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COMMUNICATION

SYNTHESIS, STRUCTURE AND PROPERTIES OF MONONUCLEAR AND DINUCLEAR MOLYBDENUM(III) BROMIDE COMPOUNDS. LIGAND-INDUCED, REVERSIBLE BREAKAGE OF A METAL–METAL BOND IN $Mo_2Br_6(dppe)_2$

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Abstract—$MoBr_3(THF)_3$ reacts with 1 equivalent of bis(diphenylphosphino)ethane (dppe) in THF to yield $MoBr_3$(dppe)(THF) (**1**). The THF ligand in the latter molecule can be easily replaced by MeCN to afford $MoBr_3$(dppe)(MeCN) (**2**). When treated in a non-donor solvent, **1** loses THF and dimerizes to one of two isomeric $Mo_2Br_6(dppe)_2$ molecules (green, **3**, kinetic product; purple, **4**, thermodynamic product) depending on experimental conditions. An X-ray analysis of **4** shows an edge-sharing bioctahedral structure and the presence of a Mo—Mo bond. Both **3** and **4** can be reconverted to the parent compound **1** by warming in the presence of excess THF. Compound **2** can also be transformed into the dinuclear compound **4**.

The chemistry of molybdenum compounds in oxidation state III is extremely vast and offers many possible applications, ranging from catalysis to materials science to biochemistry. The chemistry of molybdenum(III) is also among the richest in the field of metal–metal bonding.[1] The simple mononuclear, octahedral compounds of stoichiometry MoX_3L_3 (X = anionic ligand, L = neutral ligand) have been prepared with a variety of different neutral ligands, but most of the studies have been restricted to the trichloride system.[2] This fact can be attributed to the lack of simple preparative procedures for useful starting materials such as $MoX_3(THF)_3$ (X = Br, I; THF = tetrahydrofuran), similar to the widely used $MoCl_3(THF)_3$ where the THF ligands are easily replaced by other ligands. This is unfortunate for several reasons: a comparative study of different molybdenum(III) halide derivatives can be helpful for assessing the importance of electronic and steric factors on chemical reactivity; the bromide and iodide compounds may provide alternative and possibly better starting materials for the generation of other molybdenum(III) compounds as well as compounds of molybdenum in different oxidation states; finally, new types of reactivity and/or structural features may be found.

Cotton and Poli recently reported the synthesis, structure and THF replacement chemistry of $MoI_3(THF)_3$.[3] We successfully applied the same strategy to the large-scale preparation of the already known[4] $MoBr_3(THF)_3$.[‡] We report here preliminary studies on THF substitution chemistry on $MoBr_3(THF)_3$ which led to the observation, to our knowledge unprecedented, of a ligand-induced and reversible interconversion between a mononuclear and a metal–metal bonded dinuclear compound.

A suspension of $MoBr_3(THF)_3$ in THF reacts smoothly at room temperature with an equimolar amount of bis(diphenylphosphino)ethane (dppe) to afford a clear orange solution containing $MoBr_3$(dppe)(THF) (**1**), which can be isolated as a yellow, slightly air-sensitive microcrystalline solid in good yields by addition of diethyl ether to con-

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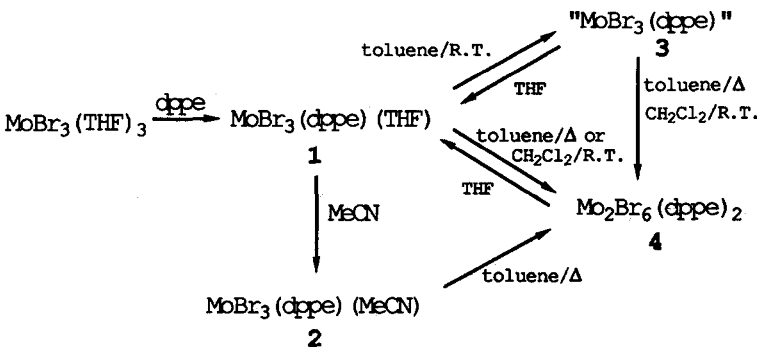
[‡] $Mo_2Br_4(CO)_8$ and Br_2 in equimolar amounts were stirred together in THF for a few hours at 0°C, then overnight at room temperature. A 90% yield of analytically pure material was obtained.



Scheme 1.

centrated solutions.† We believe **1** is a mononuclear, octahedral complex, with a *mer* arrangement of the three bromo ligands, on the basis of an X-ray crystal structure determination on the corresponding triiodide molecule[5] and the similarity of the IR spectra of the two compounds. Also, octahedral trihalide complexes of molybdenum, as well as of other metals, are known to prefer the *mer* arrangement with only a few documented exceptions.[6]

The THF molecule in **1** can be easily replaced by other ligands (see Scheme 1). Compound **2**, $MoBr_3(dppe)(MeCN)$, can be obtained by adding an excess of acetonitrile to THF solutions of **1**, although better yields can be obtained by reacting the isolated **1** with pure MeCN.‡

When compound **1** is dissolved in a solvent other than THF and no other ligand is present, it slowly loses the coordinated THF molecule and converts into a different product, the nature of which depends upon the experimental conditions employed. In toluene at room temperature a green–brown compound, **3**, precipitates. In CH_2Cl_2 or in refluxing toluene a purple compound, **4**, is obtained. **3** can be converted into **4** under the same conditions where the latter is obtained directly from **1**. Both compounds **3** and **4** analyse correctly for $MoBr_3(dppe)$.§ The recrystallization of **3** and **4** is rather problematic. Any attempt to recrystallize **3** results in its partial conversion to **4**. Compound **4** easily incorporates the crystallization solvent§ to afford very poorly soluble forms of the compound that are then impossible to separate from other insoluble impurities. Compound **4** is slightly soluble in polar chlorinated hydrocarbons but an attempt to recrystallize it from hot 1,1,2-trichloroethane resulted in decomposition. The change of colour from purple to orange–red and the shift of a visible absorption band, λ_{max}, from 558 to 495 nm suggest that at least partial halide exchange with the solvent may have taken place. $Mo_2Cl_6(dppe)_2$ has $\lambda_{max} = 507$ in CH_2Cl_2.[7]

Single crystals of **4** that were suitable for an X-ray analysis were obtained from $CHCl_3$.‖ The compound is dinuclear with an edge-sharing bioctahedral configuration, the six bromo ligands occupy-

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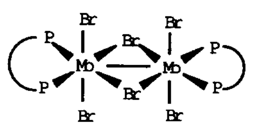
† Compound **1**. Found: C, 44.4; H, 3.8; Br, 30.6. Calc. for $C_{30}H_{32}Br_3MoP_2O$: C, 44.7; H, 4.0; Br, 29.7%. IR (Nujol mull/cm^{-1}): 3055 m, 1590 w, 1575 w, 1485 m, 1440 s, 1415 w, 1345 w, 1310 vw, 1195 w, 1165 w, 1100 m, 1075 w, 1045 vw, 1030 w, 990 vw, 920 vw, 850 m, br., 745 s, 725 w, 695 s, 680 w, 650 w, 620 w, 520 s, 500 w.

‡ Compound **2**. Found: C, 43.3; H, 3.3; Br, 30.6; N, 1.8. Calc. for $C_{28}H_{27}Br_3MoNP_2$: C, 43.4; H, 3.5; Br, 30.9; N, 1.8%. IR (Nujol mull/cm^{-1}): 3055 m, 2310 w, 2275 m, 1575 w, 1490 m, 1440 s, 1415 m, 1360 w, 1345 vw, 1325 w, 1195 w, 1160 w, 1115 w, 1100 m, 1080 w, 1030 w, 1000 w, 860 m, 820 w, 765 m, 745 s, 715 m, 700 s, 695 s, 675 m, 645 m, 620 vw, 525 m, 520 m, 490 m, 475 w, 420 w.

§ Compound **3**. Found: C, 42.5; H, 3.5; Br, 30.7. Calc. for $C_{26}H_{24}Br_3MoP_2$: C, 42.5; H, 3.3; Br, 32.7%. Compound **4** typically gave analyses consistent with the incorporation of variable amounts of the crystallization solvent. An X-ray analysis confirmed the presence of interstitial solvent (see text). A sample of compound **4** obtained in **1** in refluxing toluene analysed correctly. Found: C, 42.8; H, 3.2; Br, 32.2. IR (Nujol mull/cm^{-1}): 3050 w, 1590 w, 1580 w, 1490 m, 1415 w, 1440 s, 1195 w, 1160 w, 1100 m, 1075 w, 1030 w, 1005 w, 870 w, 830 w, 815 w, 745 m, 705 m, 695 s, 675 w, 650 vw, 620 vw, 525 m, 520 m, 500 w, 475 w. UV–vis [CH_2Cl_2, R.T., λ_{max}/nm (ε)]: 345(25810), 555(2040).

‖ Crystal data for compound $\mathbf{4}\cdot 4CHCl_3$: monoclinic; space group $I2/m$; $a = 15.653(2)$; $b = 19.180(4)$; $c = 13.723(2)$ Å; $\beta = 108.52(1)°$; $V = 3907(2)$ Å^3; $d_c = 1.65$ g cm^{-3}; $\mu(\text{Mo-}K_\alpha) = 40.85$ cm^{-1}. At the end of the structure refinement for $Mo_2Br_6(dppe)_2$, a few clusters of peaks appeared in the difference Fourier map in the proximity of the crystallographic mirror planes, but it was not possible to assign a reasonable model to any of them. The number of interstitial chloroform molecules (four per dimer) is inferred by comparison with the published isostructural $Mo_2Cl_6(dppe)_2\cdot 4CH_2Cl_2$,[7] considering that CH_2Cl_2 and $CHCl_3$ occupy roughly the same volume. The final agreement factor reached ($R = 0.13$) is for the model not including any disordered solvent molecules.



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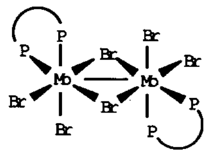

II

ing the four axial and the two bridging positions, as illustrated in I. Because of disorder in the interstitial solvent molecules we have not been able to refine the structure to a perfectly acceptable R factor† and we wish to report here these crystallographic data insofar as they establish the geometry of the complex and to indicate the presence of a metal–metal interaction [Mo—Mo′ = 2.799(7) Å].

Other edge-sharing bioctahedral compounds of molybdenum(III) with bridging chloro, hydroxo and alkylsulphido ligands have been structurally characterized. They exhibit a Mo—Mo distance in the range 2.47–2.79 Å.[8] $Mo_2Cl_6(dppe)_2$ has also been recently reported,[7] having a Mo—Mo distance of 2.762(1) Å. The metal–metal interaction in this type of compound has been described in terms of either a $\sigma^2\pi^2\delta^2$ or a $\sigma^2\pi^2\delta^{*2}$ electronic configuration.[7,9]

Even at the level of structure refinement which was achieved, it seems that compound **4** has a slightly larger metal–metal distance than any of the molybdenum(III) edge-sharing bioctahedral dimers reported to date.[8] This is consistent with the higher bulk of the bridging ligand and should reflect on the strength of the metal–metal interaction and ultimately on the chemical reactivity of the compound.

Compound **4** is converted back to the parent compound **1** when warmed in neat THF or in 1,1,2-trichloroethane containing a large excess of THF, as shown by UV–vis spectroscopic monitoring of the reaction. The attainable temperature in refluxing CH_2Cl_2 is insufficient to cause the same transformation.

There are several examples in the literature of dinuclear, halide-bridged compounds that are reversibly converted to mononuclear complexes by addition/removal of donor solvent molecules[10] but, to the best of our knowledge, none of these contain a direct metal–metal interaction. $MoCl_3(PMe_3)_3$ is reported to lose one PMe_3 ligand in refluxing toluene to afford a product described as the edge-sharing bioctahedral $Mo_2Cl_6(PMe_3)_4$, but no structural data are reported for the product and the "back-reaction" has not been described.[11]

Compound **2** is stable at room temperature towards loss of the monodentate neutral ligand and dimerization to compounds **3** and/or **4**. Heating in toluene at the reflux temperature smoothly converts compound **2** into compound **4**. This observation suggests a Mo^{III}–ligand bond strength in the order THF < MeCN.

Concerning the nature of compound **3**, if we exclude the unlikely possibility of a five-coordinate monomer, the most reasonable guess is that we have a dinuclear structure as represented in II. Although most of the edge-sharing bioctahedral compounds with bis-chelating diphosphines that have been structurally characterized show an arrangement of type I,[8a] there is at least one precedent for a structure of type II, $Mo_2Cl_6(EtSCH_2CH_2SEt)_2$.[8b] Consistent with our structural assignment, compound **3** is also converted into compound **1** when heated in THF. We are planning to undertake kinetic and equilibrium studies on this system and on others containing diphosphine ligands with different steric/electronic properties.

No chemical reactivity has been reported for the chloride analogue of compound **4**, $Mo_2Cl_6(dppe)_2$,[7] but on the basis of its reported metal–metal bond distance, its conversion to the mononuclear compound $MoCl_3(dppe)(THF)$ should be harder. Conversely, the transformation of the hypothetical monomer into the dimer should be easier. With the triiodide system, however, the opposite behaviour is expected because of the higher bulk of the iodo ligands. Work is in progress in our laboratory to test these hypotheses.

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† See footnote || on opposite page.

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