Deprotonation of a Heterodinuclear Transition-metal Hydride Complex and Reactions of the Anion with Electrophiles: *X*-Ray Crystal Structures of $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}Ag(PPh_3)\}(\mu\text{-}PPh_2)Mn(CO)_4]$ and $[(\eta\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}I)(\mu\text{-}PPh_2)Mn(CO)_4]$†

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Deprotonation of $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}H)(\mu\text{-}PPh_2)Mn(CO)_4]$ with base gives the heterodinuclear anion $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}PPh_2)Mn(CO)_4]^-$ which has been isolated as its $[NEt_4]^+$ salt. This anion reacts with complexes of Group 1 B metals to give heterotrinuclear complexes of the type $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}ML)(\mu\text{-}PPh_2)Mn(CO)_4]$ [ML = $Au(PPh_3)$, $Au(PMe_2Ph)$, or $Ag(PPh_3)$]. A single-crystal *X*-ray diffraction study established the structure of the silver-containing complex. The metal atom triangle [Mo–Mn 3.190(2), Ag–Mn 2.664(2), and Ag–Mo 2.874(2) Å] is bridged by a PPh_2 group along the Mo–Mn edge [Mo–P 2.387(4) and Mn–P 2.272(4) Å]. The bridging phosphorus atom lies 0.3 Å out of the plane of the three metal atoms resulting in an angle between this plane and the Mo–Mn–(μ-P) plane of 7.59°. The phosphorus atom in the PPh_3 group lies 0.11 Å out of the Mo–Mn–Ag plane on the same side of the plane as the phosphido ligand. The heterodinuclear anion reacts with iodine to give, as the major product, the iodo-bridged compound $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}I)(\mu\text{-}PPh_2)Mn(CO)_4]$ which has been characterised by a single-crystal *X*-ray diffraction study. The two metal atoms in this complex are 3.978(2) Å apart indicating the absence of a metal-metal bond and the angle between the planes defined by Mo–Mn–(μ-I) and Mo–Mn–(μ-P) is 145.0°. Loss of one molecule of CO during the reaction of the heterodinuclear anion with I_2 accounts for the formation of $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}I)(\mu\text{-}PPh_2)Mn(CO)_3]$ which is obtained as a minor product. The major product is converted in near quantitative yield into the minor product on photolysis and the minor product is similarly converted into the major product on treatment with CO.

The deprotonation of hydrogen-bridged metal–metal bonds is a common route to anionic homodinuclear metal carbonyl complexes[1–3] and has been extended in a limited number of cases to the formation of anionic heteronuclear derivatives.[4] The reactions of anions formed in this way have not been widely studied, although treatment with complexes of other metals and, in particular, those of Groups 1B,[1,2,5–8] 2B,[9] and 8[2] has been used to obtain a variety of mixed-metal complexes.

The reaction of $[Mn(CO)_5]^-$ with $[Mo(CO)_6]$ gives a molybdenum–manganese anionic complex, $[MoMn(CO)_{10}]^-$, which was isolated as its tetramethylammonium salt.[9] This complex undergoes metal–metal bond fission under mild conditions and a neutral protonated analogue could not be obtained. We have previously reported the preparation of the phosphido-bridged molybdenum–manganese complex, $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}H)(\mu\text{-}PPh_2)Mn(CO)_4]$,[10] and, in this paper, we describe its deprotonation to give the corresponding anion. The reactions of this anion with complexes of Group 1B metals and with I_2 are also reported. The preparation of the closely related anion $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}P(C_6H_4Me\text{-}p)_2\}Mn(CO)_4]^-$ has recently been described by Casey and Bullock[11] but its protonation was the only reaction of this anion which was investigated.

Results and Discussion

Preparation and Properties of $[NEt_4][(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}PPh_2)Mn(CO)_4]$.—Reaction of $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}H)(\mu\text{-}PPh_2)Mn(CO)_4]$ (**1**) with KOH in absolute ethanol leads to the formation of a dark red solution of $K[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}PPh_2)Mn(CO)_4]$ from which $[NEt_4][(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}PPh_2)Mn(CO)_4]$ (**2**) was obtained as an orange solid after metathesis with $[NEt_4]Br$ and precipitation from Et_2O–CH_2Cl_2 (1:1). Complex (**2**) was identified by comparison of its i.r. and ^1H n.m.r. spectra with those of the analogous complex prepared by Casey and Bullock.[11] The temperature dependence of the ^1H n.m.r. resonances due to the phenyl group over the range 213—321 K is again attributed to a fluxional process which interconverts the environments of the two phenyl groups in a similar manner to that postulated for the $\mu\text{-}P(C_6H_4\text{-}p)_2$ complex[11] and to that which interconverts the methyl groups in $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}AsMe_2)Fe(CO)_4]$.[12]

Reactions of the Anion (**2**) *with Group* 1B *Metal Complexes.*—Reaction of complex (**2**) at room temperature in CH_2Cl_2 solution with a small excess of $[AuI(PPh_3)]$, $[AuCl(PMe_2Ph)]$, or $[\{AgCl(PPh_3)\}_4]$ gives the heterotrinuclear complexes $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}ML)(\mu\text{-}PPh_2)Mn(CO)_4]$ [M = Au, L = PPh_3 (**3a**) or PMe_2Ph (**3b**); M = Ag, L = PPh_3 (**3c**)] in high yield. The complexes have been characterised on the basis of i.r. and ^1H n.m.r. spectroscopy and, in the case of (**3c**), by an *X*-ray diffraction study.

The i.r. [ν(CO)] spectra of (**3a**)—(**3c**) show, in each case, six absorption bands in an overall pattern similar to that observed for (**1**). However, the absolute frequencies of the carbonyl

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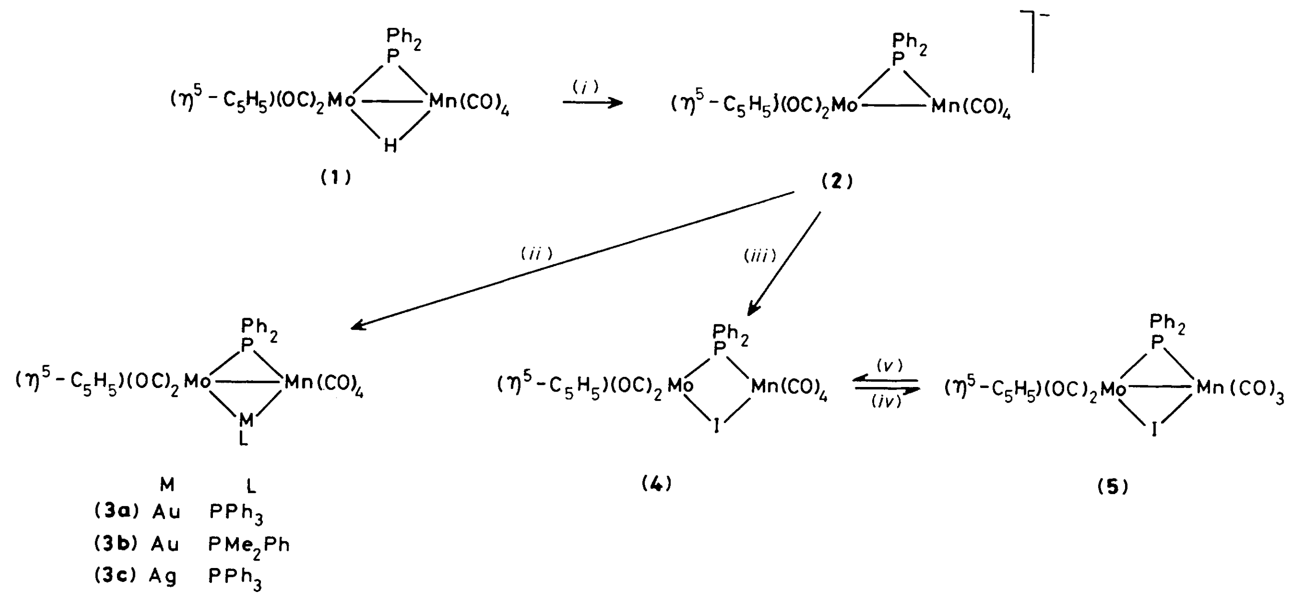
† 1,1,1,1,2,2-Hexacarbonyl-2-η-cyclopentadienyl-μ-diphenylphosphido-μ-triphenylphosphineargentio-manganesemolybdenum(*Mn*–*Mo*) and 1,1,1,1,2,2-hexacarbonyl-2-η-cyclopentadienyl-μ-diphenylphosphido-μ-iodo-manganesemolybdenum.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



Scheme. Synthesis and proposed structures of the new complexes. Reagents: (*i*) KOH, ethanol, $[NEt_4]Br$; (*ii*) $[AuI(PPh_3)]$, $[AuCl(PMe_2Ph)]$, or $[\{AgCl(PPh_3)\}_4]$, CH_2Cl_2; (*iii*) I_2, CH_2Cl_2; (*iv*) *hν*, hexane–benzene (5:1); (*v*) CO, hexane–benzene (5:1)

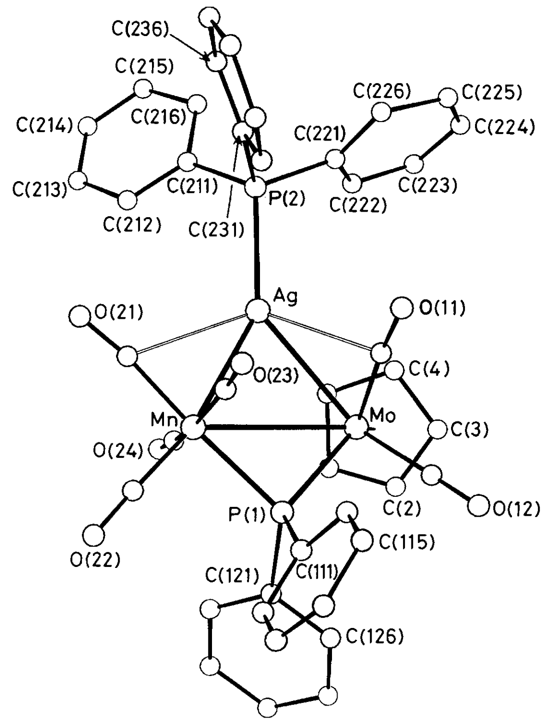


Figure 1. Molecular structure of $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}Ag(PPh_3)\}(\mu\text{-}PPh_2)Mn(CO)_4]$ (**3c**) showing the crystallographic numbering

absorptions are intermediate between those of complexes (**1**) and (**2**) suggesting that the M′–Au(Ag) bonds are polarised with significant negative charge on the molybdenum and manganese centres (M′).[13] The ^1H n.m.r. spectra of the complexes are consistent with the presence in solution of a single isomer, containing a μ-AuL or μ-AgL group. Few complexes containing a μ-bridging silver atom have been structurally characterised [14,15] and, to examine the effect of replacement of a μ-H by a μ-AgL group, an *X*-ray diffraction study has been carried out on (**3c**). Suitable crystals of complex (**3c**) were grown by slow evaporation of a hexane–CH_2Cl_2 (1:1) solution at 0 °C.

The molecular structure of (**3c**) is shown in Figure 1. Table 1 lists selected bond lengths and bond angles. The silver atom lies 0.30 Å above the Mo–Mn–P(1) plane, resulting in an angle between this plane and the Mo–Mn–Ag plane of 7.59°. The deviation from coplanarity in (**3c**) is somewhat greater than in the related complex, $[Mn_2\{\mu\text{-}Au(PMe_2Ph)\}(\mu\text{-}PPh_2)(CO)_8]$,[1] in which the gold atom is situated only 0.06 Å above the Mn–Mn–P(1) plane. The difference may be related to steric interaction between the bulky cyclopentadienyl and μ-$Ag(PPh_3)$ groups in (**3c**). The phosphorus atom in the PPh_3 group lies 0.11 Å above the Mo–Mn–Ag plane, on the same side of the plane as the phosphido ligand.

The reduced covalent radius of Mn compared to Mo may only partially explain the asymmetric bridging of the μ-$Ag(PPh_3)$ group [Ag–Mn 2.664(2), Ag–Mo 2.874(2) Å]. Thus the difference in the two metal–metal distances of *ca.* 0.21 Å compares with a difference of only *ca.* 0.12 Å in the two metal-bridging phosphorus distances. The Ag–Mn bond distance is only slightly shorter than the average Au–Mn bond distance (2.688 Å) in $[Mn_2\{\mu\text{-}Au(PMe_2Ph)\}(\mu\text{-}PPh_2)(CO)_8]$.[1] The manganese centre is approximately octahedrally co-ordinated by the silver atom, phosphido ligand, and four carbonyl ligands. The ligands around the molybdenum centre adopt the familiar approximate square-pyramidal geometry (if the Mo–Mn bond is ignored). The greater steric requirement of the μ-AgL group, compared to the μ-H group, results in the movement of the equatorial carbonyl ligands on Mn away from the former group, with an increase in the Mo–Mn–CO (*trans* to PPh_2) angle from 116.1(2)° in (**1**)[10] to 129.3(5)° in (**3c**) and a decrease in the Mo–Mn–CO (*trans* to Ag) angle from 148.6(2) to 135.6(5)°. This increase of 13.2° in the displacement from the μ-ML group of the carbonyl (*trans* to PPh_2) may be compared to the increase of 8.4° for the related Mn_2Au system.[1] Steric crowding involving the bulky μ-$Ag(PPh_3)$ group may also partly explain the increase in the Mo–Mn bond distance from 3.088(1) Å in (**1**) to 3.190(2) Å in (**3c**). The average Mn–CO and Mo–CO bond distances are the same within error limits in (**1**) and (**3c**). Further, all the carbonyl ligands in (**3c**) are near-linear; the greatest deviation, an Mn–CO interbond angle of 172(1)°, is

Table 1. Selected bond lengths (Å) and angles (°) for complexes (**3c**) and (**4**)

	(**3c**)	(**4**)		(**3c**)	(**4**)
Mo–Mn	3.190(2)	3.978(2)	Mo–C(11)	1.954(16)	1.951(12)
Mo–Ag	2.874(2)		Mo–C(12)	1.950(17)	2.009(13)
Mo–I		2.865(1)	Mn–C(21)	1.830(16)	1.815(12)
Mn–Ag	2.664(2)		Mn–C(22)	1.755(18)	1.810(13)
Mn–I		2.710(2)	Mn–C(23)	1.883(18)	1.873(12)
Mo–P(1)	2.387(4)	2.545(3)	Mn–C(24)	1.829(17)	1.849(12)
Mn–P(1)	2.272(4)	2.388(3)			
Ag–P(2)	2.414(4)		Range of C–O	1.113—1.165(17)	1.127—1.151(12)

(**3c**)

Mn–Ag–Mo	70.2(1)	P(2)–Ag–Mo	139.4(1)	C(22)–Mn–Mo	135.6(5)	C(23)–Mn–Ag	80.9(5)
P(2)–Ag–Mn	150.2(1)	C(11)–Ag–Mo	41.0(3)	C(22)–Mn–C(21)	95.1(7)	C(23)–Mn–P(1)	90.5(5)
C(11)–Ag–Mn	88.6(4)	C(11)–Ag–P(2)	112.7(4)	C(23)–Mn–Mo	88.4(5)	C(23)–Mn–C(22)	97.3(7)
C(21)–Ag–Mo	109.9(3)	C(21)–Ag–Mn	39.8(3)	C(23)–Mn–C(21)	87.8(7)	C(24)–Mn–Mo	84.0(5)
C(21)–Ag–P(2)	110.7(3)	C(21)–Ag–C(11)	121.2(5)	C(24)–Mn–Ag	83.1(5)	C(24)–Mn–C(21)	86.1(7)
Mn–Mo–Ag	51.8(1)	P(1)–Mo–Ag	96.8(1)	C(24)–Mn–P(1)	94.9(5)	C(24)–Mn–C(23)	164.0(7)
C(11)–Mo–Ag	64.4(4)	C(11)–Mo–Mn	89.8(5)	C(24)–Mn–C(22)	98.0(8)	C(111)–P(1)–Mo	123.5(5)
P(1)–Mo–Mn	45.3(1)	C(11)–Mo–P(1)	107.8(5)	Mn–P(1)–Mo	86.4(1)	C(121)–P(1)–Mo	113.5(5)
C(12)–Mo–Ag	142.0(4)	C(12)–Mo–Mn	119.2(5)	C(111)–P(1)–Mn	113.7(5)	C(121)–P(1)–C(111)	101.1(6)
C(12)–Mo–P(1)	81.4(5)	Mo–Mn–Ag	58.0(1)	C(121)–P(1)–Mn	120.0(5)	C(221)–P(2)–Ag	112.9(5)
C(12)–Mo–C(11)	79.9(6)	P(1)–Mn–Mo	48.3(1)	C(211)–P(2)–Ag	115.6(5)	C(231)–P(2)–Ag	111.7(5)
P(1)–Mn–Ag	106.0(1)	C(21)–Mn–Mo	129.3(5)	C(221)–P(2)–C(211)	104.0(7)	C(231)–P(2)–C(221)	105.2(7)
C(21)–Mn–Ag	71.5(5)	C(22)–Mn–Ag	166.4(5)	C(231)–P(2)–C(211)	106.7(7)		
C(21)–Mn–P(1)	177.1(5)	C(22)–Mn–P(1)	87.5(5)				
				Range of M–C–O	175—179(2)		

(**4**)

P–Mo–I	73.7(1)	C(11)–Mo–P	118.0(4)	C(24)–Mn–I	88.7(4)	C(23)–Mn–C(22)	90.6(5)
C(12)–Mo–I	129.4(3)	C(12)–Mo–C(11)	77.1(4)	C(24)–Mn–C(21)	88.8(5)	C(24)–Mn–P	90.4(3)
P–Mn–I	79.1(1)	C(12)–Mo–P	78.9(3)	C(24)–Mn–C(23)	177.3(5)	C(24)–Mn–C(22)	92.1(5)
C(21)–Mn–P	172.4(4)	C(21)–Mn–I	93.4(4)	Mn–P–Mo	107.5(1)	Mn–I–Mo	91.0(1)
C(22)–Mn–P	94.2(3)	C(22)–Mn–I	173.2(3)	C(111)–P–Mn	107.3(3)	C(111)–P–Mo	114.8(3)
C(23)–Mn–I	88.7(4)	C(22)–Mn–C(21)	93.3(5)	C(121)–P–Mn	115.5(3)	C(121)–P–Mo	110.0(3)
C(23)–Mn–C(21)	90.7(5)	C(23)–Mn–P	89.8(3)			C(121)–P–C(111)	101.9(4)
				Range of M–C–O	175—179(1)		

seen for CO(21) (*trans* to PPh_2), and is ascribed to the bending back of the oxygen from the PPh_3 ligand on Ag for steric reasons. Although the separation of the silver atom and the two adjacent carbonyl ligands, CO(21), 2.711(16) Å, and CO(11), 2.688(14) Å, approaches that required for incipient bridging of the Ag–Mn and Ag–Mo bonds, there is no evidence for such an interaction in the i.r. [ν(CO)] spectrum of (**3c**).

The Mn–P(1) bond distance, 2.272(4) Å, and the Mo–P(1) distance, 2.387(4) Å, are reduced from the corresponding distances in (**1**) of 2.294(2) and 2.435(1) Å respectively. The greater reduction in the Mo–P(1) distance may reflect a greater increase in the electron density, available for π bonding to phosphorus, at the molybdenum centre, as a result of the asymmetric bridging of the μ-Ag(PPh_3) group. In contrast, the similar Mn_2Au complex shows no significant change in Mn–P bond distances on replacement of the μ-H by the μ-AuL group.[1] The modification of the metal–phosphorus bond distances in the Mo–Mn–P triangle results in a large increase in the phosphido group bite angle (Mn–P–Mo) from 81.5(0)° in (**1**) to 86.4(1)° in (**3c**).

Reaction of Complex (**2**) *with Iodine*.—The reaction of complexes containing metal–metal bonds with electrophiles may lead to cleavage of the metal–metal bonds in some cases. This is particularly true of electrophiles such as X^+ (X = halogen) which may bridge metal–metal bonds as three-electron donor ligands. Thus the reaction of I_2 with $[Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ proceeds *via* electrophilic attack to give an iodo-bridged cationic intermediate which then reacts with I^- to give $[Fe(CO)_2(\eta^5\text{-}C_5H_5)I]$.[16] The reaction of I_2 with heterodinuclear metal–metal bonded complexes, *e.g.* with $[(OC)_5MnAu(PPh_3)]$ to give $[Mn(CO)_5I]$ and $[AuI(PPh_3)]$,[17] may proceed similarly and, in an attempt to isolate an iodo-bridged heterodinuclear intermediate in the Mo–Mn system, the reaction of (**2**) with I_2 has been studied.

On stirring complex (**2**) in CH_2Cl_2 with an equimolar quantity of I_2 a dark red crystalline solid is obtained in 76% yield. This yield is halved if the amount of I_2 used is halved, indicating that 1 mol of I_2 is needed per mol of (**2**) as expected if electrophilic attack of I^+ is involved.

The molecular structure of the dark red crystalline solid has been determined by an *X*-ray diffraction study, which reveals that it is the iodo-bridged complex $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}I)(\mu\text{-}PPh_2)Mn(CO)_4]$ (**4**). Crystals of (**4**) suitable for the *X*-ray study were grown by slow evaporation of a solution in hexane–CH_2Cl_2 (1 : 1) at 0 °C. The molecular structure of (**4**) is shown in Figure 2 and Table 1 lists selected bond lengths and bond angles.

The phosphido and iodo ligands bridge the two metal atoms, which are separated by a distance of 3.978(2) Å, compared to 3.088(1) Å in the μ-H complex, (**1**).[10] This large separation is consistent with the absence of a Mo–Mn bond in (**4**), as expected on the basis of the 18-electron rule, and may be compared to a Mo–Mo separation of 4.441(1) Å in the bis(iodo)-bridged complex, $[Mo_2(\mu\text{-}I)_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$.[18] Even allowing for differences in the covalent radius between Mo and Mn the intermetal separation in (**4**) is significantly reduced compared to the bis(iodo) complex, indicating lower geometrical flexibility of the μ-PR_2 ligand compared to the μ-I

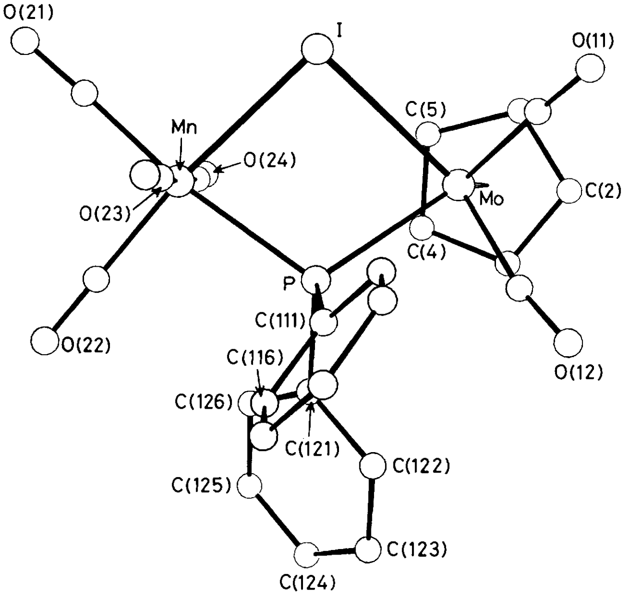


Figure 2. Molecular structure of $[(\eta^5\text{-}C_5H_5(OC)_2Mo(\mu\text{-}I)(\mu\text{-}PPh_2)\text{-}Mn(CO)_4]$ (**4**) showing the crystallographic numbering

ligand. The Mn–I bond distance of 2.710(2) Å compares to 2.689(2) Å in the only previous *X*-ray structural determination on an iodo-bridged heterodimetallic complex, $[(OC)_4Mn\text{-}(\mu\text{-}I)(\mu\text{-}COCH_2CH_2CH_2)Pt(PBu^t{}_2Me)_2]$.[19] The Mo–I bond distance of 2.865(1) Å compares closely to that of 2.853(1) Å in $[Mo_2(\mu\text{-}I)_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$.[18] The Mo–I–Mn angle of 91.0(1)° is at the lower end of the range of values for iodo ligands bridging two non-bonded metals; the corresponding angle in $[Mo_2(\mu\text{-}I)_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ is 102.24(2)° and in $[Os_4H_3(\mu\text{-}I)\text{-}(CO)_{12}]$[20] is 87.9(2)°. The bridging angle of the phosphido group, Mo–P–Mn, of 107.5(1)° compares with 81.5(0)° for (**1**), which contains a Mo–Mn bond. The M–P bond distances in (**4**) are *ca.* 0.1 Å greater than in (**1**). The iodo and phosphido groups adopt a relative orientation (with respect to the Mo–Mn vector) intermediate between transoid and cisoid: the angle between the planes containing Mo–Mn–I and Mo–Mn–P is 145.0°. The relative geometry of the bridging groups may be determined by the requirement to minimise steric interaction between the ligands on the two metals.

The distribution of the six ligands on Mn, comprising four carbonyl groups and the phosphido and iodo groups, is close to octahedral, the largest deviation from ideal being the P–Mn–I interbond angle of 79.1(1)°. The mean Mn–CO bond distance of 1.832(10) Å is equal, within error limits, to the corresponding distance in (**1**), with the longest Mn–CO distance being observed for the axial carbonyl ligands as expected on the basis of the relative π-acid character of the *trans* ligands on Mn. The ligands on Mo adopt a square-pyramidal geometry with mean Mo–CO and mean Mo–C(cyclopentadienyl) bond distances identical within error limits to the corresponding distances in (**1**).

The infrared [ν(CO)] and ^{13}C n.m.r. spectra of complex (**4**) show the same pattern of resonances as observed for (**1**),[10] indicating that (**1**) and (**4**) have similar structures in solution. The absence of a metal–metal bond in (**4**), however, is revealed by its ^{31}P n.m.r. spectrum, which shows a resonance at δ −135.4 p.p.m. attributable to the μ-PPh_2 group as compared to the resonance at δ 17.5 p.p.m. for this group in (**1**). These values are consistent with data on a wide range of μ-PR_2 complexes which suggest that, in most cases, resonances in the range δ −100 to −350 p.p.m. may be expected if a metal–metal bond is absent and in the range δ 150 to −100 p.p.m. if such a bond is present.[21]

In the reaction of complex (**2**) with I_2 small quantities of an orange solid are isolated in addition to the major product (**4**). The yield of this minor product increases if the reaction mixture is stirred in daylight after the initial reaction with I_2 is complete, and (**4**) is converted into it in near-quantitative yield on irradiation with u.v. light. On the basis of spectroscopic evidence the minor product is formulated as $[(\eta^5\text{-}C_5H_5)(OC)_2\text{-}Mo(\mu\text{-}I)(\mu\text{-}PPh_2)Mn(CO)_3]$ (**5**) which is derived from (**4**) by loss of a CO ligand and concomitant metal–metal bond formation. Thus the ^{13}CO n.m.r. spectrum of (**5**) shows three resonances of relative intensity 1 and a 'triplet' resonance of relative intensity 2. This latter resonance may be ascribed to two superimposed doublets. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum shows a singlet resonance at δ −49.3 p.p.m., this shift [as compared to the corresponding resonance in (**4**)] being consistent with metal–metal bond formation.[21]

There are two possible structures for (**5**), one with four CO ligands on Mn and one on Mo, the other with three CO ligands on Mn and two on Mo. The latter structure, shown in the Scheme, is preferred on the basis of the close similarity of the i.r. [ν(CO)] spectrum of (**5**) to that of a related μ-acyl complex, $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}C(O)C_6H_{11}\}(\mu\text{-}PPh_2)Mn(CO)_3]$, the structure of which has been determined by *X*-ray analysis.[22]

Stirring a solution of (**5**) under CO at room temperature leads, after 1 h, to near-quantitative regeneration of (**4**). Such reversible metal–metal bond cleavage in bridged heterodinuclear complexes on reaction with two-electron donor ligands has been observed in related systems.[23]

Experimental

All reactions were carried out under a nitrogen atmosphere in nitrogen-saturated solvents distilled from an appropriate drying agent and stored over 4A molecular sieves. The instrumentation used to obtain spectroscopic data has been previously described.[1] Phosphorus-31 n.m.r. chemical shifts are given relative to $P(OMe)_3$ with upfield shifts negative. All n.m.r. spectra were recorded at 298 K unless otherwise specified. Preparative thin-layer chromatography (t.l.c.) was carried out on commercial Merck plates coated with a 0.25 mm layer of silica. Complex (**1**) was prepared as previously described by us.[10]

Synthesis of $[NEt_4][(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}PPh_2)Mn\text{-}(CO)_4]$ (**2**).—A mixture of complex (**1**) (0.23 g, 0.4 mmol) and powdered KOH (0.023 g, 0.41 mmol) were stirred in absolute ethanol (10 cm^3) for 24 h at room temperature to give a dark red solution. A solution of $[NEt_4]Br$ (0.084 g, 0.4 mmol) in absolute ethanol (10 cm^3) was added by syringe and the solvent removed *in vacuo*. The residue was extracted with acetone and the acetone then removed *in vacuo*. Precipitation from Et_2O–CH_2Cl_2 (1:1) solution gave (**2**) (0.18 g, 64%) as an orange solid (Found: C, 51.9; H, 5.1; N, 1.9. $C_{31}H_{35}MnMoNO_6P$ requires C, 53.2; H, 5.0; N, 2.0%); $\nu_{max.}$(CO) at 2 003m 1 911s, 1 873s, and 1 785m cm^{-1} (CH_2Cl_2). N.m.r.: ^1H (CD_3COCD_3) at 215 K, δ 7.8—7.0 (m, 10 H, Ph), 4.82 (s, 5 H, C_5H_5), 3.46 (m, 8 H, CH_2CH_3), and 1.33 (m, 12 H, CH_2CH_3).

Reactions of Complex (**2**) *with Group* 1B *Metal Complexes*.—(*a*) *With* $[AuI(PPh_3)]$. A solution of complex (**2**) (0.024 g, 0.034 mmol) and $[AuI(PPh_3)]$ (0.023 g, 0.039 mmol) in CH_2Cl_2 (5 cm^3) changed colour instantly (10 s) from orange to bright red on being stirred at room temperature. I.r. monitoring indicated that the reaction had gone *ca.* 90% to completion and the addition of further small quantities of $[AuI(PPh_3)]$ or longer reaction times did not increase the product yield. The solvent was removed *in vacuo* and the residue applied to t.l.c. plates. Elution with light petroleum (b.p. 40—60 °C) in ethyl acetate (9:1) gave a trace of an unidentified yellow product,

Table 2. Fractional atomic co-ordinates for [(η^5-C_5H_5)(OC)$_2$Mo{μ-Ag(PPh_3)}μ(PPh_2)Mn(CO)$_4$] (**3c**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag	0.270 17(7)	0.019 06(7)	0.192 96(8)	C(115)	0.218 5(13)	0.450 9(14)	0.184 9(12)
Mo	0.198 84(8)	0.127 92(8)	0.300 76(8)	C(116)	0.204 6(11)	0.363 2(11)	0.202 0(10)
Mn	0.143 49(13)	0.118 93(13)	0.101 54(13)	C(121)	0.011 0(9)	0.212 9(9)	0.200 8(9)
P(1)	0.103 6(2)	0.210 8(2)	0.193 0(2)	C(122)	−0.076 6(10)	0.165 1(11)	0.150 2(10)
P(2)	0.386 0(2)	−0.086 1(2)	0.202 2(3)	C(123)	−0.159 6(11)	0.161 4(12)	0.167 7(11)
C(1)	0.087 8(10)	0.036 8(11)	0.320 6(11)	C(124)	−0.177 4(11)	0.207 6(11)	0.231 8(11)
C(2)	0.110 9(12)	0.091 8(10)	0.387 3(10)	C(125)	−0.111 7(10)	0.257 3(11)	0.282 2(10)
C(3)	0.196 7(13)	0.075 8(11)	0.432 1(10)	C(126)	−0.028 0(9)	0.260 9(9)	0.266 7(9)
C(4)	0.228 1(12)	0.005 4(12)	0.391 2(12)	C(211)	0.351 6(9)	−0.191 5(9)	0.154 2(9)
C(5)	0.161 7(12)	−0.021 1(10)	0.322 1(11)	C(212)	0.277 4(10)	−0.195 2(11)	0.089 2(10)
C(11)	0.319 6(11)	0.153 7(10)	0.298 0(10)	C(213)	0.250 9(13)	−0.275 9(13)	0.051 2(13)
O(11)	0.391 8(7)	0.173 2(9)	0.300 9(8)	C(214)	0.297 6(12)	−0.348 5(13)	0.077 4(12)
C(12)	0.214 0(10)	0.241 1(11)	0.355 6(10)	C(215)	0.369 9(12)	−0.346 5(12)	0.140 6(11)
O(12)	0.221 5(9)	0.305 6(8)	0.390 8(8)	C(216)	0.400 6(11)	−0.267 3(11)	0.180 6(10)
C(21)	0.181 1(10)	0.044 4(10)	0.031 5(10)	C(221)	0.441 1(9)	−0.112 0(9)	0.306 5(9)
O(21)	0.198 3(9)	0.003 3(8)	−0.018 9(8)	C(222)	0.395 2(11)	−0.158 6(11)	0.356 4(11)
C(22)	0.067 0(11)	0.172 8(12)	0.021 5(10)	C(223)	0.436 2(14)	−0.175 0(14)	0.438 8(15)
O(22)	0.016 7(9)	0.209 0(9)	−0.030 6(8)	C(224)	0.517 8(15)	−0.147 3(15)	0.475 0(16)
C(23)	0.240 9(12)	0.189 6(10)	0.100 8(10)	C(225)	0.564 2(18)	−0.106 8(16)	0.429 8(16)
O(23)	0.297 5(8)	0.230 8(8)	0.095 8(9)	C(226)	0.527 4(14)	−0.088 2(14)	0.342 6(14)
C(24)	0.072 8(11)	0.029 8(10)	0.118 0(10)	C(231)	0.470 2(9)	−0.046 1(10)	0.155 6(9)
O(24)	0.027 9(8)	−0.027 2(8)	0.125 0(8)	C(232)	0.477 0(12)	0.044 7(12)	0.148 1(12)
C(111)	0.121 7(9)	0.327 5(9)	0.173 0(9)	C(233)	0.542 8(13)	0.080 2(14)	0.114 4(12)
C(112)	0.054 2(11)	0.374 8(11)	0.122 9(10)	C(234)	0.600 7(13)	0.027 0(14)	0.089 0(12)
C(113)	0.072 6(12)	0.463 7(13)	0.103 8(12)	C(235)	0.593 9(13)	−0.062 6(14)	0.095 0(12)
C(114)	0.149 5(14)	0.496 3(14)	0.136 1(13)	C(236)	0.528 8(11)	−0.099 3(12)	0.127 4(11)

Table 3. Fractional atomic co-ordinates for [(η^5-C_5H_5)(OC)$_2$Mo(μ-I)(μ-PPh_2)Mn(CO)$_4$] (**4**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
I	−0.015 39(3)	−0.227 59(7)	−0.034 18(7)	C(23)	−0.006 9(4)	−0.089 1(12)	−0.323 7(13)
Mo	−0.135 89(3)	−0.272 43(8)	−0.056 40(8)	O(23)	0.004 1(3)	0.012 9(8)	−0.335 5(10)
Mn	−0.021 90(6)	−0.260 83(13)	−0.307 97(16)	C(24)	−0.035 5(4)	−0.429 7(11)	−0.283 5(11)
P	−0.119 4(1)	−0.213 3(2)	−0.295 7(2)	O(24)	−0.040 8(3)	−0.534 9(7)	−0.267 8(9)
C(1)	−0.136 2(5)	−0.433 6(10)	0.099 4(12)	C(111)	−0.130 8(4)	−0.046 8(8)	−0.339 6(9)
C(2)	−0.192 0(5)	−0.397 3(10)	0.048 8(12)	C(112)	−0.124 8(4)	0.044 6(9)	−0.238 6(11)
C(3)	−0.203 4(5)	−0.426 1(10)	−0.091 9(13)	C(113)	−0.129 9(5)	0.173 0(11)	−0.273 6(12)
C(4)	−0.154 5(5)	−0.483 8(9)	−0.126 8(12)	C(114)	−0.141 8(5)	0.208 7(12)	−0.409 7(13)
C(5)	−0.112 6(5)	−0.488 1(9)	−0.009 7(12)	C(115)	−0.146 4(5)	0.120 7(11)	−0.511 7(13)
C(11)	−0.124 8(5)	−0.142 7(11)	0.085 1(12)	C(116)	−0.141 3(4)	−0.008 7(10)	−0.477 1(11)
O(11)	−0.121 4(4)	−0.070 3(9)	0.171 5(10)	C(121)	−0.173 3(4)	−0.290 1(8)	−0.426 0(9)
C(12)	−0.202 0(5)	−0.155 4(12)	−0.116 7(11)	C(122)	−0.228 5(4)	−0.239 6(9)	−0.453 6(11)
O(12)	−0.240 4(4)	−0.089 2(9)	−0.149 2(9)	C(123)	−0.270 0(5)	−0.298 6(11)	−0.555 3(12)
C(21)	0.053 9(5)	−0.296 4(11)	−0.292 7(13)	C(124)	−0.255 9(5)	−0.402 9(11)	−0.619 1(12)
O(21)	0.101 0(4)	−0.321 7(10)	−0.287 0(12)	C(125)	−0.203 8(4)	−0.454 8(10)	−0.592 9(11)
C(22)	−0.035 0(5)	−0.277 1(10)	−0.492 9(13)	C(126)	−0.161 5(4)	−0.396 1(9)	−0.495 3(10)
O(22)	−0.043 4(4)	−0.285 9(9)	−0.608 7(9)				

followed by a bright red band which, on evaporation of the solvent, gave bright red crystals of [(η^5-C_5H_5)(OC)$_2$Mo{μ-Au(PPh_3)}(μ-PPh_2)Mn(CO)$_4$] (**3a**) (0.03 g, 86%); $\nu_{max.}$(CO) at 2 028m, 1 959s, 1 942s, 1 936s, 1 925m, and 1 857m cm^{-1} (n-hexane). N.m.r.: ^1H ($CDCl_3$), δ 7.9—7.2 (m, 25 H, Ph) and 4.65 (s, 5 H, C_5H_5).

(*b*) *With* [AuCl(PMe_2Ph)]. A solution of complex (**2**) (0.024 g, 0.034 mmol) and [AuCl(PMe_2Ph)] (0.014 g, 0.038 mmol) in CH_2Cl_2 (5 cm^3) were allowed to react as in (*a*) to give an unidentified purple product (0.002 g) and bright red crystalline [(η^5-C_5H_5)(OC)$_2$Mo{μ-Au(PMe_2Ph)}(μ-PPh_2)Mn(CO)$_4$] (**3b**) (0.025 g, 81%) (Found: C, 40.7; H, 3.0. $C_{46}H_{38}MnMoO_6P_2$ requires C, 41.2; H, 2.9%); $\nu_{max.}$(CO) at 2 030m, 1 961s, 1 944s, 1 937s, 1 921m, and 1 853m cm^{-1} (n-hexane). N.m.r.: ^1H ($CDCl_3$), δ 7.9—7.2 (m, 15 H, Ph), 4.80 (s, 5 H, C_5H_5), and 1.99 [d, 6 H, ^2J(PH) 8.9 Hz, P*Me*$_2$Ph].

(*c*) *With* [{AgCl(PPh_3)}$_4$]. A solution of complex (**2**) (0.024 g, 0.034 mmol) and [{AgCl(PPh_3)}$_4$] (0.016 g, 0.01 mmol) in CH_2Cl_2 (5 cm^3) were allowed to react as in (*a*) to give an unidentified yellow complex (0.002 g) and bright red crystalline [(η^5-C_5H_5)(OC)$_2$Mo{μ-Ag(PPh_3)}(μ-PPh_2)Mn(CO)$_4$] (**3c**) (0.023 g, 72%); $\nu_{max.}$(CO) at 2 033m, 1 955m, 1 942s, 1 935s, 1 911m, and 1 843m cm^{-1} (n-hexane). N.m.r.: ^1H ($CDCl_3$), δ 7.8—7.2 (m, 25 H, Ph) and 4.67 (s, 5 H, C_5H_5).

Reaction of Complex (**2**) *with Iodine*.—Complex (**2**) (0.024 g, 0.034 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and I_2 (0.0045 g, 0.018 mmol) added to give an instant colour change from orange to bright red. I.r. monitoring showed *ca.* 50% conversion of (**2**) into a new product. Addition of a further quantity of I_2 (0.045 g, 0.018 mmol) resulted in essentially complete conversion of (**2**). The solvent was removed *in vacuo* and the residue applied to the base of a t.l.c. plate. Elution with hexane–CH_2Cl_2 (9:1) gave a red band followed by an orange band. The red band, after evaporation of the solvent, gave dark red crystals of $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}I)(\mu\text{-}PPh_2)Mn(CO)_4]$ (**4**) (0.018 g, 76%) (Found: C, 39.5; H, 2.2; P, 4.7. $C_{23}H_{15}IMnMoO_6P$ requires C, 39.7; H, 2.2; P, 4.5%); mass spectrum, *m/e* 696 (M^+), $M^+ - n$CO (n = 1—6); $\nu_{max.}$(CO) at 2 077m, 2 010s, 1 981s, 1 967s, 1 960s, and 1 894s cm^{-1} (n-hexane). N.m.r.: ^{1}H (CDCl$_3$), δ 8.0—7.3 (m, 10 H, Ph) and 5.20 (s, 5 H, C_5H_5); ^{13}C (CDCl$_3$, 233 K, ^{1}H gated decoupled), δ 250.7 [d, ^2J(PC) 22.9, 1 MoCO(*cis*)], 247.2 [s, 1 MoCO(*trans*)], 219.7 [d, ^2J(PC) 13.8, 1 MnCO], 214.6 [d, ^2J(PC) 17.6, 1 MnCO], 211.2 [d, ^2J(PC) 13.8, 1 MnCO], 208.5 [d, ^2J(PC) 3.9 Hz, 1 MnCO], 143.7—128.2 (m, Ph), and 94.9 (s, C_5H_5); ^{31}P (CDCl$_3$, ^{1}H gated decoupled), δ −135.4 p.p.m. (s, μ-PPh$_2$). The orange band, after evaporation of the solvent, gave as an orange solid the complex $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}I)(\mu\text{-}PPh_2)Mn(CO)_3]$ (**5**) (Found: C, 39.2; H, 2.3; P, 4.6. $C_{22}H_{15}IMnMoO_5P$ requires C, 39.6; H, 2.3; P, 4.6%); $\nu_{max.}$(CO) at 2 028s, 1 991m, 1 952m, 1 931m, and 1 920 (sh) cm^{-1} (n-hexane). N.m.r.: ^{1}H (CDCl$_3$), δ 7.6—7.2 (m, 10 H, Ph), 5.56 (s, 5 H, C_5H_5); ^{13}C (CDCl$_3$, 233 K, ^{1}H gated decoupled), δ 229.4 [d, ^2J(PC) 14.8, 1 CO)], 229.2 [d, ^2J(PC) 14.1, 1 CO], 226.4 (s, 1 CO), 224.8 [d, ^2J(PC) 18.9, 1 CO], 220.9 [d, ^2J(PC) 19.9 Hz, 1 CO], 141.3—127.2 (m, Ph), and 90.8 (s, C_5H_5); ^{31}P (CDCl$_3$, ^{1}H gated decoupled), δ −49.3 p.p.m. (s, μ-PPh$_2$).

Photolysis of Complex (**4**).—A solution of complex (**4**) (0.01 g, 0.014 mmol) in a mixture of hexane (25 cm^3) and benzene (5 cm^3) was irradiated with u.v. light (Hanovia, medium-pressure lamp) at room temperature for 1 h. The solvent was removed *in vacuo* and the residue applied to t.l.c. plates. Elution with hexane–CH_2Cl_2 (9:1) gave a trace of unreacted (**4**) and (**5**) (0.0085 g, 90%).

Reaction of Complex (**5**) *with Carbon Monoxide*.—Carbon monoxide was bubbled through a solution of complex (**5**) (0.01 g, 0.015 mmol) in hexane (25 cm^3)–benzene (5 cm^3) for 2 h at room temperature. T.l.c. separation of the products in the dark gave (**4**) (0.095 g, 91%) and a trace of (**5**).

Crystal Structure Determinations.—*Crystal data*. (**3c**), $C_{41}H_{30}AgMnMoO_6P_2$, M = 939.35, monoclinic, a = 15.745(3), b = 15.382(3), c = 16.536(3) Å, β = 104.69(2)°, U = 3 873.9 Å^3, space group $P2_1/c$, Z = 4, D_c = 1.610 g cm^{-3}, $F(000)$ = 1 872.

(**4**), $C_{23}H_{15}IMnMoO_6P$, M = 696.08, monoclinic, a = 23.689(5), b = 10.639(2), c = 9.894(2) Å, β = 99.95(2)°, U = 2 456.0 Å^3, space group $P2_1/n$, Z = 4, D_c = 1.882 g cm^{-3}, $F(000)$ = 1 344.

Data collection. Data were collected on a Philips PW1100 diffractometer in the θ range 3—25°, with a scan width of 0.80°, using Mo-K_α radiation [μ(Mo-K_α) 11.59 (**3c**) and 22.11 cm^{-1} (**4**)] by the technique described previously.[24] Lorentz polarisation corrections were applied, and equivalent reflections were merged to give 3 445 (**3c**) and 2 618 (**4**) data with $I/\sigma(I) > 3.0$.

Structure solution and refinement.[25] The co-ordinates of the metal atoms were deduced from Patterson syntheses, and the remaining non-hydrogen atoms were located from subsequent Fourier-difference syntheses. The hydrogen atoms were included in geometrically idealised positions and were constrained to 'ride' on the relevant carbon atoms with common isotropic thermal parameters which were refined [final values 0.12 (**3c**), and 0.068 (phenyl) and 0.10 (cyclopentadienyl) (**4**)]. All non-hydrogen atoms were assigned anisotropic thermal parameters in the final cycles of full-matrix refinement which converged at R 0.0712 (R' 0.0701) (**3c**) and 0.0449 (0.0445) (**4**) with weights of $w = 1/\sigma^2F_o$ assigned to the individual reflections.

The final atomic co-ordinates are given in Tables 2 and 3 respectively for (**3c**) and (**4**). Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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