Rhenium(V) Oxo−Alkoxide Complexes: Syntheses and Oxidation to Aldehydes†

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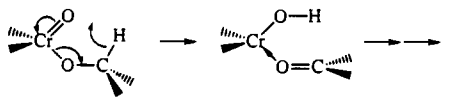
Received June 24, 1995®

New rhenium(V) oxo−alkoxide compounds $(HBpz_3)ReO(OR)_2$ (R = Me (**1**), Et (**2**), ^{i}Pr (**3**), ^{n}Bu (**4**), CH_2Ph (**5**)) have been prepared in good yields from reaction of $(HBpz_3)ReOCl_2$ with excess alcohol in the presence of NEt_3 [$HBpz_3$ = hydrotris(1-pyrazolyl)borate]. Treatment of these compounds with Me_3SiOTf (OTf = OSO_2CF_3) forms the reactive triflate compounds $(HBpz_3)ReO(OR)(OTf)$ (**6**−**8**). The triflate complexes are rapidly oxidized by the oxygen atom donors pyridine *N*-oxide and Me_2SO to give aldehydes or ketones, alcohols, and $(HBpz_3)ReO_3$ (**9**). Addition of DMSO to **2** initially gives the sulfoxide adduct $[(HBpz_3)ReO(OEt)(OSMe_2)]OTf$ (**10**). Mechanistic studies indicate that **10** rapidly and reversibly loses SMe_2 (k_{298} = 8.2 (6) s^{-1}) to give a cationic rhenium(VII) dioxo complex, $[(HBpz_3)ReO_2(OEt)]OTf$ (**11**), in which oxidation of the ethoxide ligand occurs. An isotope effect of 4.6 is determined for C−H bond cleavage. Oxidation of the ethoxide ligand in **11** is proposed to occur by hydride transfer to an oxo group. The oxo ligands in **11** are shown to be electrophilic, based on the relative rates of Me_2S and Me_2SO oxidation, which explains their ability to act as hydride acceptors.

Introduction

Metal-mediated oxidations of organic compounds are receiving increasing attention because of their importance in industrial processes and their involvement in biochemical transformations.[1] The oxidation of alcohols to aldehydes, ketones, and carboxylic acids is a standard organic reaction, accomplished by a variety of reagents.[2] The mechanism of alcohol oxidation by chromium(VI) reagents was shown by Westheimer to involve formation of a chromate "ester", in which net hydride transfer from the alkoxide to a chromium oxo group generates the aldehyde or ketone product (eq 1).[3]



(1)

Reported here are oxidations of rhenium(V) alkoxide complexes that result in oxidation of the alkoxide ligand to the corresponding aldehyde or ketone. Unlike classical oxidation reactions where the substrate is brought to an oxidizing metal center such as Cr^{VI}, these reactions start with stable alkoxide complexes of an essentially nonoxidizing metal center, rhenium(V).[4] The rhenium is oxidized by oxygen atom transfer, from pyridine *N*-oxide or DMSO, to form a more reactive rhenium(VII) complex in which alkoxide oxidation occurs. Oxygen atom transfer[5] has become a popular route for generating oxidizing metal centers, most notably in the biomimetic chemistry of metal porphyrin and related complexes.[6] Our approach of adding an oxygen atom to a metal center that bears an oxidizable organic group has already proven valuable in the discovery of the first well-defined phenyl-to-oxo migration reaction.[7]

Experimental Section

General Considerations. All experiments were performed under an inert atmosphere using standard vacuum, Schlenk, and glovebox techniques, except where noted. Solvents were degassed and dried according to standard procedures.[8] Reagents were purchased from Aldrich and used as received unless otherwise noted. Deuterated solvents, $H_2{}^{18}O$, and CH_3CHDOH were purchased from Cambridge Isotope Laboratories. $Me_2S^{18}O$ [9] and $(HBpz_3)ReOCl_2$[10] were synthesized according to published procedures. NEt_3 was degassed, dried over CaH_2, and vacuum transferred prior to use. Alcohols were

† Abbreviations: $HBpz_3$ = hydrotris(1-pyrazolyl)borate; OTf = triflate, OSO_2CF_3; pz = pyrazole; pyO = pyridine *N*-oxide; DMSO = dimethyl sulfoxide, Me_2SO; DMS = dimethyl sulfide, Me_2S.

® Abstract published in *Advance ACS Abstracts,* November 15, 1995.

(1) (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981. (b) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley-Interscience: New York, 1992. (c) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(2) *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 7 (Oxidation).

(3) (a) Westheimer, F. *Chem. Rev.* **1949**, *45*, 419. For more recent reviews of chromium(VI) oxidations, see: ref 2. (b) Wiberg, K. B. In *Oxidation in Organic Chemistry*, Part A; Wiberg, K. B., Ed.; Academic Press: New York, 1965; pp 69−184. (c) Freeman, F. In *Organic Syntheses by Oxidation with Metal Compounds;* Mijs, W. J., de Jonge, C. R. H. I., Eds.; Plenum: New York, 1986; Chapter 2, pp 41−118. (d) Müller, P. In *The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulfur Analogues, Part 1 (The Chemistry of Functional Groups, Supplement E);* Patai, S., Ed.; Wiley-Interscience: New York, 1980; pp 469−539. (e) For the final chapter in the story of chromium(VI) alcohol oxidation mechanisms, see: Scott, S. L.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1992**, *114*, 4205−4213. Espenson, J. H. *Acc. Chem. Res.* **1992**, *25*, 222−227.

(4) Rhenium(V) oxo complexes will oxidize phosphines to phosphine oxides but to our knowledge have not been reported to oxidize alcohols. (a) Rouchias, G. *Chem. Rev.* **1974**, *74*, 531−566. (b) *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1987; Vol. 4, pp 125−215. (c) Conry, R. R.; Mayer, J. M. *Inorg. Chem.* **1990**, *29*, 4862−4867, and references therein. Reduction of $(HBpz_3)Re(O)XY$ complexes by PR_3: (d) Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82 (2)*, 125−128. (e) Degnan, I. A.; Behm, J.; Cook, M. R.; Herrman, W. A. *Inorg. Chem.* **1991**, *30*, 2165−2170. (f) Brown, S. N.; Masui, C. S.; Mayer, J. M. Unpublished results.

(5) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401−1449. Holm, R . H.; Donahue, J. P. *Polyhedron* **1993**, *12*, 571−589.

(6) Watanabe, Y.; Groves, J. T. In *The Enzymes*, 3rd ed.; Academic Press: New York, 1992; Vol. XX, pp 405−452. Munier, B. *Bull. Soc. Chim. Fr.* **1986**, 578.

(7) (a) Brown, S. N.; Mayer, J. M. Manuscript in preparation. (b) Brown, S. N. Ph.D. Thesis, University of Washington, 1994.

(8) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd Ed.; Pergamon: New York, 1988.

(9) Fenselaw, A. H.; Moffat, J. G. *J. Am. Chem. Soc.* **1966**, *88*, 1762−1765.

(10) (a) Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82*, 125. (b) A modified synthesis is found in: Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091−4100.

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degassed and dried over 3 or 4 Å sieves and then vacuum transferred prior to use. Pyridine *N*-oxide and dimethyl sulfone were sublimed and kept under nitrogen. DMSO was degassed and dried over 4 Å molecular sieves. Me_2S was degassed, dried over sodium, and vacuum transferred prior to use. HCl gas (technical grade) was obtained from Matheson.

NMR spectra were recorded on Bruker AC-200 (^1H, ^{19}F) and AF-300 (^1H, ^{13}C) FT NMR spectrometers at ambient temperatures unless otherwise noted. Chemical shifts are reported in parts per million, referenced to the residual protons in the solvent (^1H, ^{13}C) or to neat CF_3COOH (^{19}F); coupling constants are reported in hertz. The pyrazole protons all have $J_{HH} = 2$ Hz, so this value is not included in the spectra reported below. Probe temperatures for low-temperature ^1H and $^{13}C\{^1H\}$ NMR spectra were calibrated by use of the ^1H chemical shifts for methanol.[11] IR spectra were recorded using a Perkin-Elmer 1600 FTIR with samples prepared as Nujol mulls or evaporated films on NaCl plates or as solution spectra in CD_2Cl_2. IR bands are reported in cm^{-1}. All of the compounds show bands for the $HBpz_3$ ligand at 3112 (m), 1503 (m), 1409 (s), 1312 (s), 1212 (s), 1116 (s), 1072 (m), 1051 (vs), 987 (w), 762 (s), 715 (s), 657 (m), and 615 (m). Unique bands are listed with the respective compounds. Electron impact mass spectra were recorded using a Kratos Analytical mass spectrometer using direct probe techniques with samples packed into glass capillaries and heated typically to 100 °C. GC-MS data were obtained using a Kratos Analytical mass spectrometer and a 5890 Hewlett-Packard GC-MS equipped with cooling units. Elemental analyses were performed by Canadian Microanalytical Services Ltd.

($HBpz_3$)$ReO(OMe)_2$ (1). ($HBpz_3$)$ReOCl_2$ (416 mg, 0.855 mmol) was placed in a 150 mL thick walled glass bomb with a stir bar. NEt_3 (0.6 mL, 4.31 mmol, 5 equiv), methyl alcohol (2.1 mL, 51.8 mmol, 61 equiv), and CH_3CN (80 mL) were vacuum transferred in and the solution was placed in an 81 °C oil bath and stirred for 7 days. The volatiles were removed in vacuo, leaving a dark blue residue, which was extracted twice with C_6H_6 (40 mL) and filtered. The solvent was removed, and the residue was recrystallized from CH_2Cl_2/pentane, yielding 248 mg (61%) of blue solid after washing with 2 × 15 mL of pentane and drying in vacuo. ^1H NMR (C_6D_6): δ 7.82 (d, 2H, pz); 7.52 (d, 1H, pz); 7.14 (d, 2H, pz); 6.86 (d, 1H, pz); 5.76 (t, 2H, pz); 5.50 (t, 1H, pz); 4.92 (s, 6H, $Re(OCH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.2, 137.7, 107.6 (pyrazoles cis to the oxo); 142.9, 134.3, 106.0 (pyrazole trans to the oxo); 73.3 (OCH_3). IR: 2498 (w, ν_{BH}); 1162(w); 1031 (s); 951 (s, ν_{ReO}); 623 (w). MS: *m/z* = 479 (M^+). Anal. Calcd for $C_{11}H_{16}BN_6O_3Re$: C, 27.68; H, 3.38; N, 17.61. Found: C, 27.57; H, 3.62; N, 17.48.

($HBpz_3$)$ReO(OEt)_2$ (2). ($HBpz_3$)$ReOCl_2$ (363 mg, 0.747 mmol) was placed in a 100 mL thick walled glass bomb with a magnetic stir bar. NEt_3 (0.52 mL, 13.7 mmol, 5 equiv), ethyl alcohol (0.80 mL, 13.7 mmol, 18.3 equiv), and CH_3CN (60 mL) were vacuum transferred into the bomb and then placed in an 81 °C oil bath and stirred for 3 days. Within 2 h the solution was a deep blue. The bomb was removed from the bath, the volatiles were removed in vacuo, and the blue residue was extracted with C_6H_6 (15 mL) and filtered to remove $[NEt_3H][Cl]$. Recrystallization from benzene/pentane gave 324 mg of a sky blue powder (86%). The ethoxy-d_1 variant was synthesized by using CH_3CDHOH (D, 98%; 32% yield). ^1H NMR (C_6D_6): δ 7.85 (d, 2H, pz); 7.59 (d, 1H, pz); 7.17 (d, 2H, pz); 6.86 (d, 1H, pz); 5.78 (t, 2H, pz); 5.50 (t, 1H, pz); 5.21, 5.05 (both d of q, 2H, $ReOCHH'CH_3$, $J_{HH} = 6$, $J_{HH'} = 10$); 1.60 (t, 6H, $J_{HH} = 6$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.2, 137.7, 107.2 (pyrazoles cis to the oxo); 143.1, 133.7, 105.7 (pyrazole trans to the oxo); 78.8 ($ReOCH_2CH_3$); 19.6 ($ReOCH_2CH_3$). IR: 2503 (w, ν_{BH}); 1157(w); 960 (s, ν_{ReO}). MS: *m/z* = 507 (M^+). Anal. Calcd for $C_{13}H_{20}BN_6O_3Re$: C, 30.90; H, 3.99; N, 16.63. Found: C, 30.81; H, 4.02; N, 16.50.

($HBpz_3$)$ReO(O^iPr)_2$ (3). Following the procedure for **2**, ($HBpz_3$)$ReOCl_2$ (325 mg, 0.668 mmol), NEt_3 (0.5 mL, 3.59 mmol, 5.4 equiv), ^iPrOH (2.0 mL, 26.1 mmol, 39.1 equiv), and CH_3CN (60 mL) were placed in a 150 mL thick walled bomb and stirred at 80 °C for 6 days (the solution turned dark brown after 3 h). Extraction with C_6H_6 (15 mL) and addition of pentane (30 mL) gave a deep blue solution and a brown precipitate. The solution was filtered and the solvent removed in vacuo, leaving a blue residue. The residue was recrystallized from toluene/heptane. A blue solid precipitated out and was filtered and then dried in vacuo; yield 189 mg (53%). ^1H NMR ($CDCl_3$): δ 7.81 (d, 2H, pz); 7.68 (d, 2H, pz); 7.66 (d, 1H, pz); 7.37 (d, 1H, pz); 6.36 (t, 2H, pz); 5.99 (t, 1H, pz); 5.65 (sept, 2H, $ReOCH(CH_3)_2$, $J_{HH} = 6$); 1.39, 1.18 (each d, 6H, $ReOCH(CH_3)(CH'_3)$, $J_{HH} = 6$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.0, 144.7, 137.4, 134.2, 107.4, 105.3 (pyrazole carbons); 83.3 ($ReOCH(CH_3)_2$); 25.9, 25.0 ($OCH(CH_3)(C'H_3)$. IR: 2493 (w, ν_{BH}); 1162(w); 952 (s, ν_{ReO}); 842 (w); 639(w). MS: *m/z* = 535 (M^+). Anal. Calcd for $C_{15}H_{24}BN_6O_3Re$: C, 33.05; H, 4.47; N, 15.76. Found: C, 33.17; H, 4.59; N, 15.89.

($HBpz_3$)$ReO(O^nBu)_2$ (4). Following the procedure for **2**, ($HBpz_3$)$ReOCl_2$ (240 mg, 0.494 mmol), NEt_3 (0.34 mL, 3.36 mmol, 6.8 equiv), ^nBuOH (0.89 mL, 9.9 mmol, 20 equiv), and CH_3CN (50 mL) were placed in a 150 mL thick walled glass bomb and stirred at 81 °C for 7 days. Extraction with C_6H_6 (5 mL), filtration to remove the ammonium salts, and recrystallization from toluene/heptane gave 165 mg of a blue solid (59%). ^1H NMR (C_6D_6): δ 7.87 (d, 2H, pz); 7.63 (d, 1H, pz); 7.17 (d, 2H, pz); 6.88 (d, 1H, pz); 5.79 (t, 2H, pz); 5.52 (t, 1H, pz); 5.13, 2.01, 1.67 (each m, 4H, $ReOCH_2CH_2CH_2CH_3$); 1.05 (t, 6H, $ReO(CH_2)_3CH_3$, $J_{HH} = 6$). $^{13}C\{^1H\}$ (NMR) (C_6D_6): δ 147.2, 143.1, 137.2, 133.8, 107.3, 105.6 (pyrazoles); 83.0 ($Re(OCH_2-$); 36.5, 20.3, 14.6 ($ReOCH_2CH_2CH_2CH_3$). IR: 2497 (w, ν_{BH}); 1027 (w); 959 (s, ν_{ReO}); 858 (w); 792 (w); 638 (w). MS: *m/z* = 563 (M^+). Anal. Calcd for $C_{17}H_{28}BN_6O_3Re$: C, 36.37; H, 5.03; N, 14.96. Found: C, 36.01; H, 4.95; N, 14.94.

($HBpz_3$)$ReO(OCH_2Ph)_2$ (5). Following the procedure for ($HBpz_3$)$ReOCl_2$ (133.4 mg, 0.274 mmol), $PhCH_2OH$ (1.0 mL, 8.85 mmol, 32 equiv, added via syringe), NEt_3 (0.26 mL, 1.87 mmol, 6.8 equiv), and CH_3CN (30 mL) were placed in a 100 mL thick walled glass bomb and stirred at 80 °C for 186 h. The glassy dark blue residue remaining after removal of the volatiles was recrystallized from toluene/heptane and benzene/pentane several times to give 48 mg of deep blue powder (28%). ^1H NMR (C_6D_6): δ 7.77 (d, 2H, pz); 7.59 (d, 4H, $J_{HH} = 7$, ortho); 7.40 (d, 1H, pz); 7.28 (m, 4H, meta); 7.16 (d, 2H, pz); 7.15 (t, 2H, $J_{HH} = 8$, para); 6.85 (d, 1H, pz); 6.21 (AB pattern, 4H, apparent $J_{HH} = 14$, $ReOCH_2Ph$); 5.72 (t, 2H, pz); 5.40 (t, 1H, pz). $^{13}C\{^1H\}$ NMR (C_6H_6): δ 147.0, 144.8, 143.6, 137.4, 107.5, 105.8 (pyrazoles); 128.5, 127.2, 126.7, 124.3 (phenyl); 85.1 ($ReOCH_2Ph$). IR: 3083 (w); 3059 (w); 3028 (s); 2503 (w, ν_{BH}); 1602.8 (s); 1450 (s); 1392 (w); 1358 (s); 1265 (w); 1101 (w); 1024 (w); 961 (w, ν_{ReO}); 816 (w); 791 (w); 734 (s); 700 (w); 675 (w). MS: *m/z* = 630 (M^+).

($HBpz_3$)$ReO(OEt)(OTf)$ (6). ($HBpz_3$)$ReO(OEt)_2$ (101 mg, 0.200 mmol) was placed in a 100 mL round bottom flask with a stir bar. C_6H_6 (30 mL) was vacuum transferred in, and Me_3SiOTf (0.040 mL, 0.20 mmol) was added via syringe. The solution was stirred for 12 h, with formation of a purple precipitate. The solution was chilled with an ice bath and filtered, producing a purple solid which was washed with 2 × 5 mL of C_6H_6 and 2 × 10 mL of pentane. Recrystallization from CH_2Cl_2/pentane gave 62.3 mg of a lavender solid (51%). The ethoxy-d_1 variant was also synthesized in 56% yield from ($HBpz_3$)$ReO(OCDHCH_3)_2$. ^1H NMR ($CDCl_3$): δ 8.12, 7.91, 7.89, 7.69, 7.62, 7.47, (each d, 1H, pz); 6.51, 6.44, 6.16 (each t, 1H, pz); 5.03, 4.76 (each d of q, 1H, $ReOCHH'CH_3$, $J_{HH} = 6$, 12); 1.98 (t, 3H, $ReOCH_2CH_3$, $J_{HH} = 6$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.3, 149.2, 145.3, 140.7, 137.6, 135.3, 109.1, 108.1, 106.7 (pyrazole carbons); 82.7 ($ReOCH_2CH_3$); 18.5 ($ReOCH_2CH_3$); $ReSO_3CF_3$ not observed. ^{19}F NMR ($CDCl_3$): δ −1.51 (s). IR: 2523 (w, ν_{BH}); 1350 (s, ν_{OTf}); 1236 (w, ν_{OTf}); 1180 (w, ν_{OTf}); 1157 (w, ν_{OTf}); 958 (s, ν_{ReO}); 918 (w); 644 (w). MS: *m/z* = 611 (M^+). Anal. Calcd for $C_{12}H_{15}BF_3N_6O_4ReS$: C, 23.65; H, 2.48; N, 13.79. Found: C, 23.71; H, 2.41; N, 13.60.

($HBpz_3$)$ReO(O^iPr)(OTf)$ (7). Following the procedure for **6**, ($HBpz_3$)$ReO(O^iPr)_2$ (48 mg, 0.089 mmol), C_6H_6 (10 mL), and Me_3SiOTf (0.017 mL, 0.089 mmol) were stirred for 16 h in a 50 mL round bottom flask (the solution turned purple within 1 h). Pentane (30 mL) was added, and the solution was allowed to stand in an ice bath for 5 h before filtering. Washing with 3 × 10 mL of cold pentane and drying in vacuo gave 32 mg of a dark lavender powder (58%). ^1H NMR (C_6D_6): δ 8.52, 7.91, 7.24, 6.92, 6.91, 6.68 (each d, 1H, pz); 6.34 (sept, 1H, $ReOCHMe_2$, $J_{HH} = 5$), 5.70, 5.56, 5.45 (each t, 1H, pz); 1.42, 1.33 (each d, 3H, $ReOCH(CH_3)(CH_3')$, $J_{HH} = 5$). $^{13}C\{^1H\}$ NMR (C_6D_6):

(11) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley-Interscience: New York, 1972, p 303.

δ 150.2, 147.5, 144.9, 139.9, 137.0, 134.9, 108.7, 107.8, 106.2 (pyrazoles); 85.5 ($ReOCHMe_2$); 25.6, 24.7 ($ReOCH(CH_3)(CH_3')$); $ReSO_3CF_3$ not observed. IR: 2521 (w, ν_{BH}); 1444(w); 1391 (w, ν_{OTf}); 1237(w, ν_{OTf}); 1199 (s, ν_{OTf}); 982 (s, ν_{ReO}); 910 (w); 790 (w); 731 (w); 671(w). MS: m/z = 625 (M + 1).

(HBpz$_3$)ReO(O^{n}Bu)(OTf) (8). Following the procedure for **7**, (HBpz$_3$)$ReOCl_2$ (105 mg, 0.216 mmol), C_6H_6 (10 mL), and Me_3SiOTf (0.043 mL, 0.217 mmol) were stirred for 4 h in a 50 mL round bottom flask (the solution turned brown within 1 min). Adding pentane (15 mL), chilling, and filtering gave a lavender solid that was recrystallized from toluene/pentane; yield 56.6 mg (41%). ^1H NMR (CD_2Cl_2): δ 8.12, 7.91, 7.87, 7.68, 7.60, 7.47 (each d, 1H, pz); 6.52, 6.43, 6.15 (each t, 1H, pz); 4.95, 4.73 (each d of t, 1H, $ReOCHH'CH_2CH_2CH_3$, J_{HH} = 6, $J_{HH'}$ = 4); 1.77, 1.33 (m, 1H, $ReOCH_2CHH'CH_2CH_3$); 1.49 (m, 2H, $ReOCH_2CH_2CH_2CH_3$); 0.92 (t, 3H, $ReO(CH_2)_3CH_3$, J_{HH} = 7). $^{13}C\{^1H\}$ (NMR) (CD_2Cl_2): δ 149.3, 146.2, 141.1, 137.0, 135.1, 133.7, 108.2, 107.5, 106.7 (pyrazoles); 84.3, 37.8, 22.1, 17.9 ($ReOCH_2$-$CH_2CH_2CH_3$); $ReSO_3CF_3$ not observed. IR: 2525 (w, ν_{BH}); 1392 (w, ν_{OTf}); 1237 (w, ν_{OTf}); 1197(s, ν_{OTf}); 1158 (w, ν_{OTf}); 1027 (w); 964 (s, ν_{ReO}); 912 (vw); 865 (w); 815 (w); 772 (s); 733 (w); 669(w). MS: m/z = 639 (M^+).

[(HBpz$_3$)ReO(OEt)(OSMe$_2$)][OTf] (10) is formed on addition of 1 equiv of Me_2SO to **6** in methylene chloride and is isolated as an impure purple solid on solvent removal. ^1H NMR ($CDCl_3$): δ 7.91 (d, 2H, pz); 7.85, 7.71, 7.64, 7.50 (each d, 1H, pz); 6.51, 6.48, 6.19 (each t, 1H, pz); 4.58, 4.28 (each d of q, 1H, $OCHH'CH_3$, J_{HH} = 6, $J_{HH'}$ = 11); 3.39, 3.33 (each s, 3H, $OS(CH_3)(CH'_3)$); 1.43 (t, 3H, OCH_2CH_3, J_{HH} = 5). IR: 2494 (w, ν_{BH}); 1249 (w, ν_{OTf}); 960 (s, ν_{ReO}); 872 (s, ν_{SO}; 839 cm^{-1} for $Re^{18}OSMe_2$).

[(HBpz$_3$)ReO(O^{i}Pr)(OSMe$_2$)][OTf] is formed on addition of 1 equiv of Me_2SO to **7** in methylene chloride. ^1H NMR (CD_2Cl_2): δ 8.18, 7.95, 7.85, 7.82, 7.70, 7.63 (each d, 1H, pz); 6.57, 6.52, 6.19 (each t, 1H, pz); 6.02 (sept, 1H, $ReOCHMe_2$, J_{HH} = 6), 3.42, 3.30 (each s, 3H, $OS(CH_3)(CH'_3)$); 1.51, 1.43 (each d, 3H, $ReOCH(CH_3)(CH_3')$, J_{HH} = 6).

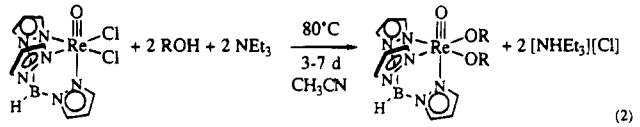
[(HBpz$_3$)ReO(O^{n}Bu)(OSMe$_2$)][OTf] is formed on addition of 1 equiv of Me_2SO to **8** in methylene chloride. ^1H NMR (CD_2Cl_2): δ 7.99, 7.95, 7.92, 7.75 (each d, 1H, pz); 7.58 (d, 2H, pz); 6.58, 6.52, 6.19 (each t, 1H, pz); 4.55, 4.25 (each d of t, 1H, $ReOCHH'CH_2$–, J_{HH} = 6, $J_{HH'}$ =5); 3.39, 3.30 (each s, 3H, $OS(CH_3)(CH'_3)$); 1.84 (m, 2H, $ReOCH_2CH_2CH_2CH_3$); 1.47 (m, 2H, $ReOCH_2CH_2CH_2CH_3$); 0.97 (t, 3H, $ReO(CH_2)_3CH_3$, J_{HH} = 8).

General Procedure for NMR Tube Experiments. Many of the experiments examined were done in sealed NMR tubes. In a typical procedure, (HBpz$_3$)ReO(OEt)(OTf) (6.7 mg, 0.011 mmol) was placed, in the glovebox, in a sealable NMR tube attached to a ground glass joint. PyO (3.2 mg, 0.034 mmol) was added, and the contents were dissolved in $CDCl_3$ (0.4 mL). A needle valve with a Teflon stopcock was attached to the tube, and the apparatus was placed on the vacuum line. The tube was freeze–pump–thawed three times (to −77 °C), then frozen again at −77 °C, and sealed with a torch. This procedure was modified depending on the nature of the reactants and/or the conditions of the experiment. The *isotope effects* were measured by reaction **6**-α-d^1 (98% D) with Me_2SO or pyO in a sealed NMR tube. The ratios of CH_3CHO to CH_3CDO were measured by NMR integration. The volatiles were then vacuum transferred off and examined by GC-MS; spectra were analyzed using the known fragmentation patterns.

Magnetization transfer in [(HBpz$_3$)ReO(OEt)(OSMe$_2$)]OTf was performed on solutions containing a large (>20 equiv) excess of free dimethyl sulfide. The $(CH_3)_2S$ peak at 2.10 ppm was selectively inverted using a DANTE pulse sequence, and the resulting free induction decay (FID) (acquired after the desired delay) was subtracted from an FID acquired in an analogous manner but with inversion carried out well off-resonance. The difference spectra therefore show positive peaks whose magnitude is proportional to the nonequilibrium extent of magnetization of the relevant signals. Analysis of the growth of the [(HBpz$_3$)ReO(OEt)($OS(CH_3)_2$)]OTf signals is complicated by differential relaxation of free Me_2S and bound Me_2SO, so the data were analyzed using the equations in ref 7. Corrections for differential relaxation were <20% at or above room temperature but were substantial below room temperature (e.g., $k = 3.4k_{obs}$ at 277 K).

Results

Syntheses of (HBpz$_3$)ReO(OR)$_2$ and (HBpz$_3$)ReO(OR)(OTf). Refluxing (HBpz$_3$)$ReOCl_2$[10] with an alcohol and NEt_3 in acetonitrile for several days results in replacement of the chlorides by alkoxide ligands, giving the bisalkoxide species (HBpz$_3$)$ReO(OR)_2$ (eq 2).



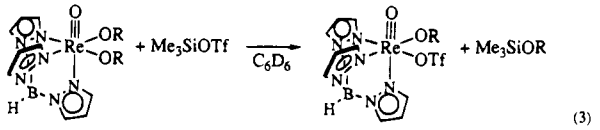
(2)

R = Me (**1**), Et (**2**), ^{i}Pr (**3**), ^{n}Bu (**4**), CH_2Ph (**5**)

This general synthesis works well with 20 equiv of the ethanol, isopropyl alcohol, 1-butanol, and benzyl alcohol, while 60 equiv of methanol are required to prevent substantial decomposition. Attempts to synthesize the *tert*-butoxide compound by this method were not successful. Multiple recrystallizations are required to obtain pure materials; their solubility in hydrocarbon solvents roughly increases with the size of the alkyl group.

Following reaction 2 by ^1H NMR shows that (HBpz$_3$)ReO(OR)Cl complexes are formed initially and then converted to the bisalkoxides **1**–**5**. Attempts to separate the alkoxy chloride complexes from the bisalkoxide species by chromatography on silica gel or recrystallization have been unsuccessful. Complex **2** is also formed on reaction of (HBpz$_3$)$ReOCl_2$ with thallium ethoxide, but in lower yield and purity. Analogous glycolate and bis(phenoxide) complexes have been prepared by similar routes,[7b,10b] and related alkoxide compounds have been formed by other approaches.[12]

One alkoxide ligand is cleanly removed from **2**, **3**, or **4** by 1 equiv of Me_3SiOTf (OTf = triflate, OSO_2CF_3) to give the alkoxy–triflate complexes (HBpz$_3$)ReO(OR)(OTf) (R = Et (**6**), ^{i}Pr (**7**), ^{n}Bu (**8**), eq 3). Complexes **6**–**8** are isolated as purple



(3)

OTf = OSO_2CF_3 R = Et (**6**), ^{i}Pr (**7**), ^{n}Bu (**8**)

or lavender solids in reasonable yields (40–60%), using their limited solubilities in hydrocarbon solvents. For instance, the ethoxide **6** is essentially insoluble in benzene and is isolated by filtration, washing with benzene to remove any **2**, and recrystallizing from CH_2Cl_2/pentane to remove residual Me_3SiOEt. (HBpz$_3$)$ReO(OTf)_2$[7b] is not observed unless excess Me_3SiOTf and extended reaction times are used.

The composition and stereochemistry of **1**–**8** are indicated by their NMR, IR, and mass spectra and their analytical data. For **1**–**5**, ^1H NMR spectra show that the three pyrazoles of the $HBpz_3$ ligand are in a 2:1 ratio and that the hydrogens or methyl groups on the α-carbon are diastereotopic (except in **1**). These data indicate molecular C_s symmetry. Spectra of the alkoxy–triflates **6**–**8** show three inequivalent pyrazole rings, indicative of C_1 symmetry, as expected because of the three different oxygen ligands. Protons on the alkoxide α-carbon appear unusually downfield in these complexes: δ 4–7 ppm for **1**–**5**

(12) Thomas, J. A.; Davison, A. *Inorg. Chim. Acta* **1991**, *190*, 2131–2135. Paulo, A.; Domingos, A.; Marçalo, J.; de Matos, A. P.; Santos, I. *Inorg. Chem.* **1995**, *34*, 2113–2120.

Table 1. Product Yields in Reactions of $(HBpz_3)ReO(OR)(OTf)$ with Oxygen Atom Donors

compound	oxidant	yields, %		
		$(HBpz_3)ReO_3$ (**9**)	aldehyde/ketone	alcohol
$(HBpz_3)ReO(OEt)(OTf)$ (**6**)	pyO[a]	81	46	37
$(HBpz_3)ReO(OEt)(OTf)$ (**6**)	DMSO[a]	66	30	34
$(HBpz_3)ReO(OEt)(OTf)$ (**6**)	Me_3NO[b]	67	42	21
$(HBpz_3)ReO(O^iPr)(OTf)$ (**7**)	pyO[a]	78	46	30
$(HBpz_3)ReO(O^iPr)(OTf)$ (**7**)	DMSO[a]	63	34	29
$(HBpz_3)ReO(O^nBu)(OTf)$ (**8**)	pyO[b]	78	46	33
$(HBpz_3)ReO(O^nBu)(OTf)$ (**8**)	DMSO[b]	60	26	32

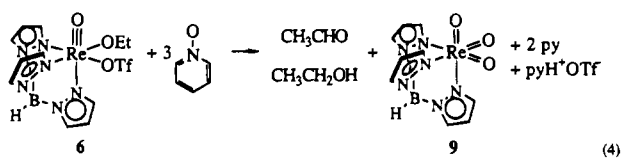
[a] Reaction in CD_2Cl_2 solvent. [b] Reaction in $CDCl_3$ solvent.

and δ 6−8 ppm for **6**−**8**. IR spectra and ^{19}F NMR chemical shifts indicate the presence of coordinated, rather than ionic, triflate.[13]

Solutions of the bisalkoxide complexes are somewhat air sensitive, due to reaction with atmospheric moisture. The methoxide **1** is the most sensitive, forming methanol and a green NMR-silent material within 15 min, while **2** requires 3 h, and the butoxide **4** is stable in solution for 2 days in air (all react with added H_2O in minutes). Compounds **1**−**5** thermally decompose only over a period of a week or more at 81 °C in benzene, acetonitrile, or methylene chloride solution. The alkoxy−triflate complexes **6**−**8** are much more reactive, decomposing in air within minutes in solution and in under 30 min as solids. All of the alkoxide compounds are very reactive toward acids. Benzene solutions of **2**, for instance, react rapidly with gaseous HCl to give ethanol and $(HBpz_3)ReOCl_2$. Reaction of **6** with dry HCl or triflic acid forms ethanol and $(HBpz_3)ReOCl_2$ or $(HBpz_3)ReO(OTf)_2$. NH_4Cl converts **6** to $(HBpz_3)ReO(OEt)Cl$ (by ^1H NMR in CD_3CN), indicating that the triflate ligand is labile. The lability of the triflate ligands in **6**−**8** is also shown by the chemistry described below.

Oxidation of Alkoxide Complexes. The bisalkoxide complexes **1**−**5** react slowly with 3 equiv of pyO over 36 h in C_6D_6, CD_2Cl_2, or $CDCl_3$ solution. The products observable by NMR are the rhenium(VII) trioxo complex $(HBpz_3)ReO_3$ (**9**)[14] (55−65% yield), the corresponding alcohol (20−25% yield), and aldehyde or ketone (30−35% yield). Thus, **2** forms acetaldehyde and ethanol, **3** gives acetone and isopropyl alcohol, etc. Oxidations with 3−4 equiv of DMSO give similar products but at a much slower rate (months). Compounds **1**−**5** are unreactive to Me_2SO_2, N_2O, and dry O_2.

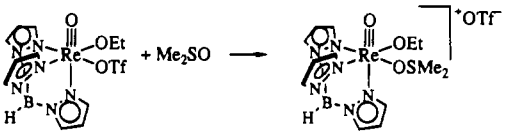
The alkoxy−triflate compounds **6**−**8** are much more reactive toward pyO and DMSO, though dry O_2 is still unreactive. Reaction of **6** with 2.6 equiv of pyO in CD_2Cl_2 gives a light brown solution that turns clear in less than a minute. ^1H NMR spectra of the reaction mixture show the formation of $(HBpz_3)ReO_3$ (**9**), acetaldehyde, ethanol, pyridine, and pyridinium triflate (eq 4). Similarly, oxidation of **7** by pyO produces acetone and



6 **9** (4)

isopropyl alcohol, and oxidation of **8** gives *n*-butyraldehyde and 1-butanol, along with **9** and py + pyH^+OTf^-. The organic products are formed in roughly equal yields (30−50%), and the amount of **9** formed is roughly equal to the sum of the organic yields (60−80%; Table 1). The rate and product distribution of these reactions are unaffected by the presence of excess pyO.

The reaction of **6** with 2.8 equiv of DMSO in $CDCl_3$ immediately gives a light blue solution whose ^1H NMR spectrum shows that all of the rhenium has been converted to a cationic DMSO adduct, $[(HBpz_3)ReO(OEt)(OSMe_2)]OTf$ (**10**; eq 5). Similar adducts are observed in reactions of **7** and **8**.



6 **10** (5)

Three inequivalent pyrazoles and diastereotopic methyl groups ($OSMe_2$) and methylene hydrogens (OCH_2Me) in the ^1H NMR of **10** indicate C_1 symmetry at the metal. The IR spectrum of **10** shows a band at 872 cm^{-1}, which is assigned as the S−O stretch of the DMSO ligand because it shifts to 839 cm^{-1} when $Me_2S^{18}O$ is used (calculated, 825 cm^{-1} for a diatomic S−O stretch). This assignment shows that the sulfoxide oxygen is bound to rhenium, since the S−O stretching frequency decreases on coordination in O-bound sulfoxide complexes and increases in S-bound complexes[15] (ν_{SO} = 1057 cm^{-1} for free Me_2SO in CH_2Cl_2). The 872 cm^{-1} band in **10** is an unusually low S−O stretch, as typical values in O-bound complexes are in the 900−1000 cm^{-1} range.[15] This band is almost as low in energy as the 858 cm^{-1} band observed in the very similar phenyl−DMSO adduct $[(HBpz_3)ReO(Ph)(OSMe_2)]OTf$.[7] Complex **10** is not very stable, but it has been isolated as a purple solid, always contaminated with small amounts of $(HBpz_3)ReO_3$ (**9**). Solutions of **10** in the absence of added DMSO decompose to form trace amounts of ethanol and acetaldehyde, **9**, and a number of yet unidentified $HBpz_3$ compounds, with most of the rhenium (>85%) not observed by ^1H NMR spectroscopy.

In the presence of excess DMSO, **10** is oxidized more cleanly to **9** (64% yield) and ~30% each of acetaldehyde and ethanol. Me_2S and a small amount of triflic acid are also observed in the ^1H NMR spectrum, identified by comparison with authentic spectra and by spiking the reaction mixture with authentic samples. Over the 3 days that **10** is consumed, there is also some oxidation of Me_2SO to Me_2SO_2 (which is inert under these conditions). Analogous products are observed on treatment of the other alkoxy−triflate complexes **7** and **8** with excess DMSO. If insufficient DMSO is present, the reaction stops when the DMSO is consumed and the adduct slowly decomposes. The rate of oxidation is inhibited by the presence of excess Me_2S but is unaffected by the amount of DMSO above 3 equiv. The

(13) (a) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17−33. (b) Conry, R. R.; Mayer, J. M. *Organometallics* **1993**, *12*, 3179−3186.
(14) Degnan, I. A.; Herrman, W. A.; Herdtweck, E. *Chem. Ber.* **1990**, *123*, 1347.
(15) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3d ed.; Wiley: New York, 1978; pp 344−346. Davies, J. A. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 115−187. Furukawa, N.; Fujihara, H. In *The Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; Wiley: New York, 1988; pp 541−581.

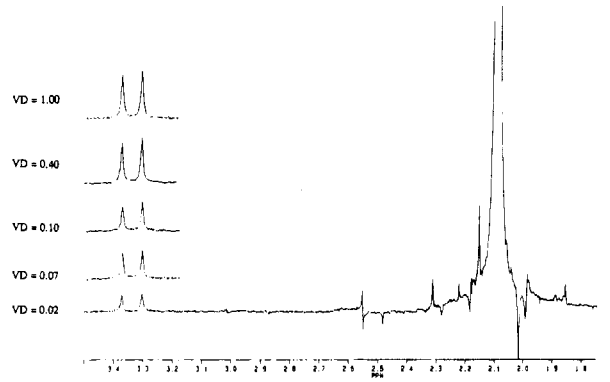
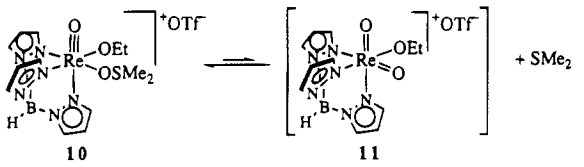


Figure 1. ^{1}H NMR spectra from a magnetization transfer experiment on a sample containing [(HBpz$_3$)ReO(OEt)(OSMe$_2$)]OTf (**10**) and a large excess of Me$_2$S. The Me$_2$S resonance at 2.10 ppm is selectively inverted, and the intensities of the two resonances for bound Me$_2$SO at different delay times are displayed. (The Me$_2$S peak at 2.10 is well off scale and thus shows various side bands and subtraction errors.)

time for conversion of **10** to **9** is unchanged over a factor of 50 in the concentration of **10**, at constant Me$_2$S and Me$_2$SO concentrations, indicating that the alkoxide oxidation is unimolecular in rhenium.

Inhibition of the oxidation of **10** by Me$_2$S suggests the pre-equilibrium loss of Me$_2$S to give a rhenium(VII) dioxo complex, [(HBpz$_3$)Re(O)$_2$(OEt)]OTf (**11**, eq 6).



10 **11** (6)

Consistent with this equilibrium is the observed rapid incorporation of protium into the bound $(CD_3)_2SO$ on addition $(CH_3)_2S$ to a solution of [(HBpz$_3$)ReO(OEt)[OS$(CD_3)_2$]OTf (**10**-d^6). The rhenium(VII) complex has not, however, been observed, even at 198 K in CD_2Cl_2 using Me$_2$SO or pyO as the oxygen atom transfer agent. Facile dissociation of Me$_2$S is consistent with the low S−O stretching frequency observed in the IR spectrum of **10**. Also consistent with Me$_2$S dissociation is the observation that treatment of **6** with Me$_2$S^{18}O gives **10** labeled at both the DMSO and oxo groups.

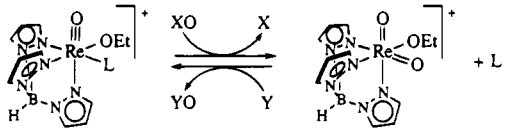
Dissociation of Me$_2$S from **10** can also be observed and quantified by ^{1}H NMR magnetization transfer experiments. Inversion of the free Me$_2$S signal results in partial loss of intensity of the resonances for the bound Me$_2$SO ligand (Figure 1). The observed rate of exchange is independent of the concentration of free Me$_2$S, indicating unimolecular dissociation of Me$_2$S from **10**, with a rate constant of 8.2 (6) s^{-1} at 298 K. This is slightly faster than Me$_2$S loss from the analogous phenyl−DMSO complex, [(HBpz$_3$)ReO(OPh)(OSMe$_2$)]OTf (k_{298} = 2.9 (4) s^{-1}).[7] From the rates of exchange measured from −3 to +32 °C, $\Delta H^{\ddagger}$ = 14.9 (8) kcal/mol and $\Delta S^{\ddagger}$ = −4.5 (16) eu.

Oxidations of **6**-α-d^1, (HBpz$_3$)ReO(OCHDCH$_3$)(OTf), give both CH$_3$CHO and CH$_3$CDO, and their ratio reflects the isotope effect for C−H vs C−D bond cleavage. Oxidation with pyO gives a CH$_3$CDO/CH$_3$CHO ratio of 4.5 (2) by ^{1}H NMR (4.6 (3) by GC-MS). With DMSO as the oxidant, 4.6 (3) (by ^{1}H NMR, 4.7 (4) by GC-MS) is obtained. The equivalence of these values is consistent with the same intermediate undergoing C−H bond cleavage, regardless of which oxygen atom transfer agent is used.

Discussion

Rhenium(V) oxo−alkoxide complexes are stable species. They do not readily decay by internal redox reactions involving reduction of the rhenium and oxidation of the alkoxide. Reaction of these species with the oxygen atom donors pyridine *N*-oxide and DMSO results in oxidation of both the rhenium and the alkoxide ligand. The reactions are much faster with the alkoxy−triflate species **6**−**8** than with the bisalkoxide complexes **1**−**5**, because the oxygen atom transfer reagent must coordinate to the metal prior to reaction, as is typically assumed.[5,16] Such initial adducts—*e.g.*, [(HBpz$_3$)ReO(OEt)(OSMe$_2$)]OTf (**10**)—have been observed in the reactions of **6**−**8** with DMSO. Pyridine *N*-oxide is a much more potent oxygen atom donor than DMSO,[5] so presumably an initial adduct loses pyridine too rapidly to be observed. The requirement for initial coordination explains the lack of reaction of O_2 and N_2O, thermodynamically very potent oxygen atom transfer reagents[5] but quite poor ligands.

The chemistry and spectroscopy of the DMSO adduct **10** indicate that it undergoes facile equilibrium loss of Me$_2$S to form a rhenium(VII) dioxo complex (eq 6). Since added Me$_2$S inhibits the alkoxide oxidation reaction, this S−O bond cleavage must be a pre-equilibrium on the oxidation pathway. The observation of the same isotope effect in reactions of **6**-α-d^1 with both DMSO and pyO suggests that the C−H bond cleavage occurs in same intermediate in the two cases, after liberation of Me$_2$S or pyridine. The inhibition, exchange, and magnetization transfer studies all indicate that this intermediate is the cationic rhenium(VII) dioxo complex [(HBpz$_3$)ReO$_2$(OEt)]OTf (**11**). Complex **11** is formed by oxygen atom transfer and can be consumed by oxygen atom transfer, to Me$_2$S or Me$_2$SO (eq 7); this is the origin of the Me$_2$SO$_2$ observed in reactions of **6**−**8** with DMSO.



6 **11** (7)

Complex **11** oxidizes Me$_2$S much more readily than Me$_2$SO: the equilibrium between **10** and **11** (eq 6) is very fast, while Me$_2$SO$_2$ formation is slow. Me$_2$SO$_2$ formation is inhibited by the presence of excess Me$_2$S, as predicted by this mechanism because the equilibrium concentration of **11** is reduced. The initial rate of sulfone formation, $R_{Me_2SO\rightarrow Me_2SO_2}$, can be estimated from the NMR spectra of the reaction. The rate of sulfide oxidation ($R_{Me_2S\rightarrow Me_2SO}$) is—at equilibrium—equal to the rate of Me$_2$S loss, which was measured by magnetization transfer. Dividing the rate expression in eq 8 by that in eq 9 and rearranging give eq 10, which gives the ratio of rate constants for oxidation of Me$_2$S and Me$_2$SO by **11**. The conclusion is that **11** oxidizes Me$_2$S 8 × 10^4 times faster than Me$_2$SO.

$$R_{Me_2SO\rightarrow Me_2SO_2} = k_{Me_2SO}[\mathbf{11}][Me_2SO] \quad (8)$$

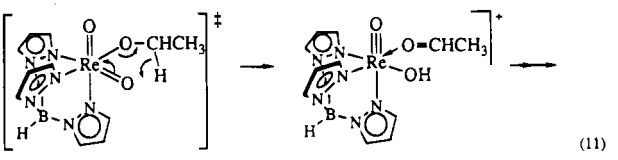
$$R_{Me_2S\ dissociation} = R_{Me_2S\rightarrow Me_2SO} = k_{Me_2S}[\mathbf{11}][Me_2S] \quad (9)$$

$$\frac{k_{Me_2S}}{k_{Me_2SO}} = \frac{R_{Me_2S\ dissociation}[Me_2SO]}{R_{Me_2SO\rightarrow Me_2SO_2}[Me_2S]} \quad (10)$$

The relative rate of sulfide vs sulfoxide oxidation is a measure of the electrophilicity of an oxidant, according to a reactivity

scale set out by Adam, Di Furia, and others.[17] Basic H_2O_2 is nucleophilic and selectively oxidizes the electron poor sulfoxide sulfur (>100:1), while H_2O_2 in strongly acidic solution prefers to oxidize the more electron rich thioether (≤1:4). On this scale, **11** is an extremely electrophilic oxidant.[18] This analysis and the conclusions follow closely those worked out for the analogous dioxo−phenyl cation, $[HBpz_3ReO_2Ph]^+$, which can be observed at low temperatures.[7] Complex **11** is roughly as electrophilic as $[HBpz_3ReO_2Ph]^+$, which oxidizes Me_2S 1.2×10^5 times faster than Me_2SO.[7]

The dioxo−alkoxide complex **11** can oxidize Me_2S, Me_2SO, or the internal alkoxide ligand. Oxidation of an alkoxide to a ketone or aldehyde occurs formally by loss of hydride. Chromium(VI) oxidations of alcohols most likely occur by hydride transfer from the alkoxide to an oxo group (eq 1),[3] and our data are consistent with such a pathway (eq 11).

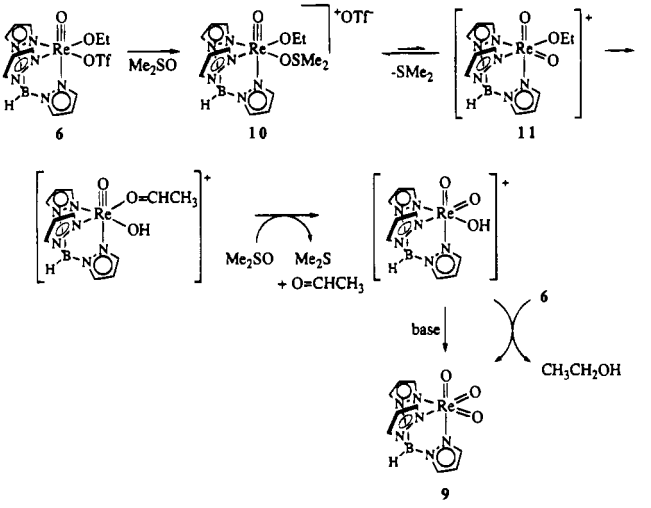


(11)

Hydride transfer to an oxo ligand is a two-electron reduction of the metal center, reforming rhenium(V) and generating a hydroxide ligand. The ability of the oxo groups in **11** to accept a hydride is related to their electrophilicity. The isotope effect of 4.6 for this oxidation is within the range seen in Cr^{VI} alcohol oxidations, where k_H/k_D is typically between 2 and 5.[3d] We cannot rule out an alternative mechanism of hydride transfer to the metal (β-elimination from the alkoxide) followed by migration to an oxo ligand. This would, however, involve a seven coordinate intermediate, and it is not clear why β-elimination should occur in **11**, without an open coordination site, while **6** is stable despite the labile triflate. The hydride transfer is rapid, as reactions of **6**−**8** with pyO are complete within minutes at ambient temperatures. This contrasts with the relative stability of neutral rhenium(VII) trioxo−alkoxide complex $ReO_3(OMe)$,[19] which likely has less electrophilic oxo groups.

Putting these results together gives the mechanism shown in Scheme 1 for the oxidation of **6** by DMSO or pyO to give acetaldehyde, ethanol, and $(HBpz_3)ReO_3$ (**9**). The acetaldehyde formed via eq 11 is a poor ligand and should be readily displaced by DMSO or pyO, resulting in oxidation of the rhenium back to Re(VII). This removal of the aldehyde from the coordination sphere of the metal is likely the reason for its lack of further oxidation to acetic acid. The rhenium(VII) dioxo−hydroxide cation $[(HBpz_3)ReO_2(OH)]^+$ is an extremely strong acid, as **9**

Scheme 1



is a very poor base (like perrhenate). Independent NMR tube reactions show that **9** is unaffected by triflic acid in benzene solution. With DMSO as the oxidant, $[(HBpz_3)ReO_2(OH)]^+$ protonates either a triflate anion, to give the observed HOTf, or an alkoxide complex, which gives the free alcohol observed. Reactions of pyridine *N*-oxide consistently give higher yields of **9** and of aldehyde/ketone product (Table 1), presumably because the pyridine produced can deprotonate $[(HBpz_3)ReO_2(OH)]^+$, forming pyH^+OTf^-, and reduce the formation of alcohol and other side reactions. The trioxo complex **9** is a reaction dead end in this process and prevents any catalytic turnover. A catalytic cycle could occur if the hydroxy−aldehyde complex in Scheme 1 were intercepted by alcohol rather than oxidant, but complex **6** is not stable in the presence of excess ethanol.

Conclusions

The rhenium(V) oxo−alkoxide complexes $(HBpz_3)ReO(OR)_2$ and $(HBpz_3)ReO(OR)(OTf)$ are oxidized by the oxygen atom donors pyridine *N*-oxide and DMSO to give $(HBpz_3)ReO_3$ (**9**) and the corresponding aldehyde or ketone in moderate yield. No further oxidation of aldehydes to carboxylic acids is observed, apparently because of displacement of the aldehyde from the rhenium coordination sphere. The DMSO oxidation of $(HBpz_3)ReO(OEt)(OTf)$ (**6**) proceeds via initial formation of a sulfoxide adduct, $[(HBpz_3)ReO(OEt)(OSMe_2)]OTf$ (**10**). Complex **10** reversibly loses SMe_2 to give a cationic rhenium(VII) dioxo complex $[(HBpz_3)ReO_2(OCH_2CH_3)]OTf$ (**11**), which is not observed but is indicated by kinetic, labeling, and magnetization transfer studies. Complex **11** oxidizes Me_2S to Me_2SO 8×10^4 times faster than it oxidizes Me_2SO to Me_2SO_2, indicating it to be a very electrophilic oxidant. Oxidation of the ethoxide ligand occurs in **11** by hydride transfer to an oxo group, consistent with the electrophilic character of the oxo ligands.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this work. We especially thank Seth Brown for his invaluable comments and guidance and for his example in working with this system. We thank Dr. Tom Pratum for assistance with the NMR experiments.

IC950781I

(16) Mayer, J. M. In *Advances in Transition Metal Chemistry;* Che, C.-M., Ed.; in press.

(17) (a) Adam, W.; Haas, W.; Lohray, B. B. *J. Am. Chem. Soc.* **1991**, *113*, 6202−6208, and references cited therein. (b) Ballistreri, F. P.; Tomaselli, G. A.; Toscono, R. M.; Conte, V.; Di Furia, F. *J. Am. Chem. Soc.* **1991**, *113*, 6209−6212.

(18) The comparison of main-group oxidants vs **11** may be biased somewhat by the fact that the rhenium binds Me_2SO more strongly than Me_2SO_2. However, these reactions are downhill and rapid, indicating an early transition state which should not be strongly affected by the stability of the products. Me_2S oxidation by $[HBpz_3ReO2Ph]^+$ has been shown to occur at 10^5 M^{-1} s^{-1}, with essentially no enthalpic barrier.[7]

(19) Edwards, P.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1984**, 2695.