

A TRIMETHYLSILYL GROUP MIGRATION IN THE CHEMISTRY OF $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SiMe}_3$

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Summary

Reaction of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SiMe}_3$ with either *n*-BuLi or lithium diisopropylamide (LDA) results in a migration of the trimethylsilyl group from iron to the complexed Cp ligand. The resulting $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3\text{Fe}(\text{CO})_2$ anion is readily alkylated to give σ -bonded derivatives. The unique reactivity of the trimethylsilyl system is underscored by comparison with the behavior of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Me}$ under identical conditions. Some chemical transformations of $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3\text{Fe}(\text{CO})_2\text{R}$ derivatives involving migratory insertion and β -hydride abstraction are also reported.

Since the original report of an iron organosilyl compound in 1956 [1], a number of silyl derivatives of iron have been prepared [2–8]. Relatively little is known, however, about the chemical reactivity of the iron–silicon bond. Nucleophilic cleavage of dicarbonylcyclopentadienyliron silyl compounds by alkoxides to give the $\text{CpFe}(\text{CO})_2$ anion ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) has been demonstrated [4,9], and electrophilic cleavage has been observed with reagents such as Cl_2 and HCl [10]. The potential for interesting new chemistry of the iron–silicon

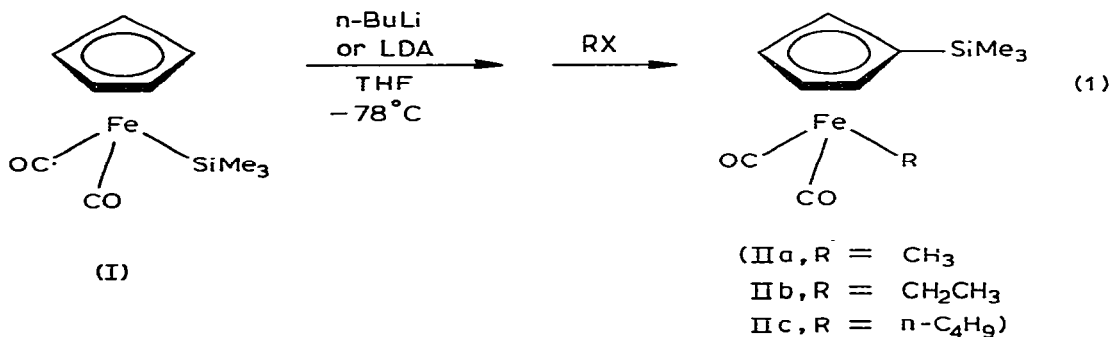


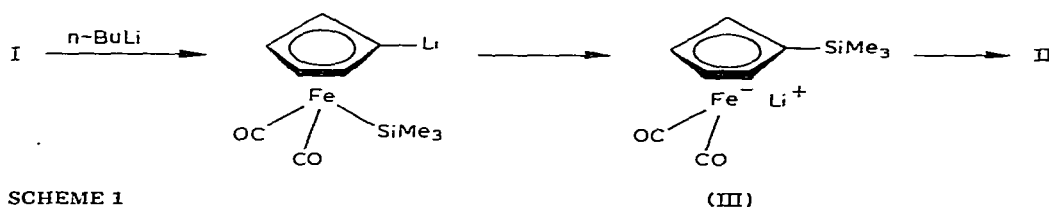
TABLE 1
YIELDS OF $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3\text{Fe(CO)}_2\text{R}$ PRODUCTS (eq. 1)

Product	Alkylating agent R-X	Product yields as function of base (%)	
		LDA	n-BuLi
IIa	MeI	73	95, 57 ^a
IIb	EtBr	74	87
IIc	n-BuBr	79	65 ^a

^a Entire reaction sequence run at 0°C; all others at -78°C.

bond is suggested by the recent report of the reaction of $(\text{CO})_4\text{Fe}[\text{Si}(\text{CH}_3)_3]_2$ with the carbonyl group of benzaldehyde [11].

This paper describes a new reaction of $\text{CpFe(CO)}_2\text{SiMe}_3$ (I) discovered while examining the possibility of ring metalation of dicarbonylcyclopentadienyliron derivatives. As shown in eq. 1, treatment of I at -78°C in THF with either n-BuLi or lithium diisopropylamide (LDA) followed by alkylation at -78°C gives products IIa-IIIc which are the result of a trimethylsilyl migration from iron to the bonded cyclopentadienyl ligand. Compounds IIa-IIIc are air-sensitive yellow liquids whose spectroscopic properties* are consistent with the presence of a $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ ligand and an alkyl group σ -bonded to iron. Typical yields of alkylated products IIa-IIIc are given in Table 1. A possible mechanism for the rearrangement is suggested in Scheme 1. The same type of mechanism has been advanced to explain a migration of the triphenylgermyl group from metal to cyclopentadienyl ligand observed when $\text{CpM(CO)}_3\text{GePh}_3$ (M = Mo, W) is treated with alkyllithium reagents [12].



SCHEME 1

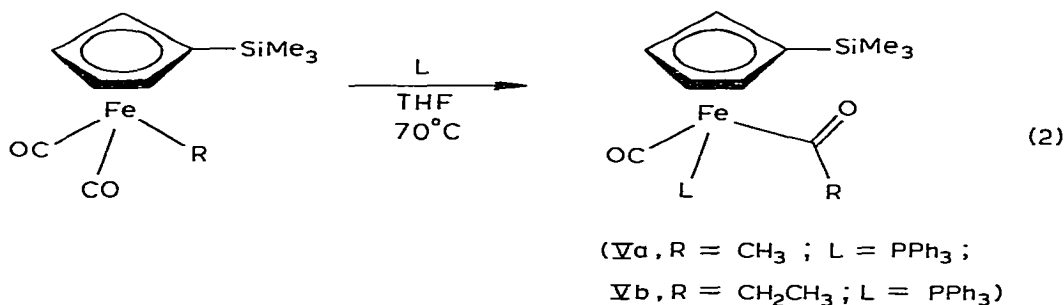
Reactions involving base-induced migrations of organosilyl groups are well known [13], but the one reported here is the first example in which the organosilyl group is bonded to a transition metal. Anion III has been identified by IR spectroscopy as an intermediate in the conversion of I to II. An infrared spectrum of the reaction mixture several minutes after n-BuLi is added dropwise to a THF solution of I at -78°C shows four intense carbonyl bands at 1875, 1861, 1806, and 1743 cm^{-1} . The bands at 1861 and 1743 cm^{-1} may be

* IIa IR(CHCl_3): 1991, 1937 cm^{-1} , NMR(CS_2): δ 4.67-4.90 (m, 4, Cp), 0.31 (s, 9, SiMe_3), 0.18 ppm (s, 3, CH_3). IIb IR(CHCl_3): 1993, 1937 cm^{-1} , NMR(CS_2): δ 4.63-4.82 (m, 4, Cp), 1.03-1.84 (12 lines, 5, CH_2CH_3), 0.29 ppm (s, 9, SiMe_3), MS m/e 278 (M^+), 250 ($M^+ - \text{CO}$), 222 ($M^+ - 2 \text{CO}$), 194 ($M^+ - 2 \text{CO} - \text{C}_2\text{H}_4$). IIc IR(CHCl_3): 1987, 1929 cm^{-1} , NMR(CS_2): δ 4.64-4.88 (m, 4, Cp), 1.46 (m, CH_2) 0.91 (m, CH_3), 0.27 ppm (s, 9, SiMe_3), MS m/e 306 (M^+), 278 ($M^+ - \text{CO}$), 250 ($M^+ - 2 \text{CO}$ or $M^+ - \text{C}_4\text{H}_8$), 249 ($M^+ - \text{C}_4\text{H}_9$), 194 ($M^+ - 2 \text{CO} - \text{C}_4\text{H}_8$).

assigned to a carbonyl-bridged ion pair and those at 1875 and 1806 cm^{-1} to a tight ion pair, following the interpretation of the almost identical spectrum of $\text{CpFe}(\text{CO})_2\text{Li}$ [14]. The absence of other bands in the carbonyl portion of the spectrum indicates a rapid and complete trimethylsilyl rearrangement. Formation of the stable, coordinatively saturated 18-electron anion III may provide the driving force for the rearrangement. The alkylation of III parallels the well-established chemistry of the $\text{CpFe}(\text{CO})_2$ anion [14].

The detailed mechanism of the reported reaction is currently under investigation, but the unique reactivity of the iron silyl compound I is emphasized by comparison with the behavior of $\text{CpFe}(\text{CO})_2\text{Me}$ (IV) under the same conditions. When IV in THF solution at -78°C is treated with one equivalent of *n*-BuLi followed by ethyl bromide, the tractable portion of the product (accounting for about 30% of the Fe atoms in the starting material) consists of $\text{CpFe}(\text{CO})_2\text{Et}$, IV, and ferrocene in a 4 : 3 : 1 ratio*. Both $\text{CpFe}(\text{CO})_2\text{Et}$ and ferrocene are probably products of electron transfer processes, as is the polymeric non-carbonyl material which makes up the bulk of the reaction product.

Compounds IIa and IIb undergo chemical reactions typical of $\text{CpFe}(\text{CO})_2\text{R}$ (R = alkyl) derivatives. Migratory insertion of a carbonyl ligand is a well-known process [16]. The formation of metal acyl complexes Va (NMR(CDCl_3): δ 7.41 (m, Ph), 4.08–4.68 (m, Cp), 2.21 (s, CH_3), 0.32 ppm (s, SiMe_3); Anal. Found: C, 66.04; H, 5.85. $\text{C}_{29}\text{H}_{31}\text{O}_2\text{PSiFe}$ calcd: C, 66.16; H, 5.93%) and Vb (IR-(CH_2Cl_2): 1905, 1592 cm^{-1} ; Anal. Found: C, 66.17; H, 6.09. $\text{C}_{30}\text{H}_{33}\text{O}_2\text{PSiFe}$ calcd: C, 66.67; H, 6.15%) by migratory insertion is shown in eq. 2 (20% excess of phosphorus ligand, 72 h, 60–70% yield).

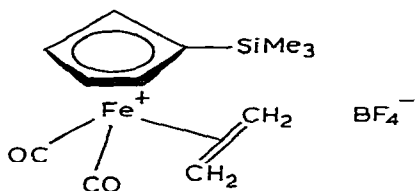


Another transformation characteristic of the $\text{CpFe}(\text{CO})_2\text{R}$ system is elimination of a β -hydride to give a cationic olefin complex [17]. When IIb is allowed to react with trityl fluoroborate (CHCl_3 , 0°C , 1.5 h) the ethylene π -complex VI is formed in 68% yield (IR(CH_3CN): 2077, 2040 cm^{-1} ; NMR (acetone- d_6) δ 5.99 (s, Cp), 3.97 (s, vinyl), 0.48 ppm (s, SiMe_3); Anal. Found: C, 39.32; H, 4.84. $\text{C}_{12}\text{H}_{17}\text{BF}_4\text{O}_2\text{SiFe}$ calcd.: C, 39.59; H, 4.71%).

The reaction reported here is the first example of a base-induced silyl rearrangement involving a compound with a transition metal to silicon bond. Additional work in progress is focusing on the mechanism of the rearrangement and

* These three compounds are eluted together by chromatography of the crude reaction product on Florisil; the ratio is determined by integration of the NMR spectrum and is reproducible to $\pm 3\%$ in different experiments. The remainder of the reaction product is a dark, viscous, polymeric material whose IR spectrum shows no significant carbonyl absorptions.

extension of this chemistry to other cyclopentadienyliron triorganosilyl compounds.



(VI)

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