Pentagonal-bipyramidal Molybdenum- and Tungsten-(II) Derivatives: Crystal and Molecular Structure of 1—3-η-Allyldicarbonylchlorobis-(trimethyl phosphite)molybdenum(II)

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Compounds of the type $[MX(CO)_2(\eta^3\text{-}C_3H_4R)L_2]$ [M = Mo or W; X = halide; R = H, L = $P(OMe)_3$ or $P(OEt)_3$; R = Me, L = $P(OMe)_3$] have been prepared. A crystal-structure determination has been carried out on the title compound as a representative member of the series. Crystals are triclinic, space group $P\bar{1}$, with a = 13.309(11), b = 10.093(10), c = 8.148(7) Å, α = 114.9(8), β = 93.1(7), γ = 100.6(7)°, and Z = 2. A total of 1534 independent reflections above background were collected on a diffractometer and refined to R 0.072. The geometry around the metal atom is best considered in terms of a distorted pentagonal bipyramid with a chlorine atom [Mo–Cl 2.606(6) Å] and a carbonyl group [Mo–C 1.91(3) Å] in axial positions, and the equatorial girdle occupied by two phosphite ligands [Mo–P 2.432(6), 2.425(6) Å], one carbonyl group [Mo–C 2.03(3) Å], and the allyl ligand which occupies two adjacent sites. The molecule has approximate C_s symmetry with the mirror plane containing the metal atom, both carbonyl groups, and the central carbon atom of the allyl group. The Mo–C(allyl) bond lengths are 2.403(20), 2.347(24), and 2.407(22) Å. Carbon-13 and ^1H n.m.r. data indicate that this geometry is retained in solution below 230 K, but at room temperature the molecule is fluxional. The two cationic complexes $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)\{P(OMe)_3\}_3][BF_4]$ (R = H or Me) have also been characterised.

MANY allyl complexes of the early transition elements are known to be fluxional at room temperature, but in many instances the mechanisms of their rearrangement processes have not been established.[1,2] A combination of single-crystal X-ray diffraction, to reveal preferred solid-state configurations, and dynamic n.m.r. studies is desirable when studying stereochemical non-rigidity. Using these methods the dynamic behaviour of $[MoCl(CO)_2(\eta\text{-}C_3H_5)(Ph_2PCH_2CH_2PPh_2)]$ [3] and $[Mo(CO_2)(\eta\text{-}C_3H_5)(pd)(py)]$ [4] (pd = pentane-2,4-dionate, py = pyridine) has been explained in terms of a trigonal twist mechanism, which involves rotation of the triangular face formed by the halogen or pyridine nitrogen atom, and the donor atoms of the bidentate ligand, relative to the face formed by the allyl and two carbonyl groups. We were interested to ascertain whether the chelating ligands present in both these molecules had a major influence on the structure and rearrangement of this type of complex, and whether a similar non-bond-breaking mechanism would also apply to dynamic $[M(CO)_2(\eta\text{-}C_3H_5)L_3]$ (M = Mo or W) complexes containing only unidentate ligands. In order to spectroscopically monitor the maximum number of atoms directly bonded to the metal, we chose to investigate complexes containing unidentate phosphorus-donor ligands. As tertiary phosphines are known to readily break the metal-allyl linkage in these species and form allylphosphonium salts,[5,6] the less nucleophilic tertiary phosphites were used to prepare complexes of the types $[MX(CO)_2(\eta^3\text{-}C_3H_4R)\{P(OR')_3\}_2]$ (M = Mo, R = H or Me, R′ = Me or Et; M = W, R = H, R′ = Me or Et) and $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)\{P(OMe)_3\}_3][BF_4]$ (R = H or Me). Both series of complexes were found to be stereochemically non-rigid at, or near, room temperature and were therefore suitable for such an investigation.

EXPERIMENTAL

All preparations were performed in an atmosphere of dry N_2 gas using solvents and liquid reagents freed from moisture and oxygen by standard procedures. The phosphites $P(OR')_3$ (R′ = Me or Et) were left to stand over lead–sodium alloy for 1 week and then fractionally distilled from fresh alloy and stored over molecular sieves. In addition, triethyl phosphite was fractionally distilled at least twice immediately before use. The starting materials $[MX(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_2]$ (M = Mo or W; X = Cl, Br, or I; R = H or Me) were prepared from $[M(CO)_3(NCMe)_3]$ by literature methods.[7]

Solution and mull i.r. spectra in the region 200—4 000 cm^{-1} were recorded on a Perkin-Elmer 597 spectrophotometer. Far-i.r. spectra from 40 to 400 cm^{-1} were obtained using a Beckmann RIIC FS 720 interferometer on samples pressed in Polythene discs. Hydrogen-1 and ^{31}P n.m.r. were recorded on a JEOL PS 100 instrument, and JEOL PTF-100 and FX-90 spectrometers were used to obtain ^{13}C n.m.r. spectra.

Synthesis of $[MX(CO)_2(\eta^3\text{-}C_3H_4R)L_2]$[M = Mo *or* W; R = H, L = $P(OMe)_3$ *or* $P(OEt)_3$; R = Me, L = $P(OMe)_3$].—A solution of $[MX(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_2]$ (1.0 mmol) dissolved in acetone (10 cm^3) was treated with $P(OR')_3$ (2.0 mmol) at room temperature. After 1 h the solution was reduced to low bulk *in vacuo*. The precipitated product was filtered off, washed with a little cold acetone (−20 °C), and vacuum dried. The $P(OEt)_3$ complexes crystallised with difficulty and an alternative procedure was adopted to obtain pure products. After mixing, the solvent was completely removed and the residue evacuated for 2 h. Approximately 2 cm^3 of acetone were added at −20 °C and the mixture stored at −30 °C overnight. The product was filtered off and washed as above.

Attempts to prepare triphenyl phosphite analogues by this procedure were unsuccessful.

$[Mo(CO)_2(\eta^3\text{-}C_3H_4R)\{P(OMe)_3\}_3][BF_4]$.—The salt $Ag[BF_4]$ (1.0 mmol) was added to a solution of $[MoCl(CO)_2(\eta^3\text{-}C_3H_4R)\{P(OMe)_3\}_2]$ (1 mmol) dissolved in acetone (20 cm^3). The mixture was stirred for 10 min, filtered, and the filtrate added to a solution of $P(OMe)_3$ (*ca.* 1.5 mmol) in acetone (5 cm^3) at room temperature. After 0.5 h, the solution was evaporated at reduced pressure to a volume of 6 cm^3 and treated dropwise with Et_2O to initiate precipitation. The product was filtered off and recrystallised from $CHCl_3$–Et_2O.

The conductivity (Λ) of a 10^{-3} mol dm^{-3} solution of (9; R = H) in nitromethane was 92.4 S cm^2 mol^{-1}.

Crystal Data.—$C_{11}H_{23}ClMoO_8P_2$, $M = 476.5$, Triclinic, $a = 13.309(11)$, $b = 10.093(10)$, $c = 8.148(7)$ Å, $\alpha = 114.9(8)$, $\beta = 93.1(7)$, $\gamma = 100.6(7)°$, $U = 965.1$ Å^3, D_m (flotation) = 1.64 g cm^{-3}, $Z = 2$, $D_c = 1.64$ g cm^{-3}, $F(000) = 484$, λ(Mo-K_α) = 0.710 7 Å, μ(Mo-K_α) = 10.0 cm^{-1}, space group $P\bar{1}$ from the successful structure determination.

A crystal of approximate size 0.4 × 0.3 × 0.2 mm was mounted with a^* parallel to the instrument axis of a G.E. XRD 5 diffractometer which was used to measure diffraction intensities and unit-cell dimensions. The apparatus was equipped with a manual goniostat scintillation counter and pulse-height analyser. The stationary-crystal–stationary-counter method was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken for those reflections whose counts were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of 2θ. Several standard reflections monitored during the course of the experiment showed no significant changes in intensities. 2 135 Independent reflections were measured for $2\theta < 40°$, of which 1 534 with $I > 3\sigma(I)$ were used in subsequent refinement. No absorption or extinction corrections were applied.

Structure Determination.—The positions of the molybdenum atoms were obtained from the Patterson map and the positions of remaining atoms were found from Fourier analysis. The hydrogen-atom positions of the allyl or methyl groups could not of course be calculated; some were observed in a difference Fourier but refinement was not successful, and therefore they were not included in the final refinement. All atoms were refined anisotropically to R 0.072 by full-matrix least squares. Calculations were done using SHELX 76 [8] at the University of London Computer Centre. The weighting scheme used was $w^{\frac{1}{2}} = 1$ for $F_o < 40$ and $w^{\frac{1}{2}} = 40/F_o$ for $F_o > 100$. Scattering factors and dispersion corrections were taken from ref. 9. The final difference-Fourier map showed no unusual features. In the final cycle of refinement all shifts were less than 0.05σ. The final positions are given in Table 1, and bond lengths and angles in Table 2. Structure-factor tables and anisotropic thermal parameters are given in Supplementary Publication No. SUP 22774 (11 pp.).*

TABLE 1

Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Mo(1)	7 735(1)	7 758(2)	5 076(2)
Cl(1)	6 608(5)	7 308(8)	7 391(8)
P(1)	7 504(4)	10 212(6)	5 506(8)
P(2)	7 583(4)	5 165(6)	2 912(7)
O(21)	8 708(11)	4 835(17)	2 391(20)
O(22)	7 174(12)	3 821(16)	3 461(21)
O(23)	6 845(11)	4 488(17)	981(20)
C(21)	8 795(19)	3 308(28)	1 026(33)
C(22)	6 063(20)	3 470(32)	3 723(42)
C(23)	6 909(21)	5 214(31)	−264(25)
O(11)	8 578(11)	11 294(16)	5 682(21)
O(12)	7 040(13)	11 218(17)	7 264(20)
O(13)	6 729(12)	10 284(16)	3 961(20)
C(11)	8 623(21)	12 925(29)	6 107(37)
C(12)	5 986(18)	10 733(28)	7 592(36)
C(13)	6 915(22)	9 804(31)	2 101(36)
C(1)	8 816(18)	9 499(27)	7 906(30)
C(2)	9 312(20)	8 348(34)	6 946(35)
C(3)	8 898(19)	6 856(32)	6 501(35)
C(4)	8 562(18)	8 027(21)	3 342(30)
O(4)	9 095(14)	8 195(20)	2 283(25)
C(5)	6 278(22)	7 219(24)	3 727(28)
O(5)	5 467(15)	6 924(20)	3 098(26)

RESULTS AND DISCUSSION

Neutral Complexes.—Reaction of tertiary phosphites with the molybdenum- or tungsten-nitrile starting materials at room temperature yielded a series of substituted complexes $[MX(CO)_2(\eta^3\text{-}C_3H_4R)\{P(OR')_3\}_2]$ (Table 3). There was no evidence of nucleophilic attack of the phosphites on the allyl ligand even in refluxing MeCN, Me_2CO, or MeOH in the presence of excess of phosphite, in marked contrast to the analogous reactions of tertiary phosphines.[5,6] However, the spectral properties of the whole series of complexes were inconsistent with the pseudo-octahedral geometry which has been established by single-crystal *X*-ray diffraction studies for 15 other complexes containing the $M(CO)_2(\eta\text{-}C_3H_5)$ entity;[3,4,10-13] consequently a crystal-structure determination was carried out on $[MoCl(CO)_2(\eta\text{-}C_3H_5)\{P(OMe)_3\}_2]$, (1), as a representative member of the series. A preliminary report of this structure has appeared recently.[14]

TABLE 2

Molecular dimensions, distances (Å) and angles (°)

Mo(1)–Cl(1)	2.606(6)	P(2)–O(22)	1.613(15)
Mo(1)–P(1)	2.432(6)	P(2)–O(23)	1.609(15)
Mo(1)–P(2)	2.425(6)	O(21)–C(21)	1.504(28)
Mo(1)–C(1)	2.403(20)	O(22)–C(22)	1.503(29)
Mo(1)–C(2)	2.347(24)	O(23)–C(23)	1.479(28)
Mo(1)–C(3)	2.407(22)	O(11)–C(11)	1.521(30)
Mo(1)–C(4)	1.914(25)	O(12)–C(12)	1.475(28)
Mo(1)–C(5)	2.035(27)	O(13)–C(13)	1.435(31)
P(1)–O(11)	1.589(15)	C(1)–C(2)	1.403(36)
P(1)–O(12)	1.603(16)	C(2)–C(3)	1.384(37)
P(1)–O(13)	1.618(16)	C(4)–O(4)	1.192(26)
P(2)–O(21)	1.632(16)	C(5)–O(5)	1.099(25)
Cl(1)–Mo(1)–P(1)	100.79(21)	C(4)–Mo(1)–C(5)	101.9(8)
Cl(1)–Mo(1)–P(2)	98.71(21)	Mo(1)–P(1)–O(11)	111.1(5)
P(1)–Mo(1)–P(2)	146.12(20)	Mo(1)–P(1)–O(12)	119.8(6)
Cl(1)–Mo(1)–C(1)	80.0(6)	Mo(1)–P(1)–O(13)	117.7(5)
P(1)–Mo(1)–C(1)	75.0(6)	O(11)–P(1)–O(12)	102.2(8)
P(2)–Mo(1)–C(1)	135.9(6)	O(11)–P(1)–O(13)	106.0(8)
Cl(1)–Mo(1)–C(2)	94.5(6)	O(12)–P(1)–O(13)	97.9(8)
P(1)–Mo(1)–C(2)	102.6(7)	Mo(1)–P(2)–O(21)	111.5(5)
P(2)–Mo(1)–C(2)	103.2(7)	Mo(1)–P(2)–O(22)	120.7(6)
C(1)–Mo(1)–C(2)	34.3(8)	Mo(1)–P(2)–O(23)	119.3(6)
Cl(1)–Mo(1)–C(3)	80.5(6)	O(21)–P(2)–O(22)	99.7(8)
P(1)–Mo(1)–C(3)	135.4(6)	O(21)–P(2)–O(23)	105.1(8)
P(2)–Mo(1)–C(3)	75.1(6)	O(22)–P(2)–O(23)	97.7(8)
C(1)–Mo(1)–C(3)	61.2(8)	P(2)–O(21)–C(21)	120.7(13)
C(2)–Mo(1)–C(3)	33.8(8)	P(2)–O(22)–C(22)	119.8(13)
Cl(1)–Mo(1)–C(4)	178.3(6)	P(2)–O(23)–C(23)	123.2(14)
P(1)–Mo(1)–C(4)	80.9(5)	P(1)–O(11)–C(11)	119.8(13)
P(2)–Mo(1)–C(4)	79.6(5)	P(1)–O(12)–C(12)	122.2(14)
C(1)–Mo(1)–C(4)	100.9(8)	P(1)–O(13)–C(13)	122.4(15)
C(2)–Mo(1)–C(4)	85.6(9)	Mo(1)–C(1)–C(2)	70.7(13)
C(3)–Mo(1)–C(4)	98.7(9)	Mo(1)–C(2)–C(1)	75.0(13)
Cl(1)–Mo(1)–C(5)	78.0(6)	Mo(1)–C(2)–C(3)	75.4(14)
P(1)–Mo(1)–C(5)	78.8(6)	C(1)–C(2)–C(3)	122.8(25)
P(2)–Mo(1)–C(5)	78.5(6)	Mo(1)–C(3)–C(2)	70.7(13)
C(1)–Mo(1)–C(5)	141.8(9)	Mo(1)–C(4)–O(4)	178.7(18)
C(2)–Mo(1)–C(5)	172.5(9)	Mo(1)–C(5)–O(5)	175.4(20)
C(3)–Mo(1)–C(5)	142.7(9)		

Solid-State Structure.—The structure consists of discrete units of $[MoCl(CO)_2(\eta\text{-}C_3H_5)\{P(OMe)_3\}_2]$ as

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

TABLE 3

Analytical data (calculated values in parentheses), melting points, yields, and selected i.r. data

Compound	Analysis (%)		M.p. (θ_c/°C)	Yield (%)	Carbonyl i.r. data *		M(CO)$_2$ angle (°)	ν(M–X) /cm^{-1}
	C	H			2*A′*	others		
(1) [MoCl(CO)$_2$(η-C$_3$H$_5$){P(OMe)$_3$}$_2$]	27.5 (27.2)	4.8 (4.9)	76—78	58	1 985, 1 860	1 960m	109	237
(2) [MoBr(CO)$_2$(η-C$_3$H$_5$){P(OMe)$_3$}$_2$]	25.4 (25.5)	4.5 (4.5)	85—88	51	1 985, 1 855	1 953m	108	151
(3) [MoI(CO)$_2$(η-C$_3$H$_5$){P(OMe)$_3$}$_2$]	23.2 (23.3)	4.0 (4.1)	77—79	88	1 985, 1 860	1 960 (sh)	113	120
(4) [MoCl(CO)$_2$(η^3-C$_4$H$_7$){P(OMe)$_3$}$_2$]	29.2 (29.4)	5.1 (5.1)	95—97	38	1 992, 1 847		109	239
(5) [MoCl(CO)$_2$(η-C$_3$H$_5$){P(OEt)$_3$}$_2$]	35.1 (36.4)	6.1 (6.3)	38—41	46	1 985, 1 856	1 960 (sh)		232
(6) [MoI(CO)$_2$(η-C$_3$H$_5$){P(OEt)$_3$}$_2$]	31.4 (31.3)	5.4 (5.4)	46—48	50	1 983, 1 859		110	108
(7) [WCl(CO)$_2$(η-C$_3$H$_5$){P(OMe)$_3$}$_2$]	23.2 (23.4)	4.1 (4.1)	95—97	57	1 974, 1 848	1 944 (sh)	111	239
(8) [WCl(CO)$_2$(η-C$_3$H$_5$){P(OEt)$_3$}$_2$]	31.5 (31.5)	5.2 (5.4)	49—52	51	1 967, 1 843	1 942 (sh)	112	227
(9) [Mo(CO)$_2$(η-C$_3$H$_5$){P(OMe)$_3$}$_3$][BF$_4$]	25.7 (25.8)	5.0 (5.0)	104 (decomp.)	72	2 010, 1 923		114	
(10) [Mo(CO)$_2$(η^3-C$_4$H$_7$){P(OMe)$_3$}$_3$][BF$_4$]	26.1 (27.1)	5.0 (5.2)	79—82	71	2 000, 1 917		112	

* In CHCl$_3$.

shown in Figure 1, which also gives the atomic numbering scheme. The structure has C_s symmetry within experimental error, with the mirror plane containing the metal atom, both carbonyl groups, the chlorine atom, and the central carbon of the allyl group. The most striking feature of the structure is the P(1)–Mo–P(2) angle of 146.1(2)°, which is not an angle observed in previous [Mo(CO)$_2$(η-C$_3$H$_5$)L$_3$]$^{n\pm}$ structures where the allyl and carbonyl groups occupy three *fac* sites in a pseudo-octahedron, and the L–Mo–L angles vary between 71 and 92°.[3,4,10-13] Indeed the geometry observed for (1) is best considered in terms of a pentagonal bipyramid (p.b.) with Cl(1) and C(4) in axial positions [Cl(1)–Mo–C(4) 178.3(6)°], and the allyl ligand occupying two adjacent sites in the equatorial girdle.* The root mean square (r.m.s.) deviation[15] of the co-ordination sphere from the ideal polyhedron is 0.16 Å, a large value indicating severe distortion from the p.b. However, the deviation from other seven-co-ordinate polyhedra is considerably larger.

The distortions of (1) from an ideal p.b. are indicated by the angles subtended by the Mo-Cl(1) bond with Mo-C(5), Mo-C(1), and Mo-C(3) which are 78.0(6), 80.0(6), and 80.5(6)°, and with Mo–P(1) and Mo–P(2) which are 100.8(2) and 98.7(2)°. Calculation of the least-squares plane through the pentagonal girdle shows a maximum deviation of 0.57 Å for an atom from the six-atom plane [plane (1) in Table 4]. However there is a good explanation for this distortion from the ideal geometry.

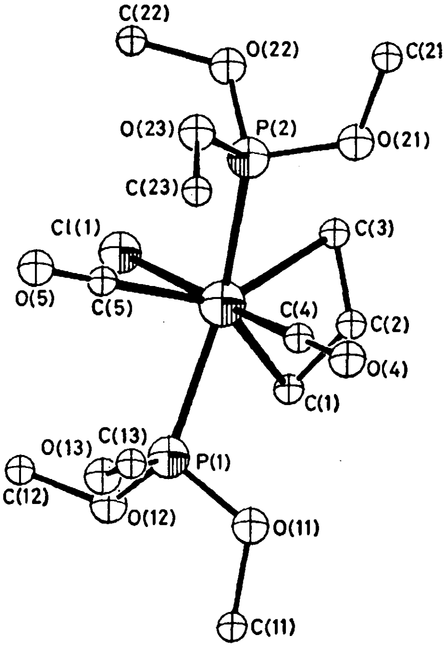

FIGURE 1 Structure of [MoCl(CO)$_2$(η-C$_3$H$_5$){P(OMe)$_3$}$_2$]

Our starting point is plane (2) in Table 4 which shows that Mo, P(1), P(2), C(1), and C(3) are almost coplanar (maximum deviation 0.17 Å) and that C(5) is 1.14 Å from this plane (which intersects the allyl plane at an angle of 78.7°). The position of C(5) relative to plane (2) is determined by the positions of the OMe groups. Study of the torsion angles shows that the six C(1)–Mo–P(1)–O(1*m*) and C(3)–Mo–P(2)–O(2*m*) angles (*m* = 1—3) are all within 6° of 60, −60, or 180°. Thus the P–O bonds are staggered with respect to the allyl group, a conformation which maximises OMe contacts with the allyl hydrogen atoms. Consequentially they are also staggered with respect to the Mo–C(4) bond, but not to Mo–Cl(1) and Mo–C(5). The smallest torsion angles involv-

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* In these η^3-allyl structures, all three carbon atoms are involved in some degree of bonding with the metal. While the allyl group can be considered as *formally* bidentate, from a purely structural point of view it can be described as bi- or uni-dentate. Our choice is made on the grounds of whether the resulting geometry can best be explained in terms of a six- or seven-co-ordinate polyhedron. In the case of the M(CO)$_2$(η^3-allyl) structures usually described as *fac*-octahedral, there is little to choose between this description and that of a capped trigonal prism with the bidentate allyl occupying the unique edge.[15] In these structures the plane of the allyl group is approximately parallel to a plane containing the metal and four donor atoms and thus the carbon atoms do not distort the octahedron to any appreciable extent. A plane through Mo, C(1), C(3) is close to just one other donor atom, that *trans* to the allyl group. (Thus for example in ref. 4, the *trans* atom is 0.08 Å and the other four donor atoms over 1.45 Å from this plane.) By contrast in (1), as shown in Table 4, both phosphorus atoms are close to the plane of Mo, C(1), and C(3) while C(5) is also within 1 Å. Thus the allyl group has a major effect on the geometry of the complex and the only reasonable description of the geometry is as a seven-co-ordinate pentagonal bipyramid with the allyl group bidentate. Furthermore, the allyl ligand, with a small normalised bite of 1.02, is well suited to occupy the equatorial girdle of such a structure.[15]

ing these latter two bonds are Cl(1)–Mo–P(n)–O(n2) 15.3, −15.9° for $n = 1,2$ and C(5)–Mo–P(n)–O(n3) −28.1, 29.1° for $n = 1,2$. It is interesting and significant that the Mo–P(n1)–O(n1) angles are considerably less (by an average of 8.1°) than the Mo–P(n2)–O(n2) and Mo–P(n3)–O(n3) angles. Clearly this is because these O(n1) atoms are not involved in close contacts with either Cl(1) or C(4).

A consequence of the staggering of the phosphite OMe groups with respect to the allyl group is that O(23) and O(13) are very close to the girdle plane (Table 4). If C(5) were in the girdle plane (as in an ideal pentagonal bipyramid) it would be involved in impossibly short contacts with O(13) and O(23), so atom C(5) moves out of the plane by over 1 Å to give C(5)–Mo–P(n)–O(n3) torsion angles of −28.1, 29.1° and C(5) · · · O(13), O(23) distances of 2.96, 2.99 Å respectively. This movement of C(5) causes the axial atoms Cl(1) and C(4) to move out of the perpendicular with respect to the girdle plane (Figure 2). Even so the Cl(1)–Mo–P(n) angles are 100.8(2), 98.7(2)° and together with the long Mo–Cl(1) bond [2.606(6) Å compared to a mean of 2.52 Å in ten molybdenum(II) seven-co-ordinate structures] [15] ensure that the small torsion angles Cl(1)–Mo–P(n)–O(n2) do not lead to short Cl · · · O distances. Other distances in the complex are as expected except that the Mo–C(1),C(3) bonds at 2.403(20), 2.407(22) Å are *ca.* 0.1 Å longer than the mean molybdenum–allyl distances in the *fac*-octahedral structures (see Table 3 in ref. 4). This is presumably a consequence of the crowding in the present molecule. The Mo–C(carbonyl) bond lengths are not significantly different particularly as the Mo · · · O(4) and Mo · · · O(5) distances are comparable.

TABLE 4

Least-squares planes with deviations (Å) of atoms from the planes. Atoms not contributing to the planes are marked with an asterisk

Plane (1): Mo −0.05, P(1) −0.42, P(2) −0.39, C(1) 0.17, C(3) 0.12, C(5) 0.57, C(2) * −0.47

Plane (2): Mo −0.17, P(1) 0.08, P(2) 0.05, C(1) −0.01, C(3) 0.05, Cl(1) * −2.67, C(2) * 0.68, C(4) * 1.67, C(5) * −1.14, O(23) * 0.09, O(13) * 0.09

Plane (3): Mo, C(1), C(3) 0.00, P(1) * 0.36, P(2) * 0.22, C(5) −0.80, C(2) * 0.64

Angles between the allyl group C(1), C(2), C(3) and planes (1) and (2) are 68.0 and 78.7° respectively.

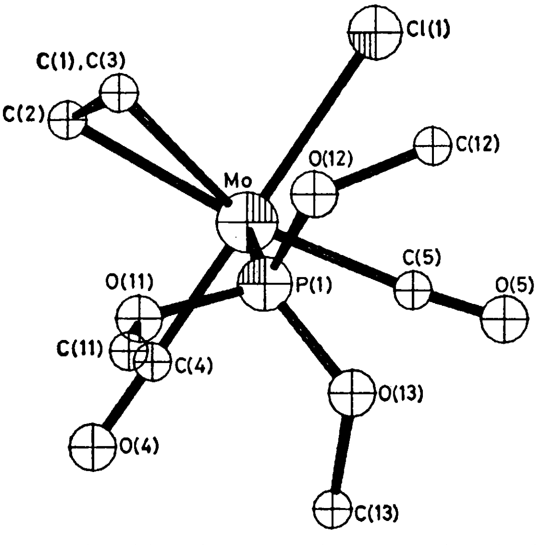

FIGURE 2 Disposition of the $\mathrm{P(OMe)_3}$ groups. A projection of the molecule onto the approximate mirror plane through atoms Mo, Cl(1), C(4), O(4), C(5), O(5), and C(2). In this projection C(1), C(3) are coincident as are the two $\mathrm{P(OMe)_3}$ groups. The disposition of the OMe groups maximises O · · · allyl contacts

We have shown therefore that the bulkiness of the $\mathrm{P(OMe)_3}$ groups is a cause of the distortions from the ideal seven-co-ordinate pentagonal-bipyramidal geometry, and it seems likely that steric effects are also important in determining this particular polytopal form, since severe crowding would occur in the usual pseudo-octahedral structure found for all other $[\mathrm{Mo(CO)_2(\eta\text{-}C_3H_5)L_3}]^{n\pm}$ complexes. However, such a geometry is by no means impossible and is adopted by $[\mathrm{MoCl(CO)_2(\eta\text{-}C_3H_5)(Ph_2PCH_2CH_2PPh_2)}]$ in which the cone angle of the phosphorus ligand (128°) is considerably larger than that of $\mathrm{P(OMe)_3}$ (107°).[16] Consequently we believe that electronic considerations are also important in establishing the polytopal form. With only one exception, all previous structure determinations on this class of complex have been carried out on molecules containing bi- or tri-dentate ligands, which prevent the formation of a structure analogous to (1). The one exception is $[\mathrm{Mo(CO)_2(\eta\text{-}C_3H_5)(NCMe)_3}]^+$ which adopts a pseudo-octahedral structure [10] with the usual *fac* arrangement of carbonyl and allyl ligands, which we previously suggested [4] to be electronically favoured in other complexes, all of which lack additional strong π-acceptor ligands. However, for the phosphite complexes, not only are there steric problems associated with a pseudo-octahedral structure, but at least one phosphite ligand would be *trans* to a carbonyl group and hence competing as a π acceptor. In view of the small energy difference between the various idealized seven-co-ordinate geometries,[15] the stereochemistry of these molybdenum- and tungsten-(II) derivatives may well be particularly sensitive to ligand properties.

Solution Behaviour.—In Nujol mulls, compounds (1)—(8) each exhibited the expected two A' carbonyl modes at approximately 1 980 and 1 850 cm^{-1}. The solution spectra of several of the complexes dissolved in $\mathrm{CCl_4}$, $\mathrm{CHCl_3}$, or $\mathrm{CH_2Cl_2}$ however revealed additional bands between 1 940 and 1 960 cm^{-1} (Table 1) which did not increase in intensity with time. Evaporation of the solutions regenerated the original two-band solid-state spectra indicating that a second isomeric species is formed in solution and is responsible for these spectral changes. This feature complicated the calculation of $\mathrm{Mo(CO)_2}$ bond angles from the relative intensities of the two major carbonyl bands,[17] but in those complexes where such calculations could be performed, values of 108—113° were obtained (Table 3). These values are in reasonable agreement with the solid-state $\mathrm{Mo(CO)_2}$ angle of 102° in (1), and considered together with the n.m.r. data indicate that the whole series of neutral complexes have the same basic structure.

The n.m.r. spectra of (1) below 230 K were in complete accord with the solid-state structure, with the exception of additional weak absorptions probably attributable to the isomeric species mentioned earlier. Thus for the major isomer ^{13}C n.m.r. measurements at 170 K showed equivalence of the ends of the allyl group and of the methyl groups of the phosphite ligands (Table 5). The two carbonyl groups are inequivalent, with both carbons strongly coupled with the two phosphorus atoms. In other phosphine-substituted carbonyl complexes of molybdenum and tungsten, *trans* $^{31}P-^{13}C$ coupling has been reported to be larger than *cis* coupling,[18] and consequently the more strongly coupled triplet centred at 233.0 p.p.m. is tentatively assigned to the axial carbonyl group in view of the slightly larger P(*n*)-Mo-C(4) angles compared with P(*n*)-Mo-C(5) (Table 2). By 260 K the carbonyl signals had coalesced into a single broad resonance at 228.4 p.p.m., which sharpened into a triplet by room temperature showing the carbonyls to be equivalent, and coupled equally with both phosphorus atoms. The free energy of activation of this rearrangement process, calculated by Kessler's procedure,[19] was found to be 55 ± 5 kJ mol^{-1}. The terminal allyl carbons, which showed a downfield shift of 10—15 p.p.m. compared with other Group 6 complexes of a similar type,[3,4] remained equivalent throughout. In addition, for this one room-temperature spectrum, couplings between ^1H and ^{13}C in the co-ordinated allyl and phosphite ligands were measured. For the former ligand, values of $^1J(C^2-H) = 161.1$ and average $^1J(C^{1,3}-H) = 161.6$ Hz are similar to the limited data reported on other complexes containing the allyl group [20,21] and are consistent with sp^2 hybridisation of the allylic carbon atoms. For the phosphite ligand $^1J(C-H) = 147.5$ Hz which differs little from the free-ligand value (144.5 Hz).

TABLE 5

^{13}C-{^1H} n.m.r. data

		^{13}C [δ/p.p.m. relative to $SiMe_4$, $J(C-P)$/Hz]				
			Allyl			
Complex (solvent)	(θ_c/°C)	Carbonyl	C^2	C^1C^3	Me	Phosphite
(1) (CD_2Cl_2)	−90	233.0 (t, 35.9)	114.4 (s)	76.0 (s)		53.6 (d, 4.6)
		225.0 (t, 27.2)				
	0	228.4 (br)	113.6 (s)	75.1 (s)		53.6 (br)
	32	228.0 (t, 29.3)	112.9 (s)	74.7 (s)		53.1 (d, 4.9)
(4) ($CDCl_3$)	−30	231.8 (t, 35.9)	130.0 (s)	75.4 (s)	25.1 (s)	53.2 (d, 4.6)
		225.4 (t, 26.7)				
(9) ($CDCl_3$)	−80	225.7 (dt, 33.3, 19.8)	103.1 (s)	62.1 (s)		53.6 (d, 9.2)
		216.4 (dt, 58.0, 21.4)				54.5 (d, 9.2)
	32		101.3 (s)	61.2 (s)		54.3 (br)

The ^1H n.m.r. spectrum of (1) was typical of symmetrical η^3-allyl complexes, but significant $P-H_{syn}$ (allyl) coupling at all temperatures resulted in two overlapping AA'XX' patterns rather than the doublet (or doublet of triplets) usually observed for the *syn*-allyl proton signal. At low temperatures this spin system simplified and approximated to overlapping AX spectra in which each *syn*-proton was strongly coupled to only one phosphorus (*J* 7.0 Hz), while at room temperature both *syn* protons were coupled equally with two phosphorus atoms (*J* 3.5 Hz) resulting in an A_2X_2 pattern for the ^1H-decoupled spectrum. Preparation of the 2-methylallyl derivative (4) in which homonuclear coupling effects were absent resulted in simpler spectra with similar P-H coupling constants, but a higher temperature dependence. Thus complex (4) was rigid on the ^1H n.m.r. time scale at room temperature and the limiting high-temperature A_2X_2 spectrum was not reached until *ca.* 335 K, under which conditions decomposition occurred. The remaining complexes in Table 6 showed similar effects in their ^1H n.m.r. spectra, with coalescence temperatures (as determined from the *syn*-proton signals) in the same range (235—260 K) as (1), and considerably lower than the more sterically hindered 2-methylallyl derivative (4).

The triethyl phosphite complexes [(5), (6), and (8)] showed additional temperature-dependent phenomena in their ^1H n.m.r. spectra. At room temperature the methylene proton signals of the phosphite ligands appeared as a pseudo-quintet, since $^3J(P-H) \approx {}^3J(H-H)$ caused overlapping of the expected quartet of doublets, whereas at low temperatures rotation about the P-O-C bonds was prevented resulting in two sets of overlapping quintets of equal intensity. The molecular symmetry of the neutral complex is such that both P atoms are chemically equivalent, and in solution at low temperature the ^{31}P n.m.r. spectrum of (1) consisted of a single broad band centred at 181 p.p.m. downfield from 85% H_3PO_4. At room temperature no significant changes occurred in the spectrum, although we were unable to observe fine structure on the JEOL PS 100 instrument at either high or low temperatures.

These n.m.r. studies show that all the neutral complexes undergo a fast rearrangement in solution at room temperature or above, which results in equivalence of the carbonyl groups, equivalence of the phosphite ligands, and coupling of the allyl *syn*-protons with two equivalent phosphorus atoms with coupling constants equal to the average of those at the low-temperature limit. These observations are inconsistent with a simple allyl-rotation mechanism such as that found for $[Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$,[22] since this could not result in the carbonyl groups becoming equivalent. Addition of free $P(OMe)_3$ had no effect on the ^1H n.m.r. spectrum of (1), and therefore a rearrangement involving dissociation of the phosphite ligand seems unlikely. Since no information could be obtained on any involvement of the axial halogen atoms in the rearrangement process, and as the spectra of the neutral complexes were complicated by signals from isomeric species, we cannot at present define the rearrangement mechanism further.

Cationic Derivatives.—Two $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)\{P(OMe)_3\}_3][BF_4]$ (R = H or Me) complexes (9) and (10) were readily prepared from the neutral halogeno-complexes by an analogous method to that described by Powell[23] for the preparation of related cationic complexes $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)(bipy)L][BF_4]$ (bipy = 2,2′-bipyridyl). Infrared ν(CO) band-intensity measurements indicated $M(CO)_2$ angles similar to those of the neutral phosphite complexes and far too large for the usual pseudo-octahedral structure found for other cations of the type $[Mo(CO)_2(\eta\text{-}C_3H_5)L_3]^+$. Furthermore, low-temperature ^1H [and ^{13}C on complex (9)] n.m.r. data clearly show two chemical environments for the phosphite ligands in the ratio 2 : 1, and a symmetrically bonded allyl group. Consequently it seems reasonable to presume that at low temperatures the cationic species also adopt a basically pentagonal-bipyramidal structure derived from (1) by replacement of the halogen by trimethyl phosphite, although different distortions from those of (1) are anticipated. Unequivocal confirmation could not be obtained from the ^{13}C n.m.r. spectrum of (9). A clearly defined doublet of triplets, with ^{31}P coupling constants in the ratio *ca.* 3 : 1, as expected for a combination of *trans*- and *cis*-phosphorus atoms,[18] could be assigned to the axial carbonyl groups in (9), but the position and fine structure of the other carbonyl signal is more tentative (Table 5) because of interference from spurious resonances, presumably due to decomposition products. The room-temperature spectrum was even less informative as no carbonyl signals could be detected, and the two phosphite resonances collapsed to a broad singlet. The ^1H n.m.r. spectra of (7) below 240 K contained two doublets of intensity ratios 1 : 2 centred at δ 3.66 and 3.78 p.p.m. respectively which were assigned to the $P(OMe)_3$ ligands. Two ^{31}P decoupling frequencies were found. One decoupled the phosphite signal at δ 3.66 p.p.m. [the unique $P(OMe)_3$] and also the overlapping doublet of doublets centred at δ 2.96 p.p.m. arising from the *anti*-allyl protons [$^3J(P\text{-}H) = 12$ Hz], the other decoupled the phosphite signal at δ 3.78 p.p.m. [$P(OMe)_3$ *trans* to allyl] and slightly sharpened the signal from the *anti*-allyl protons, suggesting weak coupling with these protons also. As the temperature was raised from −30 °C the two phosphite signals coalesced and sharpened to a doublet centred at δ 3.71 [$^3J(P\text{-}H) = 11$ Hz], but did not exchange with added $P(OMe)_3$ indicating a non-dissociative phosphite rearrangement. The *anti*-allyl proton signal was also temperature dependent and became a broad doublet by 300 K. Unfortunately the resonances from the *syn*-allyl protons completely obscured by the phosphite signals at all temperatures. The ^1H n.m.r. of (10) showed similar features, but as with the neutral 2-methylallyl derivatives the fully dynamic state was reached at a relatively high temperature (>350 K), when decomposition became significant.

TABLE 6

Hydrogen-1 and $^{31}P\text{-}\{^1H\}$ n.m.r. data at 303 K

		^1H [δ/p.p.m. relative to $SiMe_4$, $J(H\text{-}H)$ and $J(P\text{-}H)$/Hz]			
		Allyl			
Complex	^{31}P(δ/p.p.m. relative to H_3PO_4)	H_{anti}	H_{syn}	H or Me	Phosphite
(1)	181	3.24 (d, 13.3)	4.52 (d, 7.9, 3.5)	4.92 (m)	3.85 (d, 11.5)
(2)	179	3.49 (d, 13.2)	4.42 (dt, 7.8, 3.5)	4.74 (m)	3.80 (d, 11.4)
(3)	177	*	4.21 (dt, 7.4, 3.5)	4.64 (m)	3.79 (d, 11.0)
(4)	187	3.17 (s)	4.35 (d, 7.0)	1.81 (s)	3.82 (d, 11.8)
(5)	176	3.23 (d, 13.5)	4.40 (dt, 7.5, 3.3)	4.85 (m)	1.33 (t, 7.0), 4.16 (q, 7.0)
(6)	172	3.77 (d, 13.5)	*	4.60 (m)	1.30 (t, 7.0), 4.10 (q, 7.0)
(7)	150	2.88 (d, 13.5)	4.33 (dt, 8.0, 3.7)	4.95 (m)	3.76 (d, 11.8)
(8)		2.87 (d, 13.5)	4.22 (dt, 7.8, 3.5)	4.90 (m)	1.32 (t, 7.2), 4.09 (q, 7.3)
(9)	168	2.81 (br d, 12)	*	4.98 (m)	3.71 (d, 11.0)
(10)		3.13 (br, *ca.* 16)	*	2.03 (br)	3.85 (br d, *ca.* 8)

* Hidden by $P(OR')_3$ signal.

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