

# Alcoholysis of *gauche*-1,2-( $\eta^3$ -Cp)<sub>2</sub>W<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>: Structural evidence for W≡W bond cleavage and proton transfer to bound cyclopentadiene

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## Abstract

1,2-Cp<sub>2</sub>W<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> undergoes W≡W bond scission in the presence of excess aliphatic alcohols ROH where R = Me, Et, Pr<sup>n</sup> giving yellow, crystalline Cp<sub>2</sub>WH<sub>2</sub> and presumably W(OR)<sub>6</sub>. In reactions with excess CF<sub>3</sub>CH<sub>2</sub>OH, two crystalline products are obtained from the pentane wash of the crude product. The first product is formulated as 1,1-W<sub>2</sub>( $\eta^5$ -Cp)( $\eta^3$ -C<sub>5</sub>H<sub>7</sub>)( $\mu$ -OCH<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(OCH<sub>2</sub>CF<sub>3</sub>)<sub>4</sub>, (W–W, 2.705(1) Å avg. for two independent molecules) wherein six equivalents of CF<sub>3</sub>CH<sub>2</sub>OH have reacted with the amide precursor. The unusual  $\eta^3$ -C<sub>5</sub>H<sub>7</sub> ligand present in this compound arises from the transfer of two protons to one of the Cp rings. The second product is formulated as the complex salt [W(OCH<sub>2</sub>CF<sub>3</sub>)<sub>6</sub>] [H<sub>2</sub>NMe<sub>2</sub>][Cp<sub>2</sub>W(H)<sub>x</sub>(OCH<sub>2</sub>CF<sub>3</sub>)] wherein a H<sub>2</sub>NMe<sub>2</sub> cation bridges the neutral W(OR)<sub>6</sub> moiety and the Cp<sub>2</sub>W(H)<sub>x</sub>(OCH<sub>2</sub>CF<sub>3</sub>) (x = 1 or 2) anion through hydrogen bonding. The formation of the alcoholysis products suggests the importance of oxidative addition in the mechanism of alcoholysis of ditungsten dimethylamides.

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1,2-W<sub>2</sub>R<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> compounds are well-explored templates for the organometallic chemistry associated with the (W≡W)<sup>6+</sup> unit [1]. When R = Et, Pr, or Bu, these compounds undergo alcoholysis reactions with R' OH to form both W<sub>2</sub>R<sub>2</sub>(OR')<sub>4</sub> and W<sub>2</sub>R(OR')<sub>5</sub>. In the latter, only one equivalent of alkyl ligand is exchanged for alkoxide [2]. Under mild conditions, alcoholysis of these species occurs without complete loss of the alkyl ligands, even in cases where the alkyl ligand contains  $\beta$ -hydrogen atoms. Dimolybdenum dialkylamides are considerably more susceptible to reductive elimination than their tungsten analogues [3,4].

Reactions of 1,2-W<sub>2</sub>Et<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> with propionic anhydride leads to reductive elimination of ethane and ethene, giving the quadruply bonded W<sub>2</sub>(O<sub>2</sub>CET)<sub>4</sub> paddlewheel compound [5]. A similar reaction employing 1,2-W<sub>2</sub>( $\eta^3$ -

Cp)<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> (**1**) gives incomplete loss of the dimethylamide ligands and the formation of 1,2-( $\eta^5$ -Cp)<sub>2</sub>W<sub>2</sub>( $\mu$ -NMe<sub>2</sub>)(O<sub>2</sub>CET)<sub>3</sub> [6]. The recently reported clean and facile alcoholyses of W<sub>2</sub>COT(NMe<sub>2</sub>)<sub>4</sub> to give [W<sub>2</sub>COT(OR)<sub>4</sub>]<sub>n</sub> [n = 1 where R = Bu<sup>t</sup>, Pr<sup>i</sup>, CH<sub>2</sub>Bu<sup>t</sup> and n = 2 where R = Me, Et, Pr] led us to believe that similar reactivity might be observed for **1** given the proper choice of alcohol [7,8]. The X-ray crystal structure of **1** was recently reported [9].

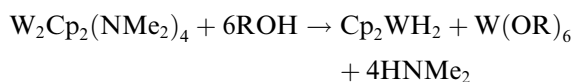
Compound **1** undergoes slow reactions with aliphatic alcohols such as methanol and isopropanol in hydrocarbon solutions [10]. The reaction with MeOH-*d*<sub>4</sub> proceeds slowly enough at room temperature that even after one hour in solution it is possible to obtain <sup>1</sup>H NMR spectra of the dimethylamido compound in 4:1 benzene-*d*<sub>6</sub>:MeOH-*d*<sub>4</sub> mixtures. This resistance to alcoholysis is unusual among the dimethylamido ditungsten compounds, which usually react with aliphatic alcohols in the course of only a few seconds. The light yellow reaction solutions darken over several days when stored at –20 °C, but the solid products obtained by cooling these solutions often contain mostly unreacted dimethylamide starting material as shown by

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$^1\text{H}$  NMR spectroscopy [10]. The reported crystal structure of **1** shows that the ditungsten unit is quite crowded by the  $\eta^3\text{-Cp}$  and dimethylamido ligands [9].

When **1** is dissolved in neat, dry EtOH or Pr<sup>n</sup>OH and left at  $-20^\circ\text{C}$  for ca. 48 h, yellow crystalline needles are obtained. These were first thought to be starting material but single-crystal X-ray diffraction studies revealed that the product was  $\text{Cp}_2\text{WH}_2$  (Fig. 1) [11,12]. The identity of this hydride was also confirmed by comparison with previously reported  $^1\text{H}$  NMR data [12]. No structural record for this hydride was found in the Cambridge Database, however, the compound is isostructural with  $\text{Cp}_2\text{MoH}_2$  [13]. The bis-hydride is formed in yields near 50% based on W. It is believed that the volatile  $\text{W(OR)}_6$  species are also formed according to the following reaction:



It was hoped that the rate of alcoholysis of **1** could be increased by using more acidic alcohols.  $\text{CF}_3\text{CH}_2\text{OH}$  was chosen for such a study due to its relatively high acidity ( $\text{pK}_a = 12.43$ ) [14] and its steric similarity to  $\text{Bu}^i\text{CH}_2\text{OH}$  (neopentanol). The neopentoxide ligand has been shown to provide steric protection for ditungsten and dimolybdenum double and triple bonds [15].

$1,2\text{-W}_2\text{Cp}_2(\text{NMe}_2)_4$  reacts immediately with neat  $\text{CF}_3\text{CH}_2\text{OH}$  to give dark brown solutions accompanied by rapid evolution of gas ( $\text{HNMe}_2$ ).  $^1\text{H}$  and  $^{19}\text{F}$  NMR studies of the gelatinous, brown product, obtained after removal of the excess  $\text{CF}_3\text{CH}_2\text{OH}$ , yield complicated spectra that indicate a variety of products are formed. The pentane washings of this crude material are dark blue. Slow evaporation of the pentane washings, at room temperature, in the drybox gives a mixture of two crystalline products

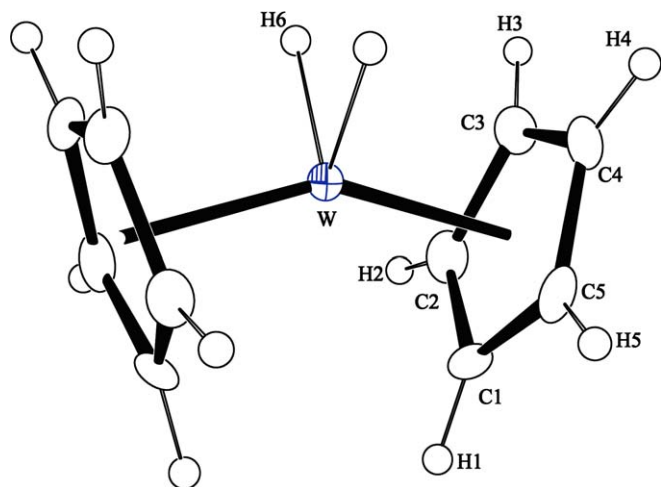


Fig. 1. ORTEP diagram of  $\text{Cp}_2\text{WH}_2$ . The molecule contains a twofold rotation axis. Anisotropic displacement parameters for the non-hydrogen atoms are drawn at the 50% probability level. Pertinent bond distances and angles for  $\text{Cp}_2\text{WH}_2$ : W–H, 1.57(3) Å; W–C (avg.), 2.28(1) Å; H–W–H, 80(2)°. A complete list of pertinent bond distances and angles are included in the [supplementary information](#).

consisting mostly of blue needles with a small amount of interdispersed amber prisms [16]. The product crystals were manually separated and subjected to X-ray crystal structure determination.

The blue needles were shown by X-ray crystallography to be a product formulated as  $1,1\text{-W}_2\text{Cp}(\eta^3\text{-C}_5\text{H}_7)(\text{OCH}_2\text{CF}_3)_6$  (**2**) [17] which contains the unusual  $\eta^3\text{-C}_5\text{H}_7$  ligand. There is one other compound containing such a ligand for which crystallographic data is on deposit in the CCDC:  $\text{Mo}(\eta^5\text{-Cp})(\eta^3\text{-C}_5\text{H}_7)(\text{dppe})$  [18]. The latter compound was synthesized *via* the reaction of  $\text{Cp}_2\text{Mo}(\text{dppe})$  with two equivalents of  $\text{H}^-$ . The asymmetric unit of (**2**) contains two independent molecules, one of which is depicted in Fig. 2.

The amber crystals were shown by X-ray crystallography to be the complex salt  $[\text{W}(\text{OCH}_2\text{CF}_3)_6][\text{H}_2\text{NMe}_2][\text{Cp}_2\text{W(H)}_{x=1,2}(\text{OCH}_2\text{CF}_3)]$  (**3**, Fig. 3) wherein the W–W bond has undergone complete rupture to give two W-containing fragments [19]. Only one hydride ligand was crystallographically located on the tungsten atom within the anionic portion of this salt, but we suspect there might be two hydride ligands on this tungsten atom due to the absence of any evidence of paramagnetism in NMR experiments on the mixture of **2** and **3**. Hydride signals were not detected at high field in the  $^1\text{H}$  NMR of the mixture of **1** and **2** most likely due to the relatively low concentration of **2** and the presence of  $^{183}\text{W-H}$  coupling.

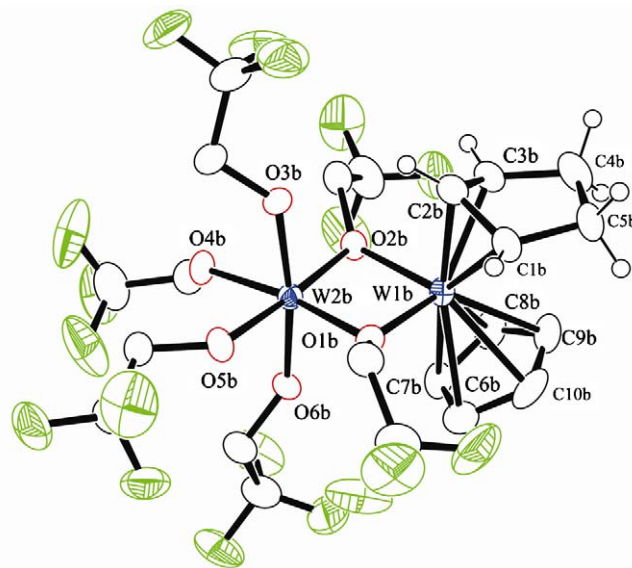


Fig. 2. ORTEP diagram of **2**. Anisotropic displacement parameters for the non-hydrogen atoms are drawn at the 50% probability level. This is one of the two independent but essentially identical dimers within the asymmetric unit of **2**. Alkoxide and  $\eta^5\text{-Cp}$  hydrogen atoms are omitted for clarity. Pertinent bond distances and angles for **2**: C4b–C5b, 1.525(6) Å; W1b–W2b, 2.7134(2) Å; W2b–O1b, 2.016(2) Å; W2b–O2b, 2.032(2) Å; W2b–O3b, 1.901(2) Å; W2b–O4b, 1.979(2) Å; W2b–O5b, 1.959(2) Å; W2b–O6b, 1.897(2) Å; W1b–C1b, 2.211(4) Å; W1b–C2b, 2.129(4) Å; W1b–C3b, 2.220(4) Å; W1b–C<sub>Cp</sub> (avg.), 2.35(1) Å; W1b–W2b–O3b, 96.47(7)°; W1b–W2b–O4b, 140.19(7)°; W1b–W2b–O5b, 131.55(7)°; W1b–W2b–O6b, 91.81(7)°. A complete list of bond distances and angles, for both independent molecules of **2**, is included with the [supplemental information](#).

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