Organometallics 1988, 7, 2524–2528

29.81, 23.13, 20.96, 20.81 (α anomer). The resonances assigned to the β anomer is δ 95.51. Anal. Calcd for $B_{10}C_{16}H_{32}O_6$: C, 44.85; H, 7.53; B, 25.23. Found: C, 45.10; H, 7.42; B, 25.20.

1-[(2,3-Dideoxy-*erythro*-hex-2-enopyranosyl)methyl]-1,2-dicarbadodecahydroundecaborate(1−) ion (8). The potassium salt of this monoanion was prepared by a general degradation procedure.[9] **3** (1.14 g, 2.95 mmol) was refluxed in ethanolic KOH (0.45 g, 0.5 M) for 20 h. The potassium salt was dissolved in water and converted to the tetramethylammonium salt by the addition of an excess of Me_4NCl. This salt was recrystallized from water to give white plates (0.79 g, 73%). IR (Nujol mull): 3480–3460 (br m), 2525 (vs), 1088 (w), 1035 (s), 1020 (s br), 949 (m) cm^{-1}. ^1H NMR (acetone-d_6): δ 5.88 (1 H, br d, $J = 10.2$), 5.68 (1 H, br d, $J = 10.2$), 5.00 and 4.90 (1 H, 2 br s), 4.10–4.01 (2 H, m), 3.82–3.56 (6 H, m), 3.45 (12 H, s), 3.35 (1 H, s), −2.6 (1 H, br s). ^{13}C NMR (MeOH-d_4): δ 132.79, 132.68, 125.79, 125.76, 92.96, 92.31, 75.47, 74.65, 71.71, 71.68, 62.39, 60.85, 60.81, 54.36, 54.33, 54.30. ^{11}B NMR (acetone): δ −9.91 (4 B, d, $J = 135$), −10.69 (1 B, d), −11.01 (1 B, d), −14.38 (1 B, d, $J = 167$), −22.48 (2 B, d, $J = 147$), −32.82 (2 B, d, $J = 121$), −37.15 (2 B, d, $J = 137$). MS: cluster of peaks between *m/e* 289 and 294, with most intense peak at *m/e* 292. This *m/e* corresponds to $^{10}B_1{}^{11}B_8C_9H_{22}O_4$.

1-[(2,3-Dideoxy-α-D-*erythro*-hex-2-enopyranosyl)methyl]-1,2-dicarba-*closo*-dodecaborane (9). K_2CO_3 (1.60 g, 11.6 mmol) was dissolved in 50 mL of 90% EtOH, with gentle heating. After the solution was cooled to room temperature, 2.01 g (5.20 mmol) of **3** was added. This solution was stirred overnight and concentrated in vacuo. The solid thus produced was washed with 3 × 15 mL H_2O and recrystallized from chloroform (0.97 g, 62%): mp 143–144.5 °C. IR (Nujol mull): 3330–3274 (br s), 3080 (m), 3060 (m), 2591–2569 (br s), 1409 (w), 1326 (m), 1305 (m), 1245 (w), 1180 (w), 1124 (m), 1095 (w), 1046 (s), 989 (m), 984 (m), 959 (m) cm^{-1}. ^1H NMR (acetone-d_6): δ 5.97 (1 H, br d, $J = 10.1$), 5.70 (1 H, ddd, $J = 10.1$), 5.03 (1 H, br s), 4.30 (1 H, d, $J = 11.4$), 4.12 (1 H, d, $J = 11.4$), 4.01 (1 H, m), 3.86–3.76 (2 H, m), 3.65–3.61 (2 H, m), 2.81 (2 H, br s, exchanges with D_2O). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 135.28, 124.08, 93.41, 74.39, 73.25, 68.22, 62.17, 61.06, 60.64. Anal. Calcd for $B_{10}C_9H_{22}O_4$: C, 35.77; H, 7.27; B, 35.77. Found: C, 35.31; H, 7.29; B, 35.42.

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Registry No. 1, 117162-37-5; α-**2**, 117162-38-6; β-**2**, 117162-39-7; α-**3**, 117162-40-0; β-**3**, 117162-41-1; α-**4**, 117162-42-2; β-**4**, 117183-74-1; α-**5**, 117162-43-3; β-**5**, 117162-44-4; α-**6**, 117162-45-5; β-**6**, 117162-46-6; α-**7**, 117162-47-7; β-**7**, 117162-48-8; **8**, 91946-38-2; **9**, 117162-49-9; $HOCH_2$-*o*-$C_2B_{10}H_{10}$-H, 19610-34-5; $HOCH_2CH_2$-*o*-$C_2B_{10}H_{10}$-H, 23835-95-2; $HOCH_2CH_2$-*o*-$C_2B_{10}H_{10}$-CH_3, 20644-51-3; $HO(CH_2)_3$-*o*-$C_2B_{10}H_{10}$-H, 23835-93-0; $HO(CH_2)_3$-*o*-$C_2B_{10}H_{10}$-CH_3, 17815-32-6; 1-*o*-acetyl-2,3,5-tri-*o*-benzoyl-β-D-ribofuranose, 6974-32-9; 3,4-di-*O*-acetyl-D-xylal, 3152-43-0; tri-*O*-acetyl-D-glucal, 2873-29-2.

Transition-Metal-Substituted Silanes. Hydrosilylation of Phenylacetylene Using $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2H]$ and $[(\eta^5\text{-}C_5H_4SiPh_2H)Fe(CO)_2R]$ (R = Me, $SiMe_3$)[1]

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The complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2H]$ ($FpSiPh_2H$, I) has been synthesized and characterized. Treatment of I with *i*-Pr_2NLi (LDA) followed by MeI or Me_3SiCl produces the silyl migration products $[(\eta^5\text{-}C_5H_4SiPh_2H)Fe(CO)_2R]$ (R = Me (IIa), $SiMe_3$ (IIb)). Addition of the Si–H bonds to phenylacetylene using chloroplatinic acid yields exceptionally high yields of the appropriate α products. The hydrosilylation products of I may be transformed into those of II by treatment with LDA followed by MeI or Me_3SiCl. The *trans*-β-silylstyrene hydrosilylation products were synthesized independently by the reaction of $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]^-Na^+$ (R = H, $SiMe_3$) with *trans*-$Ph_2Si(Cl)CH{=}CHPh$.

Introduction

Transition-metal complexes containing a Si–H bond are relatively uncommon compared to those with halogen, alkyl, or aryl groups bonded to silicon; however, those complexes that are reported exhibit much unusual chemistry.[2-4] For example, the silicon–hydrogen bond of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2H]$ ($FpSiMe_2H$), exhibits a low Si–H stretching frequency and is readily transformed into a silicon–chlorine bond upon treatment with CCl_4;[5] bridging metal–hydrogen–silicon systems are known,[6,7] and (dimethylsilyl)methyl groups readily rearrange to trimethylsilyl groups, e.g. $[(\eta^5\text{-}C_5H_5)M(CO)_nCH_2SiMe_2H] \rightarrow [(\eta^5\text{-}C_5H_5)M(CO)_nSiMe_3]$.[8,9] Given the interesting chemistry it is surprising that the most studied reaction of organosilicon hydrogen bonds, namely, hydrosilylation, has

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Table I. Spectral Data of Complexes[a]

	$(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2H$ (I)
^{13}C	84.2 (C_5H_5), 127.7, 128.4, 134.5, 141.3 (Ph), 214.3 (CO)
^1H	4.71 (C_5H_5), 5.67 (SiH), 7.36, 7.69 (Ph)
^{29}Si	27.1
ν(CO)	2008, 1956, ν(SiH) 2085

	$(\eta^5\text{-}C_5H_4SiPh_2H)Fe(CO)_2Me$ (IIa)
^{13}C	−22.7 (Me), 80.0, 87.8, 94.5 (C_5H_4), 128.1, 130.1, 132.9, 135.4 (Ph), 216.7 (CO)
^1H	0.20 (Me), 4.89 (m, C_5H_4), 5.48 (s, SiH), 7.47, 7.68 (Ph)
^{29}Si	−21.0
ν(CO)	2014, 1958, ν(SiH) 2143

	$(\eta^5\text{-}C_5H_4SiPh_2H)Fe(CO)_2SiMe_3$ (IIb)
^{13}C	7.6 ($SiMe_3$), 83.8, 87.2, 90.0 (C_5H_4), 128.1, 130.2, 132.6, 135.5 (Ph), 215 (CO)
^1H	0.43 ($SiMe_3$), 4.72 (m, C_5H_4), 5.49 (s, SiH), 7.44, 7.70 (Ph)
^{29}Si	−21.2 (C_5H_4Si), 42.0 (FeSi)
ν(CO)	1997, 1944, ν(SiH) 2140

	$(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2(Ph)C{=}CH_2$ (III)
^{13}C	84.5 (C_5H_5), 126.2, 127.5, 127.7, 127.8, 128.2, 130.1, 135.3, 142.2, 146.2, 154.0 (Ph, CH_2)), 215.3 (CO)
^1H	4.40 (C_5H_5), 5.64 (d, J = 3.0 Hz), 6.01 (d, J = 3.0 Hz, CH_2), 7.1–7.6 (Ph)
^{29}Si	37.0
ν(CO)	2008, 1956

	$(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2\text{-}trans\text{-}CH{=}CHPh$ (IV)
^{13}C	84.5 (C_5H_5), 126.6, 127.6, 127.8, 128.3, 128.4, 131.9, 135.0, 138.6, 142.0, 143.7, 215 (CO)
^1H	4.68 (C_5H_5), 6.76 (d, J = 18.7 Hz), 7.09 (d, J = 18.7 Hz, CH=CH), 7.3–7.6 (Ph)
^{29}Si	31.6
ν(CO)	2006, 1954

	$(\eta^5\text{-}C_5H_4(Ph)C{=}CH_2)Fe(CO)_2Me$ (Va)
^{13}C	−22.7 (Me), 83.1, 89.9, 92.9 (C_5H_4), 127.0, 127.5, 128.0, 128.3, 130.0, 133.6, 133.9, 136.1, 143.6, 146.4 (Ph), 216.7 (CO)
^1H	0.0 (Me), 4.45, 4.70 (C_5H_4), 5.84 (d, J = 2.1 Hz), 6.28 (d, J = 2.1 Hz), 7.2–7.7 (Ph)
^{29}Si	−16.4
ν(CO)	2014, 1957

	$(\eta^5\text{-}C_5H_4(Ph)C{=}CH_2Fe(CO)_2SiMe_3$ (Vb)
^{13}C	7.4 ($SiMe_3$), 86.8, 87.0, 90.0 (C_5H_4), 127.0, 127.5, 127.9, 128.2, 130.0, 133.7, 133.8, 136.1, 143.5, 146.6 (Ph), 214.9 (CO)
^1H	0.40 ($SiMe_3$), 4.39 (m), 4.59 (m, C_5H_4), 5.94 (d, J = 2.5 Hz), 6.37 (d, J = 2.5 Hz, C=CH_2), 7.3–7.8 (Ph)
^{29}Si	−17.0 (C_5H_4Si), 41.9 (FeSi)
ν(CO)	1997, 1942

	$(\eta^5\text{-}C_5H_4SiPh_2\text{-}trans\text{-}CH{=}CHPh)Fe(CO)_2Me$ (VIa)
^{13}C	−22.9 (Me), 83.0, 88.7, 94.0 (C_5H_5), 121.8, 126.9, 127.6, 128.0, 128.6, 130.0, 133.9, 135.7, 137.8, 149.4 (Ph), 217.1 (CO)
^1H	0.11 ($SiMe_3$), 4.87 (m, C_5H_4), 7.0–7.7 (Ph)
^{29}Si	−19.0
ν(CO)	2014, 1957

	$(\eta^5\text{-}C_5H_4SiPh_2\text{-}trans\text{-}CH{=}CHPh)Fe(CO)_2SiMe_3$ (VIb)
^{13}C	7.6 ($SiMe_3$), 86.6, 87.2, 98.9 (C_5H_4), 122.1, 126.8, 127.6, 128.0, 128.6, 129.9, 133.8, 135.8, 137.8, 149.2 (Ph), 215.2 (CO)
^1H	0.41 ($SiMe_3$), 4.69 (m), 4.75 (m, C_5H_4), 7.4–7.7 (Ph)
^{29}Si	−19.2 (C_5H_4Si), 41.6 (FeSi)
ν(CO)	1995, 1940

	$(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2SiPh_2H$ (VII)
^{13}C	0.1 ($SiMe_3$), 87.8, 89.9, 92.1 (C_5H_4), 128.1, 128.7, 134.9, 141.9 (Ph), 215 (CO)
^1H	0.49 ($SiMe_3$), 4.67, 4.88 (C_5H_4), 5.91 (SiH), 7.5–7.9 (Ph)
^{29}Si	−4.0 (C_5H_4Si), 27.4 (FeSi)
ν(CO)	2002, 1951, ν(SiH) 2080

	$(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2SiPh_2(Ph)C{=}CH_2$ (VIII)
^{13}C	−0.6 ($SiMe_3$), 88.3, 88.8, 93.0 (C_5H_4), 126.2, 127.5, 127.8, 127.9, 128.2, 130.2, 135.4, 142.4, 146.3, 154.2 (Ph), 215.6 (CO)
^1H	0.27 ($SiMe_3$), 4.33 (m), 4.40 (m, C_5H_4), 5.74 (d, J = 3.0 Hz), 6.11 (d, J = 3.0 Hz), 7.2–7.7, 216.6 (CO)
^{29}Si	−4.3 (C_5H_4Si), 36.5 (FeSi)
ν(CO)	2002, 1950

	$(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2SiPh_2\text{-}trans\text{-}CH{=}CHPh$ (IX)
^{13}C	−0.4 ($SiMe_3$), 88.2, 89.3, 92.3 (C_5H_4), 126.6, 127.6, 127.8, 128.3, 124.4, 132.1, 135.1, 138.7, 142.1, 143.7 (Ph), 215.3 (CO)
^1H	0.32 ($SiMe_3$), 4.44 (m), 4.75 (m, C_5H_4), 7.3–7.7 (Ph)
^{29}Si	−4.2 (C_5H_4Si), 30.8 (FeSi)
ν(CO)	2000, 1949

[a] ^{29}Si, ^{13}C, and ^1H NMR spectra (chemical shifts in ppm) were recorded in $CDCl_3$ with the exception of the ^{29}Si spectra of complexes I, Vb, VIb, VIII, and IX which were recorded in C_6D_6. IR spectra were recorded in hexane.

not been reported for transition-metal SiH complexes. It is the purpose of this paper to report the complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2H$ (I) and the chloroplatinic acid catalyzed addition of I and its migrated products II, $(\eta^5\text{-}C_5H_4SiPh_2H)Fe(CO)_2R$ (R = Me, $SiMe_3$), to phenylacetylene.

Results

The synthesis of the title complex $FpSiPh_2H$ (I) was accomplished by reaction 1.

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-Na^+ + Ph_2SiHCl \rightarrow \underset{\text{I}}{(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2H} \quad (1)$$

In contrast to the related dimethylsilyl complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2H$,[5]] complex I may be readily handled in air and purified by column chromatography and recrystallization. Despite a Si–H stretching frequency at 2085 cm^{-1} (hexane), cf. Ph_3SiH at 2131 cm^{-1}, I is thermally stable and treatment in refluxing toluene for 24 h does not produce a chemical reaction. The complex is photochemically active under variety of conditions, and such chemistry will be the subject of a future publication.

Treatment of I with lithium diisopropylamide (LDA) resulted in initial deprotonation of the cyclopentadienyl ring as in the case for the trialkyl-/triarylsilane complexes of the iron system.[10–13] As with previous studies, silyl group migration occurs to produce a ferrate salt, in this case $[(\eta^5\text{-}C_5H_4SiPh_2H)Fe(CO)_2]^-Li^+$. The salt was trapped using either MeI or Me_3SiCl to produce complexes IIa and IIb, respectively, in which the Si–H functionality has been

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2H \xrightarrow{\text{LDA/RX}} \underset{\text{II}}{(\eta^5\text{-}C_5H_4SiPh_2H)Fe(CO)_2R} \quad (2)$$

$$\text{RX} = \text{MeI (IIa)}, Me_3SiCl \text{ (IIb)}$$

successfully transferred from the Fe atom to the cyclopentadienyl ring. This is the first example of the migration of a silyl group with a useful functional group in such reactions. It is of interest that the Si-H stretching frequency in the intermediate ferrate salt and the resulting complexes IIa and IIb is at 2143 cm^{-1} as compared to the value of 2085 cm^{-1} in the starting complex. Clearly the electron density in the ferrate salt is quite localized upon the Fe atom, and both the salt and the complexes II behave as species very similar to Ph_3SiH in terms of the stretching

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Table II. New Complexes: Analytical Data

	complex	found (calcd)	found (calcd)	mp, °C
I	(η^5-C_5H_5)Fe(CO)$_2$SiPh$_2$H	63.16 (63.34)	4.57 (4.48)	91
IIa	(η^5-C_5H_4SiPh$_2$H)Fe(CO)$_2$Me	63.51 (64.18)	4.64 (4.85)	
IIb	(η^5-C_5H_4SiPh$_2$H)Fe(CO)$_2$SiMe$_3$	61.11 (61.10)	5.70 (5.59)	
III	(η^5-C_5H_5)Fe(CO)$_2$SiPh$_2$(Ph)C=CH$_2$	69.85 (70.13)	4.98 (4.80)	121
IV	(η^5-C_5H_5)Fe(CO)$_2$SiPh$_2$-*trans*-CH=CHPh	70.14 (70.13)	4.76 (4.80)	133
Va	(η^5-C_5H_4SiPh$_2$(Ph)C=CH$_2$)Fe(CO)$_2$Me	70.56 (70.59)	5.38 (5.08)	81
Vb	(η^5-C_5H_4SiPh$_2$(Ph)C=CH$_2$)Fe(CO)$_2$SiMe$_3$	67.36 (67.41)	5.72 (5.62)	110
VIa	(η^5-C_5H_4SiPh$_2$-*trans*-CH=CHPh)Fe(CO)$_2$Me	70.56 (70.59)	5.18 (5.08)	82
VIb	(η^5-C_5H_4SiPh$_2$-*trans*-CH=CHPh)Fe(CO)$_2$SiMe$_3$			102
VII	(η^5-C_5H_4SiMe$_3$)Fe(CO)$_2$SiPh$_2$H[a]			
VIII	(η^5-C_5H_4SiMe$_3$)Fe(CO)$_2$SiPh$_2$C(Ph)=CH$_2$	66.05 (67.41)	5.60 (5.62)	
IX	(η^5-C_5H_4SiMe$_3$)Fe(CO)$_2$SiPh$_2$-*trans*-CH=CHPh	66.87 (66.40)	5.82 (5.66)	75

[a] Complex VII is an air- and temperature-sensitive oil which cannot be purified by column chromatography or recrystallization. All spectral and chemical properties are consistent with the structure, but attempts to obtain satisfactory elemental analysis were unsuccessful.

Table III. Regioselectivity of SiH Addition to PhC≡CH

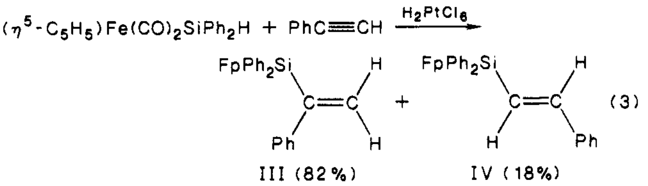
	% products	
complex	*trans*-SiCH=CH-Ph	Si(Ph)-C=CH$_2$
(η^5-C_5H_5)Fe(CO)$_2$SiPh$_2$H	18	82
(η^5-C_5H_4SiPh$_2$H)Fe(CO)$_2$Me	30	70
(η^5-C_5H_4SiPh$_2$H)Fe(CO)$_2$SiMe$_3$	67	33
(η^5-C_5H_4SiMe$_3$)Fe(CO)$_2$SiPh$_2$H	32	68

frequency of the Si-H bond.

The spectral and analytical properties of the new complexes are recorded in Tables I and II and conform with the described structures.

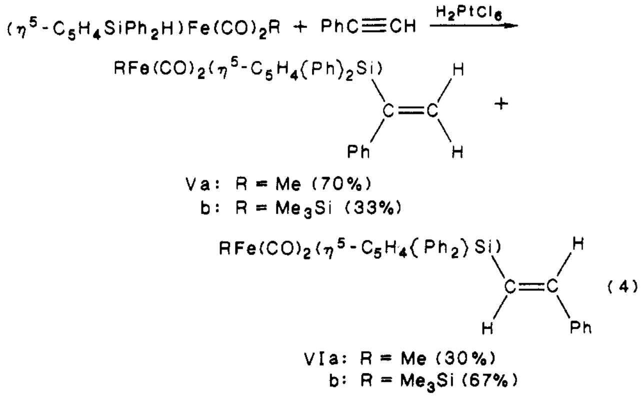
Hydrosilylation reactions of I with phenylacetylene were attempted with several different catalysts, i.e. platinum on carbon, [Rh(diphos)$_2$(norbornadiene)]$^+$PF$_6^-$, and chloroplatinic acid. Of these only chloroplatinic acid proved effective and even then elevated temperatures were required; therefore all hydrosilylation reactions were performed in refluxing toluene. The product distribution from the hydrosilylation of phenylacetylene by I is recorded in Table III.

The data indicate that of the three possible compounds that may be formed, α-silylstyrene, *trans*-β-silylstyrene, and *cis*-β-silylstyrene, the predominant isomer formed was the α-silylstyrene (82%), with 18% of the *trans*-β-styrene and a trace of the *cis*-β-styrene.



Compared to the hydrosilylation of olefins, reports on the addition of silanes to acetylenes are relatively few.[14-20] It has been established that the hydrosilylation of diphenylacetylene by optically active NpPhMeSiH resulted in a cis addition with retention of configuration at silicon.[17] A recent study of the monoaddition of Ph$_n$Me$_{3-n}$SiH to phenylacetylene catalyzed by chloroplatinic acid salts showed that the regioselectivity of addition changed as the degree of phenyl substitution changed, whereas Ph$_3$SiH yielded an β:α product ratio of 95:5; this progressively decreased upon Me substitution of Ph to a ratio of 72:28 for Me$_2$PhSiH.[20] In general, addition of silanes to acetylenes leads to predominantly *trans*-β-olefins and a study by Hill and Nile reported that use of a rhodium carbene catalyst resulted in the sole formation of β-addition products.[15] Directly related to our study is the report that cymantrenylmethylphenylsilane, (η^5-C_5H_4SiPh(Me)H)-Mn(CO)$_3$, adds to phenylacetylene to yield a ratio of 73:27 trans-β:α addition.[21]

To determine if the uniquely high yields of α-product III obtained by using I were due to the presence of the Si-Fe bond, we also performed the identical hydrosilylation reaction with the migrated complexes IIa and IIb. The reaction with IIa yielded a product distribution almost identical with that with I, clearly indicating that the abnormally high α-styrene formation was not due to the presence of a direct metal-silicon bond. Increasing the steric bulk of the complex by having a trimethylsilyl group attached to the Fe atom, IIb, did reduce the amount of α-product when compared to the results from complexes I and IIa, but even in this case the 33% yield of α-silylstyrene is still somewhat high for such a reaction when compared to a 5% or 22% yield for Ph$_3$SiH and Ph$_2$MeSiH, respectively.



These results indicate that the presence of the SiPh$_2$H group in the coordination sphere of a [(η^5-C_5H_4R)Fe(CO)$_2$] group results in a generally higher α-addition in the hydrosilylation reaction. Also, steric factors play a role in reducing the extent of this unusual regioselectivity since the greater steric bulk of the overall complex is expected to yield more of the β-product IV as observed, i.e. IIa vs IIb.

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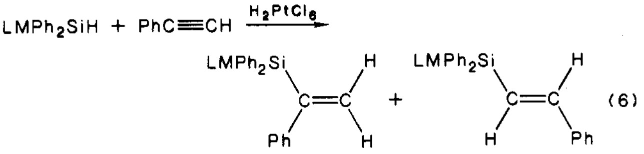
The extent of this steric role was studied by synthesizing $(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2SiPh_2H$ (VII) (eq 5) and performing

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_3 \xrightarrow{LDA} [(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2]^-Li^+ \xrightarrow{Ph_2Si(H)Cl} (\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2SiPh_2H \quad (5)$$

the same hydrosilylation reaction to determine if the extra steric bulk of the trimethylsilyl group was equally important when placed upon the cyclopentadienyl ring while the $SiPh_2H$ group was bonded to the Fe atom, i.e. interchanging the relative positions of the two Si groups (eq 6).



VIII (68%) IX (32%)

LM = $(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2$

In total, these results, all of which are tabulated in Table III, indicate that the effect of the Me_3Si group upon the regioselectivity of hydrosilylation of the $SiPh_2H$ moiety is limited to the situation when it is bonded to the Fe atom. This suggests that there may be some direct interaction between the Pt catalyst and the Fe coordination sphere during the catalytic cycle. The precise nature of this interaction is unclear but is currently under investigation.

The hydrosilylation products were separated by column chromatography and fully characterized by the appropriate spectroscopic techniques. These data are recorded in Table I. As expected, the ^{29}Si NMR data for the various complexes with a direct Si–Fe bond, I, IIb, III, IV, Vb, VIb, VII, VIII, and IX, exhibit low-field chemical shifts of approximately 35 ppm for these Si atoms when compared to the SiMe analogues, e.g. $FpSiPh_2H$ vs $MeSiPh_2H$.[22] Silicon atoms attached directly to the cyclopentadienyl ring exhibit slightly high field shifts, 3.5 ppm, as noted in previous studies.[12] Such shifts for the two types of silicon atom greatly facilitate complete identification.

Further product characterization was provided by independent synthesis. Complexes IV and IX were obtained from the reactions of the appropriate ferrate salts with *trans*-$Ph_2ClSiCH{=}CHPh$ (eq 7).

$$[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]^- + trans\text{-}Ph_2ClSiCH{=}CHPh \rightarrow (\eta^5\text{-}C_5H_4R)Fe(CO)_2\text{-}trans\text{-}SiPh_2CH{=}CHPh \quad (7)$$

$$R = H\ (IV),\ SiMe_3\ (IX)$$

Experimental Section

All manipulations were performed in N_2 atmospheres by using dry oxygen-free solvents. Starting chlorosilanes were purchased from Petrarch Systems Inc., and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ was purchased from Strem Chemicals.

NMR spectra were recorded on a Bruker NR 200 MHz multinuclear spectrometer and IR spectra on a Perkin-Elmer 580B spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

Typical reactions are described below, and all spectral and analytical data are provided in the tables.

Synthesis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2H$ (I). To 100 mL of a cooled (0 °C) THF solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-Na^+$ obtained from 5.0 g (14.1 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ was added dropwise 20 mL of a THF solution of Ph_2SiHCl (6.2 g, 28.2 mmol). The solution was stirred for 1 h and the temperature permitted to rise to room temperature. At this time the solvent was removed and the resulting thick gum extracted into 100 mL of a 40:60 methylene chloride/hexane solution and filtered. The filtrate was concentrated to 10 mL and this solution placed upon a silica gel column, 2.5 × 20 cm. Elution with a 25:75 methylene chloride/hexane solvent mixture yielded a yellow band that upon collection, concentration, and recrystallization from a 20:80 methylene chloride/hexane solution yielded 5.1 g (51%) of the title complex.

Treatment of I with Lithium Diisopropylamide. To 30 mL of a cooled (0 °C) THF solution of I (2.0 g, 5.6 mmol) was added dropwise a 10-mL solution of LDA (5.6 mmol). Monitoring by infrared spectroscopy indicated that after 40 min the corresponding ferrate salt $[(\eta^5\text{-}C_5H_4SiPh_2H)Fe(CO)_2]^-Li^+$ had formed.[23,24] To this solution was added 0.7 mL (11.3 mmol) of MeI, and the solution was stirred for 30 min. The solvent was removed under vacuum and the residue extracted with a 40:60 methylene chloride/hexane solvent mixture and purified by chromatography on a silica gel column, 2.5 × 20 cm, made up in hexane. Elution with an 85:15 hexane/methylene chloride solvent mixture produced a yellow band that was collected and after removal of the solvents yielded 1.5 g (72%) of IIa as an oil.

Reaction of the intermediate ferrate salt with Me_3SiCl was performed by a reverse addition procedure, i.e. addition of the ferrate salt to Me_3SiCl, and produced a 71% yield of IIb. Normal addition was complicated via the formation of secondary migrations due to the presence of excess LDA upon formation of IIb.

Hydrosilylation Reactions. In a typical reaction, a 100-mL round-bottomed flask equipped with a reflux condenser and magnetic stirring bar was charged with 2.20 g (6.11 mmol) of I and 1.3 mL (11.8 mmol) of phenylacetylene in 20 mL of toluene. To this mixture was added 2.0 mg of H_2PtCl_6. The solution was refluxed for 1 h after which time infrared monitoring of the Si–H stretching frequency showed that the reaction was complete. The solvent was removed under reduced pressure to yield a thick gum that was extracted into 10 mL of a 40:60 methylene chloride/hexane solvent mixture. This was placed upon a silica gel column, 2.5 × 20 cm, eluted with a 30:70 mixture of the same solvents to collect all the hydrosilylation products. This procedure resulted in the recovery of a pale yellow semisolid (2.1 g, 4.52 mmol, 74%) that was shown by NMR spectroscopy to comprise of a 82:18 ratio of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2(Ph)C{=}CH_2$ (III) and *trans*-$(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2CH{=}CHPh$ (IV). This procedure resulted in essentially the same ratio of products as determined by NMR analysis of the crude gum obtained prior to chromatography, but with significantly superior resolution. High-pressure liquid chromatographic analysis of this crude mixture indicated a trace amount (1%) of a material that may be the related *cis*-$(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2CH{=}CHPh$.

This crude reaction product was rechromatographed, eluted with an 85:15 hexane/methylene chloride solvent mixture, and the two major products were separated, complex III, the α-silylstyrene eluting first (1.6 g 3.4 mmol, 56%), and IV, the *trans*-β-silylstyrene eluting second (0.3 g, 0.6 mmol, 10%).

All other hydrosilylations were performed by using the same procedure for determining product distributions and purification if required.

Synthesis of VIb from IV by LDA Treatment. To a solution of 0.5 g (1.1 mmol) of IV in 10 mL of THF was added an equivalent of LDA in 2 mL of THF, and the mixture was stirred for 30 min at 0 °C. At this time infrared monitoring indicated the presence of the ferrate salt $[(\eta^5\text{-}C_5H_4SiPh_2\text{-}trans\text{-}CH{=}CHPh)Fe(CO)_2]^-Li^+$. This salt was quenched with an excess of Me_3SiCl and stirred for 30 min. Removal of the solvents, chromatography on silica gel, 2.5 × 20 cm column, made up in hexane and eluted with 20:80 methylene chloride/hexane solvent mixture, and final recrystallization from hexane yielded 0.39 g (0.73 mmol, 66%) of VIb.

In an analogous fashion we synthesized VIa in 55% yield and Va and Vb from III (65% and 57% yields, respectively).

Independent Synthesis of $(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2SiPh_2$-*trans*-$CH{=}CHPh$ (IX). Into a three-necked flask was charged 0.57 g (2.27 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_3$ in 10

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mL of THF. To this cooled solution (0 °C) was added an equivalent of LDA in THF, and the reaction mixture was stirred for 40 min at which time was added an equivalent of *trans*-(Cl)$SiPh_2CH{=}CHPh$ dissolved in 10 mL of THF. The solution was permitted to warm to room temperature and stirred for 30 min. After removal of the solvents and extraction with a 40:60 methylene chloride/hexane solvent mixture, the crude material was placed on a silica gel column, 2.5 × 20 cm made up in hexane, and eluted with a 20:80 methylene chloride/hexane solvent mixture. The resulting material was recrystallized from hexane to yield 0.86 g (1.61 mmol, 71%) of the title compound.

Independent Synthesis of (η^5-C_5H_5)$Fe(CO)_2SiPh_2$-*trans*-CH=CHPh (IV). To a solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-Na^+$ prepared from 1.6 g (9.04 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in THF was added an equivalent of (Cl)$SiPh_2$-*trans*-CH=CHPh. The mixture was stirred for 30 min, and workup as above yielded IV (1.5 g, 3.2 mmol, 35%).

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Synthesis and Characterization of Rhodium(I) Amino–Olefin Complexes

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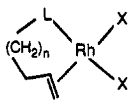
The syntheses of $[(CH_2CR_1CH_2CH_2NR_2R_3)RhClL$ complexes (R_1 = CH_3, H, R_2 = *n*-Bu, R_3 = H; R_1 = CH_3, H, R_2 = R_3 = CH_3, L = CO or dimer; **19–32** and **38–43**) are reported. The complexes are prepared by the reaction of unsaturated amines with bis(μ-chloro)tetracarbonyldirhodium(I) (**3**) or bis(μ-chloro)tetrakis(ethylene)dirhodium(I) (**4**) at ambient temperature. Compound **19**, [*N*-(*trans*-3-pentenyl)*n*-butylamine]carbonylrhodium(I) chloride, crystallized in the monoclinic space group $P2_1/c$ with cell dimensions a = 17.699 (5), b = 8.442 (1), and c = 20.119 (5) Å, and β = 120.19 (2)°.

Introduction

As part of our research program directed toward the regioselective functionalization of simple olefins by prior coordination to transition metals,[1] we found the need for Rh(I) complexes containing bidentate olefinic ligands. Numerous Rh(I) complexes with bidentate ligands are known;[2] however, none proved suitable for our purpose.

Diolefin complexes[2] would not be useful because of the question of regiocontrol during alkene functionalization if an unsymmetrical diolefin was utilized. We were interested in complexes, such as **1**, which incorporated bidentate, monoolefin ligands where a heteroatom was tethered to the olefin by a carbon chain to yield a chelated ligand. Olefinic phosphines[3,4] have been shown to give rise to Rh(I) complexes (e.g. **2**) containing bidentate ligands.[5]



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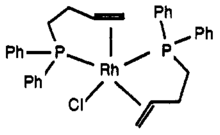

2

However, subsequent synthetic utility of the phosphine ligand after olefin functionalization was questionable. While allylic amines have been shown to give rise to polymeric materials[6a,b] upon reaction with bis(μ-chloro)tetracarbonyldirhodium(I) (**3**), we found that homoallylic and bishomoallylic amines reacted with both **3** and bis(μ-chloro)tetrakis(ethylene)dirhodium(I) (**4**) to give rise to a series of new complexes containing bidentate olefinic ligands.[6c] We now report our results on the synthesis and characterization of these new Rh(I) complexes.

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