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# Notes

## $\eta^4$-Siloles as Ligands for Cationic Cobalt and Rhodium Phosphine Complexes

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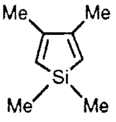
*Summary:* Reaction of 1-R-1-R′-3,4-dimethylsiloles (R = R′ = Me, **1**; R = Me; R′ = Ph, **2**; R = Me, R′ = allyl, **3**; R = R′ = allyl, **4**) with $CoBr(PMe_3)_3$ afforded the 18e $[Co(silole)(PMe_3)_3]^+$ complexes, which were precipitated as $BPh_4$ salts. Only one isomer was observed in which the larger substituent at Si was located in an exo position. Even when the silicon atom bore two allyl groups, no coordination of the endo allyl function to cobalt was apparent. This is in agreement with the higher nucleophilicity of $PMe_3$ compared to that of alkene. Complexation with the 12e rhodium fragment $[Rh(PPh_3)_2]^+$ occurred when an excess of silole was added to a hydrogenated solution of $[Rh(COD)(PPh_3)_2]PF_6$ in THF. The cationic complexes $[Rh(silole)(PPh_3)_2]PF_6$ that precipitated were characterized by $^1H$, $^{13}C$, and $^{31}P$ NMR spectroscopy and elementary analysis. As for cobalt, only one isomer was present and no coordination of the allyl group in an endo position to rhodium was observed. Comparison of the $^{13}C$ and $^1H$ chemical shifts of the carbon and proton atoms of the ring indicated that the distortion of the ring on coordination is larger in cobalt than in rhodium, in agreement with the lower nucleophilic character of Co compared to that of Rh.

It has long been known that siloles and germoles,[1] in particular the C-unsubstituted derivatives,[1d-g] can be stabilized by 14e metal carbonyl fragments, the $\pi$-acid character of CO increasing the strength of the metal–netallole bond. A few examples of mixed carbonyl–phosphine complexes were described, in which the phosphine was used as a substitute for a carbonyl group in order to increase the complex stability or to help precipitation of single crystals. Surprisingly, silole–metal complexes containing only phosphines are rare. It was thus of interest to study the reaction of siloles with metal phosphine fragments to check the influence of $PR_3$ on the bonding, the stability of the complex, the reactivity at silicon or germanium, and the possible formation of the still unknown $\eta^5$-silacyclopentadienyl or germacyclopentadienyl species.

We previously reported that the X-ray structures of (1,1,3,4-tetramethylmetallole)tris(trimethylphosphine)cobalt(I) tetraphenylborate (metallole = silole (**5**), germole)[2] surprisingly showed no significant differences in the distances and angles from those of the (silole)$Fe(CO)_3$ analogues. We decided then to explore the effect of the silole on the nature and stability of the complexes. Therefore, we studied the reaction of $CoBr(PMe_3)_3$ with the new siloles **2**–**4**.[3] However, as described herein, although **3** and **4** bear functionalized substituents at Si able to interact with the metal center,[4] coordination of the allyl groups to the cobalt center was never observed.



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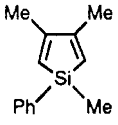

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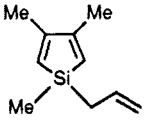

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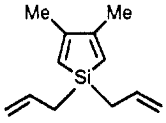

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The reaction of the 12e rhodium(I) fragments $[Rh(PR_3)_2]^+$ is particularly interesting since they are well-known for their ability to complex dienes. However, only two silole–rhodium compounds have been reported until now.[5] We describe herein the synthesis of four new 16-electron Rh–silole complexes, **9**–**12**, which were isolated as red microcrystalline powders. As for cobalt, no interaction of the allyl substituents with the rhodium center was observed.

### Experimental Section

**NMR Spectra.** Variable-temperature $^1H$, $^{31}P$, and $^{13}C$ FT NMR spectra were recorded with use of Bruker 90-, 200-, and 250-MHz spectrometers. Field frequency stabilization was achieved on an internal $^2D$ signal. $SiMe_4$ was used as an external reference for $^1H$ and $^{13}C$ chemical shifts and $H_3PO_4$ (85% in $D_2O$) for $^{31}P$. The NMR tubes were loaded in a nitrogen-filled glovebox, with $CD_2Cl_2$ or $(CD_3)_2CO$ as solvent. The NMR spectra of the cobalt(I) complexes were measured at low temperature (188–223 K) to improve the resolution of the signals, broadened at room

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[1] (a) McMahon, R. J. *Coord. Chem. Rev.* **1982,** *47,* 1 and references therein. (b) Jutzi, P.; Karl, A. *J. Organomet. Chem.* **1981,** *214,* 289. (c) Jutzi, P.; Burschla, C. *Ibid.* **1981,** *215,* 27. (d) Laporterie, A.; Iloughmane, H.; Dubac, J. *Ibid.* **1983,** *244,* C13. (e) Guimon, C.; Pfister-Guillouzo, G.; Dubac, J.; Manuel, G.; Iloughmane, H. *Organometallics* **1985,** *4,* 636. (f) Burns, G. T.; Colomer, E.; Corriu, R. J. P.; Lheureux, M.; Dubac, J.; Laporterie, A.; Iloughmane, H. *Ibid.* **1987,** *6,* 1398. (g) Burns, G. T.; Colomer, E.; Corriu, R. J. P. *Ibid.* **1983,** *2,* 1901.

[2] Ananias de Carvalho, L. C.; Dartiguenave, M.; Dahan, F.; Dartiguenave, Y.; Dubac, J.; Laporterie, A.; Manuel, G.; Iloughmane, H. *Organometallics* **1985,** *5,* 2205.

[3] Dubac, J.; Laporterie, A.; Manuel, G.; Iloughmane, H.; Beteille, J. P.; Dufour, P. *Synth. React. Inorg. Met.-Org. Chem.* **1987,** *17,* 783.

[4] Carre, F.; Corriu, R. J. P.; Guerin, C.; Henner, B. J. L.; Kolani, B.; Wong Chi Man, W. W. C. *J. Organomet. Chem.* **1987,** *328,* 15.

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

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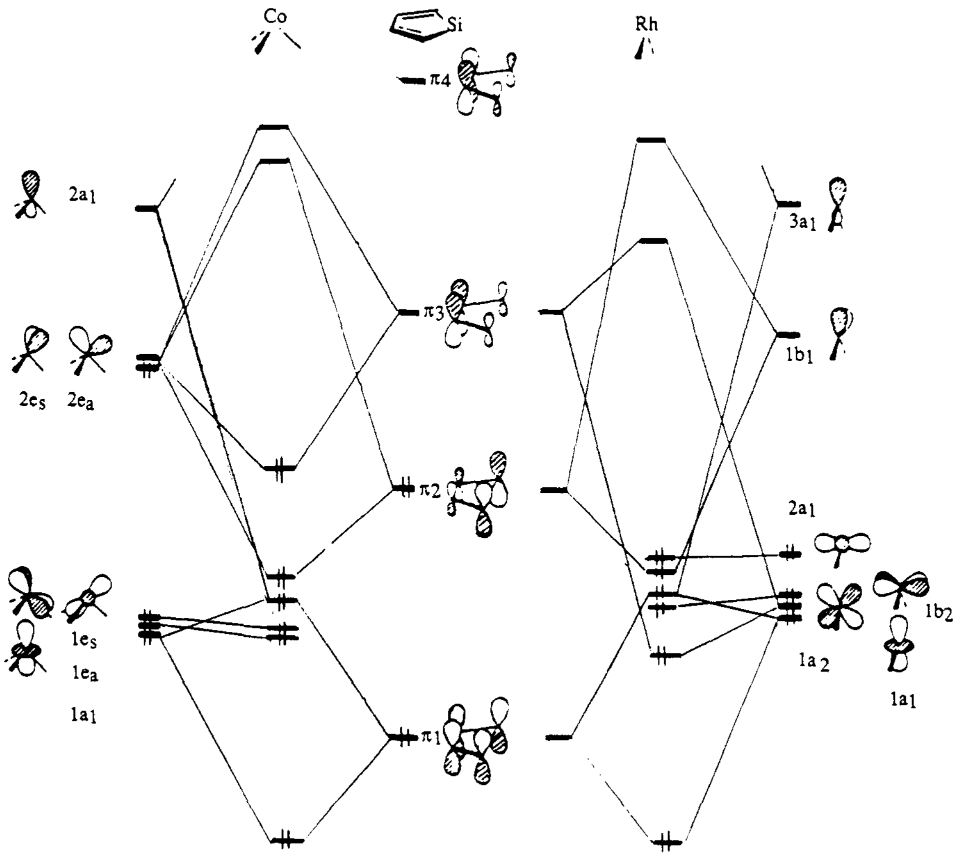
Chart I



temperature by spin–spin interaction with the quadrupole moment of the cobalt nucleus.[6,7]

All reactions were performed under argon by following the procedures already reported.[8] $CoBr(PMe_3)_3$[9] and $[Rh(COD)(PPh_3)_2]X$ ($X = PF_6^-$, $BF_4^-$, $SbF_6^-$)[10] were synthesized by following literature methods. The siloles 1–4 were prepared by a one-pot synthesis as described in ref 11. The isomeric purity of these metalloles containing the transoid isomer is about 90% for the alkyl and aryl derivatives (1, 2) and 50% for the allyl ones (3, 4). [Co($\eta^4$-1-*exo*-methyl-1-methylsilole)$(PMe_3)_3$]$BPh_4$ (5) is synthesized as described in ref 2.

**[Co($\eta^4$-1-*exo*-phenyl-1-methylsilole)$(PMe_3)_3$]$BPh_4$ (6).** To a solution of $CoBr(PMe_3)_3$ (0.9 g; 2.45 mmol) in acetone (10 mL) was added an excess of 2 (0.62 g; 3.09 mmol) with stirring. The color of the solution changed from blue to orange. $NaBPh_4$ (0.85 g; 2.45 mmol) dissolved in 10 mL of methanol was added. The solution was then filtered and concentrated. Crystallization overnight at −25 °C gave rise to orange crystals (yield 70%). Recrystallization in acetone allowed the elimination of a small amount of green crystals of $[Co(PMe_3)_4]BPh_4$ that coprecipitated with 6.

**[Co($\eta^4$-1-*exo*-allyl-1-methylsilole)$(PMe_3)_3$]$BPh_4$ (7).** By the same procedure, 0.47 g (1.28 mmol) of $CoBr(PMe_3)_3$ and 0.58 g (3.55 mmol) of 3 gave a 65% yield of 7.

**[Co($\eta^4$-1-*exo*-allyl-1-allylsilole)$(PMe_3)_3$]$BPh_4$ (8).** By the same procedure, 0.67 g (1.82 mmol) of $CoBr(PMe_3)_3$ and 0.65 g (4.55 mmol) of 4 gave a 65% yield of 8.

**[Rh($\eta^4$-1-*exo*-methyl-1-methylsilole)$(PPh_3)_2$]$PF_6$ (9).** A 0.441-g (2.5-mmol) amount of 1 in 10 mL of THF was added to the clear orange solution obtained by vigorously stirring $[Rh(COD)(PPh_3)_2]PF_6$ (0.5 g; 0.57 mmol) in 10 mL of THF under a stream of $H_2$. 9 precipitated from this dark red solution as a red powder, which was filtered off, dried, and stored under argon. Addition of diethyl ether gave rise to another crop; yield 90%. Recrystallization at −20 °C in $CH_2Cl_2$/pentane (1/1) produced 9 as a microcrystalline product.

Table I. Physical and Analytical Data for the New Complexes

| compd[c] | color | mp,[a] °C | anal.[b] % C | anal.[b] % H |
|---|---|---|---|---|
| [Co(MePhsilole)$(PMe_3)_3$]$BPh_4$ (6) | orange | *d* | 67.81 (68.48) | 7.85 (7.87) |
| [Co(Me(allyl)silole)$(PMe_3)_3$]$BPh_4$ (7) | orange | *d* | 66.76 (67.01) | 7.97 (8.23) |
| [Co((allyl)$_2$silole)$(PMe_3)_3$]$BPh_4$ (8) | orange | *d* | 67.59 (67.83) | 8.01 (8.22) |
| [Rh(Me$_2$silole)$(PPh_3)_2$]$PF_6$ (9) | red | 164[d] | 58.04 (58.03) | 4.75 (4.87) |
| [Rh(MePhsilole)$(PPh_3)_2$]$PF_6$ (10) | red | 148 | 57.83 (58.99) | 4.77 (4.95) |
| [Rh(Me(allyl)silole)$(PPh_3)_2$]$PF_6$ (11) | red | 153[d] | 59.92 (60.50) | 4.83 (4.77) |
| [Rh((allyl)$_2$silole)$(PPh_3)_2$]$PF_6$ (12) | red | 132 | 59.51 (59.88) | 5.31 (5.02) |

[a] Uncorrected melting point, in capillary tube. [b] Calculated values are given in parentheses. [c] $R_1R_2$silole = $R_1R_2SiC_6H_8$. [d] Decomposed.

**[Rh($\eta^4$-1-*exo*-phenyl-1-methylsilole)$(PPh_3)_2$]$PF_6$ (10).** By the same procedure, 0.65 g (0.74 mmol) of $[Rh(COD)(PPh_3)_2]PF_6$ and 0.83 g (3.3 mmol) of 2 gave rise to 10 in 75% yield.

**[Rh($\eta^4$-1-*exo*-allyl-1-methylsilole)$(PPh_3)_2$]$PF_6$ (11).** By the same procedure, 0.85 g (0.96 mmol) of $[Rh(COD)(PPh_3)_2]PF_6$ and 1.4 g (4.3 mmol) of 3 gave a 77% yield of 11.

**[Rh($\eta^4$-*exo*-allyl-1-allylsilole)$(PPh_3)_2$]$PF_6$ (12).** By the same procedure, 0.97 g (1.1 mmol) of $[Rh(COD)(PPh_3)_2]PF_6$ and 0.95 g (4.9 mmol) of 4 gave a 75% yield of 12.

Complex 9 and 10 have also been synthesized, by following the same procedure, as $SbF_6^-$ and $BF_4^-$ salts in good yields (70%). In no case have we been able to crystallize single crystals suitable for an X-ray study.

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[7] Fellmann, J. D.; Garrou, P. E.; Withers, H. P.; Seyferth, D.; Traficante, D. D. *Organometallics* **1983**, *2*, 818.

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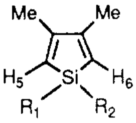
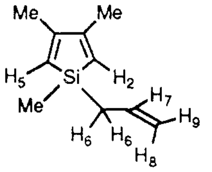
[10] Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397.

[11] Dubac, J.; Laporterie, A.; Iloughmane, H. *J. Organomet. Chem.* **1985**, *293*, 295.

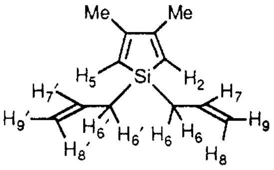
**Table II. $^1$H NMR Spectral Data (ppm) for the Free Siloles and the New Complexes**[a]



| compd ($R_1R_2Si$) | Si–Me | Me | $H_2$, $H_5$ | ref |
|---|---|---|---|---|
| $Me_2$silole (**1**) | 0.10 (s, 6 H) | 1.96 (s, 6 H) | 5.46 (s, 2 H) | 9a |
| MePhsilole (**2**) | 0.45 (s, 3 H) | 2.03 (s, 6 H) | 5.80 (s, 2 H) | 9b |
| Me(allyl)silole (**3**) | 0.10 (s, 3 H) | 1.93 (s, 6 H) | 5.48 (s, 2 H) | 9b |
| (allyl)$_2$silole (**4**) | | 2.03 (s, 6 H) | 5.66 (s, 2 H) | 9b |
| $[Co(Me_2silole)(PMe_3)_3]^+$ (**5**) | exo −0.12 (s, 3 H)<br>endo 0.61 (s, 3 H) | 2.34 (s, 6 H) | 1.50 (s, 2 H) | 2 |
| $[Co(MePhsilole)(PMe_3)_3]^+$ (**6**) | endo 0.72 (s, 3 H) | 2.06 (s, 3 H) | 1.55 (s, 2 H) | |
| $[Co(Me(allyl)silole)(PMe_3)_3]^+$ (**7**) | endo 0.42 (s, 3 H) | 2.08 (s, 6 H) | 1.50 (s, 2 H) | |
| $[Co((allyl)_2silole)(PMe_3)_3]^+$ (**8**) | | 2.02 (s, 6 H) | undeterm | |
| $[Rh(Me_2silole)(PPh_3)_2]^+$ (**9**) | exo 0.06 (s, 3 H)<br>endo 0.89 (s, 3 H) | 1.54 (s, 6 H) | 3.51 (s, 2 H) | |
| $[Rh(MePhsilole)(PPh_3)_2]^+$ (**10**) | endo 1.19 (s, 3 H) | 1.62 (s, 6 H) | 3.48 (s, 2 H) | |
| $[Rh(Me(allyl)silole)(PPh_3)_2]^+$ (**11**) | endo 0.88 (s, 3 H) | 1.47 (s, 6 H) | 3.40 (s, 2 H) | |
| $[Rh((allyl)_2silole)(PPh_3)_2]^+$ (**12**) | | 1.47 (s, 6 H) | 3.32 (s, 2 H) | |



| compd | $H_6$ | $H_7$ | $H_8$ | $H_9$ |
|---|---|---|---|---|
| **7** | hidden by $PMe_3$ | 5.51 (m, 1 H) | 4.80 (m, 2 H) | |
| **11** | 1.53 (d, 2 H, $^3J_{6,7}$ = 8 Hz) | 5.34 (tdd, 1 H, $^3J_{7,6}$ = 8 Hz, $^3J_{7,9}$ = 9.7 Hz, $^3J_{7,8}$ = 18 Hz) | 4.65 (dd, 1 H, $^3J_{8,7}$ = 18 Hz, $^2J_{8,9}$ = 1 Hz) | 4.78 (dd, 1 H, $^3J_{9,7}$ = 9.7 Hz, $^2J_{9,8}$ = 1 Hz) |



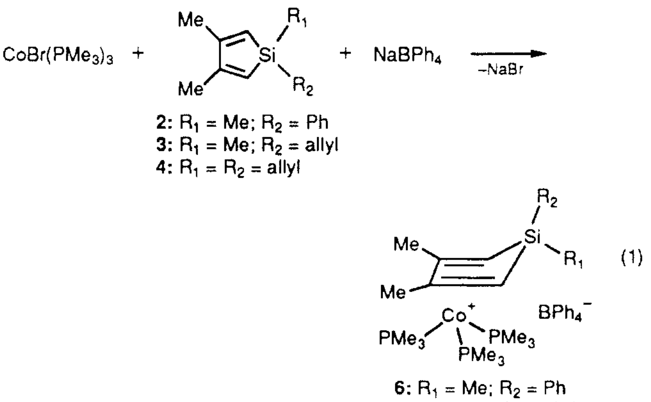
| compd | $H_6$ | $H_7$ | $H_8$ | $H_9$ |
|---|---|---|---|---|
| **8** | | two broad signals (6 H) between 5 and 5.75 | | |
| **12** (exo) | 1.55 (2 H, d, $^3J_{6,7}$ = 8.15 Hz) | 5.27 (1 H, tdd, $^3J_{7,6}$ = 8.15 Hz, $^3J_{7,9}$ = 10.05 Hz, $^3J_{7,8}$ = 21.5 Hz) | 4.58 (1 H, d, $^3J_{8,7}$ = 21.5 Hz) | 4.73 (1 H, d, $^3J_{9,7}$ = 10.05 Hz) |

| compd | $H_{6'}$ | $H_{7'}$ | $H_{8'}$ | $H_{9'}$ |
|---|---|---|---|---|
| **12** (endo) | 2.44 (2 H, d, $^3J_{6',7'}$ = 7.6 Hz) | 5.85 (1 H, tdd, $^3J_{7',6'}$ = 7.6 Hz, $^3J_{7',9'}$ = 9.97 Hz, $^3J_{7',8'}$ = 16.82 Hz) | 4.94 (1 H, d, $^3J_{8',7'}$ = 16.82 Hz) | 5.03 (1 H, d, $^3J_{9',7'}$ = 9.97 Hz) |

[a] Solvent: $CCl_4$ for **1**–**3**; $CDCl_3$ for **4**, **9**–**12**; $CD_2Cl_2$ for **5**–**8**. s = singlet. Temperature: 298 K for **1**–**4**, **9**–**12**; 223 K for **5**, **8**; 213 K for **7**; 203 K for **6**.

## Results

**[Co($\eta^4$-silole)(PMe$_3$)$_3$]BPh$_4$.** Treatment of $CoBr(PMe_3)_3$ at room temperature with siloles **2**–**4**, followed by addition of $NaBPh_4$, afforded the new cationic species **6**–**8** in good yields. The crystalline solids **6**–**8** that precipitated were handled in air for a short time. They have been completely characterized by a combination of elementary analysis and $^1$H, $^{13}$C and $^{31}$P NMR spectroscopies (Tables I–IV). They show the characteristic silacyclopentadiene signals in the $^{13}$C NMR spectra. The olefinic carbon appears in the range 100–105 ppm for the carbons $\beta$ to Si (C3, C4) and 39–43 ppm for the $\alpha$-carbons (C2, C5). The methyl carbons on the ring (C6) are at about 17 ppm. Upfield shifts of the two ring protons on coordination are also observed in the $^1$H NMR spectra. For example, the signal at 5.8 ppm in **2** shifts upfield to 1.55 ppm on coordination to Co in **6**. This is a consequence of the increase



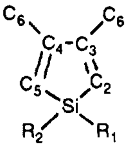
**2**: $R_1$ = Me; $R_2$ = Ph
**3**: $R_1$ = Me; $R_2$ = allyl
**4**: $R_1$ = $R_2$ = allyl

**6**: $R_1$ = Me; $R_2$ = Ph
**7**: $R_1$ = Me; $R_2$ = allyl
**8**: $R_1$ = $R_2$ = allyl

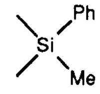
**Table III. $^{31}$P{$^1$H} NMR Data**

| compd | temp, K | solvent | $\delta$, ppm |
|---|---|---|---|
| **6** | 203 | $CD_2Cl_2$ | 7 (s) |
| **7** | 188 | $CD_2Cl_2$ | 4 (s) |
| **8** | 193 | $CD_2Cl_2$ | 4 (s) |
| **9** | 298 | $(CD_3)_2CO$ | 33 (d, $^1J_{P,Rh}$ = 179 Hz) |
| **10** | 298 | $(CD_3)_2CO$ | 33 (d, $^1J_{P,Rh}$ = 178 Hz) |
| **11** | 298 | $CD_2Cl_2$ | 30 (d, $^1J_{P,Rh}$ = 178 Hz) |
| **12** | 298 | $CD_2Cl_2$ | 30 (d, $^1J_{P,Rh}$ = 178 Hz) |

**Table IV.** $^{13}C\{^1H\}$ **NMR Data (ppm)**

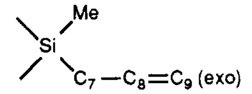


| compd | Si-$CH_3$ | $C_2$, $C_5$ | $C_3$, $C_4$ | $C_6$ | ref |
|---|---|---|---|---|---|
| **1** | -5.1 | 126.5 | 157 | 20.6 | 9b |
| **5** | exo 1.3<br>endo 6.9 | 40.9 | 102.5 | 17.3 | 2 |
| **6** | endo 0.14 | 39.5 | 103.4 | 17.1 | |
| **7** | endo -0.2 | 39.9 | 102.9 | 17.1 | |
| **8** | | 42.8 | 100.5 | 16.7 | |
| **9** | exo -2, 7<br>endo 1 | 81.7 | 123.5 | 17.4 | |
| **10** | endo -5.1 | 80.3 | 124 | 17.3 | |
| **11** | endo -4 | 79.2 | 124 | 17.3 | |
| **12** | | 77.9 | 124.2 | 17.4 | |



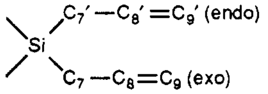
$R_2 = Ph$

**6**: δ 143.5, 131.9, 127.7
**10**: δ 133.67, 130.16, 128.35



$R_2 = -C_7-C_8=C_9$

| | $C_7$ | $C_8$ | $C_9$ |
|---|---|---|---|
| **7** | 30.9 | 134.3 | 111.9 |
| **11** | 25.2 | 114.9 | 113.1 |



$R_1 = -C_7-C_8=C_9$ (exo)
$R_2 = -C_{7'}-C_{8'}=C_{9'}$ (endo)

| | $C_7$ | $C_{7'}$ | $C_8$ | $C_{8'}$ | $C_9$ | $C_{9'}$ |
|---|---|---|---|---|---|---|
| **8** | 30.6 | 28.1 | undetermined | | 112.6 | 109.2 |
| **12** | 19.9 | 22.2 | 115.4 | | 113.5 | 116.7 |

[a] Solvent: $CD_2Cl_2$ for **1**, **5**–**8**, **11**, **12**; $(CD_3)_2CO$ for **9**, **10**. Temperature: 298 K for **1**, **9**–**12**; 203 K for **6**, **8**; 193 K for **5**; 188 K for **7**.

of the $sp^3$ character of the carbon bearing this hydrogen on coordination.

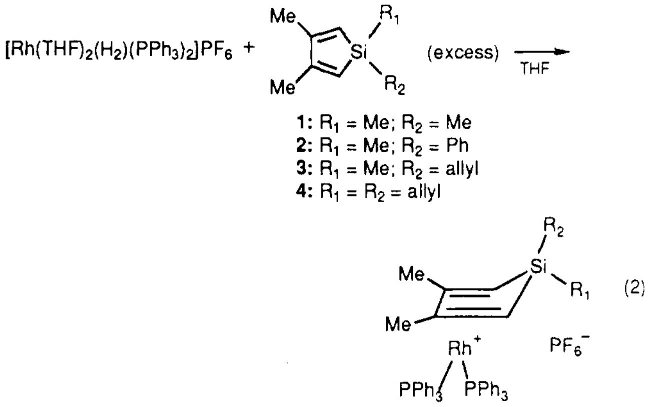
No evidence was found for the bonding of the allyl functions to cobalt, neither in **7** nor in **8**. The corresponding $^1H$ and $^{13}C$ NMR spectra indicate no change between the values in the free and the coordinated siloles (Tables II and IV). Although in **7** the allyl substituent, more sterically hindered, is located in an exo position to the cobalt, that is in such a way that no interaction is possible, the presence of two allyl functions in **8** could have provided an example where this supplementary coordination could occur. This result is related to the nucleophilic character of $PMe_3$, which is a better ligand than ethylene.

When reaction 1 was performed at higher temperature (60 °C), decomposition of complexes **6**–**8** occurred, followed by the precipitation of $[Co(PMe_3)_4]BPh_4$ as green crystals.[12]

**$[Rh(silole)(PPh_3)_2]PF_6$.** Although rhodium complexes including diene are well-known, only two binuclear rhodium compounds including silole have been synthesized, by reaction of 1,1-dimethyl-2,5-diphenylsilole with $[Rh(CO)Cl]_2$: $[RhCl(silole)]_2$ and $[Rh(CO)Cl]_2(silole)$.[5]

It was thus of interest to attempt the synthesis of the first mononuclear Rh–silole complexes by the reactions used to synthesize the diene species. Treatment of $RhCl_3 \cdot nH_2O$ with **4** in methanol afforded an unseparable mixture of compounds. Moreover, we observed no exchange of ligand by adding silole to a solution of $[Rh(COD)(PPh_3)_2]^+$, indicating that COD and $PPh_3$ are better ligands than silole. Alternatively, however, we found that the capability of the dienes to be hydrogenated in the coordination sphere of rhodium,[13] thereby giving rise to unsaturated metal centers, can be successfully used to prepare the silole derivatives (reaction 2). Bubbling $H_2$ gas through a suspension of $[Rh(COD)(PPh_3)_2]PF_6$ in THF was performed at room temperature until the solution became clear. Addition of excess siloles **1**–**4** in THF gave $[Rh(silole)(PPh_3)_2]PF_6$ rapidly. Precipitation of red microcrystals occurred on addition of ether. The four complexes have been synthesized by following the same procedure. Their identification is based on their spectroscopic ($^1H$, $^{31}P$, $^{13}C$ NMR) and analytical data (Tables I–IV).

$$[Rh(COD)(PPh_3)_2]PF_6 + H_2 \xrightarrow[THF]{} [Rh(THF)_2(H_2)(PPh_3)_2]PF_6 + C_8H_8$$



**1**: $R_1$ = Me; $R_2$ = Me
**2**: $R_1$ = Me; $R_2$ = Ph
**3**: $R_1$ = Me; $R_2$ = allyl
**4**: $R_1$ = $R_2$ = allyl

**9**: $R_1$ = Me; $R_2$ = Me
**10**: $R_1$ = Me; $R_2$ = Ph
**11**: $R_1$ = Me; $R_2$ = allyl
**12**: $R_1$ = $R_2$ = allyl

Compared to the values of the cobalt analogues, the $^{13}C$ NMR data show significant shifts to lower field for the carbon atoms of the silacyclopentadiene ring. The carbons α to Si (C2, C5) are at about 77–81 ppm (compared to 39–43 ppm for Co) and the β-carbons (C3, C4) at 123–124 ppm (compared to 100 ppm for Co), indicative of a lower deshielding of the carbons of the ring and consequently a less distorted ring with Rh compared that with Co in agreement with the trend in the nucleophilic character of the two metal centers. The same conclusion is deduced from the $^1H$ NMR spectra. As in the cobalt complexes, coordination of the allyl fragments is never observed.

Addition of $PMe_3$ to **9**–**13** *did not give rise to the trimethylphosphine analogues* but to mixtures of products, from which addition of methanol led to the precipitation of $[Rh(PMe_3)_2(PPh_3)_2]PF_6$ as the major product.[14] No oxidative addition of MeI on the rhodium center occurred, the complexes being recovered unchanged after the reaction. Addition of $SnCl_4$, which was performed in order to prepare siloles functionalized at Si,[1b,f] was also unsuccessful. Only decomposition products were obtained.

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## Discussion and Conclusion

Siloles react as 4e-donor-like conjugated dienes toward metal phosphine fragments, giving rise to five-coordinate 18e complexes with cobalt and tetracoordinated 16e complexes with rhodium as expected. Complexes were obtained in good yield. Thus, through their butadiene fragment, the siloles mimic the reaction of cyclopentadiene.

The essential interactions between silole and the $[Co(PMe_3)_3]^+$ and $[Rh(PR_3)_2]^+$ fragments are emphasized in Chart I. Only the orbitals involved in the bonding are represented. The important valence orbitals of $d^8$ $ML_3$ and $ML_2$ groups are reasonably well-known.[15] They are decomposed into three levels of low energy ($1e + 1a_1$) in $ML_3$ ($C_{3v}$ symmetry) and $1a_1$, $1b_2$, and $1a_1$ in $ML_2$ ($C_{2v}$ symmetry) and an upper set of three levels, pointing away from the cobalt, toward the silole. The major difference between the two fragments is the energy of the $d_{xz}$ set, which is significantly stabilized in the $ML_2$ fragment and consequently less involved in the bonding. The silole presents to the metal three $\pi$ orbitals: $\pi^1$, $\pi^2$, $\pi^3$. They clearly interact with the metal in a manner similar to that for butadiene, as shown by the X-ray structures of the analogous $[(\text{butadiene})Co(PMe_3)_3]^+$ and $[(\text{silole})Co(PMe_3)_3]^+$ [2,6] complexes, the silicon atom being bent away from cobalt after complexation.

Thus, qualitatively, on the basis of symmetry considerations, the basic patterns of interaction between the silole and the cobalt and rhodium fragments are very much alike. The two empty metal orbitals are destabilized by interaction with the filled $\pi^1$ and $\pi^2$ silole orbitals, giving rise to a two-electron stabilizing interaction. In $[Co(PMe_3)_3]^+$, the $\pi^3$ empty silole orbital is also well suited to interact with the filled metal d orbital and thus increase the strength of the bonding by the back-donation d (Co) → $\pi$ (silole). However, in $[Rh(PR_3)_2]^+$ the corresponding filled d orbital is of higher energy and is thus less suited to match the silole $\pi^3$ level and consequently to give extra stabilization by back-bonding. This is in accord with the higher stability of the cobalt complex compared to that of the rhodium one toward silole dissociation or phosphine substitution. As a consequence, an increase in the Co–silole interaction would strengthen the M–silole bond and weaken the C–C bond. This is in accord with the NMR data.

Moreover, the lack of empty metal d orbitals in the *xy* plane indicates why there is no coordination of the allyl substituent on Si with the cobalt or rhodium center.

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**Registry No.** **1**, 82763-95-9; **2**, 98749-91-8; **3**, 118512-97-3; **4**, 118512-99-5; **6**, 129176-16-5; **7**, 129176-18-7; **8**, 129176-20-1; **9**, 129176-22-3; **10**, 129176-24-5; **11**, 129176-26-7; **12**, 129176-28-9; $CoBr(PMe_3)_3$, 53432-07-8; $[Rh(COD)(PPh_3)_2]PF_6$, 35238-97-2; $[Rh(THF)_2(H_2)(PPh_3)_2]PF_6$, 129176-30-3.

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# Synthesis of Dimanganese Nonacarbonyl Cyclic Carbene Complexes and Molecular Structures of Two of Them

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*Summary:* The reactions of $Br(CH_2)_3Br$, $BrCH_2CH_2CH(CH_3)Br$, $Br(CH_2)_4Br$, and $BrCH_2CH_2CH_2CH(CH_3)Br$ with $Na[Mn(CO)_5]$ yield the dimanganese cyclic carbene complexes $[(CO)_5MnMn(CO)_4L]$ (where L = $\overline{\mathrm{CCH_2CH_2CH_2O}}$, $\overline{\mathrm{CCH_2CH_2CH(CH_3)O}}$, $\overline{\mathrm{CCH_2CH_2CH_2CH_2O}}$, and $\overline{\mathrm{CCH_2CH_2CH_2CH(CH_3)O}}$, respectively). The structures of the first two of these complexes have been determined by X-ray crystallography, and this confirms that the cyclic carbene ligand occupies an equatorial position. IR, $^1H$ and $^{13}C$ NMR, and mass spectra are reported and discussed for these carbene complexes.

Binuclear metal complexes containing carbene or $\mu$-hydrocarbyl ligands are of considerable current interest.[1,2] This is partly due to the proposed intermediacy of such species in a variety of catalytic reactions.[3-5]

The reaction of $Br(CH_2)_3Br$ with several metal carbonyl anions was first reported several years ago.[6-8] The orange product of the reaction of $Na[Mn(CO)_5]$ with $Br(CH_2)_3Br$ was originally reported by King to be a $\mu$-1,3-propanediyl compound,[7] with a novel structure to account for the $^1H$ NMR data. Some years later, Casey,[9] using $^1H$ NMR data and deuterium-exchange experiments, put forward very convincing evidence that King's orange manganese compound was *not* the propanediyl compound $[(CO)_5MnCH_2CH_2CH_2Mn(CO)_5]$ but an isomer of this, namely the cyclic carbene complex $[(CO)_5MnMn(CO)_4(\overline{\mathrm{CCH_2CH_2CH_2O}})]$, and explained the mechanism of its formation. Surprisingly, the structure of King's orange dimanganese compound has never been confirmed. We now report the structure of this compound and the related compound

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