# Syntheses and Characterization of Nickel(II) and **Ruthenium(II)** Complexes with the Novel Phosphine Ligands 1-((Diphenylphosphino)methyl)-1-phenyl-1-silacyclopent-3-ene and 1,1-Bis((diphenylphosphino)methyl)-1-silacyclopent-3-ene. Crystal Structure of CpRuCl[(PPh<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>(SiC<sub>4</sub>H<sub>6</sub>)]

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The reaction of the lithium salt of chlorodiphenylphosphine with 1-chloro-1-phenylsilacyclopent-3-ene (1) and 1,1-dichlorosilacyclopent-3-ene (2) gave good yields of 1-((diphenylphosphino)methyl)-1-phenyl-1-silacyclopent-3-ene (L) (3) and 1,1-bis((diphenylphosphino)methyl)-1-silacyclopent-3-ene (L') (4). Both molecules were obtained as white solids characterized by NMR. Red and red-violet diamagnetic square-planar complexes trans-NiCl<sub>2</sub>L<sub>2</sub> and *cis*-NiCl<sub>2</sub>L' were obtained by reacting NiCl<sub>2</sub>·6H<sub>2</sub>O with **3** and **4**, respectively. Substitution of two PPh<sub>3</sub> in CpRuCl(PPh<sub>3</sub>)<sub>2</sub> by 4 gave CpRuCl(L') (7) in good yield. Orange crystals of 7 contain monomeric pseudooctahedral ruthenium(II) centers surrounded by a Cl atom, a Cp ligand, and the two phosphorus atoms of the 1,1-bis((diphenylphosphino)methyl)-1-silacyclopent-3-ene ligand. The silacyclopentene ring adopts a puckered ground state configuration with a puckering angle of 10°. 7 can be described as a spirannic compound with roughly perpendicular Ru-P(1)-C(10)-Si-C(20)-P(2) and Si-C(6)-C(7)-C(8)-C(9) rings.

#### Introduction

Complexes containing silacyclopentene ligands Sibonded to one or two transition metals, either directly (A) or through an organic linker (B), are of particular interest as metal-containing monomeric starting materials to generate new polymers. Such ligands and possible coordination modes to metal centers are illustrated in Chart 1.

Even though organic silacyclopentenes have been successfully developed as monomeric precursors for silicon-containing polymers,<sup>1</sup> little is known about metalcontaining species. One reason is that there are not many metal-functionalized silacyclopentenes known and the examples have been restricted so far to iron and



cobalt complexes, in which the metal is  $\sigma$ -bonded to silicon (A).<sup>2</sup> The second reason is the scarcity of silacyclopentenes carrying functionalized substituents that can bind metal centers. A few examples are shown in Chart 2,<sup>3,4</sup> but they have not been coordinated to transition metals. No molecules bearing a phosphorus donor in a position  $\beta$  to Si has yet been described.

In the present study, we report the synthesis of two new silacyclopentenes 3 and 4 containing one and two

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two metals were chosen because they give stable monomeric phosphine complexes and they can adopt different geometries to meet the steric requirement of the ligands.<sup>5</sup> The species were characterized mainly by NMR spectroscopy. Since no X-ray diffraction work had yet been done on metal-bonded silacyclopentene, the crystal structure of the ruthenium complex CpRuCl-[(PPh<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>(SiC<sub>4</sub>H<sub>6</sub>)] was determined.

#### **Experimental Section**

Solvent distillation and all other manipulations were performed in a dry nitrogen atmosphere using standard Schlenk techniques. Tetrahydrofuran, toluene, and ether were stirred with sodium wire and distilled over Na/benzophenone prior to use. Pentane and hexane were also distilled from Na just before use. Dichloromethane was dried over P2O5. All solvents were degassed by three freeze-thaw cycles. 1-Chloro-1phenylsilacyclopent-3-ene (1) and 1,1-dichlorosilacyclopent-3ene (2) were prepared by literature methods.<sup>6</sup>  $(C_6H_5)_2PCH_2Li-$ TMEDA (where TMEDA = tetramethylethylenediamine) was synthesized as previously described.<sup>10</sup> CpRuCl(PPh<sub>3</sub>)<sub>2</sub>, prepared as described earlier,17 was recrystallized from ethanol before use. NiCl<sub>2</sub>·6H<sub>2</sub>O was purchased from Aldrich and used without purification.

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The  $^1H,\ ^{31}P\{^1H\},$  and  $^{13}C\{^1H\}$  spectra were recorded on Bruker WM-200 or WH-80 spectrometers using CDCl<sub>3</sub> as solvent. For <sup>1</sup>H and <sup>13</sup>C NMR, the chemical shifts were referenced to the residual solvent signals (CDCl<sub>3</sub>,  $\delta$ (<sup>1</sup>H) = 7.27 ppm and  $\delta$  (<sup>13</sup>C) = 77 ppm), and for <sup>31</sup>P NMR, to external H<sub>3</sub>PO<sub>4</sub> 85% in D<sub>2</sub>O ( $\delta = 0$  ppm). UV-visible measurements were carried out using a HP spectrophotometer (10.0 mm cells, CHCl<sub>3</sub>). The magnetic moments for the nickel(II) complexes were determined in the solid state by the Faraday method, using a Cahn microbalance coupled with a Drusch electromagnet. Measurements were run at room temperature. HgCo(NCS)<sub>4</sub> was used as standard ( $X_g = 16.44 \ 10^{-6} \text{ cgs emu}$ ). The experimental values were corrected for the diamagnetism of the ligands.

Microanalyses were performed by the Service Central de Microanalyse du CNRS, Lyon, and by the Service de Microanalyse du LCC, Toulouse.

1-((Diphenylphosphino)methyl)-1-phenyl-1-silacyclopent-3-ene (3). Compound 1 (2.13 g; 6.6 mmol) dissolved in THF (20 mL) was added to a solution of PPh<sub>2</sub>CH<sub>2</sub>Li-TMEDA (10% excess) in 50 mL of THF at -80 °C and the mixture stirred for 1 h. The mixture was then allowed to warm up, and it was kept at room temperature for 12 h. Removal of THF from the resulting green solution in vacuo gave an oily product which was recrystallized from ether. Workup and microdistillation gave an oil. Yield: 2.12 g, 90%. Anal. Calcd for C23H23PSi: C, 77.06; H, 6.47. Found: C, 76.58; H, 6.55.

1,1-Bis(diphenylphosphino)methyl)-1-silacyclopent-3ene (4). The same procedure applied to 2 (1.22 g, 8 mmol) gave 4 in 84% yield (3.23 g). Anal. Calcd for C<sub>30</sub>H<sub>30</sub>P<sub>2</sub>Si: C, 74.97; H, 6.29; Found: C, 75.21; H, 6.38.

trans-Dichlorobis(1-((diphenylphosphino)methyl)-1phenyl-1-silacyclopent-3-ene)nickel(II) (5). At room temperature, 353 mg (1.5 mmol) of NiCl<sub>2</sub>·6H<sub>2</sub>O was added to a solution of 1.06 g (3 mmol) of 3 in 20 mL of ethanol. After 1 h at 20 °C, the solution was filtered and the red solid washed with diethyl ether and CH<sub>2</sub>Cl<sub>2</sub>. Recrystallization from CH<sub>2</sub>-Cl<sub>2</sub>/pentane at -5 °C gave red crystals of 5. Yield: 0.70 g, 55%. Anal. Calcd for C<sub>46</sub>H<sub>46</sub>P<sub>2</sub>Si<sub>2</sub>NiCl<sub>2</sub>: C, 65.26; H, 5.48; P, 7.32; Si, 6.63; Ni, 6.93. Found: C, 65.25; H, 5.44; P, 7.23; Si, 6.60; Ni, 6.84. Mp = 182° dec.

cis-Dichloro(1,1-bis((diphenylphosphino)methyl)-1-silacyclopent-3-ene)nickel(II) (6). To a solution of 0.493 g (2 mmol) of NiCl<sub>2</sub>·6H<sub>2</sub>O in 20 mL of 2-propanol/methanol (5/ 2) was added 1.000 g (2.1 mmol) of 4 in 20 mL of 2-propanol. The solution was refluxed for 3 h. The red precipitate was filtered off, washed with ether, and dried in vacuo. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane gave a violet microcrystalline powder. Yield: 0.79 g, 65%. Anal. Calcd for C<sub>30</sub>H<sub>30</sub>P<sub>2</sub>-SiNiCl<sub>2</sub>: C, 59.05; H, 4.96; P, 10.15. Found: C, 59.36; H, 4.86; P, 10.02. Mp > 200 °C.

Chloro(cyclopentadienyl)(1,1-bis((diphenylphosphino)methyl)-1-silacyclopent-3-ene))ruthenium(II) (7). A mixture of 1.06 g (1.35 mmol) of CpRuCl(PPh<sub>3</sub>)<sub>2</sub> and 1.25 g (2.6 mmol) of 4 was refluxed in 80 mL of toluene for 3 h. Evaporation of the solvent in vacuo gave a solid, which was purified by chromatography on alumina with CH<sub>2</sub>Cl<sub>2</sub> and then with acetone as eluent. Evaporation of the solvent in vacuo

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Table 1.	Crystal	lograp	hic	Data	for
CnRuC	l[(PPh <sub>2</sub>	`H <b>ə</b> )•(S	iC₄ŀ	Ie)] (2	0

formula	C <sub>35</sub> H <sub>35</sub> ClP <sub>2</sub> RuSi			
mol wt	682.21			
cryst syst	monoclinic			
space group	$P2_1/c$			
a, Å	9.2699(7)			
b, Å	18.2490(13)			
<i>c</i> , Å	18.5500(12)			
$\beta$ , deg	102.902(6)			
V. Å <sup>3</sup>	3058.8(4)			
Z	4			
$d_{ m calcd}$ , Mg.m <sup>-3</sup>	1.481			
radiation $(\lambda, \mathbf{A})$	1.540 56			
$\mu \text{ mm}^{-1}$	6.63			
temp, K	210			
no. of measd reflns	21 729			
no. of indep reflns	5790			
no. of refins with $I > 2\sigma(I)$	5427			
$R^a$	0.025			
$R_w^a$	0.035			

<sup>a</sup>  $R = \sum(||F_{o}| - |F_{c}||) / \sum(|F_{o}|), R_{w} = [\sum [w(|F_{o}| - |F_{c}|)^{2}] / \sum [w(|F_{o}|)^{2}]^{1/2}.$ 

and recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane at -20 °C gave orange crystals of 7 suitable for X-ray work. Yield: 0.53 g, 58%. Anal. Calcd for C<sub>35</sub>H<sub>35</sub>P<sub>2</sub>SiRuCl: C, 61.62; H, 5.17; P, 9.08; Found: C, 61.67; H, 5.14; P, 8.95. Mp > 200 °C.

**Crystal Structure Analysis of 7**. Orange crystals of **7** were grown from a  $CH_2Cl_2$ /pentane solution at -20 °C. The X-ray work was carried out on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Cu K $\alpha$  radiation. The reduced cell deduced from 25 reflections detected on an oscillation photograph indicated a primitive monoclinic lattice. The 2/*m* Laue symmetry was eventually checked from the full data set, and the space group was unambiguously identified from the systematic absences. The crystal data and other relevant information are summarized in Table 1.

The  $\omega/2\theta$  scan mode was used to collect the intensity data with a scan range  $\Delta \omega$  of  $(0.80 + 0.14 \tan \theta)^{\circ}$  and a constant scan rate of 16.5  $^\circ$  min  $^{-1}$  . The orientation was monitored every 400 measurements, whereas the intensity was checked every hour with four standard reflections. Intensity fluctuation remained within  $\pm 1.0\%$ . Equivalent reflections were averaged, and corrections for Lorentz and polarization effects were applied. The data set consisted of 5790 independent reflections, of which 5427 with  $I > 2\sigma_I$  were retained for structure determination. The structure was solved by direct methods and difference Fourier syntheses using NRCVAX.7 Leastsquares refinement was based on F, and all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were initially introduced at idealized positions and then refined isotropically during the last cycles. The scattering curves were from standard sources.8 The anomalous dispersion contributions  $\Delta f'$  and  $\Delta f'$  for Ru, Si, P, and Cl were from Cromer and Liberman.<sup>9</sup> Refinement converged to R = 0.025 and  $R_w =$ 0.035. The refined parameters are provided in the Supporting Information.

### **Results and Discussion**

**Synthesis of the Ligands**. Compounds **3** and **4** were prepared following the procedure used to prepare aliphatic phosphines bearing methylsilane substituents.<sup>10,11</sup> Thus, reacting ((diphenylphosphino)methyl)-lithium–TMEDA with 1-chloro-1-phenylsilacyclopent-3-ene (**1**) and 1,1-dichlorosilacyclopent-3-ene (**2**) in THF produced the monodendate phosphine **3** and bidentate diphosphine **4**, respectively, in 85% yield (Scheme 1)

The synthesis of **4** was critically sensitive to the details of the procedure used. It was crucial to keep the lithium reactant in excess in order to get complete



Table 2. <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR Data

compd	NMR data			
<b>3</b> <sup>a</sup>	$^{31}P{^{1}H}:-22$			
	<sup>1</sup> H: 1.9 (2H, d, ${}^{2}J_{HP} = 1$ Hz, H <sub>A</sub> /H <sub>B</sub> );			
	1.5 (2H, d, ${}^{4}J_{\text{HP}} = 1$ Hz, H <sub>C</sub> /H <sub>D</sub> );			
	6.0 (2H, s, H <sub>E</sub> /H <sub>F</sub> ); 7.40 (5H, m, H <sub>Ar</sub> )			
	<sup>13</sup> C{ <sup>1</sup> H}: 12.9 (d, ${}^{1}J_{CP} = 30$ Hz, C <sub>1</sub> );			
	16.6 (d, ${}^{3}J_{CP} = 4.1$ , C <sub>2</sub> /C <sub>3</sub> );			
_	$129.5 (C_4/C_5)$			
<b>4</b> a	$^{31}P{^{1}H}:-22$			
	<sup>1</sup> H: 1.4 (4H, d, ${}^{2}J_{HP} = 1$ Hz, H <sub>A</sub> /H <sub>B</sub> );			
	1.1 (4H, d, ${}^{4}J_{HP} = 1$ Hz, H <sub>C</sub> /H <sub>D</sub> );			
	5.7 (2H, s, $H_E/H_F$ )			
	$^{13}C{^{1}H}: 12.6 (dd, ^{1}J_{CP} = 30 Hz,$			
	$^{\circ}J_{CP} = 4.6$ Hz, C1); 16.8 (t, $^{\circ}J_{CP} =$			
<b>5</b> b	4.1, $C_2/C_3$ ; 130.7 ( $C_4/C_5$ ) 31D(111) 4 9			
J	<sup>1</sup> H: 1 $A7$ (AH a (AB) $h_{\rm HX} = 17$ Hz Ha/Ha):			
	18 ( $AH H_{A}/H_{D}$ ): 58 ( $2H s H_{D}/H_{D}$ ):			
	$7.50 (5H \text{ m } \text{H} \Delta r)$			
	${}^{13}C{}^{1}H}; 9.4 (C1); 16.2 (C_2/C_3); 131.3 (C_4/C_5)$			
<b>6</b> <sup>b</sup>	<sup>31</sup> P{ <sup>1</sup> H}: 17			
	<sup>1</sup> H: 0.6 (4H, H <sub>C</sub> /H <sub>D</sub> ); 1.5 (4H, H <sub>A</sub> /H <sub>B</sub> );			
	5.5 (2H, $H_E/H_F$ )			
	<sup>13</sup> C{ <sup>1</sup> H}: 10.1 (C1); 17.5 (C <sub>2</sub> /C <sub>3</sub> ); 132.3 (C <sub>4</sub> /C <sub>5</sub> )			
<b>7</b> <sup>a</sup>	$^{31}P\{^{1}H\}: 42$			
	<sup>1</sup> H: 1.54 (2H, q, $J_{\rm HH} = 13.7$ Hz, H <sub>A</sub> /H <sub>B</sub> );			
	0.8, 1.2 (2H, dd, ${}^{3}J_{HH} = 3$ Hz, ${}^{4}J_{HH} =$			
	1.7 Hz, H <sub>C</sub> /H <sub>D</sub> ); 4.20 (5H, s, Cp);			
	5.6, 5.7 (2H, m, $H_E/H_F$ )			
	$^{13}C{^{1}H}: 11.5 (t, {}^{1}J_{CP} = 6.5 Hz, C1);$			
	18.3(S), 19.2(t) $({}^{3}J_{CP} = 5.2 \text{ Hz},$			
	$U_2/U_3$ ; $\delta U$ (S, Up); 121.7 (t. 4 L = 5.2 Hz C on C );			
	$131.7$ (L, $3_{CP} = 3.3$ Hz, $C_4$ or $C_5$ ); 132.7 (t. 4 $L_{re} = 5.5$ Hz, $C_4$ or $C_5$ )			
	152.7 (c, $5CP = 3.5$ 112, C4 01 C5)			

<sup>a</sup> CDCl<sub>3</sub>, room temperature. <sup>b</sup> CD<sub>2</sub>Cl<sub>2</sub>, 193 K.

chlorine substitution. Consequently, the chlorosilane must be added dropwise to the solution containing the lithium. Methyldiphenylphosphine, which was obtained as a byproduct, was eliminated by distillation (bp = 120-122 °C/1.5 Torr).<sup>12</sup>

The structures of 3 and 4 were deduced from the NMR results (Table 2). The  ${}^{31}P{}^{1}H{}$  NMR spectra show singlets at -22 ppm for both compounds, very close to that of free  $PPh_2Me$  (-26 ppm). This indicates that the substitution of a proton by a silacyclopentene group does not affect significantly the basicity of the phosphine. The singlet for 4 showed the equivalence of the two phosphorus atoms. The two compounds also gave similar <sup>1</sup>H NMR results. In both cases, the presence of equivalent  $H_C$  and  $H_D$  protons on the endocyclic methylene groups confirmed the planarity of the silacyclopentene ring.<sup>13</sup> They appeared as a doublet because of  ${}^{4}J_{\rm HP}$ coupling. The exocyclic methylene protons H<sub>A</sub> and H<sub>B</sub> also gave a doublet, due to  ${}^{2}J_{\rm HP}$  couplings. The  ${}^{13}{\rm C}$ -{<sup>1</sup>H} spectra of the two ligands were also very similar. Phosphorus coupling was apparent for the endocyclic  $C_2/C_3$  atoms (doublet,  ${}^3J_{CP} = 4.1$  Hz). The exocyclic methylene carbon C<sub>1</sub> showed a doublet at 12.9 ppm ( ${}^{1}J_{CP}$ = 30 Hz) for 3 and a doublet of doublets centered at 12.6 ppm ( ${}^{1}J_{CP} = 30$  Hz;  ${}^{3}J_{CP} = 4.6$  Hz) for 4.

Scheme 2



Compounds **3** and **4** are functionalized mono- and diphosphines. Therefore, they should be able to act as ligands toward transition metals.

Synthesis and Characterization of the Nickel Complexes. The reaction of 2 equiv of 3 and 1 equiv of 4 with NiCl<sub>2</sub>· $6H_2O$ , in ethanol for 3 and in methanol/ 2-propanol (1/1) for 4, gave the new complexes 5 and 6 in 55 and 65% yield, respectively (Scheme 2). They precipitated as red and red-violet air-stable powders, respectively. The formula was established from elemental analysis, and a low-spin Ni(II) square-planar structure was proposed on the basis of the zero magnetic moment in the solid state, electronic spectra and NMR data.

Coordination of phosphorus to the metal is reflected by the low-field shift of the <sup>31</sup>P NMR signal. Only one signal is present at -80 °C, at 4.8 ppm for 5 and 17.0 ppm for 6, the latter being significantly broadened even at this temperature. The presence of a single <sup>31</sup>P signal for 6 indicates that the ligand is symmetrically bonded to the metal. The relatively large shift of 6 ( $\Delta \delta = 39$ ppm) compared to 5 ( $\Delta \delta = 27$  ppm) could be attributed to the different configurations of the complexes: cis P–P in 6 and trans P–P in 5. Such variations are not uncommon in nickel complexes.<sup>5</sup>

The <sup>1</sup>H NMR spectrum of **5** showed inequivalent endocyclic methyl protons  $H_C$  and  $H_D$  (AB system, <sup>2</sup> $J_{HH}$  = 17 Hz), whereas the exocyclic methylene protons  $H_A$  and  $H_B$  were equivalent and gave a singlet (Table 2). The signals for **6** were too broad to draw conclusions. In the <sup>13</sup>C spectra, coordination gave rise to only one small negative shift on  $C_1$  ( $\Delta \delta = -3.5$  ppm for **5** and -2.7 ppm for **6**), due to increased electron density created on this carbon by the positive charge located on the nickel atom.

The electronic spectra of **5** and **6** in  $CH_2Cl_2$  have profiles similar to those of other Ni(II) complexes. Only one broad band is observed at 480 nm ( $\epsilon = 400 \text{ mol}^{-1} \text{ L}$ cm<sup>-1</sup>), and it is assigned to the d-d transition  ${}^{1}\text{A}_{1} \rightarrow$  ${}^{1}\text{B}_{2}$  for the square-planar d<sup>8</sup> complex. The spectrum of **6** shows, besides the absorption band at 485 nm ( $\epsilon =$  $400 \text{ mol}^{-1} \text{ L cm}^{-1}$ ), an extra, weaker band at 835 nm ( $\epsilon =$  $60 \text{ mol}^{-1} \text{ L cm}^{-1}$ ), which could be attributed to the  ${}^{3}\text{T}_{1} \rightarrow {}^{3}\text{A}_{2}$  transition in a tetrahedral isomer. In agreement with this interpretation are the signal broadening observed in the <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra of **6** and the fact that square-planar-tetrahedral equilibria in solution are well documented for nickel(II)-phosphine complexes.  $^{14,15}$ 

**Ruthenium Complex 7.** The CpRuCl[(PPh<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-(SiC<sub>4</sub>H<sub>6</sub>)] complex 7 was obtained in refluxing toluene<sup>16</sup> by phosphine substitution, starting from CpRuCl-(PPh<sub>3</sub>)<sub>2</sub><sup>17</sup> and 4. Complex 7 was isolated as a pure orange powder after chromatography on  $Al_2O_3$  (Scheme 3).

The orange solid was identified as complex 7 by microanalysis and NMR studies. The equivalence of the two phosphorus atoms was indicated by the presence of a single <sup>31</sup>P NMR signal at 42 ppm, in the range for phosphorus atoms bonded to ruthenium.<sup>16,17</sup> The <sup>1</sup>H NMR spectrum at 20 °C showed only one broad signal at 1.54 ppm for the exocyclic methylene protons  $H_A/H_B$ , which after <sup>31</sup>P decoupling became an AB system  $(^{2}J_{\text{HA}-\text{HB}} = 13.7 \text{ Hz})$ , indicating the inequivalence of the two protons in solution. The doublets of doublets at 0.8 and 1.2 ppm for the inequivalent endocyclic methylene protons H<sub>C</sub> and H<sub>D</sub> were not affected by phosphorus decoupling, but they both appeared as singlets after irradiation of the ethylenic protons  $H_E$  and  $H_F$  ( $^3J_{HH} =$ 3 Hz;  ${}^{4}J_{\text{HH}} = 1.7$  Hz) at room temperature. The  ${}^{13}\text{C}$ NMR spectrum shows a triplet at 11.5 ppm, corresponding to the two equivalent C1 atoms coupled with the two phosphorus atoms ( ${}^{1}J_{PC} = {}^{3}J_{PC} = 6.5$  Hz). Phosphorus coupling is also observed for C<sub>3</sub>, which appears as a triplet at 19.2 ppm ( $J_{CP} = 5.2$  Hz), and for C<sub>4</sub> and C<sub>5</sub> (triplet at 131.7 ppm ( $J_{PC} = 5.2 \text{ Hz}$ ) for C<sub>4</sub> and at 132.7  $(J_{PC} = 5.5 \text{ Hz})$  for C<sub>5</sub>). Surprisingly, no phosphorus coupling is observed for C2, which gives only a singlet at 18.3 ppm.

Since no crystallographic results were available for metal complexes with a silacyclopentene ligand, the crystal structure of **7** was determined, and it confirmed the inequivalence of the two halves of the five-membered ring revealed by NMR. Single crystals were obtained by recrystallization from a dichloromethane/ pentane mixture at -20 °C. The unit cell contains the monomeric molecule shown in Figure 1. Selected intermolecular distances and bond angles are listed in Table 3.





**Figure 1.** ORTEP drawing of the  $CpRuCl[(PPh_2CH_2)_2-(SiC_4H_6)]$  molecule.

Table 3.Selected Interatomic Distances (Å) and<br/>Bond Angles (deg)

Ru-P(1)	2.2953(5)	P(1)-C(11)	1.836(2)
Ru-P(2)	2.2753(5)	P(1)-C(11')	1.848(2)
Ru-Cl	2.4419(5)	P(2)-C(20)	1.826(2)
Ru-C(1)	2.200(2)	P(2)-C(21)	1.836(2)
Ru-C(2)	2.224(2)	P(2)-C(21')	1.835(2)
Ru-C(3)	2.216(2)	C(1)-C(2)	1.413(4)
Ru-C(4)	2.202(2)	C(1)-C(5)	1.411(3)
Ru-C(5)	2.201(2)	C(2)-C(3)	1.403(5)
Si-C(6)	1.887(2)	C(3)-C(4)	1.418(5)
Si-C(9)	1.887(2)	C(6)-C(7)	1.501(3)
Si-C(10)	1.877(2)	C(7)-C(8)	1.317(4)
Si-C(20)	1.876(2)	C(8)-C(9)	1.503(4)
P(1)-C(10)	1.827(2)		
$D(1)$ $D_{11}$ $D(9)$	02 41(9)	$D_{11}$ $D(9)$ $C(91)$	110 20(7)
P(1) = Ru = P(2) P(1) = Pu = Cl	93.41(2) 88.06(2)	Ru = P(2) = C(21) Pu = P(2) = C(21')	119.29(7)
P(1) = Ku = CI P(2) = Pu = CI	87.06(2)	Ru = F(2) = C(2T) C(20) = D(2) = C(2T)	103.64(0) 104.68(10)
$\Gamma(\mathcal{L}) = \mathbf{K}\mathbf{u} = \mathbf{C}\mathbf{I}$	07.00(2)	C(20) = F(2) = C(21) C(20) = D(2) = C(21')	104.00(10) 102.01(0)
C(0) = SI = C(0)	33.0(1)	C(20) = F(2) = C(21)	102.91(9) 100.20(0)
C(0) = SI = C(10)	109.3(1) 100.2(1)	C(21) = F(2) = C(21)	100.39(9) 107.7(9)
C(0) = SI = C(20)	109.3(1) 110.1(1)	C(2) = C(1) = C(3) C(1) = C(2) = C(3)	107.7(2) 107.0(2)
C(9) = SI = C(10)	119.1(1) 110.5(1)	C(1) = C(2) = C(3) C(2) = C(2) = C(4)	107.9(2)
C(9) = SI = C(20)	110.3(1) 112.0(1)	C(2) - C(3) - C(4)	100.4(2) 107.4(2)
C(10) = SI = C(20)	112.0(1) 115.79(7)	C(3) - C(4) - C(3)	107.4(2) 109.6(2)
Ru = F(1) = C(10) Ru = D(1) = C(11)	113.72(7) 110.12(7)	C(1) = C(3) = C(4) Si $C(6) = C(7)$	100.0(2) 102.4(2)
Ru = P(1) = C(11) Ru = D(1) = C(11')	119.13(7)	$SI^{-}C(0)^{-}C(7)$	102.4(2) 110.7(9)
$R_{\rm U} = P(1) = C(11)$	113.27(7) 104.0(1)	C(0) = C(7) = C(0)	110.7(2) 110.9(2)
C(10) = P(1) = C(11) C(10) = D(1) = C(11)	104.0(1) 101.8(1)	C(7) = C(0) = C(9)	119.0(2)
C(10) = F(1) = C(11) S: $C(10) = D(1)$	101.0(1) 120 5(1)	$SI^{-}U(3)^{-}U(3)$	101.0(2) 100.4(1)
$D_{11} = D(10) = P(1)$	120.3(1) 117.20(7)	C(11) = P(1) = C(11) Si = C(20) = P(2)	100.4(1) 119.0(1)
$\operatorname{Ku}_{\Gamma}(\lambda) = C(\lambda 0)$	117.29(7)	$SI^{-}U(\lambda 0)^{-}P(\lambda)$	110.0(1)

The coordination geometry of ruthenium is best described as a distorted octahedron, with the  $\eta^5$ -Cp ligand occupying three coordination sites. The remaining positions are filled with one chlorine atom and the two phosphorus donors of the chelating ligand. The Cp ring is planar within 0.008 Å (2.5 $\sigma$ ) and symmetrically bonded to the metal: the Ru–C distances range from 2.200(2) to 2.224(2) Å, whereas the distance to the center of the ring is 1.854(1) Å. The Ru–Cl bond (2.4419(5) Å) is typical of such systems. The Ru–P distances and the P–Ru–P angle show some variation depending on the type of phosphine. In CpRuCl(PPh<sub>3</sub>)<sub>2</sub>,<sup>18</sup> the relatively long Ru–P bonds (2.336(1) Å) and the large P–Ru–P angle (103.99(4)°) can be ascribed to the rather



large steric requirement of PPh<sub>3</sub>. With the smaller PMe<sub>3</sub> ligand,<sup>18</sup>the distance is shorter (2.274(6) Å) and the angle is 94.8(2)°. Reduced steric repulsion in the complex with a bis(diphenylphosphino)ethane (diphos) derivative<sup>19</sup> results in shorter Ru-P bonds (2.277(2) Å), whereas the P-Ru-P angle in the five-membered ring is reduced to  $82.9(1)^\circ$ . In the present case, the Ru-P bonds (2.2953(5) and 2.2753(5) Å) are comparable with those of the diphos complex, but the six-membered chelate ring opens the P-Ru-P angle to 93.41(2)°. Interestingly, the Ru-P(1)-C(10)-Si-C(20)-P(2) ring presents a cyclohexane-like chair conformation: P(1), C(10), C(20), and P(2) are coplanar, and the Si atom lies 0.65 Å above and the Ru atom 1.09 Å below this plane, which corresponds to dihedral angles of 38.0(1)° and 44.3(1)°, respectively (Chart 3).

The silacyclopentene ring becomes puckered upon coordination. It adopts an envelope conformation with a dihedral angle of 10° between the C(6)-C(7)-C(8)-C(9) and C(6)-Si-C(9) planes. The bond distances and angles in the ring are not affected,<sup>2,20</sup> but appreciable changes are noted on some of the angles around Si. Their values still average 110°, but the C(6)-Si-C(9) angle decreases to 95.0(1)° and the external C(9)-Si-C(10) angle increases to 119.3(1)° to accommodate the six-membered chelate ring. Compound 7 can be described as a spirannic compound, in which the Ru-P(1)-C(10)-Si-C(20)-P(2) and Si-C(6)-C(7)-C(8)-C(9) rings sharing the Si atom make an angle of 87°.

In conclusion, these results demonstrate that, provided appropriate linkers are devised, functionalized silacyclopentenes can be used as ligands and stable metal complexes can be made. Work is in progress to explore the reactivity of these species as inorganic monomeric precursors.

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**Supporting Information Available:** Tables of crystal data, atomic coordinates, temperature factors, bond lengths and angles, refined temperature factors, weighted least-squares planes, and torsion angles and a stereoview of the unit cell (14 pages). Ordering information is given on any current masthead page.

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