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The reactivity of a bis(μ-diphenylphosphido) dicyclopentadienyl dimolybdenum complex with an electron withdrawing ring substituent

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Abstract

The synthesis of $[(\eta^5\text{-}C_5H_4CO_2Me)_2Mo_2(CO)_6]$ (**1**), a bis(cyclopentadienyl) dimolybdenum complex with an electron withdrawing ring substituent, from the reaction of $Mo(CO)_6$ and $[Na(C_5H_4CO_2Me)]$ is described. Complex **1** reacts thermally with P_2Ph_4 to form the bis(μ-diphenylphosphido) complex $[(\eta^5\text{-}C_5H_4CO_2Me)_2Mo_2(\mu\text{-}PPh_2)_2(CO)_2]$ (**2**). Air oxidation of **2** gives *trans*-$[(\eta^5\text{-}C_5H_4CO_2Me)_2Mo_2(\mu\text{-}PPh_2)_2(O)(CO)]$ (**3a**) and the corresponding *cis*-isomer **3b**. The reactions of **3a** and of the corresponding unsubstituted cyclopentadienyl complex $[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}PPh_2)_2(O)(CO)]$ (**4**) with $[NO][BF_4]$, which yield respectively the nitrosyl substituted dimolybdenum complexes $[(\eta^5\text{-}C_5H_4CO_2Me)_2Mo_2(\mu\text{-}PPh_2)_2(O)(NO)][BF_4]$ (**5**) and $[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}PPh_2)_2(O)(NO)][BF_4]$ (**6**), are described. Single crystal X-ray diffraction was used to determine the molecular structures of **1** (which crystallises in the monoclinic space group $P2_1/c$ with $a=9.811$ (4), $b=12.109$ (2), $c=9.919$ (3) Å, $\beta=110.00$ (3)° and $Z=2$), **2** (which crystallises in the triclinic space group $P\bar{1}$, $a=13.364$ (4), $b=14.535$ (4), $c=10.576$ (2) Å, $\alpha=91.33$ (2), $\beta=94.94$ (2) $\gamma=108.92$ (2)° and $Z=2$) and **3a** (which crystallises in the monoclinic space group $P2_1/c$ with $a=12.436$ (2), $b=15.300$ (3), $c=20.395$ (4) Å, $\beta=111.59$ (3)° and $Z=4$).

Keywords: Crystal structures; Molybdenum complexes; Oxo complexes; Nitrosyl complexes; Dinuclear complexes

1. Introduction

We have previously reported that air oxidation of the bis(μ-diphenylphosphido) dicyclopentadienyl dimolybdenum complex $[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}PPh_2)_2(CO)_2]$ leads to replacement of one carbonyl ligand by a terminal oxo group to give a mixture of *cis*- and *trans*-$[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}PPh_2)_2(CO)(O)]$ [1]. It was not possible by this means to replace the remaining carbonyl group by a second oxo ligand. More recently we have shown that air oxidation of the alkyne bridged complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ ($R=R'=CO_2Me$ or Ph; $R=H$, $R'=Ph$ and $R=H$, $R'=CO_2Me$) in the presence of trimethylamine *N*-oxide leads to the new high oxidation state organometallic oxo complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}RCCR')]$ in which all the carbonyl ligands have been replaced by oxo groups [2]. These latter reactions are facilitated when the substituents on the bridging alkyne ligand are electron withdrawing in character, the highest yield of product being obtained when $R=R'=CO_2Me$.

In the light of this result it was of interest to determine whether or not the introduction of electron withdrawing substituent groups onto the cyclopentadienyl rings in the bis(μ-diphenylphosphido) complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}PPh_2)_2(CO)_2]$ might similarly facilitate oxidation of the complexes and perhaps lead to species in which both carbonyl groups have been substituted by oxo ligands. To this end we have now studied the reactivity of the complex $[(\eta^5\text{-}C_5H_4CO_2Me)_2Mo_2(\mu\text{-}PPh_2)_2(CO)_2]$ (**2**). The complex $[(\eta^5\text{-}C_5H_4CO_2Me)_2Mo_2(CO)_6]$ (**1**), required as a precursor to compound **2**, has not previously been reported and although the analogous species $[(\eta^5\text{-}C_5H_4CO_2Me)_2M_2(CO)_6]$ (M = Cr, W) [3,4] are known, their reactivity has not been investigated.

2. Results and discussion

2.1. Synthesis and X-ray characterisation of $[(\eta^5\text{-}C_5H_4CO_2Me)_2Mo_2(CO)_6]$ (1)

The substituted sodium cyclopentadienide $[Na(C_5H_4CO_2Me)]$ was prepared according to the method of Rausch and co-workers [5] and complex $[Cp^*{}_2Mo_2(CO)_6]$

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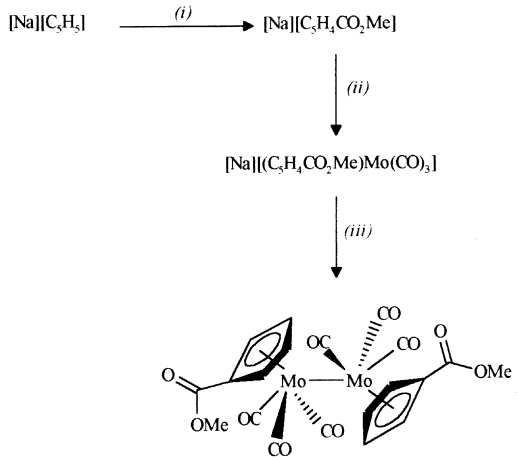


Scheme 1. Reagents and conditions: (*i*) $CO_3(CH_3)_2$ (1.5 equiv.), THF, 67°C, 6 h; (*ii*) $Mo(CO)_6$ (1 equiv.), THF, 67°C, 12 h; (*iii*) Fe(III), CH_3COOH, H_2O.

(Cp* = (η^5-$C_5H_4CO_2Me$)) (**1**) then synthesised by oxidation of the sodium salt Na[Cp*Mo(CO)$_3$] (Scheme 1) [6]. The IR spectrum of **1** in chloroform shows carbonyl absorptions at 2021, 1970 and 1924 cm^{-1}, with an additional absorption at 1724 cm^{-1} due to the substituent group on the cyclopentadienyl ring. In comparison, the carbonyl absorptions of the unsubstituted cyclopentadienyl complex [$Cp_2Mo_2(CO)_6$] (Cp = (η^5-C_5H_5)) are at significantly lower wavenumbers (1959, 1916, 1905 cm^{-1}) [6] clearly demonstrating the electron withdrawing properties of the cyclopentadienyl ring substituent. The ^1H and ^{13}C NMR spectra, FAB mass spectrum and microanalysis of **1** are in accord with the proposed formulation of the complex and are described in Section 3.

The molecular structure of **1** is shown in Fig. 1 with selected bond lengths and angles listed in Table 1 and final fractional atomic coordinates and equivalent thermal parameters listed in Table 2. The structure is similar to that of the unsubstituted analogue [1] with an *anti* disposition of the Cp* ligands, the molecule lying on a crystallographic inversion centre. The Mo–Mo bond length (3.2135(12) Å) in **1** shows a slight shortening relative to the metal–metal distance in the unsubstituted cyclopentadienyl complex (3.235(1) Å). Complex **1** is crystallographically isomorphous with the published tungsten analogue [4b], for which one metal–metal bond length was reported as 3.216(1) Å.

2.2. Synthesis and X-ray characterisation of [(η^5-$C_5H_4CO_2Me)_2Mo_2(\mu$-$PPh_2)_2(CO)_2$] (2)

The reaction of equimolar quantities of **1** and P_2Ph_4 in refluxing toluene, according to the procedure used for the analogous unsubstituted complex [1], gave on cooling a high yield of a greenish brown crystalline solid (Scheme 2). Spectroscopic characterisation of this complex, described in detail in Section 3, was consistent with the formulation [(η^5-$C_5H_4CO_2Me)_2Mo_2(\mu$-$PPh_2)_2(CO)_2$] (**2**); this was subsequently confirmed by X-ray analysis. Unlike the unsubstituted analogue which showed appreciable solubility only in dichloromethane, complex **2** is moderately soluble in most organic solvents. The electron withdrawing nature of the ring substituent is revealed by the IR spectrum of **2** in which a carbonyl absorption at 1875 cm^{-1} is observed, as compared to the reported value of 1855 cm^{-1} for the unsubstituted complex [(η^5-Cp)$_2$Mo$_2$(μ-PPh$_2$)$_2$(CO)$_2$].

Fig. 2 shows the molecular structure of **2** which consists of two crystallographically independent centrosymmetric molecules. The two molecules are shown in the same orientation to demonstrate that they are essentially the same, the sole difference between them being the configuration of the carbomethoxy cyclopentadienyl ring substituents. Selected bond lengths and angles are listed in Table 3, final fractional

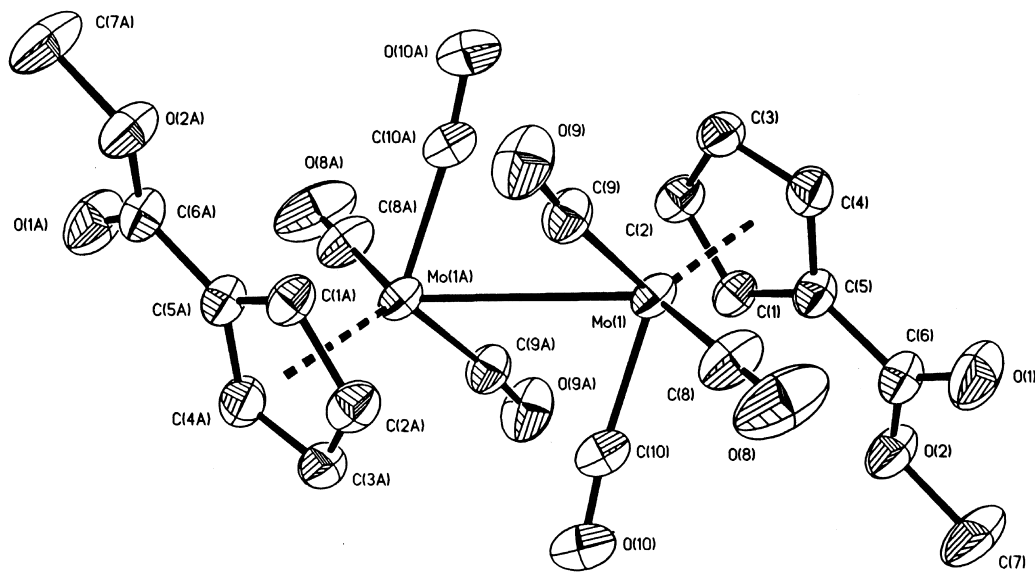


Fig. 1. ORTEP plot of the molecular structure of [(η^5-$C_5H_4CO_2Me)_2Mo_2(CO)_6$] (**1**) with thermal ellipsoids at 40% probability level. The atom numbering scheme used in Table 1 is defined.

Table 1
Selected bond lengths (Å) and angles (°) for [(η^5-$C_5H_4CO_2Me)_2Mo_2(CO)_6$] (**1**)

Mo(1)–Mo(1A)	3.2135(12)	C(3)–C(4)	1.418(8)
Mo(1)–C(8)	1.972(6)	C(4)–C(5)	1.435(7)
Mo(1)–C(9)	1.988(5)	C(1)–C(5)	1.417(7)
Mo(1)–C(10)	1.989(6)	C(8)–O(8)	1.141(7)
Mo(1)–C(1)	2.366(5)	C(9)–O(9)	1.149(6)
Mo(1)–C(2)	2.401(5)	C(10)–O(10)	1.150(7)
Mo(1)–C(3)	2.368(5)	C(5)–C(6)	1.488(7)
Mo(1)–C(4)	2.321(6)	C(6)–O(1)	1.200(7)
Mo(1)–C(5)	2.301(5)	C(6)–O(2)	1.335(7)
C(1)–C(2)	1.417(7)	C(7)–O(2)	1.455(7)
C(2)–C(3)	1.409(8)		
C(8)–Mo(1)–Mo(1A)	127.6(2)	C(8)–Mo(1)–C(1)	122.1(2)
C(9)–Mo(1)–Mo(1A)	71.4(2)	C(8)–Mo(1)–C(2)	144.7(3)
C(10)–Mo(1)–Mo(1A)	71.3(2)	C(8)–Mo(1)–C(3)	118.7(3)
C(1)–Mo(1)–Mo(1A)	103.82(13)	C(8)–Mo(1)–C(4)	87.8(3)
C(2)–Mo(1)–Mo(1A)	87.57(14)	C(8)–Mo(1)–C(5)	89.7(2)
C(3)–Mo(1)–Mo(1A)	105.75(14)	C(9)–Mo(1)–C(1)	151.4(2)
C(4)–Mo(1)–Mo(1A)	140.9(2)	C(9)–Mo(1)–C(2)	117.3(2)
C(5)–Mo(1)–Mo(1A)	139.14(14)	C(9)–Mo(1)–C(3)	95.3(2)
C(1)–C(5)–C(6)	127.6(5)	C(9)–Mo(1)–C(4)	106.1(2)
C(4)–C(5)–C(6)	123.8(5)	C(9)–Mo(1)–C(5)	141.4(2)
C(5)–C(6)–O(1)	124.6(5)	C(10)–Mo(1)–C(1)	97.5(2)
C(5)–C(6)–O(2)	110.8(5)	C(10)–Mo(1)–C(2)	121.2(2)
C(6)–O(2)–C(7)	116.4(5)	C(10)–Mo(1)–C(3)	154.6(2)
C(6)–C(5)–Mo(1)	121.2(4)	C(10)–Mo(1)–C(4)	140.5(2)
C(5)–C(1)–Mo(1)	69.8(3)	C(10)–Mo(1)–C(5)	106.2(2)
C(2)–C(1)–Mo(1)	74.1(3)	O(8)–C(8)–Mo(1)	179.0(6)
C(3)–C(2)–Mo(1)	71.6(3)	O(9)–C(9)–Mo(1)	173.6(5)
C(4)–C(3)–Mo(1)	70.6(3)	O(10)–C(10)–Mo(1)	174.0(5)
C(4)–C(5)–Mo(1)	72.7(3)		
C(8)–Mo(1)–C(9)	78.0(2)		
C(8)–Mo(1)–C(10)	78.7(2)		
C(9)–Mo(1)–C(10)	106.9(2)		

The atoms denoted 'A' are related to the equivalently numbered atoms by the symmetry operation $-x, -y, -z$.

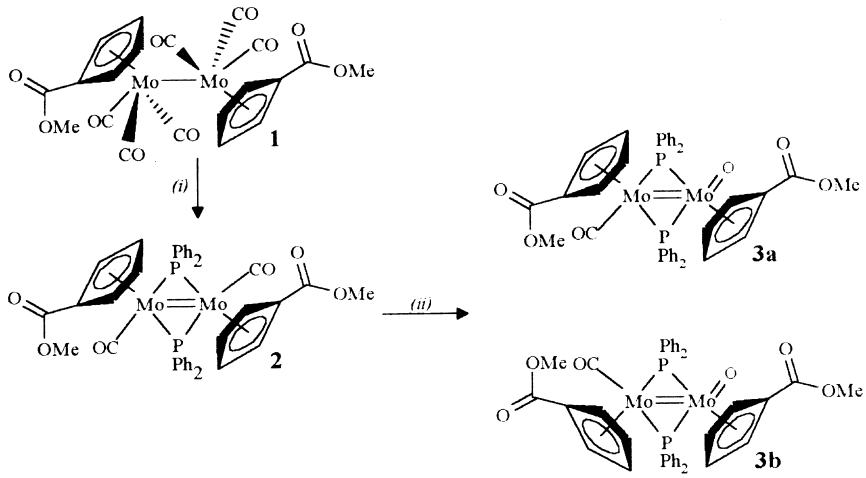
atomic coordinates and equivalent thermal parameters are listed in Table 4. The Mo_2P_2 core is planar, with the pairs of cyclopentadienyl ligands and carbonyl ligands lying in a *trans* configuration with respect to the plane. The molybdenum–molybdenum bond is symmetrically bridged by the PPh_2 groups, the separation between the metal atoms (2.7239(12) Å in molecule 1, Fig. 2 (a) and 2.7317(10) Å in molecule 2, Fig. 2 (b)) being consistent with the presence of the formal double bond required to satisfy the 18-electron rule. In comparison, the analogous unsubstituted complex [(η^5-$Cp)_2Mo_2(\mu$-$PPh_2)_2(CO)_2$] displays a slightly shorter bond length, 2.716(1) Å, the lengthening in **2** perhaps being a consequence of electron withdrawal from a metal–metal bonding orbital by the substituted cyclopentadienyl ligands.

2.3. Synthesis of trans- and cis-[(η^5-Cp)$_2$Mo$_2$(μ-PPh$_2$)$_2$-(CO)(O)] ((**3a**) and (**3b**)). X-ray characterisation of the trans-isomer **3a***

Air oxidation of [(η^5-$Cp)_2Mo_2(\mu$-$PPh_2)_2(CO)_2$] for 4 days at room temperature leads to replacement of a carbonyl ligand by a terminal oxo ligand and formation of the oxo complex [(η^5-$Cp)_2Mo_2(\mu$-$PPh_2)_2(CO)(O)$] [1]. Under the same conditions, it was found to be impossible to replace even one of the carbonyl ligands of **2**, but air purging of a solution of **2** in refluxing toluene for 8 h resulted in a good

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$\times 10^3$) for [(η^5-$C_5H_4CO_2Me)_2Mo_2(CO)_6$] (**1**)

	x	y	z	U_{eq}
Mo(1)	1417(1)	751(1)	256(1)	37(1)
O(1)	5288(6)	2125(4)	2084(5)	76(1)
C(1)	3356(5)	−526(4)	1003(5)	43(1)
O(2)	5295(5)	607(4)	3384(4)	62(1)
C(2)	2525(6)	−820(4)	−426(6)	48(1)
C(3)	2541(6)	66(5)	−1340(6)	50(1)
C(4)	3399(6)	927(5)	−499(6)	51(1)
C(5)	3894(6)	554(4)	962(6)	45(1)
C(6)	4880(6)	1204(5)	2180(6)	50(1)
C(7)	6323(9)	1128(7)	4644(8)	85(2)
C(8)	1671(7)	2323(5)	809(6)	58(2)
O(8)	1838(8)	3228(4)	1140(6)	101(2)
C(9)	−243(6)	1451(4)	−1257(6)	47(1)
O(9)	−1109(5)	1916(4)	−2160(5)	69(1)
C(10)	929(6)	742(4)	2045(6)	46(1)
O(10)	766(6)	778(4)	3139(5)	71(1)



Scheme 2. Reagents and conditions: (*i*) P_2Ph_4 (1 equiv.), toluene, 111°C, 4 h; (*ii*) air, toluene, 111°C, 8 h.

combined yield of the *trans*- and *cis*-isomers of the carbonyl–oxo complex $[(\eta^5\text{-Cp}^*)_2Mo_2(\mu\text{-PPh}_2)_2(CO)(O)]$ (**3a**) and (**3b**) (Scheme 2). The two non-interconverting isomers were easily separated by column chromatography, **3a** having a higher R_F value than **3b**. As in the case of the analogous unsubstituted cyclopentadienyl species, **3a** is formed in a much higher yield than **3b**, the ratio of **3a**:**3b** being approximately 30:1. Upon repeating the oxidation reaction of **2** in the presence of trimethylamine *N*-oxide it was found that **3a** and **3b** were formed in the same ratio but in considerably lower yield. Prolonged reflux of **3a** in toluene while purging with air, did not, as had been hoped, lead to replacement of the remaining CO group by a second oxo ligand and, in the presence of trimethylamine *N*-oxide, resulted in complete decomposition.

The IR spectra of **3a** and **3b** each show a single carbonyl ligand absorption (1842 and 1870 cm^{-1}, respectively) and two separate peaks for the ester group on the cyclopentadienyl ligand (1722, 1712 and 1718, 1711 cm^{-1}, respectively). The molecular ions of **3a** and **3b** were identical, as determined by FAB mass spectroscopy, and corresponded to $[(\eta^5\text{-}C_5H_4CO_2Me)_2Mo_2(\mu\text{-PPh}_2)_2(CO)(O)]^+$ at m/z 853 with a fragment ion peak at 28 mass units lower, arising from loss of the single carbonyl ligand. The ^1H NMR spectra of **3a** and **3b** showed the cyclopentadienyl rings to be inequivalent, each ring giving rise to two distinct resonances in the cyclopentadienyl region. Multiplet peaks characteristic of the phenyl protons on the phosphido bridges were also observed. The $^{31}P\{^1H\}$ spectra each showed a single peak, for **3a** at 27.9 ppm and for **3b** at 23.0 ppm (relative to $P(OMe)_3$ (0.0

Table 3
Selected bond lengths (Å) and angles (°) for $[(\eta^5\text{-}C_5H_4CO_2Me)_2Mo_2(\mu\text{-PPh}_2)_2(CO)_2]$ (**2**)

Mo(1)–Mo(1A)	2.7239(12)	Mo(2)–Mo(2A)	2.7317(10)	C(2)–C(3)	1.419(10)	C(22)–C(23)	1.410(9)
Mo(1)–P(1)	2.406(2)	Mo(2)–P(2)	2.401(2)	C(3)–C(4)	1.402(11)	C(23)–C(24)	1.394(10)
Mo(1)–P(1A)	2.399(2)	Mo(2)–P(2A)	2.402(2)	C(4)–C(5)	1.410(10)	C(24)–C(25)	1.393(10)
Mo(1) C(1)	1.935(6)	Mo(2)–C(21)	1.928(6)	C(5)–C(6)	1.431(9)	C(25)–C(26)	1.427(9)
Mo(1)–C(2)	2.345(6)	Mo(2)–C(22)	2.306(6)	C(2)–C(6)	1.425(9)	C(22)–C(26)	1.422(9)
Mo(1)–C(3)	2.380(6)	Mo(2)–C(23)	2.342(6)	C(6)–C(7)	1.469(9)	C(26)–C(27)	1.487(9)
Mo(1)–C(4)	2.366(7)	Mo(2)–C(24)	2.349(6)	C(7)–O(2)	1.197(8)	C(27)–O(5)	1.183(9)
Mo(1)–C(5)	2.290(7)	Mo(2)–C(25)	2.340(6)	C(1)–O(1)	1.155(7)	C(21)–O(4)	1.164(7)
Mo(1)–C(6)	2.282(6)	Mo(2)–C(26)	2.304(5)				
P(1)–C(9)	1.839(5)	P(2)–C(29)	1.837(6)				
P(1)–C(15)	1.833(6)	P(2)–C(35)	1.838(6)				
P(1)–Mo(1)–P(1A)	110.94	P(2)–Mo(2)–P(2A)	110.68(4)	Mo(1)–P(1)–Mo(1A)	69.06(5)	Mo(2)–P(2)–Mo(2A)	69.32(4)
P(1)–Mo(1)–C(2)	145.3(2)	P(2)–Mo(2)–C(22)	141.1(2)	Mo(1)–P(1)–C(9)	123.5(2)	Mo(2)–P(2)–C(29)	122.3(2)
P(1)–Mo(1)–C(3)	110.3(2)	P(2)–Mo(2)–C(23)	149.4(2)	Mo(1)–P(1)–C(15)	117.7(2)	Mo(2)–P(2)–C(35)	119.1(2)
P(1)–Mo(1)–C(4)	91.8(2)	P(2)–Mo(2)–C(24)	115.1(2)	Mo(1)–C(1)–O(1)	174.8(6)	Mo(2)–C(21)–O(4)	173.6(5)
P(1)–Mo(1)–C(5)	107.2(2)	P(2)–Mo(2)–C(25)	93.2(2)	C(9)–P(1)–C(15)	102.5	C(29)–P(2)–C(35)	103.5(3)
P(1)–Mo(1)–C(6)	143.6(2)	P(2)–Mo(2)–C(26)	105.6(2)	C(2)–C(6)–C(7)	124.0(6)	C(22)–C(26)–C(27)	122.6(6)
P(1)–Mo(1)–C(1)	85.0(2)	P(2)–Mo(2)–C(21)	85.8(2)	C(6)–C(7)–O(2)	123.6(7)	C(26)–C(27)–O(5)	124.2(6)
P(1)–Mo(1)–Mo(1A)	55.35(4)	P(2)–Mo(2)–Mo(2A)	55.36(4)				
C(1)–Mo(1)–Mo(1A)	79.1(2)	C(21)–Mo(2)–Mo(2A)	81.7(2)				
C(1)–Mo(1)–P(1A)	82.7(2)	C(21)–Mo(2)–P(2A)	84.8(2)				

The atoms denoted 'A' are related to the equivalently numbered atoms by the symmetry operation $-x, -y+1, -z+1$ in molecule 1 and $-x+1, -y, -z$ in molecule 2.

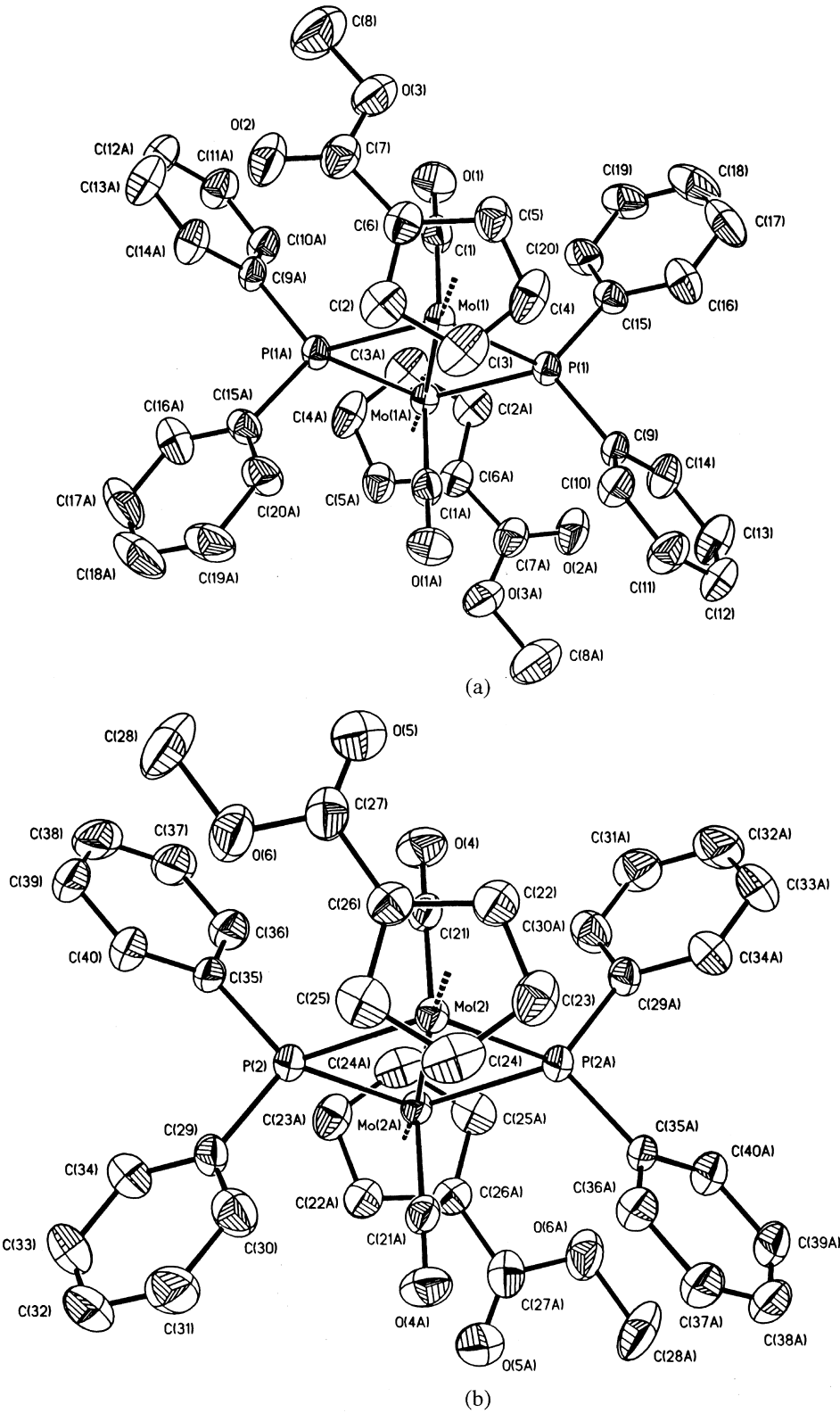


Fig. 2. ORTEP plot of the molecular structures of the two crystallographically independent molecules of [(η^5-$C_5H_4CO_2Me)_2Mo_2(\mu$-$PPh_2)_2(CO)_2$] (**2**) with thermal ellipsoids at 40% probability level, (a) molecule 1 and (b) molecule 2. The atom numbering scheme used in Table 3 is defined.

ppm)). From the spectroscopic data alone it was not possible to determine which isomer was which, although comparison with the data for the unsubstituted cyclopentadienyl analogues suggested that **3a** was *trans*-[(η^5-$Cp^*)_2Mo_2(\mu$-$PPh_2)_2(CO)(O)$] and **3b** the corresponding *cis*-isomer. An X-ray diffraction study of **3a** was undertaken in order to

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$\times 10^3$) for [(η^5-$C_5H_4CO_2Me)_2Mo_2(\mu$-$PPh_2)_2(CO)_2$] (**2**)

	x	y	z	U_{eq}
Mo(1)	274(1)	5989(1)	5092(1)	34(1)
Mo(2)	5178(1)	−18(1)	1289(1)	32(1)
P(1)	1430(1)	5112(1)	4511(1)	36(1)
P(2)	3640(1)	225(1)	196(1)	35(1)
O(1)	−699(4)	5619(4)	2296(4)	75(2)
C(1)	−331(5)	5714(5)	3339(6)	49(2)
C(2)	143(6)	7295(5)	6333(6)	55(2)
O(2)	−1694(4)	7612(4)	4914(6)	77(2)
C(3)	1199(6)	7289(5)	6605(7)	67(2)
O(3)	−916(4)	7608(5)	3129(5)	80(2)
C(4)	1718(5)	7455(5)	5494(8)	65(2)
O(4)	6311(4)	2191(3)	1152(4)	61(1)
C(5)	992(5)	7554(5)	4499(7)	57(2)
O(5)	5787(5)	1990(4)	4223(5)	79(2)
C(6)	12(5)	7463(4)	5016(6)	50(2)
O(6)	4047(4)	1231(4)	3951(5)	72(1)
C(7)	−960(6)	7569(5)	4371(7)	58(2)
C(8)	−1877(9)	7617(10)	2368(10)	123(4)
C(9)	2631(4)	5123(4)	5510(5)	39(1)
C(10)	2983(5)	5714(5)	6624(6)	52(2)
C(11)	3858(5)	5683(6)	7377(6)	62(2)
C(12)	4414(5)	5086(6)	7062(7)	63(2)
C(13)	4067(6)	4492(6)	5952(8)	72(2)
C(14)	3187(5)	4525(5)	5178(7)	55(2)
C(15)	1893(5)	5268(4)	2924(5)	45(1)
C(16)	2881(6)	5868(5)	2716(7)	64(2)
C(17)	3159(8)	6023(6)	1489(9)	84(3)
C(18)	2456(9)	5569(7)	467(8)	88(3)
C(19)	1479(8)	4957(6)	651(6)	71(2)
C(20)	1193(6)	4784(5)	1869(5)	56(2)
C(21)	5871(4)	1356(4)	1127(5)	40(1)
C(22)	6113(5)	213(5)	3272(5)	49(1)
C(23)	5914(6)	−770(5)	2879(6)	57(2)
C(24)	4816(6)	−1224(5)	2784(6)	60(2)
C(25)	4311(6)	−560(5)	3097(5)	54(2)
C(26)	5123(5)	356(4)	3406(5)	43(1)
C(27)	5045(6)	1296(6)	3890(6)	54(2)
C(28)	3951(8)	2157(7)	4413(8)	94(3)
C(29)	2307(4)	−686(4)	145(5)	42(1)
C(30)	2158(5)	−1589(5)	640(6)	56(2)
C(31)	1162(6)	−2277(6)	565(8)	69(2)
C(32)	298(6)	−2095(7)	−11(9)	83(3)
C(33)	433(6)	−1203(7)	−519(9)	86(3)
C(34)	1430(5)	−506(6)	−449(7)	64(2)
C(35)	3400(4)	1386(4)	466(5)	41(1)
C(36)	3967(5)	2213(5)	−84(6)	55(2)
C(37)	3822(6)	3095(5)	179(8)	70(2)
C(38)	3115(8)	3163(7)	994(10)	88(3)
C(39)	2537(6)	2345(7)	1570(9)	78(3)
C(40)	2687(5)	1465(5)	1314(7)	59(2)
C(01)	1285(23)	134(22)	4509(11)	160(11)
Cl(1)	918(18)	−377(16)	3093(17)	167(9)
Cl(2)	514(16)	−61(15)	5658(18)	147(7)
Cl(1′)	222(14)	120(15)	3593(18)	209(8)
Cl(2′)	1123(11)	−114(9)	5984(10)	123(4)

Site occupancy factors: C(01) = 0.50; Cl(1), Cl(2) = 0.20; Cl(1′), Cl(2′) = 0.30.

confirm its configuration and to compare its structure with that of complex **2** and the unsubstituted analogue [(η^5-$Cp)_2Mo_2(\mu$-$PPh_2)_2(CO)(O)$].

The molecular structure of **3a** is shown in Fig. 3 with selected bond lengths and angles listed in Table 5 and final fractional atomic coordinates and equivalent thermal parameters listed in Table 6. The structure is similar to that of the unsubstituted analogue possessing a *trans* arrangement of η^5-cyclopentadienyl ligands as predicted [1]. The oxo ligand is bonded to Mo(1), which is formally in oxidation state IV, while Mo(2), bonded to the carbonyl ligand, is formally in oxidation state II. The metal–metal bond is asymmetrically bridged by the two μ-PPh_2 groups, with Mo(1)–P distances of 2.455(2) and 2.454(2) Å compared to the correspondingly shorter Mo(2)–P distances of 2.341(2) and 2.336(2) Å. The bridging phosphido ligands may be positioned more closely to Mo(2) because the π back-donation from Mo(2) to the empty phosphorus d orbitals is enhanced relative to that from Mo(1) which is in a higher oxidation state. The separation between the molybdenum atoms in **3a** (2.9265(11) Å) has increased with respect to **2** (2.7243(13) Å), but is slightly shorter than that observed for the unsubstituted analogue (2.942(1) Å). The (η^5-$C_5H_4CO_2Me$) ring attached to Mo(1), the metal atom bonded to oxygen, is coordinated asymmetrically. Three of the Mo(1)–C distances (Mo(1)–C(10) 2.369(8) Å, Mo(1)–C(11) 2.369(8) Å, Mo(1)–C(14) 2.382(8) Å) are significantly shorter than the remaining two distances (Mo(1)–C(12) 2.450(8) Å, Mo(1)–C(13) 2.470(8) Å). This (η^3,η^2) mode of coordination has previously been observed in complexes of similar structure [1,7]. The distortion is attributed to the electronic effects of the strongly π-donating oxo ligand which lies *trans* to C(12)–C(13) and exerts a labilising *trans* effect [8].

2.4. Synthesis of [(η^5-Cp*)$_2$Mo$_2$(μ-PPh$_2$)$_2$(NO)(O)][BF$_4$] (5) and [(η^5-Cp)$_2$Mo$_2$(μ-PPh$_2$)$_2$(NO)(O)][BF$_4$] (6)

It was of interest to determine whether it was possible to replace the remaining carbonyl group in complex **3** by any other ligand. The *trans* complex **3a** was investigated because the yield of the *cis* complex **3b** was very low. For comparative purposes, the reactions were also carried out on *trans*-[(η^5-$Cp)_2Mo_2(\mu$-$PPh_2)_2(CO)(O)$] (**4**) since the possibility of replacing the CO group in **4** with other ligands was not explored in the original investigation [1]. Separate toluene solutions of **3a** were refluxed in the presence of each of the two-electron donor ligands $P(OMe)_3$, PPh_3, Bu^tNC for several days, but the IR and NMR spectra of the reaction solutions showed only unreacted **3a** to be present. Under the same reaction conditions **4** behaved in an identical manner, yielding only starting material and insoluble decomposition products. The IR carbonyl absorptions of **3a** and **4** (1842 and 1826 cm^{-1}, respectively) indicate a strong degree of π back-donation to the sole carbonyl group in each case, this presumably accounting for the resistance to substitution. It appears

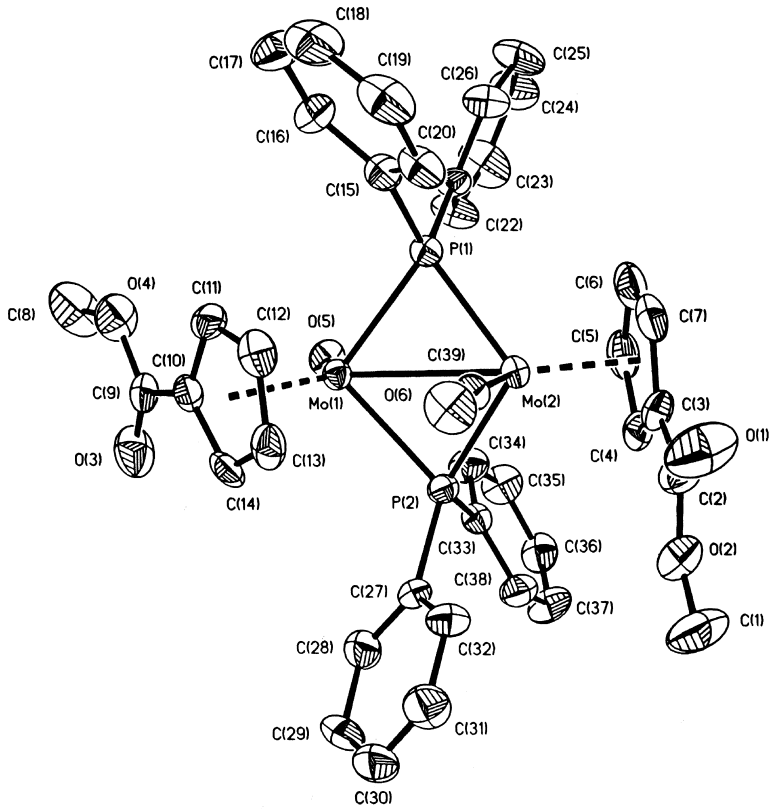


Fig. 3. ORTEP plot of the molecular structure of *trans*-[(η^5-$C_5H_4CO_2Me)_2Mo_2(\mu$-$PPh_2)_2(CO)(O)$] (**3a**) with thermal ellipsoids at 40% probability level. The atom numbering scheme used in Table 5 is defined.

Table 5
Selected bond lengths (Å) and angles (°) for *trans*-[(η^5-$C_5H_4CO_2Me)_2Mo_2(\mu$-$PPh_2)_2(CO)(O)$] (**3a**)

Mo(1)–C(13)	2.470(8)	Mo(2)–C(6)	2.359(9)	P(1)–C(21)	1.829(7)	P(2)–C(33)	1.838(8)
Mo(1)–C(14)	2.382(8)	Mo(2)–C(7)	2.314(8)	C(10)–C(11)	1.419(12)	C(3)–C(4)	1.441(12)
Mo(1)–O(5)	1.702(5)	Mo(2)–C(39)	1.954(9)	C(11)–C(12)	1.416(12)	C(4)–C(5)	1.400(13)
Mo(1)–Mo(2)	2.9265(11)	C(39)–O(6)	1.165(10)	C(12)–C(13)	1.404(13)	C(5)–C(6)	1.411(14)
				C(13)–C(14)	1.424(12)	C(6)–C(7)	1.389(13)
				C(10)–C(14)	1.440(12)	C(3)–C(7)	1.400(13)
P(1)–Mo(1)–Mo(2)	50.64(5)	P(2)–Mo(1)–Mo(2)	50.53(5)	C(10)–Mo(1)–O(5)	91.0(3)	O(6)–C(39)–Mo(2)	175.7(8)
P(1)–Mo(2)–Mo(1)	54.19(6)	P(2)–Mo(2)–Mo(1)	54.19(6)	C(11)–Mo(1)–O(5)	107.3(3)	C(15)–P(1)–Mo(1)	116.5(3)
P(1)–Mo(1)–P(2)	100.39(8)	P(2)–Mo(2)–P(1)	107.50(8)	C(12)–Mo(1)–O(5)	141.4(3)	C(15)–P(1)–Mo(2)	126.7(3)
Mo(1)–P(1)–Mo(2)	75.17(7)	Mo(1)–P(2)–Mo(2)	75.28(7)	C(13)–Mo(1)–O(5)	144.2(3)	C(21)–P(1)–Mo(1)	117.5(3)
O(5)–Mo(1)–P(1)	101.0(2)	C(39)–Mo(2)–P(1)	92.2(3)	C(14)–Mo(1)–O(5)	110.4(3)	C(21)–P(1)–Mo(2)	117.8(3)
O(5)–Mo(1)–P(2)	101.9(2)	C(39)–Mo(2)–P(2)	94.0(2)	C(4)–C(3)–C(2)	128.0(9)	C(15)–P(1)–C(21)	102.4(4)
O(5)–Mo(1)–Mo(2)	115.4(2)	C(39)–Mo(2)–Mo(1)	86.9(2)	C(7)–C(3)–C(2)	125.1(8)	C(27)–P(2)–Mo(1)	117.5(3)
C(10)–Mo(1)–Mo(2)	153.6(2)	C(3)–Mo(2)–Mo(1)	164.3(2)	C(3)–C(2)–O(1)	123.8(10)	C(27)–P(2)–Mo(2)	127.8(3)
C(11)–Mo(1)–Mo(2)	128.5(2)	C(4)–Mo(2)–Mo(1)	133.9(2)	C(3)–C(2)–O(2)	114.3(9)	C(33)–P(2)–Mo(1)	115.7(3)
C(12)–Mo(1)–Mo(2)	98.9(2)	C(5)–Mo(2)–Mo(1)	121.8(2)	C(2)–O(2)–C(1)	116.8(9)	C(33)–P(2)–Mo(2)	116.6(3)
C(13)–Mo(1)–Mo(2)	97.1(2)	C(6)–Mo(2)–Mo(1)	132.3(3)	O(1)–C(2)–O(2)	122.0(10)	C(27)–P(2)–C(33)	102.9(4)
C(14)–Mo(1)–Mo(2)	124.7(2)	C(7)–Mo(2)–Mo(1)	160.2(3)	C(11)–C(10)–C(9)	129.0(8)	C(9)–O(4)–C(8)	116.8(9)
C(10)–Mo(1)–P(1)	129.1(2)	C(3)–Mo(2)–P(1)	141.3(2)	C(14)–C(10)–C(9)	123.5(8)	O(3)–C(9)–O(4)	125.2(9)
C(11)–Mo(1)–P(1)	95.1(2)	C(4)–Mo(2)–P(1)	140.1(3)	C(10)–C(9)–O(3)	124.4(9)		
C(12)–Mo(1)–P(1)	87.0(2)	C(5)–Mo(2)–P(1)	105.5(3)	C(10)–C(9)–O(4)	110.3(8)		
C(13)–Mo(1)–P(1)	111.5(2)	C(6)–Mo(2)–P(1)	88.1(3)				
C(14)–Mo(1)–P(1)	143.2(2)	C(7)–Mo(2)–P(1)	106.1(3)				
C(10)–Mo(1)–P(2)	125.3(2)	C(3)–Mo(2)–P(2)	110.2(2)				
C(11)–Mo(1)–P(2)	143.5(2)	C(4)–Mo(2)–P(2)	87.5(2)				
C(12)–Mo(1)–P(2)	113.8(2)	C(5)–Mo(2)–P(2)	101.8(3)				
C(13)–Mo(1)–P(2)	87.0(2)	C(6)–Mo(2)–P(2)	136.3(3)				
C(14)–Mo(1)–P(2)	91.7(2)	C(7)–Mo(2)–P(2)	144.5(3)				

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$\times 10^3$) for *trans*-[(η^5-$C_5H_4CO_2Me)_2Mo_2(\mu$-$PPh_2)_2(CO)(O)$] (**3a**)

	x	*y*	*z*	U_{eq}
Mo(1)	9485(1)	2345(1)	9855(1)	29(1)
Mo(2)	8129(1)	2514(1)	10756(1)	29(1)
P(1)	10149(2)	2480(1)	11143(1)	31(1)
P(2)	7404(2)	2132(1)	9563(1)	31(1)
O(1)	5881(7)	3972(6)	11249(5)	99(3)
O(2)	4896(6)	3098(5)	10380(4)	70(2)
O(3)	10301(7)	1894(5)	8192(4)	74(2)
O(4)	11959(6)	2144(5)	9101(4)	67(2)
O(5)	9932(5)	1313(4)	9772(3)	42(1)
O(6)	7997(6)	4520(4)	10471(4)	59(2)
C(1)	4040(10)	3803(9)	10092(8)	97(4)
C(2)	5790(9)	3281(7)	10946(6)	54(3)
C(3)	6648(7)	2578(5)	11179(5)	42(2)
C(4)	6606(8)	1727(6)	10867(5)	48(2)
C(5)	7611(9)	1281(6)	11278(5)	52(3)
C(6)	8283(10)	1838(7)	11826(5)	59(3)
C(7)	7690(9)	2623(6)	11761(5)	52(2)
C(8)	12573(12)	1490(9)	8833(7)	101(5)
C(9)	10831(8)	2250(6)	8732(5)	46(2)
C(10)	10341(8)	2892(5)	9075(4)	39(2)
C(11)	10877(8)	3322(5)	9732(5)	42(2)
C(12)	10046(9)	3877(5)	9841(5)	48(2)
C(13)	8989(9)	3783(6)	9272(5)	50(2)
C(14)	9145(8)	3154(6)	8800(4)	45(2)
C(15)	11141(8)	3381(5)	11542(4)	41(2)
C(16)	12296(8)	3372(7)	11611(5)	56(3)
C(17)	13036(10)	4068(8)	11896(6)	76(4)
C(18)	12605(13)	4767(8)	12150(6)	86(5)
C(19)	11502(12)	4790(7)	12110(5)	70(3)
C(20)	10742(9)	4103(5)	11802(5)	52(3)
C(21)	10898(7)	1542(5)	11671(4)	34(2)
C(22)	10725(9)	704(5)	11411(5)	53(3)
C(23)	11187(11)	−8(6)	11855(6)	76(4)
C(24)	11796(10)	116(7)	12555(6)	68(3)
C(25)	11938(10)	940(7)	12831(5)	68(3)
C(26)	11527(8)	1650(6)	12392(5)	55(3)
C(27)	6408(7)	2760(6)	8819(4)	38(2)
C(28)	6176(8)	2507(6)	8128(5)	52(2)
C(29)	5393(9)	2977(8)	7572(5)	63(3)
C(30)	4835(9)	3689(7)	7708(6)	66(3)
C(31)	5090(9)	3953(6)	8385(6)	60(3)
C(32)	5859(8)	3484(6)	8946(5)	47(2)
C(33)	6879(7)	1005(5)	9351(4)	33(2)
C(34)	7618(9)	289(6)	9584(5)	52(2)
C(35)	7176(9)	−561(6)	9502(5)	56(3)
C(36)	6012(9)	−703(6)	9168(5)	55(3)
C(37)	5283(9)	−10(7)	8945(6)	62(3)
C(38)	5704(8)	830(6)	9025(5)	50(2)
C(39)	8082(7)	3768(6)	10567(4)	39(2)

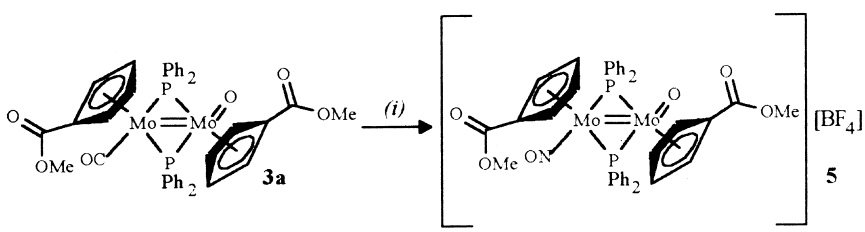
that the electron withdrawing substituent on the cyclopentadienyl rings does not significantly increase the ease of substitution of the carbonyl group of complex **3a** as compared to the unsubstituted analogue **4**.

However, when **3a** and **4** were treated with [NO][BF_4] at room temperature, a substitution reaction occurred almost instantaneously in each case, with the CO ligand being replaced by NO^+ to give a near quantitative yield of [(η^5-Cp*)$_2Mo_2(\mu$-$PPh_2)_2(NO)(O)$][BF_4] (**5**) and [(η^5-Cp)$_2Mo_2(\mu$-$PPh_2)_2(NO)(O)$][BF_4] (**6**), respectively (Scheme 3). There are relatively few known examples of dimolybdenum nitrosyl complexes [9] and, to our knowledge, the recently reported complexes [$Mo_2(\mu$-H)(μ-$Ph_2P(CH_2)_nPPh_2)(CO)_7(NO)$] ($n$=1–4) [10] are the only other dimolybdenum nitrosyls to be prepared by the use of [NO][BF_4]. The oxo- and nitrido-bridged species [(η^5-C_5Me_5)Mo(NO)(CH_2SiMe_3)]$_2(\mu$-O) [11] and [(η^5-C_5Me_5)Mo(NO)(CH_2SiMe_3)](μ-N)[(η^5-C_5Me_5)Mo(O)-(CH_2SiMe_3)] [12] are the only other reported dimolybdenum complexes containing both nitrosyl and oxo ligands.

Complexes **5** and **6** were fully characterised spectroscopically, as described in Section 3 and a single crystal of **6** was grown in an attempt to determine the molecular structure of **6** by X-ray diffraction. The crystallographic data obtained could not be fully refined due to the disorder within the structure but confirmed the proposed atom arrangement [13].

Complex **5** displays no carbonyl ligand absorptions in its IR spectrum, although there is a peak at 1730 cm^{-1} due to the ester group of the substituted cyclopentadienyl ligand, and a single NO stretching frequency at 1701 cm^{-1}. Complex **6** displays a single nitrosyl absorption at 1692 cm^{-1}. The ^1H NMR spectrum of each complex reveals the inequivalence of the cyclopentadienyl ligands, while the $^{31}P\{^1H\}$ spectra for **5** and **6** each show a single peak at 37.1 and 36.0 ppm, respectively, due to the equivalent diphenylphosphido bridges. The ^{19}F NMR of each complex shows a broad single peak at −152.8 ppm which confirms the presence of the [BF_4]$^-$ anion, while the FAB mass spectra, run in positive ion mode, display molecular ion signals for the cations only, at m/z 855 and 739 for **5** and **6**, respectively.

In conclusion, the above reactions show that the introduction of electron withdrawing substituents onto the cyclopentadienyl rings in **2** does not facilitate the displacement of the carbonyl groups by other ligands. Indeed, the presence of the carbomethoxy groups as ring substituents renders the displacement of a carbonyl group by an oxo ligand more difficult. The exchange of carbonyl ligands in [$Co_2(CO)_6$-



Scheme 3. Reagents and conditions: (*i*) $NOBF_4$ (excess), CH_2Cl_2, r.t.

(RCCR′)] has previously been shown to be slowed when R is an electron withdrawing substituent [14]. This was attributed to the strengthening of the metal–alkyne bond with cleavage of this bond being involved in the rate determining step. It may be that the metal–cyclopentadienyl bond is similarly strengthened by the electron withdrawing substituent on the ring and that this slows the oxidation of **2** to **3a** and **3b**, relative to the unsubstituted analogue described previously [1]. Alternatively, the increased steric bulk of the ring may adversely influence the rate of reaction.

3. Experimental

Except where stated, all reactions were carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled under nitrogen, from appropriate drying agents, and degassed prior to use. All reagents were obtained from commercial suppliers and used without further purification. The compounds *trans*-[(η^5-$C_5H_5)_2Mo_2(\mu$-$PPh_2)_2$-(CO)(O)] (**4**) and P_2Ph_4 were prepared by literature methods [1,15]. Column chromatography was performed on Kieselgel 60 (70–230 or 230–400 mesh). Products are given in order of decreasing R_F values.

The instrumentation used to obtain spectroscopic data has been described previously [16]. ^{1}H, ^{13}C and ^{31}P NMR were recorded in $CDCl_3$ at 293 K. The solvent resonance was used as internal standard, except for ^{31}P where chemical shifts are given relative to $P(OMe)_3$ with upfield shifts negative and ^{19}F where chemical shifts are given relative to $CFCl_3$. The ^{13}C and ^{31}P spectra were ^{1}H gated decoupled.

*3.1. Synthesis of [(η^5-$C_5H_4CO_2Me)_2Mo_2(CO)_6$] (**1**) by a modification of literature procedures [5,6]*

Freshly cracked cyclopentadiene (18 ml, 210 mmol, excess) was added to sodium sand (1.75 g, 76 mmol) in THF, and stirred for 1 h until complete reaction had occurred. Dimethyl carbonate (9.45 ml, 115 mmol) was added to the solution, which was then refluxed for 6 h. $Mo(CO)_6$ (20 g, 76 mmol) was added, and refluxing continued for further 12 h. The reaction mixture was then cooled to room temperature and a solution of $Fe_2(SO_4)_3 \cdot 9H_2O$ (17 g, 30 mmol) and acetic acid (10 ml) in water (250 ml) added dropwise with stirring. The purple–red precipitate was filtered and washed succesively with water (200 ml), cold methanol (20 ml) and hexane (20 ml), then dried overnight in vacuo to yield [(η^5-$C_5H_4CO_2Me)_2Mo_2(CO)_6$] (**1**) (17.6 g, 77%). Analytically pure samples were prepared by recrystallisation from dichloromethane at −4°C. *Anal*. Found: C, 39.4; H, 2.2. Calc. for $C_{20}H_{14}Mo_2O_{10}$: C, 39.6; H, 2.3%. IR (ν_{max}($CHCl_3$) cm^{-1}): (CO) 2021(sh), 1970(vs), 1924(vs) and 1724(s). ^{1}H NMR (400 MHz): δ 3.76 (6H, s, CO_2CH_3), 5.26 (4H, s, $C_5H_4CO_2Me$), 5.83 (4H, s, $C_5H_4CO_2Me$). ^{13}C NMR (400 MHz): δ 231.3 (2C, s, CO), 224.9 (2C, s, CO), 201.0 (2C, s, CO), 165.1 (2C, s, $C_5H_4CO_2Me$), 97.3 (4C, s, $C_5H_4CO_2Me$), 96.3 (2C, s, $C_5H_4CO_2Me$), 94.9 (4C, s, $C_5H_4CO_2Me$), 52.3 (2C, s, $C_5H_4CO_2CH_3$). FAB-MS: m/z 607 [(M^+)+1], 578 [(M^+)−CO], 550 [(M^+)−2CO], 522 [(M^+)−3CO], 494 [(M^+)−4CO], 466 [(M^+)−5CO] and 438 [(M^+)−6CO].

*3.2. Synthesis of [(η^5-$C_5H_4CO_2Me)_2Mo_2(\mu$-$PPh_2)_2(CO)_2$] (**2**)*

P_2Ph_4 was prepared in situ from PPh_2H (1.8 ml, 10.3 mmol) and PPh_2Cl (1.85 ml, 10.3 mmol). In order to ensure a slight excess of the ligand in the subsequent reaction, a yield of 80% was assumed, although in practice it is essentially quantitative. To the solution of P_2Ph_4 in toluene (150 ml) was added **1** (5 g, 8.25 mmol) and the mixture refluxed for 4 h. On cooling to room temperature a greenish brown solid was precipitated, collected by filtration and washed with hexane (50 ml). The solvent was removed from the combined filtrate and washings and redissolved in the minimum of dichloromethane. Silica was added (10 g), the dichloromethane removed in vacuo, and the silica loaded onto a silica chromatography column. Elution with hexane–dichloromethane (2:1) gave an orange band due to [(η^5-$C_5H_4CO_2Me)_2$-$Mo_2(\mu$-$PPh_2)(\mu$-H)$(CO)_4$] (0.29 g, 5%) and then a green–brown band due to **2**. The latter band was collected, the solvent removed, and the solid added to that already obtained by filtration, yielding [(η^5-$C_5H_4CO_2Me)_2Mo_2(\mu$-$PPh_2)_2$-$(CO)_2$] (**2**) (4.5 g, 63%). Analytically pure samples were prepared by recrystallisation from hexane–dichloromethane 1:1 at −4°C. *Anal*. Found: C, 55.45; H, 3.9; P, 7.8. Calc. for $C_{40}H_{34}Mo_2O_6P_2$: C, 55.6; H, 4.0; P, 7.9%. IR (ν_{max}($CHCl_3$) cm^{-1}): (CO) 1875(vs) and 1717(s). ^{1}H NMR (400 MHz): δ 3.19 (6H, s, CO_2CH_3), 5.65 (4H, t, J(PH) = 1.9 Hz, $C_5H_4CO_2Me$), 5.84 (4H, t, J(PH) = 2.2 Hz, $C_5H_4CO_2Me$), 7.55–7.23 (20H, m, C_6H_5). ^{13}C NMR (400 MHz): δ 208.8 (2C, s, CO), 165.9 (2C, s, $C_5H_4CO_2Me$), 143.5 (4C, d, J(PC) = 42.7 Hz, C_6H_5), 133.2–127.5 (20C, m, C_6H_5), 94.9 (4C, s, $C_5H_4CO_2Me$) 89.8 (4C, s, $C_5H_4CO_2Me$), 89.4 (2C, s, $C_5H_4CO_2Me$), 52.3 (2C, s, $C_5H_4CO_2CH_3$). ^{31}P NMR (250 MHz): δ −50.1 (2P, s, μ-PPh_2). FAB-MS: m/z 865 [(M^+)+1], 836 [(M^+)−CO] and 808 [(M^+)−2CO].

3.3. Synthesis of [(η^5-Cp)$_2Mo_2(\mu$-$PPh_2)_2(CO)(O)$] (**3a**) and (**3b**)*

Complex **2** (1 g, 1.3 mmol) was dissolved in toluene (150 ml) and refluxed for 8 h whilst purging gently with compressed air. Solvent was removed, the residue dissolved in the minimum of dichloromethane, and silica added (2 g). The dichloromethane was evaporated in vacuo and the silica loaded onto a chromatography column. Elution with hexane–dichloromethane (2:1) gave trace quantities of starting material **2**, then a purple band which was collected. The solvent was removed in vacuo, yielding crystalline *trans*-[(η^5-Cp*)$_2Mo_2(\mu$-$PPh_2)_2$(CO)(O)] (**3a**) (0.69 g, 71%). *Anal*. Found: C, 55.7; H, 3.95; P, 7.2. Calc. for $C_{39}H_{34}Mo_2O_6P_2$:

C, 54.9; H, 4.0; P, 7.3%. IR (ν_{max}($CHCl_3$) cm^{-1}): (CO) 1842(vs), 1722(s) and 1712(s). ^1H NMR (400 MHz): δ 3.01 (2H, s, $C_5H_4CO_2Me$), 3.71 (3H, s, CO_2CH_3), 3.79 (3H, s, CO_2CH_3), 4.41 (2H, s, $C_5H_4CO_2Me$), 5.45 (2H, s, $C_5H_4CO_2Me$), 6.93 (2H, s, $C_5H_4CO_2Me$), 7.16–8.10 (20H, m, C_6H_5). ^{13}C NMR (400 MHz): δ 235.6 (1C, s, CO), 167.5 (1C, s, $C_5H_4CO_2Me$), 162.0 (1C, s, $C_5H_4CO_2Me$), 147.2 (2C, d, J(PC) = 34.1 Hz, C_6H_5), 141.1 (2C, d, J(PC) = 43.0 Hz, C_6H_5), 134.9–127.6 (20C, m, C_6H_5), 110.4 (1C, s, $C_5H_4CO_2Me$) 100.1(1C, s, $C_5H_4CO_2Me$), 94.85 (2C, s, $C_5H_4CO_2Me$), 92.4 (2C, s, $C_5H_4CO_2Me$), 91.0 (2C, s, $C_5H_4CO_2Me$), 89.8 (2C, s, $C_5H_4CO_2Me$), 52.4 (1C, s, $C_5H_4CO_2CH_3$), 51.3 (1C, s, $C_5H_4CO_2CH_3$). ^{31}P NMR (250 MHz): δ 27.9 (2P, s, μ-PPh_2). FAB-MS: m/z 853 [$(M^+)+1$] and 824 [$(M^+)-CO$]. Further elution with ethyl acetate–hexane (1:1) gave another purple band which, on removal of solvent, afforded *cis*-[$(\eta^5$-$Cp^*)_2Mo_2(\mu$-$PPh_2)_2(CO)(O)$] (**3b**) (0.025 g, 2.5%). *Anal*. Found: C, 55.65; H, 4.0; P, 7.3. Calc. for $C_{39}H_{34}Mo_2O_6P_2$: C, 54.9; H, 4.0; P, 7.3%. IR (ν_{max}($CHCl_3$) cm^{-1}): (CO) 1870(vs), 1718(s) and 1711(s) ($CHCl_3$). ^1H NMR (400 MHz): δ 3.25 (2H, s, $C_5H_4CO_2Me$), 3.76 (3H, s, CO_2CH_3), 3.80 (3H, s, CO_2CH_3), 4.72 (2H, s, $C_5H_4CO_2Me$), 5.67 (2H, s, $C_5H_4CO_2Me$), 6.64 (2H, s, $C_5H_4CO_2Me$), 7.0–7.78 (20H, m, C_6H_5). ^{13}C NMR (400 MHz): δ 232.6 (1C, s, CO), 166.3 (1C, s, $C_5H_4CO_2Me$), 161.2 (1C, s, $C_5H_4CO_2Me$), 146.1 (2C, d, J(PC) = 30.9 Hz, C_6H_5), 139.8 (2C, d, J(PC) = 41.2 Hz, C_6H_5), 132.0–127.3 (20C, m, C_6H_5), 108.4 (1C, s, $C_5H_4CO_2Me$) 97.8 (1C, s, $C_5H_4CO_2Me$), 93.2 (2C, s, $C_5H_4CO_2Me$), 91.1 (2C, s, $C_5H_4CO_2Me$), 90.5 (2C, s, $C_5H_4CO_2Me$), 88.8 (2C, s, $C_5H_4CO_2Me$), 50.7 (1C, s, $C_5H_4CO_2CH_3$), 49.1 (1C, s, $C_5H_4CO_2CH_3$). ^{31}P NMR (250 MHz): δ 23.0 (2P, s, μ-PPh_2). FAB-MS: m/z 853 [$(M^+)+1$] and 824 [$(M^+)-CO$].

3.4. Synthesis of [(η^5-Cp*)$_2$Mo$_2$(μ-PPh$_2$)$_2$(CO)(O)] ((**3a**) and (**3b**)) by air oxidation of **2** in the presence of trimethylamine N-oxide

Complex **2** (1 g, 1.3 mmol) was dissolved in toluene (150 ml), excess trimethylamine *N*-oxide (0.26 g, 3.9 mmol) added and the mixture refluxed for 1 h whilst purging gently with compressed air. After this time the reaction mixture had turned blue in colour indicating that considerable decomposition had occurred. Solvent was removed, the residue dissolved in the minimum of dichloromethane, and silica added (2 g). The dichloromethane was evaporated in vacuo and the silica loaded onto a chromatography column. Elution with hexane–dichloromethane (2:1) gave a purple band which was collected and identified as *trans*-[$(\eta^5$-$Cp^*)_2Mo_2(\mu$-$PPh_2)_2(CO)(O)$] (**3a**) (0.26 g, 26%) by comparison with the fully characterised products from Section 3.3. Further elution with ethyl acetate–hexane (1:1) gave a trace of a purple band which, on removal of solvent, afforded *cis*-[$(\eta^5$-$Cp^*)_2Mo_2(\mu$-$PPh_2)_2(CO)(O)$] (**3b**) (0.009 g, 0.9%), identified by comparison with the products from Section 3.3.

3.5. Further thermolysis reactions of trans-[(η^5-Cp*)$_2$-Mo$_2$(μ-PPh$_2$)$_2$(CO)(O)] (**3a**) with O$_2$, P(OMe)$_3$, PPh$_3$ and Bu^{t}NC

3a (0.29 g, 0.33 mmol) was dissolved in toluene (50 ml) and refluxed for 18 h (111°C) while purging gently with compressed air. Spot TLC throughout the reaction showed that no new products were formed, and that the starting material was gradually decomposing. The procedure was repeated separately, under nitrogen, with trimethyl phosphite (0.11 ml, 1 mmol, excess); triphenyl phosphine (0.26 g, 1 mmol, excess) and tert-butyl isocyanide (0.11ml, 1 mmol, excess) refluxing each solution for several days. A little decomposition of **3a** was observed by spot TLC but no new products were formed. The reflux of **3a** (0.25 g, 0.3 mmol) in toluene (50 ml) was repeated in the presence of excess trimethylamine *N*-oxide (0.068 g, 0.9 mmol) whilst purging gently with compressed air. Spot TLC throughout the reaction showed that no new products were formed and after 2 h, complex **3a** had completely decomposed to an intractable blue solid.

3.6. Thermolysis reactions of trans-[(η^5-Cp)$_2$Mo$_2$(μ-PPh$_2$)$_2$-(CO)(O)] (**4**) with O$_2$, P(OMe)$_3$, PPh$_3$ and Bu^{t}NC

Following a similar procedure to Section 3.5 using **4** (0.24 g, 0.33 mmol), each reaction mixture was refluxed for 24 h. Spot TLC throughout the reaction time showed that no new products had formed.

3.7. Synthesis of [(η^5-Cp*)$_2$Mo$_2$(μ-PPh$_2$)$_2$(NO)(O)][BF$_4$] (**5**)

To a solution of **3a** (0.5 g, 0.66 mmol) in dichloromethane (100 ml) was added [NO][BF_4] (0.16 g, 1.37 mmol). The solution was stirred for 10 min, during which time the colour was observed to change from purple–red to orange. Hexane (20 ml) was added, and the solution concentrated in vacuo until a precipitate was observed. The precipitate was collected by filtration, dissolved in the minimum of diethyl ether–dichloromethane (1:1) and recrystallised at −4°C to afford orange crystals of [$(\eta^5$-$Cp^*)_2Mo_2(\mu$-$PPh_2)_2(NO)(O)$]-[BF_4] (**5**) (0.47 g, 94%). *Anal*. Found: C, 48.35; H, 3.5; N, 1.4; P, 6.65. Calc. for [$C_{38}H_{34}Mo_2NO_6P_2$][BF_4]: C, 48.5; H, 3.6; N, 1.5; P, 6.6%. IR (ν_{max}($CHCl_3$) cm^{-1}): (CO) 1730(s) and (NO) 1701. ^1H NMR (400 MHz): δ 3.77 (3H, s, CO_2CH_3), 3.90 (3H, s, CO_2CH_3), 4.74 (2H, s, $C_5H_4CO_2Me$), 5.92 (2H, s, $C_5H_4CO_2Me$), 6.57 (2H, s, $C_5H_4CO_2Me$), 6.59 (2H, s, $C_5H_4CO_2Me$), 6.86–7.87 (20H, m, C_6H_5). ^{31}P NMR (250 MHz): δ 37.1 (2P, s, μ-PPh_2). ^{19}F NMR (250 MHz): δ −152.8 (4F, BF_4). FAB-MS: m/z 855 [$(M^+)+1$].

3.8. Synthesis of [(η^5-Cp)$_2$Mo$_2$(μ-PPh$_2$)$_2$(NO)(O)][BF$_4$] (**6**)

Following a similar procedure to Section 3.7, a dichloromethane solution of [$(\eta^5$-$Cp)_2Mo_2(\mu$-$PPh_2)_2(CO)(O)$]

(0.3 g, 0.41 mmol) was treated with [NO][BF_4] (0.095 g, 0.82 mmol). The precipitate that resulted from addition of hexane (20 ml) was collected by filtration and recrystallised from the minimum of diethyl ether–dichloromethane (1:1) to afford red–orange crystals of [(η^5-Cp)$_2$$Mo_2$($\mu$-$PPh_2$)$_2$-(NO)(O)][$BF_4$] (**6**) (0.29 g, 97%). *Anal.* Found: C, 49.35; H, 3.5; N, 1.6; P, 7.35. Calc. for [$C_{34}H_{30}Mo_2NO_2P_2$][BF_4]: C, 49.5; H, 3.7; N, 1.7; P, 7.5%. IR (ν_{max}($CHCl_3$) cm^{-1}): 1692. ^{1}H NMR (400 MHz): δ 5.90 (5H, s, C_5H_5), 5.62 (5H, s, C_5H_5), 6.82–7.93 (20H, m, C_6H_5). ^{31}P NMR (250 MHz): δ 36.0 (2P, s, μ-PPh_2). ^{19}F NMR (250 MHz): δ −152.8 (4F, BF_4). FAB-MS: m/z 739 [(M^+)+1].

3.9. Crystal structure determination for complexes **1**, **2** and **3a**

The crystals were mounted on a glass fibre with epoxy resin at room temperature. Data were collected by the $\omega/2\theta$ scan method on a Rigaku AFC5R [1,3a] and AFC7R [2] four-circle diffractometer. In each case, three standard reflections measured at intervals of 100 reflections showed no significant variation in intensity. Cell parameters were obtained by least-squares refinement on diffractometer angles from 25 centred reflections ($30 \le 2\theta \le 40°$).

A semi-empirical absorption correction based on ψ-scan data was applied (teXsan) [17]. The structures were solved by direct methods (SHELXTL PLUS) [18] and subsequent Fourier difference syntheses, and refined anisotropically (non-H atoms) by full-matrix least-squares on F^2 (SHELXL 93) [19]. Hydrogen atoms were placed in geometrically idealised positions and refined using a riding model or as rigid methyl groups.

Two half-molecules of CH_2Cl_2 are associated with the inversion centre at 0, 0, 0.5. Each was disordered over two positions with a common C atom and was modelled with restraints applied to the atomic distances and isotropic thermal parameters (site occupation factors given in Table 4). Details of the data collection and structure refinements are given in Table 7.

Table 7
Details of data collection and structure refinements for complexes **1**, **2** and **3a** [a]

Complex	**1**	**2**	**3a**
Molecular formula	$C_{20}H_{14}Mo_2O_{10}$	$C_{40}H_{34}Mo_2O_6P_2 \cdot 0.5(CH_2Cl_2)$	$C_{39}H_{34}Mo_2O_6P_2$
M	606.19	906.96	852.48
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	9.811(4)	13.364(4)	12.436(2)
b (Å)	12.109(2)	14.535(4)	15.300(3)
c (Å)	9.919(3)	10.576(2)	20.395(4)
α (°)	90	91.33(2)	90
β (°)	110.00(3)	94.94(2)	111.59(3)
γ (°)	90	108.92(2)	90
U (Å^3)	1107.3(4)	1933.3(9)	3608.3(12)
Z	2	2	4
D_c (g cm^{-3})	1.818	1.558	1.569
Crystal size (mm)	0.2×0.2×0.04	0.3×0.2×0.15	0.2×0.2×0.05
Crystal habit	red plate	green prism	purple plate
F(000)	596	914	1720
μ (mm^{-1})	1.186	0.846	0.83
Relative transmission max., min.	1.000, 0.894	1.000, 0.938	1.000, 0.861
Data collection range (°)	$4.5 \le 2\theta \le 55$	$5.0 \le 2\theta \le 50$	$5.0 \le 2\theta \le 50$
Index ranges	$0 \le h \le 12$	$0 \le h \le 15$	$-14 \le h \le 13$
	$0 \le k \le 15$	$-17 \le k \le 16$	$-18 \le k \le 0$
	$-12 \le l \le 12$	$-12 \le l \le 12$	$0 \le l \le 24$
Reflections measured	2682	7113	6583
Independent reflections	2538 (R_{int} = 0.018)	6721 (R_{int} = 0.041)	6329 (R_{int} = 0.048)
Parameters, restraints	145, 0	472, 9	442, 0
$wR2$ (all data) [b]	0.1437	0.1357	0.1834
x, y [b]	0.0848, 2.82	0.0474, 4.60	0.1000, 0.00
$R1$ ($I > 2\sigma(I)$) [b]	0.0458	0.0442	0.0523
Observed reflections	2152	5304	3770
Goodness-of-fit on F^2 (all data) [b]	1.030	1.074	0.956
Maximum shift/σ	0.001	−0.003	−0.008
Peak, hole in final difference map (e Å^{-3})	1.394, −1.181	0.923, −0.653	1.262, −0.974

[a] Data in common: graphite-monochromated Mo Kα radiation, λ = 0.71073 Å, T = 293(2) K.
[b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$ where x and y are constants adjusted by the program. Goodness-of-fit = $\{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the number of parameters.

4. Supplementary material

Hydrogen atom coordinates, full tables of atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. Structure factors are available from the authors on request.

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