

Silicon containing ferrocenyl phosphane ligands

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Abstract

New ferrocenyl phosphane ligands incorporating Si–P linkages, $[(\eta\text{-C}_5\text{H}_4\text{SiMe}_2\text{PR}_2)_2\text{Fe}]$, where R = Ph and Me, and the corresponding metal complexes $[\text{Mo}(\text{CO})_4(\text{L})]$ have been prepared and characterised. The molecular structures of $[(\eta\text{-C}_5\text{H}_4\text{SiMe}_2\text{PR}_2)_2\text{Fe}]$, where R = Ph and Me have been determined by single crystal X-ray diffraction.
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1. Introduction

Transition metals containing a bidentate diphosphane ligand have played an important role in homogeneous catalysis [1]. A backbone that has attracted considerable attention in bidentate diphosphane ligands is ferrocene. The most common ligand in this class is 1,1'-bis(diphenylphosphino)ferrocene (dppf). The dppf ligand has been coordinated to most late transition metals [2] and complexes of this ligand have been used in a range of catalytic reactions including carbon–carbon coupling [3,4] and hydroformylation reactions [5]. Transition metals containing ferrocene-based ligands, such as dppf, often show superior catalytic activity when compared to complexes containing other types of bidentate diphosphane ligands [6]. The origin of this effect is thought to be due to the conformational flexibility of the ferrocene backbone in the coordinated ligand.

Ferrocene diphosphane ligands have been prepared with additional substituents at the ferrocene cyclopentadienyl ring and with a variety of groups at the phosphorus atom [7,8]. However, less attention has focused on synthesising ligands containing a group between the ferrocene cyclopentadienyl ring and the phosphorus atoms. Bidentate ferrocene diphosphane ligands containing a carbon spacer have been prepared and studied by

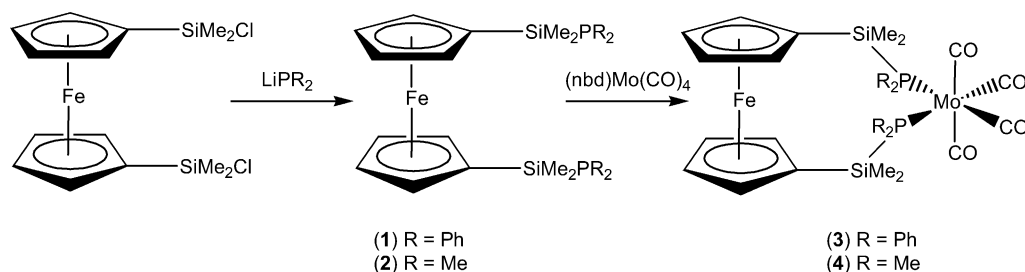
us and others [9–11]. Herein, we report the synthesis and properties of ferrocenyl phosphane ligands with a silyl spacer.

2. Results and discussion

2.1. Synthesis and characterisation of the ligands $[(\eta\text{-C}_5\text{H}_4\text{SiMe}_2\text{PR}_2)_2\text{Fe}]$ where R = Ph (**1**) and Me (**2**)

The ferrocenyl silyl-phosphane ligands $[(\eta\text{-C}_5\text{H}_4\text{SiMe}_2\text{PR}_2)_2\text{Fe}]$, where R = Ph (**1**) and Me (**2**) were prepared from the reaction of $[(\eta\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})_2\text{Fe}]$, in a diethyl ether solution with the corresponding lithium phosphide at -78°C to afford, after work-up, the ligands as air-sensitive orange solids in high yield, Scheme 1. Ligands **1** and **2** were characterised by ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and ^{29}Si NMR spectroscopy, elemental analysis and mass spectrometry. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (C_6D_6) exhibits a singlet at $\delta -54.5$ for ligand **1** and $\delta -129.0$ for ligand **2**. Unfortunately, silicon satellites were not completely resolved in either spectrum. However, the ^{29}Si NMR shows the expected doublet at $\delta -2.44$ and $\delta 0.27$ for **1** and **2**, respectively, with a $^1J_{\text{PSi}}$ coupling constant of 22.2 Hz for **1** and 18.5 Hz for **2**. The value of the ^{31}P and ^{29}Si chemical shifts and the magnitude of the $^1J_{\text{PSi}}$ coupling constants are comparable to those of similar compounds and are typical of a phosphorus(III) centre bound directly to silicon [12–14].

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Scheme 1.

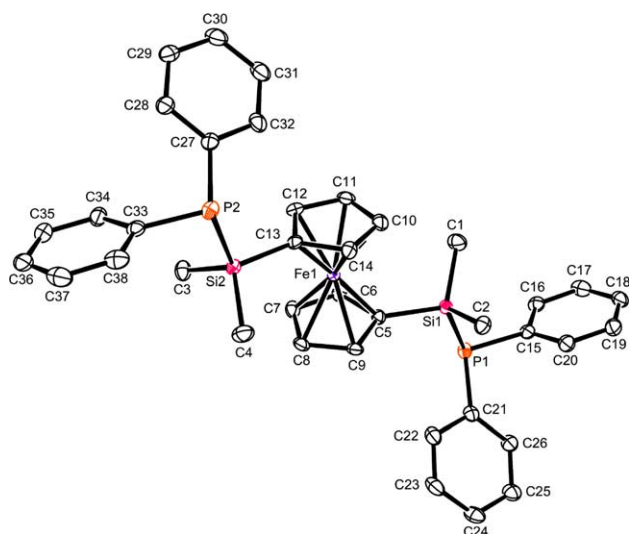


Fig. 1. ORTEP diagram of the molecular structure of ligand 1. Thermal ellipsoids are set at 40%. Hydrogen atoms are omitted for clarity.

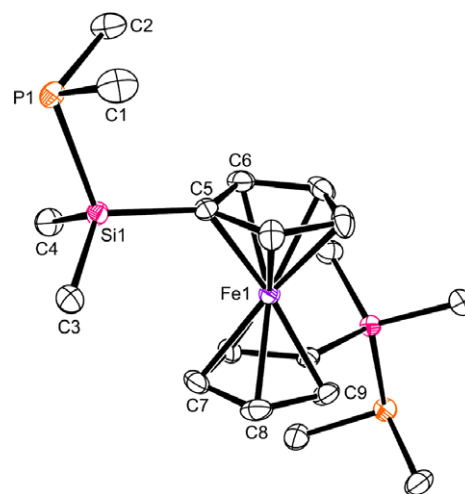


Fig. 2. ORTEP diagram of the molecular structure of ligand 2. Thermal ellipsoids are set at 40%. Hydrogen atoms are omitted for clarity.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the products obtained from each reaction were consistent with the formation of the desired ligand **1** and **2** and their data are listed in Section 3.

Exposure of ligands **1** and **2** to water results in the formation of the known siloxane bridged ferrocenophane $[\text{Fe}(\eta\text{-C}_5\text{H}_4)_2(\text{SiMe}_2)_2\text{O}]$ due to the reactivity of the Si–P linkage [15,16].

2.2. Molecular structure of ligands 1 and 2

Crystals of the ferrocenyl ligands **1** and **2**, suitable for single crystal X-ray diffraction, were obtained by slow cooling of a toluene solution and by slow evaporation of a pentane solution, respectively. An ORTEP view of the molecular structure of **1** and **2** are shown in Figs. 1 and 2, respectively, and crystallographic data given in Table 1. Selected bond lengths and angles are listed in Table 2. The asymmetric unit of ligand **1** contains two unique molecules that have similar geometry and confirmation, however, only data for one of the unique molecules is given in Table 2. The asymmetric unit of ligand **2** contains half a molecule with the rest generated by symmetry.

In ligand **1**, the lengths of the Si–P bonds, Si(1)–P(1) and Si(2)–P(2), are 2.2770(9) and 2.2837(9) Å, respectively, whereas in ligand **2**, the Si–P bond distance is 2.2578(7) Å. These are typical for a Si–P bond [17] (2.264 Å) and compare favourably to the average value of 2.275 Å found in the structurally characterised compound $\text{HC}(\text{SiMe}_2\text{PPh}_2)_3$ [18]. Similarly, the lengths of the P–C bonds are comparable. All the Si–C bonds in ligands **1** and **2** have a similar length and are comparable to the Si–C bonds found in the compound $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2$ where the average Si–C bond length was found to be 1.862 Å [19]. The average Fe–C (2.050 Å (**1**) and 2.055 Å (**2**)) and Fe–Cp centroid distance (1.6505 Å (**1**) and 1.657 Å (**2**)) are also similar to values found in $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2$ [19] and other ferrocenyl-based compounds [20]. The Cp rings of the ligands are very close to being eclipsed in **1** and are perfectly eclipsed in **2**, however, the substituents at the Cp rings in both compounds avoid an eclipsing interaction by pointing away from one another at an angle close to 180°. The remaining bond lengths and angles are unexceptional and are within expected limits.

Table 1
Summary of crystallographic data for compounds **1** and **2**

	1	2
Empirical formula	C ₃₈ H ₄₀ FeP ₂ Si ₂	C ₁₈ H ₃₂ FeP ₂ Si ₂
<i>M_r</i>	670.67	422.41
<i>T</i> (K)	150	150
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 12 ₁ 1	<i>Pbcn</i>
<i>a</i> (Å)	8.7060(10)	7.3292(1)
<i>b</i> (Å)	15.6610(10)	12.3212(3)
<i>c</i> (Å)	24.9020(10)	24.5144(6)
α (°)	90	90
β (°)	92.43(1)	90
γ (°)	90	90
<i>V</i> (Å ³)	3392.2(5)	2213.76(8)
<i>Z</i>	4	4
<i>D_c</i> (Mg m ⁻³)	1.31	1.27
μ (mm ⁻¹)	0.64	0.93
<i>F</i> ₀₀₀	1411	899
Crystal size (mm)	0.30 × 0.40 × 0.50	0.10 × 0.20 × 0.30
Description of crystal	Orange prism	Orange plate
Absorption correction	Multi-scan	Multi-scan
Transmission coefficients (min., max.)	0.743, 0.825	0.83, 0.91
θ range for data collection (°)	1 ≤ θ ≤ 27	1 ≤ θ ≤ 27
Index ranges, <i>hkl</i>	0–11, 0–20, –32–32	–9–9, –15–15, –31–31
Reflections measured	7782	4903
Unique reflections	7773	4522
<i>R</i> _{int}	0.027	0.046
Observed reflections (<i>I</i> > 3 σ (<i>I</i>))	7038	2953
Refinement method	Full-matrix least-squares on <i>F</i>	Full-matrix least-squares on <i>F</i>
Parameters refined	776	106
Weighting scheme	Chebyshev 3-term polynomial	Chebyshev 3-term polynomial
Goodness of fit	0.9607	1.0468
<i>R</i>	0.0266	0.0356
<i>wR</i>	0.0309	0.0365
Residual electron density (min., max.) (e Å ⁻³)	–0.47, 0.36	–0.62, 1.32

2.3. Coordination of ligands **1** and **2** to transition metal centres

The Mo(0) complexes [(η -C₅H₄SiMe₂PR₂)₂Fe]Mo(CO)₄, where R = Ph (**3**) and Me (**4**) were prepared, almost quantitatively, by reaction of the corresponding ligands **1** and **2** with [(nbd)MoCO₄], where nbd = 2,5-norbornadiene. The ³¹P{¹H} NMR spectra each contained a single resonance that had shifted to higher frequency when compared to that of the starting ligands indicative of coordination of tertiary phosphane ligands to the metal centre. The ³¹P{¹H} chemical shift of **3** (δ –25.3) and **4** (δ –95.7) are similar to the chemical shifts reported for a molybdenum tetracarbonyl compound containing a coordinated Ph₂PSiMe₂ group [Mo(CO)₄{Ph₂PSiMe₂Si₃CH}] (δ –17.7) [18] and

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1** and **2**

Compound 1			
Fe(1)–C _{mean}	2.050	P(1)–C(21)	1.840(3)
Fe(1)–C _{Pcentroid}	1.6505	P(2)–C(33)	1.845(3)
P(1)–Si(1)	2.2770(9)	P(2)–C(27)	1.839(3)
Si(2)–P(2)	2.2837(9)	Fe(1)–C(5)–Si(1)	125.09(14)
Si(1)–C(5)	1.857(3)	Fe(1)–C(13)–Si(2)	127.17(13)
Si(2)–C(13)	1.848(3)	P(1)–Si(1)–C(5)	107.40(9)
Si(1)–C(1)	1.874(3)	P(2)–Si(2)–C(13)	108.07(8)
Si(1)–C(2)	1.859(3)	Si(1)–P(1)–C(15)	100.27(9)
Si(2)–C(3)	1.869(3)	Si(1)–P(1)–C(21)	104.73(9)
Si(2)–C(4)	1.872(3)	Si(2)–P(2)–C(33)	98.43(9)
P(1)–C(15)	1.841(3)	Si(2)–P(2)–C(27)	105.88(9)
Compound 2			
Fe(1)–C _{mean}	2.055	P(1)–C(2)	1.844(2)
Fe(1)–C _{Pcentroid}	1.657	Fe(1)–C(5)–Si(1)	125.7(1)
P(1)–Si(1)	2.2578(7)	P(1)–Si(1)–C(5)	109.93(6)
Si(1)–C(3)	1.868(2)	Si(1)–P(1)–C(1)	100.41(8)
Si(1)–C(5)	1.862(2)	Si(1)–P(1)–C(2)	99.72(7)
P(1)–C(1)	1.844(2)		

a SiMe₂PMe₂ unit [Mo(CO)₄(PMe₂SiMe₂CH₂PMe₂)] (δ –88.1) [21]. The ¹H and ¹³C{¹H} NMR spectra showed the expected peaks for the ferrocene ligand framework and, in each case, two further high frequency peaks in the ¹³C{¹H} spectra which are assigned to the carbonyl groups, δ 210.3 (triplet, ²*J*_{PC} = 9.5 Hz), δ 216.5 (doublet, ²*J*_{PC} = 11.8 Hz) and δ 210.3 (triplet, ²*J*_{PC} = 9.2 Hz), δ 216.5 (doublet, ²*J*_{PC} = 14.0 Hz) for complex **3** and **4**, respectively, with the lower frequency signal corresponding to carbon-*trans*-carbon and the higher frequency signal to carbon-*trans*-phosphorus. The coupling pattern observed for the carbonyl resonances are consistent with the formation of the *cis*-coordinated products, with the apparent doublet pattern for carbon-*trans*-phosphorus observed presumably due to unresolved ²*J*_{CP} *cis* coupling which should have afforded a doublet of doublets. The *cis* coordination of the phosphane ligands to the metal centres were further confirmed by IR measurements which showed the presence of four bands in the carbonyl stretching region as required for C_{2v} local symmetry at the metal centre. The EI mass spectra of complexes **3** and **4** showed the parent ions of the desired complexes.

In summary, new ferrocene-based bidentate phosphine ligands have been prepared containing an unusual Si–P linkage and coordinated, in a *cis* fashion, to Mo(CO)₄ units.

3. Experimental

3.1. General procedures

All manipulations were carried out under an inert atmosphere of dinitrogen using standard Schlenk line

techniques, or in an inert atmosphere dry box containing dinitrogen. All solvents were dried over the appropriate drying agents and distilled under nitrogen. NMR spectra were recorded using either a Varian Mercury 300 (^1H , 300 MHz; ^{13}C , 75.5 MHz; ^{31}P , 121.6 MHz) or a Varian UNITYplus (^1H , 500 MHz; ^{13}C , 125.7 MHz; ^{31}P , 202.4 MHz; ^{29}Si , 99.3 MHz) spectrometer, and at room temperature unless otherwise stated. The spectra were referenced internally relative to the residual protio-solvent (^1H) and solvent (^{13}C) resonances and chemical shifts reported relative to tetramethylsilane (^1H , ^{13}C , ^{29}Si , $\delta=0$) or externally to H_3PO_4 (^{31}P , $\delta=0$). Infrared spectra were recorded on a 6020 Galaxy Series FT-IR in the range 4000–400 cm^{-1} . Samples were prepared in the glovebox as a Nujol-mull between KBr plates. Electron impact mass spectra were obtained using a Micromass GCT Probe EI/FI MS. Microanalyses were performed by the microanalytical department of the Inorganic Chemistry Laboratory, University of Oxford.

All reagents were purchased from Aldrich and used as received unless otherwise stated. $\text{LiPMe}_2 \cdot 0.5\text{Et}_2\text{O}$ was prepared by deprotonating HPMe_2 using a modification of Issleib's method [22] with $^t\text{BuLi}$ was used as the base instead of PhLi . The reagents LiPPh_2 [23], $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})_2]$ [24], and $(\text{nb})\text{Mo}(\text{CO})_4$ [25] were prepared using published procedures.

4. Syntheses

4.1. Preparation of 1,1'-bis[dimethyl(diphenylphosphino)silyl]ferrocene (1)

1,1'-Bis(chlorodimethylsilyl)ferrocene (1.86 g, 5.0 mmol) was dissolved in Et_2O (40 ml). The clear orange solution was cooled to -78°C and a suspension of lithium diphenylphosphide (2.02 g, 10.5 mmol) in Et_2O (20 ml) was then added dropwise. After addition was complete, the reaction mixture was allowed to warm to room temperature and the resulting orange solution stirred for 12 h. The solvent was then removed under vacuum and the resulting orange solid extracted with benzene (3×20 ml). The benzene extracts were combined and pumped down to dryness to yield a crystalline orange solid. Yield = 2.83 g, 84%.

^1H NMR (C_6D_6 , 300 MHz): δ 0.47 (d, $^3J_{\text{PH}} = 4.70$ Hz, 12H, SiCH_3), 3.93 (m, 4H, Cp-H), 4.21 (m, 4H, Cp-H), 7.10–7.70 (20H, Ar-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75.5 MHz): δ -1.33 (d, $^2J_{\text{PC}} = 14.36$ Hz, SiCH_3), 69.92 (d, $^2J_{\text{PC}} = 15.56$ Hz, $\text{Cp}_{\text{ipso}}\text{-C}$), 72.20 (s, Cp-C), 73.94 (s, Cp-C), 128.51 (s, Ar-C), 128.78 (s, Ar-C), 134.43 (s, Ar-C), 136.31 (d, $^1J_{\text{PC}} = 16.76$ Hz, Ar-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.5 MHz): δ -54.51 (s, SiPPh_2). ^{29}Si NMR (C_6D_6 , 99.3 MHz): δ -2.44 (d, $^1J_{\text{SiP}} = 22.2$ Hz, SiPPh_2). MS (EI) m/z 592 [$\text{MH}^+ - \text{Ph}$] (100%).

Elemental analysis (%): Found (Calc.): C, 67.61 (68.05); H, 6.27 (6.01); P, 9.28 (9.24)%.

4.2. Preparation of 1,1'-bis[dimethyl(dimethylphosphino)silyl]ferrocene (2)

1,1'-Bis(chlorodimethylsilyl)ferrocene (3.71 g, 10.0 mmol) was dissolved in Et_2O (40 ml) and cooled to -78°C . A suspension of $\text{LiPMe}_2 \cdot 0.5\text{Et}_2\text{O}$ (2.31 g, 22.0 mmol) in Et_2O (20 ml) was then added dropwise to the cooled solution. The reaction mixture was allowed to warm to room temperature and stirred for 6 h. The solvent was then removed under vacuum leaving an orange solid. The solid was extracted with pentane (2×30 ml) and upon removal of the volatiles a waxy orange solid was obtained. Yield = 4.01 g, 95%.

^1H NMR (C_6D_6 , 300 MHz): δ 0.07 (s, 12H, SiCH_3), 0.64 (d, $^2J_{\text{PH}} = 2.35$ Hz, 12H, PCH_3), 3.93 (m, 4H, Cp-H), 4.22 (m, 4H, Cp-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75.5 MHz): δ -3.31 (d, $^2J_{\text{PC}} = 13.16$ Hz, SiCH_3), 7.16 (d, $^2J_{\text{PC}} = 17.95$ Hz, PCH_3), 72.02 (s, Cp-C), 73.64 (s, Cp-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.5 MHz): δ -128.99 (s, SiPMe_2). ^{29}Si NMR (C_6D_6 , 99.3 MHz): δ 0.27 (d, $^1J_{\text{SiP}} = 18.5$ Hz, SiPMe_2). MS (EI) m/z 422 [M^+] (26%). Elemental analysis (%): Found (Calc.) C, 50.46 (51.18); H, 7.04 (7.64)%.

4.3. Preparation of tetracarbonyl[*P,P'*-bis(dimethyl(diphenylphosphino)silyl]ferrocene]-molybdenum (3)

1,1'-Bis(dimethyl(diphenylphosphino)silyl]ferrocene (1) (1.06 g, 1.6 mmol) was dissolved in THF (20 ml) to produce an orange solution. This solution was added dropwise to a stirred solution of (norbornadiene)tetracarbonylmolybdenum (0.47 g, 1.6 mmol) dissolved in THF (30 ml). On addition the green-yellow solution changed to a dark orange colour. Once addition was complete, the reaction was heated to 65°C under nitrogen for 3 h. After cooling to room temperature, volatiles were removed under vacuum and the resulting orange solid was washed with pentane (2×10 ml). The solid was then dried under vacuum. Yield = 0.91 g, 66%.

^1H NMR (CD_2Cl_2 , 500 MHz): δ 0.38 (br s, 12H, SiCH_3), 3.55 (m, 4H, Cp-H), 4.04 (m, 4H, Cp-H), 6.78–7.39 (20H, Ar-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 125.7 MHz): δ -1.76 (t, $^3J_{\text{PH}} = 5.91$ Hz, SiCH_3), 67.40 (d, $^1J_{\text{PC}} = 9.67$ Hz, $\text{Cp}_{\text{ipso}}\text{-C}$), 72.04 (s, Cp-C), 74.64 (s, Cp-C), 127.81 (s, Ar-C), 128.27 (s, Ar-C), 133.49 (s, Ar-C), 133.96 (d, $^1J_{\text{PC}} = 9.67$ Hz, Ar-C), 210.25 (t, $^2J_{\text{PC}} = 9.47$ Hz, *cis*-CO), 216.49 (d, $^2J_{\text{PC}} = 11.82$ Hz, *trans*-CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 202.4 MHz): δ -25.33 (s, SiPPh_2Mo). MS (EI) m/z 880 [M^+] (100%). Selected IR data ($\nu(\text{CO})$ cm^{-1} , nujol mull, KBr plates) 2012 (m), 1912 (s), 1904 (s), 1888 (vs). Elemental analysis (%): Found (Calc.) C, 57.15 (57.41); H, 5.16 (4.59)%.

4.4. Preparation of tetracarbonyl[*P,P'*-bis(dimethyl(dimethylphosphino)silyl]ferrocene]-molybdenum (**4**)

1,1'-Bis(dimethyl(dimethylphosphino)silyl]ferrocene (**2**) (0.58 g, 1.4 mmol) was dissolved in THF (20 ml) and added dropwise to a stirred solution of (norbornadiene)tetracarbonylmolybdenum (0.41 g, 1.4 mmol) dissolved in THF (30 ml). On addition the green-yellow solution changed to an orange colour. Once addition was complete, the reaction was heated to 65 °C under nitrogen for 3 h. After cooling to room temperature, volatiles were removed under vacuum and the resulting light orange solid was washed with 5 ml of pentane. The solid was then dried under vacuum. Yield = 0.69 g, 80%.

¹H NMR (CD₂Cl₂, 500 MHz): δ 0.35 (d, ³J_{PH} = 4.39 Hz, 12H, SiCH₃), 1.52 (d, ²J_{PH} = 5.37 Hz, 12H, PCH₃), 4.28 (t, ³J_{HH} = 3.42 Hz, 4H, Cp-H), 4.39 (t, ³J_{HH} = 3.42 Hz, 4H, Cp-H). ¹³C{¹H} NMR CD₂Cl₂, 125.7): δ -2.22 (t, 4.30 Hz, SiCH₃), 15.50 (dd, ¹J_{PC} = 8.06 Hz, ³J_{PC} = 3.22 Hz, PCH₃), 67.76 (d, ¹J_{PC} = 5.90 Hz, Cp_{ipso}-C), 71.31 (s, Cp-C), 74.08 (s, Cp-C), 210.49 (t, ²J_{PC} = 9.16 Hz, *cis*-CO), 215.82 (d, ²J_{PC} = 13.97 Hz, *trans*-CO). ³¹P{¹H} NMR (CD₂Cl₂, 202.4 MHz): δ -95.74 (s, SiPMe₂Mo). MS (EI) *m/z* 632 [M⁺] (34%). Selected IR data (ν(CO) cm⁻¹, nujol mull, KBr plates) 2008 (m), 1908 (s), 1900 (s), 1880 (s, br). Elemental analysis (%): Found (Calc.) C, 42.68 (41.92); H, 5.34 (5.12)%.

5. X-ray crystallography

Crystals were isolated under dinitrogen, covered with a perfluoropolyether oil, and mounted on the end of a glass fibre. Crystal data are summarised in Table 1.

All data were collected at 150 K using an Enraf-Nonius KappaCCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å), as summarised in Table 1. The images were processed with the DENZO and SCALEPACK programs [26]. All solution, refinement, and graphical calculations were performed using the CRYSTALS program suite [27]. The crystal structures were solved by direct methods using the SIR92 program [28] and were refined by full-matrix least squares on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 224907 for compound **1** and 224908 for compound **2**.

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