First aminosilyl bridging ligand in a bimetallic complex: structure of $[(OC)_3\{(Me_2N)_2(MeO)P\}Fe\{\mu\text{-}Si(OMe)_2(NMe_2)\}Cu(PPh_3)]$

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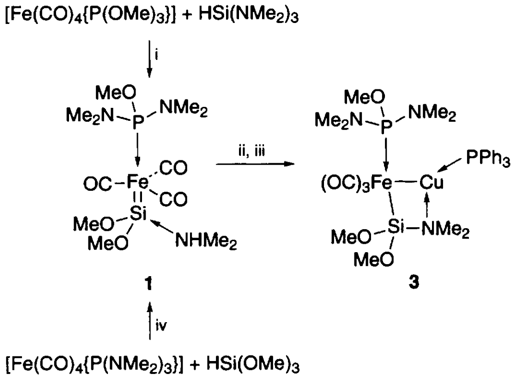
The first example of a bridging aminosilyl ligand between two transition metals is reported and the crystal structure of the bimetallic complex $[(OC)_3\{(Me_2N)_2(MeO)P\}Fe\{\mu\text{-}Si(OMe)_2(NMe_2)\}Cu(PPh_3)]$ establishes the presence of an unprecedented four-membered cycle; selective metal-promoted OMe/NMe$_2$ substituent exchange between P and Si occurs during the synthesis of the iron–silylene precursor.

Silyl- and silylene–metal complexes represent very interesting classes of molecules owing to their rich chemistry and their involvement in a number of catalytic processes.[1] We have recently reported that oxidative addition of $HSi(NMe_2)_3$ to $[Fe(CO)_5]$ afforded the amine-stabilized bis(dimethylamino)-silylene complex $[(OC)_4Fe{=}Si(NMe_2)_2(NHMe_2)]$[2] whereas the corresponding reaction with $HSi(OMe)_3$ yields the hydridosilyl complex *cis*-$[FeH(CO)_4\{Si(OMe)_3\}]$.

With the aim of preparing the first tris(amino)silyl iron metalate of the type *trans*-$[Fe\{Si(NMe_2)_3\}(CO)_3L]^-$ (L = two-electron phosphorus donor), we reacted $[Fe(CO)_4\{P(OMe)_3\}]$ with $HSi(NMe_2)_3$ under photochemical conditions.† Oxidative addition led to the amine-stabilized iron–silylene complex **1** in which two methoxy groups on phosphorus have exchanged with two amino groups on silicon. Since **1** was only obtained in *ca.* 30–40% yield (based on $^{31}P\{^1H\}$ NMR, other products not yet characterized), we attempted an alternative synthesis based on the reaction of $[Fe(CO)_4\{P(NMe_2)_3\}]$ with $HSi(OMe)_3$; this also led to **1** but in *ca.* 80% yield. These cross-experiments indicate that the subtle balance between the oxophilicity of the phosphorus and silicon centres may lead to highly selective substituent exchange reactions. A remarkable rearrangement of this type has been recently observed with OEt/NMe$_2$ groups and shown to be metal promoted.[2]

Deprotonation of **1** with excess KH in thf afforded the metalate complex $K[Fe(CO)_3\{P(OMe)(NMe_2)_2\}\{Si(OMe)_2(NMe_2)\}]$ **2** as shown by IR spectroscopy [ν(CO) (thf) 1810s, 1841vs, 1922m cm^{-1}]. Its reaction with $[CuCl(PPh_3)]$ at low temperature in a 1 : 1 Fe : Cu stoichiometry afforded the heterobimetallic complex $[(OC)_3\{(Me_2N)_2(MeO)P\}Fe\{\mu\text{-}Si(OMe)_2(NMe_2)\}Cu(PPh_3)]$ **3**, without any further ligand rearrangement (Scheme 1).†

The ^1H NMR spectrum of **3** contains a doublet centred at δ 2.56 for the twelve $P(NMe_2)_2$ protons and a singlet at δ 2.98 for the six $Si(NMe_2)$ protons. The P(OMe) protons give rise to a doublet centred at δ 3.44 and the Si(OMe) protons to a singlet at δ 3.79. In order to establish the nature of the bonding interactions involving the copper centre, an X-ray diffraction study was performed on single crystals of **3**.‡ This revealed the presence of a novel four-membered $Fe{-}Si{-}N{\rightarrow}Cu$ ring (Fig. 1). The N(1)–Cu distance of 2.151(4) Å corresponds to a bonding interaction. When the metal–metal bond is not considered, the coordination around the Fe centre is closer to trigonal bipyramidal than to octahedral, as also observed in related complexes containing a trialkoxysilyl ligand.[3] The Si–N(1)–Cu angle of 88.7(2)° is associated with a much wider C(7)–N(1)–C(8) angle of 111.3(5)°. The geometry at the Cu^I centre is distorted trigonal planar [sum of the valency angles = 359.90(18)°]. The Fe–Cu distance of 2.530(2) Å is comparable to the values found in the trinuclear complex $[Fe(CO)_4\{Cu(PPh_3)_2\}_2]$ which contains a nearly linear chain Cu–Fe–Cu [2.499(4), 2.522(4) Å][4a] and longer than found in complexes where the Fe–Cu bond is supported by a bridging dppm ligand [2.497(2) Å,[4b] 2.540(2) Å[4c]]. Compared with



Scheme 1 *Reagents and conditions*: i, pentane, −20 °C, *hν*, yield 30–40%; ii, KH, thf; iii, $[CuCl(PPh_3)]$, −78 °C; iv, pentane, −20 °C, *hν*, yield 80%

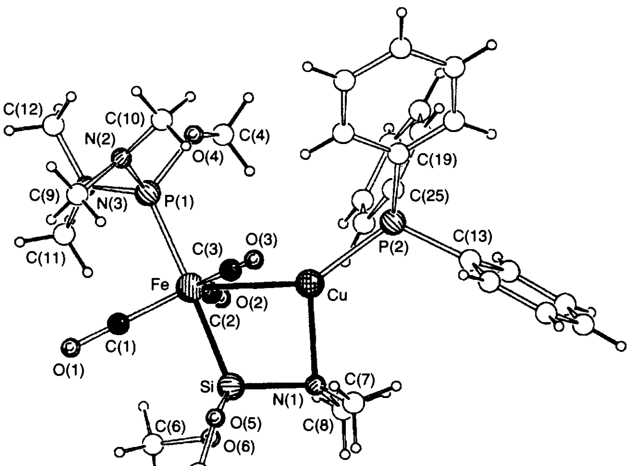
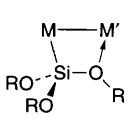


Fig. 1 View of the molecular structure of **3**. Selected bond distances (Å) and angles (°): Fe–C(1) 1.747(5), Fe–C(2) 1.748(3), Fe–C(3) 1.756(5), Fe–P(1) 2.194(2), Cu–P(2) 2.198(2), Si–O(5) 1.660(4), Si–O(6) 1.633(4), P(1)–O(4) 1.631(3), P(1)–N(2) 1.689(4), P(1)–N(3) 1.654(4); C(1)–Fe–C(2) 113.6(2), C(1)–Fe–C(3) 109.4(2), C(2)–Fe–C(3) 135.4(2), P(1)–Fe–Si 178.04(5), O(5)–Si–O(6) 108.3(2), O(5)–Si–N(1) 107.3(2), O(6)–Si–N(1) 101.7(2), N(2)–P(1)–N(3) 102.1(3), O(4)–P(1)–N(2) 94.4(2), O(4)–P(1)–N(3) 104.4(2), Fe–Cu–N(1) 90.80(12), Fe–Si–N(1) 110.28(14), Cu–Fe–Si 70.23(7), Fe–Cu–P(2) 145.22(5), P(2)–Cu–N(1) 123.88(12).

silylamines which have Si–N distances in the range 1.70–1.76 Å,[5] the lengthening observed in **3** may be ascribed to the bridging interaction. However, the Si–N(1) distance of 1.793(4) Å is much shorter than the Si–N distances [1.940(4), 1.958(4) Å] in the amino-bridged bis(silylene)iron complex $[(C_5Me_5)(OC)Fe\{Me_2Si\cdots NEt_2\cdots SiMe_2\}]$[6] and in the ethoxy analogue of **1** [1.916(5) Å].[2] As expected the Fe–Si distance of 2.268(2) Å is longer than the Fe–Si formal double bond [2.218(2) Å] in the ethoxy analogue of **1**.

Although the first four-membered cycles of the type M–Si–O→M′ (**A**) (M = Fe, M′ = transition or post-transition element) were discovered in 1989,[3a] their nitrogen analogues were unknown.



A

With the exception of a few homometallic rhenium complexes,[7] and of Fe–Cd[8a] and Fe–In complexes,[8b] units of type **A** have always been stabilized by an additional assembling ligand such as $Ph_2PCH_2PPh_2$. This is also the reason why four-membered cycles of the type Fe–Si–O→Cu have not yet been reported: coordination of the dppm phosphorus to the Cu centre leads to a trigonal-planar coordination around this metal which prevents coordination of a ligand *trans* to P. This geometrical constraint is lifted in **3** (Fig. 2).

It will now be interesting (*i*) to investigate the behaviour of the metalate derived from **1** with other metal centres since we have now established that both Si–OMe and $Si–NMe_2$ groups can form suitable bridges, and (*ii*) to explore whether the thermodynamic stability and kinetic lability which often characterize units **A** and confer unique properties to the corresponding molecules[9] will also be observed in M–Si–N→M systems.

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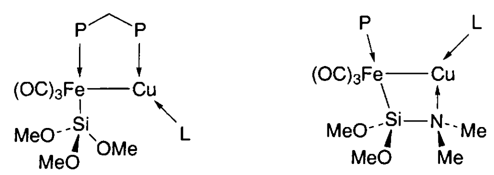

Fig. 2 Coordination geometry of the Cu centre in dppm-stabilized complexes and in **3**

Footnotes

† All reactions were performed under purified N_2, using carefully dried solvents.

Synthesis: **1**; a sample of $[Fe(CO)_4\{P(NMe_2)_3\}]$ (0.806 g, 2.0 mmol) and $HSi(OMe)_3$ (0.80 ml, 6.28 mmol) in pentane (60 ml) was irradiated with a 150 W lamp for 4 h at −20 °C. A white powder precipitated during irradiation. The solvent was decanted and the solid lightly dried *in vacuo*. Yield: 0.72 g (84%). FTIR (diethyl ether): ν(CO) 1859vs cm^{-1}; ^1H NMR (200 MHz, C_6H_6–C_6D_6, 25 °C, $SiMe_4$) δ 4.8 (s, vbr, 1 H, NH), 3.80 (s, 6 H, $SiOCH_3$), 3.67 [d, $^3J(HP)$ 13.6 Hz, 3 H, $POCH_3$], 2.77 [d, $^3J(HP)$ 10.2 Hz, 12 H, $PNCH_3$], 2.19 (s, 6 H, $SiNCH_3$); $^{31}P\{^1H\}$ NMR (81 MHz, C_6H_6–C_6D_6, 25 °C, H_3PO_4) δ 199.4; $^{13}C\{^1H\}$ NMR (50 MHz, C_6H_6–C_6D_6, 25 °C, $SiMe_4$) δ 215.3 [d, $^2J(CP)$ 28.5 Hz, 3 C, CO], 51.7 (s, 2 C, $SiOCH_3$), 51.5 (s, 1 C, $POCH_3$), 37.6 [d, $^2J(CP)$ 7.1 Hz, 4 C, $PNCH_3$], 37.35 (s, 2 C, $SiNCH_3$); ^{29}Si INEPT (39.8 MHz, C_6H_6–C_6D_6, 25 °C, $SiMe_4$) δ 64.4 [d, $^2J(SiP)$ 35.75 Hz]; MS(FAB$^+$): *m*/*z*: 381 [$MH^+ - NMe_2H$].

3; complex **1** (0.174 g, 0.41 mmol) was dissolved in 20 ml thf at 0 °C. An excess of KH was then added and the deprotonation monitored by IR. The filtered solution was then added to a stirred suspension of $[CuCl(PPh_3)]$ (0.148 g, 0.41 mmol) in thf at −78 °C. After *ca.* 1 h, IR monitoring showed completion of the reaction and the solvent was removed *in vacuo*. The residue was then extracted with diethyl ether. Addition of hexane caused the precipitation of **3**. Yield: 0.215 g (70%). FTIR (C_6D_6): ν(CO) 1842vs, 1870s, 1943m cm^{-1}; ^1H NMR (C_6D_6, 25 °C) δ 6.9–7.7 (m, 15 H, Ph), 3.79 (s, 6 H, $SiOCH_3$), 3.44 [d, $^3J(HP)$ 13.3 Hz, 3 H, $POCH_3$], 2.98 (s, 6 H, $SiNCH_3$), 2.56 [d, $^3J(HP)$ 10.2 Hz, 12 H, $PNCH_3$]; $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C) δ 194.6 (1 P, FeP), 0.6 (1 P, CuP); $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C) δ 213.8 [d, $^2J(CP)$ 22.8 Hz, 3 C, CO], 127.5–134.4 (m, Ph), 51.2 (s, 3 C, $POCH_3$ and $SiOCH_3$), 39.5 (s, 2 C, $SiNCH_3$), 37.4 [d, $^2J(CP)$ 7.2 Hz, 4 C, $PNCH_3$]; satisfactory elemental analyses were obtained.

‡ *Crystal data* for **3** (yellow crystals from diethyl ether–hexane): $C_{30}H_{42}CuFeN_3O_6P_2Si$, $M = 750.09$, triclinic, space group $P\bar{1}$, $a = 9.653(9)$, $b = 11.977(11)$, $c = 16.05(2)$ Å, $\alpha = 100.55(7)$, $\beta = 96.14(7)$, $\gamma = 95.03(8)°$, $U = 1803(3)$ Å^3, $Z = 2$, $D_c = 1.382$ Mg m^{-3}, Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu = 1.156$ mm^{-1}. Siemens Stoe AED2 diffractometer, ω–θ scan type, room temp., direct and Fourier methods. 5652 unique reflections measured in the range $1.74 < \theta < 24°$; 4578 with $I > 2\sigma(I)$; empirical absorption correction was made by ψ-scans; refinement by full-matrix least-squares methods; anisotropic thermal parameters for all non-H atoms in the final cycles; the H atoms were refined on a riding model in their ideal geometric positions; $R = 0.0500$ and $wR_2 = 0.1301$ [$I > 2\sigma(I)$]. SHELXS-86 and SHELXL-93 computer programs were used. 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 182/218.

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