A Tetrameric Copper(I) Phosphide and its Conversion into a Bis(phosphido)cuprate and a Bis(phosphine)-complexed Tetrameric Copper(I) Thiolate

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The reaction of Bu^tPSiMe_3 with CuCl affords the tetrameric copper(I) phosphide, $(CuPBu^t_2)_4$, which in turn produces $[Li(thf)_2][Cu(PBu^t_2)_2]$ (thf = tetrahydrofuran) and $(Bu^t_2PH)_2(CuSBu^t)_4$ on reaction with $Li[PBu^t_2]$ and $Li[SBu^t]$, respectively.

Recent literature reflects a sustained interest in heteroatom cuprates.[1] In particular, we note that Cu^I phosphides play an important role as synthetic intermediates,[1a,d] but, despite being known for 25 years,[2] compounds of this type are not well characterised. Herein we report the synthesis and structure of $(CuPBu^t_2)_4$, (**1**), and results of a preliminary reactivity study. To the best of our knowledge, this compound is the first structurally characterised homoleptic phosphide of a late transition metal.

A key feature of the present work is the use of $Bu^t_2PSiMe_3$[3] as a phosphide-transfer agent.† In our hands, the reaction of $Li[PBu^t_2]$ with copper(I) halides was unsuccessful owing to extensive $Cu^I \rightarrow Cu^0$ reduction. However, treatment of anhydrous CuCl with $Bu^t_2PSiMe_3$ in tetrahydrofuran (thf) solution (25 °C), followed by solvent evaporation, extraction with n-hexane, cooling of the filtrate to −20 °C resulted in high (>90%) yields of colourless, crystalline (**1**).‡ The tetrameric nature of (**1**) was indicated by electron-impact mass spectroscopy (M^+, m/z 834) and structural details for the solid state were provided by an X-ray diffraction study.§ The centrosymmetric Cu_4P_4 core (Figure 1) consists of an essentially planar ring of alternating Cu and P atoms. The average P–Cu–P and Cu–P–Cu angles are 169.4(2) and 100.6(2)°, respectively. The average Cu–P distance [2.209(5) Å] is shorter than that in the heteroleptic complex, $(Ph_2PCu{\cdot}diphos)_2{\cdot}2C_6H_6$ (diphos = $Ph_2PCH_2CH_2PPh_2$) [av. 2.354(3) Å], the only other structurally characterised copper phosphide.[5] The planar Cu_4X_4 core of (**1**) resembles those of $(CuCH_2SiMe_3)_4$[6] and $(CuOBu^t)_4$[7] but contrasts with the somewhat non-planar Cu_4N_4 geometry

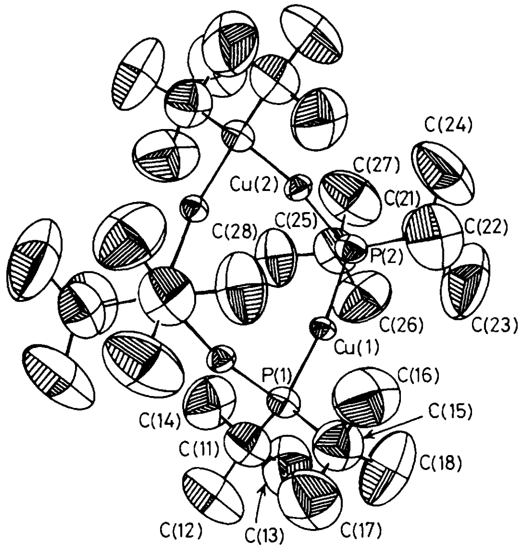

Figure 1. ORTEP view of $(CuPBu^t_2)_4$ (**1**), showing the atom numbering scheme. Selected bond lengths and angles: Cu(1)–P(1) 2.214(4), Cu(1)–P(2) 2.214(4), Cu(2)–P(1) 2.207(5), Cu(2)–P(2) 2.203(5) Å, Cu(1)–P(1)–Cu(2) 100.1(2), P(1)–Cu(1)–P(2) 169.2(2), Cu(1)–P(2)–Cu(2) 101.0(2), P(1)–Cu(2)–P(2) 169.6(2)°.

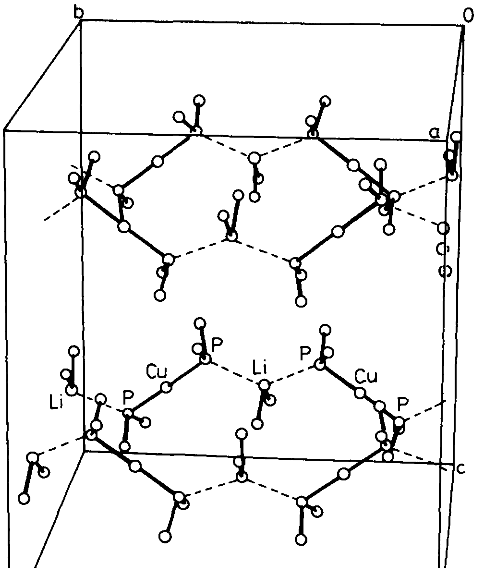

Figure 2. Unit cell packing diagram for $[Li(thf)_2][Cu(PBu^t_2)_2]$, (**2**). The Me groups of each Bu^t group have been removed for clarity. Only the O atoms of each thf ligand are shown.

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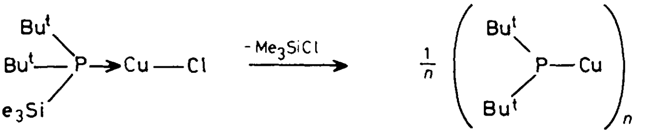
† It is possible that this reaction proceeds *via* prior co-ordination of the silylphosphine followed by 1,2 elimination of Me_3SiCl.[4]



‡ ^{31}P n.m.r. data (121.5 MHz, thf, relative to external 85% H_3PO_4): (**1**), δ 37.2 p.p.m. (s); (**2**), δ 43.2 p.p.m. (s); (**3**), δ 24.3 p.p.m. (d, $^1J_{PH}$ 287.0 Hz).

§ *Crystal data* for (**1**): $C_{32}H_{72}C_4P_4$, triclinic, $P\bar{1}$ (No. 2), $a = 8.668(2)$, $b = 11.877(2)$, $c = 12.207(2)$ Å, $\alpha = 67.73(1)$, $\beta = 70.56(2)$, $\gamma = 84.42(2)°$, $U = 1096$ Å^3, $Z = 1$, $D_c = 1.265$ g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 20.8$ cm^{-1}. For (**2**): $C_{24}H_{52}CuLiO_2P_2$, monoclinic, $C2/c$ (No. 15), $a = 16.796(10)$, $b = 17.529(9)$, $c = 20.482(9)$ Å, $\beta = 102.39(7)°$, $U = 5890$ Å^3, $Z = 8$, $D_c = 1.139$ g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 8.6$ cm^{-1}.

Totals of 3847 and 4255, unique reflections were collected for (**1**) and (**2**), respectively, on an Enraf-Nonius CAD-4 diffractometer at 25 °C. The data were corrected for Lorentz, polarisation, decay, and absorption. Of these, 2119 and 1625 reflections were considered observed [$I > 3.0\,\sigma(I)$] and used to solve (Patterson syntheses) the structures of (**1**) and (**2**) respectively, with final residuals, $R = 0.0790$ for (**1**) and $R = 0.0804$ for (**2**). The carbon atoms of (**1**) exhibit high thermal motion due to poor crystal quality.

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.

of $(CuNEt_2)_4$.[8] As expected, the non-bonded Cu···Cu distances in (**1**) (av. 3.398 Å) are considerably larger than those in the analogous light atom systems.

Compound (**1**) is a versatile reagent. For example, treatment with $Li[PBu^t_2]$ affords the yellow crystalline bis(phosphido) cuprate, $[Li(thf)_2][Cu(PBu^t_2)_2]$ (**2**), in virtually quantitive yield.‡ The P–Cu–P backbone of the $[Cu(PBu^t_2)_2]^-$ anion is approximately linear [176.5(2)°] and the two Cu–P bond lengths [2.266(4) and 2.246(5) Å] are slightly longer than those of (**1**).§ Both phosphido groups adopt pyramidal geometries as evidenced by the sums of bond angles at the phosphorus atoms [314.9(8) and 318.6(7)°]. The implied dihedral angle between the phosphorus lone pairs is close to 180°. Approximately tetrahedral co-ordination around each $[Li(thf)_2]^+$ cation is completed by a weak interaction with two phosphorus atoms on different anions (Li–P av. 2.83 Å). The infinite zig-zag chain of solvated lithium cations and cuprate moieties (Figure 2) is reminiscent of that found in $[\{Li(thf)_2PPh_2\}_\infty]$.[9]

In view of the foregoing, it was anticipated that treatment of (**1**) with $[SBu^t]^-$ would produce the analogous thiolate anion, $[Cu(SBu^t)(PBu^t_2)]^-$. However, the product of this reaction is $(Bu^t_2PH)_2(CuSBu^t)_4$, (**3**), which can be regarded as a bis(phosphine) complex of the tetramer, $(CuSBu^t)_4$. The structure of (**3**) was established by *X*-ray crystallography and details will be given in a subsequent publication.

We are grateful to the National Science Foundation (Grants CHE-8506029 and CHE-8517759), the Robert A. Welch Foundation (Grants F-135 and F-816) and the Texas Advanced Technology Research Program for financial support. R. A. J. thanks the Alfred P. Sloan Foundation for a fellowship (1985—1987).

Received, 23rd July 1987; Com. 1070

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