

Radical-Type Reactivity of Metalla[1.1.1]**propellanes of Group 14**: Syntheses, Structures, and Reduction Chemistry of Transition Metal-Terminated Bicyclo[1.1.1]pentastannanes

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Two selected metalla[1.1]propellanes of group 14, Sn_5Dep_6 (1) and Ge_5Mes_6 (2) (Dep = 2,6- $Et_2C_6H_3$, Mes = 2,4,6-Me_3C_6H_2), were reacted with $[FeCp(CO)_2]_2$ and $[RuCp(CO)_2]_2$. While 2 did not show any reaction with $[FeCp(CO)_2]_2$ or did not lead to any isolable product in the case of $[RuCp(CO)_2]_2$, the tin propellane 1 quantitatively (monitored by ¹H NMR) afforded the first transition metal-terminated bicyclo[1.1.1]pentastannanes, [{MCp(CO)}_2 $_2$ { μ -Sn₅Dep₆}] (M = Fe (3), Ru = (4), in 68% (3) and 66% (4) isolated yield. This behavior confirms the radical-type reactivity of metalla[1.1.1]propellanes, in this case 1. The title compounds 3 and 4 have been characterized in detail using various methods. X-ray structure analyses corroborated that the two ligand-free bridgehead tin atoms within the Sn₅ scaffold are bonded to the transition metal fragments. Electrochemical studies revealed the reduction chemistry of 3 and 4 in THF solutions to be very interesting. A detailed preparative and electrochemical study, including the isolation and characterization of the monosubstituted cobaltocenium salt $[CoCp_{2}^{+}]^{+}[FeCp(CO)_{2}]\{Sn_{5}Dep_{6}\}]^{-}$ (5), elucidated a complex redox cycle consisting of a cascade of bond-breaking and bond-making processes.

Introduction

Propellane molecules¹ intrigue chemists for a number of reasons, not at least because their core structures resemble *"eponymous macroscopic propellers*".² In particular, the question about the interaction between the bridgehead atoms in propellanes has been extensively discussed in the literature.^{3,4} All efforts are mainly directed toward clarifying fundamental aspects of the nature of the interaction between the "inverted" bridgehead atoms. Even the simplest

all-carbon [1.1.1]propellane⁵ has attracted renewed interest, from both experimentalists⁶ and theoreticians.⁷ For the heavier congeners of carbon, however, the situation is even more complicated.^{3,8} They were shown to be fundamentally different from their carbon counterparts.^{3,9} Several quantum chemical calculations⁴ on these heavy metalla[1.1.1]propellanes $[E_5R_6]$ (E = Si, Ge, Sn; Chart 1) predicted some biradical character of the ground state and that "it would be misleading to represent the structure by drawing a line between the bridgehead atoms".^{4a} Clearly, the inherent singlet ground state of these species points toward noticeable $E_{b} \cdots E_{b}$ interactions, but it appears that this interaction is perturbed to such an extent ("stretched bonds") that quantum chemistry provides evidence for some biradicaloid¹⁰ characteristics. This nicely illustrates the continuous nature¹¹ of the conversion of an ordinary closed-shell molecule into a biradicaloid and eventually into a "perfect" biradical¹² by

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⁽¹⁾ Wiberg, K. B. Chem. Rev. 1989, 89, 975.

⁽²⁾ Yeston, J. Science 2009, 323, 563.

⁽³⁾ Breher, F. Coord. Chem. Rev. 2007, 251, 1007.

 ^{(4) (}a) Schleyer, P.; von, R.; Janoschek, R. Angew. Chem. 1987, 99,
 1312; Angew. Chem., Int. Ed. 1987, 26, 1267. (b) Schoeller, W. W.;
 Dabisch, T.; Busch, T. Inorg. Chem. 1987, 26, 4383. (c) Nagase, S.; Kudo, T. Organometallics 1987, 6, 2456. (d) Nagase, S.; Kudo, T. Organometallics 1988, 7, 2534. (e) Nagase, S. Polyhedron 1991, 10, 1299. (f) Gordon, M. S.; Nguyen, K. A.; Carroll, M. T. *Polyhedron* **1991**, *10*, 1247. (g) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem.* **1991**, *103*, 916; *Angew. Chem.*, *Int. Ed.* **1991**, *30*, 902. (h) Gallego-Planas, N.; Whitehead, M. A. J. Mol. Struct. (THEOCHEM) 1992, 260, 419. (i) Gallego-Planas, N.; Whitehead, M. A. J. Mol. Struct. (THEOCHEM) 1997, 391, 51. (j) Holder, A. J.; Earley, C. W. J. Mol. Struct. (THEOCHEM) 1993, 281, 131.

^{(5) (}a) Wiberg, K. B.; Walker, F. H. J. Am. Chem. Soc. 1982, 104, 5239. (b) Semmler, K.; Szeimies, G.; Belzner, J. J. Am. Chem. Soc. 1985, 107, 6410. (c) Levin, M. D.; Kaszynski, P.; Michl, J. Chem. Rev. 2000, 100, 169.

^{(6) (}a) Messerschmidt, M.; Scheins, S.; Grubert, L.; Pätzel, M.; Szeimies, G.; Paulmann, C.; Luger, P. Angew. Chem. 2005, 117, 3993; Angew. Chem., Int. Ed. 2005, 44, 3925. (b) Coppens, P. Angew. Chem. 2005, 117, 6970; Angew. Chem., Int. Ed. 2005, 44, 6810.

^{(7) (}a) Wu, W.; Gu, J.; Song, J.; Shaik, S.; Hiberty, P. C. Angew. Chem. 2009, 121, 1435; Angew. Chem., Int. Ed. 2009, 48, 1407. (b) Shaik, S.; Danovich, D.; Wu, W.; Hiberty, P. C. Nat. Chem. 2009, 1, 443.

^{(8) (}a) Grützmacher, H.; Breher, F. Angew. Chem. 2002, 114, 4178; Angew. Chem., Int. Ed. 2002, 41, 4006. (b) Karni, M.; Apeloig, Y.; Kapp, Vice and State an

Comm. Inorg. Chem. 2009, 30, 131.

^{(10) &}quot;A biradicaloid is a closed shell species derived from a singlet biradical by a weak interaction between the radical centers." Dewar, M. J. S.; Healy, E. F. Chem. Phys. Lett. 1987, 141, 521.
(11) Bonačić-Koutecký, V.; Koutecký, J.; Michl, J. Angew. Chem.

^{1987, 99, 216.;} Angew. Chem., Int. Ed. Engl. 1987, 26, 170.

^{(12) (}a) Borden, W. T. In Enzyclopedia of Computational Chemistry; Schleyer, P. v. R., Ed.; Wiley: New York, 1998; p 708. (b) Biradicals; Borden, W. T., Ed.; Wiley: New York, 1982. (c) Berson, J. A. Acc. Chem. Res. **1997**, 30, 238. (d) Dougherty, D. A. Acc. Chem. Res. **1991**, 24, 88. (e) Salem, L.; Rowland, C. Angew. Chem. 1972, 84, 86; Angew. Chem., Int. Ed. 1972, 11, 92; (f) Borden, W. T.; Iwamura, H.; Berson, J. A. Acc. Chem. Res. 1994, 27, 109. (g) Rajca, A. Chem. Rev. 1994, 94, 871.



the introduction of a suitable perturbation. Apart from fundamental aspects addressing the bonding in biradicaloid species, they have attracted considerable recent interest due to the unusual reactivity involving main group elements.^{9,13}

Although numerous quantum chemical calculations have been performed for metalla[1.1.1]propellanes^{3,4} as well as hetero[1.1.1]propellanes,¹⁴ synthetically accessible and structurally characterized species are very rare. Apart from closely related cluster compounds [E₈R₆] containing silicon,¹⁵ germanium,¹⁶ and tin,¹⁷ seminal work was performed by Sita and co-workers in the early 1990s.¹⁸ They succeeded in isolating the pentastanna[1.1.1]propellane Sn_5Dep_6 (Dep = 2,6-Et₂C₆H₃) and a further derivative.¹⁹ Analogous group 14 metalla[1.1.1]propellanes such as Sn_5R_6 (R = 2,6-(*i*-PrO)₂- C_6H_3) and $Ge_2{Sn(Cl)R}_3$ (R = 2,6-Mes₂C₆H₃; Mes = 2,4,6-Me₃C₆H₂) were reported later by Drost²⁰ and Power,²¹ respectively. To shed more light on the accessibility and stability of metallapropellanes of this type and to study fundamental aspects of their bonding, we have recently investigated the Messubstituted pentagerma-²² and pentasila[1.1.1]propellanes²³ in combined experimental and quantum chemical studies. In each case it was found that the central distance between the "naked" bridgehead atoms (E_b) within the [1.1.1] scaffold of heavy

(13) Review on REER (E = group 14 element) showing in some cases biradicaloid behavior: Power, P. P. Organometallics **2007**, *26*, 4362.

(14) See for example: (a) Nguyen, K. A.; Carroll, M. T.; Gordon, M. S. J. Am. Chem. Soc. 1991, 113, 7924. (b) Sandström, N.; Ottosson, H. Chem.—Eur. J. 2005, 11, 5067. (c) Wang, Y.; Ma, J.; Inagaki, S. Tetrahedron Lett. 2005, 46, 5567. (d) Ebrahimi, A.; Deyhimi, F.; Roohi, H. J. Mol. Struct. (THEOCHEM) 2003, 626, 223. (e) Kitchen, D. B.; Jackson, J. E.; Allen, L. C. J. Am. Chem. Soc. 1990, 112, 3408.

(15) (a) Fischer, G.; Huch, V.; Mayer, P.; Vasisht, S. K.; Veith, M.; Wiberg, N. *Angew. Chem.* **2005**, *117*, 8096; *Angew. Chem., Int. Ed.* **2005**, *44*, 7884. For a Si cluster of the formula $Si_5Tip_6(Tip = 2,4,6-i-Pr_3C_6H_2)$ consisting of only one ligand-free Si atom see: (b) Scheschkewitz, D. *Angew. Chem.* **2005**, *117*, 3014; *Angew. Chem., Int. Ed.* **2005**, *44*, 2954.

(16) (a) Schnepf, A.; Köppe, R. Angew. Chem. 2003, 115, 940; Angew. Chem., Int. Ed. 2003, 42, 911. (b) Schnepf, A.; Drost, C. Dalton Trans.
 2005, 3277. See also: (c) Schnepf, A. Chem. Soc. Rev. 2007, 36, 745.

 (17) (a) Wiberg, N.; Lerner, H.-W.; Wagner, S.; Nöth, H.; Seifert, T.
 Z. Naturforsch. B 1999, *54*, 877. (b) See also: Wiberg, N.; Power, P. P. In Molecular Clusters of the Main Group Elements; Driess, M.; Nöth, H., Eds.; Wiley-VCH: Weinheim, 2004.

(19) (a) Sita, L. R.; Kinoshita, I. J. Am. Chem. Soc. 1992, 114, 7024.
(b) Sita, L. R.; Kinoshita, I. J. Am. Chem. Soc. 1991, 113, 5070. (c) Sita, L. R.; Kinoshita, I. J. Am. Chem. Soc. 1990, 112, 8839. (d) Sita, L. R.;

Bickerstaff, R. D. J. Am. Chem. Soc. 1989, 111, 6454.

propellanes is considerably stretched by between 13% and 20% of a regular E–E single bond. On the basis of this elongation, these molecules have frequently been described as singlet biradicaloids.³ Although highly correlated CASSCF calculations predicted the biradicaloid character²⁴ to be fairly small, experimental studies indeed revealed some radical-type reactivity.^{22,23} To the best of our knowledge, no further experimental studies on the biradicaloid behavior of these species are known. Only Sita et al. studied the reactivity of Sn₅Dep₆ toward MeLi and MeI and observed formation of unstable adducts.¹⁹

Results and Discussion

In order to extend our studies in the area of biradicaloids, we have investigated the reactivities of some selected homonuclear propellanes in homolytic bond cleavage reactions by using transition metal precusors containing M-M bonds. For this case study we used Sn_5Dep_6 (1)¹⁹ and Ge_5Mes_6 (2)²² and reacted both with [FeCp(CO)₂]₂ and [RuCp(CO)₂]₂. The latter were chosen because of the moderate metalmetal bond strengths²⁵ and their well-known electrochemical properties.²⁶ In addition, we have a general interest in metalterminated clusters/cage compounds for studies addressing electronic communications between metal centers. Metalterminated bicyclo[1.1.1]pentastannanes are promising candidates for such investigations since the metal atoms are arranged in close spatial proximity.

In general, homolytic M–M bond activation of these transition metal precursors and addition of two $[MCp(CO)_2]^{\bullet}$ fragments to the bridgehead atoms should strongly depend on the amount of interaction between the bridghead atoms in 1 and 2. In terms of bond energies alone, it is the subtle balance between M–M and $E_b \cdots E_b$ bond cleavage and M–E bond formation that governs the overall reactivity. On the basis of our experimental and theoretical findings,^{22,23} we expected the tin propellane 1 to be more reactive in these types of reactions, although differences in the steric accessibility of the bridgeheads should not be neglected. Furthermore, we speculated that the general reactivity of metallapropellanes might be influenced by light due to the facile accessibility of the excited singlet (¹A₂) and triplet states (³A₂) in the UV/vis region.^{22,23}

For this comparative case study, the tin compound Sn_5Dep_6 (1), known from the seminal work of Sita et al.,¹⁹ was prepared in a modified procedure by reacting the cyclotristannane Sn_3Dep_6 with 6 equiv of lithium chunks and 3 equiv of $SnCl_2$ as additional Sn source in THF as solvent. We optimized the purification steps and rerecorded the UV/vis spectrum of 1 in pentane (Figure 1). The absorption bands were assigned by using our previous TD-DFT calculations.^{22,27} The lowest energy absorbance at $\lambda_{max} = 558$ nm belongs to the transition HOMO (e) \rightarrow LUMO (a₂)

⁽¹⁸⁾ Reviews: (a) Sita, L. R. Adv. Organomet. Chem. 1995, 38, 189.
(b) Sita, L. R. Acc. Chem. Res. 1994, 27, 191.

⁽²⁰⁾ Drost, C.; Hildebrand, M.; Lönnecke, P. Main Group Met. Chem. 2002, 25, 93.

^{(21) (}a) Richards, A. F.; Brynda, M.; Power, P. P. *Organometallics* **2004**, *23*, 4009. See also: (b) Richards, A. F.; Brynda, M.; Olmstead, M. M.; Power, P. P. *Organometallics* **2004**, *23*, 2841.

⁽²²⁾ Nied, D.; Klopper, W.; Breher, F. Angew. Chem. 2009, 121, 1439; Angew. Chem., Int. Ed. 2009, 48, 1411.

⁽²³⁾ Nied, D.; Köppe, R.; Klopper, W.; Schnöckel, H.; Breher, F. J. Am. Chem. Soc. 2010, 131, 10264.

⁽²⁴⁾ It is important to note that the quantity of radical *character* is fundamentally different from the theory of radical *behavior*. Radical character serves as a theoretical measure, whereas radical behavior is experimentally observed for such species.

^{(25) (}a) Bitterwolf, T. E. Coord. Chem. Rev. 2000, 206–207, 419.
(b) Bitterwolf, T. E. J. Organomet. Chem. 2004, 689, 3939. (c) Meyer, T. J.; Caspar, J. V. Chem. Rev. 1985, 85, 197. (d) Szaciłowski, K.; Macyk, W.; Stochel, G.; Stasicka, Z.; Sostero, S.; Traverso, O. Coord. Chem. Rev. 2000, 208, 277.

^{(26) (}a) Dessy, R. E.; Weissman, P. M.; Pohl, R. L. J. Am. Chem. Soc.
1966, 88, 5117. (b) Miholová, D.; Vlček, A. A. Inorg. Chim. Acta 1980, 41, 119. (c) Bullock, J. P.; Palazotto, M. C.; Mann, K. R. Inorg. Chem. 1991, 30, 1284. (d) Pugh, J. R.; Meyer, T. J. J. Am. Chem. Soc. 1992, 114, 3784.



Figure 1. Experimental UV/vis spectrum of 1 in pentane and TD-DFT-calculated UV/vis transitions of A₂ (HOMO-1 \rightarrow LUMO transition) and E symmetry (HOMO \rightarrow LUMO transition). The possible ${}^{3}A_{2}$ transition is marked by an asterisk.

(97.8%, E in Figure 1) and the characteristic band at $\lambda = 381$ nm to the transition HOMO-1 (a₁) \rightarrow LUMO (a₂) (67.9%, A_2 in Figure 1).²² The broad shoulder located around 500 nm can most likely be attributed to the triplet transition $({}^{3}A_{2}, HOMO-1 (a_{1}) \rightarrow LUMO (a_{2}))$, for which we calculated a value of $\lambda_{calcd} = 522.1$ nm. These transitions are usually not visible in the UV/vis spectrum but obviously are allowed due to spin-orbit coupling effects for the heavier propellanes. This effect is also known for other metalla-[1.1.1]propellanes of group 14.28

1 and 2 were reacted with the iron and ruthenium compounds [MCp(CO)₂]₂ in the stoichiometric ratio of 1:1 in C₆D₆ at room temperature. The germanium compound 2 did not show any reaction with $[FeCp(CO)_2]_2$. The analogous reaction using the ruthenium precursor did not lead to any isolable product. The tin popellane 1, however, quantitatively (monitored by ¹H NMR) afforded the first transition metalterminated bicyclo[1.1.1]pentastannanes,²⁹ [{MCp(CO)₂}₂- $\{\mu$ -Sn₅Dep₆ $\}$] (M = Fe (3), Ru = (4), Scheme 1) in 68% (3) and 66% (4) isolated yield (reactions in THF solution).³⁰ Analytically pure crystals were obtained from toluene/ acetonitrile solutions. It is important to note that no reaction is observed (or very slow) in the absence of daylight. We are not able to comment on whether this enhanced reactivity is due to the excited singlet or triplet A_2 state of 1 or the Nied et al.

photochemistry of the M-M bonded bimetallic transition metal precursors.³¹ This is work in progress. Furthermore, we noticed that only decomposition products are obtained in these reactions in cases where we used light sources of much higher intensities (i.e., $\lambda < 400$ nm, 200 W).

The title compounds 3 and 4 are soluble in toluene, diethyl ether, and tetrahydrofuran and moderately soluble in pentane. The thermally stable (mp > 250 °C (dec)) dark green solids form almost black crystals when recrystallized from toluene/acetonitrile. In crystalline form, both compounds can shortly be handled under aerobic conditions. Yellowgreen solutions of 3 and 4, however, are sensitive to oxygen and/or moisture. In addition, both solutions are unstable at room temperature if stored for longer periods (some weeks), even under argon. The UV/vis spectra (THF) showed characteristic absorptions at $\lambda_{max}(3) = 436, \sim 330$ (sh), 254, and 212 nm and $\lambda_{\text{max}}(4) = 414$, ~350 (sh), 254 (sh), and 213 nm (see Supporting Information).³² IR spectroscopic investigations exposed in each case two characteristic vibrations in the CO region centered at $\nu = 1985$, 1947 cm⁻¹ (3) and 2003, 1958 cm^{-1} (4), respectively. Most revealingly, no bridging CO entities could be detected, which is consistent with the structures proposed in Scheme 1.33

The ¹H NMR spectra of **3** and **4** in C_6D_6 solutions further corroborated the formation of metal-terminated tin clusters. For instance, we detected two triplets for nonequivalent Me protons with chemical shifts of $\delta = 0.81$ and 1.00 ppm (3) and $\delta = 0.81$ and 1.01 ppm (4). The corresponding methylene protons of the ethyl groups appear around $\delta \approx 2.0$ and 3.0-3.1 ppm, alongside the aromatic protons of the aryl substituent ($\delta = 7.0-7.2$ ppm). The Cp rings show sharp singlets at $\delta = 4.54$ (3) and 4.91 ppm (4). The structural integrity in solution was confirmed by ¹H-¹H NOESY experiments, showing characteristic NOEs between the Cp^H and the protons of the CH_2 and CH_3 entities (see Supporting Information).

For tin clusters of this type, ¹¹⁹Sn NMR spectroscopy is a powerful tool to determine the connectivity between the metal atoms. Both title compounds were analyzed in detail, showing in each case the expected 119 Sn $^{-119}$ Sn and 119 Sn $^{-117}$ Sn couplings between the bridgehead (Sn_b) and bridging (Sn_{br}) tin atoms. A typical example of an experimental ¹¹⁹Sn NMR spectrum, showing also the simulated satellites,³⁴ is depicted in Figure 2. Of particular interest in this case was to compare the $J(Sn_b \cdots Sn_b)$ coupling constant in 1 with those observed for 3 and 4. Since both bridgehead atoms are bonded to the metal fragments and, accordingly, the formal bonding interaction between them is eliminated, couplings may still arise either through the bridging {SnDep₂} units or via

⁽²⁷⁾ DFT calculations on D_3 symmetric model compounds predicted in each case the following order of the frontier molecular orbitals: (a) HOMO-1: $E_b \cdots E_b$ bonding orbital of a_1 symmetry; (b) HOMO: degenerate set of $E_b - E_{br}$ cluster bonding orbitals of e symmetry; (c) LUMO: $E_b \cdots E_b$ antibonding orbital of a_2 symmetry (E_b : bridgehead (28) Nied, D.; Klopper, W.; Breher, F. Manuscript in preparation.
(29) For a closely related bicyclo[1.1.1]pentasilane derivative see:

⁽a) Kabe, Y.; Kawase, T.; Okada, J.; Yamashita, O.; Goto, M.; Masamune, S. *Angew. Chem.* **1990**, *102*, 823; *Angew. Chem., Int. Ed.* **1990**, *29*, 794. See also for some tricyclo[2.1.0.0^{2.5}]pentane derivatives: (b) Lee, V. A.; Yokoyama, T.; Takanashi, K.; Sekiguchi, A. *Chem.*(c) Lee, V. A.; Yokoyama, T.; Takanashi, K.; Sekiguchi, A. *Chem.*(c) Lee, V. A.; Ichinoe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* 2002, *124*, 9962.
(30) Moreover, ¹H NMR spectroscopic monitoring of a reaction of 1

with a mixture of $[FeCp(CO)_2]_2$ and $[RuCp(CO)_2]_2$ in C_6D_6 provided the typical signals of the symmetrical products 3 and 4. Furthermore, we observed via ²D NMR spectra the unsymmetrical, heterobimetallic Fe/Ru adduct, which exhibits the same ¹H NMR chemical shifts (see Supporting Information).

⁽³¹⁾ Photochemical investigations on M-M bonded bimetallic Cp/ carbonyl compounds like $[MCp(CO)_2]_2$ showed M-M bond homolysis and CO-loss photochemical channels. It is by far out of the scope of this article to cite all original papers dealing with the photochemistry of these types of molecules. The reader is referred to excellent review articles cited in ref 25. We thank one referee for helpful comments.

⁽³²⁾ Unfortunately, 3 and 4 could not be analyzed by mass spectrometry because the electron impact (EI) ionization method tends to result in decomposition of the compounds. The smoother electrospray ionization method (ESI), however, was shown to be too gentle to ionize the compounds.

⁽³³⁾ For comparison: ν (CO) for [FeCp(CO)₂]₂ = 1958, 1936, 1771, 1757 cm⁻¹; ν(CO) for [RuCp(CO)₂]₂ = 1957, 1940, 1773, 1761 cm⁻¹. Fischer, R. D.; Vogler, A.; Noack, K. J. Organomet. Chem. **1967**, 7, 135.

^{(34) (}a) Programs WinNMR and WinDaisy, Bruker Daltonik: Bremen, 1999. (b) Hägele, G.; Engelhardt, M.; Boenigk, W. Simulation und Automatisierte Analyse von NMR-Spektren; VCH: Weinheim, 1987.



Scheme 1. Reactivity of the Metalla[1.1.1]propellanes 1 and 2; Synthesis of the Transition Metal-Terminated Bicyclo[1.1.1]pentastannanes 3 (M = Fe) and 4 (M = Ru)^{*a*}





Figure 2. Experimental ¹¹⁹Sn NMR spectrum of 4 (C_6D_6 , bottom) and the simulated ³⁴ coupling constants (top traces); only the satellites are shown in the simulated spectra. See also Table 1 and the main text for further details.

"through-space interactions" due to the close spatial proximity of the bridgeheads.³⁵

Table 1 summarizes and compares the coupling constants observed for **3** and **4** with those reported for **1**. Compared to the latter, we observed smaller values for the one-bond couplings ${}^{1}J({}^{119}\mathrm{Sn_b}-{}^{117/119}\mathrm{Sn_{br}})$, which in turn strongly vary

 Table 1. Tin Coupling Constants [Hz] for 3 and 4; Those Reported for 1 Are Given for Comparison

coupling	3	4	1 ¹⁹
$^{1}J(^{119}\mathrm{Sn_{b}}-^{117}\mathrm{Sn_{br}})$	1623	1230	3975
$^{1}J(^{119}\text{Sn}_{b}-^{119}\text{Sn}_{br})$	1699	1291	4159
$^{2}J(^{119}Sn_{b}\cdots ^{117}Sn_{b})$	2908	3896	8145 ^a
$^{2}J(^{119}\mathrm{Sn}_{\mathrm{br}}-^{117}\mathrm{Sn}_{\mathrm{br}})$	1270	1348	262

^a Remeasured for completeness.

⁽³⁵⁾ Hoffmann, R. Acc. Chem. Res. 1971, 4, 1.



Figure 3. Molecular structures of **3** (a) and **4** (b). Displacement ellipsoids are drawn at the 30% probability level; hydrogen atoms have been omitted and carbon atoms of the 2,6-Et₂C₆H₃ substituents have been drawn with arbitrary radii for clarity. Selected bond lengths [pm] and angles [deg]: (**3**) Sn₃...Sn₅ 357.3(1), Sn₁–Sn₃ 286.1(1), Sn₂–Sn₃ 281.8(1), Sn₃–Sn₄ 283.2(1), Sn₁–Sn₅ 284.4(1), Sn₂–Sn₅ 284.5(1), Sn₄–Sn₅ 287.4(1), Fe₁–Sn₅ 258.8(1), Fe₂–Sn₃ 256.5(1), Fe₋Cp^{Centroid} 171.7, Fe₋CO 174.1, CO 114.7, Sn₋C 217.4(6)–219.9(6); Sn₃–Sn₁–Sn₅ 77.57(1), Sn₃–Sn₂–Sn₅ 78.25(1), Sn₃–Sn₄–Sn₅ 77.55(2), Sn₁–Sn₃–Sn₄ 85.05(1), Sn₁–Sn₃–Sn₄ 83.09(1), Sn₂–Sn₃–Sn₄ 86.61(1), Sn₂–Sn₅–Sn₄ 85.32(1), C–Sn₋C 106.1; (**4**) Sn₁...Sn₁/ 355.1(1) {357.4(1)}, Sn₁–Sn₂ 283.2(1) {283.7(1)}, Sn₁–Sn₂/2 87.6(1) {285.8(1)}, Sn₁–Sn₃ 283.7(1) {285.2(1)}, Ru₁–Sn₁ 266.3(1) {266.2(1)}, Ru₋Cp^{Centroid} 189.7 {188.3}, Ru₋CO 185.5 {184.6}, CO 114.3 {114.7}, Sn₋C 219.8(7) – 220.6(7) {219.1(7)–220.6(7)}; Sn₁–Sn₂–Sn₁/ 76.96(2) {77.60(3)}, Sn₁–Sn₃–Sn₁/ 77.50(3) {77.74(3)}, Sn₂–Sn₁–Sn₂/ 83.46(2) {85.41(3)}, Sn₃–Sn₁–Sn₂ 86.51(2) {84.72(2)}, C–Sn₋C 102.8 {101.6}; the values given in face brackets correspond to the second molecule in the asymmetric unit; equivalent atoms generated by $-x + {}^{3}/{2}$, y, $-z + {}^{1}/{2}$; Cp^{Centroid} = centroid of the Cp ring.

with the nature of the metal fragments (1623/1699 Hz for **3** vs 1230/1291 Hz for **4**). Interestingly, the two-bond coupling constant ${}^{2}J({}^{119}Sn_{br}-{}^{117}Sn_{br})$ of 1348 Hz for **3** was revealed to be larger than the one-bond coupling ${}^{1}J({}^{119}Sn_{b}-{}^{117}Sn_{br})$ (1230 Hz). The most striking feature, however, is the comparably large coupling between the bridgehead tin atoms, which were found to amount to 2908 (**3**) and 3896 (**4**) Hz (absolute values).

The crystal structure determination of 3 (space group *Iba2*) and 4 $(P2/n)^{36}$ verified the formation of the metalterminated tin clusters (Figure 3).³⁷ Relevant structural parameters are given in the figure caption. As expected, the Sn_5 scaffold consisting of three bridging { $SnDep_2$ } units and two ligand-free bridgehead tin atoms is preserved in both compounds. The latter are coordinated to iron (3) and ruthenium (4), which in turn consist of two CO ligands and one η^5 -coordinated Cp moiety. Most importantly, the central $Sn_b \cdots Sn_b$ distances of 357.3(1) pm (3) and 355.1(1) pm (4) (357.4(1) pm)³⁸ are significantly elongated by ca. 20 pm as compared to the starting material 1. This observation contrasts earlier findings of Sita and co-workers, which showed no structural changes upon MeI addition to the all-tin propellane 1 (cf. 336.1(1) and 336.7(1) pm).¹⁹ In 3 and 4, however, the trigonal bipyramids composed of the five tin atoms are

stretched in the direction of the bridgehead atoms. As a result of this structural distortion, the $Sn_b-Sn_{br}-Sn_b$ angles are increased (77.55(2)–78.25(1)° for **3** and 76.96(2)–77.50(3)° (77.60(3)–77.74(3)°)³⁸ for **4** vs 72.2(1)° for **1**) and the $Sn_{br}-Sn_b-Sn_{br}$ angles of 83.09(1)-86.61(1)° for **3** and 83.46(2)-86.51(2)°(84.35(3)-85.41(3)°)³⁸ for **4** are decreased with respect to the parent propellane **1** (cf. 88.2(1)–89.9(1)°). The transition metal tin bond lengths of 256.5(1) and 258.8(1) pm for Fe–Sn (**3**) and 266.3(1) pm (266.2(1) pm)³⁸ for Ru–Sn (**4**) fall within the expected ranges.³⁹

Since redox-active transition metal atoms are present in both compounds, it was of interest to study their electrochemical properties using cyclic voltammetry (CV) under strictly anaerobic and dry conditions. In particular, we studied the reduction chemistry of **3** and **4** in THF solutions. As can be seen from Figure 4, the CVs of both compounds were revealed to be much more complicated than anticipated. The cyclovoltammogram of **3** shows three irreversible reduction waves centered at $E_{\rm pc} = -1.90, -2.24$, and -2.93 V. On the basis of the peak current intensities it appears that the first two waves correspond to one-electron processes, while the last event comprises a two-electron reduction process (for further studies see below). Furthermore, a broad oxidation event between -3.0 and -2.5 V is observed in the return sweep, followed by two electrochemically irreversible

⁽³⁶⁾ Hahn, T. International Tables for Crystallography, Vol. A, 5th ed.; Kluwer Academic Publishers: Dordrecht, 2002.

⁽³⁷⁾ For a closely related structure, [{CpFe(CO)₂}₂Sn₂Fe₃(CO)₉], see: McNeese, T. J.; Wreford, S. S.; Tipton, D. L.; Bau, R. J. Chem. Soc., Chem. Commun. **1977**, 390.

⁽³⁸⁾ Values for the second independent molecule in the asymmetric unit are given in brackets.

⁽³⁹⁾ See for instance Sn-Fe: 254.5 pm in [Cp(py)(CO)Fe-SnEt₃]. Itazaki, M.; Kamitani, M.; Nakazawa, H. Acta Crystallogr. Sect. E 2008, 64, m1578. Sn-Ru: 265.0 pm in [Cp₂Ru₂(μ-CH₂)(CO)₂(SnMe₃)₂]. Akita, M.; Hua, R.; Oku, T.; Tanaka, M.; Moro-oka, Y. Organometallics 1996, 15, 4162.

Scheme 2. Synthesis of 5





Figure 4. Cyclic voltammetry of **3** at 15 °C in THF vs the Fc/Fc^+ couple. Scan rate 100 mV s⁻¹, Pt/[(nBu)_4N]PF₆/Ag. All redox waves show completely the same behavior in a second CV cycle; only one is shown here for clarity. The oxidation wave of very small intensity located at ca. -2.4 V can most likely be attributed to the reoxidation of trace amounts of [1]²⁻ (see text).

oxidations at $E_{pa} = -1.61$ and -1.00 V (Figure 4). To put this electrochemical behavior into perspective, it is instructive to recall that metalla[1.1.1]propellanes such as 1 show two quasi-reversible one-electron reduction waves at $E_{1/2}^0 =$ -1.96 and -2.48 V (vs Fc/Fc⁺). These redox couples correspond to the processes $1 + e^- \Rightarrow [1]^{--}$ and $[1]^{--} + e^- \Rightarrow [1]^{2^-}$. Furthermore, it is important to note that all redox waves of **3** show completely the same behavior in a second CV cycle, which means that the overall reduction is chemically reversible, consisting of several electrochemically irreversible couples.⁴⁰ The electrochemistry of **4** is very similar (see the Supporting Information).

In order to shed more light on this fascinating electrochemistry, we performed some preparative reductions. As a suitable entry point we decided to examine the first reduction event ($E_{pc} = -1.90$ V). To this end, we treated a THF solution of **3** with a slight excess of CoCp*₂ (Cp* = C₅Me₅; $E^{0}_{1/2} = -1.94$ V vs Fc/Fc⁺), which resulted in a quantitative formation of the cobaltocenium salt [CoCp*₂]⁺[{CpFe $(CO)_2$ {Sn₅Dep₆]⁻ (**5**) and [CpFe(CO)₂]₂ (Scheme 2). For the isolation of **5**, the solvent THF was removed *in vacuo* and the crude product washed with toluene in order to remove the excess CoCp*₂ and the byproduct [FeCp(CO)₂]₂. Recrystallization from acetonitrile at -40 °C affords analytically pure, dark red crystals of **5** (yield 85%; mp 245 °C (dec)), which are soluble in THF and sparingly soluble in acetonitrile and DMSO.

The ¹H NMR spectrum of 5 in DMSO- d_6 was consistent with a monosubstituted cluster: the CH₃ protons of the Dep ligand appear as four triplets and the methylene protons as several sets of multiplets. Alongside the aryl ring protons, the Cp entity was detected as a singlet at $\delta = 4.68$ ppm. In contrast to 3 and 4, crystals of 5 are extremely sensitive to air and moisture. Solutions of 5 immediately decolorize when exposed to air. Furthermore, they turned out to be unstable when stored at room temperature for a prolonged time. Due to the instability of 5 in solution, we were not able to record satisfactory ¹³C and ¹¹⁹Sn NMR spectra. However, the elemental analysis of bulk 5 was consistent with the composition $[CoCp_2^*][{FeCp(CO)_2}{Sn_5Dep_6}]$. In the ESI mass spectrum we found the correct molecular ion envelope and isotope distribution centered at m/z 1569.08 (ion envelope for the anionic cluster, see Figure 5). The UV/vis spectrum of 5 in THF shows characteristic bands at $\lambda_{\text{max}} = 492, 294, 264$ (sh), and 214 nm (see the Supporting Information).

An X-ray structure analysis was conducted on single crystals of **5** (space group *Pbca*),³⁶ unambiguously confirming the formation of the cobaltocenium salt of the anionic cluster. As shown in Figure 6, only one of the bridgehead tin atoms is bonded to the [FeCp(CO)₂] entity. The tin cage is stretched along the Sn_b···Sn_b-Fe vector, which leads to a very large distance of d = 380.8(1) pm between the Sn_b atoms. The Sn-Fe bond (267.3(1) pm) is 11 pm longer than that found for **3**. Other relevant distances and angles are given in the figure caption.

With this first result in hand we were able to explain the redox processes of **3** as follows: the first irreversible reduction of **3** at $E_{pc} = -1.90$ V (Figure 4) can be assigned to the splitting of one Sn–Fe bond, which results in the formation of **5** and "[FeCp(CO)₂]*". At this potential, the resulting fragment "[FeCp(CO)₂]*" immediately dimerizes to form a half of an equivalent of [FeCp(CO)₂]₂. This oneelectron process is depicted in eq 1. Since the electrochemistry of [FeCp(CO)₂]₂ is very well known,²⁶ the second reduction process in the CV of **3** ($E_{pc} = -2.24$ V) can be assigned to the reductive splitting of [FeCp(CO)₂]₂ into two anionic [FeCp(CO)₂]⁻ fragments (overall a one-electron

^{(40) (}a) Geiger, W. E. Organometallics **2007**, *26*, 5738. (b) Evans, D. H. Chem. Rev. **2008**, *108*, 2113.



Figure 5. Electrospray ionization (ESI) mass spectrum of 5 (inset: enlargement of the experimental and simulated molecular ion envelope for $[{FeCp(CO)_2} {Sn_5Dep_6}]^-)$. Since 5 is very sensitive, the ion signals of low intensities are due to decomposition products.



Figure 6. Molecular structure of **5**. Displacement ellipsoids are drawn at the 30% probability level; the hydrogen atoms have been omitted and carbon atoms of $2,6-Et_2C_6H_3$ and Cp* ligands have been drawn with arbitrary radii for clarity. Selected bond lengths [pm] and angles [deg]: Sn1...Sn2 380.8(1), Sn1–Sn3 289.0(1), Sn1–Sn4 285.8(1), Sn1–Sn5 288.8(1), Sn2–Sn3 285.0(1), Sn2–Sn4 285.9(1), Sn2–Sn5 287.3(1), Fe1–Sn1 267.3(1), Sn2...Co1 606.2, Fe1–Cp^{Centroid} 172.1, Co–Cp^{Centroid} 163.1, Fe–CO 173.6, CO 115.3, Sn–C 219.3(6)–221.2(6); Sn1–Sn3–Sn2 83.11(1), Sn1–Sn4–Sn2 83.53(1), Sn1–Sn5–Sn2 82.76(1), Sn3–Sn1–Sn4 80.05(1), Sn3–Sn1–Sn5 80.12(1), Sn4–Sn1–Sn5 81.23(1), Sn3–Sn2–Sn4 80.72(1), Sn3–Sn2–Sn5 81.06(1), Sn4–Sn2–Sn5 81.47(1), C–Sn–C 103.7; Cp^{Centroid} = centroid of the Cp ring.

process, eq 2). Since it is reasonable to assume that the most negative reduction process at $E_{\rm pc} = -2.93$ V again leads to a splitting of the Fe–Sn bond in **5**, formation of $[1]^{2-}$, and a reduction of the resulting "[FeCp(CO)₂]*" fragment at this potential, we propose eq 3 for this two-electron process. Furthermore, we assume that the broad oxidation peak around $E_{\rm pa} \approx -2.75$ V in the return sweep can be assigned to



Figure 7. Cyclic voltammetry of **5** at 15 °C in THF vs Fc/Fc⁺. Scan rate: 100 mV s⁻¹, Pt/[$(nBu)_4N$]PF₆/Ag. All redox waves show completely the same behavior in a second CV cycle; only one is shown here for clarity. CoCp₂*: quasi-reversible redox waves of the CoCp₂* entity. Relevant redox processes of the anion of **5** are marked with an asterisk (note the similarities to those observed for **3**, Figure 4).

the re-formation of 5 (eq 4; reverse of eq 3). The oxidation event at $E_{pa} = -1.61$ V belongs to the reoxidation of [FeCp(CO)₂]⁻, as known from the literature (eq 5).²⁶

$$3 + e^- \rightarrow 5 + \frac{1}{2} [FeCp(CO)_2]_2 \quad E_{pc} = -1.90 \text{ V} \quad (1)$$

$$\frac{1}{2} [\text{FeCp(CO)}_2]_2 + e^- \rightarrow [\text{FeCp(CO)}_2]^- \quad E_{\text{pc}} = -2.24 \text{ V}$$
(2)

5+2e⁻ →
$$[1]^{2^-}$$
 + $[FeCp(CO)_2]^ E_{pc} = -2.93 V$
(3)

$$[1]^{2^{-}} + [FeCp(CO)_2]^{-} \rightarrow 5 + 2e^{-} \quad E_{pa} \approx -2.75 \text{ V} \quad (4)$$

$$[\operatorname{FeCp}(\operatorname{CO})_2]^- \to \frac{1}{2} [\operatorname{FeCp}(\operatorname{CO})_2]_2 + e^- \quad E_{\operatorname{pa}} = -1.61 \text{ V}$$
(5)

So far, all proposed equations comprise only diamagnetic species. This is in accord with supplementary EPR studies. As expected, we were not able to detect any paramagnetic species by repeated *in situ* reduction of **3** within an EPR tube. In order to fully explore the CV of **3** and to bolster the proposed equations, we have investigated the fate of **5** a little further by examining the electrochemistry of the latter. The electrochemical responses of **5** (Figure 7) are very similar to those found for **3**, with some important exceptions: (a) two quasi-reversible redox processes of the CoCp₂* entity are present (i.e., $CoCp_{2}^{*} \rightleftharpoons [CoCp_{2}^{*}]^{+} + e^{-}$, $E^{0}_{1/2} = -1.85$ V; $CoCp_{2}^{*} + e^{-} \leftrightarrows [CoCp_{2}^{*}]^{-}$, $E^{0}_{1/2} = -3.15$ V);⁴¹ (b) the

⁽⁴¹⁾ Braunschweig, H.; Breher, F.; Kaupp, M.; Gross, M.; Kupfer, T.; Nied, D.; Radacki, K.; Schinzel, S. *Organometallics* **2008**, *27*, 6427 (and cited references).



Figure 8. Proposed cascade of bond-breaking and bond-making processes during the chemically reversible though electrochemically irreversible redox cycle of 3. The numbers correspond to the equations given in the text.

redox waves of $[FeCp(CO)_2]_2$ (eq 2) and $[FeCp(CO)_2]^-$ (eq 5) are missing. All other features, i.e., peak current intensities and potentials for 5, directly correspond to those observed for 3. Especially the first reduction peak at $E_{pc} = -1.90$ V, which was assigned to the splitting of one Sn-Fe bond in 3, is also visible in the CV of 5. Furthermore, the so far unexplained irreversible oxidation peak centered at $E_{pa} = -1.0$ V in the CV of 3 is also present in the voltammogram of 5. From these studies it can be concluded that identical tin clusters species must be involved in the electrochemistry of both compounds!

In order to clarify this last piece of the puzzle, we performed some preparative oxidation experiments on an NMR tube scale. The anionic cluster **5** was reacted with 1 equiv of [Fc][PF] (with [PF]⁻ = [Al{OC(CF₃)₃}₄]⁻)⁴² in d_8 -THF. Again, we were not able to detect any paramagnetic species by EPR spectroscopy. Most revealingly, the sample gave clean NMR signals, which were easily assigned to **3** and **1**. Hence, the most positive oxidation event at $E_{pa} = -1.0$ V corresponds to a dismutation reaction (eq 6).

$$5 \rightarrow \frac{1}{2}\mathbf{1} + \frac{1}{2}\mathbf{3} + e^{-} \quad E_{\text{pa}} = -1.0 \text{ V}$$
 (6)

The absence of the redox waves of $[FeCp(CO)_2]_2$ in the CV of **5** can be explained as follows: once the first amounts of **3** are reduced (eq 1), the resulting $[FeCp(CO)_2]_2$ immediately reacts with **1** to form **3** (see above), which in turn is again reduced to **5**.⁴³ Thus, no electrochemical responses of $[FeCp(CO)_2]_2$ and/or $[FeCp(CO)_2]^-$ are visible in the cyclic voltammogram of **5**.

By summing up all equations and assumptions, we were able to propose the redox cycle depicted in Figure 8. The complicated though very appealing reduction chemistry of 3 consists of a cascade of bond-breaking and bond-making processes, fully in accord with the chemically reversible redox cycle of 3 consisting of electrochemical irreversible couples.

Conclusions

Metal-terminated bicyclo[1.1.1]pentastannanes of the general formula [{ $MCp(CO)_2$ } $_2$ { μ -Sn₅Dep₆}] (M = Fe (3), Ru = (4)) are available by reacting the heavy propellane Sn_5Dep_6 (1) with the transition metal precursors [MCp- $(CO)_{2}_{2}$. In each case, the latter can readily be added to the bridgehead atoms, nicely confirming the radical-type reactivity of metalla[1.1.1]propellanes, in this case 1. The title compounds 3 and 4 have been characterized in detail using various methods. X-ray structures of both compounds corroborated that the two ligand-free bridgehead tin atoms within the Sn_5 scaffold are bonded to iron (3) and ruthenium (4). The reduction chemistry of 3 and 4 in THF solutions was shown to be considerably more complicated than anticipated. A detailed preparative and electrochemical study elucidated a complex redox cycle consisting of a cascade of bond-breaking and bond-making processes, fully in accord with the chemically reversible redox cycle of 3 consisting of electrochemical irreversible couples. Further studies on this type of metal-terminated clusters are currently in progress in our laboratory.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon. Solvents were freshly distilled under argon from the appropriate drying agent. Deuterated solvents were refluxed over the appropriate drying agent, distilled, and stored under argon in Teflon valve ampules. NMR samples were prepared under an inert atmosphere in 5 mm Wilmad 507-PP tubes, either sealed or fitted with J. Young Teflon valves. ¹H, ¹³C{¹H}, ²⁹Si, and ¹¹⁹Sn NMR spectra were recorded on Bruker Avance 400 and Avance III 300 spectrometers and are referenced according to IUPAC recommendations.⁴⁴ ¹H, ¹³C, and ²⁹Si chemical shifts are given relative to TMS and ¹¹⁹Sn to Me₄Sn. Coupling constants J are given in Hertz as absolute values regardless of their real individual signs. The multiplicity of the signals is indicated as s, d, t, dq, or m for singlets, doublets, triplets, doublets of quadruplets,

⁽⁴²⁾ Krossing, I.; Raabe, I. Angew. Chem. 2004, 116, 2116; Angew. Chem., Int. Ed. 2004, 43, 2066.

⁽⁴³⁾ Another possible mechanism: (a) reduction of 1 to $[1]^{\bullet-}$; (b) reaction of $[1]^{\bullet-}$ with "[FeCp(CO)₂][•]" or [FeCp(CO)₂]₂ to furnish 5.

⁽⁴⁴⁾ Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Goodfellow, R.; Granger, P. Pure Appl. Chem. 2001, 73, 1795.

and multiplets, respectively. The abbreviation br is given for broadened signals. Assignments were confirmed as necessary with the use of 2D correlation experiments. Cyclic voltammetry measurements were performed with an EG&G potentiostat (PAR model 263A) and an electrochemical cell for sensitive compounds.45 We used a freshly polished Pt disk working electrode, a Pt wire as counter electrode, and a Ag wire as (pseudo) reference electrode ([n-Bu₄N][PF₆] (0.1 M) as electrolyte). Potentials were calibrated against the Fc/Fc^+ couple,⁴⁶ which has a potential of $E_{1/2}^0 = 0.35$ V vs Ag/AgCl. Continuous wave electron paramagnetic resonance spectroscopy was performed at X-band on a Bruker EMXplus spectrometer (microwave frequency 9.43 GHz) equipped with a liquid nitrogen cryostat. The samples were measured with a modulation amplitude of 10 G and a modulation frequency of 100 kHz, and the field was calibrated by using 2,2-diphenyl-1-picrylhydrazyl with a g value of 2.0036. IR spectra were recorded on a Bruker Vertex 70 spectrometer in the range from 4000 to 400 cm⁻¹ using a KBr beamsplitter. Samples were prepared by using the ATR technique (attenuated total reflection) on bulk material, and the data are quoted in wavenumbers (cm^{-1}) . The intensity of the absorption band is indicated as vw (very weak), w (weak), m (medium), s (strong), vs (very strong), br (broad), or sh (shoulder). UV/vis spectra were recorded on a Varian Cary 100 Scan UV/vis spectrometer. ESI mass spectra of 5 (THF solution under nitrogen) were measured on a FTICR (Fourier Transform Ion Cyclotron Resonance) IonSpec Ultima mass spectrometer equipped with a 7 T magnet (Cryomagnetics, Inc.). The end plate of the ESI source was typically held at a potential of 3.25 kV while the potential of the entrance of the metal coated quartz glass capillary was set to 3.20 kV. Dry nitrogen was used as nebulizing gas. The ions were stored in a hexapole for 4 s prior to transfer into the ICR cell in order to increase the signal-to-noise ratio. Elemental analyses were recorded by the institutional technical laboratories of the Karlsruhe Institute of Technology (KIT). The elemental analysis (carbon) of compound 4 is slightly out of the admitted error, which can be attributed to either the sensitivity or the varying solvent content of the sample. As indicated by the formula $[C_{74}H_{88}Ru_2O_4Sn_5 \cdot 1/2 toluene \cdot 1/4 thf]$, we have consistently used the composition detected by X-ray crystallography for the calculated values.

Starting Materials. Sn_3Dep_6 ,⁴⁷ Sn_5Dep_6 (1),¹⁹ Ge_5Mes_6 (2),²² and $[RuCp(CO)_2]_2^{48}$ were prepared according to literature methods. $[FeCp(CO)_2]_2$ and $CoCp*_2$ were used as purchased from ABCR without further purification.

[{FeCp(CO)₂}₂Sn₅Dep₆] (3). A THF solution (10 mL) of 1 (100 mg, 71.8 μ mol) and [FeCp(CO)₂]₂ (25.4 mg, 71.8 μ mol) was stirred for 48 h at room temperature. After the solvent of the dark yellow solution was removed *in vacuo*, the crude product was redisolved in toluene (3 mL), layered with acetonitrile (10 mL), and stored at -40 °C to afford dark yellow-green crystals suitable for single-crystal X-ray diffraction. Yield: 85 mg (48.7 μ mol, 68%). Mp: 255 °C (dec). Anal. Found: C, 52.87; H, 5.23. Calcd for [C₇₄H₈₈Fe₂O₄Sn₅·toluene·1/2CH₃CN] [1859.26 g mol⁻¹]: C, 52.97; H, 5.29; N, 0.38. ¹H NMR (C₆D₆, 400.1 MHz, ppm): δ 0.81 (t, ³J_{HH} = 7.3 Hz, 18 H, CH₃), 1.00 (t, ³J_{HH} = 7.3 Hz, 18 H, CH₂), 2.02 (dq, ³J_{HH} = 7.3 Hz, ²J_{HH} = 15.4 Hz, 6 H, CH₂), 3.03 (m, 12 H, two overlapping methylene groups), 3.12 (dq, ³J_{HH} = 7.3 Hz, ²J_{HH} = 14.5 Hz, 6 H, CH₂), 4.54 (s, 10 H, Cp), 6.98–7.02 (m, 12 H, H³-Ph and H⁵-Ph) 7.21 (t, ³J_{HH} = 7.6 Hz, 6 H, H⁴-Ph). ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, ppm): δ 14.8 and 16.2 (CH₃), 35.4 and 35.7 (CH₂), 83.4 (Cp), 125.8, 125.9, 127.1, 150.2, 150.5,

and 152.4 (Ph), 214.9 (CO). ¹¹⁹Sn^{{1}H} NMR (C₆D₆, 149.0 MHz, ppm): δ –260 (¹*J*(¹¹⁹Sn_{br}, ^{117/119}Sn_b) = 1623/1699 Hz, ²*J*(¹¹⁹Sn_{br}, ¹¹⁷Sn_{br}) = 1270 Hz), -296 (¹*J*(¹¹⁹Sn_b, ^{117/119}Sn_{br}) = 1623/1699 Hz, ²*J*(¹¹⁹Sn_b, ¹¹⁷Sn_b) = 2908 Hz). IR-ATR (cm⁻¹): ν 404 (w), 415 (w), 426 (m), 445 (m), 464 (m), 485 (m), 501 (m), 570 (vs), 630 (w), 694 (vw), 717 (vw), 729 (w), 756 (vw), 802 (w), 832 (w), 1010 (vw), 1371 (vw), 1413 (vw), 1429 (vw), 1448 (w), 1466 (vw), 1947 (m), 1985 (m), 2852 (w), 2921 (m), 2955 (vw). UV/vis (nm): $\lambda_{max} = 436 (\varepsilon = 14500), 368-300$ shoulder, 254 ($\varepsilon = 68500$ M⁻¹ cm⁻¹), 212 ($\varepsilon = 150500$ M⁻¹ cm⁻¹).

 $[{RuCp(CO)_2}_2Sn_5Dep_6]$ (4). A THF solution (10 mL) of 1 (80.0 mg, 57.4 µmol) and [RuCp(CO)₂]₂ (26.1 mg, 57.4 µmol) was stirred for one week at room temperature. After the solvent of the dark yellow solution was removed in vacuo, the crude product was redisolved in toluene (3 mL), layered with acetonitrile (10 mL), and stored at -40 °C to afford dark yellow-green crystals suitable for single-crystal X-ray diffraction. Yield: 70 mg (38.1 µmol, 66%). Mp: 270 °C (dec). Anal. Found: C, 50.52; H, 5.06. Calcd for $[C_{74}H_{88}Ru_2O_4Sn_5 \cdot 1/2 toluene \cdot 1/4 thf]$ [1899.1 g mol⁻¹]: C, 49.59; H, 4.98. ¹H NMR (C₆D₆, 400.1 MHz, ppm): $\delta 0.81$ (t, ³J_{HH} = 7.4 Hz, 18 H, CH₃), 1.01 (t, ³J_{HH} = 7.4 Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ²J_{HH} = 15.5 Hz, 6 H, Hz, 18 H, CH₃), 2.07 (dq, ³J_{HH} = 7.4 Hz, ³J_H CH₂), 3.08 (m, 18 H, three overlapping methylene groups), 4.91 (s, 10 H, Cp), 6.99 and 7.01 (2d, ${}^{3}J_{HH} = 7.9$ Hz, 12 H, H³-Ph and H⁵-Ph), 7.22 (t, ${}^{3}J_{\text{HH}} = 7.6$ Hz, 6 H, H⁴-Ph). ${}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR (C₆D₆, 100.6 MHz, ppm): δ 14.9 and 16.3 (CH₃), 35.5 and (C₆D₆, 100.0 MH2, ppm). δ 14.9 and 10.3 (CH₃), 53.5 and 35.6 (CH₂), 86.4 (Cp), 125.8, 125.9, 130.4, 150.3, 150.5, and 152.3 (Ph), 215.2 (CO). ¹¹⁹Sn^{{1}H} NMR (C₆D₆, 149.0 MHz, ppm): δ -285 (¹J(¹¹⁹Sn_{br}, ^{117/119}Sn_b) = 1230/1291 Hz), ²J(¹¹⁹Sn_{br}, ¹¹⁷Sn_b) = 1348 Hz), -287 (¹J(¹¹⁹Sn_b, ^{117/119}Sn_{br}) = 1230/1291 Hz, ²J(¹¹⁹Sn_b, ¹¹⁷Sn_b) = 3896 Hz). IR-ATR (cm⁻¹): 476 (s), 512 (s), 548 (vs), 592 (w), 694 (w), 715 (w), 729 (w), 756 (vw), 802 (m), 816 (m), 833 (vw), 1010 (w), 1038 (vw), 1062 (vw), 1091 (vw), 1170 (vw), 1225 (vw), 1320 (vw), 1351 (vw), 1372 (w), 1421 (w), 1449 (m), 1562 (vw), 1953 (s), 1962 (s), 2003 (vs), 2852 (m), 2921 (m), 2955 (w), 3044 (vw). UV/vis (nm): λ_{max} 414 ($\varepsilon = 73500 \text{ M}^{-1} \text{ cm}^{-1}$), 382–335 shoulder, 254 shoulder, 213 ($\varepsilon = 285000 \text{ M}^{-1} \text{ cm}^{-1}$).

[CoCp*2][{FeCp(CO)2}Sn5Dep6] (5). To a THF solution (5 mL) of 3 (20.0 mg, 11.5 μ mol) was added a THF solution (3 mL) of CoCp*₂ (5 mg, 15.2 μ mol) at room temperature, and the solution was stirred for 20 min. The reaction mixture was evaporated to dryness, and the residue was washed several times with toluene. The ruby-colored powder was redisolved in acetonitrile and stored at -30 °C to form dark red crystals suitable for X-ray diffraction. Yield: 19 mg (9.8 µmol, 85%). Mp: 245 °C (dec). ESI-MS (3.6 kV) m/z: 1569.08. Anal. Found: C, 55.05; H, 5.92. Calcd for [C₈₇H₁₁₃CoFeO₂Sn₅] [1899.2 g/mol]: C, 55.02; H, 6.00; Co, 3.10; Fe, 2.94; O, 1.68; Sn, 31.25. ¹H NMR (DMSO d_6 , 400.1 MHz, ppm): δ 0.53 (t, ${}^{3}J_{HH} = 7.4$ Hz, 9 H, CH₃), 0.61 (2t, ${}^{3}J_{HH} = 7.4$ Hz, 18 H, CH₃), 0.96 (t, ${}^{3}J_{HH} = 7.4$ Hz, 9 H, CH₃), 1.62 (m, 3 H, CH₂), 1.96 (m, 3 H, CH₂), 2.45 (m, 3 H, CH₂), 2.67 (m, 3 H, CH₂), 2.96 (m, 12 H, CH₂), 4.68 (s, 5 H, Cp), $6.43 (d, {}^{3}J_{HH} = 7.6 Hz, 3 H), 6.56 (d, {}^{3}J_{HH} = 7.6 Hz, 3 H) and 6.71 (t, {}^{3}J_{HH} = 6.4, 6 H, H^{3}-Ph and H^{5}-Ph), 6.91 (2t, {}^{3}J_{HH} = 7.5 Hz, 6 H, H^{4}-Ph). IR-ATR (cm^{-1}): 445 (m), 490 (m), 508 (m), 572$ (vs), 643 (m), 722 (m), 739 (w), 753 (m), 802 (m), 889 (wv), 1013 (w), 1021 (w), 1058 (vw), 1165 (vw), 1225 (vw), 1268 (vw), 1324 (w), 1371 (m), 1425 (m), 1447 (s), 1562 (vw), 1638 (vw), 1906 (vs), 1953 (vs), 2000 (vw), 2869 (w), 2927 (w), 2958 (w), 3040 (vw). UV/vis (nm): λ_{max} 492 ($\varepsilon = 24500 \text{ M}^{-1} \text{ cm}^{-1}$), 294 ($\varepsilon = 140000 \text{ M}^{-1} \text{ cm}^{-1}$), 264 shoulder, 214 ($\varepsilon = 315000 \text{ M}^{-1} \text{ cm}^{-1}$).

Crystal Structure Determinations of 3, 4, and 5. Crystal data collection and processing parameters are given in Table 2. In order to avoid degradation, the single crystals were mounted on glass fibers using perfluoropolyether oil and cooled rapidly in a stream of cold N_2 using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using a STOE STADI 4 diffractometer equipped with a CCD detector and graphitemonochromated Mo K α (0.71073 Å) radiation. All calculations

^{(45) (}a) Hinkelmann, K.; Heinze, J.; Schacht, H.-T.; Field, J. S.; Vahrenkamp, H. J. Am. Chem. Soc. **1989**, 111, 5078. (b) Heinze, J. Angew. Chem. **1984**, 96, 823; Angew. Chem., Int. Ed. **1984**, 23, 831.

⁽⁴⁶⁾ Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

⁽⁴⁷⁾ Sita, L. R.; Bickerstaff, R. D. J. Am. Chem. Soc. 1989, 111, 3769.

⁽⁴⁸⁾ Doherty, N. M.; Knox, S. A. R.; Morris, M. J. Inorg. Synth. 1990, 28, 189.

Table 2. Crystal Data.	Data Collection,	and Structure	Refinement for 3, 4, and 5

	3	4	5
empirical formula	$C_{74}H_{88}O_4Fe_2Sn_5 \cdot C_7H_8 \cdot \frac{1}{2} CH_3CN$	$2 C_{74}H_{88}O_4Ru_2Sn_5 \cdot C_7H_8 \cdot \frac{1}{2}C_4O$	C ₆₇ H ₈₃ O ₂ FeSn ₅ ,C ₂₀ H ₃₀ Co
M^{\uparrow}	1859.26	3798.22	1899.00
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	<i>Iba</i> 2 (no. 45)	<i>P</i> 2/ <i>n</i> (no. 13)	<i>Pbca</i> (no. 61)
a/pm	21.362(4)	20.896(4)	25.077(5)
b/pm	40.586(8)	14.802(3)	24.040(5)
c/pm	17.613(4)	25.759(5)	26.596(5)
β/deg		107.59(3)	
$V/10^{6} \text{ pm}^{3}$	15271(5)	7595(3)	16033(6)
$\mu/\mathrm{mm}^{\pm 1}$	2.026	2.050	1.955
$D_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.617	1.661	1.573
cryst dimens/mm	$0.25 \times 0.15 \times 0.15$	0.15 imes 0.10 imes 0.10	$0.40 \times 0.25 \times 0.20$
Z	8	2	8
T/K	150	200	200
$2\theta_{\rm max}/{\rm deg}$	52.00	52.00	52.00
reflns measd	54 993	55 1 38	11 1 307
reflns unique	$14738 (R_{int} = 0.0643)$	$14885(R_{\rm int}=0.0638)$	$15667(R_{\rm int}=0.0890)$
params/restraints	858/149	923/141	907/4
$R_1 [I \ge 2\sigma(I)]$	0.0406	0.0581	0.0647
wR_2 (all data)	0.0906	0.1498	0.1224
max./min.	1.534/-1.088	2.620/-2.020	0.850/-1.074
resid electron	,	,	,
$dens/e \times 10^{-6} pm^{-3}$			

were performed using the SHELXTL (ver. 6.12) program suite.^{49,50} The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against either For F^2). All non-hydrogen atoms were refined anisotropically (for exceptions see below). The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Upon convergence, the final Fourier difference map of the X-ray structures showed no significant peaks.

Several ethyl groups of the Dep ligands in 4 and one in 5 were disordered over two sites. In these cases, the two positions were refined against each other using one free variable with occupation factors of $2 \times 42\%$ and 45% (4) and 40% (5) for the disordered position. Attempts to refine other Et groups showing unusually large displacement ellipsoids were not successful. 3 crystallizes with one toluene and $1/_2$ CH₃CN molecule in the crystal lattice. The toluene C atoms (refined with some DFIX restraints) and one CO oxygen atom and four C atoms of the Dep ligands (disordered Et substituents) have been refined using the ISOR restraint. As indicated by SHELXL (Flack x parameter around 0.3), the structure of 3 showed racemic twinning. By using an appropriate TWIN card in SHELXL and a batch scale factor of BASF = 0.31 the structure was suitably refined. Two molecules of **4** crystallize with one toluene and $^{1}/_{2}$ THF molecule, as indicated by the formula $2C_{74}H_{88}O_4Ru_2Sn_5 \cdot C_7H_8 \cdot ^{1}/_2C_4O$ in Table 2. The latter was located on a special crystallographic position and was refined isotropically without hydrogen atoms. Since the toluene solvent molecule was also located on a special crystallographic position, it was refined by using appropriate restraints and the instruction PART-1 in SHELXL. The toluene C atoms and two other C atoms of the Dep ligands (disordered Et substituents) have been refined using the ISOR restraint.

All details of the structure solution and refinements are given in the Supporting Information (CIF data). Full listings of atomic coordinates, bond lengths and angles, and displacement parameters for all the structures have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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Supporting Information Available: X-ray crystallographic data in CIF format for the structure determinations of **3**, **4**, and **5**. UV/vis spectra of **3**, **4**, and **5**, NOESY and ¹¹⁹Sn NMR spectra for **3**, cyclic voltammetry of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

 ⁽⁴⁹⁾ SHELXTL v6.12; Bruker AXS Inst. Inc.: Madison, WI, USA, 2000.
 (50) Sheldrick, G. M. Acta Crystallogr., Sect. A 2008, 64, 112.