$PdCl_2$, $CuCl_2$, HCl, CO, and O_2 (i.e., in the absence of the olefin). If the mixture is filtered and the filtrate is treated with 1-decene for 48 h (CO/O_2), then carboxylic esters are formed in 42% yield, with the branched/linear ratio being 6.0. Furthermore, exposure of the filtered solid to fresh *n*-butyl formate, 1-decene, CO, O_2, and HCl (but no $PdCl_2$ or $CuCl_2$) for 24 h afforded the esters in 43% yield (branched/linear ratio of 6.9). These observations show that the thus far uncharacterized solid material, as well as the filtrate, are active catalysts for converting olefins and formate esters to carboxylic esters.

The following general procedure was used; carbon monoxide was bubbled through a dioxane (10 mL)–formate ester (4 mL) solution for 15 min. Palladium chloride (0.3 mmol) was then added, followed by 0.3 mL of concentrated hydrochloric acid. Once most of the palladium chloride had dissolved, cupric chloride (1.5 mmol) was added, oxygen bubbling was begun together with carbon monoxide, and the olefin (5.4 mmol) was added. After being stirred at room temperature and 1 atm, the mixture was filtered, the filtrate was treated with an equal volume of water (∼15 mL), and the products were extracted with ether and distilled.

Polysilane–Metal Interactions. Migration, with Rearrangement, of the Disilylmethyl Group from Iron to the Cyclopentadienyl Group in (η⁵-C₅H₅)Fe(CO)₂-CH₂SiMe₂SiMe₃[1]

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Summary: Treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}R$ (R = CH_2SiMe_3, $CH_2SiMe_2SiMe_3$) with lithium diisopropylamide at −80 °C leads to cyclopentadienyl ring metalation. Reaction of the metalated product with CH_3I gives $(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2\text{-}R$. If the reaction is performed at 0 °C, the same product is obtained for R = CH_2SiMe_3; however, with R = $CH_2SiMe_2SiMe_3$ a new product is obtained involving migration, with rearrangement, of the disilylmethyl group $(\eta^5\text{-}Me_3SiCH_2SiMe_2C_5H_4)Fe(CO)_2\text{-}CH_3$.

There is current interest in deprotonation reactions of transition-metal cyclopentadienyl carbonyls that lead to ring metalations with or without[2-6] migrations of σ-bonded

groups from the transition metal, and we recently reported migrations of polysilyl groups from Fe to the cyclopentadienyl group of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(SiMe_2)_nSiMe_3$ upon treatment with *n*-butyllithium.[7]

We found that deprotonation of the related iron disilylmethyl complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}CH_2SiMe_2SiMe_3$ (1) at −78 °C resulted only in ring metalation with no migration, and the same result was observed with $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2SiMe_3$ (2) (eq 1).
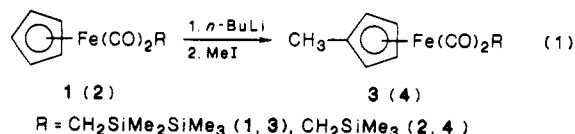
This result was in keeping with previous studies which showed that simple alkyl groups σ-bonded to metals were not prone to migration,[2] in contrast to silyl,[2,3,7] germyl,[8,9] stannyl,[9] plumbyl,[9] and acyl groups.[4,6]

Our continuing studies have indicated that changes in temperature have a profound effect upon the outcome of the reaction of the disilylmethyl complex with *n*-butyllithium. When we performed the reaction at room temperature instead of −78 °C, different results were observed; a high yield of a product (5) was obtained in which the original $Me_5Si_2CH_2$ group had migrated *and* rearranged (eq 2).
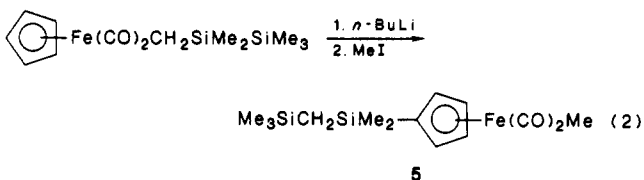
We found that the yields were higher when the reaction was carried out at 0 °C, using lithium diisoproplyamide (LDA) as the base. In a typical reaction, 0.54 g (1.75 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2SiMe_2SiMe_3$ dissolved in oxygen-free THF at 0 °C was treated with 4.0 mL (2.2 mmol) of freshly prepared LDA in THF. The solution immediately changed color from orange to deep red, and after 20 min the CO stretching frequencies of the starting material (2002, 1945 cm^{-1}) had been replaced by bands typical of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ (ν(CO) 1881, 1865, 1811, 1751 cm^{-1}[11,12]). An excess of methyl iodide (2.0 g, 14.1 mmol) was added, and the solution was stirred for 20 min after which time all anion CO bands had been replaced by two bands at 2001 and 1944 cm^{-1}. The solvent was removed in vacuo and the residue dissolved in a minimum of hexane and chromatographed (1 × 10 cm alumina column). A single yellow band was eluted with hexane to produce 0.39 g (70%) of $(\eta^5\text{-}Me_3SiCH_2SiMe_2C_5H_4)Fe(CO)_2CH_3$ (5).[10] Pertinent spectral data for this and other complexes are recorded in Table I.

(1) Part 14 of "Organometalloidal Derivatives of the Transition Metals". For part 13 see: Pannell, K. H.; Rozell, J.; Tsai, W.-M. *Organometallics*, in press. For part 12, see ref 7.

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Table I. ^{13}C and ^{29}Si NMR Data for New Complexes (ppm, C_6D_6)

complex	^{13}C^a		^{29}Si $(\Delta\delta)^b$		
	CH_2	CH_3	Si_α	Si_β	Si_γ
$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2Si_2Me_5$ (1)	-25.2			-6.6 (13.0)	-19.9 (-0.36)
$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2SiMe_3$ (2)	-23.5			9.2 (7.2)	
$(\eta^5\text{-}MeC_5H_4)Fe(CO)_2CH_2Si_2Me_5{}^c$ (3)	-23.9	12.7		-7.0 (12.6)	-19.9 (-0.36)
$(\eta^5\text{-}MeC_5H_4)Fe(CO)_2CH_2SiMe_3$ (4)	-22.1	12.7		8.3 (6.3)	
$(\eta^5\text{-}Me_3SiCH_2Me_2SiC_5H_4)Fe(CO)_2Me$ (5)	4.2	-22.6	-4.3 (-4.6)		0.45 (0.13)
$(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2CH_2SiMe_3$ (6)	12.8		42.8 (42.5)		0.36 (0.04)

^{a} Resonances for the CO groups are singlets in the range 218 ± 2 ppm and those for the cyclopentadienyl carbons either singlets (complexes 1, 2, and 6) or three singlets (complexes 3–5), in the range 84–93 ppm. $^b \Delta\delta = [\delta(\text{Fe–Si}) - \delta(\text{Me–Si})]$. ^{c} Analyses for the new complexes 3–5 are presented in ref 10.

The migrated/rearranged complex **5** was also synthesized independently by the route outlined in eq 3 for further structure confirmation.
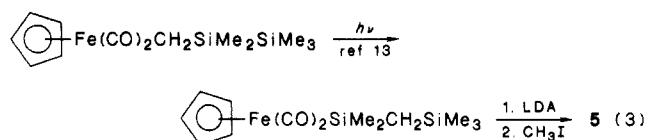
This reaction sequence takes advantage of the facility of $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}CH_2SiMe_2SiMe_3$ to photochemically rearrange to $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}SiMe_2CH_2SiMe_3$ (6)^{13} and the ability of the silyl group of **6** to migrate from Fe to the deprotonated cyclopentadienyl group. We also synthesized both the methylcyclopentadienyl silylmethyl complexes **3** and **4** via the route outlined in eq 4.

R = $Me_3SiMe_2SiCH_2$ (3), Me_3SiCH_2 (4)
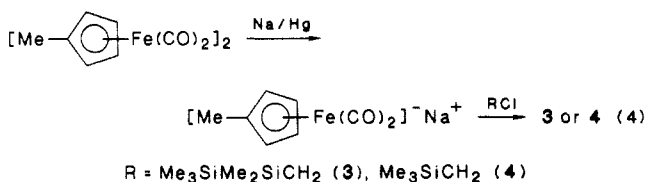
The spectral data reported in Table I are in accord with the proposed structures. Particularly useful are the ^{29}Si NMR data. We have previously reported that for polysilyl complexes of the $[\eta^5\text{-}C_5H_5)Fe(CO)_2]$ system, the chemical shifts of the various Si atoms are very dependent upon their location with respect to the metal center.^{14} Thus, compared to the methylsilicon analogues, when the polysilyl chain is bonded to the metal atom, Si atoms directly bonded to Fe, (Si_α), exhibit chemical shift differences, $\Delta\delta = (\delta (\text{Fe–Si}) - \delta (\text{Me–Si}))$, of $\simeq$ +35 ppm, for Si_β this shift is $\simeq$ +10 ppm, and for Si_γ it is $\simeq$ 0. When the chain is bonded to the cyclopentadienyl ring, $\Delta\delta$ values are as follows: Si_α, $\simeq$ –4.0 ppm, Si_β, $\simeq$ +0.5 ppm, Si_γ, $\simeq$ 0.^{7} Analysis of the data for complexes **3** and **4**, those in which no migration of the silylmethyl groups had occurred, reveals $\Delta\delta(Si_\beta)$ = +12.6 ppm (3) and +6.3 ppm (4), with $\Delta\delta(Si_\gamma)$ = –0.36 ppm (3). The migrated/rearranged complex **5** exhibits two ^{29}Si resonances with $\Delta\delta$ = –4.6 (Si_α) and +0.13 ppm (Si_γ). These $\Delta\delta$ values are those expected for the assigned structures based upon the previously reported data.

^{13}C NMR data are also very useful for additional structure verification. α-Carbon atoms of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$-alkyl complexes exhibit chemical shifts around –23 ppm relative to Me_4Si. Since the new complexes discussed in this communication (1–5) have alkyl substituents σ-bonded to iron, simple chemical shift data of the Fe–C C atom do not help in determining whether or not migrations have taken place, i.e., whether the alkyl group is a methyl or silylmethyl group. However, for the nonmigrated complexes **3** and **4** with a $CH_2Si_2Me_5$ or CH_2SiMe_3 group attached to the metal, ^{13}C NMR spectra with C–H coupling exhibit a triplet in the region for Fe–C C atoms whereas for the migrated/rearranged complex **5** the coupled spectrum exhibits a quartet for the methyl group attached to iron.

The rearrangement observed for the migrated product is an example of an intramolecular anion-induced silyl rearrangement.^{15}
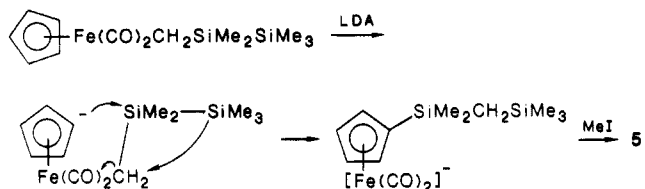
This rearrangement is similar to that previously observed for the photochemical transformation of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}CH_2SiMe_2SiMe_3$ complex, shown in reaction 3.^{13} It is also related to the long established thermal transformation of (pentamethyldisilyl)methyl acetate to ((trimethylsilyl)methyl)dimethylsilyl acetate, $Me_3SiMe_2SiCH_2OAc \rightarrow Me_3SiCH_2Me_2SiOAc$.^{16}

Crocco and Gladysz have shown that deprotonation of the cyclopentadienyl ring in $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)H$ occurs at –78 °C upon treatment with n-butyllithium–TMEDA and that the anion may be methylated to produce $(\eta^5\text{-}MeC_5H_4)Re(NO)(PPh_3)H$.^{5} If the methylation, or other trapping experiment, is performed at an elevated temperature, H migration from Re to the cyclopentadienyl ring occurs to produce a metal-centered anion which upon methylation yields $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)Me$. Our results extend such behavior to iron, with the added interest of the rearrangement induced by the cyclopentadienyl anion attack upon the Si–Si bond of the disilylmethyl group,^{17} indicating for the first time that the cyclopentadienyl ring centered anion will attack bonds other than the direct σ-bond to the metal atom.

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(17) In ref 6, base treatment of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2R]$ complexes produced acyl deprotonation at –78 °C, but cyclopentadienyl deprotonation was a very effective competitive route at 20 °C.