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Alkyne Adducts of $[W_2(OCH_2{}^tBu)_8]_n$ (M = M): Comparisons of Bridging and Terminal Addition Products

Malcolm H. Chisholm,*,† Damon R. Click,† Judith C. Gallucci,† Christopher M. Hadad,† and Paul J. Wilson‡

Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210 and Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

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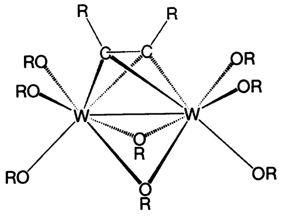
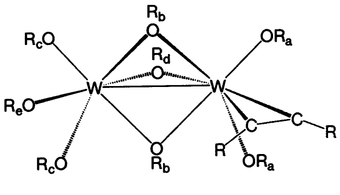
Alkyne adducts of dinuclear metal complexes typically show either μ-perpendicular or μ-parallel modes of alkyne bonding[1] as exemplified by $Co_2(CO)_6(\mu\text{-PhCCPh})$[2] and $Os_2(CO)_8(\mu\text{-RCCR})$.[2,3] Bridged skewed bonding is much less common but is now well documented and has in general an electronic origin arising from a second-order Jahn−Teller distortion.[4] There are also some examples of dinuclear complexes, where other ligands are used to form the bridges and the alkyne is terminal for example, $Cp^*(CO)_2Re(\mu\text{-}CO)Re(CO)(\eta^2\text{-}CH_3C{\equiv}CCH_3)Cp^*$.[5] We describe herein our studies of the alkyne adducts of $[W_2(OCH_2{}^tBu)_8]$ which reveal for the first time the existence of bridged and terminally bonded adducts represented by **A** and **B,** respectively.



A



B

$[W_2(OCH_2{}^tBu)_8]$ (M = M) and each of the alkynes MeCCH, PhCCH, PhCCMe, MeCCMe, and Me_3SiCCH (1 equiv) in hexanes at 25−45 °C, yield 1:1 alkyne adducts as crystalline air-sensitive solids. The molecular structures of the PhCCH, MeCCMe, and PhCCMe adducts are shown in Figures 1, 2, and 3, respectively. For PhCCH a μ-perpendicular mode of alkyne bonding exists with a (C−C)−(W−W) twist angle of 84.1(1)° (μ-perpendicular = 90°), whereas the MeCCMe adduct is severely twisted with a (C−C)−(W−W) twist angle of 67.9(1)° (similar to the μ-ethyne adduct).[6] In contrast, the PhCCMe adduct has an η^2-PhCCMe ligand. Both of the structural types, **A** and **B**, are derived from a confacial-bioctahedral geometry.

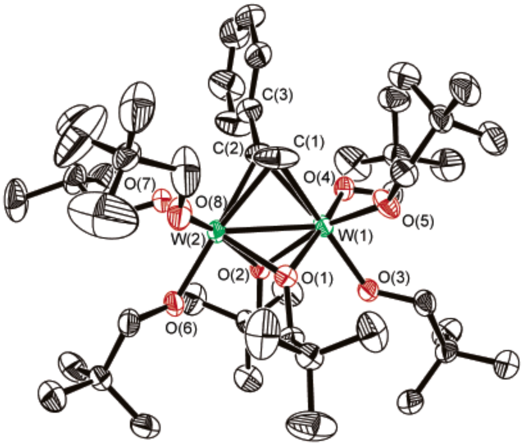


Figure 1. Solid-state molecular structure of $W_2(\mu\text{-}\eta^2,\eta^2\text{-PhCCH})(\mu\text{-}OCH_2{}^tBu)_2(OCH_2{}^tBu)_6$,[11] with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): W(1)−W(2) = 2.5927(2), W(1)−C(1) = 2.195(4), W(1)−C(2) = 2.320(3), W(2)−C(1) = 2.259(4), W(2)−C(2) = 2.237(4), C(1)−C(2) = 1.251(5), (W−W)−(PhC−CH) = 84.1(1).

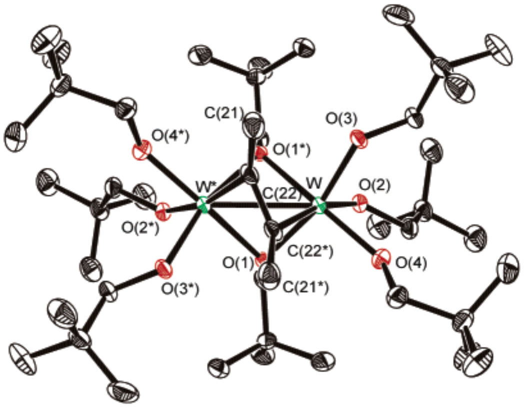


Figure 2. Solid-state molecular structure of $W_2(\mu\text{-}\eta^2,\eta^2\text{-MeCCMe})(\mu\text{-}OCH_2{}^tBu)_2(OCH_2{}^tBu)_6$,[11] with thermal ellipsoids drawn at the 50% probability level. * indicates the following symmetry transformation: $-x + 1$, y, $-z + {}^1/_2$. Selected bond distances (Å) and angles (deg): W−W* = 2.6361(2), W*−C(22) = 2.396(3), W−C(22*) = 2.085(3), C(22)−C(22*) = 1.354 (5), (W−W)−(MeCCMe) = 67.9 (1).

The solution structure of the alkyne adducts can be deduced from NMR spectroscopic studies (^1H, $^{13}C\{^1H\}$). In toluene-d_8 the low-temperature limiting spectrum for the PhCCH adduct is consistent with a μ-perpendicular bridged adduct having C_s symmetry.[7] Significantly, the CH proton of the PhCCH ligand sees two equivalent ^{183}W nuclei as judged from $J_{^{183}W-H}$ and $J_{^{183}W-^{13}C}$ coupling constants (^{183}W, $I = {}^1/_2$, 14.5% nat. abund.). In contrast the Me_3SiCCH adduct also shows C_s symmetry at room temperature, but the related $J_{^{183}W-H}$ and $J_{^{183}W-^{13}C}$ values and the relative intensities of the satellites indicate that the alkyne is bonded to only one tungsten atom.[7] In the case of the adduct involving MeCCH, the isomers **A** and **B** are present in a 75:25 ratio, while for the MeCCMe adduct, which adopts the bridged structure in the solid-state, the ratio of A:B is 10:90 in toluene-d_8. The PhCCMe adduct has an η^2- coordination mode in the solid-state (Figure 3), but is present as a 25:75 **A**:**B** isomer ratio in toluene-d_8. It is thus clear that the

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* To whom correspondence should be addressed. E-mail: chisholm@chemistry.ohio-state.edu.
† The Ohio State University.
‡ University of Bath.

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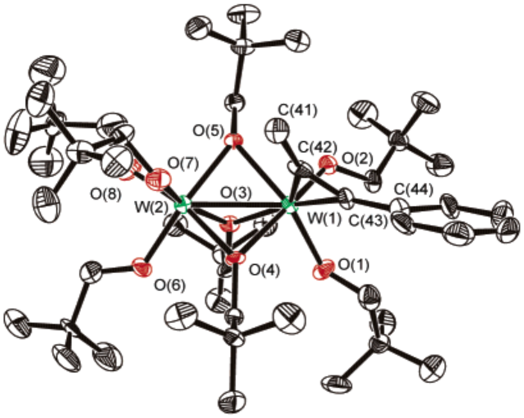

Figure 3. Solid-state molecular structure $W_2(\eta^2\text{-PhCCMe})(\mu\text{-OCH}_2{}^t\text{Bu})_3(\text{OCH}_2{}^t\text{Bu})_5$,[11] with thermal ellipsoids drawn at the 50% probability level.

Table 1. Selected Experimental and DFT Calculated Bond Distances and Angles for $W_2(\eta^2\text{-PhCCMe})(\mu\text{-OCH}_2{}^t\text{Bu})_3(\text{OCH}_2{}^t\text{Bu})_5$

bond	exptl	calcd	bond	exptl	calcd
Distance (Å)			Angle (deg)		
W(1)−W(2)	2.6536(5)	2.71	O(4)−W(1)−O(2)	166.2(2)	167.4
W(1)−C(42)	2.057(9)	2.05	O(4)−W(2)−-O(8)	168.2(3)	169.3
W(1)−C(43)	2.081(9)	2.08	C(42)−W(1)−C(43)	37.9(3)	37.2
C(42)−C(43)	1.35(1)	1.32	C(41)−C(42)−C(43)	140.6(9)	140.2
W(1)−O(1)	1.981(6)	1.99	C(44)−C(43)−C42)	135.8(9)	137.3
W(1)−O(2)	1.922(6)	1.94			
W(1)−O(3)	2.201(6)	2.23			
W(1)−O(4)	2.115(6)	2.15			
W(1)−O(5)	2.158(6)	2.19			
W(2)−O(3)	2.055(6)	2.08			
W(2)−O(4)	2.062(5)	2.08			
W(2)−O(5)	2.069(6)	2.09			
W(2)−O(6)	1.919(6)	1.95			
W(2)−O(7)	1.856(7)	1.89			
W(2)−O(8)	1.914(6)	1.94			

energy difference between the bridged and terminal alkyne adducts is very small and that they readily interconvert in solution. This interconversion, though chemically rapid, is not rapid on the NMR time-scale although we observed that each isomer form is fluxional. Specifically the μ-alkyne adducts show rapid bridge-terminal OR group exchange at room temperature, whereas the η^2-alkyne products are stereochemically rigid on the NMR time-scale at 25 °C. Upon heating, however, the isomers of structural type **B** show selective alkoxide group exchange involving the preferential exchange of alkoxide ligands b, c, d, and e.[9] In the case of the MeCCMe η^2-bound adduct we also observe alkyne rotation by ^1H NMR spectroscopy[7] and we can infer the same for the PhCCMe adduct on the basis of $^{13}C\{^1H\}$ data.[7] Neither alkyne dissociation, nor alkyne exchange occurs in solution.

We have previously noted that many alkoxide-supported clusters of molybdenum and tungsten can be related to later transition metal carbonyl clusters via isolobal relations for example, $d^3\text{-M(OR)}_3$ and $d^9\text{-M(CO)}_3$.[8] If we similarly relate $d^2\text{-W(OR)}_4$ and $d^8\text{-M(CO)}_4$ (M = Fe, Ru, Os)[9] fragments then the alkyne adducts reported here may be contrasted with alkyne adducts of $[\text{Os}_2(\text{CO})_8]$ (M = M)[3] which are well-known to adopt the μ-parallel mode of bonding and may be called dimetallacyclobutenes. Clearly the bonding and structural relationship between alkoxide and carbonyl clusters noted above is a qualitative one.

We are now carrying out electronic structure calculations on a number of alkyne adduct model compounds employing density functional theory where $W_2(\text{OCH}_3)_8$[10] has been employed as the template in place of $W_2(\text{OCH}_2{}^t\text{Bu})_8$. A preliminary calculation has reproduced the ground-state geometry for the PhCCMe alkyne adduct remarkably well (see Table 1). Calculations revealed the similarity in energies of the bridged and η^2- bonded structures (less than 5.6 kcal/mol), and suggest that in the bridged isomer **A,** the interconversion of μ-perpendicular and μ-parallel isomers would have a low energy barrier. The observed structure for the PhCCMe adduct in the solid state (see Figure 3) and the solution behavior attributed to the η^2-bound alkyne adducts indicates a low barrier to metal alkyne bond rotation. However, despite the fluxional nature of the isomers of form **A** and **B**, they do not interconvert on the NMR time scale. Thus, the energy involved for interconversion of μ- and η^2-alkyne ligands must be greater than bridge−terminal alkoxide exchange. Further studies are in progress.

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Supporting Information Available: Crystallographic data for Figures 1, 2, and 3 and full experimental preparations and NMR data for all compounds are given (PDF/CIF). This material is available free of charge via the Internent at http://www.pubs.acs.org

References

(1) Hoffmann, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858−3875.
(2) Sly, W. G.; *J. Am. Chem. Soc.* **1959**, *81*, 18.
(3) Burke, M. R.; Takats, J. *J. Organomet. Chem.* **1986**, *302*, C25.
(4) (a) Calhorda, M. J.; Hoffman, R. *Organometallics* **1986**, *5*, 2187. (b) Cotton, F. A.; Feng, X. *Inorg. Chem.* **1990**, *29*, 3187−3192. (c) Chisholm, M. H.; Lynn, M. A. *J. Organomet. Chem.* **1998**, *550*, 141−150.
(5) (a) Casey, C. P.; Carino, R. S.; Hayashi, R. K.; Schladetzky, K. D. *J. Am. Chem. Soc.* **1996**, *118*, 1617−1623. (b) Casey, C. P.; Carino, R. S.; Sakaba, H. *Organometallics* **1997**, *16*, 419−426.
(6) Chisholm, M. H.; Streib, W. E. Tiedtke, D. B.; Wu, De-Dong. *Chem. Eur. J.* **1998**, *4*, 1470−1479.
(7) Please see Supporting Information for Experimental section.
(8) Chisholm, M. H.; Clark, D. L.; Hampden-Smith, M. J.; Hoffman, D. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 432−444.
(9) (a) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 142.(b) Xie, Y.; Schaefer, H. F., III; King, B. R. *J. Am. Chem. Soc.* **2000**, *122*, 8746−8761 and references therein. (c) Grevels, F.-W.; Klotzbücher, Schrickel, J.; Schaffner, K. *J. Am. Chem. Soc.* **1994**, *116*, 6229−6237.
(10) Electronic structure calculations were carried out using [B3LYP(SDD,6-31G*)] basis sets. Please see Supporting Information for references.
(11) Crystal Stucture data has been deposited with the Cambridge Crystallographic Data Center, Figure 1: CCDC No. 188146; Figure 2: CCDC No. 187844; and Figure 3: CCDC No. 187843.

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