The Chemistry of Copper(I) β-Diketonate Compounds. Part 4.[1] Syntheses and Characterization of $CuXL_n$ (X = β-diketonate or Cl, L = PMe_3, $n = 2$ or 4; L = PEt_3, $n = 2$)†

Kai-Ming Chi,[a] Janos Farkas,[b] Mark J. Hampden-Smith,*[,a] Toivo T. Kodas*[,b] and Eileen N. Duesler[a]

[a] *Department of Chemistry and Center for Micro-Engineered Ceramics, University of New Mexico, Albuquerque, NM 87131, USA*

[b] *Department of Chemical Engineering and Center for Micro-Engineered Ceramics, University of New Mexico, Albuquerque, NM 87131, USA*

The salts $[Cu(PMe_3)_4]^+[CuCl_2]^-$ and $[Cu(PMe_3)_4]^+[\beta\text{-diketonate}]^-$[β-diketonate = 1,1,1,5,5,5-hexafluoroacetylacetonate (hfacac), 1,1,1-trifluoroacetylacetonate (tfacac) or acetylacetonate (acac)] were prepared by the displacement of the co-ordinating anions Cl^- and β-diketonate from the copper(I) complexes $[CuX(PMe_3)]$ (X = Cl or β-diketonate) by addition of an excess of PMe_3. These species were characterized by a variety of spectroscopic methods including ^{31}P NMR spectroscopy which revealed coupling between ^{31}P and $^{63,65}Cu$ in the cation. Two examples were characterized in the solid state by single-crystal X-ray diffraction: $[Cu(PMe_3)_4]^+[CuCl_2]^-$, space group $P2_13$, $a = 13.584(1)$ Å and $Z = 12$; $[Cu(PMe_3)_4]^+[hfacac]^-$, space group *Pmmn*, $a = 10.703(2)$, $b = 15.077(3)$, $c = 8.997(2)$ Å and $Z = 2$. The cations exhibit an approximately tetrahedral co-ordination environment and the anion $[CuCl_2]^-$ is linear. The addition of excess of PEt_3 to $[CuX(PEt_3)]$ resulted in formation of $[CuX(PEt_3)_2]$ in contrast to the PMe_3 analogues. The compound $[CuCl(PEt_3)_2]$ was found to be monomeric in benzene solution by cryoscopic molecular weight determination and has high volatility.

There has been extensive discussion of the factors which affect the co-ordination number and geometry of metal complexes containing Group 15 ligands. It is generally believed that the steric and electronic requirements of the ligands, and the metals to which they are co-ordinated, are the dominant factors. However, distinction between the influence of steric and electronic requirements of ligands is extremely difficult. In cases where steric requirements are likely to be dominant, such as the zerovalent $[PtL_n]$, where L = a triorganophosphine ligand and $n = 2$–4, predictions based on Tolman's cone-angle[2] measurements have to be modified due to 'intermeshing' of the organic phosphorus substituents.[3–5] As a result, compounds such as $[Pt\{P(C_6H_{11})_3\}_3]$ have been prepared and structurally characterized,[6] but would not have been predicted based on the sum of the cone angles for three $P(C_6H_{11})_3$ ligands (510°). Recently, Baiada *et al.*[7–9] have investigated the structural chemistry of two-, three- and four-co-ordinate complexes of monovalent coinage metals with triorgano-Group 15 donor ligands, $[M(ER_3)_n]^+X^-$ (M = Cu, Ag or Au; E = P, As or Sb; R = alkyl or aryl; $n = 2$–4; and X = *a non-co-ordinating anion* BF_4^- or ClO_4^-). They have proposed that the steric dividing line between three- and four-co-ordinate $[ML_n]^+$ complexes lies close to the steric demands of PPh_3. Steric arguments can also be used to rationalize the formation of three- and four-co-ordinate amine adducts of copper(I) such as $[Cu(py)_4]^+[ClO_4]^-$ (py = pyridine)[10] and $[Cu(2Me\text{-}py)_3]^+[ClO_4]^-$ (2Me-py = 2-methylpyridine).[11]

In this work we report the syntheses and characterization of a number of new copper(I) salts containing the stable $[Cu(PMe_3)_4]^+$ cation including the solid-state X-ray structural characterization of $[Cu(PMe_3)_4]^+[CuCl_2]^-$ and $[Cu(PMe_3)_4]^+[hfacac]^-$ (hfacac = 1,1,1,5,5,5-hexafluoroacetylacetonate). These salts were formed *via* displacement of *co-ordinating* anions such as Cl^- and β-diketonate from the co-ordination environment of copper(I) by addition of an excess of trimethylphosphine to $[CuX(PMe_3)]$ complexes (X = Cl or β-diketonate). In contrast, the addition of an excess of triethylphosphine to $[CuX(PEt_3)]$ complexes does not result in salt formation, but in new volatile $[CuX(PEt_3)_2]$ species, one of which is amongst the most volatile copper(I) compounds prepared to date. The factors affecting these reactions are discussed. Furthermore, we are primarily interested in the chemistry of copper(I) species related to chemical vapour deposition (CVD)[12] and etching[13] of copper, so a knowledge of the conditions under which involatile copper(I) salts are formed is crucial.

Experimental

General Procedures.—All manipulations were carried out under an atmosphere of dry (molecular sieves) dinitrogen using standard Schlenk techniques. All hydrocarbon and ether solvents were dried and distilled from sodium–benzophenone and stored over 4 Å molecular sieves. Copper(I) chloride and the trialkylphosphines PMe_3 and PEt_3 were purchased from Aldrich and used without further purification. The β-diketone starting materials were purchased from Aldrich, distilled under nitrogen and stored over 4 Å molecular sieves before use. Sodium salts of β-diketones were prepared by the reaction of the free acid with sodium hydride, as previously described.[12,14] The compounds $[\{CuCl(PMe_3)\}_n]$ and $[CuX(PMe_3)_2]$ (X = β-diketonate) were prepared by the literature methods.

Elemental analyses were performed either by Oneida Research Services, New York, or by Ms. R. Ju at the University of New Mexico, Department of Chemistry. The NMR spectra were recorded on a Bruker AC-250P spectrometer by using the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

protio impurities of the deuteriated solvents (^1H) or the ^{13}C resonance of the solvents as reference. Temperatures were calibrated with either ethylene glycol or methanol. The ^{31}P NMR spectra were recorded on the same instrument using phosphoric acid as reference; ^{31}P chemical shifts are quoted using the high frequency = positive sign convention. Infrared spectra were recorded on a Perkin Elmer model 1620 FTIR spectrophotometer, mass spectra on a Finnegan GC-mass spectrometer. Molecular weights were measured cryoscopically by the freezing point depression of benzene. Vapour pressures were measured using an apparatus that has been previously described.[14]

Syntheses.—(*a*) $[CuCl(PEt_3)_2]$. Triethylphosphine (5 cm^3, 4 g, 33.8 mmol) was added dropwise to a slurry of CuCl (1.63 g, 16.5 mmol) in Et_2O (100 cm^3). The solution became clear when the addition was complete. After stirring for 1 h and removal of the volatile components *in vacuo* a white solid was obtained. Recrystallization of the product from pentane provided 5.02 g (91% yield) of analytically pure $[CuCl(PEt_3)_2]$, m.p. 40 °C. NMR (C_6D_6, 20 °C): ^1H (250 MHz), δ 1.01 (m, 3 H, J_{PH} = 6.0, J_{HH} = 3.0 Hz, CH_3) and 1.40 (m, 2 H, CH_2); $^{13}C-\{^1H\}$ (62.9 MHz), δ 8.6 (d, J_{PC} = 3.0, CH_3) and 17.2 (d, J_{PC} = 13.4 Hz, CH_2); $^{31}P-\{^1H\}$ (101.3 MHz), δ −12.6. IR (KBr disc): 2958s, 2932s, 2902s, 2874s, 1458m, 1416m, 1379m, 1259w, 1036m, 763s, 730w, 711m, 668w and 622w cm^{-1} (Found: C, 43.20; H, 9.20. Calc. for $C_{12}H_{30}ClCuP_2$: C, 43.0; H, 9.00%).

The molecular weight of $[CuCl(PEt_3)_2]$ was determined in solution *via* the freezing point depression of benzene. Measurements were made at three different concentrations and the results were as follows: 0.08, 322(7); 0.12, 337(5); 0.17 mol dm^{-3}, 378(5). The molecular weight of monomeric $[CuCl(PEt_3)_2]$ is 334.5.

(*b*) $[CuX(PEt_3)_2]$ (X = β-*diketonate*). These compounds where β-diketonate = 1,1,1,5,5,5-hexafluoroacetylacetonate (hfacac), 1,1,1-trifluoroacetylacetonate (tfacac) and acetylacetonate (acac) were prepared in a similar manner. One representative example is described in detail.

$[Cu(hfacac)(PEt_3)_2]$. Addition of pentane (100 cm^3) to a Schlenk flask (250 cm^3) which contained $[CuCl(PEt_3)_2]$ (7.53 g, 22.47 mmol) and Na(hfacac) (5.31 g, 23.09 mmol) immediately gave an orange-yellow solution. After stirring for 2 h the solution was filtered and the solvent removed under vacuum. An oily, orange product was obtained in 92% yield (10.47 g) which analysed correctly as $[Cu(hfacac)(PEt_3)_2]$. Using a similar procedure, $[Cu(tfacac)(PEt_3)_2]$ and $[Cu(acac)(PEt_3)_2]$ were obtained in yields of 87 and 85%, respectively. NMR (20 °C, C_6D_6): ^1H (250 MHz), δ 6.02 (s, 1 H, CH of hfacac), 1.17 (m, 12 H, CH_2 of PEt_3) and 0.88 (m, 18 H, CH_3 of PEt_3); $^{13}C-\{^1H\}$ (62.9 MHz), δ 176 (q, 32 Hz, CO), 119 (q, *J* 289, CF_3), 86.5 (s, CH), 17.8 (d, *J* 15.8, CH_2 of PEt_3) and 8.30 (d, *J* 3.6 Hz, CH_3 of PEt_3); $^{31}P-\{^1H\}$ (101.3 MHz), δ −11.6 (s, br) (Found: C, 40.35; H, 6.00. Calc. for $C_{17}H_{31}CuF_6O_2P_2$: C, 40.30; H, 6.15%).

$[Cu(tfacac)(PEt_3)_2]$. NMR (20 °C, C_6D_6): ^1H (250 MHz), δ 5.58 (s, 1 H, CH of tfacac), 1.83 (s, 3 H, CH_3 of tfacac), 1.25 (m, 12 H, CH_2 of PEt_3) and 0.96 (m, 18 H, CH_3 of PEt_3); $^{13}C-\{^1H\}$ (62.9 MHz), δ 195.0 (s, CO), 170 (q, *J* 29, CO), 120 (q, *J* 289, CF_3), 91.9 (s, CH), 29.5 (s, CH_3), 17.5 (d, *J* 12.5 Hz, CH_2 of PEt_3) and 8.50 (s, br, CH_3 of PEt_3); $^{31}P-\{^1H\}$ (101.3 MHz), δ −12.5 (s, br) (Found: C, 45.10; H, 7.95. Calc. for $C_{17}H_{34}CuF_3O_2P_2$: C, 45.10; H, 7.55%).

$[Cu(acac)(PEt_3)_2]$. NMR (20 °C, C_6D_6): ^1H (250 MHz), δ 5.22 (s, 1 H, CH of acac), 1.95 (s, 6 H, CH_3 of acac), 1.31 (m, 12 H, CH_2 of PEt_3) and 1.02 (m, 18 H, CH_3 of PEt_3); $^{13}C-\{^1H\}$ (62.9 MHz), δ 188 (s, CO), 97.0 (s, CH), 29.0 (s, CH_3), 17.8 (d, *J* 12.8, CH_2 of PEt_3) and 8.58 (d, *J* 4.15 Hz, CH_3 of PEt_3); $^{31}P-\{^1H\}$ (101.3 MHz), δ −13.2 (s, br) (Found: C, 51.30; H, 9.80. Calc. for $C_{17}H_{37}CuO_2P_2$: C, 51.20; H, 9.35%).

(*c*) $[Cu(PMe_3)_4]^+[CuCl_2]^-$. Trimethylphosphine (10.5 cm^3, 7.72 g, 101.4 mmol) was added to a flask (250 cm^3) which contained a slurry of CuCl (5.0 g, 50.5 mmol) in benzene (100 cm^3). The solution became clear after addition of the first half of PMe_3 and then a white solid formed. The mixture was stirred for 2 h after addition of PMe_3 was complete. Removal of volatile components gave a white crystalline solid which was dried *in vacuo* for 1 h. Analytically pure $[Cu(PMe_3)_4]^+[CuCl_2]^-$ (12.4 g, 98% yield) was obtained. NMR: ^1H ([$^2H_8$]toluene, 20 °C), δ 1.00 [s, $P(CH_3)_3$]; (C_6D_6, 20 °C), δ 1.00 [d, J_{PH} = 5.0 Hz, $P(CH_3)_3$]; ([$^2H_6$]acetone, 20 °C), δ 1.29 (s); (0 °C), δ 1.29 (s); (−20 °C) δ 1.31 (br, s); (−40 °C) δ 1.15 (s) and 1.33 (s); (−60 °C), δ 1.14 (s) and 1.32 (s); (−70 °C), δ 1.13 (s) and 1.31 (s); $^{13}C-\{^1H\}$ (C_6D_6, 20 °C), δ 15.8 [d, J_{PC} = 14.8 Hz, $P(CH_3)_3$]; ([$^2H_6$]acetone, 20 °C), δ 17.2 [d, J_{PC} = 13 Hz, $P(CH_3)_3$]; $^{31}P-\{^1H\}$ ([$^2H_6$]acetone, 20 °C), δ −38.2 (br, s); (−30 °C), δ −35.2 (q, J_{CuP} = 792) and −39.0 (s); (−50 °C), δ −34.6 [q, J_{CuP} = 794 Hz] and −38.3 (s). IR (KBr disc): 2963w, 2901w, 1433w, 1282w, 955s, 727m and 666w cm^{-1} (Found: C, 28.85; H, 7.55. Calc. for $C_{12}H_{36}Cl_2Cu_2P_4$: C, 28.70; H, 7.20%).

(*d*) $[Cu(PMe_3)_4]^+$[β-diketonate]$^-$. One representative synthetic procedure is described in detail. The other species were prepared by a similar method.

Addition of PMe_3 (1 cm^3, 9.76 mmol) to a solution of $[Cu(hfacac)(PMe_3)_2]$ (1.1 g, 2.6 mmol) in pentane (50 cm^3) immediately gave a white precipitate. After stirring for 1 h the white solid was filtered off, washed with pentane (2 × 20 cm^3) and dried *in vacuo* for 1 h. A nearly quantitative yield of $[Cu(PMe_3)_4]^+[hfacac]^-$ (1.47 g, 98%) was obtained. NMR: ^1H ([$^2H_6$]acetone, 20 °C): δ 1.35 [s, $P(CH_3)_3$] and 5.34 (s, CH in hfacac); $^{13}C-\{^1H\}$ (62.9 MHz, CD_2Cl_2, 20 °C) δ 17.6 [s, $P(CH_3)_3$], 82.7 (s, CH in hfacac), 119.4 (q, J_{CF} = 294, CF_3 in hfacac) and 171.6 (q, J_{CF} = 28 Hz, CF_3*C*O in hfacac); $^{31}P-\{^1H\}$ (CD_2Cl_2), δ(20 °C) −36.8 [q, *J*(Cu–P) = 796, $P(CH_3)_3$]; (−10 °C) −38.9[twoq,*J*(^{63}Cu–P) = 795,*J*(^{65}Cu–P) = 852Hz, $P(CH_3)_3$]. IR (KBr disc): 2978w, 2908w, 1671s, 1563s, 1528m, 1511w, 1429w, 1307w, 1290w, 1243m, 1169s, 1125s, 950s, 782w, 731m, 658m and 568w cm^{-1} (Found: C, 35.60; H, 6.20; Cu, 11.05; F, 18.20; P, 20.95. Calc. for $C_{17}H_{37}CuF_6O_2P_4$: C, 35.50; H, 6.50; Cu, 11.05; F, 19.85; P, 21.55%).

$[Cu(PMe_3)_4]^+[tfacac]^-$. NMR: ^1H ([$^2H_6$]acetone, 20 °C), δ 1.36 [s, $P(CH_3)_3$], 2.22 (s, CH_3 in tfacac) and 4.93 (s, CH in tfacac); (CD_2Cl_2, 20 °C), δ 1.23 [s, $P(CH_3)_3$], 2.21 (s, CH_3 in tfacac) and 4.91 (s, CH in tfacac); $^{13}C-\{^1H\}$ (62.9 MHz, CD_2Cl_2, 20 °C), δ 17.6 [s, $P(CH_3)_3$], 29.5 (s, CH_3 in tfacac), 93.5 (s, CH in tfacac), 121.1 (q, J_{CF} = 293, CF_3 in tfacac), 169.0 (q, J_{CF} = 27 Hz, CF_3*C*O in tfacac) and 195.3 (s, CH_3*C*O in tfacac); $^{31}P-\{^1H\}$ (101.3 MHz, [$^2H_6$]acetone, 20 °C), δ −39.7 [q, *J*(Cu–P) = 796, $P(CH_3)_3$]; (−10 °C), δ −38.8 [two q, *J*(^{63}Cu–P) = 795, *J*(^{65}Cu–P) = 852, *P*$(CH_3)_3$]; (CD_2Cl_2, 20 °C), δ −40.2 [q, *J*(Cu–P) = 797 Hz, $P(CH_3)_3$]. IR (KBr disc): 2972m, 2907m, 2361w, 1647m, 1611m, 1569s, 1458m, 1428m, 1355w, 1280m, 1242s, 1149m, 1114m, 998w, 946s, 867w, 770w, 729m, 668w and 520w cm^{-1} (Found: C, 39.20; H, 7.90. Calc. for $C_{17}H_{40}CuF_3O_2P_4$: C, 39.20; H, 7.75%).

$[Cu(PMe_3)_4]^+[acac]^-$. NMR: ^1H (250 MHz, CD_2Cl_2, 20 °C), δ 1.19 [s, $P(CH_3)_3$], 2.22 (br s, CH_3 in acac) and 4.67 (s, CH in acac); $^{13}C-\{^1H\}$ (62.9 MHz, CD_2Cl_2, 20 °C), δ 17.4 [s, $P(CH_3)_3$], 28.6 (s, *C*H_3CO in acac), 99.1 (s, CH in acac) and 188.3 (s, CH_3*C*O in acac); $^{31}P-\{^1H\}$ ([$^2H_6$]acetone, 20 °C), δ −36.6 [q, *J*(^{63}Cu–P) = 795, $P(CH_3)_3$]; (CD_2Cl_2, 20 °C), δ −40.3 [q, *J*(^{63}Cu–P) = 791 Hz, $P(CH_3)_3$]. IR (KBr disc): 2963m, 2901m, 1724w, 1617m, 1508m, 1459s, 1412s, 1283m, 1235w, 1010w, 955s, 809w, 760w, 727m, 668w and 522w cm^{-1} (Found: C, 43.75; H, 9.50. Calc. for $C_{17}H_{43}CuO_2P_4$: C, 43.75; H, 9.30%).

X-Ray Crystallographic Studies.—(*a*) $[Cu(PMe_3)_4]^+$ $[CuCl_2]^-$. Clear prisms of $[Cu(PMe_3)_4]^+[CuCl_2]^-$ were grown by slow crystallization from toluene solution at −30 °C and were mounted under dry nitrogen in a glass capillary. The crystal data collection and refinement parameters are collected in Table 1. The determination of the space group $P2_13$ in the cubic crystal system was unambiguous. The structure was solved by direct methods which located the copper atom. The remaining non-hydrogen atoms were located through subsequent least-squares full-matrix refinement cycles and Fourier difference calculations. All non-hydrogen atoms were refined anisotropically, with all hydrogen atoms in idealized positions with isotropic U values set to 1.25 U (equiv.) of the parent atoms. The final Fourier difference map had a highest peak of 0.374 e Å^{-3} and a lowest peak of -0.518 e Å^{-3}. For the 1108 reflections collected with $F > 3.0\sigma(F)$, this model refined to $R = 0.0338$, $R' = 0.0295$. Atomic coordinates are given in Table 2, and selected bond lengths and angles in Table 3. The atom numbering scheme of the molecule is shown in Fig. 1 and the crystal structure packing diagram in Fig. 2.

(*b*) $[Cu(PMe_3)_4]^+[hfacac]^-$. Clear, colourless prisms of $[Cu(PMe_3)_4]^+[hfacac]^-$ were grown at -30 °C from tetrahydrofuran (thf) solution and mounted in capillary tubes under a nitrogen atmosphere. The crystal data collection and refinement parameters are presented in Table 1. The space group was determined to be *Pmmn* in the orthorhombic crystal system. The structure was solved by direct methods. When all non-hydrogen atoms were refined isotropically and anisotropically, large U values were observed for both C(6) and C(7). In an attempt to eliminate the large anisotropic character of C(6) and C(7), the data were refined in the space group *Pnm*2(1), but the resulting bond lengths and angles were highly distorted. After returning to *Pmmn*, hydrogen atoms were added (riding model) with isotropic U values set to 1.25 U (equiv.) of the parent atom. The anisotropic U of C(6) became very large and the methyl groups on P(2) were found to be disordered; therefore a three-fold model was introduced consisting of two sets of methyl carbon {set 1: C(6), C(7) and C(7″) [by symmetry from C(7)]; set 2: C(8), C(9) and C(10)}. Finally, all non-hydrogen atoms were refined anisotropically, the disordered methyl groups on P(2) were refined isotropically, and all hydrogen atoms were included in idealized or calculated positions with fixed isotropic U values equal to 1.25 U (equiv.) of parent atoms. The hydrogen-atom positions of the disordered methyl groups were calculated from the methyl positions of the previous refinement. All software and source of scattering factors are contained in the SHELXTL program library.[15] The 1123 reflections with $F > 3.0\sigma(F)$ refined to $R = 0.0748$, $R' = 0.0858$. In the final difference map the highest amplitude was 0.881 e Å^{-3} and the lowest -0.540 e Å^{-3}. Atom coordinates are given in Table 2 and selected bond lengths and angles in Table 4. The atom numbering scheme of $[Cu(PMe_3)_4]^+[hfacac]^-$ is shown in Fig. 4(*a*) and 4(*b*) and the crystal structure packing diagram in Fig. 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The synthesis of the series of compounds $[CuX(PMe_3)_2]$ (X = hfacac, tfacac or acac) has previously been described.[14] The two methods used are presented in equations (1) and (2).

$$[CuX(PMe_3)] + PMe_3 \longrightarrow [CuX(PMe_3)_2] \qquad (1)$$

$$Na^+X^- + \text{‘}CuCl(PMe_3)_2\text{’} \longrightarrow [CuX(PMe_3)_2] + NaCl \qquad (2)$$

The starting material, ‘$CuCl(PMe_3)_2$’, was prepared from reaction (3).

$$[CuCl(PMe_3)] + PMe_3 \longrightarrow \text{‘}CuCl(PMe_3)_2\text{’} \qquad (3)$$

During these syntheses some unusual observations were noted. The species ‘$CuCl(PMe_3)_2$’, unlike other examples of $[CuCl(PR_3)_2]$ complexes, exhibited low solubility in non-polar aromatic hydrocarbon solvents, and much higher solubility in polar solvents such as acetone and thf. These solubility characteristics are more consistent with the existence of a salt rather than a covalent compound. In $[^2H_8]$toluene and C_6D_6 solution, ^1H and ^{13}C-$\{^1H\}$ NMR spectroscopy revealed only one type of PMe_3 chemical environment. In $[^2H_8]$toluene, at room temperature, ^{31}P NMR spectroscopy revealed the presence of a broad singlet at δ -47.9 superimposed on a much broader resonance ($\Delta\nu_{\frac{1}{2}} \approx 1200$ Hz) centred at approximately δ -39. On cooling, the sharper resonance moved to δ -44.5 and the broader resonance broadened further ($\Delta\nu_{\frac{1}{2}} \approx 4040$ Hz) at -30 °C. The ^1H NMR spectrum of the same solution exhibited a single peak on cooling to -70 °C. In $(CD_3)_2CO$ solution quite different behaviour was observed. Room-temperature ^1H NMR spectroscopy revealed a single resonance (doublet) at δ 1.28. On cooling, this resonance broadened and split into two broad resonances at -17 °C which sharpened to two resonances at δ 1.31 and 1.13 at -67 °C with relative intensities of 3 : 1. The value of the chemical shift observed at room temperature is close to that expected for the weighted average for rapid exchange between the two resonances observed at -67 °C.

In the room-temperature ^{31}P NMR spectrum of ‘$CuCl(PMe_3)_2$’ in $(CD_3)_2CO$ solution a single broad ($\Delta\nu_{\frac{1}{2}} \approx 1200$ Hz) resonance was observed at δ -38.2. On cooling to -10 °C this resonance was split into a 1 : 1 : 1 : 1 broad quartet with a broad singlet resonance which overlapped one of the quartet resonances. Further cooling to -50 °C did not result in any change of the position or ratio of these peaks. The 1 : 1 : 1 : 1 quartet is likely to have arisen from coupling between ^{31}P and the two NMR-active isotopes of copper, ^{63}Cu (70% natural abundance, $I = \frac{3}{2}$) and ^{65}Cu (30% natural abundance, $I = \frac{3}{2}$).[16] The approximate ratio of the two peaks, the singlet and the quartet, was estimated to be 1 : 3, respectively, by integration. This ratio of these species is the same as that observed by low-temperature ^1H NMR spectroscopy and is consistent with the presence of two species in rapid equilibrium at room temperature in solution.

In general, couplings to quadrupolar nuclei are observed when the quadrupolar nucleus possesses a symmetrical electric field gradient.[17] This is often the case for homoleptic transition-metal complexes with high symmetry. In the present case the existence of a salt such as $[Cu(PMe_3)_4]^+[CuCl_2]^-$, where it is expected that the copper cation electric field symmetry is high, is consistent with these observations. A similar observation has previously been made for the species $[Cu(PMe_3)_4]^+[CuMe_2]^-$, where $J(^{31}P\text{–}Cu) = 805$ Hz, while for $[Cu(PMe_3)_4]^+$-$[CuCl_2]^-$, $J(^{31}P\text{–}Cu) = 794$ Hz.[17] The broad singlet observed by low-temperature ^{31}P NMR spectroscopy is likely to arise from a species with a less-symmetrical copper environment since no phosphorus–copper coupling was observed. This species has not been identified yet, but at present we speculate that it may be a *covalent* compound, such as $[\{CuCl(PMe_3)_2\}_n]$.

Addition of approximately 0.25 equivalent of PMe_3 to the $(CD_3)_2CO$ solution of $[Cu(PMe_3)_4]^+[CuCl_2]^-$ resulted in two overlapping broad resonances in the ^{31}P NMR spectrum at $\delta \approx -38$ and ≈ -45, at room temperature. Cooling to -10 °C and further to -30 °C resulted in the observation of a 1 : 1 : 1 : 1 quartet at δ -38 together with a singlet at δ -56.9, consistent with the presence of free PMe_3.

To probe the nature of $[Cu(PMe_3)_4]^+[CuCl_2]^-$ further, single crystals were grown from toluene solution and characterized by single-crystal X-ray diffraction. A summary of the crystal data is presented in Table 1, atomic coordinates are given in Table 2 and relevant bond lengths and angles in Table 3. An ORTEP drawing of the molecular structure of $[Cu(PMe_3)_4]^+[CuCl_2]^-$ showing the atom numbering scheme is presented in Fig. 1, and a crystal-packing diagram in Fig. 2. As it can be seen from the figures the species crystallized exists as an ionic salt. There is no evidence for any interaction between the halogenocuprate anion, $[CuCl_2]^-$, and the cation $[Cu(PMe_3)_4]^+$. The anion $[CuCl_2]^-$ is linear, analogous to the structure of $[CuMe_2]^-$. The two Cu–Cl bond distances in

Table 1 Summary of crystallographic data for $[Cu(PMe_3)_4]^+[CuCl_2]^-$ and $[Cu(PMe_3)_4]^+[hfacac]^-$ *

	$[Cu(PMe_3)_4]^+[CuCl_2]^-$	$[Cu(PMe_3)_4]^+[hfacac]^-$
Chemical formula	$C_{12}H_{36}Cl_2Cu_2P_4$	$C_{17}H_{37}CuF_6O_2P_4$
M	502.2	574.9
Colour, habit	Clear, colourless prism	Clear, colourless prism
Space group	$P2_13$	*Pmmn*
a/Å	13.584(1)	10.703(2)
b/Å	—	15.077(3)
c/Å	—	8.997(2)
U/Å^3	2506.2(2)	1451.7(5)
F(000)	1040	596
Z	12	2
D_c/g cm^{-3}	1.331	1.315
R	0.0338	0.0748
R'	0.0295	0.0858

* Parameters in common include: temperature, 293 K; diffractometer, Siemens $R3_m/V$; radiation, Mo-Kα (λ = 0.710 73 Å); $R = \Sigma\Delta F/\Sigma F_o$, $R' = \Sigma w^{\frac{1}{2}}\Delta F/\Sigma w^{\frac{1}{2}}(2F)$, $w^{-1} = \sigma^2(F) + 0.0053F^2$.

Table 2 Atomic coordinates (× 10^4)

Atom	*x*	*y*	*z*
(*a*) $[Cu(PMe_3)_4]^+[CuCl_2]^-$			
Cu	434(1)	434(1)	434(1)
P(1)	−526(1)	−526(1)	−526(1)
C(1)	−760(6)	−1758(5)	−73(5)
P(2)	616(1)	1937(1)	−273(1)
C(2)	1529(4)	2744(4)	261(5)
C(3)	−460(4)	2720(4)	−265(6)
C(4)	957(6)	1954(5)	−1562(4)
Cu(2)	3665(1)	3665(1)	3665(1)
Cl(1)	4550(1)	4550(1)	4550(1)
Cl(2)	2793(1)	2793(1)	2793(1)
(*b*) $[Cu(PMe_3)_4]^+[hfacac]^-$			
Cu	2500	2500	−122(1)
P(1)	765(2)	2500	1332(3)
C(4)	−745(12)	2500	547(13)
C(5)	613(11)	3342(10)	2606(14)
P(2)	2500	3723(2)	−1591(3)
C(6)	2500	4670	−366
C(7)	1220(32)	3911(21)	−2908(38)
C(8)	3132	4632	−525
C(9)	1055(32)	4127(20)	−2312(36)
C(10)	3505(32)	3604(22)	−3264(33)
C(1)	7500	2500	5773(13)
C(2)	7500	1685(7)	5027(10)
O(1)	7500	1511(6)	3701(8)
C(3)	7500	877(9)	6059(16)
F(1)	7500	1006(5)	7469(9)
F(2)	6541(7)	345(5)	5734(8)

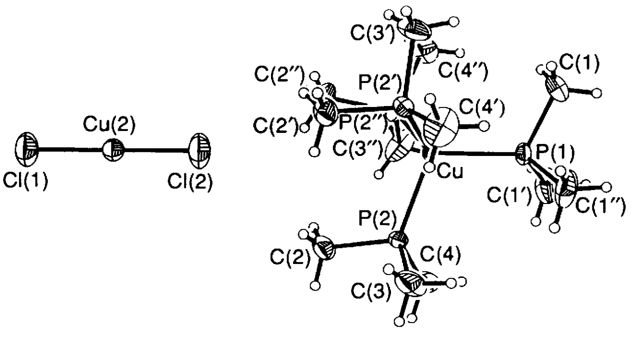

Fig. 1 An ORTEP plot of the molecular structure of $[Cu(PMe_3)_4]^+[CuCl_2]^-$ showing the atom numbering scheme

Table 3 Selected bond lengths (Å) and angles (°) for $[Cu(PMe_3)_4]^+[CuCl_2]^-$

Cu–P(1)	2.259(2)	Cu–P(2)	2.270(1)
Cu–P(2')	2.270(1)	Cu–P(2'')	2.270(1)
P(1)–C(1)	1.810(6)	P(1)–C(1')	1.810(6)
P(1)–C(1'')	1.810(6)	P(2)–C(2)	1.807(6)
P(2)–C(3)	1.807(5)	P(2)–C(4)	1.812(6)
Cu(2)–Cl(1)	2.082(3)	Cu(2)–Cl(2)	2.051(3)
P(1)–Cu–P(2)	109.8(1)	P(1)–Cu–P(2')	109.8(1)
P(2)–Cu–P(2')	109.2(1)	P(1)–Cu–P(2'')	109.8(1)
P(2)–Cu–P(2'')	109.2(1)	P(2A)–Cu–P(2'')	109.2(1)
Cu–P(1)–C(1)	116.0(2)	Cu–P(1)–C(1')	116.0(2)
C(1)–P(1)–C(1')	102.2(3)	Cu–P(1)–C(1'')	116.0(2)
C(1)–P(1)–C(1'')	102.3(3)	C(1A)–P(1)–C(1'')	102.3(3)
Cu–P(2)–C(2)	116.8(2)	Cu–P(2)–C(3)	116.0(2)
C(2)–P(2)–C(3)	101.3(3)	Cu–P(2)–C(4)	116.6(2)
C(2)–P(2)–C(4)	101.8(3)	C(3)–P(2)–C(4)	101.8(3)
Cl(1)–Cu(2)–Cl(2)	180.0(1)		

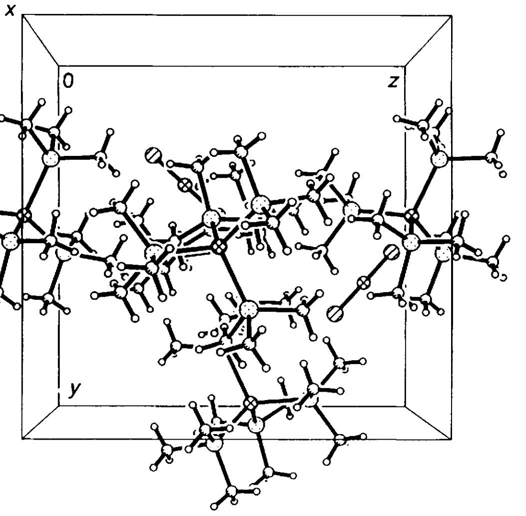

Fig. 2 Packing diagram for $[Cu(PMe_3)_4]^+[CuCl_2]^-$

$[CuCl_2]^-$ are different within the limits of the X-ray diffraction experiment, but the reason for this asymmetry is unclear at present and may depend on crystal-packing effects. In the cation the copper atom is in a tetrahedral environment of PMe_3 ligands. The Cu–P bond lengths of 2.270 and 2.259 Å are similar to those observed for $[Cu(PMe_3)_4]^+[CuMe_2]^-$ (2.269 and 2.253 Å).[17]

The presence of a symmetrical, tetrahedral $[Cu(PMe_3)_4]^+$ cation in the solid state is consistent with the low-temperature ^{31}P NMR spectrum where $J(^{31}P–Cu)$ coupling was observed. The absence of copper–phosphorus coupling at higher temperatures is consistent with a dynamic rearrangement process, probably *via* Cu–P bond cleavage, which results in lowered symmetry.

In contrast, addition of 1 equivalent of PEt_3 to $[CuCl(PEt_3)]$ resulted in formation of $[CuCl(PEt_3)_2]$, a white, volatile, low-melting solid that dissolved readily in non-polar aromatic hydrocarbon solvents. The vapour pressure at 90 °C was approximately 900 mTorr (*ca.* 120 Pa), close to the value for copper(I)[14] and copper(II)[18] β-diketonate compounds. The possibility that the high vapour pressure was derived from the loss of PEt_3 was discounted by ^1H NMR analysis of the starting material after the molecular weight measurement which showed no evidence for formation of $[CuCl(PEt_3)]$. Furthermore, $[CuCl(PEt_3)_2]$, could be sublimed unchanged *in vacuo*. To investigate the degree of oligomerization of $[CuCl(PEt_3)_2]$ in solution a cryoscopic molecular weight determination was carried out in benzene. Molecular weight data recorded at

Table 4 Selected bond lengths (Å) and angles (°) for $[Cu(PMe_3)_4]^+[hfacac]^-$ *

Cu–P(1)	2.272(2)	Cu–P(2)	2.269(3)	P(2)–C(10)	1.858(31)	C(1)–C(2)	1.400(12)
P(1)–C(4)	1.764(13)	P(1)–C(5)	1.718(14)	C(1)–C(2′)	1.400(12)	C(2)–O(1)	1.222(12)
P(2)–C(7)	1.833(34)	P(2)–C(6)	1.803(3)	C(2)–C(3)	1.532(17)	C(3)–F(1)	1.284(16)
P(2)–C(9)	1.784(33)	P(2)–C(8)	1.804(3)	C(3)–F(2)	1.335(11)		
P(1)–Cu–P(2)	109.6(1)	C(9)–P(2)–C(10)	103.9(15)	C(8)–P(2)–C(9)	105.0(10)	C(2)–C(3)–F(2)	107.9(8)
P(2)–Cu–P(1′)	109.6(1)	C(6)–P(2)–C(7′)	105.8(10)	C(8)–P(2)–C(10)	106.7(10)	F(1)–C(3)–F(2*)	107.9(8)
P(2)–Cu–P(2′)	108.8(2)	C(6)–P(2)–C(7″)	96.7(21)	Cu–P(2)–C(7′)	120.1(10)		
Cu–P(1)–C(4)	121.2(4)	P(1)–Cu–P(1′)	109.7(1)	Cu–P(2)–C(9′)	119.3(10)	C(1)–C(2)–C(3)	114.1(9)
C(4)–P(1)–C(5)	100.4(5)	P(1)–Cu–P(2′)	109.9(1)	Cu–P(2)–C(10′)	113.1(10)	C(2)–C(3)–F(2)	110.2(8)
Cu–P(2)–C(6)	106.7(1)	Cu–P(1)–C(5)	117.5(4)	C(1)–C(2)–O(1)	131.0(10)	C(2)–C(3)–F(2*)	110.2(8)
C(6)–P(2)–C(7)	105.8(10)	C(5)–P(1)–C(5′)	95.3(9)	O(1)–C(2)–C(3)	114.9(10)	F(2)–C(3)–F(2*)	100.5(11)
Cu–P(2)–C(9)	119.3(10)	Cu–P(2)–C(7)	120.1(10)	C(2)–C(3)–F(1)	118.6(11)		
Cu–P(2)–C(10)	113.1(10)	Cu–P(2)–C(8)	107.9(1)				

* P(1′), P(2′) generated by transformation $\frac{1}{2} - x, \frac{1}{2} - y, z$. P(2′), C(5*) generated by transformation $x, \frac{1}{2} - y, z$.

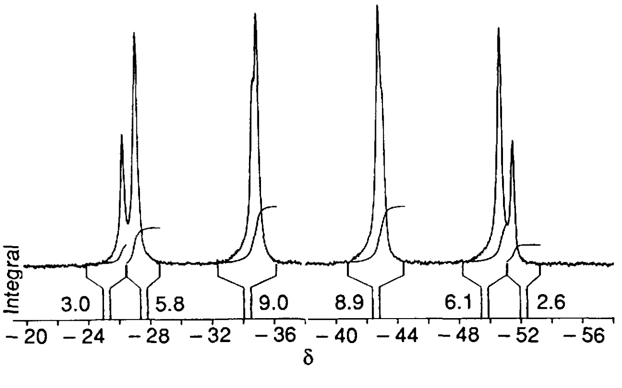

Fig. 3 Low-temperature ^{31}P NMR spectrum of $[Cu(PMe_3)_4]^+$-$[hfacac]^-$ showing coupling between ^{31}P and both NMR-active copper nuclei, ^{63}Cu and ^{65}Cu

three different concentrations revealed that $[CuCl(PEt_3)_2]$ was monomeric in this solvent. Based on these observations, it seems likely that $[CuCl(PEt_3)_2]$ exists as a covalent compound, unlike the analogous PMe_3 compound.

It seems unlikely that the β-diketonate compounds $[CuX(PR_3)_2]$ where $PR_3 = PMe_3$ or PEt_3 exist as salts $[Cu(PR_3)_4]^+[CuX_2]^-$, based on their physical properties. No evidence was found for a quartet arising from $J(^{31}P–Cu)$ that is characteristic of the $[Cu(PMe_3)_4]^+$ cation in solution. However, the addition of an excess of PMe_3 to $[CuX(PMe_3)_n]$, $n = 1$ or 2, resulted in formation of white species with the physical characteristics of ionic salts and which analysed as $[CuX(PMe_3)_4]$ (see Experimental section).

$$[CuX(PMe_3)_n] + \text{excess of } PMe_3 \longrightarrow [Cu(PMe_3)_4]^+[X]^- \quad (4)$$

The presence of the $[Cu(PMe_3)_4]^+$ cation in solution is consistent with the room-temperature ^{31}P NMR data for hfacac, tfacac and acac derivatives which all exhibit coupling to *both* spin-active isotopes of copper, ^{63}Cu and ^{65}Cu. A typical ^{31}P NMR spectrum is shown in Fig. 3. All three species exhibit similar ^{31}P and ^{1}H NMR chemical shifts. Cooling below room temperature sharpens the ^{31}P NMR quartets to reveal more clearly coupling to ^{63}Cu and ^{65}Cu which was not observed previously for either $[Cu(PMe_3)_4]^+[CuCl_2]^-$ or $[Cu(PMe_3)_4]^+[CuMe_2]^-$.[17] The coupling to both spin-active copper isotopes is manifest in *two* overlapping 1:1:1:1 quartets with measured intensity ratio of 70:30 for ^{63}Cu:^{65}Cu, respectively, as shown in Fig. 3. Further confidence in this assignment comes from a comparison of the ratio of ^{31}P to ^{63}Cu and ^{65}Cu coupling constants of 795 and 852 Hz, respectively, which is very close to the ratio of the magnetogyric ratios of ^{63}Cu and ^{65}Cu.[16] No evidence for any other phosphorus-containing species was observed in $(CD_3)_2CO$ solution. The addition of an excess of PMe_3 to $(CD_3)_2CO$ solutions of $[Cu(PMe_3)_4]^+$-$[hfacac]^-$ resulted in the presence of a new singlet resonance at δ −57.0, but no change of the quartets. Cyclic voltammetry of $[Cu(PMe_3)_4]^+[hfacac]^-$ in acetonitrile–tetra-*n*-butylammonium chloride indicated a reversible oxidation at 0.982 V relative to calomel, and an irreversible reduction.

To provide a firm basis for these assignments, single crystals of $[Cu(PMe_3)_4]^+[hfacac]^-$ were subject to X-ray analysis. The crystal data are summarized in Table 1, the atomic positional parameters in Table 2 and selected bond lengths and angles in Table 4. Fig. 4 shows an ORTEP plot with the atom numbering scheme while Fig. 5 shows the crystal-packing diagram for $[Cu(PMe_3)_4]^+[hfacac]^-$. The co-ordination environment of copper in $[Cu(PMe_3)_4]^+$ is very similar to that in $[Cu(PMe_3)_4]^+[CuX_2]^-$ where X = Me or Cl. The P–Cu–P angles are close to the tetrahedral angle and the Cu–P distances of 2.272 and 2.269 Å are similar. The $[hfacac]^-$ ligand is clearly not associated with the cation as shown by Fig. 5. The negative charge appears to be delocalized over the O(1)–C(2)–C(1)–C(2′)–O(1′) atom core in the C_{2v} symmetric anion. The O–C and C(1)–C(2) distances of 1.22 and 1.40 Å respectively are similar to those observed in analogous co-ordinated β-diketonate ligands such as in $[Cu(hfacac)(PMe_3)]$ where O–C and C–C distances are 1.23 and 1.24 Å and 1.37 and 1.39 Å, respectively.[14,19,20]

Again, the analogous reactions with the PEt_3 species are quite different. Addition of an excess of PEt_3 to any of $[CuX(PEt_3)_n]$ (X = hfacac, tfacac or acac; $n = 1$ or 2) does not result in any reaction. When these reactions are carried out in a 5 mm NMR tube and investigated by ^{1}H and ^{31}P NMR spectroscopy the resonances arising from both free and co-ordinated PEt_3 are significantly broadened, indicating the presence of an exchange process on the NMR time-scale.

Conclusion

In the complexes $[CuX(PMe_3)_n]$ (X = β-diketonate with $n = 1$ or 2 or Cl with $n = 1$) the addition of PMe_3 resulted in complete displacement of the β-diketonate and chloride ligands from the copper(I) co-ordination sphere. In contrast, addition of PEt_3 to the analogous triethylphosphine complexes does not result in this reaction, although phosphine-ligand exchange was observed. Since PMe_3 and PEt_3 exhibit similar basicities[21] it seems likely that the difference in reactivity is best explained by the different steric demands of these ligands, and their ability to form a four-co-ordinate $[CuL_4]^+$ complex. It has been shown previously that the steric dividing line between three- and four-co-ordinate $[Cu(PR_3)_n]^+$ complexes occurs at ligands with the steric demands of PPh_3.[9] However, in this work, three-co-

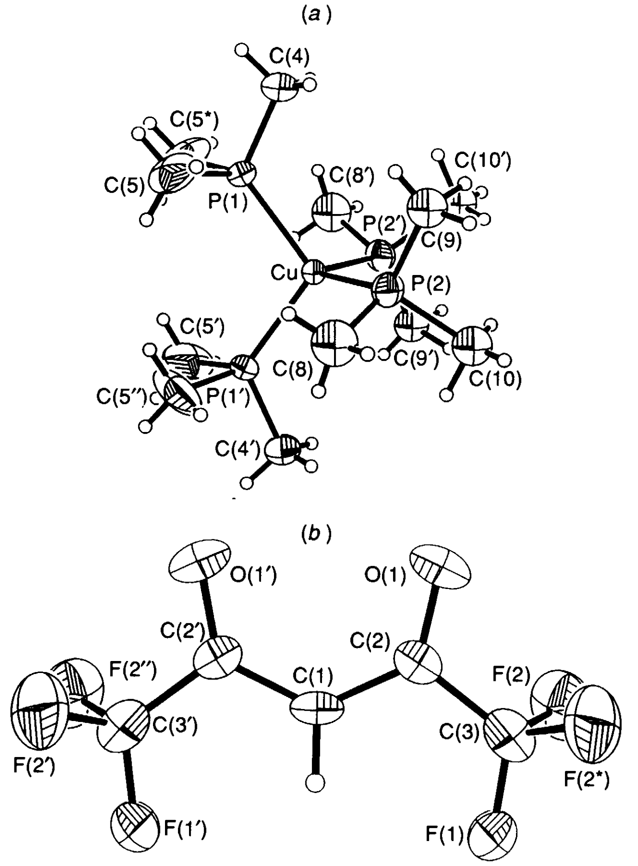

Fig. 4 An ORTEP plot of the molecular structure of (*a*) $[\mathrm{Cu(PMe_3)_4}]^+$ {one component of the disordered methyl groups [C(6) and C(7) around P(2) and their symmetry equivalents around P(2')] have been omitted for clarity} and (*b*) $[\mathrm{hfacac}]^-$ in $[\mathrm{Cu(PMe_3)_4}]^+[\mathrm{hfacac}]^-$ showing the atom numbering scheme

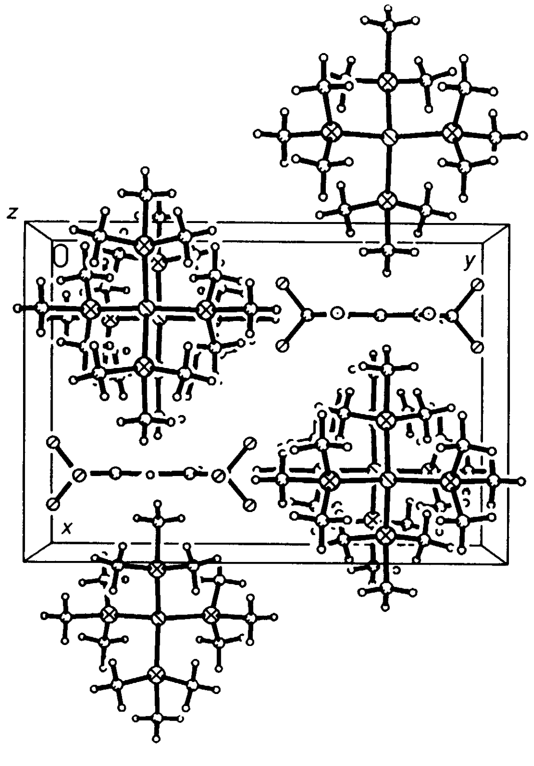

Fig. 5 Crystal packing diagram for $[\mathrm{Cu(PMe_3)_4}]^+[\mathrm{hfacac}]^-$

ordinate species such as $[\mathrm{Cu(PEt_3)_3}]^+[\mathrm{X}]^-$ (X = β-diketonate) were not observed. If the thermodynamic driving force for the displacement of the hard anions, $\mathrm{Cl^-}$ and β-diketonate, from the copper(I) co-ordination sphere is the preference for soft Lewis bases $\mathrm{PR_3}$, then perhaps the formation of three copper–phosphine bonds is insufficient, while formation of *four* (together with the steric protection afforded the copper centre by four ligands) is adequate.

Furthermore, if the phosphorus-containing material observed by ^{1}H and ^{31}P NMR spectroscopy in $[\mathrm{Cu(PMe_3)_4}]^+[\mathrm{CuCl_2}]^-$ is $[\mathrm{CuCl(PMe_3)_2}]$, then these species may exist in equilibrium as described by equation (5). This reaction may provide insight

$$2[\mathrm{CuCl(PMe_3)_2}] \rightleftharpoons [\mathrm{Cu(PMe_3)_4}]^+[\mathrm{CuCl_2}]^- \quad (5)$$

into thermally induced copper(I) disproportionation reactions, as exemplified by equation (6) (X = β-diketonate) which leads

$$2\mathrm{Cu^IXL}_n \rightleftharpoons \mathrm{Cu^0} + [\mathrm{Cu^{II}X_2}] + 2n\mathrm{L} \quad (6)$$

to chemical vapour deposition of copper.[12] Further studies are in progress to explore these possibilities.

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