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The synthesis of dinuclear molybdenum and tungsten complexes with the bridging heterodifunctional ligand $C_5H_4PPh_2$: X-ray crystal structure of $Mo_2(\mu-C_5H_4PPh_2)(\eta^5-C_5H_5)(CO)_5$

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Abstract

The synthesis and some reactions of dinuclear metal–metal bonded complexes of molybdenum and tungsten bridged by the heterodifunctional ligand $C_5H_4PPh_2$ are reported. The new complexes $MoM(\mu-C_5H_4PPh_2)(\eta^5-C_5H_5)(CO)_5$ [$M = Mo$ (**1a**); $M = W$ (**1b**)], and $Mo_2(\mu-C_5H_4PPh_2)(\eta^5-C_5H_4PPh_2)(CO)_5$ (**1c**) have been characterized, together with the phosphine substituted derivatives $MoM(\mu-C_5H_4PPh_2)(\eta^5-C_5H_5)(CO)_4L$ [$M = Mo$, $L = PPh_2Me$ (**2a**); $M = Mo$, $L = P(OMe)_3$ (**2b**); $M = W$, $L = PPh_2Me$ (**2c**)] and the di-bridged complex $Mo_2(\mu-C_5H_4PPh_2)_2(CO)_4$ (**3**). The molecular structure of $Mo_2(\mu-C_5H_4PPh_2)(\eta^5-C_5H_5)(CO)_5$ (**1a**) has been determined by X-ray diffraction. Treatment of **1a**, **1b** and **3** with HBF_4 gives the corresponding monoprotonated derivatives **4a**, **4b** and **5**, respectively, in which the proton occupies a bridging site between the metal centres. The new mononuclear complexes $Mo(\eta^5-C_5H_4PPh_2)(CO)_3I$ (**6**) and $Mo(\eta^5-C_5H_4PPh_2)(CO)_2NO$ (**7**) have also been prepared.

Introduction

The heterodifunctional cyclopentadienylphosphine $C_5H_4PPh_2$ has been widely used as a bridging ligand in the synthesis of homodimetallic and heterodimetallic complexes [1,2]. Such complexes are of widespread interest because of the possibility of cooperative effects between the two metal centres [2,3]. Despite this interest, the number of structurally characterized complexes containing one or more bridging $C_5H_4PPh_2$ ligands in which the metal centres are sufficiently close for a direct metal–metal bond to be present remains small [3–5], and there are none involving two Group VI metals.

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In this paper we report the synthesis and some reactions of the metal-metal bonded complexes $\text{MoM}(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5$ [$\text{M} = \text{Mo}$ (**1a**); $\text{M} = \text{W}$ (**1b**)], $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_5$ (**1c**) and $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{CO})_4$ (**3**), together with the results of an X-ray crystal structure determination on **1a**. In the course of this work, we have prepared two stable mononuclear molybdenum complexes containing the $\text{C}_5\text{H}_4\text{PPh}_2$ ligand, $\text{Mo}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_3\text{I}$ and $\text{Mo}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_2\text{NO}$, although a previous report [5] suggested that complexes of this type were unstable.

Results and discussion

The complexes $\text{MoM}(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5$ [$\text{M} = \text{Mo}$ (**1a**); $\text{M} = \text{W}$ (**1b**)], were prepared in moderate yields from the reaction of $\text{Li}[\text{Mo}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_3]$ with $\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{I}$ ($\text{M} = \text{Mo}$ or W) in tetrahydrofuran under reflux. Analogous methods were used previously to prepare other homodimetallic and heterodimetallic complexes with a bridging $\text{PPh}_2\text{C}_5\text{H}_4$ ligand [5,6].

The crystal structure of $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5$ (**1a**) was determined by an X-ray diffraction study. The molecular structure is shown in Fig. 1; selected bond lengths and angles are given in Table 1 and fractional atom coordinates in Table 2. The structure consists of discrete dinuclear molecules with

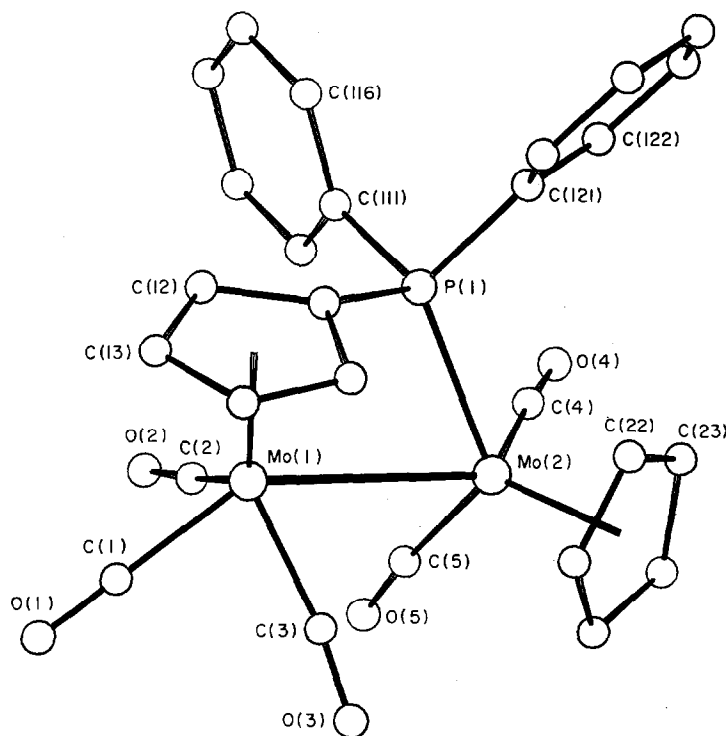


Fig. 1. The molecular structure of $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5$ (**1a**) including the atom numbering scheme.

Table 1

Selected bond lengths (Å) and angles (°) for $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5$ (**1a**)

Selected bond lengths			
Mo(1)–Mo(2)	3.255(2)	Mo(1)–C(11)	2.322(13)
Mo(1)–C(12)	2.382(15)	Mo(1)–C(13)	2.374(15)
Mo(1)–C(14)	2.320(14)	Mo(1)–C(15)	2.299(14)
Mo(1)–C(1)	1.962(16)	Mo(1)–C(2)	1.903(14)
Mo(1)–C(3)	1.962(17)	Mo(2)–P(1)	2.431(4)
Mo(2)–C(21)	2.413(17)	Mo(2)–C(22)	2.373(18)
Mo(2)–C(23)	2.301(18)	Mo(2)–C(24)	2.319(19)
Mo(2)–C(25)	2.362(17)	Mo(2)–C(4)	1.966(17)
Mo(2)–C(5)	1.956(16)	P(1)–C(11)	1.811(13)
P(1)–C(111)	1.833(7)	P(1)–C(121)	1.828(7)
C(11)–C(12)	1.463(17)	C(11)–C(15)	1.479(18)
C(12)–C(13)	1.412(19)	C(13)–C(14)	1.389(19)
C(14)–C(15)	1.420(19)	C(21)–C(22)	1.423(23)
C(21)–C(25)	1.453(22)	C(22)–C(23)	1.326(22)
C(23)–C(24)	1.512(25)	C(24)–C(25)	1.427(23)
C(1)–O(1)	1.160(16)	C(2)–O(2)	1.199(15)
C(3)–O(3)	1.169(17)	C(4)–O(4)	1.137(16)
C(5)–O(5)	1.162(16)		
Selected angles			
C(1)–Mo(1)–Mo(2)	140.0(4)	C(2)–Mo(1)–Mo(2)	82.6(4)
C(2)–Mo(1)–C(1)	80.6(6)	C(3)–Mo(1)–Mo(2)	68.7(5)
C(3)–Mo(1)–C(1)	79.0(7)	C(3)–Mo(1)–C(2)	100.2(6)
P(1)–Mo(2)–Mo(1)	67.0(1)	C(4)–Mo(2)–Mo(1)	127.9(5)
C(4)–Mo(2)–P(1)	82.4(4)	C(5)–Mo(2)–Mo(1)	80.7(4)
C(5)–Mo(2)–P(1)	115.8(4)	C(5)–Mo(2)–C(4)	76.1(6)
C(11)–P(1)–Mo(2)	107.0(4)	O(1)–C(1)–Mo(1)	179(1)
O(2)–C(2)–Mo(1)	172(1)	O(3)–C(3)–Mo(1)	171(1)
O(4)–C(4)–Mo(2)	176(1)	O(5)–C(5)–Mo(2)	173(1)

no unusually short intermolecular contact. The heterodifunctional ligand bridges the two molybdenum atoms. Mo(1) is additionally coordinated by three carbonyl groups and Mo(2) by two carbonyl groups and a cyclopentadienyl ring. This cyclopentadienyl ring lies to one side of a plane bisecting the $\text{PPh}_2\text{C}_5\text{H}_4$ ligand and passing through the two metal atoms and the central CO ligand on the other molybdenum atom.

The metal–metal distance in **1a** at 3.255(2) Å, is slightly longer than that in $\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6$ [7], but is consistent with the presence of a single bond between the metal centres as required by the effective atomic number (EAN) rule. The geometry of the ligands about Mo(1) is a distorted piano stool arrangement similar to that in the molybdenum–manganese complex $\text{MoMn}(\mu\text{-C}_5\text{H}_4\text{-PPh}_2)(\text{CO})_7$ [5]. The angles between the metal–metal bond and the *trans* carbonyl [C(1)–Mo(1)–Mo(2)], and between the two *cis* carbonyls [C(3)–Mo(1)–C(2)], are 140.0 and 100.2°, respectively, compared with 141.2 and 98.2° in the Mo–Mn complex. However, unlike the arrangement in the Mo–Mn complex, the *cis* carbonyls on Mo(1) in **1a** are asymmetrically placed with respect to the metal–metal bond axis, with angles [C(2)–Mo(1)–Mo(2)] = 82.6° and [C(3)–Mo(1)–Mo(2)] = 68.7°. This difference is presumably due to the asymmetric arrangement of the ligands on Mo(2) in **1a** compared with those on manganese in the MoMn complex.

Table 2

Fractional atomic coordinates for $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5$ (**1a**)

Atom	x	y	z
Mo(1)	0.25224(14)	0.23145(7)	-0.14282(7)
Mo(2)	0.10082(15)	0.05422(7)	-0.16634(7)
P(1)	0.1433(4)	0.1155(2)	-0.2815(2)
C(1)	0.2639(19)	0.3196(10)	-0.0729(9)
O(1)	0.27227(16)	0.3712(7)	-0.0310(7)
C(2)	0.0216(16)	0.2591(9)	-0.1578(7)
O(2)	-0.1176(12)	0.2853(7)	-0.1703(7)
C(3)	0.2738(18)	0.1752(9)	-0.0481(9)
O(3)	0.2928(16)	0.1506(8)	0.0125(7)
C(4)	-0.1106(22)	0.0208(9)	-0.2284(8)
O(4)	-0.2322(15)	-0.0021(7)	-0.2623(7)
C(5)	-0.0710(18)	0.1021(8)	-0.1184(8)
O(5)	-0.1796(15)	0.1226(7)	-0.0894(6)
C(11)	0.3045(15)	0.1893(7)	-0.2571(7)
C(12)	0.2803(17)	0.2744(8)	-0.2637(8)
C(13)	0.4091(18)	0.3103(9)	-0.2125(8)
C(14)	0.5115(17)	0.2518(9)	-0.1760(8)
C(15)	0.4542(17)	0.1755(8)	-0.1995(8)
C(21)	0.3614(21)	0.0063(10)	-0.0961(10)
C(22)	0.3353(23)	-0.0286(11)	-0.1679(10)
C(23)	0.1971(22)	-0.0716(11)	-0.1775(10)
C(24)	0.1165(23)	-0.0680(11)	-0.1093(11)
C(25)	0.2240(22)	-0.0174(11)	-0.0600(10)
C(111)	-0.0228(9)	0.1693(5)	-0.3422(4)
C(112)	-0.1781(9)	0.1829(5)	-0.3222(4)
C(113)	-0.3018(9)	0.2237(5)	-0.3702(4)
C(114)	-0.2701(9)	0.2510(5)	-0.4381(4)
C(115)	-0.1148(9)	0.2374(5)	-0.4582(4)
C(116)	0.0089(9)	0.1966(5)	-0.4102(4)
C(121)	0.2177(10)	0.0483(5)	-0.3464(4)
C(122)	0.1048(10)	-0.0045(5)	-0.3864(4)
C(123)	0.1589(10)	-0.0574(5)	-0.4354(4)
C(124)	0.3259(10)	-0.0574(5)	-0.4442(4)
C(125)	0.4388(10)	-0.0046(5)	-0.4042(4)
C(126)	0.3847(10)	0.0483(5)	-0.3552(4)

The spectroscopic properties of the complexes **1a** and **1b** in solution (Table 3) are consistent with their having the same structure as found for **1a** in the solid state. Thus the ^1H NMR spectra of the complexes each show four multiplets of relative intensity one in the region δ 5.5–3.2 which may be assigned to the inequivalent ring protons of the $\mu\text{-C}_5\text{H}_4\text{PPh}_2$ ligands. This confirms the lack of a plane of symmetry such as is present in the related complex $\text{MoMn}(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_7$ [5]; this latter complex shows only two multiplets due to the ring protons. The upfield shift of one of the cyclopentadienyl proton resonances in **1a** and **1b** of *ca.* 1.2 ppm relative to the other three signals is an effect which has been seen previously in the zirconium–iron complex $\text{ZrFe}(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_5)_2(\text{O}^i\text{Bu})(\text{CO})$ [8] and it may be attributed to the proximity of the proton to the other cyclopentadienyl ring [9].

Table 3
Infrared and ¹H NMR data for the new complexes

Compound	$\nu(\text{CO})$ (cm ⁻¹) ^a	¹ H NMR (δ in ppm) ^c
1a Mo ₂ (μ -C ₅ H ₄ PPh ₂)(η ⁵ -C ₅ H ₅)(CO) ₅	1933s, 1943m, 1887m, 1878m	7.2–7.7 (m, 10H, Ar); 5.49 (m, 1H, C ₅ H ₄ P); 5.28 (m, 1H, C ₅ H ₄ P); 4.95 (s, 5H, C ₅ H ₅); 4.46 (m, 1H, C ₅ H ₄ P); 3.20 (m, 1H, C ₅ H ₄ P); 7.0–7.7 (m, 10H, Ar); 5.40 (m, 1H, C ₅ H ₄ P); 5.34 (m, 1H, C ₅ H ₄ P); 5.10 (s, 5H, C ₅ H ₅); 4.52 (m, 1H, C ₅ H ₄ P); 3.30 (m, 1H, C ₅ H ₄ P); 7.2–7.8 (m, 20H, Ar); 5.46 (br, s, 1H, μ -C ₅ H ₄ PPh ₂); 5.36 (br, s, 2H, η ⁵ -C ₅ H ₅ PPH ₂); 5.26 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 4.56 (br, s, 1H, η ⁵ -C ₅ H ₄ PPH ₂); 3.15 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 7.1–7.8 (m, 20H, Ar); 4.93 (s, 5H, C ₅ H ₅); 4.56 (br, s, 1H, C ₅ H ₄ P); 4.33 (br, s, 1H, C ₅ H ₄ P); 4.21 (br, s, 1H, C ₅ H ₄ P); 3.33 (br, s, 1H, C ₅ H ₄ P); 2.10 (d, <i>J</i> (PH) = 8.2, 3H, PPh ₂ Me)
1b MoW(μ -C ₅ H ₄ PPh ₂)(η ⁵ -C ₅ H ₅)(CO) ₅	1933s, 1939m, 1887m, 1867m	7.2–7.8 (m, 20H, Ar); 5.46 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 5.36 (br, s, 2H, η ⁵ -C ₅ H ₅ PPH ₂); 4.45 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 3.15 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 7.1–7.8 (m, 20H, Ar); 4.93 (s, 5H, C ₅ H ₅); 4.56 (br, s, 1H, C ₅ H ₄ P); 4.33 (br, s, 1H, C ₅ H ₄ P); 4.21 (br, s, 1H, C ₅ H ₄ P); 3.33 (br, s, 1H, C ₅ H ₄ P); 2.10 (d, <i>J</i> (PH) = 8.2, 3H, PPh ₂ Me)
1c Mo ₂ (μ -C ₅ H ₄ PPh ₂)(η ⁵ -C ₅ H ₄ PPh ₂)(CO) ₅	1994s, 1947m, 1890m, 1885m, sh	7.2–7.8 (m, 20H, Ar); 5.46 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 5.36 (br, s, 2H, η ⁵ -C ₅ H ₅ PPH ₂); 4.45 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 3.15 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 7.1–7.8 (m, 20H, Ar); 4.93 (s, 5H, C ₅ H ₅); 4.56 (br, s, 1H, C ₅ H ₄ P); 4.33 (br, s, 1H, C ₅ H ₄ P); 4.21 (br, s, 1H, C ₅ H ₄ P); 3.33 (br, s, 1H, C ₅ H ₄ P); 2.10 (d, <i>J</i> (PH) = 8.2, 3H, PPh ₂ Me)
2a Mo ₂ (μ -C ₅ H ₄ PPh ₂)(η ⁵ -C ₅ H ₅)(CO) ₄ PPh ₂ Me	1948s, 1880w, 1860m, 1827m	7.2–7.8 (m, 20H, Ar); 5.46 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 5.36 (br, s, 2H, η ⁵ -C ₅ H ₅ PPH ₂); 4.45 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 3.15 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 7.1–7.8 (m, 20H, Ar); 4.93 (s, 5H, C ₅ H ₅); 4.56 (br, s, 1H, C ₅ H ₄ P); 4.33 (br, s, 1H, C ₅ H ₄ P); 4.21 (br, s, 1H, C ₅ H ₄ P); 3.33 (br, s, 1H, C ₅ H ₄ P); 2.10 (d, <i>J</i> (PH) = 8.2, 3H, PPh ₂ Me)
2b Mo ₂ (μ -C ₅ H ₄ PPh ₂)(η ⁵ -C ₅ H ₅)(CO) ₄ P(OMe) ₃	1947s, 1889w, 1861m, 1843m	7.2–7.8 (m, 20H, Ar); 5.46 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 5.36 (br, s, 2H, η ⁵ -C ₅ H ₅ PPH ₂); 4.45 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 3.15 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 7.1–7.8 (m, 20H, Ar); 4.93 (s, 5H, C ₅ H ₅); 4.56 (br, s, 1H, C ₅ H ₄ P); 4.33 (br, s, 1H, C ₅ H ₄ P); 4.21 (br, s, 1H, C ₅ H ₄ P); 3.33 (br, s, 1H, C ₅ H ₄ P); 2.10 (d, <i>J</i> (PH) = 8.2, 3H, PPh ₂ Me)
2c MoW(μ -C ₅ H ₄ PPh ₂)(η ⁵ -C ₅ H ₅)(CO) ₄ PPh ₂ Me	1943s, 1880w, 1851m, 1826m	7.2–7.8 (m, 20H, Ar); 5.46 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 5.36 (br, s, 2H, η ⁵ -C ₅ H ₅ PPH ₂); 4.45 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 3.15 (br, s, 1H, μ -C ₅ H ₄ PPH ₂); 7.1–7.8 (m, 20H, Ar); 4.93 (s, 5H, C ₅ H ₅); 4.56 (br, s, 1H, C ₅ H ₄ P); 4.33 (br, s, 1H, C ₅ H ₄ P); 4.21 (br, s, 1H, C ₅ H ₄ P); 3.33 (br, s, 1H, C ₅ H ₄ P); 2.10 (d, <i>J</i> (PH) = 8.2, 3H, PPh ₂ Me)
3 Mo ₂ (μ -C ₅ H ₄ PPh ₂) ₂ (CO) ₄	1953s, 1909s, 1861m	7.2–7.9 (m, 20H, Ar); 5.32 (m, 2H, C ₅ H ₄ P); 4.69 (m, 2H, C ₅ H ₄ P); 3.69 (m, 2H, C ₅ H ₄ P); 3.29 (m, 2H, C ₅ H ₄ P); 7.0–7.8 (m, 10H, Ar); 6.15 (br, s, 2H, C ₅ H ₄ P); 5.75 (br, s, 1H, C ₅ H ₄ P); 5.45 (s, 5H, C ₅ H ₅); 3.73 (br, s, 1H, C ₅ H ₄ P); -17.37 (d, <i>J</i> (PH) = 15.9, 1H, MoHMo)
4a [Mo ₂ (μ -C ₅ H ₄ PPh ₂)(μ -HX)(η ⁵ -C ₅ H ₅)(CO) ₅][BF ₄]	2058s, 1991s, 1970m, sh, 1920w ^b	7.3–7.7 (m, 20H, Ar); 5.05 (s, 5H, C ₅ H ₅); 4.57 (br, s, 1H, C ₅ H ₄ P); 4.35 (br, s, 1H, C ₅ H ₄ P); 4.28 (br, s, 1H, C ₅ H ₄ P); 3.40 (br, s, 1H, C ₅ HP); 2.08 (d, <i>J</i> (PH) = 8.2, 3H, PPh ₂ Me)
4b [MoW(μ -C ₅ H ₄ PPh ₂)(μ -HX)(η ⁵ -C ₅ H ₅)(CO) ₅][BF ₄]	2061s, 1984s, br, 1908w ^b	7.3–7.7 (m, 20H, Ar); 6.25 (br, s, 1H, C ₅ H ₄ P); 6.22 (br, s, 1H, C ₅ H ₄ P); 5.70 (br, s, 1H, C ₅ H ₄ P); 5.58 (s, 5H, C ₅ H ₅); 3.82 (br, s, 1H, C ₅ H ₄ P); -18.62 (d, <i>J</i> (PH) = 11.3, W satellites <i>J</i> (¹⁸³ WH) = 36.1, 1H, MoHW)
5 [Mo ₂ (μ -C ₅ H ₄ PPh ₂) ₂ (μ -HX)(CO) ₄][BF ₄]	2000s, 1979s, 1991m ^b	7.1–7.9 (m, 20H, Ar); 5.43 (br, s, 6H, C ₅ H ₄ P); 4.12 (br, s, 2H, C ₅ H ₄ P); -16.93 (t, <i>J</i> (PH) = 22.9, 1H, MoHMo)
6 Mo(η ⁵ -C ₅ H ₄ PPh ₂)(CO) ₃ I	2044s, 1970s, 1950s	7.3–7.8 (m, 10H, Ar); 5.83 (t, <i>J</i> = 2.2, 2H, C ₅ H ₄ P); 5.40 (td, <i>J</i> = 2.2, 0.75, 2H, C ₅ H ₄ P)
7 Mo(η ⁵ -C ₅ H ₄ PPh ₂)(CO) ₂ NO	2021s, 1951s [$\nu(\text{NO})$ 1687s]	7.3–7.5 (m, 10H, Ar); 5.63 (d, <i>J</i> = 1.4, 2H, C ₅ H ₄ P); 5.61 (d, <i>J</i> = 1.7, 2H, C ₅ H ₄ P)

^a Recorded in hexane solution unless otherwise indicated. ^b Recorded in CH₂Cl₂ solution. ^c Recorded at 298 K in CDCl₃ solution. All coupling constants are in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.

The ^{31}P NMR spectra of **1a** and **1b** each show a single peak which may be attributed to the phosphorus of the $\mu\text{-C}_5\text{H}_4\text{PPh}_2$ ligand. In the case of **1b**, this peak is accompanied by tungsten satellites with $J(^{183}\text{W}\text{-}^{31}\text{P})$ of 295 Hz, showing that the ligand is coordinated through phosphorus to tungsten and through the C_5H_4 ring to molybdenum.

The reactions of **1a** with PPh_2Me and P(OMe)_3 and of **1b** with PPh_2Me were studied in order to determine whether substitution would take place and, if so, at which of the metal atom sites. From these reactions, which proceeded in refluxing toluene at 383 K, the monosubstituted derivatives $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_4\text{L}$ [$\text{L} = \text{PPh}_2\text{Me}$ (**2a**); $\text{L} = \text{P(OMe)}_3$ (**2b**)] and $\text{MoW}(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_4\text{L}$ [$\text{L} = \text{PPh}_2\text{Me}$ (**2c**)] were obtained. There was no evidence in any of the reactions for the formation of disubstituted products.

The ^{31}P NMR spectra of the complexes [**2**] strongly suggest that the substituting ligand is bound to the metal atom which is not coordinated by the phosphorus of the $\mu\text{-C}_5\text{H}_4\text{PPh}_2$ ligand. Thus the ^{31}P signal due to this latter ligand occurs at virtually the same position in the substituted complexes as in the relevant unsubstituted complex **1a** or **1b**. In addition, whereas in **2c** the phosphorus signal due to the $\mu\text{-C}_5\text{H}_4\text{PPh}_2$ ligand shows ^{183}W satellites, the phosphorus signal due to the PPh_2Me ligand does not. Instead this latter signal is a simple doublet with $J(\text{P-P}) = 10$ Hz.

The carbonyl ligands on the molybdenum atom in **1a** at which substitution takes place are all non-equivalent and there are therefore three possible sites for the phosphorus ligand in the complexes **2**. These cannot be distinguished on the basis of the spectroscopic data but only one isomer seems to be present in each case. This isomer is tentatively assigned the structure shown in Fig. 2 since, for steric reasons, the reactions are most likely to proceed in such a way that the carbonyl group furthest from the C_5H_5 ligand on the other metal atom is displaced.

The reaction of **1a** or **1b** with excess HBF_4 at 195 K gives brown air-sensitive products which are formulated on the basis of their ^1H NMR spectra as the protonated derivatives, $[\text{MoM}(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\mu\text{-H})(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5][\text{BF}_4]$ ($\text{M} = \text{Mo}$ (**4a**); $\text{M} = \text{W}$ (**4b**)), with the structures shown in Fig. 2. Thus doublet signals are seen for **4a** at $\delta -17.37$ [$J(\text{P-H}) = 15.9$ Hz] and for **4b** at $\delta -18.62$ [$J(\text{P-H}) = 11.3$ Hz] which may be assigned to a bridging hydride ligand. In the case of **4b** the central doublet is accompanied by two satellite doublets [$J(^{183}\text{W-H}) = 36.1$ Hz]. Similar spectra have been reported previously for the protonated derivatives of $\text{MoMn}(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_7$ and $\text{MoRe}(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_7$ [10]. The values of $J(\text{P-H})$ for these previously reported complexes (6.2 Hz and unresolved, respectively) are, however, considerably less than for the complexes **4**. This difference is presumably due to the altered geometry round manganese or rhenium compared to that of the corresponding molybdenum atom in **4**.

Many dimetallic complexes are known that contain two bridging $\text{C}_5\text{H}_4\text{PPh}_2$ ligands. In the majority of these, the two cyclopentadienyl ligands are coordinated to one metal atom and the two phosphorus atoms to the other [1,2,11,12]. A head to tail arrangement is much less common and the only structurally characterized examples all involve Group VIII metals, namely $\text{Pt}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Ph}_2$ [13], $\text{Rh}_2(\mu\text{-C}_5\text{H}_4\text{PR}_2)_2(\text{CO})_2$ ($\text{R} = \text{Ph}$ [14]; $\text{R} = \text{Me}$ [15]), $[\text{Rh}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{CO})\text{COMe}][\text{PF}_6]$ [3] and $[\text{Rh}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{py}_2][\text{BF}_4]_2$ [4]. A metal-metal bond is present only in the last two of these examples. We have now synthesized in three

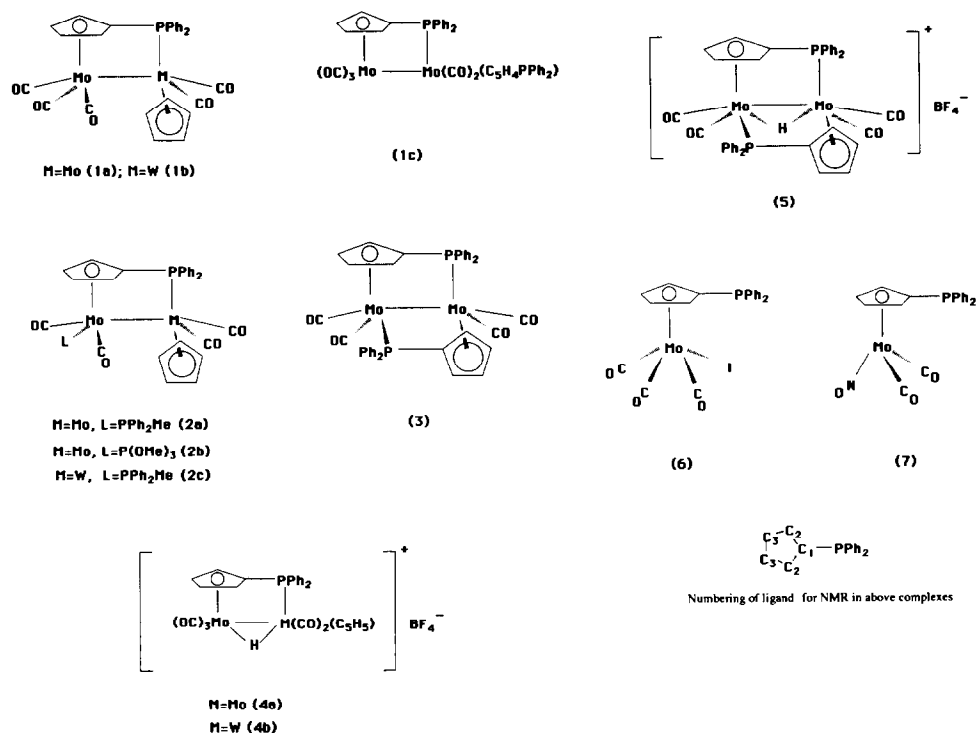


Fig. 2. Proposed structures of the new dinuclear molybdenum and tungsten complexes.

different ways the metal-metal bonded complex $Mo_2(\mu-C_5H_4PPh_2)_2(CO)_4$ (3) which contains a head to tail arrangement of the two $C_5H_4PPh_2$ ligands. The best of these methods involves the reaction of $Mo(\eta^5-C_5H_4PPh_2)(CO)_3I$ (6) with $Li[Mo(CO)_3(\eta^5-C_5H_4PPh_2)]$, a method which is analogous to that used for the synthesis of 1a and 1b. At 338 K this reaction leads to the synthesis of 3 in 32% yield together with a second complex, $Mo_2(\mu-C_5H_4PPh_2)(\eta^5-C_5H_4PPh_2)(CO)_5$ (1c) in 6% yield. Complex 3 may also be obtained in 10% yield by the oxidation of $Li[Mo(CO)_3(\eta^5-C_5H_4PPh_2)]$ with ferric sulphate in the presence of ethanoic acid or in 34% yield by the thermolysis of 1c (see Experimental section).

In the proposed structure for 3 (Fig. 2), the two heterodifunctional ligands, although occupying equivalent positions, are arranged in a cisoid configuration with respect to each other. Such an arrangement is also found in the metal-metal bonded complexes $[Rh_2(\mu-C_5H_4PPh_2)_2(CO)COMe][PF_6]$ [3] and $[Rh_2(\mu-C_5H_4PPh_2)_2py_2][BF_4]_2$ [4] but not in the complexes $Pt_2(\mu-C_5H_4PPh_2)_2Ph_2$ [13], $Rh_2(\mu-C_5H_4PR_2)_2(CO)_2$ ($R=Ph$ [14]; $R=Me$ [15]), in which a metal-metal bond is absent. In these latter complexes, the two heterodifunctional ligands are arranged *trans* to each other so that the two metal atoms, the two phosphorus atoms, and the centroids of the two cyclopentadienyl rings lie in a plane. The two arrangements can be distinguished by a consideration of the NMR data for the complexes concerned. Thus in the 1H NMR spectrum of 3, four signals, each of

relative intensity two, are observed at δ 5.32, 4.69, 3.69 and 3.29 and these are assigned to the four non-equivalent protons on each of the two cyclopentadienyl rings. The two upfield resonances at 3.69 and 3.29 probably correspond to H¹ and H² due to their proximity to aromatic rings [9]. The ³¹P NMR spectrum also confirms the equivalence of the two heterodifunctional ligands with a single resonance at δ -72.8. In the ¹³C NMR spectrum only two signals are observed in the carbonyl region, one a doublet at δ 243.9 [$J(\text{P}-\text{C}) = 27.4$ Hz] and the other a singlet at δ 231.9. On this basis [16], the former is assigned to the two carbonyl ligands (CO¹) which are *trans* to the phosphine ligands and the latter to the two carbonyl ligands (CO²) which are *cis* to the phosphine ligands. It should be noted that the relative positions of the two cyclopentadienyl rings in **3** in the proposed structure are similar to those found for the cyclopentadienyl rings in **1a** from the crystal structure determination.

Complex **1c** is assigned a structure analogous to that of **1a** and **1b** on the basis of spectroscopic data, with one heterodifunctional ligand in a bridging position and one which is coordinated only to a single metal atom through the cyclopentadienyl group (Fig. 2). In accordance with this proposal, the ³¹P {¹H} NMR spectrum of **1c** shows two singlet signals at δ -78.0 and -157.8. The first of these is assigned to the bridging C₅H₄PPh₂ ligand, since it has a chemical shift very close to that observed for this ligand in **1a**. The second signal, which has a chemical shift similar to that observed in Li[Mo(η^5 -C₅H₄PPh₂)(CO)₃] and also in **6** and **7** described below, is assigned to a C₅H₄PPh₂ group in which the phosphorus atom remains uncoordinated.

It is tempting to suggest that **1c** is an intermediate in the reaction leading to **3**, especially in view of the similarity in the positions of the cyclopentadienyl rings in the two complexes, and that **3** is formed on displacement of a carbonyl group in **1c** by the uncoordinated phosphorus atom. That this is a reasonable suggestion is shown by the thermolysis of **1c** at 338 K, which yields **3** as the only product.

Protonation of complex **3** with excess HBF₄ at 195 K gives a single dark red complex which is formulated as [Mo₂(μ -C₅H₄PPh₂)₂(μ -H)(CO)₄][BF₄] (**5**). The bridging hydride ligand in **5** gives rise to a triplet signal in the ¹H NMR of the complex at δ -16.93 [$J(\text{P}-\text{H}) = 22.9$ Hz] which is consistent with the structure shown in Fig. 2 in which the hydride is symmetrically placed between the two metal atoms. A non-symmetrical but fluxional structure cannot, however, be excluded.

The mononuclear complex Mo(η^5 -C₅H₄PPh₂)(CO)₃I (**6**), used in the preparation of **3**, is itself a new species and was prepared from the reaction of the anionic complex Li[Mo(CO)₃(η^5 -C₅H₄PPh₂)] with iodine (see Experimental section), although a previous attempt to halogenate this anion or to prepare other mononuclear neutral derivatives from it was not successful [5]. To demonstrate that an extended range of neutral mononuclear derivatives of Li[Mo(CO)₃(η^5 -C₅H₄PPh₂)] can be obtained as stable entities, we have also synthesized and characterized the nitrosyl complex Mo(η^5 -C₅H₄PPh₂)(CO)₂NO (**7**) both by reaction of the anion with diazald, *p*-MeC₆H₄SO₂N(Me)NO, and by reaction of the anion with NOBF₄. The spectroscopic properties of **7** are similar to those of the cyclopentadienyl complex Mo(η^5 -C₅H₅)(CO)₂NO [17] and it is assigned an analogous structure (Fig. 2). Complex **7** was subjected to thermolysis and photolysis in attempts to eliminate one or more CO groups, and hence to form higher nuclearity species, but no new complexes could be isolated from these reactions.

Experimental

All reactions were carried out under nitrogen by standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use. Preparative thin-layer chromatography (TLC) was carried out on commercial Merck plates coated with a 0.25-mm layer of silica, or on 1-mm silica plates prepared at the University Chemical Laboratory, Cambridge; products are presented in order of decreasing R_f values.

The instruments used to obtain spectroscopic data have been specified previously [18]. Phosphorus-31 NMR chemical shifts are given relative to $P(OMe)_3$ with upfield shifts negative. Unless otherwise stated, all reagents were obtained from commercial suppliers and used without further purification. The compounds $Mo(\eta^5-C_5H_5)(CO)_3I$ and $W(\eta^5-C_5H_5)(CO)_3I$ were prepared by slight modifications (see below) of the published method [19] from $Na[Mo(\eta^5-C_5H_5)(CO)_3] \cdot 2DME$ and $Na[W(\eta^5-C_5H_5)(CO)_3] \cdot 2DME$ [20], respectively. The compound $Li[Mo(CO)_3(\eta^5-C_5H_4PPh_2)]$ [5] was prepared from $Li[PPh_2C_5H_4]$ [21] and $Mo(CO)_3(MeCN)_3$ [22] rather than from the lithium reagent and $Mo(CO)_6$. This modification enabled the compound to be prepared in 15 min at room temperature, rather than by overnight reflux, and gave a purer solution of the anion.

Preparation of complexes

(i) $Mo(\eta^5-C_5H_5)(CO)_3I$ [19]. The complex $Na[Mo(\eta^5-C_5H_5)(CO)_3] \cdot 2DME$ (3.1 g, 7.08 mmol) was dissolved in tetrahydrofuran (THF) (40 cm³) and iodine (1.75 g, 6.62 mmol) in THF (20 cm³) was added. The mixture was stirred for 20 min at room temperature and the solvent then removed under vacuum to yield a red solid. A suspension of this in toluene was stirred for 20 min and the insoluble sodium iodide then filtered off. Removal of solvent from the filtrate under vacuum left $Mo(\eta^5-C_5H_5)(CO)_3I$ (2.3 g, 89%) as a red powder.

(ii) $W(\eta^5-C_5H_5)(CO)_3I$ [19]. This was prepared in a similar fashion to the molybdenum analogue using $Na[W(\eta^5-C_5H_5)(CO)_3] \cdot 2DME$ (0.40 g, 0.758 mmol) and iodine 0.19 g, 0.748 mmol) to give $W(\eta^5-C_5H_5)(CO)_3I$ (0.33 g, 95%) as a red powder.

(iii) $Mo_2(\mu-C_5H_4PPh_2)(\eta^5-C_5H_5)(CO)_5$ (**1a**). The complex $Mo(\eta^5-C_5H_5)(CO)_3I$ (1.10 g, 2.96 mmol) was added to a solution of $Li[Mo(CO)_3(\eta^5-C_5H_4PPh_2)]$ prepared *in situ* from $Li(C_5H_4PPh_2)$ (0.75 g, 2.93 mmol) and $Mo(CO)_3(NCMe)_3$ (0.80 g, 2.93 mmol) in THF (100 cm³). The mixture was heated under reflux at 338 K for 16 h, then allowed to cool and the solvent was removed under vacuum. The residue was adsorbed on alumina and purified by column chromatography on alumina (UG1 grade). Elution of the column with CH_2Cl_2 /hexane (1:2) gave a brown band which yielded $Mo_2(\mu-C_5H_4PPh_2)(\eta^5-C_5H_5)(CO)_5$ (**1a**) (0.85 g, 45%) as a brown powder on evaporation of the solvent. **1a**: Anal. Found: C, 50.2; H, 2.9; P, 4.7. $C_{27}H_{19}Mo_2O_5P$ calc.: C, 50.2; H, 2.9; P, 4.8%. MS: m/e 646 (M^+), $M^+ - n(CO)$ ($n = 1-5$). ^{13}C NMR: $CDCl_3$ at 298 K) δ 140.7 (d, $J(P-C) = 38.8$, *ipso-Ar*); 135.2 (d, $J(P-C) = 13.0$, *o-Ar*); 131.3 (s, *p-Ar*); 130.2 (s, *p-Ar*); 129.6 (d, $J(P-C) = 11.6$, *o-Ar*); 129.1 (d, $J(P-C) = 9.6$, *m-Ar*); 128.3 (d, $J(P-C) = 11.3$, *m-Ar*); 95.5 (d, $J(P-C) = 17.1$, C_5H_4P , C_2 or C_3); 93.2, (d, $J(P-C) = 6.2$, C_5H_4P , C_2 or C_3); 92.5 (s, C_5H_5); 90.9 (d, $J(P-C) = 8.2$, C_5H_4P , C_2 or

C₃); 86.9 (d, $J(\text{P}-\text{C}) = 6.5$, C₅H₄P, C₂ or C₃); 54 (d, $J(\text{P}-\text{C}) = 40$, C₅H₄P, C₁). ³¹P NMR: (CDCl₃ at 298 K) δ -78.7 (s, PPh₂C₅H₄).

(iv) *MoW*(μ -C₅H₄PPh₂)(η^5 -C₅H₅)(CO)₅ (**1b**). The complex *W*(η^5 -C₅H₅)(CO)₃I (0.156 g, 0.339 mmol) was added to a solution of Li[Mo(CO)₃(η^5 -C₅H₅PPh₂)] prepared *in situ* from Li(C₅H₄PPh₂) (0.087 g, 0.340 mmol) and Mo(CO)₃(NCMe)₃ (0.093 g, 0.341 mmol) in THF (20 cm³) and the reaction carried out as in (iii). The residue was purified by TLC with CH₂Cl₂/hexane (1:3) as the eluent. A red band and a brown band were eluted and yielded, respectively, *W*(C₅H₅)(CO)₃I (0.042 g, 27%) and *MoW*(μ -C₅H₄PPh₂)(η^5 -C₅H₅)(CO)₅ (**1b**) (0.078 g, 31%). **1b**: Anal. Found: C, 44.0; H, 2.6. C₂₇H₁₉MoO₅PW calc.: C, 44.2; H, 2.6%. MS: m/e 734 (M^+), $M^+ - n(\text{CO})$ ($n = 1-5$). ³¹P NMR (CDCl₃ at 298 K): δ -109.6 (s, W satellites $J(\text{W}-\text{P}) = 295$, PPh₂C₅H₄).

(v) *Mo*₂(μ -C₅H₄PPh₂)(η^5 -C₅H₅)(CO)₄PPh₂Me (**2a**). To a solution of *Mo*₂(μ -C₅H₄PPh₂)(η^5 -C₅H₅)(CO)₅ (**1a**) (0.175 g, 0.271 mmol) in toluene (50 cm³) was added PPh₂Me (0.050 cm³). The mixture was heated under reflux at 383 K for 40 h after which infrared monitoring indicated that no further reaction was occurring. The solution was allowed to cool, the solvent removed under vacuum, and the residue purified by TLC with CH₂Cl₂/hexane (1:1) as the eluent. The single dark red band obtained yielded *Mo*₂(μ -C₅H₄PPh₂)(η^5 -C₅H₅)(CO)₄PPh₂Me (**2a**) (0.140 g, 63%) as a brown powder. **2a**: Anal. Found: C, 53.0; H, 3.7. C₃₉H₃₂Mo₂O₄P calc.: C, 53.2; H, 3.9%. MS: m/e 818 (M^+), $M^+ - n(\text{CO})$ ($n = 1-3$). ³¹P NMR (CDCl₃ at 298 K): δ -78.0 (s, PPh₂C₅H₄); -85.4 (s, PPh₂Me).

(vi) *Mo*₂(μ -C₅H₄PPh₂)(η^5 -C₅H₅)(CO)₄P(OMe)₃ (**2b**). In an analogous procedure to that described in (v), *Mo*₂(μ -C₅H₄PPh₂)(η^5 -C₅H₅)(CO)₅ (**1a**) (0.040 g, 0.062 mmol) and P(OMe)₃ (0.010 g, 0.085 mmol) in toluene (20 cm³) was heated under reflux at 383 K for 16 h. The residue was purified by TLC with CH₂Cl₂/hexane (1:4) as the eluent to give a brown and a red band. These yielded, respectively, *Mo*₂(μ -C₅H₄PPh₂)(η^5 -C₅H₅)(CO)₅ (**1a**) (0.006 g, 15%) and *Mo*₂(μ -C₅H₄PPh₂)(η^5 -C₅H₅)(CO)₄P(OMe)₃ (**2b**) (0.025 g, 54%) as brown powders. Complex **2b**: MS: m/e 744 (M^+), $M^+ - n(\text{CO})$ ($n = 1-4$). ³¹P NMR (CDCl₃ at 298 K): δ -77.3 (d, $J(\text{P}-\text{P}) = 13$, PPh₂C₅H₄); 55.2 (d, P(OMe)₃).

(vii) *MoW*(μ -C₅H₄PPh₂)(η^5 -C₅H₅)(CO)₄PPh₂Me (**2c**). In an analogous procedure to that described in (v), a mixture of *MoW*(μ -C₅H₄PPh₂)(η^5 -C₅H₅)(CO)₅ (**1b**) (0.040 g, 0.054 mmol) and PPh₂Me (0.015 cm³, 0.081 mmol) in toluene (20 cm³) was heated under reflux at 383 K for 16 h. The residue was purified by TLC with CH₂Cl₂/hexane (2:3) as the eluent to give a brown and a dark red band. These yielded, respectively, *MoW*(μ -C₅H₄PPh₂)(η^5 -C₅H₅)(CO)₅ (**1b**) (0.008 g, 20%) and *MoW*(μ -C₅H₄PPh₂)(η^5 -C₅H₅)(CO)₄PPh₂Me (**2c**) (0.014 g, 28%) as brown powders. **2c**: Anal. Found: C, 49.7; H, 3.5. C₂₇H₁₉MoO₅P₂W calc.: C, 48.5; H, 3.4%. MS: m/e 906 (M^+), $M^+ - n(\text{CO})$ ($n = 1-4$). ³¹P NMR (CDCl₃ at 298 K): δ -109.0 (d, $J(\text{P}-\text{P}) = 10$, W satellites $J(\text{W}-\text{P}) = 310$, PPh₂C₅H₄), -85.8 (d, PPh₂Me).

(viii) *Mo*(η^5 -C₅H₄PPh₂)(CO)₃I (**6**). A solution of iodine (0.075 g, 0.295 mmol) in THF (5 cm³) was added to a solution of Li[Mo(CO)₃(η^5 -C₅H₅PPh₂)] prepared *in situ* from Li(C₅H₄PPh₂) (0.075 g, 0.293 mmol) and Mo(CO)₃(NCMe)₃ (0.080 g, 0.293 mmol) in THF (30 cm³) as described in (i). The mixture was stirred at room temperature for 15 min after which the solution had turned red and none of the anion remained. The solvent was removed under vacuum and the residue purified

by TLC using $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:3) as eluent. The single red band obtained yielded $\text{Mo}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_3\text{I}$ (**6**) (0.072 g, 44%) as a slightly oily red material. ^{13}C NMR (CDCl_3 at 298 K): δ 232.0 (s, $\text{Mo}(\text{CO})$); 219.5 (s, $\text{Mo}(\text{CO})$); 217.9 (s, $\text{Mo}(\text{CO})$); 128–136 (m, Ar); 100.8 (br, s, $\text{C}_5\text{H}_4\text{P}$, C_1); 98.8 (s, $\text{C}_5\text{H}_4\text{P}$, C_3); 97.7 (d, $J(\text{P}-\text{C}) = 12.1$, $\text{C}_5\text{H}_4\text{P}$, C_2). ^{31}P NMR (CDCl_3 at 298 K): δ -159.4 (s, $\text{PPh}_2\text{C}_5\text{H}_4$).

(ix) $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{CO})_4$ (**3**). (a) A solution of $\text{Mo}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_3\text{I}$ (**6**) (0.200 g, 0.360 mmol) in THF (5 cm^3) was added to one of $\text{Li}[\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)]$ prepared *in situ* from $\text{Li}(\text{C}_5\text{H}_4\text{PPh}_2)$ (0.086 g, 0.336 mmol) and $\text{Mo}(\text{CO})_3(\text{NCMe})_3$ (0.086 g, 0.315 mmol) in THF (20 cm^3) as described in (i). The mixture was heated under reflux at 338 K for 16 h and then allowed to cool and the solvent was removed under vacuum. The residue was purified by TLC with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (2:3) as eluent, giving a brown and a red band. These yielded, respectively, $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_5$ (**1c**) (0.015 g, 6%) as a brown powder and $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{CO})_4$ (**3**) (0.080 g, 32%) as a dark red powder.

Complex **1c**: MS: m/e 802 ($\text{M}^+ - \text{CO}$), $\text{M}^+ - n(\text{CO})$ ($n = 1-5$). ^{31}P NMR (CDCl_3 at 298 K): δ -78.0 (s, $\mu\text{-PPh}_2\text{C}_5\text{H}_4$); -157.8 (s, $\eta^5\text{-PPh}_2\text{C}_5\text{H}_4$). Complex **3**: Anal. Found: C, 56.8; H, 3.6. $\text{C}_{38}\text{H}_{28}\text{Mo}_2\text{O}_4\text{P}_2$ calc.: C, 56.9; H, 3.5%. MS: m/e 802 (M^+), $\text{M}^+ - n(\text{CO})$ ($n = 1-4$). ^{13}C NMR (CDCl_3 at 298 K): δ 243.9 (d, $J(\text{P}-\text{C}) = 27.4$ $\text{Mo}(\text{CO})_2$); 231.9 (s, $\text{Mo}(\text{CO})_2$), 138.5 (d, $J(\text{P}-\text{C}) = 40.2$ *ipso*-Ar); 133.9 (d, $J(\text{P}-\text{C}) = 13.2$, *o*-Ar); 132.6 (d, $J(\text{P}-\text{C}) = 48.6$, *ipso*-Ar); 131.1 (d, $J(\text{P}-\text{C}) = 11.5$, *o*-Ar); 130.6 (s, *p*-Ar); 128.6 (d, $J(\text{P}-\text{C}) = 9.4$, *m*-Ar); 128.3 (d, $J(\text{P}-\text{C}) = 10.6$ *m*-Ar); 93.5 (br, s, $\text{C}_5\text{H}_4\text{P}$, C_2 or C_3); 91.0 (d, $J(\text{P}-\text{C}) = 14.3$, $\text{C}_5\text{H}_4\text{P}$, C_2 or C_3); 87.6 (d, $J(\text{P}-\text{C}) = 6.4$, $\text{C}_5\text{H}_4\text{P}$, C_2 or C_3); 87.1 (br, s, $\text{C}_5\text{H}_4\text{P}$, C_2 or C_3); 53.1 (d, $J(\text{P}-\text{C}) = 40.6$, $\text{C}_5\text{H}_4\text{P}$, C_1). ^{31}P NMR (CDCl_3 at 298 K): δ -72.8 (s, $\text{PPh}_2\text{C}_5\text{H}_4$).

(b) A solution of $\text{Li}[\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)]$ was prepared from $\text{Li}(\text{C}_5\text{H}_4\text{-PPh}_2)$ (0.068 g, 0.266 mmol) and $\text{Mo}(\text{CO})_3(\text{NCMe})_3$ (0.070 g, 0.256 mmol) in THF (20 cm^3) as described in (i). A solution of $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ (0.080 g, 0.152 mmol) in distilled water and a few drops of concentrated ethanoic acid were added [23] and the mixture was stirred at room temperature for 30 min. The red precipitate formed was filtered off and dried under vacuum. It was purified by TLC with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:1) as the eluent. A dark red band and a brown band eluted, which yielded, respectively, $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_5$ (**1c**) (0.006 g, 3%) and $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{CO})_4$ (**3**) (0.020 g, 10%).

(c) A solution of $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_5$ (**1c**) (0.015 g, 0.018 mmol) in THF (15 cm^3) was heated under reflux at 338 K for 16 h and then allowed to cool. The solvent was removed under vacuum and the residue purified by TLC with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (2:3) as the eluent. A single red band was obtained which yielded $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{CO})_4$ (**3**) (0.005 g, 34%) as a red solid.

(x) $\text{Mo}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_2\text{NO}$ (**7**). (a) Diazald (0.130 g, 0.607 mmol) in THF (5 cm^3) was added to a solution of $\text{Li}[\text{Mo}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_3]$ prepared *in situ* from $\text{Li}(\text{C}_5\text{H}_4\text{PPh}_2)$ (0.160 g, 0.643 mmol) and $\text{Mo}(\text{CO})_3(\text{NCMe})_3$ (0.175 g, 0.614 mmol) in THF (20 cm^3) in a procedure analogous to that described under (viii). The reaction mixture was stirred at room temperature for 30 min after which the mixture had become dark brown and infrared monitoring indicated that no anion remained. The solvent was removed under vacuum and the residue was purified by TLC with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:10) as the eluent. The single yellow band obtained yielded $\text{Mo}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_2\text{NO}$ (**7**) (0.120 g, 48%) as a yellow powder.

Complex 7: MS: m/e 403 ($M^+ - \text{CO}$), $M^+ - n(\text{CO}) - \text{NO}$ ($n = 1, 2$). ^{31}P NMR (CDCl_3 at 298 K): δ -161.7 (s, $\text{PPh}_2\text{C}_5\text{H}_4$).

(b) NOBF_4 (0.008 g, 0.068 mmol) was added to a solution of $\text{Li}[\text{Mo}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_3]$ prepared *in situ* from $\text{Li}(\text{C}_5\text{H}_4\text{PPh}_2)$ (0.017 g, 0.066 mmol) and $\text{Mo}(\text{CO})_3(\text{NCMe})_3$ (0.020 g, 0.073 mmol) in THF (20 cm^3) which had been previously cooled to 195 K. The mixture was allowed to warm to room temperature and stirred for 30 min, after which the solution had turned dark brown and none of the anion remained. The solvent was removed under vacuum and the residue purified by TLC with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:5) as eluent. The single yellow band obtained yielded $\text{Mo}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_2\text{NO}$ (7) (0.010 g, 34%) as a yellow powder.

Protonation experiments

(i) Protonation of $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5$ (1a). A solution of 1a (0.010 g, 0.015 mmol) in CH_2Cl_2 (20 cm^3) was cooled to 195 K, an excess of HBF_4 was added, and the mixture allowed to warm to room temperature. After 15 min infrared monitoring indicated that no starting material remained and the solvent was removed under vacuum. The residue was washed with Et_2O to yield $[\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\mu\text{-H})(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5][\text{BF}_4]$ (4a) as a brown powder, which was stored under nitrogen.

(ii) Protonation of $\text{MoW}(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5$ (1b). Complex 1b (0.008 g, 0.011 mmol) was used in an analogous procedure to that followed for 1a. The protonated complex $[\text{MoW}(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\mu\text{-H})(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5][\text{BF}_4]$ (4b) was obtained as a brown solid, which was stored under nitrogen.

(iii) Protonation of $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{CO})_4$ (3). Complex 3 (0.013 g, 0.016 mmol) was used in an analogous procedure to that described for 1a. The protonated complex $[\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2(\mu\text{-H})(\text{CO})_4][\text{BF}_4]$ (5) was obtained as a dark red solid, which was stored under nitrogen.

X-Ray data collection, structure solution and refinement of $\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5$ (1a)

Crystal data for 1a. $\text{C}_{27}\text{H}_{19}\text{O}_5\text{P}_1\text{Mo}_2$, $M = 646.30$, monoclinic, space group $P2_1/c$, $a = 8.124(2)$, $b = 17.008(4)$, $c = 18.312(5)\text{\AA}$, $\beta = 100.35(2)^\circ$, $Z = 4$, $U = 2.489.05\text{\AA}^3$, $\mu(\text{Mo-K}\alpha) = 9.9\text{ cm}^{-1}$, $D_c = 1.73\text{ g cm}^{-3}$, $F(000) = 1280$. A dark red crystal of size $0.10 \times 0.08 \times 0.46\text{ mm}^3$, was used in the data collection.

Data collection. Data were collected in the θ -range $3\text{--}25^\circ$, with a scan width of 0.90° , using the technique described previously [24]. Equivalent reflections were merged to give 2170 data with $I/\sigma(I) > 3.0$. Absorption corrections were applied to the data after initial refinement with isotropic thermal parameters for all atoms [25].

Structure solution and refinement [26]. The coordinates of the molybdenum atoms were deduced from a Patterson synthesis, and the remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses. The phenyl rings were constrained to idealized hexagonal geometry (C-C 1.395 and C-H 1.08 \AA) with fixed thermal parameters of 0.08\AA^2 assigned to the hydrogen atoms. The molybdenum, phosphorus, and the carbon and oxygen atoms of the five carbonyl ligands were assigned anisotropic thermal parameters in the final cycles of full-ma-

trix refinement which converged at $R = 0.0605$ and $R' = 0.0597$ with weights of $w = 1/\sigma^2 F_o$ assigned to the individual reflections.

Additional material is available from the Cambridge Crystallographic Data Centre.

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