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COMMUNICATION

Dimeric 2,2-dimethyl-2-silabut-3-enyldiphenylphosphinecopper(I) bromide: a chelating olefinic-phosphine copper(I) complex

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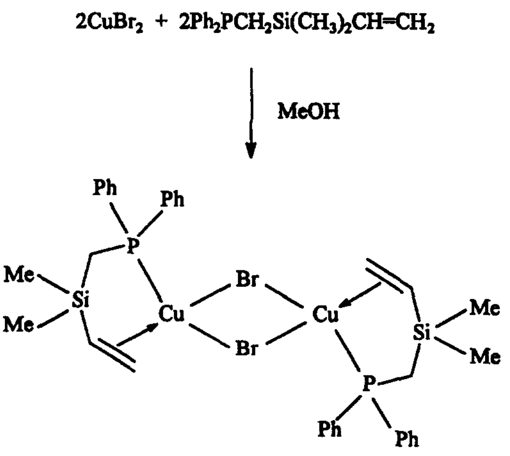
Abstract—The reaction between $CuBr_2$ and 2,2-dimethyl-2-silabut-3-enyldiphenylphosphine (L^1) in methanol produced the title complex **1**; the single crystal X-ray crystal structure of **1** reveals a centrosymmetric dimeric bromo-bridged species, with the copper(I) atoms bound to both the olefin and phosphorus donor sites on the ligands. © 1997 Elsevier Science Ltd

Keywords: mixed-donor ligand; phosphorus-olefin donation; copper bromide; crystal structure.

Olefin-phosphorus donor ligands can function solely as phosphorus donors or can coordinate to a metal centre *via* the olefin and the phosphorus [1]. An example of the latter is *trans*-2,2′-*o*-(di-*o*-tolylphosphino) stilbenerhodium chloride [2]. Here we report the complex $[(Ph_2PCH_2Si(CH_3)_2CH{=}CH_2)CuBr]_2$ **1**, the first example of a group 11 metal coordinated in this fashion. The X-ray structure of molecule **1** is also the first to feature the novel chelating ligand L^1, whose synthesis and spectroscopic characterisation we have previously reported [3]. The incorporation of a dimethylsilicon backbone not only improves complex solubility but also provides a marked increase in the tendency of such ligands to chelate [4].

Copper(II) is typically reduced to copper(I) upon coordination to phosphorus donor ligands [1], indeed, the addition of free ligand to copper(II) salts forms the basis for a wide range of copper(I)-phosphine syntheses [5] and was the preparative route undertaken here. The addition of one equivalent of L^1 to $CuBr_2$ in methanol produced a clear, colourless solution. Overnight stirring of the reaction mixture and subsequent solvent removal *in vacuo* produced a white solid, Scheme 1. Recrystallisation from methanol-CH_2Cl_2 afforded clear, colourless, lath crystals of the title complex in 45% yield.

Examination of the ^1H NMR spectrum of the complex[†] at 298 K revealed marked changes from the free ligand. A complex splitting pattern was observed in



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Scheme 1.

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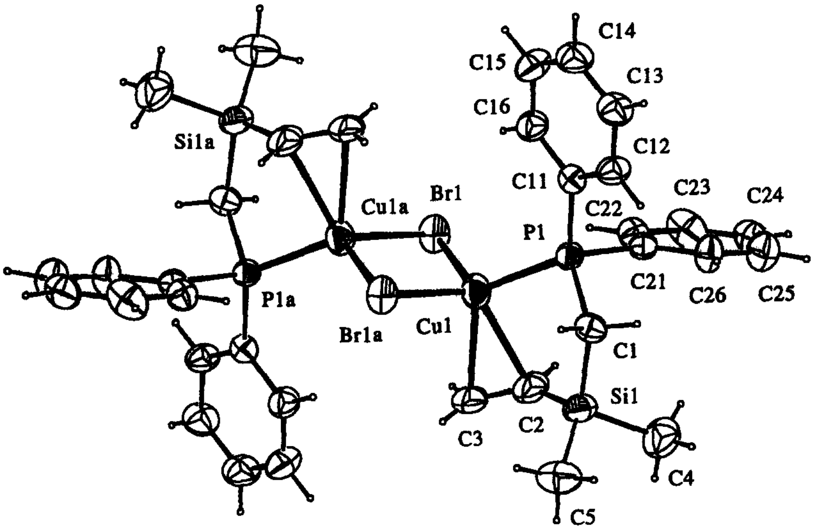

Fig. 1. Molecular structure of **1** showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Cu1-Br1 2.4770(12), Cu1-Br1a 2.4962(12), Cu1-P1 2.240(2), Cu1-Cu2 2.246(8), Cu1-C3 2.267(7), C2-C3 1.262(9), Cu1-Br1-Cu1a 72.34(4), P1-Cu1-Br1 121.87, P1-Cu1-C2 87.5(2), Cu1-C2-Si1 105.7(4). Labels ending with an 'a' refer to atoms at equivalent position *-x*, *-y*, *-z*. Anisotropic displacement ellipsoids are drawn at the 30% probability level; H atoms are indicated by small spheres of an arbitrary size.

the olefinic region, while the doublet assigned to the P—CH$_2$ backbone protons is shifted 0.4 ppm downfield, a clear indication of the change in the phosphorus environment upon complexation. ^{31}P NMR studies of the complex showed a sharp singlet at -14.98 ppm, shifted markedly downfield from the free L^1 (-27.50 ppm). There was no conclusive evidence in the infra-red spectrum for a phosphine-oxide side-product; the strong band at 1590 cm^{-1} for L^1 cannot be unambiguously assigned since both olefinic and phenylic C═C vibrations occur in this region.

The X-ray crystal structure ‡ of **1** shows that the molecule is a dimer, sitting about an inversion centre located at the centre of the Cu$_2$Br$_2$ moiety. An ORTEP view of **1** is shown in Fig. 1, together with selected important bond lengths and angles. The unique metal atom is a five coordinate, 18-electron centre; pairs of copper atoms are bridged by bromine atoms, Cu(1)—Br(1) 2.4770(12) and Cu(1)—Br(1a) 2.4962(12) Å. Alternatively, considering the olefinic bond to be monodentate, the species is pseudo-tetrahedral, with angles ranging from 104.1(2)° (P(1)—Cu(1)—olefin) to 121.87(7)° (Br(1)—Cu(1)—Br(1a). The Cu···Cu separation is 2.935(2) Å. The Cu(1)—P(1) bond length of 2.240(2) Å is non-controversial. A noteworthy feature of the complex concerns the olefinic donor group. Although a search of the October 1996 release of the Cambridge Structural Database [6] showed that the distances of 2.246(8) (Cu(1)—C(2)) and 2.267(7) Å (Cu(1)—C(3)) each lie within the literature-observed range (1.977 [7]–2.549 [8] mean 2.105 Å) for such bonds, the olefinic C═C bond length is unusually short. Values as low as 1.180 Å have been noted [9] for C═C distances in Cu-olefins (mean 1.357 Å), but the value of 1.262(9) Å observed for **1** is the fourth shortest example known to date [6]. The 5-membered ring comprising Cu(1), P(1), C(1), Si(1) and C(2) shows a high degree of strain, with bond angles ranging from 87.5(2) (P(1)—Cu(1)—C(2)) to 108.9(3)° (P(1)—C(1)—Si(1)): it is most readily described as having a half-chair conformation, twisted about the Cu(1)—P(1) bond.

Extensive studies into the complexation of a range of transition metal salts with L^1 and related ligands are under way. An investigation into the reactivity of **1** with monodentate phosphine and phosphite ligands is also in progress.

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† Selected spectroscopic data for **1**. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.63–7.29 (m, 10H, C$_6$H$_5$), 5.75–5.28 (m, 3H, CH═CH$_2$), 1.72 (d, 2H, CH$_2$), 0.02 (s, 6H, SiMe$_2$).

‡ Selected crystal data for **1**: C$_{34}$H$_{42}$Br$_2$Cu$_2$P$_2$Si$_2$, $M_r = 855.72$, orthorhombic, space group *Pbca*, $a = 18.444(2)$, $b = 10.0570(8)$, $c = 20.179(3)$ Å, $U = 3743.0(7)$ Å^3, $Z = 4$, $D_c = 1.518$ g cm^{-3}, $F(000) = 1728$, $R(F_{obs}) = 0.0517$ for 1342 observed reflections with $I > 2\sigma(I)$, $wR2(F^2) = 0.1141$ for all 3301 unique reflections, total number of parameters 199. Data were collected on an Enraf-Nonius CAD4 diffractometer and corrected for Lorentz, polarization and absorption effects. The structure was solved using NRCVAX96 [10] and refined using SHELXL93 [11]. All non-H atoms were allowed anisotropic motion. H atoms were allowed for as riding atoms. Methyl C5 is disordered over two adjacent sites. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number.

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