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Preliminary communication

Photochemical synthesis and structural characterization of $(\eta^5\text{-}C_5Me_5)_3Mo_3(CO)_4(\mu_2\text{-}H)(\mu_3\text{-}O)$: an unprecedented 46-electron trimolybdenum cluster containing a localized monoprotonated Mo–Mo double bond

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Abstract

Irradiation of the 30-electron $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$ and $Re_2(CO)_{10}$ in toluene solution (containing H_2O) afforded (in 1–2% yields) a novel triangular metal cluster, $(\eta^5\text{-}C_5Me_5)_3Mo_3(CO)_4(\mu_2\text{-}H)(\mu_3\text{-}O)$ (**1**), which was characterized by a single-crystal X-ray diffraction study. Compound **1**, of pseudo C_s-m symmetry, has a triangulo-$Mo_3(\mu_3\text{-}O)$ core with composite Mo–H–Mo and Mo–Mo electron-pair bonds along one unusually short edge (2.660(1) Å) and Mo–Mo electron-pair bonds along the other two edges (2.916(1) and 2.917(1) Å). The edge-bridged hydride ligand, which displays a characteristic high-field proton NMR resonance at δ −17.79 ppm, was not found from the crystallographic determination but was located via a quantitative potential-energy-minimization method. This procedure unambiguously established that the optimized hydrogen position, which corresponds to a distinct coordination site with identical Mo–H distances of 1.85 Å, is the only one that can be sterically occupied by a metal-bound hydride ligand. This 46-electron species is the first electron-deficient trimolybdenum cluster containing a monoprotonated Mo–Mo double bond; its existence is attributed to ligand over-crowding due to the bulky pentamethylcyclopentadienyl rings. Black $(\eta^5\text{-}C_5Me_5)_3Mo_3(CO)_4(\mu_2\text{-}H)(\mu_3\text{-}O) \cdot 1/2THF$ crystallizes with two formula species in a triclinic unit cell of $P\bar{1}$ symmetry with a 8.603(4), b 11.115(4), c 19.412(11) Å, α 80.69(4)°, β 101.10(4)°, and γ 98.88(3)° at −40 °C. Least-squares refinement (RAELS with 221 variables) of one independent Mo_3 molecule and a centrosymmetrically-disordered THF molecule converged at $R_1(F)$ 5.62%, $R_2(F)$ 6.88% for 8460

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independent diffractometry data ($I_0 > 3\sigma(I_0)$) collected at −40 °C with Mo-K_α radiation.

Mixed-metal clusters containing molybdenum are of particular interest due to the extensive use of molybdenum-based heterogeneous catalysts. Our investigations [1–6] of the photochemical reactions of the 30-electron acetylene-like $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$ (**2**) [7,8] with various monomeric metallic carbonyl or nitrosyl species have led to the synthesis of a wide variety of unusual molybdenum-based mixed-metal clusters. As an extension of this work, we have studied the photochemical reactions of **2** with several different dimeric organometallic species [1]. Herein we report the isolation and structural-bonding analysis of an unprecedented 46-electron triangular metal cluster containing a localized monoprotonated metal–metal double bond.

In a typical experiment, 180 ml of "wet" toluene containing a mixture of 0.52 g (0.90 mmol) of **2** and 0.33 g (0.51 mmol) of $Re_2(CO)_{10}$ (**3**) were placed in a water-cooled Pyrex photolysis unit (equipped with a stir bar) and irradiated for 18 h with a Hanovia 450 W, medium-pressure Hg vapor lamp. A slow stream of N_2 was bubbled through the solution during the photolysis to facilitate the removal of evolved CO; an infrared spectral monitoring showed the gradual disappearance of the carbonyl absorption bands due to **3** together with the appearance of a number of new carbonyl bands between 1725 and 1950 cm^{-1}. Separation of the products via column chromatography (alumina) yielded a large amount of unreacted **2** along with minor products including the black $(\eta^5\text{-}C_5Me_5)_3Mo_3(CO)_4(\mu_2\text{-}H)(\mu_3\text{-}O)$ (**1**) which was isolated several times in 1–2% yields by elution with a THF/toluene mixture. Recent attempts to obtain **1** by the photolysis of solutions of **2** per se (including pretreatments with H_2O and/or O_2 [9*,10]) have (as yet) been unsuccessful.

An X-ray diffraction study [11*–13] was carried out on a crystal obtained by the slow evaporation of a THF solution of **1**; the asymmetrical part of the centrosymmetric triclinic unit cell was found to contain one molecule of **1** and a centrosymmetrically disordered THF molecule, for which atomic coordinates are presented in Table 1. The molecular structure of **1** was found to possess a pseudo C_s-m geometry (Fig. 1) consisting of one $(C_5Me_5)Mo(CO)_2$ fragment and two mirror-related $(C_5Me_5)Mo(CO)$ fragments linked together by metal–metal bonds, by a trimetal-capped oxide atom [9*,10], and by semibridging carbonyl interactions [14*,15] involving both carbonyl ligands of the $(C_5Me_5)Mo(CO)_2$ fragment. The $Mo_3(\mu_3\text{-}O)$ core possesses one unusually short Mo–Mo distance of 2.660(1) Å between the two $(C_5Me_5)Mo(CO)$ fragments and two electron-pair bonding Mo–Mo distances of 2.916(1) and 2.917(1) Å between the $(C_5Me_5)Mo(CO)_2$ fragment and the two $(C_5Me_5)Mo(CO)$ fragments. These molecular parameters are completely consistent with the short Mo–Mo bond having localized multiple-bond character.

Of prime interest is the indirect but convincing evidence that the short Mo–Mo edge in **1** is spanned by a symmetrically bridging hydrogen atom; thus, the multiple metal–metal bond corresponds to a composite (three-center)-(two-electron) Mo–H–Mo bond and an electron-pair Mo–Mo bond (alternatively viewed as a

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* This and other references marked with asterisks indicate notes occurring in the list of references.

monoprotonated metal–metal double bond) [16]. Although the hydrogen atom was not unambiguously located from difference Fourier maps calculated after the X-ray structural refinement of **1**, the existence of a metal-bound hydrogen atom is clearly indicated by the characteristic high-field proton NMR resonance [17*]. A detailed ligand-packing analysis showed that the hydride ligand could only occupy one unfilled coordination site on the pseudo mirror plane bisecting the short Mo–Mo edge (Fig. 2). A placement of the hydrogen atom at this coordination site at a distance of 1.86 Å from each of the two mirror-related Mo atoms (as was previously ascertained [18*–20*] for the symmetrical, bent Mo–H–Mo bond in $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu_2\text{-}H)(\mu_2\text{-}PMe_2)$) gives rise to reasonable intramolecular Van der Waals contacts. Corroboration of the existence of a symmetrical, bent Mo–H–Mo bond was obtained by the use of a potential-energy-minimization procedure which was developed and shown by Orpen [21] to be highly successful for locating hydride ligands in a large number of transition metal clusters. Application of the quantitative Orpen Program XHYDEX [22] to locate the hydride ligand in **1** resulted in an optimized, lowest-energy hydrogen site which was virtually identical with that initially deduced from packing considerations. Since the metal–metal separation is normally longer in a metal–H–metal bond than in a deprotonated metal–metal bond [16,18*,23,24], it is apparent that substantial metal–metal bonding must exist between Mo(1) and Mo(3) as the Mo(1)–Mo(3) distance is 0.26 Å shorter than the two electron-pair Mo–Mo bonds.

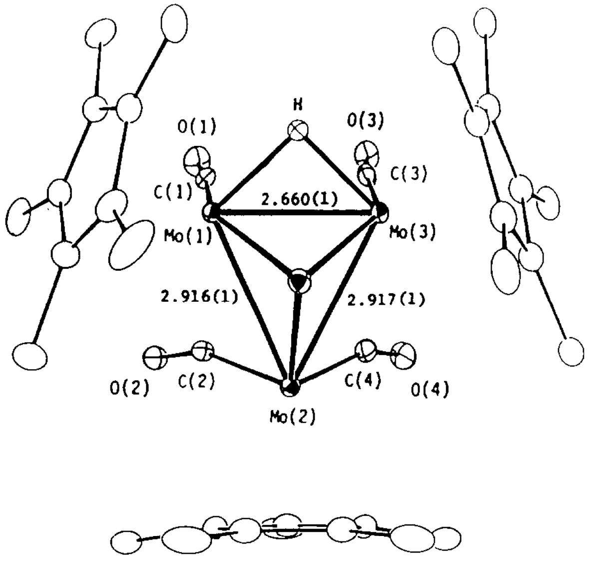

Fig. 1. Molecular configuration of the oxo-capped $(\eta^5\text{-}C_5Me_5)_3Mo_3(CO)_4(\mu_2\text{-}H)(\mu_3\text{-}O)$ (**1**) which closely conforms to C_s-m symmetry with normal single-bond Mo(1)–Mo(2) and Mo(2)–Mo(3) edges and an abnormally short Mo(1)–Mo(3) edge. The 0.26 Å shorter Mo(1)–Mo(3) edge in this 46-electron triangular metal cluster is ascribed to composite Mo–H–Mo and Mo–Mo bonds which may be conceptually considered as a monoprotonated Mo–Mo double bond. The hydride atom was unambiguously located via a quantitative potential-energy-minimization procedure [21,22] at a symmetrical edge-bridged Mo(1)–Mo(3) site (on the pseudo mirror plane) with equivalent Mo(1)–H and Mo(3)–H distances of 1.85 Å.

Table 1

Atomic coordinates [a] for $(\eta^5\text{-}C_5Me_5)_3Mo_3(CO)_4(\mu_2\text{-}H)(\mu_3\text{-}O)\cdot\frac{1}{2}C_4H_8O$

Atom	x	y	z
Mo(1)	0.4777(7)	0.3119(5)	0.1762(5)
Mo(2)	0.6279(7)	0.2371(5)	0.3217(3)
Mo(3)	0.6139(7)	0.4898(5)	0.2531(3)
O	0.4521(5)	0.3412(4)	0.2744(2)
C(1)	0.6490(9)	0.3383(6)	0.1188(4)
O(1)	0.7432(6)	0.3463(5)	0.0830(3)
C(2)	0.6748(8)	0.1683(6)	0.2430(4)
O(2)	0.7268(6)	0.1007(4)	0.2140(3)
C(3)	0.7878(8)	0.5273(6)	0.1974(4)
O(3)	0.8952(6)	0.5585(5)	0.1675(3)
C(4)	0.8222(8)	0.3525(6)	0.3206(4)
O(4)	0.9593(6)	0.3927(5)	0.3357(3)
Cp(1)	0.3728(6)	0.1696(5)	0.0941(2)
Cp(2)	0.3266(5)	0.2847(4)	0.0630(3)
Cp(3)	0.2270(6)	0.3203(5)	0.1049(2)
Cp(4)	0.2113(6)	0.2234(5)	0.1641(3)
Cp(5)	0.3041(6)	0.1302(5)	0.1558(3)
Me(1)	0.4691(9)	0.0909(7)	0.0676(3)
Me(2)	0.3703(8)	0.3611(7)	−0.0032(3)
Me(3)	0.1439(9)	0.4333(6)	0.0905(3)
Me(4)	0.1055(8)	0.2185(7)	0.2178(3)
Me(5)	0.3006(10)	0.0123(6)	0.2060(3)
Cp(6)	0.5680(6)	0.1715(5)	0.4405(2)
Cp(7)	0.4993(7)	0.0752(4)	0.4001(2)
Cp(8)	0.6242(5)	0.0289(5)	0.3774(3)
Cp(9)	0.7730(7)	0.0984(5)	0.4044(2)
Cp(10)	0.7363(7)	0.1866(5)	0.4435(2)
Me(6)	0.4777(9)	0.2387(7)	0.4773(3)
Me(7)	0.3244(7)	0.0302(6)	0.3896(4)
Me(8)	0.6147(7)	−0.0853(6)	0.3443(4)
Me(9)	0.9338(7)	0.0726(7)	0.3965(3)
Me(10)	0.8674(10)	0.2601(7)	0.4875(3)
Cp(11)	0.6315(6)	0.6990(4)	0.2392(3)
Cp(12)	0.4805(7)	0.6503(3)	0.2600(3)
Cp(13)	0.5070(6)	0.5900(5)	0.3305(3)
Cp(14)	0.6746(6)	0.5998(4)	0.3553(3)
Cp(15)	0.7536(7)	0.6671(3)	0.2993(3)
Me(11)	0.6593(8)	0.7865(6)	0.1746(3)
Me(12)	0.3176(7)	0.6643(5)	0.2187(4)
Me(13)	0.3804(7)	0.5312(6)	0.3724(3)
Me(14)	0.7620(8)	0.5596(6)	0.4275(3)
Me(15)	0.9297(7)	0.7047(5)	0.3088(4)
H(1A)	0.5374(52)	0.0473(42)	0.1088(4)
H(1B)	0.3955(13)	0.0291(36)	0.0407(27)
H(1C)	0.5385(52)	0.1437(13)	0.0358(25)
H(2A)	0.3026(48)	0.3277(32)	−0.0456(3)
H(2B)	0.3519(64)	0.4480(12)	−0.0038(15)
H(2C)	0.4854(20)	0.3587(43)	−0.0044(15)
H(3A)	0.1256(62)	0.4544(31)	0.1363(5)
H(3B)	0.2118(34)	0.5033(14)	0.0672(28)
H(3C)	0.0390(32)	0.4174(20)	0.0587(25)
H(4A)	0.0256(48)	0.2776(41)	0.1997(15)
H(4B)	0.0486(56)	0.1333(16)	0.2264(25)
H(4C)	0.1720(16)	0.2412(56)	0.2632(11)

Table 1 (continued)

Atom	*x*	*y*	*z*
H(5A)	0.2890(75)	−0.0586(6)	0.1788(5)
H(5B)	0.4023(35)	0.0131(25)	0.2411(21)
H(5C)	0.2082(46)	0.0039(28)	0.2315(24)
H(6A)	0.3766(37)	0.2587(51)	0.4451(13)
H(6B)	0.4515(67)	0.1859(25)	0.5214(16)
H(6C)	0.5445(31)	0.3166(29)	0.4899(30)
H(7A)	0.2643(9)	0.0947(23)	0.3585(26)
H(7B)	0.3038(15)	−0.0466(31)	0.3669(28)
H(7C)	0.2880(18)	0.0125(50)	0.4366(7)
H(8A)	0.5002(8)	−0.1200(30)	0.3314(28)
H(8B)	0.6646(63)	−0.0650(14)	0.3007(18)
H(8C)	0.6729(59)	−0.1472(20)	0.3788(13)
H(9A)	0.9272(18)	0.0467(53)	0.3489(13)
H(9B)	1.0122(18)	0.1486(19)	0.4010(32)
H(9C)	0.9696(34)	0.0053(40)	0.4343(20)
H(10A)	0.9439(41)	0.3067(45)	0.4568(8)
H(10B)	0.8208(17)	0.3192(40)	0.5090(26)
H(10C)	0.9251(48)	0.2037(12)	0.5259(21)
H(11A)	0.7607(34)	0.7737(34)	0.1605(17)
H(11B)	0.5681(32)	0.7717(34)	0.1351(9)
H(11C)	0.6676(64)	0.8728(5)	0.1849(10)
H(12A)	0.2451(18)	0.5860(18)	0.2275(23)
H(12B)	0.2753(27)	0.7328(33)	0.2340(21)
H(12C)	0.3232(15)	0.6834(49)	0.1671(4)
H(13A)	0.4306(10)	0.5066(46)	0.4227(7)
H(13B)	0.3035(38)	0.5908(20)	0.3710(24)
H(13C)	0.3222(45)	0.4567(30)	0.3517(18)
H(14A)	0.8633(32)	0.5297(46)	0.4234(4)
H(14B)	0.7877(56)	0.6306(15)	0.4553(10)
H(14C)	0.6937(27)	0.4917(34)	0.4522(11)
H(15A)	0.9860(7)	0.6331(15)	0.3330(26)
H(15B)	0.9619(13)	0.7329(46)	0.2614(6)
H(15C)	0.9590(12)	0.7733(33)	0.3383(24)
THF(1)	0.0510(17)	0.0199(14)	−0.0578(6)
THF(2)	0.1034(14)	−0.0911(15)	−0.0411(8)
THF(3)	0.1126(19)	−0.1950(11)	0.0070(13)
THF(4)	0.0352(18)	−0.1543(12)	0.0480(8)
THF(5)	0.0195(13)	−0.0470(9)	0.0034(5)
THFH(0)	−0.0340(23)	0.0326(19)	−0.0964(7)
THFH(1)	0.1261(23)	0.0921(15)	−0.0565(9)
THFH(2)	0.0528(25)	−0.1240(21)	−0.0832(9)
THFH(3)	0.2129(15)	−0.0645(22)	−0.0434(12)
THFH(4)	0.0557(29)	−0.2692(11)	−0.0081(17)
THFH(5)	0.2158(21)	−0.2097(17)	0.0318(17)
THFH(6)	−0.0600(22)	−0.2084(17)	0.0533(12)
THFH(7)	0.1001(28)	−0.1488(18)	0.0932(8)
THFH(8)	−0.0931(14)	−0.0473(15)	−0.0058(9)
THFH(9)	0.0670(24)	0.0122(12)	0.0340(6)

[a] Although the hydrogen atoms were placed in idealized positions. RAELS [12] provides both positional and thermal esd's for these atoms. The positional esd's reflect the errors associated with the orientations of the local axial systems (which are calculated from the crystallographic coordinates of the ring carbon atoms) and do not reflect actual esd's of the fractional coordinates of these atoms. In light of the oxygen atom of the centrosymmetrically disordered THF molecules not being unambiguously discriminated from the other four ring carbon atoms in difference Fourier syntheses, the THF molecule was approximated in the final refinement as an idealized cyclopentane species.

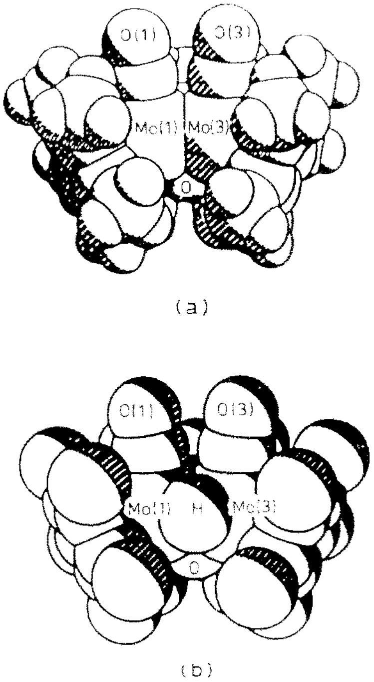

Fig. 2. Views of the space-filling atoms in $(\eta^5\text{-}C_5Me_5)_3Mo_3(CO)_4(\mu_2\text{-}H)(\mu_3\text{-}O)$ (**1**) showing (a) the only available unfilled coordination site (situated along the Mo(1)–Mo(3) edge) which can be sterically occupied by a metal-bound hydride ligand, and (b) this site containing the symmetrically bridging hydrogen atom. A lowest-energy position (with coordinates of x 0.4838, y 0.4813, z 0.1655) was obtained for this edge-bridged hydrogen atom by use of the Orpen XHYDEX program [22].

The molecular geometry of **1** is virtually identical to that of the corresponding 48-electron $(\eta^5\text{-}C_5Me_5)_3Mo_3(CO)_4(\mu_3\text{-}O)(\mu_2\text{-}NCO)$ [1c,6] which possesses a nitrogen-coordinated isocyanate ligand (instead of the edge-bridged hydrido ligand in **1**) symmetrically attached along the Mo(1)–Mo(3) edge to the triangulo-$Mo_3(\mu_3\text{-}O)$ core. Upon a formal replacement of the three-electron (pseudo-halide) μ_2-NCO donor by the one-electron μ_2-H donor, the only major geometrical variation is a 0.09 Å decrease in the Mo(1)–Mo(3) bond. This change is in harmony with the metal–metal bond-orbital character for the Mo(1)–Mo(3) bond being markedly larger in the 46-electron **1** than in the 48-electron isocyanate-bridged analogue.

A symmetrical linkage of the bridging hydride atom to both Mo atoms results in the assignment of a formal oxidation state of +2 to each of the three Mo atoms in **1**. The fact that the two longer Mo–Mo distances of 2.916(1) and 2.917(1) Å in the $Mo_3(\mu_3\text{-}O)$ core of **1** are within the single-bond range of 2.89–2.99 Å found [1–6] in other oxo-capped Mo^{II} clusters containing $Mo(\eta^5\text{-}C_5Me_5)$ moieties provides a self-consistent representation of the metal–metal bonding in this 46-electron triangular metal cluster. Work is in progress to obtain a rational (high-yield) synthetic route to **1** in order to explore its chemical reactivity [25*,26*,27,28].

Supplementary material available. Tables presenting the atomic parameters and selected intramolecular distances and bond angles for $(\eta^5\text{-}C_5Me_5)_3Mo_3(CO)_4(\mu_2\text{-}H)(\mu_3\text{-}O)$ (**1**) and/or $(\eta^5\text{-}C_5Me_5)_2Mo_2Re(CO)_7(\mu_2\text{-}H)(\mu_3\text{-}O)$ (**4**) as well as tables listing observed and calculated structure factor amplitudes are available upon request from L.F.D.

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11 $(\eta^5\text{-}C_5Me_5)_3Mo_3(CO)_4(\mu_2\text{-}H)(\mu_3\text{-}O)\cdot\frac{1}{2}C_4H_8O$ (f. wt., 858.6): A small parallelepiped-shaped fragment ($0.7\times0.3\times0.5$ mm) was carefully cleaved from a large single crystal that was grown by the slow evaporation of a THF solution of **1**; intensity data were collected at $-40\,^\circ C$ with a Syntex (Nicolet) $P\bar{1}$ diffractometer; triclinic, $P\bar{1}$; a 8.603(4), b 11.115(4), c 19.412(11) Å, α 80.69(4)°, β 101.10(4)°, γ 98.88(3)°; d_{calcd} 1.60 g/cm^3 for $Z = 2$. The crystal structure (with the independent unit consisting of one Mo_3 molecule and a centrosymmetrically disordered THF molecule) was determined from an interpretation of a Patterson map followed by successive Fourier and difference Fourier syntheses. Least-squares refinement was carried out with RAELS [12] in which anisotropic thermal parameters were utilized for all non-hydrogen atoms. The librational-like thermal motion of the crystal-disordered THF molecule and of each of the C_5Me_5 rings was treated by use of a TLX model [13]. Hydrogen atoms at idealized positions were included as fixed-atom contributors. This refinement with 221 variables converged at $R_1(F)$ 5.62%, $R_2(F)$ 6.88% for 8460 independent diffractometry data ($I_0 > 3\sigma(I_0)$) collected with Mo-K_α radiation.

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14 Evidence for the existence of these π-acceptor semibridging carbonyl ligands is given by: (1) abnormally small Mo(2)–C(2)–O(2) and Mo(2)–C(4)–O(4) bond angles of 157.6(5) and 158.6(6)°, respectively; (2) the sharply acute Mo(1)–Mo(2)–C(2) and Mo(3)–Mo(2)–C(4) bond angles of 58.9(2) and 59.6(2)°, respectively; and (3) the relatively short carbonyl carbon distance to the second metal atom of 2.535(7) Å for the C(2)$\cdots$Mo(1) interaction and 2.559(7) Å for the C(4)$\cdots$Mo(3) interaction. These values are entirely consistent with the structural data recently tabulated by Crabtree and Lavin [15] in their detailed analysis of the bent semibridging carbonyl ligand.

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17 A proton NMR spectrum of **1** in $CDCl_3$ exhibited resonances at δ 1.89, δ 1.78, and δ −17.79 ppm with a 30/15/1 ratio. The former two resonances are ascribed to the C_5Me_5 ligands that are bound to the mirror-related and unique Mo atoms, respectively; the latter high-field resonance is readily attributed to a molybdenum-bound hydride ligand [18,19].

18 The bent (three-center)-(two-electron) Mo–H–Mo bond [19b,c] in the 34-electron $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu_2\text{-}H)(\mu_2\text{-}PMe_2)$ molecule [19a] forms a closed-type Mo–H–Mo fragment with a bond angle of 122.9(2)° and chemically equivalent Mo–H distances of 1.854(4) and 1.869(4) Å. A comparative X-ray diffractometry analysis of this protonated (Mo–Mo)-bonded dimer [19d] and its deprotonated monoanion [20] established that the loss of the proton from the Mo–H–Mo linkage decreases the Mo–Mo distance by 0.105 Å from 3.262(2) Å in the monohydrido neutral parent to 3.157(2) Å in the deprotonated monoanion. A proton NMR spectrum of this dimolybdenum complex in $CDCl_3$ displayed a high-field doublet for the hydrido atom at δ −11.73 ppm (J(HP) 36.6 Hz) [19a].

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25 A brown by-product, $(\eta^5\text{-}C_5Me_5)_2Mo_2Re(CO)_7(\mu_2\text{-}H)(\mu_3\text{-}O)$ (**4**), was also isolated in low yields from the above photochemical reaction by elution with toluene. The stoichiometry and atomic arrangement of the non-hydrogen framework of **4** were determined from an X-ray diffraction study [26] which revealed a triangulo-$Mo_2Re(\mu_3\text{-}O)$ core with the rhenium atom coordinated to three terminal carbonyl ligands and each molybdenum atom bonded to a C_5Me_5 ring and two carbonyl ligands. The observed 0.1 Å-elongation of one Re–Mo edge in the completely bonding $Mo_2Re(\mu_3\text{-}O)$ core (which has a Mo–Mo distance of 2.916(1) Å and two Re–Mo distances of 2.913(1) and 3.010(1) Å) is attributed to a Re–H–Mo bond in which the hydrogen atom occupies a distinct edge-bridged coordination site about both the Re and Mo atoms. Compelling evidence for the existence and location of this bridging hydrogen atom in the 48-electron **4** was obtained from a ligand-packing analysis which revealed this site to be the only sterically favorable one. Utilization of the quantitative Orpen procedure [21,22] substantiated this conclusion; the optimized hydrogen position gives a symmetrical Re–H–Mo bond with identical metal–hydrogen distances of 1.86 Å. The formulation of **4** as a monohydrido 48-electron cluster is in accordance with other triangular rhenium carbonyl clusters [24,27,28] (e.g., the oxo-capped $[Re_3(CO)_9(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^{2-}$ dianion [28]) which invariably form 48-electron closed-shell electronic systems.

26 $(\eta^5\text{-}C_5Me_5)_2Mo_2Re(CO)_7(\mu_2\text{-}H)(\mu_3\text{-}O)\cdot\frac{1}{2}C_6H_{14}$ (f.wt., 904.7): Crystals were grown from a hexane-toluene solution of **4**. A room-temperature data set was obtained from a parallelepiped-shaped crystal (0.5×0.3×0.2 mm) with a Syntex (Nicolet) P$\bar{1}$ diffractometer; triclinic, $P\bar{1}$; a 11.219(4), b 15.369(7), c 10.555(5) Å, α 103.11(4)°, β 97.85(3), γ 110.93(3)°; d_{calcd} 1.87 g/cm³ for $Z = 2$. The non-hydrogen atoms of one independent Mo_2Re molecule and a centrosymmetrically ordered one-half hexane molecule were located from a Patterson map (which gave initial metal coordinates) and subsequent Fourier and difference maps. Least-squares refinement (RAELS [12]) with 238 variables converged at $R_1(F)$ 4.09%, $R_2(F)$ 4.57% for 3172 independent diffractometry data ($I_0 > 3\sigma(I_0)$) collected with Mo-K_α radiation. In the final refinement, the thermal motion of each C_5Me_5 ring was described via a TLX model [13] (with methyl hydrogen atoms included in idealized tetrahedral positions); all other non-hydrogen atoms were refined with individual anisotropic thermal parameters.

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