

Molybdenum tricarbonyl complexes containing unidentate diphosphine. NMR study of *fac-mer* isomers and crystal structure of *fac*-Mo(CO)₃(η^2 -phen)(η^1 -dppm)

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Abstract

The preparation of Mo(CO)₃(η^2 -NN)(η^1 -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(η^2 -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, ¹³C and ³¹P 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, *P*2₁/*c*, *a* 16.843(3), *b* 11.220(2), *c* 19.358(4) Å, β 111.72(2)°, *V* 3398 Å³, *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(η^2 -dppm)(η^1 -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(η^2 -NN)(η^1 -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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$\text{Mo}(\text{CO})_3(\eta^2\text{-NN})(\eta^1\text{-dppm})$ (dppm = bis(diphenylphosphino)methane) (NN = bipy, phen) have been recently prepared by use of trimethylamine-*N*-oxide (TMNO) as a decarbonylation agent [3,4]. We describe here the preparation of $\text{Mo}(\text{CO})_3(\eta^2\text{-NN})(\eta^1\text{-dppm})$ (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 $\text{Mo}(\text{CO})_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$.

Results and discussion

A recently described synthesis of mixed ligand tricarbonyl complexes of type $\text{M}(\text{CO})_3(\eta^2\text{-NN})(\eta^1\text{-dppm})$ (M = Cr, Mo, W; NN = bipy, phen) by use of TMNO as a decarbonylation agent involves a 2-step reaction of $\text{M}(\text{CO})_6$ 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 $\text{Mo}(\text{CO})_3(\eta^2\text{-NN})(\eta^1\text{-dppm})$ (NN = bipy, phen, dmp) by treating $\text{Mo}(\text{CO})_4(\eta^2\text{-NN})$ 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 $\text{Mo}(\text{CO})_3(\eta^2\text{-NN})(\eta^1\text{-dppm})$ (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 $\text{Mo}(\text{CO})_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$ show three strong carbonyl absorptions in **A**, and two strong bands (one broad) in **B**. Some other differences appear in the phen- $\gamma(\text{CH})$ region ($800\text{--}850\text{ cm}^{-1}$). 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 stretching region.

The distinction between *fac* and *mer* isomers in $\text{M}(\text{CO})_3\text{L}_3$ 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 $\text{Mo}(\text{CO})_3(\eta^2\text{-dppm})(\eta^1\text{-dppm})$ [1] and Shaw et al. for $\text{Cr}(\text{CO})_3(\eta^2\text{-dppm})(\eta^1\text{-dppm})$ [9] observed two carbonyl stretching 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 $\text{Mo}(\text{CO})_3(\eta^2\text{-NN})(\text{Ph}_3\text{P})$ (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 $\text{Mo}(\text{CO})_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$ 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; $^2J(\text{P}^{\text{a}}\text{--P}^{\text{b}})$ 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) ($^2J(\text{C--P})$ 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 $\text{Mo}(\text{CO})_3(\eta^2\text{-NN})(\eta^1\text{-dppm})$ (NN = bipy, phen, dmp)

NN	Type ^a	IR (cm ⁻¹)		CH ₂ Cl ₂ $\nu(\text{C}\equiv\text{O})$	$\delta(^1\text{H})$ (ppm) ^b (CH ₂ in dppm)	$\delta(^{13}\text{C})$ ^b (ppm)	$\delta(^{31}\text{P})$ ^b (ppm)
		solid state					
		$\nu(\text{C}\equiv\text{O})$	$\gamma(\text{CH})$				
bipy	A	1908vs		1915vs	2.60 (dd)	27.5(dd, CH ₂	27.9(d, P ^a)
	B	1805s 1780vs	765s	1818s 1790s	$J(\text{H}-\text{P}^a)$ 4.9 Hz $J(\text{H}-\text{P}^b)$ 2.4 Hz	in dppm) $J(\text{C}-\text{P}^a)$ 39.3 Hz $J(\text{C}-\text{P}^b)$ 28.6 Hz	$-27.5(\text{d}, \text{P}^b)$ $J(\text{P}^a-\text{P}^b)$ 67.5 Hz
phen	A	1905vs 1810vs 1760vs	845s	1915vs 1819s 1790s	2.48 (dd) $J(\text{H}-\text{P}^a)$ 4.8 Hz $J(\text{H}-\text{P}^b)$ 2.7 Hz	217.15(d,CO, $J(\text{C}-\text{P}^a)$ 39.3 Hz) 228.85(s,CO) 228.97(s,CO) 27.82(dd, CH ₂ in dppm $J(\text{C}-\text{P}^a)$ 32.7 Hz $J(\text{C}-\text{P}^b)$ 21.4 Hz)	28.7(d, P ^a) $-27.5(\text{d}, \text{P}^b)$ $J(\text{P}^a-\text{P}^b)$ 66.1 Hz
	B	1900s 1785s	835s	1915vs 1819s 1790s	2.55(br)	28.0(br, CH ₂ in dppm)	20.3(d, P ^a) $-27.7(\text{d}, \text{P}^b)$ $J(\text{P}^a-\text{P}^b)$ 61.8 Hz
dmp	A	1902vs		1915vs	2.12 (br, CH ₂	28.0 (br, CH ₂	<i>fac</i> :
	B	1788vs	848s	1815s 1785s	in dppm) 3.28, 3.18 (s, CH ₃ in dmp)	in dppm)	25.6 (d, P ^a) $-29.1 (\text{d}, \text{P}^b)$ $J(\text{P}^a-\text{P}^b)$ 62.3 Hz <i>mer</i> : 27.9 (d, P ^a) $-29.0 (\text{d}, \text{P}^b)$ $J(\text{P}^a-\text{P}^b)$ 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; $^2J(\text{P}^a-\text{P}^b)$ 61.8 Hz) which were assigned to the phosphorus atoms of the new isomer (Fig. 1). The ^1H and ^{13}C NMR data agree with the presence of *fac* and *mer* isomers (^1H NMR: *fac*: δ 2.48 ppm (dd), $^2J(\text{H}-\text{P}^a)$ 4.8 Hz, $^2J(\text{H}-\text{P}^b)$ 2.7 Hz; *mer*: δ 2.55 ppm (br); ^{13}C NMR: δ 28 ppm (m) for CH_2 of dppm).

For the $\text{Mo}(\text{CO})_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ complex, the NMR data (^1H , ^{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, $^2J(\text{P}^a-\text{P}^b)$ 67.5 Hz) (Fig. 1) appears in the same range that for *fac*- $\text{Mo}(\text{CO})_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$ and agrees with the literature data for the *fac* isomer [3]. The ^1H and ^{13}C NMR spectra confirm the presence of one isomer as judged from the resonances of CH_2 group of the dppm ligand (^1H NMR: δ 2.60(dd) ppm, $^2J(\text{H}-\text{P}^a)$ 4.9 Hz, $J(\text{H}-\text{P}^b)$ 2.4 Hz; ^{13}C NMR: δ 27.5 (dd) ppm, $J(\text{C}-\text{P}^a)$ 39.3 Hz, $J(\text{C}-\text{P}^b)$ 28.6 Hz).

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

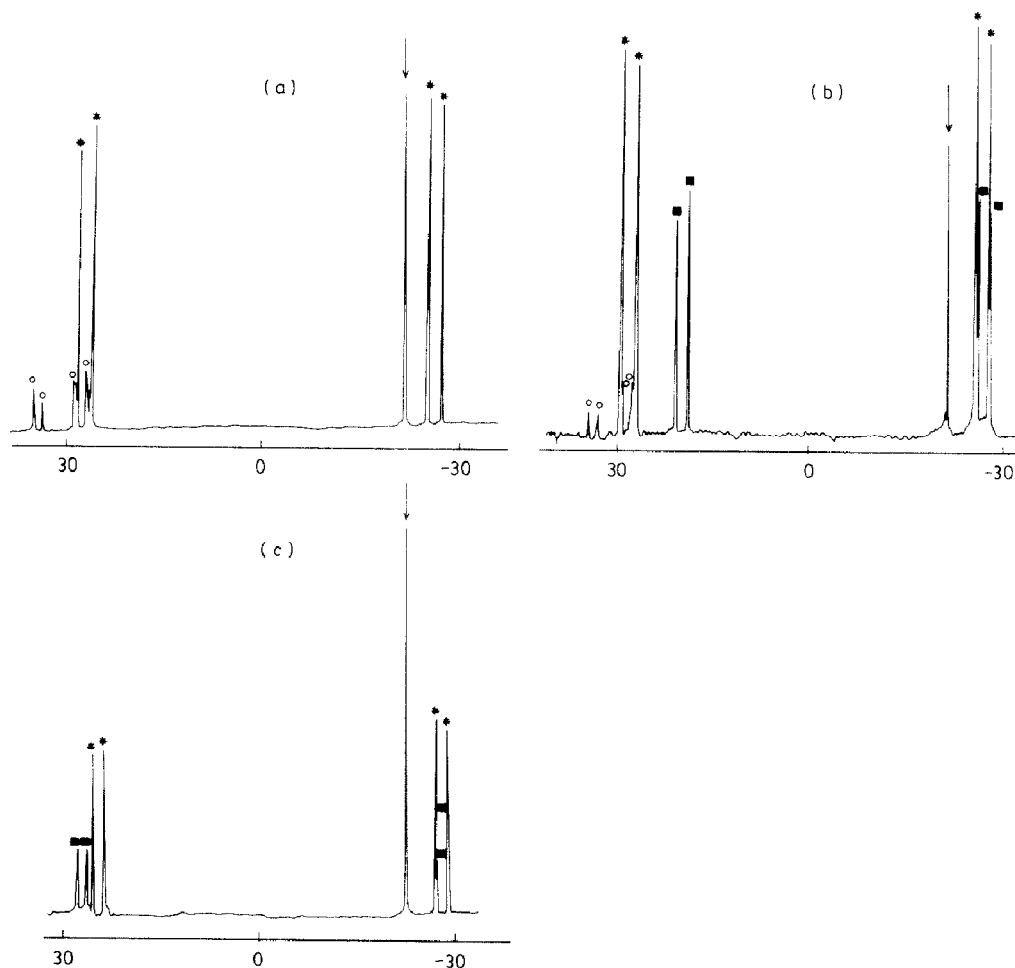


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $\text{Mo}(\text{CO})_3(\eta^2\text{-NN})(\eta^1\text{-dppm})$; (a) $\text{NN} = \text{bipy}$; (b) $\text{NN} = \text{phen}$; (c) $\text{NN}^3 = \text{dmp}$. * *fac* isomer, ■ *mer* isomer, ○ dicarbonyl intermediate, ↓ free dppm.

25.6 ppm, $^2J(\text{P}^a\text{-P}^b)$ 62.4 Hz; δ 27.9 ppm, $^2J(\text{P}^a\text{-P}^b)$ 50.3 Hz), and two doublets at highest field (δ -29.1 ppm, $^2J(\text{P}^a\text{-P}^b)$ 62.4 Hz; δ -29.0 ppm, $^2J(\text{P}^a\text{-P}^b)$ 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 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*- $\text{Mo}(\text{CO})_2(\eta^2\text{-NN})(\eta^2\text{-dppm})$ ($\text{NN} = \text{bipy}$, δ 35.8 (d, 1P) and 28.4 (d, 1P) ppm, $^2J(\text{P-P})$ 37.9 Hz; $\text{NN} = \text{phen}$, δ 33.3 (d, 1P) and 29.1 (d, 1P) ppm, $^2J(\text{P-P})$ 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 disappearing, leaving those of the *fac*

Fig. 2. Crystal structure of *fac*-Mo(CO)₃(η²-phen)(η¹-dppm).

The angle N(1)–Mo–N(2) is $73.0(3)^\circ$, 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 $\text{Mo}(\text{CO})_4(\eta^2\text{-NN})$ (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 $(\text{CH}_3)_4\text{Si}$ 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 $\text{Mo}(\text{CO})_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$. Procedure A. A solution of $\text{Mo}(\text{CO})_4(\eta^2\text{-phen})$ (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 $\text{Mo}(\text{CO})_4(\eta^2\text{-phen})$ (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. $\text{C}_{40}\text{H}_{30}\text{MoP}_2\text{N}_2\text{O}_3$ calcd.: C, 63.9; H, 4.50; N, 3.50%).

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

Preparation of $\text{Mo}(\text{CO})_3(\eta^2\text{-dmp})(\eta^1\text{-dppm})$. 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 $\text{C}_{42}\text{H}_{34}\text{MoP}_2\text{N}_2\text{O}_3$ 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

$$U_{eq} = \frac{1}{3} \sum [U_{ij} a_i^* a_j^* a_i a_j \cos(a_i a_j)] \times 10^4 \text{ for MoP}_2\text{N}_2\text{O}_3\text{C}_{40}\text{H}_{30}$$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{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 ₂ N ₂ O ₃ C ₄₀ H ₃₀
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	16.843(3)
<i>b</i> , Å	11.220(2)
<i>c</i> , Å	19.358(4)
β , °	111.72(2)
<i>V</i> , Å ³	3398(1)
ρ (calcd), g cm ^{−3}	1.46
temperature, °C	22
μ , cm ^{−1}	5.08
crystal dimensions, cm	0.04 × 0.02 × 0.02
diffractometer	Enraf–Nonius CAD4
radiation	graphite-monochromated Mo- <i>K</i> 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>I</i>) ≥ 3 σ (<i>I</i>)	3381
<i>R</i> (int), %	1.89
decay	≤ 5% variation
<i>R</i> _F , %	4.9
<i>R</i> w _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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