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Linking metal centres with 1,4-bis(diphenylphosphino)-2,5-difluorobenzene (dpfb): syntheses and molecular structures of [{$Mo(CO)_4(\mu$-dpfb)}$_2$] and [{$Mo(CO)_4$}$_2(\mu$-dpfb)(μ-dppa)] (dppa = $Ph_2PC{\equiv}CPPh_2$)

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The rigid diphosphine 1,4-bis(diphenylphosphino)-2,5-difluorobenzene (dpfb) has been prepared *via* addition of 2 equivalents of lithium diphenylphosphide to 1,2,4,5-tetrafluorobenzene and characterised by multinuclear NMR spectroscopy. Reaction with *cis*-[$Mo(CO)_4(pip)_2$] (pip = piperidine) afforded doubly bridged [{$Mo(CO)_4(\mu$-dpfb)}$_2$] **1**, while with equimolar amounts of dpfb and bis(diphenylphosphino)acetylene (dppa) the mixed-ligand complex [{$Mo(CO)_4$}$_2(\mu$-dpfb)(μ-dppa)] **2** was isolated. Both **1** and **2** have been characterised crystallographically. The dfpb ligand always adopts a *syn*-type configuration. Complex **1** shows a weak π-stacking interaction between the bridging aryl rings, while in **2** the dppa ligand adopts an *anti* conformation. Variable-temperature multinuclear NMR experiments revealed that **1** undergoes two fluxional processes in solution; twisting of the central core of the molecule and a low-energy process involving the flipping up and down of molybdenum tetracarbonyl units which interconverts the *anti* and *syn* conformations of the diphosphines.

We have recently been interested in the concept of linking metal centres together with rigid phosphorus-containing ligands[1,2] and have successfully prepared and crystallographically characterised dimolybdenum complexes [{$Mo(CO)_4(\mu$-dppa)}$_2$] and [{$Mo(CO)_3$}$_2(\mu$-dppa)$_3$], in which the rigid diphosphine, bis(diphenylphosphino)acetylene (dppa), bridges the metal centres.[3] In order to extend this work, we wondered whether zerovalent molybdenum centres could be spanned by other rigid diphosphines such as 1,4-bis(diphenylphosphino)benzene (dppb). While this compound was prepared some time ago[4] its co-ordination chemistry remains relatively unexplored. Puddephatt and co-workers[5] have utilised dppb in order to link gold centres giving complexes of the type [$(AuX)_2(\mu$-dppb)] (X = Cl or $C{\equiv}CPh$), while Wright *et al.*[6] have prepared polymeric complexes [{Rh(CO)Cl(μ-dppb)[η^6-$Cr(CO)_2L$]}$_n$] (L = CO or PBu^n_3) in which dppb links rhodium centres *via* phosphorus ligation while being bound to chromium through the central aryl ring in an η^6-type manner. Closely related to the latter, and particularly relevant in terms of this publication, Elschenbroich *et al.*[7] have prepared complexes such as [{$Ni(CO)_2(\mu$-dppb)}$_2$Cr], whereby the dppb is bound to nickel through phosphorus and chromium through the central aryl rings. We were, then, interested to see whether two dppb ligands could span molybdenum tetracarbonyl fragments in the *absence* of the central metal atom. If such a complex could be prepared, then in light of the above results it might be capable of later encapsulating metal atoms. For reasons outlined below, rather than employing dppb as the linking unit, we have prepared and utilised the new rigid diphosphine, 1,4-bis(diphenylphosphino)-2,5-difluorobenzene (dpfb), and describe herein the syntheses and molecular structures of two complexes in which it bridges molybdenum tetracarbonyl fragments.

Results and Discussion

1,4-Bis(diphenylphosphino)-2,5-difluorobenzene (dpfb)

Our initial attempts centred on the preparation of dppb, however, in our hands the literature preparation[4] was slow and gave mixtures of the diphosphine and its oxides which proved difficult to separate. We have recently followed a related preparation (slightly modified) of 1,2,4,5-tetrakis(diphenylphosphino)benzene by McFarlane and McFarlane[8] starting from 1,2,4,5-tetrafluorobenzene. In the light of this, and coupled with the known enhancement of the rate of nucleophilic aromatic substitution reactions upon incorporation of electronegative substituents on the aryl ring,[9] we attempted the reaction of 1,2,4,5-tetrafluorobenzene with 2 equivalents of lithium diphenylphosphide in tetrahydrofuran (thf). Slow addition of the latter to the fluorinated organic results in a rapid reaction from which the new diphosphine 1,4-bis(diphenylphosphino)-2,5-difluorobenzene (dpfb) was isolated in 52% yield as a white crystalline solid, soluble in common organic solvents. Selective formation of the 1,4-disubstituted compound is expected, and results from both electronic and steric factors. After the initial substitution reaction, *ortho* and *para* positions are activated towards further substitution, however, the former is disfavoured due to greater steric congestion. The new diphosphine was characterised on the basis of analytical and spectroscopic data, with multinuclear NMR spectroscopy proving particularly useful as might be expected for an $A_2M_2X_2$ system. Fig. 1 shows the ^{31}P, ^{19}F and ^1H (in part) NMR spectra together with relevant coupling constants as determined from simulations. Noteworthy is the relatively large four-bond phosphorus–phosphorus coupling constant of 17.7 Hz, which contrasts with the much smaller values assumed for related diphosphines.[8]

[{$Mo(CO)_4(\mu$-dpfb)}$_2$]

Room-temperature addition of dpfb to a dichloromethane solution of *cis*-[$Mo(CO)_4(pip)_2$] (pip = piperidine) resulted in the formation of [{$Mo(CO)_4(\mu$-dpfb)}$_2$] **1** in 87% yield, isolated as an air-stable, pale yellow solid. Characterisation as a *cis*-substituted molybdenum tetracarbonyl-containing complex was made on the basis of IR spectroscopy, four carbonyl absorptions being observed. Further characterisation revealed the equivalence of the phosphorus environments (see below) and the stoichiometric formula, so to fully elucidate the molecular structure a crystallographic study was carried out. Suitable single crystals were grown upon slow diffusion of methanol into a dichloromethane solution and the results are summarised in Table 1 and Figs. 2 and 3.

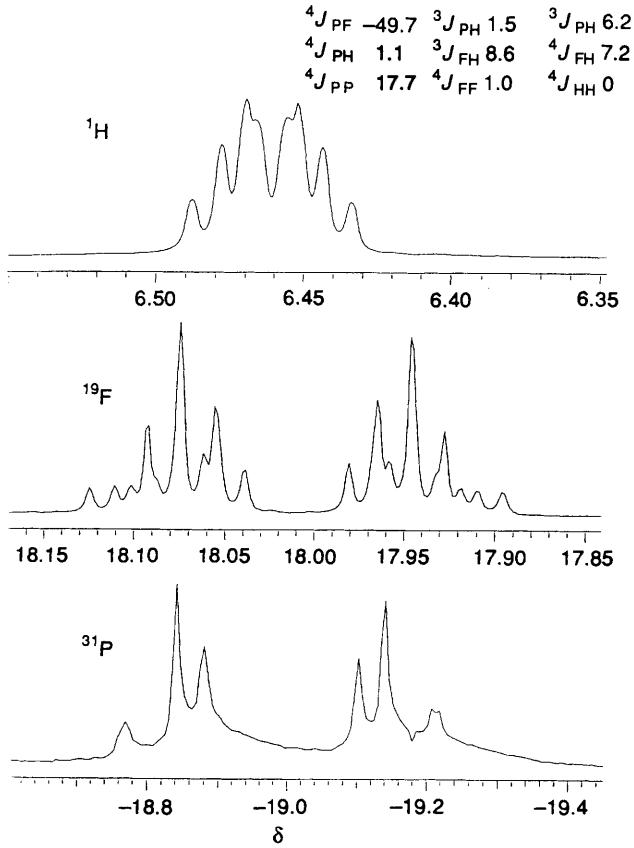


Fig. 1 The NMR spectra for 1,4-bis(diphenylphosphino)-2,5-difluorobenzene. Coupling constants (J) in Hz

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**·CH_2Cl_2

Mo(1)–P(1)	2.536(2)	Mo(1)–P(2)	2.586(2)
Mo(2)–P(3)	2.550(3)	Mo(2)–P(4)	2.596(2)
Mo(1)–C(1)	2.044(8)	Mo(1)–C(2)	2.031(8)
Mo(1)–C(3)	1.969(8)	Mo(1)–C(4)	1.980(7)
Mo(2)–C(5)	2.020(8)	Mo(2)–C(6)	2.011(9)
Mo(2)–C(7)	1.968(9)	Mo(2)–C(8)	1.975(8)
F(1)–C(91)	1.373(7)	F(2)–C(101)	1.351(8)
F(3)–C(94)	1.369(7)	F(4)–C(104)	1.362(7)
P(1)–Mo(1)–P(2)	103.6(1)	P(3)–Mo(2)–P(4)	102.8(1)
P(1)–Mo(1)–C(1)	88.3(2)	P(2)–Mo(1)–C(2)	91.0(2)
P(1)–Mo(1)–C(3)	85.7(2)	P(2)–Mo(1)–C(4)	86.9(2)
P(1)–Mo(1)–C(4)	169.2(2)	P(2)–Mo(1)–C(3)	170.5(2)
C(1)–Mo(1)–C(2)	179.0(3)	C(3)–Mo(1)–C(4)	84.0(3)
P(3)–Mo(2)–C(5)	94.8(2)	P(4)–Mo(2)–C(6)	93.6(2)
P(3)–Mo(2)–C(7)	168.4(3)	P(4)–Mo(2)–C(8)	170.9(2)
P(3)–Mo(2)–C(8)	85.7(2)	P(4)–Mo(2)–C(7)	87.8(3)
C(5)–Mo(2)–C(6)	174.8(3)	C(7)–Mo(2)–C(8)	84.0(3)
Mo(1)–P(1)–C(90)	120.3(2)	Mo(1)–P(2)–C(100)	122.5(2)
Mo(2)–P(3)–C(93)	119.6(2)	Mo(2)–P(4)–C(103)	122.2(2)

As can be clearly seen (Fig. 2), the molecule consists of molybdenum tetracarbonyl centres spanned by a pair of diphosphines to give a large ring system. The molydenum–phosphorus bond lengths are unexceptional ranging between 2.536 and 2.596 Å, and the phosphorus centres subtend a 'bite angle' at the molybdenum centres of 103.6(1) and 102.8(1)° respectively. As a result of the latter, the co-ordination geometry about molybdenum is somewhat distorted from an ideal octahedron. Both diphosphines adopt a *syn*-type arrangement, that is the metal centres are substituted on the same side, and the molybdenum centres are appreciably staggered with respect to one another (Fig. 3). The bond angles at phosphorus to the central aryl ring are significantly distorted from tetrahedral, ranging from 119.6(2) to 122.5(2)°, being indicative of significant steric strain. Indeed, the phosphorus centres are displaced from the plane of the aryl ring by up to 0.164 Å. The Mo_2P_4 framework is fairly flat and the two central aryl rings lie above one another in a staggered arrangement, the fluorine substituents being related by an approximate S_4 axis. Construction of a simple molecular model suggests that the central core of the molecule is easily distorted and thus the conformation adopted in the solid state may result from the minimisation of unfavourable F ••• F and maximisation of favourable H ••• F interactions. Perhaps the most interesting feature of the molecule is the 'stacking' of the central aryl rings, the intercentroid distance of 3.6 Å being close enough to account for a weak π-stacking interaction. In relation to the work of Elschenbroich *et al.*[7] noted in the Introduction, the structure of **1** suggests that incorporation of a metal atom between the two central aryl rings would not lead to a significant perturbation of the system. For example, the distance between ring centroids in bis(benzene)chromium is approximately 3.2 Å.[10] While in the latter the benzene rings are believed to adopt an eclipsed conformation, rotational barriers are low for metal-bound arenes even in the solid state.[11]

Elschenbroich *et al.*[7] have previously noted that the related complex [{Ni(CO)(μ-dppb)}$_2$Cr] is fluxional in solution, an observation they attribute to the interchange between *syn* and *anti* arrangements of the diphosphines [Scheme 1 (*a*)]. Variable-temperature ^{1}H, ^{19}F and ^{31}P NMR studies were carried out on **1**, the first being most informative. At room temperature two broad resonances are observed at δ 7.42 and 6.56, being assigned to external and central aromatic protons respectively. Upon cooling to −70 °C, however, considerable changes occur, resulting in a series of sharp multiplets between δ 7.6 and 7.1, and while the linewidth of the high-field signal associated with the central rings also narrows no fine structure develops. Further cooling to −100 °C led to a dramatic broadening of aromatic resonances, such that those associated with the outer phenyl rings became very broad, while the signal assigned to the central rings remained much the same. Similar changes were noted in the ^{19}F and ^{31}P NMR spectra, both showing broad singlets at room temperature which narrowed upon cooling to −70 °C. Again significant broadening of both occurred between −70 and −100 °C, indeed while at −70 °C both spectra showed some fine structure at −100 °C the linewidths of the signals increased dramatically. Thus for the ^{31}P NMR spectrum the linewidth increased from 72 to 215 Hz over this temperature range, while the increase from 106 to *ca.* 1000 Hz in the ^{19}F spectrum over the same range is even more dramatic. Bearing in mind that the width of the ^{19}F signal for the non-fluxional free dpfb is 87 Hz, we associate these broadenings with the development of more than one isomer in solution. This will clearly be the case if the up–down flipping of metal centres is frozen out, since both *syn* and *anti* conformations of the diphosphines are possible, and thus we suggest that the low-energy fluxional process is similar to that postulated by Elschenbroich *et al.*[7] and shown in Scheme 1(*a*). The precise nature of the high-energy process remains less clear, however it must be associated with the central core of the molecule. Construction of a simple molecular model suggests that a twisting of the two central aryl rings from the mutually staggered array seen in the solid state to an eclipsed arrangement can occur with little strain developing in other parts of the ring. Thus we propose such a process [Scheme 1(*b*)] to account for the changes in the NMR spectra between room temperature and −70 °C.

In an attempt to determine the degree of interaction between metal centres in complex **1** an electrochemical study was performed. In dichloromethane at room temperature a single irreversible oxidation wave was seen at +1.01 V. This behaviour is similar to that found for *cis*-[Mo(CO)$_4$(PPh$_3$)$_2$], which also exhibits an irreversible oxidation at +1.15 V

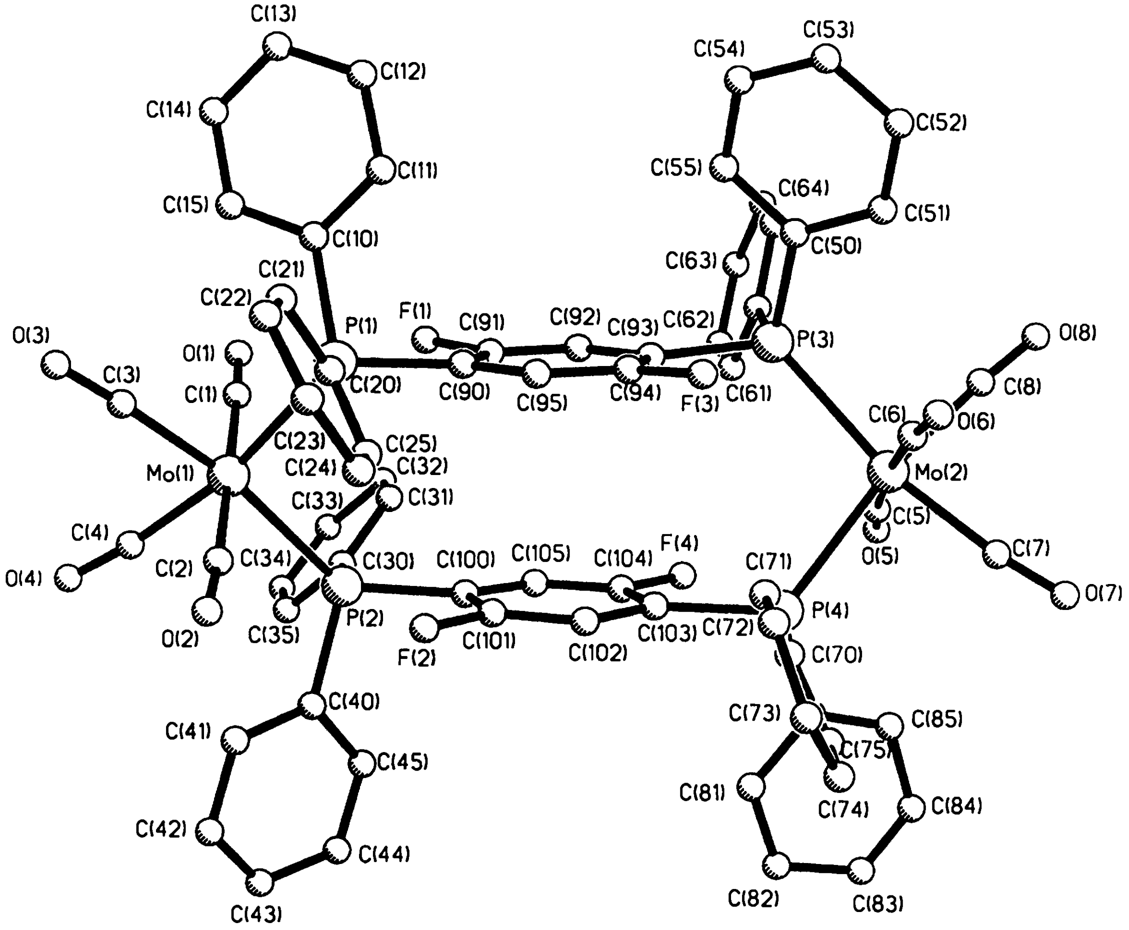


Fig. 2 Molecular structure of complex **1**

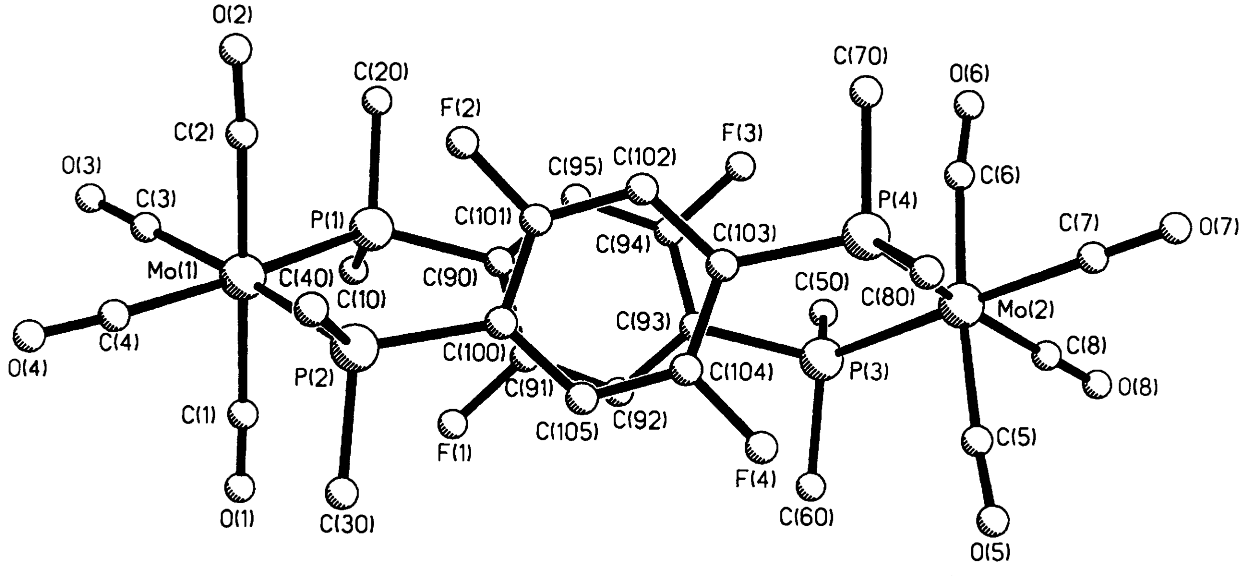


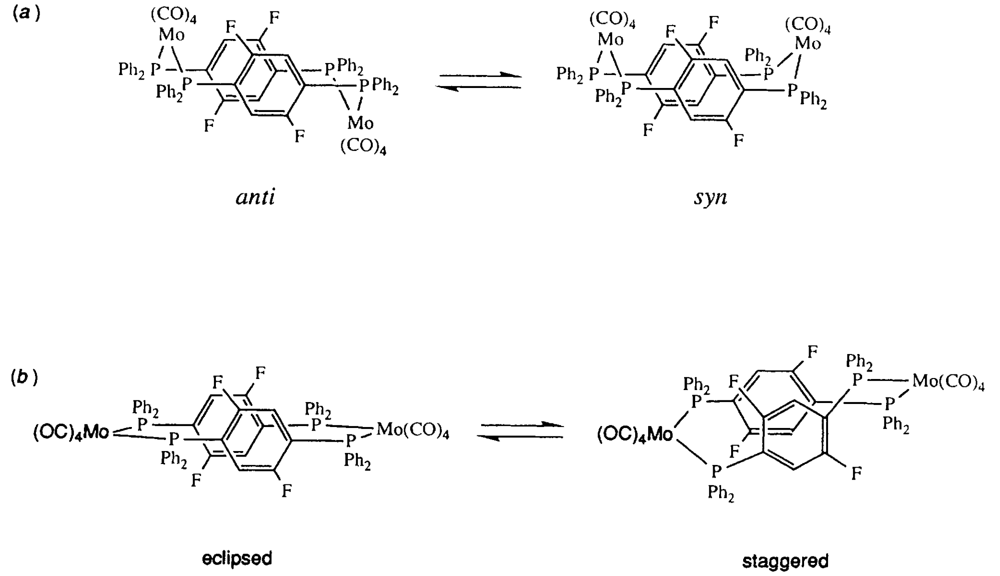
Fig. 3 Side-on view of the structure of complex **1** (phenyl rings omitted for clarity)

at room temperature, becoming partially reversible at −78 °C.[12]

[{Mo(CO)$_4$}$_2$(μ-dpfb)(μ-dppa)]

Room-temperature addition of equimolar amounts of dpfp and dppa to 2 equivalents of *cis*-[Mo(CO)$_4$(pip)$_2$] in dichloromethane resulted in the formation of yellow [{Mo(CO)$_4$}$_2$(μ-dpfb)(μ-dppa)] **2** in 83% yield. The IR spectrum again indicated a *cis*-disubstituted molybdenum tetracarbonyl fragment, while in the ^{31}P NMR spectrum two complex multiplets centred at approximately δ 32 and 16 are assigned to the dpfb and dppa ligands respectively. In order to elucidate the molecular structure and solid-state configuration a crystallographic study was performed the results of which are summarised in Table 2 and Figs. 4 and 5.

As shown in Fig. 4, the two molybdenum tetracarbonyl units are now spanned by both dpfb and dppa moieties in a somewhat similar fashion to that seen in complex **1**. This ligand set, however, subtends a significantly reduced 'bite angle' at molybdenum [P(1)–Mo(1)–P(3) 99.0(1), P(2)–Mo(2)–P(4) 99.6(2)°], while there is also less steric strain at phosphorus as



Scheme 1 Proposed fluxionality in dppb- and dpfb-containing complexes

Table 2 Selected bond lengths (Å) and angles (°) for complex $2{\cdot}CH_2Cl_2$

Mo(1)–P(1)	2.562(4)	Mo(1)–P(3)	2.561(3)
Mo(2)–P(2)	2.554(5)	Mo(2)–P(4)	2.558(5)
Mo(1)–C(1)	1.943(17)	Mo(1)–C(2)	1.938(22)
Mo(1)–C(3)	1.968(22)	Mo(1)–C(4)	2.007(20)
Mo(2)–C(5)	1.908(20)	Mo(2)–C(6)	1.938(21)
Mo(2)–C(7)	1.987(20)	Mo(2)–C(8)	1.956(19)
F(1)–C(91)	1.369(19)	F(2)–C(94)	1.349(19)
C(96)–C(97)	1.197(23)		
P(1)–Mo(1)–P(3)	99.0(1)	P(2)–Mo(1)–P(4)	99.6(2)
P(1)–Mo(1)–C(1)	170.4(6)	P(3)–Mo(1)–C(2)	172.7(6)
P(1)–Mo(1)–C(3)	95.9(6)	P(3)–Mo(1)–C(4)	93.2(6)
P(1)–Mo(1)–C(4)	87.6(5)	P(3)–Mo(1)–C(3)	88.9(6)
C(1)–Mo(1)–C(2)	84.5(8)	C(3)–Mo(1)–C(4)	175.6(7)
P(2)–Mo(2)–C(5)	173.5(5)	P(4)–Mo(2)–C(6)	170.2(6)
P(2)–Mo(2)–C(7)	85.1(7)	P(4)–Mo(2)–C(8)	85.0(6)
P(2)–Mo(2)–C(8)	95.4(7)	P(4)–Mo(2)–C(7)	96.6(6)
C(5)–Mo(2)–C(6)	85.5(9)	C(7)–Mo(2)–C(8)	178.2(9)
Mo(1)–P(1)–C(90)	116.1(5)	Mo(2)–P(2)–C(93)	113.5(5)
Mo(1)–P(3)–C(97)	118.6(6)	Mo(2)–P(4)–C(96)	115.0(6)
P(3)–C(97)–C(96)	174.8(15)	P(4)–C(96)–C(97)	171.7(15)

manifested in the smaller Mo–P–C(central) bond angles [dpfb, Mo(1)–P(1)–C(90) 116.1(5), Mo(2)–P(2)–C(93) 113.5(5); dppa, Mo(1)–P(3)–C(97) 118.6(6), Mo(2)–P(4)–C(96) 115.0(6)°]. That there is still some strain is shown clearly by the deviation of P(1) and P(2) out of the plane of the aryl ring by 0.144 and 0.283 Å respectively in dpfb, and the bowing of the P–C≡C–P vector in the dppa ligand [P(3)–C(97)–C(96) 174.8(15), P(4)–C(96)–C(97) 171.7(15)°]. In the latter the carbon–carbon triple bond distance of 1.197(23) Å is close to that of 1.209(5) Å found in free dppa.[13] Fig. 5 shows a side-on view of the molecule which reveals that the carbon–carbon triple bond lies directly over the aryl ring and reinforces the similarity between **1** and **2**. Perhaps the most notable difference between the two is highlighted in Fig. 6 which gives end-on views of **1**, **2** and $[\{Mo(CO)_4(\mu\text{-dppa})\}_2]$[3] looking down the molybdenum–molybdenum vectors. Thus in **2** the octahedral molybdenum centres are approximately eclipsed with respect to one another which differs from their more staggered mutual arrangement in **1**. The major consequence of this twisting is seen in the conformation of the dppa ligand. Thus, while the top diphosphine is essentially in the same environment, the lower one varies significantly such that the dppa moiety in **2** is substantially twisted with respect to the dpfb moiety in **1**. The net result of this twisting is that while the dpfb moiety maintains its *syn*-type arrangement of metal centres, the dppa ligand is best described as adopting a more *anti* configuration, that is the molybdenum centres are ligated on opposite sides of the diphosphine. The latter configuration of diphosphine ligands is as found in the related complex $[\{Mo(CO)_4(\mu\text{-dppa})\}_2]$[3] [Fig. 6(*c*)] and indicates that while dppa and dpfb are similar in their ability to link metal centres the former is more conformationally flexible.

An electrochemical study of complex **2** carried out in dichloromethane at room temperature revealed a single irreversible oxidation at +1.06 V. This is very similar to that found for **1** and again suggests that the two ligands, dpfb and dppa are interchangeable.

Conclusion

The work described herein suggests that rigid diphosphine ligands based on acetylenic and *para*-disubstituted aryl backbones have very similar co-ordination properties and can be interchanged with only minor structural consequences. While a large number of complexes have been prepared in which two dppa ligands span metal centres,[3] examples of analogous complexes based on dppb and related *para*-disubstituted aryl ligands are relatively rare. Such complexes should, however, be readily accessible.

Experimental

General comments

General techniques and instrumentation were as previously described.[3] The synthesis of *cis*-$[Mo(CO)_4(pip)_2]$ was *via* a modification of the literature method[14] and utilised the thermolysis of molybdenum hexacarbonyl and piperidine in a microwave oven. The compound dppa was obtained from Aldrich and used as supplied.

Preparations

1,4-bis(diphenylphosphino)-2,5-difluorobenzene (dpfb). Triphenylphosphine (17.48 g, 66 mmol) was stirred in thf (200 cm^3) and thin strips of lithium (0.93 g, 130 mmol) were added. The mixture was stirred overnight to give a blood-red solution. A reflux condenser was fitted, and dry NH_4Cl (3.65 g, 66 mmol)

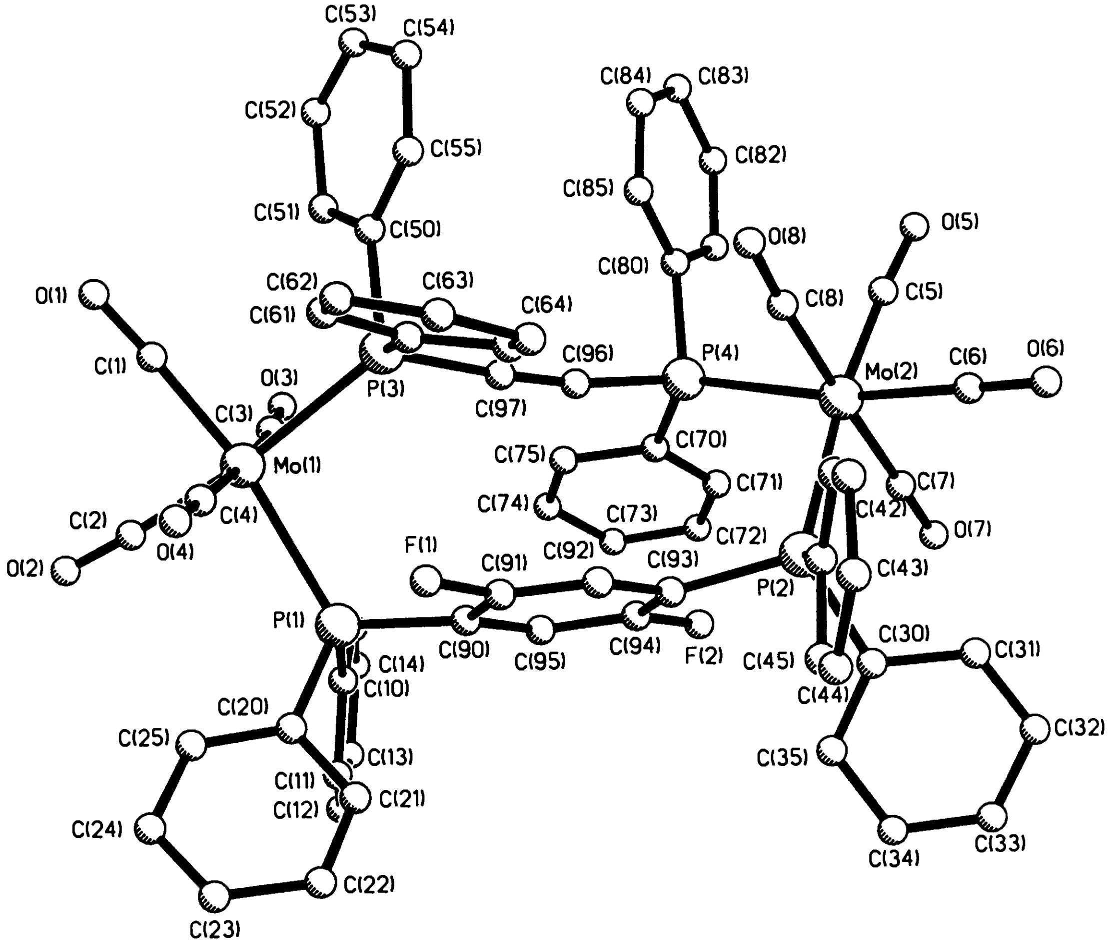


Fig. 4 Molecular structure of complex **2**

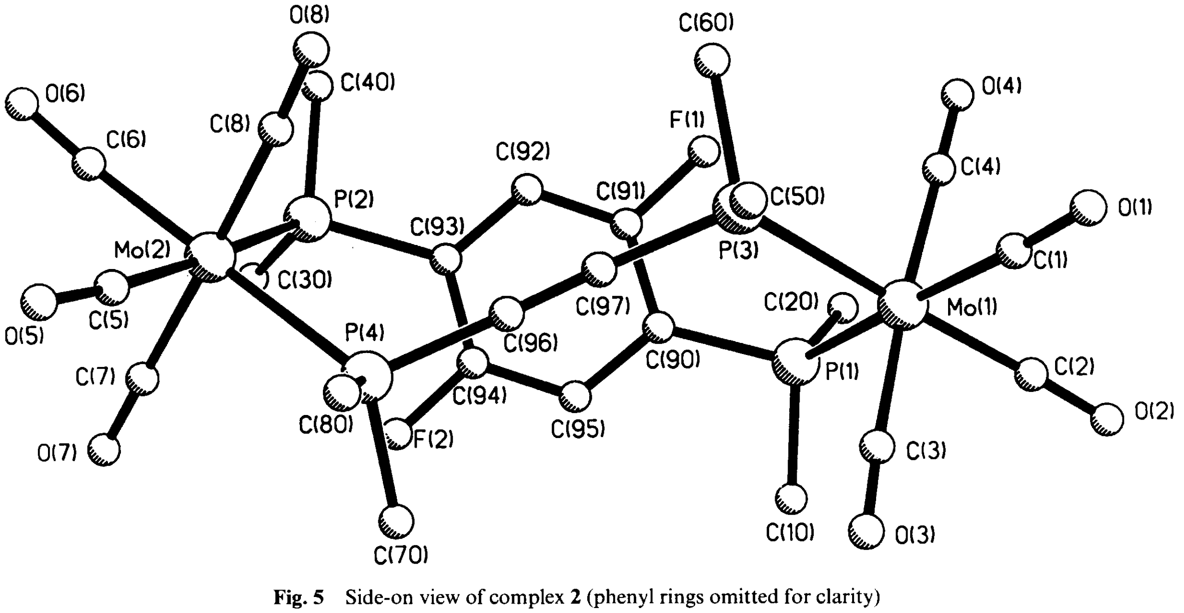


Fig. 5 Side-on view of complex **2** (phenyl rings omitted for clarity)

added over 3 h. A thf solution (80 cm^3) of 1,2,4,5-tetrafluorobenzene was slowly added over 90 min, resulting in decolorisation of the solution. The mixture was stirred for 2 h and degassed water (100 cm^3) was added causing precipitation of a white solid which was filtered off, washed with water (2 × 50 cm^3) and dried under vacuum. Crystallisation from dichloromethane–methanol afforded dpfb (8.30 g, 52%) as a fine white powder (Found: C, 72.20; H, 4.70; P, 12.15. Calc. for $C_{30}H_{22}F_2P_2$·MeOH: C, 72.35; H, 5.10; P, 12.05%). IR(KBr): 3068m, 3049m, 3027m, 3014m, 3001m, 1584w, 1476m, 1455s, 1365s, 1270m, 1176m, 1162s, 1155s, 1092m, 1070m, 1027m and 880s cm^{-1}. NMR (CDCl$_3$): ^{1}H, δ 7.44–7.32 (m, 20 H, Ph) and 6.46 (m, 2 H, $C_6H_2F_2$); ^{19}F, δ 18.0 (m); ^{31}P-{^{1}H}, δ −19.0 (m) (see Fig. 1).

[{Mo(CO)$_4$(μ-dpfb)}$_2$] 1. The complex *cis*-[Mo(CO)$_4$(pip)$_2$] (0.40 g, 1.06 mmol) and dpfb (0.51 g, 1.06 mmol) were stirred in dichloromethane (30 cm^3) for 80 min. Volatiles were removed under reduced pressure and the resulting yellow solid was washed with light petroleum (b.p. 40–60 °C) (2 × 20 cm^3).

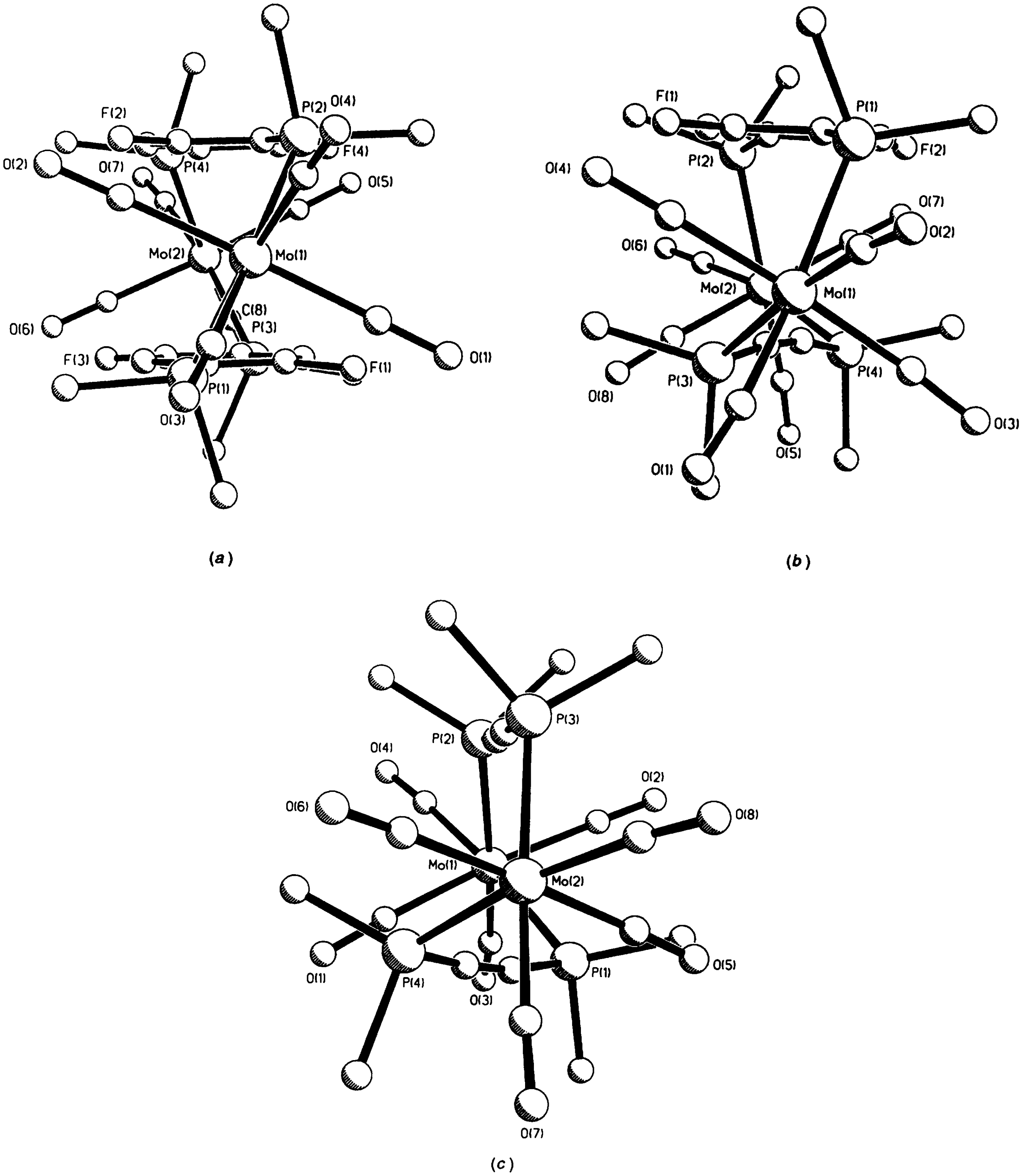


Fig. 6 Molecular structures of complexes **1** (*a*), **2** (*b*) and [{Mo(CO)$_4$(μ-dppa)}$_2$] **3** (*c*) looking down the molybdenum–molybdenum vectors (phenyl rings omitted for clarity)

Crystallisation from dichloromethane–methanol yielded **1** (0.63 g, 87%) as a yellow crystalline solid. Crystals suitable for X-ray diffraction were grown upon slow diffusion of methanol in concentrated dichloromethane solutions (Found: C, 58.80; H, 3.40; P, 8.65. Calc. for $C_{68}H_{44}F_4Mo_2O_8P_4$: C, 59.15; H, 3.20; P, 8.95%). IR(KBr)(CO): 2029m, 1930s, 1914m and 1888m cm^{-1}. NMR (CD_2Cl_2, −70 °C): ^{1}H, δ 7.60–7.10 (m, 40 H, Ph) and 6.56 (br s, 4 H, $C_6H_2F_2$); ^{19}F, δ 27.1 (broad with a 'doublet' feature, *J* 5.1); ^{31}P-{^{1}H}, δ 36.3 (broad with a 'quartet' feature, *J* 7.5 Hz).

[{Mo(CO)$_4$}$_2$(μ-dpfb)(μ-dppa)] 2. The complex *cis*-[Mo(CO)$_4$(pip)$_2$] (0.40 g, 1.06 mmol), dppa (0.21 g, 0.53 mmol) and dpfb (0.26 g, 0.53 mmol) were stirred in dichloromethane (60 cm^3) for 50 min. Volatiles were removed under reduced pressure and the resulting yellow solid was washed with light petroleum (b.p. 40–60 °C) (2 × 30 cm^3). Crystallisation from dichloromethane–methanol yielded **2** (0.57 g, 83%) as a pale yellow crystalline solid. Crystals suitable for X-ray diffraction were grown upon slow diffusion of methanol in concentrated dichloromethane solutions (Found: C, 56.60; H, 3.25; P, 9.00.

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

	1·CH_2Cl_2	**2**·CH_2Cl_2
Formula	$C_{69}H_{46}Cl_2F_4Mo_2O_8P_4$	$C_{65}H_{44}Cl_2F_2Mo_2O_8P_4$
a/Å	22.609(4)	13.162(3)
b/Å	11.690(2)	23.148(5)
c/Å	25.037(5)	20.307(4)
β/°	99.05(2)	100.09(2)
U/Å^3	6535.20(1.86)	6091.69(2.03)
$F(000)$	2952	2776
D_c/g cm^{-3}	1.49	1.50
Crystal size/mm	0.85 × 0.60 × 0.45	0.58 × 0.22 × 0.18
μ(Mo-Kα)/cm^{-1}	6.16	6.52
Orientation reflections, 2θ range/°	30, 18–27	25, 11–20
Data measured	10 213	8613
Unique data	9858	8240
Unique with $I \geqslant 3.0\sigma(I)$	6995	4055
No. parameters	787	354
R	0.056	0.076
R'	0.063	0.081
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.000\,702F^2$	$\sigma^2(F) + 0.000\,869F^2$
Largest shift/e.s.d., final cycle	0.03	0.008
Largest peak/e Å^{-3}	1.38	1.57

* Details in common: monoclinic, space group $P2_1/n$; yellow; $Z = 4$; $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$; $R' = \Sigma w^{\frac{1}{2}}[|F_o| - |F_c|]/\Sigma w^{\frac{1}{2}}|F_o|$.

Table 4 Atomic coordinates (× 10^4) for complex **1**·CH_2Cl_2

Atom	x	y	z	Atom	x	y	z
Mo(2)	3878(1)	2121(1)	1634(1)	C(41)	6784(3)	2343(7)	5220(3)
Mo(1)	6959(1)	−460(1)	4410(1)	C(42)	6819(4)	3145(9)	5629(3)
P(1)	6223(1)	−1622(2)	3758(1)	C(43)	6773(4)	4260(9)	5507(4)
P(2)	6701(1)	1633(2)	4131(1)	C(44)	6652(5)	4609(8)	4982(4)
P(3)	4668(1)	580(1)	1594(1)	C(45)	6617(4)	3825(7)	4575(3)
P(4)	4126(1)	2851(1)	2623(1)	C(50)	4407(3)	−843(6)	1338(3)
F(1)	6656(2)	−372(4)	2871(2)	C(51)	3849(3)	−1011(7)	1043(3)
F(2)	5474(2)	1130(4)	4310(2)	C(52)	3663(4)	−2072(8)	866(3)
F(3)	4239(2)	−564(3)	2506(2)	C(53)	4029(4)	−2997(7)	974(4)
F(4)	5371(2)	3451(4)	2445(2)	C(54)	4579(5)	−2867(7)	1248(4)
O(1)	7873(3)	−583(5)	3571(3)	C(55)	4775(4)	−1788(6)	1432(3)
O(2)	6079(3)	−422(6)	5281(2)	C(60)	5249(3)	943(6)	1188(3)
O(3)	7392(3)	−2782(5)	4939(3)	C(61)	5594(3)	1922(6)	1316(3)
O(4)	8011(3)	425(6)	5280(3)	C(62)	6036(3)	2194(8)	1025(4)
O(5)	4649(3)	4166(6)	1280(3)	C(63)	5793(4)	593(9)	448(3)
O(6)	2930(3)	292(7)	1879(3)	C(64)	5352(3)	287(7)	750(3)
O(7)	2740(3)	3646(7)	1455(4)	C(65)	6133(4)	1544(9)	589(4)
O(8)	3466(3)	1684(6)	407(2)	C(70)	3584(3)	2379(6)	3054(3)
C(1)	7539(3)	−533(6)	3862(3)	C(71)	3500(4)	1244(6)	3134(3)
C(2)	6382(3)	−419(7)	4955(3)	C(72)	3081(4)	853(8)	3427(3)
C(3)	7234(3)	−1942(7)	4731(3)	C(73)	2753(5)	1581(10)	3665(4)
C(4)	7612(3)	170(7)	4950(3)	C(74)	2794(6)	2717(10)	3557(7)
C(5)	4389(4)	3410(7)	1422(3)	C(75)	3207(5)	3112(8)	3259(5)
C(6)	3304(4)	922(8)	1816(3)	C(80)	4093(3)	4410(6)	2705(3)
C(7)	3174(4)	3134(8)	1544(3)	C(81)	4319(5)	4905(8)	3195(5)
C(8)	3622(4)	1798(7)	858(3)	C(82)	4248(6)	6083(10)	3272(6)
C(10)	6508(3)	−2832(6)	3397(3)	C(83)	3945(5)	6730(8)	2854(5)
C(11)	6139(4)	−3365(7)	2979(4)	C(84)	3752(8)	6268(9)	2427(5)
C(12)	6340(5)	−4313(7)	2734(4)	C(85)	3828(6)	5102(9)	2326(5)
C(13)	6917(5)	−4733(7)	2895(5)	C(90)	5768(3)	−930(5)	3179(2)
C(14)	7280(4)	−4201(8)	3302(4)	C(91)	6041(3)	−380(5)	2801(2)
C(15)	7089(4)	−3261(7)	3553(3)	C(92)	5753(3)	116(5)	2329(2)
C(20)	5659(3)	−2320(7)	4098(3)	C(93)	5129(3)	83(5)	2226(2)
C(21)	5674(4)	−3482(8)	4186(4)	C(94)	4850(3)	−456(5)	2605(3)
C(22)	5282(5)	−3935(12)	4509(6)	C(95)	5144(3)	−952(5)	3068(3)
C(23)	4867(5)	−3285(13)	4688(5)	C(100)	5992(3)	2034(5)	3689(2)
C(24)	4829(4)	−2171(11)	4600(4)	C(101)	5460(3)	1704(6)	3839(3)
C(25)	5248(3)	−1661(8)	4308(3)	C(102)	4895(3)	1936(6)	3552(3)
C(30)	7291(3)	2252(6)	3796(3)	C(103)	4847(3)	2519(5)	3061(2)
C(31)	7323(3)	2049(6)	3254(3)	C(104)	5391(3)	2867(5)	2918(2)
C(32)	7790(4)	2444(7)	3014(3)	C(105)	5936(3)	2649(6)	3208(3)
C(33)	8252(4)	3032(8)	3335(4)	C(200)	5719(9)	5969(19)	127(8)
C(34)	8239(4)	3231(9)	3860(4)	Cl(1)	5275(2)	7180(4)	59(2)
C(35)	7757(3)	2848(7)	4106(3)	Cl(2)	5841(3)	5408(6)	707(3)
C(40)	6689(3)	2664(6)	4689(3)				

Calc. for $C_{64}H_{42}F_2Mo_2O_8P_4{\cdot}CH_2Cl_2$: C, 56.65; H, 3.20; P, 9.00%). IR(KBr)(CO): 2028m, 1932s, 1922s, 1910s, 1898m and 1883m cm^{-1}. NMR ($CDCl_3$): ^1H, δ 7.52–6.93 (m, 40 H, Ph) and 6.45 (br s, 2 H, $C_6H_2F_2$); $^{31}P-\{^1H\}$, δ 32.0 (m, dpfb) and 16.0 (m, dppa).

Crystallography

A yellow single crystal of complex **1**•CH_2Cl_2 was mounted on a glass fibre. All geometric and intensity data were taken from this sample using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo-Kα radiation (λ = 0.710 73 Å). The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of reflections taken from a rotation photograph and centred by the diffractometer. The ω-scan technique was used to measure 10 213 reflections (9858 unique) in the range $5 \leqslant 2\theta \leqslant 46°$. Three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The unique data with $I \geqslant 3.0\sigma(I)$ were used to solve and refine the structure in the monoclinic space group $P2_1/n$.

The structure was solved by direct methods and developed by using alternating cycles of least-squares refinement (performed on *F*) and Fourier-difference synthesis. All non-hydrogen atoms except the dichloromethane solvate were refined anisotropically while hydrogens were placed in idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter (U = 0.08 Å ^{2}). The final Fourier-difference map contained two peaks close to the dichloromethane solvate of greater than 1.00 e Å^{-3}. The structure solution used the SHELXTL PLUS[15] program package on a microVax II computer.

Crystallographic analysis of complex **2**•CH_2Cl_2 was carried out in an analogous manner on a yellow single crystal. The ω-scan technique was used to measure in the range $5 \leqslant 2\theta \leqslant 45°$. Molybdenum and phosphorus atoms were refined anisotropically while all other non-hydrogen atoms were refined isotropically. The positions of the solvate atoms were fixed during the final cycles of refinement. All important crystallographic parameters for both structures are summarised in Table 3 and atomic coordinates in Tables 4 and 5.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Acknowledgements

We thank Dr. J. Edgar Anderson for his interest in this work and help with NMR simulations and Dr. David Humphrey for help with electrochemical experiments.

Table 5 Atomic coordinates (× 10^4) for complex **2**•CH_2Cl_2

Atom	*x*	*y*	*z*
Mo(1)	2328(1)	124(1)	2861(1)
Mo(2)	−3227(1)	1881(1)	2235(1)
P(1)	1364(3)	75(2)	1652(2)
P(2)	−2351(3)	1948(2)	1210(2)
P(3)	1276(3)	924(2)	3297(2)
P(4)	−2372(3)	960(2)	2767(2)
F(1)	1471(7)	1349(4)	1623(5)
F(2)	−2491(7)	660(4)	1058(5)
C(1)	3266(14)	142(8)	3714(9)
C(2)	3201(16)	−498(9)	2649(10)
C(3)	1467(16)	−452(9)	3218(10)
C(4)	3299(14)	686(8)	2544(9)
C(5)	−4008(15)	1876(8)	2943(9)
C(6)	−3890(16)	2616(9)	1989(10)
C(7)	−4364(17)	1492(9)	1622(11)
C(8)	−2135(16)	2284(9)	2839(10)
O(1)	3886(13)	184(7)	4198(8)
O(2)	3696(13)	−894(7)	2563(8)
O(3)	1006(13)	−789(7)	3468(8)
O(4)	3845(13)	1010(7)	2366(8)
O(5)	−4520(12)	1914(7)	3374(8)
O(6)	−4235(12)	3071(7)	1843(8)
O(7)	−5046(14)	1249(8)	1264(9)
O(8)	−1530(12)	2528(7)	3231(8)
C(10)	756(12)	−612(7)	1363(8)
C(11)	752(13)	−826(8)	729(9)
C(12)	297(15)	−1348(9)	533(10)
C(13)	−183(14)	−1676(8)	939(9)
C(14)	−191(16)	−1467(9)	1569(10)
C(15)	276(14)	−936(8)	1775(9)
C(20)	2146(13)	223(7)	1002(8)
C(21)	1752(15)	512(8)	428(9)
C(22)	2337(17)	632(9)	−70(11)
C(23)	3327(16)	420(9)	18(10)
C(24)	3732(16)	134(9)	570(10)
C(25)	3131(15)	35(8)	1058(10)
C(30)	−3177(14)	1831(8)	403(9)
C(31)	−4146(17)	2110(10)	288(11)
C(32)	−4812(18)	2078(9)	−307(10)
C(33)	−4517(17)	1763(9)	−799(11)
C(34)	−3573(18)	1492(10)	−708(12)
C(35)	−2937(15)	1498(8)	−85(9)
C(40)	−1702(14)	2628(8)	1055(9)
C(41)	−1475(15)	3041(9)	1506(10)
C(42)	−979(18)	3538(11)	1383(12)
C(43)	−735(18)	3640(11)	777(12)
C(44)	−933(18)	3214(10)	300(12)
C(45)	−1435(16)	2707(10)	422(10)
C(50)	1239(13)	908(7)	4184(8)
C(51)	1310(22)	417(14)	4541(15)
C(52)	1262(22)	391(14)	5258(16)
C(53)	1168(17)	883(10)	5553(12)
C(54)	1012(22)	1357(14)	5228(15)
C(55)	1133(20)	1371(13)	4537(14)
C(60)	1675(13)	1667(7)	3164(8)
C(61)	2701(15)	1803(9)	3369(9)
C(62)	3040(21)	2355(11)	3279(12)
C(63)	2389(20)	2767(12)	2966(12)
C(64)	1317(17)	2642(10)	2766(11)
C(65)	984(15)	2098(8)	2888(9)
C(70)	−2716(12)	233(7)	2462(8)
C(71)	−3656(14)	94(8)	2139(8)
C(72)	−3955(16)	−452(9)	1935(9)
C(73)	−3231(17)	−879(10)	2027(10)
C(74)	−2270(19)	−767(11)	2371(11)
C(75)	−1968(16)	−210(9)	2584(9)
C(80)	−2536(13)	910(7)	3648(8)
C(81)	−3390(17)	666(9)	3802(10)
C(82)	−3545(17)	657(9)	4472(10)
C(83)	−2852(18)	935(10)	4959(12)
C(84)	−2019(18)	1197(10)	4775(11)
C(85)	−1858(16)	1183(8)	4136(10)
C(93)	−1300(12)	1421(7)	1217(8)
C(94)	−1500(13)	837(7)	1185(8)
C(95)	−731(12)	424(7)	1284(7)
C(90)	309(12)	572(7)	1433(7)
C(91)	468(13)	1167(7)	1470(8)
C(92)	−266(12)	1581(7)	1355(7)
C(96)	−995(13)	945(7)	2861(8)
C(97)	−73(13)	947(7)	3008(8)
C(100)	2919	2155	628
Cl(1)	1581	2615	760
Cl(2)	3513	2728	1273

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Received 28*th September* 1995; *Paper* 5/06401E