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Chemistry of Strained Organometallic Rings: Unusual Reactivity of Tin-Bridged [1]Ferrocenophanes with Metal Carbonyls

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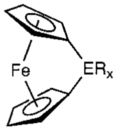
*Summary: The reactivity of the stanna[1]ferrocenophane $Fe(\eta\text{-}C_5H_4)_2Sn(tBu)_2$ (**8**) toward transition-metal carbonyls was investigated. Insertion of an $Fe(CO)_4$ fragment into an Sn−Cp bond of **8** was observed on treatment with $Fe_2(CO)_9$, forming the ferrostanna[2]ferrocenophane **9** whereas in the case of $Co_2(CO)_8$, a highly unusual rearrangement/transfer of CO occurred, forming the ketone-bridged dimer **10**.*

Although the study of strained organic compounds has received considerable attention,[1] analogous investigations of strained organometallic compounds are rare. One class of strained metal-containing ring compounds, the [1]ferrocenophanes, is particularly suited for detailed studies, as their structure can be systematically varied. The molecules consist of a single-element bridge spanning the two cyclopentadienyl (Cp)[2] ligands of ferrocene.[3] The first example, **1** (E = Si, R = Ph, x = 2), was synthesized by Osborne and co-workers in 1975.[4] More recently, the range of [1]ferrocenophanes has been extended to include those bridged with group 13 (B),[5,6] group 14 (Ge, Sn),[7−12] group 15 (P, As),[7,13−16] and group 16 (S, Se)[17,18] elements as well as the group 4 metals (Ti, Zr, Hf)[19] and even an actinoid (U).[20] The Cp ligands of the [1]ferrocenophane are tilted relative to the parallel arrangement found in ferrocene in order to accommodate this single-atom bridge. The degree of ring tilting (α) depends on the size and geometrical preferences of the bridging element and ranges from ca. 0° in the case of the uranium-bridged [1]ferrocenophane[20] to as high as 32° for the bora[1]ferrocenophanes.[5,6] The associated “tunability” of the ring strain makes the [1]ferrocenophanes excellent candidates for fundamental studies of reactivity.



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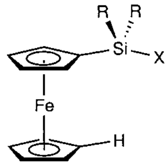

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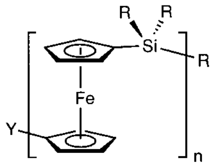

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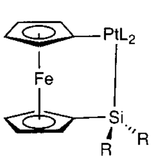

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The sila[1]ferrocenophanes (**1**, E = Si) are the most well-studied subclass of [1]ferrocenophanes. These compounds possess appreciable ring strain (RS) (α = 16−20°, RS = 60−80 kJ mol^{-1} by DSC; cf. norbornane, RS = ca. 60 kJ mol^{-1})[21] and display enhanced reactivity. For example, ring opening at an Si−Cp bond is observed with protic reagents such as HCl and MeOH, forming **2** (X = Cl, OH, respectively).[22,23] In addition, nucleophiles such as LiR[24] or thermal treatment[25] induce

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(1) For example, see: (a) Bodwell, G. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2085. (b) Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421. (c) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312 and references therein.

(2) In this manuscript the abbreviation Cp is used to denote both substituted and unsubstituted cyclopentadienyl ligands.

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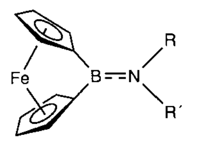
Si−Cp bond cleavage, yielding polyferrocenylsilanes **3** via ring-opening polymerization. Platinum(0) complexes have also been shown to undergo insertion reactions into an Si−Cp bond, yielding either platinasila[2]ferrocenophanes **4** or ring-opened polymers **3**, depending on the ancillary ligands.[26]

In contrast, the highly strained boron-bridged [1]-ferrocenophanes **5** (α = ca. 32°, RS = ca. 95 kJ mol^{-1}) have been shown to undergo facile ring-opening chemistry at the *Fe*−Cp rather than the B−Cp bond. For example, treatment of **5** with the metal carbonyl complexes $Fe_2(CO)_9$ and $Co_2(CO)_8$ yields the novel bi- and trimetallic species **6** and **7**, respectively.[6] In this communication we report on analogous studies of the reactivity of a tin-bridged [1]ferrocenophane (**8**) with the same metal carbonyl reagents and the novel products that ensue.



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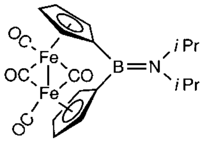

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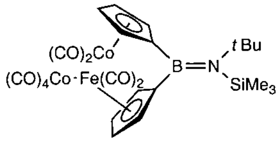

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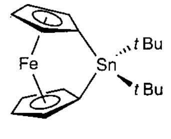

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The successful isolation of stanna[1]ferrocenophanes required the presence of sterically demanding substituents at tin.[9] Studies to date have shown that although the structures possess only moderate ring tilt and strain (α = ca. 14−15°; RS = ca. 18−36 kJ mol^{-1}), the weaker Sn−Cp bond results in remarkable reactivity.[10,11] For example, ring-opening polymerization is observed at room temperature in the presence of amine initiators,[27] and the insertion of Pt^0 fragments into the Sn−Cp bond has been detected.[10] We have now found that a facile and selective reaction occurs between equimolar quantities of $Fe_2(CO)_9$ and stanna[1]ferrocenophane **8** in THF solution.[28] Analysis by ^{1}H NMR after 3 h at 25 °C revealed the formation of a new product, giving rise to four pseudotriplet resonances in the Cp region. The ^{1}H NMR data were indicative of a loss of symmetry from that of the starting material, which possesses only two signals in the Cp region, and were consistent with the insertion of an $Fe(CO)_4$ fragment into an Sn−Cp bond to afford **9**. The ^{1}H NMR resonance arising from the CH_3 groups of the *t*Bu functionality was shifted slightly downfield from that of the starting material (δ 1.47 ppm; cf. **8** at δ 1.36 ppm), and a decrease in the coupling constant observed between the ^{1}H and $^{117/119}$Sn nuclei was apparent (J_{H-Sn} = 36 Hz; cf. **8** at J_{H-Sn} = 75 Hz).[28] Consistent with the assigned structure for **9**, the ^{13}C NMR spectrum showed three separate resonances in the carbonyl region (δ 212.1, 205.8, 202.4 ppm), which also indicated that there is no exchange of the CO ligands at room temperature. A single resonance was observed in the ^{119}Sn NMR spectrum at a chemical shift of 142.4 ppm (C_6D_6), which is shifted considerably downfield from that for **8** (δ −23.7, $CDCl_3$).

Confirmation of the structure of **9** was obtained by single-crystal X-ray diffraction.[28] This showed that the product was indeed the novel ferrostanna[2]ferrocenophane **9** shown in Figure 1, formed from the insertion of an iron tetracarbonyl fragment into an Sn−Cp bond

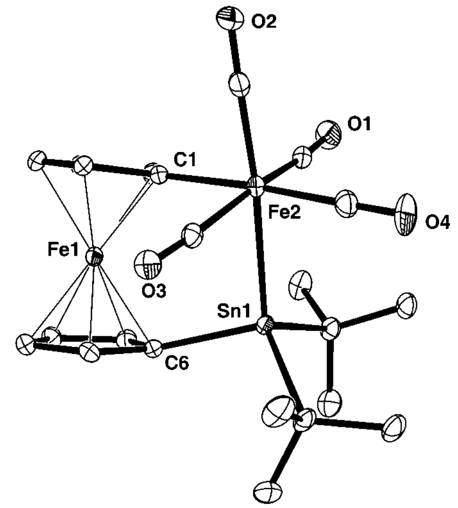
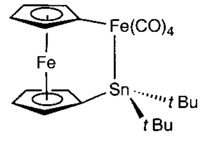


Figure 1. Molecular structure of **9** (thermal ellipsoids at 30% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)−C(6), 2.156(2); Sn(1)−Fe(2), 2.7004(4); C(1)−Fe(2), 2.069(2); C(11)−Fe(2), 1.793(3); C(12)−Fe(2), 1.832(3); C(13)−Fe(2), 1.810(3); C(14)−Fe(2), 1.802(3); C(6)−Sn(1)−Fe(2), 103.35(6); C(15)−Sn(1)−C(19), 107.92(10); C(1)−Fe(2)−Sn(1), 87.24(7); C(12)−Fe(2)−Sn(1), 173.92(8); C(1)−Fe(2)−C(14), 176.27(12); C(11)−Fe(2)−C(13), 165.36(12); α, 4.2(2).



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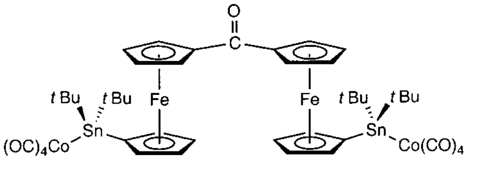

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(26) Platinum fragments with comparatively strongly bound ancillary phosphine ligands tend to lead to the platinasila[2]ferrocenophane as product, whereas those with more weakly bound (e.g. 1,5-cod) ligands have been found to lead to the formation of polymer. See: Temple, K.; Jäkle, F.; Sheridan, J. B.; Manners, I. *J. Am. Chem. Soc.* **2001**, *123*, 1355.

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(28) For full experimental details please refer to the Supporting Information.

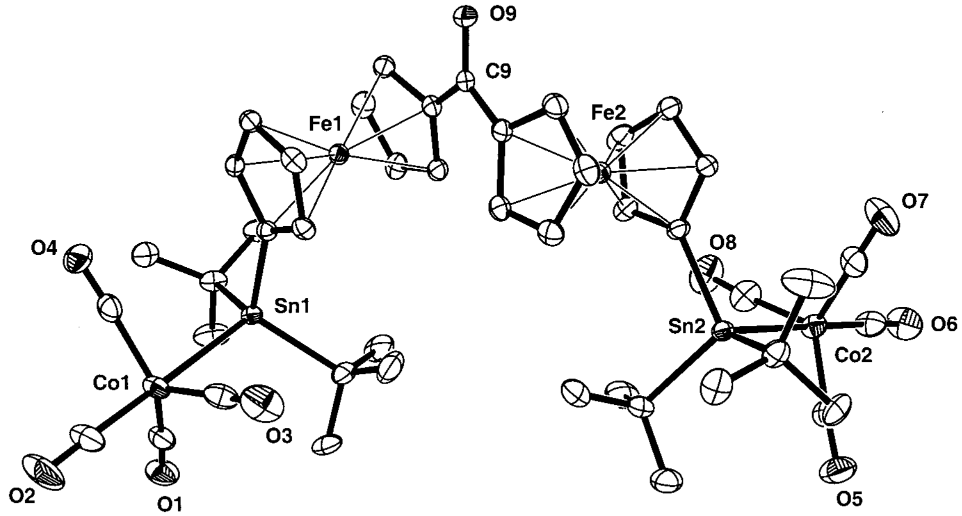

Figure 2. Molecular structure of **10** (thermal ellipsoids at 30% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(30)−Sn(1), 2.149(3); Sn(1)−Co(1), 2.6463(5); C(20)−Sn(2), 2.143(3); Sn(2)−Co(2), 2.6495(5); C(35)−C(9)−C(25), 121.6(3); C(35)−C(9)−O(9), 119.1(3); C(25)−C(9)−O(9), 119.3(4); C(30)−Sn(1)−Co(1), 101.77(8); Sn(1)−Co(1)−C(2), 179.03(17); C(20)−Sn(2)−Co(2), 101.92(9); Sn(2)−Co(2)−C(6), 179.38(17).

of **8**. Although considerably less strained than the stanna[1]ferrocenophane **8** (α = 14.1(2)°), **9** still possesses a very slight tilting of the Cp rings (α = 4.2(2)°). The distance between the Sn and Fe(bridge) atoms was measured to be 2.7004(4) Å, which is nearly identical with the average Fe−Sn bond length (2.72 Å).[29] The iron in the bridging position lies in a slightly distorted octahedral geometry.

Reaction of equimolar amounts of $Co_2(CO)_8$ and the stanna[1]ferrocenophane **8** in hexanes solution was also found to result in the selective formation of a single iron-containing new product by ^{1}H NMR spectroscopy. An extensive crystallization procedure was employed to extract reasonably pure (>95%) samples of this air- and moisture-sensitive product from the cobalt-containing byproducts of the reaction.[28] Resonances arising from the protons of the cyclopentadienyl rings were observed at δ 5.14, 4.40, 4.38, and 4.08 ppm. The signals in the Cp region of the ^{1}H NMR spectrum of **8** appear at δ 4.38 and 4.19 ppm. The signal at δ 5.14 is therefore shifted strongly downfield from that of the starting material. Another notable feature is the decrease in symmetry of the product (four signals) from that of **8** (two signals). The chemical shift of the signal arising from the *t*Bu groups was virtually unchanged from that of **8** (δ = 1.37; for **8**, δ 1.36 ppm). However, the coupling between the *t*Bu protons and the $^{117/119}$Sn nuclei was again significantly less (40 Hz) than in **8** (75 Hz). The ^{119}Sn NMR spectrum of the product showed a single signal (δ 149.8 ppm), and the electron impact mass spectrum showed peaks of low intensity (1%) at 589 and 616 amu corresponding to the fragments $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)Sn(t\mathrm{Bu})_2Co(CO)_4]^+$ and $[Fe(\eta\text{-}C_5H_4)_2Sn(t\mathrm{Bu})_2Co(CO)_5]^+$, respectively. X-ray diffraction was also used to unequivocally determine the structure of the product.[28] This showed that the compound possessed a remarkable structure (**10**) comprised of two $(CO)_4CoSn(t\mathrm{Bu})_2$-substituted ferrocenes linked by a ketone bridge (see Figure 2).

The length of the Sn−Co bonds was determined to be 2.6463(5) and 2.6495(5) Å, which is only slightly longer than the average length of an Sn−Co bond (2.60 Å).[29] The geometry around the cobalt atoms is approximately trigonal bipyramidal. The geometry around the central ketone functionality is trigonal planar ($\sum\Delta = 360°$). The ferrocene moieties adopt a trans arrangement about the central carbon atom, presumably to reduce interactions between the bulky substituents on the Cp rings. The detailed mechanism of formation of **10** is not obvious; however, one of the steps presumably results in the transfer of a CO ligand from $Co_2(CO)_8$ to link the Cp rings of the ferrocene groups.

The results of this study clearly illustrate the distinct differences in reactivity between the subclasses of [1]-ferrocenophanes. Significantly, for the first time, we are able to demonstrate that reactions of different [1]-ferrocenophanes (boron-bridged species **5** and tin-bridged species **8**) with the same reagents ($Fe_2(CO)_9$ and $Co_2(CO)_8$) lead to distinctly different pathways and products. Thus, whereas the bora[1]ferrocenophane **5** yields **6** and **7** via *Fe*−Cp cleavage chemistry,[6] species **9** and **10** arise from reactions of the *Sn*−Cp bond in stanna[1]ferrocenophane **8**.

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Supporting Information Available: Crystallographic data for compounds **9** and **10**, including tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters, and text giving full experimental details for **9** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[29] Calculated from data obtained from molecules listed in the Cambridge Structural Database version 5.21 (April 2001).