834 *Organometallics* **2001,** *20,* 834−843

Reactions of the Si−H Functionalized Silicon-Bridged [1]Ferrocenophane $Fe(\eta\text{-}C_5H_4)_2SiMeH$ with Dicobalt Octacarbonyl: Ring-Opening Metalization and the Synthesis of a Novel Sila[1]ferrocenophane with a $Co(CO)_4$ Substituent

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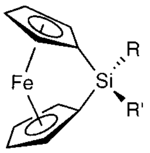
Reaction of $Co_2(CO)_8$ with the Si−H-functionalized sila[1]ferrocenophane $Fe(\eta\text{-}C_5H_4)_2SiMeH$ (**1a**) was found to result in metalation of silicon and ring-opening of the ferrocenophane, affording the orange crystalline silylene-bridged dicobalt heptacarbonyl complex $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)Si[\mu\text{-}Co_2(CO)_7](Me)$ **6** in 45% yield. The novel red, crystalline sila[1]ferrocenophane $Fe(\eta\text{-}C_5H_4)_2Si[Co(CO)_4](Me)$ (**8**), the first with a direct Si−M bond, was isolated in 23% yield when the reaction between **1a** and $Co_2(CO)_8$ was conducted in NEt_3 as a proton trap. The dinuclear complex **6** and metalated silicon-bridged ferrocenophane **8** were each characterized by multinuclear NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction. [1]Ferrocenophanes $Fe(\eta\text{-}C_5H_4)_2Si(Et)(H)$ (**9**) and $Fe(\eta\text{-}C_5H_4)_2Si(Me)(D)$ (**10**) were prepared in order to investigate whether the ring-opening reaction that afforded **6** was an intramolecular or an intermolecular process. Mass spectral analysis of the products of the reaction of an equimolar mixture of **9** and **10** with $Co_2(CO)_8$ showed only the presence of $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)Si[\mu\text{-}Co_2(CO)_7](Et)$ (**11**) and $(\eta\text{-}C_5H_4D)Fe(\eta\text{-}C_5H_4)Si[\mu\text{-}Co_2(CO)_7](Me)$ (**12**); neither $(\eta\text{-}C_5H_4D)Fe(\eta\text{-}C_5H_4)Si[\mu\text{-}Co_2(CO)_7](Et)$ (**11′**) nor $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)Si[\mu\text{-}Co_2(CO)_7](Me)$ (**12′**) were detected, which indicated that the ring-opening process was intramolecular. Compounds **11** and **12** were synthesized separately to provide comparative spectroscopic data for the mechanistic investigation.

Introduction

[1]Ferrocenophanes are interesting organometallic species in which the presence of a single atom bridge between the cyclopentadienyl (Cp) ligands leads to a strained, ring-tilted structure.[1] The first example, a strained silicon-bridged [1]ferrocenophane **1** (R = R′ = Ph), was synthesized in 1975 by Osborne and coworkers.[2] Subsequent work on this compound and a range of analogues has shown that such species possess tilt angles between the planes of the cyclopentadienyl ligands of 16−21°, and the appreciable ring strain has been estimated to be 70−80 kJ mol^{-1}.[3] The release of ring strain provides the driving force for reactivity at the Si−Cp bond,[4] which has been exploited to prepare high molecular weight, well-defined polyferrocenes **2** via ring-opening polymerization (ROP) reactions.[5−7]



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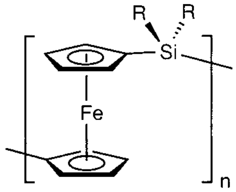

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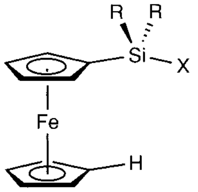

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Stoichiometric ring-opening reactions of sila[1]ferrocenophanes have also proved to be of broad interest. For example, **1** reacts with water, methanol, or silanol groups to generate monosubstituted ferrocenylsilanes **3** (X = OR) containing Si−O bonds.[8,9] This strategy has been used to generate ferrocenyl-substituted mesopo-

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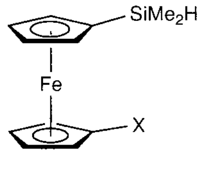
rous silica and has been utilized in the fabrication of novel composites and magnetic nanostructures.[9−12] Similarly, the reaction of HCl with sila[1]ferrocenophanes leads to the formation of ferrocenyl-substituted chlorosilanes, which are of synthetic utility in the preparation of ferrocenylsilane oligomers and for silica and electrode derivatization.[13,14] Very recently it has been shown that reaction of an acid containing a noncoordinating anion such as tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate with sila[1]ferrocenophanes can lead to the formation of ions with silylium character.[15] Ring-opening of sila[1]ferrocenophanes also occurs with the Lewis acids BCl_3 and $PhBCl_2$ to give functionalized ferrocenylboranes.[16]

Substitution at the bridging silicon atom without ring-opening has been recently achieved. For example, reaction of the Si−Cl moiety in **1** (R = R′ = Cl and R = Me, R′ = Cl) with alcohols or amines in the presence of NEt_3 as a proton scavenger (to prevent the aforementioned ring-opening processes) has resulted in the formation of sila[1]ferrocenophanes with alkoxy, aryloxy, or amino substituents.[17] This strategy has been utilized in the synthesis of hydrophilic polyferrocenes when a suitable polyether alcohol was chosen.[18]

To date, no silicon-bridged [1]ferrocenophanes with direct Si−M bonds have been prepared.[19] These molecules would be of interest as precursors to highly metalized ring-opened polyferrocenes. To explore a potential route to such species, we report on the reaction of sila[1]ferrocenophanes containing Si−H bonds with the metal carbonyl $Co_2(CO)_8$.

Results and Discussion

The intent of this work was to study the reactivity of the Si−H functionality of the hydromethylsilicon-bridged ferrocenophane **1a** (R = Me, R′ = H) toward dicobalt octacarbonyl. The reactivity of Si−H bonds toward transition metal complexes is well documented in the literature.[20] In fact, the reaction of dicobalt octacarbonyl with hydrodimethylsilyl-substituted ferrocenes **4** has been shown to result in the replacement of the hydride with a $Co(CO)_4$ fragment to form **5**.[21] It was with this in mind that we first studied the reaction of **1a** with $Co_2(CO)_8$ with the formation of a $Co(CO)_4$-substituted sila[1]ferrocenophane as our target.



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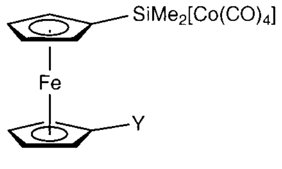
X = H, $SiMe_2H$



5

Y = H, $SiMe_2[Co(CO)_4]$

Reaction of $Co_2(CO)_8$ with 1a: Synthesis and Characterization of 6. Room-temperature addition of 0.5 or 1 equiv of $Co_2(CO)_8$ to a stirred solution of **1a** in hexanes led to the isolation of a highly air and moisture sensitive light orange crystalline solid. The ^{1}H NMR spectrum of this material showed three peaks in the Cp region at chemical shifts of δ 4.17 (2 H), 4.14 (2 H), and 3.92 (5 H) ppm, which was indicative of a ring-opened structure rather than a $Co(CO)_4$-substituted sila[1]-ferrocenophane as we initially expected. The resonance due to the Si−Me group protons (δ 1.03 ppm) was considerably downfield-shifted from that of the starting material (0.44 ppm) and was also significantly different from that of **5**, which displays a resonance at δ 0.80 ppm.

The ^{13}C NMR spectrum showed a resonance at δ 205.4 ppm (cf. $Co_2(CO)_8$ = 201.3 ppm), which suggested that a cobalt carbonyl fragment was present in the product. The chemical shift of the methyl group carbon (6.7 ppm) was also considerably downfield-shifted with respect to that of the starting material (−5.7 ppm). The ^{29}Si NMR spectrum showed a single resonance at δ 137.5 ppm. Solution FTIR spectroscopy (hexanes) showed the presence of both bridging and terminal carbonyl resonances. To assign the structure of this compound unequivocally, an X-ray diffraction study was performed on crystals obtained from hexanes at −30 °C. This showed that the product was a ferrocenyl-substituted, silylene-bridged dicobalt heptacarbonyl (**6**)[22] formed via metalation and ring-opening of **1a** (Scheme 1). Complex **6** crystallized with two independent molecules in the unit cell and one molecule of *n*-hexane present for every four molecules

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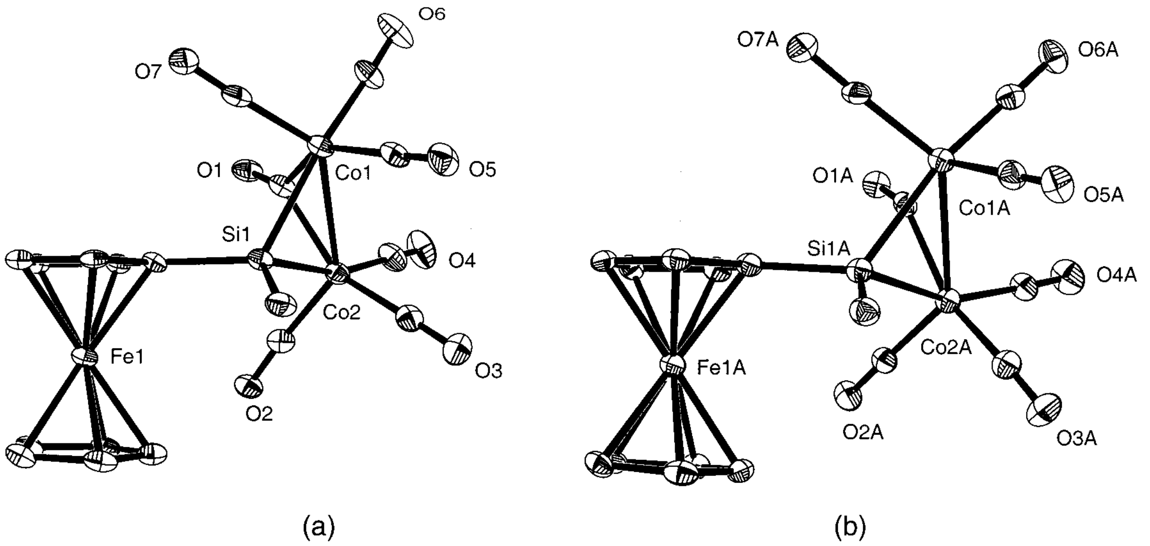
Table 1. Selected Bond Lengths [Å] and Angles [deg] for $\mathbf{6_A}$ and $\mathbf{6_B}$

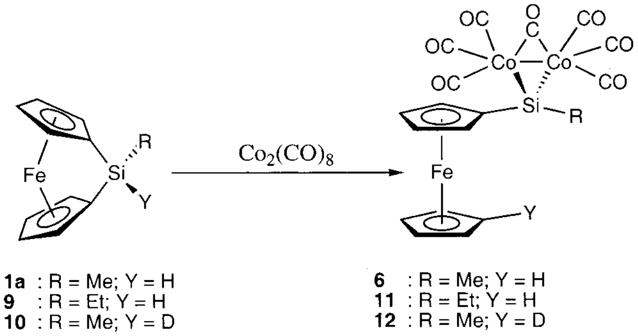
	$\mathbf{6_A}$	$\mathbf{6_B}$		$\mathbf{6_A}$	$\mathbf{6_B}$
Co(1)−Co(2)	2.5420(11)	2.5544(11)	Co(1)−Si−Co(2)	67.01(5)	67.59(5)
Co(1)−Si(1)	2.2842(17)	2.2813(18)	Co(1)−C(12)−Co(2)	82.8(3)	82.6(3)
Co(2)−Si(1)	2.3208(18)	2.3112(18)	C(1)−Si−Co(1)	119.4(2)	119.03(19)
Co(1)−C(12)	1.930(7)	1.955(7)	C(1)−Si−Co(2)	117.4(2)	115.5(2)
Co(2)−C(12)	1.915(6)	1.915(7)	Co(2)−Co(1)−C(13)	136.3(2)	137.1(2)
Co(1)−C(13)	1.776(7)	1.772(7)	Co(2)−Co(1)−C(14)	105.1(2)	100.19(19)
Co(1)−C(14)	1.815(8)	1.804(8)	Co(2)−Co(1)−C(15)	101.1(2)	108.2(2)
Co(1)−C(15)	1.832(7)	1.812(7)	Co(1)−Co(2)−C(16)	98.0(2)	98.8(2)
Co(2)−C(16)	1.836(8)	1.816(8)	Co(1)−Co(2)−C(17)	110.5(2)	111.4(2)
Co(2)−C(17)	1.795(7)	1.815(7)	Co(1)−Co(2)−C(18)	132.01(19)	132.9(2)
Co(2)−C(18)	1.785(7)	1.769(7)			



(a) (b)

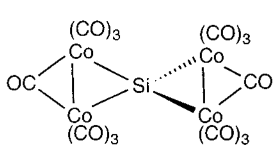
Figure 1. Molecular structure of $\mathbf{6_A}$ (a) and $\mathbf{6_B}$ (b) (thermal ellipsoids at 30% probability).

Scheme 1. Reaction of $Co_2(CO)_8$ with Sila[1]ferrocenophanes 1a, 9, and 10



of **6**. Selected bond lengths and angles are given in Table 1, and the molecular structure of **6** is shown in Figure 1.

The Si−Co bond lengths of 2.2842(17)/2.2813(18) and 2.3208(18)/2.3112(18) Å in **6** are within the reported range for Si−Co bonds (2.209−2.381 (49) Å)[20] and are similar to those reported for the spirocyclic species **7** (2.276(1) and 2.301(1) Å).[23] The Co(1)−C(12) and Co(2)−C(12) bond lengths in **6** of 1.930(7)/1.955(7) and 1.915(6)/1.915(7) Å are slightly different from those found for both $Co_2(CO)_8$ (1.940(1)/1.939(1), 1.937(1)/1.924(1) Å)[24] and **7** (1.964(4), 1.926(3) Å).[23] The Co(1)−Co(2) bond length in **6** was found to be 2.5420(11)/2.5544(11) Å, which is slightly larger than the Co−Co distance in both $Co_2(CO)_8$ (2.5301(8)/2.5278(8) Å)[24] and **7** (2.528(1) Å).[23] The Co(1)−Si−Co(2) angle in **6** of 67.01(5)/67.59(5)° is similar to that reported for **7** (67.0(1)°)[23] but is significantly smaller than the Co(1)−C(12)−Co(2) angle of **6** 82.7(3)° (average) or the Co(1)−C_B−Co(2) angle in $Co_2(CO)_8$ (average = 81.38(7)°).[24] This difference can most likely be accounted for by the increased length of Co−Si bonds in comparison to the Co−C bonds.



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Reaction of 1a with $Co_2(CO)_8$ in the Presence of NEt_3: Isolation of 8. Although the metalization and ring-opening processes that led to the formation of **6** are of interest (and will be discussed in more detail later), we attempted to modify the synthesis to allow for the isolation of the initial target: a $Co(CO)_4$-substituted sila[1]ferrocenophane. As no reaction is observed between the sila[1]ferrocenophane **1b** (R = R′ = Me) and $Co_2(CO)_8$[4] and taking into consideration the observed ring-opening reactions at an Si−Cp bond by protic reagents as well as the prevention of this process by the addition of a tertiary amine, we decided to investigate the effect of added NEt_3. We postulated that this might result in the formation of $[HNEt_3][Co(CO)_4]$ and the cobalt-substituted sila[1]ferrocenophane **8**. Slow addition of a hexanes solution of $Co_2(CO)_8$ to a stirred, dilute solution

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Table 2. Selected Bond Lengths [Å] and Angles [deg] for 8

Co(1)−Si(1)	2.3672(5)	Si(1)−C(11)	1.8676(19)	Si(1)−Co(1)-C(15)	172.33(7)
Co(1)−C(12)	1.780(2)	C(1)−Si(1)−C(6)	96.38(8)	O(1)−C(12)−Co(1)	179.24(19)
Co(1)−C(13)	1.7887(19)	C(11)−Si(1)−Co(1)	110.89(7)	O(2)−C(13)−Co(1)	178.50(17)
Co(1)−C(14)	1.799(2)	Si(1)−Co(1)−C(12)	79.00(6)	O(3)−C(14)−Co(1)	175.04(16)
Co(1)−C(15)	1.814(2)	Si(1)−Co(1)−C(13)	79.94(6)	O(4)−C(15)−Co(1)	179.5(2)
Fe(1)−Si(1)	2.6941(6)	Si(1)−Co(1)−C(14)	92.13(6)	α	19.98(5)

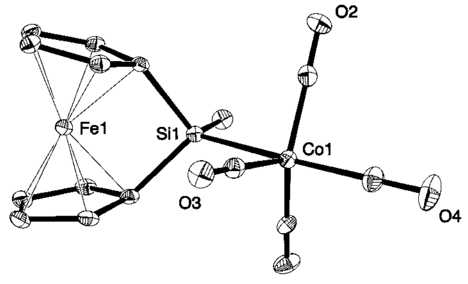
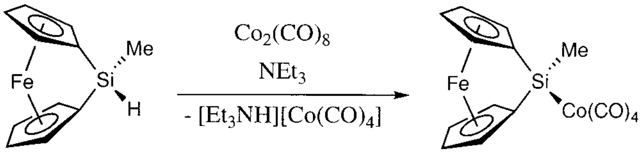


Figure 2. Molecular structure of **8** (thermal ellipsoids at 30% probability).

of **1a** in hexanes with excess NEt$_3$, however, did not result in the production of the desired product, but instead still resulted in the formation of the ring-opened product **6**. On the other hand, addition of a NEt$_3$ solution of Co$_2$(CO)$_8$ to a stirred solution of **1a** in NEt$_3$ resulted in the formation of a new product **8** in addition to **6** (Scheme 2). Analysis of the reaction mixture by ^{1}H NMR spectroscopy showed a resonance at 8.49 ppm, corresponding to the proton of the cation HNEt$_3$$^+$, which indicated that the desired acid−base reaction had occurred.[25]

Scheme 2. Reaction of 1a with Co$_2$(CO)$_8$ in NEt$_3$



1a **8**

Sublimation followed by recrystallization from hexanes led to the isolation of red crystalline **8**. The ^{1}H NMR spectrum of the product showed four separate signals in the Cp region (4.45, 4.36, 4.25, 3.85 ppm) indicative of an unsymmetrically substituted [1]ferrocenophane. The resonance due to the methyl protons appeared at 0.83 ppm, which is downfield-shifted from that of **1a** (0.44 ppm), but upfield from that of **6** (1.03 ppm). The ^{13}C NMR spectrum showed a resonance at a chemical shift of 199.0 ppm corresponding to the carbonyl carbons. The ^{29}Si NMR spectrum showed a signal at 24.3 ppm, which is considerably downfield from that of the starting material (−21.2 ppm), but at much higher field than that of **6** (137.5 ppm).

A single-crystal X-ray diffraction study was performed on **8** in order to confirm the assigned structure (see Figure 2 for molecular structure and Table 2 for selected bond distances and angles). The Co−Si distance of 2.3672(5) Å is slightly longer than those for **6** (2.28 and 2.32 Å average) but is still within the typical range of Si−Co bond lengths. The geometry about the Co atom appears to be distorted trigonal bipyramidal. The tilt angle between the Cp rings (α) was measured to be 19.98(5)°, which is within the range of tilt angles found for sila[1]ferrocenophanes (16−21°).

Investigation of the Mechanism for the Formation of 6. Following the successful isolation of the desired metalated sila[1]ferrocenophane **8**, we were further motivated to investigate the process by which the ring-opened species **6** is formed. The mechanism for the formation of **6** can likely be divided into two steps: first, the addition of the Si−H bond to the cobalt center, and second, the ring-opening of an Si−Cp bond. The initial step has been studied by other research groups;[26] however the ring-opening step is unique to the strained ferrocenophane system. We decided for the purpose of this study that we would focus our efforts on the novel second step of the reaction.

Deuterium-Labeling Studies. We initially undertook deuterium-labeling studies in order to determine whether the ring-opening was an intermolecular process or an intramolecular process. For these studies, the ethylhydro species **9** and the deuteriomethyl species **10** were prepared. We envisioned that if equal amounts of **9** and **10** were reacted with Co$_2$(CO)$_8$, one should be able to obtain information from the mass spectrum of the product mixture (Scheme 3) with respect to whether species such as free HCo(CO)$_4$/DCo(CO)$_4$ are generated that could induce ring-opening chemistry. For example, if Co$_2$(CO)$_8$ reacts with **9** and generates HCo(CO)$_4$, and if Co$_2$(CO)$_8$ reacts with **10** and generates DCo(CO)$_4$, then one would expect to see some evidence for crossover reactions in the mass spectrum. If (η-C$_5$H$_4$D)Fe(η-C$_5$H$_4$)Si[μ-Co$_2$(CO)$_7$](Et) (**11′**) and (η-C$_5$H$_5$)Fe(η-C$_5$H$_4$)Si[μ-Co$_2$(CO)$_7$](Me) (**12′**) were observed as well as (η-C$_5$H$_5$)Fe(η-C$_5$H$_4$)Si[μ-Co$_2$(CO)$_7$](Et) (**11**) and (η-C$_5$H$_4$D)Fe(η-C$_5$H$_4$)Si[μ-Co$_2$(CO)$_7$](Me) (**12**), it would indicate that a species such as free HCo(CO)$_4$/DCo(CO)$_4$ is formed. If, on the other hand, only **11** and **12** were observed in the product mixture, then it would provide evidence for an intramolecular proton (deuterium) transfer.

Synthesis and Characterization of 9 and 10. Sila[1]ferrocenophane **9** was prepared from low-temperature reaction of HSiCl$_2$Et with a suspension of dilithioferrocene·*n*TMEDA in diethyl ether. After workup **9** was isolated as a red oil. The ^{1}H NMR spectrum of this compound showed a triplet at 5.32 ppm corresponding to the Si−H moiety. Three multiplets at chemical shifts of 4.36 (4 H), 4.15 (2 H), and 3.95 (2 H) ppm were assigned to the protons on the Cp rings of the ferrocenophane. A triplet at a chemical shift of 1.16 ppm and a quartet of doublets centered at 0.95 ppm were as-

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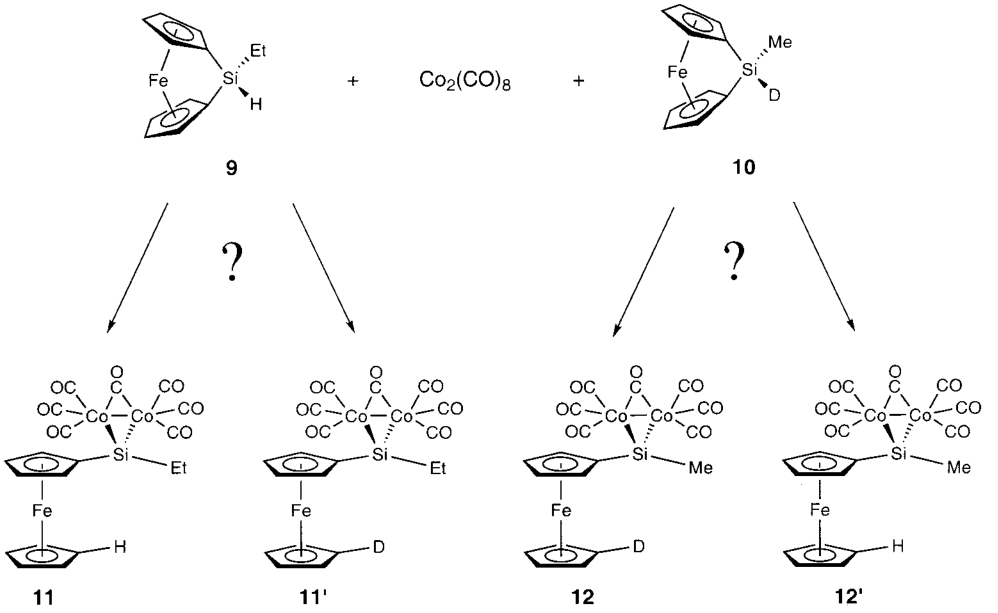
[25] The reaction of **10** with Co$_2$(CO)$_8$ was also performed. A peak of very low intensity in the ^{1}H NMR spectrum at 8.7 ppm was observed which was assigned to the N−H of [NEt$_3$H][Co(CO)$_4$] arising from small amounts of nondeuterated impurities in the starting material, **10**. For details, see the Experimental Section.

[26] See, for example: (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1967**, *89*, 1640. (b) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151, and references therein. (c) Reference 20 and references therein.

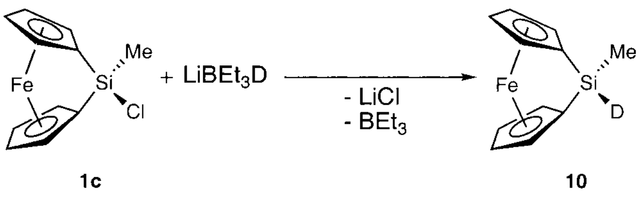
Scheme 3. Possible Products from Labeling Experiments



signed to the CH_3 and CH_2 protons, respectively, of the ethyl substituent. The ^{29}Si NMR spectrum (proton-decoupled) showed a single signal at a chemical shift of -16.1 ppm, and the proton-coupled ^{29}Si NMR spectrum consisted of a doublet of multiplets centered at -16.1 ppm.

Synthesis of Deuterated [1]Ferrocenophane 10. Preparation of the deuterated sila[1]ferrocenophane **10** was not as straightforward. Unlike the analogous hydrosilane, $HSiCl_2Me$, the deutero analogue is not readily available from commercial sources. Although it would, in principle, be possible to form the deuterated analogue, $DSiCl_2Me$ from a deuterated reducing agent and Cl_3SiMe, this reaction would not be expected to result in the selective formation of the desired compound. To obtain **10** in the most convenient manner, the reaction of the sila[1]ferrocenophane **1c** (R = Me; R′ = Cl) with a source of nucleophilic deuteride was explored.

Scheme 4. Deuteration of the Sila[1]ferrocenophane 1c



It was found that a slight excess of $Li[BEt_3D]$ when reacted with a chloro-substituted sila[1]ferrocenophane resulted in the formation of the desired deuteriosilane *without any ring-opening of the ferrocenophane* (Scheme 4). The desired product was isolated by room-temperature sublimation under vacuum as a red crystalline solid in 32% yield. The ^1H NMR spectrum of **10** showed three signals, which were assigned to the protons on the Cp rings at chemical shifts of 4.36 (4 H), 4.14 (2 H), and 3.93 (2 H) ppm. A signal at a chemical shift of 0.40 ppm was assigned to the methyl group protons. The *ipso*-carbon signal was observed in the ^{13}C NMR spectrum at a chemical shift of 27.6 ppm. Due to the presence of

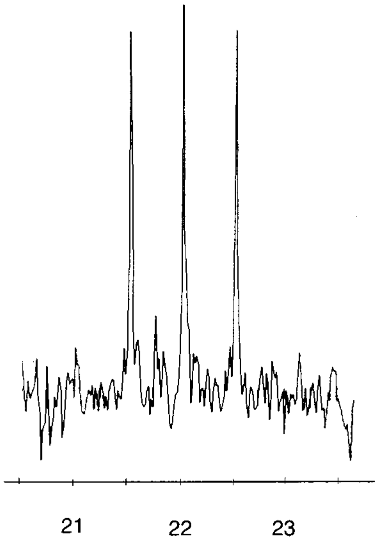


Figure 3. NMR spectral evidence for deuterium substitution at the silicon bridge: ^{29}Si NMR spectrum of **10** (in C_6D_6).

the deuterium on the bridging silicon, the signal is split into a poorly resolved triplet. The ^1H-decoupled ^{29}Si NMR spectrum also showed evidence for deuterium substitution on the silicon with a triplet centered at -22.0 ppm (see Figure 3).

Reaction of Sila[1]ferrocenophanes 9 and 10 with $Co_2(CO)_8$. To ensure that the proposed reaction of $Co_2(CO)_8$ with a mixture of **9** and **10** would be viable, first, separate reactions of $Co_2(CO)_8$ with **9** and with **10** were performed.

Addition of 1 mL of C_6D_6 to a 1:1 mixture of **9** and $Co_2(CO)_8$ immediately led to the formation of a deep red solution and the release of CO. After 3 h gas evolution had ceased, and the ^1H NMR spectrum showed that a ring-opened species analogous to **6** was formed in nearly quantitative spectroscopic yield. Compound **11** was isolated as a light orange oil in a 20% yield. The ^1H NMR spectrum was consistent with the structure proposed. Signals at δ 4.27 (2 H) and 4.17 (2 H) ppm were assigned to the protons on the substituted rings,

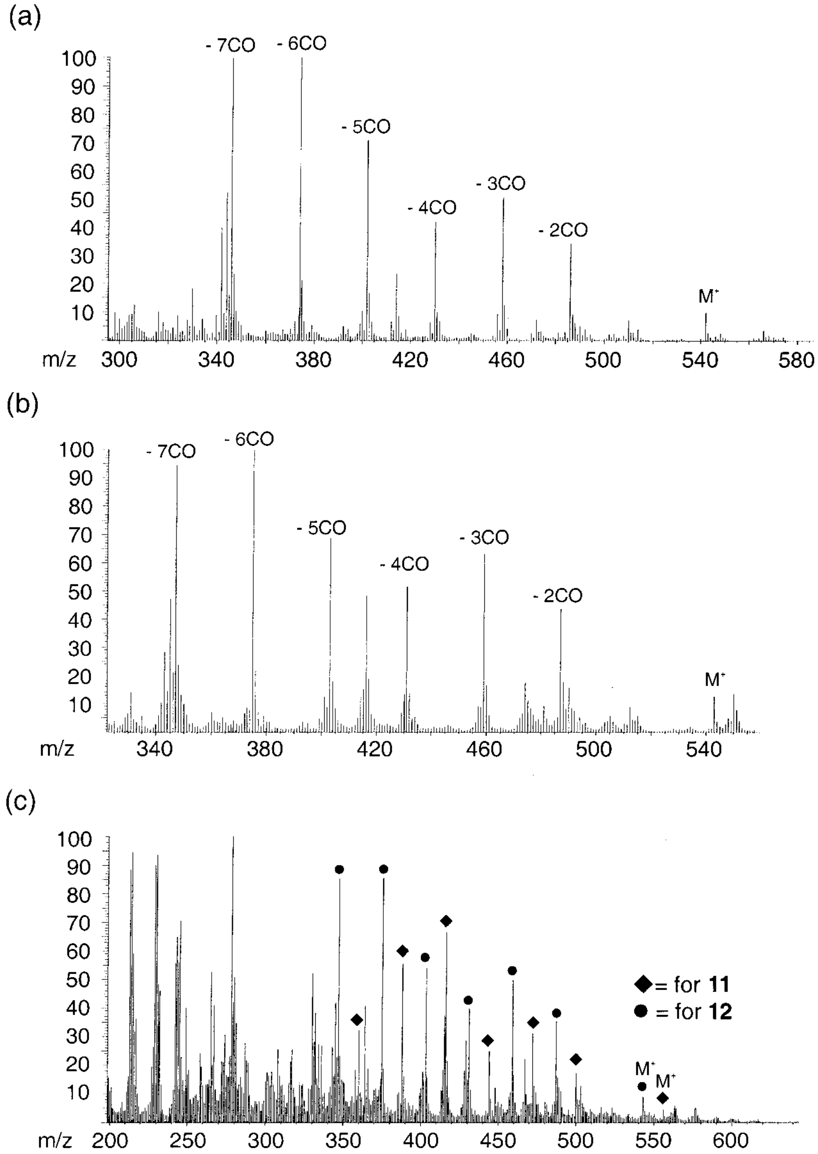


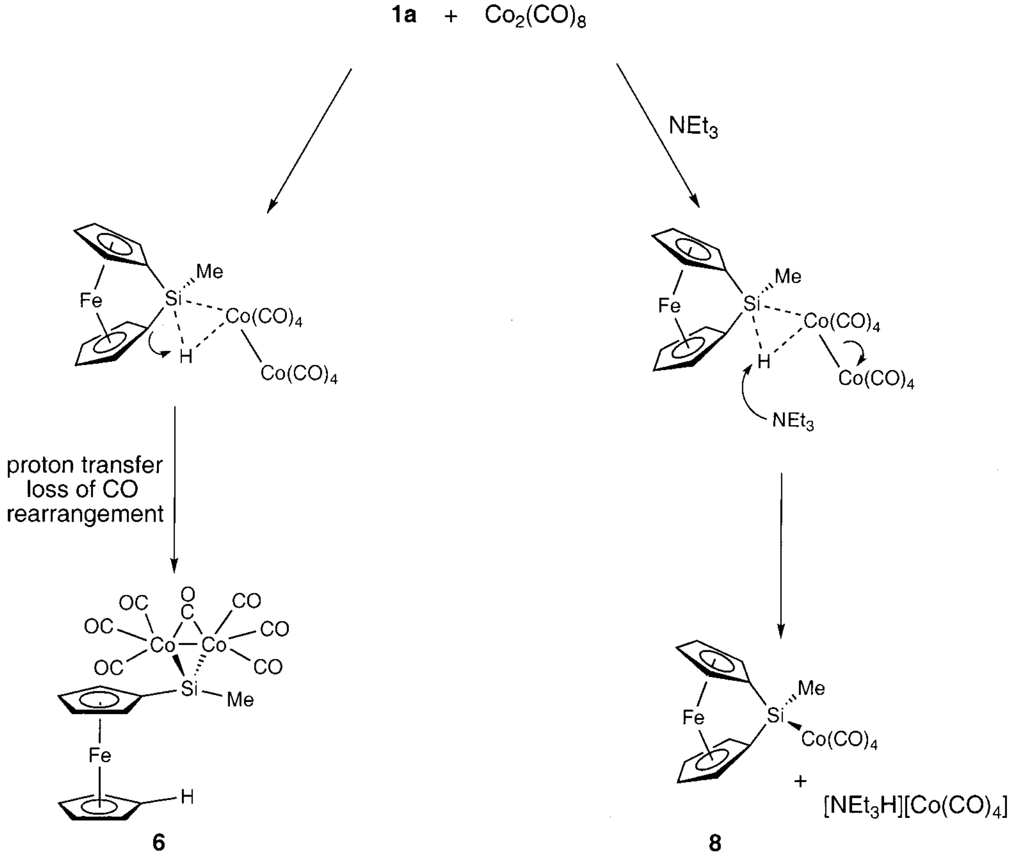
Figure 4. Selected mass spectra: (a) mass spectrum of **6** showing successive loss of carbonyls from a small M$^+$ (542 amu); (b) mass spectrum of **12** also showing successive loss of carbonyls from a small M$^+$ (543 amu); (c) mass spectrum of the products from reaction of Co$_2$(CO)$_8$ with a mixture of **9** and **10**. Note M$^+$ at (543 amu, **12**) and (556 amu, **11**) but not (542 amu, **12′**) or (557 amu, **11′**).

and the signal at 3.96 (5 H) ppm was assigned to the unsubstituted Cp ring of **11**. A quartet centered at 1.57 ppm was assigned to the CH$_2$ protons of the ethyl group (cf. 0.95 ppm for **9**), and a triplet centered at 1.25 ppm (cf. 1.16 ppm for **9**) was assigned to the CH$_3$ protons of the ethyl group. The ^{29}Si NMR spectrum showed a signal at 147.5 ppm, which is downfield-shifted from that of **6** (137.5 ppm). The electron impact (EI) mass spectrum of **11** showed a small molecular ion peak at $m/z = 556$ (ca. 2%) and peaks corresponding to the successive loss of 2−7 carbonyls.

The reaction of **10** with Co$_2$(CO)$_8$ was performed in the same manner. After 3 h, the ^{1}H NMR spectrum showed that the expected ring-opening had occurred and that the product was formed in a nearly quantitative spectroscopic yield. Compound **12** was isolated in 36% yield as light orange needlelike crystals. Multinuclear NMR spectroscopy was used to confirm the assigned structure via comparison with **6**. The ^{1}H NMR spectrum was almost identical to that of **6** except that integration of the signal due to the protons on the free Cp ring indicated the presence of only four, not five protons. The ^{13}C NMR spectrum was also almost completely identical except for the signals arising from the deuterium-substituted ring. Instead of one signal for the free Cp ring as in **6**, the deuterated compound **12** gave two signals (69.6, 69.5 ppm). The Cp carbon attached to deuterium was presumably overlapping with the resonances of the other carbon atoms. The ^{29}Si NMR spectrum showed one signal at a chemical shift of 137.7 ppm (cf. 137.5 ppm for **6**). The EI mass spectrum of the product showed a small signal (ca. 3%) for the molecular ion at 543 amu as well as signals corresponding to the successive loss of 2−7 carbonyls. Important for our studies was the fact that the mass spectrum of **12** can clearly be distinguished from that of **6** (see Figure 4a,b).

Reaction of Co$_2$(CO)$_8$ with a Mixture of 9 and 10. Co$_2$(CO)$_8$ was added to a C$_6$D$_6$ solution containing equimolar amounts of **9** and **10**. ^{1}H NMR spectroscopy after 3 h showed the formation of ring-opened products. To obtain structural information on these products, the reaction mixture was studied via mass spectroscopy.

Scheme 5. Possible Mechanism for the Formation of 6 and 8 from 1a and $Co_2(CO)_8$



Peaks at $m/z = 556$ and 543 were observed corresponding to the molecular ions of **11** and **12**, respectively. Peaks corresponding to the successive loss of carbonyls from both of these compounds were also identified. Importantly, there was no evidence apparent in the mass spectrum for the formation of the molecular ions of compound **11′** (557 amu) or compound **12′** (542 amu) in quantities above baseline noise or for ions corresponding to subsequent loss of carbonyl groups (see Figure 4c). This evidence suggests that a species such as free $HCo(CO)_4$/$DCo(CO)_4$ is not present during the course of this reaction and points to a scenario in which intramolecular hydrogen (deuterium) transfer occurs.

Scheme 5 depicts one possible mechanism to form **6** and **8** in light of the experimental evidence obtained in these studies. Interaction between the Si−H bond and one of the Co metal centers leads to "arrested" oxidative addition and the formation of a three-centered intermediate. In the absence of NEt_3, hydrogen transfer occurs to one of the Cp rings, causing cleavage of one of the Si−Cp bonds. Rearrangement, including addition of the second metal center to the silicon, loss of one molecule of CO, and formation of a bridging carbonyl moiety ensues, forming **6** as the final product. It is proposed that loss of CO occurs at some point after the three-centered intermediate is formed since in the case of NEt_3 addition no loss of CO is noted. In the presence of NEt_3 it is proposed that the bridging hydrogen is abstracted by the base. Formation of **8** and $[NEt_3H][Co(CO)_4]$ can then occur. It should be noted that **8** is not observed to form unless the reaction is conducted in NEt_3 as solvent, and even under these conditions some **6** is produced. This indicates that the intramolecular hydrogen transfer must occur very fast since NEt_3 must make up the solvent cage around the proposed intermediate in order for hydrogen abstraction to occur.

An alternative radical mechanism analogous to that proposed by Markó and co-workers[27] for the reaction between Et_3SiH and $Co_2(CO)_8$ to form $Et_3SiCo(CO)_4$ also needs to be considered (Scheme 6). An oxidative elimination reaction between the 17-electron species $[Co(CO)_4]^\bullet$ and **1a** is the key initial step. Once again the observed products can be accounted for by the alternative possibilities for hydrogen transfer to the cyclopentadienyl ring or to NEt_3.

To investigate the possibility of radical intermediates in the reaction of **1a** with $Co_2(CO)_8$, a series of NMR experiments were carried out with varying concentrations (0−100 mol % based on $Co_2(CO)_8$) of galvinoxyl (2,6-di-*tert*-butyl-α-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy, free radical). The results of this study were that the galvinoxyl did slow the rate of the reaction, and the higher the concentration of the galvinoxyl, the slower the rate. Although further detailed studies are needed, the fact that rate inhibition occurs upon addition of a free radical trap to the system is indicative of the presence of radicals in the reaction between **1a** and $Co_2(CO)_8$, which suggests that a mechanism of the type shown in Scheme 6 may be correct.

Summary

The reactivity of Si−H functionalized sila[1]-ferrocenophanes was investigated as a route to metal-

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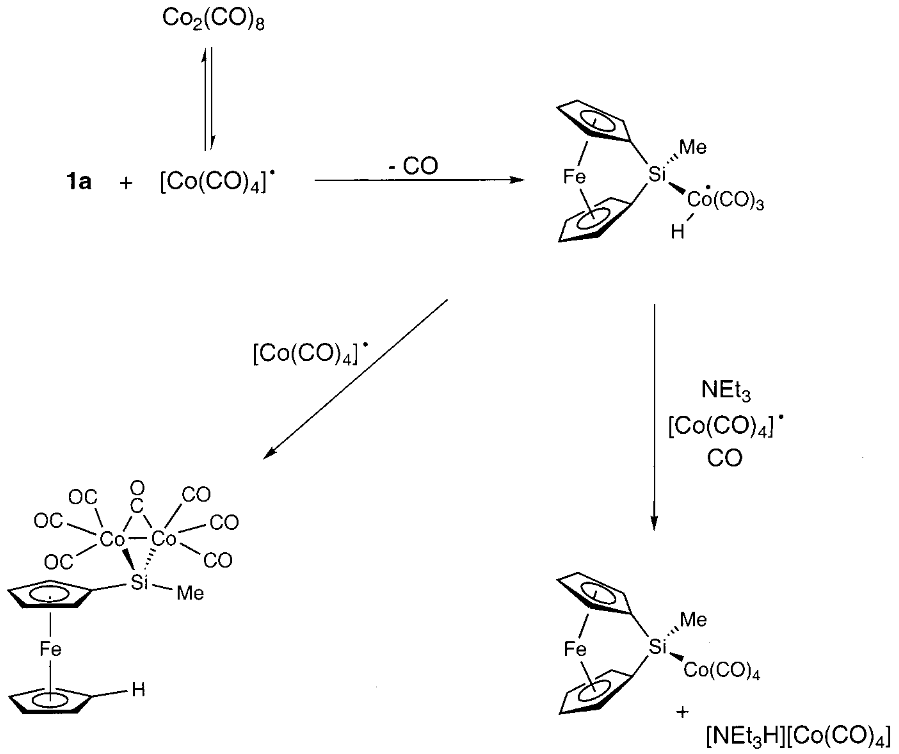
[27] Sisak, A.; Ungváry, F.; Markó, L. *Organometallics* **1986**, *5*, 1019.

Scheme 6. Alternative Radical Mechanism for the Formation of 6 and 8 from 1a and $Co_2(CO)_8$



6 8

ized silicon-bridged [1]ferrocenophanes. In hydrocarbon solvents reaction of the Si−H functionality with $Co_2(CO)_8$ does occur; however, an additional process leads to transfer of the hydride to a Cp ring and, subsequently, ring-opening of the ferrocenophane producing the silylene-bridged dicobalt heptacarbonyl **6**. This ring-opening step can be prevented by performing the reaction in NEt_3 as solvent, which leads instead to the isolation of the novel $Co(CO)_4$-substituted sila[1]ferrocenophane **8**. The mechanism by which the hydride is transferred from the silicon to the Cp ring was first explored by selective deuterium-labeling studies. It was found that the hydrogen (deuterium) transfer from the silicon to the Cp ring to form **6** occurs via an *intra*molecular process; evidence supporting the presence of radical species was found in studies involving the addition of galvinoxyl as a radical trap. Further work will focus on the synthesis of metalized polymers obtained from the ROP of **8** and related species to obtain high molecular weight bimetallic materials which may be of interest as ceramic precursors or as polymeric catalysts.

Experimental Section

The $Li[BEt_3H]$ (1.0 M in THF), $Li[BEt_3D]$ (1.0 M in THF), and galvinoxyl were purchased from Aldrich and were used without further purification. $Co_2(CO)_8$ (95% in hexanes) was puchased from STREM and was sublimed before use. Silanes were obtained from Gelest. TMEDA (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) and NEt_3 were distilled from Na and stored under an atmosphere of N_2. Dilithioferrocene·*n*TMEDA,[28,29] **1a**,[30] **1b**,[8] and **1c**[17] were synthesized according to literature procedures.

All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox. Solvents were distilled from Na, stored over NaK under N_2, and filtered through dried neutral alumina prior to use. ^1H NMR spectra (400 MHz), ^{13}C NMR spectra (100.4 MHz), and ^{29}Si NMR spectra (79.3 MHz) were recorded on a Varian Unity 400 spectrometer. All solution ^1H and ^{13}C NMR spectra were referenced internally to protonated solvent shifts. ^{29}Si NMR spectra were referenced externally to $SiMe_4$. 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. Elemental analyses were performed by Quantitative Technologies, Inc., Whitehouse, NJ.

Preparation of 6. Dicobalt octacarbonyl (0.37 g, 1.1 mmol) and **1a** (0.25 g, 1.1 mmol) were dissolved in 25 mL of hexanes, and the reaction mixture was allowed to stir for 1 h at room temperature. The solution was filtered through glass wool to remove small amounts of insoluble impurities, and the solvent was removed under high vacuum. The product was recrystallized multiple times from hexanes at −55 °C and was obtained in 45% yield (0.26 g).

For 6: ^1H NMR (400 MHz, C_6D_6, 20 °C) δ 4.17 (ps t, 2 H, Cp), 4.14 (ps t, 2 H, Cp), 3.92 (br s, 5 H, Cp), 1.03 (s, 3 H, Me); $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 20 °C) δ 205.4 (CO), 74.4, 73.4, 70.8, 69.6 (Cp), 6.7 (Me); ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C) δ 137.5; IR (hexanes, 25 °C) 2089 (m), 2063 (w), 2053 (s), 2030 (s), 2012 (m), 1994 (w) (CO), 1840 (m) (μ-CO); MS (70 eV, EI) *m/z* (%) 542 (4) [M^+], 486 (6) [$M^+ - 2$ CO], 458 (8) [$M^+ - 3$ CO], 430 (7) [$M^+ - 4$ CO], 402 (12) [$M^+ - 5$ CO], 374 (17) [$M^+ - 6$ CO], 346 (17) [$M^+ - 7$ CO], 186 (100) [$C_{10}H_{10}Fe^+$]. Multiple attempts made at obtaining accurate EA values for **6** were unsuccessful due to apparent decomposition before reaching the external analytical laboratory. For evidence of purity the reader is referred to copies of the NMR spectra deposited in the Supporting Information. HRMS (70 eV, EI) calcd 541.836566; found 541.838890; fit 4.3 ppm.

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[28] Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, R. E.; Merrill, J. C.; Smart, J. *J. Organomet. Chem.* **1971**, *27*, 241.

[29] Butler, I. R.; Cullen, W. R.; Ni, J.; Rettig, S. J. *Organometallics* **1985**, *4*, 2196.

[30] See ref 19a.

Preparation of 8 from 1a. A solution of 0.19 g (0.56 mmol) of $Co_2(CO)_8$ in NEt_3 (25 mL) was added dropwise to a stirring solution of 0.125 g (0.55 mmol) of **1a** in NEt_3 (25 mL) at room temperature. After stirring for 1 h, the volatile components of the reaction were removed under high vacuum, and a hexanes extract of the residue was collected. Removal of the solvent, followed by sublimation of the residue (25 °C, 10^{-3} mmHg), gave **8** as a red solid. Crystals suitable for X-ray diffraction studies were grown from hexanes solution at −30 °C. Yield: 50 mg (23%).

For 8: ^{1}H NMR (400 MHz, C_6D_6, 20 °C) δ 4.45 (m, 2 H, Cp), 4.36 (m, 2 H, Cp), 4.25 (m, 2 H, Cp), 3.85 (m, 2 H, Cp) 0.83 (s, 3 H, Me); $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 20 °C) δ 199.0 (CO), 78.2, 77.9, 76.5, 75.5 (Cp), 38.2 (*ipso*-Cp), 5.0 (Me); ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C) δ 24.3; IR (hexanes, 25 °C) 2095 (m), 2034 (m), 2003 (s) (CO); MS (70 eV, EI) *m/z* (%) 398 (17) [M^+], 342 (28) [$M^+ - 2CO$], 314 (54) [$M^+ - 3CO$], 286 (100) [$M^+ - 4CO$], 227 (28) [$M^+ - Co(CO)_4$], 186 (10) [$C_{10}H_{10}Fe^+$]; for $C_{15}H_{11}O_4CoFeSi$ (398) calcd C 45.25, H 2.78; found C 43.82, H 2.79. The low value found for carbon may reflect partial decomposition or the difficult combustion of the highly sensitive product. For evidence of purity the reader is referred to copies of the NMR spectra deposited in the Supporting Information. HRMS (70 eV, EI) calcd 397.910800; found 397.911334; fit 1.3 ppm.

For [NEt$_3$H][Co(CO)$_4$]: isolated, ^{1}H NMR (400 MHz, C_6D_6, 20 °C) δ 8.27 (br s, 1 H, N−H), 2.48−2.42 (q, *J* (H_{CH2}, H_{CH3}) = 7.2 Hz, 6 H, CH_2), 0.84−0.80 (t, *J* (H_{CH3}, H_{CH2}) = 7.2 Hz, 9 H, CH_3); IR (THF, 25 °C) 1887 (s), 555 (s) (cf. [C_5H_5NH][Co(CO)$_4$] (pyridine) 1883 (vs), 555 (s));[31] in reaction mixture, ^{1}H NMR (400 MHz, C_6D_6, 20 °C) δ 8.49, all other signals are overlapping with free NEt_3.

Preparation of 8 from 10. Approximately 0.3 mL of NEt_3 was added to a mixture of 25 mg (0.11 mmol) of **10** and 40 mg (0.12 mmol) of $Co_2(CO)_8$ in an NMR tube. Approximately 0.5 mL of C_6D_6 was added, and the reaction mixture kept at room temperature overnight. Analysis of the ^{1}H NMR spectrum showed signals indicative of the formation of **8** as the major product and **12** as a minor product. A small signal was observed at a chemical shift of 8.7 ppm due to the nondeuterated impurities in the starting material.

Preparation of 9. Fe(η-$C_5H_4Li)_2$·2/3TMEDA (10.0 g, 36.1 mmol) was suspended in ether (200 mL) at −78 °C. $EtSiCl_2H$ (4.7 mL, 39.7 mmol) was added dropwise via syringe. After warming to room temperature and stirring for an additional 2 h, the reaction mixture was filtered through a fritted glass disk, and all volatile components were removed under high vacuum. The residue was taken up in hexanes (200 mL) and filtered once more through a fritted glass disk, and the solvent was removed under high vacuum. Purification by multiple low-temperature recrystallizations gave 2.0 g (23%) of **9** as a red oil.

For 9: ^{1}H NMR (400 MHz, C_6D_6, 20 °C) δ 5.32 (t, *J* (H_{SiH}, H_{CH2}) = 3.6 Hz, 1 H, Si−H), 4.36 (m, 4 H, Cp), 4.15 (m, 2 H, Cp), 3.95 (m, 2 H, Cp), 1.16 (t, *J* (H_{CH3}, H_{CH2}) = 7.8 Hz 3 H, CH_3), 0.95 (qd, *J* (H_{CH2}, H_{CH3}) = 7.8 Hz, *J* (H_{CH2}, H_{SiH}) = 3.6 Hz, 2 H, CH_2); $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 20 °C) δ 78.1, 77.6, 76.8, 75.2 (Cp), 27.4 (*ipso*-Cp), 7.3 (CH_3), 3.6 (CH_2); ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C) δ -16.1 (dm, *J* (Si, H) = 200 Hz); MS (70 eV, EI) *m/z* (%) 242 (100) [M^+], 213 (36) [$M^+ - CH_2CH_3$], 186 (9) [fc^+].

Preparation of 10. Compound **1c** (2.0 g, 7.6 mmol) was dissolved in 100 mL of toluene. $LiBEt_3D$ (1.0 M in THF, 7.6 mL, 7.6 mmol) was added dropwise at −78 °C. After warming to room temperature and stirring for an additional 1 h, the resulting red solution was decanted from the sticky white precipitate, and all volatile components were removed from the solution under high vacuum. Light red crystals of **10** were obtained via room-temperature vacuum (10^{-3} mmHg) sublimation from the reaction mixture to a coldfinger (4 °C). Yield after repeated sublimations: 0.55 g (32 %).

For 10: ^{1}H NMR (400 MHz, C_6D_6, 20 °C) δ 4.36−4.35 (m, 4 H, Cp), 4.14 (m, 2 H, Cp), 3.93 (m, 2 H, Cp), 0.40 (s, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 20 °C) δ 78.1, 77.7, 76.4, 75.0 (Cp), 27.6 (ps.t, *ipso*-Cp), −5.8 (CH_3); ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C) δ −22.0 (t, *J* (Si, D) = 32 Hz); MS (70 eV, EI) *m/z* (%) 229 (100) [M^+], 214 (51) [$M^+ - CH_3$].

Preparation of 11. Dicobalt octacarbonyl (85 mg, 0.25 mmol) and **9** (50 mg, 0.21 mmol) were dissolved in 1 mL of C_6D_6 and allowed to react for 3 h at room temperature. NMR spectroscopic analysis of the reaction mixture showed complete reaction at this time. Removal of the volatile materials, followed by repeated crystallizations (hexanes, −30 °C), gave **11** as a light orange oil. Yield: 20 mg (17%).

For 11: ^{1}H NMR (400 MHz, C_6D_6, 20 °C) δ 4.27 (ps t, 2 H, Cp), 4.17 (ps t, 2 H, Cp), 3.96 (br s, 5 H, Cp), 1.57 (q, *J* (H_{CH2}, H_{CH3}) = 8.0 Hz 2 H, CH_2), 1.25 (t, *J* (H_{CH3}, H_{CH2}) = 8.0 Hz 3 H, CH_3); $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 20 °C) δ 205.5 (CO), 74.6, 73.2, 69.7 (Cp), 16.7 (CH_2), 10.6 (CH_3), not observed (*ipso*-Cp); ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C) δ 147.5; MS (70 eV, EI) *m/z* (%) 556 (2) [M^+], 500 (5) [$M^+ - 2$ CO], 472 (7) [$M^+ -$ 3 CO], 444 (4) [$M^+ - 4$ CO], 416 (7) [$M^+ - 5$ CO], 388 (9) [M^+ − 6 CO], 360 (5) [$M^+ - 7$ CO], 186 (100) [fc^+].

Preparation of 12. Dicobalt octacarbonyl (85 mg, 0.25 mmol) and **10** (50 mg, 0.22 mmol) were dissolved in 1 mL of C_6D_6 and allowed to react for 3 h at room temperature. NMR spectroscopic analysis of the reaction mixture showed complete reaction at this time. Removal of the volatile materials followed by repeated crystallizations (hexanes, −30 °C) gave **12** as light orange needlelike crystals. Yield: 41 mg (34%).

For 12: ^{1}H NMR (400 MHz, C_6D_6, 20 °C) δ 4.17 (m, 2 H, Cp), 4.15 (m, 2 H, Cp), 3.92 (s, 4 H, Cp), 1.04 (s, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 20 °C) δ 205.5 (CO), 74.4, 73.4, 69.6, 69.5 (Cp), 6.7 (CH_3), not observed (*ipso*-Cp); ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C) δ 137.7; MS (70 eV, EI) *m/z* (%) 543 (3) [M^+], 487 (8) [$M^+ - 2$ CO], 459 (12) [$M^+ - 3$ CO], 431 (9) [$M^+ - 4$ CO], 403 (13) [$M^+ - 5$ CO], 375 (18) [$M^+ - 6$ CO], 347 (17) [$M^+ - 7$ CO], 187 (100) [(η-C_5H_4D)Fe(η-$C_5H_5)^+$].

Reaction of 9 and 10 with Co$_2$(CO)$_8$. The reaction was performed twice with identical results. In a representative reaction, dicobalt octacarbonyl (85 mg, 0.25 mmol) in 1 mL of C_6D_6 was added to a mixture of **9** (25 mg, 0.10 mmol) and **10** (24 mg, 0.10 mmol) in 0.5 mL of C_6D_6 in an NMR tube. The reaction was allowed to proceed for 3 h at room temperature. Analysis by ^{1}H NMR spectroscopy confirmed the presence of ring-opened products. Volatile components of the reaction mixture were removed under high vacuum, and multiple samples of the remaining product mixture were submitted for mass spectrometric analysis in sealed glass capillary tubes.

For the product mixture: MS (70 eV, EI) *m/z* (%) 556 (1) [M^+ **11**], 543 (1) [M^+ **12**], 500 (2) [M^+ **11** − 2 CO], 487 (3) [M^+ **12** − 2 CO], 472 (3) [M^+ **11** − 3 CO], 459 (4) [M^+ **12** − 3 CO], 444 (3) [$M^+ - 4$ CO], 431 (4) [M^+ **12** − 4 CO], 416 (6) [M^+ **11** − 5 CO], 403 (5) [M^+ **12** − 5 CO], 388 (6) [M^+ **11** − 6 CO], 375 (6) [M^+ **12** − 6 CO], 360 (3) [M^+ **11** − 7 CO], 347 (6) [M^+ **12** − 7 CO], 187 (92) [(η-C_5H_4D)Fe(η-$C_5H_5)^+$], 186 (100) [Fe(η-$C_5H_5)_2{}^+$].

Reaction of 1a with Co$_2$(CO)$_8$ in the Presence of Galvinoxyl. Dicobalt octacarbonyl (30 mg, 0.088 mmol) and **1a** (20 mg, 0.088 mmol) were placed in an NMR tube with varying amounts of galvinoxyl (0, 2, 10, 100 mol % based on $Co_2(CO)_8$) in a glovebox. The tube was connected to a Schlenk attachment, placed under N_2, and cooled to −78 °C in a dry ice/acetone bath. A syringe was utilized to freeze 0.5 mL of C_6D_6 at a point above the solid materials. The bath was removed (time = 0 for all trials) and the reaction monitored via NMR (25 °C) for ca. 1 h. Relative rates of reaction were estimated by NMR integration of the signals corresponding to the methyl group of **6** and **1a**. After ca. 45 min the

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Table 3. Crystal Data and Structure Refinement

	6	**8**
formula	$C_{18}H_{12}O_7Co_2FeSi\cdot 1/4\ C_6H_{14}$	$C_{15}H_{11}CoFeO_4Si$
M_r	563.62	398.11
T, K	100.0(1)	150(1)
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	7.4145(5)	10.6991(5)
b, Å	14.9247(8)	8.5875(3)
c, Å	21.0325(12)	16.7277(8)
α, deg	110.546(4)	90
β, deg	92.745(3)	94.455(2)
γ, deg	100.003(3)	90
V, Å^3	2131.3(2)	1532.27(12)
Z	4	4
$\rho_{calc,}$ g cm^{-3}	1.757	1.726
μ(Mo Kα), mm^{-1}	2.305	2.120
F(000)	1130	800
cryst size, mm	0.30 × 0.15 × 0.08	0.35 × 0.30 × 0.24
θ range, deg	4.11−26.42	2.67−27.51
no. of reflns collected	23 722	11 756
no. of ind reflns	8587	3447
abs corr	Denzo-SMN	Denzo-SMN
min. and max. transmn coeff	0.5447/0.8371	0.5241/0.6302
no. of params refined	552	201
GoF on F^2	0.991	1.032
R1[a] ($I > 2\sigma(I)$)	0.0668	0.0249
wR2[b] (all data)	0.1768	0.0595
peak/hole (e Å^{-3})	0.893/−1.128	0.302/−0.309

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

conversion of **1a** into **6** was estimated to be 77%, 69%, 61%, and 46% for 0, 2, 10, and 100 mol % galvinoxyl, respectively.

X-ray Structural Characterization. A summary of selected crystallographic data is given in Table 3. Data were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A combination of 1° phi and omega (with kappa offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.[32]

The structures were solved and refined using the SHELXTL\PC V5.1[33] package. Refinement was by full-matrix least squares on F^2 using all data (negative intensities included). Hydrogen atoms were included in calculated positions.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-155697 (**6**) and CCDC-155698 (**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336−033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Crystallographic data for compounds **6** and **8**, including tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters. Copies of NMR spectra obtained for compounds **6** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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