for the complex $(hubM_3)_1(R'CA)_3$ (R_f 0.35–0.45) and minor spots for uncomplexed $hubM_3$ (R_f 0.15–0.30) and uncomplexed R'CA (R_f 0.0).[11]

These data establish the composition and structure of $(hubM_3)_1(R'CA)_3$. Preorganization, i.e., joining the three melamine units by using the 1,3,5-$C_6H_3R_3$ hub and spokes conformationally compatible with the desired structure (Scheme 1), is an important factor contributing to the stability of the complex. Reaction of monomeric derivatives of M and CA in solution forms complexes having approximately the correct molecular weight for $CA_3{\cdot}M_3$ by VPO,[12] but crystallization of these complexes yields extended linear structures.[13] The apparent solution molecular weight in these systems may represent a true cyclic hexamer $CA_3{\cdot}M_3$ or an average of linear and cyclic oligomers.

Acknowledgment. NMR instrumentation was supported by National Science Foundation Grant CHE-84-10774. Mass spectra were obtained by Dr. Andrew Tyler (Harvard University Mass Spectrometry Facility) using instrumentation provided by JEOL (USA) Inc. We thank Professor Robert Cohen (MIT, Chemical Engineering) for the loan of the vapor pressure osmometer and for helpful discussions.

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[11] We have not obtained crystals of the 1:3 complex that are suitable for X-ray diffraction.

[12] VPO indicated a MW of 2710 for a 1:1 mixture of *N,N'*-bis(4-*tert*-butylphenyl)melamine and 3,3,3-triphenylpropyl cyanurate (calculated for (*N,N'*-bis(4-*tert*-butylphenyl)melamine)$_3$(3,3,3-triphenylpropyl cyanurate)$_3$ = 2370) over the concentration range 6–20 mM in $CHCl_3$ at 37 °C. The MW estimated by VPO depends strongly on concentration at lower concentrations.

[13] Lehn, J. M.; Mascal, M.; DeCian, A.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1990**, 479–481. Zerkowski, J.; Seto, C.; Whitesides, G. M., unpublished results.

Synthesis and X-ray Structure of a Simple Metallaoxetane. Metal-Based Selectivity in Oxidative Addition

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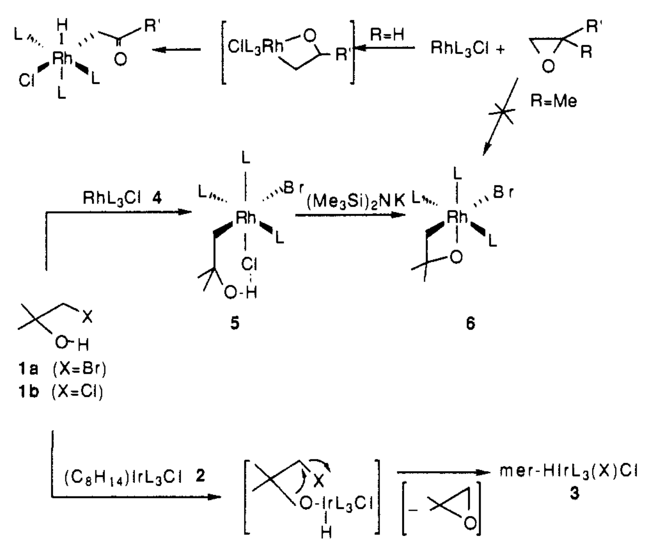
2-Metallaoxetanes are often invoked as crucial intermediates in metal-catalyzed oxidations,[1] including cytochrome P-450 and biomimetic olefin epoxidations.[2] Their intermediacy is also postulated in various metal-mediated reactions of epoxides,[3] in olefin metathesis,[4] and in conversions of carbonyls to alkenes by metal alkylidenes.[5] However, such complexes are exceedingly scarce and have been isolated in special cases where the metallaoxetane ring is stabilized by multiple cyano substitution[6] or by an exocyclic double bond.[7] Only recently has the first example of a simply substituted 2-metallaoxetane been reported.[8] We report here (a) a straightforward route for the preparation of a simple metallaoxetane; (b) the crystallographic characterization of such a complex; (c) the structure of an analogous β-hydroxyalkyl complex, allowing direct evaluation of the structural consequences of ring closure; and (d) unusual metal-based chemoselectivity in oxidative addition of a bifunctional substrate.

Scheme I[a]



[a] L = PMe_3; C_8H_{14} = cyclooctene.

We had reported that epoxides undergo C–O oxidative addition to electron-rich rhodium and iridium complexes to yield β-oxoalkyl metal hydrides, possibly by β-hydride elimination of an intermediate metallaoxetane.[3g,9] However, attempts to isolate the primary oxidative addition product by use of a geminally disubstituted epoxide were not successful. Hence we planned the preparation of a metallaoxetane indirectly from the corresponding halohydrin (Scheme I).

Addition of an equimolar amount of a 0.14 M toluene solution of the halohydrins **1** to a 0.04 M solution of the electron-rich iridium complex **2** in toluene under nitrogen at -30 °C leads after 30 min to formation of the hydrides **3**[10] (ca. 70% yield), possibly by O–H rather than C–X oxidative addition, followed by epoxide elimination. We find this surprising, since oxidative addition of alkyl halides to low valent metal complexes is usually a facile process,[11] taking place even in alcoholic solvents,[12] whereas such

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[1] For example: (a) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120. (b) Schröder, M.; Constable, E. C. *J. Chem. Soc., Chem. Commun.* **1982**, 734. (c) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. (d) Jorgensen, K. A. *Chem. Rev.* **1989**, *89*, 431.

[2] See, for example: (a) Collman, J. P.; Brauman, J. L.; Meunier, B.; Hayashi, T.; Kodadek, T.; Raybuck, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 2000. (b) Collman, J. P.; Kodadek, T.; Raybuck, S. A.; Brauman, J. L.; Papazian, L. M. *Ibid.* **1985**, *107*, 4343. (c) Collman, J. P.; Brauman, J. L.; Meunier, B.; Raybuck, S. A.; Kodadek, T. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 3245. (d) Groves, J. T.; Avaria-Neisser, G. E.; Fish, K. N.; Imachi, M.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 3837. (e) Groves, J. T.; Watanabe, Y. *Ibid.* **1986**, *108*, 507. (f) Rappe, A. K.; Goddard, W. A. *Ibid.* **1982**, *104*, 3287.

[3] (a) De Pasquale, R. J. *J. Chem. Soc., Chem. Commun.* **1973**, 157. (b) Milstein, D.; Buchman, O.; Blum, J. *J. Org. Chem.* **1977**, *42*, 2299. (c) Blum, J.; Zinger, B.; Milstein, D.; Buchman, O. *J. Org. Chem.* **1978**, *43*, 2961. (d) Kamiya, Y.; Kawato, K.; Ohta, H. *Chem. Lett.* **1980**, 1549. (e) Schwartz, J.; Hayasi, Y. *Inorg. Chem.* **1981**, *20*, 3473. (f) Suzuki, M.; Watanabe, A.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 2095. (g) Milstein, D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3773. (h) Osborne, R. B.; Ibers, J. A. *J. Organomet. Chem.* **1982**, *232*, 273; (i) *Ibid.* **1982**, *232*, 371. (j) Alper, H.; Arzoumanian, H.; Petrignani, J.-F.; Saldana-Maldonado, M. *J. Chem. Soc., Chem. Commun.* **1985**, 340. (k) Miyashita, A.; Ishida, J.; Nohira, H. *Tetrahedron Lett.* **1986**, *27*, 2127. (l) Hase, T.; Miyashita, A.; Nohira, H. *Chem. Lett.* **1988**, 219. (m) Aye, K. T.; Ferguson, G.; Lough, A. J.; Puddephatt, R. J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 767.

[4] Ivin, K. J.; Reddy, B. S. R.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1062.

[5] (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Buchwald, S. L.; Grubbs, R. H. *Ibid.* **1983**, *105*, 5490. (c) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *Ibid.* **1980**, *102*, 3270.

[6] (a) Schlodder, R.; Ibers, J. A.; Lenarda, M.; Graziani, M. *J. Am. Chem. Soc.* **1974**, *96*, 6893. (b) Lenarda, M.; Pahor, N. B.; Calligaris, M.; Graziani, M.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1978**, 279. (c) Lenarda, M.; Ros, R.; Traverso, O.; Pitts, W. D.; Baddley, W. H.; Graziani, M. *Inorg. Chem.* **1977**, *16*, 3178.

[7] Ho, S. C.; Hentges, S.; Grubbs, R. H. *Organometallics* **1988**, *7*, 780.

[8] Klein, P. D.; Hayes, J. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3704.

[9] Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 5227.

[10] **3a**: IR (Nujol) 2161 (m, ν_{Ir-H}), 951 (vs, ν_{P-C}); ^{1}H NMR (pyridine-d_5) δ 1.49 (t, J_{P-H} = 3.7 Hz, 18 H, 2PMe$_3$), 1.20 (d, J = 10 Hz, 9 H, PMe$_3$), −21.6 (dt, J_{P1-H} = 19.4 Hz, J_{P2-H} = 14 Hz, 1 H); ^{31}P{^{1}H} NMR (pyridine-d_5) δ −40 (d, J_{P-P1} = 20 Hz, 2 P), −44 (t, J_{P-P1} = 20 Hz, 1 P).

[11] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 284–321. (b) Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434.

[12] Oxidative addition of organic halides in the presence of alcohols is a key step in metal-catalyzed carbalkoxylation of these substrates. See, for example: Milstein, D. *Acc. Chem. Res.* **1988**, *21*, 428 and references therein.

0002-7863/90/1512-6411$02.50/0

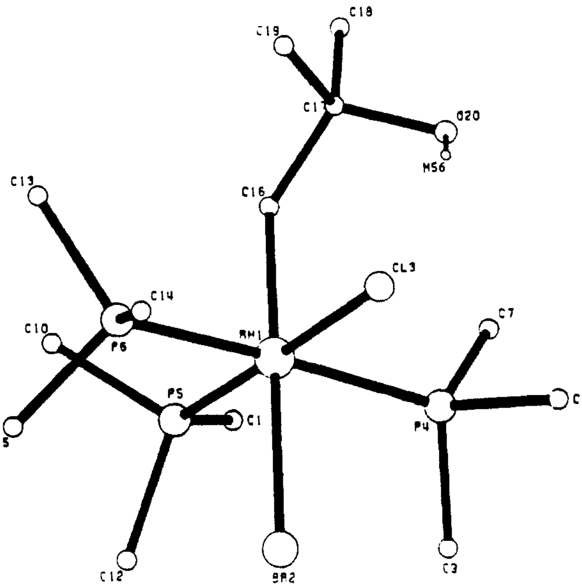

Figure 1. Molecular structure of **5** (C–H hydrogens are omitted for clarity). Selected bond distances (Å) and angles (deg): Rh(1)–C(16), 2.131 (8); Rh(1)–P(4), 2.367 (4); Rh(1)–P(5), 2.271 (4); Rh(1)–P(6), 2.367 (4); C(16)–C(17), 1.542 (11); C(17)–O(20), 1.452 (9); C(17)–C(18), 1.519 (11); C(17)–C(19), 1.529 (12); P(6)–Rh(1)–P(4), 91.2; P(5)–Rh(1)–Cl(3), 88.4; C(16)–Rh(1)–P(4), 91.2 (3); Rh(1)–C(16)–C(17), 123.2 (5); C(16)–C(17)–O(20), 112.1 (6); C(17)–O(2)–H(56), 106.7 (6).

reactions involving O–H bonds are less common.[13] In addition, we find that reaction of **2** with *tert*-butyl alcohol is approximately 2 orders of magnitude slower than with **1a**. A possible explanation for the facility of the above reaction invokes prior coordination of the Ir(I) complex to the halogeno substituent,[14] although a base-type mechanism involving deprotonation of **1** by **2** prior to an internal nucleophilic attack may also be possible.

In complete contrast, reaction of the analogous rhodium complex **4** with **1a** in toluene at 25 °C result in selective C–Br oxidative addition to yield complex **5**[15] (in 65% isolated yield), the O–H bond remaining intact. Since neopentyl halides are known to undergo nucleophilic displacement with difficulty,[16] the relative facility of this reaction with **4** may be a result of assistance by the hydroxo group. No reaction is observed with the chlorohydrin **1b** under these conditions. Experiments aimed at clarification of this unusual metal-based chemoselectivity are underway.

An X-ray structural study of crystals of complex **5**[17] shows that trans oxidative addition has taken place (Figure 1). The OH···Cl distance of 2.416 Å indicates the presence of one of the strongest intramolecular hydrogen bonds known for a metal-bound halide ligand.[18] The difference in Rh–P bond lengths reflects the weak chloride trans effect.

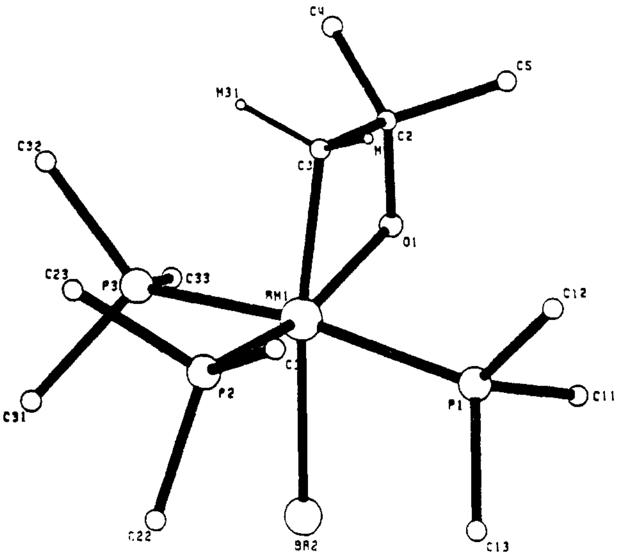

Figure 2. Molecular structure of **6** (methyl hydrogens are omitted for clarity). Selected bond distances (Å) and angles (deg): Rh(1)–O(1), 2.099 (8); Rh(1)–C(3), 2.069 (10); Rh(1)–P(1), 2.352 (4); Rh(1)–P(2), 2.255 (4); Rh(1)–P(3), 2.331 (4); C(3)–C(2), 1.537 (14); C(2)–O(1), 1.416 (12); P(3)–Rh(1)–P(1), 161.1 (1); O(1)–Rh(1)–P(2), 163.6 (2); C(3)–Rh(1)–O(1), 67.6 (4); C(3)–C(2)–O(1), 103.5 (7); C(2)–C(3)–Rh(1), 93.2 (6); C(2)–O(1)–Rh(1), 95.7 (5).

Treatment of a 0.014 M THF solution of **5** with the hindered base $(Me_3Si)_2NK$ (0.03 M in THF, 1.8 equiv) under nitrogen at −30 °C, followed by filtration and solvent evaporation, results in a solid residue. Extraction with C_6D_6 yields the crude rhodaoxetane **6** in 80% yield.[19] Slow, repeated freeze–thaw concentration of the benzene solution results in colorless crystals suitable for an X-ray structural study (Figure 2).[20]

It is noteworthy that ring closure proceeds by substitution of the chloride rather than the bromide ligand, especially since the latter is trans to the alkyl group, which has a stronger trans effect than PMe_3. This may indicate involvement of the base silyl group in a halide abstraction process.

As expected, the Rh–P(2) bond length is shorter than Rh–P(1) or Rh–P(3), reflecting the small trans effect of the alkoxy ligand relative to that of PMe_3. Interestingly, the structure clearly shows the presence of an essentially planar rhodaoxetane ring, deviations of the atoms from the plane Rh–O–C(3)–C(2) being effectively 0°. For example, the dihedral angle between the C(2)–C(3)–O and O–Rh–C(3) planes of 0.3° is less than the standard deviation (1.5°). This can be compared with the structure of cyano-substituted platinaoxetanes, exhibiting a considerably puckered ring, the dihedral angle being as large as 30°,[6b] although this may be due to unfavorable staggered conformation of the cyano groups in a planar ring, or perhaps to interaction of the cyano group with the metal. On the basis of solution NMR studies, it is concluded that a 3-methylenetitanaoxetane is considerably puckered, and it is suggested that this is required for optimum orbital overlap involving donation of the oxygen lone pair to an empty a_1 orbital.[7] This reasoning is compatible with a planar ring involving the saturated rhodium center in **6**.[21]

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(13) For O–H oxidative addition to Ir(I), see: Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387.

(14) For an example of coordination of organic halides to a metal, see: Burk, M. J.; Segmuller, B.; Crabtree, R. H. *Organometallics* **1987**, *6*, 2241.

(15) **5**: IR (Nujol) 3361 (s, ν_{O-H}), 945 (vs, ν_{P-C}); $^{31}P\{^1H\}$ NMR (THF) δ 11.7 (dt, J_{Rh-P} = 133 Hz, J_{P-P1} = 35 Hz, 1 P), −8 (dd, J_{Rh-P1} = 96 Hz, J_{P-P1} = 35 Hz, 2 P). The β-hydroxyalkyl protons are obscured by PMe_3 signals in ^1H NMR.

(16) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985; pp 298–299.

(17) Crystal data for **5**: $C_{13}H_{36}OP_3ClBrRh$: M = 519.61; monoclinic, space group $P2_1/c$; a = 16.418 (9) Å, b = 8.792 (9) Å, c = 14.375 (9) Å; V = 2177 (2) Å^3; Z = 4, D_{calcd} = 1.63 g cm^{-3}; μ(Mo Kα) = 30.11 cm^{-1}; crystal dimensions 0.1 × 0.1 × 0.1 mm. Data were measured on a Rigaku AFC5 diffractometer at 90 K and corrected for Lorentz, polarization, and absorption effects. The hydrogen atoms were found from the difference Fourier map. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of R = 0.044 and R_w = 0.046. Details are given in the supplementary material.

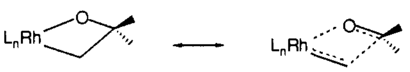
(18) For other recently reported intramolecular hydrogen bonds involving a halogen ligand, see: Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 2803.

(19) **6**: IR (Nujol) 1040 (m, ν_{C-O}), 947 (vs, ν_{P-C}); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −5 (dt, J_{Rh-P} = 118 Hz, J_{P-P1} = 35 Hz, 1 P), −11 (dd, J_{Rh-P} = 104 Hz, J_{P-P1} = 35 Hz, 2 P). The ring protons in ^1H NMR (C_6D_6, 270 MHz) are obscured by ligand protons.

(20) Crystal data for **6**: $C_{13}H_{35}OP_3BrRh$, M = 483.15; orthorhombic, space group $P2_12_12_1$ (No. 19); a = 15.069 (2) Å, b = 15.525 (2) Å, c = 8.662 (4) Å; V = 2026 (1) Å^3; Z = 4, D_{calcd} = 1.58 g cm^{-1}; μ(Mo Kα) = 30.11 cm^{-1}; crystal dimensions 0.3 × 0.3 × 0.1 mm. Data were measured as in ref 17. The hydrogen atoms were found from the difference Fourier map and refined with an overall temperature factor of U_{over} = 0.038 (2) Å^2 × 10^3. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of R = 0.042 and R_w = 0.044. Details are given in the supplementary material.

(21) Although less relevant, the recently reported 3-oxaplatinacyclobutanes also exhibit a planar ring: Hoover, J. F.; Stryker, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 6466; *Organometallics* **1989**, *8*, 2973.

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]



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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]

Acknowledgment. We thank Prof. J. P. Collman for helpful discussions. This research was supported by Grant No. 86-00316 from the U.S.-Israel Binational Science Foundation (BSF), Jerusalem, Israel, and by the Fund for Basic Research, administered by the Israel Academy of Sciences and Humanities. We also thank the Johnson-Matthey Co. for a loan of $RhCl_3$.

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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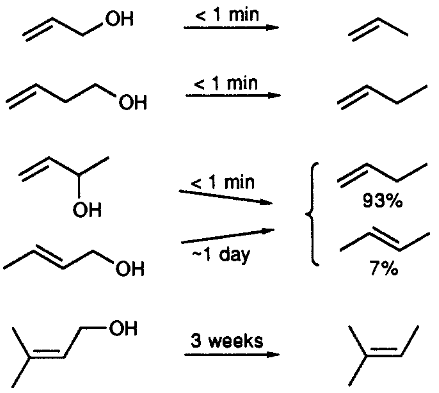
A variety of chemical processes involve metal-mediated addition or removal of an oxygen or sulfur atom from an organic substrate, ranging from oxidation[2] and hydrodesulfurization[3] reactions to enzymatic processes.[4] We have found that the tungsten(II) complex $WCl_2(PMePh_2)_4$ (**1**)[5] readily 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 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]

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

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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 $\nu_{CO} = 1096$ 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 $\nu_{CO} = 1097$ 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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