was washed with the precooled (−30 °C) solvents *n*-hexane (4 × 10 mL) and ether (4 × 5 mL). The residue was digested at −20 °C with 12 mL of methanol. Most of the red liquid phase was inversely filtered off at −50 °C. The remaining slurry was redissolved in 15 mL of acetone, inversely filtered, and cooled on dry ice, giving at first 60 mg and after concentrating the mother liquor to half its volume, another 360 mg of bright yellow, microcrystalline **4a**. Isolated yield: 420 mg (31%) of **4a**. For spectroscopic properties cf. Table I.

To NMR monitor the formation of **4a** and **5a**, the reaction was carried out in a 10-mm NMR tube as follows. To a THF/THF-d_6 (2.5 mL) solution of 0.48 g (1.1 mmol) of **1a** at −78 °C was added neat DMAD (0.17 mL, 1.38 mmol) with stirring and then at −50 °C was added 0.13 mL (1.1 mmol) of $P(OMe)_3$. The mixture was left standing for 4 days at −30 °C. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra indicated a virtually complete transformation into **4a**. The solution was further kept at 0 °C for 6 days, giving, after evaporation of the solvent and drying in high vacuum, 0.76 g (102%) of crude **5a**. The residue was redissolved in 8 mL of THF and cooled to −30 °C, giving a pale yellow precipitate and a dark brown mother liquor. At 0 °C the precipitate was washed with 1 mL of THF and dryed in vacuo. Spectroscopically, the sample was found pure enough to be combined with **5a** that had been prepared analogously from spectroscopically pure microcrystalline **4a** that had been prepared as described above. Anal. Calcd for $C_{28}H_{33}FeN_2O_{11}P$: C, 50.93; H, 5.04; N, 4.24. Found: C, 50.44; H, 5.18; N, 4.06. For spectroscopic properties of **5a** cf. Table II.

Crystal Structure of 5a. Single crystals suitable for X-ray diffraction were obtained by slowly cooling an acetone solution of **5a**. A pale yellow crystal of ca. $0.3 \times 0.2 \times 0.5$ mm^3 was chosen, and 10 022 intensities ($\theta \le 30°$, h −16 to 16, k −19 to 19, l 0 to 16) were measured on a Nonius CAD4 diffractometer employing graphite-monochromated Mo Kα radiation. A total 4160 intensities were below the $2.5\sigma(I)$ level and were treated as unobserved. Pertinent experimental and crystallographic details are collected in Tables IV and V. Fe, P, and one ring were found by means of direct methods (SIMPEL[14]); subsequent Fourier syntheses yielded the rest of the structure including one molecule of acetone. Refinement proceeded by means of block-diagonal least-squares calculations. An empirical absorption correction (DIFABS[15]) was applied. The positions of the H atoms were indicated in a ΔF synthesis and included in the refinement with isotropic temperature parameters. Continued refinement converged to an R value of 0.048 ($R_w = 0.075$) for the 5862 observed reflections. A weighting scheme $w = 1/(5.8 + F_o + 0.019F_o^2)$ was applied, and the anomalous scattering of Fe was taken into account. The further programs used were from XRAY 76.[16]

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Registry No. **1a**, 65016-01-5; **3a**, 122190-26-5; **4a**, 122190-27-6; **5a**, 122190-29-8; N(*p*-anisyl)C(O)C(COOMe)=C(COOMe)C(Me)C(Me)=N(*p*-anisyl), 122190-25-4.

Supplementary Material Available: Tables of fractional coordinates of the hydrogen atoms and isotropic thermal parameters and anisotropic thermal parameters of the non-hydrogen atoms and complete lists of bond distances and angles of the non-hydrogen atoms (4 pages); a listing of structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of Group 14 Metalloles. 5.[1] Use of Dicarbonyl(η^5-cyclopentadienyl)(1-methyl-2,5-diphenylsilacyclopentadien-1-yl)iron as a Four-Electron Ligand: Chemical Properties and Dynamic Stereochemistry of the Complexes

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Chlorine is displaced in 1-chloro-1-methyl-2,5-diphenylsilole by dicarbonyl(η^5-cyclopentadienyl)ferrate(I) to give a silole with a Si–Fe σ bond. Attempts to displace the carbonyl ligands to give the corresponding silaferrocene were unsuccessful. This new silole behaves as an efficient η^4-ligand with transition metals, giving a new series of complexes which present an interesting reactivity. Thus the Si–Fe bond can be cleaved without decoordination of the η^4-ligand, and the Co–Co bond in $(CO)_6(\eta^4\text{-silole})Co_2$ can be cleaved without cleavage of the Fe–Si bond. These η^4-complexes are fluxional as observed for other series. The interconversion, in solution, of the two enantiomers cis-Δ_{uu} and cis-Λ_{uu} has an activation energy of ~35 kJ mol^{-1} and a coalescence temperature of ~200 K. However, contrary to other cases, the presence of diastereoisomers cannot be detected.

Introduction

In the rapidly developing field of group 14 metalloles,[2,3] numerous papers have dealt with the search for the η^5-metallacyclopentadienyl species. The similarities between cyclopentadienes and siloles make attractive the stabilization of the latter by coordination to a transition metal. Its observation in mass spectrometry has been reported[4,5] without further evidence.

Functionalization at silicon could be approach to η^5-

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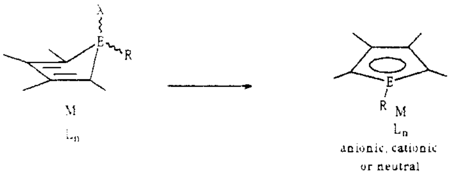
species, by participation of the group 14 metal in the coordination sphere of the transition metal (eq 1).



(1)

E = Si, Ge M = transition metal, R = hydrocarbon radical, X = functional group

Complexes with functional silicon atoms have been obtained both by cleavage of the exo substituent and by complexation of functional metalloles.[6–15] Unfortunately, neither of these procedures led to the expected η^5-metallacyclopentadienyl complex. Also, a μ-germylene complex was formed from the reaction of a germole with diiron nonacarbonyl instead of the expected dicarbonyl(η^5-germolyl)iron dimer.[16] These facts contrast with the development of the chemistry of the η^5-phospholyl complexes.[17]

In this report we describe the use of a silole with a silicon–iron σ bond as a η^4-ligand and the properties of the new complexes.

Experimental Section

All reactions were carried out under nitrogen using a vacuum line and Schlenk tubes. Solvents were dried and distilled before use. The following starting materials were prepared by literature methods: 1-chloro-1-methyl-2,5-diphenylsilole,[11] $Cr(CO)_4(COD)$[15] (COD = 1,5-cyclooctadiene), $Mo(CO)_4(COD)$,[18] $W(CO)_4(COD)$,[19] $Fe_2(CO)_9$,[20] and $Ni(COD)_2$.[21] The following starting materials were commercially available: $Co_2(CO)_8$, $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$, $Ru_3(CO)_{12}$, and Ph_3SnCl.

Photochemical reactions were performed with a 100- or a 450-W medium-pressure Hanovia mercury lamp in a quartz vessel. Melting points were taken in an oil-circulating apparatus in vacuo. IR spectra were recorded with a Perkin-Elmer 298 spectrophotometer, NMR spectra with a Varian EM 360 or a Bruker WM 360 WB spectrometer (chemical shifts, δ, are relative to Me_4Si), and mass spectra on a JEOL JMS-DX 300 spectrometer.

Dicarbonyl(η^5-cyclopentadienyl)(1-methyl-2,5-diphenylsilacyclopentadien-1-yl)iron (1). A solution of $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$,[22] prepared from 2 g of $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ (5.65 mmol) and 10 mL of 1% sodium amalgam in THF (30 mL), was added dropwise to a stirred solution of 1-chloro-1-methyl-2,5-diphenylsilole, 3 g (10.7 mmol) in 30 mL of THF at −78 °C. After the addition was complete, the solution was allowed to warm to room temperature and was stirred for 12 h. The solvent was evaporated in vacuo, and the residue was dissolved in the minimum amount of toluene. Column chromatography on acidic alumina (toluene/hexane, 1/1) gave a yellow band that was collected, concentrated to ~20 mL, and cooled at −78 °C to precipitate the product. Recrystallization from CH_2Cl_2/hexane at −20 °C afforded 3.75 g of yellow needles of 1 (yield 83%): mp 121–122 °C; ^1H NMR (CCl_4) δ 7.50–6.80 (m, 12 H, aromatic and olefinic), 4.31 (s, 5 H, C_5H_5), 0.90 (s, 3 H, CH_3); IR (cyclohexane) ν_{CO} 2015 (s), 1955 (s) cm^{-1}; mass spectrum, *m/e* (assignment) 424 (molecular peak for ^{56}Fe), 368 (M^+ − 2CO). Anal. Calcd for $C_{24}H_{20}O_2FeSi$: C, 67.95; H, 4.72. Found: C, 67.86; H, 4.76.

Carbonyl(η^5-cyclopentadienyl)(1-methyl-2,5-diphenylsilacyclopentadien-1-yl)(triphenylphosphine)iron (2). A solution of 1 (700 mg, 1.65 mmol) and triphenylphosphine (432 mg, 1.65 mmol) in 300 mL of hexane was irradiated for 2.5 h (100-W lamp). The reaction was monitored by IR (disappearance of the ν_{CO} bands due to 1). The solvent was evaporated in vacuo, the residue was chromatographed on a silica gel column (toluene/hexane, 9/1), and the orange band was collected. The solvent was evaporated in vacuo, and the residue was crystallized from toluene/hexane (1/3) at −20 °C to give 350 mg of orange crystals of 2 (yield 32%): mp 193–195 °C; ^1H NMR ($CDCl_3$) δ 7.27 (m, 27 H, aromatic and olefinic), 3.87 (d, $J_{H,P}$ = 1.8 Hz, 5 H, C_5H_5), 0.60 (s, 3 H, CH_3); IR (toluene) ν_{CO} 1909 (s) cm^{-1}; mass spectrum, *m/e* (assignment) 658 (molecular peak for ^{56}Fe), 630 (M^+ − CO), 368 (M^+ − CO − PPh_3). Anal. Calcd for $C_{41}H_{35}FeOPSi$: C, 74.77; H, 5.32. Found: C, 74.83; H, 5.32.

UV Irradiation of 1 in Methanol. A solution of 1 (200 mg, 0.472 mmol) in 60 mL of methanol was irradiated for 8 h (100-W lamp) to given an orange solution. The reaction was monitored by IR. The ν_{CO} bands due to 1 disappeared, and a new band at 1939 cm^{-1} (in addition to those of $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$) was observed. Fractional crystallization from hexane at −20 °C afforded the iron dimer (25 mg, yield 31%) and 1-methoxy-1-methyl-2,5-diphenylsilole (20 mg, yield 15%) which was identified by comparison to an authentic sample.[11] The new carbonyl-containing complex decomposed upon attempted isolation.

UV Irradiation of 1 in Hexane. The experimental conditions were the same as above except using hexane, and the solution was irradiated for 16 h. After this time, the ν_{CO} bands due to 1 had disappeared; the solvent was evaporated in vacuo. Column chromatography of the residue on acidic alumina gave 1,4-diphenylbuta-1,3-diene (hexane) (30 mg, yield 31%, identified by comparison with an authentic sample[23]) and $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ (toluene) (30 mg, yield 37%). An orange compound, eluted with toluene/hexane (9/1), decomposed upon attempted purification (ν_{CO} 1938 cm^{-1}).

***cis*-Dicarbonylbis[η^4-*exo*-1-{dicarbonyl(η^5-cyclopentadienyl)ferrio}-*endo*-1-methyl-2,5-diphenylsilole]molybdenum (3).** A solution of 1.05 g of 1 (2.5 mmol) and 400 mg of $Mo(CO)_4(COD)$ (1.26 mmol) in 15 mL of octane was refluxed for 1.5 h. The solvent was evaporated in vacuo, and the residue was extracted with four 20-mL portions of hexane. Hexane was evaporated in vacuo, and the residue was chromatographed on a silica gel column (toluene/hexane, 9/1) to afford unreacted 1, a red band, and $[Fe(CO)_2(\eta^5\text{-}C_5H_5]$. The red solution was left at −20 °C to afford 295 mg of 3 (yield 20%), orange crystals. Complex 3 crystallizes with two molecules of toluene (^1H NMR and elemental analysis): mp 223–226 °C; ^1H NMR ($CDCl_3$) δ 7.27–7.17 (m, 30 H, aromatic), 5.10 (s, 4 H, olefinic), 4.24 (s, 10 H, C_5H_5), 2.35 (s, 6 H, toluene), 1.29 (s, 6 H, *endo*-CH_3); IR (toluene) ν_{CO} 1988 (s), 1973 (m), 1933 (s) cm^{-1}. Anal. Calcd for $C_{64}H_{56}Fe_2MoO_6Si_2$: C, 64.85; H, 4.73. Found: C, 64.63; H, 4.68.

***cis*-Dicarbonylbis[η^4-*exo*-1-{dicarbonyl(η^5-cyclopentadienyl)ferrio}-*endo*-1-methyl-2,5-diphenylsilole]tungsten (4).** Complex 1 (1.05 g, 2.5 mmol) and $W(CO)_4(COD)$ (485 mg, 1.2 mmol) in 15 mL of octane were refluxed for 8 h. A similar work up as above afforded 732 mg of orange crystals of 4 (yield 48%). Complex 4 crystallizes also with two molecules of toluene: mp 260–262 °C; ^1H NMR ($CDCl_3$) δ 7.27–7.17 (m, 30 H, aromatic),

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4.90 (s, 4 H, olefinic), 4.21 (s, 10 H, C_5H_5), 2.35 (s, 6 H, toluene), 1.30 (s, 6 H, *endo*-CH_3); IR (toluene) ν_{CO} 1988 (s), 1976 (m), 1932 (s) cm^{-1}. Anal. Calcd for $C_{64}H_{56}Fe_2O_6Si_2W$: C, 60.38; H, 4.44. Found: C, 59.86; H, 4.18.

Dicarbonyl(η^5-cyclopentadienyl)[1-methyl-2-(tricarbonylphenylchromium)-5-phenylsilacyclopentadien-1-yl]iron (5). A solution of 500 mg of 1 (1.18 mmol) and 320 mg of $Cr(CO)_4(COD)$ (1.18 mmol) in 20 mL of octane was refluxed for 1.5 h. The solvent was evaporated in vacuo, and the residue was chromatographed on a silica gel column (hexane/toluene, 7/3) to give a yellow band of unreacted 1 and an orange one. The last fraction was left at −20 °C to give 130 mg of orange crystals of 5 (yield 20%): mp 170–172 °C; ^1H NMR ($CDCl_3$) δ 7.34 (m, 5 H, aromatic), 7.17 (s, 2 H, olefinic), 5.48 (s, 5 H, η^6-C_6H_5), 4.47 (s, 5 H, C_5H_5), 0.82 (s, 3 H, CH_3); IR (toluene) ν_{CO} 1995 (m), 1970 (s), 1952 (m), 1900 (m), 1895 (m) cm^{-1}; mass spectrum, *m/e* (assignment) 560 (molecular peak for ^{52}Cr and ^{56}Fe), 504 (M^+ − 2CO), 476 (M^+ − 3CO), 420 (M^+ − 5CO). Anal. Calcd for $C_{27}H_{20}CrFeO_5Si$: C, 57.86; H, 3.57. Found: C, 58.70; H, 3.84 (a more satisfactory result could not be obtained).

Tricarbonyl[η^4-*exo*-1-{dicarbonyl(η^5-cyclopentadienyl)-ferrio}-*endo*-1-methyl-2,5-diphenylsilole]iron (6). A mixture of 310 mg of $Fe_2(CO)_9$ (0.852 mmol) and 227 mg of 1 (0.535 mmol) in 30 mL of benzene was heated at 65 °C for 16 h. The solvent was evaporated in vacuo; the residue was extracted with hexane and filtered through a fritted funnel (G4). The red solution was left at −78 °C to afford orange-red crystals of 6 (118 mg, yield 39%); mp 149.5–151 °C; ^1H NMR (C_6D_6) δ 7.28 (m, 10 H, aromatic), 5.76 (s, 2 H, olefinic), 3.93 (s, 5 H, C_5H_5), 1.53 (s, 3 H, *endo*-CH_3); IR (hexane) ν_{CO} 2040 (s), 2000 (s), 1988 (s), 1975 (s), 1945 (s) cm^{-1}; mass spectrum, *m/e* (assignment) 564 (molecular peak for ^{56}Fe), 536 (M^+ − CO), 508 (M^+ − 2CO), 480 (M^+ − 3CO). Anal. Calcd for $C_{27}H_{20}Fe_2O_5Si$: C, 57.48; H, 3.57. Found: C, 57.45; H, 3.56.

Tricarbonyl[η^4-*exo*-1-{dicarbonyl(η^5-cyclopentadienyl)-ferrio}-*endo*-1-methyl-2,5-diphenylsilole]ruthenium (7). A mixture of 213 mg of $Ru_3(CO)_{12}$ (0.333 mmol) and 424 mg of 1 (1 mmol) in 30 mL of toluene was refluxed for 3 h. Similar workup as above followed by crystallization at −78 °C afforded 180 mg of golden crystals of 7 (yield 29%): mp 103–105 °C; ^1H NMR (C_6D_6) δ 7.17 (m, 10 H, aromatic), 5.77 (s, 2 H, olefinic), 3.93 (s, 5 H, C_5H_5), 1.47 (s, 3 H, *endo*-CH_3); IR (toluene) ν_{CO} 2058 (s), 1989 (s, br), 1933 (s) cm^{-1}. Anal. Calcd for $C_{27}H_{20}FeO_5RuSi$: C, 53.20; H, 3.28. Found: C, 53.26; H, 3.61.

Hexacarbonyl[η^4-*exo*-1-{dicarbonyl(η^5-cyclopentadienyl)ferrio}-*endo*-1-methyl-2,5-diphenylsilole]dicobalt (8). A solution of 544 mg of 1 (1.28 mmol) and 285 mg of $Co_2(CO)_8$ (0.835 mmol) in 25 mL of hexane was stirred for 12 h at room temperature. The solution was cooled at −20 °C, and the brown precipitate was filtered and chromatographed on an acid alumina column (hexane/CH_2Cl_2, 1/1). The orange band was collected, the solvent was evaporated in vacuo, and the orange residue was crystallized four times from toluene/hexane at −20 °C to give 90 mg of orange crystals of 8 (yield 15%): mp 168 °C dec; ^1H NMR (CD_2Cl_2) δ 7.30 (m, 10 H, aromatic), 5.87 (s, 2 H, olefinic), 4.35 (s, 5 H, C_5H_5), 1.30 (s, 3 H, *endo*-CH_3); IR (CH_2Cl_2) ν_{CO} 2070 (s), 1990 (s), 1935 (w), 1825 (m) cm^{-1}. Anal. Calcd for $C_{30}H_{20}Co_2FeO_8Si$: C, 50.78; H, 2.82. Found: C, 51.17; H, 2.98.

***cis*-Dicarbonylbis(η^4-*exo*-1-methoxy-*endo*-1-methyl-2,5-diphenylsilole)tungsten (10).** To a solution of 500 mg of 4 (0.393 mmol) in 30 mL of toluene was added dropwise a solution of 200 mg of iodine (0.786 mmol) in 10 mL of toluene at −78 °C. The reaction mixture was allowed to warm to −50 °C, 3 mL of methanol (excess) in 10 mL of toluene was added, and the mixture was stirred for 12 h at room temperature. The solvent was evaporated in vacuo, and the residue was chromatographed on a silica gel column to give a black band (toluene/hexane, 9/1) and a yellow one (CH_2Cl_2).

The black solution was evaporated in vacuo to give 160 mg of $Fe(CO)_2(\eta^5$-$C_5H_5)I$ (yield 78%) which was identified by comparison with an authentic sample (Strem).

The second fraction was evaporated in vacuo, and the residue was crystallized from toluene/hexane (1/5) at −78 °C to give 150 mg of orange-yellow crystals of 10 (yield 47%): mp 201–202 °C; ^1H NMR ($CDCl_3$) δ 7.23 (m, 20 H, aromatic), 4.80 (s, 4 H, olefinic), 3.01 (s, 6 H, *exo*-CH_3O), 0.90 (s, 6 H, *endo*-CH_3); IR (hexane) ν_{CO} 1993 (s); 1948 (s) cm^{-1}; mass spectrum, *m/e* (assignment) 796 (molecular peak for ^{184}W), 768 (M^+ − CO), 740 (M^+ − 2CO), 710 (M^+ − 2CO − $2CH_3$). Anal. Calcd for $C_{38}H_{36}O_4Si_2W$: C, 57.28; H, 4.52. Found: C, 57.04; H, 4.36.

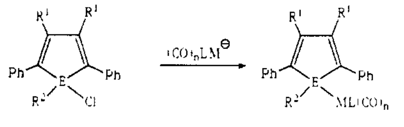
***cis*-Dicarbonylbis(η^4-*exo*-1-benzyl-*endo*-1-methyl-2,5-diphenylsilole)tungsten (11).** Similarly as above, to 140 mg of 4 (0.110 mmol) in 15 mL of toluene was added 56 mg of iodine (0.220 mmol) in 10 mL of toluene. The reaction mixture was allowed to warm to −30 °C, and 0.286 mL of a 1.75 M solution of $PhCH_2MgBr$ in ether was added. After 12 h, the solvent was evaporated in vacuo and the residue was chromatographed on a silica gel column. A yellow band was obtained (hexane), and after evaporation of the solvent, the compound was identified as $Fe(CH_2Ph)(CO)_2(\eta^5$-$C_5H_5)$ by comparison of its IR spectrum to that of an authentic sample.[24] Elution with toluene/hexane (1/1) gave an orange band, the solvent was evaporated in vacuo, and the residue was crystallized from hexane at −78 °C to give 50 mg of orange crystals of 11 (yield 50%): mp 135–137 °C; ^1H NMR ($CDCl_3$) δ 7.41 (m, 20 H, aromatic), 6.66 (m, 10 H, aromatic), 4.66 (s, 4 H, olefinic), 1.69 (s, 4 H, benzylic), 0.82 (s, 6 H, *endo*-CH_3); IR (hexane) ν_{CO} 1985 (s), 1940 (s) cm^{-1}; mass spectrum, *m/e* (assignment) 916 (molecular peak for ^{184}W), 825 (M^+ − CH_2Ph), 706 (M^+ − $2CH_2Ph$ − CO). Anal. Calcd for $C_{50}H_{44}O_2Si_2W$: C, 65.50; H, 4.80. Found: C, 65.01; H, 5.20.

Tricarbonyl(η^4-*exo*-1-methoxy-*endo*-1-methyl-2,5-diphenylsilole)iron (12). A solution of 300 mg of 6 (0.532 mmol) in 50 mL of methanol was irradiated (500-W lamp, external) for 14 h; a red color developed. The solvent was evaporated in vacuo, and the residue was crystallized from THF/hexane at −78 °C to give violet crystals of $[Fe(CO)_2(\eta^5$-$C_5H_5)]_2$ (60 mg, yield 63%). The mother liquors were evaporated in vacuo and extracted with hexane; the solution was filtered through a fritted funnel (G4) and was left at −78 °C to afford a yellow microcrystalline powder (45 mg) of 12 (yield 20%) which was identified by comparison with an authentic sample.[25]

Dicarbonyl[η^4-*exo*-1-{dicarbonyl(η^5-cyclopentadienyl)-ferrio}-*endo*-1-methyl-2,5-diphenylsilole](triphenylstannyl)cobalt (13). A solution of 500 mg of 8 (0.50 mmol) in 50 mL of THF was stirred for 2 h with 10 mL of 1% sodium amalgam. After this time it was added dropwise to 385 mg of Ph_3SnCl (1 mmol) in 30 mL of THF at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The solvent was evaporated in vacuo, and the residue was chromatographed on an acid alumina column. The red-orange band (CH_2Cl_2/hexane, 1/1) was collected, the solvent was evaporated in vacuo, and the residue was crystallized from hexane at −78 °C to give 85 mg of red crystals of 13 (yield 19%): mp 80–82 °C; ^1H NMR (C_6D_6) δ 7.7–6.9 (m, 25 H, aromatic), 6.00 (s, 2 H, olefinic), 3.80 (s, 5 H, C_5H_5), 1.53 (s, 3 H, *endo*-CH_3); IR (hexane) ν_{CO} 2010 (s), 2000 (s), 1980 (s), 1950 (s) cm^{-1}. Anal. Calcd for $C_{44}H_{35}CoFeO_4SiSn$: C, 59.41; H, 3.94. Found: C, 59.92; H, 3.83.

Results and Discussion

A few group 14 metalloles bearing silicon–transition-metal σ bonds have been prepared[26,27] by reaction of the corresponding 1-chloro-substituted metallole with the appropriate metal carbonyl anion (eq 2).



(2)

E = Si; R^1 = Ph, R^2 = Ph, Me; $(CO)_nLM$ = $(CO)_2(\eta^5$-$C_5H_5)Fe$

E = Ge; R^1 = R^2 = Ph; $(CO)_nLM$ = $(CO)_5Mn$, $(CO)_4Co$, $(CO)_2(\eta^5$-$C_5H_5)Fe$

An analogous procedure allows the formation of dicarbonyl(η^5-cyclopentadienyl)(1-methyl-2,5-diphenylsilacyclopentadien-1-yl)iron (1; R^1 = H, R^2 = Me; $(CO)_nLM$ = $(CO)_2(\eta^5$-$C_5H_5)Fe$).

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[25] Carré, F.; Corriu, R. J. P.; Guérin, C.; Henner, B. J. L.; Wong Chi Man, W. W. C. *Organometallics* **1989**, *8*, 313.

[26] Curtis, M. D. *J. Am. Chem. Soc.* **1969**, *91*, 6011.

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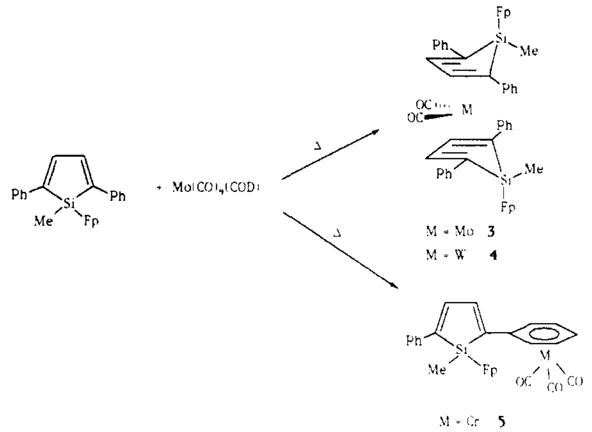
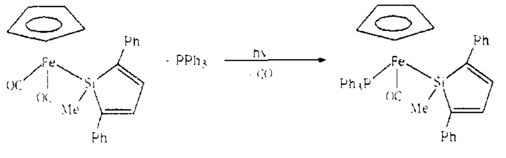
Scheme I



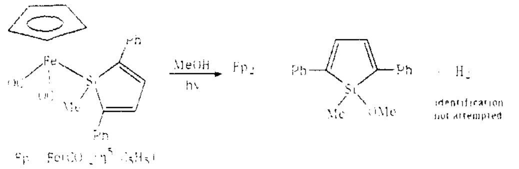
UV Irradiation of 1. UV irradiation of 1, in hexane, in the presence of PPh_3 resulted in the substitution of one carbonyl ligand and formation of 2 (eq 3).



(3)

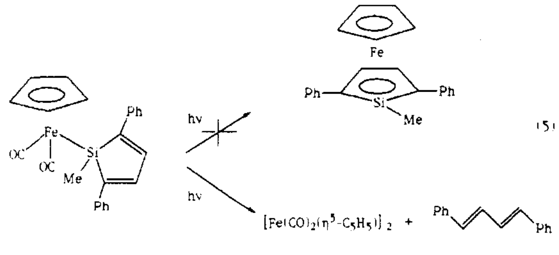
1 2

Substitution of only one carbonyl ligand by triphenylphosphine has already been observed.[28] Much decomposition also took place with formation of $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$. In order to understand how the Fe–Si bond is cleaved, the irradiation was performed in methanol, without phosphine. The iron dimer was the major product together with some 1-methoxy-1-methyl-2,5-diphenylsilole (eq 4) (the latter is not formed by nucleophilic cleavage of the Fe–Si σ bond).[28b]



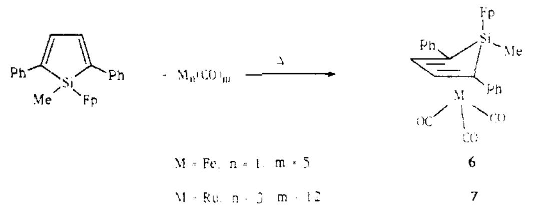
(4)

Irradiation in hexane did not lead to the expected silaferrocene; instead formation of the iron dimer and 1,4-diphenylbuta-1,3-diene was observed; silicon-containing products could not be isolated (eq 5). This result is to be compared to the observations of Curtis in the C-tetraphenylated series[26] and Abel with phosphole analogues.[29]

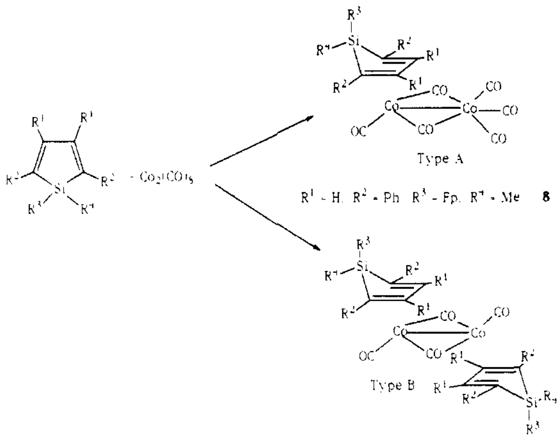


(5)

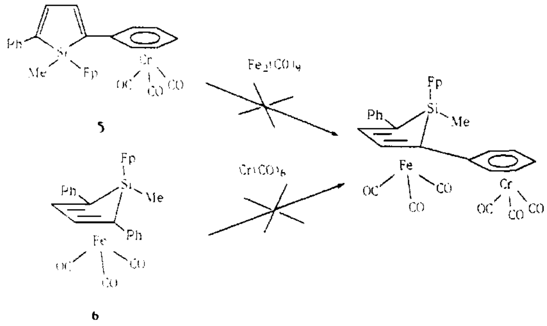
Scheme II



Scheme III



Scheme IV



Use of Complex 1 as a η^4-Ligand. Complex 1 displaced thermally 1,5-cyclooctadiene and two carbonyls in $M(CO)_4(COD)$ (M = Mo, W) to give the corresponding bis(silole) complexes 3 and 4 (Scheme I). It is interesting to note that the $M(CO)_4(\eta^4\text{-silole})$ complexes are not obtained, contrary to other siloles which, depending on the experimental conditions, give mono- or bis(silole) complexes.[15] The formation of 3 and 4 is stereospecific since only the isomers bearing the bulky Fp groups in the exo position were observed in the crude reaction mixture. This specificity is also noted for other bis(silole) complexes in which the silicon atom is unsymmetrically substituted.[30] The stereochemistry was confirmed by ^1H NMR.[11,15]

The situation is quite different for M = Cr, since only the (arene)tricarbonylchromium complex 5 was formed (Scheme I), in contrast to previous observations. Indeed, the (arene)chromium derivative was obtained with $Cr(CO)_6$,[31] but the η^4-silole complex was formed with $Cr(CO)_4(COD)$ for 1-phenyl- and 2,5-diphenyl-substituted siloles.[13,25,30]

Reaction of 1 with $Fe_2(CO)_9$ or $Ru_3(CO)_{12}$ led to the corresponding η^4-silole complexes (Scheme II), with the Fp groups in the exo position. This is in agreement with previous observations since when the difference in steric crowding of the 1-substituents is large, only the isomer bearing the bulkier group in the exo position is obtained.[14,15,32]

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[28] (a) King, R. B.; Pannell, K. H. *Inorg. Chem.* **1968**, 7, 1510. (b) Cerveau, G.; Colomer, E.; Corriu, R.; Douglas, W. E. *J. Organomet. Chem.* **1977**, *135*, 373.

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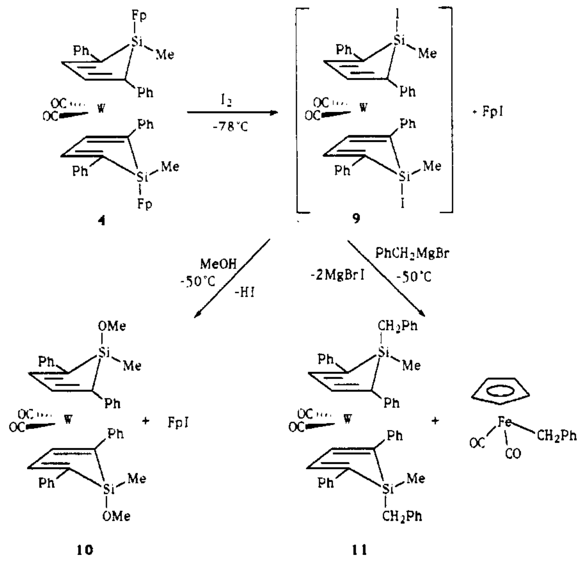
[31] Abel, E. W.; Blackmore, T.; Whitley, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2484.

[32] Wong Chi Man, W. W. C. Thèse, Université des Sciences et Techniques du Languedoc, Montpellier, 1987.

Scheme V



Coordination of siloles by carbonyl displacement in $Co_2(CO)_8$ can lead to two different types of complexes[11,13-15,25,31] (Scheme III). Two carbonyl ligands were substituted by reaction with silole 1 and complex 8 (type A) was obtained; the yield, however, was low (15%) in contrast with 60-90% in other cases. Complex 8 also bears the bulky Fp in the exo position, but it is difficult to assert that the reaction is stereospecific since no ^1H NMR spectra of the crude material could be recorded, due to paramagnetic impurities.

Contrary to other siloles[11,15] no complexation occurred with $Ni(COD)_2$. The starting material 1 was recovered almost quantitatively. Complex 5 did not react with $Fe_2(CO)_9$ to give the expected η^4-silole complex, nor did 6 react with $Cr(CO)_6$ (Scheme IV).

Reactivity of the Complexes. These complexes, as already observed for other siloles,[3] are very stable once isolated. Nevertheless they possess two reactive sites: (i) the silicon atom and (ii) the transition metal.

(i) Reactions at the Silicon Atom. Treatment of 4 with iodine leads to the cleavage of the Fe–Si sigma bond (as normally expected[28b]) to give complex 9 and dicarbonyl(η^5-cyclopentadienyl)iodoiron. This reaction was carried out at low temperature to avoid any eventual oxidation of tungsten by the halogen.[33] Complex 9 was not stable and was treated *in situ* with methanol or with benzylmagnesium bromide. These nucleophiles displace iodide and lead to complexes 10 and 11 respectively (Scheme V).

These reactions occur with retention of configuration at silicon in agreement with the general trends for coordinated siloles,[12,13,15,25] although halosilanes always undergo nucleophilic substitution with inversion of configuration.[34]

Surprisingly, reaction of MeLi on 9 did not give the expected dicarbonylbis(η^4-1,1-dimethyl-2,5-diphenylsilole)tungsten;[31] instead, decomposition occurred. IR monitoring did not show the appearance of the ν_{CO} absorption bands due to a carbenic species arising from the attack of MeLi at a carbonyl ligand. Lack of reactivity of 1-chlorosiloles coordinated to a transition metal has already been reported.[15]

Scheme VI

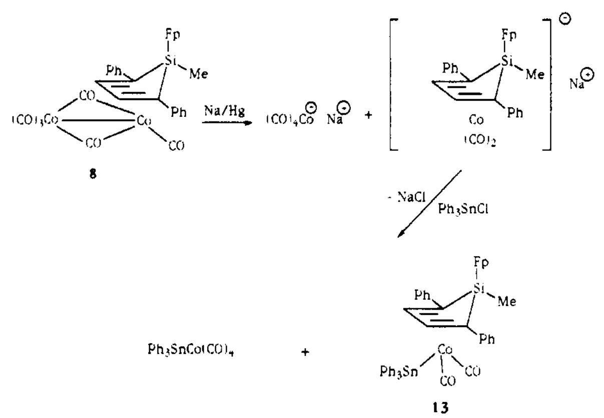
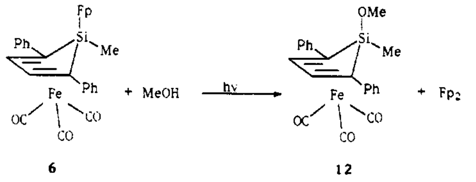


Table I. Variable-Temperature Spectra (Olefinic Protons) and Activation Energies of Complexes 3 and 4 in CD_2Cl_2/CS_2 Solution

complex	T, K	δ, ppm	$\Delta\nu$,[a] Hz	$\Delta G^*_{T_c}$,[b] kJ mol^{-1}
3	300	5.10	237	34
3	163	5.30, 4.64		
4	300	4.90	263	38
4	163	5.13, 4.40		

[a] 360-MHz spectrometer. [b] T_c for 3: 178 K. T_c for 4: 205 K.

The Fe–Si bond in 4 was not cleaved by MeOH or MeONa, in agreement with previous observations,[28b] but neither by water. $LiAlH_4$ attacked 4 but the expected *cis*-dicarbonylbis(η^4-*endo*-methyl-2,5-diphenylsilole)tungsten could not be isolated. The enhanced reactivity of the exo Si–H bond[13,15,25] could explain this observation. Diisobutylaluminum hydride did not react with 4. Complex 6 reacted with MeOH under UV light in a manner analogous to that of 1, without decoordination of the η^4-ligand, giving 13 (eq 6).



(6)

(ii) Reactions at the Transition Metal. Attempted substitution of a carbonyl ligand by PPh_3 in complex 6 did not lead to a defined complex since a lack of selectivity was observed between the $Fe(CO)_2$ and $Fe(CO)_3$ groups. When 2 mol of PPh_3/mol of 6 were used, much decomposition occured and only *trans*-$Fe(CO)_3(PPh_3)_2$[35] could be identified.

The cobalt–cobalt bond in 8 was cleaved by sodium amalgam, as already observed for other silole complexes;[11,15] the corresponding cobaltate(I) anions that were obtained reacted with Ph_3SnCl to afford the complexes with Co–Sn σ bonds (Scheme VI) (the formation of tetracarbonyl(triphenylstannyl)cobalt is assumed by analogy to previous reports[11]).

Dynamic Stereochemistry. We have shown previously[1] that complexes of the type *cis*-$M(CO)_2(\eta^4\text{-metallole})_2$ (M = Mo, W) exhibit fluxionality. Indeed, the magnetic nonequivalence of protons (predicted on the basis of the molecular structure of the complex) was not observed at room temperature. Variable-temperature NMR studies

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(35) Lewis, J.; Nyholm, R. S.; Sandhu, S. S.; Stiddard, M. H. B. *J. Chem. Soc.* **1964**, 2825. Clifford, A. F.; Mukherjee, A. K. *Inorg. Synth.* **1966**, *8*, 185.

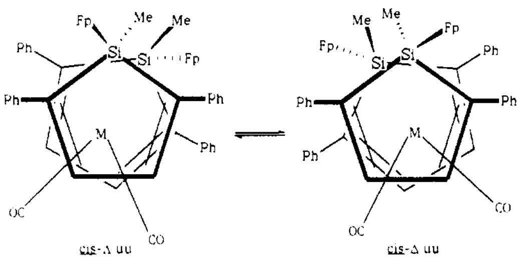

Figure 1. Ring rotation explains the equivalence of protons H_a and H_b in complexes **3** and **4**.

showed an interconversion between two enantiomers with a $\Delta G^*_{\mathrm{coal}} \sim$ 35–40 kJ mol^{-1}. In addition, the presence of diastereoisomers was deduced from the multiplicity of the IR absorption bands in the ν_{CO} region.

Complexes **3** and **4** (the molecular structure of which is assumed to be also cis) showed comparable behavior in the variable-temperature ^{1}H NMR study. Indeed, the olefinic protons showed a single resonance at room temperature, but at low temperature two signals of the same intensity were observed. From their $\Delta\nu$, the activation energy can be calculated by means of the Eyring equation. Table I brings the most important values. These results can be explained by the interconversion of isomer cis-Δ_{uu} and *cis*-Λ_{uu} (Figure 1) via a ring rotation mechanism.[36] The presence of the *exo*-Fp groups does not make any dramatic change with respect to the previously studied complexes since both activation energies and coalescence temperatures are in the same range.

Nevertheless, the coexistence of diastereoisomers cannot be proved since the ν_{CO} absorptions are broad (as observed in *cis*-dicarbonylbis(η^4-1,1-dimethyl-2,5-diphenylsilole)-molybdenum[31]) and the resolution becomes lower than 10 cm^{-1}.[1] Two possibilities can exist: (i) diastereoisomers coexist but cannot be observed or (ii) the presence of the phenyl groups in the 2,5-positions might change the situation, with respect to complexes with non *C*-phenyl substituted metalloles, and avoids the interconversion of diastereoisomers.

Conclusion

The substitution by a transition-metal moiety in the 1-position of a silole does not change the coordination capability of the metallole. As observed for other C-phenylated siloles, only two carbonyl ligands are displaced in $Co_2(CO)_8$.[11] It is interesting to note the stereospecific coordination of **1** since the Fp substituent occupies always the exo position.

The reactivity of the η^4-complexes does not show particular features, except for the cleavage of the Si–Fe bond by iodine. Indeed, functionalization at silicon, in order to form a Si–Fe bond, seems to be necessary for an approach to the η^5-silacyclopentadienyl species.

Contrary to other *cis*-$M(CO)_2(\eta^4\text{-metallole})_2$ complexes, the presence of diastereoisomers in solution cannot be ascertained; nevertheless a rapid interconversion of cis-Δ_{uu} and cis-Λ_{uu} enantiomers has been observed.

Registry No. **1**, 121919-41-3; **2**, 121919-42-4; **3**, 121919-43-5; **4**, 121962-47-8; **5**, 121919-44-6; **6**, 121919-45-7; **7**, 121919-46-8; **8** (type A), 121919-47-9; **10**, 121919-48-0; **11**, 121919-49-1; **12**, 112218-88-9; **13**, 121919-51-5; Fp_2, 12154-95-9; $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$, 12152-20-4; PPh_3, 603-35-0; $Mo(CO)_4(COD)$, 12109-74-9; $W(CO)_4(COD)$, 12129-70-3; $Cr(CO)_4(COD)$, 12301-34-7; $Fe_2(CO)_9$, 10210-68-1; $Ru_3(CO)_{12}$, 15243-33-1; $Co_2(CO)_8$, 10210-68-1; $Fe(CO)_2(\eta^5\text{-}C_5H_5)I$, 12078-28-3; $PhCH_2MgBr$, 1589-82-8; Ph_3SnCl, 639-58-7; 1-chloro-1-methyl-2,5-diphenylsilole, 100840-06-0; 1-methoxy-1-methyl-2,5-diphenylsilole, 100840-04-8.

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