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Transition Metal Stannyl Complexes. 9.[1] Reactivity of $Li[Cp_2M(SnPh_3)]$ toward Metal Halides

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Reaction of the anionic stannyl complexes $[Cp_2MSnPh_3]^-$ (M = Mo, W) with HgX_2 (X = Br, I) in THF resulted in the formation of the di- or trinuclear complexes $Cp_2M(SnPh_3)HgX$ or $[Cp_2M(SnPh_3)]_2Hg$ respectively, depending on the molar ratio of the reactants (1:1 or 2:1, respectively). $[Cp_2M(SnPh_3)]_2Hg$ was also formed by the reaction of $[Cp_2MSnPh_3]^-$ with PhHgBr. $Cp_2W(SnPh_3)HgI$ crystallizes as unbridged monomers in the orthorhombic space group *Pbcn* with $a = 1646.1(3)$ pm, $b = 1780.1(3)$ pm, $c = 1788.7(3)$ pm (W−Hg 263.4(1) pm, Hg−I 251.1(3) pm, W−Sn 276.8(2) pm; W−Hg−I 177.2(1)°, Hg−W−Sn 78.87(6)°). Reaction of $[Cp_2M\text{-}SnPh_3]^-$ with $CdCl_2$ or $ZnBr_2$ only gave the trinuclear complexes $[Cp_2M(SnPh_3)]_2M'$ (M′ = Cd, Zn), independent of the employed molar ratio.

Introduction

Despite the rich chemistry of the group VI metallocene derivatives, there are only few complexes in which the Cp_2M fragment (Cp = π-C_5H_5, M = Mo, W) is directly bonded to another metal atom. All of them were synthesized from Cp_2MH_2. The polymeric complexes $[Cp_2MZn]_n$ were prepared by reaction with $ZnEt_2$,[2] while the use of $ZnCp_2$ led to the formation of $Cp_2M(ZnCp)_2$ instead.[3] The mercury derivatives $Cp_2M(HgX)_2$ (X = Cl, OAc, SR) were obtained by reaction of Cp_2MH_2 with HgX_2.[4]

In the last few years we developed the chemistry of anionic silyl and stannyl complexes, $[L_nMER_3]^-$ (E = Si, Sn).[5] We have used these complexes, *inter alia*, to prepare heteronuclear complexes of the type $[L_n(R_3E)M]_xM'L'_m$ with unsupported metal−metal bonds.[6] Stable complexes were obtained with sterically nondemanding metal complex fragments $M'L'_m$ and rather unpolar M−M′ bonds. Stabilization of the heteronuclear complexes by bridging phosphine ligands and, thus, an extension of the preparative possibilities was achieved by Knorr et al. starting from $[(CO)_3(\eta^1\text{-dppe})FeSiR_3]^-$ or a related phosphine-substituted anionic complexes.[7]

We recently prepared $Li[Cp_2M\text{-}SnPh_3]$ (**1a**: M = Mo, **1b**: M = W) by deprotonation of $Cp_2M(H)SnPh_3$ with butyllithium.[1] While the corresponding anionic silyl complex was not accessible due to silyl migration from the metal to the Cp ring, the stannyl derivative turned out to be a valuable reagent for the preparation of $Cp_2M(X)SnPh_3$ derivatives.[8] In this paper we report reactions of **1** with transition metal halides for the syntheses of di- and trinuclear complexes containing the Cp_2M fragment with unsupported M−M′ bonds.

Results and Discussion

Reaction of **1** with HgX_2 (X = Br, I) in THF resulted in the formation of the di- or trinuclear complexes **2** or **3**, respectively, depending on the molar ratio of the reactants (1:1 or 2:1) (eq 1). With 1 equiv of $HgBr_2$ there was immediate reaction already at −78 °C, while reaction with HgI_2 only proceeded when the reaction mixture was warmed to room temperature. There was no indication for the formation of $[Cp_2\text{-}M\text{-}Hg]_n$ by Ph_3SnX elimination in any reaction. The trinuclear complexes **3** underwent the redistribution reactions with HgX_2 typical of compounds of the type $L_nM\text{-}Hg\text{-}ML_n$. Reaction of **3** with $HgBr_2$ in CH_2Cl_2 at room temperature quantitatively gave the dinuclear complexes **2a,c**.

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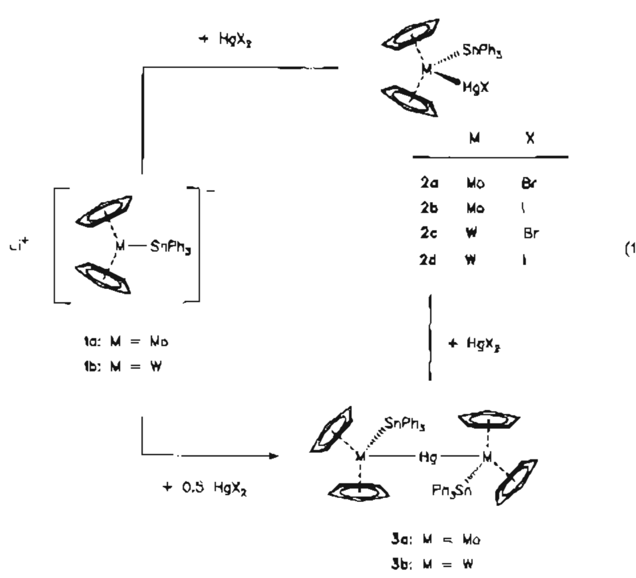
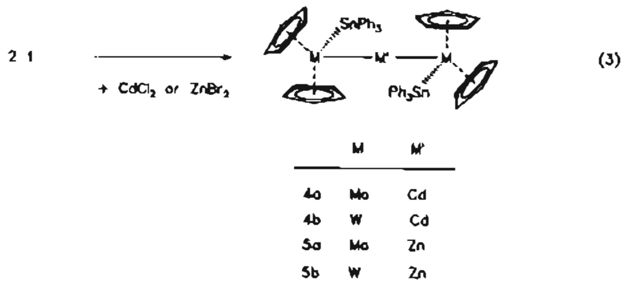


The complexes **2** and **3** were orange red to light red solids. They dissolved in coordinating or halogenated solvents, but were only sparingly soluble in aromatic hydrocarbons. While the dinuclear complexes **2** were very stable, the trinuclear complexes **3** slowly decomposed both as solids and in solution by precipitation of elemental Hg, even in an inert gas atmosphere.

When **1** was reacted with PhHgBr, the anticipated substitution product $Cp_2M(SnPh_3)HgPh$ was not isolated, but instead the trinuclear complexes **3**, and $HgPh_2$ (eq 2).

$$2\,\mathbf{1} + 2PhHgBr \rightarrow \mathbf{3} + HgPh_2 + 2LiBr \qquad (2)$$

Reaction of **1** with $^1/_2$ equiv of $CdCl_2$ or $ZnBr_2$ at low temperatures resulted in the formation of the yellow, trinuclear complexes **4** and **5** in moderate yields (eq 3). Contrary to the corresponding Hg complexes **3**, they were only moderately stable even under an inert gas atmosphere. Stability decreased in the order Hg > Cd > Zn. Due to their instability, the Zn complexes **5** were only characterized spectroscopically. Solubility of **4** and **5** was even lower than that of **3**; they were only sparingly soluble in CH_2Cl_2 and spontaneously decomposed in $CHCl_3$.



Reaction of **1** with excess $CdCl_2$ or $ZnBr_2$ did not give the dinuclear complexes $Cp_2MM'X$, but instead only the trinuclear complexes **4** or **5** and decomposition products. Partial decomposition, but no formation of the dinuclear complexes was observed when a mixture of **4** and $CdCl_2$ in CH_2Cl_2 was stirred at room temperature for 20 h.

The dinuclear complexes **2** are distinguished from their trinuclear counterparts **3**–**5** by their NMR spectroscopic data. Both the ^1H and ^{13}C resonances of the Cp ligands in **2** are shifted to lower field (^1H NMRl, 4.65–4.70 ppm; ^{13}C NMR, Mo complexes 76.8 ppm and W complexes 72.9 ppm) relative to the trinuclear complexes **3**–**5** (^1H NMR, 4.30–4.45 ppm; ^{13}C NMR, Mo complexes 70.9–74.5 ppm and W complexes 67.7–70.2 ppm). A similar trend was found for the coupling constants of the Cp protons with the $^{117/119}Sn$ isotope ($^3J_{SnMCH}$). It increases from 6.2 to 6.4 Hz in **2** to 7.8–10.0 Hz in **3**–**5**. The $^3J_{HgMCH}$ coupling was only well resolved in the molybdenum complexes **2a,c**.

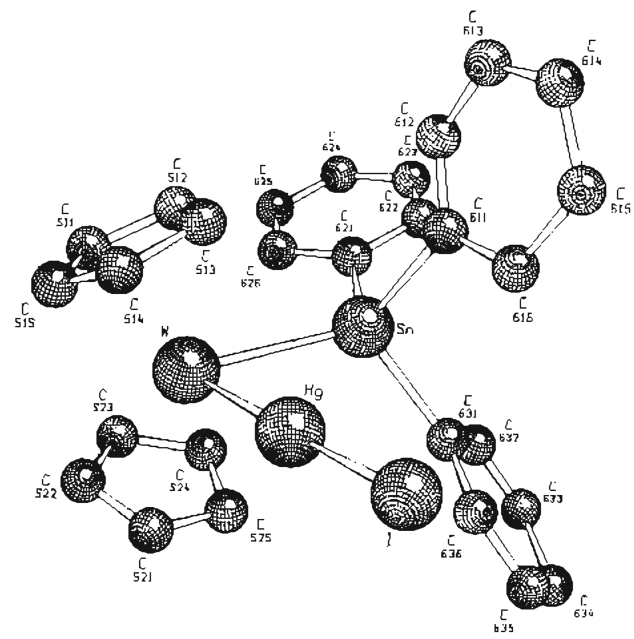


Figure 1. Molecular structure of $Cp_2(Ph_3Sn)WHgI$ (**2d**). Selected bond distances (pm) and angles (deg): W–Hg = 263.4(1), Hg–I = 251.1(3), W–Sn = 276.8(2), W–Cp(1) = 196.1, W–Cp(2) = 194.7 pm (Cp = centroids of the Cp ligands); W–Hg–I = 177.2(1), Hg–W–Sn = 78.87(6), W–Sn–C(611) = 114.9(8), W–Sn–C(621) = 110.8(6), W–Sn–C(631) = 116.5(7), Cp(1)–W–Cp(2) = 140.5.

The complex $Cp_2(Ph_3Sn)WHgI$ (**2d**) crystallized in discrete molecules (Figure 1). The X-ray structure analysis gave no indication for a secondary halogen interaction, as was observed, for instance, in $(CO)_3(Me_3P)(Ph_2MeSi)FeHgBr$,[6f] or $Cp(CO)_3WHgBr$.[10] As a consequence, the W–Hg–I grouping in **2d** is nearly linear (177.2(1)°). The geometry of the Cp_2W moiety is as expected for complexes of this kind, and the Hg–W–Sn angle of 78.87(6)° agrees very well for the theoretically predicted value of 78° for Cp_2MX_2 complexes with a d^2 electron configuration.[9] The W–Hg and W–Sn vectors are nearly symmetrical relative to the C_2 axis of the Cp_2W fragment (39 and 40°, respectively). In the series of MeHgX compounds (X = Cl, Br, I) the Hg–X distance increases from 228.3 pm (X = Cl) to 240.6 pm (X = Br) and 257.1 pm (X = I).[11] In $Cp(CO)_3MoHgCl$ (Hg–Cl 243.7(8)pm) and $Cp(CO)_3WHgBr$ (Hg–Br 256.5(8) pm)[10] the Hg–X distances are about 15 pm *longer* than in MeHgX. Contrary to that, the Hg–I bond length in **2d** (251.1(3)pm) is *shorter* than in MeHgI. Since the W–Hg distance in **2d** (263.4(1) pm) is also shorter than in $Cp(CO)_3WHgBr$ (269.8 pm), the shortening of the Hg–I bond length cannot be due to π-donation from I to Hg, but is probably another consequence of the absence of a secondary halogen interaction.

There was also spontaneous reaction at −78 °C of **1** with $(Ph_3P)MCl$ (M = Au, Ag, Cu), (dppe)AgCl, $[(Ph_3P)_2Cu]NO_3$, $(Ph_3P)_2MCl_2$ (M = Ni, Pd, Pt), Cp_2TiCl_2 or $Cp(CO)_2FeI$. However, in none of these reactions stable heteronuclear

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complexes were obtained. In most cases there was decomposition already at −78 °C. From these mixtures only $Cp_2M(H)SnPh_3$ and smaller quantities of $Cp_2M(Cl)SnPh_3$ (**6**) were isolated as the only Cp-containing products.

The halide-substituted complexes $Cp_2M(X)SnPh_3$ (**6**: X = Cl, **7**: X = Br) were independently synthesized for comparison by reaction of $Cp_2M(H)SnPh_3$ with the alkyl halides CCl_4, CHX_3 or $PhCH_2Br$ (eq 4). The corresponding $SnMe_3$ derivatives were already prepared by Lappert *et al.* by the same route.[13] Contrary to the $SnMe_3$ derivatives, the M−Sn bonds in **6** and **7** were not cleaved by an excess of RX, even at elevated temperatures.

$$Cp_2M(H)SnPh_3 + RX \rightarrow Cp_2M(X)SnPh_3 + RH \quad (4)$$

6a: M = Mo, X = Cl
6b: M = W, X = Cl
7a: M = Mo, X = Br
7b: M = W, X = Br

The formation of **6** according to eq 4 indicates that formation of these complexes in the reaction of **1** with metal halides is due to a secondary reaction, in which part of the hydride complex $Cp_2M(H)SnPh_3$ is halogenated. In the light of our previous experience, the formation of $Cp_2M(H)SnPh_3$ is not unusual. In systematic studies carried out with the anionic stannyl complexes $[(\pi\text{-arene})(CO)_2CrSnR_3]^-$ we showed that the corresponding hydride complexes $(\pi\text{-arene})(CO)_2Cr(H)SnR_3$ are formed in redox reactions, which compete with the substitution reactions.[11] The redox reactions are not only favored by electronic factors also but to a great extent also by an increasing size of either the anionic complexes or the halides.

Steric factors also seem to play a decisive role in the reactions of **1** with metal halides or halogeno complexes. Even the complexes $Cp_2(Ph_3Sn)MM'PPh_3$ (M′ = Cu, Ag, Au) with a linear coordination of M′ would be more crowded than the complexes **3**, because there would be a stronger steric interference between the PPh_3 ligand and a $Cp_2(Ph_3Sn)M$ moiety than between the two $Cp_2(Ph_3Sn)M$ moieties in **3**. The steric situation is even more severe for $M'L_n$ moieties with higher coordination numbers. Steric interactions probably also help to prevent aggregation of **2d** via iodo bridges. From a steric point of view, however, it is surprising that no complexes $Cp_2(Ph_3Sn)MM'X$ (M′X = CdCl, ZnBr) were obtained.

Experimental Section

All operations were performed in an atmosphere of dry and oxygen-free argon, using dried and argon-saturated solvents. Instrumentation: melting points, DuPont thermal analyzer; ^1H and ^{13}C NMR spectra, Bruker AC 200 (200.1 or 50.3 MHz, respectively); ^{119}Sn NMR spectra, Jeol FX 90Q (33.4 MHz) relative to external $SnMe_4$.

General Procedure for the Preparation of $Cp_2M(SnPh_3)HgX$ (2). To a solution of **1**[1] in THF at −78 °C was added a solution of excess HgX_2 in THF dropwise under vigorous stirring. The mixture was kept at −78 °C for 30 min and then warmed to room temperature within 1 h. Addition of $HgBr_2$ resulted in an immediate color change of the solution to orange red. Upon addition of HgI_2, the solution turned green first and only turned an orange color on warming to room temperature. Stirring was continued for 15 min, and then the solvent was removed *in vacuo*. The residue was redissolved in CH_2Cl_2. After filtration the filtrate was concentrated to 15 mL. Upon addition of 60 mL of petroleum ether the complexes **2** precipitated. They were separated from the solution, washed with several portions of petroleum ether, and dried *in vacuo*. Crystals were obtained from CH_2Cl_2 solutions by adding half the amount of petroleum ether and keeping the solution at −25 °C.

2a. Reaction of 0.39 mmol of **1a** in 5 mL of THF with 180 mg (0.49 mmol) of $HgBr_2$ in 10 mL of THF gave orange red crystals: yield 227 mg (68%). Mp: 109 °C dec. Anal. Found (calcd for $C_{28}H_{25}BrHgMoSn$): C, 38.36 (39.26); H, 2.78 (2.94). ^1H NMR ($CDCl_3$, δ): 7.56–7.21 (m, Ph, 15 H), 4.69 (s, Cp, 10 H, $^3J_{SnMoCH}$ = 6.3 Hz, $^3J_{HgMoCH}$ = 15.5 Hz). ^{13}C NMR ($CDCl_3$, δ): 146.17 (*ipso*-C_6H_5), 136.84 (*o*-C_6H_5, $^2J_{SnCC}$ = 34.3 Hz), 128.30 (*m*-C_6H_5, $^3J_{SnCCC}$ = 39.7 Hz), 127.76 (*p*-C_6H_5), 76.88 (Cp). ^{119}Sn NMR ($CDCl_3$, δ): 104.62.

2b. Reaction of 0.55 mmol of **1a** in 6 mL of THF with 325 mg (0.70 mmol) of HgI_2 in 12 mL of THF gave light red crystals: yield 323 mg (65%). Mp: 102 °C dec. Anal. Found (calcd for $C_{28}H_{25}HgIMoSn$): C, 36.35 (37.22); H, 3.42 (2.79). ^1H NMR ($CDCl_3$, δ): 7.57–7.24 (m, Ph, 15 H), 4.66 (s, Cp, 10 H, $^3J_{SnMoCH}$ = 6.4 Hz). ^{13}C NMR ($CDCl_3$, δ): 146.35 (*ipso*-C_6H_5), 136.86 (*o*-C_6H_5, $^2J_{SnCC}$ = 33.7 Hz), 128.18 (*m*-C_6H_5, $^3J_{SnCCC}$ = 39.6 Hz), 127.69 (*p*-C_6H_5), 76.78 (Cp). ^{119}Sn NMR ($CDCl_3$, δ): 97.61.

2c. Reaction of 0.46 mmol of **1b** in 6 mL of THF with 208 mg (0.57 mmol) of $HgBr_2$ in 12 mL of THFgave orange red crystals: yield 308 mg (71%). Mp: 188 °C dec. Anal. Found (calcd for $C_{28}H_{25}BrHgSnW$): C, 35.28 (35.60); H, 2.38 (2.67). ^1H NMR ($CDCl_3$, δ): 7.54–7.24 (m, Ph, 15 H), 4.66 (s, Cp, 10 H, $^3J_{SnWCH}$ = 6.2 Hz, $^3J_{HgWCH}$ = 14.6). ^{13}C NMR ($CDCl_3$, δ): 145.98 (*ipso*-C_6H_5), 136.79 (*o*-C_6H_5, $^2J_{SnCC}$ = 33.4 Hz), 128.18 (*m*-C_6H_5, $^3J_{SnCCC}$ = 39.4 Hz), 127.70 (*p*-C_6H_5), 72.96 (Cp). ^{119}Sn NMR ($CDCl_3$, δ): −27.33.

2d. Reaction of 0.54 mmol of **1b** in 6 mL of THF with 310 mg (0.68 mmol) of HgI_2 in 12 mL of THF gave orange red crystals: yield 358 mg (67%). Mp: 167 °C dec. Anal. Found (calcd for $C_{28}H_{25}HgISnW$): C, 32.91 (33.9); H, 2.21 (2.54). ^1H NMR ($CDCl_3$, δ): 7.54–7.23 (m, Ph, 15 H), 4.65 (s, Cp, 10 H, $^3J_{SnWCH}$ = 6.3 Hz). ^{13}C NMR ($CDCl_3$, δ): 146.20 (*ipso*-C_6H_5), 136.85 (*o*-C_6H_5, $^2J_{SnCC}$ = 33.2 Hz), 128.12 (*m*-C_6H_5, $^3J_{SnCCC}$ = 38.2 Hz), 127.67 (*p*-C_6H_5), 72.90 (Cp). ^{119}Sn NMR ($CDCl_3$, δ): −32.50.

Preparation of 2a,c by Redistribution. Solid $HgBr_2$ (47 mg [0.13 mmol] or 36 mg [0.10 mmol], respectively) was added to a solution of 175 mg (0.13 mmol) of **3a** or 153 mg (0.10 mmol) of **3b** in 15 mL of CH_2Cl_2 at room temperature. The reaction mixture was stirred for 6 h, while the $HgBr_2$ dissolved. The solution was then concentrated *in vacuo*, redissolved in 30 mL of CH_2Cl_2, and filtered. After concentration to 10 mL volume and addition of 40 mL of petroleum ether, the complexes **2a,c** precipitated. They were separated from the solution, washed with several portions of petroleum ether, and dried *in vacuo*. The spectroscopic data are identical with the samples obtained by reaction of **1** with $HgBr_2$. Yields: **2a**, 214 mg (96%); **2c**, 178 mg (94%).

X-ray Structure Analysis of 2d. Red crystals (0.2 × 0.1 × 0.4 mm) were obtained from $CHCl_3$. Crystal data: orthorhombic, space group *Pbcn*; a = 1646.1(3) pm, b = 1780.1(3) pm, c = 1788.7(3) pm; V = 5241 × 10^6 pm^3; Z = 8; d_{ber} = 2.51 g/cm^3. Data collection: The cell constants were determined by refinement of 25 reflections with high diffraction angles from different parts of the reciprocal space. The reflection intensities were measured in the range 4° ≤ 2Θ ≤ 50° at an Enraf-Nonius CAD4 diffractometer at 298 K with Mo Kα radiation (λ = 71.069 pm) using the ω -scan method. Following Lorentz, polarization, empirical absorption (μ = 124.46 cm^{-1}; minimum transmission 38.0%) and linear decay correction (intensity decay 24%) 5123 independent reflections were measured. 2862 reflections with $F_o > 3\sigma(F_o)$ were used for the solution of the structure by the Patterson method. The positions of the hydrogen atoms were calculated according to an ideal geometry. The heavy atoms were refined with anisotropic thermal parameters by full-matrix least-squares methods with the full matrix. R = 0.057, R_w = 0.071. The residual electron density was 1.12 × 10^6 e/pm^3. Crystallographic data are given in Table 1.

Table 1. Crystallographic Data for $Cp_2(Ph_3Sn)WHgI$ (**2d**)

formula	$C_{28}H_{25}HgISnW$	d_{ber}, g/cm^3	2.51
fw	991.6	space group	*Pbcn*
a, pm	1646.1(3)	T, K	298
b, pm	1780.1(3)	λ, pm	71.069
c, pm	1788.7(3)	μ, cm^{-1}	124.46
V, pm^3	5241 × 10^6	R, R_w[a]	0.057, 0.071
Z	8		

[a] $R = \Sigma|F_o - F_c|/\Sigma|F_o|$. $R_w = \{\Sigma w(F_o - F_c)^2/\Sigma wF_o^2\}^{1/2}$, $w = 1/\sigma(F)^2$

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General Procedure for the Preparation of [$Cp_2M(SnPh_3)$]$_2$M′ (3–5). For the preparation of **3** and **4**, $CdCl_2$ was added to a suspension of **1**[1] in 20 mL of DME at −50 °C. For the preparation of **5**, $ZnBr_2$ is added to a solution of **1** in 20 mL of THF. The reaction mixtures were warmed to room temperature within 30 min under vigorous stirring, while the color changed from red to yellow. After 1h the solvent was removed *in vacuo*. The residue was redissolved in CH_2Cl_2 and filtered over 3 cm silica at −5 °C. The filtrate was concentrated to 20−50 mL. Upon addition of 60 mL of petroleum ether, complexes **4** and **5** precipitated at 0 °C. They were separated from the solution, washed with several portions of petroleum ether, and dried *in vacuo*. Analytically pure samples of **4** were obtained by recrystallization from CH_2Cl_2/petroleum ether.

3a. Reaction of 0.64 mmol of **1a** with 115 mg (0.32 mmol) of $HgBr_2$ gave an orange red powder: yield 268 mg (62%). Mp: 128 °C dec. Anal. Found (calcd for $C_{56}H_{50}HgMo_2Sn_2$): Found C, 48.63 (49.72); H, 3.60 (3.73). ^{1}H NMR ($CDCl_3$, δ): 7.48−7.22 (m, Ph, 15 H), 4.41 (s, Cp, 10 H, $^3J_{SnMoCH} = 8.4$ Hz). ^{13}C NMR ($CDCl_3$, δ): 149.16 (*ipso*-C_6H_5, $^1J_{^{119}SnC} = 238.5$ Hz, $^1J_{^{117}SnC} = 227.9$ Hz), 137.07 (*o*-C_6H_5, $^2J_{SnMoC} = 31.7$ Hz), 127.78 (*m*-C_6H_5, $^3J_{SnMoCC} = 33.5$ Hz), 127.08 (*p*-C_6H_5), 74.51 (Cp). ^{119}Sn NMR ($CDCl_3$, δ): 100.68.

3b. Reaction of 0.70 mmol of **1b** with 126 mg (0.35 mmol) of $HgBr_2$ gave an orange red powder: yield 370 mg (69%). Mp: 144 °C dec. Anal. Found (calcd for $C_{56}H_{50}HgSn_2W_2$): C, 43.69 (44.00); H, 3.44 (3.30). ^{1}H NMR ($CDCl_3$, δ): 7.47−7.19 (m, Ph, 15 H), 4.35 (s, Cp, 10 H, $^3J_{SnMoCH} = 7.8$ Hz). ^{13}C NMR ($CDCl_3$, δ): 148.77 (*ipso*-C_6H_5), 137.06 (*o*-C_6H_5, $^2J_{SnMoC} = 31.7$ Hz), 127.71 (*m*-C_6H_5, $^3J_{SnMoCC} = 33.3$ Hz), 127.03 (*p*-C_6H_5), 70.18 (Cp). ^{119}Sn NMR ($CDCl_3$, δ): −42.39.

4a. Reaction of 0.71 mmol of **1a** with 66 mg (0.36 mmol) of $CdCl_2$ gave a yellow powder: yield 171 mg (38%). Mp: 112 °C dec. Anal. Found (calcd for $C_{56}H_{50}CdMo_2Sn_2$): Found C, 53.28 (53.18); H, 3.75 (3.99). ^{1}H NMR (DMSO-*d*$_6$, δ): 7.38−7.20 (m, Ph, 15 H), 4.36 (s, Cp, 10 H, $^3J_{SnMoCH} = 9.1$ Hz). ^{13}C NMR (*d*$_6$-DMSO, δ): 150.02 (*ipso*-C_6H_5), 136.73 (*o*-C_6H_5), 127.87 (*m*-C_6H_5), 127.11 (*p*-C_6H_5), 70.86 (Cp). ^{119}Sn NMR (CH_2Cl_2/C_6D_6, δ): 118.65.

4b. Reaction of 0.63 mmol of **1b** with 58 mg (0.32 mmol) of $CdCl_2$-gave a yellow powder: yield 195 mg (43%). Mp: 60 °C dec. Anal. Found (calcd for $C_{56}H_{50}CdSn_2W_2$): C, 46.11 (46.69); H, 3.05 (3.50). ^{1}H NMR (CD_2Cl_2, δ): 7.44−7.20 (m, Ph, 15 H), 4.29 (s, Cp, 10 H, $^3J_{SnMoCH} = 8.3$ Hz). ^{13}C NMR (CD_2Cl_2, δ): 149.80 (*ipso*-C_6H_5), 137.34 (*o*-C_6H_5), 128.15 (*m*-C_6H_5), 127.44 (*p*-C_6H_5), 67.73 (Cp).

5a. Reaction of 0.61 mmol of **1a** with 69 mg (0.31 mmol) of $ZnBr_2$ gave a yellow powder: yield 102 mg (27%). ^{1}H NMR (THF-*d*$_8$, δ): 7.49−7.15 (m, Ph, 15 H), 4.43 (s, Cp, 10 H, $^3J_{SnMoCH} = 10.0$ Hz). ^{13}C NMR (THF-*d*$_8$, δ): 151.13 (*ipso*-C_6H_5), 138.11 (*o*-C_6H_5), 128.36 (*m*-C_6H_5), 127.57 (*p*-C_6H_5), 73.47 (Cp).

5b. Reaction of 0.72 mmol of **1b** with 81 mg (0.36 mmol) of $ZnBr_2$ gave a yellow powder: yield 123 mg (25%). ^{1}H NMR (THF-*d*$_8$, δ): 7.48−7.14 (m, Ph, 15 H), 4.36 (s, Cp, 10 H, $^3J_{SnMoCH}$ 9.0 = Hz). ^{13}C NMR (THF-*d*$_8$, δ): 150.51 (*ipso*-C_6H_5), 138.04 (*o*-C_6H_5), 128.20 (*m*-C_6H_5), 127.45 (*p*-C_6H_5), 69.23 (Cp).

Preparation of $Cp_2M(SnPh_3)Cl$ (6). To a solution of 483 mg (0.84 mmol) of $Cp_2Mo(H)SnPh_3$ [683 mg (0.96 mmol) $Cp_2W(H)SnPh_3$] in 20 mL of THF was added 0.40 mL (4.18 mmol) [0.46 mL (4.80 mmol)] of CCl_4 dropwise. The solution was stirred for 15 h. During this time the yellow solution turned into a dark red suspension. The solvent was then removed *in vacuo* and the residue redissolved in 30 mL of CH_2Cl_2. The solution was filtered and concentrated to about 20 mL. Addition of 60−70 mL of petroleum ether resulted in the precipitation of **6**. The solid was separated from the solution, washed with three portions of 20 mL of petroleum ether each, and dried *in vacuo*. Analytically pure samples were obtained by recrystallization from CH_2Cl_2 (**6a**) or CH_2Cl_2/petroleum ether (2:1) (**6b**). The complexes **6** can also be prepared by reaction of $Cp_2M(H)SnPh_3$ in refluxing $CHCl_3$ in about the same yields.

6a: Violet crystals, yield 426 mg (83%). Mp: 70 °C dec. Anal. Found (calcd for $C_{28}H_{25}ClMoSn$): C, 54.86 (54.99); H, 4.13 (4.12). ^{1}H NMR ($CDCl_3$, δ): 7.63−7.23 (m, Ph, 15 H), 4.95 (s, Cp, 10 H, $^3J_{SnMoCH} = 4.8$ Hz). ^{13}C NMR ($CDCl_3$, δ): 146.03 (*ipso*-C_6H_5), 137.32 (*o*-C_6H_5, $^2J_{SnMoC}$ 29.7 Hz), 127.96 (*m*-C_6H_5, $^3J_{SnMoCC} = 38.2$ Hz), 127.75 (*p*-C_6H_5), 88.64 (Cp). ^{119}Sn NMR (acetone-*d*$_6$/THF, δ): 41.74.

6b: Dark red crystals, yield 483 mg (72%). Mp: 100 °C dec. Anal. Found (calcd for $C_{28}H_{25}ClSnW$): C, 47.82 (48.08); H, 3.57 (3.60). ^{1}H NMR ($CDCl_3$, δ): 7.61−7.24 (m, Ph, 15 H), 4.93 (s, Cp, 10 H, $^3J_{SnWCH} = 5.4$ Hz). ^{13}C NMR ($CDCl_3$, δ): 145.34 (*ipso*-C_6H_5), 137.48 (*o*-C_6H_5), 127.87 (*m*-C_6H_5), 127.58 (*p*-C_6H_5), 84.96 (Cp). ^{119}Sn NMR (acetone-*d*$_6$/THF, δ): −183.45.

Preparation of $Cp_2M(SnPh_3)Br$ (7). To a solution of 265 mg (0.46 mmol) of $Cp_2Mo(H)SnPh_3$ [256 mg (0.38 mmol) $Cp_2W(H)SnPh_3$] in 15 mL of CH_2Cl_2 was added 42 μL (0.48 mmol) [0.17 mL (1.90 mmol)] of $CHBr_3$ dropwise. The solution was refluxed for 30 min (2 h). During this time the yellow solution turned dark red. The workup was the same as for **6**. Complex **7** can also be prepared by reaction of $Cp_2M(H)SnPh_3$ with $PhCH_2Br$ at room temperature (15 h).

7a: Dark blue crystals, yield 251 mg (87%). Mp: 80 °C dec. Anal. Found (calcd for $C_{28}H_{25}BrMoSn$): C, 51.23 (51.26); H, 3.84 (3.84). ^{1}H NMR ($CDCl_3$, δ): 7.60−7.16 (m, Ph, 15 H), 4.96 (s, Cp, 10 H, $^3J_{SnMoCH} = 4.4$ Hz). ^{13}C NMR ($CDCl_3$, δ): 146.28 (*ipso*-C_6H_5), 137.36 (*o*-C_6H_5, $^2J_{SnMoC} = 29.4$ Hz), 127.91 (*m*-C_6H_5, $^3J_{SnMoCC} = 39.2$ Hz), 127.75 (*p*-C_6H_5), 87.89 (Cp).

7b: Violet red crystals, yield 232 mg (82%). Mp: 105 °C dec. Anal. Found (calcd for $C_{28}H_{25}BrSnW$): C, 44.93 (45.20); H, 3.34 (3.39). ^{1}H NMR ($CDCl_3$, δ): 7.60−7.16 (m, Ph, 15 H), 4.93 (s, Cp, 10 H, $^3J_{SnWCH} = 5.3$ Hz). ^{13}C NMR ($CDCl_3$, δ): 145.59 (*ipso*-C_6H_5), 137.55 (*o*-C_6H_5, $^2J_{SnWC} = 29.5$ Hz), 127.83 (*m*-C_6H_5, $^3J_{SnWCC} = 36.6$ Hz), 127.59 (*p*-C_6H_5), 84.23 (Cp). ^{119}Sn NMR (acetone-*d*$_6$/THF, δ): −175.12.

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Supporting Information Available: Tables of the final atomic coordinates, thermal parameters, bond lengths, and bond angles (7 pages). Ordering information is given on any current masthead page.

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