When does a Nitrogen attached to a λ^3-Phosphorus assume a Pyramidal Geometry? Crystal Structures of Group 6 Metal Carbonyl Complexes of Isomeric Forms of λ^3-Cyclotriphosphazanes†

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The reaction of $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) with *trans*-$[EtNP(OC_6H_3Me_2\text{-}2,6)]_3$ (L^1) or *cis*-$[EtNP(OCH_2CF_3)]_3$ (L^2) yields the mono- and di-nuclear molybdenum(0) complexes $[Mo(CO)_4(L^1)]$ **1** and $[\{Mo(CO)_4(\mu\text{-}L^2)\}_2]$ **2**, respectively. They represent the first organometallic transition-metal derivatives of λ^3-cyclotriphosphazanes and have been characterised by elemental analysis and IR and NMR spectroscopy and their structures confirmed by X-ray crystallography. The different co-ordination behaviour of the *cis* and *trans* isomeric forms of this type of ligand is revealed. A pyramidal geometry observed around one of the nitrogen atoms of the P_3N_3 ring in complex **1** is unprecedented among λ^3-phosphazanes.

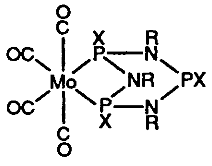
Whereas the co-ordination chemistry of acyclic λ^3-diphosphazanes has been extensively studied,[1] investigations on the transition-metal complexes of λ^3-cyclophosphazanes are sparse.[2-4] Recent work from our laboratory[3] has demonstrated that the cyclodiphosphazanes of the type $[RNP(OR)]_2$ (R = alkyl or aryl) can function as versatile ligands and the *cis* and *trans* isomers of the P_2N_2 ring exhibit different co-ordination behaviour. Cyclotriphosphazanes, $(RNPR')_3$, which possess three λ^3-phosphorus centres in close proximity would be interesting ligands too but there has been no report on their complexation behaviour. On the other hand, Paddock and co-workers[4] have investigated the synthesis, spectra and structure of transition-metal complexes of the cyclotetraphosphazanes $(MeNPR)_4$ (R = Me, Et or Ph).

In the course of our studies on the conformations of λ^3-cyclotriphosphazanes[5] and their use as ligands in transition-metal chemistry, we have isolated the metal carbonyl complexes $[Mo(CO)_4(L^1)]$ **1** {L^1 = *trans*-$[EtNP(OC_6H_3Me_2\text{-}2,6)]_3$} and $[\{Mo(CO)_4(\mu\text{-}L^2)\}_2]$ **2** {L^2 = *cis*-$[EtNP(OCH_2CF_3)]_3$} and determined their crystal structures. They represent the first examples of organometallic derivatives of λ^3-cyclotriphosphazanes. The structural features of complexes **1** and **2**, conformational changes in the ligands as a result of complexation and implications of the results for the understanding of the nature of the P–N bond are reported in this paper.

Results and Discussion

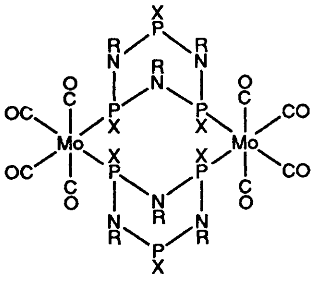
Syntheses and Spectra.—The (aryloxy)cyclotriphosphazane L^1 reacts with $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) in boiling hexane to give the mononuclear complex $[Mo(CO)_4(L^1)]$ **1** (60% yield) whereas the reaction of L^2 with $[Mo(CO)_4(nbd)]$ under similar conditions yields the dinuclear complex $[\{Mo(CO)_4(\mu\text{-}L^2)\}_2]$ **2** (70% yield). Complexes **1** and **2** have been characterised by elemental analysis and IR and NMR spectroscopy.

The IR spectra of **1** and **2** show four absorption bands in the ν(CO) region (*ca.* 1900–2100 cm^{-1}) suggesting that these compounds contain a $Mo(CO)_4$ moiety with an approximate local C_{2v} symmetry. The ^{31}P NMR spectra of both complexes show an A_2X pattern. The phosphorus resonances shift downfield upon complexation to the metal. However, the shifts (Δδ) are not of the same magnitude ($\Delta\delta_P$ +15 for **1** and +51.3 for **2**), which suggests that the mode of co-ordination of the cyclotriphosphazane ligand may be different in the two complexes.



R = Et, X = $OC_6H_3Me_2$–2,6

1



R = Et, X = OCH_2CF_3

2

X-Ray Crystal Structures.—The molecular structures of compounds **1** and **2** have been established by single-crystal X-ray diffraction and are shown in Figs. 1 and 2 respectively together with the atom numbering scheme used. Selected structural parameters are listed in Tables 1 and 2, respectively.

Molecular structure of complex **1**. The cyclotriphosphazane ligand in complex **1** is chelated to the metal. The central molybdenum atom is in a highly distorted octahedral geometry. The *cis* angles vary over a wide range (60.2–105.7°) with P(1)–Mo–P(2) being the smallest [60.17(3)°] and the *trans* angles (160.1–167.2°) are much smaller than the ideal value of 180°. The average Mo–P, Mo–C and C–O distances are 2.461(1), 2.013(4) and 1.142(6) Å respectively and are comparable with values found for complexes of acyclic diphosphazanes,[1] cyclodiphosphazanes[3] and cyclotetraphosphazanes.[4] There are two sets of P–N distances in the P_3N_3 ring. The bonds originating from N(1) and P(3) are slightly longer (1.716–1.723 Å) than the middle P–N bonds (1.701–1.706 Å). The average P–N bond length is considerably lengthened (1.713 Å) compared to that observed for *trans*-[EtNP-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

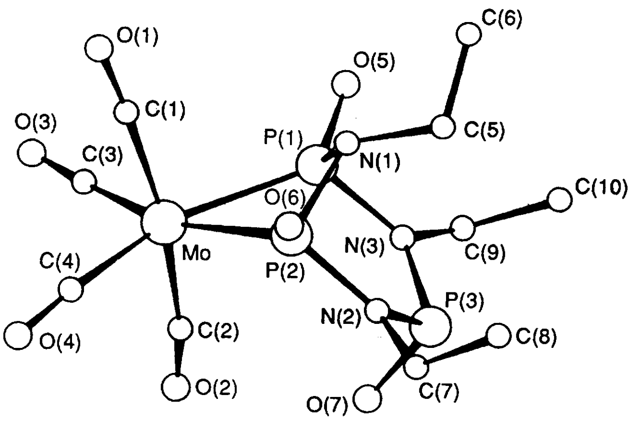


Fig. 1 Molecular core structure of complex **1** (carbon atoms of the aryl group are not shown for clarity)

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

Mo–P(1)	2.4612(8)	Mo–P(2)	2.4607(9)
Mo–C(1)	2.021(5)	Mo–C(2)	2.035(5)
Mo–C(3)	2.016(4)	Mo–C(4)	1.990(5)
P(1) ··· P(2)	2.467(1)	P(1)–N(1)	1.716(3)
P(1)–N(3)	1.706(3)	P(1)–O(5)	1.616(3)
P(2)–N(1)	1.716(2)	P(2)–N(2)	1.701(3)
P(2)–O(6)	1.625(3)	P(3)–N(2)	1.723(3)
P(3)–N(3)	1.717(3)	P(3)–O(7)	1.658(3)
N(1)–C(5)	1.490(4)	N(2)–C(7)	1.499(5)
N(3)–C(9)	1.493(4)	C(1)–O(1)	1.144(5)
C(2)–O(2)	1.143(6)	C(3)–O(3)	1.136(6)
C(4)–O(4)	1.147(6)	O(5)–C(11)	1.416(4)
O(6)–C(21)	1.421(4)	O(7)–C(31)	1.406(4)
C(3)–Mo–C(4)	93.9(2)	C(2)–Mo–C(4)	84.8(2)
C(2)–Mo–C(3)	84.7(2)	C(1)–Mo–C(4)	92.3(2)
C(1)–Mo–C(3)	83.1(2)	C(1)–Mo–C(2)	167.2(2)
P(2)–Mo–C(4)	100.8(1)	P(2)–Mo–C(3)	163.5(1)
P(2)–Mo–C(2)	103.9(1)	P(2)–Mo–C(1)	88.9(1)
P(1)–Mo–C(4)	160.1(1)	P(1)–Mo–C(3)	105.7(1)
P(1)–Mo–C(2)	93.8(1)	P(1)–Mo–C(1)	93.2(1)
P(1)–Mo–P(2)	60.17(3)	Mo–P(1)–O(5)	130.5(1)
Mo–P(1)–N(3)	119.41(9)	Mo–P(1)–N(1)	94.51(9)
Mo–P(1)–P(2)	59.91(3)	N(3)–P(1)–O(5)	99.7(1)
N(1)–P(1)–O(5)	108.6(1)	N(1)–P(1)–N(3)	99.3(1)
P(2)–P(1)–O(5)	151.9(1)	P(2)–P(1)–N(3)	92.85(9)
P(2)–P(1)–N(1)	44.04(9)	Mo–P(2)–P(1)	59.93(3)
P(1)–P(2)–O(6)	148.8(1)	P(1)–P(2)–N(2)	95.3(1)
P(1)–P(2)–N(1)	44.03(9)	Mo–P(2)–O(6)	129.3(1)
Mo–P(2)–N(2)	122.3(1)	Mo–P(2)–N(1)	94.52(9)
N(2)–P(2)–O(6)	99.6(1)	N(1)–P(2)–O(6)	106.1(1)
N(1)–P(2)–N(2)	99.8(1)	N(3)–P(3)–O(7)	99.0(1)
N(2)–P(3)–O(7)	104.5(1)	N(2)–P(3)–N(3)	103.9(1)
P(1)–N(1)–P(2)	91.9(1)	P(2)–N(1)–C(5)	119.0(2)
P(1)–N(1)–C(5)	125.3(2)	P(2)–N(2)–P(3)	121.7(2)
P(3)–N(2)–C(7)	112.4(2)	P(2)–N(2)–C(7)	125.9(3)
P(1)–N(3)–P(3)	124.1(2)	P(3)–N(3)–C(9)	112.1(2)
P(1)–N(3)–C(9)	123.8(2)	Mo–C(1)–O(1)	174.2(4)
Mo–C(2)–O(2)	169.8(4)	Mo–C(3)–O(3)	176.0(5)
Mo–C(4)–O(4)	175.3(4)		

$(OC_6H_4Br-4)]_3$ [1.66(1) Å].[5] The P(3)–O(7) bond is longer [1.658(3) Å] than the other two P–O bonds [1.616(3) and 1.625(3) Å].

The P_3N_3 ring of the cyclotriphosphazane adopts a sofa conformation, the nitrogen atom N(1) deviating by 1.152(2) Å from the mean plane formed by the other five atoms. The exocyclic substituents on both the co-ordinated phosphorus atoms occupy equatorial positions and the substituent on the unco-ordinated phosphorus, the axial position. More significantly, the geometry around the nitrogen [N(1)] flanking the two co-ordinated phosphorus atoms becomes pyramidal ($\Sigma\hat{N}$ = 336.3°) whilst the geometry around both N(2) and N(3) is trigonal planar. The pyramidal geometry observed around N(1) is unusual and, as a consequence, the endocyclic angle at N(1) is considerably reduced (91.9°) compared to the angles at N(2) and N(3).

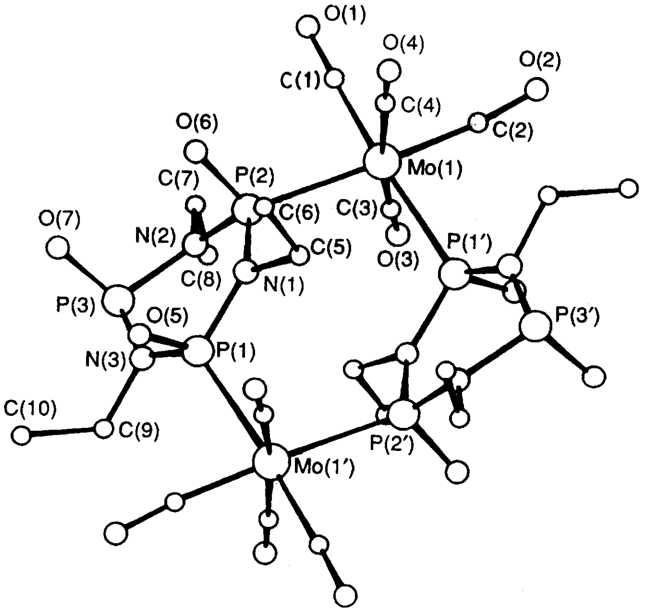


Fig. 2 Molecular core structure of complex **2** (carbon and fluorine atoms of the trifluoroethoxy group are not shown for clarity)

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

Mo(1)–P(1)	2.554(3)	Mo(1)–P(2)	2.545(2)
Mo(1)–C(1)	2.01(1)	Mo(1)–C(2)	1.98(1)
Mo(1)–C(3)	2.06(1)	Mo(1)–C(4)	2.02(1)
C(1)–O(1)	1.14(1)	C(2)–O(2)	1.15(1)
C(3)–O(3)	1.12(1)	C(4)–O(4)	1.13(1)
P(1)–N(1)	1.704(6)	P(1)–N(3)	1.693(8)
P(2)–N(1)	1.699(7)	P(2)–N(2)	1.701(8)
P(3)–N(2)	1.691(8)	P(3)–N(3)	1.686(6)
P(1)–O(5)	1.615(7)	P(2)–O(6)	1.635(7)
P(3)–O(7)	1.651(9)		
P(1)–Mo(1)–P(2)	94.7(1)	C(4)–Mo(1)–P(2)	87.4(3)
C(4)–Mo(1)–P(1)	96.8(3)	C(3)–Mo(1)–P(2)	98.0(3)
C(3)–Mo(1)–P(1)	85.0(3)	C(3)–Mo(1)–C(4)	174.2(4)
C(2)–Mo(1)–P(2)	175.2(3)	C(2)–Mo(1)–P(1)	89.2(3)
C(2)–Mo(1)–C(4)	89.4(4)	C(2)–Mo(1)–C(3)	85.1(5)
C(1)–Mo(1)–P(2)	90.8(3)	C(1)–Mo(1)–P(1)	172.2(3)
C(1)–Mo(1)–C(4)	89.0(5)	C(1)–Mo(1)–C(3)	88.7(5)
C(1)–Mo(1)–C(2)	85.6(4)	Mo(1)–C(1)–O(1)	177(1)
Mo(1)–C(2)–O(2)	179(1)	Mo(1)–C(3)–O(3)	172(1)
Mo(1)–C(4)–O(4)	175.7(9)	Mo(1)–P(1)–O(5)	104.6(3)
Mo(1)–P(1)–N(3)	119.6(3)	Mo(1)–P(1)–N(1)	119.2(2)
N(3)–P(1)–O(5)	104.9(3)	N(1)–P(1)–O(5)	103.4(4)
N(1)–P(1)–N(3)	103.2(4)	Mo(1)–P(2)–O(6)	114.5(2)
Mo(1)–P(2)–N(2)	116.5(3)	N(2)–P(2)–O(6)	105.6(4)
N(1)–P(2)–N(2)	103.9(5)	N(2)–P(3)–N(3)	102.6(5)
N(2)–P(3)–O(7)	101.1(4)	P(1)–N(1)–C(5)	111.6(5)
P(1)–N(1)–P(2)	135.3(4)	P(2)–N(2)–C(7)	117.6(7)
P(2)–N(2)–P(3)	129.7(5)	P(3)–N(2)–C(7)	109.5(6)
P(1)–N(3)–C(9)	114.8(6)	P(3)–N(3)–P(1)	134.1(4)

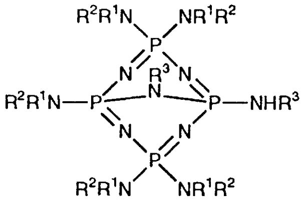
Molecular structure of complex **2**. In contrast to the chelating mode of binding of the *trans*-cyclotriphosphazane in **1**, the *cis*-cyclotriphosphazane in **2** bridges two $Mo(CO)_4$ moieties. The co-ordination geometry around the metal deviates only slightly from the ideal octahedral geometry. The average Mo–P distance of 2.550(2) Å is the longest observed for a Mo^0–P(phosphazane) bond, is 0.09 Å longer than the value observed for **1** and 0.07 Å longer compared to the dinuclear complex $[Mo_2(CO)_8\{[PhNP(OC_6H_4Me\text{-}4)]_2\}_2]$ [2.484(2) Å][3a,6] which has a similar structure to that of **2**. The average Mo–C and C–O distances are 2.02(1) and 1.14(1) Å respectively.

As in the case of the chelate complex **1**, there is a pronounced change in the ring conformation in the dinuclear complex **2**. The P_3N_3 ring adopts a sofa conformation, the pendant phosphorus atom P(3) deviating from the plane formed by the other five atoms. However, the extent of the deviation [0.411(5) Å] is smaller than that found for complex **1**. All three 1,1,1-trifluoroethoxy groups occupy axial positions on the P_3N_3 ring as observed for the chair triaxial form of *cis*-$[EtNP(OC_6H_4Br\text{-}4)]_3$.[5] The geometry around all the ring nitrogen atoms is trigonal planar ($\Sigma\hat{N} = 358.9°$) in contrast to the pyramidal geometry around one of the ring nitrogen atoms in **1**. The mean P–N bond length of 1.696 Å is close to the average P–N distance observed for *cis*-$[EtNP(OC_6H_4Br\text{-}4)]_3$ [1.69(1) Å].[5]

Origin of the Pyramidal Geometry around Nitrogen Attached to Phosphorus.—A three co-ordinated nitrogen atom attached to a λ^3- or λ^5-phosphorus atom invariably assumes a planar geometry.[7] The observation of a pyramidal geometry at N(1) and the equatorial disposition of the $OC_6H_3Me_2$-2,6 substituent at P(1) and P(2) in complex **1** is in contrast to the boat triaxial conformation of *trans*-$[EtNP(OC_6H_4Br\text{-}4)]_3$ in which all three nitrogen atoms exhibit trigonal-planar geometry.[5] Our recent results[5] show that the *cis*-chair triaxial and *trans*-boat triaxial forms are favoured for the six-membered λ^3-P_3N_3 ring because of minimal vicinal lone-pair repulsions and stabilising negative hyperconjugative interactions between the nitrogen lone pairs and adjacent P–O σ^* orbitals.[8] Assuming that L^1 has a *trans*-boat triaxial conformation as found in the 4-bromophenoxy derivative, upon complexation to a $Mo(CO)_4$ moiety an inversion occurs around the two phosphorus atoms co-ordinated to the metal accompanied by a flipping of the P_3N_3 ring to the sofa form. In the resulting arrangement the lone pair on N(1) cannot orient itself parallel to the P–O σ^* orbitals (an essential geometric constraint for negative hyperconjugation to be operative); consequently N(1) assumes a pyramidal geometry. This argument is also consistent with the short P–O bonds at P(1) and P(2) compared to the longer one at P(3).

To our knowledge apart from complex **1**, only two other types of P–N compounds display a pyramidal geometry around a nitrogen atom. In the case of bicyclic tetraphosphazenes of the type **I**, a pyramidal geometry is observed around the bridging nitrogen atom.[9] In the case of aziridinyl phosphorus derivatives such as **II**, the aziridinyl nitrogen atoms[10–12] exhibit pyramidal geometry. The observed pyramidal geometry around the bridging nitrogen of **I** can be explained on the basis of the inability of this nitrogen lone pair to orient itself parallel to a formal P–N single bond.[13] Apparently, the lone pair of a nitrogen atom attached to a phosphorus centre prefers to be parallel to a P–X σ^* (X = N or O) orbital to maximise negative hyperconjugation, failing which it assumes a pyramidal geometry.

The observed pyramidal geometry of nitrogen atoms in aziridinyl phosphorus derivatives is a special case that is linked to the larger barrier for pyramidal inversion at an aziridinyl nitrogen atom.[14] If an aziridinyl nitrogen atom attached to phosphorus were to adopt a planar geometry, the exocyclic angles would have values close to 150° and such an arrangement would be energetically unfavourable.[14] It would appear that for aziridinyl phosphorus compounds, the above destabilisation cannot be overcome by stabilising negative hyperconjugative interactions that would result when the nitrogen assumes a planar geometry. The absence of a negative hyperconjugative interaction is manifested in the larger P–N distances in $P(NC_2H_4)_3$ (1.75 Å)[12] and aziridinyl cyclophosphazenes [*e.g.* $N_3P_3(NC_2H_4)_6$, 1.676 Å][10b] compared to the corresponding values in $P(NMe_2)_3$ (1.70 Å)[12] and aminocyclophosphazenes [*e.g.* $N_3P_3(NMe_2)_6$, 1.652 Å].[10b]



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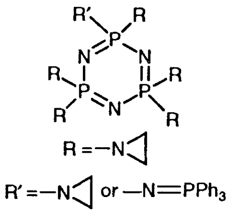

II

Conclusion

Limited studies reported in this paper reveal the different co-ordination behaviour of λ^3-cyclotriphosphazanes depending on the geometrical disposition of the substituents attached to the phosphorus atoms. The *trans* derivative behaves as a chelating bidentate ligand whereas the *cis* derivative bridges two metal centres. Further studies are required to explore the reactivity of the geometrical isomers of λ^3-cyclotriphosphazanes towards a variety of organometallic derivatives. The complexes reported here bear unco-ordinated λ^3-phosphorus centres and would be useful building blocks for both homo- and hetero-polynuclear complexes. The structural data for complexes **1** and **2** provide further insight into the nature of the P–N bond which is one of the most intriguing in chemistry and many of its more subtle aspects still elude a detailed and satisfactory description.[15]

Experimental

General.—All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk-line techniques. Solvents were distilled under nitrogen and degassed prior to use. The IR spectra were recorded on a BioRad FTS-7 spectrometer and NMR spectra on a Bruker ACF-200 or Bruker AMX-400 (^1H NMR, standard $SiMe_4$; ^{31}P NMR, H_3PO_4 external reference) spectrometer. All chemical shifts are expressed on the δ scale with upfield shifts negative. Elemental analyses were performed on an Heraeus CHN-O-Rapid elemental analyser.

The cyclotriphosphazanes *trans*-$[EtNP(OC_6H_3Me_2\text{-}2,6)]_3$ (L^1) and *cis*-$[EtNP(OCH_2CF_3)]_3$ (L^2) were prepared by the treatment of the chlorocyclotriphosphazane[16] $(EtNPCl)_3$ with 2,6-dimethylphenol in the presence of 1,4-diazabicyclo[2.2.2]-octane or with sodium trifluoroethoxide, respectively.[5] The precursor complex $[Mo(CO)_4(nbd)]$ was prepared according to the literature procedure.[17]

Synthesis of Complexes.—$[Mo(CO)_4(L^1)]$ **1**. The compounds $[Mo(CO)_4(nbd)]$ (50 mg, 0.17 mmol), L^1 (100 mg, 0.17 mmol) and hexane (15 cm^3) were charged into a 50 cm^3 double-necked round-bottom flask. The mixture was heated gently to 50 °C, stirred for 5 h and then cooled to 25 °C. The reaction mixture was passed through a silica gel column (1 × 10 cm) using CH_2Cl_2–light petroleum (b.p. 60–80 °C) (1 : 1) as the eluent to remove any decomposed material. Evaporation of the solvent *in vacuo* gave an oily residue which was redissolved in hexane (5 cm^3) and recrystallised at 0 °C to yield **1** (60%), m.p. 155–158 °C (Found: C, 51.3; H, 5.3; N, 5.5. $C_{34}H_{42}MoN_3O_7P_3$ requires C, 51.5; H, 5.3; N, 5.3%). IR (Nujol): ν_{CO} 2026, 1947, 1917 and 1893 cm^{-1}; ^{31}P NMR (CH_2Cl_2): A_2X pattern, δ_A 132.2 (d), δ_X 113.2 (t, J 39.5 Hz).

$[\{Mo(CO)_4(\mu\text{-}L^2)\}_2]$ **2**. Complex **2** was prepared similarly from $[Mo(CO)_4(nbd)]$ (115 mg, 0.4 mmol) and L^2 (200 mg, 0.4 mmol) in hexane (15 cm^3) and recrystallised from CH_2Cl_2–hexane (1 : 10) at 0 °C. Yield 70% (Found: C, 26.1; H, 2.7; N, 5.9. $C_{32}H_{42}F_{18}Mo_2N_6O_{14}P_6$ requires C, 26.4; H, 2.9; N, 5.8%). IR (Nujol): ν_{CO} 2080, 2035, 1947 and 1935 cm^{-1}; ^{31}P NMR

(CH_2Cl_2): A_2X pattern, δ_A 144.9 (d), δ_X 123.8 (t); coupling constants not resolved at 25 °C.

X-Ray Crystal Structure Analysis.—Colourless crystals of **1** and **2** suitable for X-ray crystallographic studies were obtained from CH_2Cl_2–light petroleum (1 : 1). In each case, a suitable crystal was mounted on a glass fibre and coated with paraffin oil to prevent any decomposition. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromatised Mo-Kα radiation and a ω–2θ scan mode. The unit-cell parameters were derived and refined from 25 reflections in the range $26 < 2\theta < 34°$ for **1** and $26 < 2\theta < 40°$ for **2**. The crystal data and details of data collection and refinement procedure are given in Table 3. The data were corrected for Lorentz and polarisation effects. An absorption correction was not made as the absorption coefficients were very small for both compounds.

The structures were solved by direct methods using SHELXS 86.[18] The hydrogen atoms were located from successive difference maps and included in subsequent calculations. Least-squares refinement was carried out minimising the function $w(|F_o| - |F_c|)^2$ using SHELX 76.[19] For complex **1**, all non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically. Anisotropic least-squares refinement on 4482 observed reflections with $F_o > 5.0\sigma(F_o)$ and 597 variables converged at $R = 0.035$ and $R' = 0.038$ with a goodness of fit of 1.253. For complex **2**, two of the fluorine atoms of the OCH_2CF_3 group attached to the unco-ordinated

Table 3 Crystal data for complexes **1** and **2**

Complex	1	2
Formula	$C_{34}H_{42}MoN_3O_7P_3$	$C_{32}H_{42}F_{18}Mo_2N_6O_{14}P_6$
M	0.15 × 0.25 × 0.35	1454.4
Crystal size/mm	Monoclinic	0.15 × 0.15 × 0.25
Crystal system	$P2_1/n$	Monoclinic
Space group	793.6	$P2_1/n$
a/Å	11.2253(7)	13.995(12)
b/Å	24.987(3)	13.349(4)
c/Å	13.524(1)	15.741(3)
β/°	93.879(7)	106.33(4)
U/Å^3	3784.6(6)	2822(3)
Z	4	2
D_c/g cm^{-3}	1.393	1.712
F(000)	1640	1448
μ(Mo-Kα)/cm^{-1}	4.7	7.2
λ(Mo-Kα)/Å	0.7107	0.7107
Octants collected	$+h, +k, \pm l$	$+h, +k, \pm l$
2θ Range/°	50	50
Decay (%)	< 2	< 2
Unique reflections	6637	4951
Observed reflections	4482[$F_o > 5.0\sigma(F_o)$]	3170[$F_o > 5.0\sigma(F_o)$]
No. of parameters	597	378
R^a	0.035	0.069
R'^b	0.038	0.078
Goodness of fit^c	1.25	1.97
Largest shift/e.s.d.	0.015	0.01
Largest residual peak/e Å^{-3}	0.42	1.5

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$. [c] Goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs}-N_{param})]^{\frac{1}{2}}$.

Table 4 Fractional atomic coordinates for complex **1**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	0.102 15(3)	0.156 84(1)	0.020 28(2)
P(1)	0.263 73(7)	0.119 47(3)	0.131 57(6)
P(2)	0.130 61(8)	0.188 96(3)	0.192 26(6)
P(3)	0.119 89(8)	0.085 31(3)	0.301 81(7)
N(1)	0.281 2(2)	0.176 3(1)	0.202 3(2)
N(2)	0.087 6(3)	0.152 5(1)	0.289 9(2)
N(3)	0.229 8(2)	0.075 2(1)	0.221 5(2)
C(1)	0.203 8(3)	0.218 4(2)	−0.022 1(3)
C(2)	−0.004 0(4)	0.091 3(2)	0.030 1(3)
C(3)	0.130 4(4)	0.128 7(2)	−0.115 9(3)
C(4)	−0.048 4(4)	0.194 3(2)	−0.024 6(3)
O(1)	0.260 9(3)	0.251 3(1)	−0.053 8(2)
O(2)	−0.064 7(3)	0.054 7(1)	0.020 5(3)
O(3)	0.150 1(4)	0.115 5(2)	−0.193 5(3)
O(4)	−0.139 0(3)	0.213 9(1)	−0.045 7(3)
O(5)	0.394 3(2)	0.097 5(1)	0.108 2(2)
O(6)	0.114 2(2)	0.248 9(1)	0.235 9(2)
O(7)	0.008 0(2)	0.054 9(1)	0.238 2(2)
C(5)	0.346 7(3)	0.179 5(2)	0.301 7(2)
C(6)	0.477 8(4)	0.188 5(2)	0.297 8(3)
C(7)	0.020 0(4)	0.173 3(2)	0.373 7(3)
C(8)	0.097 1(6)	0.182 1(3)	0.466 5(4)
C(9)	0.292 9(3)	0.023 2(1)	0.239 9(3)
C(10)	0.373 1(4)	0.023 5(2)	0.332 2(4)
C(11)	0.430 4(3)	0.096 6(1)	0.009 9(2)
C(12)	0.391 7(3)	0.055 0(2)	−0.052 3(3)
C(13)	0.435 7(4)	0.054 4(2)	−0.148 0(3)
C(14)	0.513 7(5)	0.092 9(2)	−0.175 2(3)
C(15)	0.549 5(4)	0.133 6(2)	−0.111 7(3)
C(16)	0.507 0(3)	0.136 4(2)	−0.018 0(3)
C(17)	0.308 6(4)	0.012 3(2)	−0.024 6(3)
C(18)	0.543 2(4)	0.182 0(2)	0.049 6(3)
C(21)	0.086 7(3)	0.292 3(1)	0.170 4(2)
C(22)	−0.031 3(4)	0.303 7(1)	0.144 9(3)
C(23)	−0.056 0(4)	0.347 5(2)	0.082 2(3)
C(24)	0.037 1(5)	0.378 1(2)	0.049 8(3)
C(25)	0.153 2(4)	0.366 7(2)	0.080 4(3)
C(26)	0.181 0(4)	0.323 4(1)	0.142 0(3)
C(27)	−0.132 2(4)	0.271 6(2)	0.184 6(4)
C(28)	0.307 6(4)	0.312 2(2)	0.178 4(4)
C(31)	−0.089 7(3)	0.039 7(1)	0.291 6(3)
C(32)	−0.192 3(3)	0.070 1(2)	0.280 6(3)
C(33)	−0.289 3(4)	0.054 8(2)	0.333 8(3)
C(34)	−0.283 3(4)	0.010 2(2)	0.392 4(3)
C(35)	−0.182 6(4)	−0.020 5(2)	0.399 3(3)
C(36)	−0.081 9(3)	−0.006 2(2)	0.348 8(3)
C(37)	−0.204 3(4)	0.118 4(2)	0.213 3(4)
C(38)	0.026 1(4)	−0.040 8(2)	0.356 0(4)

Table 5 Fractional atomic coordinates for complex **2**

Atom	X/a	Y/b	Z/c
Mo(1)	0.293 40(5)	0.113 38(6)	0.388 14(5)
C(1)	0.175 4(8)	0.179 5(9)	0.413 2(7)
C(2)	0.230 8(7)	0.151 1(9)	0.263 4(7)
C(3)	0.361 1(7)	0.251 3(9)	0.398 3(7)
C(4)	0.216 7(7)	−0.017 1(8)	0.367 0(6)
O(1)	0.108 3(5)	0.220 4(6)	0.424 6(5)
O(2)	0.195 1(7)	0.172 8(8)	0.190 8(5)
O(3)	0.392 0(7)	0.328 1(6)	0.394 5(7)
O(4)	0.169 1(7)	−0.086 7(8)	0.351 7(7)
P(1)	0.445 5(2)	0.050 9(2)	0.344 4(1)
N(1)	0.554 6(5)	0.032 4(5)	0.424 7(4)
P(2)	0.359 5(2)	0.060 9(2)	0.549 5(1)
N(2)	0.409 3(6)	0.153 1(6)	0.623 2(5)
P(3)	0.484 3(2)	0.144 4(2)	0.727 9(2)
N(3)	0.435 8(5)	−0.052 5(6)	0.280 2(4)
C(5)	0.578 4(6)	0.119 3(6)	0.489 1(5)
C(6)	0.641 0(8)	0.202 0(8)	0.467 0(7)
C(7)	0.357 1(10)	0.255 1(8)	0.610 2(7)
C(8)	0.428 0(13)	0.339 1(11)	0.615 4(11)
C(9)	0.336 3(7)	−0.064 8(8)	0.211 2(6)
C(10)	0.332 4(9)	−0.020 3(12)	0.124 5(7)
O(5)	0.471 7(5)	0.140 6(5)	0.285 8(4)
C(11)	0.547 0(8)	0.137 5(7)	0.243 2(7)
C(12)	0.543 8(10)	0.229 2(11)	0.191 7(9)
F(1)	0.553 0(8)	0.311 7(6)	0.240 7(6)
F(2)	0.617 3(7)	0.229 9(7)	0.155 4(7)
F(3)	0.459 7(8)	0.241 5(7)	0.127 9(5)
O(6)	0.278 0(4)	0.004 3(5)	0.589 5(4)
C(13)	0.183 0(8)	0.039 2(9)	0.587 3(9)
C(14)	0.128 0(9)	−0.035 6(11)	0.616 3(10)
F(4)	0.039 5(5)	−0.008 5(7)	0.618 6(6)
F(5)	0.109 8(8)	−0.113 2(7)	0.560 5(9)
F(6)	0.171 3(8)	−0.084 3(10)	0.688 7(7)
O(7)	0.411 1(6)	0.084 7(5)	0.777 0(5)
C(15)	0.380 4(13)	0.144 9(13)	0.839 4(11)
C(16)	0.340 1(16)	0.094 2(15)	0.891 9(13)
F(8)	0.309 2(7)	0.132 8(6)	0.955 0(6)
F(9)*	0.297 4(14)	−0.000 6(13)	0.874 2(11)
F(10)*	0.442 5(17)	0.075 9(16)	0.954 7(14)
F(11)*	0.366 9(20)	−0.003 5(18)	0.913 3(15)
F(12)*	0.248 2(23)	0.070 4(24)	0.840 8(19)

* Disordered atom; site occupancy factor 0.5.

phosphorus atom P(3) were disordered. The disordered atoms and the hydrogen atoms were refined isotropically and all other atoms anisotropically. Least-squares refinement on 3170 observed reflections with $F_o > 5.0\sigma(F_o)$ and 378 variables converged at $R = 0.069$ and $R' = 0.078$ with a goodness of fit of 1.97. The final difference maps were free from any appreciable residual electron density. Final fractional atomic coordinates for complexes **1** and **2** are listed in Tables 4 and 5 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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