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Synthesis and Properties of Organometallic Rings and Macrocycles Containing Ferrocene, Silicon, and Unsaturated Hydrocarbon Units: X-ray Crystal Structures of the Novel Ferrocenophanes $Fe(\eta\text{-}C_5H_4)_2(SiMe_2)_2(CH{=}CH)$ and *trans,trans*-$Fe(\eta\text{-}C_5H_4)_2(SiMe_2)_2(CH_2CH{=}CHCH_2)_2$

Wolfgang Finckh, Ben-Zhong Tang, Alan Lough, and Ian Manners*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, M5S 1A1 Ontario, Canada

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A range of novel cyclic organometallic compounds containing ferrocene, silicon, and unsaturated hydrocarbon units have been synthesized and characterized. These species were prepared via the insertion of alkynes or butadiene into the silicon–silicon bond of the ferrocenyldisilane $Fe(\eta\text{-}C_5H_4)_2(SiMe_2)_2$ (1). Thus, the reaction of 1 with the acetylenes $HC{\equiv}CH$ and $HC{\equiv}CPh$ in the presence of $Pd(PPh_3)_4$ catalyst in toluene at 110 °C yielded the organometallic ring products $Fe(\eta\text{-}C_5H_4)_2(SiMe_2)_2(RC{=}CR')$ (2, R = R' = H; 3, R = H, R' = Ph). Reaction of 1 with $MeO_2CC{\equiv}CCO_2Me$ under the same conditions yielded mainly the monoinsertion product $Fe(\eta\text{-}C_5H_4)_2(SiMe_2)_2(RC{=}CR)$ (4; R = CO_2Me) together with trace amounts of the diinsertion product $Fe(\eta\text{-}C_5H_4)_2(SiMe_2)_2(RC{=}CR)_2$ (5; R = CO_2Me). Significant quantities of the acetylene cyclotrimerization derivative $C_6(CO_2Me)_6$ (6) were also formed. By contrast, reaction of 1 with butadiene under the same conditions exclusively yielded the macrocyclic diinsertion product $Fe(\eta\text{-}C_5H_4)_2(SiMe_2)_2(CH_2CH{=}CHCH_2)_2$ (7). Characterization of the latter by ^{13}C, ^{29}Si, and ^1H NMR spectroscopy indicated the presence of an approximate 7:3 mixture of the trans,trans and cis,trans isomers. The X-ray crystal structures of 2 and *trans,trans*-7 were determined. Crystals of 2 are monoclinic, space group $P2_1/n$, with $a = 6.3131\ (8)$ Å, $b = 15.7160\ (12)$ Å, $c = 16.8650\ (22)$ Å, $\beta = 95.087\ (11)°$, $V = 1666.7\ (3)$ Å^3, and $Z = 4$. Crystals of 7 are orthorhombic, space group *Pcnb*, with $a = 11.188\ (4)$ Å, $b = 13.530\ (5)$ Å, $c = 14.654\ (8)$ Å, $V = 2218\ (2)$ Å^3, and $Z = 4$.

Introduction

Cyclic molecules continue to attract considerable attention because of the interesting questions they pose concerning structure, bonding, and reactivity and their function as precursors to solid-state materials and new polymer systems.[1,2] We are particularly interested in investigating the ring-opening polymerization of cyclic compounds containing inorganic elements or organometallic units as a route to new macromolecules with novel and potentially useful properties.[3] Ring-opening polymerization represents a well-established route to organic polymers and an increasingly successful method for the synthesis of polymers constructed of inorganic elements.[3-6] Ring-opening methods may also prove of great utility in the preparation of organometallic polymers, but apart from the cases of several cyclic organosilicon compounds, very few attempts to investigate this approach have been reported.[7,8]

One of the problems hindering the development of this area is the relative lack of cyclic organometallic compounds which are likely to function as polymerization monomers. For this reason we have attempted to develop routes to a series of organometallic rings containing the relatively robust ferrocene unit as a skeletal component together with silicon atoms and/or olefinic groups. Silicon atoms function as sites for the anionically initiated ring-opening polymerization of cyclotetrasilanes and silacyclopentenes.[5c,7] Carbon–carbon multiple bonds, on the other hand, are the sites of attack in transition-metal-catalyzed ring-opening metathesis polymerization (ROMP) reactions.[8]

In this paper we report full details of our synthetic work aimed at developing routes to cyclic organometallic species which contain skeletal ferrocene moieties together with both organosilicon and unsaturated hydrocarbon units.

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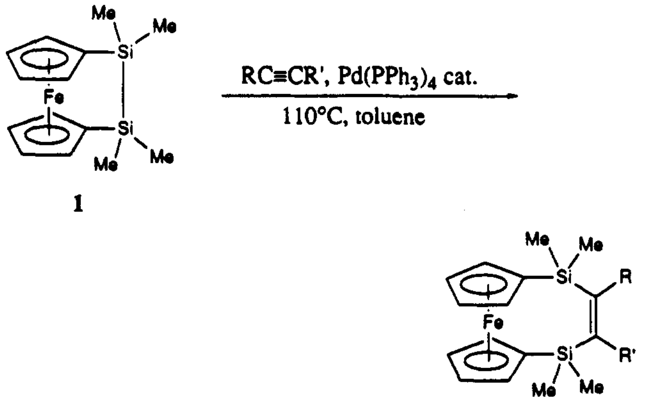
Scheme I



1

2 R = R' = H

3 R = H, R' = Ph

4 R = R' = CO_2Me

Thus, the synthesis, structural characterization, and properties of several novel ferrocenophanes are described. Studies of the polymerization behavior of these and other related cyclic organometallic species will be reported elsewhere.[9]

Results and Discussion

Synthesis of the Ferrocenyldisilane 1. Our synthetic strategy to assemble cyclic organometallic compounds containing ferrocene together with organosilicon and unsaturated hydrocarbon units consisted of exploiting the ability of alkynes and dienes to insert into silicon-silicon bonds in the presence of transition-metal catalysts. The key starting material in our work was the ferrocenyldisilane 1. Insertion of unsaturated hydrocarbons into strained and unstrained silicon-silicon bonds catalyzed by palladium(0) complexes has ample precedent in organosilicon chemistry, but the extension of this approach to metal-containing rings was unexplored prior to this work.[10]

The ferrocenyldisilane 1 was prepared in high yield as an orange, sublimable compound by the previously reported method, which involved the reaction of dilithioferrocene-tmeda (tmeda = tetramethylethylenediamine) with the dichlorodisilane $ClMe_2Si$–$SiMe_2Cl$.[11] The latter was prepared in two high-yield steps from Me_3SiCl. These involved, first, a Wurtz coupling reaction with sodium-potassium alloy to yield Me_3Si–$SiMe_3$ and, second, replacement of a methyl group at each silicon atom by chlorine using Me_3SiCl in the presence of $AlCl_3$.[12,13] The identity of 1 was confirmed by ^1H NMR spectroscopy, mass spectrometry, and the melting point, which afforded data consistent with that reported in the literature.[11] In addition, compound 1 was further characterized by ^{13}C and ^{29}Si NMR spectroscopy, which also gave data consistent with the assigned structure.

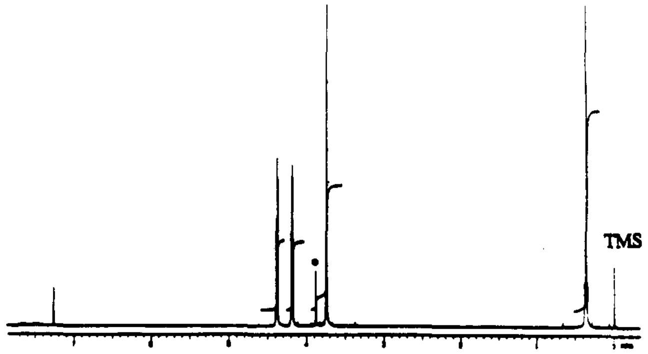
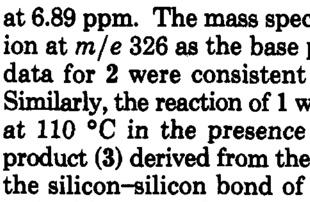


Figure 1. 200-MHz ^1H NMR spectrum of 4. The resonance marked with an asterisk is assigned to the arene $C_6(CO_2Me)_6$, which is an impurity.

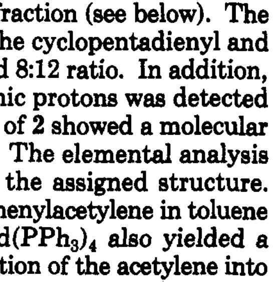
Palladium-Catalyzed Insertion of Acetylenes into the Si–Si Bond of 1: Synthesis of Compounds 2–4. Attempts were made to insert a variety of unsaturated hydrocarbons into the Si–Si bond of 1 in the presence of palladium(0) complexes. The first reactions that were investigated utilized a range of different alkynes.

Reaction of 1 with acetylene at 110 °C in toluene in the presence of catalytic amounts of $Pd(PPh_3)_4$ yielded the deep orange insertion product 2. Compound 2 was characterized by ^1H, ^{13}C, and ^{29}Si NMR, mass spectrometry, elemental analysis, and X-ray diffraction (see below). The ^1H NMR spectrum of 2 showed the cyclopentadienyl and methyl resonances in the expected 8:12 ratio. In addition, a low-field resonance of the olefinic protons was detected at 6.89 ppm. The mass spectrum of 2 showed a molecular ion at m/e 326 as the base peak. The elemental analysis data for 2 were consistent with the assigned structure. Similarly, the reaction of 1 with phenylacetylene in toluene at 110 °C in the presence of $Pd(PPh_3)_4$ also yielded a product (3) derived from the insertion of the acetylene into the silicon-silicon bond of 1. Compound 3 was characterized by methods similar to those for 2. In particular, the ^{29}Si NMR spectrum of 3 in $CDCl_3$ showed two singlet resonances of equal intensity arising from the nonequivalent silicon atoms present. The ^1H and ^{13}C NMR spectra, mass spectrum, and elemental analysis data for 3 were also consistent with the assigned structure.

In contrast to the palladium-catalyzed reaction of 1 with acetylene and phenylacetylene, the reaction of 1 with the activated acetylene $MeO_2CC{\equiv}CCO_2Me$ yielded a mixture of products. The main product was identified as the expected monoinsertion product 4. Interestingly, trace quantities of the diinsertion product 5 were also formed.



5



6

The other major component of the reaction mixture was identified as the acetylene cyclotrimerization product 6. Evidence for the presence of small quantities of 5 was

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Table I. Summary of Crystal Data and Intensity Collection Parameters

compd	2	7
empirical formula	$C_{16}H_{22}FeSi_2$	$C_{22}H_{32}FeSi_2$
M_r	326.4	408.5
cryst class	monoclinic	orthorhombic
space group	$P2_1/n$	$Pcnb$
a, Å	6.3131 (8)	11.188 (3)
b, Å	15.7160 (12)	13.530 (4)
c, Å	16.8650 (22)	14.654 (5)
β, deg	95.087 (11)	
V, Å^3	1666.7 (3)	2218.1 (12)
Z	4	4
D_{calc}, g cm^{-3}	1.30	1.22
μ(Mo Kα), cm^{-1}	10.3	7.9
$F(000)$	688	872
ω scan width, deg	$0.6 + 0.35 \tan \theta$	$0.6 + 0.35 \tan \theta$
θ range collected, deg	1–27 ($\pm h,k,l$)	1–25 (hkl)
total no. of rflns	3870	2240
no. of unique rflns	3614	
R_{int}	0.063	
no. of obsd data ($I > 3\sigma(I)$)	2662	1188
weighting g	0.0005	0.00177
R	0.049	0.047
R_w	0.053	0.052
goodness of fit	2.22	1.20
largest Δ/σ	0.006	0.007
no. of params refined	174	125
max density in ΔF map, e/Å^3	0.55	0.32

Table II. Final Fractional Coordinates and Thermal Parameters for the Non-Hydrogen Atoms of 2

atom	x	y	z	U_{eq}, Å^2 [a]
Fe	0.11465 (8)	0.10801 (3)	0.37275 (2)	0.0472 (2)
Si1	0.12134 (17)	0.17463 (6)	0.16768 (5)	0.0543 (4)
Si2	0.11275 (14)	0.33001 (5)	0.34311 (6)	0.0453 (4)
C1	0.1525 (5)	0.09929 (18)	0.25233 (17)	0.0467 (7)
C2	0.3378 (5)	0.07303 (28)	0.29955 (21)	0.0791 (7)
C3	0.2836 (6)	0.00345 (26)	0.34783 (23)	0.1004 (7)
C5	0.0725 (6)	−0.01363 (23)	0.33303 (24)	0.1029 (7)
C4	−0.0111 (5)	0.04314 (21)	0.27500 (19)	0.0677 (7)
C6	0.0780 (5)	0.23340 (17)	0.40356 (17)	0.0455 (7)
C7	0.2412 (5)	0.19326 (19)	0.45558 (19)	0.0589 (7)
C8	0.1528 (6)	0.12309 (21)	0.49307 (19)	0.0704 (7)
C9	−0.0599 (6)	0.11837 (20)	0.46689 (22)	0.0732 (7)
C10	−0.1106 (5)	0.18577 (19)	0.41114 (21)	0.0614 (7)
C11	−0.0455 (5)	0.26975 (21)	0.18404 (20)	0.0590 (7)
C12	−0.0486 (5)	0.32427 (20)	0.24471 (21)	0.0562 (7)
C13	−0.0185 (6)	0.11513 (25)	0.08257 (23)	0.0996 (8)
C14	0.3873 (6)	0.2076 (3)	0.13966 (28)	0.1114 (8)
C15	0.4020 (5)	0.34266 (24)	0.33386 (23)	0.0690 (7)
C16	0.0139 (5)	0.42455 (22)	0.39502 (26)	0.0748 (7)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

Table III. Selected Bond Lengths (Å) and Angles (deg) for 2[a]

Distances			
Fe–C1	2.070 (3)	Si2–C12	1.871 (4)
Fe–C2	2.030 (4)	Si2–C15	1.857 (3)
Fe–C3	2.023 (4)	Si2–C16	1.860 (4)
Fe–C4	2.038 (3)	C1–C2	1.417 (5)
Fe–C5	2.035 (4)	C1–C5	1.436 (4)
Fe–C6	2.056 (3)	C2–C3	1.423 (6)
Fe–C7	2.046 (3)	C3–C4	1.360 (6)
Fe–C8	2.036 (3)	C4–C5	1.393 (5)
Fe–C9	2.018 (4)	C6–C7	1.439 (4)
Fe–C10	2.024 (3)	C6–C10	1.421 (4)
Si1–C1	1.852 (3)	C7–C8	1.411 (5)
Si1–C11	1.863 (3)	C8–C9	1.378 (5)
Si1–C13	1.868 (4)	C9–C10	1.434 (5)
Si1–C14	1.858 (4)	C11–C12	1.336 (5)
Si2–C6	1.8527 (29)		
Angles			
C11–Si1–C1	114.93 (14)	C12–Si2–C6	111.52 (14)
C13–Si1–C1	106.44 (16)	C15–Si2–C6	107.42 (15)
C14–Si1–C1	109.74 (18)	C16–Si2–C6	109.54 (16)
C2–C1–Si1	130.19 (24)	C7–C6–Si2	125.55 (22)
C4–C1–Si1	124.65 (22)	C10–C6–Si2	128.47 (23)
C13–Si1–C11	106.28 (16)	C15–Si2–C12	113.13 (16)
C14–Si1–C11	110.48 (18)	C16–Si2–C12	106.07 (16)
C12–C11–Si1	132.43 (26)	C11–C12–Si2	131.79 (25)
C14–Si1–C13	108.68 (19)	C16–Si2–C15	109.12 (16)

[a] Estimated standard deviations are given in parentheses.

found in the mass spectrum of the crude product mixture. This showed the presence of a peak at *m/e* 584, which was assigned to the molecular ion of 5. However, an analysis of the product mixture at this stage by ^{1}H and ^{13}C NMR spectroscopy showed no resonances which could be assigned to this species. Thus, the yield of 5 must be below ca. 3–5%, the detection limit for NMR spectroscopy. Compound 4 was successfully separated from the small quantities of 5 by repeated high-vacuum sublimation, as indicated by mass spectrometry of the purified product, which showed no peaks that could be assigned to 5. However, although partial separation of 4 from the acetylene cyclotrimerization product 6 was also possible via fractional sublimation, significant loss of material occurred during this process and a pure sample of 4 could not be isolated. The presence of the arene 6 as an impurity in the isolated monoinsertion product 4 was apparent from the mass spectrum, which showed a molecular ion derived from 6 at *m/e* 426 and another peak at *m/e* 395 which corresponded to the loss of a methoxy group from the molecular ion. Moreover, the ^{1}H NMR spectrum of the isolated product (Figure 1) showed, in addition to the expected resonances for 4, a resonance at 3.90 ppm assigned to the methoxy groups of 6. Integration of this spectrum indicated that the purity of isolated compound 4 was ca. 95%. Although compound 4 could not be completely purified, the identity of this species was clear from the ^{1}H and ^{13}C NMR spectra and mass spectra of the 95% pure product. For example, the mass spectrum of the product showed, in addition to a molecular ion from 6, a peak at *m/e* 442 which was assigned to the molecular ion derived from 4, and this corresponded to the base peak. The reaction of 1 with diphenylacetylene was also investigated under the same reaction conditions as those that were used to prepare compounds 2–4. However, in this case no reaction was detected.

In order to provide additional structural characterization of one of the new compounds prepared, a single-crystal X-ray diffraction study of the acetylene insertion product 2 was undertaken.

X-ray Structure of 2. Single crystals of 2 suitable for an X-ray diffraction study were grown by cooling a solution of the compound in hexanes to −6 °C for 24 h.

The molecular structure of 2 is shown in Figure 2a, and an alternative view of the molecule is shown in Figure 2b. A summary of cell constants and data collection parameters is included in Table I. Final fractional atomic coordinates and selected bond lengths and angles are given in Tables II and III, respectively.

The X-ray crystal structure of 2 confirmed the presence of a ring comprising a ferrocene unit, two silicon atoms, and an unsaturated hydrocarbon fragment containing a C═C bond. The most interesting structural feature of 2 is that the silicon atoms attached to the C═C bond lie slightly above and below the planes of the respective cyclopentadienyl rings, which are therefore slightly tilted such that the pairs of atoms C3, C4, and C8, C9 are the closest to one another. This can be appreciated by comparing the Fe–C3 and Fe–C4 distances (2.023 (4) and 2.038 (3) Å) and the Fe–C8 and Fe–C9 distances (2.036 (3) and 2.018 (4) Å) with the slightly longer Fe–C1 distance (2.070

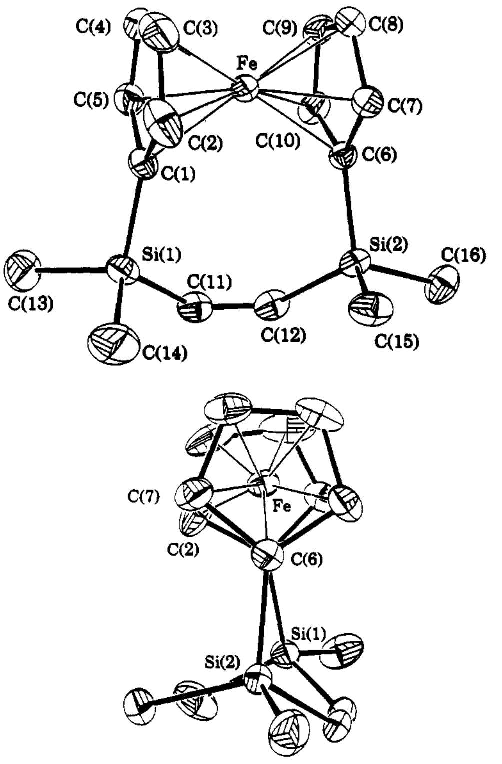


Figure 2. (a, top) Molecular structure of 2 (with thermal ellipsoids drawn at the 25% probability level). (b, bottom) Alternative view of a molecule of 2 (with thermal ellipsoids drawn at the 25% probability level).

(3) Å) and the Fe–C6 distance (2.056 (3) Å). The tilt angle between the mean planes of the cyclopentadienyl ligands in 2 is 3.43 (21)°. The cyclopentadienyl rings in 2 are slightly staggered, with an angle of 11.10 (15)° between the projection of the Fe–C bonds on the mean plane of the cyclopentadienyl rings. This is slightly larger than the analogous angle in Fe(η-$C_5H_4SiMe_2SiMe_3$)$_2$, which has a value of 6.0 (17)°.[14] The C–C bonds between the two carbon atoms of the cyclopentadienyl ligand opposite to the silicon atoms have lengths of 1.360 (6) and 1.378 (5) Å, which is significantly shorter than the other C–C bond lengths in the cyclopentadienyl ligand, which range from 1.393 (5) to 1.439 (4) Å. This is analogous to the situation in Fe(η-$C_5H_4SiMe_2SiMe_3$)$_2$. When projected on the mean plane of the cyclopentadienyl rings, the bonds C1–Si1 and C6–Si2 make an angle of 15.01 (15)°. The corresponding bonds in Fe(η-$C_5H_4SiMe_2SiMe_3$)$_2$ make a much larger angle of 149 (2)°. This is again a consequence of the lack of a bridge between the cyclopentadienyl ligands in the latter, which allows steric interactions to be minimized via the adoption of an almost trans arrangement of silyl groups.[14] The C=C bond length (1.336 (5) Å) is slightly longer than the typical value for carbon–carbon double bonds (1.317 Å).[15] Interestingly, the Si—C=C bond angles are particularly wide (131.79 (25) and 132.43 (26)°) compared to the usual values for sp^2 carbon centers (120°). The bonds joining the silicon atoms to the carbon atoms of the cyclopentadienyl groups in 2 have the lengths 1.852 (3) and 1.853 (3) Å, which are similar to the analogous bonds in Fe(η-$C_5H_4SiMe_2SiMe_3$)$_2$ (1.85 (2) and 1.88 (3) Å). The bond lengths and angles within the $SiMe_2$ groups are normal.

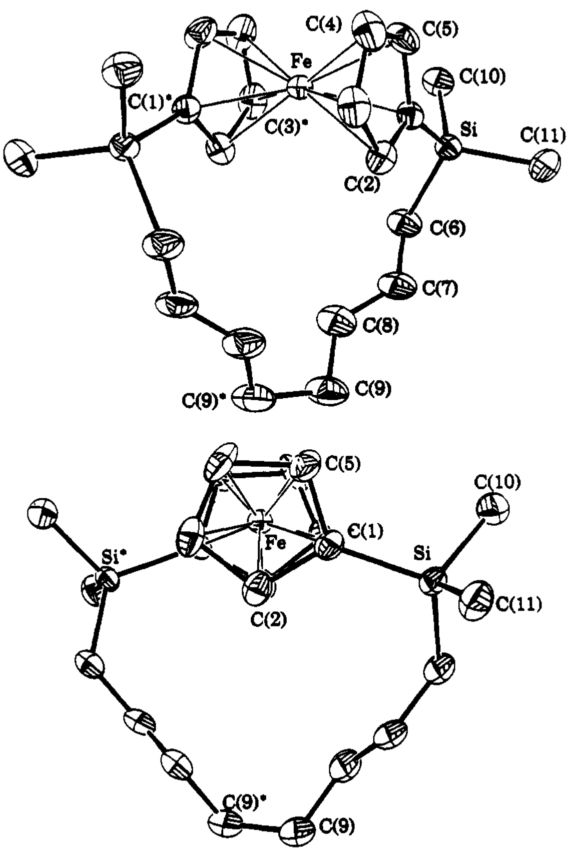
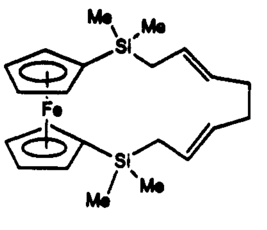


Figure 3. (a, top) Molecular structure of 7 (probability ellipsoids are drawn at the 25% level, and symmetry-related atoms are starred). (b, bottom) Alternative view of a molecule of 7 (probability ellipsoids are drawn at the 25% level, and symmetry-related atoms are starred).

Palladium-Catalyzed Insertion of Butadiene into the Si–Si Bond of 1: Synthesis of 7. The reaction of 1 with other unsaturated hydrocarbons was also explored. No reaction was detected between 1 and 1,3-cyclooctadiene, 1,5-cyclooctadiene, or cyclopentadiene in the presence of a catalytic quantity of $Pd(PPh_3)_4$ in toluene at 110 °C. In contrast, the reaction of 1 with butadiene under similar conditions yielded the orange, crystalline product 7, which was exclusively derived from the insertion of two molecules of butadiene into the Si–Si bond of 1. Thus, the mass spectrum of 7 showed a molecular ion at *m*/*e* 408 which represented the base peak. In addition, elemental analysis data and integration of the ^1H NMR spectrum of 7 were consistent with the incorporation of two diene units into the organometallic ring structure.



7

$Me_3SiCH_2CH{=}CHCH_2SiMe_3$

8

In principle, compound 7 might contain molecules which possess any of three different structures, depending on the geometry at the C=C bonds. Thus, trans,trans, cis,trans, or cis,cis structures might be envisaged. On the basis of accepted mechanisms for the insertion of alkynes into Si–Si bonds, a cis,cis structure would be expected in the product (see below).[10d,g,j] To help resolve this structural ambiguity and because of the unusual molecular structure, a single

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[14] Hirotsu, K.; Higuchi, T.; Shimara, A. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1557.

[15] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 1* **1987**, S1.

Table IV. Final Fractional Coordinates and Thermal Parameters for the Non-Hydrogen Atoms of 7

atom	x	y	z	U_{eq}, Å$^{2\,a}$
Fe	0.00	0.25	0.12958 (6)	0.0425 (5)
Si	0.11171 (12)	0.48081 (8)	0.20256 (9)	0.0475 (7)
C1	−0.0078 (4)	0.3981 (3)	0.1603 (3)	0.049 (3)
C2	−0.0944 (4)	0.3429 (3)	0.2117 (4)	0.056 (3)
C3	−0.1725 (5)	0.2928 (4)	0.1498 (5)	0.067 (3)
C4	−0.1361 (6)	0.3160 (4)	0.0614 (5)	0.083 (4)
C5	−0.0362 (5)	0.3801 (4)	0.0658 (4)	0.071 (4)
C6	0.1810 (5)	0.4349 (4)	0.3106 (4)	0.070 (4)
C7	0.1020 (6)	0.4114 (5)	0.3871 (4)	0.078 (4)
C8	0.0996 (6)	0.3242 (5)	0.4326 (4)	0.079 (4)
C9	0.0240 (6)	0.3019 (5)	0.5089 (4)	0.092 (5)
C10	0.2312 (5)	0.4906 (4)	0.1156 (3)	0.071 (4)
C11	0.0446 (5)	0.6047 (4)	0.2219 (4)	0.073 (4)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

Table V. Selected Bond Lengths (Å) and Angles (deg) for 7[a]

	Distances		
Fe–C1	2.055 (4)	C1–C2	1.436 (7)
Fe–C2	2.035 (5)	C1–C5	1.441 (7)
Fe–C3	2.037 (5)	C2–C3	1.430 (8)
Fe–C4	2.029 (6)	C3–C4	1.395 (10)
Fe–C5	2.033 (5)	C4–C5	1.416 (8)
Si–C1	1.851 (5)	C6–C7	1.462 (8)
Si–C6	1.869 (6)	C7–C8	1.355 (9)
Si–C10	1.851 (5)	C8–C9	1.434 (9)
Si–C11	1.858 (5)	C9–C9*	1.503 (10)
	Angles		
C1*–Fe–C1	154.66 (19)	C11–Si–C10	109.42 (25)
C6–Si–C1	112.46 (23)	C5–C1–C2	105.5 (4)
C10–Si–C1	109.57 (23)	C3–C2–C1	109.1 (5)
C11–Si–C1	107.73 (23)	C4–C5–C1	108.7 (5)
C2–C1–Si	128.8 (4)	C4–C3–C2	107.7 (5)
C5–C1–Si	125.6 (4)	C5–C4–C3	109.0 (6)
C10–Si–C6	107.89 (25)	C8–C7–C6	125.5 (6)
C11–Si–C6	109.75 (26)	C9–C8–C7	125.4 (6)
C7–C6–Si	118.1 (4)	C9*–C9–C8	114.0 (5)

[a] Estimated standard deviations are given in parentheses.

crystal of 7 was analyzed by X-ray diffraction methods.

X-ray Structure of the Trans,trans Isomer of 7. Single crystals of 7 suitable for an X-ray diffraction study were grown by cooling a solution of the compound in hexanes to −6 °C for 24 h.

The molecular structure of 7 is shown in Figure 3a, and an alternative view of the molecule is shown in Figure 3b. A summary of cell constants and data collection parameters is included in Table I. Final fractional atomic coordinates and selected bond lengths and angles are given in Tables IV and V, respectively.

The X-ray structure of 7 confirmed the presence of a ring structure containing a ferrocene nucleus attached to two organosilicon units linked to two coupled butadiene molecules and indicated the presence of crystallographic C_2 symmetry. The most surprising feature of the structure was the presence of a trans,trans geometry with respect to the two C=C bonds. This is unusual, as products with cis stereochemistry usually result from the transition-metal-catalyzed insertion of unsaturated hydrocarbons into Si–Si bonds (see below). In most respects the bond angles and bond lengths in 7 are as would be expected on the basis of structural data for molecules containing the individual fragments present in this species. Thus, the bond lengths and bond angles in the ferrocenyl unit are normal and the cyclopentadienyl ligands are coplanar. When projected on the mean plane of the cyclopentadienyl ligands, the C1–Si and C1*–Si* bonds make an angle of 131.8 (4)°, which is much closer to the corresponding value of 149 (2)° in Fe(η-$C_5H_4SiMe_2SiMe_3$)$_2$[14] than the value of 15.01 (15)° in 2. This can be explained by the presence of a relatively long and flexible bridge in 7 which allows steric congestion to be minimized in a way similar to that for Fe(η-$C_5H_4SiMe_2SiMe_3$)$_2$ by the adoption of an almost trans arrangement of the silyl groups bonded to the ferrocene ring. In contrast, because the bridge between the cyclopentadienyl ligands in 2 is shorter and more rigid, steric interactions between the silyl groups in 2 cannot be relieved by cyclopentadienyl ligand rotation. Thus, the silyl groups are held in virtually a cis arrangement. The C–C bonds in the cyclopentadienyl groups which are opposite the silyl substituent have a bond length of 1.395 (10) Å, which is significantly shorter than the other C–C bonds present, which vary from 1.416 (8) to 1.441 (7) Å. A similar distortion was noted in 2. The angle between the projection of the Fe–C bonds on the mean plane of the cyclopentadienyl ligands is 6.4 (1)°, which indicates that the rings are slightly staggered. The Si–C bonds joining the silicon atom to the cyclopentadienyl ligands are of length 1.851 (5) Å, which is similar to the lengths of the analogous bonds in Fe(η-$C_5H_4SiMe_2SiMe_3$)$_2$ (average 1.865 (25) Å).[14] The C=C bond lengths have the value 1.355 (9) Å, which is significantly longer than that normally found for trans CH=CH units (1.312 Å).[15] Otherwise, the geometry of the organic unit is similar to that present in *cis,cis*-$Ph_2Si(CH_2CH{=}CHCH_2)_2SiPh_2$.[8b]

NMR Spectroscopic Characterization of the Trans,trans and Cis,trans Isomers of 7. Although the X-ray diffraction study of a single crystal of 7 indicated that the trans,trans isomer was present, the possibility existed that the crystal selected was not fully representative of the sample. That this was indeed the case was confirmed by the ^{13}C and ^{29}Si NMR spectra for 7, which indicated the presence of an approximate 7:3 mixture of the trans,trans and cis,trans isomers. Comparison of the ^{13}C NMR spectrum of 7 (Figure 4a) with that reported for the cis and trans isomers of $Me_3SiCH_2CH{=}CHCH_2SiMe_3$ (8) provides excellent evidence for the presence of these two isomers.[7a] For example, in the CH_2 region of the ^{13}C NMR spectrum of 7 (Figure 4b) two large resonances of equal intensity and four smaller resonances of equal intensity were present. The two large resonances at 23.26 and 32.20 ppm can be attributed to the trans,trans isomer of 7 and can be assigned to the sets of two equivalent methylene carbons bound to silicon and to the two equivalent methylene carbons furthest removed from the ferrocene moiety, respectively. The former resonance has a chemical shift virtually identical with that of the methylene carbons present in *trans*-8 (δ 23.2 ppm), as would be expected. The set of four smaller equal-intensity resonances can be assigned to the cis,trans isomer of 7. Thus, the higher field resonances at 23.75 and 17.22 ppm can be assigned to the methylene groups bonded to silicon next to the trans C=C bond and to the methylene groups bonded to silicon next to the cis C=C bond, respectively. Again, support for these assignments comes from the ^{13}C NMR spectra of the different isomers of 8. Thus, the carbon nuclei of the methylene groups bonded to silicon for the cis isomer of 8 resonate at significantly higher field (18.2 ppm) than those of the trans isomer (23.2 ppm). The two lower field singlet resonances at 32.82 and 27.22 ppm are assigned to the methylene groups furthest from the ferrocene moiety. Because of the similarity of the chemical shift of the former to that for the trans,trans isomer (32.20 ppm), the former is assigned to the CH_2 group closest to the trans C=C bond, while the latter is assigned to the CH_2 group closest to the cis C=C unit. Similar arguments

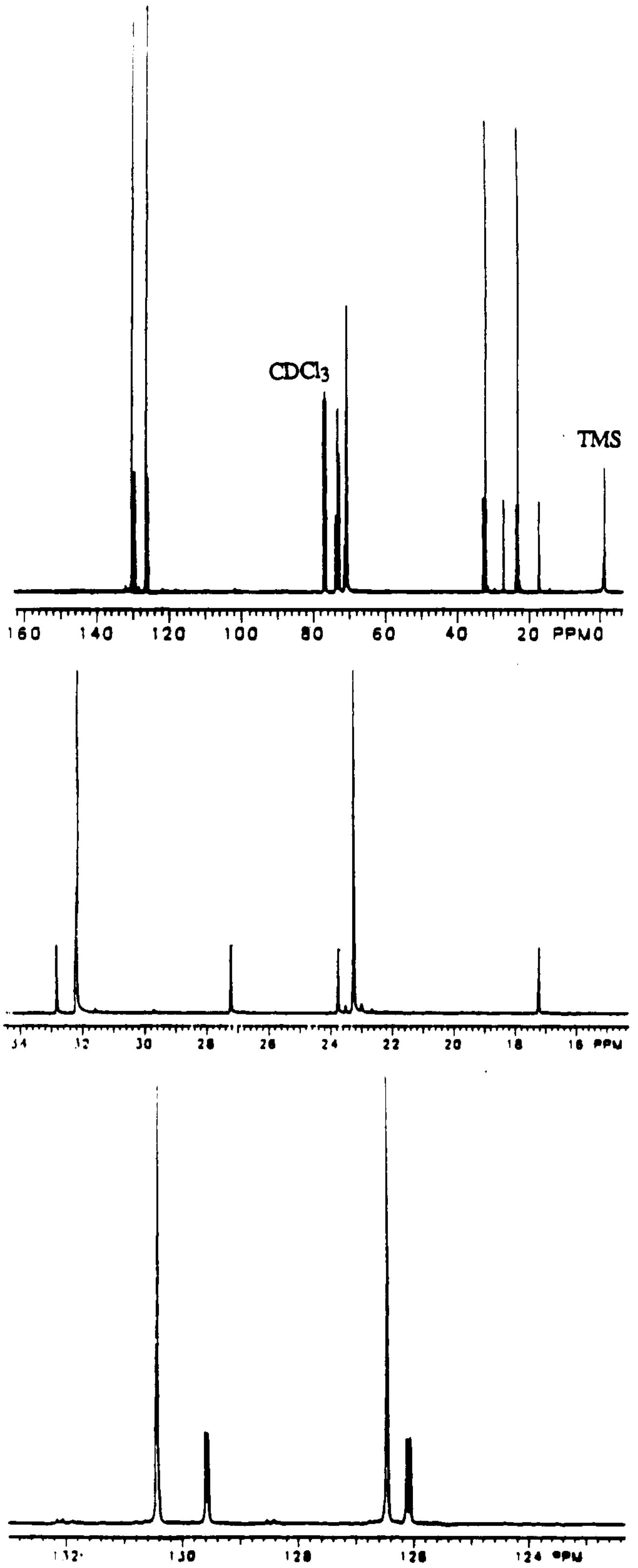

Figure 4. (a, top) 100.5-MHz ^{13}C NMR spectrum of 7. (b, middle) Expansion of the methylene carbon region of the 100.5-MHz ^{13}C NMR spectrum of 7. (c, bottom) Expansion of the olefinic carbon region of the 100.5-MHz ^{13}C NMR spectrum of 7.

using the reported data for the cis and trans isomers of 8 permitted resonance assignments to the trans,trans and cis,trans isomers of 7 in other regions of the ^{13}C NMR spectrum. For example, in the olefinic carbon region (Figure 4c) the large resonances at 130.43 and 126.47 ppm can be assigned to the trans,trans isomer and the four less intense resonances at 129.60, 129.55, 126.06, and 126.04 ppm to the four inequivalent multiply bonded carbon atoms present in the cis,trans species. The ^{29}Si NMR spectrum of 7 was consistent with the presence of a 7:3 mixture of trans,trans and cis,trans isomers. Thus, this spectrum showed a large singlet resonance at −5.1 ppm, which was assigned to the two equivalent silicon atoms present in the trans,trans isomer, and a much smaller pair of singlets of approximately equal intensity at −5.6 and −3.9 ppm, which were assigned to the inequivalent silicon atoms in the cis,trans isomer. Integration of this spectrum indicated the ratio of the trans,trans to cis,trans isomers to be approximately 7:3.

Mechanisms for the Palladium-Catalyzed Si–Si Bond Insertion Reactions. The insertion of unsaturated hydrocarbons such as acetylenes into both strained and unstrained silicon–silicon bonds in the presence of transition-metal catalysts is a relatively well-studied reaction.[10] In general, the reaction tends to be most facile if the Si–Si bond is strained or if electron-withdrawing substituents are present at silicon. Furthermore, the isolated products invariably possess predominantly cis stereochemistry at the C=C bonds.[10] A mechanism has been proposed for the palladium-catalyzed insertion processes involving acetylenes.[10d,g,j] The reaction is believed to initially proceed via the oxidative addition of the silicon–silicon bond at the palladium center to give an intermediate containing two Pd–Si bonds. The next steps are postulated to be the insertion of the acetylene into one of the Pd–Si single bonds followed by reductive elimination to yield the monoinsertion product. In general, this overall process generates a product with cis stereochemistry, as a cis configuration is believed to be necessary for the insertion step to occur.[10d] The formation of diinsertion products, which has previously been observed in the case of dienes, can be explained by the rapid additional insertion of an unsaturated hydrocarbon molecule into the other palladium–silicon bond present in the postulated intermediate before reductive elimination to yield a monoinsertion product can occur. Reductive elimination from the resulting species would then yield a diinsertion product.[10k] These pathways are illustrated for the case of the insertion of butadiene in Scheme II. The formation of a diinsertion product in the reaction of 1 with butadiene contrasts with the formation of monoinsertion products in the analogous reactions involving acetylene and phenylacetylene. This suggests that the second insertion into the Pd–Si bond of the postulated intermediate is more rapid for the former than for the latter two hydrocarbons (Scheme II). Interestingly, the detection of very small quantities of the diinsertion product 5 in the palladium-catalyzed reaction of 1 with $MeCO_2C{\equiv}CCO_2Me$ suggests that diinsertion is on the brink of competing with the formation of the monoinsertion product for this particular acetylene.

The surprising isolation of products with predominantly trans stereochemistry at the C=C bonds in the reaction of 1 with butadiene contrasts markedly with other reports of palladium-catalyzed mono- and diinsertion reactions into Si–Si bonds, which invariably yield products with cis olefinic units.[10,16] However, in work by Matsumoto et al. the formation of small amounts (7–21%) of trans products in the reaction of acetylene with chlorodisilanes in the presence of $Pd(PPh_3)_4$ was attributed to the existence of palladium-catalyzed cis–trans isomerization reactions which occur under the reaction conditions used.[10e] Ex-

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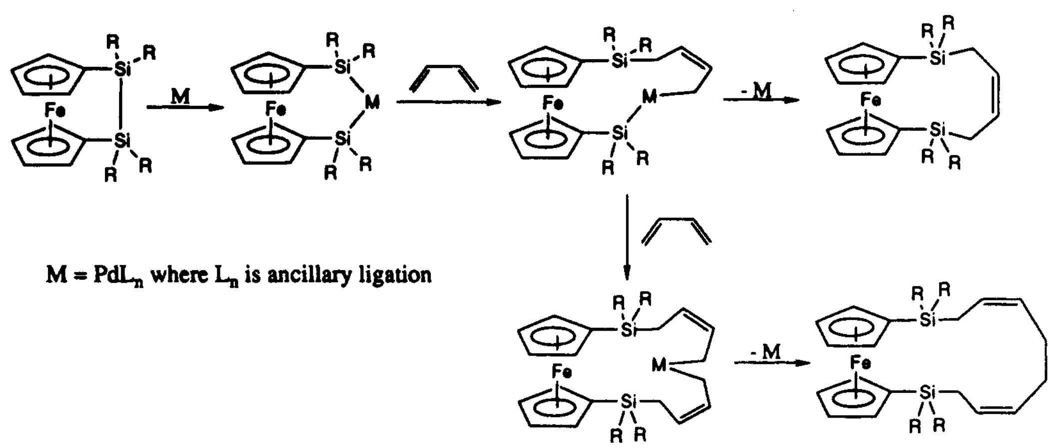
(16) Very recently evidence for palladium-catalyzed cis–trans isomerization reactions has also been found during studies of the insertion of unsaturated hydrocarbons into Ge–Ge bonds. See: Hayashi, T.; Yamashita, H.; Sakakura, T.; Uchimaru, Y.; Tanaka, M. *Chem. Lett.* 1991, 245.

Scheme II



M = PdL$_n$ where L$_n$ is ancillary ligation

perimental evidence in favor of this explanation was also found. Thus, Pd(PPh$_3$)$_4$ was shown to catalyze the cis–trans isomerization of *cis*-Cl$_2$MeSiCH=CHSiMeCl$_2$ in the presence of the disilane Cl$_2$MeSi–SiMeCl$_2$, although no detailed mechanism was proposed.[10e] Similar observations have also been made in related systems by Watanabe.[10d] Thus, it appears likely that a similar isomerization of the initially formed cis,cis isomer to the cis,trans and ultimately the trans,trans isomer occurs during the formation of the butadiene diinsertion product 7.

Experimental Section

Materials. Trimethylchlorosilane, sodium metal, potassium metal, ferrocene, 1.6 M butyllithium in hexanes, tetramethylethylenediamine (tmeda), tetrakis(triphenylphosphine)palladium, phenylacetylene, 1,3-cyclooctadiene, 1,5-cyclooctadiene, dicyclopentadiene, and dimethyl acetylenedicarboxylate were purchased from Aldrich and were used as received. Acetylene and butadiene were purchased from Matheson and were dried by passage through columns of Linde 4A molecular sieves. The dichlorodisilane ClMe$_2$Si–SiMe$_2$Cl was prepared via the reaction of Me$_3$Si–SiMe$_3$ with Me$_3$SiCl in the presence of AlCl$_3$.[12] The synthesis of Me$_3$Si–SiMe$_3$ involved the reaction of Me$_3$SiCl with sodium–potassium alloy.[13]

Equipment. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Vacuum Atmospheres). Solvents were dried by standard methods, distilled, and stored under nitrogen over activated molecular sieves. ^{1}H NMR spectra (200 or 400 MHz) and ^{13}C NMR spectra (50.3 or 100.5 MHz) were recorded on either a Varian Gemini 200 or Varian XL 400 spectrometer. The 39.7-MHz ^{29}Si NMR spectra were referenced externally to SiMe$_4$ (TMS) and were recorded on a Varian XL 400 spectrometer utilizing either a normal (proton coupled) or a DEPT pulse sequence (proton decoupled) with a $^2J_{\mathrm{SiH}}$ coupling of 6.7 Hz. All NMR spectra were referenced internally to TMS. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer operating in an electron impact (EI) mode. Elemental analyses were performed by Canadian Microanalytical Services, Delta, BC, Canada.

Synthesis of the Ferrocenyldisilane 1. This compound was prepared by a modification of literature procedures.[11] To ferrocene (3.0 g, 16 mmol) in hexanes (20 mL) containing tetramethylethylenediamine (tmeda; 5 mL, 33 mmol) was slowly added a solution of butyllithium in hexanes (20 mL, 1.6 M, 32 mmol). After 15 h at room temperature the stirred reaction solution was cooled to −78 °C and a cooled (−78 °C) solution of ClMe$_2$SiSiMe$_2$Cl (3.0 g, 16 mmol) in diethyl ether (50 mL) was added over 30 s using a double-tipped needle. The reaction mixture was slowly warmed to room temperature over 3 h and was then stirred at 25 °C for a further 20 h. The reaction mixture was then filtered and the solvent removed from the filtrate by rotary evaporation. Residual tmeda was then removed under vacuum (80 °C, 12 mmHg). The dark red tacky residue was then sublimed twice (100 °C, 0.1 mmHg) to yield the orange crystalline product. Recrystallization from boiling dry hexanes (30 mL) afforded 1 as diamond-shaped platelets: yield 2.0 g (42%); mp 134 °C. The melting point, ^{1}H NMR spectrum, and mass spectrum of 1 were consistent with those reported in the literature.[11] Additional NMR data for 1: ^{13}C NMR (CDCl$_3$) δ 74.0 (Cp), 70.4 (Cp), 72.4 (Cp C–Si), −1.5 (SiMe$_2$) ppm; ^{29}Si NMR (CDCl$_3$) δ −8.8 ppm.

Pd-Catalyzed Insertion of Acetylenes into the Si–Si Bond of 1. Synthesis of 2. A solution of 1 (4.50 g, 15 mmol) and Pd(PPh$_3$)$_4$ (0.32 g, 0.3 mmol) in toluene (10 mL) was heated to gentle reflux, and acetylene gas was bubbled through for 24 h (the flow rate was estimated to be ca. 5 mL/min). The reaction mixture was then transferred to a silica gel–hexanes column. Elution with hexanes yielded an orange band, which was collected. Solvent removal followed by several vacuum condensations at 100–150 °C (0.03 mmHg) afforded the product as orange crystals: yield of 2 2.55 g (52%); mp 26 °C. Spectral and analytical data for 2: ^{13}C NMR (CDCl$_3$) δ 151.80 (C=C), 73.64 (Cp), 71.37 (Cp), 67.46 (Cp C–Si), 0.21 (SiMe$_2$) ppm; ^{1}H NMR (CDCl$_3$) δ 6.89 (s, 2 H, HC=CH), 4.33 (dd, $^3J_{\mathrm{HH}}$ = 1.7 Hz, 4 H, Cp), 4.08 (dd, $^3J_{\mathrm{HH}}$ = 1.7 Hz, 4 H, Cp), 0.26 (s, $^2J_{\mathrm{SiH}}$ = 7 Hz, 12 H, SiMe$_2$) ppm; ^{29}Si NMR (CDCl$_3$) δ −14.9 ppm; MS (EI, 70 eV; *m/z* (%)) 326 (100, M$^+$), 311 (81, M$^+$ − CH$_3$), 285 (16, M$^+$ − C$_2$H$_2$ − CH$_3$), 253 (20, M$^+$ − SiMe$_2$ − CH$_3$). Anal. Calcd for C$_{16}$H$_{22}$FeSi$_2$: C, 58.90; H, 6.75. Found: C, 58.48; H, 6.75.

Synthesis of 3. Compound 3 was prepared similarly to compound 2, except that phenylacetylene was used in place of acetylene and the liquid product was isolated by vacuum distillation (bp ca. 50 °C, 0.005 mmHg). Purification was achieved by reprecipitation from CH$_2$Cl$_2$–hexanes: yield of 3 1.91 g (95%). Spectral and analytical data for 3: ^{13}C NMR (CDCl$_3$) δ 164.9 (Ph*C*=C), 151.1 (ipso Ph), 149.9 (C=*C*H), 128.5 (*m* Ph), 127.3 (*o* Ph), 126.4 (*p* Ph), 74.4 (β-C, Cp), 74.1 (β-C, Cp), 71.9 (coincident resonances γ-C, Cp) 69.8 (Cp C–Si), 68.1 (Cp C–Si), 1.9 (SiMe$_2$), 1.5 (SiMe$_2$) ppm; ^{1}H NMR (CDCl$_3$) δ 7.32–7.52 (m, 3 H, *m* and *p* Ph), 7.28 (d, 2 H, *o* Ph), 6.80 (s, 1 H, C=CH), 4.54 (dd, $^3J_{\mathrm{HH}}$ = 1.5 Hz, 4 H, Cp), 4.33 (dd, $^3J_{\mathrm{HH}}$ = 1.5 Hz, 4 H, Cp), 0.52 (s, 6 H, SiMe$_2$), 0.40 (s, 6 H, SiMe$_2$) ppm; ^{29}Si NMR (CDCl$_3$) δ −11.8 (s, 1 Si, *Si* CPh and −14.2 (s, 1 Si, *Si* CH) ppm; MS (EI, 70 eV; *m/z* (%)) 402 (100, M$^+$), 387 (28, M$^+$ − CH$_3$). Anal. Calcd for C$_{22}$H$_{26}$FeSi$_2$: C, 65.65; H, 6.51. Found: C, 66.30; H, 6.36.

Synthesis of 4. Dimethyl acetylenedicarboxylate (1.1 g, 7.7 mmol) was added dropwise over a period of 3 h to a refluxing solution of 2 (1.03 g, 3.43 mmol) and Pd(PPh$_3$)$_4$ (0.08 g, 0.07 mol %) in toluene (10 mL). After 24 h the mixture was poured into a 1:1 mixture of diethyl ether and hexanes (100 mL). Filtration, followed by solvent removal, afforded a brown semisolid, which was dissolved in diethyl ether. Addition of cold (ca. −40 °C) hexanes at −78 °C yielded a yellow amorphous solid, which was further purified by sublimation (100 °C, 0.02 mm): yield of 4 1.22 g (80%). Spectral and analytical data for 4: ^{13}C NMR (CDCl$_3$) δ 73.95 (Cp), 71.77 (Cp), 66.25 (Cp C–Si), 51.74 (s, OCH$_3$), 0.15 (SiMe$_2$) ppm; ^{1}H NMR (CDCl$_3$) δ 4.36 (dd, $^3J_{\mathrm{HH}}$ = 1.7 Hz, 4 H, Cp), 4.16 (dd, $^3J_{\mathrm{HH}}$ = 1.7 Hz, 4 H, Cp), 3.72 (s, 6 H, OMe), 0.34 (s, $^2J_{\mathrm{SiH}}$ = 7 Hz, 12 H, SiMe$_2$) ppm; ^{29}Si NMR (CDCl$_3$) δ −9.2 (s) ppm; MS (EI, 70 eV for 95% pure product with 6 as impurity; *m/z* (%)) 442 (100, M$^+$), 427 (16, M$^+$ − CH$_3$), 411 (29, M$^+$ − OCH$_3$).

A peak at m/z 395 (12%) was assigned to $M^+ - OCH_3$ for **6**. In the crude product this corresponded to the base peak. In addition, the crude product showed a peak at m/z 584, which corresponded to the molecular ion derived from **5**.

Pd-Catalyzed Insertion of Butadiene into the Si–Si Bond of 1. Synthesis of the Trans,trans and Cis,trans Isomers of 7. A solution of **1** (1.5 g, 5.0 mmol) and $Pd(PPh_3)_4$ (0.10 g, 0.09 mmol) in toluene (10 mL) was heated to gentle reflux, and butadiene gas was bubbled through for 24 h (the flow rate was estimated to be ca. 5 mL/min). The reaction mixture was then poured into hexanes (100 mL). Filtration followed by removal of the solvent gave orange crystals which were recrystallized from hexanes: yield of **6** 1.55 g (76%).

Spectral and analytical data for **7**: MS (EI, 70 eV; m/z (%)) 408 (100, M^+) 354 (35, $M^+ - C_4H_6$), 300 (23, $M^+ - 2C_4H_6$). Anal. Calcd for $C_{22}H_{32}FeSi_2$: C, 64.70; H, 7.86. Found: C, 64.64; H, 7.84.

Spectral data for *trans,trans*-**7**: ^{13}C NMR ($CDCl_3$) δ 130.43 (C=*C*—C—C), 126.47 (Si—C—*C*=C), 73.38 (Cp), 73.02 (Cp C—Si), 70.90 (Cp), 32.20 (C=C—*C*—C), 23.26 (s, $^2J_{SiC}$ = 200 Hz, Si—*C*—C=C), −1.09 ($SiMe_2$) ppm; ^1H NMR ($CDCl_3$) δ 5.58 (dt, $^3J_{HH}$ = 15 Hz, $^3J_{HH}$ = 7 Hz, 2 H, H7), 5.37 (br d, $^3J_{HH}$ = 15 Hz, 2 H, H8), 4.35 (br s, 4 H, Cp), 4.24 (br s, 4 H, Cp), 2.29 (br s, 4 H, H9), 1.70 (d, $^3J_{HH}$ = 7 Hz, 4 H, H6), 0.14 (s, 12 H, $SiMe_2$) ppm; ^{29}Si NMR ($CDCl_3$) δ −5.1 ppm.

Spectral data for *cis,trans*-**7**: unless noted below, the NMR resonances for this isomer are obscured by those of the trans,trans isomer; ^{13}C NMR ($CDCl_3$) δ 129.60 (trans C=*C*—C—C), 129.55 (cis C=*C*—C—C), 126.06 (trans Si—C—*C*=C), 126.04 (cis Si—C—*C*=C), 74.00 (Cp), 71.39 (Cp C—Si), 71.20 (Cp C—Si), 70.87 (Cp), 32.82 (trans C=C—*C*—C), 27.22 (cis C=C—*C*—C), 23.75 (trans Si—*C*—C=C), 17.22 (cis Si—*C*—C=C), −1.25 ($SiMe_2$ near trans C=C), −1.09 ($SiMe_2$ near cis C=C) ppm; ^1H NMR ($CDCl_3$) δ 0.26 (s, 12 H, $SiMe_2$) ppm; ^{29}Si NMR ($CDCl_3$) δ −5.6 (s, 1 Si, Si near trans C=C), −3.9 (s, 1 Si, Si near cis C=C) ppm.

Other Reactions. A solution of **1** and $Pd(PPh_3)_4$ (ca. 0.02 mol equiv) in toluene was heated to gentle reflux in the presence of diphenylacetylene, 1,3-cyclooctadiene, 1,5-cyclooctadiene, or cyclopentadiene for 24 h. In each case unreacted **1** was recovered as the only ferrocene-containing product detected by ^1H NMR spectroscopy.

X-ray Structure Determination Technique. Crystals of both **2** and **7** had dimensions in the range 0.25–0.45 mm. Intensity data for both compounds were collected on an Enraf-Nonius CAD4 diffractometer at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The $\omega/2\theta$ scan technique was applied with variable scan speeds. Intensities of three standard reflections measured every 2 h showed no decay. The space groups were determined from systematic absences. An empirical absorption correction[17] was applied to the data for **2** (relative maximum and minimum corrections 1.264 and 0.502) and **7** (relative maximum and minimum corrections 2.171 and 0.667).

The positions of the non-hydrogen atoms for both **2** and **7** were determined by direct methods using SHELXS86.[18] For both structures all non-hydrogen atoms were refined anisotropically by full-matrix least squares to minimize $\sum w(F_o - F_c)^2$, where $w = 1/(\sigma^2(F_o) + gF_o^2)$. Hydrogen atoms were positioned on geometric grounds (C–H = 0.95 Å) and general hydrogen atom thermal parameters for **2** and **7** refined to 0.113 (6) and 0.111 (1) Å^2. Crystal data, details of the data collection, and least-squares parameters for **2** and **7** are given in Table I. Figures 2 and 3 are views of the molecules prepared using ORTEP. Atomic scattering factors were taken from ref 21. All calculations were carried out using SHELX76,[19] SHELXS86,[18] and NRCVAX[20] on a 486-33 PC and an Apollo computer.

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Supplementary Material Available: Listings of atomic coordinates, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, and torsion angles for **2** and **7** (19 pages). Ordering information is given on any current masthead page.

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