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# Some Copper(I) Complexes of 1-Diphenylphosphino-*ortho*-carborane

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## Abstract

Coordination compounds of the type Cu(HPC)X, $Cu(HPC)_{1.5}X$ and $Cu(HPC)_2X$ where X = Cl, Br or I and HPC = 1-diphenylphosphino-*o*-carborane have been prepared and characterized by IR, Raman, electronic spectroscopy and magnetic and conductivity measurements.

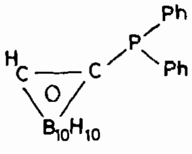
The Cu(HPC)X compounds have been formulated as tetramers possessing a cubane (X = Cl) or chair (X = Br or I) structures. The $Cu(HPC)_{1.5}X$ species are dimeric in the solid state and structures containing both tri and tetracoordinate copper(I) ions linked by halogen bridges are proposed.

Halogen-bridged dimeric structures of $D_{2h}$ symmetry have been found for the solids with formula $Cu(HPC)_2X$.

## Introduction

In previous papers [1–3] we reported the studies of a number of complexes of Pd(II), Co(II) and Ni(II) with a series of tertiary phosphines containing *ortho*-carborane as a backbone. The ditertiary phosphines 1,2-bis(diphenylphosphine)-*o*-carborane and 1-bis(dimethylamino)phosphino-2-diphenylphosphino-*o*-carborane produce the expected *cis* square-planar $PdLX_2$ or the pseudotetrahedral $CoLX_2$ complexes where X = Cl, Br, or I.

The tertiary phosphine 1-diphenylphosphino-*o*-carborane (HPC) yielded the *trans* planar $PdL_2X_2$ species. In the present paper we report the coordination compounds of this phosphine with copper(I) halides



· HPC

Copper(I) halides form a series of complexes with tertiary phosphines in which the ligand/metal ratio varies from 1 to 4. The stabilities of these species seem to be controlled by steric rather than electronic effects. In fact, the stability increases in the order $PPh_3 \ll MePh_2 \simeq Me_2PhP$. For the $Cu(Me_3P)_nX$ species a tetrameric structure has been proposed when $n = 1$, whereas for $n = 3$ a tetrahedral monomeric species has been found [4].

X-ray crystal structure determinations have shown that the $[Cu(PR_3)X]_4$ complexes possess either a cubane or a chair conformation [5, 6]. In fact, when X is chloride a cubane structure is found [7], whereas for the bromide and iodide derivatives the tetrameric complexes have a chair conformation [7, 8]. In the cubane and chair structures each copper(I) atom is bonded to a phosphine ligand and is connected with other copper(I) atoms through halogen bridges.

The $Cu_2Cl_2(PPh_3)_3$ species possesses a structure that contains three and four coordinate copper(I) atoms [9, 10].

The reaction of copper(I) halides with the tertiary phosphine HPC in different molar ratios produces complexes of the type Cu(HPC)X, $Cu(HPC)_{1.5}$-X (hereafter formulated as $Cu_2(HPC)_3X_2$) and $Cu(HPC)_2X$ which have been analytically and spectroscopically characterized. By analogy with previously reported phosphine complexes of copper(I), tetrameric or simple halogen-bridged structures are proposed.

## Experimental

### *Preparation*

The HPC ligand was prepared as described elsewhere [11, 12], whereas the complexes were prepared as follows:

#### *Cu(HPC)X; X = Cl, Br or I*

To an ethanolic solution of 1 mmol of $CuX_2$, 2 mmol of HPC dissolved in the same solvent were added. The reaction mixtures were reflexed under nitrogen for 1 h, then cooled to 0 °C and left at this temperature for 48 h. The powdered solids so obtained were filtered off, washed with cold ethanol and dried.

#### *$Cu_2(HPC)_3X_2$; X = Cl, Br*

To prepare these complexes the same procedure described above was used, but the $CuX_2$/HPC molar ratio was 1:3.

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TABLE I. Analytical, Conductivity and Magnetic Data for the HPC Complexes of Copper(I) Halides[a]

| Complex | | C% | H% | Cu% | $\Lambda_M^{20}$ [b] | $\chi_M^{corr} \times 10^6$ |
|---|---|---|---|---|---|---|
| CuCl(HPC) | I | 39.4(39.3) | 5.8(5.0) | 14.9(14.9) | 0.06 | 117.8 |
| CuBr(HPC) | II | 35.0(35.6) | 4.5(4.5) | 13.3(13.5) | 0.23 | 121.5 |
| CuI(HPC) | III | 32.5(32.4) | 4.2(4.1) | 12.2(12.3) | 0.00 | 91.2 |
| $CuCl(HPC)_{1.5}$ | IV | 42.9(42.6) | 6.0(5.3) | 10.3(10.7) | 0.00 | 61.5 |
| $CuBr(HPC)_{1.5}$ | V | 40.0(39.7) | 5.6(5.0) | 10.4(10.0) | 0.12 | 54.7 |
| $CuCl(HPC)_2$ | VI | 44.9(44.5) | 5.2(5.6) | 8.7(8.4) | 0.23 | 80.6 |
| $CuBr(HPC)_2$ | VII | 41.7(42.0) | 5.8(5.3) | 7.3(7.9) | 0.13 | 86.4 |
| $CuI(HPC)_2$ | VIII | 40.1(39.7) | 4.9(5.0) | 7.7(7.5) | 0.08 | 65.0 |

[a] HPC = $B_{10}H_{21}C_{14}P$; calculated values are given in parentheses. [b] Molar conductivities for mM solution.

*$Cu(HPC)_2X$; X = Cl, Br or I*

To a warmed ethanolic solution of 1 mmol of the Cu(HPC)X complexes, 2 mmol of HPC dissolved in the same solvent were added dropwise. The reaction mixture was then refluxed for 1 h to obtain a clear solution. The solvent was partially pumped off and the remaining was left at 0 °C for several hours. The solids were filtered off, washed with cold ethanol and dried.

Table I presents the analytical, conductivity and magnetic data for the compounds reported here.

*Physical Measurements*

The conductivity and magnetic measurements were carried out as described previously [1, 2]. The electronic and IR spectra were obtained as described elsewhere [3]. The Raman spectra were obtained on powdered solid in capillary tubes as described in ref. 13.

## Results and Discussion

The conductivity measurements show that the complexes are non-electrolytes in dichloromethane. Typical values for such electrolytes are 0–10 mhos $cm^2$ $mol^{-1}$ [14]. The magnetic data indicate that all compounds are diamagnetic and hence they can confidently be formulated as Cu(I) complexes.

The IR spectra show the typical bands of the HPC ligand. The *o*-carborane vibrations are shifted only a few $cm^{-1}$ implying that the cage is not strongly perturbed on coordination (see Table II). The compounds **I** to **VIII** show a medium to weak band at *ca.* 3030 $cm^{-1}$ which has been assigned to the C–H stretching mode of the carborane cage. The shift of *ca.* 20 $cm^{-1}$ detected in the complexes can be attributed to a weakening of the C–H bond due to a probable C–H···X interaction in the solid state [15] and not to a carbon coordination. The in-plane deformation modes of the phenyl groups are shifted to higher frequencies as a result of the phosphine coordination [16]. In fact, Sandhu and Mehta [17] have observed shifts of such magnitudes in some $PPh_3$ complexes and used them as a criterion for phosphorus coordination. The P–C (phenyl) stretching mode is also shifted in keeping with a phosphorus coordination of the HPC ligand.

TABLE II. Selected IR Bands of the HPC Complexes of Copper(I)

| Compound | $\nu$(C–H) | Phenyl deformation[a] | $\nu$(P–C) phenyl | Deformation cage |
|---|---|---|---|---|
| HPC | 3050m | 1435s | 1090s | 740s, 720m |
| I | 3030w | 1449s | 1099s | 741s, 730m |
| II | 3030w | 1445s | 1095s | 744s, 738m |
| III | 3012m | 1437s | 1094s | 735s, 719m |
| IV | 3049w | 1449s | 1099s | 750s, 729s |
| V | 3012m | 1439s | 1094s | 746s, 736s |
| VI | 3021m | 1436s | 1093s | 744s, 739s |
| VII | 3030m | 1437s | 1093s | 741s, 720m |
| VIII | 3049m | 1436s | 1093s | 742s, 737s |

[a] In-plane deformation mode of the phenyl ring.

The Raman spectra of the solids are given in Table III. The observed Raman frequencies agree well with the far-IR absorption bands given by Boon-Keng Teo and Barnes [18] for some $PPh_3$ complexes of the type $Cu_mX_m(PPh_3)_n$ where $n = 3$ or 4 and $m = 1, 2$ or 4. In the cubane-like $(PPh_3)_4Cu_4Cl_4$ species the two bands located at 181 and 162 $cm^{-1}$ were assigned to $\nu_3$ triple bridging stretching modes. In fact, complex **I** shows the above modes at 180 and 169 $cm^{-1}$ implying that this compound would also possess such a structure. For complexes **II** and **III** two bands located in the same frequency region of the triple bridging stretching mode of a chair conformation were observed.

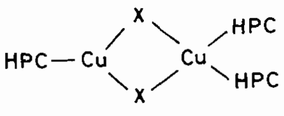
The Raman spectrum of compound **III** also shows a band at *ca.* 178 $cm^{-1}$ probably due to the double bridging stretching mode of the chair conformation. In compound **II** this mode is likely to be covered by the broad band at 177 $cm^{-1}$. Unfortunately the low solubility of these compounds precluded their molecular weight determinations, although it is worth

TABLE III. Raman Bands of the HPC Complexes of Copper(I) Halides

| Complex | $\nu$(Cu–X) | $\nu$(Cu–P) | Other bands |
|---|---|---|---|
| I | 180ms<br>169mw | 111m | 333ms, 256m, 216w |
| II | 177ms, br<br>129m | 109m | 402w, 334m, 259m<br>216w |
| III | 178w<br>164s<br>130ms | 109ms | 381w, 329m, 268mw<br>215w |
| IV | 229m | 102m | 356mw |
| V | 175ms<br>140ms | 108ms | 333m, 222mw |
| VI | 218m | 121m | 187m |
| VII | 172ms | 103m | 126mw |
| VIII | 168s | 110m | 71w |

noting that the cubane structure proposed for the solid Cu(HPC)Cl may not be present in solution. In fact, as pointed out by Churchill and Kabra [19] the stabilization of a cubane or a chair conformation will depend on (i) the minimization of the X---X non-bonding contacts; (ii) the relative stability of the trigonal coordination with respect to the tetrahedral one; (iii) the relative stability of the double over the triple bridge; (iv) the steric and electronic factors of the other ligands attached to Cu(I); and (v) crystal packing effects. In the tetrameric [Cu(HPC)X]$_4$ the replacement of a chloride by the bulkier bromide or iodide increases the non-bonding repulsions and therefore the chair conformation should be preferred.

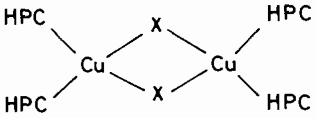
For the $(PPh_3)_3Cu_2X_2$ complex bands at *ca.* 220 and 179 cm$^{-1}$ (X = Cl), 180 and 128 cm$^{-1}$ (X = Br) and 163 and 107 cm$^{-1}$ (X = I) were reported [18]. In compounds **IV** and **V** which have the same stoichiometry, we observed just one band located at 229 cm$^{-1}$ (**IV**) which has been assigned to the double-bridging Cu–X–Cu stretching mode, whereas in complex **V** the two bridging modes were detected in keeping with a structure of the type **A**.



**A**

This unusual structure has been found in similar complexes whose X-ray crystal structure determinations [9, 10] reveal the presence of a trigonal and a tetrahedral copper(I) atom.

The compounds with $Cu(HPC)_2X$ stoichiometry (**VI–VIII**) are probably dimers with halogen bridges. In fact, the Raman spectra of these compounds show the Cu–X stretching modes in the region of a halogen-bridged structure. Unfortunately no other structural information can be obtained in the absence of the far-IR spectra. These species would possess a type **B** structure



**B**

of $D_{2h}$ symmetry and hence the natural exclusion selection rule must be operating.

The electronic spectrum (Table IV) of the free HPC shows a strong unstructured absorption band at 274 nm which has been assigned to a transition within the phenyl groups [1–3]. In the coordination

TABLE IV. Electronic Spectra (nm) of the HPC Complexes of Copper(I) Halides[a]

| Compound | $\lambda_{max}$ | | | Assignment[c] |
|---|---|---|---|---|
| | X = Cl | X = Br | X = I | |
| CuX(HPC) | 275(4235)[b]<br>268(5200)[b]<br>261(5540)[b]<br>234(11200) | 275(4730)[b]<br>268(5730)[b]<br>260(6380)[b]<br>236(17700) | 275(4600)[b]<br>268(5630)[b]<br>260(6040)[b]<br>233(12440) | $^1L_a$ $\pi \to \pi^*$<br>$^1L_a$ $\pi \to \pi^*$<br><br>$n \to \pi^*$ |
| $Cu_2X_2(HPC)_3$ | 275(7940)[b]<br>268(9800)[b]<br>258(10500)[b]<br>236(33200) | 274(10370)[b]<br>266(14600)[b]<br>258(18160)[b]<br>236(44200) | | $^1L_a$ $\pi \to \pi^*$<br>$^1L_b$ $\pi \to \pi^*$<br><br>$n \to \pi^*$ |
| $CuX(HPC)_2$ | 275(6130)[b]<br>269(6900)[b]<br>261(7100)[b]<br>239(15100) | 275(4450)[b]<br>268(5770)[b]<br>260(6500)[b]<br>236(18800) | 275(6870)[b]<br>268(8640)[b]<br>261(9300)[b]<br>237(14380) | $^1L_a$ $\pi \to \pi^*$<br>$^1L_b$ $\pi \to \pi^*$<br><br>$n \to \pi^*$ |

[a] Molar absorptivity at band maximum given in parentheses. [b] Shoulder. [c] Notation after Platt [20].

compounds reported here the vibrational structure of the phenyl transition has been restored in keeping with a decrease in the perturbation of the phenyl groups upon coordination. In the free $PPh_3$ the unstructured form of the band located at 261 nm is attributed to a resonance interaction over the whole molecule by the lone-pair of electrons on the phosphines atom [21, 22]. Therefore, the appearance of this vibrationally structured band can also be taken as evidence for phosphorus coordination.

## Conclusions

The IR, Raman and electronic spectra provide reasonable evidence for a cubane structure of compound I, whereas **II** and **III** would possess a chair conformation. Compounds **IV** and **V** are of interest since they contain both trigonal and tetracoordinate copper(I) ions. The compounds **VI**, **VII** and **VIII** possess halogen-bridged structures with both copper(I) atoms being four-coordinated.

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