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Structure and Reactivity of Distanna[2]metallocenophanes of Ruthenium and Osmium

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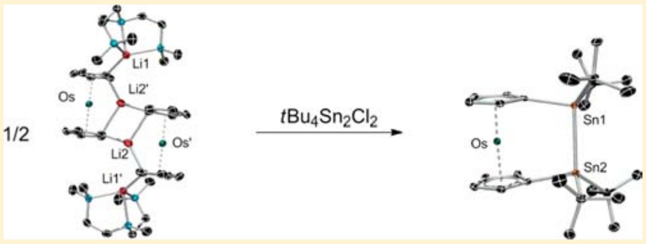
S *Supporting Information*

ABSTRACT: We report the molecular structures of 1,1′-dilithiometallocenes of ruthenium and osmium. These compounds served as precursors for the synthesis and subsequent structural characterization of the first [2]-osmocenophanes with disilane and distannane bridges, as well as of a distanna[2]ruthenocenophane. In addition, the insertion of sulfur and selenium into the Sn−Sn bridges was studied and it was observed that the presence of the Lewis base pmdta (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine) dramatically accelerates the reaction.



■ INTRODUCTION

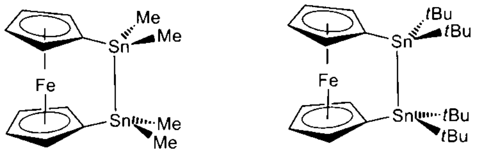
Since their discovery in the 1950s, metallocenes and their bridged analogues ("metallocenophanes") have constituted an important class of transition metal compounds and have therefore been studied rather intensively.[1] Various *ansa* bridges with different chemical properties and reactivity patterns have been developed, the most strained examples of which are in many cases susceptible to ring-opening polymerization.[2]

The oldest and best studied metallocenophanes are ferrocenophanes featuring *ansa* bridges of group 14 elements, whereas a broad variety of corresponding noniron *ansa* complexes have been disclosed much more recently.[3] From the 3d metals, strained metalloarenophanes have been synthesized for Ti,[4] V,[5] Cr,[6] Mn,[7] Fe,[3] Co,[8] and Ni.[9] However, higher homologues of the 4d row have only been reported for groups 6 (Mo[10]) and 8 (Ru[11]). Even more scarce are 5d metalloarenophanes, which are known solely for osmium.[11e,12] Although many different homoatomic bridges are known for the 3d metals and ruthenium, osmocenophanes feature exclusively three-atom bridges (e.g., trithia-[12a] and trisila-[11e] moieties) and not smaller bridges with only one or two atoms.

Two-atom bridges most commonly feature carbon and silicon, which are found with a wide variety of substituents for most metallocenophanes. Their higher homologue tin, however, is restricted to $Me_2Sn{-}SnMe_2$ and $t\text{-}Bu_2Sn{-}Sn\text{-}t\text{-}Bu_2$ units spanning the two Cp rings of ferrocene (Chart 1).[13]

1,1′-Dilithiated metallocenes have proven to be the most versatile starting materials for the preparation of strained metallocenophanes. Thus, high yield syntheses and structural characterizations have been achieved for most of the 1,1′-dilithio derivatives of the 3d metal sandwich complexes.[4c,5c,6c,7,14] Although the structure of 1,1′-dilithioferrocene with different supporting bases such as tmeda (*N,N,N′,N′*-tetramethylethylenediamine) and THF has been known since 1978,[14b] the corresponding dianions of ruthenium and osmium have not been characterized in the solid state as yet. However, in 2004 Mulvey et al. reported the molecular structures of the corresponding tetra-anions of all three group 8 metallocenes.[15]

Chart 1. Distanna[2]ferrocenophanes by Herberhold (1) and Braunschweig (2)



1 **2**

In this paper, we report the solid-state structures of dilithiated rutheno- and osmocene, which further serve as starting materials for the synthesis of new metallocenophanes. We describe the synthesis and molecular structures of the first osmocenophanes with two-atom bridges as well as a distanna[2]ruthenocenophane. By investigating their reactivity, we found a base-accelerated chalcogen insertion into the Sn−Sn bond of the *ansa* bridge.

■ RESULTS AND DISCUSSION

In order to disclose the hitherto unknown molecular structures of dilithioruthenocene and -osmocene, we prepared these species in the form of their pmdta (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine) adducts $[Ru(\eta^5\text{-}C_5H_4Li)_2(pmdta)]$ (**4**) and $[Os(\eta^5\text{-}C_5H_4Li)_2(pmdta)]$ (**5**).[11e] In 2008 Wagner et al. reported that the corresponding 1,1′-dilithioferrocene pmdta adduct crystallizes from an excess of THF as the dimeric species $[Fe(\eta^5\text{-}C_5H_4Li)_2(THF)_3]_2$ (**3**) in which all amine bases have been replaced by THF molecules.[14] The same behavior was

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observed for the ruthenocene derivative (Figure 1); thus, [Ru(η^5-C_5H_4Li)$_2$(pmdta)] (**4**) crystallizes from THF as the dimer [Ru(η^5-C_5H_4Li)$_2$(THF)$_3$]$_2$ (**6**) in the triclinic space group $P\bar{1}$ as colorless blocks.

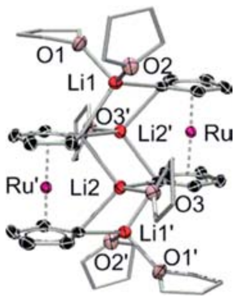


Figure 1. Molecular structure of **6** (thermal ellipsoids depicted at 50% probability). Hydrogen atoms were omitted and THF molecules were simplified for clarity. Selected bond lengths [Å]: centroid−centroid, 3.634; C_{ipso}−Li1, 2.191(6); C_{ipso}−Li2, 2.370(6); C_{ipso}−Li2′, 2.252(6); $C_{ipso'}$−Li2, 2.322(6); $C_{ipso'}$−Li1′, 2.191(6); Li1−O1, 1.988(6); Li1−O2, 2.006(7); Li2−O3, 2.058(7).

The dimeric structure resembles the known structure of **3** with two THF molecules coordinating the peripheral lithium atoms and one THF molecule coordinating each of the central lithium atoms.[14b] Thereby, each lithium atom adopts a tetrahedral coordination sphere. From a noncoordinating solvent such as toluene, we were able to crystallize the aforementioned pmdta adducts [Ru(η^5-C_5H_4Li)$_2$(pmdta)] (**4**) and [Os(η^5-C_5H_4Li)$_2$(pmdta)] (**5**) as the dimeric compounds [Ru(η^5-C_5H_4Li)$_2$(pmdta)]$_2$ (**7**) and [Os(η^5-C_5H_4Li)$_2$(pmdta)]$_2$ (**8**), respectively (Figure 2).

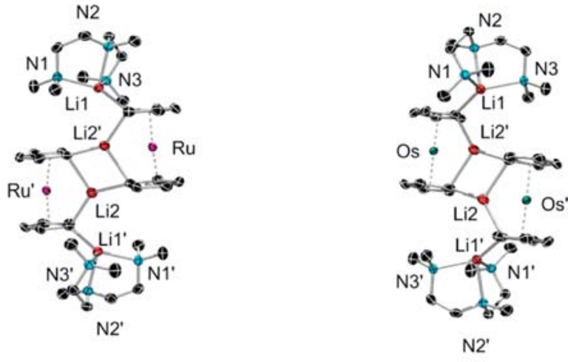
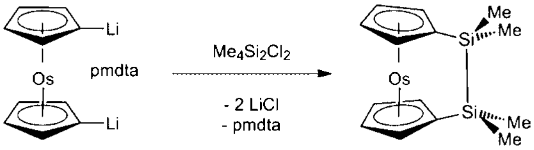


Figure 2. Molecular structures of **7** and **8** (thermal ellipsoids depicted at 50% probability). Both structures are generated by a C_i symmetry operation from the asymmetric unit. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å]. **7**: centroid−centroid, 3.63; C_{ipso1}−Li1, 2.147(3); C_{ipso1}−Li2, 2.186(3); C_{ipso2}−Li2, 2.128(3); C_{ipso2}−Li2′, 2.294(3); Li1−N, 2.143(3), 2.132(3), and 2.113(3). **8**: centroid−centroid, 3.63; C_{ipso1}−Li1, 2.143(6); C_{ipso1}−Li2, 2.179(6); C_{ipso2}−Li2, 2.128(7); C_{ipso2}−Li2′, 2.309(7); Li1−N, 2.137(6), 2.124(6), and 2.112(6).

Both dinuclear species crystallize in the monoclinic space group $P2_1/c$ and show structural details similar to the corresponding ferrocene derivative published in 1978 by Stucky et al.[14b] The peripheral lithium atoms are bound to one carbon atom of the Cp ring and coordinated by the three nitrogen atoms of the pmdta ligand, whereas the central lithium atoms are only bound to three carbon atoms of the Cp rings (sum of bond angles is 354.1°).

Next, we turned our attention to the reactivity of these dilithio species targeting in particular the synthesis of osmocenophanes with smaller bridges. From the reaction of **8** with $Me_4Si_2Cl_2$ in hexanes, we were indeed able to obtain the first osmocenophane with a two-atom linker (Scheme 1). After reaction at room temperature for 16 h and workup, [Os(η^5-C_5H_4)$_2$$Si_2Me_4$] (**9**) was obtained by sublimation at 80 °C and 10^{-2} mbar as a colorless solid in 35% yield. Although the solid compound is stable toward air and moisture, it decomposes within a few days in solution. However, under an inert atmosphere, we found no signs of decomposition, neither in solid form nor in solution.

Scheme 1. Synthesis of the Disilaosmocenophane (9)



The ^1H NMR spectrum in C_6D_6 shows two multiplets at 5.02 and 4.90 ppm with an integration of 4, indicating the AA′BB′ systems of the Cp-bound hydrogens, and a singlet at 0.19 ppm integrating to 12 for the methyl protons. The ^{29}Si NMR spectrum displays one resonance at −11.5 ppm for the equivalent silicon atoms. The NMR data is thus in agreement with those of related [2]disilametallocenophanes.[16b] Crystals suitable for a single-crystal X-ray analysis were grown from pentane at −30 °C (Figure 3). Complex **9** crystallizes in the monoclinic space group $P2_1/n$. With a tilt angle α of 7.1°, it exhibits a higher strain than the analogous iron compound (4.2°)[16b] and is thus comparable to its ruthenium derivative with a tilt angle of 7.8°.[16c] Likewise, the Si−Si distance of 2.367(1) Å is comparable to that found in the related Fe (2.351(1) Å) and Ru (2.370(2) Å) complexes. The Cp-centroid−Cp-centroid distance (3.60 Å) deviates only slightly from that of the parent osmocene (3.61 Å).[16]

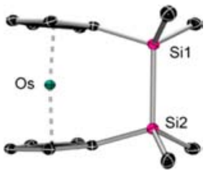
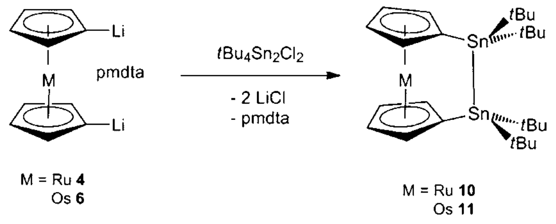


Figure 3. Molecular structure of **9** (ellipsoids depicted at 50% probability). Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1−Si1, 2.367(1); C_{ipso}−Si1, 1.881(3); $C_{ipso'}$−Si2, 1.881(3); Si1−Me, 1.871(3) and 1.872(3); Si2−Me, 1.876(3) and 1.878(3); C_{ispo}−Si1−Si2, 106.83(8); $C_{ipso'}$−Si2−Si1, 106.73(8).

By extending this chemistry to the heavier group 14 elements, we were also able to synthesize the first distanna-bridged ruthenocenophane and osmocenophane by reaction of the dilithiated precursors with 1,2-dichlorotetra-*tert*-butyldistannane (Scheme 2).

To this end, the dilithiated precursors were stirred with *t*-$Bu_4Sn_2Cl_2$ in hexane at 0 °C for 16 h. After workup and crystallization from pentane, 24% (**10**) and 23% (**11**) yields of slightly yellow, air- and moisture-sensitive crystals were

Scheme 2. Synthesis of the Distannametallocenophanes 10 and 11



obtained. In their ^{1}H NMR spectra, both metallocenophanes show the two typical multiplets for the eight Cp protons at 4.81 and 4.76 ppm for **10** and 5.10 and 4.90 ppm for **11** as well as a singlet for the *tert*-butyl protons at 1.45 (**10**) and 1.44 ppm (**11**). The latter shows a coupling to the two NMR-active tin nuclei ($^3J_{\text{Sn-H}}$ = 63 and 65 Hz). In the ^{119}Sn NMR spectrum, we found signals at 8.2 (**10**) and 21.3 ppm (**11**) with a one-bond ^{117}Sn–^{119}Sn coupling of 1925 (**10**) and 2046 Hz (**11**), respectively.

Crystals suitable for a single-crystal X-ray analysis of both distannametallocenophanes could be obtained from saturated solutions in pentane at −30 °C (Figure 4). Both species show a very similar solid-state structure with rather small tilt angles of 3.40° for **10** and 3.58° for **11**. However, due to the larger interplanar distance, the angles are more than doubled in comparison to those of the ferrocenophane [Fe(η^5-C_5H_4)$_2$Sn$_2$(t-Bu)$_4$] (**12**) (1.4°). The Sn–Sn distances (2.8407(3) (**10**) and 2.852(2) Å (**11**)) are only slightly longer than in **12** (2.827(2) Å). The ring–ring separations of 3.63 and 3.65 Å are in the normal range for rutheno- and osmocenophanes.

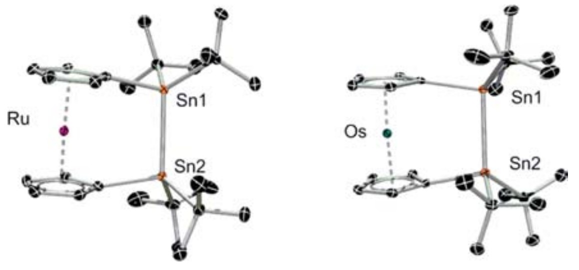


Figure 4. Molecular structures of **10** and **11** (thermal ellipsoids depicted at 50% probability). Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [deg]. **10**: centroid–centroid, 3.626; Sn1–Sn2, 2.8407(3); Sn1–C_{ipso}, 2.164(2); Sn2–$C_{\text{ipso}'}$, 2.165(2); Sn1–$C_{t\text{-Bu}}$, 2.207(2) and 2.211(2); Sn2–$C_{t\text{-Bu}}$, 2.165(2) and 2.205(2); C_{ipso}–Sn1–Sn2, 99.03(4); $C_{\text{ipso}'}$–Sn2–Sn1, 99.25(4). **11**: centroid–centroid, 3.649; Sn1–Sn2, 2.853(2); Sn1–C_{ipso}, 2.174(4); Sn2–$C_{\text{ipso}'}$, 2.171(4); Sn1–$C_{t\text{-Bu}}$, 2.215(4) and 2.220(4); Sn2–$C_{t\text{-Bu}}$, 2.219(4) and 2.228(4); C_{ipso}–Sn1–Sn2, 99.38(9); $C_{\text{ipso}'}$–Sn2–Sn1, 99.21(9).

As the work of Puff et al. in 1987 has shown, chalcogens can insert into Sn–Sn bonds.[18] Wrackmeyer et al. and later our group extended this methodology to bridged distanna[2]-ferrocenophanes.[13] Although the chalcogen insertion into organodistannanes by Puff et al. and tetramethyldistanna[2]-ferrocenophane by Wrackmeyer et al. proceeds in 12 h at 110 °C, the bulkier *tert*-butyl substituents slow down the reaction to 5 days at 100 °C in the case of tetra-*tert*-butyldistanna[2]-ferrocenophane.[6c]

A similarly slow reaction can be observed for the tin-bridged *ansa* metallocenes **10** and **11** (Scheme 3). Although the insertion of selenium into the distanna bridge of **10** requires 6 days in an ultrasonic bath for completion (determined by ^{1}H NMR) or alternatively 12 days at 100 °C, the insertion into the tin–tin bond of **11** is complete after 11 days at 100 °C but shows no signs of insertion upon sonification. However, in the presence of 1 equiv of pmdta, the reaction only requires 16 h at 80 °C until full conversion. The same decrease of reaction time could be observed for the ferrocene analogue, whereas the addition of tmeda had no influence (Table 1). The effect of the tertiary nitrogen base pmdta on the rate of chalcogen insertion and especially its different behavior compared to that of tmeda remains unclear to us at this stage.

Scheme 3. Insertion of Chalcogens into the Tin–Tin Bridge of 10 and 11

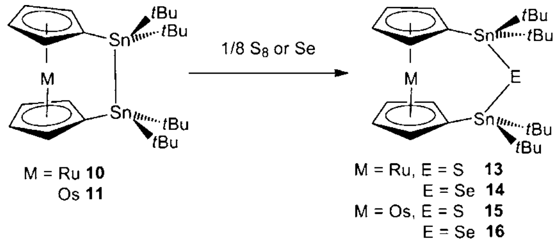


Table 1. Reaction Conditions for the Insertion of Chalcogens into the Sn–Sn Bond

metal	chalcogen	base	temperature	time
Fe	S		100 °C	5 d
	Se		100 °C	5 d
	Se	tmeda	100 °C	5 d
	Se	pmdta	80 °C	16 h
Ru	S		RT, ultrasonic bath	6 d
	Se		RT, ultrasonic bath	6 d
	S	pmdta	80 °C	16 h
	Se	pmdta	80 °C	16 h
Os	S		100 °C	11 d
	Se		100 °C	11 d
	S	pmdta	80 °C	16 h
	Se	pmdta	80 °C	16 h

The sulfur insertion product **13** could be obtained in 24% yield after workup as a yellow solid, and the selenium analogue **14** was obtained in 31% yield as a colorless solid material. The relatively modest yields are mainly due to the difficulty in separating the products from the excess chalcogen. The ^{1}H NMR data show the expected multiplets for the Cp protons at 4.70 and 4.53 ppm for **13** and at 4.69 and 4.53 ppm for **14**. In addition, a singlet could be observed at 1.41 ppm displaying the two expected $^3J_{\text{Sn-H}}$ couplings of 73 and 75 Hz for the butyl protons. The ^{119}Sn NMR signals can be found at 30.1 ppm with a $^2J_{\text{Sn-Sn}}$ coupling of 246 Hz for **13** and at 26.3 ppm with a $^2J_{\text{Sn-Sn}}$ coupling of 220 Hz for **14**. This set of data is consistent with the insertion of a chalcogen atom into the tin–tin bond and comparable to that of analogous ferrocene complexes.[13c]

Similarly, the osmocene derivatives **15** and **16** were synthesized upon reaction of the distanna[2]metallocenophane precursor **11** with elemental sulfur and selenium and isolated in yields of 22% and 24%, respectively. Both complexes display (the same) characteristic multiplets in the ^{1}H NMR spectra for the Cp protons at 4.90 and 4.68 ppm, as well as a singlet at 1.41 ppm for the *tert*-butyl groups with two $^3J_{\mathrm{Sn-H}}$ couplings of 73 and 75 Hz. The ^{119}Sn NMR signals are found at 26.5 (**15**) and 26.6 ppm (**16**) with $^2J_{\mathrm{Sn-Sn}}$ couplings of 235 (**15**) and 208 Hz (**16**), thus confirming the expansion of the bridge.

■ CONCLUSION

In summary, we have reported the solid-state structures of the THF- and pmdta-stabilized 1,1′-dilithiated ruthenocene and osmocene. With these compounds in hand, we were able to synthesize the first osmocenophane featuring a two-atom bridge. We have also expanded this methodology toward a higher homologue of silicon and prepared tetra-*tert*-butyldistanna[2]metallocenophanes of ruthenium and osmium. Furthermore, we have shown that the Sn−Sn bond of the *ansa* bridge in these species is capable of chalcogen insertions, which were found to be accelerated in the presence of pmdta.

■ EXPERIMENTAL SECTION

General Considerations. All experiments were performed under an inert atmosphere of dry argon using standard Schlenk techniques or in a glovebox. Solvents were dried according to standard procedures, freshly distilled prior to use, degassed, and stored under argon over activated molecular sieves (4 Å). Deuterated solvents were degassed by three freeze−pump−thaw cycles and stored over molecular sieves. *t*-$\mathrm{Bu_4Sn_2Cl_2}$ was prepared according to published methods,[19] and $\mathrm{Me_4Si_2Cl_2}$, $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5H_5})_2]$, and $[\mathrm{Os}(\eta^5\text{-}\mathrm{C_5H_5})_2]$ were purchased from ABCR and used without further purifications. All other compounds were obtained commercially and used without further purification. NMR spectra were recorded on a Bruker AMX 400 or a Bruker Avance 500 NMR spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external TMS via the residual protio solvent (^{1}H) or the solvent itself (^{13}C). ^{29}Si{^{1}H} NMR spectra were referenced to external TMS and ^{119}Sn NMR spectra to $\mathrm{Me_4Sn}$. Assignments were made from the analysis of ^{1}H,^{13}C−HMQC and ^{1}H,^{1}H−COSY NMR spectroscopic experiments. All chemical shifts are reported in ppm. Elemental analyses were performed on a Vario Micro Cube (Elementar Analysensysteme GmbH) or a CHNS-932 (Leco) elemental analyzer.

$[\mathrm{Os}(\eta^5\text{-}\mathrm{C_5H_4})_2\mathrm{Si_2Me_4}]$ (9). **8** (200 mg, 0.39 mmol) in 30 mL of hexane was treated over the course of 2 h with $\mathrm{Me_4Si_2Cl_2}$ (74.5 mg, 0.39 mmol) in 15 mL of hexane. After stirring for 16 h, the solution was filtered and the solvent was removed in vacuo. After sublimation at 80 °C at 10^{-2} mbar, 60 mg (0.14 mmol, 35%) of a colorless solid was obtained. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 5.01−5.02 (m, 4H, $\mathrm{C_5H_4}$), 4.90−4.91 (m, 4H, $\mathrm{C_5H_4}$), 0.188 (s, 12H, $\mathrm{CH_3}$) ppm. ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 70.10, 68.13, 66.51, 0.20 ppm. ^{29}Si NMR (79 MHz, $\mathrm{C_6D_6}$, 293 K, δ): −11.51 ppm. Anal. Calcd for $\mathrm{C_{14}H_{20}OsSi_2}$ (436.1): C, 38.68; H, 4.64. Found: C, 39.03; H, 4.71.

$[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5H_4})_2\mathrm{Sn_2}\text{-}t\text{-}\mathrm{Bu_4}]$ (10). **7** (100 mg, 0.24 mmol) in 20 mL of hexane was treated with *t*-$\mathrm{Bu_4Sn_2Cl_2}$ (128 mg, 0.24 mmol) at 0 °C. After 16 h, all solid materials were removed by filtration, and the solvent was removed in vacuo. After crystallization at −30 °C from pentane, 40 mg (0.06 mmol, 24%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 4.81−4.80 (m, 4H, $\mathrm{C_5H_4}$), 4.77−4.76 (m, 4H, $\mathrm{C_5H_4}$), 1.45 (s, 36H, *t*-Bu,$^3J_{\mathrm{Sn-H}}$ = 63, 65 Hz) ppm. ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 79.24, 76.23, 73.44, 32.89, 31.99 ppm. ^{119}Sn NMR (149 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 8.16 (s, $^1J_{\mathrm{Sn-Sn}}$ = 1925.43 Hz) ppm. Anal. Calcd for $\mathrm{C_{26}H_{44}RuSn_2}$ (698.1): C, 43.76; H, 6.24. Found: C, 44.41; H, 6.45.

$[\mathrm{Os}(\eta^5\text{-}\mathrm{C_5H_4})_2\mathrm{Sn_2}\text{-}t\text{-}\mathrm{Bu_4}]$ (11). **8** (166 mg, 0.33 mmol) in 20 mL of hexane was treated with *t*-$\mathrm{Bu_4Sn_2Cl_2}$ (176 mg, 0.33 mmol) at 0 °C. After 16 h, all solid materials were removed by filtration, and the solvent was removed in vacuo. After crystallization at −30 °C from pentane, 60 mg (0.076 mmol, 23%) of a yellow solid was obtained.

^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 5.10 (m, 4H, $\mathrm{C_5H_4}$), 4.90−4.91 (m, 4H, $\mathrm{C_5H_4}$), 1.438 (s, 36H, *t*-Bu, $^3J_{\mathrm{Sn-H}}$ = 63, 65 Hz) ppm. ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 72.79, 69.89, 67.57, 32.81, 31.39 ppm. ^{119}Sn NMR (149 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 21.32 (s, $^1J_{\mathrm{Sn-Sn}}$ = 2046 Hz) ppm. Anal. Calcd for $\mathrm{C_{26}H_{40}OsSn_2}$ (788.1): C, 39.82; H, 5.65. Found: C, 39.97; H, 5.73.

$[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5H_4})_2\mathrm{Sn_2}\text{-}t\text{-}\mathrm{Bu_4S}]$ (13). (a) **10** (20 mg, 0.029 mmol) in 1 mL of $\mathrm{C_6D_6}$ were treated with sulfur (1.9 mg, 0.058 mmol). After 6 days in an ultrasonic bath, the solvent was removed in vacuo, and the precipitate was treated with 5 mL of hexane and filtered over Celite. After removal of the solvent, 5 mg (0.007 mmol, 24%) of **13** was obtained as a yellow solid. (b) **7** (30 mg, 0.072 mmol) in 1 mL of $\mathrm{C_6D_6}$ was treated with *t*-$\mathrm{Bu_4Sn_2Cl_2}$ (0.039 mg, 0.072 mmol) at 0 °C. After 16 h, all solid materials were removed by filtration. Sulfur (4 mg, 0.1 mmol) was added, and the suspension was warmed to 80 °C for 16 h. After removal of the solvent and treatment with 2 mL of hexane, the insoluble substances were removed by filtration over Celite. After crystallization at −30 °C from hexane, 9 mg (0.01 mmol, 17%) of **13** was obtained.

^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 4.70−4.69 (m, 4H, $\mathrm{C_5H_4}$), 4.54−4.53 (m, 4H, $\mathrm{C_5H_4}$), 1.41 (s, 36H, *t*-Bu, $^3J_{\mathrm{Sn-H}}$ = 75, 78 Hz) ppm. ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 77.45, 73.05, 72.66, 32.34, 31.32 ppm. ^{119}Sn NMR (149 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 26.27 (s, $^2J_{\mathrm{Sn-Sn}}$ = 246 Hz) ppm. Anal. Calcd for $\mathrm{C_{26}H_{44}RuSSn_2}$ (730.0): C, 40.34; H, 5.73; S, 4.41. Found: C, 43.05; H, 6.11; S, 5.16.

$[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5H_4})_2\mathrm{Sn_2}\text{-}t\text{-}\mathrm{Bu_4Se}]$ (14). (a) **10** (20 mg, 0.029 mmol) in 1 mL of $\mathrm{C_6D_6}$ was treated with red selenium (4.6 mg, 0.058 mmol). After 6 days in an ultrasonic bath, the solvent was removed in vacuo, and the precipitate was treated with 5 mL of hexane and filtered over Celite. After removal of the solvent, 7 mg (0.009 mmol, 31%) of **14** was obtained as a yellow solid. (b) **7** (30 mg, 0.072 mmol) in 1 mL of $\mathrm{C_6D_6}$ was treated with *t*-$\mathrm{Bu_4Sn_2Cl_2}$ (0.039 mg, 0.072 mmol). After 16 h, all solid materials were removed by filtration. Red selenium (11 mg, 0.14 mmol) was added, and the suspension was warmed to 80 °C for 16 h. After removal of the solvent and treatment with 2 mL of hexane, the insoluble substances were removed by filtration over Celite. Crystallization at −30 °C from hexane yielded 5 mg (0.006 mmol, 8%) of the product.

^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 4.70−4.69 (m, 4H, $\mathrm{C_5H_4}$), 4.54−4.53 (m, 4H, $\mathrm{C_5H_4}$), 1.41 (s, 36H, *t*-Bu, $^3J_{\mathrm{Sn-H}}$ = 75, 78 Hz) ppm. ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 77.45, 73.05, 72.66, 32.34, 31.32 ppm. ^{119}Sn NMR (149 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 26.27 (s, $^2J_{\mathrm{Sn-Sn}}$ = 220 Hz) ppm. Anal. Calcd for $\mathrm{C_{26}H_{44}RuSeSn_2}$ (778.0): C, 40.34; H, 5.73. Found: C, 41.13; H, 5.44.

$[\mathrm{Os}(\eta^5\text{-}\mathrm{C_5H_4})_2\mathrm{Sn_2}\text{-}t\text{-}\mathrm{Bu_4S}]$ (15). (a) **11** (30 mg, 0.038 mmol) in 1 mL of $\mathrm{C_6D_6}$ was treated with sulfur (2.44 mg, 0.076 mmol). After 6 days at 80 °C, the solvent was removed in vacuo, and the precipitate was treated with 5 mL of hexane and filtered over Celite. After removal of the solvent, 7 mg (0.009 mmol, 22%) of **15** was obtained as a yellow solid. (b) **8** (30 mg, 0.059 mmol) in 1 mL of $\mathrm{C_6D_6}$ was treated with *t*-$\mathrm{Bu_4Sn_2Cl_2}$ (31.7 mg, 0.059 mmol). After 16 h, all solid materials were removed by filtration. Sulfur (4 mg, 0.1 mmol) was added, and the suspension was warmed to 80 °C for 16 h. After removal of the solvent and treatment with 2 mL of hexane, the insoluble substances were removed by filtration over Celite. Storage at −30 °C in hexane yielded 9 mg (0.01 mmol, 19%) of **15** as a white powder.

^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 4.90−4.90 (m, 4H, Cp), 4.68−4.68 (m, 4H, Cp), 1.41 (s, 36H, *t*-Bu, $^3J_{\mathrm{Sn-H}}$ = 74, 78 Hz) ppm. ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 70.40, 67.20, 65.22, 32.33, 31.36 ppm. ^{119}Sn NMR (149 MHz, $\mathrm{C_6D_6}$, 293 K, δ): 26.54 (s, $^2J_{\mathrm{Sn-Sn}}$ = 235 Hz).

$[\mathrm{Os}(\eta^5\text{-}\mathrm{C_5H_4})_2\mathrm{Sn_2}\text{-}t\text{-}\mathrm{Bu_4Se}]$ (16). (a) **11** (30 mg, 0.038 mmol) in 1 mL of $\mathrm{C_6D_6}$ was treated with red selenium (6.0 mg, 0.076 mmol). After 6 days at 80 °C, the solvent was removed in vacuo, and the precipitate was treated with 5 mL of hexane and filtered over Celite. After removal of the solvent, 8 mg (0.009 mmol, 24%) of a yellow solid was obtained. (b) **8** (30 mg, 0.059 mmol) in 1 mL $\mathrm{C_6D_6}$ was treated with *t*-$\mathrm{Bu_4Sn_2Cl_2}$ (31.7 mg, 0.059 mmol). After 16 h, all solid materials were removed by filtration. Red selenium (9.32 mg, 0.072 mmol) was added, and the suspension was warmed to 80 °C for 16 h. After removal of the solvent and treatment with 2 mL of hexane, the insoluble substances were removed by filtration over Celite.

Crystallization at −30 °C from hexane yielded 8 mg (0.009 mmol, 16%) of **16** as a white solid.

^{1}H NMR (400 MHz, C_6D_6, 293 K, δ): 4.89−4.91 (m, 4H, C_5H_4), 4.67−4.68 (m, 4H, C_5H_4), 1.41 (s, 36H, *t*-Bu, $^3J_{Sn-H}$ = 74, 78 Hz) ppm. ^{13}C NMR (100 MHz, C_6D_6, 293 K, δ): 70.41, 67.21, 65.21, 32.33, 31.36 ppm. ^{119}Sn NMR (149 MHz, C_6D_6, 293 K, δ): 26.59 ($^2J_{Sn-Sn}$ = 208 Hz) ppm. Anal. Calcd for $C_{26}H_{40}OsSeSn_2$ (868.0): C, 36.18; H, 5.14. Found: C, 37.18; H, 5.39.

Crystallographic Analysis. The crystal data of **5** was collected using a Bruker X8APEX diffractometer with a CCD area detector and multilayer mirror monochromated Mo Kα radiation. The crystal data of **7**, **8**, **9**, **10**, and **11** were collected using a Bruker X8APEXII diffractometer with a CCD area detector and multilayer mirror monochromated Mo Kα radiation. The structures were solved using direct methods, refined with the ShelX software package[20] and expanded by using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and included in structure factors calculations.

*Crystal Data for **5**.* $C_{44}H_{64}Li_4O_6Ru_2$, M_r = 918.85, colorless block, 0.18 × 0.15 × 0.09 mm^3, triclinic space group $P\bar{1}$, a = 9.964(11) Å, b = 10.737(12) Å, c = 11.29(2) Å, α = 101.23(5)°, β = 98.60(5)°, γ = 111.73(4)°, V = 1067(3) Å^3, Z = 1, ρ_{calcd} = 1.430 g cm^{-3}, μ = 0.752 mm^{-1}, $F(000)$ = 476, T = 293(2) K, R_1 = 0.0422, wR_2 = 0.0737, 4375 independent reflections [$2\theta \le 52.74°$] and 263 parameters.

*Crystal Data for **7**.* $C_{38}H_{62}Li_4N_6Ru_2$, M_r = 832.84, colorless block, 0.31 × 0.25 × 0.18 mm^3, monoclinic space group $P2_1/c$, a = 8.5778(5) Å, b = 17.2387(9) Å, c = 14.0546(8) Å, β = 100.259(2)°, V = 2045.0(2) Å^3, Z = 2, ρ_{calcd} = 1.353 g cm^{-3}, μ = 0.771 mm^{-1}, $F(000)$ = 864, T = 193(2) K, R_1 = 0.0205, wR_2 = 0.0460, 4176 independent reflections [$2\theta \le 52.74°$] and 231 parameters.

*Crystal Data for **8**.* $C_{38}H_{62}Li_4N_6Os_2$, M_r = 1011.10, colorless block, 0.26 × 0.18 × 0.13 mm^3, monoclinic space group $P2_1/c$, a = 8.561(6) Å, b = 17.202(12) Å, c = 14.003(9) Å, β = 100.20(2)°, V = 2030(2) Å^3, Z = 2, ρ_{calcd} = 1.654 g cm^{-3}, μ = 6.287 mm^{-1}, $F(000)$ = 992, T = 193(2) K, R_1 = 0.0273, wR_2 = 0.0480, 4134 independent reflections [$2\theta \le 52.74°$] and 231 parameters.

*Crystal Data for **9**.* $C_{14}H_{20}OsSi_2$, M_r = 434.68, colorless block, 0.05 × 0.05 × 0.05 mm^3, monoclinic space group $P2_1/n$, a = 12.3312(9) Å, b = 8.3327(7) Å, c = 14.8501(12) Å, β = 109.441(4)°, V = 1438.9(2) Å^3, Z = 4, ρ_{calcd} = 2.007 g cm^{-3}, μ = 9.005 mm^{-1}, $F(000)$ = 832, T = 100(2) K, R_1 = 0.0152, wR_2 = 0.0345, 3107 independent reflections [$2\theta \le 53.54°$] and 159 parameters.

*Crystal Data for **10**.* $C_{26}H_{44}RuSn_2$, M_r = 695.06, colorless block, 0.42 × 0.35 × 0.23 mm^3, monoclinic space group $P2_1/n$, a = 16.7387(14) Å, b = 9.1760(7) Å, c = 18.5670(15) Å, β = 110.2720(10)°, V = 2675.1(4) Å^3, Z = 4, ρ_{calcd} = 1.726 g cm^{-3}, μ = 2.420 mm^{-1}, $F(000)$ = 1376, T = 100(2) K, R_1 = 0.0143, wR_2 = 0.0489, 5707 independent reflections [$2\theta \le 53.62°$] and 274 parameters.

*Crystal Data for **11**.* $C_{26}H_{44}OsSn_2$, M_r = 784.19, colorless block, 0.23 × 0.16 × 0.06 mm^3, monoclinic space group $P2_1/n$, a = 16.831(11) Å, b = 9.216(6) Å, c = 18.629(12) Å, β = 110.178(15)°, V = 2712(3) Å^3, Z = 4, ρ_{calcd} = 1.920 g cm^{-3}, μ = 6.510 mm^{-1}, $F(000)$ = 1504, T = 100(2) K, R_1 = 0.0289, wR_2 = 0.0450, 5667 independent reflections [$2\theta \le 53.18°$] and 274 parameters.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data (CIF) for compounds **5** and **7**−**11**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC-929183 (**6**), -929186 (**7**), -929184 (**8**), -928379 (**9**), -929185 (**10**) and -929182 (**11**) 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.

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Notes

The authors declare no competing financial interest.

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