

Preliminary communication

# Reversible carbon–hydrogen bond oxidative addition across a W–W multiple bond<sup>1</sup>

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## Abstract

As previously reported, the reaction between  $W_2(NMe_2)_6$  and 2,2'-methylenebis(6-*tert*-butyl-4-methyl-phenol), HO–CH<sub>2</sub>–OH, in hydrocarbon solvents leads to  $W_2(\mu-H)(\mu-NMe_2)(\eta^2-O-CH_2-O)(\eta^3-O-CH-O)(HNMe_2)(NMe_2)$ , **1**, by oxidative cyclometallation to the ditungsten center. Upon heating **1** to greater than 60°C under dynamic vacuum  $W_2(NMe_2)_2(\eta^2-O-CH_2-O)_2$ , **2**, is formed with elimination of HNMe<sub>2</sub>. Compound **2** is proposed to have an ethane-like O<sub>2</sub>NW≡WO<sub>2</sub>N core based on NMR data. Addition of HNMe<sub>2</sub> to **2** at room temperature converts **2** to **1**. The addition of other neutral ligands (pyridine, PMe<sub>3</sub>) to hydrocarbon solutions of **2** promotes the C–H oxidative addition to the W<sub>2</sub> center and the pyridine adduct  $W_2(\mu-H)(\mu-NMe_2)(NMe_2)(py)(\eta^2-O-CH_2-O)(\eta^3-O-CH-O)$ , **3**, has been fully characterized by an X-ray study. Addition of PMe<sub>3</sub> to **2** at low temperatures reveals that Lewis base association occurs prior to C–H activation. There is no evidence for an agostic interaction for **2** by NMR or IR spectroscopy.

**Keywords:** Tungsten; Alkoxide; Metal–metal bond; Oxidative addition

Although oxidative-addition and reductive-elimination reactions are well documented for compounds with M–M multiple bonds [1,2], there are very few that are reversible and allow for the establishment of a catalytic cycle [3]. The reversible uptake of H<sub>2</sub> by Cp<sub>2</sub>W<sub>2</sub>Cl<sub>4</sub> [4] and W<sub>2</sub>(X)<sub>2</sub>(silox)<sub>4</sub> [5], where Cp' = C<sub>5</sub>H<sub>4</sub>Pr, X = Cl and H, and silox = OSi<sup>t</sup>Bu<sub>3</sub>, provide to our knowledge the only simple reversible interconversions of M–M triple and double bonds; in Ref. [5], reversible cyclometallation involving a silox ligand with the elimination of H<sub>2</sub> was observed upon heating W<sub>2</sub>(H)<sub>2</sub>(silox)<sub>4</sub>. We describe here the first reversible oxidative addition of a C–H bond to a ditungsten center which interconverts W–W triple and double bonds.

The reaction between  $W_2(NMe_2)_6$  and 2,2'-methylenebis(6-*tert*-butyl-4-methyl-phenol), HO–CH<sub>2</sub>–OH in toluene or hexane at 22°C leads to the replacement of only four NMe<sub>2</sub> ligands and a product  $W_2(\mu-H)(\mu-NMe_2)(NMe_2)(\eta^2-O-CH_2-O)(\eta^3-O-CH-O)(HNMe_2)$ , **1**, wherein one of the O–CH<sub>2</sub>–O diolate ligands has

undergone C–H activation to the W<sub>2</sub> center [6]. The structure of **1** has been previously reported, and the presence of the W<sub>2</sub>(μ-H) signal in the <sup>1</sup>H NMR spectrum in C<sub>6</sub>D<sub>6</sub> is clearly identifiable at δ 11.54 with  $J^{W-H} = 129$  and 95 Hz. We now find when **1** is heated in a dynamic vacuum at 60°C for 10 min that HNMe<sub>2</sub> is evolved and the compound  $W_2(NMe_2)_2(\eta^2-O-CH_2-O)_2$ , **2**, is formed.

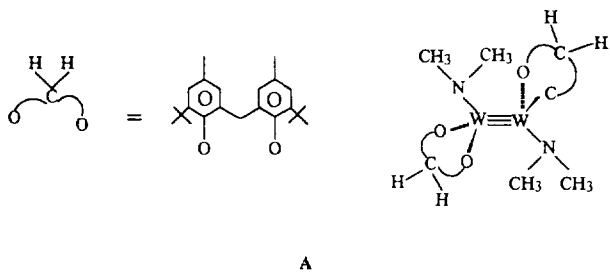
<sup>1</sup>H NMR data for **2**, C<sub>6</sub>D<sub>6</sub> at 22°C, 300 MHz: δ 7.20 and 6.90 (8 H, s, aromatic-CH); 4.75 (2H, *J* = 15 Hz, d, CH<sub>a</sub>); 4.40 (6 H, s, NCH<sub>3</sub>); 3.75 (2H, *J* = 15 Hz, d, CH<sub>b</sub>); 2.05 (12 H, s, aromatic-CH<sub>3</sub>); 1.62 (36 H, s, *tert*-Bu); 1.60 (6 H, s, NCH<sub>3</sub>). Anal. Found: C, 52.43; H, 6.21; N, 2.47. C<sub>50</sub>H<sub>72</sub>O<sub>4</sub>N<sub>2</sub>W<sub>2</sub>. Calc.: C, 53.01; H, 6.40; N, 2.47%.

The structure of **2** can be reliably formulated as that depicted by **A** (below) based on the <sup>1</sup>H NMR spectrum, which shows only one type of O–CH<sub>2</sub>–O ligand having equivalent <sup>1</sup>Bu, Me, and aromatic protons (see NMR data above). The molecule must have a time-averaged mirror plane of symmetry. The O–CH<sub>2</sub>–O protons form an AX spectrum, as one is proximal and the other distal with respect to the W≡W bond. Similarly, there is only one type of NMe<sub>2</sub> group, but restricted rotation about the W–N bond leads to downfield (proximal) and up-

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<sup>1</sup> Dedicated to Professor M.L.H. Green on the occasion of his 60th birthday.

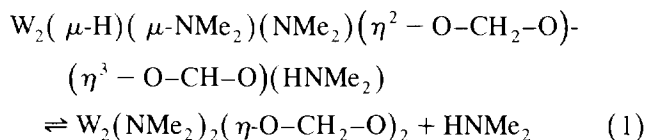
field (distal) *N*-methyl resonances [7]. For  $\text{Mo}_2(\text{NMe}_2)_2(\eta^2\text{-O-CH}_2\text{-O})_2$  we have obtained [8] the X-ray structure of the gauche form of the related complex, which in solution shows similar NMR properties to **2**, indicating that gauche  $\rightleftharpoons$  anti isomerization is facile on the NMR time scale. Thus, we cannot rule out that **2** may crystallize in the gauche rotamers.



The  $^1\text{H}$  NMR spectrum of **2** is, however, quite different from that of the structurally characterized compound  $\text{Mo}_2(\text{NMe}_2)_2(\mu\text{-O-CH}_2\text{-O})_2$ , which has  $C_2$  symmetry with the  $\mu\text{-O-CH}_2\text{-O}$  ligands spanning the  $\text{Mo}\equiv\text{Mo}$  triple bond to form nine-membered rings [6].

The addition of  $\text{HNMe}_2$  to a hydrocarbon solution of **2** at room temperature regenerates **1**, and the dynamic

equilibrium shown in Eq. (1) can be monitored by variable-temperature  $^1\text{H}$  NMR spectroscopy in toluene- $d_8$ . The interconversion of **1** and **2** in Eq. (1) has been monitored for many cycles and in the absence of air and moisture no side reactions have been observed.



A question arises: does the formation of **1** occur by a reversible C–H activation at the  $\text{W}_2$  center followed by trapping in the presence of  $\text{HNMe}_2$ , or is it that addition of  $\text{HNMe}_2$  promotes the C–H activation?

We are not in a position to provide an unequivocal answer at this time, but we can present evidence which is consistent with the latter pathway, namely that Lewis base association promotes C–H activation.

(1) We have examined the C–H coupling constants for the O–CH<sub>2</sub>–O groups of **2** and find these to be normal. ( $J_{\text{C-H}} = 128\text{ Hz}$  for  $\text{CH}_a$  and  $\text{CH}_b$ ). If an agostic M–H–C interaction were present in **2** then a smaller  $J_{\text{C-H}}$  might have been observed [9].

(2) The C–H oxidative addition is promoted by Lewis bases other than  $\text{HNMe}_2$ , thereby ruling out some potential role of the N–H groups in facilitating C–H activation. The addition of pyridine, for example,

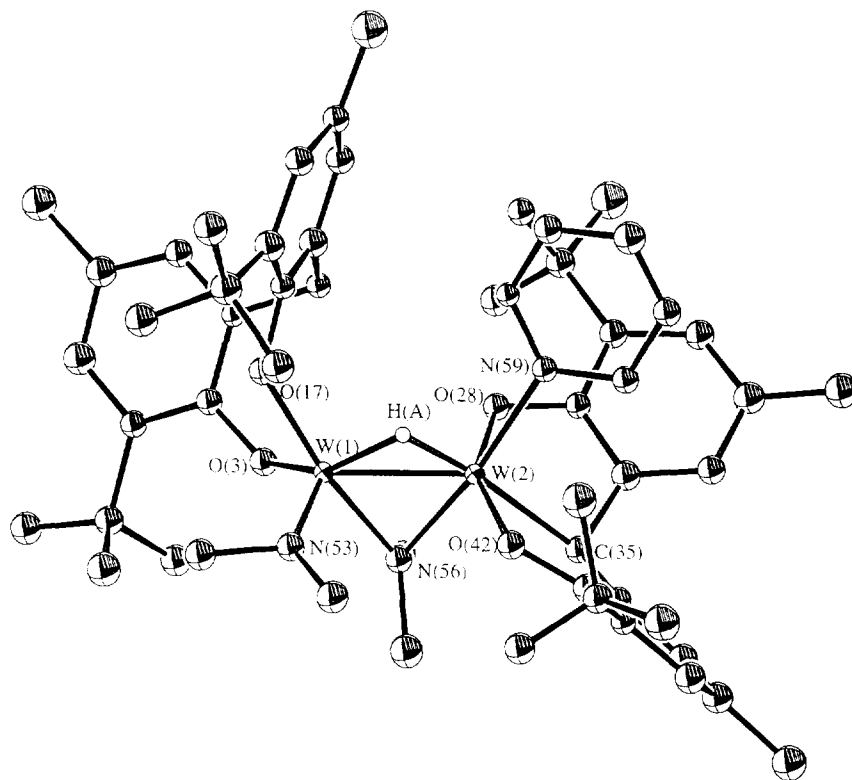


Fig. 1. An ORTEP drawing of compound **3**. Selected bond distances ( $\text{\AA}$ ) and angles (deg) are:  $\text{W}(1)\text{-W}(2) = 2.4704(14)$ ;  $\text{W}(1)\text{-O}(3) = 1.995(13)$ ;  $\text{W}(1)\text{-O}(17) = 1.936(16)$ ;  $\text{W}(1)\text{-N}(53) = 1.871(14)$ ;  $\text{W}(1)\text{-N}(56) = 2.137(22)$ ;  $\text{W}(1)\text{-H(A)} = 1.5709(9)$ ;  $\text{W}(2)\text{-O}(28) = 1.949(12)$ ;  $\text{W}(2)\text{-O}(42) = 1.990(10)$ ;  $\text{W}(2)\text{-C}(35) = 2.243(23)$ ;  $\text{W}(2)\text{-N}(59) = 2.233(15)$ ;  $\text{W}(2)\text{-N}(56) = 2.149(14)$ ;  $\text{W}(2)\text{-H(A)} = 1.4817(11)$ ;  $\text{O}(3)\text{-W}(1)\text{-O}(17) = 86.4(6)$ ;  $\text{O}(28)\text{-W}(2)\text{-O}(42) = 152.5(3)$ ;  $\text{W}(1)\text{-N}(56)\text{-W}(2) = 70.4(7)$ ;  $\text{W}(1)\text{-H(A)}\text{-W}(2) = 108.01(6)$ .

to hydrocarbon solutions of **2** at room temperature leads to  $W_2(\mu-H)(\mu-NMe_2)(NMe_2)(\eta^2-O-CH_2-O)(\eta^3-O-CH-O)(py)$ , **3**, which has been structurally characterized.

Summary of crystal data for  $C_{66}H_{72}N_3O_4W_2 \cdot 1/2C_3H_5N$  at  $-172^\circ C$ :  $a = 21.834(13) \text{ \AA}$ ,  $b = 16.952(9) \text{ \AA}$ ,  $c = 31.332(18) \text{ \AA}$ ,  $\beta = 110.04(2)^\circ$ ,  $Z = 8$ ,  $d_{\text{calcd}} = 1.516 \text{ g cm}^{-3}$ , space group  $C2/c$ ,  $V = 10895(10) \text{ \AA}^3$ . Of 11 665 reflections collected ( $MoK\alpha$   $6 < 2\theta < 45^\circ$ ), 5181 had  $F > 2.33\sigma(F)$  and were used in the least squares refinement. A peak located in the expected region for a  $\mu-H$  atom was found, H(A), and was included in the final cycles of refinement as a fixed atom contributor. Final residuals are  $R(F) = 0.0618$  and  $Rw(F) = 0.0579$ . Only the W atoms were anisotropically refined.

An ORTEP view of the molecular structure of **3** is shown in Fig. 1 and reveals the close similarity to **1**. The  $\mu$ -hydride is seen in the  $^1H$  NMR spectrum at  $\delta$  11.1 flanked by coupling to  $^{183}W$ ,  $I = \frac{1}{2}$ , 14.5% nat. abundance,  $J = 128$  and 88 Hz.

(3) When the addition of  $PMe_3$  to a toluene- $d_8$  solution of **2** is carried out in an NMR tube at low temperature, and the  $^1H$  and  $^{31}P\{^1H\}$  spectra are recorded with increasing temperature, there is first the appearance of a  $^{31}P$  signal for a coordinated  $PMe_3$  ligand at  $-70^\circ C$ . No hydride signal is observed until the temperature is raised to ca.  $-20^\circ C$ , at which time a new  $^{31}P\{^1H\}$  signal grows in along with a  $^1H$  signal at  $\delta$  12.4 which now appears as a doublet due to coupling to  $^{31}P$ ,  $I = \frac{1}{2}$ , 100% nat. abundance,  $J = 9$  Hz, flanked by satellites due to coupling to two inequivalent tungsten nuclei,  $J = 127$  and 90 Hz.

In conclusion we have discovered a rare, if not the first, example of the reversible C–H oxidative-addition to an M–M multiple bonded complex. (Irreversible cyclometallation of  $PPh_3$  ligands at  $[Rh-Rh]^{4+}$  centers has been noted previously. See Ref. [1] and references cited therein.) In the present case this is facilitated by a favorable cyclometallation reaction and by Lewis base association. The intimate mechanism of this reaction is under further investigation.

### Acknowledgements

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