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X-Ray crystallographic studies of three heterocyclic complexes of the type *cis*-$\mathrm{Mo(CO)_4\{(R_2PO)_2Si(Me)R'\}}$ ($\mathrm{R_2 = OCH_2CMe_2CH_2O}$; $\mathrm{R' = Me, Bu^t}$ or $\mathrm{R_2 = Ph_2}$; $\mathrm{R' = Bu^t}$)

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Abstract

X-Ray crystal structures for three complexes of the type *cis*-$\mathrm{Mo(CO)_4\{(R_2PO)_2Si(Me)R'\}}$ (I: $\mathrm{R_2 = OCH_2CMe_2CH_2O}$, $\mathrm{R' = Me}$; II: $\mathrm{R_2 = OCH_2CMe_2CH_2O}$, $\mathrm{R' = Bu^t}$; III: $\mathrm{R_2 = Ph_2}$, $\mathrm{R' = Bu^t}$) are reported. Complex I crystallizes in the monoclinic space group $P2_1/n$ (a 15.373(1), b 10.617(2), c 16.053(1) Å; β 110.336(6)°; V 2460(7) Å^3; $Z = 4$), complex II crystallizes in the triclinic space group $P\bar{1}$ (a 9.6203(9), b 10.6899(15), c 16.0098(25) Å; α 69.4716(2), β 68.8474(2), γ 66.7698(2)°; V 1368.7(3) Å^3; $Z = 2$) and complex III crystallizes in the orthorhombic space group $P2_12_12_1$ (a 11.500(2), b 16.430(2), c 17.892(3) Å; V 3380(2) Å^3; $Z = 4$). The conformations of the chelate rings in these complexes are affected by the nature of the P and Si substituents. The conformations of the chelate rings in I, II and III are best described as a twist boat, a distorted chair and a chaise longue, respectively. In contrast, the conformations of the 1,3,2-dioxaphosphorinane rings in I and II do not appear to be affected by the nature of the Si substituents and are distorted chairs for both complexes. These studies indicate that the P and Si substituents have very different effects upon the steric and electronic properties of these ligands.

Introduction

The reactions of coordinated P-donor ligands have been used to prepare a variety of complexes with chelating ligands of the type $\{(\mathrm{PR_2O})_2\mathrm{Y}\}$ (R = alkoxy, alkyl, aryl; Y = H [1–17], $\mathrm{BF_2}$, [5,18–21], M^{n+} [19,20,22–25], P(O)R (R = alkyl, aryl, metal complex) [26–31] and SiRR′ (R, R′ = alkyl, aryl) [5,26,29–32]). Multinuclear NMR and IR spectroscopic studies of *cis*-$\mathrm{(CO)_4Mo}$ complexes of some of these ligands (Y = P(O)R, SiRR′) have demonstrated that it is possible to independently vary the steric and electronic properties of the ligands in these complexes [29–31].

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X-ray crystallography is a powerful tool in understanding how variations in the P substituents and the Y groups affect the conformations of the six-membered chelate rings. A number of X-ray crystallographic studies of complexes with Y = H [6,9–14,16,33–35] have been carried out, however only a few studies of complexes with other Y groups have been reported (Y = BF_2 [21], $UO_2(OH)_2$ [25], $P(O)\{Pt(Et_3P)_2Cl\}$) [27]. We have begun an X-ray crystallographic study of complexes of the type *cis*-$(CO)_4Mo\{(R_2PO)_2Y\}$ ($R_2 = Ph_2$, $OCH_2CMe_2CH_2O$; Y = BF_2, P(O)R, SiRR′; R, R′ = alkyl, aryl). In this paper, we report the results of our X-ray crystallographic studies of three complexes of the type *cis*-$(CO)_4$-$Mo\{(R_2PO)_2Si(Me)R'\}$ ($R_2 = OCH_2CMe_2CH_2O$, R′ = Me, I; $R_2 = OCH_2CMe_2CH_2O$, R′ = Bu^t, II; $R_2 = Ph_2$; R′ = Bu^t, III).

Experimental

Synthetic procedures for I, II and III have been previously reported [29,31]. The complexes are air stable in the solid state but were handled under N_2 when in solution to avoid oxidation. All recrystallization solvents were reagent grade and were used as received from the supplier.

Collection and reduction of the X-ray data

Hot, saturated THF/heptane solutions of I, II and III were slowly cooled to −10 °C to yield crystals of the complexes. Suitable crystals were mounted on glass fibers with epoxy cement and mounted on an Enraf–Nonius CAD4 diffractometer. Standard peak search and automatic indexing routines of the CAD4 version 4.0 software followed by least squares fits of 25 accurately centered reflections ($2\theta >$ 25°) gave the cell constants. Data collections were carried out with Ni-filtered Cu-K_α (λ 1.5418 Å) radiation. Three reflections were remeasured periodically to monitor for decay, and linear decay corrections were applied. The data were processed using the Enraf–Nonius SDP series of programs. Variances were assigned to the I's on the basis of counting statistics with the addition of an instrumental uncertainty term. Lorentz, polarization and analytical absorption corrections were made to I's and σ^2's.

Solution and refinement of the structure

The cell parameters and systematic absences uniquely indicated the space groups for I ($P2_1/n$) and III ($P2_12_12_1$) and indicated that the space group for II was either P1 or P$\bar{1}$. The P$\bar{1}$ space group was chosen to be correct for II on the basis of the successful refinement of the structure. Both enantiomers of III were refined, and the one giving the lowest R and R_w values is reported. For all structures, the positions of the Mo, P and Si atoms were obtained from the Patterson functions, and the remainder of the atoms were located by Fourier methods. The structure was refined by a full matrix least-squares procedure that minimized $w(|F_o| - 1/k|F_c|^2)$, where $w = 1/\sigma^2(F_o)$. All non-H atoms were refined anisotropically, and H atoms were included in calculated positions (staggered for methyl Hs) and were not refined. The thermal parameters of the H atoms were calculated from those of the C atoms to which they were attached. Data with $I > 3\sigma I$ were used in the refinement, and the 2θ range for the data was chosen to minimize R $(\Sigma(|F_o| - |F_c|)/\Sigma|F_o|)$ and R_w $((\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2)^{0.5})$ and to give the best goodness of fit

Table 1

Experimental data for crystallographic studies of I, II and III.

	I	II	III
Formula	$C_{16}H_{26}MoO_{10}P_2Si$	$C_{19}H_{32}MoO_{10}P_2Si$	$C_{30}H_{26}MoO_6P_2Si$
MW, Daltons	564.35	606.43	688.51
Space group	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$
a (Å)	15.373(1)	9.6203(9)	11.500(2)
b (Å)	10.617(2)	10.6899(15)	16.430(2)
c (Å)	16.053(1)	16.0098(25)	17.892(3)
α (°)	90.000(0)	69.4716(2)	90.000(0)
β (°)	110.336(6)	68.8474(2)	90.000(0)
γ (°)	90.000(0)	66.7698(2)	90.000(0)
V (Å^3)	2457(7)	1368.7(3)	3380(2)
Z	4	2	4
d_{calc} (g/cm^3)	1.526	1.471	1.313
Cryst. dim., mm	0.11×0.05×0.30	0.27×0.14×0.14	0.16×0.48×0.57
Abs. coeff. (cm^{-1})	65.937	59.556	47.731
Ext. coeff.	8.0149×10^{-7}	1.4076×10^{-6}	1.9349×10^{-7}
Data collection			
θ limits (°)	0.1–76.0	0.1–74.0	0.1–74.0
refl. meas.	4984	5545	3839
scan width (°)	1.14	2.14	1.34
Structure refinement			
θ limits	1.0–60.0	1.0–70.0	1.0–70.0
n ($I \geq n\sigma I$)	3.0	3.0	3.0
refl. obs.	2983	4644	3464
no. of variables	272	299	389
R, %	2.93	6.69	4.38
R_w, %	3.97	8.67	6.04
GOF, electrons	1.706	1.857	2.940

Table 2

Fractional coordinates with e.s.d.s for I

Atom	x	y	z	Atom	x	y	z
Mo	0.21336(2)	0.11898(3)	0.49355(2)	C2	0.1206(2)	0.0796(4)	0.5542(2)
P1	0.31925(6)	0.17521(9)	0.63973(5)	C3	0.1684(3)	0.2975(4)	0.4774(2)
P2	0.32758(6)	0.1783(1)	0.42749(6)	C4	0.2664(3)	−0.0596(4)	0.5089(3)
Si	0.45821(7)	0.3204(1)	0.58490(6)	C5	0.5816(3)	0.2838(5)	0.6172(3)
O1	0.0702(2)	0.0499(4)	0.3050(2)	C6	0.4299(3)	0.4856(5)	0.5913(3)
O2	0.0700(2)	0.0617(3)	0.5898(2)	C7	0.4001(3)	0.0930(4)	0.8031(2)
O3	0.1435(2)	0.4011(3)	0.4684(2)	C8	0.3450(2)	0.1844(4)	0.8386(2)
O4	0.2972(2)	−0.1580(3)	0.5155(2)	C9	0.4048(3)	0.2169(4)	0.9343(2)
O5	0.4185(2)	0.2332(3)	0.6488(2)	C10	0.2535(3)	0.1239(4)	0.8345(3)
O6	0.4055(2)	0.2771(3)	0.4805(2)	C11	0.3267(3)	0.3031(4)	0.7827(2)
O7	0.3512(2)	0.0627(2)	0.7096(1)	C12	0.4499(3)	0.1004(4)	0.3586(3)
O8	0.2782(2)	0.2761(2)	0.6896(2)	C13	0.3957(3)	0.1587(4)	0.2690(3)
O9	0.3881(2)	0.0692(3)	0.4078(2)	C14	0.4659(3)	0.1995(5)	0.2255(3)
O10	0.2857(2)	0.2473(2)	0.3342(1)	C15	0.3265(4)	0.0633(5)	0.2115(3)
C1	0.1223(3)	0.0739(4)	0.3733(2)	C16	0.3457(3)	0.2750(4)	0.2834(2)

Table 3

Fractional coordinates with e.s.d.s for II

Atom	x	y	z	Atom	x	y	z
Mo	0.22178(3)	0.06797(3)	0.20144(2)	C4	0.1837(5)	0.2015(5)	0.0778(3)
P1	−0.0524(1)	0.1657(1)	0.27529(7)	C5	−0.3228(6)	−0.0454(7)	0.2829(4)
P2	0.1466(1)	−0.1106(1)	0.18278(7)	C6	−0.1700(6)	−0.2136(5)	0.4467(4)
Si	−0.1584(2)	−0.0884(1)	0.33159(9)	C7	−0.1729(8)	−0.3527(6)	0.4389(5)
O1	0.5673(5)	−0.0766(5)	0.1023(3)	C8	−0.0267(8)	−0.2405(8)	0.4787(5)
O2	0.3185(5)	0.2897(4)	0.2375(3)	C9	−0.3230(9)	−0.1517(8)	0.5151(5)
O3	0.3015(5)	−0.1258(5)	0.3886(3)	C10	−0.3194(6)	0.3466(6)	0.2424(4)
O4	0.1669(5)	0.2775(5)	0.0100(3)	C11	−0.3251(6)	0.4362(5)	0.3004(3)
O5	−0.1463(4)	0.0569(3)	0.3408(2)	C12	−0.4964(8)	0.5101(7)	0.3428(5)
O6	0.0088(4)	−0.1605(3)	0.2618(3)	C13	−0.2380(9)	0.5424(6)	0.2391(5)
O7	−0.1593(4)	0.2665(3)	0.2059(2)	C14	−0.2517(6)	0.3399(5)	0.3785(3)
O8	−0.0909(3)	0.2587(3)	0.3444(2)	C15	0.0708(6)	−0.1841(5)	0.0684(3)
O9	0.0923(4)	−0.0747(3)	0.0925(2)	C16	0.2182(6)	−0.3084(5)	0.0617(3)
O10	0.2799(4)	−0.2568(3)	0.1801(2)	C17	0.1851(7)	−0.4238(5)	0.0433(4)
C1	0.4438(5)	−0.0221(5)	0.1361(4)	C18	0.3521(9)	−0.2623(8)	−0.0162(5)
C2	0.2836(6)	0.2105(5)	0.2228(4)	C19	0.2577(6)	−0.3640(5)	0.1537(3)
C3	0.2680(5)	−0.0576(5)	0.3225(4)				

($[\Sigma w(||F_o| - 1/k|F_c||)^2/\nu]^{0.5}$) while maintaining an observation to parameter ratio of at least 9/1. In the last stage of refinement no parameter varied by more than 0.03 of its standard deviation. The final difference Fourier maps had no

Table 4

Fractional coordinates with e.s.d.s for III.

Atom	x	y	z	Atom	x	y	z
Mo	0.90846(4)	0.93760(3)	0.88038(2)	C13	0.809(1)	1.2329(6)	0.6355(6)
P1	0.9957(1)	1.06412(9)	0.82741(8)	C14	1.1361(6)	1.1034(4)	0.7057(4)
P2	0.7215(1)	0.95676(8)	0.81365(8)	C15	1.2344(6)	1.0937(4)	0.6586(4)
Si	0.8029(2)	1.0916(1)	0.7183(1)	C16	1.3151(7)	1.0380(5)	0.6748(5)
O1	0.8151(6)	0.7750(3)	0.9475(3)	C17	1.3025(6)	0.9888(5)	0.7380(5)
O2	1.1215(5)	0.9002(4)	0.9855(3)	C18	1.2067(6)	0.9968(5)	0.7821(4)
O3	0.8017(6)	1.0565(3)	1.0009(3)	C19	1.0111(9)	1.2190(4)	0.8923(4)
O4	1.0127(6)	0.8475(4)	0.7403(3)	C20	1.056(1)	1.2781(5)	0.9388(5)
O5	0.9101(4)	1.1195(2)	0.7755(2)	C21	1.1406(9)	1.2569(6)	0.9896(5)
O6	0.7078(4)	1.0418(2)	0.7681(2)	C22	1.1787(8)	1.1752(6)	0.9960(5)
C1	0.8460(7)	0.8331(4)	0.9227(4)	C23	1.1305(7)	1.1184(5)	0.9462(4)
C2	1.0474(7)	0.9158(4)	0.9447(4)	C24	0.5969(7)	0.9059(4)	0.6888(4)
C3	0.8389(6)	1.0116(4)	0.9597(4)	C25	0.5578(7)	0.8487(5)	0.6374(4)
C4	0.9765(6)	0.8766(4)	0.7904(4)	C26	0.5921(7)	0.7711(5)	0.6413(4)
C5	0.8623(8)	1.0301(6)	0.6428(5)	C27	0.6697(8)	0.7478(5)	0.6955(5)
C6	0.7291(7)	1.1828(5)	0.6831(5)	C28	0.7083(7)	0.8029(4)	0.7466(4)
C7	1.1229(5)	1.0531(4)	0.7668(3)	C29	0.5411(7)	1.0369(4)	0.8888(5)
C8	1.0481(6)	1.1401(4)	0.8927(4)	C30	0.4465(8)	1.0418(5)	0.9359(5)
C9	0.6744(6)	0.8809(4)	0.7448(3)	C31	0.4080(7)	0.9702(6)	0.9718(4)
C10	0.5929(5)	0.9637(4)	0.8748(3)	C32	0.4563(7)	0.8996(5)	0.9550(5)
C11	0.6195(8)	1.1569(6)	0.6417(6)	C33	0.5514(7)	0.8939(5)	0.9081(4)
C12	0.698(1)	1.2391(6)	0.7486(9)				

Table 5

Bond distances and selected bond angles with e.s.d.s for I

Atoms	Distance	Atoms	Distance	Atoms	Distance
Mo-P1	2.4204(8)	P2-O10	1.589(2)	O9-C12	1.469(6)
Mo-P2	2.429(1)	Si-O5	1.649(3)	O10-C16	1.457(5)
Mo-C1	2.009(3)	Si-O6	1.653(2)	C7-C8	1.523(6)
Mo-C2	2.030(4)	Si-C5	1.826(4)	C8-C9	1.531(4)
Mo-C3	2.003(4)	Si-C6	1.819(5)	C8-C10	1.528(6)
Mo-C4	2.045(4)	O1-C1	1.140(4)	C8-C11	1.515(5)
P1-O5	1.604(3)	O2-C2	1.131(5)	C12-C13	1.521(5)
P1-O7	1.594(2)	O3-C3	1.158(5)	C13-C14	1.537(7)
P1-O8	1.593(3)	O4-C4	1.136(5)	C13-C15	1.525(6)
P2-O6	1.598(3)	O7-C7	1.462(4)	C13-C16	1.515(6)
P2-O9	1.586(3)	O8-C11	1.449(4)		
Atoms	**Angle**	**Atoms**	**Angle**	**Atoms**	**Angle**
P1-Mo-P2	90.84(3)	Mo-P2-O9	117.4(1)	P2-O9-C12	118.4(2)
P1-Mo-C1	178.3(1)	Mo-P2-O10	114.4(1)	P2-O10-C16	119.5(2)
P1-Mo-C2	86.19(9)	O5-Si-O6	108.5(1)	O7-C7-C8	111.7(3)
P1-Mo-C3	88.74(9)	O5-Si-C5	106.1(2)	C7-C8-C9	107.6(3)
P1-Mo-C4	90.4(1)	O5-Si-C6	111.0(2)	C7-C8-C10	109.8(3)
P2-Mo-C1	90.6(1)	O6-Si-C5	108.9(2)	C7-C8-C11	108.8(3)
P2-Mo-C2	176.2(1)	O6-Si-C6	106.4(2)	O8-C11-C8	111.7(3)
P2-Mo-C3	88.1(1)	C5-Si-C6	115.8(2)	O9-C12-C13	110.9(3)
P2-Mo-C4	88.5(1)	P1-O5-Si	134.9(1)	C12-C13-C14	107.7(3)
Mo-P1-O5	118.7(1)	P2-O6-Si	137.3(2)	C12-C13-C15	109.8(4)
Mo-P1-O7	115.85(9)	P1-O7-C7	118.7(2)	C12-C13-C16	109.1(3)
Mo-P1-O8	113.75(8)	P1-O8-C11	120.0(2)	O10-C16-C13	112.0(3)
Mo-P2-O6	117.4(1)				

interpretable peaks (for I, maximum 0.337 e/Å^3 near Mo; for II, -2.210 e/Å^3 near Mo; for III, maximum 1.581 e/Å^3 near Si). Neutral atom scattering factors were taken from the compilations of Cromer and Weber [36], and those for hydrogen atoms were taken from International Tables for X-ray Crystallography [37]. Corrections for the real and imaginary components of anomalous dispersion were taken from the compilations of Cromer and Liberman [38] and were applied to the Mo, P and Si atoms. Details of the data collection and structure solution procedures are summarized in Table 1. The final values for the positional parameters of I, II and III are given in Tables 2, 3 and 4 and selected bond lengths and angles for these compounds are given in Tables 5, 6 and 7.

Results and discussion

The molecular structures of compounds I, II and III are shown in Fig. 1, 2 and 3, respectively. The conformations of the heterocyclic rings in compounds I, II and III are shown in Fig. 4, 5 and 6, respectively. The structures of compounds I, II and III have a number of interesting features. These include the coordination geometries of the molybdenum atoms, the conformations of the chelate rings and the conformations of the 1,3,2-dioxaphosphorinane rings. These are discussed below.

Table 6

Selected bond distances and angles with e.s.d.s for II

Atoms	Distance	Atoms	Distance	Atoms	Distance
Mo-P1	2.426(1)	Si-O5	1.662(4)	C6-C7	1.55(1)
Mo-P2	2.429(1)	Si-O6	1.661(3)	C6-C8	1.53(1)
Mo-C1	2.014(4)	Si-C5	1.840(7)	C6-C9	1.543(8)
Mo-C2	2.005(7)	Si-C6	1.855(5)	C10-C11	1.53(1)
Mo-C3	2.020(5)	O1-C1	1.120(6)	C11-C12	1.531(8)
Mo-C4	2.055(5)	O2-C2	1.143(9)	C11-C13	1.526(9)
P1-O5	1.599(4)	O3-C3	1.129(7)	C11-C14	1.511(7)
P1-O7	1.602(3)	O4-C4	1.126(6)	C15-C16	1.514(6)
P1-O8	1.592(4)	O7-C10	1.452(5)	C16-C17	1.53(1)
P2-O6	1.587(4)	O8-C14	1.452(5)	C16-C18	1.539(8)
P2-O9	1.583(4)	O9-C15	1.458(8)	C16-C19	1.510(8)
P2-O10	1.586(3)	O10-C19	1.460(8)		

Atoms	Angle	Atoms	Angle	Atoms	Angle
P1-Mo-P2	86.87(4)	Mo-P2-O10	114.8(2)	Si-C6-C7	108.8(5)
P1-Mo-C1	175.3(2)	O5-Si-O6	107.6(2)	Si-C6-C8	109.2(4)
P1-Mo-C2	92.7(1)	O5-Si-C5	110.1(3)	Si-C6-C9	109.1(3)
P1-Mo-C3	92.4(1)	O5-Si-C6	107.8(3)	O7-C10-C11	111.0(5)
P1-Mo-C4	89.1(1)	O6-Si-C5	109.8(3)	C10-C11-C12	108.9(6)
P2-Mo-C1	88.6(2)	O6-Si-C6	106.6(2)	C10-C11-C13	109.2(5)
P2-Mo-C2	177.4(1)	C5-Si-C6	114.6(3)	C10-C11-C14	108.2(4)
P2-Mo-C3	90.0(2)	P1-O5-Si	134.3(2)	O8-C14-C11	111.7(3)
P2-Mo-C4	93.1(2)	P2-O6-Si	137.2(2)	O9-C15-C16	111.0(5)
Mo-P1-O5	117.0(1)	P1-O7-C10	119.4(3)	C15-C16-C17	108.7(5)
Mo-P1-O7	114.9(1)	P1-O8-C14	119.6(4)	C15-C16-C18	109.5(4)
Mo-P1-O8	116.8(1)	P2-O9-C15	119.9(2)	C15-C16-C19	108.2(4)
Mo-P2-O6	117.4(2)	P2-O10-C19	119.6(3)	O10-C19-C16	111.8(4)
Mo-P2-O9	116.6(1)				

Table 7

Selected bond distances and angles with e.s.d.s for III

Atoms	Distance	Atoms	Distance	Atoms	Distance
Mo-P1	2.495(2)	P1-C8	1.813(6)	O1-C1	1.112(8)
Mo-P2	2.480(2)	P2-O6	1.624(4)	O2-C2	1.150(9)
Mo-C1	2.009(7)	P2-C9	1.835(6)	O3-C3	1.127(9)
Mo-C2	2.002(7)	P2-C10	1.843(6)	O4-C4	1.097(9)
Mo-C3	2.034(7)	Si-O5	1.667(4)	C6-C11	1.52(1)
Mo-C4	2.052(6)	Si-O6	1.631(4)	C6-C12	1.54(2)
P1-O5	1.630(4)	Si-C5	1.821(9)	C6-C13	1.50(1)
P1-C7	1.830(6)	Si-C6	1.833(8)		

Atoms	Angle	Atoms	Angle	Atoms	Angle
P1-Mo-P2	93.42(5)	P2-Mo-C4	90.8(2)	O5-Si-C5	109.3(3)
P1-Mo-C1	177.2(2)	Mo-P1-O5	116.0(2)	O5-Si-C6	109.2(3)
P1-Mo-C2	92.7(2)	Mo-P1-C7	117.6(2)	O6-Si-C5	112.2(3)
P1-Mo-C3	85.7(2)	Mo-P1-C8	117.5(2)	O6-Si-C6	106.7(3)
P1-Mo-C4	87.5(2)	Mo-P2-O6	115.7(2)	C5-Si-C6	111.9(4)
P2-Mo-C1	88.8(2)	Mo-P2-C9	119.5(2)	P1-O5-Si	130.0(2)
P2-Mo-C2	172.7(2)	Mo-P2-C10	114.7(2)	P2-O6-Si	129.9(3)
P2-Mo-C3	85.3(2)	O5-Si-O6	107.3(2)		

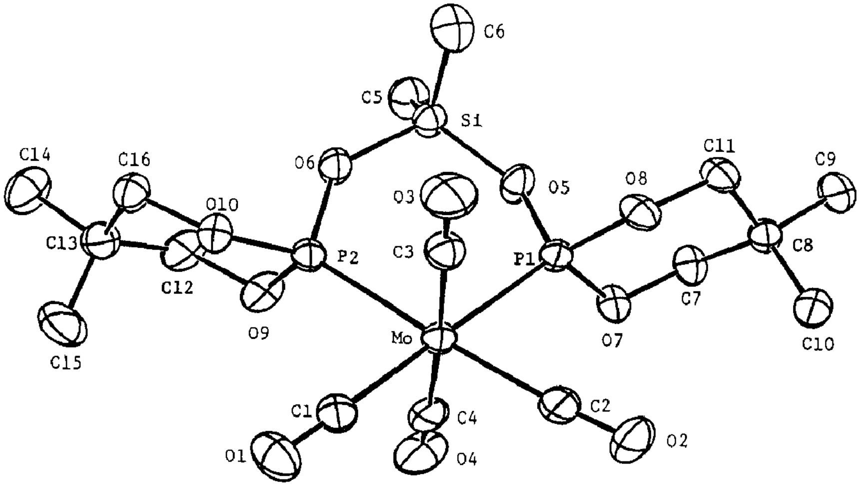

Fig. 1. ORTEP drawing [45] of the molecular structure of I. Thermal ellipsoids are drawn at the 25% level and H atoms are omitted for clarity.

Coordination geometry at molybdenum

The coordination geometry of the Mo in each of these complexes is a slightly distorted octahedron composed of four carbonyls and two P-donor sites *cis* to each other. The average Mo–P distances are shorter in I and II (2.428 and 2.425 Å) than in III (2.488 Å). This is consistent with the fact that phosphites (the P-donor groups in I and II) are poorer σ-electron donors and better π-electron acceptors than are phosphinites (the P-donor groups in III). The greater π-acceptor ability of the phosphites results in a greater degree of multiple bonding between the Mo and the P and thus in shorter Mo–P bond lengths.

The Mo–C bond lengths in these complexes are quite variable. In all of the complexes, the Mo–C bond length for one of the carbonyls *cis* to both P's (*cis*

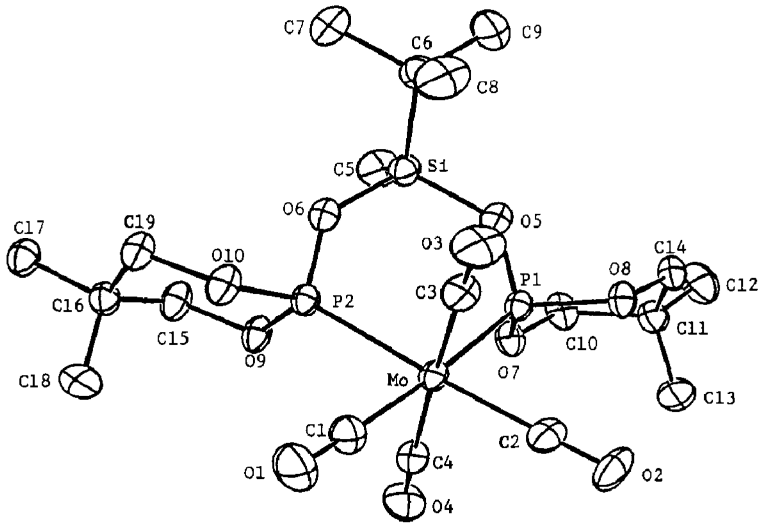

Fig. 2. ORTEP drawing [45] of the molecular structure of II. Thermal ellipsoids are drawn at the 25% level and H atoms are omitted for clarity.

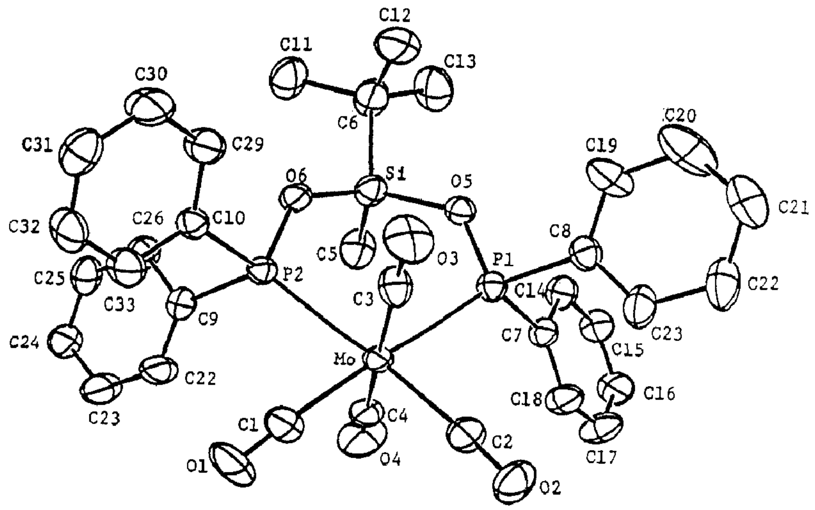

Fig. 3. ORTEP drawing [45] of the molecular structure of III. Thermal ellipsoids are drawn at the 25% level and H atoms are omitted for clarity.

carbonyl) is longer (0.018 to 0.040 Å) than that of the other *cis* carbonyl. This phenomenon is also observed for the carbonyls *trans* to one of the P's in I but not in II or III. The reasons for this are not obvious from the structures of the complexes and do not appear to be due to any close intermolecular contacts with the carbonyl ligands (none significantly less than the sum of the Van der Waal's radii).

The average Mo–C bond lengths for the *trans* carbonyls in II and III are shorter than those for the *cis* carbonyls (2.010 vs. 2.038 Å in II and 2.006 vs. 2.043 Å in III) but not for I (2.020 vs. 2.024 Å). These differences are dependent upon the natures of both the P and Si substituents. The dependence upon the natures of the P substituents is not surprising because the greater π-acceptor abilities of the phos-

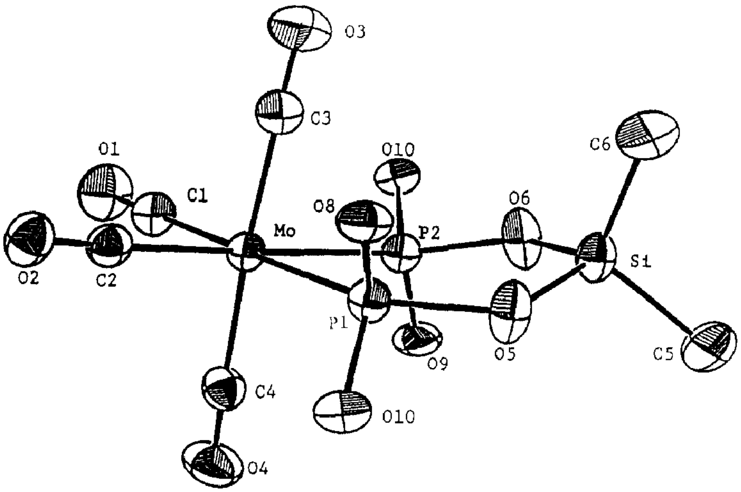

Fig. 4. ORTEP drawing [45] of the chelate ring in I. Thermal ellipsoids are drawn at the 25% level and H atoms are omitted for clarity.

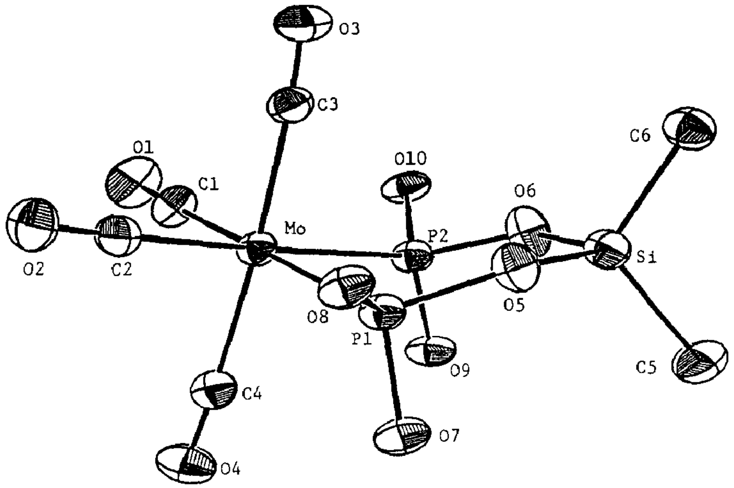

Fig. 5. ORTEP drawing [45] of the chelate ring in II. Thermal ellipsoids are drawn at the 25% level and H atoms are omitted for clarity.

phites should result in less multiple bonding between the Mo and the C of the carbonyls *trans* to the P and thus in longer Mo–C bond lengths. The dependence upon the nature of the Si substituent is more surprising, because these groups are too far from the P to have significant electronic effects. Therefore, they must influence the Mo–C bonding either by through-space steric interactions with the carbonyl ligands or by causing variations in the conformations of the chelate ring and thus in the electron donor abilities of the P-donor groups. This first explanation appears to be the more likely on the basis of earlier solution NMR spectroscopic studies of these complexes which demonstrated that the two *cis* carbonyl ligands are chemically inequivalent when the steric bulk of the two Si alkyl substituents is different [29–31].

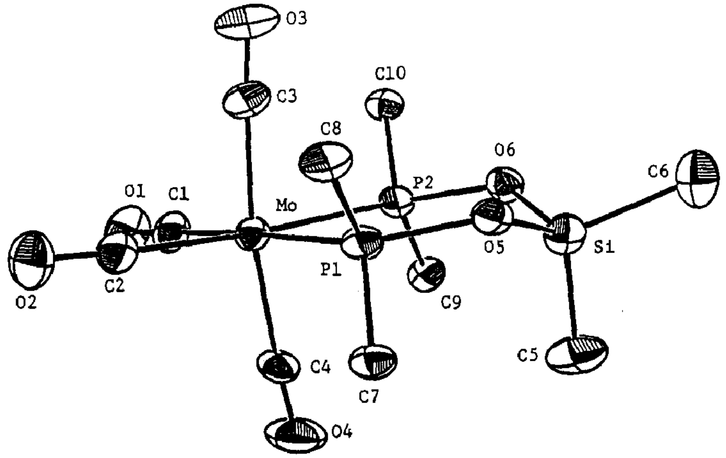

Fig. 6. ORTEP drawing [45] of the chelate ring in III. Thermal ellipsoids are drawn at the 25% levels and H atoms are omitted for clarity.

Conformations of the chelate rings

The six-membered chelate rings in I, II and III exhibit different conformations as shown in Fig. 4, 5 and 6. The conformation of the ring in I is best described as a twist boat with the Mo, P1, P2 and O5 atoms in one plane and the P2, O5, O6 and Si atoms in a second plane. The two planes intersect on a line drawn through the P2 and O5 atoms at an angle of 27.6(2)°. In contrast, the conformation of the chelate ring in II is best described as a distorted chair. The P1, P2, O5 and O6 atoms are in a plane (with deviations of 0.022(1), −0.022(1), −0.027(4) and 0.028(4) Å, respectively) while the Mo lies 0.947(1) Å above this plane and the Si lies 0.298(1) Å below this plane. The planes formed by the Mo, P1 and P2 and by the O5, O6 and Si are not parallel but are bent away from each other at a 14.9(4)° angle. Finally, the conformation of the chelate ring in III is best described as a chaise longue. The O5 and O6 atoms are located 0.105(4) and 0.156(4) Å, respectively, above the plane formed by the Mo, P1 and P2 atoms while the Si atom is located 0.443(2) Å below this plane. The structures of the chelate rings in II and III are similar except that there is less deviation of the Mo and more deviation of the Si from the plane formed by the P1, P2, O5 and O6 atoms in III than in II. This is most likely a result of the very different steric properties of the 1,3,2-dioxaphosphorinane and diphenylphosphino groups in these complexes.

These different conformations of the six-membered chelate rings indicate that both the P and Si substituents affect the conformations of the rings in the solid state. This conclusion is supported by the results from two previous crystallographic studies of compounds with chelate ligands of the type $(R_2PO)_2Y$ where Y is neither H nor a metal ion. In $Pt\{(P(OMe)_2O)_2BF_2\}_2$, the chelate rings are in a distorted chair configuration [21], but in *cis*-$Cl_2Pt\{(P(OEt)_2O)_2P(O)[Pt(PEt_3)_2Cl]\}$, the chelate ring is in a chaise longue conformation.

The reasons for the variations that are observed in the conformations of the chelate rings in these complexes are the differing effects that the P and Si substituents have upon the bond distances and angles in the chelate rings. The P substituents affect the Mo–P and P–O bond lengths and the P–Mo–P and P–O–Si bond angles with the phosphite complexes (I, II) having shorter Mo–P and P–O bonds and larger P–O–Si angles than the phosphinite complex. The Si substituents also affect the P–Mo–P bond angles as well as the O–Si–O bond angles with the Bu^t complexes having smaller O–Si–O bond angles. The combined effects of the P and Si substituents on the P–Mo–P bond angle are quite dramatic with the bond angle varying from 86.87(4)° for II to 93.42(5)° for III. The differences in the lengths of the Mo–P and P–O bonds in the phosphite and phosphinite complexes are very similar to those observed in the dinuclear complex, $(CO)_5Mo(Ph_2POP(OCH_2CMe_2CH_2O))Mo(CO)_5$ [39]. These differences are probably due both to the very different electronegativities and steric bulks of the P substituents. The P–O bond lengths in I and II are identical to those in $M_3[P_3O_9]\cdot H_2O$ (range of 1.60(1) to 1.63(1) Å) [40–43] and those in the $P(OEt)_2O$ group in *cis*-$Cl_2Pt\{(P(OEt)_2O)_2P(O)[Pt(PEt_3)_2Cl]\}$ (average of 1.601(8) Å). It should be noted that energy differences between the conformations of rings in the solid state is often quite small. Thus, the differences noted above may not be sufficient to affect the conformations of the rings in solution.

Conformations of the phosphorinane rings

The conformations of the phosphorinane rings in I and II are also of interest. In these complexes, each of the phosphorinane rings adopts a chair conformation that is somewhat flattened about the $P(OC)_2$ group. This is due to the fact that P–O–C angles (average of 119.2(2)° for I and 119.6(3)° for II) are significantly larger than 109.5° while the O–P–O angles (average of 103.0(1)° for I and 103.0(2)° for II) are significantly smaller than 109.5°. These angles are very similar to those reported for 1,3,2-dioxaphosphorinane ligands in other transition metal complexes [39,44], and this suggests that the 1,3,2-dioxaphosphorinane ring is quite rigid.

The 1,3,2-phosphorinane rings in I and II are different from those in earlier complexes in that they contain spiro P atoms. However, this does not affect the sites occupied by the Mo carbonyl and chelate-ring O groups in these complexes. The Mo carbonyl groups occupy the equatorial sites and the chelate-ring O's occupy axial sites. These results are consistent with the earlier studies [39,44] of complexes of 1,3,2-dioxaphosphorinane ligands with O-bonded 2-substituents.

Conclusions

The conformations that are observed for the 6-membered chelate rings in complexes of the type *cis*-$(CO)_4Mo\{(R_2PO)_2Si(Me)R'\}$ depend upon both the P and Si substituents present in these molecules. Variations in the P substituents affect the lengths of the Mo–P and P–O bonds and the P–Mo–P and P–O–Si bond angles while variations in the Si substituents affect the P–Mo–P and O–Si–O bond angles. Combinations of these effects result in conformations ranging from twist boat to distorted chair for the chelate ring. These results suggest that it may be possible to vary the electronic and steric properties of ligands of the type, $(R_2PO)_2Y$, in a controlled fashion by varying the P and Si substituents.

In contrast, the conformation of the 1,3,2-phosphorinane rings in these complexes are distorted chairs in all cases and are very similar to those reported for other 1,3,2-dioxaphosphorinane complexes. The conformations of these rings do not appear to be sensitive to the nature of the Si substituents present in the complexes.

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