ca. 0.2 Å longer than the C≡N distance in $Me_2NC{\equiv}N$,[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 Mo_2N-CNC_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 $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(\mu\text{-}CO)$.[12]

Though crystallography is rarely a reliable method for the elucidation of reaction pathways,[13] we do believe the molecular structure of $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}NCNMe_2)$ provides some insight into the metathesis reactions involving W≡W and C≡N bonds. In $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}NCNMe_2)$, the Mo–Mo and Me_2NC–*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 M≡M + —C≡N → M≡N + M≡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 $(W{\equiv}W)^{6+}$ unit is oxidized to two 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. $[(t\text{-}BuO)_3W{\equiv}N]_x$, 86832-67-9; $(t\text{-}BuO)_3W{\equiv}CNMe_2$, 86767-54-6; $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(M\text{-}NCNMe_2)$, 86784-87-4; $W_2(O\text{-}t\text{-}Bu)_6$, 57125-20-9; $Mo_2(OCH_2\text{-}t\text{-}Bu)_6$, 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, $MH_x(PR_3)_y$ ($x \geq 3$), 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.

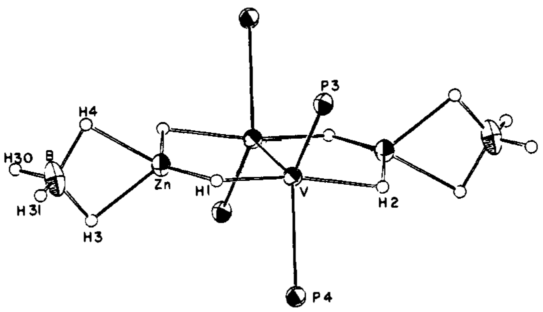


Figure 1. ORTEP view of the inner coordination spheres of $V_2Zn_2H_4(BH_4)_2(PMePh_2)_4$. Unlabeled atoms (primed) are related to those given by a crystallographic center of symmetry lying between the two vanadium atoms. Selected structural data: V–P3 = 2.548 (1), V–P4 = 2.529 (1), V–H1 = 1.80 (5), 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)°.

Reaction of a THF slurry of $[V_2(\mu\text{-}Cl)_3(THF)_6]_2Zn_2Cl_6$[3] with $PMePh_2$ (2 equiv/mol of V), followed by addition of $LiBH_4$ (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 $^{11}B\{^1H\}$ resonance at −30.6 ppm (in C_6D_6 at 25 °C) and a broad $^{31}P\{^1H\}$ 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-BH_4 units. An X-ray diffraction study[7] shows this material to contain centrosymmetric molecules of formula $V_2Zn_2H_4(BH_4)_2(PMePh_2)_4$ (Figure 1). The structure may be described as a diamond-shaped 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.

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

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

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 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 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 $VCl_2(THF)_2$[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

Acknowledgment is made to the Indiana University Office of Research and Graduate Development, to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Stauffer Chemical Co. for support of this research. NATO Grant 070-82 and the consultation of David Hoffman, Jan Teuben, and Reinder Bouma were of crucial importance to this work. We thank Scott Horn for skilled technical assistance. The high-field NMR spectrometer employed was purchased under NSF Grant CHE-81-05004.

Registry No. $V_2Zn_2H_4(BH_4)_2(PMePh_2)_4$, 86690-01-9; $[V_2(\mu\text{-}Cl)_3(THF)_6]_2Zn_2Cl_6$, 86690-03-1; $VCl_2(THF)_2$, 21729-44-2.

Supplementary Material Available: Table of fractional atomic coordinates, thermal parameters, and structure factors for $V_2Zn_2H_4(BH_4)_2(PMePh_2)_4$ (18 pages). Ordering information is given on any current masthead page.

α-Haloalkanesulfonyl Bromides in Organic Synthesis. 1. Formation and Base-Induced Reactions of α,β-Unsaturated Halomethyl Sulfones[1a,b]

Eric Block* and Mohammad Aslam

Department of Chemistry
State University of New York at Albany
Albany, New York 12222

Received April 15, 1983

The Ramberg–Bäcklund reaction is a synthetically useful process in which α-haloalkyl sulfones afford olefins upon treatment with base (eq 1).[2] We report a novel variant of the Ramberg–

$$RCH_2SO_2CH_2X \xrightarrow{\text{base}} R\overset{-}{C}HSO_2CH_2X \xrightarrow{-X^-} R\overline{CHSO_2C}H_2 \rightarrow RCH{=}CH_2 + SO_2 \quad (1)$$

Bäcklund reaction in which α,β-unsaturated α′-bromoalkyl sulfones **1** afford 1,3-dienes on base treatment (eq 2). This communication

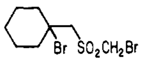
$$\underset{\mathbf{1}}{RCH_2CH{=}CHSO_2CH_2Br} \xrightarrow{\text{base}} R\overset{-}{C}H\overset{-}{C}H\overset{-}{C}HSO_2CH_2Br \xrightarrow{-Br^-} RCH{=}CH\overline{CHSO_2C}H_2 \rightarrow RCH{=}CHCH{=}CH_2 + SO_2 \quad (2)$$

describes a general synthesis of previously unknown compounds of type **1**, using the useful reagent $BrCH_2SO_2Br$ (**2**, bromomethanesulfonyl bromide), as well as unusual stereochemical features of the reaction of **1** with base. The accompanying communication[1c] illustrates the broad utility of this reaction.

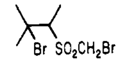
Compounds **1** are formed in excellent yield in a two-step process involving light-catalyzed addition of **2** to olefins at −20 °C followed by treatment of the adduct with triethylamine (eq 3). Reagent

$$RCH_2CH{=}CH_2 + \underset{\mathbf{2}}{BrCH_2SO_2Br} \xrightarrow[\text{30 min, −20 °C}]{h\nu,\ CH_2Cl_2} \underset{\mathbf{3}}{RCH_2CHBrCH_2SO_2CH_2Br} \xrightarrow{Et_3N} \underset{\mathbf{1}}{RCH_2CH{=}CHSO_2CH_2Br} \quad (3)$$

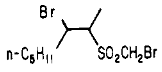
2 may be conveniently prepared in 46% yield by bromination of an aqueous slurry of 1,3,5-trithiane.[3,4] Olefin–**2** adducts are formed in nearly quantitative yields by a process that most likely involves a free radical chain reaction analogous to free radical additions of other sulfonyl halides.[2,6,7] We find the light-catalyzed process to be cleaner and more easily controlled than thermal addition of **2**. A wide range of olefins react with **2**. With mono-, 1,1-di-, and 1,1,2-trisubstituted olefins the addition is regiospecific, consistent with formation of the more stabilized radical intermediate (see products **3**, R = *n*-C_5H_{11}, **4**, and **5**, from 1-octene, methylenecyclohexane, and 2-methyl-2-butene, respectively[8]).



4



5



6

Even unsymmetrical 1,2-disubstituted olefins show a high degree of regioselectivity in the addition, e.g., as demonstrated by the formation of **6** as the major (79%) adduct from addition of **2** to 2-octene. The facile S–Br bond homolysis of **2** makes it superior to sulfonyl chlorides such as $BrCH_2SO_2Cl$, which showed only 10% addition to 1-octene after irradiation for 1 h.[7,10]

Addition of **2** to olefins and subsequent reaction of the adducts with base is nicely illustrated with 1-octene. Thus, 1-octene, diluted with an equal volume of CH_2Cl_2 and irradiated in a Pyrex tube for 30 min at −20 °C after addition of an equivalent amount of **2**, afforded a single 1:1 olefin–**2** adduct in 94% yield. Direct treatment of this crude adduct with Et_3N in CH_2Cl_2 at 0 °C for 15 min gave in 97% yield a 10:1 mixture of (*E*)- and (*Z*)-bromomethyl 1-octenyl sulfones, **1E** and **1Z** (R = *n*-C_5H_{11}), respectively.[8,9] Crystallization readily afforded a pure sample of **1E** while isomer **1Z** could be isolated from the mother liquor by preparative HPLC. Treatment of **1E** with 2.5 equiv of *t*-BuOK in 7:3 *tert*-butyl alcohol/THF at −20 °C for 1 h gave in 59% distilled yield a 83:17 mixture of (*Z*)- and (*E*)-1,3-nonadiene. In a similar manner **1Z** gave in 61% distilled yield a 6:94 mixture of (*Z*)- and (*E*)-1,3-nonadiene.

The remarkable stereoselectivity of the reaction of **1E** with base, which may be termed a "*vinylogous Ramberg–Bäcklund reaction*", is attributed to a "syn effect"[11] involving interaction between the developing negative charge at the α-position and the CH_2 group at the δ-position favoring transition state **1E′** over **1E″** for deprotonation (eq 4 and 5). Our observation that (*E*)-1-octenyl phenyl sulfone undergoes base-catalyzed isomerization to (*Z*)-2-octenyl phenyl sulfone[8,12] provides support for this model, if it

---

[1] (a) The material covered in this communication is the subject of a U.S. Patent Application filed by the Research Foundation of the State University of New York. (b) Presented in part at the International Symposium on Heteroatoms for Organic Synthesis, Montreal, August 16, 1983 and at the 186th ACS National Meeting, Washington, D.C., September 1, 1983. (c) Block, E.; Aslam, M.; Eswarakrishnan, V.; Wall, A. *J. Am. Chem. Soc.*, following communication in this issue.

[2] Reviews: (a) Bordwell, F. G. In "Organosulfur Chemistry"; Janssen, M. J., Ed.; Interscience: New York, 1967; Chapter 16. (b) Paquette, L. A., *Org. React.* (*N.Y.*) **1977**, *25*, 1–71. (c) Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978; p 77.

[3] Kostsova, A. G. *Tr. Voronezh. Gos. Univ.* **1935**, *8*, 92–117; *Chem. Abstr.* **1938**, *32*, 6618; a 15% yield of **2** is claimed.

[4] Bromine (9.5 equiv) is added dropwise to a vigorously stirred aqueous slurry of 1,3,5-trithiane at or below 35 °C. The product is extracted into CH_2Cl_2, and the organic phase is washed with ice-cold 5% $NaHSO_3$ and water, dried, concentrated, and distilled giving **2** as a pale yellow liquid: $bp_{0.025mm}$ 62 °C, NMR δ 4.92 (s); IR 1362 (vs), 1205 (s), 1160 (vs), 1105 (m), 830 (s), 680 (s) cm^{-1}. Compound **2** is stable at 25 °C for at least 2 weeks. An alternative synthesis of **2** is given in ref 5.

[5] Block, E.; Aslam, M. *Tetrahedron Lett.* **1982**, *23*, 4203–4206.

[6] Truce, W. E.; Wolf, G. C. *J. Org. Chem.* **1971**, *36*, 1727–1732. Also cf.: Gancarz, R. A.; Kice, J. L. *Tetrahedron Lett.* **1980**, *21*, 4155–4158.

[7] Goldwhite, H.; Gibson, M. S.; Harris, C. *Tetrahedron* **1964**, *20*, 1613–1624.

[8] All new compounds have been fully characterized by spectral means.

[9] The use of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) at −23 °C in place of triethylamine gave a mixture containing >97% **1E**.

[10] (a) 1-Octene fails to add $ClCH_2SO_2Cl$ on heating in the presence of Cu^I: Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1964**, 4962–4971. (b) *t*-$BuOOH/ZnCl_2$-catalyzed addition of $ClCH_2SO_2Br$ to 2,5-dihydrofuran and Et_3N treatment gives 3-(chloromethylsulfonyl)-2,5-dihydrofuran in 26% yield: Böll, W. *Liebigs Ann. Chem.* **1979**, 1665–1674.

[11] (a) Block, E.; Penn, R. E.; Bazzi, A. A.; Cremer, D. *Tetrahedron Lett.* **1981**, *22*, 29–32. (b) Houk, K. N.; Strozier, R. W.; Rondan, N. G.; Fraser, R. R.; Chuaqui-Offermanns, N. *J. Am. Chem. Soc.* **1980**, *102*, 1426–1429 and references therein.

[12] Product stereochemistry in the base-induced isomerization of α,β-unsaturated sulfones to β,γ-unsaturated sulfones[13] has not been previously reported. Exclusive formation of (*Z*)-2-octenyl tosyl sulfone when Bu_2CuLi adds to (*E*)-1,3-butadienyl tosyl sulfone[14] is consistent with a syn effect in the anionic intermediate.

[13] O'Connor, D. E.; Lyness, W. I. *J. Am. Chem. Soc.* **1964**, *86*, 3840–3846. Broaddus, C. D. *Ibid.* **1968**, *90*, 5504–5511.

[14] Näf, F.; Decorzant, R.; Escher, S. D. *Tetrahedron Lett.* **1982**, *23*, 5043–5046.

0002-7863/83/1505-6164$01.50/0