DOI: 10.1002/ejic.200700292

Synthesis of Half-Sandwich Tungsten Chlorogermyl and Chlorostannyl Complexes

Holger Braunschweig,*[a] Holger Bera,[a] Barbara Geibel,[a] Rainer Dörfler,[a] Daniel Götz,[a] Fabian Seeler,[a] Thomas Kupfer,[a] and Krzysztof Radacki[a]

Keywords: Half-sandwich complexes / Tungsten complexes / Germanes / Stannanes / Stannylcyclopentadienes

The reaction of the dichlorogermane Me_2GeCl_2 and stannanes R_2SnCl_2 (R = Me, Bu) with the alkali tungsten salts $M[(\eta^5\text{-}C_5R'_5)L(OC)_2W]$ (L = CO, PPh_3; M = Li, Na; R′ = H, Me) yields via alkali salt elimination a range of novel chlorostannyl- and chlorogermyl-functionalized tungsten complexes of the general formula $[(\eta^5\text{-}C_5R'_5)L(OC)_2W(ER_2Cl)]$ (R′ = H, Me; L = CO, PPh_3; E = Ge, Sn; R = Me, Bu) (**3a**–**e**). The use of the phosphane-substituted tungsten anion $Na[(\eta^5\text{-}C_5Me_5)(Ph_3P)(OC)_2W]$ (**1c**) and Me_2SnCl_2 leads to a mixture consisting of the mono- (**3e**) as well as the di-substituted stannyl compound $[\{(\eta^5\text{-}C_5H_5)(Ph_3P)(OC)_2W\}_2(SnMe_2)]$ (**4**). Access to **3a** is also given by reaction of $ClMe_2Sn\text{–}C_5H_5$ (**5**) with $[(MeCN)_3W(CO)_3]$ which includes chemoselective tin shift from the cyclopentadiene to the tungsten atom. In addition, a successive chlorination of $[(\eta^5\text{-}C_5H_5)(OC)_3W(SnMe_3)]$ (**6**) via $[(\eta^5\text{-}C_5H_5)(OC)_3W(SnMe_2Cl)]$ (**3a**) and $[(\eta^5\text{-}C_5H_5)(OC)_3W(SnMeCl_2)]$ (**7**) to $[(\eta^5\text{-}C_5H_5)(OC)_3W(SnCl_3)]$ (**8**) is presented. All new compounds have been fully characterized by elemental analyses and in solution by IR and multinuclear NMR spectroscopy. The crystal structures of complexes **3b**–**d** and **8** were presented and discussed, showing bond lengths of 2.6272(4) Å for Ge–W, 2.7959(5) (**3b**), 2.7866(3) (**3d**) and 2.7244(3) (**8**) Å for the Sn–W bonds.

Introduction

The first germanium and tin complexes of molybdenum and tungsten have been prepared in the 1960’s[1] and since that time [M]–SnR_3 bonds are ubiquitous up to the present day.[2] The chemistry of such complexes has been the object of extensive studies due to their potential in many catalytic and stoichiomtric processes.[3] Two important reactions of transition-metal stannyl complexes [M]–SnR_3 (R = organic group) are the chlorination with hydrogen halides[4] and the stanna-tropic shift from the transition-metal to the cyclopentadienyl ligand in half-sandwich complexes, induced by a strong base.[5] Despite this fact, the amount of complexes owing a chlorogermyl or chlorostannyl moiety, which allow further functionalization and reaction chemistry, is fairly limited – in particular in the case of germanium, and only little work has been carried out concerning investigations of the Cl–Sn unit of a transition metal. One of them – the most recent work – deals with chloride displacement by nucleophilic sulfur or oxygen groups with the latter (pyridinedicarboxylic acid) leading to an iron complex with fivefold-coordinated tin[6] (Figure 1). Another investigation topic is the Lewis basicity of the Cl_3Sn group. In this context, some interesting molybdenum and tungsten *ansa* complexes were built up showing an intramolecular Lewis acid–base interaction of a cyclopentadienyl-bound donor group (with N and O as donor atoms) and the transition-metal bound Cl_3Sn moiety giving a sixfold-coordinated tin centre[7] (Figure 1).

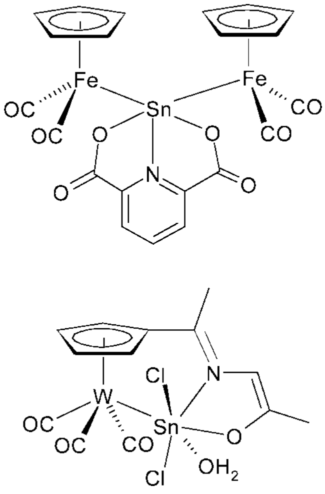


Figure 1. Iron and tungsten half-sandwich complexes with fivefold- and sixfold-coordinated tin atoms.

Nevertheless, with regard to the facile chemistry of R_3ECl (E = Ge, Sn) which includes a wide variety of reactions with alkali metals, organolithium compounds, hydroxides, sulfides, Lewis bases, amides, alkoxides, etc., it seems self-evident that much of it can be yet transferred to chlorogermyl and chlorostannyl transition-metal complexes.

---

[a] Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074, Würzburg, Germany

In an extension of our work on the reactivity of boryl-, borylene-,[8] or diborane(4)yl[9] moieties linked to half-sandwich metal fragments (e.g. compound [(η^5-C_5Me_5)-$(OC)_2$Fe–(BX_2←py)] (X = Cl, Br; py = pyridine),[8f] [(η^5-C_5H_5)(R_3P)$(OC)_2$W–{B(NMe_2)–B(NMe_2)Cl}] (R = Me, Ph)[9a] in Figure 2) which included the addition of Lewis bases to BCl_2 ligands[8f,8i] analogous to Cl_3Sn complexes, we became interested in some aspects of the chemistry of corresponding halogermyl and stannyl complexes.

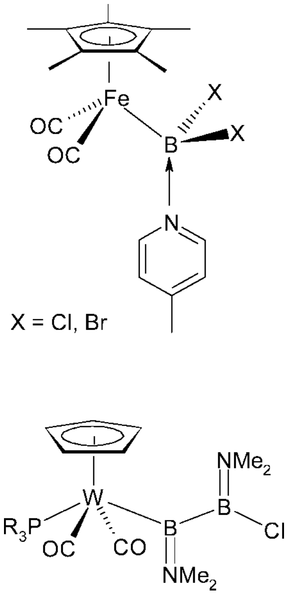


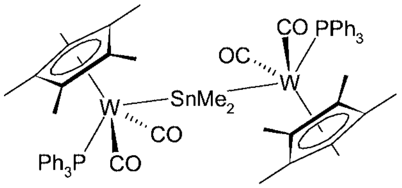
Figure 2. Methylpyridine Lewis base adduct of a X_2B-substituted iron complex and phosphane-substituted diborane(4)yl tungsten half-sandwich complex.

In this paper we report on the synthesis, spectroscopic and structural characterisation of the novel chlorodiorgano germyl and stannyl complexes of tungsten. The synthetic method chosen is straightforward and widely variable and so should give access to a range of analogue complexes. Additionally, we have developed three convenient and new methods for a facile preparation of **3a**, and established a chlorination chemistry which allows the facile synthesis of tungsten complexes with mono, di- and trichlorinated stannyl ligands.

Results and Discussion

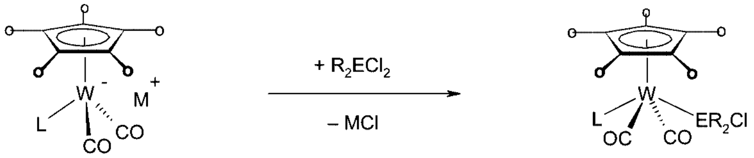
The complexes of the general formula [(η^5-$C_5R'_5$)L$(OC)_2$-W(ER_2Cl)] (R′ = H, Me; L = CO, PPh_3; E = Ge, Sn; R = Me, Bu) (**3a**–**e**) are obtained from the corresponding dichlorogermanes and stannanes R_2ECl_2 (E = Ge, Sn; R = Me, Bu) (**2a**–**c**) with the alkali tungsten salts M[(η^5-$C_5R'_5$)-L$(OC)_2$W] (L = CO, PPh_3; M = Li, Na; R′ = H, Me) (**1a**–**c**) after 16–22 h reaction time at ambient temperature in diethyl ether, according to Equation (1). The new compounds are isolated as yellow and dark yellow (**3e** and **3a**,**b**), ochre (**3d**) and brown (**3c**) powders in yields between 70% (**3b**) and 85% (**3d**). These results demonstrate that the synthetic method chosen is straightforward and widely variable and hence should give access to a range of analogue complexes. **3a**–**e** show moderate solubility in pentane or hexane and dissolve readily in diethyl ether and aromatic solvents. They can be stored under argon atmosphere at –30 °C for several months without signs of decomposition. **3d** can be even stored at ambient temperature.

The reaction of the triphenylphosphane-substituted tungsten anion **1c** with dichlorodimethylstannane (**2b**) does not give exclusively **3e**. Instead, a product mixture of **3e** and the dinuclear complex **4** is obtained (Figure 3). The ratio of **3e** and **4** is determined by integration of the ^{1}H NMR spec-



4

Figure 3. Disubstituted dimethylstannane *trans*-**4**.



(1)

1	a	b	c
o-	H	Me	Me
L	CO	CO	PPh_3
M	Li	Li	Na

2	a	b	c
R	Me	Me	Bu
E	Ge	Sn	Sn

3	a	b	c	d	e
o-	H	H	Me	Me	Me
L	CO	CO	CO	CO	PPh_3
R	Me	Bu	Me	Me	Me
E	Sn	Sn	Ge	Sn	Sn

trum and amounts to 2:1. The formation of **3e** and **4** proceeds stereospecifically and only the *trans*-products are observed, which is consistent with the synthesis of the parent $[(\eta^5\text{-}C_5H_5)(Ph_3P)(OC)_2W(SnMe_3)]$.[10] Due to the different solubility in hexane both compounds can be easily separated from each other. This reaction demonstrates the higher nucleophilic character of the phosphane-substituted tungsten anion **1c** in comparison to the tricarbonyl derivative (**1b**) in spite of its higher steric demands.

All new complexes were characterised in solution by IR and multinuclear NMR spectroscopy. The complexes **3a**,**c**–**e** show singlets for the dimethyl groups attached to the germanium and tin atom in the ^1H NMR spectra between 0.87 (**3a**) and 1.17 (**3c**) ppm, characteristic for an element nucleus being deshielded with respect to those of the starting dichlorogermane and stannanes. These values are in good agreement to the corresponding signal found for $[\{H_2C(O)\text{-}C(\eta^5\text{-}C_5H_4)\}(OC)_3W(SnMe_2Cl)]_2$ (δ = 0.95 ppm).[11] The signals of the Sn-bound methyl moieties are accompanied by $^{117/119}Sn$ satellites showing $^2J_{HCSn}$ coupling constants of 45.3, 47.3 (**3a**), 42.5, 44.4 (**3d**) and 40.2, 41.8 (**3e**) Hz, thus reflecting the increasing electron density of the tungsten fragments in this row. The ^{119}Sn NMR resonances of **3a**,**d**,**e** are detected in close proximity at 227.0 (**3a**), 233.0 (**3d**) and 233.8 (**3e**) ppm, whereas the one of the butyl derivative **3b** differs significantly and appears at δ = 26.7 ppm due to the electron-releasing effect of the butyl groups. Only in two cases the $^1J_{SnW}$ coupling was observed amounting to 162.8 (**3b**) and 347.0 Hz (**3d**). Due to the fact that in the case of **3e** and **4** the *trans*-product is exclusively formed, in the ^{31}P NMR spectra appears in each case one resonance at 38.61 (**3e**) and 44.50 ppm (**4**), accompanied by ^{183}W [$^1J_{WP}$ = 293.6 Hz (**3e**), 267.3 Hz (**4**)] and $^{117/119}Sn$ satellites [$^2J_{SnWP}$ = 123.9 and 128.8 Hz (**3e**), 125.4 and 130.8 Hz (**4**)]. As expected, **3a**,**c**,**d** show three CO-stretching frequencies ($A_{(1)}'$, A'' and $A_{(2)}'$) each in the IR spectra between 1901 and 2010 cm^{-1}, as expected for such tungsten complexes.[11] Surprisingly, the butyl derivative **3b** shows only two bands (1999 and 1981 cm^{-1}), one of which, however, is thus possibly indicating an overlap of two bands. In contrast, the observed number of two CO-stretching frequencies for **3e** and **4** is in agreement with phosphane-substituted tungsten stannyl complexes, as loss of a carbonyl group usually decreases the number of absorption bands from 3 to 2. As expected, the carbonyl stretching frequencies decrease in comparison to **3a**,**c**,**d** and are found for **3e** and **4** at 1904, 1835 and 1901, 1832 cm^{-1}, respectively which lie very close to those of $[(\eta^5\text{-}C_5H_5)(Ph_3P)(OC)_2W(SnMe_3)]$.[10]

X-ray diffraction analyses. The molecular structures of $[(\eta^5\text{-}C_5H_5)(OC)_3W(SnBu_2Cl)]$ (**3b**), $[(\eta^5\text{-}C_5Me_5)(OC)_3W\text{-}(GeMe_2Cl)]$ (**3c**) and $[(\eta^5\text{-}C_5Me_5)(OC)_3W(SnMe_2Cl)]$ (**3d**) have been confirmed by X-ray diffraction studies and are presented in Figure 4, Figure 5, and Figure 6. Selected bond lengths and angles are listed below each Figure and crystal data and refinement parameters in Table 2 in the experimental section. In all cases, crystals, suitable for X-ray analysis, are obtained upon slow evaporation of saturated benzene solutions at room temperature. The compounds crystallize in triclinic (**3b**) and monoclinic (**3c**,**d**) crystal systems with space groups $P\bar{1}$ (**3b**), $P2_1/c$ (**3c**) and $C2/c$ (**3d**), respectively.

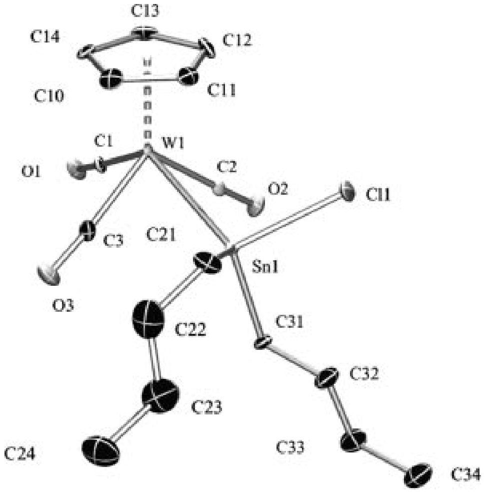


Figure 4. Molecular structure of $[(\eta^5\text{-}C_5H_5)(OC)_3W(SnBu_2Cl)]$ (**3b**) in the solid state with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: W1–C1 1.983(7), W1–C3 1.984(8), W1–C2 1.985(7), W1–Sn1 2.7959(5), Sn1–C31 2.156(7), Sn1–C21 2.168(8), Sn1–Cl1 2.4203(18), C31–Sn1–C21 114.6(3), C31–Sn1–Cl1 99.1(2), C21–Sn1–Cl1 99.6(2), C31–Sn1–W1 120.56(19), C21–Sn1–W1 114.1(2), Cl1–Sn1–W1 104.34(5).

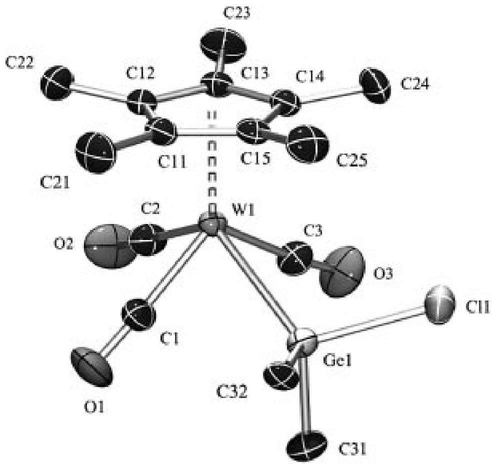


Figure 5. Molecular structure of $[(\eta^5\text{-}C_5Me_5)(OC)_3W(GeMe_2Cl)]$ (**3c**) in the solid state with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: W1–C1 1.971(4), W1–C2 1.982(4), W1–C3 1.982(4), W1–Ge1 2.6272(4), Ge1–C31 1.948(4), Ge1–C32 2.008(3), Ge1–Cl1 2.2428(10), C1–W1–Ge1 70.04(11), C2–W1–Ge1 123.98(11), C3–W1–Ge1 72.07(12), C31–Ge1–C32 106.44(17), C31–Ge1–Cl1 101.62(13), C32–Ge1–Cl1 101.97(10), C31–Ge1–W1 117.55(13), Cl1–Ge1–W1 109.74(3).

The coordination sphere around each tungsten atom can be considered as a pseudo square-pyramid, with the three carbonyl ligands [mean W–C 1.984 (**3b**), 1.978 (**3c**) and 1.978 Å (**3d**)] and the germyl or rather stannyl group forming the base, while the aromatic ring systems occupie the

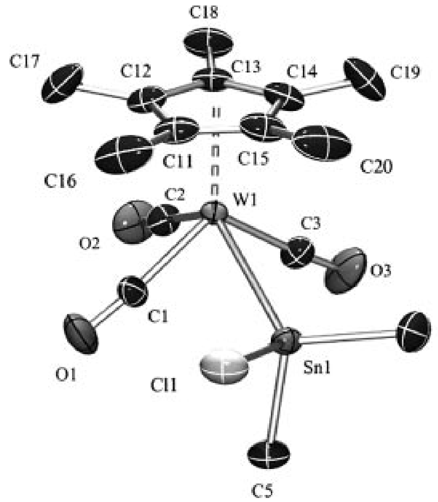


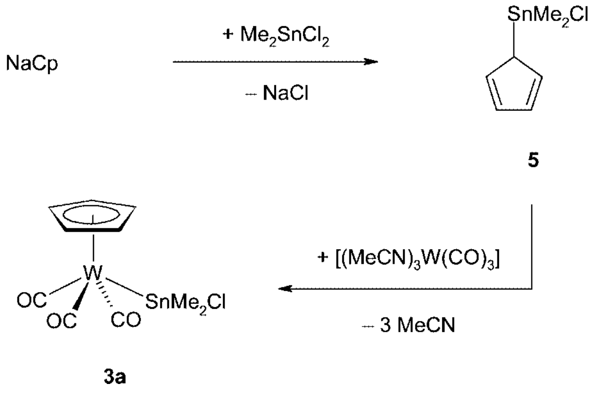
Figure 6. Molecular structure of [(η^5-C_5Me_5)$(OC)_3W(SnMe_2Cl)$] (**3d**) in the solid state with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: W1–C3 1.976(4), W1–C1 1.977(3), W1–C2 1.982(4), W1–Sn1 2.7866(3), Sn1–C5 2.146(4), Sn1–C4 2.157(4), Sn1–Cl1 2.4215(10), C5–Sn1–C4 107.61(16), C5–Sn1–Cl1 99.75(12), C4–Sn1–Cl1 100.48(13), Cl1–Sn1–W1 108.97(3), C5–Sn1–W1 118.56(11), C4–Sn1–W1 118.31(12).

apical position ("four-legged piano stool" complex). In the case of **3c**,**d**, the five methyl groups are slightly bent out of the plane of the cyclopentadienyl ligand [mean 6.7° (**3c**) and 6.5° (**3d**)]. All these structural parameters lie in the range reported in literature for comparable compounds.[7,11,12] The base-forming angles lie all between 70 and 75°. The determined W–Ge distance amounts to 2.6272(4) Å, which is about 0.1 Å shorter than the values in the PMe_3-substituted trichlorogermanium complexes *cis*- and *trans*-[(η^5-C_5Me_5)$(Me_3P)(OC)_2W(GeCl_3)$] [2.559(5) (*cis*) and 2.5159(14) Å (*trans*)].[12a] This finding supports the observation that increased electron density at a central transition metal atom – evoked by the introduction of a phosphane ligand – strengthens the transition metal–element bond. The determined Ge–C bond lengths are 1.948(4) (Ge1–C31) and 2.008(3) (Ge1–C32) Å. For the germanium–chlorine bond a length of 2.2428(10) Å is found, which is only slightly longer than the corresponding bonds in the Cl_3Ge derivative [mean 2.206 (*cis*) and 2.199 Å (*trans*)].[12a] The tetrahedral coordination geometry of the germanium atom is strongly distorted indicated by angles in the range from 101.62(13) (C31–Ge1–Cl1) to 117.55(13)° (C31–Ge1–W1). Only Cl1–Ge1–W1 shows an almost ideal tetrahedron angle [109.74(3)°].

The determined W–Sn bond lengths are 2.7959(5) (**3b**) and 2.7866(3) Å (**3d**), thus being in the range of tin-substituted tricarbonyl tungsten complexes.[7,11] The Sn–C bonds of **3b** are slightly longer [2.168(8) (Sn1–C21) and 2.156(7) Å (Sn1–C31)] than those of **3d** [2.146(4) (Sn1–C5) and 2.157(4) Å (Sn1–C4)]. For the tin–chlorine bonds, distances of 2.4203(18) (**3b**) and 2.4215(10) Å (**3d**) are found, which is very similar to those in tungsten complexes with sixfold-coordinated tin atoms, e.g. 2.404(1) and 2.459(2) Å in the tungsten complex in Figure 1.[7] As expected, the tetrahedral coordination geometry of the tin atoms of **3b**,**d** is significantly distorted almost to the same extent as already mentioned for the Ge analogue and thus, angles between 99.1(2) (C31–Sn1–Cl1) and 120.56(19) (C31–Sn1–W1) (**3b**) or rather 99.75(12) (C5–Sn1–Cl1) and 118.56(11) Å (C5–Sn1–W1) (**3d**) were found. Interestingly, in both compounds the W–Sn–C angles are widened whereas the C–Sn–Cl angles are more acute in comparison to the ideal tetrahedron angle. This characteristic could also be observed in the Ge compound and was found in diorganostannyl molybdenum complexes, too.[11,13] In **3b**, there is an interaction of one carbonyl oxygen (O1) with a hydrogen atom of the second molecule of the same cell (H51A) which can be classified as moderate hydrogen bond according to the value of 2.508 Å (O1···H51A).

Alternative syntheses of ***3a*** *and chlorination reactions.* Even though the following compounds were already mentioned in literature, not all of them have been isolated and their characterisation has not been carried out to full extent. For example, up to now, it was only possible to obtain the di-chlorinated complex **7** together with **3a** as an inseparable mixture by treatment of **6** with hydrogen chloride.[4] Therefore, we developed new and convenient syntheses for these chlorostannyl compounds, isolated them and completed their characterization.

One alternative route leading to **3a** proceeds via the chlorodimethylstannyl-cyclopentadiene **5** which is literature-known,[14] but was here synthesized in a more convenient way. The alkali salt elimination of sodium cyclopentadienide and dichlorodimethylstannane yields after 18 h stirring at ambient temperature **5** according to Scheme 1. **5** is obtained as a yellow oil in 84% and can be stored at –30 °C under Ar atmosphere over a period of months. Due to the fast stannatropic shift of the $ClMe_2Sn$ group with respect to the NMR time-scale, a singlet at δ = 5.99 ppm is observed for the cyclopentadiene protons at ambient temperature. This chemical shift agrees very well with the literature data (δ = 6.02 ppm[14a]) and the signal shows the expected



Scheme 1. Alternative synthesis of **3a** via the chlorostannyl-functionalized cyclopentadiene **5** which is obtained from alkali salt elimination of sodium cyclopentadienyl and dichlorodimethyl stannane.

tin satellites with coupling constants of 29.0 and 30.0 Hz. In the ^{119}Sn NMR spectrum a singlet is observed at δ = 101.45 ppm.[14b]

In the last step, **5** is treated with [(MeCN)$_3$W(CO)$_3$] in refluxing THF over a period of 18 h, leading to **3a** in 90% yield (Scheme 1). **3a** is obtained as an analytically pure yellow solid. The reaction proceeds chemoselectively and only the chlorostannyl group shifts to the tungsten centre – no complex tungsten hydride is observed as by-product. This insertion of a coordinatively unsaturated transition-metal fragment (W) into a Sn–C bond which is accompanied by oxidation of the W centre has precedence but only for trimethylgermanium- and -tin-functionalized cyclopentadienes.[15] In contrast, in Me$_3$Si-substituted cyclopentadienes the Si–C unit tends to remain intact due to a stronger and less polar bond.[15a]

Besides, we developed not only a selective synthesis of **7**, but also a controlled, successive chlorination of the trimethylstannyl tungsten complex **6** to the trichlorostannyl derivative **8** (Scheme 2) via isolable intermediates.

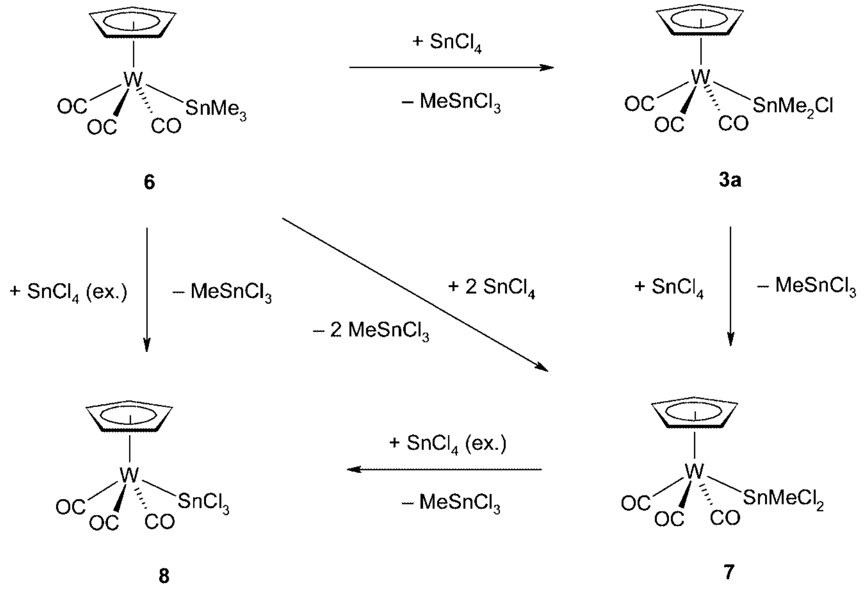
The first Me/Cl exchange is achieved by use of exactly one equivalent of SnCl$_4$ at ambient temperature, leading after two hours exclusively to **3a**. After work up, **3a** can be obtained analytically pure in 92% yield. The second chlorination is realized with a further equivalent of SnCl$_4$ at ambient temperature, too. The reaction is finished after two hours and yields **7** in 88%. The di-chlorination product **7** can also be obtained directly from **6** if an excess of SnCl$_4$ is employed. **7** is characterized by a high stability even towards concentrated hydrochloric acid. For the tin-bound methyl group a singlet at δ = 1.11 ppm is observed, showing the expected $^{117/119}$Sn satellites of 45.2 and 46.2 Hz, respectively. The ^{119}Sn signal is detected at δ = 198.9 ppm. An excess of SnCl$_4$ in refluxing chloroform gives access to the trichlorostannyl complex **8**, when the mixture is heated over a period of six days. **8** can be obtained in 60% as a yellow powder, which can be also exposed to air for a prolonged period without decomposition. The detected ^{1}H NMR chemical shift at 5.77 for the Cp is in accordance with literature (δ = 5.6 ppm) as well as the IR data.[16] The ^{119}Sn NMR resonance was detected at δ = –89.4 ppm, which is about 115 ppm shifted to higher field in comparison to the Mo analogue [(η^5-C$_5$H$_5$)(OC)$_3$Mo(SnCl$_3$)] (δ = 26 ppm).[6] Due to the fact that only IR data of **7** are published[16] (except for ^{1}H NMR of **8**,[16b]), we characterized **7** and **8** by ^{1}H, ^{13}C and ^{119}Sn NMR as well as elemental and melting point analysis. Some of these data are listed in Table 1.

Table 1. NMR spectroscopic features depending on the chlorination degree of the W-bound tin atom.[a]

	[WpSnMe$_3$] (**6**)	[WpSnMe$_2$Cl] (**3a**)	[WpSnMeCl$_2$] (**7**)	[WpSnCl$_3$] (**8**)
^{1}H(MeSn)	0.51	0.87	1.11	–
^{119}Sn	42.3[b]	227.0	198.9[c]	–89.4
$^2J_{\mathrm{HCSn}}$	48.4, 46.4	47.3, 45.3	46.2, 45.2	–

[a] NMR spectroscopic data in ppm (in C$_6$D$_6$, except **8**: CDCl$_3$), coupling constants in Hz. For a more detailed discussion of the IR data and bonding energies see ref.[16a]. Wp ≡ (η^5-C$_5$H$_5$)(OC)$_3$W. [b] $^1J_{\mathrm{SnW}}$ = 150.5 Hz. [c] $^1J_{\mathrm{SnW}}$ = 596.8 Hz.

For better comparison of the compounds of **6**, **3a**, **7** and **8**, we determined the ^{1}H and ^{119}Sn NMR chemical shifts and the coupling constants $^2J_{\mathrm{HCSn}}$ of the Sn-attached methyl groups (Table 1). The trends of the ^{1}H NMR chemical shifts in the row [(η^5-C$_5$H$_5$)(OC)$_3$W(SnMe$_3$)] (**6**), [(η^5-C$_5$H$_5$)(OC)$_3$W(SnMe$_2$Cl)] (**3a**), [(η^5-C$_5$H$_5$)(OC)$_3$W(SnMeCl$_2$)] (**7**) and [(η^5-C$_5$H$_5$)(OC)$_3$W(SnCl$_3$)] (**8**) are very regular and behave as expected – the more electronegative chlorine atoms are bound at the tin atom the higher is the detected chemical shift value. Parallel, the $^2J_{\mathrm{HCSn}}$ coupling constants (MeSn) decrease continuously. In contrast to



Scheme 2. Stepwise chlorination of **6** via mono- and dichlorinated stannyl tungsten complexes **3a** and **7** leading to the trichlorostannyl complex **8** and direct synthesis of **7** and **8**.

these findings, the ^{119}Sn NMR shifts display no regular trend, and after the first Me/Cl substitution a maximum shift value of 227.0 ppm is observed. Further chlorine substitution leads to a decrease of the ^{119}Sn chemical shift up to –89.4 ppm for **8**. Apparently, two effects are responsible for this feature namely the electronegative character of chlorine as well as the π-back bonding of the *p*-lone pairs of the chlorine. The latter effect increases with a growing number of chlorine atoms due to the fact that the Lewis acid character of the tin atom is increasing at the same time.

X-ray diffraction analysis. The molecular structure of [(η^5-C_5H_5)$(OC)_3W(SnCl_3)$] (**8**) has been confirmed by X-ray diffraction study and is depicted in Figure 7. Selected bond lengths and angles are listed below the Figure and crystal data and refinement parameters in Table 2 in the experimental section. Suitable crystals are obtained upon slow evaporation of saturated $CDCl_3$ solution at room temperature. **8** crystallizes in a triclinic crystal system with space group $P\bar{1}$.

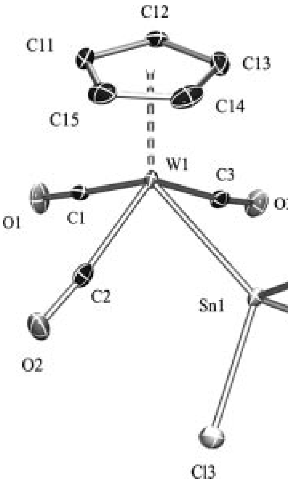


Figure 7. Molecular structure of [(η^5-C_5H_5)$(OC)_3W(SnCl_3)$] (**8**) in the solid state with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: W1–C1 1.998(5), W1–C2 2.011(5), W1–C3 2.001(4), W1–Sn1 2.7244(3), Sn1–Cl1 2.3450(11), Sn1–Cl3 2.3616(11), Sn1–Cl2 2.3681(11), C1–W1–Sn1 126.42(12), C3–W1–Sn1 75.08(12), C2–W1–Sn1 76.17(12), Cl1–Sn1–Cl3 96.41(4), Cl1–Sn1–Cl2 98.94(4), Cl3–Sn1–Cl2 99.45(4), Cl1–Sn1–W1 121.81(3), Cl3–Sn1–W1 119.57(3), Cl2–Sn1–W1 116.14(3).

8 shows the typical piano-stool arrangement as expected for a half-sandwich compound. The geometrical features of **8** in the solid state are very similar to that found for the Mo analogue [(η^5-C_5H_5)$(OC)_3Mo(SnCl_3)$]:[6] the tetrahedral coordination geometry of the tin atom is strongly distorted and resemble a trigonal pyramid also found for the Mo compound. All Cl–Sn–Cl angles are acute (mean: 98.27°) whereas the Cl–Sn–W angles are more obtuse showing values between 116.14(3) (Cl2–Sn1–W1) and 121.81(3)° (Cl1–Sn1–W1). Not only the Sn–Cl distances (mean: 2.358 Å) are similar to those of the Mo complex, but also the transition-metal–tin distances, which amount to 2.7244(3) Å in the tungsten and 2.7223(4) in the molybdenum case. Additionally, we found a short distance of 2.925 Å between the chlorine atom Cl2 and the proton bound to C14, which can be classified as a weak, intramolecular hydrogen bond interaction.

It is known that organotin halides tend to build up associated arrangements with formation of σ-donor bridges in the solid state. It is interesting that **8** shows not such a intermolecular association behaviour. Presumably, this finding is caused by the transition-metal fragment but it remains open whether steric or electronic effects are responsible.

Conclusions

We were able to show that the alkali salt elimination has to be regarded as a straightforward route to synthesize chlorogermyl and chlorostannyl tungsten complexes and allows the variation of the organo groups being attached to the element as well as the transition-metal fragment itself. The chlorination degree of the transition-metal bound tin atom can be varied successively and selectively by use of $SnCl_4$. Thus, the work reported in this paper opens the door to a range of chlorogermyl and chlorostannyl tungsten complexes which enables further investigations of the chemical behaviour, e.g. with respect to alkali metals, organolithium compounds, hydroxides, sulfides, Lewis bases, amides or alkoxides.

Experimental Section

All manipulations were conducted either under an atmosphere of dry argon or in vacuo using standard Schlenk line or glovebox techniques. Solvents (benzene and pentane) were purified by distillation from appropriate drying agents (sodium and sodium wire) under dry argon, immediately prior to use. C_6D_6 was degassed by three freeze-pump-thaw cycles and stored over molecular sieves. IR spectra were recorded as CH_2Cl_2 solutions between KBr plates on a Bruker Vector 22 FT-IR spectrometer. ^{1}H, ^{31}P{^{1}H} and ^{119}Sn{^{1}H} NMR spectra were acquired on a Bruker Avance 200 NMR spectrometer at 200.1, 121.5 and 111.9 or 186.5 MHz, respectively and referenced to external TMS or $SnMe_4$ (^{119}Sn). ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AMX 400 NMR spectrometer at 125.8 MHz and referenced to the solvent. Microanalyses for C, H and N were performed by Mrs. L. Michels (University of Würzburg) on a Vario Micro instrument (Elementar Analysensysteme). Starting materials were prepared according to literature procedures: Li[W(η^5-C_5H_5)$(CO)_3$][17] (**1a**), [(η^5-C_5Me_5)$(OC)_3WCl$],[18] [(η^5-C_5H_5)$(OC)_3WSnMe_3$][1b] (**6**) and [$(MeCN)_3W(CO)_3$].[19] The reagents Me_2GeCl_2 (**2a**), Me_2SnCl_2 (**2b**), $SnCl_4$ and Bu_2SnCl_2 (**2c**) were purchased from commercial sources and not further purified prior use.

Preparation of Starting Material

1. Li[W(η^5-C_5Me_5)$(CO)_3$] (1b)

Lithium Tricarbonyl(pentamethylcyclopentadienyl)tungstate

A solution of 1.80 g (4.45 mmol) of (η^5-C_5Me_5)$(OC)_3WH$ in 15 mL Et_2O was treated with 2.09 mL (5.35 mmol) of BuLi (2.5 M) at 0 °C. The color of the solution changed from yellow to brown and after 15 min **1b** started to precipitate. The mixture was stirred for 1.5 h at ambient temperature. After reaction the precipitate consisting of

1b was filtered off, washed twice with 10 mL of hexane and finally dried in vacuo. Yield 1.64 g (4.01 mmol; 90%). Pale brown, pyrophoric powder. Elemental analysis was not carried out due to the pyrophoric behaviour of **1b**.

2. [(η^5-C_5Me_5)(Ph_3P)$(OC)_2$WCl] (9)

Dicarbonyl(chloro)(η^5-pentamethylcyclopentadienyl)(triphenylphosphanyl)tungsten(II)

A solution of 3.20 g (7.30 mmol) of [(η^5-C_5Me_5)$(OC)_3$WCl] and 1.91 g (7.30 mmol) PPh_3 in 10 mL benzene in was irradiated with UV light for 5 d. The solvent was removed in vacuo, the crude residue washed with 20 mL hexane and the product dried in vacuo. Yield 4.11 g (6.11 mmol, 84%). Orange powder. ^{1}H NMR (300.4 MHz, C_6D_6): δ = 7.62–7.52 (m, 6 H, Ph), 7.08–6.98 (m, 9 H, Ph), 1.65 (s, 15 H, C_5Me_5) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ = 250.75 (d, $^2J_{CWP}$ = 18.5 Hz, *cis*-CO), 237.99 (d, $^2J_{CWP}$ = 7.3 Hz, *trans*-CO), 135.85 (d, $^1J_{CP}$ = 47.4 Hz, *ipso*-C_6H_5), 132.28 (d, $^3J_{CCCP}$ = 10.1 Hz, *meta*-C_6H_5), 130.95 (d, $^4J_{CCCCP}$ = 2.4 Hz, *para*-C_6H_5), 128.69 (d, $^2J_{CCP}$ = 9.0 Hz, *ortho*-C_6H_5), 112.80 (d, $^2J_{CWP}$ = 1.2 Hz, H_3CC_5), 11.00 (s, H_3CC_5) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ = 26.57 (s, $^1J_{PW}$ = 274.6 Hz) ppm. IR (Et_2O): ṽ(C=O) = 1947 (vs), 1870 (m) cm^{-1}. $C_{30}H_{30}ClO_2PW$ (672.82): calcd. C 53.55, H 4.49; found C 53.68, H 4.66.

3. Na[W(η^5-C_5Me_5)$(CO)_2$(PPh_3)] (1c)

Sodium Dicarbonyl(η^5-pentamethylcyclopentadienyl)(triphenylphosphanyl)tungstate

Na amalgam was prepared by dissolving 0.28 g (12.22 mmol) sodium in 50 g mercury. 35 mL THF were added and then 4.11 g (6.10 mmol) of [(η^5-C_5Me_5)(Ph_3P)$(OC)_2$WCl] (**9**). The reaction mixture was stirred for 18 h at ambient temperature. The suspension was separated from the sodium amalgam and the solvents evaporated to dryness. The crude solid was washed with three 10 mL portions of hexane and dried in vacuo. Yield 3.75 g (5.67 mmol, 93%). Yellow-green, pyrophoric powder. ^{1}H NMR (300.4 MHz, [D$_8$]THF): δ = 7.84–7.82 (m, 6 H, Ph), 7.13–7.02 (m, 9 H, Ph), 1.89 (s, $^4J_{HCCWP}$ = 29.4 Hz, 5 H, Cp) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ = 31.44 (s, $^1J_{PW}$ = 278.9 Hz) ppm. IR (THF): ṽ(C=O) = 1780 (s), 1729 (s) cm^{-1}. $C_{30}H_{30}NaO_2PW$ (660.36). Elemental analysis was not carried out due to the pyrophoric behaviour of **1c**.

Preparation of Germyl and Stannyl Tungsten Complexes

1. [(η^5-C_5H_5)$(OC)_3$W($SnMe_2Cl$)] (3a)

Tricarbonyl(chlorodimethylstannyl)(η^5-cyclopentadienyl)tungsten(II)

To a suspension of 635 mg (1.87 mmol) of Li[W(C_5H_5)$(CO)_3$] (**1a**) in 10 mL diethyl ether were added 411 mg (1.87 mmol) of Me_2SnCl_2 and the mixture was stirred at ambient temperature overnight. The solvent was removed in vacuo and the residue was extracted with of hexane (3 × 10 mL). The combined extracts were filtered through celite and the filtrate was evaporated to dryness. Yield 793 mg (1.53 mol, 72%). Dark yellow powder. M.p. 91 °C. ^{1}H NMR (300 MHz, C_6D_6): δ = 4.52 (s, 5 H, Cp), 0.87 (s, $^2J_{HCSn}$ = 47.3, 45.3 Hz, 6 H, $SnMe_2$) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ = 89.04 (s, Cp), 2.99 (s, $SnMe_2$) ppm. ^{119}Sn{^{1}H} NMR (111.9 MHz, C_6D_6): δ = 227 (s) ppm. IR (hexane): ṽ(C=O) = 2010 (m), 1940 (m), 1911 (m) cm^{-1}. $C_{10}H_{11}ClO_3SnW$ (517.20): calcd. C 23.22, H 2.14; found C 23.44, H 2.24.

2. [(η^5-C_5H_5)$(OC)_3$W($SnBu_2Cl$)] (3b)

(Dibutylchlorostannyl)(tricarbonyl)(η^5-cyclopentadienyl)tungsten(II)

Similar to paragraph **1.** above, from 570 mg (1.68 mmol) of Li[W(C_5H_5)$(CO)_3$] (**1a**) and 380 mg (1.25 mmol) of Bu_2SnCl_2 in 10 mL diethyl ether. The mixture was stirred at ambient temperature overnight. The ether was removed under reduced pressure and the oily residue was extracted with pentane (3 × 10 mL). The combined extracts were filtered through celite and the filtrate was evaporated to dryness. The sticky residue was washed with ice-cold pentane (3 × 2 mL) and was dried in vacuo. Yield 526 mg (0.88 mol, 70%). Dark yellow powder. M.p. 74 °C. ^{1}H NMR (300 MHz, C_6D_6): δ = 4.82 (s, 5 H, Cp), 1.91–1.73 (m, 8 H, CH_2-CH_2), 1.55–1.52 (m, 4 H, $SnCH_2$), 1.05 (t, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ = 88.43 (s, Cp), 31.64 (s, CH_2), 27.40 (s, CH_2), 19.24 (s, CH_2), 13.69 (s, CH_3) ppm. ^{119}Sn{^{1}H} NMR (111.9 MHz, C_6D_6): δ = 26.7 (s, $^1J_{SnW}$ = 162.8 Hz) ppm. IR (hexane): ṽ(C=O) = 1999 (m), 1981 (m) cm^{-1}. $C_{16}H_{23}ClO_3SnW$ (601.35): calcd. C 31.96, H 3.86; found C 32.29, H 3.99.

3. [(η^5-C_5Me_5)$(OC)_3$W($GeMe_2Cl$)] (3c)

Tricarbonyl(chlorodimethylgermyl)(η^5-pentamethylcyclopentadienyl)tungsten(II)

0.52 g (1.27 mmol) of Li[W(η^5-C_5Me_5)$(CO)_3$] (**1b**) were suspended in 10 mL Et_2O and treated with 0.18 mL (1.27 mmol, 0.22 g) of Me_2GeCl_2. The reaction mixture was stirred for 22 h at ambient temperature. After reaction LiCl was filtered off by use of a celite pad. The filtrate was evaporated to dryness giving a dark brown residue which was washed with 3 mL hexane at –40 °C and dried in vacuo. Yield 0.56 g (81%). Brown solid, m.p. 62 °C. ^{1}H NMR (200.1 MHz, C_6D_6): δ = 1.71 [s, 15 H, $C_5(CH_3)_5$], 1.17 [s, 6 H, Ge$(CH_3)_2$] ppm. ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ = 217.95 (s, CO-*trans*), 202.29 (s, CO-*cis*), 102.52 (s, C_5Me_5), 28.67 [s, Ge$(CH_3)_2$], 9.00 [s, $C_5(CH_3)_5$] ppm. IR (hexane): ṽ(C=O) = 2003 (s), 1931 (s), 1907 (s) cm^{-1}. $C_{15}H_{21}ClGeO_3W$ (541.23): calcd. C 33.29, H 3.91; found C 32.62, H 3.81.

4. [(η^5-C_5Me_5)$(OC)_3$W($SnMe_2Cl$)] (3d)

Tricarbonyl(chlorodimethylstannyl)(η^5-pentamethylcyclopentadienyl)tungsten(II)

To a suspension of 0.66 g (1.16) of Li[W(η^5-C_5Me_5)$(OC)_3$] (**1b**) in 20 mL Et_2O were added 0.36 g (1.64 mmol) of Me_2SnCl_2 and the reaction mixture stirred for 17 h at ambient temperature. After reaction LiCl was filtered off over celite and the filtrate evaporated to dryness. The crude brown product was washed with 5 mL of hexane at –40 °C and dried in vacuo. Yield 0.80 g (85%). Ochre solid, m.p. 122 °C. ^{1}H NMR (200.1 MHz, C_6D_6): δ = 1.70 (s, 15 H, C_5Me_5), 0.91 [s, $^2J_{HCSn}$ = 42.5 and 44.4 Hz, 6 H, $(H_3C)_2Sn$] ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 220.89 (s, CO-*trans*), 217.87 (s, CO-*cis*), 103.70 (s, C_5Me_5), 10.71 [s, $C_5(CH_3)_5$], 2.48 [s, $^1J_{CSn}$ = 245.5 and 259.9 Hz, Sn$(CH_3)_2$] ppm. ^{119}Sn NMR (186.5 MHz, C_6D_6): δ = 233.04 [s, $^1J_{WSn}$ = 347.0 Hz] ppm. IR (hexane): ṽ(C=O) = 1901 (s), 1927 (s), 1997 (s) cm^{-1}. $C_{15}H_{21}ClO_3SnW$ (587.33): calcd. C 30.67, H 3.60; found C 30.34, H 3.67.

5. [(η^5-C_5Me_5)$(OC)_2$(Ph_3P)W($SnMe_2Cl$)] (3e) and {[(η^5-C_5Me_5)-$(OC)_2$(Ph_3P)W]$_2$($SnMe_2$)} (4)

Dicarbonyl(trimethylstannyl)(η^5-pentamethylcyclopentadienyl)(triphenylphosphanyl)tungsten(II)

600 mg (0.83 mmol) of Na[W(η^5-C_5Me_5)$(OC)_2$(PPh_3)] (**1c**) were suspended in 20 mL Et_2O and treated with 183 mg (0.83 mmol) of Me_2SnCl_2. The reaction mixture was stirred for 16 h at ambient temperature and NaCl filtered through by use of a celite pad. The filtrate was evaporated to dryness and the residue consisting of **3e** and **4** extracted with 25 mL of hexane. **3e** dissolves readily in hexane whereas **4** remains as an yellow solid which was dried in vacuo. The combined hexane extracts were concentrated and crystallized at –30 °C. The hexane phase was separated and the solid dried in

vacuo. **3e**: Yield 340 mg (0.42 mmol, 51%). Yellow solid, m.p. 87 °C. ^{1}H NMR (200.13 MHz, C_6D_6): δ = 7.68–7.43 (m, 6 H, Ph), 7.09–6.93 (m, 9 H, Ph), 1.68 (s, 15 H, Me_5C_5), 1.05 [s, $^2J_{HCSn}$ = 40.2 and 41.8 Hz, 6 H, MeSn] ppm. ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ = 230.06 [d, $^2J_{CP}$ = 132.3 Hz, CO], 134.54 [d, $^1J_{CP}$ = 46.6 Hz, *ipso*-C_6H_5], 134.29 [d, $^1J_{CP}$ = 10.0 Hz, *meta*-C_6H_5], 130.53 [d, $^3J_{CCCP}$ = 2.4 Hz, *para*-C_6H_5], 128.56 [d, $^2J_{CCP}$ = 9.9 Hz, *ortho*-C_6H_5], 101.16 [s, $^1J_{CW}$ = 5.4 Hz, C_5Me_5], 11.25 (s, C_5Me_5), 2.88 (s, CH_3Sn) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ = 38.61 [s, $^1J_{PW}$ = 293.6, $^2J_{PWSn}$ = 128.8 und 123.9 Hz] ppm. ^{119}Sn{^{1}H} NMR (300.13 MHz, C_6D_6): δ = 233.80 [d, $^2J_{SnWP}$ = 132.1 Hz] ppm. IR (Et_2O): ṽ(C=O) = 1904 (vs), 1835 (vs) cm^{-1}. $C_{32}H_{36}ClO_2PSnW$ (821.60): calcd. C 46.78, H 4.42; found C 46.67, H 4.25.

4: Yield 138 mg (0.11 mmol, 13%). Yellow solid, m.p. 123 °C. ^{1}H NMR (300.4 MHz, C_6D_6): δ = 7.68–7.43 (m, 6 H, Ph), 7.09–6.93 (m, 9 H, Ph), 1.78 (s, 30 H, Me_5C_5), 0.91 [d, $^4J_{HCSnWP}$ = 1.2, $^2J_{HCSn}$ = 44.0 and 48.0 Hz, 6 H, H_3CSn] ppm. ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ = 44.50 [s, $^1J_{PW}$ = 267.3, $^2J_{PWSn}$ = 130.8 und 125.4 Hz] ppm. IR (Et_2O): ṽ(C=O) = 1901 (vs), 1832 (vs) cm^{-1}. $C_{52}H_{46}O_4P_2SnW_2$ (1283.26): calcd. C 48.67, H 3.61; found C 48.47, H 4.05.

6. $C_5H_5SnMe_2Cl$ (5)

(Chlorodimethylstannyl)cyclopentadiene

A suspension of 418 mg (4.75 mmol) of NaCp and 15 mL Et_2O was treated with 1.04 g (4.75 mmol) of Me_2SnCl_2. The mixture was stirred for 18 h at ambient temperature and NaCl was removed by filtration through a celite pad. The filtrate was evaporated under reduced pressure (70 mbar) at ambient temperature. Yield 1.00 g (4.01 mmol, 84%). Yellow oil. ^{1}H NMR (200.1 MHz, C_6D_6): δ = 5.99 (s, $^3J_{HCCSn}$ = 30.0 and 29.0 Hz, 5 H, C_5H_5), 0.03 [s, $^2J_{HCSn}$ = 59.2 and 56.8 Hz, 6 H, $(H_3C)_2Sn$] ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 114.91 (s, $^1J_{CSn}$ = 96.8 Hz, C_5H_5Sn), –2.96 [s, $(H_3C)_2Sn$] ppm. ^{119}Sn NMR (186.5 MHz, C_6D_6): δ = 101.45 (s) ppm. $C_7H_{11}ClSn$ (249.32): calcd. C 33.72, H 4.45; found C 33.34, H 4.67.

7. [(η^5-C_5H_5)(OC)$_3$W(SnMe$_2$Cl)] (3a) by Reaction of 5 with [(MeCN)$_3$W(CO)$_3$]

A suspension of 450 mg (1.80 mmol) of $C_5H_5SnMe_2Cl$ (**5**), 704 mg (1.80 mmol) of [(MeCN)$_3$W(CO)$_3$] and 10 mL THF was refluxed over the period of 18 h. After cooling to room temperature, all volatiles were removed in vacuo and the residue was extracted with hexane (3 × 10 mL). The hexane extracts were combined and filtered through a celite pad. The filtrate was concentrated and stored at –70 °C over the period of one week. The hexane phase was removed and the solid dried in vacuo. Yield 837 mg (1.62 mmol, 90%). Yellow solid.

8. [(η^5-C_5H_5)(OC)$_3$W(SnMe$_2$Cl)] (3a) by Reaction of 6 with $SnCl_4$

A solution of 270 mg (0.54 mmol) of [(η^5-C_5H_5)(OC)$_3$W(SnMe$_3$)] (**6**) in 5 mL benzene was treated with 142 mg (0.54 mmol) of $SnCl_4$ and the mixture was stirred at ambient temperature for 2 h. All volatiles were removed in vacuo and the residue was extracted with hexane (3 × 19 mL). The combined extracts were filtered through celite and the filtrate was evaporated to dryness. Yield 258 mg (0.50 mmol, 92%). Dark yellow powder.

9. [(η^5-C_5H_5)(OC)$_3$W(SnMeCl$_2$)] (7) by Reaction of 3a with $SnCl_4$

Tricarbonyl(dichloromethylstannyl)(η^5-cyclopentadienyl)tungsten(II)

A solution of 258 mg (0.50 mmol) of [(η^5-C_5H_5)(OC)$_3$W-(SnMe$_2$Cl)] (**3a**) in 5 mL diethyl ether was treated slowly with 131 mg (0.50 mmol) of $SnCl_4$ at 0 °C and the mixture was stirred at ambient temperature for 2 h. All volatiles were removed in vacuo and the residue was extracted with Et_2O (2 × 10 mL). The combined extracts were filtered through celite and the filtrate was evaporated to dryness. Yield 237 mg (0.44 mmol, 88%). Yellow powder. M.p. 189 °C. ^{1}H NMR (300 MHz, C_6D_6): δ = 4.49 (s, 5 H, Cp), 1.11 (s, $^2J_{HCSn}$ = 46.2, 45.2 Hz, 3 H, SnMe$_2$) ppm. ^{13}C{^{1}H} NMR

Table 2. Crystal data and refinement parameters for the compounds **3b**–**d** and **8**.

Compound	**3b**	**3c**	**3d**	**8**
Empirical formula	$C_{16}H_{23}ClO_3SnW$	$C_{15}H_{21}ClGeO_3W$	$C_{15}H_{21}ClO_3SnW$	$C_8H_5Cl_3O_3SnW$
Formula weight (g mol^{-1})	601.33	541.21	587.31	558.01
Temperature [K]	100(2)	193(2)	173(2)	97(2)
Radiation, λ [Å]	0.71073 (Mo-K_α)			
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$P\bar{1}$
Unit cell dimensions				
a [Å]	7.8200(6)	8.2325(5)	30.036(3)	7.7851(3)
b [Å]	11.4910(9)	25.4316(15)	8.3148(7)	8.2946(3)
c [Å]	21.0814(16)	9.4108(6)	17.7603(15)	11.1925(4)
α [°]	79.768(3)	90.00	90.00	93.7950(10)
β [°]	89.533(3)	111.8140(10)	122.8430(10)	108.7020(10)
γ [°]	89.927(3)	90.00	90.00	108.2510(10)
Volume [Å^3]	1864.2(2)	1829.21(19)	3726.6(5)	638.90(4)
Z	4	4	8	2
Calculated density (g cm^{-3})	2.143	1.965	2.094	2.901
Absorbtion coefficient [mm^{-1}]	7.657	8.078	7.658	11.563
F(000)	1136	1032	2208	504
Theta range for collection	0.98 to 31.95°	2.46 to 26.08°	2.30 to 26.39°	1.95 to 26.08°
Reflections collected	88054	3624	24318	15287
Independent reflections	11465	3481	6061	2513
Refinement method	Full-matrix last-squares on F^2			
Data/parameters	11465 –397/6	3624/190	3826/190	2513/145
Goodness-of-fit on F^2	1.138	1.170	1.096	1.088
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0497, wR_2 = 0.1287	R_1 = 0.0205, wR_2 = 0.0509	R_1 = 0.0198, wR_2 = 0.0462	R_1 = 0.0234, wR_2 = 0.0605
R Indices (all data)	R_1 = 0.0532, wR_2 = 0.1342	R_1 = 0.0217, wR_2 = 0.0514	R_1 = 0.0215, wR_2 = 0.0469	R_1 = 0.0238, wR_2 = 0.0608

(75.5 MHz, C_6D_6): δ = 215.16 (s, *trans*-CO), 211.89 (s, $^1J_{CW}$ = 144.6 Hz, *cis*-CO), 89.91 (s, $^1J_{CW}$ = 4.9 Hz, Cp), 11.46 (s, $^1J_{CSn}$ = 7.7 Hz, MeSn) ppm. $^{119}Sn\{^1H\}$ NMR (111.9 MHz, C_6D_6): δ = 198.88 (s, $^1J_{WSn}$ = 596.8 Hz) ppm. $C_9H_8Cl_2O_3SnW$ (537.61): calcd. C 20.11, H 1.50; found C 20.03, H 1.80.

10. [(η^5-C_5H_5)$(OC)_3$W($SnMeCl_2$)] (7) by Reaction of 6 with 2 Equiv. of $SnCl_4$

Analogously to paragraph 9., from 320 mg (0.64 mmol) of [(η^5-C_5H_5)$(OC)_3$W($SnMe_3$)] (**6**) and 335 mg (1.28 mmol) of $SnCl_4$ in 10 mL diethyl ether over the period of 4 h. Yield 242 mg (0.45 mol, 90%). Yellow powder.

11. [(η^5-C_5H_5)$(OC)_3$W($SnCl_3$)] (8) by Reaction of 7 with $SnCl_4$ (ex.)

Tricarbonyl(trichlorostannyl)(η^5-cyclopentadienyl)tungsten(II)

To a suspension of 266 mg (0.49 mmol) of [(η^5-C_5H_5)$(OC)_3$W($SnMeCl_2$)] (**7**) in 10 mL chloroform were added 1.28 mg (4.90 mmol) of $SnCl_4$ and the mixture was heated and stirred under reflux over the period of 6 d. All insoluble material was filtered off and the solvent and unreacted $SnCl_4$ were removed in vacuo. The residue was washed with hexane (3 × 10 mL) and the solvents evaporated to dryness. Yield 164 mg (0.29 mol, 60%). Yellow powder. M.p. 91 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.77 (s, $^3J_{HCWSn}$ = 3.4 Hz, 5 H, Cp) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 89.17 (s, Cp) ppm. $^{119}Sn\{^1H\}$ NMR (111.9 MHz, $CDCl_3$): δ = –89.4 (s) ppm. $C_8H_5Cl_3O_3SnW$ (558.03): calcd. C 17.22, H 0.90; found C 17.44, H 1.24.

12. [(η^5-C_5H_5)$(OC)_3$W($SnCl_3$)] (8) by Reaction of 6 with $SnCl_4$ (ex.)

Tricarbonyl(trichlorostannyl)(η^5-cyclopentadienyl)tungsten(II)

Analogously to paragraph 11., from 326 mg (0.60 mmol) of [(η^5-C_5H_5)$(OC)_3$W($SnMe_3$)] (**6**) and 1.28 mg (4.90 mmol) of $SnCl_4$ in 15 mL chloroform over the period of 6 d. Yield 148 mg (0.26 mol, 55%). Yellow powder.

Crystal Structure Determination: The crystal data of **3b**–**d** and **8** (Table 2) were collected with a Bruker APEX2 diffractometer with a CCD area detector and multi-layer mirror monochromated Mo-K_α radiation. The structures were solved by direct methods, refined with the Shelx software package (G. Sheldrick, University of Göttingen, 1997) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized position and were included in structure factor calculations.

CCDC-644418 (for **3b**), -636078 (for **3c**), -636079 (for **3d**) and -640077 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We thank Deutsche Forschungsgemeinschaft (DFG) and Fonds der Chemischen Industrie (FCI) for financial support.

---

[1] a) D. J. Cardin, S. A. Keppie, M. F. Lappert, *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 365; b) H. R. H. Patil, W. A. G. Graham, *Inorg. Chem.* **1966**, *5*, 1401; c) F. Bonati, G. Wilkinson, *J. Chem. Soc.* **1964**, 179.

[2] M. S. Holt, W. L. Wilson, J. H. Nelson, *Chem. Rev.* **1989**, *89*, 11.

[3] a) T. Szymanska-Buzar, T. Gtowiak, *Polyhedron* **1998**, *17*, 3419; b) L. Benczene, G. Szalai, T. L. Overton, *Inorg. Chim. Acta* **1997**, *254*, 5; c) T. Szymanska-Buzar, T. Gtowiak, *J. Organomet. Chem.* **1995**, *489*, 207; d) P. K. Baker, *Adv. Organomet. Chem.* **1996**, *40*, 45.

[4] R. E. J. Bichler, H. C. Clark Hunter, A. T. Rake, *J. Organomet. Chem.* **1974**, *69*, 367.

[5] a) J. Cervantes, St. P. Vincenti, R. N. Kapoor, K. H. Pannell, *Organometallics* **1989**, *8*, 744; b) W. K. Dean, W. A. G. Graham, *Inorg. Chem.* **1977**, *16*, 1061.

[6] J. L. Neto, G. M. Lima, A. O. Porto, J. D. Ardisson, A. C. Doriguetto, J. Ellena, *J. Mol. Struct.* **2006**, *782*, 110.

[7] L.-F. Tang, X.-M. Zhao, Z.-H. Zou, H.-B. Song, Y.-P. Zhai, *J. Organomet. Chem.* **2005**, *690*, 4142.

[8] For reviews seea) H. Braunschweig, C. Kollann, D. Rais, *Angew. Chem.* **2006**, *118*, 5380; *Angew. Chem. Int. Ed.* **2006**, *45*, 5254; b) H. Braunschweig, *Adv. Organomet. Chem.* **2004**, *51*, 163; c) H. Braunschweig, M. Colling, *Eur. J. Inorg. Chem.* **2003**, 393; d) H. Braunschweig, M. Colling, *Coord. Chem. Rev.* **2001**, *223*, 1; e) H. Braunschweig, *Angew. Chem.* **1998**, *110*, 1882; *Angew. Chem. Int. Ed.* **1998**, *37*, 1786. For selected examples on the reactivity of metal bound boron halides see:; f) H. Braunschweig, K. Radacki, F. Seeler, G. R. Whittell, *Organometallics* **2006**, *25*, 4605; g) H. Braunschweig, K. Radacki, D. Rais, D. Scheschkewitz, *Angew. Chem.* **2005**, *117*, 5796; *Angew. Chem. Int. Ed.* **2005**, *44*, 5651; h) H. Braunschweig, K. Radacki, D. Rais, F. Seeler, K. Uttinger, *J. Am. Chem. Soc.* **2005**, *127*, 1386; i) H. Braunschweig, K. Radacki, D. Rais, G. R. Whittell, *Angew. Chem.* **2005**, *117*, 1217; *Angew. Chem. Int. Ed.* **2005**, *44*, 1192; j) H. Braunschweig, M. Müller, *Chem. Ber./Recueil* **1997**, *130*, 1295.

[9] a) H. Braunschweig, H. Bera, D. Götz, K. Radacki, *Z. Naturforsch., Teil B* **2006**, *61*, 29; b) H. Braunschweig, M. Koster, K. W. Klinkhammer, *Angew. Chem.* **1999**, *111*, 2368; *Angew. Chem. Int. Ed.* **1999**, *38*, 2229; c) H. Braunschweig, M. Koster, R. Wang, *Inorg. Chem.* **1999**, *38*, 415; d) H. Braunschweig, B. Ganter, M. Koster, T. Wagner, *Chem. Ber.* **1996**, *129*, 1099.

[10] T. A. George, C. D. Turnipsed, *Inorg. Chem.* **1973**, *12*, 394.

[11] L.-F. Tang, J.-F. Chai, Zh.-H. Hong, W.-L. Jia, J.-T. Wang, *Polyhedron* **2001**, *20*, 403.

[12] a) A. C. Filippou, J. G. Winter, M. Feist, G. Kociok-Köhn, I. Hinz, *Polyhedron* **1998**, *17*, 1103; b) A. C. Filippou, J. G. Winter, M. Feist, G. Kociok-Köhn, C. Troll, I. Hinz, *Organometallics* **1999**, *18*, 2649.

[13] J.-T. Wang, H.-Y. He, Y.-M. Xu, J. Sun, X.-F. Kong, *Heteroat. Chem.* **1998**, *9*, 169.

[14] a) K. D. Bos, E. J. Bulten, J. G. Noltes, *J. Organomet. Chem.* **1974**, *67*, C13; b) V. N. Torocheshnikov, A. P. Tupciauskas, Y. A. Ustynyuk, *J. Organomet. Chem.* **1974**, *81*, 351.

[15] a) S. A. Keppie, M. F. Lappert, *J. Chem. Soc. A* **1971**, 3216; b) E. W. Abel, S. A. Keppie, M. F. Lappert, *J. Organomet. Chem.* **1970**, *22*, C31; c) S. A. Keppie, M. F. Lappert, *J. Organomet. Chem.* **1969**, *19*, P5.

[16] a) H. Willemen, L. F. Wuyts, D. F. Van der Vondel, G. P. Van der Kelen, *J. Electron Spectrosc. Relat. Phenom.* **1977**, *11*, 245; b) F. Bonati, S. Cenini, R. Ugo, *J. Chem. Soc. A* **1967**, 932.

[17] W. Baumann, W. Malisch, *J. Organomet. Chem.* **1986**, *303*, C33.

[18] Th. Straub, M. Haukka, M. Brunner, A. M. P. Koskinen, T. A. Pakkanen, *J. Organomet. Chem.* **2005**, *690*, 674–677.

[19] F. Edelmann, P. Behrens, S. Behrens, U. Behrens, *J. Organomet. Chem.* **1986**, *310*, 333.

Received: March 15, 2007