Synthesis and molecular structure of the first tetranuclear copper(I) silylphosphido cluster [Cu(CyPSiMe$_2$PHCy)]$_4$

Markus Faulhaber, Matthias Driess*† and Klaus Merz

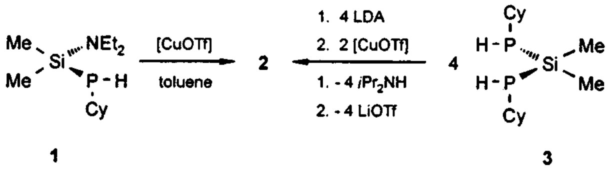
Lehrstuhl für Anorganische Chemie I, Ruhr-Universität, Universitätsstr. 150, D-44801 Bochum, Germany

The reaction of *N*,*N*-diethylamino(cyclohexylphosphino)dimethylsilane 1 with the benzene solvate of copper(I) trifluoromethylsulfonate furnishes the title complex 2, which has been structurally characterized by X-ray diffraction; the same product results on conversion of bis(cyclohexylphosphino)dimethylsilane 3 with copper(I) trifluoromethylsulfonate in the presence of lithium diisopropylamide as an auxilliary base.

Secondary phosphido anions [RRP]$^-$ are of considerable interest as ligands in the coordination chemistry of transition metals and clusters thereof.[1] Such complexes are also attractive as soft nucleophilic transphosphination reagents for selective synthesis of functionalized phosphane ligands. This has recently been shown for oligomeric copper(I) phosphido complexes.[2] Hitherto knowledge of the structural chemistry and the structure–reactivity relationship of copper phosphido aggregates has been relatively scarce and a silylphosphido cluster has not been described. A convenient method for the preparation of phosphido bridged transition metal complexes and clusters is the electrophilic cleavage of Si–P bonds in silylphosphanes through the corresponding metal halides and alkoxides.[3] However, we recently reported on the template synthesis of the first hexaphosphahexasilacyclododecane by the reaction of a triphosphatrisilacyclohexane with copper(I) or silver(I) trifluoromethylsulfonate, where the building up of new Si–P bonds instead of cleavage was observed.[4] In order to extend this building up method for the preparation of acyclic silylphosphane and −phosphido chelate ligands, we are exploring the reactivity of Si-functionalized silylphosphanes toward coin metal(I) complexes.

Here we report on two preparation routes to the first tetranuclear copper(I) silyl phosphido complex **2** (Fig. 1), containing the [CyPHSiMe$_2$CyP]$^-$ ligand, and we describe its molecular structure which was elucidated by single-crystal X-ray diffraction.

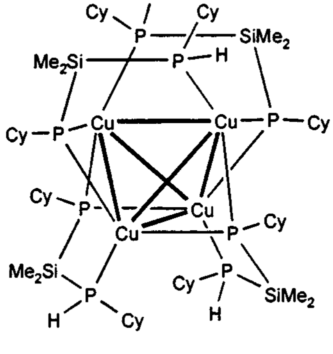
While it was anticipated that the P–H bond in a secondary silylphosphane of the type R$_3$Si–PH–R would be metalated by copper(I) trifluoromethylsulfonate ([CuOTf]), surprisingly, transphosphination–silylation reactions were observed, leading to a Cu$^{\text{I}}$ silylphosphidophosphane aggregate. Hence the *N*,*N*-diethylamino(cyclohexylphosphino)dimethylsilane **1** reacts with the benzene solvate of [CuOTf] in toluene to give **2** in the form of dark red crystals in 75% yield (Scheme 1).



Scheme 1

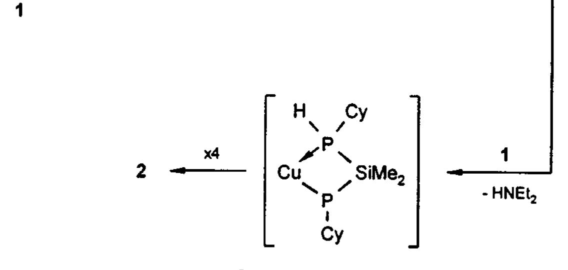
Compound **1** (colourless liquid, bp$_{0.01\text{Torr}}$ = 85 °C) is readily accessible *via* a procedure analogous to that for the synthesis of *N*,*N*-diethylamino(methylphosphino)dimethylsilane.[5] The reaction mechanism for the formation of **2** is unknown, but we suggest the stepwise process as outlined in Scheme 2.

Apparently, the first step is the electrophilic cleavage of the Si–P bond in **1** to give the corresponding copper phosphide as intermediate and the corresponding silyl(amino)triflate. The copper phosphide intermediate could then co-ordinate another molecule of **1** and subsequent replacement of the NEt$_2$ group leads to the PSiP chelate moiety in the co-ordination sphere of the Cu$^{\text{I}}$ centre. Compound **2** (Fig. 2) is also accessible starting from bis(cyclohexylphosphino)dimethylsilane **3** and [CuOTf] in the presence of LDA (lithium diisopropylamide) as base in 70% yield. Compound **3** was prepared through phosphination of dimethyldichlorosilane with LiAl(PHCy)$_4$ (Cy = cyclohexyl).[5] The composition of **2** was confirmed by elemental analysis. As expected, the ^{1}H NMR spectrum of **2** shows two signals at δ 0.3 and 0.4 for the diastereomeric methyl groups of the SiMe$_2$ moiety. The cyclohexyl groups exhibit unresolved multiplets between δ 0.7 and 2.9, and the signal of the chemically equivalent P–H protons is observed as a doublet at δ 3.7 ($^1J_{\text{PH}}$ = 267 Hz). The ^{31}P NMR spectrum of **2** shows multiplets at δ −100 and −72, which are relatively broad due to the quadrupole moment of the $^{63/65}$Cu nuclei (I = 3/2) . The P–H stretching vibration is observed in the IR spectrum at 2290 cm^{-1}.



2

Fig. 1 Chelated cluster **2**



Scheme 2

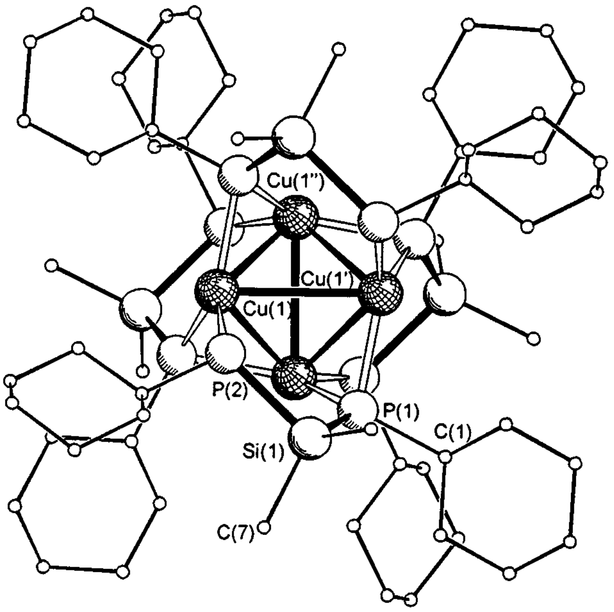


Fig. 2 Molecular structure of **2**. Hydrogen atoms omitted for clarity. Selected distances (Å) and angles (°): P(1)–Si(1) 2.207(5), P(2)–Si(1) 2.263(5), P(1)–C(1) 1.882(9), Si(1)–C(7) 1.890(11), P(2)–Cu(1) 2.261(4), P(1)–Cu(1) 2.270(3), P(1)–Cu(1") 2.235(4), Cu(1)–Cu(1) 3.071(3), Cu(1)–Cu(1") 2.911(2); P(1)–Si(1)–P(2) 98.7(2), Cu(1)–P(1)–Cu(1") 80.5(1), Cu(1")–Cu(1)–Cu(1") 63.67(6).

The X-ray crystallographic analysis‡ proves that **2** exists as a discrete tetramer and its core consists of a distorted Cu_4 tetrahedron. The latter is the result of the chelate property of the ($CyPSiMe_2PHCy$) ligand and, at the same time, of 'metallophilic' dispersion-type interactions between the co-ordinatively unsaturated Cu^I centres. Each phosphane-like P atom is only bonded to one Cu centre while the phosphido-like P atoms are μ_2-co-ordinated. Therefore, two of the six edges of the Cu_4 tetrahedron are not bridged by phosphorus. Accordingly, each Cu center has six neighbouring atoms, three of which are copper and three are phosphorus. The Cu–Cu distances are different: those for the four edges bridged by phosphorus (2.91 Å) are about 0.16 Å shorter than for the two unbridged edges (3.07 Å) of the Cu_4 tetrahedron. Other compounds containing cluster cores of four or more Cu atoms have also been reported. For example, the tetrameric compound $Cu_4I_4[As(C_2H_5)_3]_4$[6] and others with sulfur and nitrogen ligands[7,8] possess a tetrahedral core of Cu^I centres. A structurally related Cu_4 cluster to **2** was reported, where O,O-diisopropyldithiophosphate coordinates *via* η^1 and μ_2 sulfur centres to the Cu centres of the Cu_4 tetrahedron. The Cu–Cu distances in the latter are shorter (2.74 Å for the bridged and 2.95 Å for the unbridged edges of the tetrahedron) than in **2**. The Cu–Cu and Cu–P distances in **2** are within the range observed in other phosphido bridged Cu clusters.[2,7] According to the different co-ordination modes of the phosphino and the phosphido P centres of the ligands, the Si–P distances are not identical: the Si(1)–P(1) distance of the μ_2-coordinating phosphido group (2.207 Å) is about 0.5 Å shorter than the Si(2)–P(1) bond of the η^1-coordinating P atom. The present results underline the value of silylphosphanes for the synthesis of new oligophosphane ligands in the co-ordination sphere of Cu^I centres.

Notes and References

† E-mail: driess@ibm.anch.ruhr-uni-bochum.de

‡ *Crystal data* for **2**: $C_{56}H_{112}Cu_4P_8Si_8$, M = 1399.7, tetragonal, space group $I4_1/a$, a = 23.952(6), c = 12.799(4) Å, U = 7342 Å^3, Z = 4, intensity data were collected on a Siemens P4 diffractometer (Mo-Kα radiation, λ = 0.71707 Å, ω-scan, T = 203 K), $2\theta_{max}$ = 45°, 2381 measured reflections, 164 parameters, μ = 1.414 mm^{-1} $R1$ = 0.070 for 921 observed reflections $\{I > 2\sigma(I)$, $wR2$ = 0.206 (all reflections, wR2 = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^4)]^{\frac{1}{2}}\}$. The structure was solved by direct methods and refined by full-matrix least squares using SHELXL-93.[9] All non-hydrogen atoms were refined using anisotropic thermal parameters; hydrogen atoms were included by use of a riding model and fixed isotropic thermal parameters. CCDC 182/926.

1 A. J. Carty, S. A. McLaughlin and D. Nucciarone, in *Phosphorous-31 NMR Spectroscopy in Stereochemical Analysis*, ed. J. G. Verkade and L. D. Quin, Verlag Chemie, Weinheim, 1987, p. 559.
2 A. H. Cowley, D. M. Giolando, R. A. Jones, C. M. Nunn and J. M. Power, *J. Chem. Soc., Chem. Commun.*, 1988, 208; C. Meyer, H. Grützmacher and H. Pritzkow, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2471.
3 D. Fenske, in *Clusters and Colloids—From Theory to Applications*, ed. G. Schmid, Verlag Chemie, Weinheim, 1994, p. 219; D. J. Brauer, G. Hessler, P. C. Knüppel and O. Stelzer, *Inorg. Chem.*, 1990, **29**, 2370.
4 M. Driess, M. Faulhaber and H. Pritzkow, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1892.
5 L. D. Balashova, A. B. Bruker and L. Z. Soborovskii, *J. Gen. Chem. USSR*, 1966, **36**, 76.
6 A. F. Wells, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, 1936, **94**, 447.
7 V. Schramm, *Inorg. Chem.*, 1978, **17**, 714; C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1976, 2153; J. R. Nicholson, I. L. Abrahams, W. Clegg and C. D. Garner, *Inorg. Chem.*, 1985, **24**, 1092; M. Driess, S. Martin, K. Merz, H. Pritzkow, V. Pintchouk, H. Grützmacher and M. Kaupp, *Angew. Chem., Int. Ed. Engl.*, 1997, **9**, 1894.
8 S. L. Lawton, W. J. Rohrbaugh and G. T. Kokotailo, *Inorg. Chem.*, 1972, **11**, 612.
9 G. M. Sheldrick, SHELXL-93, A Program for Crystal Structure Refinement, University of Göttingen, 1990.

Received in Basel, Switzerland, 6th May 1998; 8/03394C