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MIXED-VALENCE DINUCLEAR MOLYBDENUM COMPLEXES: SYNTHESIS AND MOLECULAR STRUCTURE OF $(Cp^{\circ}Mo)_2(\mu\text{-}Cl)_n(\mu\text{-}PPh_2)_{3-n}$ ($n = 1$, 0; $Cp^{\circ} = \eta^5\text{-}C_5Me_4Et$)

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Abstract—$(Cp^{\circ}Mo)_2(\mu\text{-}Cl)_4$ reacts with PMe_3 to give $Cp^{\circ}MoCl_2(PMe_3)_2$ (**1**) ($Cp^{\circ} = \eta^5\text{-}C_5Me_4Et$). The reaction of the molybdenum(III) complexes $(Cp^{\circ}Mo)_2(\mu\text{-}Cl)_4$ and $Cp^{\circ}MoCl_2(PMe_3)_2$ with $KPPh_2(dioxane)_2$ yields the mixed-valence dinuclear complexes $(Cp^{\circ}Mo)_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)_2$ (**2**) and $(Cp^{\circ}Mo)_2(\mu\text{-}PPh_2)_3$ (**3**) as reduction/substitution products. Complexes **1**–**3** were characterized by IR and MS techniques and an X-ray structure determination was carried out on **2** and **3**.

Mixed-valence solid-state compounds in which the metal is present in two oxidation states, such as Fe_3O_4, Pb_3O_4 and hexacyanoferrates, have been known for a long time.[1] Biologically relevant molecules (e.g. the ferredoxins) have been the focus of much interest.[2] In contrast, analogous molecular compounds only became the subject of intensified investigation with the synthesis of the "Creutz–Taube complex" $[(NH_3)_5Ru(\mu\text{-}1,4\text{-}N_2C_4H_4)Ru(NH_3)_5]^{5+}$, in which a pyrazine ring links a Ru^{II} centre with a Ru^{III} centre.[3] Other compounds of this type are the mixed-valence complexes $Ru_2Cl_5(PR_2R')_4$ (R = Me, R′ = Me or Ph; R = R′ = Bu; R = Et, R′ = Ph)[4] and $[Ru_2(NH_3)_6Cl_3]^{2+}$,[5] in which three chloro ligands bridge an Ru^{II} and an Ru^{III} centre.

Mixed-valence organometallic complexes are rare. Known examples are $(Cp^*Ru)_2(\mu\text{-}Cl)_3$ ($Cp^* = \eta^5\text{-}C_5Me_5$) $[Ru^{II}/Ru^{III}]$,[6] which was not structurally characterized; the thio-bridged Mo^{III}/Mo^{IV} complexes $(CpMo)_2(\mu\text{-}S)(\mu\text{-}SMe)(S_2CH_2)$[7] and $[(CpMo)_2(\mu\text{-}SMe)_4]^+$,[8] which were characterized by EPR spectroscopy and absorption spectroscopy;[9] and $[(Cp^*Mo)_2(\mu\text{-}Br)_4]^+$.[10] The symmetrically fourfold-bridged cationic complexes are structurally closely related to their neutral precursors[8,10] and $(Cp^{\circ}Mo)_2(\mu\text{-}Cl)_4$ ($Cp^{\circ} = \eta^5\text{-}C_5Me_4Et$).[11]

We now report on the synthesis and structure of $(Cp^{\circ}Mo)_2(\mu\text{-}Cl)_n(\mu\text{-}PPh_2)_{3-n}$ [$n = 1$ (**2**), 0 (**3**)], the first structurally characterized neutral phosphido-bridged mixed-valence Mo^{II}/Mo^{III} complexes.

RESULTS AND DISCUSSION

Synthesis and Properties of $Cp^{\circ}MoCl_2(PMe_3)_2$ (**1**), $(Cp^{\circ}Mo)_2(\mu\text{-}Cl)_n(\mu\text{-}PPh_2)_{3-n}$ ($n = 1$ (**2**), 0 (**3**))

On attempting successively to substitute the chloro bridges of $(Cp^{\circ}Mo)_2(\mu\text{-}Cl)_4$[11] with $KPPh_2(dioxane)_2$[12] to give phosphido-bridged binuclear Mo^{III} complexes, we were able to isolate the monosubstituted complex $(Cp^{\circ}Mo)_2(\mu\text{-}Cl)_3(\mu\text{-}$

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PPh_2).[11] Using excess $KPPh_2(dioxane)_2$ failed to give products of composition $(Cp^\circ Mo)_2(\mu\text{-}Cl)_n(\mu\text{-}PPh_2)_{4-n}$ ($n = 2$, 1, 0). Instead the green, mixed-valence, dinuclear complex $(Cp^\circ Mo)_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)_2$ (**2**) was obtained, which formally is formed by reduction and substitution of the corresponding Mo^{III} complex. Similarly, $(Cp^\circ Mo)_2(\mu\text{-}PPh_2)_3$ (**3**) can be prepared from $Cp^\circ MoCl_2(PMe_3)_2$ (**1**) and a large excess of $KPPh_2(dioxane)_2$. $Cp^\circ MoCl_2(PMe_3)_2$ (**1**) can be obtained analogously to the synthesis of $Cp^R MoCl_2(PMe_3)_2$ ($Cp^R = \eta^5\text{-}C_5H_4Pr^i$)[13] from $(Cp^\circ Mo)_2(\mu\text{-}Cl)_4$ and PMe_3.

In the mass spectra, molecular ion peaks are observed for **2** and **3** at $m/z = 896$ (**2**) and $m/z = 1047$ (**3**), respectively. Fragment ions arising through loss of phenyl rings are also seen.

Crystal structure of $(Cp^\circ Mo)_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)_2$ (**2**) and $(Cp^\circ Mo)_2(\mu\text{-}PPh_2)_3$ (**3**)

An X-ray structure analysis was performed on dark-green, rhombic crystals of $(Cp^\circ Mo)_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)_2$ (**2**). Complex **2** crystallizes in the monoclinic space group C2/c (no. 15) and forms dimeric units in which two Mo atoms are bridged by a chloro ligand and two PPh_2 ligands. The molecule lies on a crystallographic twofold rotational axis (0, *y*, 1/4, (e)) through the chlorine atom and the midpoint of the Mo—Mo bond. Rotation about this axis converts one half of the molecule to the other [designated with (′)] (Fig. 1, Table 1).

Complex **3** crystallizes in the monoclinic space group $P2_1/c$ (no. 14). The asymmetric unit contains two independent molecules, almost perpendicular to one another. These are dimeric units in which two Mo atoms are bridged by three PPh_2 ligands (Fig. 3, Table 2). Thus, formally the chloro ligand of **2** is substituted by a PPh_2 group.

In **2** and **3**, each Mo atom is coordinated by a Cp° ligand. The two Cp° ligands in **2** are almost eclipsed and, due to steric interaction with the phenyl rings (C(201)–C(206) and C(201′)–C(206′)) of the bridging ligands, are tilted toward the chloro ligand (angle between Cp° and the plane P, P′, Cl: 6.5°) (Fig. 2). In **3**, the Cp° ligands are staggered and are almost parallel to one another (angle between planes: 9.4° for molecule 1 and 12.1° for molecule 2) and to the plane formed by the three bridging P atoms (angles of 4.9° and 4.5° for molecule 1, and 7.0° and 5.6° for molecule 2) (Fig. 3). On viewing the compounds perpendicular to the Mo—Mo bond (Figs 2 and 3) the steric interaction between the bridging ligands and the methyl C atoms of the Cp° rings, which leads to displacement of the methyl C atoms out of the plane of the ring C atoms, becomes apparent.

Comparing the structural data of the Mo_2P_2Cl fragment in **2** with those of the Mo_2P_3 fragment in **3** shows the influence of the size and type of the bridging ligands on the bonding parameters (Table 3).

The Mo—Cl bond length of 2.519(2) Å and the

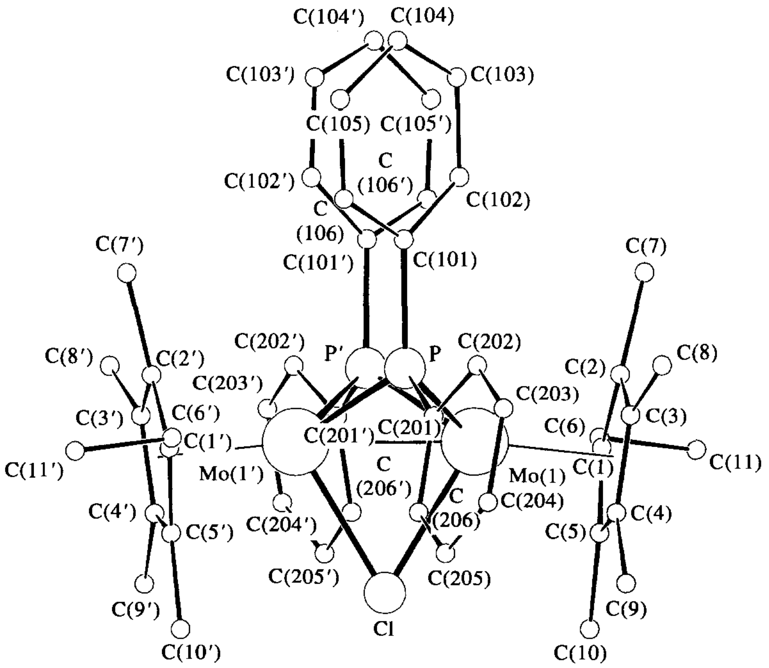

Fig. 1. Molecular structure of $(Cp^\circ Mo)_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)_2$ (**2**) showing the numbering scheme employed. Hydrogen atoms are omitted for clarity.

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

Mo(1)—P′	2.373(2)
Mo(1)—P	2.381(2)
Mo(1)—Cl	2.519(2)
Mo(1)—Mo(1′)	2.5925(14)
P—C(101)	1.829(5)
P—C(201)	1.840(5)
P—Mo(1′)	2.373(2)
Cl—Mo(1′)	2.519(2)
C(1)—C(6)	1.509(7)
C(6)—C(11)	1.534(7)
Mo(1)—C(Cp°)	2.336(5)–2.364(5)
C(Cp°)—C(Cp°)	1.416(7)–1.429(7)
C(Cp°)—C(Me, Cp°)	1.498(8)–1.514(8)
C(Ph)—C(Ph)	1.348(11)–1.401(7)
P′—Mo(1)—P	90.45(6)
P′—Mo(1)—Cl	95.93(5)
P—Mo(1)—Cl	95.74(5)
P′—Mo(1)—Mo(1′)	57.09(4)
P—Mo(1)—Mo(1′)	56.82(5)
Cl—Mo(1)—Mo(1′)	59.03(3)
C(101)—P—C(201)	101.8(2)
C(101)—P—Mo(1′)	123.2(2)
C(201)—P—Mo(1′)	121.7(2)
C(101)—P—Mo(1)	126.1(2)
C(201)—P—Mo(1)	116.6(2)
Mo(1′)—P—Mo(1)	66.09(5)
Mo(1)—Cl—Mo(1′)	61.93(7)
C(5)—C(1)—C(6)	125.9(5)
C(2)—C(1)—C(6)	125.4(5)
C(1)—C(6)—C(11)	111.7(5)
C(102)—C(101)—P	120.6(4)
C(106)—C(101)—P	122.0(4)
C(202)—C(201)—P	123.6(4)
C(206)—C(201)—P	118.0(4)
C(Cp°)—C(Cp°)—C(Cp°)	107.5(5)–108.5(5)
C(Cp°)—C(Cp°)—C(Me)	125.3(5)–126.4(5)
C(Ph)—C(Ph)—C(Ph)	117.3(5)–121.5(6)

Mo—Cl—Mo bond angle of 61.93(7)° in **2** are comparable to those in $(\mathrm{Cp^{\circ}Mo})_2(\mu\text{-Cl})_3(\mu\text{-PPh}_2)$ [2.487(2)–2.513(2) Å, 63.43(5)–63.81(4)°].[11]

The Mo—P bond lengths of 2.373(2) and 2.381(2) Å (**2**) and 2.389(2)–2.427(2) Å (**3**) are comparable to those in $(\mathrm{CpMo})_2(\mu\text{-PPh}_2)_2(\mu\text{-CO})$ [2.373(3)–2.389(3) Å],[14] but considerably shorter than those in $(\mathrm{Cp^{\circ}Mo})_2(\mu\text{-Cl})_3(\mu\text{-PPh}_2)$ [2.487(2), 2.513(2) Å].[11] The longer Mo—P bond lengths in **3** compared with **2** lead to widening of the Mo—P—Mo bond angle in **3** by *ca* 2° [66.09(5)°, **2**; 67.84(7)–68.92(7)°, **3**]. The Mo—P—Mo bond angles in **2** and **3** are larger than those in $(\mathrm{CpMo})_2(\mu\text{-PPh}_2)_2(\mu\text{-CO})$ [64.0(1), 63.6(1)°][14] and $(\mathrm{Cp^{\circ}Mo})_2(\mu\text{-Cl})_3(\mu\text{-PPh}_2)$ [64.94(5)°].[11] The difference in the structural parameters of these complexes

Table 2. Selected bond lengths (Å) and bond angles (°) for **3**

Molecule 1	
Mo(1)—P(1)	2.397(3)
Mo(1)—P(2)	2.403(3)
Mo(1)—P(3)	2.416(2)
Mo(1)—Mo(2)	2.697(2)
Mo(1)—C(Cp°)	2.363(8)–2.388(8)
Mo(2)—P(1)	2.396(3)
Mo(2)—P(2)	2.402(2)
Mo(2)—P(3)	2.417(3)
Mo(2)—C(Cp°)	2.346(10)–2.391(9)
P(1)—C(101)	1.814(10)
P(1)—C(201)	1.838(9)
P(2)—C(301)	1.858(9)
P(2)—C(401)	1.865(4)
P(3)—C(501)	1.828(4)
P(3)—C(601)	1.858(8)
C(1)—C(6)	1.484(13)
C(6)—C(11)	1.52(2)
C(12)—C(17)	1.500(13)
C(17)—C(22)	1.515(14)
C(Cp°)—C(Cp°)	1.398(14)–1.454(12)
C(Cp°)—C(Me, Cp°)	1.496(12)–1.536(12)
C(Ph)—C(Ph)	1.33(2)–1.436(14)
P(1)—Mo(1)—P(2)	101.13(9)
P(1)—Mo(1)—P(3)	85.99(8)
P(2)—Mo(1)—P(3)	86.20(8)
P(1)—Mo(1)—Mo(2)	55.74(6)
P(2)—Mo(1)—Mo(2)	55.84(6)
P(3)—Mo(1)—Mo(2)	56.11(7)
P(1)—Mo(2)—P(2)	101.18(8)
P(1)—Mo(2)—P(3)	85.98(9)
P(2)—Mo(2)—P(3)	86.19(9)
P(1)—Mo(2)—Mo(1)	55.78(6)
P(2)—Mo(2)—Mo(1)	55.87(6)
P(3)—Mo(2)—Mo(1)	56.05(6)
C(101)—P(1)—C(201)	97.6(4)
C(101)—P(1)—Mo(2)	122.6(3)
C(201)—P(1)—Mo(2)	124.8(4)
C(101)—P(1)—Mo(1)	127.4(4)
C(201)—P(1)—Mo(1)	117.2(3)
Mo(2)—P(1)—Mo(1)	68.48(7)
C(301)—P(2)—C(401)	99.9(3)
C(301)—P(2)—Mo(2)	119.7(3)
C(401)—P(2)—Mo(2)	123.2(2)
C(301)—P(2)—Mo(1)	120.2(3)
C(401)—P(2)—Mo(1)	125.6(2)
Mo(2)—P(2)—Mo(1)	68.29(7)
C(501)—P(3)—C(601)	95.9(3)
C(501)—P(3)—Mo(1)	121.1(2)
C(601)—P(3)—Mo(1)	125.4(3)
C(501)—P(3)—Mo(2)	124.1(2)
C(601)—P(3)—Mo(2)	124.5(3)
Mo(1)—P(3)—Mo(2)	67.84(7)
C(106)—C(101)—P(1)	122.5(7)
C(102)—C(101)—P(1)	120.5(9)
C(202)—C(201)—P(1)	120.2(8)
C(206)—C(201)—P(1)	121.4(8)

Table 2.—*continued*

C(306)—C(301)—P(2)	123.4(7)
C(302)—C(301)—P(2)	119.0(7)
C(402)—C(401)—P(2)	121.75(14)
C(406)—C(401)—P(2)	121.10(14)
C(502)—C(501)—P(3)	121.21(14)
C(506)—C(501)—P(3)	122.1(4)
C(606)—C(601)—P(3)	120.3(7)
C(602)—C(601)—P(3)	121.5(7)
C(5)—C(1)—C(6)	126.5(10)
C(2)—C(1)—C(6)	126.6(10)
C(1)—C(6)—C(11)	110.9(10)
C(16)—C(12)—C(17)	124.6(10)
C(13)—C(12)—C(17)	127.5(10)
C(12)—C(17)—C(22)	113.5(10)
C(Cp°)—C(Cp°)—C(Cp°)	106.0(9)–109.9(8)
C(Cp°)—C(Cp°)—C(Me)	121.3(13)–128.6(12)
C(Ph)—C(Ph)—C(Ph)	115.2(9)–124.1(13)
Molecule 2	
Mo(3)—P(4)	2.397(3)
Mo(3)—P(5)	2.397(3)
Mo(3)—P(6)	2.427(2)
Mo(3)—Mo(4)	2.708(2)
Mo(3)—C(Cp°)	2.364(8)–2.414(8)
Mo(4)—P(4)	2.422(3)
Mo(4)—P(5)	2.389(2)
Mo(4)—P(6)	2.399(2)
Mo(4)—C(Cp°)	2.380(8)–2.391(8)
P(4)—C(701)	1.848(8)
P(4)—C(801)	1.847(9)
P(5)—C(901)	1.851(8)
P(5)—C(111)	1.841(9)
P(6)—C(121)	1.859(8)
P(6)—C(131)	1.838(9)
C(34)—C(39)	1.513(12)
C(39)—C(44)	1.56(2)
C(23)—C(28)	1.497(12)
C(28)—C(33)	1.42(2)
C(Cp°)—C(Cp°)	1.393(13)–1.453(13)
C(Cp°)—C(Me, Cp°)	1.495(13)–1.535(12)
C(Ph)—C(Ph)	1.355(14)–1.40(2)
P(5)—Mo(3)—P(4)	101.36(9)
P(5)—Mo(3)—P(6)	88.85(9)
P(4)—Mo(3)—P(6)	82.05(8)
P(5)—Mo(3)—Mo(4)	55.40(6)
P(4)—Mo(3)—Mo(4)	56.25(7)
P(6)—Mo(3)—Mo(4)	55.39(6)
P(5)—Mo(4)—P(6)	89.69(8)
P(5)—Mo(4)—P(4)	100.87(9)
P(6)—Mo(4)—P(4)	82.11(9)
P(5)—Mo(4)—Mo(3)	55.68(7)
P(6)—Mo(4)—Mo(3)	56.35(6)
P(4)—Mo(4)—Mo(3)	55.38(7)
C(801)—P(4)—C(701)	98.1(4)
C(801)—P(4)—Mo(3)	121.2(3)
C(701)—P(4)—Mo(3)	122.3(3)
C(801)—P(4)—Mo(4)	125.3(3)
C(701)—P(4)—Mo(4)	122.4(3)

Table 2.—*continued*

Mo(3)—P(4)—Mo(4)	68.37(8)
C(111)—P(5)—C(901)	102.2(4)
C(111)—P(5)—Mo(4)	124.4(3)
C(901)—P(5)—Mo(4)	117.9(3)
C(111)—P(5)—Mo(3)	121.8(3)
C(901)—P(5)—Mo(3)	120.5(3)
Mo(4)—P(5)—Mo(3)	68.92(7)
C(131)—P(6)—C(121)	94.4(4)
C(131)—P(6)—Mo(4)	123.8(3)
C(121)—P(6)—Mo(4)	122.8(3)
C(131)—P(6)—Mo(3)	123.9(3)
C(121)—P(6)—Mo(3)	126.3(3)
Mo(4)—P(6)—Mo(3)	68.26(7)
C(702)—C(701)—P(4)	123.0(7)
C(706)—C(701)—P(4)	119.5(7)
C(806)—C(801)—P(4)	119.8(7)
C(802)—C(801)—P(4)	121.7(7)
C(906)—C(901)—P(5)	117.8(6)
C(902)—C(901)—P(5)	123.9(7)
C(112)—C(111)—P(5)	121.7(7)
C(116)—C(111)—P(5)	120.4(7)
C(126)—C(121)—P(6)	120.7(7)
C(122)—C(121)—P(6)	120.6(7)
C(136)—C(131)—P(6)	121.4(7)
C(132)—C(131)—P(6)	122.2(7)
C(24)—C(23)—C(28)	127.5(9)
C(27)—C(23)—C(28)	122.5(9)
C(33)—C(28)—C(23)	116.8(12)
C(35)—C(34)—C(39)	124.2(8)
C(38)—C(34)—C(39)	125.9(9)
C(34)—C(39)—C(44)	112.1(9)
C(Cp°)—C(Cp°)—C(Cp°)	105.3(9)–109.1(8)
C(Cp°)—C(Cp°)—C(Me)	122.5(9)–128.0(9)
C(Ph)—C(Ph)—C(Ph)	116.4(9)–122.5(10)

can be attributed to the different number (three or four) of bridging ligands and to the greater steric bulk of a PPh_2 group compared to a chloro ligand.

Whereas **2** has an P—Mo—P bond angle of 90.45(6)°, **3** exhibits two P—Mo—P bond angles of *ca* 85° and a third P—Mo—P bond angle which is *ca* 15° larger. The different P—Mo—P bond angles in **3** can be explained by packing effects in the solid state. A space-filling model of **3** shows how close together the phosphido phenyl groups of the two independent molecules are. The phenyl rings **I** (C(201)–C(206)) and **II** (C(301)–C(306)) of molecule 1 and **III** (C(801)–C(806)) and **IV** (C(121)–C(126)) of molecule 2 are arranged so that rings **III** and **IV** occupy the gap between rings **I** and **II**. The latter are coordinated to the P atoms with the largest P(1)—Mo—P(2) bond angle of *ca* 101°.

As a result of the above-mentioned structural parameters of the Mo_2P_2Cl fragment in **2** and the Mo_2P_3 fragment in **3** (smaller Mo—P—Mo and

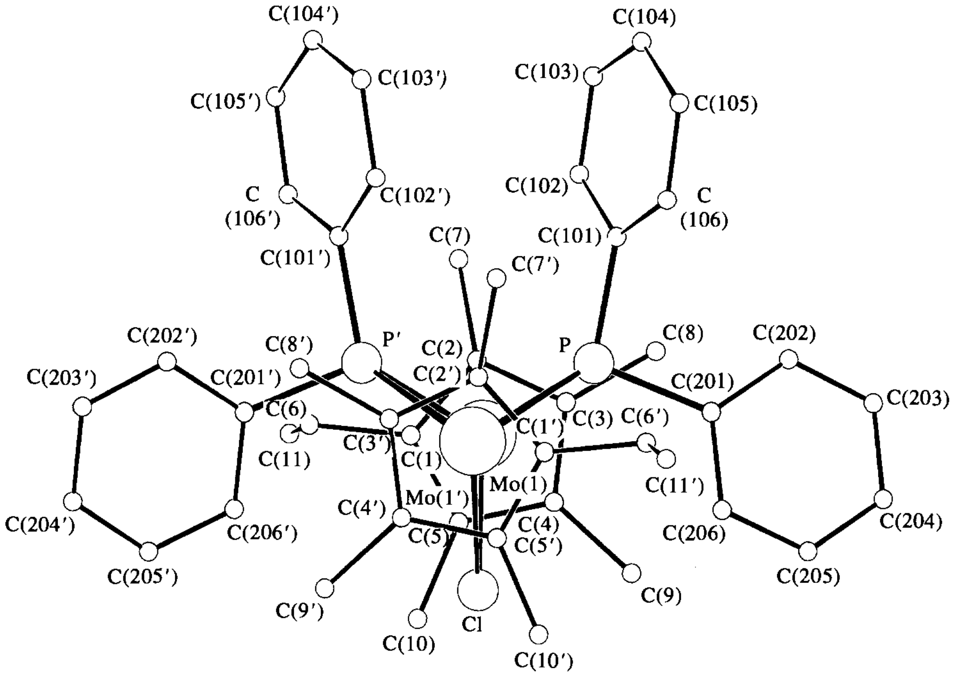

Fig. 2. View along the Mo—Mo bond axis of $(Cp^{\circ}Mo)_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)_2$ (**2**). Hydrogen atoms are omitted for clarity.

Mo—Cl—Mo bond angles in **2**), the Mo—Mo bond length in **2** [2.593(1) Å] is shorter than in **3** [2.697(2), 2.708(2) Å]. Comparable values are observed in $(Cp^{\circ}Mo)_2(\mu\text{-}Cl)_4$ [Mo—Mo 2.600(2), 2.596(2) Å],[11] $(Cp^{\circ}Mo)_2(\mu\text{-}Cl)_3(\mu\text{-}PPh_2)$ [Mo—Mo 2.6388(8) Å],[11] $\{(C_5H_4Pr^i)Mo\}_2(\mu\text{-}Cl)_4$ [Mo—Mo 2.607(1) Å],[15] $(Cp^*Mo)_2(\mu\text{-}Br)_4$ [Mo—Mo 2.645(2) Å][10] and $[(Cp^*Mo)_2(\mu\text{-}Br)_4]^+$ [Mo—Mo 2.691(4) Å],[10] in which, according to theoretical investigations on dimeric quadrupally-bridged complexes of type $(CpM)_2(\mu\text{-}X)_4$,[16] an Mo—Mo single bond is present. That the metal–metal bond length is a poor indicator for the bond order is shown by comparison with $(CpMo)_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)$,[14] which has an Mo≡Mo triple bond length of 2.515(2) Å.

In summary, the formal replacement of the chloro ligand in **2** by the sterically more demanding PPh_2 group in **3** leads to lengthening of the Mo—P and Mo—Mo bond distances. The differences are restricted to bonding parameters of the triply-bridged Mo—Mo fragment. The peripherally bonded Cp° groups are largely unaffected.

EXPERIMENTAL

All experiments were carried out under purified dry nitrogen. Solvents were dried and freshly distilled under nitrogen. The IR spectra were recorded on a Perkin–Elmer 883 in the range 200–4000 cm^{-1}, MS: Varian MAT 711 (EI, 70 eV, source temperature 180°C). The melting points were determined in sealed capillaries under nitrogen and are uncorrected. $(Cp^{\circ}Mo)_2(\mu\text{-}Cl)_4$,[11] $KPPh_2(dioxane)_2$[12] and PMe_3[17] were prepared by literature procedures.

Synthesis of $Cp^{\circ}MoCl_2(PMe_3)_2$ (**1**)

PMe_3 (1.2 cm^3, 19.0 mmol) was added to a solution of 3.00 g $(Cp^{\circ}Mo)_2(\mu\text{-}Cl)_4$ (4.71 mmol) in 30 cm^3 pentane and the solution stirred for several days at r.t. The colour of the solution changed from yellow to red. The product (**1**) was isolated as a dark red powder by removal of the solvent. Small amounts of yellow $MoCl_2(PMe_3)_4$ were also formed. Cooling a saturated pentane solution of the impure product to −25°C gave first yellow $MoCl_2(PMe_3)_4$, which was isolated, and then dark red, rhombic crystals of **1**. Yield 4.1 g (93%), m.p. 131–134°C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2964 s, 2909 s, 1762 w, 1728 vw, 1712 vw, 1699 vw, 1683 vw, 1624 m, 1558 w, 1451 m, 1420 s, 1377 m, 1291 m, 1268 sh, 1098 m, 1050 m, 1022 m, 951 vs, 848 vw, 801 m, 746 m, 725 m, 667 m, 604 w, 549 vw, 472 vw, 422 w, 402 w, 389 w, 378 w, 344 m, 329 m cm^{-1}. EI-MS (70 eV), *m/z* (%): 392 (12.3) (M^+-PMe_3 = $[Cp^{\circ}MoCl_2(PMe_3)]^+$), 316 (18.7) ($M^+$-$2PMe_3$ = $[Cp^{\circ}MoCl_2]^+$), 281 (17.3) (M^+-$2PMe_3$-Cl = $[Cp^{\circ}MoCl]^+$), and fragmentation products thereof. No molecular ion peak is observed at 180°C source temperature for **1**. The observed isotope pat-

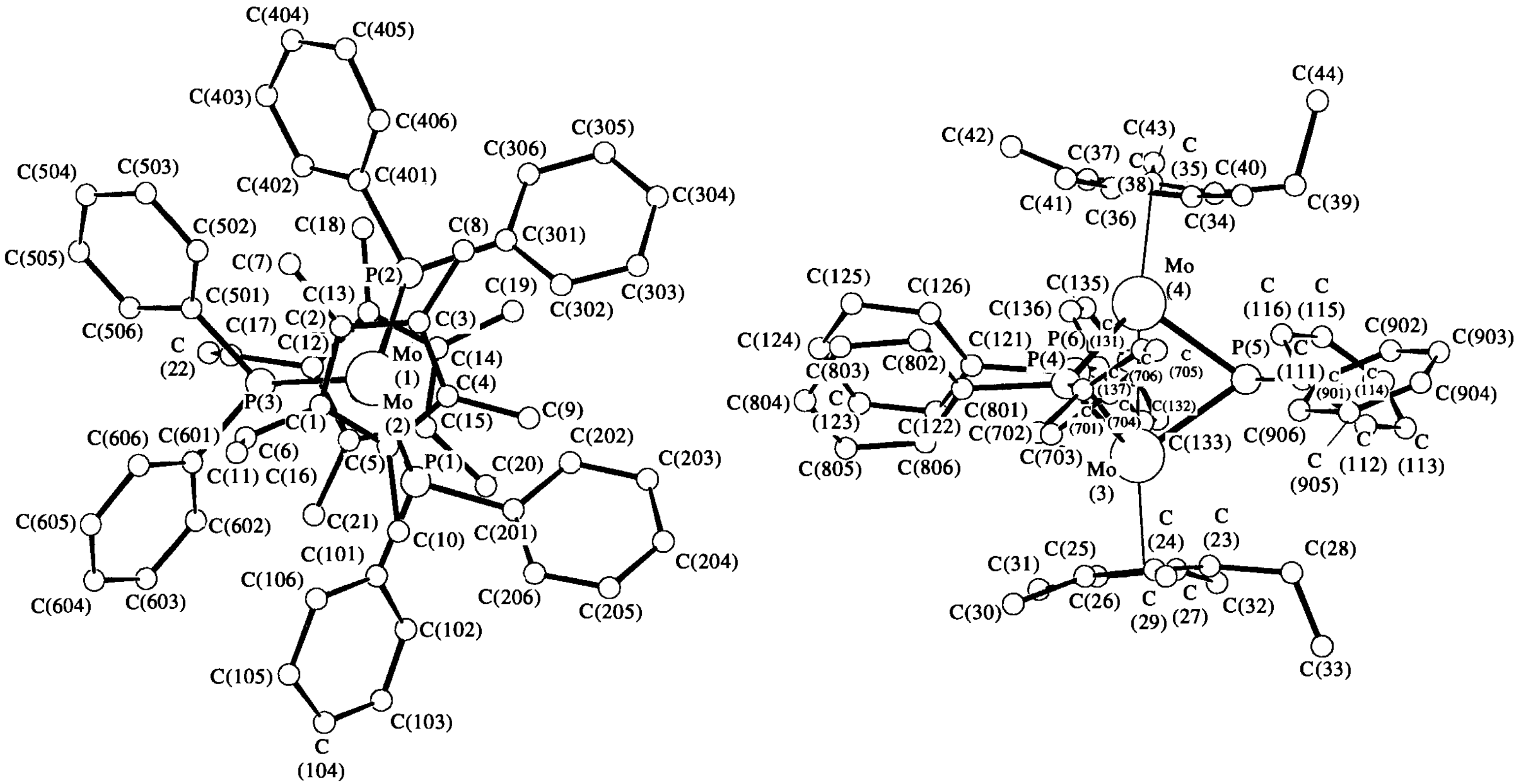

Fig. 3. Molecular structure of $(Cp^{\circ}Mo)_2(\mu\text{-}PPh_2)_3$ (**3**) showing the numbering scheme employed. Hydrogen atoms are omitted for clarity.

Table 3. Comparison of selected bond lengths (Å) and bond angles (°) of **2** and **3**

	2	**3**	
		Molecule 1	Molecule 2
Mo—Mo	2.593(1)	2.697(2)	2.708(2)
Mo—Cl	2.519(2)	—	—
Mo—P	2.373(2), 2.381(2)	2.396(3)– 2.417(3)	2.389(2)– 2.427(2)
Mo—C(Cp°)	2.336(5)– 2.364(5)	2.346(10)– 2.391(9)	2.364(8)– 2.414(8)
Mo—Cl—Mo	61.93(7)	—	—
Mo—P—Mo	66.09(5)	67.84(7)– 68.48(7)	68.26(7)– 68.92(7)
Cl—Mo—P	95.74(5), 95.93(5)	—	—
P—Mo—P	90.45(6)	85.99(9), 86.19(9), 101.18(8)	82.06(8), 88.85(9), 101.36(9)

tern of the peak at *m/z* 392 is in good agreement with the calculated isotope distribution for $[Cp^{\circ}MoCl_2(PMe_3)]^+$.

Synthesis of $(Cp^{\circ}Mo)_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)_2$ (**2**)

A solution of 2.78 g $KPPh_2(dioxane)_2$ (6.94 mmol) in 35 cm^3 THF was added dropwise to a solution of 2.20 g $(Cp^{\circ}Mo)_2(\mu\text{-}Cl)_4$ (3.48 mmol) in 25 cm^3 THF. A green solution had already formed after the addition of a few drops of the potassium phosphide solution. After addition was complete the solution was stirred for 6 h. The solution was reduced to half its volume and cooled to −25°C. After 2 days **2** was obtained as green rhombic crystals. Yield 1.7 g (55%), m.p. 130°C. IR (CsI windows, nujol, cm^{-1}): $\tilde{\nu}$ = 1555 w, 1302 m, 1259 m, 1152 sh, 1072 m, 1052 m, 1019 s, 963 m, 800 w, 752 w, 672 w, 578 w, 544 w, 496 w, 470 m, 413 w, 350 m, 272 sh cm^{-1}. EI-MS (70 eV), *m/z* (%): 896 (43.0) ($M^+ = [(Cp^{\circ}Mo)_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)_2]^+$), 859 (53.0) ($M^+\text{-}Cl = [(Cp^{\circ}Mo)_2(\mu\text{-}PPh_2)_2{}^+]$), 782 (17.0) ($M^+\text{-}Cl\text{-}Ph = [(Cp^{\circ}Mo)_2(\mu\text{-}PPh_2)(\mu\text{-}PPh)]^+$), 705 (16.4) ($M^+\text{-}Cl\text{-}2Ph = [(Cp^{\circ}Mo)_2(\mu\text{-}PPh)_2]^+$), 628 (15.5) ($M^+\text{-}Cl\text{-}3Ph = [(Cp^{\circ}Mo)_2(\mu\text{-}PPh)(\mu\text{-}P)_2]^+$), and fragmentation products thereof. The observed isotope pattern of the molecular ion peak at *m/z* 896 is in good agreement with the calculated isotope distribution.

Synthesis of $(Cp^{\circ}Mo)_2(\mu\text{-}PPh_2)_3$ (**3**)

$Cp^{\circ}MoCl_2(PMe_3)_2$ (**1**) (0.76 g, 1.62 mmol) and a fivefold excess of $KPPh_2(dioxane)_2$ (3.25 g, 8.12 mmol) were weighed into a 100 cm^3 flask, and 15 cm^3 ether added with stirring. After 10 min the solution became dark green. The mixture was allowed to stand for 3 days at r.t. without stirring, whereby a red–brown solution, an orange powder [excess $KPPh_2(dioxane)_2$], and large, black rod-shaped crystals of **3** were obtained. Yield 0.22 g (26%), m.p. 207°C (dec.), IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3060 m, 2962 m, 2924 s, 2851 m, 1938 vw, 1818 vw, 1767 w, 1728 w, 1711 w, 1699 w, 1664 m, 1649 w, 1578 w, 1475 m, 1455 m, 1431 s, 1374 m, 1364 m, 1305 w, 1260 s, 1178 m, 1152 m, 1089 s, 1050 s, 1025 s, 946 w, 801 s, 738 s, 694 s, 618 w, 524 s, 479 s, 442 w, 423 w cm^{-1}. EI-MS (70 eV), *m/z* (%): 1047 (22.3) ($M^+ = [(Cp^{\circ}Mo)_2(\mu\text{-}PPh_2)_3]^+$), 969 (2.9) ($M^+\text{-}Ph = [(Cp^{\circ}Mo)_2(\mu\text{-}PPh_2)_2(\mu\text{-}PPh)^+]$, 888 (4.6) ($M^+\text{-}2Ph = [(Cp^{\circ}Mo)_2(\mu\text{-}PPh_2)(\mu\text{-}PPh)_2]^+$), 484 (6.7) ($M^+\text{-}2Cp^{\circ}\text{-}2Ph\text{-}PPh = [Mo_2(\mu\text{-}PPh_2)(\mu\text{-}PPh)]^+$), and fragmentation products thereof. The observed isotope pattern of the molecular ion peak at *m/z* 1047 is in good agreement with the calculated isotope distribution.

Data collection and structural refinement

Data (Mo-K_α = 0.71069 Å) were collected with a STOE Stadi IV diffractometer. Twenty-five reflections (2θ range: 2–25°) were used for determination of the unit cell parameters. Absorption correction: psi scans. The structure was solved by direct methods (SHELXS-86)[18] and subsequent difference Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXL-93).[19] Restrictions for **2**: Mo, Cl, P and C atoms anisotropic, H atoms of the Cp° ligand isotropic in calculated positions, H atoms of the phenyl rings located by difference maps and refined isotropically. Restrictions for **3**: Mo, P and C atoms anisotropic, H atoms isotropic in calculated positions. A summary of data collection parameters is given in Table 4. Anisotropic atomic parameters, full lists of bond lengths and angles and lists of F_o/F_c values have been deposited as supplementary material with the Cambridge Crystallographic Data Centre.

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Table 4. Crystal data and structure refinement for $(\mathrm{Cp}^{\circ}\mathrm{Mo})_2(\mu\text{-Cl})(\mu\text{-PPh}_2)_2$ (**2**) and $(\mathrm{Cp}^{\circ}\mathrm{Mo})_2(\mu\text{-PPh}_2)_3$ (**3**)

	2	**3**
Formula	$C_{46}H_{54}ClMo_2P_2$	$C_{58}H_{64}Mo_2P_3$
Molecular weight	896.16	1045.88
Temperature (K)	203	203
Crystal system	monoclinic	monoclinic
Space group	C2/c (no. 15)	$P2_1/c$ (no. 14)
Cell constants:		
a (Å)	20.088(10)	19.525(12)
b (Å)	10.652(5)	26.315(13)
c (Å)	23.746(12)	19.648(10)
β (°)	124.16(12)	98.49(4)
V (Å^3)	4205	9984
Z	4	8
d_{calc} (g cm^{-3})	1.416	1.392
Scan technique	ω/θ-scan	ω/θ-scan
2θ range (°)	4–54	3–48
h (min, max)	0/16	$-4/18$
k (min, max)	0/13	$-3/30$
l (min, max)	$-30/25$	$-22/22$
Total reflections	4114	15636
Independent reflections	3818 [R(int.) 0.1092]	14997 [R(int.) 0.0650]
F(000)	1844	4328
Parameters	236	1132
Absorption coefficient (μ cm^{-1})	7.20	5.97
Largest diff. peak/hole (e Å^{-3})	$0.8/-1.6$	$1.5/-0.8$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0422$ $wR_2 = 0.1021$	$R_1 = 0.0592$ $wR_2 = 0.1201$
R indices (all data)	$R_1 = 0.0808$ $wR_2 = 0.1180$	$R_1 = 0.1464$ $wR_2 = 0.1537$
Goodness-of-fit (F^2)	1.030	1.029

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