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Thermal and Photochemical Properties of [(1-Heptamethyltrisilyl)methyl]iron and [(2-Heptamethyltrisilyl)methyl]iron Complexes $(\eta^5\text{-L})Fe(CO)_2CH_2Si_3Me_7$ ($L = C_5H_5, C_5Me_5, C_9H_7$)[1]

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[(1-Heptamethyltrisilyl)methyl]iron and [(2-heptamethyltrisilyl)methyl]iron complexes $(\eta^5\text{-L})Fe(CO)_2CH_2Si_3Me_7$ have been synthesized from 1-(chloromethyl)-1,1,2,2,3,3,3-heptamethyltrisilane and 2-(chloromethyl)-1,1,1,2,3,3,3-heptamethyltrisilane and the iron carbonylate complexes $[(\eta^5\text{-L})Fe(CO)_2]^-Na^+$ (L = cyclopentadienyl (Cp), pentamethylcyclopentadienyl (Cp*), indenyl (Ind)). Photochemical treatment of the (1-heptamethyltrisilyl)methyl complexes yielded chain-rearranged products $(\eta^5\text{-L})Fe(CO)_2$–$SiMe_2CH_2SiMe_2SiMe_3$. Photochemical treatment of the isomeric [(2-heptamethyltrisilyl)methyl]iron complexes results in different chemistry due to the initial formation of a complex containing the grouping Fe–Si–Si. Such complexes undergo Si–Si bond cleavage and elimination of an SiR_2 fragment; thus the complexes isolated from photolysis of $(\eta^5\text{-L})Fe(CO)_2CH_2SiMe(SiMe_3)_2$ are a mixture of $(\eta^5\text{-L})Fe(CO)_2SiMe_3$ and $(\eta^5\text{-L})Fe(CO)_2SiMe_2CH_2SiMe_3$, resulting from the elimination of $MeSiCH_2SiMe_3$ and $SiMe_2$, respectively. The thermal stability in refluxing hexane of the (1-heptamethyltrisilyl)methyl complexes varied depending on the η^5-L ligand, with the stability being Cp ≫ Cp* ≫ Ind: Cp, no reaction; Cp*, formation of $[(\eta^5\text{-Cp})^*Fe(CO)_2]_2$; Ind, chain rearrangement. The photochemical reaction of $(\eta^5\text{-Cp})Fe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$ in the presence of PPh_3 resulted in the initial formation of an unstable phosphine-substituted intermediate $CpFe(CO)(PPh_3)CH_2SiMe_2SiMe_2SiMe_3$, which rearranged photochemically and/or thermally to $CpFe(CO)(PPh_3)SiMe_2CH_2SiMe_2SiMe_3$. The thermal reaction of $(\eta^5\text{-L})Fe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$ (L = Cp, Ind) in the presence of PPh_3 gave $LFe(CO)(PPh_3)COCH_2SiMe_2SiMe_2SiMe_3$, which photochemically or thermally decarbonylated to give $LFe(CO)(PPh_3)SiMe_2CH_2SiMe_2SiMe_3$.

Introduction

A large number of (trimethylsilyl)methyl and bis(trimethylsilyl)methyl transition-metal complexes are known, due primarily to their stability imposed by lack of suitable low-energy decomposition pathways.[2,3] This feature may be partially attributed to the absence of β-hydrogen elimination since the silylmethyl groups have no labile hydrogen atoms. On the other hand, (dimethylsilyl)methyl complexes, $LMCH_2SiMe_2H$, have been shown to rearrange rapidly via silene metal hydrides to form trimethylsilyl–metal complexes.[4,5]

Despite the many monosilylmethyl–metal complexes, only a handful of higher homologs are reported which contain Si–Si bonds.[6] Thus, (pentamethyldisilyl)methyl complexes, $LM\text{–}CH_2SiMe_2SiMe_3$, are known where LM = $(\eta^5\text{-L})Fe(CO)_2$ ($L = C_5H_5$ (Fp), C_5Me_5, C_9H_7), $(\eta^5\text{-}C_5H_5)W(CO)_3$, and $(\eta^5\text{-}C_5H_5)_2MCl$ (M = Ti, Zr, Hf). Such complexes have the potentially labile Me_3Si group in the β-position with respect to the metal center, and the cyclopentadienyl metal carbonyl complexes exhibit a facile rearrangement to $LM\text{–}SiMe_2CH_2SiMe_3$ complexes (eq 1). A

$$FpCH_2SiMe_2SiMe_3 \xrightarrow{h\nu} FpSiMe_2CH_2SiMe_3 \quad (1)$$

similar skeletal rearrangement occurs when these same complexes are treated with a base, and the disilylmethyl group migrates, with rearrangement, to the cyclopentadienyl ring (eq 2).[7]

$$FpCH_2SiMe_2SiMe_3 \xrightarrow{(1)\ \text{LDA}\ (2)\ \text{MeI}} Me_3SiCH_2SiMe_2\text{–}Fe(CO)_2CH_3 \quad (2)$$

Recently, we developed a new general synthetic route for the formation of (chloromethyl)oligosilanes, and have initiated an investigation into the chemistry of such systems, including their transition-metal derivatives.[8] We now wish to report the syntheses and chemical transformations of [(1-heptamethyltrisilyl)methyl]iron and [(2-heptamethyltrisilyl)methyl]iron complexes using the reaction between 1- and $2\text{-}ClCH_2Si_3Me_7$ and $[(\eta^5\text{-L})Fe(CO)_2]^-Na^+$ ($L = C_5H_5, C_5Me_5, C_9H_7$ (indenyl)).

Results and Discussion

The reactions between 1- and 2-(chloromethyl)heptamethyltrisilanes and the various $[(\eta^5\text{-L})Fe(CO)_2]^-Na^+$ salts ($L = C_5H_5, C_5Me_5, C_9H_7$) yielded moderate to good yields of the corresponding (trisilylmethyl)iron complexes (eq 3). An exception was our inability to synthesize $(\eta^5\text{-}C_9H_7)Fe(CO)_2CH_2SiMe(SiMe_3)_2$.

$$[(\eta^5\text{-L})Fe(CO)_2]^-Na^+ \xrightarrow{ClCH_2(SiMe_2)_2SiMe_3} (\eta^5\text{-L})Fe(CO)_2CH_2(SiMe_2)_2SiMe_3 \quad (3a)$$

$$[(\eta^5\text{-L})Fe(CO)_2]^-Na^+ \xrightarrow{ClCH_2SiMe(SiMe_3)_2} (\eta^5\text{-L})Fe(CO)_2CH_2SiMe(SiMe_3)_2 \quad (3b)$$

$L = C_5H_5$ (Cp), C_5Me_5 (Cp*), C_9H_7 (Ind, 3a only)

The spectroscopic data for the new complexes are recorded in Table I and are in accord with the proposed structures. The ^{29}Si NMR data show the expected chem-

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ical shifts previously observed for oligosilyl metal derivatives,[9] with significant low-field shifts compared to the totally permethylated oligosilanes for the Si atom β with respect to the Fe atom, but little or no shifts for the Si atoms in γ- and δ-positions.

Thermal and Photochemical Stability. The thermal stability of the [(1-heptamethyltrisilyl)methyl]iron complexes was examined under reflux conditions in hexane. The reactivity varied depending upon the η^5-ligand, as noted in eqs 4–6.

$$\mathrm{CpFe(CO)_2CH_2SiMe_2SiMe_2SiMe_3} \rightarrow \text{no reaction} \quad (4)$$

$$\mathrm{Cp^*Fe(CO)_2CH_2SiMe_2SiMe_2SiMe_3} \rightarrow \mathrm{[Cp^*Fe(CO)_2]_2} \quad (5)$$

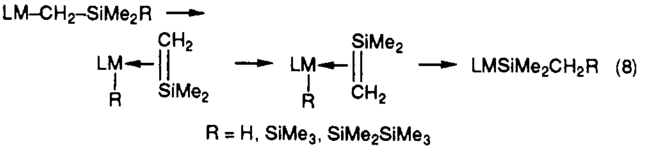
$$\mathrm{IndFe(CO)_2CH_2SiMe_2SiMe_2SiMe_3} \rightarrow \mathrm{IndFe(CO)_2SiMe_2CH_2SiMe_2SiMe_3} \quad (6)$$

This pattern is similar to the behavior of the related disilylmethyl complexes $\mathrm{LMCH_2SiMe_2SiMe_3}$,[6b] with facile rearrangement of the indenyl complex, stability of the cyclopentadienyl complex, and cleavage of the Fe–C bond for the bulky pentamethylcyclopentadienyl complex. The skeletal rearrangement observed for the indenyl complex (eq 6) was effected in high yield for all the (1-heptamethyltrisilyl)methyl complexes via photochemical irradiation in hydrocarbon solvents (eq 7).

$$(\eta^5\text{-L})\mathrm{Fe(CO)_2CH_2SiMe_2SiMe_2SiMe_3} \xrightarrow{h\nu} (\eta^5\text{-L})\mathrm{Fe(CO)_2SiMe_2CH_2SiMe_2SiMe_3} \quad (7)$$

$$\mathrm{L} = \mathrm{C_5H_5, C_5Me_5, C_9H_7}$$

The thermal/photochemical rearrangement is analogous to those reported for the $\mathrm{LMCH_2SiMe_2SiMe_3}$ complexes noted in the Introduction and may be assumed to proceed via a similar mechanism. The suggested mechanism is related to that determined for the transformation of (dimethylsilyl)methyl complexes to trimethylsilyl complexes [eq 8 (R = H)].[4,5]



$$\mathrm{LM{-}CH_2{-}SiMe_2R} \longrightarrow \mathrm{LM}\!\leftarrow\!\underset{\mathrm{R}}{}\overset{\mathrm{CH_2}}{\underset{\mathrm{SiMe_2}}{\|}} \longrightarrow \mathrm{LM}\!\leftarrow\!\underset{\mathrm{R}}{}\overset{\mathrm{SiMe_2}}{\underset{\mathrm{CH_2}}{\|}} \longrightarrow \mathrm{LMSiMe_2CH_2R} \quad (8)$$

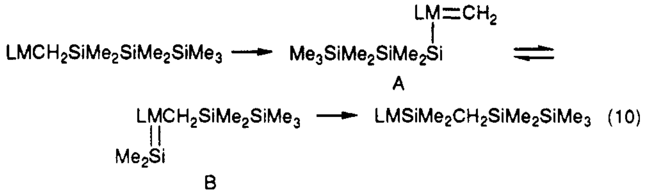
$$\mathrm{R = H, SiMe_3, SiMe_2SiMe_3}$$

The driving force of this reaction is scission of the weak Si—Si or Si—H bond coupled to the stability of the silene intermediate. Recently, related silene complexes of the transition metals have been isolated and completely characterized, including single-crystal X-ray analysis, by both the Berry and Tilley groups.[11,12] A report by Thompson and Young on the thermal rearrangement of [bis(trimethylsilyl)methyl]platinum complexes also proposed intermediacy of η^2-silene complexes formed by a β-elimination process (eq 9).[13] The facile rotation of

$$\mathrm{(R_3P)_2Pt(CH_2SiMe_3)_2} \xrightarrow{\Delta,\,-\mathrm{PR_3}} \mathrm{(R_3P)Pt(Me)(CH_2SiMe_3)(CH_2{=}SiMe_2)} \xrightarrow{\mathrm{R_3P}} \mathrm{(R_3P)_2Pt(Me)(CH_2SiMe_2CH_2SiMe_3)} \quad (9)$$

alkenemetal complexes about the metal–alkene bond is well established in a variety of systems.[14] Examples include the closely related $(\eta^5\text{-C}_5\text{H}_5)\mathrm{Fe(CO)(CH_2{=}CH_2)SnR_3}$ complexes (R = Ph, Me) and a series of cationic $[\mathrm{Fp(CR_2{=}CR_2)}]^+$ complexes. The barriers to such rotations are in the 8–14 kcal/mol range.[15]

A second more complex process was also considered and indeed has merit, as pointed out by a referee. Such a scheme involves α-silyl migration followed by a 1,3-Si shift and final migration of a silylalkyl group back to silicon (eq 10).



$$\mathrm{LMCH_2SiMe_2SiMe_2SiMe_3} \longrightarrow \underset{\mathbf{A}}{\mathrm{Me_3SiMe_2SiMe_2}\overset{\mathrm{LM{=}CH_2}}{\overset{|}{\mathrm{Si}}}} \rightleftharpoons \underset{\mathbf{B}}{\underset{\mathrm{Me_2Si}}{\underset{\|}{\mathrm{LM}}}\mathrm{CH_2SiMe_2SiMe_3}} \longrightarrow \mathrm{LMSiMe_2CH_2SiMe_2SiMe_3} \quad (10)$$

A positive aspect of this mechanism is that all species are well established and 1,3-silyl and 1,3-alkyl shifts in the oligosilyl Fp systems are now well accepted. However, a drawback is the fact that, as noted in the Fp–oligosilane chemistry for $\mathrm{Fp(SiMe_2)_nMe}$ (n = 2, 3), we might reasonably expect loss of the $\mathrm{Me_2Si}$ group in intermediate B leading to $\mathrm{FpCH_2SiMe_2SiMe_3}$ and thus eventually $\mathrm{FpSiMe_2CH_2SiMe_3}$. No such complex was observed during the course of the reaction to the extent of <1%. Similarly, one might also expect loss of methylene to yield $\mathrm{Fp(SiMe_2)_3Me}$ with further degradation to $\mathrm{FpSiMe_3}$ via $\mathrm{FpSiMe_2SiMe_3}$ and $\mathrm{FpSiMe(SiMe_3)_2}$ and methyl migration from Si to the carbene in intermediate A to yield ethyl groups. No complexes derived from such chemistry were observed during the course of the reactions studied. On the basis of all the evidence we have obtained thus far in our continuing studies on these and related systems, coupled with application of Occam's Razor, we presently favor the mechanism outlined in eq 8.

Prolonged photolysis of $\mathrm{CpFe(CO)_2CH_2SiMe_2SiMe_2SiMe_3}$ in the presence of $\mathrm{PPh_3}$ yielded $\mathrm{CpFe(CO)(PPh_3)SiMe_2CH_2SiMe_2SiMe_3}$ in high yield. However, close monitoring of this reaction by infrared spectroscopy revealed that the initial photoproduct was $\mathrm{CpFe(CO)(PPh_3)CH_2SiMe_2SiMe_2SiMe_3}$. This complex could be isolated in approximately 80% purity, mixed with $\mathrm{CpFe(CO)(PPh_3)SiMe_2CH_2SiMe_2SiMe_3}$; however, thermal or photochemical treatment of this mixture led to the formation of the rearranged phosphine substitution product. The rearrangement also occurred slowly at room temperature. It has been shown that photochemical substitution of carbon monoxide in $\mathrm{FpCH_2SiMe_3}$ by $\mathrm{PPh_3}$ produced $\mathrm{CpFe(CO)(PPh_3)CH_2SiMe_3}$; thus these new results suggest that after primary photodissociation of the CO ligand, subsequent coordination of $\mathrm{PPh_3}$ to the vacant site is a very

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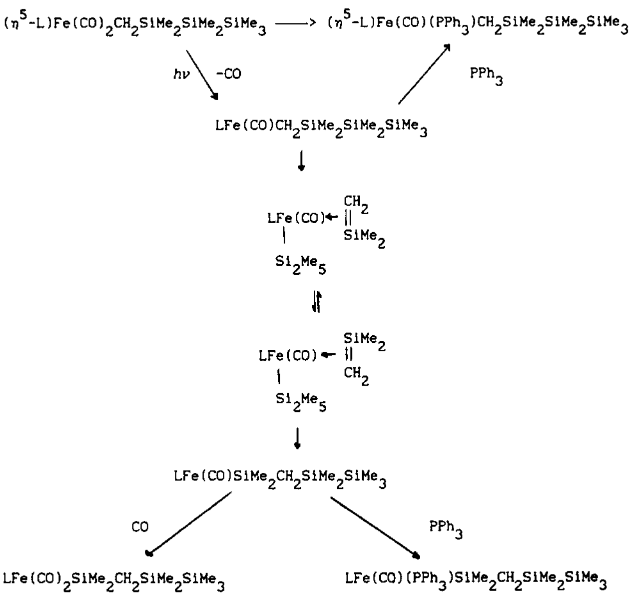
Table I. Spectroscopic and Analytical Data for New Complexes[a]

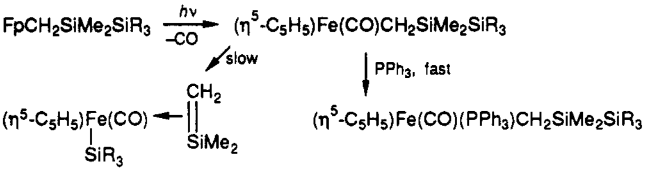
	$\mathrm{CpFe(CO)_2CH_2SiMe_2SiMe_2SiMe_3}$ (Orange Oil)
^{1}H	−0.16 ($\mathrm{CH_2}$), 0.14 (broad, 7 Me), 4.24 (Cp)
^{13}C	−24.19 ($\mathrm{CH_2}$), −6.17, −0.92, 0.47 (Me), 84.82 (Cp), 217.70 (CO)
^{29}Si	−48.01 (Si–*Si*$\mathrm{Me_2}$–Si), −16.14 ($\mathrm{SiMe_3}$), −3.31 ($\mathrm{SiMe_2CH_2}$)
ν(CO)	2010.6, 1959.0
	Anal. Calcd: C, 47.35; H, 7.42. Found: C, 46.67; H, 7.59
	$\mathrm{CpFe(CO)_2SiMe_2CH_2SiMe_2SiMe_3}$ (Orange Oil)
^{1}H	0.16 ($\mathrm{SiMe_3}$), 0.27 ($\mathrm{SiMe_2}$), 0.30 ($\mathrm{CH_2}$), 0.59 ($\mathrm{SiMe_2}$), 4.08 (Cp)
^{29}Si	−19.48, −18.14 ($\mathrm{SiMe_2SiMe_3}$), 44.09 (Fe–$\mathrm{SiMe_2}$)
ν(CO)	1996.1, 1943.3
	Anal. Calcd: C, 47.35; H, 7.42. Found: C, 47.46; H, 7.55
	$\mathrm{CpFe(CO)(PPh_3)CH_2SiMe_2SiMe_2SiMe_3}$ (Waxy Solid (Purity 80%))
^{1}H	0.1–0.5 (7 Me, $\mathrm{CH_2}$), 4.20 (Cp), 7.0–7.6 (Ph)
^{29}Si	−49.43 ($\mathrm{SiSiMe_2Si}$), −16.21 ($\mathrm{SiMe_3}$), −2.89 ($\mathrm{SiMe_2CH_2}$, $J_{\mathrm{Si-P}}$ = 5.0 Hz)
ν(CO)	1913.6
	$\mathrm{CpFe(CO)(PPh_3)SiMe_2CH_2SiMe_2SiMe_3}$ (Orange Oil)
^{1}H	0.16 ($\mathrm{SiMe_3}$), 0.21 ($\mathrm{CH_2}$), 0.23 ($\mathrm{SiMe_2}$), 0.42 ($\mathrm{SiMe_2}$), 4.06 (Cp), 7.0–7.8 (Ph)
^{29}Si	−19.58, −18.20 ($\mathrm{SiMe_2SiMe_3}$), 38.77 (Fe–$\mathrm{SiMe_2}$, $J_{\mathrm{Si-P}}$ = 29.6 Hz)
ν(CO)	1910.2
	Anal. Calcd: C, 62.53; H, 7.04. Found: C, 62.64; H, 6.93
	$\mathrm{Cp^*Fe(CO)_2CH_2SiMe_2SiMe_2SiMe_3}$ (Orange Oil)
^{1}H*	1.67 ($\mathrm{Me_5}$), 0.03 (broad, 7 Me), −0.70 ($\mathrm{CH_2}$)
^{13}C*	219.88 (CO), 95.54 ($\mathrm{C_5}$), 9.84 ($\mathrm{Me_5}$), 0.07, −0.81, −6.14 (Me), −13.24 ($\mathrm{CH_2}$)
^{29}Si*	−48.78 (Si–*Si*–Si), −16.05 ($\mathrm{SiMe_3}$), −5.08 ($\mathrm{SiCH_2}$) [($\mathrm{C_6D_6}$) −48.72 (Si–*Si*–Si), −16.14 ($\mathrm{SiMe_3}$), −5.03 ($\mathrm{SiCH_2}$)]
ν(CO)	1988.3, 1935.5
	Anal. Calcd: C, 53.31; H, 8.50. Found: C, 53.27; H, 8.67
	$\mathrm{CpFe(CO)(PPh_3)COCH_2SiMe_2SiMe_2SiMe_3}$ (Yellow Solid, Mp 140.0–141.2 °C)
^{1}H	0.17, 0.34 (broad, Me), 2.22, 3.08 ($\mathrm{CH_AH_B}$, d, $J_{\mathrm{H_AH_B}}$ = 11.0 Hz), 4.35 (Cp), 7.0–8.0 (Ph), 8.0 (Ph)
^{29}Si	−47.76 (Si–*Si*–Si), −16.64, −16.12 (*Si*–Si–*Si*)
^{13}C	−6.41 (Si–*Si*$\mathit{Me_2}$–Si), −2.05 (*SiMe*–$\mathrm{CH_2}$), −1.68 (*SiMe*–$\mathrm{CH_2}$), −0.94 ($\mathrm{SiMe_3}$), 57.0 (d, J_{CP} = 6.2 Hz, $\mathrm{CH_2}$), 86.5 (Cp), 128.4, 129.9, 134.1 (d, J_{CP} = 9.4 Hz), 137.3 (d, J_{CP} = 42.1 Hz), 221.6 (d, J_{CP} = 31.3 Hz, CO), 231.2 (d, J_{CP} = 23.0 Hz, CO)
ν(CO)	1922.2, 1586.5
	Anal. Calcd: C, 61.67; H, 6.73. Found: C, 61.48; H, 6.95
	$\mathrm{Cp^*Fe(CO)_2SiMe_2CH_2SiMe_2SiMe_3}$ (Orange Waxy Solid)
^{1}H	1.56 ($\mathrm{Me_5}$), 0.62, 0.29, 0.16 ($\mathrm{CH_3}$) ($\mathrm{CH_2}$ hidden)
^{13}C	218.34 (CO), 94.67 ($\mathrm{C_5}$), 9.99 ($\mathrm{Me_5}$), 7.96, 7.90, −0.71, −1.89 (Me, $\mathrm{CH_2}$)
^{29}Si	−19.58, −17.77 ($\mathrm{SiMe_2SiMe_3}$), 44.14 (Fe–$\mathrm{SiMe_2}$)
ν(CO)	1978.0, 1925.2
	Anal. Calcd: C, 53.31; H, 8.50. Found: C, 53.26; H, 8.60
	$\mathrm{IndFe(CO)_2SiMe_2CH_2SiMe_2SiMe_3}$ (Yellow Crystalline Solid)
^{1}H	7.15, 6.86, 4.42 (η^5-$\mathrm{C_9H_7}$), 0.58, 0.35, 0.27, 0.17 (Me and $\mathrm{CH_2}$)
^{13}C	215.55 (CO), 126.75, 124.34, 105.84, 92.87, 72.28 (η^5-$\mathrm{C_9H_7}$), 9.73, 8.85, −0.71, −1.89 (Me and $\mathrm{CH_2}$)
^{29}Si	50.28 (Fe–Si), −18.11, −19.45 ($\mathrm{SiMe_2SiMe_3}$)
ν(CO)	1993.3, 1941.8
	Anal. Calcd: C, 53.00; H, 7.02. Found: C, 51.87; H, 7.59
	$\mathrm{CpFe(CO)_2CH_2SiMe(SiMe_3)_2}$ (Orange Oil)
^{1}H	−0.02 ($\mathrm{CH_2}$), 0.18 ($\mathrm{SiMe_3}$), 0.24 (SiMe), 4.22 (Cp)
^{13}C	−29.85 ($\mathrm{CH_2}$), −4.15 (SiMe), −0.22 ($\mathrm{SiMe_3}$), 85.29 (Cp), 217.97 (CO)
^{29}Si	−32.36 (SiMe), −16.70 ($\mathrm{SiMe_3}$)
ν(CO)	2009.8, 1958.2
	Anal. Calcd: C, 47.35; H, 7.42. Found: C, 46.08; H, 7.12
	$\mathrm{IndFe(CO)(PPh_3)}$-CO-$\mathrm{CH_2SiMe_2SiMe_2SiMe_3}$ (Orange Solid)
^{1}H	−0.10, −0.01, 0.25 ($\mathrm{SiMe_2SiMe_2SiMe_3}$), 1.53, 2.66 ($\mathrm{CH_AH_B}$, d, $J_{\mathrm{H_AH_B}}$ = 12.5 Hz), 4.57, 4.97, 5.10, 6.07, 6.71, 6.9–7.6 (Ind and Ph)
^{13}C	−6.48 (Si–$\mathrm{SiMe_2}$–Si), −2.03, −1.75 (*Si*$\mathit{Me_2}$–$\mathrm{CH_2}$), −1.01 ($\mathrm{SiMe_3}$), 56.22 ($\mathrm{CH_2}$, d, J_{PC} = 6.6 Hz), 66.57, 79.99, 103.29, 105.84, 111.46, 122.7, 125.57, 126.49, 127.89, 129.81, 134.36 (d, J_{PC} = 10.5 Hz), 135.95 (d, J_{PC} = 41.8 Hz), 221.82 (CO, d, J_{PC} = 24.8 Hz), 232.50 (CO, d, J_{PC} = 22.1 Hz)
^{29}Si*	−48.11 (Si–*Si*–Si), −16.09, −15.78 (*Si*–Si–*Si*)
ν(CO)	1921.9, 1594.0
	Anal. Calcd: C, 64.14; H, 6.55. Found: C, 64.73; H, 6.41
	$\mathrm{IndFe(CO)(PPh_3)SiMe_2CH_2SiMe_2SiMe_3}$ (Red Solid)
^{1}H	0.10, 0.26, 0.29, 0.57 (Me and $\mathrm{CH_2}$), 3.77, 4.43, 4.96, 6.38–7.24 (Ind and Ph)
^{29}Si	−19.40, −18.03 ($\mathrm{SiMe_2SiMe_3}$), 45.13 (Fe–Si, d, J_{PSi} = 30.3 Hz)
ν(CO)	1910.5
	Anal. Calcd: C, 65.04; H, 6.82. Found: C, 65.20; H, 6.91
	$\mathrm{Cp^*Fe(CO)_2CH_2SiMe(SiMe_3)_2}$ (Yellow-Orange Oil)
^{1}H	−0.43 ($\mathrm{CH_2}$), 0.26 ($\mathrm{SiMe_3}$), 0.37 (SiMe), 1.42 ($\mathrm{Me_5}$)
^{13}C	−19.2 ($\mathrm{CH_2}$), −4.22 (SiMe), −0.27 ($\mathrm{SiMe_3}$), 9.28 ($\mathrm{Me_5}$), 95.2 ($\mathrm{C_5}$), 220.0 (CO)
^{29}Si	−33.64 (Si–*Si*–Si), −16.71 (*Si*–Si–*Si*)
ν(CO)	1988.1, 1935.2
	Anal. Calcd: C, 53.31; H, 8.50. Found: C, 52.80; H, 8.43
	Mixture of $\mathrm{IndFe(CO)_2CH_2SiMe_2SiMe_2SiMe_3}$[b] and $\mathrm{IndFe(CO)_2SiMe_2CH_2SiMe_2SiMe_3}$
^{29}Si	50.4, (−4.2), (−16.1), −18.1, −19.4, (−48.44)
ν(CO)	(2006.1), 1993.3, (1953.7), 1941.7

[a] NMR spectra (δ, ppm) recorded in $\mathrm{C_6D_6}$ unless noted by an asterisk which refers to spectra recorded in $\mathrm{CDCl_3}$; IR (cm^{-1}) spectra recorded in hexane. [b] Data in parentheses.

Scheme I. Photochemical Rearrangement of $LFe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$



rapid process compared to the formation of silene intermediates required for the rearrangement process.



The fact that thermal treatment of $CpFe(CO)(PPh_3)CH_2SiMe_2SiMe_2SiMe_3$ produces a skeletal rearrangement to $CpFe(CO)(PPh_3)SiMe_2CH_2SiMe_2SiMe_3$, whereas $FpCH_2SiMe_2SiMe_2SiMe_3$ does not, further illustrates the need for initial ligand expulsion to form a 16e$^-$ intermediate prior to silyl migration to form the silene intermediate. Thermal elimination of PPh_3 from such systems is well established whereas only photochemical elimination of CO has been previously observed. The overall process is illustrated in Scheme I.

Photochemical treatment of the (2-heptamethyltrisilyl)methyl complexes, $(\eta^5\text{-L})Fe(CO)_2CH_2SiMe(SiMe_3)_2$ ($L = C_5H_5$, C_5Me_5) resulted in markedly different chemistry (eq 11).

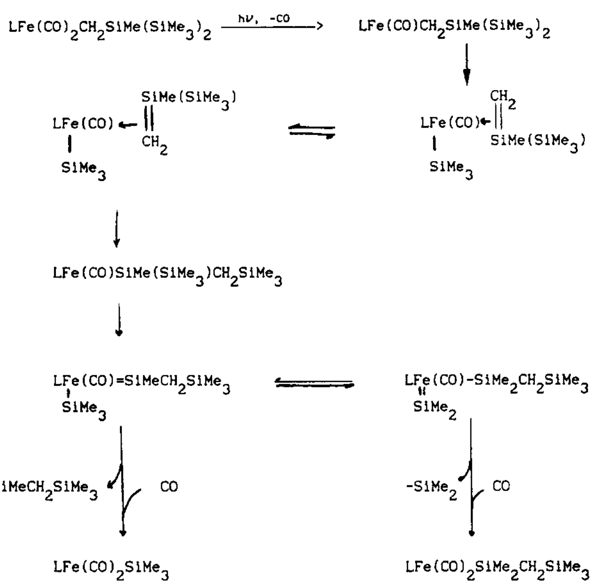
$$\mathrm{Fp{-}CH_2SiMe(SiMe_3)_2 \xrightarrow{h\nu} FpSiMe_3 + FpSiMe_2CH_2SiMe_3} \qquad (11)$$

This difference in chemistry is in accord with our studies on the photochemical properties of oligosilanes directly bonded to the Fp system via a Fe–Si bond, Scheme II.[9]

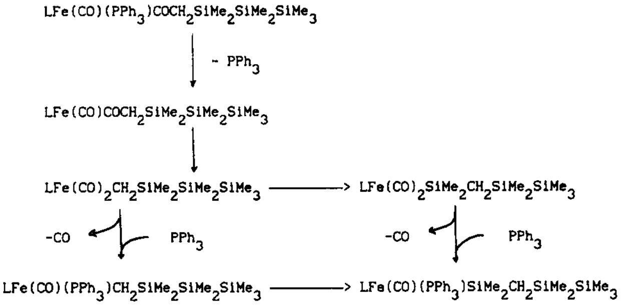
The key step in distinguishing the two types of chemistry exhibited by the Fp–CH_2–trisilanes is the initial formation of the $FpSiMe(SiMe_3)CH_2SiMe_3$ complex from $FpCH_2SiMe(SiMe_3)_2$ via the silylmethyl rearrangement. This product contains the Fe–Si–Si grouping which, as previously noted, photoeliminates the elements of a silylene fragment.[9] In the present case this results in either elimination of $SiMe_2$ to form $FpSiMe_2CH_2SiMe_3$ or elimination of $MeSiCH_2SiMe_3$ to form $FpSiMe_3$. As noted from the results, both processes occur; however, we cannot observe any selectivity between elimination of $SiMe_2$ or $MeSiCH_2SiMe_3$ since the ratio for the two group losses are 40:60 and 60:40 for the Fp and Fp* complexes, respectively.

Overall the photochemistry of the two trisilanes is an interesting example of the potential of the Fp type of substituent to discriminate between two isomeric positions in an oligosilane. This aspect will be the subject of future studies.

Scheme II. Photochemistry of $LFe(CO)_2CH_2SiMe(SiMe_3)_2$



Scheme III. Decarbonylation of Acyl Complexes $LFe(CO)(PPh_3)COCH_2SiMe_2SiMe_2SiMe_3$



Thermal Reaction of $(\eta^5\text{-L})Fe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$ with PPh_3. A CO insertion reaction occurred when $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$ was treated with PPh_3 in refluxing THF (eq 12a). Since we

$$\mathrm{FpCH_2SiMe_2SiMe_2SiMe_3 \xrightarrow[THF]{PPh_3} (\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2SiMe_2SiMe_2SiMe_3} \qquad (12a)$$

were unable to obtain the indenyl complex $(\eta^5\text{-}C_9H_7)Fe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$ in a pure form, due to the facile transformation into $(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe_2CH_2SiMe_2SiMe_3$, and since it is thermally unstable with respect to rearrangement, we obtained the CO insertion product, albeit in low yield, by performing the initial reaction between the carbonylate salt and (chloromethyl)trisilane in the presence of PPh_3 (eq 12b).

$$\mathrm{[(\eta^5\text{-}C_9H_7)Fe(CO)_2]^-Na^+ + ClCH_2SiMe_2SiMe_2SiMe_3 + PPh_3 \rightarrow (\eta^5\text{-}C_9H_7)Fe(CO)(PPh_3)COCH_2SiMe_2SiMe_2SiMe_3} \qquad (12b)$$

Prior to isomerization to $IndFe(CO)_2SiMe_2CH_2SiMe_2SiMe_3$, the intermediate $IndFe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$ is clearly trapped by PPh_3, forming $IndFe(CO)(PPh_3)COCH_2SiMe_2SiMe_2SiMe_3$. It is well established that η^5-indenyl complexes of the type $(\eta^5\text{-}C_9H_7)Fe(CO)_2R$ undergo CO insertion reactions much more rapidly than their cyclopentadienyl analogs due to the ability of the indenyl ligand to exhibit η^5–η^3 ring slippage during associative reactions with incoming ligands.[10] If a similar associative process is occurring in the present case, it becomes apparent that intermolecular association between a phosphine ligand and the indenyl complex is more favored than an intramolecular silyl migration to form the transient silene complex. If the reactions observed here and are more dissociative, i.e. η^5–η^3 slippage occurs prior to silyl migration or phosphine coordination, a similar conclusion is reached: the intermediate is more prone to phosphine substitution than silyl migration and silene formation. This situation parallels the initial formation of (η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$ upon photochemical treatment of (η^5-C$_5$H$_5$)Fe(CO)$_2$CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$ with PPh$_3$ reported above which are presumably dissociative. Similarly, the facile thermal rearrangement of IndFe(CO)$_2$CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$ leaves open to question the associative vs dissociative aspects of these migration rearrangement processes; however, in general the migration of the silyl group to iron in a coordinatively unsaturated intermediate is clearly slow compared to ligand substitution.

Thermal decarbonylation of the new acyl complexes was observed to proceed slowly in refluxing hexane to yield (η^5-L)Fe(CO)(PPh$_3$)SiMe$_2$CH$_2$SiMe$_2$SiMe$_3$. The rates of this transformation were dependent upon the nature of L, with the indenyl complex transforming over a period of 5 days, while for the Fp complex only trace amounts of the final product were observed after 75 h. During these reactions we observed the formation of (η^5-L)Fe(CO)$_2$CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$ as intermediates. Photochemical treatment of the two acyl complexes produced (η^5-L)Fe(CO)(PPh$_3$)SiMe$_2$CH$_2$SiMe$_2$SiMe$_3$ efficiently. In the case of L = Cp we could observe the intermediacy of both (η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$ and (η^5-C$_5$H$_5$)Fe(CO)$_2$SiMe$_2$CH$_2$SiMe$_2$SiMe$_3$ via NMR spectroscopic monitoring.

Experimental Section

General Information. NMR spectra were recorded on a Bruker 200-MHz spectrometer in C$_6$D$_6$ solutions, unless otherwise noted. IR spectra were recorded on a Perkin-Elmer 580B spectrophotometer, in hexane. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. All reactions were performed in a dry N$_2$ or argon atmosphere with dry, oxygen-free solvents. Photolyses were performed using a 450-W Hanovia 679A medium-pressure mercury lamp.

Materials. [CpFe(CO)$_2$]$_2$ and [Cp*Fe(CO)$_2$]$_2$ were purchased from Strem Chemicals, Newburyport, MA, [IndFe(CO)$_2$]$_2$ was prepared by the literature procedures,[16] and ClCH$_2$SiMe$_2$SiMe$_2$SiMe$_3$ and ClCH$_2$SiMe(SiMe$_3$)$_2$ were synthesized as reported previously.[8] Solvents were dried by the conventional methods and distilled under dry nitrogen. Purifications via column chromatography used silica gel that was either Merck, grade 60 (230–240 mesh) or Mallinkrodt grade 60 (mesh 60–240). Analytical and spectral properties for all new complexes are recorded in Table I.

Syntheses of CpFe(CO)$_2$CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$. To an ice-cooled solution of [CpFe(CO)$_2$]$^-$Na$^+$ prepared from Hg (2 mL), Na (270 mg, 11.7 mmol), and [CpFe(CO)$_2$]$_2$ (2.0 g, 5.6 mmol) in THF (20 mL) was added ClCH$_2$SiMe$_2$SiMe$_2$SiMe$_3$ (2.7 g, 11.3 mmol). The reaction mixture was stirred at room temperature for 1 h, and after the solvent was removed in vacuo, the residue was extracted into 50 mL of hexane. This solution was concentrated and then placed on a 2.5-cm × 20-cm silica gel column. Elution with hexane developed an orange band which was collected to produce 3.9 g (10.2 mmol, 91%) of CpFe(CO)$_2$CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$ as an orange oil.

Thermal Reaction of CpFe(CO)$_2$CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$. A 10-mL hexane solution of CpFe(CO)$_2$CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$, 102 mg (0.213 mmol), was refluxed for 14 h and monitored by infrared spectroscopy. No change was observed.

Photolysis of CpFe(CO)$_2$CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$. A solution of CpFe(CO)$_2$CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$, 130 mg (0.342 mmol), in hexane (20 mL) was photolyzed in a 200-mL Pyrex flask and monitored by IR spectroscopy. After 1 h the IR spectrum showed 100% removal of the starting material. The solvent was evaporated in vacuo, and the residue was purified by silica gel column chromatography, 1 cm × 8 cm, using hexane as eluent to give CpFe(CO)$_2$SiMe$_2$CH$_2$SiMe$_2$SiMe$_3$ as an orange oil, 98 mg (0.258 mmol, 75%).

Prolonged Photolysis of CpFe(CO)$_2$CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$ in the Presence of PPh$_3$. A solution of CpFe(CO)$_2$CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$, 0.570 g (1.50 mmol), and PPh$_3$, (0.393 g, 1.50 mmol), in hexane (30 mL) was photolyzed in a 250-mL Pyrex flask and monitored by IR spectroscopy. This indicated the formation of a new band at 1912.9 cm^{-1} (1 h, 60% conversion), which shifted to 1911.1 (2 h, 95% conversion), 1910.2 (4 h, 100% conversion), and 1910.3 cm^{-1} (5 h). After evaporation of the solvent, the residue was chromatographed on a silica gel column using hexane as eluent to give CpFe(CO)(PPh$_3$)SiMe$_2$CH$_2$SiMe$_2$SiMe$_3$, 0.85 g (1.38 mmol, 92%), as an orange oil.

Brief Photolysis of CpFe(CO)$_2$CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$ in the Presence of PPh$_3$: Detection of CpFe(CO)(PPh$_3$)CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$. A solution of CpFe(CO)$_2$CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$, 550 mg (1.45 mmol), and PPh$_3$, 379 mg (1.45 mmol), in hexane (50 mL) was photolyzed in a 100-mL Pyrex flask and monitored by IR spectroscopy. The resulting spectra exhibited a new CO stretching frequency as noted: 1913.7 (40 min, 30% conversion), 1913.3 (1 h 10 min, 50% conversion), and 1912.8 cm^{-1} (1 h 40 min, 70% conversion). The solvent was removed in vacuo, and the residue was chromatographed on a silica gel column using hexane as eluent to give starting material, 130 mg (0.34 mmol), and a waxy solid, 560 mg (0.91 mmol, 62.8%), which exhibited a ν(CO) at 1913.6 cm^{-1}. ^{29}Si NMR analysis showed that this material was a mixture of CpFe(CO)(PPh$_3$)CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$ and CpFe(CO)(PPh$_3$)SiMe$_2$CH$_2$SiMe$_2$SiMe$_3$ (about 80:20 ratio). This mixture slowly converted to rearranged product CpFe(CO)(PPh$_3$)SiMe$_2$CH$_2$SiMe$_2$SiMe$_3$, even in the semisolid state. The spectral properties are recorded in Table I.

Photolytic Rearrangement of CpFe(CO)(PPh$_3$)CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$. CpFe(CO)(PPh$_3$)CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$, 100 mg (0.163 mmol), was dissolved in hexane (26 mL) and divided into two Pyrex test tubes, 2.5 cm × 20 cm. The sample had already somewhat rearranged even during dark, cold storage. The IR spectrum exhibited ν(CO) at 1912.6 cm^{-1}. One tube was photolyzed in an ice bath, and the other was kept in the dark at the same temperature. After 30 min the photolyzed sample exhibited a ν(CO) band at 1910.3 cm^{-1}, which showed that the conversion to CpFe(CO)(PPh$_3$)SiMe$_2$CH$_2$SiMe$_2$SiMe$_3$ was essentially complete. Another 30-min photolysis gave only little change, ν(CO) 1910.2 cm^{-1}. On the other hand, the IR spectrum of the other sample tube kept in the dark in an ice bath exhibited a band at ν(CO) 1912.5 cm^{-1} after 1 h, showing that the photolysis significantly accelerated the rearrangement.

Thermal Rearrangement of CpFe(CO)(PPh$_3$)CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$. A solution of CpFe(CO)(PPh$_3$)CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$, 100 mg (0.163 mmol), in hexane (20 mL) was refluxed in the dark. The reaction was monitored by IR spectroscopy, and the CO stretching frequency changed as follows; 1912.7 (start), 1910.4 (10 min), 1910.2 (20 min), and 1910.2 cm^{-1} (50 min). This result showed thermal rearrangement was also possible to give the rearranged product CpFe(CO)(PPh$_3$)SiMe$_2$CH$_2$SiMe$_2$SiMe$_3$.

Thermal Reaction of CpFe(CO)$_2$CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$ in the Presence of PPh$_3$: Formation of CpFe(CO)(PPh$_3$)COCH$_2$SiMe$_2$SiMe$_2$SiMe$_3$. A 30-mL THF solution of CpFe(CO)$_2$CH$_2$SiMe$_2$SiMe$_2$SiMe$_3$, 1.60 g (4.2 mmol), and PPh$_3$, 1.32 g (5.0 mmol), was refluxed, and the reaction was monitored by IR spectroscopy. After 22.5 h, all the starting material had disappeared and the solvent was evaporated, and the residue was chromatographed on a silica gel column. Elution by hexane/

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(16) Forschner, T. C.; Cutler, A. R. *Inorg. Chim. Acta* **1985**, *102*, 113.

CH_2Cl_2 (3:1) gave $CpFe(CO)(PPh_3)COCH_2SiMe_2SiMe_2SiMe_3$ as an orange solid, 1.2 g (1.87 mmol, 44.5%). An analytical sample was obtained by recrystallization from a CH_2Cl_2/hexane solvent system.

Thermal Decarbonylation of $CpFe(CO)(PPh_3)COCH_2SiMe_2SiMe_2SiMe_3$. A solution of $CpFe(CO)(PPh_3)COCH_2SiMe_2SiMe_2SiMe_3$, 50 mg (0.078 mmol), in 10 mL of hexane was refluxed, and the progress of the reaction was monitored by IR spectroscopy. Initially, a pair of small ν(CO) bands appeared at 2010.6 and 1959.6 cm^{-1}, which could be assigned to $CpFe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$. The reaction was very slow, and after refluxing for 40 h, the solvent was changed to cyclohexane to achieve a faster reaction rate. After an additional 35 h of refluxing in cyclohexane, in addition to the bands assignable to $CpFe(CO)(PPh_3)COCH_2SiMe_2SiMe_2SiMe_3$ and $CpFe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$ (nearly equal peak size) a small band appeared at 1910.3 cm^{-1}, assignable to $CpFe(CO)(PPh_3)SiMe_2CH_2SiMe_2SiMe_3$. We made no attempt to separate the mixture.

Photochemical Decarbonylation of $CpFe(CO)(PPh_3)COCH_2SiMe_2SiMe_2SiMe_3$. $CpFe(CO)(PPh_3)COCH_2SiMe_2SiMe_2SiMe_3$ (100 mg, 0.156 mmol) in 0.3 mL of C_6D_6 was photolyzed in a sealed Pyrex NMR tube. The progress of the reaction was monitored by ^{29}Si NMR spectroscopy. After 1 h of irradiation, the NMR spectrum showed the presence of starting material (about 50% conversion), $CpFe(CO)(PPh_3)CH_2SiMe_2SiMe_2SiMe_3$, $CpFe(CO)_2SiMe_2CH_2SiMe_2SiMe_3$, and $CpFe(CO)(PPh_3)SiMe_2CH_2SiMe_2SiMe_3$. After an additional 4 h of irradiation, only $CpFe(CO)(PPh_3)SiMe_2CH_2SiMe_2SiMe_3$ was observed by ^{29}Si NMR spectroscopy. IR spectroscopy of this solution showed $CpFe(CO)(PPh_3)SiMe_2CH_2SiMe_2SiMe_3$ was the main product, along with trace amounts of $[CpFe(CO)_2]_2$.

Synthesis of $Cp^*Fe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$. To an ice-cooled solution of $Cp^*Fe(CO)_2^-Na^+$ prepared from Hg (3 mL), Na (0.38 g, 17 mmol), and $[Cp^*Fe(CO)_2]_2$ (1.2 g, 24 mmol) in THF (60 mL) was added $ClCH_2SiMe_2SiMe_2SiMe_3$ (1.2 g, 50 mmol). After the mixture was stirred at room temperature overnight, THF was evaporated in vacuo and the residue was extracted with hexane (50 mL). Evaporation of the hexane gave a yellow oil, 0.8 g (18 mmol, 37.5%). An analytical sample was purified by silica gel column chromatography, eluting with hexane.

Thermal Reaction of $Cp^*Fe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$. A hexane solution of $Cp^*Fe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$ was refluxed and monitored by IR spectroscopy. The IR spectrum changed gradually to that of $[Cp^*Fe(CO)_2]_2$, and after 50 h the conversion was complete. No other ν(CO) bands were observed during this process.

Photolytic Isomerization of $Cp^*Fe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$. A solution of $Cp^*Fe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$, 0.4 g (0.89 mmol), in 0.5 mL of C_6D_6 was photolyzed in a sealed Pyrex NMR tube. The progress of the reaction was checked by NMR spectroscopy at 1 h. No starting material was observed, and ^1H, ^{13}C, and ^{29}Si NMR signals assignable to a single product, $Cp^*Fe(CO)_2SiMe_2CH_2SiMe_2SiMe_3$, were observed. The product was purified by silica gel column chromatography. Elution of the yellow band with hexane gave a yellow oil, 0.35 g (0.78 mmol, 87.5%), which solidified in the refrigerator.

Attempted Synthesis of $IndFe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$: In Situ Conversion to $IndFe(CO)_2SiMe_2CH_2SiMe_2SiMe_3$. To an ice-cooled solution of $[IndFe(CO)]^-Na^+$ prepared from Hg (4 mL), Na (0.4 g, 17 mmol), and $[IndFe(CO)_2]_2$ (2.0 g, 44 mmol) in 60 mL of THF was added $ClCH_2SiMe_2SiMe_2SiMe_3$ (1.9 g, 80 mmol). The reaction mixture was stirred overnight, and after removal of the solvent in vacuo, the residue was extracted with hexane (70 mL). Removal of hexane in vacuo yielded a brown liquid whose infrared spectrum exhibited two sets of two ν(CO) signals (2006.1 and 1953.7 cm^{-1}; 1993.3 and 1941.7 cm^{-1}) and whose ^{29}Si NMR spectrum exhibited two sets of three signals (δ −48.44, −16.14 and −4.17; δ −19.44, −18.11 and 50.35). These spectral data indicated two main products, assignable to $IndFe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$ and $IndFe(CO)_2SiMe_2CH_2SiMe_2SiMe_3$, respectively. The ratio varied from 40:60 to 10:90 depending on the minor change of the reaction conditions since the rearrangement process is quite facile. After passing through a silica gel column, 2.5 cm × 20 cm and eluting with hexane, a mixture of the two compounds was obtained, 1.2 g (28 mmol, 35%).

The mixture of the two compounds (ratio 40:60), 0.8 g (1.9 mmol), was dissolved in 50 mL of hexane, and the solution was heated to reflux. The reaction was monitored by IR spectroscopy, and after 2 h only the rearranged product was observed. After passing through a silica gel column, 2.5 cm × 12 cm, the product $IndFe(CO)_2SiMe_2CH_2SiMe_2SiMe_3$, 0.5 g (1.2 mmol, 63%), was isolated.

In a separate experiment, the crude mixture, 0.5 g, was dissolved in 25 mL of hexane and the solution was irradiated in a Pyrex tube, 1 cm × 15 cm, for 1 h. NMR and IR analysis showed complete transformation to $IndFe(CO)_2SiMe_2CH_2SiMe_2SiMe_3$.

In Situ Reaction of $[(\eta^5\text{-Ind})Fe(CO)_2]^-Na^+$, $ClCH_2SiMe_2SiMe_2SiMe_3$, and PPh_3. To $[(\eta^5\text{-Ind})Fe(CO)_2]^-Na^+$ prepared from Hg (4 mL), Na (0.3 g, 0.013 mol), and $[(\eta^5\text{-Ind})Fe(CO)_2]_2$ (2 g, 4.4 mmol) in THF (60 mL) was added PPh_3 (2.1 g, 8.0 mmol). After 1 h of stirring, the solution was cooled in an ice bath and $ClCH_2SiMe_2SiMe_2SiMe_3$ (2.0 g, 8.4 mmol) was added. After an additional 4 h of stirring, THF was removed in vacuo, the residue was dissolved in dichloromethane, and the product was purified by silica gel column chromatography. Elution with CH_2Cl_2/Hexane (1:1) gave $(\eta^5\text{-Ind})Fe(CO)(PPh_3)\text{–}CO\text{–}CH_2SiMe_2SiMe_2SiMe_3$ 1.4 g (0.0020 mol, 23.8%).

Thermal Decarbonylation of $IndFe(CO)(PPh_3)\text{–}CO\text{–}CH_2SiMe_2SiMe_2SiMe_3$. A 10-mL hexane solution of $(\eta^5\text{-Ind})Fe(CO)(PPh_3)\text{–}CO\text{–}CH_2SiMe_2SiMe_2SiMe_3$ (0.05 g, 0.072 mmol) was refluxed and monitored by IR spectroscopy. After 5 days, the starting material had almost disappeared. A new infrared band at 1910.4 cm^{-1} was observed, assignable to $IndFe(CO)(PPh_3)SiMe_2CH_2SiMe_2SiMe_3$. The product was purified by silica gel column chromatography, 0.03 g (0.045 mmol, 62.5%). During the reaction, infrared monitoring showed the presence of a pair of weak ν(CO) bands assignable to $IndFe(CO)_2CH_2SiMe_2SiMe_2SiMe_3$. No other bands were observed.

Photochemical Decarbonylation of $IndFe(CO)(PPh_3)\text{–}CO\text{–}CH_2SiMe_2SiMe_2SiMe_3$. A solution of $(\eta^5\text{-Ind})Fe(CO)(PPh_3)\text{–}CO\text{–}CH_2SiMe_2SiMe_2SiMe_3$ (0.05 g, 0.072 mmol) dissolved in C_6D_6 (4 mL) was irradiated in a sealed NMR tube. The reaction was monitored by ^{29}Si NMR spectroscopy. After 1.5 h of irradiation ^{29}Si NMR spectroscopy showed no starting material remained. The product was purified by silica gel column chromatography; elution with CH_2Cl_2/Hexane (1:1) gave $IndFe(CO)(PPh_3)SiMe_2CH_2SiMe_2SiMe_3$, the same product as thermal decarbonylation.

Synthesis of $CpFe(CO)_2CH_2SiMe(SiMe_3)_2$. To an ice-cooled solution of $[CpFe(CO)_2]^-Na^+$ prepared from Hg (2 mL), Na (300 mg, 13 mmol), and $[CpFe(CO)_2]_2$ (2.0 g, 6.6 mmol) in THF (20 mL) was added $ClCH_2SiMe(SiMe_3)_2$ (2.27 g, 0.0095 mol). The reaction mixture was stirred at room temperature for 30 min, and the solvent was removed in vacuo. The orange-red residue was purified by silica gel column chromatography; eluting with hexane gave $CpFe(CO)_2CH_2SiMe(SiMe_3)_2$, 2.6 g (6.8 mmol, 72.0%), as an orange oil.

Photolysis of $CpFe(CO)_2CH_2SiMe(SiMe_3)_2$ in Hexane. A solution of $CpFe(CO)_2CH_2SiMe(SiMe_3)_2$, 301 mg (0.792 mmol), in hexane (30 mL) was photolyzed in a 2.0-cm × 30-cm Pyrex tube. The reaction was monitored by IR spectroscopy, and after 20 min of irradiation, conversion was 100%, and the new ν(CO) bands were 1997.7 and 1944.4 cm^{-1}, assignable to the presence of a complex containing an Fe–Si bond, $CpFe(CO)_2\text{–}SiR_3$. An additional 10 min of irradiation (total 30 min) did not change the IR spectrum. After removal of the solvent in vacuo and passing through a silica gel column, ^1H and ^{29}Si NMR spectra showed the products were $CpFe(CO)_2SiMe_3$ and $CpFe(CO)_2SiMe_2CH_2SiMe_3$ (about 60:40 ratio).[7]

Photolysis of $CpFe(CO)_2CH_2SiMe(SiMe_3)_2$, Monitored by NMR Spectroscopy. A solution of $CpFe(CO)_2CH_2SiMe(SiMe_3)_2$, 104 mg (0.27 mmol), in C_6D_6 (0.3 mL) in a 5-mm Pyrex NMR tube was photolyzed, and the reaction was monitored by ^{29}Si NMR spectroscopy. After 5 min of irradiation, only the photoproducts $CpFe(CO)_2SiMe_3$ and $CpFe(CO)_2SiMe_2CH_2SiMe_3$ were observed besides starting material. No peaks assignable to postulated intermediate $CpFe(CO)_2\text{–}SiMe(SiMe_3)CH_2\text{–}SiMe_3$ were observed, although small unknown resonances appeared and disappeared. We have been unable to identify the source of these resonances.

Synthesis of Cp*Fe(CO)$_2$CH$_2$SiMe(SiMe$_3$)$_2$. To an ice-cooled solution of [Cp*Fe(CO)$_2$]$^-$Na$^+$ prepared from Hg (4 mL), Na (0.3 g, 13 mmol), and [Cp*Fe(CO)$_2$]$_2$ (1.5 g, 3.0 mmol) in THF (50 mL) was added ClCH$_2$SiMe(SiMe$_3$)$_2$ (1.35 g, 5.7 mmol). The reaction mixture was stirred at room temperature overnight. THF was removed in vacuo, and subsequent to extraction into 50 mL of hexane, the residue was purified by silica gel column chromatography. Elution with hexane gave pure Cp*Fe(CO)$_2$CH$_2$SiMe(SiMe$_3$)$_2$ (30%) as a yellow orange oil.

Photolysis of Cp*Fe(CO)$_2$CH$_2$SiMe(SiMe$_3$)$_2$. A solution of Cp*Fe(CO)$_2$CH$_2$SiMe(SiMe$_3$)$_2$ in C$_6$D$_6$ in a NMR tube was photolyzed, and the reaction was monitored by ^{29}Si NMR spectroscopy. After 1 h of irradiation, ^{29}Si NMR spectroscopy showed a complex mixture, composed of starting material Cp*Fe(CO)$_2$CH$_2$SiMe(SiMe$_3$)$_2$ (δ −33.65, −16.72), final products Cp*Fe(CO)$_2$SiMe$_3$ (δ 40.13) and Cp*Fe(CO)$_2$SiMe$_2$CH$_2$SiMe$_3$ (δ 0.37, 42.0),[6b] and reactive intermediates and/or unstable byproducts with resonances at δ −13.17 (or −11.30), 1.50 (or 0.52), and 14.95 that were tentatively assignable to intermediate Cp*Fe(CO)$_2$SiMe(SiMe$_3$)CH$_2$SiMe$_3$, which could be degraded to each of the two final products. After 8.5 h of irradiation only the two final products were found besides broad signals at $\delta \simeq -16$, and $\simeq 0$ assignable to polymeric materials.

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Phosphinomethyl Complexes of Niobocene

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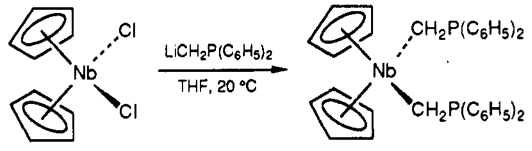
Reaction of LiCH$_2$P(C$_6$H$_5$)$_2$ with Cp$_2$NbCl$_2$ gives paramagnetic Cp$_2$Nb[CH$_2$P(C$_6$H$_5$)$_2$]$_2$ (1); Cp$_2$Nb(Cl)CH$_2$P(C$_6$H$_5$)$_2$ (4) is observed only as an unstable intermediate. Oxidation of 1 by AgBF$_4$ gives Cp$_2$Nb[CH$_2$P(C$_6$H$_4$)$_2$]$_2$$^+BF_4$$^-$ (6); reduction by Na/C$_{10}$H$_8$ gives Na$^+${Cp$_2$Nb[CH$_2$P(C$_6$H$_4$)$_2$]$_2$}$^-$ (5), both isolable in analytically pure form as stable, diamagnetic solids. The anion of the latter crystallizes as its Na(18-crown-6)(THF)$_2$$^+$ salt in the monoclinic space group $C2/c$ with cell parameters a = 27.088 (15) Å, b = 9.560 (5) Å, c = 25.903 (14), β = 126.19 (3)°, and Z = 4. The structure was refined to R = 0.044 and R_w = 0.046 using 3493 uniquely observed reflections. Reaction of 1 with (C$_7$H$_8$)Mo(CO)$_4$ gives Cp$_2$Nb[μ-CH$_2$P(C$_6$H$_5$)$_2$]$_2$Mo(CO)$_4$ (7), which crystallizes in the monoclinic space group $P2_1/n$ with cell parameters a = 13.401 (5) Å, b = 17.188 (5) Å, c = 19.768 (6), β = 99.25 (3)°, and Z = 4. The structure was refined to R = 0.081 and R_w = 0.085 using 1851 uniquely observed reflections. Both 5$^-$ and 7 possess pseudotetrahedral Nb atoms, the latter octahedral Mo. Both Nb and Na in 5 lie on crystallographic 2-fold axes; no interaction between Nb and P is evident. The C–Nb–C angles to the phosphinomethyl groups are found to be 74.2 (2)° in 5$^-$ (d^2 Nb), ca. 80–85° in 1 (d^1 Nb, estimated from ESR data), and 90.4° in 7 (d^1 Nb).

Introduction

The phosphinomethyl ligand, R$_2$PCH–, has proved to be a source of interesting and, in several cases, quite unusual chemistry, especially upon attachment to early transition metals. We and others have explored both mono- and dinuclear complexes of this ligand with group 4 metals,[1-3] as well as with metals in groups 8–10.[4] We anticipated that attachment of R$_2$PCH$_2$– to a group 5 metal such as niobium might lead in several directions unavailable to the group 4 analogues due in part to the availability of three rather than two readily accessible oxidation states. We herein describe the preparation and properties of the first such systems, phosphinomethyl derivatives of niobocene, including the structural characterization of a cyclic niobium-containing heterobimetallic lacking a metal–metal bond.

Results and Discussion

Phosphinomethyl Nb(IV) Derivatives. Addition of 2 equiv of either LiCH$_2$P(C$_6$H$_4$)$_2$ or its TMEDA complex to Cp$_2$NbCl$_2$ (Cp = η^5-C$_5$H$_5$) at 20 °C leads to ca. 65% isolated yields of analytically pure Cp$_2$Nb[CH$_2$P(C$_6$H$_5$)$_2$]$_2$ (1) as a thermally stable but air-sensitive tan solid (eq 1).



1

(1)

Spectroscopic characterization is limited to ESR analysis at ambient temperature: the paramagnetic Nb(IV) center gives rise to a 10-line pattern (^{93}Nb, I = $^9/_2$, 100%) centered about g = 1.99 with a(^{93}Nb) = 90.0 G. In toluene, further (poorly resolved) splitting is observed for the four equivalent methylene hydrogens with a(^{1}H) ≈ 7 G. These values compare well with other dialkylniobocenes, e.g. for Cp$_2$Nb(CH$_3$)$_2$, g = 1.998, a(^{93}Nb) = 88.8 G, and a(^{1}H) =

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