# REACTIONS OF Co(II) WITH SODIUM CYANOTRIHYDROBORATE
# IN THE PRESENCE OF A SERIES
# OF BIDENTATE AND SOME MONODENTATE PHOSPHINES

By

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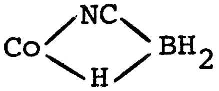
# ABSTRACT

The reactions between $Co(ClO_4)_2 \cdot 6H_2O$ or $CoCl_2 \cdot 6H_2O$, $NaBH_3CN$ and some monodentate ($PPh_3$ and $Pcy_3$) and a series of bidentate phosphines of the type $Ph_2P-(CH_2)_n-PPh_2$ (n = 1-4) and also cis and trans $Ph_2P-(CH)_2-PPh_2$ have been studied under a very wide range of experimental conditions. The reactions are affected by (1) the amount of $NaBH_3CN$ used, (2) the rate of addition of $NaBH_3CN$, (3) the temperature, (4) the solvent used and (5) the reaction time. A number of cyanotrihydroborato and other complexes have been produced and others observed but not yet isolated.

Co(II), Co(I) and one Co(0) complexes have been obtained. Complexes having formulae $Co(B)(L-L)_2X$ ($B=BH_3CN^-$, L-L=bidentate phosphine, $X=ClO_4^-$ or $Cl^-$), $Co(B)_2(L-L)_2$, $CoH(B)L_3$ ($L=PPh_3$), $Co(CN)(L-L)_2X$, $Co(B)_2(L-L)_{1.5}$, $Co(B)(L-L)$, $Co(B)(L-L)_2$, $CoH(L-L)_2$, and $Co(L-L)_2$ have been synthesized and their structures discussed on the basis of physical data, especially IR, $^1H$ and $^{31}P$ NMR spectroscopy.

Most of the reactions were much more complex at high temperature and some, particularly those with the bidentate phosphines with n=1 and 2, were very difficult to reproduce. Of the two monodentate phosphines used, only $PPh_3$ was effective in forming cobalt-cyanotrihydroborato complexes, and the crystal structure of one of these is under study.

An interpretation of available physical data suggests that $BH_3CN^-$ coordinates to the cobalt in a number of different ways, including $Co\text{-}NCBH_3$,  $\mathrm{Co}\overset{\mathrm{NC}}{\underset{\mathrm{H}}{\lozenge}}\mathrm{BH_2}$ and $Co\text{-}H\text{-}BH_2CN$ to give diamagnetic Co(I) or (usually) low spin Co(II) complexes. If these interpretations are correct, then the last two examples represent the first time $BH_3CN^-$ has been observed in these types of coordination modes.

Cleavage of the B-C bond in $BH_3CN^-$ has been observed in reactions of some complexes with organic solvents at room temperature and from several reactions at elevated temperatures. Cobalt cyanide complexes are generally produced.

The important factors influencing the reaction pathways, the non reproducibility of some of the reactions and the difficulties encountered in the identification of some complexes will be discussed at length.

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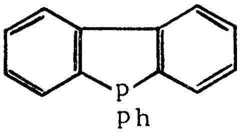
## ABBREVIATIONS

| | |
|---|---|
| Cy | Cyclohexyl |
| DBP | 5-Phenyl-5H-Dibenzophosphole<br> |
| Diphos | 1,2-Bis(diphenylphosphino)ethane |
| Dmf or DMF | Dimethylformamide |
| DPPM | 1,2-Bis(diphenylphosphino)methane |
| DPPB | 1,2-Bis(diphenylphosphino)butane |
| DPPP | 1,2-Bis(diphenylphosphino)propane |
| DPPPe | 1,2-Bis(diphenylphosphino)pentane |
| DPPH | 1,2-Bis(diphenylphosphino)hexane |
| *cis* and *trans* DPPE | 1,2-Bis(diphenylphosphino)ethylene |
| en | 1,2-Diaminoethane (ethylenediamine) |
| Et | Ethyl |
| EtOH | Ethanol |
| Me | Methyl |
| MeOH | Methanol |
| $Me_5$dien | 1,1,4,7,7-Pentamethyldiethylenetriamine |
| P | 1,1,1-Tris(diphenylphosphino methyl)ethane |
| $Pcy_3$ | Tricyclohexylphosphine |
| Ph | Phenyl |
| Phen | 1,10-Phenanthroline |

| | |
|---|---|
| $PPh_3$ | Triphenylphosphine |
| $PPr_3^i$ | Tri-isopropylphosphine |
| Siphos | Tris(trimethylsilylmethyl)phosphine |
| THF | Tetrahydrofuran |
| Tren | 2,2',2"-triaminotriethylamine |

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I wish to express my sincere gratitude to my two supervisors, Dr. D. G. Holah and Dr. A. N. Hughes for their far-sighted guidance, invaluable suggestions and constant encouragement throughout the course of this work. Grateful acknowledgments are also made to Dr. T. J. Griffith, Mr. C. Mallard and Mr. K. Pringnitz of the Science Instrumentation laboratory for their endless cooperation. Special thanks are also due to Mr. D. A. Jones, Mr. B. K. Morgan, Mr. A. J. Harding and Miss V. Petrovich for their frequent help.

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# DEDICATIONS

TO MY PARENTS

# CHAPTER I

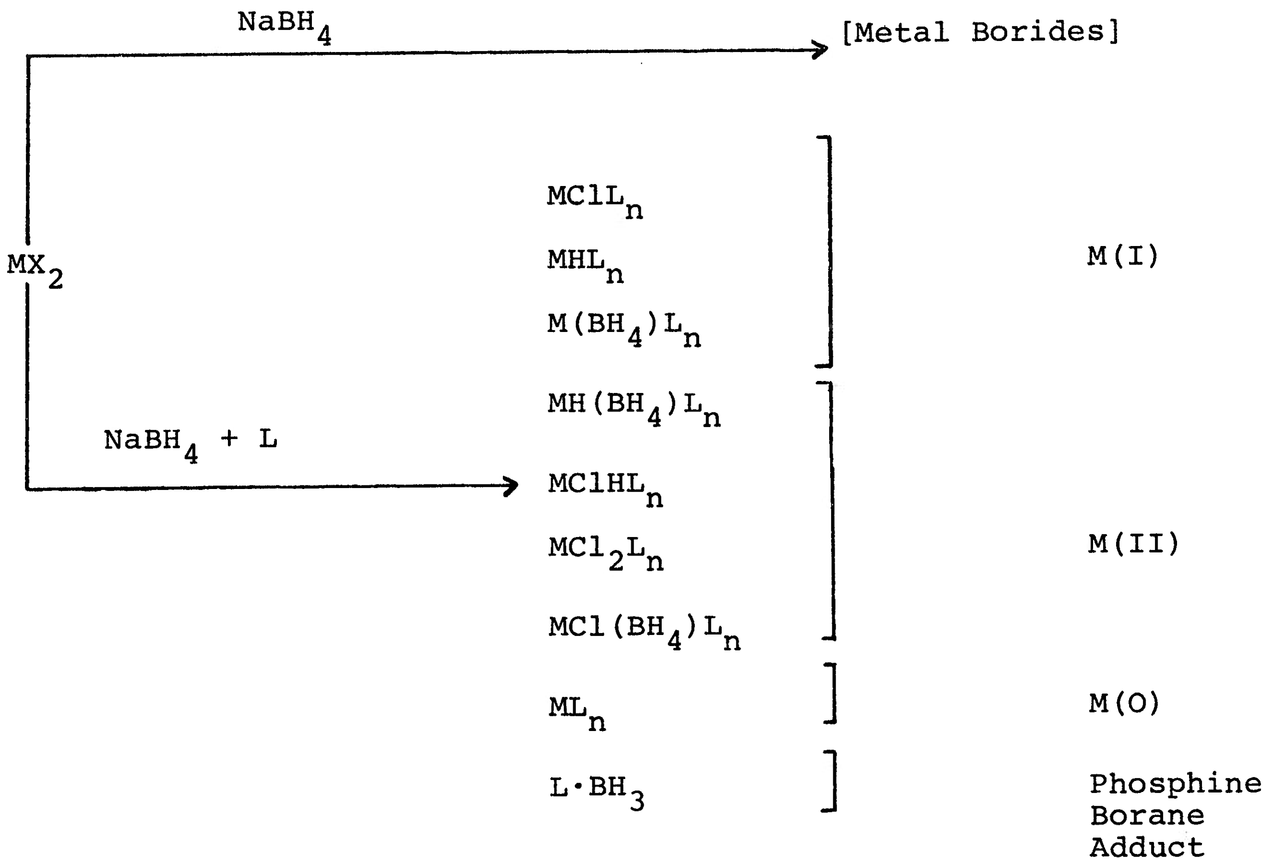
## 1 Introduction

The general importance of phosphine complexes with transition metals is reflected by the large number of papers on this subject which have been published in recent years. The interest in this field has been stimulated by the very wide range of chemical, structural, catalytic (1,2,3) and spectroscopic properties displayed by such complexes. For example, certain phosphine ligands may allow the formation of compounds containing transition metals with low or unusual oxidation states and they are among the few types of ligands which promote the formation of otherwise generally unstable transition metal compounds, such as certain organometallics, dinitrogen complexes (4), hydrides (5,6a,b,c), tetrahydroborates (7) etc.

Moreover, the fact that the phosphines may form complexes with a particular metal in different oxidation states and coordination numbers make this class of compound important for many catalytic processes in solution. In particular, hydrido and tetrahydroborato complexes containing phosphorus donor ligands have occupied the attention of organic, inorganic and physical chemists to a considerable degree in recent years because there is much more we need to know about such complexes. For example, the mechanisms of reduction of transition metal ions by various hydroborate systems in the presence of phosphines require much more study as do the mechanisms of the processes catalyzed by some of the resulting complexes.

By far the most common (7,8) method for the preparation of such tetrahydroborate derived complexes is the simple substitution of a $BH_4^-$ group for, in most cases, a halide ion, where the source of $BH_4^-$ is an ionic alkali metal-tetrahydroborate salt e.g. $NaBH_4$. It has been found that such reactions are very sensitive to reaction conditions. While the reactions of $MX_2$ (metal salts) with $NaBH_4$ with no complexing ligand present lead to only metal "borides" (3), the presence of ligands (especially phosphines) may allow the isolation of several types of products (3,9) as depicted in fig. (I) which, of course, represents a very simplified scheme for such complex reactions and which will be discussed in more detail, later in this thesis.

## Various Products Formed During Reactions Between $MX_2/L/NaBH_4$



(I)

The use of sodium tetrahydroborate, which is a strong reducing agent, makes these reactions fast and extremely sensitive to such factors as the rate of addition of sodium tetrahydroborate, the solvent system used, the molar ratio of metal to ligand to reducing agent and the temperature. Because of such sensitivity to conditions and the transient nature of some probable and proven intermediates, very little is known about the mechanisms of the reactions leading to hydrido and tetrahydroborato complexes.

One possible way to gain further information regarding these reactions is to use a milder reducing agent such as sodium cyanotrihydroborate. This thesis therefore reports the results of a preliminary investigation of the behaviour of transition metal-phosphine systems towards the cyanotrihydroborate ion.

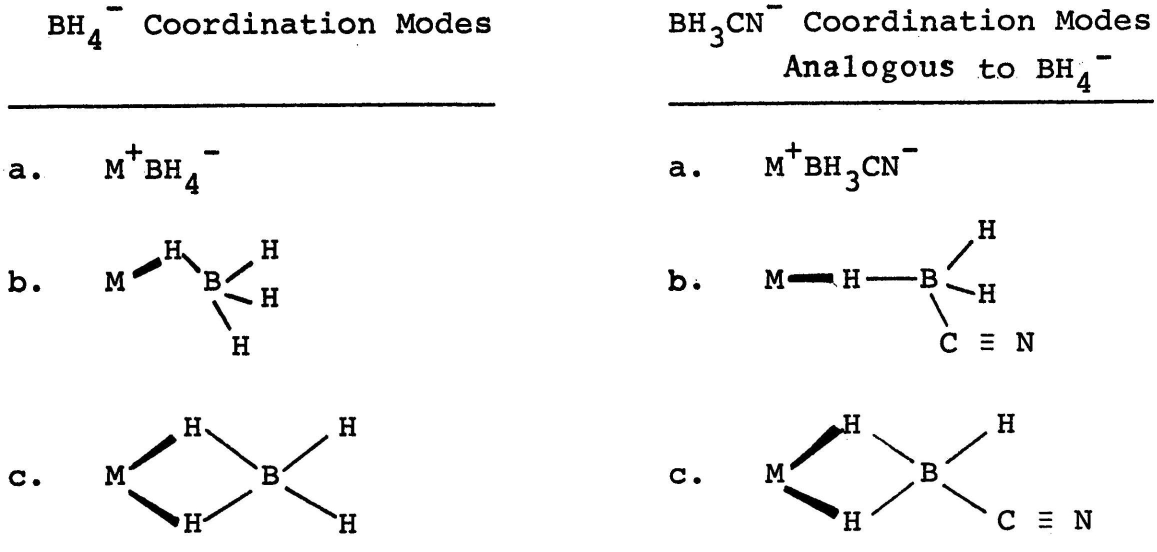
As our studies are mainly concerned with the reactions of sodium cyanotrihydroborate with cobalt(II) salts, the following sub-section of this thesis deals with several interesting aspects of the known chemistry of the cyanotrihydroborate ion.

## II. Some Aspects of the Chemistry of $BH_3CN^-$

### A. Bonding Abilities

The cyanotrihydroborate anion was first isolated as the lithium salt by Wittig (10a,b) in 1951. Eleven years elapsed before the first metal complex containing the $BH_3CN^-$ grouping was reported by Shriver (11) and, since then, the literature records few examples where complexes with cyanotrihydroborate have been synthesized. Nevertheless, the possibility of coordination of $BH_3CN^-$ by transition metal ions is obvious. When compared to $BH_4^-$, it offers some unique bonding possibilities as shown in fig. (II).

A Comparison of the Conceivable Coordination Modes of the $BH_3CN$ and $BH_4$ Anions



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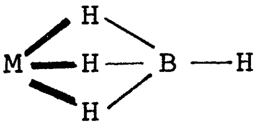

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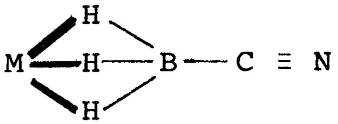

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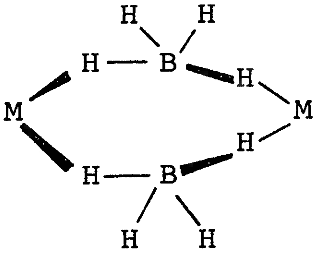

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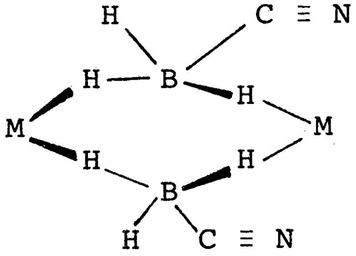

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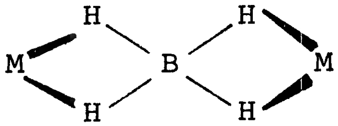

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## $BH_3CN^-$ Coordination Modes Different From $BH_4^-$

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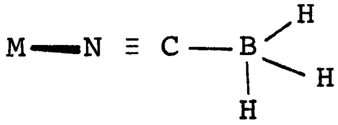

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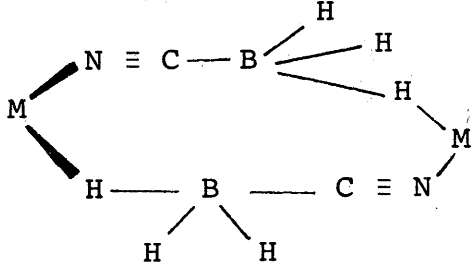

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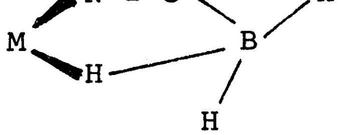

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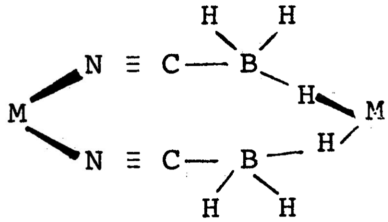

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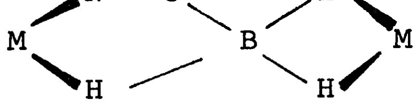
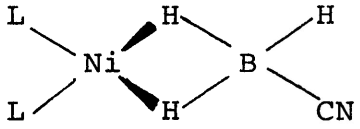


(II)

Besides all of the above possible modes of association of $BH_3CN^-$ with transition metals, there is every possibility for this ligand to isomerize, whereby the role of the nitrogen atom of the cyano group is taken by the carbon. The only literature report in this respect is that of Haines (12), who reports the reaction of $BH_3CN^-$ with $[Ru(\eta\text{-}C_5H_5)(PPh_3)_2(Me_2CO)]^+$. The authors have claimed on the basis of infrared spectral data alone the formation of at least two products in the above reaction, a cyanide complex, $Ru(CN)(\eta\text{-}C_5H_5)(PPh_3)_2$ and an isocyanotrihydroborate complex, $Ru(BH_3N\underline{C})(\eta\text{-}C_5H_5)(PPh_3)_2$, the separations of which were not effected. However, such claims require much more evidence than infrared data alone before such an interpretation can be considered as correct.

More understanding of the bonding abilities of $BH_3CN^-$ has been gained by the excellent work of Lippard and coworkers. These workers have synthesized and characterized the solid state structures of $[Ni(BH_3CN)(tren)]_2(BPh_4)_2$ (13), $Cu(BH_3CN)_2(Me_5dien)$ (14) and $[Cu(BH_3CN)(PPh_3)_2]_2$ (15). Both the nickel and the copper triphenylphosphine complexes involve a bridging cyanotrihydroborate structure as depicted in fig. (II, i ), whereas the other copper complex involves monodentate bonding of $BH_3CN^-$ as shown in fig. (II, f ).

However, in addition to the above solid state structural studies, Holah and coworkers (16) have strongly argued (on the basis of spectroscopic data alone) that only the hydrogens of $BH_3CN^-$ are involved in bonding in certain of the complexes that were synthesized in their laboratories. For example, one such nickel complex $Ni(BH_3CN)(PPh_3)_2$ has been assigned the following structure:



(III)

In summary, all the data which have been discussed above strongly suggest great versatility in the potential bonding abilities of $BH_3CN^-$. Furthermore, as shown in fig. (II), there are many more potential coordinating modes possible for $BH_3CN^-$, which still remain to be characterized.

Returning now to the simple $BH_4^-$ group, solid state studies involving single crystal X-ray diffraction, single crystal neutron diffraction and gas phase electron diffraction have shown that the $BH_4^-$ group can adopt mono, bi and tridentate modes of ligation in complexes of transition metals. Such coordination modes of $BH_4^-$ will be discussed in more detail in section VII. However, it should be pointed out at this stage that almost all of the conceivable coordination modes of the tetrahydroborate group have been characterized.

## B. Spectroscopic and Chemical Properties

Table 1 lists the observed infrared bands for sodium cyanotrihydroborate, sodium isocyanotrihydroborate and the Raman bands for potassium cyanotrihydroborate, together with the band assignments as proposed by Purcell and coworkers (17). The band assignments have been made with the aid of Raman polarization data and are consistent with assignments which have been made (18,19) for a large number of $BH_3X$($X=CO,Me_2S,NH_3$ etc) compounds. The position of the cyanide stretching frequency (2179 $cm^{-1}$) lies intermediate between that of ionic (20) (2080 $cm^{-1}$) and covalently bound cyanide (2267 $cm^{-1}$, as for example, in $CH_3CN$). For sodium isocyanotrihydroborate, the $\nu$CN shifts to a lower position (2070 $cm^{-1}$) with a corresponding shift in the BH

TABLE 1

Infrared and Raman Spectral Bands for $MBH_3CN$ [M=Na, K]

| IR<br>$NaBH_3CN$ | IR<br>$NaBH_3NC$ | Raman<br>$KBH_3CN$ | Polarizn. | Assignment |
|---|---|---|---|---|
| 2390(m) | - | 2390(vw) | p | |
| 2350(sh) | - | 2352(sh) | dp | e BH($^{10}B$) |
| 2320(s) | 2350 | 2334(s) | p | e BH($^{11}B$) |
| 2260(sh) | - | 2258(sh) | p | $a_1$ BH($^{10}B$) |
| 2240(m) | 2290 | 2239(m) | p | $a_1$ BH($^{11}B$) |
| 2179(s) | 2070 | 2177(vs) | p | $a_1$ CN |
| 1195(m) | 1175 | 1195(m) | dp | e BH |
| 1145(sh) | - | 1136(sh) | p | $a_1$ BH($^{10}B$) |
| 1135(s) | 1105 | 1123(m) | p | $a_1$ BH($^{11}B$) |
| 1020(w) | - | | | |
| 890(w) | 760 | 888(vw) | | $p^e$ BH |
| 865(w) | 645 | 870(vw) | | $a_1$ BC,BN |
| 385(m) | 330 | 358(w) | dp | e BCN |

ABBREVIATIONS: s, strong; m, medium; w, weak; sh, shoulder; v, very; p, polarized; dp, depolarized.

stretching frequency which shifts to a higher position (2350 $cm^{-1}$).

The proton NMR spectrum of $KBH_3CN$ in $D_2O$ consists of a sharp and well resolved quartet and septet. These arise from coupling of the protons with $^{11}B(I=3/2)$ and $^{10}B(I=3)$ nuclei respectively, with $J^{11}BH$ = 90 HZ and $J^{10}BH$ = 30 HZ. The centers of the proton multiplets were reported to coincide at $\delta$ = 4.2 upfield from the impurity water resonance signal (17).

The $^{11}B$ NMR spectrum of pure sodium cyanotrihydroborate in THF shows a well resolved quartet at $\delta$ =-62.2 with respect to the external $B(OCH_3)_3$ signal (21). However, when isocyanotrihydroborate ($BH_3NC^-$) is also present the $^{11}B$ NMR shows two quartets, one well resolved and strong at $\delta$ = -62.5 (relative to $B(OCH_3)_3$ and another much more diffuse at $\delta$ =-45.5 (relative to $B(OCH_3)_3$) with $J^{11}BH$ of 91 and 94 HZ respectively. This second quartet at $\delta$ =-45.5 has been assigned to $BH_3NC^-$ (21).

With regards to the chemical properties of $BH_3CN^-$ an early initial investigation carried out by Purcell (17) showed that $BH_3CN^-$ rapidly hydrolyses in strongly acidic solutions. The hydrolysis reaction was represented by the following equation:

$$BH_3CN^- + 3H_2O + HCl \longrightarrow H_3BO_3 + HCN + 3H_2 + Cl^-$$

The rate of hydrolysis in neutral aqueous solution is very slow, though some decomposition does occur after longer times (0.5% in 24 hr). However, such studies do not include the as yet unknown behaviour of $BH_3CN^-$ in solutions at elevated temperatures. This is important for our purposes, as will be seen later in this thesis.

More recently, Kay and associates (22), have found that certain metals can oxidize $BH_3CN^-$ to $[BH_3(CN)BH_2(CN)]^-$ This was found when cyclic voltammetry studies were carried out in acetonitrile solutions of $NaBH_3CN$ at molybdenum and vanadium electrodes. In both cases, the major borane-containing product was found to be the new anion $[BH_3(CN)BH_2(CN)]^-$, which was characterized as the sodium and tetra-n-butylammonium salts. Similar oxidized species are formed by mercury halides in donor solvents such as THF and $CH_3CN$. When mercury(I) halide is replaced by the stronger oxidizing agent, mercury(II), the reaction is faster and more complex and oligomerized $BH_2CN$ species are also formed. The authors have also interpreted the IR spectrum of $[BH_3(CN)BH_2(CN)]^-$. Thus a strong sharp band at 2255 $cm^{-1}$ and a sharp medium intensity band at 2205 $cm^{-1}$ were assigned to cyanide stretching modes for the bridging and the terminal cyanide groups respectively. On the other hand, two broad and strong bands at 2395 and 2355 $cm^{-1}$ were assigned to BH terminal stretching modes. The possibility of similar reactions occurring with Co(II) salts in this work will be discussed later in the thesis.

## III. Syntheses and Chemical Properties of $BH_3CN^-$ Complexes

Several different methods of synthesis have been employed to prepare complexes with the cyanotrihydroborate anion. Most of the complexes reported (so far) have been prepared in the presence of phosphine ligands, but a few complexes also involve a nitrogen donor ligand or a metal carbonyl species. However, the number of such complexes is quite low and, therefore, all the complexes prepared so far will be discussed, under appropriate headings, according to the metals involved.

### A. Group II-B to V-B:

No complexes of the cyanotrihydroborate ion with these groups of metals have been reported so far.

### B. Chromium, Molybdenum and Tungsten:

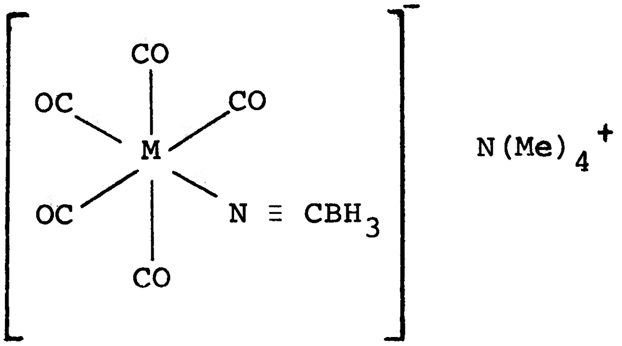
The complexes reported so far for this group are summarized in Table 2. All three complexes were synthesized (23) by boiling the metal hexacarbonyl with sodium cyanotrihydroborate in glyme for a period of 48 hours for chromium and 90 hours for molybdenum and tungsten. The appropriate anionic complexes ($[M(BH_3CN)(CO)]^-$) were then precipitated from aqueous solution as their tetramethylammonium salts. The compounds are less air sensitive in the solid state than in solution. For a given type of complex the sequence of relative air stability, both in the solid state and in solution is as follows: tungsten > chromium > molybdenum. The infrared spectra of all the above complexes show the cyanide stretching frequency of $BH_3CN^-$ at $\sim$2200 $cm^{-1}$, that is, an increase of $\sim$21 $cm^{-1}$ from the $C \equiv N$ stretching frequency in free $BH_3CN^-$ (2179 $cm^{-1}$). This led the authors (23) to propose structure (IV) for these cyanotrihydroborato derived complexes. It is

TABLE 2

Cyanotrihydroborate Complexes of the Chromium Triad

| No. | Complex | Colour | Reagents Used | Ref. |
|---|---|---|---|---|
| 1. | $[Me_4N][Cr(BH_3CN)(CO)_5]$ | Yellow | $Cr(CO)_6 + NaBH_3CN$ | 23 |
| 2. | $[Me_4N][Mo(BH_3CN)(CO)_5]$ | Yellow | $Mo(CO)_6 + NaBH_3CN$ | 23 |
| 3. | $[Me_4N][W(BH_3CN)(CO)_5]$ | Yellow | $W(CO)_6 + NaBH_3CN$ | 23 |

interesting to note that in this synthesis a carbonyl was replaced by $BH_3CN^-$ group without affecting the oxidation state of a metal.



(IV)

## C. Manganese, Technetium and Rhenium

Again no cyanotrihydroborato complexes have been reported for this triad.

## D. Iron, Ruthenium and Osmium:

Quite a number of complexes have been reported for this group and these are summarized in Table 3. Osmium is the only member of this triad for which there is no cyanotrihydroborate complex yet reported.

With iron, both chemical and electrochemical methods have been employed for the synthesis of the complexes.

## TABLE 3

### Cyanotrihydroborate Complexes of the Iron Triad

| No. | Complex | Colour | Reagents Used | Ref. |
|---|---|---|---|---|
| 1. | $Fe(BH_3CN)_2(CH_3CN)_4$ | | Electrochemical reaction | 22 |
| 2. | Cis $Fe(BH_3CN)_2(P(OR)_3)_4$<br>(R=Me or Et) | Yellow | $FeCl\cdot 2H_2O + P(OR)_3 + NaBH_3CN$<br>in $CH_3CN$ | 24 |
| 3. | Trans $Fe(BH_3CN)(P(OR)_3)_4$<br>(R=Me or Et) | Yellow | $FeCl_2\cdot 2H_2O + P(OR)_3 + NaBH_3CN$<br>in $CH_3OH$ | 24 |
| 4. | $Fe(BH_3N\underline{C})_2(Phen)_2$ * | Red | $Fe(CN)_2(Phen)_2 + BH_3/THF$ | 25 |
| | | | or | |
| | | | $Fe(CN)_2(Phen)_2 + B_2H_6$ (1 atm) | 11 |
| 5. | $Fe(BH_3CN)_2(Phen)_2$ | Purplish Red | $FeCl_2(Phen)_2 + KBH_3CN$ | 25 |

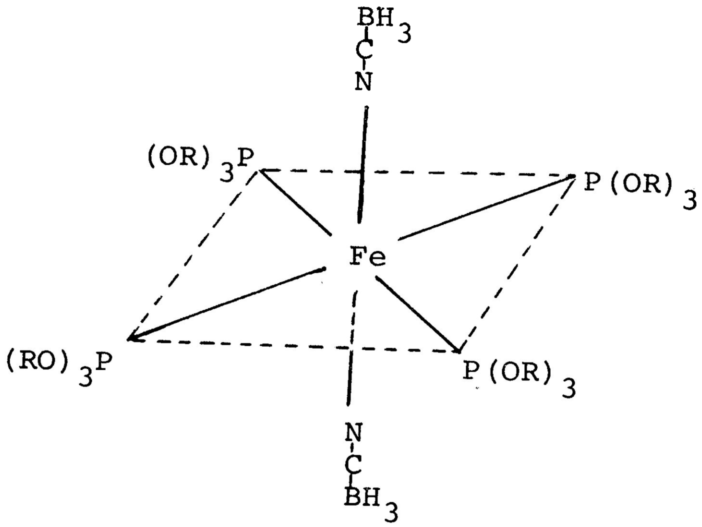
TABLE 3 continued....

| No. | Complex | Colour | Reagents Used | Ref. |
|---|---|---|---|---|
| 6. | $[Ru(BH_3CN)(NH_3)_5]Br$ | Yellow Green | $[Ru(NH_3)_5(H_2O)]^{2+}$ + NaBr + $NaBH_3CN$ in argon atmosphere | 26 |
| 7. | $[Ru(BH_3CN)(NH_3)_5]Br_2$ | | $[Ru(NH_3)_5(H_2O)]^{2+}$ + NaBr + $NaBH_3CN$ in air | 26 |
| 8. | $RuH(BH_3CN)(CO)_2(DBP)_2$ | Yellow | Ru(11)Carbonyl + DBP + $NaBH_3CN$ | 27 |

* The bar under C indicates coordination through carbon

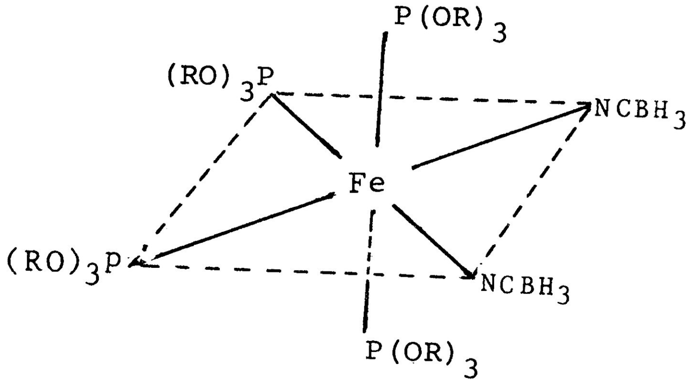
Drummond and coworkers (24) prepared the complex $Fe(BH_3CN)_2(P(OR)_3)_4$ by the reaction (in different solvents) of $FeCl_2.2H_2O$ with an excess of $NaBH_3CN$ in the presence of $P(OR)_3$ (R = Me or Et). Thus, when metathetical reactions were carried out in methanol, only the <u>trans</u> isomers were obtained (fig. V) as shown by the $^1H$-NMR, $^{31}P$-NMR and IR spectra of the products. The same reactions in acetonitrile yielded a mixture of isomers in the <u>cis</u>:<u>trans</u> ratio of 3:7. On the other hand, the electrochemical reaction in acetonitrile yields a mixture containing 65% of the <u>cis</u> isomer when R = Me, while when R = Et, the <u>cis</u> content of the mixture is only 30%.Electrochemical reactions in methanol were unsuccessful.

Purcell (25), has reported the synthesis of <u>cis</u> $Fe(BH_3CN)_2(Phen)_2$ and <u>cis</u> $Fe(BH_3N\underline{C})_2(Phen)_2$. The cyanotrihydroborato complex was prepared by displacement of chloride from $FeCl_2(Phen)_2$ by the $BH_3CN^-$ group in THF solution at reflux temperatures whereas the isocyanotrihydroborato complex was prepared by the addition of $BH_3$ to $Fe(CN)_2(Phen)_2$ in THF solution at elevated temperatures. In both cases there was no reduction of the metal ion. The authors report that no suitable solvents were found for these complexes for solution studies. When the



Trans Isomer of $Fe(BH_3CN)_2(P(OR)_3)_4$

(V-A)



Cis Isomer of $Fe(BH_3CN)_2(P(OR)_3)_4$

(V-B)

cyanotrihydroborate complex is heated under reduced pressure at 170°C for several days small changes in the infrared spectrum result, whereas the same treatment of the isocyanotrihydroborato complex results in drastic changes in the infrared spectrum, indicating loss of $BH_3$. Shriver (11) has also synthesized the same isocyanotrihydroborate complex by treating $Fe(CN)_2(Phen)_2$ with diborane at a pressure of 1 atmosphere for 5 to 9 days at room temperature. It is interesting to note that this report was the first to appear in the literature which described the coordination of the cyanotrihydroborate ion.

Other examples where reductions of metals were not effected by $NaBH_3CN$ are $[Ru(BH_3CN)(NH_3)_5]Br$ and $RuH(BH_3CN)(CO_2)(DBP)_2$, This yellow solid, $RuH(BH_3CN)(CO)_2(DBP)_2$, is the first example of a mixed hydride cyanotrihydroborate complex in this triad reported in the literature (27).

## E. Cobalt, Rhodium and Iridium

Cyanotrihydroborate complexes of all the three members of this group have been reported and these are listed in Table 4.

TABLE 4:

Cyanotrihydroborate Complexes of the Cobalt Triad

| No. | Complex | Colour | Reagents Used | Ref. |
|---|---|---|---|---|
| 1. | $Co(BH_3CN)(Diphos)_2$ | Yellow Green | $CoCl_2 \cdot 6H_2O$ + Diphos + $NaBH_3CN$ | 16 |
| 2. | $Co(BH_3CN)(DBP)_4$ | Yellow Green | $CoCl_2 \cdot 6H_2O$ + DBP + $NaBH_3CN$ | 16 |
| 3. | $Rh(BH_3CN)(PPh_3)_3$ | Yellow | $RhCl(PPh_3)_3$ + $NaBH_3CN$ | 9 |
| 4. | $Rh(BH_3CN)(CO)(PPh_3)_2$ | Yellow | $Rh(ClO_4)(CO)(PPh_3)_2$ + $NaBH_3CN$ | 28 |
| 5. | $Rh(BH_3CN)(CO)(DBP)_3$ | Orange | $RhCl_2(CO)_2$ + DBP + $NaBH_3CN$ | 9 |
| 6. | $Rh(BH_3CN)(CO)(N_2)(DBP)_3$ | Yellow | $RhCl_3(DBP)_3$ + $NaBH_3CN$ | 9 |
| 7. | $IrH(BH_3CN)(PPh_3)_3$ | White | $IrClH(PPh_3)_3$ + $NaBH_3CN$ | 29 |
| 8. | $Ir(BH_3CN)(CO)(Pcy_3)_2$ | Yellow | $Ir(ClO_4)(CO)(Pcy_3)_2$ + $NaBH_3CN$ | 28 |

Both $Co(BH_3CN)(DBP)_4$ and $Co(BH_3CN)(Diphos)_2$ were prepared in an analogous way. Thus, when $CoCl_2{\cdot}6H_2O$ was treated with an excess of $NaBH_3CN$ in the presence of the appropriate ligand, yellow green complexes were precipitated. Unlike the Diphos complex, recrystallization of the DBP complex from nitrogen-saturated solvents resulted in the uptake of varying amounts of dinitrogen.

The air-stable rhodium and iridium complexes, $Rh(BH_3CN)(PPh_3)_2(CO)$ and $Ir(BH_3CN)(Pcy_3)_2(CO)$ were prepared according to the following equation:

$$\underline{\text{trans}}\ M(ClO_4)L_2(CO) + NaBH_3CN \text{ — } \underline{\text{trans}}\ M(BH_3CN)L_2(CO) + NaClO_4$$

In general, the stability and/or inertness of these compounds show the sequence Rh > Ir. The cyanotrihyroborate grouping in these complexes is coordinated through the nitrogen of the cyano group as inferred from the vibrational spectra which show a small increase ($\sim$ 13 to 20 $cm^{-1}$) in the $C \equiv N$ stretching frequency as compared with that of the free ion.

Several other Rh(I) and Rh(III) cyanotrihydroborato complexes have been synthesized by Holah and coworkers (9). Thus when $[RhCl(CO_2)]_2$ is treated with $NaBH_3CN$ in the presence of DBP, $Rh(BH_3CN)(DBP)_3(CO)$ resulted, that is, a rhodium(I) complex is formed. A similar reaction with $RhCl_3(DBP)_3$ produces $Rh(BH_3CN)(DBP)_3(CO)(N_2)$. The reduction by $NaBH_3CN$ of Rh(III) to Rh(I) is thought (9) to involve a Rh(III)-dihydride intermediate which, under a nitrogen atmosphere undergoes exchange of dihydrogen for molecular nitrogen. This suggestion is well supported by the preparation of the closely related compound $RhH_2(BH_3CN)(PPh_3)_3$ from $RhCl(PPh_3)_3$ in the presence of an excess of $NaBH_3CN$, by the same authors. This complex is very unstable in solution and decomposes immediately by eliminating a gas in solvents such as benzene and chloroform.

### F. Nickel, Palladium and Platinum

Nickel is the only member of this group for which $BH_3CN^-$ complexes are known. Table 5 summarizes the complexes of this triad.

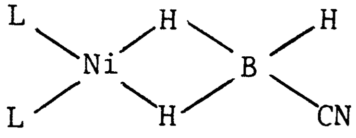
As has been the case with most of the transition metals discussed in the previous pages, the complexes

TABLE 5:

Cyanotrihydroborate Complexes of the Nickel Triad

| No. | Complex | Colour | Reagents Used | Ref. |
|---|---|---|---|---|
| 1. | $Ni(BH_3CN)(PPh_3)_2$ | Yellow | $NiCl(PPh_3)_3 + NaBH_3CN$ | 16,29 |
| 2. | $NiH(BH_3CN)(DBP)_3$ | Brown | $NiCl_2 \cdot 6H_2O + DBP + NaBH_3CN$ | 16,29 |
| 3. | $NiCl(BH_3CN)(Diphos)_2$ | Orange | $NiCl_2 \cdot 6H_2O + Diphos + NaBH_3CN$ | 16,29 |
| 4. | $Ni(BH_3CN)(en)_2 \cdot THF$ | Purple | $NiCl_2(en)_2 + NaBH_3CN$ | 30 |
| 5. | $[Ni(BH_3CN)(tren)]_2(BPh_4)_2$ | Purple | $NiSO_4 \cdot 6H_2O + tren + NaBH_3CN$ | 14 |
| 6. | $NiH(BH_3CN)(PPh_3)_2$ | Orange | $NiCl_2 \cdot 6H_2O + PPh_3 + NaBH_3CN$ | 16,29 |

prepared for nickel by the milder reducing agent $NaBH_3CN$ are not formed by reduction of the metal(II) ion. Thus a variety of nickel(II) cyanotrihydroborato complexes have been synthesized by Holah and coworkers (16,29), such as $NiH(BH_3CN)(PPh_3)_2$, $NiH(BH_3CN)(DBP)_3$ and $NiCl(BH_3CN)(Diphos)_2$. All these complexes were synthesized using essentially the same experimental conditions whereby $NiCl_2 \cdot 6H_2O$ was treated with $NaBH_3CN$ in the presence of the appropriate phosphine. However, a Ni(I)-$BH_3CN$ complex has also been reported (by the same group) and this was prepared by replacing a halide grouping from $NiClL_2$ ($L=PPh_3$) by treatment with $NaBH_3CN$, again with no change in the oxidation state of the metal. This Ni(I) complex is interesting and in particular its electronic and vibrational spectra are consistent with the proposed structure, as shown below:



(III)

The same studies also showed that the nature of the phosphine ligand is also important in determining the product formed from $NaBH_3CN$ reactions. Thus, the Ni(I) triphenylphosphine complex $Ni(BH_3CN)(PPh_3)_2$ is formed when $NiCl(PPh_3)_3$ is treated with $NaBH_3CN$, whereas the closely related $NiCl(DBP)_3$ - $NaBH_3CN$ reaction yields only $Ni(DBP)_2$.

Lippard and group (14) have also synthesized and characterized a nickel cyanotrihydroborato complex with a nitrogen donor ligand. The complex, $[Ni(BH_3CN)(tren)]_2(BPh_4)_2$, was synthesized by treating $NiSO_4$ with tren in chloroform and then adding the $NaBH_3CN$. The dark purple complex was precipitated by adding sodium tetraphenylborate to the reaction mixture. The compound was characterized by X-ray diffraction, which showed a bridging $BH_3CN^-$ structure. More details on the structure of this complex will appear later in section IV-A.

### G. Copper, Silver and Gold:

More cyanotrihydroborato complexes are known for this triad than for any other group of transition metals.

Copper has been most extensively studied while few complexes are known for silver and none for gold. All the known complexes of this triad are depicted in Table 6.

The common method employed for the preparation of copper-cyanotrihydroborate complexes in the presence of a phosphine ligand, is the displacement of a halide, either from a Cu(I) or (II) salt and/or from a Cu(I) or (II)-phosphine-halide complex, by the $BH_3CN^-$ grouping. However, slight differences in reaction conditions can lead to significantly different compounds. Thus, when $CuCl(PPh_3)_3$ in ethanol/chloroform is treated with $NaBH_3CN$, colorless crystals of $Cu(BH_3CN)(PPh_3)_3$ with melting point 157-158°C are formed. This complex is insoluble in cold benzene whereas in hot benzene it decomposes to $[Cu(BH_3CN)(PPh_3)_2]_2$. On the otherhand, $CuCl_2 2H_2O$ and triphenylphosphine in methanol, when treated with $NaBH_3CN$, form a complex with the same empirical formula as shown above i.e. $Cu(BH_3CN)(PPh_3)_3$, although the two compounds show significant differences in terms of solubilities melting points and vibrational spectra. These differences were explained (16, 29) in terms of differences in bonding between the metal and the $BH_3CN^-$, the first one involving a $Cu\text{-}NCBH_3$

TABLE 6:

Cyanotrihydroborate Complexes of the Copper Triad

| No. | Complex | Colour | Reagents Used | Ref. |
|---|---|---|---|---|
| 1. | $Cu(BH_3CN)(PPh_3)_3$ | White | $CuCl_2 \cdot 2H_2O + PPh_3 + NaBH_3CN$ | 16,29 |
| 2. | $Cu(BH_3CN)(PPh_3)_3 \cdot CHCl_3$ | White | $CuCl(PPh_3)_3 + NaBH_3CN$ | 31,16 |
| 3. | $Cu(BH_3CN)(AsPh_3)_3 \cdot CHCl_3$ | White | $CuCl + AsPh_3 + NaBH_3CN$ | 31 |
| 4. | $Cu(BH_3CN)(SbPh_3)_3$ | White | $CuCl + SbPh_3 + NaBH_3CN$ | 31 |
| 5. | $[Cu(BH_3CN)(PPh_3)_2]_2$ | White | $CuCl(PPh_3)_2 + NaBH_3CN$ | 31 |
| 6. | $Cu(BH_3CN)(DBP)_3$ | White | $CuCl_2 \cdot 2H_2O + PPh_3 + NaBH_3CN$ | 16,29 |
| 7. | $Cu(BH_3CN)(PEt(Ph)_2)_3$ | White | $CuCl_2 \cdot 2H_2O + PEt(Ph)_2 + NaBH_3CN$ | 16 |

TABLE 6 continued...

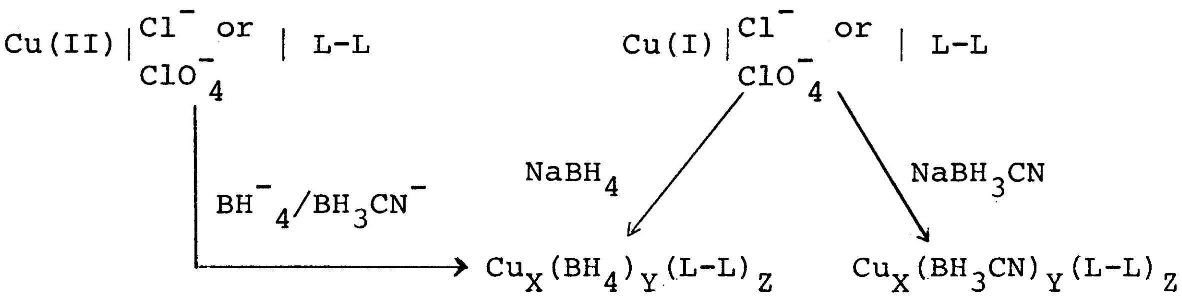
| No. | Complex | Colour | Reagents Used | Ref. |
|---|---|---|---|---|
| 8. | $Cu(BH_3CN)(Diphos)_{1.5}$ | White | $CuCl_2 \cdot 2H_2O$ + Diphos + $NaBH_3CN$ | 16 |
| 9. | $Cu(BH_3CN)_2(Me_5dien)$ | Royal Blue | $CuBr_2$ + $(Me_5dien)$ + $NaBH_3CN$ | 13 |
| 10. | $Ag(BH_3CN)(PPh_3)_3 \cdot CHCl_3$ |  | $CuCl(PPh_3)_3$ + $NaBH_3CN$ | 31 |
| 11. | $Ag(BH_3CN)(P(p\text{-}MeC_6H_4)_3)_4$ | White | AgCl + $P(p\text{-}MeC_6H_4)_3$ + $NaBH_3CN$ | 31 |

type of linkage and the second a Cu-H-$BH_2CN$ type of linkage.

Another interesting complex is the paramagnetic, $Cu(BH_3CN)_2(Me_5dien)$. This complex was synthesized (13), by treating copper(II) bromide with $NaBH_3CN$ in the presence of $Me_5dien$. The deep royal blue compound so formed was recrystallized from warm methanol. The complex is unstable at high temperatures and decomposes in acetone. The complex has been fully characterized spectroscopically and crystallographically (see section IV-A). This synthesis reveals that in the presence of nitrogen donor ligands, Cu(II) is not reduced to Cu(I) by $NaBH_3CN$ alone.

All the copper cyanotrihydroborato complexes prepared by Lippard's group (31) in the presence of group V-A donor ligands involves the same technique. A typical representative, $[Cu(BH_3CN)(PPh_3)]_2$, was synthesized by dissolving $CuCl(PPh_3)_2$ in chloroform and adding to it an ethanolic solution of $NaBH_3CN$. The reaction mixture, on standing for 24 hrs., deposits large colorless crystals. Occasionally, such complexes also take up a molecule of chloroform during crystallization from that solvent.

More recently (32) a variety of cyanotrihydroborato, tetrahydroborato and some other metal phosphine complexes of copper have been prepared in our laboratories. At this stage complete details regarding these reactions are not available. However, the reactions being studied are between Cu(II) salts or Cu(I)-bidentate phosphine complexes and $NaBH_3CN$ or $NaBH_4$ in the presence or absence of the appropriate phosphine. The bidentate phosphines used in these syntheses were of the type $Ph_2P-(CH_2)_n-PPh_2$ (where, n=1-6). The types of products obtained and the general sequence followed for their reaction can be represented as follows:



where X = 1 or 2, Y = 1 or 2, and Z = 1, 2, or 3.

(VI)

## H. Lanthanides and Actinides:

Marks and Kolb (33) have synthesized $U(BH_3CN)(C_5H_5)$, which is the only cyanotrihydroborate complex known among these elements. The synthesis can be best represented by the following equation:

$$UCl(C_5H_5) + NaBH_3CN \xrightarrow[N_2\text{atmosphere}]{\text{THF}} U(BH_3CN)(C_5H_5) + NaCl$$

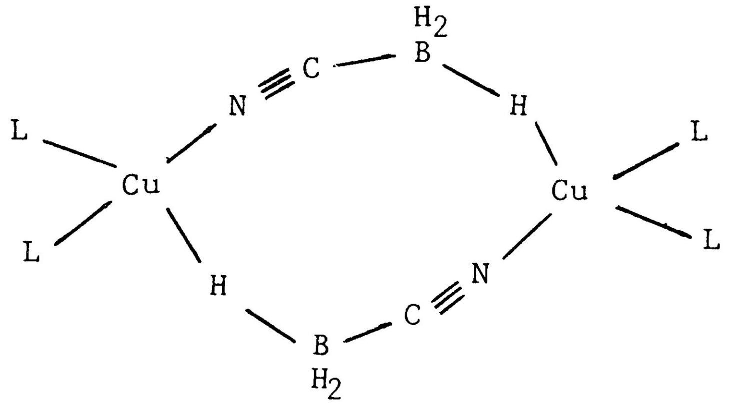
The green cyanotrihydroborate complex so formed immediately blackens and burns on exposure to air. Because of the difficulty in finding a suitable solvent, purification of the solid was done by soxhlet extraction with benzene. Structural details of the complex are unclear; its infrared spectrum suggests a structure similar to the dimeric copper complex $[Cu(BH_3CN)(PPh_3)_2]_2$ whereas $^1H$-NMR suggests a structure like $M\text{-}\underline{N}CBH_3$.

## IV. Structural Analysis of $BH_3CN^-$ Complexes:

### A. Single Crystal X-ray Diffraction:

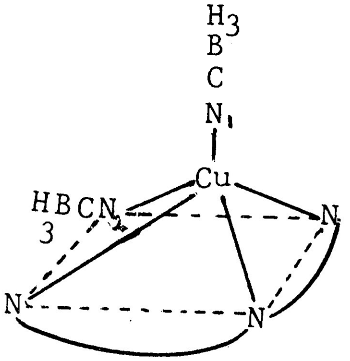
A complete understanding of the properties of a molecular system must rest upon a firm structural foundation. Then, by comparison of the physical properties (particularly infrared spectra) of complexes of known structure with the physical properties of other complexes, the structures of the latter may hopefully be deduced. Lippard (31, 14, 13) and his coworkers have contributed significantly in this respect by establishing the structures of three cyanotrihydroborato complexes viz. $[Cu(BH_3CN)(PPh_3)_2]_2$, $Cu(BH_3CN)_2(Me_5dien)$ and $[Ni(BH_3CN)(tren)]_2(BPh_4)_2$. Unfortunately these are the only published complexes of the cyanotrihydroborate ion for which structures have been definitely established although the structure determination of one interesting cyanotrihydroborate complex of cobalt made in this work is currently in progress.

The complex $[Cu(BH_3CN)(PPh_3)_2]_2$ contains four coordinate copper in a distorted tetrahedral geometry, defined by two phosphorus atoms (of $PPh_3$) and a hydrogen and nitrogen of two different $BH_3CN^-$ groupings. Thus the dimeric unit contains bridging $BH_3CN^-$ involving a single hydrogen from the $BH_3$ grouping and a nitrogen from the cyano grouping to form a bridge between two Cu atoms as shown in fig. VIII. This is a rare example of the type of co-ordination where only a single hydrogen of a hydroborate group is bonded to a metal. The ten-membered ring so formed with this bridging structure is considerably distorted, where the local site symmetry at the boron atoms of the two cyanotrihydroborate ligands is distinctly different. This accounts for the appearance of two strong cyanide stretching bands (2190, 2207 $cm^{-1}$) in the infrared spectrum of the complex.



(VIII)

Another structure involving bridging $BH_3CN^-$ is the complex $[Ni(BH_3CN)(tren)]_2(BPh_4)_2$. Here, the nickel is octahedrally bonded to all four nitrogens of the (tren) ligand and a nitrogen and hydrogen of two different cyanotrihydroborate groupings. The ten-membered ring in this complex is almost planar and the two site symmetries at the $BH_3CN^-$ grouping are the same. This accounts well for the single strong cyanide stretching frequency observed (14) at 2221 $cm^{-1}$ in the vibrational spectrum of the complex. This shift to higher frequency, compared with that of the Cu dimer, discussed previously, is consistent with the measured C-N distances of $BH_3CN^-$ in the two complexes. These are 1.122 $A^0$ for the nickel complex and 1.15 $A^0$ for the copper complex.



(IX)

The third complex $Cu(BH_3CN)_2(Me_5dien)$ studied crystallographically shows a geometry based on a square base pyramid where one of the $BH_3CN^-$ ligands occupies the apical position as shown in fig. IX. In this complex, the Cu-N distances of the two cyanotrihydroborate groupings are strikingly different ($Cu-N_1$, 1.980 A°, $Cu-N_2$, 2.153 A°, see fig. IX). Also the basal $BH_3CN^-$ has a long N-C bond (1.137 A°) whereas the one at the apical position has a shorter N-C distance (1.126 A°). Again, these observations explain very well the vibrational spectrum of the complex which shows two strong cyanide stretching signals at 2210 and 2190 $cm^{-1}$. The one at the higher position has been assigned to the apical and other to the basal $BH_3CN^-$ ligands.

## B. Vibrational Spectroscopy

It is apparent therefore that for metal-cyanotrihydroborate complexes, one of the most significant structural questions concerns the mode by which the cyanotrihydroborato group is attached to the metal atom.

Although our definite structural information has

TABLE 7:

Selected Features of the Infrared Spectral Data of Cyanotrihydroborate Complexes

| No. | Complex | Inferred Bonding | BH Deformation | νBH Terminal | M-H-B Bridge | νCN | Others | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1. | $[Me_4N][Cr(BH_3CN)(CO)_5]$ | $M—NCBH_3$ | | 2337(w,br)<br>2310(w,sh) | | 2207(vw)<br>Δ28 | 1937(s)<br>CO | 23 |
| 2. | $[Me_4N][Mo(BH_3CN)(CO)_5]$ | | | 2335(vw,br)<br>2290(vw,br) | | 2200(vw)<br>Δ21 | 1935(s)<br>CO | 23 |
| 3. | $[Me_4N][W(BH_3CN)(CO)_5]$ | | | 2335(vw,br)<br>2312(vw,sh) | | 2200(vw)<br>Δ21 | 1928(s)<br>CO | 23 |
| 4. | $Fe(BH_3CN)_2(CH_3CN)_4$ | | | 2350<br>2370(sh) | | 2210<br>Δ31 | 2290<br>$CN(CH_3CN)$ | 22 |
| 5. | Cis $Fe(BH_3CN)_2(P(OR)_3)_4$<br>[R = Me or Et] | | | | | 2208(s)<br>Δ27<br>2212(s)<br>Δ33 | | 24 |
| 6. | Trans $Fe(BH_3CN)_2(P(OR)_3)_4$<br>[R = Me or Et] | | | 2323<br>2368 | | 2202<br>Δ23 | | 24 |
| 7. | $Fe(BH_3N\underline{C})_2(Phen)_2$ | $M—\underline{C}NBH_3$ | | | | 2161<br>- Δ18<br>2146<br>- Δ33 | | 25 |

TABLE 7: continued...

| No. | Complex | Inferred Bonding | BH Deformation | ν BH Terminal | M-H-B Bridge | ν CN | Others | Ref. |
|---|---|---|---|---|---|---|---|---|
| 8. | $Fe(BH_3CN)_2(Phen)_2$ | M —NCBH$_3$ | | | | 2198<br>Δ19<br>2186<br>Δ7 | | 25 |
| 9. | $[Ru(BH_3CN)(NH_3)_5]Br$ | | | | | 2170(s)<br>Δ9 | | 25 |
| 10. | $[Ru(BH_3CN)(NH_3)_5]Br_2$ | | | | | 2206(s)<br>Δ27 | | 26 |
| 11. | $RuH(BH_3CN)(CO)_2(DBP)_2$ | | 1120 | 2340(s) | | 2110<br>-Δ169 | 1845<br>M-H | 27 |
| 12. | $Co(BH_3CN)(Diphos)_2$ | | 1112(s) | 2336(s) | | 2190<br>Δ11 | | 16 |
| 13. | $Co(BH_3CN)(DBP)_4$ | | 1112(s) | 2340(sh) | | 2188(s)<br>Δ9 | | 16 |
| 14. | $RhH_2(BH_3CN)(PPh_3)_3$ | | 1118(s) | 2328(s)<br>2260(sh) | | 2207<br>Δ28 | 2060<br>2048 MH | 9 |
| 15. | $Rh(BH_3CN)(CO)(PPh_3)_2$ | | | 2360 | | 2192<br>Δ13 | 1997<br>CO | 28 |

TABLE 7: continued...

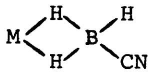
| No. | Complex | Inferred Bonding | BH Deformation | $\nu$ BH Terminal | M-H-B Bridge | $\nu$ CN | Others | Ref. |
|---|---|---|---|---|---|---|---|---|
| 16. | $Rh(BH_3CN)(CO)(DBP)_3$ | $M$ —$NCBH_3$ | 1114(m) | 2340(m) |  | 2202(m)<br>Δ23<br>2188(sh)<br>Δ9 | 1984<br>CO | 9 |
| 17. | $Rh(BH_3CN)(CO)(N_2)(DBP)_3$ |  | 1114(m) | 2335 |  | 2205<br>Δ26 | 2108<br>$N_2$ | 9 |
| 18. | $IrH(BH_3CN)(PPh_3)_3$ |  | 1122(s) | 2328(sb) |  | 2180(m)<br>Δ1 | 2135(w)<br>MH | 29 |
| 19. | $Ir(BH_3CN)(CO)(Pcy_3)_2$ |  | 1113 | 2375(sb) |  | 2200<br>Δ21 | 1957<br>CO | 28 |
| 20. | $Ni(BH_3CN)(PPh_3)_2$ |  | 1118(s) | 2340(sb) | 2070 | 2185<br>Δ6 |  | 16 |
| 21. | $NiH(BH_3CN)(DBP)_3$ |  | 1133(m) | 2334(sb) | 2138(m) | 2201(s)<br>Δ22 |  | 16 |
| 22. | $NiCl(BH_3CN)(Diphos)_2$ | $M$ —$NCBH_3$ | 1103(s) | 2340(sb) |  | 2192(s)<br>Δ13 | 343(m)<br>M-Cl | 16 |

TABLE 7: continued...

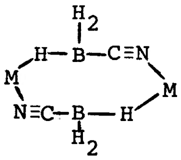
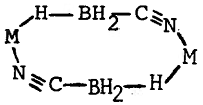
| No. | Complex | Inferred Bonding | BH Deformation | ν BH Terminal | M-H-B Bridge | νCN | Others | Ref. |
|---|---|---|---|---|---|---|---|---|
| 23. | $Ni(BH_3CN)(en)_2 \cdot THF$ | M —NCBH$_3$ |  | 2340<br>2370 |  | 2200<br>Δ21 |  | 30 |
| 24. | $NiH(BH_3CN)(PPh_3)_2$ |  | 1120 | 2336 | 2140(m) | 2200(s)<br>Δ21 |  | 16 |
| 25. | $[Ni(BH_3CN)(tren)](BPh_4)_2$* |  | 1130(sh)<br>1114(m) | 2380(s)<br>2372(sh)<br>2350(sh) | 2200(m)<br>2241(m)<br>2276(m) | 2221<br>Δ42 |  | 14 |
| 26. | $Cu(BH_3CN)(PPh_3)_3$ | - | 1115(s) | 2340(sb)<br>2280(sh) | 2122(ms) | 2185(s)<br>Δ6 |  | 16 |
| 27. | $Cu(BH_3CN)(PPh_3)_3 \cdot CHCl_3$ | M —NCBH$_3$ | 1125(sh)<br>1115(s) | 2358(sh)<br>2330(s) |  | 2192(s)<br>Δ13 |  | 31 |
| 28. | $[Cu(BH_3CN)(PPh_3)_2]_2$* |  | 1100(vs) | 2376(s)<br>2350(m)<br>2388(sh)<br>2407(sh) | 2200(b) | 2190(s)<br>Δ11<br>2207(s)<br>Δ28 |  | 31 |
| 29. | $Cu(BH_3CN)(AsPh_3)_3 \cdot CHCl_3$ | M —NCBH$_3$ | 1123(sh)<br>1113(s) | 2360(sh)<br>2325(s) |  | 2187(s)<br>Δ8 |  | 31 |

TABLE 7: continued...

| No. | Complex | Inferred Bonding | BH Deformation | νBH Terminal | M-H-B Bridge | ν CN | Others | Ref. |
|---|---|---|---|---|---|---|---|---|
| 30. | $Cu(BH_3CN)(SbPh_3)_3$ | M —NCBH$_3$ | 1127(sh)<br>1115(s) | 2360(sh)<br>2331(s) | | 2191(s)<br>Δ12 | | 31 |
| 31. | $Cu(BH_3CN)_2(Me_5dien)$* | | 1123(s)<br>1112(s) | 2346(s)<br>2396(sh)<br>2284(sh) | | 2192(s)<br>Δ13<br>2210(s)<br>Δ31 | | 13 |
| 32. | $Cu(BH_3CN)(DBP)_3$ | | 1119(s) | 2350(sb)<br>2290(sh) | | 2188(s)<br>Δ9 | | 16 |
| 33. | $Cu(BH_3CN)(Diphos)_{1.5}$ | | 1116(s) | 2340(sb) | 2106(sb) | 2188(s)<br>Δ9 | | 16 |
| 34. | $Cu(BH_3CN)(PEtPh_2)_3$ | M —NCBH$_3$ | 1112(s) | 2336(s) | | 2190(s)<br>Δ11 | | 16 |
| 35. | $Ag(BH_3CN)(PPh_3)_3 \cdot CHCl_3$ | " | 1126(sh)<br>1113(s) | 2350(sh)<br>2321(s) | | 2180(s)<br>Δ1 | | 31 |
| 36. | $U(BH_3CN)(C_5\text{-}H_5)_3$ | | 1104 | 2462(w)<br>2360(m)<br>2240(ms) | | 2178<br>- Δ1 | | 33 |

FOOTNOTE: Δ represents the difference between the observed $^{\nu}CN$ in the complex and $^{\nu}CN$ in free $BH_3CN^-$

+ towards higher frequency

- towards lower frequency

* Structure known through X-ray crystallography

ABBREVIATIONS:

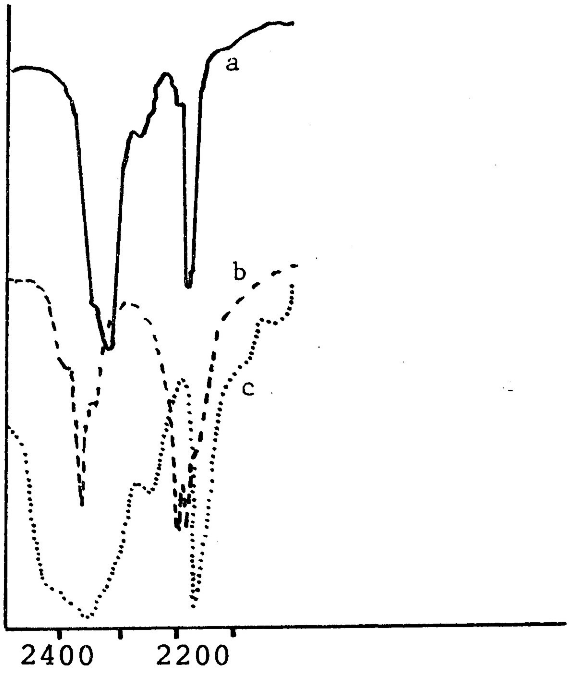
s, strong; m, medium; v, very; w, weak; sh, shoulder; br, broad.

been obtained from X-ray crystallography, infrared spectroscopy is also an indispensible adjunct and has been used in its own right to infer structures. Thus, the selected features of the vibrational spectral data published for the various cyanotrihydroborate complexes, prepared so far, are listed in Table 7.

As discussed earlier (page 9 ) the infrared spectrum of the $BH_3CN$ ion shows (Table 1) a strong cyanide stretching frequency at 2179 $cm^{-1}$ and a strong and broad BH stretching frequency at 2320 $cm^{-1}$. Clearly, therefore, in metal-cyanotrihydroborato complexes this region in their infrared spectra (i.e. from 2000 to 2400 $cm^{-1}$) is important for structural elucidations.

The infrared spectral data for all the proposed and known $BH_3CN^-$ complexes of the type $M \leftarrow NCBH_3$, show stretching vibrations of the $C \equiv N$ unit of $BH_3CN^-$ ranging from 2080 to 2212 $cm^{-1}$, compared with the value of 2179 $cm^{-1}$ in ionic $NaBH_3CN$. These shifts in $\nu CN$ are considerably smaller when compared to the corresponding nitrile (34) and cyanotriphenylborato (31), complexes which show corresponding shifts in the range of $\sim$40 to 50 $cm^{-1}$. In fact, cyanotrihydroborate complexes such as $Ag(BH_3CN)(PPh_3)_2 \cdot CHCl_3$ and $IrH(BH_3CN)_2(PPh_3)_3$ which show the $\nu$ CN at 2180 $cm^{-1}$ (i.e. virtually unshifted from the position in $NaBH_3CN$ contain either an extremely weak $M \leftarrow NCBH_3$ coordination or, more likely, a coordination which involves only the hydrogen atom(s) of the $BH_3$ unit of $BH_3CN^-$.

A well recognized complex $Cu(BH_3CN)_2(Me_5dien)$ is the only cyanotrihydroborato complex where X-ray crystallography has confirmed (fig. IX) the monodentate ($M \leftarrow NCBH_3$ type) coordination of $BH_3CN^-$ with the metal. The two cyanide stretching vibrations in this complex occur at 2210 and 2191 $cm^{-1}$, showing an increase of 31 and 17 $cm^{-1}$ respectively from uncoordinated $BH_3CN^-$ grouping.



Comparison of Infrared Spectra for

(A) $Cu(BH_3CN)(PPh_3)_3$

(B) $[Cu(BH_3CN)(PPh_3)_2]_2$

(C) $NaBH_3CN$

(X)

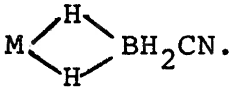
Lippard and coworkers (13, 15) have confirmed through X-ray crystallography for two of the cyanotrihydroborate complexes a structure which involves a bridging $BH_3CN^-$ unit, as shown in fig. VIII. The infrared spectra of both of these complexes are very similar and show significant differences from the monodentate complexes of the type $M \leftarrow NCBH_3$ discussed above. Fig. (X) illustrates these differences and compares the spectra of $[Cu(BH_3CN)(PPh_3)_2]_2$ (bridging structure) and $Cu(BH_3CN)(PPh_3)_3$ (monodentate structure) with that of free $BH_3CN^-$ ion. These spectral differences between the $BH_3CN^-$ group as a bridging ligand and as a monodentate ligand can be summarized as follows:

1. The terminal BH stretching frequency appears at 2320 to 2350 $cm^{-1}$ (Table 7) when $BH_3CN^-$ is monodentate, whereas in bridging $BH_3CN^-$ complexes it appears at a higher frequency, 2376 $cm^{-1}$ in $[Cu(BH_3CN)(PPh_3)_2]_2$ and 2380 $cm^{-1}$ in the $[Ni(BH_3CN)(tren)]_2^{+2}$ cation.

2. In dimeric complexes there is a broad band at $\sim$2200 $cm^{-1}$ attributed to a $M{-}H_b{-}B$ stretching vibration (31, 13). This band is absent in the monodentate complexes.

3. The terminal BH deformation mode occurs at $\sim$1115 $cm^{-1}$

for monodentate $BH_3CN^-$ complexes whereas it shifts to a lower position ∿1100 $cm^{-1}$ in the copper bridged dimer.

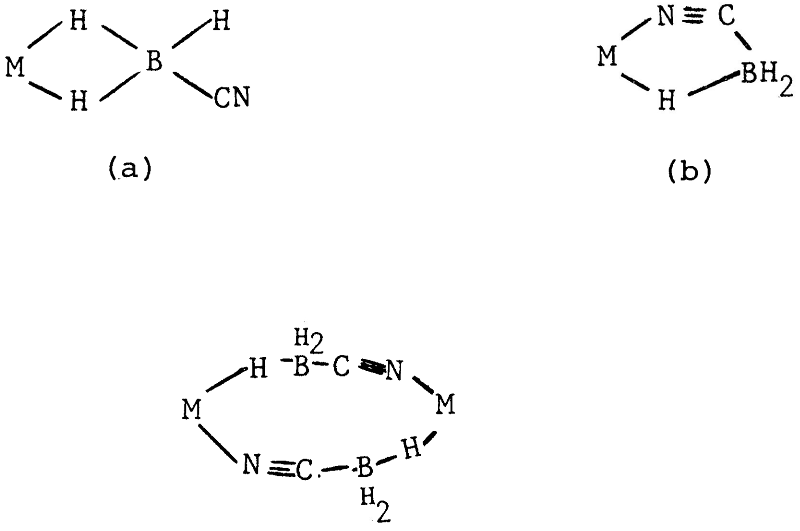
There is a significant number of complexes listed in Table 7 (e.g. No. 20, 21, 24, 26 and 35) for which infrared spectral data cannot be unambigiously interpreted in terms of monodentate or bridging $BH_3CN^-$ ligands as discussed above. For all such complexes it appears likely that in addition to possible cyanide bonding, one or more of the hydrogen of the $BH_3$ unit of $BH_3CN^-$ are also involved in bonding with the metal ions. For example, $Ni(BH_3CN)(PPh_3)_2$ shows a medium intensity band at 2070 $cm^{-1}$ and only a small shift in the cyanide stretching frequency (2185 $cm^{-1}$) from the uncoordinated $BH_3CN^-$ (2179 $cm^{-1}$), and is therefore, thought (16) to involve a chelating structure like . The band at 2070 $cm^{-1}$ has been assigned to the $M-H_b-B$ stretching frequency (16). Similar bands at around 2100 $cm^{-1}$ occur in the infrared spectra of several other cyanotrihydroborate complexes of copper and nickel, as specified above, and the implication is that the $M-H_b-B$ bonding is also present in all these complexes. However, as pointed out by Holah and coworkers (16), there is little difference in the C≡N stretching frequency between the compounds which show the extra band at ∿2100 - 2200 $cm^{-1}$ and those which do not ($M-NCBH_3$ type), and thus there remains an element of doubt regarding the detailed mode of coordination in these complexes. To give information which is as complete as possible, such extra bands, whose tentative assignments require more evidence for the M-$H_b$-B type of stretch, are also included under the M-$H_b$-B heading in Table 7. However, bands due to the M-$H_b$-B vibration will be further discussed later for the M-$BH_4$ complexes.

It is therefore clear from the above discussion that much structural work (X-ray diffraction) is required before any firm conclusions regarding the structure of cyanotrihydroborato complexes can be made from infrared spectroscopy. Furthermore, there is a great need for a detailed normal coordinate analysis for the various possible geometries adopted by the $BH_3CN^-$ (Fig. II) during complexation with the metals.

## C. Nuclear Magnetic Resonance Spectroscopy

A literature survey of the cyanotrihydroborate complexes has indicated that proton NMR spectroscopy has not been utilized in an effort to obtain structural details for these complexes. However, considerable work has been done on the corresponding tetrahydroborate complexes where unfortunately, $^1H$ NMR studies have not been very helpful because of the fluxional behaviour of the $BH_4$ grouping (7). That is, at room temperature, the bridge and the terminal hydrogen atoms of the B-H bonds in tetrahydroborate complexes are magnetically equivalent. This is due to rapid interchange (on the NMR time scale) between the bridge and the terminal hydrogen atoms of the $BH_4^-$ group. Thus, most of the $BH_4^-$ complexes studied show a broad quartet ($^{11}B$, $I=3/2$) at room temperature in their $^1H$ NMR spectra. Studies at low temperatures show the collapse of the multiplet and eventually washing out of the B-H coupling. This spectral collapse is attributed to rapid spin lattice relaxation of the $^{11}B$ and $^{10}B$ nuclei (35) and is not due to slowing (or speeding up) of the fluxional process (36). This phenomenon is named "thermal decoupling" (35) or "correlation time decoupling" (7). However, as will be seen in section VII-C, some nonfluxional $BH_4^-$ complexes are known, whereas in some other complexes apparent (but not real) slowing down of the fluxional process has been observed (37) at low temperatures.

Returning now to the cyanotrihydroborato complexes fluxionality is probably of no importance for structures like $M \leftarrow NCBH_3$, but in complexes where hydrogen atoms of $BH_3CN^-$ group are also involved in bonding with the metal ion, for example as shown in the structures below, then it is possible that simple rotation about the B-C bond may possibly give some degree of fluxional behaviour in solution. The bridging and terminal B-H bonds may again, therefore, be equivalent at room temperature.



(a) (b)

(c)

(XI)

This is because the boron atoms in $BH_3CN^-$ are tetrahedral, and such a rotation would remove a coordinated B-H and replace it by what was an instant before a terminal B-H. However, we are not aware of any such studies on $BH_3CN^-$ complexes and these are largely speculations on our part.

Perhaps a more useful method to study the mode of coordination of $BH_4^-$ in tetrahydroborate complexes, is the solid state NMR because it appears that the fluxional processes do not operate in the solid state in a crystal lattice (38). Thus, information about shifts and couplings for bridging and terminal B-H bonds may possibly be obtained from solid state "magic angle" spectra. Such techniques are becoming more widely available now.

For some $BH_3CN^-$ complexes $^{11}B$ NMR spectra have been recorded. Thus, trans-$Fe(BH_3CN)_2(P(OR)_3)_4$ in which the $M \leftarrow NCBH_3$ linkage is present (Table 3), shows (24) a quartet at $\delta = -40$ in the ratio of 1:3:3:1 with JBH=91 HZ, which is consistent with the shifts and couplings expected for a $BH_3CN^-$ ligand. On the other hand, the $^{11}B$ NMR spectrum of the paramagnetic $Fe(CH_3CN)(BH_3CN)_2$ shows (24) a broad singlet at $\delta = -66$. The very large shift of the boron atom resonance may possibly arise as a result of either bulk susceptibility effects or a paramagnetic shift (24).

Cyanotrihydroborato complexes where phosphine ligands are also involved mean that $^{31}P$ NMR studies may also give very useful information. Thus, the arrangement of phosphorus atoms around the metal atom can be inferred from $^{31}P$ NMR studies. For example, in trans-Fe$(BH_3CN)_2(P(OR)_3)_4$ (referred to above) (R=Me or Et), where the four phosphite ligands are planar (fig. V, page 20) the $^{31}P$-NMR shows a singlet at $\delta$=154.4. On the other hand, the cis form of the same complex (fig. V B page 20) shows two areas of resonances in an $A_2B_2$ pattern, where the chemical shifts and coupling constants depend on the nature of R. For R=Me, $\delta$ values are 163.3 and 150.2 with $JP_A$-$P_B$=131 HZ and for R=Et, $\delta$ values are 158.8 and 145.9 with $JP_A$-$P_B$= 129 HZ.

## V. Tetrahydroborate Complexes

The purpose of discussing the chemistry of tetrahydroborate complexes in this introduction is to illustrate the close resemblance and the obvious differences such systems have with the cyanotrihydroborate complexes, as this discussion will be useful later in the thesis. This section, however, is not meant to be very comprehensive and only selected examples will be discussed. Some special emphasis will be given to complexes of the cobalt triad although, again, coverage will not be exhaustive.

## VI. Syntheses and Chemical Properties of Tetrahydroborate Complexes

### A. Iron, Ruthenium and Osmium

A variety of ruthenium tetrahydroborate complexes have been synthesized by Holah and coworkers (27), as depicted in Table 8. The method of synthesis for all of these complexes is similar to that already discussed for the $BH_3CN^-$ complex $RuH(BH_3CN)(CO)_2(DBP)_2$ earlier in this survey. The Ru(II) complex $RuH(BH_4)(PPh_3)_3$ was the only product isolated by treating $RuCl_3$ with an excess of $NaBH_4$ in the presence of triphenylphosphine, but the formation of tetrahydroborate complexes of ruthenium appears to be very sensitive to the electronic and steric effects operating in the ligand. For example, with Ru(II) or Ru(III) chloride, under conditions similar to those already outlined, $AsPh_3$ forms only $RuHCl(AsPh_3)_3$, while the rigid and bulky DBP gives the ruthenium dihydride $RuH_2(DBP)_4$. Thus, only

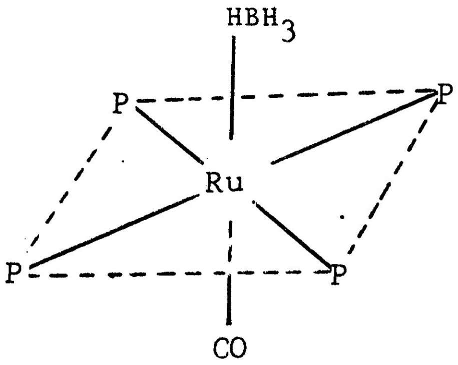
TABLE 8:

Tetrahydroborate Complexes of the Iron Triad

| No. | Complex | Colour | Reagents Used | Ref. |
|---|---|---|---|---|
| 1. | $RuH(BH_4)(PPh_3)_3$ | Yellow | Ru(II) Carbonyl + $NaBH_4$ | 27 |
| 2. | $RuH(BH_4)(CO)(PPh_3)_3$ | Yellow | Ru(II) Carbonyl + $NaBH_4$ | 27 |
| 3. | $RuH(BH_4)(CO)_2(Pcy_3)_2$ | Yellow | Ru(II) Carbonyl + $NaBH_4$ | 27 |
| 4. | $Ru(BH_4)(n\text{-}C_5H_5)(PPh_3)_2$ | White | $RuCl(n\text{-}C_5H_5)(PPh_3)_2$ + $NaBH_4$ | 39 |

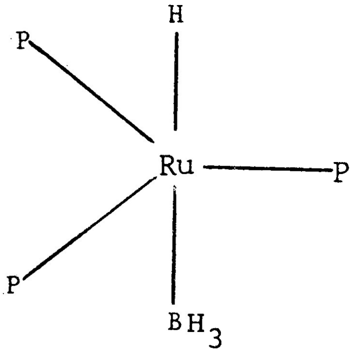
triphenylphosphine and tricyclohexylphosphine are effective in forming tetrahydroborate complexes as isolable products whereas with $NaBH_3CN$ (as already discussed), only the rigid DBP is similarly effective.

Steric factors as well as infrared data have led the authors (27) to postulate the following structure for the ruthenium tetrahydroborate complexes, where only



(XII-A)

one of the hydrogens of $BH_4^-$ is involved in bonding with the metal. Another interesting ruthenium complex,



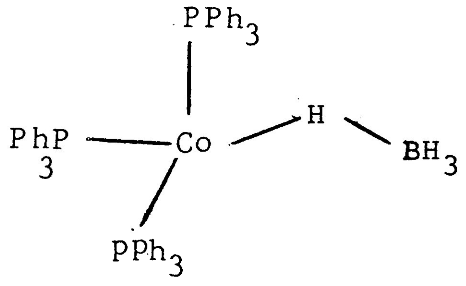
(XII-B)

$Ru(BH_4)(n\text{-}C_5H_5)(PPh_3)_2$, was prepared by another group (39) by treating $Ru(Cl(n\text{-}C_5H_5)(PPh_3)_2$ with $NaBH_4$ in THF solution. However, as pointed out earlier (page 7 ), a similar reaction in acetone between $[Ru(n\text{-}C_5H_5)(PPh_3)_2(Me_2CO)]^+$ and $NaBH_3CN$, reported by Haines (12), was more complex. The IR of the reaction mixture revealed the formation of at least two products, $Ru(CN)(n\text{-}C_5H_5)(PPh_3)_2$ ( $\nu$ CN, 2083 in $CH_2Cl_2$) and $Ru(\underline{C}NBH_3)(n\text{-}C_5H_5)(PPh_3)_2$ ( $\nu$ $\underline{C}$N, 2141 in $Me_2CO$), although separation was not effected. Thus, the formation of the above cyanide and isocyanotrihydroborato complexes can only be tentative. As will be seen later in this thesis, we have also seen decomposition of $BH_3CN^-$ at reflux temperatures in certain solvents, where $BH_3$ has been abstracted from the $BH_3CN^-$ group.

## B. Cobalt, Rhodium and Iridium

A large number of tetrahydroborate complexes has been synthesized in this triad and some are tabulated in Table 9.

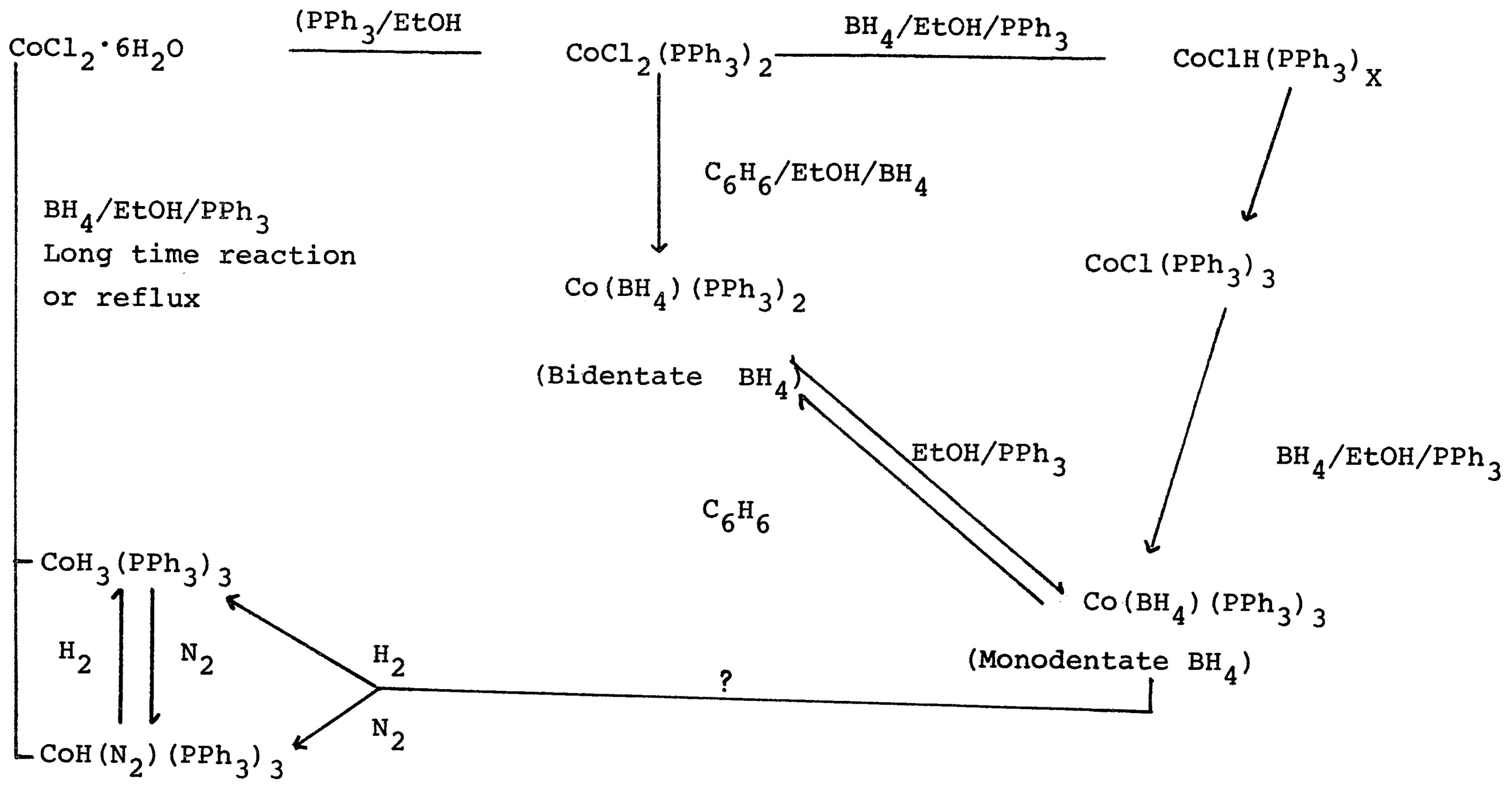
One of the earliest such complexes, $CoH(BH_4)(Pcy_3)_2$, has been fully characterized by X-ray diffraction methods (41). The complex was synthesized by treating $CoCl_2.6H_2O$ with an excess of $NaBH_4$ in the presence of free ligand in toluene/ethanol. If only ethanol is used and the ligand is replaced by $PPh_3$, reduction to Co(I) occurs and $Co(BH_4)(PPh_3)_3$ is formed (16). An improved synthesis for this complex was reported later by the same authors, and involves the reaction of $CoCl(PPh_3)_3$ with $NaBH_4$ in ethanol for 4 days. The dark green complex so formed is very air sensitive and when attempts to recrystallize it from nitrogen saturated solvents are made, it invariably takes up dinitrogen and gives a complex which approximates to the formula $Co(BH_4)(PPh_3)_3(N_2)$. The infrared and the solid state electronic spectra of the complex have been interpretated (16, 40) in terms of the structure shown in fig. XIII where monodentate $BH_4^-$ links to cobalt in a tetrahedral geometry.



(XIII)

This structure has also been supported by X-ray powder diffraction data which shows it to be isostructural with the known tetrahedral $CoCl(PPh_3)_3$.

A very interesting feature of this monodentate $BH_4^-$ complex is that it changes to $Co(BH_4)(PPh_3)_2$ in benzene and this complex involves a bidentate $BH_4^-$ grouping as evidenced by infrared and solid state electronic spectral data. Both of these mono and bidentate tetrahydroborate complexes have been very extensively studied by Holah and coworkers (40), and have been synthesized in a variety of ways. Thus, the reaction schemes leading to these mono and bidentate $BH_4^-$ complexes, as outlined by the authors (3), is depicted in figure XIV.



Tetrahydroborate-reduced cobalt system

(xiv)

TABLE 9:

Tetrahydroborate Complexes of the Cobalt Triad

| No. | Complex | Colour | Reagents Used | Ref. |
|---|---|---|---|---|
| 1. | $Co(BH_4)(PPh_3)_3$ | Yellow | $CoCl_2 + PPh_3 + NaBH_4$ | 40 |
| 2. | $Co(BH_4)(PPh_3)_2$ | Green | $CoCl_2 + PPh_3 + NaBH_4$<br>or<br>$CoCl(PPh_3)_3 + NaBH_4$ | 40 |
| 3. | $CoH(BH_4)(Pcy_3)_2$ | Brownish Yellow | $CoCl_2 + Pcy_3 + NaBH_4$ | 41 |
| 4. | $Co(BH_4)(DPPB)$ | Green | $CoCl_2 + DPPB + NaBH_4$ | 42 |
| 5. | $Co(BH_4)(DPPPe)$ | Green | $CoCl_2 + DPPPe + NaBH_4$ | 42 |
| 6. | $Co(BH_4)P$ | Green | $[Co(H_2O)_6](BF_4)_2 + P + NaBH_4$ | 43 |
| 7. | $Rh(BH_4)(PPh_3)_2$ |  | $RhCl(PPh_3)_2 + NaBH_4$ | 9 |
| 8. | $Rh(BH_4)(Pcy_3)_2(CO)$ | Yellow | $RhCl(CO)(Pcy_3)_2 + NaBH_4$ | 28 |

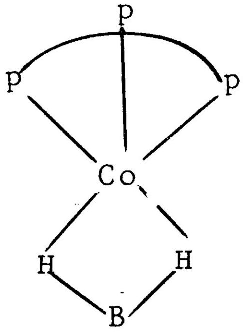
TABLE 9: continued...

| No. | Complex | Colour | Reagents Used | Ref. |
|---|---|---|---|---|
| 9. | $RhH(BH_4)L_2$<br>(L = tertiary bulky phosphine) | Yellow | $RhCl_2HL_2 + NaBH_4$ | 44 |
| 10. | $Rh(BH_4)(Siphos)_2(CO)$ | Yellow | $RhCl(Siphos)_2(CO) + NaBH_4$ | 45 |
| 11. | $RhH(BH_4)(\underline{o}\text{-tolyl}_3P)$ | Greenish Brown | $RhCl(\underline{o}\text{-tolyl}_3P)_2 + \underline{o}\text{-tolyl}_3P + NaBH_4$ | 9 |
| 12. | $RhCl(BH_4)(Py)_2(dmf)$ | Red | $RhCl_3(Py)_3 + dmf + NaBH_4$ | 46 |
| 13. | $Rh(BH_4)(PPh_3)_2(CO)$ | Yellow | $Rh(ClO_4)(PPh_3)_2(CO) + NaBH_4$ | 28 |
| 14. | $RhCl_2(BH_4)(Py)_2(C_5H_{12}NCl)$ | Brown | $Rh(Cl)(BH_4)(Py)_2(dmf) + H_2 + CHCl_3$ | 46 |
| 15. | $Ir(BH_4)(Pcy_3)_2(CO)$ | White | $Ir(Clo_4)(CO)(Pcy_3)_2 + NaBH_4$ | 28 |

TABLE 9: continued...

| No. | Complex | Colour | Reagents Used | Ref. |
|---|---|---|---|---|
| 16. | $Ir(BH_4)(Siphos)_2(CO)$ | Yellow | $IrCl(CO)(Siphos)_2 + NaBH_4$ | 45 |
| 17. | $IrH(BH_4)(PR_3)_2$ | Yellow | $IrCl_2H(PR_3)_2 + NaBH_4$ | 44 |

Some tripod phosphine ligands (P) have also been utilized to stabilize tetrahydroborate complexes of cobalt (43). Thus, when an ethanolic suspension of $NaBH_4$ is added slowly to a THF solution of $[Co(H_2O)_6](BF_4)_2$ and P, $Co(BH_4)P$ is formed. This can be purified by recrystallization from DMF/1-butanol. Single crystal X-ray diffraction studies (43) of this complex show a distorted square pyramidal geometry where cobalt is linked to the three phosphorus atoms of the phosphine ligand and two of the hydrogen atoms of the $BH_4^-$ as depicted below in fig. XV.



(XV)

More recently (42) a series of reactions involving $CoCl_2 \cdot 6H_2O$, $NaBH_4$ and bidentate phosphines of the type $Ph_2P-(CH_2)_n-PPh_2$ (n=1-6), have been investigated in our laboratories under a variety of reaction conditions. It appears that no stable tetrahydroborate complexes could be isolated for these phosphines where n=1, 2 or 3, whereas careful reactions in the presence of phosphines where n=4 and 5 lead to green $Co(BH_4)(L-L)$ complexes. However, for phosphines where n=3 and 6, there is some $^{31}P$ NMR evidence for such tetrahydroborate derived complexes but they have not been isolated so far.

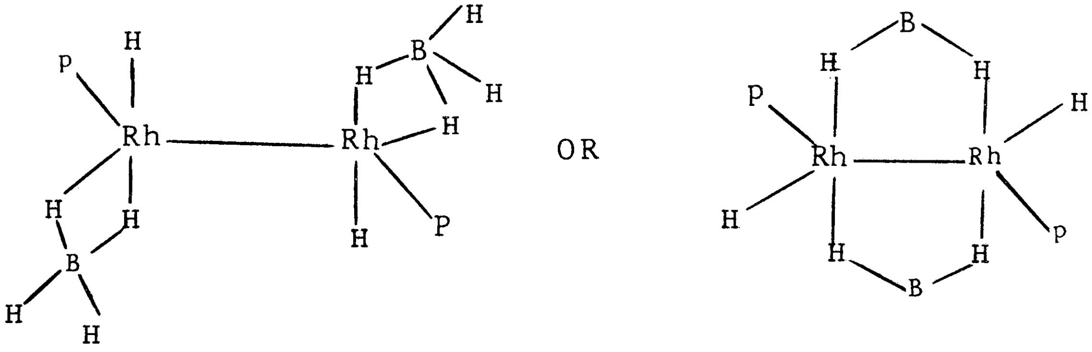
A readily formed product in these reactions is a five-coordinate hydride, $CoH(L-L)_2$ and therefore, in order to isolate the $BH_4^-$ complexes it is necessary to carefully control and stop the reactions when appropriate changes in the colour of the reaction mixture take place. For example, when $NaBH_4$ is added to a mixture of $CoCl_2 \cdot 6H_2O$ and the free phosphine (approximate ratio of M:L-L is 1:4) in a mixture of ethanol and benzene and the reaction stopped when the original blue solution changed to green, the tetrahydroborate complexes can be isolated. The formation of these $Co(BH_4)(L-L)$ complexes is very sensitive to the reaction conditions and the nature of the solvent system, the amount of $NaBH_4$ used, the rate of $NaBH_4$ addition and the temperature are often critical factors in these reactions. Thus, $Co(BH_4)(L-L)$ (L-L, n=4) is obtained when the reaction is carried out in a 1:1 EtOH/$C_6H_6$ mixture but when this ratio is changed to 6:1, an unidentified insoluble polymer-like product is formed. Also a similar product is formed when the temperature is increased.

The $BH_4^-$ group in the above complexes is most probably bonded in a bidentate manner, as inferred from infrared data. However, this point will be clarified when an X-ray crystal and molecular structure determination of $Co(BH_4)(L{-}L)$ (L-L, n=5) has been determined (currently in progress).

The remaining well studied $BH_4^-$ complexes in this triad are those of rhodium. For example, the interesting Rh(II) complex $RhH(BH_4)(O\text{-tolyl}_3P)$ was synthesized (9) by the route

$$RhCl_2(\underline{o}\text{-tolyl}_3P)_2 + \underline{o}\text{-tolyl}_3P + NaBH_4 \xrightarrow{EtOH} RhH(BH_4)(\underline{o}\text{-tolyl}_3P)_2.$$

In the above reaction, the presence of free ligand is important since, without this, a complex mixture of products is obtained. Magnetic measurements coupled with other physical data such as $^1H$ NMR spectra led the authors to propose the following possibilities for the structure of this complex.



(XVI)

## C. Nickel, Palladium and Platinum

Tetrahydroborate complexes with this group are recorded in Table 10.

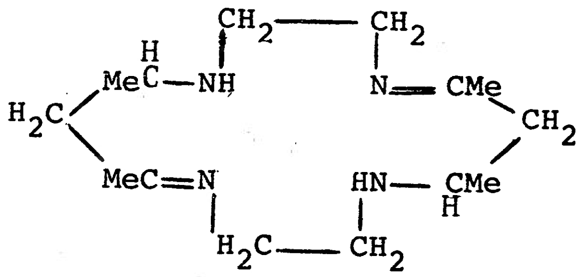
Like the Co(II)|$PPh_3$|$NaBH_4$ system (discussed previously) the Ni(II)|$PPh_3$|$NaBH_4$ system has also been extensively investigated by Holah and coworkers (48). Unlike Co(II), the Ni(II)|$PPh_3$|$NaBH_4$ reactions produce essentially two complexes, $Ni(BH_4)(PPh_3)_3$ and $Ni(BH_4)(PPh_3)_{1.5}$, both of which are thought (48) to be dimeric. Another major difference between the Co(II) and Ni(II)|$PPh_3$|$NaBH_4$ reactions is the effect of the nature of the starting materials on the course of the reactions. Thus, unlike cobalt, when

TABLE 10:

Tetrahydroborate Complexes of the Nickel Triad

| No. | Complex | Colour | Reagents Used | Ref. |
|---|---|---|---|---|
| 1. | $NiH(BH_4)(Pcy_3)_2$ | Yellow | $NiClH(Pcy_3)_2 + NaBH_4$ | 47 |
| 2. | $NiH(BH_4)(PPr_3^i)_2$ | Orange | $NiClH(PPr_3^i)_2 + NaBH_4$ | 47 |
| 3. | $Ni(BH_4)(PPh_3)_3$ | Yellow Brown | $NiCl(PPh_3)_3 + NaBH_4$ | 48 |
| 4. | $Ni(BH_4)(PPh_3)_{1.5}$ | Dark Green | $NiI_2(PPh_3)_2 + NaBH_4$ | 48 |
| 5. | $Ni(BH_4)(ClO_4)L$ | Blue Violet | $LNi(ClO_4)_2 + NaBH_4$ | 49 |
| 6. | $Ni(BH_4)_2L$ | Mauve | $LNiCl_2 + NaBH_4$ | 49 |
| 7. | $PdH(BH_4)(Pcy_3)_2$ | White | $PdClH(Pcy_3)_2 + NaBH_4$ | 47 |
| 8. | $PdH(BH_4)(PPr_3^i)_2$ | White | $PdClH(PPr_3^i) + NaBH_4$ | 47 |

L =



and different isomers

$NiX_2(PPh_3)_2$ (X=Cl, Br, I, preferably the last because of its greater reactivity), is treated with $NaBH_4$ in ethanol, a highly crystalline pyrophoric solid with the empirical formula $Ni(BH_4)(PPh_3)_{1.5}$ can be isolated. This diamagnetic, non-conducting complex can be recrystallized from cold benzene or THF but decomposes to $Ph_3P{\cdot}BH_3$ and unidentified Ni complexes in acetonitrile and nitromethane. The other Ni(I) species, $Ni(BH_4)(PPh_3)_3$ has been prepared (48) by treating $NiCl_2$ and $PPh_3$ (minimum molar ratio 1:6) with $NaBH_4$. However, unlike the cobalt complex, $Co(BH_4)(PPh_3)_3$, the nickel compound is thought (48) to be dimeric with a bridging $BH_4^-$ group because of its diamagnetism and infrared spectrum.

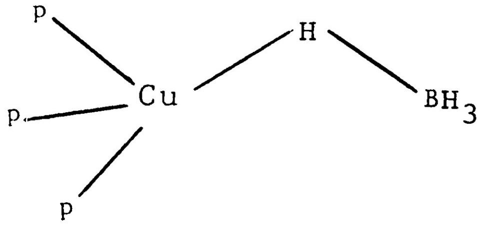
Other tetrahydroborato phosphine Ni(II) complexes, $NiH(BH_4)L_2$ (L=$Pcy_3$ or triisopropyl phosphine), were prepared (47) by the reaction of the corresponding $NiClHL_2$ with $NaBH_4$. These complexes contain a double hydrogen-bridged structure. The tricyclohexyl phosphine complex has been well characterized through single crystal X-ray diffraction methods (see section VII A) and is known (50) to contain a bidentate $BH_4^-$ group. An analogus palladium complex, prepared by a similar method (47), also involves a similar type of structure.

In addition to phosphines, nitrogen donor ligands have also been used to stablize tetrahydroborate complexes of nickel (49) but discussion of these species is outside the scope of this thesis.

There is apparently no platinum complex containing the tetrahydroborate grouping known.

## D. Copper, Silver and Gold

The complex, $Cu(BH_4)(PPh_2Me)_3$ (47) has been characterized by single crystal X-ray (52) and neutron diffraction (38) methods. Both of these structure determinations confirm the monodentate mode of coordination of $BH_4^-$ with the metal. This is in fact the first example of an unambiguous structure which shows the type of $BH_4^-$ bonding shown below.



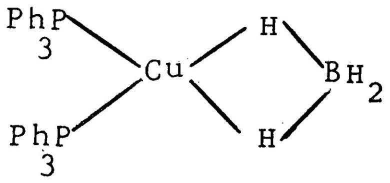
(XVII)

The complex was synthesized by treating $CuCl(PPh_2Me)_3$ with $NaBH_4$ in chloroform. Further discussion of this structure will appear later.

Another very intersting copper tetrahydroborate complex is $Cu(BH_4)(PPh_3)_2$ which was synthesized by the sequence,

$$CuX + PPh_3 + NaBH_4 \xrightarrow{CHCl_3} Cu(BH_4)(PPh_3)_2$$

This complex has also been fully characterized by X-ray diffraction (53) and unlike the previous complex it involves the bidentate coordination of $BH_4^-$.



(XVIII)

The synthesis of these two tetrahydroborate complexes of copper has clearly demonstrated that for copper, which likes to be four coordinate, the steric

TABLE 11:

Tetrahydroborate Complexes of the Copper Triad

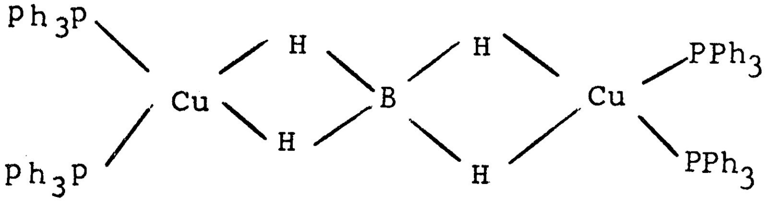
| No. | Complex | Colour | Reagents Used | Ref. |
|---|---|---|---|---|
| 1. | $Cu(BH_4)(PPh_3)_2$ | Yellow | $CuCl_2 + PPh_3 + NaBH_4$ | 16 |
| | | White | $CuCl + PPh_3 + NaBH_4$ | 55 |
| 2. | $Cu(BH_4)(PPh_2Me)_3$ | White | $CuCl(PPh_2Me)_3 + NaBH_4$ | 51 |
| 3. | $Cu(BH_4)(DBP)_2 \cdot C_6H_6$ | White | $CuCl_2 + DBP + NaBH_4$ | 16 |
| 4. | $Cu(BH_4)(PPh_3)(Phen)$ | | | 56 |
| 5. | $Cu(BH_4)(P(p\text{-}MeC_6H_4)_3)$ | White | $CuCl + P(\underline{p}\text{-}MeC_6H_4)_3 + NaBH_4$ | 55 |
| 6. | $Cu(BH_4)(P(p\text{-}MeOC_6H_4)_3)_2$ | White | $CuCl + P(\underline{p}\text{-}MeOC_6H_4)_3 + NaBH_4$ | 55 |

TABLE 11: continued...

| No. | Complex | Colour | Reagents Used | Ref. |
|---|---|---|---|---|
| 7. | $Cu(BH_4)(P(\underline{m}\text{-}MeC_6H_4)_3)_2$ | White | $CuCl + P(\underline{m}\text{-}MeC_6H_4)_3 + NaBH_4$ | 55 |
| 8. | $Cu(BH_4)$(Diphos) | White | $CuCl$ + Diphos + $NaBH_4$ | 55 |
| 9. | $[Cu_2(BH_4)(PPh_3)_4]^+X^-$ | White | $Cu(BH_4)(PPh_3)_2 + HClO_4$ | 54 |
| 10. | $Cu(BH_4)(P(MeO)_3)_2$ | Clear Non-Viscous Liquid | $CuCl + P(MeO)_3 + NaBH_4$ | 37 |
| 11. | $Cu(BH_4)P$ | White | $CuClP + NaBH_4$ | 43 |
| 12. | $Ag(BH_4)(PPh_3)_2$ | White | $AgCl(PPh_3)_3 + PPh_3 + NaBH_4$ | 56 |

factors associated with a ligand play an important role in determining whether the $BH_4^-$ group will act as a monodentate or a bidentate ligand. This fact becomes more evident by the behaviour of $Cu(BH_4)(PPh_2Me)_3$ in solution, where it releases a phosphine ligand forming $Cu(BH_4)(PPh_2Me)_2$. The infrared spectrum of this newly formed complex shows a bidentate $BH_4^-$ grouping (see section VII-A for more details).

In addition, Cariati and Naldini (54) have prepared $[(PPh_3)_2Cu(BH_4)Cu(PPh_3)_2]^+X^-$. These cationic species (where $X^-$ can be $ClO_4^-$, $BF_4^-$, or $BPh_4^-$) have been tentatively assigned the following structure where the $BH_4^-$ group acts as a tetradentate ligand.



(XIX)

These novel compounds were prepared by the reaction of $Cu(BH_4)(PPh_3)_2$ with perchloric acid or $HBF_4$ in methanol solution. The tetraphenyl borate derivative was obtained by exchanging perchlorate with $BPh_4^-$ from $[Cu_2(BH_4)(PPh_3)_4]ClO_4$.

Several other copper tetrahydroborate complexes have been recently synthesized in our laboratories and a deatailed discussion of these can be found elsewhere (32).

Finally for this triad, when $AgCl(PPh_3)_3$ and $PPh_3$ are treated with $NaBH_4$, the little studied $Ag(BH_4)(PPh_3)_2$ is formed. This is analogous to the corresponding copper complex discussed before.

There are no reports for tetrahydroborate complexes of gold in the literature.

### E. Other Metals

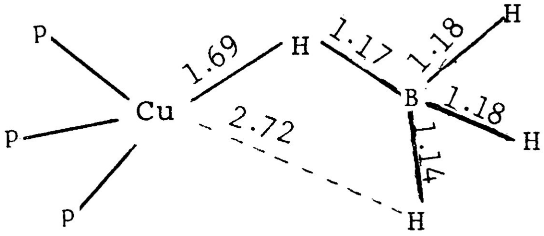
A significant number of tetrahydroborate complexes have been prepared with transition metals other than group VIII. However, their detailed discussion is outside the scope of this thesis although, where necessary, such complexes will be discussed while dealing with the topic of structural analysis of tetrahydroborate complexes.

## VII. Structural Analysis of $BH_4^-$ Complexes

### A. X-ray, Electron and Neutron Diffraction Studies

Precise location of hydrogen atoms in transition metal compounds through X-ray diffraction methods is extremely difficult because of the close proximity of the hydrogen atoms to the heavy transition metal atoms. This problem is further complicated by the large vibrational motions associated with light atoms, like hydrogen, which makes X-ray scattering more diffuse. Thus, for transition metal tetrahydroborate complexes where the $BH_4^-$ group is involved in bonding with a metal atom through one or more of its hydrogen atoms, different methods have been applied to study these structural details. These methods include X-ray, electron and neutron diffraction techniques.

Table 12 lists some interesting transition metal tetrahydroborate complexes for which structural details are now available. A very interesting complex among these is the already mentioned $Cu(BH_4)(PPh_2Me)_3$. X-ray (52) and neutron diffraction (38) studies of this complex have now confirmed that the tetrahydroborate group is bonded with only a single hydrogen atom to the copper atom, which approximates a pseudotetrahedral geometry, the other three positions being occupied by the phosphorus atoms of the phosphine ligands, as shown below:



(XVII)

As mentioned earlier this is the only $BH_4^-$ complex characterized by solid state studies where the $BH_4^-$ group is unambiguously unindentate, although similar $BH_4^-$ bonding has been claimed (16, 27) previously for some

TABLE 12:

X-ray and Neutron Diffraction Data for Tetrahydroborate Complexes

| No. | Complex | Geometry | M-$BH_4$ Linkage | Method Used | M-$H_b$ $A^o$ | M-B $A^o$ | B-$H_t$ $A^o$ | $BH_b$ $A^o$ | M-H-B Degree | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. | $Cu(BH_4)(PPh_2Me)_3$ | Quasi tetrahedral | M | X-ray | 1.47 | 2.65 | 1.02<br>1.19<br>1.14 | 1.19 | 170 | 52 |
| | | " | M | Neutron | 1.697 | 2.518 | 1.13<br>1.18<br>1.18 | 1.17 | 121.9 | 38 |
| 2. | $Ti(BH_4)(C_5H_5)_2$ | " | B | X-ray | 1.75 | 2.37 | 1.40 | 1.23 | 108 | 57 |
| 3. | $Nb(BH_4)(C_5H_5)_2$ | " | B | X-ray | 2.0 | 2.26 | 1.1 | 1.1 | - | 58 |
| 4. | $(PPh_3)_2\ N[Mo(BH_4)(CO)_4]$ | Distorted octahedron | B | X-ray | 2.02 | 2.41 | 1.11 | 1.20 | 107 | 59 |
| 5. | $CoH(BH_4)(Pcy_3)_2$ | Distorted square pyramid | B | X-ray | 1.80<br>1.87 | 2.13 | 1.35<br>1.22 | 1.30<br>1.39 | | 41 |
| 6. | $Co(BH_4)P$ | " | B | X-ray | 1.80<br>1.87 | 2.14 | 1.39 | | | 43 |
| 7. | $Co(BH_4)$(terpyridine) | - | B | Neutron | 1.72 | 2.15 | 1.22 | 1.29 | 90 | 60 |
| 8. | $NiH(BH_4)(Pcy_3)_2$ | Distorted trigonal bipyramid | B | X-ray | 1.73<br>1.76 | 2.20 | 1.12<br>1.05 | 1.27<br>1.30 | - | 50 |

TABLE 12: continued...

| No. | Complex | Geometry | M-$BH_4$ Linkage | Method Used | M-$H_b$ $A^o$ | M-B $A^o$ | B-$H_t$ $A^o$ | $BH_b$ $A^o$ | M-H-B Degree | Ref |
|---|---|---|---|---|---|---|---|---|---|---|
| 9. | $Cu(BH_4)(PPh_3)_2$ | Quasi tetrahedral | B | X-ray | 1.82 | 2.18 | 1.09 | 1.07 | 94 | 53 |
| 10. | $Zr(BH_4)_4$ | Tetrahedral | T | Electron | 2.21 | 2.30 | 1.17 | 1.27 | - | 61 |
| 11. | $Hf(BH_4)_4$ | Tetrahedral | T | Neutron | 2.66 | 2.25 | 1.31 | 1.19 | 114 | 7 |
| 12. | $U(BH_4)_4$ | Tetrahedral | T | Neutron | 2.34 | 2.52 | 1.24 | 1.23 | 113 | 62 |

FOOTNOTE: M = Monodentate
B = Bidentatate
T = Tridentate

cobalt, nickel and ruthenium complexes on the basis of less precise physical data.

It is interesting to see that X-ray diffraction studies on the above complex, carried out by two different groups produced strikingly different results although both studies agreed on monodentate $BH_4^-$ bonding. Thus, the initial investigation (52) indicated that the $M-H_b-BH_3$ bridge is almost linear, with the $M-H_b-BH_3$ bond angle of $170^o$ and the $M-H_b$ bond length of 1.4 $A^o$, significantly shorter than in other tetrahydroborate complexes. More recently, other X-ray diffraction studies have shown (38) that the $M-H_b-B$ bridge is highly angular with an angle of $126^o$ and a $M-H_b$ bond length of 1.6 $A^o$. This later study has been confirmed by a much more exact and reliable method, the neutron diffraction technique, which showed (38) an $M-H_b-B$ angle of $121.7^o$ with a $M-H_b$ bond length of 1.697 $A^o$.

Another interesting feature of this molecule, revealed by neutron diffraction studies, is that, unlike other tetrahydroborate complexes where $B-H_t$ distances are shorter than the $B-H_b$, the $B-H_b$ and $B-H_t$ bonds lengths are nearly equal except for one of the $B-H_t$ bonds (see fig. XVII). However, there is no satisfactory explanation for this abnormal behaviour unless it is a crystal packing phenomenon. Yet another important feature of the structure is the close proximity of one of the non-coordinating hydrogens of the $BH_4^-$ group to the copper atom. This last feature of the structure might explain the chemical behaviour of this complex in solution where $PPh_2Me$ and $Cu(BH_4)(PPh_2Me)_2$ are formed. This new complex contains a bidentate $BH_4^-$ group Thus, one can imagine the hydrogen atom close to the copper coordinating to the metal when one of the phosphines dissociates. This has been described (38) as an "incipient Cu-H bonding interaction". In addition, the particular orientation of the $BH_4^-$ group found in this complex has been considered as a model for suspected monodentate intermediates formed during scrambling processes ($M(H)_2BH_2 \rightleftharpoons M(H)BH_3$) in solution.

Some other interesting complexes for which the structures have been ivestigated by X-ray diffraction include $CoH(BH_4)(Pcy_3)_2$ (41), $Cu(BH_4)(PPh_3)_2$ (53), $NiH(BH_4)(Pcy_3)_2$ (50) and $Co(BH_4)P$ (43), all of which involve a bidentate $BH_4^-$ group. Some of the tridentate $BH_4^-$ compounds with heavier transition metals have also been studied (61, 62). By comparing the structural data for all of these compounds, Takusagawa et al., (38) have generalized that:

a) except for $Cu(BH_4)(PPh_2Me)_3$ and $U(BH_4)_4$ the $B-H_t$ distances are shorter than the $B-H_b$ lengths, indicating strong metal hydrogen interaction.

b) the $M-H_b-B$ angles are distinctly bent and become smaller along the series monodentate > bidentate > tridentate.

## B. Vibrational Spectroscopy:

A complete normal coordinate analysis has been carried out (63, 64) for the various symmetry geometries adopted by ionic and coordinated $BH_4^-$. Marks and Kolb (7) have tabulated these expected vibrations which are reported in Table 13. An examination of the data in Table 13 reveals that it should be possible, theoretically, to use infrared spectroscopy to distinguish between the different modes of coordination which the $BH_4^-$ group can adopt. Besides these theoretical studies, tetrahydroborate complexes involving mono, bi and tridentate $BH_4^-$ groupings have been extensively studied crystallographically. A combination of infrared and crystallographic data can therefore be used to set criteria which, hopefully, may be used to help interpret data from and assign structures to other complexes involving coordinated $BH_4^-$ groups. However, the interpretation of infrared spectra of tetrahydroborate complexes is not always easy and some of the difficulties are:

a) sometimes the expected absorptions do not appear in the spectra or, if they do, they can occur at somewhat different locations from those expected. For example, for complexes where the $BH_4^-$ group is monodentate, the $B\text{-}H_b$ stretching frequency is expected (Table 13) as a strong signal at around 2000 $cm^{-1}$. Most of the complexes which are thought (from other evidence) to contain the $M\text{-}H\text{-}BH_3$ type of coordination (see Table 14) do not show this absorption in their vibrational spectra although $Cu(BH_4)(PPh_2Me)_3$, for which the structure has been determined in the solid state (38), shows this band at 2050 $cm^{-1}$. In the absence of other evidence, this might be interpreted as being good evidence that

TABLE 13:

Infrared-Active Fundamental Vibrational Transitions for Mononuclear $MBH_4$ Configurations

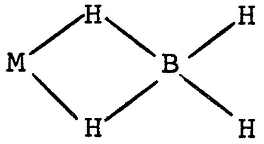
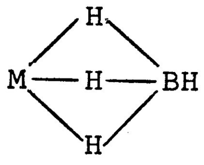
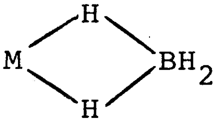
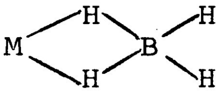
| Structure | Approximate frequency $cm^{-1}$ | Type of internal coordinate change | Symmetry type | Comment |
|---|---|---|---|---|
| M —$HBH_3$ | 2300 - 2450 | $B\text{-}H_t$ stretching | $A_1$,E | strong, possibly doublet |
| (monodentate) | ∿2000 | $B\text{-}H_b$ stretching | $A_1$ | strong |
| | ∿2000 - 1700 | $M\text{-}H_b$ stretching | $A_1$ | may be broad |
| | ∿1000 - 1150 | $BH_3$ deformation | $A_1$, E | strong |
|  | 2400 - 2600 | $B\text{-}H_t$ stretching | $A_1$, $B_1$ | strong doublet |
| | 1650 - 2150 | $B\text{-}H_b$ stretching | $A_1$, $B_2$ | strong, possibly shoulder |
| | 1300 - 1500 | Bridge stretching | $A_1$ | strong, broad |
| (bidentate) | 1100 - 1200 | $BH_2$ deformation | $B_2$ | strong |

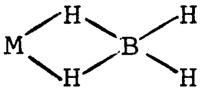
TABLE 13: continued...

| Structure | Approximate frequency $cm^{-1}$ | Type of internal coordinate change | Symmetry type | Comment |
|---|---|---|---|---|
|  (tridentate) | 2450 - 2600 | B-$H_t$ stretching | $A_1$ | strong singlet |
| | 2100 - 2200 | B-$H_b$ stretching | $A_1$, E | doublet |
| | 1150 - 1250 | Bridge deformation | E | strong |
| $M^+BH_4^-$ (ionic) | 2200 - 2300 | B-$H_t$ stretching | $T_2$ | strong, broad |
| | 1050 - 1150 | B-$H_2$ deformation | $T_2$ | strong, broad |

monodentate $BH_4^-$ does <u>not</u> in fact occur in these other complexes.

b) frequently, ligand vibrations overlap $BH_4^-$ absorptions or make it difficult, because of their number and complexity, to distinguish some of the more important coordinated $BH_4^-$ vibrations. Thus for complexes with a bidentate $BH_4^-$ group a ring breathing mode, 

, is expected as a broad absorption in the region 1300-1500 cm$^{-1}$ (this stretching frequency is unique for such structures). However, $Cu(BH_4)(PPh_3)_2$ which is known to contain the 

type of structure by X-ray crystallography does not show this stretch which, most probably, is obscured by ligand absorptions. Furthermore, very few 

type complexes do in fact show such a stretching frequency (Table 14), a further specific example being $CoH(BH_4)(Pcy_3)_2$. This is unfortunate, because the presence of such a stretch should be, theoretically at least, reasonably

TABLE 14

Selected Features of the Infrared Spectra of Tetrahydroborate Complexes

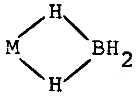
| No. | Complex | M-$BH_4$ Linkage | δBH | $\nu BH_t$ t = terminal | $\nu BH_b$ b = bridge | Bridge Stretch | Ref. |
|---|---|---|---|---|---|---|---|
| 1. | $RuH(BH_4)(PPh_3)_3$ | M-H-$BH_3$ P | 1119(m) P | 2382(s)<br>2340(sh) | | | 27 |
| 2. | $RuH(BH_4)(PPh_3)_3(CO)$ | P | 1119(m) | 2382(s)<br>2350(sh) | | | 27 |
| 3. | $RuH(BH_4)(Pcy_3)_2(CO)_2$ | P | | 2480(m)<br>2430(m) | | | 27 |
| 4. | $Co(BH_4)(PPh_3)_3$ | P | 1105(m) | 2390(s)<br>2340(sh) | | | 40 |
| 5. | $Ni(BH_4)(PPh_3)_3$ | P | 1120(m) | 2388(s)<br>2350(sh) | | | 48 |
| 6. | $Cu(PH_4)(PPh_2Me)_3$ | " K | 1060(vs)<br>1975(m) | 2335(sh)<br>2315(s) | 2050(s, br) | | 51 |
| 7. | $Co(BH_4)P$ |  K | | 2370(mw)<br>2330 | 2015(w) | | 43 |
| 8. | $CoH(BH_4)(Pcy_3)_2$ | K | | 2390<br>2360 | 1958 | 1379 | 41 |
| 9. | $Co(BH_4)(PPh_3)_2$ | P | | 2450(s)<br>2390(w,sh) | 2040<br>1970 | | 40 |
| 10. | $Co(BH_4)(DPPB)$ | | | 2415(s) | | | 42 |

TABLE 14: continued....

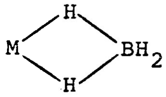
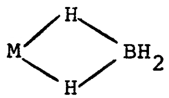
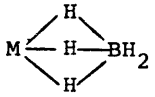
| No. | Complex | $M-BH_4$ Linkage | δBH | $\nu BH_t$ t = terminal | $\nu BH_b$ b = bridge | Bridge Stretch | Ref. |
|---|---|---|---|---|---|---|---|
| 11. | C $(BH_4)(DPPPe)$ |  |  | 2420(s) | 2030(m)<br>1985(cm) |  | 42 |
| 12. | $Ni(BH_4)(Pcy_3)_2$ | " K | 1140 | 2340 | 2050<br>2020<br>1860 |  | 47 |
| 13. | $Ni(BH_4)(PPh_3)_{1.5}$ | P |  | 2440 | 1970 | 1380 | 48 |
| 14. | $Ni(BH_4)(PPr_3{}^i)_2$ | P | 1130 | 2360 | 2060<br>1860 |  | 47 |
| 15. | $Rh(BH_4)(PPh_3)_2(CO)$ | P | 1149 | 2452<br>2416 |  |  | 28 |
| 16. | $Rh(BH_4)(Pcy_3)_2(CO)$ | P | 1174 | 2462<br>2402 |  |  | 28 |
| 17. | $Rh(BH_4)(Diphos)_2(CO)$ | P |  | 2385<br>2370 |  |  | 45 |
| 18. | $Ir(BH_4)(Pcy_3)(CO)$ | P |  | 2485<br>2425 |  |  | 28 |
| 19. | $PdH(BH_4)(Pcy_3)_2$ | P | 1070 | 2330<br>2260 | 1980<br>1800 |  | 47 |
| 20. | $Cu(BH_4)(PPh_3)_2$ | K | 1065 | 2340 | 2030 |  | 16,55 |

TABLE 14 continued...

| No. | Complex | M-BH$_4$ Linkage | | δBH | νBH$_t$ t = terminal | νBH$_b$ b = bridge | Bridge Stretch | Ref. |
|---|---|---|---|---|---|---|---|---|
| 21. | $Cu(BH_4)[(POMe)_3]$ |  | P | 1135 | 2380(s)<br>2345(sh) | 1995(s)<br>1935(s) | 1390(m) | 37 |
| 22. | $Cu(BH_4)(P(p\text{-}MeOC_6H_4)_3)_2$ | " | P | | 2382<br>2382 | 1961 | | 55 |
| 23. | $Cu(BH_4)(P(p\text{-}MeC_6H_4)_3)_2$ | | P | | 2382<br>2382 | 1930<br>1930 | | 55 |
| 24. | $Cu(BH_4)(P(m\text{-}MeC_6H_4)_3)_2$ | | P | | 2380<br>2343 | 2010<br>1944 | | 55 |
| 25. | $Cu(BH_4)P_3$ | | P | 2 | 2300(s) | 1980 | | 43 |
| 26. | $U(BH_4)(\pi C_5H_5)_2$ |  | P | 1160 | 2480 | 2220<br>2160 | | 43 |

FOOTNOTE: P stands for structures proposed by the authors
K stands for structures known through diffraction studies

conclusive evidence for a bidentate $BH_4^-$ group.

Another bidentate complex studied crystallographically (43) is $Co(BH_4)P$. The infrared spectrum of this complex is consistent with the bidentate $BH_4^-$ grouping but shows the $B-H_t$ stretch at a higher position than in other strictly covalent tetrahydroborate complexes with bidentate $BH_4^-$ e.g. $Ti(BH_4)(C_5H_5)_2$. However, the electronic spectrum of the cobalt complex shows a close similarity with that of the <u>isomorphous</u> <u>tetrahedral</u> compound, CoClP. Thus for such complexes Sacconi and coworkers (43) have described the $M-BH_4$ bonding in terms of a spherical $BH_4$ anion with a largely ionic bond to the metal, instead of the conventional three centre bonds where empty metal orbitals and the appropriate BH orbitals overlap (63).

Thus, the above discussion clearly reflects the need for further attention to the bonding between metal ions and the tetrahydroborate group. Furthermore, a very careful assessment of infrared data is necessary before any deductions regarding the structures of tetrahydroborate complexes can be made and even then such interpretations cannot be regarded as conclusive.

Finally, as pointed out earlier (page 47), a normal coordinate analysis for the various possible geometries $BH_3CN^-$ can adopt during complexation, has not been done so far. However, in cases where $BH_3CN^-$ and $BH_4^-$ coordination is similar (fig. II), it may be possible to use the data in Table 13 to assist in the interpretation of the infrared spectra of coordination complexes of $BH_3CN^-$.

## C. Nuclear Magnetic Resonance Spectroscopy

As pointed out earlier $^1H$ NMR spectroscopy has been of very little use for tetrahydroborate complexes because of the fluxional behaviour of the $BH_4^-$ grouping. However, the slowing of the fluxional process has been observed for some tetrahydroborate complexes. Thus for $IrH_2(BH_4)(PR_3)_2$ ($PR_3$=bulky tertiary phosphine) the $^1H$ NMR spectra were resolved at -51°C when $(H_b)_2$ and $(H_t)_2$ occur at $\delta = -6.87$ and $\delta = 6.86$ respectively (44).

More recently, the slowing down of the fluxional process has been demonstrated (37) for the diamagnetic copper tetrahydroborate complex, $Cu(BH_4)(P(OMe)_3)_2$. The $^1H$ NMR spectrum was recorded by dissolving the complex in a halocarbon mixture to give low temperature solubility. A broad quartet (undecoupled from $^{11}B$) observed for the protons of the $BH_4^-$ group at ambient temperatures at $\delta$=0.69 collapses to a broad doublet at -90°C and completely collapses to baseline at -165°C. However, the low solubility of the complex precluded further lowering of temperature to observe the $(H_b)_2$ signal. This complete collapse was attributed to "slowing of the hydrogen permutation" in the complexed $BH_4^-$ grouping (37). The vanadium complex, $V(BH_4)(n\text{-}C_5H_5)_2$, also shows a slowing down of the fluxional process at low temperatures (65). The $^{11}B$ decoupled spectrum of this complex shows a sharp singlet ($\delta$=-19) at room temperature. This singlet collapses to the base line at -92°C and further lowering of temperatures (-103°C) gives rise to a new signal at $\delta$=-34. This appearance of a new signal shows a static structure where the bridging and terminal protons of the $BH_4^-$ group can no longer undergo rapid exchange. Thus the signal at $\delta$=-34 has been assigned to the $(H_b)_2$ protons where as the signal due to the $(H_t)_2$ protons could not be observed due to solvent interferance.

Thus, these examples and some others (7, 33) not discussed here, show that the slowing of the fluxional behaviour in $BH_4^-$ complexes can be observed at low temperatures. However, in reality much lower temperatueres are required for genuine slowing to be observed.

## VIII Aim of the Present Work

From the previous introductory discussions it is now clear that the obviously very interesting interactions of the cyanotrihydroborate anion with transition metals has received little attention compared with the wide range of studies undertaken for the corresponding tetrahydroborate systems. This project is therefore undertaken with several objectives in mind. These are:

a) to study $BH_3CN^-$ as a ligand and in particular to investigate by the use of physical methods the versatility in the coordination modes of $BH_3CN^-$ with new cobalt complexes prepared in this work. Of course, the reaction conditions necessary for isolating such cyanotrihydroborato derived complexes are also of interest to us.

b) to contribute to our understanding of the factors determining the reaction pathways for the M|L|$BH_4$ systems extensively investigated in our laboratories in the past by using the milder reducing properties of $NaBH_3CN$. For example, in the usually very fast M|L|$BH_4$ reactions, the existence of a number of intermediate complexes were predicted. The use of the milder reducing properties of $NaBH_3CN$ may be of particular significance in this respect, and may therefore lead to valuable information on reaction mechanisms particularly if new intermediate complexes are found.

c) to determine how changes in ligand steric and electronic factors such as bite and basicity influence the ability of the ligand to interact with and stabilize cobalt in different oxidation states. The phosphine ligands to be used are $PPh_3$, $Pcy_3$, $Ph_2P(CH_2)_nPPh_2$ (n=1-4) and <u>Cis</u> and <u>Trans</u>-DPPE.

# CHAPTER II

## Experimental

### 1. Materials

The phosphines, $Pcy_3$, DPPM, Diphos, Cis and Trans DPPE, DPPP and DPPB were purchased from Strem Chemicals Inc. and were used without further purification. Triphenylphosphine, purchased from Alpha Inorganics, was recrystallized from alcohol and was stored under nitrogen. Tricyclohexylphosphine was also stored under nitrogen. Sodium cyanotrihydroborate and sodium cyanotrideuteridoborate (98% isotopic purity) were purchased from Aldrich Chemical Company and the Alpha Division of Ventron Corporation respectively and were also used without further purification. However, due to the hygroscopic nature of the cyano compounds they were stored over $CaCl_2$ in a desicator. Cobalt(II) chloride and perchlorate were purchased as their hydrates from British Drug House Chemicals Limited and Alpha Inorganics Inc. respectively and were used without further purifications.

All solvents used were reagent grade and were distilled, degassed with oxygen free nitrogen and stored over 4-A molecular sieves in the glove box.

Synthetic work was done in a glove box (unless otherwise specified) which was constantly flushed with dry nitrogen. When not in use the glove box was always maintained at a positive pressure of nitrogen to stop the inward diffusion of atmospheric oxygen.

## II Analysis and Physical Measurements

Samples were suitably protected from atmospheric oxidation during weighings or data collection.

The infrared spectra were recorded on a Beckman IR-12 spectrophotometer (calibrated with a polystyrene reference film) as Nujol mulls (unless otherwise specified) between NaCl (650-4000 $cm^{-1}$) or polyethylene plates (200-600 $cm^{-1}$).

Electronic spectra in the 16,000 to 3000 $A^o$ range were recorded on a Cary-14 recording spectrophotometer. The solution spectra were measured using cells of 1 cm pathlength and the solid state reflectance spectra were recorded against the reference MgO.

$^{1}H$ and $^{31}P$ NMR spectra were obtained from a Bruker WP-80 fourier transform instrument equipped with an automatic temperature control device B-VF 1000. The chemical shifts in 32.3 MHZ-$^{31}P$ NMR spectra were measured relative to $H_3PO_4$, although the direct use of $H_3PO_4$ in routine NMR measurements was avoided. This was done by first measuring the position of the $H_3PO_4$ signal against either $D_2O$ or $(CD_3)_2CO$, which were used as frequency lock systems, and which were sealed in thin glass capillaries inside the NMR tubes. The positions of $H_3PO_4$ against these frequency locking solvents were found to be 2800 HZ ($D_2O$) and 2910 HZ $(CD_3)_2CO$. Samples were run using these lock solvents as external standards and the chemical shifts were then calculated with reference to the above mentioned frequencies. This method offered two main advantages. First, if $H_3PO_4$ is used as an external reference, the $H_3PO_4$ signal can easily be saturated which means that weak signals from a sample may not be observed. Use of the above method allows spectra to be run for longer times so that weak signals due to, for example, low sample solubility may be observed without saturation problems. Secondly, solutions of pure samples or solutions of reaction mixtures may be run without contamination by and possible reaction with $H_3PO_4$ (if added as an internal standard).

28.7 MHZ - $^{11}B$ NMR spectra were recorded with the courtesy of the Chemistry Department, Duke University, North Carolina, on a Jeol FX-90Q NMR spectrometer using $BF_3 \cdot OEt_2$ as an external reference.

Chemical shifts, $\delta$, are quoted as being negative to the high field of the reference standards ($SiMe_4$ for $^1H$ NMR, 85% $H_3PO_4$ for $^{31}P$ NMR and $BF_3 \cdot OEt_2$ for $^{11}B$ NMR).

Mass spectra of the samples were recorded on a Hitachi-Perkin-Elmer Model RMU-7 double focussing mass spectrometer.

Microanalytical analyses for nitrogen, carbon and hydrogen were done on a Perkin Elmer 240 Analyser. For samples where combustion was incomplete under normal conditions, $V_2O_5$ was used as a catalyst.

Samples for X-ray powder diffraction were sealed in Lindeman capillaries (0.3 mm) and were photographed on a Debye-Scherrer type camera using nickel filtered copper $K_{\alpha}$ radiation from a Phillips PW-1130 X-ray generator. Exposure time was 80 minutes.

Solid state magnetic moments were measured using the Gouy method. The double ended Gouy tube was calibrated with $Hg[Co(CNS)_4]$ and $Ni(en_3)(S_2O_3)$ for different settings of a varian V-2900 Regulated Magnet Power supply which controlled the current to a Varian V-4005 electromagnet. In solution, magnetic measurements were done by the NMR method devised by Evans (66).

## III Syntheses

The general pattern followed for the syntheses to be described in this chapter involved the addition of the reducing agent, $NaBH_3CN$, to Co(II) chloride or perchlorate in the presence of the appropriate phosphine. Mostly the reaction media was either ethanol/benzene or ethanol/toluene, chosen because the phosphines used are completely soluble in benzene or toluene whereas the cobalt salts are soluble in ethanol. The reactions were studied under a wide variety of conditions and the critical factors found to affect the course of these reactions, and which will be fully discussed later in this thesis, are:

a) amount of $NaBH_3CN$ used

b) rate of $NaBH_3CN$ addition

c) temperature

d) reaction time

e) solvent system

f) ratio of metal to ligand (phosphine).

The products were obtained in approximately 30% yield unless otherwise specified.

## 1. $Co(II)|PPh_3|NaBH_3CN$

### A. Hydrido(Cyanotrihydroborato)tris(triphenylphosphine) Cobalt(II)

$CoH(BH_3CN)(PPh_3)_3$

$Co(ClO_4)_2 \cdot 6H_2O$ (.457 g, ∿1.25 mM) and $PPh_3$ (1.74 g, ∿7.5 mM) were dissolved in toluene/ethanol (1:1, 10 ml). The light pink solution so formed was stirred for 10 mins.

and then a solution of $NaBH_3CN$ (1.0 g, ∿16 mM) in ethanol (10 ml) was added dropwise to the stirred mixture over a period of 10 mins. The colour of the solution had turned to red-violet when the addition of $NaBH_3CN$ was complete. The solution was stirred for 1 hr, filtered and the filtrate allowed to stand at room temperature for 18 hrs during which time a wine red crystalline solid was formed. The red solid was separated by filtration washed with ethanol (∿10 ml) and n-Hexane (∿5 ml) and dried under reduced pressure.

It was not possible to recrystallize this complex due to its rapid (within 10-30 mins ) decomposition in all solvents in which the compound showed solubility, that is, $C_6H_6$, PhMe, THF, $CH_2Cl_2$, MeCN, DMF and DMSO. Attempts to recrystallize the complex in the presence of free ligand also failed, although the presence of free ligand does increase the time, to a maximum of ∿50 mins in benzene, before the red colour of the solution has completely changed to green. In air, the solid is stable for ∿48 hrs.

<u>Analysis</u> Calc. for $CoH(BH_3CN)(PPh_3)_3$

C = 74.52, H = 5.53, N = 1.58

found

C = 74.60, H = 5.67, N = 1.49

## B. Formation of Crystals for X-ray Studies

In an attempt to obtain crystals large enough for X-ray diffraction studies the above reaction was performed in a large volume of solvents (PhMe:EtOH, 1:1, 40 ml) while keeping all other weights and conditions the same as specified above. After the reaction, the mixture was stirred for 1 hr. before being filtered. The filtrate was kept at ∿$3^{o}C$ for 48 hrs with a slow stream of nitrogen flowing over the solution. Large red plate shaped crystals were formed along with some blue solid (see 1-C). The mixture was separated by repeated decantation with EtOH in which the blue solid forms a suspension, the large red crystals remaining in the bottom of the flask. The crystals were then washed with EtOH (∿10 ml) and n-Hexane (∿5 ml) and dried under vacuum. Selected crystals were sealed in Lindemann capillaries (.3 mm dia.) for single crystal X-ray diffraction studies.

## C. Unidentified Blue Solid

During several syntheses of $CoH(BH_3CN)(PPh_3)_3$ the formation of the above mentioned blue compound has been repeatedly seen. The following describes a method for its synthesis in higher yields.

C.1. $CoCl_2 \cdot 6H_2O$ (0.3 g, ∿1.26 mM) and $PPh_3$ (1.74 g, ∿6.64 m M) were dissolved in toluene/ethanol (1:1, 25 ml). The light green solution so formed was heated to boiling (77°C) and a solution of $NaBH_3CN$ (1.0 g, ∿16.0 mM) in ethanol (∿10 ml) was added dropwise over a period of ∿20 mins while keeping the temperature constant. The very dark green solution so formed was filtered and kept at ∿3°C for 24 hrs with a slow stream of nitrogen flowing over the solution. During this time blue crystals were formed which were washed with $C_6H_6$, EtOH and n-Hexane. When dried under vacuum for 24 hrs the crystals disintegrated slowly to form a blue powder. The air sensitive blue solid is insoluble in $C_6H_6$, THF, MeCN, $CH_2Cl_2$, $CHCl_3$ and EtOH but can be rapidly recrystallized unchanged from DMF/EtOH or DMF/$H_2O$. However, clear blue solutions of the solid in DMF cannot be kept for longer than ∿30 mins after which they turn to green.

<u>Analysis</u> The blue solid obtained from two different reactions analysed as follows:

Reaction 1. C = 57.8 H = 4.47 N = 8.15
Reaction 2. C = 57.86 H = 4.80 N = 8.13

C.2. As mentioned earlier (1.A, page 98) the blue solid was also formed when $CoH(BH_3CN)(PPh_3)_3$ crystals were grown. Thus the blue solid can be purified by washing with either benzene or THF, in which $CoH(BH_3CN)(PPh_3)_3$, but not the blue solid, is soluble.

C.3. Similarly the reaction between $Co(ClO_4)_2 \cdot 6H_2O$ (.457 g, 1.25 mM), $PPh_3$ (0.87 g, 3.45 mM) and $NaBH_3CN$ (.696 g, ∿11 mM) in toluene/ethanol (1:1, 10 ml) also produces a mixture of $CoH(BH_3CN)(PPh_3)_3$ and the blue solid. In this case the reaction was stirred for 1 hr and then kept at ∿3°C for 24 hrs. The mixture so obtained was washed repeatedly with benzene until the washings were colorless (this removes all the free phosphine and $CoH(BH_3CN)(PPh_3)_3$ from the mixture). The blue solid was dried under vacuum for 24 hrs.

## 2. $Co(II)|Pcy_3|NaBH_3CN$

It has not yet been possible to isolate any product from reactions, both at room temperature and at elevated temperatures, between Co(II), $Pcy_3$ and $NaBH_3CN$.

## 3. $Co(II)|DPPM|NaBH_3CN$

This system has been investigated under a wide range of conditions and has produced a number of different compounds. It is by far the most complex system studied in this work and the course of reactions are exceptionally sensitive to small changes in reaction conditions.

### A. (Cyanotrihydroborato) bis [bis(diphenylphosphino) methane] Cobalt(II) perchlorate

### $[Co(BH_3CN)(DPPM)_2]\ ClO_4$

This complex has been synthesized from reactions where the molar ratios between $Co(ClO_4)_2 \cdot 6H_2O$ and $NaBH_3CN$ were varied from between 1:1 to 1:16 while keeping the Co:DPPM ratio constant at 1:3.

### A.1. From $Co(ClO_4)_2 \cdot 6H_2O|DPPM|NaBH_3CN$ (1:3:1)

An ethanolic solution (∿10 ml) of $NaBH_3CN$ (.0775 g, ∿1.25 mM) was added dropwise over a period of 10 mins to a stirred solution containing a mixture of $Co(ClO_4)_2 \cdot 6H_2O$ (.45 g, ∿1.25 mM) and DPPM (1.44 g, ∿3.75 mM) in toluene/ethanol (2.5:1, 10 ml). The mixture was stirred for 24 hrs during which time a yellow solid was precipitated. The yellow solid was filtered off, washed with benzene (∿20 ml), ethanol (∿ 10 ml) and n-Hexane (∿5 ml) and was dried under vacuum for 24 hrs. The complex decomposes in $CH_2Cl_2$, $CHCl_3$, THF, MeCN and DMSO. However it can be recrystallized unchanged either from DMF/EtOH or from hot methanol. The product recrystallized from DMF/EtOH retains a molecule of DMF which could not be removed even under vacuum ($10^{-4}$ torr) for 24 hrs.

The above reaction has also been carried out with $NaBD_3CN$. The deuterated complex was purified as discussed above.

Analysis Calc. for $[Co(BH_3CN)(DPPM)_2]ClO_4$

C = 63.32 H = 4.86 N = 1.45

found

C = 63.43 H = 5.10 N = 1.71

Calc. for $[Co(BH_3CN)(DPPM)_2]ClO_4 \cdot DMF$

C = 62.33 H = 5.2 N = 2.7

found

C = 61.66   H = 5.62   N = 2.65

Calc. for $[Co(BD_3CN)(DPPM)_2]ClO_4$

C = 63.12   H = 5.15   N = 1.44

found

C = 64.36   H = 5.24   N = 1.36

### A.2. From $Co(ClO_4)_2\cdot 6H_2O|DPPM|NaBH_3CN$ (1:3:10)

$Co(ClO_4)_2$ (.457 g, ∿1.25 mM) and DPPM (1.44 g, ∿3.75 mM) were mixed in benzene/ethanol (2.5:1, 10 ml) and a solution of $NaBH_3CN$ (.610 g, ∿10 mM) in ethanol (∿10 ml) was added dropwise over a period of 20 mins. The light pink coloured solution had changed to dark brown-green by the time the addition of $NaBH_3CN$ was completed. The solution was stirred for 12 hours during which time a yellow-green solid precipitated. This was filtered off, washed and purified as described above.

### A.3. From $Co(ClO_4)_2\cdot 6H_2O|DPPM|NaBH_3CN$ (1:3:16)

A solution of $NaBH_3CN$ (1.0 g, ∿16 mM) in ethanol

(∿10 ml) was added to a mixture of $Co(ClO_4)_2 \cdot 6H_2O$ (.454 g, ∿1.25 mM) and DPPM (1.44 g, ∿3.75 mM) dissolved in benzene/ethanol (2.5:1, 10 ml). The mixture was stirred for 24 hrs after which time the precipitated yellow solid was separated, washed and recrystallized as described above.

## B. (Cyanotrihydroborato)[bis(diphenylphosphino) methane] Cobalt(I)

## $Co(BH_3CN)(DDPM)$

The above complex was prepared both from $CoCl_2 \cdot 6H_2O$ and from $Co(ClO_4)_2.6H_2O$ as follows:

### B.1. From $CoCl_2.6H_2O|DPPM|NaBH_3CN$

$CoCl_2.6H_2O$ (0.3 g, ∿1.25 mM) and DPPM (1.44 g, ∿3.75 mM) were mixed in a benzene/ethanol mixture (2.5:1, 10 ml) and immediately formed a dark blue-green solution. A solution of $NaBH_3CN$ (.310 g, ∿5 mM) in ethanol (∿10 ml) was added dropwise to the above solution over a period of 10 mins (addition for the first 5 mins was very slow). During the addition of $NaBH_3CN$ the blue-green solution changes colour to dark green and finally to dark brown-green. The solution was then stirred for 24 hrs during which time a yellowish-green solid was precipitated. The compound can be purified either by washing throughly with benzene (to remove all the traces of free phosphine) and ethanol (∿10 ml, to remove unreacted $NaBH_3CN$) or by recrystallization either from a DMF/EtOH (6:1) mixture or from hot methanol. However both the crude and the recrystallized products always retain a mole of solvent (as seen from the $^1H$-NMR and mass spectra. The complex decomposes in $CH_2Cl_2$, $CHCl_3$, THF, MeCN and DMSO.

<u>Analysis</u> Calc. for $Co(BH_3CN)(DPPM)\cdot C_6H_6$

C = 68.44 H = 5.52 N = 2.49

found C = 68.60 H = 5.80 N = 2.66

Calc. for $Co(BH_3CN)(DPPM).MeOH$

C = 63.0 H = 5.66 N = 2.73

found

C = 64.48 H = 5.89 N = 2.41

Calc. for $Co(BH_3CN)(DPPM).DMF$

C = 62.91 H = 5.78 N = 5.06

found

C = 60.28 H = 6.16 N = 4.78

## B.2. From $Co(ClO_4)_2.6H_2O|DPPM|NaBH_3CN$

A solution of $NaBH_3CN$ (1.55 g, ∿24.5 mM) in ethanol (∿10 ml) was added dropwise over a period of 15 mins to a stirred solution containing a mixture of $Co(ClO_4)_2.6H_2O$ (.454 g, ∿1.25 mM) and DPPM (1.44 g, ∿3.75 mM) in benzene/ethanol (2.5:1, 10 ml). The dark brown-green coloured solution formed after the addition of the $NaBH_3CN$ was stirred for 24 hrs during which time a greenish-yellow solid was precipitated. The crude product was separated and purified as described above.

## C. Unidentified Green and Blue Solids

A green and blue solid obtained from reactions between $CoCl_2.6H_2O$, DPPM and $NaBH_3CN$ have not yet been identified due to a number of practical difficulties as outlined below.

C.1. To a stirred green solution containing a mixture of $CoCl_2.6H_2O$ (0.3 g, ∿1.25 mM) and DPPM (1.44 g, ∿3.75 mM) in benzene/ethanol (2.5:1, 10 ml) a solution of $NaBH_3CN$ (.0775 g, ∿1.25 mM) in ethanol (∿10 ml) was added over a period of 10 mins. The resulting dark green solution was stirred for 24 hrs during which time a light green solid was precipitated. The solid was filtered off and to the resulting dark green filtrate was added n-Hexane (∿20 ml) to precipitate more of the green solid. All the light green solid was combined and washed with benzene and n-Hexane. When the crude green solid was dissolved in $CH_2Cl_2$, $CHCl_3$, THF, MeCN or $Me_2CO$ and filtered a clear green filtrate resulted with some undissolved bluish-white solid remaining. Addition of n-Hexane to the filtrate resulted in the formation of a green solid which, after filtration, is <u>not completely soluble</u> in the solvent used for recrystallization (e.g. $CH_2Cl_2$ or THF). However, the mixture is completely soluble in DMSO and showed, as expected, signals due to more than one compound in the $^{31}P$ NMR spectrum. When a solution of the green solid in $CH_2Cl_2$ was left for 24 hrs either inside or outside the glove box a mixture of blue and green crystals resulted. The separation of these compounds has not yet been achieved.

When the crude green solid was treated with alcohol (MeOH and EtOH) a clear yellow solution was formed from which a mixture of yellow and green solids was obtained by the addition of n-Hexane. More details regarding this reaction will be found in the results and discussion section. Analysis of both the crude and recrystallized compounds from different reactions showed wide variations as shown below.

Recrystallized from $CH_2Cl_2$/Hexane

C = 63.53    H = 5.51    N = 2.19

Recrystallized from THF/Hexane

C = 60.55    H = 5.26    N = 1.9 to 2.5

The analysis for the crude product were in the following range

C = 53 - 63   H = 4.4 - 5.3   N = 1.9 - 2.5

C.2 A solution of $NaBH_3CN$ (.155 g, ∿2.5 mM) in ethanol (∿10 ml) was added over a period of 10 mins to a stirred solution of $CoCl_2 \cdot 6H_2O$ (0.3 g, ∿3.75 mM) and DPPM (1.44 g, ∿3.75 mM) in ethanol/benzene (2.5:1, 10 ml). The mixture was stirred for 12 hrs and the green solid which precipitated was collected and treated as described above.

## D. Attempted Syntheses

A deep red, highly crystalline sample of $CoH(DPPM)_2$ was prepared (42) in these labs from a reaction between $CoCl_2 \cdot 6H_2O$, (1.35 g, ∿2.6 mM), DPPM, (136 g, ∿3.5 mM) and $NaBH_4$. (.1 g, ∿2.6 mM).

Many repeated attempts to reproduce this reaction failed, not only to produce a pure sample of the above hydride, but to produce reaction mixtures which contained, from $^{31}P$ NMR data, more than a <u>trace</u> of the complex. The following reactions between $NaBH_3CN$, Co(II) and DPPM were carried out in an effort to obtain the Co(I) hydride by an alternate route.

D.1. $CoCl_2 \cdot 6H_2O$ (0.3 g, ∿1.2 mM) and DPPM (1.44 g, ∿3.75 mM) were mixed in ethanol/benzene (1:1, 15 ml) and the temperature raised to 70°C. A solution of $NaBH_3CN$ (2.0 g, ∿32 mM) in ethanol (∿10 ml) was added dropwise over a period of 20 mins to the above boiling mixture. As the $NaBH_3CN$ was added the initial green coloured solution changed to olive-green then to dark-brown and finally to very dark red. The heating was stopped, the solution stirred for 10 mins and a yellow solid percipitated. The solid was filtered off and the remaining dark red filtrate shown to contain, from $^{31}P$ NMR data, a complex mixture of compounds but no trace of the hydride. The yellow solid also proved to be a mixture of compounds as shown from IR spectral data. We were unable to isolate any identifiable compounds from this reaction.

D.2. $Co(ClO_4)_2 \cdot 6H_2O$ (.457 g, ∿1.25 mM) and DPPM (1.44 g, ∿3.75 mM) were mixed in $C_6H_6$/EtOH (2:1, 10 ml) and a solution of $NaBH_3CN$ (2.5 g, ∿39.78 mM) in ethanol (15 ml) was added with stirring during a period of 15 mins. The mixture turned dark brown-green in colour and precipitated a greenish-yellow solid when stirred for 24 hrs. The solid was shown to be a complex mixture of compunds. No identifiable compound was obtained from the remaining red filtrate which also showed no trace of the Co(I) hydride complex in the $^{31}P$ NMR.

## 4. Co(II)|Diphos|$NaBH_3CN$

### A. (Cyanotrihydroborato)bis[bis(diphenylphosphino) ethane] Cobalt(II) perchlorate.

### $[Co(BH_3CN)(Diphos)_2]ClO_4$

The above complex has been synthesized according to the following methods.

A.1. $Co(ClO_4)_2 \cdot 6H_2O$ (.914 g, ∿2.5 mM) and Diphos (2.985 g, ∿7.5 mM) were mixed in ethanol/toluene (6:1, 10 ml), and immediately produced a yellow precipitate of Co(Diphos)$_2$(ClO$_4$)$_2$. To this stirred mixture a solution of NaBH$_3$CN (.930 g, ∿15 m M) in ethanol (∿10 ml) was added dropwise over a five minute period. The orange-yellow solid so formed was separated immediately by filtration, as prolonged stirring leads to reduction and the formation of a Co(I) complex (see 4-C). Approximately 90% of the crude product was highly soluble in CH$_2$Cl$_2$ and was recrystallized from CH$_2$Cl$_2$/hexane (3:1) as an orange-red solid. The complex is air stable in the solid state but decomposes to a green compound in solution. The complex reacts with acetone (see 4-B).

Analysis: Calc. for [Co(BH$_3$CN)(Diphos)$_2$]ClO$_4$

C = 63.95 H = 5.10 N = 1.40

found

C = 64.02 H = 5.29 N = 1.42

A.2. A solution of NaBH$_3$CN (.310 g, ∿5 m M) in ethanol (∿ 10 ml) was added dropwise over a 10 min period to a stirred mixture of Co(ClO$_4$)$_2$·6H$_2$O (.914 g, ∿2.5 m M) and Diphos (2.98 g, ∿7.5 m M) in ethanol/toluene (6:1, 5 ml).

The mixture was stirred for 3 hrs before the resulting orange-yellow solid was filtered off and purified as described above.

## B. (Cyano)bis[bis(diphenylphosphino)ethane] Cobalt(II) perchlorate. Acetone

### $[Co(CN)(Diphos)_2](ClO_4)\cdot Me_2CO$

When $[Co(BH_3CN)(Diphos)_2](ClO_4)$ was treated with acetone an immediate and unusual reaction occurred. Thus the orange coloured complex dissolves in acetone to form a brown coloured solution from which a dark brown crystalline solid was obtained by the addition of a small amount of n-Hexane. The dark brown solid so formed is not completely soluble in acetone. It dissolves in $CH_2Cl_2$ but decomposes within 20 mins. It appears to be air stable for approximately 24 hrs.

Analysis: Calc. for $[Co(CN)(Diphos)_2](ClO_4)\cdot Me_2CO$

C = 64.36 H = 5.1 N = 1.34

found

C = 65.24 H = 5.09 N = 1.31

## C. (Cyanotrihydroborato)bis[bis(diphenylphosphino)ethane] Cobalt(I)

### $Co(BH_3CN)(Diphos)_2$

The above complex was first synthesized by Holah and coworkers (16) from the reaction between $CoCl_2$, Diphos and $NaBH_3CN$ ($Co:BH_3CN^-$, 1:10) in ethanol. This synthesis has been reproduced and, additionally, the complex has been made from a number of reactions carried out under different conditions, as follows:

C.1. A solution of $NaBH_3CN$ (.930 g, ∿15 mM) in ethanol (∿15 ml) was added over a period of 10 mins to a stirred mixture of $Co(ClO_4)_2 \cdot 6H_2O$ (9.14 g, ∿2.5 mM) and Diphos (2.98 g, ∿7.5 mM) in ethanol/toluene (6:1, 5 ml). The initial yellow coloured mixture turned to orange-yellow during addition of the $NaBH_3CN$, and finally to deep yellow after stirring for 24 hrs. The resulting yellow solid was filtered off and washed with benzene (∿15 ml), ethanol (∿15 ml) and n-Hexane (∿10 ml). The yellow solid is sparingly soluble in benzene and toluene. It is soluble in DMSO, $CH_2Cl_2$, THF and $CHCl_3$ but decomposes to a green solution within ∿5 mins in DMSO and 1 hr in the other solvents. The crude product can be recrystallized unchanged from DMF/EtOH (2:1) as small orange-yellow crystals, which, even after 24 hrs under high vacuum ($10^{-5}$ torr), retained a molecule of DMF (yield ∿60%). It appears to be stable in air for approximately 12 hrs.

Analysis: Calc. for $Co(BH_3CN)(Diphos)_2 \cdot DMF$

C = 69.42 H = 5.99 N = 2.90

found

C = 69.07 H = 6.29 N = 3.06

C.2. A solution of $NaBH_3CN$ (.310 g, ∿5 mM) in ethanol (∿10 ml) was added quickly (within 4 mins) to a boiling solution (74°C) containing $CoCl_2 \cdot 6H_2O$ (.595 g, ∿2.5 mM) and Diphos (2.985 g, ∿7.5 mM) in ethanol/toluene (6:1, 5 ml). The dark green coloured solution turned to dark brown as the $NaBH_3CN$ was added. Precipitation of a yellow solid started immediately and continued while the mixture was stirred for a further 1 hr at room temperature. The yellow solid was filtered off and purified as described above.

C.3. This method was essentially the same as described by Holah and coworkers (16), except that the solvent system used was ethanol/toluene (6:1, 5 ml) instead of ethanol only.

D. The reactions between $CoCl_2 \cdot 6H_2O$, Diphos and $NaBH_3CN$ at elevated temperatures were also found to be very sensitive to slight changes in reaction conditions. The following subsections describe the synthesis of $Co(CN)Cl(Diphos)_2$ and $Co(BH_3CN)_2(Diphos)_2$ although repeated attempts to reproduce these compounds in the pure form have so far failed.

## D.1. (Cyano) (Chloro) bis [bis (diphenylphosphino) ethane] Cobalt(II).

## $Co(CN)Cl(Diphos)_2$

$CoCl_2 \cdot 6H_2O$ (.595 g, ∿2.5 m M) and Diphos (2.98 g, ∿7.5 mM) were mixed in ethanol/toluene (5:1, 5 ml) and the temperatures of the solution raised to 63°C. The temperature was kept constant while a solution of $NaBH_3CN$ (.155 g, ∿2.5 mM), in ethanol (∿10 ml) was added over a period of 15 mins. The dark green coloured solution changed slowly to dark brown during the addition of $NaBH_3CN$. The heating was stopped and the mixture was stirred for 1 hr during which time a yellow-brown solid precipitated. The reaction mixture was again heated to 63°C (at which temperature the yellow-brown solid completely dissolved in the reaction mixture) and another addition of $NaBH_3CN$ (.155g, ∿2.5 m M) in ethanol (∿10 ml) was made over a period of 10 mins. The total $Co:BH_3CN^-$ ratio at this point was 1:2. Again the heating was stopped and the dark red solution formed after the second addition of $NaBH_3CN$ was stirred for 1 hr during which time a small quantity of a yellow solid was precipitated (see 4-E). The mixture was filtered and n-Hexane (∿15 ml) was added to the dark brown filtrate. This was kept at -10°C for 48 hrs and produced dark brown crystals which were separated, washed with ethanol and n-Hexane and dried under vacuum. The complex was recrystallized from toluene/ethanol (4:1). The compound seems to be stable in air for short periods of time (∿4 hrs).

<u>Analysis</u> Calc. for $Co(CN)Cl(Diphos)_2$

C = 69.39 H = 5.32 N = 1.52

found

C = 69.28 H = 6.12 N = 1.34

## E. Bis(cyanotrihydroborato)bis[bis(diphenylphosphino)ethane] Cobalt(II)

### $Co(BH_3CN)_2(Diphos)_2$

During attempts to reproduce the synthesis of $Co(CN)Cl(Diphos)_2$ several reactions at elevated temperatures involving Diphos, $CoCl_2 \cdot 6H_2O$ and $NaBH_3CN$ were carried out. In these reactions several parameters were changed including the Co:L ratio (varied between 1:3 and 1:2), the time of $NaBH_3CN$ addition (varied between 5 and 15 mins) and the Co:$NaBH_3CN$ ratio (varied between 1:2 and 1:6). From each of these reactions small amounts of yellow or yellow-green solids were produced and separated from the dark brown reaction mixtures. These yellow solids from several different reactions were combined together and treated with $CH_2Cl_2$ producing a deep yellowish-red solution with a large amount of a white solid remaining undissolved. Addition of n-Hexane to this yellowish-red solution, after filtration, produced a yellow solid. The solid decomposes to a dark green solution in $CH_2Cl_2$ after ∿1 hr (yield ∿2%).

Analysis: Calc. for $Co(BH_3CN)_2(Diphos)_2$

C = 69.30 H = 5.77 N = 2.99

found

C = 69.28 H = 5.99 N = 2.90

## F. Unidentified Complexes

The complex nature of the reactions between $CoCl_2.6H_2O$, Diphos and $NaBH_3CN$ at elevated temperature will be further illustrated in this subsection. Thus, in addition to $Co(CN)Cl(Diphos)_2$, the formation of several other, as yet unidentified, products were observed as described below.

F.1. $CoCl_2 \cdot 6H_2O$ (.595 g, ∿2.5 mM) and Diphos (2.0 g, ∿5 mM) were mixed in ethanol/toluene (5:1, 5 ml) and the solution was heated to boiling (70°C). To this boiling solution was added a solution of $NaBH_3CN$ (.31 g, ∿5 mM) in ethanol (∿10 ml) over a period of 5 mins. The heating was stopped and, while the solution was being stirred for 1 hr, a yellowish-green solid precipitated. The solid was filtered off and the resulting green-brown filtrate was not investigated further. The infrared spectrum of the yellow-green solid is very similar to that of $Co(BH_3CN)(DPPM)$. The solid immediately decomposed in $CH_2Cl_2$ giving a dark green solution. Attempts to reproduce the synthesis of this compound have so far failed.

F.2. $CoCl_2 \cdot 6H_2O$ (.595 g, ∿2.5 mM) and Diphos (2.98 g, ∿7.5 mM) were mixed in toluene/ethanol (1:5, 10 ml) and the temperature raised to 63°C. At this temperature a solution of $NaBH_3CN$ (.310 g, ∿5 mM) in ethanol (∿10 ml) was added very slowly over a period of 25 mins. The heating was stopped and the solution stirred for 1 hr during which time a brown solid precipitated. The solid was filtered off and the dark brown filtrate kept at ∿3°C for 24 hrs producing more brown crystalline solid. This was recrystallized from ethanol/toluene (1:5). However, the $^{31}P$-NMR spectrum of the recrystallized product showed it to be a mixture of $CoH(Diphos)_2$, $Co(CN)Cl(Diphos)_2$ and several other unknown products. The IR spectrum showed no evidence for a Co-H signal. The separation of these products has not yet been possible.

## 5. Co(II)|*Cis* DPPE|$NaBH_3CN$

### A. Bis(cyanotrihydroborato)bis[bis-cis(diphenyl phosphino)ethylene] Cobalt(II).Ethanol

## $Co(BH_3CN)_2(DPPE)_2 \cdot EtOH$

$Co(ClO_4)_2 \cdot 6H_2O$ (.457 g, ∿1.24 mM) and *cis* DPPE (1.492 g, ∿3.03 mM) were mixed together in ethanol/ toluene (2:1, 10 ml) to form a yellow-green mixture. To this a solution of $NaBH_3CN$ (.696 g, ∿8.87 mM) in ethanol (∿10 ml) was added over a period of 10 mins. As the $NaBH_3CN$ was added the colour of the mixture changed to orange-yellow and finally, after being stirred for 1 hr to orange-red. The resulting solid was then separated by filtration, washed repeatedly with benzene (to remove free phosphine) and ethanol and dried under reduced pressure for 24 hrs.

The orange coloured complex is soluble in DMF and insoluble in $CH_2Cl_2$, $CHCl_3$, THF, $C_6H_6$ and PhMe. It was recrystallized from DMF/EtOH (2:1). The crude and the recrystallized products all retain a molecule of ethanol which could not be removed even after pumping under high vacuum ($10^{-5}$ torr) for 24 hrs.

*Analysis*: Calc. for $Co(BH_3CN)_2(DPPE)_2 \cdot EtOH$

C = 68.80 H = 5.70 N = 2.87

found

C = 68.75    H = 5.81    N = 2.57

## B. Unidentified Co-(CN) Complex

An unidentified brown solid was produced in the following reaction.

$CoCl_2 \cdot 6H_2O$ (.238 g, ∿1 mM) and cis-DPPE (1.194 g, ∿3.0 mM) were mixed in ethanol/toluene (2:1, 10 ml) and the temperature of the mixture raised to the boiling point (76°C). While keeping the temperature constant, a solution of $NaBH_3CN$ (.5028 g, ∿8 m M) in ethanol (∿10 ml) was added over a period of 10 mins. The heating was stopped and the mixture stirred for 24 hrs during which time a dark brown solid was precipitated. This was collected by filtration and washed with benzene, ethanol and n-Hexane. The dark brown filtrate was not investigated further.

The brown solid (yield ∿5%) was soluble in $CH_2Cl_2$ and $CHCl_3$ but decomposed within 1 hr (red solution turning green). The infrared spectrum of the solid showed, as its major feature, a strong peak at 2100 $cm^{-1}$ ($\nu$CN). Insufficient solid was obtained for further studies, and the reaction has not yet been reproduced. The product appears to be a Co-CN-L complex.

### 6. Co(II)|*trans* DPPE|$NaBH_3CN$

At room temperature $Co(ClO_4)_2 \cdot 6H_2O$, *trans* DPPE and $NaBH_3CN$ (approx. ratio 1:3:9 respectively) in ethanol/toluene (1:1) do not react, even after 24 hrs of stirring. However, at elevated temperatures a reaction does occur forming a dark brown solution. It has not yet been possible to isolate any identifiable compound from the above dark brown solution.

### 7. Co(II)|DPPP|$NaBH_3CN$

### A. Tetrakis(cyanotrihydroborato)tris[bis(diphenylphosphino)propane]dicobalt(II)

## $[Co(BH_3CN)_2(DPPP)_{1.5}]_2$

The following methods were used to prepare this compound.

A.1. A solution of $NaBH_3CN$ (.310 g, ∿5 mM) in ethanol (∿10 ml) was added over a period of 10 mins to a stirred solution containing a mixture of $Co(ClO_4)_2 \cdot 6H_2O$ or $CoCl_2 \cdot 6H_2O$ (∿1.25 mM) and DPPP (1.545 g, ∿3.75 mM) in ethanol/toluene (1:1, 15 ml). As the $NaBH_3CN$ was added the light pink solution (blue for $CoCl_2 \cdot 6H_2O$) changed to green and finally to dark green-brown. Precipitation of a green solid started immediately and continued as the solution was stirred for 1 hr (after complete addition of the $NaBH_3CN$). The green solid was filtered off (the resulting brown-green filtrate will be discussed in 7-C) and recrystallized unchanged from $CH_2Cl_2$/Hexane (5:1), THF/Hexane (4:1), $CHCl_3$/Hexane (5:1) or $C_6H_6$/Hexane (2:1) as small olive green crystals. However, prolonged standing (for more than 2-3 hrs) of the complex in the above solvents resulted in decomposition to an unidentified dark coloured solid. The green complex immediately decomposes in DMF, DMSO, MeCN and $Me_2CO$. The solid appears to be stable in air (more than 3 days) but decomposes in solution.

<u>Analysis:</u> Calc. for $[Co(BH_3CN)_2(DPPP)_{1.5}]_2$

C = 67.4 H = 5.95 N = 3.70 Co = 7.8

found

a) product recrystallized from $CH_2Cl_2$/Hexane

C = 67.04 H = 5.74 N = 3.47 Co = 7.3*

b) product recrystallized from THF/Hexane

C = 67.4 H = 5.95 N = 3.70 Co = 6.2

c) product recrystallized from $CHCl_3$/Hexane

C = 67.69 H = 6.20 N = 3.64 Co = 6.8

d) product recrystallized from $C_6H_6$/Hexane

C = 67.41 H = 6.16 N = 3.72 Co = -

<u>A.2.</u> $Co(ClO_4)_2 \cdot 6H_2O$ (4.57 g, ∿1.25 mM) and DPPP (1.545 g, 3.75 mM) were mixed in THF (∿30 ml) and the mixture stirred for 20 mins. A solution of $NaBH_3CN$ (.310 g, ∿5 mM)

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NOTE: The author wishes to thank Mrs. E. Jenson of the Geology Department, Lakehead University, for carrying out the Cobalt analyses by atomic absorption spectrophotometry.

in ethanol (∿10 ml) was then added to the stirred mixture over a period of 10 mins. The resulting dark green solution was stirred for 1 hr during which time a green solid was precipitated. The solid was separated and purified as described above.

## B. Hydrido bis[bis(diphenylphosphino)propane] Cobalt(I)

### $CoH(DPPP)_2$

$CoCl_2 \cdot 6H_2O$ (.2379 g, ∿1 mM) and DPPP (1.545 g, ∿3.75 mM) were mixed in benzene/ethanol (1:1, 15 ml) and the temperature of the mixture raised to the boiling point (68°C). A solution of $NaBH_3CN$ (.620 g, ∿9.8 mM) in ethanol (∿10 ml) was then added dropwise over a period of 10 mins to the reaction mixture maintained at a constant temperature of 68°C. The blue coloured solution turned dark green. Heating was stopped and the mixture stirred for 1 hr before a further addition, over a 10 min period, of a solution of $NaBH_3CN$ (.910 g, ∿14.5 mM) in ethanol (∿10 ml) was made, again at 68°C. The dark green solution turned deep red and was stirred at room temperature for 3 hrs during which time a small amount of a brown solid precipitated. This was separated by filtration and the resulting dark red filtrate kept at ∿6°C for 24 hrs producing large brown crystals. The compound was finally recrystallized from benzene/ethanol (3:1). The highly air sensitive compound decomposes within 10-15 mins in $CHCl_3$, $CH_2Cl_2$, THF and DMF.

Analysis: Calc. for $CoH(DPPP)_2$

C = 73.38 H = 5.93

found

C = 74.00 H = 6.08

### C. Bis[bis(diphenylphosphino)propane]cobalt(0)

### $Co(DPPP)_2$

This cobalt zero complex was isolated from the brown-green coloured filtrate after the separation of $[Co(BH_3CN)_2(DPPP)_{1.5}]_2$ in reaction 7-A. When this filtrate was kept at ∿6°C, light red crystals, in a very small yield (∿4%) were produced after 24 hrs. The complex is very air sensitive and immediately decomposes in solvents like $CH_2Cl_2$, $CHCl_3$ and DMSO. However, it can be recrystallized from benzene/ethanol.

Analysis Calc. for Co(DPPP)$_2$

$C = 73.0 \quad H = 6.1$

found

$C = 73.16 \quad H = 5.92$

8. Co(II)|DPPB|NaBH$_3$CN

A. Bis(cyanotrihydroborato)bis[bis(diphenylphosphino)butane] cobalt(II)

Co(BH$_3$CN)$_2$(DPPB)$_2$

The above complex has been synthesized by the following methods.

A.1. Co(ClO$_4$)$_2$·6H$_2$O (.365 g, ∿1 mM) and DPPB (o.87 g, ∿2.2 mM) were dissolved in benzene/ethanol (5:1, 10 ml) and stirred for 30 mins to give a clear pink solution. A solution of NaBH$_3$CN (1.0 g, ∿16 mM) in ethanol (∿15 ml) was then added dropwise over a period of 15 mins to the stirred solution. The resulting deep green-brown coloured solution was stirred for 1 hr and then filtered. The filtrate was kept at ∿4°C for 24 hrs during which time an olive green solid was precipitated. The solid was filtered off and the resulting dark brown filtrate was treated further (see 8-B). The green solid is insoluble in $C_6H_6$, $CH_2Cl_2$, $CHCl_3$, THF, MeCN, and (even) DMF and DMSO. The solid was purified by washing with benzene (∿15 ml), $CH_2Cl_2$ (∿20 ml) ethanol (∿20 ml) and n-Hexane (∿5 ml). The products obtained from several different reactions and purified by the above method consistently analysed for $Co(BH_3CN)_2(DPPB)_2$. The complex is air stable.

<u>Analysis</u> Calc. for $Co(BH_3CN)_2(DPPB)_2$

C = 70.2 H = 6.25 N = 2.82

found

C = 69.85 H = 6.03 N = 2.92

<u>A.2.</u> The deep blue mixture of $CoCl_2 \cdot 6H_2O$ (.23 g, ∿1 mM) and DPPB (1.27 g, ∿3 mM) in ethanol/benzene (1:1, 10 ml) was heated to reflux temperatures (68°C) and a solution of $NaBH_3CN$ (0.85 g, ∿13.5 mM) in ethanol (∿10 ml) was added over a period of 5 mins. The resulting dark brown-green solution was stirred for 1 hr at room temperature, during which time a green solid was precipitated, separated and purified as described above.

## B. (Cyanotrihydroborato)bis[bis(diphenylphosphino)butane]cobalt(I)

## $Co(BH_3CN)(DPPB)_2$

The above complex was isolated from the dark brown filtrate of reaction 8-A after the removal of the green $Co(BH_3CN)_2(DPPB)_2$ . n-Hexane (∿10 ml) was added to the brown solution which was kept at ∿4°C for 24 hrs. The orange solid so produced was separated (∿5% yield) and washed with benzene (∿15 ml), ethanol (∿10 ml) and n-Hexane (∿5 ml) and dried under vacuum. The complex is extremely air sensitive. It is insoluble in $C_6H_6$, EtOH, PhMe and THF and it decomposes in DMF, DMSO and $CHCl_3$.

Analysis Calc. for $Co(BH_3CN)(DPPB)_2$

C = 71.92 H = 6.20 N = 1.47

found

C = 68.8 H = 6.48 N = 1.66

Note: The low percentage of carbon might be the result of decomposition during analysis as the compound is very air sensitive.

# CHAPTER III

## Results and Discussion

### 1 Reactions of Co(II), $PPh_3$ and $NaBH_3CN$

The above system was initally studied by Holah and coworkers and in a preliminary communication (29) a wine coloured complex tentatively assigned the formula, $Co(BH_3CN)_2(PPh_3)_3$ was reported. However, in a later report (16) the same authors mentioned that they were unable to isolate any identifiable product from reactions between $Co(II)|PPh_3|NaBH_3CN$. Thus it was felt necessary to reinvestigate the above system under a wider range of conditions than previously studied. It has now been found that the initially reported wine red solid was almost certainly a mixture of two complexes, the wine red coloured $CoH(BH_3CN)(PPh_3)_3$ and an as yet unidentified very interesting blue solid. The carbon and hydrogen content of the latter are comparable with the content of the red complex, but the blue compound contains a much higher percentage of nitrogen. Thus, very small amounts of the blue solid mixed with the hydridocyanotrihydroborato complex can radically change the percentage of nitrogen in a sample and this might have misled the authors in initially formulating the wine red complex as $Co(BH_3CN)_2(PPh_3)_2$.

## A. $CoH(BH_3CN)(PPh_3)_3$

The very precise reaction conditions which are necessary to produce the hydridocyanotrihydroborato complex in the pure form have been established. Thus reactions between cobalt perchlorate hexahydrate, $PPh_3$ and $NaBH_3CN$ in a 1:6:14 molar ratio in a mixture of ethanol and toluene lead to highly crystalline samples of $CoH(BH_3CN)(PPh_3)_3$ which form in reaction filtrates after about 24 hrs at room temperature. Smaller amounts of either phosphine (1:3:14) or $NaBH_3CN$ (1:6:9) lead to mixtures of $CoH(BH_3CN)(PPh_3)_3$ and the blue compound.

$CoH(BH_3CN)(PPh_3)_3$ forms blood red solutions in $C_6H_6$, PhMe, THF, $CH_2Cl_2$ and DMF but these turn green very rapidly although the presence of free phosphine slows slightly the rate of decomposition. This indicates that it is unlikely that decomposition in solution is the result of simple dissociation of $PPh_3$ as shown below,

$$CoH(BH_3CN)(PPh_3)_3 \rightleftharpoons CoH(BH_3CN)(PPh_3)_2 + PPh_3$$

since even the addition of very large amounts of phosphine is unable to prevent decomposition. Loss of the $BH_3CN^-$ may also be involved. Due to the sensitivity of the complex in solution recrystallization was not possible. Nor was it possible to recover the red compound from the reactions where a mixture of red and blue compounds were formed. It is, however, possible to obtain the 'pure' blue solid by extracting the red compound into organic solvents (e.g. $C_6H_6$, THF) in which the blue material is insoluble.

In spite of the sensitivity of this complex in solutions, it was possible to grow single crystals directly from the reaction mixture by carrying out reactions in dilute solutions. At the time of writing, data collection is complete and the structure will be known shortly.

The infrared spectrum of the complex is shown in fig. XX and the important frequencies are listed in Table 15. No changes were seen in the infrared spectrum of the complex after exposure of the sample to air for 24 hrs, but slow decomposition occurs after longer times. As seen from fig. XX there is a strong and sharp signal at 2190 $cm^{-1}$ assignable to the cyanide stretching frequency of the $BH_3CN^-$ grouping. This is a shift of only 11 $cm^{-1}$ from the ionic $BH_3CN$ (2179 $cm^{-1}$) and suggests that the coordination of $BH_3CN$ to the cobalt is through the nitrogen atom of the cyanide group. Such a small shift in the $\nu CN$ is indicative of a weak coordination ($M \text{---} NCBH_3$ type) of the $BH_3CN^-$ grouping to the metal. A similar situation has been observed for $Cu(BH_3CN)_2(Me_5dien)$ which has two significantly different Cu-N distances (see fig. IX, page 36). These give rise to two different CN stretching frequencies, one at 2210 $cm^{-1}$ (assigned to the CN grouping where the Cu-N distance is shorter) and the other at 2192 $cm^{-1}$. Moreover this copper complex in solution was found to be a 1:1 electrolyte which was explained in terms of the almost complete dissociation of the weakly coordinated $BH_3CN^-$ grouping. Thus, as mentioned before, the extreme sensitivity of the hydridocyanotrihydroborato complex in solution might be the result of a very weakly coordinated $BH_3CN^-$ grouping.

The $BH_3$ stretching vibrations in the infrared spectrum occur as a strong and broad band at 2340 $cm^{-1}$ with weak bands at 2210 and 2280 $cm^{-1}$. A medium intensity peak at 1962 $cm^{-1}$ has been assigned to the Co-H stretching vibration. The Co-H and the $BH_3$ deformation modes which occur in the range 700 - 900 $cm^{-1}$ (67) and 1000 - 1150 $cm^{-1}$ (7) respectively, were obscured by the strong phosphine vibrations in these regions.

The complex is paramagnetic with a magnetic moment of 1.9 B.M. showing that the complex is low spin. The fact that the cobalt is subjected to such a strong ligand field is surprising since $PPh_3$-Co(II) complexes are generally high spin (68,69) and the $Co-NCBH_3$ interaction is apparently weak. This suggests that the hydride must be strongly bonded.

It is unfortuante that we have not been able to see the metal hydride signal in the $^1H$ NMR spectrum due to the instability of the complex in solutions even with added phosphine. The spectrum recorded at low temperatures (-70°C) also failed to show the hydride. The $^{31}P$ NMR spectrum of a freshly prepared solution is also consistent with decomposition of the sample. The spectrum shows a broad signal centered at $\delta = -1.67$, which is close to the free phosphine signal at $\delta = -6.57$ (42). The line broadening in this spectrum might also be the result of the paramagnetism associated with the cobalt. However, as will be seen later such broad signals close to the free phosphine

TABLE 15:

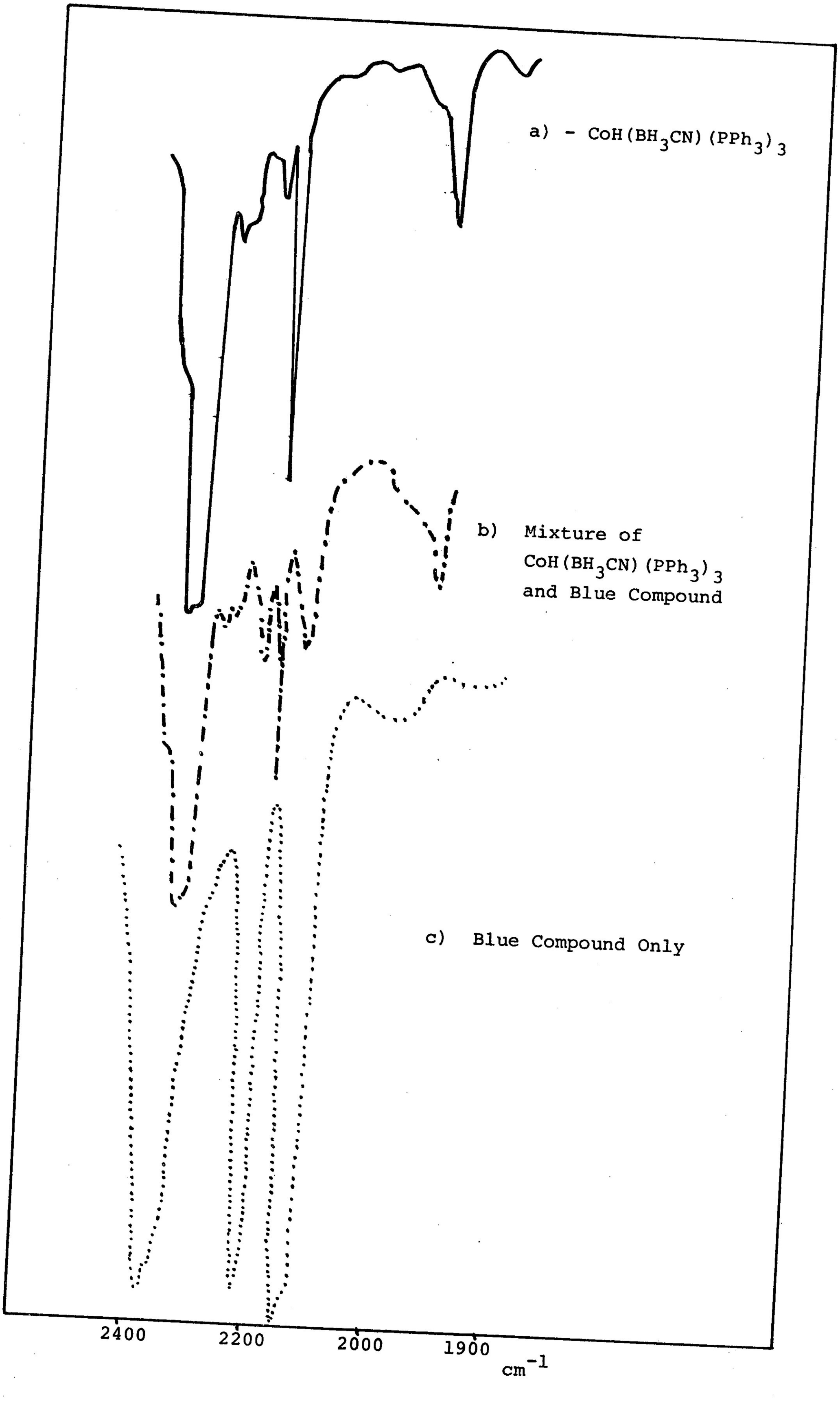
Infrared, NMR, Electronic and Magnetic Measurement Data on Complexes Derived from Co(II), $PPh_3$ and $NaBH_3CN$ Reactions

| No. | Complexes | $\nu BH$ $cm^{-1}$ | $\delta BH$ $cm^{-1}$ | $\nu CN$ $cm^{-1}$ | $\nu CO\text{-}H$ $cm^{-1}$ | $\delta$ $^{31}P$ NMR | $\delta$ $^{1}H$ MNR | $\mu$ (B.M.) | Electronic Spectra $cm^{-1}$ Solid State | Electronic Spectra $cm^{-1}$ Solution ($\varepsilon$ in Bracket) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. | $CoH(BH_3CN)(PPh_3)_3$ | 2340(s,b)<br>2210(w)<br>2280(w) | | 2190(s) | 1962(m) | -1.67(b) | 7.8 | 1.9 | 8333(b)<br>11,111(sh) | 7692(42)<br>16,666(28) |
| 2. | Blue Solid | 2380(s,b) | | 2210(s)<br>2120(s,b)? | | 89.59(b) | | | 18,181<br>9090 | |

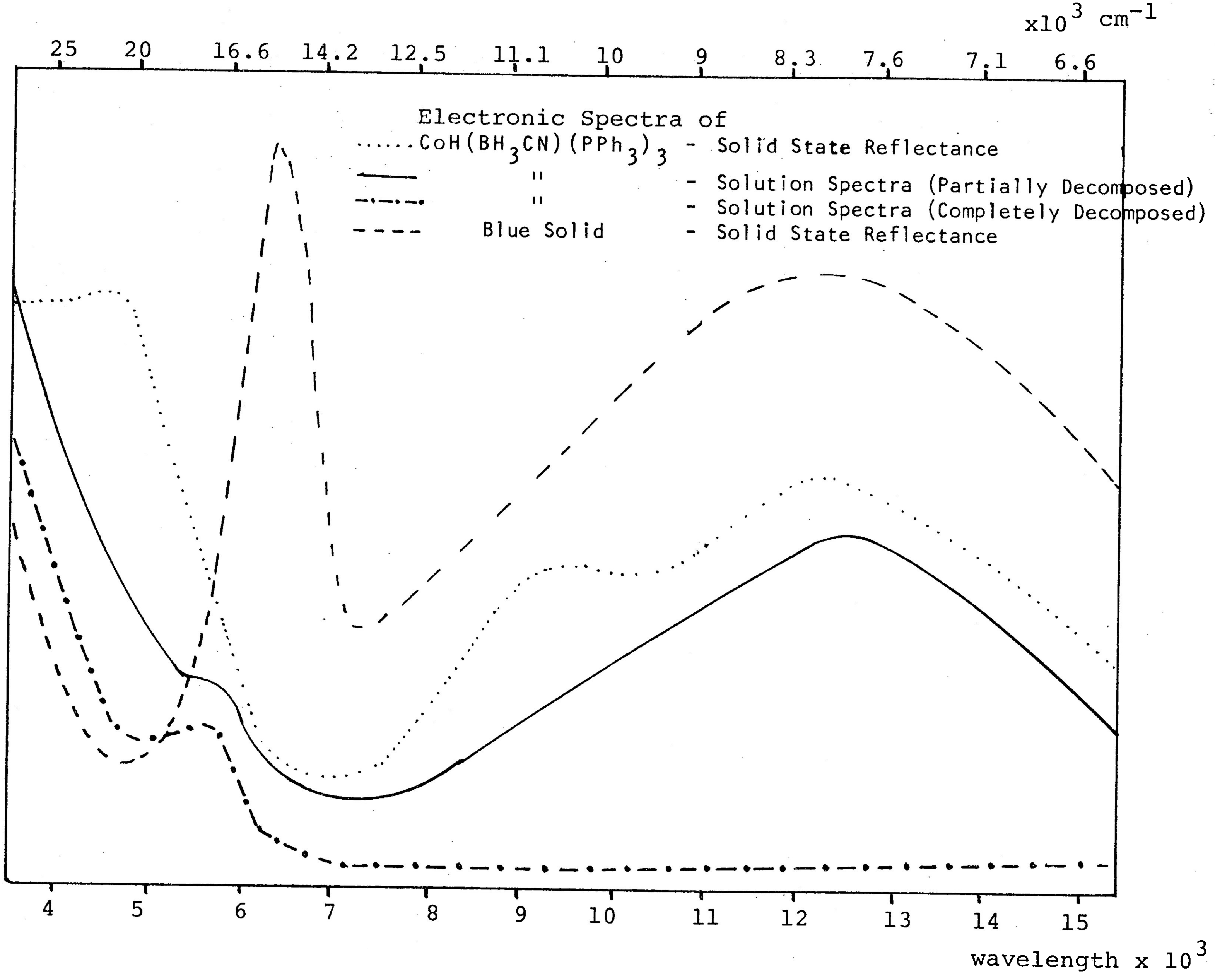
Abbreviations

w, weak
s, strong
b, broad
m, medium
sh, shoulder

Selected Features of the Infrared Spectra of



(XX)


x10$^3$ cm$^{-1}$
25
20
16.6
14.2
12.5
11.1
10
9
8.3
7.6
7.1
6.6
Electronic Spectra of
...... $CoH(BH_3CN)(PPh_3)_3$ - Solid State Reflectance
" - Solution Spectra (Partially Decomposed)
" - Solution Spectra (Completely Decomposed)
Blue Solid - Solid State Reflectance
4
5
6
7
8
9
10
11
12
13
14
15
wavelength x 10$^3$ A$^o$

(XXI)

signals in $^{31}P$ NMR spectra have also been observed for diamagnetic complexes (e.g. $Co(BH_3CN)(Diphos)_2$, see page 174) and the implication is that the broadening is the result of extensive ligand (phosphine) exchange in solution. However, this behaviour is not properly understood at present and more studies in this regard are underway in our laboratories.

The electronic spectra of the complex both in solution and in the solid state are shown in fig. XXI. The solid state reflectance spectrum shows basically two regions of absorption, a broad peak at 8333 $cm^{-1}$ and another shoulder at 11,111 $cm^{-1}$. As might be expected, even the rapidly obtained spectrum of a freshly prepared solution of this complex is different from the spectrum in the solid state. Peaks now occur at 7692 $cm^{-1}$ ($\varepsilon = 42$) and 16,666 $cm^{-1}$ ($\varepsilon = 28$), whereas the spectrum when the solution finally turns green shows only the absorption at 16,666 $cm^{-1}$. The reflectance spectrum of the complex shows no resemblance to the spectra of any other cyanotrihydroborato complexes prepared in this work. Also there does not appear to be any close similarity to the spectra reported in the literature for low spin Co(II) complexes either in square pyramidal (70,71) or trigonal bipyramidal (72) geometries. However, the solution spectrum of the partially decomposed sample does show some resemblance to the spectrum of the blue solid (to be discussed shortly), which also shows strong bands in its relectance spectrum at 9090 $cm^{-1}$ and 18,181 $cm^{-1}$. Perhaps after the true structure of the complex is known, it will be possible to interprete these spectra. At the present time, all the data seem to point towards a five coordinated cobalt(II) structure for this complex.

## B. Unidentified Blue Solid

Although we have not yet been able to identify the blue solid which appears in several reactions where $CoH(BH_3CN)(PPh_3)_3$ is formed, suitable reaction conditions have very recently been established to prepare this complex in higher yields. Thus the reactions at reflux temperatures involving $CoCl_2 \cdot 6H_2O$, $PPh_3$ and a large excess of $NaBH_3CN$ leads to deep royal blue coloured, highly crystalline samples of this solid. These crystals unfortunately disintegrate when dried under vacuum and a blue powder results. Attempts to dry samples under a slow nitrogen flow were also not successful.

The chemical analyses of similarly treated samples obtained from two different reactions were found to be the same, although the $^1H$ NMR spectra of the samples showed the presence of quite different amounts of toluene, ethanol and water. Attempts to remove these solvent molecules under vacuum for periods of up to 36 hrs have not been successful. The high nitrogen content and IR data (see later) suggest that $N_2$ may be present and mass spectral data indicate that (due to the significant increase in the peak at M/e = 28), this $N_2$ is released at relatively low temperatures (<90°C). Drying at higher than ambient temperatures has therefore been avoided. The above results make it difficult to formulate this complex at the present time.

The complex shows in its infrared spectrum (see fig. XX ) strong and broad peaks at 2120 and 2210 $cm^{-1}$. The peak at 2210 $cm^{-1}$ is certainly due to the cyanide stretching frequency of the $BH_3CN$ grouping. The equally strong peak at 2120 $cm^{-1}$ can be due either to the $N{\equiv}N$ stretching frequency of coordinated $N_2$ or to the isocyanide stretching frequency (if the $BH_3CN^-$ has isomerized, $\nu NC$ = 2070 $cm^{-1}$, see Table 1). It seems more probable that this peak is due to $N_2$ because of the very high nitrogen content of the complex and the mass spectral data mentioned earlier.

The $BH_3$ stretching vibrations show a considerable shift from ionic $BH_3CN$ (2340 $cm^{-1}$) and appear as a broad band at 2380 $cm^{-1}$. In addition there are two other bands, one at 1675 $cm^{-1}$ which is strong and broad and another broad band at 3500 $cm^{-1}$. These are probably due to the large amounts of solvent impurities in the complex.

As discussed before, the reflectance spectrum (fig.XXI) of the complex shows two strong absorptions at 18,181 $cm^{-1}$ and 9090 $cm^{-1}$. The appearance of the spectrum appears to be similar to those of some trigonal bipyramidal Co(I) complexes (73,74).

As mentioned earlier, the $^1H$ NMR spectrum of the complex shows the presence of a variety of solvent molecules but no signal in the high field region and no signal due to the $BH_3$ protons. The $^{31}P$ NMR spectrum of the compound shows free phoshpine ($\delta = -5.47$) and a broad signal at $\delta = 89.59$. Such a large chemical shift might indicate that the complex is paramagnetic, but clearly considerably more work is required before this complex can be identified. It would also be interesting to prepare this complex under a different inert gas (such as argon) to establish if indeed $N_2$ is present.

## ii Reactions of Co(II), DPPM and $NaBH_3CN$

Of the many products which form in reactions between either $CoCl_2$ or $Co(ClO_4)_2$, DPPM and $NaBH_3CN$, two proved relatively easy to isolate, two are produced together and have not yet been separated from each other and the presence of several others has been seen in $^{31}P$ NMR spectra.

A readily formed product from the reactions of cobalt perchlorate hexahydrate, DPPM and $NaBH_3CN$ is the yellow, $[Co(BH_3CN)(DPPM)_2](ClO_4)$. This can be produced from reactions where Co:$NaBH_3CN$ ratios range from 1:1 to 1:16, while reactions where even larger amounts of $NaBH_3CN$ are used (1:∿19) result in the reduction of Co(II) to Co(I) and the formation of a complex tentatively formulated as $Co(BH_3CN)(DPPM)$. With still larger amounts of the reducing agent, complex unresolvable mixtures of solids are obtained, as seen from the infrared spectra of the solids which show a number of absorptions in the $BH_3CN^-$ region.

Reactions between cobalt chloride hexahydrate and $NaBH_3CN$ in the presence of DPPM behave differently.

Thus with a 1:1 ratio of $CoCl_2 \cdot 6H_2O$ to $NaBH_3CN$ an as yet unresolved mixture of green and blue solids is obtained. When the above ratio is increased to 1:4, reduction of Co(II) to Co(I) appears to take place and $Co(BH_3CN)(DPPM)$ is produced. A further increase in the amount of $NaBH_3CN$ leads to a mixture of unknown compounds. Similarly, reactions at elevated temperatures were also found to lead to mixtures of compounds, the presence of which has been observed through IR and NMR spectroscopy.

The complexes which have been isolated will now be considered in more detail.

## A. $[Co(BH_3CN)(DPPM)_2](ClO_4)$

As mentioned above the addition of a wide range of concentrations of $NaBH_3CN$ over a 10-20 min period to $Co(ClO_4)_2 \cdot 6H_2O$ and DPPM in a mixture of benzene and ethanol yields the yellow coloured Co(II) cyanotrihydroborato complex, $[Co(BH_3CN)(DPPM)_2](ClO_4)$. Reactions were generally stirred for 24 hrs.

The reactions are sensitive to the rate of addition of the $NaBH_3CN$, the solvent and the reaction time period. Thus in reactions, especially where large amounts of $NaBH_3CN$ are involved, when the $NaBH_3CN$ is added too fast (<5 mins), large amounts of a dirty white solid are precipitated. The infrared spectrum of this shows no significant absorptions in the $BH_3CN^-$ region and is presumably the free phosphine. Perhaps in these reactions there is not enough time for the phosphine to coordinate to and stabilize the cyanotrihydroborato complex. Only a small yield of yellow complex is also seen when the solvent is changed from the usual benzene and ethanol mixture to only ethanol. This is probably due to the low solubility of DPPM in alcohol, so that there is little ligand in solution to stabilize the cobalt-cyanotrihydroborato complex. The reactions where large excesses of $NaBH_3CN$ (∿16 mM) are used and which are left for longer periods of time (>24 hrs) lead to mixtures of green solids. This is apparent from the complicated pattern of absorptions in the 2000 - 2400 $cm^{-1}$ region in the infrared spectra of the isolated solids.

The infrared spectrum of $[Co(BH_3CN)(DPPM)_2](ClO_4)$ and the analogous complex formed when $NaBD_3CN$ is used are shown in fig. XXII, with the important frequencies tabulated in

TABLE 16:

Infrared, NMR, Electronic and Magnetic Measurement Data on Complexes Derived from Co(II), DPPM and $NaBH_3CN$ Reactions

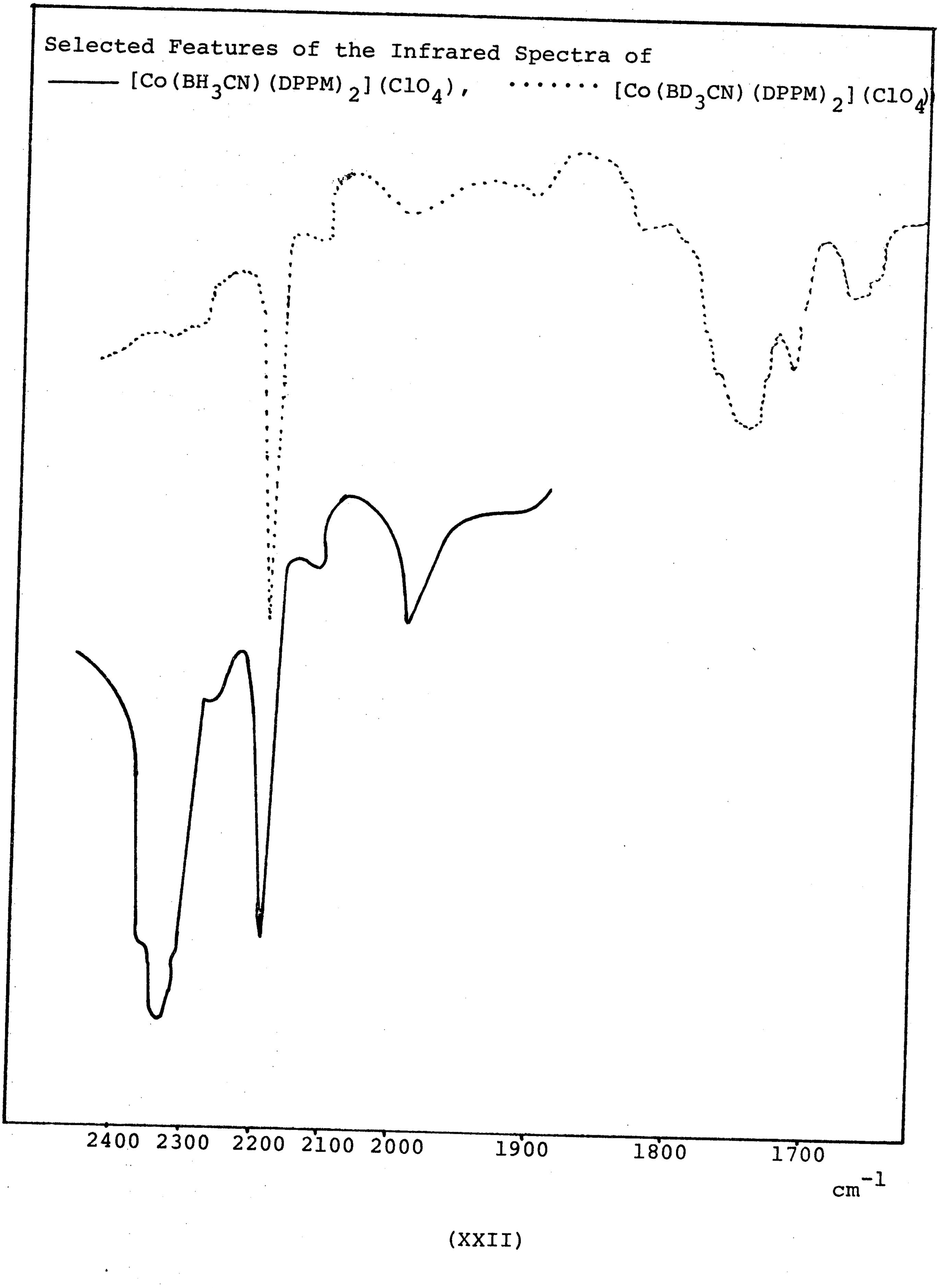
| | Complexes | $\nu BH$ $cm^{-1}$ | $\delta BH$ $cm^{-1}$ | $\nu CN$ $cm^{-1}$ | $\nu Co\text{-}H_b\text{-}B$ $cm^{-1}$ | $\delta$ $^{31}P$ NMR | $\delta$ $^{1}H$ MNR | $\mu$ (B.M.) | Electronic Spectra $cm^{-1}$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Solid State | Solution |
| 1. | $[Co(BH_3CN)(DPPM)_2](ClO_4)$ | 2345(s,b)<br>2245(sh)<br>2375(sh) | | 2200(s) | 2000(m) | 2.02 | -14.76(Q)<br>JPH=47.5 HZ | 1.9 | 16,666 | 16,666 |
| 2. | $[Co(BD_3CN)(DPPM)_2(ClO_4)$ * | 1755(m,b) | | 2200(s) | | 2.04 | | | | |
| 3. | $Co(BH_3CN)(DPPM)$ | 2340(s,b) | 1100(s) | 2160(s) | 1990(m) | 2.02 | a) O(Qt)<br>JBH=90 HZ<br>b) -15.30(Q)<br>JPH=48 HZ | Diamagnetic | 9090<br>16,666 | 16,666 |
| 4. | $Co(BH_3CN)(DPPM)\cdot MeOH$ | 2350(s,b) | 1100(s)<br>1120(s) | 2180(s)<br>2202(s) | 1990(m) | 2.02 | " | " | " | " |
| 5. | Impure Green Solid ‡ | 2340(s,b) | 1100(s) | 2200(s)<br>2140(w) | | a) 2.02<br>b) 59.5<br>c) 84.27 | -14.71(Q)<br>JPH=48 HZ<br>-11(b), -30(b)<br>-40(b), -51(b) | | | 16,700 |

* $\nu ClO_4$ —— 1100(s)

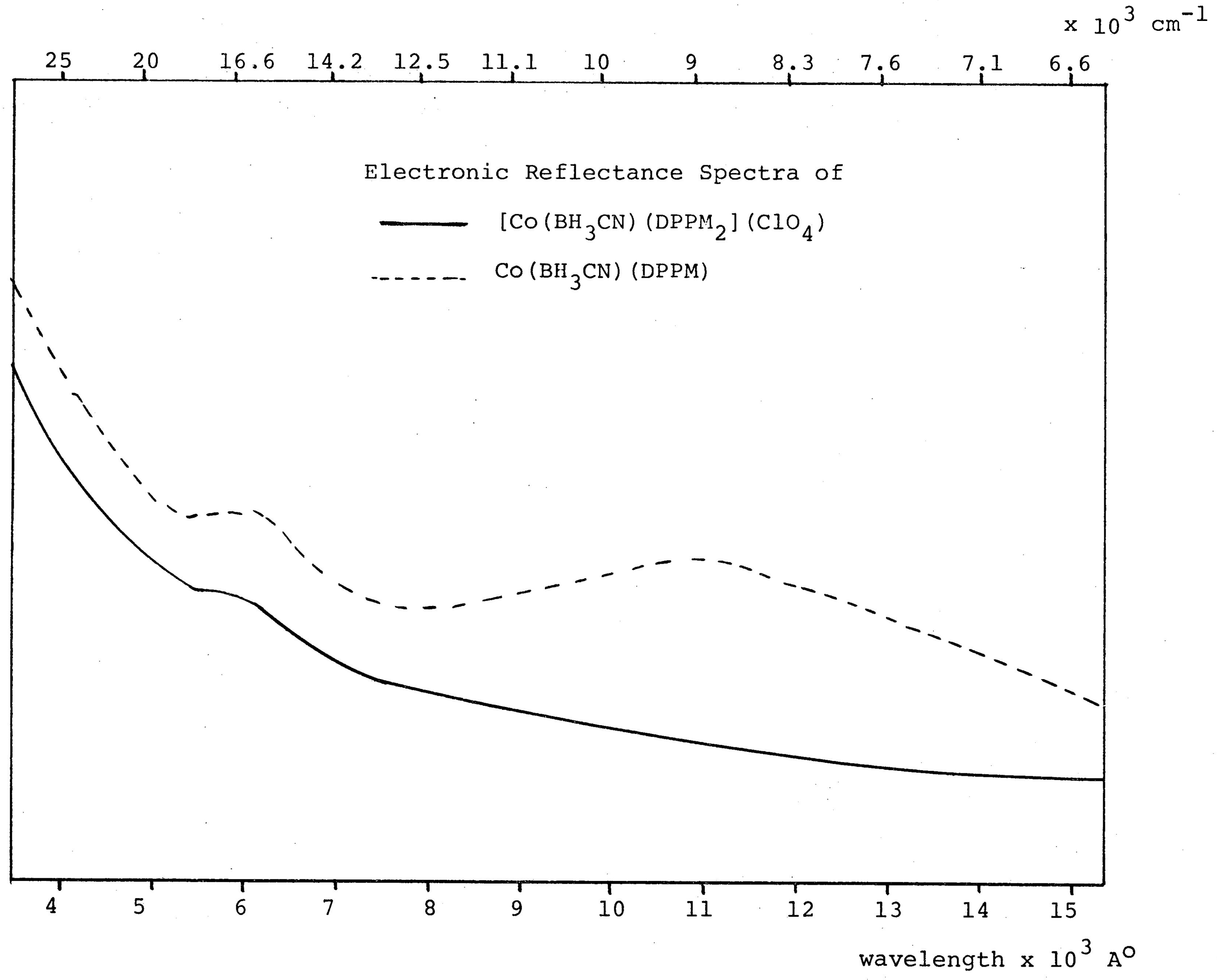
‡ $\nu Co\text{-}Cl$ —— 330(m)

Abbreviations

b, broad
m, medium
s, strong
sh, shoulder
Q, Quintet
Qt, Quartet


Selected Features of the Infrared Spectra of
——— [Co(BH$_3$CN)(DPPM)$_2$](ClO$_4$), ······· [Co(BD$_3$CN)(DPPM)$_2$](ClO$_4$)
2400
2300
2200
2100
2000
1900
1800
1700
cm$^{-1}$

(XXII)


x $10^3$ cm$^{-1}$
25
20
16.6
14.2
12.5
11.1
10
9
8.3
7.6
7.1
6.6
Electronic Reflectance Spectra of
$[Co(BH_3CN)(DPPM_2](ClO_4)$
$Co(BH_3CN)(DPPM)$
4
5
6
7
8
9
10
11
12
13
14
15
wavelength x $10^3$ A°

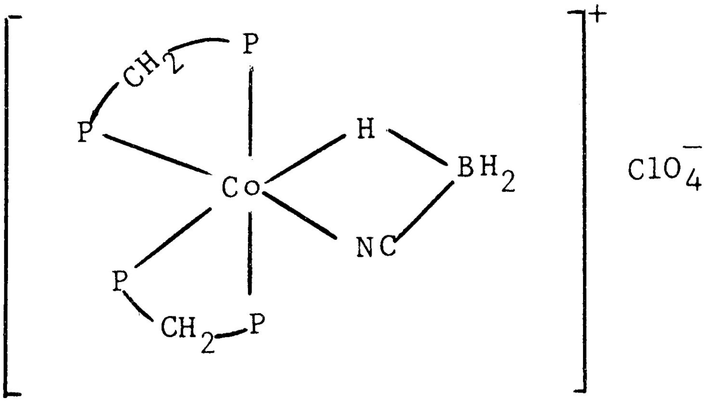
(XXIII)

Table 16. The large and broad peak at 1100 cm$^{-1}$ clearly shows the presence of the $ClO_4^-$ grouping and is consistent with the stretching vibrations of ionic perchlorate (75). The $BH_3$ stretching modes occur at 2345 cm$^{-1}$ as a strong and broad band with shoulders at 2245 and 2375 cm$^{-1}$. In the spectrum of the deuterated complex the broad band shifts to 1755 cm$^{-1}$, very close to the calculated value of 1720 cm$^{-1}$. The cyanide stretching vibrations of the $BH_3CN^-$ grouping occurs as a strong and sharp signal at 2200 cm$^{-1}$ showing an increase of 21 cm$^{-1}$ from the ionic $BH_3CN$ grouping. Such a large shift in $\nu CN$ is reasonably conclusive evidence that the nitrogen of $BH_3CN^-$ is involved in coordination to the metal ion (13). However there is a weak band at ∿2000 cm$^{-1}$ which may be assigned to a $M\text{-}H_b\text{-}B$ stretching frequency. In the deuterated complex this band is expected at ∿1475 cm$^{-1}$ but is obscured by strong ligand vibration in this region. A band at 2070 cm$^{-1}$ in the spectrum of $Ni(BH_3CN)(PPh_3)_2$ has also been assigned to the $M\text{-}H_b\text{-}B$ stretching frequency by Holah and coworkers (16). It appears therefore that as well as the nitrogen atom, one hydrogen of the $BH_3CN^-$ grouping is also involved in coordination to the metal. If this is the case, this is the first reported complex of the cyanotrihydroborato ion where both the nitrogen and a hydrogen of the $BH_3CN^-$ grouping are involved in bonding with the same metal.

Further evidence for the involvement of a hydrogen is shown by the $^1H$ NMR spectrum of the complex which shows a well resolved quintet at $\delta = -14.76$ with JPH = 47.5 HZ, indicating that four magnetically equivalent phosphorus atoms of the two DPPM ligands are coupling with the coordinated hydrogen of the $BH_3CN^-$ grouping. The $^{31}P$ NMR spectrum of the cyanotrihydroborato complex shows one signal at $\delta = 2.02$, again showing that the phosphorus atoms in the molecule are equivalent, at least in solution. An additional very weak signal at $\delta = -23$ due to the free phosphine (76) is always seen in the $^{31}P$ NMR spectrum. The absence of other signals in the $^{31}P$ NMR spectrum rules out any possibility that this complex is contaminated by either of the Co-H-DPPM complexes recently prepared in this laboratory (42). For example, the five coordinate red colured $CoH(DPPM)_2$ shows a signal at $\delta = 57.2$ whereas the signal due to the other yellow complex (presumably with bridging dihydrides) $[CoH(DPPM]_2$, appears at $\delta = -16$. In addition the metal hydride stretching frequencies in the infrared spectra of these hydrides occur at 1855 and 1968 $cm^{-1}$ respectively, and neither of these absorptions occur in the spectrum of the $BH_3CN^-$ complex. However, the yellow dihydride shows a quinet at $\delta = -17.2$ with JPH = 52 HZ in its $^1H$ NMR spectrum.

It does not seem reasonable that the complex can contain a cobalt(III)-hydride link (i.e. $CoH(BH_3CN)(DDPM)_2(ClO_4)$) to account for the quintet in the $^1H$ NMR spectrum and the peak at 2000 $cm^{-1}$ (Co-H) in the IR spectrum of the complex. This can be further discounted by the fact that the complex is paramagnetic with a magnetic moment of 1.9 B.M. due to one unpaired electron.

All the evidence therefore points to a structure for the complex as shown below.



(XXIV)

As pointed out earlier, if the above is the structure of the complex then it represents the first example of a phosphine-metal-$H_b$-$BH_2CN$ arrangement where the $H_b$ appears to be behaving as a terminal hydride (as in, for example, $CoH(DPPM)_2$) coupled to four equivalent phosphorus atoms in solution. What is still not clear is why, in such an arrangement, the $BH_2$ protons are not seen, coupled to $H_b$ and why $H_b$ and $H_t$'s are not coupled to B. There appears the possibility that the $B(H_2)_t$ resonance might be obscured by the strong signal due to the aromatic protons of DPPM ($\delta = 7.2$), as sometimes the $B(H_2)_t$ resonances do occur way down field in this region (44). Thus for $IrH_2(BH_4)(PR_3)_2$, a complex which contains a bidentate $BH_4$ grouping, the $B(H_2)_t$ protons appear at $\delta = 6.86$ to 7.8, while the $B(H_2)_b$ are at $\delta = -6.79$ to $-6.87$.

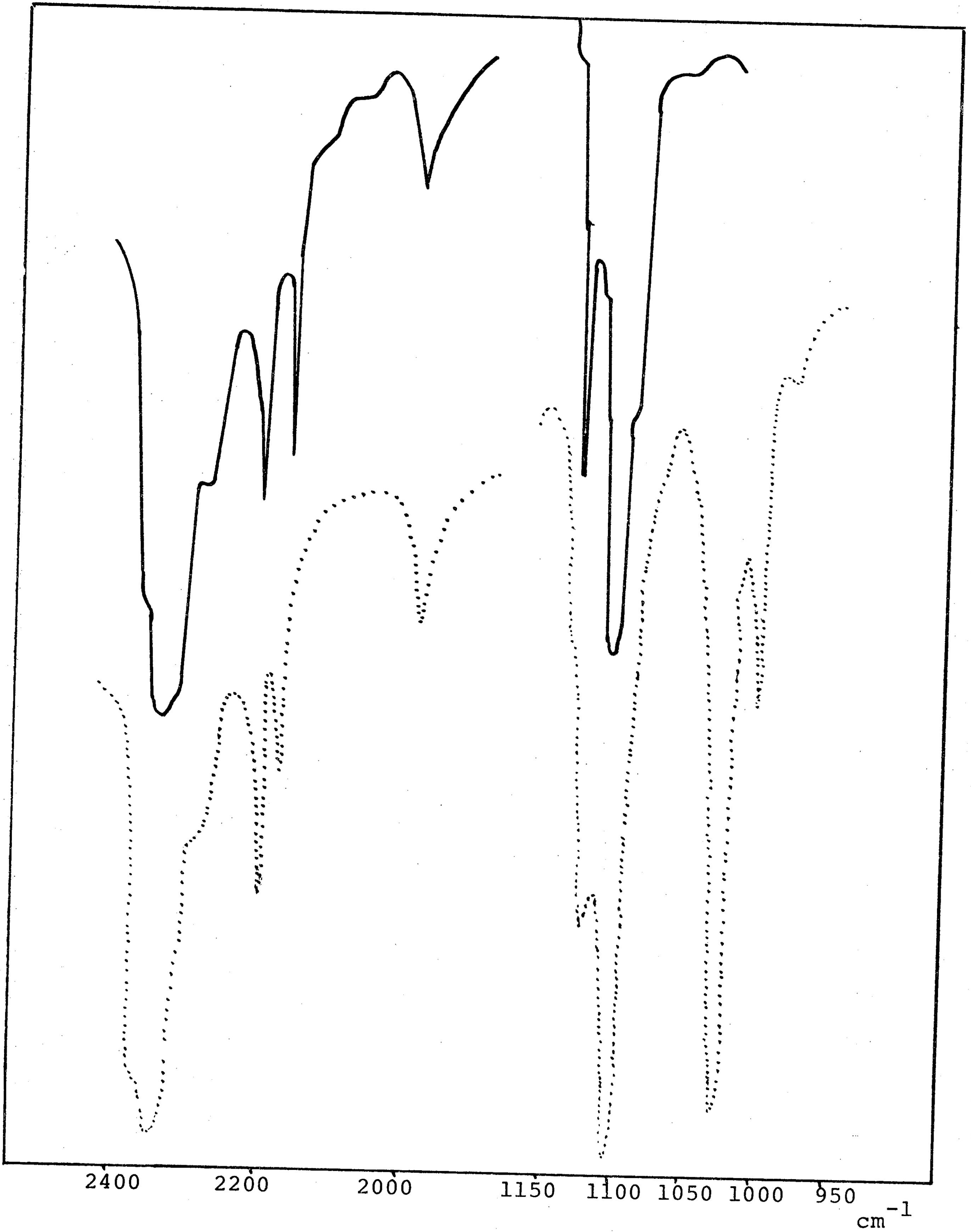
The solid state reflectance spectrum of the complex, which remains essentially unaltered in solution, shows only one weak band at 16,666 $cm^{-1}$ and will be discussed shortly with other DPPM complexes. However, a Diphos complex with the same empirical formula, $[Co(BH_3CN)(Diphos)_2](ClO_4)$ has also been synthesized in this work. It will be shown later that it is fundamentally different from the DPPM complex in, for example, its IR and reflectance spectra.

## B. $Co(BH_3CN)(DPPM)$

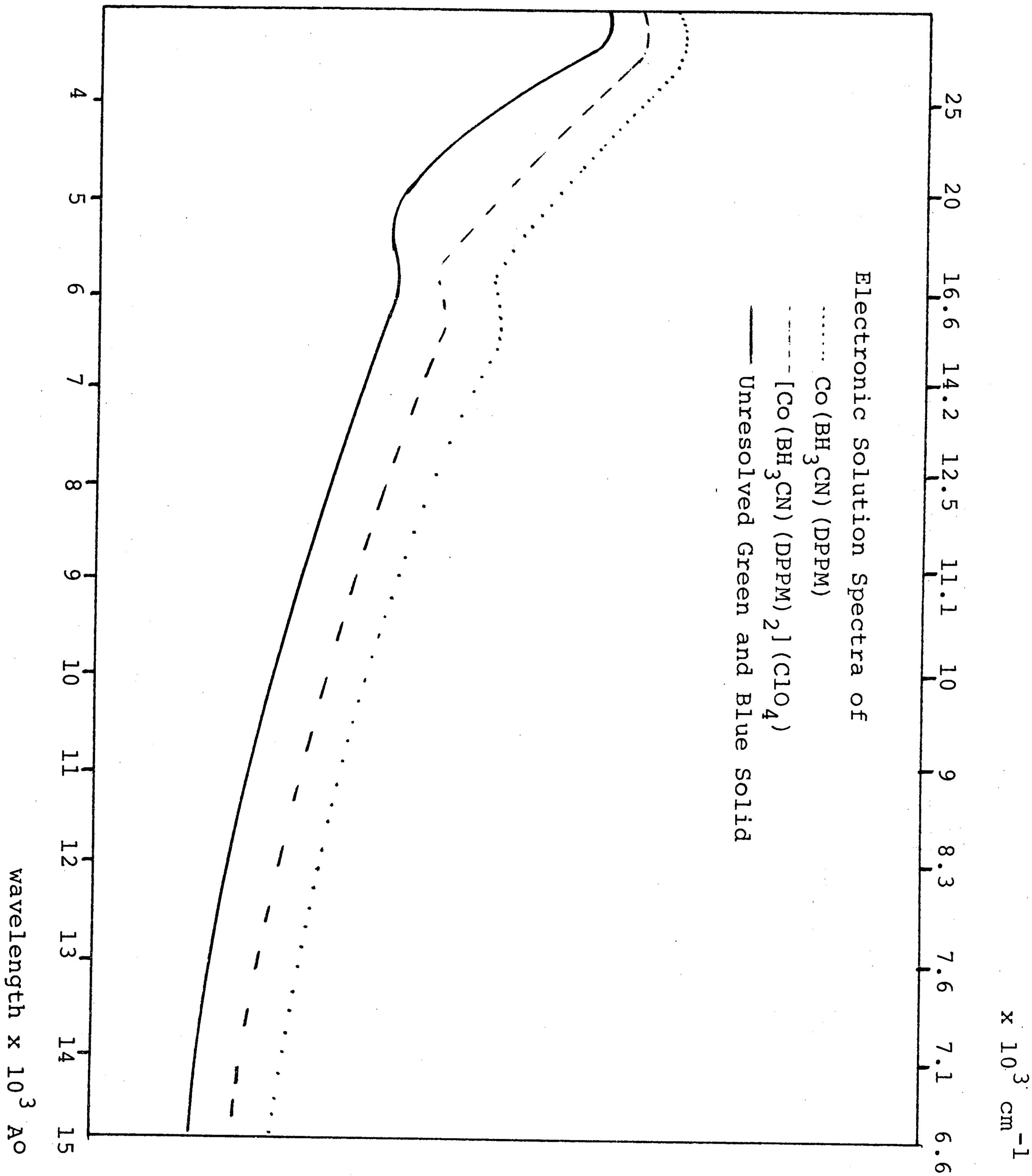
This greenish-yellow complex is formed both from $Co(ClO_4)_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$. However, when the former is used a much larger excess of $NaBH_3CN$ (∿19 mM) is requried than when the latter is used where only a 4 mM excess is needed. The reactions have been reproduced several times and different samples recrystallized from either $CH_2Cl_2$, MeOH or DMF. In each case one solvent molecule is retained in the lattice and these also cause slight changes in the IR spectra of the products in the region of the $BH_3CN^-$ absorptions.

The infrared spectrum of the sample purified by washing with benzene and ethanol and the one recrystallized from hot methanol are shown in fig.XXV, and the important frequencies listed in Table 16. Thus, in the unrecrystallized sample, there are two strong bands at 2160 and 2202 $cm^{-1}$ assigned to the stretching frequencies of the cyanide group of $BH_3CN^-$, whereas the $BH_3$ stretching

Selected Features of the Infrared Spectra of
—— $Co(BH_3CN)(DPPM)$
······· $Co(BH_3CN)(DPPM) \cdot MeOH$



(XXV)


Electronic Solution Spectra of
Co(BH$_3$CN)(DPPM)
[Co(BH$_3$CN)(DPPM)$_2$](ClO$_4$)
Unresolved Green and Blue Solid
x 10$^3$ cm$^{-1}$
25
20
16.6
14.2
12.5
11.1
10
9
8.3
7.6
7.1
6.6
4
5
6
7
8
9
10
11
12
13
14
15
wavelength x 10$^3$ A°

(XXVI)

vibrations occur as a strong band at 2340 $cm^{-1}$ with a shoulder at 2280 $cm^{-1}$. In the sample recrystallized either from hot methanol or from DMF the band at 2160 $cm^{-1}$ shifts to 2180 $cm^{-1}$ and also the $BH_3$ stretch now appears at 2350 $cm^{-1}$. The other features of the infrared spectra remains essentially unchanged in both the unrecrystallized and the recrystallized products. Thus there is a medium intensity band at 1990 $cm^{-1}$ and the BH deformation mode occurs as a strong doublet at 1100 and 1120 $cm^{-1}$. Thus it is difficult to account for two different cyanide stretching signals in $Co(BH_3CN)(DPPM)$ unless the complex is at least dimeric with two different $BH_3CN^-$ groups.

One of the most interesting aspects of this compound is its $^1H$ NMR spectrum, which shows a broad quartet centered at $\delta = 0$ with JBH = 90 HZ and a well defined quintet at $\delta = -15.30$ with JPH = 48 HZ. This is the only one of a great many cyanotrihydroborato complexes prepared in this and other work in these laboratories which shows a broad quartet which is a characteristic of free $BH_3$ protons coupling with $^{11}B$ ($I = 3/2$) (17). The significance of this is not clear, but the upfield quintet suggests either the presence of a hydride or the coordination of a hydrogen from $BH_3CN^-$ coupled to four equivalent phosphorus atoms.

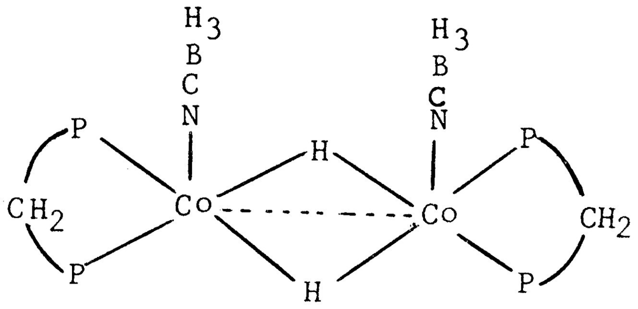
For the product recrystallized from hot methanol, careful integration of the $CH_3$ protons against the aromatic protons have confirmed that very close to one molecule of MeOH is retained by the complex during recrystallization from this solvent. However, similar studies could not be done for the product recrystallized from DMF due to its low solubility in MeOH, but the presence of these solvent molecules are clearly visible in IR spectra which show strong peaks at 1030 and 1685 $cm^{-1}$ due to the OH deformation (from MeOH) and the CO (from DMF).

The $^{31}P$ NMR spectrum of the complex, surprisingly, shows the same chemical shift as observed for $[Co(BH_3CN)(DPPM)_2](ClO_4)$, that is, $\delta = 2.02$. Like the Co(II) complex there is always a very small amount of free phosphine present which appears at $\delta = -23$. There are no other signals in the spectrum and thus any contamination due to the cobalt hydrides mentioned earlier can be ruled out.

The complex is diamagnetic and its reflectance spectrum shows (fig. XXIII) two regions of absorption, a broad band at around 9090 $cm^{-1}$ and a shoulder at 16,666 $cm^{-1}$. However, in solution the spectrum shows only one band (Fig. XXVI) at 16,666 $cm^{-1}$ very similar to that of

$[Co(BH_3CN)(DPPM)_2](ClO_4)$, and suggests that in solution the two complexes are very closely related. This is confirmed by the similarity of the two $^{31}P$ NMR spectra and thus raises the question as to whether the complex can contain Co(I) as suggested in the experimental section.

Since some of the (unexpected) data on this complex have been obtained very recently, it is now necessary to consider an alternative formulation to account for the new results. One possibility must be that the complex contains Co(II), and is related to the dimeric, hydride bridged $[CoH(DPPM)]_2$ complex recently characterized (42). The following structure would account for some of the data.



(XXVII)

This complex should, like CoH(DPPM)$_2$, be diamagnetic, show an upfield quintet due to H-P coupling in the $^1$H NMR spectrum and show a band in the 1900 - 2000 cm$^{-1}$ region of the IR spectrum. In addition the complex might be expected to show the quartet due to B-H coupling, but does not readily account for two different CN stretching frequencies.

The similarity of the $^{31}$P NMR and solution electronic spectra of this and the $ClO_4^-$ compound (discussed earlier) are difficult to explain. It should be noted, (fig. XXVI) that the reflectance and solution spectra of the $ClO_4^-$ complex are essentially the same. How the proposed structure shown above leads to a solution spectrum (fig. XXVI) which is so closely related to that of the $ClO_4^-$ complex is not clear.

Crystallographic data on this interesting complex are obviously needed before these questions can be properly resolved.

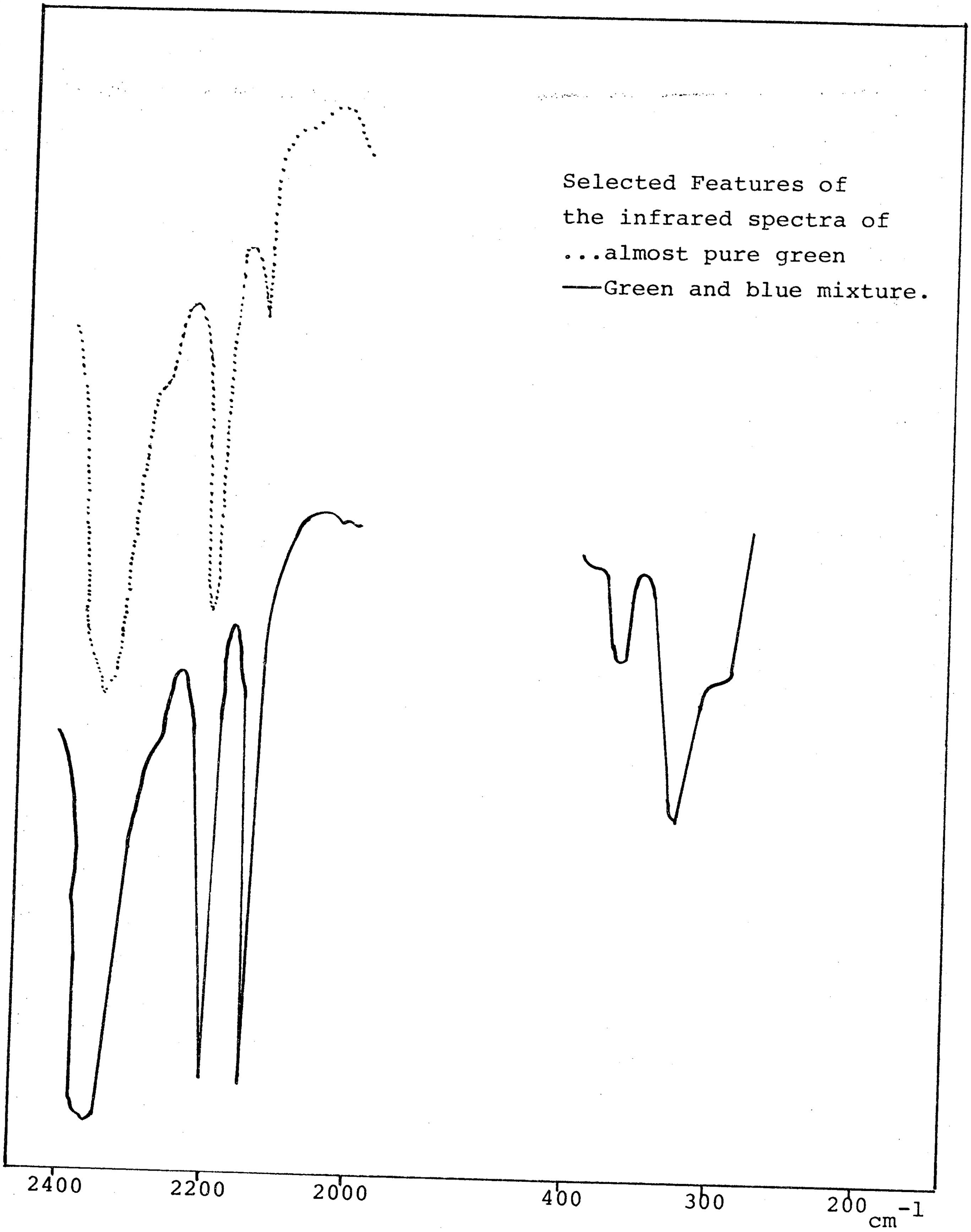
## C. The Unresolved Green and Blue Solids

The reactions of $CoCl_2 \cdot 6H_2O$, DPPM and $NaBH_3CN$ where the molar ratios between the $CoCl_2$ and $NaBH_3CN$ were 1:1 or 1:2, lead to a bright emerald green highly crystalline solid, which was always contaminated with varying amounts of a blue (turquoise) compound. Although the green compound is soluble in $CH_2Cl_2$, $CHCl_3$, THF, MeCN and $Me_2CO$ to form bright green solutions it could not be recovered unchanged from these solvents and dissolution always appears to be accompanied by decomposition and formation of more of the blue compound, both in the absence and in the presence of oxygen. The crude green solid reacts with methanol to form a clear yellow solution from which a mixture of green and yellow solids were precipitated. Attempts to preferentially extract either the green or the blue solid into an organic solvent have also been unsuccessful. Attempts to convert all the green to the blue simply by allowing the bright green solution to stand for long periods (48 hrs) also failed. The amount of the blue compound certainly increased significantly but this was accompanied by the formation of additional unknown compounds which have not yet been separated from the resulting mixture.

The infrared spectrum of the 'almost pure' green compound shows (fig. XXVIII) a strong band at 2200 $cm^{-1}$ and a very weak band at 2140 $cm^{-1}$ due to the cyanide stretching frequencies of the $BH_3CN^-$ groupings. The intensity of this weak band at 2140 $cm^{-1}$ depends on the concentration of the blue impurity and in mixtures where the latter is in greater quantity the infrared spectrum shows these two sharp strong bands at almost equal intensity. As usual the $BH_3$ stretching and deformation modes occur at 2340 and 1100 $cm^{-1}$. The far infrared region shows a medium intensity band at 330 $cm^{-1}$ which may be assigned to a Co-Cl stretching frequency.

Like other DPPM complexes, the $^1H$ NMR spectrum of the green compound dissolved in $CD_2Cl_2$ also shows a quintet at $\delta = -14.71$ with JPH = 48 HZ. In addition there are at least four broad unresolved signals at $\delta = -11$, -30, -40 and -51.

The $^{31}P$ NMR spectra of bright green solutions of the complex show a strong signal at $\delta = 2.02$ together with other weak signals due to impurities of the blue and


Selected Features of
the infrared spectra of
...almost pure green
—Green and blue mixture.
2400
2200
2000
400
300
200
$cm^{-1}$

(XXVIII)

some other unknown compounds. The solution spectrum of the complex is very similar (fig. XXVI) to the other DPPM complexes discussed before, and clearly all these complexes are very closely related in solution. In fact the green complex may be [Co(BH$_3$CN)(DPPM)$_2$]Cl. More studies are underway in an effort to achieve complete separation of the green and blue solids and little more can be concluded until this has been achieved.

## D. Other Products

It is clear that the reactions between Co(II), DPPM and NaBH$_3$CN are extremely complex and result in the formation of number of complexes. Similar reactions where NaBH$_4$ has been used and which have been investigated in this laboratory are also more complicated than reactions where other bidentate phosphines are used. Some of these reactions have proved to be very difficult to reproduce. For example, CoH(DPPM)$_2$ produced in the reactions of NaBH$_4$, DPPM and a Co(II) salt has not been reproduced although a number of attempts have been made both from reactions of NaBH$_4$ and NaBH$_3$CN. Reactions have been studied where different parameters were systematically changed in an effort to reproduce the above hydride, but these have led to the isolation of several new compounds while some others have been seen in $^{31}P$ NMR spectra and still remain to be isolated. The reactions where $NaBH_3CN$ instead of $NaBH_4$ have been used as the reducing agent in attempts to synthesize $CoH(DPPM)_2$, both a room temperature and at elevated temperatures have only led to complex mixtures of compounds. Such a wide variety of complexes has only been seen from reactions with the phosphines DPPM and (see later) Diphos, i.e. those ligands with small bite distances. The other appear to behave differently and in general reactions involving them are easier to study (see later).

## iii Reactions of Co(II), Diphos and $NaBH_3CN$

### A. Room Temperature Reactions

The reactions between Co(II), Diphos and $NaBH_3CN$ have been extensively investigated under a wide variety of conditions. A number of complexes have been characterized and the presence of several others (as yet unidentified), was seen in $^{31}P$ NMR and IR spectra. The formation of these complexes is very dependent upon reaction conditions.

Two complexes have been characterized from reactions at room temperature, a cobalt(II) complex, $[Co(BH_3CN)(Diphos)_2](ClO_4)$ and an already known (16) cobalt(I) complex $Co(BH_3CN)(Diphos)_2$. Thus the addition of an ethanolic solution of $NaBH_3CN$ to a mixture of $Co(ClO_4)_2 \cdot 6H_2O$ and Diphos ($\sim$1:3 ratio) produces an orange-yellow mixture containing both $[Co(BH_3CN)(Diphos)_2](ClO_4)$ and $Co(BH_3CN)(Diphos)_2$. However, the reaction conditions can be adjusted so that either the Co(I) or the Co(II) complex forms preferentially. This is achieved either by varying the amount of $NaBH_3CN$ added or by varying the reaction time. As might perhaps be expected, when the reaction is allowed to take place for short periods of time, or when small amounts of $NaBH_3CN$ are used, then the major product is the Co(II) compound. For example, with a 1:6 ratio of Co:$NaBH_3CN$ and a time of 5 mins or with a 1:2 ratio and a time of 3 hrs little reduction occurs. But with both a 1:6 and a 1:2 ratio and a time of 24 hrs, the Co(I) complex is the major product.

The separation of the Co(I) and Co(II) complexes can be easily effected because $[Co(BH_3CN)(Diphos)_2](ClO_4)$ is highly soluble in $CH_2Cl_2$ whereas the solubility of $Co(BH_3CN)(Diphos)_2$ is very low in this solvent. Moreover the Co(II) complex is reasonably stable (more than 1 day) in $CH_2Cl_2$ from which it can be recrystallized, whereas the Co(I) complex decomposes within 1 hr in chlorinated solvents. The Co(I) complex can be recrystallized unchanged from DMF/EtOH but it decomposes very quickly (within 15 mins) in other solvents like DMSO, MeCN and THF.

## 1. $[Co(BH_3CN)(Diphos)_2](ClO_4)$

This orange-red solid appears to be stable in $CH_2Cl_2$ and there was no significant decomposition even after 48 hours. However, prolonged standing (more than 2 days) of the dark red $CH_2Cl_2$ solution does lead to decomposition of the complex and the solution turns green. This green solution was not investigated further.

The infrared spectrum of $[Co(BH_3CN)(Diphos)_2](ClO_4)$ is shown in fig.XXIX and the important frequencies are listed in Table 17. As seen in fig.XXIX there is a strong and sharp peak at 2185 $cm^{-1}$ assigned to the cyanide stretching frequency of the $BH_3CN^-$ grouping. There is another strong and broad band centered at 2340 $cm^{-1}$ with shoulders at 2260 and 2370 $cm^{-1}$, assignable to the $BH_3$ stretching modes. A very broad peak centered at 1100 $cm^{-1}$

TABLE 17:

Infrared, NMR, Electronic and Magnetic Measurement Data on Complexes Derived from Co(II), Diphos and $NaBH_3CN$ Reactions

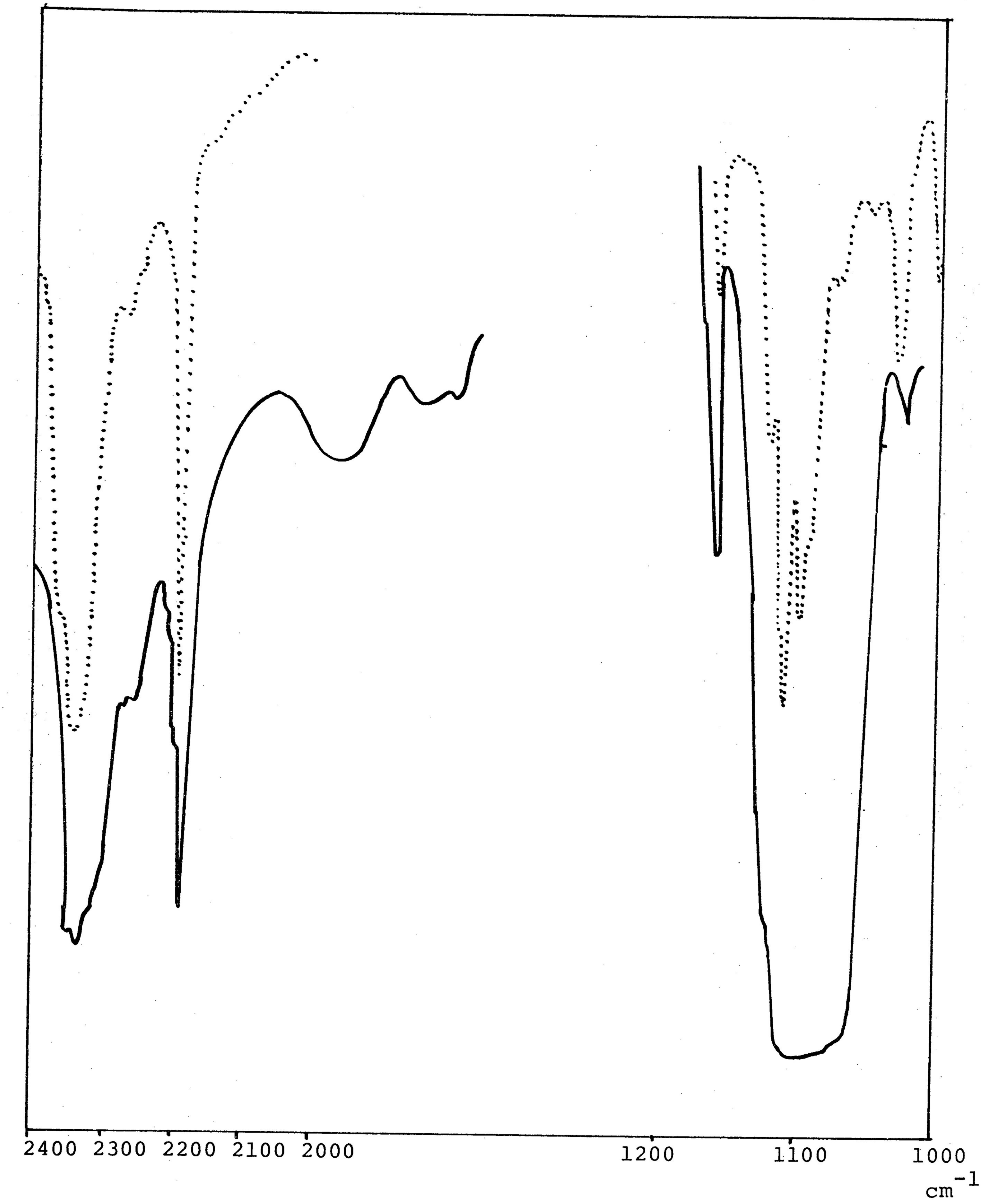
| No. | Complexes | νBH cm$^{-1}$ | δBH cm$^{-1}$ | νCN cm$^{-1}$ | νCo-$H_b$-B cm$^{-1}$ | δ $^{31}$P NMR | δ $^1$H MNR | μ (B.M.) | Electronic Spectra cm$^{-1}$ Solid State | Electronic Spectra cm$^{-1}$ Solution (ε in Bracket) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. | $[Co(BH_3CN)(Diphos)_2]$ $(ClO_4)$ * | 2340(s,b)<br>2260(sh)<br>2370(sh) | | 2185(s) | | 64.08 | -22.50(Q)<br>JPH=52 HZ | 2.1 | 14,285<br>8097 | 14,285(22)<br>8097(94) |
| 2. | $Co(BH_3CN)(Diphos)_2$ | 2340(s,b)<br>2260(sh)<br>2360(sh) | 1100 | 2192(s) | | -10.85(b) | 7.2 (Aromatic Protons) | Diamagnetic | 10,000(b,s) | 8500 |
| 3. | $[Co(CN)(Diphos)_2]$ $(ClO_4)$ ‡ | | | 2100(s) | | | | | | |
| 4. | $Co(CN)Cl(Diphos)_2$ ⊕ | | | 2060(s)<br>2075(s,sh) | | 60.46 | | | 10,810 | 10,900 |
| 5. | $Co(BH_3CN)_2(Diphos)_2$ | 2342(s,b) | 1100(s)<br>1150(sh) | 2200(s)<br>2170(vw) | 1990 | 64.04 | | | No Absorption | |
| 6. | $Co(BH_3CN)(Diphos)$ | 2360(s,b) | 1100(s) | 2160(s)<br>2200(s) | 2000 | | | | | |
| 7. | $(Bu_4N)^+(BH_3CNBH_2CN)$ | 2395(b,s)<br>2355(b,s) | | 2205(w) | | | | | | |

*$\nu ClO_4$ —— 1100 cm$^{-1}$; *δ, $^{11}$B NMR —— -42.2; ‡ $\nu ClO_4$ —— 1100 cm$^{-1}$; ⊕ νCo-Cl —— 375 cm$^{-1}$

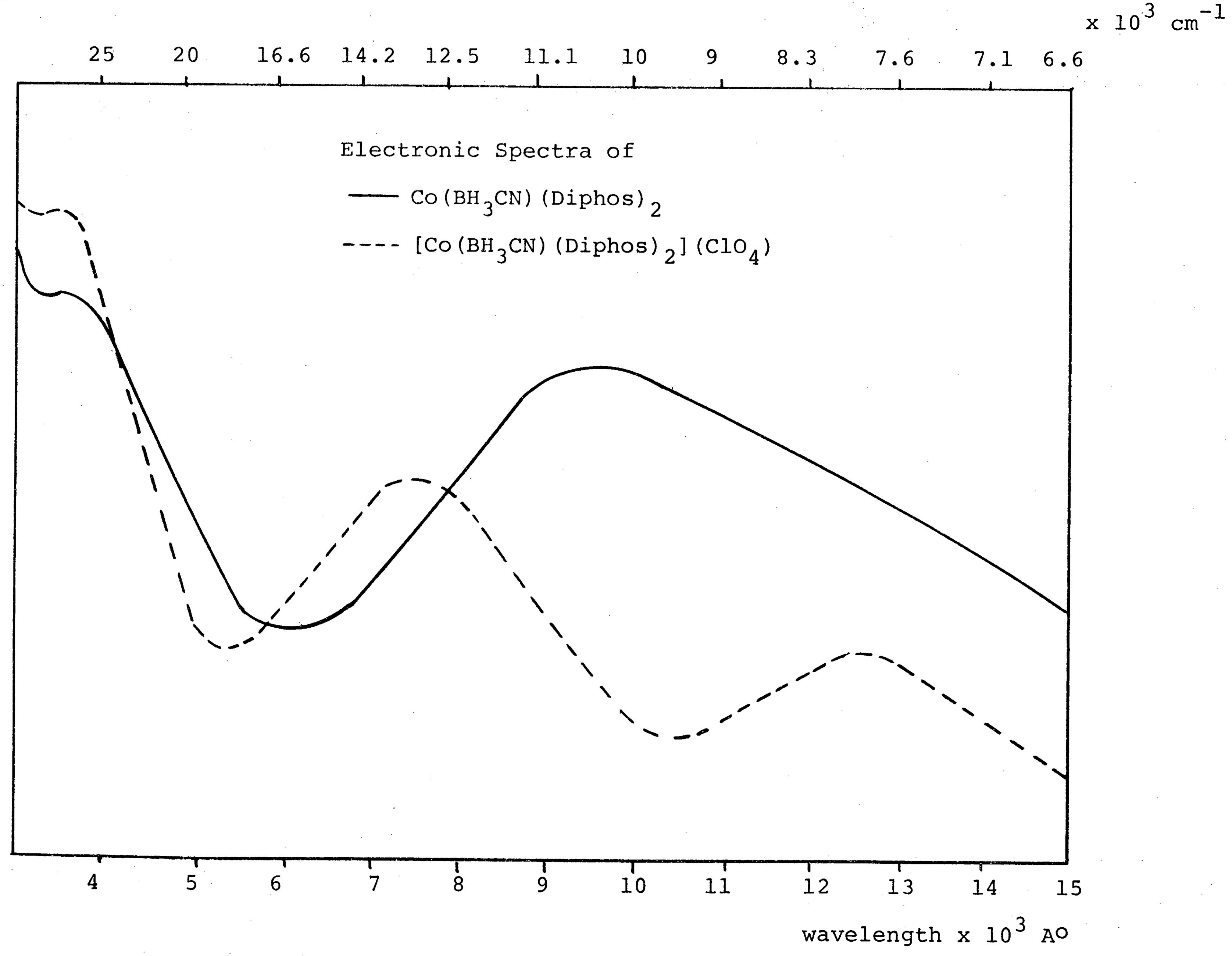
Abbreviations b, broad; m, medium; s, strong; sh, shoulder; Q, Quintet; v, very.

Selected Features of the Infrared Spectra of

—— [Co($BH_3CN$)(Diphos)$_2$]($ClO_4$), .......... Co($BH_3CN$)(Diphos)$_2$



(XXIX)


Electronic Spectra of
—— $Co(BH_3CN)(Diphos)_2$
---- $[Co(BH_3CN)(Diphos)_2](ClO_4)$
25
20
16.6
14.2
12.5
11.1
10
9
8.3
7.6
7.1
6.6
x $10^3$ $cm^{-1}$
4
5
6
7
8
9
10
11
12
13
14
15
wavelength x $10^3$ Ao

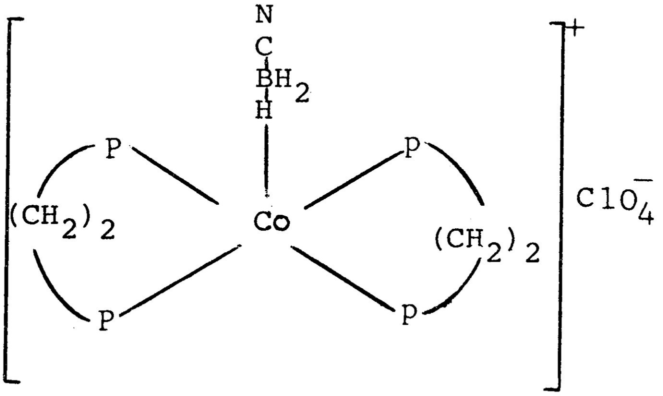
(XXX)

indicates the presence of an ionic $ClO_4^-$ grouping and obscures the BH deformation modes which usually appear around 1000 - 1150 $cm^{-1}$.

The $^{31}P$ NMR spectrum of the solid dissolved in $CH_2Cl_2$ shows only one sharp resonance at $\delta = 64.08$. The $^{11}B$ NMR spectrum of the sample in $CD_2Cl_2$ after approximately 20,000 pulses shows a broad resonance at $\delta = -42.2$ which broadens further in the proton undecoupled spectrum. The $^{1}H$ NMR spectrum in $CD_2Cl_2$ shows as its major feature a well defined quintet at $\delta = -22.50$ with JPH = 52 HZ. Other significant resonances in the $^{1}H$ NMR spectrum are the strong signal at $\delta = 7.2$ due to the aromatic protons of Diphos and a broad and very weak signal at $\delta = 3.08$ due to the methylene protons of Diphos (76).

The magnetic moment of 2.1 B.M. indicates the presence of one unpaired electron and therefore the complex contains low spin Co(II), $d^7$. The electronic spectrum shows (fig. XXX) basically two regions of absorption, one at 8097 $cm^{-1}$ ($\varepsilon = 94$) and the other at 14,285 $cm^{-1}$ ($\varepsilon = 22$). Both the solid state and the solution spectra are the same.

All the above data strongly support the structure where the $BH_3CN^-$ grouping is bonded to the cobalt through a hydrogen atom only, and most likely the structure of the complex is as follows:



(XXXI)

Considering the infrared spectrum of the complex, the cyanide stretching frequency (2185 $cm^{-1}$) of the $BH_3CN^-$ unit shows only a marginal shift compared to ionic $BH_3CN^-$ (2179 $cm^{-1}$). As discussed in the introduction of this thesis such small shifts in the νCN reflects either an ionic $BH_3CN$ unit (which is very unlikely in this compound), a very weak coordination of $BH_3CN^-$ through nitrogen or a coordination involving only the hydrogen atoms of the $BH_3CN^-$ grouping. Indeed the presence of the latter type of bonding has been suggested in a number of complexes e.g. $Ni(BH_3CN)(PPh_3)_2$ (16). For this cobalt complex perhaps the most convincing evidence for the proposed structure is the $^1H$ NMR spectrum. Thus, the well resolved quintet at $\delta = -22.5$ (JPH = 52 HZ) can be explained by the coupling of the four magnetically equivalent phosphorus atoms of the two Diphos ligands with the coordinated hydrogen of the $BH_3CN$ grouping, as discussed previously with DPPM complexes. However, the possibility exists, like the DPPM case, that the complex is contaminated with or decomposes to $CoH(Diphos)_2$, which has been recently prepared in this laboratory and which also shows (42) a well defined quintet in $CDCl_3$ at $\delta = -25.5$ with JPH = 55 HZ. That the complex does not decompose to $CoH(Diphos)_2$ in the solvent ($CD_2Cl_2$) was proved by the following studies.

(a) The infrared spectrum of the solid obtained by evaporating under vacuum the solvent from a solution of the complex immediately after recording its NMR spectrum was unchanged from that of the starting material, and showed no Co-H signal.

(b) The $^1H$ NMR spectrum of a freshly prepared solution of the cyanotrihydroborato complex was taken and the spectrum remeasured after three different intervals of time, the longest being 28 hrs from the time the solution was prepared. All the spectra were identical. This is perhaps the strongest evidence that CoH(Diphos)$_2$ is not present since it decomposes within 1 hr in $CH_2Cl_2$ (42), the solvent used for the above studies. It therefore seems reasonable to conclude that the quintet in the spectrum of the $BH_3CN^-$ complex is not due to the hydride, since, even if it were present in quantities too small to be detected in either the IR or the $^{31}P$ NMR spectra, it could not survive in $CH_2Cl_2$ over the time period mentioned above.

Further supporting evidence for the proposed structure is obtained from $^{31}P$ and $^{11}B$ NMR spectra. Thus, the single peak in the $^{31}P$ NMR spectrum at $\delta = 64.08$ confirms that all the four phosphorus atoms from the two Diphos ligands are equivalent, that the compound is not decomposing in the solvent ($CH_2Cl_2$) and that there is no formation of the hydride which shows a signal at $\delta = 70.8$ (42) in its $^{31}P$ NMR spectrum. The $^{11}B$ NMR spectrum when run for 24 hours also shows a broad peak at $\delta = -42.2$. This broad singlet could not be resolved by recording the $^1H$ undecoupled spectrum for 24 hrs at room temperature, which only broadens the peak even more. Such line broadening does in fact indicate some residual coupling. This may be due to the protons associated with $BH_3$. However, the signal broadening can also be the result of interaction of the quadrupole moment of cobalt (I = 7/2) with the boron. Low temperature studies to resolve this broad singlet were not done because such temperatures will induce thermal decoupling.

Although the IR, $^{31}P$, $^{11}B$ and $^{1}H$ NMR spectra of the complex do support the proposed structure and essentially rule out the possibility of any Co-H impurity, the structure is by no means conclusive. Thus, there appears no resonance in the $^{1}H$ NMR spectrum due to the terminal $BH_2$ hydrogens neither does the spectrum show any coupling due to the $^{10}B$ and $^{11}B$ protons. It is possible that the resonance due to the terminal $BH_2$ protons is obscured by the strong signal due to the aromatic protons of Diphos, as discussed previously in the case of DPPM.

However, exact structural details can only be revealed by crystallographic studies and attempts are being made to grow suitable crystals of the above complex.

## 2. $Co(BH_3CN)(Diphos)_2 \cdot DMF$

This complex has been reported in the literature by Holah and coworkers (16) and has been re-made in this work by a wider variety of methods than originally reported. As mentioned earlier, reduction to form the Co(I) complex can be achieved by (a) increasing the amount of $NaBH_3CN$ (b) increasing the time of the reaction or (c) increasing the temperature. In addition, it was found that the solvent plays an important role in the formation of the above complex. Thus all the reactions done at room temperature involving only ethanol instead of the usual mixture of ethanol and toluene resulted in the formation of an olive green solid which proved to be a mixture of compounds as seen from the infrared spectrum. However, from this mixture of solids the yellow, $Co(BH_3CN)(Diphos)_2$ can be isolated by treating the mixture with acetone which dissolves most of the green impurities leaving behind the yellow Co(I) complex.

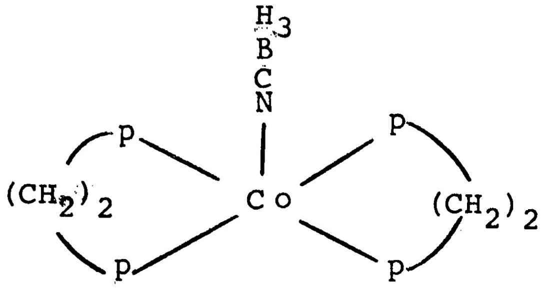
Table 17 lists the important frequencies of the infrared spectrum of $Co(BH_3CN)(Diphos)_2$ part of which is also shown in fig. XXIX. There are some differences between this and the spectrum of the Co(II) complex,

$[Co(BH_3CN)(Diphos)_2](ClO_4)$. For example the $\nu CN$ occurs at 2191 $cm^{-1}$ (a shift of 13 $cm^{-1}$ from ionic $BH_3CN$) and the $BH_3$ stretching modes occur at 2340 $cm^{-1}$ as a strong peak with shoulders at 2260 and 2360 $cm^{-1}$. The BH deformation modes appear at 1100 and 1120 $cm^{-1}$ as a strong doublet. Considering the infrared data alone it appears as if the $BH_3CN^-$ is coordinated through its nitrogen to the cobalt. Indeed such an arrangement is supported by the $^1H$ NMR spectrum of the complex which, unlike the Co(II) complex discussed previously, does not show any resonance in the high field region. Also, like most other cyanotrihydroborato complexes prepared in this work, the resonance due to the $BH_3$ protons were not observable at both ambient and low temperatures.

The $^{31}P$ NMR spectrum of the complex in DMF shows a broad peak (with a half width of 320 HZ) at $\delta$ = -10.85. The position of this signal is close to the free phosphine (Diphos) signal which occurs at $\delta$ = -14.3 (76). As discussed earlier such a broad signal which usually indicates the presence of unpaired electrons on the metal ion, is rather surprising because this complex is diamagnetic. Attempts to record the spectrum in other solvents such as $CH_2Cl_2$ and $CHCl_3$ were unsuccessful because of limited solubility and rapid decomposition of the complex.

The electronic reflectance spectrum (shown in fig. XXX) of the complex has a strong band at 10,000 $cm^{-1}$ which shifts to 8500 $cm^{-1}$ in solution (DMF). Such spectra appear to be typical of pentacoordinated low spin $d^8$ systems with trigonal bipyramidal (actually $C_{3v}$) symmetry (73, 74).

Thus combining all the above data it appears as if the complex has the following structure:



(XXXII)

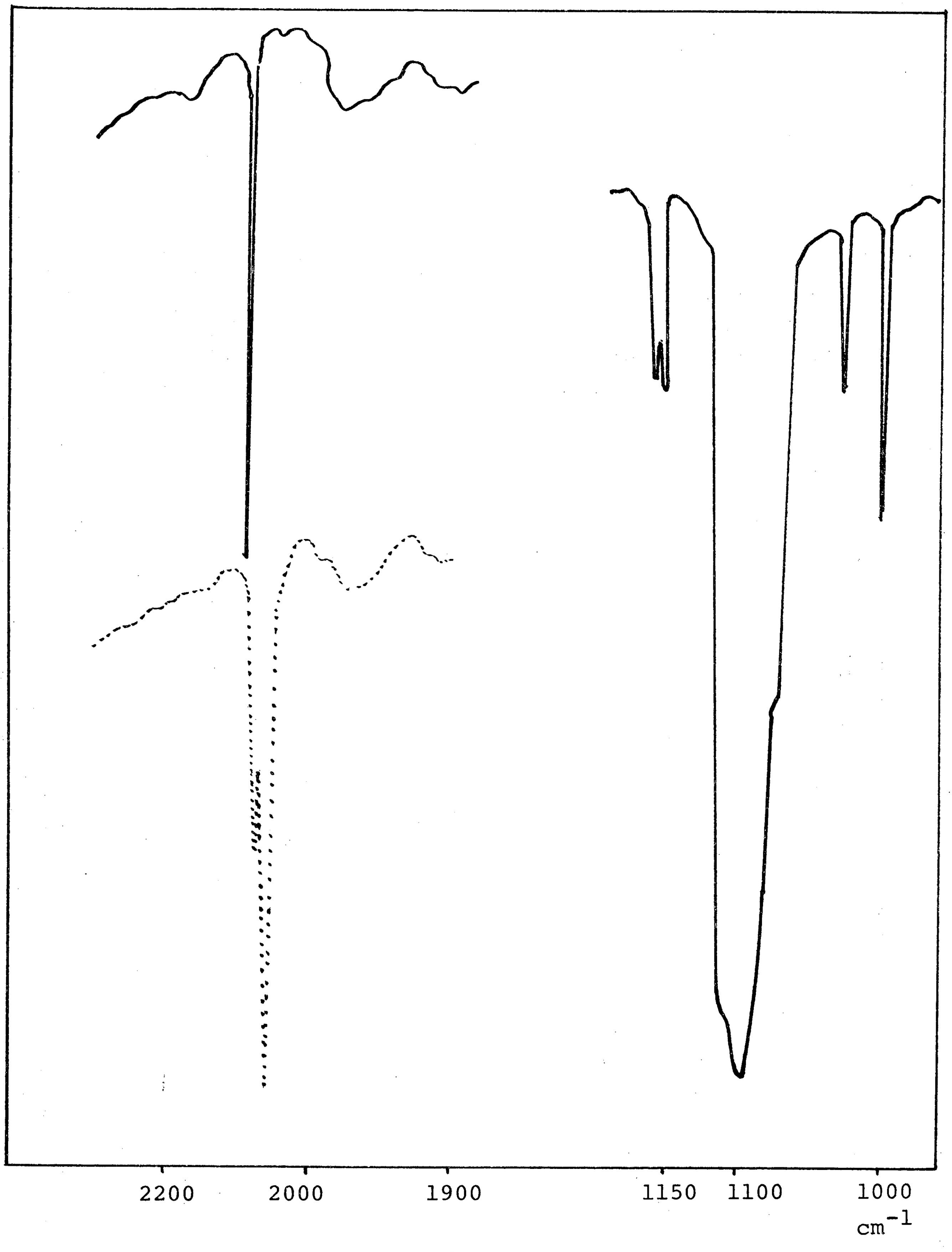
## 3. $[Co(CN)(Diphos)_2](ClO_4)\cdot Me_2CO$

A very unusual reaction takes place when the orange coloured complex $[Co(BH_3CN)(Diphos)_2](ClO_4)$ is treated with acetone. The complex dissolves in acetone to form a brown solution from which a dark brown crystalline solid $[Co(CN)(Diphos)_2](ClO_4)\cdot Me_2CO$ was obtained. The cyanide complex does not redissolve completely in acetone, but its analysis and infrared spectrum are consistent with the above formulation. The infrared spectrum shows (fig.XXXIII, Table 17) a strong cyanide stretching frequency at 2100 $cm^{-1}$ and a strong and broad absorption at 1100 $cm^{-1}$ which indicates an ionic $ClO_4^-$ grouping. The carbonyl group of the acetone trapped in crystal lattice, shows as an absorption at 1710 $cm^{-1}$. The intensity of this peak reduces when the sample is kept under vacuum for 24 hrs but complete removal of the molecule of acetone could not be achieved.

As discussed in the introduction of this thesis the formation of related cyanide complex, $[Ru(n\text{-}C_5H_5)(PPh_3)_2(CN)]$ was observed by Haines (12) when $[Ru(n\text{-}C_5H_5)(PPh_3)_2(Me_2CO)]^+$ was treated with $NaBH_3CN$ in acetone. However, the complex was not isolated in the pure form, and was

Slected Features of the Infrared Spectra of

—— $[Co(CN)(Diphos)_2](ClO_4)$, ……… $Co(CN)Cl(Diphos)_2$



(XXXIII)

identified only from the infrared spectrum of the reaction mixture which showed $\nu$CN at 2083 $cm^{-1}$. A related reaction between a cyanotrihydroborto - DPPP complex and methylene chloride leading to the formation of a cyanide complex has also been observed and will be discussed later in the thesis. A further specific example where the B-C bond is broken is the formation of the complex $PtH(CN)L_2 \cdot 5C_6H_6$ (L = $PPh_3$ or DBP) which was produced from the reaction of $PtCl_2L_2$ (L = $PPh_3$ or DBP) with $NaBH_3CN$ at _room temperature_ (16). However, as will be seen later in this discussion the formation of a cyanide complex from reactions of $BH_3CN^-$ with Co(II) in the presence of a phosphine ligand has been repeatedly seen at elevated temperatures. Such reactions are complex and very difficult to reproduce. Thus the breaking of the B-C bond occurs under a variety of circumstances and exactly what role metal ions, organic solvent or temperature play in the cleaving of this bond are not clear.

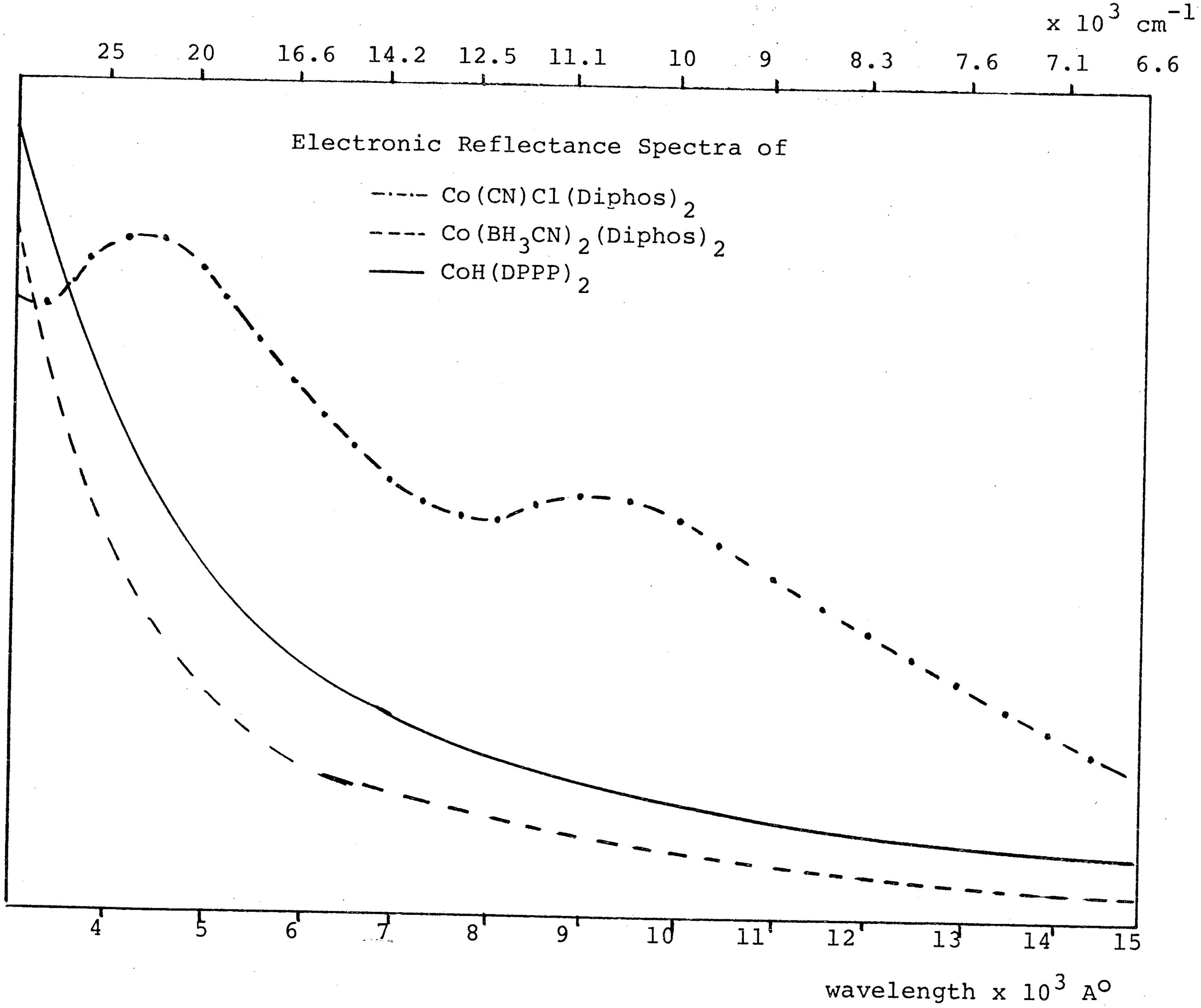
## B. High Temperature Reactions

The reactions between $CoCl_2 \cdot 6H_2O$, Diphos and $NaBH_3CN$ at elevated temperatures were found to be more complex and, once again, problems in reproducing some reactions have been encountered. While the fast addition of $NaBH_3CN$ to a mixture of $CoCl_2 \cdot 6H_2O$ and Diphos results in the immediate precipitation of $Co(BH_3CN)(Diphos)_2$, the reaction involving the slow and periodic addition of $NaBH_3CN$ afforded a number of complexes, some of which have been identified while the complete separation of others has not yet been achieved.

### 1. $\underline{Co(CN)Cl(Diphos)_2}$

One complex that has been isolated from the reaction at elevated temperatures is $Co(CN)Cl(Diphos)_2$.

The infrared spectrum (fig. XXXIII, Table 17) of the complex clearly shows that the CN group has again been abstracted from $BH_3CN^-$. No B-H absorptions are seen and peaks at 2060 and 2075 $cm^{-1}$ are due to cyanide stretching frequencies. A peak at 375 $cm^{-1}$ in the far infrared region is thought to be due to the Co-Cl stretching frequency. The presence of the chloride ion has also been verified chemically. The $^{31}P$ NMR spectrum of the complex shows a sharp single resonance at $\delta = 60.46$.


x 10$^3$ cm$^{-1}$
25
20
16.6
14.2
12.5
11.1
10
9
8.3
7.6
7.1
6.6
Electronic Reflectance Spectra of
Co(CN)Cl(Diphos)$_2$
Co(BH$_3$CN)$_2$(Diphos)$_2$
CoH(DPPP)$_2$
4
5
6
7
8
9
10
11
12
13
14
15
wavelength x 10$^3$ A$^o$

(XXXIV)

The differences between the infrared of this complex and that of the cyanide complex obtained from the acetone reaction are apparent from the fig. XXXIII. Thus the chlorocyano complex shows a cyanide signal which is split and is 20 $cm^{-1}$ lower in frequency than the single sharp $\nu CN$ in the perchlorato-cyano complex. Moreover there is a sharp doublet at 803 and 820 $cm^{-1}$ in the chlorocyano complex whereas there is only one peak at 820 $cm^{-1}$ in the perchlorato-cyano complex. The significance of these bands is not clear, but they are probably associated with ligand vibrations and may reflect different geometries of the phosphines in the two complexes.

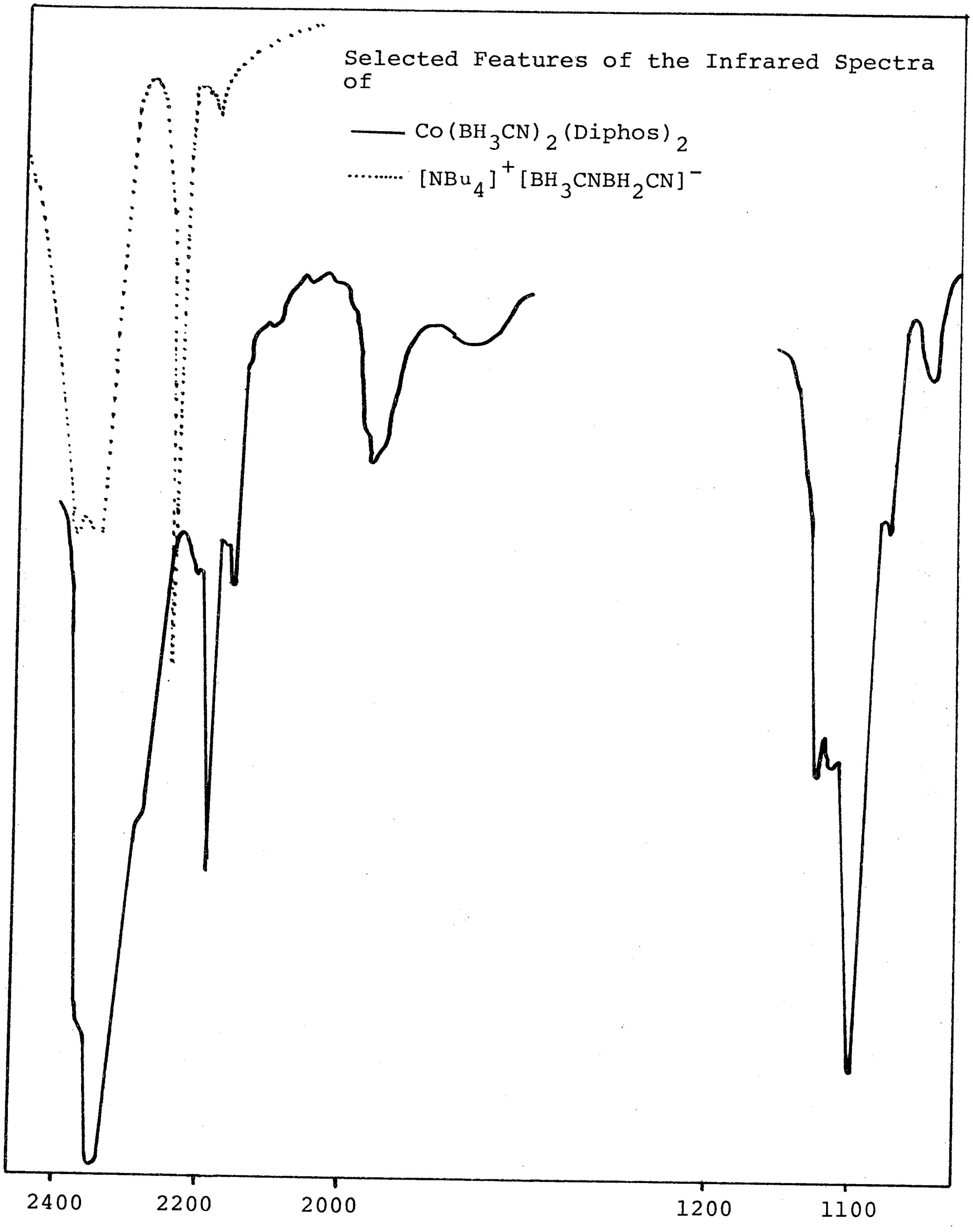
The solid state electronic reflectance spectrum of $Co(CN)Cl(Diphos)_2$ which remains virtually unaltered in $CH_2Cl_2$ shows (fig. XXXIV) a single absorption at 10,810 $cm^{-1}$. In the absence of magnetic moment and $^1H$ NMR data for the complex, it is difficult to interpret the spectrum. However, it is close to the DPPM complexes discussed previously.

Repeated attempts to reproduce the above complex in the pure form again have failed, although the presence of the complex was always seen when the reactions were monitored through $^{31}P$ NMR spectroscopy. This has shown, in the reaction mixtures, the presence of several unknown compounds as well as the already known $CoH(Diphos)_2$ (42). The hydride and the cyanide complexes were easily recognized by their chemical shifts, $\delta = 70.8$ for the hydride and $\delta = 60.46$ for the cyanide complex. Addition of n-Hexane to such reaction mixtures produces large amounts of free phosphine and an unresolved mixture of compounds.

## 2. $Co(BH_3CN)_2(Diphos)_2$

Attempts to synthesize the cyano complex either by repeating the original high temperature reaction or by varying the reaction conditions have led only to mixtures of compounds. However, in all these reactions small amounts of yellow or yellow-green solids were obtained. These were separated from each of the dark red reaction mixtures and, because of the small quantities involved, combined together. The resulting solid was extracted into methylene chloride to produce a yellowish-red solution which was separated by filtration from a large amount of an insoluble white residue. The addition of n-Hexane to the filtrate produced a small amount of a yellow solid which analysed for $Co(BH_3CN)_2(Diphos)_2$.

The infrared spectrum of the complex is shown in fig. XXXV and the important frequencies listed in Table 17 Unlike the spectrum of $[Co(BH_3CN)(Diphos)_2](ClO_4)$, there is a medium intensity band at 1990 $cm^{-1}$ together with a sharp and strong cyanide stretching vibration at 2200 $cm^{-1}$, and a weak band at 2170 $cm^{-1}$. The BH stretching vibrations appear at 2342 $cm^{-1}$ and the deformation modes are at 1100 $cm^{-1}$ with a shoulder at 1150 $cm^{-1}$. The complex appears to be very pure as seen from the $^{31}P$ NMR which shows a single component at $\delta = 64.04$. What is surprising is that this chemical shift is at the same position as seen for the perchlorate complex ($\delta = 64.08$). Thus from the $^{31}P$ NMR data it appears as if the two compounds should be formulated in very similar ways, such as $[Co(BH_3CN)(Diphos)_2]^+X^-$ ($X = ClO_4^-$ or $BH_3CN^-$) which would account for the exceedingly close chemical shifts in the $^{31}P$ NMR spectra. However, this is difficult to substantiate from an examination of the infrared spectrum of the complex which does not show the two separate cyanide stretching


Selected Features of the Infrared Spectra of
Co(BH$_3$CN)$_2$(Diphos)$_2$
[NBu$_4$]$^+$[BH$_3$CNBH$_2$CN]$^-$
2400
2200
2000
1200
1100
cm$^{-1}$

(XXXV)

frequencies which presumably should be visible if both ionic and coordinated $BH_3CN^-$ groupings are present. The significance of the very weak signal at 2170 $cm^{-1}$ is not clear. The large shift (21 $cm^{-1}$) in the strong cyanide stretching frequency at 2200 $cm^{-1}$ from the position in ionic $BH_3CN^-$ strongly suggests that the latter is coordinated through its nitrogen atom. The broad weak absorption at $\sim$2000 $cm^{-1}$ in Diphos is significantly more intense (fig. XXXV) in the complex and indicates that, in addition to a Co-N-C-B arrangement, the hydrogen atoms of $BH_3CN^-$ are also involved in bonding to the metal. Unfortunately, the $^1H$ NMR spectrum of the complex has not yet been obtained.

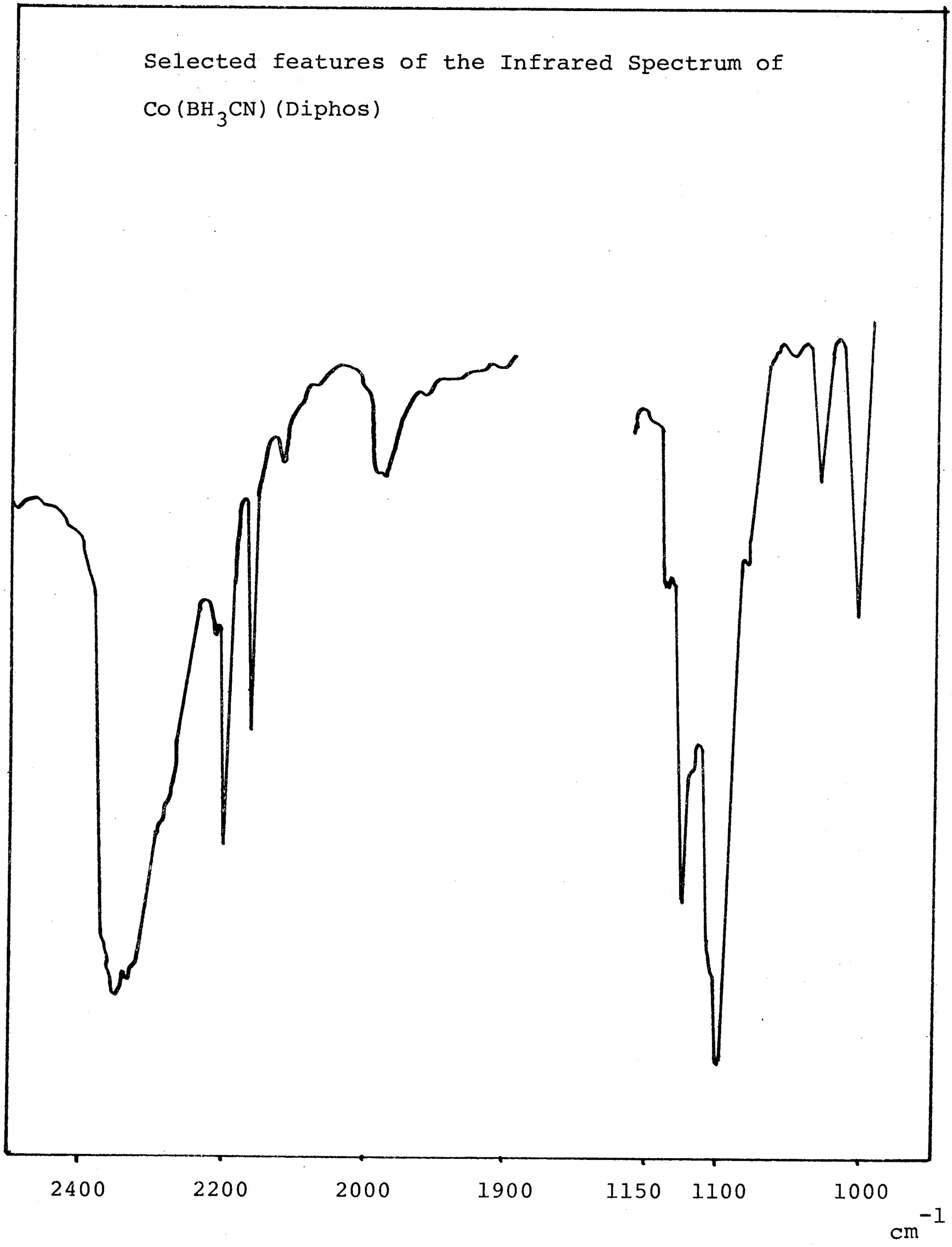
Further evidence that the complex is not closely structurally related to $[Co(BH_3CN)(Diphos)_2](ClO_4)$ is seen in the electronic reflectance spectrum of the complex, which is shown in fig. XXXIV. The featureless electronic spectrum is very similar to that of $CoH(DPPP)_2$ which has recently been shown to be diamagnetic ($d^8$), with a five coordinate slightly distorted square pyramidal geometry (78). Insufficient material has so far been obtained to allow the measurement of the magnetic moment. Thus insufficient information is presently available about this complex to resolve the dilema as to whether it is paramagnetic (Co(II)), diamagnetic (Co(I)) or polymeric (Co(II)) and to account for the $^{31}P$ NMR data.

If it is indeed a Co(I) complex then an alternative formulation has to be considered to satisfy the analytical data. It was mentioned in the introduction that Hg(II) and Hg(I) react with $BH_3CN^-$ to form $(BH_3CNBH_2CN)^-$ and in fact the $Bu_4N^+$ salt (but no metal complex) of this species was isolated. The infrared spectrum of $(Bu_4N)^+$ $(BH_3CNBH_2CN)^-$ is reproduced in fig.XXXV and the frequencies are given in Table 17 . Thus the authors assigned the stretching frequency of the terminal cyanide group to the surprisingly weak band at 2205 cm$^{-1}$ whereas the bridging cyanide stretching frequency was assigned to the strong band at 2255 cm$^{-1}$. There is some similarity between the shape of this spectrum and that of the Co complex in the region of the cyanide stretching frequencies, although there are significant shifts in the position of these signals in the spectrum of the cobalt complex. Such large shifts in $\nu$CN might be the result of coordination of $(BH_3CNBH_2CN)^-$ with the metal ion in, for example $Co(BH_3CNBH_2CN)(Diphos)_2$.

Clearly more information is needed on this complex. Its method of preparation is not satisfactory and considerably more work is necessary to investigate the reactions between Co(II), Diphos and $NaBH_3CN$ in a more reproducible way in higher yields.

## 3. $Co(BH_3CN)(Diphos)$

There is one additional product which has been separated from these reactions. Thus in one of the many reactions aimed at producing $Co(CN)Cl(Diphos)_2$, where the Co:Diphos ratio was changed from the usual 1:3 to 1:2, a small amount of a yellow-green solid was obtained. The infrared spectrum of this solid is shown in fig. XXXVI, and is clearly very similar to the $Co(BH_3CN)(DPPM)$ complex, already discussed. Thus like the DPPM complex there are two cyanide stretching bands at 2160 and 2200 $cm^{-1}$ with the same intensity ratio as shown in the DPPM complex, and like the latter there is also a medium intensity band at $\sim$2000 $cm^{-1}$. Also the BH stretching and deformation modes occur at the same position, 2360 and 1100 $cm^{-1}$ respectively. The structure of the two species are therefore closely related. Moreover, like the DPPM complex, the Diphos complex is also very sensitive to



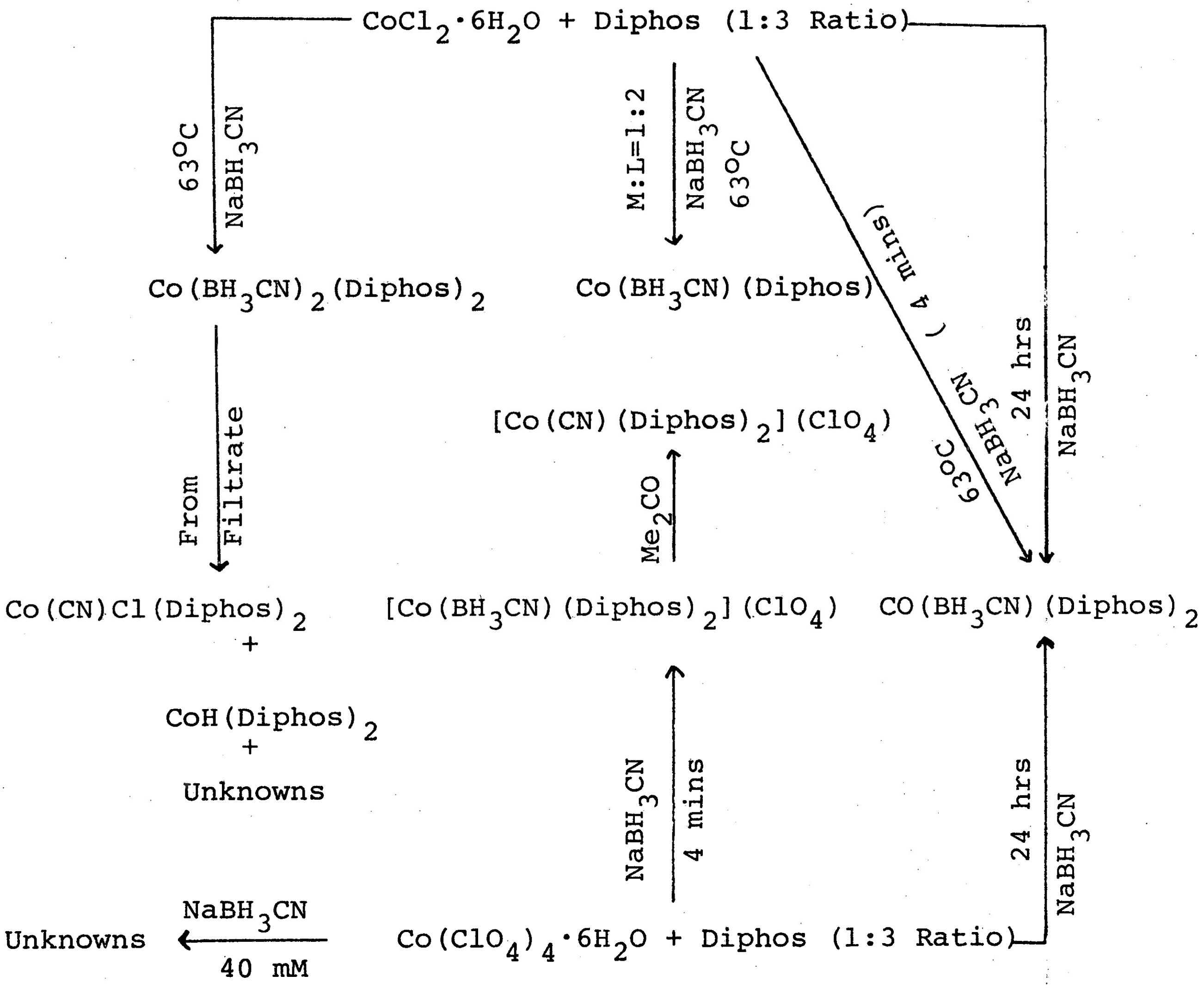
Selected features of the Infrared Spectrum of $Co(BH_3CN)(Diphos)$

(XXXVI)

$CH_2Cl_2$ and immediately decomposes. Again due to small amounts of solid further studies could not be done, and like several other reactions already mentioned, this particular one has also not been reproduced.

This study of reactions at elevated temperatures between Diphos, $CoCl_2$ and $NaBH_3CN$ has been repeatedly frustrated because the reactions are very difficult to reproduce due to the extreme sensitivity of the reactions to factors like the rate of addition of $NaBH_3CN$, the amount of $NaBH_3CN$ used, the reaction time and the metal:ligand ratio. However, it has been possible to isolate some of the wide variety of complexes which results from these reactions as summarized in fig. XXXVII.

It is interesting to note that both Co(I) and Co(II) complexes have been isolated from reactions using $NaBH_3CN$, whereas in the analogus reactions where stronger reducing agent $NaBH_4$ was used, only $CoH(Diphos)_2$ (42) and $Co(Diphos)_2$ (77) were the isolable products. It appears as if the hydride complex is quite stable because there is no reaction between $CoH(Diphos)_2$ and $NaBH_3CN$.


CoCl2·6H2O + Diphos (1:3 Ratio)
63°C
NaBH3CN
M:L=1:2
NaBH3CN
63°C
(4 mins)
NaBH3CN
63°C
24 hrs
NaBH3CN
Co(BH3CN)2(Diphos)2
Co(BH3CN)(Diphos)
From
Filtrate
[Co(CN)(Diphos)2](ClO4)
Me2CO
Co(CN)Cl(Diphos)2
+
CoH(Diphos)2
+
Unknowns
[Co(BH3CN)(Diphos)2](ClO4)
CO(BH3CN)(Diphos)2
NaBH3CN
4 mins
24 hrs
NaBH3CN
Unknowns
NaBH3CN
40 mM
Co(ClO4)4·6H2O + Diphos (1:3 Ratio)

(XXXVII)

## IV. Reactions of Co(II), *Cis* DPPE and $NaBH_3CN$

Reactions between the unsaturated phosphines, *cis* or *trans* DPPE, Co(II) and $NaBH_3CN$ have not shown the wide variety of complexes as has been seen with Diphos. While there is no reaction at room temperature when Co(II) is treated with $NaBH_3CN$ in the presence of *trans* DPPE, reactions in the presence of *cis* DPPE produced an orange-red coloured solid, which has analysed for $Co(BH_3CN)_2(DPPE)_2.EtOH$.

### A. $Co(BH_3CN)_2(DPPE)_2 \cdot EtOH$

The complex is readily formed when a large excess of $NaBH_3CN$ (∿9 mM) is added to a mixture of *cis* DPPE and either $Co(ClO_4) \cdot 6H_2O$ or $CoCl_2 \cdot 6H_2O$ in ethanol and toluene. However, the product isolated retains a molecule of ethanol in the lattice and all efforts to remove it by drying the sample under high vacuum ($10^{-5}$ torr) for 24 hrs or even by recrystallizing the sample from DMF have not been fruitful. Thus both the unrecrystallized and the recrystallized (from DMF/EtOH) product show a sharp peak in their infrared spectra at 3550 $cm^{-1}$ due to the OH stretching frequency of ethanol. Such a sharp peak due to the OH absorption (see fig. XXXVIII), which usually appears as a broad band, indicates strong interaction of the ethanol molecule with the complex. The $^1H$ NMR spectrum of the sample, dissolved in d-DMF, has also confirmed the presence of one mole of ethanol per mole of the sample by the careful integration of the methyl protons of ethanol against the aromatic protons of the ligand DPPE.

Other significant features of the infrared spectrum are shown in fig. XXXVIII and the important frequencies are listed in Table 18 . There is a strong and sharp band at 2200 $cm^{-1}$ due to the $\nu$CN of the $BH_3CN^-$ grouping, and this indicates that the two $BH_3CN^-$ groups must be equivalent in the complex and most probably <u>trans</u> to each other. Furthermore, a shift of 21 $cm^{-1}$ in the $\nu$CN from ionic $BH_3CN$ also strongly suggests a coordinatin through the nitrogen atom to the cobalt. It has been suggested that a similar shift in the single strong peak due to $\nu$CN in the infrared spectrum of $Fe(BH_3CN)_2(P(OR)_3)_4$ which are <u>trans</u> to each other (see fig. V-A , page 20 ) whereas the <u>cis</u> isomer of the iron complex shows two separate cyanide stretching frequencies (24).

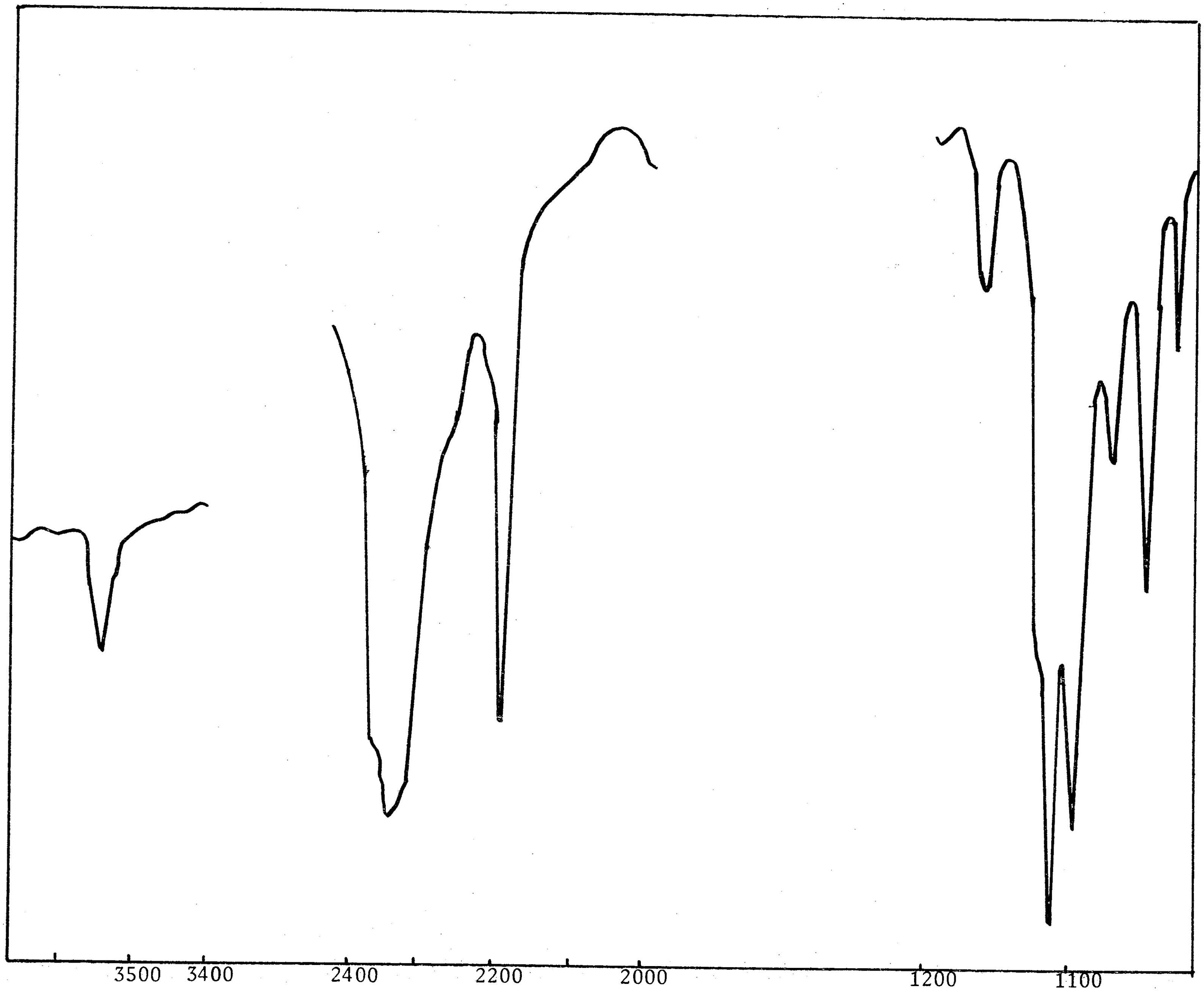
TABLE 18:

Infrared, NMR, Electronic and Magnetic Measurement Data on Complexes Derived from Reactions of Co(II), DPPE and $NaBH_3CN$ and Co(II), DPPP and $NaBH_3CN$

| No. | Complexes | νBH $cm^{-1}$ | δBH $cm^{-1}$ | νCN $cm^{-1}$ | νCO-H $cm^{-1}$ | δ $^{31}P$ NMR | δ $^{1}H$ MNR | μ (B.M.) | Electronic Spectra $cm^{-1}$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Solid State | Solution |
| 1. | $Co(BH_3CN)_2(DPPE)_2 \cdot EtOH$ | 2350(s,b) | 1100(s)<br>1115(s) | 2200(s) | | 72.56 | | 1.73 | 11,764(b) | 15,384<br>8333 |
| 2. | $Co(BH_3CN)_2(DPPP)_{1.5}$ | 2380(s,b) | 1100(s) | 2185(s) | | | 7.2(b) (aromatic protons) | 1.91 | 7550<br>11,000<br>14,200 | 7340<br>12,000<br>16,600 |
| 3. | $CoH(DPPP)_2$ | | | | 1960(m) | 31.7 | -14.61(Q)<br>JPH=25 HZ | Diamagnetic | No Absorption | |
| 4. | $Co(DPPP)_2$ | | | | | 11.62 | | | | |

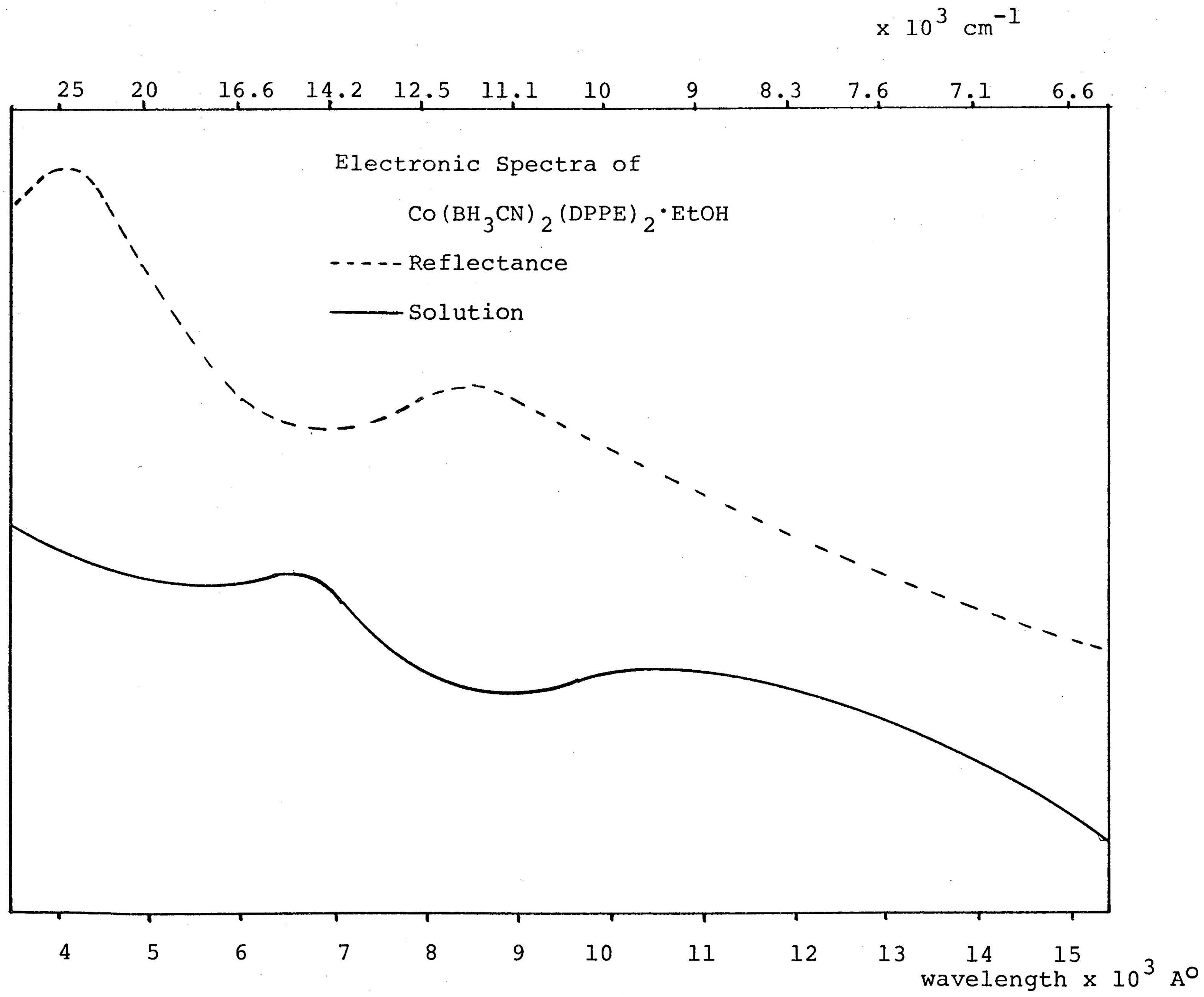
Abbreviations

b, broad
s, strong
Q, Quintet



Selected Features of the Infrared Spectrum of $Co(BH_3CN)_2(DPPE)_2 \cdot EtOH$

(XXXVIII)


x $10^3$ cm$^{-1}$
25
20
16.6
14.2
12.5
11.1
10
9
8.3
7.6
7.1
6.6
Electronic Spectra of
$Co(BH_3CN)_2(DPPE)_2 \cdot EtOH$
- - - - -Reflectance
———Solution
4
5
6
7
8
9
10
11
12
13
14
15
wavelength x $10^3$ A°

(XXXIX)

The $BH_3$ stretching and deformation modes occur in the infrared spectrum as a strong and broad band at 2350 $cm^{-1}$ and a sharp doublet at 1100 and 1115 $cm^{-1}$ respectively. There is no vibration at ∿2000 $cm^{-1}$ usually associated with a M-H-B arrangement and this rules out the possibility of hydrogen coordination with the cobalt. This is confirmed by the $^{1}H$ NMR spectrum of the complex which shows no significant features in the high field region.

The $^{31}P$ NMR spectrum of the complex exhibits a sharp peak at $\delta = 72.56$ and also a signal due to the presence of a significant amount of free phosphine at $\delta = -24.36$. The complex has a magnetic moment of 1.73 B.M. and is therefore a low spin $d^7$ system, i.e. Co(II). As has been mentioned before, such a large chemical shift might be the result of paramagnetism but surprisingly the unpaired electron does not seem to affect the signal shape which has a half width of only 60 HZ. However, the presence of free phosphine in solution does indicate some dissociation of the complex. This is also supported by the electronic spectra of the complex, as shown in fig. XXXIX. Thus the solid state reflectance spectrum shows a broad band at 11,764 $cm^{-1}$ due to a d-d transition whereas another strong band at 25,329 $cm^{-1}$ is probably charge transfer in origin. In solution (DMF) there are two regions of absorption, one at 15,384 $cm^{-1}$ and the other at 8333 $cm^{-1}$. However, as the complex can be recovered unchanged from solution, it therefore appears that the dissociation process might only involve the phosphine ligand and not the $BH_3CN^-$ group.

The reflectance spectrum of the complex shows some resemblance to the solution spectra of the DPPM complexes which, as already discussed, are $d^7$ low spin six coordinate systems. On the basis of its empirical formula the complex also shows a resemblance to $Co(BH_3CN)_2(DPPB)_2$ (see later) although in the latter the Co(II) is high spin and the $BH_3CN^-$ group is N-bonded to cobalt. It is surprising that the cis DPPE complex is low spin since the ligand field is being created by the phosphine and the relatively weakly bound $BH_3CN^-$ groups (shift in $\nu CN$ of only 21 $cm^{-1}$ from ionic $BH_3CN$). It should be noted that in all other low spin Co(II) complexes prepared in this work, Co-H interactions also appear to be involved. The possibility must therefore remain that the structure of the complex is not as straightforward as being suggested i.e. six coordinated Co(II).

## B. Other Complexes

Other reactions at room temperature between cis DPPE, Co(II) and $NaBH_3CN$ where the amount of $BH_3CN^-$ or the reaction time was changed have not shown the formation of any other complex except the one discussed above. However, at high temperatures the reactions are complex and behave in a more or less similar way to those involving Diphos. Although most of the reactions at high temperatures have not led to any characterizable product, a small amount of a dark brown air sensitive cyanide complex was produced in one reaction. The infrared spectrum of this solid showed a strong peak at 2100 $cm^{-1}$ assigned to $\nu CN$ and no vibrations due to the $BH_3$ grouping. Due to the small amounts of the product obtained and due to the complex nature of the reactions, complete identification has not been achieved. The X-ray powder pattern of the brown solid has ruled out the possibility that the brown solid might be contaminated with NaCN which may also form as a byproduct in these reactions. This again illustrates the sensitivity of the B-C bond, particularly in high temperature reactions.

## V. Reactions of Co(II), DPPP and $NaBH_3CN$

The reaction between Co(II), DPPP and $NaBH_3CN$ have yielded essentially three products, a Co(II) complex with empirical formula $Co(BH_3CN)_2(DPPP)_{1.5}$, a Co(I) hydride $CoH(DPPP)_2$, and a Co(O) complex $Co(DPPP)_2$. Furthermore the reactions are very clean and no problems in reproducing these reactions have been encountered.

### A. $Co(BH_3CN)_2(DPPP)_{1.5}$

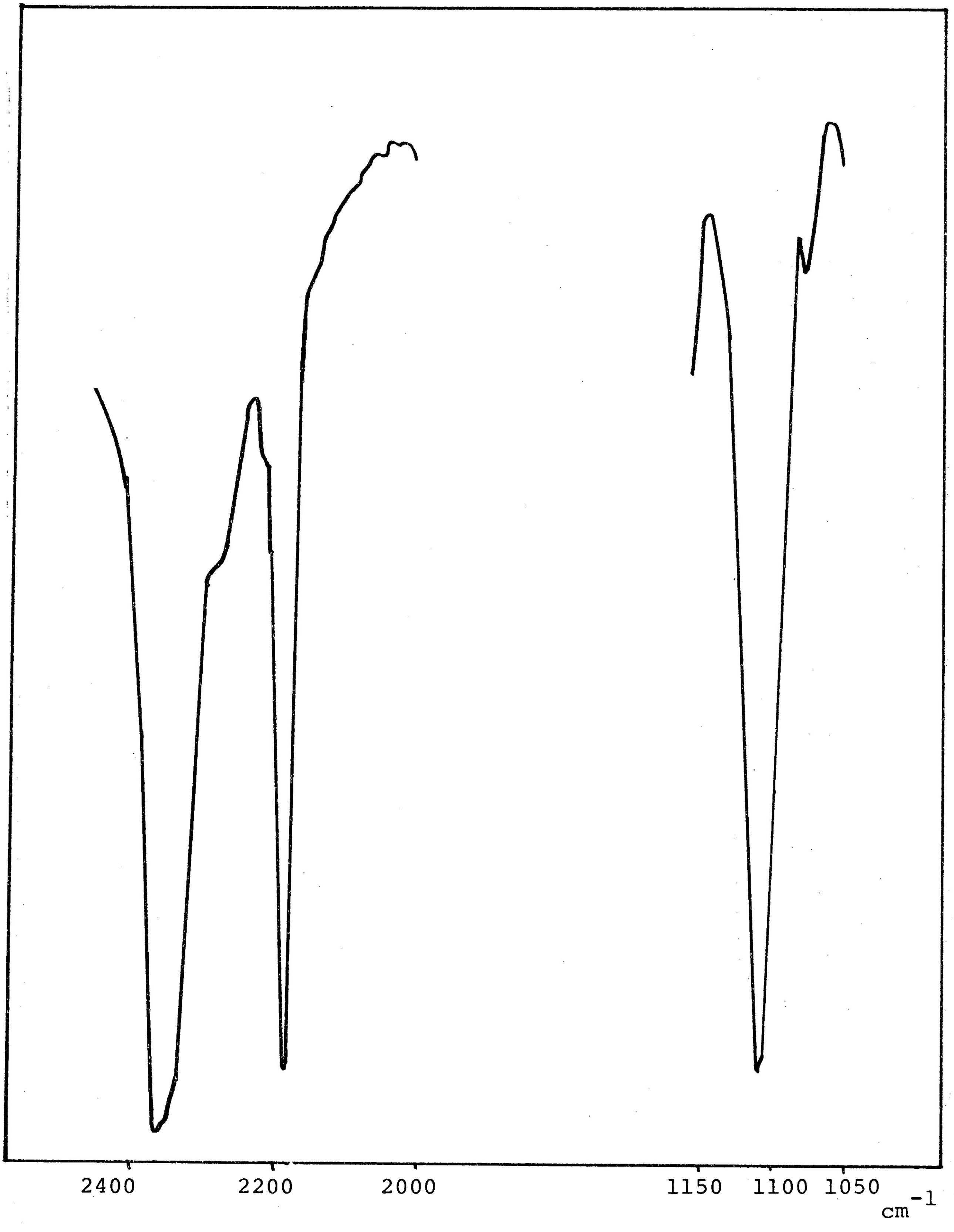
The synthesis of $Co(BH_3CN)_2(DPPP)_{1.5}$ is apparently much less sensitive, than the syntheses of other complexes in this study, both to the solvent used for the reaction medium, and to the starting material. For example, the olive green complex was successfully synthesized in almost identical yields from reactions carried out in either benzene and ethanol or THF and ethanol, between either $CoCl_2 \cdot 6H_2O$ or $Co(ClO_4)_2 \cdot 6H_2O$, DPPP and $NaBH_3CN$ (∿5 M excess). However, when the amounts of $NaBH_3CN$ were increased up to an 18 molar excess, green-brown mixtures of solids were produced from which no identifiable product could be isolated.

Quick recrystallizations of different crude products from $CH_2Cl_2$, $CHCl_3$, THF and benzene have essentially led to the same product, as seen from IR spectra and chemical analysis (see experimental). However, attempts to grow larger crystals by keeping the complex in solution for longer periods of time have led to interesting observations, which will be discussed shortly.

The infrared spectrum of the complex is shown in fig. XL and Table 18. When compared to the spectra of other complexes made in this work, this spectrum is very simple and possibly reflects a very symmetrical structure. The B-H stretching vibrations occur at 2380 $cm^{-1}$ and the deformation modes are at 1110 as a strong peak. A single sharp cyanide stretching frequency of the $BH_3CN^-$ group at 2185 $cm^{-1}$, which is shifted by only 6 $cm^{-1}$ from the position in ionic $BH_3CN^-$ (2179 $cm^{-1}$), suggests that, if the $BH_3CN^-$ is coordinated to the cobalt through its nitrogen, the bond is very weak.

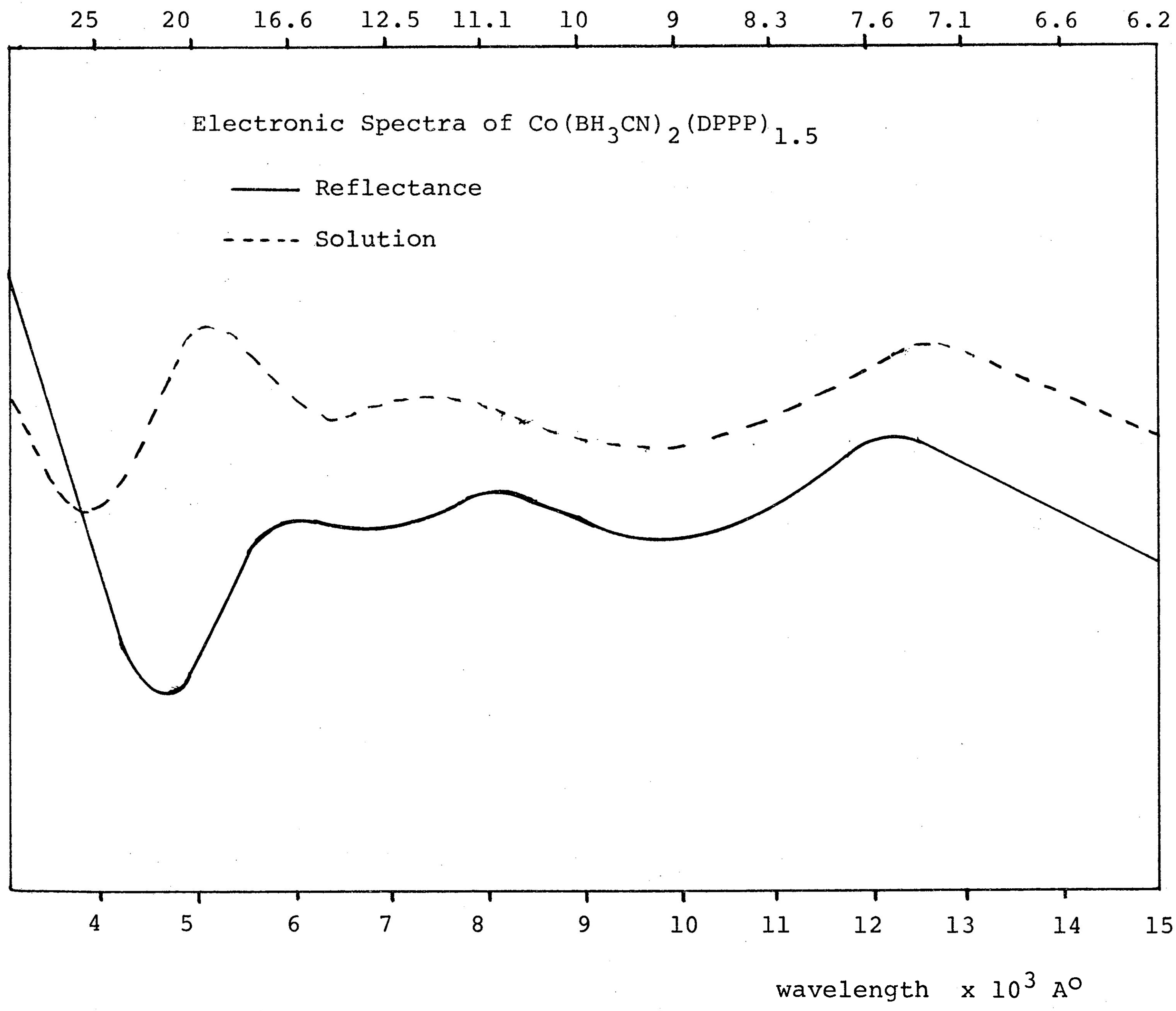
One of the most interesting observations regarding this complex concerns the $^{31}P$ and $^{1}H$ NMR spectra. No signal has been detected after many attempts to measure the $^{31}P$ NMR spectrum both at ambient and at low temperatures and in different solvents ($CH_2Cl_2$, THF or $C_6H_6$). The

Selected Features of the Infrared Spectrum of $Co(BH_3CN)_2(DPPP)_{1.5}$



(XL)

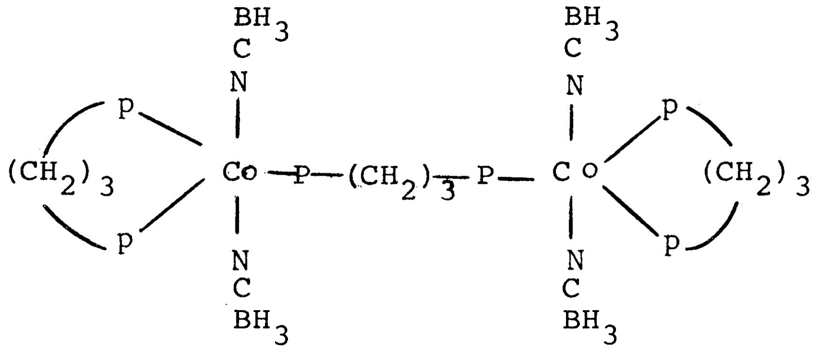
possibility exists that the signals are shifted so far downfield, due to paramagnetism associated with the complex ($\mu = 1.9$ B.M.), that they are not observed under normal operating conditions which covers a range of ∿8 - 10,000 HZ. For this reason, several spectra were recorded over the widest range possible (20,000 HZ) for this instrument, but no signals could be found. The $^{1}H$ NMR spectrum shows the aromatic protons of the DPPP as an unusually broad signal at $\delta = 7.2$. At present this behaviour of the complex is not properly understood. As this complex was made quite early in these studies, it was originally thought that paramagnetic effects were causing these effects. However, many normal $^{31}P$ and $^{1}H$ NMR spectra have now been recorded on paramagnetic complexes and so the answer to the problem must lie elsewhere. A similar situation has been observed for two other complexes (a phosphole complex and a Ni-DPPP-cyanotrihydroborato complex) recently prepared in these labs. No signals were observed in their $^{31}P$ NMR spectra, despite the fact that there is no doubt as to the presence of phosphorus atoms in these molecules. Certainly more work is required in this direction to explain this curious behaviour on some of these phosphine complexes.



Electronic Spectra of $Co(BH_3CN)_2(DPPP)_{1.5}$

(XLI)

As mentioned before the complex is paramagnetic with a magnetic moment of 1.91 B.M. and therefore the Co(II) ion ($d^7$) is in the low spin state. The reflectance and solution electronic spectra of the complex are shown in fig.XLI, from which it is apparent that, apart from slight shifts in the positions of the absorptions the two spectra are the same. This means that the solid state structure is retained in solution. The shape of these spectra is quite different from those of the other cyanotrihydroborato complexes prepared in this work. Comparison of this spectrum with those of other Co(II) low spin complexes of square pyramidal or trigonal bipyramidal geometries has not revealed any significant similarities. It is therefore difficult to formulate the complex with any certanity. The most reasonable possibility would seem to be the structure shown below:

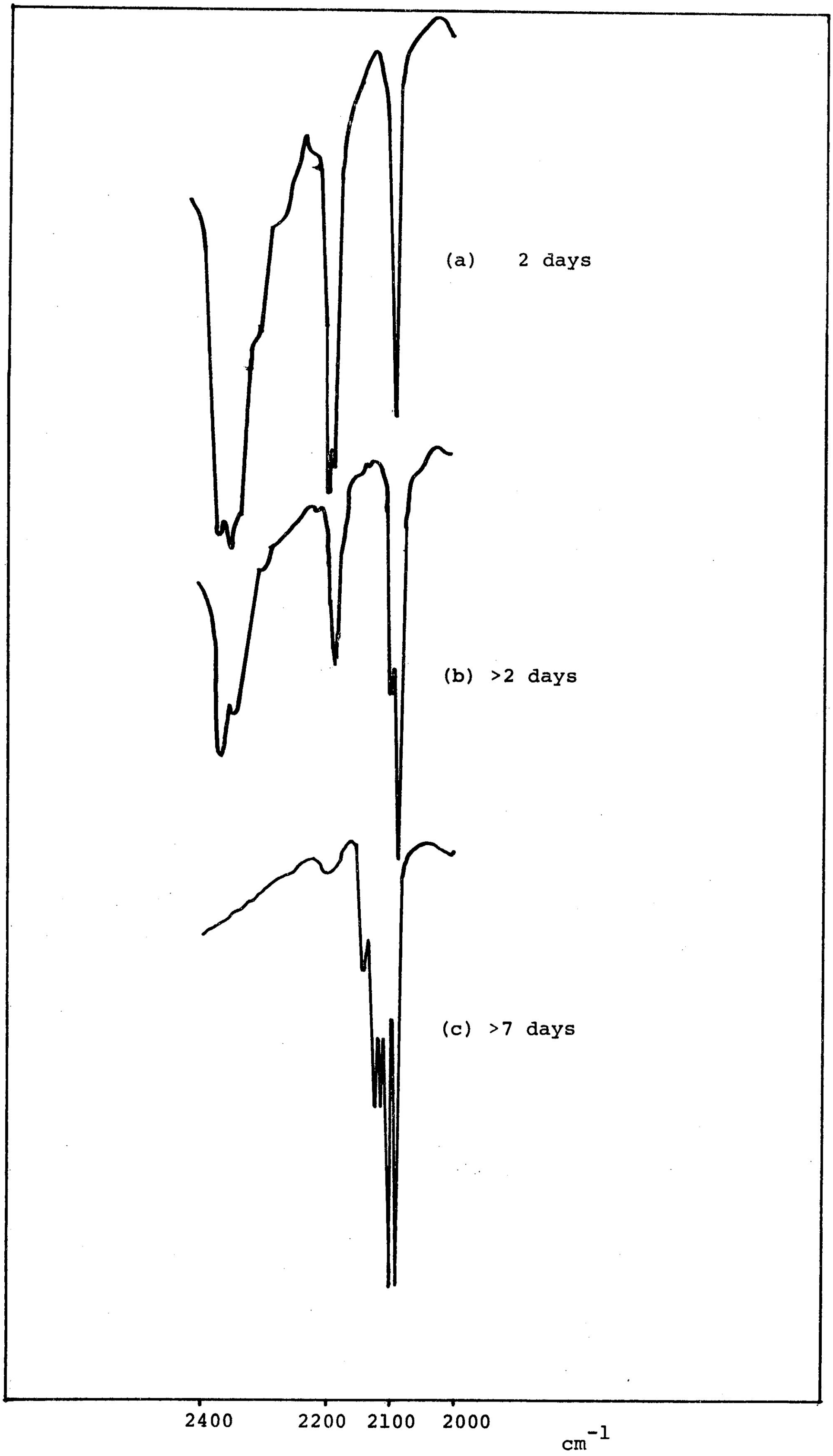


(XLII)

which might be distorted significantly from regular $C_{4v}$ or $D_{5h}$ symmetries. This type of dimeric arrangement with chelating and bridging phosphines has been confirmed in, for example, $Cu_2(Diphos)_3Cl_2$ (79). DPPM is also a well known bridging bidentate phosphine ( 80—84) but it is not common for the longer chain bidentate phosphines to bridge in this way (85).

As mentioned earlier, when solutions of this complex in organic solvents are kept for prolonged periods, decomposition results. Fig. XLIII shows how the IR spectrum of the starting material is dramatically changed as a function of time. Thus when a solution of the complex in $CH_2Cl_2$ is kept for 2 days under a slow stream of nitrogen, a dark coloured (almost black) crystalline solid is obtained. This shows (fig. XLIII) the appearance of a new sharp and strong peak at 2090 $cm^{-1}$ accompanied by the splitting of the peak at 2185 and 2380 $cm^{-1}$. When a different sample in $CH_2Cl_2$ solution is kept for more than two days a brown crystalline solid is obtained (fig. XLIII) where both the peaks at 2185 $cm^{-1}$ and 2380 $cm^{-1}$ are significantly reduced in intensity and a shoulder at 2100 has appeared on the peak at 2100 $cm^{-1}$. Finally when a sample is left for more than 7 days a reddish-brown crystalline solid is obtained.

Infrared Spectra of Products Obtained at Different Stages of Decomposition of Co$(BH_3CN)_2(DPPP)_{1.5}$



(XLIII)

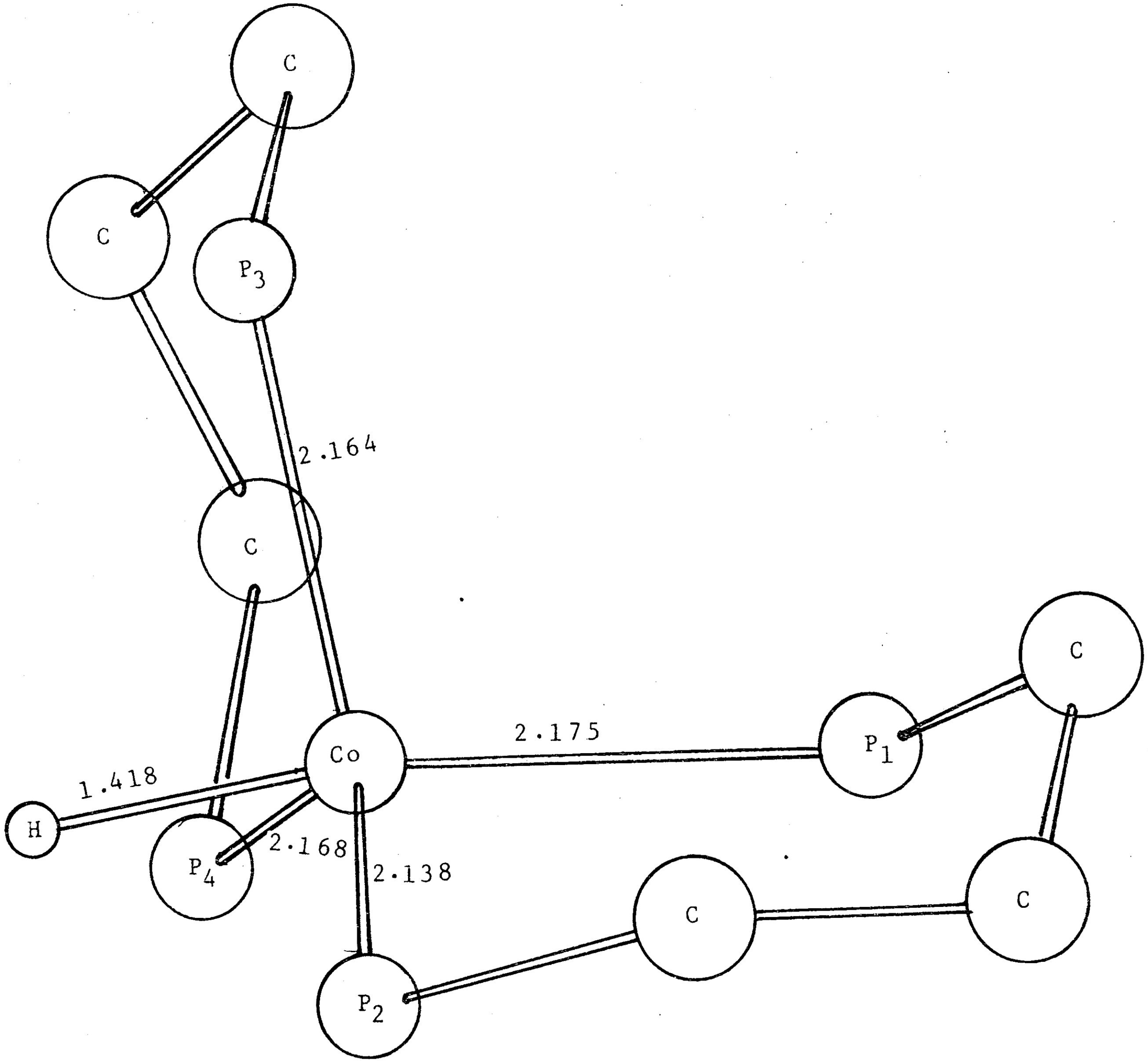
This shows (fig. XLIII) a strong doublet at 2090 and 2100 $cm^{-1}$, a medium intensity doublet at 2118 and 2122 $cm^{-1}$ together with a very weak band at 2141 $cm^{-1}$. The peak due to $BH_3$ absorptions at 2380 $cm^{-1}$ has completely vanished, so that, once again, the B-C bond in $BH_3CN^-$ has been broken and the $BH_3$ group abstracted. There are no significant changes in the remaining region of the infrared spectra which remain essentially the same as that of $Co(BH_3CN)_2(DPPP)_{1.5}$. Although the complexes produced in this study appeared to be crystalline, they were in fact impure and, unfortunately, decomposed further during attempts at recrystallization.

These are the first studies on $BH_3CN^-$ complexes where B-C bond breaking has been observed in organic solvents ($CH_2Cl_2$ and $Me_2CO$, see page 177). However, as mentioned earlier in the discussion of Diphos complexes, it is not known whether this is a general reaction or what role is played by the metal ion. Certainly more studies in this regard would be rewarding.

## B. $CoH(DPPP)_2$

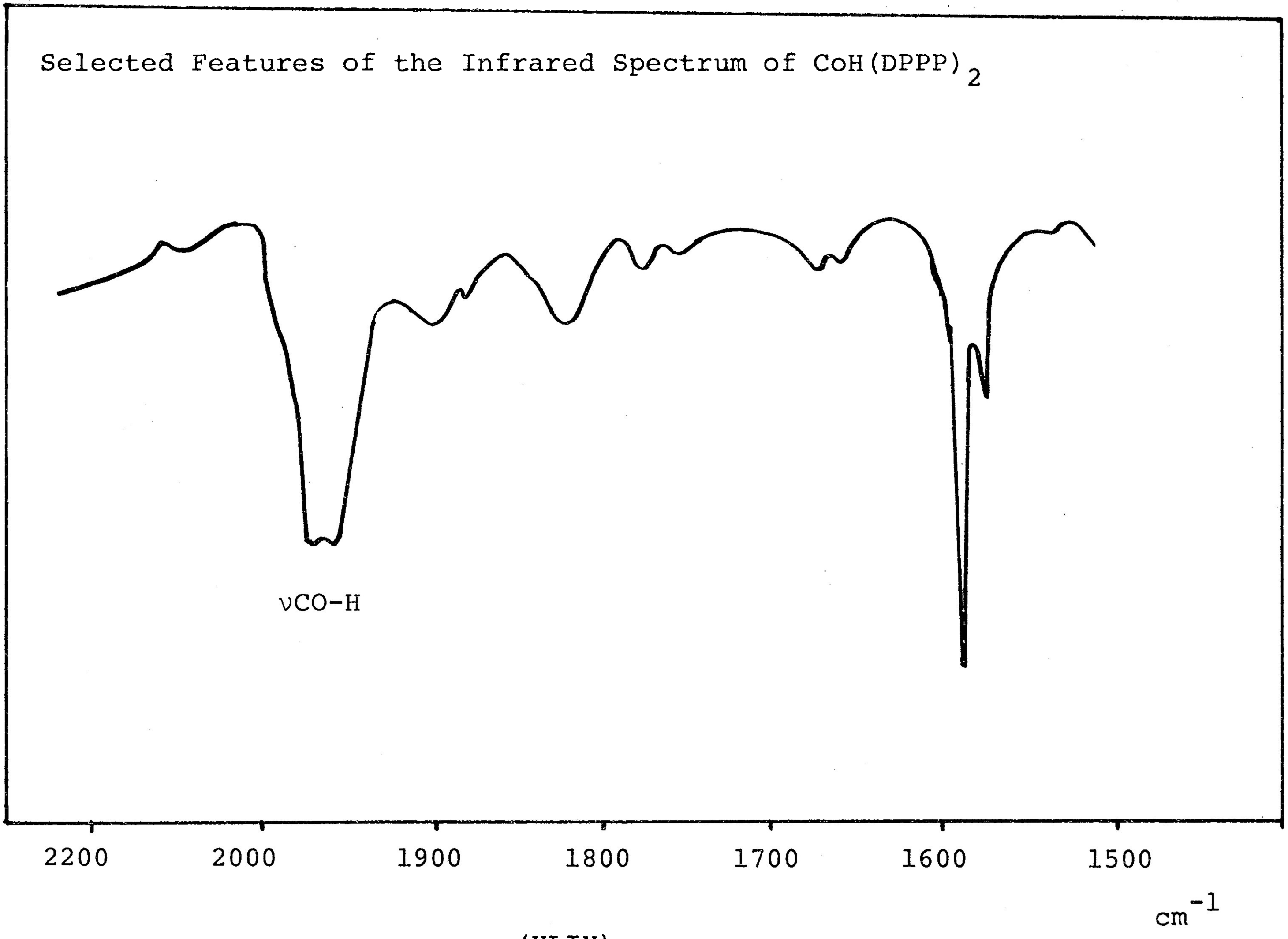
The above cobalt hydride complex has already been prepared in these labs from reactions at room temperatures between Co(II), DPPP and $NaBH_4$ (42). However, the complex has also been made in this work by using the milder reducing agent, $NaBH_3CN$. In this case considerably more forcing reaction conditions are required. Thus the complex is formed at elevated temperatures when a very large molar excess ($\sim$24) of $NaBH_3CN$ is added periodically to a mixture of $CoCl_2 \cdot 6H_2O$ and DPPP. The highly air sensitive complex can be recrystallized from benzene or toluene as large dark brown crystals. It decomposes quickly in chlorinated solvents and in DMF, DMSO and THF.

The metal hydride stretching frequency in the infrared spectrum of the complex (shown in fig. XLIV) occur as a medium intensity band at 1960 $cm^{-1}$, but the deformation mode is obscured by the ligand vibrations. The $^1H$ NMR spectrum of the complex shows a distinct quintet at $\delta = -14.61$, with JPH = 25 HZ, due to coupling of four phosphoros atoms of two DPPP ligand with the hydride. The



Structure of $CoH(DPPP)_2$ as Determined by X-ray Crystallography

(XLV)



Selected Features of the Infrared Spectrum of $CoH(DPPP)_2$

(XLIX)

$^{31}$P NMR spectrum of the complex exhibits a single sharp peak at $\delta = 31.7$, showing that all the four phosphorus atoms of the two DPPP ligands are equivalent.

Recently the solid state structure of the complex, prepared from $NaBH_4$ reactions, has been determined by single crystal X-ray diffraction (78). The presence of hydride has been clearly seen and the structure is a ditorted square base pyramid ( fig. XLV), showing one of the M-P bonds to be longer than the other three. However, due to the single peak in the $^{31}$P NMR spectrum it appears that in solution all the four phosphorus atoms are equivalent.

The complex is low spin $d^8$ system and has a featureless electronic spectrum as shown in fig. XXXIV.

## C. Co(DPPP)$_2$

The zero valent cobalt complex has been isolated in very small yields (∿4%) from the filtrates after the isolation of $Co(BH_3CN)_2(DPPP)_{1.5}$. Consistent with the above formulation, the infrared spectrum of the complex shows only the vibrations associated with the phosphine. The $^{31}P$ NMR spectrum of the sample shows a single strong peak at $\delta = 11.62$ indicating that all the four phosphorus atoms are equivalent, at least in solution. The cobalt is probably tetradedrally coordinated.

The formation of this cobalt(0) complex indicates that even small amounts of the mild reducing agent, $NaBH_3CN$, can cause reduction of Co(II). However, the major product in the reaction is the Co(II) species, $Co(BH_3CN)_2(DPPP)_{1.5}$ and it therefore appears that some as yet not isolated intermediate Co(I) complexes may have also been formed in these reactions.

## VI. Reactions of Co(II), DPPB and $NaBH_3CN$

The complexity of and diversity of products from the reactions between Co(II), $NaBH_3CN$ and bidentate phosphines is considerably reduced as the length of the carbon chain increases in these phosphines. Moreover, in the presence of the longer chain bidentate phosphine DPPB, much larger amounts of $NaBH_3CN$ or higher temperatures are required to achieve complexation. Thus all the reactions at room temperatures where the Co:DPPB:$NaBH_3CN$ ratio was varied from 1:3:1 to 1:4:8, produced only dark green solutions from which no identifiable products could be isolated. However, when larger excesses of $NaBH_3CN$ (∿16 molar) were used a Co(II) and a Co(I) complex was formed.

### A. $Co(BH_3CN)_2(DPPB)_2$

The olive green Co(II) complex has been synthesized in the presence of a large excess of $NaBH_3CN$, both at room temperature from $Co(ClO_4)_2 \cdot 6H_2O$ and at high temperatures from $CoCl_2 \cdot 6H_2O$. As might perhaps be expected it requires much longer time (24 hrs) for the complex to form at room temperature than at elevated temperatures (1 hr). However, in both these reactions a Co(I) complex is also formed which will be discussed later.

The green complex, $Co(BH_3CN)_2(DPPB)_2$, slowly precipitates from the filtrates of reaction mixtures which were kept for 24 hrs at low temperatures. The green solid could not be purified by recrystallization as it is insoluble in all organic solvents tried i.e. $C_6H_6$, $CH_2Cl_2$, $CHCl_3$, THF, MeCN, DMSO and DMF. The complex was purified by washing with EtOH, $C_6H_6$ and $CH_2Cl_2$. The X-ray powder diffraction pattern of the complex showed no NaCl or NaCN impurities. Several different products from various reactions treated in the above manner have consistently analysed for $Co(BH_3CN)_2(DPPB)_2$.

The infrared spectrum of this air stable complex shows (fig. XLVI) a strong doublet with maxima at 2189 and 2200 $cm^{-1}$. These two strong signals can be assigned to the cyanide stretching frequencies of the two $BH_3CN^-$ groups. Clearly the large shift in the cyanide stretching frequencies indicates that the two $BH_3CN^-$ groups are coordinated through

TABLE 19:

Infrared, NMR, Electronic and Magnetic Measurement Data on Complexes Derived From Co(II), DPPB and $NaBH_3CN$ Reactions

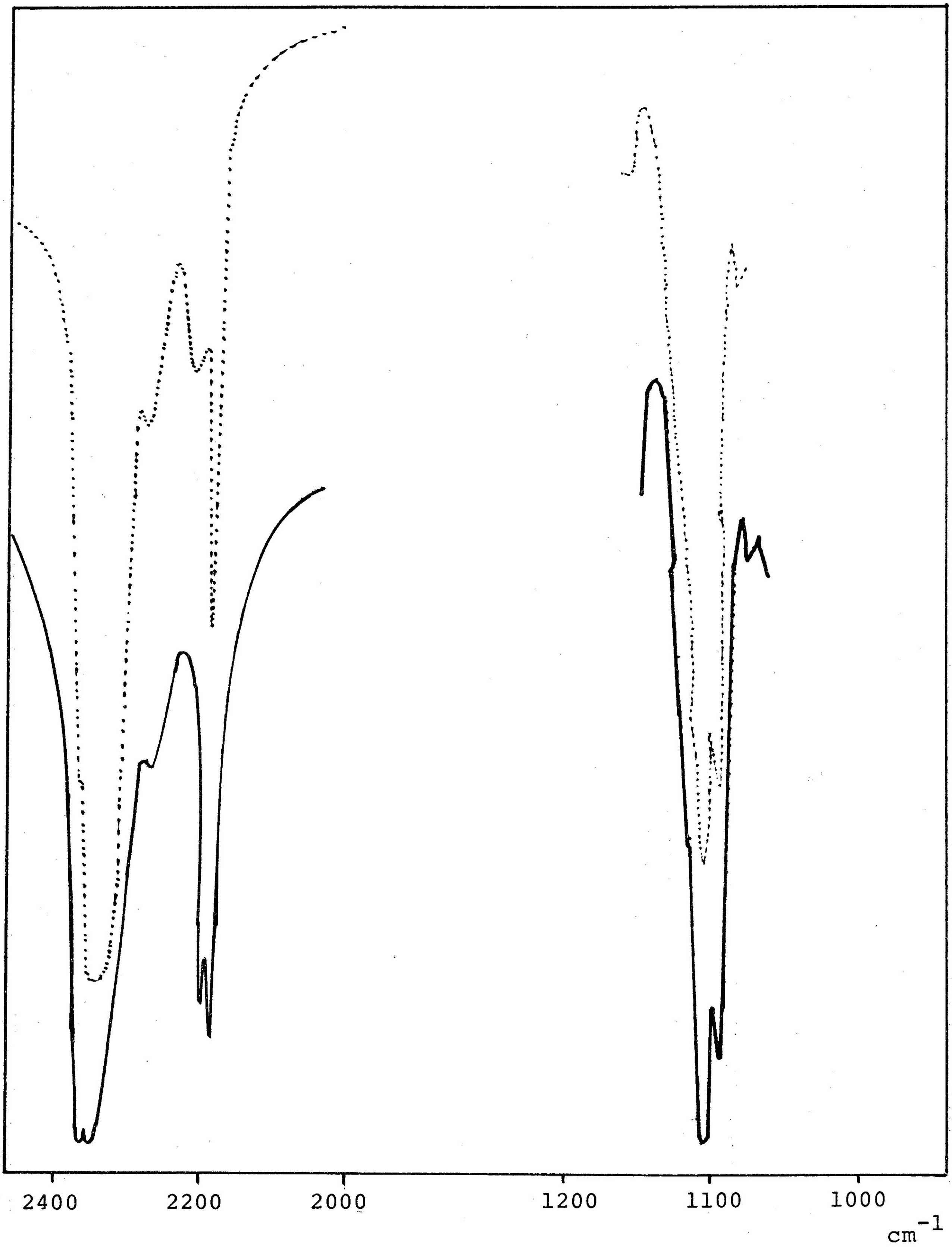
| No. | Complexes | $\nu BH$ $cm^{-1}$ | $\delta BH$ $cm^{-1}$ | $\nu CN$ $cm^{-1}$ | $\mu$(B.M.) | Electronic Spectra ($cm^{-1}$) | |
|---|---|---|---|---|---|---|---|
| | | | | | | Solid State | Band Assignments |
| 1. | $Co(BH_3CN)_2(DPPB)_2$ | 2360(s) | 1100(s) | 2189(s) | 3.5 | 7407 | $^4T_1g$ — $^4T_2g$ |
| 2. | $Co(BH_3CN)(DPPB)_2$ | 2360(s) | 1100(s)<br>1110(sh) | 2200(s) | | 9000 | $^4T_1g$ — $^4A_2g$ |

Abbreviations

b, broad; s, strong; sh, shoulder.

Selected Features of the Infrared Spectra of

——— $Co(BH_3CN)_2(DPPB)_2$, ……… $Co(BH_3CN)(DPPB)$



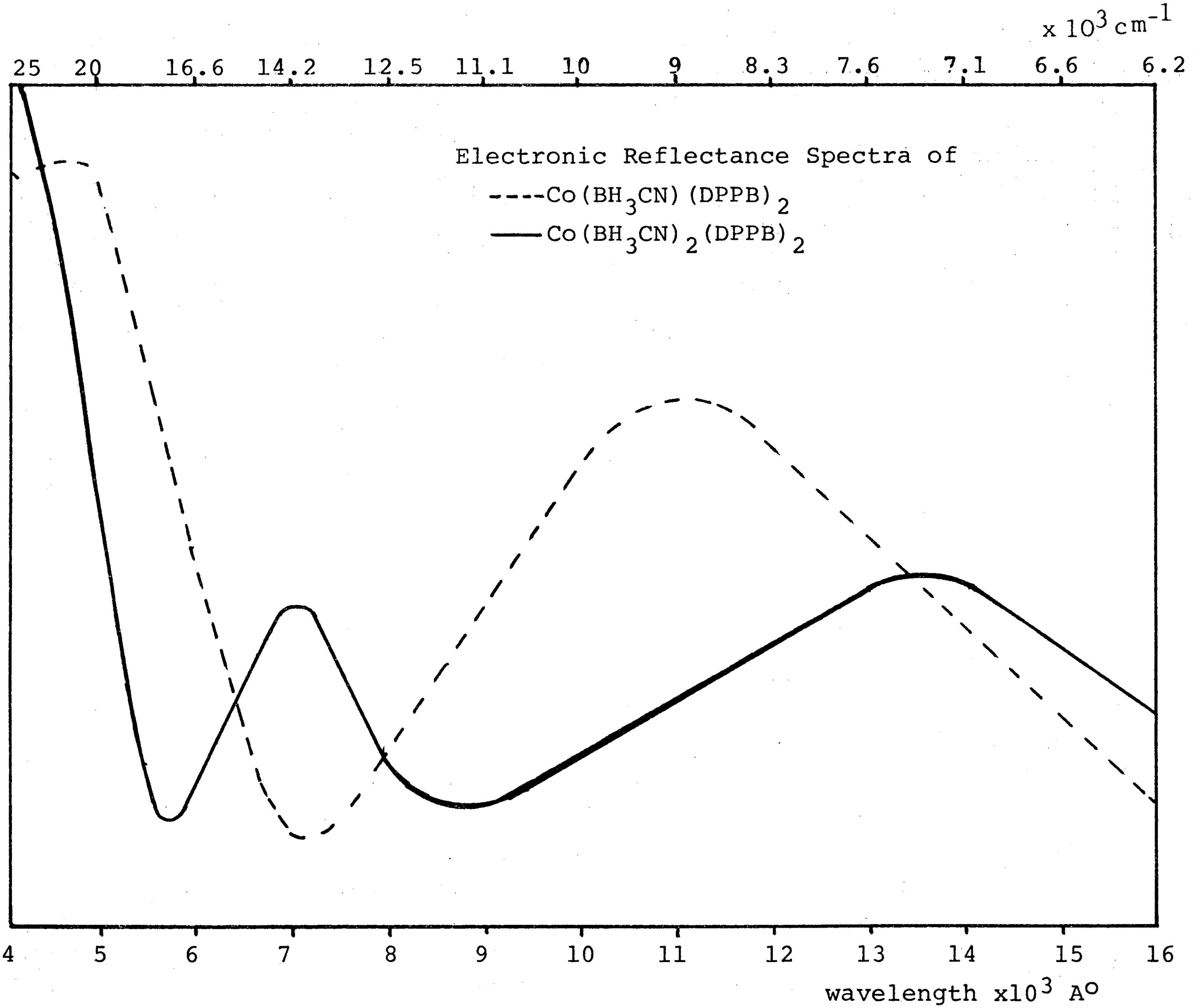
(XLVI)

their nitrogen atoms to the cobalt. The small splitting in the signal probably reflects slightly different site symmetries of the two $BH_3CN^-$ groups.

As usual the $BH_3$ stretching modes occur as a broad signal centered at 2360 $cm^{-1}$ with a shoulder at 2260 $cm^{-1}$ and the deformation frequencies occur at 1100 and 1110 $cm^{-1}$ as a strong doublet.

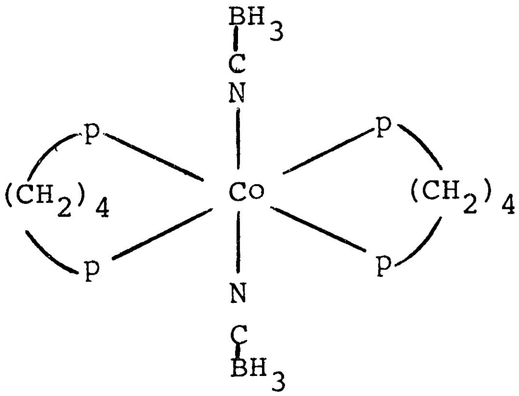
Due to the insolubility of the complex, solution studies could not be done. The reproducible (as samples from different reactions) solid state magnetic measurement shows this complex to be high spin with a magnetic moment of 3.5 B.M. This is an unusually low value for 3 unpaired electrons in a $d^7$ system. As the presence of simple inert impurities, such as NaCl, has been largely ruled out from the X-ray patterns, the low value might be the result of very low orbital contribution in a geometry which is significantly disorted from an octahedral symmetry. Magnetic measurements at different temperatures would be interesting.

The solid state electronic reflectance spectrum of the complex is shown in fig. XLVII. The spectrum can be


x 10$^3$ cm$^{-1}$
25
20
16.6
14.2
12.5
11.1
10
9
8.3
7.6
7.1
6.6
6.2
Electronic Reflectance Spectra of
----Co(BH$_3$CN)(DPPB)$_2$
——Co(BH$_3$CN)$_2$(DPPB)$_2$
4
5
6
7
8
9
10
11
12
13
14
15
16
wavelength x10$^3$ A$^o$

(XLVII)

interpreted assuming a six coordinated cobalt in an octahedral environment, although as mentioned earlier this may be significantly distorted. The peaks at 7407 and 14,285 $cm^{-1}$ can be tentatively assigned to transitions from the $^4T_1g$ ground state to $^4T_2g$ and $^4A_2g$ levels respectively, with the peak at 23,529 $cm^{-1}$ probably arising from charge transfer. Thus the above limited data on this complex point towards a structure as shown below.



(XLVIII)

B. $Co(BH_3CN)(DPPB)_2$

This very air sensitive orange coloured cobalt(I) complex has been isolated from the dark brown-green reaction filtrates left after the separation of the green $Co(BH_3CN)_2(DPPB)_2$, from reactions between $Co(ClO_4)_2 \cdot 6H_2O$, DPPB and

$NaBH_3CN$ carried out at room temperature. The complex also appears to form in the filtrates from high temperature reactions which lead to $Co(BH_3CN)_2(DPPB)_2$ as the major product, but it was found to be contaminated by some other unknown compounds which were clearly seen in the IR spectra of the mixture. It has not been possible to recrystallize this, like the other DPPB complex, because it is either insoluble in some solvents (e.g. $C_6H_6$, PhMe, and EtOH) or it decomposes very rapidly in others (orange solution turning green in DMF, DMSO and $CHCl_3$).

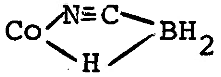
The infrared spectrum of the complex shows (fig. XLVI) some differences from its Co(II) analog, $Co(BH_3CN)_2(DPPB)_2$. Thus, there is only one sharp signal at 2200 $cm^{-1}$ due to the $\nu CN$ of $BH_3CN$ group whereas the BH stretching and deformation modes occur essentially at the same position i.e. 2360 and 1100 and 1110 $cm^{-1}$ respectively.

As mentioned earlier, due to the extreme sensitivity of the complex in solution, NMR studies could not be carried out. Also, insufficient material has so far been obtained for magnetic measurements. However, the electronic reflectance spectrum of the complex, shown in fig. XLVII, has a very close similarity to the Co(I) Diphos complex, $Co(BH_3CN)(Diphos)_2$ which, as already discussed, is thought to have a trigonal bipyramidal structure.

## VII. Conclusions

The primary aims of this work were set out in Chapter I (page 89). After the discussion of the results obtained in this thesis, it is appropriate to comment on the extent to which these aims were realized.

### 1. $NaBH_3CN$ as a Ligand

It is clear from the variety of complexes synthesized that $NaBH_3CN$ is an extremely versatile ligand. Complexes involving $Co-H-BH_2CN$, $Co-NCBH_3$ and  types of $BH_3CN^-$ coordination have been tentatively characterized. Not only are the coordination modes of $BH_3CN^-$ varied, but the structures adopted by the complexes so formed appear to be equally diverse, at least, judging by, for example, their many different reflectance spectra. A considerable part of the effort was spent in establishing the precise reaction conditions which are often necessary for the isolation of some of these complexes. The reactions have proved to be very sensitive to the following parameters a) amount of $NaBH_3CN$ used, b) rate of $NaBH_3CN$ addition, c) reaction time, d) temperature, e) solvent system, and f) metal:ligand (phosphine) ratio.

## 2. Relationship to M-Phosphine-$BH_4^-$ Reactions

The M-Phosphine-$NaBH_4$ reactions (M=Co and Ni) lead essentially to the rapid reduction of M(II) to form M(I) or M(O) complexes ( 3 ). It has been proposed that, for example, $MH(BH_4)(Phosphine)_X$ and $MCl(BH_4)(Phosphine)_X$ are two types of complexes that, although never seen, are intermediates in reactions as metal(II) salts are reduced to M(O) by $NaBH_4$. In this work it is significant that, by using the milder reducing properties of $NaBH_3CN$, it has proved possible to isolate $CoH(BH_3CN)(PPh_3)_3$, analogous to one of the above complexes. In addition, the as yet unidentified green DPPM complex is quite likely of the type $CoCl(BH_3CN)(DPPM)_X$, similar to the second type of system. As more of the complexes made in this work are more completely characterized, hopefully by crystallography, it should be possible to better assess detailed mechanisms of reduction.

## 3. Phosphine Properties

One of the reasons for using bidentate phosphines in this work is the relatively little attention they have received compared to the vast literature on monodentate tertiary phosphines. From the complexities of the reactions described in the previous pages, it is clear that bidentate phosphines with smaller bite distances (e.g. DPPM, Diphos) are generally more effective in forming cyanotrihydroborato complexes, than are those with larger bite distances (e.g. DPPP, DPPB). This may be the result of the formation of more flexible and sterically less hindered systems involving DPPM and Diphos. Also the smaller chain length phosphines have greater potentials for acting as bridging ligands, which obviously results in a greater variety of products.

Of the two monodentate tertiary phosphines used, only $PPh_3$ gave $BH_3CN^-$ complexes. The related phosphine, $Pcy_3$, gave no complexes. Another rigid and flattened phosphine, DBP, which has a very similar donor character to $PPh_3$ is also known to form $BH_3CN^-$ complexes (see Chapter I). Thus it appears that steric rather than electronic factors play a major role in the formation of cyanotrihydroborato complexes with tertiary phosphines like $PPh_3$ and $Pcy_3$.

## VIII Suggestions for Future Work

In these studies on the reactions of $NaBH_3CN$ with Co(II) in the presence of phosphines, some extremely interesting coordination compounds have been produced. In some cases the reactions are far more complex than had been expected. As is often the case in research more questions have been raised by this work than really answered in it and, as a result the section with the above title is probably the easiest section of the thesis to write.

Perhaps the most immediate need is X-ray diffraction studies on some of the $BH_3CN^-$ complexes already isolated, particularly those where hydrogen coordination is suspected, as these complexes are the first of their kind to be reported. It is also difficult to draw conclusions about the mechanims of these reactions until more coordination geometries have been established.

Attempts to study some of the reactions in this work, particularly those at elevated temperatures, have been repeatedly frustrated by problems of reproducibility in spite of very careful attempts to control conditions. This is particularly evident in reactions involving DPPM and

Diphos. This problem must clearly be solved. Perhaps it will be necessary to prepare standard solutions of the reagents so that very precise concentrations can be delivered to reaction vessels e.g. from burettes, over very specific time intervals.

Some potentially very interesting compounds in these studies have not yet been identified for a variety of reasons. For example, the method of preparation of the blue Co-$PPh_3$-$BH_3CN$ complex has been established, but varying amounts of solvents in the crystals have made characterization difficult. In the case of the green and blue solids obtained from reactions involving DPPM, the problem appears to be of compound stability and separation. Still other complexes have not been identified because of the reaction reproducibility problems mentioned above. All of these difficulties could, it is felt, be overcome with more work.

There has been practically no $^1H$ NMR studies of $BH_3CN^-$ complexes done in the past. In this work several very interesting observations have been made which need further attention. For example, neither the resonance due to the terminal $BH_2$ protons nor coupling of the bridging as well as the terminal protons to the boron atom in M-$H_b$-B- structures has been observed in any of the spectra of the cyanotrihydroborato complexes made in this work. Significantly more work is required to find out why this is so. One obvious direction would be to investigate the spectra of these complexes at low temperatures particularly with fluxional processes in mind.

The $^{31}P$ NMR spectra of these and related complexes also require more attention. It is not clear what role a paramagnetic ion plays in signal broadening. In some cases signals are broadened to such an extent that it is not possible to see anything above background in the spectra while, in other cases, unpaired electrons on metal ions do not seem to affect the signal shape in any way. Moreover, significant signal broadening has been observed for diamagnetic complexes.

One additional aspect in the very interesting behaviour of $BH_3CN^-$ is the B-C bond cleavage at both room and elevated temperatures in certain organic solvents. There is considerable scope for more detailed studies to investigate the role of metal ion and the organic solvents in such reactions.

Thus continued research in this area promises to be very challenging, exciting and full of surprises.

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