(1) Å, respectively, are observed. However, the greater number or larger size of the $\sigma$-donor ligands attached to each Mo atom in these compounds as compared to **4** requires a greater canting of the corresponding pairs of five-membered rings. In turn, the resultant smaller average Fv(n)-Mo-Cp(n) angles in **5** and **6** of 140.4° and 134.8°, respectively, provide additional space to accommodate a shorter Mo-Mo separation. In contrast, the more parallel orientation of the corresponding pairs of rings in **4** introduces a greater degree of interring repulsion (between the two methylcyclopentadienyl rings) that can only be relieved by a longer Mo-Mo distance. The closest inter-ring contacts (calculated on the basis of an idealized C-H bond distance of 1.09 Å) are 1.97 and 2.11 Å for H5···H19 and H6···H18, respectively. Weak metal-metal single bonds are not that uncommon in sterically crowded dinuclear organometallic compounds. Similar arguments have been presented by Cotton, Muetterties, and their co-workers to rationalize the elongated Cr-Cr bonds of 3.281 (1) Å in $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$[24] and of 3.341 (1) Å in $[(\eta^5\text{-}C_5H_5)Cr(CO)_2P(OCH_3)_3]_2$.[25]

Since the methyl substituents do not play a significant steric role in the structure of **4**, one would expect a similarly elongated Mo-Mo bond in **3**. This structural feature presumably explains the relative ease by which the Mo-Mo bond in **3** can be ruptured by CO as well as accounts for the compound's apparent fluxional behavior in solution.[3]

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**Registry No.** 4, 101033-26-5; $KC_5H_4CH_3$, 41066-45-9; $Mo_2(O_2CCH_3)_4$, 14221-06-8; Mo, 7439-98-7.

**Supplementary Material Available:** Tables of refined thermal parameters, hydrogen bond distances and angles, least-squares planes of interest, and observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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# Coordination Chemistry of Group 14 Metalloles. 2.[†] Functional 2,5-Diphenylsilacyclopentadienes[‡] and Their Use as $\eta^4$-Ligands

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The reactions of 1,4-dilithio-1,4-diphenylbutadiene with several di- and trichloro- (or trimethoxy-) silanes lead to the formation of the corresponding silicon-substituted 2,5-diphenylsilacyclopentadienes. The compounds thus obtained are **1** (H, Cl), **2** (Me, H), **3** (Me, $Me_3Si$), **4** (Me, vinyl), **5** (Me, MeO), **6** (vinyl, MeO), **7** (allyl, MeO), **8** ($Me_3Si$, MeO), **9** (H, H), **10** (Me, Cl), **11** (Me, allyl), **12** (vinyl, H), **13** (allyl, H), and **14** ($Me_3Si$, H). The use of siloles **2**, **3**, **11**, and **15** as ligands was studied, and $\eta^4$-silole complexes with iron, cobalt, and nickel are described. Reaction of monosubstituted cobalt complexes with an excess of the ligand gives the corresponding disubstituted ones. The cobalt-cobalt bonds are cleaved with sodium amalgam, and the anions thus formed are trapped with triphenyltin chloride. The crystal structure of bis($\eta^4$-1,1-dimethyl-2,5-diphenylsilacyclopentadiene)nickel (**16**) shows that nickel is tetrahedral and that the quasi-planar free ligand is bent (dihedral angle between the dienic plane and the C(2)-Si-C(5) one $\approx 20°$). This complex crystallizes with one molecule of cyclohexane per three molecules of **16**.

## Introduction

Transition-metal complexes of siloles are well-known,[3] and in all complexes reported thus far the silole functions as an $\eta^4$-ligand. The earliest studies focused on the readily available 2,3,4,5-tetraphenylsilacyclopentadiene complexes and later on the 2,5-diphenylsilacyclopentadiene system. Since the most recent summary of silole derivative chemistry,[3] metal carbonyl complexes of C-unsubstituted siloles[1,4] as well as of 3,4-dimethylsilacyclopentadiene[5] have been reported.

Still unreported, however, is the generation or detection of an ($\eta^5$-silacyclopentadienyl)metal complex. A complex of $\eta^5$-silole could, in principle, be formed from reaction of an ionic silole with a metal derivative or by reaction of a coordinated $\eta^4$-silole. In either approach, silicon functional

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[†] Part 1, see ref 1.

[‡] For a preliminary communication see ref 2.

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precursors are required. Although attractive from the standpoint of simplicity, functional siloles without substituents on carbon have not yet been prepared as the methods used to introduce unsaturation at carbon are not compatible with the presence of the normal functional groups at silicon.[6] Of the carbon-substituted siloles where the method of synthesis lends itself to incorporation of functional groups at silicon, the system chosen for study was the 2,5-diphenyl series in preference to the 2,3,4,5-tetraphenyl series. By eliminating two phenyl substituents, some simplification in isolation, purification, and identification is anticipated. Also, with increased phenyl substitution, access to the $\eta^5$-system may be more difficult as observed in the carbon analogue.[7]

Functional siloles are known in the 2,3,4,5-tetraphenyl series,[8] and 1-methyl-2,5-diphenylsilole is briefly mentioned in one report[9] without any suitable synthesis.

The functional siloles of the 2,5-diphenyl series will allow the investigation of reactivity at the silicon atom, the use as $\eta^4$-ligands in transition-metal chemistry, and the comparison of the reactivity of complexed and uncomplexed siloles in addition to possible preparation of ($\eta^5$-silacyclopentadienyl)metal complexes.

In this report we describe the synthesis of functional 2,5-diphenylsiloles and conditions for the preparation of complexes with iron, cobalt, and nickel. The first crystal structure of a bis(silole) derivative of nickel is also included.

## Experimental Section

All reactions were carried out under nitrogen or argon by using a vacuum line and Schlenk tubes in the case of the transition-metal complexes. Solvents were dried and distilled before use. (Vinyl)Si(OMe)$_3$, (allyl)Si(OMe)$_3$, and MeHSiCl$_2$ were kindly provided by Rhône-Poulenc Spécialités Chimiques. Me(CH$_2$=CH)SiCl$_2$ was purchased from Fluka. The following starting materials were prepared by literature methods: MePh$_2$SiSiMe$_3$,[10] Ph$_3$SiSiMe$_3$,[11] MeCl$_2$SiSiMe$_3$,[12] Cl$_3$SiSiMe$_3$,[12] 1,1-dimethyl-2,5-diphenylsilacyclopentadiene (**15**),[8d] 1,4-dilithio-1,4-diphenylbutadiene,[8d] Fe$_2$(CO)$_9$,[13a] Ni(COD)$_2$,[14] and Me$_3$SiSi(OMe)$_3$.[15] 1-(Trimethylsilyl)-1-methyl-2,5-diphenylsilacyclopentadiene (**3**) was prepared according to Barton[16] but with a mixture of hexane/THF (1/1) as a solvent and a reaction time of 30 h at 50 °C.

Photochemical reactions were performed with a 100-W or a 450-W medium-presure 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 or EM 390 spectrograph (chemical shifts, $\delta$, are relative to Me$_4$Si), and mass spectra on a JEOL JMS-D 100 spectrometer.

The functional siloles obtained are yellow crystals which usually change with time, giving sticky compounds. In several cases (**2**, **4**, **6**, **7**, **9**, **11**, and **12**) these decompositions made it impossible to obtain a good analysis. They are best kept under nitrogen at −20 °C. The nickel complex **20** also decomposed with time.

**1-Hydro-1-methyl-2,5-diphenylsilacyclopentadiene (2).** A solution of 1,4-dilithio-1,4-diphenylbutadiene, prepared from 10 g (27.5 mmol) of the corresponding dibromide in 300 mL of diethyl ether at 0 °C, was added dropwise to a solution of 2.9 mL (27.5 mmol) of MeHSiCl$_2$ in 50 mL of diethyl ether and stirred for 1 h at 0 °C. Hydrolysis with a cold saturated solution of NH$_4$Cl, followed by extraction with diethyl ether, drying over MgSO$_4$, and evaporation of the solvent, gave an oil which was crystallized from hexane to give 2.86 g (42 %) of yellow **2**: mp 97–98 °C; $^1$H NMR (CCl$_4$) $\delta$ 7.5–7.2 (m, 12 H, aromatic and ethylenic), 5.00 (q, 1 H, Si–H), 0.60 (d, 3 H, methyl); IR (CCl$_4$) $\nu_{\mathrm{SiH}}$ 2125 cm$^{-1}$. Anal. Calcd for C$_{17}$H$_{16}$Si: C, 85.66; H, 5.23. Found: C, 84.66; H, 5.75.

**1-Methyl-1-vinyl-2,5-diphenylsilacyclopentadiene (4).** A solution of 1,4-dilithio-1,4-diphenylbutadiene prepared from 3.64 g (10 mmol) of the corresponding dibromide in 25 mL of hexane at 0 °C was added dropwise to a solution of 1.3 mL (10 mmol) of Me(CH$_2$=CH)SiCl$_2$ in 10 mL of THF at 0 °C and stirred at room temperature for 24 h. Workup as above gave 1.45 g (51%) of silole **4**: mp 51 °C; $^1$H NMR (CCl$_4$) $\delta$ 7.7–6.9 (m, 12 H, aromatic and ethylenic), 6.35–6.00 (m, 3 H, vinyl), 1.55 (s, 3 H, methyl); mass spectrum, *m/e* (assignment) 274 (molecular peak).

**Synthesis of Compounds 5–8.** These compounds were prepared by using the same procedure as for **2**, except that the reaction mixture was stirred at room temperature for 4 h (prolonged stirring markedly decreased the yields). The starting silanes were the corresponding trimethoxysilanes: RSi(OMe)$_3$ with R = Me, CH$_2$=CH, CH$_2$=CHCH$_2$, Me$_3$Si, and OMe.

**5**: 70% yield; mp 122–124 °C; $^1$H NMR (CCl$_4$): $\delta$ 7.5–7.0 (m, 12 H, aromatic and ethylenic), 3.4 (s, 3 H, CH$_3$O), 0.50 (s, 3 H, methyl). Anal. Calcd for C$_{18}$H$_{18}$OSi: C, 77.60; H, 6.47. Found: C, 77.41; H, 6.49.

**6**: 50% yield; mp 86–90 °C; $^1$H NMR (CCl$_4$) $\delta$ 7.5–7.0 (m, 12 H, aromatic and ethylenic), 6.20 (s, 3 H, vinyl), 3.5 (s, 3 H, CH$_3$O); mass spectrum, *m/e* (assignment) 290 (molecular peak).

**7**: 40% yield; mp 62–64 °C; $^1$H NMR (CCl$_4$) $\delta$ 7.5–7.0 (m, 12 H, aromatic and ethylenic), 6.0–4.5 (m, 3 H, vinyl), 3.50 (s, 3 H, CH$_3$O), 2.00 (d, 2 H, $J$ = 8 Hz, CH$_2$).

**8**: not isolated pure; characterized as the hydro derivative **14** (see below).

**8a**: 70% yield; mp 103–104 °C; $^1$H NMR (CCl$_4$) $\delta$ 7.5–7.0 (m, 12 H, aromatic and ethylenic), 3.5 (s, 6 H, OMe). Anal. Calcd for C$_{18}$H$_{18}$O$_2$Si: C, 73.53; H, 6.12. Found: C, 73.44; H, 6.19.

**1,1-Dihydro-2,5-diphenylsilacyclopentadiene (9).** A solution of 1,4-dilithio-1,4-diphenylbutadiene, prepared from 5 g (13.7 mmol) of the corresponding dibromide in 150 mL of diethyl ether at 0 °C, was added dropwise to a solution of 1.4 mL (13.7 mmol) of HSiCl$_3$ in 30 mL of diethyl ether and the mixture stirred at 0 °C for 1 h. The solution was then filtered, added to a slurry of 0.520 g (13.7 mmol) of LiAlH$_4$ in 50 mL of diethyl ether, and stirred at room temperature for 1 h. The hydrolysis was performed by using a cold saturated NH$_4$Cl solution. After standard workup, the yellow solid obtained was recrystallized from hexane to give 1.92 g of yellow crystals of **9**; 60% yield; mp 145–146 °C (briefly mentioned by Rühlmann et al.[17]); $^1$H NMR (CCl$_4$) $\delta$ 7.5–7.0 (m, 12 H, aromatic and ethylenic), 4.80 (s, 2 H, SiH$_2$); IR (CCl$_4$) $\nu_{\mathrm{Si-H}}$ 2130 cm$^{-1}$; mass spectrum, *m/e* (assignment) 234 (molecular peak). Anal. Calcd for C$_{16}$H$_{14}$Si: C, 82.02; H, 6.02. Found: C, 81.36; H, 6.26.

**Synthesis of Compounds 12–14.** The reduction of the corresponding methoxysiloles was performed with LiAlH$_4$ in diethyl ether (*i*-Bu$_2$AlH in hexane in the case of **12**), at room temperature, using a 1:1 ratio of the reagents, a reaction time of 1 h, and a cold, saturated solution of NH$_4$Cl for the hydrolysis. The recrystallizations were performed with hexane as the solvent.

**12**: 90% yield; mp 63–65 °C; $^1$H NMR (CCl$_4$) $\delta$ 7.5–7.0 (m, 12 H, aromatic and ethylenic), 6.20 (s, 3 H, vinyl), 5.00 (m, 1 H, SiH); IR (CCl$_4$) $\nu$(Si–H) 2140 cm$^{-1}$; mass spectrum, *m/e* (assignment) 260 (molecular peak).

**13**: 60% yield; mp 65–67 °C; $^1$H NMR (CCl$_4$) $\delta$ 7.5–7.0 (m, 12 H, aromatic and ethylenic), 6.00–5.30 (m, 1 H, CH=), 4.95 (t, 1 H, SiH), 4.9–4.6 (m, 2 H, =CH$_2$), 2.00 (d, br, 2 H, CH$_2$); mass

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spectrum, *m/e* (assignment) 304 (molecular peak). Anal. Calcd for $C_{19}H_{18}Si$: C, 83.21; H, 6.56. Found: C, 83.04; H, 6.19.

14: 5% yield; mp 114–118 °C; $^1H$ NMR ($CCl_4$) $\delta$ 7.5–7.0 (m, 12 H, aromatic and ethylenic), 4.90 (s, 1 H, SiH), 0.10 (s, 9 H, $Me_3Si$); IR ($CCl_4$) $\nu_{Si-H}$ 2105 $cm^{-1}$.

**1-Methyl-1-chloro-2,5-diphenylsilacyclopentadiene (10).** A solution of 2 (3.01 g, 1.21 mmol) and $PCl_5$ (2.86 g, 1.37 mmol) in 60 mL of $CCl_4$ was heated at ~60 °C for 4 H. After this time the solvent was evaporated, and the residue was dissolved in hot hexane, filtered, and cooled at −20 °C. The yellow crystals were recrystallized from hot hexane to give 2.58 g (75%) of analytically pure material: mp 136–137.5 °C; $^1H$ NMR ($C_6D_6$) $\delta$ 7.5–6.6 (m, 12 H, aromatic and ethylenic), 0.56 (s, 3 H, methyl). Anal. Calcd for $C_{17}H_{15}ClSi$: C, 72.19; H, 5.35; Cl, 12.53. Found: C, 72.46; H, 5.64; Cl, 12.30.

**1-Methyl-1-allyl-2,5-diphenylsilacyclopentadiene (11).** To a solution of 4 g (16.1 mmol) of 2 in 100 mL of diethyl ether was added 0.211 g (~2%) of $(PPh_3)_2NiCl_2$ and then, dropwise, a tenfold excess of a solution of allylmagnesium bromide in diethyl ether (~1 M). After stirring at room temperature for 1 day (the disappearance of the $\nu_{SiH}$ was monitored by IR), standard workup gave 3 g (67%) of 11, after crystallization from hexane at −78 °C. Silole 11 is best stored at −20 °C: mp 58–59 °C; $^1H$ NMR ($CCl_4$) $\delta$ 7.25 (br m, 12 H, aromatic and ethylenic), 6.0–5.3 (m, 1 H, =CH), 4.75 (br d, 2 H, $=CH_2$), 2.00 (d, 2 H, $J$ = 7–8 Hz, $CH_2$), 0.55 (s, 3 H, methyl); mass spectrum, *m/e* (assignment) 288 (molecular peak).

**Bis($\eta^4$-1,1-dimethyl-2,5-diphenylsilacyclopentadiene)nickel (16).** To a solution of 15 (2.62 g, 10 mmol) and anhydrous nickel acetylacetonate (1.05 g, 5 mmol) in 50 mL of hexane cooled at 0 °C was added dropwise 25 mL of a 0.6 M solution of $Et_3Al$ in hexane for 30 min. The green solution turned deep red. The reaction mixture was stirred for 1 h at room temperature and then concentrated to ca. 25 mL and left at −78 °C. A gummy precipitate formed. Several crystallizations from hexane at −78 °C afforded deep red crystals of 16 (3.02 g, 50%); mp 125–126 °C; $^1H$ NMR ($C_6D_6$) $\delta$ 7.6–7.0 (m, 20 H, aromatic), 5.58 (d, 2 H, $J_{AB}$ = 4 Hz, $H_B$), 5.22 (d, 2 H, $J_{AB}$ = 4 Hz, $H_A$), 1.35 (s, 4 H, cyclohexane), 0.12 (s, 6 H, endo methyl), −0.05 (s, 6 H, exo methyl); mass spectrum, *m/e* (assignment for $^{58}Ni$) 582 (molecular peak). This complex crystallizes with one-third of a molecule of cyclohexane (see crystal structure). Anal. Calcd for $C_{38}H_{40}NiSi_2$: C, 74.67; H, 6.55. Found: C, 74.52; H, 6.33.

The same procedure using other solvents (*n*-pentane or *n*-heptane) and another reducing agent (*i*-$Bu_2AlH$) afforded 16 as a dark red gum, except when cyclohexane was added, in which case crystals were obtained as above.

**($\eta^4$-*exo*-1-(Trimethylsilyl)-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron (17).** Silole 3 (1.11 g, 3.43 mmol) and $Fe_2(CO)_9$ (1.87 g, 5.14 mmol) were heated at 50–60 °C in toluene (25 h). The originally yellow solution turned brick-red. The solvent was pumped off, and the remaining oil was extracted with hexane. Fractional crystallization gave brick-red crystals of 17 (1.0 g, 63%): mp 130 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 7.15–7.00 (m, 10 H, aromatic), 6.15 (s, 2 H, ethylenic), 1.23 (s, 3 H, methyl), −0.15 (s, 9 H, $Me_3Si$); IR (hexane) $\nu_{CO}$ 2040 (s, sh), 1980 (s, br) $cm^{-1}$; mass spectrum, *m/e* (assignment) 460 (molecular peak, 10), 432 ($M^+ - CO$, 32), 404 ($M^+ - 2CO$, 25), 376 ($M^+ - 3CO$, 100). Anal. Calcd for $C_{23}H_{24}FeO_3Si_2$: C, 59.99; H, 5.25. Found: C, 60.12; H, 5.36.

**($\eta^4$-*endo*-1-Allyl-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron (18).** The same procedure as for 17 was used, with a reaction time of 30 h. The solution became deep yellow and orange crystals were obtained: 30% yield; mp 156.5–157 °C; $^1H$ NMR ($C_6D_6$) $\delta$ 7.4–6.1 (m, 13 H, aromatic, ethylenic and =CH), 5.65 (s, 2 H, $=CH_2$), 1.70 (d, 2 H, $CH_2$), 0.10 (s, 3 H, methyl); IR (hexane) $\nu_{CO}$ 2050 (sh), 1980 (br) $cm^{-1}$; mass spectrum, *m/e* (assignment, relative intensity) 428 (molecular peak, 6), 400 ($M^+ - CO$, 33), 372 ($M^+ - 2CO$, 70), 344 ($M^+ -3CO$, 100), 288 ($M^+ - Fe(CO)_3$, 37), 247 ($M^+ - Fe(CO)_3 -$ allyl, 20). Anal. Calcd for $C_{23}H_{20}FeO_3Si_2$: C, 64.49; H, 4.71. Found: C, 64.81; H, 4.25.

**($\eta^4$-*exo*-1-(Trimethylsilyl)-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)hexacarbonyldicobalt (23).** A solution of the silole 3 (0.697 g, 2.18 mmol) in 20 mL of hexane was added to dicobaltoctacarbonyl (0.745 g, 2.18 mmol), and the mixture was stirred at room temperature for 35 h (the reaction was monitored by IR). The brown-red solution was filtered and cooled at −20 °C to give dark brown crystals of the title compound (0.834 g, 63%): mp 84 °C; $^1H$ NMR ($C_6D_6$) $\delta$ 7.5–6.8 (m, 10 H, aromatic), 6.00 (s, 2 H, ethylenic), 1.10 (s, 3 H, methyl), −0.20 (s, 9 H, $Me_3Si$); IR (hexane) $\nu_{CO}$ 2078, 2022, 1868, 1850 $cm^{-1}$. Anal. Calcd for $C_{26}H_{24}Co_2O_6Si$: C, 51.49; H, 3.99. Found: C, 51.19; H, 3.95.

**($\eta^4$-*exo*-1-Allyl-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)hexacarbonyldicobalt (24).** The same procedure as for 23 was used, with a reaction time of 6 h: brown crystals; 84% yield; mp 80 °C; $^1H$ NMR ($C_6D_6$) $\delta$ 7.60–6.76 (m, 10 H, aromatic), 5.85 (s, 2 H, ethylenic), 5.25–4.85 (m, 1 H, =CH), 4.65 (d, 2 H, $=CH_2$), 1.17 (d, 2 H, $CH_2$), 0.97 (s, 3 H, methyl); IR (hexane) $\nu_{CO}$ 2075, 2025, 2015 (sh), 1868, 1852 $cm^{-1}$. Anal. Calcd for $C_{26}H_{20}Co_2O_6Si$: C, 54.37; H, 3.51. Found: C, 54.15; H, 3.34.

**Bis[($\eta^4$-*exo*-1-(trimethylsilyl)-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)dicarbonylcobalt] (26).** A mixture of the complex 23 (0.476 g, 0.77 mmol) and 3 (0.247 g, 0.77 mmol) was heated in refluxing hexane (20 mL) for 4 h. The solution was filtered and cooled at −20 °C to give the title complex (0.400 g, 60%): mp 197 °C; $^1H$ NMR ($C_6D_6$) $\delta$ 7.45–6.65 (m, 20 H, aromatic), 5.90 (s, 4 H, ethylenic), 1.05 (s, 6 H, methyl), −0.10 (s, 18 H, $Me_3Si$); IR (hexane) $\nu_{CO}$ 2020, 1995, 1840 $cm^{-1}$. Anal. Calcd for $C_{44}H_{48}Co_2O_4Si_4$: C, 60.67; H, 5.55. Found: C, 60.37; H, 5.52.

**Bis[($\eta^4$-*exo*-1-allyl-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)dicarbonylcobalt] (27).** The same procedure as for 26 was used: red crystals; 60% yield; mp 118 °C; $^1H$ NMR ($C_6D_6$) $\delta$ 7.40–6.85 (m, 20 H, aromatic), 5.75 (s, 4 H, ethylenic), 5.88–5.08 (m, 2 H, =CH), 4.75 (d, 4 H, $=CH_2$), 1.35 (d, 4 H, $CH_2$), 0.95 (s, 6 H, methyl); IR (hexane) $\nu_{CO}$ 2020, 1995, 1842, 1822 $cm^{-1}$.

**($\eta^4$-*exo*-1-(Trimethylsilyl)-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)(triphenylstannyl)dicarbonylcobalt (28).** A solution of complex 23 (0.372 g, 0.61 mmol) in THF (20 mL) was treated with sodium amalgam (1 g of Na in 300 g of Hg, 4 h). The resulting solution was added to a solution of triphenyltin chloride (0.473 g, 1.23 mmol) in 10 mL of THF at room temperature and stirred for 2 h. The solvent was evaporated, and the dark red residue was extracted with hexane; fractional crystallization afforded first off-white crystals of $Ph_3SnCo(CO)_4$[13b] and then, after filtration, red crystals of the title compound (0.232 g, 45%): mp 122 °C; $^1H$ NMR ($C_6D_6$) $\delta$ 7.85–6.85 (m, 25 H, aromatic), 6.05 (s, 2 H, ethylenic), 1.15 (s, 3 H, methyl), −0.10 (s, 9 H, $Me_3Si$); IR (hexane) $\nu_{CO}$ 2018, 1975 $cm^{-1}$. Anal. Calcd for $C_{40}H_{39}CoO_2Si_2Sn$: C, 61.16; H, 5.00. Found: C, 61.05; H, 5.09.

**($\eta^4$-*exo*-1-Allyl-*endo*-1-methyl-2,5-diphenylsilacyclopentadiene)(triphenylstannyl)dicarbonylcobalt (29).** The same procedure as for 28 was used: 59% yield of red crystals; mp 132–132.5 °C; $^1H$ NMR ($C_6D_6$) $\delta$ 7.60–6.45 (m, 25 H, aromatic), 5.77 (s, 2 H, ethylenic), 5.60–4.90 (m, 1 H, =CH), 4.62 (d, 2 H, $=CH_2$), 1.30 (d, 2 H, $CH_2$), 1.00 (s, 3 H, methyl); IR (hexane) $\nu_{CO}$ 2015, 1915 $cm^{-1}$. Anal. Calcd for $C_{40}H_{35}CoO_2SiSn$: C, 63.77; H, 4.68. Found: C, 63.40; H, 4.84.

**($\eta^4$-1,1-Dimethyl-2,5-diphenylsilacyclopentadiene)(triphenylstannyl)dicarbonylcobalt (30).** The same procedure as above starting with 1.508 g (2 mmol) of 25.[21] The THF solution containing the anion was added dropwise to a solution of $Ph_3SnCl$ (1.54 g, 4 mmol) in 30 mL of THF at −78 °C. After 2 h the solution was allowed to warm to room temperature, the solvent was pumped off, and the residue was dissolved in ether and chromatographed on neutral alumina. An orange band was eluted (hexane/ether, 1/1). The solvent was pumped off and the residue crystallized from toluene/hexane to leave 1.3 g (45%) of orange crystals of 30: mp 156–157 °C; $^1H$ NMR ($C_6D_6$) $\delta$ 8.2–6.1 (m, 25 H, aromatic), 5.81 (s, 2 H, ethylenic), 1.00 (s, 3 H, *endo*-methyl), −0.12 (s, 3 H, *exo*-methyl); IR (hexane) $\nu_{CO}$ 2030, 1980 $cm^{-1}$. Anal. Calcd for $C_{38}H_{33}CoO_2SiSn$: C, 62.72; H, 4.54. Found: C, 62.72; H, 4.58.

**($\eta^4$-1-(Trimethylsilyl)-1-methyl-2,5-silacyclopentadiene)($\eta^4$-1,5-cyclooctadiene)nickel (20).** The reactions with nickel complexes were carried out under argon and in the dark. Silole 3 (1.247 g, 3.89 mmol), dissolved in 20 mL of toluene, was added dropwise to a suspension of $Ni(COD)_2$ (1.070 g, 3.89 mmol) in 30 mL of toluene at −78 °C, and then the mixture was allowed to warm slowly to room temperature. $Ni(COD)_2$ disappeared quickly, and a change of color from yellow to deep red was noticed at ~-40 °C. The reaction mixture was stirred at room temperature for 24 h. The solvent was pumped off and the residue extracted with hexane; the solution was left at -20 °C and gave 568 mg (30%) of red crystals of the title compound: mp 92 °C; $^1$H NMR ($C_6D_6$) (the complex is extremely sensitive in solution, and paramagnetic impurities were present; lines are broad, but the integrations are satisfactory; endo–exo assignments were not possible) $\delta$ 7.0 (10 H, aromatic), 5.1 (2 H, ethylenic), 4.6 and 3.9 (4 H, COD ethylenic), 1.6 (8 H, $CH_2$), 0.5 (3 H, methyl), 0.0 (9 H, $Me_3Si$); mass spectrum, *m/e* (assignment, relative intensity) 487 (molecular peak, 1.3), 378 ($M^+$ - COD, 4), 320 ($M^+$ - Ni(COD), 93), 305 ($M^+$ - Ni(COD) - Me, 100), 247 ($M^+$ - Ni(COD) - $Me_3Si$, 8).

**($\eta^4$-1-Allyl-1-methyl-2,5-diphenylsilacyclopentadiene)($\eta^4$-1,5-cyclooctadiene)nickel (21).** The same procedure as for **20** was used: red crystals; 68% yield; mp 73 °C dec; $^1$H NMR ($C_6D_6$) (same remarks as above) $\delta$ 7.15 (10 H, aromatic), 5.85 (1 H, =CH), 4.95, 4.5, 4.1 (8 H, other ethylenic protons), 1.7 (10 H, all $CH_2$), 0.2 (3 H, methyl). Anal. Calcd for $C_{28}H_{32}NiSi$: C, 73.86; H, 7.08. Found: C, 73.43; H, 7.23.

**($\eta^4$-*exo*-1-Methyl-*endo*-1-hydro-2,5-diphenylsilacyclopentadiene)tricarbonyliron (19).** The same procedure as for **17** was used, with a reaction time of 20 h. The solution became brown and yellow-brown crystals were obtained in 14% yield: mp 159–160 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.53–6.96 (m, 10 H, aromatic), 6.02 (s, 2 H, ethylenic), 5.47 (q, 1 H, SiH), 0.06 (d, 3 H, methyl); IR (hexane) $\nu_{CO}$ 2050, 1990, 1983 cm$^{-1}$; $\nu_{SiH}$ 2150 cm$^{-1}$; mass spectrum, *m/e* (assignment, relative intensity) 388 (molecular peak, 10), 360 ($M^+$ - CO, 60), 332 ($M^+$ - 2CO, 58), 304 ($M^+$ - 3CO, 100), 248 ($M^+$ - $Fe(CO)_3$, 26), 223 ($M^+$ - $Fe(CO)_3$ - Me, 23). Anal. Calcd for $C_{20}H_{16}FeO_3Si$: C, 61.87; H, 4.15. Found: C, 61.81; H, 4.08.

**($\eta^4$-*exo*-1-Methyl-*endo*-1-hydro-2,5-diphenylsilacyclopentadiene)($\eta^4$-1,5-cyclooctadiene)nickel (22).** To a suspension of $Ni(COD)_2$(1.2 g, 4 mmol) in 40 mL of toluene at -78 °C was added dropwise a solution of **2** (0.992 g, 4 mmol) in 20 mL of toluene. After the addition, the reaction mixture was allowed to warm slowly. At ~-25 °C it turned orange and was stirred for 12 h at room temperature. Then it was concentrated to ca. 15 mL, 50 mL of hexane was added, and the solution was left at -20 °C. A first crop of off-white crystals, identified as 1,4-diphenylbutadiene, was collected; the mother liquor was left at -20 °C to afford red-orange crystals which were recrystallized from toluene–hexane at -20 °C. Complex **22** (1.1 g, 66 %) was obtained as red-orange microcrystals: mp 115–116 °C; $^1$H NMR ($C_6D_6$) $\delta$ 7.6–7.0 (m, 10 H, aromatic), 5.20 (d, 2 H, *J* = 2 Hz, silole =CH), 4.63 (m, 1 H, *J* = 2 Hz and *J* = 5 Hz, SiH), 4.30, 4.16 (br s, 4 H, COD ethylenic), 1.73 (br s, 8 H, $CH_2$), 0.23 (d, 3 H, *J* = 5 Hz, methyl); IR ($C_6H_6$) $\nu_{SiH}$ 2120 cm$^{-1}$; mass spectrum, *m/e* (assignment for $^{58}$Ni) 414 (molecular peak). Anal. Calcd for $C_{25}H_{28}NiSi$: C, 72.34; H, 6.74. Found: C, 71.98; H, 6.66.

**Crystal Structure of Bis($\eta^4$-1,1-dimethyl-2,5-diphenylsilacyclopentadiene)nickel (16). Crystal Preparation.** Crystals of complex **16** were grown by slowly cooling to -18 °C a hexane solution in a nitrogen atmosphere. Black, elongated rectangular blocks were obtained. Preliminary Weissenberg and precession photographs established an orthorhombic unit cell with space group *Fdd*2 (no. 43). A small block was cut from a needle and was sealed inside a Lindemann glass capillary with the [001] direction parallel to the $\phi$ axis of the diffractometer.

**X-ray Data Collection.** Data were collected on a CAD-4 automated diffractometer with graphite-monochromatized Mo K$\alpha$ radiation ($\lambda$ = 0.710 69 Å). Lattice constants (Table I) came from a least-squares refinement of 24 reflections obtained in the range $12 < 2\theta < 30°$. 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 $\sigma(F)/F < 0.35$ were considered to be observed. The changes in the intensities due to absorption were calculated. The largest effect found was a 13% decrease of the observed intensity, and hence, absorption corrections on the *F*'s were neglected.

**Structure Determination and Refinement.** The Ni and Si coordinates were given by direct methods (1980 version of the MULTAN program). A Fourier map phased on these atoms revealed 17 carbon atoms belonging to the methyl groups, to the silole rings, and partly to the phenyl rings. The remaining carbon atoms were located in two succeeding difference Fourier syntheses. The atomic scattering factors were taken from ref 18. Three cycles of least-squares refinement decreased the *R* factor to 0.09.

**Table I. Summary of Crystal Data, Intensity Collection, and Refinement**

| | |
|---|---|
| formula | $C_{36}H_{36}NiSi_2$ |
| cryst system | orthorhombic |
| space group | *Fdd*2 |
| *a*, Å | 24.8425 (35) |
| *b*, Å | 48.3145 (83) |
| *c*, Å | 11.2110 (29) |
| vol, Å$^3$ | 13 456 |
| mol wt | 583.6–625.6$^a$ |
| *Z* | 16 |
| $d_{calcd}$, g cm$^{-3}$ | 1.152–1.235$^a$ |
| $d_{measd}$, g cm$^{-3}$ | 1.22 (7) |
| cryst size, mm$^3$ | 0.35 × 0.30 × 0.08 |
| cryst color | dark red |
| recrystn solv | hexane |
| mp, °C | 125–126 |
| method of data collectn | moving cryst–moving counter |
| radiatn (graphite monochromated) | Mo K$\alpha$ |
| $\mu$, cm$^{-1}$ | 6.23 |
| $2\theta$ limits, deg | 4–40; 40–50 |
| no. of unique reflectns | 3243 |
| no. of obsd reflectns | 973 |
| final no. of variables | 165 |
| *R* | 0.062 |
| $R_w$ | 0.061 |
| residual elect density | 0.48 |

$^a$Calculated with 0.5 molecule of cyclohexane per molecule of complex **16**.

At this stage three broad and weak peaks appeared in the difference Fourier map. As they were located near a 2-fold axis, these peaks could reveal the presence of either a benzene or a disordered cyclohexane molecule inside a cavity surrounded by eight phenyl rings belonging to *six* different molecules of the complex. A careful examination of the $^1$H NMR spectrum of the complex showed no detectable benzene signal, but the impurity at 1.35 ppm could match with the cyclohexane signal. This was further checked by adding a slight amount of cyclohexane to the NMR sample. Several refinement cycles showed that the cavity was only partially occupied. An occupancy factor of 0.6 was determined from the NMR spectrum. This factor, along with a large common isotropic temperature factor, was kept fixed in the last least-squares refinements (see Table II). Due to the low number of observed intensities, every increase in the number of parameters failed to improve the accuracy of the refinement: an attempt to convert Ni and Si isotropic thermal parameters to anisotropic ones, keeping the same set of 973 reflections, did not lead to convergence but to values of $|\delta/\sigma|$ as large as 3.1; another attempt to use slightly more reflections ($\sigma(F)/F < 0.37$) and anisotropic thermal parameters of the Ni and Si atoms gave the following results $N_0$ = 1009, $N_v$ = 180, *R* = 0.057, and $R_w$ = 0.056; but the standard deviations computed in the last cycle for bond distances and angles were generally slightly larger than those in Tables III and IV.

The final atomic coordinates with the associated thermal parameters are listed in Table II. The labeling scheme is given in Figure 1. Individual bond lengths are listed in Table III and important bond angles in Table IV. A list of observed and calculated structure factors (Table V) is available as supplementary material.

## Results and Discussion

**Preparation of Functional Silacyclopentadienes.** Reaction of 1,4-dilithio-1,4-diphenylbutadiene[8d] with

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(18) Doyle, P. A.; Turner, P. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 390.

**Table II. Fractional Atomic Parameters ($\times 10^4$) and Thermal Parameters for Complex 16**

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| Ni | 2408.3 (9) | 985.8 (4) | 5000 | 3.38 (6) |
| Si(1) | 2032 (2) | 784 (1) | 2820 (7) | 4.07 (14) |
| Si(2) | 2761 (2) | 781 (1) | 7170 (7) | 3.98 (14) |
| C(1) | 1712 (6) | 762 (4) | 4331 (17) | 2.8 (4) |
| C(2) | 1608 (7) | 1029 (4) | 4714 (22) | 4.0 (5) |
| C(3) | 1922 (7) | 1245 (4) | 4064 (22) | 4.0 (4) |
| C(4) | 2246 (8) | 1159 (4) | 3155 (22) | 3.9 (4) |
| C(5) | 2632 (8) | 1153 (4) | 6811 (21) | 4.0 (4) |
| C(6) | 2959 (7) | 1234 (4) | 5854 (22) | 3.9 (4) |
| C(7) | 3213 (7) | 1000 (4) | 5232 (23) | 4.5 (5) |
| C(8) | 3062 (7) | 735 (4) | 5673 (21) | 3.8 (5) |
| C(11) | 1433 (8) | 521 (4) | 4830 (24) | 4.7 (5) |
| C(12) | 1682 (8) | 255 (5) | 4753 (24) | 5.2 (5) |
| C(13) | 1396 (10) | 31 (5) | 5283 (29) | 7.0 (7) |
| C(14) | 907 (11) | 67 (5) | 5885 (28) | 6.9 (7) |
| C(15) | 670 (9) | 319 (5) | 5984 (25) | 6.0 (6) |
| C(16) | 942 (9) | 566 (5) | 5455 (22) | 5.3 (5) |
| C(21) | 2588 (7) | 1330 (4) | 2468 (23) | 3.7 (4) |
| C(22) | 2534 (9) | 1611 (5) | 2562 (27) | 6.3 (6) |
| C(23) | 2882 (10) | 1791 (6) | 1827 (27) | 7.1 (7) |
| C(24) | 3230 (10) | 1687 (6) | 1061 (29) | 6.9 (7) |
| C(25) | 3272 (10) | 1415 (5) | 939 (27) | 7.1 (7) |
| C(26) | 2962 (9) | 1226 (5) | 1663 (25) | 6.4 (6) |
| C(31) | 2315 (7) | 1362 (4) | 7514 (22) | 3.6 (4) |
| C(32) | 2190 (9) | 1298 (5) | 8704 (25) | 5.8 (6) |
| C(33) | 1901 (9) | 1480 (5) | 9418 (25) | 6.5 (6) |
| C(34) | 1733 (10) | 1742 (5) | 8945 (28) | 6.5 (6) |
| C(35) | 1882 (9) | 1800 (5) | 7727 (26) | 6.1 (6) |
| C(36) | 2161 (8) | 1610 (4) | 7060 (21) | 4.8 (5) |
| C(41) | 3295 (8) | 485 (4) | 5153 (23) | 4.4 (5) |
| C(42) | 3060 (8) | 232 (5) | 5466 (23) | 5.4 (5) |
| C(43) | 3264 (10) | −32 (5) | 4921 (29) | 7.3 (6) |
| C(44) | 3694 (11) | −13 (5) | 4219 (26) | 6.2 (6) |
| C(45) | 3967 (10) | 226 (5) | 3968 (26) | 6.6 (7) |
| C(46) | 3757 (8) | 486 (4) | 4461 (23) | 4.6 (5) |
| Me(1) | 1534 (8) | 785 (5) | 1589 (22) | 5.3 (6) |
| Me(2) | 2566 (8) | 532 (4) | 2403 (26) | 5.5 (5) |
| Me(3) | 2152 (8) | 559 (5) | 7593 (25) | 5.5 (5) |
| Me(4) | 3272 (9) | 714 (5) | 8390 (23) | 5.4 (6) |
| Hx(1)[a] | 1927 (21) | 2555 (12) | 4862 (76) | 12 |
| Hx(2) | 2122 (22) | 2265 (11) | 4772 (60) | 12 |
| Hx(3) | 2717 (23) | 2223 (11) | 4807 (66) | 12 |

[a] Hx(1) to Hx(3) are half of the atoms of a molecule of cyclohexane located around the special positon: $^1/_4$, $^1/_4$, 0.4813 (see text).

**Table III. Bond Lengths (Å) for Complex 16 (Esd's in Parentheses)**

| | | | |
|---|---|---|---|
| Ni–C(1) | 2.175 (17) | C(11)–C(12) | 1.43 (3) |
| Ni–C(2) | 2.025 (18) | C(12)–C(13) | 1.43 (4) |
| Ni–C(3) | 2.032 (21) | C(13)–C(14) | 1.40 (4) |
| Ni–C(4) | 2.268 (24) | C(14)–C(15) | 1.36 (3) |
| Ni–C(5) | 2.256 (23) | C(15)–C(16) | 1.49 (3) |
| Ni–C(6) | 2.057 (21) | C(16)–C(11) | 1.42 (3) |
| Ni–C(7) | 2.017 (18) | C(21)–C(22) | 1.37 (3) |
| Ni–C(8) | 2.162 (20) | C(22)–C(23) | 1.48 (4) |
| | | C(23)–C(24) | 1.32 (4) |
| Si(1)–Me(1) | 1.855 (24) | C(24)–C(25) | 1.32 (4) |
| Si(1)–Me(2) | 1.859 (22) | C(25)–C(26) | 1.45 (4) |
| Si(1)–C(1) | 1.875 (20) | C(26)–C(21) | 1.39 (3) |
| Si(1)–C(4) | 1.925 (22) | C(31)–C(32) | 1.40 (4) |
| Si(2)–Me(3) | 1.914 (22) | C(32)–C(33) | 1.39 (4) |
| Si(2)–Me(4) | 1.896 (25) | C(33)–C(34) | 1.43 (4) |
| Si(2)–C(5) | 1.870 (22) | C(34)–C(35) | 1.44 (4) |
| Si(2)–C(8) | 1.853 (23) | C(35)–C(36) | 1.37 (3) |
| | | C(36)–C(31) | 1.36 (3) |
| C(1)–C(11) | 1.47 (3) | C(41)–C(42) | 1.40 (3) |
| C(1)–C(2) | 1.38 (3) | C(42)–C(43) | 1.50 (4) |
| C(2)–C(3) | 1.50 (3) | C(43)–C(44) | 1.33 (4) |
| C(3)–C(4) | 1.36 (3) | C(44)–C(45) | 1.37 (4) |
| C(4)–C(21) | 1.41 (3) | C(45)–C(46) | 1.47 (3) |
| | | C(46)–C(41) | 1.39 (3) |
| C(5)–C(31) | 1.50 (3) | | |
| C(5)–C(6) | 1.40 (3) | Hx(1)–Hx(3′) | 1.39 (8) |
| C(6)–C(7) | 1.47 (3) | Hx(1)–Hx(2) | 1.49 (8) |
| C(7)–C(8) | 1.42 (3) | Hx(2)–Hx(3) | 1.49 (8) |
| C(8)–C(41) | 1.46 (3) | Hx–Hx | 1.452[a] |

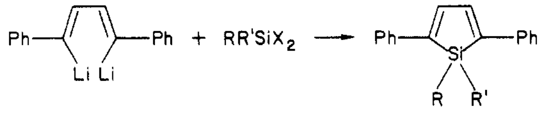
[a] Calculated value for a hexagone corresponding to a cyclohexane molecule projection on a plane perpendicular to the $\vec{C}$ axis of the crystal.

**Table IV. Important Bond Angles (deg) for Complex 16**

| | | | |
|---|---|---|---|
| C(1)–Ni–C(2) | 38.3 (8) | Si(1)–C(1)–C(11) | 126.2 (15) |
| C(2)–Ni–C(3) | 43.3 (8) | Si(1)–C(1)–C(2) | 107.9 (15) |
| C(3)–Ni–C(4) | 36.5 (8) | C(11)–C(1)–C(2) | 122.2 (18) |
| C(1)–Ni–C(4) | 74.1 (7) | C(1)–C(2)–C(3) | 113.7 (18) |
| C(5)–Ni–C(6) | 37.6 (8) | C(2)–C(3)–C(4) | 117.3 (19) |
| C(6)–Ni–C(7) | 42.3 (9) | C(21)–C(4)–C(3) | 125.6 (20) |
| C(7)–Ni–C(8) | 39.6 (8) | Si(1)–C(4)–C(3) | 105.8 (15) |
| C(5)–Ni–C(8) | 72.6 (8) | Si(1)–C(4)–C(21) | 127.5 (17) |
| C(1)–Si(1)–C(4) | 89.7 (9) | Si(2)–C(5)–C(31) | 128.4 (17) |
| C(1)–Si(1)–Me(1) | 113.0 (9) | Si(2)–C(5)–C(6) | 109.5 (15) |
| C(1)–Si(1)–Me(2) | 119.6 (11) | C(31)–C(5)–C(6) | 121.3 (19) |
| C(4)–Si(1)–Me(1) | 109.1 (10) | C(5)–C(6)–C(7) | 113.4 (19) |
| C(4)–Si(1)–Me(2) | 117.8 (9) | C(6)–C(7)–C(8) | 114.5 (20) |
| Me(1)–Si(1)–Me(2) | 106.9 (12) | C(41)–C(8)–C(7) | 120.0 (19) |
| | | Si(2)–C(8)–C(7) | 108.3 (16) |
| C(5)–Si(2)–C(8) | 89.4 (10) | Si(2)–C(8)–C(41) | 128.5 (17) |
| C(5)–Si(2)–Me(3) | 117.2 (9) | | |
| C(5)–Si(2)–Me(4) | 115.8 (10) | Hx(3′)–Hx(1)–Hx(2) | 121 (5)[a] |
| C(8)–Si(2)–Me(3) | 118.4 (11) | Hx(1)–Hx(2)–Hx(3) | 117 (5) |
| C(8)–Si(2)–Me(4) | 111.3 (10) | Hx(2)–Hx(3)–Hx(1′) | 122 (5) |
| Me(3)–Si(2)–Me(4) | 104.7 (11) | | |

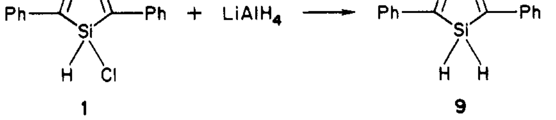
[a] Hx(3′) and Hx(1′) are derived from the coordinates of carbons Hx(3) and Hx(1) through the symmetry transformation ($^1/_2 - x$, $^1/_2 - y$, $z$)

chloro- and alkoxysilanes provides cyclized products as shown in eq 1. The cyclization reaction has some limitations when the chlorosilanes are employed. Attempts to condense the dilithio reagent with the dichlorosilane $MeSi(CH_2Cl)Cl_2$ gave product mixtures that did not appear to contain the expected silole. Only the trifunctional chlorosilanes $HSiCl_3$ and $MeHSiCl_2$ could be successfully converted to siloles, and an attempt to prepare a spiro derivative from LiPhC=CHCH=CPhLi and $SiCl_4$ failed. Such difficulties in silole formation have not been reported for reactions of LiPhC=CPhPhC=CPhLi where condensation with both $MeSi(CH_2Cl)Cl_2$ and $SiCl_4$ (to give the spiro derivative) are known.[8f,19] In contrast to the chlorosilanes, alkoxysilanes, $RSi(OMe)_3$, can be converted to 2,5-diphenylsiloles without difficulty with the exception of R = H where only gummy products where obtained.


(1)

X = Cl: **1**, R = H, R′ = Cl; **2**, R = Me, R′ = H; **3**, R = Me, R′ = $Me_3Si$; **4**, R = Me, R′ = $CH_2{=}CH$
X = OMe: **5**, R = OMe, R′ = Me; **6**, R = OMe, R′ = $CH_2{=}CH$; **7**, R = OMe, R′ = $CH_2{=}CHCH_2$; **8**, R = OMe, R′ = $Me_3Si$; **8a**, R = OMe, R′ = OMe

Several conversions of these new functional siloles were successfully completed without ring cleavage. The in situ reduction of silole 1 with $LiAlH_4$ provides the stable dihydro derivative 9 (eq 2). The stability of 9 is somewhat surprising since the hydrosilole 2 decomposes slowly at


(2)

**1** **9**

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(19) (a) Braye, E. H.; Hübel, W.; Caplier, I. *J. Am. Chem. Soc.* **1961**, *83*, 4406. (b) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 1883.

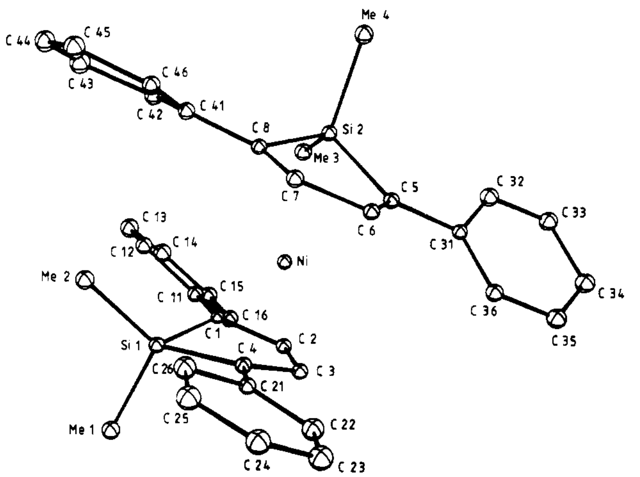
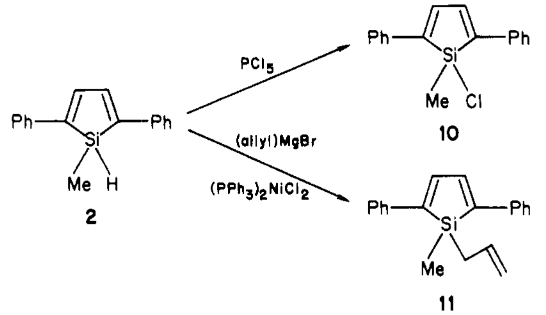


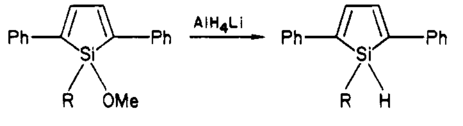
**Figure 1.** ORTEP drawing of complex **16** with the numbering of the atoms. The spheres enclose 30% of the electron density.

room temperature. Chlorination of **2** by PCl$_5$ occurs readily to give **10**, and the SiH bond of **2** couples with allylmagnesium bromide in the presence of a nickel catalyst (Eq 3).[20] Reduction of the methoxy derivatives **6** with



(3)

$i$-Bu$_2$AlH, **7**, and **8** with LiAlH$_4$ occurs smoothly to give the hydrosiloles **12**, **13**, and **14**, respectively (eq 4).



(4)

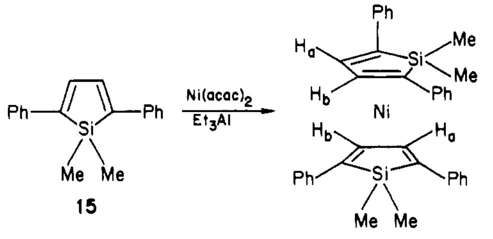
**6**
**7**
**8**

**12**, R = CH$_2$=CH
**13**, R = CH$_2$=CHCH$_2$
**14**, R = Me$_3$Si

The attempted direct synthesis of 1,1-dichloro-2,5-diphenylsilole from SiCl$_4$ was unsuccessful and gave only an intractable residue (reaction of LiPh$_4$C$_4$Li with SiCl$_4$ gives Ph$_4$C$_4$SiCl$_2$).[8f] However, with Si(OMe)$_4$ the dimethoxysilole is obtained in good yield (one compound only in the $^1$H NMR spectrum of the reaction mixture). If LiAlH$_4$ is added to the reaction mixture produced from Si(OMe)$_4$ and LiCPh=CHCH=CPhLi, the dihydrosilole **9** is produced in 25% yield. The reaction of silole **9** with PCl$_5$, SOCl$_2$, SO$_2$Cl$_2$, CCl$_4$, or $N$-chlorosuccinimide in the presence of benzoyl peroxide did not give the expected mono- or dichlorosiloles.

**Reactions of 2,5-Diphenylsiloles with Transition Metals.** $\eta^4$-Complexes of 1,1-dimethyl-2,5-diphenylsilole (**15**) with cobalt, ruthenium, molybdenum, and rhodium[21] have been reported. In this study we have discovered that **15** reacts with nickel metal when it is generated in situ by reduction of Ni$^{II}$ salt (eq 5). The tetrahedral structure of complex **16** has been verified by crystallographic analysis (next section) but may also be predicted from the $^1$H NMR spectrum which shows a typical AB pattern for protons H$_a$ and H$_b$ ($J_{ab} \approx 4$ Hz). The assignments for the exo and *endo* methyl resonances (−0.05 and 0.12, respectively) are given by comparison with other diene complexes[22] and especially with ($\eta^4$-1,1-dimethyl-2,5-diphenylsilole)($\eta^5$-cyclopentadienyl)cobalt.[23]

Complex **16** crystallizes with one-third molecule of cyclohexane per molecule of complex. When the original complexation reaction is carried out in cyclohexane-free solvent ($n$-pentane, $n$-heptane), **16** is formed but does not crystallize. Addition of a small amount of cyclohexane provides the crystalline solvate. When Et$_3$Al is replaced by $i$-Bu$_2$AlH, **16** is produced and precipitated as the solvate in the presence of cyclohexane.



**16**

(5)

One of the long term goals of the study of metal complexes of siloles is the possibility of the generation of $\eta^5$-silacyclopentadienyl derivatives. Two approaches to the $\eta^5$-silole complexes may be envisioned: trapping of a silacyclopentadienide anion by an appropriate metal derivative or by reaction at silicon in a preformed complex. Our initial focus has been on the latter strategy. In a preliminary study modeled after the reported cleavage of the *exo*-methyl substituent in (Ph$_4$C$_4$SiMe$_2$)Fe(CO)$_3$ by SnCl$_4$,[8g,24] reaction of **15** and SnCl$_4$ was examined. Unfortunately, at least seven products were obtained from this combination which could not be separated by conventional methods. A more provising route to $\eta^5$-silacyclopentadienyl derivatives will require silafunctional siloles. Such functional siloles may include conventional groups such as SiH or SiCl but also allyl or trimethylsilyl groups which can be considered as pseudofunctional substituents. The latter groups are attractive for two reasons: (i) siloles with exocyclic organic substituents are complexed more easily without the side reaction often observed for hydrosilanes; and (ii) the complexes thus formed should react with electrophiles to cleave the Me$_3$Si and CH$_2$=CHCH$_2$ groups and provide the more conventional functionalized siloles coordinated to a metal.

To this end, the reactions of siloles **2**, **3**, and **11** with Fe$_2$(CO)$_9$, Co$_2$(CO)$_8$, and Ni(COD)$_2$ were examined, and the results are summarized in Scheme I. Reaction of **3** and **11** with Fe$_2$(CO)$_9$ gives the ($\eta^4$-silacyclopentadiene)tricarbonyliron derivatives **17** and **18**, respectively. The complexation reaction is stereospecific with the Me$_3$Si group in **17** and the Me group in **18** occupying the exo position. When the hydrosilole **2** reacts with Fe$_2$(CO)$_9$, the complex **19** is formed in poor yield, probably due to side reactions of the SiH bond (which can undergo oxidative addition to iron[25]). The larger methyl group in **19** occupies

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[20] Colomer, E.; Corriu, R. J. P.; Meunier, B. *J. Organomet. Chem.* **1979**, *71*, 197 and references therein.

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

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[23] (a) Sakurai, H.; Hayashi, J. *J. Organomet. Chem.* **1973**, *63*, C7. (b) Sakurai, H.; Hayashi, J. *J. Organomet. Chem.* **1973**, *63*, C10.

[24] Sakurai, H.; Hayashi, J.; Kobayashi, T. *J. Organomet. Chem.* **1976**, *110*, 303.

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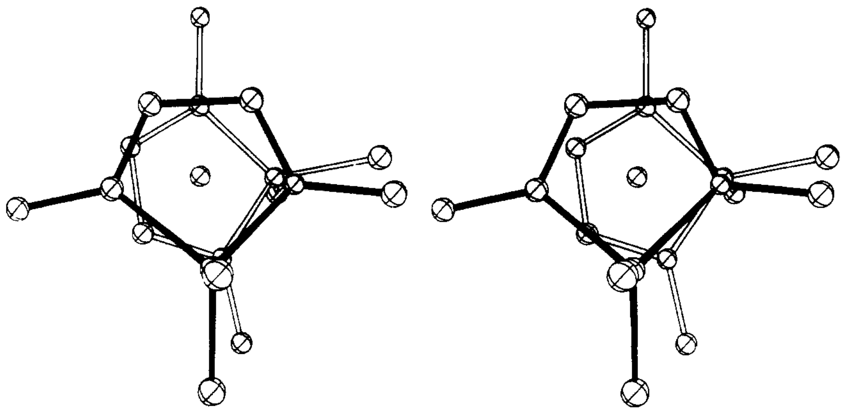


**Figure 2.** Stereoscopic diagram of the molecule of complex **16** viewed along a line going through the two silole ring centers. The thermal ellipsoids are at the 10% probability level. Silole Si(1)–C(1–4) is represented with the plain black bonds. The carbons C(2) to C(6) of each of the phenyl rings have been omitted for clarity.

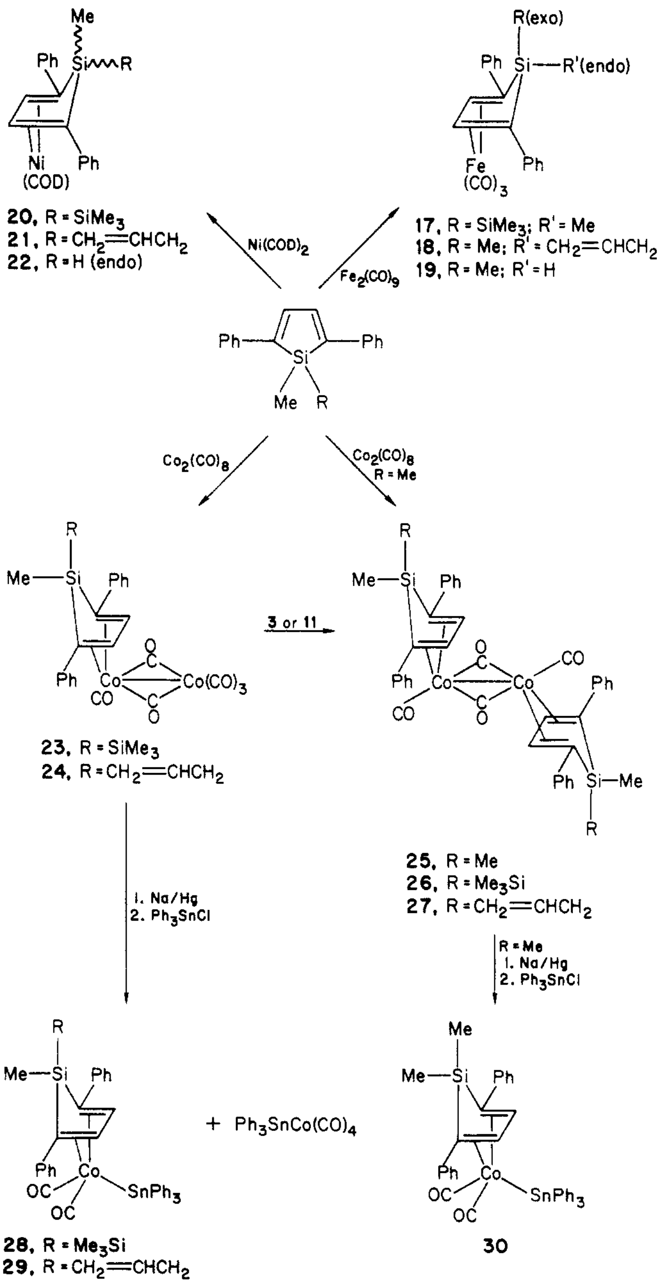
the exo position as deduced from the chemical shift ($^1H$ NMR) relative to that of the analogous complex in the tetraphenyl series.[21,24] When no substituents are present on C(2) and C(5), as in the case of the 3,4-dimethylsilacyclopentadiene series, a greater proportion of the bulky substituent appears in the endo position; i.e., in the complex formed from 1,3,4-trimethyl-1-butylsilacyclopentadiene and $Fe_2(CO)_9$ the product complex is an isomeric mixture with *endo*-Me to *exo*-Me roughly 2/1.[5b]

Siloles **3** and **11** react with $Ni(COD)_2$ to generate the monosubstituted complexes **20** and **21** which are unstable in solution. The methyl groups in the complexes exhibit resonances very close to those of the uncomplexed siloles which prevents an assignment of exo and endo positions. Silole **2** also reacts with $Ni(COD)_2$ through displacement of one COD ligand to give complex **22**. In this case, however, the methyl group occupies the exo position (by analogy to complex **16**). It should be noted that the bis-substituted silole complex **16** cannot be prepared by double displacement of COD from $Ni(COD)_2$. Conversely, Ni complexes of the hydrosilole **2** cannot be prepared by the technique of reduction of $Ni^{II}$. In both of these instances a nickel mirror was obtained.

Dimethyldivinylsilane may be considered as an open-chain analogue of silole **15**. Complexes of structural type **20**–**22** have been prepared from $Me_2Si(CH{=}CH_2)_2$ either with $Ni(acac)_2/Et_2AlOEt$ (in the presence of $PPh_3$) or from $Ni(COD)_2/PPh_3$ which gives $Me_2Si(CH{=}CH_2)_2NiL_2$ and $Me_2Si(CH{=}CH_2)_2NiL$ (L = $PPh_3$), respectively.[26]

In contrast to previously reported results of the reaction of **15** with $Co_2(CO)_8$ where only the dimer **25** was obtained on workup, siloles **3** and **11** react with dicobalt octacarbonyl to give monosubstituted $\eta^4$-silacyclopentadiene derivatives **23** and **24**, respectively. Again, the larger substituent occupies the exo position. Monosubstituted diene derivatives of $Co_2(CO)_8$ have been reported by Wilkinson and Manning,[27,28] however, in low yield (5% for norbornadiene or 2,3-dimethylbutadiene). Both mono- and disubstituted derivatives have been isolated from the reaction of 1,1,3,4-tetramethylsilacyclopentadiene and $Co_2(CO)_8$.[29] The monosubstituted cobalt complexes **23** and **24** react with an excess of silole to give the corresponding disubstituted derivatives **26** and **27**.

### Scheme I



The dicobalt silole derivatives **23**–**25** are reduced by sodium amalgam to an anionic species which could be

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(26) Isaeva, L. S.; Peganova, T. A.; Petrovskii, P. V.; Kayumov, F. F.; Yusupova, F. G.; Yur'en, V. P. *J. Organomet. Chem.* **1983**, *248*, 375.

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(28) Newmann, J.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1593.

(29) Colomer, E.; Corriu, R. J. P.; Lheureux, M.; Dubac, J.; Iloughmane, H.; Laporterie, A., to be submitted for publication.

trapped by addition of $Ph_3SnCl$ (but not by $Me_3SiCl$) to give the silole complexes **28**–**30**. Related $\eta^4$-diene cobalt–tin derivatives have also been obtained from ($\eta^4$-diene)$Co_2(CO)_6$ or $[(\eta^4\text{-diene})Co(CO)_2]_2$ by reaction with $SnX_4$.[28]

**Crystallographic Study of Bis($\eta^4$-1,1-dimethyl-2,5-diphenylsilacyclopentadiene)nickel (16).** The computer-drawn model displayed in Figure 1 shows the essential features of the disilole nickel complex. The four carbon–carbon double bonds are arranged about the nickel atom to generate the tetrahedral geometry similar to that of $Ni(CO)_4$. With the assumption that the nickel atom lies on a line passing through the two silole ring centers, an angle of ca. 93.6° between the plane defined by Si(1), Ni, and the midpoint of the C(2)–C(3) bond and the plane is defined by Si(2), Ni, and the midpoint of the C(6)–C(7) bond is generated.

The roughly planar butadiene unit C(1)–C(2)–C(3)–C(4) and the C(1)–Si(1)–C(4) plane make a dihedral angle of ca. 22.0°. The corresponding fold angle for the other silole ring is 20.3°. These values are consistent with the observations of Muir[30] for the complex of the same silole ligand with a tricarbonylruthenium moiety. In the ruthenium complex this angle opens to 32°, possibly due to the presence of a metal that is bulkier than nickel.

The phenyl rings are not coplanar with the butadiene unit: phenyl groups 1 and 2 are rotated in the same sense (ca. 23.6 and 6.5°, respectively) with atoms C(12) and C(26), nearest to silicon, both in endo positions, whereas phenyls 3 and 4 are rotated in the opposite sense (29° and 17.3°, respectively) with atom C(32) laying in the exo position and atom C(42) again in the endo position. This leads to a total absence of symmetry for a molecule of complex **16**. The carbon atoms C(11), C(21) and C(31), C(41) are lying in the planes of the corresponding butadiene units.

The presence of the metal atom causes perturbation of the bond lengths of the silole ring but to a lesser extent compared to the Ru complex.[30] The double bond lengthens from 1.345 (4) Å in the free ligand to 1.39 (3) Å (average of this work) and to 1.453 (4) Å (Ru complex). The formal single bond decreases from 1.466 (6) to 1.406 (7) Å for the Ru complex, but in the present work, the average value, 1.48 (3) Å, is in the range of the single bond of the uncoordinated ligand. The mean Si–C(silole) bond length, 1.88 (2) Å, is identical with that reported by Muir.

As described in the Experimental Section, some cyclohexane molecules were trapped inside the crystals of the complex, giving what may be described as a 2/1 clathrate. Whether benzene or smaller molecules would fit into the cages produced by the eight phenyl groups was not determined. We are also unable to determine whether or not these cages communicate with each other alone the *c* axis of the crystal.

## Conclusion

In this report we have described the synthesis and reactions of functional and pseudofunctional siloles and the conditions for generation of a variety of metal complexes. In general, only one isomer of the metal complex is produced and it is the one in which the bulkier of the two substituents is in a position exo to the metal. The possible exception to this occurs in silole **11** where the allyl group occupies the endo position in complex **18** but the exo position in complexes **24**, **27**, and **29**.

In terms of substitution and reaction chemistry at coordinated siloles, previous observations suggest that the reacting group must be exo to the metal center. As an example, in the complexes of the silole $Ph_4C_4SiMeH[Fe(CO)_3]$, the hydrogen atom in the exo position is chlorinated by $CCl_4$ or adds to acetone. However, similar conversions of the endo isomer are not observed under the same conditions.[24] Since complexes of **2** contain H in the endo or a least favorable site for reaction, it is anticipated that in the absence of isomerization, complexes such as **17** will give coordinated siloles with a functional group in the desired exo position.[31]

The preliminary studies of 1,1-dimethylsilole (C-unsubstituted) as a ligand for transition metals suggest some enhanced stability over other diene complexes that do not contain silicon,[28] as though the silole behaves as a $\eta^5$-cyclopentadienyl ligand.[1] The electronic nature of siloles and germoles, both free and complexed to $Fe(CO)_3$, have been studied by photoelectron spectroscopy. The results show a strong electron donation from iron to the metallole ring, and the authors conclude that these compounds may have some aromatic character.[32] The derivatives of interest, however, will be those in which a charge is generated at Si (Ge) in the silole (germole) and subsequent evaluation of whether that charge is delocalized to give a $\eta^5$-ligand.[23b,33] In a preliminary report of the properties of the cationic species $(Ph_4C_4GeMe)Fe(CO)_3{}^+$, the positive charge appeared to be localized on the Ge center and $\eta^4$-coordination of the germole was favored.[34]

With our recent development of the generation of the silacyclopentadienyl anion[35] and the formation of the functional and pseudofunctional complexed siloles described in this report, we are actively pursuing the possible generation of $\eta^5$-silole ligands 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. 233, Université des Sciences et Techniques du Languedoc, for the use of their Weissenberg and precession cameras.

**Registry No.** **2**, 76713-22-9; **3**, 70606-51-8; **4**, 100840-03-7; **5**, 100840-04-8; **6**, 97538-88-0; **7**, 97538-89-1; **8**, 97538-90-4; **8a**, 100840-05-9; **9**, 19923-45-6; **10**, 100840-06-0; **11**, 97538-87-9; **12**, 97538-91-5; **13**, 97538-92-6; **14**, 97538-93-7; **15**, 7688-03-1; **16**, 100815-42-7; **16**$\cdot{}^1/_3C_6H_{12}$, 100815-43-8; **17**, 100815-44-9; **18**, 100815-45-0; **19**, 100815-46-1; **20**, 100815-47-2; **21**, 100815-48-3; **22**, 100815-49-4; **23**, 100815-50-7; **24**, 100815-51-8; **25**, 100896-64-8; **26**, 100815-52-9; **27**, 100815-53-0; **28**, 100815-54-1; **29**, 100815-55-2; **30**, 100815-56-3; $MeHSiCl_2$, 75-54-7; $Me(CH_2{=}CH)SiCl_2$, 124-70-9; $MeSi(OMe)_3$, 1185-55-3; $CH_2{=}CHSi(OMe)_3$, 2768-02-7; $CH_2{=}CHCH_2Si(OMe)_3$, 2551-83-9; $Me_3SiSi(OMe)_3$, 18000-25-4; $MeOSi(OMe)_3$, 681-84-5; $HSiCl_3$, 10025-78-2; $Fe_2(CO)_9$, 15321-51-4; $Co_2(CO)_8$, 10210-68-1; $Ni(COD)_2$, 33221-58-8; Co, 7440-48-4; Sn, 7440-31-5; 1,4-dilithio-1,4-diphenylbutadiene, 7641-46-5; allylmagnesium bromide, 1730-25-2; nickel acetylacetonate, 3264-82-2.

**Supplementary Material Available:** A listing of structure factor amplitudes (Table V) (9 pages). Ordering information is given on any current masthead page.

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[30] Muir, K. W.; Walker, R.; Abel, E. W.; Blackmore, T.; Whitley, R. J. *J. Chem. Soc. Chem. Commun.* **1975**, 698.

[31] Cleavage of Ph in $Ph_4C_4SiPh(exo)MeFe(CO)_3$ occurs with retention of configuration.[24]

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