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## Mixed-valence dimolybdenum complexes containing hard oxo and soft carbonyl ligands: Synthesis, structure, and electrochemistry of $Mo_2(O)(CO)_2(\mu-\kappa^2-S(CH_2)_nS)_2(\kappa^2-diphosphine)$

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Mixed-valence dimolybdenum complexes  $Mo_2(O)(CO)_2\{\mu-\kappa^2-S(CH_2)_nSJ_2(\kappa^2-Ph_2P(CH_2)_mPPh_2) (n=2,3; m=1,2) (1-4)$  have been synthesized from one-pot reactions of *fac*-Mo(CO)\_3(NCMe)\_3 and dithiols, HS(CH\_2)\_nSH, in the presence of diphosphines. The dimolybdenum framework is supported by two thiolate bridges, with one molybdenum carrying a terminal oxo ligand and the second two carbonyls. The dppm (m = 1) products exist as a pair of diastereomers differing in the relative orientation of the two carbonyls (*cis* and *trans*) at the Mo(CO)\_2(dppm) center, while dppe (m = 2) complexes are found solely as the *trans* isomers. Small amounts of Mo(CO){ $\kappa^3-S(CH_2CH_2S_2)$ { $\kappa^2-dppe$ } (5) also result from the reaction using HS(CH\_2)\_2SH and dppe. The bonding in isomers of 1-4 has been computationally explored by DFT calculations, *trans* diastereomers being computed to be more stable than the corresponding pair of *cis* diastereomers for all. The calculations confirm the existence of Mo=O and Mo-Mo bond orders and suggest that the new dimeric compounds are best viewed as Mo(V)-Mo(I) mixed-valence systems. The electrochemical properties of 1 have been investigated by CV and show a reversible oneelectron reduction associated with the Mo(V) centre, while two closely spaced irreversible oxidation waves are tentatively assigned to oxidation of the Mo(I) centre of the two isomers.

## Introduction

Metal-catalyzed oxygen atom transfer (OAT) reactions are not only important in biological systems but also in industry. In biology, molybdoenzymes mainly catalyze important OAT reactions in the living cells, the mechanistic details of which are still unclear despite the determination of many crystal structures.<sup>1-5</sup> As a result, studies on new molybdenum and tungsten oxo complexes as functional and structural models of the oxotransferase enzymes continue to be of interest.<sup>6-12</sup> Industrial OAT reactions include epoxidation of alkenes, such as styrene and propylene, and the resulting epoxides are used for the manufacture of important commercial products (e.g., epoxy resins, cosmetics, surface coatings, sweeteners, perfume, drugs,

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<sup>d</sup> Department of Chemistry, King's College London, Britannia House, 7 Trinity Street, London, SE1 1DB, UK. etc.).<sup>13-17</sup> Molybdenum and tungsten dithiolene complexes have been studied as models of the active site of a range of oxotransferase enzymes since the molybdenum atom in the common molybdenum cofactor of these enzymes is bonded to the pterin ligand through a dithiolene linkage.<sup>6-8</sup>

Recently, we and others reported that a variety of molybdenum complexes containing up to three metal centers could be synthesized from one-pot reactions involving *fac*-Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub> and pyridine-2-thiol in the presence of various phosphorus-donor ligands.<sup>18,19</sup> Following this synthetic strategy, we herein report the unexpected synthesis of some new mixed-valence dimolybdenum complexes, containing hard (oxo) and soft (carbonyl) supported centres linked via two dithiolate bridges together with studies on their redox behavior, supported by DFT calculations in an attempt to understand the valency of each metal ion and the nature of the metal-metal interaction.

## **Results and discussion**

#### Synthesis and characterization

Reactions between fac-Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>, dppm and dithiols HS(CH<sub>2</sub>)<sub>n</sub>SH at 50-55 °C in MeCN furnished the mixed-valence molybdenum complexes Mo<sub>2</sub>(O)(CO)<sub>2</sub>{ $\mu$ - $\kappa$ <sup>2</sup>-S(CH<sub>2</sub>)<sub>n</sub>S}<sub>2</sub>( $\kappa$ <sup>2</sup>-dppm) [**1** 

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Scheme 1. Synthesis of dimolybdenum complexes 1-4.

(18%), n = 2; **2** (11%), n = 3)] together with Mo(CO)<sub>4</sub>( $\kappa^2$ -dppm)<sup>19</sup> (21 and 23%, respectively). The nature of the diphosphine ligand in the reaction was next investigated by exchanging the rigid dppm ligand for the more flexible dppe. Heating *fac*-Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>, dppe, and 1,2-ethanedithiol gave Mo<sub>2</sub>(O)(CO)<sub>2</sub>{ $\mu$ - $\kappa^2$ -S(CH<sub>2</sub>)<sub>2</sub>S}<sub>2</sub>( $\kappa^2$ -dppe) (**3**) and Mo(CO)<sub>4</sub>(dppe)<sup>20</sup> in 14% and 11% yields respectively, while with 1,3-propanedithiol, Mo<sub>2</sub>(O)(CO)<sub>2</sub>{ $\mu$ - $\kappa^2$ -S(CH<sub>2</sub>)<sub>3</sub>S}<sub>2</sub>( $\kappa^2$ -dppe) (**4**) and Mo(CO)<sub>4</sub>( $\kappa^2$ -dppe) were isolated in 13% and 10% yields (Scheme 1).

Dppm complexes **1-2** exist as mixture of *trans* and *cis* isomers (Scheme 1), the *trans* and *cis* descriptors having as their reference point the orientation of the ancillary CO groups at the  $Mo(CO)_2(dppm)$  center since the diphosphine ligand is constrained to occupy mutually *cis* sites in each isomer, in ratios of 2:5 and 1:4 respectively, based on <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. *Trans*-1 shows a single <sup>31</sup>P{<sup>1</sup>H} resonance at  $\delta$  8.6 that is consistent with it possessing an idealized plane of symmetry (C<sub>s</sub>) that bisects the dppm ligand and contains the two molybdenum atoms, two CO groups, and the oxo ligand, while the *cis*-1 isomer displays a pair of doublets (<sup>2</sup>J<sub>PP</sub> 21.4 Hz) centered at  $\delta$  14.4 and 12.0. The isomer ratio in **1** remained relatively constant between different preparative batches and also upon heating to 60 °C. Above this temperature, it gradually decomposed and we abandoned further thermal equilibration studies.

We have been unable to separate isomers of **1** or **2** except in single crystal X-ray studies (see later), so all spectroscopic data relate to mixtures. Both show a pair of carbonyl in the IR spectrum; in CH<sub>2</sub>Cl<sub>2</sub> appearing at 1989 and 1876 for **1** and 1973 and 1865 cm<sup>-1</sup> for **2**. Complexes **3-4** were isolated as a single diastereomer based on singlets at  $\delta$  44.3 and 32.6 respectively in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. In analogy to the dppm derivatives **1-2**, the dppe ligand in **3-4** is assumed to occupy equatorial sites at the octahedral

molybdenum center. The *trans* disposition of carbonyls is shown by the presence of two carbonyl bands of very different intensities in the IR spectrum; appearing (KBr) at 1975w and 1876vs for 3 and 1977w and 1879vs  $\text{cm}^{-1}$  for **4**, the weak band being associated with the symmetric stretch. The DFT computed v(CO) for trans isomers are 1972 and 1888 cm<sup>-1</sup> which is in good agreement with the IR spectra of **3-4**. For *cis* isomers DFT values are 1950 and 1870 cm<sup>-1</sup>. The lower value fits well with that seen in 1 (1876 cm<sup>-1</sup>) but the higher energy vibration is too low. It is unclear why this should be but we do note that there are some significant differences in the IR stretching frequencies found in 1 and 2, and hence changing the nature of the dithiolate bridge clearly has a significant effect on the distribution of electron density. All four complexes show a single Mo=O band between 935-955 cm<sup>-1</sup> (KBr), consistent with the computed v(Mo=O) in *trans* isomers of 948 cm<sup>-1</sup>, but significantly lower than that predicted for *cis* isomers of 988 cm<sup>-1</sup>.

Also isolated from the dppe/ethanedithiol reaction in very low yield (3%) was  $Mo(CO){\kappa^3-S(CH_2CH_2S)_2}(\kappa^2-dppe)$  (5), which likely results due to an impurity in the ethanedithiol; this compound was characterized primarily by X-ray crystallographic study (see below).

#### Crystallographic studies

The solid-state structures of *cis*-**1** and *trans*-**2** were established by single-crystal X-ray diffraction analysis (Table S1). The structure of *cis*-**1** is shown in Figure 1 and confirms the presence of a dimolybdenum framework ligated by two edt ligands and whose coordination sphere also contains a terminal oxo moiety at one Mo center and a  $\kappa^2$ -dppm and two carbonyls at the second. The CO groups are situated *cis* to each other, and the P(1) atom is oriented *cis* to the O(3) oxo group, the Mo(2)–O(3) of 1.683(5) Å is within the

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expected range. The C(2)-Mo(1)-C(1) angle is  $88.4(3)^\circ$  and the P(1)-Mo(1)-Mo(2)-O(3) dihedral angle is  $9.0(2)^\circ$ . The molybdenum atoms have distinctly different coordination geometries; Mo(2) is five-coordinate and best viewed as a distorted square pyramid, while Mo(1) exhibits a distorted octahedral geometry. The two are joined via the edge-bridging S(1) and S(3) moieties and the Mo(1)-Mo(2) vector is 2.7764(8) Å.

The structure of *trans*-**2** (Figure 2) confirms the *trans* orientation of the two carbonyls. The dppm ligand and the bridging S(1) and S(3) atoms occupy the equatorial sites at the formally octahedral Mo(1) center. Structurally speaking, apart from the extra CH<sub>2</sub> unit in the pdt ligand and the disposition of the CO and dppm ligands at the Mo(1) center, the bond distances and angles in *trans*-**2** follow those trends reported for *cis*-**1**. The Mo-Mo distance is 2.8233(8) Å and the Mo=O distance 1.671(3) Å, being slightly longer and shorter respectively than similar distances in *cis*-**1**.

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Fig. 1. Molecular structure of  $Mo_2(O)(CO)_2(\mu - \kappa^2 - edt)_2(\kappa^2 - dppm)$  (*cis*-1, right) showing 50% probability thermal ellipsoids and DFT-optimized structure of A2 (right). Selected X-ray diffraction bond distances [Å] and angles [ $^{9}$ ]: Mo(1)–Mo(2) 2.7764(8), Mo(1)–P(1) 2.5715(18), Mo(1)–P(2) 2.5213(17), Mo(2)–O(3) 1.683(5), Mo(1)–S(1) 2.4095(19), Mo(1)–S(3) 2.4384(19), Mo(2)–S(1) 2.425(2), Mo(2)–S(2) 2.383 (2), Mo(2)–S(3) 2.420(2), Mo(2)–S(4) 2.399(2), Mo(1)–C(1) 2.019(8), Mo(1)–C(2) 1.949(8), P(1)–Mo(1)–P(2) 66.63(6), P(1)–Mo(1)–S(1) 96.80(6), P(1)–Mo(1)–S(3) 88.27(6), P(1)–Mo(1)–C(1) 89.7(2), P(1)–Mo(1)–C(2) 166.8(2), C(1)–Mo(1)–C(2) 88.4(3), P(1)–Mo(1)–Mo(2) 109.63(5), P(2)–Mo(1)–Mo(2) 139.66(5), O(3)–Mo(2)–Mo(1) 118.05(16), O(3)–Mo(2)–S(1) 95.31(18), O(3)–Mo(2)–S(2) 112.17(18), S(1)–Mo(2)–S(2) 82.65(8), S(1)–Mo(2)–S(4) 152.06(9), Mo(1)–S(1)–Mo(2) 70.102(5), Mo(1)–S(3)–Mo(2) 69.71(5), S(1)–Mo(2)–50.2(5), S(1)–Mo(2)–Mo(1) 54.69(4).



Fig. 2. Molecular structure of  $Mo_2(O)(CO)_2(\mu+\kappa^2-pdt)_2(\kappa^2-dppm)$  (*trans*-2, left) showing 50% probability thermal ellipsoids and DFT-optimized structure **B1** (right). Selected X-ray diffraction bond distances [Å] and angles [P]: Mo(1)-Mo(2) 2.8233(8), Mo(1)-P(1) 2.5383(14), Mo(1)-P(2) 2.4927(15), Mo(2)-O(10) 1.671(3), Mo(1)-S(1) 2.3886(14), Mo(1)-S(3) 2.4055(15), Mo(2)-S(1) 2.4575(15), Mo(2)-S(2) 2.4135(16), Mo(2)-S(3) 2.4513(15), Mo(2)-S(4) 2.4156(17), Mo(1)-C(8) 2.013(6), Mo(1)-C(9) 2.035(6), P(1)-Mo(1)-P(2) 67.82(5), P(1)-Mo(1)-S(3) 94.31(5), P(1)-Mo(1)-C(8) 92.99(16), P(1)-Mo(1)-C(9) 89.92(15), C(8)-Mo(1)-C(9) 176.0(2), P(1)-Mo(1)-Mo(2) 149.38(4), P(2)-Mo(1)-Mo(2) 142.47(4), O(10)-Mo(2)-Mo(1) 106.88(13), O(10)-Mo(2)-S(1) 96.11(14), O(10)-Mo(2)-S(2) 111.25(13), S(1)-Mo(2)-S(2) 83.60(5), S(1)-Mo(2)-S(4) 152.81(6), Mo(1)-S(1)-Mo(2) 71.25(4), Mo(1)-S(3)-Mo(2) 71.08(4), S(1)-Mo(1)-Mo(2) 55.51(4), S(1)-Mo(2)-Mo(1) 53.24(3).

## Relative isomer stablity - DFT studies

The stability of *cis*-**1** relative to the other diastereomers based on  $Mo_2(O)(CO)_2\{\mu-\kappa^2-S(CH_2)_2S\}_2(\kappa^2-dppm)$  was explored by DFT calculations. The DFT-optimized structure of *cis*-**1** (A2) is shown in Figure 1 and closely mirrors the crystallographic structure. The

structure of *trans*-1 (A1) was also computationally examined, and the B3LYP-optimized structure is shown in Figure 3. The computed free energy difference between these two species is 3.9 kcal/mol in favor of A1. The observed ratio of the two diastereomeric products in the reaction between fac-Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>, dppm and

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HS(CH<sub>2</sub>)<sub>2</sub>SH favors **A2**, suggesting that *trans*-**1** and *cis*-**1** are formed in a kinetically controlled process. This premise is strengthened by the fact that the 2:5 ratio of Isolated samples of *trans*-**1** and *cis*-**1** remain unchanged on heating at 60 °C. An alternative isomer exists that possesses *cis* CO groups. Here one of the phosphine moieties from the dppm ligand occupies an axial site that is proximal to the edt rings. Such an isomer is represented by **A3**, and it is the least stable of the three computed diastereomers, lying 8.5 kcal/mol above **A1**. The O(oxo)-Mo-Mo-P dihedral angle in **A3** is 173.6° in keeping with the antiperiplanar disposition of the oxo group and the axial phosphine moiety. The greater destabilization of A3 relative to A2 and A1 is attributed to the extant intramolecular contacts between the carbocyclic portion of the edt ligands and the phenyl groups associated with the axial  $Ph_2P$  moiety. The DFT-optimized structure of B1 is shown alongside the X-ray diffraction structure, and good agreement exists between the two structures. Of the corresponding *cis* diastereomers (B2 and B3, not shown), B1 is predictably more stable by 4.1 and 9.3 kcal/mol, respectively. The DFT-optimized structures of **3-4** (species D-E, Fig. S1) are consistent with the formulated structure and analogous to that of species A1.



Fig. 3. B3LYP-optimized structures and ground-state energy ordering for the different diastereomers of  $Mo_2(O)(CO)_2(\mu-\kappa^2-det)_2(\kappa^2-dppm)$  (1). The free energy ( $\Delta G$ ) values are in kcal/mol relative to *trans*- $Mo_2(O)(CO)_2(\mu-\kappa^2-edt)_2(\kappa^2-dppm)$  (A1).

## Crystallographic study of $Mo(CO){\kappa^3-S(CH_2CH_2S)_2}(\kappa^2-dppe)$ (5)

The structure of **5** was established by X-ray crystallography (Figure 4). It contains a single molybdenum atom ligated by a carbonyl, a chelating dppe, and a facially coordinated  $S(CH_2CH_2S)_2$  ligand, which formally derives from bis(2-mercaptoethyl)sulfide, possibly as an impurity in the ethanedithiol. The coordination of this S<sub>3</sub>-type ligand at a Mo(CO)(dppe) center is unprecedented to our knowledge. A check of the current Cambridge Structural Data Center (CSD), while showing related Mo(CO)<sub>3</sub>(S<sub>3</sub>) and Mo(CO)<sub>n</sub>(alkene)(S<sub>3</sub>) derivatives, reveals no phosphine-substituted analogues.<sup>21</sup> The molybdenum atom shows a distorted octahedral geometry and may be assigned a formal oxidation state of +2. **5** may be viewed as a 16-electron complex provided the S(CH<sub>2</sub>CH<sub>2</sub>S)<sub>2</sub> ligand formally serves as a 4-electron donor.

The bonding in 5 was examined, and the DFT-optimized structure of **C** is shown in Figure 4. The orientation of the ancillary ligands in C is similar to the solid-state structure, and the DFT computed v(CO) for **C** is 1823 cm<sup>-1</sup> in excellent agreement with the IR spectrum of 5 [ $\nu$ (CO) 1822 cm<sup>-1</sup>]. The low energy associated with this band confirms the existence of a high degree of electrondonation from the  $S_3$  and dppe ligands. The  ${}^{31}P{}^{1}H{}$  NMR spectrum displays a singlet for the dppe ligand, showing that it has  $C_{\rm s}$ symmetry in solution. A number of different binding modes of the S(CH<sub>2</sub>CH<sub>2</sub>S)<sub>2</sub> ligand are known (Figure 5).<sup>22</sup> The *facial* binding mode (A) in 5 appears to be novel; more common binding modes are in an approximately planar mer fashion (B) to a single metal centre, or bridging modes involving two metals (C-E).



Fig. 4. Molecular structure of  $Mo(CO)(\kappa^2-dppe)(\kappa^3-SCH_2CH_2SCH_2CH_2S)$  (5) showing 50% probability thermal ellipsoids and DFT-optimized structure C (right). Selected bond distances [Å] and angles [ $^{9}$ ]: Mo(1)-P(1) 2.521(3), Mo(1)-P(2) 2.544(2), Mo(1)-S(1) 2.365(3), Mo(1)-S(2) 2.519(2), Mo(1)-S(3) 2.353(2), Mo(1)-C(31) 1.925(4), P(1)-Mo(1)-P(2) 77.30(7), P(1)-Mo(1)-S(1) 162.79(4), P(1)-Mo(1)-S(2) 96.20(7), P(1)-Mo(1)-S(3) 84.96(9), P(1)-Mo(1)-C(31) 86.90(11), P(2)-Mo(1)-S(3) 161.86(4), C(31)-Mo(1)-S(2) 175.83(9), S(1)-Mo(1)-S(2) 83.77(6), C(31)-Mo(1)-S(1) 94.09(11), S(1)-Mo(1)-S(3) 112.10(7), S(2)-Mo(1)-S(3) 84.40(8).

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## Oxidation states, the nature of the Mo-Mo interaction, and DFT calculations

Assigning oxidation states to individual metal atoms in 1-4 is difficult. Figures 6a-c show possible bonding scenarios. Overall the Mo<sub>2</sub> centre carries a formal +6 charge in each case. One view (Figure 6a) involves lone electron pairs on each bridging sulfur to act as soft 2-electron donors to the molybdenum carbonyl moiety, thus making this an 18-electron Mo(0) centre and the molybdenum-oxo centre is then a hard Mo(VI) site. Clearly then the Mo-Mo interaction is best throught of as a donor-acceptor (dative) interaction. Another possibility (Figure 6b) again has asymmetrical  $\mu_2$  sulfur bridges where one bridging ligand functions as a 2-electron donor to the Mo(oxo) moiety. Here the two metals are formally Mo(I) and Mo(V) centres, and the observed diamagnetism would then result from the formation of a Mo-Mo single bond. The third option (Figure 6c) contains a Mo(IV)-Mo(II) formalism where the two bridging sulfur symmetrically bridge the two molybdenum atoms that are connected by a formal Mo=Mo double bond. While we cannot easily assign oxidation states to each molybdenum centre, these complexes are undoubtedly mixedvalent.



Fig. 6. Possible bonding pictures for 1-4 (a-c) and the related cyclopentadienyl complexes  $Cp_2Mo_2(O)(CO)(\mu$ -PPh\_2)( $\mu$ -X) (d-f).

Closely related to **1-4** are the cyclopentadienyl complexes  $Cp_2Mo_2(O)(CO)(\mu$ -PPh<sub>2</sub>)( $\mu$ -X) (X = PPh<sub>2</sub>, CH<sub>2</sub>PPh<sub>2</sub>, CH=CHPh)<sup>23-26</sup> whose metal-metal bond order and oxidation state at each molybdenum atom may be viewed in a number of possible

between these and our oxo derivatives is that each molybdenum atom carries a cyclopentadienyl ligand whose presence precludes a mixed-valence state based on Mo(VI)-Mo(0) centers. A Mo(III)-Mo(III) state is a possibility, although not one we would favor based on an electron count of 20 electrons at the molybdenum-oxo moiety. One way of potentially differentiating between different valence forms would be to use Mo-Mo distances to assign a bond order as (formally) this differs based on oxidation states; however, this approach can be problematic, especially in compounds with a constraining bridging ligand(s).<sup>27</sup> Mays and coworkers have suggested a Mo=Mo double bond in previously  $Cp_2Mo_2(O)(CO)(\mu-PPh_2)_2^{23}$  based on a valence electron count (VEC) of 32. However, we believe this assignment to be erroneous as it was based on the assumption that the oxo ligand functioned as a 2-electron donor (Type B), in contrast to the established view that favours a single oxo ligand as a 4electron donor (Type A), except for cases where there is only a single vacant metal orbital of the right symmetry to take part in the  $\pi$ -bonding.<sup>28</sup> The latter scenario is particularly common in early metal compounds where the electronic deficiency facilitates multiple  $\pi$ -bonding between the metal and the oxo moiety. One might expect the Mo-O bond distance to be distinctive between Type A and B bonding modes but as the difference is only a second  $\pi$ -component to the bond, then again this is not a good measure of bond order. Counting the oxo ligand as a 4-electron donor leads to a VEC of 34 in  $Cp_2Mo_2(O)(CO)(\mu-PPh_2)(\mu-X)$ , an electron count that supports the presence of a metal-metal single bond. Counting each dithiolate ligand as a 4-electron donor (1+1+2) suggests that complexes 1-4 have a VEC of 32 and this is commensurate with a Mo-Mo single bond provided the high valent centre is a 16electron moiety. The Mo-O bond distance of 1.684(3) and 1.670(3) Å in cis-1 and trans-2, respectively, are similar to those reported in the cyclopentadienyl complexes discussed above.<sup>23-26</sup> Further in support of a proposed Mo(V)-Mo(I) mixed valence arrangement for 1-4, the Mo-O distances are also very similar to those found in Mo(V) complexes [MoO( $\kappa^2$ edt)<sub>2</sub>][PPh<sub>4</sub>] (Mo=O 1.678(5) Å)<sup>29</sup> and [MoO( $\kappa^2$ -pdt)<sub>2</sub>][PPh<sub>4</sub>]

ways (shown for  $X = PPh_2$  in Figures 6d-f). The difference

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(Mo=O 1.667(8) Å).<sup>30</sup> Indeed, [MoO( $\kappa^2$ -pdt)<sub>2</sub>][PPh<sub>4</sub>] reacts with hydrazoic acid in methanol to afford binuclear [Mo<sub>2</sub>(O)<sub>2</sub>( $\kappa^2$ -pdt)( $\mu$ -N<sub>3</sub>)( $\mu$ - $\kappa^2$ -pdt)<sub>2</sub>][PPh<sub>4</sub>] in which the two Mo(V) centres are linked via a Mo-Mo bond of 2.893(3) Å and Mo=O bonds are 1.66(1) and 1.67(1) Å.<sup>30</sup>

The general nature of the bonding in 1, especially with respect to the metal-metal and the metal-oxo bond orders, was investigated through the aid of electronic structure calculations. Figure 7 shows selected orbital plots for the important bonding orbitals for the metal-oxo and metal-metal vectors in species A2. Depicted at the top of Figure 7 is MO 149 that represents the Mo-oxo  $\sigma$  bond, and at slightly higher energy two Mo-oxo  $\pi$ -bonds (MO 153 and 154) confirm the presence of a "Type A" oxo in species A2. The bonding between the two molybdenum centres is illustrated by MO 176 and consists of a strong overlap between the two metals. Our DFT calculations revealed no evidence for the existence of a Mo=Mo bond in A2, and these data support a Mo(V)-Mo(I) mixed-valent complex that possesses an oxo moiety that functions as a 4-electron donor in accord with species **b** in Figure 6. Species A1 and A3 gave similar orbital plots (not shown) in terms of the Mo-O and Mo-Mo bonds.



Fig. 7. Selected orbital plots for the Mo-oxo and Mo-Mo moieties in species A2. The top two listed orbitals represent the  $\sigma$  and  $\pi$  components for the Mo-oxo bond and the bottom plot shows the Mo-Mo bond in A2. All plots are shown at a common isovalue of 0.055.

We also examined the effect of the ligand distribution on the natural charges and bond indices in A1-A3 by NBO analysis. Table 1 shows the atomic charges and Wiberg bond indices for selected atoms in the three stereoisomers. As expected, the oxo-substituted molybdenum center is considerably less electron-rich than the dppm-substituted molybdenum atom. The charge on Mo1 for the three species does not vary much (average value -0.05) while the atomic charge on the Mo<sub>2</sub> center varies slightly, ranging from -1.85 (A1) to -1.69 (A3), with an average of -1.75. The oxo ligand in each is electron rich, and the average charge is -0.34. The bridging S1 and S2 atoms are electron poor relative to the terminal S<sub>3</sub> and S<sub>4</sub> donor groups, while the two phosphorus atoms have a positive charge, as found in other phosphinesubstituted complexes.<sup>31,32</sup> The average index for Mo-Mo and Mo=O bonds is 0.63 and 2.09 respectively, values in excellent agreement with the computed indices of 0.60 and 2.09 for the same bonds in trans-Mo<sub>2</sub>Cp<sub>2</sub>(PPh<sub>2</sub>)<sub>2</sub>(O)(CO).<sup>33</sup> As an added check on the validity of the computed WBI for the Mo≡O triple bond in our compounds, we also examined Cp<sub>2</sub>MoOC(O)CHCC(O)OMe, whose structure is depicted in Figure 8.<sup>34</sup> This complex is electronically saturated and cannot exhibit multiple  $\pi$ -bonding with the metal without accompanying slippage of a cyclopentadienyl ring(s). The Mo-O bond distance of 2.113(5) Å is over 0.4 Å longer than those in 1-4, providing a benchmark for a Mo-O single bond. The structure of Cp<sub>2</sub>MoOC(O)CHC(O)OMe was optimized, and the Mo-O bond index examined by Wiberg analysis. The computed WBI for the Mo-O vector (Figure 8) is 0.69, gratifyingly exactly 33% of the WBI value for the Mo-O bond in 1-4. Finally, the different Mo-S Wiberg indices computed are consistent with the number of electrons donated by the different sulfur atoms. The bridging S<sub>1</sub> and S<sub>2</sub> centers show slightly smaller Mo-S indices (average WBI 0.81) compared to the average Mo-S index of 1.06 for the two  $\kappa^1$  S<sub>3</sub> and S<sub>4</sub> donors. Each bridging sulfur moiety ( $S_1$  and  $S_2$ ) donates 3e and this gives rise to a pair of three-center, two-electron interactions whose Mo-S Wiberg index should be slightly smaller than the Mo-S index produced by the electron-precise interaction between the  $Mo_1-S_{3,4}$ bonds whose slightly larger values also reflect the contribution of additional electron donation from the sulfur lone-electron pair(s) to the metal centre.



Figure 8. Reaction of  $Cp_2MoH_2$  with DMAD to give  $Cp_2MoOC(0)CHCC(0)OMe$ . The computed WBI of the Mo-O bond is 0.69.

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Table 1Selected natural charges and Wiberg bond indices for species A1-A3.<sup>a</sup>



	A1	A2	A3
Natural charges			
Mo <sub>1</sub>	-0.04	-0.06	-0.05
Mo <sub>2</sub>	-1.85	-1.72	-1.69
0	-0.34	-0.37	-0.32
S <sub>1</sub> (bridging)	0.36	0.40	0.40
S <sub>2</sub> (bridging)	0.36	0.33	0.36
S <sub>3</sub> (terminal)	0.06	0.07	0.04
S <sub>4</sub> (terminal)	0.05	0.07	0.03
P <sub>1</sub>	1.32	1.23	1.20
P <sub>2</sub>	1.29	1.29	1.30
Wiberg bond indices			
Mo-Mo	0.64	0.66	0.59
Mo <sub>1</sub> -O	2.11	2.05	2.11
Mo <sub>1</sub> -S <sub>1</sub>	0.74	0.79	0.82
Mo <sub>2</sub> -S <sub>1</sub>	0.88	0.84	0.82
Mo <sub>1</sub> -S <sub>2</sub>	0.76	0.78	0.84
Mo <sub>2</sub> -S <sub>2</sub>	0.86	0.79	0.79
Mo <sub>1</sub> -S <sub>3</sub>	1.08	1.08	1.06
Mo <sub>1</sub> -S <sub>4</sub>	1.05	1.08	1.02
Mo <sub>2</sub> -P <sub>1</sub>	0.73	0.63	0.63
Mo <sub>2</sub> -P <sub>2</sub>	0.73	0.72	0.73

<sup>a</sup> The numbering scheme for species **A1-A3** is depicted immediately below the table heading. The phenyl groups associated with the  $P_1$  and  $P_2$  atoms are omitted for clarity.

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#### Electrochemistry

A CV of 1 recorded in MeCN at a scan rate of 0.1 Vs<sup>-1</sup> is shown in Figure 9. It shows a quasi-reversible reduction at  $E_{1/2} = -1.44$ V, together with two irreversible oxidations at  $E_p = 0.60$  V and  $E_{\rm p}$  = 0.78 V (wrt Fc<sup>+</sup>/Fc couple). The reversible reduction, despite its large peak-to-peak separation ( $\Delta E_p$ ) of 200 mV, shows good chemical reversibility ( $i_{\rm pa}/i_{\rm pc}$  ~ 0.90). A small oxidative feature on the return scan at  $E_p = -0.68$  V is associated with the quasi-reversible reduction (Fig. S2), and the overlapping reductive features observed on the return scan around -0.22 V are due to species generated by the irreversible oxidations (Fig. S2). The CV does not show any discernable change when the scan rate scan rate is varied (Fig. S3). The plot of peak current  $(i_p)$  vs. square root of scan rate for the quasi-reversible reduction response shows that the redox wave originates from a diffusion-controlled solution process (Fig. S4). The current function  $(i_p/Vv)$  associated with this reduction deviates from linearity at slow scan rates (Fig. S5), and this behavior supports a multielectron process on longer timescales. The reduction is a well-behaved one electron process at higher scan rates ( $\geq 1 \text{ Vs}^{-1}$ ). The peak current ratio,  $i_{red}/i_{ox}$ , of *ca*. 1.5 ( $i_{red}$  = reductive peak current of the reduction wave and  $i_{ox}$  = oxidative peak current of the first reduction) at scan rate 0.1 Vs<sup>-1</sup> provides further support that more than one electron is involved in the reduction process of 1. The reversible reduction is attributed to a Mo(V) to Mo(IV) process and we note that  $[MoO(\kappa^2-pdt)_2][PPh_4]$  shows a similar reversible one-electron reduction observed at -0.615 V in MeCN.<sup>30</sup> Since solutions of 1 contain both isomers (trans:cis-1 ratio is 2:5), we suggest that the two oxidation peaks may originate from the  $1 \rightarrow 1^+$  oxidation of the individual isomers.



Figure 9. CV of  $Mo_2(O)(CO)_2(\kappa^2-dppm)(\mu-\kappa^2-edt)_2$  (1) in MeCN (0.5 mM solution, supporting electrolyte [NBu<sub>4</sub>][PF<sub>6</sub>], scan rate 0.1 Vs<sup>-1</sup>, glassy carbon electrode, potential vs. Fc<sup>+</sup>/Fc).

#### DFT studies on principal orbital contributions

To better understand the redox properties we computed the HOMO and LUMO of 1 [trans-1 (A1) and cis-1 (A2)] (Figure 10) and D (see ESI). The LUMO of all is delocalized over the dimolybdenum framework and similar relative to the principal orbital contributions from the two metals and bridging thiolate ligands. The minor difference between the LUMO is the presence of an in-phase Mo-CO  $\pi$ -contribution involving the equatorial CO group in A2. The HOMO in the trans-based structure of A1 is identical and largely localized on the two peripheral thiolate groups with a minor contribution from the oxo moiety. That the disposition of the ancillary ligands is important in controlling the nature of the HOMO is verified by comparison of A1 and D with A2. In the case of the latter species, the orbital parentage in the HOMO of A2 is very different and essentially localized on the dppm-bound molybdenum center. Also noted in the metal-based HOMO of A2 are minor out-of-phase interactions with one of the CO and bridging thiolate groups. The energy difference ( $\Delta E$ ) computed for the HOMO-LUMO levels in A2 is 65.3 kcal/mol, which is significantly smaller than the  $\Delta E$  of 75.3 and 74.4 kcal/mol computed for the *trans* species A1 and D, respectively.



Figure 10. HOMO (left) and LUMO (right) for species *trans*-1 (A1, top), *cis*-1 (A2, bottom). The orbitals are printed with an isovalue of 0.055.

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### Summary and conclusions

This work describes the fortuitous synthesis of mixed-valence  $Mo_2(O)(CO)_2{\mu-\kappa^2-S(CH_2)_nS}_2(\kappa^2$ dimolybdenum complexes Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>m</sub>PPh<sub>2</sub>) (n=2,3; m=1,2) (1-4) containing closely linked hard and soft molybdenum centres which we believe are best described as Mo(V) and Mo(I) resepctively. Exactly how they are formed remains unclear and our best guess is that mononuclear  $Mo(CO)_{2}{\kappa^{1}-S(CH_{2})_{n}S}_{2}{\kappa^{2}-Ph_{2}P(CH_{2})_{m}PPh_{2}}$  are initially formed and in turn react with further fac-Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub> to initially afford  $Mo_2(CO)_3{\mu-\kappa^2-S(CH_2)_nS}_2(\kappa^2-Ph_2P(CH_2)_mPPh_2)$  which in turn are oxidised to the observed products; certainly oxidation of molybdenum-carbonyl to molybdenum-oxo species is quite  $\mathsf{common}^{^{23,28e,35}}$  although we cannot discount the possibility of thermally-induced carbonyl loss followed by hydrolysis from water. The dppm-derivatives exist as a mixture of cis and trans isomers which do not interconvert in solution. DFT studies indicate that the major cis isomer is the least stable and thus we conclude that the observed ratios are the result of kinetic factors, possibly relating to the stability or rate of further reactions of mononuclear presursors  $cis/trans-Mo(CO)_{2}{\kappa^{1}-S(CH_{2})_{n}S}_{2}{\kappa^{2}-dppm}$ . Interestingly for the dppe derivatives only the trans isomer is seen which may suggest that  $trans-Mo(CO)_2{\kappa^1-S(CH_2)_nS}_2(\kappa^2-dppe)$  is exclusively initially formed.

An understanding of the bonding in these complexes has led to a reevaluation of the nature of the Mo-Mo bond in related cyclopentadienyl complexes  $Cp_2Mo_2(O)(CO)(\mu-PPh_2)(\mu-PP$ X) (X = PPh<sub>2</sub>, CH<sub>2</sub>PPh<sub>2</sub>, CH=CHPh)<sup>23-26</sup> which are almost certainly 34-electron complexes containing a Mo-Mo single bond rather than 32-electron species with a metal-metal double bond as the Mo-oxo bond is clearly a 4-electron interaction (neutral counting). Interestingly 1-4 are best considered as 32-electron complexes and likely contain a low valent 17-electron centre linked to the high valent 15-electron oxo-supported centre. The later is, however, based on a lack of  $\pi$ -donation from the terminally bonded sulfur atoms and may be a somewhat simplified view. Preliminary electrochemical measurements on 1 support the Mo(V)-Mo(I) view of these complexes as the reversible one-electron reduction observed is consistent with a Mo(V)-Mo(IV) couple as noted in related mononuclear Mo(V) complexes.

## Experimental

General and instrumentation

All the reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated.  $Mo(CO)_6$  was purchased from Strem Chemical Inc. and used without further purification. Dithiols and diphosphines were purchased from Acros Chemicals Inc. and used as received, while  $Mo(CO)_3(NCMe)_3$  (1) was prepared according to a published procedure.<sup>36</sup> All products were separated in the air by TLC over 0.5 mm silica gel 60 Å F<sub>254</sub> glass plates. Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer, and the <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a 400 MHz Bruker-VNMRS spectrometer. All NMR chemical shift and coupling constant data are reported in  $\delta$  units and Hz, respectively. Elemental analyses were performed by the Microanalytical Laboratory of Wazed Miah Research Centre at Jahangirnagar University.

#### Reaction of fac-Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub> with dppm and HS(CH<sub>2</sub>)<sub>2</sub>SH

To 15 mL of MeCN in a Schlenk flask containing Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub> (0.23 g, 0.74 mmol) and dppm (0.29 mg, 0.76 mmol) was added HS(CH<sub>2</sub>)<sub>2</sub>SH (0.29 mg, 3.01 mmol). The solution was heated to 50-55 °C for 18 h during which time the color changed from yellow to dark brown. After cooling to room temperature, volatiles were removed under reduced pressure. The crude product was purified by chromatography on silica gel. Elution with cyclohexane/acetone (7:3, v/v) developed eight bands. The third band afforded the known compound  $Mo(CO)_4(\kappa^2$ -dppm) (90 mg, 21%) as yellow crystals, while the fifth band afforded  $Mo_2(O)(CO)_2(\kappa^2-dppm)(\mu-\kappa^2$ edt)<sub>2</sub> (1) (56 mg, 18%) as red crystals after recrystallization from hexane/CH<sub>2</sub>Cl<sub>2</sub> at 4° C. The contents of the other bands were too small for complete characterization. Data for 1: Anal. Calcd. for C31H30M02O3P2S4: C, 44.61; H, 3.62. Found: C, 44.95; H, 3.78%. IR (CH<sub>2</sub>Cl<sub>2</sub>): 1989s (CO), 1876s (CO) cm<sup>-1</sup>; (KBr): 1989s (CO), 1974s (CO), 935w (Mo=O) cm<sup>-1</sup>. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): 364 nm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): for both diastereomers: δ 7.85 (m, 2H), 7.64 (m, 2H), 7.52-7.34 (m,14H), 7.25 (m, 2H), 4.88-4.19 (m, 8H), 3.88 (m, 1H), 3.38 (m, 1H). major diastereomer: δ 12.0 (d, J 21.4, 1P), -14.4 (d, J 21.4, 1P); minor diastereomer:  $\delta$  8.6 (s). ratio major:minor diastereomer = 5:2

## Reaction of fac-Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub> with dppm and HS(CH<sub>2</sub>)<sub>3</sub>SH

To a MeCN (15 ml) solution of  $Mo(CO)_3(NCMe)_3$  (0.23 g, 0.74 mmol) was added dppm (0.29g, 0.76 mmol) and  $HS(CH_2)_3SH$  (0.32g, 3.03 mmol). The mixture was stirred at 50-55 °C for 18 h, the color changing from yellow to dark brown. After cooling to room temperature, volatiles were removed under vacuum and the

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residue separated by TLC on silica gel. Elution with cyclohexane/acetone (4:1, v/v) developed eight bands. The third band gave Mo(CO)<sub>4</sub>( $\kappa^2$ -dppm) (0.10g, 23%) as yellow crystals, while the sixth afforded Mo<sub>2</sub>(O)(CO)<sub>2</sub>( $\kappa^2$ -dppm)( $\mu$ - $\kappa^2$ -pdt)<sub>2</sub> (2) (34 mg, 11%) as red crystals after recrystallization from hexane/CH<sub>2</sub>Cl<sub>2</sub> at 4 <sup>o</sup>C. Data for **2**: Anal. Calcd for C<sub>33</sub>H<sub>34</sub>Mo<sub>2</sub>O<sub>3</sub>P<sub>2</sub>S<sub>4</sub>: C, 45.94; H, 3.97. Found: C, 46.35; H, 4.11%. IR (CH<sub>2</sub>Cl<sub>2</sub>): 1973s (CO), 1865s (CO) cm<sup>-1</sup>; (KBr): 1954s (CO), 1854s (CO), 949w (Mo=O) cm<sup>-1</sup>. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): 372 nm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): for both diastereomers:  $\delta$  7.72-6.97 (m, 20H), 4.75-3.74 (m, 12H), 2.37-2.15 (m, 2H). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): major isomer:  $\delta$  1.2.4 (d, J 24.2, 1P), -15.2 (d, J 24.2, 1P); minor isomer:  $\delta$  7.9 (s), with a ratio of major:minor diastereomer = 4:1. UV-vis (

#### Reaction of fac-Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub> with dppe and HS(CH<sub>2</sub>)<sub>2</sub>SH

MeCN (15 ml) was added to a misture of Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub> (0.23g, 0.74 mmol) and dppe (0.30g, 0.76 mmol), and HS(CH<sub>2</sub>)<sub>2</sub>SH (0.28 g, 3.04 mmol) was then added. The solution was stirred at 50-55 °C for 18 h. Chromatographic separation and workup as described above gave eight bands. The third band gave Mo(CO)<sub>4</sub>( $\kappa^2$ -dppe) (51 mg, 11%) as yellow crystals, the fourth band gave  $Mo(CO){\kappa^3}$ - $S(CH_2CH_2S)_2$  ( $\kappa^2$ -dppe) (5) (14 mg, 3%) as green crystals, and the fifth band afforded  $Mo_2(O)(CO)_2(\kappa^2-dppe)(\mu-\kappa^2-edt)_2$  (3) (38 mg, 12%) as red crystals after recrystallization from hexane/CH<sub>2</sub>Cl<sub>2</sub> at 4 °C. Data for **3**: Anal. Calcd for  $C_{32}H_{32}Mo_2O_3P_2S_4$ : C, 45.29; H, 3.80. Found: C, 46.45; H, 3.97%. IR (KBr): 1975w (CO), 1874s (CO), 955w (Mo=O) cm<sup>-1</sup>. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): 368 nm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.81 (m, 8H), 7.45 (m, 12H), 3.75 (d, J 4.0 Hz, 4H), 2.58-2.10 (m, 8H). <sup>31</sup>P{<sup>1</sup>H} NMR ( $CD_2Cl_2$ ):  $\delta$  44.3 (s). Data for **5**: Anal. Calcd for  $C_{31}H_{32}MoOP_2S_3$ : C, 55.19; H, 4.78. Found: C, 55.96; H, 4.85%. IR (u(CO), CH<sub>2</sub>Cl<sub>2</sub>): 1822s cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.06 (m, 4H), 7.47 (m, 6H), 7.32 (m, 6H), 7.21 (m, 4H), 2.74 (m, 2H), 2.58 (m, 4H), 2.34 (m, 2H), 2.02 (m, 2H) 1.71 (m, 2H). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 52.9 (s).

## Reaction of fac-Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub> with dppe and HS(CH<sub>2</sub>)<sub>3</sub>SH

Following a similar procedure to that described above but with dppe (0.30g, 0.76 mmol) and HS(CH<sub>2</sub>)<sub>3</sub>SH (0.33 g, 3.03 mmol). Eight bands were developed on the TLC plate of which the fifth band gave  $Mo(CO)_4(\kappa^2$ -dppe) (45 mg, 10%) as yellow crystals, and the eighth band  $Mo_2(O)(CO)_2(\kappa^2$ -dppe)( $\mu$ - $\kappa^2$ -pdt)<sub>2</sub> (4) (42 mg, 13%) as red crystals after recrystallization from hexane/CH<sub>2</sub>Cl<sub>2</sub> at 4 °C. Data for 4: Anal. Calcd for C<sub>34</sub>H<sub>36</sub>Mo<sub>2</sub>O<sub>3</sub>P<sub>2</sub>S<sub>4</sub>: C, 46.58; H, 4.14. Found: C, 47.96; H, 4.25%. IR (KBr): 1977w (CO), 1976vs (CO), 955w (Mo=O) cm<sup>-1</sup>. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): 360 nm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.72 (m, 6H), 7.53 (m, 4H), 7.47 (m, 10H), 4.10-3.60 (m, 12H), 2.68 (m, 2H), 2.33 (m,2H).<sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 32.6 (s).

#### **Electrochemical studies**

The cyclic voltammetric studies on **1** and **3** were carried out in deoxygenated acetonitrile (MeCN) solution with tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte. The working electrode was a 3 mm diameter glassy

carbon electrode that was polished with a 0.3  $\mu$ m alumina slurry before each scan. The counter electrode was a Pt wire, and the quasi-reference electrode was a silver wire. All CVs were referenced to the Fc/Fc<sup>+</sup> redox couple. An Autolab potentiostat (EcoChemie, Netherlands) was used for all electrochemical measurements.

#### X-ray crystallography

Single crystals of *cis*-1, *trans*-2, and 5 suitable for X-ray structure analysis, were grown by slow diffusion of hexane into a dichloromethane solution containing each compound at 4° C. The selected crystals were attached to a MiTeGen loop by Apiezon H grease and mounted on a Rigaku Mercury375R/M CCD (XtaLAB mini) diffractometer using graphite monochromated Mo-K $\alpha$  radiation at 293(2) K (for *trans*-2 and 5) and 296(2) K (for *cis*-1). Data collection and subsequent data processing of these compounds were performed using the available diffractometer software Crystal Clear (Rigaku). The data were corrected for Lorentz and polarization effects. All three structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined using a riding model for all three compounds. Table S1 summarizes the X-ray processing and data collection parameters.

#### Computational details and modeling

The DFT calculations were carried out with the Gaussian 09 package of programs,<sup>37</sup> using the B3LYP hybrid functional. This functional is comprised of Becke's three-parameter hybrid exchange functional (B3)<sup>38</sup> and the correlation functional of Lee, Yang, and Parr (LYP).<sup>39</sup> The molybdenum atoms were described with the Stuttgart-Dresden effective core potential and SDD basis set,<sup>40</sup> and the 6-31G(d') basis set<sup>41</sup> was employed for all remaining atoms.

The reported geometries have been fully optimized and the analytical second derivatives were evaluated, confirming that the geometry was an energy minimum (no negative eigenvalues). Unscaled vibrational frequencies were used to make zero-point and thermal corrections to the electronic energies. The vibrational analysis of the v(CO) band in **C** employed a scaling factor of 0.94. The natural charges and Wiberg indices were computed using Weinhold's NaturalBond Orbital (NBO) program.<sup>42,43</sup> The geometry-optimized structures have been drawn with the *JIMP*2 molecular visualization and manipulation program.<sup>44</sup>

#### **Supplementary Information**

Additional computational, electrochemical and crystallographic information are given in Figs. S1-S6 and Table S1. CCDC 1400764 (for *cis*-1), CCDC 1400765 (for *trans*-2) and CCDC 1400766 (for 4) contain supplementary crystallographic data. These data may be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data\_request/cif.

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## **Notes and References**

- 1 M.J. Romao, M. Archer, I. Moura, J.J.G. Moura, J. LeGall, R. Engh, M. Schneider, P. Hof, R. Huber, *Science* 1995, *270*, 1170.
- 2 R. Hille, Arch. *Biochem. Biophys.* 2005, *433*, 107.
- 3 R. Hille, Eur. J. Inorg. Chem. 2006, 1913.
- 4 M.J. Romao, *Dalton Trans.* 2009, 4053.
- 5 R. Hille, J. Hall, P. Basu, Chem. Rev. 2014, 114, 3963.
- 6 D. Collison, C.D. Garner, J.A. Joule, *Chem. Soc. Rev.* 1996, *25*, 25.
- 7 J.H. Enemark, J.J.A. Cooney, J.-J. Wang, R.H. Holm, *Chem. Rev.* 2004, *104*, 1175.
- 8 F.J. Hine, A.J. Taylor, C.D. Garner, Coord. Chem. Rev. 2010, 254, 1570.
- 9 H. Sugimoto, H. Tsukube, Chem. Soc. Rev. 2008, 37, 2609.
- G. Lyashenko, G. Saischek, M.E. Judmaier, M. Volpe, J. Baumgartner, F. Belaj, V. Jancik, R. Herbst-Irmer, N.C. Mösch-Zanetti, *Dalton Trans.* 2009, 5655.
- 11 M.E. Judmaier, A. Wallner, G.N. Stipicic, K. Kirchner, J. Baumgartner, F. Belaj, N.C. Mösch-Zanetti, *Inorg. Chem.* 2009, 48, 10211.
- 12 C. Schulzke, Eur. J. Inorg. Chem. 2011, 1189.
- 13 J.-M. Brégeault, Dalton Trans. 2003, 3289.
- 14 D.V. Deubel, G. Frenking, P. Gisdakis, W.A. Herrmann, N. Roesch, J. Sundermeyer, *Acc. Chem. Res.* 2004, *37*, 645.
- 15 F.E. Kühn, A.M. Santos, W.A. Herrmann, *Dalton Trans.* 2005, 2483.
- 16 L. Shechter, J. Wynstra, R. Kurkjy, *Ind. Eng. Chem.* 1957, *49*, 1107.
- 17 J.A. Schachner, P. Traar, C. Sala, M. Melcher, B.N. Harum, A.F. Sax, M. Volpe, F. Belaj, N.C. Mösch-Zanetti, *Inorg. Chem.* 2012, 51, 7642.
- 18 Y. Shi, S. Lu, H. Guo, Q. Wu, N. Hu, J. Organomet. Chem. 1996, 514, 183.
- 19 M.R. Haque, S. Ghosh, G. Hogarth, M.G. Richmond, S.E. Kabir, Inorg. Chim. Acta 2015, 434, 150.
- 20 The identity of Mo(CO)<sub>4</sub>(dppe) was ascertained through TLC and spectral comparison with an independently prepared sample. See ref. 19.
- For related molybdenum carbonyl compounds containing S<sub>3</sub> ligands, see: a) M.T. Ashby, D.L. Lichtenberger, *Inorg. Chem.* 1985, *24*, 636; b) M.T. Ashby, J.H. Enemark, D.L. Lichtenberger, R.B. Ortega, *Inorg. Chem.* 1986, *25*, 3154; c) G.J. Grant, J.P. Carpenter, W.N. Setzer, D.G. VanDerveer, *Inorg. Chem.* 1989, *28*, 4128; d) C.A. Gamelas, N.A.G. Banderira, C.C.L. Pereira,

M.J. Calhorda, E. Herdtweck, M. Machuqueiro, C.C. Romão, L.F. Veiros, *Dalton Trans*. 2011, *30*, 10513.

- See for example: a) G.A. Barclay, E.M. McPartlin, N.C. Stephenson, Acta Cryst. 1969, B25, 1262; b) K.P. Maresca, G.H. Bonavia, J.W. Babich, J. Zubieta, Inorg. Chim. Acta 1999, 284, 252; c) K.P. Maresca, F.J. Femia, G.H. Bonavia, J.W. Babich, J. Zubieta, Inorg. Chim. Acta 2000, 297, 98; d) V.E. Kaasjager, R.K. Henderson, E. Bouwman, M. Lutz, A.L. Spek, J. Reedijk, Angew. Chem., Int. Ed. 1998, 37, 1668. e) C.-Y. Chaing, M.L. Miller, J.H. Reibenspies, M.Y. Darensbourg, J. Am. Chem. Soc. 2004, 126, 10867.
- 23 T. Adatia, M. McPartlin, M.J. Mays, M. J.; Morris, P.R. Raithby, Dalton Trans. 1989, 1555.
- 24 K. Endrich, R. Korswagen, T. Zahn, M.L. Ziegler, *Angew. Chem., Int. Ed. Engl.* 1982, *21*, 919; *Angew. Chem.* Suppl. 1982, 1906.
- 25 V. Riera, M.A. Ruiz, F. Villafañe, C. Bois, Y. Jeannin, Organometallics 1993, 12, 124.
- 26 G. Garcia, M.E. Garcia, S. Melón, V. Riera, M.A. Ruiz, Organometallics 1997, 16, 624.
- See for example: a) M.-H. Baik, R.A. Friesner, G. Parkin, Polyhedron 2004, 23, 2879; b) M.C. Neary, G. Parkin, *Inorg.* Chem. 2017, 56, 1511.
- a) G. Parkin, J.E. Bercaw, *Polyhedron* 1988, *7*, 2053; b) G.
  Parkin, J.E. Bercaw, *J. Am. Chem. Soc.* 1989, *111*, 391; c) M.E.
  Garcia, D. Carcia-Vivó, S. Melón, M.A. Ruiz, C. Graiff, A.
  Tiripicchio, *Inorg. Chem.* 2009, *48*, 9282; d) F. Cimadevilla, M.E.
  Garcia, D. Carcia-Vivó, M.A. Ruiz, M.T. Rueda, *J. Organomet. Chem.* 2012, *699*, 67; e) M.A. Alvarez, M.E. Garcia, D. Carcia-Vivó, S. Menéndez, M.A. Ruiz, *Organometallics* 2013, *32*, 218.
- 29 S.R. Ellis, D. Collison, C.D. Garner, W. Clegg, Chem. Comm. 1986, 1483.
- 30 P.T. Bishop, J.R. Dilworth, J.P. Hutchinson, J.A. Zubieta, Trans. Met. Chem. 1990, 15, 177.
- 31 C.-H. Lin, V.N. Nesterov, M.G. Richmond, J. Organomet. Chem. 2013, 744, 24.
- 32 L. Yang, V.N. Nesterov, X. Wang, M.G. Richmond, *J. Clust. Sci.* 2012, *23*, 685.
- 33 We have confirmed that the orbital composition for the Mo-Mo and Mo-O moieties in *trans*-Mo<sub>2</sub>Cp<sub>2</sub>(PPh<sub>2</sub>)<sub>2</sub>(O)(CO) parallel those found in species A1-A3, namely, a Mo-Mo single bond and a Mo≡O triple bond ("Type A"). Unpublished results.
- 34 M. Cariou, M.M. Kubicki, R. Kergoat, J.E. Guerchais, P. L'Haridon, J. Organomet. Chem. 1986, 304, 127.
- 35 H. Adams, Y.K. Booth, E.S. Cook, S. Riley, M.J. Morris, *Organometallics* 2017, *36*, 2254.
- 36 D.P. Tate, W.R. Knipple, J.M. Augl, *Inorg. Chem.* 1962, *1*, 433.
- 37 M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J.

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Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.

- 38 A.D. Becke, J. Chem. Phys. 1993, 98, 5648.
- 39 C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 1988, 37, 785.
- a) M. Dolg, U. Wedig, H. Stoll, H. Preuss, J. Chem. Phys. 1987, 86, 866; b) S.P. Watch, C.W. Bauschlicher, J. Chem. Phys. 1983, 78, 4597.
- a) G.A. Petersson, A. Bennett, T.G. Tensfeldt, M.A. Al-Laham,
  W.A. Shirley, J. Mantzaris, *J. Chem. Phys.* 1988, *89*, 2193; b)
  G.A. Petersson, M.A. Al-Laham, *J. Chem. Phys.*, 1991, *94*, 6081.
- 42 A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 1988, 88, 899.
- 43 K.B. Wiberg, Tetrahedron 1968, 24, 1083.
- a) JIMP2, version 0.091, a free program for the visualization and manipulation of molecules: M.B. Hall, R. F. Fenske, *Inorg. Chem.* 1972, *11*, 768; b) J. Manson, C.E. Webster, M.B. Hall, Texas A & M University, College Station, TX, 2006: http://www.chem.tamu.edu/jimp2/index.html.