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The Utility of Sodium Diisopropylamide (NADA): Formation of a New Transition Metalate via Silyl Migration Chemistry, $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(CO)(PPh_3)]^-Na^+$ (SiFpPNa), and Resulting Thermal Rearrangements of the Complexes SiFpP$-CH_2SiMe_2R$ (R = H, $SiMe_3$) to SiFpP$-SiMe_2CH_2R$

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A new transition metalate system, $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(CO)(PPh_3)]^-M^+$ (SiFpPM; M = Li, Na), was synthesized via treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)SiMe_3$ with sodium and lithium diisopropylamides (MN(iPr$_2$); NADA and LDA, respectively). The utility of NADA was far superior to that of LDA, with shorter reaction times, lower reagent concentrations, and higher yields. Infrared spectroscopic analysis of the new ferrates indicated that their stability and utility were dependent upon the tight ion pairs Fe$-$CO$-$M; in the presence of coordinating solvents and ionophores the separated ion pairs formed led to the expulsion of the PPh_3 and CO scavenging led to formation of the dicarbonylferrate $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(CO)_2]^-M^+$. Hexane was the solvent of choice for formation and use of the ferrates. Reactions of the new ferrates with MeI led to $[SiFpP]CH_3$, whereas reactions with $ClCH_2SiMe_2R$ (R = H, $SiMe_3$) did not lead to the expected Fe$-$C bonded complexes $[SiFpP]CH_2SiMe_2R$ but to high yields of the rearranged complexes $[SiFpP]SiMe_2CH_2R$. The presence of the thermally labile phosphine group readily produces a coordinatively unsaturated 16e species that permits Fe$-CH_2-SiMe_2R$ to $FeSiMe_2CH_2R$ rearrangements (previously observed photochemically with the simple Fp derivatives) to occur thermally.

Introduction

Transition-metal carbonylate salts are key reagents for the formation of metal$-$carbon (and related metal$-$element) bonds.[1] Their use has been demonstrated to be solvent dependent, and their solution and solid-state structures often involve ion pairs which vary as a function of the cationic species present, the solvent, the temperature, and the nature of the ligands substituted at the metal center.[2]

A transition metalate system that has been particularly well-used and studied is the cyclopentadienyliron dicarbonyl system, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ (Fp^-), and an imperfect search of the literature indicates > 20 000 references to compounds of the general type Fp$-$E (E = any element). One of the aspects of the Fp$-$E system is the ability to substitute the CO groups by phosphine ligands either thermally or photochemically to introduce interesting diasteroisomeric properties, including optical activity at the metal center.[3] However, there is only a single literature report on the availability and reactivity of a phosphine-substituted ferrate, $[(\eta^5\text{-}C_5H_5)Fe(CO)(PR_3)]^-Li^+$.[4] Such ferrates would be of interest for the direct formation of interesting new complexes and/or derivatives where photochemical treatment of Fp derivatives is not plausible.

We report such a system using a modified base-induced silyl group migration from iron to a η^5-cyclopentadienyl ligand previously well-established for the reaction of Fp$-SiR_3$ and sodium or lithium diisopropylamide (NADA, LDA) that results in the formation of $[(\eta^5\text{-}R_3SiC_5H_4)Fe(CO)_2]^-M^+$ (M = Na, Li).[5] Thus, using $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]SiMe_3$ we form the new ferrates $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(CO)(PPh_3)]^-M^+$ (SiFpPM). These salts exhibit ion-pairing characteristics which indicate that only tight ion pairs stabilize the needed phosphine-substituted salts. Furthermore, whereas the ferrates readily react with MeI and Me_3SiCl to generate the corresponding Fe$-$C and Fe$-$Si bonded complexes, their reactions with $ClCH_2SiMe_2R$ (R = H, $SiMe_3$) lead to rearranged materials containing Fe$-$Si bonds.

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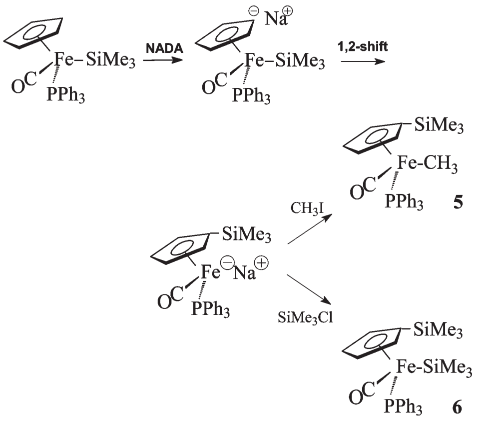
Results and Discussion

Synthesis and Spectral Characterization of [(η^5-Me$_3$SiC$_5$H$_4$)Fe(CO)(PPh$_3$)]$^-$M$^+$. The complex (η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)SiMe$_3$ (**1**)[6] readily reacts with NADA to form the silyl-migrated product [(η^5-Me$_3$SiC$_5$H$_4$)Fe(CO)(PPh$_3$)]$^-$Na$^+$ (**2a**), which can then be trapped by addition of either CH$_3$I or SiMe$_3$Cl to form (η^5-Me$_3$SiC$_5$H$_4$)Fe(CO)(PPh$_3$)ER$_3$ (eq 1; ER$_3$ = CH$_3$ (**5**), SiMe$_3$ (**6**)). Small amounts of Fp$-$ER$_3$ derivatives are also obtained.



(1)

Published infrared spectroscopic analysis of [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$^-$Na$^+$ illustrated three distinct ion-paired species in equilibrium: an Fe$-$Na tight ion pair (1877, 1806 cm^{-1}), an Fe$-$CO- - -Na tight ion pair (1862, 1770 cm^{-1}), and a solvent-separated ion pair (1862, 1786 cm^{-1}).[7] Similar data were obtained for the Li analog.[8] In the present case a 25 mL THF solution of NADA (4.9 mmol) and **1** (1.5 mmol; ν_{CO} 1902 cm^{-1}) at -78 °C resulted in the formation of **2a** with a new ν_{CO} band at 1730 cm^{-1} within 30 min (Figure 1). Similarly, addition of lithium disopropylamide (LDA; 10 equiv, 24 h, 0 °C) to **1** resulted in formation of a new ν_{CO} band at 1710 cm^{-1} for species **2b**.

Both stretching frequencies are in accord with the presence of a single species involving a Fe$-$CO- - -Na(Li) tight ion pair.[7,8] As expected for Li, with a greater electrostatic potential and thereby a stronger interaction with the terminal CO, the increased retrodative bonding between the Fe and CO π^* orbitals results in a greater reduction of the CO triple-bond character and hence a lower ν_{CO}. Progressive addition of 4′-bromobenzo-18-crown-6 (0.13 M solution in THF) to a THF solution of **2a** resulted in the appearance of a new ν_{CO} band at 1771 cm^{-1}, at a higher frequency as expected for a solvent- or ionophore-separated ion pair (**3a**). Further addition of the crown ether solution resulted in the development of two new ν_{CO} bands at 1862 and 1789 cm^{-1}, indicating the presence of the solvent (ionophore)-separated ion pair of the *dicarbonyl* salt [(η^5-Me$_3$SiC$_5$H$_4$)Fe(CO)$_2$]$^-$Na$^+$ (**4**) (Figure 2).

Indeed, upon treatment of this solution with methyl iodide, two products were isolated, the phosphine-substituted methyl compound SiPFpCH$_3$ (1905 cm^{-1}) and the dicarbonyl methyl compound FpCH$_3$ (2001, 1944 cm^{-1}) (Scheme 1). A similar result was obtained upon addition of [PPN]$^+$Cl$^-$ to a solution of **2a**.

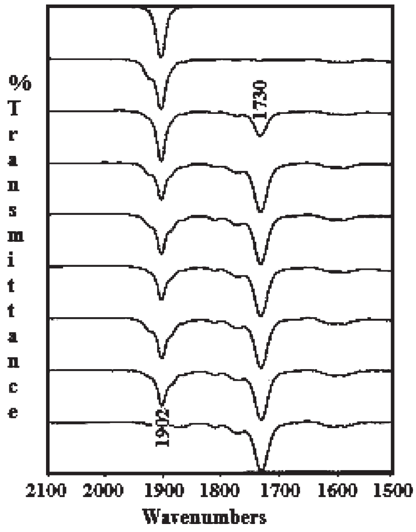


Figure 1. Infrared changes during formation of [(η^5-Me$_3$SiC$_5$H$_4$)Fe(CO)(PPh$_3$)]$^-$Na$^+$ over a 30 min time period.

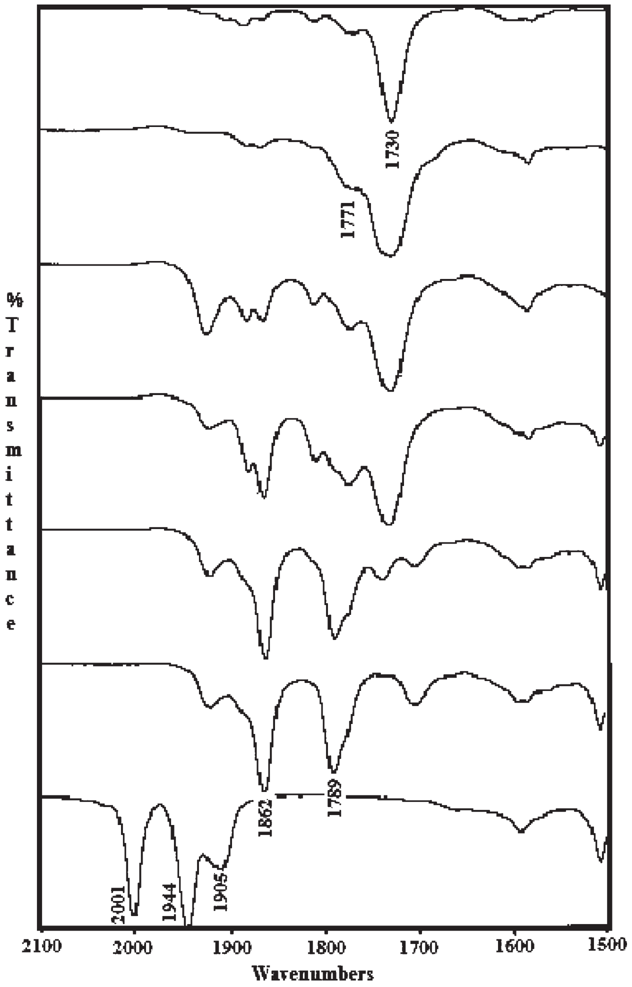


Figure 2. Infrared spectral changes upon addition of a crown ether to **2a** followed by quenching with MeI (bottom spectrum).

Due to the reduced π-accepting ability of PPh$_3$ compared with that of CO, the substitution of a CO ligand in Fp$^-$ by PPh$_3$ greatly increases the electron density at the iron atom. As a result, in the tight ion pair Fe$-$CO- - -Na the dπ(Fe) → π^*(CO- - -Na) interaction is facilitated, relieving some of the

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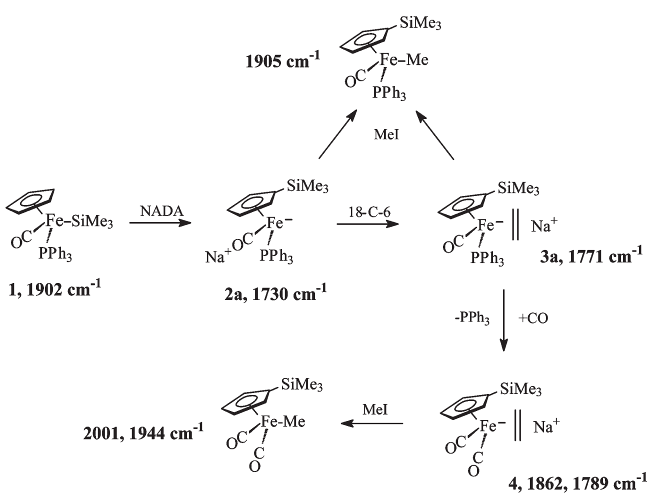
Scheme 1. Formation and Reactivity of [(η^5-$Me_3SiC_5H_4$)Fe(CO)(PPh_3)]$^-$Na$^+$



electron density at the transition-metal center. When this tight ion pair is perturbed by addition of a crown ether, or $[PPN]^+Cl^-$, increasing electron density at Fe facilitates loss of the PPh_3 ligand and the resulting 16-electron system scavenges CO to produce the dicarbonyl anion. Such loss of the poorer π-acceptor is consistent with observations by Chen and Ellis upon reduction of metal complexes containing both CO and PR_3.[9] The fate of the Fe atom that was the source of the second CO is not clear at this time.

To our surprise, the silyl migration chemistry and formation of [(η^5-$Me_3SiC_5H_4$)Fe(CO)(PPh_3)]$^-$Na$^+$ also proceed smoothly in hexanes. The reaction is complete in 3 h upon addition of only 3 equiv of NADA at room temperature to produce a species with a single ν_{CO} band at 1693 cm^{-1} (and shoulder at 1745 cm^{-1}). The anion is readily quenched as above, with higher yields and little or no formation of dicarbonyl derivatives. Similarly, when LDA is added to **1** in hexane, a new broad ν_{CO} band at 1681 cm^{-1} is formed (however, only after adding 20 equiv at room temperature and stirring for 12 days). To our knowledge, no ν_{CO} bands as low as 1681 and 1693 cm^{-1} have been seen for cyclopentadienyliron carbonyl compounds.

When the hexane solution of [(η^5-$Me_3SiC_5H_4$)Fe(CO)(PPh_3)]$^-$Na$^+$ is titrated with THF, the Fe–CO- - -M ν_{CO} band at 1730 cm^{-1} reemerges until it completely replaces the ν_{CO} band at 1693 cm^{-1}. The ν_{CO} band at 1693 cm^{-1} reflects a maximization of the dπ(Fe) → π*(CO- - -M) interaction suggestive of a considerable C=O character. In addition, the convenient solubility of the salt in hexanes suggests salt aggregation between Na^+ and the metalate. The well-established solubility of alkyllithium reagents in hexanes (whether because of Li–C covalency[10a,b] or, as some quantum mechanical calculations suggest, the encapsulation of the lithium atom core by the hydrophobic alkyl groups[10c]) is augmented in the present case by the large hydrophobic Me_3Si group on the cyclopentadienyl ring and PPh_3, thus distinguishing these new metalates from the simple $[Fp]^-$ salts.

We suggest that an aggregate of the type illustrated in Figure 3, in which the oxygen of the carbonyl group is coordinated to the face of a cationic metallic tetramer, is a probable structure for the species in hexane. This type of arrangement, which would increase solubility, maximize dπ(Fe)→ π*(CO- - -M), and produce the very low ν_{CO} bands, i.e. 1693 cm^{-1} (Na) and 1681 cm^{-1} (Li), is known in alkali-metal chemistry and the crystal structure of methyllithium contains a lithium tetramer with a carbon atom coordinated to each face of the tetrahedron.[11] In addition many dimers and aggregates of lithium and sodium are known.[12]

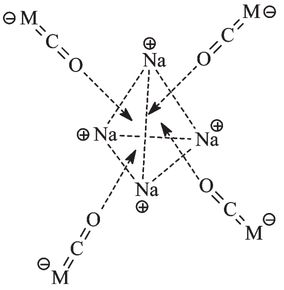
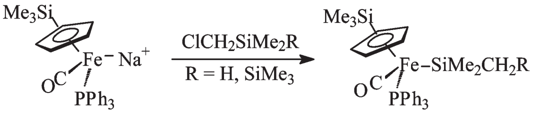


Figure 3. Proposed aggregation of **2a** in hexanes solution (M^- = [(η^5-$Me_3SiC_5H_4$)Fe(CO)(PPh_3)]).

Reactivity of [(η^5-$Me_3SiC_5H_4$)Fe(CO)(PPh_3)]$^-$M$^+$ with $ClCH_2SiMe_2R$ (R = H, $SiMe_3$). An important potential of the new metalate system of interest to us is the capacity to synthesize oligosilyl (and related) complexes where the phosphine-substituted Fp complex cannot be prepared via the usual photochemical treatment due to photochemically induced rearrangements.[5d,13] It has been noted that photochemical reactions of disilanes (e.g., $Me_3SiSiMe_2H$) lead to silylene formation/expulsion when catalyzed by FpR complexes, but non-photochemical thermal rearrangement chemistry is observed when the phosphine-substituted analogues are the catalysts or reagents.[14a,b]

The new ferrate **2** reacts readily as noted in eq 1 to form the simple alkyl and silyl complexes **5** and **6**, and full spectroscopic analysis of these materials is provided in the Experimental Section. Additionally, we have reacted [(η^5-$Me_3SiC_5H_4$)Fe(CO)(PPh_3)]$^-$Na$^+$ with the chloromethylsilane species $ClCH_2SiMe_2R$ (R = H, $SiMe_3$). The reactions are rapid, and the final products (η^5-$Me_3SiC_5H_4$)Fe(CO)(PPh_3)$SiMe_2CH_2R$ (R = H (**6**), $SiMe_3$ (**7**)) are obtained in good yield (eq 2).



(2)

This chemistry is different from that using the parent Fp anion, where in both cases the initially isolated product was $FpCH_2SiMe_2R$.[13a,d,e] Similarly, the reaction of the

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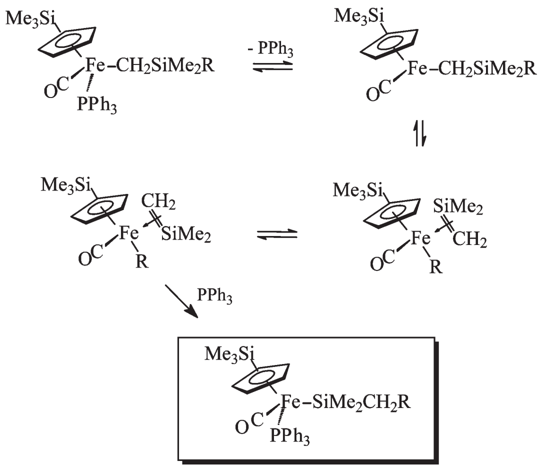
Scheme 2



tungsten analogue $[(\eta^5\text{-}C_5H_5)W(CO)_3]^-Na^+$ with $ClCH_2SiMe_2SiMe_3$ results in the formation of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2SiMe_2SiMe_3$ and only upon photochemical irradiation is a rearranged material with the WSiCSi chain formed.[15] Apparently the initially formed analogous product $(\eta^5\text{-}Me_3SiC_5H_4)Fe(CO)(PPh_3)CH_2SiMe_2R$ is thermally unstable at ambient temperature with respect to loss of PPh_3 to form the 16e system that we have previously suggested leads to silene formation and ultimately the $Fe{-}SiMe_2CH_2R$ rearranged product (Scheme 2; R = H, $SiMe_3$).

Such chemistry signifies that the PPh_3 ligand is labile in the system, and thus we are hopeful that similar thermal rearrangements of oligosilyl, oligosilylmethyl, and related chains may be observed in the future using this and similar metalates.

The crystal structures of complexes **5** and **7** are illustrated in Figures 4 and 5, respectively, and the various bond lengths and bond angles in the structures are normal (Tables 1 and 2, respectively). The Newman projections of each of the structures reveal the organization of the groups around the Fe atom and $SiMe_3$ group (Figure 6). The larger size of the $SiMe_2CH_2SiMe_3$ substituent at the Fe atom forces the cyclopentadienyl Me_3Si group to adopt a non-trans orientation with respect to the PPh_3 ligand.

The geometrical parameters of the silane group in **7** are essentially the same as those of other metalla-silylmethylsilanes that we have reported, $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)SiMe_2CH_2SiMe_3$[15] (**8**) and $Fp\text{-}SiMe_2CH_2SiMe_2\text{-}Fp$ (**9**).[16] From observation of a Newman projection along the metal−Si bond the orientation of the cyclopentadienyl groups with respect to the silane chain is gauche for the two Fe complexes, with dihedral angles of 60.7 (**7**) and 67.2° (**9**), respectively. In the case of the W complex a transoid arrangement is observed with a dihedral angle of 173.9°. The Si−C−Si angles are 122.5 (**6**), 122.7 (**7**), and 123.7° (**9**), and the $C_{bridge}{-}Si$ bonds are different in **7** and **8**, the $C{-}SiMe_2$ bond being slightly longer compared to the $C{-}SiMe_3$ bond (1.898 and 1.868 Å (**7**); 1.886 and 1.855 Å (**8**)) while in **9**, as expected, both bonds are the same length (1.885 Å).

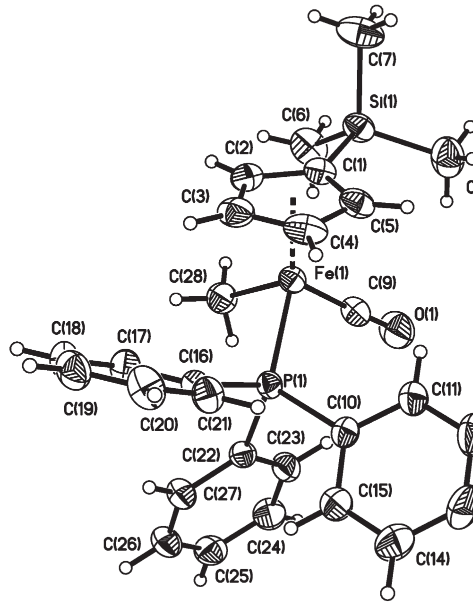


Figure 4. Ortep view of compound **5**. The ellipsoids are drawn at the 35% probability level.

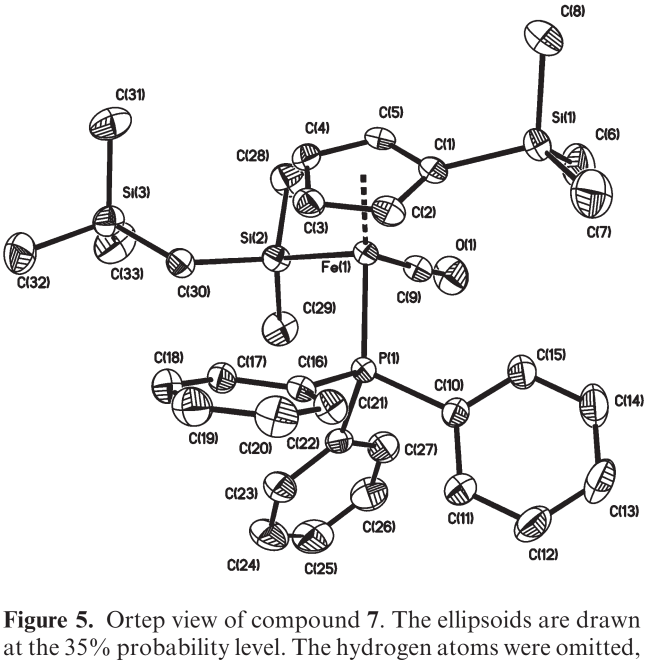


Figure 5. Ortep view of compound **7**. The ellipsoids are drawn at the 35% probability level. The hydrogen atoms were omitted, and the disordered benzene solvent molecule is not included.

In conclusion, we have demonstrated that NADA is a significantly superior base compared to LDA in effecting the formation of silyl-migrated metalate salts of the type $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(CO)(PPh_3)]^-M^+$ (much lower amounts of base, much shorter reaction times, and higher yields). In solution this salt exhibits a tight ion pair in the form of Fe-CO- - -Na, which is needed to provide stability to the reagent, since solvent-separated ion pairs decompose via loss of phosphine and CO scavenging to produce the dicarbonyl analogue. The new metalate is a useful synthon for studying the thermal rearrangements of Fe−Si complexes due to facile phosphine elimination to form 16e transients.

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Table 1. Crystal Data and Refinement Parameters for Complexes 5 and 7

	5	**7**
formula	$C_{28}H_{31}FeOPSi$	$C_{33}H_{45}FeOPSi_3\cdot{}^1/_2C_6H_6$
formula wt	498.44	667.83
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	9.2213(4)	9.2515(9)
b (Å)	15.9784(8)	18.0499(16)
c (Å)	17.5446(8)	22.205(2)
α (deg)	90	90
β (deg)	95.5160(10)	94.349(2)
γ (deg)	90	90
V (Å^3)	2573.1(2)	3697.4(6)
Z	4	4
ρ_{calcd} (g cm^{-3})	1.287	1.200
μ(Mo Kα) (mm^{-1})	0.713	0.574
F(000)	1048	1420
T (K)	298(2)	296(2)
$2\theta_{max}$ (deg), completeness (%)	53.98, 99.9	54.00, 99.7
index ranges: h, k, l	−11 to +11, −20 to +20, −22 to +22	−11 to +11, −17 to +23, −27 to +28
total no. of rflns	28 610	22 503
no. of indep rflns (R_{int})	5616 (0.0382)	8043 (0.0412)
refinement methods	full-matrix least squares on F^2	
no. of data/restraints/params	5616/0/293	8043/120/415
goodness of fit on F^2	1.040	1.093
R1 ($I > 2\sigma(I)$)	0.0435	0.0628
largest diff in peak and hole (e Å^{-3})	0.382 and −0.279	0.575 and −0.272

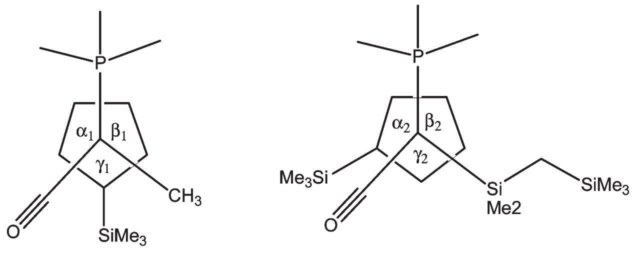
Experimental Section

All syntheses were performed under a nitrogen atmosphere using standard Schlenk line techniques. Reagent grade tetrahydrofuran (THF) was dried and distilled under nitrogen from a sodium benzophenone ketyl solution; benzene and hexanes were dried and distilled from Na ribbon. Sodium *tert*-butoxide, *n*-butyllithium, and iodomethane were purchased from Aldrich and used as received. Diisopropylamine was purchased from Aldrich and distilled over NaOH prior to use. Trimethylchlorosilane, chloromethyldimethylsilane, and trimethylchlorogermane were purchased from Gelest and used as received. Cyclopentadienyliron dicarbonyl dimer was purchased from Strem Chemicals and used as received. The iron silicon complexes $FpSiMe_3$,[6,17] (η^5-C_5H_5)Fe(CO)(PPh_3)$SiMe_3$ (**1**),[6] and (chloromethyl)pentamethyldisilane[18] were synthesized using literature methods. Lithium diisopropylamide (LDA) was freshly prepared from *n*-BuLi and diisopropylamine. NMR spectra were recorded on a Bruker 300 MHz spectrometer in C_6D_6, except where indicated. Infrared spectra were recorded on an ATI Mattson Infinity Series FTIR. Elemental analyses were performed by Galbraith Laboratories.

Crystals of **5** and **7** were mounted on glass fibers. The X-ray intensity data were measured on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube (λ = 0.710 73 Å). Frames were collected with a scan width of 0.30° in ω and an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The structures were solved and refined using the Bruker SHELXTL (version 6.1012) software package. The corresponding experimental parameters for each compound are summarized in Table 1 and selected bond lengths and angles in Table 2.

Table 2. Selected Geometrical Parameters for 5 and 7

Compound **5**			
Fe(1)−C(9)	1.731(2)	Si(1)−C(1)	1.865(2)
O(1)−C(9)	1.147(2)	Si(1)−C(6)	1.850(3)
Fe(1)−C(28)	2.068(2)	Si(1)−C(7)	1.867(3)
Fe(1)−P(1)	2.1873(6)	Si(1)−C(8)	1.860(3)
C(9)−Fe(1)−C(28)	88.78(10)	C(28)−Fe(1)−P(1)	90.65(7)
C(9)−Fe(1)−P(1)	93.79(7)	O(1)−C(9)−Fe(1)	177.9(2)
C(9)−Fe(1)−P(1)−C(22)			−58.46(10)
C(9)−Fe(1)−P(1)−C(16)			179.70(10)
C(9)−Fe(1)−P(1)−C(10)			61.33(10)
C(6)−Si(1)−C(1)−Fe(1)			52.61(19)
C(7)−Si(1)−C(1)−Fe(1)			172.95(16)
C(8)−Si(1)−C(1)−Fe(1)			−69.39(18)
C(9)−Fe(1)−C(1)−Si(1)			30.66(16)
C(28)−Fe(1)−C(1)−Si(1)			−60.52(16)
P(1)−Fe(1)−C(1)−Si(1)			153.44(8)
Si(1)−C(1)−C(2)−C(3)			−176.00(15)
Compound **7**			
Fe(1)−C(9)	1.719(3)	Si(2)−C(29)	1.883(4)
Fe(1)−P(1)	2.1945(8)	Si(2)−C(30)	1.898(3)
Fe(1)−Si(2)	2.3565(9)	Si(3)−C(33)	1.863(4)
Si(1)−C(1)	1.868(3)	Si(3)−C(31)	1.865(4)
Si(1)−C(6)	1.836(5)	Si(3)−C(32)	1.867(4)
Si(1)−C(7)	1.854(5)	Si(3)−C(30)	1.868(3)
Si(1)−C(8)	1.856(4)	O(1)−C(9)	1.158(4)
Si(2)−C(28)	1.904(3)		
C(9)−Fe(1)−P(1)	95.46(11)	C(33)−Si(3)−C(32)	107.5(2)
C(9)−Fe(1)−Si(2)	81.54(11)	C(31)−Si(3)−C(32)	108.1(2)
P(1)−Fe(1)−Si(2)	99.27(3)	C(33)−Si(3)−C(30)	113.08(19)
C(29)−Si(2)−Fe(1)	119.41(12)	C(31)−Si(3)−C(30)	110.14(18)
C(28)−Si(2)−Fe(1)	107.33(13)	C(32)−Si(3)−C(30)	108.52(17)
C(30)−Si(2)−Fe(1)	114.24(10)	O(1)−C(9)−Fe(1)	177.1(3)
C(33)−Si(3)−C(31)	109.4(2)	Si(3)−C(30)−Si(2)	122.52(17)
C(9)−Fe(1)−P(1)−C(22)			−51.29(16)
C(9)−Fe(1)−P(1)−C(16)			−176.67(14)
C(9)−Fe(1)−P(1)−C(10)			65.72(15)
C(9)−Fe(1)−Si(2)−C(30)			168.81(15)
C(6)−Si(1)−C(1)−Fe(1)			33.2(3)
C(7)−Si(1)−C(1)−Fe(1)			−92.1(3)
C(8)−Si(1)−C(1)−Fe(1)			151.9(3)
C(9)−Fe(1)−C(1)−Si(1)			−27.5(3)
P(1)−Fe(1)−C(1)−Si(1)			75.7(3)
Si(2)−Fe(1)−C(1)−Si(1)			−117.8(2)
Si(1)−C(1)−C(2)−C(3)			167.2(2)
Fe(1)−Si(2)−C(30)−Si(3)			145.89(16)



$\alpha_1 = 129$
$\beta_1 = 116$
$\gamma_1 = 115$

$\alpha_2 = 137$
$\beta_2 = 123$
$\gamma_2 = 100$

Figure 6. Angles between each pair of substituents about the Fe atom for **5** and **7**.

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Synthesis of Sodium Diisopropylamide (NADA). A 50 mL Schlenk flask was charged with 0.60 g (6.2 mmol) of *t*-BuONa and LDA (6.8 mmol) in hexanes (20 mL) at room temperature. The insoluble *t*-BuONa very rapidly dissolves upon addition of LDA, followed by the immediate precipitation of NADA. After 3 h of stirring, the solid white precipitate was allowed to sit for 30 min and settle to the bottom of the flask. The hexanes (and soluble LDA and *t*-BuOLi) were removed via syringe. Approximately 10 mL of dry hexanes was then added to the NADA, and the mixture was stirred for 10 min and allowed to sit and settle for 30−40 min, upon which the solvent removal was repeated. This process of washing NADA was repeated three times. If the NADA was to be used in a THF solution, then all hexanes were removed via vacuum, the flask with NADA was cooled to −52 °C, and THF (5 mL) was added via syringe. If, however, the NADA was to be used as a hexanes slurry, a larger (200 mL) Schlenk flask was used to prepare NADA, and approximately 150 mL of hexanes at room temperature was added after the last wash to create the slurry needed.

Synthesis of (η^5-$Me_3SiC_5H_4$)Fe(CO)(PPh_3)Me (5). A 50 mL Schlenk flask was charged with 1 g of **1** (2.1 mmol) in 20 mL of THF. The solution was cooled to −78 °C, after which a precooled (−52 °C) THF solution of NADA was added dropwise via syringe. The reaction mixture was maintained at −78 °C for the formation of the salt $[(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)(PPh_3)]^-Na^+$, whose formation was monitored by IR (ν_{CO} at 1730 cm^{-1}). When all the starting material was consumed and complete formation of the anion was observed (approximately 15 min), the reaction was quenched with methyl iodide (6.2×10^{-3} mol, 0.87 g, 0.38 mL) and the mixture was warmed to room temperature and stirred for 16 h. The solvent was removed under reduced pressure, the product was extracted with a solvent mixture of 80 mL of hexanes and 2 mL of benzene, and the extract was subsequently filtered to remove NaCl. The crude material was purified by column chromatography using silica and eluted with a hexanes/benzene solution (80:20) to afford solid red crystalline (η^5-$Me_3SiC_5H_4$)Fe(CO)(PPh_3)Me (**5**): yield 0.612 g (59%); mp 164−166 °C.

^{1}H NMR (C_6D_6): δ 0.30 (3H, s, CH_3); 0.41 (9H, s, $Si(CH_3)_3$); 7.6−6.9 (15H, m, Ph); 4.6, 4.5, 4.2, 3.8 (4H, m, C_5H_4). ^{13}C NMR (C_6D_6): δ −20.7 ($\mathit{C}H_3$, d, $^2J_{13}\mathrm{C}-^{31}\mathrm{P}$ = 21.8 Hz); 0.38 (CpSi*Me*$_3$); 81.9, 85.2, 86.9, 89.6, 103.3 (C_5H_4); 137.7 (d, $^1J_{13}\mathrm{C}-^{31}\mathrm{P}$ = 39.2 Hz), 133.6 (d, $^2J_{13}\mathrm{C}-^{31}\mathrm{P}$ = 9.4 Hz), 128.2 (d, $^3J_{13}\mathrm{C}-^{31}\mathrm{P}$ = 9.4 Hz), 129.5 (d, $^4J_{13}\mathrm{C}-^{31}\mathrm{P}$ = 1.5 Hz) (Ph); 224.3 (*C*O, d, $^2J_{13}\mathrm{C}-^{31}\mathrm{P}$ = 34.2 Hz). ^{29}Si NMR (C_6D_6): δ −3.6 (Cp−$SiMe_3$). ^{31}P NMR (C_6D_6): δ 86.9. IR (CCl_4): ν_{CO} 1910 cm^{-1}. Anal. Calcd for $C_{28}H_{31}OPSi$: C, 67.46; H, 6.27. Found: C, 67.51; H, 6.08.

Synthesis of (η^5-$Me_3SiC_5H_4$)Fe(CO)(PPh_3)$SiMe_3$ (6). One gram (1 g) of **1** (2.1 mmol) was added to a NADA slurry in 200 mL of hexanes at room temperature. The slurry was stirred for 3 h until the formation of the salt $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(CO)(PPh_3)]^-Na^+$, whose formation was monitored by IR (ν_{CO} at 1693 cm^{-1}), was complete. The reaction mixture was cooled to 0 °C, quenched with freshly distilled trimethylchlorosilane (0.673 g, 6.2 mmol), warmed to room temperature, and stirred for 16 h. The product was directly filtered to remove NaCl. The crude material was purified by column chromatography using neutral alumina and eluted with a hexanes/benzene solution (80:20) to afford solid orange crystalline (η^5-$Me_3SiC_5H_4$)Fe(CO)(PPh_3)$SiMe_3$.

Alternative Synthesis of 6. The above synthetic method was repeated, with the exception that the $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(CO)(PPh_3)]^-Na^+$ salt was quenched with chloromethyldimethylsilane (6.2 mmol, 0.672 g, 0.752 mL). Workup as above resulted in a 68% yield of (η^5-$Me_3SiC_5H_4$)Fe(CO)(PPh_3)$SiMe_3$.

Note on Synthesis of 7. The formation of **7** is a result of quenching $[(\eta^5\text{-}Me_3SiC_5H_4)Fe(CO)(PPh_3)]^-Na^+$ with chloromethylpentamethyldisilane (6.2 mmol, 1.12 g). Workup as above resulted in a 58% yield of (η^5-$Me_3SiC_5H_4$)Fe(CO)(PPh_3)$SiMe_2CH_2SiMe_3$.

Data for (η^5-$Me_3SiC_5H_4$)Fe(CO)(PPh_3)$SiMe_3$ (6). Yield: 0.432 g (38%) (yield is when R = $ClCH_2SiMe_2$; when R = $ClSiMe_3$ the yields are lower, 14%). ^{1}H NMR (C_6D_6): δ 0.41 (18H, s, $Si(CH_3)_3$); 7.7−7.0 (15H, m, Ph); 4.5, 4.3, 4.2, 3.6 (4H, m, C_5H_4). ^{13}C NMR (C_6D_6): δ 90.6, 89.6, 89.0, 88.8, 82.2 (C_5H_4); 221.2 (*C*O, d, $^2J_{13}\mathrm{C}-^{31}\mathrm{P}$ = 27.6 Hz); 0.12 (CpSi*Me*$_3$); 9.3 (Fe−Si*Me*$_3$); 139.2 (d, $^1J_{13}\mathrm{C}-^{31}\mathrm{P}$ = 40.0 Hz), 133.8 (d, $^2J_{13}\mathrm{C}-^{31}\mathrm{P}$ = 10.2 Hz), 129.4 (d, $^3J_{13}\mathrm{C}-^{31}\mathrm{P}$ = 2.2 Hz) (Ph). ^{29}Si NMR (C_6D_6): δ −3.5 (Cp−$SiMe_3$); 32.9 (d, $^2J_{29}\mathrm{Si}-^{31}\mathrm{P}$ = 31.6 Hz). ^{31}P NMR (C_6D_6): δ 81.3. IR (hexanes): ν_{CO} 1907 cm^{-1}. Anal. Calcd for $C_{30}H_{37}OPSi_2$: C, 64.74; H, 6.71. Calcd: C. 64.95; H. 6.72.

Data for (η^5-$C_5H_4SiMe_3$)Fe(CO)(PPh_3)$SiMe_2CH_2SiMe_3$ (7). Yield: 0.33 g (25%). ^{1}H NMR (C_6D_6): δ 0.53 (3H, s, Si−CH_3); 0.43 (3H, s, Si−CH_3 and 9H, s, C−$Si(CH_3)_3$); 0.01 (1H, d, CH); 0.10 (1H, d, CH); 0.19 (9H, s, Cp−$Si(CH_3)_3$); 7.7−7.0 (15H, m, Ph); 3.6, 4.2, 4.3, 4.5 (4H, m, C_5H_4). ^{13}C NMR (C_6D_6): δ 0.67 (CpSi*Me*$_3$); 2.6 (C−Si($\mathit{C}H_3$)$_3$; 9.6 (FeSi−$\mathit{C}H_3$); 10.4 (FeSi−$\mathit{C}H_3$); 13.1 (*C*−$Si(CH_3)_3$); 221.8 (*C*O, d, $^2J_{13}\mathrm{C}-^{31}\mathrm{P}$ Hz); 139.4 (d, $^1J_{13}\mathrm{C}-^{31}\mathrm{P}$ = 39.2 Hz), 133.9 (d, $^2J_{13}\mathrm{C}-^{31}\mathrm{P}$ = 10.2 Hz), 129.4 (d, $^3J_{13}\mathrm{C}-^{31}\mathrm{P}$ = 2.2 Hz) (Ph); 91.1, 89.9, 89.3, 82.6, 82.57 (C_5H_4). ^{29}Si NMR (C_6D_6): δ −3.5 (Cp*Si*Me_3); 35.3 (d, $^2J_{29}\mathrm{Si}-^{31}\mathrm{P}$ = 31.1 Hz); 0.14 (CH_2*Si*Me_3). ^{31}P NMR (C_6D_6): δ 80.9. IR (hexanes): ν_{CO} 1911 cm^{-1}.

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Supporting Information Available: CIF files giving crystallographic data for **5** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org. These data were also deposited at the CCDC with deposit numbers 737883 and 737882, respectively, and can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.