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Molybdenum tricarbonyl complexes containing unidentate diphosphine. NMR study of *fac-mer* isomers and crystal structure of *fac*-$Mo(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$

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Abstract

The preparation of $Mo(CO)_3(\eta^2\text{-NN})(\eta^1\text{-dppm})$ (NN = 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (dmp); dppm = bis(diphenylphosphino)methane) by reactions of $Mo(CO)_4(\eta^2\text{-NN})$ with dppm have given a *fac* isomer or a *fac-mer* mixture depending on the nature of the NN ligand and on the reaction conditions. ^1H, ^{13}C and ^{31}P NMR spectroscopy have been used for the characterization of *fac* and *mer* isomers. The X-ray structure of one of the phen derivative shows a *fac* configuration (monoclinic, $P2_1/c$, *a* 16.843(3), *b* 11.220(2), *c* 19,358(4) Å, *β* 111.72(2)°, *V* 3398 Å^3, $Z = 4$).

A transformation in solution has been observed for both isomers, and the *fac* judged to be more stable than the *mer* isomer.

Introduction

Mixed ligand tricarbonyl complexes of type $Mo(CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppm})$ are well known, and their ability to form dinuclear heterobimetallic complexes by reactions with other metal derivatives has been established [1,2]. Related reactions with $Mo(CO)_3(\eta^2\text{-NN})(\eta^1\text{-dppm})$ (NN = 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (dmp)) have not been investigated, and we decided to study them.

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$Mo(CO)_3(\eta^2\text{-}NN)(\eta^1\text{-}dppm)$ (dppm = bis(diphenylphosphino)methane) (NN = bipy, phen) have been recently prepared by use of trimethylamine-*N*-oxide (TMNO) as a decarbonilation agent [3,4]. We describe here the preparation of $Mo(CO)_3(\eta^2\text{-}NN)(\eta^1\text{-}dppm)$ (NN = bipy phen, dmp) by a different route. We have observed the formation of *fac*, *mer* or mixtures of both isomers, depending on the NN ligand and the reaction conditions, and have also examined the behaviour of the isomers in solution. We report the crystal structure of one of the isolated forms for $Mo(CO)_3(\eta^2\text{-}phen)(\eta^1\text{-}dppm)$.

Results and discussion

A recently described synthesis of mixed ligand tricarbonyl complexes of type $M(CO)_3(\eta^2\text{-}NN)(\eta^1\text{-}dppm)$ (M = Cr, Mo, W; NN = bipy, phen) by use of TMNO as a decarbonilation agent involves a 2-step reaction of $M(CO)_6$ with NN and dppm ligands [3,4]. It was shown that in the second step conventional thermolytic or photolytic routes generally do not apply to diphosphine possibly because of complications arising from chelation, bridge formation, or ligand displacement reactions.

However, we have now prepared the $Mo(CO)_3(\eta^2\text{-}NN)(\eta^1\text{-}dppm)$ (NN = bipy, phen, dmp) by treating $Mo(CO)_4(\eta^2\text{-}NN)$ with dppm in refluxing acetone or xylene. Two solid products, **A** and **B**, were obtained for phen derivative, but when NN was bipy or dmp, the same products were isolated by both routes.

The tricarbonyl complexes $Mo(CO)_3(\eta^2\text{-}NN)(\eta^1\text{-}dppm)$ (NN = bipy, **1**; phen, **2**; dmp, **3**) have been characterized and the IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopic data are shown in Table 1. Complex **3** is new, but the *fac*-isomer of **1** and **2** have been briefly mentioned in the literature [3,4].

The IR spectra (in KBr pellets) of $Mo(CO)_3(\eta^2\text{-}phen)(\eta^1\text{-}dppm)$ show three strong carbonyl absorptions in **A**, and two strong bands (one broad) in **B**. Some others differences appear in the phen-γ(CH) region (800–850 cm^{-1}). However, for bipy or dmp derivatives, only one pattern of bands was observed in both cases. In dichloromethane three bands were observed in all cases in the carbonyl streching region.

The distinction between *fac* and *mer* isomers in $M(CO)_3L_3$ compounds is often made on the basis of IR spectroscopy [5–8]. However, there are some slight ambiguities in the literature; thus Isaac et al. for $Mo(CO)_3(\eta^2\text{-}dppm)(\eta^1\text{-}dppm)$ [1] and Shaw et al. for $Cr(CO)_3(\eta^2\text{-}dppm)(\eta^1\text{-}dppm)$ [9] observed two carbonyl streching bands for the *fac* isomer and three for the *mer*, but Hor et al. for **1** and **2** [3,4] and Stone et al. for $Mo(CO)_3(\eta^2\text{-}NN)(Ph_3P)$ (NN = bipy, phen) [10] suggested a *fac* configuration on the basis of three strong absorptions. Thus, IR spectroscopy may not always conclusively distinguish between the isomers.

We had previously found that the form of $Mo(CO)_3(\eta^2\text{-}phen)(\eta^1\text{-}dppm)$ isolated from acetone solution (**A**) could be unequivocally identified as the *fac* isomer on the basis of the crystal structure and NMR (^{31}P, ^{13}C) spectroscopy. Thus in the ^{31}P NMR spectrum, two doublets (δ 28.7 and −27.5 ppm; $^2J(P^a\text{-}P^b)$ 66.1 Hz), assigned to the coordinated and uncoordinated phosphorus atoms, are consistent with the presence of only one isomer, and are consistent with literature reports [4]. Three signals (δ 217.15(d) ($^2J(C\text{-}P)$ 39.3 Hz), 228.85(s) and 228.97(s) ppm) in the ^{13}C NMR spectrum, assigned to the carbon atoms of the three carbonyl groups, confirm the *fac* configuration for this isomer.

Table 1

IR and NMR spectroscopic data for Mo(CO)$_3$(η^2-NN)(η^1-dppm) (NN = bipy, phen, dmp)

NN	Type [a]	IR (cm^{-1})			δ(^{1}H) (ppm) [b] (CH$_2$ in dppm)	δ(^{13}C) [b] (ppm)	δ(^{31}P) [b] (ppm)
		solid state		CH$_2$Cl$_2$			
		ν(C≡O)	γ(CH)	ν(C≡O)			
bipy	**A** **B**	1908vs 1805s 1780vs	 765s	1915vs 1818s 1790s	2.60 (dd) J(H–P^a) 4.9 Hz J(H–P^b) 2.4 Hz	27.5(dd, CH$_2$ in dppm) J(C–P^a) 39.3 Hz J(C–P^b) 28.6 Hz	27.9(d, P^a) −27.5(d, P^b) J(P^a–P^b) 67.5 Hz
phen	**A**	1905vs 1810vs 1760vs	 845s	1915vs 1819s 1790s	2.48 (dd) J(H–P^a) 4.8 Hz J(H–P^b) 2.7 Hz	217.15(d,CO, J(C–P^a) 39.3 Hz) 228.85(s,CO) 228.97(s,CO) 27.82(dd, CH$_2$ in dppm J(C–P^a) 32.7 Hz J(C–P^b) 21.4 Hz)	28.7(d, P^a) −27.5(d, P^b) J(P^a–P^b) 66.1 Hz
phen	**B**	1900s 1785s	 835s	1915vs 1819s 1790s	2.55(br)	28.0(br, CH$_2$ in dppm)	20.3(d, P^a) −27.7(d, P^b) J(P^a–P^b) 61.8 Hz
dmp	**A** **B**	1902vs 1788vs	 848s	1915vs 1815s 1785s	2.12 (br, CH$_2$ in dppm) 3.28, 3.18 (s, CH$_3$ in dmp)	28.0 (br, CH$_2$ in dppm)	*fac*: 25.6 (d, P^a) −29.1 (d, P^b) J(P^a–P^b) 62.3 Hz *mer*: 27.9 (d, P^a) −29.0 (d, P^b) J(P^a–P^b) 50.3 Hz

[a] **A**: isolated from acetone; **B**: isolated from xylene. [b] P^a: coordinated phosphorus atom; P^b: uncoordinated phosphorus atom.

When the reaction was carried out in refluxing xylene, the product isolated, (**B**), was a mixture of *fac* and *mer* isomers. The ^{31}P NMR spectrum of **B** shows the same signals as **A** along with two new doublets (δ 20.3 and −27.7 ppm; ^2J(P^a–P^b) 61.8 Hz) which were assigned to the phosphorus atoms of the new isomer (Fig. 1). The ^{1}H and ^{13}C NMR data agree with the presence of *fac* and *mer* isomers (^{1}H NMR: *fac*: δ 2.48 ppm (dd), ^2J(H–P^a) 4.8 Hz, ^2J(H–P^b) 2.7 Hz; *mer*: δ 2.55 ppm (br); ^{13}C NMR: δ 28 ppm (m) for CH$_2$ of dppm).

For the Mo(CO)$_3$(η^2-bipy)(η^1-dppm) complex, the NMR data (^{1}H, ^{13}C, ^{31}P) showed that only one isomer was formed in both procedures. The resonance for the coordinated phosphorus atom (δ 27.9 ppm, ^2J(P^a–P^b) 67.5 Hz) (Fig. 1) appears in the same range that for *fac*-Mo(CO)$_3$(η^2-phen)(η^1-dppm) and agrees with the literature data for the *fac* isomer [3]. The ^{1}H and ^{13}C NMR spectra confirm the presence of one isomer as judged from the resonances of CH$_2$ group of the dppm ligand (^{1}H NMR: δ 2.60(dd) ppm, ^2J(H–P^a) 4.9 Hz, J(H–P^b) 2.4 Hz; ^{13}C NMR: δ 27.5 (dd) ppm, J(C–P^a) 39.3 Hz, J(C–P^b) 28.6 Hz).

In the Mo(CO)$_3$(η^2-dmp)(η^1-dppm) complex, the ^{31}P NMR spectra of **A** and **B** (Fig. 1) indicate four types of phosphorus atoms; two doublets at lowest field (δ

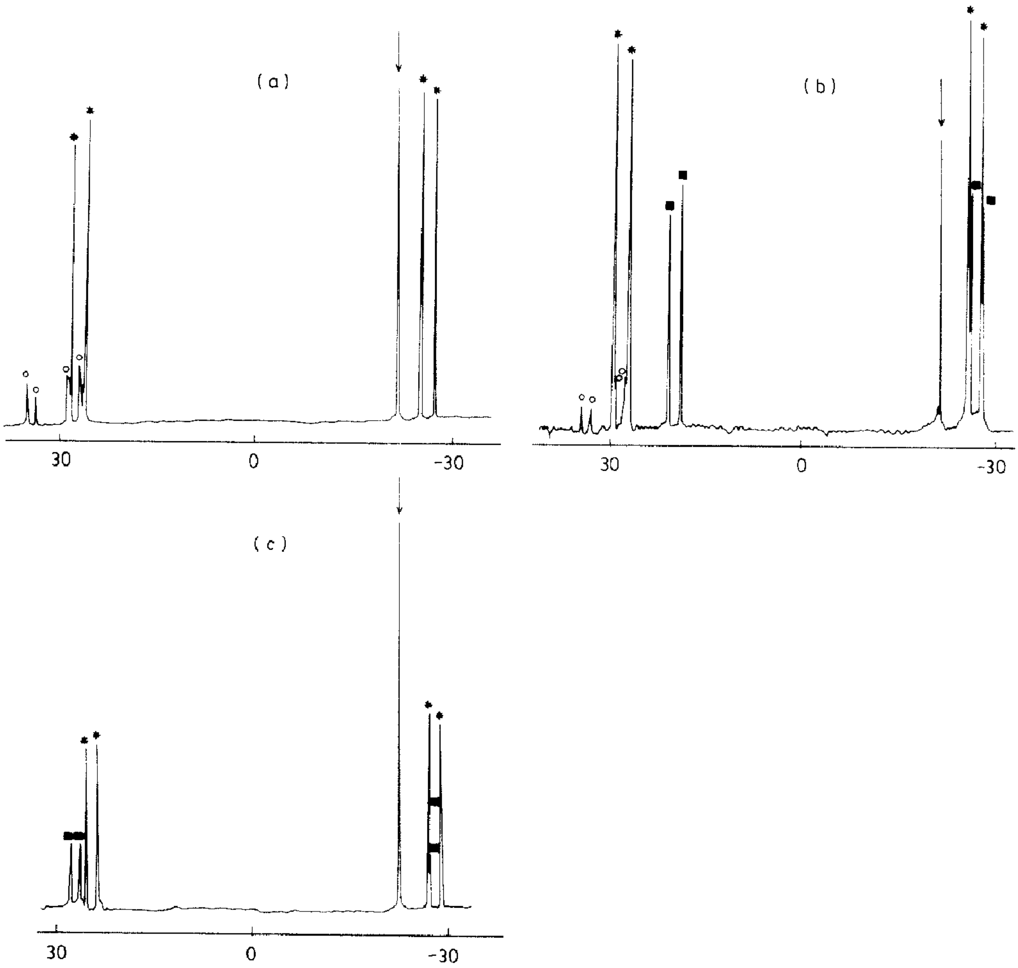

Fig. 1. $^{31}P\{^1H\}$ NMR spectra of $Mo(CO)_3(\eta^2\text{-NN})(\eta^1\text{-dppm})$; (a) NN = bipy; (b) NN = phen; (c) NN^3 = dmp. * *fac* isomer, ■ *mer* isomer, ○ dicarbonyl intermediate, ↓ free dppm.

25.6 ppm, $^2J(P^a\text{–}P^b)$ 62.4 Hz; δ 27.9 ppm, $^2J(P^a\text{–}P^b)$ 50.3 Hz), and two doublets at highest field (δ −29.1 ppm, $^2J(P^a\text{–}P^b)$ 62.4 Hz; δ −29.0 ppm, $^2J(P^a\text{–}P^b)$ 50.3 Hz) were assigned to the coordinated and uncoordinated phosphorus atoms of the *fac* and *mer* isomers, respectively. The ^{13}C NMR spectrum shows a multiplet for the carbon methylene atom which can be attributed to the presence of a mixture of isomers (δ 28 ppm). The ^1H NMR spectrum shows the signal corresponding to the CH_2 group of dppm ligand, and two singlets (δ 3.28 and 3.18 ppm) from to the two different methyl groups of dmp in this compound.

A signal (δ −22.2 ppm) corresponding to free dppm ligand [12] and two weak doublets at low field appear in all the ^{31}P NMR spectra. These doublets are consistent with the chemical inequivalence of the two coordinated phosphorus atoms, and may come from a dicarbonyl complex such as *cis*-$Mo(CO)_2(\eta^2\text{-NN})(\eta^2\text{-dppm})$ (NN = bipy, δ 35.8 (d, 1P) and 28.4 (d, 1P) ppm, $^2J(P\text{–}P)$ 37.9 Hz; NN = phen, δ 33.3 (d, 1P) and 29.1 (d, 1P) ppm, $^2J(P\text{–}P)$ 30 Hz).

The ^{31}P NMR spectra of all the complexes show significant changes in solution after 24 h, the signals of the *mer* isomer dissapearing, leaving those of the *fac* isomers. This is not surprising in view of the higher stability suggested for the *fac* isomers. In addition, new signals, characteristic of a unidentate coordination of dppm, were observed and suggest the presence of new products in solution. Sometimes the bands from a tetracarbonyl complex, together with other bands, could be observed in the IR spectra of the final solutions.

The isolation of the *fac* isomer for bipy and phen derivatives but of the mixture of *fac* and *mer* isomers for dmp indicates that the steric demands of the NN ligands are important for the stabilization of one or the other isomer. Our work has confirmed that the *fac* is more stable than the *mer* isomer, but decomposition was observed for both. Further studies are in progress.

Crystal structure

Single crystals of Mo(CO)$_3$(η^2-phen)(η^1-dppm) suitable for an X-ray diffraction study were obtained as violet prisms from dichloromethane/methanol. Table 3 lists the bond lengths and angles. Figure 2 shows the structure and the atom labelling [13]. The result confirms that the *fac* isomer is formed in procedure A.

The molybdenum atom is in a distorted octahedral coordination. One bidentate phenanthroline ligand and two carbonyl groups are in equatorial positions. The apical positions are occupied by a unidentate dppm ligand and the third carbonyl group, giving a *fac* configuration.

The angle P(1)–C(28)–P(2) is similar to that for the monodentate dppm in Mo(CO)$_2$(NCS)$_2$(η^2-dppm)(η^1-dppm) [14]. The distances and angles are normal.

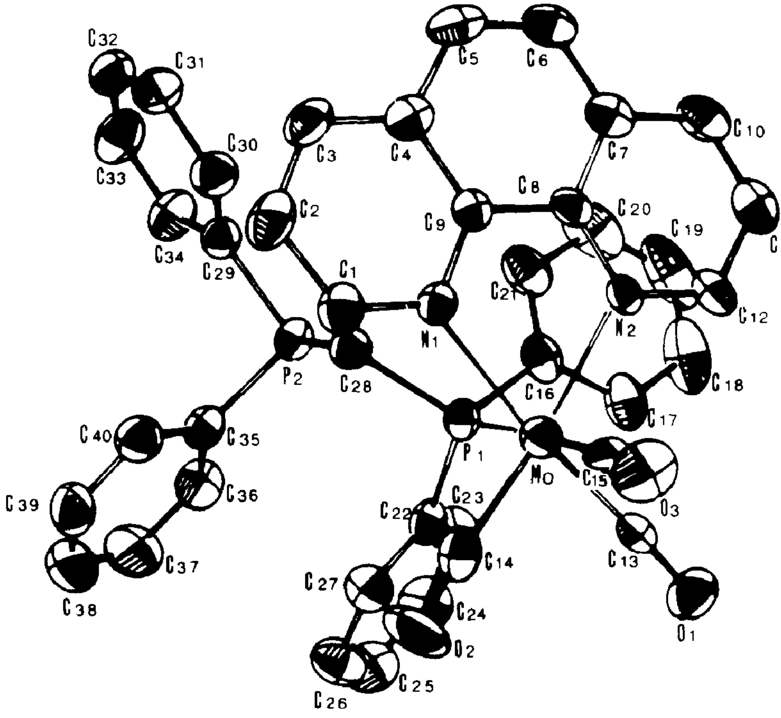

Fig. 2. Crystal structure of *fac*-Mo(CO)$_3$(η^2-phen)(η^1-dppm).

The angle N(1)–Mo–N(2) is 73.0(3)°, a value in the range expected for a bidentate phenanthroline.

The packing of the crystal is determined only by Van der Waals forces and there are no significant intermolecular interactions.

Experimental

General

All reactions were carried out under oxygen-free dry nitrogen. Analytical grade solvents were used. The $Mo(CO)_4(\eta^2\text{-NN})$ (NN = bipy, phen, dmp) were prepared as previously described [15–17]. C, H and N analyses were carried out by Elemental Micro-Analysis Ltd. Laboratories (Devon). IR spectra were recorded on a Perkin–Elmer 1300 spectrophotometer with KBr pellets and CH_2Cl_2 solutions. The NMR spectra were recorded on a Varian XL-300 spectrometer at room temperature, operated at 299.95 MHz for ^1H, 75.43 MHz for ^{13}C, and 121.42 MHz for ^{31}P, with $(CH_3)_4Si$ as internal standard for ^1H and ^{13}C, and 85% phosphoric acid as external standard for ^{31}P; the solvent in all cases was $CDCl_3$.

Reactions

Preparation of $Mo(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$. Procedure **A**. A solution of $Mo(CO)_4(\eta^2\text{-phen})$ (1.0 mmol) and dppm (1.0 mmol) in acetone (15 ml) was refluxed for 30 min, then cooled to room temperature. The precipitate was filtered off, washed with hexane and dried in vacuo (yield: 80%).

Procedure **B**. A solution of $Mo(CO)_4(\eta^2\text{-phen})$ (1.0 mmol) and dppm (1.0 mmol) in xylene (15 ml) was refluxed for 1 h, then cooled to room temperature. The precipitate was filtered off and dried in vacuo (yield: 70%. Analysis. Found C, 63.5; H, 4.10; N, 3.58. $C_{40}H_{30}MoP_2N_2O_3$ calcd.: C, 63.9; H, 4.50; N, 3.50%).

Preparation of $Mo(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$. The procedures were similar to that used for the phen derivative. The same product was obtained from the two procedures (yield: 75%).

Preparation of $Mo(CO)_3(\eta^2\text{-dmp})(\eta^1\text{-dppm})$. The procedure was similar to that for the phen derivative. The same, product was obtained from both procedures (yield: 70%. Analysis, Found: C, 64.7; H, 4.26; N, 3.44 $C_{42}H_{34}MoP_2N_2O_3$ calcd.: C, 65.3; H, 4.44; N, 3.63%.

Structure determination.

Table 2 shows the final atomic parameters. Crystal data and details of the procedure are given in Table 4. The cell dimensions were refined by least-squares fitting of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo and P were taken from ref. 18. The structure was solved by direct [19] and Fourier methods. An empirical absorption correction [20] was applied at the end of the isotropic refinement.

Final refinement with fixed isotropic factors and coordinates for hydrogen atoms and unit weights led to R 4.9%. Final difference synthesis showed no significantly electron density. Most of the calculations were carried out with X-RAY 80 system [21].

Table 2

Atomic coordinates and thermal parameters as

$U_{eq} = \frac{1}{3}\sum[U_{ij}a_i^{\star}a_j^{\star}a_ia_j\cos(a_i a_j)]\times 10^4$ for $MoP_2N_2O_3C_{40}H_{30}$

Atom	x	y	z	U_{eq}
Mo	0.89981(6)	0.48394(7)	0.25050(5)	305(3)
P(1)	0.75198(17)	0.38634(24)	0.21635(15)	284(10)
P(2)	0.65372(18)	0.16634(25)	0.24867(16)	329(10)
N(1)	0.93917(50)	0.36927(72)	0.35285(44)	277(31)
N(2)	0.86650(51)	0.58469(71)	0.33666(46)	276(33)
O(1)	0.83238(54)	0.65899(75)	0.11765(45)	512(36)
O(2)	0.96428(69)	0.34013(92)	0.14540(56)	758(52)
O(3)	1.08096(50)	0.59120(80)	0.28696(47)	529(37)
C(1)	0.97633(68)	0.26490(99)	0.36095(61)	373(43)
C(2)	0.99227(74)	0.19179(107)	0.42354(68)	473(50)
C(3)	0.96854(74)	0.23236(103)	0.48070(60)	412(44)
C(4)	0.93055(65)	0.34190(97)	0.47469(57)	345(40)
C(5)	0.90471(75)	0.39628(118)	0.53144(59)	447(48)
C(6)	0.86896(65)	0.50318(115)	0.52337(55)	407(43)
C(7)	0.85478(63)	0.57271(100)	0.45768(58)	343(40)
C(8)	0.87780(60)	0.52476(95)	0.40068(50)	293(34)
C(9)	0.91656(60)	0.41030(86)	0.40942(54)	272(36)
C(10)	0.81896(75)	0.68664(112)	0.44710(66)	439(50)
C(11)	0.80775(78)	0.74719(109)	0.38229(71)	474(51)
C(12)	0.83235(71)	0.69332(98)	0.32832(61)	394(45)
C(13)	0.85606(64)	0.59314(92)	0.16861(57)	307(40)
C(14)	0.93637(74)	0.38846(100)	0.18535(67)	423(48)
C(15)	1.01276(68)	0.55309(88)	0.27598(50)	289(38)
C(16)	0.67924(64)	0.48683(104)	0.23890(62)	404(41)
C(17)	0.65621(75)	0.59294(109)	0.19783(76)	505(54)
C(18)	0.60869(84)	0.67826(133)	0.21809(107)	725(74)
C(19)	0.58467(95)	0.65968(166)	0.27734(121)	837(89)
C(20)	0.60817(95)	0.55741(164)	0.31785(97)	751(77)
C(21)	0.65521(75)	0.46934(119)	0.29874(70)	516(51)
C(22)	0.69106(69)	0.33653(94)	0.12124(61)	361(42)
C(23)	0.60529(71)	0.36646(114)	0.08235(71)	484(50)
C(24)	0.56247(77)	0.32209(129)	0.01138(74)	568(53)
C(25)	0.60403(86)	0.24994(138)	−0.02153(69)	607(59)
C(26)	0.68720(84)	0.21847(124)	0.01591(72)	550(56)
C(27)	0.73161(72)	0.26320(107)	0.08721(65)	429(46)
C(28)	0.75408(65)	0.24964(94)	0.27031(56)	335(39)
C(29)	0.67592(67)	0.07821(96)	0.33316(61)	342(42)
C(30)	0.74920(75)	0.08504(107)	0.39767(65)	449(48)
C(31)	0.75638(83)	0.01952(123)	0.46036(62)	542(50)
C(32)	0.69017(96)	−0.05294(113)	0.46093(74)	553(61)
C(33)	0.61876(84)	−0.06207(118)	0.39774(81)	559(60)
C(34)	0.61080(72)	0.00301(116)	0.33504(67)	502(48)
C(35)	0.66478(72)	0.04987(95)	0.18657(63)	385(45)
C(36)	0.59727(75)	0.02841(119)	0.12123(68)	516(48)
C(37)	0.60352(104)	−0.06026(144)	0.07209(79)	708(68)
C(38)	0.67660(111)	−0.12382(133)	0.08749(87)	680(72)
C(39)	0.74429(95)	−0.10190(115)	0.15309(88)	595(67)
C(40)	0.73922(72)	−0.01739(114)	0.20272(61)	451(45)

Table 3

Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Mo–P(1)	2.572(3)	Mo–N(1)	2.247(8)
Mo–N(2)	2.252(9)	Mo–C(13)	1.922(10)
Mo–C(14)	1.922(14)	Mo–C(15)	1.942(11)
P(1)–C(16)	1.833(13)	P(1)–C(22)	1.833(10)
P(1)–C(28)	1.848(11)	P(2)–C(28)	1.840(11)
P(2)–C(29)	1.827(12)	P(2)–C(35)	1.831(12)
N(1)–C(1)	1.309(14)	N(1)–C(9)	1.364(15)
N(2)–C(8)	1.359(13)	N(2)–C(12)	1.332(14)
O(1)–C(13)	1.177(13)	O(2)–C(14)	1.175(19)
O(3)–C(15)	1.169(14)	C(1)–C(2)	1.403(17)
C(2)–C(3)	1.387(20)	C(3)–C(4)	1.369(16)
C(4)–C(5)	1.457(18)	C(4)–C(9)	1.422(15)
C(5)–C(6)	1.325(18)	C(6)–C(7)	1.434(16)
C(7)–C(8)	1.405(17)	C(7)–C(10)	1.395(17)
C(8)–C(9)	1.423(14)	C(10)–C(11)	1.377(19)
C(11)–C(12)	1.397(20)	C(16)–C(17)	1.404(17)
C(16)–C(21)	1.374(20)	C(17)–C(18)	1.395(22)
C(18)–C(19)	1.365(33)	C(19)–C(20)	1.363(26)
C(20)–C(21)	1.399(24)	C(22)–C(23)	1.401(15)
C(22)–C(27)	1.381(19)	C(23)–C(24)	1.385(17)
C(24)–C(25)	1.371(22)	C(25)–C(26)	1.364(18)
C(26)–C(27)	1.397(16)	C(29)–C(30)	1.396(14)
C(29)–C(34)	1.394(18)	C(30)–C(31)	1.385(18)
C(31)–C(32)	1.382(21)	C(32)–C(33)	1.365(17)
C(33)–C(34)	1.380(20)	C(35)–C(36)	1.374(14)
C(35)–C(40)	1.396(17)	C(36)–C(37)	1.406(22)
C(37)–C(38)	1.357(24)	C(38)–C(39)	1.379(19)
C(39)–C(40)	1.374(20)		
C(14)–Mo–C(15)	82.4(5)	C(13)–Mo–C(15)	89.7(5)
C(13)–Mo–C(14)	86.1(5)	N(2)–Mo–C(15)	95.7(4)
N(2)–Mo–C(14)	174.1(4)	N(2)–Mo–C(13)	99.6(4)
N(1)–Mo–C(15)	93.6(4)	N(1)–Mo–C(14)	101.5(4)
N(1)–Mo–C(13)	172.1(4)	N(1)–Mo–N(2)	73.0(3)
P(1)–Mo–C(15)	178.3(3)	P(1)–Mo–C(14)	96.3(4)
P(1)–Mo–C(13)	91.2(3)	P(1)–Mo–N(2)	85.5(2)
P(1)–Mo–N(1)	85.7(2)	Mo–P(1)–C(28)	113.2(4)
Mo–P(1)–C(22)	121.1(4)	Mo–P(1)–C(16)	110.2(4)
C(22)–P(1)–C(28)	101.6(5)	C(16)–P(1)–C(28)	104.5(5)
C(16)–P(1)–C(22)	104.6(5)	C(29)–P(2)–C(35)	99.5(5)
C(28)–P(2)–C(35)	101.7(5)	C(28)–P(2)–C(29)	101.8(5)
Mo–N(1)–C(9)	115.8(6)	Mo–N(1)–C(1)	126.1(7)
C(1)–N(1)–C(9)	117.9(9)	Mo–N(2)–C(12)	125.7(7)
Mo–N(2)–C(8)	116.0(7)	C(8)–N(2)–C(12)	118.2(9)
N(1)–C(1)–C(2)	124 (1)	C(1)–C(2)–C(3)	118 (1)
C(2)–C(3)–C(4)	119 (1)	C(3)–C(4)–C(9)	119 (1)
C(3)–C(4)–C(5)	125 (1)	C(5)–C(4)–C(9)	117 (1)
C(4)–C(5)–C(6)	123 (1)	C(5)–C(6)–C(7)	121 (1)
C(6)–C(7)–C(10)	123 (1)	C(6)–C(7)–C(8)	119 (1)
C(8)–C(7)–C(10)	118 (1)	N(2)–C(8)–C(7)	122.7(9)
C(7)–C(8)–C(9)	120.0(9)	N(2)–C(8)–C(9)	117.2(9)
C(4)–C(9)–C(8)	120.7(9)	N(1)–C(9)–C(8)	117.5(9)
N(1)–C(9)–C(4)	121.8(9)	C(7)–C(10)–C(11)	119 (1)
C(10)–C(11)–C(12)	119 (1)	N(2)–C(12)–C(11)	123 (1)
Mo–C(13)–O(1)	177 (1)	Mo–C(14)–O(2)	173 (1)
Mo–C(15)–O(3)	175.4(9)	P(1)–C(16)–C(21)	122.9(9)

Table 3 (continued)

P(1)-C(16)-C(17)	117.1(9)	C(17)-C(16)-C(21)	119 (1)
C(16)-C(17)-C(18)	119 (1)	C(17)-C(18)-C(19)	121 (1)
C(18)-C(19)-C(20)	120 (1)	C(19)-C(20)-C(21)	121 (1)
C(16)-C(21)-C(20)	120 (1)	P(1)-C(22)-C(27)	118.0(9)
P(1)-C(22)-C(23)	123.3(9)	C(23)-C(22)-C(27)	119 (1)
C(22)-C(23)-C(24)	120 (1)	C(23)-C(24)-C(25)	120 (1)
C(24)-C(25)-C(26)	120 (1)	C(25)-C(26)-C(27)	120 (1)
C(22)-C(27)-C(26)	120 (1)	P(1)-C(28)-P(2)	118.0(6)
P(2)-C(29)-C(34)	116.6(8)	P(2)-C(29)-C(30)	126.2(9)
C(30)-C(29)-C(34)	117 (1)	C(29)-C(30)-C(31)	121 (1)
C(30)-C(31)-C(32)	120 (1)	C(31)-C(32)-C(33)	119 (1)
C(32)-C(33)-C(34)	121 (1)	C(29)-C(34)-C(33)	121 (1)
P(2)-C(35)-C(40)	122.7(9)	P(2)-C(35)-C(36)	118.6(9)
C(36)-C(35)-C(40)	119 (1)	C(35)-C(36)-C(37)	120 (1)
C(36)-C(37)-C(38)	121 (1)	C(37)-C(38)-C(39)	119 (1)
C(38)-C(39)-C(40)	121 (1)	C(35)-C(40)-C(39)	120 (1)

Table 4

Crystal and refinement data for *fac*-Mo(CO)$_3$(η^2-phen)(η^1-dppm)

formula	$MoP_2N_2O_3C_{40}H_{30}$
crystal system	monoclinic
space group	$P2_1/c$
a, Å	16.843(3)
b, Å	11.220(2)
c, Å	19.358(4)
β, °	111.72(2)
V, Å^3	3398(1)
ρ(calcd), g cm^{-1}	1.46
temperature, °C	22
μ, cm^{-1}	5.08
crystal dimensions, cm	0.04×0.02×0.02
diffractometer	Enraf-Nonuis CAD4
radiation	graphite-monochromated Mo-K_α (λ = 0.71069 Å)
scan technique	$\theta/2\theta$
data collected	(−20,0,0) to (20,13,23)
reflections collected	7531
unique data	6667
unique data (I) ≥ 3σ(I)	3381
R(int), %	1.89
decay	≤ 5% variation
R_F, %	4.9
Rw_F, %	7.4
average shift/error	0.0035
maximum shift/error	0.032
maximum absorption correction	1.229
minimum absorption correction	0.713

Tables of anisotropic temperature factors and final structure factors are available from the authors.

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