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Unprecedented $W_2(0)$ quadruply bonded complex supported by π -donor ligands†

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A quadruply bonded complex $W_2(\text{DippF})_2K_2$ with a $W_2(0)$ core was synthesized and structurally characterized. The observed W - W distance of 2.407(1) Å and DFT calculations are consistent to the unprecedented electronic structure in D_{2h} symmetry of $\sigma^2\pi^2\pi^2\delta^2\delta^2\delta^{*2}$ where the HOMO is the δ^* orbital.

The chemistry of W_2 complexes has recently been the subject of renewed interest by many research groups due to its potential in small molecule activation reactions.^{1–7} However, in contrast to the rich chemistry of the other two group 6 bimetallics (Cr_2 and Mo_2), the chemistry of W_2 complexes has been characterized by their propensity to be easily oxidized. In fact, W_2 compounds are so easily oxidized that tetragonal compounds bridged by guanidinate ligands are the most easily ionizable complexes measured to date, and have potential uses as strong reductants.¹

Bimetallic complexes bridged by π -acceptor ligands such as CO allow the formation of singly-bonded staggered complexes such as $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $MnRe(CO)_{10}$ and $Co_2(CO)_8$,^{8–10} whose chemistry has been well-studied. These bimetallic complexes supported by π -acceptor ligands can be considered as being formed by two $M(CO)_5$ fragments that are isolobal with the methyl radical and behave accordingly,^{8–10} yet no W_2 complexes of this type are known to exist. While π -acceptor ligands can help stabilize electron rich metals thanks to back-bonding, ligands of increased basicity, such as π -donors, are needed to support bimetallic complexes with higher oxidation states. The most common ligands of this type are carboxylates, formamidinates, and guanidinate.^{5,11} The lowest oxidation state of W - W bonded complexes when bridged by π -donor ligands is $W(II)$ - $W(II)$. In contrast, dichromium and dimolybdenum bimetallic systems have been isolated with oxidation states of $Cr(I)$ - $Cr(I)$ and $Mo(I)$ - $Mo(I)$. Currently, no tungsten analogs are known, in part, due to the difficulty of

their synthesis. While the $W(I)$ - $W(I)$ complex is still unreported (but still pursued by us and others), herein we report the synthesis and characterization of an *even more* highly reduced $W(0)$ - $W(0)$ bimetallic complex (Figure 1) supported by two DippF ligands (DippF = bis-diisopropylphenyl formamidinate) and its precursors.

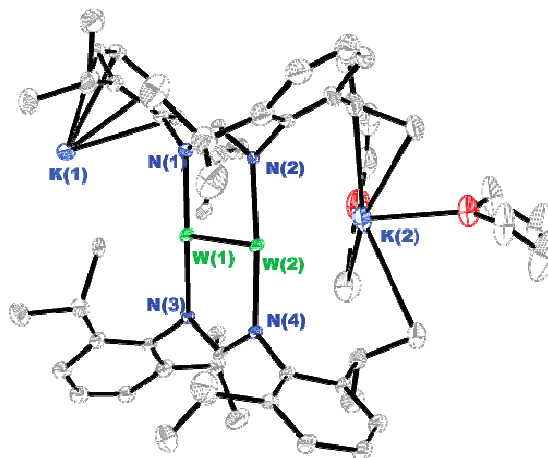


Figure 1. ORTEP diagram of **3** plotted at the 50% probability value. $W(1)$ - $W(1)$ distance 2.407(1) Å, $W(1)$ - $N(1)$ distance 2.08(2) Å.

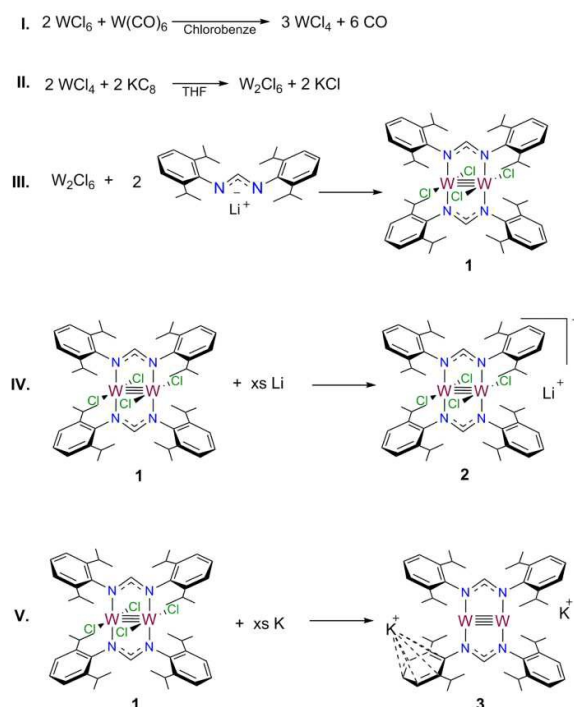
The multi-step synthesis of the title compound starts with WCl_6 as a starting material, which is reacted with $W(CO)_6$ to form WCl_4 as depicted in Scheme 1. Reduction of WCl_4 with KC_8 in the presence of stoichiometric amounts of the lithium salt of DippF, yields the bimetallic precursor **1** (26% yield) which has a W_2^{6+} core. A cyclic voltammogram (CV) of **1**, Figure 3, shows a reversible reduction at -1.28 V (vs Fc/Fc^+) followed by an irreversible reduction at -1.89 V. A third reversible reduction event at -2.28 V is also observed.

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Reduction of **1** with one equivalent of lithium metal in THF yields **2** in 99% yield (see Supplementary Information). Compound **2** has been characterized by x-ray crystallography, and has a W–W bond distance of 2.280(1) Å. This distance is consistent with a bond order of 3.5.¹² NMR spectroscopy shows broad signals consistent with having a paramagnetic sample. EPR spectroscopy shows an anisotropic signal with $g = 1.86$ (Figure S2) also in agreement with similar W–W complexes with bond order of 3.5.^{4,13,14}

Scheme 1. Synthetic pathway for $W_2(\text{DippF})_2K_2$



Reduction of **1** in refluxing THF with excess potassium sand yields **3** in 14% yield (Scheme 1.V). Crystals grown at -10°C from a concentrated solution of **3** in ether were analyzed under single-crystal x-ray diffraction. The structure of **3** is shown in Figure 1. The W–W bond distance of 2.407(1) Å is longer than the range of classical $\sigma^2\pi^4\delta^2$ quadruply bonded complexes (spanning distances between 2.155(2) Å and 2.375(1) Å).^{15,16} The bond distances between the metal center and the N atom in the ligand are between 2.081(2) – 2.121(2) Å. The distances between the potassium cations and the isopropyl groups of the ligand fall in the range of 3.262(6) – 3.303(4) Å. On the other hand the distances between the isopropyl groups and the W atoms are between 2.216(2) – 2.223(6) Å.

DFT calculations were performed on a geometry optimized dianionic model of **3** to gain insight into its electronic structure. The top six highest occupied molecular orbitals of

the model of **3** shows that they all are metal based (Figure 2).

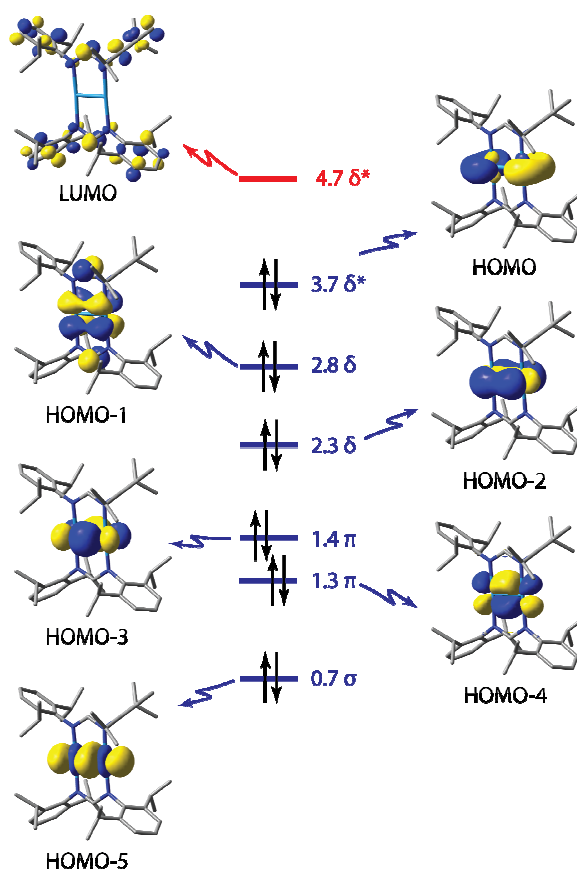


Figure 2. Molecular orbital diagram plotted at the 0.04 isodensity value for a dianionic model of **3**.

Starting from HOMO-5 and going up in energy until the HOMO, we see the molecular orbital manifold of bimetallic systems with D_{2h} symmetry,^{5,17–19} namely a σ -orbital (HOMO-5, 93% metal character), two π -orbitals close in energy (but not degenerate) (HOMO-4 and HOMO-3, 82 and 96% metal character, respectively), a distorted δ -orbital composed by two d_x^2 orbitals (HOMO-2, 87% metal), a second δ -orbital formed by two d_{xy} orbitals (51% metal), and finally a δ^* antibonding orbital as the HOMO (79% metal). The HOMO has a large s orbital contribution to the MO (22% s orbital character vs 20% d orbital character) also consistent with previous calculations on similar W_2 systems.²⁰ This molecular orbital manifold shows that the net bond order of this system is four and it is consistent with the experimentally observed long W–W distance. The electronic spectrum of **3** shows a broad signal from 600 to 350 nm (Figure S7) suggesting the availability of low-lying excited states.²¹

The strong π interactions between the metal and the ligand are described pictorially in Figure 4. The π system of each DippF ligand yields three orbitals composed of different combinations of the NCN p_z orbitals, namely a bonding combination (all p_z orbitals in phase), a non-bonding (no p_z character in the central C atom), and an antibonding orbital combination (left side of Figure 4, from bottom to top). Since there are two DippF ligands, the in-phase and out-of-phase

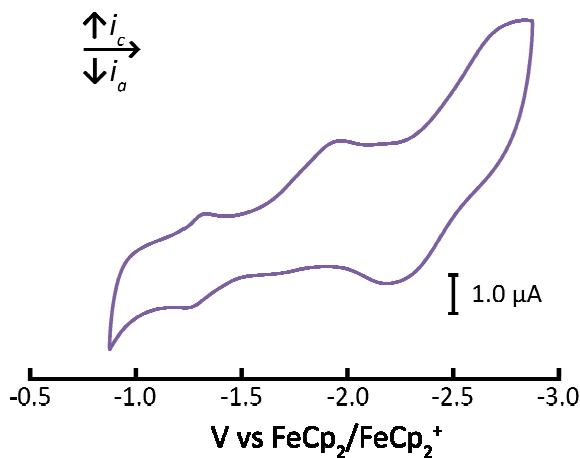


Figure 3. Cyclic voltammogram of **1** depicting two reversible redox events and one non-reversible oxidation.

interactions of each are expected. In an idealized D_{2h} symmetry each combination has the following Mulliken labels: b_{3g} , b_{1u} for bonding, a_u , b_{2g} for non-bonding and b_{3g} , b_{1u} for antibonding. The bonding and nonbonding orbitals are occupied, while the antibonding orbital is not.²²

The out-of-phase combinations of the bonding, non-bonding and antibonding (b_{3g} , a_u , and b_{3g} respectively) interact with one set of the δ and δ^* . The ligand based antibonding b_{3g} interacts with the b_{3g} δ orbital. The empty π^* b_{3g} stabilizes the delta b_{3g} in a back-bonding interaction. In the potassium salt of the deprotonated DippF ligand the carbon-nitrogen distances of the NCN π system are 1.312(3) and 1.319(3) Å.²³ When DippF is associated to the ditungsten core, W_2 , in **3** those distances increase to 1.37(3) and 1.36(3) Å, suggesting that the b_{3g} antibonding ligand orbital is occupied, and consistent with the depicted molecular orbital in Figure 4.²⁴ Three signals of different intensity were observed in the Raman spectrum of **3** (Figure S3). We assigned these vibrations with the aid of DFT calculations. Strong signals at 343.7 and 421.8 cm^{-1} are attributed to ligands vibrations while a signal centered at 299.4 cm^{-1} corresponds to the tungsten-tungsten vibration which is in the range of quadruply bonded systems.¹³ To the best of our knowledge, compound **3** is the first example of a M_2 core with a metal center in the zero oxidation state with π -donating ligands. Moreover, the low oxidation state of the metal centers makes this an unprecedented electron rich metal core. We are currently working on oxidizing **3** to yield the $W(I)$ - $W(I)$ analog to those of the Cr_2 and Mo_2 quintuply bonded complexes,^{5,17,19} as well as exploring its reactivity.

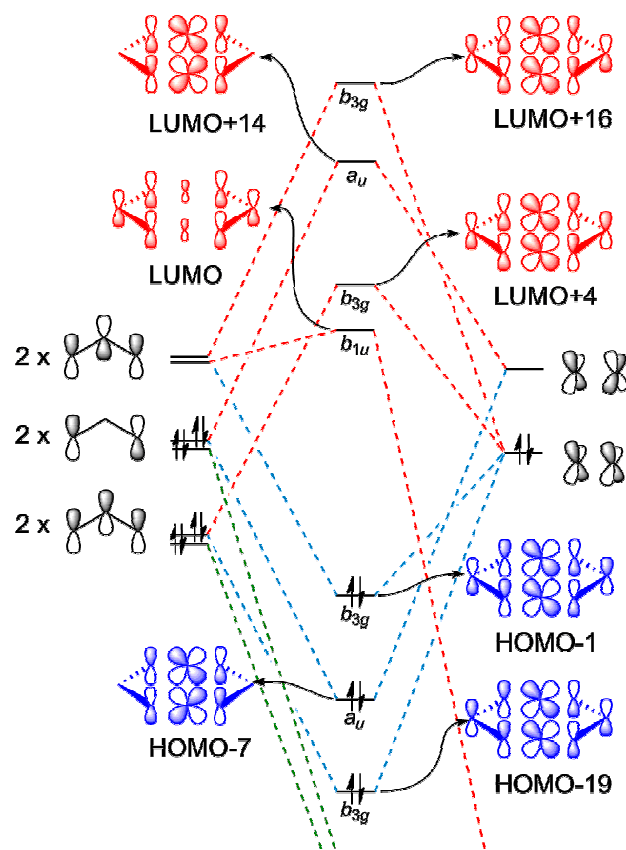


Figure 4. Molecular orbital depicting ligand-metal interactions of compound **3**

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Notes and references

- (1) Cotton, F. A.; Donahue, J. P.; Lichtenberger, D. L.; Murillo, C. A.; Villagrán, D. *J. Am. Chem. Soc.* **2005**, *127* (31), 10808.
- (2) Dolinar, B. S.; Berry, J. F. *Dalton Trans.* **2014**, 43 (16), 6165.
- (3) Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1991**, *113* (23), 8709.
- (4) Ventura, K.; Veleta, J. M.; Metta-Magaña, A.; Villagrán, D. *Inorganica Chim. Acta* **2015**, *424*, 286.
- (5) Tsai, Y.-C.; Chen, H.-Z.; Chang, C.-C.; Yu, J.-S. K.; Lee, G.-H.; Wang, Y.; Kuo, T.-S. *J. Am. Chem. Soc.* **2009**, *131* (35), 12534.

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Journal Name

- (6) Kol, M.; Schrock, R. R.; Kempe, R.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116* (10), 4382.
- (7) Nippe, M.; Goodman, S. M.; Fry, C. G.; Berry, J. F. *J. Am. Chem. Soc.* **2011**, *133* (9), 2856.
- (8) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20* (5), 1609.
- (9) Sweany, R. L.; Brown, T. L. *Inorg. Chem.* **1977**, *16* (2), 415.
- (10) Brimm, E. O.; Lynch, M. A.; Sesny, W. J. *J. Am. Chem. Soc.* **1954**, *76* (14), 3831.
- (11) Bailey, P. J.; Pace, S. *Coord. Chem. Rev.* **2001**, *214* (1), 91.
- (12) While the crystal structure of **1** has not yet been obtained we can compare this W-W distance to the triple bonded W2tpg2Cl4 (where tpg is the anion of N,N',N''-triphenylguanidine) that has a W-W bond distance of 2.261(2), consistent with the stronger basicity of the guanidinate ligand.
- (13) Eglin, J. L. In *Multiple Bonds Between Metal Atoms*; Springer US; pp 183–202.
- (14) While we have probed and spectroscopically characterized the second reduction event yielding a putative W(I)-W(I) quintuply bonded complex, the crystal structure of this has remained elusive, and it is not a matter of this communication.
- (15) Eglin, J. L.; Smith, L. T.; Staples, R. J.; Valente, E. J.; Zubkowski, J. D. *J. Organomet. Chem.* **2000**, *596* (1–2), 136.
- (16) Cotton, F. A.; Murillo, C. A. In *Multiple Bonds Between Metal Atoms*; pp 183–202.
- (17) Nguyen, T.; Sutton, A. D.; Brynda, M.; Fettinger, J. C.; Long, G. J.; Power, P. P. *Science* **2005**, *310* (5749), 844.
- (18) Murillo, C. A. *Comments Inorg. Chem.* **2015**, *35* (1), 39.
- (19) Noor, A.; Kempe, R. *Inorganica Chim. Acta* **2015**, *424*, 75.
- (20) Landis, C. R.; Weinhold, F. *J. Am. Chem. Soc.* **2006**, *128* (22), 7335.
- (21) These excited states would be antibonding in nature with respect to the W-W bond, and thus consistent with the observed long W-W bond.
- (22) The in-phase combination of each of these ligand orbitals do not have the symmetry to interact with the metal d orbitals (b1u, b2g), and they are not depicted graphically except for the b1u of the antibonding that is LUMO and has some interaction with metal π orbitals.
- (23) Cole, M. L.; Junk, P. C. *J. Organomet. Chem.* **2003**, *666* (1–2), 55.
- (24) In compound **2** the NCN distances are of 1.3214 and 1.3404 Å consistent with the metal-ligand interactions.