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mation **2** → **4** shows that on protonation **2** leads selectively under mild conditions to monosubstitution products of precursor **1**.

Finally, we have examined whether complex **2** could transfer its hydride to another substrate, namely, $Ru_3(CO)_{12}$ (ref 16) as a possible route to cluster anions or used to elaborate other phosphido-bridged polynuclear complexes. Complex **2** was reacted with 1 equiv of $Ru_3(CO)_{12}$ at 60 °C, and after chromatography a small amount (12%) of the hydrido cluster $Ru_3(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_8$ (**5**) was isolated (Scheme I). This complex **5** was produced previously in better yields by simple thermolysis of $Ru_3(PPh_2H)_2(CO)_{10}$.[13] Nevertheless the formation of **5** indicates the possibility of transfer of the $RuH(PPh_2)(CO)_n$ unit by cleavage of the Ru–Co bond of **2**.

Conclusion

Displacement of a carbonyl group of $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ by anionic hydride or halide donors leads to thermodynamic products in which regiospecific substitution of CO at the ruthenium site has occurred. For the anion $[(H)(CO)_3Ru(\mu\text{-}PPh_2)Co(CO)_3]^-$ the hydride occupies an axial cis site with respect to the $Ru(\mu\text{-}P)Co$ plane and the phosphido bridge whereas for $[(X)(CO)_3Ru(\mu\text{-}PPh_2)Co(CO)_3]^-$ the halide has an equatorial trans configuration. Thus the present results serve to confirm the previous observations on CO substitution in **1** by tertiary phosphines, namely, that the stable products of substitution have the Lewis base coordinated at the ruthenium site.

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Registry No. **1**, 82544-75-0; **2**, 95392-70-4; **3a**, 118142-02-2; **3b**, 118142-04-4; *cis*-**4**, 99094-59-4; *trans*-**4**, 99094-58-3; **5**, 87552-32-7; $Ru_3(CO)_{12}$, 15243-33-1; Co, 7440-48-4; Ru, 7440-18-8.

Supplementary Material Available: A table of thermal parameters (1 page); a listing of structure factors (14 pages). Ordering information is given on any current masthead page.

Coordination Chemistry of Siloles: Synthesis, Reactions, and Stereochemistry of Silicon-Substituted (η^4-2,5-Diphenylsilacyclopentadiene)transition-metal Complexes.[1] Crystal Structure of Dicarbonyl[phenyl((η^4-*exo*-1-methyl-2,5-diphenylsilacyclopentadien-1-yl)oxy)carbene]iron

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New silicon-monosubstituted and -disubstituted (η^4-2,5-diphenylsilacyclopentadiene)transition-metal complexes are described. These complexes undergo a variety of substitution reactions at silicon, in which the exo leaving groups showed enhanced reactivity. The stereochemistry of substitution reactions at silicon with nucleophiles (RMgX, $LiAlH_4$, ROH, H_2O) differs significantly from that established for optically active silanes. (η^4-1-Chloro-2,5-diphenylsilacyclopentadiene)tricarbonyliron complexes undergo displacement at silicon with complete retention at both exo and endo positions. These observations are discussed in terms of electronic factors. Reactions of the endo-chloro derivative with organolithiums resulted in the formation of new carbene complexes; the crystal structure of dicarbonyl[phenyl((η^4-*exo*-1-methyl-2,5-diphenylsilacyclopentadien-1-yl)oxy)carbene]iron is reported. In the case of the exo-chloro isomer, the reaction course depends on the nature of the solvent and of the organolithium reagent; either attack at silicon or at a carbonyl ligand was observed.

Introduction

Transition-metal complexes of nonfunctional siloles are well-known,[2,3] and in all complexes reported thus far the silole functions as an η^4-ligand. Still unreported, however, is the generation or detection of a (η^5-silacyclopentadienyl)metal complex. One route could be, in principle, the reaction of a silicon functional coordinated η^4-silole.

In terms of substitution and reaction at coordinated siloles, previous studies have been carried out by Sakurai et al.[3] and Jutzi et al.[4] and suggested that the reacting group at silicon must be exo to the metal center. However the experiments were restricted to a few exo isomers of (η^4-2,3,4,5-tetraphenylsilacyclopentadiene)transition-metal

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(1) For preliminary communications: Corriu, R. J. P.; Guerin, C.; Henner, B. J. L.; Wong Chi Man, W. W. C. *J. Organomet. Chem.* **1987**, *320*, C1; **1987**, *320*, C7. Carré, F.; Corriu, R. J. P.; Guerin, C.; Henner, B. J. L.; Wong Chi Man, W. W. C. *J. Organomet. Chem.* **1987**, *336*, C1.

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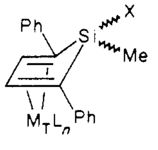
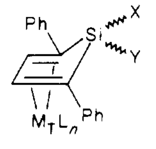
complexes (metal = Fe or Co) since the functional derivatives were only accessible by preferential cleavage of an exo Si–Me bond by Lewis acid reagents.

Recently, we described the synthesis of a variety of functional 2,5-diphenylsiloles and conditions for the generation of the corresponding metal complexes.[5] The new complexes allowed us to investigate in more detail the reactivity at a silicon center with functional groups either in the exo or in the endo position with respect to the metal center. We now report our data for (η^4-diphenylsilacyclopentadiene)tricarbonyliron and -tetracarbonylchromium, **1** and **2**, respectively, which bear either one or two leaving groups bonded to silicon.



1



2

M_TL_n = Fe(CO)$_3$ or Cr(CO)$_4$; X and Y = a leaving group

Experimental Section

All reactions were carried out under nitrogen or argon by using a vacuum line and Schlenck tubes in the case of the transition-metal complexes. Solvents were dried and distilled before use. The following starting materials were prepared by literature methods: $ClSi(OMe)_3$;[6] 1-methyl-1-methoxy-, 1-methyl-1-hydro-, 1-methyl-1-chloro-, 1,1-dimethoxy-2,5-diphenylsilacyclopentadiene;[7] (η^4-*exo*-1-methyl-*endo*-1-hydro-2,5-diphenylsilacyclopentadiene)tricarbonyliron (**4**).[5b] *i*-$PrSi(OMe)_3$ was prepared in 30% yield from *i*-PrMgBr and $ClSi(OMe)_3$ at −50 °C.

Melting points were taken by using an oil circulating apparatus and are uncorrected. IR spectra were recorded with a Perkin-Elmer 298 spectrophotometer, NMR spectra with a Varian EM 360 or EM 390 spectrograph (chemical shifts, δ, are relative to Me_4Si), and mass spectra on a JEOL JMS-D 100 spectrometer (electronic impact).

1-Isopropyl-1-methoxy-2,5-diphenylsilacyclopentadiene. This derivative was obtained from *i*-$PrSi(OMe)_3$ (2.3 g, 13.75 mmol) and 1,4-dilithio-1,4-diphenylbutadiene prepared from 5 g (13.75 mmol) of dibromo-1,4-diphenylbutadiene by using the general procedure published before:[5b] 80% yield; mp 94–96 °C; ^1H NMR (CCl_4) δ 7.6–7.1 (m, 12 H, aromatic + ethylenic), 3.55 (s, 3 H, OCH_3), 1.3–0.8 (m, 7 H, *i*-Pr); mass spectrum, *m/e* (assignment) 306 (molecular peak). Anal. Calcd for $C_{20}H_{22}OSi$: C, 78.43; H, 7.18. Found: C, 78.08; H, 7.50.

1-Isopropyl-1-hydro-2,5-diphenylsilacyclopentadiene. This compound was obtained from the corresponding methoxy derivative (3.06 g, 10 mmol) using $LiAlH_4$ (0.38, 10 mmol) as the reducing agent[5b] and diethyl ether as solvent: 80% yield; mp 87–89 °C; ^1H NMR (CCl_4) δ 7.5–7.0 (m, 12 H, aromatic and ethylenic), 4.95 (s, 1 H, SiH), 1.15–0.85 (m, 7 H, *i*-Pr); IR (CCl_4) ν_{Si-H} 2095 cm^{-1}. Anal. Calcd for $C_{19}H_{20}Si$: C, 82.60; H, 7.24. Found: C, 82.36; H, 7.24.

1-Isopropyl-1-chloro-2,5-diphenylsilacyclopentadiene. This compound was obtained from 1-isopropyl-1-hydro-2,5-diphenylsilacyclopentadiene (0.55 g, 2 mmol) and PCl_5 (0.41 g, 2.2 mmol) by using the procedure of the preparation of 1-methyl-1-chloro-2,5-diphenylsilacyclopentadiene[5b] (reaction time, 6 h): 0.248 g, 40% yield; mp 137 °C; ^1H NMR (CCl_4) δ 7.6–7.0 (m, 12 H, aromatic + ethylenic), 1.5–0.9 (m, 7 H, *i*-Pr); mass spectrum, *m/e* (assignment for ^{35}Cl) 310 (molecular peak), 268 (M^+ − (*i*-Pr)), 231 (M^+ − (*i*-Pr − Cl)). Anal. Calcd for $C_{19}H_{19}ClSi$: C, 73.41; H, 6.28. Found: C, 72.85; H, 6.20.

(η^4-*exo*-1-Methoxy-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)- and (η^4-*exo*-1-Methyl-*endo*-1-methoxy-2,5-diphenylsilacyclopentadiene)tricarbonyliron. These derivatives were obtained from 1.22 g (4.4 mmol) of 1-methoxy-1-methyl-2,5-diphenylsilacyclopentadiene and 1.6 g (4.4 mmol) of $Fe_2(CO)_9$ by using the general procedure[5b] (reaction time, 36 h): 1 g, 54% yield; ^1H NMR indicated an exo:endo methoxy isomer ratio of 70:30 (for the physical properties see the synthesis of the pure isomer). Anal. Calcd for the mixture of isomers ($C_{21}H_{18}FeO_4Si$): C, 60.30; H, 4.34. Found: C, 59.89; H, 4.36.

(η^4-*exo*-1-Hydro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)- and (η^4-*exo*-1-Methyl-*endo*-1-hydro-2,5-diphenylsilacyclopentadiene)tricarbonyliron. A solution of 1 g (2.4 mmol) of (η^4-1-methoxy-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron (70:30, exo:endo methoxy isomers) in hexane was cooled at −30 °C, and 0.42 mL (2.4 mmol) of a molar solution of *i*-Bu_2AlH in hexane was added slowly, and the reaction mixture was allowed to warm to room temperature. After being stirred for 1 h and filtered, the reaction mixture was cooled at −20 °C to give 0.23 g (0.6 mmol, 25% yield) of (η^4-*exo*-1-methyl-*endo*-1-hydro-2,5-diphenylsilacyclopentadiene)tricarbonyliron (**4**) (same physical characteristics as an authentic sample;[5b] ^{29}Si NMR (C_6D_6, C_6H_6) δ −14.86 (J_{Si-H} = 212 Hz)). The residual solution was cooled at −78 °C to give yellow-orange crystals of (η^4-*exo*-1-hydro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron (**3**): 0.61 g, 1.6 mmol, 66% yield; mp 70–71 °C; ^1H NMR (CCl_4) δ 7.4–7.0 (m, 10 H, aromatic), 6.03 (s, 2 H ethylenic), 5.35 (q, 1 H, Si–H, *J* = 4 Hz), 1.15 (d, 3 H, Me, *J* = 4 Hz); ^{29}Si (C_6H_6, C_6D_6) δ −12.09, J_{Si-H} = 182 Hz); IR (hexane) ν_{CO} 2050, 1980 cm^{-1}, ν_{Si-H} 2073 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity), 388 (molecular peak, 12), 370 (M^+ − CO, 29), 332 (M^+ − 2CO, 27), 304 (M^+ − 3CO, 100). Anal. Calcd for $C_{20}H_{16}FeO_3Si$: C, 61.87; H, 4.15. Found: C, 61.96; H, 4.23.

(η^4-*exo*-1-Isopropyl-*endo*-1-chloro-2,5-diphenylsilacyclopentadiene)tetracarbonylchromium. A mixture of silole (0.310 g, 1 mmol) and $(COD)Cr(CO)_4$ (0.272 g, 1 mmol) in hexane (10 mL) was heated at 50 °C for 1 h (the disappearance of $(COD)Cr(CO)_4$ was monitored by IR). The mixture was concentrated and cooled at −20 °C to give 0.2 g (0.43 mmol) of orange crystals of the title complex: 43% yield; mp 139 °C; ^1H NMR (CCl_4) δ 7.40–6.50 (m, 10 H, aromatic), 5.83 (s, 2 H, ethylenic), 1.30–0.40 (m, 7 H, *i*-Pr); IR (hexane) ν_{CO} 2042, 1994, 1957, 1946 cm^{-1}; mass spectrum, *m/e* (assignment for ^{35}Cl, relative intensity) 446 (M^+ − CO, 1), 418 (M^+ − 2CO, 0.2), 390 (M^+ − 3CO, 1), 362 (M^+ − 4CO, 7), 310 (M^+ − $Cr(CO)_4$, 100). Anal. Calcd for $C_{23}H_{19}ClCrO_4Si$: C, 58.17; H, 4.03. Found: C, 57.89; H, 4.15.

Reactions of (η^4-*exo*-1-Hydro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. With Methanol: Formation of (η^4-*exo*-1-Methoxy-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. To a solution of **3** (100 mg, 0.258 mmol) in hexane (10 mL) cooled at 0 °C was added methanol (1 mL), and the solution was stirred at room temperature for 15 h. The solvent was removed in vacuo and the residue extracted with 20 mL of hot hexane, filtered, concentrated to 10 mL, and cooled at −20 °C to give 0.093 g (0.222 mmol, 86% yield) of yellow crystals of the title complex: mp 122 °C; ^1H NMR ($CDCl_3$) δ 7.4–6.80 (m, 10 H, aromatic), 5.80 (s, 2 H, ethylenic), 3.10 (s, 3 H, OMe), 1.03 (s, 3 H, Me); IR (hexane) ν_{CO} 2052, 1982 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 418 (molecular peak, 12), 390 (M^+ − CO, 14), 362 (M^+ − 2CO, 39), 334 (M^+ − 3CO, 100), 274 (M^+ − $Fe(CO)_3$, 14).

With PCl_5: Formation of (η^4-*exo*-1-Chloro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. A solution of **3** (150 mg, 0.387 mmol) in 5 mL of CCl_4 was added to a suspension of PCl_5 (100 mg, 0.480 mmol) in the same solvent cooled at 0 °C. The mixture was allowed to warm to room temperature and was stirred for 1 h. The solvent was removed under vacuum, and the yellow residue was extracted with 20 mL of hexane, filtered, and concentrated to 10 mL. The solution was cooled at −20 °C to give 0.147 g (0.348 mmol) of yellow crystals of the title compound: 90% yield; mp 124 °C; ^1H NMR ($CDCl_3$) δ 7.50–6.80 (m, 10 H, aromatic), 6.0 (s, 2 H, ethylenic), 1.40 (s, 3 H, Me); IR (hexane) ν_{CO} 2058, 1995, 1988 cm^{-1}; mass spectrum, *m/e* (assignment for ^{35}Cl, relative intensity) 422 (molecular peak,

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[7] Brunet, J. C.; Demey, N. *Ann. Chim. (Rome)* **1973**, *8*, 123.

7), 394 (M^+ – CO, 10), 366 (M^+ – 2CO, 27). Anal. Calcd for $C_{20}H_{15}ClFeO_3Si$: C, 56.83; H, 3.58. Found: C, 56.88; H, 3.44.

With Water: Formation of (η^4-*exo*-1-Hydroxy-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. To a solution of **3** (100 mg, 0.258 mmol) in 5 mL of acetone was added 0.4 mL of water, and the mixture was stirred at 42 °C for 3 h. The solvents were pumped off and the yellow residue extracted with 20 mL of hot hexane. After filtration, the solution was concentrated to 10 mL and cooled at –20 °C to give 0.093 g (0.232 mmol) of yellow crystals of the title compound: 90% yield; mp 117 °C; ^1H NMR (CCl_4) δ 7.35–7.00 (s, br, 10 H, aromatic), 5.80 (s, 2 H, ethylenic), 2.13 (s, 1 H, OH), 1.07 (s, 3 H, Me). IR (hexane) ν_{CO} 2050, 1985 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 404 (molecular peak, 11), 376 (M^+ – CO, 17), 348 (M^+ – 2CO, 29), 320 (M^+ – 3CO, 100), 264 (M^+ – $Fe(CO)_3$, 19). Anal. Calcd for $C_{20}H_{16}FeO_4Si$: C, 59.42; H, 3.99. Found: C, 59.43; H, 4.05.

With *p*-Methoxyphenol: Formation of (η^4-*exo*-1-(*p*-Methoxyphenoxy)-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. The same procedure as for the reaction of **3** with methanol (vide supra) was used. To a solution of **3** (0.150 g, 0.387 mmol) in hexane (10 mL) was added a solution of *p*-methoxyphenol (0.048 g, 0.387 mmol) in 5 mL of hexane, and the mixture was stirred at 45 °C for 20 h. Yellow crystals (0.154 g, 0.3 mmol, 78%) of the title complex were obtained: mp 123 °C; ^1H NMR (CCl_4) δ 7.30–6.90 (s, 10 H, aromatic from silole), 6.60–6.07 (m, 4 H, aromatic), 5.55 (s, 2 H, ethylenic), 3.60 (s, 3 H, OMe), 1.17 (s, 3 H, Me); IR (hexane) ν_{CO} 2051, 1989, 1981 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 510 (molecular peak, 42), 482 (M^+ – CO, 21), 426 (M^+ – 3CO, 100).

With Benzaldehyde: Formation of (η^4-*exo*-1-(Benzyloxy)-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. The same procedure as for the reaction of **3** with methanol (vide supra) was used. To a solution of **3** (0.100 g, 0.258 mmol) in hexane (10 mL) was added a solution of benzaldehyde (0.027 g, 0.258 mmol) in 5 mL of the same solvent, and the reaction mixture was stirred at 45 °C for 3 h. Yellow crystals of the title complex (0.061 g, 0.124 mmol, 48% yield) were obtained: mp 102 °C; ^1H NMR (CCl_4) δ 7.33–6.83 (m, 15 H, aromatic), 5.83 (s, 2 H, ethylenic), 4.40 (s, 2 H, CH_2), 1.10 (s, 3 H, Me); IR (hexane) ν_{CO} 2050, 1981 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 494 (molecular peak, 18), 466 (M^+ – CO, 10), 410 (M^+ – 3CO, 100).

With Phenylacetylene: Formation of (η^4-*exo*-1-Styryl-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. The same procedure as for the reaction of **3** with methanol (vide supra) was used. To a solution of **3** (0.100 g, 0.258 mmol) in hexane was added 0.1 mL (0.093 mg, 0.9 mmol) of phenylacetylene, and the mixture was stirred at 45 °C for 16 h. Yellow crystals (0.044 g, 0.09 mmol, 35% yield) of the title complex were obtained: mp 112 °C; ^1H NMR (CCl_4) δ 7.20 (s, br, 15 H, aromatic), 6.67–6.10 (mainly 2 doublets, J = 18 Hz, 2 H, vinylic), 6.00 (s, 2 H, ethylenic), 1.23 (s, 3 H, Me); ^1H NMR corresponded mainly to the trans isomer; IR (hexane) ν_{CO} 2050, 1984 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 462 (M^+ – CO, 1), 434 (M^+ – 2CO, 2), 406 (M^+ – 3CO, 34), 350 (M^+ – $Fe(CO)_3$, 100).

With $Ph_3C^+BF_4^-$: Formation of (η^4-*exo*-1-Fluoro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. A solution of **3** (100 mg, 0.258 mmol) in 10 mL of CH_2Cl_2 was added to a solution of $Ph_3C^+BF_4^-$ (85 mg, 0.258 mmol) in 10 mL of CH_2Cl_2 cooled at –50 °C. The mixture was allowed to warm to room temperature and was stirred for 1 h. The solvent was removed in vacuo, and the yellow residue was extracted with hexane, filtered, and cooled to –20 °C. Fractional crystallization gave first white crystals of Ph_3CH and then yellow crystals of the title complex: 65% yield; mp 81 °C; ^1H NMR (CCl_4) δ 7.47–6.87 (s, 10 H, aromatic), 5.94 (s, 2 H, ethylenic), 1.17 (d, J_{H-F} = 6 Hz, 3 H, Me); ^{19}F NMR (CCl_4, freon 11) δ –100, 7 (q, J_{F-H} = 6 Hz); IR (hexane) ν_{CO} 2050, 1988, 1983 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 406 (molecular peak, 12), 378 (M^+ – CO, 25), 350 (M^+ – 2CO, 50), 322 (M^+ – 3CO, 100), 266 (M^+ – $Fe(CO)_3$, 44). Anal. Calcd for $C_{20}H_{15}FFeO_3Si$: C, 59.13; H, 3.72. Found: C, 59.06; H, 3.79.

With $Co_2(CO)_8$: Formation of (η^4-*exo*-1-(Tetracarbonylcobaltio)-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. A mixture of complex **3** (0.170 g, 0.438 mmol) and $Co_2(CO)_8$ (0.075 g, 0.219 mmol) dissolved in 10 mL of hexane was stirred at room temperature for 2 h. The reaction mixture was filtered and cooled at –20 °C to give 0.186 g (0.333 mmol, 76% yield) of pale brown crystals of the title compound: mp 125 °C; ^1H NMR (C_6D_6) δ 7.40–6.70 (m, 10 H, aromatic), 5.43 (s, 2 H, ethylenic), 1.50 (s, 3 H, Me); IR (hexane) ν_{CO} 2085, 2053, 2023, 1990 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 558 (molecular peak, 9), 446 (M^+ – 4CO, 20), 387 (M^+ – $Co(CO)_4$, 100), 359 (M^+ – $Co(CO)_4$ – CO, 44), 331 (M^+ – $Co(CO)_4$ – 2CO, 63), 303 (M^+ – $Co(CO)_4$ – 3CO, 52). Anal. Calcd for $C_{24}H_{15}CoFeO_7Si$: C, 51.64; H, 2.71. Found: C, 51.82; H, 2.99.

Reduction of (η^4-*exo*-1-Chloro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)- and (η^4-*exo*-1-Methoxy-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron Using $LiAlH_4$ and *i*-Bu_2AlH. A solution of the complex (0.470 mmol) in 10 mL of diethyl ether was added to a suspension of $LiAlH_4$ (2 mmol) in 10 mL of the same solvent cooled at 0 °C and stirred for 5 min. Hexane was added to precipitate the excess of $LiAlH_4$, and the mixture was filtered, the solvent removed under vacuum, and the yellow residue extracted with 10 mL of hexane and cooled at –78 °C to give the expected complex with 65–70% yield. (same physical properties as an authentic sample, vide supra.) To a solution of the exo-methoxy complex (0.170 g, 0.4 mmol) in 10 mL of hexane at –30 °C was added 0.4 mL of a molar solution of *i*-Bu_2AlH in the same solvent. The reaction mixture was allowed to warm to room temperature and was stirred for 1 h. Cooling the solution at –78 °C gave a 66% yield (0.102 g, 0.26 mmol) (same physical properties as an authentic sample, vide supra).

Reaction of (η^4-*exo*-1-Methoxy-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron with SbF_5 Intercalated in Graphite. A solution of the exo-methoxy complex (0.115 g, 0.275 mmol) in hexane (10 mL) was added to a suspension of SbF_5 intercalated in graphite (0.229 g, 1.376 mmol) in the same solvent, and the mixture was stirred at 40 °C for 30 h. The mixture was filtered and cooled at –20 °C to give 0.036 g (0.09 mmol) yellow-orange crystals of (η^4-*exo*-1-fluoro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron: 32% yield (same physical properties as an authentic sample, vide supra).

Reactions of (η^4-*endo*-1-Hydro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron (4). With the same experimental conditions as for its exo-hydro isomer no reaction of **4** was observed with H_2O, MeOH, PCl_5, $Ph_3C^+BF_4^-$, or $Co_2(CO)_8$.

Reactions of (η^4-*exo*-1-Chloro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. With Methanol: Formation of (η^4-*exo*-1-Methoxy-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. To a solution of exo-chloro complex (0.175 g, 0.414 mmol) dissolved in CCl_4 and cooled at 0 °C was added methanol (1 mL), and the mixture was allowed to warm up to room temperature. The solvent was removed in vacuo, and recrystallization from hexane (–20 °C) gave 0.154 g (0.368 mmol, 89% yield) of the title compound (same physical properties as an authentic sample, vide supra).

With Water: Formation of (η^4-*exo*-1-Hydroxy-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. To a mixture of the exo-chloro complex (0.100 g, 0.236 mmol) in acetone (10 mL) was added water (1 mL), and the mixture was stirred at room temperature for 0.5 h. The solvent was removed under vacuum and recrystallization from hexane (–20 °C) gave 0.089 g (0.22 mmol, 93%) yield of the title complex (same physical properties as an authentic sample, vide supra).

Formation of the Siloxane. To a mixture of the exo-chloro complex (0.100 g, 0.236 mmol) in acetone (10 mL) was added water (1 mL), and the mixture was stirred at 50 °C for 24 h. The solvent was removed under vacuum and recrystallization from hexane (–20 °C) gave 0.084 g (0.106 mmol, 90% yield) of yellow crystals of the corresponding siloxane: mp 188 °C; ^1H NMR ($CDCl_3$) δ 7.50–6.80 (m, 20 H, aromatic), 5.36 (s, 4 H, ethylenic), 0.85 (s, 6 H, SiMe); IR (hexane) ν_{CO} 2045, 1980 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 790 (molecular peak, 4), 762 (M^+ – CO, 5), 706 (M^+ – 3CO, 40), 622 (M^+ – 6CO, 100). Anal. Calcd for $C_{40}H_{30}Fe_2O_7Si_2$: C, 60.77; H, 3.83. Found: C, 61.05; H, 3.91.

With EtMgBr: Formation of (η^4-*exo*-1-Ethyl-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. To a solution of the exo-chloro complex (0.150 g, 0.355 mmol) in diethyl ether (10 mL) cooled at 0 °C was added 1 mL of a 1.2 molar solution of EtMgBr. The mixture was allowed to warm to room temperature and was stirred for 30 h. The solvent was removed under vacuum and the orange residue extracted with hot hexane, filtered, and cooled at -20 °C to give 0.093 g (0.224 mmol, 63% yield) of orange crystals of the title complex: mp 127 °C; ^{1}H NMR ($CDCl_3$) δ 7.50–6.90 (m, 10 H, aromatic), 6.03 (s, 2 H, ethylenic), 1.03 (s, 3 H, SiMe), 0.87–0.3 (m, 5 H, Et); IR (hexane) ν_{CO} 2048, 1979 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 416 (molecular peak, 0.3), 388 (M^+ - CO, 1.7), 360 (M^+ - 2CO, 2.5), 332 (M^+ - 3CO, 8.2), 276 (M^+ - $Fe(CO)_3$, 100), 261 (M^+ - $Fe(CO)_3$ - Me, 16), 247 (M^+ - $Fe(CO)_3$ - Et, 58).

(η^4-*exo*-1-Chloro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)- and (η^4-*endo*-1-Chloro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. These derivatives were obtained from $Fe_2(CO)_9$ (2 g, 5.5 mmol) and 1-chloro-1-methyl-2,5-diphenylsilacyclopentadiene (1.2 g, 4.25 mmol) in toluene (50 mL) using the general procedure.[5b] The title complexes were obtained in a 58% yield (1.04 g, 2.46 mmol). ^{1}H NMR indicated a 65:35 endo:exo chloro isomers ratio. Fractional recrystallization from hexane gave 0.628 g (1.49 mmol, 35% yield) of (η^4-*endo*-1-chloro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron: mp 112 °C; ^{1}H NMR ($CDCl_3$) δ 7.50–6.80 (m, 10 H, aromatic), 5.93 (s, 2 H, ethylenic), 0.47 (s, 3 H, Me); IR (hexane) ν_{CO} 2055, 2000, 1985 cm^{-1}; mass spectrum, *m/e* (assignment for ^{35}Cl, relative intensity) 422 (molecular peak, 25), 394 (M^+ - CO, 49), 387 (M^+ - Cl, 100), 366 (M^+ - 2CO, 11) 338 (M^+ - 3CO, 21) 282 (M^+ - $Fe(CO)_3$, 6). Anal. Calcd for $C_{20}H_{15}ClFeO_3Si$: C, 56.83; H, 3.58. Found: C, 57.08; H, 3.78 (for the physical properties of the exo-chloro isomer see the pure complex).

Reactions of (η^4-*endo*-1-Chloro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. With Methanol or Water: Formation of (η^4-*endo*-1-Methoxy-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)- or (η^4-*endo*-1-Hydroxy-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. The same procedures and amounts as for the reactions with the exo-chloro isomers were used.

MeOH: reaction time, 3 h; 71% yield; mp 135 °C; ^{1}H NMR ($CDCl_3$) δ 7.40–6.80 (m, 10 H, aromatic), 5.73 (s, 2 H, ethylenic), 3.77 (s, 3 H, OMe), 0.17 (s, 3 H, Me); IR (hexane) ν_{CO} 2052, 1993, 1978 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 418 (molecular peak, 5), 390 (M^+ - CO, 12), 362 (M^+ - 2CO, 32), 334 (M^+ - 3CO, 100), 319 (M^+ - 3CO - Me, 40), 304 (M^+ - 3CO - 2Me, 50), 278 (M^+ - $Fe(CO)_3$, 8).

H_2O: reaction time, 3 h; 71% yield; mp 135–136 °C; ^{1}H NMR (CCl_4) δ 7.33–6.87 (m, 10 H, aromatic), 5.85 (s, 2 H, ethylenic), 2.80–2.63 (m, 1 H, OH), 0.17 (s, 3 H, Me); IR (hexane) ν_{CO} 2047, 1985, 1967 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 404 (molecular peak, 11), 376 (M^+ - CO, 49), 348 (M^+ - 2CO, 100), 320 (M^+ - 3CO, 100), 305 (M^+ - $Fe(CO)_3$, 14). Anal. Calcd for $C_{20}H_{16}SiO_4Fe$: C, 59.42; H, 3.99. Found: C, 59.55; H, 4.14.

With $LiAlH_4$: Formation of (η^4-*endo*-1-Hydro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron. A solution of the endo-chloro complex (0.150 g, 0.355 mmol) in diethyl ether (5 mL) was added to a slurry of $LiAlH_4$ (0.057, g, 1.5 mmol) in 10 mL of the same solvent cooled to 0 °C, and the mixture was stirred at that temperature for 1 h. Hexane was added to precipitate $LiAlH_4$, the mixture was filtered, and the solvents were removed under vacuum. Crystallization from hexane gave 0.106 g (0.273 mmol, 77% yield) of yellow crystals of the title complex. Same physical properties as an authentic sample.[5b]

Reaction of a 65:35 Isomer Mixture of (η^4-*endo*-1-Chloro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)- and (η^4-*exo*-1-Chloro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron with MeOH, H_2O, and $LiAlH_4$. These reactions were performed by using the same reaction conditions as for the pure (η^4-*endo*-1-chloro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron isomer. ^{1}H NMR indicated in all three cases a 65:35 mixture of the endo:exo isomers: MeOH, 86% yield; H_2O, 72%; $LiAlH_4$, 53%.

Reaction of (η^4-*endo*-1-Chloro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron with RLi (R = Me, Ph) and *i*-Pr_2NLi: Formation of Carbenes 5. To a solution of 0.200 g (0.473 mmol) of the endo-chloro complex in diethyl ether (10 mL) cooled at -50 °C was added 1 equiv of the lithium reagent, and the solution was allowed to warm to room temperature (the yellow solution turned black around -20 °C). The solvent was removed under vacuum, and the black residue was extracted with 20 mL of a 50:50 mixture of hexane–dichloromethane. The mixture was filtered, concentrated to 10 mL, and cooled at -20 °C to give black crystals of the neutral carbene. (Scheme VI).

R = Ph: 0.154 g, 0.331 mmol, 70% yield; mp 172 °C; ^{1}H NMR ($CDCl_3$) δ 8.40–8.07 and 7.63–7.30 (m, 5 H, C_{carb} phenyl), 7.10 (s, 10 H, aromatic), 5.97 (s, 2 H, ethylenic), 1.00 (s, 3 H, Me); ^{13}C NMR ($CDCl_3$) δ 339.91 (C_{carb}); IR (hexane) ν_{CO} 2002, 1952 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 464 (molecular peak, 6), 436 (M^+ - CO, 15), 408 (M^+ - 2CO, 78), 380 (M^+ - 3CO, 100). Anal. Calcd for $C_{26}H_{20}FeO_3Si$: C, 67.25; H, 4.34. Found: C, 66.94; H, 4.31.

The same reaction performed in toluene–diethyl ether (98:2) gave the same neutral carbene with 80% yield.

R = Me: 0.120 g, 0.3 mmol, 63% yield; mp 73 °C; ^{1}H NMR ($CDCl_3$) δ 7.05 (s, 10 H, aromatic), 5.77 (s, 2 H, ethylenic), 3.03 (s, 3 H, CMe), 0.97 (s, 3 H, SiMe); ^{13}C NMR ($CDCl_3$) δ 365.92 (C_{carb}); IR (hexane) ν_{CO} 2008, 1953 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 402 (molecular peak, 9), 374 (M^+ - CO, 21), 346 (M^+ - 2CO, 100), 247 (M^+ - $Fe(CO)_2$ - COMe, 46). Anal. Calcd for $C_{21}H_{18}FeO_3Si$: C, 62.70; H, 4.51. Found: C, 63.02; H, 4.69.

R = *i*-Pr_2N: 0.076 g, 0.156 mmol, 33% yield; mp 163–164 °C; ^{1}H NMR ($CDCl_3$) δ 7.05 (s, 10 H, aromatic), 5.67 (s, 2 H, ethylenic), 3.60 (m, 1 H, CH), 4.80 (m, 1 H, CH), 1.57 (d, J_{H-H} = 7 Hz, 6 H, Me), 1.17 (d, J_{H-H} = 7 Hz, 6 H, Me) (two different isopropyl groups); ^{13}C NMR ($CDCl_3$) δ 215.36 (C_{carb}); IR (hexane) ν_{CO} 2047, 1985, 1930 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 487 (molecular peak, 11), 459 (M^+ - CO, 9), 431 (M^+ - 2CO, 100). Anal. Calcd for $C_{26}H_{29}FeNO_3Si$: C, 64.06; H, 6.00; N, 2.87. Found: C, 64.09; H, 6.09; N, 2.63.

Reaction of (η^4-*endo*-1-Chloro-*exo*-1-isopropyl-2,5-diphenylsilacyclopentadiene)tetracarbonylchromium with PhLi. The same reaction conditions as for (η^4-*endo*-1-chloro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron were used except with 0.200 g (0.421 mmol) of the chloro complex: solvent, toluene–diethyl ether (98:2); 0.176 g (0.321 mmol, 81% yield) of the carbene was obtained; mp 186 °C; ^{1}H NMR ($CDCl_3$) δ 8.37–8.10 and 7.60–7.30 (m, 5 H, C-phenyl), 6.90 (s, 10 H, aromatic), 5.60 (s, 2 H, ethylenic), 2.05–1.03 (m, 7 H, *i*-Pr). ^{13}C NMR ($CDCl_3$) δ 359.64 (C_{carb}); IR (hexane) ν_{CO} 2002, 1954, 1932 cm^{-1}. Anal. Calcd for $C_{29}H_{24}CrO_4Si$: C, 67.43; H, 4.68. Found: C, 67.29; H, 4.73.

Reaction of (η^4-*exo*-1-Chloro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron with RLi (R = Ph, Me). The same reaction conditions as for the endo-chloro isomer were used.

R = Ph: solvent, Et_2O; using 0.422 g (1 mmol) of the chloro complex, 0.023 g (0.05 mmol, 5% yield) of dicarbonyl[phenyl((η^4-*exo*-1-methyl-2,5-diphenylsilacyclopentadien-1-yl)oxy)carbene]iron was obtained. (same physical properties as an authentic example; vide supra.)

Solvent:toluene–diethyl ether (98:2); with 0.200 g (0.473 mmol) of chloro complex, 0.156 g (0.379 mmol, 80%) of the same carbene was obtained.

R = Me. The reaction was performed by using 0.200 g (0.473 mmol) of the chloro complex. The solution did not turn black, and after workup 0.114 g (0.284 mmol, 60% yield) of orange crystals of (η^4-1,1-dimethyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron were obtained (diethyl ether as solvent) or 0.137 g (0.340 mmol, 72% yield) (toluene–hexane, 98:2). Physical properties corresponded to the literature values.[7]

Complexation Reactions of 1,1-Dimethoxy-2,5-diphenylsilacyclopentadiene. With (COD)Cr(CO)$_4$. A mixture of the dimethoxysilole (0.147 g, 0.5 mmol) and (COD)Cr(CO)$_4$ (0.136 g, 0.5 mmol) in hexane (10 mL) was heated at 50 °C for 1 h. (The disappearance of (COD)Cr(CO)$_4$ was IR monitored.) The mixture was concentrated and cooled at -20 °C to give orange crystals of (η^4-1,1-dimethoxy-2,5-diphenylsilacyclopentadiene)tetracarbonylchromium (0.126 g, 55%): mp 153 °C dec; ^{H} NMR (C_6D_6) δ 7.30–6.80 (m, 10 H, aromatic), 5.30 (s, 2 H, ethylenic), 3.75 (s, 3 H, OMe endo), 3.03 (s, 3 H, OMe exo); IR (hexane) ν_{CO} 2041, 1993, 1954, 1942 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 458 (molecular peak, 12), 430 (M$^+$ − CO, 7), 402 (M$^+$ − 2CO, 9), 374 (M$^+$ − 3CO, 29), 346 (M$^+$ − 4CO, 100), 294 (M$^+$ − Cr(CO)$_4$, 79). Anal. Calcd for $C_{22}H_{18}CrO_6Si$: C, 57.64; H, 3.96. Found: C, 57.50; H, 4.00. The dimethoxysilole reacted also with $Cr(CO)_5$·THF in THF at room temperature (5 h) to give the same complex with 50% yield.

With $Co_2(CO)_8$. A mixture of the dimethoxysilole (0.735 g, 2.5 mmol) and $Co_2(CO)_8$ (0.855 mg, 2.5 mmol) in hexane (40 mL) was stirred at room temperature for 8 h (the disappearance of $Co_2(CO)_8$ was monitored by IR). The solvent was removed under vacuum; the residue was extracted with hexane, concentrated, and cooled at −20 °C to give brown crystals of (η^4-1,1-dimethoxy-2,5-diphenylsilacyclopentadiene)hexacarbonyldicobalt (1.1 g, 77%): mp 128 °C dec; ^{1}H NMR (C_6D_6) δ 7.73–6.83 (m, 10 H, aromatic), 5.66 (s, 2 H, ethylenic), 3.73 (s, 3 H, OMe endo), 2.95 (s, 3 H, OMe exo); IR (hexane) ν_{CO} 2075, 2047, 2017, 1854 (w) cm^{-1}. The poor stability of the complex prevented good analysis.

Synthesis of Bis[(η^4-1,1-dimethoxy-2,5-diphenylsilacyclopentadiene)dicarbonylcobalt]. A mixture of (η^4-1,1-dimethoxy-2,5-diphenylsilacyclopentadiene)hexacarbonyldicobalt (0.580 g, 1 mmol) and 1,1-dimethoxy-2,5-diphenylsilacyclopentadiene in hexane (20 mL) was heated at 50 °C for 5 h (monitored by IR). A red solid precipitated during the reaction. When all the cobalt derivative was consumed, CH_2Cl_2 (5 mL) was added to dissolve the red precipitate; the mixture was filtered and cooled at −20 °C to give red crystals of the title complex (0.672 mg, 82%): mp 165 °C dec; ^{1}H NMR (CD_2Cl_2) δ 7.50–7.00 (m, 10 H, aromatic), 5.77 (s, 2 H, ethylenic), 3.80 (s, 3 H, OMe endo), 3.10 (s, 3 H, OMe exo); IR (CCl_4) ν_{CO} 2042, 1835 (w) cm^{-1} (the poor stability of the complex prevented good analysis).

Reaction of Bis[(η^4-1,1-dimethoxy-2,5-diphenylsilacyclopentadiene)dicarbonylcobalt] with Iodine. A solution of iodine (0.590 g, 0.232 mmol) in 10 mL of CCl_4 was added to a solution of the complex (0.190 g, 0.232 mmol) in CCl_4 (10 mL) cooled to −10 °C. The mixture was allowed to warm to room temperature, the solvent was removed under vacuum, and the black residue was extracted with a mixture of hexane/dichloromethane (80:20). After filtration the solution was cooled to −20 °C to give black crystals of iodo(η^4-1,1-dimethoxy-2,5-diphenylsilacyclopentadiene)dicarbonylcobalt: 80% yield; mp 107 °C dec; ^{1}H NMR (C_6D_6) δ 7.98–7.05 (m, 10 H, aromatic), 6.22 (s, 2 H, ethylenic), 3.93 (s, 3 H, OMe endo), 2.80 (s, 3 H, OMe exo); IR (CCl_4) ν_{CO} 2076, 2048 cm^{-1}. Anal. Calcd for $C_{20}H_{18}CoIO_4Si$: C, 44.79; H, 3.38. Found: C, 44.49; H, 3.50.

Reaction of (η^4-1,1-Dimethoxy-2,5-diphenylsilacyclopentadiene)tricarbonyliron with *i*-Bu_2AlH. The same reaction conditions as for (η^4-*exo*-1-methoxy-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron were used (vide supra). With 0.434 g (1 mmol) of the dimethoxy derivative, 0.227 g (0.59 mmol, 59% yield) of the complex (η^4-1,1-dihydro-2,5-diphenylsilacyclopentadiene)tricarbonyliron was obtained: mp 132 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.63–7.17 (m, 10 H, aromatic), 6.27 (d, $J^4_{\text{H-H}}$ = 1.2 Hz, 2 H, ethylenic), 5.80 (dt, $J^1_{\text{H-H}}$ = 24 Hz, $J^4_{\text{H-H}}$ = 1.2 Hz, 1 H, SiH endo), 5.33 (d, $J^1_{\text{H-H}}$ = 24 Hz, 1 H, SiH exo); ^{29}Si NMR ($CDCl_3$) δ −39.24 (q, $J_{\text{Si-H}_\text{endo}}$ = 188 Hz, $J_{\text{Si-H}_\text{exo}}$ = 220 Hz); IR (hexane) ν_{CO} 2050, 1988, 1985 cm^{-1}, $\nu_{\text{Si-H}}$ 2156 (endo), 2080 (exo) cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 374 (molecular peak, 10), 346 (M$^+$ − CO, 36), 318 (M$^+$ − 2CO, 42), 290 (M$^+$ − 3CO, 100), 234 (M$^+$ − Fe(CO)$_3$, 16). Anal. Calcd for $C_{19}H_{14}FeO_3Si$: C, 60.98; H, 3.77. Found: C, 61.20; H, 3.54.

Reaction of (η^4-1,1-Dimethoxy-2,5-diphenylsilacyclopentadiene)tricarbonyliron with SbF_5 Intercalated in Graphite. The same reaction conditions as for (η^4-*exo*-1-methoxy-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron (vide supra) were used. Starting from 0.200 g (0.46 mmol) of dimethoxy derivative, 0.087 g (0.212 mmol, 46% yield) of yellow crystals of (η^4-1,1-difluoro-2,5-diphenylsilacyclopentadiene)tricarbonyliron were obtained: mp 171 °C; ^{1}H NMR ($CDCl_3$) δ 7.67–7.07 (m, 10 H, aromatic), 6.07 (dd, $J^4_{\text{H-F}}$ = 5 Hz, $J^1_{\text{H-H}}$ = 1.7 Hz, 2 H, ethylenic); ^{19}F NMR ($CDCl_3$, freon 11) δ −113.7 (d, $J_{\text{F-F}}$ = 71 Hz, 1 F, F exo), −156.3 (dt, $J^4_{\text{F-H}}$ = 5 Hz, $J^1_{\text{F-F}}$ = 71 Hz, 1 F, F endo); IR (hexane) ν_{CO} 2060, 2010, 1995 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 410 (molecular peak, 8), 382 (M$^+$ − CO, 18), 354 (M$^+$ − 2CO, 31), 326 (M$^+$ − 3CO, 100), 270 (M$^+$ − Fe(CO)$_3$, 40). Anal. Calcd for $C_{19}H_{12}F_2FeO_3Si$: C, 55.63; H, 2.95. Found: C, 55.45; H, 2.90.

Reactions of (η^4-1,1-Dihydro-2,5-diphenylsilacyclopentadiene)tricarbonyliron. The same general procedure as for the (η^4-1-hydro-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron complexes was used.

With H_2O. The dihydro complex (0.200 g, 0.535 mmol) was heated in wet acetone at 50 °C for 2 h; a yellow precipitate appeared, and after the mixture was cooled to room temperature, filtration gave the corresponding disiloxane (hydrogen in endo position): 0.181 g 0.238 mmol, 80% yield; mp 244 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.23 (s, 20 H, aromatic), 5.47 (d, $J^4_{\text{H-H}}$ = 1.5 Hz, 2 H, ethylenic), 5.33 (m, 1 H, SiH endo); IR (hexane) ν_{CO} 2048, 1986 cm^{-1}, $\nu_{\text{Si-H}}$ 2180 (vw) cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 762 (molecular solubility prevented good crystallization and elemental analysis).

The dihydro complex (0.200 g, 0.535 mmol) in wet acetone was stirred at room temperature for 0.5 h during which time a yellow precipitate appeared. Filtration gave 0.137 g (0.180 mmol, 67%) of a yellow solid corresponding to the siloxane. The solution was evaporated under vacuum: the residue was extracted with hexane, filtered and cooled at −20 °C to give 0.042 g (0.107 mmol, 20% yield) of yellow crystals of (η^4-*exo*-1-hydroxy-*endo*-1-hydro-2,5-diphenylsilacyclopentadiene)tricarbonyliron: mp 236 °C; ^{1}H NMR ($CDCl_3$) δ 7.60–6.90 (m, 10 H, aromatic), 5.97 (d, 2 H, ethylenic, $J^4_{\text{H-H}}$ = 1.5 Hz), 5.60 (t, 1 H, SiH endo, $J^4_{\text{H-H}}$ = 1.5 Hz), 2.70–2.30 (m, 1 H, SiOH); IR (hexane) ν_{CO} 2053, 1993, ν_{SiOH} 3670, ν_{SiH} 2200 (vw) cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 390 (molecular peak, 2), 362 (M$^+$ − CO, 14), 334 (M$^+$ − 2CO, 35), 306 (M$^+$ − 3CO, 100). Anal. Calcd for $C_{19}H_{14}FeO_4Si$: C, 58.48; H, 3.62. Found: C, 58.42; H, 3.85.

With MeOH. To a solution of the dihydro complex (0.100 g, 0.267 mmol) in hexane was added an excess of MeOH, and the mixture was stirred at room temperature for 3 h. Yellow crystals of (η^4-*exo*-1-methoxy-*endo*-1-hydro-2,5-diphenylsilacyclopentadiene)tricarbonyliron were obtained: 0.100 g, 0.248 mmol, 93% yield; mp 155 °C; ^{1}H NMR ($CDCl_3$) δ 7.70–7.00 (m, 10 H, aromatic), 6.13 (d, $J^4_{\text{H-H}}$ = 1–1.5 Hz, 2 H, ethylenic), 5.60 (m, 1 H, SiH), 3.30 (s, 3 H, OMe exo); IR (hexane) ν_{CO} 2052, 1990 cm^{-1}, $\nu_{\text{Si-H}}$ 2194 (vw) cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 404 (molecular peak, 22) 376 (M$^+$ − CO, 56), 348 (M$^+$ − 2CO, 85), 320 (M$^+$ − 3CO, 100), 305 (M$^+$ − 3CO − Me, 86).

With *p*-$CH_3OC_6H_4OH$. A solution of the dihydro complex (0.100 g, 0.267 mmol) and 0.035 g (0.267 mmol) of *p*-$CH_3OC_6H_4OH$ in hexane was heated at 40 °C for 3 h. Orange crystals of (η^4-*exo*-1-(*p*-methoxyphenoxy)-*endo*-1-hydro-2,5-diphenylsilacyclopentadiene)tricarbonyliron were obtained: 0.094 g, 0.195 mmol, 73% yield; mp 114 °C; ^{1}H NMR (CCl_4) δ 7.60–7.10 (m, 10 H, aromatic), 6.73–6.43 (m, 4 H, OC_6H_4O), 5.90 (d, $J^4_{\text{H-H}}$ = 1.5 Hz, 2 H, ethylenic), 5.70 (t, br, 1 H, SiH endo), 3.63 (s, 3 H, OMe); IR (hexane) ν_{CO} 2056, 1993 cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 468 (M$^+$ − CO, 4), 412 (M$^+$ − 3CO, 100), 356 (M$^+$ − Fe(CO)$_3$, 10), 233 (M$^+$ − Fe(CO)$_3$ − $OC_6H_4OCH_3$, 6). Anal. Calcd for $C_{26}H_{20}FeO_5Si$: C, 62.91; H, 4.06. Found: C, 62.83; H, 4.14.

With PCl_5. A solution of the dihydro complex (0.100 g, 0.267 mmol) and 0.060 g (0.290 mmol) of PCl_5 in hexane was stirred at room temperature for 1 h. Yellow crystals of (η^4-*exo*-1-chloro-*endo*-1-hydro-2,5-diphenylsilacyclopentadiene)tricarbonyliron were obtained: 0.077 g, 0.189 mmol, 71% yield; mp 184 °C; ^{1}H NMR ($CDCl_3$) δ 7.67–7.10 (m, 10 H, aromatic), 6.30 (t, $J^4_{\text{H-H}}$ = 1.5 Hz, 1 H, SiH endo), 6.17 (d, $J^4_{\text{H-H}}$ = 1.5 Hz, 2 H, ethylenic); IR (hexane) ν_{CO} 2049, 1992 cm^{-1}, $\nu_{\text{Si-H}}$ 2203 (vw) cm^{-1}; mass spectrum, *m/e* (assignment for ^{35}Cl, relative intensity) 408 (molecular peak, 62), 380 (M$^+$ − CO, 19), 373 (M$^+$ − Cl, 100), 352 (M$^+$ − 2CO, 11), 324 (M$^+$ − 3CO, 7), 268 (M$^+$ − Fe(CO)$_3$, 8). Anal. Calcd for $C_{19}H_{13}ClFeO_3Si$: C, 55.84; H, 3.21. Found: C, 55.90; H, 3.28.

With PBr_5. A solution of the dihydro complex (0.175 g, 0.468 mmol) and 0.220 g (0.510 mmol) of PBr_5 in THF was allowed to warm from −40 °C to room temperature and stirred for half an hour. Yellow crystals of (η^4-*exo*-1-bromo-*endo*-1-hydro-2,5-diphenylsilacyclopentadiene)tricarbonyliron were obtained: 0.173 g, 0.384 mmol, 82% yield; mp 198 °C dec; ^{1}H NMR (C_6D_6) δ

Table I. Summary of Crystal Data, Intensity Collection, and Refinement for Compound 5 (R = Me, R^1 = Ph)

formula	$C_{26}H_{20}FeO_3Si$
cryst system	monoclinic
space group	$P2_1/n$
a, Å	15.0542 (27)
b, Å	15.1040 (22)
c, Å	9.6296 (24)
β, deg	92.155 (17)
V, Å^3	2188
mol wt	464.4
Z	4
d_{calcd}, g cm^{-3}	1.410
d_{measd}, g cm^{-3}	1.38 (2)
cryst size, mm^3	0.10 × 0.40 × 0.45
cryst color	dark red
recrystn solv	$CHCl_3$–hexane, 1:4, room temp
mp, °C	172
method of data collectn	moving crystal, moving counter
radiatn (graphite monochromated)	Mo Kα
μ, cm^{-1}	7.12
2θ limits, deg	4–50
no. of unique reflectns	3372
no. of obsd reflectns	1998
final no. of variables	285
R	0.028
R_W	0.028
residual electron density, e Å^{-3}	0.36

7.60–6.80 (m, 10 H, aromatic), 6.60 (br t, 1 H, SiH endo), 5.30 (d, J^4_{H-H} = 1.5 Hz, 2 H, ethylenic); IR (hexane) ν_{CO} 2051, 1993 cm^{-1}, ν_{Si-H} 2195 (vw) cm^{-1}; mass spectrum, m/e (assignment for ^{81}Br, relative intensity) 454 (molecular peak, 5), 426 (M$^+$ – CO, 11), 398 (M$^+$ – 2CO, 17), 370 (M$^+$ – 3CO, 56), 314 (M$^+$ – Fe(CO)$_3$, 8), 233 (M$^+$ – Fe(CO)$_3$ – Br, 40). Good elemental analysis was not obtained because of the hydroscopicity of the complex.

With $Ph_3C^+BF_4^-$. A mixture of the dihydro complex (0.050 g, 0.134 mmol) and 0.045 g (0.137 mmol) of $Ph_3C^+BF_4^-$ in CH_2Cl_2 (5 mL) was stirred at room temperature for 2 h. Yellow crystals of (η^4-*exo*-1-fluoro-*endo*-1-hydro-2,5-diphenylsilacyclopentadiene)tricarbonyliron were obtained: 0.046 g, 0.117 mmol, 87% yield; mp 140 °C; ^{1}H NMR ($CDCl_3$) δ 7.60–7.10 (m, 10 H, aromatic), 5.72 (dt, J^4_{H-H} = 1.5 Hz, J_{H-F} = 86 Hz, 1 H, SiH endo), 6.13 (d, J^4_{H-H} = 1.5 Hz, 2 H, ethylenic); IR (hexane) ν_{CO} 2058, 1997 cm^{-1}, ν_{Si-H} 2193 (vw) cm^{-1}; mass spectrum, m/e (assignment, relative intensity) 392 (molecular peak, 20), 364 (M$^+$ – CO, 17), 336 (M$^+$ – 2CO, 40), 308 (M$^+$ – 3CO, 100), 252 (M$^+$ – Fe(CO)$_3$, 25). Anal. Calcd for $C_{19}H_{13}FFeO_3Si$: C, 58.18; H, 3.34. Found: C, 58.02; H, 3.66.

Crystal Structure of Dicarbonyl[phenyl((η^4-*exo*-1-methyl-2,5-diphenylsilacyclopentadien-1-yl)oxy)carbene]iron (5). Crystals of the title complex 5 (R^1 = Me; R^1 = Ph) were grown at room temperature by diffusion of hexane in a chloroform solution in a nitrogen atmosphere. Dark red plates were obtained. Preliminary Weissenberg photographs established a monoclinic unit cell with space group $P2_1/n$ (No. 14). A small plate was sealed inside a Lindeman glass capillary with the [101] direction parallel to the ϕ axis of the diffractometer.

X-ray Data Collection. Data were collected on a CAD-4 automated diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). Lattice constants (Table I) came from a least-squares refinement of 25 reflections obtained in the range 16 < 2θ < 29°. The intensities of three standard reflections were monitored after intervals of 60 min; no significant change in these intensities occurred during data collection. The structure amplitudes were obtained after the usual Lorentz and polarization reduction. Only the reflections having $\sigma(F)/F < 0.33$ were considered to be observed. No absorption corrections were made.

Structure Determination and Refinement. The direct methods (1980 version of the MULTAN program) were first tried but failed to give any useful information about the structure. A Patterson calculation revealed the coordinates of the iron atom, which were used to phase a Fourier map. This Fourier map gave the coordinates of the silicon atom, and a subsequent Fourier synthesis revealed the carbon atoms of the silole ring and the phenyl ring and the carbon and oxygen atoms of the carbene moiety. The remaining carbon and oxygen atoms were located in two succeeding difference Fourier synthesis. The atomic scattering factors were taken from ref 8. After three cycles of least-squares refinement with isotropic thermal parameters to all atoms and five cycles with anisotropic thermal parameters, the hydrogen atoms were positioned by calculation (SHELX 76 program) and five isotropic thermal parameters were attributed to these hydrogen according to the groups they were attached: methyl, silole ring, and phenyl rings (11), (41), and (61) (see Figure 1). Refinement was resumed and converged to the final R value of 0.028.

The final atomic coordinates are listed in Table II. Individual bond lengths are listed in Table III, and important bond angles are in Table IV. A list of observed and calculated structure factors (Table V) is available as supplementary material. The anisotropic thermal parameters and the hydrogen atoms coordinates are also given as supplementary material (Tables VI and VII).

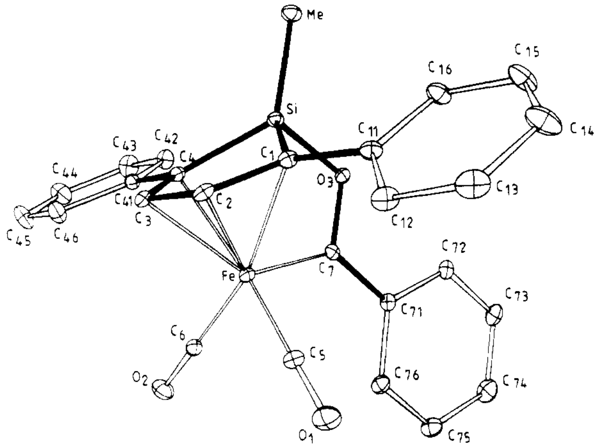

Figure 1. ORTEP drawing of the molecule of complex 5 (R = Me, R^1 = Ph) with the numbering of the atoms. Thermal ellipsoids are at the 10% probability level.

Table II. Fractional Atomic Parameters (×10^4) for Complex 5 (R = Me, R^1 = Ph)

atom	x/a	y/b	z/c
Fe	509.4 (3)	3217.9 (3)	–144.2 (5)
Si	2228.8 (6)	3048.1 (6)	–85.5 (10)
C(1)	1550 (2)	3148 (2)	1463 (3)
C(2)	1095 (2)	3975 (2)	1437 (4)
C(3)	1126 (2)	4431 (2)	159 (4)
C(4)	1600 (2)	3973 (2)	–896 (4)
C(5)	–387 (2)	2817 (2)	829 (4)
C(6)	–199 (2)	3527 (2)	–1571 (4)
C(7)	967 (2)	2141 (2)	–863 (3)
O(1)	–969 (2	2546 (2)	1417 (3)
O(2)	–631 (2)	3715 (2)	–2523 (3)
O(3)	1853 (1)	2086 (1)	–866 (2)
Me	3456 (2)	2958 (3)	–100 (4)
C(11)	1556 (2)	2539 (2)	2679 (3)
C(12)	936 (3)	2604 (3)	3735 (4)
C(13)	1000 (3)	2056 (4)	4874 (4)
C(14)	1654 (3)	1432 (4)	5000 (5)
C(15)	2255 (3)	1348 (3)	3970 (5)
C(16)	2209 (3)	1905 (3)	2818 (4)
C(41)	1659 (2)	4308 (2)	–2330 (4)
C(42)	2129 (3)	3837 (2)	–3290 (4)
C(43)	2191 (3)	4137 (3)	–4650 (4)
C(44)	1787 (3)	4905 (3)	–5075 (5)
C(45)	1312 (3)	5381 (3)	–4142 (5)
C(46)	1253 (3)	5087 (3)	–2779 (5)
C(71)	534 (2)	1329 (2)	–1364 (3)
C(72)	1023 (3)	569 (2)	–1572 (4)
C(73)	604 (3)	–204 (3)	–2001 (5)
C(74)	–297 (3)	–225 (3)	–2233 (5)
C(75)	–800 (3)	527 (3)	–2054 (4)
C(76)	–390 (2)	1301 (2)	–1620 (4)

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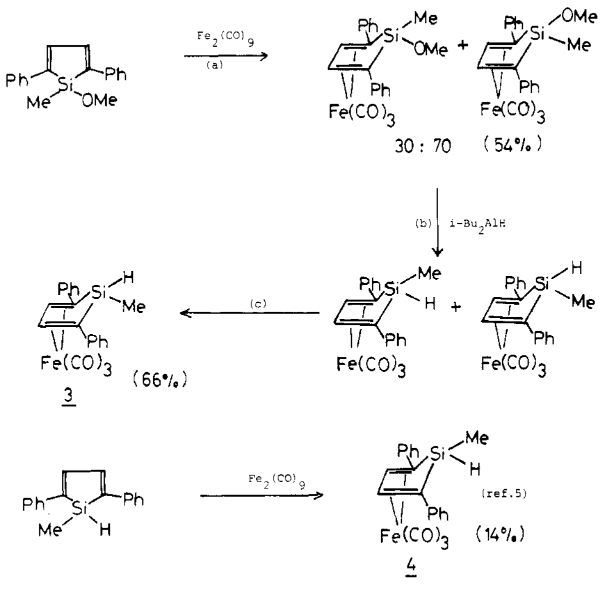
Table III. Interatomic Distances (Å) for Complex 5 (R = Me, R^1 = Ph) (Esd's in Parentheses)

Fe-C(1)	2.163 (3)	C(11)-C(12)	1.410 (5)
Fe-C(2)	2.074 (4)	C(12)-C(13)	1.374 (6)
Fe-C(3)	2.070 (3)	C(13)-C(14)	1.364 (8)
Fe-C(4)	2.147 (3)	C(14)-C(15)	1.374 (7)
Fe-C(5)	1.778 (4)	C(15)-C(16)	1.392 (6)
Fe-C(6)	1.770 (4)	C(16)-C(11)	1.375 (5)
Fe-C(7)	1.908 (3)		
		C(41)-C(42)	1.383 (5)
Si-C(1)	1.845 (3)	C(42)-C(43)	1.393 (6)
Si-C(4)	1.844 (3)	C(43)-C(44)	1.366 (6)
Si-Me	1.853 (4)	C(44)-C(45)	1.373 (7)
Si-O(3)	1.721 (2)	C(45)-C(46)	1.392 (7)
		C(46)-C(41)	1.388 (5)
C(5)-O(1)	1.136 (5)		
C(6)-O(2)	1.140 (5)	C(7) -C(71)	1.460 (4)
C(7)-O(3)	1.337 (4)	C(71)-C(72)	1.384 (5)
		C(72)-C(73)	1.382 (6)
C(1)-C(11)	1.488 (5)	C(73)-C(74)	1.368 (7)
C(1)-C (2)	1.425 (5)	C(74)-C(75)	1.379 (6)
C(2)-C (3)	1.412 (5)	C(75)-C(76)	1.379 (6)
C(3)-C (4)	1.440 (5)	C(76)-C(71)	1.403 (5)
C(4)-C(41)	1.477 (5)		

[a] Si···Fe distance = 2.660 (1) Å.

Scheme I. Synthesis of (η^4-*exo*-1-Hydro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)- and (η^4-*endo*-1-Hydro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron Complexes[a]



[a] a, $Fe_2(CO)_9$, toluene, 50–60 °C, 54%; b, i-Bu_2AlH, hexane, −30 °C, 1 h; c, fractional crystallization.

Results and Discussion

1. Synthesis and Chemical Behavior of the (η^4-*exo*-1-Hydro-1-methyl-2,5-diphenylsilacyclopentadiene)- and (*endo*-1-Hydro-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron (3 and 4, Respectively).

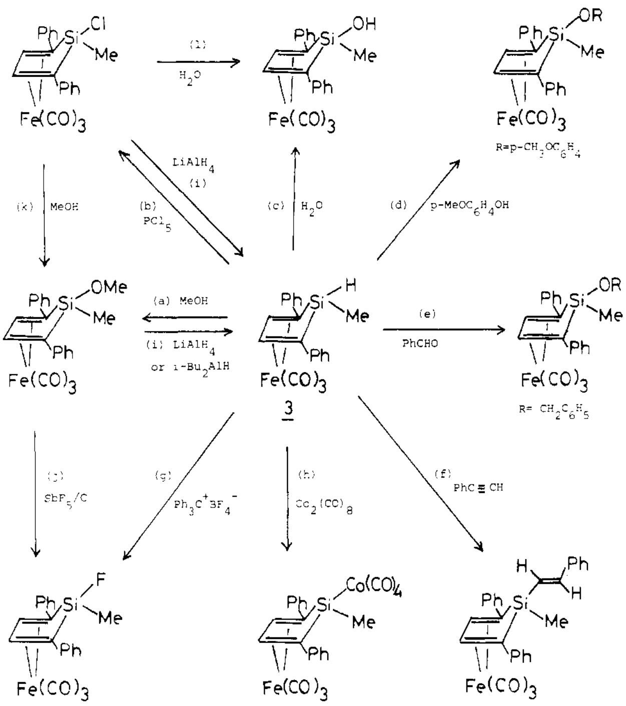
The starting complexes were prepared as summarized in Scheme I.

Treatment of 1-methoxy-1-methyl-2,5-diphenylsilacyclopentadiene with 1 equiv of $Fe_2(CO)_9$ in toluene at 50 °C gave a good yield (54%) of a 70:30 mixture of the exo-methoxy and endo-methoxy isomers. Reduction with diisobutylaluminium hydride in hexane afforded a mixture of exo-hydro and endo-hydro derivatives (70:30) from which the pure exo isomer was separated by fractional crystallization in good yield. The endo isomer was prepared as described previously.[5b]

Table IV. Important Bond Angles (deg) in Compound 5 (R = Me, R^1 = Ph)

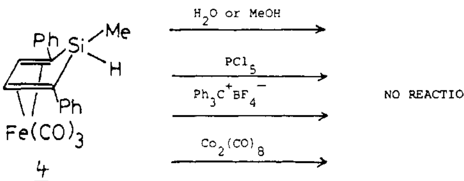
C(5)-Fe-C(6)	93.0 (2)	C(11)-C(1)-Si	126.7 (3)
C(6)-Fe-C(7)	99.0 (1)	C(11)-C(1)-C(2)	123.0 (3)
C(7)-Fe-C(5)	101.2 (2)	Si-(C1)-C(2)	109.7 (2)
		C(1)-C(2)-C(3)	114.3 (3)
Fe-C(5)-O(1)	178.0 (3)	C(2)-C(3)-C(4)	114.4 (3)
Fe-C(6)-O(2)	177.4 (3)	C(3)-C(4)-Si	109.0 (2)
		C(41)-C(4)-Si	127.4 (2)
C(1)-Si-C(4)	89.4 (2)	C(41)-C(4)-C(3)	122.9 (3)
C(1)-Si-Me	126.5 (2)		
C(4)-Si-Me	123.3 (2)	Si-O(3)-C(7)	105.1 (2)
Me-Si-O(3)	104.2 (1)	Fe-C(7)-O(3)	115.2 (2)
C(1)-Si-O(3)	103.8 (1)	Fe-C(7)-C(71)	132.2 (2)
C(4)-Si-O(3)	107.5 (1)	C(71)-C(7)-O(3)	112.5 (3)

Scheme II. Chemical Behavior of (η^4-*exo*-1-Hydro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron[a]



[a] a, MeOH, hexane, 20 °C, 15 h, 86%; b, PCl_5, CCl_4, 20 °C, 1 h, 90%; c, H_2O, acetone, 40 °C, 3 h, 90%; d, p-$MeOC_6H_4$ OH, hexane, 45 °C, 20 h, 78%; e, PhCHO, hexane, 45 °C, 34, 48%; f, $PhC\equiv CH$, hexane, 45 °C, 16 h, 35%; g, $Ph_3C^+BF_4^-$, dichloromethane, −50 °C to +20 °C, 65%; h, $Co_2(CO)_8$, hexane, 20 °C, 2 h, 76%; i, AlH_4Li, diethyl ether, 0 °C, 1 h, 65%; j, SbF_5 intercalated in graphite, hexane, 40 °C, 30 h, 32%; k, MeOH, CCl_4, 0–20 °C, 89%; l, H_2O, acetone, 20 °C, 0.5 h, 93%.

Scheme III. Chemical Behavior of (η^4-*endo*-1-Hydro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron



(η^4-2,5-Diphenylsilacyclopentadiene)tricarbonyliron complexes are good stereomodels for nucleophilic displacements at silicon. The position of the groups attached at silicon, i.e., endo or exo with respect to the $Fe(CO)_3$ moiety, can be unequivocally assigned by ^1H NMR spectroscopy,[9] and, thus, the stereochemistry of the reactions can be easily studied.

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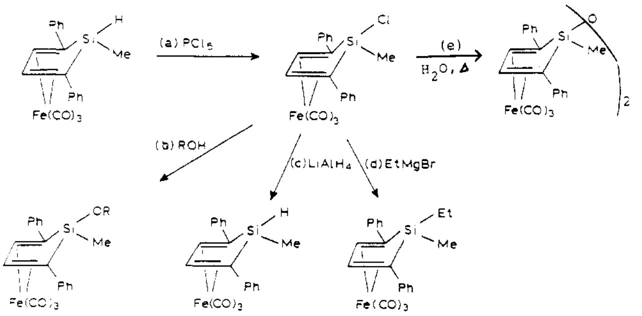
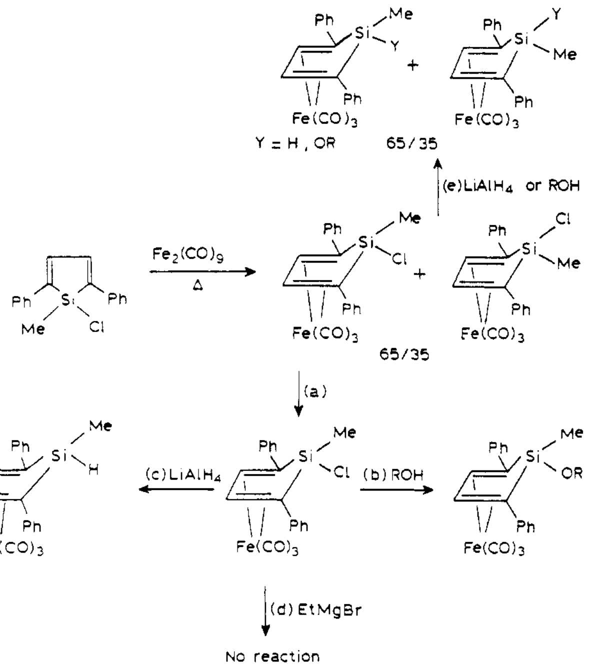
(9) Sakurai, H.; Hayashi, J. *J. Organomet. Chem.* **1973**, *63*, C7.

Scheme IV. Synthesis and Stereochemical Behavior of (η^4-*exo*-1-Chloro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron[a]



[a] Stereochemical assignments were made by ^{1}H NMR spectroscopy:[9] a, PCl_5, Et_2O, −20 °C, 1 h (90%); b, ROH, rt, 1 h, ROH = MeOH (90%), ROH = H_2O (90%); c, $LiAlH_4$, Et_2O, 0, 5 h (80%); d, EtMgBr, Et_2O, rt, 3 h (70%; e, H_2O, 50 °C, 24 h (90%).

Scheme V. Synthesis and Stereochemical Behavior of (η^4-*endo*-1-Chloro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron[a]



[a] Stereochemical assignments were made by ^{1}H NMR spectroscopy.[9] a, fractional recrystallization (40%); b, ROH, room temp., 3 h, ROH = MeOH (90%), ROH = H_2O (90%); c, $LiAlH_4$, Et_2O, 1 h (80%); d, EtMgBr, Et_2O, room temp., 30 h; e, ROH[b], AlH_4Li[c].

We studied the reactivity of **3** and **4** toward various reagents; the most significant data are summarized in Schemes II and III.

The features of the results are as follows.

(i) The (η^4-*exo*-1-hydro-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron shows enhanced reactivity whatever the nature of the reagent. **3** reacts with H_2O or MeOH in high yield at room temperature under neutral conditions without any catalyst. This great reactivity is also evidenced by its facile reaction with phenylacetylene; uncatalyzed cis addition afforded in 30% yield yellow crystals of the (*E*)-1-silylethylene derivative.

(ii) In contrast, under similar conditions, the endo isomer **4** was completely unreactive (Scheme III) toward H_2O, MeOH, $Co_2(CO)_8$, and even $Ph_3C^+BF_4^-$.

(iii) As previously observed for the (η^4-2,3,4,5-tetraphenylsilole) analogue,[3,4] the (η^4-*exo*-1-hydro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron undergoes exclusive displacement of the Si–H bond with retention of configuration at silicon (exo from exo). For instance chlorination of **3** with PCl_5 resulted in the exclusive formation of the exo-chloro isomer. Reaction of **3** with $Ph_3C^+BF_4^-$ in dichloromethane afforded exclusively the exo-fluoro,endo-methyl derivative as did the reaction with $Co_2(CO)_8$ (0.5 equiv) leading to the formation of the *exo*-silyltetracarbonylcobalt complex.

(iv) At the same time, it should be noted that other groups in the exo position are significantly activated and displaced with retention. For instance, the exo-methoxy isomer was reduced with either $LiAlH_4$ or *i*-Bu_2AlH to **3**; treatment with SbF_5 intercalated in graphite gave the exo-fluoro isomer. Hydrolysis or methanolysis of the (η^4-*exo*-1-chloro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron afforded exclusively the corresponding exo-hydroxy or exo-methoxy derivatives.

In view of such an enhanced reactivity of the exo leaving groups, the results could be consistent with the control of the reaction by steric factors.[3] Attack on the side away from the bulky $Fe(CO)_3$ is favored; consequently retention of configuration would be the expected displacement for an exo isomer as observed experimentally (Scheme II). From this point of view, an endo leaving group should be displaced with inversion.

However another interpretation is also possible. Increased angular strain at silicon is known to lead to a significant change in the stereochemistry toward retention;[10] this general trend is particularly evident with the most angle-strained silacyclobutanes. The data have been explained in terms of a change in the hybridization around the tetracoordinated silicon atom;[11] this change implies a shift in the stereochemistry toward retention. These hybridization arguments may be compared with our data relative to the structure of the (η^4-2,5-diphenylsilacyclopentadiene)tricarbonyliron complexes; these molecules were found to exhibit a great deal of angular distortion at silicon (C(1)–Si–C(2) ≈ 90°).[12] Consequently, retention of configuration should be favored for both exo and endo isomers. From this point of view, we investigated the easily available (η^4-1-chloro-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron.

2. Stereochemical Behavior of (η^4-*exo*-1-Chloro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)- and (η^4-*endo*-1-Chloro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron Complexes. a. Reactions with MeOH, H_2O, $LiAlH_4$, and EtMgBr as Nucleophiles. The synthesis and reactivity toward nucleophiles of both (η^4-*exo*-1-chloro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)- and (η^4-*endo*-1-chloro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron are listed in Schemes IV and V.

The following comments can be made.

(i) It is known that acyclic chlorosilanes react with inversion of the configuration at silicon. The results (Scheme IV) show that the exo-chloro isomer reacted always with retention of the configuration. This behavior is similar to the reduction of (η^4-*exo*-1-chloro-*endo*-1-methyl-2,3,4,5-tetraphenylsilacyclopentadiene)tricarbonyliron with $LiAlH_4$ observed by Sakurai et al.[3] Retention of the configuration was also observed previously for the highly strained chlorosilacyclobutanes.[12]

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(10) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231; *Adv. Organomet. Chem.* **1982**, *20*, 265. Corriu, R. J. P.; Guerin, C.; Moreau, J. *Top. Stereochem.* **1982**, *5*, 45 and references therein.

(11) Minot, C.; Anh, N. T. *J. Am. Chem. Soc.* **1980**, *102*, 103.

(12) Muir, K. W.; Walker, R.; Abel, E. W.; Blackmore, T.; Whitley, R. J. *J. Chem. Soc. Chem. Commun.* **1975**, 698.

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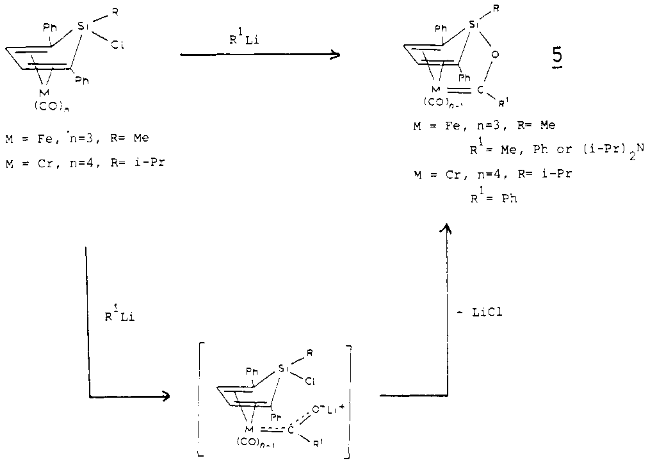
Scheme VI. Chemical Behavior of (η^4-*endo*-1-Chloro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron and of (η^4-*endo*-1-Chloro-*exo*-1-isopropyl-2,5-diphenylsilacyclopentadiene)tetracarbonylchromium toward Organolithiums



(ii) More interesting is the stereochemistry observed for the endo-chloro isomer. All the reactions also took place selectively with retention (endo from endo) (Scheme V) instead of inversion as would be expected on the basis of steric considerations.

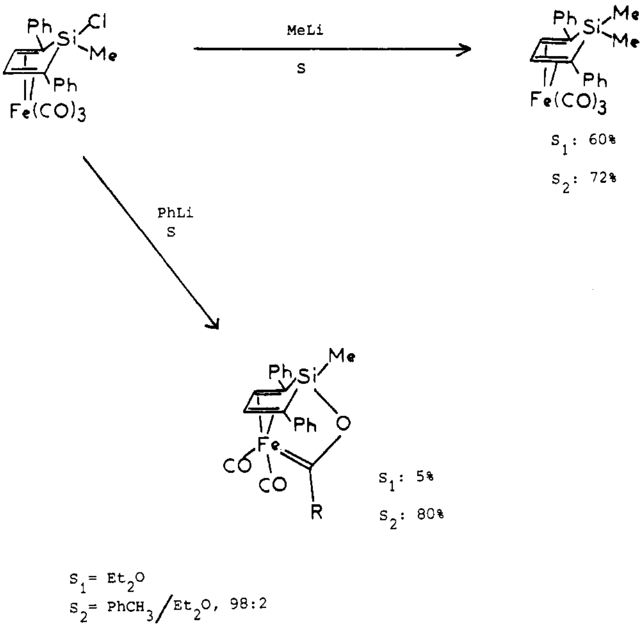
(iii) The retention of the configuration may be explained either by nucleophilic substitution giving retention or by inversion of the configuration followed by isomerization of the product. To rule out thermodynamic control of the stereochemistry in these reactions, a mixture of endo- and exo-chloro isomers (65:35) was used in the reaction with H_2O, MeOH, and $LiAlH_4$. The product, in each case, showed the same isomer ratio after complete reaction (Scheme V).

(iv) If the same stereochemical route was observed with both exo- and endo-chloro derivatives, we observed a difference in the rate of the reactions. For instance the exo-chloro compound is 35 times more reactive than its endo isomer in the methanolysis reaction at −20 °C; half-reaction times (determined by ^{1}H NMR technique with respect to the starting chlorosilane) are respectively $t_{1/2}$ = 5 min for the exo isomer and $t_{1/2}$ = 180 min for the endo isomer. The reactivity difference is even larger in the reaction with EtMgBr, in which the exo-chloro group was clearly displaced whereas no reaction was detected with the endo-chloro derivative.

The above data are clearly consistent with a control of the stereochemistry by electronic factors. As pointed out before (vide supra), angle strain at silicon (C(1)–Si–C(2) = 90°[10]) implies a change of the hybridization of the Si–X bond (X = leaving group) when the (C(1)–Si–C(2)) angle becomes smaller than the tetrahedral value:[11] the $\sigma^*_{\text{Si-X}}$ MO has large amount of s character at silicon, leading to a more dissymmetric hybrid atomic orbital at silicon with a bigger lobe between Si and X. Frontside attack is thus favored and retention, the expected stereochemical outcome for an exo or endo leaving group. The steric factors that may arise from $Fe(CO)_3$ group account for the enhanced reactivity of the exo Si–X bond but do not control the stereochemistry of the reaction.

b. Reactions with Organolithium Reagents. The reactions of organolithium reagents are more complex because of the competition between the substitution at silicon and the addition to a carbonyl leading to a Fischer-type carbene complex. The main data can be summarized as follows.

Scheme VII. Chemical Behavior of (η^4-*exo*-1-Chloro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron toward Organolithium Reagents



(i) The reaction of RLi (R = Me, Ph, or *i*-Pr_2N) with the (η^4-*endo*-1-chloro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron resulted in attack at a carbonyl ligand and the formation of the intermediate acylmetal anion; the subsequent intramolecular reaction on the endo-chloro group allowed the formation of the corresponding carbene complexes (Scheme VI). The displacement of the Si–Cl bond occurred with retention, i.e., the expected stereochemical outcome. Similar data were obtained with the (η^4-silole)tetracarbonylchromium (Scheme VI).

The crystal structure of dicarbonyl[((η^4-*exo*-1-methyl-2,5-diphenylsilacyclopentadien-1-yl)oxy)carbene]iron **5** confirmed the presence of a carbene moiety (vide infra).

(ii) In the case of the exo-chloro isomer (Scheme VII), treatment with MeLi either in diethyl ether or in a 98:2 mixture of toluene and diethyl ether as the solvent only led to the nucleophilic displacement of the Si–Cl bond with retention, as observed previously with ROH, $LiAlH_4$, and RMgX.

In contrast the reaction with PhLi in a 98:2 mixture of toluene/diethyl ether proceeded giving the corresponding carbene complex **5**, in good yield (80%). The latter derivative originates from an intramolecular displacement of the exo-chloro group with inversion; it is the only case where we observed inversion as the stereochemical outcome. The same reaction with PhLi carried out in Et_2O afforded the carbene complex in very low yield (5%) (Scheme VII). The formation of the intermediate acylmetal anion can be detected by IR spectroscopy: the subsequent intramolecular displacement of the Si–Cl bond which implied inversion at silicon, failed in diethyl ether and decomposition of the intermediate acyl anion occurred.

The above data can be easily explained on the basis of the well-known observation that the stereochemistry of nucleophilic displacements at silicon is extremely sensitive to the solvating power of the solvent toward the nucleophile.[10] It suggests in our case that the solvatation of the intermediate acyl anion modifies the electronic character of the nucleophile and hence the stereochemical course of the reaction. The more coordinating solvent (diethyl ether) polarized the oxygen–metal bond and increased the

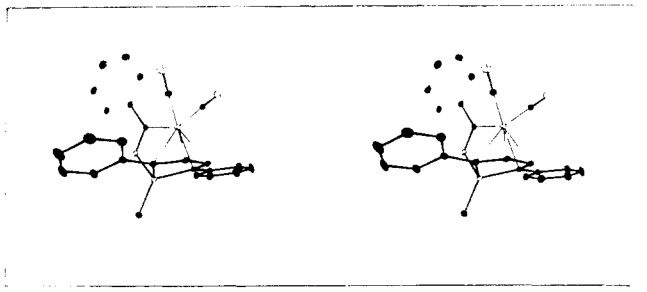


Figure 2. Stereoview of the molecule of complex **5** (R = Me, R^1 = Ph).

hardness of the nucleophile, orienting the stereochemistry toward retention as observed previously;[12] thus the displacement of the exo Si–Cl bond was made impossible. In contrast, in toluene, the acylmetal anion behaved as a softer nucleophile; the inversion was favored and the displacement of the exo-chloro leaving group occurred in good yield.

3. Crystallographic Study of Dicarbonyl[phenyl((*η*⁴-*exo*-1-methyl-2,5-diphenylsilacyclopentadien-1-yl)oxy)carbene]iron (5). The crystal structures of **5** (R = Me, R^1 = Ph) have been determined by X-ray crystallography; ORTEP views for this complex are shown in Figures 1 and 2 and interatomic distances and bond angles in Tables III and IV.

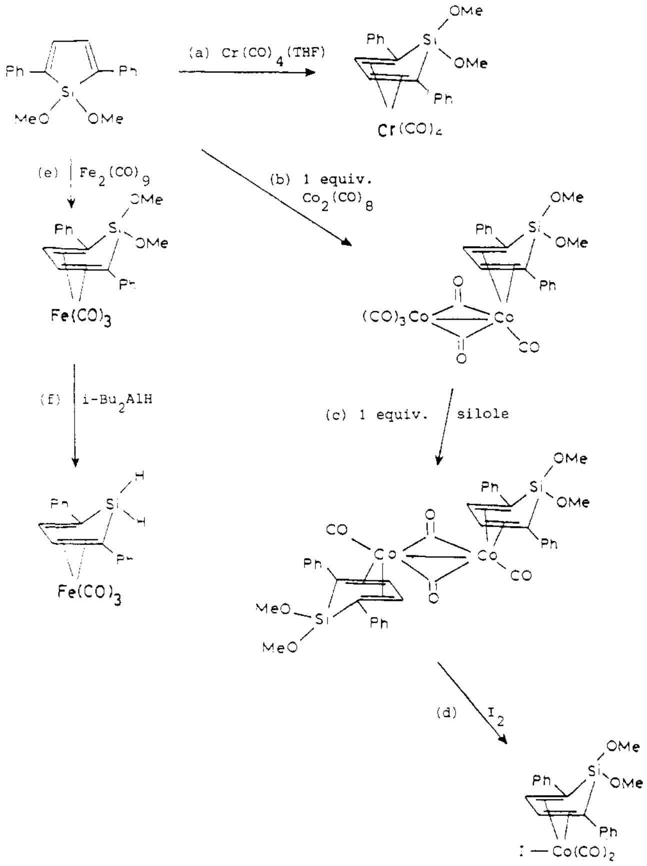
Interestingly, the X-ray study confirms the presence of a carbene moiety. The sum of the angles around the carbene atom C(7) shows that the three bonds around this atom lie in a plane. The distance between iron and the carbenic carbon (Fe—C(7) = 1.908 Å) is significantly shorter than the distance found by Huttner et al.[14] (Fe=C = 2.008 Å) in the case of (1,3-dimethylimidazolinylidenyl)tetracarbonyliron. The repulsion between the Fe and Si atoms (d = 2.600 (1) Å) causes the Si–O(3) bond length (1.721 (2) Å) to be slightly longer than the Si–O bonds in $Ph_3SiOSiPh_3$ (1.616 (1) Å)[15a] and $Me_3SiOSiMe_3$ (1.66 (4) Å).[15b] The C–O distance in the carbene moiety (1.337 (4) Å) is also slightly longer than in other carbenic compounds, viz., $(Ph_3Ge)(CO)_3Co(OEt)Et$ (1.29 (1) Å)[16a] and $MePh(1\text{-}Np)Ge(CO)_4Mn\{C(OEt)Et\}$ (1.31 (3) Å),[16b] but is similar to that (1.33 Å) observed for $(CO)_5Cr\{C(OMe)Ph\}$.[17]

The linkage of the silicon atom down to the iron atom through atoms O(3) and C(7) results in a silole ring closer to planarity (the dihedral angle between the planar butadiene unit and the plane C(1)SiC(4) is 16.6°) than those in other coordinated siloles complexes (20–37°).[12,18]

4. Synthesis and Reactivity of Silicon-Disubstituted (*η*⁴-Silole) Complexes. We discussed above the lability of the exo substituent and the displacement of both exo and endo leaving groups in the case of silicon-monosubstituted (*η*⁴-2,5-diphenylsilacyclopentadiene)tricarbonyliron complexes. The availability of new silicon-disubstituted *η*⁴-silole derivatives allowed us to make a direct comparison of the relative reactivity of exo and endo substituents both bonded to the same silicon atom.

Treatment of 1,1-dimethoxy-2,5-diphenylsilacyclopentadiene with 1 equiv of $Fe_2(CO)_9$ in toluene at 50 °C gave a good yield (60%) of (*η*⁴-1,1-dimethoxy-2,5-diphenylsilacyclopentadiene)tricarbonyliron (Scheme VIII). The reduction with $(i\text{-}Bu)_2AlH$ provided the stable dihydro derivative. The reaction with SbF_5 intercalated in graphite afforded the corresponding (*η*⁴-difluoro-2,5-diphenylsilacyclopentadiene)tricarbonyliron.

Scheme VIII. Synthesis of Silicon-Disubstituted (*η*⁴-Silole) Complexes[a]



[a] (a) hexane, 50 °C, 12 h, 55%; (b) hexane, room temp., 7 h, 77%; (c) hexane, 40 °C, 4 h, 82%; (d) CCl_4, room temp., 1 h, 80%; (e) toluene, 50 °C, 15 h, 60%; (f) hexane, room temp., 1 h, 70%.

The 1,1-dimethoxy-2,5-diphenylsilacyclopentadiene reacted with $Co_2(CO)_8$ to give a monosubstituted *η*⁴-silacyclopentadiene complex (Scheme VIII). As observed previously,[5] the latter complex reacted with an excess of silole to give the corresponding disubstituted derivative. Treatment with iodine in carbon tetrachloride[19] gave iodo(*η*⁴-1,1-dimethoxy-2,5-diphenylsilacyclopentadiene)dicarbonylcobalt. Finally, reaction of the 1,1-dimethoxy-2,5-diphenylsilacyclopentadiene with $Cr(Co)_5(THF)$ or $Cr(CO)_4(COD)$ proceeded similarly to give the (*η*⁴-silole)-$Cr(CO)_4$ complex.

The data observed in the case of the (*η*⁴-1,1-dihydro-2,5-diphenylsilacyclopentadiene)tricarbonyliron complex (**6**) are summarized in Scheme IX.

Whatever the nature of the reagent (PX_5, ROH, or BF_4^-), the reaction led selectively to the substitution of the exo groups in good yields (70–100%); the position of the hydrogen atom bonded to silicon, i.e., endo or exo with respect to the $Fe(CO)_3$ moiety, can be unequivocally assigned by ^1H NMR spectroscopy.[9] Cleavage of the Si–H bond is well-known to occur with retention at silicon.[12] Retention was also demonstrated in the case of the (*η*⁴-

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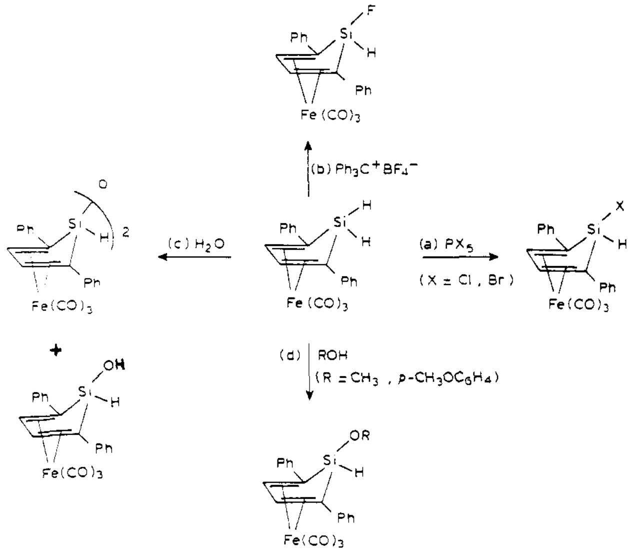
Scheme IX. Chemical Behavior of the (η^4-1,1-Dihydro-2,5-diphenylsilacyclopentadiene)tricarbonyliron[a]



[a] (a) X = Cl, CCl_4, room temp., 1 h, 71%; X = Br, THF, −40 °C to room temp., 0.5 h, 82%; (b) CH_2Cl_2, room temp., 2 h, 82%; (c) acetone, room temp., 0.5 h, 67% siloxane, 20% silanol; acetone, 50 °C, 2 h, 89% siloxane; (d) R = CH_3, hexane, room temp., 3 h, 93%; R = p-$CH_3OC_6H_4$, hexane, 40 °C, 3 h, 73%.

exo-1-hydro-*endo*-1-methyl-2,3,4,5-tetraphenylsilacyclopentadiene)-[2] and (η^4-*exo*-1-hydro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron (vide supra). These results show clearly that whatever the group in endo position (Me or H) there is enhanced reactivity of the exo SiH bond and the cleavage occurs always with retention of the configuration at silicon.

Conclusion

In this report, we have described the synthesis and the reactivity of several new functional (η^4-2,5-diphenylsilacyclopentadiene)metal complexes.

In terms of substitution and reaction chemistry at coordinated siloles, the data show enhanced reactivity of the exo leaving group (H, MeO, or Cl), as observed previously in the tetraphenyl series. Moreover both exo- and endo-chloro leaving groups are displaced by nucleophiles (MeOH, $LiAlH_4$, RMgX) with retention of configuration at silicon (exo from exo and endo from endo). These observations suggest that the stereochemistry is only controlled by electronic factors. The steric factors due to the metal center account for the enhanced reactivity of the exo Si–X bond. Depending on the nature of the reagent and the solvent, organolithiums led to competitive reactions at silicon or at a carbonyl ligand, leading in the latter case to the formation of new Fischer-type carbene complexes.

Finally, the above observations allowed us to have access to a new class of silicon hetero-disubstituted (η^4-silole)metal complexes.

With our recent development of the generation of the silacyclopentadienyl anion[20] and the formation of functional complexed siloles described in this report, we are actively pursuing the possible generation of the η^5-silole ligand and the question of charge delocalization in such complexes.

Acknowledgment. F.H.C. thanks Prof. J. Lapasset, Groupe de Dynamique des Phases Condensées, LA au CNRS No. 223, U.S.T.L., for the use of their Weissenburg and precession cameras.

Registry No. 3, 112296-18-1; 4, 100815-46-1; 5 (M = Fe, n = 3, R = Me, R^1 = Ph), 117687-89-5; 5 (M = Fe, n = 3, R = R^1 = Me), 117687-90-8; 5 (M = Fe, n = 3, R = Me, R^1 = (i-Pr)$_2$N), 117687-91-9; 5 (M = Cr, n = 4, R = i-Pr, R^1 = Ph), 117687-92-0; i-PrSi(OMe)$_3$, 14346-37-3; PCl_5, 10026-13-8; (COD)Cr(CO)$_4$, 12301-34-7; p-MeOCClH$_4$-OH, 150-76-5; PhCHO, 100-52-7; $Fe_2(CO)_9$, 15321-51-4; $Ph_3C^+BF_4^-$, 341-02-6; $Co_2(CO)_8$, 10210-68-1; SbF_5, 7783-70-2; EtMgBr, 925-90-6; PBr_5, 7789-69-7; Cr(CO)$_5$·THF, 15038-41-2; (η^4-*exo*-1-methoxy-*endo*-1-methyl-2,5-diphenylcyclopentadiene)tricarbonyl iron, 112218-88-9; (η^4-*exo*-1-methyl-*endo*-1-methoxy-2,5-diphenylcyclopentadiene)tricarbonyl iron, 112295-32-6; (η^4-*exo*-1-isopropyl-*endo*-1-chloro-2,5-diphenylsilacyclopentadiene)tetracarbonylchromium, 117687-83-9; (η-*exo*-1-chloro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 112296-19-2; (η^4-*exo*-1-hydroxy-*endo*-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 112296-20-5; (η^4-*exo*-1-(p-methoxyphenoxy)-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 117687-84-0; (η^4-*exo*-1-(benzyloxy)-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 117687-85-1; (η^4-*exo*-1-styryl-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 117687-86-2; (η^4-*exo*-1-fluro-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 117687-87-3; (η^4-*exo*-1-(tetracarbonylcobaltio-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 117709-58-7; (η^4-*exo*-1-ethyl-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 112295-31-5; (η^4-*exo*-1-methyl-*endo*-1-chloro-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 112218-89-0; (η^4-1,1-dimethoxy-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 111825-64-0; (η^4-1,1-dihydro-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 111801-35-5; (η^4-1,1-difluoro-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 117687-95-3; (η^4-*exo*-1-methoxy-*endo*-1-hydro-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 111801-32-2; (η^4-*exo*-1-chloro-*endo*-1-hydro-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 111801-29-7; (η^4-*exo*-1-bromo-*endo*-1-hydro-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 111801-30-0; (η^4-*exo*-1-fluoro-*endo*-1-hydro-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 111801-28-6; (η^4-*exo*-1-methyl-*endo*-1-hydroxy-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 112218-90-3; oxybis[(η^4-*endo*-1-methyl-2,5-diphenylsilacyclopentadien-1-yl)tricarbonyl iron], 117687-88-4; (η^4-1,1-dimethoxy-2,5-diphenylsilacyclopentadiene)dicarbonyl chromium, 111825-65-1; (η^4-1,1-dimethoxy-2,5-diphenylsilacyclopentadiene)dicarbonyl cobalt], 117687-93-1; bis[(η^4-1,1-dimethoxy-2,5-diphenylsiliacyclopentadiene)dicarbonylcobalt], 111801-38-8; iodo(η^4-1,1-dimethoxy-2,5-diphenylsilacyclopentadiene)dicarbonyl cobalt, 111801-39-9; oxybis[(η^4-*endo*-1-hydro-2,5-diphenylsilacyclopentadien-1-yl)tricarbonyliron], 111801-27-5; (η^4-1,1-dimethyl-2,5-diphenylsilacyclopentadiene)tricarbonyl iron, 49539-48-2; 1-isopropyl-1-methoxy-2,5-diphenylsilacyclopentadiene, 117687-96-4; 1-isopropyl-1-hydro-2,5-diphenylsilacyclopentadiene, 117687-97-5; 1-isopropyl-1-chloro-2,5-diphenylsilacyclopentadiene, 117687-98-6; 1-methoxy-1-methyl-2,5-diphenylsilacyclopentadiene, 100840-04-8; 1-chloro-1-methyl-2,5-diphenylsilacyclopentadiene, 100840-06-0; 1,1-dimethoxy-2,5-diphenylsilacyclopentadiene, 100840-05-9; phenylacetylene, 536-74-3; 1,4-dilithio-1,4-diphenylbutadiene, 7641-46-5.

Supplementary Material Available: Listings of anisotropic thermal parameters and hydrogen atoms coordinates (Tables VI and VII, respectively) (2 pages); a listing of structure factor amplitudes (Table V) (9 pages). Ordering information is given on any current masthead page.

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