should uncover further information about the fundamental importance of these processes.

Acknowledgment. Support for this research was from grants from the National Institutes of Health (GM-27251) and the National Science Foundation (CHE-09813). Preliminary efforts conducted by Lario V. Yerino are acknowledged.

Reactions of M-M Triple Bonds with C-N Triple Bonds: Adduct Formation (M = Mo) and Metathesis (M = W) As Seen in the Reactions between Dimethylcyanamide and Hexaalkoxides of Dimolybdenum and Ditungsten

Malcolm H. Chisholm,* John C. Huffman, and
Nancy S. Marchant

*Department of Chemistry and Molecular Structure Center
Indiana University, Bloomington, Indiana 47405*

Received May 18, 1983

Metal-metal multiple bonds[1] provide the basis for extensive reactivity, which includes redox reactions, cluster syntheses, activation of small unsaturated molecules, and cleavage reactions, yielding new or alternate syntheses of mononuclear compounds.[2] The reactions between $W_2(OR)_6(M{\equiv}M)$ compounds and alkyl or aryl nitriles $R'C{\equiv}N$, which give nitrides, $(RO)_3W{\equiv}N$, and carbynes, $(RO)_3W{\equiv}CR'$, are striking examples of the latter.[3] We report here some observations on the reactions between $M_2(OR)_6(M{\equiv}M)$ compounds (M = Mo, W) and dimethylcyanamide, $Me_2NC{\equiv}N$, which we believe provide insight into the reaction pathway leading to the metathesis of $W{\equiv}W$ and $C{\equiv}N$ bonds.

Hexane solutions of $W_2(O\text{-}t\text{-}Bu)_6$[4] and Me_2NCN (1 equiv) react[5] at room temperature to give a white precipitate of the linear polymer $[(t\text{-}BuO)_3W{\equiv}N]_x$[6] and the hydrocarbon-soluble compound $(t\text{-}BuO)_3W{\equiv}CNMe_2$. The reaction is complete within minutes. The carbyne compound is obtained in analytically pure, crystalline form by (i) filtering off the hexane-insoluble nitride, (ii) stripping the solvent from the filtrate, and (iii) sublimation at 25 °C, 10^{-4} torr. The molecular structure deduced from a single-crystal X-ray study[7] revealed the weakly associated dimer shown in Figure 1. Through the agency of a pair of OR bridges, two TBP tungsten atoms are united along a common axial-equatorial edge. The molecule has virtual C_{2h} symmetry and a crystallographically imposed mirror plane containing the central $[NC{\equiv}W\text{-}\mu\text{-}O]_2$ unit.

Addition of dimethylcyanamide (1 equiv) to $Mo_2(OR)_6$[8] compounds under directly analogous conditions gives 1:1 adducts $Mo_2(OR)_6(\mu\text{-}NCNMe_2)$, where R = *t*-Bu,[9] *i*-Pr[9], and $CH_2\text{-}t\text{-}Bu$.

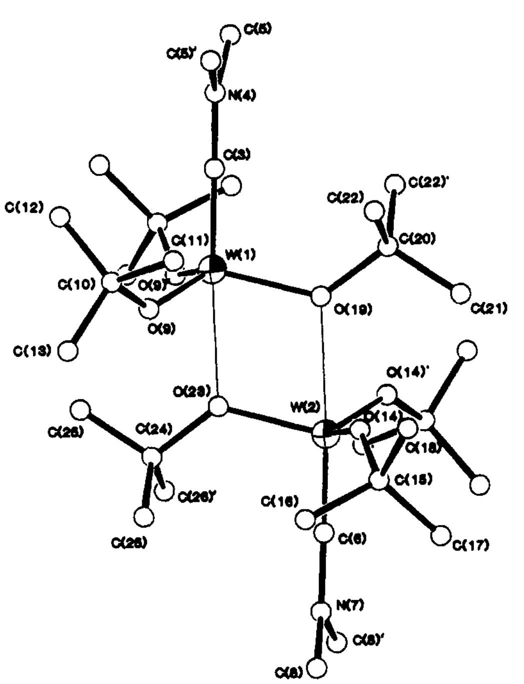

Figure 1. Ball and stick view of the $[(t\text{-}BuO)_3W{\equiv}CNMe_2]_2$ molecule emphasizing the trigonal-bipyramidal coordination at each tungsten atom. Pertinent distances (Å) and angles (deg) are W(1)–O(9) = 1.89 (1), W(1)–O(19) = 1.95 (1), W(1)–O(23) = 2.42 (1), W(1)–C(3) = 1.77 (2), W(2)–O(14) = 1.88 (1), W(2)–O(19) = 2.43 (1), W(2)–O(23) = 1.94 (1), W(2)–C(6) = 1.75 (2), N(4)–C(3) = 1.34 (2), N(7)–C(6) = 1.39 (2); ∠W(1)–C(3)–N(4) = ∠W(2)–C(6)–N(7) = 179 (2), ∠O(23)–W(1)–C(3) = ∠O(19)–W(2)–C(6) = 177 (1).

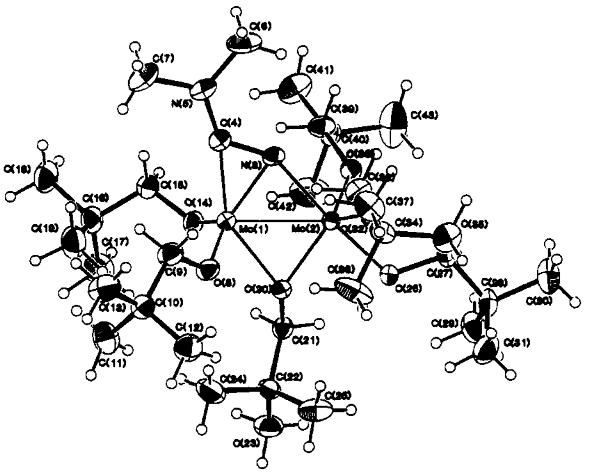

Figure 2. ORTEP view of the $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}NCNMe_2)$ molecule. Pertinent distances (Å) and angles (deg) are Mo–Mo = 2.449 (1), Mo–O (terminal OR) = 1.92 (2) (averaged), Mo(1)–O(20) = 2.146 (2), Mo(1)–N(3) = 1.908 (3), Mo(1)–C(4) = 2.014 (4), Mo(2)–O(20) = 1.999 (2), Mo(2)–N(3) = 2.134 (2), N(3)–C(4) = 1.333 (4), C(4)–N(5) = 1.324 (4); ∠Mo(1)–C(4)–N(5) = 167.0 (3), ∠(3)–C(4)–N(5) = 127.1 (3), ∠C–N(5)–C = 120 (1) (averaged).

Crystals suitable for an X-ray study were obtained for the neopentoxide from hexane and thereafter revealed[7] the fascinating molecular structure shown in Figure 2. Superficially, the central $Mo_2(\mu\text{-}NCNMe_2)$ unit appears similar to that in $Cp_2Mo_2(CO)_4(\mu\text{-}NCNMe_2)$,[10] as indeed was suggested[9] for the compounds $Mo_2(OR)_6(\mu\text{-}NCNMe_2)$, where R = *t*-Bu and *i*-Pr, on the basis of IR and NMR spectroscopic data. However, in the structure of $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}NCNMe_2)$, we see (relative to $Cp_2Mo_2(CO)_4(NCNMe_2)$) (i) a much longer $Me_2NC\text{-}N$ distance, 1.333 (4) Å (cf. 1.236 (9) Å), comparable to that in pyridine and

---

[1] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

[2] Chisholm, M. H. *ACS Symp. Ser.* **1981**, *No. 155*.

[3] Schrock, R. R.; Listerman, M. L. Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

[4] Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266.

[5] All reactions and manipulations were carried out using dry and oxygen-free solvents and atmospheres.

[6] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.*, in press.

[7] Crystal data for $(t\text{-}BuO)_3W{\equiv}CNMe_2$: orthorhombic, space group *Pnma* with $a = 23.246$ (9), $b = 17.031$ (5), $c = 9.719$ (2) Å; $D_{calcd} = 1.586$ gm cm^{-3} for $Z = 8$; temperature, −104 °C. Phase transition (reversible) at ca. −120 °C, yielding triclinic cell of approximately the same dimensions; $R = 0.045$ and $R_w = 0.043$ for 2336 observed data to $2\Theta = 45°$ (Mo$K\alpha$). Crystal data for $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}NCNMe_2)$: triclinic, space group $P\bar{1}$ with $a = 19.738$ (6), $b = 11.390$ (2), $c = 10.112$ (2) Å, $\alpha = 85.42$ (1), $\beta = 104.69$ (1), $\gamma = 104.20$ (1)°; $D_{calcd} = 1.232$ gm cm^{-3} for $Z = 2$; temperature, −120 °C; $R = 0.031$ and $R_w = 0.032$ for 4771 observed data to $2\Theta = 45°$ (Mo $K\alpha$). A second phase, also triclinic, occurs below −140 °C, yielding an identical structure with the exception of a different conformer for one of the terminal $OCH_2\text{-}t\text{-}Bu$ groups.

[8] Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801.

[9] Chisholm, M. H.; Kelly, R. L. *Inorg. Chem.* **1979**, *18*, 2321.

[10] Chisholm, M. H.; Cotton, F. A.; Extine, M. Ws.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 807.

0002-7863/83/1505-6162$01.50/0

ca. 0.2 Å longer than the C$\equiv$N distance in $\mathrm{Me_2NC{\equiv}N}$,[11] (ii) a smaller N–C–N angle, 127° (vs. 135°), and a larger Mo–C–NMe$_2$ angle, 167° (vs. 150°), and (iii) a planar central $\mathrm{Mo_2NCNC_2}$ unit. The Mo–Mo distance, 2.45 Å, is comparable to those seen in compounds containing Mo–Mo double bonds, e.g., Mo–Mo = 2.49 Å in $\mathrm{Mo_2(O\text{-}\mathit{i}\text{-}Pr)_6(py)_2(\mu\text{-}CO)}$.[12]

Though crystallography is rarely a reliable method for the elucidation of reaction pathways,[13] we do believe the molecular structure of $\mathrm{Mo_2(OCH_2\text{-}\mathit{t}\text{-}Bu)_6(\mu\text{-}NCNMe_2)}$ provides some insight into the metathesis reactions involving W$\equiv$W and C$\equiv$N bonds. In $\mathrm{Mo_2(OCH_2\text{-}\mathit{t}\text{-}Bu)_6(\mu\text{-}NCNMe_2)}$, the Mo–Mo and Me$_2$NC–*N* bonds appear poised for metathesis, and it is difficult to imagine that this is prevented because of a kinetic barrier. We suggest that the reaction $\mathrm{M{\equiv}M + {-}C{\equiv}N \rightarrow M{\equiv}N + M{\equiv}C{-}}$ proceeds for tungsten because of thermodynamic factors and that these are not favorable for molybdenum. This metathesis reaction can be viewed as an oxidative cleavage reaction wherein the $\mathrm{(W{\equiv}W)^{6+}}$ unit is oxidized to two $\mathrm{W^{6+}}$ units. As such, the reaction provides another example of the greater susceptibility of W–W multiple bonds toward oxidations relative to Mo–Mo multiple bonds.[14]

Further studies of these interesting reactions and compounds are in progress.[15]

Registry No. $[(\mathit{t}\text{-}\mathrm{BuO})_3\mathrm{W{\equiv}N}]_x$, 86832-67-9; $(\mathit{t}\text{-}\mathrm{BuO})_3\mathrm{W{\equiv}CNMe_2}$, 86767-54-6; $\mathrm{Mo_2(OCH_2\text{-}\mathit{t}\text{-}Bu)_6(M\text{-}NCNMe_2)}$, 86784-87-4; $\mathrm{W_2(O\text{-}\mathit{t}\text{-}Bu)_6}$, 57125-20-9; $\mathrm{Mo_2(OCH_2\text{-}\mathit{t}\text{-}Bu)_6}$, 62521-24-8.

Supplementary Material Available: Listing of fractional coordinates (2 pages). Ordering information is given on any current masthead page.

---

(11) Li, Y. S.; During, J. R. *J. Mol. Struct.* **1973**, *16*, 433.

(12) Chisholm, M. H.; Huffman, J. C.; Leonelli, J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1982**, *104*, 7030.

(13) Wilson, S. R.; Huffman, J. C. *J. Org. Chem.* **1980**, *45*, 560.

(14) Cotton, F. A. *Chem. Soc. Rev.* **1983**, *12*, 35.

(15) We thank the National Science Foundation for support.

A Bimetallic Vanadium(I) Polyhydride

Rick L. Bansemer, John C. Huffman, and
Kenneth G. Caulton*

Department of Chemistry and Molecular Structure Center
Indiana University
Bloomington, Indiana 47405

Received May 19, 1983

Our examination of the reaction chemistry of polyhydride complexes, $\mathrm{MH}_x(\mathrm{PR_3})_y$ ($x \geq 3$), has relied principally on photochemical[1] and oxidative[2] methods in order to enhance the reactivity of these coordinatively saturated species. We have more recently been attempting to produce polyhydride species of the first row transition metals since these metals (a) often violate the 18-electron rule as synthesized and (b) exhibit more rapid reaction rates than their heavier analogues. This report suggests that such a goal is indeed realizable, incorporating vanadium in a bimetallic polyhydride aggregate.

Reaction of a THF slurry of $\mathrm{[V_2(\mu\text{-}Cl)_3(THF)_6]_2Zn_2Cl_6}$[3] with $\mathrm{PMePh_2}$ (2 equiv/mol of V), followed by addition of $\mathrm{LiBH_4}$ (2 mol/mol of metal) at 25 °C yields a green solution. Vacuum removal of solvent leaves a red residue, which can be recrystallized from benzene/pentane to give a 50% yield (based on Zn) of dark red air-sensitive crystals. This material is homogeneous by two spectral criteria: It shows a broad $^{11}\mathrm{B}\{^1\mathrm{H}\}$ resonance at −30.6 ppm (in $\mathrm{C_6D_6}$ at 25 °C) and a broad $^{31}\mathrm{P}\{^1\mathrm{H}\}$ resonance at +22.7 ppm (in toluene-d_8 at −80 °C). The infrared spectrum of the red product shows bands characteristic[6] of η^2-$\mathrm{BH_4}$ units. An X-ray diffraction study[7] shows this material to contain centrosymmetric molecules of formula $\mathrm{V_2Zn_2H_4(BH_4)_2(PMePh_2)_4}$ (Figure 1). The structure may be described as a diamond-shaped $\mathrm{V_2Zn_2}$ aggregate (a squashed butterfly) with four edge-bridging hydrogens. The η^2-borohydride hydrogens and the hydrogens bridging V to Zn furnish tetrahedral ligation about zinc. The formal oxidation states Zn(II) and V(I) follow naturally.

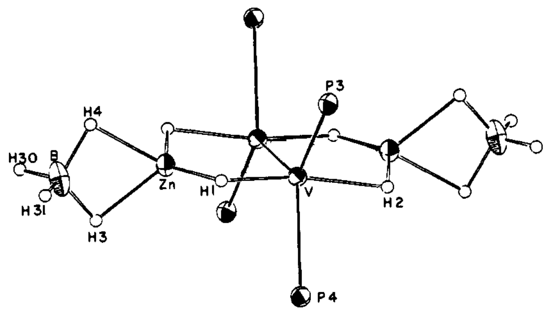

Figure 1. ORTEP view of the inner coordination spheres of $\mathrm{V_2Zn_2H_4(BH_4)_2(PMePh_2)_4}$. Unlabeled atoms (primed) are related to those given by a crystallographic center of symmetry lying between the two vanadium atoms. Selected structural data: V–P3 = 2.548 (1), V–P4 = 2.529 (1), V–H1 = 1.80 (5), V–H2 = 1.85 (5), Zn–H1 = 1.70 (5), Zn–H2′ = 1.59 (5), Zn–H3 = 1.78 (5), Zn–H4 = 1.82 (5) Å; ∠P3–V–P4 = 106.4 (0)°, ∠H1–V–H2 = 159 (2)°.

An alternative description of this molecule, and one which permits reliance on existing theory,[8] considers it to be composed of the unit $\mathrm{V_2H_4(PMePh_2)_4}^{2-}$ with eclipsed hydride ligands bridged end-to-end by two electrophilic $\mathrm{Zn(BH_4)^+}$ counterions. Support for this dissection of the molecule (which deemphasizes Zn–V bonding) comes from comparison of the Zn–V distances (2.633 (2) and 2.656 (1) Å) to the sum of the covalent radii of these metals (2.50 Å). This model, which is predated by the lithium bridging seen in $\mathrm{Li_4Cr_2Me_4{\cdot}4THF}$[9] and $\mathrm{Li_4Cr_2(C_4H_8)_4{\cdot}4THF}$,[10] reduces the bonding problem to that of a d^4-d^4 $\mathrm{M_2X_8}^{q-}$ dimer. The observed V–V distance of 2.400 (2) Å is longer than the ~2.3 Å found among $\mathrm{Cr_2(O_2CR)_4L_2}$ complexes[8] and cannot be considered a quadruple bond. Since the distance essentially duplicates that of the V=V double bond in $\mathrm{Cp_2V_2(CO)_5}$ (2.46 Å),[11] we suggest the bonding described by I, where the pair of d-electrons

$$\mathrm{(Ph_2MeP)_2H_2\ddot{V}{=}\ddot{V}H_2(PMePh_2)_2}^{2-}$$

I

withheld from metal–metal bonding is drawn explicitly. An alternative rationale for this depiction is that the large ∠V′–V–P (126.1° and 127.0°) in the planar $\mathrm{V_2P_4}$ unit destabilizes one V–V π orbital (it becomes V–P σ-antibonding) to an energy above both the δ and δ^* orbitals. The resulting electron configuration is $(\sigma)^2(\pi_1)^2(\delta)^2(\delta^*)^2(\pi_2)^0$; the lone pairs of I thus correspond to the filled δ and δ^* orbitals.

Aspects of the unusual synthesis of this $\mathrm{Zn_2V_2}$ aggregate, as well as its utility in hydrogen transfer, are under investigation.

---

(1) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *243*, C78.

(2) Rhodes, L. F.; Zubkowski, J. D.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1982**, *21*, 4185.

(3) The compound previously claimed to be $\mathrm{VCl_2(THF)_2}$[4] has been shown[5] to in fact be this mixed-metal salt.

(4) Hall, V. M.; Schmulbach, C. D.; Soby, W. N. *J. Organomet. Chem.* **1981**, *209*, 69.

(5) Bansemer, R. L.; Huffman, J. C.; Caulton, K. G.; Bouma, R.; Teuben, J. H., unpublished results.

(6) 2450, 2390, and 2020 cm^{-1}. See: Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

(7) Crystallographic data (−162 °C): a = 12.678 (3) Å, b = 13.775 (3) Å, c = 10.483 (2) Å, α = 111.58 (1)°, β = 110.70 (1)°, γ = 111.53 (1)°, V = 1306.9 Å^3, Z = 1 in space group $P\bar{1}$; R_f = 2.9%. All hydrogen atoms were refined isotropically.

(8) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

(9) Krausse, J.; Marx, G.; Schödl, G. *J. Organomet. Chem.* **1970**, *21*, 159.

(10) Krausse, J.; Schödl, G. *J. Organomet. Chem.* **1971**, *27*, 59.

(11) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

0002-7863/83/1505-6163$01.50/0