Compounds of Germanium and Tin, 20[◇]

Stannylene Complexes of Iron and Nickel without Donor Stabilization[☆]

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Treatment of $[Fe_2(CO)_9]$, $[Fe_3(CO)_{12}]$ or $[Ni(CO)_4]$ with the alkylarylstannylene RR'Sn: [R = 2,4,6-tBu$_3$C$_6$H$_2$, R' = CH$_2$C(CH$_3$)$_2$-3,5-tBu$_2$C$_6$H$_3$] furnishes the stannylene complexes $[(OC)_4Fe{=}SnRR']$ (**5**) and $[(OC)_3Ni{=}SnRR']$. The X-ray structure analysis of **5** reveals a trigonal-bipyramidal environment of the iron atom with the tricoordinated tin atom occupying an axial site, thus indicating that RR'Sn: is a strong σ-donor but weak π-acceptor.

Reports on unambiguously characterized transition-metal stannylene complexes containing a tricoordinated tin atom are still scarce[2]. This is particularly apparent for complexes of the lighter transition metals with stannylenes that do not experience inter- or intramolecular stabilization from the free electron pairs of donor atoms[2c]. Thus, in the case of iron and nickel for example, the heterosubstituted iron-stannylene complex **1**[3] and the homoleptic, heterosubstituted nickel complex **2**[4] were prepared and their structures elucidated.

Scheme 1. Ar = 2,6-tBu$_2$-4-MeC$_6$H$_2$

$$\underset{\mathbf{1}}{[(OC)_4Fe{=}Sn(OAr)_2]} \qquad \underset{\mathbf{2}}{[Ni\{{=}Sn(N\mathit{t}Bu)_2SiMe_2\}_4]}$$

We recently prepared compound **3** as an example of a diarylstannylene lacking stabilization by donor atoms[5]. Although compound **3** is stable in the solid state, it undergoes irreversible rearrangement in solution to furnish the alkylarylstannylene **4**, the formation of which was demonstrated indirectly by means of trapping reactions and preparation of the isotypic complexes $[(OC)_5M{=}SnRR']$ where M = Cr, Mo, W[6,7]. Large M–Sn bond lengths and small C–Sn–C bond angles are characteristic of these complexes and indicate that compound **4** behaves mainly as a σ-donor in such compounds while its π-acceptor properties are only weakly effective. The different positions that a ligand can occupy in a trigonal bipyramid serve as a criterion for the evaluation of its donor or acceptor properties[8]. Hence, we attempted to prepare an iron complex of the type **1** and now report on the formation and structure of the stannylene complex **5**.

Although the reaction of pentacarbonyliron with the alkylarylstannylene **4** affords the complex **5** in only low yield, an analogous reaction with nonacarbonyldiiron[3a] furnishes the same product in good yield. Complex **5** can also be obtained from the reaction of **4** with dodecacarbonyltriiron, albeit in markedly lower yield in comparison with the reaction with $[Fe_2(CO)_9]$. Even so, the latter reaction is worthy of note since the corresponding reactions of $[Fe_3(CO)_{12}]$ with diarylstannylenes give trinuclear iron–tin clusters of the type $[Fe_2(CO)_8(\mu\text{-}SnR_2)]$ in which the tin atoms are tetracoordinated[9].

Scheme 2. R = 2,4,6-tBu$_3$C$_6$H$_2$, R' = CH$_2$C(CH$_3$)$_2$-3,5-tBu$_2$C$_6$H$_3$

$$\underset{\mathbf{3}}{R_2Sn{:}} \rightarrow \underset{\mathbf{4}}{RR'Sn{:}}$$

$$[Fe_2(CO)_9] + \mathbf{4} \rightarrow \underset{\mathbf{5}}{[(OC)_4Fe{=}SnRR']} \leftarrow \mathbf{4} + [Fe_3(CO)_{12}]$$

First evidence for the presence of a tricoordinated tin atom in **5** was provided by the ^{119}Sn-NMR spectrum which consists of a singlet at δ = 889. This signal is thus only slightly shifted to higher field in comparison with the signal of the free stannylene **4** [δ(^{119}Sn) = 960]. The structure of **5** was confirmed by X-ray crystallography (Figure 1) which revealed some surprising details.

In the solid state, compound **5** has a slightly distorted trigonal-bipyramidal structure in wich the tin atom, together with its coplanar substituents, occupies an axial position. In agreement with theoretical predictions[8], the stannylene **4** thus functions as a strong σ-donor but weak π-acceptor ligand. In contrast, the heteroelement-substituted stannylene in complex **1** is in an equatorial position. This finding can be attributed to the weak σ-donor/strong π-acceptor properties of the Sn(OAr)$_2$ ligand[3]. Although the tin–iron bond in **5** is shorter than those found in most complexes containing tetracoordinated tin[9], it is markedly longer than the corresponding value of the complex **1**; this is most likely an indication of the weak π-acceptor nature

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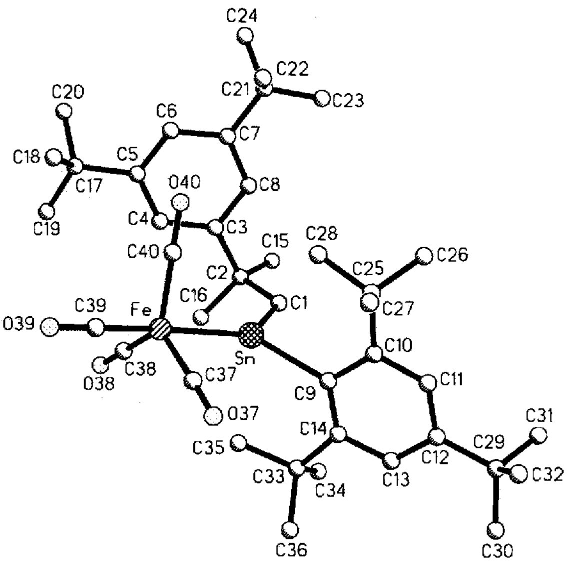
[◇] Part 19: Ref.[1].

Figure 1. Molecular structure of **5** in the crystal (hydrogen atoms omitted)[a]



[a] Selected bond lengths [pm] and angles [°]: Fe–Sn 248.8(1), Sn–C(1) 216.4(4), Sn–C(9) 218.7(3), Fe–C(37) 178.9(4), Fe–C(38) 179.4(5), Fe–C(39) 176.6(6), Fe–C(40) 177.2(6); C(1)–Sn–C(9) 98.0(1), Fe–Sn–C(1) 135.8(1), Fe–Sn–C(9) 126.2(1), Sn–Fe–C(37) 84.6(2), Sn–Fe–C(38) 90.3(2), C(37)–Fe–C(38) 122.5(3), Sn–Fe–C(39) 174.4(1), C(37)–Fe–C(39) 89.3(3), C(38)–Fe–C(39) 93.2(3), Sn–Fe–C(40) 88.7(2), C(37)–Fe–C(40) 121.1(2), C(38)–Fe–C(40) 116.0(2), C(39)–Fe–C(40) 93.6(3).

of **4**. Even the iron–tin bond in a stannyl–iron complex containing the structural unit $[(OC)_4Fe{-}Sn{\equiv}(O)_3{\equiv}]$ is slightly shorter than that of **5**[10].

On heating of **5** the color changes from dark yellow to brick red and reconverts to dark yellow on cooling. This thermochromic behavior is attributable to a change of the coordination polyhedron about the iron atom in the sense of a reversible interchange between a trigonal bipyramid and a square pyramid. Transformations of this type have been unequivocally demonstrated in other classes of compounds[11].

Scheme 3

$$4 + [Ni(CO)_4] \xrightarrow[-CO]{} [(OC)_3Ni{=}SnRR']$$

6

In contrast to pentacarbonyliron which exhibits only a low reactivity towards **4**, the reaction of this stannylene with tetracarbonylnickel takes place smoothly even at low temperatures to furnish the complex **6** as light yellow crystals. The constitution of this product was confirmed by analytical and spectral data. The strong deshielding of ^{119}Sn ($\delta = 956$) is almost the same as that in the free stannylene **4**. This indicates that the π-acceptor properties of this ligand in complex **6** are even weaker than those in the iron complex **5**. The markedly higher lability of complex **6** in comparison with complex **5** substantiates this assumption. For example, solutions of complex **6** decompose with slow deposition of elemental tin on exposure to daylight.

Attempts to confirm the structure of **6** by X-ray crystallography were not satisfactory because the crystals also decomposed slowly on exposure to X-rays. Thus, only an incomplete data set was obtained which does fully substantiate the constitution of **6**. The nickel atom has a distorted tetrahedral environment of its ligands with widened C–Ni–C and smaller C–Ni–Sn angles. In comparison with the values for **2**, the appreciably increased Ni–Sn bond length of 245.7(5) pm and the small C–Sn–C bond angle of 101.8(10)° indicate that, as in **5**, the π-acceptor nature of the stannylene ligand is very small. However, the data obtained are not sufficient for an in-depth discussion of the structure.

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Experimental

All manipulations were performed by using standard Schlenk techniques under dry argon. – ^{119}Sn (inverse-gated, ^{1}H-decoupled, Me_4Sn ext.), ^{1}H and ^{13}C NMR: Bruker AM 300. – IR: Bio-Rad FTS-7. MS: Varian-MAT 212. – Elemental analyses: Analytische Laboratorien, D-51779 Lindlar, Germany.

Tetracarbonyl{[2-(3,5-di-tert-butylphenyl)-2-methylpropyl]-(2,4,6-tri-tert-butylphenyl)stannylene}iron(0) (**5**). – (a) *From [$Fe_2(CO)_9$]:* A solution of 0.50 g (1.37 mmol) of [$Fe_2(CO)_9$] in 30 ml of toluene was added to a solution of 0.91 g (1.49 mmol) of **4** in 20 ml of toluene and the reaction mixture was stirred for 3 d at room temperature. The resultant dark brown solution was concentrated to a volume of 25 ml, cooled to −24 °C, and the unreacted $Fe_2(CO)_9$ was filtered off. Toluene was distilled off and the residue dissolved in 15 ml of *n*-hexane. Standing of the solution at room temperature for 2 d yielded 0.83 g of **5** (71%) as dark yellow crystals, m.p. 130–132 °C. – ^{1}H NMR (C_6D_6, 25 °C): δ = 1.23 (s, 9H), 1.24 (s, 9H), 1.31 (s, 18H), 1.63 (s, 6H), 2.48 (s, 2H), 7.37 (d, 2H, $^4J_{H,H}$ = 1.96 Hz), 7.41 (t, 1H), 7.44 (s, 2H). – ^{13}C NMR (C_6D_6, 25 °C): δ = 31.21 (C_p), 31.63 (C_p), 31.76 (C_p), 33.04 (C_p), 33.44 (C_p), 34.80 (C_q), 35.12 (C_q), 38.68 (C_q), 39.71 (C_q), 57.61 (CH_2), 119.60 (CH), 121.03 (CH), 123.72 (CH), 125.64 (CH), 144.93 (C_q), 148.48 (C_q), 150.95 (C_q), 151.21 (C_q), 155.48 (C_q), 214.47 (CO); C_p and C_q refer to primary and quaternary carbon atoms. – ^{119}Sn NMR: δ = 888.8. – IR (KBr): $\tilde{\nu}$ = 2029, 1954, 1929, 1910 cm^{-1} (CO). – MS (CI, isobutane); *m/z* (%): 779 (100) [MH$^+$]. – $C_{40}H_{58}FeO_4Sn$ (777.4): calcd. C 61.80, H 7.52; found C 61.73, H 7.39.

(b) *From $Fe_3(CO)_{12}$:* A solution of 1.23 g (2.12 mmol) of **4** in 30 ml of toluene was added dropwise to a solution of 0.75 g (1.49 mmol) of $Fe_3(CO)_{12}$ in 40 ml of toluene over a period of 15 min at room temperature. Separation as described above and recrystallization from 15 ml of *n*-hexane afforded 0.38 g of **5** (24%) as dark yellow crystals which were identified by m.p., IR, ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectra and comparison with data of an authentic sample fo **5**.

Tricarbonyl{[2-(3,5-di-tert-butylphenyl)-2-methylpropyl](2,4,6-tri-tert-butylphenyl)stannylene}iron(0) (**6**): A solution of 1.38 g (2.26 mmol) of **4** in 20 ml of *n*-hexane was added to a solution of 3 g (large excess) of $Ni(CO)_4$ in 20 ml of *n*-hexane at −10 °C. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. After this time, all volatile materials were removed in vacuo. The resulting brown residue was dissolved in 20 ml of toluene and all insoluble products were filtered off. Cooling of the solution for 16 h at −50°C provided 1.29 g (76%) of pale yellow, rhombohedral crystals of **6**, m.p. 77–78°C. – ^{1}H NMR (C_6D_6, 25°C): δ = 1.27 (s, 18H), 1.31 (s, 9H), 1.38 (s, 18H), 1.60 (s, 6H), 1.99 (s, 2H), 7.40 (d, 2H, $^4J_{H,H}$ = 1.67 Hz), 7.43 (t, 1H), 7.48 (s, 2H). – ^{13}C NMR (C_6D_6, 25°C): δ = 31.45 (C_p), 33.78 (C_p), 34.53 (C_p), 34.74 (C_p), 39.04 (C_q), 39.58 (C_q), 57.42 (CH_2), 120.78 (CH), 122.86 (CH), 124.35 (CH), 149.75 (C_q), 149.99 (C_q), 156.42 (C_q), 156.81 (C_q), 198.54 (CO). – ^{119}Sn NMR (C_6D_6, 25°C): δ = 955.8. – IR (KBr): $\tilde{\nu}$ = 2056 s, 1995 s, 1977 cm^{-1} s (CO). – MS (CI, isobutane); *m/z* (%): 697 (10) [MH$^+$ − 2 CO]. – $C_{39}H_{58}NiO_3Sn$ (752.3): calcd. C 62.27, H 7.77; found C 62.09, H 7.70.

X-ray Structure Analysis of **5**: $C_{40}H_{58}FeO_4Sn \times n\text{-}C_6H_{14}$ (863.69); crystal dimensions 0.45 × 0.5 × 0.3 mm. Siemens R3m/V diffractometer, Wyckoff scan; temperature 296(2) K; triclinic; space group $P\bar{1}$; a = 1230.3(1), b = 1426.2(1), c = 1566.8(1) pm, α = 94.488(5), β = 108.842(5), γ = 109.109(5)°; V = 2395.4(1) × 10^6 pm^3; $d_{calcd.}$ = 1.197 g/cm^3; Z = 2; $2\Theta_{max}$ = 55°; μ(Mo-K_α) = 0.86 mm^{-1}; total no. of reflections 12464; unique reflections 10925; observed [$F > 3\sigma(F)$] 9683; data-to-parameter ratio 22.62. The structure was solved by direct phase determination using the SHELXTL PLUS program system and refined by full-matrix least-squares techniques. Hydrogen atoms were placed in calculated positions, and all other atoms were refined anistropically; R = 0.055, R_w = 0.056; residual electron density 0.86 and −0.79 e · Å^{-3}[12].

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[12] Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-405548, the names of the authors, and the journal citation.

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