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Insertion reactions of electrophilic iron carbene complexes with organosilanes: a synthetic and mechanistic study ☆

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Abstract

Cationic iron carbene complexes of the type $Cp(L)(CO)Fe{=}C(H)(R)^+$ ($L{=}PPh_3$, $R{=}CH_3$,Ph), ($L{=}PEt_3$, R=Ph, CH_3, CH_2CH_3, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_2CH_3$) have been prepared and shown to react with organosilanes to give the products resulting from insertion of the carbene unit into the Si–H bond. These reactions occur rapidly at low temperature, but yields are ca. 50% and a counterion-dependent by-product is formed. A mechanism consistent with the experimental observations is proposed. Variable temperature NMR studies are reported which have allowed for the independent observation of several of the intermediates proposed in the mechanistic pathway.

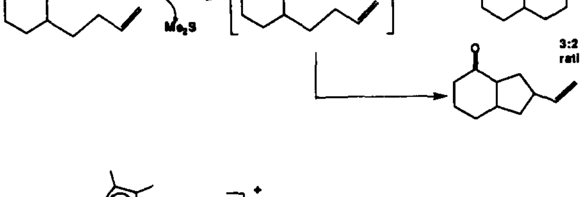
Keywords: Iron; Silicon; Iron carbene complexes; Insertion reactions; Reaction mechanism

1. Introduction

Numerous isolable or spectroscopically observable transition metal carbene complexes have been shown to carry out stoichiometric carbene transfer reactions with alkenes to generate cyclopropanes [1–9]. These well characterized complexes have served as models for transient metal carbene complexes presumed to be intermediates in catalytic cyclopropanation reactions [10]. While not widely used synthetically, studies of cyclopropanation reactions using stable carbene complexes have provided detailed information concerning the mechanism of the transfer reaction.

Numerous examples of metal-catalyzed carbene insertion reactions have been reported, particularly intramolecular insertions [11,12], but few studies have focused on stoichiometric insertions employing stable or spectroscopically observable transition metal carbene complexes. Fischer et al. demonstrated that the tungsten phenyl carbene complex $(CO)_5W{=}C(H)Ph$ reacts with diethyl ether and THF to give products resulting from insertion of the carbene moiety into the C–H bond alpha to oxygen (Eq. (1)) [13]. Helquist et al. reported an example of an intramolecular C–H insertion in competition with intramolecular cypropanation upon generation of a transient iron carbene complex (Eq. (2)) [14]. Guerchais et al. have shown that the cationic methoxycarbene complex, $Cp(CO)_2Fe{=}C(H)(OCH_3)^+$ reacts with triethylsilane to generate the insertion product $Et_3SiCH_2OCH_3$ (Eq. (3)) [15]

(1)



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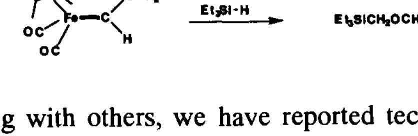

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Along with others, we have reported techniques for preparing nonheteroatom-stabilized carbene complexes

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☆ Dedicated to Professor Hans-H. Brintzinger on the occasion of his 60th birthday.

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of the type $Cp(CO)(L)Fe{=}C(H)(R)^+$, as well as reactions of these species with olefins to generate cyclopropanes [1–8,16]. In view of the extensive cyclopropanation chemistry reported for these species, we wished to extend the scope of reactivity of these species to include insertion into X–H bonds. A study of the reactions of these species $Cp(CO)(L)Fe{=}C(H)(R)^+$ (R = Ph, CH_3, L = PPh_3; R = Ph, CH_3, CH_2CH_3, $(CH_2)_3CH_3$, $(CH_2)_4CH_3$, L = PEt_3) with various organosilanes to yield insertion products is reported here.

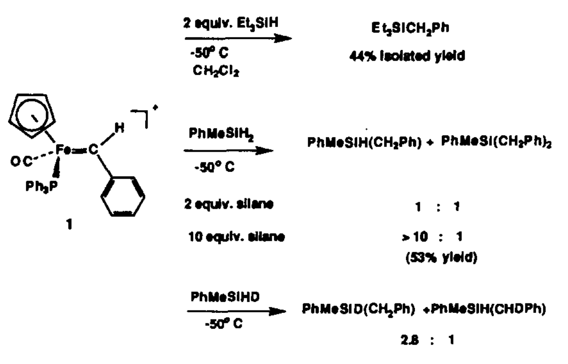
2. Results and discussion

2.1. Insertion chemistry of phenyl carbene complexes

The phenyl carbene complex $Cp(CO)(PPh_3)Fe{=}C(H)(Ph)^+$ (**1**), reacts with triethylsilane and methylphenylsilane to give the products of insertion of the carbene unit into the Si–H bond (Scheme 1) [17]. Using methods previously described [16], **1** was generated at −78 °C and treated with two equivalents of Et_3SiH. No reaction occurred at −78 °C, but upon warming to −50 °C the solution changed rapidly from a dark orange color to a deep green color. Upon workup, Et_3SiCH_2Ph was obtained in a 44% yield.

Insertion reactions using **1** and $PhMeSiH_2$ were also examined. Using two equivalents of $PhMeSiH_2$, significant amounts of both mono and di-insertion products, phenylmethylbenzylsilane and phenylmethyldibenzylsilane were obtained, indicating that the second insertion is competitive with the first insertion. The di-insertion product could be avoided by employing 10 equivalents of $PhMeSiH_2$ and with this procedure, only the mono-insertion product was obtained in a 53% yield.

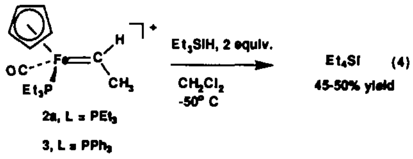
The kinetic isotope effect of the insertion reaction was investigated by using phenylmethylmonodeuterosilane (PhMeSiHD) which was synthesized by the reduction of phenylmethylchlorosilane with lithium aluminum deuteride. The labeled silane (10 equivalents) was treated with **1** and products from insertion into both the Si–H bond and the Si–D bond were obtained. Analysis by ^1H NMR spectroscopy indicated that formation of $PhMeSi(D)CH_2Ph$, (the product of insertion into the Si–H bond) was favored by a factor of 2.8 over PhMeSi(H)CHDPh which is indicative of significant Si–H(D) bond breaking in the transition state for insertion [18].



Scheme 1.

2.2. Insertion reactions of alkyl-substitued carbene complexes, $Cp(CO)(PR_3)Fe{=}C(H)(R)^+$ ($R = CH_3$, C_2H_5, C_4H_9, C_5H_{11})

Insertion reactions of methyl substituted carbene complexes $Cp(CO)(PEt_3)Fe{=}C(H)(CH_3)^+$ (**2**) and $Cp(CO)(PPh_3)Fe{=}C(H)(CH_3)^+$ (**3**) were also investigated employing Et_3SiH. The carbene complexes were generated in situ in CH_2Cl_2 by reaction of the α-ether complexes $Cp(CO)(L)FeC(H)(OCH_3)(CH_3)$ (L = PPh_3, PEt_3) with trimethylsilyltriflate as previously reported [16]. As in the case of the phenyl carbene complex, treatment of these −78 °C solutions with 2 equivalents of Et_3SiH results in no immediate reaction. Raising the temperature to −50 °C induces a rapid reaction and color change to green. In each case, the insertion product, Et_4Si, is formed in ca. 50% yield:



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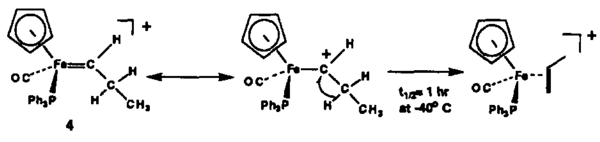
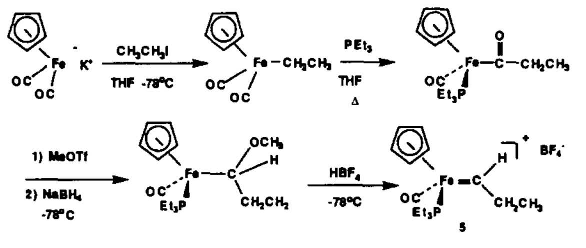


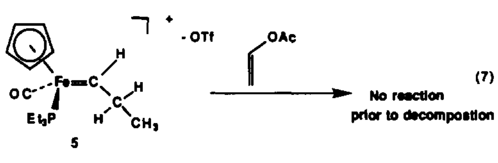
(5)

Most reactivity studies on cationic iron carbene complexes of the type $Cp(CO)(L)Fe{=}C(H)(R)^+$ have involved systems containing methyl or phenyl substituents on C_α. There are far fewer examples of longer chain alkyl carbene complexes due to the fact that they undergo a rapid isomerization via a 1,2-hydride migration from C_β to C_α. In the transition state for this process, substantial positive charge buildup occurs at C_β which is stabilized by the β alkyl substituent. For example, complex **4** undergoes rapid hydride migration from C_β to the electrophilic C_α carbon atom even at low temperatures (Eq. 5) [19]. In an attempt to stabilize these alkyl-substituted carbene complexes, the PPh_3 ligand was replaced by the more electron-donating PEt_3 ligand. This substitution was expected to reduce the electrophilicity of C_α and significantly retard the rate of 1,2-hydride migration. The PEt_3-substituted ethyl carbene complex, **5**, was synthesized using standard methods [16]. $Cp(CO)_2Fe^-K^+$ was treated with iodoethane to give the iron ethyl complex which was then thermolyzed in the presence of PEt_3 to yield the phosphine-substituted acyl complex. Subsequent methylation with methyl triflate followed by treatment with $NaBH_4$ gave the α-ether complex:



(6)

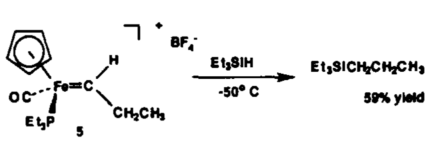
Carbene complex **5** was generated and spectroscopically observed at low temperature [20]. At −100 °C, two rotamers were observed with resonances for H_α at 17.5 and 15.5 ppm. Complex **5** did not decompose until 0 °C whereas the PPh_3 analog had a half-life of only 1 h even at −40 °C. However, the decrease in electrophilicity at C_α not only slows hydride migration, but concurrently reduces the reactivity of the carbene complex. As a consequence, complex **5** did not react with vinyl acetate to give cyclopropanes prior to decomposition



(7)

Stable up to 0 °C

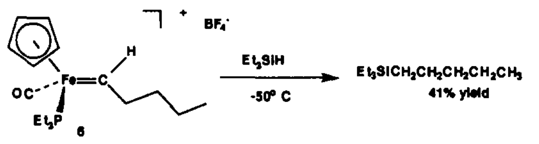
As noted earlier, the Si–H insertion reactions of complexes **1**, **2** and **3** occurred at low temperature (ca. −50 °C). While cyclopropanation was unsuccessful, complex **5** is stable indefinitely at −50 °C and thus Si–H insertion chemistry appeared feasible. Indeed, generation of **5** at −78 °C in CH_2Cl_2 and treatment with two equivalents of triethylsilane at −50 °C gave triethylpropylsilane, the insertion product, in 59% yield:



(8)

From these results, it can be inferred that insertion of the carbene moiety into a Si–H bond occurs significantly faster than both the cyclopropanation reaction and 1,2-hydride migration which results in decomposition of the carbene complex.

As an extension of this methodology, two other long chain alkyl carbene complexes were synthesized using the same procedure as shown in Eq. (6). As noted below, both the butyl, (**6**) and pentyl (**7**) carbene complexes react with triethylsilane to give triethylpentylsilane and triethylhexylsilane, respectively:



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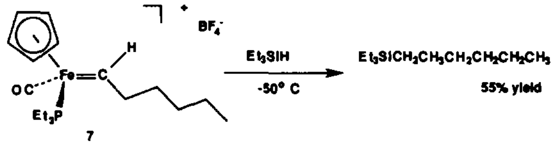
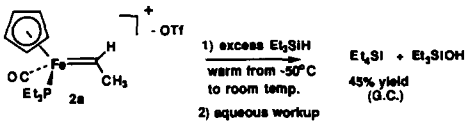


(10)

2.3. Mechanistic studies

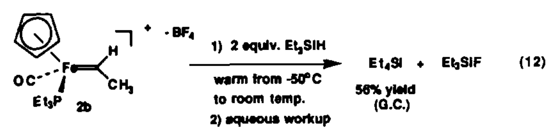
It was clear that the electrophilic iron carbene complexes were capable of carrying out insertion reactions with organosilanes, and as noted in the previous section, the insertion reactions occur rapidly at very low temperatures (−50 °C). Since decomposition of the carbene complexes at these temperatures is quite slow, we expected that the yields of these reactions should be high. However, the yields were consistently around 50% and this led us to investigate the reaction sequence more closely in an attempt to explain the apparent anomalies.

A careful analysis of products from a typical insertion reaction was carried out. $Cp(CO)(PEt_3)Fe{=}C(H)(CH_3)^+$ OTf (**2a**) was treated with excess Et_3SiH and the products were examined by gas chromatography (Eq. (11)). In addition to Et_4Si, Et_3SiOH was also present. This was thought to be a by-product formed upon hydrolysis of Et_3SiOTf which most likely forms upon reaction of the counterion with some intermediate.



(11)

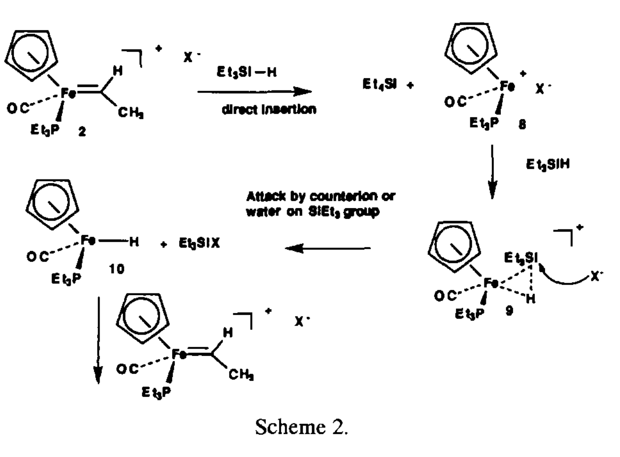
More evidence for this hypothesis was obtained when the insertion reaction was carried out with the BF_4^- salt of the carbene complex, **2b** (Eq. (12)). Upon examination of the products of this reaction, only trace amounts of Et_3SiOH were detected (< 1%). Now, however, triethylsilylfluoride, a byproduct derived from the BF_4^- counterion, was present along with tetraethylsilane in approximately a 1 : 1.5 ratio.



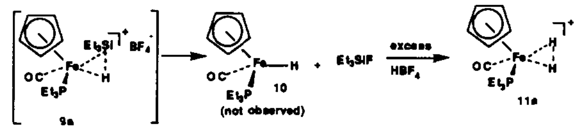
(12)

The consistent formation of insertion products in ca. 50% yields and the counterion-dependent formation of by-products, R_3SiX, led us to propose the general reaction sequence shown in Scheme 2.The initial step involves the direct insertion of the carbene moiety of **2** into the Si–H bond which gives Et_4Si and a cationic iron fragment, **8**. This highly electrophilic, unsaturated iron center can coordinate free silane giving a nonclassically bound silane complex **9**, for which there is some precedent [21]. By binding to the metal center, the silicon atom is rendered highly electrophilic and is therefore extremely susceptible to nucleophilic attack by counterion (OTf^-, BF_4^-) or trace water. This leads to formation of the by-product (Et_3SiX) and a neutral iron hydride, **10**. The electron-rich iron hydride species is likely to be quite reactive toward the highly electrophilic carbene complex, but the nature of the reaction products which may result is unclear [22]. If the steps subsequent to initial insertion are rapid relative to this insertion, then two equivalents of carbene complex are consumed for each equivalent of insertion product generated. Therefore, yields based on the carbene complex will fall in the 50% range [23].

Several additional experiments were carried out, the results of which support the general mechanistic scheme proposed. Particularly informative was a low temperature NMR study of the silane insertion reaction. The carbene complex, $Cp(CO)(PEt_3)Fe{=}C(H)(CH_3)^+BF_4^-$ (**2b**) was generated by protonation of the α-ether complex with excess HBF_4 and observed by ^1H NMR spectroscopy at low temperature. At −80 °C, two equivalents of Et_3SiH were added and the sample was warmed slightly and returned to the NMR probe (−80 °C). Immediate observation indicated that the carbene complex had been completely consumed. No intermediates were observed, but Et_4Si and Et_3SiF were observed as expected. The major organometallic species formed was the cationic η^2-H_2 complex, **11a**. These observations are consistent with Scheme 2. Insertion generates Et_4Si and $Cp(CO)(PEt_3)Fe^+$ (**8**) which then coordinates Et_3SiH to give complex **9a**. This species is not observed but, as presumed in Eq. (13), reacts rapidly with BF_4^- to generate Et_3SiF and $Cp(CO)(PEt_3)FeH$, **10**. In the presence of excess HBF_4, the Fe–H complex is rapidly protonated to generate the observed cationic iron η^2-H_2 complex, **11a** [24].

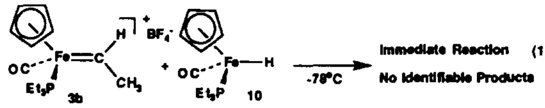


Scheme 2.



(13)

Experiments were also performed to probe the reactivity of the iron hydride complex **10** with carbene complex **2b**, which is the final step in the reaction sequence shown in Scheme 2. The PEt_3-substituted iron hydride, **10** [25] was added to a −78 °C solution of **2b** and an instantaneous color change occurred.



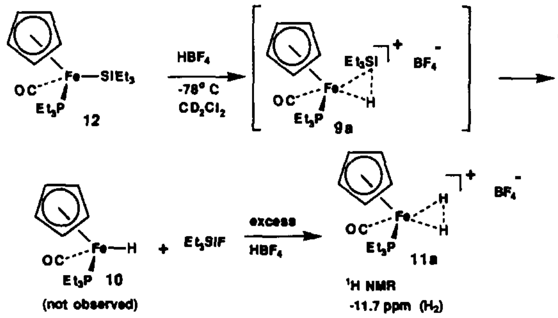
(14)

Unfortunately, no identifiable products could be isolated. But, this experiment clearly shows that the iron hydride and the carbene complex react rapidly at temperatures far below that required for insertion to occur (−50 °C), and this lends support to Scheme 2.

Low temperature NMR spectroscopy was next utilized in an attempt to observe the initially formed products in this reaction. For this experiment, the PPh_3-substituted iron hydride complex was employed because of its relative ease of handling compared with the PEt_3 analog. Complex **2b** was generated and observed by ^1H NMR spectroscopy at −80 °C. Upon addition of the iron hydride at this temperature, the solution darkened slightly. Immediate NMR observation at −80 °C showed that none of the carbene complex remained and that a complex mixture of organometallic products was present which could not be identified. This experiment further confirmed that the reaction of an iron hydride complex with a cationic carbene complex is rapid at low temperature.

Finally, we sought spectroscopic evidence for the cationic iron η^2-silane complex **9** that was proposed as a key intermediate in Scheme 2. We felt that these compounds could be accessed by protonation of neutral iron silyl complexes, but since the cationic species were expected to be highly reactive, we attempted to observe them by low temperature NMR spectroscopy.

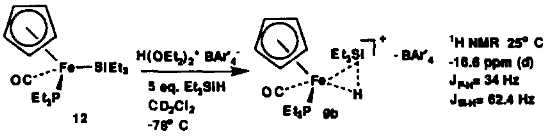
$Cp(CO)(PEt_3)FeSiEt_3$, (**12**) was prepared by methods described elsewhere [23] and was protonated with HBF_4 at low temperature. Protonation should occur across the Fe–Si bond giving the nonclassically bound silane complex, **9a**. However, even at −90 °C, the only organometallic species observed by ^1H NMR spectroscopy was an η^2-H_2 complex **11a**. Et_3SiF, the expected product from reaction of the silane complex with the counterion, was also observed. This is consistent with the NMR observations made for the insertion reaction (Eq. (13)). As noted earlier, the best way to account for these products is through the initial formation of an η^2-silane complex, **9a**, followed by the reactions shown in Eq. (15).



(15)

Although this experiment provided strong evidence for the intermediacy of an η^2-silane complex, we wished to actually observe such a species. The BAr'^-_4 counterion (Ar′ = bis(3,5-trifluoromethyl)phenyl) is a nonreactive, noncoordinating counterion that has been used successfully to stabilize highly electrophilic organometallic complexes [27]. These features are necessary in a counterion if the cationic silane complex is to be observed since BF_4^-, usually considered a nonreactive counterion, reacted rapidly with **9a**.

In the same manner as before, the neutral iron silyl complex **12** was protonated in an NMR tube at −78 °C (Eq. (16)). But this time, $H(OEt_2)_2^+$ BAr'^-_2 was used as the acid instead of HBF_4.



(16)

At −80 °C, the silane complex **9b** was observed, and in fact it was even stable at room temperature in the presence of excess silane [26]. Silicon satellites were discernible and a value of $J_{Si-H} = 62$ Hz was obtained, which is consistent with a non-classically bound silane complex as shown [21]. This observation provides strong evidence for this type of intermediate in the insertion pathway as is proposed in Scheme 1.

2.4. Conclusions

Electrophilic iron carbene complexes of the type $Cp(CO)(PR_3)Fe{=}C(H)(R)^+$ (R = CH_3, Ph) were shown to carry out insertion reactions with organosilanes. Long chain alkyl carbene complexes, which do not carry out cyclopropanation reactions, were shown to be effective for insertion chemistry. Although reaction of the carbene complexes with organosilanes was rapid at low temperature, yields were moderate. Mechanistic studies were carried out to investigate this problem and a counterion-dependent by-product was found to form in competition with the insertion product. Through further experiments it was determined that after the carbene complex reacts with the silane to give the insertion product, the resultant cationic iron fragment reacts with free silane to give a highly reactive cationic iron silane complex, which has been independently observed. This complex rapidly reacts with the counterion giving the by-product (Et_3SiX) and a neutral iron hydride complex. The latter species has been shown to react rapidly with the carbene complex at temperatures much lower than those required for insertion which limits the amount of carbene complex available for insertion. This mechanism thus accounts for both the moderate yields of insertion product and the formation of the by-product.

3. Experimental

3.1. General

Unless otherwise noted, all reactions were carried out under a dry N_2 atmosphere using Schlenk techniques or a Vacuum Atmospheres dry box. Methylene chloride was distilled from P_2O_5; THF, Et_2O, hexanes, and toluene were distilled from sodium-benzophenone ketyl and methanol was distilled from $Mg(OMe)_2$ prior to use. Solvents used for chromatography were degassed via a N_2 purge for 10 min. Fisher brand alumina (80–200 mesh) was used for chromatography. CD_2Cl_2 was dried over CaH_2 and vacuum transferred to a Kontes flask. C_6D_6 was used as received. $Cp(CO)_2Fe^-K^+$ was prepared by a published method [28], as were the carbene complexes $Cp(CO)(PR_3)Fe{=}C(H)(R)^+$ (R=CH_3, Ph) [16]. Et_3SiH, $PhMeSiH_2$, ethyl iodide, butyl iodide, and pentyl iodide were used as received from Aldrich or Petrarch. TMSOTf and MeOTf were transferred to Kontes flasks in the dry box and stored under N_2.

^1H and ^{13}C NMR spectra were recorded on Bruker AC-200, WM-250 and Varian XL-400 spectrometers. Chemical shifts were referenced using the protonated residue of the deuterated solvents ($C\mathit{H}Cl_3$, δ 7.24 ppm, $CD\mathit{H}Cl_2$, δ 5.32 ppm, $C_6\mathit{H}D_5$ δ 7.15 ppm). IR spectra were taken in solution using a CaF_2 cell on a

Mattson Polaris FT–IR spectrometer. Gas chromatographic experiments were conducted on a Hewlett Packard 5890 gas chromatograph using a 20 ft × 1/4 inch column of 20% QF-1 on Chromasorb (thermal conductivity detector) or a 30 m DB-5 capillary column (flame ionization detector). Elemental analyses were performed by Oneida Research Services of Whitesboro, NY.

3.2. General syntheses of Cp(CO)$_2$FeR complexes

All of the long chain alkyl complexes were synthesized in the same manner with the only difference being the starting alkyl halide.

3.2.1. R = CH$_2$CH$_3$

Cp(CO)$_2$Fe$^-$K$^+$ (0.49 g, 2.3 mmol) was weighed into a Schlenk flask in the drybox and dissolved in ca. 130 ml of freshly distilled THF. The stirring solution was cooled to −50 °C and then 1.5 equivalents of ethyl iodide (0.55 g, 3.5 mmol) were syringed into the flask. The reaction mixture was allowed to slowly warm to room temperature at which time the reaction was determined to be complete by IR spectroscopy. The KI salts were allowed to settle and the brown solution was then transferred via cannula through Celite and collected in another flask. Solvent was removed in vacuo giving a brown oil which was redissolved in 2-methylbutane and chromatographed on an alumina column. A yellow band quickly eluted and was collected as a yellow liquid. Solvent was removed giving FpCH$_2$CH$_3$ (0.30 g, 64% yield) as a brown oil. Note: the lower molecular weight iron alkyl complexes, such as this one, are prone to sublimation upon prolonged exposure to a vacuum. ^{1}H NMR (CD$_2$Cl$_2$) δ 4.8 ppm (s, C$_5$H$_5$); 1.57 (q, J_{HH} = 7.2 Hz, CH$_2$); 1.25 (t, J_{HH} = 7.2 Hz, CH$_3$). ^{13}C{^{1}H}NMR (C$_6$D$_6$, 25 °C) δ 218.2 ppm (*C*O); 85.3 (s, *C*$_5$H$_5$); 22.5 (s, CH$_3$); −2.8 (CH$_2$). IR (THF)ν(CO) (2000, 1942 cm^{-1}).

3.2.2. R = CH$_2$CH$_2$CH$_2$CH$_3$

FpCH$_2$CH$_2$CH$_2$CH$_3$ was obtained as a brown oil in a 92% yield. ^{1}H NMR (C$_6$D$_6$) δ 4.1 ppm (s, C$_5$H$_5$); 1.8–1.6, 1.2–0.8 (2 broad peaks, 9H CH$_2$CH$_2$CH$_2$CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C) δ 218 ppm (*C*O); 85.3 (*C*$_5$H$_5$); 41, 28.1, 14.0, 3.5 (CH$_2$CH$_2$CH$_2$CH$_3$). IR (THF)ν(CO) (2000, 1940 cm^{-1}).

3.2.3. R = CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$

FpCH$_2$CH$_2$CH$_2$CH$_2$CH$_3$ was obtained as a brown oil in a 92% yield. ^{1}H NMR (C$_6$D$_6$) δ 4.0 ppm (s, C$_5$H$_5$); 1.6–0.6 (3 broad peaks, 11 H, CH$_2$CH$_2$CH$_2$ CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C) δ 218 ppm (*C*O); 85.3 (*C*$_5$H$_5$); 38.4, 32.7, 22.8, 14.5, 3.9 (CH$_2$CH$_2$CH$_2$CH$_2$-CH$_3$). IR (THF)ν(CO) (2000, 1940 cm^{-1}).

3.3. Synthesis of Cp(CO)(PEt$_3$)FeC(O)R complexes

3.3.1. R = CH$_2$CH$_3$

FpCH$_2$CH$_3$ (0.3 g, 2.3 mmol) was dissolved in 30 ml of THF in a reflux apparatus equipped with a sidearm. Nitrogen was introduced through the top of the condenser. PEt$_3$ (3 equivalents, 0.81 g, 6.9 mmol) was syringed into the reaction vessel and the mixture was heated to reflux. The reaction was monitored by IR spectroscopy and judged to be complete after 6 h. Solvent was removed leaving an orange oil. This was redissolved in 2-methylbutane and chromatographed on an alumina column. A yellow band (product) remained at the top of the column while starting material and excess phosphine were washed away. Diethyl ether was subsequently used as the eluant and the yellow band quickly eluted and was collected as an orange liquid. Removal of solvent gave 0.35 g (78% yield) of Cp(CO)(PEt$_3$)FeC(O)CH$_2$CH$_3$ as an orange oil. ^{1}H NMR (C$_6$D$_6$) δ 4.25 ppm (d, J_{PH} = 0.9 Hz, C$_5$H$_5$); 3.05 (q of d, J_{HH} = 7.4 Hz, J_{PH} = 2.4 Hz, C(O)C*H*$_2$); 1.5–1.2 (d of mult., 6H, PC*H*$_2$CH$_3$); 1.1 (t, J_{HH} = 7.4 Hz, CH$_3$); 0.78 (d of t, J_{PH} = 14.5 Hz, J_{HH} = 7.8 Hz, 9H, PCH$_2$C*H*$_3$). ^{13}C NMR (C$_6$D$_6$, 25 °C) δ 272.7 ppm (d, J_{PC} = 23 Hz, C(O)); 221.2 (d, J_{PC} = 31 Hz, CO); 83.3 (m, J_{CH} = 176 Hz, *C*$_5$H$_5$); 59.2 (t of mult., J_{CH} = 127 Hz, J_{PC} = 5 Hz, C(O)*C*H$_2$); 20.6 (t of d, J_{CH} = 127 Hz, J_{PC} = 25 Hz, P*C*H$_2$CH$_3$); 10.4 (q, J_{CH} = 127 Hz, CH$_3$); 8.1 (q of d, J_{CH} = 127 Hz, J_{PC} = 3.0 Hz, PCH$_2$*C*H$_3$). IR (THF)ν(CO) (1905, 1608 cm^{-1}) Anal. Found: C, 55.51; H, 7.70. C$_{15}$H$_{25}$FeO$_2$P Calc.: C, 55.58; H, 7.78%.

3.3.2. R = CH$_2$CH$_2$CH$_2$CH$_3$

Using a similar procedure, Cp(CO)(PEt$_3$)FeC(O)-CH$_2$CH$_2$CH$_2$CH$_3$ was obtained as an orange solid in a 73% yield. ^{1}H NMR (C$_6$D$_6$) δ 4.25 ppm (d, J_{PH} = 1.0 Hz, C$_5$H$_5$); 3.15(t of d, J_{HH} = 6.9 Hz, J_{PH} = 2.6 Hz, C(O)C*H*$_2$); 1.8–1.2 (2 sets of mult., 10 H, C(O)CH$_2$C*H*$_2$C*H*$_2$CH$_3$ and PC*H*$_2$CH$_3$); 0.95 (t, J_{HH} = 7.8 Hz, CH$_3$); 0.8 (mult, PCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C) δ 272.6 ppm (d, J_{PC} = 24 Hz, C(O)); 221.2 (d, J_{PC} = 32 Hz, CO); 83.3 (s, C$_5$H$_5$); 66.5 (d, J_{PC} = 5 Hz, C(O)*C*H$_2$); 28.1, 23.0 (s, C(O)CH$_2$*C*H$_2$*C*H$_2$CH$_3$); 20.7 (d, J_{PC} = 25.0 Hz, P*C*H$_2$CH$_3$); 14.4 (s, CH$_3$); 8.0 (d, J_{PC} = 3 Hz, PCH$_2$*C*H$_3$). IR (Et$_2$O)ν(CO) (1911, 1612 cm^{-1}). Anal. Found C, 58.28; H, 8.41. C$_{17}$H$_{29}$FeO$_2$P Calc.: C, 57.97, H, 8.30%.

3.3.3. R = CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$

Using the procedure described above, Cp(CO)(PEt$_3$)-FeC(O)CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$ was obtained as an orange solid in a 60% yield. ^{1}H NMR (C$_6$D$_6$) δ 4.25 ppm (d, J_{PH} = 1.1 Hz, C$_5$H$_5$); 3.1 (q, J_{HH} = 6.9 Hz, C(O)C*H*$_2$); 1.52–1.4 (mult, 12 H,

$\mathrm{C(O)CH_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3}$ and $\mathrm{PC\mathit{H}_2CH_3}$); 0.9 (t, $J_{\mathrm{HH}} = 6.9$ Hz, $\mathrm{CH_3}$); 0.78 (d of t, $J_{\mathrm{PH}} = 14.6$ Hz, $J_{\mathrm{HH}} = 7.7$ Hz, 9H, $\mathrm{PCH_2C\mathit{H}_3}$). $^{13}\mathrm{C}$ NMR ($\mathrm{C_6D_6}$, 25 °C) δ 272.9 ppm (d, $J_{\mathrm{PC}} = 23$ Hz, C(O)); 221.4 (d, $J_{\mathrm{PC}} = 30$ Hz, CO); 83.3 (mult, $J_{\mathrm{CH}} = 176$ Hz, $\mathit{C}_5\mathrm{H}_5$); 66.7 (t of d, $J_{\mathrm{CH}} = 126$ Hz, $J_{\mathrm{PC}} = 5$ Hz, $\mathrm{C(O)\mathit{C}H_2}$); (32.2 (t, $J_{\mathrm{CH}} = 128$ Hz), 25.7 (t, $J_{\mathrm{CH}} = 125$ Hz), 23.1 (t, $J_{\mathrm{CH}} = 121$ Hz), ($\mathrm{C(O)CH_2\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2CH_3}$)); 20.7 (t of d, $J_{\mathrm{CH}} = 127$ Hz, $J_{\mathrm{PC}} = 25$ Hz, $\mathrm{P\mathit{C}H_2CH_3}$); 14.3 (q, $J_{\mathrm{CH}} = 124$ Hz, $\mathrm{CH_3}$); 8.1 (q, $J_{\mathrm{CH}} = 127$ Hz, $\mathrm{PCH_2\mathit{C}H_3}$). IR ($\mathrm{Et_2O}$)ν(CO) (1909, 1608 $\mathrm{cm^{-1}}$). Elemental Anal. Found: C, 59.14; H, 8.48. $\mathrm{C_{18}H_{31}FeO_2P}$ Calc.: C, 59.03; H, 8.53%.

3.4. Synthesis of $\mathrm{Cp(CO)(PEt_3)FeC(H)(R)(OCH_3)}$

3.4.1. $R = \mathrm{CH_2CH_3}$

$\mathrm{Cp(CO)(PEt_3)C(O)CH_2CH_3}$ (1.14 g, 3.7 mmol) was dissolved in 20 ml of methylene chloride. Then, 2 equivalents of methyl triflate (Caution! HIGHLY TOXIC, 1.2 g, 7.4 mmol) were added to the stirring solution. After 1 h, methylation of the acyl oxygen was judged to be complete by IR spectroscopy (1969 $\mathrm{cm^{-1}}$). A solution of methanol/sodium methoxide was prepared by the addition of 8 equivalents of sodium (0.68 g, 30 mmol) to 160 ml of methanol. After the sodium had completely reacted, the solution was cooled to 0 °C, and 4 equivalents of $\mathrm{NaBH_4}$ (0.56g, 14.8 mmol) were added. The solution was allowed to stir for 45 min to dissolve the $\mathrm{NaBH_4}$.

The methoxy carbene solution was transferred via cannula into the methanol solution which had been cooled to −50 °C. An immediate color change from yellow to bright orange was observed. The stirring solution was allowed to warm to −10 °C at which point 150 ml of saturated aqueous $\mathrm{K_2CO_3}$ solution were added. (Note: the vinyl complex $\mathrm{Cp(CO)(PEt_3)FeCH\text{-}CH_2}$ can be formed upon elimination of MeOH from the α-ether. By keeping the solution at low temperature, formation of this by-product is avoided.) This mixture was stirred vigorously for 1 min and then allowed to settle. The organic layer was transferred via cannula into a flask containing $\mathrm{K_2CO_3}$ as a drying agent. The $\mathrm{K_2CO_3}$ solution was washed with two 50 ml portions of $\mathrm{CH_2Cl_2}$ and these were also dried. The orange solution was allowed to dry for fifteen minutes, and then it was filtered through a cannula into another flask. Solvent was removed in vacuo giving $\mathrm{Cp(CO)(PEt_3)FeC(H)(CH_2CH_3)(OCH_3)}$ (1.1 g, 91% yield) as an orange oil. $^1\mathrm{H}$ NMR spectroscopy indicated that two diastereomers were present in a 5.6 : 1 ratio. These were not separated. $^1\mathrm{H}$ NMR ($\mathrm{C_6D_6}$) δ 4.38 ppm (s, $\mathrm{C_5\mathit{H}_5}$, minor); 4.33 (s, $\mathrm{C_5\mathit{H}_5}$, major); 4.25–4.15 (mult., $\mathrm{C\mathit{H}(R)(OCH_3)}$, major); 3.86–3.80 (mult, $\mathrm{C\mathit{H}(R)(OCH_3)}$, minor); 3.47 (s, $\mathrm{OC\mathit{H}_3}$, major); 3.25 (s, $\mathrm{OC\mathit{H}_3}$, minor); 2.4–2.3, 2.2–2.1 (mult, 1H, $\mathrm{C\mathit{H}H'CH_3}$); 1.9–1.7 (mult, 1H, $\mathrm{C\mathit{H}H'CH_3}$); 1.5–1.2 (mult, 9H, $\mathrm{CH_3}$ and $\mathrm{PCH_2CH_3}$); 0.9–0.7 (mult., 9H, $\mathrm{PCH_2CH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 25 °C) δ 223.8 ppm (d, $J_{\mathrm{PC}} = 34$ Hz, CO); 86.2 (d, $J_{\mathrm{PC}} = 20$ Hz, $\mathrm{\mathit{C}H(CH_2CH_3)(OCH_3)}$); 83.4 (s, $\mathit{C}_5\mathrm{H}_5$); 58.5 (s, $\mathrm{O\mathit{C}H_3}$); 39.7 (s, $\mathrm{\mathit{C}H_2CH_3}$); 20.4 (d, $J_{\mathrm{PC}} = 23$ Hz, $\mathrm{P\mathit{C}H_2CH_3}$); 15.4 (s, $\mathrm{CH_2\mathit{C}H_3}$); 8.1 (s, $\mathrm{PCH_2\mathit{C}H_3}$). IR ($\mathrm{CH_2Cl_2}$)ν(CO) (1890 $\mathrm{cm^{-1}}$).

3.4.2. $R = \mathrm{CH_2CH_2CH_2CH_3}$

Applying the procedure described above, $\mathrm{Cp(CO)(PEt_3)FeC(H)(CH_2CH_2CH_2CH_3)(OCH_3)}$ was obtained as an orange oil in a 91% yield. $^1\mathrm{H}$ NMR spectroscopy indicated that two diastereomers were present in a 9.1 : 1 ratio. These were not separated. $^1\mathrm{H}$ NMR ($\mathrm{C_6D_6}$) δ 4.38 ppm (d, $J_{\mathrm{PH}} = 1.1$ Hz, $\mathrm{C_5\mathit{H}_5}$, minor); 4.36 (d, $J_{\mathrm{PH}} = 1.0$ Hz, $\mathrm{C_5\mathit{H}_5}$, major); 4.27 (mult., $\mathrm{C\mathit{H}(R)(OCH_3)}$, major); 4.0 (mult, $\mathrm{C\mathit{H}(R)(OCH_3)}$, minor); 3.48 (s, $\mathrm{OC\mathit{H}_3}$, major); 3.26 (s, $\mathrm{OC\mathit{H}_3}$, minor); 2.24 (mult, 1H), 2.05 (mult, 1H), 1.78 (mult, 1H), ($\mathrm{C(H)(OCH_3)C\mathit{HH'}C\mathit{H}H'CH_2CH_3}$); 1.5–1.1 (mult, 9H, $\mathrm{C(H)(OCH_3)CHH'CH\mathit{H'}C\mathit{H}_2CH_3}$ and $\mathrm{P(C\mathit{H}_2CH_3)_3}$); 1.0 (t, $J_{\mathrm{HH}} = 7.1$ Hz, $\mathrm{CH_3}$); 0.78 (d of t, $J_{\mathrm{PH}} = 13.9$ Hz, $J_{\mathrm{HH}} = 7.6$ Hz, $\mathrm{P(CH_2C\mathit{H}_3)_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 25 °C) δ 223.8 ppm (d, $J_{\mathrm{PC}} = 34$ Hz, CO); 84.2 (d, $J_{\mathrm{PC}} = 19$ Hz, $\mathrm{\mathit{C}H(CH_2CH_2CH_2CH_3)(OCH_3)}$); 83.6 (s, $\mathit{C}_5\mathrm{H}_5$); 58.5 (s, $\mathrm{OCH_3}$); 47.4 (s, $\mathrm{C(H)(OCH_3)\mathit{C}H_2}$); 33.5 (s, $\mathrm{C(H)(OCH_3)CH_2\mathit{C}H_2}$); 23.5 (s, $\mathrm{C(H)(OCH_3)CH_2CH_2\mathit{C}H_2}$); 20.6 (d, $J_{\mathrm{PC}} = 23$ Hz, $\mathrm{P\mathit{C}H_2CH_3}$); 14.7 (s, $\mathrm{CH_3}$); 8.2 (s, $\mathrm{PCH_2\mathit{C}H_3}$). IR ($\mathrm{CH_2Cl_2}$)ν(CO) (1888 $\mathrm{cm^{-1}}$).

3.4.3. $R = \mathrm{CH_2CH_2CH_2CH_2CH_3}$

Using the procedure described above, $\mathrm{Cp(CO)(PEt_3)FeC(H)(CH_2CH_2CH_2CH_2CH_3)(OCH_3)}$ was obtained as an orange oil in a 74% yield. $^1\mathrm{H}$ NMR spectroscopy indicated that two diastereomers were present in a 6.6 : 1 ratio. These were not separated. $^1\mathrm{H}$ NMR ($\mathrm{C_6D_6}$) δ 4.39 ppm (d, $J_{\mathrm{PH}} = 1.1$ Hz, $\mathrm{C_5\mathit{H}_5}$, minor); 4.36 (d, $J_{\mathrm{PH}} = 1.2$ Hz, $\mathrm{C_5\mathit{H}_5}$, major); 4.3 (mult., $\mathrm{C\mathit{H}(R)(OCH_3)}$, major); 4.05 (broad, $\mathrm{C\mathit{H}(R)(OCH_3)}$, minor); 3.5 (s, $\mathrm{OCH_3}$, major); 3.25 (s, $\mathrm{OCH_3}$, minor); 2.4–2.2 (mult.), 2.1–1.9 (mult.), 1.8–1.6 (mult.), (3H, $\mathrm{C(H)(OCH_3)C\mathit{HH'}C\mathit{H}H'CH_2CH_2CH_3}$); 1.54–1.16 (mult. 11H, $\mathrm{C(H)(OCH_3)CHH'CH\mathit{H'}C\mathit{H}_2C\mathit{H}_2CH_3}$ and $\mathrm{PC\mathit{H}_2CH_3}$); 0.96 (t, $J_{\mathrm{HH}} = 7.0$ Hz, $\mathrm{C\mathit{H}_3}$); 0.9–0.72 (mult. 9H, $\mathrm{PCH_2C\mathit{H}_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 25 °C) δ 223.8 ppm (d, $J_{\mathrm{PC}} = 34$ Hz, CO); 84.2 (d, $J_{\mathrm{PC}} = 20$ Hz, $\mathrm{\mathit{C}H(CH_2CH_2CH_2CH_2CH_3)(OCH_3)}$); 83.6 (s, $\mathit{C}_5\mathrm{H}_5$); 58.5 (s, $\mathrm{OCH_3}$); 47.6 (s, $\mathrm{C(H)(OCH_3)\mathit{C}H_2CH_2CH_2CH_2CH_3}$); 32.8 (s), 30.7 (s), 23.4 (s), ($\mathrm{C(H)(OCH_3)CH_2\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2CH_3}$); 20.7 (d, $J_{\mathrm{PC}} = 23$ Hz, $\mathrm{P\mathit{C}H_2CH_3}$); 14.5 (s, $\mathrm{CH_3}$); 8.2 (s, $\mathrm{PCH_2CH_3}$). IR ($\mathrm{CH_2Cl_2}$)ν(CO) (1890 $\mathrm{cm^{-1}}$).

3.5. Generation of $Cp(CO)(PEt_3)Fe=C(H)(R)^+$ complexes from $Cp(CO)(PEt_3)FeCH(OCH_3)R$

Two methods to generate the carbene complexes were utilized: Method 1 in which the triflate salt was generated, and Method 2 in which the BF_4^- salt was generated.

3.5.1. Method 1

$C_5H_5(CO)(PEt_3)FeC(H)(OCH_3)(CH_3)$ (0.29 g, 0.88 mmol) was dissolved in 15 ml of CH_2Cl_2 and the solution was cooled to −78 °C. TMSOTf (1.1 equivalents, 0.97 mmol, 0.21 g) was added and the solution turned a deep red–orange color. NMR data for this compound has been previously reported [16].

3.5.2. Method 2

In a Schlenk flask, 0.62 g (1.9mmol) of $C_5H_5(CO)(PEt_3)FeC(H)(OCH_3)(CH_3)$ was dissolved in 50 ml of freshly distilled diethyl ether. The solution was stirred and cooled to −40 °C. HBF_4–Me_2O (3 equivalents, 5.7 mmol, 0.76 g) was syringed into the solution and a fine yellow powder immediately precipitated. Stirring was stopped and the solid was allowed to settle. The ether was removed via cannula and the carbene salt was washed with two more 30 ml portions of diethyl ether. The remaining ether was then pumped away while maintaining low temperatures. NMR data has been previously reported for this compound [16].

3.6. NMR observation of $Cp(CO)(PEt_3)Fe=C(H)(CH_2CH_3)^+\ BF_4^-$

This complex was generated by Method 2. ^1H NMR (−30 °C, 400 MHz, CD_2Cl_2) δ 17.2 ppm (s, H_a); 5.4 (s, C_5H_5); 3.4 (mult., CH_2); 2.0–1.6 (mult, PCH_2CH_3); 1.2 (t, J_{HH} = 7.4 Hz, CH_3); 1.0–0.8 (mult., PCH_2CH_3). At −100 °C, signals were observed at 17.5 ppm (major isomer, anticlinal) and at 15.5 ppm (minor isomer, synclinal) in a 8.3 : 1 ratio. Upon warming, the signals broadened and coalesced at about −80 °C. After further warming, a broad singlet was observed at 17.2 ppm. The carbene complex was stable to ca. 0 °C, but upon further warming, decomposition to unidentified products occurred.

3.7. Reaction of Et_3SiH with $Cp(CO)(PEt_3)Fe=C(H)(CH_3)^+OTf^-$

Complex **3a** (2.2 mmol) was generated by Method 1 at −60 °C in 25 ml of CH_2Cl_2. Et_3SiH (2 equivalents, 4.3 mmol, 0.5 g) was then syringed into the solution and it was allowed to warm. At ca. −50°C, the solution turned a dark green color. After stirring for an additional 30 min, 50 ml of a saturated aqueous $NaHCO_3$ solution were added to quench the reaction. Hexanes (50 ml) was added and the reaction was shaken in a separatory funnel. The organic layer was washed with 2 × 50 ml of water and then dried over $MgSO_4$. The aqueous layer was then washed with 50 ml of fresh hexanes and this was also dried. The solution was filtered and concentrated by simple distillation giving the organosilane product. GC analysis indicated that Et_4Si was formed in 45% yield by comparison to an internal standard (dodecane). GC also indicated that Et_3SiOH was present. NMR and GC data for Et_4Si and Et_3SiOH matched those of authentic samples. ^1H NMR ($CDCl_3$, 250 MHz, 25°C) δ 0.95–0.85 ppm (t, J_{HH} = 8.1 Hz, CH_3); 0.55–0.4 (q, J_{HH} = 8.1 Hz, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 250 MHz, 25°C) δ 7.4 ppm (s, CH_3); 3.1 (s, CH_2).

3.8. Reaction of Et_3SiH with $Cp(CO)(PEt_3)Fe=C(H)(CH_3)^+BF_4^-$

$Cp(CO)(PEt_3)Fe=C(H)(CH_3)^+BF_4^-$ (1.9 mmol) was generated by Method 2. The carbene salt was dissolved in 40 ml of CH_2Cl_2 at −50°C giving a light orange solution. Et_3SiH (2 equivalents, 3.8 mmol, 0.44 g) was then added. The solution darkened and within minutes was a green color. However, upon warming, the solution became lighter again. Workup of the solution was the same as described in the previous case. Product analysis by GC indicated that Et_4Si was formed in a 56% yield as determined by comparison to an internal standard (dodecane). ^{13}C NMR spectroscopy showed Et_3SiF (δ 6.0 ppm, 4.9 (d,J_{CF} = 13.2 Hz)) to be present as a byproduct (Et_4Si : Et_3SiF, 1.5 : 1).

3.9. Reaction of Et_3SiH with $Cp(CO)(PPh_3)Fe=C(H)(Ph)^+OTf^-$

$Cp(CO)(PPh_3)Fe=C(H)(Ph)^+OTf^-$ (0.43 mmol) was prepared by Method 1 at −78°C. Et_3SiH (2 equivalents, 0.86 mmol, 0.1 g) was then added. No reaction appeared to occur until about −50°C at which point the solution turned a green color. After allowing the solution to warm to room temperature, the reaction mixture was worked up as above. Et_3SiCH_2Ph was obtained in a 44% isolated yield. NMR data matched that of an independently prepared sample. ^1H NMR ($CDCl_3$, 250 MHz, 25°C) δ 7.4–7.0 ppm (mult., 5H, aryl); 2.1 (s, 2H, benzylic); 1.0 (t, J_{HH} = 6.9 Hz, CH_3); 0.6 (q, J_{HH} = 6.9 Hz, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 250 MHz, 25°C) δ 140.6 ppm (s), 128.4 (s), 128.0 (s), 123.7 (s) (aryl); 21.6 (s, benzylic); 7.2 (s, CH_3); 3.0 (s, CH_2).

3.10. Reaction of $Ph(CH_3)SiH_2$ with $Cp(CO)(PPh_3)Fe=C(H)(Ph)^+OTf^-$

$Cp(CO)(PPh_3)Fe=C(H)(Ph)^+OTf^-$(0.26 mmol) was prepared by Method 1 at −78°C. $PhMeSiH_2$ (10 equivalents, 2.6 mmol, 0.3 g) was then added. As in the above case, no reaction appeared to occur until about −50°C at which point the solution turned green. The reaction mixture was allowed to warm and then worked up as before. Methylphenylbenzylsilane was obtained in a 53% isolated yield. NMR data matched that of an independently prepared sample. ^{1}H NMR ($\mathrm{CDCl_3}$, 250 MHz, 25°C) δ 7.7–7.0 ppm (mult., 10H, aryl); 4.6 (mult., 1H, SiH); 2.55 (d of d, $J_{\mathrm{HHgem}} = 13.7$ Hz, $J_{\mathrm{HH''}} = 2.9$ Hz, 1H, $\mathrm{SiC\mathit{H}H'Ph}$); 2.45 (d of d, $J_{\mathrm{HHgem}} = 13.7$ Hz, $J_{\mathrm{HH''}} = 3.9$ Hz, 1H, $\mathrm{SiCH\mathit{H'}Ph}$); 0.42 (d, $J_{\mathrm{HH}} = 3.7$ Hz, $\mathrm{CH_3}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 250 MHz, 25°C) δ 139.1 ppm (s), 134.4 (s), 129.4 (s), 128.4 (s), 128.3 (s), 127.8 (s), 127.5 (s), 124.3 (s) (aryl); 23.5 (s, $\mathrm{\mathit{C}H_2Ph}$); −6.2 (s, $\mathrm{CH_3}$).

3.11. Reaction of $\mathrm{PhCH_3SiHD}$ with $\mathrm{Cp(CO)(PPh_3)Fe{=}C(H)(Ph)^+OTf^-}$

PhMeSiHD was prepared by adding PhMeSiHCl (32 mmol, 5 g) to lithium aluminum deuteride (38 mmol, 1.6 g) dissolved in 40 ml of $\mathrm{Et_2O}$ at −78°C. After allowing this to stir overnight, the reaction was quenched by addition of water at −30°C. The organic layer was extracted and dried on $\mathrm{MgSO_4}$. It was then filtered and concentrated by simple distillation. A GC trace of this compound matched that of the unlabeled compound. ^{1}H NMR spectroscopy indicated that close to quantitative incorporation of deuterium had been achieved as determined by the 3 : 1 ratio for the methyl protons to the Si–H proton.

Carbene complex **2** (0.34 mmol) was prepared by Method 1 and dissolved in 10 ml of $\mathrm{CH_2Cl_2}$ at −78°C. To this solution was added 10 equivalents (3.4 mmol, 0.42 g) of PhMeSiHD. This was allowed to warm and worked up as above. Analysis of the ^{1}H NMR spectrum indicated that products from insertion into the Si–H bond ($\mathrm{PhMeSi(D)CH_2Ph}$) and into the Si–D bond (PhMeSi(H)CHDPh) were present in a 2.8 : 1 ratio.

3.12. Reaction of $\mathrm{Et_3SiH}$ with $\mathrm{C_5H_5(CO)(PEt_3)Fe{=}C(H)(CH_2CH_3)^+\ BF_4^-}$

$\mathrm{C_5H_5(CO)(PEt_3)Fe{=}C(H)(CH_2CH_3)^+BF_4^-}$ (0.8 mmol) was prepared by Method 2. At −50°C, the carbene salt was dissolved in 35 ml of methylene chloride. Triethylsilane (2 equivalents, 1.5 mmol, 0.2 g) was then added to the stirring solution, and it was allowed to warm. Triethylpropylsilane was obtained in a 59% yield as determined by GC comparison to an internal standard (dodecane). NMR data matched that of an independently prepared sample. ^{1}H NMR ($\mathrm{CDCl_3}$, 250 MHz, 25°C) δ 1.3 ppm (mult., 2H, $\mathrm{SiCH_2C\mathit{H}_2CH_3}$); 1.0–0.9 (mult., 12H, $\mathrm{(C\mathit{H}_3CH_2)_3SiCH_2CH_2C\mathit{H}_3}$); 0.6–0.4 (mult., 8H, $\mathrm{(CH_3C\mathit{H}_2)SiC\mathit{H}_2CH_2CH_3}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 250 MHz, 25°C) δ 18.6 ppm (s, $\mathrm{SiCH_2\mathit{C}H_2CH_3}$); 17.4 (s, $\mathrm{SiCH_2CH_2CH_3}$); 14.2 (s, $\mathrm{SiCH_2CH_2CH_3}$); 7.4 (s, $\mathrm{(\mathit{C}H_3CH_2)_3SiCH_2CH_2CH_3}$); 3.4 (s, $\mathrm{(CH_3\mathit{C}H_2)_3SiCH_2CH_2CH_3}$).

3.13. Reaction of $\mathrm{Et_3SiH}$ with $\mathrm{C_5H_5(CO)(PEt_3)Fe{=}C(H)(CH_2CH_2CH_2CH_3)^+BF_4^-}$

$\mathrm{C_5H_5(CO)(PEt_3)Fe{=}C(H)(CH_2CH_2CH_2CH_3)^+BF_4^-}$ (0.5 mmol) was prepared by Method 2. The carbene salt was dissolved in 30 ml of $\mathrm{CH_2Cl_2}$ at −40°C. $\mathrm{Et_3SiH}$ (2 equivalents, 1 mmol, 0.15 g) was added and the solution darkened quickly. Upon workup, triethylpentylsilane was obtained in a 41% yield (GC). NMR data matched the reported values [26]. ^{1}H NMR ($\mathrm{CDCl_3}$, 250 MHz, 25°C) δ 1.4–1.3 ppm (broad, 6H, $\mathrm{SiCH_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3}$); 1.0–0.8 (mult., 12H, $\mathrm{(C\mathit{H}_3CH_2)_3SiCH_2CH_2CH_2CH_2C\mathit{H}_3}$); 0.6–0.4 (mult., 8H, $\mathrm{(CH_3C\mathit{H}_2)_3SiC\mathit{H}_2CH_2CH_2CH_2CH_3}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 250 MHz, 25°C) δ 36.2 ppm (s), 23.5 (s), 22.3 (s) ($\mathrm{SiCH_2\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2CH_3}$); 14.0 (s, $\mathrm{SiCH_2CH_2CH_2CH_2\mathit{C}H_3}$); 11.3 (s, $\mathrm{Si\mathit{C}H_2CH_2CH_2CH_2CH_3}$); 7.5 (s, $\mathrm{(\mathit{C}H_3CH_2)_3SiCH_2CH_2CH_2CH_2CH_3}$); 3.4 (s, $\mathrm{(CH_3\mathit{C}H_2)_3SiCH_2CH_2CH_2CH_2CH_3}$).

3.14. Reaction of $\mathrm{Et_3SiH}$ with $\mathrm{C_5H_5(CO)(PEt_3)Fe{=}C(H)(CH_2CH_2CH_2CH_2CH_3)^+BF_4^-}$

$\mathrm{C_5H_5(CO)(PEt_3)Fe{=}C(H)(CH_2CH_2CH_2CH_2CH_3)^+BF_4^-}$ (1.6 mmol) was prepared by Method 2. The salt was then dissolved in 40 ml of methylene chloride at −45°C and 2 equivalents of triethylsilane (3.3 mmol, 0.4 g) were added. Within 5 min the solution had turned green. After 0.5 h the solution was quenched with an aq. $\mathrm{NaHCO_3}$ solution, and worked up as described above. Triethylhexylsilane was formed in a 55% yield as determined by GC comparison to an internal standard (dodecane). NMR data matched the reported values [29]. ^{1}H NMR ($\mathrm{CDCl_3}$, 250 MHz, 25°C) δ 1.3–1.2 ppm (broad, 8H, $\mathrm{SiCH_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3}$); 1.0–0.8 (mult., 12H, $\mathrm{(C\mathit{H}_3CH_2)_3SiCH_2CH_2CH_2CH_2CH_2CH_3}$); 0.6–0.4 (mult., 8H, $\mathrm{(CH_3C\mathit{H}_2)_3SiC\mathit{H}_2CH_2CH_2CH_2CH_2CH_3}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 250 MHz, 25°C) δ 33.7 ppm (s), 31.6 (s), 23.9 (s), 22.7 (s) $\mathrm{(CH_3CH_2)_3SiCH_2\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2CH_3}$); 14.1 (s, $\mathrm{SiCH_2CH_2CH_2CH_2CH_2\mathit{C}H_3}$); 11.4 (s, $\mathrm{Si\mathit{C}H_2}$); 7.5 (s, $\mathrm{(\mathit{C}H_3CH_2)_3Si}$); 3.4 (s, $\mathrm{(CH_3\mathit{C}H_2)_3Si}$).

*3.15. NMR observation of the reaction of **3b** with $\mathrm{Et_3SiH}$*

Complex **3b** (0.037 mmol) was prepared by Method 2, dissolved in 0.7 ml of $\mathrm{CD_2Cl_2}$ and transferred to an NMR tube at −78°C. Spectroscopic observation showed the carbene complex to be present ($\mathrm{H_a}$ 17.1 ppm). The tube was removed from the probe and kept at −78°C.

Et_3SiH (2 equivalents, 0.074 mmol, 0.009 g) was added to the solution. Just before it was returned to the probe, the tube was quickly inverted to ensure complete mixing. Immediate observation at −78°C indicated that all of the carbene complex had been consumed. $Cp(CO)(PEt_3)FeH_2^+BF_4^-$ was present along with Et_4Si, Et_3SiF and Et_3SiH. ^{1}H NMR (CD_2Cl_2, 400 MHz, −80°C) δ 5.0 ppm (s, C_5H_5); 2.0–1.8 (mult., PCH_2CH_3); 1.1–1.0 (mult., PCH_2CH_3); −11.8 (broad, H_2).

3.16. $Cp(CO)(PEt_3)Fe(HSiEt_3)^+BAr_4'^-$

In the drybox, an NMR tube was charged with 10.3 mg (0.027 mmol) of $Cp(CO)(PEt_3)FeSiEt_3$ and 27.4 mg (0.027 mmol) of $H(OEt_2)_2^+BAr_4'^-$. The tube was capped with a septum and removed from the drybox. The sample was kept under N_2 via a syringe needle and cooled to −78°C. CD_2Cl_2 (0.8 ml) was added via syringe. The needle was removed and the septa was wrapped in parafilm and covered with grease. The tube was quickly inverted to ensure complete mixing and then returned to the cold bath.

The tube was introduced into a cold NMR probe (−80°C) and the Et_3SiH complex was observed if very little trace water was present. The η^2-H_2 complex was present along with the dihydride complex as discussed earlier.

After initial observation, the tube was removed from the probe and returned to the coldbath. Under a N_2 atmosphere, 5 equivalents of Et_3SiH (0.14 mmol, 0.015 g) were added. The tube was shaken and warmed to room temperature briefly. H_2 was observed to evolve. The tube was then reintroduced to the cooled NMR probe and now the Et_3SiH complex was the only species present. This complex was relatively stable at room temperature in the presence of excess Et_3SiH. ^{1}H NMR (400 MHz, 25°C, CD_2Cl_2) δ 7.8–7.7 ppm (broad s, aryl, 8H); 7.6–7.5 (broad s, 4 H, aryl); 4.9 (s, C_5H_5); 2.0–1.8 (mult., PCH_2CH_3); 1.2–1.1 (mult., PCH_2CH_3); 1.0–0.9 (mult., partially obscured, $SiCH_2CH_3$); 0.7–0.6 (mult., partially obscured, $SiCH_2CH_3$); −16.6 (d, $J_{PH} = 34$ Hz, $J_{SiH} = 62.4$ Hz, Fe–H–Si). $^{13}C\{^1H\}$ NMR (400 MHz, 25°C, CD_2Cl_2) δ 213.5 ppm (d, $J_{PC} = 27$ Hz, CO); 162 (q, $J_{BC} = 50$ Hz, *ipso* C); 135 (s, *ortho* C); 129 (q, $J_{CF} = 26$ Hz, *meta* C); 125 (q, $J_{CF} = 271$ Hz, CF_3); 118 (s, *para* C); 84.5 (s, C_5H_5); 22.9 (d, $J_{PH} = 30$ Hz, PCH_2CH_3); 11.2 (s, $SiCH_2CH_3$); 9.0 (s, $SiCH_2CH_3$) 8.2 (s, PCH_2CH_3).

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