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Silylated diphosphite complexes of molybdenum. Crystal structures of the compounds $\text{Mo}(\text{CO})_4[\text{P}(\text{OMe})_2\text{O}]_2\text{SiR}^2\text{R}^3$ ($\text{R}^2 = \text{R}^3 = \text{Ph}$ or $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{Ph}$)

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Abstract

The crystal structures of two silylated diphosphite complexes of molybdenum, $\text{Mo}(\text{CO})_4[\text{P}(\text{OMe})_2\text{O}]_2\text{SiPh}_2$ (**1**) and $\text{Mo}(\text{CO})_4[\text{P}(\text{OMe})_2\text{O}]_2\text{SiMePh}$ (**2**) have been determined. Both complexes crystallize in the triclinic system (space group $P\bar{1}$) with unit cell parameters: (**1**) $a = 909.5(1)$ pm, $b = 1059.8(1)$ pm and $c = 1442.4(2)$ pm; $\alpha = 80.84(1)^\circ$, $\beta = 72.73(1)^\circ$ and $\gamma = 73.51(1)^\circ$; $U = 1.2687(3)$ nm³; $Z = 2$; (**2**) $a = 927.7(1)$ pm, $b = 1058.4(1)$ pm and $c = 1279.5(2)$ pm; $\alpha = 96.23(1)^\circ$, $\beta = 99.17(1)^\circ$ and $\gamma = 110.48(1)^\circ$; $U = 1.1434(3)$ nm³; $Z = 2$. Both **1** and **2** consist of discrete, slightly distorted octahedral monomers in which the six-membered chelate rings adopt unusual twist-boat conformations in contrast to the chair type geometry normally found in complexes containing the formally analogous diphosphine ligand $[\text{PPh}_2\text{CH}_2]_2\text{CH}_2$ (dppp).

The applications of chelating polyphosphorus ligands in coordination and organometallic chemistry are widely exploited [1], particularly in the areas of homogeneous catalysis and catalytic asymmetric synthesis where the detailed structure of the chelate ring is crucial in determining the stereochemical outcome of the reaction [2]. We are currently examining the chemistry of a family of silylated organophosphorus compounds of the form $[\text{PR}_2\text{O}]_n\text{SiR}'_{4-n}$ ($\text{R} = \text{Ar}$, OMe , OEt ; $\text{R}' = \text{Me}$, Ph , $\text{CH}=\text{CH}_2$ and H ; $n = 1-3$) some of which are good chelating ligands towards transition metals [3]. Within this class of ligands, there is an opportunity for studying the effects that changing substituents on both silicon and phosphorus atoms have on the spectroscopic and structural properties of their complexes. Certain of these properties have recently been investigated [4] and here we wish to report the results of single-crystal X-ray diffraction analyses on the complexes, $\text{Mo}(\text{CO})_4[\text{P}(\text{OMe})_2\text{O}]\text{SiPh}_2$ (**1**) and $\text{Mo}(\text{CO})_4[\text{P}(\text{OMe})_2\text{O}]\text{SiMePh}$ (**2**).

Experimental

Compounds **1** and **2** were synthesized by the reported procedure [4]. Suitable single crystals of both **1** and **2** were grown by slow cooling of saturated solutions to -30°C ; toluene was used as the crystallizing solvent for **1**, whereas for **2** a layered mixture of CH_2Cl_2 /pentane ($\sim 1:1$, v/v) was used. In each case, a single crystal was sealed within a Pyrex capillary under dry dinitrogen prior to mounting on the diffractometer.

X-Ray diffraction analysis

All diffraction measurements were made at 200 K on a Stoe STADI4 diffractometer operating in the ω - θ scan mode using graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 71.069$ pm). Crystal data are listed in Table 1 together with details of data collection and structure refinement. The data sets were corrected for Lorentz and polarization factors and also for absorption using azimuthal psi scans.

Both structures were solved by standard heavy-atom techniques and were refined by full-matrix least squares using SHELX76 [5]. In both cases, all non-hydrogen atoms were refined with anisotropic thermal parameters. All phenyl groups

Table 1

Crystallographic data for compounds **1** and **2**^a

	1	2
<i>Crystal data</i>		
Formula	$\text{C}_{20}\text{H}_{22}\text{MoO}_{10}\text{P}_2\text{Si}$	$\text{C}_{15}\text{H}_{20}\text{MoO}_{10}\text{P}_2\text{Si}$
<i>M</i>	608.36	546.29
Crystal dimensions (mm)	$0.55 \times 0.3 \times 0.1$	$0.84 \times 0.53 \times 0.38$
<i>a</i> (pm)	909.5(1)	927.7(1)
<i>b</i> (pm)	1059.8(1)	1058.4(1)
<i>c</i> (pm)	1442.4(2)	1279.5(2)
α ($^{\circ}$)	80.84(1)	96.23(1)
β ($^{\circ}$)	72.73(1)	99.17(1)
γ ($^{\circ}$)	73.51(1)	110.48(1)
<i>U</i> (nm ³)	1.2687(3)	1.1434(3)
<i>D_x</i> (g cm ⁻³)	1.59	1.59
<i>F</i> (000)	615.91	555.91
μ (cm ⁻¹)	6.84	7.54
<i>Data collection</i>		
No. of data collected	4478	4150
No. of data observed ^b	3452	3302
<i>Refinement</i>		
$\rho_{\text{max}}, \rho_{\text{min}}$ (e \AA^{-3})	0.41, -0.41	0.79, -0.59
$\Delta/\sigma_{\text{max}}$	0.025	0.098
<i>R</i> ^c	0.0263	0.0332
<i>R'</i> ^d	0.0339	0.0347
No. of parameters	296	266

^a Common to both compounds: crystal system triclinic, space group $P\bar{1}$, $Z = 2$, ω scan widths $1.05^{\circ} + \alpha$ -doublet splitting, scan speeds 1.5 – $8.0^{\circ} \text{ min}^{-1}$, $4.0 < 2\theta < 50.0^{\circ}$. ^b Criterion for observed reflection, $|F_o| > 4.0\sigma(|F_o|)$. ^c $R = \Sigma(|F_o|) - |F_c| / \Sigma|F_o|$. ^d $R' = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2)^{1/2}$ with $w = [\sigma^2(|F_o|) + 0.0004(|F_o|)^2]^{-1}$.

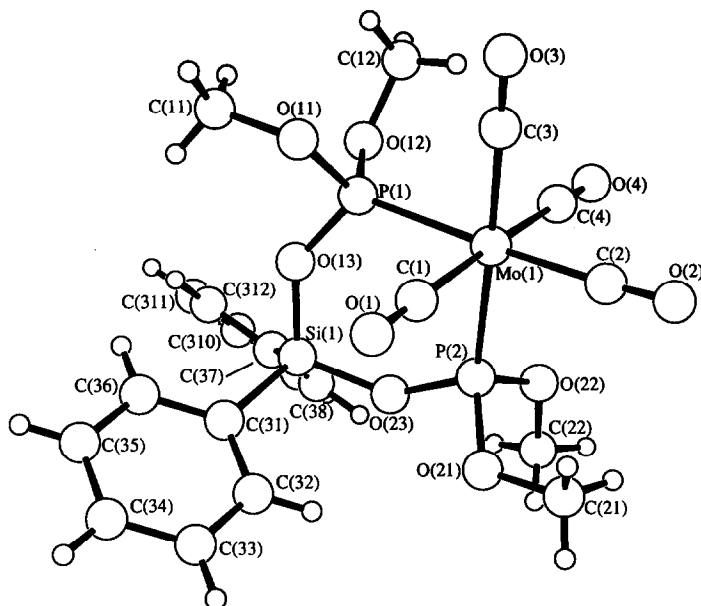


Fig. 1. The molecular structure of **1**.

were treated as rigid bodies with idealized hexagonal symmetry (C–C = 139.5 pm). In both cases the hydrogen atoms were included in calculated positions (C–H = 96 pm) and were refined with an overall isotropic thermal parameter. The weighting scheme $w^{-1} = \sigma^2(F) + 0.0004(F)^2$ was used for both complexes.

Further details of data collection and structure refinement, non-hydrogen atomic coordinates, H atom coordinates, and isotropic and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. Lists of observed and calculated structure factors are available from the authors.

Results and discussion

The molecular structures of **1** and **2** are illustrated in Figs. 1–4 and atomic coordinates, bond lengths and bond angles are reproduced in Tables 2–7.

Both **1** and **2** consist of slightly distorted, octahedral monomers in which the diphosphite ligands occupy mutually *cis* positions. The Mo–P distances range from 244.2(3) to 245.3(3) pm and appear to be relatively insensitive to the nature of the substituents on silicon. These distances are approximately 20 pm longer than those in $\text{MnBr}(\text{CO})_3[\text{P}(\text{OMe})_2\text{O}]_2\text{SiMe}_2$ [4], presumably reflecting the larger atomic radius of Mo^0 over Mn^1 . They are also approximately 4–5 pm shorter than the corresponding distances in $\text{Mo}(\text{CO})_4[\text{PPh}_2\text{O}]_2\text{SiMe}^t\text{Bu}$ [6], supportive of increasing phosphorus *s*-character in the Mo–P bond, and hence shorter Mo–P distances, as the electronegativity of the phosphorus substituents increases [7]. Within both **1** and **2** the Mo–C distances for the carbon monoxide ligands *trans* to the phosphorus atoms are consistently shorter (by *ca.* 3 pm) than those to the carbon monoxide ligands *trans* to each other. This presumably reflects the greater *trans* influence of

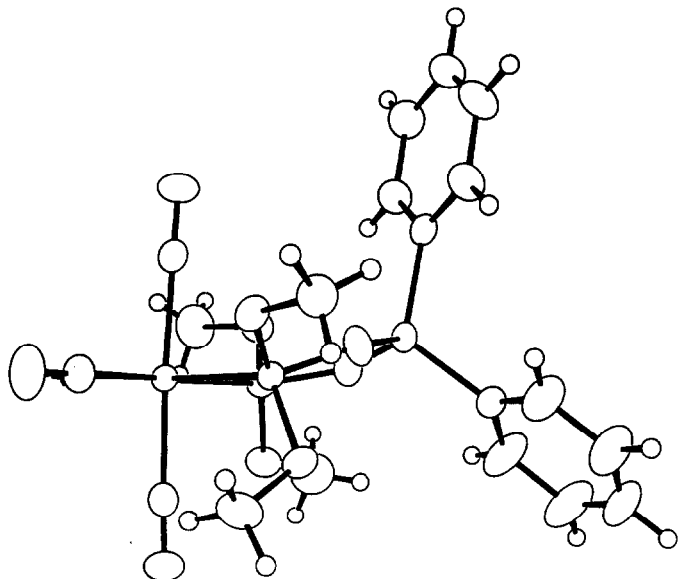


Fig. 2. View of 1 emphasizing the conformation of the chelate ring.

the carbon monoxide ligands over that of the phosphite ligands in these complexes. The Mo–C distances of the carbon monoxide ligands *trans* to each other are little different from those found in the related molybdenum compounds [6].

The only chemical difference between 1 and 2 is the nature of the substituents on silicon; consequently, we might envisage that this would have a greater influ-

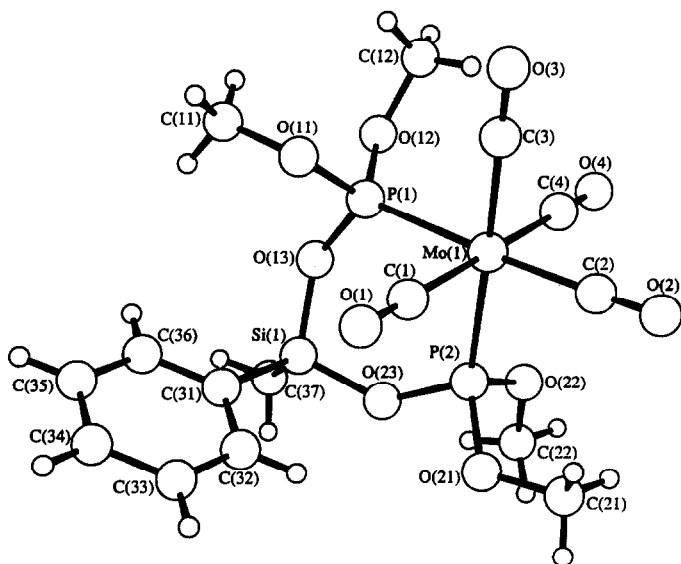


Fig. 3. The molecular structure of 2.

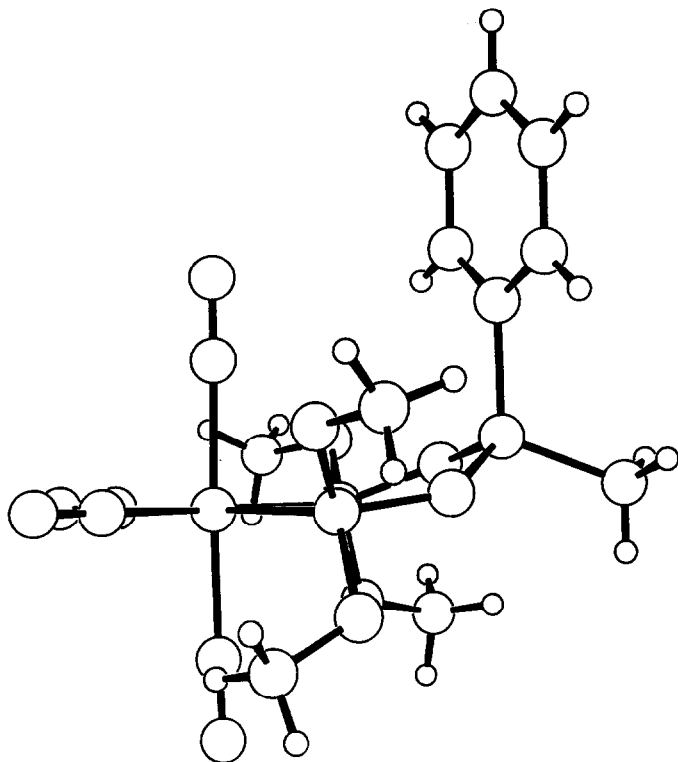


Fig. 4. View of **2** emphasizing the conformation of the chelate ring.

ence on the structural parameters associated with the chelate ring than on the more remote, ancillary CO ligands. However, the two chelate rings have very similar parameters. There is a small difference between the chelate bite angles in **1** and **2** ($90.5(1)$ and $89.7(1)^\circ$, respectively) although the values fall within the range found for other six-membered diphosphorus ligands [8] and are within 3° of those values reported in the $\text{Mo}(\text{CO})_4[\text{PR}_2\text{O}]_2\text{SiMeR}'$ systems [6]. Within the chelate rings, the corresponding P–O distances and Si–O distances in the two complexes are the same and the O(13)–Si–O(23) angle is only about 1° smaller in **2** than that in **1**.

Six-membered chelate rings based on the closely related ligand bis(diphenylphosphino)propane (dppp) often exhibit the chair conformation but both **1**, **2** and the analogues reported by Gray and co-workers adopt conformations ranging from twist-boat to “chaise-longue”: a related complex of manganese containing the diphosphite ligand $[\text{P}(\text{OMe})_2\text{O}]_2\text{SiMe}_2$ has a similar chaise longue conformation [4]. The conformations of the rings in both **1** and **2** are best described as “twist boat”. Thus, both the silicon and molybdenum atoms are disposed on the same side of the best fit plane through atoms P(1)–O(13)–Si–O(23)–P(2), although the deviations of the silicon atoms from this plane are small, $1.4(1)$ pm (**1**) and $4.3(1)$ pm (**2**), respectively, compared to the metal atoms, $53.7(1)$ pm (**1**) and $64.6(1)$ pm (**2**), respectively. The degree to which the chelate rings are twisted may be gauged by the dihedral angle between the planes P(1)–O(13)–P(2) and P(2)–O(23)–P(1)

Table 2

Non-hydrogen atomic coordinates ($\times 10^4$) for compound **1** with e.s.d.s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Mo(1)	1833.4(3)	1176.9(2)	3336.4(2)
P(1)	2441(1)	3245(1)	3437(1)
P(2)	1104(1)	2055(1)	1811(1)
Si(1)	826(1)	4943(1)	1948(1)
C(1)	-457(4)	1979(3)	4085(2)
O(1)	-1735(3)	2434(2)	4489(2)
C(2)	1308(4)	-548(3)	3364(2)
O(2)	1022(3)	-1553(2)	3436(2)
C(3)	2473(4)	522(3)	4588(3)
O(3)	2854(3)	157(3)	5289(2)
C(4)	4076(4)	448(3)	2498(3)
O(4)	5320(3)	54(3)	2012(2)
O(11)	1922(3)	3668(2)	4516(2)
C(11)	2092(4)	4914(3)	4717(3)
O(12)	4241(2)	3386(2)	3030(2)
C(12)	5412(4)	2555(4)	3502(3)
O(13)	1647(3)	4542(2)	2863(2)
O(21)	-583(3)	1997(2)	1702(2)
C(21)	-914(5)	727(4)	1764(4)
O(22)	2352(3)	1399(2)	876(2)
C(22)	2132(6)	1799(5)	-95(3)
O(23)	899(3)	3599(2)	1486(2)
C(31)	-1300(2)	5813(2)	2448(2)
C(32)	-2509(2)	5332(2)	2335(2)
C(33)	-4098(2)	5952(2)	2744(2)
C(34)	-4478(2)	7054(2)	3266(2)
C(35)	-3270(2)	7535(2)	3379(2)
C(36)	-1681(2)	6915(2)	2970(2)
C(37)	2056(3)	5918(2)	1020(2)
C(38)	2648(3)	5627(2)	48(2)
C(39)	3644(3)	6341(2)	-611(2)
C(310)	4047(3)	7346(2)	-299(2)
C(311)	3455(3)	7637(2)	673(2)
C(312)	2460(3)	6923(2)	1333(2)

which is $9.7(1)^\circ$ in **1** and $13.1(1)^\circ$ in **2**. A further indication of this ring distortion is given by the twisting of the phosphorus-bound methoxy groups away from the fully eclipsed position: the relevant angles between the planes O(11)–P(1)–O(12) and O(21)–P(2)–O(22) are $15.7(1)^\circ$ (**1**) and $20.0(1)^\circ$ (**2**), respectively. We presume that the conformational flexibility of these six-membered chelate rings is relatively high in solution since we could not observe inequivalent phosphorus methoxy substituents as would be required in the static, twist-boat conformation by $^1\text{H}\{^{31}\text{P}\}$ NMR spectroscopy upon cooling a toluene- d_8 solution of **1** to -90°C : there is however an increase in line width ($\Delta_{1/2}$) by a factor of 3 over that at 25°C suggesting that the rate of ring fluxionality may be slowing.

Although a combination of several factors are likely to be important in governing the conformational preferences of six-membered chelate rings such as those described here, the following points may be relevant.

Table 3

Bond lengths (pm) for compound 1 with e.s.d.s in parentheses

P(1)–Mo(1)	244.2(3)	P(2)–Mo(1)	245.2(3)
C(1)–Mo(1)	204.4(5)	C(2)–Mo(1)	200.8(5)
C(3)–Mo(1)	201.8(5)	C(4)–Mo(1)	203.9(5)
O(11)–P(1)	158.6(4)	O(12)–P(1)	160.8(4)
O(13)–P(1)	158.9(4)		
O(21)–P(2)	160.8(4)	O(22)–P(2)	159.0(4)
O(23)–P(2)	160.2(4)		
O(13)–Si(1)	164.5(4)	O(23)–Si(1)	164.3(4)
C(31)–Si(1)	186.6(4)	C(37)–Si(1)	185.4(4)
O(1)–C(1)	113.7(5)	O(2)–C(2)	114.8(5)
O(3)–C(3)	144.0(5)	O(4)–C(4)	114.0(5)
C(11)–O(11)	145.5(5)	C(12)–O(12)	144.3(5)
C(21)–O(21)	144.3(5)	C(22)–O(22)	145.4(5)

Table 4

Bond angles (°) for compound 1 with e.s.d.s in parentheses

P(2)–Mo(1)–P(1)	90.5(1)	C(1)–Mo(1)–P(1)	87.8(2)
C(1)–Mo(1)–P(2)	88.9(2)	C(2)–Mo(1)–P(1)	175.7(1)
C(2)–Mo(1)–P(2)	93.5(2)	C(2)–Mo(1)–C(1)	90.5(2)
C(3)–Mo(1)–P(1)	87.1(2)	C(3)–Mo(1)–P(2)	177.5(1)
C(3)–Mo(1)–C(1)	91.5(2)	C(3)–Mo(1)–C(2)	88.9(2)
C(4)–Mo(1)–P(1)	91.6(2)	C(4)–Mo(1)–P(2)	86.9(2)
C(4)–Mo(1)–C(1)	175.8(1)	C(4)–Mo(1)–C(2)	90.3(2)
C(4)–Mo(1)–C(3)	92.7(2)		
O(11)–P(1)–Mo(1)	113.0(2)	O(12)–P(1)–Mo(1)	120.0(2)
O(12)–P(1)–O(11)	103.5(2)	O(13)–P(1)–Mo(1)	118.3(2)
O(13)–P(1)–O(11)	102.4(2)	O(13)–P(1)–O(12)	96.9(2)
O(21)–P(2)–Mo(1)	119.6(2)	O(22)–P(2)–Mo(1)	113.7(2)
O(22)–P(2)–O(21)	103.9(2)	O(23)–P(2)–Mo(1)	118.7(2)
O(23)–P(2)–O(21)	95.9(2)	O(23)–P(2)–O(22)	102.2(2)
O(23)–Si(1)–O(13)	109.7(2)	C(31)–Si(1)–O(13)	107.2(2)
C(31)–Si(1)–O(23)	108.8(2)	C(37)–Si(1)–O(13)	105.9(2)
C(37)–Si(1)–O(23)	109.0(2)	C(37)–Si(1)–C(31)	116.1(2)
O(1)–C(1)–Mo(1)	179.0(3)	O(2)–C(2)–Mo(1)	175.8(3)
O(3)–C(3)–Mo(1)	179.0(3)	O(4)–C(4)–Mo(1)	178.5(3)
C(11)–O(11)–P(1)	121.1(3)	C(12)–O(12)–P(1)	118.1(3)
Si(1)–O(13)–P(1)	138.5(1)		
C(21)–O(21)–P(2)	119.1(3)	C(22)–O(22)–P(2)	121.7(3)
Si(1)–O(23)–P(2)	138.3(1)		
C(32)–C(31)–Si(1)	120.1(2)	C(36)–C(31)–Si(1)	119.9(2)
C(38)–C(37)–Si(1)	122.1(2)	C(312)–C(37)–Si(1)	117.8(2)

Table 5

Non-hydrogen atomic coordinates ($\times 10^4$) for compound **2** with e.s.d.s in parentheses

	x	y	z
Mo(1)	4475.3(3)	1338.7(3)	2041.7(2)
P(1)	3939(1)	3453(1)	2087(1)
P(2)	6482(1)	2381(1)	3708(1)
Si(1)	6913(1)	5316(1)	3600(1)
C(1)	6144(4)	2103(4)	1168(3)
O(1)	7059(4)	2519(3)	670(2)
C(2)	4841(5)	-424(4)	1944(3)
O(2)	5006(4)	-1443(3)	1856(3)
C(3)	2852(4)	539(4)	668(3)
O(3)	1945(4)	68(3)	-120(3)
C(4)	2849(5)	634(4)	2960(3)
O(4)	1958(4)	264(3)	3480(3)
O(11)	3956(3)	3963(2)	969(2)
C(11)	3679(6)	5194(4)	786(4)
O(12)	2340(3)	3499(2)	2386(2)
C(12)	843(4)	2506(4)	1781(4)
O(13)	5063(3)	4777(2)	2951(2)
O(21)	8137(3)	2188(3)	3859(3)
C(21)	8168(7)	839(6)	3848(6)
O(22)	5853(3)	1964(3)	4749(2)
C(22)	6785(7)	2550(7)	5819(4)
O(23)	7251(3)	4012(3)	4001(2)
C(31)	8244(3)	5999(2)	2690(2)
C(32)	9358(3)	5437(2)	2518(2)
C(33)	10390(3)	5966(2)	1851(2)
C(34)	10307(3)	7057(2)	1356(2)
C(35)	9193(3)	7620(2)	1528(2)
C(36)	8161(3)	7091(2)	2195(2)
C(37)	7174(6)	6580(5)	4784(4)

Table 6

Bond lengths (pm) for compound **2** with e.s.d.s in parentheses

P(1)–Mo(1)	245.3(3)	P(2)–Mo(1)	245.2(3)
C(1)–Mo(1)	204.3(6)	C(2)–Mo(1)	200.5(6)
C(3)–Mo(1)	200.4(6)	C(4)–Mo(1)	204.5(6)
O(11)–P(1)	158.4(4)	O(12)–P(1)	160.5(4)
O(13)–P(1)	159.6(4)		
O(21)–P(2)	160.3(5)	O(22)–P(2)	158.3(5)
O(23)–P(2)	159.5(5)		
O(13)–Si(1)	164.9(5)	O(23)–Si(1)	163.4(5)
C(31)–Si(1)	184.9(4)	C(37)–Si(1)	183.3(6)
O(1)–C(1)	113.6(5)	O(2)–C(2)	113.7(5)
O(3)–C(3)	113.9(5)	O(4)–C(4)	113.4(6)
C(11)–O(11)	144.9(5)	C(12)–O(12)	144.7(5)
C(21)–O(21)	143.6(7)	C(22)–O(22)	143.9(6)

Table 7

Bond angles (°) for compound **2** with e.s.d.s in parentheses

P(2)–Mo(1)–P(1)	89.7(1)	C(1)–Mo(1)–P(1)	89.2(2)
C(1)–Mo(1)–P(2)	89.8(2)	C(2)–Mo(1)–P(1)	177.5(1)
C(2)–Mo(1)–P(2)	92.8(2)	C(2)–Mo(1)–C(1)	90.7(3)
C(3)–Mo(1)–P(1)	88.9(2)	C(3)–Mo(1)–P(2)	178.4(1)
C(3)–Mo(1)–C(1)	89.3(2)	C(3)–Mo(1)–C(2)	88.5(3)
C(4)–Mo(1)–P(1)	89.7(2)	C(4)–Mo(1)–P(2)	88.4(2)
C(4)–Mo(1)–C(1)	177.9(1)	C(4)–Mo(1)–C(2)	90.4(3)
C(4)–Mo(1)–C(3)	92.5(3)		
O(11)–P(1)–Mo(1)	111.6(2)	O(12)–P(1)–Mo(1)	120.4(2)
O(12)–P(1)–O(11)	104.1(2)	O(13)–P(1)–Mo(1)	119.2(2)
O(13)–P(1)–O(11)	104.3(2)	O(13)–P(1)–O(12)	94.7(2)
O(21)–P(2)–Mo(1)	121.1(2)	O(22)–P(2)–Mo(1)	113.1(2)
O(22)–P(2)–O(21)	104.2(3)	O(23)–P(2)–Mo(1)	118.0(2)
O(23)–P(2)–O(21)	94.5(3)	O(23)–P(2)–O(22)	102.9(3)
O(23)–Si(1)–O(13)	108.5(2)	C(31)–Si(1)–O(13)	110.1(2)
C(31)–Si(1)–O(23)	108.3(2)	C(37)–Si(1)–O(13)	107.8(3)
C(37)–Si(1)–O(23)	108.8(3)	C(37)–Si(1)–C(31)	113.3(3)
O(1)–C(1)–Mo(1)	179.1(3)	O(2)–C(2)–Mo(1)	177.5(4)
O(3)–C(3)–Mo(1)	178.6(3)	O(4)–C(4)–Mo(1)	178.9(3)
C(11)–O(11)–P(1)	122.6(3)	C(12)–O(12)–P(1)	119.4(3)
Si(1)–O(13)–P(1)	133.8(2)	C(21)–O(21)–P(2)	119.5(4)
C(22)–O(22)–P(2)	122.6(4)	Si(1)–O(23)–P(2)	137.7(2)
C(32)–C(31)–Si(1)	119.6(2)	C(36)–C(31)–Si(1)	120.4(2)

(a) The closest intermolecular contacts in **1** are H(32)–H(39) at 248.9(1) pm and H(312)–O(2) at 248.0(1) pm. The former is within the range of H–H van der Waals distances (240–290 pm [9]) whilst the latter is shorter than normal non-bonded contacts for H–O (270–295 pm [9]). For **2**, there is one very short non-bonded contact between H(34) and H(11c) which at 197.2(1) pm is approximately 40 pm shorter than the lower limit of H–H van der Waals distances. The effect that these interactions have on the conformations of the chelate ring is difficult to ascertain.

(b) For both **1** and **2**, there are no non-bonded intramolecular contacts closer than 350 pm between (i) the substituents on silicon and those on phosphorus, (ii) the substituents on silicon and the carbon monoxide ligands and (iii) the methoxy groups and the carbon monoxide ligands, suggesting that there are no restrictive steric interactions between these pairs of groups. The transoid arrangement of the methoxy methyl groups presumably reflects a relief of steric strain between the adjacent methyls C(11)–C(12) and C(21)–C(22). Indeed, the pairs of methoxy oxygen atoms O(11)–O(12) and O(21)–O(22) in **1** have close non-bonded contacts of 250.9(1) pm (251.4(5) pm in **2**) and 251.7(5) pm (251.3(5) pm in **2**) respectively (a representative O–O van der Waals separation is 300 pm [9]).

(c) Within six-membered, saturated organic rings such as cyclohexane, the boat form is disfavoured with respect to the chair conformation, even though the former is a more flexible structure, mainly because of prohibitively close approach of the “flag-pole” hydrogens on the bow and stern carbons and significant eclipsing of

the port and starboard methylene hydrogens [10]. A similar situation likely exists for dppp ligation. However, replacing two methylene groups with isoelectronic oxo groups, in the ligands $[\text{P}(\text{OMe})_2\text{O}]_2\text{SiR}_2$, should result in the boat form being less disfavoured since the steric influences of the methylene hydrogens are removed. For both **1** and **2**, the full boat form is presumably disfavoured by the resulting close contacts between the silicon substituents and the carbon monoxide ligands *cis* to the diphosphite. We presume that the large dihedral angles of $162.0(3)^\circ$ (**1**) and $158.4(3)^\circ$ (**2**) between the P(1)–Mo–P(2) planes and the best fit planes through the atoms P(1)–O(13)–Si–O(23)–P(2) reflect the tendency to reduce these steric repulsions.

The above results, together with those on the closely related systems $\text{Mo}(\text{CO})_4[\text{PR}_2\text{O}]_2\text{SiMeR}'$, support the view that variations in the steric and electronic nature of the substituents on silicon have relatively subtle effects on the structural parameters of the complexes. Precisely to what extent these structural variations affect the stereoelectronic environment and hence the chemistry of the metal centres is currently under investigation.

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