Chemistry of Phosphido-bridged Dimolybdenum Complexes. Part 3.[1] Reinvestigation of the Reaction between $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ and P_2Ph_4; *X*-Ray Structures of $[Mo_2(\mu\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(CO)_2]$, $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$, and *trans*-$[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2O(CO)]$†

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The thermal reaction of $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ with P_2Ph_4 in toluene gives $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(CO)_2]$ in high yield. An *X*-ray diffraction study shows a Mo–Mo double bond [2.712(2) Å] symmetrically bridged by two PPh_2 groups, with a planar Mo_2P_2 core. Under u.v. irradiation, further decarbonylation occurs to give $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$, in which two PPh_2 groups and a carbonyl ligand bridge a Mo–Mo triple bond of length 2.515(2) Å. Oxidation of either of these complexes gives *cis*- and *trans*-$[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2O(CO)]$; the structure of the *trans* isomer has been determined by *X*-ray diffraction. Protonation of $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(CO)_2]$ occurs across the metal–metal bond to give $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)_2(CO)_2][BF_4]$.

The chemistry of dinuclear complexes stabilised by bridging phosphido groups (μ-PR_2) has received much attention in recent years. One of the earliest and most successful methods for the preparation of such complexes involved the reaction of metal carbonyls with diphosphanes, P_2R_4.[2] In general, thermal cleavage of the diphosphane resulted in the production of compounds containing two bridging PR_2 units, with or without a metal–metal bond depending on the electronic requirements of the metal–ligand fragments concerned.

In 1963 Hayter[3] reported that whereas the reaction of $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ (**1**) with P_2Me_4 in refluxing toluene gave the expected orange-red complex $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PMe_2)_2(CO)_4]$, an analogous reaction with P_2Ph_4 afforded instead a relatively insoluble dark green compound which, on the basis of its i.r. spectrum, elemental analysis, and a molecular weight determination, was formulated as $[Mo_3(\eta\text{-}C_5H_5)_3(\mu\text{-}PPh_2)_3(CO)_3]$ with the structure shown in Figure 1. In Part 1 of this Series we described the synthesis of $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ through the reaction of (**1**) with PPh_2H in toluene or decalin at 110 °C.[1] The green compound reported by Hayter was a low-yield by-product of this synthesis and, in order to characterise the complex more fully, it was decided to reinvestigate the original preparation. This paper describes the identification and structural characterisation of the green complex, together with details of its protonation, decarbonylation, and oxidation.

Results and Discussion

(*a*) *Synthesis and* X-*Ray Analysis of* $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(CO)_2]$ (**2**).—Following the procedure of Hayter,[3] refluxing a toluene solution containing approximately equimolar amounts of $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ and P_2Ph_4 gave, after cooling, dark green powdery crystals which were collected by filtration, washed with acetone, and dried. Further product could be obtained by extraction and column chromatography of the filtrate, bringing the total yield to 70%.

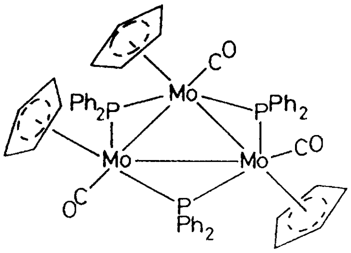

Figure 1. Structure proposed by Hayter[3] for '$[Mo_3(\eta\text{-}C_5H_5)_3(\mu\text{-}PPh_2)_3(CO)_3]$,' now shown to be the dimer $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(CO)_2]$ (**2**)

As previously reported, the complex is appreciably soluble only in dichloromethane. The i.r. spectrum in this solvent shows an absorption at 1 855 cm^{-1} with a shoulder at 1 890 cm^{-1} (Table 1). The n.m.r. spectra of the complex (Table 2) are not inconsistent with the formulation proposed by Hayter. Thus the ^1H n.m.r. spectrum in CD_2Cl_2 showed the presence of only phenyl and cyclopentadienyl protons, the latter appearing as a singlet at δ 5.42, and the ^{31}P-$\{^1H\}$ spectrum consisted of a singlet resonance in the region associated with μ-PR_2 groups [-50.25 p.p.m. relative to $P(OMe)_3$ (0.0 p.p.m.)]. However the mass spectrum showed a highest mass peak at *m*/*z* 748 (^{96}Mo) with successive loss of two carbonyl groups; moreover these peaks displayed a dimolybdenum isotope pattern. These data are consistent with the formulation of the green complex as $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(CO)_2]$ (**2**) (Scheme), a proposal which was subsequently confirmed by an *X*-ray diffraction study.

The molecular structure of (**2**) is shown in Figure 2, with selected bond lengths and angles listed in Table 3. The structure consists of two crystallographically independent centrosymmetric molecules with only minor differences between them. Each molybdenum atom is ligated by a η^5-C_5H_5 ring and a terminal carbonyl. The co-ordination of the former is unremarkable, and the CO ligands are effectively linear [mean Mo–C–O angle 172.8(8)°]; the relatively large deviation from 180° may be due to steric effects, as proposed for the alkyne complexes $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}RC_2R)(CO)_4]$.[4] The cyclopenta-

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† Bis(μ-diphenylphosphido)-bis[carbonyl(η-cyclopentadienyl)molybdenum] (*Mo=Mo*), μ-carbonyl-bis(μ-diphenylphosphido)-bis[(η-cyclopentadienyl)molybdenum] (*Mo≡Mo*), and *trans*-1-carbonyl-1,2-bis(η-cyclopentadienyl)-bis(μ-diphenylphosphido)-2-oxodimolybdenum (*Mo=Mo*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Analytical and physical data for dimolybdenum complexes

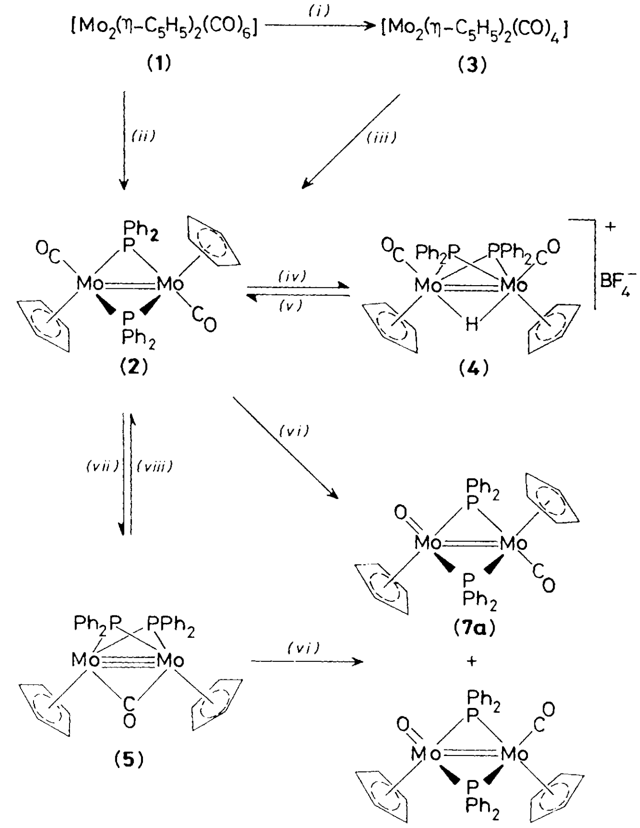
	Compound	Colour	M.p. (°C)	Yield (%)	Mass spectrum (*m*/*z*)	I.r. spectrum[a] ν(CO) (cm^{-1})	Analysis[b] (%) C	H	P
(2)	$[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(CO)_2]$	Green	decomp. 300	70	748, 720, 692	1 890 (sh), 1 855s	57.3 (57.8)	3.9 (4.0)	8.3 (8.3)
(4)	$[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)_2(CO)_2][BF_4]$	Red	decomp. 262	100		2 010	51.9 (51.7)	3.6 (3.7)	7.2 (7.4)
(5)	$[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$	Red-purple	decomp. 261	58	720, 692	1 674	58.5 (58.3)	4.3 (4.2)	8.1 (8.6)
(7a)	*trans*-$[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2O(CO)]$	Red	289—292	79[c]	736, 708	1 826[d]	57.5 (57.1)	4.2 (4.1)	8.4 (8.4)
(7b)	*cis*-$[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2O(CO)]$	Red	decomp. 204	52[e]	736, 708	1 859[d]	56.8 (57.1)	3.9 (4.1)	8.6 (8.4)

[a] In CH_2Cl_2 solution. [b] Calculated values in parentheses. [c] From (**2**). [d] ν(Mo=O) at 895 cm^{-1} KBr. [e] From (**5**).

Table 2. Hydrogen-1, carbon-13, and phosphorus-31 n.m.r. data for the complexes[a]

Complex	^1H (δ)	^{13}C (δ)	^{31}P (δ)
(2)	7.76—7.19 (m, 20 H, Ph) 5.42 (s, 10 H, C_5H_5)[b]	131.5, 126.0, 125.9 (Ph) 88.3 (C_5H_5)[b,c]	−50.3 (s)[b]
(4)	7.78—6.84 (m, 20 H, Ph) 5.48 (s, 10 H, C_5H_5) −13.35 (t, 1 H, *J* 56.3, μ-H)[b]	234.0 (s, CO) 144.0 (d, *J* 38, P–C) 137.6 (d, *J* 46, P–C) 135.1—128.9 (m, Ph) 92.1 (s, C_5H_5)	71.7 (s)
(5)	7.25—6.54 (m, 20 H, Ph) 5.58 (s, 10 H, C_5H_5)	306.2 (t, *J* 7, CO) 152.1 (t, *J* 16, P–C) 151.8 (t, *J* 16, P–C) 142.2 (t, *J* 16, P–C) 141.8 (t, *J* 16, P–C) 134.7—128.5 (m, Ph) 92.4 (s, C_5H_5)	57.1 (s)
(7a)	8.28—7.15 (m, 20 H, Ph) 4.97 (t, 5 H, *J* 0.7, C_5H_5) 4.78 (t, 5 H, *J* 1.2, C_5H_5)	238.2 (t, *J* 9, CO) 148.6 (d, *J* 30, P–C) 142.1 (d, *J* 41, P–C) 135.4—124.7 (m, Ph) 104.5 (s, C_5H_5)	27.5 (s)
(7b)	8.05—6.78 (m, 20 H, Ph) 5.26 (t, 5 H, *J* 0.9, C_5H_5) 5.06 (t, 5 H, *J* 0.8, C_5H_5)	87.6 (s, C_5H_5) 232.7 (t, *J* 10, CO) 147.5 (d, *J* 26, P–C) 141.6 (d, *J* 42, P–C) 134.7—127.6 (m, Ph) 100.9 (s, C_5H_5) 85.6 (s, C_5H_5)	22.3 (s)

[a] Chemical shifts (δ) in p.p.m., couplings constants in Hz; ^1H and ^{13}C shifts relative to $SiMe_4$ (0.0 p.p.m.), ^{31}P shifts relative to $P(OMe)_3$ (0.0 p.p.m.) (upfield shifts negative). The ^{13}C and ^{31}P spectra were ^1H gated decoupled. Measured in $CDCl_3$ at 298 K. [b] Measured in CD_2Cl_2. [c] CO and P–C not observed due to low solubility.



Scheme. Proposed structures for the new dimolybdenum complexes: (*i*) toluene, 111 °C, N_2 purge, 18 h; (*ii*) P_2Ph_4 (1 equiv.), toluene, 111 °C, 15 h, yield 70%; (*iii*) P_2Ph_4 (1 equiv.), toluene 111 °C, 1.5 h, 50%; (*iv*) HBF_4, OEt_2, CH_2Cl_2, 100%; (*v*) base; (*vi*) CH_2Cl_2, air; (*vii*) u.v. light, argon purge, 16 h, 58%; (*viii*) CO, CH_2Cl_2, room temperature, 100%

dienyl ligands are disposed in a *trans* arrangement, as are consequently the carbonyls. Although there are two possible isomers of (**2**), no evidence was found for the *cis* isomer either in the solid state or in solution; thus only one phenyl environment was observed in the ^{13}C n.m.r. spectrum.

The metal–metal axis is symmetrically bridged by two diphenylphosphido groups. The Mo–P distances of 2.402(2) and 2.393(2) Å in molecule 1 and 2.396(2) and 2.400(2) Å in molecule 2 of (**2**) are slightly shorter than those found in $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3\{P(OMe)_3\}]$,[1] for which the average Mo–(μ-P) bond length is 2.422(3) Å. On the other hand, the bridging angle of the phosphido group (*i.e.* the Mo–P–Mo angle) is considerably reduced [69.0(1) and 68.8(2)° in the second molecule] compared with the corresponding angle in the latter complex [84.2(1)°]. The Mo_2P_2 core of the centrosymmetric molecule of (**2**) is strictly planar. Ignoring the metal–metal bond and regarding the cyclopentadienyl ligand as occupying three co-ordination sites, the geometry around each Mo atom is close to octahedral. The molybdenum–molybdenum separation is 2.716(1) [2.711(1) Å in the second molecule] which is consistent with the presence of the formal double bond required on the basis of the 18-electron rule. The range of Mo–Mo double-bond lengths is wide,[5,6] but perhaps the most relevant comparison is with the analogous thiolato-bridged complex $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}SBu^t)_2(CO)_2]$, prepared by

Table 3. Selected bond lengths (Å) and angles (°) for $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(CO)_2]$ (**2**)

Molecule 1		Molecule 2		Molecule 1		Molecule 2	
Mo(1)–P(1)	2.402(2)	Mo(2)–P(2)	2.396(2)	Mo(1)–P(1a)	2.393(2)	Mo(2)–P(2a)	2.400(2)
Mo(1)–C(1)	1.945(7)	Mo(2)–C(19)	1.940(9)	P(1)–C(7)	1.829(9)	P(2)–C(25)	1.843(8)
Mo(1)–C(2)	2.309(10)	Mo(2)–C(20)	2.295(10)	P(1)–C(13)	1.840(7)	P(2)–C(31)	1.838(8)
Mo(1)–C(3)	2.347(9)	Mo(2)–C(21)	2.306(9)	C(2)–C(3)	1.403(16)	C(20)–C(21)	1.403(11)
Mo(1)–C(4)	2.346(8)	Mo(2)–C(22)	2.320(8)	C(2)–C(6)	1.400(12)	C(20)–C(24)	1.382(5)
Mo(1)–C(5)	2.321(8)	Mo(2)–C(23)	2.347(11)	C(3)–C(4)	1.388(12)	C(21)–C(22)	1.398(14)
Mo(1)–C(6)	2.303(10)	Mo(2)–C(24)	2.337(11)	C(4)–C(5)	1.407(15)	C(22)–C(23)	1.399(12)
Mo(1)–Mo(1a)	2.716(1)	Mo(2)–Mo(2a)	2.711(1)	C(5)–C(6)	1.401(13)	C(23)–C(24)	1.388(13)
P(1)–Mo(1)–C(2)	110.1(2)	P(2)–Mo(2)–C(20)	135.9(2)	P(1)–Mo(1)–P(1a)	111.0(1)	P(2)–Mo(2)–P(2a)	111.2(1)
P(1)–Mo(1)–C(3)	94.1(2)	P(2)–Mo(2)–C(21)	101.8(2)	C(1)–Mo(1)–P(1a)	83.1(2)	C(19)–Mo(2)–P(2a)	82.7(2)
P(1)–Mo(1)–C(4)	111.9(3)	P(2)–Mo(2)–C(22)	93.7(2)	Mo(1)–P(1)–Mo(1a)	69.0(1)	Mo(2)–P(2)–Mo(2a)	68.8(2)
P(1)–Mo(1)–C(5)	146.9(3)	P(2)–Mo(2)–C(23)	118.4(2)	Mo(1)–P(1)–C(7)	125.9(2)	Mo(2)–P(2)–C(25)	117.4(2)
P(1)–Mo(1)–C(6)	145.3(2)	P(2)–Mo(2)–C(24)	150.9(2)	Mo(1)–P(1)–C(13)	118.5(2)	Mo(2)–P(2)–C(31)	123.7(3)
P(1)–Mo(1)–C(1)	82.9(3)	P(2)–Mo(2)–C(19)	83.1(2)	C(7)–P(1)–C(13)	100.8(3)	C(25)–P(2)–C(31)	100.9(3)
P(1)–Mo(1)–Mo(1a)	55.3(1)	P(2)–Mo(2)–Mo(2a)	55.7(1)	Mo(1)–C(1)–O(1)	172.2(7)	Mo(2)–C(19)–O(2)	173.6(7)
C(1)–Mo(1)–Mo(1a)	77.5(3)	C(19)–Mo(2)–Mo(2a)	77.3(2)				

The atoms denoted 'a' are related to the equivalently numbered atoms by the symmetry operation $\bar{x}, \bar{y}, 1 - z$ in molecule 1 and $-2 - x, -1 - y, \bar{z}$ in molecule 2.

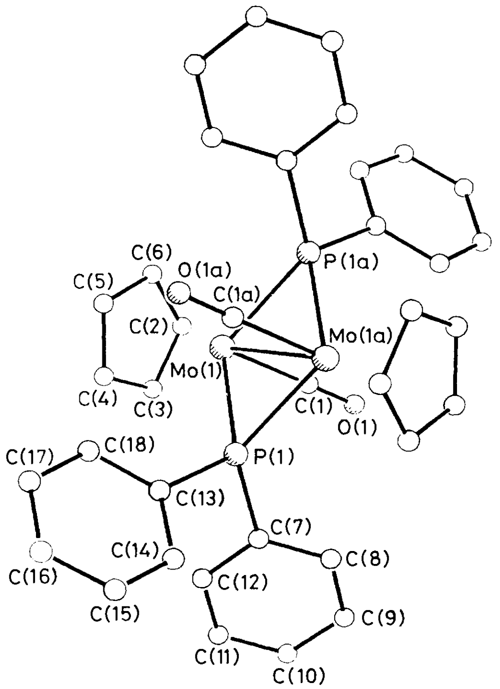


Figure 2. Molecular structure of $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(CO)_2]$ (**2**) including the atom numbering scheme

Knox and co-workers,[7] which has a similar *trans* arrangement of C_5H_5 and CO ligands, a planar Mo_2S_2 core, and a formal Mo–Mo double bond of length 2.616(2) Å. The longer bond in (**2**) may reflect the increased steric crowding due to the PPh_2 groups. By comparison, the Mo–Mo bond length in $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3\{P(OMe)_3\}]$ is 3.254(1) Å,[1a] and in the compounds $[Mo_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^3\text{-}CH{=}CHC({=}O)Ph\}(\mu\text{-}PPh_2)(CO)_2]$[8] and $[Mo_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^3\text{-}C(CO_2Me){=}CHCO_2Me\}(\mu\text{-}PPh_2)(CO)_2]$,[9] which have a formal bond order of one, the corresponding distances are 2.954(1) and 2.930(1) Å.

Several other complexes containing a metal–metal double bond bridged by two phosphido groups have been prepared, including $[Ir_2(\mu\text{-}PPh_2)_2(CO)_2(PPh_3)_2]$,[10] $[Ru_2(\mu\text{-}PPh_2)_2(NO)_2(PMePh_2)_2]$,[11] $[V_2(\mu\text{-}PMe_2)_2(CO)_8]$,[12] $[Co_2(\mu\text{-}PPh_2)_2(CO)_2(PEt_2Ph)_2]$,[13] $[Rh_2(\mu\text{-}PBu^t{}_2)_2(CO)_2(PMe_3)_2]$,[14] and $[Rh(\mu\text{-}PHBu^t)_2(PMe_3)_4]$.[15] In all of these cases, *X*-ray crystallography revealed a centrosymmetric structure with a planar M_2P_2 core, similar to that found in (**2**).

There are several possible pathways for the formation of complex (**2**) from $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$. It is known, for instance, that (**1**) reacts under thermal conditions with triarylphosphines to give monosubstituted products $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_5L]$.[16] Formation of such a derivative, followed by P–P bond cleavage and loss of CO, could lead to (**2**); however, the monosubstituted complexes are known to disproportionate in the presence of an excess of ligand to give salt-like products,[17] none of which was observed in the synthesis of (**2**), and the intermediacy of such a complex is thus doubtful.

A more plausible route is a free-radical process involving the reaction of P_2Ph_4 with $Mo(\eta\text{-}C_5H_5)(CO)_3{}^{\bullet}$, which is known to be in equilibrium with (**1**) under the conditions of the reaction,[18] to give ${}^{\bullet}PPh_2$ and $[Mo(\eta\text{-}C_5H_5)(PPh_2)(CO)_3]$. The latter has been obtained previously[19,20] and was reported to dimerise to $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(CO)_4]$, though neither the dimer nor the monomer was well characterised. We have reinvestigated this reaction, and find that the mononuclear complex is transformed readily into (**2**) on heating. Thus addition of PPh_2Cl to $Na[Mo(\eta\text{-}C_5H_5)(CO)_3]{\cdot}2dme$[21] (dme = dimethoxyethane) in toluene[19] gave a solution containing predominantly $[Mo(\eta\text{-}C_5H_5)(PPh_2)(CO)_3]$ [$\nu_{max.}$(CO) in toluene at 2 005, 1 934, and 1 925 cm^{-1}]. On heating, the orange solution turned rapidly green, and the i.r. spectrum showed that the peaks due to the mononuclear species had disappeared and had been replaced by a strong absorption at 1 862 cm^{-1} due to (**2**). Chromatographic work-up afforded $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ (9%) followed by a 52% yield of (**2**). There was no evidence for the formation of $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(CO)_4]$. The fact that complex (**2**) is obtained in this reaction shows that the free-radical process above is a possible route to at least a proportion of the (**2**) obtained in our original reaction.

A second plausible mechanism for the production of complex (**2**) involves the reaction of the diphosphane with $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (**3**), which is known to be formed slowly from (**1**) under the conditions of the reaction.[22] Indeed, in a separate experiment, addition of 1 equivalent of P_2Ph_4 to a refluxing toluene solution of preformed (**3**) produced a 50% yield of (**2**) after 1 h. Addition of 1 equivalent of P_2Ph_4 to preformed (**3**) at room temperature gives an unstable complex which on attempted purification decomposes to (**1**), (**2**), and [Mo$_2$-

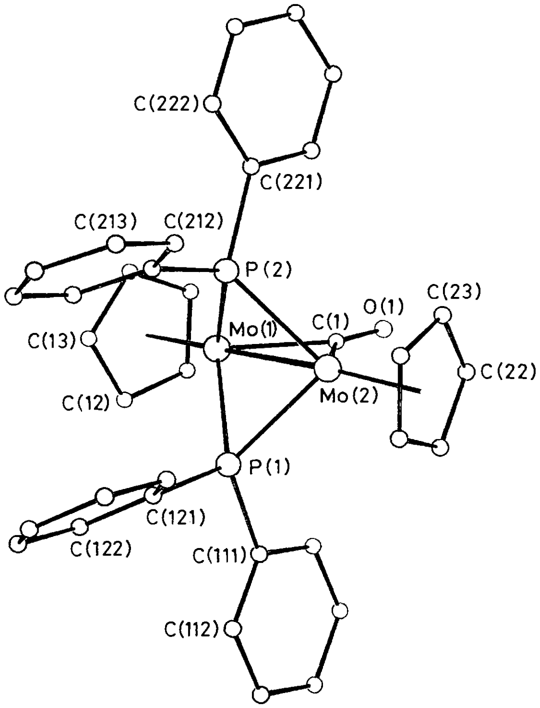


Figure 3. Molecular structure of $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ (5) including the atom numbering scheme

$(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$. The i.r. spectrum of this unstable species is reminiscent of those of the alkyne complexes $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}RC_2R)(CO)_4]$[4] and we therefore tentatively ascribe to it the formula $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}P_2Ph_4)(CO)_4]$. Interestingly, a related di-iron complex containing a bridging P_2Ph_4 has recently been reported.[23]

The degree of decarbonylation of phosphido-bridged dimolybdenum complexes appears to depend on the steric properties of the bridging groups. Thus, Hayter's compound, $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PMe_2)_2(CO)_4]$,[3] was not reported to decarbonylate under the conditions of its preparation whereas, more recently, Heck[24] has shown that $[Mo_2(\eta^5,\eta^5\text{-}C_5H_4SiMe_2C_5H_4)(\mu\text{-}PMe_2)_2(CO)_4]$, produced from $[Mo_2(\eta^5,\eta^5\text{-}C_5H_4SiMe_2C_5H_4)(CO)_6]$ and P_2Me_4, does decarbonylate on heating to give $[Mo_2(\eta^5,\eta^5\text{-}C_5H_4SiMe_2C_5H_4)(\mu\text{-}PMe_2)_2(CO)_3]$, with a single metal–metal bond. With PPh_2 bridges, further decarbonylation to the dicarbonyl complex (2) must be favoured since no evidence for the formation of $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(CO)_x]$ (x = 4 or 3) could be obtained.

(*b*) *Synthesis of* $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)_2(CO)_2][BF_4]$ (**4**).—Addition of an excess of $HBF_4 \cdot OEt_2$ to a green dichloromethane solution of (**2**) at −78 °C, followed by warming to room temperature, caused a colour change to red with an accompanying shift of ν(CO) to higher wavenumber, consistent with the formation of a protonated species. Treatment with diethyl ether afforded the salt (**4**) in virtually quantitative yield. The nature of the cation is demonstrated by its ^1H n.m.r. spectrum (Table 2) which exhibits a triplet resonance at δ −13.35 due to a hydride ligand bridging the two metal atoms and coupled to two equivalent phosphorus nuclei [J(PH) = 56.3 Hz]. The two C_5H_5 ligands give rise to a singlet at δ 5.48, suggesting that they are in equivalent environments, whereas the ^{13}C n.m.r. spectrum reveals that there are two environments for the phenyl groups. A *trans* isomer would contain inequivalent cyclopentadienyl rings unless the Mo_2P_2 core was still planar with the hydride ligand lying in this plane. This arrangement for the *trans* isomer is ruled out by the observation of inequivalent phenyl groups, and (**4**) must therefore exist exclusively as the *cis* isomer. For the *cis* isomer one C_5H_5 and two phenyl environments are expected regardless of whether or not the Mo_2P_2 unit is planar, and it is not possible to determine this on the basis of the n.m.r. data.

Since (**2**) exists exclusively as the *trans* isomer and (**4**) as the *cis*, there is clearly an interchange of C_5H_5 and CO ligands during the protonation reaction. Initial protonation to give a terminal H ligand would create a five-co-ordinate molybdenum centre which could then rearrange by a trigonal twist mechanism, followed by migration of the hydride ligand to a bridging position to give the observed isomer.

(*c*) *Synthesis and X-Ray Analysis of* $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ (**5**).—Irradiation with u.v. light of $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(CO_2)]$ in toluene while purging the solution slowly with argon results in decarbonylation and the production of complex (**5**) in 58% yield. Owing to the low solubility of (**2**) in toluene, the reaction can only be carried out on a small scale; larger quantities of (**5**) may be synthesised through the reaction of (**2**) with ethyl diazoacetate, followed by anaerobic decomposition of the resulting blue intermediate.[25]

Complex (**5**), a dark red solid, was characterised by i.r., mass, ^1H, ^{13}C, and ^{31}P n.m.r. spectroscopy, and elemental analysis (Tables 1 and 2). The i.r. spectrum showed ν(CO) at the unusually low frequency of 1 674 cm^{-1}, indicating the presence of a bridging carbonyl ligand. The ^1H n.m.r. spectrum established the presence of only phenyl and cyclopentadienyl protons, with the two C_5H_5 rings giving rise to a singlet. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum consisted of a single peak at 57.1 p.p.m., and a molecular ion was observed at m/z 720 in the mass spectrum.

A crystal of complex (**5**) suitable for *X*-ray diffraction was grown by diffusion of hexane into a dichloromethane solution. The molecular structure is depicted in Figure 3, and selected bond parameters are summarised in Table 4. The crystal consists of discrete molecules with no unusually short intermolecular contacts.

The Mo–Mo separation of 2.515(2) Å in (**5**) is consistent with a triple bond between the metal atoms as required on the basis of electron counting, although it is significantly longer than the Mo–Mo bond in (**3**) which is 2.448(1) Å.[26] The molybdenum atoms are bridged symmetrically by two diphenylphosphido groups [Mo–P(1) 2.374(3) and 2.373(3) Å, Mo–P(2) 2.389(3) and 2.384(3) Å] and a carbonyl ligand [Mo–C(1) 2.075(13) and 2.080(12) Å]. The mean Mo–P distance of 2.380(3) in (**5**) is slightly shorter than that of 2.401(3) in (**2**), perhaps reflecting increased donation from the metal atom to the μ-PPh_2 groups in (**5**) resulting from loss of a CO ligand. The shortening of the metal–metal bond in (**5**) compared with that in (**2**) is accompanied by a reduction of *ca.* 5° in the bridging angle of the μ-PPh_2 groups in (**5**) [Mo–P(1)–Mo 64.0(1), Mo–P(2)–Mo 63.6(1)°]. Due to the presence of the third bridging ligand, the Mo_2P_2 unit is no longer planar as in (**2**), but adopts a butterfly structure, with a dihedral angle between the two Mo_2P planes of 113.6°. The geometry around each molybdenum atom is still pseudo-octahedral. Whereas in (**2**) the cyclopentadienyl ligands are disposed in a *trans* orientation, in (**5**) they adopt a *cis* geometry on the same side of the molecule as the CO ligand, thus minimising steric interactions with the phenyl groups. A closely related complex, $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PhPC_6H_4PPh)(\mu\text{-}CO)]$ (**6**), has been reported by Kyba *et al.*[27] In this complex the metal–metal bond length is 2.532(1) Å, very similar to that seen in (**5**). However, due to the constraining link between them, the bridging phosphorus atoms in (**6**) are slightly asymmetrically co-ordinated and, in contrast to (**5**), the C_5H_5 ligands adopt a *trans* configuration.

Table 4. Selected bond lengths (Å) and angles (°) for $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ (**5**)

Mo(1)–Mo(2)	2.515(2)	Mo(1)–P(1)	2.374(3)	Mo(2)–C(21)	2.350(10)	Mo(2)–C(22)	2.326(11)
Mo(1)–P(2)	2.389(3)	Mo(1)–C(1)	2.075(13)	Mo(2)–C(23)	2.328(11)	Mo(2)–C(24)	2.352(11)
Mo(1)–C(11)	2.355(13)	Mo(1)–C(12)	2.378(13)	Mo(2)–C(25)	2.365(11)	P(1)–C(111)	1.849(9)
Mo(1)–C(13)	2.375(12)	Mo(1)–C(14)	2.349(11)	P(1)–C(121)	1.830(11)	P(2)–C(211)	1.834(10)
Mo(1)–C(15)	2.336(12)	Mo(2)–P(1)	2.373(3)	P(2)–C(221)	1.855(8)		
Mo(2)–P(2)	2.384(3)	Mo(2)–C(1)	2.080(12)				
P(1)–Mo(1)–Mo(2)	58.0(1)	P(2)–Mo(1)–Mo(2)	58.1(1)	C(21)–Mo(2)–P(1)	101.0(3)	C(21)–Mo(2)–P(2)	158.3(3)
P(2)–Mo(1)–P(1)	90.4(1)	C(1)–Mo(1)–Mo(2)	52.8(3)	C(22)–Mo(2)–Mo(1)	139.7(3)	C(22)–Mo(2)–P(1)	133.2(3)
C(1)–Mo(1)–P(1)	93.7(3)	C(1)–Mo(1)–P(2)	92.1(4)	C(22)–Mo(2)–P(2)	136.2(3)	C(23)–Mo(2)–Mo(1)	147.1(3)
C(11)–Mo(1)–Mo(2)	141.6(3)	C(11)–Mo(1)–P(1)	115.1(3)	C(23)–Mo(2)–P(1)	154.9(3)	C(23)–Mo(2)–P(2)	104.4(3)
C(11)–Mo(1)–P(2)	153.4(3)	C(12)–Mo(1)–Mo(2)	149.7(3)	C(24)–Mo(2)–Mo(1)	157.6(3)	C(24)–Mo(2)–P(1)	123.1(3)
C(12)–Mo(1)–P(1)	94.7(3)	C(12)–Mo(1)–P(2)	142.5(3)	C(24)–Mo(2)–P(2)	99.8(3)	C(25)–Mo(2)–Mo(1)	154.2(3)
C(13)–Mo(1)–Mo(2)	157.6(3)	C(13)–Mo(1)–P(1)	107.7(3)	C(25)–Mo(2)–P(1)	96.2(3)	C(25)–Mo(2)–P(2)	126.0(3)
C(13)–Mo(1)–P(2)	108.7(3)	C(14)–Mo(1)–Mo(2)	152.0(3)	Mo(2)–P(1)–Mo(1)	64.0(1)	C(111)–P(1)–Mo(1)	120.2(3)
C(14)–Mo(1)–P(1)	142.1(3)	C(14)–Mo(1)–P(2)	97.0(3)	C(111)–P(1)–Mo(2)	117.8(3)	C(121)–P(1)–Mo(1)	122.8(4)
C(15)–Mo(1)–Mo(2)	142.7(3)	C(15)–Mo(1)–P(1)	150.1(3)	C(121)–P(1)–Mo(2)	123.4(3)	C(121)–P(1)–C(111)	105.0(4)
C(15)–Mo(1)–P(2)	118.5(3)	P(1)–Mo(2)–Mo(1)	58.0(1)	Mo(2)–P(2)–Mo(1)	63.6(1)	C(211)–P(2)–Mo(1)	125.4(3)
P(2)–Mo(2)–Mo(1)	58.3(1)	P(2)–Mo(2)–P(1)	90.6(1)	C(211)–P(2)–Mo(2)	124.8(3)	C(211)–P(2)–Mo(1)	117.7(3)
C(1)–Mo(2)–Mo(1)	52.6(4)	C(1)–Mo(2)–P(1)	93.6(4)	C(221)–P(2)–Mo(2)	120.0(3)	C(221)–P(2)–C(211)	102.9(4)
C(1)–Mo(2)–P(2)	92.1(4)	C(21)–Mo(2)–Mo(1)	143.2(3)	Mo(2)–C(1)–Mo(1)	74.5(4)	O(1)–C(1)–Mo(1)	144(1)
				O(1)–C(1)–Mo(2)	142(1)		

Complexes (**5**) and (**6**) serve to illustrate further how the presence of bulky Ph groups on the bridging phosphorus atoms favours the loss of CO ligands and the formation of Mo–Mo multiple bonds. The decarbonylation of (**2**) to (**5**) is reversible; thus, bubbling CO gas through a dichloromethane solution of (**5**) at room temperature regenerates (**2**), apparently quantitatively (i.r. spectrum). This system thus provides a rare instance of a reversible change in bond order in multiply bonded dinuclear complexes with uptake or loss of CO, a previous example being provided by the diosmium compounds $[Os_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}H)_2(CO)_2]$ and $[Os_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}H)_2(\mu\text{-}CO)]$.[28] An interesting comparison can also be drawn with (**1**) and (**3**), where interconversion between singly and triply bonded species involves the reversible loss of two CO ligands.

(*d*) *Synthesis of Complex* (**7**) *and* X-*Ray Analysis of one Isomer* $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2O(CO)]$ (**7a**).—Although the phosphido-bridged complexes (**2**) and (**5**) may be handled in air without special precautions, prolonged exposure to atmospheric oxygen of either complex [*e.g.* 3 d in CH_2Cl_2 solution or *ca.* 3 weeks in the solid state for (**2**)] results in the production of red, air-stable $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2O(CO)]$ (**7**), derived from (**2**) by the replacement of one carbonyl ligand by a terminal oxo group. The complex exists as two isomers: (**7a**), $\nu_{max.}$(CO) 1 826 cm^{-1}; and (**7b**), $\nu_{max.}$(CO) 1 859 cm^{-1}. The isomers are easily separated by preparative t.l.c. with (**7a**) having the higher R_F value. No interconversion between them was observed even on refluxing in toluene or on u.v. irradiation.

The identical formulae of (**7a**) and (**7b**) were established by the appearance of molecular ions in their mass spectra at *m*/*z* 736. In addition, the i.r. spectrum of each isomer in a KBr disc showed a strong absorption at 895 cm^{-1} characteristic of a terminal Mo=O group; no such absorption was present in the spectrum of (**2**) or (**5**). The ^1H n.m.r. spectrum of each isomer comprised multiplet peaks due to phenyl protons and two resonances due to inequivalent C_5H_5 rings. Each cyclopentadienyl peak was observed as a triplet with small couplings (*ca.* 1 Hz) to the two equivalent phosphorus atoms, whereas no such coupling was seen for (**2**), (**4**), or (**5**) (Table 2); however on the basis of our further results in this system, see below, no special significance can be attached to this splitting. The ^{31}P n.m.r. spectrum of each isomer consisted of a single peak, that of (**7a**) appearing at 27.5 p.p.m. and that of (**7b**) at 22.3 p.p.m.

It was not possible to decide from the spectroscopic data alone which of the two isomers of (**7**) is the *trans* and which the *cis*. However a useful indication was given by the different ratios of (**7a**) and (**7b**) obtained from (**2**) and (**5**). Thus, oxidation of (**2**) leads mainly to (**7a**), the isomer with the higher R_F value [(**7a**):(**7b**) ratio 20:1]. The *X*-ray diffraction study of (**2**) (Figure 2) had shown that the C_5H_5 ligands are arranged in a *trans* configuration. Assuming this structure to be maintained in solution, and the relative orientation of the C_5H_5 rings to be unaffected by the oxidation reaction, it seemed likely that (**7a**) was the *trans* isomer, which agreed with its greater mobility on a t.l.c. plate compared with the more polar *cis* isomer. In accord with this idea, oxidation of (**5**), which in the solid state has a *cis* geometry (Figure 3), affords mainly (**7b**) [(**7a**):(**7b**) ratio 1:27].

In each of the complexes (**7**) one of the molybdenum atoms is formally in oxidation state II whereas the other, bearing the oxo ligand, is in oxidation state IV. In order to investigate the effect of this change on the molecular geometries of (**7**) as compared with (**2**) and to confirm the assignment of the isomers, an *X*-ray diffraction study of (**7a**) was undertaken. Suitable crystals were grown by diffusion of hexane into a toluene solution of (**7a**). The crystal structure consists of discrete molecules of (**7a**), with no abnormally short intermolecular contacts, together with solvent molecules which displayed major positional disorder. The molecular structure is depicted in Figure 4 with selected bond parameters listed in Table 5.

The Mo(1)–Mo(2) distance in (**7a**) of 2.942(1) Å is 0.22 Å longer than that found for the Mo–Mo double bond in (**2**). It is, however, comparable to the corresponding double-bond distance of 2.885(1) Å found in the related complex $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}\sigma{:}\eta^2\text{-}CH{=}CHPh)(\mu\text{-}PPh_2)O(CO)]$ (**8**),[6] in which the Mo atoms are in similar oxidation states to those in (**7a**). The slightly longer bond in (**7a**) may be due to increased steric effects resulting from the presence of a second PPh_2 group.

The two bridging phosphido ligands in (**7a**) are asymmetrically co-ordinated, being closer to Mo(1) [average Mo(1)–P 2.326, average Mo(2)–P 2.461 Å]. This is presumably the consequence of better π donation to the phosphorus *d* orbitals from the Mo^{II} than from the Mo^{IV} atom. The Mo(1)–P–Mo(2) angles of 75.7(1) and 75.9(1)° are considerably larger than those found in (**2**) [mean 69.0(1)°]. Within experimental error the Mo_2P_2 core in (**7a**) is planar.

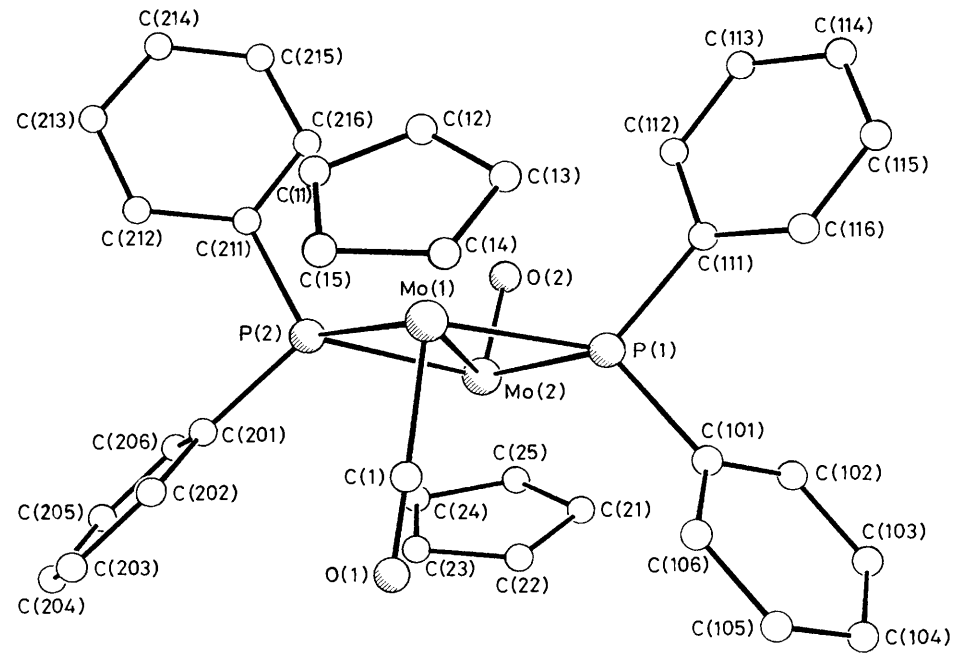


Figure 4. Molecular structure of *trans*-[$Mo_2(\eta$-$C_5H_5)_2(\mu$-$PPh_2)_2O(CO)$] (**7a**) including the atom numbering scheme

Table 5. Selected bond lengths (Å) and angles (°) for [$Mo_2(\eta$-$C_5H_5)_2(\mu$-$PPh_2)_2O(CO)$]·$0.5C_6H_{14}$ (**7a**)

Mo(1)–Mo(2)	2.942(1)	Mo(1)–P(1)	2.326(1)	Mo(2)–C(25)	2.363(4)	P(1)–C(101)	1.837(4)
Mo(1)–P(2)	2.326(1)	Mo(1)–C(1)	1.917(6)	P(1)–C(111)	1.835(5)	P(2)–C(201)	1.837(5)
Mo(1)–C(11)	2.323(6)	Mo(1)–C(12)	2.341(7)	P(2)–C(211)	1.835(5)	C(11)–C(12)	1.337(15)
Mo(1)–C(13)	2.314(8)	Mo(1)–C(14)	2.320(6)	C(11)–C(15)	1.369(9)	C(12)–C(13)	1.365(15)
Mo(1)–C(15)	2.317(5)	Mo(2)–P(1)	2.464(1)	C(13)–C(14)	1.391(18)	C(14)–C(15)	1.388(10)
Mo(2)–P(2)	2.457(1)	Mo(2)–O(2)	1.700(4)	C(21)–C(22)	1.425(8)	C(21)–C(25)	1.414(7)
Mo(2)–C(21)	2.358(5)	Mo(2)–C(22)	2.455(5)	C(22)–C(23)	1.387(8)	C(23)–C(24)	1.405(8)
Mo(2)–C(23)	2.466(6)	Mo(2)–C(24)	2.375(5)	C(24)–C(25)	1.416(9)		

P(1)–Mo(1)–Mo(2)	54.3(1)	P(2)–Mo(1)–Mo(2)	54.1(1)	C(21)–Mo(2)–O(2)	111.2(2)	C(22)–Mo(2)–Mo(1)	98.9(1)
P(2)–Mo(1)–P(1)	108.2(1)	C(1)–Mo(1)–Mo(2)	88.8(1)	C(22)–Mo(2)–P(1)	85.4(1)	C(22)–Mo(2)–P(2)	109.3(1)
C(1)–Mo(1)–P(1)	91.5(1)	C(1)–Mo(1)–P(2)	90.4(1)	C(22)–Mo(2)–O(2)	145.4(2)	C(23)–Mo(2)–Mo(1)	101.2(1)
C(11)–Mo(1)–Mo(2)	132.0(2)	C(11)–Mo(1)–P(1)	138.8(2)	C(23)–Mo(2)–P(1)	112.1(1)	C(23)–Mo(2)–P(2)	85.7(1)
C(11)–Mo(1)–P(2)	89.9(1)	C(12)–Mo(1)–Mo(2)	119.2(2)	C(23)–Mo(2)–O(2)	142.4(1)	C(24)–Mo(2)–Mo(1)	130.2(2)
C(12)–Mo(1)–P(1)	105.5(3)	C(12)–Mo(1)–P(2)	104.6(3)	C(24)–Mo(2)–P(1)	141.5(1)	C(24)–Mo(2)–P(2)	94.6(1)
C(13)–Mo(1)–Mo(2)	130.3(4)	C(13)–Mo(1)–P(1)	88.4(3)	C(24)–Mo(2)–O(2)	108.7(2)	C(25)–Mo(2)–Mo(1)	155.0(1)
C(13)–Mo(1)–P(2)	138.6(3)	C(14)–Mo(1)–Mo(2)	161.1(2)	C(25)–Mo(2)–P(1)	124.1(1)	C(25)–Mo(2)–P(2)	128.9(2)
C(14)–Mo(1)–P(1)	107.4(2)	C(14)–Mo(1)–P(2)	143.3(2)	C(25)–Mo(2)–O(2)	92.7(2)	Mo(2)–P(1)–Mo(1)	75.7(1)
C(15)–Mo(1)–Mo(2)	162.3(1)	C(15)–Mo(1)–P(1)	142.1(1)	C(101)–P(1)–Mo(1)	128.4(2)	C(101)–P(1)–Mo(2)	116.4(1)
C(15)–Mo(1)–P(2)	108.8(1)	P(1)–Mo(2)–Mo(2)	50.0(1)	C(111)–P(1)–Mo(1)	118.1(1)	C(111)–P(1)–Mo(2)	117.8(1)
P(2)–Mo(2)–Mo(1)	50.1(1)	P(2)–Mo(2)–P(1)	100.0(1)	C(111)–P(1)–C(101)	100.4(2)	Mo(2)–P(2)–Mo(1)	75.9(1)
O(2)–Mo(2)–Mo(1)	112.2(1)	O(2)–Mo(2)–P(1)	102.7(1)	C(201)–P(2)–Mo(1)	127.9(1)	C(201)–P(2)–Mo(2)	116.0(1)
O(2)–Mo(2)–P(2)	102.4(1)	C(21)–Mo(2)–Mo(1)	126.1(1)	C(211)–P(2)–Mo(1)	118.4(1)	C(211)–P(2)–Mo(2)	116.8(2)
C(21)–Mo(2)–P(1)	90.4(1)	C(21)–Mo(2)–P(2)	141.6(2)	O(1)–C(1)–Mo(1)	176.2(4)		

The Mo(2)–O(2) distance of 1.700(4) Å is typical for such a grouping and is equal within experimental error to the corresponding bond length in (**8**) of 1.688(6) Å. As expected, the cyclopentadienyl ligands in (**7a**) are in a *trans* configuration. An interesting feature of the structure is the asymmetric co-ordination of the C_5H_5 ring attached to Mo(2). Three of the Mo–C distances are short [Mo(2)–C(21) 2.358(5), Mo(2)–C(24) 2.375(5), and Mo(2)–C(25) 2.363(4) Å] while the remaining two are significantly longer [Mo(2)–C(22) 2.455(5) and Mo(2)–C(23) 2.466(6) Å]. In addition the C(22)–C(23) bond of 1.387(8) Å is somewhat shorter than the other C–C distances in the ring [although this difference is marginal in terms of the estimated standard deviations (e.s.d.s) on these distances], consistent with a 'η^3,η^2' component to the mode of co-ordination. This phenomenon has been observed previously in related complexes [29] and may be attributed to the strong *trans* influence of the oxo ligand.

The production of oxo complexes of molybdenum is commonly observed, but the isolation of a carbonyl complex and its subsequent high-yield oxidation to a single oxo-containing product is more unusual. The formation of (**7**) from (**2**) is assumed to proceed with release of CO_2, though no attempt to detect this was made. Under the conditions of the reaction, no evidence was found for further oxidation and loss of the remaining carbonyl ligand. In contrast, the oxidation of (**1**) under similar conditions proceeds with complete loss of the CO ligands to give [$Mo_2(\eta$-$C_5H_5)_2(\mu$-$O)_2O_2$],[30] in which each molybdenum is in oxidation state v.

Experimental

General techniques and instrumentation were described in Part 1 of this Series.[1a] The complex [Mo$_2$(η-C$_5$H$_5$)$_2$(CO)$_6$] was prepared by the method of King.[31] Tetraphenyldiphosphane was prepared in heptane by the method of Kuchen and Buchwald.[32] The compounds PPh$_2$H and PPh$_2$Cl were purchased from Aldrich and used without further purification. In order to ensure a slight excess of the diphosphane in the subsequent reaction, a yield of 80% in the synthesis of P$_2$Ph$_4$ was assumed although in practice it is essentially quantitative.

(*i*) *Synthesis of* [Mo$_2$(η-C$_5$H$_2$)$_2$(μ-PPh$_2$)$_2$(CO)$_2$] (**2**).—Solid P$_2$Ph$_4$ was prepared *in situ* from PPh$_2$H (4.0 cm^3, 22.99 mmol) and PPh$_2$Cl (4.13 cm^3, 22.99 mmol). To this were added [Mo$_2$(η-C$_5$H$_5$)$_2$(CO)$_6$] (9.01 g, 18.39 mmol) and toluene (300 cm^3). The solution was refluxed for 17 h then cooled to room temperature and the green precipitate was collected by filtration and washed with acetone. The solvent was removed from the combined filtrate and washings, and the residue extracted with acetone to give a red solution. Further (**2**) remained undissolved, and was added to the previous precipitate.

After addition of silica (5 g) the solvent was removed from the acetone extract and the silica was loaded onto a silica chromatography column. Elution with hexane–CH$_2$Cl$_2$ (6:4) gave a red band due to [Mo$_2$(η-C$_5$H$_5$)$_2$(μ-H)(μ-PPh$_2$)(CO)$_4$] (1.08 g, 9.6%). Further elution with hexane–CH$_2$Cl$_2$ (1:1) changing progressively to pure CH$_2$Cl$_2$ gave a green band due to (**2**). After elution from the column and removal of solvent, the green solid was washed with acetone, and added to that recovered previously. The total yield of (**2**) was 9.57 g (69.6%). The complex was stored under nitrogen. Analytically pure samples were prepared by recrystallisation from dichloromethane–hexane (1:1).

(*ii*) *Thermolysis of* [Mo(η-C$_5$H$_5$)(PPh$_2$)(CO)$_3$].—A solution of PPh$_2$Cl (0.52 cm^3, 2.90 mmol) in toluene (50 cm^3) was added from a dropping funnel over a period of 0.5 h to an ice-cooled suspension of Na[Mo(η-C$_5$H$_5$)(CO)$_3$]·2dme[21] (1.30 g, 2.90 mmol) in the same solvent (100 cm^3). After filtering the solution through a frit to remove NaCl, the i.r. spectrum in toluene showed strong absorptions at 2 005, 1 934, and 1 925 cm^{-1} due to [Mo(η-C$_5$H$_5$)(PPh$_2$)(CO)$_3$], with small peaks due to impurities at 2 053, 1 950, and 1 891 cm^{-1}. The solution was then heated to reflux, and turned dark green rapidly. After refluxing for 1.5 h the i.r. spectrum showed an impurity peak at 1 970 cm^{-1}, a peak due to [Mo$_2$(η-C$_5$H$_5$)$_2$(μ-H)(μ-PPh$_2$)(CO)$_4$] at 1 935 cm^{-1}, and a very strong absorption due to [Mo$_2$(η-C$_5$H$_5$)$_2$(μ-PPh$_2$)$_2$(CO)$_2$] at 1 862 cm^{-1}. After addition of silica (3 g) the solvent was evaporated and the residue loaded onto a silica chromatography column. Elution with hexane–dichloromethane (7:3) produced a red band, identified as [Mo$_2$(η-C$_5$H$_5$)$_2$(μ-H)(μ-PPh$_2$)(CO)$_4$] (82.1 mg, 9%) by i.r. and ^{1}H n.m.r. spectra. A strong green band was obtained on elution with CH$_2$Cl$_2$. After removal of the solvent the solid was washed with acetone to remove a small amount of *trans*-[Mo$_2$(η-C$_5$H$_5$)$_2$(μ-PPh$_2$)$_2$O(CO)] (identified by its i.r. spectrum) leaving (**2**) (563.6 mg, 52%) undissolved.

Elution with dichloromethane–acetone (9:1) produced small amounts of two unidentified red complexes.

(*iii*) *Synthesis of* [Mo$_2$(η-C$_5$H$_5$)$_2$(μ-H)(μ-PPh$_2$)$_2$(CO)$_2$][BF$_4$] (**4**).—An excess of HBF$_4$·OEt$_2$ (0.3 cm^3) was added to a solution of complex (**2**) (75.8 mg, 0.10 mmol) in CH$_2$Cl$_2$ at −78 °C. The green solution was allowed to warm to room temperature, during which time the colour changed to red. After stirring for 10 min at room temperature the solvent was removed *in vacuo* to leave a red oil which, on washing with diethyl ether (3 × 5 cm^3), gave a red-brown powder. Recrystallisation of (**4**) to give an analytically pure material was achieved by diffusion of ether into a dichloromethane solution. The yield of crude material was apparently quantitative; no other carbonyl-containing products were observed in the i.r. spectrum.

(*iv*) *Synthesis of* [Mo$_2$(η-C$_5$H$_5$)$_2$(μ-PPh)$_2$)$_2$(μ-CO)] (**5**).—A solution of complex (**2**) (110.9 mg, 0.148 mmol) in toluene (125 cm^3) was irradiated with u.v. light (Hanovia 125-W medium-pressure immersion lamp) for 16 h with a slow stream of argon passing through the solution. After removal of the solvent from the dark red-brown solution the residue was purified by t.l.c. with CH$_2$Cl$_2$ as the eluting solvent. Three zones were separated: (*a*) a red band, R_F 0.95, due to *trans*-[Mo$_2$(η-C$_5$H$_5$)$_2$(μ-PPh$_2$)$_2$O(CO)] (**7a**) (11.1 mg, 10.2%); (*b*) a purple-brown band, R_F 0.25, consisting of [Mo$_2$(η-C$_5$H$_5$)$_2$(μ-PPh$_2$)$_2$(μ-CO)] (**5**) (61.5 mg, 57.6%); and (*c*) a red band, R_F 0.15, due to *cis*-[Mo$_2$(η-C$_5$H$_5$)$_2$(μ-PPh$_2$)$_2$O(CO)] (**7b**) (15.1 mg, 13.8%).

(*v*) *Synthesis of* [Mo$_2$(η-C$_5$H$_5$)$_2$(μ-PPh$_2$)$_2$O(CO)] (**7a**), (**7b**).—(*a*) *From* [Mo$_2$(η-C$_5$H$_5$)$_2$(μ-PPh$_2$)$_2$(CO)$_2$] (**2**). Complex (**2**) (154.6 mg, 0.207 mmol) was dissolved in CH$_2$Cl$_2$ (10 cm^3) and the solution stirred for 4 d in an open flask, with more solvent being added when necessary. The residue was purified by t.l.c. with hexane–CH$_2$Cl$_2$ (1:1) as the eluting solvent, producing (**7a**) as a red band, R_F 0.5, yield 120.8 mg, 79.4%. A second red band, R_F 0.1, afforded (**7b**) (6.2 mg, 4.1%).

(*b*) *From* [Mo$_2$(η-C$_5$H$_5$)$_2$(μ-PPh$_2$)$_2$(μ-CO)] (**5**). In a similar manner, a solution of complex (**5**) (133.1 mg, 0.185 mmol) in CH$_2$Cl$_2$ (10 cm^3) was stirred in air for 4 d. T.l.c. separation as above provided (**7a**) (2.6 mg, 1.9%) and (**7b**) (70.7 mg, 52.0%) as red bands.

Crystal Structure Determination for Complexes (**2**), (**5**), *and* (**7a**).—Suitable single crystals of the complexes were mounted on glass fibres with epoxy-resin, and transferred to a four-circle *X*-ray diffractometer. Details of the data-collection procedures, structure solution and refinements are presented in Table 6. For complex (**5**) reflections for which $I > 3\sigma(I)$ were rejected after a prescan and were not recorded.

In the structure of (**7a**) a disordered solvent molecule, thought to be a hexane, was located. Six possible carbon atom positions were included in the refinement, each site being assigned half occupancy. In the refinement of (**5**) the phenyl groups were treated as rigid hexagons (C–C 1.395 Å) and their hydrogen atoms included in the structure-factor calculation in fixed positions (C–H 1.08 Å) with a common isotropic thermal parameter set at 0.08 Å^2. The cyclopentadienyl rings were constrained to be rigid pentagons (C–C 1.450 Å); hydrogen atoms for these carbons were not included in refinement. For complexes (**2**) and (**7a**) the phenyl and cyclopentadienyl hydrogen atoms were placed in idealised positions and allowed to ride 1.08 Å from the relevant carbon; each type of H atom was assigned a common isotropic thermal parameter.

All the structures were refined to convergence. Weighting schemes were applied, analyses of the variations of the sum of $w\Delta^2$ [$\Delta = (F_o - |F_c|)$] according to $|F_o|$ and sinθ indicated that the schemes were appropriate. The final residuals were calculated on the basis $R = \Sigma|F_o - |F_c||/\Sigma F_o$, $R' = \Sigma w^{\frac{1}{2}}|F_o - |F_c||/\Sigma w^{\frac{1}{2}}F_o$, and $w = 1/[\sigma^2(F_o) + gF_o^2]$ where $\sigma(F_o)$ is the estimated standard derivation in F_o from counting statistics. The final atomic co-ordinates for the non-hydrogen atoms for all three structures are listed in Tables 7—9, respectively. All atoms were assigned complex neutral-atom scattering factors taken from ref. 33. Calculations were performed on the

Table 6. Data for crystal structure analyses

	(2)	**(5)**	**(7a)**
Molecular formula	$C_{36}H_{30}Mo_2O_2P_2$	$C_{25}H_{30}Mo_2OP_2$	$C_{35}H_{30}Mo_2O_2P_2\cdot0.5C_6H_{14}$
M	748.42	599.8	779.50
Crystal system	Triclinic	Monoclinic	Triclinic
Crystal colour	Green	Dark red	Red
Crystal dimensions (mm)	0.08 × 0.19 × 0.30	0.15 × 0.22 × 0.25	0.27 × 0.35 × 0.44
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	10.085(1)	17.517(2)	9.559(2)
b/Å	10.970(1)	17.531(2)	13.411(1)
c/Å	15.198(1)	9.978(3)	14.353(2)
α/°	90.13(1)	90	76.60(1)
β/°	101.02(1)	95.46(2)	71.60(1)
γ/°	109.17(1)	90	87.90(1)
U/Å^3	1 553.0	3 050.3	1 697.1
Z	2	4	2
D_c/g cm^{-3}	1.60	1.30	1.52
F(000)	752	1 448	790
Radiation	Mo	Mo	Mo
λ/Å	0.710 69	0.710 69	0.710 69
μ/cm^{-1}	9.19	8.52	8.16
Diffractometer	Stoe	Phillips PW1100	Stoe
Scan mode	ω—θ	ω—2θ	ω—θ
2θ Range/°	5—45	6—50	5—50
Index limits	$\pm h, \pm k, +l$	$\pm h, +k, +l$	$\pm h, -k, \pm l$
No. data measured	4 239	2 985	6 241
Method of absorption correction	Empirical 300 azimuthal scans	None	Numerical face indexing
Transmission factors	0.92—0.81		0.81—0.74
No. unique data	4 058	2 755	5 963
No. observed data	2 816	2 755	4 846
Criteria (n) for observed [$F > n\sigma(F)$]	4	6	4
Solution method	Direct methods	Patterson	Direct methods
Refinement method	Blocked cascade	Full matrix	Blocked full matrix
No. parameters refined	382	133	396
Anisotropic atoms	Mo, P, O, C	Mo, P	Mo, P, O, C (not solvent)
Weighting scheme	$[\sigma^2(F) + 0.000\ 12F^2]$	$1/\sigma^2F$	$1.744/[\sigma^2(F) + 0.001F^2]$
Final R	0.048	0.062	0.039
Final R'	0.042	0.062	0.045
Max. final electron density difference (e Å^{-3})	1.16	0.85	0.66

Table 7. Atomic co-ordinates (× 10^4) for complex **(2)**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo(1)	1 166(1)	410(1)	4 615(1)	Mo(2)	−8 909(1)	−4 691(1)	−450(1)
P(1)	−1 128(2)	597(2)	3 990(1)	P(2)	−8 762(2)	−3 744(2)	1 003(1)
C(7)	−1 546(8)	2 099(7)	3 921(5)	C(25)	−8 288(8)	−1 972(7)	1 128(5)
C(8)	−2 990(9)	2 006(8)	3 789(6)	C(26)	−9 307(9)	−1 387(7)	991(5)
C(9)	−3 369(11)	3 109(10)	3 765(6)	C(27)	−8 908(10)	−29(8)	1 036(5)
C(10)	−2 335(12)	4 293(9)	3 877(6)	C(28)	−7 493(11)	707(9)	1 222(5)
C(11)	−936(11)	4 406(8)	3 994(6)	C(29)	−6 494(10)	124(8)	1 364(6)
C(12)	−540(10)	3 308(8)	4 019(5)	C(30)	−6 879(9)	−1 214(8)	1 319(6)
C(13)	−2 078(7)	−211(7)	2 876(5)	C(31)	−7 667(8)	−4 035(7)	2 041(5)
C(14)	−2 866(8)	−1 512(7)	2 759(5)	C(32)	−7 693(10)	−3 476(8)	2 855(6)
C(15)	−3 496(8)	−2 084(8)	1 901(5)	C(33)	−6 932(14)	−3 712(12)	3 645(7)
C(16)	−3 346(9)	−1 371(9)	1 161(6)	C(34)	−6 127(15)	−4 474(13)	3 636(9)
C(17)	−2 550(9)	−75(8)	1 272(5)	C(35)	−6 111(11)	−5 055(11)	2 852(10)
C(18)	−1 935(9)	494(7)	2 126(5)	C(36)	−6 869(9)	−4 847(8)	2 038(7)
C(2)	2 521(9)	652(10)	3 522(6)	C(19)	−9 890(8)	−3 480(8)	−860(5)
C(3)	2 372(9)	1 860(10)	3 664(6)	C(20)	−7 736(10)	−4 101(9)	−1 617(6)
C(4)	3 054(9)	2 324(9)	4 542(7)	C(21)	−6 848(9)	−3 348(9)	−844(7)
C(5)	3 637(9)	1 409(9)	4 944(7)	C(22)	−6 447(8)	−4 201(8)	−255(6)
C(6)	3 302(8)	367(9)	4 311(6)	C(23)	−7 069(9)	−5 457(9)	−663(6)
C(1)	235(8)	−1 364(7)	4 106(5)	C(24)	−7 850(9)	−5 378(9)	−1 506(7)
O(1)	−177(7)	−2 400(5)	3 767(4)	O(2)	−10 390(6)	−2 725(5)	−1 161(4)

Polytechnic of North London DEC 10 computer, and the University of Cambridge IBM 3081 mainframe computer using modified versions of SHELX 76.[34]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Table 8. Fractional atom co-ordinates for complex (**5**)

Atom	x	y	z
Mo(1)	0.213 88(6)	0.220 81(6)	0.019 63(11)
Mo(2)	0.251 95(7)	0.102 49(6)	0.152 10(11)
P(1)	0.331 2(2)	0.212 4(2)	0.159 2(3)
P(2)	0.241 8(2)	0.103 6(2)	−0.087 8(3)
C(1)	0.151 5(7)	0.165 3(7)	0.157 0(13)
O(1)	0.092 6(6)	0.166 6(6)	0.209 5(10)
C(111)	0.344 3(4)	0.266 5(5)	0.318 8(9)
C(112)	0.415 2(4)	0.295 0(5)	0.371 9(9)
C(113)	0.421 5(4)	0.333 1(5)	0.495 3(9)
C(114)	0.357 0(4)	0.342 5(5)	0.565 6(9)
C(115)	0.286 2(4)	0.313 9(5)	0.512 5(9)
C(116)	0.279 8(4)	0.275 9(5)	0.389 1(9)
C(121)	0.425 0(6)	0.214 8(4)	0.051 0(11)
C(122)	0.455 9(6)	0.283 3(4)	−0.011 4(11)
C(123)	0.523 8(6)	0.282 8(4)	−0.032 3(11)
C(124)	0.560 9(6)	0.214 0(4)	0.009 3(11)
C(125)	0.530 0(6)	0.145 6(4)	0.071 7(11)
C(126)	0.462 0(6)	0.146 0(4)	0.092 5(11)
C(211)	0.332 0(5)	0.087 9(4)	−0.190 2(9)
C(212)	0.349 8(5)	0.014 5(4)	−0.208 2(9)
C(213)	0.412 5(5)	0.003 3(4)	−0.282 4(9)
C(214)	0.447 3(5)	0.065 6(4)	−0.338 8(9)
C(215)	0.419 4(5)	0.139 1(4)	−0.320 8(9)
C(216)	0.356 8(5)	0.150 3(4)	−0.246 6(9)
C(221)	0.161 3(4)	0.053 4(5)	−0.184 7(8)
C(222)	0.166 5(4)	0.021 1(5)	−0.311 3(8)
C(223)	0.103 4(4)	−0.016 0(5)	−0.377 5(8)
C(224)	0.034 9(4)	−0.020 8(5)	−0.317 1(8)
C(225)	0.029 6(4)	0.011 5(5)	−0.190 6(8)
C(226)	0.092 8(4)	0.048 6(5)	−0.124 4(8)
C(11)	0.146 6(7)	0.336 3(7)	0.035 3(11)
C(12)	0.219 6(7)	0.355 5(7)	−0.005 9(11)
C(13)	0.225 5(7)	0.322 4(7)	−0.134 4(11)
C(14)	0.156 2(7)	0.282 8(7)	−0.172 7(11)
C(15)	0.107 4(7)	0.291 3(7)	−0.067 9(11)
C(21)	0.279 4(7)	0.055 3(6)	0.371 8(10)
C(22)	0.207 6(7)	0.025 5(6)	0.318 1(10)
C(23)	0.220 4(7)	−0.021 9(6)	0.207 1(10)
C(24)	0.300 2(7)	−0.021 4(6)	0.192 2(10)
C(25)	0.336 7(7)	0.026 3(6)	0.294 0(10)

Table 9. Atomic co-ordinates (× 10^4) for complex (**7a**)

Atom	x	y	z
Mo(1)	8 782(1)	1 828(1)	6 340(1)
Mo(2)	6 420(1)	1 789(1)	8 252(1)
P(1)	8 047(1)	3 226(1)	7 058(1)
P(2)	7 433(1)	379(1)	7 442(1)
C(1)	7 327(6)	2 068(3)	5 658(4)
O(1)	6 493(5)	2 216(3)	5 186(3)
O(2)	7 068(3)	1 566(3)	9 254(2)
C(101)	7 133(5)	4 374(3)	6 592(3)
C(102)	6 487(5)	5 027(4)	7 210(4)
C(103)	5 784(6)	5 888(4)	6 838(5)
C(104)	5 721(6)	6 093(4)	5 885(5)
C(105)	6 371(6)	5 447(4)	5 264(4)
C(106)	7 088(5)	4 590(3)	5 603(4)
C(111)	9 361(4)	3 805(3)	7 495(3)
C(112)	9 871(5)	3 248(4)	8 259(4)
C(113)	10 977(5)	3 664(5)	8 501(4)
C(114)	11 598(6)	4 633(5)	7 993(4)
C(115)	11 101(6)	5 183(4)	7 229(4)
C(116)	9 996(5)	4 763(4)	6 988(4)
C(201)	6 091(5)	−418(3)	7 232(3)
C(202)	6 104(5)	−402(3)	6 264(4)
C(203)	5 081(7)	−987(4)	6 104(5)
C(204)	3 992(7)	−1 566(4)	6 927(6)
C(205)	3 999(6)	−1 597(4)	7 881(5)
C(206)	5 033(5)	−1 026(4)	8 051(4)
C(211)	8 395(5)	−598(4)	8 109(3)
C(212)	8 546(6)	−1 566(4)	7 899(4)
C(213)	9 421(7)	−2 278(5)	8 332(6)
C(214)	10 103(7)	−2 004(6)	8 954(5)
C(215)	9 955(7)	−1 077(6)	9 146(5)
C(216)	9 111(5)	−350(5)	8 721(4)
C(11)	10 849(6)	852(5)	5 938(5)
C(12)	11 206(6)	1 553(9)	6 360(7)
C(13)	11 177(8)	2 503(8)	5 764(10)
C(14)	10 832(8)	2 367(5)	4 929(6)
C(15)	10 602(6)	1 322(5)	5 052(4)
C(21)	4 401(5)	2 873(4)	8 482(4)
C(22)	4 496(5)	2 594(4)	7 565(4)
C(23)	4 212(5)	1 544(4)	7 779(4)
C(24)	3 941(5)	1 142(4)	8 818(4)
C(25)	3 984(5)	1 973(4)	9 264(4)
C(0S)	4 694(15)	4 118(8)	348(8)
C(1S)	2 706(16)	4 840(12)	355(11)
C(2S)	6 018(18)	4 910(14)	−75(12)
C(3S)	6 913(18)	4 312(12)	44(11)
C(4S)	3 725(19)	4 219(13)	426(11)
C(5S)	5 516(18)	4 034(11)	289(10)

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