Addition of 1,3-Butadiene to a Metal–Metal Triple Bond. Preparation and Structure of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(C_4H_6)$

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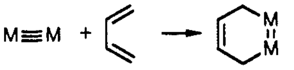
Summary: $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ and butadiene react reversibly in hydrocarbon solvents to give $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}\eta^1{:}\eta^4\text{-}C_4H_6)(py)$ (I), which has been isolated as a blue-black crystalline solid. In solution I exists in equilibrium with $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_n$, where $n = 0$ and 2, and butadiene. The W–W distance of 2.49 Å is suggestive of a M–M double bond. One tungsten atom is in a pseudooctahedral environment, being coordinated by three terminal and two bridging OR ligands along with one carbon of the C_4H_6 ligand. This carbon atom bridges the metal atoms. The second tungsten is coordinated by all four of the butadiene carbon atoms and one terminal and the two bridging OR groups in addition to a pyridine ligand.

$M_2(OR)_6$ (M≡M) compounds (M = Mo, W) provide remarkably versatile templates for the uptake of unsaturated organic molecules.[1] A rich coordination and reaction chemistry has already been noted with respect to alkynes,[1] nitriles,[1] carbon monoxide,[2] ethylene,[3] and allene.[4] We have for some time been intrigued by the possible reaction involving 1,3-butadiene, since this could provide an organometallic analogue of the Diels–Alder reaction (eq 1).



(1)

Of course, because metal–ligand bonding is in general stronger than metal–metal bonding, one might well expect that more metal–carbon bonds would be formed than those realized in a simple cycloaddition reaction that would produce a dimetallacyclohexadiene (eq 1). A number of plausible structures could be anticipated on the basis of the now well-established coordination chemistry of the butadiene ligand to mono- and dinuclear centers.[5]

We describe here the preparation and structural characterization of $W_2(OCH_2\text{-}t\text{-}Bu)_6(C_4H_6)(py)$ (I), which reveals a quite unanticipated and novel mode of coordination.[6]

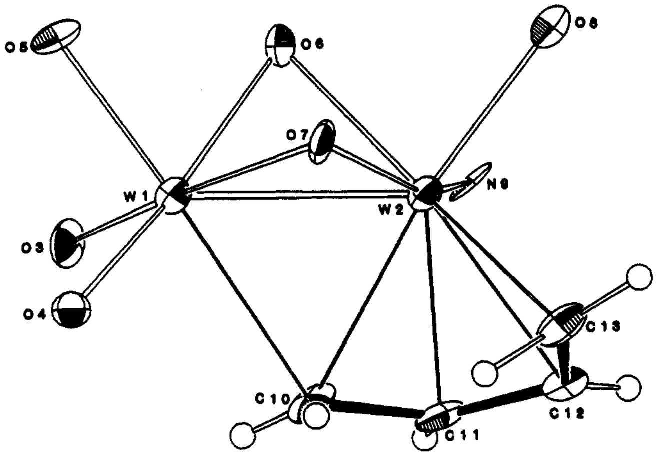


Figure 1. ORTEP drawing of the central $W_2O_6NC_4H_6$ skeleton of the $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(C_4H_6)$ molecule. Selected bond distances (Å) and angles (deg) are as follows: W–W = 2.4706 (8), W(1)–O(3) = 1.909 (7), W(1)–O(4) = 1.918 (7), W(1)–O(5) = 1.987 (7), W(1)–O(6) = 2.078 (7), W(1)–O(7) = 2.083 (7), W(1)–C(10) = 2.443 (10), W(2)–O(6) = 2.095 (7), W(2)–O(7) = 2.146 (7), W(2)–O(8) = 2.049 (7), W(2)–N(9) = 2.221 (8), W(2)–C(10) = 2.318 (11), W(2)–C(11) = 2.242 (10), W(2)–C(12) = 2.279 (10), W(2)–C(13) = 2.255 (10); O(3)–W(1)–O(4) = 95.3 (3), O(3)–W(1)–O(5) = 95.2 (3), O(3)–W(1)–O(6) = 92.4 (3), O(3)–W(1)–O(7) = 168.2 (3), O(3)–W(1)–C(10) = 90.1 (3), O(4)–W(1)–O(5) = 90.2 (3), O(4)–W(1)–O(6) = 169.1 (3), O(4)–W(1)–O(7) = 94.4 (3), O(4)–W(1)–C(10) = 82.8 (3), O(5)–W(1)–O(6) = 81.5 (3), O(5)–W(1)–O(7) = 91.4 (3), O(5)–W(1)–C(10) = 171.6 (3), O(6)–W(1)–O(7) = 78.9 (3), O(6)–W(1)–C(10) = 104.8 (3), O(7)–W(1)–C(10) = 84.5 (3), C(10)–C(11)–C(12) = 118.8 (9), C(11)–C(12)–C(13) = 118.9 (9), W(1)–O(6)–W(2) = 72.6 (2), W(1)–O(7)–W(2) = 71.5 (2), W(1)–C(10)–W(2) = 62.6 (3).

When a toluene solution of $W_2(OCH_2CMe_3)_6(py)_2$[7] is stirred under an atmosphere of butadiene, the initially deep orange solution quickly darkens to blue-black over a period of a few minutes. Cooling this solution to −20 °C for several days leads first to the development of an intense blue-purple color and then to deposition of blue-black needlelike crystals. Decanting the mother liquor and drying the crystals under vacuum leads to the isolation of an analytically pure, X-ray-quality crystalline solid, I, in about 60% yield.

When the reaction is carried out with $W_2(OCD_2CMe_3)_6(py)_2$ in a sealed NMR tube under 1 atm of butadiene in toluene-d_8, the ^1H NMR spectrum shows that $W_2(OCD_2CMe_3)_6(py)_2$ has been about 95% consumed, and new signals for a complex of the formula $W_2(OCD_2CMe_3)_6(py)$(butadiene) (I*) are observed. The existence of six different CMe_3 singlets and six different multiplets for the protons on butadiene indicate that the complex lacks any element of symmetry. In addition, the signals for butadiene span a very wide range, at δ 1.56, 3.47, 4.07, 4.82, 5.25, and 5.79 ppm (compared with signals at

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[1] For recent reviews see: Chisholm, M. H.; Clark, D. L.; Hampden-Smith, M. J.; Hoffman, D. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 432. Chisholm, M. H.; Conroy, B. K.; Eichhorn, B. W.; Folting, K.; Hoffman, D. M.; Huffman, J. C.; Marchant, N. S. *Polyhedron* **1987**, *6*, 783. Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Chem. Soc. Rev.* **1985**, *14*, 69.

[2] Blower, P. J.; Chisholm, M. H.; Clark, D. L.; Eichhorn, B. W. *Organometallics* **1986**, *5*, 2125.

[3] Chisholm, M. H.; Huffman, J. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5284. Cayton, R. H.; Chacon, S. T.; Chisholm, M. H.; Huffman, J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1026.

[4] Cayton, R. H.; Chacon, S. T.; Chisholm, M. H.; Hampden-Smith, M. J.; Huffman, J. C.; Folting, K.; Ellis, P.; Huggins, B. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *29*, 1523. Chacon, S. T.; Chisholm, M. H.; Huffman, J. C. *Organometallics*, in press.

[5] For a summary of the typical $M\text{–}C_4$ and M_2C_4 binding modes for 1,3-butadiene see: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 1153. For recent reviews see: Erker, G. *Adv. Organomet. Chem.* **1985**, *24*, 1. Kreiter, C. G. *Adv. Organomet. Chem.* **1986**, *26*, 297.

[6] A $\mu\text{-}\eta^1{:}\eta^3\text{-}C_4H_4$ ligand uniting two non-M-M-bonded centers [Cp^*_2Ln] has recently been reported and would appear to be the closest precedent for the present structure: Scholz, A.; Smola, A.; Scholz, J.; Loebel, J.; Schumann, H.; Thiele, K.-H. *Angew Chem., Int. Ed. Engl.* **1991**, *30*, 435. In this structure the metal atoms are on opposite sides of the C_4 ligand.

[7] All reactions were carried out under an inert atmosphere (N_2) and employed dried and deoxygenated solvents. The preparation and structure of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ is analogous to that of $W_2(O\text{-}i\text{-}Pr)_6(py)_2$. See: Chisholm, M. H. *Polyhedron* **1983**, *2*, 681 and references therein.

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δ 4.94, 5.05, and 6.22 for free butadiene), suggesting a very asymmetric mode of binding to the dimetal center.

The butadiene ligand in I is labile. If the reaction flask (after complete development of the blue-purple color but before crystal growth) is placed under vacuum for a few seconds, the blue-purple color becomes blacker, and if crystals are grown at this point, a significant number of bright yellow crystals of $W_2(OCH_2CMe_3)_6$ and orange crystals of $W_2(OCH_2CMe_3)_6(py)_2$ form along with the blue-black needles of I. Furthermore, if pure I is dissolved in C_6D_6 under a nitrogen atmosphere in an NMR tube fitted with a septum cap, a black solution results, and ^1H NMR resonances for free butadiene and $W_2(OCH_2CMe_3)_6$ can be seen along with signals attributable to I. On the basis of the relative intensities of these signals, ignoring that the free butadiene may not be completely dissolved in the C_6D_6 solution, the complex appears to be roughly 90% dissociated in solution.

An ORTEP drawing of the central $W_2O_6N(C_4H_6)$ moiety of the $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(C_4H_6)$ molecule is shown in Figure 1.[8] The core structure can be viewed in terms of a confacial bioctahedron. The octahedral geometry is clearly appropriate for W(1). For W(2) the η^4-C_4H_6 ligand would have to occupy cis sites. An alternative geometric description for W(2) might be based on a four-legged stool capped by the η^4-C_4H_6 ligand. The bridging carbon atom, C(10), is slightly closer to W(2) than to W(1) (cf. W(2)–C(10) = 2.32 (1) Å vs W(1)–C(10) = 2.43 (1) Å. However, the significance of the W(1)–C(10) bond is evident from its trans influence, which produces a notably long W(1)–O(5) bond in relation to the other terminal W–O alkoxide bonds. Also of note are the metric parameters associated with the W(2)–η^4-C_4 moiety. The C(10)–C(11) distance appears longer (1.457 (15) Å) compared to the two other C–C distances (1.40 (1) Å (av)). Collectively the structural data are consistent with the existence of a W–W double bond, $(W{=}W)^{8+}$, wherein the butadiene is counted as the sum of a bridging alkyl and a π-allyl ligand. The ^{13}C NMR data are also interpretable in this way. Specifically, the high-field carbon resonance of the C_4H_6 ligand occurs at δ 44.8 and shows coupling to two inequivalent hydrogen atoms ($J_{^{13}C-^{1}H}$ = 149 and 124 Hz) as well as coupling to ^{183}W ($J_{^{183}W-^{13}C} \approx 34$ Hz, I = 25%), indicative of the bridging carbon C(10). The other carbon resonances are further downfield and show larger values of $^1J_{^{13}C-^{1}H}$ and smaller values of $J_{^{183}W-^{13}C}$: δ 66.2 (t, $J_{^{13}C-^{1}H}$ = 157 Hz, $J_{^{183}W-^{13}C} \approx 24$ Hz, I = 14%); δ 102.9 (d, $J_{^{13}C-^{1}H}$ = 164 Hz); δ 111.8 (d, $J_{^{13}C-^{1}H}$ = 174 Hz).[9]

Greater insight into the bonding in I might be gained from MO calculations, and this together with studies of the reactivity of I are planned.

Acknowledgment. We thank the Department of Energy, Office of Basic Sciences, Chemical Division, for support.

Supplementary Material Available: Listings of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances and angles, and least-squares planes and stereoviews and VERSORT drawings giving the atom-numbering scheme for I (10 pages); a listing of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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[8] Crystals of I suitable for X-ray analysis were grown from the reaction of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ and 1,3-butadiene (1 atm) in toluene at −20 °C. Crystal data at −173 °C: a = 13.006 (2) Å, b = 17.583 (2) Å, c = 10.351 (2) Å, α = 98.61 (1)°, β = 104.13 (1)°, γ = 80.60 (1)°, Z = 2, d_{calcd} = 1.511 g cm^{-3}, and space group $P\bar{1}$. Of the 10 405 reflections collected (Mo Kα, 6° ≤ 2θ ≤ 45°) 8858 were unique and the 5514 having $F > 3\sigma(F)$ were used in the refinement. The tungsten, oxygen, carbon, and nitrogen atoms were refined with anisotropic thermal parameters. Several of the hydrogen atoms were located, including those on the bridging carbon atom, C(10). The remainder were included in calculated positions. It should be noted that there are short (2.5–2.6 Å) interatomic distances involving W(1) and the H atoms on C(10). The final residuals are $R(F)$ = 0.0418 and $R_w(F)$ = 0.0430.

[9] NMR data reported herein were obtained from toluene-d_8 solutions at 22 °C on a Varian 300 spectrometer.

Enantioselective Allylation of Grignard Reagents with Nickel–Diphosphine Catalysts

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Summary: A highly enantioselective (up to 94% ee) alkylation of cyclic allyl phenyl ethers with Grignard reagents catalyzed by nickel complexes of C_2-symmetric chiral diphosphine ligands is described; for the ligands related to (+)-(*R*,*R*)-cyclopentane-1,2-diylbis(diphenylphosphine) the enantioselectivity of the reaction appears to be influenced much more by steric than by electronic factors, which, however, strongly affect the chemoselectivity of the process.

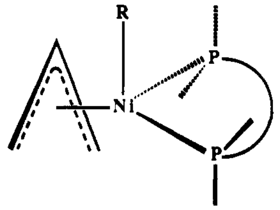

Figure 1.

The enantioselective allylation reactions of organometallic derivatives of the main-group elements (hard nucleophiles) such as Grignard reagents have been much less investigated than those of stabilized nucleophiles (soft nucleophiles).[1,2] Synthetic, stereochemical, and mecha-