Differing degrees of five-coordination for similar tin atoms in the polymetallic complex $[(OC)_3Fe(\mu\text{-}Ph_2Ppy)(SnPh_2)(\mu\text{-}Cl)(SnClPh_2)]$

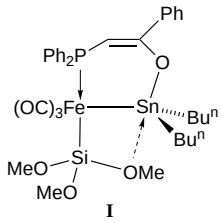
Pierre Braunstein,*[a] Chantal Charles,[a] Guido Kickelbick[b] and Ulrich Schubert[b]

[a] *Laboratoire de Chimie de Coordination, URA 416 CNRS, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France*

[b] *Institut für Anorganische Chemie, Technische Universität Wien, Getreidemarkt 9/153, A-1060 Wien, Austria*

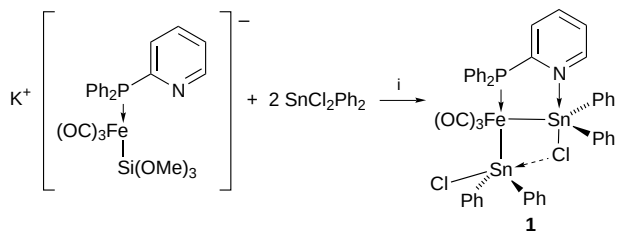
The unusual iron–bistin complex, $[(OC)_3Fe(\mu\text{-}Ph_2Ppy)(SnPh_2)(\mu\text{-}Cl(SnClPh_2)]$, obtained by silicon–tin exchange from a Si–Fe–Sn precursor, contains two tin atoms showing different degrees of five-coordination, a unique feature of relevance to hypercoordination of main-group elements.

The structural chemistry of tin in its complexes is diversified and the preferred geometries are tetrahedral, trigonal bipyramidal or octahedral.[1] Structural deformations encountered in crystallographically characterized molecules may often be analysed as representing snap-shots along the reaction coordinates of nucleophilic displacements at the tin centre.[2] It is also known that hypercoordination of a main-group element strongly influences its reactivity and may be used to promote catalytic behaviour. In transition-metal tin compounds M–Sn–R (R = alkyl or aryl), the bond angles decrease in the order M–Sn–R > R–Sn–R as there is more s character in the metal–tin bond.[3] Following our report of the structure of an unusual phosphinoenolate-bridged Si–Fe–Sn complex **I** in which the coordination at the tin centre was distorted tetrahedral, toward trigonal bipyramidal, with the oxygen donor ligands being *trans* to each other,[4] we have now observed that varying the nature of the assembling ligand led *via* a silicon–tin exchange reaction to a $FeSn_2$ complex in which the tin centres display different degrees of hypercoordination. This feature is of particular interest since it occurs in the same molecule, with tin ions in the same formal oxidation state.



I

The reaction of the iron metalate $K[Fe(CO)_3\{Si(OMe)_3\}(Ph_2Ppy\text{-}P)]$[5] [$Ph_2Ppy$ = 2-(diphenylphosphino)-pyridine] with $[SnCl_2Ph_2]$ (Scheme 1) required 2 equiv. to reach completion.† The product **1** was characterised by three ν(CO) absorptions (2041m, 2001m, 1969s cm^{-1}) consistent with a *mer*-arrangement of the carbonyl ligands. Its $^{31}P\{^1H\}$ NMR spectrum contains a singlet at δ 77.9 attributed to the iron-bound P atom, coupled to two sets of $^{117,119}Sn$ isotopes with $^2J(P^{117,119}Sn)$ 161.7 and 217.6 Hz. This is consistent with the presence of two different tin atoms in the molecule, *cis* and *trans* to the P → Fe bond, respectively.[6a]



1

Scheme 1 *Reagents and conditions*: i, thf, room temp., 30 min, − $SiCl(OMe)_3$, −KCl

A perspective view of the molecular structure of this complex is shown in Fig. 1.‡ The iron atom has a slightly distorted octahedral environment with three meridional carbonyl ligands, two *cis* tin atoms and the P atom of the bridging phosphinopyridine ligand. The nitrogen atom is coordinated to Sn(1) which has a trigonal-bipyramidal environment with the phenyl groups and the Fe atom in the equatorial plane, the sum of the corresponding bond angles being 359.2°. The Sn(1)–Cl(1) bond length of 2.557(2) Å is slightly longer than the average value for this bond.[7] This is probably due to the presence of a rather

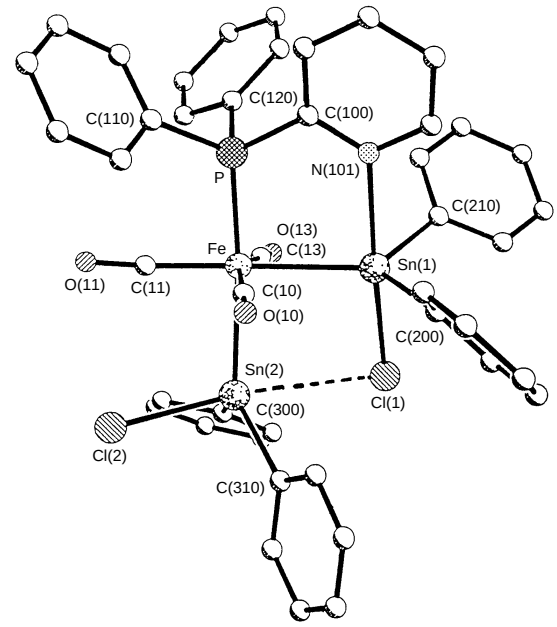


Fig. 1 View of one molecule of **1**. Selected bond distances (Å) and angles (°): Fe–C(10) 1.796(9), Fe–C(11) 1.785(9), Fe–C(13) 1.799(9), Fe–P 2.241(2), Fe–Sn(1) 2.6111(12), Fe–Sn(2) 2.6026(12), P–C(100) 1.831(8), Sn(1)–Cl(1) 2.557(2), Sn(1)–C(200) 2.163(8), Sn(1)–C(210) 2.156(8), Sn(1)–N(101) 2.499(7), Sn(2)–Cl(2) 2.485(2), Sn(2)–C(300) 2.149(9), Sn(2)–C(310) 2.150(8), Sn(2)–Cl(1) 3.076(2); C(10)–Fe–C(11) 100.5(4), C(11)–Fe–C(13) 96.3(4), C(10)–Fe–C(13) 159.5(4), P–Fe–Sn(1) 92.73(6), P–Fe–Sn(2) 175.12(7), Sn(1)–Fe–Sn(2) 91.74(4), C(200)–Sn(1)–Fe 122.4(2), C(210)–Sn(1)–Fe 124.7(2), N(101)–Sn(1)–Fe 87.3(2), Cl(1)–Sn(1)–Fe 95.31(6), N(101)–Sn(1)–Cl(1) 176.4(2), C(200)–Sn(1)–C(210) 112.1(3), C(200)–Sn(1)–N(101) 88.2(3), C(210)–Sn(1)–N(101) 85.6(3), C(200)–Sn(1)–Cl(1) 92.6(2), C(210)–Sn(1)–Cl(1) 90.9(2), C(300)–Sn(2)–Fe 114.8(2), C(310)–Sn(2)–Fe 126.0(2), Cl(2)–Sn(2)–Fe 102.08(7), Cl(1)–Sn(2)–Cl(2) 171.6(3), Cl(2)–Sn(2)–Fe 102.08(7), Cl(2)–Sn(2)–C(300) 95.7(3), Cl(2)–Sn(2)–C(310) 92.5(2), C(300)–Sn(2)–C(310) 115.1(3).

strong N–Sn(1) bond [2.499(7) Å][7b,8] *trans* to it and to an intramolecular coordination of Cl(1) to Sn(2). Although the Sn(2)–Cl(1) separation of 3.076(2) Å is relatively long, it is only 0.04 Å longer than in the five-coordinated tin complex $[SnCl_2Me_3]^-$.[9] The bond angles around Sn(2) are consistent with a distorted trigonal-bipyramidal geometry, the Cl(1)–Sn(2)–Cl(2) angle of 171.6(3)° and the sum of the interligand angles involving Fe, C(200) and C(210) of 355.9(2)° being close to the ideal values for a trigonal bipyramid. The angles between Cl(2) and the three equatorial substituents [Fe, C(300), C(310)] [between 92.5(2) and 102.08(7)°] are again consistent with a distortion of the tetrahedral geometry around Sn(2) towards trigonal bipyramidal as a result of the Sn(2)–Cl(1) interaction. The value of the Cl(1)–Sn(2)–Cl(2) angle illustrates the view of this structure representing a snap-shot along the reaction coordinates of an intramolecular nucleophilic substitution at the Sn(2) centre.[2] Accordingly, the Sn(2)–Cl(2) distance of 2.485(2) Å is longer than in tetrahedral tin complexes. Complex **1** represents therefore a unique example where in the same molecule, two hypercoordinated tin atoms displaying different degrees of Sn–Cl interactions are present. It is also interesting that although the Fe–Sn(1) bond is supported by an assembling ligand in contrast to the Fe–Sn(2) bond, their lengths of 2.6111(12) and 2.6026(12) Å are only marginally different and compare well with those in relevant molecules.[6]

The reactivity of the Fe–Si bond, *trans* to P in the iron metalate, is dependent on the nature of the assembling ligand, as shown by the differences observed when Ph_2Ppy (this work), dppm[6a] or $Ph_2PCH_2C(O)Ph$ are used. In the former cases, $FeSn_2$ complexes are formed whereas in the latter, spontaneous deprotonation of the Fe-coordinated ketophosphine ligand occurred to give a phosphino enolate bridging ligand.[4]

We are grateful to Dr J. Rocha (Aveiro, Portugal) for the solid-state NMR data, to the Ministère de l'Enseignement Supérieur et de la Recherche for a Ph. D. Grant for C. C. and to the Centre National de la Recherche Scientifique (Paris) and the Commission of the European Communities (contract ERBCHRXCT93 277) for financial support.

Acknowledgements

Dedicated to Professor R. B. King (Athens, GA) on the occasion of his 60th birthday.

Footnotes and References

* E-mail: braunst@chimie.u-strasbg.fr

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

Synthesis of mer-$[Fe(CO)_3\{SnClPh_2\}_2(Ph_2Ppy)]$ **1**: to a stirred solution of $K[Fe(CO)_3\{Si(OMe)_3\}(Ph_2Ppy\text{-}P)]$ prepared *in situ* from the corresponding hydride (0.525 g, 1.0 mmol) and a slight excess of KH (0.05 g) in thf, was added $[SnCl_2Ph_2]$ (0.688 g, 2.0 mmol). Rapid formation of a white precipitate occurred. The solution was stirred for 30 min, slowly concentrated and filtered through Celite to eliminate KCl. The product was precipitated by addition of hexane and washed with hexane and a small amount of diethyl ether. Crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of **1**. Yield: 79%. IR ν(C≡O) (CH_2Cl_2): 2041m, 2001w, 1969s cm^{-1}; (KBr): 2037m, 1994w, 1967s cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.90–8.35 (m, 34 H, aromatics), 8.85 [d, 1 H, H_{ortho}(py), ^2J(HH) 4.7 Hz]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 77.9 [s, P(Fe), $^2J(P^{119,117}Sn)$ 161.7, $^2J(P^{119,117}Sn)$ 217.6 Hz]. ^{31}P NMR (solid state, CP MAS, 15 kHz) : δ 74.1. ^{119}Sn NMR (solid state, CP MAS, 15 kHz): δ 2 and −65. Mass spectrum (FAB^+): 984 (M^+ − Cl, 84), 947 (M^+ − 2Cl, 32), 919 (M^+ − 2Cl − CO, 18), 891 (M^+ − 2Cl − 2CO, 15%).

‡ *Crystal data* for **1** (pale orange crystals, 0.24 × 0.20 × 0.14 mm): $C_{44}H_{34}Cl_2Fe\,NO_3PSn_2{\cdot}CH_2Cl_2$, M = 1104.75. The crystals were mounted on a Siemens SMART CCD area detector diffractometer. Mo-Kα radiation was used for the measurement (λ = 0.710 73 Å, graphite monochromated). Monoclinic, space group $P2_1/c$, a = 11.4534(2), b = 11.6281(3), c = 34.1379(6) Å, β = 97.643(1), U = 4506 Å^3, Z = 4, D_c = 1.628 g cm^{-3}. The cell dimensions were refined with all unique reflections. The data collection at 293(2) K covered a hemisphere of the reciprocal space, by a combination of three sets of exposures. Each set had a different ϕ angle for the crystal and each exposure took 20 s and covered 0.3° in ω. The collected data range was $1.20 \leqslant \theta \leqslant 25.00°$ ($-13 \leqslant h \leqslant 16$, $-16 \leqslant k \leqslant 15$, $-48 \leqslant l \leqslant 48$) by a crystal-to-detector distance of 3.85 cm. 25 359 reflections were collected and 7942 unique reflections (R_{int} = 0.057) were obtained after correction of polarization and Lorentz effects and an empirical absorption correction (program SADABS, μ = 1.73 mm^{-1}).[10] The structure was solved by direct methods (SHELXS86). Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL93). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were added in idealized positions and were refined with a riding model. The carbon atom of the solvent molecule was refined with constrained C–Cl distances. R = 0.071, R_w = 0.145 for 6395 reflections with $I = 2.0\,\sigma(I)$; $w = 1/[\sigma^2(F_o^2) + (0.1402P)^2 + 28.94P]$ [$P = (F_o^2 + 2F_c^2)/3$]. The largest residual electron density was 1.5 e Å^{-3} at Sn(1) and Sn(2). CCDC 182/587.

1 A. G. Davies, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, vol 2, p. 217.
2 H. B. Bürgi and J. D. Dunitz, *Acc. Chem. Res.*, 1983, **16**, 153; *Structure Correlations*, ed. H. B. Bürgi and J. D. Dunitz, VCH, Weinheim, 1994.
3 M. S. Holt, W. L. Wilson and J. H. Nelson, *Chem. Rev.*, 1989, **89**, 11; J. A. Zubieta and J. J. Zuckerman, *Prog. Inorg. Chem.*, 1978, **24**, 251.
4 P. Braunstein, C. Charles, A. Tiripicchio and F. Ugozzoli, *J. Chem. Soc., Dalton Trans.*, 1996, 4365.
5 G. Reinhard, B. Hirle, U. Schubert, M. Knorr, P. Braunstein, A. DeCian and J. Fischer, *Inorg. Chem.*, 1993, **32**, 1656.
6 (*a*) P. Braunstein, M. Knorr, M. Strampfer, A. DeCian and J. Fischer, *J. Chem. Soc., Dalton Trans.*, 1994, 117; (*b*) M. Knorr, H. Piana, S. Gilbert and U. Schubert, *J. Organomet. Chem.*, 1990, **388**, 327; (*c*) P. Braunstein, C. Charles, R. D. Adams and R. Layland, *J. Cluster Sci.*, 1995, **7**, 145; (*d*) F. W. B. Einstein and R. Restivo, *Inorg. Chim. Acta*, 1971, **5**, 501.
7 (*a*) W. Clegg, C. M. J. Grievson and K. Wade, *J. Chem. Soc., Chem. Commun.*, 1987, 969; (*b*) J. Vicente, M. T. Chicote, M. C. Ramirez-de-Arellano, G. Pelizzi and F. Vitali, *J. Chem. Soc., Dalton Trans.*, 1990, 279; (*c*) A. L. Balch, H. Hope and F. E. Wood, *J. Am. Chem. Soc.*, 1985, **107**, 6936; (*d*) H. Weichmann, J. Meunier-Piret and M. van Meerssche, *J. Organomet. Chem.*, 1986, **309**, 267.
8 J. T. B. H. Jastrzebski, G. van Koten, C. T. Knaap, A. M. M. Schreurs, J. Kroon and A. L. Spek, *Organometallics*, 1986, **5**, 1551; J. T. B. H. Jastrzebski, J Boersma, P. M. Esch and G. van Koten, *Organometallics*, 1991, **10**, 930; (*c*) J. T. B. H. Jastrzebski, E. Wehman, J. Boersma, G. van Koten, K. Goubitz and D. Heijdenrijk, *J. Organomet. Chem.*, 1991, **409**, 157; (*d*) S. K. Lee and B. K. Nicholson, *J. Organomet. Chem.*, 1986, **309**, 257.
9 S. E. Johnson, K. Polborn and H. Nöth, *Inorg. Chem.*, 1991, **30**, 1410.
10 SADABS, Program for empirical absorption correction for Siemens area detectors; G. M. Sheldrick, University of Göttingen, 1996.

Received in Cambridge, UK, 4th July 1997; 7/04749E