

87938-61-2; *trans*-2a, 87938-51-0; *cis*-3, 83447-54-5; *trans*-3, 83447-55-6; *cis*-4, 108167-72-2; *trans*-4, 108150-17-0; *trans*-4 *cis*-2-butene derivative, 108150-18-1; *cis*-5, 85977-35-1; *trans*-5, 85977-36-2; 6, 87938-58-7; 7, 108167-73-3; 9, 108167-74-4; 10, 108167-76-6; 11, 108167-75-5; MgBr₂, 7789-48-2; potassium

tert-butoxide, 865-47-4; *cis*,4-di-*tert*-butoxyhexamethyl-1,4-disilacyclohexa-2,5-diene, 108189-52-2; *trans*-1,4-di-*tert*-butoxyhexamethyl-1,4-disilacyclohexa-2,5-diene, 108167-71-1; ethylene dibromide, 106-93-4; dichloromethylsilane, 75-54-7; catechol, 120-80-9; *cis*-2-butene-1,4-diol, 6117-80-2.

Coordination Chemistry of Group 14 Metalloles. 3.¹ Synthesis and Reactivity of 1,1-Dimethyl- and 1,1,3,4-Tetramethylsilole and 1,1,3,4-Tetramethylgermole Complexes²

Gary T. Burns, Ernest Colomer, Robert J. P. Corriu,* and Marc Lheureux

Laboratoire "Hétérochimie et Aminoacides", U.A. CNRS 1097, Institut de Chimie Fine, USTL, Place Eugène Bataillon, F-34060-Montpellier Cédex, France

Jacques Dubac, André Laporterie, and Hafida Iloughmane

Laboratoire des Composés Organiques du Germanium, U.A. CNRS 477, Université Paul Sabatier, F-31062-Toulouse Cédex, France

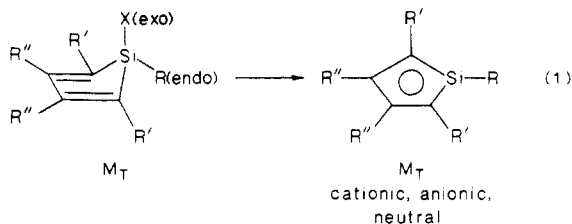
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Silacyclopentadienes and germacyclopentadienes (metalloles) without phenyl substituents are effective ligands for transition-metal complexes. Direct displacement of carbonyl ligands from Fe₂(CO)₉, Ru₃(CO)₁₂, or Co₂(CO)₈ results in stable complexes (η⁴-metallole)M(CO)₃ (M = Fe, Ru), (η⁴-metallole)Co₂(CO)₆, and [(η⁴-metallole)Co(CO)₂]₂. (η⁴-metallole)Fe(CO)₃ undergoes carbonyl replacement with PPh₃. Cleavage of the cobalt-cobalt bond is achieved with both iodine and sodium amalgam; the anions obtained react with Ph₃SnCl. Displacement of 1,5-cyclooctadiene in (1,4-COD)₂Ni affords (η⁴-silole)NiCOD. Displacement of COD in (1,5-COD)M(CO)₄ (M = Cr, Mo, W) leads to (η⁴-metallole)M(CO)₄ and also (η⁴-metallole)₂M(CO)₂. In iron complexes, the *exo* methyl is cleaved by SnCl₄. Chlorine can be displaced by some nucleophiles (CH₃Li, PhLi, H₂O, alcohols). No evidence for the formation of η⁵-silacyclopentadienyl complexes has been obtained.

Introduction

Since the first silacyclopentadiene, 1,1,2,3,4,5-hexaphenyl-1-silacyclopentadiene (hexaphenylsilole), was prepared in 1959 by Braye and Hübel,³ the chemistry of siloles has been considerably developed; in particular their use as ligands with transition metals.⁴ Interest has been directed to the similarities between cyclopentadienes and siloles, especially for the preparation of the silacyclopentadienyl anion⁵ and the η⁵-silacyclopentadienyl ligand. The observation of the latter in mass spectrometry has been suggested^{6,7} without any further evidence, however.

Functionalization at silicon could be an efficient way for the transformation of η⁴-silole to η⁵-silolyl (eq 1).



M_T = transition metal; R = hydrocarbon radical; R' = Ph; R'' = Ph, H;
X = functional group

Functional complexes have been obtained both by cleavage of the *exo* methyl⁸ and complexation of functional siloles.¹ Unfortunately, neither of these ways led to the expected η⁵-silolyl complex. In the case of the parent germole, a cationic species coordinated to iron has been obtained but shown to be an η⁴-complex with the positive charge mainly localized at the germanium atom.⁹ Also a μ-germylene complex was formed from reaction of germole with diiron enneacarbonyl, instead of the expected (η⁵-germylyl)dicarbonyliron dimer.¹⁰ These facts contrast with the recent development of the chemistry of the η⁵-phospholyl complexes¹¹ since one would expect similar behavior for silole (or germole) and phosphole. Since all these attempts have been carried out with *C*-phenyl-substituted siloles, the failure to obtain the η⁵-system could be explained by the observation of Pauson et al.,^{12,13} who pointed out that phenyl substitution on the ring rendered the formation of η⁵-cyclopentadienyl more difficult.

Recently, some of us have reported the synthesis of *C*-unsubstituted siloles^{14,15} as well as of 3,4-dimethyl-silacyclopentadienes^{16,17} and their iron tricarbonyl com-

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plexes.^{14,16-19} The availability of nonphenyl-substituted siloles and the stability of their complexes with iron tricarbonyl prompted us to develop their coordination chemistry.

In this report we describe the synthesis of transition-metal complexes of 1,1-dimethylsilole and 1,1,3,4-tetramethylsilole (and germole), their properties, and their reactivity.

Experimental Section

All reactions were carried out under nitrogen (or argon in the case of chromium and nickel complexes) by using a vacuum line and Schlenk tubes. Solvents were dried and distilled before use. The following starting materials were prepared by literature methods: (COD)Mo(CO)₄,²⁰ (COD)W(CO)₄,²¹ Fe₂(CO)₉,²² (CO-D)₂Ni,²³ [(η⁴-2,3-dimethyl-1,3-butadiene)Co(CO)₂]₂,²⁴ and [(η⁴-1,3-cyclohexadiene)Co(CO)₂]₂.²⁴ 1,1-Dimethylsilole was prepared as described¹⁵ immediately before use, dissolved in the appropriate solvent at -78 °C, and transferred dropwise with a cannula to the reaction vessel.

In column chromatography the Florisil used was purchased from Fluka (ref no. 46384). Florisil from other sources caused decomposition of several complexes.

Photochemical reactions were performed with a 100- or a 450-W medium-pressure Hanovia mercury lamp. Melting points were taken by using an oil circulating apparatus, under vacuum, and are uncorrected. IR spectra were recorded with a Perkin-Elmer 298 spectrophotometer, NMR spectra with a Varian EM 360, EM 390, or a Bruker WM 360 WB spectrometer (chemical shifts, δ, are relative to Me₄Si), and mass spectra on a JEOL JMS-D100 spectrometer.

The electrochemical measurements were recorded following the described procedure.²⁵ Reduction potentials were measured against an aqueous saturated calomel electrode (SCE), separated from the nonaqueous solution by a salt bridge containing the same solvent (1,2-dimethoxyethane, DME) and supporting electrolyte (0.1 M tetrabutylammonium perchlorate, TBAP) as the solution being studied, in order to prevent water diffusion into the medium. The working electrodes, besides a platinum wire anode, were a dropping mercury cathode in the polarographic measurements and a hanging mercury cathode in the case of voltammetry. The supporting electrolyte concentration was 0.12 M in TBAP. All measurements were recorded at room temperature under nitrogen: the concentration was 10⁻⁴ M in complex. The polarograms were recorded at 10 mV s⁻¹ and the voltammograms at 100 mV s⁻¹.

Bis(η⁴-1,1-dimethylsilole)dicarbonylmolybdenum (5). To a refluxing hexane solution (50 mL) of 3.95 g (12.5 mmol) of (COD)Mo(CO)₄ was added, dropwise, a hexane solution of 1,1-dimethyl-4-(benzoyloxy)-1-silacyclopent-2-ene. After addition, the solution was refluxed for one additional hour and cooled and the solvent removed in vacuo. The dimethylsilole dimer, which formed during the reaction, was eliminated by distillation at ~90–100 °C (oil bath) under ~1 Pa. The residue was chromatographed on Florisil with hexane, the yellow band was collected, and the solvent was pumped off. The yellow oil was dissolved in pentane.

Standing at -78 °C afforded 2.02 g of **5** (yield 43% based on (COD)Mo(CO)₄): mp 61–62 °C; ¹H NMR (C₆D₆) δ 4.84 (m, 4 H, β-ethylenic), 1.83 (m, 4 H, α-ethylenic), 0.40 (s, 6 H, endo methyls), -0.08 (s, 6 H, exo methyls); IR (hexane) ν_{CO} 1990 (s), 1940 (s) cm⁻¹; mass spectrum, *m/e* (assignment) 374 (molecular peak for ⁹⁸Mo),

318 (M⁺ - 2CO). Anal. Calcd for C₁₄H₂₀MoO₂Si₂: C, 45.15; H, 5.37. Found: C, 45.15; H, 5.49.

(η⁴-1,5-Cyclooctadiene)tetracarbonylchromium. Since conventional methods for preparing this compound are reported to give a very low yield,²⁶ a similar method to that described for an efficient synthesis of benzochrene was used.²⁷

Chromium carbonyl (4 g, 18.2 mmol) was refluxed for 6 h in a mixture of butyl ether (120 mL), THF (10 mL), and 1,5-cyclooctadiene (25 mL). After this time solvents were pumped off, and the residue was crystallized from hexane at -78 °C to give 2.16 g (44% yield) of yellow crystals. 1,5-Cyclooctadiene was chromatographed over neutral alumina, dried, and distilled prior to use.

Reaction of 1 with (COD)Cr(CO)₄. The same procedure as for the synthesis of **5** was used. (COD)Cr(CO)₄ (2.2 g, 8 mmol) was treated with **1** (from 5.9 g (25 mmol) of the benzoate ester). Chromatography on Florisil was made before distillation of the dimer, and the crude material (yellow orange band) was proved to be a mixture of the silole dimer and a new compound which showed in ¹H NMR (C₆D₆) spectrum two singlets at δ 0.50 and -0.26 (endo and exo methyls). The complex decomposed during distillation of the silole dimer.

(η⁴-1,1,3,4-Tetramethylsilole)tetracarbonyltungsten (9). A THF solution (60 mL) of silole **2** (0.60 g, 4.35 mmol) and (COD)W(CO)₄ (0.875 g, 2.17 mmol) was refluxed for 2 h. The reaction was monitored by IR spectroscopy and stopped when the carbonyl absorption due to W(CO)₆ was observed. The solvent was pumped off and the residue extracted with hexane, filtered through a fritted funnel (G4), and chromatographed on Florisil with hexane. The yellow band was collected and the solvent pumped off. The residue was crystallized four times from hexane at -78 °C; yellow crystals of **9** were obtained: 0.235 g (25% yield); mp 67–68 °C; ¹H NMR (C₆D₆) δ 2.19 (s, 6 H, C-CH₃), 2.09 (s, 2 H, ethylenic), 0.37 (s, 3 H, endo methyl), -0.21 (s, 3 H, exo methyl); IR (hexane) ν_{CO} 2042 (s), 1975 (s), 1937 (s), 1927 (s) cm⁻¹; mass spectrum, *m/e* (assignment) 434 (molecular peak for ¹⁸⁴W), 406 (M⁺ - CO), 378 (M⁺ - 2CO), 350 (M⁺ - 3CO), 322 (M⁺ - 4CO). Anal. Calcd for C₁₂H₁₄O₄SiW: C, 33.18; H, 3.22. Found: C, 33.20; H, 3.28.

Bis(η⁴-1,1,3,4-tetramethylsilole)dicarbonyltungsten (8). A solution of **2** (0.7 g, 5 mmol) and (COD)W(CO)₄ (1.0 g, 2.5 mmol) in 40 mL of hexane was refluxed for 1 day. After this time solvent was pumped off; the W(CO)₆ formed was sublimed under vacuum and the residue chromatographed on Florisil by using hexane as eluant. The yellow band was collected, concentrated, and left at -78 °C; yellow crystals were obtained (250 mg, yield 20%): mp 81–82 °C; ¹H NMR (C₆D₆) δ 2.36 (s, 12 H, C-CH₃), 1.50 (s, 4 H, ethylenic), 0.44 (s, 6 H, endo methyl), 0.00 (s, 6 H, exo methyl); IR (hexane) ν_{CO} 1976 (s), 1970 (s), 1917 (s), 1908 (s) cm⁻¹; mass spectrum, *m/e* (assignment) 516 (molecular peak for ¹⁸⁴W), 503 (M⁺ - CH₃), 475 (M⁺ - CH₃ - CO), 460 (M⁺ - 2CO). Anal. Calcd for C₁₈H₂₈O₂Si₂W: C, 41.90; H, 5.43. Found: C, 41.95; H, 5.46.

Complex **8** is also obtained by thermal reaction of **2** with a THF solution of THF·W(CO)₅.²⁸

(η⁴-1,1,3,4-Tetramethylsilole)tetracarbonylchromium (4). The same procedure as for the synthesis of **9** was used. (COD)Cr(CO)₄ (0.80 g, 2.90 mmol) and **2** (1.00 g, 6 mmol) were refluxed in 60 mL of hexane for 3 h. Yellow crystals were obtained after crystallization from hexane (300 mg, 35% yield): mp 39–40 °C; ¹H NMR (C₆D₆) δ 1.95 (s, 6 H, C-CH₃), 1.91 (s, 2 H, ethylenic), 0.45 (s, 3 H, endo methyl), -0.30 (s, 3 H, exo methyl); IR (hexane) ν_{CO} 2035 (s), 1940 (s), 1935 (s) cm⁻¹; mass spectrum, *m/e* (assignment) 302 (molecular peak for ⁵²Cr), 274 (M⁺ - CO), 246 (M⁺ - 2CO), 218 (M⁺ - 3CO), 190 (M⁺ - 4CO). Anal. Calcd for C₁₂H₁₄CrO₄Si: C, 47.68; H, 4.63. Found: C, 47.18; H, 5.08.

Bis(η⁴-1,1,3,4-tetramethylsilole)dicarbonylmolybdenum (6) and Bis(η⁴-1,1,3,4-tetramethylgermole)dicarbonylmolybdenum (7). These complexes were prepared in a similar manner to that of **8**. From **2** (1.38 g, 10 mmol) and (COD)Mo(CO)₄ (1.58 g, 5 mmol) was obtained 600 mg (28% yield) of **6**: yellow crystals; mp 91–92 °C; ¹H NMR (C₆D₆) δ 2.18 (s, 12 H, C-CH₃), 1.73 (s, 4 H, ethylenic), 0.40 (s, 6 H, endo methyl), 0.00

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(s, 6 H, exo methyl); ^{13}C NMR (CD_2Cl_2) δ 230.4 (CO), 105.6 (C, β to Si), 53.7 (C, α to Si, this signal is masked by the solvent), 19.0 (methyl bonded to carbon), 12.0 (endo methyl), 0.00 (exo methyl); IR (hexane) ν_{CO} 1978 (s), 1972 (s), 1919 (s), 1912 (s) cm^{-1} ; mass spectrum, m/e (assignment) 430 (molecular peak for ^{98}Mo), 402 ($\text{M}^+ - \text{CO}$), 374 ($\text{M}^+ - 2\text{CO}$). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{MoO}_2\text{Si}_2$: C, 50.45; H, 6.74. Found: C, 50.44; H, 6.63.

From **3** (0.25 g, 1.36 mmol) and $(\text{COD})\text{Mo}(\text{CO})_4$ (0.22 g, 0.68 mmol) in 25 mL of hexane, 72 mg (20% yield) of yellow crystals of **7** were obtained (however chromatography on Celite was used instead of Florisil to avoid decomposition): mp 102–103 °C; ^1H NMR (C_6D_6) δ 2.28 (s, 12 H, C-CH₃), 2.03 (s, 4 H, ethylenic), 0.53 (s, 6 H, endo methyl), 0.19 (s, 6 H, exo methyl); IR (hexane) ν_{CO} 1970 (s), 1963 (s), 1912 (s), 1905 (s) cm^{-1} ; mass spectrum, m/e (assignment) 518 (molecular peak for ^{98}Mo and ^{74}Ge), 490 ($\text{M}^+ - \text{CO}$), 462 ($\text{M}^+ - 2\text{CO}$). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{Ge}_2\text{MoO}_2$: C, 41.70; H, 5.40. Found: C, 41.52; H, 5.31. (The IR spectra of **6**–**8** suggest the presence of isomers. This problem will be discussed in a forthcoming publication).

(η^4 -1,1-Dimethylsilole)tricarbonyliron (10). A THF solution of **1** (generated from 5.60 g (24 mmol) of the benzoate ester) was added to a suspension of 14.83 g (41 mmol) of $\text{Fe}_2(\text{CO})_9$ in 200 mL of THF at 0 °C. The mixture was stirred at 0 °C for 40 min, allowed to warm to room temperature, and stirred for 2 h. The solvent was pumped off, and the residue was chromatographed on a silica gel column containing 10% AgNO_3 , using hexane. The yellow orange band was collected, the solvent was pumped off to afford a yellow-orange oil (3.14 g, yield 52% based on the benzoate ester): ^1H NMR (CCl_4) δ 5.89 (m, 2 H, β -ethylenic), 1.96 (m, 2 H, α -ethylenic), 0.83 (s, 3 H endo methyl), -0.18 (s, 3 H, exo methyl); IR (cyclohexane) ν_{CO} 2055 (s), 1985 (s, br) cm^{-1} ; mass spectrum, m/e (assignment) 250 (molecular peak for ^{56}Fe), 222 ($\text{M}^+ - \text{CO}$), 194 ($\text{M}^+ - 2\text{CO}$).

10 was also obtained by treating a mixture of **1** and Me_2NO (equimolar amounts) in toluene by $\text{Fe}(\text{CO})_5$ at -12 °C and then by warming the mixture to room temperature.

UV irradiation of **1** and $\text{Fe}(\text{CO})_5$ in hexane at 0 °C also afforded **10** in low yield.

(η^4 -1,1,3,4-Tetramethylsilole)tricarbonyliron (11) and (η^4 -1,1,3,4-Tetramethylgermole)tricarbonyliron (12). These complexes were prepared according to the literature;^{17,29} however they were purified by crystallization from pentane at -78 °C. **11** was filtered at low temperature since it melts at ~ 0 °C. **12**: mp 52–52.5 °C.

(η^4 -1,1,3,4-Tetramethylsilole)tricarbonylruthenium (13). A mixture of $\text{Ru}_3(\text{CO})_{12}$ (600 mg, 0.98 mmol) and **2** (400 mg, 2.90 mmol) in 50 mL of toluene was refluxed for 3 h. The solvent was pumped off, and the residue was taken up in hexane and filtered. The yellow solution was evaporated and the residue distilled at 105 °C (oil bath) under ~ 1 Pa to give an orange-yellow oil: ^1H NMR (C_6D_6) δ 2.03 (s, 6 H, C-CH₃), 1.66 (s, 2 H, ethylenic), 0.43 (s, 3 H, endo methyl), 0.19 (s, 3 H, exo methyl); IR (hexane) ν_{CO} 2058 (s), 1990 (s), 1982 (s) cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_3\text{RuSi}$: C, 40.86; H, 4.33. Found: C, 40.01; H, 4.19.

The residue of the distillation was essentially $(\text{CH}_3)_{12}\text{Si}_6$ which was compared to an authentic sample.³⁰

Reaction of 1 with $\text{Co}_2(\text{CO})_8$. A hexane solution of **1** (from 8.21 g (35.4 mmol) of the benzoate ester) was added to a stirred solution of 2.61 g (7.63 mmol) of $\text{Co}_2(\text{CO})_8$ in 100 mL of hexane at 0 °C. After being stirred for 2 h, the solution was allowed to warm to room temperature and stirred for an additional 2 h. The solvent was pumped off, the residue dissolved in ether (or CH_2Cl_2) and filtered through a fritted funnel (G4), and the solvent pumped off. Several crystallizations from hexane afforded orange crystals which were a mixture of **14** and **17**. ^1H NMR (C_6D_6): δ 5.48 and 5.18 (m, β -ethylenic), 2.71 (m, α -ethylenic), 0.51 and 0.45 (s, endo methyls), -0.22 and -0.45 (s, exo methyls). Column chromatography on acid alumina using hexane and crystallization of the orange band from hexane at -78 °C afforded 1.37 g (40% yield) of orange crystals of **17**: mp 161–161.5 °C dec; ^1H NMR (C_6D_6) δ 5.18 (m, 4 H, β -ethylenic), 2.71 (m, 4 H, α -ethylenic), 0.51 (s, 6 H, endo methyl), -0.22 (s, 6 H, exo methyl); IR (cyclohexane)

ν_{CO} 2020 (s), 2000 (s), 1830 (m) cm^{-1} ; mass spectrum, m/e (assignment) 450 (molecular peak), 422 ($\text{M}^+ - \text{CO}$), 394 ($\text{M}^+ - 2\text{CO}$). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{Co}_2\text{O}_4\text{Si}_2$: C, 42.67; H, 4.44. Found: C, 42.52; H, 4.40.

(η^4 -1,1,3,4-Tetramethylsilole)hexacarbonyldicobalt (15) and (η^4 -1,1,3,4-Tetracarboxylgermole)hexacarbonyldicobalt (16). A solution of 0.62 g (4.50 mmol) of **2** in 10 mL of hexane was added dropwise to a solution of 1.48 g (4.33 mmol) of $\text{Co}_2(\text{CO})_8$ in 80 mL of hexane at -78 °C. The mixture was allowed to warm to room temperature and stirred overnight. The solvent was pumped off at 0 °C and the residue chromatographed on neutral alumina with hexane. The orange solution was concentrated and left at -20 °C to afford 1.24 g (yield 68%) of **15**: orange crystals; mp 97–98 °C; ^1H NMR (C_6D_6) δ 2.54 (s, 2 H, ethylenic), 1.68 (s, 6 H, C-CH₃), 0.37 (s, 3 H, endo methyl), -0.50 (s, 3 H, exo methyl); IR (hexane) ν_{CO} 2075 (s), 2025 (s), 2008 (s), 1858 (w), 1838 (s) cm^{-1} ; mass spectrum, m/e (assignment) 424 (molecular peak), 396 ($\text{M}^+ - \text{CO}$), 368 ($\text{M}^+ - 2\text{CO}$), 340 ($\text{M}^+ - 3\text{CO}$), 312 ($\text{M}^+ - 4\text{CO}$), 284 ($\text{M}^+ - 5\text{CO}$), 256 ($\text{M}^+ - 6\text{CO}$). Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{Co}_2\text{O}_6\text{Si}_2$: C, 39.62; H, 3.33. Found: C, 39.49; H, 3.49.

Complex **16** was obtained in a similar manner. From 2.34 g (12.8 mmol) of **3** and 2.19 g (6.40 mmol) of $\text{Co}_2(\text{CO})_8$ in 100 mL of hexane, **16** (1.35 g, yield 45%), red-orange crystals, was formed: mp 102–103 °C; ^1H NMR (C_6D_6) δ 2.80 (s, 2 H, ethylenic), 1.75 (s, 6 H, C-CH₃), 0.50 (s, 3 H, endo methyl), -0.26 (s, 3 H, exo methyl); IR (hexane) ν_{CO} 2070 (s), 2025 (s), 2008 (s), 1858 (w), 1938 (s) cm^{-1} ; mass spectrum, m/e (assignment) 413 (molecular peak - 2CO for ^{74}Ge), 385 ($\text{M}^+ - 3\text{CO}$), 357 ($\text{M}^+ - 4\text{CO}$), 329 ($\text{M}^+ - 5\text{CO}$), 301 ($\text{M}^+ - 6\text{CO}$). Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{Co}_2\text{GeO}_6$: C, 35.85; H, 3.01. Found: C, 35.63; H, 2.93.

Bis[(η^4 -1,1,3,4-tetramethylsilole)dicarbonylcobalt] (18) and Bis[(η^4 -1,1,3,4-tetramethylgermole)dicarbonylcobalt] (19). A solution of **15** (875 mg, 2.06 mmol) and **2** (284 mg, 2.06 mmol) in 80 mL of methylcyclohexane was heated at 80 °C for 2.5 h to give a dark red solution. The reaction was monitored by IR, and heating was stopped after disappearance of the ν_{CO} bands due to **15**. The solvent was pumped off and the residue chromatographed on neutral alumina with hexane. After the mixture was concentrated and left standing at -78 °C, garnet crystals of **18** (500 mg, yield 50%) were obtained: mp 179–181 °C; ^1H NMR (C_6D_6) δ 2.21 (s, 4 H, ethylenic), 1.91 (s, 12 H, C-CH₃), 0.47 (s, 6 H, endo methyl), -0.22 (s, 6 H, exo methyl); IR (hexane) ν_{CO} 1990 (s), 1820 (s) cm^{-1} ; mass spectrum, m/e (assignment) 506 (molecular peak), 478 ($\text{M}^+ - \text{CO}$), 450 ($\text{M}^+ - 2\text{CO}$), 422 ($\text{M}^+ - 3\text{CO}$), 394 ($\text{M}^+ - 4\text{CO}$). Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{Co}_2\text{O}_4\text{Si}_2$: C, 47.41; H, 5.57. Found: C, 47.20; H, 5.44.

Complex **19** was prepared by heating at 45 °C for 10 h a solution of **16** (250 mg, 0.55 mmol) and **3** (250 mg, 1.37 mmol) in 60 mL of hexane. The same procedure as above gave 115 mg (yield 35%) of red crystals: mp 160–161 °C; ^1H NMR (C_6D_6) δ 2.56 (s, 4 H, ethylenic), 1.97 (s, 12 H, C-CH₃), 0.60 (s, 6 H, endo methyl), -0.13 (s, 6 H, exo methyl); IR (hexane) ν_{CO} 1982 (s), 1812 (s) cm^{-1} ; mass spectrum, m/e (assignment) 597 (molecular peak for ^{74}Ge), 569 ($\text{M}^+ - \text{CO}$), 541 ($\text{M}^+ - 2\text{CO}$), 513 ($\text{M}^+ - 3\text{CO}$), 485 ($\text{M}^+ - 4\text{CO}$). Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{Co}_2\text{Ge}_2\text{O}_4$: C, 40.33; H, 4.74. Found: C, 40.69; H, 4.16.

Bis(η^4 -1,1-dimethylsilole)nickel (21). To a suspension of $(\text{COD})_2\text{Ni}$ (600 mg, 2.18 mmol) in 50 mL of toluene at -78 °C was added a solution of **1** (prepared from 1.72 g (7.47 mmol) of the benzoate ester) in toluene. The solution was allowed to warm, and at ~ -30 °C an orange color developed. Toluene was pumped off at room temperature and the residue taken up in hexane and filtered through a fritted funnel (G4). Evaporation of the solvent left a red-orange oil. The ^1H NMR (C_6D_6) spectrum showed the signals of the dimer of **15** and additional signals at δ 0.26 and 0.00 which were attributed to the endo and exo methyls of **21**, respectively. Mass spectrum: m/e (assignment) 278 (molecular peak for ^{58}Ni), 263 ($\text{M}^+ - \text{CH}_3$), 168 ($\text{M}^+ - \text{silole}$). Lack of success was found in attempted purifications.

(η^4 -1,1,3,4-Tetramethylsilole) (η^4 -1,5-cyclooctadiene)nickel (22). Silole **2** (621 mg, 4.5 mmol) and $\text{Ni}(\text{COD})_2$ (620 mg, 2.25 mmol) were treated in 40 mL of toluene as above. Several crystallizations from hexane at -78 °C afforded 170 mg (yield 25%) of **22**: orange crystals; mp 100–101 °C; mass spectrum, m/e (assignment) 304 (molecular peak for ^{58}Ni), 196 ($\text{M}^+ - \text{COD}$), 181 ($\text{M}^+ - \text{COD} - \text{CH}_3$), 166 ($\text{M}^+ - \text{COD} - 2\text{CH}_3$). Anal. Calcd for

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(30) West, R.; Brough, L.; Wojnowski, W. *Inorg. Synth.* **1979**, *19*, 265.

$C_{16}H_{26}NiSi$: C, 62.97; H, 8.59. Found: C, 63.30; H, 8.51. The 1H NMR (C_6D_6) spectrum showed the presence of paramagnetic impurities (broad signals) even after 10 crystallizations; however, the following signals were observed: δ 3.33 (s, 4 H, ethylenic COD), 2.16 (two s, 10 H, aliphatic COD and ethylenic silole), 1.66 (s, 6 H, C-CH₃), 0.00 (s, 6 H, endo and exo methyls).

Bis(η^4 -1,1-dimethylsilole)(triphenylphosphine)carbonylmolybdenum (23). A solution of **5** (1.093 g, 2.94 mmol) and PPh_3 (754 mg, 2.88 mmol) in 200 mL of benzene was irradiated with a 450-W Hanovia lamp through a Pyrex filter for 10 h. The solvent was pumped off and the residue dissolved in hexane. Crystallization at $-78^\circ C$ afforded 626 mg of **23**. Concentration of the mother liquor afforded 617 mg of **5**; the yield of **23** is 81% on the basis of reacted **5**. Complex **23** is obtained as yellow crystals: mp 193–194 $^\circ C$; 1H NMR (C_6D_6) δ 7.70–6.90 (m, 15 H, aromatic), 5.20 and 4.40 (m, 2 H each, β -ethylenic), 2.00 and 1.50 (m, 2 H each, α -ethylenic), 0.65 (s, 6 H, endo methyls), 0.10 (s, 6 H, exo methyls); IR (cyclohexane) ν_{CO} 1916 (s), 1890 (s) cm^{-1} ; mass spectrum, m/e (assignment) 608 (molecular peak for ^{98}Mo), 580 ($M^+ - CO$), 346 ($M^+ - PPh_3$). Anal. Calcd for $C_{31}H_{35}MoOPSi_2$: C, 61.37; H, 5.82. Found: C, 61.50; H, 5.70.

(η^4 -1,1-Dimethylsilole)(triphenylphosphine)dicarbonyliron (24) and (η^4 -1,1,3,4-Tetramethylsilole)(triphenylphosphine)dicarbonyliron (25). A solution of **10** (3.14 g, 12.6 mmol) and PPh_3 (3.31 g, 12.6 mmol) in 50 mL of hexane was irradiated with a 100-W Hanovia lamp for 8 h. The solvent was pumped off and the residue chromatographed on silica gel with hexane/benzene (1/1). The orange-yellow band was collected, the solvent pumped off, and the residue crystallized from hexane at $-20^\circ C$ to afford 2.54 g (yield 42%) of **24**: yellow crystals; mp 170.5–171.5 $^\circ C$; 1H NMR (C_6D_6) δ 7.63–6.73 (m, 15 H, aromatic), 5.00 (m, 2 H, β -ethylenic), 1.17 (m, 2 H, α -ethylenic), 0.70 (s, 3 H, endo methyl), -0.14 (s, 3 H, exo methyl); IR (cyclohexane) ν_{CO} 1975 (s), 1920 (s) cm^{-1} ; mass spectrum, m/e (assignment) 484 (molecular peak for ^{56}Fe). Anal. Calcd for $C_{26}H_{25}FeO_2PSi$: C, 64.46; H, 5.17; P, 6.40. Found: C, 64.61; H, 5.35; P, 6.53.

The same procedure as above with **11** (3.3 g, 11.9 mmol) and PPh_3 (3.14 g, 12 mmol) in 300 mL of hexane afforded 2.5 g (yield 41%) of **25**: orange crystals; mp 151–152 $^\circ C$; 1H NMR (C_6D_6) δ 7.47 and 6.90 (m, 15 H, aromatic), 1.93 (s, 6 H, C-CH₃), 1.18 (d, $J_{HP} = 3.5$ Hz, 2 H, ethylenic), 0.79 (s, 3 H, endo methyl), -0.10 (s, 3 H, exo methyl); IR (hexane) ν_{CO} 1975 (s), 1920 (s) cm^{-1} ; mass spectrum, m/e (assignment) 512 (molecular peak for ^{56}Fe), 484 ($M^+ - CO$), 456 ($M^+ - 2CO$). Anal. Calcd for $C_{28}H_{29}FeO_2PSi$: C, 65.62; H, 5.66. Found: C, 65.76; H, 5.17.

(η^4 -1,1-Dimethylsilole)(triphenylstannyl)dicarbonylcobalt (26), (η^4 -1,1,3,4-Tetramethylsilole)(triphenylstannyl)dicarbonylcobalt (27), (η^4 -1,1-Dimethylsilole)(triphenylphosphine)(triphenylstannyl)dicarbonylcobalt (28), and (η^4 -2,3-Dimethyl-1,3-butadiene)(triphenylstannyl)dicarbonylcobalt (29). These compounds are prepared by using the techniques described previously³¹ for Fe–Si complexes.

Complex **26** is prepared from **14** (785 mg, 1.76 mmol) and Ph_3SnCl (1.49 g, 3.88 mmol). Yellow crystals (from hexane at $-78^\circ C$) are obtained: 770 mg (yield 38%); mp 85.5–86.5 $^\circ C$; 1H NMR (C_6D_6) δ 7.73 and 7.17 (m, 15 H, aromatic), 5.18 (m, 2 H, β -ethylenic), 2.72 (m, 2 H, α -ethylenic), 0.47 (s, 3 H, endo methyl), 0.36 (s, 3 H, exo methyl); IR (cyclohexane) ν_{CO} 2030 (s), 1980 (s) cm^{-1} ; mass spectrum, m/e (assignment) 576 (molecular peak for ^{120}Sn). Anal. Calcd for $C_{26}H_{25}CoO_2SiSn$: C, 54.29; H, 4.35. Found: C, 54.34; H, 4.42.

Complex **27** (from 330 mg (0.65 mmol) of **15** and 500 mg (1.3 mmol) of Ph_3SnCl) is obtained in low yield (10%, 80 mg) as yellow crystals: mp 127–127.5 $^\circ C$; 1H NMR (C_6D_6) δ 7.90 and 7.26 (m, 15 H, aromatic), 2.90 (s, ethylenic), 1.70 (s, 6 H, C-CH₃), 0.33 (s, 3 H, endo methyl), -0.30 (s, 3 H, exo methyl); IR (cyclohexane) ν_{CO} 2005 (s), 1960 (s) cm^{-1} . Anal. Calcd for $C_{28}H_{29}CoO_2SiSn$: C, 55.72; H, 4.81. Found: C, 55.71; H, 4.91.

UV irradiation of **26** (720 mg, 1.34 mmol) in the presence of PPh_3 (365 mg, 1.40 mmol) gave 273 mg of **28** (yield 25%): orange crystals; mp 160–161 $^\circ C$ dec; 1H NMR (C_6D_6) δ 7.98–6.38 (m, 30 H, aromatic), 5.90 and 4.95 (m, 1 H each, β -ethylenic), 2.85 and 1.82 (m, 1 H each, α -ethylenic), 0.73 (s, 3 H, endo methyl), -0.33

(s, 3 H, exo methyl); IR (benzene) ν_{CO} 1970 (s, br) cm^{-1} ; mass spectrum, m/e (assignment) 733 (molecular peak for $^{120}Sn - C_6H_5$), 690 ($M^+ - C_6H_5 - CO - CH_3$). Anal. Calcd for $C_{44}H_{42}Cl_2CoOPSiSn$ (crystallizes with one molecule of CH_2Cl_2): C, 57.97; H, 4.40; Cl, 7.97. Found: C, 58.03; H, 4.69; Cl, 8.13.

From 600 mg (1.52 mmol) of bis[$(\eta^4$ -dimethylbutadiene)dicarbonylcobalt] and 1.17 g (3 mmol) of Ph_3SnCl , 450 mg (yield 36%) of **29**, was obtained: orange crystals; mp 95–96 $^\circ C$; 1H NMR (C_6D_6) δ 7.76 and 7.18 (m, 15 H, aromatic), 2.45 (d, $J_{ab} \approx 2$ Hz, 2 H, H_a), 1.58 (s, 6 H, C-CH₃), 0.59 (d, $J_{ab} \approx 2$ Hz, 2 H, H_b); IR (hexane) ν_{CO} 2022 (s), 1970 (s) cm^{-1} ; mass spectrum, m/e (assignment) 520 (molecular peak for $^{120}Sn - CO$). Anal. Calcd for $C_{26}H_{25}CoO_2Sn$: C, 57.04; H, 4.60. Found: C, 56.71; H, 4.67.

(η^4 -1,1-Dimethylsilole)dicarbonyliron (30) and (η^4 -1,1,3,4-Tetramethylsilole)dicarbonyliron (31). To a stirred chloroform solution (20 mL) of 460 mg (1.02 mmol) of **14** at room temperature was added 10 mL of a chloroform solution of iodine (283 mg, 1.11 mmol) over a 15-min interval. After the solution was stirred for 3 h, the solvent was pumped off and the residue extracted with hexane/ CH_2Cl_2 . The extracts were filtered through a fritted funnel (G4), concentrated to ~ 10 mL, and cooled at $-78^\circ C$. Complex **30** was obtained (371 mg, yield 52%) as violet crystals: mp 69.5–71 $^\circ C$; 1H NMR (C_6D_6) δ 5.97 (m, 2 H, β -ethylenic), 2.40 (m, 2 H, α -ethylenic), 0.40 (s, 3 H, endo methyl), -0.36 (s, 3 H, exo methyl); IR (cyclohexane) ν_{CO} 2070 (s), 2040 (s) cm^{-1} ; mass spectrum, m/e (assignment) 352 (molecular peak). Anal. Calcd for $C_8H_{10}CoIO_2Si$: C, 27.29; H, 2.86. Found: C, 26.78; H, 3.01.

Similarly, **15** (200 mg, 0.40 mmol) afforded 30 mg (yield 10%) of **31** black crystals: mp 89–92 $^\circ C$; 1H NMR (C_6D_6) δ 2.16 (s, 6 H, C-CH₃), 2.05 (s, 2 H, ethylenic), 0.28 (s, 3 H, endo methyl), -0.50 (s, 3 H, exo methyl); IR (hexane) ν_{CO} 2060 (s), 2030 (s) cm^{-1} ; mass spectrum, m/e (assignment) 380 (molecular peak), 352 ($M^+ - CO$), 324 ($M^+ - 2CO$), 197 ($M^+ - 2CO - I$). Anal. Calcd for $C_{10}H_{14}CoIO_2Si$: C, 31.58; H, 3.68. Found: C, 31.00; H, 3.82.

(η^4 -exo-1-Chloro-endo-1-methyl-3,4-dimethylsilole)tricarbonyliron (32) and (η^4 -exo-1-Chloro-endo-1-methyl-3,4-dimethylgermole)tricarbonyliron (33). A solution of **11** (870 mg, 3.13 mmol) in 20 mL of toluene was treated dropwise with 375 μL (3.20 mmol) of $SnCl_4$ at $0^\circ C$. The yellow-orange solution turned red-brown after being stirred for 12 h at room temperature. Solvent was pumped off and the residue taken up in hexane and filtered. Several crystallizations at $-20^\circ C$ (three to seven) afforded orange crystals of **32** (350 mg, yield 37%); mp 64–66 $^\circ C$; 1H NMR (C_6D_6) δ 1.70 (s, 8 H, C-CH₃ and ethylenic), 0.75 (s, 3 H, endo methyl); 1H NMR (CD_2Cl_2) δ 2.27 (s, 6 H, C-CH₃), 2.16 (s, 2 H, ethylenic), 0.87 (s, 3 H, endo methyl); IR (hexane) ν_{CO} 2053 (s), 1986 (s, br), 1945 (w) cm^{-1} ; mass spectrum, m/e (assignment) 298 (molecular peak for ^{56}Fe), 270 ($M^+ - CO$), 263 ($M^+ - Cl$), 242 ($M^+ - 2CO$), 235 ($M^+ - CO - Cl$), 216 ($M^+ - 3CO$). Anal. Calcd for $C_{10}H_{11}ClFeO_3Si$: C, 40.23; H, 3.69; Cl, 11.90. Found: C, 39.21; H, 3.66; Cl, 10.11 (not satisfactory analysis, due to thermal instability).

From the mother liquors, after evaporation, CH_3SnCl_3 was obtained by sublimation and compared to an authentic sample.³²

Complex **33** was obtained in a similar manner from **12** (580 mg, 1.80 mmol) and $SnCl_4$ (840 μL , 7.2 mmol). Crystallization from hexane at $-20^\circ C$ gave 480 mg (yield 78%) of yellow crystals: mp 82–83 $^\circ C$; 1H NMR (C_6D_6) δ 2.11 (s, 2 H, ethylenic), 1.75 (s, 6 H, C-CH₃), 0.94 (s, 3 H, endo methyl); IR (hexane) 2055 (s), 1990 (s), 1980 (s), 1960 (w) cm^{-1} ; mass spectrum, m/e (assignment) 344 (molecular peak for ^{56}Fe), 316 ($M^+ - CO$), 288 ($M^+ - 2CO$), 260 ($M^+ - 3CO$). Anal. Calcd for $C_{10}H_{11}ClFeGeO_3$: C, 35.00; H, 3.21; Cl, 10.35. Found: C, 35.23; H, 3.35; Cl, 10.24.

Chlorine Substitution Reactions of Complex 32. All reactions were carried out in inert solvents (hydrocarbons, ether).

Complex **34** was identified by comparison with an authentic sample.³³

Treatment of **32** (50 mg, 0.17 mmol) in 5 mL of water–acetone at room temperature for 30 min, followed by evaporation of the solvent and crystallization from hexane, afforded 46 mg (yield 100%) of yellow crystals of **35**: mp 92–94 $^\circ C$; 1H NMR (C_6D_6)

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(32) Barbier, G.; Taddei, F. *J. Chem. Soc., Perkins Trans.* 2 1972, 1327.

(33) Colomer, E.; Corriu, R. J. P.; Lheureux, M., unpublished results.

δ 1.82 (s, 12 H, C-CH₃), 1.77 (s, 4 H, ethylenic), 0.43 (s, 6 H, endo methyls); IR (hexane) ν_{CO} 2046 (s), 1982 (s), 1977 (s), 1940 (w) cm^{-1} ; mass spectrum, m/e (assignment) 542 (molecular peak for ⁵⁶Fe), 514 (M - CO), 458 (M⁺ - 3CO), 430 (M - 4CO), 402 (M⁺ - 5CO), 374 (M - 6CO). Anal. Calcd for C₂₀H₂₂Fe₂Si₂O₇: C, 44.31; H, 4.06. Found: C, 44.29; H, 4.29.

Reaction of **32** in C₆D₆ with the stoichiometric amount of methanol in an NMR tube showed instantaneously the disappearance of the resonances due to the starting material and new signals at δ 2.97 (s, 3 H, exo-OCH₃) 1.87 (s, 6 H, C-CH₃) 1.62 (s, 2 H, ethylenic), and 0.50 (s, 3 H, endo methyl). Attempts to isolate complex **36** on a larger scale were unsuccessful, and instead **35** was obtained.

Reaction of **32** with stoichiometric amounts of NaCp, *i*-PrMgBr, or PhC≡CLi in ether or THF, followed by evaporation of the solvent, dissolution in hexane, filtration, and crystallization, afforded **35** in reasonable yields (50–80%).

Chlorine Substitution Reactions of Complex 33. Treatment of **33** (250 mg, 0.73 mmol) in the same conditions as **32** (water-acetone) resulted in the formation of **39** (160 mg, yield 70%): yellow crystals; mp 128–129 °C; ¹H NMR (C₆D₆) δ 2.00 (s, 4 H, ethylenic), 1.85 (s, 12 H, C-CH₃), 0.67 (s, 6 H, endo methyl); IR (hexane) ν_{CO} 2055 (s), 1980 (s, br), 1940 (w) cm^{-1} . Anal. Calcd for C₂₀H₂₂Fe₂Ge₂O₇: C, 38.05; H, 3.49. Found: C, 38.36; H, 3.17.

Complex **33** in hexane was treated at -50 °C by the stoichiometric amount of DIBAH (in hexane solution). The temperature was allowed then to reach -10 °C, an aliquot was syringed, the solvent was pumped off, and the residue was dissolved in C₆D₆; the ¹H NMR spectrum showed at δ 6.03 a quartet attributed to Ge-H ($J \approx 4$ Hz) in **37**. After column chromatography (neutral alumina, using hexane as eluent) the complex was converted presumably into **38** [IR (hexane) $\nu_{\text{Ge-OH}}$ 3350 (br), 3230 (sh) cm^{-1}], which decomposed upon an attempted purification.

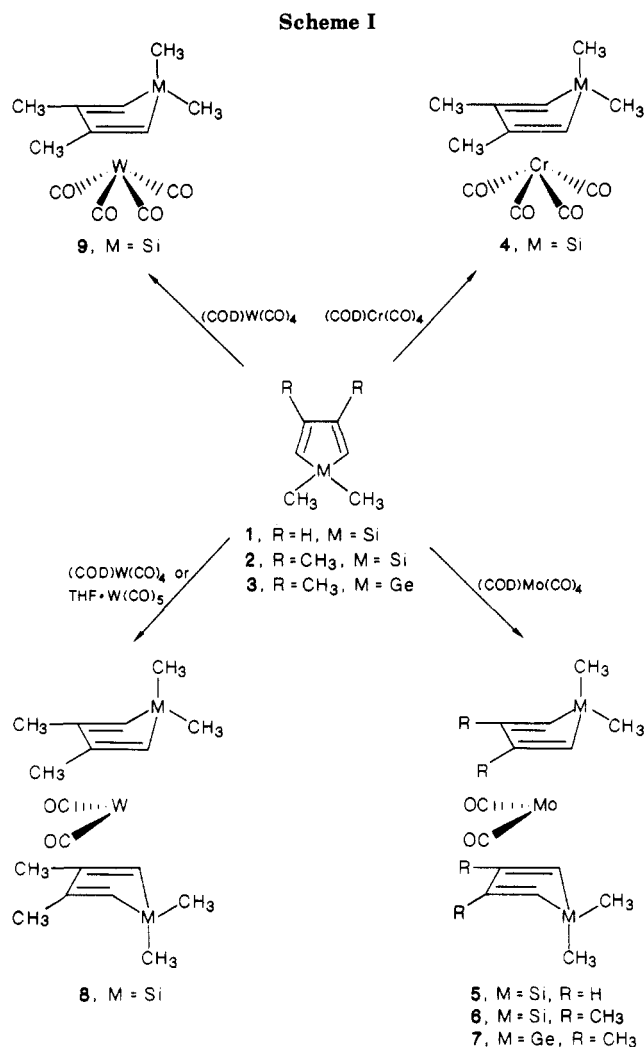
Results and Discussion

Crystallographic studies show that the uncomplexed silole ring is almost planar,³⁴ but, in metal complexes, the dihedral angles between the planes defined by the Si, C², and C⁵ atoms and by the diene moiety have values between 20 and 32°. The magnetic nonequivalence of the substituents at silicon is essential to the determination of the configuration at silicon: the exo methyl groups show resonances at higher field than endo methyl groups.^{1,6} This behavior allows an assessment of the success of a complexation reaction by observation of the ¹H NMR spectrum of the reaction mixture before isolation and full characterization of products.

Synthesis of Complexes with Group 6 Metals. Thermal reactions of 1,1-dimethylsilole (**1**), 1,1,3,4-tetramethylsilole (**2**), and 1,1,3,4-tetramethylgermole (**3**) can lead to complexation with Cr, Mo, and W (Scheme I). Silole **1** reacts with (η^4 -1,5-cyclooctadiene)tetracarbonylmolybdenum, [(COD)Mo(CO)₄], to give the bis(silole) complex **5**; complexation also takes place with (COD)Cr(CO)₄ as shown by ¹H NMR spectroscopy of the crude compound (singlets at 0.50 and -0.26 ppm, attributed to the endo and exo methyls of the complexed silole), but attempts to isolate the complex result in decomposition. With (COD)W(CO)₄, dimerization of **1**^{14,15} occurs prior to complexation.

The tetramethyl analogue **2** is more easily coordinated, and in this case complexes with either one or two silole ligands are obtained. However, only with (COD)W(CO)₄ can both of them be isolated. Formation of either **8** or **9** is a function of the solvent used for the reaction (hexane or THF). Complex **8** is also obtained from (THF)W(CO)₅ in THF by UV irradiation.

In the reaction with (COD)Cr(CO)₄, only a mono(silole) complex can be isolated, and a bis(silole) complex is ob-



tained with (COD)Mo(CO)₄. In both reactions, the other expected complexes are also formed but decompose upon any attempted purification.

The germole **3** has only been complexed with (COD)Mo(CO)₄ to show that complexation also occurs. The complex is less stable than its silicon analogue and decomposes during attempted chromatography. Thus a filtration on Celite of the crude reaction mixture is the most convenient purification, followed by crystallization from hexane.

Synthesis of Complexes with Group 8 Metals. Siloles **1** and **2** and germole **3** coordinate with iron tricarbonyl, as shown previously,^{14,16,19} by decomposition of Fe₂(CO)₉ in an inert solvent at 40–60 °C.

However, silole **1** reacts also with Fe(CO)₅ under UV irradiation or in the presence of trimethylamine oxide (Scheme II). These techniques avoid the high temperatures required when Fe(CO)₅ is employed in a thermal reaction.^{35,36} Ru₃(CO)₁₂ reacts thermally with silole **2** leading to complex **13**. Its isolation is rather difficult, however, since dodecamethylhexasilacyclohexane arising from ring cleavage is also formed. This ring opening can be related to the one observed with the parent germole.¹⁰

Synthesis of Complexes with Cobalt. As shown previously for conjugated dienes³⁷ and phenyl-substituted

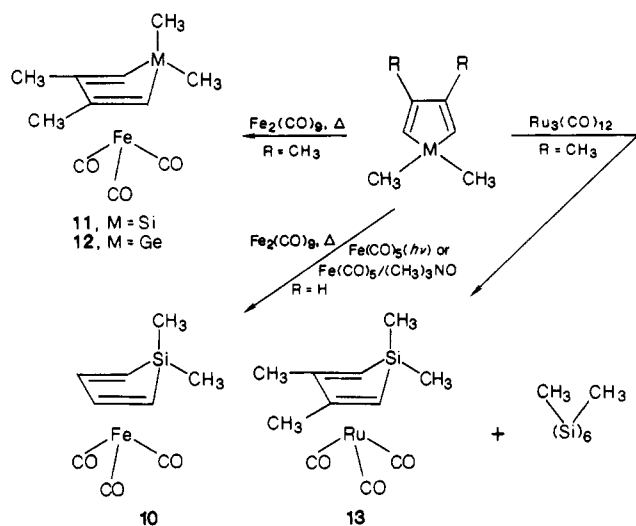
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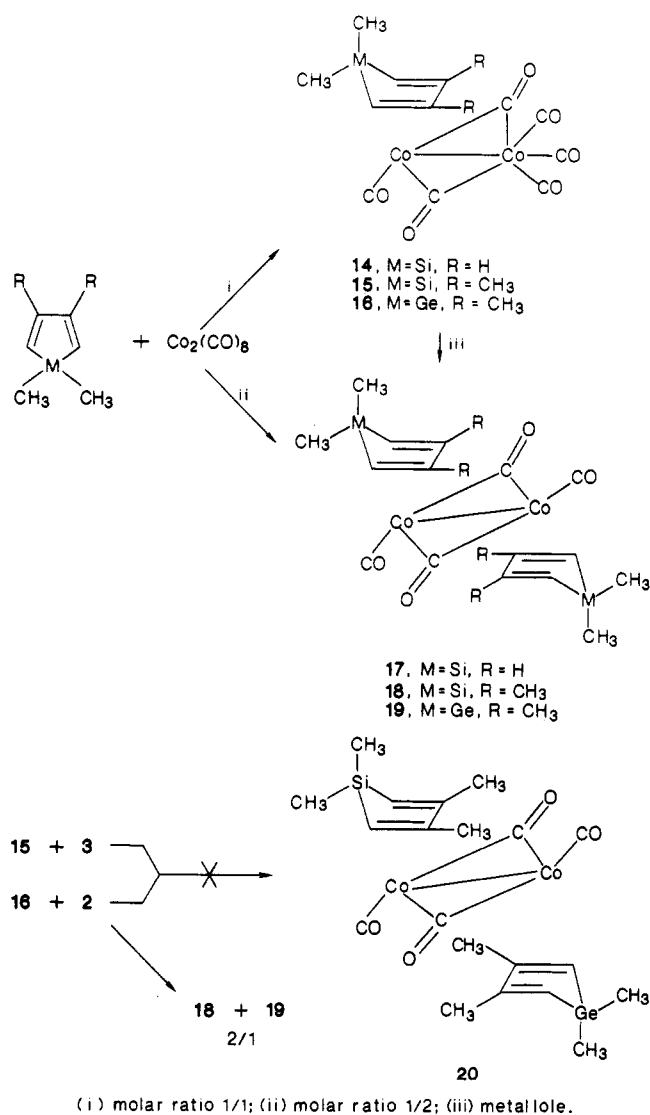
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Scheme II



Scheme III

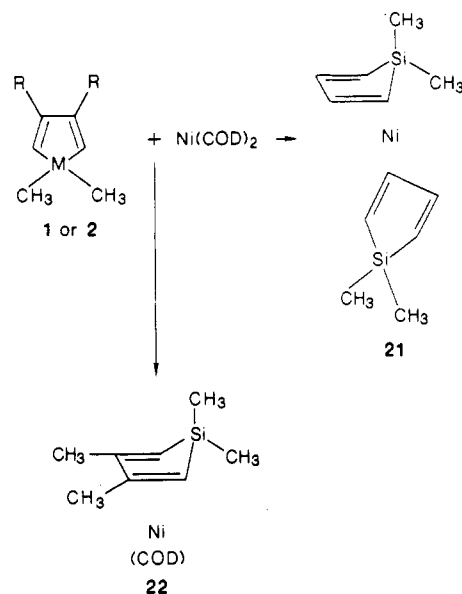


siloles,^{1,38} the cobalt carbonyl $\text{Co}_2(\text{CO})_8$ undergoes carbonyl replacement by thermal reaction with 1, 2, and 3 (Scheme

 Table I. IR Spectra in Hexane of 17, 18, 19, and $[\eta^5\text{-C}_5\text{R}_5]\text{Fe}(\text{CO})_2)_2$ (Carbonyl Absorptions in cm^{-1})

Compound	Carbonyl Absorptions (cm^{-1})
17	2030, 2000, 1830
18	1990, 1820
19	1982, 1812
$[\eta^5\text{-C}_5\text{R}_5]\text{Fe}(\text{CO})_2)_2$ (R = H)	2001, 1958, 1786 ^{39,40}
$[\eta^5\text{-C}_5\text{R}_5]\text{Fe}(\text{CO})_2)_2$ (R = CH ₃)	1932, 1764 ⁴¹

Scheme IV



III) at room temperature or below. A mixture of complexes with one or two metallole units is obtained at room temperature. Pure 15 or 16 can be prepared by reaction of equimolar amounts of both reagents at -40°C and purified by column chromatography followed by crystallization. Compounds 18 and 19 can be obtained by allowing a twofold excess of metallole to react with $\text{Co}_2(\text{CO})_8$ at room temperature. However, they are more easily prepared by reacting 15 or 16 with the corresponding metallole. Thermal decomposition of 15 or 16 in refluxing toluene also yields 18 or 19 in less than 50% yield. Complexes 14 and 17 are obtained when silole 1 is treated with $\text{Co}_2(\text{CO})_8$ at 0°C ; however, 14 cannot be isolated since it decomposes rapidly to give 17 even in an attempted isolation by column chromatography. The presence of 14 is deduced by comparison of the ^1H NMR and IR spectra with those of compounds 15, 16, 18, and 19 and with those reported previously.^{1,38}

In a preliminary communication,² we reported the formation of cis and trans isomers of 17; however, in light of the results obtained with silole 2 and germole 3, it appeared that the assumed cis isomer was in fact complex 14, which cannot be isolated and easily decomposes giving 17 and $\text{Co}_4(\text{CO})_{12}$. Interestingly, compounds 17-19 are isoelectronic with $[\eta^5\text{-C}_5\text{R}_5]\text{Fe}(\text{CO})_2)_2$ (R = H, CH₃). The similarities between the IR spectra (in solution) of the cobalt and the iron complexes (Table I) show that 17 is isostructural with the iron complex in which R = H, while 18 and 19 are isostructural with the one in which R = CH₃.

Attempts to prepare complex 20 by reaction of the monosubstituted complex 15 or 16 with metallole 3 or 2, respectively, did not give the expected compound but a mixture of the homodisubstituted complexes 18 and 19. The ^1H NMR spectrum of this mixture, after crystallization, appears to be a superimposition of the spectra of 18

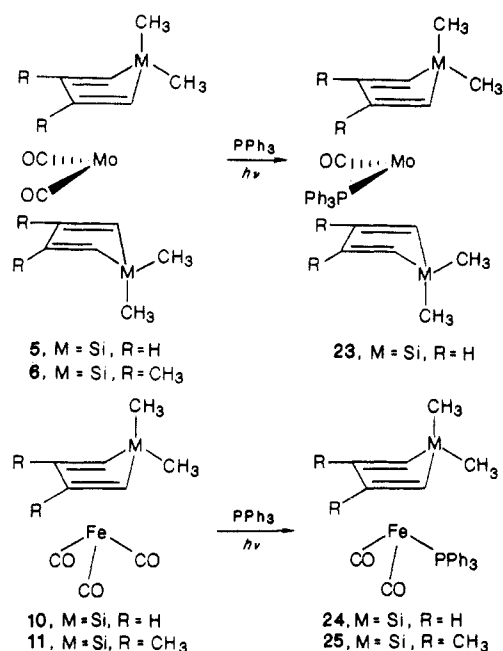
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Scheme V



and 19 (in a ratio 2:1), and its mass spectrum corresponds to those of 18 and 19 (the molecular peak of 20 is not observed). The behavior can be related to the conversion of 14 into 17, both by thermal reaction or by column chromatography. Complexes 15 and 16, upon standing, both in the solid state or in solution, at low or at room temperature yield 18 or 19, respectively, along with some decomposition, under periods going from some hours to several weeks.

Synthesis of Complexes with Nickel. Bis(cyclooctadiene)nickel reacts with metalloles 1, 2, and 3 (Scheme IV). The reaction of 1 with the nickel complex affords an orange oil that is shown by ¹H NMR and mass spectroscopy to be complex 21. Silole 2 displaces only one cyclooctadiene ligand to give complex 22.

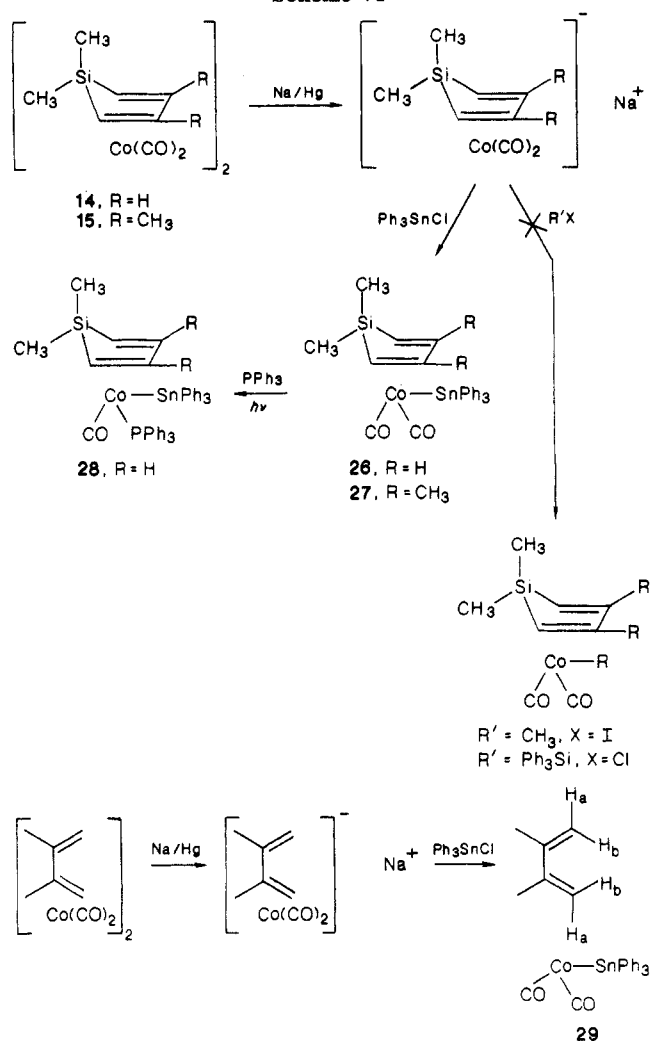
Compounds 21 and 22 are assumed to possess a tetrahedral geometry; their structures are given by comparison with the nickel complexes obtained in the 2,5-diphenylsilole series.¹ Germole 3 also reacts with (COD)₂Ni to give a complex which decomposes during any attempted purification. Its structure, reasonably, should be analogous to that of 22.

Reactivity of the New Complexes. These metallole complexes appear to be very stable once isolated, both in the solid state and in solution. Nevertheless, two types of reactions are observed: (i) reactions at the transition-metal atom and (ii) reactions at silicon (or germanium).

(i) Reactions at the Transition Metal. The good ligating ability of these metalloles is demonstrated by the replacement of one carbonyl, rather than the metallole, by UV irradiation of complexes 5, 10, and 11 in the presence of triphenylphosphine (Scheme V). It is interesting to note that complex 6 does not undergo carbonyl replacement by triphenylphosphine under mild conditions and prolonged irradiation leads to decomposition. Thermal treatment of 11 with triphenylphosphine at 110 °C for 6 h does not result in any reaction. It is known that olefin complexes of transition metals undergo easy replacement of the olefin ligand by phosphines.⁴²

Sodium amalgam reduces the cobalt-cobalt bond in 14 and 15 giving the corresponding anion which reacts with

Scheme VI

Table II. Electrochemical Reduction of Complexes [(η^4 -Diene)Co(CO)₂]₂ and (η^4 -Diene)Co₂(CO)₆

complex	diene	red. potential ^a <i>E</i> _{1/2} , V
[(η^4 -diene)Co(CO) ₂] ₂	1,1-dimethylsilole	-1.46
	1,1,3,4-tetramethylsilole	-1.55
	1,1,3,4-tetramethylgermole	-1.50
	2,3-dimethylbutadiene	-1.63
(η^4 -diene)Co ₂ (CO) ₆	1,1,3,4-tetramethylsilole	-1.57
	1,1,3,4-tetramethylgermole	-1.62
[(η^5 -C ₅ H ₅)Fe(CO) ₂] ₂ (CO) ₈ Co ₂		-1.49 ⁴⁵
		-0.3 ⁴⁵

^a Irreversible. Vs. a calomel-saturated electrode.

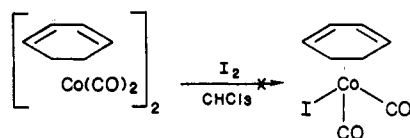
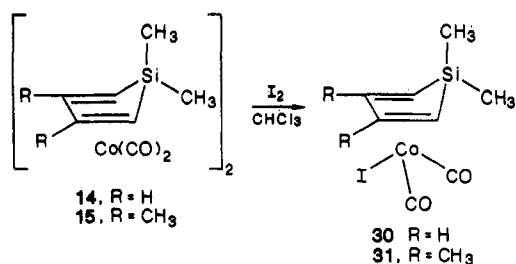
triphenylchlorotin (Scheme VI) affording complexes 26 and 27 which possess a cobalt-tin σ -bond. The same reaction is also possible with other diene complexes since 29 is obtained in a similar way. This behavior seems quite interesting since these cobalt anions are analogous to [(η^5 -C₅H₅)Fe(CO)₂]⁻ which is the only transition-metal anion which reacts with R₃SiCl giving products with Fe-Si bonds.⁴³ Unfortunately, these cobalt anions do not react with either R₃SiCl (R₃ = Ph₃, Ph₂Me) or with RI (R = CH₃, allyl, benzyl).

Complex 26 undergoes easy replacement of carbonyl by a phosphine under UV irradiation affording 28, which possesses a chiral cobalt atom. This reaction is also

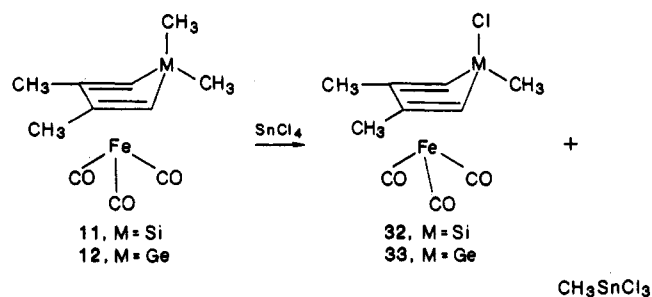
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Scheme VII



Scheme VIII



characteristic of complexes having iron-group 14 element σ -bonds.⁴⁴

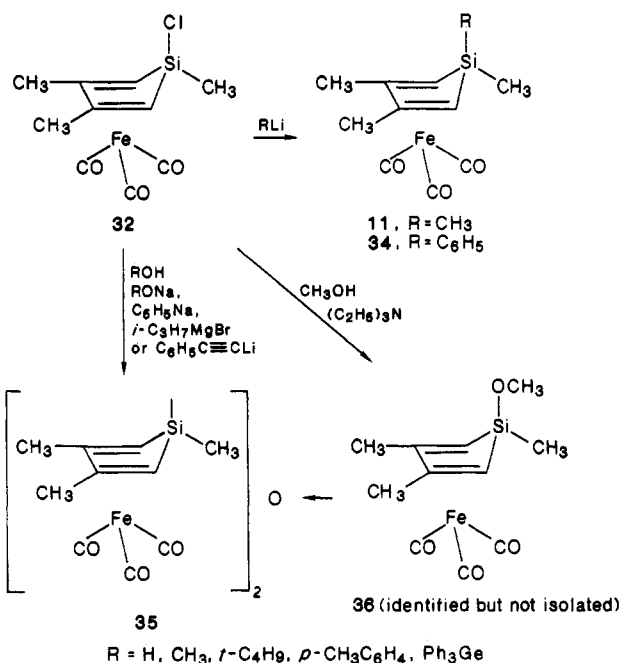
In order to test the similarities and differences between the iron and cobalt anions, we have studied the electrochemical reduction of a variety of dimers (Table II).

The reduction potentials of the metallole cobalt dimers are quite close to that of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ and much lower than that of $\text{Co}_2(\text{CO})_8$.⁴⁵ However, $[(\eta^4\text{-dimethylbutadiene})\text{Co}(\text{CO})_2]_2$ has a reduction potential in the same range, showing the small influence of the group 14 element. The reductions of the $(\eta^4\text{-diene})\text{cobalt}$ complexes are all irreversible in cyclic voltammetry.

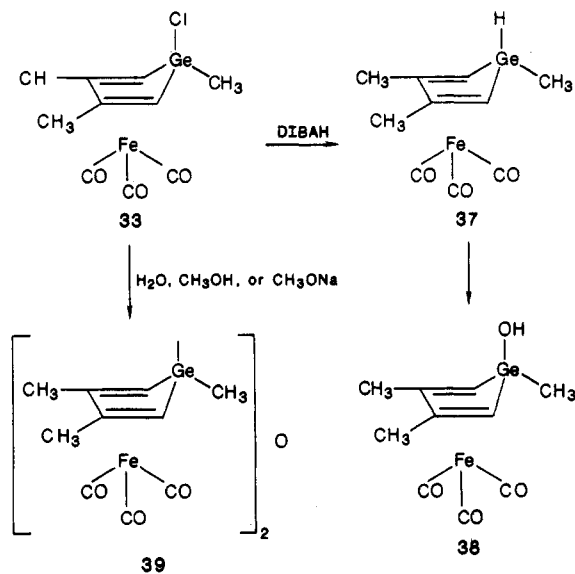
Treatment of bimetallic complexes **14** and **15** with iodine leads to the cleavage of the metal-metal bond, affording the corresponding iodides **30** and **31**, respectively (Scheme VII). This is a typical reaction of bimetallic complexes;⁴⁶ however, in the case of $[(\eta^4\text{-diene})\text{Co}(\text{CO})_2]_2$ the products can not be isolated.³⁷ The gain in stability seems to be due to the presence of the silicon atom in the ring rather than to the cyclic system itself, since bis $[(\eta^4\text{-1,3-cyclohexadiene})\text{dicarbonylcobalt}]$ does not lead to an isolable iodide.

(ii) **Reactions at Silicon or Germanium.** C-Phenylated silole and germole complexes of iron tricarbonyl show a peculiar reactivity of the exo substituent at silicon, which is easily cleaved by a variety of reagents.^{8,47,48} Iron tricarbonyl complexes of the non-phenylated metalloles, described here, undergo exo methyl cleavage with SnCl₄ (Scheme VIII). From the cleavage of CH₃-Si, CH₃SnCl₃ is identified by its ¹H NMR spectrum and by its melting point.³² Treatment of **11** with other reagents (ICl, CH₃OH under UV light, or HClO₄/Hg-

Scheme IX



Scheme X



(OAc)₂) does not lead to isolable products.

The silicon-chlorine bond in complex **32** is very reactive; however, there are some limitations to the isolation of the products. Reactions of complex **32** are summarized in Scheme IX. Only methyl- and phenyllithium replace the Si-Cl bond, while, surprisingly, sodium cyclopentadienide, isopropylmagnesium bromide, and lithium phenylacetylide lead to the siloxane complex **35**, the formation of which is also observed when **32** is treated with water, alcohols, phenols, alkoxides, and phenoxides. Complex **32** is not converted into **35** during a similar workup in the absence of the other reagents. In the presence of triethylamine, the methoxy complex **36** is identified by ¹H NMR in the reaction mixture but converts into **35** during crystallization or standing in a dry atmosphere.

Reaction of **32** with $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ gives mostly $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$, but traces of a complex having an Fe-Si σ -bond are obtained as indicated by its IR spectrum.³¹

The germanium chloride **33** reacts with diisobutyl-aluminum hydride, giving the hydrido derivative **37**

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(Scheme X). Complex **37** is identified in the crude mixture by ^1H NMR spectroscopy, which shows the Ge-H as a quartet and Ge-CH₃ as a doublet, but during isolation it converts into the hydroxy complex **38** which decomposes during attempted isolation. The germoxane complex **39** is obtained by treatment of **33** with water or with sodium methoxide in methanol. Reaction of **33** with AgBF₄ does not give a cationic complex, contrary to the previous observation in the phenyl-substituted series.⁹

The formation of siloxane or germoxane complexes is difficult to rationalize. Siloxanes can be obtained from alkoxy silanes, but only by employing vigorous conditions.⁴⁹ The presence of water or oxygen is carefully avoided; however, in another set of reactions, Curtis⁴³ pointed out that the affinity of silicon for oxygen is such that an oxygen atom could be abstracted from the carbonyl ligands.

Conclusion

Siloles and germoles, without phenyl substituents, behave as good η^4 -ligands in transition-metal chemistry. They are strongly attached to the metal and are not displaced by phosphines.⁴² The absence of aromatic groups

avoids the competition between coordination to the diene or to the aromatic system³⁸ with chromium.

In some cases the silicon atom is probably responsible for new properties, compared to other related η^4 -diene complexes, especially the cleavage of the dinuclear cobalt compounds by iodine. In this case, the η^4 -silole ring behaves as a pseudo η^5 ligand. This observation is in agreement with studies by photoelectron spectroscopy²⁹ that show a certain aromatic character of the silole ring in iron tricarbonyl complexes.

The reactivity of the silole ring is rather disappointing, since the only clean reaction is the cleavage with SnCl₄. Chlorine can be displaced by several nucleophiles, but in many cases the product is a siloxane complex.

The η^5 -silacyclopentadienyl system is not formed, confirming the difficulties in stabilizing sp² silicon atoms by coordination to a transition metal.⁵⁰

Acknowledgment. We are grateful to Drs. Guy Dabosi and Monique Martineau for help in the polarographic measurements.

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Photochemical Silene Syntheses. 3-Vinylsilacyclobutanes and Their Thermal Reactions

Robert T. Conlin* and Kevin L. Bobbitt

Center for Organometallic Research and Education, Department of Chemistry, North Texas State University, Denton, Texas 76203

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Photolysis of 1,1,2,2-tetramethyl-1,2-divinyl-1,2-disilane at room temperature in a cyclohexane solution of methoxytrimethylsilane yields 1,1-dimethyl-2-((vinyl dimethylsilyl)methyl)silene which is trapped in nearly quantitative yield by the methoxysilane. Reaction of the silene with butadiene affords the (*E*)- and (*Z*)-1,1-dimethyl-2-((vinyl dimethylsilyl)methyl)-3-vinyl-1-silacyclobutanes in 42 and 29% yields, respectively, along with minor amounts of 1,1-dimethyl-2-((vinyl dimethylsilyl)methyl)-1-silacyclohex-3-ene (8%). Low-pressure flow pyrolysis at 450 °C of either the *E* or *Z* isomer provides a relatively mild thermal source of the silene in the gas phase. Two products, 1,1,3,3-tetramethyldisilacyclohex-4-ene and 2,2,5,5-tetramethyl-2,5-disilabicyclo[2.1.1]hexane, are formed from an intramolecular rearrangement of the silene. Other reactions of the 3-vinylsilacyclobutanes include geometric isomerization, ring expansion to the silacyclohex-3-ene, and a homodienyl 1,5-hydrogen shift to 3,3,6,6-tetramethyl-3,6-disiladeca-1,4,8-triene.

Until the recent isolation and convincing spectroscopic characterization of molecules possessing a silicon-carbon π bond by Brook,^{1,2} the existence of silenes had been inferred from analogy to the reactivity of alkenes. In the early stages, perhaps the clearest example of an expected similarity was the facility with which silacyclohex-3-enes are formed in the thermal reactions between the silicon-carbon π bond and butadiene.³ The 2 + 4 cycloaddition

thus, with a singular exception, served as a diagnostic for the formation of a silene. That exception was one reported by Jones⁴ in which the silene, generated at low temperature by a novel method, produced predominantly 2- and 3-vinyl-substituted silacyclobutanes. This atypical example prompted further investigation of the silene/diene reaction at temperatures where the vinylsilacyclobutane might remain stable.⁵

A clean photochemical source of silenes is 1,2-divinyl-1,1,2,2-tetramethyldisilane (1).⁶ Ishikawa and co-workers

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(5) We have learned recently that another silene, generated photochemically from an acylpolysilane, gives predominantly 2 + 2 products with butadiene. In addition, the 2 + 2 pathway with butadiene proceeds in the absence of light with a stable silene. Brook, A. G. XXI Organosilicon Symposium, Tarrytown, NY Apr 1986.