Comparison of the structures of **5** and **6** is quite instructive, showing that both the Rh–C and C–O bonds are significantly shorter in the rhodaoxetane. As a matter of fact, the C–O bond of **6** is even shorter than that of oxetane itself [1.444 (2) Å],[22] contrary to the expectation of increased bond length upon strain relief.[6a,23] These features indicate some contribution of structure **7**, i.e., partial metathesis to a metal carbene and a ketone. This is also compatible with the planar ring structure. In accordance with this, the other reported simply substituted metallaoxetane, $CpIr(CH_2CMe_2O)PMe_3$, undergoes photoextrusion of acetone to generate an iridiacarbene.[24]

7

We are currently studying the properties and reactivity of the rhodaoxetane, emphasizing model transformations. We are also planning to prepare analogous complexes by the same route.[25]

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Supplementary Material Available: Crystal data and tables of atom coordinates, anisotropic temperature factors, hydrogen atom coordinates, bond lengths, and bond angles for **5** and **6** and torsion angles for **6** (12 pages). Ordering information is given on any current masthead page.

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[22] Chan, S. I.; Zinn, J.; Gwinn, W. D. *J. Chem. Phys.* **1961**, *34*, 1319.

[23] For example, the C–O bond length of oxirane is slightly shorter than that of oxetane; see ref 22 and the following: Cunningham, G. L.; Boyd, A. W.; Myers, R. J.; Gwinn, W. D.; Le Van, W. I. *J. Chem. Phys.* **1951**, *19*, 676.

[24] Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3079.

[25] Two other metallaoxetanes were reported after submission of this paper. (a) Iridiaoxetane: Day, V. W.; Klemperer, W. G.; Lockledge, S. P.; Main, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 2031. (b) Rhenaoxetane: Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 3234.

Deoxygenation of Alcohols and Desulfurization of Thiols by $WCl_2(PMePh_2)_4$

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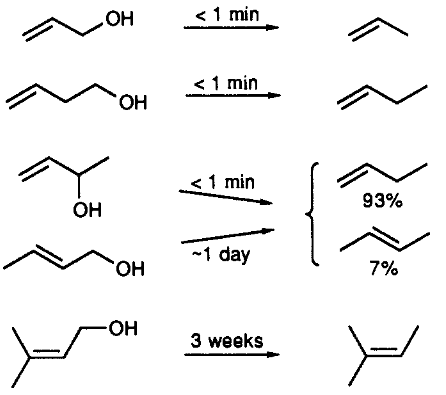
A variety of chemical processes involve metal-mediated addition or removal of an oxygen or sulfur atom from an organic substrate, ranging from oxidation[2] and hydrodesulfurization[3] reactions to enzymatic processes.[4] We have found that the tungsten(II) complex $WCl_2(PMePh_2)_4$ (**1**)[5] readily abstracts an oxygen or a sulfur atom from a variety of substrates, including epoxides and episulfides, ketones, and heterocumulenes such as CO_2 and RNCS.[6] The metal product of these reactions is a terminal oxo or terminal sulfido complex such as $W(O)Cl_2(PMePh_2)_3$ (**2**) or $W(S)Cl_2(PMePh_2)_3$ (**3**).[6] This report describes the reduction of alcohols and thiols by **1**, including their novel deoxygenation or desulfurization to hydrocarbons. Selected ethers are also deoxygenated.

Scheme I. Deoxygenation of Unsaturated Alcohols by $WCl_2(PMePh_2)_4$ (**1**), Forming $W(O)Cl_2(PMePh_2)_3$ (**2**)



A benzene solution of **1** reacts with simple alcohols such as methanol or ethanol over >1 week at ambient temperatures to give two sets of products in roughly equal amounts: The tungsten(IV) oxo complex **2** and the corresponding alkane, together with a bis(alkoxide) complex (**4**) and hydrogen (eq 1; R = Me, Et, $PhCH_2$).[7,8] Compounds **2** and **4** together are formed in high

$$\underset{\mathbf{1}}{WCl_2(PMePh_2)_4} + ROH \rightarrow \underset{\mathbf{2}}{W(O)Cl_2(PMePh_2)_3} + RH + \underset{\mathbf{4}}{W(OR)_2Cl_2(PMePh_2)_2} + H_2 \quad (1)$$

yield when the reaction is carried out in a sealed NMR tube.[9] Formation of a metal–oxo complex from an alcohol has been previously observed[10] (including from $WCl_2(PMe_3)_4$ and CH_3OH[11]), but concomitant alkane formation is, to our knowledge, unprecedented. With phenol and *p*-cresol the predominant products are a bis(aryl oxide) complex $W(OAr)_2Cl_2(PMePh_2)_2$ (**5**) and H_2.[7-9] C–O bond cleavage does not occur in this case presumably because the aromatic ring-to-oxygen bond is almost 20 kcal/mol stronger than aliphatic C–O bonds.[12]

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[1] Presidential Young Investigator, 1988–1993. Alfred P. Sloan Research Fellow, 1989–1991.

[2] (a) Hucknall, D. J. *Selective Oxidation of Hydrocarbons*; Academic: New York, 1974. Cullis, C. F.; Hucknall, D. J. *Catalysis* (*London*) **1982**, *5*, 273. (b) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic: New York, 1981. (c) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988, particularly Chapter 7.

[3] Furimsky, E. *Catal. Rev.—Sci. Eng.* **1980**, *22*, 371–400.

[4] Examples include reactions of cytochrome P-450 (*Cytochrome P-450: Structure, Mechanism, and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986) and various molybdenum enzymes (*Molybdenum Enzymes*; Spiro, T. G., Ed.; Wiley: New York, 1985). See also: Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401–1449. Reference 2c, pp 296–298.

[5] (a) Sharp, P. R. *Organometallics* **1984**, *3*, 1217–1223. (b) Sharp, P. R.; Bryan, J. C.; Mayer, J. M. *Inorg. Synth.*, in press.

[6] (a) Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826–2828. (b) Su, F.-M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Polyhedron* **1989**, *8*, 1261–1277. (c) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 7213–7214. (d) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298–2308.

[7] Selected NMR (C_6H_6) and IR (Nujol) data: $W(OMe)_2Cl_2(PMePh_2)_2$: ^1H NMR δ 2.99 (s, OCH_3), 1.99 (t, J_{PH} = 3 Hz, PCH_3); ^{31}P NMR −31.7 (J_{WP} = 322 Hz); IR ν_{CO} = 1096 cm^{-1}. $W(OC_6H_4Me)_2Cl_2(PMePh_2)_2$ (from *p*-cresol): ^1H NMR δ 2.09 (s, $OC_6H_4CH_3$), 1.87 (t, 4 Hz, PCH_3); ^{31}P NMR 54.0 (J_{WP} = 314 Hz); IR ν_{CO} = 1097 cm^{-1}. Complexes **4** and **5** have not been obtained in pure form because of difficulties in separation and isolation; their compositions are indicated by NMR and IR spectra[8] and by reactions with $H_2O/PMePh_2$ to give **2** + 2ROH.

[8] H_2 was identified by oxidative addition to $Ir(CO)Cl(PPh_3)_2$, CH_4 by NMR and gas-phase IR.

[9] Yields determined in situ by ^1H NMR using a ferrocene standard. In situ yields are difficult to determine accurately because of the high reactivity of **1** and difficulty in its purification, and because of its broad NMR resonances. Difficulties in workup prevent determination of meaningful yields from preparative procedures.

[10] Reference 2c, pp 64–65.

[11] Chiu, K. W.; Lyons, D.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *Polyhedron* **1983**, *2*, 803–810.

[12] Bond strengths calculated by using $H_f°$ values from the following: *JANAF Thermochemical Tables*, 3rd ed.; *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1. *Thermochemical Tables*; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1986. Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969. Benson, S. W. *Thermochemical Kinetics*, Wiley: New York, 1968.

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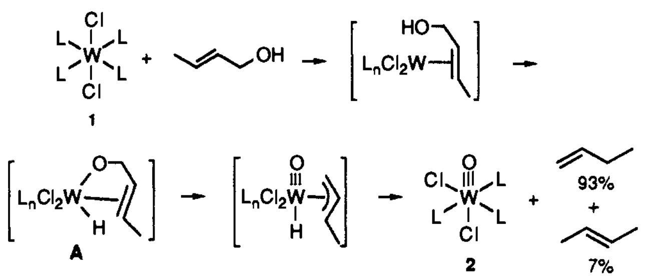
Scheme II



Thiols are desulfurized by **1** to form alkanes and the tungsten sulfido complex **3**, without any evidence for the formation of thiolate complexes (eq 2; R = Et, ${}^tBu$). These reactions are much

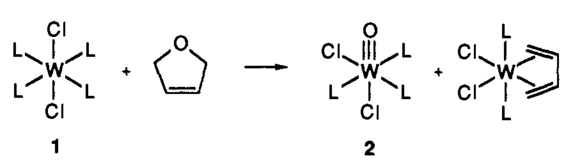
$$\underset{\mathbf{1}}{WCl_2(PMePh_2)_4} + RSH \rightarrow \underset{\mathbf{3}}{W(S)Cl_2(PMePh_2)_3} + RH + PMePh_2 \quad (2)$$

more rapid than those with alcohols: ethanethiol is desulfurized in 10 min at ambient temperatures and ${}^tBuSH$ within an hour, while deoxygenation of ethanol requires 3 weeks and ${}^tBuOH$ is unreactive. The reaction of **1** and ${}^tBuSH$ initially forms **3** and isobutane in high yields,[9] but **3** reacts further with the thiol to give a complex mixture of products including $SPMePh_2$. With EtSH, degradation of **3** by the thiol is competitive with its formation and **3** does not accumulate in the reaction mixture. Aryl thiols yield hydrogen[8] and apparently paramagnetic products which have not been characterized.

In contrast to the slow reactions of **1** with saturated alcohols, allyl alcohol is very rapidly (<1 min) and quantitatively[9] converted to **2** and propene (Scheme I).[13] Similarly, allyl mercaptan is desulfurized within 1 min. 3-Buten-1-ol is also rapidly deoxygenated, to 1-butene, indicating that conjugation is not responsible for the faster rates of unsaturated substrates. Rates are affected by steric hindrance about the double bond (Scheme I), with the trisubstituted olefin reacting as slowly as aliphatic alcohols. The rate enhancement thus seems to result from coordination of the double bond to the tungsten center, consistent with the rapid formation of a bis(ethylene) complex from **1** and ethylene.[5a] Double-bond migration is observed on deoxygenation of 3-buten-2-ol and 2-buten-1-ol, both isomers yielding 93:7 mixtures of 1-butene and *trans*-2-butene (by NMR).

The deoxygenation does not appear to proceed via free-radical intermediates, as no ethane is observed on methanol reduction, nor butane or ethylene from EtOH, and CH_3OH is reduced to CH_4 even in toluene-d_8. The reaction of benzyl alcohol with **1** is similar to that of methanol, both in rate and in the ratio of products. In C_6D_6 solution, CD_3OD is reduced to CD_4 and allyl alcohol-*O*-*d* forms $CH_2{=}CHCH_2D$. Carbocations also seem unlikely as aromatic alkylation and ether formation are not observed.[14] The observation of the same nonthermodynamic product mixture from isomeric butenols (Scheme I) suggests a common intermediate, probably an η^3 or fluxional 1-methylallyl complex. These data are consistent with a mechanism for the deoxygenation of allyl alcohols (Scheme II) involving initial coordination of the double bond, followed by oxidative addition of the O–H bond[15] to form an allyloxy intermediate (A). The rate enhancement for unsaturated alcohols is then due to oxidative addition being an intramolecular process. Intermediate A can rearrange[16] to an oxo–allyl–hydride species[17] which reductively eliminates alkene. An alternative involving loss of RH directly from A[18] is difficult to reconcile with the observed double-bond migration.

This chemistry has been extended to ethers by using the idea that the double bond acts as a tether to bring the oxygen to the metal center. Thus 2,5-dihydrofuran and diallyl ether are rapidly deoxygenated to give **2** (e.g., eq 3[19]), while THF and Et_2O do not react with **1** at ambient temperatures.



(3)

Deoxygenation of alcohols and ethers (net oxygen atom transfer) is a quite unusual reaction. The formation of the very strong tungsten–oxygen multiple bond in **2**[20] provides a driving force for this pathway as opposed to the more common reduction of alcohols to alkoxide compounds. Further studies of the mechanism and the scope of these unusual transformations are in progress, including the differences between alcohols, thiols, and amines (which are not reduced to imido complexes[21]).

Acknowledgment. We thank Dr. Jeff Bryan for discovering reaction 3 and for his insightful advice. This work was supported by the National Science Foundation and the Chevron Research Co.

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[13] With excess allyl alcohol, $W(O)Cl_2(CH_2{=}CHCH_2OH)(PMePh_2)_2$ is formed in equilibrium with **2** and can be the predominant product.[6b] Similar equilibria are observed for the other terminal alkenols as well. All of the unsaturated alcohol reactions appear to proceed in high yield.[9]

[14] Cf.: Noble, A. M.; Winfield, J. M. *J. Chem. Soc. A* **1970**, 501–506.

[15] Cf.: Reference 11. Wilkinson, G.; Chiu, K. W.; Jones, R. A.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1981**, 1204. Oxidative addition of the C–O bond instead of the C–H bond is also possible, followed by loss of alkene from a W(OH)(allyl) species; cf.: Herrmann, W. A.; Kuchler, J. G.; Weichselbaumer, G.; Herdtweck, E.; Kiprof, P. *J. Organomet. Chem.* **1989**, *372*, 351–370.

[16] Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21–39.

[17] Oxo-allyl complexes: Spaltenstein, E.; Erikson, T. K. G.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 617–623. Atagi, L. A.; Mayer, J. M., unpublished results.

[18] Listemann, M. L.; Schrock, R. R.; Dewan, J. C.; Kolodziej, R. M. *Inorg. Chem.* **1988**, *27*, 264–271.

[19] Bryan, J. C. Ph.D. Thesis, University of Washington, 1988. Reaction with dihydrofuran proceeds in high yield[9] to a roughly 3:1 mixture of **2** and $WCl_2(C_4H_6)(PMePh_2)_2$.

[20] D(W≡O) is estimated to be >138 kcal/mol.[6d]

[21] Over, D.; Mayer, J. M., unpublished results.

Ruthenium–Tungsten and Iron–Tungsten Complexes with Ethynyl and Ethynediyl Bridges

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Small carbon fragments are important in the surface chemistry of many heterogeneous catalysts,[1] often as reactive intermediates[2] or as precursors to graphitic overlayers.[1] While metal cluster carbides are relatively common,[3] complexes with carbide[4] and

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[1] (a) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: Ithaca, NY, 1981; pp 494–499. (b) Viswanathan, B. *J. Mol. Catal.* **1986**, *37*, 157–163. (c) Bianchi, D.; Tau, L. M.; Borcar, S.; Bennett, C. O. *J. Catal.* **1983**, *84*, 358–374. (d) Erdōhelyi, A.; Solymosi, F. *J. Catal.* **1983**, *84*, 446–460. (e) Erly, W.; McBreen, P. H.; Ibach, H. *J. Catal.* **1983**, *84*, 229–234. (f) Orita, H.; Naito, S.; Tamaru, K. *J. Catal.* **1988**, *111*, 464–467. (g) Stockwell, D. M.; Bianchi, D.; Bennett, C. O. *J. Catal.* **1988**, *113*, 13–25. (h) Shincho, E.; Egawa, C.; Naito, S.; Tanaru, K. *Surf. Sci.* **1985**, *155*, 153. (i) Duncan, T. M.; Winslow, P.; Bell, A. T. *J. Catal.* **1985**, *93*, 1.

[2] (a) Anderson, R. B. *The Fischer-Tropsch Synthesis*; Academic Press: 1984. (b) Chisholm, M. H.; Folting, K.; Hampden-Smith, M. J.; Hammond, C. E. *J. Am. Chem. Soc.* **1989**, *111*, 7283–7285.

[3] (a) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Nicholls, J. N.; Vargas, M. D. *J. Organomet. Chem.* **1983**, *249*, 255–272. (b) Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1. (c) Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203. (d) Hriljac, J. A.; Swepston, P. N.; Shriver, D. F. *Organometallics* **1985**, *4*, 158–166. (e) Chisholm, M. H. *J. Organomet. Chem.* **1987**, *334*, 77–84.

0002-7863/90/1512-6414$02.50/0