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Preparation and Alkylation Reactions of $K^+[(CO)_4FeSi(CH_3)_3]^-$; Reductive Elimination of Tetramethylsilane from Isolable $(CO)_4FeRSi(CH_3)_3$ Complexes

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The increasingly recognized unique reactivity modes available to transition metal trialkylsilanes [1] have prompted us to synthesize new organometallic compounds containing the trimethylsilyl group [2]. Objectives include the development of new metal-carbon bond forming reactions, and clarification of the mechanistic steps involved in the catalytic hydrosylation of organic molecules [1]. In this communication, we report (a) the synthesis of a new transition metal anion $K^+[(CO)_4FeSi(CH_3)_3]^-$ (*1*), which can be alkylated to yield isolable $(CO)_4FeRSi(CH_3)_3$ complexes (*2*), and (b) the facile reductive elimination of $RSi(CH_3)_3$ from *2* when R = CH_3 or $CH_2H_6H_5$. The latter event is of particular significance, since the key postulated step in catalytic olefin hydrosilylation – alkyl silane elimination from a $L_nM(R)(SiR_3)$ intermediate [3, 4] – has not previously been directly observed.

When a THF slurry of $K_2^+[(CO)_4Fe]^=$ [5] was reacted for 0.5 hr at 0 °C with 1 equiv. of $(CH_3)_3SiBr$, a new iron silane formed. Ether extraction of the reaction residue yielded a crude product (*ca.* 50%) whose spectral properties (NMR, acetone-d_6: ^1H, δ 0.34; ^{13}C, 221.3, 8.0 ppm. IR (THF, cm^{-1}): 1980 m, 1887 s, 1872 s, 1832 m) suggested it to be $K^+[(CO)_4FeSi(CH_3)_3]^-$ (*1*: Scheme 1). Metathesis with $[(C_6H_5)_3P]_2N^+Cl^-$ (PPN^+Cl^-) afforded white, air stable $PPN^+[(CO)_4FeSi(CH_3)_3]^-$ whose spectral properties were similar to *1* and analytical properties (*Anal.* Calcd. for $C_{43}H_{39}FeNO_4P_2Si$: C, 66.24; H, 5.04; Fe, 7.16; N, 1.80; P, 7.95; Si, 3.60. Found: C, 65.95; H, 5.21; Fe, 6.86; N, 2.02; P, 7.73; Si, 3.24%) unequivocally established its composition. *1* could be independently prepared by treatment of $(CO)_4FeHSi(CH_3)_3$ [6] with KH. Also, the reaction of *1* (petroleum ether slurry) with $(CH_3)_3SiBr$ yielded the known compound $(CO)_4Fe[Si(CH_3)_3]_2$ [7].

Ether slurries of *1* reacted with CH_3SO_3F and $CH_3CH_2SO_3F$ within 2 minutes at 0 °C. After filtra-

TABLE I. Spectroscopic Properties of *cis*-$(CO)_4FeRSi(CH_3)_3$ Complexes Prepared.

R	^1H NMR (δ)	^{13}C NMR^a (ppm)	IR (cm^{-1}, hexane)
CH_3 (*2a*)	0.34 (s, 9H) 0.03 (s, 3H)^{c,d}	210.3, 206.5, 204.8 (CO's)^b 5.5 ($SiCH_3$), –12.7 ($FeCH_3$)^{c,e}	2088 m, 2027 s 2000 vs
CH_2CH_3 (*2b*)	1.31 (m, 3H) 1.13 (m, 2H) 0.33 (s, 9H)^{c,d}	211.1, 206.0, 205.3 (CO's)^b 6.8 ($FeCH_2$–), 5.4 ($SiCH_3$)^{c,e,f}	2086 m, 2023 s, 1997 vs
$CH_2C_6H_5$ (*2c*)	7.28–6.95 (m, 5H) 2.45 (s, 2H) 0.40 (s, 9H)^{e,g}	211.7, 205.6, 202.7 (CO's)^b 150.9, 125.0 (C_6H_5)^e 16.0 ($FeCH_2$–), 5.7 ($SiCH_3$)^{e,g,h}	2085 m, 2028 s, 1998 vs
$CH_2CH{=}CH_2$ (*2d*)	6.57–5.77 (m, 1H) 5.03 (d of m), overlapping with 4.88 (d of d, J = 2, 10 Hz), 2H total 1.86 (d, J = 9 Hz, 2H) 0.37 (s, 9H)^{e,g}	210.7, 205.8, 204.3 (CO's)^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 $CH_3C_6H_5$ 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.

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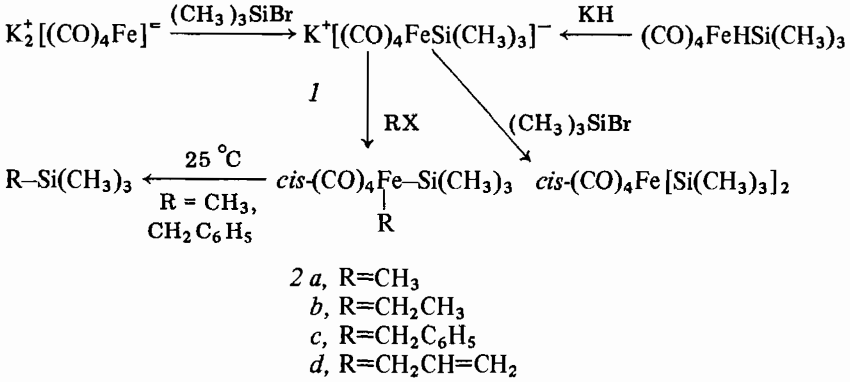

Scheme 1. Formation and Reactions of *1* and *2*.

tion, solvent removal, and distillation at 25 °C and $<10^{-3}$ mm, iron alkyls *2a* and *2b* (Scheme 1) were isolated as colorless liquids in 46 and 56% yields, respectively. Benzyl bromide reacted similarly with *1* (0.5 hr, 25 °C) to yield *2c* (75%). The reaction of allyl bromide with *1* (7 minutes, 25 °C) afforded the iron allyl *2d*, which underwent partial decomposition upon distillation. The spectral properties of *2a–d* (Table I) are in full accord with the assigned structures. In particular, the ^{13}C NMR spectra show three carbonyl absorptions in a 2:1:1 height ratio, as would be expected of non-fluxional *cis* geometric isomers [8].

2a–d are all air sensitive and undergo decomposition at room temperature over periods ranging from 6 hr (*2d*) to 5–6 days (*2c*). The decompositions of *2b* and *2d* are complex and still under study: volatile $RSi(CH_3)_3$ species are not produced in appreciable quantities (<5%), and *2d* does not appear to give rise to a π-allyl $Fe(CO)_3SiR_3$ complex [9]. However, *2a* clearly yields $(CH_3)_4Si$ (identified by ^{1}H NMR and GLC) as the only proton-containing decomposition product and $(CH_3)_3SiCH_2C_6H_5$ is obtained in 63% GLC yield from *2c*; significant amounts (<1%) of bibenzyl are not formed.

The preceding results are noteworthy in several respects. First, osmium homologs of *1* and *2* were prepared in important earlier work by Stone and Knox [10]. However, no observation of $RSi(CH_3)_3$ elimination was reported. Secondly, $Fe(CO)_5$ has been previously demonstrated to be an effective olefin hydrosilylation catalyst precursor [4, 6, 11]. Thus species closely related to *2* may under certain conditions be *bona fide* catalytic intermediates. However, decomposition pathways other than simple reductive elimination are available to $(CO)_4FeRSi(CH_3)_3$ complexes; previously we noted that $(CO)_4Fe[(CH(C_6H_5)OSi(CH_3)_3]Si(CH_3)_3$ undergoes facile iron–carbon bond homolysis at room temperature [1]. Dimerization of resulting stabilized $\cdot[CH(C_6H_5)OSi(CH_3)_3]$ radical occurs. Collman has observed that $(CO)_4FeRR'$ complexes thermally decompose to ketones [12], implying that alkyl group migration to coordinated CO precedes reductive elimination. The fact $Fe(CO)_5$-based olefin hydrosilylation catalysts often afford appreciable quantities of 'abnormal' products such as vinyl silanes may be relevant to these alternative decomposition modes.

In summary, this study has made available two new types of iron–$Si(CH_3)_3$ complexes for which useful applications can be envisioned. Finally, since numerous examples exist of M–H bond addition to olefins [13] and several L_nMHSiR_3 species have been prepared by $HSiR_3$ addition to metals [6, 14] direct precedent now exists for all steps postulated to occur in catalytic olefin hydrosilylation.

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