1,5,9-Triphosphacyclododecane Complexes of Molybdenum and Tungsten; Crystal Structure of Tricarbonyl[1,5,9-tris(isopropyl)-1,5,9-triphosphacyclododecane]-molybdenum(0) †

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The first tritertiary 1,5,9-triphosphacyclododecane ligand complexes of molybdenum were prepared from the trisecondary 1,5,9-triphosphacyclododecane precursor. The tungsten trisecondary 1,5,9-triphosphacyclododecane analogue has been synthesised and also serves as an intermediate to the first tungsten complexes of the tertiary phosphine macrocyclic ligands. The synthetic routes are general and allow access to a range of macrocyclic triphosphines with alkyl, ω-aminoalkyl and alkenyl functions on phosphorus. All the compounds have been characterised spectroscopically and the molybdenum triisopropyl derivative, $[Mo(CO)_3\{cyclo\text{-}(Pr^iPC_3H_6)_3\}]$, structurally.

There is only one reported example of a 1,5,9-triphosphacyclododecane macrocycle complex.[1] The free macrocycle has not been reported. A number of cyclotriphosphines have been reported by Kyba *et al.*[2] derived from 1,2-bis(phosphino)-benzene. The synthetic routes employed in these cases do not ideally lend themselves to extensive study of macrocyclic phosphines and their complexes, since the high-dilution methods used tend to be tedious for reasonable-scale preparations, the chemical yields may be low and a mixture of isomers is often generated, causing difficulty in separation and further reduction in yields of individual compounds. In the latter case, applicability of the complexes towards further derivatisation and other chemistry is restricted. These comments are generally true for all phosphorus macrocycles. Consequently the study of the chemistry of macrocyclic phosphines is remarkably slight, especially since the known chemistry of similar nitrogen and sulfur systems is both very extensive and important.

Norman and co-workers[1] first published the elegant synthesis of the only 1,5,9-triphosphacyclododecane complex in 1982, it involved the template coupling of three co-ordinated allylphosphine ligands on tris(allylphosphine)tricarbonyl molybdenum. The complex was structurally and spectroscopically characterised, however there have been no subsequent reported studies of any chemical properties. Using a similar route, the 1,6,11-triphosphacyclopentadecane analogue was also prepared.[1b] We have a number of reasons for investigating the chemistry of triphosphine macrocycle complexes. We are currently interested in the chemistry of complexes stabilised by linear triphosphorus ligand systems which have led to new classes of transition[3] and actinide[4] metal complexes. Although these complexes show new and unusual structural and chemical properties that are of interest, the co-ordination and electronic versatility of these ligands complicates the study of individual complexes and systems. Whereas this versatility is an advantage in some circumstances, *e.g.* in producing substitution labile and reactive compounds, there is also an advantage in restricting ligand freedom in order further to stabilise the metal–ligand interaction. Such an approach would be possible with macrocyclic triphosphines since clearly the phosphorus donors would be quite strictly restricted to specific co-ordination behaviour. Another motivation of this study is the observation that these compounds would act as cyclic, tridentate, six-electron ligands with close similarities to the η^5-C_5R_5, (R = H, alkyl, *etc.*) family of ligands. Furthermore, since the phosphorus donors have the potential to carry a wide variety of functions (in tertiary phosphine ligand systems) and in principle the connecting 'backbone' of the macrocycle may be variable, these compounds have the attractive and important features of versatile electronic and steric properties. Since they are also formally neutral, they may also lead to a wide range of chemistry that is more restricted to cyclopentadienyl and related complexes (*e.g.* access to low oxidation states). Should relatively general routes to the macrocycles derivatised at phosphorus be developed, the approach may be extended in a number of directions including the incorporation of pendant donors. In this paper we describe a synthetic study of cyclotriphosphadodecane derivatives which addresses the points above.

Results and Discussion

Molybdenum Complexes.—The NMR data for the molybdenum complexes described below are collected in Table 1; IR and analytical data are in Table 3. Tris(allylphosphine)tricarbonylmolybdenum **1** and the trisecondary phosphine precursor complex to the new tertiary phosphines described below, $[Mo(CO)_3\{cyclo\text{-}(HPC_3H_6)_3\}]$ **2**, were prepared in good yield according to the methods described by Norman and co-workers.[1] Our approach to the synthesis of tertiary derivatives was two-fold, one involving the precedented[5] deprotonation followed by alkylation at co-ordinated phosphorus by alkyl halide, the other being radical-initiated coupling of allylamine with the secondary PH functions of **2**; the synthetic routes to the new compounds are illustrated in Scheme 1. In individual cases, the progress and degree of substitution was readily followed by ^{31}P NMR spectroscopy. For example, in the preparation of **3**, addition of 3 equivalents of LiBu followed by 3 equivalents of MeI gave rise to mixtures of the monotertiary–disecondary and ditertiary–monosecondary macrocycle derivatives as indicated by multiplets at δ +1.5 and −6.9 in the ^{31}P-$\{^1H\}$ NMR spectra. The proton-coupled spectra were broad and lacked the necessary detail unequivocally to assign these resonances and no further effort was made

† *Supplementary data available:* See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 The NMR data for the molybdenum complexes

Complex	$\delta(^{31}P)$ (J_{PH}/Hz)	$\delta(^{1}H)$	$\delta[^{13}C\text{-}\{^{1}H\}]$
1 $[Mo(CO)_3\{PH_2(C_3H_5)\}_3]$	−57.5 (t, 295)	5.90, 5.10, 5.00, C=CH 2.36 CH_2P 3.92 PH_2	26.4 PCH_2 135.4, 117.6 C=C 217.7 CO
2 $[Mo(CO)_3\{cyclo\text{-}(HPC_3H_6)_3\}]$	−32.1 (d, 318)	4.70 PH 1.8 CH_2	
3 $[Mo(CO)_3\{cyclo\text{-}(MePC_3H_6)_3\}]$	−8.6 (s)	1.8 (m) CH_2 1.1 (br) CH_3	31.9 (m) PCH_2 22.7 (m) PCH_2CH_2 14.7 (m) CH_3 220.1 CO
4 $[Mo(CO)_3\{cyclo\text{-}(C_3H_5PC_3H_6)_3\}]$	−1.4 (s)	5.71, 5.07 (m) C=CH 1.77 (m) PCH_2 1.21 (m) PCH_2CH_2	21.2 (m) PCH_2 24.2 (m) PCH_2 118.1 (s), 145.4 (s) C=C 222.1 (m) CO
5 $[Mo(CO)_3\{cyclo\text{-}(Pr^iPC_3H_6)_3\}]$	10.1 (s)	1.84 (m) PCH_2 1.64 (m) PCH_2CH_2 1.50 (m) PCH 1.22 (s) CH_3	18.1 (s) CH_3 20.9 (m) PCH 27.3 (m) PCH_2CH_2 32.7 (dd, J_{PC} 13.7, 9.6) PCH_2 221.1 (m) CO
6 $[Mo(CO)_3\{cyclo\text{-}(Me_3SiCH_2PC_3H_6)_3\}]$	3.5 (s)	0.16 (s) $SiCH_3$ 1.18 (m) $SiCH_2$ 1.26 (m) PCH_2CH_2 1.66 (m) PCH_2CH_2	1.6 (s) $SiCH_3$ 21.4 (m) $SiCH_2$ 23.8 (m) PCH_2CH_2 33.4 (m) PCH_2CH_2 219.1 (m) CO
7 $[Mo(CO)_3\{cyclo\text{-}(NH_2C_3H_6PC_3H_6)_3\}]$	1.2 (s)	2.0 (m) NH_2, PCH_2 1.4 (m) PCH_2CH_2, NH_2CH_2	20.4 (s) $NH_2CH_2CH_2$ 23.7 (br m) PCH_2CH_2 29.2, 42.8 (br m) PCH_2CH_2 67.0 (s) NH_2CH_2 220.1 (br m) CO

to separate the mixture. Similarly, in the preparation of **4**, additional multiplets were observed at δ +20.0 and −1.7 in the $^{31}P\text{-}\{^{1}H\}$ NMR spectrum of the reaction mixture. Addition of further aliquots of $LiBu^n$ followed by the appropriate alkyl halide to these solutions resulted in the formation of the methyl (**3**) and allyl (**4**) derivatives respectively and for these compounds, it was generally found best to perform the deprotonation/alkylation cycles stepwise resulting in the clean formation of the tritertiary macrocycle complexes in good yield.

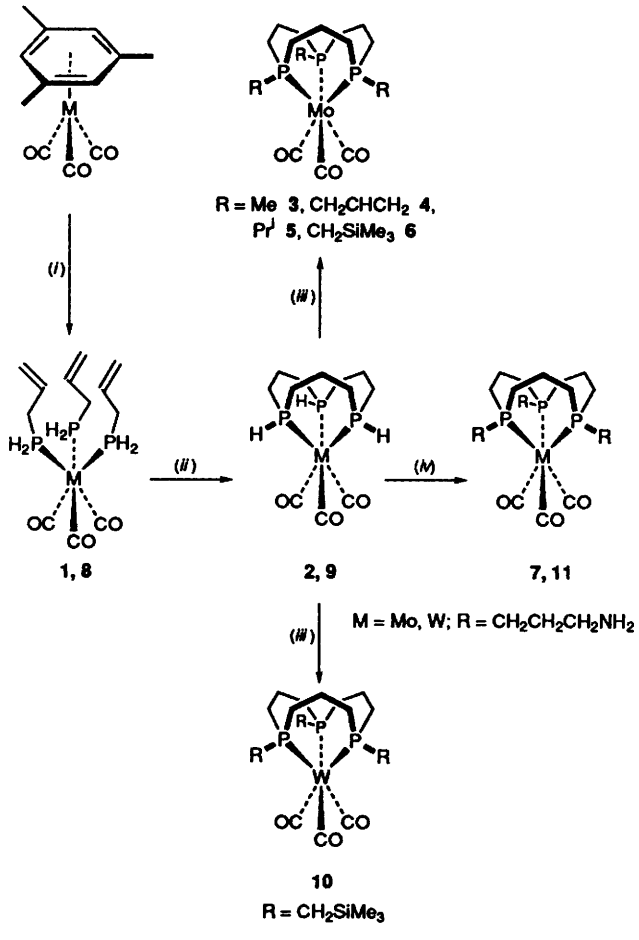
Such behaviour was not observed in the preparations of the isopropyl (**5**) and trimethylsilylmethyl (**6**) macrocycle complexes. In both cases, direct addition of 3 mol equivalents of $LiBu^n$ followed by 3 mol equivalents of the appropriate alkyl halide gave rise to only the desired tritertiary phosphine products; there was no evidence of partially alkylated intermediates (NMR spectroscopy). This difference is probably associated with the relative rates of halide substitution in the alkyl halides studied.[6] The inter- or intra-molecular radical-promoted coupling of co-ordinated primary and secondary phosphines with alkenes is well documented.[7] This approach clearly lends itself to the incorporation of a variety of aliphatic substituents and the use of functionalised alkenes would lead to functionally derivatised phosphorus macrocycles such as those with other pendant donor atoms. The radical-catalysed addition of allylamine to **2** gave rise to the desired tris(3-aminopropyl)-1,5,9-triphosphadodecane complex **7** in reasonable yield. The product was isolated from hydrocarbons as an air-stable white powder; attempts to obtain crystallographic quality crystals have not been successful. Proton NMR data are not informative since a number of complex multiplets of similar chemical shift overlap. The characterisation of **7** is supported by analytical, IR, ^{31}P and ^{31}C NMR data, all of which are consistent with the formulation. In the $^{31}P\text{-}\{^{1}H\}$ NMR spectrum a singlet is observed (δ +1.2) which is readily assigned to the three magnetically equivalent tertiary phosphines. In the $^{13}C\text{-}\{^{1}H\}$ NMR spectrum, resonances due to all carbons are observed and can be assigned, those α to N appearing at relatively low field (δ 67.0) and the carbonyl carbons (δ 220.1) appear as a broadened multiplet due to coupling with phosphorus.

Attempts to synthesise the chromium analogue of **2** by reaction of tricarbonylmesitylenechromium(0) with allylphosphine have so far not been successful. The triallylphosphine precursor is not readily formed since the conditions required to effect the substitution of mesitylene cause oligomerisation of the allylphosphine to take precedence. The route is viable for tungsten.

Tungsten Complexes.—The NMR data for the new tungsten complexes are collected in Table 2; IR and analytical data are in Table 3. The synthetic approaches to the molybdenum complexes above are readily applied to tungsten, however significant differences in reactivities were observed. Reaction of tricarbonylmesitylenetungsten with allylphosphine in a manner similar to that for Mo (at ambient temperature) did not result in clean conversion into the required tris(allylphosphine)tricarbonyl complex; the mixture had to be heated (80°C) to effect complete substitution of mesitylene. Under these conditions some by-products due to oligomerisation/polymerisation of allylphosphine were formed as insoluble orange materials which were readily separated from the product by filtration. The tris(allylphosphine)tricarbonyltungsten product **8** was characterised spectroscopically in solution and no attempts at further identification were made. The ^{1}H NMR spectrum has resonances attributable to alkeneic and aliphatic protons as well as a doublet in a position characteristic of PH protons (δ +3.5) in primary aliphatic phosphines.[8] The $^{31}P\text{-}\{^{1}H\}$ and ^{31}P NMR spectra clearly indicate the formation of a primary phosphine complex (δ −80.1, triplet), thus the co-ordination chemical shift of the primary allylphosphine is 54.3 ppm from the free phosphine (δ −134.4) but significantly less than that in the molybdenum analogue **1** (Δδ = 76.9). The P–H coupling

Table 2 The NMR data for the tungsten complexes

Complex	$\delta(^{31}P)$ (J_{PH}/Hz)	J_{PW}/Hz	$\delta(^1H)$	$\delta[^{13}C\text{-}\{^1H\}]$
8 $[W(CO)_3\{PH_2(C_3H_5)\}_3]$	−80.1 (319)	204	5.6, 5.1, 4.9, C=CH 2.2 PCH_2 3.5 PH_2	28.4 (d, J_{PC} 59) PCH_2 117.2, 135.3 (s) C=C 217.9 (m) CO
9 $[W(CO)_3\{cyclo\text{-}(HPC_3H_6)_3\}]$	−60.8 (312)	195	4.82 (m) PH 1.95 (m) CH_2	22.9 (m) PCH_2CH_2 25.0 (d, J_{PC} 38) PCH_2 220.0 (m) CO
10 $[W(CO)_3\{cyclo\text{-}(Me_3SiCH_2PC_3H_6)_3\}]$	−22.4	205	0.24 (s) $SiCH_3$ 1.24 (m) $SiCH_2$ 1.38 (m) PCH_2CH_2 1.81 (m) PCH_2CH_2	0.6 (s) $SiCH_3$ 21.8 (d, J_{PC} 12.4), $SiCH_2$ 23.9 (br m) PCH_2CH_2 31.8 (br m) PCH_2CH_2 213.3 (br m) CO
11 $[W(CO)_3\{cyclo\text{-}(NH_2C_3H_6PC_3H_6)_3\}]$	−24.0	203	1.42 (m) CH_2CH_2 2.02 (s) NH_2 2.58 (m) PCH_2	21.5 (s) $NH_2CH_2CH_2$ 28.9 (m) PCH_2CH_2 32.2 (m), 42.6 (m) PCH_2 67.6 (m) NH_2CH_2 212.3 (m) CO



Scheme 1 Synthesis of molybdenum and tungsten 1,5,9-triphosphacyclododecane complexes. (*i*) Allylphosphine (3 : 1); (*ii*) azoisobutyronitrile (aibn), heat; (*iii*) (*a*) 3LiBu^n, (*b*) 3RX; (*iv*) allylamine (3 : 1), aibn

constant ($^1J_{PH}$ = 319 Hz) also increases relative to that of the free phosphine (195 Hz). The $^{13}C\text{-}\{^1H\}$ NMR spectrum has resonances in positions characteristic of aliphatic and alkeneic carbons, the former exhibiting P–C coupling ($^1J_{PC}$ = 59 Hz) and a multiplet attributed to the carbonyl carbons. The formation of the trisecondary macrocyclic tungsten complex **9**, proceeded in a manner very similar to that of **2** but directly from the filtered reaction mixture containing the intermediate **8**. Complex **9** was then obtained in good overall yield (58%) from tricarbonylmesitylenetungsten as a white, microcrystalline air-stable solid. The compound is readily identified by its ^{31}P NMR spectrum in which a doublet is observed (δ −60.8, $^1J_{PH}$ = 312 Hz) due to co-ordinated secondary phosphines and again to high field of the corresponding resonance observed for the molybdenum analogue **2**. In addition, satellites due to coupling with ^{183}W (14.4% abundant) are observed ($^1J_{PW}$ = 195 Hz). The ^1H NMR spectrum shows multiplets assignable to the PCH_2 and central CH_2 protons, which appear coincident, and the PH proton. In the mass spectrum, an intense (40%) molecular ion is observed (*m*/*z* 490) along with peaks due to sequential loss of three carbonyl ligands.

There were significant differences between the reactivities of complexes **2** and **9** in the preparations of tertiary phosphine derivatives. The attempted synthesis of the trimethyl derivative by addition of LiBu^n followed by MeI resulted in the formation of two tritertiary phosphine complexes as indicated by two resonances in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of the reaction mixture (δ −21.5, −31.7). The IR spectrum showed four ν(C–O) bands at 1918, 1821, 1771 and 1628 cm^{-1}, the last in a position consistent with acyl or bridging carbonyl functions. Unfortunately, the $^{13}C\text{-}\{^1H\}$ and ^1H NMR spectra were complex, broadened and uninformative and attempts to separate the mixture by crystallisation and chromatography have failed. The tungsten trimethylsilylmethyl and 3-aminopropyl derivatives **10** and **11** are however readily prepared in a manner directly analogous to their molybdenum analogues **6** and **7**. In both cases the compounds are satisfactorily characterised by analytical and spectroscopic data (Tables 2 and 3). Again in the $^{31}P\text{-}\{^1H\}$ NMR spectra there is a consistent high-field shift of 20–25 ppm for the tungsten compounds relative to the molybdenum analogues, and $^1J_{PW}$ is observed.

The interpretation of the IR spectra of metal carbonyl phosphine complexes is a classical approach to providing a view of the nature of the metal–ligand bonding in such systems.[9] All the complexes reported here show two C–O stretching vibrations consistent with the A_1 and E modes expected for a facial, C_{3v} X_3MY_3 co-ordination structure[10] and consistent with the reported IR spectrum of **2**. For the molybdenum compounds **2**–**7**, the lower-frequency ν(C–O) absorption decreases as the substituents on phosphorus vary in the order H > C_3H_5 > Me ≈ Me_3SiCH_2 > Me_2CH ≈ $H_2NCH_2CH_2CH_2$. These trends may infer a similar order of π-bonding ability in these ligands but a similar order of σ-donor abilities might also be expected. Since these data are unavailable for these ligands,

Table 3 Infrared (cm^{-1}) and analytical data for the molybdenum and tungsten complexes

Complex	ν(CO)	ν(PH)	ν(C=C)	Analysis (%) * C	H	N
1	1954, 1864	2299	1633	35.7 (35.8)	5.40 (5.25)	0.00 (0.00)
2	1954, 1844	—	—	36.0 (35.8)	5.40 (5.25)	0.00 (0.00)
3	1920, 1827	—	—	40.1 (40.5)	5.65 (6.15)	0.00 (0.00)
4	1926, 1834	—	1633	47.6 (48.3)	6.00 (6.40)	0.00 (0.00)
5	1915, 1813	—	—	47.6 (46.5)	7.80 (7.40)	0.00 (0.00)
6	1923, 1828	—	—	42.2 (43.6)	8.15 (7.30)	0.00 (0.00)
7	1912, 1813	—	—	43.8 (44.0)	7.10 (7.35)	7.65 (7.35)
8	1935, 1825	2350	1630	—	—	—
9	1910, 1825	2305	—	28.5 (29.4)	4.60 (4.30)	0.00 (0.00)
10	1910, 1813	—	—	36.2 (37.0)	7.25 (6.75)	0.00 (0.00)
11	1912, 1813	—	—	38.3 (37.6)	6.55 (6.25)	7.45 (7.15)

* Calculated values in parentheses.

an analysis of relative π-bonding abilities is not possible.† For the tungsten complexes a similar trend is observed [*i.e.* ν(C–O) varies in the order of macrocycle phosphine substituents H > Me_3SiCH_2 ≈ $H_2NCH_2CH_2CH_2$ and primary phosphine > secondary macrocycle] although the magnitude of the variation in ν(C–O) is not as great as it is for the molybdenum complexes. Since the bulk of the macrocycle substituents varies in these series, steric influences on the ν(C–O) absorptions cannot be ruled out. Detailed analysis of the structures of representative examples from the series is of value in this context; compounds **2** and **5** were chosen since the structure of **2** has been reported, **5** exhibits one of the largest shifts in ν(C–O) and forms crystals amenable to X-ray crystallography.

Structural Studies.—The crystal structure of the triisopropyl derivative **5** with the full atom-labelling scheme is displayed in Fig. 1; views of the two crystallographically independent molecules showing minor conformational differences are in Fig. 2. The overall geometry is distorted octahedral, the major source of distortion from idealised geometry arising from the difference between the Mo–C and Mo–P bond lengths [averages 1.981(2) and 2.5269(8) Å respectively]. Direct comparison with the secondary phosphine precursor **2** is informative; selected bond lengths and angles for both compounds are collected in Table 4, fractional atomic coordinates for **5** are in Table 5. The average Mo–C distance in **5** is identical to that in **2** [1.977(3) Å] within experimental error; the average C–O distances [1.159(3) Å and 1.150(4) Å for **5** and **1** respectively] are also very similar. There is a significant difference in Mo–P bonding however, the average in **5** being longer than that in **2** [2.476(1) Å] by *ca.* 0.05 Å (62σ). This relative lengthening of the Mo–P bonds may be due at least in part to the relative bulk of the substituents on the tertiary phosphines. The structural data do not distinguish between electronic and steric causes of the observed bond lengthening, but the spectroscopic data (see above) are consistent with the tertiary phosphine in **5** promoting a more electron-rich centre than does the secondary phosphine in **2**.

Comparison with the bis(tertiary phosphine)tetracarbonylmolybdenum complexes $[Mo(CO)_4(PR_3)]$[12] (R_3 = Me_3, Et_3, Bu^n_3, Me_2Ph, $MePh_2$, or Ph_3) is of interest since in these examples the phosphine ligands have freedom to move towards positions that may more readily accommodate compromises between idealised bonding and steric influences. The shortest Mo–P bond lengths to the smaller tertiary phosphines are similar to those in **5** [2.522(1) Å where R_3 = Me_3] but are significantly longer for more bulky phosphines

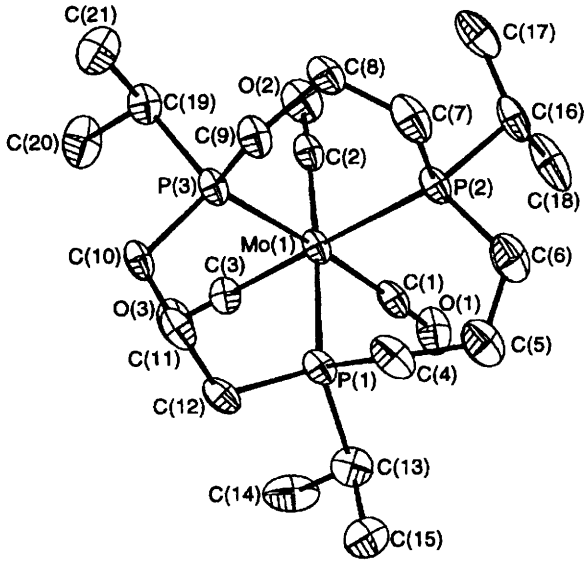


Fig. 1 View of the structure and atom-labelling scheme of $[Mo(CO)_3\{cyclo\text{-}(Pr^iPC_3H_6)_3\}]$ **5** looking down the approximate C_3 axis

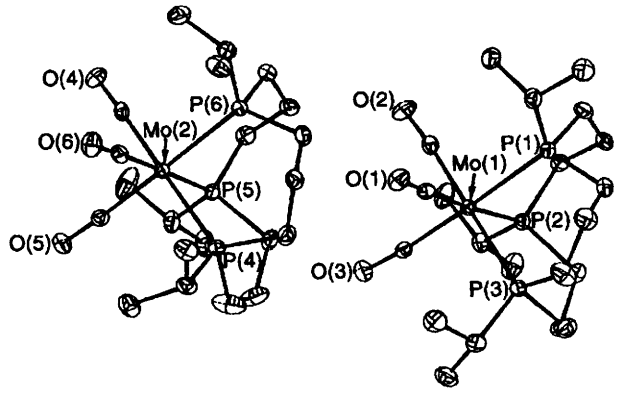


Fig. 2 Diagram of the two crystallographically independent molecules of complex **5**. The main structural differences concern the conformations of the macrocycle ligands and the orientations of the isopropyl substituents

† A referee pointed out that ^{13}C NMR data have been used to determine relative electron densities at the metal in carbonyl complexes. However in the tertiary phosphine macrocycle complexes of both Mo and W there is not a significant variation in δ (^{13}C–O). There is a difference in δ (^{13}C–O) between the secondary and tertiary tungsten derivatives but this still does not distinguish between relatively poor σ-donor ability *vs.* relatively enhanced π acceptance for the secondary phosphine.

Table 4 Selected bond angles (°) and lengths (Å) for compounds **2**[1] and **5**

	2	5*
Mo–P(1)	2.507(1)	2.5118(7)
Mo–P(2)	2.455(1)	2.5531(8)
Mo–P(3)	2.465(1)	2.5163(8)
Mo–C(1)	1.983(4)	1.982(2)
Mo–C(2)	1.987(3)	1.988(2)
Mo–C(3)	1.962(3)	1.974(3)
C(1)–O(1)	1.142(5)	1.165(3)
C(2)–O(2)	1.162(4)	1.159(3)
C(3)–O(3)	1.146(4)	1.156(3)
P(1)–Mo–P(2)	89.27(3)	87.86(2)
P(1)–Mo–P(3)	88.18(3)	85.53(3)
P(3)–Mo–P(2)	89.18(3)	89.57(3)
C(1)–Mo–C(2)	90.5(1)	88.08(9)
C(1)–Mo–C(3)	93.5(1)	86.54(10)
C(3)–Mo–C(2)	91.2(1)	85.79(9)
P(1)–Mo–C(1)	92.8(1)	92.41(7)
P(1)–Mo–C(2)	176.6(1)	177.10(7)
P(1)–Mo–C(3)	87.7(1)	91.38(6)
P(2)–Mo–C(1)	88.4(2)	93.23(7)
P(2)–Mo–C(2)	91.7(2)	94.97(7)
P(2)–Mo–C(3)	176.5(2)	179.19(6)
P(3)–Mo–C(1)	177.4(1)	176.47(7)
P(3)–Mo–C(2)	88.6(1)	93.83(8)
P(3)–Mo–C(3)	89.0(1)	90.64(7)
Mo–C(1)–O(1)	177.4(3)	175.2(2)
Mo–C(2)–O(2)	178.5(3)	174.3(2)
Mo–C(3)–O(3)	179.5(3)	174.8(2)
Mo–P(1)–C(4)	120.2(1)	114.26(8)
Mo–P(1)–C(12)	117.6(1)	117.76(7)
Mo–P(1)–C(13)		116.52(8)
Mo–P(2)–C(6)	118.7(1)	117.36(9)
Mo–P(2)–C(7)	119.3(1)	119.50(9)
Mo–P(2)–C(16)		118.05(9)
Mo–P(3)–C(9)	118.5(1)	117.64(8)
Mo–P(3)–C(10)	119.3(1)	115.70(7)
Mo–P(3)–C(19)		115.35(8)

* Values for one of the two independent molecules [Mo(1)] have been listed; the second molecule shows no significant differences in relevant structural parameters. The atom-labelling scheme is consistent with that of **2**.

[2.577(2) Å where $R_3 = Ph_3$] The average *cis*-P–Mo–P angles are greater than the idealised 90° and vary over a wide range from 92.52(5) (for $R_3 = MePh_2$) to 104.62(7)° (for $R_3 = Ph_3$). In our example there are some obvious constraints on the metal-ligand bonding imposed by the macrocycle 'backbone'. The confinement or containment of the three mutually *cis* phosphorus donors by the backbone in **2** results in a more regular distribution of *cis* interligand angles, all of which are close to 90° [averages: P–Mo–P 88.88(3), C–Mo–C 91.7(1) and C–Mo–P 89.7(1)° respectively]. In the triisopropyl derivative **5** these angles deviate from those observed in **2** [averages P–Mo–P 87.65(3), C–Mo–C 86.8(1), C–Mo–P 92.74(4)°] and reflect two features. The relative lengthening of the Mo–P bonds results in a decrease of the P–Mo–P angles, which combined with the greatly increased bulk of the substituents on phosphorus results in an expansion of the P–Mo–C angles and a considerable compression of the C–Mo–C angles. Although the influences on the P–Mo–P and C–Mo–P angles could be viewed as a result of stretching the pseudo-three-fold axis, this does not explain the compression of the C–Mo–C angles (since the Mo–C bond lengths in **2** and **5** are so similar) which may be a result of steric interactions between the phosphorus substituents in the macrocycle and the carbonyl ligands. This interaction does appear to be weak however since the shortest intramolecular O(CO)–H(CH_3) contact is > 2.7 Å. There also appears to be considerable freedom of orientation for the isopropyl functions in **5** since two are canted such that the methyl groups lie above and below the plane of the three phosphorus atoms, and in the third both methyl groups lie below that plane towards the Mo atom; freedom of rotation of the P–C (Pr^i) bonds in solution is indicated by NMR data. Again, these arguments do not distinguish steric from electronic influences on the molybdenum-macrocycle bonding.

The conformations of the three six-membered chelate rings in each of the two molecules of **5** vary. One adopts a chair, chair, boat arrangement as observed in **2** and the other adopts three chair conformations (Fig. 2).

Experimental

Techniques and Instruments.—All reactions were carried out in an atmosphere of dry nitrogen. All solvents were dried by boiling under reflux over standard drying agents. The compounds $[Mo(CO)_3\{cyclo\text{-}(HPC_3H_6)_3\}]$ **2**,[1b] $[Mo(CO)_3(C_6H_3Me_3\text{-}1,3,5)]$[13], $[W(CO)_3(C_6H_3Me_3\text{-}1,3,5)]$[14], and allylphosphine,[15] were prepared by literature methods. All other reagents were obtained from the Aldrich Chemical Company and, where appropriate, were degassed before use. The NMR spectra were recorded on a Bruker WM360 instrument operating at 360.13 (^{1}H) or 90.53 MHz (^{13}C) or a JEOL FX-90 instrument operating at 36.23 MHz (^{31}P). All spectra were recorded in $CDCl_3$ solution, with the ^{1}H and ^{13}C chemical shifts quoted in ppm relative to solvent and ^{31}P chemical shifts quoted in ppm relative to 85% external H_3PO_4. The infrared spectra were recorded in Nujol on a Nicolet 510 FT-IR spectrometer, mass spectra by the SERC Mass Spectrometry service in Swansea. Microanalyses were obtained from the Microanalysis Group within this department.

CAUTION: The organophosphines and some of their complexes described are *highly malodorous* and likely *highly toxic*. Great care should be exercised in their handling.

Preparations.—The syntheses of compounds **3**–**6** and **10** were similar; the detailed experimental procedure is given for $[Mo(CO)_3\{cyclo\text{-}Pr^iPC_3H_6)_3\}]$ **5**. To a cooled (−78 °C) solution of $[Mo(CO)_3\{cyclo\text{-}(HPC_3H_6)_3\}]$ **2** (0.20 g, 0.50 mmol) dissolved in tetrahydrofuran (thf) (20 cm^3) was added dropwise a solution of $LiBu^n$ (0.25 mol dm^{-3}, 0.50 mmol) in hexane (2 cm^3) and the mixture allowed to warm to − 20 °C. The mixture was cooled to −78 °C and a solution of Pr^iBr (0.06 g, 0.50 mmol) in thf (3 cm^3) was added dropwise. The mixture was allowed to stir for 20 min. This process was repeated twice such that 3 equivalents of $LiBu^n$ and Pr^iBr had both been added sequentially. The solvent was removed *in vacuo* to give a pale orange, oily product. This was taken up in CH_2Cl_2 (50 cm^3) and passed through a short (3.8 cm) silica column with CH_2Cl_2 as eluent, to give a pale solution. Evaporation *in vacuo* gave complex **5** as an off-white powder; yield 0.18 g, 68%. Positive-ion electron impact (EI) mass spectrum: *m/z* 530 (M^+, 32), 502 ($[M - CO]^+$, 24) and 472 ($[M - 2CO]$, 44%).

$[Mo(CO)_3\{cyclo\text{-}(MePC_3H_6)_3\}]$ **3**. From complex **2** (0.2 g), other reagents being in the same stoichiometric ratio and using MeI as the alkylating agent; **3** was isolated as off-white prisms from light petroleum (b.p. 40–60 °C) and is soluble in all common hydrocarbons, ethers and chlorinated hydrocarbons; yield 0.11 g, 48%.

$[Mo(CO)_3\{cyclo\text{-}(C_3H_5PC_3H_6)_3\}]$ **4**. From complex **2** (0.2 g), other reagents being in the same stoichiometric ratio and using C_3H_5Br as the alkylating agent; **4** was isolated as off-white prisms from light petroleum and is soluble in all common hydrocarbons, ethers and chlorinated hydrocarbons; yield 0.11 g, 41%.

$[Mo(CO)_3\{cyclo\text{-}(Me_3SiCH_2PC_3H_6)_3\}]$ **6**. From complex **2** (0.2 g), other reagents being in the same stoichiometric ratio and using $Me_3Si(CH_2Cl)$ as the alkylating agent; **6** was isolated as white needles from light petroleum and is very soluble in

Table 5 Atomic coordinates ($\times 10^4$) for complex **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo(1)	2 465(1)	2 171(1)	8 070(1)	C(15)	4 552(2)	980(2)	10 871(1)
Mo(2)	2 440(1)	2 174(1)	3 006(1)	C(16)	1 345(2)	3 961(1)	8 396(1)
P(1)	3 063(1)	1 307(1)	9 327(1)	C(17)	689(2)	4 109(2)	7 495(1)
P(2)	1 578(1)	2 880(1)	8 629(1)	C(18)	2 147(2)	4 434(2)	8 632(2)
P(3)	1 311(1)	1 131(1)	8 629(1)	C(19)	740(1)	1 105(2)	6 290(1)
P(4)	1 549(1)	2 800(1)	3 593(1)	C(20)	1 332(2)	792(2)	5 969(1)
P(5)	1 207(1)	1 221(1)	2 308(1)	C(21)	−107(2)	648(2)	5 883(1)
P(6)	3 041(1)	1 190(1)	4 169(1)	C(22)	3 075(1)	1 634(1)	2 510(1)
O(1)	4 011(1)	3 368(1)	8 852(1)	C(23)	1 949(1)	2 896(1)	2 039(1)
O(2)	1 821(1)	3 187(1)	6 459(1)	C(24)	3 401(2)	2 941(1)	3 517(1)
O(3)	3 581(1)	1 349(1)	7 391(1)	C(25)	393(2)	2 788(2)	2 890(2)
O(4)	3 455(1)	1 344(1)	2 214(1)	C(26)	−76(2)	2 058(2)	2 509(2)
O(5)	1 709(1)	3 314(1)	1 479(1)	C(27)	387(1)	1 258(1)	2 646(1)
O(6)	3 963(1)	3 398(1)	3 767(1)	C(28)	549(1)	1 307(2)	1 173(1)
C(1)	3 426(1)	2 938(1)	8 586(1)	C(29)	−282(2)	814(2)	783(2)
C(2)	2 016(1)	2 818(1)	7 049(1)	C(30)	1 077(2)	1 138(2)	745(1)
C(3)	3 161(1)	1 618(1)	7 653(1)	C(31)	1 491(2)	159(1)	2 447(1)
C(4)	2 589(2)	1 482(2)	7 653(1)	C(32)	1 931(2)	−139(1)	3 333(1)
C(5)	2 703(2)	2 355(2)	10 297(1)	C(33)	2 863(1)	−132(1)	3 855(1)
C(6)	2 043(2)	2 944(2)	9 768(1)	C(34)	4 223(1)	1 166(2)	4 860(1)
C(7)	501(2)	2 503(2)	8 363(1)	C(35)	4 723(1)	1 055(2)	4 398(2)
C(8)	23(1)	2 005(1)	7 580(1)	C(36)	4 539(2)	1 893(2)	5 410(2)
C(9)	419(1)	1 172(1)	7 673(1)	C(37)	2 655(2)	1 215(2)	4 934(1)
C(10)	1 667(1)	91(1)	7 709(1)	C(38)	2 484(2)	2 052(2)	5 163(1)
C(11)	2 056(2)	−106(1)	8 629(1)	C(39)	1 600(2)	2 379(2)	4 540(1)
C(12)	2 959(1)	213(1)	9 177(1)	C(40)	1 704(2)	3 875(1)	3 863(1)
C(13)	4 231(1)	1 413(2)	10 053(1)	C(41)	2 580(2)	4 014(2)	4 620(1)
C(14)	4 761(1)	1 185(2)	9 636(1)	C(42)	1 617(2)	4 384(2)	3 149(1)

aliphatic hydrocarbons, ethers and chlorinated hydrocarbons; yield 0.25 g, 75%.

$[Mo(CO)_3\{cyclo\text{-}(NH_2C_3H_6PC_3H_6)_3\}]$ **7**. To a solution of complex **2** (0.20 g, 0.50 mmol) dissolved in toluene (20 cm^3) and allylamine (5 cm^3) was added azoisobutyronitrile (*ca* 1%). The mixture was heated to 70 °C for 4 h. The solvent was removed *in vacuo* to give a yellow oil. The residue was dissolved in CH_2Cl_2 (30 cm^3) and passed through a short (1.3 cm) Celite column. Solvent was removed *in vacuo* to give the crude product as a yellow solid. The product **7** was obtained as off-white needles by recrystallisation from CH_2Cl_2–Et_2O; yield 0.13 g, 45%.

$[W(CO)_3\{PH_2(C_3H_5)\}_3]$ **8**. To a frozen solution of allylphosphine (1.5 g, 20.2 mmol) in toluene (30 cm^3) was added $[W(CO)_3(C_6H_3Me_3\text{-}1,3,5)]$ (0.81 g, 0.21 mmol). The apparatus was fitted with a solid CO_2 condenser and the mixture heated to 80 °C for 4 h. After this time the mixture was allowed to cool to room temperature. Solvent and unreacted phosphine were removed *in vacuo* to give an orange solid. Toluene was added and the mixture was filtered through a short Celite column to give a clear pale orange solution which was used without further purification for the synthesis of $[W(CO)_3\{cyclo\text{-}(HPC_3H_6)_3\}]$ **9** and was identified by spectroscopic methods only.

$[W(CO)_3\{cyclo\text{-}(HPC_3H_6)_3\}]$ **9**. This complex was prepared according to the method for **2**, using $[W(CO)_3\{PH_2(C_3H_5)\}_3]$ **8**. The off-white product was soluble in aromatic hydrocarbons (sparingly in aliphatic hydrocarbons) and quite soluble in chloroform and dichloromethane; yield 58% based on $[W(CO)_3(C_6H_3Me_3\text{-}1,3,5)]$. Positive-ion EI mass spectrum: *m/z* 490 (M^+, 40) 462 ($[M - CO]^+$, 15), 432 ($[M - 2CO]^+$, 28), and 404 ($[M - 3CO]^+$, 35%).

$[W(CO)_3\{cyclo\text{-}(Me_3SiCH_2PC_3H_6)_3\}]$ **10**. This compound was prepared by the same method as that used for **5**, using $[W(CO)_3\{cyclo\text{-}(HPC_3H_6)_3\}]$ **9** (0.2 g), other reagents in the same stoichiometric ratio and $SiMe_3(CH_2Cl)$ as the alkylating agent. Complex **7** was isolated as white needles from light petroleum and was soluble in aliphatic hydrocarbons, more so in aromatic hydrocarbons and dichloromethane; yield 0.15 g, 40%.

$[W(CO)_3\{cyclo\text{-}(NH_2C_3H_6PC_3H_6)_3\}]$ **11**. This compound was prepared by the same method as that used for **7**, using $[W(CO)_3\{cyclo\text{-}(HPC_3H_6)_3\}]$ **9** (0.2 g). It was isolated as a white powder which was soluble in dichloromethane and sparingly soluble in aliphatic hydrocarbons; yield 0.12 g, 36%.

X-ray Crystallography.—Crystal data $C_{21}H_{39}MoO_3P_3$, $M = 528.37$, monoclinic, space group $P2_1/a$ (alternative no. 14), $a = 17.740(5)$, $b = 16.797(5)$, $c = 18.5280(11)$ Å, $\beta = 118.450(14)$, $U = 4854(2)$ Å^3, $Z = 8$, $D_c = 1.446$ g cm^{-3}, $F(000) = 2208$, μ(Mo-Kα) = 7.57 cm^{-1}.

Data collection and processing. A pale yellow prism of approximate dimensions 0.24 × 0.24 × 0.1 mm was mounted on a glass fibre using silicone oil. Data were collected at 120 K, on a FAST TV Area detector diffractometer at the window of a rotating-anode FR591 generator (50 kV, 40 mA), with Mo-Kα radiation ($\lambda = 0.71069$ Å) controlled by a Micro Vax 3200 computer with MADNES[16] software and following previously described procedures.[17] 19562 Data were recorded ($1.78 < \theta < 25.03°$), index ranges $-20 < h < 12$, $-19 < k < 19$, $-20 < l < 22$, to give 7328 unique data ($R_{int} = 0.0594$ after absorption correction, DIFABS[18]).

Structure solution and refinement. The structure was solved *via* heavy-atom methods (SHELXS)[19] and refined by full-matrix least squares on all F_o^2 data (SHELX 93)[20] to give two independent molecules in the asymmetric unit. All non-hydrogen atoms were refined anisotropically with all hydrogens included in idealised positions (C–H 0.97 Å, C/H–C–H angles 109.5°). The weighting scheme used was $w = 1/[\sigma^2(F_o^2)]$. The final R_1 and wR_2 values for 5452 data with $F_o > 4\sigma(F_o)$ and 517 parameters {ρ_{max},ρ_{min} = 2.18, −0.521 e Å^{-3}; $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR_2 = \Sigma[(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{\frac{1}{2}}$ were 0.0404 and 0.1002 for 517 parameters. The corresponding R_1 and wR_2 values for all 7328 data were 0.0456 and 0.1078 respectively. Diagrams were drawn with SNOOPI.[21] All calculations were

performed on a 486DX2 personal computer. Sources of scattering factor data are given in ref. 20.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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