ELSEVIER

Journal of Organometallic Chemistry 560 (1998) 125–129

Journal of Organo metallic Chemistry

An octahedral stannylmanganese stannylene complex[1,2]

Manfred Weidenbruch [a,*], Artur Stilter [a], Wolfgang Saak [a], Karl Peters [b], Hans Georg von Schnering [b]

[a] *Fachbereich Chemie der Universität Oldenburg, Carl-von-Ossietzky-Straße 9-11, D-26111 Oldenburg, Germany*
[b] *Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70506 Stuttgart, Germany*

Received 24 November 1997

Abstract

Treatment of decacarbonyldimanganese with the alkylarylstannylene RR′Sn (**2**), R = 2,4,6-$t\mathrm{Bu}_3\mathrm{C}_6\mathrm{H}_2$, R′ = $\mathrm{CH_2C(CH_3)_2}$-3,5-$t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3$, furnishes the tetracarbonyl-stannylmanganese stannylene complex **3**, in which the tin atom of the stannyl group is part of a stannaindan ring system. Reaction of **2** with $[\mathrm{(OC)_2Fe(NO)_2}]$ yields the tetrahedral iron stannylene complex $[\mathrm{OC(NO)_2Fe{=}SnRR'}]$ (**4**). The structures of **3** and **4** were determined by X-ray crystallography. © 1998 Elsevier Science S.A. All rights reserved.

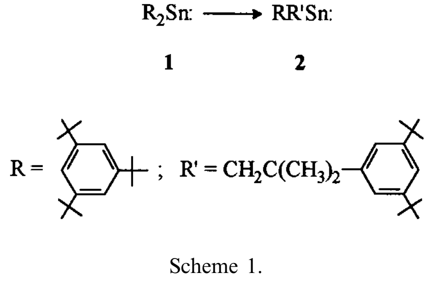
Keywords: Manganese; Iron; Stannylene; Crystal structures

---

1. Introduction

Although the first transition metal-stannylene complex without donor stabilization, namely the compound $[\mathrm{(OC)_5Cr=Sn\{CH(SiMe_3)_2\}_2}]$, was described more than 20 years ago [2], the number of completely characterized complexes of this type is still very small [3]. Thus, for example, reactions of tin(II) chloride with various manganese complexes lead to compounds containing the structural unit Mn–Sn–Mn in which, however, the tin atom achieves the coordination number 4 by means of either bridging halogen ligands or solvent molecules [4,5]. One exception is the compound $(\mu_3\text{-Sn})[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn(CO)}_2]_3$ prepared by Herrmann et al. in which the naked tin atom has the coordination number three and forms one short and two long bonds to the three manganese atoms [6].

We recently succeeded in preparing the diarylstannylene **1** which is stable in the solid state but undergoes slow rearrangement to the alkylarylstannylene **2** in solution (Scheme 1) [7]. Starting from the stannylene **2** we have been able to synthesize the isotypical complexes $[\mathrm{(OC)_5M=SnRR'}]$, M = Cr, Mo, W [8,9] and to isolate the compounds $[\mathrm{(OC)_4Fe=SnRR'}]$ and $[\mathrm{(OC)_3Ni=SnRR'}]$. However, because of its ready decomposition in the crystal state it was not possible to obtain a complete X-ray crystal structure of the tetrahedrally coordinated nickel complex [10]. Characteristic features of these complexes are long M–Sn bond lengths and small C–Sn–C bond angles, indicating that the stannylene **2** behaves mainly as a σ-donor with only weak π-acceptor properties. Accordingly, the stannylene occupies an axial position in the trigonal bipyramidal iron complex [10] which, as predicted by theoretical calcula-



Scheme 1.

---

* Corresponding author. Fax: +49 441 7983352.

[1] See ref. [1].

[2] Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday.

0022-328X/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII S0022-328X(98)00479-3

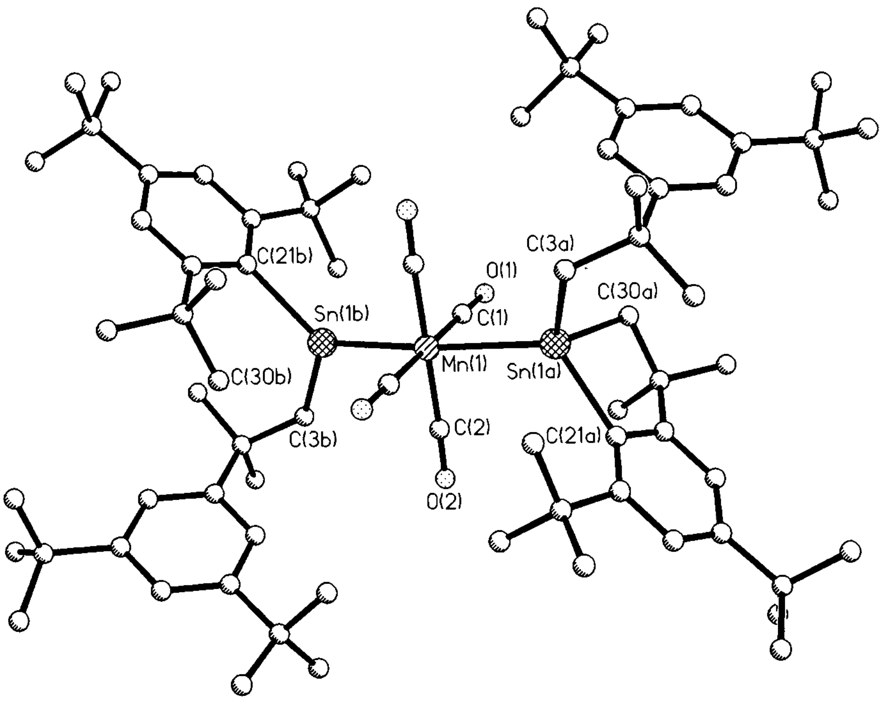


Fig. 1. Molecular structure of **3** in the crystal (hydrogen atoms omitted).

tions, is preferentially occupied by strong σ-donor and weak π-acceptor ligands [11].

In the present communication we report on the reaction of decacarbonyldimanganese with **2**, a reaction following a different course to the previously described, complex-forming processes, and on the formation of an iron-stannylene complex with tetrahedral coordination.

2. Results and discussion

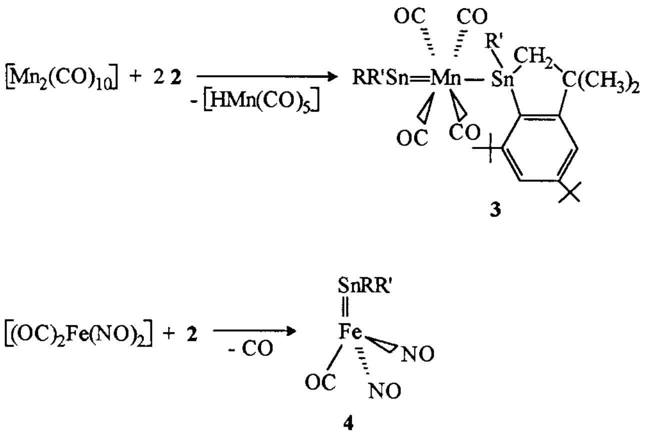
The reaction of excess **2** with decacarbonyldimanganese proceeds with evolution of a gas and is complete within a few hours. Work-up of the reaction mixture results in the isolation of a pale yellow, crystalline compound composed, according to its analytical data, of one tetracarbonylmanganese fragment and two stannylene units. Since a mononuclear manganese compound with CO and the stannylene **2** as ligands should possess an odd number of electrons, we attempted to prove the presence of the unpaired electron by ESR spectroscopy. However, the obtained spectrum indicated the existence of a diamagnetic complex.

Although the ^{1}H- and ^{13}C-NMR at first did not allow any unequivocal conclusions to be drawn about the structure of the obtained complex, the ^{119}Sn-NMR signals at 109 and 906 ppm demonstrated the presence of one tri- and one tetra-coordinated tin atom in the molecule. An X-ray crystallographic analysis (Fig. 1, Table 1) not only confirmed the deductions from the ^{119}Sn-NMR spectrum but also revealed some other interesting features (Scheme 2).

The X-ray study confirmed the formation of the 18 electron complex **3** containing both a tri- and a tetracoordinated tin atom in *trans*-positions with the tin atom of the stannyl group being incorporated in a stannaindan ring system. The Sn–Mn–Sn bond angle of 168.2(2)° is presumably attributable to the differing coordination polyhedra of the two tin atoms. The two Sn–Mn bond lengths differ appreciably [251.3(2) and 270.0(2) pm] and indicate the existence of one single and one double bond. Although the Mn–Sn single bond length correlates well with that of the reference complex [$(OC)_5Mn-SnMe_3$] [$d = 267$ pm] [12], the double bond length is considerably larger than that of 244.5(1) pm determined by Herrmann et al. [6] and again reflects the reduced π-acceptor capacity of **2** in transition metal complexes. However, in spite of the comparable covalent radii of chromium and manganese, the value determined here is noticeably shorter than that of 261.4(1) pm for [$(OC)_5CrSnRR'$], a compound with similar, octahedral coordination in which

Table 1
Selected bond lengths (pm) and angles (°) for 3

Mn–Sn(1a)	270.0(2)	Mn–Sn(1b)	251.3(2)
Mn–C(1)	181.1(9)	Mn–C(2)	182.9(7)
Sn(1a)–C(3a)	224.7(6)	Sn(1a)–C(21a)	219.4(3)
Sn(1a)–C(30a)	224.7(6)	Sn(1b)–C(3b)	216.2(6)
Sn(1b)–C(31b)	225.5(3)		
Sn(1a)–Mn–Sn(1b)	168.4(2)	C(3b)–Sn(1b)–C(21b)	113.3(2)
Mn–Sn(1b)–C(3b)	118.8(2)	Mn–Sn(1b)–C(21b)	127.8(1)



Scheme 2.

the bond is markedly lengthened. In harmony with this observation, the trigonal bipyramidally coordinated tin atom in **3** exhibits an appreciably widened C–Sn–C angle of 113.2(2)° in comparison to a value of merely 91.2(2)° in the chromium compound.

The formation of the manganese complex **3** from $[(OC)_{10}Mn_2]$ and **2** can be interpreted most simply in terms of a primary insertion of **2** into the Mn–Mn bond with subsequent cleavage of one of the *ortho-tert*-butyl methyl CH bonds to form the stannyl group under elimination of $[HMn(CO)_5]$. Indeed, the ^{1}H-NMR spectrum of the volatile reaction products did show a signal at -6.9 ppm that is characteristic for a hydrogen atom attached to a manganese carbonyl fragment. Final substitution of a CO ligand by **2** then furnishes the isolated product.

In order to obtain, in addition to the octahedrally and trigonal bipyramidally coordinated transition metal complexes, a completely characterizable complex with a tetrahedral arrangement containing **2** as a ligand, stannylene **2** was allowed to react with $[(OC)_2Fe(NO)_2]$ in a 1:1 molar ratio. The dark red, crystalline compound **4** was isolated in 77% yield and its ^{119}Sn-NMR signal at 1006 ppm is indicative of the formation of a stannylene complex.

An X-ray crystallographic analysis of **4** (Fig. 2, Table 2) revealed a distorted tetrahedral iron-stannylene complex with an Fe–Sn bond length of 248.4(1) pm. This length is somewhat shorter than those of the single bonds in similarly substituted stannyl componds (values between 260 and 270 pm) and thus indicative of multiple bond character [13,14]. It is interesting to note that the value determined here is almost identical with the Fe–Sn bond length of 248.8(1) pm in the complex $[(OC)_4FeSnRR']$ [10] in spite of the incorporation of **2** into different polyhedra.

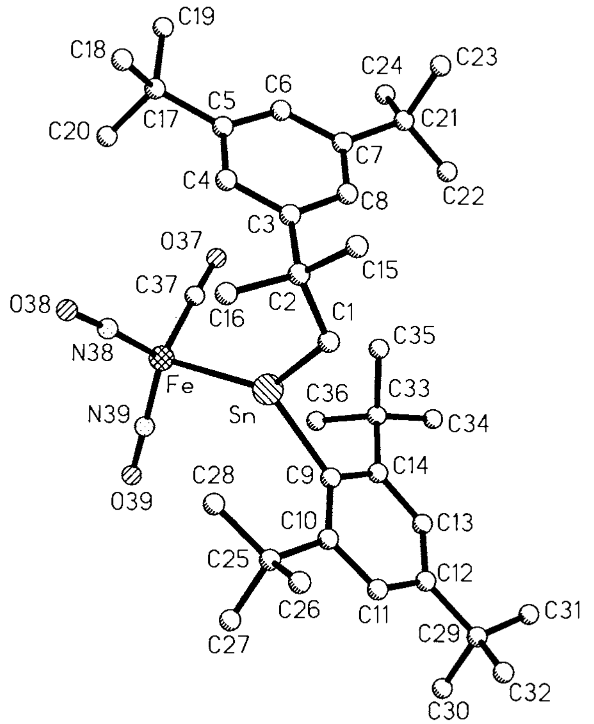


Fig. 2. Molecular structure of **4** in the crystal (hydrogen atoms omitted).

3. Experimental section

3.1. General procedure

All reactions were carried out in oven-dried glassware under an atmosphere of dry argon.

The ^{1}H-, ^{13}C-, and ^{119}Sn-NMR spectra were obtained on a Bruker AM 300 spectrometer using C_6D_6 as solvent. IR spectra were taken on a Bio-Rad FTS-7 spectrometer. Mass spectra were recorded on a Varian-MAT 212 instrument. Elemental analyses were performed by Analytische Laboratorien, D-51779 Lindlar, Germany.

3.2. Formation of the tetracarbonylstannylmanganese stannylene complex (3)

At 35°C a solution of **2** (1.10 g, 1.80 mmol) in 20 ml of THF was added to a solution of $[Mn_2(CO)_{10}]$ (0.30 g, 0.77 mmol) in 20 ml of THF over a period of 2 h. To

Table 2
Selected bond lengths (pm) and angles (°) for 4

Fe–Sn	248.4(1)	Fe–N(38)	165.9(5)
Fe–N(39)	165.7(5)	Fe–C(37)	179.1(8)
Sn–C(1)	218.1(5)	Sn–C(9)	219.2(4)
C(1)–Sn–C(9)	100.5(2)	Fe–Sn–C(9)	127.0(1)
Fe–Sn–C(1)	132.5(1)		

complete the reaction, the mixture was stirred for an additional 3 h at this temperature. The mixture was filtered and the solvent removed. Recrystallization of the residue from 10 ml of DME at −24°C yielded 0.69 g (65% yield) of pale yellow crystals of **3**, m.p. 178°C. ^{1}H-NMR: δ 1.24 (s, 9 H), 1.25 (s, 9 H), 1.27 (s, 18 H), 1.29 (s, 18 H), 1.35 (s, 18 H), 1.43 (s, 3 H), 1.47 (s, 3 H), 1.53 (s, 3 H), 1.59 (s, 6 H), 1.61 (s, 3 H), 1.80 (s, 9 H), 2.15 (s, 2 H), 2.46 (s, 2 H), 2.65 (AB-system, 2 H, $^2J = 13.1$ Hz), 7.37 (m, 3 H), 7.42 (t, 1 H, $^4J = 1.7$ Hz), 7.44 (s, 2 H), 7.45 (d, 2 H, $^4J = 1.6$ Hz), 7.66 (d, 2 H, $^4J = 1.7$ Hz) ppm. ^{13}C-NMR: δ 31.29 (C_p), 31.86 (C_p), 32.93 (C_p), 33.54 (C_p), 33.77 (C_p), 34.18 (C_p), 34.84 (C_p), 35.46 C_p), 37.35 (C_q), 37.56 (C_q), 38.48 (C_q), 39.04 (C_q), 39.91 (C_q), 40.20 (C_q), 45.39 (CH_2), 59.14 (CH_2), 119.30 (CH), 119.49 (CH), 119.88 (CH), 120.69 (CH), 122.41 (CH), 123.82 (CH), 125.65 (CH), 137.43 (C_q), 149.44 (C_q), 150.07 (C_q), 150.62 (C_q), 150.96 (C_q), 155.86 (C_q), 156.31 (C_q), 160.69 (C_q), 203.62 (CO), 221.83 (CO) ppm. C_p and C_q refer to primary and quaternary carbon atoms respectively. ^{119}Sn{^{1}H}-NMR: δ 108 (broad), 960 (broad) ppm. IR (KBr) ν: 1935, 1925 (CO) cm^{-1}. MS (CI, isobutane): m/z 1386 (MH$^+$, 6%). Anal. Found: C, 65.66; H, 8.12. $C_{76}H_{115}MnO_4Sn_2$ (1385.06) calc.: C, 65.90; H, 8.37%.

3.3. *Formation of the carbonyldinitrosyliron stannylene complex (**4**)*

At −50°C a solution of $[(OC)_2Fe(NO)_2]$ (0.27 g, 1.69 mmol) in 50 ml of toluene was added dropwise to a solution of **2** (1.03 g, 1.69 mmol) in 50 ml of toluene. To complete the reaction, the resulting mixture was stirred for 18 h at r.t. The solution was concentrated to a volume of 10 ml. After the addition of 10 ml of n-hexane, the solution was cooled to −50 °C. After 3 days at this temperature rhombohedral, dark red crystals of **4** were obtained. Yield: 0.98 g (77%), m.p. 111–112°C. ^{1}H-NMR: δ 1.23 (s, 18 H), 1.29 (s, 9 H), 1.37 (s, 18 H), 1.55 (s, 6 H), 2.04 (s, 2 H), 7.37 (d, 2 H, $^4J = 1.65$ Hz), 7.44 (t, 1 H), 7.47 (s, 2 H) ppm. ^{13}C-NMR: δ 31.37 (C_p), 31.72 (C_p), 33.14 (C_p), 35.19 (C_q), 38.91 (C_q), 39.20 (C_q), 57.77 (CH_2), 119.51 (CH), 121.08 (CH), 122.96 (CH), 125.64 (CH), 149.06 (C_q), 149.97 (C_q), 150.50 (C_q), 150.83 (C_q), 156.26 (C_q), 223.59 (CO) ppm. ^{119}Sn-NMR: δ 1006 ppm. IR (KBr) ν: 1983 (s) (CO), 1748 (s), 1707 (s) (NO) cm^{-1}. MS (CI, isobutane): m/z 755 (MH$^+$, 100%). UV–vis: $\lambda_{max}(\varepsilon)$ 280 (broad, tailing off into the visible region) (9000) nm. Anal. Found: C, 58.85; H, 7.88; N, 3.76. $C_{37}H_{58}FeN_2O_3Sn$ (753.44) calc.: C, 58.98; H, 7.76; N, 3.72%.

3.4. *X-ray structure analyses of **3** and **4***

Crystal and numerical data of the structure determinations are given in Table 3. Compound **4** crystallizes with a molecule of toluene. In each case, the crystal was mounted in a thin-walled glass capillary. Data collection was performed at 296(2) K on a Siemens STOE AED 2 (**3**) or a Siemens P4 diffractometer (**4**) using graphite-monochromated Mo–K_α radiation.

Table 3
Crystallographic data for **3** and **4**

	3	**4**
Empirical formula	$C_{76}H_{115}MnO_4Sn_2$	$C_{37}H_{58}FeN_2O_3Sn \cdot C_7H_8$
Molar mass	1385.00	845.88
Unit cell dimenstions		
a (pm)	989.0(1)	917.34(5)
b (pm)	1421.4(2)	1179.26(7)
c (pm)	1470.3(1)	2166.3(1)
α (°)	94.11(1)	89.904(5)
β (°)	98.02(1)	83.017(5)
γ (°)	110.07(1)	82.118(5)
V ($\times 10^6$) (pm^3)	1906.4(4)	2303.9(2)
Z	1	2
D_{calcd} (g cm^{-3})	1.206	1.219
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Crystal size (mm^3)	$0.38 \times 0.38 \times 0.15$	$0.5 \times 0.55 \times 0.2$
Data collection mode	ω-2θ-scan	ω-scan
$2\theta_{max}$ (°)	48	55
No. of reflections	6250	12 551
No. of unique reflections	5963	10 567
No. of observed reflections	4880 ($I > 2\sigma(I)$)	9285 ($F > 3\sigma(F)$)
Linear abs. coefficient (mm^{-1})	0.37	0.89
Data to parameter ratio	16.78	21.80
R, (R_w)	0.060	0.061 (0.064)
wR_2 (all data)	0.160	—
Residual electron density (e Å^{-3})	0.673 and −0.344	0.88 and −0.94

The structures were solved by direct phase determination using the SHELX's program systems and refined by full-matrix least-squares techniques against F^2 (**3**) or F (**4**) with the SHELXL 93 [15] or SHELXTL PLUS program systems. Hydrogen atoms were placed in calculated positions, and all other atoms were refined anisotropically.

The molecules of **3** are chiral with an Sn–Mn–Sn angle of 168.4(2)°. Owing to racemic twinning an inversion center is observed so that the space group $P\bar{1}$ results [1].

Acknowledgements

Financial support of our work from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

References

[1] Compounds of germanium and tin; part XXIII. Part XXII: A. Schäfer, W. Saak, M. Weidenbruch, H. Marsmann, G. Henkel, Chem. Ber. 130 (1997) 1733.

[2] (a) J.D. Cotton, P.J. Davidson, D.E. Goldberg, M.F. Lappert, K.M. Thomas, J. Chem. Soc. Chem. Commun. (1974) 893. (b) J.D. Cotton, P.J. Davidson, M.F. Lappert, J. Chem. Soc. Dalton Trans. (1976) 2275.

[3] Reviews: (a) W. Petz, Chem. Rev. 86 (1986) 1019. (b) M.F. Lappert, R.S. Rowe, Coord. Chem. Rev. 100 (1990) 267.

[4] H.-J. Haupt, T. Keppler, U. Flörke, Y. Calage, Z. Anorg. Allg. Chem. 571 (1989) 51.

[5] B. Schiemenz, G. Huttner, L. Zsolnai, P. Kircher, T. Diercks, Chem. Ber. 128 (1995) 187.

[6] W.A. Herrmann, H.-J. Kneuper, E. Herdtweck, Chem. Ber. 122 (1989) 437.

[7] M. Weidenbruch, J. Schlaefke, A. Schäfer, K. Peters, H.G. von Schnering, H. Marsmann, Angew. Chem. 106 (1994) 1938; Angew. Chem. Int. Ed. Engl. 33 (1994) 1846.

[8] M. Weidenbruch, A. Stilter, J. Schlaefke, K. Peters, H.G. von Schnering, J. Organomet. Chem. 501 (1995) 67.

[9] M. Weidenbruch, A. Stilter, K. Peters, H.G. von Schnering, Z. Anorg. Allg. Chem. 622 (1996) 534.

[10] M. Weidenbruch, A. Stilter, K. Peters, H.G. von Schnering, Chem. Ber. 129 (1996) 1565.

[11] A.R. Rossi, R. Hoffmann, Inorg. Chem. 14 (1975) 365.

[12] H.P. Weber, R.T. Bryan, Acta Crystallogr. 22 (1967) 822.

[13] R.M. Sweet, C.J. Fritchie, R.A. Schunn, Inorg. Chem. 6 (1967) 749.

[14] P.G. Harrison, T.J. King, J.A. Richards, J. Chem. Soc. Dalton Trans. (1975) 2097.

[15] G.M. Sheldrick, SHELXL 93, Universität Göttingen, Germany, 1993.

[16] Further details of the crystal structure determinations may be obtained from the Fachinformationsdienst Karlsruhe, D-76334 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-407 953 (**4**) and CSD-407 992 (**3**).