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**Registry No.** **1**, 110077-84-4; **2**(OTf)$_2$, 122070-54-6; **2**($PF_6$)$_2$, 122070-55-7; **2**($BF_4$)$_2$, 110077-73-1; **2**(I)$_2$, 122070-69-3; CpRu($PPh_3$)$_2$Cl, 32993-05-8; CpRu($PPh_3$)$_2$H, 34676-08-9; [CpRu($PPh_3$)]$_2$$S_6$, 122070-48-8; CpRu($PPh_3$)(CO)(SH), 122070-50-2; [CpRu($PPh_3$)$_2$($SH_2$)]OTf, 122070-52-4; CpRu($PPh_3$)$_2$OTf, 113322-93-3; [CpRu($PPh_3$)$_2$$H_2$]OTf, 122070-53-5; [CpRu($PPh_3$)$_2$]$_2$($\mu$-$S_2H_2$)[$PF_6$]$_2$, 122070-57-9; CpRu($PPh_3$)$_2$I, 34692-10-9; [CpRu($PPh_3$)$_2$]$_2$($\mu$-$S_2$)[OTf], 122070-58-0; [CpRu($PPh_3$)$_2$($SC_2H_4$)]OTf, 113322-95-5; [CpRu($PPh_3$)$_2$]$_2$($\mu$-SH)[OTf], 122070-60-4; [CpRu($PPh_3$)$_2$($CH_3SH$)]OTf, 122070-62-6; [(ThiCp)Ru($PPh_3$)$_2$]OTf, 122070-63-7; (ThiCp)Ru($PPh_3$)$_2$Cl, 98217-94-8; (ThiCp)Ru($PPh_3$)$_2$SH, 122092-65-3; (ThiCp)Ru($PPh_3$)$_2$H, 122092-66-4; [(ThiCp)Ru($PPh_3$)$_2$]$BF_4$, 98217-96-0; $H_2S$, 7783-06-4; [(ThiCp)Ru($PPh_3$)$_2$($SH_2$)]$BF_4$, 122070-65-9; [(ThiCp)Ru($PPh_3$)$_2$$H_2$]OTf, 122092-68-6; [(ThiCp)Ru($PPh_3$)$_2$$H_2$]$BF_4$, 122170-09-6; [CpRu($PPh_3$)$_2$(HSPr)]$BF_4$, 122070-67-1; [CpRu($PPh_3$)$_2$(HSPr)]$BF_4$·$CH_2Cl_2$, 122070-68-2; [CpRu($PPh_3$)]$_2$$S_4$, 122070-49-9; thiirane, 420-12-2; thiophene, 110-02-1.

**Supplementary Material Available:** Tables of idealized hydrogen coordinates and thermal parameters (4 pages); a table of structure factors (18 pages). Ordering information is given on any current masthead page.

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# Structural, Vibrational, and Solid-State NMR Studies of the Halogenocuprate(I) Complexes $[(PPh_3)_2CuI_2]^-$ and $[(PPh_3)CuI_3Cu(PPh_3)]^-$

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Single-crystal X-ray diffraction, vibrational spectroscopy, and solid state $^{31}P$ NMR spectroscopy have been used to characterize two new types of ionic copper(I) complexes. The anion in $[PPh_3Me]^+[(PPh_3)_2CuI_2]^-$ contains two $PPh_3$ ligands coordinated to the copper atom of a $CuI_2$ unit in a pseudotetrahedral arrangement, with Cu–P = 2.292 (2), 2.288 (2) Å, Cu–I = 2.692 (1), 2.702 (1) Å, P–Cu–P = 121.24 (9)°, and I–Cu–I = 108.62 (4)° (monoclinic, $P2_1/c$, $a$ = 12.138 (5) Å, $b$ = 14.776 (6) Å, $c$ = 28.197 (14) Å, $\beta$ = 103.76 (4)°, $Z$ = 4, $R$ = 0.040 for 4490 "observed" ($I > 3\sigma(I)$) reflections). The far-IR spectrum shows a strong band at 118 $cm^{-1}$ that is assigned to the antisymmetric Cu–I stretching mode of the $CuI_2$ unit. The CPMAS $^{31}P$ NMR spectrum shows a strong singlet at 18.1 ppm (relative to 85% $H_3PO_4$) due to the cation and a weaker quartet centered at −16.7 ppm due to the coordinated $PPh_3$ in the anion, with line spacings due to Cu–P coupling of 1.08, 1.20, and 1.23 kHz. The anion in $[PPh_3Me]^+[(PPh_3)CuI_3Cu(PPh_3)]^-$ consists of an approximately $D_{3h}$ $Cu_2I_3$ unit with three iodine atoms bridging the two copper atoms and with one $PPh_3$ molecule completing a pseudotetrahedral arrangement around each copper atom. The crystallographically imposed symmetry of the ion is $C_{3v}$, with the 3-fold axis passing through the P–Cu bonds. The core structural parameters are Cu–P = 2.215 (3), 2.202 (3) Å, Cu–I = 2.701 (2), 2.730 (2) Å, P–Cu–I = 116.83 (8), 118.05 (8)°, I–Cu–I = 101.21 (5), 99.70 (5)°, and Cu–I–Cu = 54.88 (4)° (cubic, $P2_13$, $a$ = 17.744 (10) Å, $Z$ = 4, $R$ = 0.036 for 1390 "observed" reflections). This is the first reported example of a binuclear copper(I) complex with three bridging ligands and is an example of an unusual bonding situation in which two coordination tetrahedra are linked by sharing a common face. This has the effect of producing an unusually short Cu- - -Cu separation of 2.50 Å. The far-IR spectrum shows a band at 127 $cm^{-1}$ that is assigned to the doubly degenerate perpendicular Cu–I stretching mode of the $Cu_2I_3$ unit. The CPMAS $^{31}P$ NMR spectrum shows a strong singlet at 20.1 ppm due to the cation and a broad quartet centered at −15.8 ppm due to the coordinated $PPh_3$ in the anion. The splitting pattern for this quartet does not conform to expectations for an AX spin system involving coupling between $I = {}^1/_2$ and $I = {}^3/_2$ nuclei. The assignments of the $\nu$(Cu–I) IR bands in both complexes are supported by approximate normal-coordinate analyses, and the resulting Cu–I force constants are compared with the values obtained in similar analyses of related iodocopper(I) complexes.

## Introduction

Copper(I) exhibits a remarkable diversity in its structural chemistry. This is demonstrated by the wide variety of structural types that are encountered in complexes of the copper(I) halides. Copper(I) halides form mononuclear or multinuclear complexes with neutral phosphine or amine ligands in which the copper coordination number ranges from 2 to 4.[2-4] Halogenocuprate(I) complexes, formed by the reaction of copper(I) halides with halide ion, likewise show a wide diversity of mononuclear and multinuclear structures, although there is a noticeable preference for lower coordination numbers; in such complexes the coordination number 4 is only found in oligomeric or infinite polymeric structures.[2,3,5,6]

Little work has been done to investigate the structures and properties of complexes that result from the reaction of the potentially coordinatively unsaturated halogenocuprates(I) (e.g. $[CuX_2]^-$, $[CuX_3]^{2-}$, $[Cu_4X_6]^{2-}$, etc.) with neutral ligands such as phosphines and amines. We have recently shown that the anionic bromocuprate(I) complex $[CuBr_2]^-$ reacts with 1 mol of triphenylphosphine, $PPh_3$, to yield the species $[(PPh_3)CuBr_2]^-$, in which the copper(I) ion has the unusual coordination number of

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**Table I.** Summary of Crystal Data for $[PPh_3Me][(PPh_3)_2CuI_2]$ and $[PPh_3Me][(PPh_3)_2Cu_2I_3]$

| | $[PPh_3Me]$-$[(PPh_3)_2CuI_2]$ | $[PPh_3Me]$-$[(PPh_3)_2Cu_2I_3]$ |
|---|---|---|
| formula | $C_{55}H_{48}CuI_2P_3$ | $C_{56}H_{49}Cl_3Cu_2I_3P_3$ |
| $M_r$ | 1119.3 | 1429.1 |
| cryst syst | monoclinic | cubic |
| space group | $P2_1/c$ ($C_{2h}^5$, No. 14) | $P2_13$ ($T^4$, No. 198) |
| $a$/Å | 12.138 (5) | 17.744 (10) |
| b/Å | 14.776 (6) | |
| $c$/Å | 28.197 (14) | |
| $\beta$/deg | 103.76 (4) | |
| $V$/Å$^3$ | 4912 (4) | 5589 (8) |
| $Z$; $D_c$/g cm$^{-3}$ | 4; 1.51 | 4; 1.70 |
| $\mu_{Mo}$/cm$^{-1}$ | 17.1 | 25.3 |
| $N$, $N_o$ | 8137, 4490 | 1837, 1390 |
| $R$ | 0.040 | 0.036[a] |
| $R_w$ | 0.036 | 0.029 |

[a] Preferred chirality.

3.[7] We now report the results of similar experiments carried out to characterize the products of reaction of $PPh_3$ with iodocuprate(I) complexes. Two different compounds have been identified to date. The first is $[PPh_3Me][(PPh_3)_2CuI_2]$, which contains the mononuclear anion $[(PPh_3)_2CuI_2]^-$. The second is $[PPh_3Me][(PPh_3)_2Cu_2I_3]$, which contains the binuclear anion $[(PPh_3)_2Cu_2I_3]^-$. In both cases the copper atoms exhibit 4-coordination. We report the preparation of these compounds and their characterization by X-ray diffraction and vibrational and solid-state (CPMAS) NMR spectroscopy.

## Experimental Section

**Preparation of Compounds. Methyltriphenylphosphonium Bis(triphenylphosphine)diiodocuprate(I), $[PPh_3Me][(PPh_3)_2CuI_2]$.** Copper(I) iodide (0.48 g, 2.5 mmol), methyltriphenylphosphonium iodide (1.01 g, 2.5 mmol), and triphenylphosphine (1.31 g, 5.0 mmol) were added to dichloromethane (20 mL), and the mixture was stirred until all the solid material had dissolved. The colorless product was precipitated from the resulting pale yellow solution by the addition of diethyl ether. The product was recrystallized from dichloromethane/diethyl ether; mp 189–190 °C. Anal. Calcd for $C_{55}H_{48}CuI_2P_3$: C, 59.0; H, 4.3; Cu, 5.7; I, 22.7; P, 8.3. Found: C, 58.9; H, 4.1; Cu, 5.8; I, 23.2; P, 8.2. The crystals for the X-ray diffraction study were obtained by recrystallization from acetone/*n*-heptane.

**Methyltriphenylphosphonium Bis(triphenylphosphine)triiododicuprate(I), $[PPh_3Me][(PPh_3)_2Cu_2I_3]$.** Bis(methyltriphenylphosphonium) hexaiodotetracuprate(I), $[PPh_3Me]_2[Cu_4I_6]$,[8] (0.63 g, 0.4 mmol) and triphenylphosphine (0.45 g, 1.7 mmol) were dissolved in dichloromethane (25 mL). The colorless product was precipitated from the resulting solution by the addition of diethyl ether. The product was recrystallized from dichloromethane/diethyl ether; mp 167–168 °C. Anal. Calcd for $C_{55}H_{48}Cu_2I_3P_3$: C, 50.4; H, 3.7; Cu, 9.7; P, 7.1. Found: C, 50.8; H, 3.6; Cu, 9.5; P, 7.2. The crystals for the X-ray diffraction study were obtained by recrystallization from chloroform and included a solvate chloroform molecule.

**Structure Determinations.** A summary of crystal data is presented in Table I. Unique data sets were measured at ≈295 K by using specimens mounted in capillaries, within the limits $2\theta_{max} = 50$ and 45°, respectively (ENRAF-Nonius CAD-4 "four-circle" diffractometer, monochromatic Mo K$\alpha$ radiation $\lambda = 0.7106_9$ Å), conventional $2\theta/\theta$ scan mode), yielding $N = 8137$ and 1837 independent reflections; of these $N_o$ with $I > 3\sigma(I)$ were considered "observed" and used in the full-matrix least-squares refinement on $|F|$, minimizing $\sum w\Delta^2$ after Gaussian absorption correction and solution of the structures by vector and direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Weights of $1/\sigma^2(F)$, the derivative of $\sigma^2(I_{diff}) + 0.000n\sigma^4(I_{diff})$, were used. Each structure refined smoothly in the chosen space group; in the second structure, the chloroform of solvation was modeled as disordered. No correction for extinction was required. Neutral atom complex scattering factors were employed,[9] computation using the XTAL 2.4 program system.[10] Conventional residuals on $|F|$, $R$, and $R_w$ are quoted. Non-hydrogen atom coordinates are given in Tables II and III. The structures of the anions are given in Figures 1 and 2.

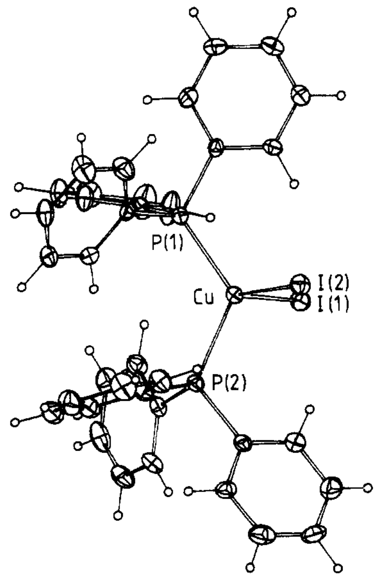

**Figure 1.** Structure of $[(PPh_3)_2CuI_2]^-$ in $[PPh_3Me][(PPh_3)_2CuI_2]$. 20% thermal ellipsoids are shown. Hydrogen atoms have an arbitrary radius of 0.1 Å.

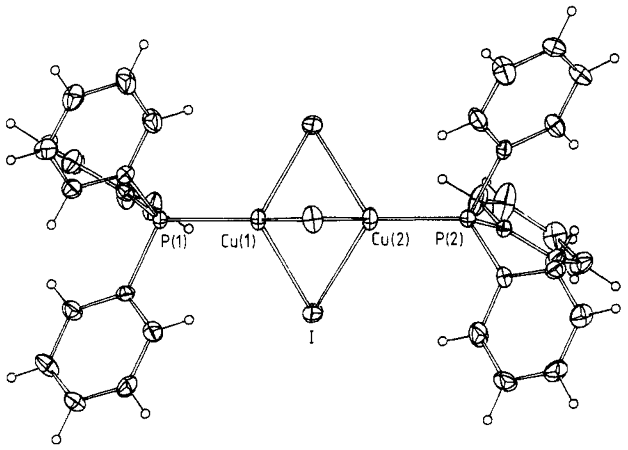

**Figure 2.** Structure of $[(PPh_3)_2Cu_2I_3]^-$ in $[PPh_3Me][(PPh_3)_2Cu_2I_3]$. 20% thermal ellipsoids are shown. Hydrogen atoms have an arbitrary radius of 0.1 Å.

**Spectroscopy.** Far-infrared spectra were recorded at room temperature as petroleum jelly mulls between polythene plates on a Digilab FTS-60 Fourier transform infrared spectrometer employing a FTS-60V vacuum optical bench with a 6.25-$\mu$m Mylar film beam splitter, a mercury-lamp source, and a TGS detector. Raman spectra were recorded at room temperature and ca. 77 K by using a Dilor OMARS 89 Raman spectrometer with a Princeton Applied Research multichannel (512 channels) detector. The spectra were recorded by using the 514.5-nm line of a Spectra Physics Series 2000 $Ar^+$ laser and were recorded for powdered samples by using 0° backscattering. Solid-state $^{31}P$ NMR spectra were obtained at room temperature on a Bruker CXP-300 spectrometer at 121.47 MHz by using $^1H$–$^{31}P$ cross-polarization with radio-frequency fields of 8 and 20 G for $^1H$ and $^{31}P$ respectively. Chemical shifts were referenced to 85% $H_3PO_4$ via solid triphenylphosphine ($\delta = -9.9$ ppm).

## Results and Discussion

Copper(I) iodide, iodide ion, and triphenylphosphine combine in a 1:1:2 ratio to form the bis(triphenylphosphine)diiodocuprate(I)

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**Table II.** Non-Hydrogen Atom Coordinates for $[PPh_3Me][(PPh_3)_2CuI_2]$

| | ligand 1 | | | ligand 2 | | | cation 3 | | |
|---|---|---|---|---|---|---|---|---|---|
| atom | *x* | *y* | *z* | *x* | *y* | *z* | *x* | *y* | *z* |
| P | 0.6848 (2) | 0.7551 (1) | 0.01141 (7) | 0.9261 (2) | 0.6632 (1) | 0.12287 (8) | 0.5168 (2) | 0.0150 (2) | 0.20072 (8) |
| C(11) | 0.7645 (6) | 0.8082 (5) | −0.0292 (3) | 0.9113 (6) | 0.5435 (5) | 0.1056 (3) | 0.6161 (6) | −0.0332 (5) | 0.2512 (3) |
| C(12) | 0.8028 (9) | 0.8944 (7) | −0.0178 (4) | 0.8255 (7) | 0.4950 (6) | 0.1175 (3) | 0.6834 (7) | −0.1036 (6) | 0.2433 (3) |
| C(13) | 0.8636 (10) | 0.9404 (6) | −0.0455 (4) | 0.8081 (8) | 0.4034 (6) | 0.1052 (4) | 0.7663 (8) | −0.1379 (7) | 0.2826 (5) |
| C(14) | 0.8896 (8) | 0.9006 (7) | −0.0848 (4) | 0.8773 (9) | 0.3617 (6) | 0.0803 (4) | 0.7783 (8) | −0.1019 (8) | 0.3281 (4) |
| C(15) | 0.8533 (8) | 0.8145 (7) | −0.0960 (3) | 0.9614 (8) | 0.4092 (7) | 0.0660 (4) | 0.7132 (9) | −0.0315 (7) | 0.3367 (4) |
| C(16) | 0.7898 (7) | 0.7684 (5) | −0.0691 (3) | 0.9803 (7) | 0.5001 (6) | 0.0795 (3) | 0.6304 (7) | 0.0013 (5) | 0.2977 (4) |
| C(21) | 0.5510 (6) | 0.8176 (5) | −0.0068 (3) | 0.9791 (6) | 0.6566 (6) | 0.1893 (3) | 0.5417 (7) | 0.1342 (5) | 0.2001 (3) |
| C(22) | 0.5095 (6) | 0.8598 (5) | 0.0286 (3) | 0.9712 (7) | 0.7311 (6) | 0.2173 (4) | 0.4582 (7) | 0.1926 (6) | 0.1760 (3) |
| C(23) | 0.4060 (7) | 0.9057 (6) | 0.0153 (3) | 1.0157 (8) | 0.7298 (7) | 0.2678 (4) | 0.4802 (9) | 0.2822 (7) | 0.1720 (4) |
| C(24) | 0.3444 (7) | 0.9073 (6) | −0.0318 (4) | 1.0659 (8) | 0.6514 (10) | 0.2894 (4) | 0.5860 (10) | 0.3164 (6) | 0.1920 (4) |
| C(25) | 0.3865 (8) | 0.8658 (6) | −0.0671 (3) | 1.0734 (7) | 0.5769 (7) | 0.2616 (4) | 0.6695 (8) | 0.2618 (8) | 0.2162 (4) |
| C(26) | 0.4893 (8) | 0.8212 (6) | −0.0544 (3) | 1.0303 (6) | 0.5785 (6) | 0.2119 (3) | 0.6481 (7) | 0.1702 (7) | 0.2204 (5) |
| C(31) | 0.6511 (6) | 0.6428 (5) | −0.0152 (3) | 1.0553 (6) | 0.6983 (5) | 0.1040 (3) | 0.3734 (6) | −0.0042 (6) | 0.2051 (3) |
| C(32) | 0.7387 (6) | 0.5809 (6) | −0.0112 (3) | 1.0396 (7) | 0.7449 (6) | 0.0605 (3) | 0.3087 (8) | −0.0695 (6) | 0.1757 (3) |
| C(33) | 0.7203 (7) | 0.4941 (6) | −0.0294 (3) | 1.1346 (9) | 0.7711 (6) | 0.0432 (4) | 0.1979 (8) | −0.0834 (7) | 0.1799 (4) |
| C(34) | 0.6122 (8) | 0.4661 (5) | −0.0515 (3) | 1.2410 (9) | 0.7508 (7) | 0.0708 (5) | 0.1547 (8) | −0.0340 (7) | 0.2121 (5) |
| C(35) | 0.5236 (8) | 0.5255 (7) | −0.0542 (4) | 1.2550 (7) | 0.7077 (6) | 0.1138 (4) | 0.2198 (8) | 0.0304 (7) | 0.2415 (4) |
| C(36) | 0.5425 (7) | 0.6127 (6) | −0.0366 (4) | 1.1625 (7) | 0.6806 (5) | 0.1313 (3) | 0.3307 (7) | 0.0453 (6) | 0.2376 (3) |
| C(0) | | | | | | | 0.5369 (7) | −0.0331 (6) | 0.1461 (3) |
| Cu | 0.77044 (7) | 0.75181 (6) | 0.09311 (3) | | | | | | |
| I | 0.83916 (5) | 0.92031 (4) | 0.12240 (2) | 0.61511 (4) | 0.69793 (4) | 0.14178 (2) | | | |

**Table III.** Non-Hydrogen Atom Coordinates for $[PPh_3Me][(PPh_3)_2Cu_2I_3]$

| | moiety *n* | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | ligand 1 | | | ligand 2 | | | cation 3 | | |
| atom | *x* | *y* | *z* | *x* | *y* | *z* | *x* | *y* | *z* |
| P(*n*) | 0.8408 (1) | $x - {}^{1}/_{2}$ | $1 - x$ | 0.6157 (1) | $x - {}^{1}/_{2}$ | $1 - x$ | 0.8172 (2) | $1^{1}/_{2} - x$ | $x - {}^{1}/_{2}$ |
| C(*n*1) | 0.9080 (5) | 0.4000 (5) | 0.2093 (5) | 0.6570 (5) | 0.0850 (5) | 0.4741 (6) | 0.7251 (6) | 0.6434 (6) | 0.3157 (6) |
| C(*n*2) | 0.9410 (6) | 0.3698 (6) | 0.2717 (6) | 0.7022 (6) | 0.1361 (7) | 0.5139 (6) | 0.7141 (6) | 0.5702 (6) | 0.2978 (6) |
| C(*n*3) | 0.9978 (7) | 0.4080 (8) | 0.3093 (6) | 0.7308 (8) | 0.1194 (8) | 0.5831 (6) | 0.6417 (8) | 0.5429 (6) | 0.2947 (6) |
| C(*n*4) | 1.0178 (6) | 0.4784 (7) | 0.2838 (7) | 0.7196 (7) | 0.0491 (7) | 0.6120 (6) | 0.5801 (7) | 0.5865 (8) | 0.3066 (7) |
| C(*n*5) | 0.9863 (6) | 0.5101 (6) | 0.2235 (8) | 0.6761 (7) | −0.0013 (6) | 0.5752 (7) | 0.5906 (6) | 0.6618 (8) | 0.3241 (7) |
| C(*n*6) | 0.9307 (6) | 0.4711 (6) | 0.1851 (6) | 0.6453 (6) | 0.0170 (6) | 0.5062 (6) | 0.6630 (6) | 0.6914 (6) | 0.3287 (7) |
| C(*n*0) | | | | | | | 0.8747 (6) | $1^{1}/_{2} - x$ | $x - {}^{1}/_{2}$ |
| Cu(*n*) | 0.76878 (6) | $x - {}^{1}/_{2}$ | $1 - x$ | 0.68735 (6) | $x - {}^{1}/_{2}$ | $1 - x$ | | | |
| I(*n*) | 0.82920 (4) | 0.13773 (4) | 0.27957 (4) | | | | | | |
| | | | | Solvent[a] | | | | | |
| C | 1.011 (2) | $x - {}^{1}/_{2}$ | $2 - x$ | 1.059 (1) | $x - {}^{1}/_{2}$ | $2 - x$ | | | |
| Cl | 0.9518 (10) | 0.554 (1) | 0.947 (1) | 0.9714 (4) | 0.5872 (4) | 0.9123 (4) | | | |

[a] Isotropic refinement; populations 0.30 (1) and 1 − 0.30 (1), respectively.

**Table IV.** Core Geometries for Molecules Containing the $[(PPh_3)_2CuI_2]$ Fragment

| param[a] | $[(PPh_3)_2CuI_2]^-$ | $[(PPh_3)CuI_2Cu(PPh_3)_2]$[b] |
|---|---|---|
| Cu–I(1) | 2.692 (1) | 2.707 (1) |
| Cu–I(2) | 2.702 (1) | 2.819 (1) |
| Cu–P(1) | 2.292 (2) | 2.259 (3) |
| Cu–P(2) | 2.288 (2) | 2.267 (3) |
| I(1)–Cu–I(2) | 108.62 (4) | 102.24 (5) |
| P(1)–Cu–P(2) | 121.24 (9) | 125.2 (1) |
| P–Cu–I | 104.36 (6)–108.79 (6)[c] | 99.94 (8)–110.66 (9) |

[a] Distances in Å; angles in deg. [b] Reference 12. [c] Individual values: I(1)–Cu–P(1,2) = 108.79 (6), 104.36 (6)°; I(2)–Cu–P(1,2) = 108.20 (7), 105.09 (7)°.

ion, $[(PPh_3)_2CuI_2]^-$, which was crystallized from dichloromethane as its $[PPh_3Me]^+$ salt. Hexaiodotetracuprate(I) ion, $[Cu_4I_6]^{2-}$,[8] and triphenylphosphine combine in a 1:4 ratio to form the bis(triphenylphosphine)tris($\mu$-iodo)dicuprate(I) ion, $[(PPh_3)CuI_3Cu(PPh_3)]^-$, which was crystallized from dichloromethane/diethyl ether as its $[PPh_3Me]^+$ salt. The same compound could be prepared by reacting $[PPh_3Me]I$, CuI, and $PPh_3$ in a 1:2:2 ratio in dichloromethane and precipitating the product with diethyl ether. Attempts to prepare the 1:1 adduct of $PPh_3$ with $[CuI_2]^-$, analogous to the previously reported bromo complex $[(PPh_3)CuBr_2]^-$,[7] by reacting $[PPh_3Me]I$, CuI, and $PPh_3$ in a 1:1:1 ratio in dichloromethane and precipitating the product with diethyl ether resulted only in the isolation of $[PPh_3Me][(PPh_3)CuI_3Cu(PPh_3)]$. Attempts to prepare the bromo analogue of the latter complex by reacting $[PPh_3Me]Br$, CuBr, and $PPh_3$ in a 1:2:2 ratio in dichloromethane and precipitating the product with diethyl ether did not result in a well-defined compound.

It might appear from the above results that the presence of more than one terminal halide ion in the primary coordination sphere of copper(I) exerts a significant effect on the preferred coordination number of the copper(I) atom. Thus, in the presence of two terminal bromide ligands, the copper coordination number cannot be increased beyond 3 by addition of triphenylphosphine. In contrast to this, compounds with coordination numbers less than 4 cannot be produced by addition of triphenylphosphine in the presence of two terminal iodide ligands. In line with this trend, we have not yet been able to prepare any adduct of triphenylphosphine with $[CuCl_2]^-$. It is not yet clear whether this indicates an increasing preference for lower coordination numbers in the series $[L_nCuX_2]^-$ from X = I to X = Cl or whether the observed trend has some other cause (e.g. a difference in crystal lattice energies). Further work is necessary to decide this point, but we note that, with the ligand 2,2′-dipyridylamine (dpa), complex salts $[(dpa)_2Cu][(dpa)CuX_2]$ for X = Cl, Br have been isolated.[11]

**X-ray Crystal Structure Determination.** The structure of the $[(PPh_3)_2CuI_2]^-$ ion is shown in Figure 1. The two $PPh_3$ ligands

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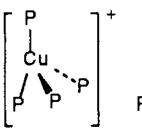
**Table V.** Core Geometries for Molecules Containing the [$(PPh_3)CuI_3$] Fragment

| param[a] | [$(PPh_3)CuI_3Cu(PPh_3)$]$^-$ Cu(1) | [$(PPh_3)CuI_3Cu(PPh_3)$]$^-$ Cu(2) | [$(PPh_3)CuI$]$_4$ "cubane"[b] | [$(PPh_3)CuI$]$_4$ "step"[c] |
|---|---|---|---|---|
| Cu-I | 2.701 (2) | 2.730 (2) | 2.653 (3)-2.732 (3) | 2.620 (2)-2.728 (2) |
| Cu-P | 2.215 (3) | 2.202 (3) | 2.251 (6)-2.258 (7) | 2.242 (4) |
| Cu---Cu | 2.503 (2) | | 2.874 (5)-3.164 (4) | 2.834 (3), 3.404 (4) |
| P-Cu-I | 116.83 (8) | 118.05 (8) | 106.5 (1)-116.9 (2) | 112.0 (1)-114.5 (1) |
| I-Cu-I | 101.21 (5) | 99.70 (5) | 103.0 (1)-115.0 (1) | 110.10 (8)-104.20 (7) |
| Cu-I-Cu | 54.88 (4) | | 67.78 (9)-71.75 (9) | 77.55 (7) |

[a] Distances in Å; angles in deg. [b] References 16. [c] References 17.

are coordinated to the copper atom of the $CuI_2$ unit in a four-coordinate tetrahedral arrangement. There is no crystallographically imposed symmetry on the structure of the ion. The core geometry of the complex is compared in Table IV with that of the [$(PPh_3)_2CuI_2$] fragment in [$(PPh_3)CuI_2Cu(PPh_3)_2$].[12] Most of the parameters are similar in magnitude, the main differences being a slight decrease in the Cu-I bond length and a slight increase in the Cu-P bond length in the mononuclear anionic complex relative to the binuclear neutral complex. The Cu-I distance increases on coordination of two $PPh_3$ molecules to [$CuI_2$]$^-$ from a mean value of 2.389 Å in the uncomplexed linear [$CuI_2$]$^-$ ion[13] to a mean value of 2.697 Å in [$(PPh_3)_2CuI_2$]$^-$, while the I-Cu-I angle decreases from linearity (180°) to 108.6°, which is close to the tetrahedral angle (109.5°). However, the other bond angles in the core depart further from the tetrahedral angle. In particular, the P-Cu-P angle of 121.2° is considerably larger than the tetrahedral angle, probably as a consequence of the steric requirements of the triphenylphosphine ligands. Structurally, this ion is a member of the series [$(PPh_3)_nCuI_{4-n}$]$^{(3-n)-}$ (I-V). The first two species, I and II, have been reported previously,[14,15] and III is the compound characterized in the present work. No evidence for the existence of IV or V has yet been presented. It has previously been noted that, in a series of triphenylphosphine complexes of copper(I) halides, there is a monotonic increase in the Cu-P bond length as halogen atoms are replaced by P in the tetrahedral coordination environment.[14] The series of compounds I-III provides a further example of this trend, with mean Cu-P bond lengths of 2.585 Å (I),[14] 2.355 Å (II),[15] and 2.290 Å (III) (this work). The present study establishes this trend more definitely, as previous comparisons have involved compounds with both bridging and terminal halogen atoms, whereas the iodine atoms in II and III are all terminally bound.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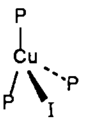
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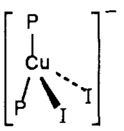
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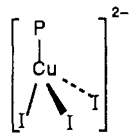
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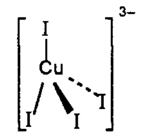
V

The structure of the [$(PPh_3)CuI_3Cu(PPh_3)$]$^-$ ion is shown in Figure 2. The anion lies on a crystallographically imposed 3-fold axis, as does the cation. The chloroform of crystallization is disordered. The $PPh_3$ ligand molecules have chirality opposite to that of the [$PPh_3Me$]$^+$ cation. The core geometry of the anion is compared in Table V with those of the "cubane"[16] and "step"[17] isomers of [$(PPh_3)CuI$]$_4$, both of which contain the [$(PPh_3)CuI_3$] fragment. The Cu-P and Cu-I bond lengths are similar in all three cases, but there are significant differences in some of the bond angles and in the Cu---Cu distances. The main reason for these differences is that in the tetranuclear complexes any two copper atoms which are connected to three iodine atoms are bridged by only two of these three iodine atoms, whereas in the binuclear complex the two copper atoms are bridged by all three iodine atoms. Another way of describing this in the case of the binuclear and the "cubane" tetranuclear complexes, both of which contain only 4-coordinate tetrahedrally coordinated copper atoms, is shown in Figure 3. The tetranuclear complex is made up of four $PCuI_3$ tetrahedra that are linked by sharing the edges of the $I_3$ faces of the tetrahedra, whereas the binuclear complex is made up of two $PCuI_3$ tetrahedra that are linked by sharing a common $I_3$ face. For perfectly regular tetrahedra, it can be shown that the bridging Cu-I-Cu angles for these two cases would be 65.96 and 38.93° and that the Cu---Cu distance would be equal to 1.09*d* and 0.67*d*, respectively, where *d* is the Cu-I bond length. Thus it is clear that the face-sharing structure results in a much smaller bridging Cu-I-Cu angle and a much shorter Cu---Cu distance than the edge-sharing structure. Indeed, it has sometimes been assumed that structures involving face-sharing linked coordination tetrahedra would not occur, as these would result in very short metal-metal contacts.[18a] However, a number of multinuclear iodocuprate(I) complexes whose structures consist of face-sharing $CuI_4$ tetrahedra have been reported.[6] In these structures, the Cu-I-Cu bridging angles at the shared faces lie in the range 54.6-56.6° and the corresponding Cu---Cu distances lie in the range 2.45-2.58 Å. These values are similar to those of the corresponding parameters in [$(PPh_3)CuI_3Cu(PPh_3)$]$^-$ and are rather larger than those predicted for structures involving undistorted face-sharing tetrahedra with a Cu-I bond length of 2.7 Å (Cu-I-Cu = 38.93°; Cu---Cu = 1.81 Å). This is because the coordination tetrahedra distort in such a way as to increase these parameters. Nevertheless, the Cu---Cu distances of about 2.5 Å in these complexes are quite short (cf. *d*(Cu-Cu) = 2.55 Å in copper metal[18b]). Shorter Cu---Cu distances have been observed in several organometallic copperI) complexes with bridging carbon donor atom ligands (e.g. [$(CH_2SiMe_3)Cu$]$_4$, *d*(Cu---Cu) = 2.42 Å[19]) and in a few other complexes involving bridging nitrogen

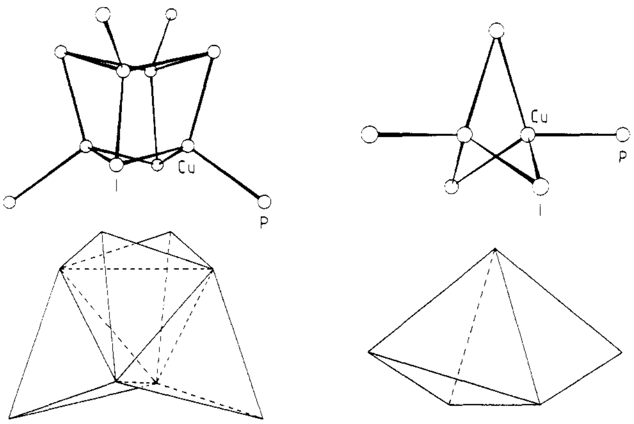

**Figure 3.** Core structures of "cubane" [$(PPh_3)CuI$]$_4$ (left) and [$(PPh_3)_2Cu_2I_3$]$^-$ (right) and the linking of the associated $PCuI_3$ coordination tetrahedra.

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**Table VI.** Observed and Calculated $\nu$(CuI) Wavenumbers and Cu–I Bond Stretching Force Constants $f_r$ for Iodocopper(I) Complexes

| complex | $\tilde{\nu}$/cm$^{-1}$ obs | $\tilde{\nu}$/cm$^{-1}$ calc | $f_r$/N m$^{-1}$ | ref |
|---|---|---|---|---|
| $[CuI_2]^-$ | 279 | 279 ($\Sigma_u^+$) | 140 | 22 |
|  | 148 | 148 ($\Sigma_g^+$) |  |  |
| $[(PPh_3)_2CuI_2]^-$ | 118 | 121 ($B_1$) | 30 | this work |
|  |  | 104 ($A_1$) |  |  |
| $[(PPh_3)_3CuI]$ | 138 | 138 | 48 | 4 |
| $[(PPh_3)CuI_2Cu(PPh_3)_2]$ | 163 | 165 ($B_1$), 132 ($A_1$) | 52 (trigonal Cu) | 23 |
|  | 107 | 108 ($B_1$), 102 ($A_1$) | 26 (tetrahedral Cu) |  |
| $[(PPh_3)CuI]_4$ "cubane" | 140 | 144 ($T_2$) | 33 | 24 |
|  | 100 | 95 ($T_2$) |  |  |
| $[(PPh_3)CuI_3Cu(PPh_3)]^-$ | 127 | 131 (E′) | 30 | this work |
|  |  | 104 ($A_2''$) |  |  |

donor atom ligands (e.g. [(tolyl-NNNNN-tolyl)Cu]$_3$, $d$(Cu- - -Cu) = 2.35 Å[20]). The possible existence of weak attractive Cu(I)- - -Cu(I) interactions in such situations has been discussed by Hoffmann et al.[21] Whether such an interaction could contribute significantly to the stabilization of the structure of $[(PPh_3)CuI_3Cu(PPh_3)]^-$ is an open question. However, it may have other observable consequences. This question is considered further in the discussion of the solid-state $^{31}P$ NMR of this complex.

While binuclear complexes form a significant class of copper(I) complex, the examples reported to date involve bridging by one and two but not three ligands.[2] The complex $[(PPh_3)CuI_3Cu(PPh_3)]^-$ thus represents the first reported example of this latter class of complex.

**Vibrational Spectra.** The far-infrared spectra of the two compounds reported in this paper are shown in Figure 4. Assignments of the $\nu$(Cu–I) wavenumbers for these and for some related iodocuprate(I) and triphenylphosphine complexes of copper(I) iodide are given in Table VI. Only one band for each complex, in the range 120–130 cm$^{-1}$, can be unambiguously assigned as $\nu$(Cu–I). For $[(PPh_3)_2CuI_2]^-$, two $\nu$(Cu–I) bands are expected for the approximately $C_{2v}$ $CuI_2$ unit in this complex. In the complex $[(PPh_3)CuBr_2]^-$, two bands at 195 (s) and 150 (m) cm$^{-1}$ were assigned as the antisymmetric ($B_1$) and symmetric ($A_1$) $\nu$(Cu–Br) stretches respectively.[7] By analogy with this the strong band at 118 cm$^{-1}$ in $[(PPh_3)_2CuI_2]^-$ is assigned as the antisymmetric ($B_1$) $\nu$(Cu–I) stretch.

Assuming the $Cu_2I_3$ core in $[(PPh_3)CuI_3Cu(PPh_3)]^-$ to have idealized $D_{3h}$ symmetry, the $\nu$(Cu–I) vibrations of this complex have the following symmetries and activities: $A_1'$ (Raman) + E′ (IR, Raman) + $A_2''$ (IR) + $E''$(Raman). Thus, in this case too, two IR bands are expected but only one is observed.

In order to estimate the expected relative positions of the two IR bands in each complex, we have carried out an approximate normal-coordinate analysis. We have previously found that the metal–halogen vibrational frequencies of the metal–halogen core in phosphine/metal halide complexes can be calculated with reasonable accuracy by carrying out a normal coordinate analysis on the metal–halogen core only.[24,25] We have used this approach here to calculate the frequencies of a $C_{2v}$ $CuI_2$ unit with an I–Cu–I angle of 109°, and of a $D_{3h}$ $Cu_2I_3$ unit with a bridging Cu–I–Cu angle of 55°. A simple diagonal force field was used that involves a Cu–I bond stretching force constant $f_r$ and an I–Cu–I angle bending force constant $f_\alpha$, with $f_\alpha = 0.1f_r$. The frequencies of the IR-active modes obtained from these calculations, with $f_r$ = 30 N m$^{-1}$ for both species, are given in Table VI. Reasonable agreement between the higher of the two calculated frequencies and the observed frequency is obtained in each case.

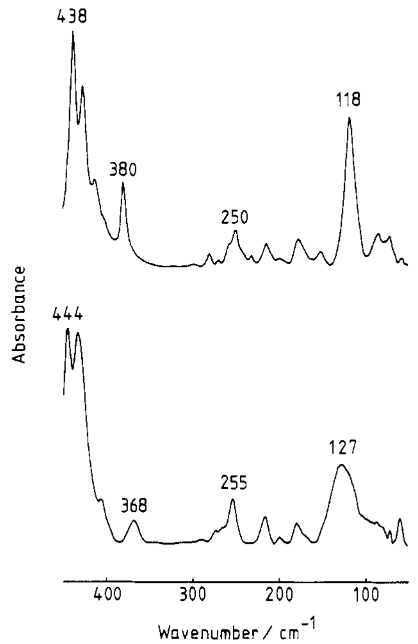

**Figure 4.** Far-IR spectra of $[PPh_3Me][(PPh_3)_2CuI_2]$ (upper) and $[PPh_3Me][(PPh_3)_2Cu_2I_3]$ (lower).

The Raman spectra of both complexes in the range 20–450 cm$^{-1}$ are dominated by strong, partially split bands in the region 90–120 cm$^{-1}$. In the compound $[PPh_3Me][(PPh_3)_2CuI_2]$ this band consists of a peak at 89 cm$^{-1}$ and a shoulder at about 119 cm$^{-1}$. The latter agrees well with the wavenumber of the antisymmetric ($B_1$) $\nu$(Cu–I) mode in the IR spectrum. The peak at 89 cm$^{-1}$ is assigned to the symmetric ($A_1$) $\nu$(Cu–I) mode. The observed difference between the wavenumbers of the $B_1$ and the $A_1$ modes is somewhat greater than that calculated (Table VI), as was found in the case of $[PPh_3Me][(PPh_3)CuBr_2]$.[7] This is probably due to the fact that the same bond stretching force constant was used for each of the two Cu–X bonds in the ion, whereas the crystal structures show these bonds to be slightly inequivalent. The $\nu$(Cu–I) Raman band in $[PPh_3Me][(PPh_3)_2Cu_2I_3]$ is less well resolved, and the resolution did not improve much on cooling the sample to 77 K. The band covers the range of wavenumbers calculated for the normal modes of the $Cu_2I_3$ unit, but there are apparently too many Raman-active bands within this range to allow satisfactory resolution.

As expected from the comparison of bond lengths discussed above, the Cu–I bond stretching force constant in $[(PPh_3)_2CuI_2]^-$ is much lower than the value found for $[CuI_2]^-$ (Table VI). This result parallels those found previously for the series of complexes $[(PPh_3)_nMX]$ (M = Cu, Ag, Au; X = Cl, Br, I) where the $\nu$(M–X) frequency and the M–X bond force constant are found to be strongly dependent on the coordination number of M and the M–X bond length.[4,25,26]

Table VI also contains data for the neutral iodocopper(I) species $[(PPh_3)_3CuI]$[4] and $[(PPh_3)CuI_2Cu(PPh_3)_2]$,[23] and the "cubane" form of $[(PPh_3)CuI]_4$.[24] The relationship between these and the data for the iodocuprate(I) complexes of the present study provides further support for the $\nu$(Cu–I) assignments made here.

**Solid-State $^{31}P$ NMR Spectra.** The solid-state CPMAS $^{31}P$ NMR spectra of the two compounds studied in this work are shown in Figure 5. The spectrum of $[PPh_3Me][(PPh_3)_2CuI_2]$ consists of a strong singlet at 18.1 ppm due to the phosphonium cation, and a weaker quartet centered at −16.7 ppm due to the coordinated $PPh_3$ molecules in the anion. Despite the crystallographic inequivalence of the two phosphorus atoms in the complex, only one quartet pattern is resolved, showing the near chemical equivalence of these two atoms. As described previously, the quartet structure is due to spin–spin coupling of the phosphorus nuclei to the copper nucleus ($^{63}Cu$, $^{65}Cu$; $I = {}^3/_2$). The line

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**Table VII.** CPMAS Solid-State $^{31}$P NMR Parameters for (Triphenylphosphine)copper(I) Iodide Complexes[a]

| complex | $\delta$ | $\Delta\nu_1$ | $\Delta\nu_2$ | $\Delta\nu_3$ | $\langle\Delta\nu_i\rangle$ | $\Delta\nu_3/\Delta\nu_1$ | ref |
|---|---|---|---|---|---|---|---|
| $[(PPh_3)_2CuI_2]^-$ | −16.7 | 1.08 | 1.20 | 1.23 | 1.17 | 1.14 | this work |
| $[(PPh_3)_3CuI]$ | −15.6 | 0.90 | 0.93 | 0.92 | 0.92 | 1.02 | 15 |
| | −18.9 | 0.90 | 0.93 | 0.93 | 0.92 | 1.03 | |
| $[(PPh_3)_2CuI]$ | −3.6 | 0.88 | 1.20 | 1.43 | 1.17 | 1.63 | 29 |
| $[(PPh_3)CuI]_4$ "step" | −6.5 | 1.32 | 1.70 | 1.86 | 1.63 | 1.41 | 16 |
| | −14.4 | 1.43 | 1.65 | 1.77 | 1.62 | 1.24 | |
| $[(PPh_3)CuI]_4$ "cubane" | −19.3 | 1.41 | 1.58 | 1.68 | 1.56 | 1.19 | 16 |
| | −25.7 | 1.39 | 1.56 | 1.63 | 1.53 | 1.17 | |
| $[(PPh_3)CuI_3Cu(PPh_3)]^-$ | −15.8 | | | | | | this work |

[a] $\delta$ is the chemical shift in ppm relative to 85% $H_3PO_4$ ($\delta$ for solid $PPh_3$ = −9.9 ppm); $\Delta\nu_i$ is the splitting in kHz between each of the four peaks of the quartet; $\langle\Delta\nu_i\rangle$ is the average of the $\Delta\nu_i$ values for each quartet.

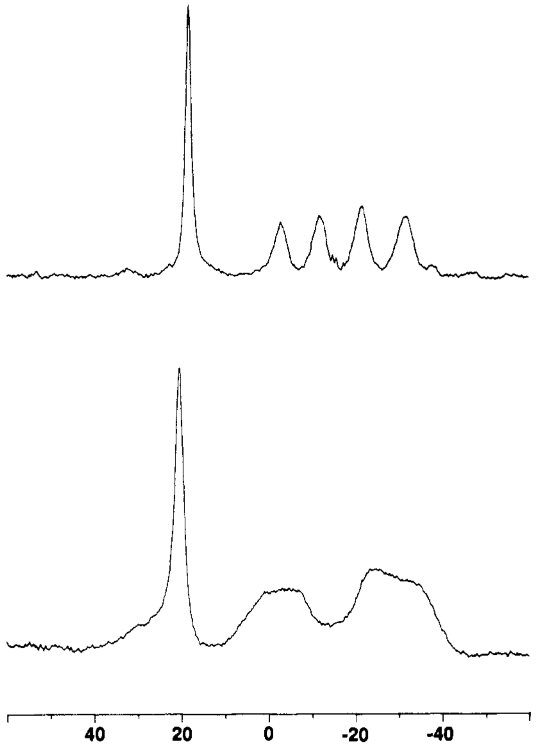

**Figure 5.** Solid-state CPMAS $^{31}$P NMR spectra of $[PPh_3Me][(PPh_3)_2CuI_2]$ (upper) and $[PPh_3Me][(PPh_3)_2Cu_2I_3]$ (lower).

spacings in the quartet are unequal, due to the presence of a nuclear quadrupole coupling interaction between the copper nucleus and its surroundings.[27,28] For a spherically symmetrical charge distribution about the copper nucleus, such as would be encountered in a $CuL_4$ complex with perfect tetrahedral coordination geometry, the nuclear quadrupole coupling constant would be zero and the components of the quartet would be equally spaced. The asymmetry of the line spacings can be represented by the ratio $\Delta\nu_3/\Delta\nu_1$ where $\Delta\nu_1$ and $\Delta\nu_3$ are the low- and high-field line spacings in the quartet.[28]

In order to investigate possible relationships between the $^{31}$P NMR parameters and the coordination environment about the copper atom, the solid-state $^{31}$P data obtained for $[(PPh_3)_2CuI_2]^-$ in the present study are compared with those of some related species in Table VII. Two aspects of these results are worthy of comment. First, the scalar $^{31}P-^{63,65}Cu$ coupling constant (which is measured by the average line spacing $\langle\Delta\nu_i\rangle$ of the quartet) appears to depend only on the number of phosphine molecules coordinated to the copper. The observed values are about 1.6 (one coordinated phosphine), 1.2 (two coordinated phosphines) and 0.9 kHz (three coordinated phosphines). It should be noted that this is true even when the total coordination number and the number of coordinated iodine atoms are different (e.g. $[(PPh_3)_2CuI]$ and $[(PPh_3)_2CuI_2]^-$ have almost identical $\langle\Delta\nu_i\rangle$ values). Similar observations have been made previously for a range of copper(I) chloride and copper(I) bromide complexes.[7,28] This suggests that only the phosphine, and not the halide, can change the degree of copper s-orbital involvement in the metal–ligand bonding.

The second feature of the results in Table V that reflects the nature of the coordination environment about the copper atom is the splitting ratio $\Delta\nu_3/\Delta\nu_1$. Comparing again the complexes $[(PPh_3)_2CuI]$ and $[(PPh_3)_2CuI_2]^-$, we see that this ratio is greater for the former than for the latter complex. As discussed previously, the divergence of this ratio from unity is approximately proportional to the copper nuclear quadrupole coupling constant.[28] The results therefore indicate that the addition of an extra iodide ligand to $[(PPh_3)_2CuI]$ to give $[(PPh_3)_2CuI_2]^-$ results in a considerable decrease in the copper nuclear quadrupole coupling constant. This is as expected, since the coordination geometry in the latter complex is closer to perfect tetrahedral, for which the quadrupole coupling constant would be zero.

The spectrum of $[PPh_3Me][(PPh_3)CuI_3Cu(PPh_3)]$ is more difficult to interpret. The strong singlet at 20.1 ppm can readily be assigned to the phosphonium cation. A quartet centered at −15.8 ppm is assigned to the coordinated $PPh_3$ molecules, but the outermost components of the quartet are almost unresolved, and the quartet pattern does not show the expected line spacing pattern with $\Delta\nu_1 < \Delta\nu_2 < \Delta\nu_3$. The coordination environment in this complex is similar to that in the "cubane" form of $[(PPh_3)CuI]_4$ (Table V), and on this basis, the spectra of these two compounds should be similar. The main difference between these is the considerably shorter Cu- - -Cu distance in the binuclear complex, but it is not yet clear whether this has anything to do with the unexpected form of the spectrum. Similar broad, unresolved signals have been observed in the $^{31}$P CPMAS spectrum of the hydride cluster complex $[(PPh_3)CuH]_6$.[30] The Cu- - -Cu distances in this cluster lie in the range 2.49–2.67 Å.[31]

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**Supplementary Material Available:** Tables Sup I–Sup IX, listing non-hydrogen thermal parameters, the derived hydrogen positions, ligand non-hydrogen geometries, and crystal data and drawings of the structures of the phosphines in the complexes (19 pages); tables of calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

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