Synthesis and Reactivity of [2]Ferrocenophanes with C−Ge and C−Sn Bridges

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The synthesis, characterization, and reactivity of novel carbogerma[2]ferrocenophanes, (η-C_5Me_4)Fe(η-C_5H_4)CH_2GeR_2, **11** (**a**, R = Ph; **b**, R = Me), and carbostanna[2]ferrocenophanes, (η-C_5Me_4)Fe(η-C_5H_4)CH_2SnR_2, **12** (**a**, R = *t*Bu; **b**, R = Mes; **c**, R = Me), are reported. Compounds **11a**,**b** and **12a**−**c** were isolated as orange crystals from the reaction of (η-C_5Me_4)Fe(η-C_5H_4Li)CH_2Li·*x*TMEDA with Cl_2ER_2 (E = Ge, R = Ph, Me or E = Sn, R = *t*Bu, Mes, Me) and were characterized by ^1H, ^{13}C, and ^{119}Sn NMR, UV/vis, MS, and in representative cases elemental analysis. X-ray diffraction analysis of these species revealed structures possessing moderate ring-tilt with values in the range $\alpha = 10.99(2)-11.81(5)°$ for **11a**,**b** and $\alpha = 6.64(2)-7.5(1)°$ for **12a**−**c**. The presence of a small or moderate degree of ring-strain was further substantiated through the observation of only a small (ca. 25−30 nm) bathochromic shift in the UV/vis absorption maxima when compared to pentamethylferrocene. Attempts to induce thermal ring-opening polymerization (ROP) of **11b** and **12a**−**c** proved to be unsuccessful and led only to decomposition at temperatures above 300 °C. Treatment of **11b** and **12a**−**c** with amines such as pyridine and 4-(dimethylamino)pyridine did not result in ROP of these compounds. In addition, treatment of **11b** and **12a**−**c** with $Pt(cod)_2$, $Pt(PEt_3)_3$, $PtCl_2$, Karstedt's catalyst (a Pt(0)-divinyltetramethyldisiloxane complex), $PtCl_2$(COD), and *n*BuLi for **11b** and **12c** and 2,2′-azobisisobutyronitrile (AIBN) in the presence of Bu_3SnH for **12a**,**b** failed to induce any of the insertion or ring-opening reactions that are known for the more highly strained [1]ferrocenophane analogues. However, reactions of **11b** and **12a** with strong acids such as HCl and **12a** with triflic acid (CF_3SO_3H) resulted in the formation of the corresponding ring-opened species, (η-C_5H_5)Fe(η-$C_5Me_4CH_2GeMe_2Cl$), **14**, (η-C_5H_5)Fe(η-$C_5Me_4CH_2Sn$(*t*Bu)$_2$Cl), **15**, and (η-C_5H_5)Fe(η-$C_5Me_4CH_2Sn$(*t*Bu)$_2OSO_2CF_3$), **16**, via selective ipso-Cp−Ge or ipso-Cp−Sn bond cleavage. Treatment of **12b** with HCl resulted in selective Sn−Mes bond cleavage, affording (η-C_5H_4)Fe(η-C_5Me_4)$CH_2SnMesCl$, **17**.

Introduction

The class of organometallic cyclic species known as [1]ferrocenophanes has been the focus of much recent research due to the ring-strain and resulting reactivity imparted by the presence of a single atom bridge between the cyclopentadienyl (Cp) ligands.[1−7] Molecules of this type may serve as surface derivatization agents[8] and as monomers in ring-opening polymerization (ROP) reactions.[3,4]

The ROP of strained silicon-bridged [1]ferrocenophanes such as **1** ($(ER_x)_y$ = $SiMe_2$) has been particularly well studied and provides a well-established route to high molecular weight polyferrocenylsilanes (e.g., **2**, $(ER_x)_y$ = $SiMe_2$).[3,4] This ROP methodology has also been extended to a range of other [1]ferrocenophanes (**1**) with a variety of p-block elements incorporated in the bridge (e.g., E = B, Si, Ge, Sn, P, S)[5−7] and has allowed the synthesis of well-defined homopolymers with interesting physical and preceramic properties[9−16] and also am-

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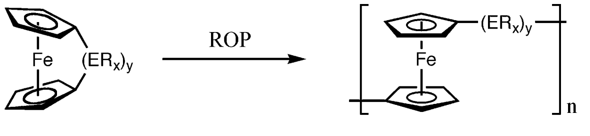
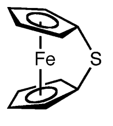
phiphilic block copolymers with intriguing applications in supramolecular chemistry.[17,18] There has also been recent interest in the use of polyferrocenylsilanes as redox-responsive photonic crystals[19] and as etch resists for the nanopatterning of subtrates.[20,21]



1 **2**

The reactivity displayed by [1]ferrocenophanes is a function of not only the ring-strain, as indicated, in part, by the angle between the planes of the Cp rings (α),[22] but also the kinetic lability which is dependent on ipso-Cp carbon−bridging element bond strength. This is illustrated by a comparison of the stability of the highly strained [1]thiaferrocenophane **3** [$\alpha = 31°$, ring-strain (as estimated by DSC) = 130 ± 5 kJ·mol^{-1}][5] and the significantly less strained di-*tert*-butyl[1]stannaferrocenophane **4a** ($\alpha = 14°$, ring-strain (as estimated by DSC) = 36 ± 5 kJ·mol^{-1}).[23] Under inert atmosphere, **3** is stable in solution at ambient temperature, whereas **4** undergoes ROP even in solution at 25 °C, presumably as a result of the weak Cp−Sn bonds.



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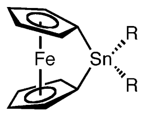
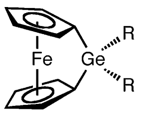
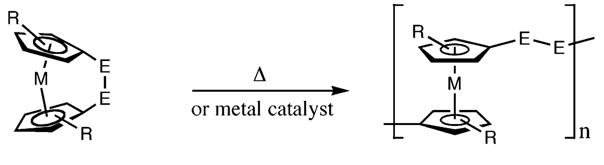


4a: R = tBu
4b: R = Mes



5: R = alkyl or aryl

While considerable work has focused on the study of the reactivity of [1]ferrocenophanes, comparatively less attention has been devoted to [2]ferrocenophane analogues. Previous work has shown that highly strained hydrocarbon-bridged monomers **6** (M = Fe, R = H, Me, $E_2 = CH_2CH_2$) and the analogous [2]ruthenocenophane **6** (M = Ru, R = H, $E_2 = CH_2CH_2$) undergo thermal ROP,[24,25] whereas ring-opening metathesis polymerization of [2]ferrocenophane **6** (M = Fe, R = H, E_2 = CH=CH) has also been described.[26] In contrast, [2]metallocenophanes with Si−Si bridges such as **6** (M = Fe or Ru, $E_2 = SiMe_2SiMe_2$) are relatively unstrained and resist ROP,[27] whereas an analogue with a Ge−Ge bridge (**6**: M = Fe, $E_2 = GeMe_2GeMe_2$) has been polymerized.[28]

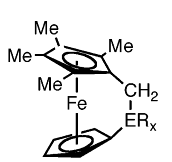


6: M = Fe or Ru,
R = H or Me,
$E_2 = CH_2CH_2$ or CH=CH
$E_2 = SiMe_2SiMe_2$ or $GeMe_2GeMe_2$

7: M = Fe or Ru,
R = H or Me,
$E_2 = CH_2CH_2$ or CH=CH
$E_2 = GeMe_2GeMe_2$

Recently, we have synthesized and studied a series of novel [2]ferrocenophanes, **8**−**10**, with unsymmetrical C−E bridges in which the covalent radius of E and hence the ring-strain present are varied.[29] The least strained of these species (**8**, $\alpha = 11.8(1)°$) was found to be completely resistant to polymerization under all conditions studied, whereas the significantly more strained species **9a** ($\alpha = 14.9(3)°$), **9b** ($\alpha = 18.2(2)°$), and **10** ($\alpha = 18.5(1)°$) were all found to readily undergo ROP reactions.

To further explore the factors that govern the reactivity and polymerizability of the [2]ferrocenophanes, we report here our studies of analogues of **8**−**10** with C−Ge and C−Sn bridges (**11a**,**b**, **12a**−**c**). The impact of the presence of weak C−E (E = Sn or Ge) bonds on the significantly less strained [2]ferrocenophane structure was envisaged to be a focal point of this work.



8 : $ER_x = SiMe_2$
9a : ER_x = PPh
9b : ER_x = PMes
10 : ER_x = S

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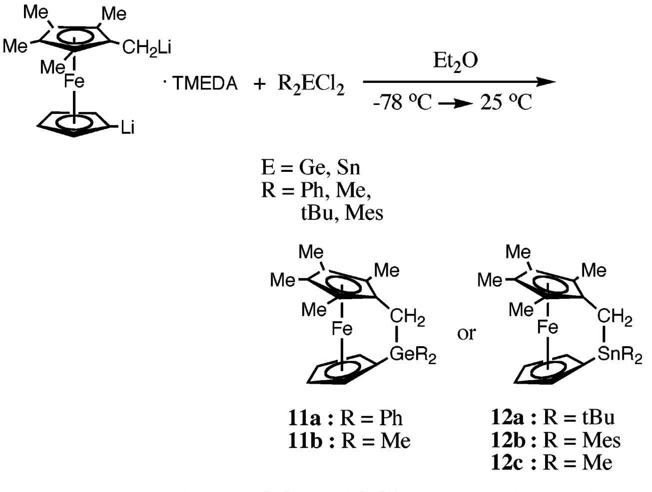
Results and Discussion

1. Synthesis and Characterization of C−Sn and C−Ge Bridged [2]Ferrocenophanes, 11a,b and 12a−c. The C−E bridged [2]ferrocenophanes (**11a**,**b**, **12a**−**c**) targeted in this study were obtained as crystalline solids through the reaction of (η-C_5Me_4)Fe(η-C_5H_4-Li)$CH_2Li \cdot x$TMEDA (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) with the corresponding organoelement dihalides Cl_2R_2E (E = Sn or Ge) in yields ranging from 26% to 49%. The former species is readily formed by the deprotonation of pentamethylferrocene [(η-C_5Me_5)-Fe(η-C_5H_5) = Cp*FeCp] in a preparation modified from literature.[30] ^{1}H, ^{13}C, and ^{119}Sn NMR analysis of the resulting products confirmed the proposed structures. Of note in the ^{13}C NMR spectra of **11a**,**b** and **12a**−**c** are the ipso-Cp and ipso-Cp′ (Cp′ = C_5Me_4) ^{13}C resonances, which range from 72.8 to 86.9 ppm and 86.2 to 92.1 ppm, respectively. In the moderately strained [1]-ferrocenophane analogues, such as **4a**, the resonances for the ipso-Cp carbons are found at 34.9 ppm,[23c] consistent with a deviation from planar sp^2 hybridization at the ipso-Cp carbon atom.[1,31,32] The ipso-Cp ^{13}C resonances found in **11a**,**b** and **12a**−**c** are consistent with those found in the nonbridged compounds fc($SnMe_2Cl)_2$ (δ = 70.7 ppm) (fc = (η-C_5H_4)Fe(η-C_5H_4)), fc($SnMe_2H)_2$ (δ = 65.8 ppm),[33] and Fc($GeMe_2Cl$) (δ = 72.4 ppm) (Fc = (η-C_5H_5)Fe(η-C_5H_4)).[34] In addition, ^{119}Sn NMR resonances for **12a**−**c** were consistent with the assigned structures. By comparing the NMR characterization data with that for the analogous [1]ferrocenophanes, it would appear that the [2]ferrocenophanes **11a**,**b** and **12a**−**c** possess relatively nonstrained structures. However, it is important to note that the corresponding ipso-Cp ^{13}C resonances for the significantly strained [2]-ferrocenophanes, **8**−**10**, also possess similar chemical shifts.[29] This suggests that the ring-strain present within this [2]ferrocenophane framework cannot be completely inferred from the ipso-Cp ^{13}C resonances alone and thus requires examination via other techniques.



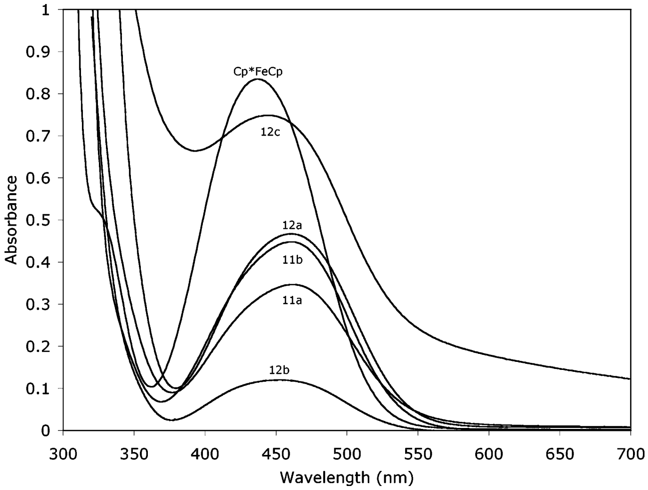


Figure 1. UV/visible spectra (hexanes) of Cp*FeCp, **11a**,**b**, and **12a**−**c**.

Previous studies on [1]- and [2]ferrocenophanes have demonstrated that the absorption maximum attributed to the lowest energy d−d transition is shifted to a longer wavelength by up to 60 nm when compared to analogous nonbridged ferrocenes.[5a,32] The UV/visible spectra in hexanes revealed absorptions at 462 nm (ϵ = 173 M^{-1} cm^{-1}) for **11a** and 461 nm (ϵ = 203 M^{-1} cm^{-1}) for **11b**, which have been assigned to the lowest energy d−d transitions (Figure 1) and which are similar to the absorptions observed for the C−Si bridged [2]ferrocenophane, **8** (α = 11.8(1)°, λ_{max} = 458, ϵ = 120 M^{-1} cm^{-1}). Similarly, the absorptions observed for **12a**−**c** were observed in the range from 453 to 462 nm. These values are significantly but not dramatically red-shifted by ca. 25−30 nm from that of Cp*FeCp (λ_{max} = 430 nm, ϵ = 120 M^{-1} cm^{-1}, in hexanes). This indicates that an appreciable but not high degree of strain is present in structures **11** and **12**.

2. X-ray Structural Analysis of [2]Ferrocenophanes 11a,b and 12a−c. To further investigate the amount of ring-strain present in **11a**,**b** and **12a**−**c**, single-crystal X-ray diffraction studies were undertaken. Suitable single crystals were obtained through low-temperature (ca. −30 °C) recrystallization of **11a**,**b** and **12c** from minimal hexanes and of **12a**,**b** from minimal Et_2O/MeCN (50/50 v/v). In all cases, only one molecule was found in the unit cell. The molecular structure of **11a** is shown in Figure 2, and selected bond lengths and angles are given in Table S1 (see Supporting Information). Of note in the structure of **11a** is the relatively moderate α angle (ca. 11.81(5)°) found between the planes of the Cp and Cp′ rings. This α angle in addition to the staggering angle (σ = 11.5(8)°) (σ = angle with which the Cp rings deviate from an eclipsed confirmation) and torsional angle (τ = 16.5(3)°) (τ = angle between the CH_2−GeR_2 bond and the plane containing the Cp centroids and iron atom) would suggest that **11a** possesses some degree of ring-strain (cf. **10**, α = 18.5-

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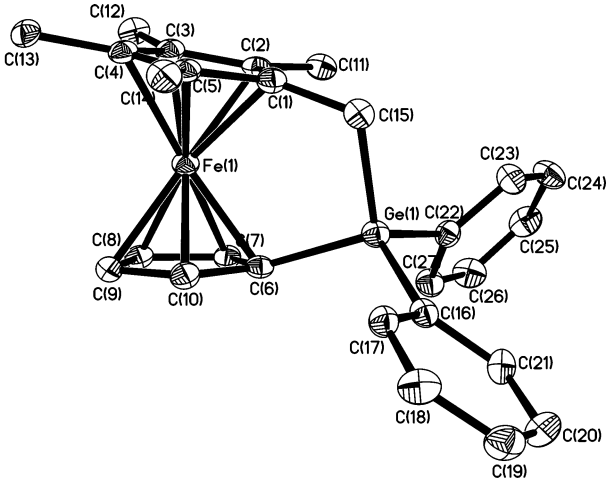

Figure 2. Molecular structure of **11a** showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

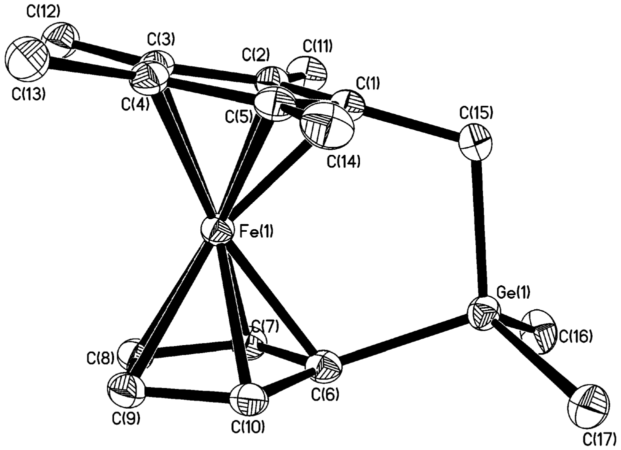

Figure 3. Molecular structure of **11b** showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

(1)°, $\Delta H_{\mathrm{ROP}} = -13 \pm 5$ kJ mol^{-1}). In addition, careful examination of the structure of **11a** revealed a β(Ge) (angle between Cp plane and ipso-Cp−Ge bond) angle of 17.6(2)° and a β(CH$_2$) (angle between Cp′ plane and ipso-Cp′−CH$_2$ bond) angle of 7.2(3)°. Given that in a nonbridged system β angles approach zero, these values suggest again that ring-strain may be present in **11a**.

The molecular structure of **11b** shown in Figure 3 has very similar characteristics to **11a**. As was seen in the structure of **11a**, the structure of **11b** suggests a small degree of ring-strain, as evidenced by the relatively moderate α angle (α = 10.99(2)°). As expected, the α angle of compound **11b** is slightly smaller compared with structure **8** (α = 11.8(1)°) due to the larger covalent radius of germanium versus silicon (Ge: $r_{\mathrm{cov}} = 1.22$ Å; Si: $r_{\mathrm{cov}} = 1.17$ Å).[35] In addition, the bond lengths of the CH$_2$−E bridge for structures **11a**,**b** are larger than that of **8**, ranging from 1.983(3) to 1.985(5) Å (cf. **8**: CH$_2$−Si = 1.914(3) Å).[29]

The molecular structures of **12a**−**c** are similar to those of **11a**,**b** and are shown in Figures 4−6. The larger covalent radius of tin compared with germanium (Sn: $r_{\mathrm{cov}} = 1.40$ Å)[35] is demonstrated by the smaller α angle values observed for species **12a**−**c** ranging from α = 6.64(2)° for **12a** to α = 7.5(1)° for **12c**. The CH$_2$−Sn bridge bond length values for **12a**−**c** range from 2.184(3) to 2.191(2) Å, which are longer than the corresponding CH$_2$−Ge bond lengths of **11a**,**b**, as expected. For comparison, selected angles for the more highly strained species **8** and **10** along with the corresponding values for **11a**,**b** and **12a**−**c** are given in Table 1. Selected bond lengths and angles for **11b** and **12a**−**c** are given in Tables S2−S5 (see Supporting Information).

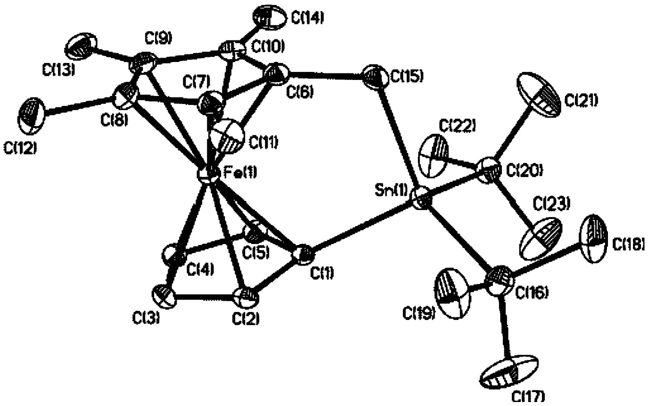

Figure 4. Molecular structure of **12a** showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

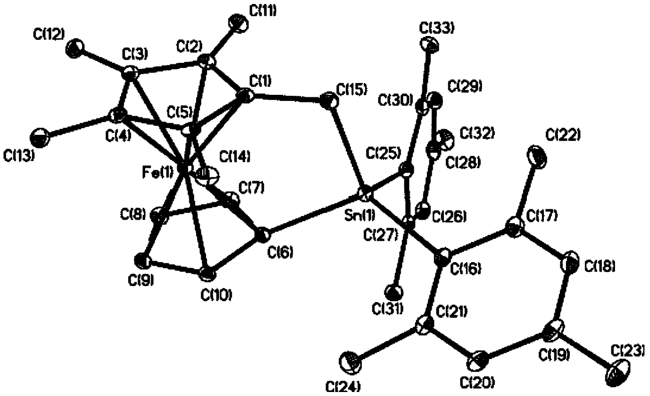

Figure 5. Molecular structure of **12b** showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

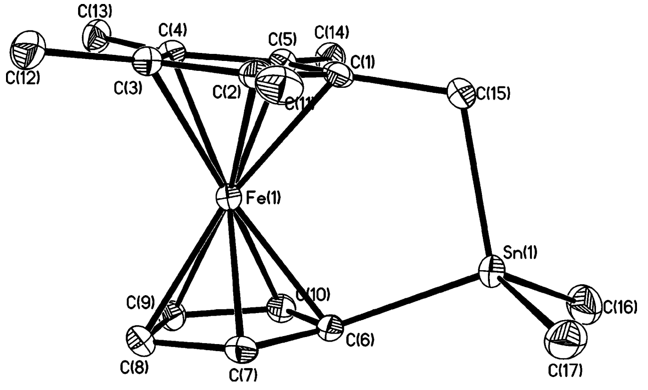

Figure 6. Molecular structure of **12c** showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

3. Electrochemical Studies of [2]Ferrocenophanes, 11b and 12a−c. The [2]ferrocenophanes **11b** and **12a**−**c** were also characterized by cyclic voltammetry. Previous studies of the electrochemical properties of [1]- and [2]ferrocenophanes have identified one-electron oxidation processes that are reversible except for the most strained examples.[5a,29,36] It was also found

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(35) Wells, A. F. *Structural Inorganic Chemistry,* 5th ed.; Oxford University Press: New York, 1984.

Table 1. Comparison of Structural Data for 8, 10, 11a,b, and 12a−c[a]

	bridging moiety	α [deg]	β^1 [deg]	β^2 [deg]	σ [deg]	τ [deg]	λ_{max} [nm][c] (ϵ, $M^{-1}cm^{-1}$)
8[b]	CH_2-SiMe_2	11.8(1)	7.3(3)	17.9(3)	0.1(2)	0.5(2)	458 (120)
10[b]	CH_2-S	18.5(1)	9.3(2)	10.6(2)	10.0(2)	17.9(3)	475 (243)
11a	CH_2-GePh_2	11.81(5)	7.2(3)	17.6(2)	11.5(8)	16.5(3)	462 (173)
11b	CH_2-GeMe_2	10.99(2)	6.1(2)	17.4(2)	0.2(5)	4.4(2)	461 (203)
12a	$CH_2-Sn(tBu)_2$	6.64(2)	4.1(2)	18.5(1)	3.0(4)	3.6(2)	462 (153)
12b	$CH_2-SnMes_2$	7.1(1)	3.8(2)	17.3(1)	2.8(3)	3.9(2)	454 (131)
12c	CH_2-SnMe_2	7.5(1)	3.3(2)	19.1(1)	4.3(3)	4.9(2)	453 (221)

[a] $\beta^1 = \beta(CH_2)$, $\beta^2 = \beta(E)$, where E = Si, S, Ge, Sn. [b] See ref 29. [c] In hexanes.

that cyclic voltammetric analysis of a 0.005 M solutionof **11b** in CH_2Cl_2 (with 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte) revealed the presence of a chemically reversible redox wave centered at −274 mV versus the ferrocene/ferrocenium redox couple. Compounds **12a**−**c** demonstrated similar reversible redox waves in the range $E_{1/2} = -279$ to −332 mV. The observed redox couples were found centered at more negative potentials than that observed for ferrocene, consistent with the more electron-rich iron center in these species arising from the presence of a tetramethylated-Cp ligand.[29]

4. Attempted Thermal Polymerization of [2]-Ferrocenophanes, 11a,b and 12a−c. The thermal polymerization behavior of **11b** was explored by heating a sample in an evacuated tube at temperatures up to 250 °C for up to 72 h. ^1H NMR analysis of the contents of the tube resulted in unreacted **11b** as well as peaks corresponding to decomposition to small quantities of free pentamethylferrocene. These observations suggest that there is inadequate ring-strain to induce thermal ROP of **11b**.

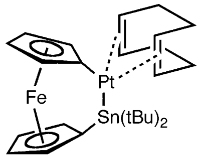
To investigate the thermal polymerization behavior of **12a**,**b**, differential scanning calorimetry studies were undertaken. In the temperature range of 25−300 °C, no exothermic transitions attributable to ROP were detected. For **12a**, a melt transition was found at 77 °C, while for **12b**, a similar transition was observed at 114 °C. When attempts were made to heat samples of **12a**,**b** beyond 300 °C, decomposition was observed in every case, which led to the formation of an insoluble black material. These observations again suggest that there is little ring-strain present in **12a**,**b**. Despite the presence of a bridging moiety possessing weak Cp−Sn bonds, the amount of ring-strain present appears to be insufficient to facilitate ROP at a temperature below that at which decomposition occurs.[37]

In a manner analogous to **11b**, the thermal polymerization of **12c** was also attempted by heating a sample in an evacuated tube at temperatures up to 250 °C for up to 72 h. ^1H NMR characterization of the resulting product resulted in very broad peaks, perhaps due to the formation of trace amounts of magnetic species such as Fe metal; however only unreacted **12c** could be isolated.

5. Ring-Opening and Insertion Reactions of [2]-Ferrocenophanes 11a,b and 12a−c. To gain insight into the ring-strain dependence of the reactivity of Ge−Cp and Sn−Cp bonds, a series of ring-opening reactions with **11b** and **12a**−**c** were attempted.

(a) Attempted Ring-Opening Reactions with 11b and 12a,c with Amine Nucleophiles and Radical Initiators. Recently it has been shown that reaction of the [1]stannaferrocenophane, **4**, with amines such as pyridine leads to ROP.[23] However, when samples of **12a** were treated with pyridine at either 25 or 60 °C, no reaction was detected by ^1H NMR even after 72 h. Similarly, no reaction was observed at 25 °C or at elevated temperatures in the presence of the much stronger nucleophile 4-(dimethylamino)pyridine for **11b**, **12a**, and **12c**. In an attempt to generate a ring-opened species through a radical pathway as previously detected for tin-bridged [1]ferrocenophanes,[23] samples of **12a** were treated with AIBN at 25 and 60 °C in the presence of Bu_3SnH. After 72 h, no ring-opening was detected by ^1H NMR. This is in contrast to the reactions of **4** with AIBN and Bu_3SnH, in which ring-opening reactions do occur.[23]

(b) Attempted Reactions of 11b, 12a, and 12c with Platinum(0) Complexes and ROP Precatalysts. Compound **4a** reacts with equimolar amounts of $Pt(cod)_2$ to form the corresponding platinastanna[2]-ferrocenophane insertion compound, **13**.[31]



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In addition to work by Tanaka et al. and ourselves concerning the transition metal-catalyzed ROP of germa-[1]ferrocenophanes,[38,39] Mochida and co-workers have recently reported platinum- and palladium-catalyzed ROP of a digerma[2]ferrocenophane to yield high molecular weight polymer.[28] In contrast, the reaction of **12a** with $Pt(cod)_2$, at 25 and 60 °C, resulted only in the formation of colloidal Pt(0), with no evidence for Pt(0) insertion into the ipso-Cp−Sn bond. Treatment of **11b** and **12c** with $PtCl_2$, Karstedt's catalyst (Pt(0)), and

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(36) Pudelski, J. K.; Foucher, D. A.; Honeyman, C. H.; Lough, A. J.; Manners, I.; Barlow, S.; O'Hare, D. *Organometallics* **1995**, *14*, 2470.

(37) A reviewer made the suggestion that the replacement of a weak E−Cp bond in a [1]ferrocenophane with a bridging atom E (E = Ge or Sn) by a stronger $E-CH_2$ bond may decrease polymerizability if this bond is cleaved in the polymerization mechanism. However, all the current evidence from studies to date indicate that during thermal polymerizations of ferrocenophanes it is the E−Cp bond that breaks, and such a bond is also present in the [2]ferrocenophanes **11** and **12** reported in this study. In addition, previous work on analogous, but more tilted and hence more strained [2]ferrocenophanes containing C−S and C−P bridges has demonstrated that these species do polymerize, even though one can similarly argue that weak E−Cp bonds (E = S or P) have been replaced by stronger $E-CH_2$ bonds relative to [1]ferrocenophane analogues. This indicates that the replacement of E−Cp by a $E-CH_2$ bond is unlikely to be mechanistically significant. For relevant discussions see: (a) Pudelski, J. K.; Manners, I. *J. Am. Chem. Soc.* **1995**, *117*, 7265. (b) Sheridan, J. B.; Lough, A. J.; Manners, I. *Organometallics* **1996**, *15*, 2195. (c) Ref 29.

(38) Reddy, N. P.; Yamashita, H.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2263.

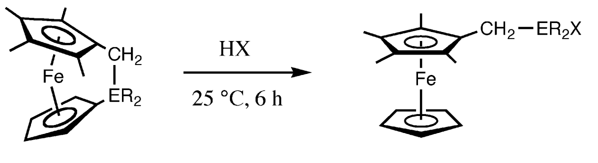
(39) Peckham, T. J.; Massey, J. A.; Edwards, M.; Foucher, D. A.; Manners, I. *Macromolecules* **1996**, *29*, 2396.

PtCl$_2$(COD) yielded only starting material, as evidenced by ^{1}H NMR. Similarly, treatment of **11b** and **12a** with equimolar amounts of Pt(PEt$_3$)$_3$ at 25 °C as well as at elevated temperatures failed to induce insertion reactions.

(c) Attempted Photolytic Ring-Opening of 11b. We have shown very recently that the ROP of [1]-silaferrocenophanes can be achieved photolytically in the presence of an initiator such as Na[η-C$_5$H$_5$] via cleavage of the Fe–Cp bond.[40] The ring-opening of **11b** was attempted using photolysis in the presence of an initiator using analogous procedures. Solutions of **11b** in THF were treated with catalytic and equimolar amounts of Na[η-C$_5$H$_5$] and irradiated for 3–6 h. In each case, only unreacted **11b** was detected by ^{1}H NMR. Similarly, there was no reaction under analogous conditions with a 5-fold excess of Na[η-C$_5$H$_5$]. In addition, treatment of a solution of **11b** with bis(diphenylphosphino)ethane and irradiation for 6 h yielded no change as observed by ^{1}H NMR.

(d) Reaction of 11a,b and 12a–c with Strong Protic Acids. The reaction of strained [1]ferrocenophanes with strong acids generally results in the formation of ring-opened products possessing a protonated Cp ring.[2,41] In addition, the cleavage of Sn–aryl bonds and sp^2-C–Sn bonds (such as the ipso-Cp–Sn bond of **12a–c**) with protic acids is well known in both strained and unstrained systems.[42] Thus, despite the moderate degree of ring-strain in **12a–c**, the presence of sp^2-C–Sn bonds would be expected to still allow ipso-Cp–Sn bond cleavage reactions. The reactivity of the ipso-Cp–Ge bond of **11a**,**b** is expected to be similar. Indeed, when samples of **11b** and **12a** were treated with an equimolar amount of HCl (in Et$_2$O), quantitative cleavage of the E–Cp bond (E = Ge, Sn) occurred, resulting in the corresponding ring-opened species, **14** and **15**. Similarly, when a sample of **12a** was treated with an equimolar amount of triflic acid (CF$_3$SO$_3$H), the corresponding ring-opened species, **16**, was isolated.

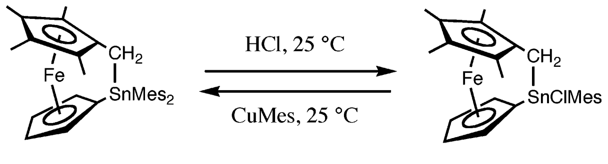
In addition, when **12c** was treated with 1 equiv of HCl, the corresponding product (η-C$_5$Me$_4$)Fe(η-C$_5$H$_5$)CH$_2$-SnMe$_2$Cl was detected by ^{1}H NMR after 10 min. However, after the solvent was removed, the only product that could be isolated was free Cp*FeCp.



11b: E = Ge, R = Me
12a: E = Sn, R = tBu

14: E = Ge, R = Me, X = Cl
15: E = Sn, R = tBu, X = Cl
16: E = Sn, R = tBu, X = SO$_3$CF$_3$

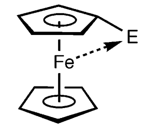
Unlike **12a**, which possesses only one sp^2-C–Sn bond, **12b** possesses both a Cp–Sn bond and two Sn–aryl-C bonds. Interestingly, when a sample of **12b** was treated with equimolar amounts of HCl, the corresponding CH$_2$–SnMesCl-bridged [2]ferrocenophane, **17**, was obtained in 50% yield. As a result of the difficulty encountered in recrystallizing **17**, the proposed structure was verified through the reaction of **17** with excess CuMes, after which complete retroconversion to **12b** was confirmed by ^{1}H, ^{13}C, and ^{119}Sn NMR.



12b **17**

(e) Attempted Reaction of 11b and 12c with an Anionic Ring-Opening Initiator. The anionic ROP of [1]silaferrocenophanes is a useful route to monodisperse polyferrocenylsilanes which allows molecular weight control and access to block copolymer architectures.[17,43] In the presence of 0.01 equiv of n-butyllithium (nBuLi), no indication of ring-opening of compound **11b** or **12c** was detected by ^{1}H NMR after 2 h. Similarily, when compounds **11b** and **12c** were treated with equimolar amounts of nBuLi, followed by quenching of any potential lithiated product with Me$_3$SiCl, only unreacted starting material was isolated.

6. X-ray Structural Analysis of Ring-Opened Species 15 and 16. Previous work has shown that certain ferrocenyl derivatives, **18a–c**, possess Fe···E interactions whose magnitude (as indicated by the β angle; angle with which the ipso-Cp–E bond bends toward the Fe atom) depends on the degree of Lewis acidity at E.[44–47]



18a: E = [CPh$_2$][BF$_4$]; β = 20.7 °
18b: E = BBr$_2$; β = 17.7 °
18c: E = GeEt$_2$Cl; β = 7.5 °

To probe the possible existence of an Fe···Sn interaction, X-ray structural analyses of compounds **15** and **16** were undertaken. The structure of **15** is shown in Figure 7, and selected bond lengths and angles are given in Table S6 (see Supporting Information). Examination of the structure of **15** reveals that the CH$_2$–Sn(tBu)$_2$Cl moiety is located above the plane of the Cp′ ligand, thereby resulting in no significant Fe···Sn interaction. The structure of **16** is shown in Figure 8, and selected bond lengths and angles are given in Table S7 (see Supporting Information). As was observed in the structure of **15**, the CH$_2$–Sn(tBu)$_2$OSO$_2$CF$_3$ moiety of **16** is also above the plane of the Cp′ ring, and thus no

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(40) Tanabe, M.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 11434. For previous work on phosphorus-bridged [1]ferrocenophanes see ref 7f.

(41) MacLachlan, M.; Bourke, S. C.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 2126.

(42) (a) Bhattacharya, S. N.; Raj, P.; Husain, I. *Indian J. Chem., Sect. A* **1978**, *16A*, 1108. (b) Olszowy, H. A.; Kitching, W. *Organometallics* **1984**, *3*, 1670. (c) Uhlig, W. *J. Organomet. Chem.* **1991**, *409*, 377.

(43) Ni, Y.; Rulkens, R.; Manners, I. *J. Am. Chem. Soc.* **1996**, *118*, 4102.

(44) Foucher, D. A.; Edwards, M.; Burrow, R. A.; Lough, A. J.; Manners, I. *Organometallics* **1994**, *13*, 4959.

(45) Behrens, U. *J. Organomet. Chem.* **1979**, *182*, 89.

(46) Koridze, A. A. *Russ. Chem. Rev.* **1986**, *55*, 113.

(47) (a) Appel, A.; Jäkle, F.; Priermeier, T.; Schmid, R.; Wagner, M. *Organometallics* **1996**, *15*, 1188. (b) Scheibitz, M.; Bats, J. W.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Organometallics* **2004**, *23*, 940.

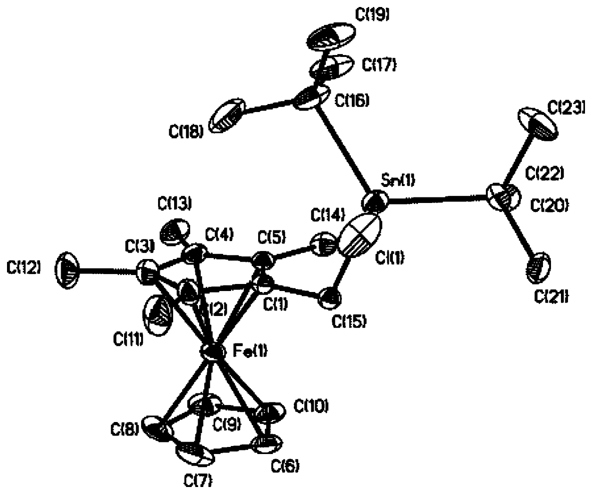

Figure 7. Molecular structure of **15** showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

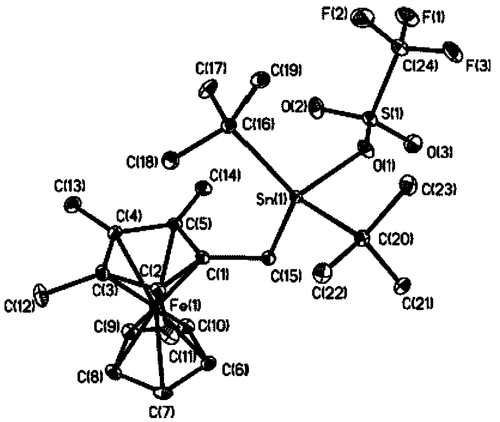

Figure 8. Molecular structure of **16** showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

significant Fe···Sn interaction is present in this case either. These observations suggest that the Sn centers present in compounds **15** and **16** do not possess the degree of Lewis acidity necessary to induce an electrophilic interaction with the electron-rich iron center.

Summary

The synthesis of novel carbogerma[2]ferrocenophanes **11a**,**b** and carbostanna[2]ferrocenophanes **12a**–**c** was accomplished via the reaction of (η-C_5Me_4)Fe(η-C_5H_4-Li)CH_2Li·xTMEDA with the appropriate dichlorodiorganogermanes and dichlorodiorganostannanes. The structures of **11a**,**b** and **12a**–**c**, as determined by X-ray structural analysis, revealed the presence of very moderate α angles with values ranging from α = 10.99(2)° to 11.81(5)° for the C–Ge-bridged species **11a**,**b** and from α = 6.64(2)° to 7.5(1)° for the C–Sn-bridged analogues **12a**–**c**, which is indicative of a small to moderate degree of ring-strain. The results of this study suggest that the presence of diminished ring-strain renders these species much less reactive than their [1]-ferrocenophane counterparts (**4**, **5**) or [2]ferrocenophanes such as **6**, **9a**,**b**, and **10** to ring-opening reactions. Furthermore, it can be concluded that the high reactivity displayed by the Sn-bridged and Ge-bridged [1]-ferrocenophanes, **4a**,**b** and **5**, is a consequence of the presence of weak Cp–E (E = Sn or Ge) bonds *and* the inherently relatively high ring-strain present in those species. The intriguing ability of **6** (M = Fe, E_2 = $GeMe_2$-$GeMe_2$) to undergo ROP[28] despite the presence of a very low degree of strain (α = ca. 4°) appears to be a consequence of the relatively labile Ge–Ge bond, whereas **11a**,**b**, which are clearly more strained, are unreactive under similar reaction conditions.

Experimental Section

Materials. All reagents, unless otherwise specified, were purchased from Aldrich Chemical Co. and were used as received. Solvents were dried by standard procedures and distilled immediately prior to use. Cl_2SnMes_2,[48] pentamethylferrocene,[49] and CuMes[50] were prepared according to standard literature procedures.

Equipment. All reactions and manipulations were performed under an inert atmosphere (prepurified N_2) using either standard Schlenk techniques or an inert-atmosphere glovebox (MBraun). ^1H (400 MHz) and ^{13}C NMR (100.5 and 75.5 MHz) spectra were recorded on Varian Unity 400 or Varian XL 300 spectrometers. The 111.8 MHz ^{119}Sn NMR spectra were recorded on a Varian XL 300 spectrometer. All solution ^1H and ^{13}C NMR spectra were referenced internally to residual protonated solvent shifts. ^{119}Sn NMR spectra were referenced externally to $SnMe_4$. UV/visible spectra were obtained using a Perkin-Elmer Lambda 900 UV/vis/near-IR spectrophotometer in hexanes at concentrations of 1.0 mmol·L^{-1}. Cyclic voltammetry (CV) was performed using an Epsilon EC instrument equipped with a Au electrode and an Ag/AgCl reference electrode. The solutions were prepared using CH_2Cl_2 (previously dried over CaH_2 and distilled under N_2) and [NBu_4][PF_6]. The concentration of [NBu_4][PF_6] was 0.1 M, and the solutions were prepared in concentrations of 0.001–0.005 M. All measurements were made under N_2 atmosphere at a scan rate of 100 mV/s, and ferrocene was used as an internal standard. Potentials are reported versus the ferrocene/ferrocenium couple. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer operating in electron impact (EI) mode. The calculated isotopic distribution for each ion was in agreement with experimental values. The photoirradiation experiments were performed by placing the reaction flask next to a 125 W high-pressure Hg arc lamp (Philips). The emission was filtered by Pyrex glass (λ > ca. 300 nm). The thermal behavior of the CH_2–Sn-bridged monomers, **12a**,**b**, was studied using a Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a TAC-7 instrument controller. Thermograms were calibrated with the melt transitions of hexane and indium and were obtained at a heating rate of 10 °C/min under a nitrogen atmosphere. Elemental analyses were performed by Quantitative Technologies, Inc., Whitehouse, NJ. In addition, elemental analyses were obtained using a Perkin-Elmer Series II 2400 CHNS analyzer maintained by the Analest facility at the University of Toronto.

Synthesis of (η-C_5Me_4)Fe(η-C_5H_4Li)CH_2Li·xTMEDA. *Note:* Reaction stoichiometries were calculated based on (η-C_5Me_4)Fe(η-C_5H_4Li)CH_2Li·0.66TMEDA. ^1H NMR analysis of reactions of (η-C_5Me_4)Fe(η-C_5H_4Li)CH_2Li·xTMEDA with Me_3SiCl suggests that x = 2; however, it was found that by employing a coefficient of x = 0.66 the overall yields were improved.

To a suspension of pentamethylferrocene (30 g) in hexanes (500 mL) were added 2.0 equiv of TMEDA (35 mL) and 4.0 equiv of nBuLi (1.6 M in hexanes). The reaction mixture was allowed to stir at 25 °C for 48 h, after which the brick red

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(48) Jäkle, F.; Manners, I. *Organometallics* **1999**, *18*, 2628.

(49) Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680.

(50) Tsuda, T.; Yazawa, T.; Watanabe, K.; Fujii, T.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 192.

precipitate was collected by filtration under N_2. The resulting pyrophoric red-orange material was washed with 3 × 200 mL aliquots of hexanes and dried under vacuum. Yield: 35 g (86%)

Synthesis of (η-C_5Me_4)Fe(η-C_5H_4)CH_2GePh_2, 11a. To a suspension of (η-C_5Me_4)Fe(η-C_5H_4Li)$CH_2Li\cdot x$TMEDA (1.0 g, 2.9 mmol) in Et_2O (200 mL) kept at −78 °C was added slowly with stirring a solution of Cl_2GePh_2 (1.03 g, 3.5 mmol) in 50 mL of Et_2O. The resulting solution was allowed to warm to 25 °C, at which point the reaction mixture was filtered under N_2, resulting in the isolation of a clear orange solution. Solvent removal under vacuum (for 24 h to ensure removal of any trace amounts of TMEDA) resulted in the isolation of a light orange gummy material. Recrystallization of this material from hexanes at −30 °C yielded **11a** as orange crystals. Yield: 0.51 g (37%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 7.76−7.74 (m, 4H, C_6H_5−Ge), 7.25−7.20 (m, 4H, C_6H_5−Ge), 7.10−7.00 (m, 2H, C_6H_5−Ge), 4.38 (ps t, 2H, C_5H_4), 3.87 (ps t, 2H, C_5H_4), 2.95 (s, 2H, CH_2−Ge), 2.16 (s, 6H, C_5Me_4), 1.74 (s, 6H, C_5Me_4) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 140.0 (*ipso*-C_6H_5), 134.4 (*o*-C_6H_5), 129.5 (*p*-C_6H_5), 129.1 (*m*-C_6H_5), 86.2 (*ipso*-C_5Me_4), 81.5 (C_5Me_4), 81.3 (C_5Me_4), 80.6 (C_5H_4), 75.0 (C_5H_4), 72.8 (*ipso*-C_5H_4), 19.2 (CH_2), 13.1 (C_5Me_4), 12.0 (C_5Me_4). UV−vis (hexanes): λ_{max} 462 nm ($\epsilon = 173\ M^{-1}\ cm^{-1}$). MS (70 eV, EI): *m/z* (%) 482 (56) [M^+], 256 (100) [M^+] − $GePh_2$. HR-MS: calcd for $C_{27}H_{28}{}^{56}FeGe$ 482.0752 g·mol^{-1}, found 482.0760 g·mol^{-1}.

Synthesis of (η-C_5Me_4)Fe(η-C_5H_4)CH_2GeMe_2, 11b. To a suspension of (η-C_5Me_4)Fe(η-C_5H_4Li)$CH_2Li\cdot x$TMEDA (3.0 g, 8.7 mmol) in Et_2O (250 mL) kept at −78 °C was added slowly with stirring a solution of Cl_2GeMe_2 (1.51 mg, 8.7 mmol) in 100 mL of Et_2O. The resulting solution was allowed to warm to 25 °C, at which point the reaction mixture was filtered under N_2, resulting in the isolation of a clear orange solution. Solvent removal under vacuum (for 24 h to ensure removal of any trace amounts of TMEDA) resulted in the isolation of a light orange gummy material. Recrystallization of this material from hexanes at −30 °C yielded **11b** as orange crystals. Yield: 0.98 g (33%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 4.20 (ps t, 2H, C_5H_4), 3.82 (ps t, 2H, C_5H_4), 2.22 (s, 6H, C_5Me_4), 2.20 (s, 2H, CH_2−Ge), 1.81 (s, 6H, C_5Me_4), 0.50 (s, 6H, Me_2−Ge) ppm. ^{13}C NMR (400 MHz, C_6D_6, 25 °C): δ 87.9 (*ipso*-C_5Me_4), 80.8 (C_5Me_4), 80.4 (C_5Me_4), 80.4 (C_5H_4), 78.9 (*ipso*-C_5H_4), 72.4 (C_5H_4), 22.4 (CH_2−Ge), 13.2 (C_5Me_4), 12.4 (C_5Me_4), 0.9 (Me_2−Ge) ppm. UV−vis (hexanes): λ_{max} 461 nm ($\epsilon = 203\ M^{-1}\ cm^{-1}$), CV (5 mM): $E_{1/2} = -274$ mV, $E_{ox} = -93$ mV, $E_{red} = -454$ mV vs Fc/Fc^+ couple. MS (70 eV, EI): *m/z* (%) 358 (100) [M^+], 254 (22) [M^+] − $GeMe_2$. Anal. Calcd for $C_{17}H_{24}FeGe$ (357): C 57.22, H 6.77. Found: C 57.22, H 6.73.

Synthesis of (η-C_5Me_4)Fe(η-C_5H_4)$CH_2Sn(t\mathrm{Bu})_2$, 12a. To a suspension of (η-C_5Me_4)Fe(η-C_5H_4Li)$CH_2Li\cdot x$TMEDA (5.0 g, 14.5 mmol) in Et_2O (200 mL) kept at −78 °C was added slowly with stirring a solution of $Cl_2Sn(t\mathrm{Bu})_2$ (4.85 g, 16 mmol) in 100 mL of Et_2O. The resulting solution was allowed to warm to 25 °C, at which point the reaction mixture was filtered under N_2, resulting in the isolation of a clear orange solution. Solvent removal under vacuum (for 24 h to ensure removal of any trace amounts of TMEDA) resulted in the isolation of a light orange powder. Recrystallization of this material at −30 °C from a concentrated Et_2O/MeCN (50/50 v/v) solution afforded **12a** as orange crystals. Yield: 3.5 g (49%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 4.30 (ps t, *J*(H/H) = 1 Hz, 2H; C_5H_4), 3.82 (ps t, *J*(H/H) = 3 Hz, 2H; C_5H_4), 2.34 (s/d, $J(^{117/119}Sn/H)$ = 40 Hz, 2H; CH_2−Sn), 2.28 (s/d, $J(^{117/119}Sn/H)$ = 48 Hz, 6H, C_5Me_4), 1.82 (s/d, $J(^{117/119}Sn/H)$ = 40 Hz, 6H; C_5Me_4), 1.42 (s/d, $J(^{117/119}Sn/H)$ = 62 Hz, 18H; CMe_3) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 90.2 (*ipso*-C_5Me_4), 80.9 ($J(^{117/119}Sn/^{13}C)$ = 40 Hz; C_5H_4), 79.9 (C_5Me_4), 78.8 (*ipso*-C_5H_4), 78.7 (C_5Me_4), 72.2 ($J(^{117/119}Sn/^{13}C)$ = 40 Hz; C_5H_4), 31.9 (CMe_3), 30.8 (CMe_3), 14.2 ($J(^{117/119}Sn/^{13}C)$ = 280 Hz; CH_2−Sn), 12.8 (C_5Me_4), 11.8 (C_5Me_4) ppm. ^{119}Sn NMR (111.8 MHz, C_6D_6, 25 °C): δ −24.9 ppm (CH_2−*Sn*) ppm. UV/vis (hexanes): λ_{max} 462 nm ($\epsilon = 153\ M^{-1}\ cm^{-1}$). CV (1 mM): $E_{1/2} = -332$ mV, $E_{ox} = -247$ mV, $E_{red} = -418$ mV vs Fc/Fc^+ couple. MS (70 eV, EI): *m/z* (%) 488 (50) [M^+], 374 (100) [M^+] − 2 $C(CH_3)_3$, 254 (51) [M^+] − $Sn(t\mathrm{Bu})_2$. HR-MS: calcd for $C_{23}H_{36}{}^{56}Fe^{120}Sn$ 488.1188 g·mol-1, found 488.1186 g·mol^{-1}.

Synthesis of (η-C_5Me_4)Fe(η-C_5H_4)CH_2SnMes_2, 12b. To a suspension of (η-C_5Me_4)Fe(η-C_5H_4Li)$CH_2Li\cdot x$TMEDA (1.0 g, 2.9 mmol) in Et_2O (100 mL) kept at −78 °C was added slowly with stirring a suspension of $Cl_2Sn(Mes)_2$ (1.36 g, 3.2 mmol) in 50 mL of Et_2O. The resulting solution was allowed to warm to 25 °C, at which point the reaction mixture was filtered under N_2, resulting in the isolation of a clear orange solution. Solvent removal under vacuum (for 24 h to ensure removal of any trace amounts of TMEDA) resulted in the isolation of a light orange powder. Recrystallization of this material at −30 °C from a concentrated Et_2O/MeCN (50/50 v/v) solution afforded **12b** as orange crystals. Yield: 0.80 g (45%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 6.80 (s/d, $J(^{117/119}Sn/H)$ = 20 Hz, 4H; *m-Mes*), 4.29 (ps t, *J*(H/H) = 3 Hz, 2H; C_5H_4), 3.79 (ps t, *J*(H/H) = 3 Hz, 2H; C_5H_4), 3.04 (s/d, $J(^{117/119}Sn/H)$ = 64 Hz, 2H, CH_2−Sn), 2.61 (s, 12H; *o-Mes*), 2.21 (s, 6H; C_5Me_4), 2.14 (s, 6H; *p-Mes*), 1.78 (s, 6H, C_5Me_4) ppm. ^{13}C NMR (75.5 MHz, C_6D_6, 25 °C): δ 144.4 ($J(^{117/119}Sn/^{13}C)$ = 35 Hz; *o*-Mes), 141.0 (*p-Mes*), 138.4 ($J(^{117/119}Sn/^{13}C)$ = 15 Hz; *ipso-Mes*), 128.9 ($J(^{117/119}Sn/^{13}C)$ = 30 Hz, *m-Mes*), 90.3 (*ipso*-C_5Me_4), 86.9 (*ipso*-C_5H_4), 81.4 ($J(^{117/119}Sn/^{13}C)$ = 56 Hz; C_5H_4), 80.4 (C_5Me_4), 79.9 (C_5Me_4), 72.1 ($J(^{117/119}Sn/^{13}C)$ = 47 Hz; C_5H_4), 26.0 (CH_2−Sn), 25.6 ($J(^{117/119}Sn/^{13}C)$ = 50 Hz; *o-Mes*), 21.0 (*p-Mes*), 12.8 (C_5Me_4), 11.7 (C_5Me_4) ppm. ^{119}Sn NMR (111.8 MHz, C_6D_6, 25 °C): δ −60.4 (CH_2−*Sn*) ppm. UV/vis (hexanes): λ_{max} 454 nm ($\epsilon = 131\ M^{-1}\ cm^{-1}$). CV (1 mM): $E_{1/2} = -280$ mV, $E_{ox} = -162$ mV, $E_{red} = -398$ mV vs Fc/Fc^+ couple. MS (70 eV, EI): *m/z* (%) 612 (100) [M^+], 493 (8) [M^+] − Mes, 254 (54) [M^+] − $Sn(Mes)_2$. Anal. Calcd for $C_{33}H_{40}FeSn$ (611): C 64.85, H 6.60. Found: C 64.62, H 6.53.

Synthesis of (η-C_5Me_4)Fe(η-C_5H_4)CH_2SnMe_2, 12c. To a suspension of (η-C_5Me_4)Fe(η-C_5H_4Li)$CH_2Li\cdot x$TMEDA (5.0 g, 14.5 mmol) in Et_2O (200 mL) kept at −78 °C was added slowly with stirring a solution of Cl_2SnMe_2 (3.8 g, 17.4 mmol) in 100 mL of Et_2O. The resulting solution was allowed to warm to 25 °C, at which point the reaction mixture was filtered under N_2, resulting in the isolation of a clear orange solution. Solvent removal under vacuum (for 24 h to ensure removal of any trace amounts of TMEDA) resulted in the isolation of a light orange powder. Recrystallization of this material at −30 °C from a concentrated hexanes solution afforded **12c** as orange crystals. Yield: 1.5 g (26%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 4.16 (ps t, *J*(H/H) = 2 Hz, 2H; C_5H_4), 3.83 (ps t, *J*(H/H) = 3 Hz, 2H; C_5H_4), 2.22 (s, 6H, C_5Me_4), 2.19 (s, 2H; CH_2−Sn), 1.82 (s, 6H; C_5Me_4), 0.36 (s, 6H; $SnMe_2$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 92.1 (*ipso*-C_5Me_4), 80.7 ($J(^{117/119}Sn/^{13}C)$ = 35 Hz; C_5H_4), 79.4 (C_5Me_4), 78.9 (*ipso*-C_5H_4), 75.2 (C_5Me_4), 72.3 ($J(^{117/119}Sn/^{13}C)$ = 40 Hz; C_5H_4), 17.5 (CH_2−Sn), 12.6 (C_5Me_4), 11.7 (C_5Me_4), −6.5 ($SnMe_2$) ppm. ^{119}Sn NMR (111.8 MHz, C_6D_6, 25 °C): δ 32.9 ppm (CH_2−*Sn*) ppm. UV/vis (hexanes): λ_{max} 453 nm ($\epsilon = 221\ M^{-1}\ cm^{-1}$). CV (5 mM): $E_{1/2} = -279$ mV, $E_{ox} = -107$ mV, $E_{red} = -450$ mV vs Fc/Fc^+ couple. MS (70 eV, EI): *m/z* (%); 404 (78) [M^+], 374 (49) [M^+] − 2 Me, 254 (100) [M^+] − $SnMe_2$. HR-MS: calcd for $C_{17}H_{24}{}^{56}Fe^{120}Sn$ 404.0249 g·mol^{-1}, found 404.0235 g·mol^{-1}.

Attempted Thermal Polymerization of 11b. A sample of **11b** (ca. 0.1 g) was sealed in an evacuated Pyrex tube and heated at temperatures of 130, 150, 180, and 250 °C for approximately 24 h at each temperature. The melt changed color from an orange to red, but there was no observable increase in viscosity. The resulting material was characterized by ^1H NMR and contained unreacted **11b** as well as (η-C_5Me_5)Fe(η-C_5H_5).

Attempted Ring-Opening Reactions of 11b. A sample of **11b** (ca. 0.05 g, 0.14 mmol) was dissolved in minimal toluene (5 mL). To this solution was added (a) 1 vol % Karstedt's catalyst (Pt(0)), (b) 1 wt % $PtCl_2$, (c) 4 mol % $PtCl_2$(COD), (d) 1 equiv (0.09 g) of $Pt(PEt_3)_3$, (e) 1 equiv (17.1 mg) of (dimethyl-

Table 2. Selected Crystal, Data Collection, and Refinement Parameters for 11a,b

	11a	**11b**
empirical formula	$C_{27}H_{28}FeGe$	$C_{17}H_{24}FeGe$
fw	480.93	356.80
temperature, K	150(1)	150(1)
wavelength, Å	0.71073	0.71073
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	7.7235(9)	7.3330(4)
b, Å	11.7744(16)	8.5260(5)
c, Å	12.8300(18)	14.2880(10)
α, deg	88.313(6)	74.826(4)
β, deg	79.831(7)	89.732(4)
γ, deg	72.316(7)	66.607(4)
volume, Å^3	1093.8(2)	786.31(8)
Z	2	2
ρ_{calc}, g cm^{-3}	1.460	1.507
abs coeff *μ*(Mo Kα), mm^{-1}	2.048	2.818
F(000)	496	368
cryst size, mm^3	0.20 × 0.12 × 0.12	0.35 × 0.30 × 0.28
θ range for data collection, deg	2.81 to 25.12	2.70 to 27.50
index ranges	$0 \le h \le 9$ $12 \le k \le 14$ $-15 \le l \le 15$	$0 \le h \le 9$ $-9 \le k \le 11$ $-18 \le l \le 18$
no. of reflns collected	7946	8124
no. of indep reflns	3834 [*R*(int) = 0.09]	3562 [*R*(int) = 0.059]
completeness to $\theta = 27.50°$	98.3%	98.4%
abs corr	multiscan	multiscan
max. and min. transmn	0.7912 and 0.6849	0.5058 and 0.4387
refinement method	full matrix least-squares on F^2	full matrix least-squares on F^2
no. of data/restraints/params	3834/0/267	3562/0/179
GoF on F^2	0.972	1.035
R1[a] [$I > 2\sigma(I)$]	R1 = 0.0586	R1 = 0.0396
wR2[b] (all data)	wR2 = 0.1456	wR2 = 0.1041
extinction coeff	0.0062(18)	0.019(3)
largest diff peak and hole, e Å^{-3}	0.815 and −0.793	0.859 and −1.011

[a] $R1 = \sum||F_o| - |F_o||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

amino)pyridine (DMAP), and (f) excess DMAP (0.15 g). The solution was stirred for 24 h at room temperature and alternatively at 120 °C for each sample, after which the solvent was removed under vacuum. In the cases of Pt(0) and $PtCl_2$, a slight broadening of the peaks was observed in the ^1H NMR; however only unreacted **11b** could be isolated. In all other cases, only unreacted **11b** was detected by ^1H NMR.

Attempted Anionic ROP of 11b. To solutions of **11b** (0.05 g, 0.14 mmol) in THF (0.5 mL) were added *n*-BuLi (1.6 M in hexanes) [(i) 1 equiv (87.5 *μ*L), (ii) 10 mol % (8.75 *μ*L)], and the mixtures were stirred for 2 h. A slight excess of TMSCl (1.1 equiv, 19.5 *μ*L) was added to each reaction, and all solvent was removed under vacuum. In each case, only unreacted **11b** was detected by ^1H NMR.

Attempted Photolytic Ring-Opening of 11b. To solutions of **11b** (0.05 g, 0.14 mmol) in THF (1 mL) were added (i) 4 mol % (2.8 *μ*L) of Na[η-C_5H_5] (2.0 M in THF), (ii) 1 equiv (70 *μ*L) of Na[η-C_5H_5], (iii) 5 equiv (0.35 mL) of Na[η-C_5H_5], and (iv) 1 equiv (56 mg) of bis(diphenylphosphino)ethane. The solution was irradiated for up to 6 h and kept at a temperature of 5 °C in a water bath. In each case, only unreacted **11b** could be detected by ^1H NMR.

Attempted Thermal Polymerization of 12a. Samples of **12a** (ca. 0.1 g) were sealed in an evacuated Pyrex tube and heated at temperatures of 200, 250, and 300 °C for 48 h. For polymerization attempts carried out at 200 and 250 °C, only unreacted **12a** was detected by ^1H NMR. At 300 °C, decomposition to an intractable black material was observed.

Attempted Ring-Opening Reactions with 12a. To a solution of **12a** (0.02 g, 0.04 mmol) in 0.6 mL of C_6D_6 was added (a) 1 equiv (3.3 *μ*L) of pyridine, (b) 1 equiv (0.005 g) of DMAP, (c) 1 equiv of AIBN (0.0067 g) and Bu_3SnH (0.012 g), (d) 1 equiv (0.017 g) of $Pt(cod)_2$, and (e) 1 equiv (0.027 g) of $Pt(PEt_3)_3$. The reaction solutions were allowed to stir at (i) 25 °C for 72 h and (ii) 60 °C for 72 h. In each case, only unreacted **12a** was detected by ^1H NMR.

Table 3. Selected Crystal, Data Collection, and Refined Parameters for 12a−c

	12a	**12b**	**12c**
empirical formula	$C_{23}H_{36}FeSn$	$C_{33}H_{40}FeSn$	$C_{17}H_{24}FeSn$
fw	487.06	611.19	402.90
temperature, K	173(2)	100.0(1)	150(1)
wavelength, Å	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a, Å	12.138(3)	7.9662(2)	9.0434(4)
b, Å	11.4142(8)	12.5838(2)	13.9146(5)
c, Å	16.3104(14)	14.0272(4)	13.0246(6)
α, deg	90	93.573(15)	90
β, deg	100.666(11)	91.389(14)	97.815(2)
γ, deg	90	101.775(15)	90
volume, Å^3	2220.6(6)	1372.91(6)	1623.73(12)
Z	4	2	4
ρ_{calc}, g cm^{-3}	1.457	1.478	1.648
abs coeff *μ*(Mo Kα), mm^{-1}	1.781	1.457	2.417
F(000)	1000	628	808
cryst size, mm^3	0.46 × 0.45 × 0.43	0.25 × 0.25 × 0.23	0.26 × 0.22 × 0.05
θ range for data collection, deg	2.54 to 27.00	2.94 to 27.47	2.59 to 27.51
index ranges	$0 \le h \le 15$ $0 \le k \le 14$ $-20 \le l \le 20$	$0 \le h \le 10$ $-16 \le k \le 15$ $-18 \le l \le 18$	$-11 \le h \le 11$ $-17 \le k \le 17$ $-14 \le l \le 16$
no. of reflns collected	5080	19 947	11 426
no. of indep reflns	4853 [*R*(int) = 0.0231]	6239 [*R*(int) = 0.025]	3696 [*R*(int) = 0.0416]
completeness to $\theta = 27.50°$		99.1%	99.1%
abs corr	empirical	multiscan (Denzo-SMN)	semiempirical from equivalents
max. and min. transmn		0.7304 and 0.7121	0.892 and 0.686
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	4853/0/237	6239/0/327	3696/0/179
GoF on F^2	1.052	1.047	1.044
R1[a] [$I > 2\sigma(I)$]	R1 = 0.0259	R1 = 0.0233	R1 = 0.0349
wR2[b] (all data)	wR2 = 0.0685	wR2 = 0.0603	wR2 = 0.0927
extinction coeff	0.0009(2)	0.0023(4)	0.0018(5)
largest diff peak and hole, e Å^{-3}	0.427 and −0.380	0.815 and −0.538	1.063 and −1.473

[a] $R1 = \sum||F_o| - |F_o||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Attempted Thermal Polymerization of 12c. A sample of **12c** (ca 0.1 g) was sealed in an evacuated Pyrex tube and heated at temperatures of 150, 180, and 250 °C for approximately 24 h at each temperature. Additionally, the sample was kept at 250 °C for 72 h. The melt changed color slightly to dark orange; however there was no observable increase in viscosity. Very broad peaks were observed in the ^{1}H NMR of the resulting material; however only unreacted **12c** could be isolated.

Attempted Ring-Opening Reactions with 12c. To a solution of **12c** (0.04 g, 0.1 mmol) in 1 mL of C_6D_6 was added (a) 0.1 wt % Karstedt's catalyst, (b) 4 mol % $PtCl_2$(COD), (c) 1 wt % $PtCl_2$, (d) 2 equiv (24 mg) of DMAP, and (e) 10 mol % (1.2 mg) DMAP. The solutions were allowed to stir for (a) 72 h at 25 °C and heated for (b) 72 h at 60−80 °C. In each case, only unreacted **12c** was detected by ^{1}H NMR.

Attempted Anionic ROP of 12c. To solutions of **12c** (0.04 g, 0.10 mmol) in THF (0.5 mL) were added *n*-BuLi (1.6 M in hexanes) [(i) 1 equiv (61.8 μL), (ii) 10 mol % (6.18 μL)], and the mixtures were stirred for 2 h. A slight excess of TMSCl (1.1 equiv, 13.8 μL) was added to each reaction, and all solvent was removed under vacuum. In each case, only unreacted **12c** was isolated and characterized by ^{1}H NMR.

Synthesis of (η-C_5Me_4)Fe(η-C_5H_5)CH_2GeMe_2Cl, 14. One equivalent of $HCl\cdot Et_2O$ (0.11 mL, 1 M in Et_2O) was added to a solution of **11b** (0.04 g, 0.11 mmol) in C_6D_6. Upon addition, the solution became yellow. This mixture was stirred for an additional 24 h and yielded a slightly greenish solution. The solvent was removed under vacuum, and the resulting powder, **14**, was recrystallized from hexanes. Yield: 35 mg (80%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 3.58 (s, 5H, C_5H_5), 2.29 (s, 2H, CH_2−Ge), 1.78 (s, 6H, C_5Me_4), 1.76 (s, 6H, C_5Me_4), 0.35 (s, 6H, Me_2GeCl) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 81.4 (*ipso*-C_5Me_4), 79.6 (C_5Me_4), 79.4 (C_5Me_4), 73.4 (C_5H_5), 21.6 (CH_2−Ge), 12.4 (C_5Me_4), 11.8 (C_5Me_4), 3.8 (−Ge(Me_2)Cl) ppm. MS (70 eV, EI): *m*/*z* (%) 394 (40) [M$^+$], 255 (100) [M$^+$] − $GeMe_2$-Cl.

Synthesis of (η-C_5Me_4)Fe(η-C_5H_5)CH_2Sn(*t*Bu)$_2$Cl, 15. To a solution of **12a** (0.20 g, 0.41 mmol) in 10 mL of toluene was added at 25 °C 1 equiv (410 μL) of HCl (1.0 M in Et_2O). The reaction solution was allowed to stir at 25 °C for 6 h, at which point the solvent was removed under vacuum. Compound **15** was obtained almost quantitatively as an orange powder. Crystals for X-ray structural analysis were obtained through low-temperature (−30 °C) recrystallization from minimal CH_3CN. Yield: 0.21 g (96%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 3.59 (s, 5H; C_5H_5), 2.54 (s/d, $J(^{117/119}Sn/H)$ = 44 Hz, 2H; CH_2−Sn), 1.96 (s, 6H; C_5Me_4), 1.81 (s, 6H; C_5Me_4), 1.15 (s/d, $J(^{117/119}Sn/H)$ = 76 Hz, 18H; CMe_3) ppm. ^{13}C NMR (100.5 MHz, C_6D_6, 25 °C): δ 84.3 (*ipso*-C_5Me_4), 80.3 (C_5Me_4), 78.1 (C_5Me_4), 71.9 (C_5H_5), 35.6 (CMe_3), 29.0 (CMe_3), 16.3 (CH_2−Sn), 12.3 (C_5Me_4), 11.5 (C_5Me_4) ppm. ^{119}Sn NMR (111.8 MHz, C_6D_6, 25 °C): δ 53.9 (CH_2−Sn) ppm. MS (70 eV, EI): *m*/*z* (%); 524 (13) [M$^+$], 255 (100) [M$^+$] − Sn(*t*Bu)$_2$Cl.

Synthesis of (η-C_5Me_4)Fe(η-C_5H_5)CH_2Sn(*t*Bu)$_2OSO_2CF_3$, 16. To a solution of **12a** (0.10 g, 0.20 mmol) in 10 mL of toluene was added at 25 °C 1 equiv (18.1 μL) of CF_3SO_3H. The reaction solution was allowed to stir at 25 °C for 6 h, at which point the solvent was removed under vacuum. Compound **16** was obtained almost quantitatively as an orange powder. Crystals for X-ray structural analysis were obtained through low-temperature (−30 °C) recrystallization from minimal CH_3CN. Yield: 0.12 g (92%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 3.58 (br, 5H; C_5H_5), 2.83 (br, 2H; CH_2−Sn), 1.88 (br, 6H; C_5Me_4), 1.75 (br, 6H; C_5Me_4), 1.09 (s/br, $J(^{117/119}Sn/H)$ = 109 Hz, 18H; CMe_3) ppm. ^{119}Sn NMR (111.8 MHz, C_6D_6, 25 °C): δ 118.2 (br, CH_2−*Sn*) ppm. MS (70 eV, EI): *m*/*z* (%) 638 (6) [M$^+$], 255 (100) [M$^+$] − Sn(*t*Bu_2)OSO_2CF_3. Anal. Calcd for $C_{24}H_{37}F_3FeO_3SSn$ (638): C 45.24, H 5.85. Found: C 45.68, H 5.94.

Table 4. Selected Crystal, Data Collection, and Refined Parameters for 15 and 16

	15	**16**
empirical formula	$C_{23}H_{37}ClFeSn$	$C_{24}H_{37}F_3FeO_3SSn$
fw	523.52	637.14
temperature, K	100(2)	100(2)
wavelength, Å	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	9.9871(6)	9.1561(3)
b, Å	11.5504(7)	13.8154(5)
c, Å	12.4486(5)	21.3416(6)
α, deg	66.703(3)	90
β, deg	75.478(3)	96.483(2)
γ, deg	69.329(2)	90
volume, Å^3	1223.65(12)	2682.35(15)
Z	2	4
ρ_{calc}, g cm^{-3}	1.421	1.578
abs coeff μ(Mo Kα), mm^{-1}	1.727	1.593
F(000)	536	1296
cryst size, mm^3	0.25 × 0.12 × 0.10	0.20 × 0.15 × 0.15
θ range for data collection, deg	2.65 to 27.45	2.68 to 27.50
index ranges	$0 \le h \le 12$ $-13 \le k \le 14$ $-15 \le l \le 16$	$0 \le h \le 11$ $0 \le k \le 17$ $-27 \le l \le 27$
no. of reflns collected	30 906	20 254
no. of indep reflns	5404 [*R*(int) = 0.038]	6039 [*R*(int) = 0.038]
completeness to θ = 27.50°	97.1%	98.1%
abs corr	multiscan (Denzo-SMN)	multiscan (Denzo-SMN)
max. and min. transmn	0.8463 and 0.6721	0.7961 and 0.7412
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	5404/30/265	6039/0/298
GoF on F^2	1.040	1.051
R1[a] [$I > 2\sigma(I)$]	R1 = 0.0431	R1 = 0.0267
wR2[b] (all data)	wR2 = 0.1004	wR2 = 0.0605
extinction coeff	0.0013(6)	
largest diff peak and hole, e Å^{-3}	1.054 and −0.935	0.642 and −0.537

[a] $R1 = \sum||F_o| - |F_o||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Synthesis of (η-C_5Me_4)Fe(η-C_5H_4)CH_2SnMesCl, 17. To a solution of **12b** (0.05 g, 0.08 mmol) in 5 mL of toluene was added at 25 °C 1 equiv (82 μL) of HCl (1.0 M in Et_2O). The reaction solution was allowed to stir at 25 °C for 6 h, at which point the solvent was removed under vacuum. Compound **17** was obtained as an orange oil in 50% yield, as determined by ^{1}H NMR. Attempts to recrystallize **17** proved to be unsuccessful. Therefore, the identity of **17** was confirmed through the reaction of **17** with excess CuMes in order to regenerate the starting material, **12b**. For **17**: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 6.71 (br, 1H; *m*-Mes), 6.81 (br, 1H; *m*-Mes), 4.88 (br, C_5H_4), 4.10 (br, C_5H_4), 3.81 (br, C_5H_4), 3.73 (br, C_5H_4), 3.12 (d, *J*(H/H) = 16 Hz, 1H; CH_2−Sn), 3.72 (d, *J*(H/H) = 16 Hz, 1H, CH_2−Sn), 2.44 (br, *o*-Mes), 2.40 (br, C_5Me_4), 2.15 (br, *o*-Mes), 2.05 (br, *p*-Mes), 1.92 (br, C_5Me_4), 1.72 (br, C_5Me_4), 1.70 (br, C_5Me_4) ppm. ^{119}Sn NMR (111.8 MHz, C_6D_6, 25 °C): δ 36.3 (CH_2−*Sn*) ppm.

Stoichometric Ring-Opening Reactions of 12c. One equivalent of $HCl\cdot Et_2O$ (99 μL, 1 M in Et_2O) was added to a solution of **12c** (0.04 g, 0.099 mmol) in C_6D_6. Upon addition, the solution became yellow. Within 10 min, ring-opened product was observed in 90% yield by ^{1}H NMR. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 3.62 (s, C_5H_5), 2.01 (br, CH_2−Sn), 1.79 (br, C_5Me_4), 0.37 (s, −SnMe_2Cl) ppm. The solvent was removed under vacuum; however the product could not be isolated. After 24 h, only (η-C_5Me_5)Fe(η-C_5H_5) could be observed by ^{1}H NMR.

X-ray Crystallography. Selected crystal, data collection, and refinement parameters for **11a**,**b**, **12a**–**c**, **15**, and **16** are given in Tables 2, 3, and 4. Selected angles are given in Table 1, and selected bond lengths and bond angles are given in Tables S1 (**11a**), S2 (**11b**), S3 (**12a**), S4 (**12b**), S5 (**12c**), S6 (**15**), and S7 (**16**) (see Supporting Information). Single-crystal X-ray diffraction data were collected at low temperature (see Tables 2–4) using a Nonius Kappa-CCD diffractometer and monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were integrated and scaled using the Denzo-SMN package.[51] The SHELXTL/PC package was used to solve and refine the structures.[52] Refinement was by full-matrix least-squares on F^2 using all data (negative intensities included). Hydrogen atoms were placed in calculated positions and included in the refinement in riding motion approximations.

In the case of **15**, the Cp ring (η-C_5H_5) and the *tert*-butyl group are both disordered. Each group was modeled over two static sites. The occupancies of the disorder components for the Cp ring and the *tert*-butyl group refined to 79:21 and 74:26, respectively.

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Supporting Information Available: Tables of atomic coordinates, bond lengths, and bond angles, anisotropic displacement parameters, and hydrogen coordinates for compounds **11a**,**b**, **12a**–**c**, **15**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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