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The electronic structure and bonding in $W_2(\mu\text{-}H)_2(O^iPr)_4(DMPE)_2$ and a comparison with $Mo_2(O^iPr)_4(DMPE)_2$

Malcolm H. Chisholm [a], Matthew A. Lynn [b,*]

[a] *Department of Chemistry, Indiana University, Bloomington, IN 47405, USA*
[b] *Department of Chemistry, The University of Arizona, Tucson, AZ 85721, USA*

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This paper is dedicated to Professor Dr. Henri Brunner on the occasion of his 65th birthday

Abstract

The bonding in the recently reported [1] $W_2(\mu\text{-}H)_2(O^iPr)_4(DMPE)_2$ (O^iPr = isopropoxide; DMPE = bis(dimethylphosphino)ethane) molecule is investigated via the computational method of Fenske and Hall and the results are compared with those of a previous study of the electronic structure of $Mo_2(O^iPr)_4(DMPE)_2$ by Bursten and coworkers [2]. In the dimolybdenum system, a Mo–Mo triple bond of configuration $\sigma^2\pi^4\delta^2_{nb}$ (nb = nonbonding) unites the two molybdenum atoms of oxidation states 0 and 4 +. The introduction of the two bridging hydrides reduces the metal–metal bond order to two in $W_2(\mu\text{-}H)_2(O^iPr)_4(DMPE)_2$ and by analogy the bonding between the tungsten atoms can be described as $\sigma^2\pi^2\delta^2_{nb}$. Although there is extensive mixing of the W–W and W–H σ bonds, an orbital can still be ascribed as a W–W σ bond. An analogy is made to the bonding in $B_2H_4^{2-}$, an ethane-type molecule, and to B_2H_6. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

A majority of the compounds that contain multiple metal-metal bonds possess metal centers that are symmetry-equivalent. Examples of such complexes include the dimetal tetracarboxylates ($M_2(O_2CR)_4$; M = Cr, Mo, W, Ru, Rh), and dimolybdenum and ditungsten hexaalkoxides ($M_2(OR)_6$) and hexaamides ($M_2(NR_2)_6$) [3]. The frontier molecular orbital (MO) scheme used to describe such systems is the well-known σπδδ*π*σ* nomenclature and ordering introduced by Cotton in the early 1960s [4]. Implicit in this description of the valence metal–metal bonding MOs is the presence of metal atoms that are located in identical environments. In such a case, the frontier MOs possess equivalent atomic orbital character from each metal atom. For example, the M–M σ bond is composed of an equal admixture of the d_{z5} atomic orbitals of each metal center. However, if the metal atoms in a dinuclear system are differently substituted, the symmetry elements that formerly related the two metal atoms are removed and the centers are no longer equivalent. Such is the case for the asymmetric complex $Mo_2(O^iPr)_4(DMPE)_2$ in which the phosphine ligands are located on one of the Mo atoms and the four isopropoxides are bound to the other [5]. The molybdenum atoms of this system have formal oxidation states of Mo(0) and Mo(IV), which therefore leads to an electron count of eight and hence the possibility of the formation of a Mo–Mo quadruple bond. Calculations by Bursten and Schneider [2], however, showed that the bond order in the related but hypothetical complex $Mo_2(OH)_4(PH_3)_4$ is three, which is consistent with the Mo–Mo bond length of 2.236 Å. This distance is 0.1 Å longer than that found in systems known to possess a Mo–Mo quadruple bond.Recently, the ditungsten compound $W_2(\mu\text{-}H)_2(O^iPr)_4(DMPE)_2$ was prepared [1,6]. This system exhibits a W–W bond length of 2.496 Å,

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[*] Corresponding author. Current address: Department of Chemistry, Old Chemistry-329 B, University of Arizona, Tuscon, AZ 25721, USA. Tel.: + 1-520-621-8407; fax: + 1-520-621-2691..
E-mail address: mlynn@u.arizona.edu (M.A. Lynn).

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which is typical of systems that contain a W–W double bond [3]. It is believed, based on structural and ^{1}H-NMR data, that this ditungsten system contains two bridging hydride ligands, thereby accounting for the reduction in bond order from three to two from the Mo to the W compound. The presence of two hydrides in bridging positions between the two tungsten atoms places each metal center in a pseudo-octahedral environment. The two octahedra are edge-sharing and the geometry around each tungsten center thus places the ligands in an eclipsed environment.

To support their argument, Bursten and Schneider proposed a molecular orbital diagram for $Mo_2(OH)_4(PH_3)_4$ [2]. Such a scheme suggests that the bond order in this complex is three, even though the total number of electrons formally assigned to the metal centers is eight. The complex contains the usual σ and two π metal–metal bonding molecular orbitals, but the δ bond is destroyed by the presence of the alkoxides around one of the tungsten atoms. Keeping in mind that molecular orbitals in the metal–metal bonding region of a molecular orbital diagram are generally antibonding with respect to the lone pairs on ancillary ligands, we wish to note that the phosphines around one of the tungsten atoms in $W_2(\mu\text{-}H)_2(O^iPr)_4(DMPE)_2$ have lone pairs that interact in a σ fashion with the metal center whereas the alkoxides bound to the other have lone pairs that have σ and π interactions with the tungsten center. The d orbitals of the tungsten atom to which the alkoxides are bound are therefore more destabilized by overlap effects than are those of the tungsten atom to which the phosphines are attached.

In the calculations on $Mo_2(OH)_4(PH_3)_4$ [2], it was shown that one σ and two π bonds can be formed between the Mo centers to give rise to a triple bond. The metal–metal σ bond is located on the axis connecting the two molybdenum atoms and, by symmetry, is little influenced by overlap effects with the lone pairs of the ancillary ligands. That is, the d_{z5} atomic orbital (AO) on each Mo atom overlaps little with any ligand lone pair; both Mo d_{z5} AOs consequently have similar energies in each fragment. A strong Mo–Mo d_{z5} σ is the result. Two π bonds also form even though the Mo d_{xz} and d_{yz} AOs interact more with the oxygen lone pairs than do the Mo d_{z5} AOs. A δ bond, however, is not formed because of the presence of the alkoxide p_π lone pairs, which destabilize the d_{xy} atomic orbital on the corresponding molybdenum atom to such a degree that the energy separation between the d_{xy} AOs on the two atoms is calculated to be more than 1 eV. A δ bond therefore does not form.

The recent preparation of what might have been taken to be a W_2 analog of the Mo_2 system raises some important questions about the bonding in this new molecule. First, the observed W–W bond length of 2.496 Å falls in the range of previously observed W–W double bonds. Therefore, does the possibility of two bridging hydrides account for this observation in a molecular orbital description of the complex? Second, if the bond order is truly two, what molecular orbitals are involved in the metal-metal bonding? Third, what effect on the molecular orbital structure do the more diffuse W 5d AOs play? That is, is there any more of a δ bond in the W_2 system than for Mo_2? Or, does it happen that because the W valence atomic orbitals are more diffuse that the W–W bonding orbitals are even more W–O antibonding? These questions have been examined via Fenske–Hall molecular orbital calculations [7] on the hypothetical system $W_2(PH_3)_4(OH)_4(H)_2$ and are presented here to explain the bonding in the noncentrosymmetric, apolarized, ditungsten complex $W_2(\mu\text{-}H)_2(O^iPr)_4(DMPE)_2$.

2. Computational details

The structure of $W_2(PH_3)_4(OH)_4(H)_2$ was generated by using bond lengths and angles from the crystal structure of $W_2(\mu\text{-}H)_2(O^iPr)_4(DMPE)_2$ [1] and was idealized to C_{2v} symmetry.. The chelating DMPE ligands have been replaced with PH_3 units and the alkoxides have been substituted with OH groups as they were in the calculations for the dimolybdenum complex. The positions of the bridging hydride ligands have been taken from the optimization performed using the program XHYDEX [8]. Various bond lengths and angles that were used are: W–W 2.496 Å, W–P_a (a = out of the W–W–H–H plane, 'out-of-plane') 2.424 Å, W–P_b (b = in the W–W–H–H plane, 'in-plane') 2.486 Å, W–O_a 1.982 Å, W–O_b 1.937 Å, W–H 1.870 Å, O–H 0.958 Å, P–H 1.415 Å, W–W–P_a 97.49°, W–W–P_b 130.32° W–W–O_a 99.35°, W–W–O_b 120.0°, W–O_a–H 123.85° W–O_b–H 133.40° and W–P–H 110.0°.

3. Discussion

A molecular orbital diagram constructed from the results of the Fenske–Hall calculation on $W_2(PH_3)_4(OH)_4(H)_2$ is presented in Fig. 1. This bonding scheme has been prepared via a fragment MO approach in which calculations on the neutral fragments $W_2(PH_3)_4(OH)_4$ and H_2 were converged separately. The orbitals of these two fragments were then allowed to interact via a transformed calculation. The fragment orbitals of the $W_2(PH_3)_4(OH)_4$ unit resemble those that were previously found [2] for $Mo_2(PH_3)_4(OH)_4$ using the DV-Xα computational method. The highest occupied fragment orbital ($1b_2$) contains the in-plane W–W π bond; the two W–W π bonds are not degenerate because of the different in-plane and out-of-plane W–W–P angles. The next most stable fragment orbital

($1a_2$) has mostly W $5d_{xy}$ character, but this orbital is essentially a tungsten lone pair because it contains such a high percentage (92%) of W character from only the tungsten atom to which the PH_3 groups are bonded. The next two most stable occupied fragment orbitals are the out-of-plane W–W π bond ($1b_1$) and the W–W σ bond ($1a_1$). Therefore, in this neutral fragment the bond order is three just as for the neutral Mo_2 compound.

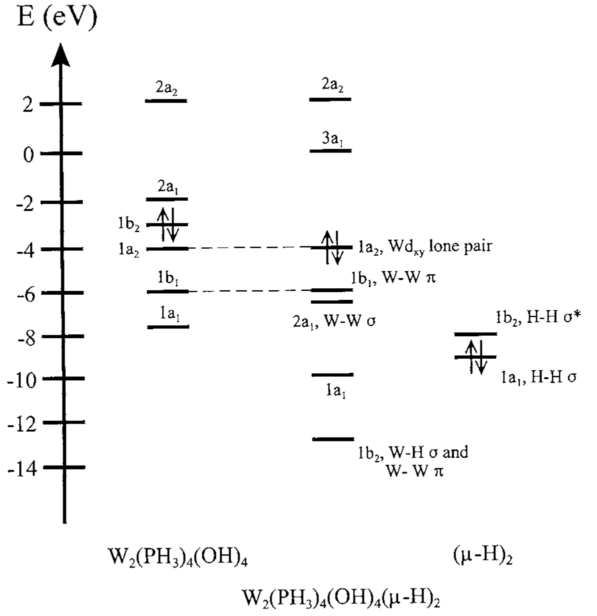

Fig. 1. Molecular orbital diagram of $W_2(PH_3)_4(OH)_4(\mu\text{-}H)_2$ prepared by mixing the orbitals of the $W_2(PH_3)_4(OH)_4$ and (μ-H)$_2$ fragments.

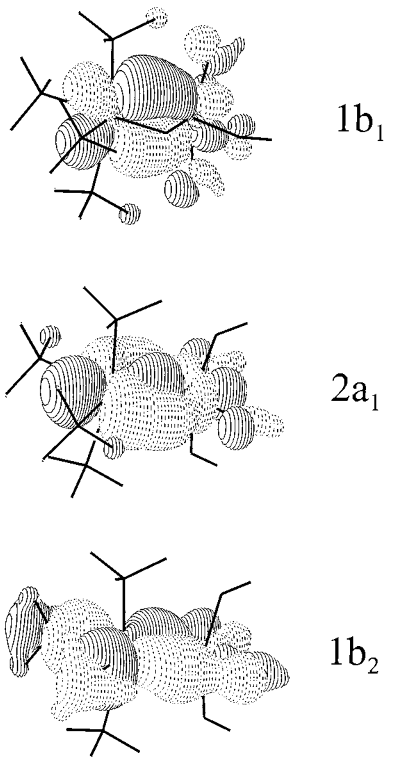

Fig. 2. Contour plots of orbitals $1b_1$ (W–W π), $2a_1$ (W–W σ), and $1b_2$ (W–H σ) of $W_2(PH_3)_4(OH)_4(\mu\text{-}H)_2$.

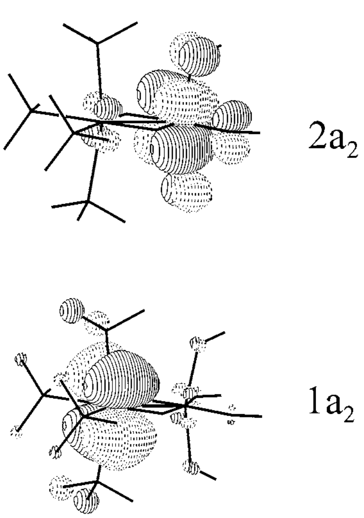

Fig. 3. Contour plots of orbitals $1a_2$ and $2a_2$ of $W_2(PH_3)_4(OH)_4(\mu\text{-}H)_2$.

Addition of the H_2 fragment allows the molecular orbitals of $W_2(PH_3)_4(OH)_4(\mu\text{-}H)_2$ to be determined and the resulting orbitals support the assignment of a W–W bond order of two for the system. In a molecule of dihydrogen, of course, there are two combinations of the H 1s AOs that give rise to the σ and σ* molecular orbitals of H_2. The symmetric combination possesses a_1 symmetry in the C_{2v} point group while the antisymmetric combination has b_2 symmetry. The $W_2(PH_3)_4(OH)_4$ valence fragment orbital that possesses a_1 symmetry and can therefore interact with the symmetric combination of the H 1s AOs is the W–W σ bond ($1a_1$). The result is the formation of the third and fourth highest occupied molecular orbitals ($2a_1$ and $1a_1$, respectively) of $W_2(PH_3)_4(OH)_4(\mu\text{-}H)_2$. Both of these orbitals possess W–W σ bonding character, but the less stable of the two is located primarily on the metal atoms while the more stable molecular orbital is located largely on the bridging hydrogen atoms. The less stable of these two molecular orbitals is the W–W σ bond, shown in Fig. 2. The π bond ($1b_1$), also shown in Fig. 2, of the $W_2(PH_3)_4(OH)_4^{2-}$ fragment has b_1 symmetry and cannot interact with either combination of the H 1s AOs. As a result, this orbital possesses essentially the same energy as it did in the fragment calculation. Likewise, the d_{xy} W lone pair ($1a_2$; shown in Fig. 3) has a_2 symmetry and does not interact with the bridging hydrogens.

The less stable W–W π bond ($1b_2$) of the $W_2(PH_3)_4(OH)_4$ fragment, unlike the more stable π bond ($1b_1$) and the σ bond ($1a_1$), is destroyed upon addition of the bridging hydrogens to form the W–H bonds. This π bond and the antisymmetric combination of the H 1s AOs each have b_2 symmetry, and the π bond, unlike the W–W σ bond, has lobes directed toward the bridging hydrogens. The result is the formation of strong W–H bonds and the removal of the W–W π bond from the metal-metal bonding region of the MO diagram. Note, though, that the W–W σ bond is not destroyed by interacting with the bridging hydrides. Rather, it is slightly destabilized and the metal–metal bonding character is maintained. The W–W bond is therefore double, comprised of the W–W d_{z5} σ and d_{yz} π bonds.

As was mentioned in the Xα calculations on $Mo_2(PH_3)_4(OH)_4$, a metal–metal δ bond is not formed because of the energy difference between the metal d_{xy} AOs, which are energetically separated from each other as a result of interactions with the lone pairs of their respective ligands. Plots of the W d_{xy} orbitals in the MO calculation of $W_2(PH_3)_4(OH)_4(H)_2$ are shown in Fig. 3. It can be seen from orbital $2a_2$ that there are four p_π-type lone pair orbitals on the OH groups that are capable of interacting with the W $5d_{xy}$ atomic orbital, thereby destabilizing this tungsten orbital and preventing it from forming a δ bond with the d_{xy} orbital on the other tungsten atom. In the contour plot of orbital $1a_2$ (the W d_{xy} lone pair), it can be seen that the orbital is essentially completely comprised of the W $5d_{xy}$ orbital; the phosphine ligands do not have p_π lone pairs to destabilize this W AO. Using polarization functions on the P atoms a bonding interaction is formed between the phosphorus and tungsten atoms; the use of these extra orbitals on the ligands gives an indication of the orbital interactions possible when the phosphines can π-accept electron density from the metal centers via hyperconjugation. The W lone pair can therefore be stabilized even further and the separation between the W d_{xy} orbitals on the two metal centers can be made to increase. According to the Fenske–Hall calculation, the energy gap between the W d_{xy} orbitals increases from 4.7 to 6.3 eV. Ultimately though, the more diffuse valence orbitals of the tungsten atoms do not help to create more of a δ bond between the two atoms. The presence on one of the tungsten atoms of substituents possessing lone pairs and on the other of ligands capable of accepting electrons is enough to prevent the formation of a metal-metal bond.

4. Conclusion

From this molecular orbital investigation of the bonding in the polarized molecule $W_2(PH_3)_4(OH)_4(\mu\text{-}H)_2$, it is evident that the compound possesses a W–W double bond composed of one σ bond and one π bond. A second W–W π bond is lost upon formation of the W–H bonds and a δ bond cannot be formed because of the electron donor ability of the alkoxide groups on one of the tungsten atoms.

Thus, in contrast to $Mo_2(OH)_4(PH_3)_4$, which has a Mo–Mo configuration of $\sigma^2\pi^4\delta^2_{nb}$ and a formal Mo–Mo triple bond, the W–W bonding configuration in $W_2(PH_3)_4(OH)_4(\mu\text{-}H)_2$ is $\sigma^2\pi^2\delta^2_{nb}$. The introduction of the two μ-H ligands effectively removes one of the W–W π bonds and mixes W–W and W–H σ bonding, but with the result that at least one molecular orbital can still be identified as a metal-metal σ bond. An analog with the bonding in diborane can be made in that $B_2H_4^{2-}$ would have a B–B orbital configuration of $\sigma^2\pi^2$, although the B–B distance is indeed too long for the formation of a true B–B σ bond The introduction of the two bridging hydrides to form B_2H_6 effectively removes the B–B π bond, but the remnants of the B–B σ bond are still present in diborane.

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