Cyclopentadienone Complexes of Molybdenum: Synthesis of Carbonyl, Acetonitrile, Phosphine and Phosphido-bridged Derivatives†

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Reaction of $[Mo(CO)_6]$ with 2 equivalents of tetraphenylcyclopentadienone (tetracyclone) in refluxing toluene gives $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$ **1a** in *ca.* 95% yield. With 1 equivalent of tetracyclone in boiling heptane, $[\{Mo(CO)_3(\sigma:\eta^4\text{-}C_4Ph_4CO)\}_2]$ **2** is produced as well as **1a**. This dimeric complex has been crystallographically characterised [triclinic, space group $P\bar{1}$ (no. 2), $a = 8.980(3)$, $b = 11.332(4)$, $c = 13.526(5)$ Å; $\alpha = 77.55(3)$, $\beta = 71.94(3)$, $\gamma = 81.02(3)^\circ$, $Z = 2$ monomer units]; each molybdenum is in a distorted-octahedral environment, co-ordinated by the η^4-diene ligand, three carbonyl ligands, and the ketonic carbonyl of the other centrosymmetrically related tetracyclone. Another convenient route into the chemistry of tetracyclone molybdenum complexes is provided by $[Mo(CO)_3(NCMe)(\eta^4\text{-}C_4Ph_4CO)]$ **5** which is formed in high yield by treating $[Mo(CO)_3(NCMe)_3]$ with tetracyclone. One (but only one) of the tetracyclone ligands of complex **1a** can be displaced by chelating phosphines to give $[Mo(CO)_2(L\text{-}L)(\eta^4\text{-}C_4Ph_4CO)]$ (L–L = $Ph_2PCH_2PPh_2$ or $Ph_2PCH_2CH_2PPh_2$); the stereochemistry and fluxionality of these complexes is briefly discussed. Thermal reaction of **1a** with monodentate phosphines (L = PPh_3 or PPh_2Me) yields $[Mo(CO)_3L(\eta^4\text{-}C_4Ph_4CO)]$ **7** by a carbonyl redistribution process; the same compounds can be prepared from **5** by displacement of the labile acetonitrile ligand, as can an analogous species with L = PPh_2H. Thermolysis of $[Mo(CO)_3(PPh_2H)(\eta^4\text{-}C_4Ph_4CO)]$ or thermal reaction of **1a** with PPh_2H gives the phosphido-bridged complex $[Mo_2(CO)_3(\mu\text{-}PPh_2)(\mu\text{-}\sigma:\eta^5\text{-}C_4Ph_4CO)(\eta^5\text{-}C_4Ph_4COH)]$ **8**. The crystal structure of **8** has also been determined [triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 12.806(10)$, $b = 14.173(8)$, $c = 17.958(7)$ Å, $\alpha = 83.75(4)$, $\beta = 86.92(5)$, $\gamma = 71.57(5)^\circ$, $Z = 2$] and reveals a formal Mo=Mo double bond [2.923(2) Å] bridged by a diphenylphosphido group and a tetracyclone ligand bonded in a $\sigma:\eta^5$ manner. The other tetracyclone is bonded as an η^5-hydroxytetraphenylcyclopentadienyl ligand, having taken up the proton released by oxidative addition of the P–H bond.

The chemistry of transition-metal complexes which contain cyclic diene ligands has been studied for over 30 years, and continues to attract considerable research interest. One of the early successes of organometallic chemistry was the stabilisation of cyclobutadiene, C_4H_4, as its iron tricarbonyl complex by Pettit and co-workers.[1] Cyclopentadienone, C_4H_4CO, is also a molecule which has only a transient existence in the free state but can be stabilised as its $Fe(CO)_3$ complex.[2] However, whereas substituted cyclobutadienes are also unstable, the Diels–Alder dimerisation of cyclopentadienones can be sterically inhibited by substitution; thus, 2,5-dimethyl-3,4-diphenylcyclopentadienone exists as a dimer which dissociates into the free monomeric dienone on heating, while tetraphenylcyclopentadienone (commonly called tetracyclone) exists solely as a stable monomer.[3]

It is therefore perhaps surprising that the chemistry of transition-metal complexes with substituted cyclopentadienone ligands has been relatively neglected compared to the large volume of research into those containing substituted cyclobutadienes, considering that the latter have to be introduced by indirect methods (*e.g.* by dimerisation of alkynes, by π-ligand transfer from other complexes, or by dechlorination of dichlorocyclobutenes).[4] Although a search of the literature reveals over 150 papers describing complexes with η^4-cyclopentadienone ligands, in the majority of cases these occur as low-yield by-products in the reactions of metal carbonyls with alkynes, with the cyclopentadienone being formed *in situ* by cyclisation of two alkyne molecules with a carbonyl ligand.[5] Such complexes have been studied in their own right only in relatively few cases. Recent work by Shvo and co-workers,[6–12] however, has shown that ruthenium complexes with substituted cyclopentadienone ligands are effective catalysts for hydrogenation and dehydrogenation reactions.

As part of our current interest in such ligands we have undertaken a study of tetracyclone molybdenum complexes. By virtue of its four phenyl groups and ketonic carbonyl the tetracyclone ligand is a relatively good π acceptor, and bonds to metals rather more strongly than labile dienes such as norbornadiene (nbd) or cycloocta-1,5-diene (cod); because of this we envisaged that further chemistry might be carried out on such complexes with retention of the dienone ligand. Prior to this work, only three tetracyclone molybdenum complexes had been isolated, by Hübel and Merenyi.[13] Reaction of $[Mo(CO)_6]$ with diphenylacetylene in benzene at 140 °C in an autoclave gave the yellow bis(cyclobutadiene) complex $[Mo(CO)_2(\eta\text{-}C_4Ph_4)_2]$, a green complex which at first was formulated as $[Mo_2(CO)_4(C_4Ph_4)_2(C_2Ph_2)]$ but later crystallographically identified as $[Mo_2(CO)_3(\mu\text{-}C_2Ph_2)(\mu\text{-}C_4Ph_4CO)(\eta\text{-}C_4Ph_4)]$ containing a bridging tetracyclone ligand,[14] and the yellow compound $[Mo(CO)_2(\eta\text{-}C_4Ph_4)(\eta^4\text{-}C_4Ph_4CO)]$ which possesses one cyclobutadiene and one tetracyclone ligand. The reaction of $[Mo(CO)_6]$ with tetracyclone itself in benzene at 160 °C for 3 d gave yellow $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$ in a yield that was described only as 'wenig', *i.e.* little.[15] Very recently, Liebeskind and Bombrun[16] have reported the synthesis of the cationic

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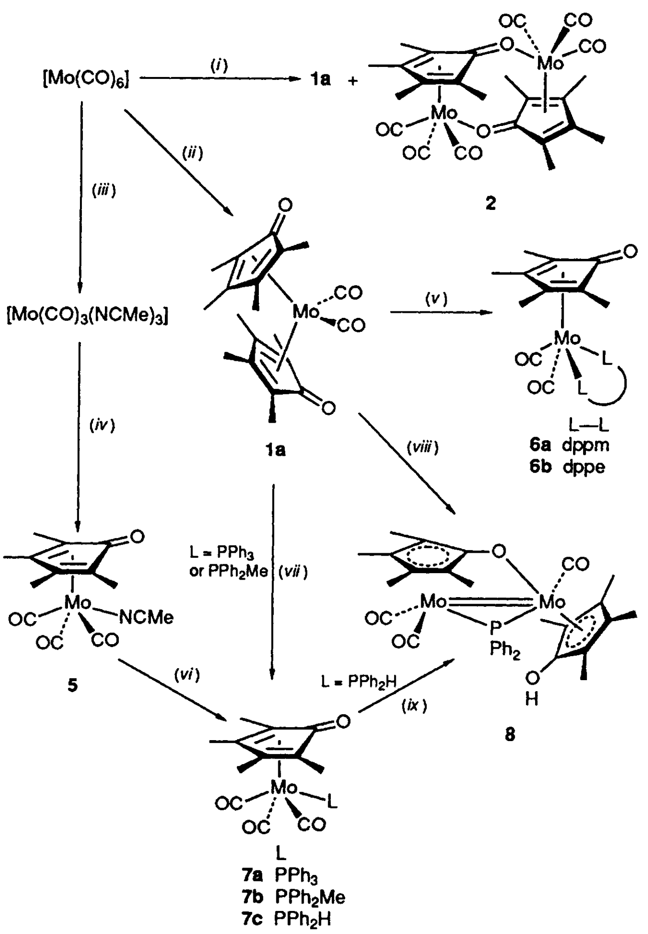
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1 Reagents and conditions: (*i*) tetracyclone (1.1 equivalent), heptane, reflux, 17 h, yield 31%; (*ii*) tetracyclone (2 equivalents), toluene, reflux, 17 h, 93%; (*iii*) MeCN, reflux, 5 h; (*iv*) tetracyclone, thf, room temperature (r.t.), 18 h, 70% overall; (*v*) L–L, toluene, reflux, 8 h, 90%; (*vi*) L, CH_2Cl_2, r.t., 18 h, 95%; (*vii*) L, toluene, reflux, 18 h, 80%; (*viii*) PPh_2H, toluene, reflux, 18 h, 51%; (*ix*) toluene, reflux, 18 h

unsubstituted cyclopentadienone complex $[Mo(CO)_2(\eta^4\text{-}C_4H_4CO)(\eta^5\text{-}C_5H_5)][PF_6]$ and its reactions with nucleophiles.

In this paper we describe simple high-yield syntheses of $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$ and the acetonitrile complex $[Mo(CO)_3(NCMe)(\eta^4\text{-}C_4Ph_4CO)]$, and demonstrate that these two compounds can serve as useful starting materials for the synthesis of complexes of the type $[Mo(CO)_2(L\text{-}L)(\eta^4\text{-}C_4Ph_4CO)]$, where L-L is a bidentate phosphine, and $[Mo(CO)_3L(\eta^4\text{-}C_4Ph_4CO)]$, where L is a monodentate phosphine. The syntheses and crystal structures of the dinuclear complex $[\{Mo(CO)_3(\mu\text{-}\sigma:\eta^4\text{-}C_4Ph_4CO)\}_2]$ and the phosphido-bridged species $[Mo_2(CO)_3(\mu\text{-}PPh_2)(\mu\text{-}\sigma:\eta^5\text{-}C_4Ph_4CO)(\eta^5\text{-}C_4Ph_4COH)]$ are also described. Parts of this work have been the subject of a preliminary communication.[17]

Results and Discussion

(*a*) *Synthesis of* $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$ *and* $[\{Mo(CO)_3(\mu\text{-}\sigma:\eta^4\text{-}C_4Ph_4CO)\}_2]$.—The reaction of $[Mo(CO)_6]$ with 2 equivalents of tetracyclone in refluxing toluene for 17 h gave the bis(dienone) complex $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$ **1a** (see Scheme 1), which could be isolated by column chromatography on silica gel as an air-stable bright yellow powder in *ca.* 95% yield. In dichloromethane solution the IR spectrum displayed the two peaks expected for a *cis*-dicarbonyl structure at 2006 and 1956 cm^{-1}, together with a peak at 1651 cm^{-1} due to the ketonic carbonyl of the dienone ligands. In the solid state (KBr disc) this peak is split into two (1651 and 1634 cm^{-1}). The ^1H NMR spectrum was relatively uninformative, but the ^{13}C NMR spectrum contained peaks due to the carbonyl ligands (δ 228.9) and the carbonyl groups of the rings (δ 167.3), as well as the expected aromatic groups. Signals were also observed at δ 108.9 and 95.3, assigned respectively to the cyclopentadienone ring carbons β and α to the ring carbonyl. All of these data support the original formulation of the complex proposed by Weiss and Hübel[15] and its structure is assumed to be similar to that of $[Mo(CO)_2(\eta\text{-}C_4Ph_4)_2]$ and other $[Mo(CO)_2(diene)_2]$ complexes.[18]

The analogous 2,5-dimethyl-3,4-diphenylcyclopentadienone complex **1b** was obtained in a similar manner using the commercially available dimer of the ligand; under the conditions of the reaction dissociation occurs to form the free monomer. The spectroscopic properties of **1b** parallel those of **1a** with appropriate additional signals for the methyl groups. Later investigation showed that **1b** was not as reactive thermally as **1a** and so this ligand system was not studied further. Attempts to prepare a tungsten analogue of **1a** failed; even after several days in refluxing toluene there was little evidence of reaction between tetracyclone and $[W(CO)_6]$, presumably because of the greater M–CO bond strength of tungsten.

The production of complex **1a** is assumed to proceed *via* the intermediate species $[Mo(CO)_4(\eta\text{-}C_4Ph_4CO)]$. In the hope of isolating this complex the reaction of $[Mo(CO)_6]$ with 1 equivalent of tetracyclone in refluxing toluene was carried out. The major product was a brown complex which could be isolated by column chromatography but subsequently decomposed to tetracyclone and insoluble material. We have so far been unable to characterise this brown complex, but it does not appear to be $[Mo(CO)_4(\eta\text{-}C_4Ph_4CO)]$, as it shows no metal carbonyl absorptions in the IR spectrum. Initially we believed it to be an arene complex in which the arene ligands were toluene or the phenyl groups of tetracyclone; however, the ^1H NMR spectrum of carefully purified material showed no evidence of η^6-arene ligands. In any case it does not appear to be an intermediate in the formation of **1a** as it does not react with additional tetracyclone, and since attempts to obtain X-ray quality crystals have been uniformly unsuccessful we have not investigated it further.

When the 1:1 ratio reaction of $[Mo(CO)_6]$ and tetracyclone was carried out in refluxing heptane solution the brown complex was not obtained; instead a precipitate was deposited consisting of an approximately 1:1 mixture of **1a** and the new complex $[\{Mo(CO)_3(\sigma:\eta^4\text{-}C_4Ph_4CO)\}_2]$ **2**. Separation of the two compounds was achieved by column chromatography, giving **2** in 31% yield as an air-stable red-brown solid.

The synthesis and characterisation of **2** are similar to that of the analogous ruthenium complex $[\{Ru(CO)_2(\sigma:\eta^4\text{-}C_4Ph_4CO)\}_2]$ **3** which we reported recently.[11] The IR spectrum of **2** consisted of a typical *fac*-$Mo(CO)_3$ pattern, and a peak was also observed at 1543 cm^{-1}, indicating the presence of a bridging tetracyclone ligand in which the ketonic carbonyl oxygen is co-ordinated to a second metal atom; the corresponding peak of **3** occurs at 1535 cm^{-1}. The ^{13}C NMR spectrum of **2** displayed two terminal CO peaks in a ratio of 1:2 consistent with a $Mo(CO)_3$ unit containing a mirror plane. The ketonic CO peak at δ 155.2 is shifted slightly upfield compared to that of **1a**, and a similar shift was observed for **3** (δ 170.4) compared to mononuclear $[Ru(CO)_3(\eta^4\text{-}C_4Ph_4CO)]$ **4** (δ 174.7).* It is interesting that for the dimeric complexes **2** and **3** the signals due to the tetracyclone ring carbons are much closer together (separations of 5.6 and 11.0 ppm respectively) than for the mononuclear

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* The ^{13}C NMR spectrum of $[\{Ru(CO)_2(\sigma:\eta^4\text{-}C_4Ph_4CO)\}_2]$ in $CDCl_3$ shows peaks at δ 200.1 (CO), 170.4 (ring CO), 99.0 (CPh) and 88.0 (CPh);[11] the corresponding peaks for $[Ru(CO)_3(\eta^4\text{-}C_4Ph_4CO)]$ in $CDCl_3$ occur at δ 195.0, 174.7, 108.4 and 82.5; this has not been previously reported. Phenyl resonances are also observed in both spectra.

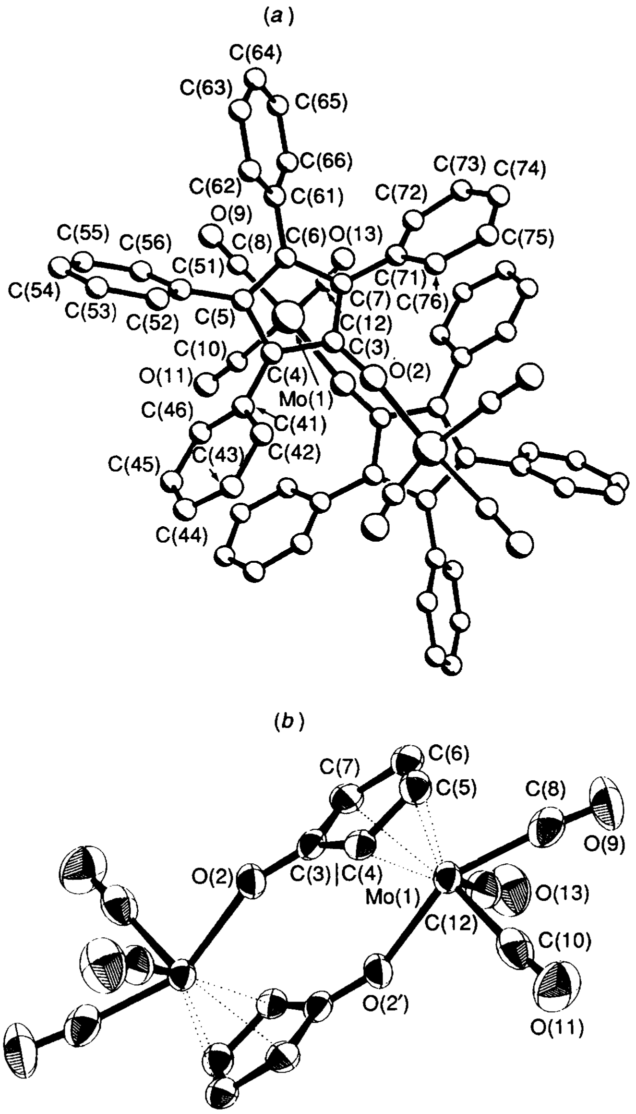

Fig. 1 Molecular structure of complex **2** in the crystal: (*a*) all non-hydrogen atoms showing the crystallographic numbering scheme; (*b*) with the phenyl rings omitted

species **1a** and **4** (13.6 and 25.9 ppm respectively). Whether any significance can be attached to this, for example concerning the planarity of the ring (as shown below, the bending back of the ketonic CO group from the diene plane appears to be somewhat reduced in bridging tetracyclone ligands), will require additional data.

Since only one other dimer of this type, $[\{Fe(CO)_2(\eta^4\text{-}C_4H_4CO)\}_2]$, is known,[2,19] it was of interest to confirm the structure of complex **2** and compare it with that of **3**. Accordingly a single-crystal X-ray structure determination was undertaken, the result of which is displayed in Fig. 1. Bond lengths and angles are presented in Table 1 and atomic coordinates in Table 2. The structure consists of centrosymmetric dimers in which each molybdenum is ligated by three terminal carbonyl ligands, a cyclopentadienone ring, and the ketonic oxygen of the second tetracyclone. Each Mo atom thus achieves an 18-electron configuration. Although in solution the ^{13}C NMR spectrum indicates that there is a mirror plane passing through the Mo atoms, carbonyl ligand C(8)–O(9), and the ketonic carbonyls, this is not the case in the solid state: carbonyl C(8)–O(9) is displaced slightly to one side, presumably because of packing forces.

Table 1 Selected bond lengths (Å) and angles (°) for complex **2**

Mo(1)–C(3)	2.534(9)	Mo(1)–C(4)	2.361(9)
Mo(1)–C(5)	2.336(10)	Mo(1)–C(6)	2.290(10)
Mo(1)–C(7)	2.367(11)	Mo(1)–C(8)	1.972(9)
Mo(1)–C(10)	2.017(12)	Mo(1)–C(12)	1.978(9)
Mo(1)–O(2a)	2.168(6)	O(2)–C(3)	1.266(9)
C(3)–C(4)	1.465(11)	C(3)–C(7)	1.449(11)
C(4)–C(5)	1.424(11)	C(4)–C(41)	1.473(11)
C(5)–C(6)	1.467(12)	C(5)–C(51)	1.478(12)
C(6)–C(7)	1.461(11)	C(6)–C(61)	1.481(12)
C(7)–C(71)	1.464(13)	C(8)–O(9)	1.151(12)
C(10)–O(11)	1.156(14)	C(12)–O(13)	1.143(11)
Mo(1) ··· Mo(1a)	5.037(3)		
C(8)–Mo(1)–C(10)	77.8(4)	C(8)–Mo(1)–C(12)	74.8(4)
C(10)–Mo(1)–C(12)	101.2(5)	C(8)–Mo(1)–O(2a)	151.1(4)
C(10)–Mo(1)–O(2a)	84.1(3)	C(12)–Mo(1)–O(2a)	87.0(3)
C(3)–O(2)–Mo(1a)	157.8(7)	O(2)–C(3)–C(4)	126.6(7)
O(2)–C(3)–C(7)	125.5(7)	C(4)–C(3)–C(7)	107.8(7)
C(3)–C(4)–C(5)	108.1(7)	C(3)–C(4)–C(41)	125.2(7)
C(5)–C(4)–C(41)	122.8(7)	C(4)–C(5)–C(6)	107.7(7)
C(4)–C(5)–C(51)	125.5(7)	C(6)–C(5)–C(51)	125.7(7)
C(5)–C(6)–C(7)	108.0(7)	C(5)–C(6)–C(61)	124.8(7)
C(7)–C(6)–C(61)	125.0(8)	C(3)–C(7)–C(6)	106.9(7)
C(3)–C(7)–C(71)	124.1(7)	C(6)–C(7)–C(71)	126.0(8)
Mo(1)–C(8)–O(9)	173.7(10)	Mo(1)–C(10)–O(11)	175.2(9)
Mo(1)–C(12)–O(13)	172.5(9)		

Symmetry operation: a $-x, -y, -z$.

Table 2 Atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*z*
Mo(1)	−1455(1)	−1554(1)	1465(1)
O(2)	1264(7)	550(5)	119(4)
C(3)	805(9)	−242(7)	937(7)
C(4)	1297(10)	−1547(7)	1059(7)
C(5)	702(10)	−2069(8)	2144(7)
C(6)	−393(9)	−1141(8)	2675(7)
C(7)	−386(10)	−20(8)	1901(7)
C(8)	−2511(11)	−2692(9)	2721(8)
O(9)	−3247(9)	−3333(7)	3420(6)
C(10)	−1542(11)	−2992(9)	837(8)
O(11)	−1549(10)	−3867(7)	529(7)
C(12)	−3693(11)	−898(10)	1838(8)
O(13)	−5001(8)	−599(8)	2160(7)
C(41)	2636(9)	−2132(8)	323(7)
C(42)	4003(11)	−1562(10)	−109(9)
C(43)	5368(12)	−2121(12)	−762(10)
C(44)	5332(14)	−3213(11)	−1003(10)
C(45)	3952(14)	−3743(11)	−612(9)
C(46)	2623(12)	−3213(9)	31(8)
C(51)	1327(11)	−3235(7)	2676(7)
C(52)	2865(14)	−3366(11)	2675(14)
C(53)	3529(19)	−4393(15)	3190(16)
C(54)	2691(15)	−5334(10)	3715(10)
C(55)	1247(17)	−5240(11)	3681(12)
C(56)	532(15)	−4196(11)	3190(11)
C(61)	−1012(11)	−1222(8)	3836(7)
C(62)	82(13)	−1443(8)	4419(7)
C(63)	−386(15)	−1476(10)	5503(8)
C(64)	−1972(18)	−1310(11)	6019(9)
C(65)	−3025(16)	−1116(11)	5468(9)
C(66)	−2575(12)	−1069(9)	4389(8)
C(71)	−1026(10)	1190(8)	2138(7)
C(72)	−2576(11)	1505(8)	2644(8)
C(73)	−3050(13)	2622(10)	2932(10)
C(74)	−2052(15)	3479(10)	2666(9)
C(75)	−520(13)	3251(8)	2083(8)
C(76)	−17(12)	2110(9)	1838(8)

The geometry around the metal can be considered as distorted octahedral. As shown recently by Wink,[20] distortion from octahedral geometry is expected in complexes of the form ML_4(diene), and takes the form of an opening up of the angle θ

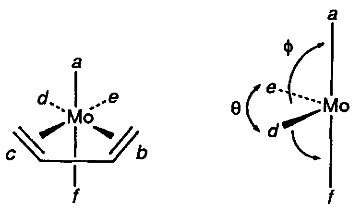

Fig. 2 Labelling scheme for octahedral $ML_4(\eta^4\text{-diene})$ complexes

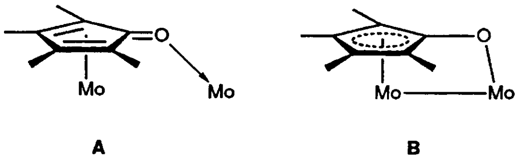

Fig. 3 Bonding in bridging cyclopentadienone ligands

between the equatorial ligands and a reduction in the angle φ between the axial ligands (see Fig. 2). For conjugated dienes average values of 104 and 154° respectively were found (compared to 90 and 180° for a perfect octahedron). The corresponding angles in complex **2** are 101.2(5) and 151.1(4)°.

There are two alternative ways of visualising the bonding in the bridging tetracyclone ligands, with the extreme situations shown in Fig. 3. In **A**, the cyclopentadienone ring is η^4 bonded, with a dative bond from the oxygen to the second molybdenum, while in **B** the ring is η^5 bonded, there is a Mo–O σ bond, and the metals have formally been oxidised (to the +I state). The latter is evidently the situation in $[Mo_2(CO)_3(\mu\text{-}C_2Ph_2)(\mu\text{-}C_4Ph_4CO)(\eta\text{-}C_4Ph_4)]$: the five carbon atoms of the cyclopentadienone ring are coplanar, and the C–O bond is considerably lengthened at 1.38(2) Å.[14] In **2** however, the carbonyl group C(3)–O(2) is bent back from the diene plane formed by C(4), C(5), C(6) and C(7) at an angle of 10.1° about the C(4) ··· C(7) hinge, in common with other η^4-cyclopentadienone complexes,[8,16,21] and the C(3)–O(2) bond length is 1.266(9) Å. The corresponding values for **3** are 6.7° and 1.270(7) Å.[11] Although the C–O bond lengths are slightly longer than those in mononuclear η^4-cyclopentadienone complexes, *e.g.* 1.224(4) Å in **4**,[8] they can still be considered as essentially C=O double bonds, and we therefore prefer to regard the bonding in both **2** and **3** as being predominantly of type **A**.

The phenyl rings in complex **2** are planar [root-mean-square (r.m.s.) deviations 0.015, 0.013, 0.005, 0.024 Å] and are twisted with respect to the C(4)–C(5)–C(6)–C(7) plane by angles of 58, 67, 64 and 125°; the rings on C(4) and C(7) thus form a 'cup' rather than a propeller arrangement. Both arrangements are known for similar highly phenylated cyclopentadienyl complexes, and it appears that the former predominates when the substituent between these two rings is relatively bulky.

(*b*) *Synthesis of* $[Mo(CO)_3(NCMe)(\eta^4\text{-}C_4Ph_4CO)]$.—It has been known for many years that the reaction of the acetonitrile complexes $[M(CO)_3(NCMe)_3]$ (M = Mo or W) with dienes generally gives the corresponding $[M(CO)_4(\eta^4\text{-diene})]$ complexes by a process involving carbonyl redistribution.[22] In the present case, however, reaction of the preformed acetonitrile complex with approximately 1 equivalent of tetracyclone in tetrahydrofuran (thf) solution at room temperature produced $[Mo(CO)_3(NCMe)(\eta^4\text{-}C_4Ph_4CO)]$ **5** in which one of the acetonitrile ligands is retained. The compound can be isolated as a stable crystalline solid by addition of hexane to the thf solution, though for large-scale syntheses it is convenient to prepare **5** in a one-pot reaction from $[Mo(CO)_6]$ and use it *in situ*.

Complex **5**, like **2**, displays the characteristic IR spectrum of a *fac*-tricarbonyl species, and in the ^{13}C NMR spectrum two CO peaks are observed in an intensity ratio of 1 : 2. Signals due to the methyl group of the co-ordinated MeCN are observed in both ^1H and ^{13}C NMR spectra, though in the latter spectrum the signal due to the nitrile carbon could not be detected and is assumed to be obscured by the phenyl region. Analytical data also indicated the presence of co-ordinated MeCN. This is borne out by the reaction chemistry of **5**, as the labile MeCN ligand is readily displaced by phosphines (see below).

The recommended IUPAC labelling scheme for octahedral diene complexes, as discussed previously by Kreiter,[23] is shown in Fig. 2. The diene ligand occupies positions *b* and *c*, with its 'open' end (in this case spanned by the ketonic carbonyl) towards position *a*. For a complex of formula $[Mo(CO)_3L(\eta^4\text{-}C_4Ph_4CO)]$ there are four possible isomers, in which the ligand occupies the *a*, *d*, *e* or *f* positions. The *a* and *f* isomers have C_s symmetry with the three CO ligands in a *fac* situation while the *d* and *e* isomers, which are enantiomers, have a *mer* disposition of the carbonyls. The IR and ^{13}C NMR data for complex **5** thus rule out the *d* and *e* isomers. Complex **2**, which of necessity exists as the *a* isomer, exhibits similar spectroscopic characteristics to **5**, as do the monosubstituted phosphine derivatives $[Mo(CO)_3L(\eta^4\text{-}C_4Ph_4CO)]$ discussed below, and we therefore propose that all of these species exist as *a* rather than *f* isomers. In the absence of overriding steric factors, a strong thermodynamic preference for *a* isomers in related complexes is well established.[23,24]

(*c*) *Synthesis of* $[Mo(CO)_2(L\text{–}L)(\eta^4\text{-}C_4Ph_4CO)]$ (L–L = dppm *or* dppe).—Treatment of a toluene solution of $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$ **1a** with 1 equivalent of a bidentate phosphine L–L [L–L = bis(diphenylphosphino)methane (dppm) or 1,2-bis(diphenylphosphino)ethane (dppe)] did not produce any reaction at room temperature. On heating the solution to reflux, however, clean displacement of one of the tetracyclone ligands occurred over a period of *ca.* 8 h to provide the complexes $[Mo(CO)_2(L\text{–}L)(\eta^4\text{-}C_4Ph_4CO)]$ (L–L = dppm **6a** or dppe **6b**) as air-stable orange powders in nearly quantitative yields after column chromatography. The same products are obtained if ⩾2 equivalents of the phosphine are used; displacement of the second tetracyclone ligand to form the known compounds $[Mo(CO)_2(L\text{–}L)_2]$ does not occur. This can be contrasted with the behaviour of $[Mo(CO)_2(nbd)_2]$ (nbd = norbornadiene), which readily loses both diene ligands on reaction with diphosphines.[25]

Reference to Fig. 2 shows that there are five possible isomers for $[Mo(CO)_2(L\text{–}L)(\eta^4\text{-}C_4Ph_4CO)]$: two pairs of enantiomers in which the diphosphine ligand occupies positions *a,d*/*a,e* or *d,f*/*e,f*, and the symmetrical *d,e* isomer. The bidentate nature of the phosphine rules out the occurrence of the *a,f* isomer. Complexes **6a** and **6b** show two strong absorptions in the carbonyl region of the IR spectrum, consistent with a *cis* disposition of the two carbonyls, thus eliminating the *d,e* isomer. In previous work on similar diene complexes of Cr, Mo and W, Kreiter[23,26] found a preference for the *a,d*/*a,e* isomers and this is also a sensible expectation for **6** since it would reduce the steric interaction between the phenyl groups of the diphosphine and those of the tetracyclone.

At room temperature the ^{31}P NMR spectra of complexes **6a** and **6b** each display only a singlet, indicating that the complexes are fluxional. In the case of **6a**, cooling the sample results only in broadening of the signal, and a low-temperature-limiting spectrum cannot be obtained. For **6b** however the spectral changes shown in Fig. 4 are observed, with the resolution of the expected AB pattern (J = 34 Hz) at low temperature. From these spectra an activation energy of 48.7 kJ mol^{-1} can be calculated. This fluxionality can also be observed in the ^{13}C NMR spectrum of **6b**: thus at room temperature the carbonyl ligands appear as an apparent triplet at δ 239.5 and only two broad signals are observed for the CPh carbons of the tetracyclone ring (δ 104.2 and 92.7). At low temperature however the CO ligands occur as a multiplet, and the four CPh carbons are now all inequivalent (δ 111.7, 96.8, 95.7 and 86.2). This type of fluxionality has been described by Kreiter[23,26] with

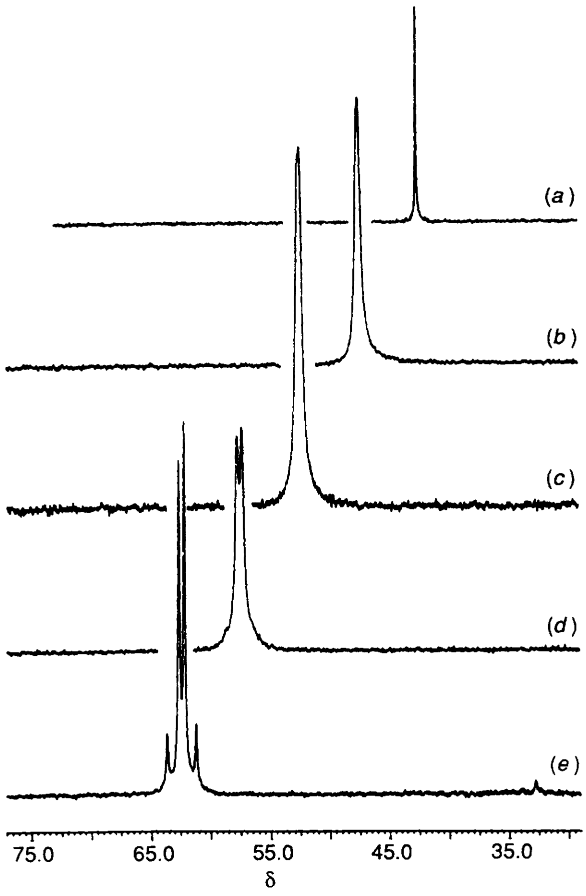

Fig. 4 Variable-temperature ^{31}P NMR spectra for $[Mo(CO)_2(dppe)(\eta^4\text{-}C_4Ph_4CO)]$ in CD_2Cl_2 solution at (*a*) 308, (*b*) 238, (*c*) 235, (*d*) 228 and (*e*) 193 K. The vertical scale is not the same for each plot

reference to complexes of the type $[Cr(CO)_2L_2(\eta^4\text{-diene})]$ and was interpreted as a rotation of the diene ligand.

(*d*) *Synthesis of* $[Mo(CO)_3L(\eta^4\text{-}C_4Ph_4CO)]$ ($L = PPh_3$, PPh_2Me *or* PPh_2H).—As expected, the acetonitrile ligand in $[Mo(CO)_3(NCMe)(\eta^4\text{-}C_4Ph_4CO)]$ **5** is relatively labile and can be readily displaced by stronger ligands such as monodentate phosphines. Thus, stirring a solution of complex **5** with 1 equivalent of the appropriate phosphine ligand overnight affords excellent yields (*ca.* 95%) of the substituted complexes $[Mo(CO)_3L(\eta^4\text{-}C_4Ph_4CO)]$ ($L = PPh_3$ **7a**, PPh_2Me **7b** or PPh_2H **7c**) as air-stable yellow crystalline solids. Each compound exists as a single isomer; their IR spectra again all show a typical *fac*-tricarbonyl pattern in the ν(CO) region, and appropriate signals for L are observed in their ^1H and ^{31}P NMR spectra (see Experimental section). The ^{13}C NMR spectra are more revealing; in the Mo–CO region each displays two doublets in an intensity ratio of approximately 1:2. That at lower field corresponds to the CO ligand *trans* to L, and has a small J_{PC} (< 5 Hz), while the second doublet corresponds to the two CO ligands *cis* to L and has a larger J_{PC} (*ca.* 20 Hz). Clearly the turnstile-like rotation of the $M(CO)_3$ fragment observed by Kreiter[23] in related $[M(CO)_3L(\eta^4\text{-diene})]$ complexes does not occur at room temperature in **7**. Only two peaks are seen for the CPh carbons of the C_4Ph_4CO ligand, and the peak due to the ring carbonyl shows a small coupling to L (not resolved for **7c**). All these data point to the existence of a single isomer with C_s symmetry, the *a* isomer, for each complex.

The synthesis of complexes **7a**–**c** can also be performed as a large-scale one-pot procedure directly from $[Mo(CO)_6]$; after the carbonyl is refluxed in MeCN for 5 h the resulting $[Mo(CO)_3(NCMe)_3]$ is suspended in thf and treated with tetracyclone to form complex **5** *in situ*. The appropriate phosphine is then added. The reaction mixture at this point contains just **7** and tetracyclone, which are easily separated by chromatography, and the yields obtained are comparable to those from purified **5**.

Heating $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$ with 2 equivalents of PPh_3 or PPh_2Me in toluene also gives complex **7a** and **7b** respectively, rather than $[Mo(CO)_2L_2(\eta\text{-}C_4Ph_4CO)]$. This requires the scavenging of carbonyl ligands, the high efficiency of which can be judged by the excellent yields obtained when calculated on the basis of the CO available. Presumably the metal centre is unable to accommodate two monodentate phosphine ligands as well as the bulky tetracyclone; previous work has shown that where L is a monodentate ligand the *af* isomer is the favoured one for complexes of the type $[M(CO)_2L_2(\eta^4\text{-diene})]$.[23] Evidently in the present case the positioning of a second phosphine ligand in the *f* position is highly unfavourable.

(*e*) *Synthesis and Crystal Structure of* $[Mo_2(CO)_3(\mu\text{-}PPh_2)(\mu\text{-}\sigma{:}\eta^5\text{-}C_4Ph_4CO)(\eta^5\text{-}C_4Ph_4COH)]$.—Treatment of $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$ with 2 equivalents of PPh_2H in refluxing toluene does not give complex **7c**. Instead a dark coloured solution is formed which on chromatography produces tetracyclone and an intense turquoise band due to the phosphido-bridged complex $[Mo_2(CO)_3(\mu\text{-}PPh_2)(\mu\text{-}\sigma{:}\eta^5\text{-}C_4Ph_4CO)(\eta^5\text{-}C_4Ph_4COH)]$ **8** which is isolated in 51% yield. Thermolysis of **7c**, either in refluxing toluene or in the solid state (melting-point tube), gives the same compound.

The IR spectrum of complex **8** shows peaks at 1947 and 1889 cm^{-1}, and the ^1H NMR spectrum contains only peaks due to phenyl protons and a singlet at δ 4.90. A singlet was observed at δ 188.9 in the ^{31}P NMR spectrum, this low-field shift being indicative of the presence of a bridging phosphido group. The dinuclear formulation was confirmed by the observation of a molecular ion in the fast atom bombardment (FAB) mass spectrum. In order to establish the structure of the complex, an X-ray diffraction study was carried out on a suitable crystal grown by diffusion of hexane into a dichloromethane solution. The molecular structure, with atom labelling, is illustrated in Fig. 5; selected bond lengths and angles with estimated standard deviations are listed in Table 3, and atomic coordinates in Table 4.

The two molybdenum atoms are linked by a metal–metal bond of length 2.923(2) Å, which is consistent with the double bond required by electron-counting considerations. This length lies in the upper range of phosphido-bridged Mo=Mo distances, which vary between 2.716(2) Å in $[Mo_2(CO)_2(\mu\text{-}PPh_2)_2(\eta\text{-}C_5H_5)_2]$ and 2.942(1) Å in $[Mo_2(CO)(\mu\text{-}PPh_2)_2O(\eta\text{-}C_5H_5)_2]$.[27]

The Mo=Mo bond is bridged somewhat asymmetrically by a diphenylphosphide ligand [Mo(1)–P 2.393(4), Mo(2)–P 2.452(3) Å] with the Mo(1)–P–Mo(2) 'bite angle' of the ligand being 74.2(1)°. The two carbonyl ligands attached to Mo(2) are both essentially linear, whereas the CO bonded to Mo(1) shows a distinct deviation from linearity [Mo(1)–C(1)–O(1) 166.9(10)°] and can be regarded as weakly semibridging [Mo(1)–C(1) 1.937(11), Mo(2) $\cdots$ C(1) 2.783(11) Å].

Each molybdenum is also ligated by a π-bound cyclopentadienone ligand. That attached to Mo(1) has become protonated to form an η^5-bound hydroxytetraphenylcyclopentadienyl ligand, which is almost perfectly planar [r.m.s. deviation 0.004 Å, with O(5) lying 0.080 Å out of this plane away from the metal]. The ring is bonded in a slightly tilted manner to the metal [perpendicular distance of Mo(1) from the mean plane 2.034 Å, with individual Mo–C distances varying between 2.310(12) for C(12) and 2.460(10) Å for C(10)]. The proton attached to O(5) was not located directly in the X-ray analysis, but its presence is inferred from the long C(9)–O(5) bond length of 1.412(12) Å, corresponding to a single bond, and also from the ^1H NMR signal at δ 4.90. The proton arises from the oxidative addition of the P–H bond of diphenylphosphine,

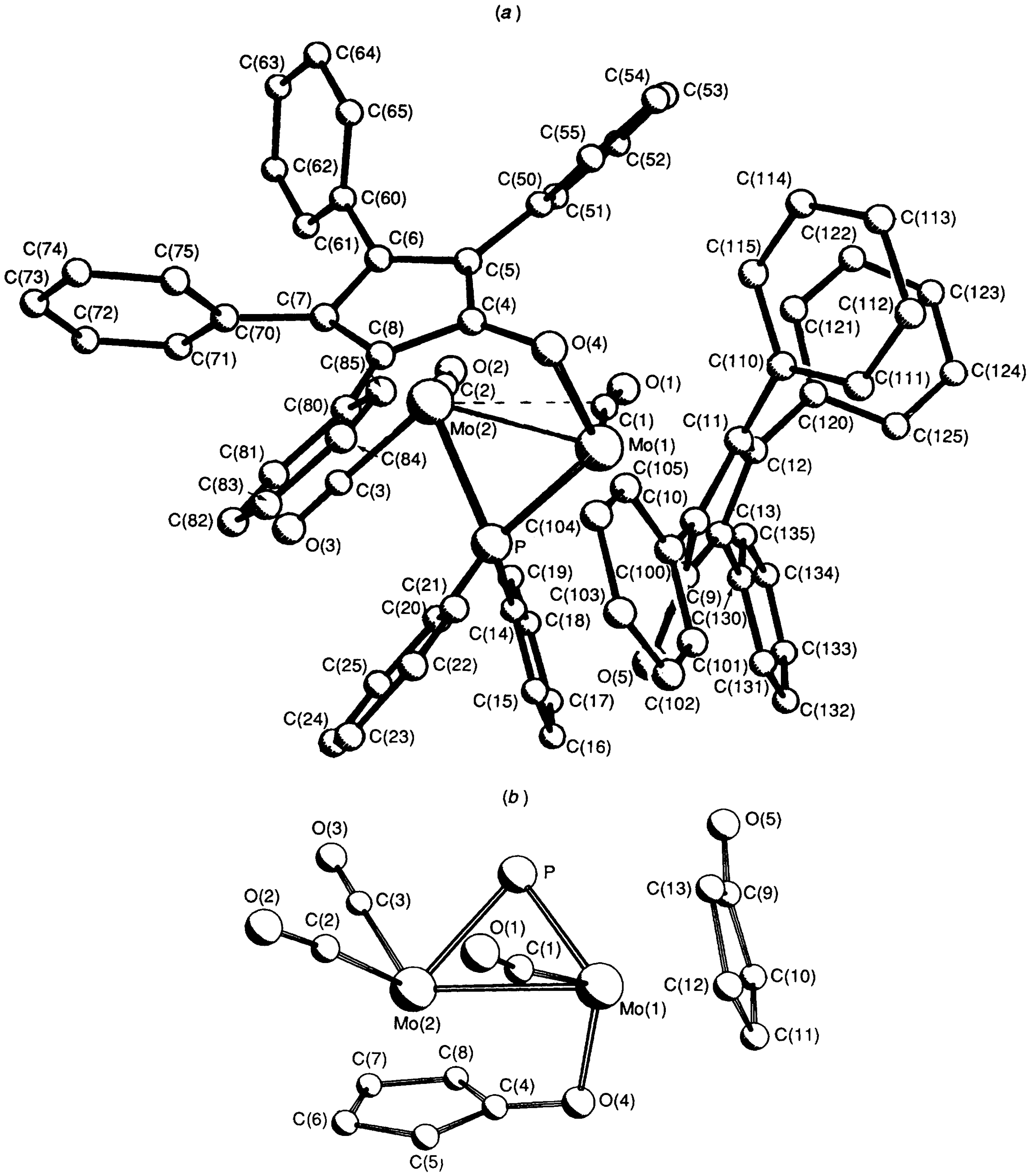

Fig. 5 Molecular structure of complex **8** in the crystal: (*a*) all non-hydrogen atoms showing the crystallographic numbering scheme; (*b*) with the phenyl rings omitted

and in related studies with ruthenium complexes we have previously observed the formation of η^5-C_5Ph_4OH ligands in oxidative-addition reactions (for example the addition of H_2 to complex **3**[11]) and as a result of cyclometallation of one of the phenyl rings of a tetracyclone ligand.[28] Whereas the OH groups in the structures of these compounds, namely [$Ru_2(\mu$-$H)(CO)_4$-(η^5:η^5-$C_5Ph_4OHOC_5Ph_4$)][11] and [$Ru_2(CO)_5\{\mu$-σ^2:η^5-OC-C_4Ph_3-η^6-$C_6H_4Ru(\eta^5$-$C_4Ph_4COH)\}$],[28] both form intramolecular hydrogen bonds in the solid state, that of the C_5Ph_4OH ligand in **8** does not.

The second tetracyclone ligand is π-bonded to Mo(2), but is also joined to Mo(1) through the carbonyl oxygen O(4). This ligand can be contrasted to those described earlier for compound **2**: in this case the ring is planar and bonded in an η^5 manner [r.m.s. deviation of five-membered ring 0.010 Å; perpendicular distance of Mo(2) from the mean plane 1.993 Å]; moreover O(4) lies 0.144 Å out of the plane in a direction *towards* the metal. The C(4)–O(4) bond length of 1.336(12) Å is considerably longer than that in **2** [1.266(9) Å] but is similar to that of 1.38(2) Å found in [$Mo_2(CO)_3(\mu$-$C_2Ph_2)(\mu$-$C_4Ph_4CO)(\eta$-$C_4Ph_4)$].[14] It is therefore clear that the bonding of the bridging tetracyclone in **8** is best described by the η^5, σ description (type **B** in Fig. 3 above).

Conclusion

In this work we have shown that the stable compounds [$Mo(CO)_2(\eta^4$-$C_4Ph_4CO)_2$] **1a** and [$Mo(CO)_3(NCMe)(\eta^4$-$C_4Ph_4CO)$] **5** are both readily prepared in high yield from [$Mo(CO)_6$] and serve as useful starting materials for the

Table 3 Selected bond lengths (Å) and angles (°) for complex **8**

Mo(1)–Mo(2)	2.923(2)	Mo(1)–P	2.393(4)	O(3)–C(3)	1.134(18)	O(4)–C(4)	1.336(12)
Mo(1)–O(4)	2.074(6)	Mo(1)–C(1)	1.937(11)	O(5)–C(9)	1.412(12)	C(4)–C(5)	1.451(12)
Mo(1)–C(9)	2.391(9)	Mo(1)–C(10)	2.460(10)	C(4)–C(8)	1.445(16)	C(5)–C(6)	1.433(16)
Mo(1)–C(11)	2.382(12)	Mo(1)–C(12)	2.310(12)	C(5)–C(50)	1.511(16)	C(6)–C(7)	1.444(14)
Mo(1)–C(13)	2.352(10)	Mo(2)–P	2.452(3)	C(6)–C(60)	1.525(13)	C(7)–C(8)	1.428(13)
Mo(2) • • • C(1)	2.783(11)	Mo(2)–C(2)	1.971(11)	C(7)–C(70)	1.477(16)	C(8)–C(80)	1.516(13)
Mo(2)–C(3)	1.999(14)	Mo(2)–C(4)	2.321(11)	C(9)–C(10)	1.424(15)	C(9)–C(13)	1.440(15)
Mo(2)–C(5)	2.354(10)	Mo(2)–C(6)	2.373(8)	C(10)–C(11)	1.445(15)	C(10)–C(100)	1.494(14)
Mo(2)–C(7)	2.329(9)	Mo(2)–C(8)	2.322(10)	C(11)–C(12)	1.434(15)	C(11)–C(110)	1.492(16)
P–C(14)	1.841(11)	P–C(20)	1.834(11)	C(12)–C(13)	1.476(16)	C(12)–C(120)	1.496(16)
O(1)–C(1)	1.191(14)	O(2)–C(2)	1.159(14)	C(13)–C(130)	1.491(16)		
Mo(2)–Mo(1)–P	53.8(1)	Mo(2)–Mo(1)–O(4)	75.4(2)	C(4)–C(5)–C(50)	126.7(10)	C(6)–C(5)–C(50)	125.0(8)
P–Mo(1)–O(4)	115.0(2)	Mo(2)–Mo(1)–C(1)	66.3(4)	C(5)–C(6)–C(7)	108.5(8)	C(5)–C(6)–C(60)	126.2(9)
P–Mo(1)–C(1)	84.8(4)	O(4)–Mo(1)–C(1)	111.1(3)	C(7)–C(6)–C(60)	124.5(10)	C(6)–C(7)–C(8)	107.9(9)
Mo(1)–Mo(2)–P	52.0(1)	Mo(1)–Mo(2)–C(2)	111.0(4)	C(6)–C(7)–C(70)	124.4(8)	C(8)–C(7)–C(70)	125.3(9)
P–Mo(2)–C(2)	103.1(3)	Mo(1)–Mo(2)–C(3)	125.6(3)	C(4)–C(8)–C(7)	108.3(8)	C(4)–C(8)–C(80)	125.5(9)
P–Mo(2)–C(3)	74.1(3)	C(2)–Mo(2)–C(3)	84.7(5)	C(7)–C(8)–C(80)	125.2(10)	O(5)–C(9)–C(10)	124.5(9)
Mo(1)–P–Mo(2)	74.2(1)	Mo(1)–P–C(14)	123.4(4)	O(5)–C(9)–C(13)	123.1(9)	C(10)–C(9)–C(13)	112.2(9)
Mo(2)–P–C(14)	122.4(3)	Mo(1)–P–C(20)	115.1(4)	C(9)–C(10)–C(11)	105.9(9)	C(9)–C(10)–C(100)	125.4(9)
Mo(2)–P–C(20)	117.7(3)	C(14)–P–C(20)	103.1(5)	C(11)–C(10)–C(100)	128.6(9)	C(10)–C(11)–C(12)	108.9(9)
Mo(1)–O(4)–C(4)	106.8(6)	Mo(1)–C(1)–O(1)	166.9(10)	C(10)–C(11)–C(110)	124.8(9)	C(12)–C(11)–C(110)	125.0(10)
Mo(2)–C(2)–O(2)	175.4(9)	Mo(2)–C(3)–O(3)	178.2(10)	C(11)–C(12)–C(13)	108.7(9)	C(11)–C(12)–C(120)	124.2(10)
O(4)–C(4)–C(5)	124.7(9)	O(4)–C(4)–C(8)	127.2(8)	C(13)–C(12)–C(120)	124.9(9)	C(9)–C(13)–C(12)	104.2(9)
C(5)–C(4)–C(8)	107.7(9)	C(4)–C(5)–C(6)	107.5(9)	C(9)–C(13)–C(130)	125.5(10)	C(12)–C(13)–C(130)	128.0(10)

synthesis of other tetracyclone complexes of the types $[Mo(CO)_2(L–L)(\eta^4\text{-}C_4Ph_4CO)]$ and $[Mo(CO)_3L(\eta^4\text{-}C_4Ph_4CO)]$. The reactions of these compounds with organic ligands will form the content of a future publication. In the synthesis of complex **8** we have also provided a further example of the conversion of an η^4-cyclopentadienone ligand into an η^5-hydroxycyclopentadienyl ligand through the addition of a hydrogen atom, arising in this instance from the oxidative addition of a P–H bond. Earlier observations of similar changes in co-ordination mode which use protons from adventitious water or from C–H bond activation indicate that this is a strong tendency and possibly one that could be used to synthetic advantage.

Experimental

General techniques and instrumentation were as described recently.[29] Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ solution at room temperature; ^1H and ^{13}C chemical shifts are reported on the δ scale relative to $SiMe_4$ (δ 0.0) and the ^{31}P spectra are given relative to 85% H_3PO_4 (δ 0.0). Coupling constants are given in Hz. Tetraphenylcyclopentadienone and 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer from Lancaster Synthesis and $[Mo(CO)_6]$ from Aldrich were used as received. Light petroleum refers to the fraction boiling in the range 60–80 °C. All of the products described are relatively air-stable.

(*a*) *Synthesis of* $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$ **1a** *and* $[Mo(CO)_2(\eta^4\text{-}C_4Me_2Ph_2CO)_2]$ **1b**.—A solution of $[Mo(CO)_6]$ (5.8 g, 22 mmol) and tetracyclone (17.0 g, 44.3 mmol) in toluene (175 cm^3) was refluxed for 17 h and then cooled. The orange precipitate of complex **1a** was filtered off, and the filtrate was absorbed onto a small amount of silica and chromatographed (Merck Kieselgel 60, 230–400 mesh, 25 × 4 cm column). After removal of a purple band of unreacted tetracyclone with CH_2Cl_2–hexane (1:1), further product was eluted as an intense yellow-orange band using CH_2Cl_2–acetone (9:1). Combined yield 18.8 g, 93%.

In a similar manner, $[Mo(CO)_6]$ (2.00 g, 7.58 mmol) and 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer (3.94 g, 7.58 mmol) reacted over 17 h in refluxing toluene to give complex **1b** (2.85 g, 56%) which was isolated by column chromatography [eluting solvent CH_2Cl_2–acetone–methanol (90:8:2)] followed by crystallisation from dichloromethane–hexane. Despite recrystallising from five different solvent mixtures we were unable to obtain a satisfactory analysis for this compound; each determination was correct for H but up to 5% low for carbon.

Complex **1a**: m.p. 207–210 °C (decomp.); IR (CH_2Cl_2) 2006, 1956, 1651; (KBr) 2008, 1960, 1651 and 1634 cm^{-1}; NMR ^1H, δ 7.29–6.83 (m, Ph); ^{13}C (CD_2Cl_2), δ 228.9 (s, CO), 167.3 (s, ring CO), 133.0–127.4 (m, Ph), 108.9 (s, CPh) and 95.3 (s, CPh) (Found: C, 77.9; H, 4.3. Calc. for $C_{60}H_{40}MoO_4$: C, 78.25; H, 4.35%); mass spectrum m/z 922 (M^+).

Complex **1b**: m.p. 230 °C (decomp.); IR (CH_2Cl_2) 2020, 1971 and 1638 cm^{-1}; NMR ^1H, δ 7.34–7.01 (m, 20 H, Ph) and 1.61 (s, 12 H, Me); ^{13}C, δ 223.7 (s, CO), 167.9 (s, ring CO), 131.1–128.2 (m, Ph), 105.7 (s, CPh), 88.9 (s, CMe) and 6.4 (s, Me) (Found: C, 70.55; H, 4.80. Calc. for $C_{40}H_{32}MoO_4$: C, 71.45; H, 4.80%); mass spectrum m/z 674 (M^+).

(*b*) *Reaction of* $[Mo(CO)_6]$ *with* 1 *equivalent of Tetracyclone in Toluene*.—A solution of $[Mo(CO)_6]$ (1.00 g, 3.79 mmol) and tetracyclone (1.45 g, 3.78 mmol) in toluene (100 cm^3) was refluxed for 17 h. The solvent was removed and the residue was chromatographed on silica. After removal of unchanged C_4Ph_4CO (284.2 mg), the unidentified major product (791.7 mg) was eluted as a brown band in CH_2Cl_2–hexane (4:1). Further elution with CH_2Cl_2–acetone (19:1) gave complex **1a** (257.1 mg, 7% based on Mo).

(*c*) *Synthesis of* $[\{Mo(CO)_3(\mu\text{-}\sigma:\eta^4\text{-}C_4Ph_4CO)\}_2]$ **2**.—A suspension of $[Mo(CO)_6]$ (2.00 g, 7.58 mmol) and tetracyclone (3.20 g, 8.3 mmol) in heptane (175 cm^3) was heated to reflux for 17 h. The orange precipitate which separated on cooling was filtered off and the filtrate, which consisted mainly of unreacted tetracyclone (TLC evidence), was discarded. The solid obtained was chromatographed on silica; elution with CH_2Cl_2–hexane (1:1) provided complex **2** as a red band (1.31 g, 31%). Subsequently a yellow band of **1a** (2.16 g, 31% based on Mo) was eluted as above.

Complex **2**: m.p. 226–228 °C; IR (CH_2Cl_2) 2026, 1948; (KBr) 2020, 1933 and 1543 cm^{-1}; NMR ^1H, δ 7.22–6.75 (m, Ph); ^{13}C (CD_2Cl_2), δ 242.7 (s, 2CO), 225.3 (s, 4CO), 155.2 (s, ring

Table 4 Atomic coordinates (× 10^4) for complex **8**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo(1)	2 728(1)	1 784(1)	2 454(1)	C(60)	4 962(9)	−2 539(8)	2 607(6)
Mo(2)	2 710(1)	−273(1)	2 448(1)	C(61)	4 365(11)	−3 094(8)	2 978(6)
P	1 137(2)	1 264(2)	2 369(2)	C(62)	4 932(15)	−4 065(10)	3 295(7)
Cl(1)	9 391(7)	6 644(6)	2 002(4)	C(63)	6 061(16)	−4 434(10)	3 215(8)
Cl(2)	11 334(7)	6 149(7)	2 850(4)	C(64)	6 668(13)	−3 862(10)	2 865(8)
O(1)	2 944(7)	782(6)	4 091(4)	C(65)	6 096(11)	−2 909(9)	2 557(7)
O(2)	2 554(8)	−1 286(7)	4 069(5)	C(70)	3 564(9)	−2 065(7)	1 147(5)
O(3)	645(7)	−893(7)	2 134(7)	C(71)	2 933(9)	−2 647(8)	1 416(6)
O(4)	4 039(5)	1 131(4)	1 753(3)	C(72)	2 849(10)	−3 425(8)	1 028(6)
O(5)	399(5)	3 732(5)	2 063(4)	C(73)	3 400(10)	−3 617(9)	365(7)
C(1)	2 875(9)	1 052(8)	3 439(7)	C(74)	4 027(10)	−3 026(10)	72(7)
C(2)	2 572(10)	−878(8)	3 476(6)	C(75)	4 104(9)	−2 238(8)	456(6)
C(3)	1 403(10)	−684(9)	2 246(7)	C(80)	3 123(8)	191(7)	517(5)
C(4)	4 109(8)	168(7)	1 771(5)	C(81)	2 224(10)	−17(8)	247(6)
C(5)	4 630(8)	−598(7)	2 358(5)	C(82)	1 882(11)	360(9)	−497(7)
C(6)	4 419(8)	−1 498(7)	2 220(5)	C(83)	2 429(12)	918(9)	−937(7)
C(7)	3 746(8)	−1 291(7)	1 565(5)	C(84)	3 297(11)	1 109(9)	−660(7)
C(8)	3 579(8)	−275(7)	1 280(5)	C(85)	3 642(9)	770(8)	56(6)
C(9)	1 497(8)	3 455(7)	2 303(6)	C(100)	2 360(8)	3 797(7)	1 002(6)
C(10)	2 413(8)	3 478(7)	1 824(6)	C(101)	1 504(9)	4 629(8)	719(6)
C(11)	3 351(8)	3 210(7)	2 306(6)	C(102)	1 461(10)	4 939(8)	−54(6)
C(12)	2 995(8)	3 040(8)	3 065(6)	C(103)	2 225(10)	4 442(8)	−544(7)
C(13)	1 798(9)	3 200(7)	3 077(6)	C(104)	3 076(11)	3 609(9)	−263(7)
C(14)	2(8)	1 495(8)	3 068(6)	C(105)	3 147(9)	3 318(8)	503(7)
C(15)	−934(10)	2 275(9)	2 964(7)	C(110)	4 446(8)	3 322(7)	2 076(5)
C(16)	−1 774(11)	2 467(10)	3 497(7)	C(111)	4 519(9)	4 249(8)	1 842(7)
C(17)	−1 690(10)	1 892(11)	4 157(7)	C(112)	5 527(10)	4 405(9)	1 656(7)
C(18)	−752(13)	1 089(15)	4 260(8)	C(113)	6 473(10)	3 605(10)	1 727(7)
C(19)	94(11)	905(12)	3 718(8)	C(114)	6 395(10)	2 680(9)	1 972(7)
C(20)	421(8)	1 657(7)	1 476(6)	C(115)	5 403(9)	2 519(9)	2 148(7)
C(21)	936(9)	2 118(8)	885(6)	C(120)	3 656(10)	2 999(9)	3 737(6)
C(22)	483(10)	2 435(8)	180(6)	C(121)	4 597(10)	2 209(9)	3 928(6)
C(23)	−518(11)	2 266(10)	53(8)	C(122)	5 251(11)	2 227(10)	4 508(7)
C(24)	−1 025(10)	1 797(9)	617(7)	C(123)	4 950(12)	3 043(10)	4 936(7)
C(25)	−554(9)	1 509(8)	1 316(7)	C(124)	4 057(13)	3 839(11)	4 741(7)
C(30)	10 009(18)	6 851(27)	2 743(18)	C(125)	3 383(12)	3 825(9)	4 146(7)
C(50)	5 415(9)	−528(7)	2 933(6)	C(130)	1 017(10)	3 368(9)	3 732(7)
C(51)	5 372(10)	−891(9)	3 677(6)	C(131)	16(11)	4 140(10)	3 668(7)
C(52)	6 139(10)	−831(10)	4 181(7)	C(132)	−708(11)	4 346(13)	4 297(9)
C(53)	6 930(11)	−424(10)	3 933(7)	C(133)	−415(15)	3 757(14)	4 969(9)
C(54)	6 994(10)	−41(10)	3 196(8)	C(134)	560(15)	3 045(13)	5 030(10)
C(55)	6 209(8)	−71(8)	2 669(6)	C(135)	1 275(13)	2 821(11)	4 433(8)

Atoms Cl(1), Cl(2), C(30) and their associated hydrogens comprise the half-occupancy dichloromethane molecule of solvation.

CO), 133.7–127.2 (m, Ph), 110.3 (s, CPh) and 104.7 (s, CPh) (Found: C, 67.9; H, 3.7; Mo, 17.0. Calc. for $C_{64}H_{40}Mo_2O_8$: C, 68.10; H, 3.55; Mo, 17.00%).

(*d*) *Synthesis of* [Mo(CO)$_3$(NCMe)(η^4-C_4Ph_4CO)] **5**.—A solution of [Mo(CO)$_6$] (2.05 g, 7.76 mmol) in MeCN (120 cm^3) was refluxed for 5 h.[30] The solvent was removed under reduced pressure and the yellow residue was redissolved in thf (150 cm^3). Solid tetracyclone (2.98 g, 7.76 mmol) was added, and the solution was stirred for 18 h, though IR monitoring indicated that the reaction was rapid. After reducing the volume to about 40 cm^3, hexane was layered on top of the orange solution. Bright orange-red crystals of [Mo(CO)$_3$(NCMe)(η^4-C_4Ph_4-CO)] (3.31 g, 70%) were deposited over a period of 3 d at −20 °C.

Complex **5**: m.p. 126 °C (decomp.); IR (CH_2Cl_2) 2019, 1934 and 1619 cm^{-1}; NMR ^{1}H, δ 7.39–6.95 (m, 20 H, Ph) and 2.30 (s, 3 H, Me); ^{13}C, δ 233.6 (s, CO), 225.6 (s, 2CO), 171.0 (s, ring CO), 132.8–126.7 (m, Ph + NCMe), 107.1 (s, CPh), 94.8 (s, CPh) and 5.0 (s, Me) (Found: C, 67.3; H, 3.9; Mo, 15.5; N, 2.0. Calc. for $C_{34}H_{23}MoNO_4$: C, 67.45; H, 3.80; Mo, 15.85; N, 2.30%); mass spectrum *m*/*z* 605 (M^+).

(*e*) *Synthesis of* [Mo(CO)$_2$(L–L)(η^4-C_4Ph_4CO)] (L–L = dppm **6a** *or* dppe **6b**).—A solution of complex **1a** (1.70 g, 1.85 mmol) and dppm (0.7096 g, 1.85 mmol) in toluene (150 cm^3) was refluxed for 8 h (IR monitoring). Removal of solvent followed by chromatography gave tetracyclone, eluted using CH_2Cl_2–hexane (1 : 1), followed by **6a** (1.57 g, 92%) eluted with CH_2Cl_2–acetone (19 : 1). An analogous reaction between **1a** (2.0 g) and dppe (0.8652 g) provided **6b** (1.83 g, 90%). Both compounds are air stable though slightly light sensitive.

Complex **6a**: m.p. 278–282 °C; IR (CH_2Cl_2) 1945, 1868; (KBr) 1936, 1871 and 1603 cm^{-1}; NMR ^{1}H, δ 7.40–6.81 (m, 40 H, Ph) and 4.27 [t, *J*(HP) 9.5, 2 H, CH_2]; ^{13}C (CD_2Cl_2, −50 °C), δ 237.3 [d, *J*(CP) 23, CO], 167.8 (s, ring CO), 135.1–125.2 (m, Ph), 103.7 (s, CPh), 89.2 (s, CPh) and 42.1 [t, *J*(CP) 23 Hz, CH_2]; ^{31}P, δ 4.2 (Found: C, 72.5; H, 4.6; Mo, 10.35; P, 6.3. Calc. for $C_{56}H_{42}MoO_3P_2$: C, 73.05; H, 4.55; Mo, 10.45; P, 6.75%); mass spectrum *m*/*z* 920 (M^+).

Complex **6b**: m.p. 246–248 °C; IR (CH_2Cl_2) 1937 and 1859 cm^{-1}; NMR ^{1}H, δ 7.81–6.69 (m, 40 H, Ph) and 2.24 [d, br, *J*(HP) 17.3, 4 H, CH_2]; ^{13}C (CD_2Cl_2, −50 °C), δ 240.5 [d, *J*(CP) 33, CO], 237.2 [d, *J*(CP) 18 Hz, CO], 168.7 (s, ring CO), 138.1–125.0 (m, Ph), 111.7 (s, CPh), 96.8 (s, CPh), 95.7 (s, CPh), 86.2 (s, CPh) and 28.8 (m, CH_2); ^{31}P (298 K, see text), δ 63.5 (Found: C, 73.20; H, 4.80; Mo, 10.30; P, 6.90. Calc. for $C_{57}H_{44}MoO_3P_2$: C, 73.25; H, 4.70; Mo, 10.30; P, 6.65%); mass spectrum *m*/*z* 934 (M^+).

(*f*) *Synthesis of* [Mo(CO)$_3$L(η^4-C_4Ph_4CO)] (L = PPh_3 **7a**, PPh_2Me **7b** *or* PPh_2H **7c**) *from* [Mo(CO)$_3$(NCMe)(η^4-

$C_4Ph_4CO)]$.—A solution of $[Mo(CO)_3(NCMe)(\eta^4\text{-}C_4Ph_4CO)]$ (199.7 mg, 0.33 mmol) and PPh_3 (93.4 mg, 0.36 mmol) in CH_2Cl_2 (15 cm^3) was stirred for 18 h. The solvent was then removed and the residue washed with hexane to give $[Mo(CO)_3(PPh_3)(\eta^4\text{-}C_4Ph_4CO)]$ **7a** as an air-stable yellow solid (262.9 mg, 96%). In a similar way, $[Mo(CO)_3(NCMe)(\eta^4\text{-}C_4Ph_4CO)]$ (238.7 mg, 0.395 mmol) reacted with PPh_2Me (0.087 cm^3, 0.47 mmol) in CH_2Cl_2 (15 cm^3) to give $[Mo(CO)_3(PPh_2Me)(\eta^4\text{-}C_4Ph_4CO)]$ **7b**, which was purified by chromatography. After elution of a small amount of tetracyclone and a small unidentified orange band [ν(CO) (CH_2Cl_2): 2011s, 1973m and 1934m cm^{-1}] the product was eluted with CH_2Cl_2–acetone (19:1) as a yellow band (282.9 mg, 94%). Complex **7c** was prepared in an analogous way from **5** (270.1 mg, 0.45 mmol) and PPh_2H (0.1 cm^3, 0.57 mmol) in CH_2Cl_2 (15 cm^3), and purified by chromatography, eluting with CH_2Cl_2–acetone (19:1). Yield: 322.3 mg, 96%. A small amount of tetracyclone and an orange complex with the same IR spectrum as that above were also eluted before the major product.

Complex **7a**: m.p. 203 °C; IR (CH_2Cl_2) 2013s, 1928s (br) and 1603m cm^{-1}; NMR ^1H, δ 7.54–6.91 (m, Ph); ^{13}C, δ 235.8 [d, *J*(CP) 2, CO], 228.3 [d, *J*(CP) 25, 2CO], 168.4 [d, *J*(CP) 5, ring CO], 133.8–125.8 (m, Ph), 133.3 [d, *J*(CP) 17 Hz, C_{ipso}], 106.3 (s, CPh) and 93.2 (s, CPh); ^{31}P, δ 38.7 (Found: C, 71.35; H, 4.85. Calc. for **7a**·$0.5MeCO_2Et$: C, 71.70; H, 4.50%); mass spectrum *m/z* 826 (M^+).

Complex **7b**: m.p. 192–194 °C (decomp.); IR (CH_2Cl_2) 2013s, 1940(sh) and 1923s cm^{-1}; NMR ^1H, δ 7.40–6.98 (m, 30 H, Ph) and 1.78 [d, *J*(HP) 9, 3 H, Me]; ^{13}C, δ 234.1 (s, CO), 227.8 [d, *J*(CP) 24, 2CO], 167.5 [d, *J*(CP) 5, CO of ring], 132.9 [d, *J*(CP) 22, C_{ipso}], 132.6–126.0 (m, Ph), 105.6 (s, CPh), 92.7 (s, CPh) and 10.1 [d, *J*(CP) 27, Me]; ^{31}P, δ 19.5 (Found: C, 70.30; H, 4.25. Calc. for $C_{45}H_{33}MoO_4P$: C, 70.70; H, 4.30%); mass spectrum *m/z* 764 (M^+).

Complex **7c**: m.p. 207 °C (decomp.); IR (CH_2Cl_2) 2016s, 1945 (sh), 1928s and 1589m cm^{-1}; NMR ^1H, δ 7.41–6.95 (m, Ph) and 5.67 [d, *J*(HP) 388, 1 H, PH]; ^{13}C, δ 231.8 [d, *J*(CP) 4, CO], 225.2 [d, *J*(CP) 20, 2CO], 164.5 (s, CO of ring), 132.3 [d, *J*(CP) 38 Hz, C_{ipso}], 132.5–126.5 (m, Ph), 104.7 (s, CPh) and 94.1 (s, CPh); ^{31}P, δ 59.6 (Found: C, 70.45; H, 4.00. Calc. for $C_{44}H_{31}MoO_4P$: C, 70.40; H, 4.15%); mass spectrum *m/z* 753 (M^+).

(*g*) *Synthesis of Complexes* **7a** *and* **7b** *from* $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$.—A solution of complex **1a** (818.1 mg, 0.89 mmol) and PPh_3 (479.1 mg, 1.83 mmol) in toluene (175 cm^3) was heated at reflux for 18 h. Column chromatography produced the liberated tetracyclone followed by an intense yellow-orange band due to **7a**, which was eluted using CH_2Cl_2–acetone (19:1). Yield: 402.9 mg, 82% based on the amount of CO available. In a similar manner, reaction of **1a** (1.00 g, 1.09 mmol) with PPh_2Me (0.21 cm^3, 1.12 mmol) in boiling toluene for 18 h produced **7b** (484.0 mg, 79%), isolated as above.

(*h*) *Synthesis of* $[Mo_2(CO)_3(\mu\text{-}PPh_2)(\mu\text{-}\sigma\text{:}\eta^5\text{-}C_4Ph_4CO)(\eta^5\text{-}C_4Ph_4COH)]$ **8**.—A solution of complex **1a** (2.004 g, 2.17 mmol) and PPh_2H (0.38 cm^3, 2.19 mmol) in toluene (175 cm^3) was heated to reflux for 18 h, producing a dark purple solution. After removal of the solvent *in vacuo* and absorption onto a small amount of silica, the products were separated on a column. Tetracyclone was removed with light petroleum–dichloromethane (7:3). The intensely turquoise complex **8** (679.1 mg, 51%) was eluted with a 1:1 mixture of the same solvents. Elution with a 3:7 mixture produced 149.8 mg of a purple complex which has not yet been identified, and elution with CH_2Cl_2–acetone (19:1) gave a small amount of starting material **1a**.

Complex **8**: m.p. 293–295 °C; IR (CH_2Cl_2) 1947s and 1889m cm^{-1}; NMR ^1H, δ 7.68–5.84 (m, 50 H, Ph) and 4.90 (s, 1 H, OH); ^{13}C δ 234.6, 234.2, 232.3 (all s, CO), 138.4 [d, *J*(CP) 31, PC_{ipso}], 137.1 [d, *J*(CP) 47 Hz, PC_{ipso}], 133.3–125.4 (m, Ph + ring COs), 119.1 (br s, CPh), 114.7, 110.4, 109.6, 105.6, 104.5, 102.3 (s, all CPh) and 98.4 (br s, CPh); ^{31}P, δ 188.9 (Found: C, 69.05; H, 4.10. Calc. for $C_{73}H_{51}Mo_2O_5P\cdot0.5CH_2Cl_2$: C, 69.35: H, 4.10; mass spectrum *m/z* 1233 [$(M + H)^+$].

Crystal Structure Determinations.—*Crystal data for complex* **2**. $C_{32}H_{20}MoO_4$, *M* = 564.41 (for monomer), crystallised by diffusion of ether vapour into a thf solution at −20 °C as red-brown prisms, crystal dimensions 0.08 × 0.16 × 0.18 mm, triclinic, space group $P\bar{1}$ (no. 2), *a* = 8.980(3), *b* = 11.332(4), *c* = 13.526(5) Å, α = 77.55(3), β = 71.94(3), γ = 81.02(3)°, *U* = 1272(1) $Å^3$, D_c = 1.47 g cm^{-3}, for *Z* = 2 monomer units, Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 5.37 cm^{-1}, *F*(000) = 571.85.

The crystal was mounted on an Enraf-Nonius CAD4 diffractometer. The unit cell was determined and refined from the setting angles of 44 reflections between θ = 3 and 11°, diffracting power being low and profiles broad. A total of 3378 unique reflections were measured up to a maximum θ of 22° [ω–2θ scan; scan width (1.5 + 0.35 tanθ)°] of which 2184 with $F > 3\sigma(F)$ were used for the computation. As $\mu R < 0.11$ no absorption correction was applied, but a linear drift correction for a total intensity drop of 12% was used.

A 20-atom solution was found using direct methods (MULTAN 80 program[31]), and a Fourier difference synthesis revealed the remaining non-hydrogen atoms. Anisotropic motion was permitted for the Mo atom only until *R* = 0.087 at which point H atoms were added at calculated positions, assigned isotropic thermal parameters 20% greater than for the adjacent carbon, and refined in riding mode. Refinement converged with all non-hydrogen atoms now anisotropic. A weighting scheme $w^{-1} = 0.008F^2$ was applied and gave uniform $(w\Delta F)^2$ distribution over the *F* range. A final Fourier difference map showed no feature >0.56 or < −0.47 e $Å^{-3}$. The final *R* = 0.0524, *R′* = 0.0571 for 334 variables with final mean and maximum δ/σ 0.002 and 0.008 respectively.

Crystal data for complex **8**·$0.5CH_2Cl_2$. $C_{73}H_{51}Mo_2O_5P\cdot0.5CH_2Cl_2$, *M* = 1273.52, crystallises from dichloromethane–hexane as deep blue blocks, crystal dimensions 0.35 × 0.20 × 0.225 mm, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), *a* = 12.806(10), *b* = 14.173(8), *c* = 17.958(7) Å, α = 83.75(4), β = 86.92(5), γ = 71.57(5)°, *U* = 3073(3) $Å^3$, D_c = 1.376 g cm^{-3}, *Z* = 2, Mo-Kα X-radiation with graphite monochromator, μ(Mo-Kα) = 5.16 cm^{-1}, *F*(000) = 1297.70.

Three-dimensional, room temperature, X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 four-circle diffractometer by the ω-scan method. The 6648 independent reflections (of 110 44 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption by the analysis of eight azimuthal scans (minimum and maximum transmission coefficients 0.819 and 0.943). The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. A molecule of dichloromethane was refined with half occupancy (on the basis of peak height and thermal parameters) and constrained geometry. Hydrogen atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode: the hydrogen on the hydroxyl O(5) was not detected and was not included in the structure-factor calculation. Refinement converged at a final *R* 0.0887 (*R′* 0.0800, 753 parameters, final mean and maximum shift/e.s.d. 0.019 and 0.097), with allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference electron-density synthesis showed minimum and maximum values of −1.13 and +1.25 e $Å^{-3}$ (in the region of the dichloromethane). Complex scattering factors were taken from the program package SHELXTL[32] as implemented on a Data General DG30 computer. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.000\,97(F)^2]$ was used in the latter stages of refinement.

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

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References

1 G. F. Emerson, L. Watts and R. Pettit, *J. Am. Chem. Soc.*, 1965, **87**, 3253.
2 W. Reppe and H. Vetter, *Justus Liebigs Ann. Chem.*, 1953, **582**, 133.
3 M. A. Ogliaruso, M. G. Romanelli and E. I. Becker, *Chem. Rev.*, 1965, **65**, 261; C. F. H. Allen and J. A. VanAllan, *J. Am. Chem. Soc.*, 1950, **72**, 5165; see also H. M. Weiss and K. Touchette, *J. Chem. Educ.*, 1990, **67**, 707.
4 P. M. Maitlis, *Adv. Organomet. Chem.*, 1966, **4**, 95; A. Efraty, *Chem. Rev.*, 1977, **77**, 691.
5 See, for example, W. Hübel, in *Organic Syntheses via Metal Carbonyls*, eds. I. Wender and P. Pino, Wiley, New York, 1968, vol. 1, p. 273.
6 Y. Blum and Y. Shvo, *Isr. J. Chem.*, 1984, **24**, 144.
7 Y. Blum, D. Czarkie, Y. Rahamim and Y. Shvo, *Organometallics*, 1985, **4**, 1459.
8 Y. Blum, Y. Shvo and D. F. Chodosh, *Inorg. Chim. Acta*, 1985, **97**, L25.
9 Y. Shvo and D. Czarkie, *J. Organomet. Chem.*, 1986, **315**, C25.
10 Y. Shvo, D. Czarkie, Y. Rahamim and D. F. Chodosh, *J. Am. Chem. Soc.*, 1986, **108**, 7400.
11 M. J. Mays, M. J. Morris, P. R. Raithby, Y. Shvo and D. Czarkie, *Organometallics*, 1989, **8**, 1162.
12 Y. Shvo and D. Czarkie, *J. Organomet. Chem.*, 1989, **368**, 357.
13 W. Hübel and R. Merenyi, *J. Organomet. Chem.*, 1964, **2**, 213.
14 J. A. Potenza, R. J. Johnson, R. Chirico and A. Efraty, *Inorg. Chem.*, 1977, **16**, 2354.
15 E. Weiss and W. Hübel, *J. Inorg. Nucl. Chem.*, 1959, **11**, 42.
16 L. S. Liebeskind and A. Bombrun, *J. Am. Chem. Soc.*, 1991, **113**, 8736.
17 R. L. Beddoes, E. S. Cook and M. J. Morris, *Polyhedron*, 1989, **8**, 1810.
18 A. Efraty, J. A. Potenza, L. Zyontz, J. Daily, M. H. A. Huang and B. Toby, *J. Organomet. Chem.*, 1978, **145**, 315; T. J. Chow, M.-Y. Wu and L.-K. Liu, *J. Organomet. Chem.*, 1985, **281**, C33; F. A. Cotton and B. A. Frenz, *Acta Crystallogr., Sect. B*, 1974, **30**, 1772.
19 G. S. D. King, personal communication.
20 D. J. Wink, *Organometallics*, 1991, **10**, 442.
21 N. A. Bailey and R. Mason, *Acta Crystallogr.*, 1966, **21**, 652; M. Gerloch and R. Mason, *Proc. R. Soc. London, Ser. A*, 1964, **279**, 170; G. C. Cash and R. C. Pettersen, *Inorg. Chem.*, 1978, **17**, 650; L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.*, 1961, **83**, 752; K. Hofmann and E. Weiss, *J. Organomet. Chem.*, 1977, **128**, 237; T. F. Smith, K. S. Kwan, H. Taube, A. Bino and S. Cohen, *Inorg. Chem.*, 1984, **23**, 1943.
22 R. B. King, *J. Organomet. Chem.*, 1967, **8**, 139; R. B. King and A. Fronzaglia, *Inorg. Chem.*, 1966, **5**, 1837.
23 C. G. Kreiter, *Adv. Organomet. Chem.*, 1986, **26**, 297.
24 M. Kotzian, C. G. Kreiter, G. Michael and S. Ozkar, *Chem. Ber.*, 1983, **116**, 3637; C. G. Kreiter and S. Ozkar, *J. Organomet. Chem.*, 1978, **152**, C13; S. Ozkar and C. G. Kreiter, *J. Organomet. Chem.*, 1986, **303**, 367.
25 T. J. Chow, C.-Y. Wang, S.-C. Sheu and S.-M. Peng, *J. Organomet. Chem.*, 1986, **311**, 339.
26 M. Kotzian and C. G. Kreiter, *J. Organomet. Chem.*, 1985, **289**, 295.
27 T. Adatia, M. McPartlin, M. J. Mays, M. J. Morris and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1989, 1555.
28 H. Adams, N. A. Bailey, P. Blenkiron and M. J. Morris, *J. Chem. Soc., Dalton Trans.*, 1992, 127.
29 H. Adams, N. A. Bailey, A. N. Day, M. J. Morris and M. M. Harrison, *J. Organomet. Chem.*, 1991, **407**, 247.
30 D. P. Tate, W. R. Knipple and J. M. Augl, *Inorg. Chem.*, 1962, **1**, 433.
31 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolfson, MULTAN 80, A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, Universities of York and Louvain, 1980.
32 G. M. Sheldrick, SHELXTL, An integrated system for solving, refining and displaying crystal structures from diffraction data (Revision 4), University of Göttingen, 1983.

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