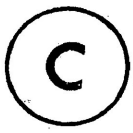
"REACTIONS OF Ni(II) WITH SODIUM CYANOTRIHYDROBORATE IN THE PRESENCE OF SOME BIDENTATE PHOSPHINES"

BY



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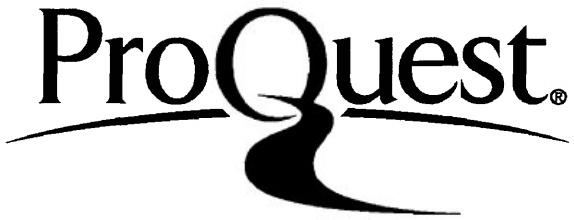
A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE

Lakehead University
Thunder Bay, Ontario, Canada

August, 1982



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ABSTRACT

Cyanotrihydroborate-transition metal ion chemistry has been reviewed.

The reactions between Ni(II) (as a ClO_4^- or Cl^- salt), $NaBH_3CN$ and a series of bidentate phosphines of the type $Ph_2P-(CH_2)_n-PPh_2$ [n = 1, (Dppm); n = 2,(Diphos); (main part of the thesis), n = 3, (Dppp); n = 4, (Dppb) and also cis-and trans-Dppe] have been studied under a wide range of experimental conditions. Most reactions and products are very sensitive to the amount and rate of addition of $NaBH_3CN$, the temperature, the solvent and the reaction time. The Dppm and Diphos ligands have produced a number of unexpected cyanide and cyanotrihydroborato complexes and several other products were observed but not yet satisfactorily purified. Complexes of Ni(II), Ni(I) and Ni(0) have been obtained.

Reactions in the presence of Dppm mainly produced Ni(I) cyanide complexes with the formulae $Ni_2(BH_3CN)_a(CN)_b(Dppm)_c.xEtOH$ (where a = 0 or 1, b = 1 or 2, c = 2 or 3 and x = ½, 1 or 4). In contrast, reactions with Diphos produced complexes of the type $[Ni(BH_3CN)(Diphos)_2Cl]_2$ and $[Ni(BH_3CN)(Diphos)Cl]_2$ containing $Ni-NCBH_3$ units and $[Ni_2(BH_3CN)_3(Diphos)_2]X$, where X = ClO_4^- or Cl^-, containing $Ni-HBH_2CN-Ni$ units. The structures of these complexes were established by a variety of physical methods and isotopic label-

ling techniques.

The other ligands Dppp, Dppb and cis-and trans-Dppe have produced a number of additional complexes for which only preliminary and incomplete data are reported.

ACKNOWLEDGMENTS

I wish to express my deepest sense of gratitude to my two Professors and Supervisors, Dr. A. N. Hughes and Dr. D. G. Holah for their invaluable guidance and sense of direction given to me throughout the progress of this work. Without their far-sighted guidance, encouragement and generous help my education would have been incomplete. Grateful acknowledgments are also made to Dr. T. Griffith, Mr. R. Chuchman and Mr. K. Pringnitz of the Science Instrumentation Laboratory for their endless patience and constant help. Special thanks are also due to Miss. V. Petrovich, Mr. D. A. Jones, Mr. B. K. Morgan and Mr. A. J. Harding for their valuable assistance.

It is also pleasure to thank the National Research Council of Canada and Lakehead University for providing generous financial support during the course of this work.

Finally, I must convey my thanks to my wife, Shireen, for her moral support, encouragement and constant inspiration which allowed me to pursue my studies and research interests.

Author
August, 1982.

LIST OF TABLES

LIST OF INFRARED SPECTRA

ABBREVIATIONS

Bu^n	n-butyl
Cy	cyclohexyl
DBP	5-phenyl-5H-dibenzophosphole
Diphos	1,2-bis(diphenylphosphino)ethane
Dppm	bis-(diphenylphosphino)methane
Dppp	1,3-bis(diphenylphosphino)propane
Dppb	1,4-bis(diphenylphosphino)butane
Dpppe	1,5-bis(diphenylphosphino)pentane
Dpph	1,6-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_5dien	1,1,4,7,7-pentamethyldiethylenetriamine
P	1,1,1-tris(diphenylphosphinomethyl)ethane
PCy_3	tricyclohexylphosphine
Ph	phenyl
Phen	1,10-phenanthroline
P(o-tolyl)$_3$	tri-o-tolylphosphine

PPh_3	triphenylphosphine
Pr^i	isopropyl
PPr^i_3	tri-isopropylphosphine
THF	tetrahydrofuran
Tren	2,2',2"-triaminotriethylamine

1. INTRODUCTION

1.1 General

During the last few years an increasing amount of attention has been paid to inorganic and organometallic studies involving complex formation between transition metal ions and phosphorus-containing (and other) ligands in the presence of sodium tetrahydroborate and, more recently, sodium cyanotrihydroborate. Until quite recently, very little was known concerning the coordinating properties and reductive capability of the cyanotrihydroborate ligand and relatively few transition metal derivatives had been described, although somewhat more is known concerning BH_4^- complexes. However, a selection of important compounds of this type has now appeared in the literature and, as will be seen in this introductory chapter, some detailed spectroscopic and other structural investigations have been undertaken, although much remains to be done. Indeed, the application of sodium cyanotrihydroborate in inorganic chemistry could be as wide as it is in organic chemistry (1).

The main interest in this area of study concerns the chemical, structural, catalytic and spectroscopic properties possessed by the wide range of complexes produced in such reactions and the mechanisms of these reactions. Such studies have already been carried out in some detail for tetrahydroborate systems (2, 3), and

some interesting results have been accumulated for both tetrahydroborate and cyanotrihydroborate-transition metal-phosphine reactions. For example, different types of phosphines in the presence of sodium cyanotrihydroborate and sodium tetrahydroborate react differently with transition metal ions. Thus, some phosphine ligands readily form complexes in which the transition metals possesses an unusual oxidation state while others may lead to the formation of less usual transition metal compounds, such as hydrido complexes (see for example, 4), tetrahydroborato (or cyanotrihydroborato) complexes (5), and even dinitrogen complexes (6).

Uncommon oxidation states of transition elements in complex chemistry have been of particular interest (7) in recent years. Many such species have appeared in the literature and quite a few of these have been obtained from reactions involving tetrahydroborate and cyanotrihydroborate ions in the presence of various ligands. More will be said of this later in this thesis.

Most phosphines studied in this context, however, give a variety of products and in general, the type of complex formation between transition metals and organic ligands (particularly with phosphorus donor ligands), in the presence of hydroborates depends upon the experimental conditions. Thus, the same phosphorus ligand may allow the formation of different types of complex with the transition metal perhaps in different oxidation states and the main

factor in determining which product is formed may be simple variation of experimental conditions, such as the rate or order of addition, reactant ratios, reaction times, and the nature of the solvent. The mechanisms of these reactions and the structural analysis of the products obviously deserve much attention and, as will be seen later, a great deal has been done in this area. Such reactions often give hydrido, tetrahydroborato or cyanotrihydroborato complexes as the resultant products.

The simplest preparation of such complexes is by the substitution of a BH_4^- (or BH_3CN^-) group (5) for, in most cases, a halide or perchlorate ion. In a number of cases this substitution by a tetrahydroborate or cyanotrihydroborate for halide ion may be accompanied by complexation by the hydroborate groups and/or a reduction in the oxidation state of the metal ion. Because of the very rapid reductive rates in reactions involving $NaBH_4$, use of the less powerful reducing agent $NaBH_3CN$ may solve some of the problems of isolation of various types of intermediate, although other complications such as a wider variety of structural types for the products obtained (see later discussion) may arise. In the absence of stabilizing ligands, other products such as the free metal or metal borides may be formed (3) and, in this context, sodium tetrahydroborate in particular forms metal borides from transition metal salts very readily.

In short, in the course of such reactions in the presence of either of these two reducing agents, several types of products (3, 8, 9, 10, 11) may be obtained from the metal salts MX_2($X = Cl^-$ and ClO_4^-) in the presence of various ligands. Many of the product types isolated so far are summarized in Fig. 1, which is, no doubt, a very simplified scheme for such complex reactions and a more detailed discussion will be presented later in this thesis.

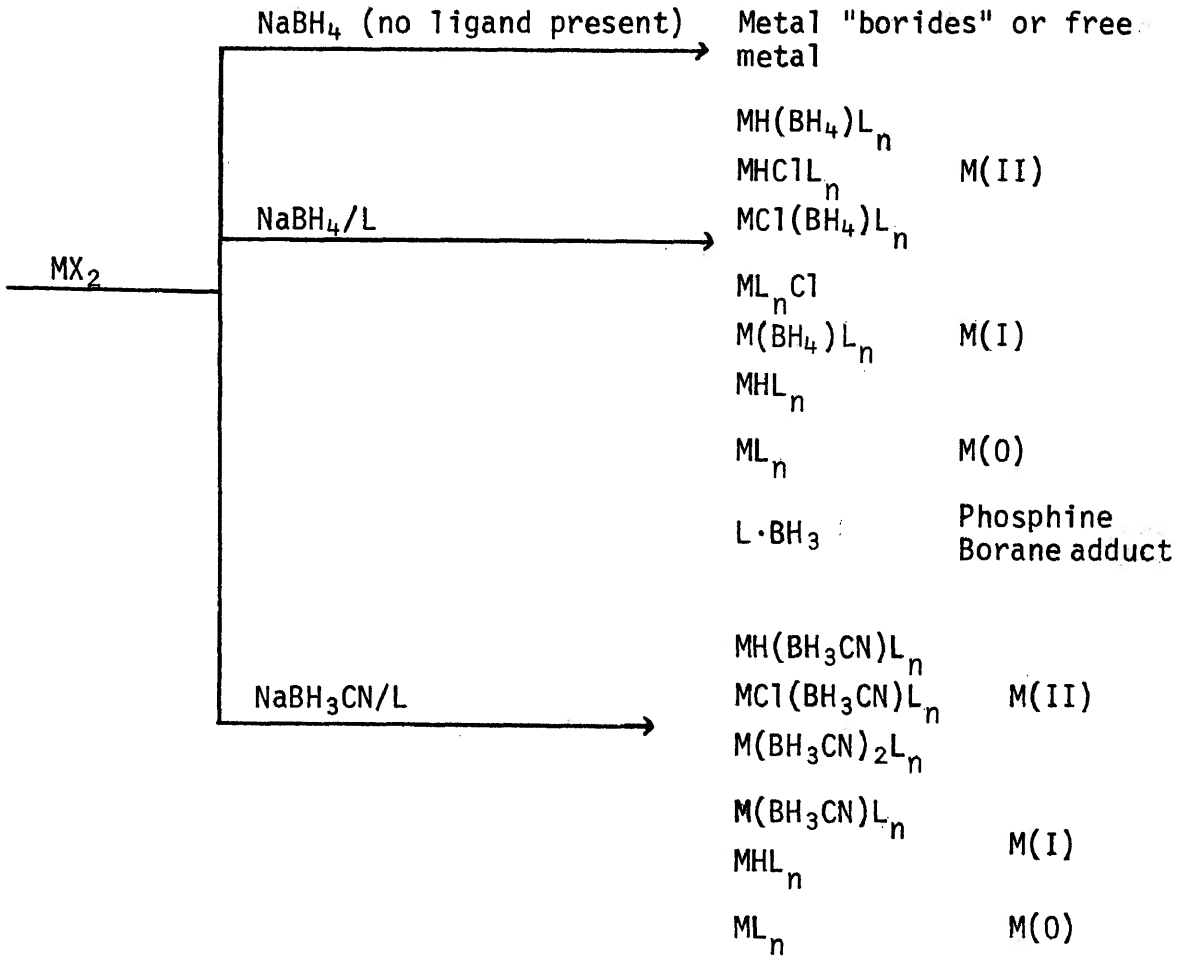


Fig. 1

Since the synthetic and structural work described in this thesis is mainly concerned with Ni(II)-cyanotrihydroborato systems in the presence of a series of bidentate phosphine ligands, the following sub sections outline the earlier work which led to the study described in this thesis.

1.2 Some aspects of the chemistry of BH_3CN^- and BH_4^-

Most of the emphasis in this and later sections is upon the BH_3CN^- system, since virtually all of the new work described later in this thesis involves this species. However, some information regarding involvement of the BH_4^- species is presented from time to time to give a better perspective to the BH_3CN^- work. Coverage of BH_4^- reactions is not intended to be exhaustive and only the more important points will be touched upon. Tetrahydroborate reactions in general have been thoroughly surveyed elsewhere (3, 5).

The first synthesis of the cyanotrihydroborate ion (as the lithium salt) from lithium tetrahydroborate and HCN was carried out by Wittig and co-workers (12a) in 1951 and the sodium salt was similarly prepared later (12b). Wittig also noted the unusual hydrolytic stability of the product towards acids. Thereafter, prior to 1960, only one brief publication appeared on the reducing power of lithium cyanotrihydroborate and that report indicated limited applicability (13). This compound received little

attention as an agent in organic reactions until 1969, when Borch and Durst (14) applied $LiBH_3CN$ in a variety of useful conversions.

Considering inorganic applications of hydroborates, in recent years a few cyanotrihydroborato complexes and many tetrahydroborato complexes have been synthesized and reported in the literature and, as already mentioned, many of these involve coordinated hydroborate ligands. Such coordination will now be briefly examined, and a further, detailed examination of certain aspects of the topic will be presented later.

1.2.1 Bonding abilities and coordination modes of BH_3CN^- and BH_4^-

The bonding ability of any group depends upon the electronic structure of the outermost orbitals. Simple coordination involves the donation of an electron pair from a ligand orbital to a vacant orbital of the acceptor. While such simple coordination is possible with BH_3CN^- (using the non-bonding pair of the nitrogen atom), it is not possible with BH_4^- where coordination would have to be through a hydrogen atom and three-centre bonding would therefore have to occur (similar bonding could occur also with BH_3CN^-). Furthermore, isomerization of BH_3CN^- to BH_3NC^- (the isocyanotrihydroborate ion) could occur during complexation giving rise to C — coordinated systems as shown in Fig. 2.

$M - CN - BH_3$

Fig. 2

Indeed there has already been one report (15) of such coordination involving the cyanotrihydroborate system. Thus, Haines et al. reported (15) a reaction between BH_3CN^- and $[Ru(Ph)(PPh_3)_2Me_2CO]^+$ and they claimed, on the basis of infrared evidence, that at least two products formed as a result of this reaction; a cyanide complex $Ru(Ph)(PPh_3)_2CN$ and a isocyanotrihydroborato complex $Ru(Ph)(PPh_3)_2$-$CNBH_3$ although separation of these two compounds was not effected. However, considerably more evidence would be required before this claim could be considered as being substantiated.

Clearly, many possible modes of coordination are open to BH_4^- and BH_3CN^- and these are listed in Fig. 3. It should be noted here that the possible BH_4^- coordination modes first received attention elsewhere (5) and unidentate (5, 16)* bidentate (5, 17), tridentate (5, 18), tetradentate in the sense of bidentate to each of two metal ions (19), and (possibly) unidentate bridging two metal ions (20) systems have been reported. Fig. 3 therefore lists the various possible bonding modes of BH_4^- and BH_3CN^- ligands and, where the appropriate mode of bonding has been detected, it is so noted by a reference in parentheses.

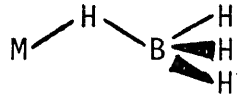
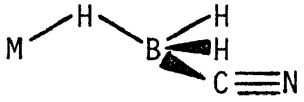
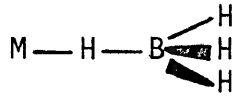
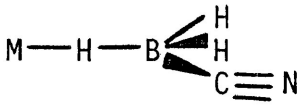
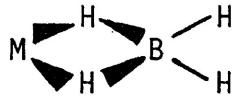
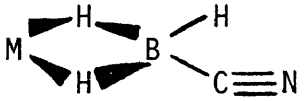
Little further will be said about coordination modes

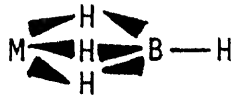
*See also ref. 59 and the more detailed account by the same authors in Inorg. Chem., 19, 587 (1980).

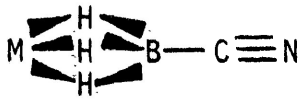
of BH_4^- here although some later mention will be made when the range of known BH_4^- complexes is briefly surveyed. It is worth noting, however, that as referenced in Fig. 3a, X-ray studies (23) of unidentate complexes first indicated a linear M — H — BH_3 arrangement while the more precise neutron diffraction method indicates (22) a non-linear linkage as does a later X-ray study (16).

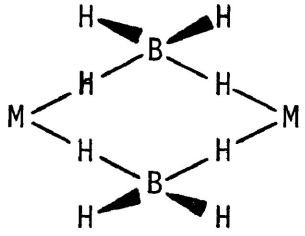
Fig. 3a

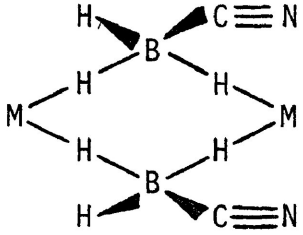
Possible similar coordination modes of BH_3CN^- and BH_4^-

Coordination of BH_4^-		Coordination of BH_3CN^-	
(a) $M^+BH_4^-$	(5)	$M^+BH_3CN^-$	(21)
(b)  Nonlinear	(22,23)		
 Linear	(16)		
(c) 	(5,17)		(?9)

(d)  (5,18)



(e) 



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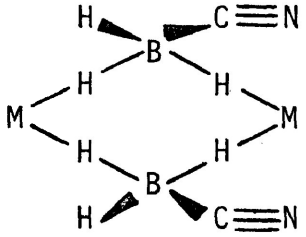

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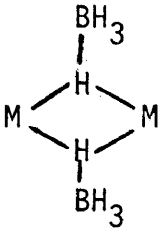
(f)  (?20)

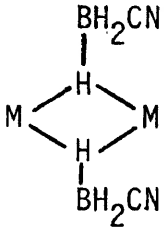
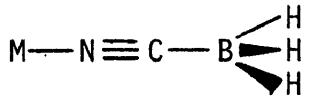
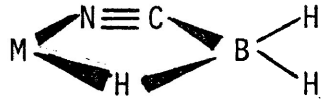


Fig. 3b

Possible coordination modes of BH_3CN^- different from those of BH_4^-

(g) 

(24)

(h) 

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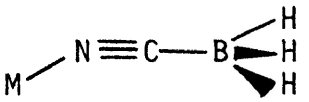
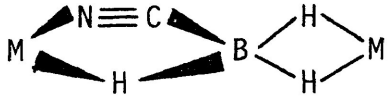
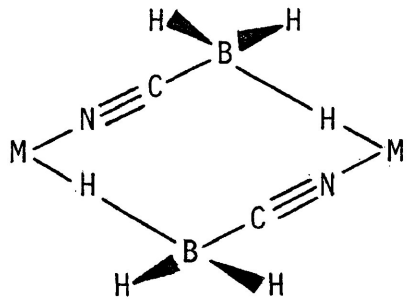
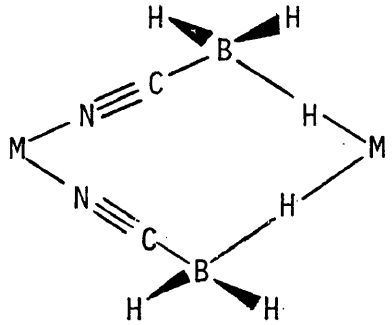


(i) 

(j) 

(10,21,25)

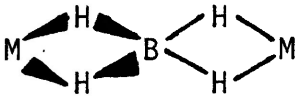
or,



(10,21,25)

Fig. 3c

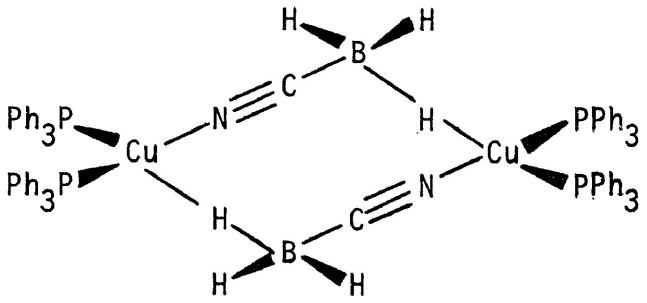
Possible coordination modes of BH_4^- different from those of BH_3CN^-

(k)  (5,19)

As noted in Fig. 3, many of these possible bonding modes for BH_3CN^- have now been observed or suggested and much work has been done in this area by several groups in recent years. For example, Lippard and co-workers (21, 25) have synthesized Cu(I)-BH_3CN complexes with PPh_3, such as $Cu(BH_3CN)(PPh_3)_3$ and $[Cu(BH_3CN)(PPh_3)_2]_2$. The structure and bonding modes of BH_3CN^- in these complexes were characterized by infrared (21) and, in the case of $[Cu(BH_3CN)(PPh_3)_2]_2$, solid state X-ray (21, 25) studies. Of particular interest, in the context of work to be reported later in this thesis, is the proven presence (25) of M — H — B — C — N — M bridges in $[Cu(BH_3CN)(PPh_3)_2]_2$ as shown in Fig. 4a (4b was briefly considered as a possibility). On the other hand, $Cu(BH_3CN)(PPh_3)_3$ apparently normally contains a unidentate nitrogen-bonded cyanotrihydroborate ligand as shown in Fig. 5a as do many other BH_3CN^- complexes (11,

see also sections 1.5.1 and 1.5.2 of this thesis). However, evidence has been presented (9) which indicates that under certain preparative conditions, the complex $Cu(BH_3CN)(PPh_3)_3$ may be isolated in the H-coordinated form as shown in Fig. 5b.

(a)



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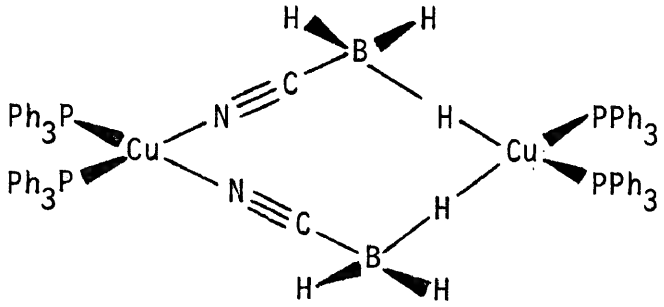
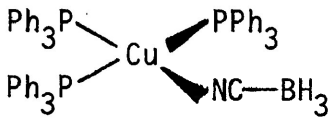


Fig. 4

(a) 

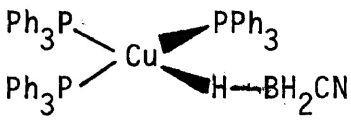
(b) 

Fig. 5

Unidentate BH_3CN^- complexes with coordination through the nitrogen atom are also of some interest because two types of bonding are apparently possible. Thus, these complexes may contain a linear M — N — C linkage in which the nitrogen atom is essentially sp hydridized or an angular M — N — C bond in which the nitrogen has some tendency towards sp^2 hybridization. Indeed, there is one complex known, $Cu(BH_3CN)_2(Me_5dien)$, which contains (24) both types of linkage. These are seen clearly from the X-ray crystal structure and the two differently bonded BH_3CN^- ligands show two different C≡N stretching frequencies. This point is discussed extensively elsewhere (24) and is touched upon later in this thesis.

One other case of BH_3CN^- acting as a bridging ligand has been recorded in the literature (10). Thus, $[Ni(BH_3CN)(tren)]_2^{2+}$ (10) contains two such bridges which have been characterized by solid state X-ray studies. More will be said about this later.

Turning now to possible bidentate coordination of BH_3CN^-, Holah and co-workers (9) prepared the complex $Ni(BH_3CN)L_2$ from $NiCl(PPh_3)_3$ and BH_3CN^-, and assigned the structure given in Fig. 6.

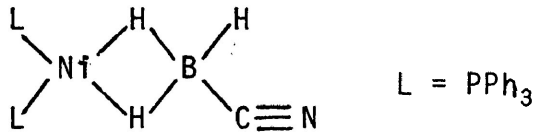


Fig. 6

This structure and bonding mode of BH_3CN^- were suggested by spectroscopic (UV,IR) evidence only and better characterization of this complex is clearly needed. More recently, S.I. Khan (11) synthesized an interesting complex formulated as $[Co(BH_3CN)(Dppm)_2]ClO_4$ for which there is some evidence that the BH_3CN^- acts similarly as a bidentate ligand as shown in Fig. 7. However, in this case, the bidentate mode arises from coordination of one N and one H atom rather than two H atoms as in Fig. 6.

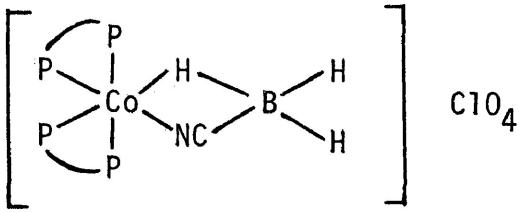


Fig. 7

However, this proposal has very recently been reconsidered (26) on the basis of other evidence and it now appears possible that the system may be better formulated as $[CoH(BH_2CN)(Dppm)_2]ClO_4$. If this is the actual structure, it would appear to be the first example of a neutral BH_2CN complex derived from BH_3CN^-. Again, more will be said of this later.

In concluding and summarizing this subsection, it can be seen from the data discussed above that BH_3CN^- possesses a potentially wide versatility in terms of its possible modes of coordination to metal ions. Clearly much work remains to be done and, later in the results and discussion section of this thesis, it will be seen that various interesting complexes of BH_3CN^- with Ni(II) and Ni(I) systems produce quite a wide variety of structural types. However, certain other aspects of BH_4^- and BH_3CN^- chemistry should be discussed before presenting these results.

1.3 Spectroscopic properties of BH_3CN^- and BH_4^-

Spectroscopic analysis, particularly infrared studies, is a fundamental technique for the investigation of the bonding mode of a group in a compound or a complex. Since this thesis is mainly concerned with cyanotrihydroborate complexes, it is clearly necessary to discuss interpretations of the infrared spectra of BH_3CN^-, and BH_4^-. Some attention will also be given to NMR spectra.

Table 1 represents the observed infrared and Raman bands of $NaBH_3CN$, KBH_3CN and $NaCNBH_3$ while Table 2 represents the corresponding IR bands of $NaBD_3CN$ and $NaCNBD_3$ with the band assignments being those proposed by Berschied and co-workers (27, 12b, 28). The band assignments have been made with the aid of the Raman polarization data for undeuterated cyanotrihydroborate ion and are consistent with assignments which have been made (29, 30, 31, 32) for a large number of BH_3X (X = CO, Me_2S and NH_3 etc.) compounds. The CN stretching vibration is observed as a sharp peak characteristic of cyanide bands. It is observed that the C≡N stretching frequency of BH_3CN^- at 2179 cm^{-1} is intermediate (33) between that of ionic cyanide (CN^-) at 2080 cm^{-1} and covalently bound cyanide (2267 cm^{-1} as in, for example, CH_3CN). For the corresponding deuterated compounds, the C≡N stretching bands do not shift measurably but the B — D stretching frequency lies, as expected, at much lower frequency than the B — H stretching frequency. For the isocyanotrihydroborate system, the C≡N stretching shifts to lower frequency at 2070 cm^{-1} (28) whereas the corresponding B — H_t (terminal) stretching frequency remains at the higher position of 2350 cm^{-1}.

For comparison with the above data, Table 3 represents the expected and observed infrared spectral bands of monodentate, bidentate and tridentate complexes of MBH_4 as well as those of ionic BH_4^-. It shows, for bidentate and tridentate complexes, that the BH terminal stretching occurs at relatively high frequency compared with

the uncomplexed cyano- and isocyano-species. Also the B — H bridging stretch for tridentate BH_4^- complexes is at higher frequency than for the other two types. As will be seen later, small changes in the frequencies of these BH and CN vibrations on complexation are extremely valuable in the assignment of coordination modes.

Considering now NMR spectra, the proton NMR spectrum of KBH_3CN in D_2O consists of a sharp and well resolved quartet and a septet (27) which arise from coupling of the protons with ^{11}B (I = 3/2) and ^{10}B (I = 3) nuclei, respectively; $J_{^{11}BH}$ = 90 Hz and $J_{^{10}BH}$ = 30 Hz. The coupling constant ratio of 3 is that expected on the basis of the magnetogyric ratio (34) for ^{11}B and ^{10}B. The centres of the proton multiplets coincide at 252 Hz upfield from the residual H_2O resonance signal at 100 MHz.

The ^{11}B NMR spectrum for pure $NaBH_3CN$ in THF shows a sharp and well resolved quartet (J = 91 Hz) at + 62.2 ppm with respect to external $B(OCH_3)_3$ (12b). This signal has been assigned to free BH_3CN^-. Another, much more diffuse, signal with a chemical shift of + 45.5 (relative to $B(OCH_3)_3$) with $J_{^{11}BH}$ = 94 Hz has been assigned to the isomeric BH_3NC^- ion.

Infrared and NMR spectroscopic properties of hydroborato complexes (as distinct from those of free hydroborate anions discussed here) will be examined in a later section.

TABLE 1

Infrared and Raman Spectral Bands for MBH_3CN (27) and MBH_3NC (12a) in KBr Disc or Nujol Mull.

IR $NaBH_3CN$	IR KBH_3CN	Raman KBH_3CN	Polarization	$NaBH_3NC$	Assignments
2390 (m)	2390 (m)	2390 (vw)	p	-	-
2350 (sh)	2350 (sh)	2352 (sh)	dp	-	^{e}BH (^{10}B)
2320 (s)	2320 (s)	2334 (s)	dp	2350	^{e}BH (^{11}B)
2260 (sh)	2240 (sh)	2258 (sh)	p	-	$^{a}1$ BH (^{10}B)
2240 (m)	2230 (m)	2239 (m)	p	2290	$^{a}1$ BH (^{11}B)
2179 (s)	2179 (s)	2177 (s)	dp	2070	$^{a}1$ CN
1195 (m)	1195 (m)	1195 (m)	dp	1175	^{e}BH
1145 (sh)	1137 (sh)	1136 (sh)	p	-	$^{a}1BH$ (^{10}B)
1135 (s)	1128 (s)	1123 (m)	p	1105	$^{a}1$ BH (^{11}B)
890 (w)	890 (w)	888 (vw)	-	760	$^{a}1$ BC, BN
865 (w)	870 (w)	870 (w)	-	645	^{e}BH
360 (m)	360 (m)	358 (w)	dp	330	^{e}BCN

TABLE 2

Infrared Spectral Bands for MBD_3CN (M=Na, K) (27) and $NaBD_3NC$ (28) in cm^{-1} in KBr Disc or Nujol Mull.

$NaBD_3CN$	KBD_3CN	$NaBD_3NC$	Assignments
2179 (s)	2179 (s)	2075	a_1 CN
2100 (vw)	2100 (vw)		-
1775 (sh)			e_{BH} (^{10}B)
1760 (s)	1760 (s)	1745 (s)	e_{BH} (^{11}B)
1670 (sh)	-	-	a_1 BH (^{10}B)
1660 (m)	1660 (m)	1640 (m)	a_1 BH (^{11}B)
790 (w)	790 (w)	665	a_1 BC (^{11}B)
926 (sh)	-	940	a_1 BH (^{10}B)
675 (w)	675 (w)	525	e_{BH}
335 (m)	330 (m)	300	e_{BCN}; e_{BNC}

TABLE 3

Infrared Spectra Commonly Observed for Mononuclear MBH_4 (5) in cm^{-1}.

Structure	BH_t terminal	BH_b bridging	Bridge($M-H_b$) stretch	BH deformation
Monodentate	2300 - 2400 (s)	2000 (s)	2000 - 1700 (b)	1000 - 1150 (b)
Bidentate	2400 - 2600 (sd)	1650 - 2150 (s)	1300 - 1500 (sb)	1100 - 1200 (s)
	50 - 80 cm^{-1} splitting			
Tridentate	2450 - 2600 (s)	2100 - 2200 (d)	-	1150 - 1250 (s)
		50 - 80 cm^{-1} splitting		
Ionic	2200 - 2300 (b)		-	1050 - 1150 (sb)

ABBREVIATIONS:- s, (strong); m, (medium); w, (weak); sh, (shoulder); vw, (very weak); b, (broad); sb, (strong broad); d, (doublet); p, (polarized); dp, (depolarized).

1.4 Some chemical properties of $NaBH_3CN$ other than coordination and organic reductions

Since $NaBH_3CN$ has widespread applications in several different branches of chemistry such as complexation, reduction and analysis, the chemical behaviour of BH_3CN^- is an important topic to be discussed here since side reactions of BH_3CN^- may have an influence upon complexation reactions in certain instances. In this connection, Purcell and co-workers (27) showed that BH_3CN^- rapidly hydrolyses in strongly acidic solutions and the reaction was represented as follows:

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

In aqueous solution, the hydrolysis is initially very slow (< 0.5% in 24 hr.). However, small amounts of acid addition cause decomposition as shown by very erratic pH readings. At 0^oC, BH_3CN^- behaves very nearly as pure water on addition of acid, indicating that BH_3CN^- behaves as a very weak base toward the protons.

Very recently, Kay and co-workers (35) have found that certain metals can oxidize BH_3CN^- to a new anion $[BH_3(CN)BH_2(CN)]^-$. This interesting chemical behaviour was found when cyclic voltammetry studies were carried out on a CH_3CN solution of $NaBH_3CN$ at molybdenum and vanadium electrodes. In both cases, the major borane containing product was found to be the new anion $[BH_3(CN)BH_2(CN)]^-$ formed as the

sodium salt which could be isolated. Although the compound was found to be hygroscopic, the anion proved to be stable to aqueous hydrolysis. The anion was characterized as the tetra-n-butylammonium salt. The reaction process at the electrodes was summarised as follows:

$$[BH_3(CN)]^- \longrightarrow BH_2CN + 1/2\ H_2 + e^-$$

$$[BH_3(CN)]^- + BH_2CN \longrightarrow [BH_2(CN)BH_3CN]^-$$

The same anion formation was observed by the same authors when mercury(I) chloride was treated with $NaBH_3CN$ in donor solvents such as THF and CH_3CN. When mercury(I) chloride is replaced by the stronger oxidising agent mercury(II) chloride, then the oxidation of BH_3CN^- in either solvent proceeded very rapidly and in a more complex manner. This reaction gives not only $[BH_3(CN)BH_2CN]^-$ but also oligomerized BH_2CN species. The authors also interpreted the IR spectrum of $[BH_3CNBH_2CN]^-$. A strong sharp band at 2255 cm^{-1} and a sharp medium-intensity band at 2205 cm^{-1} were assigned to CN stretching patterns for the bridging and the terminal cyanide groups respectively; the other two broad, strong bands at 2395 cm^{-1} and 2355 cm^{-1} were assigned to B — H terminal stretching modes.

The ^{11}B NMR spectrum of $[BH_3(CN)BH_2CN]^-$ (as the NBu_4^+ salt) shows two multiplets of equal intensity. A broad triplet

at $\delta = -28.6$ ppm [$J_{BH} = 105$ Hz] and a sharp quartet at $\delta = -43.95$ ppm [$J_{BH} = 95$ Hz] against $BF_3 \cdot Et_2O$. Both of these collapse to singlets on proton decoupling. That the triplet is broadened suggests the BH_3CN part of the species is N-bonded to the $BH_2(CN)$ grouping.

Reactions of this type which generate the BH_2CN species are of possible importance in coordination chemistry. Indeed, as already mentioned in section 1.2, the complex originally formulated (11) as $[Co(BH_3CN)(Dppm)]ClO_4$ has now been tentatively reformulated (26) as $[CoH(BH_2CN)(Dppm)_2]ClO_4$. This will be discussed again later.

1.5 Synthesis and chemical properties of BH_3CN^- complexes

Many of the cyanotrihydroborato complexes with transition metals which have appeared in the literature have been synthesized in the presence of phosphorus containing ligands. However, some of the work recently carried out in this area is as yet unpublished and arises from synthetic and structural studies carried out in these laboratories during the past three years. Most of this unpublished work concerns the formation of cyanotrihydroborato derived complexes for a series of bidentate and also monodentate phosphine ligands with Co, Ni and Cu. In addition to the phosphine-metal ion work mentioned above quite a few BH_3CN^- derived complexes have also been synthesized using nitrogen donor and other ligands. Therefore, the discussion will be divided into two parts with systems derived

from ligands other than phosphines receiving treatment first. This treatment will be arranged according to groups and, to simplify the discussion, it should be noted at the outset that for groups IIB to VB, no cyanotrihydroborato complexes have yet been reported in the literature. It should be further noted that a general survey of this topic would normally treat both phosphine and non-phosphine ligands under the same heading. However, this author feels that for ease of reference later in this thesis to work on metal-phosphine-BH_3CN^- reactions already in the literature or in as yet unpublished theses, the above-mentioned division of the topic is more appropriate here.

1.5.1 BH_3CN^- complexes, synthesized in the presence of ligands other than phosphines

1.5.1.1 Chromium, Molybdenum and Tungsten

The known cyanotrihydroborato complexes of this triad are summarized in Table 4. These complexes were synthesized (36) from reactions of sodium cyanotrihydroborate and the appropriate metal hexacarbonyl in boiling glyme over a period of several hours. The reaction mixture yielded the $[M(BH_3CN)(CO)_5]^-$ anion which was separated from an aqueous solution as the appropriate tetramethylammonium salt. These compounds were found to be less air-sensitive in the solid state than in solution. The sequence of relative air stabilities both in the solid state and in solution is as follows:

Tungsten > Chromium > Molybdenum

The C≡N stretching frequencies of these complexes were reported to be at~2200 cm^{-1} which represents a shift of about 21 cm^{-1} from the C≡N stretching observed for free BH_3CN^-. This clearly indicates that the BH_3CN^- ligand is involved in coordination with metal ions through the nitrogen atom. This evidence led the authors (36) to assign to these complexes the structure shown in Fig. 8 in which one carbonyl group has been replaced by BH_3CN^-. More will be said later about IR data in general for BH_3CN^- complexes.

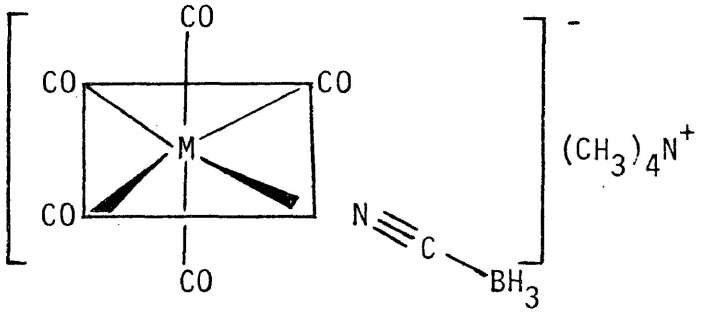


Fig. 8

1.5.1.2 Manganese, Technetium and Rhenium

No cyanotrihydroborato complexes have yet been reported for this group.

1.5.1.3 Iron, Ruthenium and Osmium

A few complexes for iron and ruthenium with ligands other than phosphines have been reported and these are summarized in Table 4. However, no cyanotrihydroborato complex for osmium has yet been reported.

The only such cyanotrihydroborato complex of iron, $Fe(BH_3CN)_2(Phen)_2$, was synthesized from $Fe(Phen)_2Cl_2$ and KBH_3CN (37) in dry THF under prolonged reflux in an inert atmosphere. The complex was isolated directly from the cooled reaction mixture. The nature of the complex and its structure were characterized by magnetic moment data together with infrared, visible and Mössbauer spectra. The BH_3CN^- unit was characterized as a ligand possessing monodentate σ- and π-donor character towards $Fe(Phen)_2^{2+}$ and the assigned structure of this complex $[Fe(BH_3CN)_2(Phen)_2]$ is shown in Fig. 9.

TABLE 4

Cyanotrihydroborato Derivatives of Transition Metals Complexed by Ligands Other Than Phosphines

Complex	Colour	Reagents Used	Ref.
$[Cr(BH_3CN)(CO)_5]Me_4N$	yellow	$Cr(CO)_6 + NaBH_3CN$	(36)
$[Mo(BH_3CN)(CO)_5]Me_4N$	yellow	$Mo(CO)_6 + NaBH_3CN$	(36)
$[W(BH_3CN)(CO)_5]Me_4N$	yellow	$W(CO)_6 + NaBH_3CN$	(36)
$Fe(BH_3CN)(Phen)_2$	purplish red	$[Fe(Phen)_2]^{2+} + NaBH_3CN$	(37)
$[Ru(BH_3CN)(NH_3)_5]Br$	yellow green	$[Ru(NH_3)_5H_2O]^{2+} + NaBH_3CN + Br^-$	(38)
$[Ru(BH_3CN)(NH_3)_5]Br_2$	yellow green	$Ru(NH_3)_5BH_3CN + NaBr$	(38)
$Ni(BH_3CN)_2(en)_2.THF$	purple	$Ni(en)_2Cl_2 + NaBH_3CN$	(39)
$[Ni(BH_3CN)(tren)]_2(BPh_4)_2$	purple	$NiSO_4.6H_2O + tren + NaBH_3CN + NaBPh_4$	(10)
$Cu(BH_3CN)_2(Me_5dien)$	royal blue	$CuBr_2 + Me_5dien + NaBH_3CN$	(24)

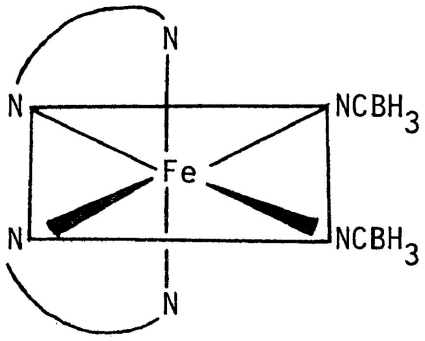


Fig. 9

In addition to the one known iron system, two ruthenium complexes, $[Ru(BH_3CN)(NH_3)_5]Br$ and $[Ru(BH_3CN)(NH_3)_5]Br_2$, have been synthesized (38) under argon from a reaction between $NaBH_3CN$ and $[Ru(NH_3)_5H_2O]^{2+}$. This reaction results in a solution of what is probably $Ru(NH_3)_5BH_3CN$ which, upon addition of NaBr, precipitates a solid formulated as the Ru(II)complex, $[Ru(BH_3CN)(NH_3)_5]Br$. When this solution is exposed to air for 1 hour, subsequent addition of Br^- precipitates a Ru(III)complex, $[Ru(BH_3CN)(NH_3)_5]Br_2$. Both of these complexes are moderately stable in aqueous solution. The coordinated BH_3CN^- of each complex hydrolyses in acidic solution leading, in the case of the former ion, to an isolable Ru(II)-hydrogen cyanide complex. However, complete structural characterizations of these complexes were not effected.

1.5.1.4 Cobalt, Rhodium and Iridium

Again, no cyanotrihydroborato complexes of these metals with ligands other than phosphines have yet appeared in the literature.

1.5.1.5 Nickel, Palladium and Platinum

Only nickel-cyanotrihydroborato complexes have been reported for this triad and they are summarized in Table 4. The first such nickel complex, containing the nitrogen donor ligand en (ethylenediamine), was synthesized (39), by heating $Ni(en)_2Cl_2$ under reflux with a stoichiometric quantity of $NaBH_3CN$ in THF for several hours, followed by Soxhlet extraction of the solid residue with the same solvent to yield, upon cooling of the extract, crystals of $[Ni(BH_3CN)_2(en)_2]\cdot THF$. The infrared spectrum of this complex showed the C ≡ N stretching vibration in the vicinity of 2200 cm^{-1} which is consistent with BH_3CN^- bonding to the metal ion through the nitrogen atom.

The second, and very much more interesting such complex, $[Ni(BH_3CN)(tren)]_2^{2+}$, has been synthesized (10) from a reaction of $NiSO_4\cdot 6H_2O$ in aqueous solution with tren in methanol-chloroform. The resulting solution was treated with a methanolic solution of $NaBH_3CN$ to give a purple reaction mixture which, on further treatment

with $NaBPh_4$, gave a solid complex formulated as $[Ni(BH_3CN)(tren)]_2$-$(BPh_4)_2$. A single crystal X-ray diffraction study (10) has shown that the system is a cyanotrihydroborate-bridged dimer in which the ring containing the two nickel atoms and two cyanotrihydroborate bridges is almost planar. The nickel atoms are octahedrally co-ordinated and a hydrogen atom of the $-NCBH_3$ ligand therefore occupies one of the coordination sites. This structure is illustrated in Fig. 10 and, as can be seen, it is similar to the bridged Cu(I) system briefly discussed in section 1.2.1 and illustrated in Fig. 4a.

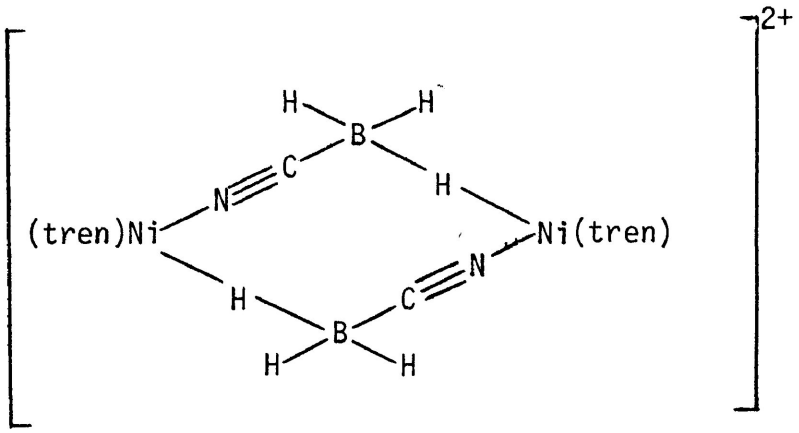


Fig. 10

This bridged Ni cation is, in fact, related to a group of ligand-bridged dimers of general formula $(tren\ MX)_2^{2+}$ characterized for the most part by Hendrickson's group (40, 41), although this system appears to be the first Ni-complex containing BH_3CN^- as a bridging ligand. More will be said of similar bridged Ni structures later in the Results and Discussion section of this thesis, where the results reported could appear to indicate that such bridging is a relatively common phenomenon in Ni — BH_3CN chemistry.

1.5.1.6 Copper, Silver and Gold

No cyanotrihydroborato complexes of silver and gold with ligands other than phosphines have been reported and only one such cyanotrihydroborato complex of copper (with Me_5dien) has been synthesized (24). This Cu(II)complex, $Cu(BH_3CN)_2(Me_5dien)$ listed in Table 4, was synthesized in ethanol from Cu(II)bromide with Me_5dien in the presence of $NaBH_3CN$ and was isolated as royal blue crystals. This solid is soluble in polar solvents but readily decomposes in acetone. The infrared spectrum of $Cu(BH_3CN)_2(Me_5dien)$ shows two distinct C ≡ N stretching frequencies, both of which occur at higher frequency than that found in free BH_3CN^-. This implies that the two BH_3CN^- groups are both present in the complex $Cu(BH_3CN)_2(Me_5dien)$ as coordinated ligands and that coordination occurs through the nitrogen atom in both cases. The authors (24) postulated on the basis of this information that the structure of this complex could be either the

dimeric cation $[Cu(BH_3CN)(Me_5dien)]_2^{2+}$ or the neutral species $Cu(BH_3CN)_2$-(Me_5dien). The structure of this complex has been fully characterized (24) by single crystal X-ray diffraction studies, which showed that the system is a distorted square-based pyramid with one of the BH_3CN^- groups occupying the apical position and the other in a basal position as illustrated in Fig. 11.

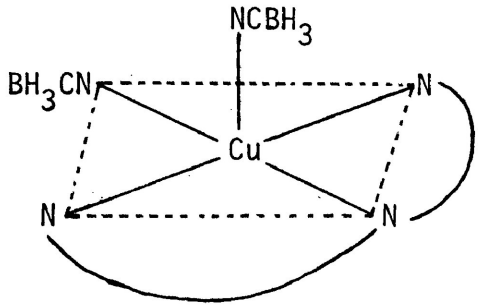


Fig. 11

The infrared spectrum of this complex will be discussed further in a later section as part of a general discussion of IR spectra of BH_3CN^- complexes.

1.5.2 Cyanotrihydroborato complexes of transition metals formed using phosphorus-containing ligands

Many cyanotrihydroborato complexes containing

phosphine ligands have been reported in the literature in contrast to the few known cyanotrihydroborato complexes formed with other ligands. A brief discussion concerning the preparative conditions required together with some physical properties of these phosphorus-containing complexes will be presented under this section.

1.5.2.1 Iron, Ruthenium and Osmium

A few such cyanotrihydroborato complexes of iron and ruthenium have been reported but as yet no similar complexes have been reported for osmium.

Drummond and co-workers (42) have synthesized cis-trans-$[Fe(BH_3CN)_2\{P(OR)_3\}_4]$ complexes and these are recorded in Table 5. Both methathetical and electrochemical methods have been employed for the preparation of these complexes in different solvents. These complexes were prepared from a reaction of $FeCl_2 \cdot 2H_2O$ with an excess of $NaBH_3CN$ in the presence of $P(OR)_3$ (R = Me or Et). However, when the methathetical reactions are carried out in methanol, only a trans-isomer is obtained, whereas this reaction in acetonitrile yields a mixture of isomers in the cis-trans ratio of 30:70 as shown by ^1H NMR and IR spectra. For the electrochemical process in acetonitrile, when R = Me, a mixture containing 65% of the cis isomer is obtained. On the basis of IR and NMR results, the authors have assigned the following octahedral structures to the cis and trans isomers.

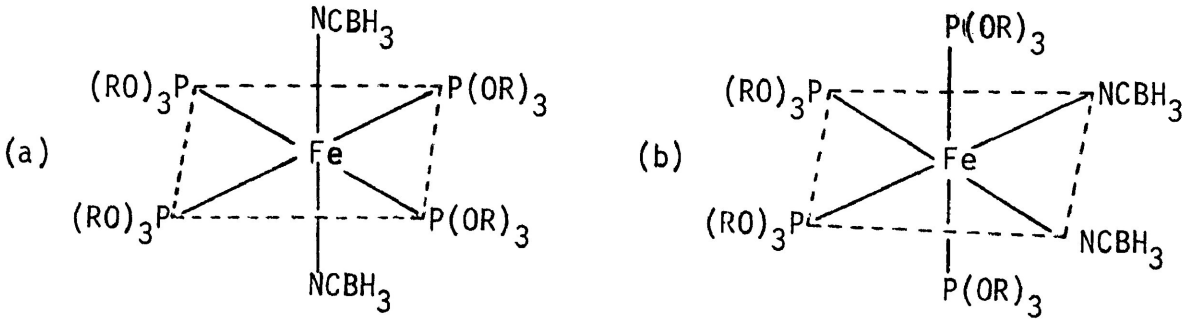


Fig. 12

The cis and trans isomers of both the trimethyl and triethyl phosphite complexes proved readily separable. For R = Me, the trans isomer was found to be preferentially soluble in benzene and repeated extraction from the mixture left the cis-isomer. For R = Et, both isomers proved to be soluble in benzene; however, addition of an excess of hexane induced precipitation of the cis form preferentially.

The only known cyanotrihydroborato complex of ruthenium (43), (Table 5), $RuH(BH_3CN)(CO)_2(DBP)_2$, was prepared by a reaction of the red Ru(II)-carbonyl solution (prepared from $RuCl_3$ hydrate and CO in ethanol) with the ligand DBP in the presence of an excess of BH_3CN^- in ethanol.

1.5.2.2 Cobalt, Rhodium and Iridium

Quite a significant number of complexes has been

TABLE 5

Known Phosphine - BH_3CN Complexes of Fe and Ru

Complex	Colour	Reagents Used	Ref.
trans-$[Fe(BH_3CN)_2\{P(OR)_3\}_4]$	yellow	$FeCl_2.2H_2O + NaBH_3CN + P(OR)_3$	(42)
cis-$[Fe(BH_3CN)_2\{P(OR)_3\}_4]$	"	$FeCl_2.2H_2O + NaBH_3CN + P(OR)_3$	(42)
$RuH(BH_3CN)(CO)(DBP)_2$		Ru(II)-Carbonyl solution in ethanol + DBP + $NaBH_3CN$	(43)

synthesized with this group, mainly with cobalt, in the presence of a series of phosphines and cyanotrihydroborate ion. They are presented in Table 6 and it should be noted that many of these complexes are formed in reactions, the details of which have not yet been published.

The first such cobalt complexes, $Co(BH_3CN)N_2(DBP)_3$ and $Co(BH_3CN)_2(PPh_3)_3$, were synthesized by Holah and co-workers (6) from reactions of $CoX_2 \cdot 6H_2O$ (X = halide) with a phosphine (PPh_3 or DBP) in the presence of $NaBH_3CN$ in ethanol. Yellow (former) and wine-red (latter) complexes were isolated from the appropriate reaction and their IR spectra show characteristic C ≡ N stretching frequencies around 2200 cm^{-1} which means almost certainly that the BH_3CN^- unit is coordinated through the nitrogen atom (see later discussion). Similarly, the cobalt complex $Co(BH_3CN)(Diphos)_2$ has been synthesized (9) from a reaction of $CoCl_2 \cdot 6H_2O$ and Diphos with an excess of $NaBH_3CN$. This last complex is diamagnetic. Again, the C ≡ N stretching frequency in the IR spectrum indicates that BH_3CN^- is coordinated to the metal ion through the nitrogen atom.

More recently, a series of cobalt-cyanotrihydroborato complexes has been synthesized (11) in these laboratories using a range of phosphines such as PPh_3, Dppm, Diphos, Dppp and Dppb in the presence of cyanotrihydroborate ion. These most interesting results are, as yet, unpublished. However, some of the better characterized systems are listed in Table 6. One particularly interesting complex arising from this study is the wine-red $CoH(BH_3CN)(PPh_3)_3$ which is

obtained from $CoCl_2 \cdot 6H_2O$ and PPh_3 with an excess of $NaBH_3CN$ in (toluene-ethanol) solvent under N_2. This complex is stable in air for up to 48 hours. On the basis of IR and reflectance data, the author proposed (11) that the complex is a five-coordinated Co(II) system with BH_3CN^- bonded through the nitrogen atom. The complex is paramagnetic (low spin). The structure of this complex has now been fully characterized by solid state X-ray methods (44) and the geometry is confirmed as a five-coordinated Co(II) species which is a trigonal bipyramid grossly distorted towards both the square pyramid (major distortion) and the monocapped tetrahedron (minor distortion).

In addition, other interesting complexes such as those tentatively formulated as $[Co(BH_3CN)(Dppm)_2]ClO_4$ and $CoH(BH_3CN)$-(Dppm) have been reported in this study (11). These were prepared from $Co(ClO_4)_2 \cdot 6H_2O$ (former) and $CoCl_2 \cdot 6H_2O$ (latter) by reaction with Dppm in the presence of an excess of $NaBH_3CN$ under nitrogen in a mixed (ethanol/benzene) solvent. Infrared spectra for both the deuterated and undeuterated (former) complex indicates that BH_3CN^- is bonded to the metal atom through the nitrogen atom (ν_{CN} at 2200 cm^{-1}). Furthermore, IR evidence was also presented for the presence of a M — H — B type of linkage and, in this connection, the ^1H NMR solution spectrum of this complex shows a well defined quintet upfield from TMS which clearly indicates the presence of a metal-hydrogen linkage at least in solution. The IR and analytical evidence led the author (11) tentatively to formulate the structure for this complex as shown in Fig. 7. The ^1H spectrum, however, remained a puzzle because it is not clear why the

the H atom of the M — H — B would couple with four phosphorus atoms each of which is two bonds away (a normal occurrence) but not with the directly attached boron atom. For this reason more recently (26), an alternative structure has been considered for this complex and this is shown in Fig. 13. In this structure a true metal hydride (terminal) is present. If this last structure is indeed correct, then the observed quintet in the ^1H NMR spectrum would be in good agreement with the proposed structure (terminal H coupled with four equivalent P). However, bonding of neutral BH_2CN in such complexes appears not to have been observed (although BH_2CN appears to be an intermediate in the formation of $(BH_3CN\ BH_2CN)^-$ previously and such a structure would be quite novel. It should be noted that a weak peak at 2000 cm^{-1} in the IR spectrum could be attributable to the Co — H linkage superimposed upon an aromatic ring vibration although it is not well defined. This peak is very much less intense in the deuterated species. It will be seen shortly that Diphos produces an apparently similar complex although there are significant IR differences.

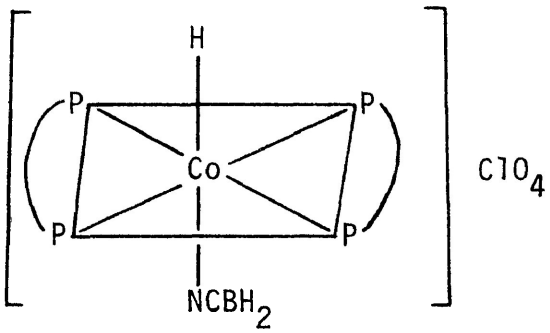


Fig. 13

TABLE 6

Cyanotrihydroborato Complexes of the Cobalt Triad.

Complex	Colour	Reagents Used	Ref.
$Co(BH_3CN)(PPh_3)_3$	yellow	$CoCl_2.6H_2O + PPh_3 + NaBH_3CN$	(6)
$CoH(BH_3CN)(PPh_3)_3$	wine-red	$CoCl_2.6H_2O + PPh_3 + NaBH_3CN$	(11)
$Co(BH_3CN)N_2(DBP)_3$	wine-red	$CoCl_2.6H_2O + DBP + NaBH_3CN$	(6)
$[Co(BH_3CN)(Dppm)_2]ClO_4$?	yellow	$Co(ClO_4)_2.6H_2O + Dppm + NaBH_3CN$	(11)
$Co(BH_3CN)(Dppm)$	yellowish green	$CoCl_2.6H_2O + Dppm + NaBH_3CN$	(11)
$Co(BH_3CN)(Diphos)_2$	yellow - green	$CoCl_2.6H_2O + Diphos + NaBH_3CN$	(9)
$[Co(BH_3CN)(Diphos)_2]ClO_4$?	orange-yellow	$Co(ClO_4)_2.6H_2O + Diphos + NaBH_3CN$	(11)
$[Co(CN)(Diphos)_2]ClO_4.Me_2CO$	dark brown	$Co(ClO_4)_2.6H_2O + Diphos + NaBH_3CN$ + acetone	(11)
$Co(BH_3CN)(Dppp)_{1.5}$	green	$Co(ClO_4)_2.6H_2O + Dppp + NaBH_3CN$	(11)
$Co(BH_3CN)(Dppb)_2$	olive green	$Co(ClO_4)_2.6H_2O + Dppb + NaBH_3CN$	(11)
$Ir(BH_3CN)CO(PPh_3)_2$		$Ir(CO)(ClO_4)_2(PPh_3)_2 + NaBH_3CN$	(46)
$Rh(BH_3CN)CO(PPh_3)_2$		$Rh(CO)(ClO_4)(PPh_3)_2 + NaBH_3CN$	(46)
$RhH_2(BH_3CN)(PPh_3)_3$		$RhCl(PPh_3)_3 + NaBH_3CN$	(6)
$Rh(BH_3CN)(CO)(DBP)_3$	orange	$[RhCl(CO)_2]_2 + DBP + NaBH_3CN$	(8)
$Rh(BH_3CN)(CO)N_2(DBP)_3$	yellow	$[RhCl(CO)_2]_2 + DBP + NaBH_3CN$	(8)

The complex $CoH(BH_3CN)(Dppm)$ which was also synthesized in these studies has been tentatively assigned the bridged structure shown in Fig. 14 on the basis of spectral data. This, if correct, would be related to another tentatively assigned bridged hydride structure (that of $[CoH(Dppm)]_2$ recently isolated (45) from $Co(II)/Dppm/NaBH_4$ reactions).

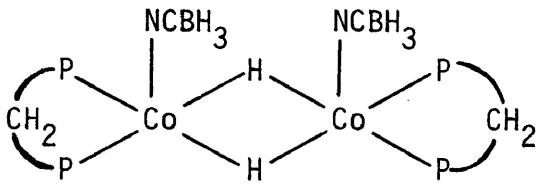


Fig. 14

In related work with the ligand Diphos, the same author (11) has synthesized a complex $[Co(BH_3CN)(Diphos)_2]ClO_4$ from $Co(ClO_4)_2 \cdot 6H_2O$ and Diphos in the presence of $NaBH_3CN$ which is apparently very similar to the Dppm complex formulated originally as $[Co(BH_3CN)(Dppm)_2]ClO_4$ and discussed in the preceding paragraphs. An interesting phenomenon was observed with this complex when it was treated with acetone. The dark brown solid thus obtained was found to be $[Co(CN)(Diphos)_2]ClO_4 \cdot Me_2CO$.

The complex $[Co(BH_3CN)(Diphos)_2]ClO_4$ shows in the infrared spectrum C ≡ N and B — H (terminal) stretching frequencies at 2185 cm^{-1} and 2340 cm^{-1} respectively and the ClO_4 peak appears as a broad peak at 1100 cm^{-1} (ionic). The 'H NMR spectrum showed, as with $[Co(BH_3CN)(Dppm)_2]ClO_4$), a well defined quintet upfield of TMS which again indicates the presence of the Co — H linkage. On the basis of these data, the structure of this complex has been tentatively formulated by the author (11) as in Fig. 15.

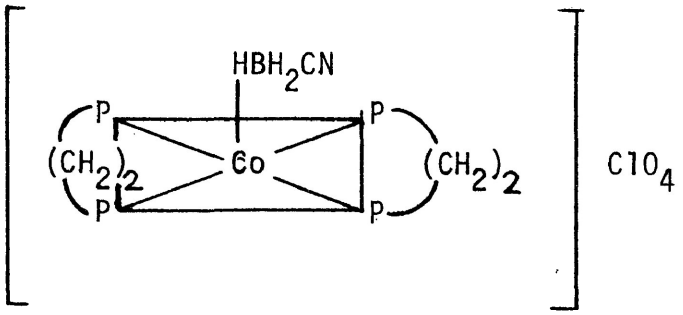


Fig. 15

However, again if this is the correct structure, the 'H spectrum is puzzling for the same reasons given for the Dppm complex and because the IR spectrum shows no Co — H stretching (or perhaps, a very weak one at around 2000 cm^{-1}). Evidence was presented for the absence of the known species CoH $(Diphos)_2$ which shows a similar 'H NMR spectrum in solution. It is also worth noting that the IR C ≡ N stretching frequency of this complex is shifted only by 6 cm^{-1} to

higher frequency from that in free BH_3CN^- and the author (11) suggested that such a small shift of the C ≡ N stretching indicates that the normal nitrogen coordination of BH_3CN^- itself is less likely. However, as will be seen in a later section, the geometry of the M — N ≡ C — linkage has a powerful effect upon the C ≡ N stretching frequency in such complexes. In view of these anomalies, it is therefore possible again that the complex may be better formulated as $[CoH(BH_2CN)(Diphos)_2]ClO_4$ as already discussed for the analogous Dppm complex.

The infrared spectrum of $[Co(CN)(Diphos)_2]ClO_4$ (derived from the above complex) shows a characteristic cyanide stretching frequency at 2100 cm^{-1}. This same complex $[Co(CN)(Diphos)_2]ClO_4$ has been synthesized (11) at elevated temperatures directly from $CoCl_2 \cdot 6H_2O$ and Diphos in the presence of a large excess of $NaBH_3CN$.

Other bidentate phosphine complexes have been isolated from similar reactions. For example, $Co(BH_3CN)(Dppp)_{1.5}$ and $Co(BH_3CN)_2(Dppb)_2$ have been synthesized (11) from $Co(ClO_4)_2 \cdot 6H_2O$ or $CoCl_2 \cdot 6H_2O$ (former) and $Co(ClO_4)_2 \cdot 6H_2O$ (latter) in the presence of $NaBH_3CN$ and the phosphine in appropriate solvents. The complex formulated as $Co(BH_3CN)_2(Dppp)_{1.5}$ was purified by recrystallization from a variety of solvents but always a molecule of solvent appears in the complex crystal lattice regardless of the solvent used. This complex has not yet been fully characterized.

The $Co(BH_3CN)_2(Dppb)_2$ complex showed in its infrared spectrum, two characteristic C ≡ N stretching frequencies as a strong doublet at 2200 cm^{-1} and 2189 cm^{-1}. This indicates that the BH_3CN^- units are both complexed through the nitrogen atoms. Perhaps with slightly different site symmetries or with one angular and another linear M — N — C unit as will be discussed for $Cu(BH_3CN)_2$-(Me_5dien) in a later section. Reflectance spectra of this complex suggest a distorted six-coordinated cobalt in an octahedral environment. Due to low solubility of the complex, solution studies were not possible. On the basis of the available evidence, the author suggested (11) the structure shown in Fig. 16 in which case the two different C ≡ N frequencies could simply be due to symmetrical and asymmetrical vibrations.

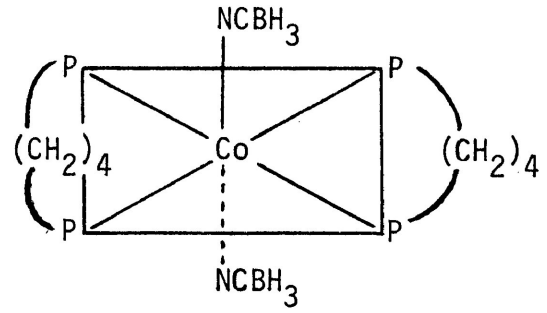


Fig. 16

Turning now to rhodium and iridium, the first cyanotrihydroborato complexes of these metals were synthesized (46) from the tertiary phosphines PPh_3 and PCy_3 in the presence of $NaBH_3CN$ by the metathetical reaction given below.

$$\underline{\text{trans}}\ [M(ClO_4)(CO)L_2]^{4+} + NaBH_3CN \rightarrow \underline{\text{trans}}\text{-}M(BH_3CN)(CO)L_2$$

$$M = Rh \text{ or } Ir\ ,\quad L = PPh_3 \text{ or } PCy_3$$

The crystalline complexes were found to be very stable in air as well as in solution and the relative stabilities of these compounds are

$$Rh > Ir\ ;\quad PCy_3 > PPh_3$$

The infrared spectra of $Ir(BH_3CN)(CO)(PCy_3)_2$ and $Rh(BH_3CN)(CO)(PPh_3)_2$ suggest that the cyanotrihydroborate unit is N — bonded as M — $NCBH_3$. Thus, the terminal B — H peaks were hardly shifted from the B — H vibration in free BH_3CN^- and, as with similar complexes already discussed, a small increase in the C ≡ N stretching frequency was observed.

Several other cyanotrihydroborato complexes of rhodium and iridium have been synthesized by Holah and his co-workers (8). For example, reaction of $[RhCl(CO)_2]_2$ with $NaBH_3CN$ in the presence of DBP gives $Rh(BH_3CN)(CO)(DBP)_3$ in which rhodium remains as Rh(I). An analogous reaction between $RhCl_3(DBP)_3$ and $NaBH_3CN$ leads to the Rh(I) complex $Rh(BH_3CN)(N_2)(CO)(DBP)_3$. This reduction of Rh(III) to Rh(I) by $NaBH_3CN$ is thought (8) to proceed through a Rh(III)-dihydride intermediate such as $RhH_2(BH_3CN)(DBP)_2$ which then undergoes an exchange of dihydrogen for molecular nitrogen under a nitrogen atmosphere. A similar dihydride, $RhH_2(BH_3CN)(PPh_3)_2$, has been prepared (6) from $RhCl(PPh_3)_3$ with an excess of $NaBH_3CN$ and this supports the above suggestion. This last complex is very solvent sensitive and decomposes in solution immediately by eliminating a gas (presumably H_2) in solvents such as

benzene or chloroform.

1.5.2.3 Nickel, Palladium and Platinum

No cyanotrihydroborato complexes of palladium or platinum with phosphines have yet been synthesized.

Holah and co-workers (9) have, however, synthesized a series of cyanotrihydroborato complexes of Ni(II), such as $NiH(BH_3CN)(PPh_3)_2$, $NiH(BH_3CN)(DBP)_3$ and $NiCl(BH_3CN)$(Diphos). These complexes were prepared by reactions between Ni(II) halide and the phosphine in the presence of an excess of $NaBH_3CN$ in ethanol. Besides these complexes, another most interesting Ni(I) complex, $Ni(BH_3CN)(PPh_3)_2$, has been prepared (9) directly from a Ni(I) precursor in the reaction between $NiCl(PPh_3)_3$ and $NaBH_3CN$ in ethanol. On the basis of the infrared and reflectance spectra of the complex, the authors proposed a novel structure of the type already shown in Fig. 6. This complex is paramagmetic and monomeric and is apparently a tetrahedral Ni(I) system. A similar reaction with $NiCl(DBP)_3$ and $NaBH_3CN$ has been carried out (9) but no BH_3CN^- complex was obtained. Instead, the reaction yielded $Ni(DBP)_2$. From this observation, the authors suggested that the nature of the ligand is once again extremely important in determining the product formed. As will be seen in the Results and Discussion section of this thesis, this is indeed correct.

Table 7 summarizes the above-mentioned complexes.

TABLE 7

Cyanotrihydroborato Complexes of Nickel - Phosphine System

Complex	Colour	Reagents Used	Ref.
$NiH(BH_3CN)(PPh_3)_2$	orange	$NiX_2.6H_2O + PPh_3 + NaBH_3CN$	(9)
$NiH(BH_3CN)(DBP)_3$	brown	$NiX_2.6H_2O + DBP + NaBH_3CN$	(9)
$NiCl(BH_3CN)(Diphos)$	orange	$NiCl_2.6H_2O + Diphos + NaBH_3CN$	(9)
$Ni(BH_3CN)(PPh_3)_2$	yellow	$NiCl(PPh_3)_3 + NaBH_3CN$	(9)

1.5.2.4 Copper, Silver and Gold

Many cyanotrihydroborato complexes of copper with different phosphine ligands have been synthesized during the last few years. Some of them have appeared in the literature, often with very thorough characterization. In more recent years, in these laboratories, Alam (47) has studied complexes of Cu with $NaBH_3CN$ and a series of (mainly bidentate) phosphines in considerable detail but the results of these studies are as yet unpublished. This subsection will therefore present the results of a variety of published and unpublished studies concerning Cu(I) or Cu(II)$|BH_3CN^-|$phosphine systems. The known Cu — BH_3CN — phosphine complexes are recorded in Table 8.

In most cases, the complexes are formed by a reaction between CuL_nX (L = ligand; X = halide or ClO_4^-) and $NaBH_3CN$ in an appropriate solvent and the BH_3CN^- becomes coordinated initially by the direct replacement of halide or ClO_4^- from Cu(I) or Cu(II) systems. One of the most interesting Cu(I) complexes, the binuclear species $[Cu(BH_3CN)(PPh_3)_2]_2$ which has already been briefly mentioned in section 1.2, has been synthesized by Lippard and co-workers (21) from a reaction of $CuCl(PPh_3)_3$ and $NaBH_3CN$ in ethanol/$CHCl_3$. The structure of this complex has been completely characterized by solid state studies such as infrared spectrophotometry (21) and single crystal X-ray diffraction (25). The structure of this complex has been assigned as shown in Fig. 4a in which two copper(I) ions are bridged

by two BH_3CN^- groups, forming a ten-membered nonplanar ring with a Cu --- Cu distance of 5.637 Å (25). It was found that two triphenylphosphine ligands are bonded to each copper(I) together with a hydrogen and a nitrogen atom from the different cyanotrihydroborate groups. The two Cu — N distances are 1.96 Å (25) and 2.10 Å (25). More will be said about this and related bridged structures later.

It is also possible to obtain monomeric Cu(I) complexes with monodentate phosphines and BH_3CN^- by variation of this method. For example, Holah and co-workers (9) have synthesized a series of cyanotrihydroborato complexes of the type $Cu(BH_3CN)\ L_3$ (L = PPh_3, DBP and $PEtPh_2$) and also $Cu(BH_3CN)(Diphos)_{1.5}$. Of particular interest is $Cu(BH_3CN)(PPh_3)_3$ since these authors also resynthesized the stoichiometrically identical but apparently chemically and spectroscopically different triphenylphosphine complex $Cu(BH_3CN)$-$(PPh_3)_3$ which was first prepared (21) by Lippard *et al.* by a somewhat different procedure. This last complex is insoluble in cold benzene but soluble in hot benzene to yield the dimeric $[Cu(BH_3CN)(PPh_3)_2]_2$ complex already described by addition of n-hexane. Holah's version of $Cu(BH_3CN)(PPh_3)_3$ (9) in chloroform showed the same IR spectrum as does a mull of the solid, indicating that it is not merely a different crystal form and the IR differences between the two complexes are of a molecular structural nature. Addition of ethanol to the chloroform solution of Holah's complex precipitates a mixture of this same complex and $[Cu(BH_3CN)(PPh_3)_2]_2$. Which of these two versions of $Cu(BH_3CN)(PPh_3)_3$

is formed depends only upon small variations in reaction conditions. These two $Cu(BH_3CN)(PPh_3)_3$ complexes, although they have the same empirical formula, differ (9), sometimes considerably, in several ways. Lippard and co-workers (21) have produced some evidence (mainly infrared) for the $Cu - NCBH_3$ linkage in $Cu(BH_3CN)(PPh_3)_3$ and such linkages also have been found (9) in several other cyanotrihydroborato complexes of copper and other metals e.g. in $Cu(BH_3CN)(Diphos)_{1.5}$. On the other hand, Holah *et al.* (9) produced evidence for the $Cu - H - BH_2CN$ bonding mode in their version of the complex. Both types of linkage (with the same BH_3CN^- group, acting as a bridging ligand) have been found (21) present in the same molecule as in the case of $[Cu(BH_3CN)-(PPh_3)_2]_2$ already discussed. As mentioned in the preceding paragraphs, this has been confirmed by solid state X-ray studies. However, there is apparently no other example in the literature of a BH_3CN^- ligand bonded through only a $M - H - BH_2CN$ type linkage.

In related studies, a series of bidentate phosphine-cyanotrihydroborato complexes of Cu(I) have been synthesized more recently (47) from metal chloride or perchlorate complexes of the type $Cu_2L_3Cl_2$, CuL_2ClO_4 and CuL_3ClO_4 (where L = Diphos, cis or trans-Dppe, Dppp or Dppb) using an excess of $NaBH_3CN$ in ethanol/benzene. In a typical reaction, the white solid $[Cu(BH_3CN)(Diphos)_{1.5}]_2$ separated from the reaction mixture upon addition of n-hexane. From the C ≡ N stretching frequency observed in the infrared spectrum, the complex appears to have a $Cu - NCBH_3$ type of bonding. On the basis of this and other evidence

TABLE 8

Cyanotrihydroborato Complexes From Copper/Phosphine/$NaBH_3CN$ Systems.

Complex	Colour	Reagents Used	Ref.
$[Cu(BH_3CN)(PPh_3)_2]_2$	white	$CuCl(PPh_3)_3 + NaBH_3CN$	(21)
$Cu(BH_3CN)(PPh_3)_3$ (H-bonded and N-bonded)	"	$CuCl(PPh_3)_3 + NaBH_3CN$	(9,21)
$Cu(BH_3CN)(DBP)_3$		$CuCl(DBP)_3 + NaBH_3CN$	(9)
$Cu(BH_3CN)(PEtPh_2)_3$		$CuCl(PEtPh_2)_3 + NaBH_3CN$	(9)
$Cu(BH_3CN)(Diphos)_{1.5}$		$CuCl_2(Diphos) + NaBH_3CN$	(9,47)
$Cu(BH_3CN)(Dppm)$		$CuCl_2.2H_2O$ + Dppm + $NaBH_3CN$	(47)
$[Cu(BH_3CN)(Dppm)]_2$		$Cu_2(Dppm)_3(ClO_4)_2 + NaBH_3CN$	(47)
$Cu(BH_3CN)_2(Dppp)_{1.5}$		$Cu_2(Dppp)_3(ClO_4)_2 + NaBH_3CN$	(47)
$[Cu(BH_3CN)_2(Dpph)]_2.CHCl_3$		$Cu(Dpph)_2ClO_4.CH_2Cl_2 + NaBH_3CN$	(47)

and the obvious similarity to related dimeric Cu(I)chloride systems, the structure has been formulated as shown in Fig. 17. Some support for this comes from ^{31}P NMR and conductivity measurements.

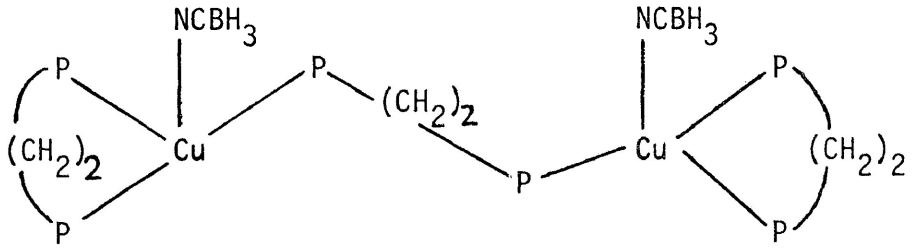


Fig. 17

Other related bidentate phosphine complexes such as $Cu(BH_3CN)(Dppm)$ and the probable dimer of identical empirical formula $[Cu(BH_3CN)(Dppm)]_2$ have been synthesized (47) by reactions between $CuCl_2 \cdot 2H_2O$ and Dppm (former) and the dimeric complex $Cu(Dppm)_2(ClO_4)_2$ (latter) in the presence of $NaBH_3CN$. These two complexes differ considerably in behaviour. Thus, $Cu(BH_3CN)(Dppm)$ is sparingly soluble in CH_2Cl_2, whereas the probable dimer $[Cu(BH_3CN)(Dppm)]_2$ is highly soluble. The latter complex shows a similar infrared spectrum to that of the apparently similar $[Cu(BH_3CN)(PPh_3)_2]_2$ (21) for which the structure is known and this led the author to formulate the structure of the $[Cu(BH_3CN)(Dppm)]_2$ complex as being similar to $[Cu(BH_3CN)(PPh_3)_2]_2$ shown in Fig. 4a. The infrared spectrum of the possibly monomeric $Cu(BH_3CN)(Dppm)$ complex shows in the BH_3CN^- region only very small shifts from the frequencies of ionic BH_3CN^-; these

small shifts suggest (but see later discussion of linear and angular M — N — C links) only weak coordination through the nitrogen atom with Cu(I). Therefore, on the basis of the IR spectrum and ^{31}P NMR data, this complex has been tentatively formulated as shown in Fig. 18. Bidentate BH_3CN^- bonding of this type has never yet been proved but has been considered for other species (see earlier discussion on bonding modes).

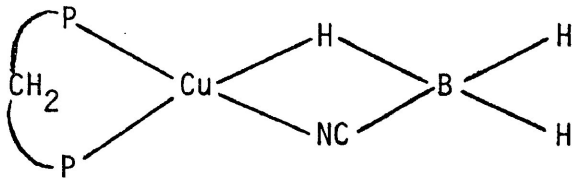


Fig. 18

Other bidentate phosphine complexes have been synthesized (47) from both $Cu(Dpph)_2Cl \cdot 0.5CH_2Cl_2$ and $Cu(Dpph)_2ClO_4 \cdot CH_2Cl_2$ in the presence of $NaBH_3CN$. The complex $Cu(BH_3CN)(Dpph)$ was also found to be very similar spectroscopically to $[Cu(BH_3CN)(PPh_3)_2]_2$ (21) and thus has been tentatively assigned a structure of the type illustrated in Fig. 4a.

Considering now silver complexes, only two such complexes of Ag(I) with phosphines have been synthesized (21). In one of these, BH_3CN^- is involved as a coordinating ligand while in the other, it is present as an ionic species. These complexes

$[Ag(BH_3CN)(PPh_3)_3]\cdot CHCl_3$ and $Ag\{(p\text{-}MePh)_3P\}^+BH_3CN^-$ were synthesized from $Ag(PPh_3)_3Cl$ (former) and AgCl with $(p\text{-}MePh)_3P$ (latter) in the presence of an excess of $NaBH_3CN$ in ethanol/chloroform. The coordinated and the ionic BH_3CN^- units in these complexes have been characterized by IR and conductivity studies.

1.6 Formation of hydrido complexes of transition metals with phosphine ligands in the presence of BH_3CN^-

As mentioned earlier in this thesis, one of the possible product types which might be formed in hydroborate reductions of transition metal ions in the presence of complexing ligands is metal hydrides. No simple (i.e. one which does not also contain a hydroborate ligand) hydrido complex of a transition metal complexed by phosphine ligands derived from BH_3CN^- has yet been reported in the literature. However, a significant number of hydrido complexes have appeared in the literature which have been derived from similar reactions in which $NaBH_4$ is the reducing agent (see next section). The lack of such BH_3CN^- derived hydrides is probably due to the fact that $NaBH_3CN$ is a milder reducing agent than $NaBH_4$ and also, this system would have a marked tendency to form cyanotrihydroborato complexes by the simpler nitrogen coordination to the metal ions. Thus, the fact that it is a mild reducing agent suggests that forcing reaction conditions might be required for the formation of hydrido complexes from BH_3CN^- reactions.

One such hydride has in fact been obtained in these reactions. Thus, very recently, Khan (11) has synthesized, in these laboratories, a series of as yet unpublished cobalt-cyanotrihydroborate complexes (at least one of which is a hydridocyanotrihydroborato system) with phosphine ligands in the presence of $NaBH_3CN$ and, in one such reaction, the hydrido complex $CoH(Dppp)_2$ has been prepared as large dark brown crystals. This particular reaction was carried out at elevated temperatures with a large excess of $NaBH_3CN$ added periodically to a mixture of $CoCl_2 \cdot 6H_2O$ and the bis-phosphine ligand Dppp. This complex is very air-sensitive and it decomposed immediately in all chlorinated solvents. Infrared spectra show the metal-hydride stretching frequency as a medium intensity band at 1960 cm^{-1}. This same hydride can also be prepared under much milder conditions using $NaBH_4$ as the reducing agent. An unpublished single crystal X-ray diffraction study (45) has determined the structure of $CoH(Dppp)_2$ prepared from the $NaBH_4$ reaction. That the complex is a metal-hydride is quite clear from the X-ray study and the structure is a highly distorted square based pyramid, a simplified version of which is shown in Fig. 19.

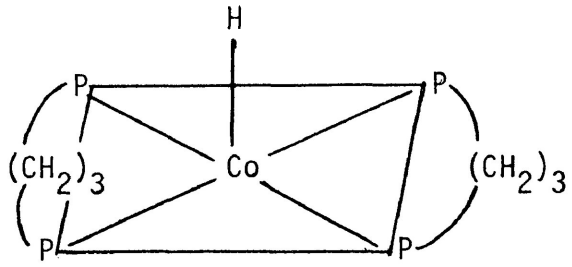


Fig. 19

The unpublished study by Khan (11) referred to above has, however, shown that, more generally, CN rather than hydride abstraction from BH_3CN^- occurs in higher temperature reactions. The complex $CoH(Dppp)_2$ therefore appears to be something of an unusual product type for these reactions.

The attention of the reader is drawn again to the more complex hydrido cyanotrihydroborato systems (related to the simple hydride discussed above) which were discussed, particularly for Co and Ni, in section 1.5.

1.7 Interaction of BH_4^- with transition metal ions in the presence of phosphorus containing ligands

As mentioned earlier, since this thesis is concerned primarily with BH_3CN^- reactions with phosphine-transition metal systems, relatively little attention will be paid to analogous BH_4^- reactions except for purposes of comparison. However, a significant number of tetrahydroborato complexes of transition metals has been synthesized during the last few years and most of the possible modes of coordination of BH_4^- with transition metal ions listed in Fig. 3 have now been characterized. While a detailed discussion concerning the synthesis and structural analysis of tetrahydroborato complexes would not be appropriate here, it is appropriate to record here the known phosphine-BH_4^- complexes which have been completely or partly

characterized. These are listed in Table 9. Other, non-hydroborate products of such reactions have, of course, also been detected (e.g. hydrides already discussed) but mention of these in this thesis will be made only when required.

It should also be noted here that, since the early part of this chapter was written, two new bonding modes of BH_4^- with transition metal ions have been reported. Thus, Meek's group (48) has shown the static nature rather than the more usual (5, 49) fluxional behaviour of a bidentate BH_4^- ligand in solution at room temperature in the Ru(II) complex, $RuH(\eta^2-BH_4)(ttp)$ [ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$] from the ^1H NMR spectrum. This appears to be the first example of non-fluxional and separately observable $B-H_t$ and $B-H_b$ using ^1H NMR spectra. These authors proposed the structure of this complex as a distorted octahedral arrangement shown in Fig. 20. which contains a bidentate BH_4^- ligand with different site symmetries for the two $B-H_b$ linkages. Fluxionality *via* a monodentate BH_4^- unit occurs at higher temperatures.

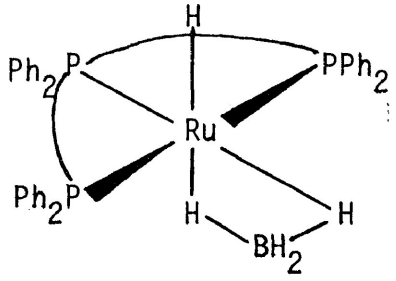


Fig. 20

TABLE 9

Tetrahydroborato Phosphine Complexes of Transition Metals

Complex	Colour	Mode of Synthesis	Ref.	Mode of Coordination	Ref.
$RuH(BH_4)(PPh_3)_3$	Yellow	$RuCl_3$aq + PPh_3 + large excess of $NaBH_4$	(43)	Monodentate ?	(43)
$RuH(BH_4)(CO)(PPh_3)_3$	"	Ru(II)CO Soln. + PPh_3 + $NaBH_4$	(43)	Monodentate ?	(43)
$RuH(BH_4)(CO)_2(PCy_3)_2$		Ru(II)CO Soln. + PCy_3 + $NaBH_4$	(43)	Monodentate ?	(43)
$RuH(\eta\text{-}BH_4)(ttp)$	--	$[RuCl_2(ttp)]_x$ + excess of $NaBH_4$	(48)	Bidentate	(48)
$CoH(BH_4)(PCy_3)_2$	Brownish Yellow	$CoCl_2 \cdot 6H_2O$ + $NaBH_4$ + PCy_3	(50,51)	Bidentate	(50)
$Co(BH_4)(PPh_3)_3$	Yellow	$CoCl_2 \cdot 6H_2O$ + PPh_3 + $NaBH_4$	(9)	Monodentate	(9, 52)
$Co(BH_4)(PPh_3)_2$	Green	$CoCl_2.6H_2O$ + PPh_3 + $NaBH_4$	(52)	Bidentate ?	(52)
$[Co(BH_4)(Dppp)]_2$	Green	$CoCl_2.6H_2O$ + Dppp + $NaBH_4$	(45)	Bridging ?	(45)
$[Co(BH_4)(Dpppe)]_2$	Green	$CoCl_2.6H_2O$ + Dpppe + $NaBH_4$	(45)	Bridging	(45)
$Co(BH_4)P$	Green	$[Co(H_2O)_6](BF_4)_2$ + P + $NaBH_4$	(53)	Bidentate	(53)
$RhH(BH_4)(o\text{-}tolyl_3P)$	Greenish Brown	$RhCl_2(o\text{-}tolyl_3P)$ + $NaBH_4$	(8)	Bidentate) ?	(8)
$MH_2(BH_4)\{P(Bu_2Me)\}_2$ {M = Ir or Rh}	--	$MCl_2(PBu_2Me)_2$ + $NaBH_4$	(54)	Bidentate ?	(54)
$Rh(BH_4)(CO)(PCy_3)_2$	Yellow	$RhCl(CO)(PCy_3)$ + $NaBH_4$	(46)	?	
$Rh(BH_4)(CO)(PPh_3)_2$	--	$RhCl(CO)(PPh_3)$ + $NaBH_4$	(46)	?	
$Rh(BH_4)(PPh_3)_2$	--	$RhCl(PPh_3)_3$ + $NaBH_4$	(8)	Bidentate ?	(8)
$Ir(BH_4)(CO)(PCy_3)_2$	White	$IrCl(CO)(PCy_3)_2$ + $NaBH_4$	(46)	?	
$Ni(BH_4)(PPh_3)_2$	Yellow Brown	$NiCl_2.6H_2O$ + PPh_3 + $NaBH_4$	(20)	Bidentate ?	(20,
trans $NiH(BH_4)(PCy_3)_2$	Yellow	$NiHCl(PCy_3)_2$ + $NaBH_4$	(17,55)	Bidentate ?	(17,55,
trans $NiH(BH_4)(PPr^i_3)_2$	Orange	$NiHCl(PPr^i_3)_2$ + $NaBH_4$	(55)	Bidentate ?	(55)
trans $PdH(BH_4)(PCy_3)_2$	White	$PdHCl(PCy_3)_2$ + $NaBH_4$	(55)	Bidentate ?	(55)
trans $PdH(BH_4)(PPr^i_3)_2$	White	$PdHCl(PPr^i_3)_2$ + $NaBH_4$	(55)	Bidentate ?	(55)
$Cu(BH_4)(PPh_3)_2$	White	$CuCl_2.2H_2O$ + PPh_3 + $NaBH_4$	(56)	Bidentate	(57,58,
$Cu(BH_4)(MePPh_2)_3$	White	$Cu(MePPh_2)_3Cl$ + $NaBH_4$	(59)*	Monodentate	(22,59,*
$[Cu_2(BH_4)(PPh_3)_4]X$	White	$Cu(BH_4)(PPh_3)_2$ + $HClO_4$	(19)	Tetradentate?	(19,

*See also the full account in Inorg. Chem., 19, 587 (1980)

In addition to this, more recently another interesting complex $[Co(BH_4)(Dpppe)]_2$ has been synthesized (45) in these laboratories. X-ray single crystal studies show that this dimeric system contains two BH_4^- units bridging the two Co(I) ions which are also bridged at right angles to the BH_4^- bridges by the two bis-phosphine ligands. Although the actual bonding mode of BH_4^- in this complex has not yet been fully characterized, the two possibilities are that each BH_4^- group bridges the two Co(I) ions either through one hydrogen atom (as in Fig. 3, structure f) or two hydrogen atoms giving a M — H — B — H — M type of linkage. The basic structure is illustrated in Fig. 21.

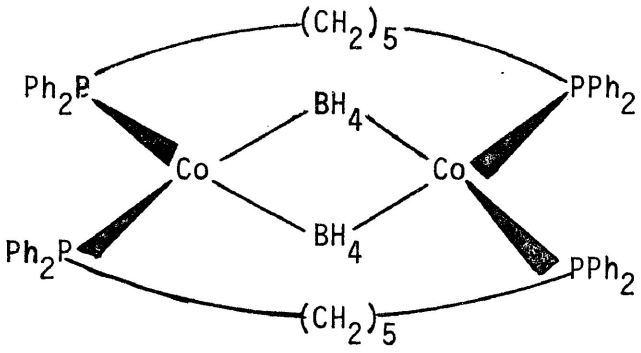


Fig. 21

1.8 Spectroscopic Studies

In the preceding sections, many references have been made to structural assignments and modes of coordination but relatively

little has been said so far about how these structures were determined except that frequent reference was made to IR methods while occasional reference was made to NMR and X-ray techniques. The X-ray structure determinations have already been discussed adequately at those points where the appropriate complexes have been introduced in the preceding discussion. However, before moving on to the discussion of new work, infrared and NMR structural studies of hydroborate complexes should be discussed in more detail so that the rationale for the structural assignments which will be made in later sections may be well understood. The discussion of infrared spectra will be confined mainly to those of cyanotrihydroborate systems but the NMR studies will be a little wider in scope to include some tetrahydroborate systems. The reason for this is that IR studies are made primarily in the solid state whereas NMR studies are made in solution where the phenomenon of fluxionality is often observed with M — H — B bonded systems. This phenomenon has been observed mainly with BH_4^- systems but could also occur in certain modes of BH_3CN^- coordination.

1.8.1 Vibrational Spectroscopy

In order to facilitate reference to published IR data on cyanotrihydroborate systems, all such systems which have so far been reported are recorded in Table 10 together with selected features of the observed spectra.

TABLE 10

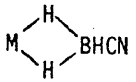
Selected Features of the Infrared Spectra of Known Cyanotrihydroborato Complexes

No.	Complex	Inferred Bonding	BH Deformation	νBH Terminal	M-H-B Bridge	νCN	Others	Ref.
1.	$Cr(BH_3CN)(CO)_5(Me_4N)$	M - $NCBH_3$	--	2337 (w.br.) 2310 (w.sh)	--	2207 (vw)	1937 (s) CO	(36)
2.	$Mo(BH_3CN)(CO)_5(Me_4N)$	"		2335 (vw.br) 2290 (vw.br)	--	2200 (vw)	1935 (s) CO	(36)
3.	$W(BH_3CN)(CO)_5(Me_4N)$		--	2335 (vw.br) 2312 (vw.br)	--	2200	1928 (s) CO	(36)
4.	$[Ni(BH_3CN)(tren)]_2^{2+}$	Two Ni-HBH_2CN-Ni bridges	1130 (w.sh) 1114 (m)	2380 (s) 2372 (sh) 2350 (sh)	2241 (m) 2276 (m) 2200 (m)	2221 (s)	--	(10)
5.	$Ni(BH_3CN)_2(en)_2 \cdot THF$	M - $NCBH_3$	--	2340 2370 2300	-- --	2200 (s)		(39)
6.	$Fe(BH_3CN)_2(Phen)_2$		--	2330 (s) 2270(vw.sh)	--	2188 2146	--	(37)
7.	$[Ru(BH_3CN)(NH_3)_5]Br$		--	--	--	2170 (s)	--	(38)
8.	$[Ru(BH_3CN)(NH_3)_5]Br_2$	"	--	--	--	2206 (s)	--	(38)
9.	$Cu(BH_3CN)_2(Me_5dien)$	M - $NCBH_3$	1123 (s) 1112 (s)	2346 (s) 2396 (sh) 2284 (sh)	--	2192 (s) 2210 (s)	--	(24)
10.	cis-$Fe(BH_3CN)_2\{P(OR)_3\}_4$		--	--		2208 (s) 2212 (s)	--	(42)
11.	trans-$Fe(BH_3CN)_2\{P(OR)_3\}_4$			2323 2368		2202	--	(42)
12.	$RuH(BH_3CN)(CO)_2(DBP)_2$		1120	2340 (s)		2110 (s)	1845 M - H	(43)
13.	$Co(BH_3CN)_2(PPh_3)_3$		1116 (s)	2340 (s,br)		2184 (s) 2218 (m)	--	(6)
14.	$Co(BH_3CN)(N_2)(DBP)_3$		1112 (s)	2350 (s,br)		2189 (s)	--	(6)

TABLE 10 (Continued)

No.	Complex	Inferred Bonding	BH Deformation	BH Terminal	M-H-B Bridge	ν CN	Others	Ref.	M-H
15.	$Co(BH_3CN)(Diphos)_2$	M - $NCBH_3$	1112 (s)	2336 (s)	--	2190 (s)	--	(9)	
16.	$CoH(BH_3CN)(PPh_3)_3$	"	--	2340 (s,br) 2210 (w) 2280 (w)	--	2190 (s)	1962 (m) M - H	(11)	
17.	$[Co(BH_3CN)(Dppm)_2]ClO_4$			2345 (s,br) 2245 (sh) 2375 (sh)	2000 (m)	2200 (s)	1100 (s) ClO_4^-	(11)	
18.	$Co(BH_3CN)(Dppm)$		1100 (s)	2340 (s,br)	1990 (m)	2160 (s)	--	(11)	
19.	$[Co(BH_3CN)(Diphos)_2]ClO_4$		--	2340 (s,br) 2260 (sh) 2370 (sh)	-- --	2185 (s)	1100 (s,br) ClO_4^-	(11)	
20.	$[Co(CN)(Diphos)_2]ClO_4$		--	--		2100 (s) M-CN	1100 (s,br) ClO_4^-	(11)	
21.	$Co(BH_3CN)_2(Dppp)_{1.5}$		1100 (s)	2380 (s,br)	--	2185 (s)	--	(11)	
22.	$Co(BH_3CN)_2(Dppb)_2$		1100 (s)	2360 (s)	--	2169 (s)	--	(11)	
23.	$Co(BH_3CN)(Dppb)_2$		1100 (s) 1110 (sh)	2360 (s)	--	2200 (s)	--	(11)	
24.	$Rh(BH_3CN)(CO)(PCy_3)_2$		1113	2375 (s,br)	--	2200 (s)	1957 CO	(46)	
25.	$Rh(BH_3CN)(CO)(PPh_3)_2$		1109	2360 (s,br)		2192	1997 CO	(46)	
26	$Rh(BH_3CN)(CO)(DBP)_3$		1114 (m)	2340 (m)	--	2202 (m) 2188 (sh)	1984 (s) CO	(8)	
27.	$Rh(BH_3CN)(CO)(N_2)(DBP)_3$		1114 (m)	2335 (m)	--	2205 (m)	1995(s) CO	(8)	
28.	$RhH_2(BH_3CN)(PPh_3)_3$		1118 (s)	2328 (s,br) 2360 (sh)	--	2207 (s)	--	(8)	2060 (s) 2046 (s)
29.	$NiH(BH_3CN)(PPh_3)_2$		1120 (s)	2336 (s)	2140 (m)	2200 (s)	722 (s) Ni-H?	(9)	

TABLE 10 (Continued)

No.	Complex	Inferred Bonding	BH Deformation	BH Terminal	M-H-B Bridge	νCN	Others	Ref.
30.	$NiH(BH_3CN)(DBP)_3$	$M-NCBH_3$	1133 (m)	2334 (s)	2138 (m)	2201 (s)	--	(9)
31.	$NiCl(BH_3CN)(Diphos)$	"	1103 (s)	2340 (s,br)	--	2192 (s)	--	(9)
32.	$Ni(BH_3CN)(PPh_3)_2$		1118 (s)	2340 (s,br)	2070 (w)	2185 (s)	--	(9)
33.	$[Cu(BH_3CN)(PPh_3)_2]_2$	Two $Cu-HBH_2CN-Cu$ bridges	1100 (s)	2376 (s) 2388 (sh) 2407 (sh)	2200 (b)	2190 (s) 2207 (s)	-- --	(10)
34.	$Cu(BH_3CN)(PPh_3)_3$	$M - NCBH_3$	1153 1125 (s)	2330 (s) 2338 (sh)		2192 (s)	--	(9)
35.	$Cu(BH_3CN)(PPh_3)$	"	1115 (s)	2340 (s) 2280 (sh)	2122 (m)	2185 (s)	--	(9)
36.	$Cu(BH_3CN)(DBP)_3$		1119 (s)	2350 (b) 2290 (sh)	--	2188 (s)	--	(9)
37.	$Cu(BH_3CN)(PEtPh_2)_3$		1112 (s)	2336 (s)	--	2190 (s)	--	(9)
38.	$Cu(BH_3CN)(Diphos)_{1.5}$	"	1116 (s)	2340 (s,br.)	2160 (m)	2188 (s)	--	(9)
39.	$Cu(BH_3CN)(Dppm)$	"	1119 (s)	2363 (s) 2340 (s)	2105 (m)	2182 (m)	--	(47)
40.	$[Cu(BH_3CN)_2(Dppm)]_2$	Two $Cu-HBH_2CN-Cu$ bridges	1116 (s)	2363 (s) 2345 (s) 2250 (m)	--	2182 (s) 2160 (m)		(47)
41.	$Cu(BH_3CN)(Dpph)$	$M - NCBH_3$	1119 (s)	2345 (s) 2360 (sh)	--	2182 (s)	--	(47)
42	$Cu_2(BH_3CN)_2(Dppp)_3$		1120 (s)	2350 (s) 2370 (sh)	--	2188 (s)	--	(47)

The infrared spectral characteristics of free BH_3CN^- (and BD_3CN^-) have been discussed earlier (Tables 1 and 2). Thus the C ≡ N stretching frequency for this system is found at 2179 cm^{-1} with the BH_t (t = terminal) stretch in the 2320 to 2350 cm^{-1} region. When this BH_3CN^- acts as a ligand (usually through the N-atom) in complexation, then the stretching frequency of C ≡ N is shifted either to higher (more usually) or lower (occasionally) frequency than that in free BH_3CN^-. Similar shifts occur on M — H — B type coordination and, as will be seen shortly, the direction of the shift observed in the B — H_t vibration can be highly informative. For most of the complexes of the type M ← $NCBH_3$ discussed earlier and presented in Table 10, the C ≡ N stretching frequency occurs in the 2110 cm^{-1} to 2220 cm^{-1} region and the BH_t stretching vibration occurs in the 2300 to 2400 cm^{-1} region. Much information can be acquired from the magnitude and direction of these shifts as will be seen in the following discussion.

For a better understanding of the essential points of the effects of coordination upon infrared spectra in the cyanotrihydroborato complexes, the spectra of several complexes of known structure will now be examined.

There are four BH_3CN^- complexes — $Cu(BH_3CN)_2(Me_5dien)$ (24), $CoH(BH_3CN)(PPh_3)_3$ (44), $[Cu(BH_3CN)(PPh_3)_2]_2$ (21), and $[Ni(BH_3CN)(tren)]_2^{2+}$ (10) — for which solid state structures have been completely characterized by single crystal X-ray studies.

Considering first the monomeric Cu(II) species $Cu(BH_3CN)_2(Me_5dien)$ the infrared spectrum shows two strong peaks corresponding to C ≡ N stretching vibrations at 2197 cm^{-1} and 2210 cm^{-1}. These are significantly higher than the frequency observed for free BH_3CN^-. The two distinct C ≡ N vibrations arise from two N-coordinated (X-ray structure) C ≡ N groups which occupy non-equivalent sites (one apical and one basal - see Fig. 11) for which there are two different Cu — N bond lengths and hence two different Cu — N bond strengths. A small C ≡ N frequency shift on coordination could suggest a weak interaction with the metal ion but examination of the structure of $Cu(BH_3CN)_2(Me_5dien)$ shows that as well as two Cu — N bond lengths, there are two Cu — N — C geometries - one linear and one angular. A linear arrangement is consistent with sp hybridization of the N-atom and coordination through an sp lone pair while an angular arrangement suggests some sp^2 character for the N-atom. The change in hybridization from sp towards sp^2 would lengthen the C — N bond and therefore reduce the vibrational frequency. In this connection, two different C — N bond lengths are observed in the above complex. Thus the most tightly bound (basal) BH_3CN^- ligand shows a short Cu — N bond length, an angular Cu — N — C linkage, and the longer of the two C — N bond lengths while the apical BH_3CN^- unit shows a long Cu — N bond but a linear Cu — N — C linkage and a short C — N bond length. For these reasons, the IR peak of smallest shift (only 13 cm^{-1}) is assigned (24) to the most strongly bound BH_3CN^- ligand with the angular Cu — N — C linkage. It therefore seems that a small N — bonded C ≡ N

frequency shift frequently observed on coordination may imply weak coordination but is more likely to imply an angular M — N — C unit. There is also the possibility in some instances that π interactions between the N atom and the metal ion may occur as is apparently the case in $CoH(BH_3CN)(PPh_3)_3$ (44). This will further affect bond lengths and M — N — C geometry. These points have been discussed extensively elsewhere (24,44).

The B — H_t stretching frequency occurs (24) at 2346 cm^{-1} (with shoulders at 2396 cm^{-1} and 2284 cm^{-1}) in the spectrum of $Cu(BH_3CN)_2(Me_5dien)$ while in the spectrum of the similar five-coordinated monomeric unit $CoH(BH_3CN)(PPh_3)_3$ it occurs (44) at 2340 cm^{-1}. As shown in Table 1 the principal B — H_t vibration in free BH_3CN^- occurs at around 2320 (broad). Generally, known or suggested N — bonded unidentate BH_3CN^- complexes show B — H_t vibrations in the range 2320 — 2345 cm^{-1} and another typical example is $Cu(BH_3CN)(PPh_3)_3$ which shows (21) this vibration at 2330 cm^{-1}. However, as will be seen shortly, shifts of the B — H_t stretching frequency to significantly higher frequency occur when one H atom of the BH_3 unit is coordinated.

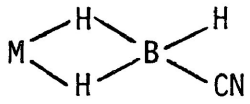
In the two structures $[Cu(BH_3CN)(PPh_3)_2]_2$ and $[Ni(BH_3CN)(tren)]_2^{2+}$, the two BH_3CN^- act as bridging ligands and structural details have been given earlier in this chapter. Thus, each of the BH_3CN^- units forms both M — H — B and M — N — C linkages

and changes should be observed in both the C ≡ N and B — H_t vibrational frequencies relative to those in free BH_3CN^-. Furthermore, a B — H_b (as in the M — H — B unit) vibration should be observable. For the dimeric copper complex, two C ≡ N vibrations are observed (at 2190 and 2207 cm^{-1}) (21) while in the spectrum of the dimeric nickel complex, only one C ≡ N vibration is seen (at 2221 cm^{-1}). The reason for this is that in the copper species, the ring containing the two Cu ions and the two BH_3CN^- ligands is non-planar and the two C ≡ N units occupy different positions with different Cu — N bond lengths. On the other hand, the nickel species is symmetrical and the two C ≡ N units are identical. It seems, therefore, that in systems containing more than one BH_3CN^- unit, the number of C ≡ N stretching vibrations is a useful guide to the symmetry or otherwise of the system.

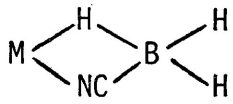
Considering now the B — H vibrations of these two dimeric systems, coordination through one of the H atoms of BH_3CN^- raises the B — H_t frequency to a value about 50 cm^{-1} above that of free BH_3CN^-. Thus, the dimeric copper system referred to above shows (21) this vibration at 2376 cm^{-1} while that of the nickel dimeric system appears (10) at 2380 cm^{-1}. On deuteration, these peaks shift into the 1780 — 1790 cm^{-1} range (with additional peaks at lower frequencies) which is somewhat higher than the value observed for BH_3CN^- systems where coordination is through only the N atom. These points will be discussed further in the Results and Discussion section of this thesis where several new BH_3CN^- bridged dimeric Ni(II) systems

are reported. Indeed, the shift to higher frequency of the $B - H_t$ vibration is, at present, the best evidence for bridging BH_3CN^- in the absence of X-ray methods. The $B - H_b$ vibration (as in the $M - H - B$ unit) appears as a fairly broad band in the 2200 – 2280 cm^{-1} region in such systems (10, 21) and sometimes lies under the intense $C \equiv N$ stretching frequency. Terminal $B - H_t$ bending vibrations appear in the 1100 – 1120 cm^{-1} range with the lower values in this range observed in the dimeric systems discussed above.

The other modes of coordination for BH_3CN^- which have possibly been identified in the literature, such as



and



(see Fig. 3), have been assigned largely on the basis of quite small changes in the BH_t and $-C \equiv N$ regions of the spectrum and further discussion here would be largely speculation. Such structures cannot yet be assigned unambiguously without X-ray structural data.

1.8.2 NMR Spectroscopy

Nuclear magnetic resonance (NMR) has, over the years, become one of the most important physical methods for chemical structural studies. Each of the many physical methods available, such

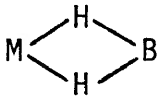
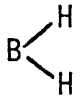
as infrared, visible, and ultraviolet spectra and mass spectrometry contribute valuable information but when structural information is obtained by NMR methods, it is usually much more precise than that yielded by the other methods listed above. We are concerned here with the structural information which can be gained regarding BH_3CN^-/-metal/phosphine complexes from magnetic resonance studies of the three nuclei ^{11}B, ^{1}H and ^{31}P.

The NMR of the ^{11}B nucleus has been generally quite well studied (60) and this is particularly true for borane derivatives. Regarding such studies with hydroborates, ^{11}B NMR has been used more with tetrahydroborato complexes than with cyanotrihydroborato complexes although relatively few studies of either type of complex have been reported. Recently, however, the ^{11}B NMR spectra of a few cyanotrihydroborato complexes have been recorded. For example, one such complex, trans-$Fe(BH_3CN)_2\{P(OR)_3\}_4$ (in which the $M - NCBH_3$ type of coordination is present), shows (42) in the ^{11}B NMR spectrum a quartet at $\delta = 40$ (relative to $BF_3 \cdot Et_2O$) in the ratio of 1:3:3:1 with a coupling constant of $J_{B-H} = 91$ Hz. This is consistent with the shifts and couplings expected for a $N -$ coordinated BH_3CN^- ligand i.e. these quantities are very similar to those exhibited by free BH_3CN^-. In another iron complex, the paramagnetic $Fe(BH_3CN)_2(CH_3CN)_4$, the ^{11}B resonance occurs at $\delta = -66$. This strong upfield shift is possibly due to paramagnetic effects. The spectra of one or two other BH_3CN^- complexes of cobalt have been briefly reported by S.I. Khan (11) but with little comment.

Most NMR studies of complexed hydroborate ligands have been carried out with ^{1}H or ^{31}P nuclei. However, even though ^{1}H NMR is so well established as a powerful structural tool, a literature survey shows that ^{1}H NMR spectrometry has not been used to any great extent in structural investigations of tetrahydroborato or cyanotrihydroborato complexes. This is mainly because of the fluxional behaviour of many complexed BH_4^- groupings in solution at room temperature and even at much lower temperatures (5, 49). A further complication in some cases is the phenomenon of "thermal decoupling" or "correlation time decoupling" in which spin-lattice relaxation effects of ^{10}B and ^{11}B effectively decouple boron from attached hydrogen (49). At room temperature, the coordinated hydrogen atoms (M — H — B) and the terminal B — H atoms in many tetrahydroborato complexes are magnetically equivalent. This happens because of rapid interchange (on the NMR time scale) between the co-ordinated and the terminal hydrogen atoms of the BH_4^- group. In certain cases this fluxional behaviour can slow down at lower temperatures to the point where separate B — H_b and B — H_t signals are observable.

One such complex which shows this behaviour (49) is the diamagnetic tetrahydroborato Cu(I) complex $Cu(BH_4)\{P(MeO)_3\}_2$ which has been thoroughly studied (49) by low temperature NMR techniques. This complex initially shows at room temperature a broadened quartet at δ = 0.69 but with lowering of temperature, the quartet gradually

collapses to a broad doublet at $-95^{o}C$ which collapses further to a broad singlet at $-128^{o}C$ because of thermal decoupling. Finally, the signal collapses to the baseline at $-165^{o}C$. However, between $-128^{o}C$ and $-165^{o}C$, the singlet first sharpens and then broadens before finally collapsing to the baseline. Further continued lowering of the temperature to $-180^{o}C$ causes no further significant changes in the B — H region of the spectrum. This collapsing and broadening process at lower temperatures was attributed to some degree of slowing of the hydrogen exchange process. This fluxional behaviour of hydrogen atoms in the BH_4^- complex limits the use of ^1H NMR spectrometry in solution to assign the structure of tetrahydroborato complexes correctly. In particular, the solution fluxional process would obscure the mode of coordination of the BH_4^- ligand (unidentate, bidentate, etc.).

While fluxionality of coordinated BH_4^- is quite common even at very low temperatures, the rate of the hydrogen exchange process can vary quite markedly from one complex to another. For example, one type of tetrahydroborato complex which is non-fluxional at moderately low temperatures has appeared in the literature (54) and the ^1H NMR information has been used to distinguish the bidentate bridging hydrogens,  , and the terminal hydrogen,  , of the tetrahydroborato grouping as two separate resonances. Thus, $IrH_2(BH_4)L_2$ [L = bulky tertiary phosphine] (54) shows the two resonances at $\delta = -6.5$ and $\delta = +6.8 - 7.8$ at $-51^{o}C$. From this evidence,

the authors suggested that the resonance at $\delta = -6.5$ is due to the bridging hydrogens in $Ir\langle^{H}_{H}\rangle B$ and that at lower field (+ 6.8 — 7.8) is therefore due to the terminal $B\langle^{H}_{H}$ hydrogen of the bidentate BH_4^- BH_4^- group. Similarly, in the ^1H spectrum of $V(BH_4)(\eta-C_5H_5)_2$ recorded (61) at -103^o, the bridging hydrogens could be observed at $\delta = -34$ but the terminal hydrogens were not observed.

Very recently, another very interesting complex which is nonfluxional at room temperature $RuH(\eta-BH_4)(ttp)$[ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$] has been reported (48) and has already been briefly discussed (section 1.7, Fig. 20) in the context of modes of BH_4^- coordination. This shows discrete ^1H NMR signals for the two non-equivalent bridging Ru — H — B protons and as well as for the two terminal B — H protons at room temperature. This appears to be the first example of a tetrahydroborato complex which is non-fluxional at ambient temperatures although fluxionality occurs at higher temperatures. Further details were given in the earlier discussion (section 1.7).

Returning now to cyanotrihydroborato complexes, ^1H spectra have been little studied. The above type of fluxionality is probably of no importance for the most common mode of coordination - i.e. $M \leftarrow NCBH_3^-$, but other types of cyanotrihydroborato complexes in which coordination of the BH_3CN^- groups may involve bonding to the metal ions through the hydrogen atoms could possibly show fluxional

behaviour. Possible structures of this type are listed (among others) in Fig. 3 and of particular importance in the context of this thesis are the bridged structures of the type illustrated in Fig. 4a of which two examples (already discussed in this thesis) have appeared in the literature (10, 24). Clearly, in these structures, simple rotation of the tetrahedral B atom about the B — C axis could interchange bridging and terminal B — H bonds. This could be temperature dependent.

Many of the BH_3CN^- complexes recorded in the literature and all of those reported in this thesis contain phosphorus. ^{31}P NMR spectrometry is a very well established powerful structural tool and its application, where appropriate, to metal/phosphine/BH_3CN^- complexes could throw considerable light upon structural problems. Very few such applications of ^{31}P NMR spectrometry have been reported in the literature but one recent application (42) has been to the cis and trans isomers of the octahedral $Fe(BH_3CN)_2\{P(OR)_3\}_4$ systems. One form (in the case where R = Me) shows a single P resonance at δ = 154.4 while the other isomer shows two regions of absorption coupled (J_{P_P} = 131 Hz) in an A_2B_2 pattern at δ 163.3 and 150.2 respectively. Clearly, the former is the trans form while the latter is the cis form since only in the cis form could two sets of non-equivalent P atoms be obtained with the type of coupling observed. Similar results were obtained when R = Et.

Other as yet unpublished observations of ^{31}P spectra have been made in this context. Thus, Alam (47) studied a series of copper/bidentate phosphine/BH_3CN^-complexes but the results were inconclusive because of the very broad nature of the ^{31}P resonances in many of the spectra. This was thought to be due to ligand dissociation phenomena and slowing of dissociation would require that spectra should be recorded at much lower temperatures. S.I. Khan (11) has carried out similar investigations with cobalt/bidentate phosphine/BH_3CN^- systems and again, although the absorptions were generally quite sharp, few conclusions were drawn. One interesting set of observations is that in the spectra of the compounds formulated (11) as $[Co(BH_3CN)(Dppm)_2]ClO_4$ and $[Co(BH_3CN)\ (Diphos)_2]ClO_4$ (now regarded as being possibly $[CoH(BH_2CN)(L\text{-}L)_2]ClO_4$ as discussed earlier in this thesis) the four phosphorus atoms were, in each case, equivalent (at δ 2·02 and 64·08 respectively) showing that either the species are highly symmetrical in solution or that ligand polytopal reorganization is very rapid at room temperature. The small ^{31}P downfield shift relative to that in the free phosphine in the case of the Dppm complexes is also of interest since it is characteristic (62) of Dppm chelation (four membered ring). The much larger shift in the Diphos case is characteristic of five membered ring chelation. The ^{31}P spectra of bidentate phosphine complexes have been extensively reviewed very recently by Garrou (62) and the ring size effects on the ^{31}P coordination shifts discussed at length in

this review may be of some considerable value in certain structural assignments of new Ni/bidentate phosphine/BH_3CN^- derived complexes to be presented later in this thesis.

1.9 Objectives of the present work

From the foregoing introductory sections, it is clear that reactions of $NaBH_3CN$ with transition metals in the presence of phosphine ligands lead to a variety of products depending upon the reaction conditions. It is equally apparent from this introduction that these most interesting interactions of the cyanotrihydroborate anion with transition metals have received relatively little attention compared with the corresponding tetrahydroborate systems. Furthermore, in recent years, a considerable amount of research has been carried out in these laboratories involving reactions between $NaBH_3CN$ and Cu(II) or Cu(I) and Co(II) systems in the presence of mainly bidentate phosphine ligands and most of this work remains unpublished. This unpublished work shows also that BH_3CN^- can adopt several bonding modes with transition metal systems. This work remains unpublished at this stage because certain points regarding mechanistic and structural problems have not yet been fully worked out although some general ideas have emerged. Similar studies with other transition metals might be more promising and might also throw light upon the Cu and Co work referred to above. The Ni(II) system would be suit-

able since it has already received some attention in the literature as already described. The project described in the following sections of this thesis is therefore centered on the Ni(II) system with the following objectives in mind:-

(a) to study the interactions of BH_3CN^- as a ligand or reducing agent with Ni(II) in the presence of bidentate phosphine ligands under different reaction conditions. The purpose of this aspect of the study is to investigate the influence of reaction conditions (solvent, temperature, rate of addition, etc.) and the nature of the bidentate phosphine ligand upon the types of product formed and the bonding mode adopted by the BH_3CN^- ligand if it is present in the product.

(b) to increase our understanding of the relatively mild behaviour of $NaBH_3CN$ as a reducing agent in these complexation reactions of Ni(II) by isolating, if possible, stable intermediate products in which Ni(I) or Ni(0) is present and to make comparisons with the behaviour of $NaBH_4$ under these conditions.

These studies to be described involve a variety of physical methods for structure determination and very careful control of reaction conditions in order to establish the sequences in which various product types are formed and the influence of reaction conditions upon these sequences.

The bisphosphines chosen for these studies were Dppm, Diphos, Dppe(*cis* and *trans*), Dppp and Dppb in which the two phosphorus atoms are separated by at least one and up to four carbon atoms. These phosphines were chosen because of the great variety of results obtained (45) in similar studies with Co(II)/$NaBH_4$ systems and also Cu(II)/$NaBH_4$ and $NaBH_3CN$ systems (47). Brief reference to these studies has already been made.

2. EXPERIMENTAL

2.1 Materials

The bidentate phosphines Dppm, Diphos, cis and trans Dppe, Dppp and Dppb were obtained from Strem Chemicals Incorporated and were used without further purification. Reagent grade $Ni(ClO_4)_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ were purchased from Alfa Inorganics Incorporated (former) and BDH Chemicals Limited (latter) and were again used without further purification. Sodium cyanotrihydroborate and sodium cyanotrideuteridoborate (98% isotopic purity) were obtained from the Aldrich Chemical Company and the Alfa Division of the Ventron Corporation respectively. Again, no further purification was necessary. Sodium cyanotrihydroborate with ^{15}N labelling was synthesized in these laboratories from $NaC^{15}N$ (purchased from Stohler Isotope Chemicals) and Borane-tetrahydrofuran complex (solution in tetrahydrofuran, stabilized with sodium borohydride) which was obtained from the Aldrich Chemical Company Incorporated. Details of this synthesis will be given shortly. Because of the hygroscopic behaviour of the cyano-compounds, they were dried under high vacuum for 24 hours and were then stored over $CaCl_2$ in a desiccator prior to use.

All solvents were reagent grade. They were purified by distillation, degassed with oxygen-free dry nitrogen, and then

stored over type 4-A molecular sieves in the glove box. Synthetic work was carried out in a glove box (unless otherwise specified) which was always flushed with a constant flow of dry nitrogen.

2.2 Analyses and Measurements

All air-sensitive samples were properly protected from atmospheric oxidation or hydrolysis during weighing or data collection.

Microanalytical data for nitrogen, carbon and hydrogen were acquired on a Perkin Elmer model 240 Analyser. For samples where combustion was incomplete under normal conditions, V_2O_5 was used as a combustion aid. Chloride analyses were determined by the Mohr titration method.

The infrared spectra of the samples were recorded on Beckman IR-12 and IR-4250 Spectrophotometers (calibrated periodically with a polystyrene reference film) as Nujol mulls pressed between NaCl plates (600 - 4000 cm^{-1}) or between polyethylene plates (200 - 600 cm^{-1}). Electronic spectra (usually reflectance) were recorded on a Cary-14 recording spectrophotometer in the 18,000 to 3,000 $\text{\AA}$ range.

A Bruker WP-80 Fourier transform instrument equipped with an automatic temperature control device (B-VT 1000) was used to record ^{1}H and ^{31}P NMR spectra at 80 mHz and 32·3 mHz respectively. The chemical shifts were measured relative to internal tetramethylsilane (TMS) and external H_3PO_4 for ^{1}H and ^{31}P respectively but, in practice, the direct use of H_3PO_4 in routine NMR measurements was avoided. The position of the H_3PO_4 signal was first recorded against either D_2O or $(CD_3)_2CO$ which were used as external frequency lock systems. These were sealed in thin capillaries coaxially fitted to the ^{31}P NMR sample tubes through the vortex plug. The position of H_3PO_4 against these solvents was found to be 2800 Hz (D_2O) and 2910 Hz [$(CD_3)_2CO$] and the chemical shifts of other ^{31}P signals were calculated relative to these frequencies. This method offered the advantage that weak signals in the samples could be measured without the saturation problems generated by a strong H_3PO_4 signal and this is particularly useful for sparingly soluble samples where pulsing for long period becomes feasible. ^{31}P spectra were normally recorded at ambient temperatures in the proton decoupled mode. The chemical shifts (δ) are positive if downfield from the reference signal.

For X-ray powder diffraction measurements, samples were sealed in Lindeman Capillaries (0.3 mm) and were photographed on a Debye-Scherrer type Camera using nickel filtered copper K_α radiation from a Philips PW-1130 X-ray generator.

Mass spectra, usually to detect solvent of crystallization, were recorded on an Hitachi-Perkin Elmer model RMU-7 double focusing mass spectrometer.

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.

Molecular weights were determined in $CHCl_3$ solution at 45°C for a few of the products using a Knauer Vapour Pressure Osmometer calibrated with Benzil in benzene at 45°C and the accuracy was checked periodically by measurement of the molecular weight of pentaerythrityl tetrastearate.

Conductivities were measured, where possible and appropriate, with a YSI model 31 conductivity bridge at 20°C and at $4{\cdot}0 \times 10^{-3}$ M concentrations in CH_2Cl_2.

2.3 Syntheses

A general pattern was followed for most of the syntheses which will be described in this section. This involved

the addition of the reducing agent, $NaBH_3CN$, to Ni(II) chloride or perchlorate in the presence of the appropriate phosphine. In most cases, the reactions were carried out either in a mixed solvent system (ethanol/benzene, ethanol/toluene) or in absolute ethanol. Mixed solvents were employed because most of the phosphines used are soluble in benzene or toluene whereas the nickel salts are soluble in ethanol. The reactions were studied under a wide variety of conditions and the more important factors which were found to affect the course of the reactions are:-

(a) the amount of $NaBH_3CN$ used

(b) the rate of addition of $NaBH_3CN$

(c) the reaction time

(d) the solvent system

(e) the ratio of metal to ligand (phosphine)

(f) the nature of the phosphine used

(g) the temperature

Yields, in most instances, were moderate and normally in the range 25 - 35% unless otherwise stated. Details of synthetic procedures for the various products formed in these reactions are given in the following subsections. Spectroscopic details are given in the Results and Discussion section later in this thesis.

2.3.1 Ni(II)/Dppm/$NaBH_3CN$ reactions

This system has been investigated under a wide range of reaction conditions and has produced a number of very interesting

compounds. It has been found that for the ligand Dppm, the course of the reaction is extremely sensitive to quite small changes in the reaction conditions. It should also be noted here that for unambiguous infared assignments in the spectra of the products of the Dppm reactions certain syntheses had to be duplicated using $NaBD_3CN$ and even ^{15}N labelled $NaBH_3CN$. The synthesis of the latter is therefore described first.

2.3.1.1 Synthesis of $NaBH_3C^{15}N$

The synthetic procedure used is similar to that used by Hui (63) for the synthesis of $NaBH_3CN$. A THF solution (24 ml) of the BH_3·THF adduct (0.98 g., 10 mM) was added dropwise over a period of 1.5 hours to a stirred solution of $NaC^{15}N$ (0.5 g., 10 mM) in 15 ml THF under N_2. The mixture was then stirred for four hours at room temperature after which it was heated under reflux for a further seven hours. A slow flow of N_2 (dry) was maintained throughout the reaction time. When the mixture was cooled to room temperature, a very small amount of white solid appeared (probably unreacted $NaC^{15}N$) and this was separated by filtration under N_2. The filtrate was evaporated to dryness at 60°C under reduced pressure. The white solid obtained in this manner from the filtrate was dried at 120°C in a vacuum oven under reduced pressure (~0·3 Torr.) over night to give the $NaBH_3C^{15}N$ in apparently pure form (analysis and IR spectra)

in 94% yield. This yield is comparable with that obtained by Hui for the unlabelled material on a much larger scale.

The infrared spectrum of this ^{15}N labelled compound shows the C ≡ ^{15}N stretching frequency as a strong and sharp band at 2152 cm^{-1} which is a frequency decrease of 27 cm^{-1} from the C ≡ ^{14}N stretching frequency observed in the spectrum of $NaBH_3C^{14}N$. In other respects the infrared spectra of $NaBH_3C^{14}N$ and $NaBH_3C^{15}N$ appear to be identical.

Analysis Found: C = 18.33%, H = 4.63%, N = 20.64%

Calc. for $NaBH_3C^{15}N$ C = 18.23%, H = 4.64%, N = 21.26%

2.3.1.2 (Cyanotrihydroborato)bis[bis(diphenylphosphino)methane] nickel(II)perchlorate

$[Ni(BH_3CN)(Dppm)_2]ClO_4$

An ethanolic solution (20 ml) of $NaBH_3CN$ (0.10 g., 1.59 mM) was added dropwise over a period of two minutes to a stirred mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.3 g., 0.82 mM) and Dppm (0.63 g., 1.63 mM) in benzene/ethanol (1:1, 20 ml.) One drop of $NaBH_3CN$ solution turned the reaction mixture instantly to brown from yellow and upon complete addition of the $NaBH_3CN$, the solution had turned to deep brown. The resultant solution was then filtered, yielding a brown solid. Prior to drying under reduced pressure, the solid was washed with benzene

(~ 10 ml), ethanol (~ 10 ml), and finally with n-hexane (~5 ml). The brown solid was found to be soluble in CH_2Cl_2, THF, DMF and acetone but it decomposes in all solvents within 30 minutes. The complex was therefore purified by precipitation from CH_2Cl_2 by very rapid addition of n-hexane. The pure solid thus obtained was dried under high vacuum (ca. 0.3 Torr.) for 12 hours. This complex appears to be air stable in the solid state. This reaction has also been carried out with $NaBD_3CN$ and the deuterated product purified as discussed above. Further discussion of this deuterated product occurs in the Results and Discussion section.

Analysis Found: C = 62.86%, H = 5.20%, N = 1.42%

Calc. for $[Ni(BH_3CN)(Dppm)_2]ClO_4$ C = 63.34%, H = 4.86%, N = 1.44%

2.3.1.3 (Cyanotrihydroborato)(cyano)bis[bis(diphenylphosphino)-methane]dinickel(I)

$Ni_2(BH_3CN)(CN)(Dppm)_2 \cdot \frac{1}{2}$ EtOH

The above complex has been synthesized from both $Ni(ClO_4)_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ reactions with the phosphine and $NaBH_3CN$ using different molar ratios of $NaBH_3CN$ to Ni(II) as follows:

(a) From $Ni(ClO_4)_2 \cdot 6H_2O$/Dppm/$NaBH_3CN$

$Ni(ClO_4)_2 \cdot 6H_2O$ (0.3g, 0.82mM) and Dppm (0.63 g., 1.63 mM) were mixed in ethanol (40 ml) and this immediately

precipitated a yellow solid. An ethanolic solution (20 ml) of $NaBH_3CN$ (0.4 g., 6.30 mM) was added dropwise to the stirred yellow suspension over a period of 10 minutes. During addition of the $NaBH_3CN$ solution, the initial yellow reaction mixture changed first to brown, then to light green, and finally to deep green when the addition was complete. The resultant mixture was left to stir for a further 3 hours, during which time a greenish brown solid precipitated. This was filtered off from the reaction mixture, washed with ethanol (~ 10 ml) and n-hexane (~ 10 ml), and dried under reduced pressure for several hours. The complex is soluble in EtOH, CH_3OH, CH_2Cl_2, THF, benzene and CH_3CN, giving a green solution in each solvent but it decomposes in solution to give light brown solutions within a few minutes. This colour changes further to violet after a few hours. Purification of this complex by recrystallization was therefore not possible due to its solvent sensitivity. However, the complex was successfully purified by washing with small amounts of cold ethanol followed by benzene. It was obtained as an ethanol solvate. Similar reactions using $NaBD_3CN$ and $NaBH_3C^{15}N$ under the above conditions were carried out and the appropriately labelled green complex obtained was also purified as discussed above. The reasons for these labelling experiements will be discussed later. This complex shows air stability and the synthesis is reproducible without serious difficulty.

Analysis	Found:	C = 65.47%, H = 5.41%, N = 2.79%
Calc. for $Ni_2(BH_3CN)(CN)(Dppm)_2 \cdot \frac{1}{2}EtOH$		C = 65.27%, H = 5.10%, N = 2.87%

The presence and the amount of EtOH was confirmed by ^{1}H NMR spectrometry. The ethanol could not be removed even by pumping at 10^{-6} Torr. for several hours.

(b) From $NiCl_2 \cdot 6H_2O$/Dppm/$NaBH_3CN$

A solution of $NaBH_3CN$ (0.079 g., 1.25 mM) in ethanol (20 ml) was added (very rapidly over a period of 2 minutes) to a stirred mixture containing $NiCl_2 \cdot 6H_2O$ (0.15 g., 0.63 mM) and Dppm (0.52 g., 1.35 mM) in ethanol (40 ml). The pink solution immediately turned to green upon addition of the $NaBH_3CN$ and the mixture was allowed to stir for 3 hours. After this, the green solid product was filtered from the reaction mixture and the crude product was purified as outlined in section 2.3.1.3a. Analysis, infrared spectra, ^{31}P spectra and deuterium labelling experiments showed this product to be identical to that described in section 2.3.1.3a.

Analysis	Found:	C = 65.35%, H = 5.20%, N = 2.80%
Calc. for $Ni_2(BH_3CN)(CN)(Dppm)_2 \cdot \frac{1}{2}EtOH$		C = 65.27%, H = 5.10%, N = 2.87%

2.3.1.4 Bis(Cyano)tris[bis(diphenylphosphino)methane]dinickel(I)

$Ni_2(CN)_2(Dppm)_3 \cdot 4EtOH$

This product was obtained (low yield) as an ethanol-solvated (analysis and ^{1}H NMR) deep green crystalline solid from the

reaction mixture filtrates of the two reactions described in sections 2.3.1.3a and b above after they were allowed to stand at room temperature for 48 hours. The crystals were filtered off, washed with ethanol (~ 10 ml), and dried under reduced pressure for 24 hours. The product is soluble in EtOH, CH_2Cl_2, benzene, THF, MeOH and DMF to give, initially, a deep green solution. However, after 24 hours, the green solutions obtained from all of these solvents turned to a deep violet, although the EtOH and MeOH solutions seemed the most stable. This compound is reproducible and appears to be air stable in the solid state for a long time. Again, the deuterated product has been prepared using $NaBD_3CN$ and a similar reaction using $NaBH_3C^{15}N$ gave the ^{15}N labelled complex. As before, these labelling experiments were carried out so that unambiguous infrared and structural assignments could be made (see Results and Discussion section).

Analysis	Found:	C = 67.49%, H = 5.08%, N = 1.89%
Calc. for $Ni_2(CN)_2(Dppm)_3 \cdot 4EtOH$		C = 67.76%, H = 5.96%, N = 1.86%

In addition to the above procedure which gave $Ni_2(CN)_2(Dppm)_3 \cdot 4EtOH$ as a minor product, when the reactions in sections 2.3.1.3a and b were allowed to stir for overnight for about 17 hours at room temperature instead of for the 3 hours mentioned in sections 2.3.1.3a and b, then they produced this deep green complex $Ni_2(CN)_2(Dppm)_3 \cdot 4EtOH$ as the major product. This separated directly from the

reaction mixture and was purified as before. The four molecules of ethanol of crystallization were obtained even after drying under high vacuum (10^{-6} Torr.) for 24 hours.

2.3.1.5 Bis(Cyano)bis[bis(diphenylphosphino)methane]dinickel(I)

$Ni_2(CN)_2(Dppm)_2 \cdot EtOH$ and $Ni_2(CN)_2(Dppm)_2 \cdot C_6H_6$.

This complex has been synthesized from room temperature and higher temperature reactions using different molar ratios of $NaBH_3CN$ in the presence of both $Ni(ClO_4)_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$.

(a) From $Ni(ClO_4)_2 \cdot 6H_2O$/Dppm/$NaBH_3CN$

To a stirred suspension containing $Ni(ClO_4)_2 \cdot 6H_2O$ (0.3 g., 0.8 mM) and Dppm (0.63 g., 1.63 mM) in ethanol (20 ml), a solution of $NaBH_3CN$ (0.05 g., 0.79 mM) in ethanol (10 ml) was added dropwise over a period of 2 minutes. The resultant mixture was then left stirring at room temperature for a further 22 hours during which time a pinkish yellow solid precipitated. This was removed by filtration leaving behind a deep violet solution. This violet solution yielded violet crystals after reducing the volume of solvent by evaporation under reduced pressure. The same violet crystals could also be obtained from washing the pinkish yellow solid mentioned above with a variety of solvents (e.g. ethanol, methanol, or benzene).

These violet crystals, though reproducible from one experiment to another, were actually a mixture of complexes (see

Results and Discussion) and final purification was effected by several recrystallizations from ethanol, methanol, or benzene. The crystals of $Ni_2(CN)_2(Dppm)_2 \cdot EtOH$ so obtained were dried under reduced pressure for 24 hours.

This complex is air stable and soluble in all common solvents in which it is stable for about 48 hours. Thereafter, the solutions turned brown. As with the Dppm complexes described earlier, the deuterated (from $NaBD_3CN$) and ^{15}N labelled violet complexes were prepared in the manner outlined above. It was found that $Ni_2(CN)_2(Dppm)_2$ always forms a solvate on recrystallization and the solvent of crystallization remains, even after drying under high vacuum for 24 hours. The presence of the solvent was confirmed by ^1H NMR(EtOH) or mass spectrometry (C_6H_6). Again, this complex is easily reproducible.

Analysis	Found:	C = 65.86%, H = 4.93%, N = 2.74% Molecular Weight = 957
Calc. for $Ni_2(CN)_2(Dppm)_2 \cdot EtOH$		C = 65.89%, H = 5.08%, N = 2.84% Molecular Weight = 983.32
	Found:	C = 68.23%, H = 4.97%, N = 2,60%
Calc. for $Ni_2(CN)_2(Dppm)_2 \cdot C_6H_6$		C = 68.54%, H = 4.92%, N = 2.75%

(b) From $NiCl_2 \cdot 6H_2O$/Dppm/$NaBH_3CN$ (a higher temperature reaction

An ethanolic solution (20 ml) of $NaBH_3CN$ (0.316 g.,

5.02 mM) was added over a period of 5 minutes to a stirred mixture of $NiCl_2 \cdot 6H_2O$ (0.15 g., 0.63 mM) and Dppm (0.519 g., 1.35 mM) in ethanol (40 ml) and the resultant mixture was allowed to stir for one hour at 77°C. After this, the heating was stopped and the solution was stirred at room temperature for a further 4 hours, during which time a small amount of purple solid was formed. This was filtered off from the reaction mixture and washed with a very little ethanol and n-hexane. The crude product was purified as discussed in section (a) above and the purified product shows the same spectroscopic and analytical features as the product $Ni_2(CN)_2(Dppm)_2$ reported in section 2.3.1.5a above.

Analysis	Found:	C = 65.47%, H = 4.93%, N = 2.74%
Calc. for $Ni_2(CN)_2(Dppm)_2 \cdot EtOH$		C = 65.89%, H = 5.08%, N = 2.84%
	Found:	C = 68.46%, H = 4.95%, N = 2.65%
Calc. for $Ni_2(CN)_2(Dppm)_2 \cdot C_6H_6$		C = 68.54%, H = 4.92%, N = 2.75%

2.3.2 Ni(II)/Diphos/$NaBH_3CN$ reactions

A number of reactions under different conditions have been carried out for both the $Ni(ClO_4)_2 \cdot 6H_2O$/Diphos/$NaBH_3CN$ and $NiCl_2 \cdot 6H_2O$/Diphos/$NaBH_3CN$ systems in a single solvent or in mixed solvents at room temperature or higher temperatures. Several

interesting complexes derived from these reactions have been reasonably well characterized and experimental details are summarized below.

2.3.2.1. Hydridobis[bis(1,2-diphenylphosphino)ethane]nickel(II) perchlorate.

$[NiH(Diphos)_2]ClO_4$

$NaBH_3CN$ (0.26 g., 4.07 mM) in ethanol (20 ml) was added dropwise over a period of 15 minutes to a stirred mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.75 g., 2.05 mM) in toluene/ethanol (10 ml, 1:1) and Diphos (2.45 g., 6.15 mM) in toluene (20 ml). The reaction mixture was stirred for a further 21 hours at room temperature under N_2, during which time an orange red solid was precipitated. This was filtered off leaving a wine red filtrate which was set aside. The crude solid product was washed with toluene (~ 5 ml) ethanol (~ 5 ml) and finally n-hexane (~ 5 ml) and then dried under reduced pressure for several hours. The complex, characterized as $[NiH(Diphos)_2]ClO_4$, is air stable and soluble in CH_2Cl_2, $CHCl_3$, THF, DMF and acetone to give solutions which are stable for up to 12 hours. After several days, a second crop of this complex was obtained from the filtrate which had been set aside at room temperature as mentioned above. The synthesis is reproducible.

Analysis	Found:	C = 65.37%, H = 5.20%
Calc. for $[NiH(Diphos)_2]ClO_4$		C = 65.32%, H = 5.12%

Note: A similar hydride of formula $[NiH(Diphos)_2]BH_3CN$ has been prepared in related reactions but only as a side reaction product. This will therefore be reported later at the appropriate point.

2.3.2.2 Tris(Cyanotrihydroborato)bis[bis(1,2-diphenylphosphino) ethane] dinickel(II) chloride or perchlorate

$[Ni_2(BH_3CN)_3(Diphos)_2]X$ where X = Cl^- or ClO_4^-

This type of complex has been synthesized both from $Ni(ClO_4)_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ using a different molar ratio of $NaBH_3CN$ and a different reaction time although both reactions were at room temperature. The complexes appear to be air stable in the solid state for a long time and the syntheses were found to be reproducible. The individual experimental procedures are described below.

(a) From $Ni(ClO_4)_2 \cdot 6H_2O$/Diphos/$NaBH_3CN$

To a stirred yellow mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.98 g., 2.68 mM) in ethanol (20 ml) and Diphos (1.96 g., 4.92 mM) in ethanol (20 ml) was added $NaBH_3CN$ (1.5 g., 23.8 mM) in ethanol (20 ml) over a period of 2 minutes. The resultant mixture was then allowed to stir for a further 30 minutes, during which time a yellow solid was

deposited. This was filtered off and the wine red filtrate set aside (see section 2.3.2.3) for further examination. The solid was washed with ethanol (~ 10 ml) and n-hexane (~ 10 ml). The crude $[Ni_2(BH_3CN)_3(Diphos)_2]ClO_4$ thus obtained was purified by precipitation from CH_2Cl_2 with rapid addition of n-hexane followed by drying under reduced pressure. The complex is soluble in CH_2Cl_2, $CHCl_3$, THF and DMF but decomposes in all solvents fairly rapidly giving brown solutions from the initially yellow solutions. Immediate decomposition occurs in DMF. A synthesis of this complex using $NaBD_3CN$ was carried out and the infrared spectrum of the deuterated product will be discussed at length later in this thesis.

Analysis	Found:	C = 61.79%, H = 5.32%, N = 4.05%
Calc. for $[Ni_2(BH_3CN)_3(Diphos)_2]ClO_4$		C = 61.44%, H = 5.30%, N = 3.91%

(b) From $NiCl_2 \cdot 6H_2O$/Diphos/$NaBH_3CN$

$NiCl_2 \cdot 6H_2O$ (0.5 g., 2.10 mM) and Diphos (1.67 g., 4.20 mM) were mixed in ethanol (20 ml) to give immediately a pink solution. While stirring this solution, an ethanolic solution (10 ml) of $NaBH_3CN$ (0.224 g., 3.57 mM) was added dropwise over a period of 4 minutes. The resultant mixture was then stirred for a further 3 hours at room temperature during which period the yellow $[Ni_2(BH_3CN)_3(Diphos)_2]$-Cl precipitated. This was filtered off leaving behind a wine red solution. The yellow solid was purified as described for

$[Ni_2(BH_3CN)_3(Diphos)_2]ClO_4$ by precipitation from $CH_2Cl_2$with rapid addition of n-hexane (slow addition allows decomposition of the complex). This yellow complex shows virtually the same spectroscopic and chemical behaviour as the complex $[Ni_2(BH_3CN)_3(Diphos)_2]ClO_4$ described in section 2.3.2.2a. It is a weak electrolyte in solution. Again, the deuterated complex $[Ni_2(BD_3CN)_3(Diphos)_2]Cl$ was prepared for infrared analysis.

Analysis	Found:	C = 61.70%, H = 5.34%, N = 3.95%
		Cl = 3.34%
Calc. for $[Ni_2(BH_3CN)_3(Diphos)_2]Cl$		C = 61.74%, H = 5.33%, N = 3.92%
		Cl = 3.32%

(c) From $NiCl_2 \cdot 6H_2O$/Diphos/$NaBH_3CN$ (large excess)

$NaBH_3CN$ (0.93 g., 14.71 mM) in ethanol (10 ml) was added dropwise over a period of 5 minutes to a stirred mixture of $NiCl_2 \cdot 6H_2O$ (0.5 g., 2.10 mM) and Diphos (1.64 g., 4.20 mM) in ethanol (20 ml). After complete addition of the $NaBH_3CN$, the mixture was allowed to stir for a further 4½ hours. A yellow solid was separated from the reaction mixture and purified as in section 2.3.2.2a. This yellow solid proved to be $[Ni_2(BH_3CN)_3(Diphos)_2]Cl$, identical to that prepared in (b) above.

Analysis	Found:	C = 61.70%, H = 5.37%, N = 3.96%
Calc. for $[Ni_2(BH_3CN)_3(Diphos)_2]Cl$		C = 61.74%, H = 5.33%, N = 3.92%

2.3.2.3 Hydridobis[bis(1,2-diphenylphosphino)ethane]nickel(II) Cyanotrihydroborate

$[NiH(Diphos)_2]BH_3CN$

From the wine red filtrate of the reaction mixture referred to in section 2.3.2.2a, a wine red crystalline solid identified as $[NiH(Diphos)_2]BH_3CN$ separated after 24 hours at room temperature. The crystals were filtered off and washed with ethanol (~ 5 ml) followed by n-hexane and then dried under reduced pressure for several hours. The crystals were purified by careful precipitation from CH_2Cl_2 with addition of n-hexane (1:1). The crystalline solid is soluble in CH_2Cl_2, THF, $CHCl_3$, DMF and acetone in which solvents it is stable for 24 hours. This complex appears to be air stable in the solid state. A deuterated version of the complex $[NiD(Diphos)_2]BD_3CN$, has also been synthesized using $NaBD_3CN$.

Analysis	Found:	C = 71.05%, H = 5.79%, N = 1.58%
Calc. for $[NiH(Diphos)_2]BH_3CN$		C = 71.10%, H = 5.84%, N = 1.60%

2.3.2.4 Bis(Cyanotrihydroborato)tetrakis[bis(1,2-diphenylphosphino)-ethane] dinickel(II) dichloride

$Ni_2(BH_3CN)_2(Diphos)_4Cl_2$

To a stirred mixture of $NiCl_2 \cdot 6H_2O$ (0.5 g., 2.10 mM) in ethanol (20 ml) and Diphos (1.67 g., 4.20 mM) in ethanol (20 ml), was added $NaBH_3CN$ (0.925 g., 14.72 mM) in ethanol (20 ml) over a period of 10 minutes. The mixture thus obtained was then left for further stirring for 48 hours, during which time a number of colour changes occurred. The reaction mixture was initially brown, it changed to orange after 18 hours, to green after 36 hours, and finally to greenish yellow. A greenish yellow solid was filtered off, washed with ethanol (~ 10 ml) and then with n-hexane (~ 5 ml). The solid was then left for drying under reduced pressure for 24 hours. The crude $Ni_2(BH_3CN)_2$-$(Diphos)_4Cl_2$ so obtained is soluble in CH_2Cl_2, $CHCl_3$, THF and DMF and the resulting solutions were found to be stable for several hours. The crude product was purified by recrystallization from CH_2Cl_2 (very carefully) with addition of n-hexane. The addition of n-hexane had to be such as to maintain a constant volume of solution and a constant time interval between the additions, otherwise decomposition occurred. The complex is air stable in the solid state and is a non-electrolyte in methylene chloride. As with previous complexes, this synthesis is reproducible.

Analysis	Found:	C = 68.53%, H = 5.54%, N = 1.52%
		Cl = 4.80%
		Molecular Weight = 1845
Calc. for $Ni_2(BH_3CN)_2(Diphos)_4Cl_2$		C = 68.38%, H = 5.48%, N = 1.50%
		Cl = 4.85%
		Molecular Weight = 1860.26

2.3.2.5 Bis(Cyanotrihydroborato)bis[bis(1,2-diphenylphosphino) ethane]dinickel(II) dichloride

$Ni_2(BH_3CN)_2(Diphos)_2Cl_2 \cdot EtOH$

An ethanolic solution (20 ml) of $NaBH_3CN$ (0.93 g., 14.72 mM) was added dropwise over a period of 5 minutes to a stirred mixture of $NiCl_2 \cdot 6H_2O$ (0.5 g., 2.10 mM) and Diphos (1.67 g., 4.20 mM) in ethanol (40 ml). The mixture was then heated at 55°C for a further 30 minutes. The mixture initially was pink but this changed to brown after complete addition of $NaBH_3CN$. After heating the mixture, a dark brown suspension was obtained from which a yellow orange solid $Ni(Diphos)_2$ was separated by filtration. The remaining dark brown solution was allowed to stand in the refrigerator at 0°C for 5 days during which time brown crystals were formed. These were filtered off, washed with ethanol (~ 10 ml) and then with n-hexane (~ 5 ml), and then dried under high vacuum for several hours. The solid was purified

by recrystallization from CH_2Cl_2 with slow addition of n-hexane in the usual manner. The complex $Ni_2(BH_3CN)_2(Diphos)_2Cl_2$ so obtained as an ethanol solvate (IR, ^1H NMR and analysis) is soluble in CH_2Cl_2, $CHCl_3$, THF and has some solution stability. An identical synthesis using $NaBD_3CN$ has been carried out for this complex for the usual spectroscopic reasons to be discussed later. The complex retains a molecule of ethanol even after drying for 24 hours under high vacuum (10^{-6} Torr.). It appears to be air stable indefinitely and is a non-electrolyte in freshly prepared solutions in methylene chloride.

Analysis	Found:	C = 60.65%, H = 5.50%, N = 2.40%
		Cl = 6.60%
		Molecular Weight = 1085
Calc. for $Ni_2(BH_3CN)_2(Diphos)_2Cl\cdot EtOH$		C = 60.45%, H = 5.39%, N = 2.51%
		Cl = 6.67%
		Molecular Weight = 1110.34

2.3.2.6 Bis[bis(1,2-diphenylphosphino)ethane]nickel(0)

$Ni(Diphos)_2$

This known (9,20) complex has been synthesized from $Ni(BF_4)_2\cdot 6H_2O$, $Ni(ClO_4)_2\cdot 6H_2O$ and $NiCl_2\cdot 6H_2O$ reactions with Diphos in the presence of $NaBH_3CN$ at room temperature and elevated temperature.

Almost all filtrates of the reactions described for Diphos so far finally yielded this complex as very fine orange crystals. However, only one typical experimental procedure leading directly to $Ni(Diphos)_2$ will be discussed. This reaction was carried out at higher temperature and, indeed, this complex was found to be more easily formed at elevated temperatures.

$Ni(BF_4)_2 \cdot 6H_2O$ (0.5 g., 1.46 mM) in ethanol (10 ml) and Diphos (1.67 g., 4.20 mM) in ethanol (10 ml) were mixed and then an ethanolic solution (10 ml) of $NaBH_3CN$ (0.92 g. , 14.72 mM) was added to this stirred mixture over a period of 3 minutes. The resultant mixture was then heated to 67°C. Initially, the yellow solid formed after the addition dissolved to give a red solution but, after 15 minutes, some orange solid appeared. Stirring of this heated suspension was continued for a further 15 minutes. The orange solid was filtered off, washed with ethanol (~ 5 ml) and then with n-hexane (~ 5 ml), and finally dried under reduced pressure overnight. The $Ni(Diphos)_2$ so obtained was found to be soluble and relatively stable in CH_2Cl_2, $CHCl_3$, THF, DMF and CH_3CN under nitrogen but the solid complex is air sensitive.

Analysis	Found:	C = 72.98%, H = 5.63%
Calc. for $Ni(Diphos)_2$		C = 73.00%, H = 5.60%

2.3.2.7 Unidentified complex

$NiCl_2 \cdot 6H_2O$ (0.5 g., 2.10 mM) and Diphos (1.67 g., 4.20 mM) were mixed in ethanol (40 ml) and the stirred mixture was heated to boiling. To this stirred and boiling mixture, an ethanolic solution (20 ml) of $NaBH_3CN$ (0.93 g., 14.72 mM) was added dropwise over 5 minutes. The resultant mixture was then further stirred for 17 hours at 76°C. After cooling the mixture to room temperature and stirring for a further 5½ hours, a yellow orange solid, $Ni(Diphos)_2$, was obtained. This was filtered off leaving behind a deep brown filtrate. This deep brown filtrate was evaporated under reduced pressure to reduce the volume and then allowed to stand in the refrigerator at 0°C for several days, during which time a pale yellow solid (very small yield) precipitated. This was separated from the solution and washed with ethanol (~ 5 ml) and n-hexane (~ 5 ml). The yield was so low that further purification by recrystallization could not be carried out. The solid appears to be very air sensitive and decomposes in air within one hour to give a green product. Analyses (several samples) for carbon, hydrogen and nitrogen, always show an unusually high percentage of nitrogen. The complex is reproducible, but always a very low yield was obtained. The infrared spectrum shows the presence of CN groups but final characterization was not carried out (see Results and Discussion).

Analysis Found: C = 49.13%, 46,07%, H = 4.00%, 4.06%, N = 7.77%, 7.63%

2.3.3 Ni(II)/Dppp/$NaBH_3CN$ reactions

This system has not been investigated as thoroughly as were the corresponding Dppm and Diphos systems already discussed. However, a number of exploratory reactions have been carried out on this system and some interesting products have been obtained. The stoichiometric compositions of these complexes have, for the most part, been well established but detailed structural assignments are only tentative as outlined in the Results and Discussion section. These tentative structural assignments form the basis of the subsection headings which follow:

2.3.3.1 Tetrakis(Cyanotrihydroborato)bis[bis(1,3-diphenylphosphino) propane] dinickel (II)

$[Ni(BH_3CN)_2(Dppp)]_2$

This compound has been synthesized both from $Ni(ClO_4)_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ reactions using the same molar ratio of $NaBH_3CN$ but different reaction times.

(a) From $Ni(ClO_4)_2 \cdot 6H_2O/Dppp/NaBH_3CN$

A solution of $NaBH_3CN$ (0.92 g., ~15 mM) in EtOH/toluene (10 ml, 1:1) was added over 2 minutes to a stirred mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.96 g., 2.61 mM) in EtOH toluene (10 ml, 1:1) and Dppp (2.94 g. 7.13 mM) in EtOH/toluene, (20 ml, 1:1) under nitrogen. The colour of the mixture was initally dark purple but this turned to light yellow after complete addition of $NaBH_3CN$. The mixture was then left stirring for a further 2 ½ hours at room temperature. The resulting light yellow solid which precipitated was then filtered off leaving behind a blood red filtrate. The crude product was washed with ethanol (~ 5 ml), toluene (~ 5 ml) and finally with n-hexane (~ 10 ml). The yellow $[Ni(BH_3CN)_2(Dppp)]_2$ appeared to be partly soluble in CH_2Cl_2, $(CH_3)_2CO$, THF, $CHCl_3$, DMF and CH_3CN but rapid decomposition occurred in all of these solvents. The crude product was, however, purified by recrystallization from CH_2Cl_2 with n-hexane (very slow addition). The yield of 30% was comparable with that of other complexes reported so far. In the solid state the complex is air stable for at least short periods.

As with the other BH_3CN^- complexes, the corresponding BD_3CN^- complex was prepared for spectroscopic analysis. After a few days, the blood red filtrate referred to above yielded orange coloured crystals and more will be said about them later in this section.

Analysis	Found:	C = 63.62%, H = 6.01%, N = 4.96%
Calc. for $[Ni(BH_3CN)_2(Dppp)]_2$		C = 63.29%, H = 5.81%, N = 5.08%

(b) From $NiCl_2 \cdot 6H_2O$/Dppp/$NaBH_3CN$

$NiCl_2 \cdot 6H_2O$ (0.3 g., 1.25 mM) in ethanol (10 ml) and Dppp (1.04 g., 2.52 mM) in toluene (20 ml) were mixed to yield a pink solution. To this solution, an ethanolic solution (10 ml) of $NaBH_3CN$ (0.56 g. , 8.83 mM) was added very rapidly over about 2 minutes with stirring under N_2. The resultant mixture was then stirred for 1 hour. A yellow solid separated from the mixture and this was washed with toluene (~ 10 ml), ethanol (~ 10 ml) and with n-hexane (~ 10 ml). This yellow solid was found to be identical to the complex $[Ni(BH_3CN)_2(Dppp)]_2$ reported in section 2.3.3.1a above.

Analysis	Found:	C = 62.95%, H = 5.69%, N = 4.87%
Calc. for $[Ni(BH_3CN)_2(Dppp)]_2$		C = 63.29%, H = 5.81%, N = 5.08%

2.3.3.2 Dihydridotetrakis[bis(1,3-diphenylphosphino)propane]dinickel (II) cyanotrihydroborate perchlorate

$Ni_2H_2(Dppp)_4(BH_3CN)(ClO_4)$ (see section 3.4.2 regarding dimeric formulation)

The compound has been synthesized from $Ni(ClO_4)_2 \cdot 6H_2O$

by using the same amount of $NaBH_3CN$ in a variety of reaction conditions. Typical syntheses are given below.

(a) From Fast addition of $NaBH_3CN$

To a stirred mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.96 g., 2.61 mM) and Dppp (2.94 g. , 7.14 mM) in ethanol/toluene (30 ml, 1:1) was added $NaBH_3CN$ (2.23 g. , 35.46 mM) in ethanol/toluene (10 ml, 1:1) over a period of 2 minutes. The resultant solution was left to stir for a further 21 hours during which time a lemon yellow precipitate was formed. This was filtered off from the reaction mixture and the crude product was washed with ethanol (~ 5 ml), toluene (~ 5 ml) and n-hexane (~ 10 ml). This crude product could not be purified by recrystallization from any of the common solvents CH_2Cl_2, $CHCl_3$, THF, DMF, ethanol, acetone or toluene because of too high a solubility.

(b) From slow addition of $NaBH_3CN$

An ethanolic solution (10 ml) of $NaBH_3CN$ (2.23 g., 35.46 mM) was added very slowly over a period of 15 minutes to a stirred mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.96 g., 2.16 mM) in ethanol/toluene (30 ml, 1:2) under N_2. The resultant solution was then stirred for 2 ½ hours during which time the lemon yellow $Ni_2H_2(Dppp)_4(BH_3CN)(ClO_4)$ precipitated. This was filtered off from the reaction mixture

leaving behind a blood red filtrate. The spectroscopic and other characteristics of this compound were found to be the same as those of the compound discussed in section 2.3.3.2a.

The filtrate, after a few days, yielded orange crystals of another product which is discussed in the following subsection.

Analysis	Found:	C = 69.17%, H = 5.65%, N = 0.62%
Calc. for	$Ni_2H_2(Dppp)_4(BH_3CN)(ClO_4)$	C = 68.70%, H = 5.72%, N = 0.73%

2.3.3.3 Bis[bis(1,3-diphenylphosphino)propane]nickel(0)

$Ni(Dppp)_2$

This complex was obtained (ca.40% yield) after a few days as orange crystals from almost all filtrates of the reactions which have been carried out for the Ni(II)/Dppp/$NaBH_3CN$ system, and which have been described above. This indicates that, in the presence of the Dppp ligand, reduction of Ni(II) to Ni(0) with the mild reducing agent $NaBH_3CN$ was found to be easier than with the Diphos ligand. In contrast Dppm seems to cause rapid reduction to Ni(I) and these points will be discussed at the appropriate point later in this thesis. This orange crystalline compound was found to be air sensitive in the solid state but stable in chlorinated solvents for a considerable time under N_2.

Analysis	Found:	C = 73.31%, H = 5.91%
Calc. for $Ni(Dppp)_2$		C = 73.41%, H = 5.89%

2.3.4 Ni(II)/Dppb/$NaBH_3CN$ reactions

These reactions were again of an exploratory nature and the remarks made at the beginning of section 2.3.3 for Dppp reactions apply here also.

2.3.4.1 Cyanotrihydroboratobis[bis(1,4-diphenylphosphino)butane] nickel(II) perchlorate

$[Ni(BH_3CN)(Dppb)_2]ClO_4$

An ethanolic solution (10 ml) of $NaBH_3CN$ (0.42 g., 6.5 mM) was added over about 10 minutes to a stirred mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.30 g., 0.82 mM) in ethanol (10 ml) and Dppb (1.05 g., 2.45 mM) in benzene (10 ml) which prior to the addition of $NaBH_3CN$ had been already stirred for about 15 minutes. The resultant mixture was left to stir for one hour under N_2. The orange-red solid which appeared was filtered off leaving behind a deep pink solution which yielded a further crop as light orange red crystals upon addition of n-hexane. The crude product was washed with ethanol (~ 10 ml),

benzene (~ 5 ml), and finally with n-hexane. The crude product was recrystallized from benzene by slow addition of n-hexane. The resulting pure solid $[Ni(BH_3CN)(Dppb)_2]ClO_4$ was found to be moderately stable in air in the solid state and soluble in benzene, THF, CH_2Cl_2, $CHCl_3$, CH_3CN and DMSO with very limited solution stability.

Analysis	Found	C = 68.41%, H = 6.21%, N = 1.57%
Calc. for $[Ni(BH_3CN)(Dppb)_2]ClO_4$		C = 68.98%, H = 5.95%, N = 1.41%

2.3.4.2 Tetrakis(Cyanotrihydroborato)bis[bis(1,4-diphenylphosphino)-butane] dinickel(II)

$[Ni(BH_3CN)_2(Dppb)]_2$

This complex has been synthesized from both $Ni(ClO_4)_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ reactions with $NaBH_3CN$ in the presence of the phosphine. Details are given below. The complex is air stable in the solid state. As with some complexes previously described in this thesis , the syntheses below were repeated using $NaBD_3CN$ for the spectroscopic reasons already outlined.

(a) From $Ni(ClO_4)_2 \cdot 6H_2O$/Dppb/$NaBH_3CN$

To a previously well stirred (15 minutes) mixture of

$Ni(ClO_4)_2 \cdot 6H_2O$ (0.3 g., 0.8 mM) in ethanol (10 ml) and Dppb (1.05 g., 2.45 mM) in benzene (10 ml) was added an ethanolic solution (10 ml) of $NaBH_3CN$ (0.41 g., 6.55 mM) very rapidly. As soon as the addition of $NaBH_3CN$ was complete, a deep yellow precipitate was formed and this was immediately filtered off from the reaction mixture, washed with ethanol (~ 5 ml), benzene (~ 50 ml), and finally with n-hexane (~ 5 ml). The product, $[Ni(BH_3CN)_2(Dppb)]_2$, was recrystallized from CH_2Cl_2 by very rapid addition of n-hexane, yielding a yellow solid soluble only in CH_2Cl_2 and $CHCl_3$. There are significant spectroscopic differences between the freshly precipitated and washed material and the recrystallized material which suggest that the former is the dimeric structure $[Ni(BH_3CN)_2(Dppb)]_2$ while the latter may be monomeric $Ni(BH_3CN)_2(Dppb)$. This is discussed in section 3 of this thesis.

Analysis		
	Found	C = 64.33%, H = 6.12%, N = 4.37%
Calc. for $[Ni(BH_3CN)_2(Dppb)]_2$		C = 63.75%, H = 6.01%, N = 4.55%

(b) From $NiCl_2 \cdot 6H_2O$/Dppb/$NaBH_3CN$

A mixture of $NiCl_2 \cdot 6H_2O$ (0.30 g., 1.20 mM) and Dppb (1.07 g., 2.51 mM) in ethanol/benzene, 1:1 (20 ml) was stirred for about 10 minutes. An ethanolic solution (10 ml) of $NaBH_3CN$ (0.24 g., 3.77 mM) was then added very rapidly over a period of 2 minutes and the resultant mixture was stirred for a further 30

minutes. A deep yellow solid appeared and this was separated from the reaction mixture and washed free of impurities as in section 2.3.4.2a above. This product is spectroscopically identical like to that obtained by the method outlined in section 2.3.4.2a.

Analysis	Found	C = 63.85%, H = 6.09%, N = 4.50%
Calc. for $[Ni(BH_3CN)_2(Dppb)]_2$		C = 63.75%, H = 6.01%, N = 4.55%

As mentioned in section 2.3.4.2a, the recrystallized material is spectroscopically different from the freshly precipitated material. Also, it crystallizes with one molecule of solvent per monomeric unit (confirmed by ^1H NMR spectrum).

Analysis	Found	C = 56.77%, H = 5.62%, N = 3.98%
Calc. for $Ni(BH_3CN)_2(Dppb)\cdot CH_2Cl_2$		C = 56.01%, H = 5.42%, N = 4.20%

2.3.5 Ni(II)/cis-Dppe/$NaBH_3CN$ reactions

Only a few exploratory reactions have been carried out on this system. From them, only two characterizable compound (containing Ni(II) and Ni(0) respectively) have been obtained so far. Once again, assignments of structures are tentative.

2.3.5.1 Bis(Cyanotrihydroborato)[cis-bis(1,2-diphenylphosphino) ethylene] nickel(II)

$Ni(BH_3CN)_2$(cis-Dppe)

This complex has been synthesized from both the $Ni(ClO_4)_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ reactions as reported below. The complex is air stable and diamagnetic. The compound is stable in CH_2Cl_2, THF and $CHCl_3$ solution for several hours.

(a) From $Ni(ClO_4)_2 \cdot 6H_2O$/cis-Dppe/$NaBH_3CN$

$Ni(ClO_4)_2 \cdot 6H_2O$ (0.15 g., 0.4 mM) in ethanol (10 ml) and cis-Dppe (0.32 g., 0.81 mM) in ethanol (10 ml) were mixed and stirred magnetically. To this stirred mixture, a solution of $NaBH_3CN$ (0.21 g., 3.27 mM) in ethanol was added dropwise over a period of 2 minutes. After this addition, the mixture was stirred for a further 30 minutes during which time a brown solid was deposited. This solid was removed by filtration, and then washed with ethanol (~ 5 ml), benzene (~ 5 ml) and n-hexane (~ 10 ml). The brown $Ni(BH_3CN)_2$(cis-Dppe) so obtained is soluble in CH_2Cl_2, THF, $CHCl_3$, DMF, acetone and DMSO. The crude product was purified by recrystallization from CH_2Cl_2 by addition of n-hexane. The complex appears to be (see Discussion) a simple monomeric cis-square planar Ni(II) system.

Analysis	Found:	C = 62.80%, H = 5.20%, N = 5.21%
Calc. for $Ni(BH_3CN)_2$(cis-Dppe)		C = 62.83%, H = 5.23%, N = 5.23%

(b) From $NiCl_2 \cdot 6H_2O$/cis-Dppe/$NaBH_3CN$

To a stirred mixture of $NiCl_2 \cdot 6H_2O$ (0.15 g., 0.63 mM) in ethanol (10 ml) and cis-Dppe (0.8 g., 1.19 mM) in ethanol (10 ml), an ethanolic solution (10 ml) of $NaBH_3CN$ (0.32 g., 5.04 mM) was added very rapidly (2 minutes). The mixture was then left to stir for a further 30 minutes and a brown solid was deposited. Prior to drying under reduced pressure, this solid was washed with ethanol (~ 5 ml), benzene (~ 10 ml) and finally n-hexane (~ 10 ml). The crude $Ni(BH_3CN)_2$(cis-Dppe) was purified by recrystallization from CH_2Cl_2 with n-hexane as outlined in part (a) above.

Analysis	Found:	C = 62.68%, H = 5.10%, N = 5.08%
Calc. for $Ni(BH_3CN)_2$(cis-Dppe)		C = 62.83%, H = 5.23%, N = 5.23%

2.3.5.2 Ni(cis-Dppe)$_2$

An ethanolic solution (10 ml) of $NaBH_3CN$ (0.21 g., 3.27 mM) was added dropwise during 2 minutes to a stirred mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.15 g., 0.409 mM) and cis-Dppe (0.32 g., 0.81 mM) in ethanol (20 ml). The mixture was left to stir overnight, after which the orange solid crude product was filtered off, and purified by washing with ethanol (~ 5 ml) followed by n-hexane (~ 5 ml).

This compound is soluble in the common chlorinated solvents and is air sensitive.

Analysis	Found:	C = 73.50%, H = 5.10%
Calc. for Ni(cis-Dppe)		C = 73.35%, H = 5.17%

2.3.6 Ni(II)/trans-Dppe/$NaBH_3CN$ reactions

Again this system has not been investigated extensively and only a few trial reactions have been carried out. Two characterized products have been obtained and structural assignments are tentative.

2.3.6.1 Tetrakis(Cyanotrihydroborato)bis[trans-bis(1,2-diphenylphosphino) ethylene] dinickel(II)

$[Ni(BH_3CN)_2(trans\text{-}Dppe)]_2$

This complex has been synthesized from both $Ni(ClO_4)_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ reactions as follows. It is air stable in the solid state and diamagnetic.

(a) From $Ni(ClO_4)_2 \cdot 6H_2O$/trans -Dppe/$NaBH_3CN$

$Ni(ClO_4)_2 \cdot 6H_2O$ (0.15 g., 0.409 mM) in ethanol(10 ml) and trans-Dppe (0.32 g., 0.81 mM) in toluene (10 ml) were mixed and magnetically stirred. An ethanolic solution (10 ml) of $NaBH_3CN$ (0.21 g., 3.2 mM) was then added dropwise over a period of 2 minutes to that stirred solution. The mixture was stirred for one more hour during which time a small amount of yellow (~ 20%) product precipitated. This was separated by filtration and was washed with ethanol (~ 5 ml), toluene (~ 5 ml), and finally n-hexane (~ 5 ml). The crude $[Ni(BH_3CN)_2(trans\text{-}Dppe)]_2$ so obtained was purified by precipitation from CH_2Cl_2 solution by addition of n-hexane. Yields of this complex were always low.

Analysis	Found:	C = 62.53%, H = 5.32%, N = 5.12%
		Molecular Weight = 1020
Calc. for $[Ni(BH_3CN)_2(trans\text{-}Dppe)]_2$		C = 62.83%, H = 5.23%, N = 5.23%
		Molecular Weight = 1029.42

(b) From $NiCl_2 \cdot 6H_2O$/trans-Dppe/$NaBH_3CN$

To a stirred mixture of $NiCl_2 \cdot 6H_2O$ (0.15 g., 0.63 mM) in ethanol (10 ml) and trans-Dppe (0.50 g., 1.26 mM) in toluene (10 ml), was added an ethanolic solution (10 ml) of $NaBH_3CN$

(0.32 g., 5.04 mM) dropwise over 2 minutes. The resulting mixture was then stirred for one more hour, during which time a small amount of yellow solid (~ 15%) was formed. This was isolated and purified as in (a) above. [The $Ni(BH_3CN)_2(\underline{trans}\text{-Dppe})]_2$ is soluble in CH_2Cl_2, $CHCl_3$, THF, DMF, DMSO and acetone.

Analysis	Found:	C = 62.80%, H = 5.38%, N = 5.37%
Calc. for $[Ni(BH_3CN)_2(\underline{trans}\text{-Dppe})]_2$		C = 62.83%, H = 5.23%, N = 5.23%

2.3.6.2 "$Ni(\underline{trans}\text{-Dppe})_2$"

This above complex was isolated as orange crystals from the reaction mixture filtrates (blood red) of reactions a) and b) in section 2.3.6.1 above after allowing them to stand at room temperature for a few days. This complex is insoluble in ethanol but is stable in the common chlorinated solvents under N_2. It is air sensitive in the solid state.

Analysis	Found:	C = 73.57%, H = 5.63%
Calc. for "$Ni(\underline{trans}\text{-Dppe})_2$"		C = 73.35%, H = 5.17%

3. RESULTS AND DISCUSSION

3.1 Introduction

As stated at the end of section 1, the investigation reported in the following pages is a detailed study of behaviour of Ni(II) towards $NaBH_3CN$ in the presence of a variety of bis-phosphines and under a variety of conditions. Several reasons were given in section 1 as to why this particular system was chosen for investigation.

Of the six bis-phosphines initially chosen for the study (Dppm, Diphos, Dppp, Dppb, cis-Dppe, and trans-Dppe), only reactions of the first two listed with $NiCl_2 \cdot 6H_2O$ or $Ni(ClO_4)_2 \cdot 6H_2O$ in the presence of $NaBH_3CN$ were studied thoroughly, although a number of similar exploratory reactions were carried out with the remaining four bis-phosphines. The reasons for this were two-fold. First, both Dppm and Diphos produced, with these nickel salts and $NaBH_3CN$, an unexpectedly wide variety of product types depending upon the nickel salt used and the conditions employed for the reactions. Clearly, these had to be thoroughly characterized and the interrelationships between the various products for each phosphine had to be established as far as possible before starting new work. Second, while some of the product types obtained with the remaining bis-phosphines were similar to those obtained with Diphos they were, in general, totally different from those obtained with Dppm and the differences between

the behaviour of these two phosphines had to be clarified. Furthermore, even though some structural similarities exist between the Diphos products and those of the remaining bis-phosphines, it proved easier to work with the Diphos systems to establish what are, in some cases, quite unusual and unexpected structural types.

In the opinion of this author, therefore, it seemed desirable to establish accurate structural and mechanistic information for the Ni(II) |Dppm and Diphos| $NaBH_3CN$ systems from which extrapolations might be made later to the behaviour of the remaining bis-phosphines under similar conditions.

The results obtained with the various systems studied are presented and discussed in the following subsections.

3.2 Reactions of Ni(II), Dppm, and $NaBH_3CN$

From the many reactions carried out in this study between either $Ni(ClO_4)_2 \cdot 6H_2O$ or $NiCl_2 \cdot 6H_2O$ with Dppm and $NaBH_3CN$, four major products have been characterized and their structures reasonably firmly established. Three of the four compounds can be synthesized from both $Ni(ClO_4)_2 \cdot 6H_2O$ and $NiClO_2 \cdot 6H_2O$ under a variety of conditions which include variations in the amount of $NaBH_3CN$ used, the reaction time, and the temperature of the reactions. These three compounds are found to be very interesting in that they are Ni(I)

species with structures and properties which are unexpected by analogy with other $NaBH_3CN$ transition metal reactions in the literature. The fourth compound characterized is a nickel (II) species which can only be synthesized from $Ni(ClO_4)_2 \cdot 6H_2O$.

The behaviour of the Ni(II) | Dppm | BH_3CN system was found to be very sensitive to the amount of $NaBH_3CN$ added and the nature of the Ni(II) salts used in a particular reaction. Furthermore, two of the Ni(I) complexes are very unstable in solution which made characterization extremely difficult. The Ni(II) complex, while more stable than the Ni(I) complexes contains a perchlorate ion and shows a tendency to explode unless treated with great care. For this reason, higher temperature reactions with the perchlorate salt were not carried out.

Details of these syntheses and characterizations will now be presented and the Ni(II) species will be discussed first.

3.2.1 $[Ni(BH_3CN)(Dppm)_2]ClO_4$

This brown diamagnetic complex was prepared from a very brief reaction of the interacting species $Ni(ClO_4)_2 \cdot 6H_2O$, Dppm, and $NaBH_3CN$ in a mixed solvent system (benzene and ethanol) as outlined in the experimental section. Analytical data for the product were in excellent agreement with the above formulation. This reaction is very

sensitive to the rate of addition of the $NaBH_3CN$, the amount of $NaBH_3CN$ used and the reaction time. Thus, in reactions where a large amount of $NaBH_3CN$ is used and where the addition time of $NaBH_3CN$ and the reaction time are increased, entirely different products are obtained and these will be discussed in later subsections.

In contrast to the other Dppm products to be described later, the structure of this complex was relatively easily established. The infrared spectra of $[Ni(BH_3CN)(Dppm)_2]ClO_4$ and the corresponding deuterated system $[Ni(BD_3CN)(Dppm)_2]ClO_4$ are shown in Fig. 22 and the more important infrared spectral frequencies for these complexes are recorded in Table 11. The large and broad peak at around 1000 cm^{-1} clearly indicates (64) the presence of ionic perchlorate. The C≡N stretching frequency of the BH_3CN^- grouping occurs as a very sharp band at 2190 cm^{-1} which is 11 cm^{-1} higher in frequency than that of C≡N in ionic BH_3CN^-. This indicates that the BH_3CN^- grouping is bonded through the nitrogen atom (24). The B-H_t (terminal) stretching vibrations occur as a broad and strong absorption at 2320 cm^{-1} which is very close to the absorption of the B-H vibrations in free BH_3CN^- and which therefore indicates that no M-H-B type of coordination occurs. These B-H_t vibrations are very close to those (2340 cm^{-1}) of the N-bonded BH_3CN^- complex $CoH(BH_3CN)(PPh_3)$ where it is known (44) that no M-H-B linkages occur. A very weak shoulder on this absorption occurs at 2260 cm^{-1}.

The infrared spectrum of the corresponding deuterated

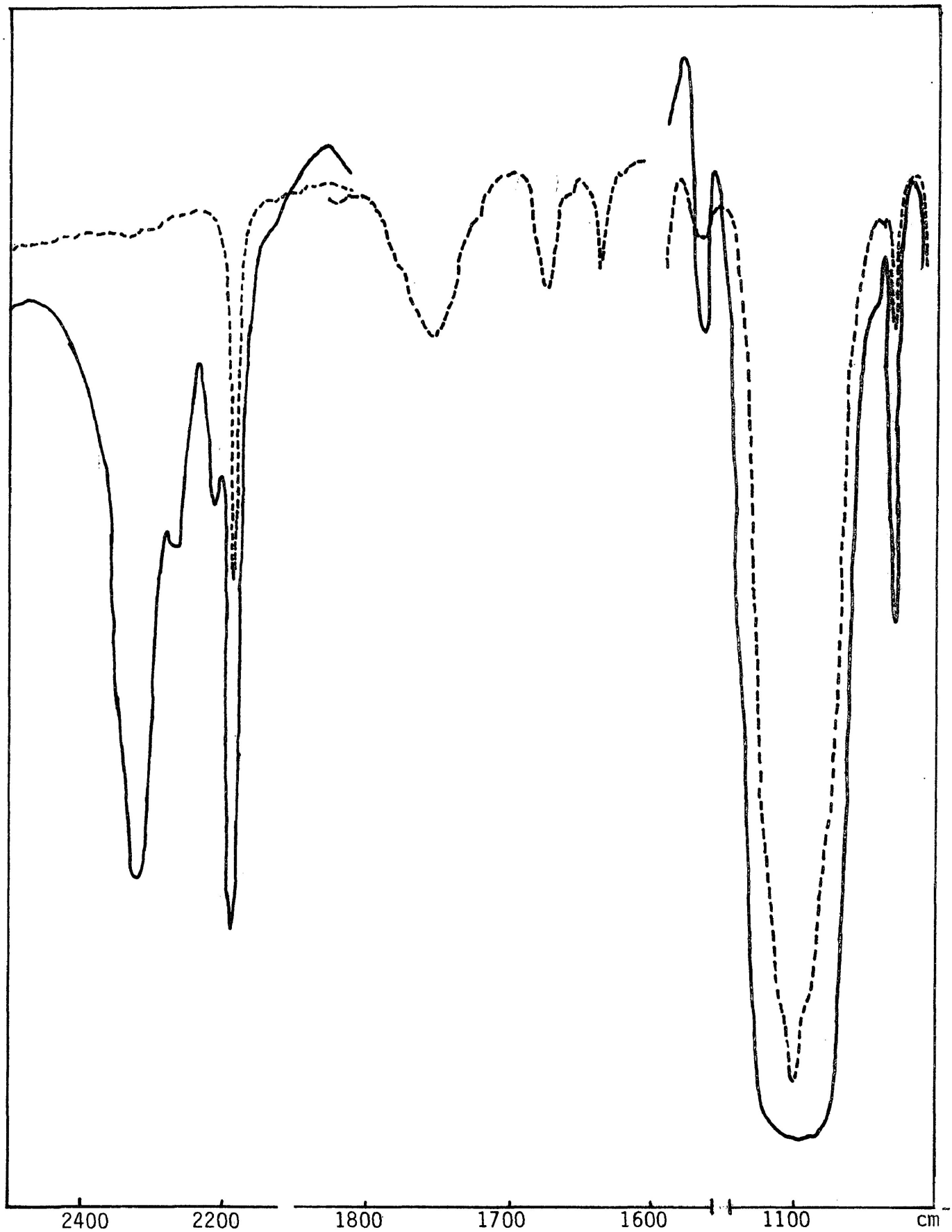


Fig. 22. Selected Features of the Infrared Spectra of

——$[Ni(BH_3CN)(Dppm)_2]ClO_4$ and ---- $[Ni(BD_3CN)(Dppm)_2]ClO_4$

TABLE II

Infrared and ^{31}P NMR Data for Ni(II)[Dppm]$NaBH_3CN$ Derived Diamagnetic Complexes

Serial No.	Complex	Colour	νBH cm^{-1}	δBH cm^{-1}	νCN (in BH_3CN^-) cm^{-1}	νCN (in NiCN) cm^{-1}	Other (EtOH)	δ ^{31}P NMR (solvent)	Mode of Coordination of BH_3CN^-
1. (a)	$[Ni(BH_3CN)(Dppm)_2]ClO_4$	Brown	2320 (s) 2265 (sh,w)	--	2190 (s)	--	--	-62.75 (CH_2Cl_2)	M - $NCBH_3$
(b)	$[Ni(BD_3CN)(Dppm_2]\ ClO_4$	Brown	1755 (s) 1675 (m) 1635 (w)	--	2190 (s)	--		--	M - $NCBD_3$
	Complex A								
2. (a)	$Ni_2(BH_3CN)(CN)(Dppm)_2\cdot\frac{1}{2}EtOH$	Greenish Brown	2320 (s) 2265 (sh,w)	1115 1095	2190 (s)	2020 (s)	3300 (b)	28.42 29.30 (EtOH)	M - $NCBH_3$
(b)	$Ni_2(BD_3CN)(CN)(Dppm)_2\cdot\frac{1}{2}\ EtOH$	"	1755 (s) 1675 (m) 1635 (w)	--	2190 (s)	2020 (s)			M - $NCBD_3$
(c)	$Ni_2(BH_3C^{15}N)(C^{15}N)(Dppm)_2\cdot\frac{1}{2}EtOH$		2320 (s) 2265 (sh,w)	1115 1095	2155 (s)	1990 (s)			M - $^{15}NCBH_3$
	Complex B								
3. (a)	$Ni_2(CN)_2(Dppm)_3\cdot 4EtOH$	Green	--	--	--	2020 (s) 2110 (w)	3400 (b)	15.98 (EtOH)	--
(b)	$Ni_2(C^{15}N)_2(Dppm)_3\cdot 4EtOH$	"	--	--	--	1970 (s) 2070 (w)	"		
	Complex C								
4. (a)	$Ni_2(CN)_2(Dppm)_2\cdot EtOH$	Violet	--	--	--	1975 (s)	3360 (b)	1.50 (EtOH)	--
(b)	$Ni_2(C^{15}N)_2(Dppm)_2\cdot EtOH$	"	--	--	--	1940 (s)	"		--
(c)	$Ni_2(CN)_2(Dppm)_2\cdot C_6H_6$	"	--	--	--	1975 (s)	--	1.45 (EtOH)	--

complex $[Ni(BD_3CN)(Dppm)_2]ClO_4$ shows the B-D_t stretching frequencies at much lower values than the B-H_t values as expected from the isotopic shift effect. The higher resolution at lower frequency causes splitting into three peaks at 1755 cm^{-1}, 1685 cm^{-1} and 1635 cm^{-1} respectively. This again indicates monocoordination of the BH_3CN^- grouping through the nitrogen atom to the metal ion, since the deuterated complex $CoD(BD_3CN)(PPh_3)_3$ (resynthesized during this work specifically to observe the location of the stretching mode of B-D_t at lower frequency) shows a virtually identical pattern with peaks at 1755 cm^{-1}, 1680 cm^{-1} and 1635 cm^{-1} . As will be seen later in the discussion of certain Diphos complexes, systems containing the M-H-BH-CN type of linkage show the B-H_t and B-D_t vibrations at significantly higher frequencies. This has also been discussed in section 1.8.

The ^{31}P NMR spectrum of $[Ni(BH_3CN)(Dppm)_2]ClO_4$ in CH_2Cl_2 shows a very strong signal at δ=-62.75 indicating that all of the phosphorus atoms are magnetically equivalent and that both phosphorus ligands chelate the same nickel ion. This is supported by the fact that a similar signal is observed at δ=-64.3 for $PtCl_2(Dppm)_2$(62). An additional weak peak occurs at δ=-34 in the spectrum of $[Ni(BH_3CN)$-$(Dppm)_2]ClO_4$. This has been attributed to a decomposition product since, as mentioned earlier, the Dppm complex is very solvent sensitive. The fact that this weak peak gradually increases in intensity with time while the strong peak at δ=-62.75 gradually decreases, finally disappearing after several hours, suggests that this interpretation is

correct. The ^{31}P spectrum indicates that the chemical change with time is a very simple one and one possiblity is slow dissociation (and perhaps subsequent decomposition) of a weakly coordinated BH_3CN^- to give the $[Ni(Dppm)_2]^{2+}$ ion as shown below.

$$[Ni(BH_3CN)(Dppm)_2]ClO_4 \xrightarrow{CH_2Cl_2} [Ni(Dppm)_2]^{2+}$$

That this is almost certainly the case is shown by the fact that $[Ni(Dppm)_2](ClO_4)_2$, a known (20) complex prepared and analytically characterized here as a yellow solid by direct reaction between $Ni(ClO_4)_2 \cdot 6H_2O$ and Dppm in ethanol, shows only one sharp peak at δ=-34 in the ^{31}P NMR spectrum in CH_2Cl_2. From all this evidence therefore, the structure of $[Ni(BH_3CN)(Dppm)_2]ClO_4$ complex has been assigned with reasonable confidence as a five coordinated Ni(II) system is as shown in Fig. 23.

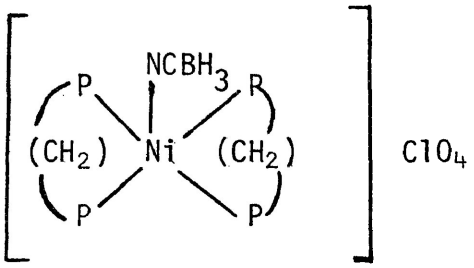


Fig. 23

The structure shown in Fig. 23 is a square pyramid with all four P atoms basal and equivalent since this agrees with the ^{31}P spectrum.

However, this may not be the actual solid state arrangement since polytopal re-arrangements of other five-coordinated structures (e,g. trigonal bipyramid) in solution at room temperature (Berry pseudorotation or turnstile rotation (65)) is well known and can lead to apparent magnetic equivalence of nuclei if the re-arrangement process is very fast.

3.2.2 $Ni_2X_aY_b(Dppm)_c \cdot xEtOH$ where $X=BH_3CN^-$, Y=CN, a=1, b=1, c=2 and x=½;
Y=CN, a=0, b=2, c=3 and x=4;
Y=CN, a=0, b=2, c=2 and x=1

As mentioned earlier, three of the complexes obtained in the Dppm reations are very closely related and the general formula given in the heading above emphasizes this close relationship. Very careful adjustments to the reaction conditions were required in order that the three complexes could be isolated as pure species. Experimental details are given in section 2 of this thesis but, briefly, the first formed product in this group is a greenish brown solid and the second is a deep green solid which is isolated from the mother liquor of the reaction mixtures which give the first formed product. The third product, a violet solid, is formed in reations which are carried out for a much longer time or at a higher temperature. In solution, both of the green products change to the violet product. All three products are diamagnetic and all can be prepared from either $NiCl_2 \cdot 6H_2O$ or $Ni(ClO_4)_2 \cdot 6H_2O$.

Normally in reactions of this kind, analytical data and infrared spectra together allow fairly rapid determination of the molecular formula and suggest a probable structure which can later be confirmed by other physical measurements and chemical reactions. However, for these three complexes, this was not possible although analytical data showed that all three complexes contain small amounts of nitrogen (1.8-2.8%). Numerous spectroscopic and chemical studies therefore had to be carried out.

Thus, initially, the three complexes were regarded as Complex A (greenish brown), Complex B (green) and Complex C (violet) while structural evidence was pieced together. These complexes are now known to be the Ni(I) species $Ni_2(BH_3CN)(CN)(Dppm)_2 \cdot \frac{1}{2}EtOH$, $Ni_2(CN)_2(Dppm)_3 \cdot 4EtOH$ and $Ni_2(CN)_2(Dppm)_2 \cdot EtOH$ respectively and to avoid confusion, these designations are used on the various spectra recorded in the next few pages. However, in the text they will be discussed as Complexes A, B and C until the evidence for each formulation becomes clear.

Looking first at the infrared spectra of these complexes, the infrared spectrum of Complex A shows three sharp stretching vibrations at 2020 cm^{-1}, 2190 cm^{-1} and 2320 cm^{-1} together with a weak broad peak at 3300 cm^{-1}. These are shown in Fig. 24 and selected infrared spectral data are recorded in Table 11. From this infrared spectrum, it is clear that on the basis of arguments used

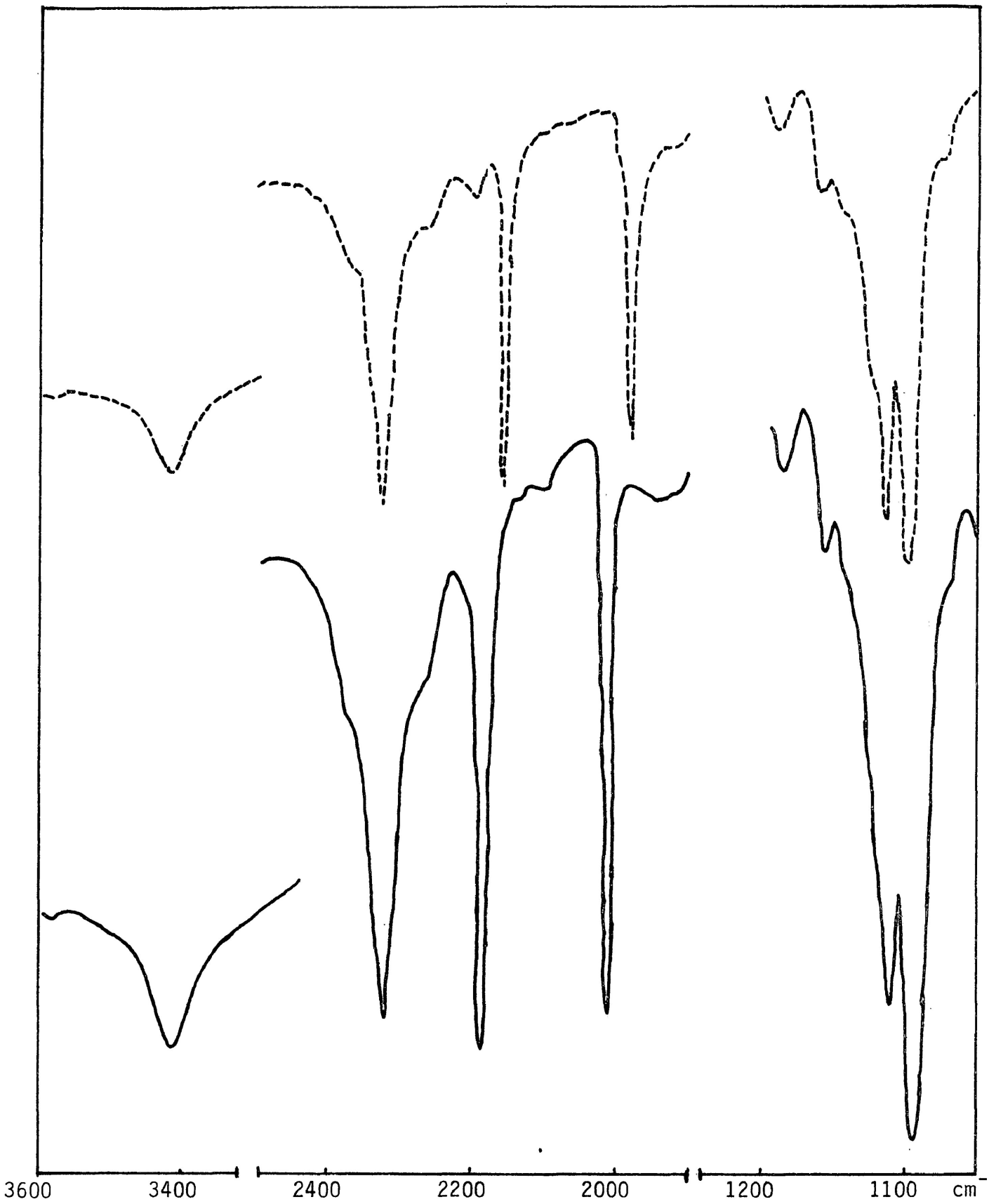


Fig. 24. Selected Features of the Infrared Spectra of
—— $Ni_2(BH_3CN)(CN)(Dppm)_2 \cdot \frac{1}{2}EtOH$ (Complex A) and
---- $Ni_2(BH_3C^{15}N)(C^{15}N)(Dppm)_2 \cdot \frac{1}{2}EtOH$.

earlier the sharp and strong peak at 2190 cm^{-1} is due to the C≡N stretching vibration of an N-coordinated BH_3CN^- grouping (11 cm^{-1} higher than the CN stretching vibration in free BH_3CN^-). This, at first sight, appears to account for the nitrogen in Complex A. The B-H_t stretching vibrations appear as a strong and broad band at 2320 cm^{-1} with a weak shoulder at 2265 cm^{-1}. This is typical (see section 1.5) of N-coordinated BH_3CN^- groupings which are not involved in any type of M-H-B linkage. Thus, two (2320 and 2190 cm^{-1}) of the four peaks in the infrared spectrum are readily explained. The other two (2020 cm^{-1} and 3300 cm^{-1}) will be discussed in conjunction with similar peaks in the spectra of Complexes B and C.

Complex B shows two absorptions in the infrared spectrum at 2110 cm^{-1} (weak) and 2020 cm^{-1} (very strong, sharp) together with a medium strength broad peak at around 3400 cm^{-1} as shown in Fig. 25, while Complex C (washed but not recrystallized-see later) shows a very strong and sharp band at 1975 cm^{-1}, a much weaker band (very sharp) at 1987 cm^{-1}, and a weak broad peak at around 3400 cm^{-1} as shown in Fig. 26. Thus, ignoring for the moment the peaks at 3300-3400 cm^{-1}, all three complexes exhibit a sharp and strong band in the 1950 cm^{-1}-2030 cm^{-1} region. The obvious possibilities for these bands are that they are due to metal hydride, metal cyanide or metal carbonyl vibrations (the latter coming from abstraction of CO from EtOH - such abstractions are well established (66)). Of these possibilities, the metal cyanide might seem the most likely since all

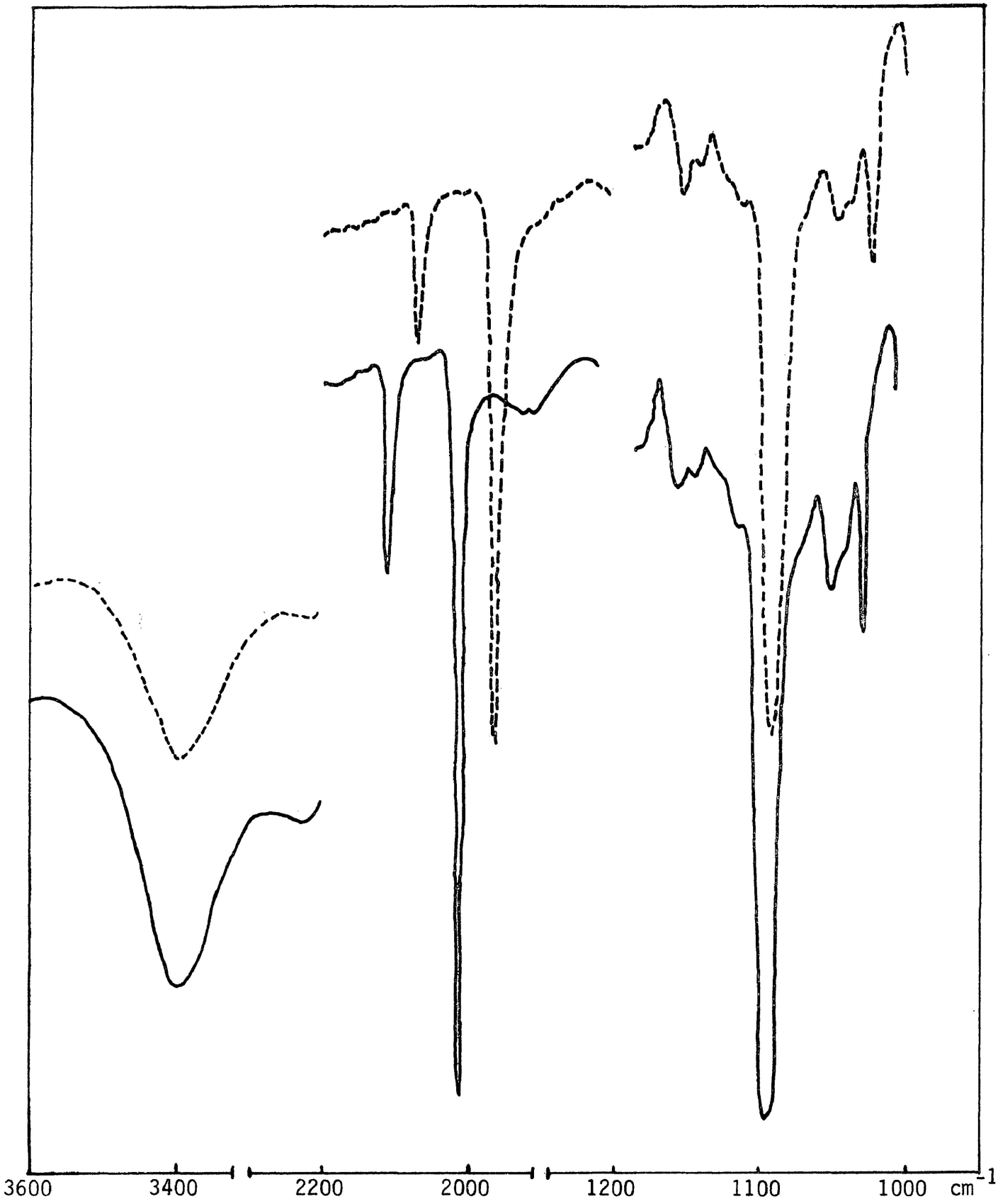


Fig. 25. Selected Features of the Infrared Spectra of

—— $Ni_2(CN)_2(Dppm)_3.4EtOH$ (Complex B) and

----- $Ni_2(C^{15}N)_2(Dppm)_3.4EtOH$.

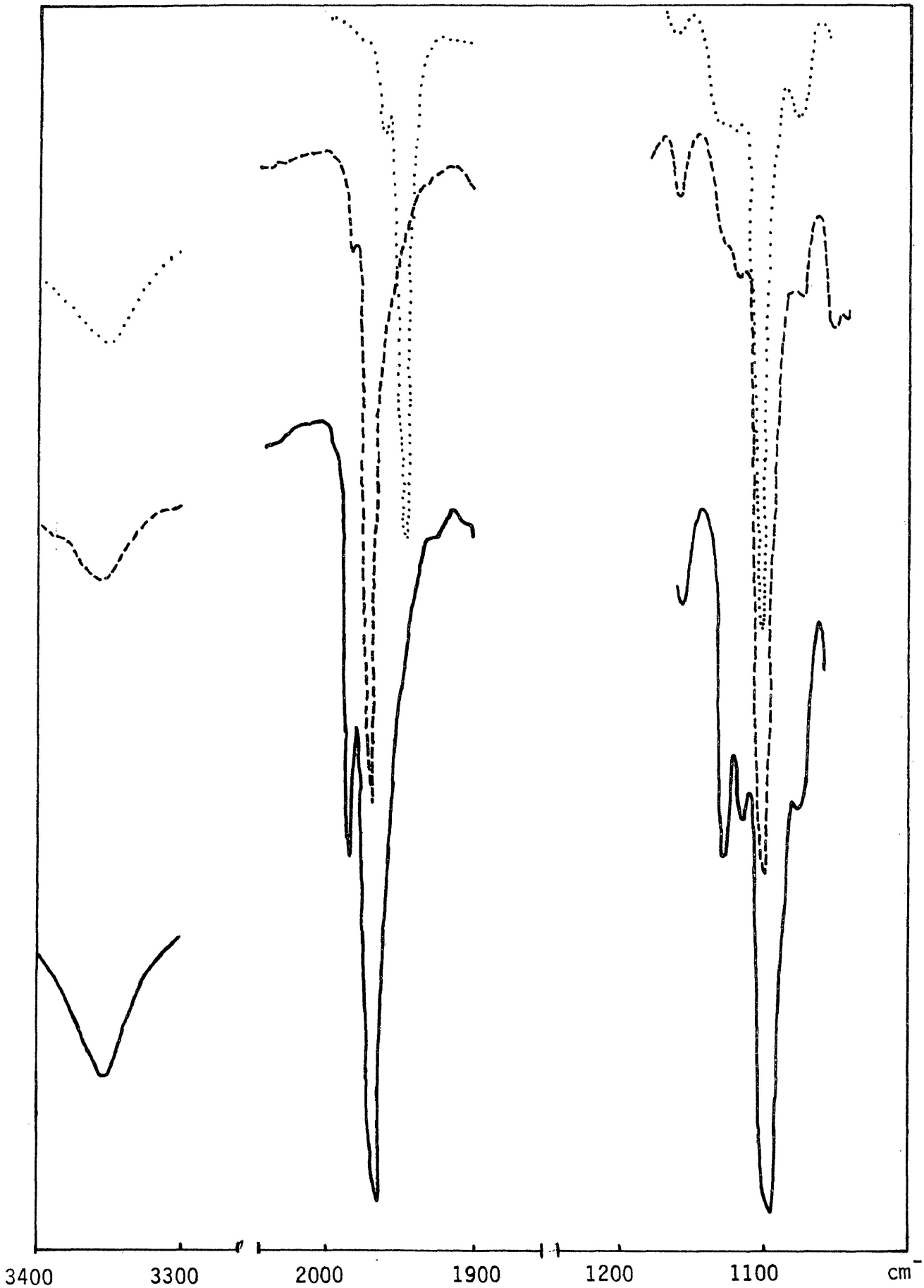


Fig. 26. Selected Features of the Infrared Spectra of—— $Ni_2(CN)_2(Dppm)_2.EtOH$ (impure Complex C),--- $Ni_2(CN)_2(Dppm)_2.EtOH$ (pure) and....$Ni_2(C^{15}N)_2(Dppm)_2.EtOH$.

three compounds contain nitrogen and only for Complex A has any nitrogen been accounted for. However, metal cyanides usually show C≡N stretching vibrations at much higher frequencies in the 2075-2200 cm^{-1} range (67a) and all possibilities must therefore be examined. For a metal carbonyl the infrared band within this range is normally strong and broad. Thus, initially, it was thought possible that these bands in all of the complexes are due to the presence of terminal metal-hydride linkages which frequently give rise to (43) a sharp and strong stretching mode within this region.

In this context ^1H NMR evidence could be a useful structural tool since metal hydrides normally give rise (11, 43, 47) to distinctive signals upfield of TMS, the multiplicity of which (if the complexes contain coordinated phosphines) gives information regarding the number and type of neighbouring phosphorus atoms. Thus, ^1H NMR spectra have been recorded for these complexes at room temperature and at lower temperatures in different solvent systems and in no case was a hydride signal observed. This could mean that the complexes are not hydrides or that solution decomposition is too fast for hydride signal observation since, as already stated, Complexes A and B are very solvent sensitive. It was, in fact, observed that the initially green solutions of these two complexes changed to violet and then deep violet (formation of Complex C as mentioned earlier) while the ^1H NMR spectra were recorded. Complex C is stable in solution but it too did not show any trace of metal

hydride signals in the ^1H NMR spectrum. Spectra were recorded for all three complexes at much lower temperatures (about -70°C) in an effort to slow decomposition but none of these three complexes showed any trace of a hydride signal in the ^1H NMR spectrum under these conditions, even though, at these temperatures, Complexes A and B appeared to be stable. From this evidence, it would appear that none of these complexes is a metal hydride although the evidence is, as yet, not conclusive. More will be said later about NMR spectrometry of these complexes in connection with different aspects of the structural problem.

If the bands in the range 1950-2030 cm^{-1} are due to metal hydride vibrations, the hydrogen would probably have come from the $NaBH_3CN$. Therefore, the corresponding deuterated complexes were synthesized using $NaBD_3CN$ in the expectation that, if these are hydride bands, they would show a charateristic isotopic shift to lower frequency on deuteration. In the infrared spectra of these complexes only the $B\text{-}H_t$ stretching bands at 2320 cm^{-1} for Complex A shift to lower frequency splitting into three bands at 1755 cm^{-1}, 1685 cm^{-1} and 1635 cm^{-1} as shown in Fig. 27. This is precisely the behaviour observed earlier for $[Ni(BD_3CN)(Dppm)_2]ClO_4$ and $CoD(BD_3CN)(PPh_3)_3$ as discussed in section 3.2.1. However, the strong bandsin the 1950-2030 cm^{-1} region for all three complexes are not shifted and they are therefore not due to metal hydride vibrations as already tentatively deduced from ^1H NMR spectra.

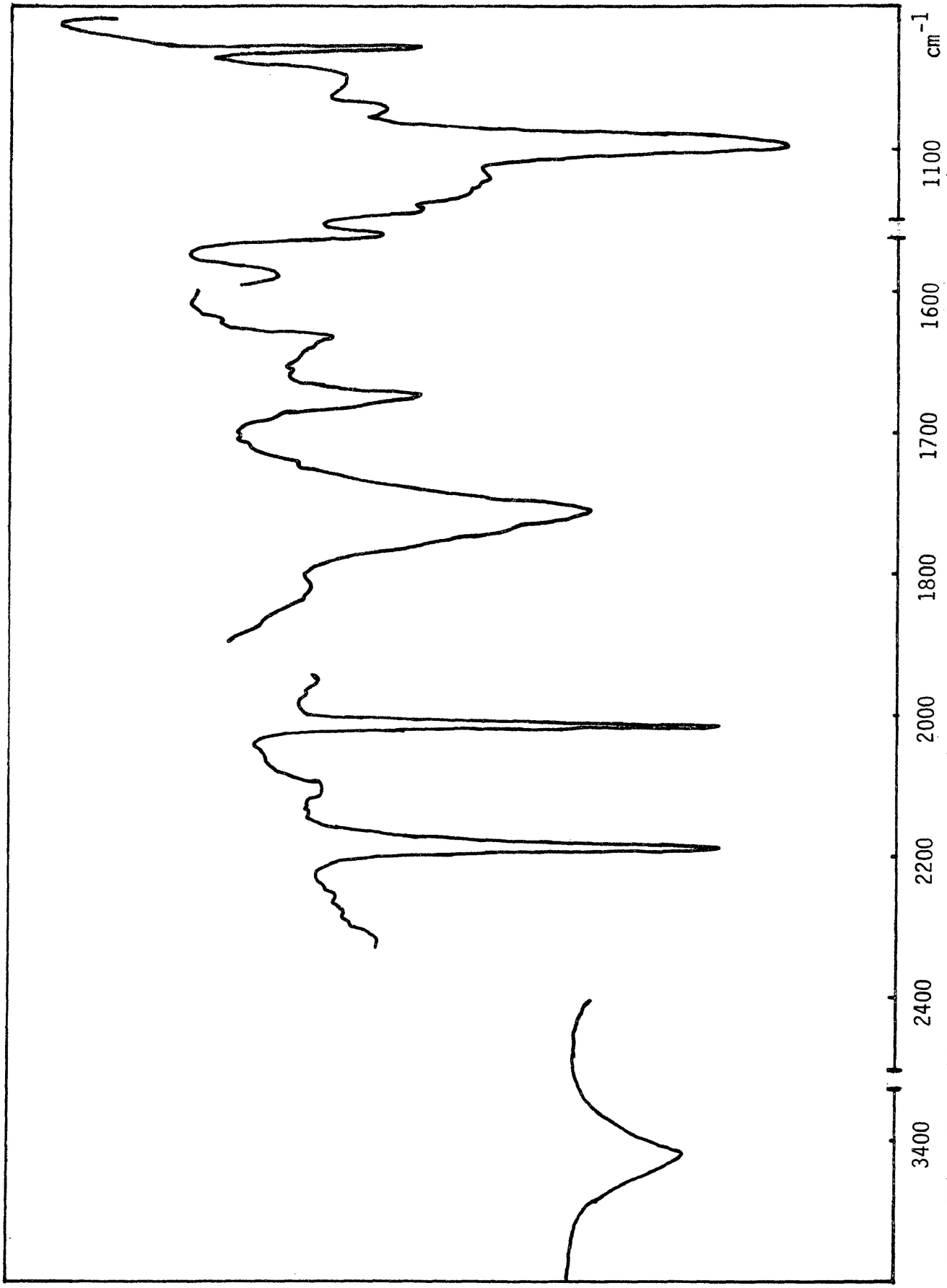


Fig. 27. Selected Features of the Infrared Spectrum of Deuterated Complex A $Ni_2(BD_3CN)(CN)(Dppm)_2 \cdot \frac{1}{2}EtOH$.

However, the sharp but weak band at 1987 cm^{-1} for Complex C vanishes from the spectrum on deuteration. No new band was observed at lower frequency but such a band could be obscured by the very strong bands for the ligand itself which crowd the lower frequency range of the spectrum. This peak at 1987 cm^{-1} is clearly due to the presence of a metal hydride linkage but the peak is weak and no other peak is affected by deuteration. The possibility that this peak is due to the presence of an impurity therefore had to be considered. Complex C was therefore rigorously purified by several successive recrystallizations from ethanol and, after three such recrystallizations, the band at 1987 cm^{-1} had completely disappeared as shown in Fig. 27 but the remainder of the spectrum was unchanged. The peak at 1987 cm^{-1} is therefore due to the presence of a hydride containing impurity. Thin layer chromatographic examination was used to examine a sample of Complex C which had not been recrystallized several times and which showed the sharp weak peak at 1987 cm^{-1}. The complex showed two separate spots in the TLC when the chromatogram was run in a mixture of chloroform:acetone, 5:1. The purified (several recrystallizations) Complex C shows only one spot but no attempt was made to isolate the impurity as only very small amounts appeared to be present.

While the infrared bands in the 1950-2030 cm^{-1} are clearly not due to metal hydride vibrations, they could still be due to either metal carbonyl or metal cyanide vibrations. This problem

was solved and these infrared bands in the 1950 cm^{-1}-2030 cm^{-1} range were completely assigned for all these complexes by synthesizing the ^{15}N labelled Complexes, A, B and C. First, however, ^{15}N labelled $NaBH_3C^{15}N$ had to be synthesized (see experimental section). If the bands appearing in the IR spectrum are due to the presence of a metal cyanide grouping then the band for the $C\equiv^{15}N$ stretch should appear at lower frequency than that for $C\equiv^{14}N$. Such ^{15}N labelled groups (not necessarily C≡N) show vibrations which are lower in frequency by up to 60 cm^{-1} (67b) compared with those of the corresponding ^{14}N species. Indeed, the $NaBH_3C^{15}N$ prepared for these reactions showed this with the $C\equiv^{15}N$ frequency at 2152 cm^{-1} which is 27 cm^{-1} lower than that observed for $NaBH_3C^{14}N$. In fact, it was found that for the infrared band under discussion, all three ^{15}N labelled complexes show in their infrared spectra, shifts to lower frequency of about 35 cm^{-1} as shown in Figs. 24, 25, 26 and Table 11. Labelling these molecules with ^{15}N would not affect metal carbonyl frequencies and these are therefore metal cyanides. This therefore accounts for the nitrogen in Complexes B and C and accounts for nitrogen additional to that of the BH_3CN grouping in Complex A. As mentioned earlier, the C≡N vibrations of metal cyanides normally occur at higher frequencies than those observed here. However, such vibrations in this range are known (67a) and they are often associated with cyanides of metal ions in lower than usual oxidation states. The possibility therefore arises that Complexes A, B and C are Ni(I) species.

As the last step in establishing molecular formulae, the broad and weak stretching frequencies at 3300-3400 cm^{-1} in the infrared spectra of all of these complexes will be examined. These vibrations may be due to an OH group in water (from $NiX_2 \cdot 6H_2O$) or ethanol (the reaction solvent) or they may be due to an N-H linkage derived from BH_3CN. This last possiblity is less likely since such absorptions are usually sharp rather than broad.

That the absorptions are not due to water was shown by carrying out the reactions under strictly anhydrous conditions. Examination of the infrared spectra of the Complexes A, B and C then obtained showed that the absorptions in the range 3300-3400 cm^{-1} remain unchanged. Equally clearly, they are not due to amine type systems since the deuteration and ^{15}N labelling experiments already discussed would have shown isotopic shifts and the peaks remain unchanged in location even after such labelling.

It therefore appears that these absorptions are due to the presence of ethanol and here, the ^1H NMR spectra already recorded to search for metal hydride signals would be potentially useful since such spectra would show not only the presence of ethanol but also the amount of ethanol present. Therefore, for Complexes A, B and C, ^1H NMR spectra were recorded again in $CDCl_3$ and it was found that all of them show a poorly resolved triplet at δ=1.25 and a quartet at δ=3.75. These values are precisely the same as those

obtained for pure ethanol in $CDCl_3$. In this context, this author felt that the solvent $CDCl_3$ should be checked for the presence of traces of ethanol but no such traces were found. It is therefore clear that the stretching vibrations in 3300 cm^{-1}-3400 cm^{-1} region in the spectra of Complexes A, B and C are due to the presence of ethanol which is either coordinated or in the crystal lattice.

Careful integrations of the ^1H spectra showed that the phosphine ligand to ethanol ratio was reproducible and different for each complex and this information, together with the analytical, magnetic and infrared data already discussed, finally allowed assignment of a molecular formula to each complex. Thus, Complexes A, B and C were found to be the binuclear Ni(I) species $Ni_2(BH_3CN)(CN)$-$(Dppm)_2 \cdot \frac{1}{2}EtOH$, $Ni_2(CN)_2(Dppm)_3 \cdot 4EtOH$ and $Ni_2(CN)_2(Dppm)_2 \cdot EtOH$ respectively. A molecular weight determination of Complex C confirmed its dimeric nature and, indeed, diamagnetic Ni(I) suggests a dimeric form.

It finally remained to determine the structure of, and the chemical relationships between these systems. First, it seemed desirable to establish if the ethanol is essential to the structures and recrystallizations from solvents other than ethanol were attempted. Complexes A and B both reverted slowly to Complex C in all sovents (including ethanol) but Complex C was sufficiently stable to be recrystallized from benzene from which it was again obtained as a solvate $Ni_2(CN)_2(Dppm)_2 \cdot C_6H_6$ in which the ethanol has

been displaced by benzene.

Final structural information was obtained from ^{31}P NMR spectrometry. The arrangements of the phosphorus atoms in the various complexes have been extensively investigated from the ^{31}P NMR spectra in methanol (for Complexes A and B) and ethanol (for Complex C) solutions. Complex A, $Ni_2(BH_3CN)(CN)(Dppm)_2 \cdot \frac{1}{2}EtOH$, is very solvent sensitive but freshly prepared samples always showed a doublet at δ=28.42 and 29.30 with the two peaks of equal area. This spectrum clearly shows nonequivalence of the phosphorus atoms in the complex and suggests that the two Dppm ligands are present in slightly different chemical environments. As time passed (e.g. 1 hour) a strong and sharp signal at δ= 1.4 appeared in the spectrum in addition to the doublet. The intensity of this signal gradually increased while that of the doublet decreased until it completely disappeared, During this time, the sample changed colour from green to violet. Further changes in the ^{31}P NMR spectrum and the colour of the same sample were not observed for about 48 hours. After this time the violet solution turned to pinkish brown. The nature of this change was not investigated. The significance of the peak which appears at δ=1.4 will be discussed shortly.

Turning now to Complex B, $Ni_2(CN)_2(Dppm)_3 \cdot 4EtOH$, this shows in the ^{31}P spectrum a single sharp peak at δ=15.98 which shows the presence of magnetically equivalent phosphorus atoms in the

complexed Dppm ligand. Again, as time passed, this sample showed similar behaviour to that exhibited by Complex A described above - i.e. freshly prepared samples (deep green) show only the peak at δ=15.98 for periods of up to 20 to 25 minutes but, after this, an extra signal appears at δ=1.4 and the intensity of this new signal gradually increases as the peak at δ= 15.98 decreases. Again, the sample turns from green to violet after several hours, and the signal at δ=15.98 completely disappears. However, this time, an additional peak at δ=-21 also appears and this signal is very close to the chemical shift observed for the free ligand Dppm. It seems, therefore that the decomposition of Complex B, unlike that of Complex A, produces free ligand in addition to the new complex ($\delta^{31}P$=1.4) produced by both complexes A and B.

The ^{31}P NMR spectrum of the violet Complex C, $Ni_2(CN)_2(Dppm)_2 \cdot EtOH$, shows a strong and very sharp signal at δ=1.5 which does not change significantly with time. This signal again indicates that all of the P atoms in the complex are magnetically equivalent at least in solution. Furthermore, the location of this signal and the colour of the sample solution strongly suggest that the main decomposition product in solution observed for Complexes A and B at δ =1.4 is Complex C. This has been confirmed by simple, slow recrystallization experiments for Complexes A and B.

In order to investigate further the relationships

between these three complexes, additional ^{31}P NMR experiments were carried out in the presence of an excess of free ligand. When an excess of free ligand was added to Complex A in ethanol (as the NMR solvent) and the ^{31}P NMR spectrum was recorded, a much more complex spectrum was produced. The spectrum showed the originally observed doublet at δ=28.42 and 29.30 together with other signals at δ=16 (very weak), δ=1.45 (medium, sharp) and δ=-21 (strong). Clearly the peak at δ=1.45 is due to the violet Complex C and the strong peak at δ=-21 is due to free ligand. However, the additional peak at approximately δ=16 (weak and poorly resolved) could well be due to small amounts of the deep green Complex B which normally shows, when pure, a sharp singlet at δ=15.98. It therefore seems likely that Complex B, $Ni_2(CN)_2(Dppm)_3 \cdot 4EtOH$, can be obtained from Complex A, $Ni_2(BH_3CN)(CN)(Dppm)_2 \cdot \frac{1}{2}EtOH$, by loss of BH_3 and addition of Dppm as shown below

$$\underset{\text{Complex A}}{Ni_2(BH_3CN)(CN)(Dppm)_2 \cdot \tfrac{1}{2}EtOH} \xrightarrow[EtOH]{\text{Dppm in excess}} \underset{\text{Complex B}}{Ni_2(CN)_2(Dppm)_3 \cdot 4EtOH} + BH_3$$

The above interconversion is indeed not unexpected because Complex B was always the second compound isolated in these reactions and it was always isolated from the filtrate of reaction mixtures from which Complex A had previously been isolated. The possiblity exists then that either Complex A and Complex B are formed

together in separate reactions pathways in the same reaction mixture or that Complex B is formed directly from Complex A. The above NMR experiments suggest however, that while the latter is possible, it is probably only a minor reaction pathway since so little of B is formed from A by direct addition of free ligand.

Similar results were observed when a ^{31}P NMR sample of Complex C (in ethanol) was treated with an excess of free ligand. In addition to the normal strong signal due to Complex C at δ=1.45, another weak peak appeared at δ=16. This phenomenon, together with the decomposition of Complex B to Complex C discussed earlier suggests that the following reversible interconversion is also possible.

$$\underset{\text{Complex C}}{Ni_2(CN)_2(Dppm)_2 \cdot EtOH} \underset{EtOH}{\overset{\text{Dppm in excess}}{\rightleftharpoons}} \underset{\text{Complex B (deep green)}}{Ni_2(CN)_2(Dppm)_3 \cdot 4EtOH}$$

Indeed, the only stoichiometric difference between Complexes B and C (apart from the ethanol of crystallization) is the number of Dppm ligands involved, and, superficially at least, such reversible interconversion seems quite reasonable. As will be seen soon, however, there are probably quite large structural differences between Complexes B and C.

There is now sufficient information available for fairly reliable suggestions to be made regarding the structures of these systems. First, the stoichiometric compositions of all three complexes are known and the synthetic procedures, together with the ^{31}P observations made in the presence of added ligand, indicated that the relationships between the complexes illustrated in Fig. 28 exist. For the purposes of this Figure, solvating molecules are ignored.

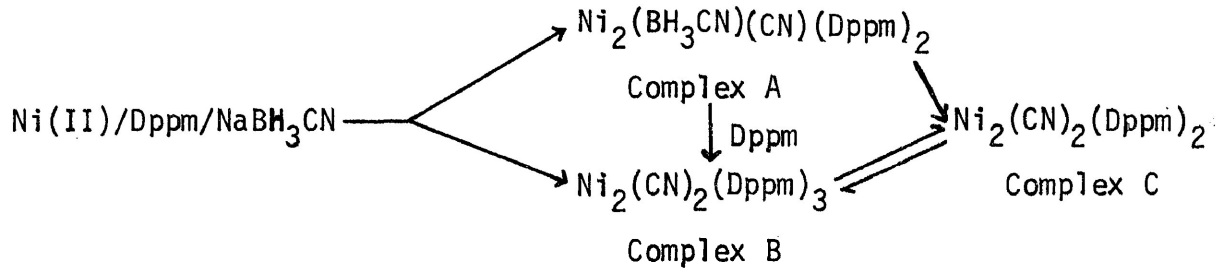
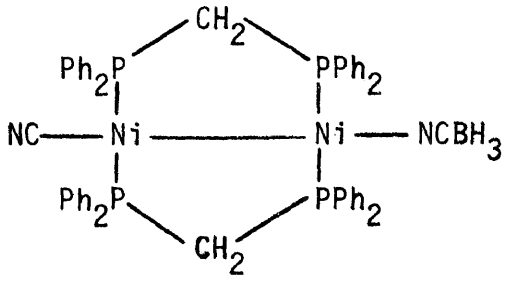
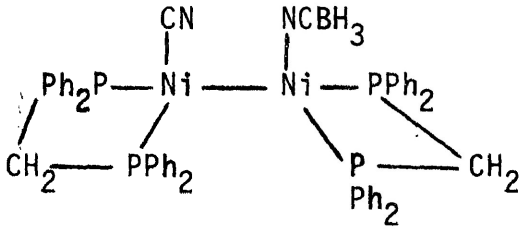


Fig. 28

Second, the ^{31}P NMR spectra of the pure complexes show that, in solution, Complex A contains two sets of phosphorus atoms which are in very similar but not identical chemical environments while Complex B and C are symmetrical species each showing only one phosphorus signal in the NMR spectrum. These observations referred to earlier suggest various possible structures for the three complexes which are illustrated in Fig. 29 a), b) and c) (no stereochemisty implied).



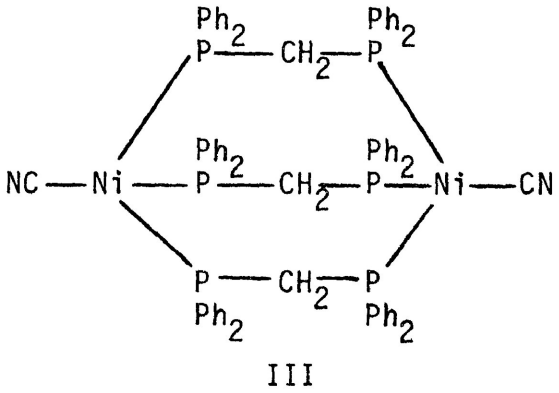
I



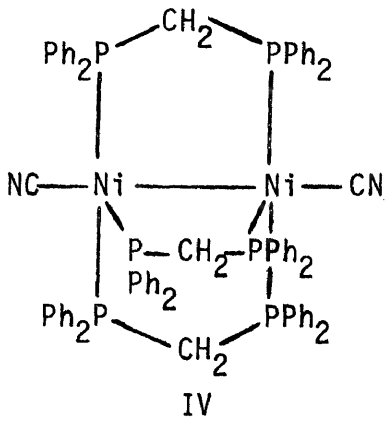
II

Fig. 29 a)

Possible Structures for $Ni_2(BH_3CN)(CN)(Dppm)_2$ (Complex A)



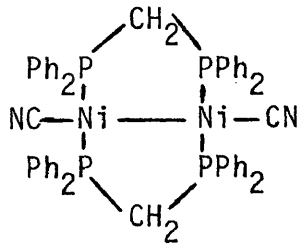
III



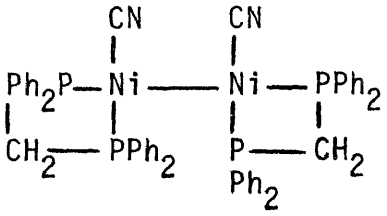
IV

Fig. 29 b)

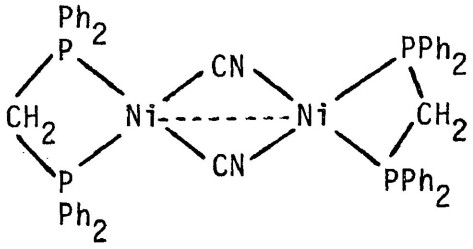
Possible Structures for $Ni_2(CN)_2(Dppm)_3$ (Complex B)



V



VI



VII

Fig. 29 c)

Possible Structures for $Ni_2(CN)_2(Dppm)_2$ (Complex C)

Both Ni-Ni bonded Ni(I) species such as that shown in Fig. 30 below (68a) and cyanide bridged species (68b) also shown are well known. However, as Nakamoto has observed (67c), bridging by cyanide groups usually leads to a significant <u>increase</u> in the C≡N stretching frequency and here one observes a significant <u>decrease</u>. It seems then that cyanide bridged structures are unlikely.

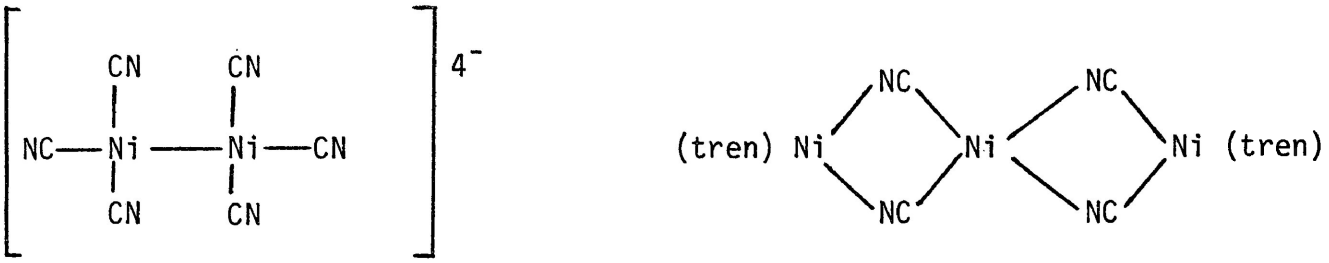


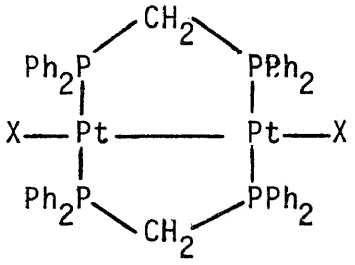
Fig. 30

In addition, it should be possible to tell the difference between bridging and chelating Dppm since the ring size effect (Δ_R) upon the coordination shift is a well known phenomenon (62). In general terms, this ring-size effect can be stated that in four-membered ring bis-phosphine chelate complexes, the phosphorus atoms are more highly shielded than those of six-membered ring chelated systems relative to a similar non-chelated complex system. On the other hand, phosphorus atoms in five-membered chelate rings are deshielded relative to those of a similar non-chelated complex. The actual values of the coordination shift will probably depend upon the nature of the metal ion, its coordination number, its oxidation state and the stereochemistry of the system.

In this context, if one considers Complex A, $Ni_2(BH_3CN)(CN)(Dppm)_2$, and Complex C, $Ni_2(CN)_2(Dppm)_2$, these two complexes differ stoichiometrically only in one BH_3 unit yet there is an upfield shift of about 27 ppm in the ^{31}P NMR spectrum and there is a considerable colour change from greenish brown to violet. It seems likely then that the loss of BH_3 from Complex A is accompanied by a profound structural change in forming Complex C. A ^{31}P chemical shift of around δ=29 for the two sets of P atoms observed for Complex A is more consistent with structure I (Fig. 29 a) than with structure II where the ring size effect due to Dppm chelation normally gives much higher field shifts (62) although the actual value of the shift observed (from slightly positive to considerably negative) depends upon the metal and the overall structure involved. On the other hand, it is quite common for coordinated but unchelated Dppm to show (62) a ^{31}P shift of the order of δ=ca.30. Similarly, the high field location (δ=1.45) of the ^{31}P signal for Complex C is more consistent with structure VI (Fig. 29 c) than structure V (structure VII is already eliminated because bridging cyanide is unlikely on infrared evidence).

This leaves Complex B, $Ni_2(CN)_2(Dppm)_3$ for structure assignment. The available evidence does not allow us to distinguish between the two possible structures III and IV (Fig. 29 b) but structure III might be preferred because it is the least hindered. They are, in any case, very similar.

One last point should be made here and that is that although there are no ^{31}P data in the literature regarding Ni(I)-Dppm complexes, there are some for similar Pt(I) complexes. Thus, Brown et al. (69) have synthesized a series of Pt(I)-Dppm bridged dimeric systems of the general structure shown in Fig. 31. These show (in



X= Cl, Br, I

Fig. 31

$C_2H_2Cl_4$ solution) ^{31}P shifts very close to 0 ppm. As stated in Garrou's review (62), ^{31}P data for Ni(II), Pd(II) and Pt(II) complexes of similar stoichiometry and coordination number show that ^{31}P shifts for the Ni(II) complexes are usually at considerably lower field (ca 15ppm) than for the corresponding Pt(II) complexes. If this trend applies also to the M(I) system then the assignment of a bridging Dppm made to Complexes A and B would appear to be quite reasonable while the higher field signal (δ=1.45) observed for Complex C would therefore again be quite compatible with a structure involving chelating Dppm ligands.

The weight of the evidence therefore favours structures I, III, and VI for Complexes A, B, and C respectively

although final confirmation of these structures will have to await X-ray crystallographic studies.

Further comments on the products of these reactions in relation to those of the other bis-phosphine ligands used will be made at the end of this Results and Discussion section.

3.3 The Ni(II)|Diphos|$NaBH_3CN$ system

Extensive investigations have been carried out on this system under a wide variety of conditions and a number of interesting products have been isolated. Seven of these have been fairly thoroughly characterized although the apparently unusual structures of some of the products make X-ray structural confirmation highly desirable. Furthermore, these reactions follow an entirely different course from the Dppm reactions since the products characterized are Ni(II) systems (or, in one case, Ni(0)) whereas Dppm gave primarily Ni(I). In addition, no characterizable metal cyanides were isolated from the Diphos system whereas Dppm gave mainly metal cyanides. The preparation of Ni-cyanotrihydroborato-Diphos complexes from the $NiCl_2 \cdot 6H_2O$|$NaBH_3CN$|Diphos system is easier than from the $Ni(ClO_4)_2 \cdot 6H_2O$|$NaBH_3CN$|Diphos system and it was observed that the products formed depend more upon the Ni(II) salt used than upon the reaction time, the amount of $NaBH_3CN$ used, and the type of solvent system.

As with Dppm, only $NiCl_2 \cdot 6H_2O$ was used in elevated temperature reactions to eliminate the possibility of formation of potentially explosive perchlorates from $Ni(ClO_4)_2 \cdot 6H_2O$.

Detailed discussions of the individual complexes formed in these reactions will now be presented.

3.3.1 [NiH(Diphos)$_2$]ClO$_4$

This diamagnetic complex was first reported by Holah and co-workers (20) and it was prepared from a reaction between $Ni(Diphos)_2(ClO_4)_2$ and $NaBH_4$ in ethanol. Superficially then it is not surprising that the same complex can be synthesized from the $Ni(ClO_4)_2 \cdot 6H_2O|Diphos|NaBH_3CN$ system in mixed solvents by an extended period reaction. As will be seen shortly, a similar but not identical complex may be prepared from $NiCl_2 \cdot 6H_2O$. However, although hydrido complexes of transition metals are fairly easily prepared from suitable metal complexes using $NaBH_4$ as a reducing agent, formation of such hydrido complexes from similar reactions with $NaBH_3CN$ is a much less common event as discussed in the Introduction.

While this is a known complex, it was felt that complete and unambiguous characterization should be carried out. The infrared spectrum of this diamagnetic complex (for which excellent analytical date were obtained) shows a stretching frequency as a sharp

and medium intensity band at 1950 cm^{-1} as is shown in Fig. 32 and this is in agreement with the Ni-H hydride (terminal) stretching frequency observed for $[NiH(Diphos)_2]ClO_4$ (20). The ionic (64) ClO_4^- band appears as a very strong and broad peak at 1100 cm^{-1}.

The ^{31}P NMR spectrum of this complex (not recorded in Holah's earlier report) in $CHCl_3$ shows only one sharp signal at δ=44.95 which shows that the phosphorus atoms of the Diphos ligands are magnetically equivalent in the complex, at least in solution.

The ^{1}H NMR spectrum in $CDCl_3$ or in C_6D_6 shows a well-defined quintet at δ=-13.10 with a coupling constant of J_{PH}=5.6Hz. This high-field signal again suggests the presence of a metal hydride linkage and the quintet nature of the signal shows that coupling of the metal hydride proton with four identical phosphorus atoms occurs. Selected features of the IR and NMR spectra of this complex are given in Table 12.

On the basis of the above evidence, a structure for this complex has been assigned is as shown in Fig. 33. The five-

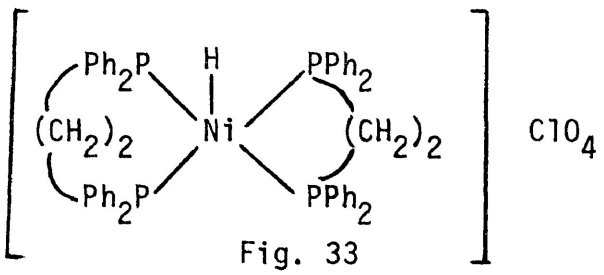


Fig. 33

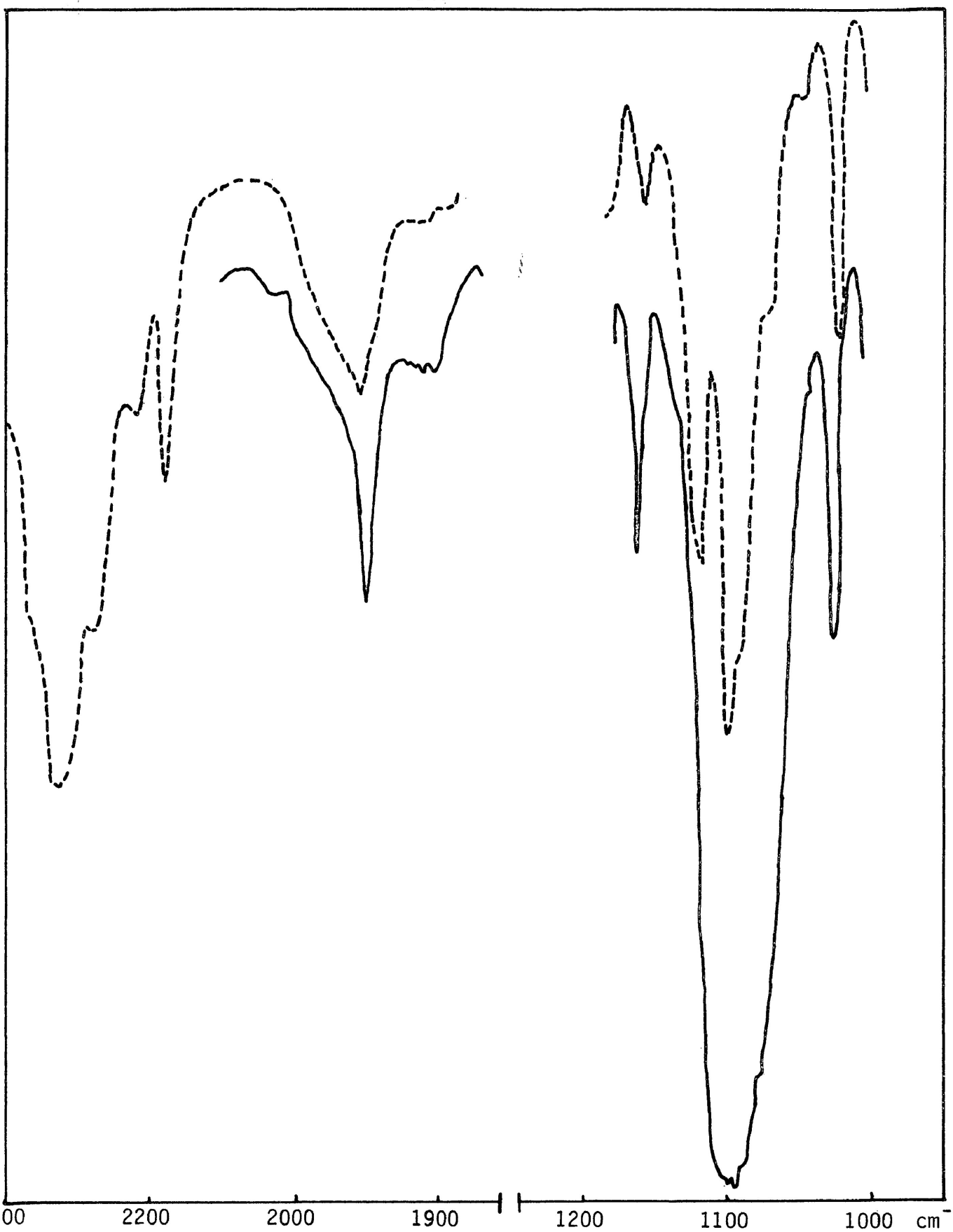


Fig. 32. Selected Features of the Infrared Spectra of the Complexes ---- $[NiH(Diphos)_2]BH_3CN$ and —— $[NiH(Diphos)_2]ClO_4$.

TABLE 12

Selected Features of the Infrared and NMR Spectra of Ni[BH_3CN^-]Diphos and Related Complexes

No.	Complex	Colour	ν BH Terminal	δ BH Deformation	ν CN	Other	M - H δ	^{31}P NMR δ	^{1}H NMR δ	Probable mode of coordination of BH_3CN^-
	$[NiH(Diphos)_2]ClO_4$	Wine-red	--	--		1100 (s) ClO_4^-	1950 (s)	44.95 ($CHCl_3$)	-13.10 quintet J_{PH}= 5.6Hz	--
2.	$[NiH(Diphos)_2]BH_3CN$	Wine-red	2330 (s,br) 2290 (w,sh) 2220 (w,sh)	--	2179 (s)	--	1950 (s)	44.95 ($CHCl_3$)	-13.10 quintet J_{PH}=5.5Hz	M+BH_3CN^-
3.a.	$[Ni_2(BH_3CN)_3(Diphos)_2]ClO_4$	Yellow	2370 (s,br) 2310 (w,sh) 2270 (w,sh)	--	2207 (s)	1100 (s,br) ClO_4^-	--	63.30 (CH_2Cl_2)	--	
b.	$[Ni_2(BH_3CN)_3(Diphos)_2]Cl$	"	2360 (s,br) 2290 (w,sh)	--	2207 (s)	--	--	63.30 (CH_2Cl_2)	--	Three M - HBH_2CN - M or M - DBD_2CN - M bridges
c.	$[Ni_2(BD_3CN)_3(Diphos)_2]ClO_4$	"	1770 (s,br) 1685 (m) 1640 (m)	--	2207 (s)	1100 (s) ClO_4^-	--	"	--	
d.	$[Ni_2(BD_3CN)(Diphos)_2]Cl$	"	1770 (s,br) 1685 (m) 1640 (m)	--	2207 (s)	--	--	"	--	
4.a.	$[Ni(BH_3CN)(Diphos)Cl]_2 \cdot EtOH$	Brown	2370 (s) 2290 (sh,w)	1120 (m)	2207 (s)	3360 OH	--	43.86 ($CHCl_3$)	--	Two M - HBH_2CN - M bridges
b.	$[Ni(BD_3CN)(Diphos)Cl]_2.EtOH$	"	1770 (s) 1685 (m) 1640 (m)	--	2207 (s)	3360 OH	--	"	--	
5.	$[Ni(BH_3CN)(Diphos_2Cl]_2$	Greenish Yellow	2330 (s,br)	1110 1125	2200	--	-- --	29.34 28.03 (CH_2Cl_2)	--	M - $NCBH_3$
6.	$CoD(BD_3CN)(PPh_3)_3$	Wine-red	1755 (s,br) 1680 (m) 1635 (m)	--	2190 (s)	--	--	--	--	M - $NCBD_3$
7.	$[Co(BD_3CN)(Dppm)_2]ClO_4$? or $[CoD(BD_2CN)(Dppm)_2]ClO_4$?	Brown	1755 (s,br) 1680 (m) 1635 (m)	--	2190 (s)	1100 (s,br) ClO_4^-	--	--	-- --	M - $NCBD_3$
8	$[Ni(BD_3CN)(Dppm)_2]ClO_4$	Brown	1755 (s,br) 1680 (m) 1635 (m)	--	2190 (s)	1100 (s,br) ClO_4^-	--	--	--	M - $NCBD_3$

coordinated species is shown as having square pyramidal type of geometry in which the hydride ligand occupies the apical position since this accounts for both the ^{1}H and ^{31}P spectra. However, the geometry may be less regular than this and, in solution, magnetic averaging of the P atoms may occur through the well-known Berry pseudorotational process.

3.3.2 [NiH(Diphos)$_2$]BH_3CN

This diamagnetic complex, which is clearly closely related to [NiH(Diphos)$_2$]ClO_4 has only been synthesized from the $NiCl_2 \cdot 6H_2O$|Diphos|$NaBH_3CN$ reaction. Experimental details are given in section 2 and, as with the ClO_4^- complex, long reaction times were required.

Once again, the analytical data obtained are in excellent agreement with this formulation and the IR spectrum of the wine-red crystals shows a medium intensity and sharp stretching frequency at 1950 cm^{-1} as shown in Fig. 32 (see also Table 12). This is virtually superimposable upon the Ni-H stretching frequency observed for [NiH(Diphos)$_2$]ClO_4 (20) also shown in Fig. 32. The C≡N stretching mode of the BH_3CN^- unit appears as a strong and sharp band at 2179 cm^{-1} which is identical in location to that of free ionic BH_3CN^- (27, 28). The BH_3 stretching frequency occurs as a very strong and broad band at 2330 cm^{-1} with a shoulder at 2290 cm^{-1} and the BH deformation

occurs as a doublet at 1130 cm^{-1} (w) and at 1110 cm^{-1} (s) as shown in Fig. 32. Again, this is consistent with ionic BH_3CN^- (28).

The ^{31}P NMR spectrum in CH_2Cl_2 shows a very strong signal at δ=44.95 which is identical in location and appearance with that observed for $[NiH(Diphos)_2]ClO_4$ and this again strongly suggests that the two complexes are strictly analogous.

This close relationship is finally proved by the ^1H NMR spectrum in $CDCl_3$ (or in C_6D_6) which shows a well-defined quintet at δ=-13.08 with a coupling constant of J_{PH}=5.6Hz - a location and pattern virtually identical to those exhibited by $[NiH(Diphos)_2]ClO_4$. The structure assigned is therefore as shown in Fig. 33 for the perchlorate complex but with ionic BH_3CN^- replacing ionic ClO_4^-. If this is the case, then it should be noted that this is possibly the first example of a Ni-hydride complex in which BH_3CN^- is present as an ionic species. This type of complex is rare because BH_3CN^- usually possesses a great tendency to occupy a vacant coordination site.

3.3.3 $[Ni_2(BH_3CN)_3(Diphos)_2]X$, where $X=Cl^-$ or ClO_4^-

This type of complex has been synthesized from both $Ni(ClO_4)_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ in reactions of short duration and the two diamagnetic complexes so formed are very sensitive towards most solvents. Analytical data (C, H, N and, where appropriate, Cl) for

several samples prepared on several different occasions were always in excellent agreement with the formulation given above. The two complexes will be treated together for structure assignment purposes.

The C≡N stretching frequencies of the BH_3CN^- grouping in these complexes appear as a very strong and sharp band at 2207 cm^{-1} in both instances. This is an increase of 28 cm^{-1} from the stretching frequency of CN in free ionic BH_3CN^- and such a large shift is reasonably conclusive evidence that the BH_3CN^- grouping is involved in coordination through the nitrogen atom as discussed earlier. The ClO_4^- stretching mode for $[Ni_2(BH_3CN)_3(Diphos)_2]ClO_4$ occurs as a strong and broad band at 1100 cm^{-1} which is consistent with the presence of the ionic ClO_4^- grouping (64). No metal-chloride band was detectable in the range 200 - 400 cm^{-1} for the analogous $[Ni_2(BH_2CN)_3(Diphos)_2]Cl$ and this implies ionic chloride is present. The two complexes are isomorphous and probably therefore isostructural by X-ray powder diffraction methods and, since ClO_4^- is clearly present in ionic form in one of the complexes, this too implies that Cl^- is ionic in the second complex. The BH_3 vibration modes occur as a broad and strong band at 2370 cm^{-1} for the ClO_4^- complex and at 2360 cm^{-1} for the Cl^- complex with a B-H deformation band at 1100 cm^{-1} for the latter. The B-H deformation mode in the spectrum of the ClO_4^- complex is obscured by the broad ClO_4^- band at around 1100 cm^{-1}. Selected features of the IR spectra of these two complexes are illustrated in Fig. 34, and are listed, together with other data, in Table 12.

These rather high values (2370 cm^{-1} and 2360 cm^{-1}) for

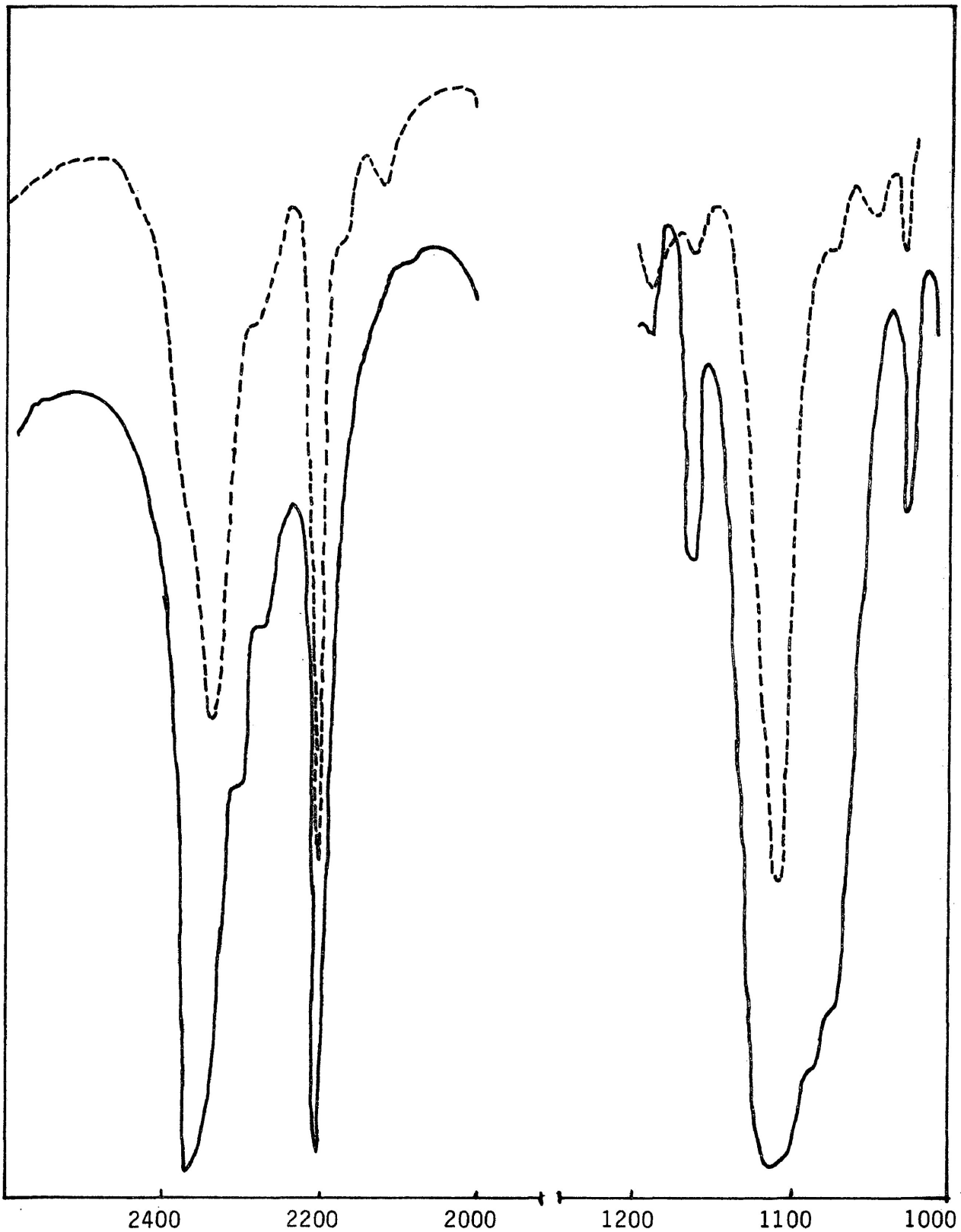


Fig. 34. Selected Features of the Infrared Spectra of —— $[Ni_2(BH_3CN)_3(Diphos)_2]ClO_4$, and ---- $[Ni_2(BH_3CN)_3(Diphos)_2]Cl$.

the B-H_t vibrations are suggestive of a M-H-BH_2CN linkage such as those which occur (X-ray crystallographic data) in the BH_3CN^- bridged species $[Cu_2(BH_3CN)_2(PPh_3)_2]_2$ (21,25) and $[Ni(BH_3CN)(tren)]_2(BPh_4)_2$ (C10) which were discussed in section 1.5. The former of these complexes shows the main B-H_t vibration at 2376 cm^{-1} while the latter shows it at 2380 cm^{-1}. As pointed out and discussed or observed elsewhere (10, 11) and as observed for other compounds in this thesis, monodentate BH_3CN^- groupings coordinated only through the nitrogen atom normally show the B-H_t vibration in the 2320-2350 cm^{-1} region.

There are two features of the IR spectra of the two complexes which should be examined before the structural discussion is taken any further. The first is that although the two complexes have the formulation $[Ni_2(BH_3CN)_3(Diphos)_2]X$ and are isostructural, there are apparently slight differences in the B-H_t stretching frequencies. Both absorptions are, however, quite broad and the apparent difference may arise merely from shape differences at the maxima of the two absorptions (Fig. 34, 35). Alternatively, in the crystalline complexes, ClC_4^- and Cl^- may interact electrostatically to different extents with the cation. Unfortunately, neither complex was sufficiently stable in solution for comparison of the solution infrared spectra where such ionic interactions should be less significant. However, as will be seen shortly, there is evidence which indicates strongly that the observed phenomenon is simply a band envelope shape effect and that the Ni and BH_3CN^- containing portions of the two complexes are of identical structure.

The second point is that although analytical data strongly suggest that three BH_3CN^- units are present in each complex (1.5 units per Ni atom), the two complexes show only one sharp C≡N stretching frequency at 2207 cm^{-1} in both cases. This suggests a very symmetrical structure.

The available evidence then indicates that the BH_3CN^- groupings in these complexes might be present as a bridging ligand in a symmetrical arrangement and, in this connection, it is interesting to note that while $[Cu(BH_3CN)(PPh_3)_2]_2$ shows (21) two C≡N frequencies in the IR spectra (at 2207 and 2190 cm^{-1}) since it is unsymmetrical (25), the symmetrical $[Ni_2(BH_3CN)(tren)]_2(BPh_4)_2$ shows only one such vibration (10) (at 2221 cm^{-1}).

This possible bridging by the BH_3CN^- groupings will now be examined further by considering the corresponding BD_3CN^- complexes where separation of the various $B\text{-}D_t$ stretching frequencies should be much clearer at lower frequency and where resolution is greater. The infrared spectra of the two deuterated complexes show that the rather broad B-H stretching frequency has been shifted, as expected, on deuteration to lower frequency and this isotopic shift is accompanied by splitting of the absorption into three individual bands at 1770 cm^{-1}(s), 1685 cm^{-1}(m) and 1640 cm^{-1} (w) for both complexes. There is some evidence of underlying shoulders on each peak. The CN stretching mode remains unchanged in the spectra of both deuterated complexes at 2207 cm^{-1}. Selected features of the infrared spectra of the deuterated complexes are shown

in Fig. 35 and tabulated in Table 12. This identical and well-resolved pattern for the B-D_t frequencies obtained for the two complexes show clearly that the minor differences observed for the corresponding B-H_t maxima are indeed band envelope shape differences.

To establish what these B-D frequencies mean in terms of bridging or monodentate BD_3CN^- groupings, it is necessary to compare the observed spectra of these two deuterated complexes $[Ni_2(BD_3CN)_3(Diphos)_2]X$ with those of known bridged species (deuterated) and known monodentate species. The two known bridged species $[Cu(BD_3CN)(PPh_3)_2]_2$ and $[Ni(BD_3CN)(tren)]_2(BPh_4)_2$ both show (10) a complex pattern of B-D vibration in the 1600-1800 cm^{-1} range. The most prominent peak in this region is at 1784 cm^{-1} for the copper complex and at 1798 cm^{-1} for the nickel complex and these two peaks have been attributed to the (^{11}B)ν B-D stretch. Other weaker peaks in this region have been attributed to the corresponding (^{10}B)νB-D peaks and various ^{11}B and ^{10}B M-D-B vibrations. It seems then that it is the strongest peak in this region which is the most definitive and, in the spectra of the two complexes $[Ni_2(BD_3CN)_3(Diphos)_2]X$, this occurs at 1770 cm^{-1}.

There are two monodentate BH_3CN^- containing species, $(Cu(BH_3CN)_2(Me_5dien)$ and $CoH(BH_3CN)(PPh_3)_3$ which have been unambiguously characterized by X-ray methods (24, 44), but there is no published IR data yet available for the deuterated versions of these systems. However, the deuterated complex $CoD(BD_3CN)(PPh_3)_3$ has been synthesized in this present work for these infrared comparisons and this shows the B-D_t frequencies

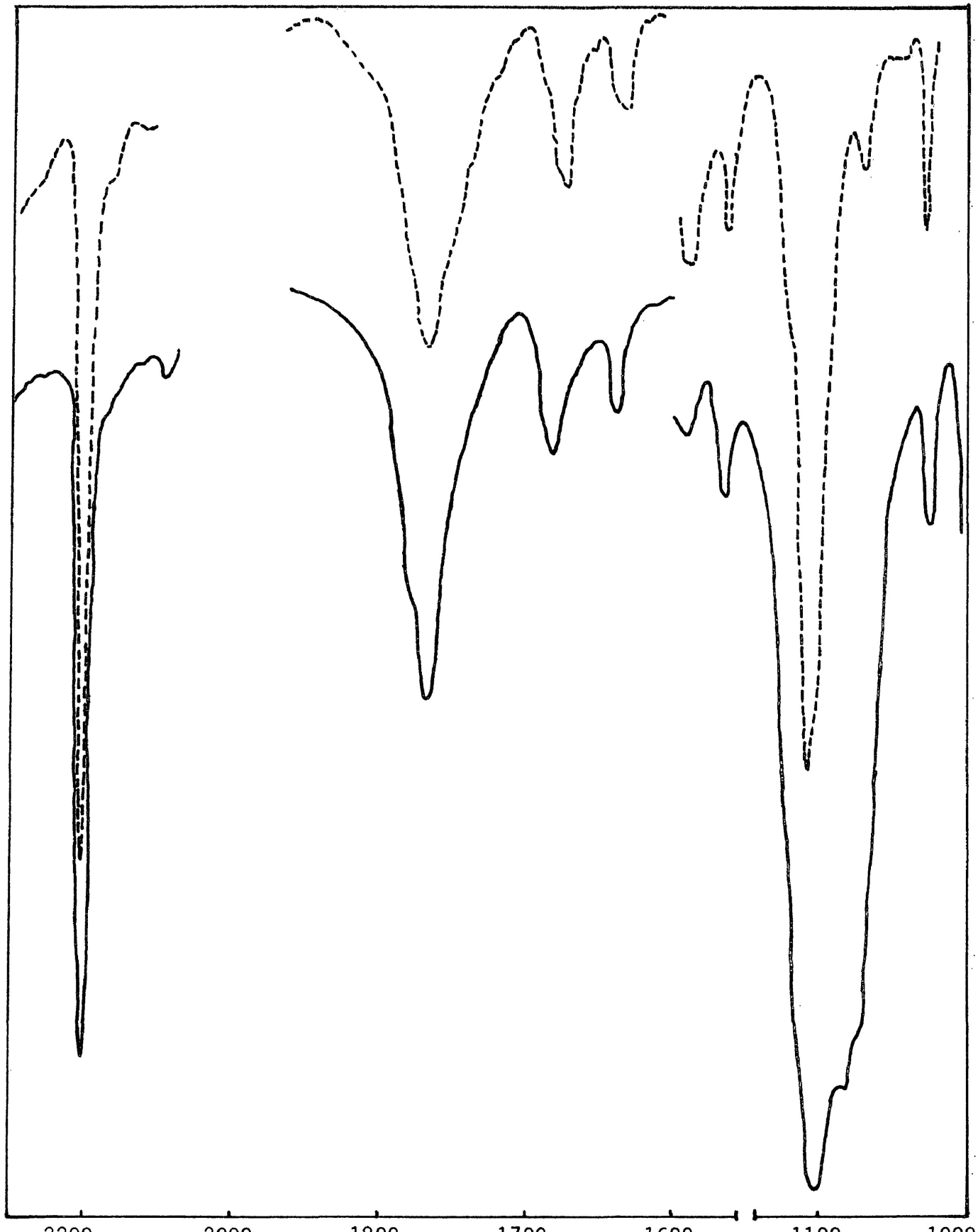


Fig. 35. Selected Features of the Infrared Spectra of —— $[Ni_2(BD_3CN)_3(Diphos)_2]ClO$ and ---- $[Ni_2(BD_3CN)_3(Diphos)_2]Cl$.

at 1755 cm^{-1}(s), 1680 cm^{-1} (m) and 1635 cm^{-1}(w) as shown in Fig. 36 and listed in Table 12. Clearly, the most intense absorption at 1755 cm^{-1} is at considerably lower frequency than the B-D vibrations discussed so far. Besides this, the deuterated version of the almost certainly monodentate BH_3CN- complex $[Ni(BH_3CN)(Dppm)_2]ClO_4$ synthesized in this work (see section 3.2.1) also shows the B-D frequencies at 1755 cm^{-1}, 1680 cm^{-1} and 1640 cm^{-1} respectively again as shown in Fig. 35 and Table 12. Similarly, the apparently related species initially reported (11) as $[Co(BH_3CN)(Dppm)_2]ClO_4$ but now tentatively reformulated (26) as $[CoH(BH_2CN)(Dppm)_2]ClO_4$ (see section 1.5.2.2.) shows an almost identical B-D pattern with the main absorption at 1755 cm^{-1} (Fig. 36 Table 12).

In this last illustration, however, the B-Dstretch may be due to monodentate BD_3CN^- or BD_2CN and, perhaps, this observation should be treated with care. However, the weight of the infrared evidence suggests that the B-H_t and B-D_t frequencies observed for $[Ni_2(BH_3CN)_3(Diphos)_2]X$ and $[Ni_2(BD_3CN)_3(Diphos)_2]X$ are more consistent with bridging BH_3CN^- than with monodentate BH_3CN^-. One final point to be noted is that the isotopic shifts observed in the infrared spectra on going from $[Ni_2(BH_3CN)_3(Diphos)_2]X$ to $[Ni_2(BD_3CN)_3(Diphos)_2]X$ shows the νB-D/νB-H = 0.746 for the peak at 2370 cm^{-1} (perchlorate) and νB-D/νB-H = 0.750 for the peak at 2360 cm^{-1} (chloride). These are consistent with the calculated ratio of νB-D/νB-H based on the reduced masses of the atom pair of 0.736 (10).

Turning now to NMR data, the ^{31}p NMR spectra of $[Ni_2(BH_3CN)_3(Diphos)_2]X$ in CH_2Cl_2 show only one sharp and strong signal

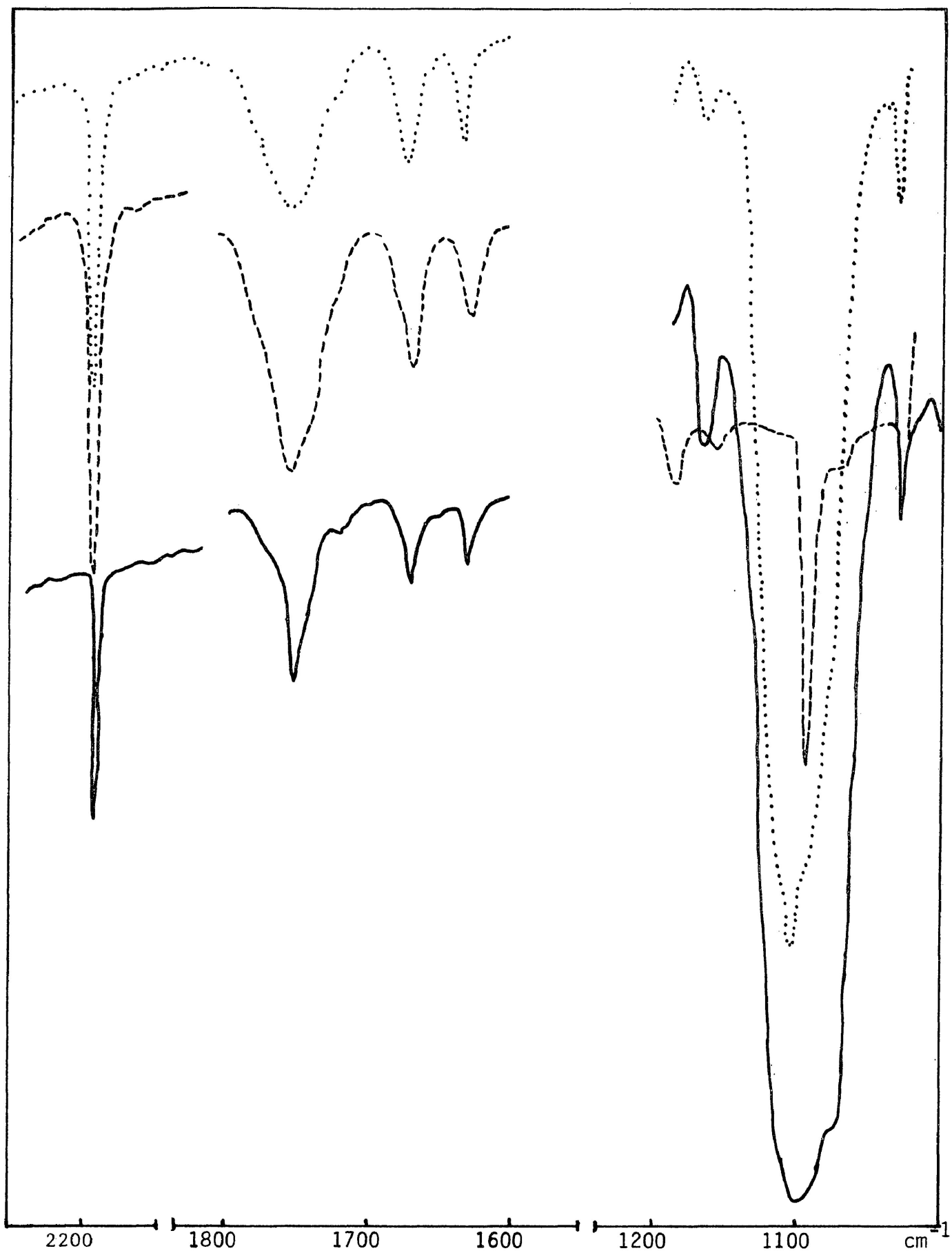


Fig. 36. Selected Features of the Infrared Spectra of the Deuterated Complexes
—— $[Co(BD_3CN)(Dppm)_2]ClO_4$ (or $[CoD(BD_2CN)(Dppm)_2]ClO_4$), ---- $CoD(BD_3CN)(PPh_3)_3$
.... $[Ni(BD_3CN)(Dppm)_2]ClO_4$.

at δ = 63.30 for freshly prepared solutions over a period of about 20 mins. This evidence indicates that the phosphorus atoms of the Diphos ligands are equivalent in the two complexes at least in solution and that both complexes contain the same Ni/BH_3CN^-/Diphos unit. These NMR data therefore apparently confirm the generally symmetrical nature of the two species which was tentatively deduced from the presence of only one sharp C≡N stretch in the IR spectra. More will be said later regarding the significance of the value of the observed shift. As mentioned earlier, however, these complexes decompose in most solvents and, as the ^{31}P NMR recording time increases, decomposition occurs. A new sharp peak at δ = 44 gradually becomes stronger with time while the intensity of the signal at δ = 63.30 decreases. After 48 hours the signal at δ = 63.30 completely disappears leaving only the signal at δ = 44. The solution colour changes from yellow to brown in this time. Clearly $[Ni_2(BH_3CN)_3(Diphos)_2]^X$ decomposes in solution to give a single phosphorus-containing product. More will be said about this product later as it has been fairly well characterized as a product in other $Ni(II)/BH_3CN^-$/Diphos reactions.

If the system is a symmetrical Ni/BH_3CN^-/Diphos containing unit then the chloride content of the molecule $[Ni_2(BH_3CN)_3(Diphos)_2]Cl$ (determined by the Mohr titration method) would have to be ionic. This ionic nature has apparently been confirmed from Molar conductivity measurements carried out in $CHCl_3$ solution (the species was generally too short lived in other solvents). Even then, these conductivity measurements had to be carried out in a very short time because the compound decomposes slowly in $CHCl_3$ and this is accompanied by a change in the

solution colour from yellow to brown. The molar conductance of 4.0×10^{-3}M solutions in $CHCl_3$ at 20^oC was found to be 11 $ohm^{-1}cm^2\ mol^{-1}$, and the system is therefore a weak electrolyte. The value obtained is rather low for the system to be considered as a true 1:1 electrolyte but three factors should be taken into account. First, in addition to the measured conductance value being low, it decreases fairly rapidly with time and the actual value is probably higher than that observed. Second, the conductance of electrolytes varies markedly with solvent (70) with lower values being observed in less polar solvents. For example, $Ph_4P^+Cl^-$ in CH_3CN shows a very high value for the conductance but this drops significantly when less polar solvents than CH_3CN are used. In this context, $CHCl_3$ is not a particularly polar solvent. The third factor is the size of the ions in the complex and since solution conductivity values are a measure of the rate of migration, large ions such as $[Ni_2(BH_3CN)_3(Diphos)_2]^+$ would move very slowly. The fact remains, however, that the system is a weak electrolyte even though it is perhaps not a classical 1:1 electrolyte.

Conductance measurements were not carried out on $[Ni_2(BH_3CN)_3(Diphos)_2]ClO_4$ partly because of solution stability problems but also because it is clear from the IR spectrum that the perchlorate grouping is ionic. This IR evidence also confirms the ionic nature of Cl^- in the solid state of $[Ni_2(BH_3CN)_3(Diphos)_2]Cl$ since X-ray powder diffraction studies show that the Cl^- and ClO_4^- complexes are isostructural. It should also be remembered that in solution, the two complexes give identical ^{31}P spectra.

In a further effort to establish ionic character, solutions in methylene chloride of both the chloride and perchlorate were reacted with solutions of $NaBPh_4$ in ethanol in an effort to make the BPh_4^- salts. The yellow colors of the starting solutions were slowly discharged, but no identifiable product could be isolated.

The changes observed with time for both the conductance values and ^{31}P NMR spectra will be considered shortly.

There is now sufficient evidence to allow possible structural assignments to be made for the species $[Ni_2(BH_3CN)_3(Diphos)_2]X$ where $X = Cl^-$ or ClO_4^-. First, the analytical data obtained agree very closely with this formulation. However, while it is clear from the analyses that the ratio of BH_3CN^-: Ni : Diphos is 1.5 : 1 : 1 and that there must be at least two nickel ions present in the structure, structures containing four or six Ni ions cannot be excluded on the basis of analytical data alone. Unfortunately, molecular weight measurements could not be carried out because of the instability of these systems and their ionic nature. Infrared data and ^{31}P NMR spectra show that the Ni/BH_3CN^-/Diphos containing fragment is a symmetrical species and infrared data again suggests strongly that the BH_3CN^- groupings are coordinated in a M—H—BH_2—CN—M mode. The two complexes are also ionic.

From this, it follows that if there are indeed only two nickel atoms present in each molecule the only possible type of structure is the five-coordinate Ni(II) structure shown in Fig. 37 although a

variation on this is to have all three C≡N groups attached to the same atom. Referring briefly back to the ^{31}P NMR data, the observed chemical shift of δ = 63.30 represents a rather large coordination shift of about 76.5 ppm downfield from the signal of the free ligand. This is entirely consistent with the fact that the Diphos unit is chelating one nickel ion rather than bridging two nickel ions since chelation by Diphos gives a five-membered ring and this particular ring size for chelating bis-phosphines leads to strong deshielding (62). Numerous examples of this ring size effect have appeared in the literature (62) and these examples suggest that bridging Diphos would be expected to have a much smaller downfield shift than that observed. However, this much depends upon the nature of the metal ion, its substitution pattern, its oxidation state and its coordination number. Thus, not only do the ^{31}P NMR spectra show that the P atoms are identical but that the Diphos units are chelating as required by the structure shown in Fig. 37.

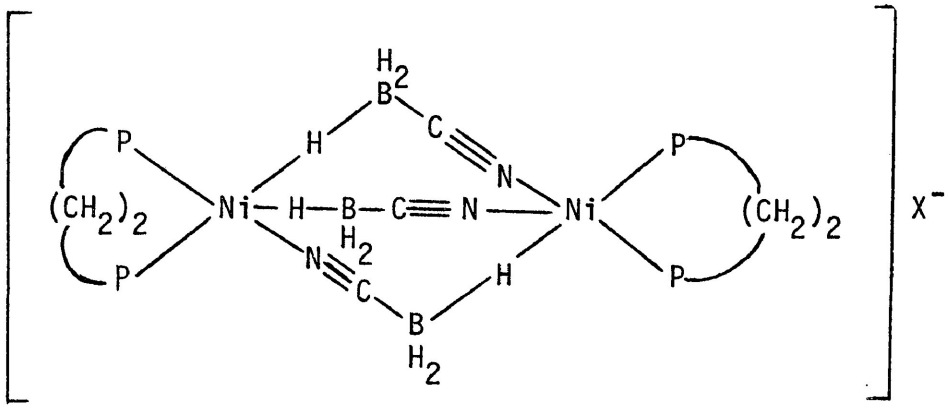


Fig. 37

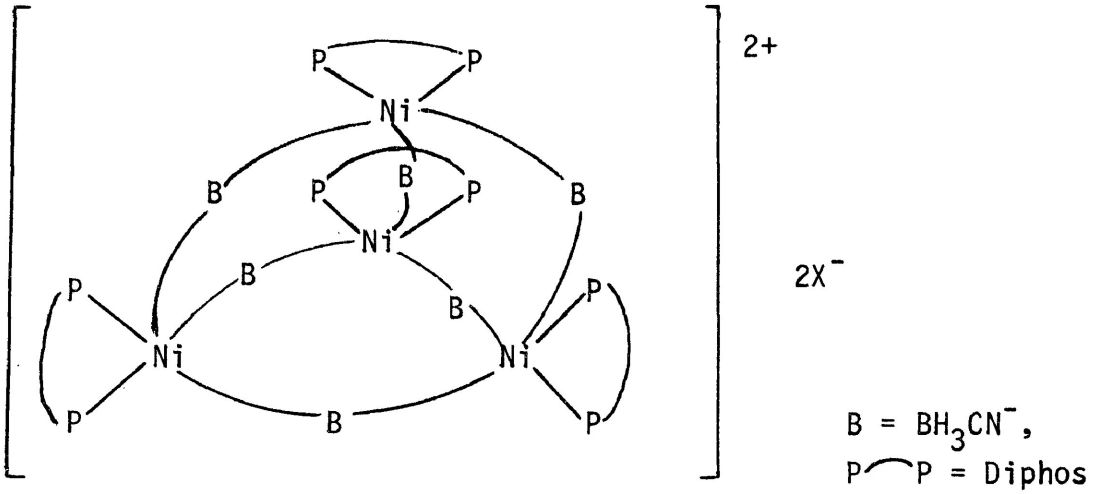


Fig. 38

If this structure is correct, then this would be the first example of triple bridging of two metal ions by BH_3CN^-. As discussed earlier, double bridging is well characterized.

If there are four nickel ions present in the molecular unit, then somewhat different types of structure consistent with the evidence, such as that shown in Fig. 38 in which there is a tetrahedral arrangement of BH_3CN^- bridged Ni ions, can be visualized. With six nickel ions, even more complex structures would arise. The structure shown in Fig. 38 involves only simple bridging by BH_3CN^- between any two Ni(II) ions.

Only an X-ray structure could solve this problem but this author feels that the binuclear, triply bridged system shown in

Fig. 37 is the most likely for several reasons. First, the only known (10, 25) BH_3CN^- bridged species are both binuclear and, while both of these are doubly bridged, there appears to be no steric or electronic reason why triple bridging could not occur. Second, as will be seen shortly, it appears that one bridging BH_3CN^- unit in $[Ni_2(BH_3CN)_3(Diphos)_2]Cl$ can be displaced by chloride ion to give an apparently doubly bridged system which is covalent and for which molecular weight data strongly indicate a binuclear structure. Finally, the two complexes are reasonably soluble (though rather unstable) in many common solvents and this would indicate that the molecular weights are not too high.

3.3.4 $[Ni(BH_3CN)(Diphos)Cl]_2.EtOH$

A diamagnetic complex of the above stoichiometry (analytical data) has been synthesized in higher temperature reactions from $NiCl_2.6H_2O$ only and it is stable in solution for long periods. The dimeric structure has been assigned on the basis of evidence which will be considered shortly.

Considering first infrared data, the C≡N stretching frequency occurs as a very strong and sharp band at 2207 cm^{-1} and, as with $[Ni_2(BH_3CN)_3(Diphos)_2]X$ which shows exactly the same stretching frequency, this shows that BH_3CN^- is coordinated through the nitrogen atom. The B-H_t stretching band appears as a strong and broad band at 2370 cm^{-1} with a weak shoulder at 2290 cm^{-1}, and, as outlined for $[Ni_2(BH_3CN)_3(Diphos)_2]X$, this strongly indicates that the BH_3CN^- unit is involved in the M-H-BH_2—CN-M type of bonding and a bridged binuclear species again seems likely. There

is also a weak and broad band at 3360 cm^{-1} which is probably due to the presence of EtOH in the lattice. Certainly, analytical data indicate the presence of half a molecule of EtOH per nickel ion and ^1H NMR studies to be discussed soon, confirm this.

Upon deuteration, $[Ni(BH_3CN)(Diphos)Cl]_2$ shows an infrared spectrum in which the CN stretching frequency remains at the same location as in the spectrum of the undeuterated complex but the $B\text{-}H_t$ vibration vanishes to be replaced by B-D vibrations at 1770 cm^{-1}, 1685 cm^{-1} and 1640 cm^{-1}. These vibrations are at virtually the same frequencies as those observed for $[Ni_2(BH_3CN)_3(Diphos)_2]X$. Thus, the locations of the $B\text{-}H_t$ and $B\text{-}D_t$ vibrations are strongly indicative of the fact that the BH_3CN^- units are present as bridging ligands. A minimum of two Ni(II) ions is therefore present in the molecular unit. Selected features of the infrared spectra of the deuterated and undeuterated complexes are illustrated in Fig. 39 and are summarized in Table 12.

The ^{31}P NMR spectrum of this complex in CH_2Cl_2 shows a strong and sharp signal at δ = 43.86 which indicates again that the phosphorus atoms of the Diphos ligands are equivalent, at least in solution. This chemical shift is virtually identical with that observed as appearing during the solution decomposition of $[Ni_2(BH_3CN)_3(Diphos)_2]X$ (discussed earlier). The decomposition product recovered from solutions which had originally contained $[Ni_2(BH_3CN)_3(Diphos)_2]Cl$ gave analytical data in good agreement with the formula $[Ni(BH_3CN)(Diphos)Cl]_2 \cdot EtOH$ and the two ^{31}P spectra are identical. One puzzling feature about this

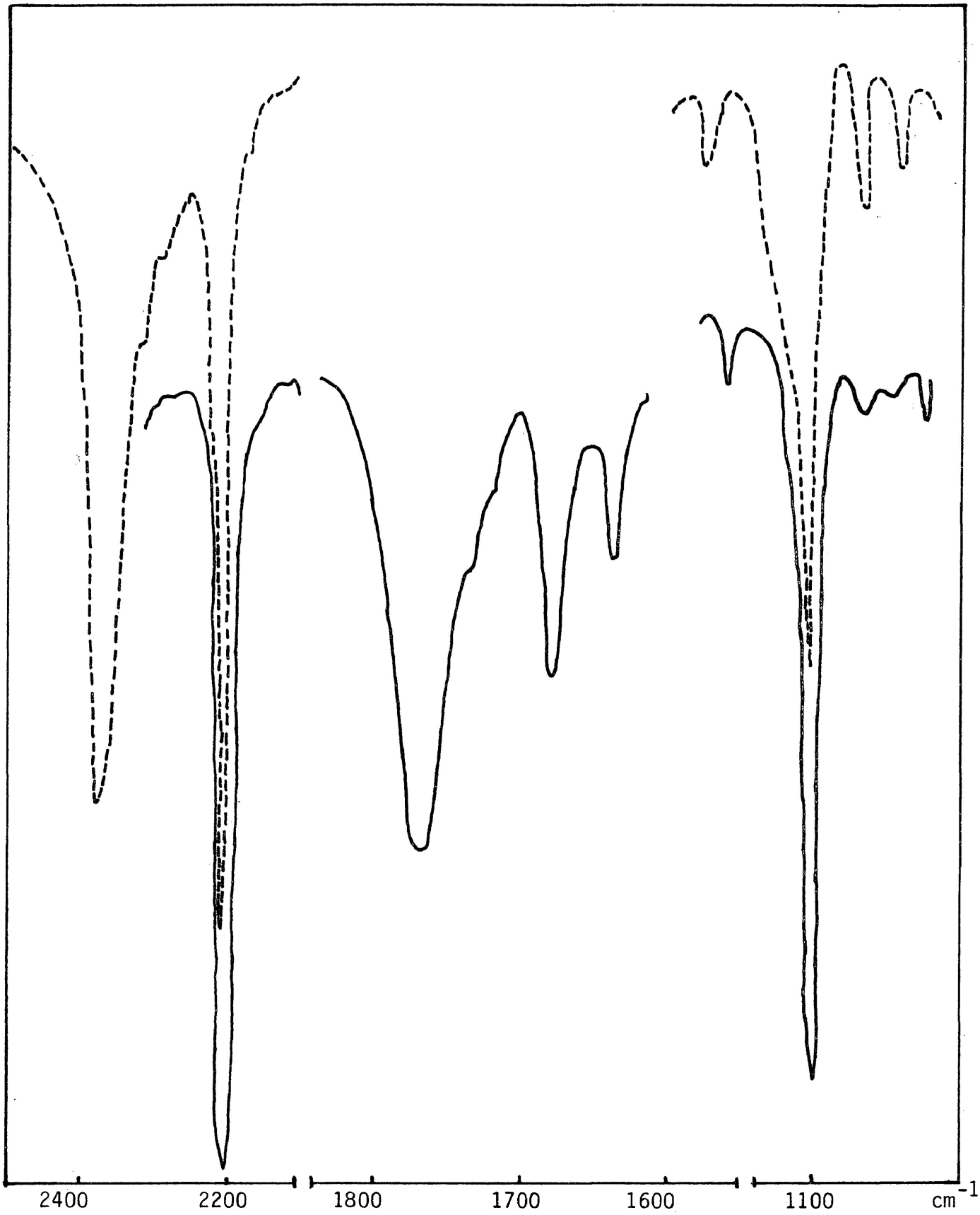


Fig. 39. Selected Features of the Infrared Spectra of

---- $[Ni(BH_3CN)(Diphos)Cl]_2$ and —— $[Ni(BD_3CN)(Diphos)Cl]_2$.

decomposition of $[Ni_2(BH_3CN)_3(Diphos)_2]X$ is that both the chloride and the perchlorate give identical ^{31}P NMR decomposition spectra. This is not in itself unexpected, but as will be seen shortly, the product obtained from decomposition of the chloride, $[Ni(BH_3CN)(Diphos)Cl]_2$.EtOH, is probably covalent in solution whereas the decomposition of the perchlorate would be expected to give a product (not isolated) which would be ionic. Different ^{31}P spectra for the two decomposition products would therefore be expected.

The presence of ethanol of crystallization was confirmed by examination of the ^1H NMR spectrum, which shows a poorly resolved quartet at δ = 3.75 and a triplet at δ = 1.25 which are identical in location (but not resolution) with those of pure ethanol under these conditions. Integration (and analysis) showed that there is half a molecule of ethanol per Diphos unit in the structure and, since IR studies indicate that the system is at least binuclear, the empirical formula is $[Ni(BH_3CN)(Diphos)Cl]_2 \cdot EtOH$.

The complex $[Ni(BH_3CN)(Diphos)Cl]_2$.EtOH is a non-electrolyte (which explains the rapid decrease in the conductance observed for solutions of $[Ni_2(BH_3CN)_3(Diphos)]^+Cl^-$). A molecular weight determination in $CHCl_3$ gave a result (see Experimental Section) in very close agreement with the dimeric formulation proposed. However, infrared studies in the 200 - 400 cm^{-1} range showed no absorption assignable to the Ni-Cl band and this, together with the unexplained points from the ^{31}P NMR spectra noted above, leave some doubts regarding the precise nature of the chlorine content.

There is now enough information for a structural assignment to be made. Thus, analytical, IR and ^1H NMR data show the empirical formula to be $[Ni(BH_3CN)(Diphos)Cl]_2$ and the infrared spectrum additionally strongly suggests that the BH_3CN^- unit is bridging. Furthermore, since only one C≡N stretching frequency is present, the system is symmetrical in the solid state. The ^{31}P NMR spectrum shows that all phosphorus atoms are equivalent in solution, while conductance measurements suggest that the chlorine is covalently bound. Molecular weight measurements support the dimeric formulation given above.

The only structure consistent with all of this data is that shown in Fig. 40 in which the two Ni(II) ions are five-coordinated and doubly bridged by BH_3CN^-.

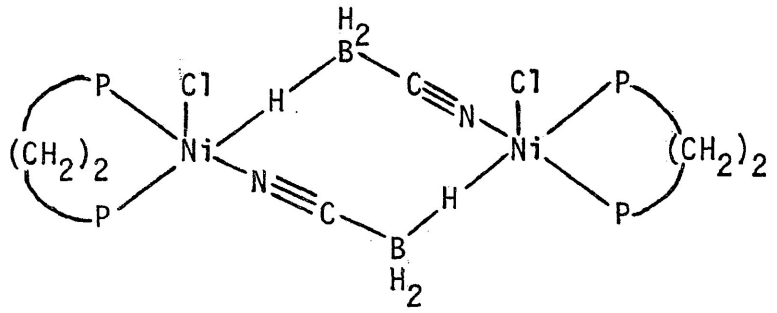


Fig. 40

Several further points should be made here. The first is that a symmetrical binuclear Ni (II) system of this doubly bridged type $[Ni(BH_3CN)(tren)]_2(BPh_4)_2$ (already discussed) has been well characterized by X-ray methods and shows precisely the same value for the C≡N stretching frequency as does $[Ni(BH_3CN)(Diphos)Cl]_2$. There are, of

course, differences in that one species is ionic with six-coordinate Ni(II) whereas the other is apparently covalent with five-coordinate Ni(II).

The second point is that if the structure shown in Fig. 40 is correct, it offers some support for the dimeric structure (Fig. 37) suggested for $[Ni_2(BH_3CN)_3(Diphos)_2]Cl$ since clearly decomposition of this species to give $[Ni(BH_3CN)(Diphos)Cl]_2$ would require only the displacement of one bridging BH_3CN^- unit by two chloride ions. However, two chloride ions would require two $[Ni_2(BH_3CN)_3(Diphos)_2]^+$ ions to be involved and the question of what happens to the second of these now arises since only one ^{31}P signal is observed after decomposition is complete. This together with the fact that both $[Ni_2(BH_3CN)_3(Diphos)_2]^+ Cl^-$ and ClO_4^- decompose to give exactly the same ^{31}P NMR spectrum again casts doubt upon the covalent nature of the chlorine in $[Ni(BH_3CN)(Diphos)Cl]_2$. If the chlorine is, after all, ionic (perhaps very closely ion paired) then the reaction shown below would explain the decomposition of $[Ni_2(BH_3CN)_3(Diphos)]X$, the isolation of $[Ni(BH_3CN)(Diphos)Cl]_2$, , the appearance of only one ^{31}P decomposition product signal, and the absence of a Ni-Cl stretching frequency in the IR spectrum of $[Ni(BH_3CN)(Diphos)Cl]_2$. Thus, the decomposition would be more of a simple disproportionation to give two products possessing a common Ni/BH_3CN^-/Diphos containing ion.

$2[Ni_2(BH_3CN)_3(Diphos)_2]X$

$\delta^{31}P = 63.30$

→ $[Ni(BH_3CN)(Diphos)]_2^{2+}\ 2X^-$

$\delta^{31}P = 43.86$

Precipitated as the chloride

→ $[Ni(BH_3CN)(Diphos)]_2^{2+}\ 2BH_3CN^-$

$\delta^{31}P = 43.86$

Possibly present in solution

i.e. the complex formulated as the covalent $[Ni(BH_3CN)(Diphos)Cl]_2$ is perhaps better formulated as the ionic $[Ni_2(BH_3CN)_2(Diphos)_2]^{2+}$ $2Cl^-$ in which case the structure would be as shown in Fig. 41

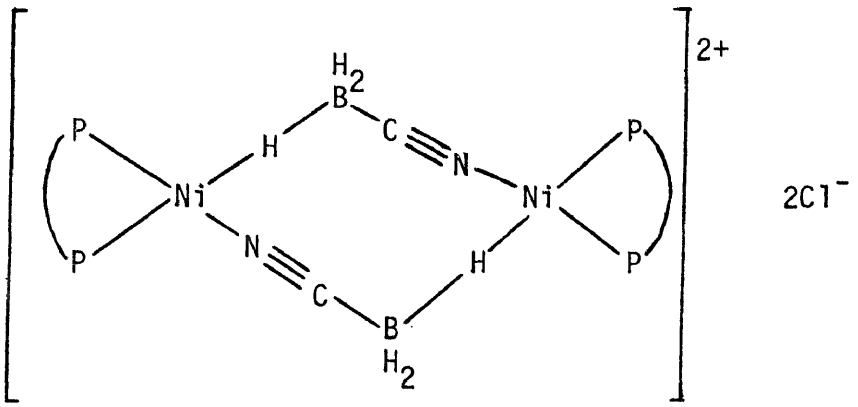


Fig. 41

where the Ni(II) ions are four-coordinate. Clearly, the conductivity and molecular weight data must be treated with caution.

A third point of interest is the actual value of the ^{31}P chemical shift of $[Ni(BH_3CN)(Diphos)Cl]_2$ at δ = 43.86. While this is less of a shift than that observed for $[Ni_2(BH_3CN)_3(Diphos)_2]X$ at δ = 63.3, it is still consistent with a chelating Diphos unit since the cis-square planar $(Diphos)NiCl_2$ shows (62) a remarkably similar shift of δ = 46.1. Perhaps this too indicates that the species formulated as $[Ni(BH_3CN)(Diphos)Cl]_2$ is best represented as the four-coordinate structure shown in Fig. 41 (the triply bridged system is five-coordinate) although the actual shift values of chelated bis phosphines are very sensitive to changes in substitution pattern, coordination number, oxidation state, etc. (62).

In conclusion, while one can be reasonably sure that the structure of $[Ni(BH_3CN)(Diphos)Cl]_2$ is either as shown in Fig. 40 or as shown in Fig. 41, X-ray data would be required before a final structural assignment is made.

3.3.5 $[Ni(BH_3CN)(Diphos)_2Cl]_2$

This compound may be synthesized from the $NiCl_2.6H_2O$ /Diphos/ BH_3CN^- system in a reaction which requires a long time (see Experimental section). The compound is stable in solution and is diamagnetic. The dimeric formulation is given on the basis of spectroscopic

and molecular weight data to be discussed shortly.

Looking first at the infrared spectrum, the C≡N stretching frequency appears as a strong and sharp band at 2200 cm^{-1} while the BH_3 vibrations occur as a strong and broad band at 2330 cm^{-1}. The B-H deformation was at first thought to occur at 1110 cm^{-1} with a shoulder at 1115 (w) cm^{-1} but, as will be seen shortly, this absorption remains when BH_3CN^- is replaced by BD_3CN^- and it is therefore probably due to a ligand vibration. Clearly, the C≡N stretching frequency is consistent with coordination to a metal ion through the nitrogen atom but the $B\text{-}H_t$ vibrational frequency indicates that no M—H—B bonding is present - i.e. in this complex, the BH_3CN^- unit is not present as a bridging unit. This deduction is supported by the infrared spectrum of the deuterated complex $[Ni(BD_3CN)(Diphos)_2Cl]_2$ which shows the C≡N stretching unchanged at 2200 cm^{-1} and the B—D vibrations at 1755 cm^{-1}, 1680 cm^{-1} and 1635 cm^{-1}. As outlined earlier this is consistent with monodentate N-coordinated BD_3CN^- and the B—D pattern observed is virtually identical with that of the well characterized complex $CoD(BD_3CN)(PPh_3)_3$ (44). There is no peak in the 200 cm^{-1} - 400 cm^{-1} range assignable to the Ni-Cl vibration and the chloride unit therefore may or may not be ionic. This will be discussed later. Selected features of the infrared spectra of the deuterated and undeuterated complexes are shown in Fig. 42 and recorded in Table 12.

The ^{31}P NMR spectrum of the complex in CH_2Cl_2 solution shows a doublet at δ = 29.34 and at δ = 30.03 showing that all P atoms

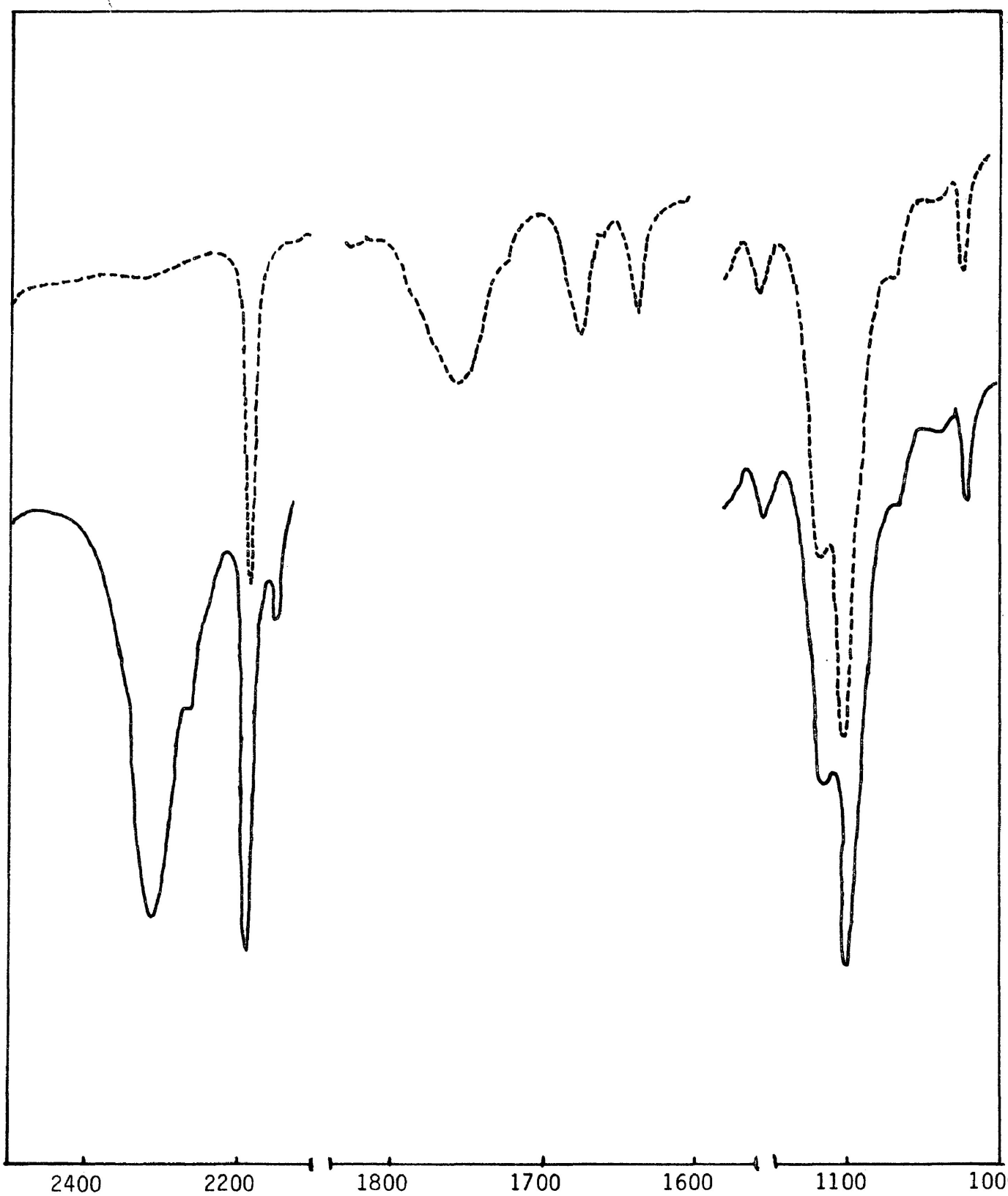


Fig. 42. Selected Features of the Infrared Spectra of the Complexes, —— $[Ni(BH_3CN)(Diphos)_2Cl]_2$ and ---- $[Ni(BD_3CN)(Diphos)_2Cl]_2$.

are coordinated. The two peaks are of approximately equal area but they are of completely different shape with the lower field peak broadened and rounded and the higher field peak sharp and intense. Clearly, in solution, there are two types of phosphorus atoms present in equal numbers. The values observed for the chemical shifts are less informative since they indicate that while coordinated, the two types of phosphorus atoms are probably not chelating. Generally, as mentioned earlier, chelated Diphos shows δ values of at least +40 and much larger shifts are quite common (62) depending upon the metal involved. The observed values, then are more consistent with Diphos coordinated to two metal atoms and, as will be seen shortly, bridging Diphos is probably involved in the structure. The shape of the lower field peak is much broader and rounded than the higher field peak. The ^{31}P Diphos peaks observed so far in all of the compounds mentioned in this thesis are very sharp and the broadened nature here may imply some sort of exchange process or the presence of two very closely spaced but unresolved signals.

The complex is a non-electrolyte in solution and a molecular weight determination shows a value which is very close to that expected for the dimeric system $[Ni(BH_3CN)(Diphos)_2Cl]_2$. This evidence apparently indicates the presence of coordinated chloride which is supported by the fact that the complex can be synthesized from the $NiCl_2 \cdot 6H_2O$ salt only. All attempts to prepare it from $Ni(ClO_4)_2 \cdot 6H_2O$ were unsuccessful. Clearly, if the product were $[Ni(BH_3CN)(Diphos)_2]^{2+} 2Cl^-$, there would be no obvious reason why the perchlorate anologue could not be formed. Note that in the ionic system $[Ni_2(BH_3CN)_3(Diphos)_2]^+X^-$, both the chloride

and perchlorate can be formed. However, as outlined in the previous subsection, molecular weight and conductivity data for these high molecular weight systems must be treated with caution.

There is now sufficient evidence for structural suggestions to be made. Thus, analytical and molecular weight data are consistent with the formula $[Ni(BH_3CN)(Diphos)_2Cl]_2$, molecular weight and conductivity data suggest that chloride is coordinated, infrared spectra show that BH_3CN^- is monocoordinated through the nitrogen, and ^{31}P NMR data suggest that at least two chemically different kinds (though magnetically very similar) of phosphorus atoms are present.

The most obvious structure which is consistent with this evidence is shown in Fig. 43. However, this structure suffers from two drawbacks. First, six coordinated nickel(II) would be expected to be paramagnetic and the two nickel ions are sufficiently far apart that spin-pairing would be unlikely.

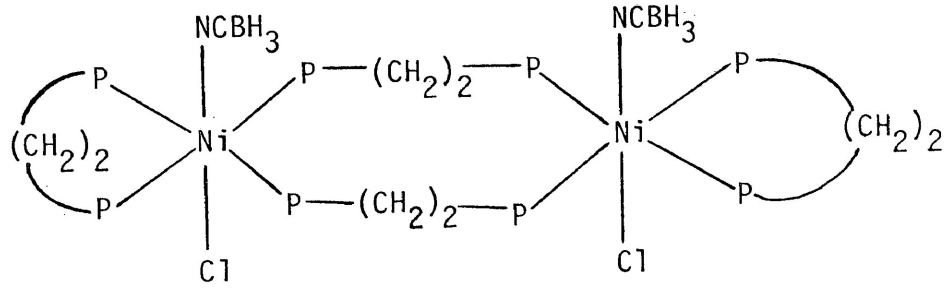


Fig. 43

Second, the ^{31}P spectra, as already outlined suggest that none of the Diphos units is chelating. Another possible structure is that shown in Fig. 44.

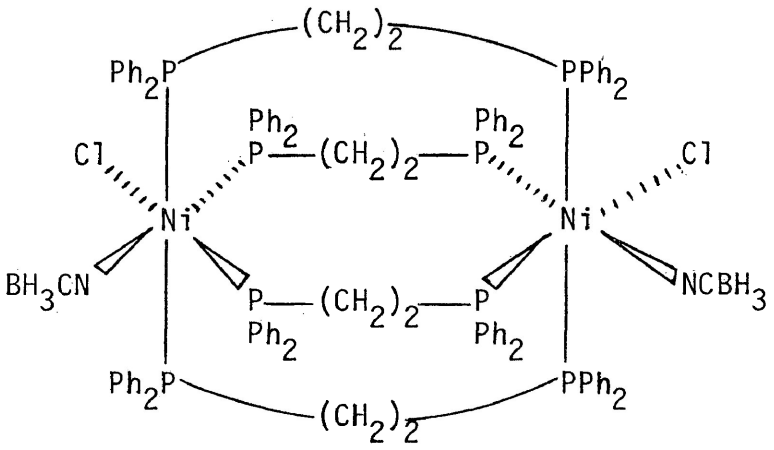


Fig. 44

This would produce spectroscopic and molecular weight data consistent with those observed except that again paramagnetism would be expected. Diamagnetism would really only be possible if the Ni(II) ions were five-coordinated with ionic chloride. This would cause problems with molecular weight and conductivity data and, again strong ion pairing may be present as outlined in the previous subsection. This complex clearly requires an X-ray crystal structure determination.

3.3.6 Ni(Diphos)$_2$

It has also been found that at higher temperatures, $NiCl_2.6H_2O$ react with $NaBH_3CN$ in the presence of Diphos to give the known (9) Ni(0) system Ni(Diphos)$_2$ (δ ^{31}P = 44.11) directly from the reaction mixtures as the major product in 40% yield. Similar results have been observed (20) with $NaBH_4$ under milder conditions.

3.3.7 Unidentified Complex

Many attempts have been made to synthesize cyanide complexes from Ni(II)/Phophine/$NaBH_3CN$ system in higher temperature reactions (see experimental) since the ligand Dppm readily yields Ni(I) cyanide systems. From only one such reaction filtrate has a very small (~20%) yield of a probable cyanide been obtained as a yellow solid. The infrared spectrum of this complex shows a single very sharp stretching frequency at 2141 cm^{-1}. The ^{31}P NMR spectrum shows only one sharp signal at δ = 35.29 which indicates the presence of equivalent phosphorus atoms.

This complex is very air sensitive and reproducible analyses for C, H and N were not obtainable. Further attempts to clarify the structure were therefore not made.

3.4. Complexes with Other Phosphines

The main part of this thesis concerns complexes synthesized from Dppm and Diphos, but several additional complexes have been obtained from exploratory reactions with Dppp, Dppb, cis-Dppe and trans - Dppe. Although most of these species have not been fully characterized, this preliminary work is briefly discussed in the following subsections.

3.4.1 $[Ni(BH_3CN)_2(Dppp)]_2$

This diamagnetic air stable complex, for which excellent chemical analyses have been obtained, has been synthesized both from $Ni(ClO_4)_2.6H_2O$ and $NiCl_2.6H_2O$ reactions and the complex was stable enough to be purified by recrystallization. The C≡N stretching frequency appears as a very strong and sharp band at 2207 cm^{-1} (an increase of 28 cm^{-1} from that of the free BH_3CN^-) and this is therefore good evidence for N-coordination of the BH_3CN^- groups (24) while the presence of only one band indicates a symmetrical structure. The BH stretching vibration which appears as a strong broad band at 2370 cm^{-1} (with a weak shoulder at 2280 cm^{-1}) is in the range consistent with bridging BH_3CN^- units (10) as previously discussed. This is further supported by the spectrum of the deuterated complex which shows that the 2370 cm^{-1} band has been shifted and split into three frequencies at 1770 cm^{-1}(s,br), 1685 cm^{-1}(w) and 1635 cm^{-1}(w), as discussed previously. Selected regions of the infrared spectra of the deuterated and undeuterated complexes are shown in Fig. 45 and 46, and are summarized in Table 13.

Although the complex can be recrystallized from methylene chloride solutions, its solubility is low and only very dilute solutions could be made for ^{31}P NMR work. Data could not be accumulated over sufficiently long periods because of decomposition of the sample, the colour of which changed from yellow through brown to green.

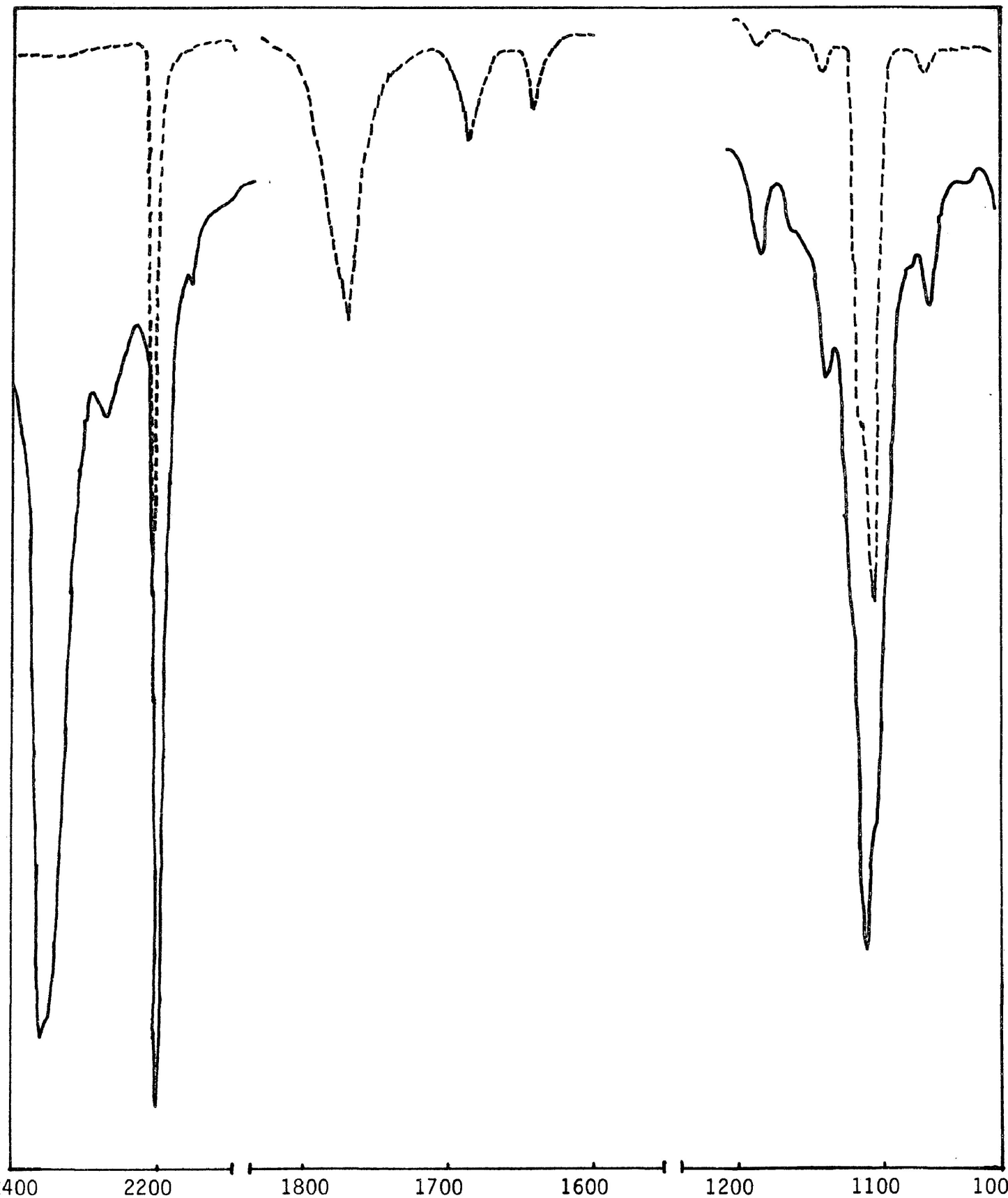


Fig. 45. Selected Features of the Infrared Spectra of the Complexes
—— $[Ni(BH_3CN)_2(Dppp)]_2$ and --- $[Ni(BD_3CN)_2(Dppp)]_2$ derived from $Ni(ClO_4)_2.6H_2O$.

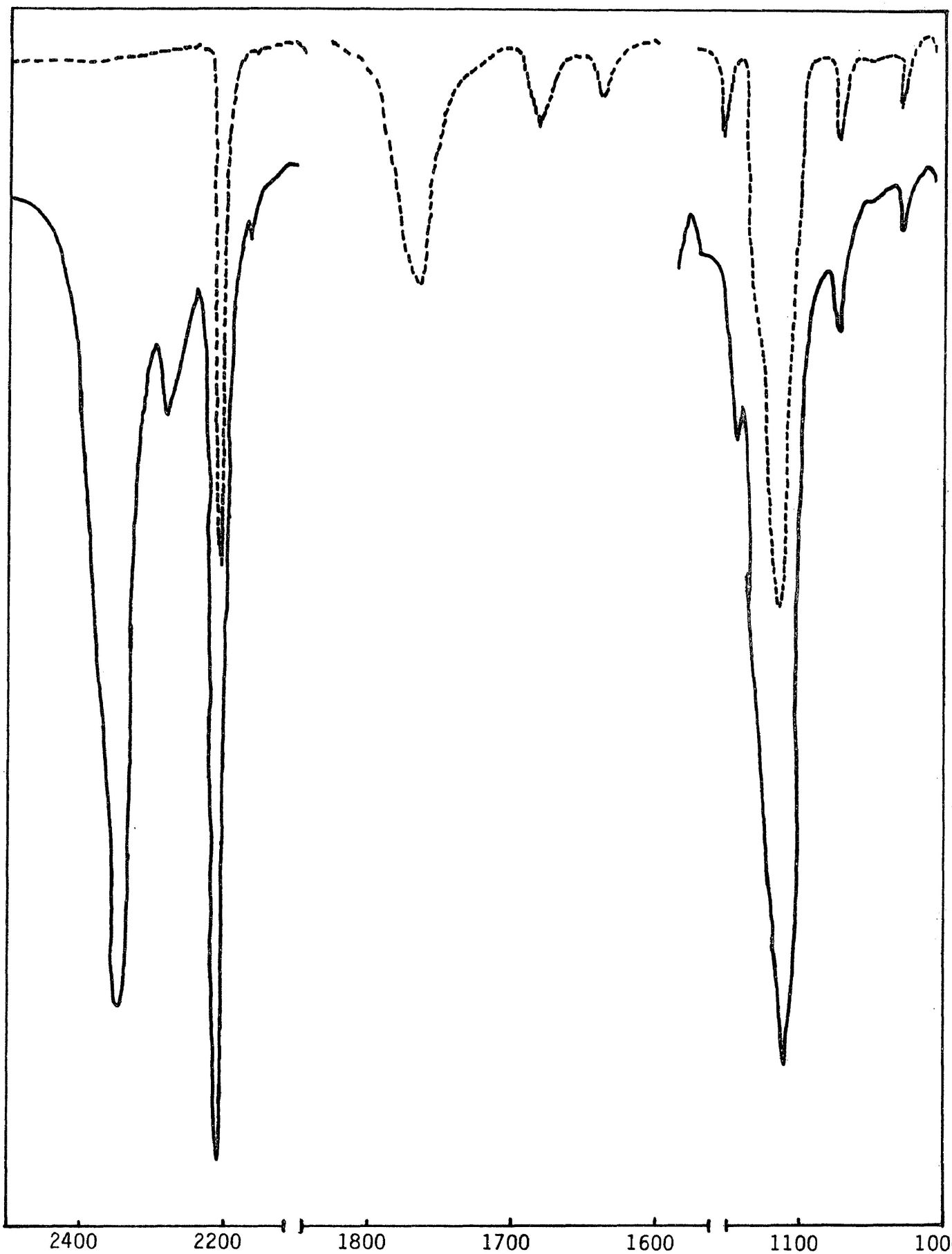
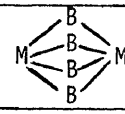
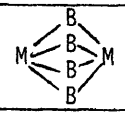


Fig. 46. Important Infrared Vibrations for the Complexes
—— $[Ni(BH_3CN)_2(Dppp)]_2$ and ---- $[Ni(BD_3CN)_2(Dppp)]_2$ derived from $NiCl_2.6H_2O$.

TABLE 13

IR, NMR, Mode of Coordination of BH_3CN^- and Magnetic Moment Data for the Complexes Derived from Dppe(Cis-trans), Dppp and Dppb Ligands

No.	Complex	Colour	νB-H cm^{-1}	δBH cm^{-1}	νCN	Other	δ^{31}PNMR (solvent)	^{1}H NMR	μ(B.M.)	Mode of coordination of BH_3CN^-
1.	$Ni(BH_3CN)_2$(cis-Dppe)	Yellow	2330 (s,br) 2270 (sh,w)	1105 (s) 1120 (sh,w)	2200 (s)	--	70.86 (CH_2Cl_2)	--	Diamagnetic	M - $NCBH_3$
2.	Ni(cis-Dppe)$_2$	Orange	--	--	--	--	49.96 (CH_2Cl_2)	--	--	--
3.	$Ni(BH_3CN)_2$(trans-Dppe)	Yellow	2340 (s,br)	1110 (s)	2207 (s)	--	63.26 (CH_2Cl_2)	--	Diamagnetic	M - $NCBH_3$
4.	"Ni(trans-Dppe)$_2$"	Orange	--	--	--	--	44.11 (CH_2Cl_2)	--	--	--
5. a	$[Ni(BH_3CN)_2(Dppp)]_2$	Greenish Yellow	2370 (s,br) 2280 (w.sh)	1115 (s)	2207 (s)	--	--	--	Diamagnetic	 ?
b	$[Ni(BD_3CN)_2(Dppp)]_2$	Greenish Yellow	1770 (m,br) 1685 (w) 1635 (w)	1115 (s)	2207 (s)	--	--	--	"	"
6.	$[NiH(Dppp)_2]_2(BH_3CN)(ClO_4)$?	Lemon Yellow	2340 (s,br) 2370 (sh,w) 2290 (sh,w)	1125	2179 (m)	1100 (s,br) ClO_4^-	7.28 (CH_2Cl_2)	δ =-14.0 Jph = 8Hz	"	M+BH_3CN^-
7.	$Ni(Dppp)_2$	Orange	--	--	--	--	30.90 (CH_2Cl_2)	--	--	--
8.	$[Ni(BH_3CN)(Dppb)_2]ClO_4$	Deep Brown	2320 (s,br) 2260 (sh,w)	1120 (m)	2200 (s)	1100 (s) ClO_4^-	16.18 (CH_2Cl_2)	--	Diamagnetic	M - $NCBH_3$
9. a	$[Ni(BH_3CN)_2(Dppb)]_2$	Deep Yellow	2360 (s,br)	1110 (s)	2207 (s)	2260 M-H-B ?	--	--	1.89	 ?
b	$[Ni(BD_3CN)_2(Dppb)]_2$	Deep Yellow	1787 (s) 1735 (s) 1685 (m) 1640 (m)	1110 (s)	2207 (s)	--	--	--	"	"
c	$Ni(BH_3CN)_2(Dppb)\cdot CH_2Cl_2$ (Recrystallized)	Yellow	2360 (s,br) 2260 (sh,w)	1110 (s)	2207 (s)	--	14.01 (CH_2Cl_2)	--	Diamagnetic	M - $NCBH_3$
10.	$Ni(BD_3CN)_2(Dppb)\cdot CH_2Cl_2$	Yellow	1755 (m) 1685 (w) 1635 (w)		2207 (s)	--	"	--	"	M - $NCBH_3$

On the basis of the (limited) available data described above, a structure of this complex has been tentatively formulated as shown in Fig. 47.

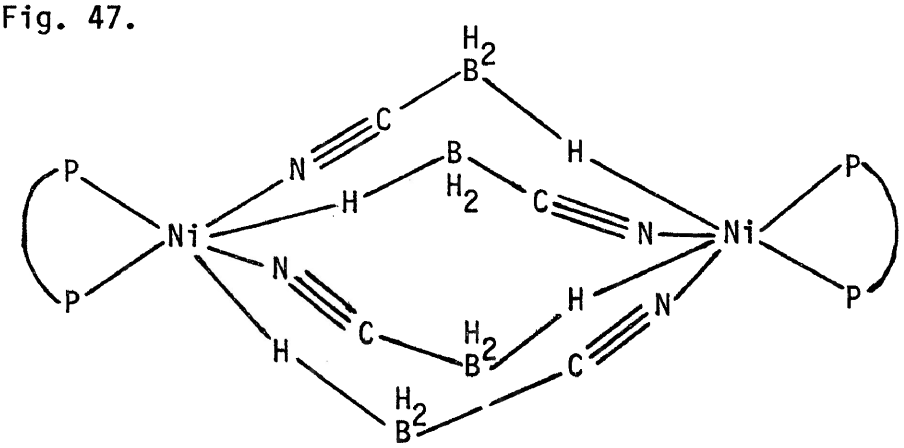


Fig. 47

In this, the Ni(II) is 6-coordinated but must be very strongly tetragonally distorted to achieve diamagnetism (68c).

3.4.2. [NiH(Dppp)$_2$]$_2$(BH$_3$CN)(ClO$_4$)

This "product" was synthesized from several reactions starting with Ni(ClO$_4$)$_2$.6H$_2$O in which the Ni|phosphine|NaBH$_3$CN ratio (~1:3:13) was kept constant and both the rate of addition of NaBH$_3$CN and the total reaction time was varied (see experimental). All attempts to purify this complex (recrystallization and column chromatography) gave products for which chemical analyses were not totally reproducible. While analyses ranged from 70.29 - 64.38% C, 5.09 - 5.94% H, and 0.54 - 0.96% N and obviously preclude an accurate formulation, several other properties were reproducible and informative enough to warrant brief

mention. For example all samples were air stable and diamagnetic.

Part of the IR spectrum is shown in Fig. 48 (and Table 13) and, at least in the B-H and C-N regions, is remarkably similar to the spectrum of the complex $[NiH(Diphos)_2]BH_3CN$ (shown in Fig. 32) which contains ionic BH_3CN^-. In addition the strong peak at 1100 cm^{-1} could be assigned to an ionic perchlorate.

The ^1H NMR spectra of several samples in $CDCl_3$ show a well defined quintet at δ = 14.01 with J_{PH} = 8 Hz and this indicates the presence of a terminal hydrogen coupled to four equivalent P atoms. A Ni-H stretching frequency could not be seen in the IR spectrum, although this is not uncommon (9).

Only a single sharp peak at δ = 7.28 is present in all samples for which ^{31}P NMR spectra were recorded. This shows that not only are the P atoms equivalent, at least in solution, but that there is only one P- containing species present in solution. This chemical shift of 7.28 ppm is entirely reasonable (62) for chelating Dppp ligands.

Therefore, until more synthetic work is done on this system, the best that can be said consistent with the above data, is that the "product" is probably a mixture of $[NiH(Dppp)_2]X$, where X = ClO_4^- or BH_3CN^-. The data recorded in the Experimental Section (section 2.3.2.2) indicate that the two products are formed in approximately equal quantities in many instances. For this reason, the binuclear formulation has been used for the purposes of section headings although a mixture of mononuclear products now seems more reasonable.

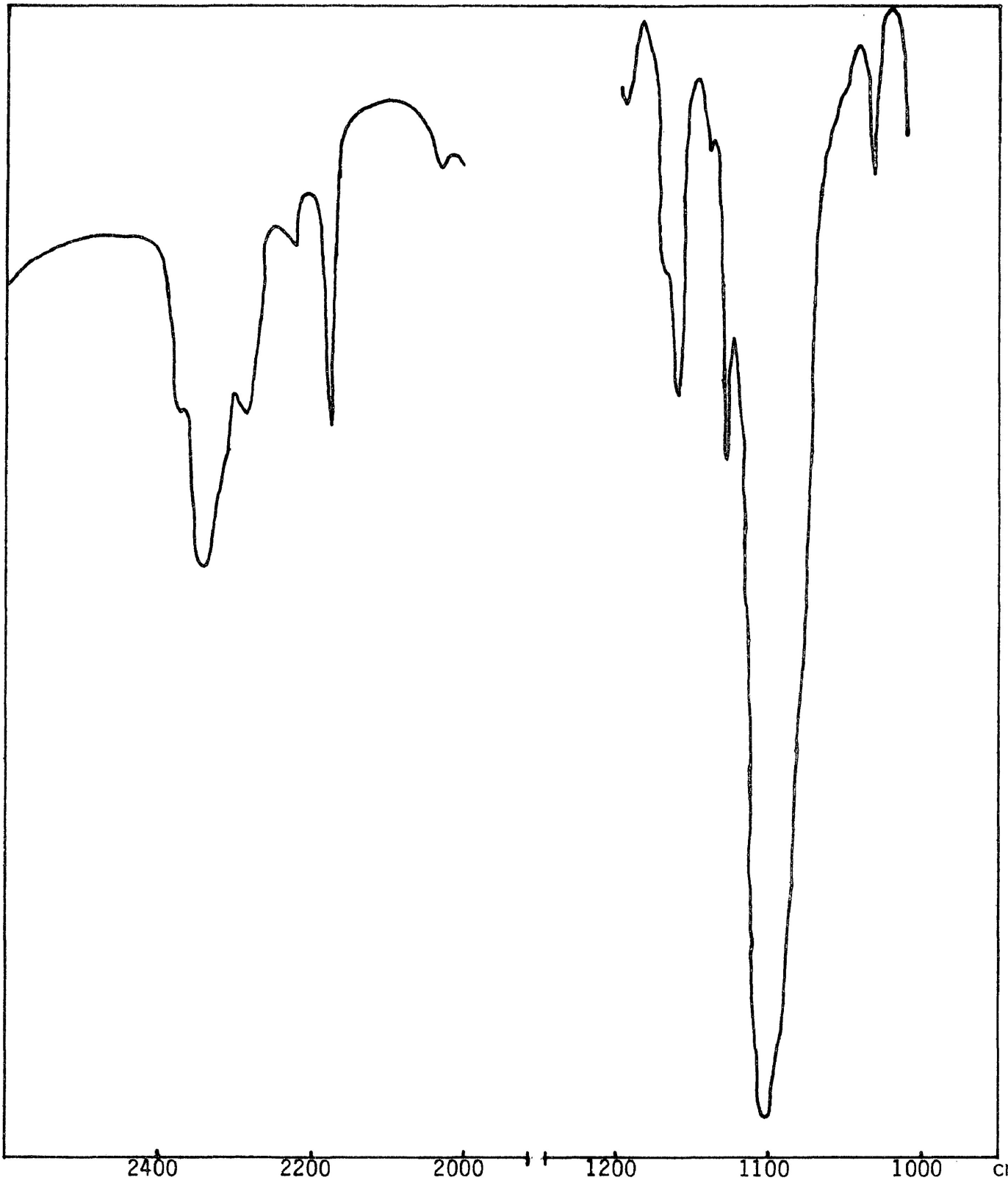


Fig. 48. Selected Features of the Infrared Spectra of the Complex $[NiH(Dppp)_2]_2$ $(BH_3CN)(ClO_4)$.

3.4.3. $[Ni(BH_3CN)(Dppb)_2]ClO_4$

This diamagnetic complex was synthesized from $Ni(ClO_4)_2.6H_2O$ and was purified by recrystallization from benzene with very slow addition of n-hexane. Reactions were reproducible and good chemical analyses were obtained for the air stable complex.

The infrared spectrum shows the C≡N stretching frequency as a sharp band at 2200 cm^{-1} (an increase of 21 cm^{-1} from BH_3CN^-) which indicates N-coordination of the BH_3CN^- group (24). The BH_3 stretching mode appears as a broad band at 2320 cm^{-1} which is in the range consistent with N-coordinated BH_3CN^-. The ClO_4^- stretching band occurs as a broad and strong band at 1100 cm^{-1}, with the B-H bending modes probably hidden under this. Selected features of the spectra are shown in Fig. 49 and are recorded in Table 13.

The ^{31}P NMR spectrum shows a single peak at $\delta = 16.18$ which implies that the phosphorus atoms are equivalent. Again, the observed shift is consistent with chelation (62). Spectra were recorded quickly on freshly prepared solutions to minimise decomposition.

A possible structure for this compound, tentatively formulated on the basis of the above evidence, is shown in Fig. 50. Why the Ni would not accept an additional BH_3CN^- ligand into its

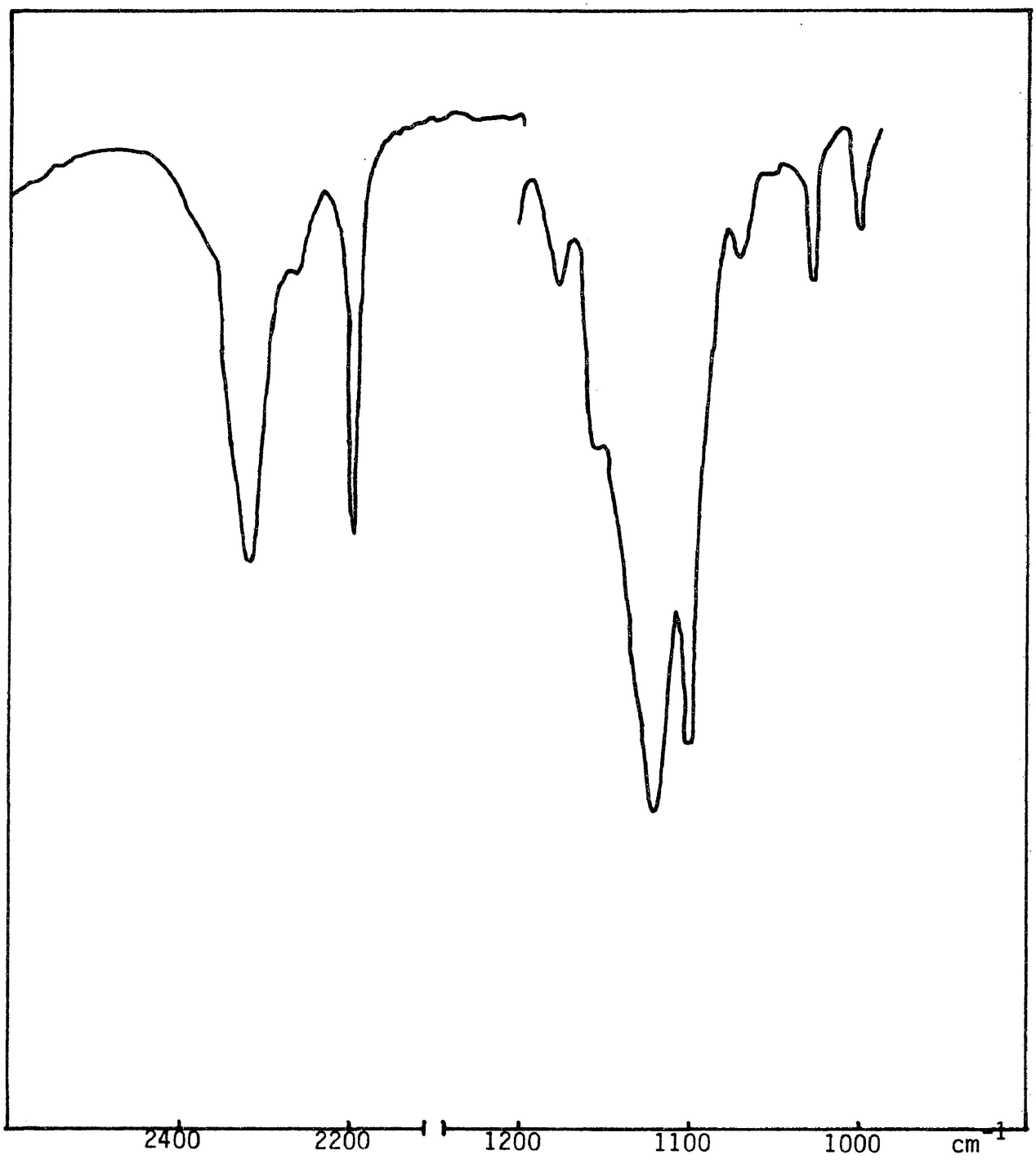


Fig. 49. Selected Features of the Infrared Spectrum of $[Ni(BH_3CN)(Dppb)_2]ClO_4$.

coordination sphere rather than an ionic ClO_4^- is possibly associated with steric requirements of the phosphines.

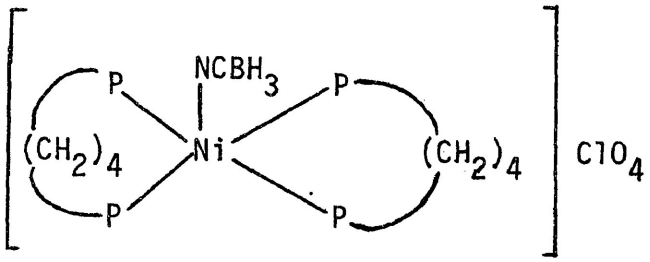


Fig. 50

3.4.4. $[Ni(BH_3CN)_2(Dppb)]_2$ and $Ni(BH_3CN)_2(Dppb).CH_2Cl_2$

The first compound $[Ni(BH_3CN)_2(Dppb)]_2$, was obtained from both $Ni(ClO_4)_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ - phosphine - $NaBH_3CN$ reactions where molar ratios of the reactants were varied but where reaction times were short (see experimental). All attempts to recrystallize this complex resulted in decomposition, and the crude product was therefore simply washed with benzene. This produced air stable samples, all of which gave good chemical analyses consistent with the above formulation. The reasons for the dimeric formulation will be discussed shortly.

The other complex, $Ni(BH_3CN)_2(Dppb) \cdot CH_2Cl_2$ was obtained as a yellow powder when $[Ni(BH_3CN)_2(Dppb)]_2$ was recrystallized from methylene chloride. Samples from different recrystallizations were

also air-stable and showed reproducible chemical analyses consistent with the above formulation. Again, the reason for the monomeric formulation will be given a little later.

The infrared spectrum of $[Ni(BH_3CN)_2(Dppb)]_2$ shows a sharp νCN at 2207 cm^{-1} (shifted by 28 cm^{-1} from $NaBH_3CN$) indicating N-coordination. The spectrum (Fig. 51) in the BH region is quite different from all other spectra reported in this work in that there are two clear peaks at 2260 and 2360 cm^{-1}, both of which shift (Fig. 52) on deuteration to give a complex pattern of bands in the 1600 - 1800 cm^{-1} region (Table 13) with the main peak at 1787 cm^{-1}. The 2360 cm^{-1} and 1787 cm^{-1}(s) peaks of the undeuterated and deuterated species respectively are in the range expected of M——HBH_2CN species. The infrared evidence then suggests a BH_3CN^- bridged species and at least a dimeric structure. The new peak at 2260 cm^{-1} is clearly associated with a BH mode and could be due either to the presence of non-equivalent bridging ligands or, possibly, the Ni-H-B frequency which so far has not been observed in any of the bridged structures discussed in this thesis.

Since $[Ni(BH_3CN)_2(Dppb)]_2$ decomposes in all solvents, no solution studies were possible. In the solid state the complex is paramagnetic with a magnetic moment of 1.89 BM, and this is not consistent with normal high spin Ni(II) complexes. It is difficult to rationalize this value without further work but it is possible that the complex is contaminated with a paramagnetic impurity (e.g. a

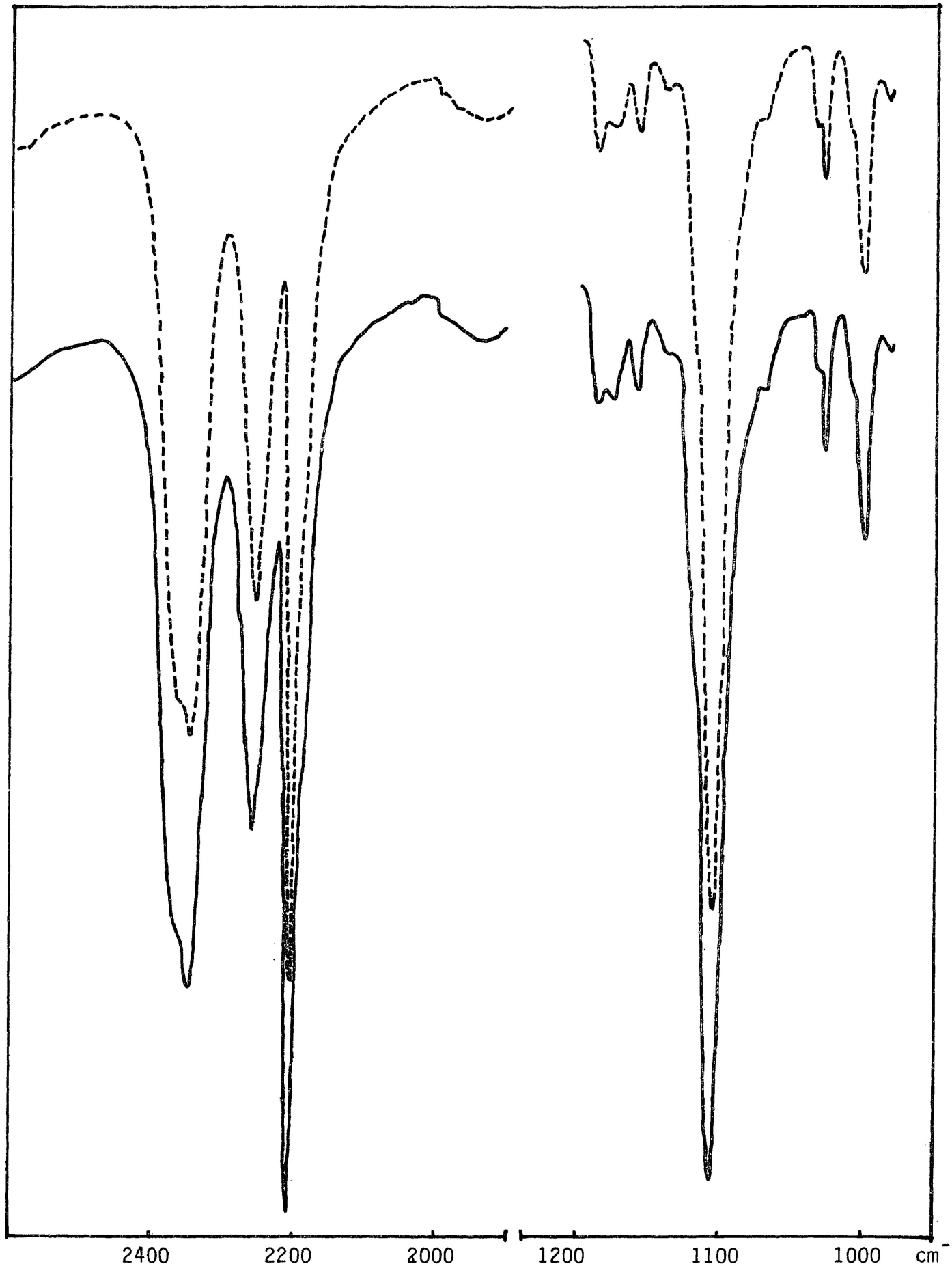


Fig. 51. Selected Features of the Infrared Spectra of the Complex $[Ni(BH_3CN)_2(Dppb)]_2$ derived from —— $Ni(ClO_4)_2.6H_2O$ and ---- $NiCl_2.6H_2O$.

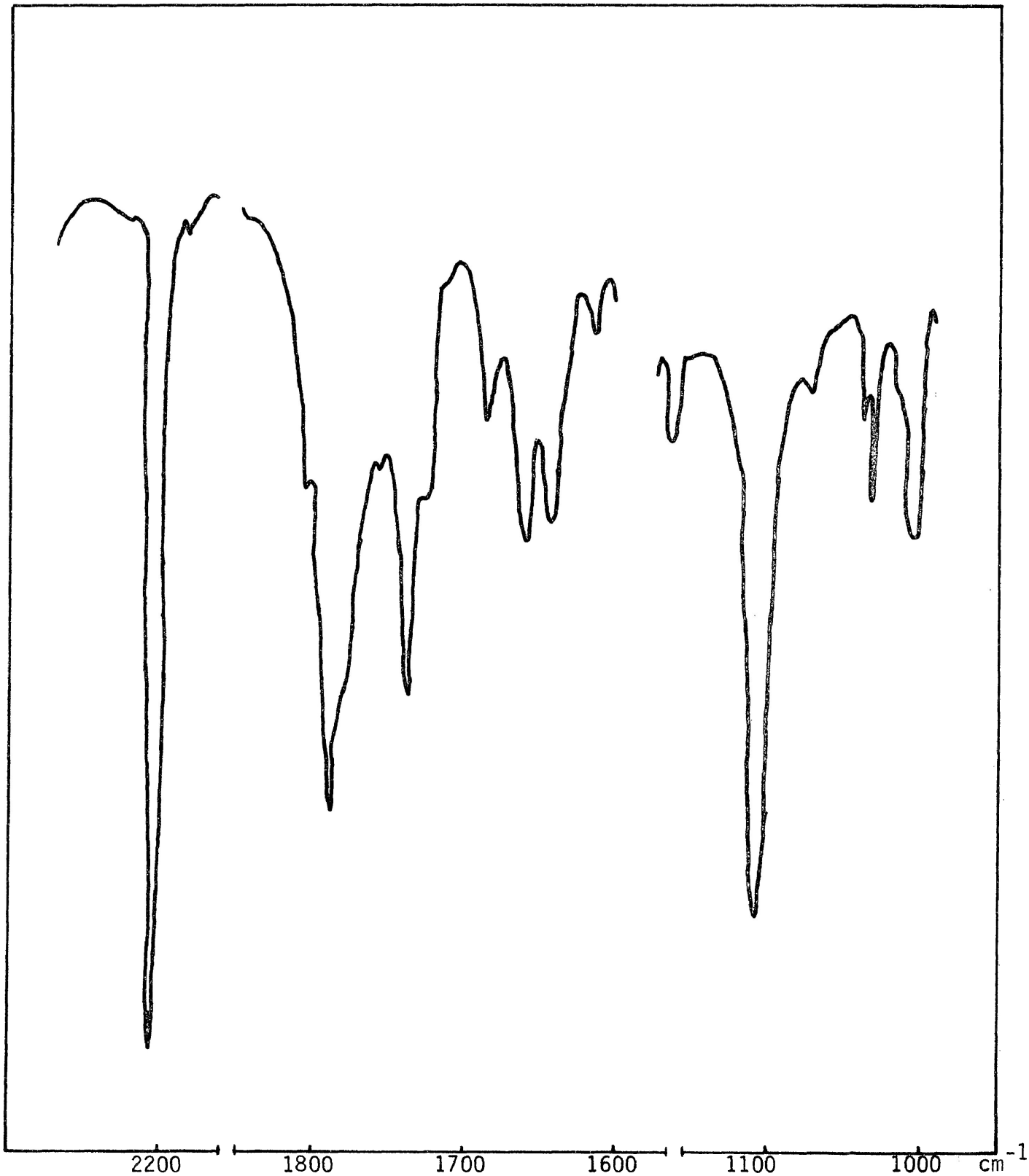


Fig. 52. Selected Features of the Infrared Spectra of the Complex $[Ni(BD_3CN)_2(Dppb)]_2$ derived from both $Ni(ClO_4)_2.6H_2O$ and $NiCl_2.6H_2O$.

boride) or that the molecule contains a mixture of diamagnetic and high spin Ni(II) species. It is therefore very difficult to draw meaningful conclusions about the structure of this species on infrared evidence alone. While this suggests the presence of bridging BH_3CN^- units (as in $[Ni(BH_3CN)_2(Dppp)]_2$ - section 3.4.1, Fig. 47) the situation is complicated by the additional B-H frequency. More work is obviously necessary.

The infrared spectra of the second (diamagnetic) complex, $Ni(BH_3CN)_2(Dppb)\cdot CH_2Cl_2$ and its BD_3CN^- analogue (Fig. 53) still show a trace of the 2260 cm^{-1} peak of the first complex and the complex is therefore very slightly contaminated with the original compound. In addition, the position of the B-H and B-D frequencies (Table 13) are consistent with the presence of non bridged, N-coordinated BH_3CN units.

The ^{31}P NMR spectrum in CH_2Cl_2 shows a single sharp peak at δ = 14.01 indicating equivalent phosphorus and this ^{31}P NMR shift is consistent with chelating Dppb (62). The presence of CH_2Cl_2 was determined from a ^1H NMR spectrum which shows, with careful integration, one molecule of CH_2Cl_2 for each phosphine ligand.

On the basis of the available spectroscopic and analytical data, a structure of the complex has been tentatively assigned as shown in Fig. 54 in which the diamagnetic behaviour is con-

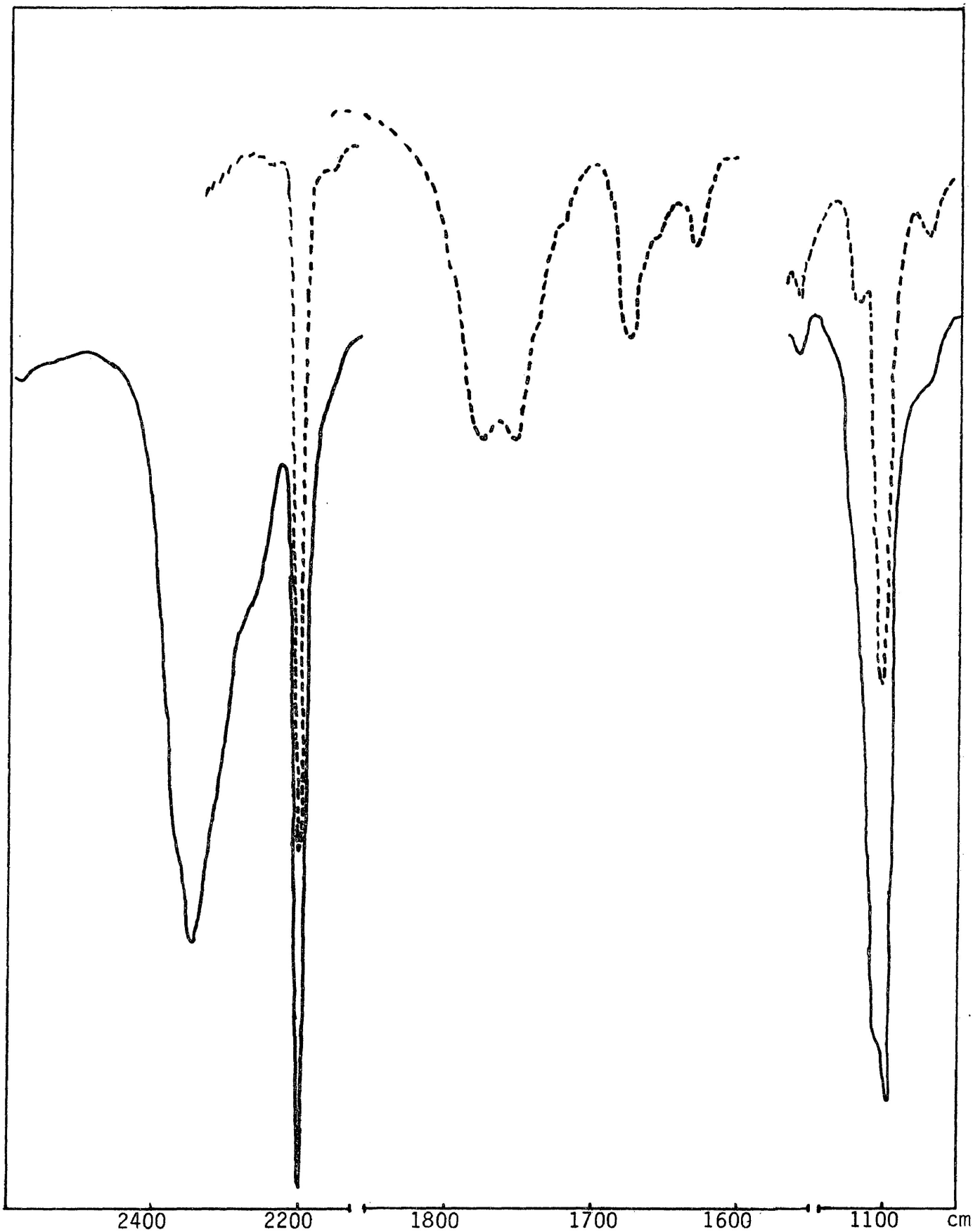


Fig. 53. Selected Features of the Infrared Spectra of the Complexes —— $Ni(BH_3CN)_2(Dppb)CH_2Cl_2$ and ---- $Ni(BD_3CN)_2(Dppb)CH_2Cl_2$ (recrystallized) derived from both $Ni(ClO_4)_2.6H_2O$ and $NiCl_2.6H_2O$.

sistent with square planar Ni(II).

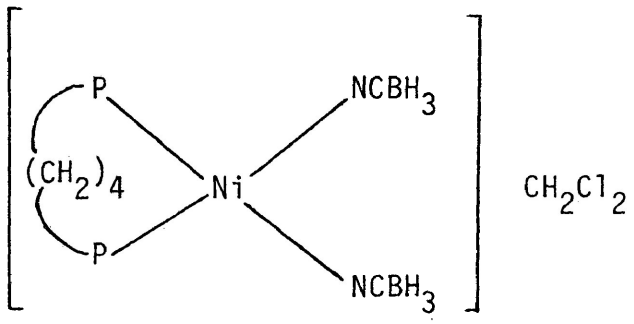


Fig. 54

3.4.5. $Ni(BH_3CN)_2$(cis-Dppe)

This diamagnetic, air stable complex was synthesized from both $Ni(ClO_4)_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ as a major product and was purified by recrystallization from CH_2Cl_2 with addition of n-hexane. Excellent and reproducible chemical analyses were obtained.

The C≡N stretching frequency occurs as a sharp band at 2200 cm^{-1}(an increase of 21 cm^{-1} from ionic BH_3CN^-) indicating N-coordination to the nickel. The BH_t vibration appears as a broad band at 2330 $cm^{-1}$with a weak shoulder at 2270 cm^{-1} (Fig. 55 and Table 13) and this suggests that the BH_3CN^- groups are acting as monodentate ligands through the nitrogen atom as discussed previously. The BH deformation mode appears as a strong band at 1105 cm^{-1} with a weak shoulder at 1120 cm^{-1}.

The ^{31}P NMR spectrum in CH_2Cl_2 shows a single sharp peak at δ = 70.86 indicating the presence of equivalent phosphorus

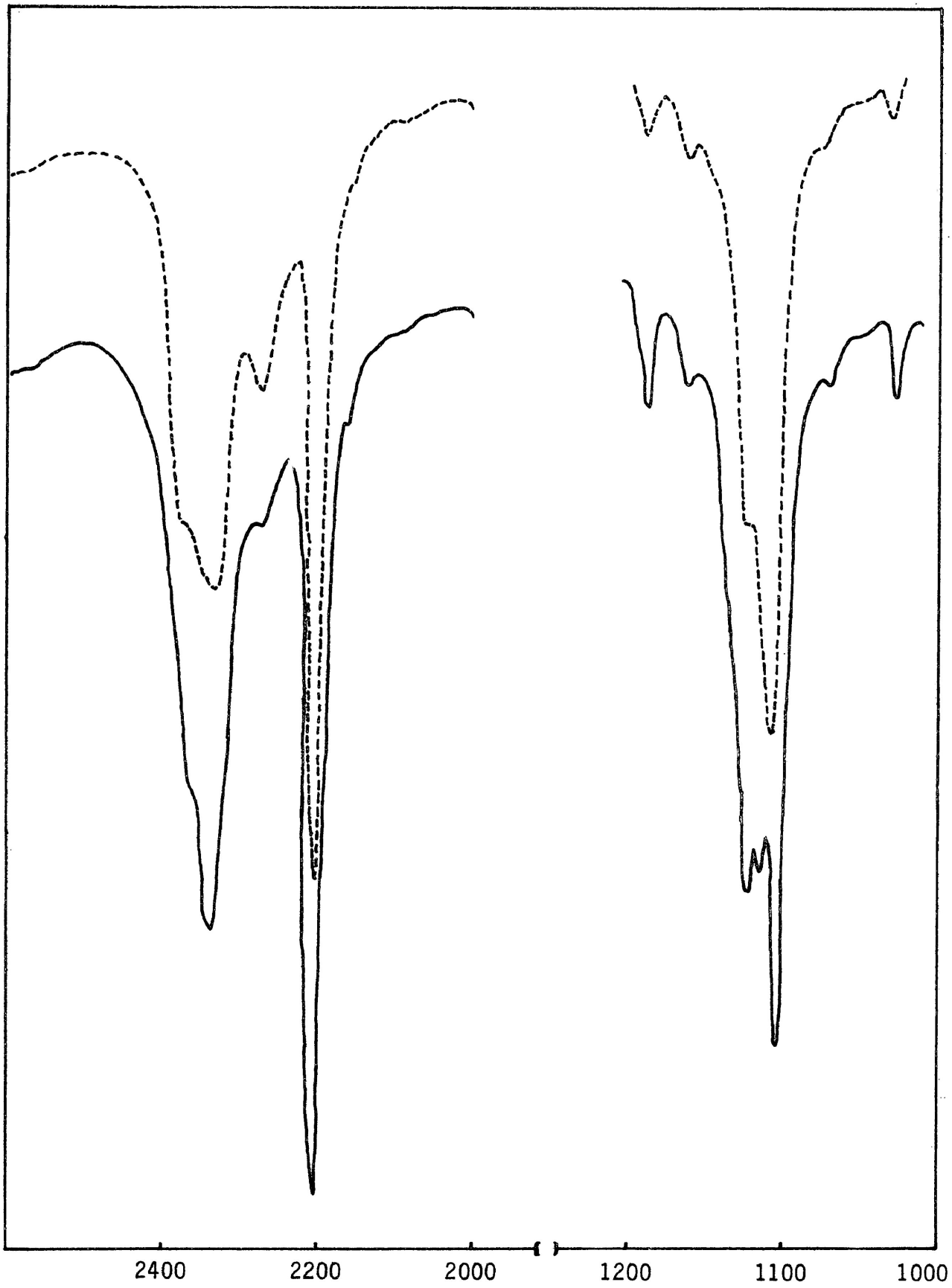


Fig. 55. Selected Features of the Infrared Spectra of the Complex $Ni(BH_3CN)_2$(cis- Dppe) derived from —— $NiCl_2.6H_2O$ and ---- $Ni(ClO_4)_2.6H_2O$.

atoms of the cis-Dppe ligands and the presence of only one P - containing species. This large shift is consistent (62) with Δ_R for a chelated five-membered ring system. No ^1H NMR spectrum or molecular weight were recorded.

A structure for this complex has been tentatively assigned on the basis of evidence obtained from the IR, NMR and analytical data discussed above and this is shown in Fig. 56. The 4-coordinated Ni(II)

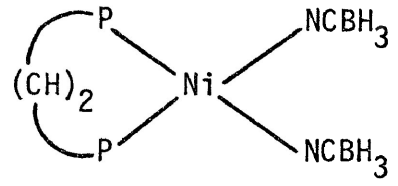


Fig. 56

species present in a square planar geometry is consistent with the diamagnetism.

3.4.6 [Ni(BH$_3$CN)$_2$(trans-Dppe)]$_2$

This reproducible, diamagnetic and air stable complex was prepared from both Ni(ClO$_4$)$_2$.6H$_2$O and NiCl$_2$.6H$_2$O reactions and was purified by recrystallization. Excellent and reproducible chemical analyses were obtained.

The infrared spectrum (Fig. 57 and Table 13) shows the C≡N stretching vibration at 2207 cm^{-1} and the BH_t stretching frequency at 2340 cm^{-1}. These are consistent with the presence of monodentate, N-bonded cyanotrihydroborato groups (as discussed in earlier sections), and are significantly different from the spectra of the related compounds $[Ni(BH_3CN)_2L]_2$, L = Dppp and Dppb. Molecular weight determinations show the complex is dimeric.

The ^{31}P NMR spectrum shows one peak at δ = 63.21 and this shift is consistent with Δ_R expected for a bis-phosphine chelating to form a 5-membered ring (62). Clearly trans-Dppe cannot chelate in this way unless isomerisation to cis-Dppe or hydrogenation to Diphos occurs during the reaction. Until this problem is resolved it is not reasonable to propose a structure for the complex. The relationship, if any, between δ = 63.21 for this complex and δ = 63.3 for $[Ni_2(BH_3CN)_3(Diphos)_2]Cl$ or ClO_4 must be investigated.

3.4.7 $Ni(Dppp)_2$, $Ni(cis\text{-}Dppe)_2$ and "$Ni(trans\text{-}Dppe)_2$"

Two of these three compounds crystallized over a period of several days from the filtrates obtained after the separation of $[Ni(BH_3CN)_2(Dppp)]_2$ and $[Ni(BH_3CN)_2(trans\text{-}Dppe)]_2$. The other complex, $Ni(cis\text{-}Dppe)_2$, was obtained directly from an overnight reaction between Ni(II), cis-Dppe and $NaBH_3CN$ as the major product. Reduction of Ni(II) to Ni(0) by $NaBH_3CN$ in the presence of Dppp and trans-Dppe is easier than in the presence of Diphos and cis-Dppe.

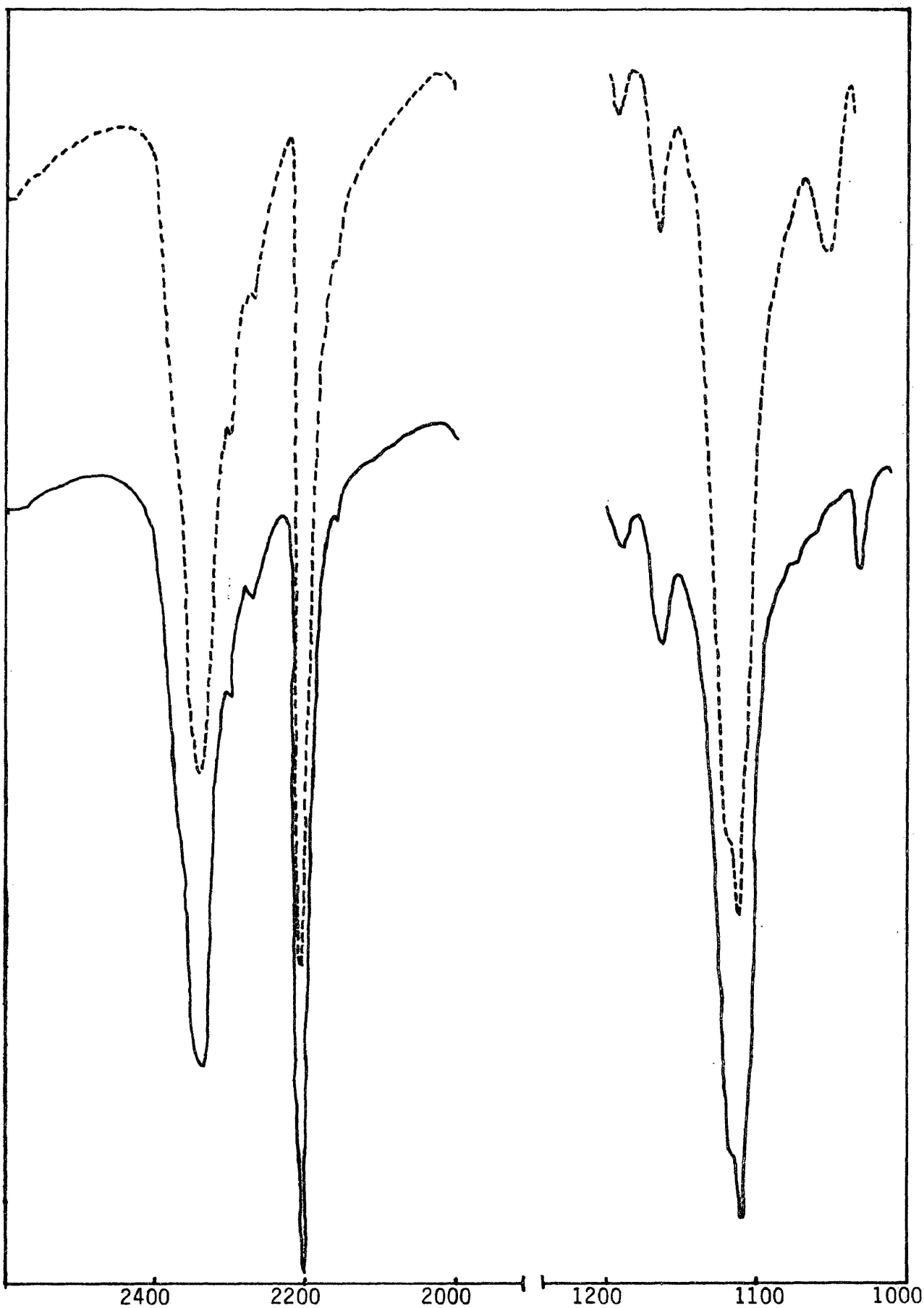


Fig. 57. Infrared Spectral Features of the Complex $[Ni(BH_3CN)_2(\underline{trans}\text{-}Dppe)]_2$ derived from —— $Ni(ClO_4)_2.6H_2O$ and ---- $NiCl_2.6H_2O$.

All these complexes are air sensitive (in the solid state) and diamagnetic and their syntheses are reproducible. Excellent chemical analyses were obtained. The complexes are stable in solution under inert atmospheres. In the IR spectra, all these above complexes show, as expected, no significant stretching vibrations in the 1600-2400 cm^{-1} region. The ^{31}P NMR spectra show only one strong peak at δ = 30.90 (Dppp), δ = 49.96 (cis-Dppe) and 44.11 (trans-Dppe) indicating the presence of equivalent phosphorus atoms in each case. The ^{31}P NMR shifts are consistent with chelating phosphines (62) although, as mentioned above trans-Dppe cannot act as a chelating ligand. The fact that the Ni(0) complex obtained from the trans-Dppe reaction has the same ^{31}P chemical shift as does $Ni(Diphos)_2$, 44.11 ppm (section 3.3.6), led us to consider the possibility that trans-Dppe might be hydrogenated to Diphos in the reaction so that the complex formulated as Ni(trans-Dppe)$_2$ may in fact be $Ni(Diphos)_2$. In an attempt to prove this, the phosphine oxides from both "Ni(trans-Dppe)$_2$" and free trans-Dppe were prepared by oxidation in ethanolic solution with 30% H_2O_2 followed by water dilution and chloroform extraction of the resulting reaction mixture. Results from these experiments were quite unexpected. The ^{31}P spectrum of the oxide (m.p.257^oC) prepared from trans-Dppe showed a strong peak at ca. δ = +22.23 and a weak peak due to a small amount of the cis-isomer at δ = 33.34. On the other hand the ^{31}P spectrum of the oxide prepared from the "trans-Dppe" metal complex (m.p. 260^oC) showed a strong peak at δ = 33.34 and a weak peak at δ = 22.23 apparently due to the trans oxide -- i.e. trans $\longrightarrow$ cis

isomerization and not hydrogenation probably occurred during the reaction with Ni(II), and the final complex appears to be a Ni(0) complex of cis-Dppe different from the one described earlier. The main spectra of the two oxides were identical showing molecular ions at m/e = 428, again confirming the presence of the C = C unit. These results may clearly have implications for section 3.4.6. The reason for the similarity in chemical shifts of this Ni complex and $Ni(Diphos)_2$ is unresolved at this point.

3.5 Conclusions

As expected, this work has shown that, compared with $NaBH_4$, $NaBH_3CN$ is a milder reducing agent. Therefore, reactions between the latter and Ni(II)-phosphine mixtures were easier to control and products easier to isolate and handle than from the corresponding $NaBH_4$ reactions. In addition, reaction products proved to be both more numerous and varied.

Reactions involving Dppm, with its small bite size, appear to be fundamentally different from reactions in the presence of the other phosphines in several ways - i.e. the majority of products contain Ni(I), cleavage of the B-C bond to form Ni-CN species readily occurs, and no Ni(0) species was obtained. On the other hand, phosphines capable of forming larger ring systems with Ni mostly form either Ni(II) or Ni(0) complexes. The former proved particularly significant in that

some of these appear to contain several bridging BH_3CN^- units. Cyanide formation was not common.

Structural assignments have been made largely on the basis of infrared and NMR work. Extensive use has been made of IR criteria already in the literature and in other theses from this laboratory to distinguish between bridging and monodentate BH_3CN^- groups and ^{31}P chemical shifts proved useful in assessing whether phosphines were chelating or bridging.

3.6 Suggestions for further work

This work has also pointed the way to further studies. For example, the IR criteria for bridging or monodentate BH_3CN^- coordination is based on only 4 X-ray structures - (two of each kind) and this is clearly insufficient. The compounds reported here are not easy to crystallize but it is felt that further attempts should be made to grow suitable crystals so that definitive X-ray work may be done.

The author feels that the synthetic work described for Dppm and Diphos is reasonably complete but there is much left to do with the other phosphines (section 3.4). Specifically, reactions must be repeated and conditions established which allow for the isolation of pure compounds. These may then be related to the better understood Dppm and Diphos complexes. Further work with cis-and trans-Dppe would

be particularly worthwhile. The isomerization described in 3.4.7 was discovered in the last week of the writing of this thesis and the role of Ni ions in this process has not yet been established. Acquisition of an ^{11}B NMR probe was too late for ^{11}B NMR studies, but this technique can now be used to study the BH_3CN^- ligand.

In the longer term, this work should allow for the assessment of the overall mechanism by which $NaBH_3CN$ reacts with and reduces Ni(II).

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