO. The ir spectrum has intense bands at 1080 and 2250 cm^{-1} assigned to the deformation and stretching modes respectively of ionic BH_4^- groups. Electronic spectra, both in solution and in the solid state, have a band at 21100 cm^{-1}, ascribed as the d-d band associated with the spin-allowed transition $'A_{1g} \rightarrow 'T_{1g}$ on an octahedral Co(III) ion.

The addition of a large excess of $NaBH_4$ (5-10 molar) to an aqueous solution of Co(II) chloride and en in a 1:3 molar ratio at room temperature gives a transient pink coloured precipitate which immediately decomposes to a black product containing 40% cobalt, thus indicating extensive decomposition to, probably, the boride. The reaction was also carried out in ammoniacal solution at 0°C using a large excess of ligand (6 molar) in an effort to stabilize the pink product, but this was also unsuccessful.

As mentioned earlier, the reduction of $[Cobipy_3](ClO_4)_3$ by $NaBH_4$ in aqueous ethanol yields $Cobipy_2(ClO_4)$ (146). However, when an aqueous solution of $NaBH_4$ (10 molar excess) is added dropwise to an aqueous solution of $CoCl_2 \cdot 6H_2O$/bipy in a 1:3 molar ratio, a dark blue solid is produced which analyses well for $Cobipy_2BH_4 \cdot H_2O$. The same dark blue complex is also obtained by adding a 10 molar excess of $NaBH_4$ to an aqueous solution of $Cobipy_2Cl_2$, and by the addition of a 10 molar excess of $NaBH_4$ to an aqueous solution of $CoCl_2$ and bipy in the ratio of 1:4.

Reactions between $CoCl_2 \cdot 6H_2O$ and $NaBH_4$ in the presence of phen have also been reexamined. According to a previous report (145), a brown black tris(phenanthroline)cobalt(I) complex, $[Cophen_3]ClO_4$ has been synthesized from the reaction of $NaBH_4$ and the cobalt(III) complex $[Cophen_3](ClO_4)_3$ in aqueous ethanol. It is interesting to note that such, presumably octahedral, metal(I) species could not be obtained in the Fe, Ru and Ni (105) systems.

The addition of an excess of an aqueous solution of $NaBH_4$ (10 molar) to a solution of $CoCl_2 \cdot 6H_2O$ and phen in the ratio of 1:3, in water produces a dark green complex which analyses well for $Cophen_2BH_4 \cdot H_2O$. The tetrahydroborate complex is also obtained when a 5 molar excess of $NaBH_4$ in the solid state is added to an aqueous solution of $Cophen_2Cl_2$. Reactions when more $NaBH_4$ is used and with longer reaction times (> 1 hour) result in the formation of an impure product, the highly paramagnetic nature of which strongly suggests the presence of ferromagnetic metal boride.

The complexes $CoL_2BH_4.H_2O$ (L=bipy and phen) are very air sensitive especially the bipy compound. Like the analogous complexes of Fe and Ni, these tetrahydroborates are insoluble in benzene, hexane and ether, but are soluble in ethanol and DMSO although they cannot be recovered from these solvents. Purification of the products therefore had to be effected by repeated washing with water, benzene and ether.

Table 8 shows that both complexes are 1:1 electrolytes in freshly prepared 10^{-3}M solutions in DMSO. The ir spectral peaks for the BH_4 groups are at 1080 and 2060, 2240, 2315, 2360 cm^{-1} for the phen complex and at 1080 and 2080, 2220, 2380 for the bipy complex. These bands are assigned to the deformation and stretching frequencies respectively of the BH_4^- group. The B-H stretching frequency region is also shown in Fig. 8, and these spectra should be compared with those reported for the iron complex in Fig. 1 from which it is apparent that the interaction between the metal and BH_4

Table 8. Some physical properties of the cobalt complexes.

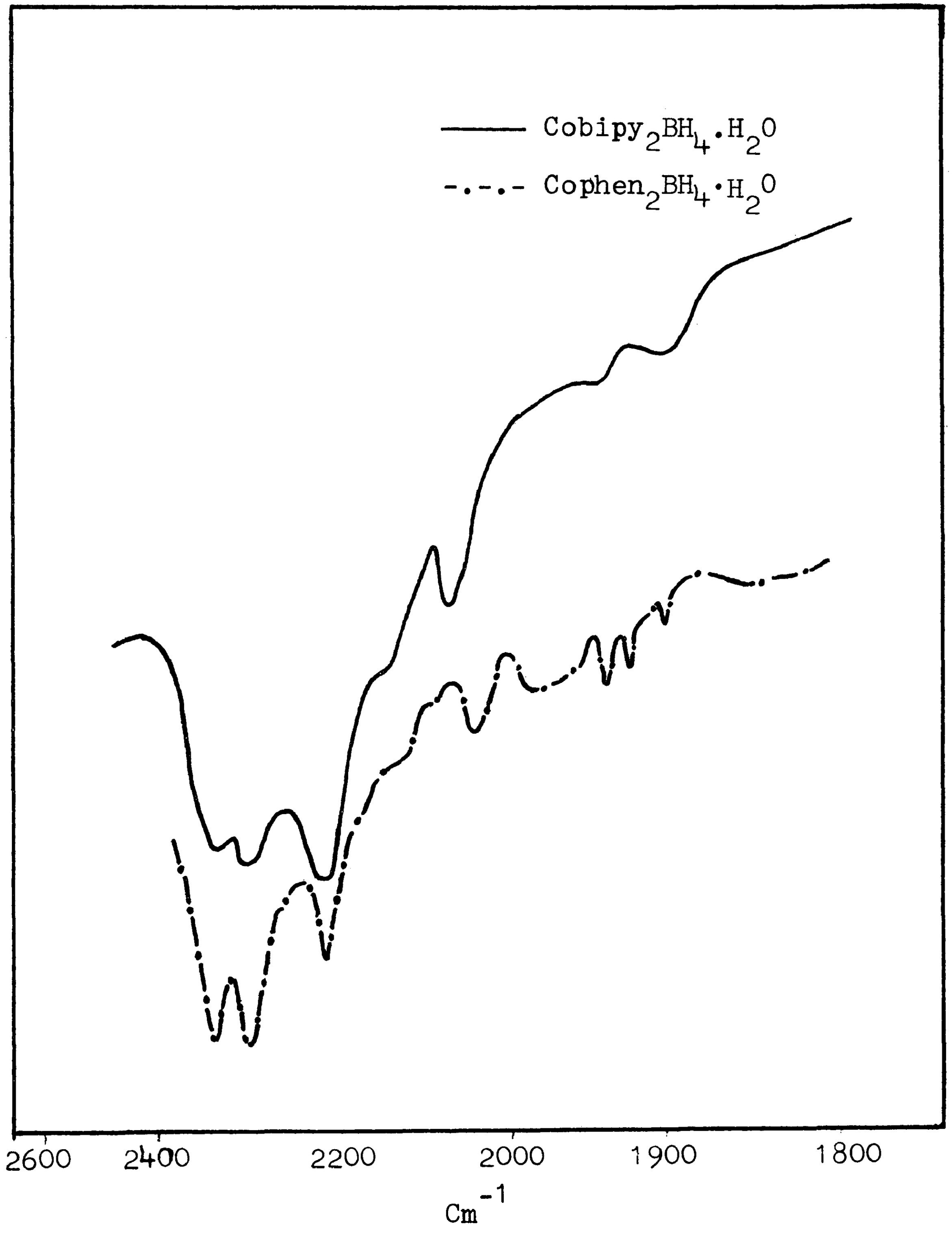
Compound	Electronic Spectra* cm^{-1}	μ eff B.M.	Conductivity** of $10^{-3}M$ DMSO solution at $25^{\circ}C$ $Ohm^{-1}cm^{2}mole^{-1}$
$[Coen_3](BH_4)_3.3H_2O$	Solid: 21100 Solution: 21270 (47.3)	Diamagnetic	92
$Cobipy_2BH_4.H_2O$	Solid: 23800, 13700, 7100 Solution: 24000(2.1x10^3) 1400(2.6x10^3),7000(40,10^3)	3.8 3.7(8.2x10^-3M) DMSO Solution	23.6
$Cophen_2BH_4.H_2O$	Solid: 22200, 7200 Solution: 21300(2.8x10^3) 7050(5.6x10^3)	3.9	15.6

* ε Values in parentheses, Solution spectra in $10^{-3}M$ DMSO Solution

** Reference Compounds conductivity of $\sim 10^{-3}M$ Solution at $25^{\circ}C$

$NaBPh_4$	(1:1)	23.4	(DMSO).
$Ni(ClO_4)_2.6H_2O$	(1:2)	68.8	(DMSO)
$Cophen_3(ClO_4)_3$	(1:3)	115.8	(DMSO)
$NaPF_6$	(1:1)	162.7	(Acetone)
$Niphen_3(BPh_4)_2$	(1:2)	222.2	(Acetone).

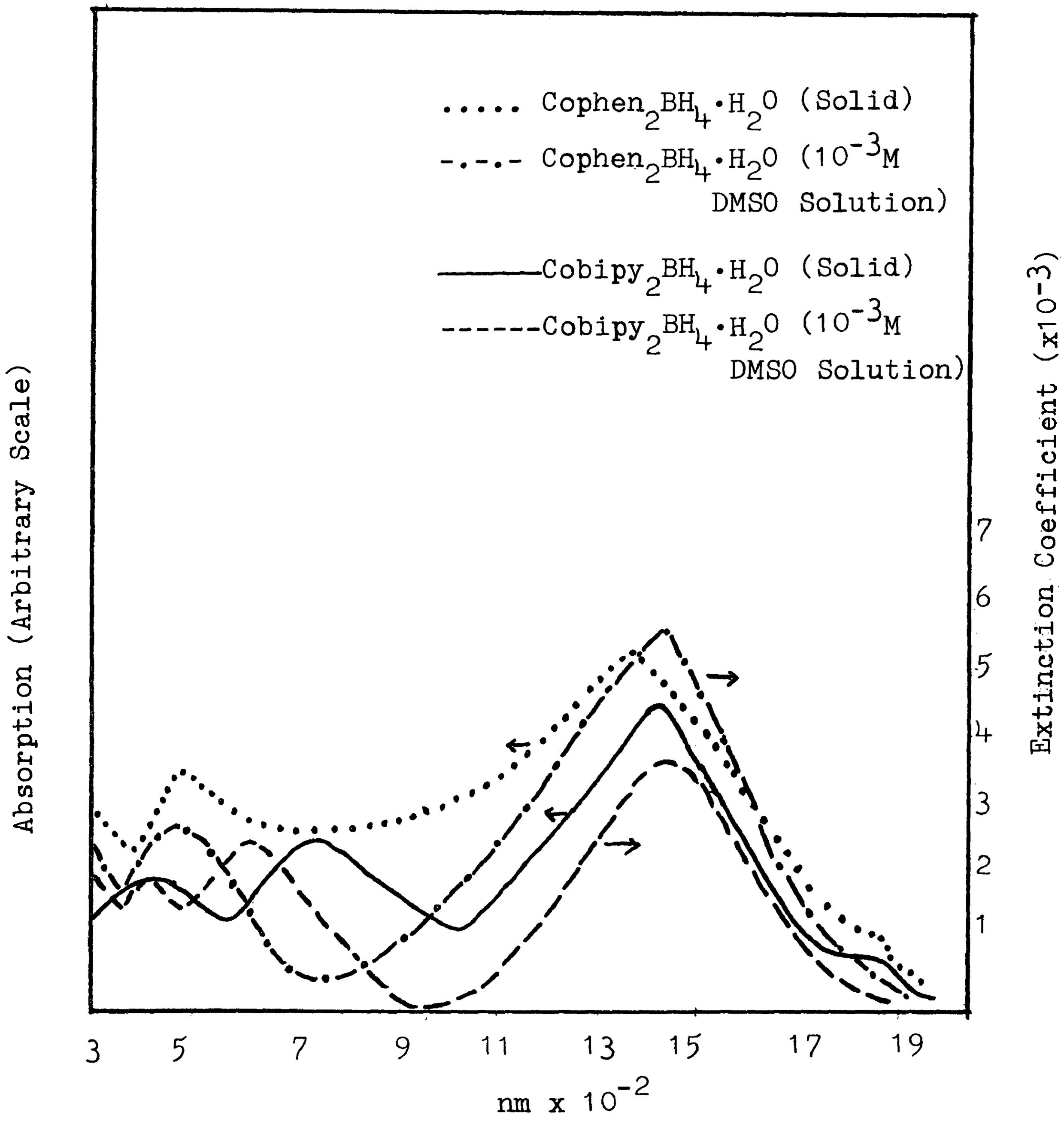
Figure 8 Infrared spectra of the Co(I) complexes in the B-H stretching region.



group is weak and probably mostly ionic. The peak at 1630 cm^{-1} and a broad peak centred at $\sim$3400 cm^{-1} for the phen complex and broad bands at 1625 and at 3400 cm^{-1} for the bipy complex, can be assigned as the bending and stretching modes of water respectively.

The reproducible values for the magnetic moments for both complexes (Table 8), not only shows the strong orbital contribution to the magnetic moments, for a high spin Co(I) d^8 system, but also rules out the possibility of the presence of any significant quantity of an impurity such as metal boride, The magnetic moment of the bipy complex is virtually unchanged when measured in solution, which again rules out the possibility of boride contamination (borides are insoluble in DMSO). Electronic reflectance and solution spectra are also recorded in Table 8 and are also shown in Figure 9, and the resemblances between the spectra not only of the different complexes but also of the same complex in both the solid state and solution are striking. The spectra are dominated by the large transition in the near infrared region with an extinction coefficient in the 6000 region. As in the Fe(I) and Ni(I) cases, the question remains as to whether these spectral bands are d-d or charge-transfer in origin. If they are charge-transfer of the type d$\rightarrow$ ligand π^* as is often the case in complexes of phen and bipy(131), then why are the energies of the π^* orbitals the same on significantly different ligands? Also, the bands are at very low energy for charge-transfer transitions, although bands as low as 6000 cm^{-1} have been reported (195) for some low-valent

Figure 9. Electronic spectra of the Co(I) complexes.



M-bipy complexes and assigned as L → M charge-transfer transitions. If on the other hand, the bands are d-d in origin, they must occur on a non centrosymmetric molecule, _e.g._ tetrahedral or a molecule showing extensive distortion. It is interesting that extinction coefficients of this order have been reported (196) for d-d transitions in low spin 5-coordinated d^8 systems, while in high spin d^8 5-coordinated Ni(II) complexes _e.g._ NiLCl, L=bis(2-dimethylaminoethyl)methylamine, a band at 7100 cm^{-1} occurs although the ϵ value is only 26. The high orbital contribution to the magnetic moment would be consistent with a tetrahedral d^8 configuration and it may be that the complexes are basically tetrahedral $[CoL_2]^+$ (L=phen and bipy) units. However, the spectra in Figure 9 show only marginal resemblance to what is characteristic of high spin tetrahedral d^8 systems (196).

The extent of the interaction of the BH_4^- group in the solid state is also uncertain and, as mentioned previously, equilibria such as

$$[CoL_2BH_4] \rightleftharpoons [CoL_2]^+ + BH_4^-$$

may be involved.

Thus, although it is clear that $NaBH_4$ has reduced Co(II) to form new Co(I) complexes the stereochemistry of these molecules remains to be established with certainty. It is interesting that the complexes reported here from the reactions involving phen and bipy are significantly different from those reported earlier from similar work (145, 146) and these differences may reflect the role of the solvent in determining the nature of the final reaction product. For example tetrahydroborate complexes, $CoL_2BH_4 \cdot H_2O$ (L=phen and bipy) are prepared from aqueous solutions, while the same reactions in aqueous ethanol solutions lead (145) to the formation of simple univalent complexes, e.g. $[Cophen_3](ClO_4)$. Similar results have been observed previously in these laboratories and for example, $Co(BH_4)(PPh_3)_2$ containing bidentate BH_4 is obtained from the $Co(II)/PPh_3/NaBH_4$ reaction in benzene, while $Co(BH_4)(PPh_3)_3$, containing mondentate BH_4 is obtained from the same reaction in ethanol (88). Thus this section presents further evidence (24) that the products of $NaBH_4$ reductions depend not only on the nature of the ligand and the ratio of the reactants but also on the solvent.

E. Other Metals

In this section four metals are considered together because much less work has been done on them.

1. Chromium

Little work on the reduction of Cr(III)/amine systems with $NaBH_4$ has been reported and this is not altogether surprising since one of the principal characteristics of Cr(III) complexes is their kinetic inertness. However, it is known that the reaction of $NaBH_4$ with $[Cr(NH_3)_6]^{3+}$ yields $[Cr(NH_3)_6](BH_4)_3$ (196), and a patent has claimed the formation of another unreduced tetrahydroborate species $[Cren_2Cl_2](BH_4)$ from the reaction of $NaBH_4$ with $[Cren_2Cl_2]Cl$ (100). In view of the brevity of the above reports, a few preliminary reactions between Cr(III) and sodium tetrahydroborate in the presence of en, bipy and phen have been studied as outlined below.

The addition of a large excess of $NaBH_4$ ($\sim$20 molar) to a concentrated solution of $[Cren_3]^{3+}$ in ammonia solution at 0°C gives a yellow product which analyses well for $[Cren_3](BH_4)_3$. This yellow product is very soluble in water, and in the initial experiments almost half of the product was lost during washing with water. It is stable at room temperature and also under reduced pressure. A band at 1080 cm^{-1} and a broad band at 2250 cm^{-1} in the ir spectrum are attributed to the deformation and stretching frequencies respectively of ionic BH_4^- groups.

The compound is a 1:3 electrolyte in a freshly prepared 10^{-3}M DMSO solution (Table 9). The electronic solution spectrum of the yellow compound shows all of the characteristic features of the Cr^{3+} ion in an octahedral arrangement with bands at 2900 cm^{-1} (ϵ =70) and at 2260.0 cm^{-1} (ϵ =85), similar to those of the $[Cren_3]^{3+}$ species (196).

All attempts to reduce the Cr(III) in $[Cren_3]^{3+}$ were unsuccessful, probably due to the high potential (0.86V) for the $Cr^{3+}/en \longrightarrow Cr^{2+}/en$ couple (197). Thus reduction is not observed even when a very large excess of $NaBH_4$ is added to an aqueous solution or alcoholic suspension of $[Cren_3]^{3+}$ at room temperature. On the other hand, when a 5 molar excess of $NaBH_4$ is added to an alcoholic solution of $CrCl_3 \cdot 6H_2O$ and bipy, in the ratio of 1:3, at room temperature, the initial green colour of the solution changes to indigo-blue and this shows the formation of the well characterized (198) $[Crbipy_3]^+$ species (potential for the

Table 9. Some physical properties of the Cr, Mn and Zn domplexes.

Compound	Infrared spectrum cm^{-1}	μ eff B.M.	Conductivity* of 10^{-3}M DMSO solution at 25°C $ohm^{-1}cm^{2}mole^{-1}$
$[Cren_3](BH_4)_3 \cdot 3H_2O$	1080 and 2250(v.b)	3.8	109.5
$[Mnbipy_3](BH_4)_2 \cdot 3H_2O$	1080 and 2250(v.b)	5.9	70.4
$[Znen_3](BH_4)_2 \cdot H_2O$	1080 and 2250(v.b)	Diamagnetic	68.0
$[Znbipy_2BH_4]BH_4 \cdot 2H_2O$	1090, 1115, 2040, 2120, 2220, 2400 and 2440	Diamagnetic	42.9

* For reference electrolytes, see Table 8.

Cr^{3+}/bipy ⟶ Cr^{2+}/bipy couple is 0.49 volts (131)). No attempts were made to isolate the product. Similar colour changes are obtained when phen is used, although no reduced species has yet been isolated.

2. Manganese.

Despite the fact that Mn(II) is the most stable oxidation state for this element, lower valent complexes in which manganese has formal oxidation states of -3, -2, -1, 0 and +1 are known. This, together with the fact that bipy and phen have the capability of stabilizing low valent complexes, could lead to some interesting complexes from reactions between $NaBH_4$ and Mn(II) in the presence of these ligands.

However, in all the reactions studied in this work, no evidence for the reduction of Mn(II) has been observed. Thus, the addition of a 5-10 molar excess of $NaBH_4$ to aqueous solutions of Mn(II) and bipy in a 1:3 molar ratio gives a pale yellow product which analyses for the manganese(II) complex $[Mnbipy_3](BH_4)_2.3H_2O$. Neither variations in molar ratios of Mn:bipy:$NaBH_4$ from 1:2:5 to 1:4:10, nor increases in reaction times from ½ hour to 6 hours lead to any reduced species. The above tetrahydroborate complex is also isolated when similar reactions are carried out in alcoholic solutions.

The yellow coloured product is insoluble in ethanol, benzene and ether, and is slightly soluble in water and DMSO. As is the case with other Mn(II) complexes, $[\mathrm{Mnbipy}_3](\mathrm{BH}_4)_2.3\mathrm{H}_2\mathrm{O}$ is high spin (Table 9) and the complex is also a 1:2 electrolyte in freshly prepared 10^{-3}M DMSO solution (Table 9). The ir spectrum shows a band at 1080 cm^{-1} and a very broad intense band at 2250 cm^{-1}, due to the deformation and stretching modes respectively of ionic BH_4 groups. The product is therefore a conventional Mn(II) complex.

Also, no evidence for reduction was obtained from the NaBH_4-Mn(II)-phen system. The addition of a 5 molar excess of NaBH_4 to an aqueous solution of Mn^{2+} and phen in the molar ratio of 1:3 gives a yellow product the ir spectrum of which shows the characteristic bands at 1080 cm^{-1} and at 2250 cm^{-1} of ionic BH_4 groups. Like the other tetrahydroborate complexes, recrystallization from DMSO solution resulted in decomposition and loss of BH_4 groups and therefore purification of the complex was effected by repeated washings with alcohol and benzene. However, even after repeated washings, satisfactory analytical results could not be obtained for a Mn(II)-phen-BH_4 complex, and the product is therefore possibly a mixture of bis, tris and tetrakis(phenanthroline) complexes, all of which have been isolated from the Mn(II)/phen system (200).

3. Copper.

Only a few preliminary reactions between $NaBH_4$ and copper(II) salts in the presence of N-donor ligand have been studied and the results are briefly presented here.

The addition of $NaBH_4$ ($\sim$5 molar excess) to an aqueous solution of $[Cuen_3]^{2+}$, causes the immediate precipitation of a dark coloured product which contains $\sim$70% Cu and which is almost certainly a mixture of metal and boride. A similar reaction also occurs when much less $NaBH_4$ ($\sim$1 mole) is added to an ammoniacal solution of $[Cuen_3]^{2+}$ and en in the ratio of 1:3 at 0°C.

It has been suggested (105) that the initial step in the reduction of metal ions (Ni^{2+} in particular) in the presence of nonπ-bonding ligands such as en, is the formation of a metal- BH_4 link which can only be prevented by repressing dissociations of the type $Men_3^{2+} \rightleftharpoons Men_2^{2+}$ + en by having a large excess of the ligand present. In the above reactions, a large excess of ligand is not present, vacant coordination sites therefore exist on the Cu^{2+} ion and rapid reduction takes place. It is interesting to note that, even in liquid ammonia, only one NH_3 is coordinated to $[Cuen_2]^{2+}$ (199).

When a 10 molar excess of $NaBH_4$ is added to ammoniacal solutions of Cu(II) and bipy in the ratio of 1:3 at 0^oC, the bluish green colour disappears and a brown precipitate is formed. This changes rapidly to a dark coloured product in the reaction vessel. Alternatively, if the initially formed brown precipitate is isolated immediately, it also changes to a dark coloured product on drying.

The ir spectrum of the brown product has bands at 1980 and at 2390 cm^{-1} in the B-H stretching region, and the dark coloured product has only one band at 2390 cm^{-1}. Preliminary analytical data suggest that the dark coloured product may be formulated as $CubipyBH_4$, although clearly more work is needed on this system.

4. Zinc.

Zinc(II) is among the few metal ions forming stable tetrahydroborates (22c) such as $Zn(BH_4)_2$ which does not decompose until heated to above 50° C (22j). A patent has also claimed the formation of $[Zn(NH_3)_4](BH_4)_2$ (107). In view of these reports it seemed quite likely that tetrahydroborate complexes could be isolated in the presence of other nitrogen donor ligands, although reduction of Zn(II) was considered unlikely.

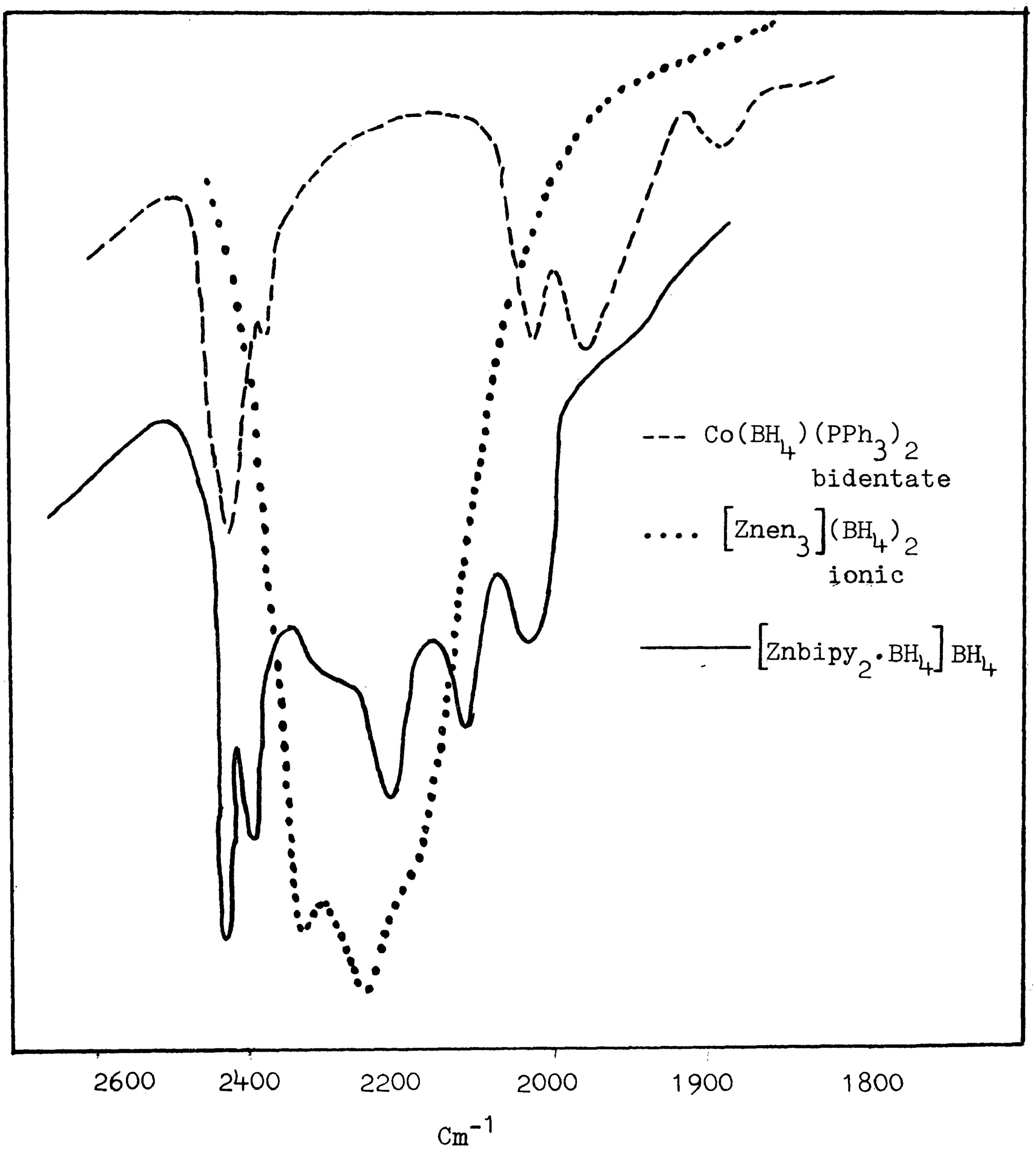
Thus the addition of a massive amount ($\sim$30 molar excess) of $NaBH_4$ to a concentrated solution of $[Znen_3]^{2+}$ in aqueous ammonia at 0° C causes the precipitation of a white product which analyses for $[Znen_3](BH_4)_2 \cdot H_2O$. The air-stable white complex is insoluble in alcohol, benzene and ether and is soluble in H_2O and DMSO but recrystallization results in the loss of the BH_4 groups. The complex was therefore purified by repeated washing with ethanol. The complex is a typical diamagnetic Zn(II) species with an electrical conductivity (Table 9) consistent with a 1:2 electrolyte and an ir which shows a band at 1080 and a broad intense band at 2250 cm^{-1}, assigned to the deformation and stretching modes respectively of ionic BH_4 groups.

The reaction of Zn(II) and $NaBH_4$ in the presence of bipy is of particular interest since the product appears to contain a coordinated BH_4 group. Thus, when 5-10 molar excess of $NaBH_4$ is added to an aqueous solution of $ZnCl_2$ and bipy in ratios between 1:3 and 1:4 a yellow product is obtained which analyses well for $Znbipy_2(BH_4)_2 \cdot 2H_2O$. The same product is also obtained from similar reactions in alcohol.

The yellow coloured complex is insoluble in ethanol, benzene and ether, slightly soluble in water and is soluble in DMSO. However, like other tetrahydroborates it cannot be recovered from DMSO and must therefore be purified by repeated washing with water, benzene and ether.

The ir spectrum of $Znbipy_2(BH_4)_2 \cdot 2H_2O$ in the B-H stretching frequency region is complex and is illustrated in Figure 10. Absorption maxima occur at 1090, 1115, 2040, 2120, 2220, 2400 and 2440 cm^{-1} and it is possible that these bands may be due to the presence of one essentially ionic and one coordinated (probably bidentate) BH_4 group. Thus the doublet at 2400 cm^{-1}, the band at 2040 and at 1115 cm^{-1} are tentatively assigned to the $B\text{-}H_t$ stretching, $B\text{-}H_b$ bending and BH_2 deformation modes respectively of a

Figure 10. Infrared spectra of the Zn complexes in the B-H stretching frequency region



bidentate BH_4 group (83), with the additional expected bridging stretch in the 1300 - 1500 cm^{-1} region not observed, as often happens with this type of coordinated BH_4 group (83). This leaves bands at 1090, 2120 and 2220 cm^{-1} which may be the BH_4 deformation and B-H stretching modes of an essentially ionic BH_4 group.

Although the electrical conductivity (Table 9) of freshly prepared $10^{-3}M$ solutions in DMSO is slightly higher than expected for a 1:1 electrolyte, some dissociation of the type

$$[Znbipy_2BH_4]^+(BH_4)^- \rightleftharpoons [Znbipy_2](BH_4)_2$$

may occur. It therefore appears that the yellow complex should be formulated as $[Znbipy_2BH_4]BH_4 \cdot 2H_2O$

The addition of a 10 molar excess of $NaBH_4$ to aqueous solutions of $ZnCl_2$ and phen in the ratio of 1:3, causes a change in colour from the original yellow to violet. A dark coloured solid started to precipitate, but the final product, after the reaction mixture had been stirred for ~1 hour was yellow in colour, which on drying under reduced pressure again changed to a dark coloured product. The ir spectrum of the latter has bands at 1080 and 2250 cm^{-1} due to BH_4^- groups. Even after repeated washing with benzene and ether consistent elemental analysis could not be obtained, possibly because, like the Mn(II) system already discussed, the product may be a mixture of mono, bis and tris(phenanthroline) complexes (200).

F. Conclusions and Suggestions for further work.

It is clear from this and earlier work that the nature of the ligand plays a critical role in determining the products formed from transition metal-ligand-$NaBH_4$ reactions. The π- acceptor ligands, phen and bipy, have stabilized the unusual Fe(I) and Ru(I) (as well as the more common Co(I)) oxidation states while with ligands with no π-bonding capability, like en, no reduction takes place or else reduction is complete to the metal or boride and no intermediate metal(I) complexes are observed. This further supports the earlier conclusions based on Ni-$NaBH_4$-N base reactions, namely that, with non π-bonding ligands, reduction takes place through the initial formation of a metal-BH_4 link. This can be prevented (and hence reduction prevented) by carrying out reactions in the presence of an excess of ligand, thus restricting the dissociation of tris(ligand) species to species having vacant coordination sites to allow the M-BH_4 link to form, e.g. Cu. To summarize, reduction in this case depends on the stability of the M-L system, and the lability and ease of dissociation of the ligands.

With π-bonding ligands, the situation appears to be different in that the very stable $ML_3^{2+,3+}$ species (L=phen, bipy) which, especially in the presence of an excess of ligand, do not dissociate and are reduced to intermediate metal(I) complexes. This reduction probably occurs through an outer sphere mechanism as already suggested in the case of Ni (105).

The solvent also plays a role in these reactions in that the metal(I)-BH_4 complexes are isolated much more readily from aqueous solutions than from ethanolic. This may be a simple solubility effect and may not necessarily reflect a major difference in mechanism although such differences have been observed previously in metal-$NaBH_4$-phosphine reductions.

Continued research in the area promises to be exciting and we can expect better understanding of the mechanism of borohydride reduction. A study of Cu^{2+}/bipy and Cu^{2+}/phen systems would be worthwhile in this aspect.

In view of the characterization of Fe(I) and Ru(I) complexes, a rare oxidation state for these metals, it would be of interest to extend this aspect to other metal systems. Pd and Pt are the obvious candidates for such a study. Regarding the role of other factors, e.g. ratio of reactants, solvent and nature of ligand, a more complete study of Zn^{2+}/phen, Mn/phen, Cr/bipy, phen should be made to further clarify the role of these factors.

Considering the catalytic potential of the tetrahydroborate complexes (23), it would also be advantageous to study the catalytic activities of any of these complexes, especially of ruthenium complexes.

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*Note: - In the final proof reading of this thesis, it was observed that references 32 & 86, 52 & 93, 56 & 87, 66 & 92, 62 & 119, 58 & 121, 129 & 156 and 130 & 155 were the same. In the interest of clarity, these duplications were left unchanged. Also, during a revision of the thesis a few more references were added. These additional references were inserted out of numerical sequence so as not to introduce errors and ambiguities during the revision.

APPENDIX

The infrared spectra of bipy complexes below 3000 cm^{-1} are tabulated on page 159, and similar information for the phen complexes is given on page 160. It has been reported (202) that the spectra of the free ligands undergo slight modification on coordination, in particular the ring frequencies (1000 - 1600 cm^{-1}) tend to undergo small but observable shifts to higher wavenumber. The other changes occur in the region of 700 - 800 cm^{-1}, e.g. the band which has been suggested to be characteristic of coordinated bipy is that which occurs at 759 cm^{-1} in the spectrum of the free ligand. This strong band frequently shifts 10 - 20 cm^{-1} to higher wavenumber on coordination (146). Also, a satellite of this band at 741 cm^{-1} (free-ligand) gains intensity and is strongly resolved from the parent peak (146) upon coordination. The low frequency region of the spectrum is of great importance, since the ν(M-N) absorptions are expected in this region. Inskeep (148) was the first to assign the M-N stretching bands of the tris-chelate complexes of bipy and phen with first row transition metals as falling in the range 530 - 250 cm^{-1}. Hutchinson et al.(203) applied the metal isotope technique for assigning the M-N vibrations. Their results indicate that M-N stretching bands for tris-bipy and phen complexes of Fe(II), Ni(II), and Zn(II) are at 375 - 360, 300 - 240 and 240 - 175 cm^{-1} respectively. On the other hand, Clark and Williams (204) could find no bands assignable to the M-N stretching modes in the far-infrared spectra (above 200 cm^{-1}) of bipy complexes of Co(II), Co(III), Fe(II) and Ni(II). However, assignments of ν(M-N) above 200 cm^{-1} have been made for a number of bipy and phen complexes (205, 206).

Inspection of the data tabulated on pages 159 and 160 shows that in their gross features, the spectra of all the bipy and phen complexes reported in this thesis are remarkably similar to the previous reports (202, 146, 148) (i.e. the ligand frequencies undergo shifts which are characteristic of coordinated ligands) except that the Nujol bands prevented observation of bands in the neighbourhood of 1380 and 1465 cm^{-1}. In PF_6^- systems a very intense band due to the PF_6^- anion also obscures frequencies due to the ligand in a region about 100 cm^{-1} wide centred around 850 cm^{-1}.
The hydrated complexes have absorptions at ~1625 and at ~3400 cm^{-1}. However, not much can be said about the bonding of these water molecules due to the poor resolution of the spectra and due to the presence of several ligand bands in the region in which bands of

coordinated water molecules would be expected (880 - 650 cm^{-1}). No attempts have been made to assign M-N frequencies because of the disputed (see earlier discussion) position of the M-N vibrational modes.

Table 10 Infrared frequencies (cm^{-1}) of bipy complexes below 3000 cm^{-1}

$Mnbipy_3(BH_4)_2.3H_2O$	$Febipy_3(BH_4)_2.6H_2O$	$Cobipy_2.BH_4 H_2O$	$[Znbipy_2.BH_4] BH_4.2H_2O$	$Rubipy_3(BH_4)_2.5H_2O$
225		245	230	
310	325	330	325	340
415	425	420, 470	400, 418	430
	540	565	560	565
625, 655	620	640*	620*	660
741*	735*	725, 745*	731, 751*	735*
775*	780*	765*	770*	780*
825, 900(w)	900(w)	892, 965*	890, 900, 970	900(w)
1015, 1045		1020, 1055	1018, 1044	
			1060	
1080* (v.b.)	1075* (v.b.)	1080	1090	1085* (v.b.)
1160, 1180	1160	1155	1160	1165
1225	1235, 1270	1250	1250	1250
1320	1315	1305	1318	1318
1495, 1570	1560	1555, 1565	1495, 1565	1560(sh)
1580, 1600	1608*	1589, 1603	1585, 1602	1608*
1625(b)	1625(b)	1625(b)	1625(b)	1625(b)
2250* (v.b.)	2250* (v.b.)	2080, 2220	1950(sh) 2040	2220* (v.b.)
		2380	2120, 2220	
			2400, 2460	

* Indicates the more intense bands.

Table 11 Infrared frequencies (cm^{-1}) of phen complexes below 3000 cm^{-1}.

Fephen$_2$.BH$_4$.H$_2$O	Cophen$_2$BH$_4$.H$_2$O	[Ruphen$_2$.BH$_4$]$_2$.3H$_2$O	Fephen$_2$PF$_6$	[Ruphen$_2$]$_2$(PF$_6$)$_2$
300, 315	290, 335	280, 320	250, 300(w)	280, 300
450(sh), 510(w)	425, 480, 508	430(sh), 490(w)	420(w), 480(sh)	
535(w), 565	555, 622	525, 560	566*	560*
595		595		
668		665		
720*	705, 720*	730*	730*	722*
780*	775*, 792	780*	780*	780*
810, 845*	835*, 862	810, 840*	850*(PF$_6$)	850*(PF$_6$)
910	890	890		
1055, 1080	1055, 1080	1055, 1085	980, 1030	980, 1055
1130,1200(sh)	1130, 1180	1130, 1180	1155, 1175	1150, 1180
1215	1280	1200(sh),1215	1215	1205, 1225
		1255	1230	
1318	1315	1315, 1350	1325	1315
1515, 1555*	1490, 1520	1512, 1550*	1520, 1560	1510, 1555
1595, 1635	1550*, 1630	1590*, 1640	1590, 1615	1590, 1605
1975(sh), 2220	2060, 2240	1950(sh)		
2290(w)	2315	2220, 2290(w)		
2380(w)	2360	2350(w)		

*Indicates the more intense bands

ADDENDUM

Certain six-coordinated bis-phenanthroline derivatives of Fe(II) show an unusual temperature dependence of their magnetic properties (207) which has been ascribed to an equilibrium between quintet and singlet states (208). Complexes of the type $[\mathrm{Fephen_2X_2}]$ exhibit high-spin properties (μeff at room temperature = 5.0 to 5.3 B.M.) for ligands of lower field strength (X= I^-, Br^-, Cl^- etc.), and low-spin properties (i.e. diamagnetic) for ligands of higher field strength (X= CN^-, CNO^-, NO_2^-). However, the intermediate ligand NCS^- appears to generate a ligand field strength close to where the energy levels cross over, since the magnetic moments drop sharply with decreasing temperature - i.e. at 170° K μeff= 5.2 B.M. falling to 0.65 B. M. at 77° K.

Recently, an unusual six-coordinated Fe(II) complex $[\mathrm{Fephen_2(NCBH_3)_2}]$ having a magnetic moment of 2.9 B. M. has been reported (209). On the basis of Mössbauer parameters and magnetic moments, a triplet ground state has been suggested for this Fe(II) complex, and the possibility of interconversion of $S = 2 \rightleftharpoons S = 1$ and $S = 1 \rightleftharpoons S = 0$ states at different temperatures has also been proposed (209).

Thus, in view of the abnormal magnetic properties of these Fe(II) bis-phenanthroline complexes, variable temperature magnetic susceptibility measurements and Mössbauer studies on the proposed Fe(I) complexes reported here would be extremely helpful in deciding the oxidation state of iron.

One further point should be made concerning BH_4^--transition metal systems in general. Recent work (90) on certain Co-phosphine-BH_4 complexes has shown that it may be very difficult to distinguish between monodentate, bidentate and even tridentate coordinated BH_4^-. The small BH_4^- grouping in such systems may just act as a spherical grouping occupying effectively one coordination site and may also have pronounced ionic character.