Preparation and Crystal Structure of $Cu_4[Pr^iP–CH_2–PPr^i_2]Cl_3(Py)_2$ (Py = pyridine): A Novel Copper Complex with a Triply Bridging Secondary Phosphido Group μ_3-PRR′ [R = Pr^i; R′ = $CH_2–PPr^i_2$]

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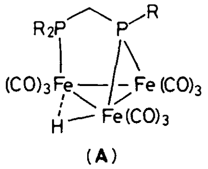
The first copper complex $Cu_4(Pr^iP–CH_2–PPr^i_2)Cl_3(Py)_2$ (Py = pyridine) containing a triply bridging secondary phosphido group μ_3-PRR′ has been synthesized and characterized by *X*-ray crystallography.

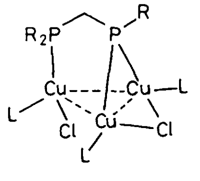
Owing to the close proximity of the phosphorus atoms, phosphidophosphines $R_2P–CH_2–PR$ may bridge triangular arrays of three transition metal atoms and thus act as five-electron donors. Thus oxidative addition reactions of tertiary secondary methylene bisphosphines[1] with excess of enneacarbonyldi-iron afford Fe_3 clusters of type (**A**).[2]

Using transition metal halides instead of carbonyl compounds, cleavage of the P–Si bond in the silyl derivatives $R_2P–CH_2–PRSiMe_3$[3] [Scheme 1(a)] might offer a route for the anionic introduction of the phosphidophosphine ligands into oligometallic complexes or clusters of type (**B**). If CuCl is employed in this reaction, peripheral copper co-ordination sites of (**B**) would be occupied by both chloride and donor ligands such as pyridine (Py).

However, when $Pr^i_2P–CH_2–PPr^iSiMe_3$ was treated with CuCl and pyridine as shown in Scheme 1(b), instead of (**B**), a yellow compound of composition $Cu_4(Pr^iP–CH_2–PPr^i_2)Cl_3(Py)_2$ (**1**) was obtained in 54% yield. Molecular weight determinations, electrical conductivity measurements, and $^{31}P-\{^1H\}$ n.m.r. spectra [δ 18.0 (Pr^i_2P), −59.7 p.p.m. (Pr^iP); $^2J_{PP}$ 85 Hz] are in agreement with a monomeric, non-ionic structure in solution.



(**A**)



(**B**) [L = pyridine (Py)]

An *X*-ray crystallographic study† established that the phosphidophosphine ligates each copper atom of (**1**). The pyridine ligands donate to the Cu(2) and Cu(4) atoms, which are bridged by the Cl(3) atom. In the solid state, (**1**) exists as an infinite polymer since the Cu(1)–Cu(1′) contact is bridged by twofold-related Cl(2) and Cl(2′) atoms while the Cu(3)–Cu(3″) contact is spanned by inversion-related Cl(1) and Cl(1″) atoms. A portion of this structure is shown in Figure 1. The ether molecule does not bond to the copper atoms but rather exists as a solvate.

The μ_3 bridging of the phosphido group is the most

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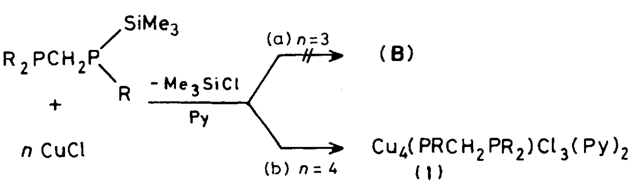
† *Crystal data* for the ether solvate of (**1**): $C_{20}H_{33}Cl_3Cu_4N_2P_2\cdot\frac{1}{2}C_4H_{10}O$, $M = 723.98 + \frac{1}{2}(74.12)$, monoclinic, space group $C2/c$, $a = 18.197(4)$, $b = 14.630(3)$, $c = 24.926(7)$ Å, $\beta = 107.88(2)°$, $U = 6315.3$ Å^3, $Z = 8$, $D_c = 1.601$ g cm^{-3}, $F(000) = 3080$, μ(Mo-K_α) = 3.04 mm^{-1}, $\lambda = 0.71073$ Å. 4122 Unique reflections were collected ($4 \leqslant 2\theta \leqslant 45°$) and corrected for absorption. The crystal structure was solved by direct methods and difference Fourier syntheses. 2778 Reflections with $F > 4\sigma(F)$ (296 parameters) were refined by large-block least-squares, all non-H atoms anisotropic, except ether (treated as O–C–C group), H atoms in calculated positions; $R = 0.050$, $R_w = 0.060$.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1

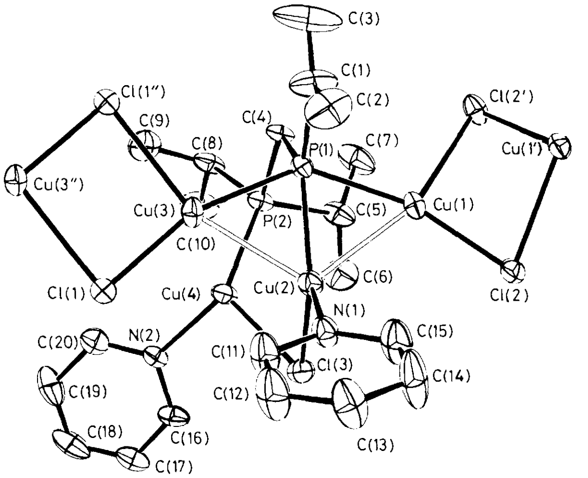


Figure 1. A segment of the polymeric structure of (**1**) with hydrogen atoms omitted. Selected bond lengths and angles: P(1)–Cu(1) 2.251(3), P(1)–Cu(2) 2.223(3), P(1)–Cu(3) 2.244(2), Cu(1)–Cl(2) 2.217(3) Cu(1)–Cl(2′) 2.473(3), Cu(2)–Cl(3) 2.281(3), Cu(3)–Cl(1) 2.193(3), Cu(3)–Cl(1″) 2.534(3), Cu(4)–Cl(3) 2.332(3), Cu(2)–N(1) 2.010(9), Cu(4)–N(2) 2.022(7), Cu(1)–Cu(2) 2.535(1), Cu(2)–Cu(3) 2.541(2) Å; Cu(1)–P(1)–Cu(3) 138.3(1), Cu(1)–Cu(2)–Cu(3) 111.71(6), P(1)–Cu(1)–Cl(2) 157.8(1), P(1)–Cu(1)–Cl(2′) 106.2(1), P(1)–Cu(3)–Cl(1) 161.2(1), P(1)–Cu(3)–Cl(1″) 105.0(1)°.

remarkable feature of the structure. Reference to the phosphido plane, defined by the atoms P(1), C(1), and C(4), facilitates the description of this interaction. Thus the P(1)–Cu(1) and P(1)–Cu(3) bond distances are inclined by 67.4 and 70.4°, respectively, to this plane and are nearly equal in length [mean 2.248(5) Å], while the P(1)–Cu(2) bond, which is 0.025(6) Å shorter, is inclined by only 1.5° to the phosphido plane. Furthermore, the P(1),Cu(1),Cu(2),Cu(3) fragment is planar to within ±0.026 Å, and the Cu(1)–Cu(2) and Cu(2)–Cu(3) distances [mean 2.538(4) Å] are sufficiently short to suggest bonding interactions.[4]

Such symmetrical μ_3 bridging by a phosphido group has previously only been reported for $[Li_2(\mu_3\text{-}Bu^t{}_2P)(\mu_2\text{-}Bu^t{}_2P)(C_4H_8O)]_2$, in which each Li–Li contact is spanned by two $Bu^t{}_2P$ species.[5]

The small variation in the P(1)–Cu bond lengths in (**1**) contrasts with the large spread (≥0.2 Å) in metal–phosphorus distances previously reported for PRR′-phosphido groups in ruthenium clusters.[6]

Because only two electron pairs are available for forming the three P(1)–Cu bonds in (**1**), the bridging must be electron deficient. Nevertheless, the P(1)–Cu bond lengths are much shorter than those of the electron-precise bridge in $[(Ph_2P\text{–}CH_2\text{–}CH_2\text{–}PPh_2)Cu(\mu_2\text{-}Ph_2P)]_2$ (**2**) [mean 2.36(1) Å[7]] which is the only previously reported copper phosphide structure. This apparent discrepancy may reflect the differences in copper co-ordination numbers [three in (**1**) and four in (**2**)] and in the basicity of the ligands. Thus the nonbridging P–Cu bond lengths in (**2**) [mean 2.30(1) Å] are also more than 0.1 Å longer than the P(2)–Cu(4) distance [2.194(3) Å] in (**1**), and the latter distance is 0.033(3) Å shorter than the analogous interaction in $[Cu(Pr^i{}_2P\text{–}CH_2\text{–}PPr^iH)Cl]_2$.[8]

While the Cu(2)–Cl(3)–Cu(4) bridge is fairly symmetrical, the Cu–Cl bonds of the Cu(1) and Cu(3) atoms are markedly dissimilar with the shorter distances roughly *trans* to the respective P(1)–Cu bonds (Figure 1). This implies a tendency for diagonal hybridization for the Cu(1) and Cu(3) atoms and suggests how (**1**) might depolymerize upon dissolution.

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