J. Am. Chem. Soc. **1994,** *116,* 389-390 389

Direct Observation of the Conversion of a Tertiary Butoxide Ligand to Hydrido–Oxo Ligands with the Liberation of Isobutylene at a Ditungsten Center

Theodore A. Budzichowski, Malcolm H. Chisholm,* and William E. Streib

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

Received June 9, 1993

There is currently considerable interest in the chemistry of metal alkoxides and their transformations to metal oxides.[1-5] Relatively little is known about the mechanisms of thermal decompositions of $M(OR)_x$ compounds, though it is already clear that the thermal stability (kinetic persistence) of such species is greatly influenced by the nature of M and R. Alkoxide ligands typically decompose by β-hydride elimination, as has been shown by Hoffman *et al.*[6] for the homoleptic isopropoxide $Re_3(\mu\text{-}OPr^i)_3(OPr^i)_6$ and by Bryndza and Tam[7] for platinum complexes such as $(DPPE)Pt(OCH_3)_2$ (DPPE = bis(diphenylphosphino)ethane).

The β-H elimination mechanism is shut down for tertiary alkoxides, but even here the thermal stability of the metal alkoxide is greatly dependent on the metal. For example, Bradley and Factor showed that $Zr(Ot\text{-amyl})_4$ is catalytically decomposed at 200 °C and 1 atm by adventitous acid sites on glass surfaces.[3]

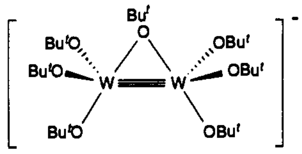
In contrast, $[Cu(OBu^t)]_4$ is a volatile precursor to Cu_2O or Cu metal in OMCVD reactions at temperatures of 240 and 400 °C, respectively.[1] $W_2(OBu^t)_6$ (**1**) decomposes similarly at *ca.* 100 °C under He(g) flow to give WO_2.[5] In both cases the decomposition is accompanied by the formation of isobutylene, Bu^tOH, and varying amounts of H_2O.[1,5]

We describe here the first example of the *selective decomposition* of a single *tert*-butoxide ligand to give hydride and oxo ligands at a dimetal center.

The addition of $KOBu^t$/18-crown-6 to a solution of **1** leads to the equilibrium shown in eq 1, which is slow on the NMR time

$$\underset{\mathbf{1}}{W_2(OBu^t)_6} + {}^-OBu^t \rightleftharpoons \underset{\mathbf{2}}{[W_2(OBu^t)_7]^-} \qquad (1)$$

scale but is fast on the time scale of chemical separations. At concentrations of *ca.* 10^{-2} M and at temperatures between +23 and +80 °C, the equilibrium lies far in favor of the purple adduct **2**, which is isolable in yields >85% for preparative reactions carried out at ≤0 °C by removing the solvent *in vacuo* and triturating the resulting purple solid with a large amount of C_6H_6. Crystalline material was obtained from THF:toluene (1:1, −34 °C).[8] The structure of **2** has not yet been determined by single crystal X-ray diffraction, but it is presumably analogous to the structurally characterized purple anion in $[K(18\text{-crown-}6)]^+[Mo_2(OCH_2Bu^t)_7]^-$ as shown in A.[9] Like the other $M_2(OR)_7^-$ anions (M = Mo, W), the alkoxide ligands in **2** are equivalent on the ^1H NMR time scale (±80 °C).[9]



A

Anion **2** decomposes irreversibly to the hydrido–oxo anion **3** according to eq 2.[10] Hydrido–oxo compounds are relatively rare,[11]

$$\underset{\mathbf{2}}{[W_2(OBu^t)_7]^-} \rightarrow \underset{\mathbf{3}}{[W_2(OBu^t)_6(\mu\text{-}O)(\mu\text{-}H)]^-} + Me_2C{=}CH_2 \qquad (2)$$

and this is the first example prepared by alkoxide decomposition. Whereas **1** decomposes autocatalytically only at elevated temperatures, the decomposition of **2** occurs at room temperature and is selective for a single $-OBu^t$ ligand.

The structure of red crystalline **3** was determined by X-ray diffraction.[12] Crystals of **3** occur in the space group $P2_1/n$, with one independent anion situated at a general position in the lattice (no crystallographically imposed symmetry). A view of the anion is shown in Figure 1. The hydride ligand was not located but may be reasonably assumed to occupy a bridging site opposite to the μ-O ligand to create a planar $W_2(\mu\text{-}O)(\mu\text{-}H)$ moiety.[13] In this way, each W atom is in a 5-coordinate trigonal-bipyramidal environment with the μ-O and two alkoxide ligands at each tungsten occupying equatorial sites.

The W–W distance of 2.4447(10) Å is typical of a W=W bond, as might be anticipated for a $W_2(OBu^t)_6(\mu\text{-}O)(\mu\text{-}H)^-$ anion with a W_2^{8+} core.[14] Furthermore, the W(μ-O) distances [1.916(12) Å and 1.888(12) Å] are inconsistent with the presence of a bridging hydroxide ligand (which would yield a W_2^{6+} core and a W≡W triple bond).

The Bu^tO ligands for **3** are equivalent on the ^1H NMR time scale even at −80 °C (300 MHz, toluene-d_8). The hydride resonance appears at δ *ca.* 6.5 and is flanked by ^{183}W satellites, $J_{W\text{-}H}$ = 125 Hz, having an intensity of *ca.* 26% at all the temperatures studied (±80 °C), indicative of a μ_2-H moiety.

The rate of reaction 2 was measured by ^1H NMR spectroscopy (23 to 80 °C, C_5D_5N) with and without added $KOBu^t$ and found to obey first-order kinetics ($\Delta H^\ddagger$ = 23.7(5) kcal/mol, $\Delta S^\ddagger$ = −3.6(5) eu) independent of [$KOBu^t$] (10^{-1}–10^{-3} M), which was always present in small amounts due to the reversibility of

---

(1) Jeffries, P. M.; Dubois, L. H.; Girolami, G. S. *Chem. Mater.* **1992**, *4*, 1169.

(2) (a) Sen, A.; Stetcher, H. A.; Rheingold, A. L. *Inorg. Chem.* **1992**, *31*, 473. (b) Nandi, M.; Rhubright, D.; Sen, A. *Inorg. Chem.* **1990**, *29*, 3066. (c) Stetcher, H. A.; Sen, A.; Rheingold, A. L. *Inorg. Chem.* **1989**, *28*, 3280.

(3) (a) Bradley, D. C.; Factor, M. M. *J. Appl. Chem.* **1959**, *9*, 435. (b) Bradley, D. C.; Factor, M. M. *J. Chem. Soc., Faraday Trans.* **1959**, *55*, 2117.

(4) Xue, Z.; Vaarstra, B. A.; Caulton, K. G.; Chisholm, M. H.; Jones, D. L. *Eur. J. Solid State Inorg. Chem.* **1992**, *29*, 213.

(5) Baxter, D. V.; Chisholm, M. H.; DiStasi, V. F.; Klang, J. A. *Chem. Mater.* **1991**, *3*, 221.

(6) Hoffman, D. M.; Lappas, D.; Wierda, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 1531.

(7) (a) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805. (b) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

(8) For **2**: ^1H NMR (300 MHz, C_5D_5N, 23 °C) δ 3.438 (s, 24 H), 1.975 (s, 63 H); $^{13}C\{^1H\}$ NMR (75 MHz, C_5D_5N, 23 °C) δ 77.54, 70.41, 35.22.

(9) Budzichowski, T. A.; Chisholm, M. H.; Martin, J. D.; Huffman, J. C.; Moodley, K. G.; Strieb, W. E. *Polyhedron* **1993**, *12*(3), 343.

(10) For **3**: ^1H NMR (300 MHz, C_5D_5N, 23 °C) δ 6.517 (s, 24 H, $J_{W\text{-}H}$ = 125 Hz), 3.475 (s, 36 H), 1.852 (s, 54 H); $^{13}C\{^1H\}$ NMR (125 MHz, C_5D_5N, 23 °C) δ 77.40, 69.90, 33.71; IR (KBr pellet) ν 2961, 2910, 1473 w, 1454 w, 1368 w, 1352, 1284 w, 1236, 1180, 1111, 1026 w, 964, 929, 866 w, 83 7 w, 773 m, 574 w, 511 w, 472 w. Anal. Calcd for $C_{42}H_{91}KO_{16}W_2$ (1.5 crown ether per K): C, 40.06; H, 7.28. Found: C, 39.98; H, 7.48.

(11) (a) Spaltenstein, E.; Erikson, T. K. G.; Critchlow, S.; Mayer, J. M. *J. Am. Chem. Soc.* **1993**, *112*, 8600. (b) Conry, R. R.; Mayer, J. M. *Organometallics* **1991**, *10*, 3160. (c) Tahmassebi, S. K.; Conry, R. R.; Mayer, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 7553. (d) Kim, Y.; Galluci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 8600. (e) van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347.

(12) For **3**·toluene [$C_{49}H_{99}KO_{16}W_2$] (FW = 1351.11): monoclinic $P2_1/n$, a = 15.982(2), b = 16.617(3), and c 24.029(4) Å; β = 97.51(1)°; V = 6326.9 Å^3; D_{calc} = 1.418 g/cm^3 (Z = 4). A total of 8272 independent reflections were collected on a Picker four-circle goniostat at −165 °C with use of graphite monochromated Mo Kα radiation. The final residuals were R_F = 0.076, R_{wF} = 0.062 for 5863 reflections observed with $F_o > 3\sigma(F_o)$. All other details regarding the crystal structure of **3** are reported in the supplementary material.

(13) (a) The molecular mechanics program HYDEX[13b] was utilized to find the optimum location for the hydride ligand. (b) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

(14) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

0002-7863/94/1516-0389$04.50/0

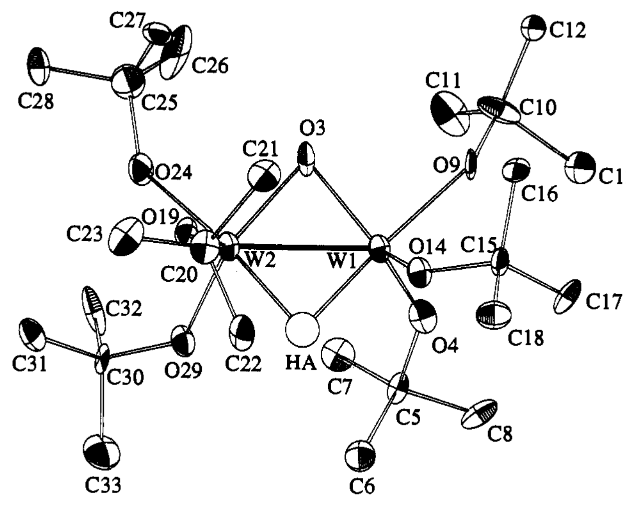


Figure 1. ORTEP plot for 3 showing all non-hydrogen atoms at the 30% probability level. The bridging hydride, HA, is also shown 1.85 Å from each W atom as placed by the program HYDEX.[13] Pertinent bond distances (Å) and angles (deg) are as follows: W(1)–W(2) = 2.4447(10), W(1)–O(3) = 1.916(12), W(1)–O(4) = 1.888(12), W(1)–O(9) = 2.013(11), W(1)–O(14) = 1.953(10), W(2)–O(3) = 1.932(11), W(2)–O(19) = 1.881(10), W(2)–O(24) = 2.025(12), W(2)–O(29) = 1.938(11), O(eq)–W–O(eq) = 120 (av), O(ax)–W–O(eq) = 89 (av), HA–W–O(ax) = 171 (av), HA–W–O(eq) = 91 (av). The counter cation is $(\eta^6$-18-crown-6)K$^+(\mu,\eta^2,\eta^2$-18-crown-6)K$^+(\eta^6$-18-crown-6), which resides at a crystallographic inversion center.

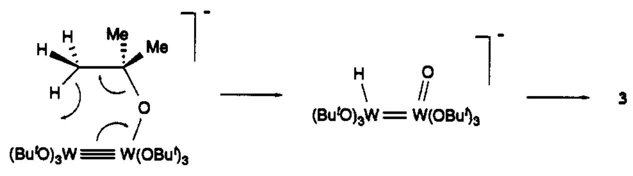
equilibrium 1.[15] No intermediates were detected during the course of these experiments. Isobutylene (δ 4.72 and 1.67) and 3 are formed in >95% yield: i.e., the reaction is quantitative by ^{1}H NMR spectroscopy.

The kinetic isotope effect, k_H/k_D, measured by comparing the rates of decomposition of 2 and [K(18-crown-6)]$^+$[W$_2$(OC(CD$_3$)$_3$)$_7$]$^-$ (2-d_{63}), was 3.5(1) at 23 °C [3.0(1) at 60.7 °C]. This clearly indicates that C–H bond breaking is significant in the transition state for the reaction (primary isotope effect), but does not, however, imply that C–H bond rupture is rate-limiting since other factors may contribute to the overall rate. In order to probe this question more thoroughly, the decomposition of [K(18-crown-6)]$^+$[W$_2$(OC(CH$_3$)(CD$_3$)$_2$)$_7$]$^-$ (2-d_{42}) was investigated.[16] In this experiment, the ratio (CD$_3$)$_2$C=CH$_2$:(CH$_3$)(CD$_3$)C=CD$_2$ is a true measure of the kinetic isotope effect *for the C–H bond-breaking component of the reaction.* The results were identical within experimental error: k_H/k_D = 3.5(4) at 23 °C [3.0(3) at 60.7 °C], verifying that C–H bond rupture is involved in the rate-determining step for the overall reaction shown in eq 2.[17]

Three plausible mechanisms by which a *tert*-butoxide ligand in 2 is converted to hydrido–oxo ligands in 3 have been considered.

A carbenium ion mechanism, wherein C–O bond heterolysis occurs, cannot be operative since we have already concluded that C–H bond rupture is involved in the rate-determining step. Furthermore, it is extremely unlikely that heterolytic cleavage of the C–O bond occurs in a rapid preequilibrium prior to the transfer of a proton in this mechanism. The second possibility, which finds precedent in recently described studies by Bercaw and coworkers[18] involves alkyl migration from an alkoxide ligand to form oxo and alkyl ligands, followed by rate-determining β-hydride elimination. This seems rather unlikely on the basis of steric considerations. Furthermore, in the few cases where alkyl group transfer to a metal has been shown to occur from an alkoxide, thiolate, or amide ligand, the migration was rate-determining and exhibited large free energies of activation ($\Delta G^\ddagger \geq$ 31 kcal/mol).[18]

Scheme 1



The remaining mechanism is shown in Scheme 1, wherein an alkoxide ligand transfers a hydride to the metal(s) in concert with the formation of a W=O bond. While there are numerous other possible ligand arrangements,[19] we are particularly attracted to the one shown because of the six-membered transition state and the ease of electronic reorganization. If concerted, this process would be related to the symmetry-allowed retro-ene reaction.[20] The small but negative entropy of activation observed for this transformation is typical of intramolecular reactions involving cyclic transition states.[21] The increase in oxidation state (W$_2^{8+}$ in 3 compared to W$_2^{6+}$ in 2) resulting from the introduction of W$_2$(μ-H) and W$_2$(μ-O) bonds must be the thermodynamic driving force for this reaction. This is clearly favored for tungsten relative to molybdenum, since it is easier to oxidize a third-row element relative to its second-row congener.[22] The negative charge associated with 2 should further facilitate this process relative to neutral complex 1.

Finally, we note two other possibilities that are in agreement with the available experimental data. The first involves transfer of a hydride to the oxygen atom of the same alkoxide to form isobutylene and a hydroxide ligand which rapidly tautomerizes to the observed final product. Alternatively, hydride transfer may occur to another alkoxide to yield isobutylene and a coordinated alcohol, which undergoes rapid oxidative addition to afford the final product. Both of these possibilities find ample precedent in the literature.[23]

Acknowledgment. We thank the National Science Foundation for support, Vincent F. Distasi for the synthesis of ^{t}BuOH-d_6, and Professor Peter T. Wolczanski for his critical reading of the manuscript.

Supplementary Material Available: Atomic coordinates and bond distances and angles for 3 (14 pages); observed and calculated structure factors (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfiche version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

[15] W$_2$(OR)$_6$ forms a reversible adduct W$_2$(OR)$_6$(py)$_2$ (py = C$_5$D$_5$N) that is fluxional on the NMR time scale at temperatures in the range 23–45 °C, which inhibits the accurate measurement of this species. For this reason, and because equilibrium 1 was so far to the right at all the temperatures studied, the temperature dependence of K_{eq} could not be determined.

[16] ^{t}BuOH-d_6 was prepared from MeMgBr and acetone-d_6 in diethyl ether.

[17] (a) A large coverage-dependent kinetic isotope effect (k_h/k_d = 11 ± 3 or 5 ± 2 extrapolated to 300 K) was previously noted for the decomposition of surface bound *tert*-butoxide on Cu(110).[17b] (b) Brainard, R. L.; Madix, R. J. *Surf. Sci.* **1989**, *214*, 396.

[18] (a) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21. (b) Nelson, J. E.; Parkin, G.; Bercaw, J. E. *Organometallics* **1992**, *11*, 2181.

[19] Considering the fluxional behavior of 2, numerous ligand arrangements/geometries may be easily accessible.

[20] (a) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. (b) Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476.

[21] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1987; pp 903–971.

[22] The Mo analogue of 2 does not decompose below 100 °C. At higher temperatures, a nonselective decomposition occurs to afford an intractible mixture of products. No hydride resonances similar to those found for 3 were observed in the ^{1}H NMR spectrum of this mixture.

[23] For metal hydroxide/hydrido–oxo tautomerization, see refs 11c, 11e, and 18a. For oxidative addition of alcohols to triply-bonded W≡W complexes, see: Chisholm, M. H.; Smith, C. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 222.