Note

Synthesis and characterization of novel intramolecularly O,C,O-coordinated heteroleptic organostannylenes and their tungstenpentacarbonyl complexes

Blanka Kašná [a,b], Roman Jambor [a,*], Markus Schürman [b], Klaus Jurkschat [b,*]

[a] Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Čs. legií 565, CZ-532 10, Pardubice, Czech Republic
[b] Lehrstuhl für Anorganische Chemie II der Technischen Universität, D-44221 Dortmund, Germany

ABSTRACT

The syntheses are reported of the novel heteroleptic organostannylenes $[2,6-(ROCH_2)_2C_6H_3]SnCl$ (**1**, R = Me; **2**, R = *t*-Bu) and of their tungstenpentacarbonyl complexes $[2,6-(ROCH_2)_2C_6H_3](X)SnW(CO)_5$ (**3**, X = Cl, R = Me; **4**, X = Cl, R = *t*-Bu; **5**, X = H, R = Me). The compounds were characterized by means of elemental analyses, ^1H, ^{13}C, ^{119}Sn NMR spectroscopies, electrospray mass spectrometry and in case of **3** and **4** also by single crystal X-ray diffraction analysis. For the two latter compounds the substituents bound at the ether oxygen atom control the strength of intramolecular O → Sn coordination. Thus, the O–Sn distances amount to 2.391(5)/2.389(5) (**3**) and 2.464(3)/2.513(3) Å (**4**).

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1. Introduction

In recent time considerable progress has been made in understanding the chemical bonding of compounds that contain multiple bonds between heavier main group elements [1–3].

One characteristic feature of heavier group 14 analogues of alkynes is their *trans*-bent geometry in the solid state as well as in solution. In fact, the real structures found are intermediate ones between the ideal structures represented by the two canonical formulas (A) and (B).
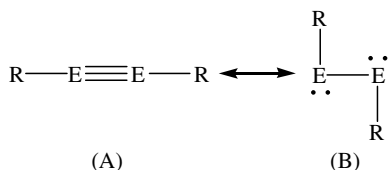
The design of a variety of rather bulky organic substituents R [2,4] was essential for the success in making compounds of type $(RE)_2$ (E = Si, Ge, Sn, Pb; R = C_6H_3-2,6-*i*-Pr$_2$, C_6H_2-2,4,6-*i*-Pr$_3$, C_6H_3-2,6-[C_6H_2-2,4,6-Me$_3$]$_2$, Si(*i*-Pr)[CH(SiMe$_3$)$_2$]$_2$). Only recently, we

demonstrated that employment of intramolecularly coordinating *built-in* ligands such as o-$C_6H_4CH_2NMe_2$ is an alternative for the stabilization of organotin(I) species $(RSn)_2$ [5].

The canonical formula (B) implies that compounds of type $(RE)_2$ should be versatile ligands for the synthesis of transition metal complexes (C).
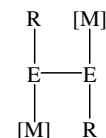
(C), [M] = transition metal fragment

Indeed, this concept was shown to be fruitful and the complexes $R[(CO)_5M]SnSn[M(CO)_5]R$ (R = {2,6-[P(O)(O*i*-Pr)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}, M = Cr, W) were prepared via reduction of the organochlorostannylene complexes $R(Cl)SnM(CO)_5$ to give the corresponding hydrides $R(H)SnM(CO)_5$ followed by evolution of hydrogen, H_2, and tin–tin bond formation [6]. The solid state structures of the ditin compounds mentioned above, as their thf and toluene solvates, respectively, are characterized by observation of different tin–tin distances ranging in between 2.8923(4) and 3.1433(7) Å, with the origin for these differences not being understood yet.

In context with this work and as part of a systematic study concerning the influence of different donor atoms on the tin–tin bond distance in complexes of type $R[(CO)_5M]SnSn-[M(CO)_5]R$ we report here the synthesis of the novel heteroleptic organostannylenes

* Corresponding authors. Fax: +420 466037068 (R. Jambor), fax: +49 231 755 5048 (K. Jurkschat).
E-mail addresses: roman.jambor@upce.cz (R. Jambor), klaus.jurkschat@uni-dortmund.de (K. Jurkschat).

RSnCl and of their tungstenpentacarbonyl complexes R(X)SnW-$(CO)_5$ (R = 2,6-$(MeOCH_2)_2C_6H_3$, 2,6-$(t$-BuOCH$_2)_2C_6H_3$; X = Cl, H) but failed to convert the latter into the corresponding ditin compounds.

2. Results and discussion

The heteroleptic organostannylenes **1** and **2** and their tungstenpentacarbonyl complexes **3** and **4** were readily obtained by reaction of the corresponding organolithium compounds 2, 6-$(ROCH_2)_2C_6H_3Li$ with SnCl$_2$ and in situ-generated $(CO)_5$WSnCl$_2$ [7], respectively (Scheme 1).

Compounds **1–4** are colourless crystalline materials that are well soluble in organic solvents such as toluene, benzene, THF and Et$_2$O but almost insoluble in *n*-hexane. Compounds **1** and **2** are rather sensitive to air and moisture whereas the stability of the transition metal complexes **3** and **4** depend on the substituent at oxygen (see below).

The ^{119}Sn NMR spectra of **1** and **2** display sharp signals at δ 230 and δ 206, respectively. These signals are high frequency-shifted as compared to the related organostannylene [C$_6$H$_3$(CH$_2$-NMe$_2$)$_2$-2,6]SnCl (δ 156) [8] that contains two intramolecularly coordinating dimethylaminomethyl groups whereas they are low frequency-shifted with respect to [C$_6$H$_3$(NMe$_2$)$_2$-2,6]SnCl (380 ppm) [9] and {C$_9$H$_6$N[CH(SiMe$_3$)]-8}SnCl (327 ppm) [10]. The latter contains one pyridine nitrogen atom that is involved in intramolecular N → Sn coordination whereas in the former only one of the two nitrogen atoms coordinates to the tin atom. Interestingly, the intramolecularly coordinated heteroleptic organostannylenes {2,6-[P(O)(OR)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl show chemical shifts of δ −100 (R = Et[11]) and −99 (R = *i*-Pr[12]). Apparently, the P=O→Sn(II) coordination in these compounds is stronger than the O → Sn(II) coordination of the ether oxygen atoms in the organostannylenes **1** and **2**. The connectivity of the atoms in these compounds is confirmed by ^{1}H and ^{13}C NMR spectroscopy (see Section 4). Most importantly, in the ^{13}C spectra there are ^1J(^{13}C–^{119}Sn) and J(^{13}C–^{119}Sn) coupling constants of 409 (**1**), 441 (**2**) and 27(**1**), 28 (**2**) Hz for the Sn*C* and O*C*H$_2$ carbon atoms, respectively. Furthermore, the identity of compounds **1** and **2** is supported by their electrospray mass spectra, hereafter referred to as ESI-MS. The spectra in the positive mode are characterized by mass clusters centred at *m*/*z* 285 (**1**), 326 (**1**), 370 (**2**), 410 (**2**) that are assigned to the corresponding cations [(ROCH$_2$)$_2$C$_6$H$_3$Sn]$^+$ and [(ROCH$_2$)$_2$-C$_6$H$_3$Sn(CH$_3$CN)]$^+$, respectively (R = Me, *t*-Bu). Attempts failed to obtain single crystals of both **1** and **2**.

Single crystals suitable for X-ray diffraction analysis of **3** and **4** were obtained by slow evaporation of benzene solutions at room temperature. The molecular structures are depicted in Figs. 1 and 2. Selected geometric parameters are given in Table 1.

Compounds **3** and **4** each contain a five-coordinate strongly distorted trigonal bipyramidally configured tin atom with the O(1) and O(2) atoms occupying the axial and the C(1), Cl(1), and W(1) atoms occupying the equatorial positions. The distortion from the
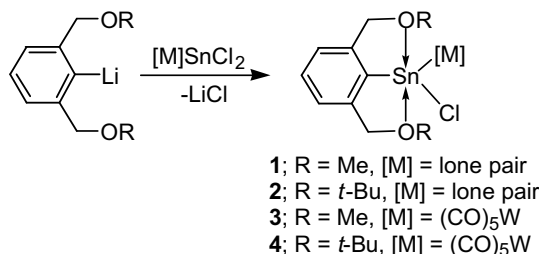
Fig. 1. General view (SHELXTL) of a molecule **3** showing 30% displacement ellipsoids and the atom numbering scheme. The hydrogen atoms are omitted for clarity.
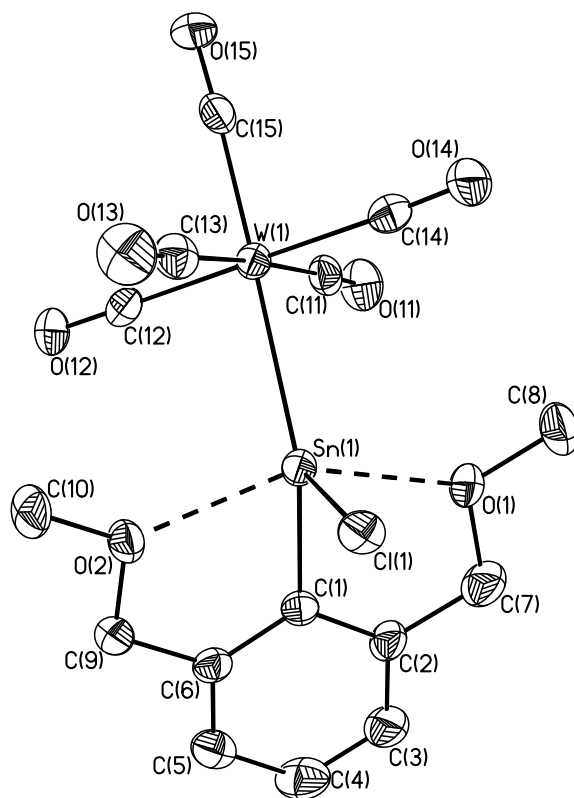

Fig. 2. General view (SHELXTL) of a molecule **4** showing 30% displacement ellipsoids and the atom numbering scheme. The hydrogen atoms are omitted for clarity.
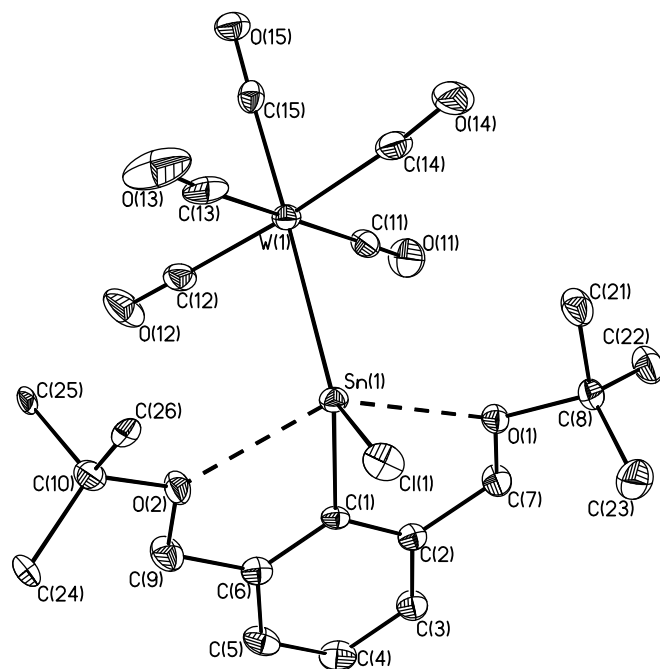
ideal trigonal bipyramidal towards the square pyramidal geometry is especially manifested by the O(1)–Sn–O(2) angles of 146.52(17)° (**3**) and 143.29(8)° (**4**) that strongly deviate from 180°, and by the W(1)–Sn(1)–C(1) (144.19(16) **3**, 130.03(10) **4**) and Cl(1)–Sn(1)–

1; R = Me, [M] = lone pair
2; R = *t*-Bu, [M] = lone pair
3; R = Me, [M] = (CO)$_5$W
4; R = *t*-Bu, [M] = (CO)$_5$W

Scheme 1.

Table 1
Crystal data and structure refinement details for compounds **3** and **4**

Compound	3	4
Empirical formula	$C_{15}H_{13}ClO_7SnW$	$C_{21}H_{25}ClO_7SnW$
Formula weight	643.24	727.40
Temperature (K)	173(1)	173(1)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Unit cell dimensions		
a (Å)	10.5640(7)	10.1356(9)
b (Å)	9.7970(6)	10.9659(7)
c (Å)	19.105(1)	12.147(1)
α (°)		77.499(4)
β (°)	104.976(4)	74.155(4)
γ (°)		72.906(5)
Volume (Å^3)	1910.2(2)	1227.7(2)
Z	4	2
Density (calculated) (mg/m^3)	2.237	1.968
Absorption coefficient (mm^{-1})	7.496	5.844
$F(000)$	1200	696
Crystal size (mm)	$0.16 \times 0.16 \times 0.16$	$0.22 \times 0.20 \times 0.20$
θ Range for data collection (°)	3.03–25.32	3.08–27.47.
Index ranges	$-12 \leqslant h \leqslant 12$	$-13 \leqslant h \leqslant 13$
	$-11 \leqslant k \leqslant 11$	$-13 \leqslant k \leqslant 14$
	$-22 \leqslant l \leqslant 22$	$-14 \leqslant l \leqslant 15$
Reflections collected/unique [$R_{(int)}$]	22664/3470 [0.052]	15964/5593 [0.043]
Reflections obs. [$I > 2\sigma(I)$]	2602	3952
Completeness to $2\theta = 27.48$	99.7%	99.5%
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3470/0/226	5593/0/307
Goodness-of-fit on F^2	0.958	0.799
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0313$, $wR_2 = 0.0726$	$R_1 = 0.0285$, $wR_2 = 0.0460$
R indices (all data)	$R_1 = 0.0457$, $wR_2 = 0.0747$	$R_1 = 0.0485$, $wR_2 = 0.0477$
Maximum shift/esd	0.001	0.001
Largest difference peak and hole (e Å^{-3})	1.248 and -0.763	1.037 and -0.809

Table 2
Selected bond lengths (Å) and angles (deg) for **3** and **4**

	3	4
Sn(1)–Cl (1)	2.440(15)	2.382(11)
Sn(1)–C(1)	2.126(7)	2.129(3)
Sn(1)–W(1)	2.732(5)	2.7655(4)
Sn(1)–O(1)	2.391(5)	2.464(3)
Sn(1)–O(2)	2.389(5)	2.513(3)
W(1)–C(15)	1.995(8)	1.971(5)
W(1)–C(14)	2.028(9)	2.041(5)
W(1)–C(13)	2.008(8)	2.015(6)
W(1)–C(12)	2.016(8)	2.050(5)
W(1)–C(11)	2.033(8)	2.033(5)
O(1)–Sn(1)–O(2)	146.52(17)	143.29(8)
C(1)–Sn(1)–O(1)	73.80(2)	73.42(12)
O(1)–Sn(1)–W(1)	105.21(13)	105.72(6)
O(1)–Sn(1)–Cl(1)	92.04(13)	89.14(7)
C(1)–Sn(1)–W(1)	144.19(16)	130.03(10)
C(1)–Sn(1)–Cl(1)	99.63(17)	104.45(10)
Cl(1)–Sn(1)–W(1)	116.31(5)	125.50(3)

C(1) (99.63(17) **3**, 104.45(10) **4**) angles considerably deviating from 120° (see Table 2).

The Sn–O distances of 2.391(5) and 2.389(5) Å in the methyl-substituted complex **3** are equal within experimental error whereas those in the *t*-butyl-substituted complex **4** (2.464(3), 2.513(3) Å) are longer and different, with the reason for this being the steric hindrance of the bulky *t*-butyl group. In both **3** and **4** the Sn–O distances are longer than those reported for {2,6-[P(O)(O*i*-Pr)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}(Cl)SnW(CO)$_5$ (2.313(2), 2.346(2) Å) [6,12] which indicates the superior donor capacity of a P=O versus the ether oxygen atoms in **3** and **4**. The different strength of the O → Sn donor–acceptor interactions in **3** and **4** is reflected by their

Sn–Cl distances. Thus, the Sn–Cl distance in the methyl-substituted complex **3** (2.440(15) Å) is longer than the corresponding distance in the *t*-butyl-substituted complex **4** (2.382(11) Å). As in {2,6-[P(O)(O*i*-Pr)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}(Cl)SnW(CO)$_5$ (Sn–Cl 2.4007(10) Å) [6,12] the Sn–Cl distances in both **3** and **4** are slightly longer as compared to the Sn–Cl distances found in [(thf)$_n$Cl$_2$Sn]W(CO)$_5$ (n = 1, 2.352(3) Å; n = 2 2.375(2) Å) [7]. The Sn(1)–W(1) distance in **3** (2.732(5) Å) is close to the corresponding distance in [(thf)$_2$Cl$_2$Sn]W(CO)$_5$ (2.737(1) Å) [7] whereas the Sn(1)–W(1) distance in **4** (2.7655(4) Å) is longer. Again, steric hindrance of the *t*-butyl substituents at the oxygen atoms in **4** might be the origin for this lengthening. The Sn–W distance in {2,6-[P(O)(O*i*-Pr)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}(Cl)SnW(CO)$_5$ amounts to 2.7263(11) Å [6,12].

Especially ^{1}H and ^{119}Sn NMR spectroscopy reveal the intramolecular O → Sn coordination in compounds **3** and **4** to be retained. Thus, the ^{1}H NMR spectra of **3** and **4** display AB spin-type resonances for the CH$_2$-protons indicating their diastereotopicity. The ^{119}Sn NMR spectra reveal signals at δ 197 [^1J(^{119}Sn–^{183}W) 1245 Hz] (**3**) and δ 257 [^1J(^{119}Sn–^{183}W) 1289 Hz] (**4**) being high frequency-shifted as compared to {2,6-[P(O)(O*i*-Pr)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}(Cl)SnW(CO)$_5$ [δ −75, ^1J(^{119}Sn–^{183}W) 1366 Hz] [6] and suggest the O → Sn interaction in **3** to be stronger than in **4**. The influence of the oxygen-bound substituent R on the strength of the O → Sn coordination has already been observed for the organotin(IV) compounds 2,6-(ROCH$_2$)$_2$C$_6$H$_3$SnPhCl$_2$ (R = Me, *t*-Bu) [13]. Interestingly, the strength of the O → Sn interaction seems to influence the stability of compounds **3** and **4** towards air. While compound **3** is stable even after one week of exposure to air, compound **4** is rather labile and rapidly decomposes upon contact with the latter.

The ^{13}C NMR spectra show two signals at δ 200.3 and 197.9 (**3**), and at δ 199.6 and 198.5 (**4**) indicating non-equivalent CO groups in both complexes, as expected.

The reaction of the intramolecularly coordinated organochlorostannylene tungstenpentacarbonyl complex **3** with K[^{sec}Bu$_3$BH] provided the corresponding hydride **5** in good yield (Eq. (1)).

$$\text{(1)}$$
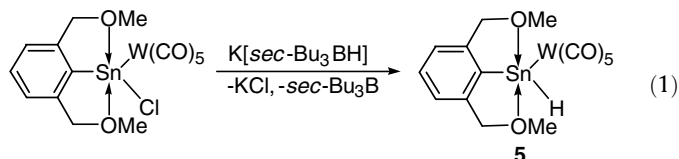
In analogy to the organochlorostannylene tungstenpentacarbonyl complex **3**, the ^{1}H NMR spectrum of **5** displays AB spin-type resonances for the CH$_2$-protons indicating their diastereotopicity. The presence of the Sn–H proton is evidenced by a sharp singlet at δ 11.5 being flanked by $^1J(^1$H–$^{117/119}$Sn) satellites of 1078/1118 Hz. The latter are rather similar to those found in the related organostannylene hydride tungstenpentacarbonyl complex {2,6-[P(O)(Oi-Pr)$_2$]$_2$-4-$tert$-Bu-C$_6$H$_2$}(H)SnW(CO)$_5$ (1198 Hz) [6] but larger than the coupling reported for the organostannylene hydride [2,6-Trip$_2$H$_3$C$_6$-Sn(μ-H)]$_2$ (Trip = 2,4,6-triisopropylphenyl) (592 Hz) [14]. The ^{119}Sn NMR spectrum of **5** reveals a sharp signal at δ 299 that is high frequency-shifted as compared to {2,6-[P(O)(Oi-Pr)$_2$]$_2$-4-$tert$-Bu-C$_6$H$_2$}(H)SnW(CO)$_5$ (δ 11) [6,12] but low frequency-shifted in comparison to the organostannylene hydride [2,6-Trip$_2$H$_3$C$_6$-Sn(μ-H)]$_2$ (δ 699) [14]. In the latter compound the bulky substituent 2,6-Trip$_2$H$_3$C$_6$ contributes to the stabilization of the Sn(II)–H bond.

Attempts failed at converting the organotin hydride tungstenpentacarbonyl complex **5** into the corresponding ditin compound [2,6-(MeOCH$_2$)$_2$C$_6$H$_3$SnW(CO)$_5$]$_2$ by heating a solution of the organotin hydride in toluene. Under the experimental conditions employed, formation of the protonated ligand 2,6-(MeOCH$_2$)$_2$C$_6$H$_4$ and of insoluble material was observed. The latter was not analyzed in more detail.

3. Conclusion

The O,C,O-coordinating pincer-type ligands [2,6-(ROCH$_2$)$_2$C$_6$H$_3$]$^-$ (R = Me, t-Bu) were shown to be useful for the synthesis of novel heteroleptic stannylenes and their transition metal complexes. However, the Lewis base donor capacity of ether-type oxygen atoms in these ligands appears to be insufficient to stabilize ditin compounds of general type (**C**).

4. Experimental

4.1. General methods

Solvents were dried by standard methods and distilled prior to use. All moisture and air sensitive reactions were carried out in an argon atmosphere using standard Schlenk techniques. The organolithium compounds 2,6-(ROCH$_2$)$_2$C$_6$H$_3$Li (R = Me, t-Bu) were prepared in situ as previously reported [13]. Elemental analyses were performed on an LECO-CHNS-932 analyzer. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were acquired on Bruker DRX400 and Bruker DPX300 FT NMR spectrometers with broad band decoupling of ^{119}Sn at 149.21 or 111.92 MHz and of ^{13}C at 100.61 MHz, using external and internal deuterium lock. The ^{1}H, ^{13}C, and ^{119}Sn NMR chemical shifts δ are given in ppm and referenced to external Me$_4$Sn (^{119}Sn) and Me$_4$Si (^{13}C, ^{1}H). IR spectra (cm^{-1}) were obtained using a Bruker FT-IR IFS 113v spectrometer. Electrospray mass spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK) using an acetonitrile mobile phase. Pressure in the mass analyzer region was usually about 4–10.5 mbar. Ions showed the expected isotopic pattern.

4.2. Synthesis of 2,6-(MeOCH$_2$)$_2$C$_6$H$_3$SnCl (**1**)

A solution of 2,6-(MeOCH2)$_2$C$_6$H$_3$Li (0.55 g, 2.2 mmol) in Et$_2$O (20 mL) was added drop-wise to a solution of SnCl$_2$ (0.42 g, 2.2 mmol) in THF (20 mL) at −78 °C. The resulting mixture was stirred for 5 h at −78 °C, and than for 3 h at room temperature. After the solvent had been evaporated the residue was suspended in toluene (30 mL) followed by filtration. The filtrate was concentrated to a volume of 5 mL and stored at −30 °C to give **1** as pale yellow powder. Yield: 0.57 g (70%); m.p. 65–66 °C. Elemental Anal. Calc. for C$_{10}$H$_{13}$ClO$_2$Sn (319.36 g/mol): C, 37.61; H, 4.10. Found: C, 37.58; H, 4.08%. Monoisotopic m.w. = 319. Positive-ion ESI-MS: m/z 285, [M−Cl]$^+$, 100%; 326 m/z [M−Cl+CH$_3$CN]$^+$, 40%. Negative-ion ESI-MS: m/z 225, [SnCl$_3$]$^-$, 100%. ^{1}H NMR (C$_6$D$_6$, 300,13 MHz): δ (ppm) 3.12 (s, 6H, CH$_3$), 4.26 (s, 4H, CH$_2$), 6.81 (d, 2H, aromatic H^3,H^5), 7.14 (t, 1H, aromatic H^4). ^{13}C NMR (C$_6$D$_6$, 100.63 MHz): δ (ppm) 58.9 (CH$_3$), 78.2 (CH$_2$,$^nJ(^{13}$C–^{119}Sn) = 27 Hz), 169.9 (C$_i$(1), $^1J(^{13}$C–^{119}Sn) = 409 Hz)), 121.8, 127.6, 144.9. ^{119}Sn NMR (C$_6$D$_6$, 111.95 MHz): δ (ppm) 231.

4.3. Synthesis of 2,6-(t-BuOCH$_2$)$_2$C$_6$H$_3$SnCl (**2**)

A solution of 2,6-(t-BuOCH$_2$)$_2$C$_6$H$_3$Li (0.66 g, 2.6 mmol) in hexane (20 mL) was added drop-wise to the solution of SnCl$_2$ (0.49 g, 2.6 mmol) in THF (20 mL). After the reaction mixture had been stirred for 12 h the solvent was removed in vacuo. The residue was suspended in toluene (40 mL) and the suspension was magnetically stirred for 10 min and then filtered. The filtrate was evaporated in vacuo to leave a solid residue that was washed with n-pentane to afford **2** as white solid. Yield: 0.62 g (60%); m.p. 75–77 °C. Elemental Anal. Calc. for C$_{16}$H$_{25}$O$_2$ClSn (403.52 g/mol): C, 47.63; H, 6.24 Found: C, 47.50; H, 6.30%. Monoisotopic m.w. = 403. Positive-ion ESI-MS: m/z 370, [M−Cl]$^+$, 100%; m/z 410 [M−Cl+CH$_3$CN]$^+$, 40%. Negative-ion ESI-MS: m/z 225, [SnCl$_3$]$^-$, 100%. ^{1}H NMR (C$_6$D$_6$, 300.13 MHz): δ (ppm) 1.24 (s, 18H, CH$_3$), 4.59 (AB system, $^2J((^1$H–^{1}H) = 13Hz, 4H, CH$_2$,), 6.96 (d, 2H, aromatic H^3,H^5), 7.21 (t, 1H, aromatic H^4). ^{13}C NMR (C$_6$D$_6$, 100.63 MHz): δ (ppm) 28.7 (CH$_3$), 67.9 (CH$_2$, $^nJ(^{13}$C–^{119}Sn) = 28 Hz), 79.2 (OC(CH$_3$)$_3$), SnC$_6$H$_3$, 167.2 (C$_i$(1), $^1J(^{13}$C–^{119}Sn) = 441 Hz), 122.2, 127.4, 145.8. ^{119}Sn NMR (C$_6$D$_6$, 111.95 MHz): δ (ppm) 206.

4.4. Synthesis of 2,6-(MeOCH$_2$)$_2$C$_6$H$_3$Sn(Cl)SnW(CO)$_5$ (**3**)

A solution of 2,6-(MeOCH$_2$)$_2$C$_6$H$_3$Li (0.59 g, 2.4 mmol) in Et$_2$O (20 mL) was added drop-wise to a solution of W(CO)$_5$SnCl$_2$ [7] (1.5 g, 2.4 mmol) in THF (20 mL) at −78 °C. The resulting mixture was stirred for further 7 h at −78 °C and for 2 h at room temperature. After the solvent had been evaporated in vacuo the residue was suspended in toluene (30 mL) and the resulting mixture was magnetically stirred for 10 min and then filtered. The solvent was evaporated in vacuo to leave a solid residue that was washed with n-pentane to give **3** as a white powder. Yield: 1.29 g (89%); m.p. 160 °C (decomposition). Elemental Anal. Calc. for C$_{15}$H$_{14}$ClO$_7$SnW (644.27 g/mol): C, 27.96; H, 2.19. Found: C, 27.90; H, 2.00%. Monoisotopic m.w. = 644. Positive-ion ESI-MS: m/z 285, [M−Cl–W(CO)$_5$]$^{+2}$, 100%; m/z 326, [M−Cl–W(CO)$_5$+CH$_3$CN]$^+$, 20%; m/z 552, [M−Cl–2CO]$^+$, 20%; m/z 608, [M−Cl]$^+$, 15%; m/z 648, [M−Cl+CH$_3$CN]$^+$, 20%. IR (KBr): ν (cm^{-1}): 2064, 1989, 1932, 1902. ^{1}H NMR (C$_6$D$_6$, 300,13 MHz): δ (ppm) 3.25 (s, 6H, CH$_3$), 4.02 (AB system $^2J((^1$H–^{1}H) = 13 Hz), 4H, CH$_2$), 6.58 (d, 2H, aromatic H^3,H^5), 7.01 (t, 1H, aromatic H^4). ^{13}C NMR (C$_6$D$_6$, 100.63 MHz): δ (ppm) 59.0 (CH$_3$), 75.8 (CH$_2$), SnC$_6$H$_3$, (C(1) not found), 122.8, 130.9, 142.6, 197.9 (CO^{eq}, $^2J(^{13}$C–^{119}Sn) = 124 Hz, $^1J(^{13}$C–^{182}W) = 58 Hz), 200.3 (CO^{ax}). ^{119}Sn NMR (C$_6$D$_6$, 111.95 MHz): δ (ppm) 197 (^1J(^{119}Sn–^{182}W) = 1245 Hz).

4.5. Synthesis of 2,6-(t-BuOCH₂)₂C₆H₃Sn(Cl)SnW(CO)₅ (**4**)

*4.5. Synthesis of 2,6-(t-BuOCH$_2$)$_2$C$_6$H$_3$Sn(Cl)SnW(CO)$_5$ (**4**)*

A solution of 2,6-(*t*-BuOCH$_2$)$_2$C$_6$H$_3$Li (0.65 g, 2.6 mmol) in hexane (20 mL) was added drop-wise to a solution of W(CO)$_5$SnCl$_2$[7] (1.55 g, 2.6 mmol) in THF (20 mL). After the reaction mixture had been stirred for 20 h at room temperature and the solvent had been evaporated in vacuo the residue was suspended in toluene (40 mL) and the suspension was stirred for 10 min followed by filtration. The filtrate was evaporated in vacuo to leave a solid residue that was washed with *n*-pentane to give **4** as pale yellow solid. Yield: 1.47 g (93%); m.p. 138–141 °C. Elemental Anal. Calc. for C$_{21}$H$_{26}$ClO$_7$SnW (728.43 g/mol): C, 34.63; H, 3.60. Found: C, 34.50; H, 3.50%. Monoisotopic m.w. = 728. Positive-ion ESI-MS: *m/z* 369, [M−Cl−W(CO)$_5$]$^+$, 100%. IR (KBr): ν (cm^{-1}): 2065, 1981, 1935, 1900. ^{1}H NMR (C$_6$D$_6$, 300,13 MHz): δ (ppm) 1.31 (s, 18H, CH$_3$), 4.49 (AB system $^2J((^{1}H–^{1}H) = 14 Hz, 4H, CH$_2$), 6.74 (d, 2H, aromatic H^3, H^5), 7.07 (t, 1H, aromatic H^4). ^{13}C NMR (C$_6$D$_6$, 100.63 MHz): δ (ppm) 28.2 (CH$_3$), 66.5 (CH$_2$), 82.4 (OC(CH$_3$)$_3$, $^nJ(^{13}$C–^{119}Sn) = 39 Hz), 151.9 (C$_i$(1)), 123.2, 129.4, 143.6, 198.5 (CO^{eq}, $^1J(^{13}$C–^{182}W) = 124 Hz, $^2J(^{13}$C–^{119}Sn) = 57 Hz), 199.6 (CO^{ax}). ^{119}Sn NMR (C$_6$D$_6$, 111.95 MHz): δ (ppm) 257 (^1J (^{119}Sn–^{182}W) = 1289 Hz).

4.6. Synthesis of 2,6-(MeOCH₂)₂C₆H₃(H)SnW(CO)₅ (**5**)

*4.6. Synthesis of 2,6-(MeOCH$_2$)$_2$C$_6$H$_3$(H)SnW(CO)$_5$ (**5**)*

A solution (0.3 mL of 1 M THF) of K[^{sec}Bu$_3$BH] (0.3 mmol) was added to a solution of **3** (0.2 g, 0.3 mmol) in THF (20 mL) at −78 °C. The resulting mixture was stirred for 4 h at this temperature and than for 4 h at −40 °C. After the solvent had been evaporated in vacuo the residue was suspended in toluene (20 mL) and the suspension was stirred for 10 min followed by filtration. The filtrate was evaporated in vacuo to leave a solid residue that was washed with *n*-pentane to afford **5** as pale yellow solid. Yield: 0.18 g (85%); m.p. 294 °C. Elemental Anal. Calc. for C$_{15}$H$_{15}$O$_7$SnW (609.82 g/mol): C, 29.54; H, 2.48. Found: C, 29.50; H, 2.45%. ^{1}H NMR (C$_6$D$_6$, 300,13 MHz): δ 3.01 (s, 6H, CH$_3$), 4.02 (AB system $^2J(^1$H–^{1}H) = 12 Hz, 4H, CH$_2$), 6.61 (d, 2H, aromatic H^3,H^5), 7.03 (t, 1H, aromatic H^4), 11.58 (s, 1H, $^1J(^1$H–^{119}Sn) = 1118 Hz). ^{13}C NMR (C$_6$D$_6$, 100.63 MHz): 59.2 (CH$_3$), 76.1 (CH$_2$), 145.9 (C$_i$(1)), 122.4, 128.2, 142.7, 200.1 (CO^{eq}, $^2J(^{13}$C–^{119}Sn) = 121 Hz, $^1J(^{13}$C–^{182}W) = 54 Hz), 202.7 (CO^{ax}). ^{119}Sn NMR (C$_6$D$_6$, 111.95 MHz): δ 299 ^1J (^{119}Sn–^{182}W) = 1242 Hz).

4.6.1. Crystallography

Intensity data for the colourless crystals **3** and **4** were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation. The data collections covered almost the whole sphere of reciprocal space with 4 sets at different κ-angles and 418 (**3**), 415 (**4**) frames via ω-rotation ($\Delta/\omega = 1°$) at two times 40 s (**3**), 20 s (**4**) per frame. The crystal-to-detector distances were 3.4 cm for both molecules. Crystal decay was monitored by repeating the initial frames at the end of data collection. Analysing the duplicate reflections there was no indication for any decay. The structures was solved by direct methods SHELXS97 [15a] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL97 [15b]. The H atoms were placed in geometrically calculated positions using a riding model with U_{iso} constrained at 1.2 for non-methyl groups and 1.5 for methyl groups times U_{eq} of the carrier atom. One *t*-butoxy group is disordered over two positions (C(24), C(25), C(26), C(24'), C(25'), C(26')) with occupancies of 0.5. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from International Tables for X–ray Crystallography [15c]. The figures were created by SHELXTL [15d]. Crystallographic data for molecules **3** and **4** are given in Table 1.

Supplementary material

CCDC 675686 and 675687 contains the supplementary crystallographic data for **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

References

[1] P.P. Power, Organometallics 26 (2007) 4362 and references cited.
[2] E. Rivard, P.P. Power, Inorg. Chem. 46 (2007) 10047 and references cited.
[3] G. Balazs, L.J. Gregorides, M. Scheer, Organometallics 26 (2007) 3058. and references cited.
[4] A. Sekiguchi, R. Kinjo, M. Ichinohe, Science 305 (2004) 1755.
[5] R. Jambor, B. Kasna, K.N. Kirschner, M. Schürmann, K. Jurkschat, Angew. Chem., Int. Ed. 47 (2008) 1650.
[6] First presented at XVth FECHEM Conference on Organometallic Chemistry, University of Zürich, 10th to 15th August 2003, Book of Abstracts OP38, and at the 11th International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin, and Lead (ICCOC-GTL-11), Santa Fe (New Mexico, USA) 27th June to 2nd July 2004, Book of Abstracts O54.
[7] A.L. Balch, D.E. Oram, Organometallics 7 (1988) 155.
[8] J.T.B.H. Jastrzebski, P.A. van der Schaaf, J. Boersma, G. van Koten, M.C. Zoutberg, D. Heijdenrijk, Organometallics 8 (1989) 1373.
[9] C. Drost, P.B. Hitchcock, M.F. Lappert, L.J.-M. Pierssens, J. Chem. Soc., Chem. Commun. (1997) 1141.
[10] W.-P. Leung, W.-H. Kwok, F. Xue, T.C.W.J. Mak, Am. Chem. Soc. 119 (1997) 1145.
[11] M. Mehring, C. Löw, M. Schürmann, F. Uhlig, K. Jurkschat, Organometallics 19 (2000) 4613.
[12] M. Henn, Ph.D. Thesis, Dortmund University, 2004.
[13] R. Jambor, L. Dostál, A. Růžička, I. Císařová, J. Brus, M. Holčapek, J. Holeček, Organometallics 21 (2002) 3996.
[14] B.E. Eichler, P.P. Power, J. Am. Chem. Soc. 122 (2000) 8785.
[15] (a) G.M. Sheldrick, Acta Crystallogr. A 46 (1990) 467–473;
(b) G.M. Sheldrick, University of Gottingen, 1997;
(c) International Tables for Crystallography, Vol. C, Kluwer Academic Publishers, Dordrecht, 1992;
(d) G.M. Sheldrick, SHELXTL. Release 5.1 Software Reference Manual, Bruker AXS, Inc., Madison, Wisconsin, USA, 1997.