Stannylene insertion into an amino-stabilized iron–silylene complex. Synthesis of $[(OC)_3\{(Me_2N)_2(RO)P\}Fe\{[NMe_2Si(OR)_2(\overline{SnNBu^tSiMe_2N}HBu^t)]\}]$ (R = Me, Et)

Pierre Braunstein,[a] Volker Huch,[b] Christine Stern[a] and Michael Veith[b]

[a] *Laboratoire de Chimie de Coordination, URA 0416 CNRS, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France*
[b] *Universität des Saarlandes, Anorganische Chemie, Postfach 15 11 50, D-66041 Saarbrücken, Germany*

Reaction of the $HNMe_2$-stabilized iron–silylene complexes (1a,b) with the stannylene reagent $\overline{SnNBu^tSiMe_2N}Bu^t$ 2 occurs selectively by insertion into the N–H bond to give novel types of base-stabilized silylene, stannylene complexes.

There is currently a renewed interest for the chemistry of molecules associating transition metals with non-transition elements. This is largely motivated by (*i*) the possibility of stabilizing by coordination moieties otherwise unstable, (*ii*) the occurrence of unusual structures and novel reactivity patterns, (*iii*) the relevance of such associations to major catalytic processes and (*iv*) their importance as single-source precursors for new materials in *e.g.* OMCVD and (*v*) the construction of clusters having direct metal–metal bonds between transition metal and main group metals.[1]

A base-stabilized iron–silylene complex **1a** has recently been reported and resulted from an unprecedented metal-promoted exchange of substituents between $P(NMe_2)_3$ and $Si(OEt)_3$ ligands.[2] Various sites for reactivity are potentially available in this molecule and we became interested in combining silylene and stannylene chemistry by using a class of cyclic stannylene reagents, such as $\overline{SnNBu^tSiMe_2N}Bu^t$ **2**,[3] which display a rich chemistry. They could lead with **1a** to ligand displacement, insertion or addition reactions.[4]

The rearrangement observed during the synthesis of **1a** could now be extended to the synthesis of the methoxy analogue **1b**, although the reaction appears very sensitive to small ligand effects.[5] The reaction of **1a,b** with 1 equiv. of **2** in toluene at room temp. yielded quantitatively (^1H NMR) complexes for which analytical and spectroscopic data clearly showed the presence of the expected Fe, Sn, Si, P and N-containing fragments. In particular, the $^{31}P\{^1H\}$ NMR spectrum of *e.g.* **3a** contained a singlet resonance at δ 199.8 (compared with δ 196.8 in **1a**) and the $^{29}Si\{^1H\}$ NMR spectrum a singlet at δ 67.7 (compared with δ 57.4 in **1a**). The IR spectrum [ν(CO) region] was only little affected, indicating a reaction at the base-stabilized silylene moiety rather than at the metal centre. A significant shift of the $SiNMe_2$ protons in the ^1H NMR spectrum (Table 1) suggested a reaction at the amine function.†

trans-$[Fe(CO)_3\{P(OR)(NMe_2)_2\}\{Si(OR)_2(NMe_2H)\}]$
1a: R = Et
1b: R = Me

An X-ray diffraction study was necessary to fully ascertain the bonding in these molecules and this was accomplished for single crystals of complex $[(OC)_3\{(Me_2N)_2(EtO)P\}Fe\{=Si(OEt)_2[NMe_2(\overline{SnNBu^tSiMe_2N}HBu^t)]\}]$ **3a** (see Scheme 1) (Fig. 1).‡

There are two symmetry independent, quasi-enantiomeric molecules in the asymetric unit. A $Sn \leftrightarrows N$ bond of the stannylene reagent **2**[7a] has formally inserted in the NH bond of the silylene unit $Si \leftarrow NMe_2H$. As expected, the newly formed Sn(1)–N(3) bond of 2.40(2) Å is significantly longer than the Sn(1)–N(2) bond [2.104(12) Å] or the Sn–N bond of **2** [2.091(8) Å].[3b] Interestingly, the H-atom which has migrated from N(3) to N(1) interacts with O(2) and the O(2)–N(1) distance of 2.953(5) Å in the resulting six-membered ring is characteristic for such a hydrogen bonding.[6] Accordingly, N(1) has acquired distorted tetrahedral coordination whereas N(2) has retained trigonal-planar coordination.

Although the solid-state structure of **3a** indicates no symmetry element in the molecule, the $SiNMe_2$ protons give rise to a singlet (δ 2.65 in $C_6D_5CD_3$) at 298 K. This results from a dynamic behaviour since at 225 K, two signals are observed (δ 2.72, 2.58 in $C_6D_5CD_3$) which coalesce at *ca.* 235 K ($\Delta G^\ddagger$ = 48.9 kJ mol^{-1}). A pseudo-mirror plane containing Si(2), N(3) and Sn(1) and relating C(18) and C(19) could be generated in the dynamic regime by pyramidal inversion at Sn, or by breaking of the N(3)→Si bond followed by rotation of the NMe_2 group about the Sn(1)–N(3) axis, inversion at N(3) and recoordination.

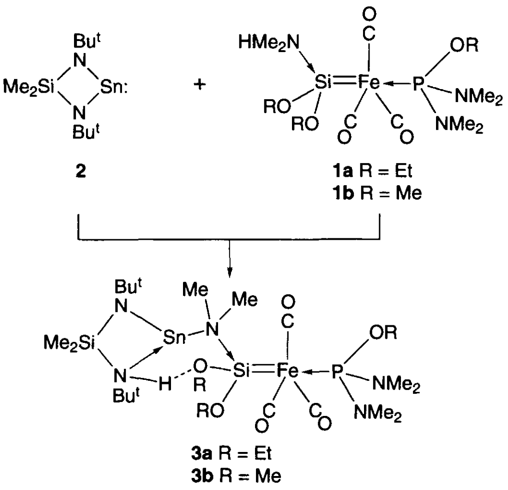
One may speculate about the course of this highly selective reaction. Displacement of the amine by the stannylene ligand followed by insertion of the amine into the Si–Sn bond appears unlikely, also on steric grounds. We favour initial addition of the N–H bond to the polar $Sn \leftrightarrows N$ bond of **2**. Formal 1,2-additions of an X–H bond (X = C_5H_5, Cl, Br, I) to an amino stannylene reagent have been observed previously.[7]

Attempts to extend this unusual addition reaction to the related germylene reagent[8] were unsuccessful. This could result from decreased reactivity owing to shorter $Ge \leftrightarrows N$ bonds. It is also interesting to note that the stannylene reagent did not displace the silylene unit from the Fe centre to give an iron–stannylene complex whereas tin(IV) reagents can readily displace an iron–silyl bond.[1g,9] Complexes **3a,b** are new

Table 1 Selected ^1H NMR chemical shifts

Complex	**1a**[a]	**3a**[c]	**1b**[c]	**3b**[b]
$SiNCH_3$	2.10 (s)	2.65 (s)	2.19 (s)	2.68 (s)
$PNCH_3$	2.80 (d, *J* 10.2 Hz)	2.86 (d, *J* 10.1 Hz)	2.77 (d, *J* 10.2 Hz)	2.91 (d, *J* 10.0 Hz)

[a] In C_6D_6. [b] In $C_6D_5CD_3$. [c] In C_6H_6–C_6D_6.



Scheme 1

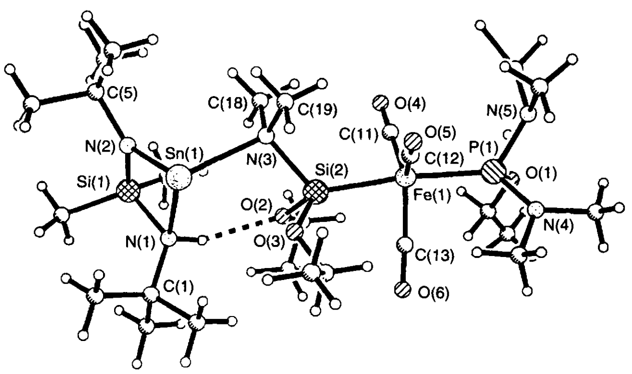


Fig. 1 View of one molecule of **3a**. Selected bond distances (Å) and angles (°): Fe(1)–C(11) 1.74(2), Fe(1)–C(12) 1.78(2), Fe(1)–C(13) 1.74(3), Fe(1)–P(1) 2.174(6), Fe(1)–Si(2) 2.220(6), Si(2)–O(2) 1.683(14), Si(2)–O(3) 1.637(13), Si(2)–N(3) 1.86(2), P(1)–O(1) 1.62(2), P(1)–N(4) 1.61(2), P(1)–N(5) 1.65(2), Si(1)–N(1) 1.81(2), Si(1)–N(2) 1.61(2), Sn(1)–N(1) 2.32(2), Sn(1)–N(2) 2.104(12), Sn(1)–N(3) 2.40(2), Sn(1)–Si(1) 2.973(6); C(11)–Fe(1)–C(12) 121.2(10), C(11)–Fe(1)–C(13) 118.8(9), C(12)–Fe(1)–C(13) 118.9(10), P(1)–Fe(1)–Si(2) 174.3(3), O(2)–Si(2)–O(3) 103.3(7), O(2)–Si(2)–N(3) 97.0(7), O(3)–Si(2)–N(3) 93.5(6), N(4)–P(1)–N(5) 97.3(9), O(1)–P(1)–N(4) 105.9(9), O(1)–P(1)–N(5) 94.2(10), Sn(1)–N(2)–Si(1) 105.4(7), N(2)–Si(1)–N(1) 94.1(8), Si(1)–N(1)–Sn(1) 91.3(7). The second molecule in the asymmetric unit has bonding parameters not significantly different.

members of the family of amine-stabilized metal–silylene complexes. The reactive N–H bond of **1a,b** is replaced by another, less reactive N–H···O system. Accordingly, a second equivalent of stannylene did not react with complexes **3a,b**.

We are grateful to the Ministère de l'Enseignement Supérieur et de la Recherche for a PhD grant to C. S., to the Centre National de la Recherche Scientifique (CNRS) for support and to the Ministère des Affaires Etrangères (Paris) and the DAAD (Bonn) for support under the PROCOPE programme.

Footnotes

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

Synthesis of **3a,b**: 0.7 mmol of **2** was slowly added at room temp. to 0.7 mmol of **1a** or **1b** previously dissolved in 15 ml toluene. The orange yellow solution was evaporated to dryness. Addition of pentane caused formation of pale yellow crystals.

Selected data **3a**: 0.429 g (78%). FTIR (toluene): ν(CO) 1842vs, 1934w cm^{-1}; ^{1}H NMR (300 MHz, C_6H_6–C_6D_6, 25 °C, $SiMe_4$), 4.50 (s, vbr, 2 H, $SiOCH_2$), 4.22 [q, ^3J(HP) 8.25, ^3J(HH) 7.6 Hz, 2 H, $POCH_2$], 4.0 (s, vbr, 2 H, $SiOCH_2$), 2.86 [d, ^3J(HP) 10.1 Hz, 12 H, $PNCH_3$], 2.65 (s, 6 H, $SiNCH_3$), 1.32 (m, 9 H, OCH_2CH_3), 1.10 (s, 9 H, NBu^t), 1.03 (s, 9 H, NBu^t), 0.30 (s, 3 H, $SiCH_3$), 0.12 (s, 3 H, $SiCH_3$); $^{31}P\{^1H\}$ NMR (81 MHz, C_6H_6–C_6D_6, 25 °C, H_3PO_4), δ 199.8 [s with Sn satellites, $^4J(P^{117/119}Sn)$ 40.1 Hz]; $^{13}C\{^1H\}$ NMR (50 MHz, $C_6D_5CD_3$, 25 °C, $SiMe_4$), δ 216.5 [d, ^2J(CP) 28.0 Hz, 3 C, CO), 60.4 (s, 2 C, $SiOCH_2$), 59.5 (s, 1 C, $POCH_2$), 54.0 (s, 1 C, C_{quat}), 51.7 (s, 1 C, C_{quat}), 40.8 (s, 2 C, $SiNCH_3$), 38.1 [d, ^2J(CP) 7.4 Hz, 4 C, $PNCH_3$), 36.5 (s, 3 C, NBu^t), 32.1 (s, 3 C, NBu^t), 19.6 (s, br, 1 C, $SiOCH_2CH_3$), 18.9 (s, br, 1 C, $SiOCH_2CH_3$), 17.0 [d, ^3J(CP) 7.8 Hz, 1 C, $POCH_2CH_3$), 9.2 (s, br, 1 C, $SiCH_3$), 8.5 (s, br, 1 C, $SiCH_3$); ^{29}Si INEPT (39.8 MHz, $C_6D_5CD_3$, 25 °C, $SiMe_4$) 67.7 [d, ^2J(SiP) 31.5 Hz, 1 Si, Fe=Si), 8.4 [s with Sn satellites, $^2J(P^{117/119}Sn)$ 21.7 Hz, 1 Si, $SiMe_2$].

3b: This compound was too unstable to be isolated pure. FTIR (benzene): ν(CO) 1844vs cm^{-1}; ^{1}H NMR (200 MHz, $C_6D_5CD_3$, 10 °C, $SiMe_4$), δ 3.96 (s, $SiOCH_3$), 3.85 (s, 6 H, $SiOCH_3$), 3.82 [d, ^3J(HP) 14.6 Hz, 3 H, $POCH_3$], 2.91 [d, ^3J(HP) 10.0 Hz, 12 H, $PNCH_3$], 2.68 (s, 6 H, $SiNCH_3$), 1.11 (s, 9 H, NBu^t), 1.08 (s, 9 H, NBu^t), 0.34 (s, 3 H, $SiCH_3$), 0.21 (s, 3 H, $SiCH_3$); $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6–C_6H_6, 25 °C, H_3PO_4), δ 203.0 [s with Sn satellites, $^4J(P^{117/119}Sn)$ 40.4 Hz]; ^{29}Si INEPT (39.8 MHz, C_6D_6–C_6H_6, 25 °C, $SiMe_4$) 70.0 [d, ^2J(SiP) 31.8 Hz, 1 Si, Fe=Si], 8.9 (s, 1 Si, $SiMe_2$).

‡ *Crystal data* for **3a** (yellow crystals from pentane, unstable under X-ray radiation, three crystals were used for the measurements): $C_{25}H_{58}FeN_5O_6PSi_2Sn$, M = 786.47, triclinic, space group $P\bar{1}$, a = 11.580(2), b = 17.500(3), c = 21.350(4) Å, α = 65.90(3), β = 78.46(3), γ = 76.00(3)°, U = 3807 Å^3, Z = 4, D_c = 1.372 Mg m^{-3}, Mo-Kα radiation: λ = 0.71073 Å, μ = 1.182 mm^{-1}. Stoe AED2 diffractometer, ω–θ scan type, 183 K. The structure was solved using direct and Fourier methods. 5000 unique reflections measured with $1.8 < \theta < 20.0°$ [$I > 2\sigma(I)$]; no absorption correction was made; refinement by full-matrix least-squares methods; anisotropic thermal parameters for all non-H atoms in the final cycles; isotropic refinement of hydrogen atoms positioned by geometry. C(25) is a terminal methyl group and suffers from disorder, a fairly common fact in such molecules. The quality of the data sets explains the poor R values obtained and the residual electron densities which, however, were far away from the neighbouring atoms. R_1 = 0.105, wR_2 = 0.28. 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 182/179.

References

1 (*a*) E. Colomer and R. J. P. Corriu, *Top. Curr. Chem.*, 1981, **96**, 79; (*b*) K. H. Whitmire, *J. Coord. Chem.*, 1988, **17**, 95; (*c*) H. Suhr, *New J. Chem.*, 1990, **14**, 523; (*d*) H. D. Kaesz, R. S. Williams, R. F. Hicks, J. I. Zink, Y.-J. Chen, H.-J. Müller, Z. Xue, D. Xu, D. K. Shuh and Y. K. Kim, *New J. Chem.*, 1990, **14**, 527; (*e*) C. Zybill, *Top. Curr. Chem.*, 1991, **160**, 1; (*f*) M. Veith and L. Stahl, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 106; (*g*) R. A. Fischer, J. Behm, I. Priermeier and W. Scherer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 746; (*h*) P. Braunstein, M. Knorr, M. Strampfer, A. De Cian and J. Fischer, *J. Chem. Soc., Dalton Trans.*, 1994, 117.

2 U. Bodensieck, P. Braunstein, W. Deck, T. Faure, M. Knorr and C. Stern, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2440.

3 (*a*) M. Veith, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 263; (*b*) M. Veith, *Z. Naturforsch., Teil B*, 1978, **33**, 7.

4 M. Veith, L. Stahl and V. Huch, *Organometallics*, 1993, **12**, 1914; M. Knorr, E. Hallauer, V. Huch, M. Veith and P. Braunstein, *Organometallics*, in the press.

5 P. Braunstein, C. Stern, C. Strohmann and N. Tong, to be submitted.

6 J. E. Huheey, E. A. Keiter and R. L. Keiter, *Anorganische Chemie*, Walter de Gruyter, Berlin, New York, 1995.

7 (*a*) M. Veith, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1; (*b*) M. Veith, M. Olbrich, W. Shihua and V. Huch, *J. Chem. Soc., Dalton Trans.*, 1996, 161.

8 M. Veith and M. Grosser, *Z. Naturforsch., Teil B*, 1982, **37**, 1375.

9 P. Braunstein, C. Charles, R. D. Adams and R. Layland, *J. Cluster Sci.*, 1996, **7**, 145.

Received, 16th May 1996; Com. 6/03422E