(7-Silanorbornadienyl)cyclopentadienyldicarbonyliron Complexes: An Approach to Iron-Substituted Silylenes

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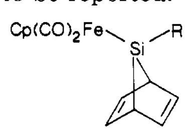
(7-Methyl-7-silanorbornadienyl)FeCp$(CO)_2$ complexes were prepared from the corresponding silole–iron complexes by Diels–Alder reaction with dimethyl acetylenedicarboxylate or benzyne. Thermolysis of the dimethyl acetylenedicarboxylate adduct in refluxing xylene led to extrusion of the iron-substituted silylene which was intercepted by the silylene-trapping reagents. With Et_3SiH, $PhSi(OMe)_3$, and $PhCH_2OH$, silylene insertion reactions took place into the Si–H, Si–O, and O–H bonds, respectively; cycloaddition products were obtained with PhC≡CPh, Ph_2CO, and PhCH=CHCH=CHPh.

In the rapidly developing field of silylene chemistry,[1] numerous papers have dealt with the search for new silylene generators and silylene-trapping reactions or for a better understanding of the nature of silylenes and their reaction mechanisms.[2] However, silylenes containing transition metals, $[L_nM(R)Si:]$ (1), have apparently not been reported. In this paper we describe the synthesis of an organo-transition-metal–silylene precursor and a preliminary investigation of its activity as a silylene source.

As the organometallic substituent, the $[CpFe(CO)_2]$ group was employed, since the facile condensation of $Na^+[CpFe(CO)_2]^-$ with organosilyl halides produces rather stable silicon–iron compounds.[3] Initially, the complex $Cp(CO)_2Fe–Si(Me)(SiMe_3)_2$ (2) was prepared[4] and investigated as a photochemical silylene precursor. However, photolysis of 2 in the presence of triethylsilane gave none of the anticipated silylene insertion product.[5] Because 7-silanorbornadienes are known to be good thermal precursors for silylenes (or silylene-like intermediates),[6] we then turned to the synthesis of (7-silanorbornadienyl)Fe$(CO)_2$Cp complexes 3. These compounds, obtained by Diels–Alder type condensations from iron-substituted siloles, are apparently the first transition-metal-substituted silanorbornadienes to be reported.



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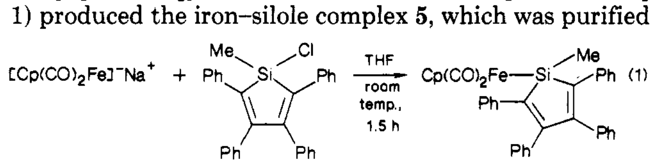
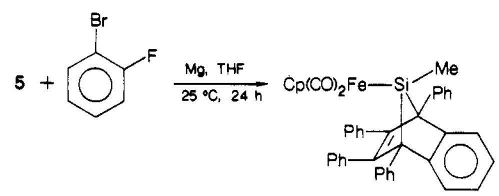
Results and Discussion

Synthesis of (7-Methyl-7-silanorbornadienyl)-FeCp$(CO)_2$ Complexes. These compounds were obtained in a two-step synthesis from 1-chloro-1-methyl-2,3,4,5-tetraphenylsilacyclopentadiene (4).[7] Reaction of 4 with the $[CpFe(CO)_2]^-$ anion in THF at room temperature[8] (eq 1) produced the iron–silole complex 5, which was purified



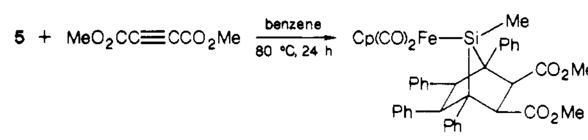
4 5 (70%)

by crystallization from toluene/hexane. In spite of the presence of electronegative phenyl substituents and the steric hindrance of the molecule, complex 5 reacted as a diene in Diels–Alder type reactions. Benzyne, generated from 1-bromo-2-fluorobenzene and magnesium, and dimethyl acetylenedicarboxylate reacted with 5 to give 7-silanorbornadienes 6 and 7 (eq 2 and 3).



(2)

6 (69%)



(3)

7 (75%)

The benzyne adduct 6 is a light yellow solid, stable to air and moisture, which was purified by chromatography on silica gel. Compound 7, which has similar properties, was obtained in 75% yield by direct crystallization from the reaction mixture. In both reactions 2 and 3 only one of the two possible isomeric products is observed, probably

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(1) For reviews, see: Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1985; Vol. 3, pp 333–427 and references cited therein.

(2) See, for example: (a) Vancik, H.; Raabe, G.; Michalczyk, M. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1985**, *107*, 4097. (b) Boo, B. H.; Gaspar, P. P. *Organometallics* **1986**, *5*, 698. (c) Lei, D.; Gaspar, P. P. *J. Chem. Soc. Chem. Commun.* **1985**, 1149. (d) Apeloig, Y.; Karni, M. *Ibid.* **1985**, 1048. (e) Colvin, M. E.; Breulet, J.; Schaefer, H. F. *Tetrahedron* **1985**, *41*, 1429. (f) Linder, L.; Revis, A.; Barton, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 2742. (g) Michalczyk, M. J.; Fink, M. J.; De Young, D. J.; Carlson, C. W.; Welsh, K. M.; West, R.; Michl, J. *Rev. Silicon, Germanium, Tin Lead Compd.*, in press.

(3) For a review on silicon–transition-metal chemistry see: Aylett, B. J. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 1.

(4) Nicholson, B. K.; Simpson, J. *J. Organomet. Chem.* **1974**, *72*, 211.

(5) Complex 2 was prepared according to the literature method[4] in 62% yield. Photolysis of 2 with a 450-W Hanovia lamp in hexane in the presence of triethylsilane gives none of the silylene trapping product **10**. Three major products have been identified as $Cp(CO)_2Fe–SiMe_3$ [^1H NMR (C_6D_6) δ 0.48 (s, 9 H, Me), 4.01 (s, 5 H, Cp); IR (benzene) ν(CO) 1995 (s), 1930 (vs) cm^{-1}; mass spectrum, exact mass calcd for $C_{10}H_{14}O_2$-FeSi 250.0112, found 250.0111], $Cp(CO)FeH(SiEt_3)_2$ [^1H NMR (C_6D_6) δ −14.06 (s, 1 H, FeH), 0.94 (m, 12 H, $SiCH_2CH_3$), 1.13 (t, ^3J = 7.5 Hz, 18 H, CH_2CH_3), 4.14 (s, 5 H, Cp); IR (benzene) ν(CO) 1935 (s) cm^{-1}], and $Cp(CO)FeH(SiEt_3)(SiMe_3)$ [^1H NMR (C_6D_6) δ −14.07 (s, 1 H, FeH), 0.51 (s, 9 H, SiMe), 0.9 (q, ^3J = 6.8 Hz, 6 H, $SiCH_2CH_3$), 1.09 (t, ^3J = 6.8 Hz, 9 H, CH_2CH_3)].

(6) Gilman, H.; Cottis, S. G.; Atwell, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 1596. Sakurai, H.; Sakaba, H.; Nakadaira, Y. *Ibid.* **1982**, *104*, 6156.

(7) Curtis, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 4241.

(8) The same reaction was shown to be successful for the synthesis of the (1,2,3,4,5-pentaphenylsilacyclopentadienyl)FeCp$(CO)_2$ complex: Curtis, M. D. *J. Am. Chem. Soc.* **1969**, *91*, 6011.

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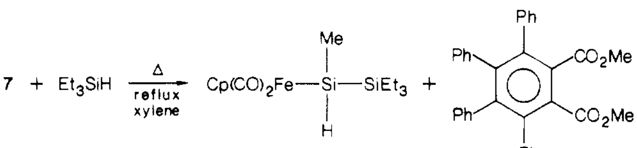
because attack of the dienophile takes place exclusively on the less hindered side of the silole **5**.[9]

A characteristic feature of the complexes **6** and **7** is the very large deshielding of the ^{29}Si NMR resonance: **7**, ^{29}Si NMR ($CDCl_3$) δ 166.6; **6**, ^{29}Si NMR (C_6D_6) δ 139. The deshielding usually observed for silicon in a bridgehead position of a norbornadiene ring[10] is here further increased by the iron substitution.[4]

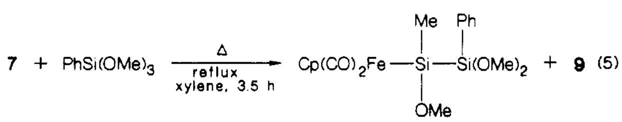
Generation and Trapping of Silylene [Cp(CO)$_2$FeSiMe] (8). In order to test for transfer of silylenes, the iron-substituted silanorbornadienes **6** and **7** were heated in the presence of triethylsilane in refluxing xylene (144 °C). Compound **7** thermolyzed under these conditions, producing dimethyl 3,4,5,6-tetraphenylphthalate (**9**) and 35% of the expected Si-H insertion product **10** (eq 4).



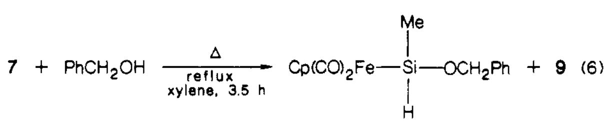
10 (35%) **9** (4)

Compound **6** was unchanged after 24 h reflux in xylene.[11] Because **7** thermolyzed at a lower temperature, it was used as the silylene source in studies with other trapping reagents.

Reactions with phenyltrimethoxysilane and benzyl alcohols occurred as shown in eq 5 and 6. Insertion of **8** into the Si–O and O–H bonds took place, analogously to well-known reactions of other silylenes.[1]



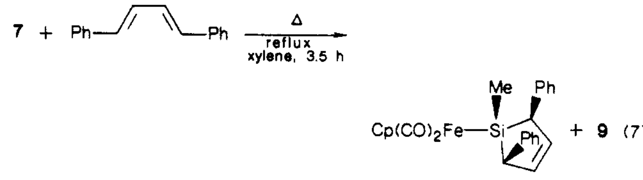
11 (40%)



12 (36%)

Yield of silylene trapping products were calculated with respect to the percentage of silylene formed, corresponding to the amount of **9** recovered. The moderate yields may reflect instability of the products at the reaction temperature (144 °C). In addition, in reaction 6 the presence of alcohol leads to cleavage of the Si–Fe bond with formation of some $[Cp(CO)_2Fe]_2$.

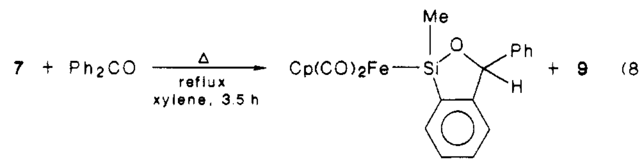
When **7** is heated in refluxing xylene in the presence of *trans,trans*-1,4-diphenyl-1,3-butadiene the silacyclopentene **13** is isolated (eq 7). Two unidentified minor products



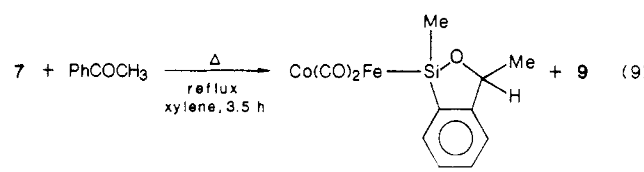
13 (30%)

are observed in the reaction mixture in about 15% yield. The (Ph) cis stereochemistry of **13** was established on the basis of its ^{1}H NMR spectrum, which showed two pairs of identical protons on the silacyclopentene ring [δ 3.47 (s, 2 H, C*H*Ph), 6.19 (s, 2 H, CH=CH)]. The relative position of the Si methyl and phenyl substituents cannot be assigned from the spectroscopic data, but the structure shown for **13** seems most likely for steric reasons.[12]

Two aromatic carbonyl compounds were heated with **7**, producing the formal silylene addition products **14** and **15**, as shown in eq 8 and 9. In each case, only one of the two possible diastereoisomers is formed in detectable amount.

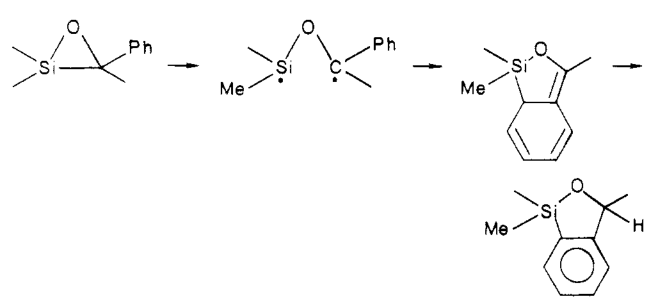


14 (70%)



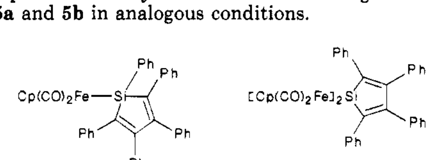
15 (44%)

An analogous cyclic compound was obtained in 17% yield in the reaction between Me_2Si: and benzophenone,[13] and its formation was attributed to the radical opening of the intermediate oxysilirene:



The isolation of a small amount of diastereomers **16a,b** in our reaction is consistent with the intermediacy of a similar biradical.[14] The normal reaction products of silylenes with acetophenone are enol ethers[15] **17**. It is possible that a

(9) We report that benzyne or DMAD failed to give clean reactions with both **5a** and **5b** in analogous conditions.



5a **5b**

(10) Sakurai, H.; Nakadaira, Y.; Koyama, T.; Sakaba, H. *Chem. Lett.* **1983**, 213.

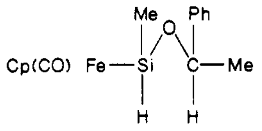
(11) When **6** was heated at 180 °C in xylene in a sealed tube in the presence of 1,4-diphenyl-1,3-butadiene, starting material disappeared within 7 h and a small amount of the trapping product **13** was detected in the reaction mixture.

(12) Silacyclopentene products like **13** are observed for the addition of Me_2Si to some conjugated dienes (Lei, D.; Hwang, R.; Gaspar, P. P. *J. Organomet. Chem.* **1984**, *271*, 1), but Me_2Si reacts in a different way with PhCH=CHCH=CHPh (Sakurai, H.; Kobayashi, Y.; Sato, R.; Nakadaira, Y. *Chem. Lett.* **1983**, 1197).

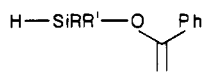
(13) Ando, W.; Ikeno, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **1977**, *99*, 6447.

(14) The mixture **16ab** was identified on the basis of its ^{1}H NMR and mass spectrum. **16a**: ^{1}H NMR (C_6D_6) δ 0.66 (d, ^3J = 2.7 Hz, 3 H, SiMe), 1.49 (d, ^3J = 6.3 Hz, 3 H, CH*Me*); 4.06 (s, 5 H, Cp), 4.95 (q, ^3J = 6.3 Hz, 1 H, C*H*Me), 6.17 (q, ^3J = 2.7 Hz, 1 H, SiH), 7–7.5 (m, Ph). **16b**: ^{1}H NMR (C_6D_6) δ 0.77 (d, ^3J = 2.7 Hz, 3 H, SiMe), 1.48 (d, ^3J = 6.3 Hz, 3 H, CH*Me*), 3.99 (s, 5 H, Cp), 4.95 (q, ^3J = 6.3 Hz, 1 H, C*H*Me), 6.15 (q, ^3J = 2.7 Hz, 1 H, SiH), 7–7.5 (m, Ph). Mass spectrum: *m/e* (relative intensity) 341 (M – H, 3), 340 (M – 2H, 2); 314 (M – CO, 13); 286 (M – 2CO, 48); exact mass calcd for $C_{16}H_{17}O_3SiFe$ 341.0296, found 341.0281; exact mass calcd for $C_{15}H_{18}O_2SiFe$ 314.0425, found 314.0430.

compound with this structure is formed in small amount in our reaction, but **15** is clearly the dominant product.



16a,b



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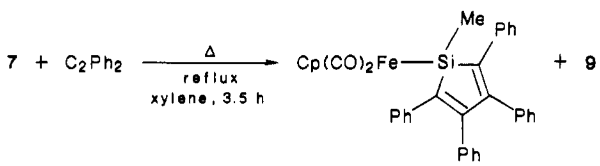
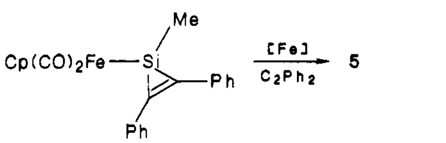
Compound **7** was also thermolyzed in the presence of diphenylacetylene (eq 10). The product **5** is unexpected,



(10)

5 (60%)

since silylenes usually add to alkynes to give silacyclopropenes which dimerize to disilacyclohexadienes.[16] Formation of **5** may be rationalized as an iron-catalyzed insertion of the acetylene derivative into the silirene **18** (eq 11) by analogy to similar Ni- and Pd-catalyzed inser-

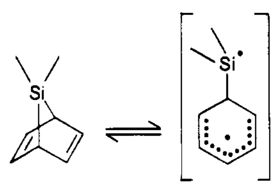


(11)

18

tion reactions.[17] Of course, this is not the only possible mechanism and more experimental evidence is needed to prove its validity.

A general view of eqs 4–10 shows that thermolysis of the iron-substituted 7-silanorbornadienes **7** in the presence of trapping reagents gives rise, without exception, to a final product containing the silylene unit bonded to the trapping species. It therefore seems reasonable to explain these reactions by the intermediacy of the iron-substituted silylene **8**. However, the possible opening of the 7-silanorbornadienes by a stepwise biradical mechanism (eq 12)



(12)

19

must be considered. Because the diradical intermediate **19** could also act as a silylene donor,[1,18] the existence of a free silylene in our reactions cannot be unequivocally established.

Nevertheless, our results show that iron-substituted silylene precursors are easily accessible and show silylene-like reactivity. Analogies and differences between organic and organometallic silylenes will have to be established through more extended studies.

Experimental Section

^{1}H NMR spectra were recorded on a Brucker WP-270 FT spectrometer. ^{13}C NMR were collected on a JEOL FX-200 operating at 50.18 MHz or a Brucker AM 500 at 125.76 MHz. ^{29}Si NMR were run on a Brucker AM 500 operating at 100.2 MHz.

Mass spectra were obtained on a Kratos MS 9020 mass spectrometer at 70 eV. All reactions were carried out under nitrogen. All solvents were dried and distilled prior to use. Chromatographic separations were performed on silica gel columns under nitrogen. Elemental analysis and/or exact mass measurements are given for any new compounds. Analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

(1-Methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)cyclopentadienyldicarbonyliron (5). A 1.0-g (2.8-mmol) sample of $[CpFe(CO)_2]_2$ in 40 mL of THF was stirred with sodium amalgam prepared from 4 mL of Hg and ca. 0.5 g of Na. After 1.5 h, this solution was transferred to a stirred solution of 2.4 g (5.6 mmol) of **4** in 30 mL of THF. After the solution was stirred for 1.5 h, hexane was added. Filtration and evaporation of the solvent, followed by crystallization of the residue from a toluene/hexane mixture, gave 2.2 g (70%) of pure **5**: mp 200 °C; light yellow solid; ^{1}H NMR (C_6D_6) δ 0.94 (s, 3 H, SiMe), 4.14 (s, 5 H, Cp), 6.8–7.3 (m, 20 H, Ph); ^{13}C NMR ($CDCl_3$) δ 0.82 (SiMe), 84.18 (Cp), 125.21, 125.82, 127.14, 127.66, 129.03, 130.38, 139.11, 141.06, 149.03, 150.84 (Ph and ring carbons), 213.97 (CO); IR (benzene) ν(CO) 1995 (vs), 1943 (vs) cm^{-1}; ^{29}Si NMR ($CDCl_3$) 47.59 ppm; mass spectrum, *m/e* (relative intensity) 576 (M, 17), 520 (M – 2CO, 100), 399 [M – FeCp(CO)$_2$, 54]; exact mass calcd for $C_{36}H_{28}O_2SiFe$ 576.1207, found 576.1222. Anal. Calcd for $C_{36}H_{28}O_2FeSi$: C, 75.00; H, 4.90. Found: C, 75.37; H, 4.88.

(1,4,5,6-Tetraphenyl-2,3-benzo-7-methyl-7-silanorbornadienyl)cyclopentadienyldicarbonyliron (6). Complex **5** (1 g, 1.7 mmol) was added to magnesium turnings (70 mg, 2.9 mmol; activated by iodine) in dry THF (5 mL). To this mixture was added 2-bromofluorobenzene (0.3 mL, 2.7 mmol) dropwise with stirring at 0 °C. The mixture was warmed to room temperature and stirred for 24 h. After evaporation of the THF, the residue was dissolved in CH_2Cl_2 and filtered. Purification by chromatography (hexane/ether, 90:10) gave **6** (0.78 g, 69%): colorless solid; decomp at ~200 °C without melting; ^{1}H NMR (C_6D_6) δ 0.21 (s, 3 H, SiMe), 3.70 (s, 5 H, Cp), 6.8–7.9 (7, Ph); ^{13}C NMR ($CDCl_3$) δ 5.43 (SiMe), 64.97 (SiCPh), 83.02 (Cp), 122.81, 123.69, 124.10, 125.85, 126.99, 127.75, 128.77, 139.51, 139.60, 147.11, 150.58 (Ph and unsaturated C ring carbons), 213.48 (CO); ^{29}Si NMR ($CDCl_3$) 138.98 ppm; IR (benzene) ν(CO) 2000 (s), 1955 (vs) cm^{-1}; mass spectrum, *m/e* (relative intensity) 652 (M, 7), 432 (Ph$_4$-naphthalene, 100); exact mass calcd for $C_{42}H_{32}O_2SiFe$ 652.1520, found 652.1527. Anal. Calcd for $C_{42}H_{32}O_2SiFe$: C, 77.29; H, 4.94. Found: C, 76.69; H, 4.95.

[1,4,5,6-Tetraphenyl-2,3-bis(methoxycarbonyl)-7-methyl-7-silanorbornadienyl]cyclopentadienyldicarbonyliron (7). Complex **5** (2 g, 3.5 mmol) and dimethyl acetylenedicarboxylate (2.1 mL, 17 mmol) were heated at 80 °C in benzene (15 mL) for 24 h. After the reaction mixture was allowed to cool to room temperature, the final product **7** began to crystallize out. Crystallization was achieved by cooling at 0–5 °C: yield 1.9 g (75%). Some more amounts of complex **7** can be obtained by chromatography of the remaining solution (ether/ethyl acetate, 90:10): light yellow solid; mp 202–203 °C; ^{1}H NMR (C_6D_6) δ 1.11 (s, 3 H, SiMe), 3.36 (s, 6 H, CO$_2$Me), 3.89 (s, 5 H, Cp), 6.8–7.5 (m, Ph); ^{13}C NMR ($CDCl_3$) δ 7.92 (SiMe), 51.71 (CO$_2$*Me*), 68.50 (Si*C*Ph), 83.54 (Cp), 124.83, 125.98, 127.28, 129.32, 130.29, 137.82, 138.67, 145.44, 147.57 (Ph and unsaturated ring carbons), 167.14 (*C*O$_2$Me), 213.48 (FeCO); ^{29}Si NMR ($CDCl_3$) 166.56 ppm; IR (benzene) ν(CO) 2000 (s), 1955 (vs), ν(co-ester) 1720 cm^{-1}; mass spectrum, only the tetraphenylphthalate fragment **9** could be detected (mass calcd 498.1831, found 498.1803) together with the Cp_2Fe (mass calcd 186.0131, found 186.0150). Anal. Calcd for $C_{42}H_{34}O_6SiFe$: C, 70.19; H, 4.77. Found: C, 70.14; H, 4.82.

Silylene-Trapping Reactions: General Procedure. Complex **7** (0.6 g, 0.8 mmol) was heated in xylene (3 mL) at 150 °C (oil bath) for 3.5 h in the presence of a sixfold excess (2.4 mmol) of trapping reagent. After evaporation of the solvent, the reaction

(15) Ando, W.; Ikeno, M. *Chem. Lett.* **1978**, 609.

(16) See, for example: Atwell, W. H.; Weyenberg, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 3438. (b) Barton, T. J.; Kilgour, J. A. *Ibid.* **1976**, *98*, 7746.

(17) See, for example: (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263. (b) Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57.

(18) (a) Mayer, B.; Neumann, W. P. *Tetrahedron Lett.* **1980**, *21*, 4887. (b) Barton, T. J.; Goure, W.; Witiak, J. L.; Wulff, W. D. *J. Organomet. Chem.* **1982**, *225*, 87.

products are purified by column chromatography with hexane/ether mixtures as eluents. The trapping product is eluted first, followed by about 0.35 g (84%) of dimethyl tetraphenylphthalate **9** [^{1}H NMR (C_6D_6) δ 3.28 (s, 6 H, Me), 6.6–7.2 (m, Ph); exact calcd mass for $C_{34}H_{26}O_4$ 498.1831, found 498.1867].

Reaction with Et_3SiH (4). The reaction mixture was heated to reflux for 5.5 h. After chromatography with hexane (R_f 0.7), 83 mg of **10** (30%) were obtained: colorless oil; ^{1}H NMR (C_6D_6) δ 0.59 (d, ^3J = 4.8 Hz, 3 H, Si*Me*), 0.78 (q, ^3J = 8.0 Hz, 6 H, CH_2CH_3), 1.12 (t, ^3J = 8.0 Hz, 9 H, CH_2CH_3), 4.12 (s, 5 H, Cp), 4.39 (q, ^3J = 4.8 Hz, 1 H, SiH); ^{13}C NMR ($CDCl_3$) δ –1.3 (SiMe), 4.74 ($SiCH_2CH_3$), 8.24 ($SiCH_2CH_3$), 83.16 (Cp), 214.64, 214.97 (FeCO); IR (benzene) ν(CO) 1995 (s), 1940 (vs) cm^{-1}; mass spectrum, m/e (relative intensity) 336 (M, 2), 308 (M – CO, 47), 280 (M – 2CO, 13), 220 (M – Et_3SiH, 51), 192 (220 – CO, 100), 164 (220 – 2CO, 53); exact mass calcd for $C_{14}H_{24}O_2Si_2Fe$ 336.0664, found 336.0668. Anal. Calcd for $C_{14}H_{24}O_2SiFe$: C, 49.99; H, 7.19. Found: C, 50.83; H, 7.48.

Reaction with $PhSi(OMe)_3$ (5). $PhSi(OMe)_3$ (0.9 mL, 5 mmol) was used. After chromatography with hexane/ether (98:2) 117 mg (34%) of **11** were obtained: colorless oil; ^{1}H NMR (C_6D_6) δ 0.95 (s, 3 H, SiMe), 3.46 (s, 3 H, SiOMe), 3.56 (s, 3 H, SiOMe), 3.57 (s, 3 H, SiOMe), 4.32 (s, 5 H, Cp), 7.0–7.9 (m, Ph); ^{13}C NMR ($CDCl_3$) δ 9.2 (SiMe), 50.87, 50.95, 51.98 (OMe), 83.66 (Cp), 127.95, 129.76, 134.17, 136.07 (Ph), 213.91 (FeCO); IR (benzene) ν(CO) 1995 (s), 1940 (vs) cm^{-1}; mass spectrum, m/e (relative intensity) 390 (M – CO, 47), 347 (M – 2CO, 36), 151 (PhSi(Me)OMe, 100); exact mass calcd for $C_{16}H_{22}O_4Si_2Fe$ 390.0406, found 390.0382.

Reaction with $PhCH_2OH$ (6). Only a threefold excess of alcohol (0.26 mL, 2.5 mmol) was used in order to lessen the side reaction of cleavage of the iron–silicon bond. After chromatography with hexane/ether (98:2), 84 mg of **12** (0.25 mmol, 30%) were isolated (R_f 0.5): colorless oil; ^{1}H NMR (C_6D_6) δ 0.75 (d, ^3J = 2.9 Hz, 3 H, SiMe), 4.06 (s, 5 H, Cp), 4.76 and 4.81 (AB, J_{AB} = 13.7 Hz, 2 H, OCH_2Ph), 6.19 (q, ^3J = 2.9 Hz, 1 H, SiH), 6.9–7.8 (m, Ph); ^{13}C NMR ($CDCl_3$) δ 5.74 (SiMe), 66.85 (OCH_2Ph), 83.34 (Cp), 125.3, 126.4, 128.6, 132.0 (Ph), 213.43, 213.76 (FeCO); IR (benzene) ν(CO) 1995 (s), 1940 (vs) cm^{-1}; mass spectrum, m/e (relative intensity) 328 (M, 1), 300 (M – CO, 38), 272 (M – 2CO, 100); exact mass calcd for $C_{15}H_{16}FeO_3Si$ 328.0218, found 328.0230.

Reaction with 1,4-Diphenyl-1,3-butadiene (7). 1,4-Diphenyl-1,3-butadiene (1.0 g, 5 mmol) was used. Repeated chromatographic separations of the reaction mixture, with hexane as eluent, allows first the recovery of the excess diene and then the silacyclopentene **13** (90 mg, 0.2 mmol, 25%): colorless solid (decomposes without melting); ^{1}H NMR (C_6D_6) δ –0.14 (s, 3 H, SiMe), 3.47 (s, 2 H, Ph*CH*), 4.07 (s, 5 H, Cp), 6.19 (s, 2 H, HC=CH), 7–7.3 (m, Ph); ^{13}C NMR ($CDCl_3$) δ 0.82 (SiMe), 46.63 (Si*C*HPh), 83.28 (Cp), 124.30, 127.14, 128.13, 135.75, 144.04 (Ph and *C*H=*C*H), 214.15 (FeCO); IR (benzene) ν(CO) 1995 (s), 1940 (vs) cm^{-1}; mass spectrum, m/e (relative intensity) 426 (M, 27), 398 (M – CO, 20), 370 (M – 2CO, 54), 249 (M – $FeCp(CO)_2$, 100); exact mass calcd for $C_{24}H_{22}O_2SiFe$ 426.0738, found 426.0734. Anal. Calcd for $C_{24}H_{22}O_2Si$: C, 67.61; H, 5.20. Found: C, 67.26; H, 5.26.

Reaction with Benzophenone (8). Ph_2CO (0.9 g, 5 mmol) was used. Column chromatography with hexane/ether (98:2) as eluent gives the excess benzophenone, and then elution with hexane/ether (94:6) gives 0.19 g of **14** (59%): colorless oil; ^{1}H NMR (C_6D_6) δ 0.85 (s, 3 H, SiMe), 4.16 (s, 5 H, Cp), 6.31 (s, 1 H, *C*HPh), 6.9–7.9 (m, Ph); ^{13}C NMR ($CDCl_3$) δ 10.93 (SiMe), 83.69 (Cp), 84.59 (*C*HPh), 123.60, 127.08, 127.63, 128.27, 128.74, 129.76, 143.40, 144.16, 149.62 (Ph), 213.77, 213.94 (FeCO); IR (benzene) ν(CO) 1995 (s), 1940 (vs) cm^{-1}; mass spectrum, m/e (relative intensity) 402 (M, 1), 374 (M – CO, 13), 346 (M – 2CO, 100), 225 (M – $FeCp(CO)_2$, 91); exact mass calcd for $C_{21}H_{18}O_3SiFe$ 402.0374, found 402.0364.

Reaction with Acetophenone (9). $PhCOCH_3$ (0.6 mL, 5 mmol) was used. Column chromatography allowed purification of the reaction mixture: hexane/ether (98:2) gives the mixture **16ab** (R_f 0.6); with hexane/ether (96:4) the excess acetophenone is removed; elution with hexane/ether (92:8) gives 105 mg of complex **15** (37%) **15**: colorless solid; mp 82 °C (hexane/ether); ^{1}H NMR (C_6D_6) δ 0.78 (s, 3 H, SiMe), 1.57 (d, ^3J = 6.5 Hz, 3 H, $CHCH_3$), 4.16 (s, 5 H, Cp), 5.44 (q, ^3J = 6.5 Hz, 1 H, $CHCH_3$), 7.0–7.8 (m, Ph); ^{13}C NMR ($CDCl_3$) δ 10.91 (SiMe), 24.26 ($CHCH_3$), 78.37 ($CHCH_3$), 83.58 (Cp), 122.00, 126.87, 128.81, 129.85 (CH-benzo), 142.68, 151.55 (C-benzo), 213.90 (FeCO); IR (benzene) ν(CO) 2000 (s), 1945 (vs); mass spectrum, m/e (relative intensity) 340 (M, 11), 312 (M – CO, 17), 284 (M – 2CO, 91), 163 (M – $FeCp(CO)_2$, 100); exact mass calcd for $C_{16}H_{16}O_3SiFe$ 340.0218, found 340.0231. Anal. Calcd for $C_{16}H_{16}O_3SiFe$: C, 56.48; H, 4.74. Found: C, 56.87; H, 4.95.

Reaction with Diphenylacetylene (11). C_2Ph_2 (0.9 g, 5 mmol) was used. Chromatography with hexane/ether (98:2) gives 243 mg of **5** (50%); R_f 0.6. The structure was confirmed by comparison with an authentic sample (see above).

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