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Oxygen Atom Transfer Reactions. Epoxide Deoxygenation by $MoO(Et_2dtc)_2$

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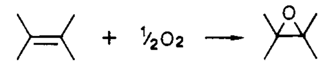
This paper documents a study of the potential use of molybdenum(VI)–oxo complexes as catalysts for olefin epoxidation with O_2. Available thermodynamic data show that the reaction $MoO_2(Et_2dtc)_2$ + olefin → $MoO(Et_2dtc)_2$ + epoxide is endothermic by 8 kcal/mol. Consistent with this data, treatment of a variety of olefins with $MoO_2(Et_2dtc)_2$ (100 psi O_2, 110 °C) does not lead to epoxidation. Interestingly, however, no other oxygenates are observed under these conditions even though the formation of these products is highly exothermic (e.g. –22 kcal/mol for ketone formation). In order to delineate the kinetic and thermodynamic barriers for these oxidations, epoxide deoxygenation by $MoO(Et_2dtc)_2$ was tested. This reaction is found to proceed smoothly with 100% olefin selectivity; rearrangement of epoxide to ketone or other oxygenates is not observed. This reaction is also highly stereoselective, as shown by the formation of *trans*-β-methylstyrene from *trans*-1-phenylpropylene oxide and *cis*-2-butene from *cis*-2,3-epoxybutane. This stereoselectivity indicates that these reactions are concerted or proceed through a cyclic intermediate. Furthermore, because the deoxygenation proceeds selectively, it is apparent that the kinetic barrier for epoxidation is lower in energy than that for other oxidation pathways. This evidence predicts that if molybdenum could be made a stronger oxidant, then selective epoxidation should result. A study has been undertaken to synthesize complexes with ligands that achieve this result.

Introduction

Epoxides are chemical intermediates finding uses in a wide variety of applications. The preparation of epoxides from olefins typically requires the use of oxidants such as peracids, alkyl hydroperoxides, hydrogen peroxide, and hypochlorous acid.[1] Although often quite efficient, these routes require the use of rather expensive reagents, multiple steps, and the formation of stoichiometric amounts of byproducts. Of course, the preferred route to epoxides is the direct oxidation of olefins with O_2, as shown in (1). This synthesis uses a cheap, readily available oxidant and

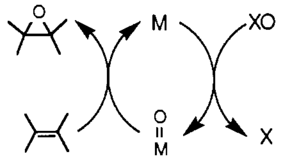


(1)

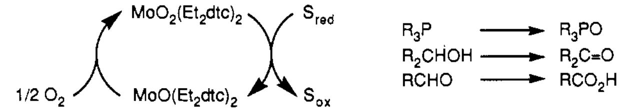
produces only the epoxide as product. However, there are only a few examples of catalysts for this reaction. The only commercial process using oxygen in this manner is the manufacture of ethylene oxide, which is catalyzed by silver on alumina. Recently, Groves showed that a ruthenium porphyrin complex catalyzes the epoxidation of a variety of olefins with O_2 under mild conditions in the liquid phase.[2] Under certain conditions, metal–nitro complexes also catalyze this reaction.[3]

Although the catalytic epoxidation of olefins with O_2 has been largely unsuccessful, there are numerous examples of catalytic epoxidation using alternative oxidants.[2,4] These examples typically employ a metal complex and an oxygen atom transfer reagent. Suitable oxygen atom transfer reagents are amine *N*-oxides, iodosoarenes, peracids, and hypochlorite. The mechanism of these catalytic reactions is shown in Scheme I. First, the oxidizing agent transfers an oxygen atom to the metal, generating an oxidized metal–oxo complex. The metal atom in these catalytic intermediates is in a very high oxidation state; Cr(V), Mn(V), Fe(V), and Ru(VI) are typical examples. These intermediates epoxidize the olefin and re-form the starting metal complex, thereby completing the catalytic cycle.

Scheme I



Scheme II



Although these systems do not use O_2 as described above, they seem to indicate a general trend: metal–oxo complexes, where the metal is in a very high oxidation state, are typically selective epoxidation reagents. This suggests that the key to finding an epoxidation catalyst which uses O_2 as oxidant would be to investigate high-valent metal–oxo complexes that may be prepared via reaction of a low oxidation state complex with O_2. Consistent with this idea, the ruthenium catalyst described above is believed to proceed via this type of mechanism. The possibility of using *cis*-dioxomolybdenum(VI) complexes in this regard has been investigated, and the results are reported here.

Results and Discussion

Preliminary investigations involved $MoO_2(Et_2dtc)_2$ (dtc = dithiocarbamate) for several reasons. Molybdenum is in its highest oxidation state, +6. Although this is certainly not an unusual oxidation state for molybdenum, the four ligating sulfur atoms make this compound one of the strongest oxidizing Mo(VI) complexes known.[5] As a result, this complex is known to partake in oxygen atom transfer reactions that are not observed for other complexes of MoO_2^{2+}. For instance, $MoO_2(Et_2dtc)_2$ readily ox-

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(1) Lutz, J. T. In *Kirk-othmer Encyclopeida of Chemical Technology*, 3rd ed.; Mark, H. F., Othmer, D. F., Overberger, C. G.; Seaborg, G. T., Eds.; Wiley-Interscience: New York, 1980; Vol. 9, pp 251-266.

(2) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790-5792.

(3) (a) Solar, J. P.; Mares, F.; Diamond, S. E. *Catal. Rev.—Sci. Eng.* **1985**, *27*, 1-28. (b) Andrews, M. A.; Chang, T. C.-T.; Chang, C. W. F.; Kelly, K. P. *Organometallics* **1984**, *3*, 1777-1785.

(4) See the following short list of references on this topic and references therein: (a) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidation of Organic Compounds*; Academic: New York, 1981; Chapter 6. (b) Collman, J. P.; Brauman, J. I.; Meunier, B.; Hayashi, T.; Kodadek, T.; Raybuck, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 2000-2005. (c) Collman, J. P.; Kodadek, T.; Raybuck, S. A.; Brauman, J. I.; Papazian, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4343-4345. (d) Samsel, K.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606-7617. (e) Srinivasan, K.; Kochi, J. K. *Inorg. Chem.* **1985**, *24*, 4671-4679. (f) Franklin, C. C.; VanAtta, R. B.; Tai, A. F.; Valentine, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 814-816. (g) VanAtta, R. B.; Franklin, C. C.; Valentine, J. S. *Inorg. Chem.* **1984**, *23*, 4123-4125. (h) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 5786-5791. (i) Groves, J. T.; Watanabe, Y.; McMurry, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 4489-4490. (j) Guilment, E.; Meunier, B. *J. Mol. Catal.* **1984**, *23*, 115-119. (k) Nee, M. W.; Bruice, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 6123-6125. (l) Enikolopyan, N. S.; Bogdanova, K. A.; Karmilova, L. V.; Askarov, K. A. *Russ. Chem. Rev. (Engl. Transl.)* **1985**, *54*, 215-230.

(5) (a) Burgmayer, S. J. N.; Stiefel, E. I. *J. Chem. Educ.* **1985**, *62*, 943-953 and references therein. (b) Berg, J. M.; Holm, R. H. *Acc. Chem. Res.* **1986**, *19*, 363-370 and references therein. (c) Harlan, E. W.; Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6992-7000. (d) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 917-925. (e) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 925-932. (f) Subramanian, P.; Kaul, B.; Spence, J. T. *J. Mol. Catal.* **1984**, *23*, 163-177. (g) Wentworth, R. A. D. *Coord. Chem. Rev.* **1976**, *18*, 1-27.

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Table I. Epoxide Deoxygenation by $MoO(Et_2dtc)_2$

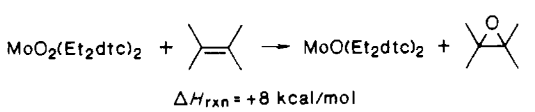
epoxide	olefin	temp, °C	time, h	yield, %
cyclohexene oxide	cyclohexene	130	36	92
endo-epoxynorbornane	norbornylene	130	50	73
trans-1-phenylpropylene oxide	*trans*-β-methylstyrene[a]	80	20	92
cis-2,3-epoxybutane	*cis*-2-butene[b]	130	45	83

[a] None of the cis isomer was detected by gas chromatography. [b] Selectivity to the cis isomer is 98%.

idizes a variety of substrates, with concomitant formation of $MoO(Et_2dtc)_2$. This Mo(IV) complex is readily oxidized to $MoO_2(Et_2dtc)_2$ with O_2. These properties have resulted in the use of $MoO_2(Et_2dtc)_2$ in a variety of catalytic oxidations[6] using O_2, as shown in Scheme II. Finally, molybdenum does not promote the free-radical autoxidation of olefins.[7]

In the present study, the reactivity of $MoO_2(Et_2dtc)_2$ with several olefins in the presence of O_2 was examined. In none of these cases was olefin oxidation observed. For instance, heating a mixture of this complex and cyclohexene in the presence of oxygen under forcing conditions (neat olefin, 110 °C, 100 psi) resulted in no detectable epoxide or other oxygenates.[8]

In retrospect, the inability of $MoO_2(Et_2dtc)_2$ to epoxidize olefins is not surprising. Thermochemical data for oxygen atom transfer by $MoO_2(Et_2dtc)_2$ have been measured by calorimetry.[9] These data show that olefin epoxidation by $MoO_2(Et_2dtc)_2$ is endothermic by +8 kcal/mol (eq 2).[10] This reaction is sufficiently high in energy or kinetically slow enough that the formation of even a small equilibrium limited amount of $MoO(Et_2dtc)_2$ and epoxide, followed by oxidation of $MoO(Et_2dtc)_2$ to $MoO_2(Et_2dtc)_2$, is insufficient to drive the reaction to completion (the oxidation of $MoO(Et_2dtc)_2$ to $MoO_2(Et_2dtc)_2$ by O_2 is exothermic by −35 kcal/mol[9]).



(2)

However, it is very interesting to note that no other oxygenates are observed under these reaction conditions, the formation of which are thermodynamically quite favorable (vide infra). This shows that a significant kinetic barrier exists for these undesired oxidation pathways. These results also confirm the inability of molybdenum to promote free-radical olefin autoxidation.

To further ensure that the epoxidation is in fact uphill, the reverse reaction was tested. Treating a variety of epoxides with $MoO(Et_2dtc)_2$ in toluene (80–130 °C, 20–40 h) does indeed lead to deoxygenation.[11] These deoxygenation reactions are 100% selective for olefin; no ketone (e.g. from epoxide rearrangement) or other oxygenates are observed. During the early portions of these reactions $Mo_2O_3(Et_2dtc)_4$ is observed as the predominant metal-containing product. This is expected on the basis of the well-known[6,12] equilibrium shown in (3) and verifies the formation of $MoO_2(Et_2dtc)_2$ as required by (2). These results are summarized in Table I.

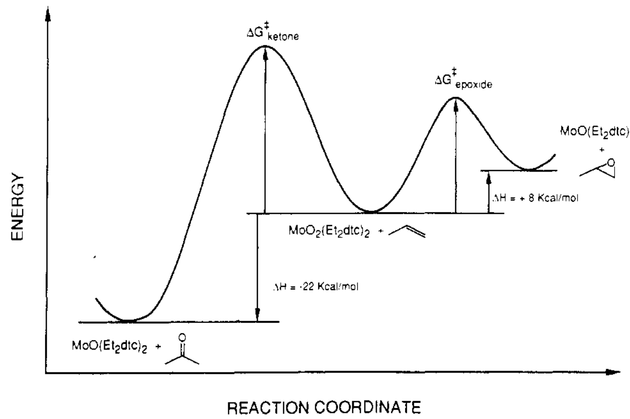
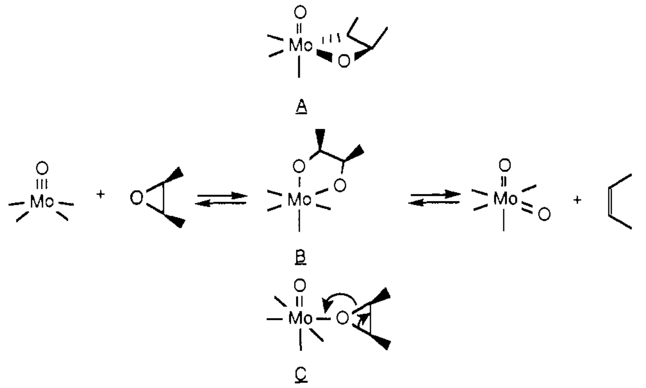


Figure 1. Energy profile for the oxidation of propylene with $MoO_2(Et_2dtc)_2$. The energy levels for the two transition states have been drawn at arbitrary positions. However, because $MoO(Et_2dtc)_2$ selectively deoxygenates epoxides, $\Delta G^{\ddagger}_{\text{ketone}} > \Delta G^{\ddagger}_{\text{epoxide}}$. The energy profiles for propylene oxidation to other oxygenates (e.g. propionaldehyde and allyl alcohol) are similar in that although they are exothermic,[16] the activation energies are higher than that for epoxidation.

Scheme III



$$Mo_2O_3(Et_2dtc)_4 \rightleftarrows MoO_2(Et_2dtc)_2 + MoO(Et_2dtc)_2 \quad (3)$$

Although highly selective, the olefin yields are less than quantitative. The reason for this is that decomposition of the molybdenum complex(es) is competitive with the deoxygenation reaction. These decomposition reactions have been recognized previously.[6c] In support of this, one such decomposition product, the Mo(V) dimer $Mo_2O_4(Et_2dtc)_2$, is isolated after the deoxygenation reactions.

Also shown in Table I are the results obtained from deoxygenation reactions with *trans*-1-phenylpropylene oxide and *cis*-2-epoxybutane. In each case >98% retention of stereochemistry is observed upon deoxygenation. These results indicate that the deoxygenation proceeds via a concerted reaction or through a cyclic

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(6) (a) Barral, R.; Bocard, C.; Seree de Roch, I.; Sajus, L. *Tetrahedron Lett.* **1972**, *17*, 1693–1696. (b) Ueyama, N.; Kamabuchi, K.; Nakamura, A. *J. Chem. Soc., Dalton Trans.* **1985**, 635–639. (c) Nakamura, A.; Nakayama, M.; Sughihashi, K.; Otsuka, S. *Inorg. Chem.* **1979**, *18*, 394–400. (d) Speier, G. *Inorg. Chim. Acta* **1979**, *32*, 139–141.

(7) This point is often unappreciated in investigations of the type described here. In fact, many transition metals are extremely proficient promoters of olefin autoxidation.[7a–c] One example of this is the recent report[7d] regarding the aerial epoxidation of olefins catalyzed by $\{Fe_3O[O_2CC(CH_3)_3]_6(HOCH_3)_3\}Cl$. Studies in this laboratory show that this cluster, as with iron complexes in general, promotes olefin autoxidation and that the olefins investigated in the original study yield large amounts of epoxides when autoxidized (Moloy, K. G., unpublished results). The high epoxide selectivities reported with this cluster are therefore an artifact of the olefins that were examined. (a) Arzoumanian, H.; Blanc, A.; Hartig, U.; Metzger, J. *Tetrahedron Lett.* **1974**, *12*, 1011–1014. (b) Fusi, A.; Ugo, R.; Fox, F.; Pasini, A.; Cenini, S. *J. Organomet. Chem.* **1971**, *26*, 417–430. (c) Gould, E. S.; Rado, M. *J. Catal.* **1969**, *13*, 238–244. (d) Ito, S.; Inoue, K.; Mastumoto, M. *J. Am. Chem. Soc.* **1982**, *104*, 6450–6452.

(8) This result has been reported as an unpublished observation; see ref 4a, Chapter 6.

(9) Watt, G. D.; McDonald, J. W.; Newton, W. E. *J. Less-Common Met.* **1977**, *54*, 415–423.

(10) This calculation is based on the epoxidation of propylene by using data found in: Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(11) Tungsten(II) complexes have recently been shown to deoxygenate epoxides: Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826–2828.

(12) (a) Jowitt, R. N.; Mitchell, P. C. H. *J. Chem. Soc. A* **1970**, 1702–1708. (b) Devore, D. D.; Maatta, E. A. *Inorg. Chem.* **1985**, *24*, 2846–2849. (c) Newton, W. E.; Corbin, J. L.; Bravard, D. C.; Searles, J. E.; McDonald, J. W. *Inorg. Chem.* **1974**, *13*, 1100–1104. (d) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2612–2615. (e) Moore, F. W.; Rice, R. E. *Inorg. Chem.* **1968**, *7*, 2510–2514.

intermediate, and several possibilities are shown in Scheme III. Recent experimental[4,13] and theoretical[14] data support the formation of oxametallacyclobutane (A) intermediates during epoxide deoxygenation as well as olefin epoxidation. Deoxygenation of an excess of *trans*-1-phenylpropylene oxide with $Mo^{18}O(Et_2dtc)_2$ leads to no detectable incorporation of labeled oxygen into the epoxide.[15] While this experiment rules out *reversible* formation of an intermediate such as B, the evidence available thus far does not allow a distinction between the possible pathways.

These results allow us to reach an important conclusion regarding olefin oxidation by molybdenum(VI)–oxo complexes: if the oxidizing ability of molybdenum could be made more favorable (by ca. 8 kcal/mol), then selective olefin epoxidation should result. This conclusion follows from the fact that the oxidation of olefins to products other than epoxides, such as ketones and alcohols, is not observed with $MoO_2(Et_2dtc)_2$ and neither is autoxidation. These oxidations are, however, very favorable. For instance, the oxidation of an olefin to a ketone by $MoO_2(Et_2dtc)_2$ is exothermic by ca. −22 kcal/mol, yet it does not occur.[16] In addition, the selective epoxide deoxygenation shows that it is possible to traverse the energy barrier between olefin and epoxide without forming more stable oxygenates. Thus, while the epoxidation with $MoO_2(Et_2dtc)_2$ is thermodynamically unfavorable, the kinetic barrier for this reaction is lower than that for other oxidation pathways. These conclusions are summarized in the energy profile diagram shown in Figure 1. A low-energy barrier to energetically less favored products is precisely the property required for selective catalysis. By microscopic reversibility, it follows that a molybdenum(VI)–oxo complex of sufficient oxidizing strength will epoxidize olefins selectively.

Because the oxidation of $MoO(Et_2dtc)_2$ to $MoO_2(Et_2dtc)_2$ by O_2 is favorable by −35 kcal/mol,[9] it should be possible to increase the oxidizing power of Mo(VI) by 8 kcal/mol and maintain a favorable oxidation of Mo(IV), thereby making a catalytic cycle for epoxidation feasible. There are numerous physicochemical studies of the variation in oxidizing ability of *cis*-MoO_2^{2+} complexes as a function of ligand environment.[6b,c,17] These studies show that ligands with electron-withdrawing groups and sulfur donor atoms significantly increase the oxidizing ability (kinetic and thermodynamic) of these complexes. The four sulfur donor atoms in $MoO_2(Et_2dtc)_2$ consequently make this complex one of the strongest oxidizing MoO_2^{2+} complexes known.

In order to systematically alter the oxidizing power of these complexes, a series of $MoO_2(R_2dtc)_2$ complexes, where R contains groups of different electron-withdrawing and electron-donating ability, was examined. New complexes used in this study were prepared and characterized by standard methodology:

$$cis\text{-}MoO_2^{2+} + 2R_2dtc^- \rightarrow cis\text{-}MoO_2(R_2dtc)_2$$

R = trifluoroethyl, benzyl, phenyl, tetramethylpiperidyl

In some cases addition of the dithiocarbamate to solutions of Mo(VI) resulted in reduction to $Mo_2O_3(R_2dtc)_4$. These species are readily identified by their intense purple color, a strong infrared absorption at ca. 940 cm^{-1} (ν_{MoO}), and reaction with a variety of oxidants (dimethyl sulfoxide, pyridine *N*-oxide) to form $MoO_2(R_2dtc)_2$.

Table II. Reduction Potentials for *cis*-Dioxomolybdenum Bis(dithiocarbamates), $MoO_2(R_2dtc)_2$

dithiocarbamate	E_{pc},[a] V vs. NHE	ΔH_{rxn},[b] kcal/mol
tetramethylpiperidyl	−1.07	
diethyl	−0.96[c]	+8.0
piperidyl	−0.94	+9.1
dibenzyl	−0.89	
dimethyl	−0.85	+7.1
morpholyl	−0.82	+6.5
diphenyl	−0.82	
bis(trifluoroethyl)	−0.58[d]	

[a] Potential at the maximum cathodic peak current. [b] Reaction enthalpy calculated for the reaction $MoO_2(R_2dtc)_2$ + propylene → $MoO(R_2dtc)_2$ + propylene oxide by using data from ref 9 and 10. [c] Literature[17] value: −0.93 V vs. NHE. [d] Estimated value; see Experimental Section.

The reduction potentials of each of these complexes was examined by cyclic voltammetry in order to measure their relative oxidizing strengths.[18] As shown in Table II, the reduction potential does become more favorable with increasing electron-withdrawing ability of the dtc ligand.[19] Also included in Table II are the calculated heats of reaction for propylene epoxidation by these complexes, where these data are available. These data, although not extensive, suggest that the epoxidation is also made more favorable.

To date, this approach has not yet lead to the preparation of a $MoO_2(R_2dtc)_2$ complex of sufficient oxidizing strength to epoxidize olefins. Attempts to prepare $MoO_2(R_2dtc)_2$ complexes with more powerful electron-withdrawing groups[20] have been unsuccessful due to the easy reduction of Mo(VI) by these ligands. This is not too surprising because thiolate is, in general, easily oxidized (eq 4). In addition, Holm[5c] recently showed that Mo(VI)

$$2RS^- \rightarrow RSSR + 2e^- \qquad (4)$$

easily oxidizes thiols to disulfides. Future work will require the use of ligands which maintain the required electronic environment about molybdenum while avoiding these types of reactions.

Conclusions

These results further underscore the observation[4] that high-valent metal–oxo complexes are inherently regioselective and stereoselective agents for olefin epoxidation. As a result, the successful synthesis of these complexes with oxygen should result in a catalytic method for olefin epoxidation. The ruthenium catalyst described by Groves[2] is an excellent example of this

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(13) (a) Berry, M.; Davies, S. G.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1978**, 99–100. (b) Lenarda, M.; Pahor, N. B.; Calligaris, M.; Graziani, M.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1978**, 279–282. (c) Sharpless, K. B.; Teranishi, A. Y.; Backvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120–3128. (d) Schlodder, R.; Ibers, J. A.; Lenarda, M.; Graziana, M. *J. Am. Chem. Soc.* **1974**, *96*, 6893–6900. (e) Sharpless, K. B.; Umbreit, M. A.; Nieh, M. T.; Flood, T. C. *J. Am. Chem. Soc.* **1972**, *94*, 6538–6540.

(14) (a) Rappe, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 448–456. (b) Rappe, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1980**, *102*, 5115–5117. (c) Rappe, A. K.; Goddard, W. A., III. *Nature (London)* **1980**, *285*, 311–312.

(15) I thank a reviewer for suggesting this experiment.

(16) This calculation is based on the oxidation of propylene to acetone using data from ref 9 and 10. The oxidation of propylene to other oxygenates by $MoO_2(Et_2dtc)_2$ is also favorable; −16 kcal/mol for propionaldehyde and −1.4 kcal/mol for allyl alcohol.

(17) (a) Topich, J. *Inorg. Chem.* **1981**, *20*, 3704–3707. (b) Topich, J.; Lyon, J. T. *Inorg. Chem.* **1984**, *23*, 3202–3206. (c) Topich, J.; Lyon, J. T. *Polyhedron* **1984**, *3*, 55–60. (d) Topich, J.; Lyon, J. T. *Polyedron* **1984**, *3*, 61–65. (e) Bristow, S.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1985**, 1617–1619.

(18) Although the cyclic voltammogram represents the one-electron reduction of Mo(VI) to Mo(V) ref 17a–d shows that there is a positive correlation between this value and the ease of reduction of Mo(VI) to Mo(IV) with loss of an oxo ligand, such as that required for oxygen atom transfer.

(19) This observation has been made with other metal dithiocarbamates: (a) Chant, R.; Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. *Inorg. Chem.* **1975**, *14*, 1894–1902. (b) Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. *Inorg. Chem.* **1974**, *13*, 1933–1939.

(20) For instance, transition-metal complexes of the pyrrole-*N*-carbodithioate ligand show a dramatic stabilization of the lower oxidation states.[20a] This increased stabilization of lower oxidation states results from aromatization of the unsaturated ring via conjugation of the nitrogen lone pair. The net result is electron withdrawal. For instance, $Fe(pyrroledtc)_3$ is easier to reduce by 0.6 V than $Fe(pyrrolidinedtc)_3$, and is 0.62 V easier than $Fe(Et_2dtc)_3$.[20a] An enhancement of this magnitude should make $MoO_2(pyrroledtc)_2$ a relatively potent oxidizing agent. All attempts to prepare this complex following procedures in the experimental section have been unsuccessful. In all cases addition of K(pyrroledtc) to solutions of Mo(VI) resulted in reduction of the metal. The known compound $Mo(CO)_3(pyrroledtc)_2$[20b] was prepared, but oxidation to the target complex by treatment with a variety of oxidizing agents (pyridine *N*-oxide, iodosylbenzene, *tert*-butyl hydroperoxide) failed. (a) El A'mma, A. G.; Drago, R. S. *Inorg. Chem.* **1977**, *16*, 2975–2977. (b) Herrick, R. S.; Nieter Burgmayer, S. J.; Templeton, J. L. *Inorg. Chem.* **1983**, *22*, 3275–3281.

methodology. The highly regio- and stereoselective epoxide deoxygenation by $MoO(Et_2dtc)_2$ demonstrates that it should be possible to use molybdenum in this regard if the appropriate ligand environment can be designed. Furthermore, molybdenum avoids the nonselective free-radical autoxidation pathways that often plague this type of chemistry.

Experimental Section

Physical and Analytical Measurements. ^1H NMR spectra were recorded on a Varian XL-100 spectrometer. ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer. Chemical shifts are reported relative to internal TMS. Infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer, and samples were prepared as KBr pellets. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Organic analysis was carried out on either a Varian 3700 (packed column) or a Hewlett-Packard 5890 (capillary column) gas chromatograph.

Where appropriate, these operations were performed in Schlenk-type glassware or a Vacuum Atmospheres drybox under a nitrogen atmosphere. All solvents were dried by standard methods and distilled under nitrogen.[21] All reagents were obtained from vendors and dried and deoxygenated before use.

The compounds $MoO_2(S_2CNR_2)_2$[R = Me, Et, $(CH_2)_5$, $(CH_2)_4O$], $MoO(S_2CNEt_2)_2$, and $Mo_2O_3(S_2CNEt_2)_4$ were prepared by the literature procedures.[12a,b]

Epoxide Deoxygenation. The following is a representative example. In the glove box, a 15-mL vessel fitted with a Solv-Seal joint, a high-vacuum Teflon stopcock, and a stir bar was charged with 0.104 g (0.254 mmol) $MoO[S_2CN(CH_2CH_3)_2]_2$ and 10 mL toluene. To this was added 0.0861 g (0.782 mmol) epoxynorbornane and 0.0111 g (0.071 mmol) undecane as an internal standard. The vessel was sealed and placed in a 130 °C oil bath. The reaction was monitored by gas chromatography on a 100-m DB 1701 capillary column with an FID detector. GC analysis showed norbornylene as the only volatile product. The olefin yield after 50 h, determined from a calibration curve, was 73%. No other products were observed in the gas chromatogram.

During the course of the reaction the color of the solution turned from rose to purple and finally to yellow. A yellow, crystalline solid formed on the vessel walls. This product was identified as the Mo(V) dimer $Mo_2O_4(Et_2dtc)_2$, as determined by IR and elemental analysis.[12a] IR (KBr): 2980 s, 2937 m, 2872 w, 1535 vs, 1460 s, 1443 s, 1382 m, 1359 m, 1281 s, 1202 s, 1154 m, 1073 w, 958 vs, 909 w, 843 w, 776 w, 702 w cm^{-1}. Anal. Calcd for $C_{10}H_{20}Mo_2N_2S_4$: C, 21.74; H, 3.65; N, 5.07. Found: C, 21.70; H, 3.68; N, 4.98.

$Mo^{18}O(Et_2dtc)_2$. A 50-mL reaction vessel fitted with a Teflon stopcock was charged with 0.261 g (0.639 mmol) of $MoO(Et_2dtc)_2$, 0.015 g (0.0035 mmol) of $MoO_2(Et_2dtc)_2$ and 30 mL of toluene. A 150-μL (8.33-mmol) aliquot of $H_2{}^{18}O$ was then added via syringe under a flush of argon. The vessel was immersed in an oil bath at 80–85 °C for 4 h. Infrared analysis indicated that label incorporation was 74%. The toluene was removed under vacuum, and the pink-red crystals were slurried into ethanol. The product was isolated by filtration, washed with 5 mL of ethanol, and dried under vacuum. The infrared spectrum (ν_{MoO}) agreed with the literature[22] ($Mo^{16}O(Et_2dtc)_2$, 958 cm^{-1}; $Mo^{18}O(Et_2dtc)_2$, 910 cm^{-1}).

trans-1-Phenylpropylene oxide was deoxygenated in the manner described above by using 0.10 g (0.24 mmol) of $Mo^{18}O(Et_2dtc)_2$ and 65 μL (0.49 mmol) of epoxide in 10 mL of toluene. After 24 h at 81 °C, gas chromatography/mass spectrometry analysis showed that the remaining *trans*-1-phenylpropylene oxide had no detectable ^{18}O incorporation.

$LiS_2CN(CH_2CF_3)_2$. We were unable to prepare this material by the literature method.[23] The following is a modification of this method. A 200-mL Schlenk flask was charged with 17.56 g (0.097 mol) of $HN(CH_2CF_3)_2$ and 50 mL of Et_2O. The solution was cooled to −78 °C and 54 mL of MeLi (1.7 M solution in Et_2O, 0.092 mol) was added dropwise. Gas evolution was immediate, and the solution turned orange. The addition was complete in 1 h, and the reaction was stirred for an additional 0.5 h. Next, 6.4 mL of CS_2 in 20 mL of Et_2O was added dropwise; the solution color became lighter. After 0.5 h the solution was allowed to warm to room temperature. After 1 h at room temperature the solution was filtered to remove a small amount of precipitate. The solvent was removed under vacuum, yielding an orange-brown syrup. The syrup was held under vacuum at ca. 50 °C for 2 days, whereupon it gradually solidified. Then 50 mL of heptane was added, and the mixture was agitated for several days until a pale yellow powder was obtained. The powder was isolated by filtration, washed with heptane, and dried in vacuo. Yield: 21.1 g, 83%. ^1H NMR (acetone-d_6): δ 5.32 (q, J_{F-H} = 9.28 Hz). $^{13}C\{^1H\}$ (acetone-d_6): δ 51.4 (q, $^2J_{F-H}$ = 33.0 Hz), 125.7 (q, $^1J_{F-H}$ = 282.3 Hz), 223.7 (s). IR (KBr): 2967 m, 2890 w, 1442 m, 1412 m, 1382 m, 1313 s, 1267 s, 1237 m, 1149 s, 1098 s, 1001 s, 964 w, 902 w, 828 m, 790 w, 687 m, 596 w, 578 m cm^{-1}.

$Mo_2O_3[S_2CN(CH_2CF_3)_2]_4{\cdot}C_7H_8$. A 100-mL flask was charged with 0.75 g (3.77 mmol) of MoO_2Cl_2 and 15 mL of THF. To this solution was added 0.41 mL (ca. 0.41 g, 1.9 mmol) of $PEtPh_2$; the nearly colorless solution turned deep green and then (5 min) deep yellow-brown. A solution of 1.98 g (7.54 mmol) of $LiS_2CN(CH_2CF_3)_2$ in 15 mL of THF was then added dropwise, resulting in an immediate color change to deep purple. After 2 h the solution was filtered and the solvent removed under vacuum. The resulting purple solid was slurried into 15 mL of EtOH, filtered, washed with 10 mL of EtOH, and dried under vacuum. Yield: 1.82 g, 76%. ^1H NMR (acetone-d_6): δ 4.94 (m). IR (KBr): 3012 w, 2970 w, 1460 s, 1409 s, 1320 m, 1296 w, 1260 s, 1234 w, 1155 vs, 1111 s, 1033 m, 978 m, 945 s, 921 w, 833 m, 690 m, 610 w, 580 m, 495 w, 436 w, 405 w cm^{-1}. The product was recrystallized as purple crystals from hot toluene. Anal. Calcd for $C_{20}H_{16}F_{24}Mo_2N_4O_3S_8{\cdot}C_7H_8$: C, 23.90; H, 1.78; N, 4.13; S, 18.90. Found: C, 23.60; H, 1.93; N, 4.00; S, 18.42.

We have been unable to prepare a pure sample of $MoO_2[S_2CN(CH_2CF_3)_2]_2$. Oxidation of $Mo_2O_3[S_2CN(CH_2CF_3)_2]_4$ with a variety of oxidants (dimethyl sulfoxide, pyridine *N*-oxide, O_2) proceeds cleanly at room temperature to form the *cis*-dioxo complex. This species has been identified by ^1H NMR (toluene-d_8, δ 3.72, q, J_{F-H} = 8.0 Hz) and by its rapid reaction with phosphines to form $Mo_2O_3[S_2CN(CH_2CF_3)_2]_4$ and phosphine oxide. Workup of these reaction mixtures results in reduction and isolation of the title dimer.

Solutions of $Mo_2O_3[S_2CN(CH_2CF_3)_2]_4$ provide a convenient source of $MoO_2[S_2CN(CH_2CF_3)_2]_2$ for reaction studies. This is a result of the disproportionation equilibrium shown in (3). Thus, the electronic spectrum of the dimer shows an intense absorption at 514 nm. Variation of the dimer concentration shows that this absorption deviates from Beer's law, consistent with an equilibrium such as that shown in (3).[12b] Also, the ^1H NMR spectrum of the dimer shows a complex multiplet of resonances attributable to the three molybdenum complexes formed by this equilibrium. From these data, the equilibrium constant for dimer disproportionation is ca. 2×10^{-3} M (25 °C), consistent with that observed for $Mo_2O_3(Et_2dtc)_4$.[24] Thus, a 100 mM solution of the dimer provides a 13 mM solution of $MoO_2[S_2CN(CH_2CF_3)_2]_2$. The reduction potential of $MoO_2[S_2CN(CH_2CF_3)_2]_2$ was estimated by comparing the reduction potential of $Fe[S_2CN(CH_2CF_3)_2]_3$ (prepared by standard methods[20a]) with $Fe[S_2CN(CH_2CH_3)_2]_3$. Cyclic voltammetry studies show that $Fe[S_2CN(CH_2CF_3)_2]_3$ is reduced 0.38 V more easily than $Fe[S_2CN(CH_2CH_3)_2]_3$.

$MoO_2(S_2CN(bz)_2)_2$. To a solution of 2.0 g (6.4 mmol) of $NaS_2CN(bz)_2{\cdot}H_2O$ in 40 mL of MeOH was added dropwise a solution of 1.1 g (3.4 mmol) of $MoO_2(acac)_2$ in 40 mL of MeOH. An orange-brown precipitate was observed. The solvent volume was reduced on a rotary evaporator, and the precipitate was isolated by filtration. The product may be recrystallized from hot toluene/hexane. ^1H NMR (CD_2Cl_2): δ 7.33 (m, 10 H), 4.97 (s, 4 H). IR (KBr): 3010 w, 1490 s, 1450 s, 1430 m, 1350 m, 1220 s, 1200 w, 1130 m, 1075 w, 1025 w, 980 m, 910 s, 875 s, 750 s, 690 s, 620 w, 545 w, 515 m, 400 w cm^{-1}. Anal. Calcd for $C_{30}H_{28}MoN_2O_2S_4$: C, 53.56; H, 4.19; N, 4.16. Found: C, 54.47; H, 4.33; N, 4.00.

$NaS_2CNPh_2{\cdot}H_2O$. To a suspension of 1.35 g (0.056 mol) of NaH in 100 mL of toluene was added a solution of 10 g (0.059 mol) of Ph_2NH in 50 mL of toluene. No immediate reaction was observed. Then, 0.5 mL of dimethoxyethane was added, and the suspension was refluxed. After 1 h gas evolution was noticeable, and reflux was continued overnight. The reaction was cooled to room temperature and colorless crystals were noted. The toluene was decanted and replaced with 60 mL of Et_2O. The solution was cooled to 0 °C and 3.8 mL (4.8 g, 0.063 mol) of CS_2 was added dropwise. The reaction was exothermic, and a yellow precipitate formed. The product was exposed to the air, isolated by filtration, and then dried under vacuum. Yield: 14.5 g, 91%. ^1H NMR (acetone-d_6): δ 7.4–7.1 (br m, 10 H), 2.05 (s, 2 H). IR (KBr): 3400 s, br, 1620 m, 1587 m, 1485 s, 1447 m, 1318 s, 1266 s, 1160 w, 1069 m, 1040 s, 1018 m, 997 m, 906 w, 878 m, 813 w, 750 s, 742 m, 699 s, 686 m, 639 m, 612 m cm^{-1}.

$MoO_2(S_2CNPh_2)_2$. This complex was prepared in the same manner as $MoO_2(S_2CNbz_2)_2$, above, and can be isolated as yellow crystals from

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hot toluene. ^{1}H NMR (CD_2Cl_2): δ 7.5–7.3 (br, m). IR (KBr): 3040 w, 1585 m, 1485 s, 1450 m, 1380 vs, 1305 w, 1260 m, 1150 w, 1070 w, 1045 s, 1020 w, 1000 m, 910 s, 885 s, 870 s, 825 w, 795 s, 730 m, 690 s, 645 s, 610 m, 515 w, 485 w, 460 w, 415 w, 355 m cm^{-1}.

$Li[S_2C\overline{NC(CH_3)_2(CH_2)_3C}(CH_3)_2]$. A 2.0-g (0.014 mol, dried over 4A sieves and deoxygenated) sample of tetramethylpiperidine and 20 mL of heptane were placed in a 100-mL Schlenk flask. The solution was cooled to 0 °C and 8.7 mL of BuLi (1.55 M in hexanes, 0.013 mol) was added dropwise. Approximately halfway through the addition a colorless precipitate was observed. After the addition the reaction was warmed to room temperature and stirred for 1 h. Next, a solution of 0.85 mL (1.08 g, 0.014 mol) of CS_2 in 10 mL of heptane was added over a 20-min period; the solution turned orange. After the solution was allowed to stand at room temperature, yellow crystals were deposited, which were filtered, washed with heptane, and dried under vacuum. Yield: 1.8 g, 60%.

$MoO_2[S_2C\overline{NC(CH_3)_2(CH_2)_3C}(CH_3)_2]_2$. A 1.0-g (4.5-mmol) sample of $Li[S_2C\overline{NC(CH_3)_2(CH_2)_3C}(CH_3)_2]$ was placed in a 50-mL flask fitted with a pressure-equalizing addition funnel containing 0.30 g (1.5 mmol) MoO_2Cl_2. To both the flask and the funnel were added 20 mL of ether, dissolving both reagents. The flask was cooled to 0 °C, and the MoO_2Cl_2 solution was added dropwise, with stirring. A purple solid precipitated during the addition and was isolated by filtration. This product was identified as $Mo_2O_3(R_2dtc)_4$ by its color and Mo–O absorption in the infrared spectrum at 940 cm^{-1}. Yield: 88%. This product was placed in 10 mL of toluene, and to it was added 0.06 g (6.0 mmol) of pyridine *N*-oxide in 10 mL of toluene. After the mixture was stirred overnight, the orange product was isolated by filtration and recrystallized from hot toluene. ^{1}H NMR ($CDCl_3$): δ 1.76 (s, 12 H), 1.55–1.95 (m, 6 H). IR (KBr): 2960 vs, 2760 m, 1587 m, 1460 m, 1380 vs, 1350 s, 1281 m, 1254 m, 1161 s, 1124 m, 1024 m, 986 m, 973 w, 904 s, 872 s, 803 m, 762 w, 601 w, 538 w.

Cyclic Voltammetry. Acetonitrile was purified by stirring over activated alumina, distilling first from a mixture of $KMnO_4$ (1 g/100 mL) and Li_2CO_3 (1 g/100 mL), and then twice from CaH_2. It was stored under nitrogen in a glass bulb fitted with a high-vacuum Teflon stopcock. Tetrabutylammonium hexafluorophosphate was recrystallized from hot H_2O/EtOH and then dried under vacuum overnight at 120 °C. Measurements were made with a Princeton Applied Research Model 173 potentiostat/galvanostat equipped with a Model 176 current to voltage converter. The voltammograms were recorded on a Houston Omnigraphic Series 2000 X-Y recorder.

All measurements were made in a nitrogen-filled glovebox. In a typical procedure, the voltammetry cell was fit with a freshly polished glassy-carbon working electrode, and a platinum-wire counter electrode. The reference electrode consisted of a silver wire immersed in a solution of solvent and electrolyte, and was separated from the voltammetry cell by a porous glass disk. The cell was then charged with 15 mL of 0.1 M n-Bu_4NPF_6 in acetonitrile. Enough of the molybdenum complex under investigation was added to make a 1 mM solution. The cyclic voltammogram was then recorded. Next, a solution of ferrocene in acetonitrile was added such that the ferrocene concentration was 0.5 mM. The potential and electrochemical reversibility of the ferrocene/ferrocenium redox couple was recorded and used as an internal standard.[25]

The molybdenum complexes described in this report exhibit irreversible redox behavior. Thus, no detectable oxidation wave is observed during reverse anodic scans. This is a general observation for *cis*-dioxomolybdenum(VI) complexes.[17] As a result, we are able to report only the potential at the maximum cathodic current, E_{pc}. Topich[17] has shown that these values may be used to relate relative oxidizing strengths in place of the true Mo(VI)/Mo(V) potentials if the voltammograms are recorded under identical conditions.[26] All measurements were made at room temperature, and the scan rate was held constant at 100 mV/s.

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Phosphine Basicities As Determined by Enthalpies of Protonation

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Enthalpies of protonation (ΔH_{HP}'s) have been determined for 12 tertiary alkyl-, aryl-, and mixed alkylarylphosphines from the heats of the reactions $R_3P + CF_3SO_3H \rightarrow R_3PH^+CF_3SO_3^-$, in 1,2 dichloroethane, by use of titration calorimetry. The ΔH_{HP}'s range from −17.9 kcal mol^{-1} for $(p\text{-}ClC_6H_4)_3P$ to −36.6 kcal mol^{-1} for $(t\text{-}Bu)_3P$. An excellent correlation of the ΔH_{HP} values with reported pK_a's is observed. Comparisons with other basicity measures and correlations with Hammett σ_{para}, Taft σ^*, and Kabachnik σ^{ph} substituent parameters are also discussed.

Introduction

A casual examination of the current literature of transition-metal complexes is all that is required to gauge the importance of phosphines as ligands in organometallic and coordination chemistry. The ability of phosphines to bind to transition metals is usually described in terms of steric and electronic properties. Quantitative determination of these binding characteristics has been the aim of a number of studies,[1] leading to parameters such as Tolman's cone angles (θ) and ν(CO) values (for the A_1 vibration in $Ni(CO)_3PR_3$) for describing steric and electronic effects, respectively, of phosphorus ligands. These parameters have often been employed to understand reactions involving phosphines.[1c,d,2] Attempts to further dissect electronic effects have led to the development of a method for quantitatively analyzing reactions in terms of the σ-bonding, π-bonding, and steric properties of phosphines.[3] Application of this method to data for ligand-dependent substitutions and reactions of phosphine-containing complexes has shown that, although π-bonding is important in some cases,[3b] most of the data can be explained in terms of steric

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