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Alkylation and Acylation of the Iron Carbonyl Anion $[(CO)_4FeSi(CH_3)_3]^-$. Evidence for 1,3-Silatropic Shifts from Iron to Acyl Oxygen

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Anions $K^+[(CO)_4FeSi(CH_3)_3]^-$ (K^+-1) and Na^+-1 are treated with CH_3OSO_2F, $CH_3OSO_2CF_3$, and $CH_3CH_2OSO_2F$ (2 min, 0 °C) and $C_6H_5CH_2Br$ and $H_2C{=}CHCH_2Br$ (0.5 h, 25 °C). Labile, air-sensitive alkyls *cis*-$(CO)_4Fe(R)Si(CH_3)_3$ (2) are subsequently isolated in 34–89% yields. When R = CH_3 (2a) or $CH_2C_6H_5$ (2c), room-temperature reductive elimination of $RSi(CH_3)_3$ occurs. Reactions of K^+-1 or Na^+-1 with acylating agents CH_3COBr, CH_3CH_2COBr, and $C_6H_5CH_2COBr$ give $H_2C{=}CHOSi(CH_3)_3$, $CH_3CH{=}CHOSi(CH_3)_3$, and $C_6H_5CH{=}CHOSi(CH_3)_3$, respectively. On the basis of low-temperature NMR and IR monitoring and literature precedent, it is proposed that initial acylation of 1 is followed by a rapid 1,3-silatropic shift to give the observable (silyloxy)carbene complex $(CO)_4Fe{=}C(CH_2R)OSi(CH_3)_3$, followed by a 1,2-hydride shift to give olefin complex $(CO)_4Fe(RCH{=}CHOSi(CH_3)_3)$, which in turn dissociates $RCH{=}CHOSi(CH_3)_3$. This interpretation is supported by (1) the independent synthesis and rearrangement of $(CO)_4Fe{=}C(CH_3)OSi(CH_3)_3$ from $Li^+(CO)_4Fe{=}C(CH_3)O^-$ and $(CH_3)_3SiBr$, (2) the synthesis of an isolable carbene complex, $(CO)_4Fe{=}C(C(CH_3)_3)OSi(CH_3)_3$, from 1 and $(CH_3)_3CCOBr$, and (3) the reaction of 2a with PPh_3 to give $(Ph_3P)(CO)_3Fe{=}C(CH_3)OSi(CH_3)_3$.

Introduction

Metal carbonyl anions are generally strong nucleophiles that undergo ready alkylation and acylation.[3] Hence they are valuable precursors to complexes with metal–carbon σ bonds. *Functionalized* metal carbonyl anions (e.g., $(CO)_xMX^-$) offer an extra dimension of reactivity in that subsequent transformations can follow metal–carbon σ bond formation. For instance, Collman has utilized the reagent $[Fe(CO)_4]^{2-}$ to effect a number of useful organic transformations via $[(CO)_4FeR]^-$ and/or $[(CO)_4Fe(COR)]^-$ intermediates.[4]

Our research group has had an ongoing interest in the fundamental chemistry of transition-metal trialkylsilanes.[5] We recently reported syntheses of the trimethylsilyl-functionalized anions $K^+[(CO)_4FeSi(CH_3)_3]^-$ (K^+–1) and $Na^+[(CO)_4FeSi(CH_3)_3]^-$ (Na^+-1).[5g] In this paper, we describe iron–carbon bond forming reactions that take place upon alkylation and acylation of these anions. A novel, and to our knowledge unprecedented, 1,3-silatropic shift from iron to oxygen accompanies the acylation of 1. A portion of this study has been communicated.[5d]

Results

Ether solutions of K^+-1 reacted with fluorosulfates CH_3OSO_2F and $CH_3CH_2OSO_2F$ within 2 min at 0 °C. After workup and careful distillation (25 °C, $<10^{-3}$ mm),

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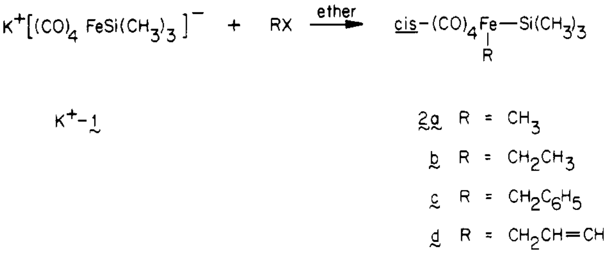
Table I. Spectroscopic Properties of Iron Alkyl Complexes cis-$(CO)_4Fe(R)Si(CH_3)_3$ (2)

complex	^1H NMR, δ	^{13}C NMR,[a] ppm	IR, cm^{-1} (hexane)
cis-$(CO)_4FeSi(CH_3)_3$ | CH_3 **2a**	0.34 (s, 9 H), 0.03 (s, 3 H)[c,d]	210.3, 206.5, 204.8 (COs)[b] 5.5 ($SiCH_3$), −2.7 ($FeCH_3$)[c,e]	2088 (m), 2027 (s), 2000 (vs)
cis-$(CO)_4FeSi(CH_3)_3$ | CH_2CH_3 **2b**	1.31 (m, 3 H), 1.13 (m, 2 H), 0.33 (s, 9 H)[c,d]	211.1, 206.0, 205.3 (COs)[b] 6.8 ($FeCH_2$), 5.4 ($SiCH_3$)[c,e,f]	2086 (m), 2023 (s), 1997 (vs)
cis-$(CO)_4FeSi(CH_3)_3$ | $CH_2C_6H_5$ **2c**	7.28–6.95 (m, 5 H), 2.45 (s, 2 H), 0.40 (s, 9 H)[e,g]	211.7, 205.6, 202.7 (COs)[b] 150.9, 125.0 (C_6H_5) 16.0 ($FeCH_2$), 5.7 ($SiCH_3$)[e,g,h]	2085 (m), 2028 (s), 1998 (vs)
cis-$(CO)_4FeSi(CH_3)_3$ | $CH_2CH{=}CH_2$ **2d**	6.57–5.77 (m, 1 H), 5.03 (d of m), overlapping with 4.88 (d of d, $J = 2, 10$ Hz, 2 H total), 1.86 (d, $J = 9$ Hz, 2 H), 0.37 (s, 9 H)[e,g]	210.7, 205.8, 204.3 (COs)[b] 145.4, 109.5 (C=C) 15.1 ($FeCH_2$), 5.5 ($SiCH_3$)[c,e]	2085 (m), 2028 (s), 2003 (vs)

[a] In the presence of $Cr(acac)_3$. [b] The low field carbonyl resonance is approximately twice as intense as the other two. [c] In toluene-d_8 at −20 °C. [d] Referenced to $C_6D_5CD_2H$ at δ 2.07. [e] Referenced to $(CH_3)_4Si$. [f] $FeCH_2CH_3$ resonance obscured by toluene-d_8; in CD_2Cl_2 (−20 °C), resonances appear at 211.3, 206.4, 205.7, 22.0, 6.7, and 5.6 ppm. [g] In benzene-d_6 at ambient probe temperature. [h] Some phenyl resonances obscured by benzene-d_6.

iron alkyl complexes cis-$(CO)_4Fe(CH_3)Si(CH_3)_3$ (**2a**) and cis-$(CO)_4Fe(CH_2CH_3)Si(CH_3)_3$ (**2b**) were isolated as colorless liquids in 46 and 56% yields, respectively (eq 1). Spectral properties, summarized in Table I, fully supported the proposed product identities. In particular, the ^{13}C NMR spectra showed three carbonyl absorptions in a 2:1:1 height ratio, as would be expected of nonfluxional cis geometric isomers.



$$K^+[(CO)_4FeSi(CH_3)_3]^- + RX \xrightarrow{\text{ether}} cis\text{-}(CO)_4\underset{\displaystyle R}{\underset{|}{Fe}}\text{—}Si(CH_3)_3 \qquad (1)$$

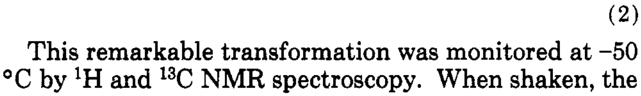
Reaction of an ether solution of Na^+-**1** with triflate $CH_3OSO_2CF_3$ (1.1 equiv, 0 °C) gave methyl complex **2a** in 89% isolated yield. Comparable results were obtained with CH_3SO_3F. The rate of formation of **2a** from Na^+-**1** and 2 equiv of $CH_3OSO_2CF_3$, CH_3OTs (OTs = p-$CH_3C_6H_4SO_3$–), and CH_3I in ether was monitored by FT IR spectroscopy at 0 °C. Conversion of Na^+-**1** to **2a** was complete within 1 min with $CH_3OSO_2CF_3$. Yields of **2a** with CH_3OTs and CH_3I were ca. 11% and 9%, respectively, after 24 and 22 min. Finally, **2a** was obtained in good yields when vigorously stirred 0 °C toluene suspensions of K^+-**1** or Na^+-**1** were treated with CH_3OSO_2F.

With alkyl substrates particularly susceptible to nucleophilic attack, bromide leaving groups could be used in eq 1. Thus, K^+-**1** and benzyl bromide reacted over the course of 0.5 h at 25 °C in ether to give cis-$(CO)_4Fe(CH_2C_6H_5)Si(CH_3)_3$ (**2c**, 75%). A similar reaction of K^+-**1** with allyl bromide gave cis-$(CO)_4Fe(CH_2CH{=}CH_2)Si(CH_3)$ (**2d**, 34%), which underwent partial decomposition upon distillation.

Alkyl complexes **2a–d** were all air sensitive and decomposed at room temperature over periods ranging from 4 to 6 h (**2a,d**) to 5–6 days (**2c**). Methyl complex **2a** gave $(CH_3)_4Si$ (84%), identified by ^1H NMR spectroscopy and GC/MS, as the only proton-containing decomposition product. Decomposition of benzyl complex **2c** gave mainly $(CH_3)_3SiCH_2C_6H_5$ (63%), as determined by ^1H NMR spectroscopy and GC; no bibenzyl (<1%) was detected. The decompositions of ethyl complex **2b** and allyl complex **2d** were complicated. Volatile $(CH_3)_3SiR$ species were not produced in appreciable quantities (<2%). Neither $(CH_3)_3SiCH{=}CH_2$ (<2% by GC from **2b**) nor a π-allyl complex of the type $(CO)_3Fe(\eta^3\text{-}C_3H_5)(SiR_3)$[6] (from **2d**) were detected.

Reactions of K^+-**1** and Na^+-**1** with acylating agents were investigated next. Exploratory experiments indicated that acyl bromides gave cleaner reactions than acyl chlorides. The reaction of acetyl bromide with a dichloromethane suspension of K^+-**1** was selected for initial study.

Anion K^+-**1** and acetyl bromide were combined in CD_2Cl_2 in a sealed NMR tube in the presence of an internal standard. The reaction was heated to 40 °C for ca. 8 h, during which time it turned a deep green. Acetaldehyde trimethylsilyl enol ether, $H_2C{=}CHOSi(CH_3)_3$,[7] cleanly formed in 70% yield (eq 2), as determined by ^1H and ^{13}C NMR spectroscopy: ^1H NMR δ 6.41 (dd, $J = 6$, 14 Hz, 1 H), 4.38 (d, $J = 14$ Hz, 1 H), 4.12 (d, $J = 6$ Hz, 1 H) 0.19 (s, 9 H); ^{13}C NMR 146.3 ($C{=}COSi$), 94.3 ($C{=}COSi$), −0.5 (SiC). In a separate experiment (below), product identity was verified by GC/MS. The only CO resonance in the ^{13}C NMR spectrum, 210.9 ppm, was assigned to $Fe_3(CO)_{12}$.[8]



(2)

This remarkable transformation was monitored at −50 °C by ^1H and ^{13}C NMR spectroscopy. When shaken, the reaction proceeded essentially instantly; otherwise, it was sluggish. New ^1H NMR resonances at δ 2.98 (s, 3 H) and 0.45 (s, 9 H) cleanly appeared, as did new ^{13}C NMR resonances (recorded at −75 °C) at 341.3 (22%), 215.2 (57%), 51.0 (39%), and 0.2 (100%) ppm. As will be rationalized below, this intermediate was assigned the silyloxycarbene structure $(CO)_4Fe{=}C(CH_3)OSi(CH_3)_3$ (**3a**). After ca. 90% conversion, other ^1H NMR resonances appeared, and the reaction was warmed in the NMR probe in 10 °C steps. From −30 to 0 °C, new ^1H NMR resonances at δ 3.06, 0.25,

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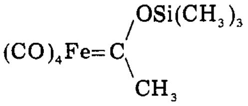
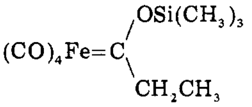
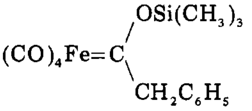
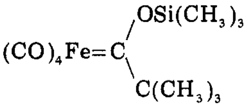
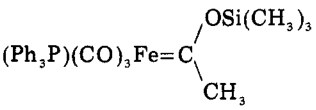
[7] (a) Blum, R. B. Ph.D. Thesis, UCLA, 1979. (b) Hudrlik, P. F.; Wan, C.-N.; Withers, G. P. *Tetrahedron Lett.* **1976**, *17*, 1449.

[8] Mann, B. E.; Taylor, B. F. "^{13}C NMR Data for Organometallic Compounds"; Academic Press: New York, 1981; pp 148, 172.

Table II. Spectroscopic Characterization of Iron Carbene Complexes (3)

complex	^{1}H NMR, δ (CD_2Cl_2)[a]	^{13}C NMR, ppm (CD_2Cl_2)[b]	IR, cm^{-1}
 $(CO)_4Fe{=}C(OSi(CH_3)_3)(CH_3)$ **3a**	2.98 (s, 3 H), 0.45 (s, 9 H)[c]	341.3 (Fe=C, 22%), 215.2 (CO, 57%), 51.0 (CCH_3, 39%), 0.2 ($SiCH_3$, 100%)[d]	2058 (m), 1988 (m), 1963 (s br), 1954 (s br), 1944 (sh br)[e]
 $(CO)_4Fe{=}C(OSi(CH_3)_3)(CH_2CH_3)$ **3b**	3.30 (q, J = 7 Hz, CH_2), 1.09 (t, J = 7 Hz, CCH_3), 0.49 (s, $SiCH_3$)[c]	347.0 (Fe=C, 14%), 215.5 (CO, 49%), 58.5 (CH_2, 44%), 12.2 (CCH_3, 37%), 0.4 ($SiCH_3$, 100%)[d]	2056 (m), 1988 (m), 1963 (sh br), 1954 (s br), 1942 (m br)[e]
 $(CO)_4Fe{=}C(OSi(CH_3)_3)(CH_2C_6H_5)$ **3c**	7.38-7.08 (m, C_6H_5), 4.71 (s, CH_2), 0.29 (s, $SiCH_3$)[f]	341.5 (Fe=C, 20%), 215.9 (CO, 61%), 135.4 (ipso-C_6H_5, 19%), 129.7 (C_6H_5, 100%), 128.8 (C_6H_5, 100%), 127.3 (p-C_6H_5, 51%), 71.6 (CH_2, 38%), −0.4 ($SiCH_3$, 44%)[g]	2056 (m), 1988 (m), 1954 (s br), 1946 (m br)[h]
 $(CO)_4Fe{=}C(OSi(CH_3)_3)(C(CH_3)_3)$ **3d**	1.20 (s, CCH_3), 0.56 (s, $SiCH_3$)[f]	361.0 (Fe=C, 19%), 216.4 (CO, 66%), 60.9 (CCH_3, 15%), 28.4 (CCH_3, 100%), 0.2 ($SiCH_3$, 56%)[g]	2051 (m), 1984 (m), 1947 (s br), 1938 (s br)[i]
 $(Ph_3P)(CO)_3Fe{=}C(OSi(CH_3)_3)(CH_3)$ **3e**	7.71-7.40 (m, C_6H_5), 3.07 (d, J_{HP} = 0.4 Hz, CCH_3), 0.50 (s, $SiCH_3$)[j]	342.3 (d, J_{CP} = 17 Hz, Fe=C, 6%), 217.9 (d, J_{CP} = 25 Hz, CO, 24%), 136.1 (d, J_{CP} = 41 Hz, ipso-C_6H_5, 20%), 133.2 (d, J_{CP} = 11 Hz, C_6H_5, 100%), 130.1 (s, p-C_6H_5, 73%), 128.4 (d, J_{CP} = 9 Hz, C_6H_5, 100%), 51.1 (d, J_{CP} = 8 Hz, CCH_3, 5%), 0.2 (s, $SiCH_3$, 10%)[k]	1907 (s br)[l]

[a] Referenced to $CDHCl_2$ (δ 5.320). [b] Referenced to CD_2Cl_2 (53.80 ppm); relative resonance intensities in parentheses. [c] −50 °C, 90 MHz. [d] −75 °C, 22.5 MHz. [e] Petroleum ether, −80 °C. [f] −42 °C, 300 MHz. [g] −42 °C, 75 MHz. [h] −42 °C, heptane. [i] −42 °C, hexane. [j] 20 °C, 300 MHz. [k] −20 °C, 75 MHz. [l] 25 °C, hexane.

and 0.04 (ca. 1:3:4) grew to a concentration of ca. 25%. Unresolved multiplets with plausible chemical shifts for coordinated olefin protons[9] also emerged from the base line. The sample was then stored for several days at −20 °C. After this time, only $H_2C{=}CHOSi(CH_3)_3$ and $Fe_3(CO)_{12}$ were evident by NMR spectroscopy.

Anion Na^+-1 and acetyl bromide also cleaned reacted in CD_2Cl_2 (−78 to −50 °C) to give **3a**, as assayed by ^{1}H NMR spectroscopy. Solvent was removed from a sample of **3a** under vacuum, and the residue was taken up in petroleum ether at −80 °C. An IR spectrum was recorded at −80 °C (Table II). The $\nu_{C{\equiv}O}$ closely matched those reported for related $(CO)_4Fe{=}C(R)OR'$ complexes.[10-12] No $\nu_{C{=}O}$ (1550–1680 cm^{-1}), which would be expected of the unrearranged acylation product *cis*-$(CO)_4Fe(COCH_3)Si(CH_3)_3$ (**4**), was observed. Some $Fe(CO)_5$ (2024 (s), 2000 vs cm^{-1})[13] was present.

An independent synthesis of (silyloxy)carbene complex **3a** was attempted. A sample of $Li^+(CO)_4Fe{=}C(CH_3)O^-$ was prepared by the attack of CH_3Li upon $Fe(CO)_5$ in ether.[10a,11,14] This anion was taken up in CD_2Cl_2 in the presence of an internal standard and cooled to −195 °C. Then $(CH_3)_3SiBr$ (1.0 equiv) was added, and the reaction was warmed. Over the course of 5 h at −15 °C, **3a** formed in 36% yield, as assayed by ^{1}H and ^{13}C NMR spectroscopy. After an additional 30 h, **3a** was present in 57% yield. A similar reaction was conducted at 25 °C for 24 h. Enol ether $H_2C{=}CHOSi(CH_3)_3$ formed in 31% yield, as assayed by ^{1}H NMR spectroscopy. Product identity was verified by GC/MS.

A (silyloxy)carbene complex that would be less prone to rearrangement than **3a** was sought. Anion Na^+-1 was treated with pivaloyl bromide, $(H_3C)_3CCOBr$, in CD_2Cl_2 in the presence of an internal standard at −29 °C. Complex $(CO)_4Fe{=}C(C(CH_3)_3)OSi(CH_3)_3$ (**3d**) formed in 83% yield over the course of 3 h, as assayed by ^{1}H NMR spectroscopy (eq 3). Complex **3d** prepared by this route was characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy in a manner similar to that of **3a** (Table II). However, pure **3d** was more conveniently isolated from the reaction of $Li^+(CO)_4Fe{=}C(C(CH_3)_3)O^-$[10a] with $(CH_3)_3SiBr$ (eq 3). It was obtained as an analytically pure red solid (67%) that melted below 0 °C.

The carbonylation of methyl complex **2a** was attempted in CH_2Cl_2 under 250 psi of CO. No evidence was observed for the formation of acyl complex **4** or carbene complex **3a**. Only reductive elimination of $(CH_3)_4Si$ from **2a** occurred. Identical results were obtained when the reaction of Na^+-1 and CH_3OSO_2F was conducted under 240 psi of

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(9) Thyret, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 520. Note that the ^{1}H NMR spectra in this paper are referenced to $[(CH_3)_3Si]_2O$, 0.0 ppm.

(10) (a) Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 4099. (b) Semmelhack, M. F.; Tamura, R. *Ibid.* **1983**, *105*, 6750.

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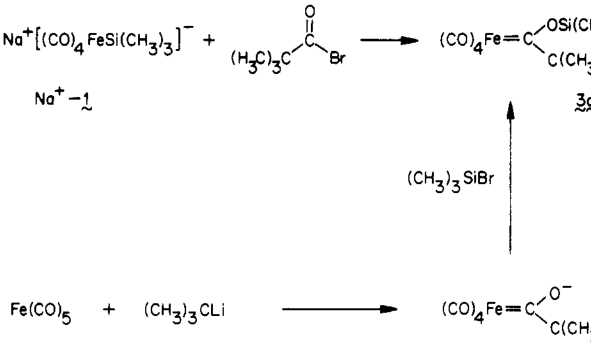
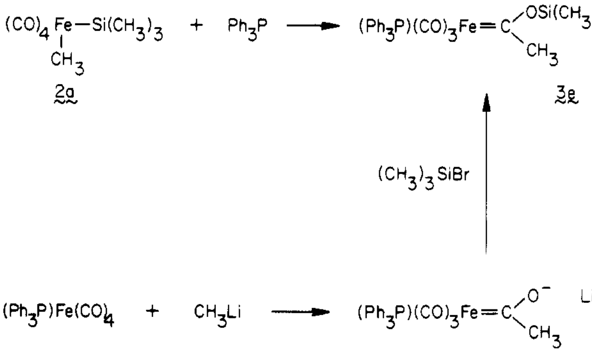
(14) Fischer, E. O.; Kiener, V. *J. Organomet. Chem.* **1970**, *23*, 215.



(3)

CO in ether. However, when **2a** was treated with PPh_3 at 0 °C, CO insertion and rearrangement occurred (eq 4) to give the (silyloxy)carbene complex $(Ph_3P)(CO)_3Fe{=}C(CH_3)OSi(CH_3)_3$ (**3e**). Minor amounts of $(Ph_3P)Fe(CO)_4$ and $(Ph_3P)_2Fe(CO)_3$ also formed in this reaction and rendered the purification of **3e** difficult. However, reaction of $Li^+(Ph_3P)(CO)_3Fe{=}C(CH_3)O^-$[11] with $(CH_3)_3SiBr$ (eq 4) gave, after workup, **3e** as a spectroscopically pure orange powder that was characterized as summarized in Table II. The single IR $\nu_{C{\equiv}O}$ observed indicates that the PPh_3 and (silyloxy)carbene ligands of **3e** occupy axial (trans) trigonal-bipyramid positions.[13b]

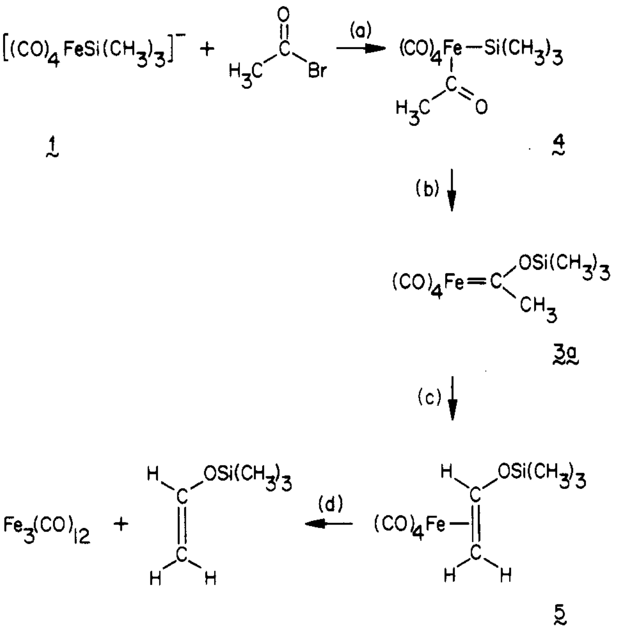


(4)

Reactions of K^+-**1** and Na^+-**1** with propionyl bromide were examined under conditions analogous to those used for acetyl bromide. At −50 °C, high conversion to (silyloxy)carbene complex $(CO)_4Fe{=}C(CH_2CH_3)OSi(CH_3)_3$ (**3b**) occurred, as assayed by ^1H NMR, ^{13}C NMR, and IR spectroscopy (Table II). When samples of **3b** were warmed to −20 °C, new ^1H NMR resonances, due to *free* olefin, appeared at ca. δ 1.5, 4.5, and 6.2. A sample was stored for 5 days at −20 °C. Careful ^1H NMR analysis indicated a ca. 75:25 mixture of *Z*/*E* $CH_3CH{=}CHOSi(CH_3)_3$ isomers. *Z*: δ 0.17 (s, 9 H), 1.53 (dd, *J* = 2, 7 Hz, 3 H), 4.25 (d quartet or pseudoquintet, *J* = 7, 7 Hz, 1 H), 6.16 (d quartet, *J* = 7, 2 Hz, 1 H). *E*: δ 0.17 (s, 9 H), ~1.5 (dd, partially obscured by *Z* resonances, *J* = 2, 7 Hz) 4.93 (d quartet or pseudosextet, *J* = 14, 7 Hz), 6.27 (low field quartet of obscured d quartet, *J* = 14, 2 Hz). These chemical shifts are in good agreement with those previously reported in the literature.[15]

Anion Na^+-**1** was similarly treated with phenylacetyl bromide in CD_2Cl_2 containing an internal standard. The reaction was monitored at −29 °C by ^1H NMR spectroscopy. Over the course of 6 h, (silyloxy)carbene complex $(CO)_4Fe{=}C(CH_2C_6H_5)OSi(CH_3)_3$ (**3c**) formed in 86% yield. Complex **3c** was characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopy (Table II). The sample of **3a** was kept at −15 °C for 14 h and 5 °C for 20 h. Analysis by ^1H NMR spectroscopy indicated a 36% yield of (*Z*)-$C_6H_5CH{=}CHOSi(CH_3)_3$: δ 7.63–7.06 (m, 5 H), 6.47 (d, *J* = 7 Hz, 1 H), 5.37 (d, *J* = 7 Hz, 1 H), 0.25 (s, 9 H). None of the corresponding *E* isomer was noted. Product identity was confirmed by synthesis of an authentic sample[16] and subsequent NMR and GC/MS comparison. Only a trace of the *E* isomer was found by GC/MS.

Scheme I. Proposed Mechanism for the Formation of Acetaldehyde Trimethylsilyl Enol Ether from 1 and Acetyl Bromide



Discussion

We were intially interested in alkyl complexes **2a–d**, and the corresponding acyl complexes such as *cis*-$(CO)_4Fe(COCH_3)Si(CH_3)_3$ (**4**), as intermediates in potentially useful synthetic transformations. Any utility, however, will be strictly limited by the instability of both classes of compounds. It can be expected that alkyls *cis*-$(CO)_4Fe(R)Si(CH_3)_3$ can be easily synthesized from K^+-**1** and Na^+-**1** when reactive alkylating agents are available. Otherwise, they will decompose at rates competitive with their formation. Interestingly, the chelated alkyl silane complex $(CO)_4\overline{FeSi(CH_3)_2CH_2CH_2CH_2}$, synthesized by Lappert, decomposes only slowly at 80 °C.[17] As expected, its spectral properties closely match those of **2a–d**.

The decomposition of **2a** and **2c** to $(CH_3)_4Si$ and $(CH_3)_3SiCH_2C_6H_5$, respectively, is of significance. Reductive elimination of an alkylsilane from a $L_nM(R)SiR_3$ intermediate has been proposed as a key step in catalytic olefin hydrosilylation.[18] To our knowledge, this elementary step has not previously been directly observed. These transformations are of additional interest in that $Fe(CO)_5$ has been demonstrated to be an effective olefin hydrosilylation precursor.[18a,19] Thus species closely related to **2** may under certain conditions be bona fide catalytic intermediates. However, it should be emphasized that **2b**, **2d**, and α-silyloxy-substituted benzyl complex $(CO)_4Fe(CH(C_6H_5)O$-

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[16] Ladjama, D.; Riehl, J. J. *Synthesis* **1979**, 504.

[17] Cundy, C. S.; Lappert, M. F. *J. Chem. Soc., Dalton. Trans.* **1978**, 665.

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[19] (a) Nesmeyanov, A. N.; Freidlina, R. Kh.; Chukovskaya, E. C.; Petrova, R. G.; Belyavsky, A. B. *Tetrahedron* **1962**, *17*, 61. (b) Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345. (c) Fischler, I.; Grevels, F. W. *Ibid.* 1980, *204*, 181.

$Si(CH_3)_3)Si(CH_3)_3$ have other decomposition pathways available. With the latter compound, iron–carbon bond homolysis occurs below room temperature.[5g]

Collman has shown that $(CO)_4Fe(R)(COR)$ intermediates generated, among other routes, by the acylation of $[(CO)_4FeR]^-$ anions, rapidly reductively eliminate ketones.[4] Hence, we anticipated that the acylation of **1** might lead to acylsilanes $(CH_3)_3Si(COR)$. Until very recently, a general synthetic route to this class of compounds was lacking.[20] However, as shown in eq 2, acetyl bromide undergoes an unprecedented reductive silylation.

On the basis of literature precedents and our NMR and IR data, we propose the mechanism depicted in Scheme I for eq 2. We suggest that initial acetylation of **1** (step a) to *cis*-$(CO)_4Fe(COCH_3)Si(CH_3)_3$ (**4**) is followed (step b) by a rapid 1,3-silatropic shift from iron to silicon to give (silyloxy)carbene complex $(CO)_4Fe{=}C(CH_3)OSi(CH_3)_3$ (**3a**).[21] Silatropic shifts are well-known in organic compounds,[22] and Berryhill has observed the migration of $-Si(CH_3)_3$ from iron to the deprotonated cyclopentadienyl ligand in $(\eta\text{-}C_5H_4Li)Fe(CO)_2Si(CH_3)_3$.[23] The principal driving force for **4** → **3a** would be the formation of a strong silicon–oxygen bond (106–127 kcal/mol).[24]

The question of whether **3a** or **4** is the species initially observed when eq 2 is monitored by NMR and IR spectroscopy deserves scrutiny. The δ 0.45 ^1H NMR chemical shift (Table II) is somewhat downfield for oxygen-bound $Si(CH_3)_3$. However, Fischer has reported that (silyloxy)carbene complexes $(CO)_5M{=}C(CH_3)OSi(CH_3)_3$ (M = Cr, W) exhibit $Si(CH_3)_3$ ^1H NMR resonances (acetone-d_6) at δ 0.53.[25] His ^{13}C NMR M=C (374.94, 346.14 ppm) and $=CCH_3$ (51.08, 55.39 ppm) chemical shifts are also in close agreement with those of **3a** (Table II). Acyl carbon ^{13}C NMR resonances in neutral iron acyl complexes are found *upfield* of 300 ppm.[8] Furthermore, only one C≡O resonance is observed in the −75 °C ^{13}C NMR spectrum of **3a**, whereas acyl complex **4** should, like **2a–d**, exhibit three resonances at sufficiently low temperature. Finally, no acyl $\nu_{C=O}$ is found in the IR spectrum of **3a**.

We suggest that (silyloxy)carbene complex **3a** subsequently rearranges by a 1,2-hydride migration (Scheme I) to olefin complex $(CO)_4Fe(H_2C{=}CHOSi(CH_3)_3)$ (**5**). Recently, abundant precedent has appeared for this step.[26] It should be noted, however, that **3a–c** appear somewhat less stable than the homologous alkoxycarbene complexes $(CO)_4Fe{=}C(CH_2R)OCH_2CH_3$ described by Semmelhack.[10]

Interestingly, **5** has been independently prepared by Thyret,[9] who reported that it decomposes at 0 °C. Its ^1H NMR spectrum was given as a mixture with free olefin $H_2C{=}CHOSi(CH_3)_3$.[9] Since this spectrum consists mainly of multiplets, we are unable to unequivocally identify **5** as a reaction intermediate; at no time does it appear to be the major species present. However, we feel that **5** is the only plausible means by which **3a** can be converted to $H_2C{=}CHOSi(CH_3)_3$.

We propose that propionyl bromide and phenylacetyl bromide are converted to their corresponding aldehyde trimethylsilyl enol ethers by mechanisms analogous to Scheme I. These constitute potentially valuable synthetic transformations. The predominant or exclusive formation of *Z* C=C geometric isomers may reflect a preference for forming the cis olefin complex in the hydrogen migration step (step c, Scheme I).

Steps analogous to a and b of Scheme I also likely occur in the reaction of Na^+-**1** with pivaloyl bromide (eq 3). However, since the resulting (silyloxy)carbene complex **3d** is devoid of hydrogens α to the carbene carbon, it exhibits greater thermal stability.

We suggest that the reaction of **2a** with PPh_3 (eq 4) initially gives the acyl complex $(Ph_3P)(CO)_3Fe(COCH_3)Si(CH_3)_3$. A subsequent silatropic shift to give product **3e** then occurs analogously to step b of Scheme I. Since the PPh_3 substituent in **3e** enhances the iron basicity and diminishes the carbene carbon electrophilicity, a subsequent 1,2-hydride shift is not as facile as with **3a**. Interestingly, Knox and Stone have reported that the osmium homolog of **2a**, *cis*-$(CO)_4Os(CH_3)Si(CH_3)_3$, undergoes substitution to $(Ph_3P)(CO)_3Os(CH_3)Si(CH_3)_3$ (23%) when treated with PPh_3 in refluxing hexane.[27]

The cobalt acyl silane complex $[(CO)_3Co(COC_6H_5)Si(C_6H_5)_3]^-$ has been synthesized by Corriu and co-workers.[28] Upon warming this complex, the acylsilane $(C_6H_5)_3Si(COC_6H_5)$ forms; no silatropic shift was noted. A silatropic shift similar to **4** → **3a** has been considered by Murai as a possible step in the $Co_2(CO)_8$ catalyzed conversion of alkenes, CO, and $HSi(CH_3)_2CH_2CH_3$ to oxo aldehyde silyl enol ethers, and related reactions.[29] The transformation **4** → **3a** also deserves consideration as a model for how M=C intermediates may be generated in the preparation of certain olefin metathesis catalysts.[30]

In summary, this study has uncovered two new reactions of transition-metal trialkylsilanes complexes: (1) alkylsilane reductive elimination and (2) metal to oxygen silatropic rearrangements. Additional novel aspects of metal silane chemistry will be the subject of forthcoming reports from this laboratory.[5k,31]

Experimental Section

General Data. All reactions were carried out under an inert atmosphere. Solvents were dried and deoxygenated as previously reported.[5g]

Spectrometers employed for the analysis of alkylation products (Table I) have been described.[5g] NMR data for the acylation experiments (Table II) were obtained on JEOL FX90Q and Varian SC-300 spectrometers. GLC analyses were conducted as prevously reported.[5f] GC/MS data were obtained on a VG Micromass 7070 spectrometer. Microanalyses were conducted by Schwarzkopf Laboratories utilizing glovebox techniques and samples that had been shipped at −78 °C.

IR Analyses. Room-temperature IR spectra (Table I) were recorded on a Perkin-Elmer 521 spectrometer. Low-temperature

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(20) (a) Seyferth, D.; Weinstein, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 5534. (b) Miller, J. A.; Zweifel, G. *Ibid.* **1981**, *103*, 6217.

(21) A reviewer has raised the possibility that step b might be intermolecular. Such mechanisms appear to be uncommon in uncatalyzed 1,3-silatropic shifts involving organic substrates[22] but are not excluded by our data.

(22) (a) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678. (b) Brook, A. G.; Bassindale, A. R. In "Rearrangement in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. II, pp 192–212.

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(30) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449.

(31) Gladysz, J. A. *Acc. Chem. Res.*, in press.

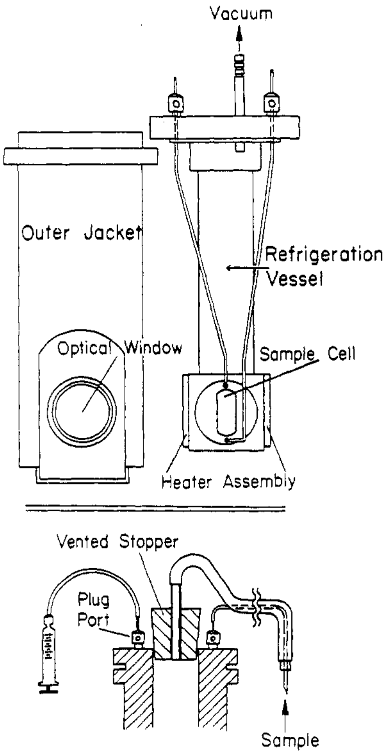

Figure 1. Modified Beckman apparatus for low-temperature IR sampling.

IR spectra (Table II) were recorded on a Perkin-Elmer 1500 (FT) spectrometer using a modified Beckman RIIC VLT-2 variable-temperature unit. This apparatus, diagrammed in Figure 1, consisted of a solution IR cell mounted beneath a liquid N_2 coolant reservoir (refrigeration vessel). An outer evacuated jacket surrounded the cell. Temperature sensing was provided by a thermocouple attached to the cell, and temperature regulation was achieved by heating coils attached to the cell and a Beckman Model CTC 250 temperature controller. To permit flow-through low-temperature reaction sampling while the outer jacket was evacuated, 20-gauge stainless-steel tubing was soldered onto the inlets of the solution sample cell (FH-01) and run up through existing inlet ports on top of the unit. A Teflon needle was connected to one end of the stainless-steel tubing and connected to a gas-tight syringe, as shown in Figure 1. The other piece of stainless-steel tubing was connected, via Teflon tubing, to a stainless-steel sampling needle. The sampling needle/tubing was kept cool by running it through a latex hose that trapped the cold liquid-nitrogen boil-off from the cooling reservoir. In operation, after the IR sample cell was cooled to the desired temperature, the sampling needle was simply inserted through a septum of the reaction vessel and a portion of the reaction mixture was withdrawn into the cell by using the gas-tight syringe.

Starting Materials. Alkyl fluorosulfates were obtained from Aldrich and used as received. Methyl triflate was obtained from Aldrich and was distilled from CaH_2 prior to use. Alkyl halides and CH_3OTs were obtained from common commercial sources and were (vacuum) distilled from CaH_2 prior to use. Alkyllithium reagents were obtained from Alfa and were standardized prior to use.

Acetyl bromide was obtained from Aldrich and was distilled from PBr_5 and then quinoline; it was distilled a third time immediately prior to use. Propionyl bromide, phenylacetyl bromide, and pivaloyl bromide were prepared from the corresponding acid chlorides and $(CH_3)_3SiBr$ as previously described,[32] except that CH_3CN was used as the reaction solvent. These acid bromides were purified by fractional (vacuum) distillation prior to use.

Phenol was purchased from MCB, recrystallized from benzene/petroleum ether, and sublimed prior to use. Phosphine PPh_3 was purchased from Pressure Chemical Co. and sublimed prior to use. Silane $(CH_3)_3SiBr$ was obtained from Petrarch Systems and was distilled from CaH_2 prior to use. Authentic samples of trimethylsilyl enol ethers, $RCH{=}CHOSi(CH_3)_3$, were prepared by literature procedures[15,16] and purified by fractional distillation. Internal standards were obtained from common commercial sources and purified by fractional distillation or recrystallization.

Hydrides NaH and KH were obtained from Alfa and were washed with THF solutions of $(CH_3)_3SiCl$ (to remove ^-OH impurities) and subsequently used in excess. Carbonyl $Fe(CO)_5$ was purchased from Aldrich and vacuum distilled prior to use. Complex $(Ph_3P)Fe(CO)_4$ was synthesized by the photolysis of $Fe(CO)_5$ (2.0 mL, 15.2 mmol) and PPh_3 (3.0 g, 11.5 mmol) in toluene (400 mL, 20 h, Rayonet reactor)[33] and purified by column chromatography. Collman's reagent $(Na^+)_2[(CO)_4Fe]^{2-}$ was prepared by a published procedure.[34] Anion K^+-1 was synthesized as previously described.[5g] Anion Na^+-1 was prepared by the following modified literature procedure,[5g] the principal change in which is the purification of intermediate $(CO)_4Fe(H)Si(CH_3)_3$.

Preparation of $Na^+[(CO)_4FeSi(CH_3)_3]^-$ (Na^+-1). A Schlenk flask was charged with $(Na^+)_2[(CO)_4Fe]^{2-}$ (2.14 g, 10.0 mmol), ether (150 mL), and a stir bar. Then phenol (0.941 g, 10.0 mmol) was added (to generate $(CO)_4FeH^-$), and the reaction was stirred at 25 °C for 1 h. The reaction was cooled to −15 °C (ethylene glycol/liquid N_2), and $(CH_3)_3SiBr$ (2.64 mL, 20.0 mmol) was added via syringe. The resulting red-purple solution was stirred for 4 h at −15 °C. The volatile components of the reaction were then vacuum transferred via a "u-tube" to another Schlenk Flask that had been charged with NaH (1.20 g, 50.0 mmol) and cooled to −195 °C. This mixture was stirred overnight at 0 °C and was then filtered to remove the excess NaH. The filtrate was concentrated under vacuum to precipitate some Na^+-1. This Na^+-1 was isolated by filtration, and remaining Na^+-1 was precipitated from the pink filtrate by the addition of cold petroleum ether. The Na^+-1 was vacuum dried at 10^{-4} torr for 12 h to give 2.096 g (7.94 mmol, 79%) of white powder. White, needle-shaped crystals slowly grew when an ether solution of Na^+-1 was layered with hexane: IR (cm^{-1}, ether) 1993 (m), 1910 (m), 1888 (s), 1803 (m); (cm^{-1}, THF)[5g] 1984 (m), 1891 (m sh), 1866 (s), 1834 (m). Anal. Calcd for $C_7H_9FeO_4NaSi$: C, 31.84; H, 3.44. Found: C, 31.78; H, 3.62.

Preparation of $Li^+(CO)_4Fe{=}C(CH_3)O^-$.[11,14] A Schlenk flask was charged with $Fe(CO)_5$ (2.0 mL, 15.2 mmol), ether (10 mL), and a stir bar and was cooled to −78 °C. Then 10 mL of 1.16 M CH_3Li (11.6 mmol) was added dropwise with stirring. The resulting amber solution was allowed to warm to 10 °C, where upon it became greenish yellow. Solvent was removd under vacuum to give a green solid, which upon extended pumping became a light tan powder. Thus obtained was 2.20 g (10.1 mmol, 91%) of $Li^+(CO)_4Fe{=}C(CH_3)O^-$: IR (KBr) 2033 (m), 1970 (s), 1879 (vs), 1522 (m) cm^{-1}.

Preparation of *cis*-$(CO)_4Fe(CH_3)Si(CH_3)_3$ (2a). A. A Schlenk flask was charged with K^+-1 (200 mg, 0.71 mmol), ether (20 mL), and a stir bar and was cooled to 0 °C. Then CH_3OSO_2F (50.6 μL, 0.71 mmol) was added via syringe. The reaction was stirred for 5 min and filtered, and the solvent was removed in vacuo. The residue was distilled (25 °C, 10^{-3} mm) onto a dry ice cooled probe to give 85 mg (0.33 mmol, 46%) of **2a** as a white solid that melted below room temperature. Characterization: Table I. In a separate experiments, hexamethylbenzene standard was added prior to distillation. A ^1H NMR spectrum indicated a 55% yield of **2a**. **B.** A Schlenk flask was charged with Na^+-1 (52.8 mg, 0.200 mmol), ether (5.0 mL), and a stir bar and was cooled to 0 °C. Then a solution of $CH_3OSO_2CF_3$ (35.4 mg, 0.216 mmol) in ether (0.5 mL) was added by syringe. The reaction was stirred for 15 min and then cooled to −15 °C (ethylene glycol/liquid N_2), whereupon solvent was removed under oil pump vacuum. The residue was sublimed onto a −78 °C cold finger to give **2a** as a white solid. This material was washed with CD_2Cl_2 into a 5-mm NMR tube that had been charged with 1,2,4,5-tetramethylbenzene (16.4 mg, 0.122 mmol) standard. Integration of a ^1H NMR spectrum of the resulting solution (δ 0.44 (9 H), 0.10 (3 H)) indicated 0.18 mmol (89%) of **2a** to be present. This tube was allowed to stand at room temperature for 36 h. The volatiles were

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(32) Schmidt, A. H.; Russ, M.; Grosse, D. *Synthesis* **1981**, 216.

(33) Conder, H. L.; Darensbourg, M. Y. *J. Organomet. Chem.* **1974**, *67*, 93.

(34) Cymbaluk, T. H.; Ernst, R. D. *Inorg. Chem.* **1980**, *19*, 2381.

vacuum transferred to another NMR tube that had been charged with tetramethylbenzene (17.2 mg, 0.128 mmol). A ^{1}H NMR spectrum showed $(CH_3)_4Si$ (0.149 mmol, 84%) to be the only volatile organic product. Product identity was confirmed by GC/MS. **C.** Each of the three vials were charged with Na^+-**1** (10 mg, 0.038 mmol), ether (3.0 mL), and a magnetic stir bar, sealed with a septum, and cooled to 0 °C. Then 0.5-mL ether solutions of $CH_3OSO_2CF_3$ (12.4 mg, 0.075 mmol), CH_3OTs (14.0 mg, 0.075 mmol), and CH_3I (10.7 mg, 0.075 mmol) were injected, and the rate of formation of **2a** at 0 °C was monitored by FT IR spectroscopy with the apparatus shown in Figure 1. Data: see Results.

Preparation of *cis*-$(CO)_4Fe(CH_2CH_3)Si(CH_3)_3$ (2b). A Schlenk flask was charged with K^+-**1** (166 mg, 0.59 mmol), ether (15 mL), and a stir bar and was cooled to 0 °C. Then $CH_3CH_2OSO_2F$ (65 μL, 0.72 mmol) was added via syringe. The reaction was stirred for 5 min and filtered, and the solvent was removed in vacuo. The residue was distilled (25 °C, ≤10^{-3} mm) into a cooled flask (−78 °C) to give 90 mg (0.33 mmol, 56%) of colorless **2b**. Characterization: Table I.

Preparation of *cis*-$(CO)_4Fe(CH_2C_6H_5)Si(CH_3)_3$ (2c). A. A Schlenk flask was charged with K^+-**1** (200 mg, 0.71 mmol), ether (20 mL), and a stir bar. Then 122 mg (0.71 mmol) of $C_6H_5CH_2Br$ in 1 mL of ether was added dropwise. The reaction was stirred for 0.5 h and filtered, and the solvent was removed in vacuo. The residue was distilled (25 °C, 4 × 10^{-4} mm) onto a dry ice cooled probe to give 175 mg (0.53 mmol, 74%) of **2c** as a white solid that melted below room temperature. Sometimes trace amounts of green $Fe_3(CO)_{12}$ colored the distilled product. Characterization: Table I. **B.** A Schlenk flask was charged with Na^+-**1** (158 mg, 0.60 mmol), ether (10 mL), and a stir bar and was cooled to 0 °C. Then 109 mg (0.50 mmol) of $C_6H_5CH_2I$ in a small amount of ether was added. The reaction was stirred for 0.5 h at 0 °C. Solvent was removed from the resulting pink solution in vacuo, and 10 mL of petroleum ether (bp 30–60 °C) was then vacuum transferred onto the residue. This mixture was filtered, and the filtrate was cooled in liquid N_2 until the freezing point of the solvent was nearly reached. A white powder, **2c**, precipitated that was isolated by cold filtration and dried in vacuo at 5 °C (benzene/liquid N_2). At 5 °C, **2c** melted to a liquid with a light green tint ($Fe_3(CO)_{12}$); it resolidified at 0 °C. Anal. Calcd for $C_{14}H_{16}FeO_4Si$: C, 50.62; H, 4.85. Found: C, 50.62; H, 4.81.

Preparation of *cis*-$(CO)_4Fe(CH_2CH{=}CH_2)Si(CH_3)_3$ (2d). A Schlenk flask was charged with K^+-**1** (100 mg, 0.36 mmol), ether (9 mL), and a stir bar. Then 43 mg (0.36 mmol) of allyl bromide in 1 mL of ether was added dropwise with stirring. The reaction was stirred for 7 min and filtered, and the solvent was removed in vacuo. The residue was extracted with petroleum ether (bp 20–40 °C), and the extract was filtered. The filtrate was taken to dryness in vacuo. A pale green oil was obtained that was washed into a 5-mm NMR tube containing *p*-di-*tert*-butylbenzene standard. A ^{1}H NMR spectrum indicated **2d** to be present in 34% yield. Characterization: Table I.

Reaction of K^+-1 with Acetyl Bromide at 40 °C. Using Schlenk and vacuum line techniques, a 5-mm NMR tube was charged with K^+-**1** (56 mg, 0.20 mmol), acetyl bromide (25 mg, 0.20 mmol), tetrachlorobenzene standard (90 mg, 0.42 mmol), and CD_2Cl_2 (1 mL). The tube was sealed and heated to 40 °C. Data: see Results.

Preparation of $(CO)_4Fe{=}C(CH_3)OSi(CH_3)_3$ (3a). A. A 5-mm NMR tube was charged with 54 mg (0.19 mmol) of K^+-**1**. On a vacuum line, ca. 0.7 mL of CD_2Cl_2 was distilled into the tube. The tube was capped with a septum under argon and was transferred to a −50 °C NMR probe. A ^{1}H NMR spectrum was recorded, and 14.5 μL (0.20 mmol) of acetyl bromide was then injected. Data: see Results and Table II. **B.** A Schlenk flask was charged with Na^+-**1** (10 mg, 0.038 mmol), and a magnetic stir bar and was cooled to −195 °C. Then acetyl bromide (9.2 mg, 0.075 mmol) and CH_2Cl_2 (2 mL) were vacuum transferred into the flask. The mixture was stirred at −78 °C for 0.5 h, and the solvent was then removed under vacuum. Onto the resulting red-brown residue (still at −78 °C) was vacuum transferred 3 mL of petroleum ether. The IR spectrum of **3a** (Table II) was obtained by using the apparatus shown in Figure 1. A small amount of $Fe(CO)_5$ (10–15%, 2024 (s), 2000 (vs) cm^{-1})[13] and excess acetyl bromide were also detected. **C.** A 5-mm NMR tube was charged with $Li^+(CO)_4Fe{=}C(CH_3)O^-$ (43.8 mg, 0.201 mmol) and 2-methylnaphthalene standard (17.8 mg, 0.125 mmol) and was capped with a septum and cooled to −195 °C. Then a solution of $(CH_3)_3SiBr$ (30.9 mg, 0.202 mmol) in CD_2Cl_2 (0.40 mL) was injected, and the tube was allowed to stand at −15 °C (ethylene glycol/CO_2) for 5 h with occasional shaking. A ^{1}H NMR spectrum (recorded at −30 °C) showed 0.0072 mmol (36%) of **3a** to be present (δ 3.02 (s), 0.47 (s)). After a total of 20 h at −15 °C, **3a** was present in 54% yield. After a total of 35 h at −15 °C, **3a** was present in 57% yield. At this point, some $H_2C{=}CHOSi(CH_3)_3$ ^{1}H NMR resonances were visible. A similar reaction was conducted at −195 to −60 °C to obtain ^{13}C NMR data: 342.4 (20%), 215.7 (100%), 50.8 (29%), −0.2 (64%) ppm.

Reaction of $Li^+(CO)_4Fe{=}C(CH_3)O^-$ with $(CH_3)_3SiBr$ at 25 °C. A 5-mm NMR tube was charged with Li^+ $(CO)_4Fe{=}C(CH_3)O^-$ (43.6 mg, 0.200 mmol), and $(CH_3)_3SiBr$ (54.0 mg, 0.353 mmol) in CD_2Cl_2 (0.60 mL) was added by vacuum transfer. The tube was flame-sealed under vacuum and allowed to stand at 25 °C for 24 h. The volatile contents of the resulting green solution were then vacuum transferred into a second 5-mm NMR tube that had been charged with Ph_3CH standard (19.9 mg, 0.0815 mmol). A ^{1}H NMR spectrum showed 0.062 mmol (31%) of $H_2C{=}CH_2OSi(CH_3)_3$ as well as some $(CH_3)_3SiBr$ and $[(CH_3)_3Si]_2O$. Products identities were confirmed by GC comparison to authentic samples and GC/MS.

Attempted Carbonylation of 2a. A. A Fischer-Porter bottle was charged with Na^+-**1** (26.4 mg, 0.100 mmol) and a stir bar and was cooled to −78 °C. Then $CH_3OSO_2CF_3$ (19.5 mg, 0.119 mmol) in ether (1.0 mL) was slowly syringed in. The solution was stirred at 0 °C for 10 min and then taken to dryness under vacuum. The residue was cooled to −78 °C, and 1.0 mL of CH_2Cl_2 was vacuum transferred into the bottle. Then the vessel was pressurized with 250 psi of CO. The solution was allowed to warm to room temperature. After 20 h, GC and GC/MS analyses were conducted. The only significant volatile products were $(CH_3)_4Si$, $Fe(CO)_5$, and $[(CH_3)_3Si]_2O$. **B.** A Fischer-Porter bottle was charged with Na^+-**1** (52.8 g, 0.200 mmol) and a stir bar and was cooled to −78 °C. Then CH_3OSO_2F (22.8 mg, 0.200 mmole in ether (3.0 mL) was syringed in. The bottle was pressurized with 240 psi of CO. The reaction was stirred and warmed to 0 °C (2 h) and then room temperature (24 h). Subsequent GC analysis showed $(CH_3)_4Si$ and $[(CH_3)_3Si]_2O$ to be present. No $H_2C{=}CHOSi(CH_3)_3$ was detected.

Preparation of $(CO)_4Fe{=}C(CH_2CH_3)OSi(CH_3)_3$ (3b). This compound was synthesized (1) identically to preparation A of **3a**, except that 18 μL (27 mg, 0.20 mmol) of propionyl bromide was used, and (2) identically to preparation B of **3a**, except that 9.2 mg (0.075 mmol) of propionyl bromide was used. Data: see Results and Table II.

Preparation of $(CO)_4Fe{=}C(CH_2C_6H_5)OSi(CH_3)_3$ (3c). A 5-mm NMR tube was charged with Na^+-**1** (28.1 mg, 0.106 mmol) and 2-methylnaphthalene standard (13.4 mg, 0.094 mmol), capped with a septum, and cooled to −195 °C. Then phenylacetyl bromide (21.1 mg, 0.106 mmol) in CD_2Cl_2 (0.40 mL) was added via syringe. The reaction was kept at −29 °C (CH_3NO_2/liquid N_2) for 6 h and was occasionally shaken. Subsequent ^{1}H NMR analysis (−30 °C) showed 0.0912 mmol (86%) of **3c** to be present. (data: Table II). The reaction was kept for 14 h at −15 °C. Subsequent ^{1}H NMR analysis (−30 °C) showed 0.0811 mmol (70%) of **3c** to be present, but no organic decomposition products were yet detectable. The reaction was kept for 20 h at 5 °C. Subsequent ^{1}H NMR analysis showed 0.038 mmol (36%) of (*Z*)-$C_6H_5CH{=}CHOSi(CH_3)_3$ to be present (data: see Results). Product identity was confirmed by ^{1}H NMR and GC comparison to an independently prepared authentic sample[16] and GC/MS. An IR spectrum of **3c** was obtained analogously to that in preparation B of **3a**.

Preparation of $(CO)_4Fe{=}C(C(CH_3)_3)OSi(CH_3)_3$ (3d). A. A 5-mm NMR tube was charged with Na^+-**1** (27.2 mg, 0.103 mmol) and 1,2,4,5-tetramethylbenzene standard (6.7 mg, 0.050 mmol), capped with a septum, and cooled to −195 °C. Then pivaloyl bromide (17.0 mg, 0.103 mmol) in CD_2Cl_2 (0.50 mL) was added via syringe. The reaction was kept at −29 °C (CH_3NO_2/liquid N_2) for 3 h and was occasionally shaken. Subsequent ^{1}H NMR analysis (−30 °C) showed 0.010 mmol of pivaloyl bromide remaining and 0.085 mmol (83%) of **3d** to be present (data: Table II). The reaction was warmed to 25 °C for 1 h. No decomposition of **3d** was noted. The reaction was stored for 1 week at −20 °C. After this time, 0.044 mmol of **3d** remained. An IR spectrum of **3d** was obtained analogously to that in preparation B of **3a**. **B.** A Schlenk flask was charged with $Fe(CO)_5$ (2.0 mL, 15.2 mmol), ether (150 mL), and a stir bar and was cooled to −78 °C. Then 6.6 mL (13.9 mmol) of 2.1 M $(CH_3)_3CLi$ in pentane was syringed in dropwise with stirring. The reaction was kept at −26 °C overnight and then cooled to −78 °C, whereupon $Li^+(CO)_4Fe{=}C(C(CH_3)_3)O^-$[10a] precipitated as a green-yellow solid. This material was isolated by filtration and vacuum dried at 0 °C: IR (cm^{-1}, ether) 2022 (7), 1944 (7), 1910 (s), 1860 (m), 1535 (w). Then 50 mL of CH_2Cl_2 was transferred by cannula onto the solid, and the solution was cooled to −78 °C. Then $(CH_3)_3SiBr$ (2.0 mL, 15.2 mmol) was added by syringe. The reaction was warmed to −15 °C (ethylene glycol/CO_2) and stirred for 1 h. Then solvent was removed under vacuum, and the resulting red oil was extracted with 50 mL of cold petroleum ether. The extract was filtered and then cooled to −110 °C (THF/liquid N_2) to precipitate **3d** as a red semicrystalline solid. Complex **3d** was isolated by cold filtration and dried at 10^{-4} torr and −23 °C (CCl_4/CO_2). The complex melted upon warming to 0 °C to give 3.042 g (9.33 mmol, 67%) of a dark red oil that resolidified upon cooling below 0 °C. Anal. Calcd for $C_{12}H_{18}FeO_5Si$: C, 44.18; H, 5.56. Found: C, 44.74; H, 5.72.

Preparation of $(Ph_3P)(CO)_3Fe{=}C(CH_3)OSi(CH_3)_3$ (3e). A. A Schlenk flask was charged with Na^+-**1** (264 mg, 1.00 mmol), ether (10 mL), and a stir bar and was cooled to 0 °C. Then $CH_3OSO_2CF_3$ (182 mg, 1.10 mmol) was added, and the solution was stirred for 5 min. A 0 °C solution of PPh_3 (524 mg, 2.00 mmol) in CH_3CN (10 mL) was then added via cannula, and the reaction was stirred for 10 min. The solvent was then removed under vacuum at 0 °C with stirring. The resulting orange-brown solid was dissolved in 25 mL of ether and cooled to 0 °C. Then $CH_3OSO_2CF_3$ (245 mg, 1.50 mmol) was added to methylate the excess PPh_3. The ether was removed under vacuum, and the solid residue was extracted with 4 × 20 mL of 3:1 (v/v) hexane/benzene). The solvent was removed under vacuum to give 445 mg of an orange-red semicrystalline solid. A 50.7-mg portion of this sample and 10.4 mg (0.073 mmol) of 2-methylnaphthalene standard were taken up in CD_2Cl_2 and analyzed by ^1H NMR (CCH_3 of **3e**) and, using a long pulse delay, ^{31}P NMR (−20 °C, 32.2 MHz, external H_3PO_4 reference). Only three products were evident: **3e** (^{31}P NMR 71.0 ppm; 0.58 mmol, 58% of theory), $(Ph_3P)Fe(CO)_4$ (71.2 ppm; 0.17 mmol, 17%) $(Ph_3P)_2Fe(CO)_4$ (81.7 ppm; 0.11 mmol, 11%). **B.** A Schlenk flask was charged with $(Ph_3P)Fe(CO)_4$ (956 mg, 2.22 mmol), THF (30 mL), and a stir bar and was cooled to −78 °C. Then 3.0 mL (3.48 mmol) of 1.16 M CH_3Li in ether was syringed in dropwise with stirring. The solution was warmed to 0 °C, and stirred for 5 min. The solvent was then removed under vacuum while a temperature of 0 °C was maintained. The resulting tan solid was dissolved in 200 mL of ether. This solution was concentrated under vacuum. A gold powder precipitated from the cold solution and was isolated by filtration, washed with cold ether, and vacuum dried at 10^{-4} torr for 16 h to give 0.950 g of $Li^+(Ph_3Ph)(CO)_3Fe{=}C(CH_3)O^-$.[11] IR ($cm^{-1}$, THF) 1852 (s br), 1541 (m). This material was suspended in CH_2Cl_2 (30 mL) and cooled to −78 °C. Then $(CH_3)_3SiBr$ (0.55 mL, 4.2 mmol) was added dropwise via syringe. The reaction was warmed to −15 °C (ethylene glycol/CO_2) and stirred for 30 min. The solvent was then removed under vacuum, and the resulting orange solid was extracted (25 °C) with 4 × 25 mL of a 3:1 (v/v) hexane/benzene mixture. Solvent was removed from the extract under vacuum to give an orange-red semicrystalline solid that was taken up in 100 mL of hexane (25 °C). The orange-red solution was cooled to −95 °C, whereupon **3e** precipitated as an orange powder. The powder was isolated by cold filtration and vacuum dried at 10^{-4} torr to give 547 mg (1.06 mmol, 48%) of spectroscopically pure **3e**: mp 62 °C dec; ^{31}P NMR (ppm, CD_2Cl_2, −30 °C) 71.1. Other data: Table II.

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Registry No. Na^+-1, 79483-28-6; K^+-1, 78240-74-1; **2a**, 78240-70-7; **2b**, 78240-71-8; **2c**, 78240-72-9; **2d**, 78240-73-0; **3a**, 90195-57-6; **3b**, 90195-58-7; **3c**, 90195-59-8; **3d**, 90195-60-1; **3e**, 90195-61-2; $Li^+(CO)_4Fe{=}C(CH_3)O^-$, 71722-65-1; $Li^+(CO)_4Fe{=}C(C(CH_3)_3)O^-$, 90195-62-3; $(Ph_3P)Fe(CO)_4$, 14649-69-5; $(Ph_3P)_2Fe(CO)_4$, 90195-63-4; $Li^+(Ph_3P)(CO)_3Fe{=}C(CH_3)O^-$, 49655-08-5; $(Na^+)_2[(CO)_4Fe]^{2-}$, 14878-31-0; $Fe(CO)_5$, 13463-40-6; $(CH_3)_3SiBr$, 2857-97-8; $H_2C{=}CHOSi(CH_3)_3$, 6213-94-1; (*Z*)-$C_6H_5CH{=}CHOSi(CH_3)_3$, 35449-04-8; propionyl bromide, 598-22-1; phenylacetyl bromide, 22535-03-1; pivaloyl bromide, 27644-18-4.