BIDENTATE PHOSPHINE COMPLEXES OF COPPER(I): THEIR SYNTHESES AND INTERACTIONS WITH SODIUM TETRAHYDROBORATE AND SODIUM CYANOTRIHYDROBORATE

BY

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ABSTRACT

Copper(I) chloride and perchlorate complexes of the types (L-L)CuCl, $(L\text{-}L)_3Cu_2X_2$ ($X=Cl^-, ClO_4^-$), $[(L\text{-}L)_2Cu]ClO_4$ (L-L=DPPM, DPPE, trans VPP, cis VPP, DPPP, DPPB, DPPPe, DPPH) have been prepared from reactions in organic solvents between the appropriate copper(II) salt and the bis phosphine in the appropriate stoichiometries. Possible arrangements of these compounds are considered on the basis of IR, ^{31}P NMR, ^{1}H NMR, conductivity, and molecular weight data. All of the evidence suggests that the complexes $[(L\text{-}L)_2Cu]$-ClO_4 should be formulated as ion pairs, whereas in the complexes $(L\text{-}L)_3Cu_2X_2$ ($X=Cl^-$, ClO_4^-), X is thought to be coordinated. The available evidence suggests the presence of both bridging monodentate and chelating bidentate phosphines in the $(L\text{-}L)_3Cu_2X_2$ complexes except for L-L =trans-VPP, where all the phosphines, appear to be monodentate and bridging. The 1:1 complexes of CuCl with L-L are all formulated as dimers, $[(L\text{-}L)CuCl]_2$ with bridging chlorides, and tetrahedrally coordinated copper.

Tetrahydroborate complexes of the type $(L\text{-}L)Cu(BH_4)$ (L-L = DPPM, DPPE, trans VPP, DPPP, DPPB, DPPPe, DPPH) have been prepared from reactions of $NaBH_4$ with a variety of the copper(I) chloride and perchlorate phosphine complexes listed above. The physical data are generally consistent with the presence of monomeric complexes involving the bidentate coordination of the BH_4 groups. Again, the possible exception to this generalization is the trans VPP

complex where a bridging phosphine dimeric structure seems likely. An insoluble complex, formulated as $[(DPPM)_2Cu_2(BH_4)]ClO_4$ has been prepared by treating the reaction mixture from $Cu(ClO_4)_2 \cdot 6H_2O$ and DPPM with $NaBH_4$. One incompletely characterized, yellow-brown, air sensitive species which on the basis of some preliminary physical and chemical evidence, is thought to contain a copper(I) hydride bond has been prepared from the reaction of $NaBH_4$ with $(DPPE)Cu_2Cl_2$.

Cyanotrihydroborate complexes, $(L-L)_3Cu_2(BH_3CN)_2$, $(L-L)Cu(BH_3CN)$, and $[(L-L)_2Cu](BH_3CN)$ have similarly been prepared from reactions of $NaBH_3CN$ with the various copper(I) chloride and perchlorate phosphine complexes. Possible structures for these complexes and the modes of coordination of the BH_3CN grouping are discussed. Several different types of BH_3CN coordination appear to be present in the variety of complexes formed and these are reflected in a series of complicated infrared spectra which are sometimes difficult to interpret.

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M.K. Alam

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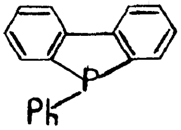
ABBREVIATIONS

Ac	acetyl
bipy	$2,2^1$-bipyridyl
Bu^n	*n*-butyl
Bu^t	*tert*-butyl
Cy	Cyclohexyl
*cis*VPP	*cis*-1,2-bis(diphenylphosphino)ethylene
DBP	5-phenyl-5*H*-dibenzophosphole 
DMF	dimethylformamide
DMSO	dimethylsulfoxide
DPAE	1,2-bis(diphenylarsino)ethane
DPPA	1,2-bis(diphenylphosphino)acetylene
DPPB	1,4-bis(diphenylphosphino)butane
DPPE	1,2-bis(diphenylphosphino)ethane
DPPPe	1,5-bis(diphenylphosphino)pentane
DPPH	1,6-bis(diphenylphosphino)hexane
DPPM	bis(diphenylphosphino)methane
DPPP	1,3-bis(diphenylphosphino)propane
en	ethylenediamine
Et	ethyl
Et_2O	ether

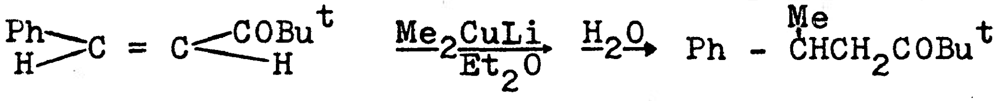
Me	methyl
Ph	phenyl
phen	1,10- phenanthroline
Th	thiourea
THF	tetrahydrofuran
*trans*VPP	trans-1,2-bis(diphenylphosphino)ethylene

1. INTRODUCTION

1.1. General:

Copper(I) compounds find widespread use in organic synthesis (1) as well as many applications in chemical (2), biochemical (3), and industrial (4) catalysis. For example, bis(phosphine) complexes of copper(I) chloride have been used as asymmetric hydrogenation catalysts to prepare amino acids (5), while μ-bis(cyanotrihydroborato)tetrakis(triphenylphosphine)dicopper(I) selectively reduces acid chlorides to aldehydes and ketones to alcohols in acidic media (6). Thus, 4-tert-butylcyclohexanone is reduced to the trans alcohol with a high degree of stereoselectivity (94:6). Furthermore, reduction of α,β - unsaturated nitriles with an unidentified copper hydride complex was found to give efficient, exclusive reduction of the double bond (7).

Copper(I)-isocyanide systems also promote several versatile organic reactions, such as dimerizations (8) and cycloadditions (8). In these reactions, an organocopper(I)-isocyanide complex is assumed to be the active intermediate (8).

Lithium organocuprates, $(R_2CuLi)_n$, rank among the most important of organometallic reagents. They are not usually isolated but are used <u>in situ</u> in ether or a similar solvent for a wide variety of organic syntheses (9). Thus, lithium organocuprates undergo reactions with organic halides (10, 11, 12), acid chlorides (13), oxiranes (14, 15), and esters (16), to form conjugate addition products. The low reactivity of these organometallic compounds towards carbonyl functional groups permits carbonyl group protection to be omitted (10, 13). Reactions of Me_2CuLi with enones (17) result in the formation of addition products, e.g.

$\begin{matrix}\mathrm{Ph}\\ \mathrm{H}\end{matrix}\!>\mathrm{C}=\mathrm{C}<\!\begin{matrix}\mathrm{COBu^t}\\ \mathrm{H}\end{matrix}\ \xrightarrow[\mathrm{Et_2O}]{\mathrm{Me_2CuLi}}\ \xrightarrow{\mathrm{H_2O}}\ \mathrm{Ph}-\overset{\mathrm{Me}}{\mathrm{C}}\mathrm{HCH_2COBu^t}$ whereas under similar conditions, reactions of these enones with MeLi, Me_2Mg or $LiAlH_4$ produce alcohols (e.g. $PhCH = CHC(OH)MeBu^t$ from the above reaction).

Studies of the mechanisms of lithium organocuprate reactions with a variety of substrates share one factor in common, namely that conclusions drawn from these studies remain premised upon an assumed structure for these reagents. The species present in solutions depend upon the solvent and the ratio of LiR to Cu (18). For example, it has been found that a 3:2 mixture of $LiCuMe_2$ and MeLi is more stereoselective towards 4-<u>tert</u>-butylcyclohexanone than either $LiCuMe_2$ or MeLi alone (19). Mixtures of $LiCuMe_2$ and MeLi react with diaryl ketones as if a reducing agent more powerful than either

$LiCuMe_2$ or MeLi were present (20). These results suggest that lithium diorganocuprates and organolithium compounds are capable of reacting to form complexes of the type Li_2CuMe_3 and Li_3CuMe_4. Thus, although lithium organocuprates are very versatile reagents, very little is known about their structures and mode of action.

Many stable copper(I) complexes have been prepared by a variety of methods in the last two decades and most of the elements of Groups V, VI and VII coordinate with the metal in this oxidation state. The stoichiometries, coordination numbers and therefore structures of copper(I) complexes depend very much upon the reaction conditions, such as reactant ratios, solvents, temperature, time of reaction, type of added ligands and nature of the counter anion. Since the experimental work to be described in this thesis concerns the synthesis of copper(I) complexes of bidentate phosphines and their reactions with $NaBH_4$ and $NaBH_3CN$, the following introduction may serve to familiarize the reader with what is known of the synthesis, structure and chemistry of copper(I) compounds.

1.2. Stability of copper(I) compounds:

1.2.1. Introduction:

The stabilities of copper(I) compounds depend very strongly upon the nature and geometry of the attached ligands, the nature of the counter anion and the solvent.

From thermodynamic relationships among copper(I), copper(II), and copper(0) (21), it can be observed that there is a strong tendency for copper(I) complexes to disproportionate:

$$2Cu^{+}_{(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + Cu^{o} \qquad (1)$$

$$K = [Cu^{2+}][Cu^{o}][Cu^{+}]^{2} = \sim 10^{6}$$

Aquocopper(I) complexes are powerful reducing agents. For example, the reduction of Co(III) complexes by copper(I) has been examined and the reactions are attributed to an electron transfer process from copper(I) to Co(III) (22).

Many copper(I) compounds are oxidized in solution by air. Thus, the autoxidations of $Cu(NH_3)_2^+$ and $Cu(imidazole)_2^+$ lead to copper(II) species and the reaction proceeds <u>via</u> peroxo species which, in turn form hydrogen peroxide by reaction with the solvent (23). Also, the complexes $(Ph_3P)_nCuNR^1R^2$ (n=2 for R^1R^2N = phthalimido, succinimido, N-phenylacetamido, acrylamido, phenylamido, and 2-oxo-1-pyrolidinyl; n=1 for R^1R^2N = acetamido) are decomposed by air in solution (24).

Of course numerous Cu(I) complexes are stable in aqueous solution, this stability being conferred by ligands. The relative stabilization effects of a ligand on copper(I) ions can be recognized by the appearence or disappearence of the blue aqueous copper(II) ion (25, 26).

Solvents that are capable of solvating copper(I) ions more effectively than water stabilize copper(I). Thus, the extremely air and moisture sensitive copper(I) acetate has been synthesized by reducing copper(II) species with copper metal in both pyridine and acetonitrile solutions under oxygen free conditions (27, 28). A further example of the effect of solvent on the stability of copper(I) is given by the fact that the ion $[(MeCN)_4Cu]^+$ can be isolated in the form of salts with large anions (e.g. ClO_4^-, PF_6^-) (29).

Copper(I) is also stabilized by suitable ligands with σ-donor and π-acceptor properties. The stabilities of copper(I) compounds with different ligand systems have been summarized in the following sections.

1.2.2. Stability of Cu(I) - N-donor ligand systems:

It is clear then that the stabilities of copper(I) complexes vary with the stereochemical and electronic environment around the metal created by the nature and geometry of the attached ligands. For example, lower aliphatic saturated amino groups stabilize the copper(II) oxidation state and promote easy disproportionation of copper(I). Thus, ethylenediamine reacts with CuCl in aqueous potassium chloride solution to give a copper(II) species (30):

$$2CuCl + 2en = [(en)_2Cu]^{2+} + 2Cl^- + Cu^o \qquad (2)$$

However, copper(I) complexes with higher amines (31) or with pyridine type ligands (32) are more stable, while thermally very stable (>260°C) copper(I) benzotriazole complexes (Fig.1)

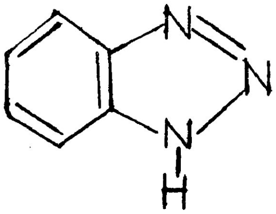


Figure 1

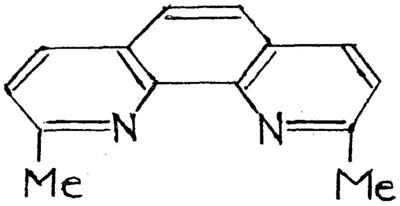


Figure 2

may be prepared in acid solutions (pH~2) (33).

Kinetic studies of the reduction of dmp—Cu(II) complexes (dmp = 2,9-dimethyl - 1,10-phenanthroline, see Fig.2) by thiocyanate ions in aqueous sodium perchlorate and by thiourea in aqueous sodium perchlorate and in methanol show that $[(dmp)_2Cu]^+$ is formed as the major product with high thermal stability (34).

1.2.3. Stability of Cu(I) -π-ligand systems:

An example of this type of stabilization is given by the fact that an aqueous solution of $Cu(ClO_4)_2$ has been reduced by metallic copper in the presence of carbon monoxide or ethylene to the corresponding copper(I)-carbon monoxide or ethylene complex (25). These explosive complexes are isolated in pure form under oxygen free conditions. Coordination of the ligand is inferred from the observed high formation constants and lower carbon monoxide stretching frequency (2130 cm^{-1} complex, 2143 cm^{-1} CO) and alkene stretching frequency (1540 cm^{-1} complex, 1623 cm^{-1} free ligand) of these complexes. However, when the carbon monoxide or ethylene are removed (by pumping) from the colourless reaction mixtures at the end of the reaction, the copper(I) ion in aqueous solution disproportionates again into copper metal and copper(II) ions.

The lability and disproportionation of copper(I) carbonyls has frustrated attempts to explore reactions of copper(I) with carbon monoxide in the presence of saturated nitrogen donor ligands (35). If unsaturated nitrogen ligands stabilize the copper(I) state, the metal center is not further available for coordinating CO molecules. A study on the reaction of (CO)CuCl with ethylenediamine in methanol at -30°C failed to produce (36) any copper(I)-en-CO complexes.

The reaction described below provides an excellent illustration of how the stability of copper(I) carbonyls and also of the copper(I) ethylenediamine system may be affected by the nature of the counter anion, the added ligand and the solvent. Though ethylenediamine induces the disproportionation of copper(I) chloride in aqueous solution (30), reactions of copper(I) iodide with ethylenediamine in the presence of carbon monoxide in methanol allows isolation of various (e.g. $[(CO)(en)_2Cu]I$, $[(CO)_2(en)_3Cu_2]I_2$) thermally stable copper(I)-en-carbon monoxide systems depending upon the reactant ratios (37). No disproportionation is observed and absorption of carbon monoxide is not reversible. The observed lower carbon monoxide stretching frequency (e.g., in $[(CO)(en)_2Cu]I$ $\nu CO[Nujol]$ 2060 cm^{-1}) is diagnostic of Cu-CO bond stabilization. No carbon monoxide absorption is observed when an en/CuI ratio lower than 1 is used. The observed reversible absorption of carbon monoxide when CuCl is used (36), may be related to the fact that chloride, in contrast to iodide, does not prevent the disproportionation of copper(I). Though the isolation and characterization of I, is difficult

$$(CO)CuCl + en \longrightarrow \underset{I}{(CO)(en)CuCl} \qquad (3)$$

(36), the addition of $NaBPh_4$ precipitates the thermally stable compound $(CO)(en)Cu(BPh_4)$ (ν_{CO} [Nujol] 2117 cm^{-1}) (37). Copper(I) carbonyl complexes are extremely sensitive to air and moisture (37).

There is an extensive literature on stable copper(I)-unsaturated nitrogen ligand systems (38), probably due to the fact that π-acceptor ligands favour copper(I) (39). Thus, the reaction shown in equation 4

$$\begin{tikzcd}
2CuI + en + 2CO \arrow[r, "MeOH"] & \underset{II}{[(CO)_2(en)_3Cu_2]I_2} \arrow[d, "4C_6H_{11}NC"'] & (4) \\
& 2\,\underset{III}{[(en)(C_6H_{11}NC)_2Cu]BPh_4} & (5)
\end{tikzcd}$$

leads to complex II (37), which reacts further (40) with cyclohexyl isocyanide ($C_6H_{11}NC$) to produce complex III, $[(en)(C_6H_{11}NC)_2Cu]BPh_4$ (ν_{CN} [Nujol] 2143 and 2177 cm^{-1}), which crystallizes out on the addition of $NaBPh_4$. Thus, the strong σ-donor ligand, cyclohexyl isocyanide, displaces ethylenediamine. Further, it has been found that the greater the basicity of the nitrogen containing ligand, the less readily is the resulting complex oxidized at an electrode. Redox potentials of

Cu(II)/Cu(I) systems are related to the relative thermodynamic stabilities of the two oxidation states in a given ligand environment. Electrochemical studies with [(L - L)Cu]ClO_4 (L - L = N,N' - bis [o- (diphenylphosphino)benzylidene] ethylenediamine, see Fig.3) showed that the Cu(I) species can be oxidized to Cu(II) and even to Cu(III). However,

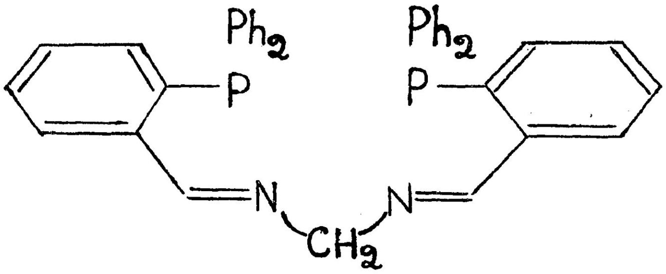


Figure 3

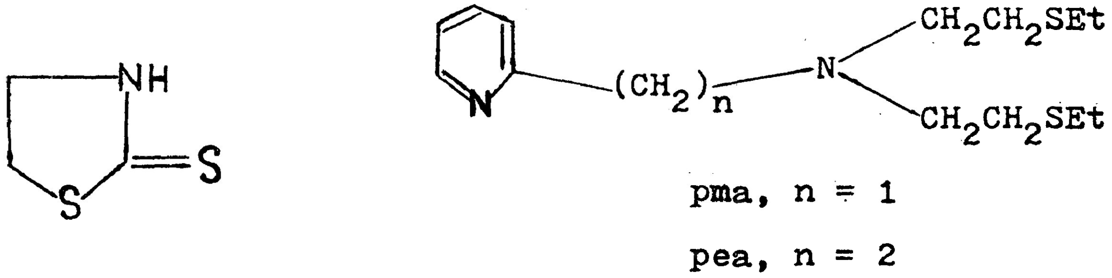
when t-BuNC is added to the copper(I) complexes of L-L, no oxidation was possible (41). This result clearly demonstrates the tendency of the isocyanide to stabilize the copper (I) oxidation state.

1.2.4. Stability of Cu(I) - S-donor ligand systems:

Monodentate anionic ligands derived from alkylthiols and thioamides (42) and also the neutral ligand thiazolidine-2-thione (Figure 4a) (43) all form stable copper (I) complexes. In addition, copper (I) complexes of thiourea and substituted thioureas are highly stable towards disproportionation - even in acidic solutions. The observed high stability constants of the bis, tris and tetrakis complexes of thiourea and substituted thioureas with copper(I) (44) is explained in terms of the synergistic effect operating between the metal atom and the ligand.

It has been observed that the number of complexes formed with different substituted thioureas decreases in the order: AcTh > PhTh > PhThPh > AcThAc (45), and also decreases as metal to ligand ratios are varied in the order: (1:2) > (1:1) > (1:3) > (1:4). It has also been observed that the number of stable solid compounds formed from reactions between different thioureas and the copper(I) ion is affected by the chemical nature of the counter anion and decreases in the order: $Cl^- > OH^- > MeCOO^- > SO_4^{2-} > NO_3^-$. These results clearly show how the nature of the ligand, the nature of the counter anion and the metal: ligand ratio influence the stability of the resulting copper(I) compounds.

Turning to other complexes, $[(pma)Cu]BPh_4$ and $[(pea)Cu]BPh_4$ (pma = 2-pyridylmethyl bis-[2-ethylthioethyl]amine; pea = 2-pyridylethyl bis-[2ethylthioethyl]amine, see Fig.4b) can be prepared from the respective mixed donor ligands (46).



(a) (b)

Figure 4

1.2.5. Stability of Cu(I) - P, As and Sb donor ligand systems:

Organophosphines, arsines, and stibines almost invariably stabilize the copper(I) state, although no stable copper(I) complexes of unsubstituted PH_3 have yet been reported. For example, simple copper(I) carboxylates are easily oxidized and disproportionate in the presence of moisture although stable carboxylatocopper(I) complexes of Ph_3P have been prepared by reducing copper(II) carboxylates in suitable solvents with Ph_3P (47). Of particular relevance is the extensive literature on the preparation of stable copper(I) halide complexes of tertiary phosphines, arsines, and stibines, particularly as a section of this thesis concerns the formation and properties of copper(I) chloride complexes with bidentate phosphines. Some Cu(I) complexes of the latter have already been reported. For example, copper(I) halide (Cl^-, Br^- and I^-) complexes of DPPM and DPPE with various Cu(I)/L-L ratios have been prepared by direct interaction of the copper(I) halide and the appropriate ligand in appropriate stoichiometries in organic solvents (50). In addition, complexes of the type $(DPPA)_3(CuX)_2$(X = Cl, Br, NO_3 NCS) were also prepared from reactions between the linear bidentate phosphine, DPPA, and the copper(II) salt in ethanolic solution (49). With monodentate phosphines complexes of the types $(Ph_3P)_3CuX$ and $[(Ph_3P)CuX]_4$ (X = Cl^-, Br^- and I^-) have been prepared from reactions of the appropriate copper(II) halide and the ligand in stoichiometric amounts (48). Similarly a series of complexes of the types, $(Ph_3As)_lCu_mX_m$ (X = halogen; l:m = 4:1, 3:1, 4:2, 3:2 and 4:4) have been prepared by reacting stoichiometric amounts of the ligand with the appropriate metal halide (51). Further stibine complexes, LCuX and L_2CuX, where L = o - $tolyl_3Sb$, m-$tolyl_3Sb$, p-$tolyl_3Sb$, o-$xylyl_3Sb$, and p-$xylyl_3Sb$; X = Cl^- and Br^-, have been prepared by prolonged heating of $CuCl_2 \cdot 2H_2O$ or $CuBr_2$ with tertiary stibines under reflux in suitable solvents (52).

The stabilities of copper(I) complexes with ligands containing P, As, and Sb donor atoms vary considerably with stereochemical and electronic environments of the copper atom. Thus, stable copper(I) hydride complexes can be prepared from reactions of $LiAlH_4$ with tertiary arylphoshine copper(I) halide complexes, while, under similar conditions, tertiary alkylphosphines give rise to decomposition to unidentified products (53). Further, it has been variously shown that the stabilities of copper(I) hydroborates depend predominantly on the stereochemical environments created by phosphines, arsines, and stibines around the copper atom (54). Thus stable complexes, $(R_3Y)_2Cu(BH_4)$, where Y is P and R an aryl group (Ph, p-MeC_6H_4, m-MeC_6H_4, p-$MeOC_6H_4$) have been prepared from the reaction between $(R_3Y)_nCuCl$ and $NaBH_4$, whereas under identical reaction conditions, trialkylphosphine, triphenylarsine and triphenylstibine give rise to decomposition to unidentified black solids (54, 55). However, under the same conditions CsB_3H_8 forms the stable complexes, $(Ph_3Y)_nCu(B_3H_8)$ for Y = P(n=2), As(n=2) and Sb(n=3) (54).

1.2.6. Stability of organocopper(I) compounds:

This section concerns Cu-C σ-bonded derivatives, as opposed to the σ and π type of bonding already discussed in Cu-π-ligand compounds.

Copper(I), but not copper(II), forms a variety of such compounds, most of which are unstable and highly reactive. Clearly the σ Cu-C bond stability depends upon the nature of the organic group attached to the Cu atom and also upon the nature of the substituents on the organic group. For example, perhalogeno alkyl- and aryl-copper(I) derivatives are thermally more stable and less oxidizable than the parent compounds (56). Similarly, cyanomethyl-copper is also relatively stable, probably owing to the electron-withdrawing properties and coordination ability of the cyano group towards copper (57).

The presence of other ligands (e.g. Ph_3P) can increase the stability of certain organocopper(I) compounds, such as Cu(2-benzyldimethylamine)(DPPE) (Figure 5) (58), and $(Ph_3P)CuMe$ (59), although attempts to stabilize the copper alkyl bond by coordination with 2, 2'-bipyridyl have been unsuccessful (60).

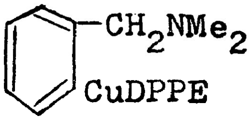
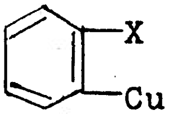


Figure 5

Arylcopper(I) compounds, such as , where X = dimethylamino, (dimethylamino) methyl, methoxy, methoxymethyl, diphenylphosphino, and dimethylsulfamoyl groups, are more thermally stable than compounds with no groups in the o-position, and are only slowly attacked by water and air (61). From the observed upfield shift of the methoxy proton resonance in the above complex when X = methoxy (62), it may be thought that the above stabilization is due to probable coordination of the hetero atom of the side group to the copper.

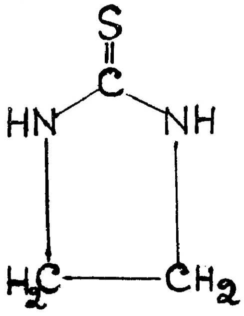
1.3. Preparation of copper(I) compounds:

1.3.1. Introduction:

A large number of copper (I) complexes has been prepared in a variety of stoichiometries by a variety of methods. Since the present thesis concerns reactions of bidentate phosphines with copper (II) salts and reactions of $NaBH_4$ and $NaBH_3CN$ with copper(I) in the presence of bidentate phosphines, the discussion in this section is organized under three reaction categories. This will allow easy comparison of the results recorded in this thesis with related material in the literature.

1.3.2. Synthesis of copper(I) complexes by direct interaction between ligands and Cu(I) species:

Typical examples of the use of this approach are the syntheses of copper(I) acetate complexes with various nitrogen-, phosphorus-, arsenic-, sulphur-, and -selenium donor ligands by direct interaction of the components in solutions under oxygen free conditions (63). With unidentate donors, compounds of the type $L_nCu(O_2CMe)$ (for L = thiourea or selenourea, n = 3, and for L = PPh_3 or imidazolidine-2-thione, [see Fig.6], n = 2) are formed (63). With bidentate donors (L-L) such as phen, 2,9-dimethyl-1,10-phenanthroline, DPPM, DPPE or DPAE, complexes of the type $(L-L)Cu(O_2CMe)$ are isolated (63), and by using different reactant ratios, the complexes $(DPPE)_3$-$[Cu(O_2CMe)]_2$ and $(DPPE)_2Cu(O_2CMe)$ have been obtained (63).



imidazolidine-2-thione

Figure 6

Complexes of the types, L_2CuX and $L_3(CuX)_2$ X = Cl^-, Br^-, I^-; L = 2-methoxycarbonylphenyldimethylarsine, 2-methoxycarbonylphenyldiphenylarsine, and 2-methoxycarbonylphenyldi-(p-tolyl)arsine have been prepared by reacting under reflux a suspension of the stoichiometric quantities of the appropriate ligand and the copper(I) halide in chloroform (64).

1.3.3. Synthesis of copper(I) complexes from copper(II) by using ligands as reducing agents:

Tertiary phosphines, arsines, and stibines almost always act both as reducing agents towards copper(II) salts and, as seen before, as complexing ligands towards copper(I). A wide variety of copper(I) complexes prepared by using phosphine, arsine, stibine and also phosphite ligands as reducing agents on copper(II) species in solution under different reaction conditions and with a variety of metal to ligand ratios has been listed in Table I.

Table I summarises a great deal of information and several points arise which need further comment. For example, tetrakis complexes of monodentate ligands can in general be prepared only with anions having poor ligand properties, e.g. ClO_4^- (66, 67). The fact that all attempts to prepare $[(Cy_3P)_4Cu]ClO_4$ with an excess of Cy_3P were unsuccessful (75) is probably a reflection of the steric hindrance of the bulky cyclohexyl group. Also, with monodentate ligands, tetrameric complexes of the type $[LCuX]_4$ ($X = Cl^-, Br^-, I^-$) can be prepared (51, 71). However, all attempts to prepare tetrameric monophosphine complexes of copper(I) fluoride were unsuccessful (48).

As Table I, for simplicity, does not contain experimental details, it is not clear from this table that the type of product formed depends in many cases upon the solvent. For

Table I. Copper(I) complexes prepared from reactions between Cu(II) salts and ligands - ligands as reducing agents

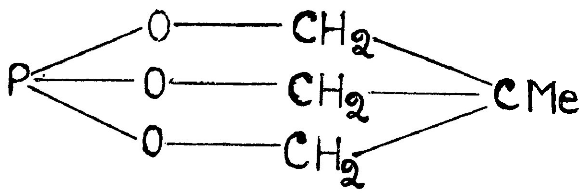
Metal salt	Ligand (as reducing agents) L or L-L	Complexes formed	Reference
$Cu(SO_3CF_3)_2$	Ph_3P	$L_nCu(SO_3CF_3)$ (n=1,2,3,4)	65
CuX_2	2-Phenylisophosphindoline, <u>o</u>-$C_6H_4[CH_2]_2PPh$	$(LCuX)_n$ and L_2CuX (X = Cl, Br, I) LCuX (I only) $[L_4Cu]X$ ($X=ClO_4^-$, NO_3^-)	66
$Cu(ClO_4)_2$	Ph_3P	$[L_4Cu]\ ClO_4$	67
CuX_2	Et_3P, Ph_3P	$[LCuCl]_4$, L_3CuF	48
$Cu(COOR)_2$	Ph_3P	$L_2Cu(COOR)$ ($R = C_6F_5$, C_2F_5, n-C_3F_5 and Ph)	69
Cu(II)-acetylacetonates	Ph_3P	LCuB (B=hexafluoroacetylacetonate, trifluoroacetylacetonate, and thienyltrifluoroacetylacetonate)	70
CuX_2	Ph_3As, Ph_3Sb	$[LCuX]_4$ (X=Br, I; $L=Ph_3As$ $L_3Cu_2X_2$ (X=Br, $L=Ph_3As$; X=I, $L=Ph_3Sb$) L_nCuBr (n=2, Ph_3Sb; n=3, $L=Ph_3As$)	71

Cont'd....

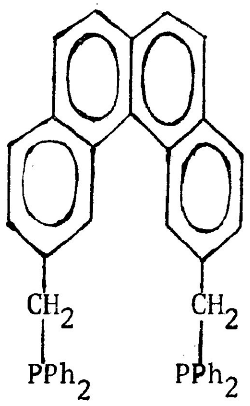
Table I. Continued.

Metal salt	Ligand (as reducing agents) L or L-L	Complexes formed	Reference
$Cu(NO_3)_2$	(Ph_3Y) (Y=P, As, Sb)	$L_3Cu(NO_3)$	72
$Cu(NO_3)_2$	Ph_3P	$L_2Cu(NO_3)$	73
$Cu(NO_3)_2$	$(m\text{-tolyl})_3P$, Cy_3P, DPPM, $EtPh_2P$, $MePh_2P$, Me_2PhP, DPPE, DPPP	$L_2Cu(NO_3)$ $L_3Cu(NO_3)$ $[(L\text{-}L)_2Cu](NO_3)$ $(L\text{-}L)_3Cu_2(NO_3)_2$	70
CuX_2 $X = NO_3^-$, ClO_4^-	$P(OCH_2)_3\ CMe^a$	$[L_4Cu]X$	74
CuX_2	Cy_3P	L_2CuX ($X=Cl^-$, Br^-, ClO_4^-) $LCuX$ ($X=Cl^-$, Br^-)	75
$CuCl_2 \cdot 2H_2O$	2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene[b]	(L-L) CuCl	76

a)



b)



example, the trisphosphine complex, $(Ph_3)_3Cu(NO_3)$ is obtained in ethanol (72), whereas, under identical reaction conditions a bisphosphine complex, $(Ph_3P)_2Cu(NO_3)$ is formed in methanol (73).

Before proceeding to other ligand systems, it is worth mentioning a slightly different synthetic approach to some Cu(I) complexes. Thus, in the isolation of the complexes $(Ph_3P)_3CuCl$, $(Ph_3As)_4CuCl$, and $(Ph_3Sb)_2CuCl$ from reactions (68) between melted ligands and the appropriate Cu(II) salt use was made of the fact that the ligands melt well below the decomposition temperature of the resulting complex.

Considering now other ligands, sulphur ligands are also known to reduce copper(II) to copper(I) . A wide variety of copper(I)-sulphur ligand complexes, prepared by using ligands as reducing agents on various copper(II) species in solutions and under a variety of reaction conditions has been listed in Table II.

Few additional comments are necessary on the data in Table II which is simply meant to illustrate the scope of this particular feature of Cu(I) chemistry. Perhaps the role of the solvent could be stressed again here. For example, complexes such as $[(bdtm)CuCl]_2$, $[(bdtm)_2Cu]ClO_4$ (84) can be prepared by using the ligands as reducing agents in ethanol or ethanol-methylenechloride solutions, whereas, the corresponding reactions in acetone lead to a copper(II) product (84).

Table II. Copper(I) complexes prepared by reducing copper(II) salts with S containing ligands

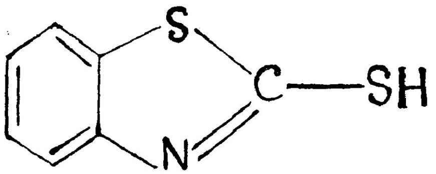
Metal salt	Reducing agents	Complex	Reference
$Cu(ClO_4)_2$	$C_7H_5NS_2$, mercaptobenzothiazole (H mbt)[a]	$Cu(mbt)_n$ $[(H\ mbt)(C_{14}H_8N_2S_5)*Cu]$- $ClO_4 \cdot CHCl_3$	77
$Cu(ClO_4)_2$	Bis(2-bipyridyl)disulphide[b] (L-L)	$[(L-L)_2Cu]ClO_4$	78
$Cu(NO_3)_2$	Thiourea (Th)	$Th_4Cu_4(NO_3)_4 \cdot 4H_2O$ $Th_9Cu_4(NO_3)_4 \cdot 4H_2O$	79
Cu(II) salts	Acetylthiourea (AcTh)	$(AcTh)_nCu(OH)$ (n=2,3,4) $(AcTh)_nCuCl$ (n=2,2.5,3) $(AcTh)_nCu(COOMe)$ (n=1,2,3) $(AcTh)_4Cu_2SO_4$	80
$CuCl_2$	Various <u>N</u>- and <u>N,N'</u>-substituted thioureas (L)	LCuCl L_2CuCl	81
CuX_2	$R_2P(S)P(S)R_2$ (R=Me, Et) (L-L)	$(L-L)_nCuX$ (n=1, X=halides; n=2, X=perchlorate)	82

Cont'd....

Table II. Continued.

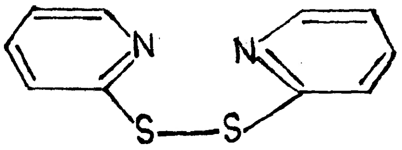
Metal salt	Reducing agents	Complex	Reference
$Cu(ClO_4)_2$	Tris(dimethylamino)phosphine sulphide, $(Me_2)N_3P = S$ (L)	$[L_4Cu]ClO_4$	83
Cu(II) salts	bdtm, bdte, bdsm, tmdpds^c (L-L)	$[(L\text{-}L)CuCl]_2$ (L-L=bdtm) $[(L\text{-}L)CuBr]_n$ (L-L=bdtm, bdte, tmdpds) $[(L\text{-}L)_2Cu]ClO_4$ (L-L=bdtm, bdsm)	84

a)



*The ligand dimerizes with the incorporation of an additional sulphur atom.

b)



c) $R_2P\cdot(:X)(CH_2)_n\cdot P(:X)R_2$

	R	X	n
bdtm	Ph	S	1
bdte	Ph	S	2
bdsm	Ph	Se	1
tmdpds	Me	S	0

1.3.4. Synthesis of copper(I) complexes by adding hydroborate ions to various copper species in the presence of ligands:

1.3.4.1. Introduction:

Reactions of ionic alkali metal hydroborates with transition metal ions in the presence of ligands may produce (a) fully reduced metal(0) compounds (55), (b) hydroborate complexes in which the hydroborate ion is coordinated to the metal ion (85) or (c) metal hydrides (86) or even mixed hydride - hydroborate type complexes (87). The tetrahydroborate ion, BH_4^-, and some of its substituted derivatives such as BH_3CN^-, $BH(OMe)_3^-$ etc., are widely used as reducing agents and as sources of H^- ion in both inorganic and organic chemistry. This next section of the thesis deals with some of the copper complexes of these species.

1.3.4.2. Synthesis of copper(I) hydroborate complexes:

Tetrahydroborate complexes of a great many metallic elements have been made. Stable hydroborate complexes are generally prepared in the presence of soft Lewis bases. A wide variety of copper(I) hydroborates have been prepared by reacting hydroborate ions with copper(I) complexes. As in previous sections, the result of these studies can be conveniently and concisely presented in tabular form, as in Table III.

Table III. Copper(I) hydroborates.

Complex	Mode of formation	Reference
$(DBP)_2Cu(BH_4)$	$CuCl_2$ + DBP + $NaBH_4$	88
$(DPPA)_3Cu_2(BH_4)_2$	$(DPPA)_3Cu_2(NO_3)_2$ + $NaBH_4$	49
$(MePh_2P)_3Cu(BH_4)$	$(MePh_2P)_3CuCl$ + $NaBH_4$	89
$[(MeO)_3P]_2Cu(BH_4)$	$[(MeO)_3P]_3CuCl$ + $NaBH_4$	90
$L_3Cu(BH_3CN)$ ($L=Ph_3P$, DBP, $EtPh_2P$, 1.5 DPPE)	$CuCl_2$ + L + $NaBH_3CN$	55
$(Ph_3P)_3Cu(BH_3CN)$	$(Ph_3P)_3CuCl$ + $NaBH_3CN$	91
$(Ph_3P)_2Cu(BH_3CN)$	$(Ph_3P)_2CuCl$ + $NaBH_3CN$	91
$L_3Cu(BH_3CN)$ ($L=Ph_3As$, Ph_3Sb)	$CuCl_2$ + L + $NaBH_3CN$	91
$(Ph_3P)_2Cu(BH_3COOR)$ (R=Me, Et)	$(Ph_3P)_3CuCl$ + KBH_3COOR	92
$(Ph_3P)_2Cu(BH_3COOH)$	$(Ph_3P)_4CuF$ + $Ca(BH_3COOH)_2$	92
$(Ph_3P)_3Cu(BH_3COOEt)$	CuCl + $MePh_2P$ + KBH_3COOEt	93
L_nCuB (L=tri-p-tolylphosphine; n=2,4; $B=B_3H_8^-$, $B_9H_{14}^-$, $B_9H_{12}S^-$)	$Cu(SO_4)$ + L + appropriate cesium hydroborate	94

Cont'd....

Table III. Continued.

Complex	Mode of formation	Reference
$[(Ph_3P)_2Cu]_2B_{10}H_{10}\cdot CHCl_3$	$(Ph_3P)_3CuCl$ + triethylammonium decahydrodecaborate	95
$(Ph_3P)_2Cu(B_4H_9)$	$(Ph_3P)_3CuCl + KB_4H_9$	96
2,3-μ-$(Ph_3P)_2Cu-RB_5H_7$ (R=H, and 1-or 4-Me)	$(Ph_3)_3CuCl + K(RB_5H_7)$	97
$(Ph_3P)Cu(C_2B_8H_{11})$	$[(Ph_3P)CuCl]_4$ + Na(5,6-$C_2B_8H_{11}$)	98

There are some very interesting chemical features of many of the complexes listed in this table. It will be convenient to discuss these aspects, e.g. mode of attachment of the hydroborate ions, ligand dissociation in solutions and fluxional behaviour data later in this chapter.

1.3.4.3. Synthesis of copper(I) hydride complexes:

Metal hydrides frequently arise as products from reactions between $NaBH_4$ and its derivatives and metal salts, especially when suitable ligands are present. They do in general form a well characterized group of complexes with well defined physical and chemical properties. However, only a few copper(I) hydride complexes are known perhaps because the spectroscopic properties (NMR, IR) which in general allow the easy recognition of most M-H bonds have not been successful when applied to Cu(I)-H bonds.

For example, the interesting hexameric complex, $(Ph_3P)_6Cu_6H_6{\cdot}HCONMe_2$ was prepared by adding solid sodium trimethoxyborohydride to a stirred solution of $(Ph_3PCuCl)_4$ in DMF under argon (99). However, the presence of the hydrides was not detected by X-ray crystallography, NMR or infrared spectroscopy, but was inferred from chemical reactions. More will be said about this complex later. The red complexes, $[(Ph_3P)CuH]_n$, $[(\underline{p}\text{-}MeC_6H_4)_3PCuH]_n$ have been prepared by adding a solution of $LiAlH_4$ in diethyl ether (less than one mole per mole of CuCl) to a reaction mixture of CuCl(4.78 mM) and phosphine (14.3 mM) in THF (53). Again no spectroscopic evidence was obtained for the hydrido ligands.

A series of stable copper(I) hydrides, of the type $Li_nCu_mH_{(n+m)}$ (for n = 1, m = 1,2; n = 2, m = 1,3; n = 3, m = 1; n = 4, m = 1; n = 5, m = 1) have been prepared by reacting $LiAlH_4$ with the corresponding lithium alkylcuprates, $Li_nCu_m(CH_3)_{(n+m)}$ in ether (100). The reactions were carried out by adding a solution of $LiAlH_4$ to a clear colourless reaction mixture of CH_3Li and CuI in appropriate ratios in ether at -78°C.

It is clear from this brief section that compounds containing Cu-H bonds are very uncommon compared to other metals and also difficult to characterize.

1.4. Structures of copper(I) compounds:

1.4.1. Introduction:

Copper(I) complexes give rise to an interesting array of stoichiometries and geometric configurations including polynuclear species (38). Simple stoichiometries do not give much information about the structures of copper(I) compounds which can be mononuclear, binuclear with bridging neutral ligands or coordinating anions, polynuclear with the copper atom two-, three-, or four-coordinate or linked in infinite chains (38). A brief summary of structural types is presented here.

1.4.2. Mononuclear species:

Traditionally, copper(I) is viewed as a metal ion prone to form two-coordinate linear (101) and four-coordinate tetrahedral (102) structures. However, mononuclear species can be of various structural types with two-, three-, or four-coordinate copper depending on the nature of counter anion and the steric bulk of the ligand.

For example, cationic complexes of the type $L_4Cu^+X^-$, where L = MeCN (29) or pyridine (103) and X = noncoordinating anions, ClO_4^- or NO_3^- are tetrahedral species. Similarly, in bis (6,6'-dimethyl-2,2'-bipyridyl)copper(I) tetrafluoroborate, the copper(I) environment (Cu_4N) is pseudotetrahedral (104).

On the other hand, copper is planar and three-coordinate in $(Cy_3P)_2CuOClO_3$ (105). Similarly, with noncoordinating anions and soft ligands containing bulky substituents, the copper is three-coordinate and planar, in complexes such as $[(Me_3PS)_3Cu]^+ClO_4^-$ (106), $[(C_6H_7N)_3Cu]^+ClO_4^-$ (107), and $[(Me_4N_2CS)_3Cu]^+BF_4^-$ (108).

In L_3CuX type complexes, in which X is a coordinating anion, a distorted tetrahedral geometry may be formed, a typical example being $(MePh_2P)_3Cu(BH_4)$ (109). Distorted tetrahedral coordination is also found for complexes of the type L_2CuX, where L = Ph_3P, X = NO_3^- (110), BH_4^- (111), $O_2NCHCMe_2OH^-$ (112), $O_2NCPhNO_2^-$ (113), $OOCCH_3^-$ (114), i.e., X is a chelating anion.

1.4.3. Binuclear species:

The compound $(Cy_3PCuCl)_2$ exists as the dimeric species (115) in contrast to the tetrameric "cubane" (116) or "step" (117) structures found for other monodentate phosphine-copper(I) halide complexes with a 1:1 ratio. Each copper atom is in a trigonal-planar coordination with a terminal phosphine and two bridging chlorides (Figure 7a, p. 34). The existence of this compound as a dimer rather than as a tetramer is due to the steric bulk of the Cy_3P ligands.

The complex $(Ph_3P)_3Cu_2Cl_2$ (118) and its benzene solvate (119) are interesting because they are both binuclear compounds containing both three- and pseudotetrahedral four-coordinate copper in the same molecule, as seen in Fig. 7b (p. 34). An X-ray investigation of the compound $[(Me_2PhAs)_2CuCl]_2$ shows that the molecule is like the above compounds in that it is a dichloride-bridged dimer, but is unlike the above compounds in that both copper atoms are pseudotetrahedral and related by an inversion center (119). A similar dimeric species is $[(Ph_3P)_2CuN_3]_2$ with four-coordinate copper atoms in tetrahedral geometries (120).

The compound $[(Ph_3P)_2Cu(BH_3CN)]_2$, which is very relevant to what will be discussed later in this thesis, is also dimeric (121), with each pseudotetrahedral copper atom bonded to two triphenylphosphine ligands and to a hydrogen and a nitrogen atom from two different cyanotrihydroborate groups (Figure 7c, p. 34). This compound is one of the very few examples where the mode of coordination of the BH_3CN group has been established by crystallography. The crystal structure of the compound $(DPPE)_3Cu_2Cl_2 \cdot 2(Me_2CO)$ is also very interesting because it shows the first example discussed so far where a bidentate phosphine acts as a bridging ligand (122). Figure 7d, (p. 34) shows clearly that each copper atom is tetrahedrally coordinated to a chlorine atom, two phosphorus atoms from one chelating DPPE molecule while the bridging ligand occupies the remaining site on each copper. Further examples of bridging ligands are shown in the crystal structures (123) of the dimeric complexes $[L_6Cu_2](BF_4)_2$ where L = Th, and S-dimethylthiourea. Each copper(I) atom is four coordinate and is bridged by the S atoms of the ligands.

1.4.4. Trinuclear species:

Only one such trinuclear structure is known and this is a 3:2 complex, $(DPPM)_2(CuI)_3$ (124). The structure, Figure 7e (p. 34), consists essentially of a triangle of copper atoms bridged by iodides and DPPM ligands such that each copper has a distorted tetrahedral configuration.

1.4.5. Tetranuclear species:

Two types of structures, "cubane" and "step", are generally observed for tetrameric complexes of the type $(LCuX)_4$ where X is halogen and L is usually a monodentate phosphine or arsine. In the cubane structure (Figure 7f, p. 34) each copper atom (located at the alternate corners of a cube) is tetrahedrally coordinated with triply bridging halides (located at the remaining corners of the cube) and a terminal phosphine. On the other hand, in the step form (Figure 7g, p. 35) there are double and triple halide bridges and two four-coordinate, tetrahedral and two three-coordinate, trigonal copper atoms.

The Cu_4Cl_4 core of $[(Ph_3P)CuCl]_4$ has the "cubane-like" structure (116), whereas the Cu_4B_4 core of the analogous bromocompound, $[(Ph_3P)CuBr]_4$, has the step structure (117). The step structure is also found in the bromo derivative, $(DPPM)_2Cu_4Br_4$ (125). Iodo derivative are known both with a cubane-like core e.g. $[(Et_3As)CuI]_4$, and $[(Et_3P)CuI]_4$ (126) and with a step structure e.g. $[(Ph_3P)_3CuI]_4$ (127). Thus, it can be seen that in $[(R_3P)CuX]_4$ (X = halogen) type complexes, the step structure is favoured over the cubane-like structure only with bulky ligands and large halogen atoms.

A number of sulphur ligand complexes have a tetrahedral or distorted tetrahedral Cu_4 core. Thus, the Cu_4S_6 core of the $[(PhS)_6Cu_4]^{2-}$ cluster consists of a tetrahedron of copper atoms inscribed in a distorted octahedron of sulphur atoms (Figure 7i, p. 35) (129). Each S atom is coordinated to two copper atoms across an edge of the Cu_4 tetrahedron, and each copper is trigonally coordinated by three sulphur atoms of three different ligands.

There are two other structures shown by tetranuclear copper complexes. Examples of the first type are $[Cu(CH_2SiMe_3)]_4$ (130) and $[CuOBu^t]_4$ (131) which have square planar Cu_4 cores (Figure 7j, p. 35), while $[CuN_3Me_2]_4$ (132) consists of a planar parallelogram of copper(I) ions (Figure 7k, p. 35). These structures however, appear to be less common than the arrangements discussed earlier.

1.4.6. Pentanuclear species:

As might be expected, these complexes are very uncommon. One example is the dianion of the benzothiolate complex, $[(\mu_2\text{-SPh})_7Cu_5]^{2-}$, which has a curious arrangement of four copper atoms, each with trigonal planar coordination, the remaining copper being two-coordinate and linear (Figure 7l, p. 35) (133).

The interesting cluster $[(\mu_2\text{-SBu}^t)_6Cu_5]^-$ has a trigonal bipyramidal arrangement of copper(I) atoms with copper-copper bonding (Figure 7m, p. 36) enclosed within a distorted octahedron of doubly-bridging thiolate ligands (134). Each of the six thiolate sulphur atoms bridge an axial-equatorial pair of copper atoms such that the two copper atoms axial in the trigonal bipyramid possess trigonal planar coordination (Cu_{trig}) and the three equatorial copper atoms possess approximately linear diagonal coordination (Cu_{dig}). Two systematic distortions force all copper atoms towards the centroid of the cluster without decreasing copper-sulphur distances, as apparent from the following observations. The $S\text{-}Cu_{dig}\text{-}S$ angles are decreased below 180^o to $170^o \pm 1^o$, and the S_6 prism is twisted by 49^o about the threefold axis. The atomic distances are decreased (compared with the idealized undistorted distances in the parenthesis); centroid-Cu_{dig}, 1.90, 1.86, 1.84 A^o (2.27 A^o); $Cu_{dig}\text{-}Cu_{trig}$, 2.72 A^o (3.14 A^o); $Cu_{dig}\text{-}Cu_{dig}$, 3.23 A^o (3.93 A^o). This type of prominent structural feature with metal-metal bonding will be discussed again in section 1.4.8.

1.4.7. Hexanuclear species:

The only example of this type known is the extremely interesting compound $[(Ph_3P)CuH]_6$, which has been mentioned earlier and which is shown in Figure 7n, (p. 36) (99). Basically, the molecule is an arrangement of six Cu atoms at the vertices of a slightly irregular octahedron, with each one bound to a Ph_3P. Two types of Cu-Cu distances have been detected. One average Cu-Cu distance is 2.65 A^o and the other is of average value 2.54 A^o. The presence of the hydrido ligands was not detected directly from the X-ray data, but they are thought to lie in bridging positions along the six longer Cu-Cu edges.

1.4.8. Octa- and decanuclear species:

A few examples of these types of arrangements are known, mainly with sulphur ligands. For example, the Cu_8S_{12} cores in the compounds, $(Ph_4P)_4[Cu_8(S_2C_4O_2)_6]$ (IV) and $(Ph_4N)_4[Cu_8\{SCC(COOEt)\}_6]$ (V) consist of a cube of copper atoms inscribed in a distorted icosahedron of sulphur atoms. Each sulphur atom is coordinated to two copper atoms across an angle of the cube, and each copper is trigonally coordinated by three sulphur atoms of three different ligands (135). Considering repulsive Cu-Cu interactions at 2.77 A^o in

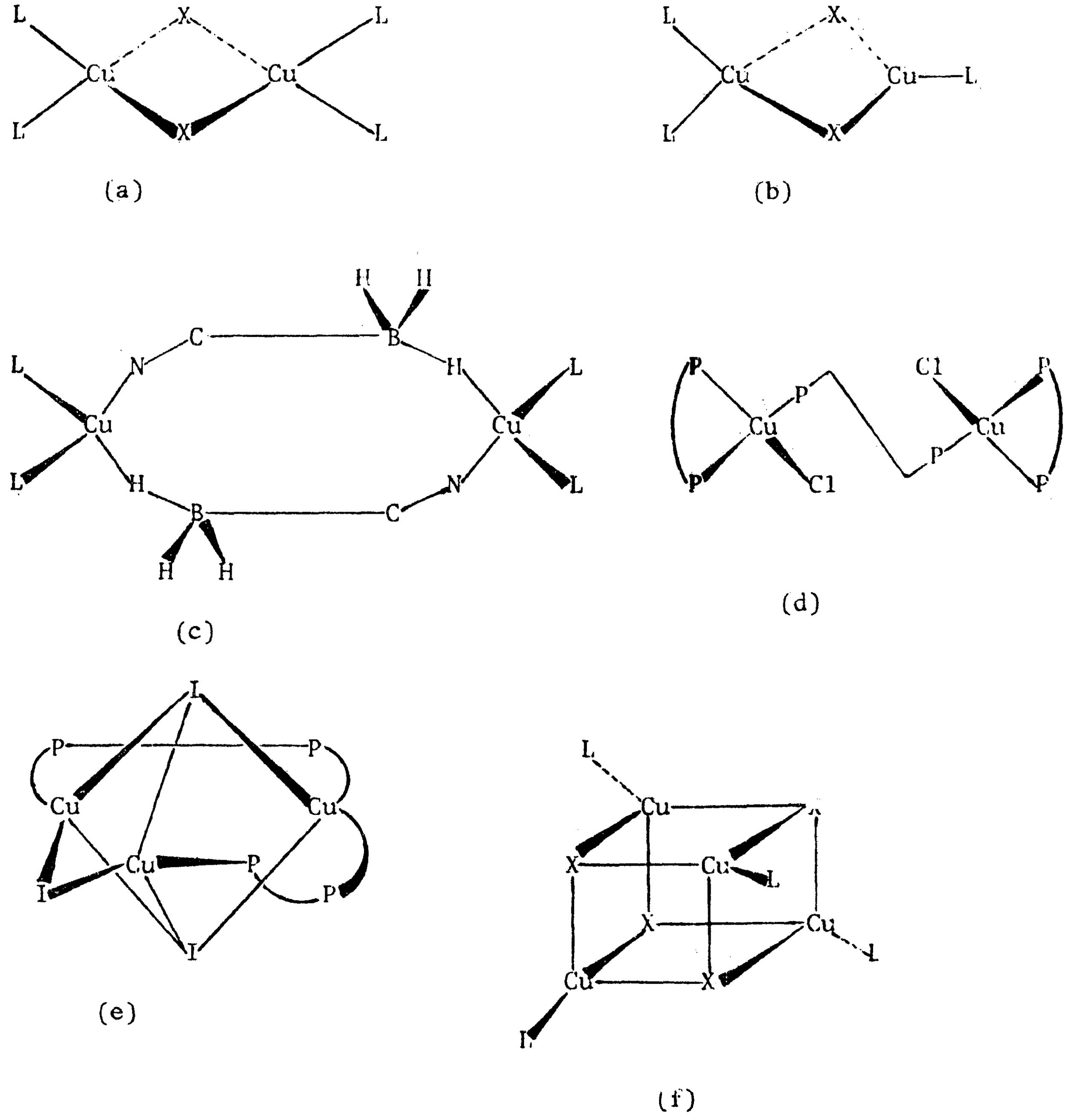
$[(\mu\text{-SPh})_6Cu_4]^{2-}$ (129), the observed Cu-Cu distance 2.844 (20) A° in (IV) and 2.790 (11) A° in (V) have been considered as the optimum conditions where the attractive interactions prevail.

1.4.9. Long chain species:

Potassium and ammonium trichloro- and tribromocuprate(I) are made up from infinite chains of Cu_4X_4 tetrahedral units sharing corners (136, 137) while in $Cs[Cu_2Cl_3]$ there are double chains formed by $CuCl_4$ tetrahedra sharing edges (138). In contrast, $KCu(CN)_2$ has a spiral polymeric structure in which each copper atom is bound to two CN- carbon atoms and one CN- nitrogen atom in a nearly trigonal coplanar array (Fig. 7o, p. 36) (139).

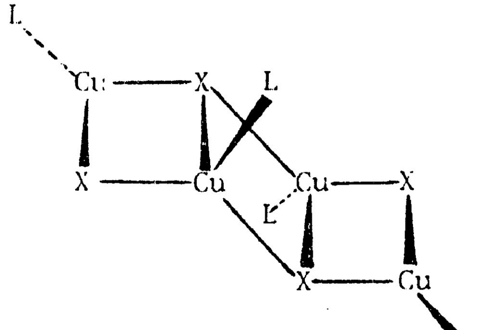
Sulphur ligands are also known to form long chain compounds. Thus, the structure of the complex $(Et_2S)_3(CuI)_4$ consists of infinite chains of sulphide-bridged Cu_4I_4 cores, each of which resembles a distorted cube with alternating vertices of copper and iodine (Figure 7h, p. 35) (128).

It is obvious from the above discussions that copper(I) complexes exist in an extraordinarily wide range of co-ordination geometries and copper(I) compounds, often with quite simple empirical formulae, can clearly have quite complicated structures. These are difficult to establish without X-ray methods, as will be emphasized again later in this thesis.



(a) (b) (c) (d) (e) (f)

Figure 7 Cont'd.....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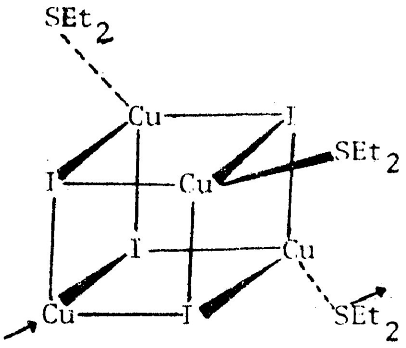
(g)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Cu
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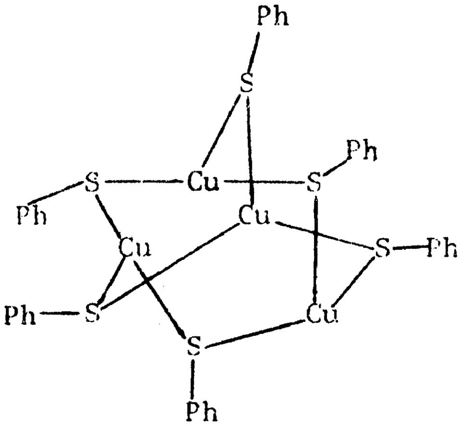
Cu
I
SEt2

(h)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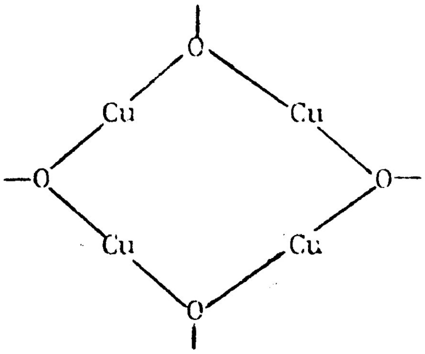
Ph

(i)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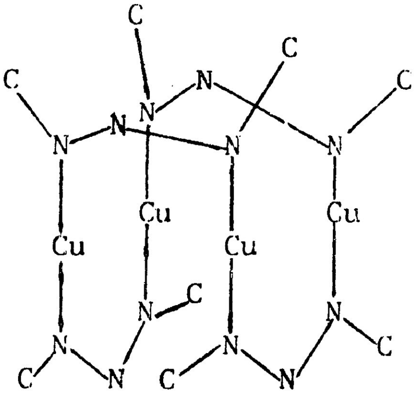
O
O
Cu
Cu
O

(j)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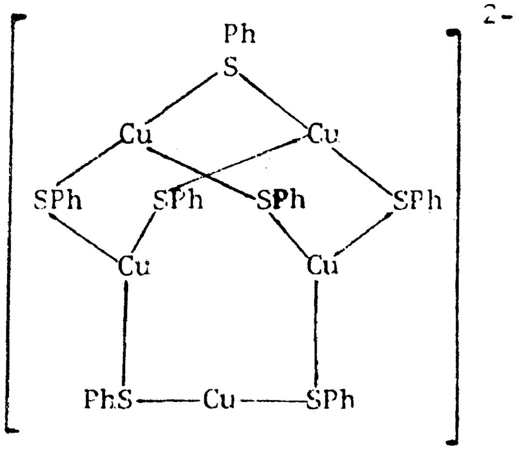
(k)


2-
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Cu
Cu
PhS
Cu
SPh

(l)

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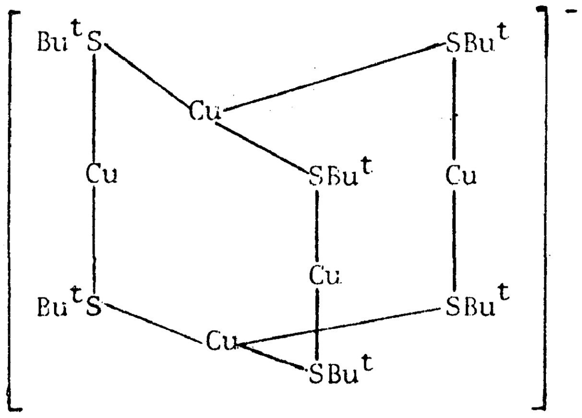

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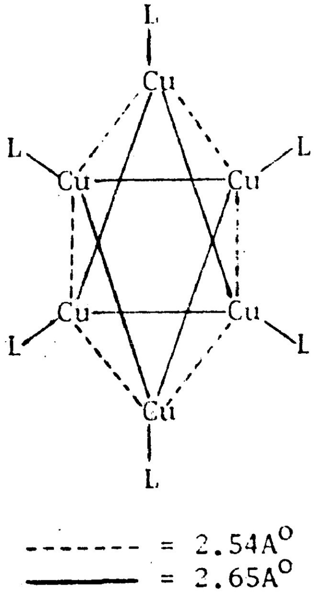

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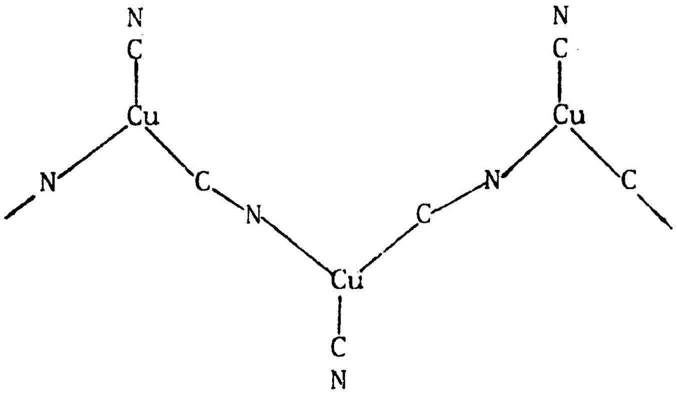

(o)

Figure 7

1.5. Properties of copper(I) compounds:

1.5.1. General:

It should perhaps be noted at this point that copper(I) compounds are diamagnetic and almost always colourless since the 3d orbitals of the copper are completely filled. Colour results only if charge-transfer bands occur or if the anion itself is coloured. This means that physical measurements based on the presence of an incompletely filled d electron shell are of no help in structural studies on copper(I) complexes.

1.5.2. Dissociation behaviour in solution:

The dissociation of tertiary phosphine, arsine and stibine complexes of copper(I) in solution is very much dependent upon the nature of the ligand, the solvent and the temperature. Thus a ^{31}P NMR study of tri-p-tolylphosphine (L) complexes of copper(I) halides in organic solvents, shows that the major species is the dimer $(L_2CuX)_2$ at -100°C. Above this temperature, at about -70 to -80°C, the complex dissociates into L_3CuX, $L_3Cu_2X_2$ and a small amount of the L_2CuX monomer (140). The equilibria occurring in chloroform solutions of complexes of the type, $[Ph_{3-n}Me_nY]_mCuX$ (n=0,1,2; m=3,2,1.5; Y=P, As; X=Cl, Br, I) have been studied osmometrically. The relative stabilities of the L_3CuCl complexes are L = $Ph_3P \ll MePh_2P \simeq Me_2PhP$ (141), an order which is different from the order of ligand basicities, and which therefore suggests that the most important influence on ligand dissociation seems to be a stereochemical one. However, the corresponding arsine analogs are much more dissociated than the phosphine complexes and suggests perhaps that the basicity of the ligand does influence the extent of dissociation. Finally, for 3:1 complexes with any given ligand the extent of ligand dissociation decreases in the order Cl > Br > I.

The labilities of arsine and stibine complexes are further manifested by the ready convertibility of complexes $(Ph_3Y)_3Cu(NO_3)$ (Y = As, Sb) into $[(L\text{-}L)_2Cu](NO_3)$ (L-L = phen, 2,2'- biquinolyl) by reacting them with an excess of the bidentate ligand (72). The triphenylphosphine analogue is not readily converted into the bidentate complex.

Further aspects of ligand dissociation will be discussed more in the next section in connection with hydroborate ion interaction.

1.6. Copper(I) - hydroborate ion interactions:

1.6.1. Introduction:

In recent years there has been considerable interest in establishing the stereochemical and electronic principles which are operative when hydroborate ions interact with metal ions. For mononuclear complexes, four possible modes of attachment of the simplest tetrahydroborate ion are conceivable:

monodentate (VI), bidentate (VII), tridentate (VIII), and ionic (IX) (142). For other B-H- containing anions, such as

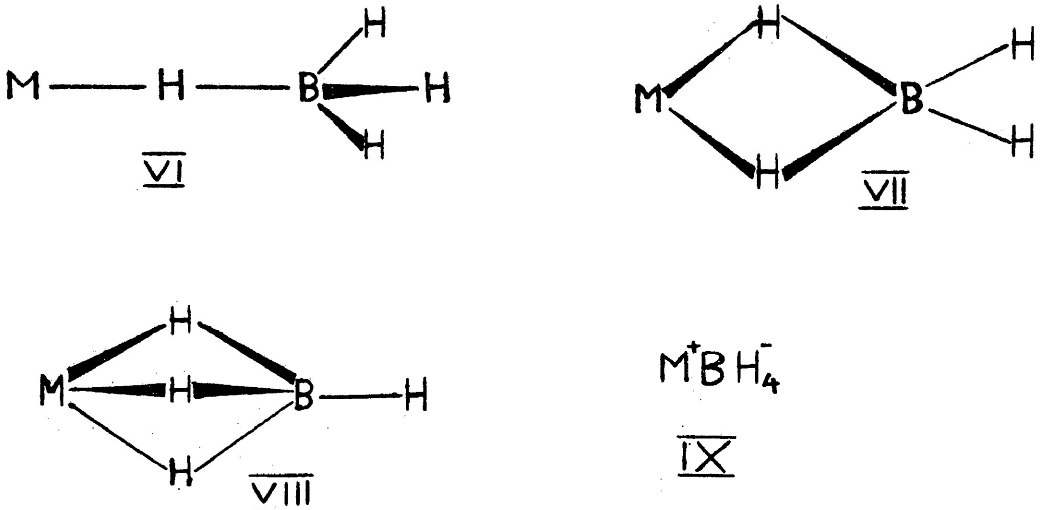

Figure 8

BH_3CN^-, similar types of binding modes might be expected, although clearly a number of different arrangements are also possible. The various types of binding possibilities are being investigated by diffraction, nuclear magnetic resonance and infrared spectral studies. Firm structural information can obviously lead to a better understanding of the properties of a molecular system. However, the most common solid-state structural technique, single-crystal X-ray diffraction, is in many cases of limited utility (143). Accurate location of hydrogen atoms near a heavy metal is extremely difficult because of the approximate proportionality of X-ray scattering to the square of the atomic number and also due to diffuse scattering for large vibrations of hydrogen atoms near a heavy metal. Thus, the molecular structure is sometimes difficult to accurately determine, due to complicated electronic, steric and also perhaps crystal packing factors. Nuclear magnetic resonance spectra in solution show that hydroborate complexes are generally nonrigid and in many cases such studies yield only limited structural information. For example, in bi- and tridentate species the bridge and terminal hydrogen atoms undergo rapid intramolecular exchange (Fluxional) and so appear equivalent on the NMR time scale (144). In contrast, infrared spectral studies can, at least in theory, provide useful data on the coordination geometry and bonding of the hydroborate ligand (145). Thus, a normal coordinate analysis shows that it should be possible to distinguish between the different modes of coordination of the BH_4^- ion as shown in Figure 8, by the number of peaks and their positions in certain regions of the IR spectrum. For example the monodentate attachment of the BH_4^- group is distinguished by the presence of the strong peak at 1000-1150 cm^{-1} assignable to the BH_3 deformation and a strong absorption at ca. 2000 cm^{-1} for the $B\text{-}H_b$ stretching frequency (145), whereas with the bidentate BH_4^- group the BH_2 deformation occurs at 1100-1200 cm^{-1} and the $B\text{-}H_b$ stretching frequency at 1650-2150 cm^{-1}. The significant distinguishing feature of the bidentate mode of attachment is the presence of a strong bridge stretch at 1300-1500 cm^{-1}. Furthermore, the position and number of peaks in the $B\text{-}H_t$ and $B\text{-}H_b$ region of IR spectrum helps to distinguish between the bidentate and monodentate attachment. The frequency difference between B-H_t (2300-2450 cm^{-1}) and B-H_b (ca . 2000 cm^{-1}) vibrations for monodentate attachment is significantly less than for the bidentate attachment (2400-2600 cm^{-1} B-H_t, and 1650-2150 cm^{-1} B-H_b). Thus, as the B-H force constants in monodentate attachment become more equal (compared to bidentate attachment), covalent interaction with the metal weakens.

The discussion in this section is organized into three categories, namely (i) mode of attachment of hydroborate ions, (ii) fluxional studies, and (iii) dissociation in solution of copper(I) hydroborate complexes.

1.6.2. Mode of attachment of hydroborate ions in copper(I) compounds:

The only conclusive reports of a BH_4^- group bonded in a monodentate way are with copper(I) , although the possibility of similar bonding in a cobalt complex (55) and a series of ruthenium complexes (87b) has been reported previously from these laboratories. Thus, the first confirmed example of a single hydrogen bridged bond between a BH_4 group and copper(I) occurs in $(MePh_2P)_3Cu(BH_4)$, reported by Bommer and Morse, initially from infrared spectroscopic data (89) as shown in Table IV. The expected infrared absorption of a monodentate BH_4 group, from the normal coordinate analysis, are given at the top of Table IV so that the reader may readily compare the expected with the observed frequencies for compounds thought to have such an arrangement.

Confirmation of the presence of a monodentate BH_4 group in $(MePh_2P)_3Cu(BH_4)$ has been shown by an X-ray crystallographic study (109). The Cu----B separation, 2.650 - (5) A°, is substantially greater than the 2.184(9)A° value for the corresponding distance in $(Ph_3P)_2Cu(BH_4)$ which is known to contain a bidentate BH_4 group (111). A nearly-linear Cu-H_b-B bridge (170°) with a Cu-H_b bond length of 1.47A° was found in this initial study. Very recently, a more accurate single crystal neutron diffraction study of $(MePh_2P)_3Cu(BH_4)$ has reaffirmed the monodentate coordination of the BH_4 group (146). However, the observed Cu-H_b bond length, 1.697(5)A° and the distinctly bent Cu-H_b-B bridge, 121.7(4)° are in marked contrast to those found in the earlier X-ray analysis (109). This difference which emphasises the difficulties of locating H atoms with X-ray, as mentioned earlier, is partly due to the fact that hydrogen atom positions are often distorted by the bonding electron density in X-ray analysis. Furthermore, the observed H_b-Cu-P angles (86°, 109°, 115°) deviate considerably from three fold symmetry. The authors rationalized these observations by postulating that a "closed" three center overlap pattern occurs in Cu-H_b-B bond.

Monodentate bonding of the BH_4^- group has also been proposed (93) in $(MePh_2P)_3Cu(BH_3COOEt)$ from IR spectroscopic data, as shown in Table IV. A decrease in covalent interaction of the $(BH_3COOEt)^-$ group in $(MePh_2)_3Cu(BH_3COOEt)$ is indicated by a decrease in frequency separation between terminal and bridging frequencies compared to the case for the BH_4 analogue (270 vs 240 cm^{-1}). The decreased value of the frequency separation between B-H_t and B-H_b in the copper (ethoxycarbonyl)trihydroborate complex may be attributed to the lower negative charge on the B-H hydrogens of $(BH_3COOEt)^-$ due to the inductive effects of the ester group.

A survey of the known structures of metal-BH_4 complexes, reveals that complexes containing bidentate hydroborate groups are most common. An X-ray diffraction investigation (111) on $(Ph_3P)_2Cu(BH_4)$ shows that this is a typical example and Table V shows the agreement between the expected and observed infrared frequencies (147) for the bidentate BH_4 group. Thus, bands at 2385 and 2353 cm^{-1} have been assigned to the terminal B-H_t stretching modes and the bands at 2001 and 1959 cm^{-1} to the B-H_b bridging modes. Table V also summarizes the solid-state infrared spectral bands for various other complexes of the type $L_2Cu(BH_4)$ all of which are thought to contain the bidentate BH_4 groups.

Infrared spectral data (Table V), are also consistent with bidentate coordination of the substituted hydroborates in the complexes $(Ph_3P)_2Cu(BH_3COOR)$, R = Me, Et, H, all of which have very similar spectra. The slightly higher frequency observed for the terminal $B\text{-}H_t$ for the substituted hydroborate complexes compared to the corresponding tetrahydroborate complex (Table V) is attributed to the less negative character of the borane hydrogens in $(Ph_3P)_2Cu(BH_3COOR)$ due to the inductive effects of the ester group.

We now turn to cyanotrihydroborate complexes. Infrared spectral data of the complexes $L_3Cu(BH_3CN)$ (L = Ph_3P, Ph_3As, Ph_3Sb), shown in Table VI, have been interpreted (91) in terms of $Cu\text{-}NCBH_3$ bonding. The C-N stretching frequencies in the complexes are slightly shifted ($\sim$1-13 cm^{-1}) to higher energy (Table VI) compared to the C-N stretching frequency in anionic BH_3CN^-. A similar small shift in the C-N stretching frequency is observed in $LiBH_3CN$ (ν_{CN} = 2198 cm^{-1}) and has also been attributed to a Li-N interaction (148). This is further supported by the infrared spectrum of the compound $(Ph_3P)_3Cu(BPh_3CN)$, where the anion can only coordinate to the copper atom in a monodentate fashion using the nitrogen atom. In this complex, the C-N stretching frequency is seen to be 38 cm^{-1} higher in energy than for the sodium salt of the ligand (Table VI). This large frequency shift has been attributed to increased C-N σ bonding upon complexation. From the similarity of the B-H stretching and BH_2 deformation frequencies in the free and coordinated BH_3CN^- ion (Table VI)

Table IV. Infrared spectral data for monodentate BH_4 and BH_3COOEt coordination.

Complex	Absorption of $B\text{-}H_n$ moieties (cm^{-1}) in monodentate copper(I) hydroborates				Reference
	BH_t terminal	BH_b bridging	Bridge stretch	BH deformation	
*	2450-2300s	2000s		1150-1000s	145
$(MePh_2P)_3Cu(BH_4)$	2335 sh 2315 s	2045		1060 s	89
$(MePh_2P)_3Cu(BH_3COOEt)$	2330 s 2260 sh	2090 s,b		1140-1130s 1045 vs	93
$(MePh_2P)_3Cu(BH_4)$ ($CHCl_3$; 0.04 g/ml)	2345 s 2370 sh 2280 sh 2240 w[a]	2010 s 1970 sh	1370 m	1125 s 1060	89
$(MePh_2P)_3Cu(BH_4)$ ($CHCl_3$; 0.7g/ml)	2370 sh 2300 s	2030 s	1380 vw	1125 m 1060 s	89
$(MePh_2P)_3Cu(BH_3COOEt)$ ($CHCl_3$; 0.04 g/ml)	2340 s	2050 s			93
$(MePh_2P)_3Cu(BH_3COOEt)$ ($CHCl_3$; 0.6 g/ml)	2320 s	2090 s			93

[a] Assigned to an overtone of a BH_2 deformation. Key: vs, very strong; s, strong; sh, shoulder; m, medium; w, weak; b, broad; str, stretch; def, deformation; H_t, terminal H; H_b, bridging H.

* Infrared absorptions expected for monodentate BH_4 groups from the normal coordinate analysis

Table V. Infrared absorptions (cm^{-1}) of bidentate copper(I) hydroborates

Compound	BH_t terminal	BH_b bridging	Bridge stretch	BH deformation	Reference
*	2600-2400 s	2150-1650 s	1500-1300 s,b	1200-1100 s	145
$(Ph_3P)_2Cu(BH_4)$	2385, 2353	2001, 1959		1135	147
$[(\underline{p}\text{-}MeOC_6H_4)_3P]_2Cu(BH_4)$	2385s, 2350sh, 2270 w, sh	2005, 1961			54
$[(\underline{p}\text{-}MeC_6H_4)_3P]_2Cu(BH_4)$	2382s, 2343, 2245w	1990, 1930			54
$[(\underline{m}\text{-}MeC_6H_4)_3P]_2Cu(BH_4)$	2380s, 2343sh, 2240w	2018, 1944			54
$[(MeO)_3P]_2Cu(BH_4)$	2380s, 2345sh	1995s, 1935s	1390m	1135s	90
$(DBP)_2Cu(BH_4)C_6H_6$	2340s	2030m		1065s	55
$(Ph_3P)_2Cu(BH_3COOEt)$	2410s, 2340w	2030s		1145s	92
$(Ph_3P)_2Cu(BH_3COOMe)$	2400s, 2340w	2040s		1135s, 1055s	92
$(Ph_3P)_2Cu(BH_3COOH)$	2410s, 2330w	2030s	1300 s,b	1135s, 1055vs	92
$(Ph_3P)_2Cu(B_3H_8)$	2495s, 2462s, 2418s, 2370w	2010b, 2045b			54
$(Ph_3As)_2Cu(B_3H_8)$	2495s, 2462s, 2418s	2100w, 2000b			54
$K^+BH_3COOEt^-$	2320s			1190	92
KBH_4	2260vs			1110vs	92

*Infrared absorptions for bidentate BH_4 group from the normal coordinate analysis. Key: Same as in Table IV.

it has been suggested that the BH_3CN^- ion approximately retains its C_{3v} symmetry in the $L_3Cu(BH_3CN)$ complexes. Infrared spectral studies of the closely related complexes $L_3Cu(BH_3CN)$, L = DBP, $EtPh_2P$ (Table VI) have also been interpreted as being due to a Cu-N type of interaction (55).

The reader may perhaps have noted that Table VI contains two sets of IR data on the complex of empirical formula $(Ph_3P)_3Cu(BH_3CN)$. There are in fact two complexes which were prepared independently, using slightly different procedures, and which differ considerably in a number of respects, such as melting points, and solubilities in organic solvents. The two complexes also differ significantly in the 2100 cm^{-1} region of their IR spectra, i.e. in the region of the $M\text{-}H_b\text{-}B$ stretching frequency. It is likely therefore that one complex has a Cu-N interaction while the second isomer has a $M\text{-}H_b\text{-}B$ arrangement. The latter is also presumably present in $(DPPE)_{1.5}Cu(BH_3CN)$ (55) which also has a band at 2106 cm^{-1}. Thus a study of the detailed method of bonding of BH_3CN^- in these copper complexes is warranted, preferably by X-ray diffraction, although IR spectroscopy can also provide very useful information.

The crystal structure of the interesting dimeric compound $[(Ph_3P)_2Cu(BH_3CN)]_2$ (121) (Figure 7c, p. 34), shows that each copper atom is bonded to a hydrogen and a nitrogen atom from two different cyanotrihydroborate groups. The infrared spectrum of this compound (Table VI), can be explained on the basis of this structure (91). In contrast to the $L_3Cu(BH_3CN)$ complexes, the B-H stretching mode has shifted to higher frequency and has split into several components, and the terminal BH_2 deformation mode has shifted to lower energy, 1100 cm^{-1}, in $L_2Cu(BH_3CN)$. However, the C-N stretching frequency remains unaltered (2190 cm^{-1}) in both types of complexes. A new absorption at 2200 cm^{-1}, underlying a broad band at ~2207 cm^{-1} is assigned to a Cu-H_b-B stretching vibration. This structure, because of the presence of two slightly different CN groups, also accounts for the two CN stretching bands in the 2200 cm^{-1} region of the IR spectrum.

An X-ray investigation of the complex $(Ph_3P)_2Cu(B_3H_8)$ (149) showed that the compound is a monomeric species in which the copper atom is in a pseudotetrahedral environment and coordinated to two Ph_3P ligands and two hydrogen atoms of the $B_3H_8^-$ group (Figure 9). The infrared spectra (Table V) of the compounds $L_2Cu(B_3H_8)$ (L = Ph_3P, Ph_3As) (54) can be explained on the basis of the above structure. Thus, the bands between 2500 and 2200 cm^{-1} have been assigned to terminal B-H_t vibrations and other bands below the latter frequency to bridging hydrogen atom vibrations.

A ^{31}P NMP study (94) of the above compound, $(Ph_3P)_2Cu(B_3H_8)$, at -120 to -85^o shows an AB pattern with

Table VI. Infrared absorptions (cm^{-1}) for cyanotrihydroborates and cyanophenylborates. (Complexed and free).

Compound	BH terminal	CN	M-H-B	BH deformation	Reference
$(Ph_3P)_3Cu(BH_3CN)$	2358sh, 2330s, 2280m, 2228sh, 2212w,	2192s		1125sh, 1115s	91
	2340s, 2280sh	2185s	2122m	1115s	55
$(Ph_3As)_3Cu(BH_3CN)$	2360sh, 2325s, 2280m, 2222sh, 2202w	2187s		1123sh, 1113s	91
$(Ph_3Sb)_3Cu(BH_3CN)$	2360sh, 2331s, 2285m, 2222sh, 2208w	2191s		1127sh, 1115s	91
$[(Ph_3P)_2Cu(BH_3CN)]_2$	2409sh, 2388sh, 2376s, 2350m	2207s 2190s	2200b	1100vs	91
$(DBP)_3Cu(BH_3CN)$	2350b, 2290sh	2188s		1119s	55
$(EtPh_2P)_3Cu(BH_3CN)$	2336s	2190s		1112s	55
$(DPPE)_{1.5}Cu(BH_3CN)$	2340s, b	2188s	2106w	1116s	55
$NaBH_3CN$	2350sh, 2325s, 2282m, 2230sh, 2220m	2179s		1145sh, 1130s	91
$NaBPh_3CN$		2168s			91

Key: same as in Table IV.

-20.4 and -22.4 ppm and J_{pp} = 91Hz at -100°. This result is consistent with the above solid-state structure (149), as the two phosphorus atoms are magnetically non-equivalent.

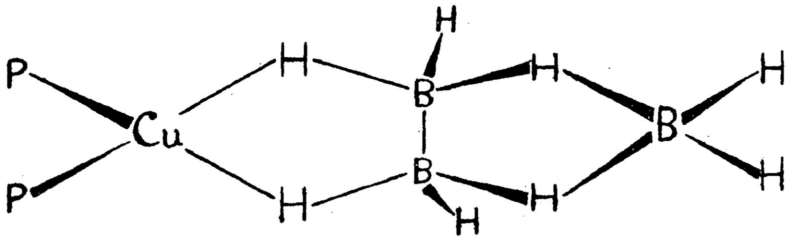

Figure 9

1.6.3. Fluxional studies on copper(I) hydroborate complexes:

Fluxional processes may be defined as rapid, degenerate, intramolecular making and breaking of chemical bonds e.g. intramolecular exchange of bridge and terminal hydrogen atoms in coordinated hydroborate complexes (e.g. see Figure 10).

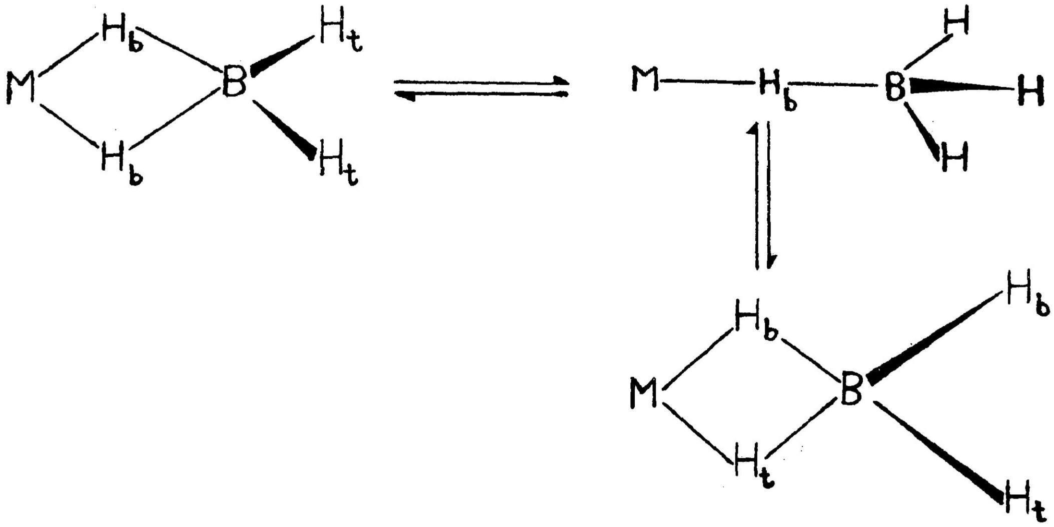

Figure 10

Individual hydrogen environments of the $B_3H_8^-$ group in $(Ph_3P)_2Cu(B_3H_8)$ has been observed with ^1H NMR by slowing down the fluxional behaviour (150). The broad resonance of the B_3H_8 hydrogens with no evident boron-hydrogen coupling in the ^1H NMR spectrum (60MHz) of $(Ph_3P)_2Cu(B_3H_8)$ at 20°C sharpens to a significantly greater degree at -14°C. The resonance of the B_3H_8 hydrogens broaden again at lower temperatures and at -93°C, two broad overlapping resonances are observed. This result clearly indicates the different hydrogen environments of the B_3H_8 group in the complex.

Subsequently it has been observed that the ^1H NMR spectrum (100 MHz) at -90°C consists of five separate resonances. This is consistent with effective thermal decoupling (i.e. washing out of ^{11}B-H coupling, which generally shows a broad featureless quartet at ambient temperatures) and slow intramolecular exchange of the bridged and terminal hydrogen atoms of the $B_3H_8^-$ group in this complex at this temperature.

The above observation is in direct contrast to $Tl(B_3H_8)$, which displays rapid equilibration on the ^1H NMR time scale even at -137°C and sharpening of the peaks due to the B_3H_8 hydrogens has not been observed until ~ -100°C (150).

The other example where the slowing of the fluxional behaviour in copper complexes has been observed is in $[(MeO)_3P]_2Cu(BH_4)$ (90). At ambient temperatures a somewhat broadened quartet has been observed for the hydrogen resonances of BH_4^- (100 MHz). The quartet for BH_4^- hydrogens broadens considerably at lower temperatures (~ -65°C) and collapses to a broad doublet at -95°C. At -128°C the ^1H NMR spectrum consists of a broad singlet which sharpens at about -147°C. At -165°C the resonance collapses to the baseline. The collapse of the BH_4 hydrogen resonance involves the slowing of the fluxional process.

1.6.4. Dissociation of copper(I) hydroborate complexes in solution:

There is an extensive report about the dissociation of copper(I) hydroborates in solution. Thus, the dilute solution ($CHCl_3$) IR spectrum of the tris complex, $(MePh_2P)_3Cu(BH_4)$, consists of doublets in the terminal and bridging B-H regions (Table IV) consistent with a bidentate mode of attachment of the BH_4 group in solution (89). The presence of very small amounts of the monodentate species has been inferred from the observed very weak absorptions at 2300 and 1060 cm^{-1}. Molecular weight measurements indicate extensive dissociation of the complex in benzene (93). From these observations it has been suggested that the second $Cu\text{-}H_b\text{-}B$ bond formation occurs in solution at the expense of one of the originally coordinated $MePh_2P$ ligands. ^{31}P NMR studies of the complex (93) at temperatures of -110 to -70°C in CD_2Cl_2 display one sharp singlet, which moves slightly upfield (from -15.7 to -16.6 ppm) at higher temperatures. This further confirmed that a rapid exchange of free and coordinated phosphine occurs in solution. Similarly, IR solution data (Table IV), conductivity and molecular weight data on the monodentate complex, $(MePh_2P)_3Cu(BH_3COOEt)$, (93) indicate the existence of an equilibrium between singly and doubly bridged species in solution.

The equivalent conductance of this last compound is much higher than for the corresponding tetrahydroborate complex, at comparable concentrations (93). Furthermore, the measurements of the degree of ligand dissociation by osmometric studies show that the BH_4^- complex dissociates to a much greater extent than does the BH_3COOEt^- complex (93). From these observations it has been suggested that the extent of neutral ligand dissociation is affected by the electron density on the coordinating portion of the anion. Thus, BH_3COOEt^- interaction is sufficiently weak (as the boron atom is less negative due to the inductive effect of the ester group) that it does not effect dissociation to the extent that BH_4^- does.

The equivalent conductance of the (ethoxycarbonyl) trihydroborate derivative (93) has been found to increase substantially by addition of excess of phosphine. This result suggests the formation of the monodentate tris (phosphine) complex at higher phosphine concentrations, for which the conductivity is higher.

From a comparative study of equivalent conductivities (which is a function of the ionic dissociation), of Ph_3P complexes of copper(I) with Cl^-, BH_4^-, $B_3H_8^-$ and BH_3CN^-, it has been observed (91) that the relative extent of dissociation of anions appears to be $B_3H_8^- \sim BH_3CN^- > BH_4^- > Cl^-$.

Equilibria such as $L_3MX + L \rightleftharpoons L_4M^+ + X^-$ are not generally important at the temperatures and concentrations available using the vapour pressure osmometric technique. The changes in equilibria in a variety of phosphite and phosphine complexes of tetrahydroborate and (ethoxycarbonyl)-trihydroborate have been observed by using IR and ^1H NMR techniques, upon lowering the temperature of the complex in the presence of an excess of phosphine and phosphite (151). In different equilibria the bidentate and monodentate coordination of the hydroborate groups are distinguished from one another by observing the position and number of peaks in the terminal and bridging stretching region. The changes in concentration with temperature of the two complexes in a given equilibrium have been observed by a gradual change in chemical shift of the borane proton resonance.

These complexes exhibit various equilibria of the type: $L_2MX + L \rightleftharpoons L_3MX$ and $L_3MX + L \rightleftharpoons L_4M^+ + X^-$, which are dependent on temperature, the particular phosphorus-containing ligand, and the hydroborate ligand. The (ethoxycarbonyl)-trihydroborate ligand is completely replaced by a phosphite, even at ambient temperatures, and this has been attributed to the weaker bonding of this trihydroborate grouping compared with the tetrahydroborate grouping. The equilibria for phosphine are observed at higher temperatures than for the corresponding phosphite. This result may reflect the differences in basicity of the ligands as well as equilibria temperature dependence.

1.7. Objectives of the present work:

From the foregoing discussion, it is obvious that reactions of bidentate phosphines with copper(II) salts have not yet been studied to any significant extent. Furthermore, the interaction of hydroborate ions of various types with copper(I) is curious in respect of the stabilities of the species formed and the mode of attachment of the hydroborate grouping. To explore reactions of bidentate phosphines with copper(II) and, overall, to study the reactions of $NaBH_4$ and $NaBH_3CN$ with copper(I) bidentate phosphine complex systems, the present work has centered mainly on the following points:

(A) to study reactions of bidentate phosphines with copper(II) salts;

(B) to study the effect of counter anions (Cl^-, ClO_4^-) upon product types;

(C) to study reactions of $NaBH_4$ and $NaBH_3CN$ with copper(I) bidentate phosphine complexes.

A detailed study of the resulting complexes will be made by using a number of physical techniques in an effort to determine the structures of the products. Of particular interest is to try to determine the mode of attachment of the BH_4 and BH_3CN groups. Thus, the following physical techniques will be used:

i. ^1H NMR and ^{31}P NMR spectral studies to investigate structural features and the behaviour of the resulting complexes in solution.

ii. Infrared spectral studies to characterize the resulting products and to ascertain the mode of attachment of BH_4 and BH_3CN groups.

iii. Molecular weight studies to determine the possible polymeric nature of the copper(I) complexes formed in the above mentioned reactions and to study the solution behaviour of these complexes.

iv. Conductivity studies to determine the ionic type (if any) of the resulting complexes.

These points, and others, form the basis for the remaining discussion of this thesis.

2. EXPERIMENTAL

2.1. Materials:

The reagent grade bidentate phosphines (DPPM, DPPE, cisVPP, transVPP, DPPP, DPPB, DPPPe, DPPH) (Strem Chemical Inc.) were used without further purification. Reagent grade $Cu(ClO_4)_2 \cdot 6H_2O$ (Alfa Division, Ventron Corporation) and $CuCl_2 \cdot 2H_2O$ (BDH Ltd., England) were used as purchased. Reagent grade $NaBH_3CN$ (Aldrich Chemical Company), $NaBH_4$ (Fisher Scientific Company), and $NaBD_4$ (Alfa Division, Ventron Corporation) were used without further purification although to prevent hydrolysis the samples were stored in a desiccator over anhydrous calcium chloride.

Solvents were purified by distillation and degassed with oxygen free dry nitrogen and stored over molecular sieves.

2.2. Analyses and physical measurements:

Air sensitive samples were suitably protected from atmospheric oxidation for analyses and physical measurements.

Infrared spectra of the samples were recorded as Nujol mulls pressed between sodium chloride plates for the 4000 cm^{-1} to 400 cm^{-1} region and between polyethylene plates for the region 600 cm^{-1} to 200 cm^{-1} using a Beckman IR-12 spectrometer (calibrated periodically with a polystyrene reference film). A Bruker WP-80 FT-NMR spectrometer was used for ^{1}H and ^{31}P NMR spectra. All chemical shifts were measured against either tetramethylsilane (TMS) in the ^{1}H or H_3PO_4(85%) in the ^{31}P NMR spectra. In practice H_3PO_4(85%) was not used as the external standard during the recording of routine ^{31}P NMR spectra to avoid saturation of the spectra by H_3PO_4. A sample of $(CD_3)_2CO$ was used in a thin capillary coaxially fitted to the sample tube through a vortex plug as the external lock. Using H_3PO_4 as the sample and $(CD_3)_2CO$ as the external lock, the H_3PO_4 signal was found to be 2920Hz and hence the chemical shifts of the samples were calculated relative to this frequency. The main advantage of this method is that weak signals in samples could be measured. This is important if a sample is only sparingly soluble.

For X-ray powder diffraction measurements, samples sealed in Lindeman capillaries were photographed on a Debye-Scherrer type camera using Ni-filtered copper $K\alpha$ radiation from a Philips PW-1130 X-ray generator. Mass spectra were recorded on a Hitachi-Perkin Elmer RMU-7 double focussing mass spectrometer. Microanalytical data were obtained with a Perkin-Elmer model 240 Elemental Analyzer. The molecular weight determinations were carried out at 25°C in methylene chloride and at 37°C in acetonitrile using a KNAUER vapour pressure osmometer calibrated with benzil. Conductivities were measured on a YSI model 31 conductivity bridge at 25°C at 10^{-2}-10^{-3}M concentrations. Redistilled analytical grade methylene chloride and acetonitrile were used for the conductance measurements.

2.3. Syntheses:

Syntheses were carried out at room temperatures either in a glove box under pure nitrogen or in a hood. Copper(I) bidentate phosphine complexes were prepared by the addition of the phosphines to copper(II) chloride or perchlorate in benzene and ethanol and the reaction mixtures stirred until the reactions were judged to be complete. A mixture of ethanol and benzene was chosen as the solvent medium because the Cu(II) salts are soluble in ethanol and phosphines are soluble in benzene. Reactions of $NaBH_4$ or $NaBH_3CN$ with the resulting copper(I) bidentate phosphine complexes were carried out by the addition of solid or solution of $NaBH_4$/$NaBH_3CN$ in ethanol to the copper(I) phosphine complexes in a mixture of benzene and ethanol (unless otherwise specified). Reaction mixtures were stirred by a magnetic stirrer for periods which varied from 20 minutes to 4 days depending on the rate of the specific reaction. The solid products which were obtained from these reaction mixtures or precipitated by adding n-hexane were isolated by filtration, washed and recrystallized from suitable solvents. Yields were generally high. Unless otherwise specified, the amount of $NaBH_4$/$NaBH_3CN$ used in the reactions amounted to a 2-10M excess over the metal concentrations.

2.4. Bidentate phosphine complexes of copper(I) perchlorate:

2.4.1. $[(L-L)_2Cu]ClO_4$ complexes:

A series of white complexes of the type $[(L-L)_2Cu]ClO_4 \cdot nCH_2Cl_2$ (n=0, L-L=DPPE, DPPP, *cis*VPP; n=1, L-L=DPPB, DPPPe, DPPH) were prepared by reactions of $Cu(ClO_4)_2 \cdot 6H_2O$ (~0.3g, 1.14mM) with the appropriate ligand (in a 4-7M excess) in mixtures of benzene and ethanol (1:1, ~50ml). The reaction mixtures were stirred at room temperature for periods which varied between 20 minutes to 14 hours (see Table VII) before isolation of the products. Solid products were obtained either directly from the reaction mixtures or after the addition of n-hexane (see Table VII) to the colourless reaction solutions, and were collected by filtration and washed successively with ethanol (~30ml), n-hexane (~15ml), benzene (~10ml), and n-hexane (~20ml). The washed products were purified by recrystallization from usually methylene chloride/n-hexane and dried under high vacuum for about 3 hours. Specific preparative conditions and analytical data appear in Table VII.

Table VII. Preparative conditions and analytical data of bidentate phosphine complexes of copper(I) perchlorate

Complex	Preparative conditions		Solid	Analyses[a]	
	L-L/Cu	Time of reaction		C	H
$[(DPPE)_2Cu]ClO_4$	4.2	~40 minutes	b	65.13 (65.06)	4.93 (5.00)
$[(\underline{cis}VPP)_2Cu]ClO_4$	6.8	~ 40 minutes	b	64.89 (65.34)	4.80 (4.60)
$[(DPPP)_2Cu]ClO_4$	6.4	~1 hour	c	65.51 (65.65)	5.36 (5.26)
$[(DPPB)_2Cu]ClO_4 \cdot CH_2Cl_2$	4.1	~1½ hour	b	61.84 (62.18)	5.12 (5.27)
$[(DPPPe)_2Cu]ClO_4 \cdot CH_2Cl_2$	4.4	~1 hour	b	62.83 (62.77)	5.57 (5.49)
$[(DPPH)_2Cu]ClO_4 \cdot CH_2Cl_2$	4.1	~2 hours	b	62.97 (63.32)	5.71 (5.70)
$(DPPM)_3Cu_2(ClO_4)_2$	4.4	~40 minutes	c	60.32 (60.89)	4.43 (4.46)
$(\underline{trans}VPP)_3Cu_2(ClO_4)_2$	5.3	~14 hours	c	61.38 (61.82)	4.36 (4.35)

[a] Calculated values in parenthesis. [b] Solid obtained by adding n-hexane to the reaction solution. [c] Solid obtained directly from the reaction mixture. All samples were recrystallized from methylene chloride/n-hexane except $(\underline{trans}VPP)_3Cu_2(ClO_4)_2$ which was recrystallized from CH_3CN/ether.

2.4.2. $(L\text{-}L)_3Cu_2(ClO_4)_2$ complexes:

Two white complexes of the type $(L\text{-}L)_3Cu_2(ClO_4)_2$ (L-L=DPPM, *trans*VPP) were prepared in the same way as described above by reacting $Cu(ClO_4)_2\cdot 6H_2O$ (~0.4g, 1.5mM) with the appropriate ligand (~5M excess) in benzene and ethanol (1:1, ~50ml). The resulting solid products were collected by filtration from the reaction mixtures after a suitable time interval (see Table VII) and washed successively with ethanol (~20ml), benzene (~10ml) and n-hexane (~10ml). The washed products were purified by recrystallization from suitable solvents (see Table VII) and dried under high vacuum for about 3 hours. Specific preparative details and analytical data appear in Table VII.

2.5. Bidentate phosphine complexes of copper(I) chloride:

2.5.1. $(L\text{-}L)_3Cu_2Cl_2$ complexes:

A series of white complexes of the type $(L\text{-}L)_3Cu_2Cl_2\cdot nCH_2Cl_2$ (n=0, L-L=DPPE, *trans*VPP; n=0.5, L-L=*cis*VPP, DPPP; n=1, L-L=DPPM) were prepared by the reactions of $CuCl_2\cdot 2H_2O$ (~0.35g, 2mM) with the appropriate ligand (in a 6-12M excess) in a mixture of benzene and ethanol (see Table VIII). The reaction mixtures were stirred at room temperatures for periods which varied from 30 minutes to 6 hours depending on the specific reaction. Except for the reaction involving DPPM, solid products were obtained either directly from the reaction mixtures or by adding n-hexane (see Table VIII) to the colourless reaction solutions, collected by filtration and washed with ethanol (~10ml) and n-hexane (~10ml).

The complex $(DPPM)_3Cu_2Cl_2 \cdot CH_2Cl_2$ was obtained by concentrating under vacuum the colourless reaction solution almost to dryness and then dissolving the concentrate in methylene chloride (~30ml) followed by the addition of n-hexane.

The washed products were purified by recrystallization from suitable solvents and dried under high vacuum for about 3 hours. Specific preparative details and analytical data are recorded in Table VIII.

2.5.2. (L-L)CuCl complexes:

A series of white complexes of the type $(L\text{-}L)CuCl \cdot nCH_2Cl_2$ (n=0, L-L=DPPM, DPPPe; n=0.5, L-L=DPPH; n=1, L-L=DPPB) were prepared by the reactions of $CuCl_2 \cdot 2H_2O$ (~0.45g, 2.6mM) with the appropriate ligand (in a 0.6 to 1M excess) in mixtures of benzene and ethanol (see Table VIII). The reaction mixtures were stirred at room temperature for periods which varied between 25 minutes and 6 hours depending on the reaction. Solid products were obtained either directly from the mixtures or by adding n-hexane to the colourless reaction solutions (see Table VIII), collected by filtration and washed with ethanol (~15ml) and n-hexane (~10ml). The washed products were purified by recrystallization from suitable solvents and dried under high vacuum for about 3 hours. Specific preparative conditions and analytical data appear in Table VIII.

The complex [(DPPM)CuCl]$_2$ was isolated from the filtrate left after the isolation of the white solid[described in 2.6.1.(ii)] from the reaction of $NaBH_4$ (0.33g, 8.72mM) with a colourless reaction mixture obtained from $CuCl_2 \cdot 2H_2O$ (0.39g, 2.28mM) and DPPM (1.67g, 4.34mM) in benzene and ethanol (~1:1, ~40ml). Addition of n-hexane to this filtrate precipitated the white product which was collected by filtraction. The product was washed with ethanol (~25ml) and n-hexane (~10ml), recrystallized from methylene chloride/n-hexane and dried under high vacuum for about 3 hours. Analytical data appear in Table VIII.

2.5.3. <u>(DPPE)Cu_2Cl_2</u>

This complex was prepared by the reaction of $CuCl_2 \cdot 2H_2O$ (0.51g, 3mM) with DPPE (1.3g, 3.2mM) in a mixture of benzene and ethanol (~1:3, ~50ml) under a nitrogen atmosphere in a glove box. The reaction mixture was stirred for 40 minutes and the white solid was precipitated by the addition of n-hexane to the colourless reaction solution. The product was purified by successive washings with benzene, n-hexane, methylene chloride, ethanol and n-hexane and dried under high vacuum for about 3 hours. Analytical data appear in Table VIII.

Table VIII. Preparative conditions and analytical data of bidentate phosphine complexes of copper(I) chloride

Complex	Preparative conditions			Solid	Analyses[a]	
	L-L/Cu	Solvents[b]	Time of reactn.		C	H
$(DPPM)_3Cu_2Cl_2 \cdot CH_2Cl_2$	6.2	(~1:1,~40ml)	1 hour	d	65.82 (66.42)	4.89 (4.95)
$(DPPE)_3Cu_2Cl_2$	10.8	(40ml)[c]	2 hours	e	67.17 (67.24)	5.17 (5.31)
$(\underline{trans}VPP)_3Cu_2Cl_2$	8.4	(~1:1,~50ml)	6 hours	e	67.76 (67.53)	4.94 (4.76)
$(\underline{cis}VPP)_3Cu_2Cl_2 \cdot 0.5CH_2Cl_2$	6.7	(~1:1,~60ml)	3 hours	d	66.07 (65.94)	5.07 (4.69)
$(DPPP)_3Cu_2Cl_2 \cdot 0.5CH_2Cl_2$	7.1	(~1:1,~60ml)	1 hour	d	66.07 (66.24)	5.39 (5.35)
$[(DPPM)CuCl]_2$	....	....	....	d	62.33 (62.11)	4.54 (4.55)
(DPPP)CuCl	1.1	(~1:1,~50ml)	30 minutes	d	62.53 (63.40)	5.04 (5.08)
$(DPPB)CuCl \cdot CH_2Cl_2$	1.1	(~1:1,~40ml)	2 hours	e	56.83 (57.05)	5.01 (4.91)
(DPPPe)CuCl	1.1	(~1:1,~50ml)	30 minutes	d	64.99 (64.56)	5.92 (5.56)
$(DPPH)CuCl \cdot 0.5CH_2Cl_2$	1.15	(~1:1,~40ml)	1 hour	d	62.05 (61.46)	5.66 (5.54)
$(DPPE)Cu_2Cl_2$	....	....	....	e	52.73 (52.35)	4.05 (4.02)

... See discussion.

a Calculated values in parenthesis. b Benzene and ethanol except c. c Ethanol only.

d Solid obtained by adding n-hexane to the reaction solution. e Solid obtained directly from the reaction mixture. All samples were recrystallized from methylene chloride/n-hexane except $(DPPE)_3Cu_2Cl_2$ which was recrystallized from benzene/n-hexane.

2.6. Tetrahydroborate complexes of copper(I):

2.6.1. (L-L)Cu(BH_4) complexes:

(i) A series of white complexes of the type (L-L)Cu(BH_4)·nCH_2Cl_2 (n=0, L-L=DPPE, *trans*VPP, DPPB, DPPH; n=0.5, L-L=DPPP, DPPPe) were prepared by the reactions of $NaBH_4$ (6-12M excess) with [(L-L)$_2$Cu]ClO_4·nCH_2Cl_2 (n=0, L-L=DPPE; n=1, L-L=DPPB, DPPPe, DPPH) or (*trans*VPP)$_3$Cu$_2$(ClO_4)$_2$ in benzene and ethanol (~1:1,~60ml). The reaction mixtures were stirred for periods which varied between 2 hours to 4 days depending on the reaction before isolation of the products. White solid products were obtained either directly from the reaction mixtures or by adding n-hexane to the filtered clear solutions, collected by filtration and washed successively with ethanol (~20ml), n-hexane (~10ml), benzene (~15ml) and n-hexane (~10ml). The washed products were purified by recrystallization from methylene chloride/n-hexane and dried under high vacuum for about 3 hours. Analytical data and preparative details are recorded in Table IX.

The same compounds were prepared from the reactions of $NaBH_4$ (3-6M excess) with either (L-L)$_3$Cu$_2$Cl$_2$·nCH_2Cl_2 (L-L=DPPE, *trans*VPP, n=0; n=0.5, L-L=DPPP) or (L-L)CuCl·nCH_2Cl_2 (n=1, L-L=DPPB; n=0, L-L=DPPPe; n=0.5, L-L=DPPH) in benzene and ethanol (~1:1,~60ml). Products were isolated and purified as described above.

(ii) (DPPM)Cu(BH_4)·H_2O

This complex was prepared in a slightly different way than described above. Solid DPPM (1.67g, 4.34mM) was added to a stirred solution of $CuCl_2 \cdot 2H_2O$ (0.39g, 2.28mM) in benzene and ethanol (~1:1,~60ml). The mixture was stirred for 20 minutes, producing a clear colourless solution. Solid $NaBH_4$ (0.33g, 8.72mM) was added slowly (~5 minutes) to the resulting clear solution and the mixture was stirred for three hours. The resulting white solid was collected by filtration and washed successively with water (~10ml), ethanol (~10ml), benzene (~10ml) and n-hexane (~10ml). The product was recrystallized from methylene chloride/n-hexane and dried under high vacuum for about 3 hours. Analytical data are recorded in Table IX.

(iii) $\underline{(DPPM)Cu(BH_4) \cdot 0.5CH_2Cl_2}$

This complex was prepared by repeated recrystallization of $(DPPM)Cu(BH_4) \cdot H_2O$ from methylene chloride/n-hexane and dried under high vacuum for about 3 hours. Analytical data are recorded in Table IX.

2.6.2. $\underline{[(DPPM)_2Cu_2(BH_4)]ClO_4}$

Solid DPPM (1.82g, 4.74mM) was added to a stirred green solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.6g, 2.28mM) in benzene and ethanol (~1:1,~30ml) and the mixture was stirred for an additional 20 minutes. Solid $NaBH_4$ (0.24g, 6.34mM) was then added slowly (~10 minutes) to the resulting colourless reaction mixture and the mixture was then stirred for 1 hour. The resulting white solid was collected by filtration and washed

Table IX. Preparative conditions and analytical data of tetrahydroborate complexes of copper(I).

Complex	Reactants^d	(Wt. of Cu complex; M $NaBH_4$)	Time of react^n.	Solid	Analyses^a	
					C	H
$(DPPM)Cu(BH_4)\cdot H_2O$	....	....	......	.....	62.58 (62.45)	5.46 (5.82)
$(DPPM)Cu(BH_4)\cdot 0.5CH_2Cl_2$	....	....	......	.....	60.59 (60.61)	5.02 (5.34)
$(DPPE)Cu(BH_4)$	A + $NaBH_4$	(1.2g; 12M excess)	4 days	b	64.89 (65.49)	5.80 (5.87)
	B + $NaBH_4$	(1.4g; 6M excess)	12 hours	b		
(<u>trans</u>VPP)$Cu(BH_4)$	C + $NaBH_4$	(0.58g; 6M excess)	2 hours	c	65.95 (65.77)	5.71 (5.48)
	B + $NaBH_4$	(0.42g; 5M excess)	3 hours	c		
$(DPPP)Cu(BH_4)\cdot 0.5CH_2Cl_2$	B + $NaBH_4$	(1.1g; 5M excess)	12 hours	c	63.22 (61.93)	6.08 (5.81)
$(DPPB)Cu(BH_4)$	A + $NaBH_4$	(1.3g; 8M excess)	2 days	c	65.26 (66.62)	6.40 (6.34)
	D + $NaBH_4$	(0.67g; 3M excess)	12 hours	c		
$(DPPPe)Cu(BH_4)\cdot 0.5CH_2Cl_2$	A + $NaBH_4$	(1.3g; 7M excess)	2 hours	c	63.31 (63.12)	6.50 (6.24)
	D + $NaBH_4$	(0.51g; 3M excess)	2 hours	c		
$(DPPH)Cu(BH_4)$	A + $NaBH_4$	(1.3g; 8M excess)	4 hours	c	67.12 (67.67)	6.94 (6.76)
	D + $NaBH_4$	(0.9g; 4.5M excess)	12 hours	c		
$[(DPPM)_2Cu_2(BH_4)]ClO_4$	....	....	......	.....	59.33 (59.44)	4.93 (4.75)

a Calculated values in parenthesis. b Solid obtained by adding n-hexane to the reaction solution. c Obtained directly from the reaction mixture.
d A= $[(L\text{-}L)_2Cu]ClO_4\cdot nCH_2Cl_2$ B= $(L\text{-}L)_3Cu_2Cl_2\cdot nCH_2Cl_2$ C= $(L\text{-}L)_3Cu_2(ClO_4)_2$
D= $(L\text{-}L)CuCl\cdot nCH_2Cl_2$. A, B, C and D were recrystallized compounds.
... See discussion.

successively with ethanol (~10ml), acetone (~10ml) and n-hexane (~10ml) and dried under high vacuum for about 3 hours. The complex is insoluble in DMF, DMSO, THF, MeCN, CH_2Cl_2 and $CHCl_3$ and therefore recrystallization was not possible.

2.7 Formation of a probable copper(I) hydride complex:

A suspension of $NaBH_4$ (0.21g, 5.55mM) in ethanol (~5ml) was slowly added (~10 minutes) to a stirred suspension of Cu_2Cl_2DPPE (1.3g, 2.18mM) in benzene and ethanol (1:1, ~50ml) under a nitrogen atmosphere in a glove box. The reaction mixture was stirred for an additional 20 minutes producing a red solution. The solution was filtered and when n-hexane was added to the filtrate a yellow solid was precipitated. The yellow solid was immediately filtered off and recrystallized three times from benzene/n-hexane, before being dried under reduced pressure. Recrystallization of the yellow powder from a mixture of benzene and toluene produced red crystals.

Analyses: Found C 53.64, H 4.61

2.8. Cyanotrihydroborate complexes of copper(I):

2.8.1. (L-L)Cu(BH_3CN) complexes:

(i) Complexes of the type (L-L)Cu(BH_3CN) (L-L=DPPM, DPPPE, DPPH) were prepared from the reactions of $NaBH_3CN$ (4-6M excess) with $[(L\text{-}L)_2Cu]ClO_4 \cdot CH_2Cl_2$ (L-L=DPPPe, DPPH and $(DPPM)_3Cu_2(ClO_4)_2$ in benzene and ethanol (~1:1, ~60ml).

The reaction mixtures were stirred for about 2 hours before collection of the products. White solids produced in the reaction mixtures or precipitated by adding n-hexane to the reaction solutions were collected by filtration and washed successively with ethanol (~15ml), n-hexane (~10ml), benzene (~10ml) and n-hexane (~10ml). The products were purified by recrystallization from suitable solvents and dried under high vacuum for about 3 hours. Specific preparative details and analytical data appear in Table X.

The same compounds for the ligands DPPPe and DPPH were also prepared from the reactions of $NaBH_3CN$ (3M excess) with $(L\text{-}L)CuCl{\cdot}nCH_2Cl_2$ (n=0, L-L=DPPPe; n=0.5, L-L=DPPH) in benzene and ethanol (~1:1, ~ 60ml). The products were isolated and purified as described above

(ii) The complex $(DPPM)Cu(BH_3CN)$, which has the same empirical formula but which is different in many respects (see later) from the isomer reported above, was prepared as follows. Solid DPPM (1.75g, 4.5mM) was added to $CuCl_2{\cdot}2H_2O$ (0.4g, 2.3mM) in benzene and ethanol (1:1, ~ 40ml) and the mixture was stirred for 30 minutes. Solid $NaBH_3CN$ (0.65g, 10.34mM) was then added slowly (~10 minutes) to the resulting colourless solution and the mixture was stirred for 2 hours. A white solid was precipitated by adding n-hexane (~20ml) to the reaction solution and was collected by filtration. The product was washed with ethanol (~ 10ml) and n-hexane (~10ml) and purified by recrystallization from methylene chloride/n-hexane and dried under high vacuum for about 3 hours. Analytical data appear in Table X.

The complex (DPPE)Cu(BH_3CN) was prepared in the same way as above. Solid DPPE (1.35g, 3.4mM) was added to $CuCl_2 \cdot 2H_2O$ (0.37g, 2.1mM) in benzene and ethanol (1:1, ~40ml) and the mixture was stirred for 40 minutes. Solid $NaBH_3CN$ (0.31g, 4.93mM) was then added slowly (~10minutes) to the colourless reaction solution and the mixture was stirred for 40 minutes. The resulting white solid was collected from the reaction mixture by filtration and washed successively with ethanol (~10ml), benzene (~10ml) and n-hexane (~10ml). The washed product was recrystallized from methylene chloride/ n-hexane and dried under high vacuum for about 3 hours. Analytical data appear in Table X.

2.8.2. $(L\text{-}L)_3Cu_2(BH_3CN)_2$ complexes:

(i) White cyanotrihydroborate complexes of the type $(L\text{-}L)_3Cu_2(BH_3CN)_2 \cdot CH_2Cl_2$ (n=0, L-L=DPPP, transVPP; n=0.5, L-L=cisVPP) were prepared from reactions of $NaBH_3CN$ (~4M excess) with $(L\text{-}L)_3Cu_2Cl_2 \cdot nCH_2Cl_2$ (n=0.5, L-L=DPPP, cisVPP; n=0, L-L=transVPP) in benzene and ethanol (~1:1, ~ 50ml). The reaction mixtures were stirred for about 6 hours. White solids which were obtained either directly from the reaction mixtures or by adding n-hexane to the reaction solutions were collected by filtration and washed thoroughly with ethanol (~15ml) and n-hexane (~10ml). The products were purified by recrystallization from methylene chloride/n-hexane and dried under high vacuum for about 3 hours. Analytical data and specific reaction conditions are recorded in Table X.

The same compounds for the ligands cisVPP and transVPP were prepared from the reactions of $NaBH_3CN$ (~7M excess) with $[(L\text{-}L)_2Cu]ClO_4$ (L-L=DPPP, cisVPP) and $(transVPP)_3Cu_2(ClO_4)_2$ in benzene and ethanol (~1:1, ~40ml). Products were isolated and purified as described above.

(ii) The complex $(DPPB)_3Cu_2(BH_3CN)_2 \cdot CHCl_3$ was prepared from the reaction of $NaBH_3CN$ (0.42g, 6.6mM) with $[(DPPB)_2Cu]ClO_4 \cdot CH_2Cl_2$ (0.81g, 0.7mM) benzene and ethanol (1:1, ~50ml). The reaction mixture was stirred over night and a white solid was produced. This was filtered off, washed with ethanol (~10ml) and n-hexane (~10ml), recrystallized from chloroform and n-hexane and dried under high vacuum for about 3 hours. Analytical data appear in Table X.

(iii) The complex $(DPPE)_3Cu_2(BH_3CN)_2$ was prepared in a slightly different procedure from that described above. An excess of phosphine (2.5g, 6.3mM) was added to a stirred solution of $CuCl_2 \cdot 2H_2O$ (0.12g, 0.7mM) in benzene and ethanol (~1:9, ~40ml) and the mixture was stirred for an additional 4 hours. Solid $NaBH_3CN$ (0.42g, 6.6mM) was then added slowly (~10 minutes) to the resulting colourless reaction mixture and the mixture was stirred for about 8 hours. The white solid which was produced was filtered off and washed with ethanol (~10ml) and n-hexane (~10ml). The product was purified by recrystallization from chloroform and n-hexane and dried under high vacuum for about 3 hours.

The complex was also prepared from the reaction of $NaBH_3CN$ (0.45g, 7.1mM) with $[(DPPE)_2Cu]ClO_4$ (0.62g, 0.64mM) in benzene and ethanol (1:2, ~40ml). The reaction mixture was stirred for about 6 hours before isolation of the product. The product was collected and purified as described above. Analytical data appear in Table X.

2.8.3. $[(\underline{cis}\ VPP)_2Cu](BH_3CN)$

*cis*VPP (2.4g, 6mM) was added to $CuCl_2 \cdot 2H_2O$ (0.14g, 0.8mM) in benzene and ethanol (~1:1, ~30ml) and the mixture was stirred for about 6 hours. $NaBH_3CN$ (0.33g, 5.25mM) was then added to this reaction mixture and the mixture was stirred for 6 hours. The resulting solution was concentrated (to ~20ml) and then n-hexane was added to this concentrate precipitating a white solid. This was collected by filtration and washed successively with ethanol (~10ml), n-hexane (~10ml), benzene (~10ml) and n-hexane (~10ml). The product was purified by recrystallization from acetone and n-hexane and dried under high vacuum for about 3 hours. Analytical data appear in Table X.

Table X. Preparative conditions and analytical data of cyanotrihydroborate complexes of copper(I)

	Preparative conditions				Analyses[a]		
Complex	Reactants[b]	(Copper complex; M $NaBH_3CN$)	Time of react^n.	Solid	N	C	H
$[(DPPM)Cu(BH_3CN)]_2$	B + $NaBH_3CN$	(1.6g; 5M excess)	2 hours	c	2.35 (2.87)	63.51 (64.02)	4.96 (5.13)
$(DPPM)Cu(BH_3CN)$	....	....	....	.....	2.76 (2.87)	63.61 (64.02)	4.98 (5.13)
$(DPPH)Cu(BH_3CN)$	A + $NaBH_3CN$ E + $NaBH_3CN$	(1.2g; 6M excess) (0.6g; 3M excess)	2 hours 6 hours	d d	2.46 (2.51)	67.07 (66.74)	6.25 (6.27)
$(DPPPe)Cu(BH_3CN)$	A + $NaBH_3CN$ E + $NaBH_3CN$	(1.1g; 4M excess) (0.51g; 2M excess)	2 hours 3 hours	c c	2.92 (2.57)	66.96 (66.25)	6.09 (6.07)
$(DPPE)Cu(BH_3CN)$	....	....	....	.....	2.57 (2.79)	64.74 (64.62)	5.48 (5.38)
$(DPPE)_3Cu_2(BH_3CN)_2$	A + $NaBH_3CN$	(1.0g; 11M excess)	6 hours	d	1.68 (1.99)	67.44 (68.53)	5.47 (5.56)
$(DPPP)_3Cu_2(BH_3CN)_2$	D + $NaBH_3CN$	(0.61g; 3.5M excess)	6 hours	c	2.12 (1.94)	69.27 (69.03)	6.03 (5.82)
$(DPPB)_3Cu_2(BH_3CN)_2 \cdot CHCl_3$	A + $NaBH_3CN$	(0.9g; 9M excess)	Over night	d	1.59 (1.74)	65.27 (65.08)	5.69 (5.67)
(<u>trans</u>VPP)$_3Cu_2(BH_3CN)_2$	B + $NaBH_3CN$ D + $NaBH_3CN$	(1.2g; 5M excess) (0.98g; 4M excess)	4 hours 6 hours	d d	2.13 (2.00)	68.80 (68.83)	4.94 (5.16)
(<u>cis</u>VPP)$_3Cu_2(BH_3CN)_2 \cdot CH_2Cl_2$	A + $NaBH_3CN$ D + $NaBH_3CN$	(0.7g; 6M excess) (0.62g; 3M excess)	2 hours Over night	c c	2.22 (1.89)	65.20 (65.69)	5.42 (5.00)
[(<u>cis</u>VPP)$_2$Cu](BH_3CN)	....	....	....	.....	1.63 (1.56)	70.51 (71.03)	5.27 (5.24)

Continued....

Table X. Continued.

a Calculated values in parenthesis. b A=[(L-L)$_2$Cu]ClO$_4$·nCH$_2$Cl$_2$, B=(L-L)$_3$Cu$_2$(ClO$_4$)$_2$, E=(L-L)CuCl, D=(L-L)$_3$Cu$_2$Cl$_2$·nCH$_2$Cl$_2$; A, B, C and D were recrystallized products. c Solid obtained by adding n-hexane to the reaction solution.

d Solid obtained in the reaction mixture. All complexes were recrystallized from methylene chloride/n-hexane except (DPPB)$_3$Cu$_2$(BH$_3$CN)·CHCl$_3$ which was recrystallized from CHCl$_3$/n-hexane. The compound (DPPH)Cu(BH$_3$CN) was the washed product.

.... See discussion.

3. RESULTS AND DISCUSSION

3.1 General:

Copper(I) chloride or perchlorate complexes were prepared from reactions of copper(II) chloride or perchlorate with a series of bidentate phosphines in benzene and ethanol at room temperatures. The products of these reactions were then treated with either $NaBH_4$ or $NaBH_3CN$. The compounds which have been isolated from all these reactions are summarized in Table XI - from which it is clear that several different types of complexes have been obtained having phosphine: Cu ratios of 1:1, 3:2, and 2:1. Further, complexes containing coordinated BH_4^- and BH_3CN^- groups have been obtained.

Regarding reactions between copper(II) chloride or perchlorate with the phosphines, reduction of Cu(II) to Cu(I) occurs most readily in mixtures of benzene and ethanol although the rate of reduction and product type depend on the type of phosphine and the nature of the counter anion. The known complexes $[(DPPM)CuCl]_2$, $(DPPE)_3Cu_2Cl_2$, and $(DPPE)Cu_2Cl_2$(50,122) were obtained in these studies by different procedures from those described in the literature, which involved direct interactions of phosphines and copper(I) chloride (50,122).

The tetrahydroborate and cyanotrihydroborate complexes were generally prepared from reactions of $NaBH_4$ and $NaBH_3CN$ with the copper(I) complexes discussed above, although the known complex $(DPPE)_3Cu_2(BH_3CN)_2$ (prepared in ethanol)(55) was prepared by a slightly different procedure (prepared in benzene and ethanol) and appears to have different properties (see later) from the complex with this formulation reported earlier (55). Reactions of $NaBH_4$ with (L-L)CuCl (L-L=DPPPe,DPPH) complexes produce trace amounts of a black solid which contaminates the main (L-L)Cu(BH_4) products. The filtrates obtained after isloation of the latter complexes were sometimes yellowish, but so far no compound has been isolated from these filtrates, nor could the black product be identified, although it can be separated from the main BH_4 complexes when they are recrystallized. It is probably formed by the decomposition of a small amount of the Cu(I)-tetrahydroborate complex (it is known that various metal salts are reduced to the corresponding metal borides, reference 160) in the presence of an excess of $NaBH_4$ or, more likely is formed by reduction of Cu(I) to Cu(0).

The complexes listed in Table XI are white and stable in air for indefinite periods. The complexes almost always retain solvent molecules, especially methylene chloride but also water, during crystallization and these molecules are sometimes difficult to remove even when the complexes are kept for prolonged periods under high vacuum. The presence of solvent was confirmed in each case by mass spectrometry. The crude complexes generally showed the presence of considerable quantities of water which could be removed by repeated recrystallization. The removal, or even partial removal of water (from a DPPM complex) was accompanied by marked changes in the IR spectrum, especially in the region of hydroborate absorptions and may indicate that the water may actually occupy coordination sites.

Considerable difficulties were encountered in obtaining reasonable elemental analyses especially with cyanotrihydroborate complexes and this might be connected with varying amounts of solvent.

The physical and chemical properties of the complexes will now be discussed and for convenience, the discussion is organized according to the type of complex formed. It is necessary to mention here that positive chemical shifts in the NMR spectral data are downfield and negative data are upfield with respect to 85% H_3PO_4 in ^{31}P spectra and to TMS in ^{1}H spectra respectively. All ^{31}P NMR spectral data reported in these studies are proton decoupled and all NMR spectra were recorded at room temperatures.

Table XI. Copper(I) complexes

Phosphine (P)	From $CuCl_2$	From $Cu(ClO_4)_2$	[a]From $NaBH_4$	[a]From $NaBH_3CN$
DPPM	$P_3Cu_2Cl_2.CH_2Cl_2$ [d]$(PCuCl)_2$	$P_3Cu_2(ClO_4)_2$	[b]$PCu(BH_4).H_2O$ [b]$PCu(BH_4).0.5CH_2Cl_2$ [c]$[P_2Cu_2(BH_4)](ClO_4)$	[b]$PCu(BH_3CN)$ [c]$[PCu(BH_3CN)]_2$
DPPE	[d]$P_3Cu_2Cl_2$ [d]PCu_2Cl_2	$[P_2Cu]ClO_4$	$PCu(BH_4)$	[d]$P_3Cu_2(BH_3CN)_2$ [b]$PCu(BH_3CN)$
trans VPP	$P_3Cu_2Cl_2$	$P_3Cu_2(ClO_4)_2$	$PCu(BH_4)$	$P_3Cu_2(BH_3CN)_2$
cis VPP	$P_3Cu_2Cl_2.0.5CH_2Cl_2$	$[P_2Cu]ClO_4$	No products	$P_3Cu_2(BH_3CN)_2.CH_2Cl_2$ [b]$[P_2Cu]BH_3CN$
DPPP	$P_3Cu_2Cl_2.0.5CH_2Cl_2$ $PCuCl$	$[P_2Cu]ClO_4$	[b]$PCu(BH_4).0.5CH_2Cl_2$ [c]No products	$P_3Cu_2(BH_3CN)_2$
DPPB	$PCuCl.CH_2Cl_2$	$[P_2Cu]ClO_4.CH_2Cl_2$	$PCu(BH_4)$	[c]$P_3Cu_2(BH_3CN)_2.CHCl_3$
DPPPe	$PCuCl$	$[P_2Cu]ClO_4.CH_2Cl_2$	$PCu(BH_4).0.5CH_2Cl_2$	$PCu(BH_3CN)$
DPPH	$PCuCl.0.5CH_2Cl_2$	$[P_2Cu]ClO_4.CH_2Cl_2$	$PCu(BH_4)$	$PCu(BH_3CN)$

a- Products obtained from both copper(I) chloride and copper(I) perchlorate complex systems unless otherwise specified.

b- From chloride. c- From perchlorate. d-Known compounds $(DPPE)_3Cu_2Cl_2$, $(DPPE)Cu_2Cl_2$, $(DPPM)CuCl$, (50,122); $(DPPE)_3Cu_2(BH_3CN)_2$, (55)

3.2 Copper(I) chloride complexes:

3.2.1 (L-L)CuCl complexes:

As seen in Table XI, complexes of this type are formed for L-L = DPPM, DPPP, DPPB, DPPPe and DPPH. ^{31}P NMR, ^{1}H NMR, conductivity, infrared and molecular weight data of representative complexes are presented in Table XII. Some actual ^{31}P NMR spectra are shown in figure 12.

The molecular weight in CH_2Cl_2 of one of these complexes, (DPPM)CuCl was found to be 1015 from which it is clear that the complex is dimeric. The same complex was found to be essentially a non-electrolyte in CH_2Cl_2(the equivalent conductivity does not increase above 5.6ohm^{-1}cm^{2}equiv $^{-1}$). So the chlorides of this complex do not apparently dissociate in this solvent.

Far infrared spectra (450-200 cm^{-1}) of all the complexes of this type do not show any absorption above 200cm^{-1} which may reasonably be assigned to Cu(I)-Cl stretching vibrations. This absence probably reflects the fact that the chlorides in these complexes are in bridging rather than in terminal positions, and would be consistent with dimeric structures as already indicated for the DPPM complex. Some support for this interpretation comes from an analysis of the far infrared spectrum of the complex $[(C_3H_2S_3)_2CuCl]_2$, where the absence of similar bands above 200cm^{-1} has been explained by suggesting that the chlorides are also in bridging positions (153).

The ^{1}H NMR spectrum of one of these compounds, $[(DPPM)CuCl]_2$ (in $CDCl_3$) exhibits a broad peak at +3.15 ppm for the methylene protons of DPPM at a position which is slightly downfield with respect to those found in the uncoordinated ligand (+2.97 ppm, CD_3COCD_3). The slight shift and the observation of a single peak might indicate that the ligand remains coordinated in solution and that there is only one type of ligand attachment. No fine structure was observed.

The ^{31}P NMR spectrum (CH_2Cl_2) of the DPPM complex (Figure 12) exhibits a singlet at -7.7 ppm and a very weak peak at -15.4 ppm. The latter is probably due to a trace amount of an impurity. The signal at -7.7 ppm is almost certainly an indication of the equivalence of the phosphorus atoms of the ligands. The ^{31}P NMR spectra of the DPPP, DPPPe and DPPH complexes of this same type exhibit a sharp singlet which can also be interpreted as being due to the equivalence of the phosphorus atoms in these molecules as would be expected from tetrahedral or trigonal Cu(I). The fact that the signals are sharp with no splitting may alternatively indicate that some exchange process occurs. A single sharp peak in the ^{31}P NMR spectrum (CD_2Cl_2) of the compound $(MePh_2P)_3Cu(BH_4)$ has been explained in terms of equivalence of the phosphines as well as to rapid exchange of phosphines on the overall structure (93).

In summary it therefore appears from IR, ^{31}P, molecular weight and conductivity data that this related group of compounds having the same metal: phosphine stoichiometry are probably all chloride bridged dimers with chelating phosphines and tetrahedrally coordinated copper as shown in figure 11.

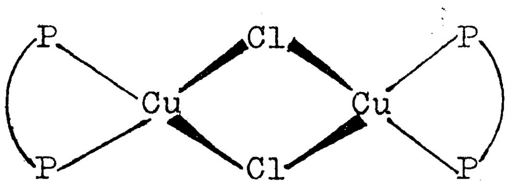

Figure 11

Turning now to chemical shift studies, coordination chemical shift, $\triangle$, may be defined as the difference between the chemical shift of the coordinated and free phosphines. It is interesting to note that the coordination shift for the chelated phosphines in these complexes are small and depend to a large extent on the size of the chelate ring (see Table XII). Thus, the four-membered chelate ring in $[(DPPM)CuCl]_2$ experiences a much larger coordination shift (Δ = +15.9) than for example, in a six-membered chelate ring in (DPPP)CuCl (Δ =+2.5). Five membered rings (strain free) commonly exhibit a larger value for Δ than a four-or six-membered rings (154). As in the present studies, no complexes containing a five-membered chelate ring of the (L-L)CuCl type could be isolated, it is not possible to compare the value of four-membered chelate ring in $[(DPPM)$-$CuCl]_2$ with a five-membered value. In view of the current interest in coordination chemical shifts and ring size effects (162), the shifts obtained in the complexes obtained in this exploratory study would merit further investigation in any extension of this work.

3.2.2 $(L-L)_3Cu_2Cl_2$ complexes:

These complexes (with L-L=DPPM, DPPE, DPPP, trans-VPP, cis VPP, see Table XI) are generally formed from reactions where a larger excess [than required for the formation of the (L-L)CuCl complexes] of phosphine has been used. Complexes of this type have been obtained only with those phosphines having bridging tendencies e.g. DPPM, DPPE and do not appear to be formed with long chain bis phosphines e.g. DPPPe,DPPH. The complex $(DPPM)_3Cu_2Cl_2$ could not be precipitated from the reaction mixture (benzene and ethanol) and was isolated by dissolving the concentrate of the reaction mixture in methylene chloride followed by the addition of n-hexane. The other complexes of this type however, are precipitated directly from the reaction mixture. The ^{31}P NMR, and some ^{1}H NMR, infrared, conductivity, and molecular weight data of these complexes (representative) appear in Table XII. Some actual ^{31}P NMR spectra are shown in figure 12.

The known compound $(DPPE)_3Cu_2Cl_2.2(Me_2CO)$ (122) is very significant in this group because its crystal structure is known and shown in figure 7d, page 34. Thus one of the DPPE ligands bridges two copper atoms each of which is also bound to a chelating DPPE and a chloride (122). Thus, in contrast to the $[(L-L)CuCl]_2$ complexes, the terminal Cu-Cl stretching frequency in the above structure is clearly visible at 248 cm^{-1} (see Table XII) in the far infrared spectrum. The related complexes with DPPM and DPPP all show strong peaks in the 262-235 cm^{-1} region which have been assigned to the terminal Cu(I)-Cl stretching frequency. For a similar complex $(DPPA)_3Cu_2Cl_2$ a strong band at 267 cm^{-1} has also been assigned to the terminal Cu(I)-Cl stretching frequency (49). However, in the complex (<u>cis</u> VPP)$_3$-$Cu_2Cl_2.0.5CH_2Cl_2$ no absorption occurs in the 300-200 cm^{-1} region. It was also not possible to assign any ionic Cu(I)-Cl stretching frequency due to ligand vibrations at about 325 cm^{-1}.

If the known solid state structure of $(DPPE)_3Cu_2Cl_2$ is retained in solution, the ^{31}P NMR spectrum should show two signals of different chemical shifts and superficially, one would expect a ratio of the areas under the two peaks of 2:1 due to the two different types of phosphine present. In fact the ^{31}P NMR spectrum (C_6H_6) of this compound does display (Figure 12) two signals-one very broad peak centered at -11.6 ppm and a second weak peak at +29.1 ppm. However, the ratio between the area of the peaks is not as expected. Furthermore, the ratio varies with the concentration of the sample and with the solvent. This behaviour is however not unexpected since magnetically different phosphorus nuclei will experience different nuclear Overhauser effects (NOE) and therefore will give different intensities from those predicted just as do magnetically different carbon atoms in ^{13}C spectra. In general ^{13}C NMR spectra cannot be integrated at all for this reason since even small changes in environment cause very large deviations from the intensity which would be predicted if NOE effects were the same for all C atoms. While the effects are less extreme in ^{31}P NMR spectra than in ^{13}C NMR spectra, considerable care has to be taken to record ^{31}P NMR spectra in which the integrations are reliable.

The ^{31}P NMR spectra of the similar complexes with DPPM, DPPP, and cis VPP also exhibit two signals -one generally in the upfield region and the other generally downfield (see Table XII). As in the case of DPPE, discussed above, integration of the two peaks in these other cases generally give values which were not in the expected ratio, although in the case of the DPPM complex, the upfield peak is seen to be almost twice the area than the downfield peak.

Considering other factors of those spectra, in the case of the DPPM complex the downfield resonance appears to be resolved into the expected triplet (J= 40Hz, in CH_2Cl_2) (arising from coupling of the bridging and chelating P atoms), with the outer two peaks being of very low intensity. As mentioned above, the spectrum varies, even in the same solvent (CH_2Cl_2), although in all cases two signals occur in the same position. Conductivity studies (CH_2Cl_2) of the

DPPM complex (see Table XII) indicate that a little ionic dissociation also occurs in solution.

The ^{31}P NMR spectrum of (cis VPP)$_3$Cu$_2$Cl$_2$.0.5CH$_2$Cl$_2$ also displays a very broad unresolved peak centered at +9.3 ppm and a sharp peak superimposed on this at +20.1ppm although, as usual, the peaks are not in a 2:1 ratio. However, bearing in mind the known solid state structure of (DPPE)$_3$Cu$_2$Cl$_2$, the fact that the ^{31}P NMR spectra of all these complexes (DPPM, DPPP, cis VPP) show two signals may be considered reasonable evidence for the presence of both bridging and chelating phosphines in the molecules.

The signals due to the chelating phosphines in the ^{31}P NMR spectra of complexes of the type (L-L)CuCl already discussed appear in the upfield region. Thus, by analogy, the upfield peak in the complexes of the type (L-L)$_3$Cu$_2$Cl$_2$ may be considered to be due to the chelating phosphines and this is supported by the fact that it is the larger area peak which occurs in this region for those phosphines.

Considering ^1H NMR spectra, one would expect that the methylene protons of the bridging phosphines might have different chemical shifts from those of the chelating phosphines at least for the shorter chain systems. There is literature precedent for this and, for example, the ^1H NMR spectrum of (CO)$_2$(DPPM)$_2$MoI$_2$ shows a triplet centered at +5.23 ppm (^{J}PH = 11Hz) and a broad singlet at +4.61 ppm assigned to the methylene protons of the chelating and monodentate bridging DPPM ligands respectively (155). Thus, the two signals for the two different DPPM ligands occur at considerably different chemical shifts in the spectrum of the above complex.

Accordingly, the ^1H NMR spectra of the complexes $(L-L)_3Cu_2Cl_2$ (L-L =DPPM, DPPP) have been carefully examined in the region of the CH_2 absorption. The spectrum of $(DPPM)_3$-$Cu_2Cl_2.CH_2Cl_2$ (in C_6D_6) clearly shows two broad signals for the methylene protons of the different DPPM ligands. One signal at +3.87 ppm may be assigned to the chelating and the one at +3.32 ppm to the bridging DPPM methylene protons respectively by analogy with the DPPM-Mo complex discussed above. The ratio between the areas of the two peaks is difficult to estimate exactly because of the presence of a partially overlapping well defined triplet (1:2:1) centered at +3.62 ppm (J=14Hz). This is possibly due to solution dissociation of the complex and some subsequent reactions. On the other hand, the CH_2 protons of DPPP in $(DPPP)_3Cu_2Cl_2$-$.0.5CH_2Cl_2$ appear as a broad featureless signal slightly downfield with respect to the free phosphine signal. This is not unexpected because even without dissociation the bridged and chelated dimeric copper(I) chloride system in this case would contain four different types of CH_2 group all with similar chemical shifts and extensive coupling with phosphorus and with each other. Considerable signal overlap would therefore be expected to lead to the broad featureless signal observed.

Thus, from the available data the complexes discussed above may be viewed (albeit tentatively bearing in mind the poorly defined spectra) as having a structure like that of $(DPPE)_3Cu_2Cl_2$(122) with each copper atom being tetrahedrally coordinated by three phosphorus atoms, (two from a chelating and one from a bridging phosphine) and one chloride ion. In such a structure with three phosphorus atoms and one chloride around each copper atom a single Cu(I)-Cl stretching frequency is expected.

There is one complex with this ligand to metal to chloride ratio recorded in Table XII which does not fit this generalization. Thus although the complex using *trans*-VPP as the ligand shows in its far infrared spectrum a strong band at 237 cm^{-1} which has been assigned to the terminal Cu(I)-Cl stretching frequency, (another band of comparatively low intensity at 277 cm^{-1} is suspected to be due to a ligand vibration) the ^{31}P NMR spectrum of the compound is different from those of the others in that it exhibits only a single very broad resonance centered at -8 ppm - the position for the free ligand. This might be due to some exchange process or dissociation of the phosphine in solution or it might indeed be characteristic of a stable complex where the trans geometry of the ligand would inhibit chelation.

On the basis of IR and ^{31}P NMR data and the rigid trans geometry of the ligand, the complex is tentatively assigned a structure where all of the phosphines are bridging. Each copper atom is probably tetrahedrally coordinated by three phosphorus atoms, one from each bridging phosphine and one terminal chloride. A similar structure has been proposed for the compound $(DPPA)_3Cu_2Cl_2$ by considering the linearity of the phosphine, the molecular weight, and the far infrared spectral data (49).

3.3 Copper(I) perchlorate complexes:

3.3.1 $[(L\text{-}L)_2Cu]ClO_4$ complexes:

Except for DPPM and transVPP, all the ligands investigated in this work produced this type of complex from reactions with $Cu(ClO_4)_2$ (see Table XI). Infrared absorptions due to the ClO_4^- group, ^{31}P NMR, conductivity and molecular weight data of these (representative) complexes are recorded in Table XIII. Some actual ^{31}P NMR spectra are shown in Figure 13.

Infrared absorptions at 625 and 1100 cm^{-1} (broad) (see Table XIII) are characteristic of ionic perchlorates (156) in these complexes. Furthermore, the ν_1 frequency at about 930 cm^{-1} characteristic for a monodentate ClO_4 group has not been seen in these complexes. Additional information to support this view comes from the solution properties of these complexes. Thus, from the conductivity data (CH_2Cl_2) (see Table XIII) of the representative complexes $[(DPPE)_2Cu]ClO_4$, and $[(DPPB)_2Cu]ClO_4 \cdot CH_2Cl_2$ it can be concluded that these complexes are uni-univalent electrolytes. Molecular weight measurements (CH_2Cl_2) of the complexes

Table XII. Molecular weight, conductivity, far infrared, and NMR spectral data of copper(I) chloride complexes

Complex	Mol. wt.[a] (F.wt)	Conductivity slope[a,d] ($cm^{1/2}$ $equiv^{-1/2}$ ohm^{-1})	$\delta^{31}P^{a}$ (ppm)	Δ^{g}	$\delta^{1}H$ (ppm)[e] CH_2	Far infrared absorptions (cm^{-1}) $\nu_{Cu(I)-Cl}$
$(DPPM)_3Cu_2Cl_2.CH_2Cl_2$	499 (1435)	263	-13.3b +26.5		+3.87 +3.32	262 s
$(DPPE)_3Cu_2Cl_2$	....	....	-11.6[h] +29.1		....	248 s
(<u>cis</u> VPP)$_3Cu_2Cl_2.0.5CH_2Cl_2$	....	....	+9.3vb +20.1		....	....
(<u>trans</u> VPP)$_3Cu_2Cl_2$	....	....	-8vb		....	237 s
$(DPPP)_3Cu_2Cl_2.0.5CH_2Cl_2$	....	....	-14.3b +30.8		+2.35b	236 vs
(DPPM)CuCl	1015 (483)	Non-electrolyte	-7.7 (-15.4w)	15.9	+3.15b[f]	....
(DPPP)CuCl	....	....	-15.9[h]	2.5	....	....
(DPPPe)CuCl	....	....	-15.2	1.2	....	....
$(DPPH)CuCl.0.5CH_2Cl_2$	....	....	-12.1mt[h]	5.1	....	....

a In CH_2Cl_2 unless otherwise specified.

d The observed slope is obtained from linear plots of $\Lambda o - \Lambda e$ against $c^{1/2}$ (152).

e In C_6D_6 unless otherwise specified.

f In $CDCl_3$

...continued

TABLE XII continued...

h In benzene.

Δ = ^{31}P coord. - ^{31}P free ligand

g = δ ^{31}P free ligand values from reference 158.

Key: b-broad; vb -very broad; mt-multiplet; s-strong; vs -very strong.

i The complex (DPPE)Cu_2Cl_2 is insoluble and the complex (DPPB)CuCl.CH_2Cl_2 is not sufficiently soluble in $CH_2Cl_2/CHCl_3$. Conductivities of reference compounds are shown in Table XIII.

.... See discussions.

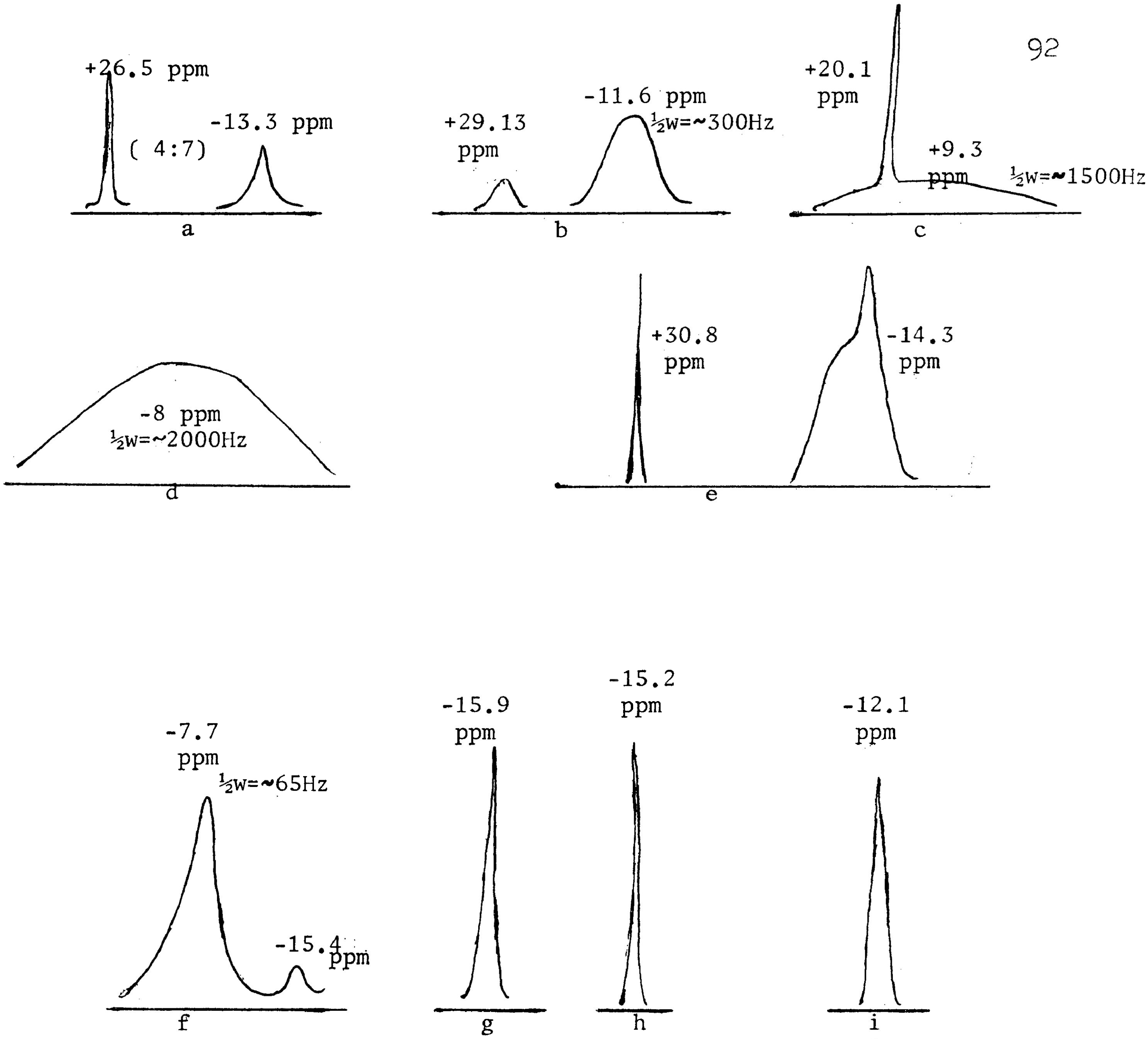

Figure 12. The $^{31}P\{H\}$ NMR spectra of (a) $(DPPM)_3Cu_2Cl_2.CH_2Cl_2$, (b) $(DPPE)_3Cu_2Cl_2$,(c) (cis VPP)$_3Cu_2Cl_2.0.5CH_2Cl_2$, (d) (trans VPP)$_3Cu_2Cl_2$, (e) $(DPPP)_3Cu_2Cl_2.0.5CH_2Cl_2$, (f) $[(DPPM)CuCl]_2$, (g) (DPPP)CuCl , (h) (DPPPe)CuCl and (i) $(DPPH)CuCl.0.5CH_2Cl_2$

$[(DPPE)_2Cu]ClO_4$ and $[(DPPP)_2Cu]ClO_4$ have shown values of considerably less than the formula weights (see Table XIII) further supporting the presence of ionic perchlorate in these complexes.

What is surprising is that the ^{31}P NMR spectra of these apparently very similar complexes fall into two main groups, one with a very broad signal and the second with a sharper and generally poorly resolved multiplet (see Figure 13). Thus the ^{31}P NMR spectra of the complexes $[(L\text{-}L)_2Cu]ClO_4$ (L-L=DPPE, cis VPP, DPPP) exhibit a very broad absorption. This might indicate the equivalence of phosphorus atoms of the ligands as well as some exchange processes. On the other hand the ^{31}P NMR spectra of the complexes $[(L\text{-}L)_2Cu]ClO_4.CH_2Cl_2$ (L-L = DPPB, DPPPe, DPPH) are all quite different and all display sharp reasonances as, generally, poorly defined multiplets with J =~40-60 Hz. In fact the spectrum of the complex with DPPB shows a well defined quintet (J = 43Hz) with a gradual lowering of intensities of the outer peaks. Though the multiplicity here is difficult to understand, the splitting of the resonance into fine structure indicates that the compound is slightly distorted with regard to the disposition of the P atoms. This could arise in a tetrahedral system through puckering of the very long chelating chains such that the P arrangement about the Cu atom becomes a distorted tetrahedral geometry. The couplings observed then might be due to magnetically slightly non-equivalent P atoms coupling through the P-Cu-P link. Why the shorter chain ligands should give broader ^{31}P signals is not at all clear and this phenomenon deserves further study when this work is extended.

The apparent equivalence (or near equivalence) of the phosphorus atoms of the ligands (whether broad or sharp ^{31}P signals are observed) and the fact that the perchlorate groups are ionic, suggest that the copper atoms in these complexes are coordinated to the four phosphorus atoms of the two chelating ligands. In this connection, an X-ray investigation of a related type of complex $[(MeCN)_4Cu]ClO_4$, has shown (29) that the copper is tetrahedrally coordinated which is also most likely the case with the bidentate ligands discussed here.

3.3.2 $(L\text{-}L)_3Cu_2(ClO_4)_2$ complexes:

Complexes of this type were obtained only with the ligands DPPM and trans VPP which, as has been noted before in this chapter, have bridging tendencies (see Table XI). The infrared absorptions (cm^{-1}) due to the ClO_4^- group, conductivity, molecular weight and ^{31}P NMR data of these (representative) complexes appear in Table XIII. Actual ^{31}P NMR spectra of these complexes are shown in Figure 13.

The infrared absorptions of the ClO_4^- group in these complexes are characteristic absorptions for a monodentate, oxygen coordinated perchlorato groups (156). Thus unlike the ionic perchlorates in the $[(L\text{-}L)_2Cu]ClO_4$ complexes, discussed earlier, these complexes show ν_1 absorptions at 930 cm^{-1} (see Table XIII) characteristic of monodentate perchlorato groups. Conductivities of these complexes in MeCN are seen to be close to the values expected for uni-univalent electrolytes, indicating that ionic dissociation occurs in solution. However, the slope is found to increase considerably ($\sim 900 cm^{1/2}\ equiv^{-1/2} ohm^{-1}$) for the DPPM complex at high dilution ($< 10^{-3}$M). Clearly complete dissociation would lead to a 1:2 electrolyte and this is only achieved at very high dilution. While most of the conductivity data have been recorded in CH_2Cl_2, it was necessary to use the more polar MeCN in these cases because the complexes have low solubilities in CH_2Cl_2.

The ionic dissociation of these complexes in solution is further supported by molecular weight measurements in the same solvent which shows only about one third of the value of the formula weights (see Table XIII).

The ^{31}P NMR spectrum (CH_2Cl_2) of the complex $(DPPM)_3$-$Cu_2(ClO_4)_2$ is hard to explain on the basis of a single compound. Thus, it exhibits a pair of doublets one centered at -2.8ppm, and the other at +46.5ppm, both with the same coupling constant (26.8Hz). By analogy with previously discussed systems one might expect these to be due to two types of P atoms of chelating and bridging DPPM ligands. However, the multiplicities apparently rule this out since they are more consistent with coupling between nonequivalent

P atoms in the same bis phosphine system with no additional couplings present. The spectrum also shows a very weak doublet centered at +32 ppm and (J=25.5Hz) and a weak broad singlet at -11.6ppm. This suggests that more than one species is present in solution (as is also suggested by the molecular weight and conductivity data) and it is impossible to make structural assignments from these data. Clearly the solid state and solution structures are entirely different.

The analytical and solid-state IR data suggests that the compound $(DPPM)_3Cu_2(ClO_4)_2$ is closely related to the corresponding chloride, and has tetrahedral copper atoms, each coordinated by three P atoms, one from a bridging and two from a chelating phosphine, and one perchlorato group. If this is the case, the Cu(I) chloride and perchlorate systems have entirely different structures in solution. X-ray structural data on the perchlorato complex discussed above would be highly desirable.

The ^{31}P NMR spectrum (MeCN) of the analytically related compound (<u>trans</u> VPP)$_3Cu_2(ClO_4)_2$ displays a well defined though relatively weak doublet centered at +20 ppm (J=31Hz), with a possible indication of monodentate coordination of the ligands. However, the spectrum (in the highly coordinative solvent MeCN) also shows very broad absorption of very much greater area than the doublet mentioned above centered at -4 ppm. This may be due to six magnetically identical or very similar P atoms coordinated to two Cu atoms. The relative areas of the doublet and the broad absorption are such as to suggest that the doublet arises from some impurity or dissociation product. The complex could be isolated from MeCN.

Thus, considering the probable presence of monodentate perchlorato groups the complex may tentatively be viewed as the binuclear species in which two tetrahedral copper atoms are bridged by three phosphines with the fourth coordination site occupied by a perchlorato group.

In summary, while the ^{31}P NMR data for these complexes must be treated with considerable caution since various equilibria clearly operate in solution, the analytical and solid state data are quite consistent with fairly conventional systems for which there are ample precedents in the literature.

3.4 Tetrahydroborate complexes of copper(I):

3.4.1 (L-L)Cu(BH_4) complexes:

Complexes of this type are obtained with L-L=DPPM, DPPE, DPPP, trans VPP, DPPB, DPPPe, DPPH (see Table XI). They can be made from reactions where complexes of the type $(L-L)_3Cu_2Cl_2$, $[(L-L)CuCl]_2$, $[(L-L)_2Cu]ClO_4$ and $(L-L)_3Cu_2(ClO_4)_2$ are used as starting materials as well as by treating a mixture obtained from the reaction of $CuCl_2.2H_2O$ and DPPM with $NaBH_4$. Clearly these reactions lead to the formation of the most common type (see the introduction to

Table XIII. Infrared spectral absorptions (cm^{-1}) of perchlorate group, molecular weight, conductivity, and ^{31}P NMR data of copper(I) perchlorate complexes.

Complex	Infrared absorptions(cm^{-1})of ClO_4^-			Mol.wt.[a] (F.wt.)	Conductivity[a] slope[c] ($cm^{1/2}equiv^{-1/2}ohm^{-1}$)	^{31}P[a] (ppm)
	ν_1	ν_3	ν_4			
$[(DPPE)_2Cu]ClO_4$		1124-1070bs	629s	665 (959)	470	+10.6vb
$[($<u>cis</u>$ VPP)_2Cu]ClO_4$		1120-1070bs	629s			+10.7vb
$[(DPPP)_2Cu]ClO_4$		1120-1060bs	628s	630 (983)		-11.8vb
$[(DPPB)_2Cu]ClO_4.CH_2Cl_2$		1125-1060bs	626s		480	- 5.8 mt(5) J=43Hz
$[(DPPPe)_2Cu]ClO_4.CH_2Cl_2$		1132-1050bs	627s			-9.53mt J=60Hz
$[(DPPH)_2Cu]ClO_4.CH_2Cl_2$		1132-1050bs	626s	674 (1156)		-7.7
$(DPPM)_3Cu_2(ClO_4)_2$	928m	1130-1065bs	626s	448[d] (1478)	600[d]	-2.8dt +46.5dt -11.6bw +32dt (w)
$($<u>trans</u>$ VPP)_3Cu_2(ClO_4)_2$	926m	1120-1069bs	625s	570[d] (1514)	490[d]	+20dt -4b
Ph_4PCl					303(1:1 type)	
$(Ph_4)_2CoCl_4$					1040 (1:2 type)	
$[(L-L)PdCl]BPh_4$[e]					580 (1:1 type)[d]	
$[(L-L)Pd](ClO_4)_2$[e]					1310 (1:2 type)[d]	

...Continued

Table XIII Continued...

a In CH_2Cl_2 unless otherwise specified.

c Slope is obtained as described in Table XII.

d In MeCN. L-L =1,2-Bis [phenyl (*o* -thiomethylphenyl) arsino] ethane.

e Reference 152c.

Key: s-strong; bs-broad and strong; m-medium; mt-multiplet; dt-doublet; vb- very broad; b-broad; bw-broad and weak.

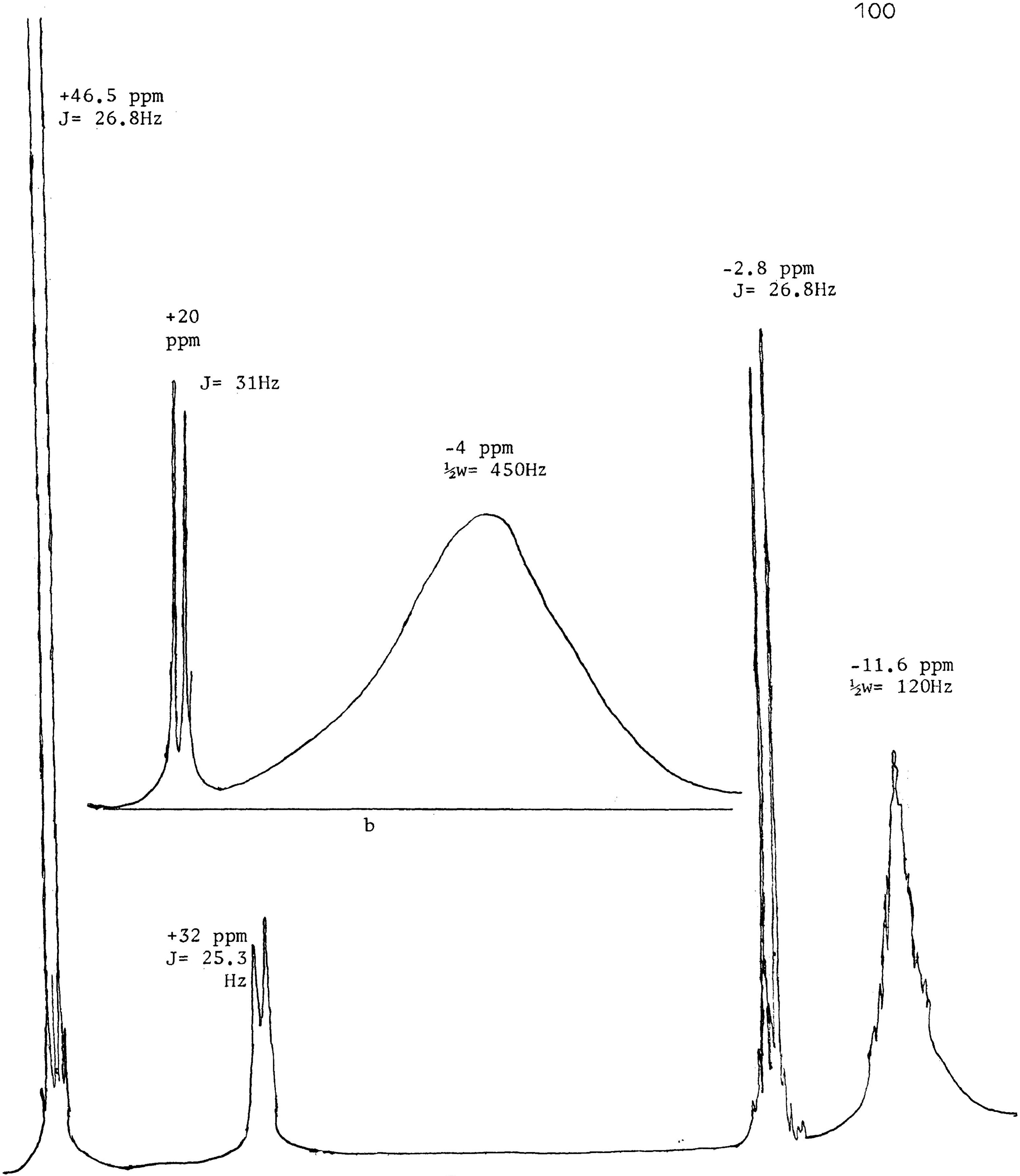

Figure 13. The $^{31}P\{H\}$NMR spectra of (a) $(DPPM)_3Cu_2(ClO_4)_2$, and (b) (<u>trans</u> VPP)$_3Cu_2(ClO_4)_2$

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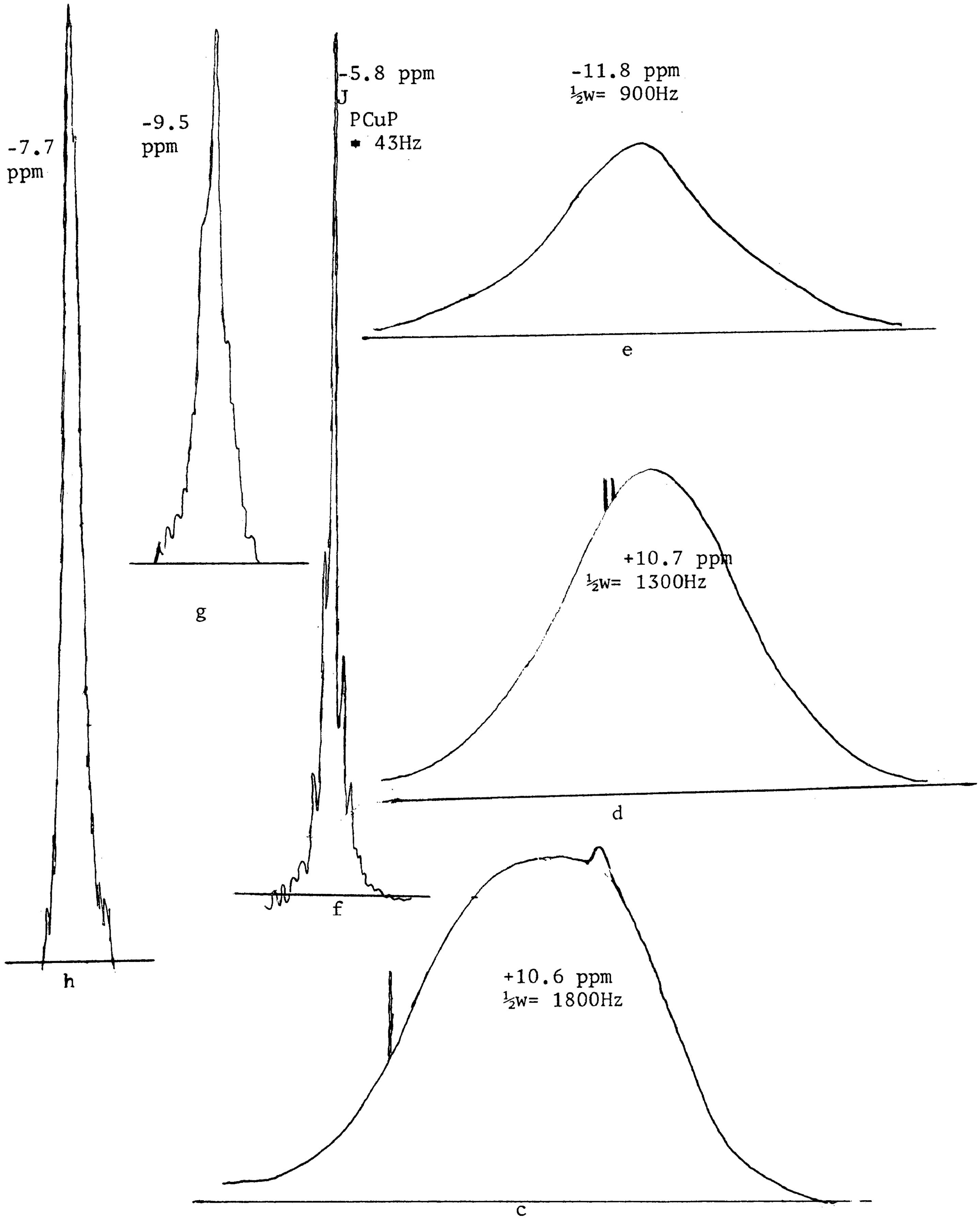

Figure 13 cont'd. (c) [(DPPE)$_2$Cu]ClO$_4$, (d) [(<u>cis</u> VPP)$_2$Cu]ClO$_4$, (e) [(DPPP)$_2$Cu]ClO$_4$, (f) [(DPPB)$_2$Cu]ClO$_4$.CH$_2$Cl$_2$ (g) [(DPPPe)$_2$-Cu]ClO$_4$.CH$_2$Cl$_2$,and (h) [(DPPH)$_2$Cu]ClO$_4$.CH$_2$Cl$_2$

this thesis) of complex containing BH_4 known. Of major interest in this work is the mode of coordination of the BH_4 group.

Physical data including molecular weights, infrared, and ^{31}P NMR are recorded in Table XIV. Molecular weight data have been obtained for three representative complexes and they indicate that the complexes appear to be monomeric in solution, although in the case of trans VPP the value is little higher than the monomeric value. (see Table XIV) On this basis alone the most reasonable arrangement would involve, assuming four-coordinate copper, bidentate BH_4 groups.

Infrared absorptions for various modes of BH_4 coordination (see Figure 8, p. 39) in tetrahydroborate complexes have been discussed earlier (section 1.6) and characteristic peaks observed for monodentate and bidentate attachments of the BH_4 group are listed in Table IV (page 45) and Table V (page 46) respectively. The solid state structure (111) of the complex $(Ph_3P)_2Cu(BH_4)$ has been shown to contain a bidentate BH_4 group, for which the characteristic infrared absorptions appear in Table V (page 46).

As mentioned above, the stoichiometries and molecular weight data mentioned above suggest that there is probably a very close relationship between the triphenylphosphine complex and the bidentate phosphine complexes $(L-L)Cu(BH_4)$, obtained in the present work. This relationship will now be examined and we will start by considering the IR data for these complexes.

Infrared absorptions attributable to the coordinated BH_4 groups of these complexes are recorded in Table XIV. Some actual IR spectra are also shown in Figure 14. For convenience and to allow easy comparison, the infrared absorptions of the bidentate BH_4 group in $(Ph_3P)_2Cu(BH_4)$ are included in Table XIV. From Table XIV it can be seen that the spectra of the $(L\text{-}L)Cu(BH_4)$ complexes are all qualitatively very similar and are in turn similar to the spectrum displayed by $(Ph_3P)_2Cu(BH_4)$. For example, the BH_t terminal and BH_b bridging regions are very similar, as is the appearence of the strong absorption at about 1135 cm^{-1} assignable to the BH deformation. A weak peak at about 2240 cm^{-1} in these complexes has been tentatively assigned to an overtone of a BH deformation, although it should be noted that it is not precisely double the frequency of the BH deformation. However, it is not possible to assign any bridge stretch in the 1500-1300 cm^{-1} region because of the presence of ligands and Nujol absorptions in this region.

It is therefore reasonable to assume on the basis of this IR data that the $(L\text{-}L)Cu(BH_4)$ complexes listed in Table XIV have the same type of bidentate BH_4 attachment to the copper(I) as in $(Ph_3P)_2Cu(BH_4)$. Presumably the phosphines act as normal chelating ligands to make the copper four-coordinated, although exactly how this could be achieved with trans VPP is not clear. In this connection it should be noted again that this complex gives a molecular weight which is superficially higher than a monomeric system would give. The possibility therefore arises that here we have a dimeric system (partially dissociated in solution) with two bridging bis phosphine ligands and two bidentate BH_4 units.

The ^{31}P NMR spectra (Table XIV) of the complexes (L-L)Cu(BH_4).nCH_2Cl_2 (n=0.5, L-L =DPPM, DPPP; n=0, L-L=DPPE, DPPB, trans VPP, DPPH) display single resonances (Figure 15), which occasionally show indications of what might be fine structure. This observation of a single resonance indicates the equivalence of the phosphorus atoms in these complexes as would be expected if the complexes have a structure analogous to that of the triphenyl phosphine complex. Such a structure is not possible for the trans-VPP complex as already observed above but the ^{31}P NMR data in this case is still consistent with the dimeric structure proposed for this complex above. The ^{31}P NMR spectrum ($CHCl_3$) of the closely related complex (DPPPe)-Cu(BH_4).0.5CH_2Cl_2 displays, however, two broad overlapping peaks (see Figure 15) in a ratio of approximately 1:1. The signal with the lower chemical shift (-15.5ppm) is at the position of the free ligand. The spectrum also contains a pair of weak unsymmetrical doublets one centered at +32 ppm (J=31.5Hz) and the other at +23.8ppm (J=9Hz). This result strongly suggests that partial neutral ligand dissociation occurs in solution in this case and that possibly, the phosphines show a tendency to become monodentate in solution.

The compound (DPPM)Cu(BH_4).H_2O (apparently analogous to the CH_2Cl_2 solvate discussed above) is obtained after the first recrystallization of the crude reaction product from methylene chloride/n-hexane [see section 2.6.1 (ii)]. That the compound is a hydrate is confirmed by the IR spectrum of the compound which exhibits a weak broad absorption at 3550 cm^{-1} with the second weak peak at 1670 cm^{-1}. While the IR spectrum is similar to that of the CH_2Cl_2 solvate discussed above (see later discussion), the ^{31}P NMR spectrum of the compound in CH_2Cl_2 (which has been reproduced several times) is entirely different and displays two sharp peaks (-16.6 ppm, -4.3 ppm) of almost equal area and intensity. This surprising result suggests that the two phosphorus atoms are not equivalent and the sharpness of the signals suggest that they are also not coupled to any significant extent. This means probably that the water molecule would have to be occupying a coordination site on the copper so that the metal ion in this case would be five coordinate, unless the compound is polynuclear in which case a more complex structure would apply - that is, if the system is five coordinate the two P atoms would have to occupy an apical-equatorial arrangement in either a trigonal bipyramid or a tetragonal pyramid.

When (DPPM)Cu(BH_4).H_2O is repeatedly recrystallized from CH_2Cl_2/n-hexane, the water molecule is eventually removed and (DPPM)Cu(BH_4).0.5CH_2Cl_2 is produced. The IR spectrum in the BH_4 region is essentially unchanged from that of the hydrate. However, the ^{31}P NMR spectrum now exhibits a single peak at -5.5 ppm. Clearly the phosphorus atoms are now equivalent and presumably the copper is again tetrahedrally coordinated. This particular compound has a molecular weight which confirms the monomeric nature of the complex (as mentioned earlier).

^1H NMR spectra for many of these complexes have been recorded but they are in general poorly resolved and frequently contain many overlapping multiplets. They provide very little useful information and will not be discussed further here. However, low temperature studies where dissociation and fluxional processes would be slowed and where correlation time decoupling (see the introduction to this thesis) of ^{11}B from ^1H could occur would be a useful extension of this work.

3.4.2 [$(DPPM)_2Cu_2(BH_4)$]ClO_4

This insoluble complex, prepared by treating the colourless mixture obtained from the reaction of $Cu(ClO_4)_2$-•$6H_2O$ and DPPM (see section 2.6.2) with $NaBH_4$ has been reproduced three times.

The perchlorate group is seen to be ionic as the compound displays in its IR spectrum a broad absorption at

1100 cm^{-1} and a strong absorption at 627 cm^{-1}(156). No absorption at about 930 cm^{-1} assignable to the ν_1 frequency characteristic of a monodentate ClO_4^- group is seen. The difference between the BH_t and BH_b absorptions is seen to be smaller (see Table XIV) in comparison with other (L-L)-$Cu(BH_4)$ complexes, and no BH deformation band was detectable. However, this might be due to the strong and broad absorption of the ClO_4^- group at 1100 cm^{-1}. The BH_b absorption in this complex is seen to be much stronger than BH_t absorption (see Figure 14).

From the data given above it is not possible to assign a structure to this most interesting complex which clearly merits further study in any extension of this work.

Table XIV. Molecular weight, ^{31}P NMR and infrared spectral data of copper(I) tetrahydroborates.

Complex	Mol. wt.[a] (F.wt.)	^{31}P[a] (ppm)	BH_4 absorptions (cm^{-1})			
			BH_t	BH_b	Bridge stretch	BH deformation
$(Ph_3P)_2Cu(BH_4)$[c]			2385 2353	2001 1959		1135
$(DPPM)Cu(BH_4).H_2O$		-16.6 - 4.3	2378s	1985b		1136s
$(DPPM)Cu(BH_4).0.5CH_2Cl_2$	594 (504.8)	- 5.5	2378s	1985b		1133s
$(DPPE)Cu(BH_4)$		- 8.3b	2385sh 2370s 2248w[d]	2005s 1975s		1133s
(<u>trans</u> VPP)$Cu(BH_4)$	616 (474.3)	- 4.4	2400s 2355s 2245w[d]	1995s 1950s 1997sh		1132s
$(DPPP)Cu(BH_4).0.5CH_2Cl_2$		-16.3	2380sh 2370s 2245w[d]	1982s 1939s		1130s
$(DPPB)Cu(BH_4)$		-11.4mt (J=37Hz)	2380s 2260w[d]	1992s 1950s		1135s
$(DPPPe)Cu(BH_4).0.5CH_2Cl_2$		-9.1,-15.5, +32,+23.8	2380s 2252w[d]	2000s 1968s		1134s
$(DPPH)Cu(BH_4)$	605 (532)	- 9.6	2385s 2260w[d]	1989s 1950s		1138s
$[(DPPM)_2Cu_2(BH_4)]ClO_4$			2380s	2078s	1370s ?	

a In CH_2Cl_2 unless other wise specified. c Included for comparison (147).

d A weak peak has been assigned to an overtone of BH deformation.

Key: b-broad; mt-multiplet; s-strong; sh-shoulder

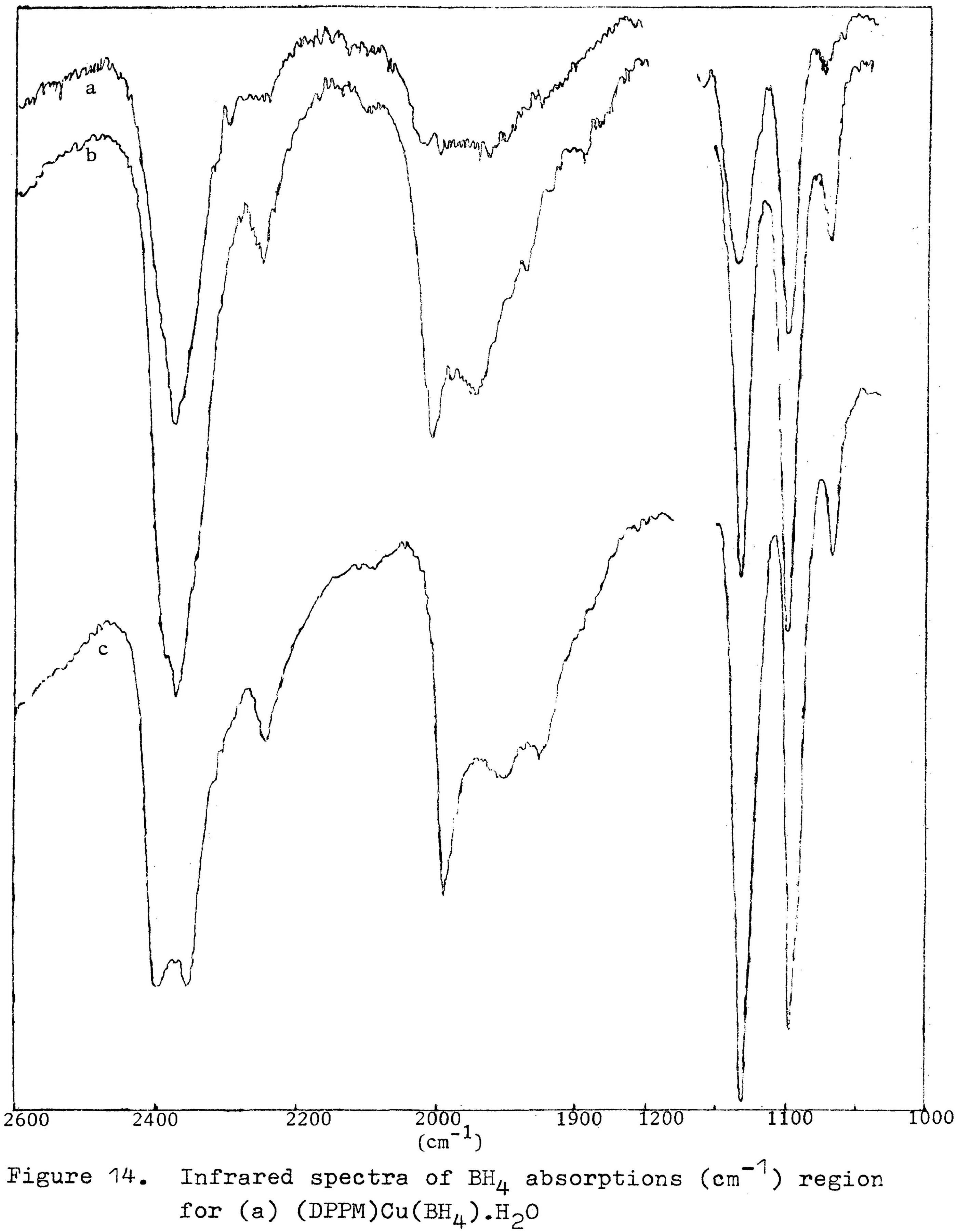

Figure 14. Infrared spectra of BH_4 absorptions (cm^{-1}) region for (a) (DPPM)Cu(BH_4).H_2O
(b) (DPPE)Cu(BH_4) and (c) (<u>trans</u> VPP)Cu(BH_4)

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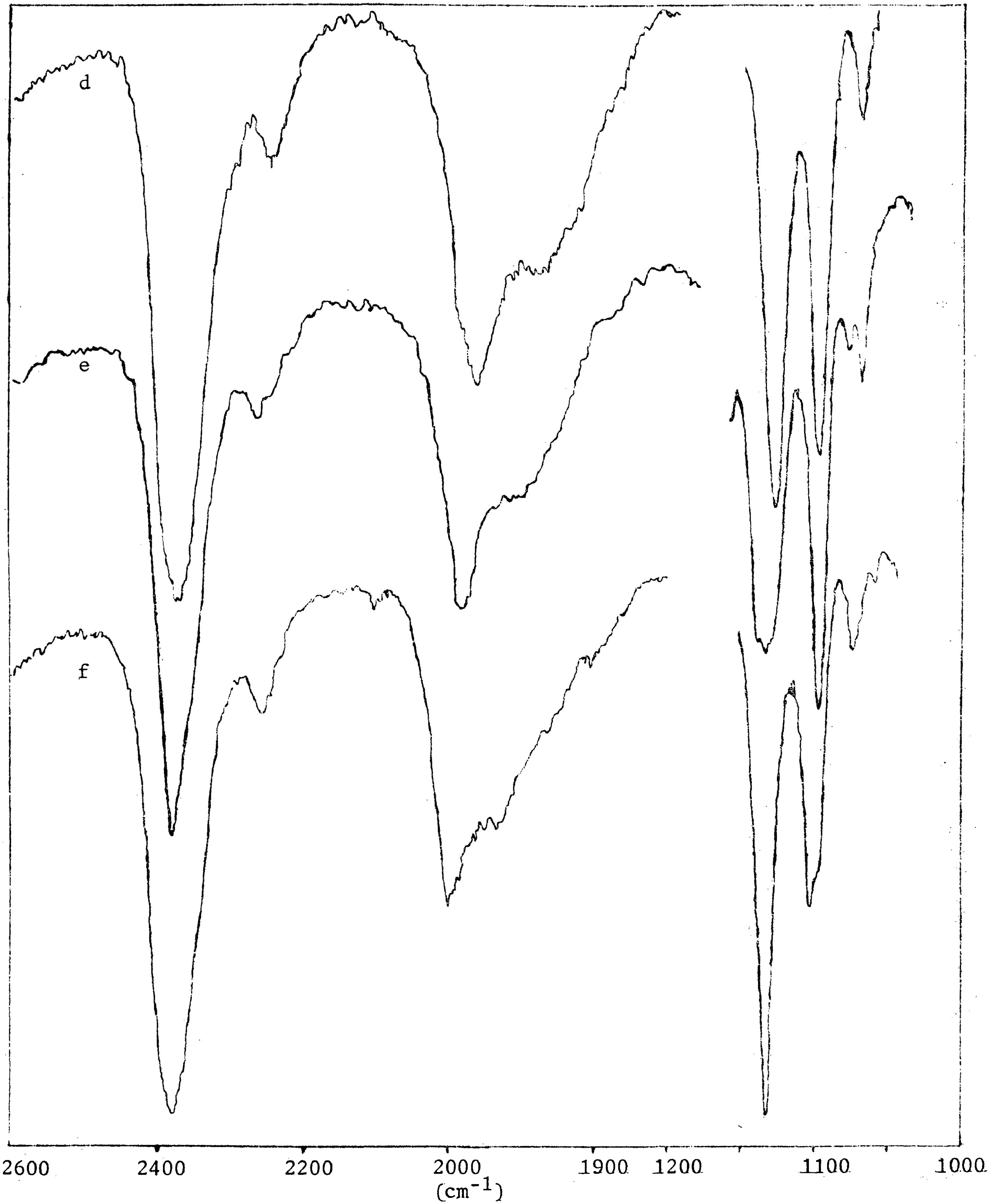

Figure 14 cont'd. (d) (DPPP)Cu(BH_4).0.5CH_2Cl_2
(e) (DPPB)Cu(BH_4) (f) (DPPPe)Cu(BH_4).0.5CH_2Cl_2

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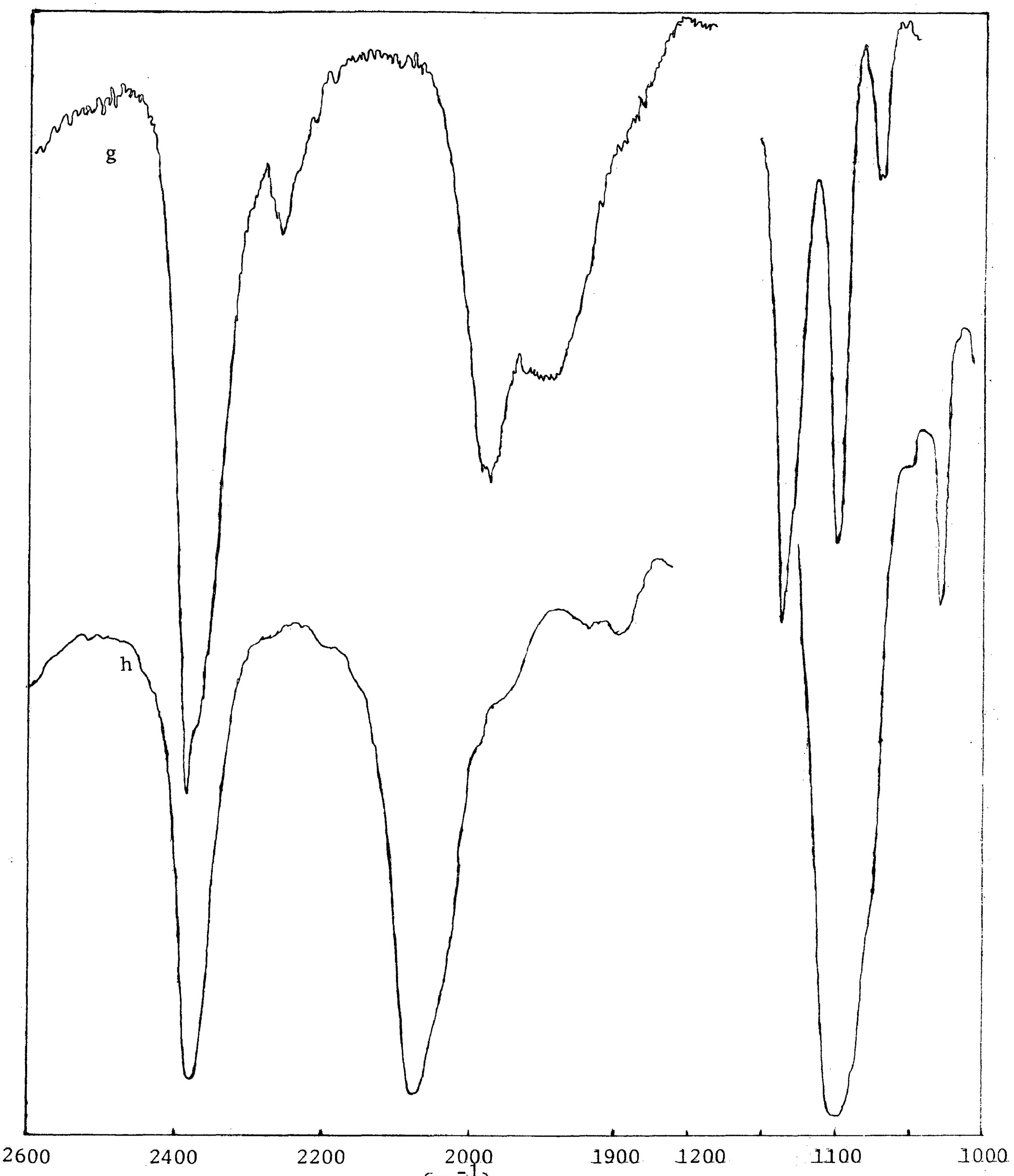

Figure 14 cont'd. (g) (DPPH)Cu(BH$_4$)

(h) [(DPPM)$_2$Cu$_2$(BH$_4$)]ClO$_4$

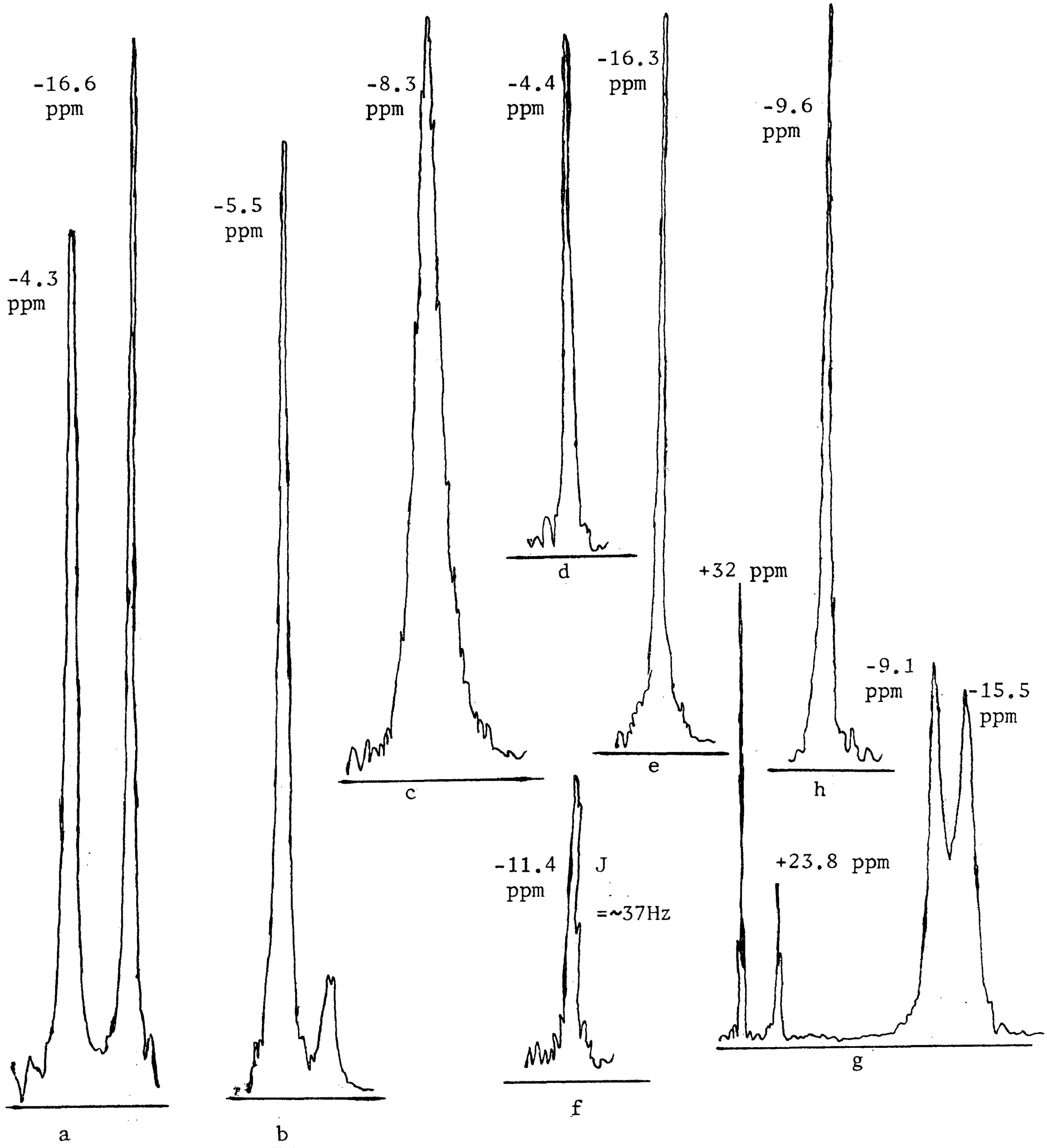

Figure 15. The $^{31}P\{H\}$ NMR spectra of (a) (DPPM)Cu(BH_4).H_2O, (b) (DPPM)Cu(BH_4).0.5CH_2Cl_2, (c) (DPPE)Cu(BH_4), (d) (trans VPP)Cu(BH_4), (e) (DPPP)Cu(BH_4).0.5CH_2Cl_2, (f) (DPPB)Cu(BH_4), (g) (DPPPe)Cu(BH_4).0.5CH_2Cl_2 and (h) (DPPH)Cu(BH_4)

3.5 Formation of a probable copper(I) hydride complex:

It is clear from the earlier discussion (section 1.3.4.3) that only a few copper(I) hydride complexes are known and those recorded in the literature have little or no conventional spectroscopic characterization. Transition metal hydride complexes are frequently obtained from reactions of hydroborate ions with metal salts in the presence of suitable ligands (see the introduction to this thesis). Thus the possibility in the present work that copper hydride complexes could be formed in such reactions required investigation Indeed, one of the main reasons why the present work was undertaken was to establish whether, in addition to copper(I)-BH_4 complexes, copper(I) hydride complexes could be prepared using bidentate phosphine ligands in these metal ion - BH_4 reactions. It would be especially interesting, to study the spectroscopic properties of such systems.

In this connection, it was found that the reaction of $NaBH_4$ with $(DPPE)Cu_2Cl_2$ in benzene and ethanol under a nitrogen atmosphere (i.e. under slightly different conditions from those outlined in the previous section) produced a yellow-red solution from which a yellow solid could be precipitated by the addition of n-hexane. The crude product is soluble in benzene and produces a red solution, from which it can be recrystallized by addition of n-hexane. In one instance the complex was recrystallized three times in this manner without any change. Although the product forms red solution in benzene, the precipitated product is obtained as a yellow solid. This synthesis has been reproduced several times, and always the same product is obtained.

This complex is, in fact, the only coloured compound obtained in all of the new reactions described in this thesis. It is unstable in air and decomposes to give a green solid after a few hours. In a CH_2Cl_2 solution (red), decomposition to give a green solution occurs after about 14 hours even under nitrogen. In the solid state, the colour of the compound also fades after a prolonged time (even under nitrogen atmosphere).

The ^{31}P NMR spectrum of the crude reaction solution (red) displays a fairly sharp signal with, possibly, some poorly resolved fine structure centered at +33.7 ppm (J= ~35 Hz) and another broader signal showing unmistakable fine structure centered at -7.9 ppm. The two major lines (poorly resolved) of this signal are of equal intensity and are separated by 53.6 Hz while a third peak of lower intensity on the lowfield site of the signal is separated from the nearest main peak by 168 Hz (see Figure 15A). However, the isolated and apparently pure yellow compound displays a broadened doublet type of resonance centered at -7.7 ppm (J=116 Hz) in its ^{31}P NMR spectrum (Figure 15A) in CH_2Cl_2 and probably all of the P atoms present are magnetically very similar. Considering briefly ^1H spectra, no resonance is seen upfield of TMS for the compound in benzene and ethanol mixture or in CH_2Cl_2. However, the crude reaction solution (red, benzene and ethanol) exhibits a single peak at -20.7 ppm in the ^1H NMR spectrum.

Solid-state IR spectrum of the recrystallized compound shows no peak in the BH_4 absorption region but a very interesting strong peak at 1685 cm^{-1}. However, no absorption in the 3550-3200 cm^{-1} region is seen, assignable to the OH stretching frequency of water or ethanol (although a very broad absorption might not be easily seen) and the peak at 1685 cm^{-1} is therefore probably not due to the coordinated OH group of EtOH or water. The peak at 1685cm^{-1} is retained even after recrystallization several times from benzene and n-hexane.

The absence of BH_4 absorptions or an OH stretching frequency in the IR spectrum, the yellow colour of the compound, and its decomposition to give a green solid suggest that the 1685cm^{-1} peak is probably due to some type of Cu(I)-H absorption even though the ^1H NMR spectra show no hydride peak above TMS. To test this hypothesis, the deuterated analogue has been prepared under identical reaction conditions using $NaBD_4$. The reaction with $NaBD_4$ proceeds in exactly same way as with $NaBH_4$ and the product is again obtained as a yellow solid, apparently identical with that obtained with $NaBH_4$, by the addition of n-hexane to the resulting red solution. The IR spectrum of the compound obtained from the $NaBD_4$ reaction does not exhibit the peak at 1685 cm^{-1}, but a new peak occurs at 1190 cm^{-1}. The IR spectra of the two complexes are otherwise identical. The shift of frequency from 1685 cm^{-1} to 1190 cm^{-1} upon introduction of deuterium is in good agreement with theoretical calculation of the isotopic shift.

It appears likely then that the yellow species discussed above is a copper(I) hydride of some type. Four elemental analyses on four samples of the compound showed it to contain carbon in the range of 52-53% and hydrogen at about 4.1 %. The percentage of copper has been found to be 27% (157) (only one sample has been analyzed). With these elemental analyses it is not possible to arrive at any reasonably simple empirical formula but it is noteworthy that the C:H ratio is almost exactly that present in the starting ligand DPPE with a slight excess of hydrogen. This would appear to rule out solvent type impurities. Moreover, on the basis of these analyses, the Cu:ligand ratio is about 2.6 to 1.

It would therefore appear that this compound is a copper cluster complex of DPPE related to the known tetrameric (117) and probably closely related to the $(Ph_3P)_6Cu_6H_6$ hexameric system characterized by S.A. Bezman et.al. (99) in which the hydrogen atoms bridge Cu atoms along edges of an octahedron.

Time considerations forced the investigation of this structure to be suspended while the other, more conventional, systems described in this thesis were investigated more fully. However, it is recognized that this complex is probably the most important isolated during this study of bidentate phosphine-Cu(I)-hydroborate systems and it is imperative that molecular weight and X-ray crystallographic data should be obtained at the earliest opportunity.

The above paragraph has been written in response to criticisms made by an examiner of this thesis.

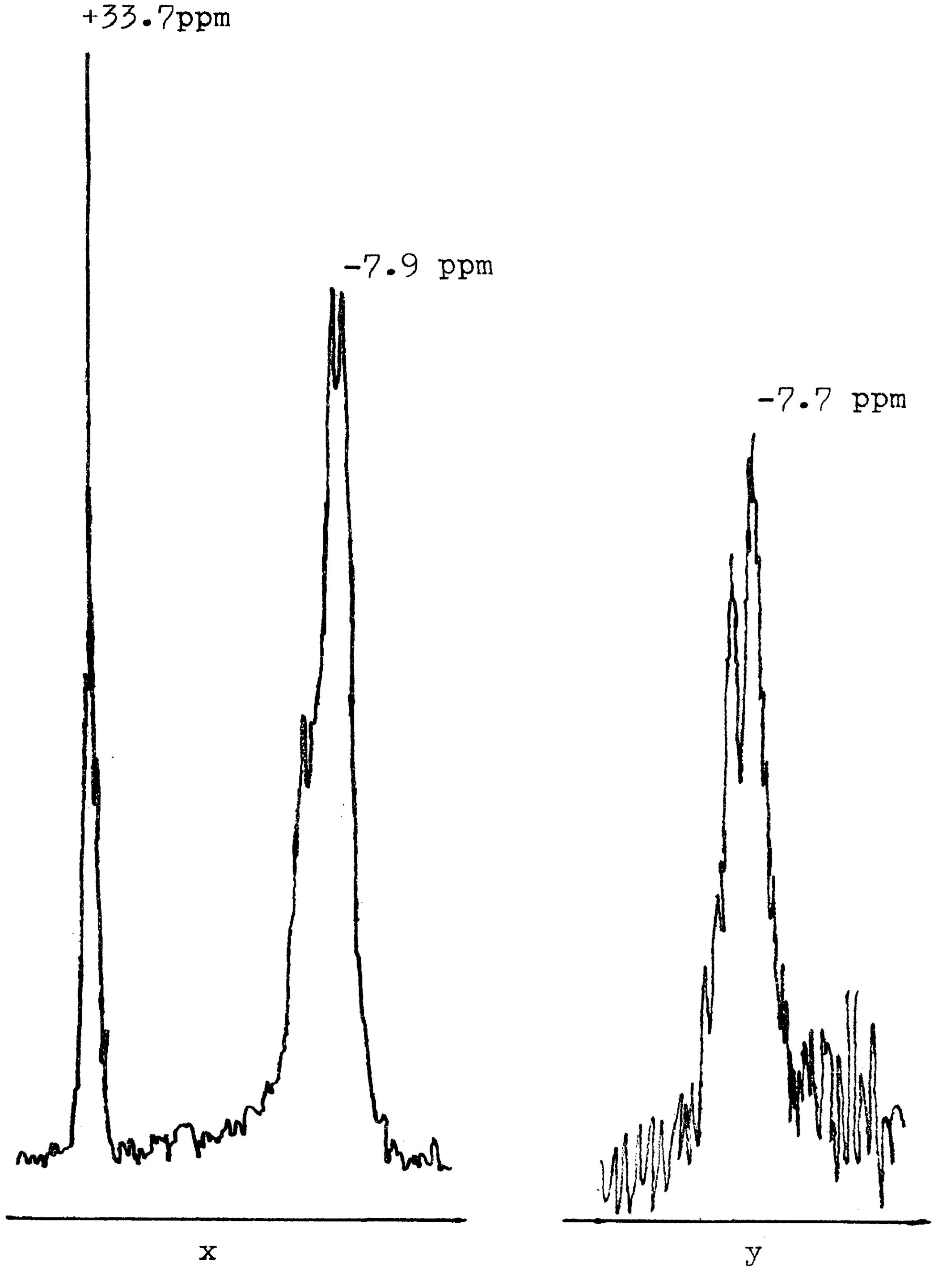

Figure 15A. The $^{31}P\{H\}$ NMR spectra of
(x) reaction solution and
(y) isolated product

3.6 Cyanotrihydroborate complexes of copper(I):

3.6.1 $(L\text{-}L)_3Cu_2(BH_3CN)_2$ complexes:

The complexes of this type obtained in the present work with L-L=DPPE, trans VPP, cis VPP, DPPP, DPPB are listed in Table XI. They can be prepared from reactions where complexes of the type $(L\text{-}L)_3Cu_2Cl_2$, $[(L\text{-}L)_2Cu]ClO_4$ and $(L\text{-}L)_3$-$Cu_2(ClO_4)_2$ are used as starting materials as well as by treating mixtures of $CuCl_2.2H_2O$ and DPPE with $NaBH_3CN$. Molecular weight, conductivity, ^{31}P NMR and assigned infrared spectral data for the BH_3CN^- groups of these complexes are presented in Table XV. Some actual IR spectra in the region of the BH_3CN absorptions are shown in Figure 16.

The stoichiometries of these complexes, $(L\text{-}L)_3Cu_2$-$(BH_3CN)_2$, are related to the composition of the $(L\text{-}L)_3Cu_2Cl_2$ complexes (section 3.2.2) and $L_3Cu(BH_3CN)$ complexes where L in these cases is a monodentate phosphine (91). Slight shifting ($\sim$1-13cm^{-1}) of the CN frequencies to higher energy compared to the CN stretching frequency in anionic BH_3CN^- (see Table VI) in the $L_3Cu(BH_3CN)$ complexes have been interpreted in terms of $Cu\text{-}NCBH_3$ bonding (91). From the stoichiometric similarities with $L_3Cu(BH_3CN)$ and with $(DPPE)_3$-Cu_2Cl_2 (122) for which the structure is known, it is reasonable to assume that the complexes $(L\text{-}L)_3Cu_2(BH_3CN)_2$ have the same structure as displayed by $(DPPE)_3Cu_2Cl_2$(see Figure 7d,p.34) with the BH_3CN groups coordinated to the copper(I) through its nitrogen atom.

However, it appears that of the five complexes of this type listed in Table XV, three are closely related (DPPE, DPPP and DPPB) and two are not only different from these, but significantly different from each other. Considering first the complexes with DPPE, DPPP and DPPB, small shifts (3-8cm^{-1}) to higher energy (see Table XV) of the CN stretching frequencies with respect to ionic $NaBH_3CN$ (2179cm^{-1}) (91) are observed in their IR spectra. These are small shifts and may possibly be attributed to weak Cu(I)-$NCBH_3$ interactions. In all these complexes the CN absorptions are seen to be a sharp band with no splitting (see Figure 16). No other absorptions in the 2180-2000 cm^{-1} region are seen which could be assigned to a Cu-H_b-B frequency. It is interesting to mention here that the complex $(DPPE)_3Cu_2(BH_3CN)_2$ prepared earlier in these Laboratories (55) shows a peak at 2106 cm^{-1} tentatively assigned to Cu-H_b-B vibration in addition to the CN peak at 2188 cm^{-1}. The earlier complex (55) was prepared in EtOH only.

Coordination through BH_3NC^-, due to possible isomerization of BH_3CN^- to BH_3NC^-, in these complexes seems very unlikely since the NC absorption in BH_3NC^- occurs at 2070 cm^{-1} (159). No absorptions in this region have been seen for the $(L-L)_3Cu_2(BH_3CN)_2$ complexes. The BH deformation frequencies in these complexes are only slightly shifted to lower energy (1300 cm^{-1} in free BH_3CN^-, see Table VI). This probably means that the BH_3CN group in these complexes retains approximately the same symmetry as in ionic BH_3CN^-.

The ^{31}P NMR spectra of these complexes exhibit two signals (see Table XV, Figure 17). The observation of two signals, as described previously, is consistent with the presence of both chelating bidentate and bridging monodentate phosphines in these complexes. The integration of these peak areas, once again, give values which vary considerably from the expected 2:1 ratio , assuming that the complexes have structures similar to $(DPPE)_3Cu_2Cl_2$ (Figure 7d,p.34). This would be consistent with the IR evidence which suggests that only $Cu-NCBH_3$ arrangement is present. Thus, once again the copper(I) ions are probably tetrahedrally coordinated.

Molecular weight measurements of these complexes indicate that dissociation occurs in solution (see Table XV). Values are approximately half the formula weights and suggest the presence of two species in solution. These results are consistent with electrical conductivities which are found to be close to values expected for 1:1 electrolytes. Thus, there is no doubt that some dissociation of these complexes is taking place in solution, though it is difficult to understand why the conductivities are so low. It would be more reasonable, considering the weak Cu-N bonding, for conductivities closer to 1:2 electrolytes to occur.

The IR spectrum of $(\underline{cis}\ VPP)_3Cu_2(BH_3CN)_2.CH_2Cl_2$ (Table XV, Figure 16e) in the 2500-2200 cm^{-1} region is unlike most other spectra of BH_3CN complexes prepared with Co, Ni, and Cu in these laboratories and in the literature. Thus, the CN stretching frequency (Figure 17) is seen to be

66 cm^{-1} higher in energy than for the free BH_3CN^- (2179 cm^{-1}). Further, the BH deformation is also shifted to lower energy (1105cm^{-1}, see Table XV) with respect to the position in the three complexes discussed above. There is no absorption in the 2200-2000 cm^{-1} region which could be assigned to a Cu-H_b-B frequency. Such a very large frequency shift for CN may be attributed to strong bonding between the nitrogen and Cu(I). A similar large shift in the CN stretching frequency has been observed for the complex $(Ph_3P)_3Cu(NCBPh_4)$ (91) and also attributed to a strong Cu-$NCBPh_4$ interaction.

Apart from the major IR difference, the solution properties of this cis VPP complex appear to be similar to those already discussed for the DPPE, DPPP and DPPB complexes. Thus, the ^{31}P NMR spectrum of this compound displays, like the others, a very broad resonance centered at +7.5ppm and a weak sharp signal at +20.7 ppm. The molecular weight of the compound (see Table XV) is close to half the formula weight and the conductivity is in the 1:1 electrolyte range (for reference see Table XIII). Thus, if the complex has the same structure as $(DPPE)_3Cu_2Cl_2$, like the other complexes, it is not clear why there is such a radical difference in the strength of the Cu-$NCBH_3$ bond.

In the remaining complex of this type with trans VPP, the IR spectrum is quite similar to those of the DPPE, DPPP and DPPB complexes discussed earlier except that in this case the CN stretching frequency is slightly shifted to lower energy (4cm^{-1}) than for the free BH_3CN(2179 cm^{-1}). There are no absorptions in the 2200-1900 cm^{-1} region assignable to a Cu-H_b-B frequency. This lowering of the CN stretching frequency has been attributed to back-donation from a π-donor metal ion to the BH_3CN group on complexation. For example, the observed CN frequency at 2170cm^{-1} in $[(NH_3)_5Ru(BH_3CN)]^+$ has been attributed to π-bonding between ruthenium (II) and the BH_3CN group (161), What is difficult to rationalize is that this type of bonding is apparently sufficiently strong that no ionic dissociation occurs in solution, as seen by the fact that the complex is a non-electrolyte. On the other hand the cis VPP complex with a very strong N-Cu bond appears to dissociate readily. The ^{31}P NMR of this complex displays a broad single resonance. This observation of single broad resonance might indicate the equivalence of phosphines and also some rapid exchange process.

3.6.2 $(L-L)Cu(BH_3CN)$ complexes:

Complexes of this type with L-L=DPPM,DPPE,DPPPe and DPPH obtained in the present work are listed in Table XI. These complexes can be prepared from reactions where $(L-L)_3$-$Cu_2(ClO_4)_2$, $[(L-L)_2Cu]ClO_4$, (L-L)CuCl type complexes are used as starting materials, as well as by treating mixtures obtained from reactions of $CuCl_2.2H_2O$ with DPPM or DPPE with $NaBH_3CN$.

Infrared spectral bands associated with the BH_3CN group, ^{31}P NMR data, and because of very low solubilities of most of these complexes, only limited conductivity and molecular weight data are presented in Table XV. Some actual IR spectra and ^{31}P NMR spectra are shown in Figure 16 and

Figure 17 respectively.

The DPPM complex obtained from the reaction of $NaBH_3CN$ with $(DPPM)_3Cu_2(ClO_4)_2$ is quite different from the complex having the same empirical formula obtained from the direct reaction of $NaBH_3CN$ with a $CuCl_2$/DPPM mixture. For example the product from the last mentioned reaction is very sparingly soluble in methylene chloride, while the product from the $(DPPM)_3Cu_2(ClO_4)_2$ complex is highly soluble in the same solvent. Because of this high solubility, it was possible to measure the molecular weight of this particular complex which from the value of 1111 clearly indicates that the molecule should be written as $[(DPPM)Cu(BH_3CN)]_2$. The IR spectra of this compound and the other complex formulated as $(DPPM)Cu(BH_3CN)$ (in the absence of molecular weight data) are also significantly different (Figure 16). However, the IR spectrum of the latter is similar to that of the corresponding DPPE complex but all the above spectra are quite different from those of the complexes with DPPPe and DPPH (Figure 16). In the absence of firm structural data on these complexes the complicated pattern of absorptions in the 2100-2500 cm^{-1} region are extremely difficult to interpret.

Thus, the IR spectrum (Figure 16f) of $[(DPPM)Cu(BH_3CN)]_2$ displays a sharp doublet at 2182 cm^{-1} and 2160 cm^{-1}, a peak at 2250 cm^{-1} and the strong broad absorption at about 2350 cm^{-1}. The latter is certainly due to the terminal BH_t absorption, but the origin of the 2250 cm^{-1} is not so obvious. It may be part of the usually broad BH_t absorption, or it may be due to a very strongly bonded Cu-$NCBH_3$ link with a shift of 71 cm^{-1} from ionic BH_3CN. That would represent an even larger shift than seen for (<u>cis</u> VPP)$_3Cu_2(BH_3CN)_2 \cdot CH_2Cl_2$ discussed earlier. The complex has basically the same stoichiometry as $[(Ph_3P)_2Cu(BH_3CN)]_2$, of known structure (see Figure 7c, p.34), in which two types of CN absorptions have been observed (91) due to slight distortions of the structure (121). In addition a broad peak at 2000 cm^{-1} has been assigned to the Cu-H_b-B frequency. However, in the DPPM complex the only peak that could be due to such an absorption would be the one at 2160 cm^{-1} on the side of the νCN. The ^{31}P NMR spectrum of the compound displays a sharp peak, probably indicating equivalence of the phosphorus atoms. On the basis of the above data, it is very difficult to draw definite conclusions about the structure of this molecule or to assess how closely it may be related to $[(Ph_3P)_2Cu(BH_3CN)]_2$.

The IR spectra of (DPPM)Cu(BH_3CN) and (DPPE)Cu(BH_3CN) are quite similar in appearance (Figure 16g and 16h), although there are slight differences in the positions of the peaks (Table XV). The sharp absorptions at 2182 and 2185 cm^{-1} have been assigned to CN stretching frequencies of weakly nitrogen coordinated BH_3CN groups, showing shifts only 4 and 6 cm^{-1} respectively from ionic BH_3CN. The peaks at 2105 (DPPM) and 2123 cm^{-1} (DPPE) are possibly due to a Cu-H_b-B frequency.

The ^{31}P NMR spectrum of the DPPM complex displays a split resonance (J=74.4 Hz) centered at -16.2 ppm, indicating the nonequivalence of phosphorus atoms. The spectrum is also accompanied by two other very weak peaks at +26.1 ppm and -6.4 ppm probably due to impurities. The ^{31}P NMR spectrum of the DPPE complex exhibit a broad type peak centered at -4.82 ppm. Thus, the complexes are tentatively formulated as structures as shown below (Figure 18) with a bidentate

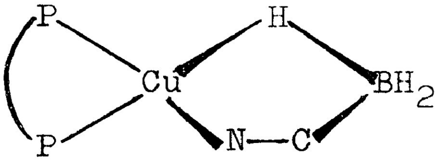

Figure 18

BH_3CN group, coordinated to the metal through both nitrogen and hydrogen. It is unfortunate that low solubilities prevented molecular weight determinations on these compounds.

The complex (DPPH)Cu(BH_3CN) is formed from reactions of both (DPPH)CuCl.0.5CH_2Cl_2 and [(DPPH)$_2$Cu] ClO_4.CH_2Cl_2 with $NaBH_3CN$ and was purified by repeated washings. The IR spectra of samples prepared from both the chloride and the perchlorate are identical and quite similar to that of [$(Ph_3P)_2Cu(BH_3CN)$]$_2$ (Figure 7c,p.34). There is a sharp strong absorption at 2193 cm^{-1} which has been assigned to the coordinated CN stretching frequency. A broad absorption at 2172 cm^{-1} overlapping the CN band has been assigned to the Cu-H_b-B bridging frequency. The terminal BH_t stretching frequency is split and the BH deformation frequency has shifted to much lower energy (1100 cm^{-1}), in comparison with other monodentate N- bonded BH_3CN complexes of the type $(L-L)_3Cu_2(BH_3CN)_2$ as seen in Table XV. The only significant difference between this spectrum and that of the dimeric copper triphenylphosphine complex is that the latter has two sharp νCN absorptions at 2207 and 2190 cm^{-1} compared to only one in the DPPH complex at 2193 cm^{-1}. Thus, the complexes are clearly very closely related structurally and appear to differ only in the site symmetries of the CN groups. This may be connected with the flexible chelating phosphines as compared with the Ph_3P groups.

The infrared spectrum of the complex (DPPPe)Cu(BH_3CN) is shown in Figure 16i. It seems reasonable that the strong peak at 2252 cm^{-1} should be assigned to the coordinated CN frequency of the BH_3CN group which means that, with a shift of 55 cm^{-1} to higher energy from ionic BH_3CN^-, there is a strong Cu-N bond. The broad absorption at 2120 cm^{-1} has been assigned to the bridging Cu-H_b-B frequency. The terminal BH_t absorption has clearly been split, with one component being shifted to higher energy (2438 cm^{-1}). It appears to be quite unusual for the BH_t vibration to occur above 2400 cm^{-1}. The BH deformation frequency has shifted to 1101 cm^{-1} as was the case with the DPPH complex.

Conductivity studies shows that the complex has a slope which is considerably less than expected for a 1:1 electrolyte, so that the conductance of the compound is quite low (see Table XV). The ^{31}P NMR spectrum of the compound displays a fairly sharp signal which seems to be a poorly defined multiplet type of resonance centered at

-7.9 ppm. If the splittings are genuine, and are not due to noise, it is difficult to see how such splittings could arise, bearing in mind the stoichiometry of the complex. However, if they are genuine it is clear that they probably arise from couplings between nonequivalent P atoms separated by not more than three bonds. It is useless to speculate further but in any extension of this work low temperature studies might be useful since, at lower temperatures, dissociation equilibria will be suppressed and more easily interpretable signals might be obtained.

3.6.3 [(cis VPP)$_2$Cu](BH$_3$CN)

This is the only complex of this type obtained with BH_3CN in this work. It is surprising that this complex is formed not from the reaction of [(cis VPP)$_2$Cu]ClO_4 and $NaBH_3CN$ but only from the reaction of $NaBH_3CN$ with a mixture of $CuCl_2.2H_2O$ and cis VPP. Infrared spectral assignments of the BH_3CN group, conductivity, and ^{31}P NMR data of this complex appear in Table XV. Part of the IR spectrum is shown in Figure 16k.

In this complex the CN stretching frequency is seen to remain unshifted with respect to $NaBH_3CN$ and looks weaker in intensity in comparison with other CN coordinated BH_3CN complexes. The terminal BH_3 absorption has not been split. Furthermore, the BH deformation (1130 cm^{-1}) remains unshifted with respect to $NaBH_3CN$. All the IR data point to an ionic BH_3CN group in this molecule. This is further supported by conductivity studies from which it is clear that the complex is a uni-univalent electrolyte (see Table XV). The ^{31}P NMR spectrum displays a very broad absorption (half width 1500Hz) centered at +11 ppm, essentially the same as shown by $[(\underline{cis}\ VPP)_2Cu]ClO_4$. Thus, from the available data the complex can be formulated as $[(\underline{cis}VPP)_2Cu]^+$–$(BH_3CN)^-$.

Table XV. Mol. wt., conductivity, ^{31}P NMR, and infrared spectral data of BH_3CN groups of copper(I) cyanotrihydroborate complexes.

Complex	Mol. wt.[a] (f. wt.)	Conductivity[a] slope[d] $cm^{1/2}equiv^{-1/2}ohm^{-1}$	^{31}P[a] (ppm)	Infrared absorptions of BH_3CN group			
				BH terminal	CN	Cu-H-B	BH deformation
$[(DPPM)Cu(BH_3CN)]_2$	1111 (974.7)		-5.9	2363s 2345s 2250m	2182s 2160m		1116a
$(DPPM)Cu(BH_3CN)$			-16.2	2363s 2340s	2182m	2105m	1119s
$(DPPH)Cu(BH_3CN)$				2380s 2340s 2348sh	2193s	2175m	1100
$(DPPPe)Cu(BH_3CN)$		140	-7.9mt	2438m 2368s	2252s	2120s	1101s
$(DPPE)Cu(BH_3CN)$			-4.82b	2363s 2343s	2185s	2123s	1120s
$(DPPE)_3Cu_2(BH_3CN)_2$	626 (1400)	400	-8.2b +32.6	2332s 2360sh	2185s		1117s
$(DPPP)_3Cu_2(BH_3CN)_2$	688 (1442)	666	-14.2b +30.3w	2370sh 2350s	2188s		1120s
$(DPPH)_3Cu_2(BH_3CN)_2 \cdot CHCl_3$		255	-8.9 +35.5 +33.8vw	2360sh 2345s	2182s		1119s
(<u>trans</u> VPP)$_3Cu_2(BH_3CN)_2$		non electrolyte	-1.96	2365sh 2340s	2176s		1112s
(<u>cis</u> VPP)$_3Cu_2(BH_3CN)_2 \cdot CH_2Cl_2$	703 (1479)	370	+7.5vb +20.6w	2425 m 2380s	2245s		1105
[(<u>cis</u> VPP)$_2$Cu](BH_3CN)		500	+11.3vb	2350s	2179m		1130s

a In CH_2Cl_2 unless otherwise specified. e In $CHCl_3$ d The observed slope is obtained as described in Table XII. Key: b-broad; vb-very broad; vw-very weak; w-weak; mt-multiplet; m-medium; s-strong; sh-shoulder. Conductivities of reference compounds are listed in Table XIII.

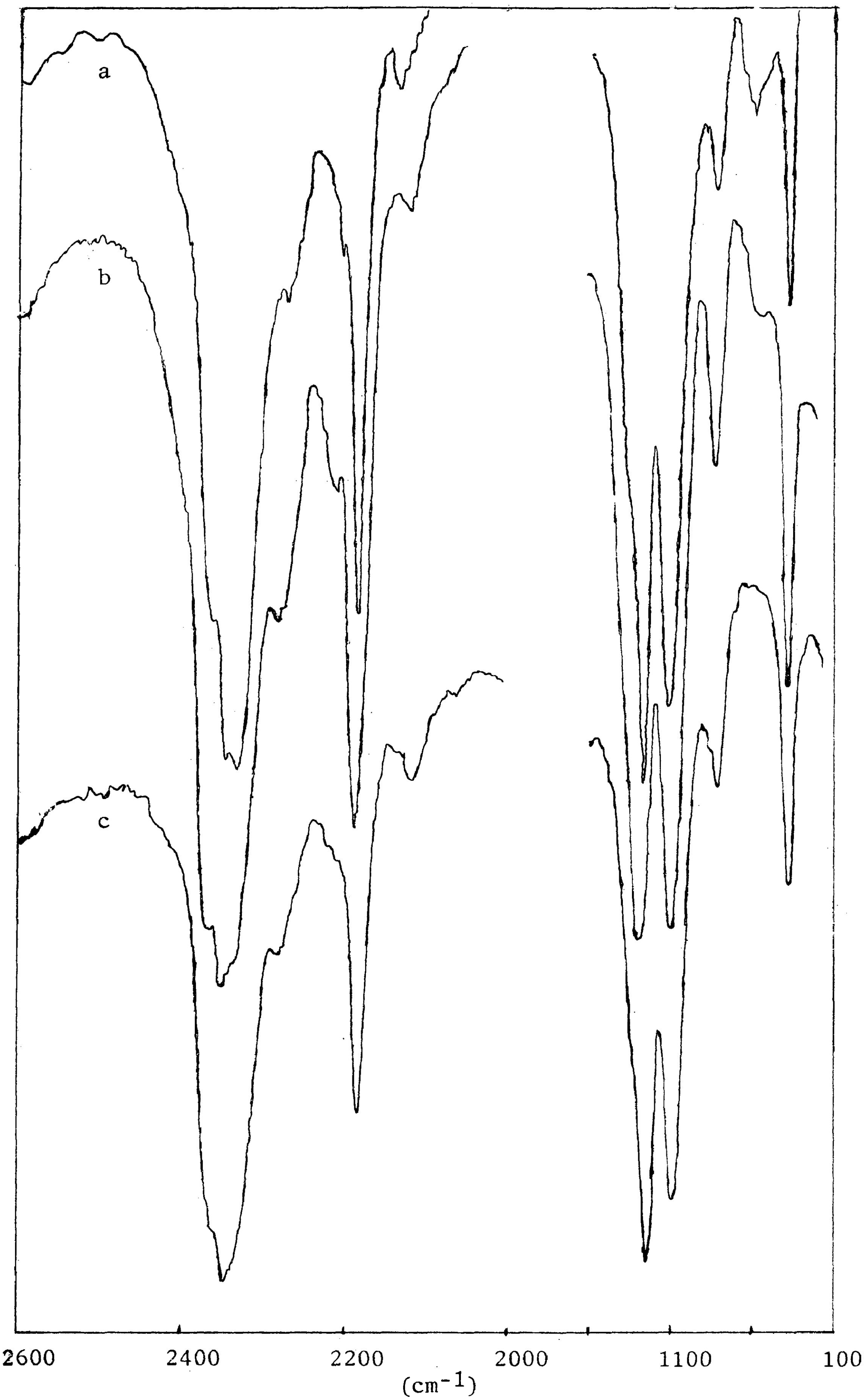

Figure 16. Infrared spectra of BH_3CN absorptions (cm^{-1}) region for (a) $(DPPE)_3Cu_2(BH_3CN)_2$, (b) $(DPPP)_3Cu_2(BH_3CN)_2$ and (c) $(DPPB)_3Cu_2(BH_3CN)_2.CHCl_3$

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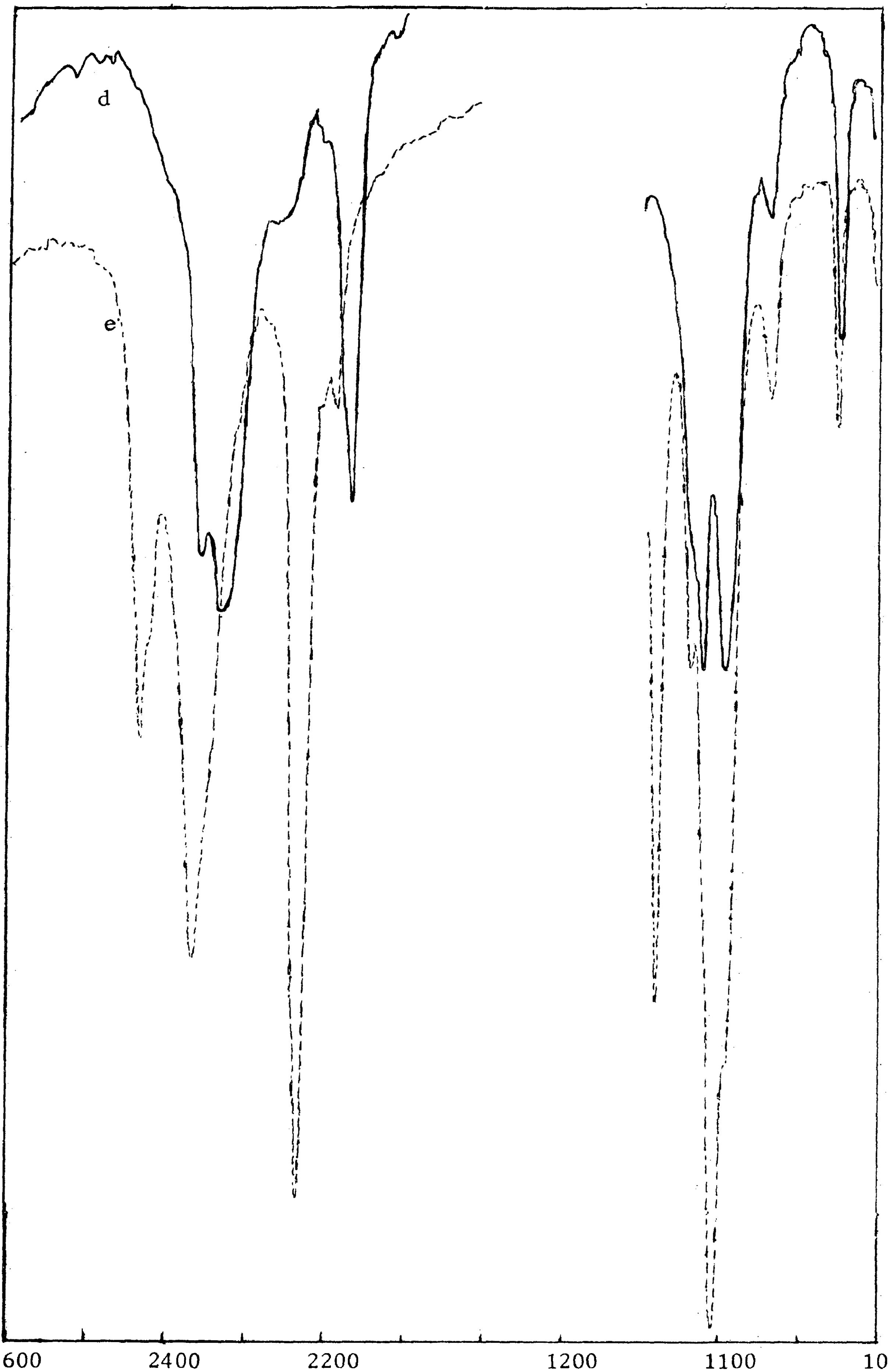

Figure 16 cont'd. (d) (trans VPP)$_3$Cu$_2$(BH$_3$CN)$_2$ and (e) (cis VPP)$_3$-Cu$_2$(BH$_3$CN)$_2$.CH$_2$Cl$_2$

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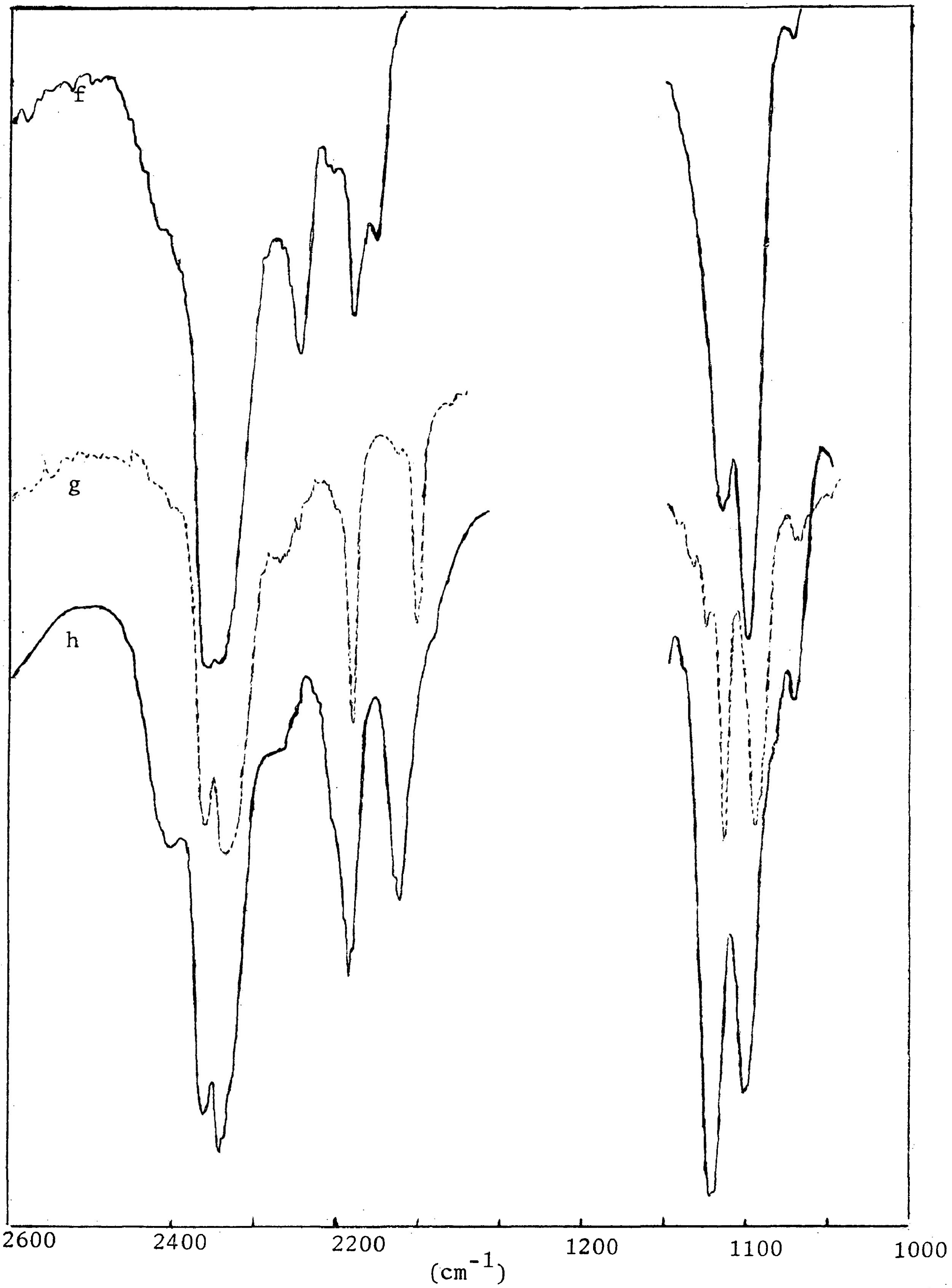

Figure 16 con't. (f) $[(DPPM)Cu(BH_3CN)]_2$, (g) $(DPPM)Cu(BH_3CN)$, and (h) $(DPPE)Cu(BH_3CN)$

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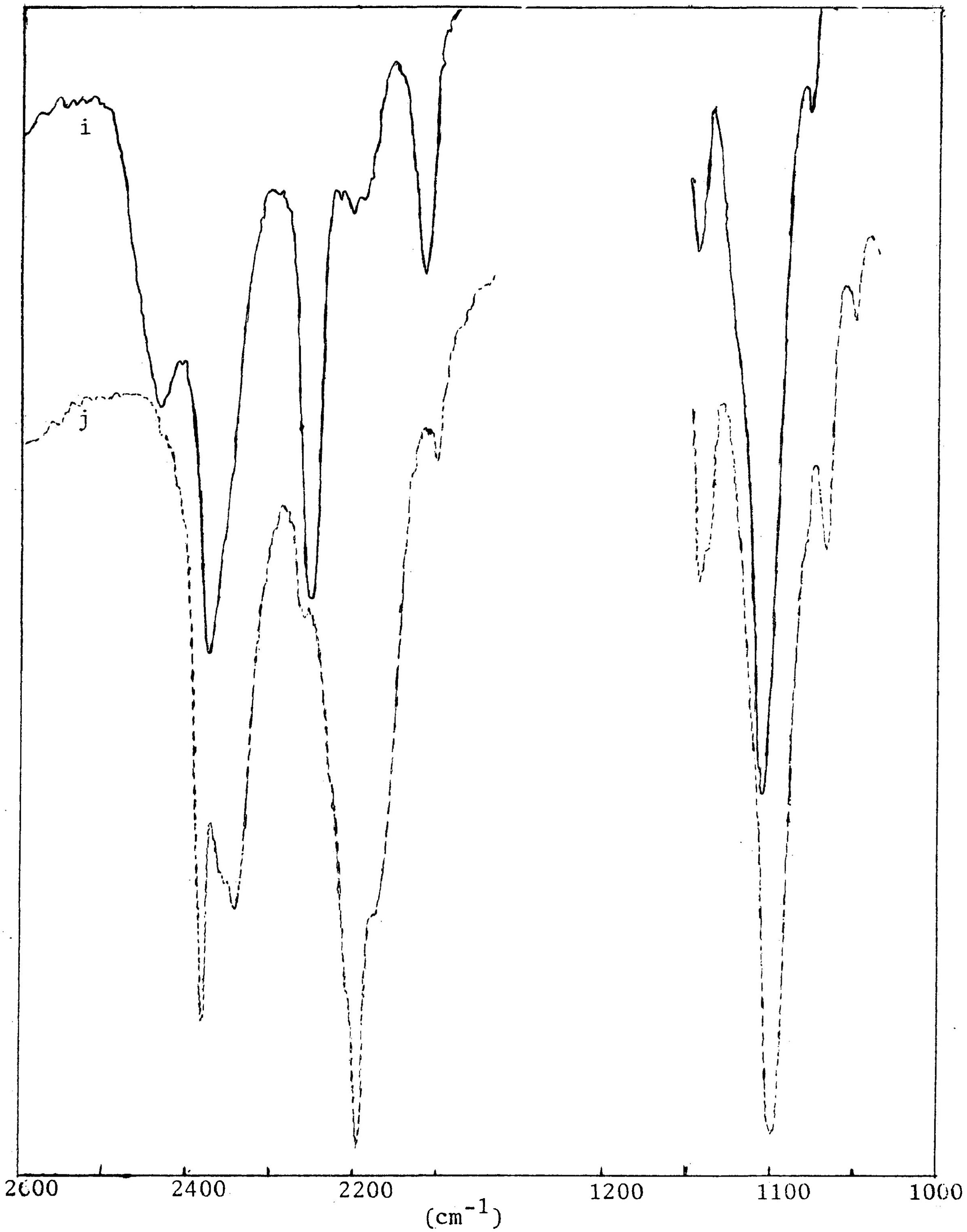

Figure 16 con't. (i) (DPPPe)Cu(BH_3CN) and (j) (DPPH)Cu(BH_3CN)

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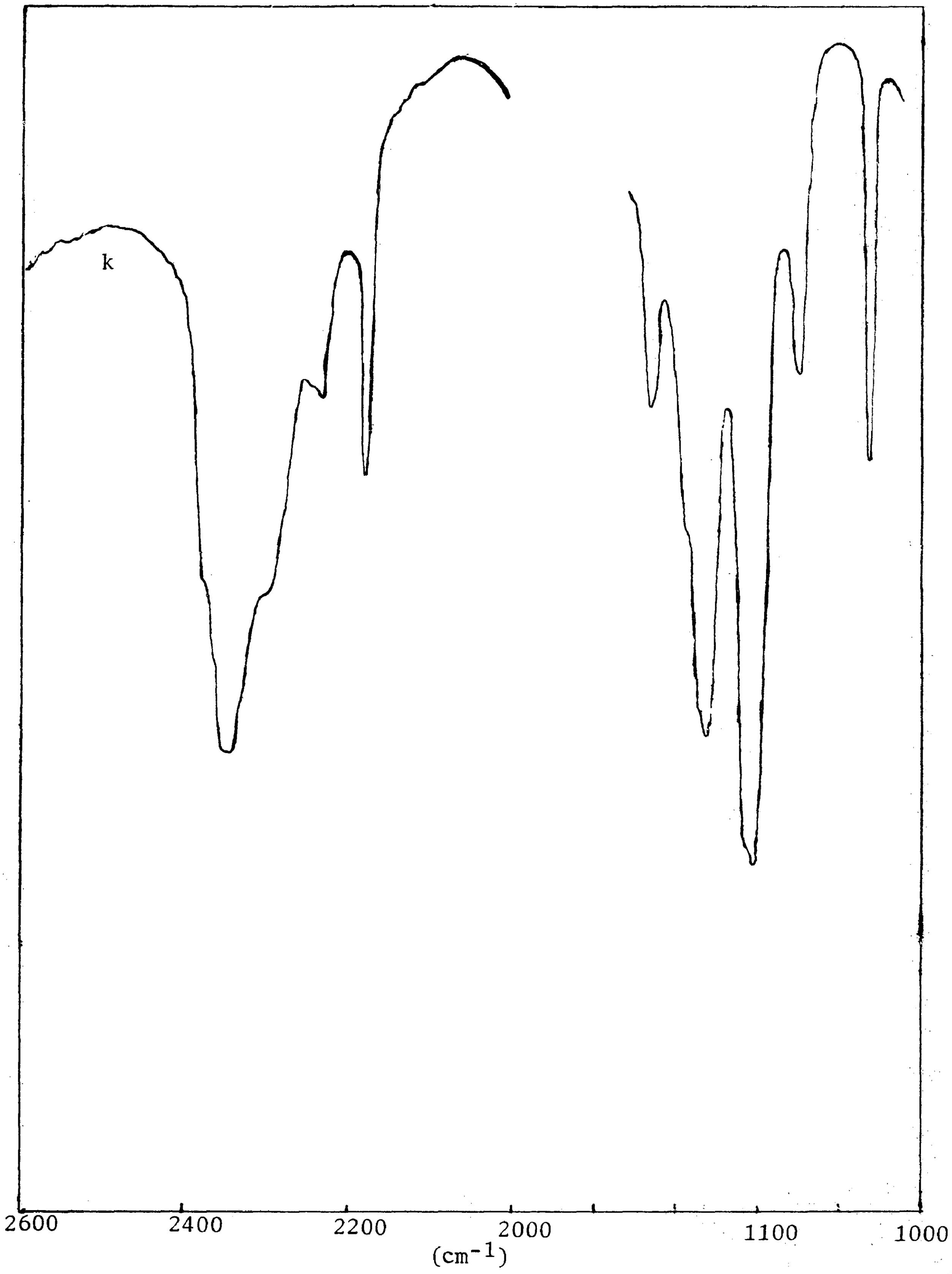

Figure 16 cont'd. (k) [(<u>cis</u> VPP)$_2$Cu] (BH$_3$CN)

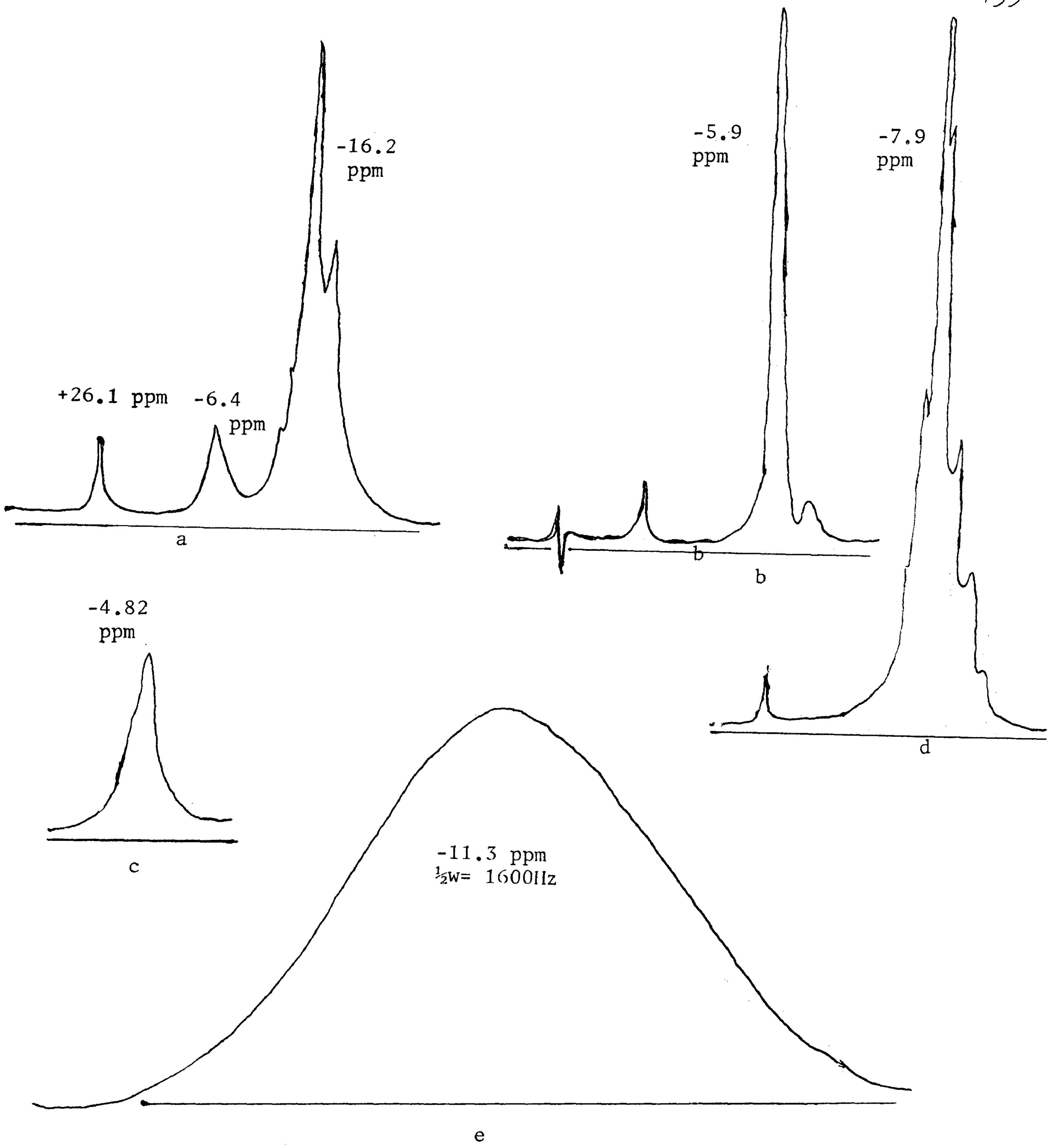

Figure 17. The $^{31}P\{H\}$NMR spectra of (a) (DPPM)Cu(BH_3CN), (b) [(DPPM)Cu(BH_3CN)]$_2$, (c) (DPPE)Cu(BH_3CN), (d) (DPPPe)Cu(BH_3CN) (e) [(cis VPP)$_2$Cu](BH_3CN)

...cont'd

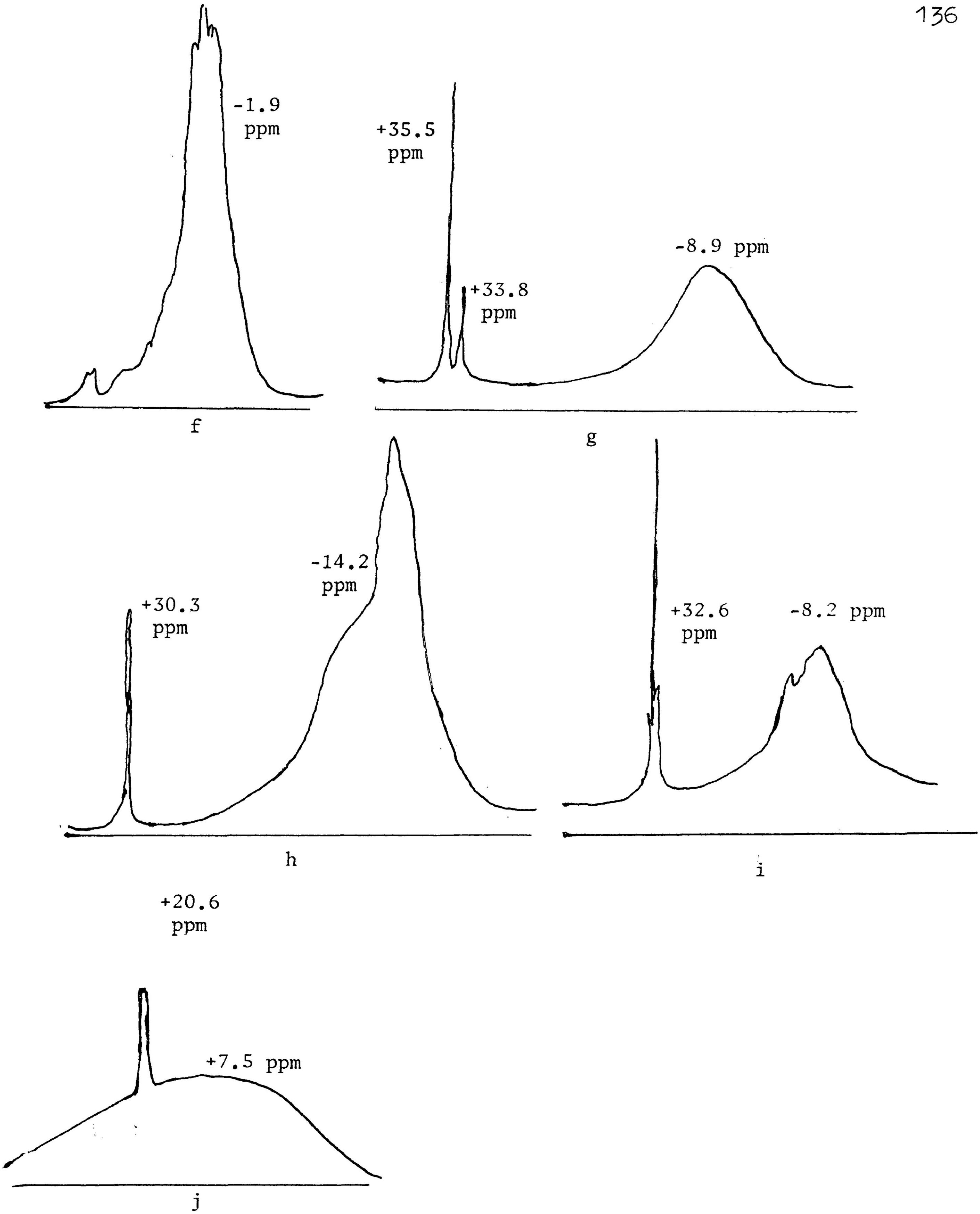

Figure 17 cont'd. (f) (<u>trans</u> VPP)$_3$Cu$_2$(BH$_3$CN)$_2$, (g) (DPPB)$_3$Cu$_2$·(BH$_3$CN)$_2$.CHCl$_3$, (h) (DPPP)$_3$Cu$_2$(BH$_3$CN)$_2$, (i) (DPPE)$_3$Cu$_2$(BH$_3$CN)$_2$ and (j) (<u>cis</u> VPP)$_3$Cu$_2$(BH$_3$CN)$_2$.CH$_2$Cl$_2$

3.7 Conclusions and suggestions for further work:

As proposed for this project (section 1.7), reactions of a series of bidentate phosphines (DPPM, DPPE, trans VPP, cis VPP, DPPP, DPPB, DPPE, DPPH) with copper(II) perchlorate and chloride have been investigated and a variety of stable copper(I) complexes (Table XI) have been obtained with all of the phosphines used. As Cu(I) is less positive than Cu(II), the stability conferred upon Cu(I) by phosphines cannot be wholly accounted for by σ bonding and must therefore involve, perhaps to a major extent, π bonding. In this connection, it is well known that phosphines are suitable π acceptor ligands.

The rate of reduction of Cu(II) to Cu(I) (there appear to be no reports about the formation of stable Cu(II) phosphine complexes in the literature) and product type are seen to be dependent upon the type of phosphine and also the nature of the counter anion. Thus, complexes of the type $(L-L)_2CuX$ are obtained with X= the noncoordinating ClO_4^- ion but not with $X = Cl^-$, since Cl^- is able to compete effectively with phosphines for coordination sites on the Cu(I). Complexes of the above type are obtained with neither L-L =DPPM nor trans VPP and $X=ClO_4^-$, probably because of the bridging tendencies of these phosphines. Instead, with these phosphines, complexes of the type $(L-L)_3Cu_2X_2$ ($X=Cl^-, ClO_4^-$) are obtained (Table XI).

Considering rates of Cu(II) to Cu(I) reduction,

reduction of Cu(II) perchlorate to Cu(I) perchlorate, for example, is seen to occur faster with DPPM than with <u>trans</u> VPP (Table VII). Similarly, Cu(II) chloride is seen to be reduced faster than Cu(II) perchlorate by <u>trans</u> VPP.

Reactions of $NaBH_4$ with all of the phosphine - copper(I) complexes isolated in this study and also with crude Cu(II)-phosphine reaction mixtures have been investigated. Stable tetrahydroborate complexes have been obtained with all of the phosphine complex systems except for L-L=<u>cis</u> VPP.

Tetrahydroborate complexes $(L\text{-}L)Cu(BH_4)$, from reactions of $[(L\text{-}L)_2Cu]ClO_4$ or $(L\text{-}L)_3Cu_2X_2$ ($X=Cl^-, ClO_4^-$) are formed with the loss of neutral phosphine. The rate at which $NaBH_4$ reacts with a given type copper(I) complex system e.g. $[(L\text{-}L)_2Cu]ClO_4$ was found to vary depending on the particular bidentate phosphine in the complex. For example, $(DPPE)Cu(BH_4)$ is formed from $[(DPPE)_2Cu]ClO_4$ by stirring with $NaBH_4$ for four days, whereas $(DPPH)Cu(BH_4)$ is formed from $[(DPPH)_2Cu]ClO_4 \cdot CH_2Cl_2$ after only four hours. Since these reactions result in the elimination of a mole of phosphine, the rate differences could be a reflection of different Cu-P bond strengths - the main difference arising due to different ring sizes, and perhaps steric crowding with longer chain phosphines, on chelation. Thus, considering that the phosphines are behaving as normal chelating ligands (discussed earlier) in $[(DPPE)_2Cu]ClO_4$, the five-membered chelate rings are therefore considerably more stable than the nine-membered ring in the DPPH complex. However, the same DPPE-BH_4 complex was formed from $(DPPE)_3Cu_2Cl_2$ more easily than from $[(DPPE)_2Cu]ClO_4$. In this chloride complex, one of the DPPE bridges two copper atoms and the remaining two DPPE molecules act as normal chelating ligands to each copper, the fourth site of Cu(I) being occupied by a chloride ion (see Figure 7d, P. 34). The first step in formation of $(DPPE)Cu(BH_4)$ from $(DPPE)_3Cu_2Cl_2$ is probably the simple substitution of Cl^- by BH_4^- (which is of almost same size as Cl^-), with the BH_4^- acting as a monodentate ligand. A second Cu-H_b-B bond would then be formed at the expense of neutral phosphine to give a final bidentate BH_4 group.

Thus, the formation of stable hydroborate complexes of Cu(I) might also be expected to depend on the availability of coordination sites on the copper(I) system. It should also be noted that no hydroborate complex could be isolated from reactions of $(DPPE)Cu_2Cl_2$ even with very small amounts of $NaBH_4$. This result possibly indicates that the steric arrangements of the neutral ligands about the Cu(I) ion also play an important role in the formation of stable tetrahydroborate complexes.

It is also apparent that what might be Cu(I)-hydride cluster complexes may be obtained under certain circumstances in reactions of this type. Again, X-ray crystallographic studies would be particularly useful here.

Reactions of $NaBH_3CN$ with all of the phosphine complexes have been investigated and stable cyanotrihydroborate complexes have been obtained with all of the systems investigated. As outlined in the previous section IR spectra of Cu(I)-cyanotrihydroborate complexes of different phosphines differ considerably from each other. Even DPPM complexes with the same empirical formulae have substantially different IR spectra. One might expect the ^{31}P and IR spectra to throw some light on the structures but, as already outlined, these spectra must be interpreted with caution. Definite structure assignments will probably have to await X-ray studies.

In summary, considerable effort has been made to follow the course of the reactions involving $NaBH_4$ and $NaBH_3CN$ to isolate intermediates and final products. Tentative structures of the compounds have been proposed from various physical measurements, but it is clear that some of the complexes obtained in this work no doubt have quite complicated structures, possibly involving polymers and or Cu atoms with different coordination numbers and geometries in the same molecule (as discussed in section 1.4). Detailed crystallographic studies would be required to verify the proposed structures. This would be particularly interesting in the case of the proposed copper(I) hydride complex and would give conclusive information about the molecular formula and the arrangement of the atoms in the molecule.

Infrared spectral studies of the deuterated analogues of the cyanotrihydroborate complexes might give valuable information concerning the tentative IR assignments made in this thesis. NMR studies at low temperatures, at which dissociations or exchange processes are generally slow, might give fine structural information, particularly on the BH_4 and BH_3CN complexes.

It has been found in other work in these laboratories, that one of the important factors which determines the products from reactions involving $NaBH_4$ and $NaBH_3CN$ is the solvent used as the reaction medium. No attempt has been made in this thesis to vary the solvent, and it may very well be that quite different reactions would be observed if the medium were changed.

Preparation of a possible Cu(I)-hydride complex from reaction of $NaBH_4$ with $(DPPE)Cu_2Cl_2$ might be indicative of the fact that hydride complexes could be prepared from reactions of $NaBH_4$ with complexes of such stoichiometry, especially with ligands having bridging tendencies. A mixture of benzene and ethanol might be a good reaction medium to follow such reactions.

It is clear then that Cu(II)-bidentate phosphines-BH_4 or BH_3CN reactions constitute an area of study which is rich in potential for the formation of novel and unexpected structural types and extensions of the work described in this thesis would contribute greatly to our as yet very incomplete understanding of metal ion-hydroborate reactions in general.

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Because of final revisions in this manuscript certain reference numbers appear out of numerical sequence. It was felt by this author that attempts to change the numbers of other references would possibly introduce errors and therefore no attempt to renumber the references was made.