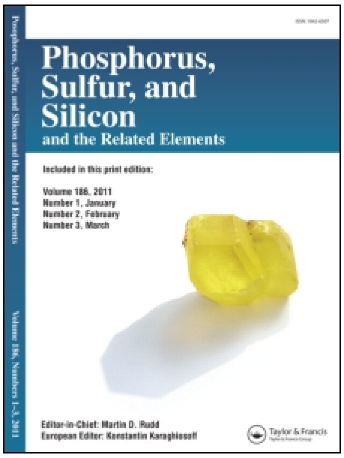


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Copper(I) Complexes with Electron Deficient μ_3-PRR' Bridging - a Novel Coordination Mode of Secondary Phosphido Groups in Transition Metal Chemistry

D. J. Brauer[a]; P. C. Knuppel[a]; O. Stelzer[a]
[a] Fachbereich 9, Anorg. Chemie, Bergische Universität-GH Wuppertal, Wuppertal 1

To cite this Article Brauer, D. J. , Knuppel, P. C. and Stelzer, O.(1990) 'Copper(I) Complexes with Electron Deficient μ_3-PRR' Bridging - a Novel Coordination Mode of Secondary Phosphido Groups in Transition Metal Chemistry', Phosphorus, Sulfur, and Silicon and the Related Elements, 49: 1, 449 — 452

To link to this Article: DOI: 10.1080/10426509008039000

URL: http://dx.doi.org/10.1080/10426509008039000

Phosphorus, Sulfur, and Silicon, 1990, Vols. 49/50, pp. 449-452
Reprints available directly from the publisher
Photocopying permitted by license only

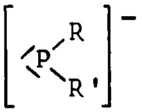
COPPER(I) COMPLEXES WITH ELECTRON DEFICIENT μ_3-PRR' BRIDGING - A NOVEL COORDINATION MODE OF SECONDARY PHOSPHIDO GROUPS IN TRANSITION METAL CHEMISTRY

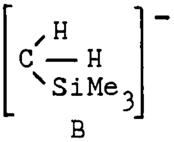
D. J. BRAUER, P. C. KNÜPPEL and O. STELZER
Fachbereich 9, Anorg. Chemie, Bergische Universität-GH Wuppertal, Gaußstraße 20, D-5600 Wuppertal 1

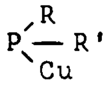
Abstract Copper(I) phosphido complexes containing electron deficient μ_3-PRR' bridges are formed by P-Si cleavage reactions in silylphosphines with CuCl or by depolymerization of polymeric $[Cu(PPh_2)]_n$ with PMe_3 or $PMe_3/CuCl$.

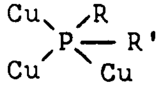
INTRODUCTION

Secondary phosphido groups PRR' (A) with their two lone electron pairs typically bind two transition metals via electron precise M-P bonds.[1] Metal-metal bridging may, however, also be achieved by ligands X providing only one pair of electrons for bonding within the M-X-M units, the tetrameric copper(I) alkyls, e. g. $[Cu(CH_2-SiMe_3)]_4$[2] being an example. The copper(I) phosphido species PRR'Cu (C) which are isoelectronic to $CH_2SiMe_3^-$ (B) should have the potential of binding two additional Cu(I) ions thus forming electron deficient μ_3-PRR'Cu_3 bridges (D).


A


B

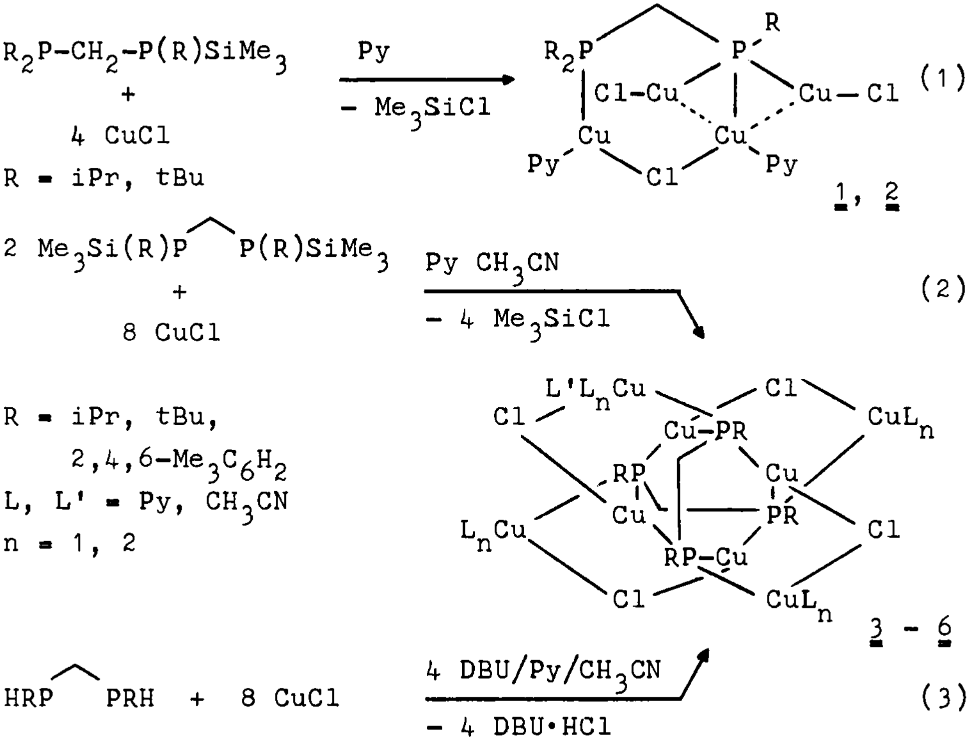

C


D

Formation of Copper(I) Phosphido Complexes with μ_3-PRR' Bridges

Copper(I) complexes showing this new type of coordination mode for secondary phosphido groups may be obtained by i) cleavage of the P-Si bonds in silylphosphines with copper(I) halides or ii) depolymerization of polymeric copper(I) phosphides by Lewis bases (e.g. pyridine, PMe_3). In preliminary work[3,4] we were able to show very recently that cleavage of the P-Si bond in the silylphosphines

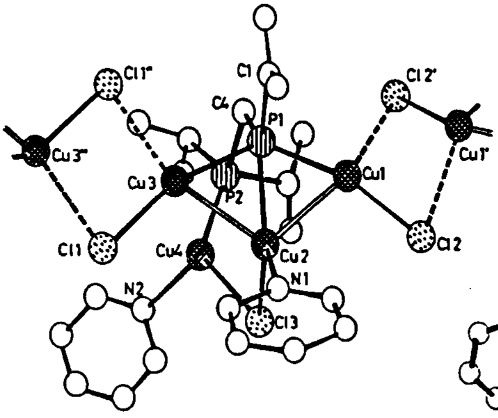
$(iPr)_2P\text{-}CH_2\text{-}P(iPr)SiMe_3$[5] or $Me_3Si(iPr)P\text{-}CH_2\text{-}P(iPr)SiMe_3$[5] with CuCl in presence of pyridine affords copper(I) phosphido complexes containing $\mu_3\text{-}P(iPr)(\text{-}CH_2\text{-})Cu_3$ units (eq. 1, 2; fig. 1, 2).



In an alternative synthetic approach to the Cu_8 clusters 3 - 6 disecondary methylenebisphosphines are employed as a source of $[RP^\frown PR]^{2-}$ bridging anions (eq. 3).

Compounds 1 - 6 were characterized by molecular weight determinations, $^{31}P\{^1H\}$-NMR spectra and conductivity measurements indicating a monomeric and nonionic structure in solution.

The x-ray structural analysis of 1 revealed that the $R_2P\text{-}CH_2\text{-}PR$ unit ligates each copper atom and established μ_3-bridging of the P(iPr)-CH_2 phosphido group (fig. 1). In the solid state 1 exists as an infinite polymer through Cu-Cl-Cu bridging of the monomers. The coordination geometry at P1 is distorted trigonal bipyramidal with P1, Cu2, C1, C4 forming the equatorial plane, the "axial" copper atoms Cu1 and Cu3 being inclined by 67.4° (Cu2-P1-Cu1) and 70.4° (Cu3-P1-Cu2) towards this plane.



1

FIGURE 1

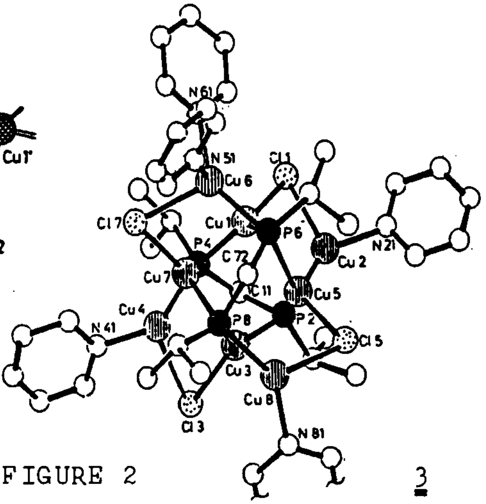
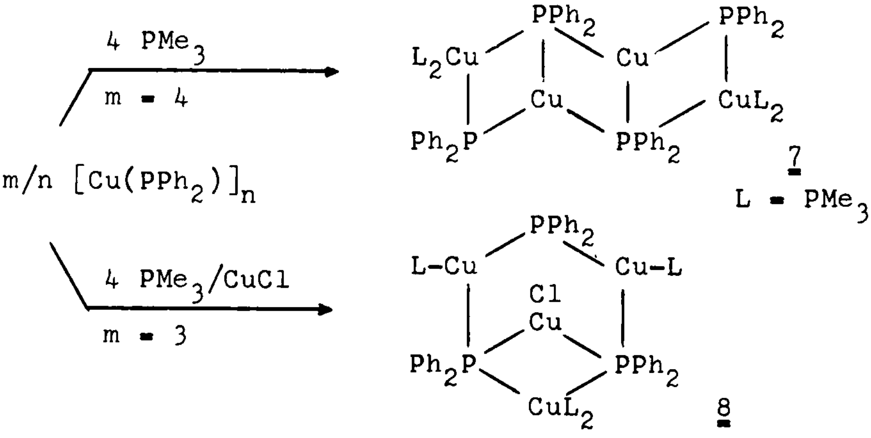


FIGURE 2

3

In the cluster type compound **3** (R = iPr) four $CuCl(Py)_n$ groups (n = 1, 2) are bound to the $Cu_4(RPCH_2PR)_2$ core via Cu-Cl-Cu and Cu-P-Cu bridges. As a result four electron deficient μ_3-$PR(CH_2)Cu_3$ units with distorted trigonal bipyramidal coordination geometry at P are formed.

Depolymerization of polymeric copper(I) phosphido complexes turned out to be an alternative synthetic procedure for the preparation of novel copper(I) phosphido complexes with μ_3-PR_2 bridges. Thus reaction of $[Cu(PPh_2)]_n$ **6** with PMe_3 or PMe_3/CuCl yielded phosphido complexes (**7**, **8**) containing μ_2-PPh_2 and μ_3-PPh_2 in the same molecule (eq. 4, 5).



(4)

(5)

The x-ray structural analysis of 8 (fig. 3, 4) shows an almost planar six-membered Cu_3P_3 ring system to which one CuCl acceptor unit is added, thus forming two μ_3-PPh_2Cu_3 units with distorted trigonal bipyramidal coordination at phosphorus.

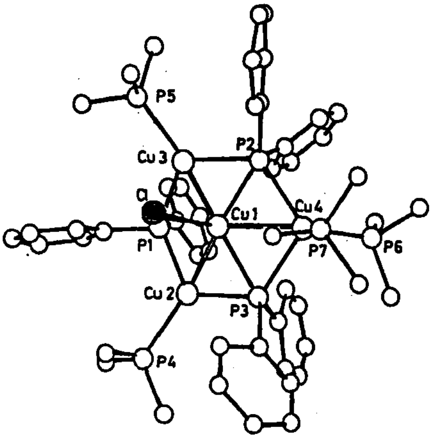


FIGURE 3

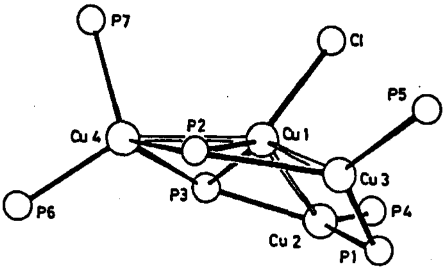


FIGURE 4

The atoms Cu1, P2, C19, C13 or Cu1, P3, C25, C31 define the equatorial planes, Cu3 and Cu4 or Cu2 and Cu4 occupy the "axial" positions. The position of the CuCl acceptor and the geometry of the six-membered Cu_3P_3 ring system is shown in fig. 4. The average values of Cu-P(μ_2-PPh_2) (229.5 pm) and Cu-P(μ_3-PPh_2) 239.0 (eq) or 246.5 ppm (ax)) are in agreement with the electron deficient nature of Cu-P bonding in the μ_3-PPh_2Cu units.

REFERENCES

1. A. J. Carty, S. A. MacLaughlin and D. Nucciarone, in Phosphorus 31 NMR Spectroscopy in Stereochemical Analysis, edited by J. G. Verkade and L. D. Quin (VCH Publishers Inc., 1987) p. 559.
2. J. A. J. Jarvis, R. Pearce and M. F. Lappert, J. C. S. Dalton Trans. 1977, 999.
3. D. J. Brauer, P. C. Knüppel and O. Stelzer, J. C. S. Chem. Commun. 1988, 551.
4. F. Gol, P. C. Knüppel, O. Stelzer and W. S. Sheldrick, Angew. Chem. 100, 1008 (1988).
5. F. Gol, G. Hasselkuß, P. C. Knüppel and O. Stelzer, Z. Naturforsch. 43b, 31 (1988).
6. K. Issleib and H. O. Fröhlich, Chem. Ber. 95, 375 (1961).