force for intramolecular electron transfer may thus differ from the voltammetrically determined value of ΔE depending upon the degree to which the reduction potential of one site is sensitive to the oxidation state of the other site close by.

In conclusion, the experiments demonstrate that interaction of proteins with electrode surfaces leading to reversible electron exchange is critically influenced by specific attachment of a single Ru complex. The loss of requirement for a cation promoter even though the sign of the protein's overall charge remains unchanged following modification (as with plastocyanin) provides support for the importance of localized protein surface charge, rather than overall charge alone, in determining its interaction with an electrode surface. The voltammetric measurements show further that the reduction potentials of redox sites in modified proteins may be significantly different from values assumed on the basis of the isolated components. In particular, the reduction potential of the histidine-attached Ru center (which is expected to be largely exposed at the protein surface) is sensitive to the composition of the electrolyte.

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Oxygen Atom Transfer Reactions of Cationic Rhenium(III), Rhenium(V), and Rhenium(VII) Triazacyclononane Complexes

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$Re(O)Cl_3(Me_2S)(OPPh_3)$ reacts readily with 1,4,7-trimethyltriazacyclononane (Me_3tacn) to form the rhenium(V) oxo cation $[Re(O)Cl_2(Me_3tacn)]^+$ (**1**) in good yield. With the unsubstituted triazacyclononane (tacn), however, both $[Re(O)Cl_2(tacn)]^+$ (**2**) and $[Re(O)_3(tacn)]^+$ (**3**) are formed, even under anaerobic conditions. Oxidation of **2** to **3** [Re(V) → Re(VII)] can be easily accomplished with a variety of mild oxidizing agents such as Me_2SO and I_2, but the oxidation of **1** requires over a month at 80 °C in aqueous nitric acid. Complex **1** is reduced [Re(V) → Re(III)] by oxygen atom transfer to phosphines, forming $[Re(OPR_3)Cl_2(Me_3tacn)]^+$ (R = Ph, **4**; Me, **5**). The $OPPh_3$ ligand in **4** is easily displaced by other neutral ligands such as acetonitrile or acetone. The acetone complex $[Re(O{=}CMe_2)Cl_2(Me_3tacn)]^+$ (**7**) is readily oxidized back to **1** [Re(III) → Re(V)] by the oxygen atom donors ^{n}BuNCO, $OAsPh_3$, Me_2SO, ethylene oxide, pyridine *N*-oxide, and N_2O. These reactions require an open coordination site at the rhenium(III) center. Surprisingly, it is not substantially easier to oxidize the rhenium(III) complex **7** than the rhenium(V) species **2**. On the basis of these reactions, simple thermochemical cycles are used to estimate the rhenium–oxo bond strength in **1** to be 141 ± 9 kcal/mol.

Transfer of an oxygen atom between a metal center and a substrate is one of the most fundamental reactions of metal oxo complexes.[2,3] Oxygen atom transfer has also received attention because of its importance in biological systems, in organic synthesis, and in industrial processes. For example, it has been suggested as the critical step in catalysis by cytochrome P-450[4] and molybdenum hydroxylase enzymes.[5] Despite the interest in this reaction, oxygen atom transfer is less well understood than transfer of a univalent atom by classical inner-sphere electron transfer.[6] Only oxygen atom transfer processes involving molybdenum have received systematic study; a recent comprehensive review states that there are no reports of oxygen atom transfer to rhenium.[2]

A primary goal of this study was to examine the effect of metal oxidation state on oxygen atom transfer reactivity. We describe here[7] a series of oxygen atom transfer reactions that interconvert rhenium(III), rhenium(V), and rhenium(VII) complexes, which enable, for the first time, a comparison of the oxygen atom transfer reactivity of two different redox couples, $d^4 \rightleftarrows d^2$ and $d^2 \rightleftarrows d^0$. Studies of the related d^3 oxo complex, which would likely have one electron in a metal–oxygen antibonding orbital,[8] were however thwarted by the instability of this compound. Triazacyclononane (tacn) and its methylated analogue (1,4,7-trimethyltriazacyclononane, Me_3tacn) have been used as supporting ligands because they bind well to both high- and low- oxidation state complexes.[9] The observed reactions are used to derive an estimate of the Re(V)≡O bond strength and to discuss the mechanism of oxygen atom transfer.

Experimental Section

Syntheses were performed with standard Schlenk or vacuum-line techniques and a continuous nitrogen flow glovebox except as indicated. Solvents were dried and deoxygenated by standard methods.[10] All reactions were executed at ambient temperatures unless otherwise stated. NMR spectra were obtained on Varian VXR-300 or Bruker WM-500 spectrometers. Chemical shifts are reported in ppm downfield from TMS: δ (multiplicity, number of hydrogens). NMR spectra in D_2O were referenced to DSS (2,2-dimethyl-2-silapentane-5-sulfonic acid, assigning the most upfield resonance to 0.015 ppm) for ^1H NMR and to MeOH (49.3 ppm) for ^{13}C. IR spectra were obtained as Nujol mulls on NaCl plates with Perkin-Elmer 283, FT 1604, or FT 1800 spectrometers and are reported in cm^{-1}. Elemental analyses were performed by Canadian

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Microanalytical (Delta, BC) or Galbraith (Knoxville, TN).

Re(O)Cl$_3$(Me$_2$S)OPPh$_3$,[11] Re(O)Cl$_3$(PPh$_3$)$_2$,[12] Bu$_4$N[Re(O)Cl$_4$],[13] and [Re(O)$_3$(tacn)]Cl[14] were synthesized by using literature methods. 1,4,7-Triazacyclononane (tacn) and 1,4,7-trimethyl-1,4,7-triazacyclononane (Me$_3$tacn) were purchased (Aldrich) and used as received, or, alternatively, tacn was synthesized.[15] NaBPh$_4$ (Aldrich), PPh$_3$ (Pressure), KReO$_4$ (Cleveland Refractory Metals), and PMe$_3$ (Aldrich) were used as received.

Kinetic experiments were run in flame-sealed NMR tubes with 2–3 mg of [Re(OPPh$_3$)Cl$_2$(Me$_3$tacn)]BPh$_4$ to which 0.4 mL of Me$_2$SO-d_6 or CD$_3$CN and a known amount of the TMS standard were added. The experiments from 35 to 65 °C were conducted on the VXR-300 and the 21 °C run utilized a large water bath whose temperature was monitored throughout the time period (20.5 °C $< T <$ 21.5 °C).

Electrochemical measurements were performed with a Bioanalytical Systems cyclic voltammograph, Model CV-27, with a Houston Instrument Model 100 recorder. The electrochemical cell employed a platinum disk as the working electrode, a platinum wire as the auxiliary electrode, a saturated calomel (SCE) reference electrode, and argon as an inert blanketing gas. The supporting electrolyte was 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Aldrich), which was recrystallized in absolute ethanol and dried in vacuo for several hours at 60–70 °C. The solvent (THF) was refluxed over lithium aluminum hydride for an hour, stored over sodium, and vacuum transferred immediately before use. Cyclic voltammograms of the ca. 10^{-3} M solutions were recorded at various scan rates, then ferrocene was added as an internal standard.

The fast atom bombardment mass spectrometry (FAB-MS) spectra were acquired with a VG 70 SEQ tandem hybrid instrument of EBqQ geometry (VG Analytical, Altrincham, U.K.). The instrument was equipped with a standard unheated VG FAB ion source and a standard saddlefield gun (Ion Tech, Ltd., Middlesex, U.K.) producing a beam of xenon atoms at 8 keV and 1 mA. The mass spectrometer was adjusted to a resolving power of 1000 and spectra were obtained at 8 kV and at a scan speed of 10 s/decade. 2-Hydroxyethyl disulfide (2-HEDS) was used as the matrix in the positive ion FAB-MS mode.

[Re(O)Cl$_2$(Me$_3$tacn)]Cl ([1]Cl). To 1.06 g (1.6 mmol) of Re(O)Cl$_3$(Me$_2$S)OPPh$_3$ was added 50 mL of CH$_2$Cl$_2$ and 0.32 mL of Me$_3$tacn (1.7 mmol). The solution was stirred for 1.5 h and then concentrated by 50% and the solids were filtered, washed with CH$_2$Cl$_2$, and stripped in vacuo to yield 0.54 g (1.2 mmol, 76%) of light brown solids. This product is impure and is purified by anion exchange to the BPh$_4^-$ salt (see below). ^{1}H NMR (D$_2$O): 2.28 (s, 3 H), 3.98 (s, 6 H) C*H*$_3$; 3.19, 3.59 (m, 4 H each), 3.54, 4.23 (m, 2 H each) CH*H*. ^{13}C{^{1}H} NMR (D$_2$O): 55.2 (2*C*H$_3$); 57.9, 61.3, 64.8, 76.1 (*C*H$_3$, *C*H$_2$). IR: 1291, 1190 w, 1157, 1119, 1048 s, 1000 s, 979 s (Re=O; ν(Re=^{18}O) seen at 933, calc 928), 968, 904 w, 893 w, 807 s, 752. [Re(^{18}O)Cl$_2$(Me$_3$tacn)]Cl was synthesized from Re(^{18}O)Cl$_3$(Me$_2$S)OPPh$_3$.[11] FAB-MS: 444/442 (M$^+$).

[Re(O)Cl$_2$(Me$_3$tacn)]BPh$_4$ ([1]BPh$_4$). On the benchtop 0.54 g (1.2 mmol) of [**1**]Cl in 200 mL of H$_2$O (distilled) was filtered through glass wool. Addition of a saturated solution of NaBPh$_4$, 0.44 g (1.3 mmol), caused immediate precipitation of [**1**]BPh$_4$, which was filtered and washed with H$_2$O and then Et$_2$O. The yield of light green-yellow solids was 0.63 g (0.82 mmol, 66% this step or 50% from Re(O)Cl$_3$(Me$_2$S)OPPh$_3$). Further purification, if needed, can be accomplished by adding CH$_3$CN, filtering out any solids, concentrating the resulting solution to the point of saturation, and adding Et$_2$O to precipitate the product, which is filtered and washed with additional Et$_2$O. ^{1}H NMR (CD$_3$CN): 2.51 (s, 3 H), 3.87 (s, 6 H) C*H*$_3$; 3.02 (m, 4 H), 3.32, 3.40, 3.57, 4.02 (m, 2 H each) CH*H*; 6.83 (t, 4 H), 6.99 (t, 8 H), 7.25 (m, 8 H) [B(C$_6$*H*$_5$)$_4$]$^-$. Anal. Calcd for C$_{33}$H$_{41}$N$_3$Cl$_2$BORe: C, 51.90; H, 5.42; N, 5.50. Found: C, 51.74; H, 5.45; N 5.48.

[Re(O)Cl$_2$(tacn)]Cl ([2]Cl).[16] ^{1}H NMR (D$_2$O): 2.46, 2.87, 3.57, 3.67, 3.79, 3.88 (m, 2 H each) CH*H*. ^{13}C{^{1}H} NMR (D$_2$O): 52.7, 51.5, 49.9 *C*H$_2$.

[Re(O)$_3$(tacn)]Cl ([3]Cl).[14] ^{1}H NMR (D$_2$O): 3.27, 3.43 (m, 6 H each) CH*H*. ^{13}C{^{1}H} NMR (D$_2$O): 49.1 *C*H$_2$.

[Re(O)$_3$(tacn)]BPh$_4$ ([3]BPh$_4$). ^{1}H NMR (CD$_3$CN): 3.19, 3.42 (m, 6 H each) CH*H*; 5.83 (br s, 3 H, NH), 6.83 (t, 4 H), 6.98 (t, 8 H), 7.25 (m, 8 H) [B(C$_6$*H*$_5$)$_4$]$^-$.

[Re(OPPh$_3$)Cl$_2$(Me$_3$tacn)]BPh$_4$ (4). To [**1**]BPh$_4$ (0.42 g, 0.55 mmol) and PPh$_3$ (0.18 g, 0.69 mmol) was added 50 mL of CH$_2$Cl$_2$ and the solution stirred for a day. Then it was concentrated by 50% and filtered away from brown solids (0.161 g). All but 2–3 mL of the CH$_2$Cl$_2$ was evaporated and then 15 mL of Et$_2$O added to precipitate orange-yellow solids, which were filtered and washed with Et$_2$O and the solvent was evaporated. This compound reacts with every solvent it is soluble in; all attempts to further purify it gave more impure material. The yield was 0.28 g (0.27 mmol, 50%) of **4**. ^{1}H NMR (CD$_2$Cl$_2$): 7.03 (s, 3 H), 7.92 (s, 6 H) C*H*$_3$; −1.39, 3.57, 5.80, 6.41, 9.22, 11.98 (m, 2 H each) CH*H*; 7.67 (t, 3 H), 7.83 (m, 6 H), 8.35 (m, 6 H) OP(C$_6$*H*$_5$)$_3$; 6.81 (t, 4 H), 6.91 (t, 8 H), 7.09 (m, 8 H) [B(C$_6$*H*$_5$)$_4$]$^-$. IR: 1579, 1119 s (P=O), 1060 s, 1048, 1032, 1000, 968, 863 w, 843, 790, 752, 737 s, 724 s, 708 s, 692 s. Anal. Calcd for C$_{51}$H$_{56}$N$_3$Cl$_2$OPBRe: C, 59.71; H, 5.50; N, 4.10. Found (average of five determinations): C, 58.37 (±0.17): H, 5.50 (±0.06); N, 4.25 (±0.15). FAB-MS: 706/704 (M$^+$), 428/426 (M − OPPh$_3^+$, 60% of M$^+$).

[Re(OPMe$_3$)Cl$_2$(Me$_3$tacn)]BPh$_4$ (5). To 75 mg (98 μmol) of [**1**]BPh$_4$ in 10 mL of CH$_3$CN was added PMe$_3$ (10–15 equiv) and the solution stirred for 15 min. Then it was evaporated to 2–3 mL and Et$_2$O added (10 mL) to precipitate solids which were filtered, washed with Et$_2$O, and evaporated in vacuo. The yield was 70 mg (83 μmol, 85%) light orange-pink solids. Further purification is accomplished by recrystallization from CH$_3$CN. ^{1}H NMR (CD$_2$Cl$_2$): 9.68 (s, 6 H), 7.32 (s, 3 H) C*H*$_3$; 0.4, 4.0, 5.3, 6.7, 9.6, 10.6 (m, 2 H each) CH*H*; 2.18 (d, 9 H, $^3J_{\mathrm{P-H}}$ = 6 Hz) OP(C*H*$_3$)$_3$; 6.80 (t, 4 H), 6.90 (t, 8 H), 7.05 (m, 8 H) [B(C$_6$*H*$_5$)$_4$]$^-$. IR: 1579, 1311, 1298, 1268 w, 1085 s (P=O), 1048, 1032, 1000 s, 970, 950, 886 w, 860, 816 w, 789, 734 s, 707 s. Anal. Calcd for **5**·CH$_3$CN: C$_{38}$H$_{53}$N$_4$Cl$_2$OPBRe: C, 51.82; H, 6.07; N, 6.36. Found: C, 51.98; H, 6.05; N, 6.41. FAB-MS: 520/518 (M$^+$).

[Re(CH$_3$CN)Cl$_2$(Me$_3$tacn)]BPh$_4$ (6). To [**1**]BPh$_4$ (0.15 g, 0.20 mmol) and PPh$_3$ (54 mg, 0.21 mmol) was added 10 mL of CH$_3$CN and the solution stirred for 6 days. Then it was filtered away from a small amount of dark solids and stripped in vacuo. About 10 mL of C$_6$H$_6$ was transferred in, the solids were triturated, filtered, and washed with C$_6$H$_6$, and the solvent removed to yield 88 mg (0.11 mmol, 57%) of light orange solids. ^{1}H NMR (acetone-d_6): 3.1 (s, 6 H), 19.4 (s, 3 H) C*H*$_3$; −9.7, −1.3, −0.8, 10.2, 18.4, 23.7 (m, 2 H each) CH*H*; 8.8 (s, 3 H) C*H*$_3$CN, 6.8 (t, 4 H), 6.9 (t, 8 H), 7.3 (m, 8 H) [B(C$_6$*H*$_5$)$_4$]$^-$. IR: 1578, 1290, 1184, 1154, 1120, 1047, 1030, 1000, 970, 918 w, 888 w, 844, 794, 744 s, 709 s, 613, 601. No ν(C≡N) was seen, in common with some other Re(III) nitrile complexes.[17] This compound appears to lose CH$_3$CN on standing and its analysis is consistent with loss of half an equivalent of CH$_3$CN. Anal. Calcd for C$_{34}$H$_{42.5}$N$_{3.5}$Cl$_2$BRe: C, 53.16; H, 5.58; N, 6.38. Found: C, 53.21; H, 5.76; N, 6.22. FAB-MS: 469/467 (M$^+$), 428/426 (M − CH$_3$CN$^+$, 70% of M$^+$).

[Re(O=CMe$_2$)Cl$_2$(Me$_3$tacn)]BPh$_4$ (7). To **4**, 0.10 g (98 μmol), was added 30 mL of acetone and the solution stirred for 3 days. Then it was concentrated to 5 mL and 20 mL of Et$_2$O added to precipitate orange-yellow solids, which were filtered, washed with Et$_2$O, and the solvent evaporated. The yield was 62 mg (77 μmol, 79%). ^{1}H NMR (CD$_3$CN): 0.2 (s, 6 H), 17.1 (s, 3 H) C*H*$_3$; −4.3, 2.7, 7.5, 10.8, 11.2, 15.3 (m, 2 H each) CH*H*; 17.4 (s, 6 H) (C*H*$_3$)$_2$CO; 6.8 (t, 4 H), 6.9 (t, 8 H), 7.3 (m, 8 H) [B(C$_6$*H*$_5$)$_4$]$^-$. IR: 1609 (C=O), 1579, 1289, 1255, 1155, 1119, 1047, 1032, 1000, 969, 886 w, 846 w, 790, 735 s, 707 s, 666.

[Re(py)Cl$_2$(Me$_3$tacn)]BPh$_4$ (8). To 19 mg (24 μmol) of **7** was added acetone (5 mL) and pyridine (20 equiv). The solution was stirred for 4 days and then evaporated to dryness, the minimum amount of acetone transferred in to dissolve the residue, the solution filtered, and Et$_2$O transferred in to crash out yellow solids. After filtration the solids were washed with Et$_2$O to yield 8 mg (9.7 μmol, 41%). ^{1}H NMR (CD$_3$CN): 4.97 (s, 6 H), 10.87 (s, 3 H) C*H*$_3$; −10.76, 0.25, 7.24, 10.40, 15.35, 20.53 (m, 2 H each), CH*H*; 1.88 (t, 2 H), 7.06 (d, 2 H), 16.63 (t, 1 H), NC$_5$*H*$_5$; 6.82 (t, 4 H), 6.98 (t, 8 H), 7.23 (m, 8 H) [B(C$_6$*H*$_5$)$_4$]$^-$. IR: 1580, 1290, 1268 w, 1148, 1119 w, 1053, 1032, 1001, 968, 863 w, 848 w, 791, 760, 746 s, 737 s, 711 s. FAB-MS: 507/505 (M$^+$), 428/426 (M − py$^+$, 55% of M$^+$).

Results

Synthesis of Rhenium(V) tacn Complexes. We have previously shown Re(O)Cl$_3$(Me$_2$S)OPPh$_3$ to be an excellent starting material for rhenium(V) oxo compounds.[11] It reacts rapidly with Me$_3$tacn in CH$_2$Cl$_2$ to precipitate [Re(O)Cl$_2$(Me$_3$tacn)]Cl, [**1**]Cl (eq 1). The product is soluble in water, MeOH, and CH$_3$CN and is

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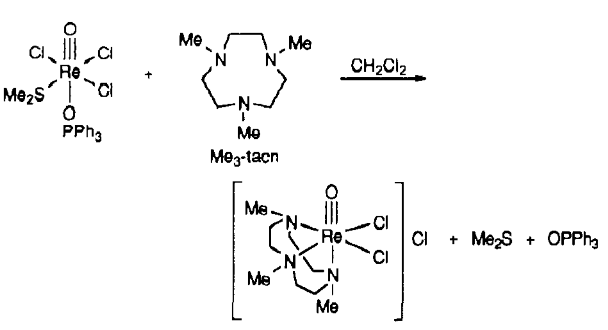
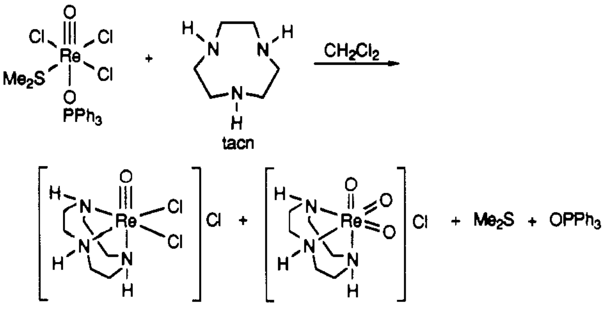


(1)

[1]Cl

purified by precipitation from water with NaBPh$_4$ to give [Re(O)Cl$_2$(Me$_3$tacn)]BPh$_4$ ([**1**]BPh$_4$). Complexes **1** are rare examples of cationic rhenium(V) monooxo complexes.[18] Compound [**1**]BPh$_4$ is an air-stable, light green-yellow solid, soluble in organic solvents such as THF, acetone, CH$_3$CN, Me$_2$SO, and CH$_2$Cl$_2$. The FAB mass spectrum shows a strong parent ion, [**1**]$^+$, at 444/442. It is diamagnetic, based on sharp unshifted ^{1}H and ^{13}C NMR spectra. The spectra indicate C_s symmetry for the cation with Me$_3$tacn coordinated facially, as is typical. The rhenium oxo stretching frequency of 979 cm^{-1} (ν(Re=^{18}O) = 933 cm^{-1}) is within the normal range for octahedral rhenium monooxo complexes.[19] Cyclic voltammetry of [**1**]BPh$_4$ in THF gives an apparently reversible reduction at $E° = -0.70$ V vs NHE (referenced to internal ferrocene at $E° = 0.40$ V). However, attempts to isolate the reduced species, for instance using cobaltocene or sodium naphthalenide as reductants, yielded intractable materials which did not exhibit the same cyclic voltammetric wave.

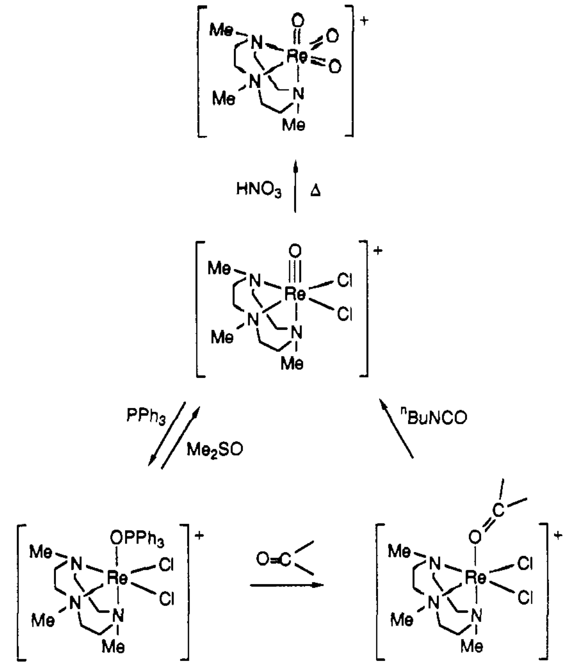
In contrast to reaction 1, addition of the nonmethylated tacn to Re(O)Cl$_3$(Me$_2$S)(OPPh$_3$) in CH$_2$Cl$_2$ results in formation of substantial amounts of both [Re(O)Cl$_2$(tacn)]Cl, [**2**]Cl, and Re(O)$_3$(tacn)]Cl, [**3**]Cl (eq 2). Compound [**3**]Cl has been previously prepared by refluxing rhenium(I) tacn compounds in aqueous H$_2$O$_2$.[14] Complex [**2**]Cl was reported[16] while this work was in progress,[7] prepared by addition of tacn to [Re(O)Cl$_4$]NBu$_4$ or Re(O)Cl$_3$(PPh$_3$)$_2$. Our attempts to prepare [**2**]Cl by these routes have also led to a mixture of **2** and **3**, and/or paramagnetic product(s); we have been unable to obtain pure samples of **2**. The formation of the rhenium(VII) complex **3** in reaction 2 is surprising, and we have not been able to identify the source of the oxygen or of the oxidizing equivalents. While Re(O)Cl$_3$(Me$_2$S)(OPPh$_3$), Re(O)Cl$_3$(PPh$_3$)$_2$, and [Re(O)Cl$_4$]NBu$_4$ are all isolated from water, spectroscopically the isolated materials do not appear to contain water, certainly not enough to account for the 50% yield of **3**. The ratio of **2**:**3** obtained varies little between reactions performed under strictly anaerobic conditions (which we have used to handle very air-sensitive materials[20]) versus reactions performed under 700 Torr of pure O$_2$ or in the presence of 3 equiv of water. A D$_2$O solution of the **2**/**3** mixture is essentially unchanged after 3 days of exposure to atmospheric oxygen. We obtain similar (or poorer) results in a variety of organic solvents; similar results are also obtained with tacn we have prepared and with that purchased from Aldrich.



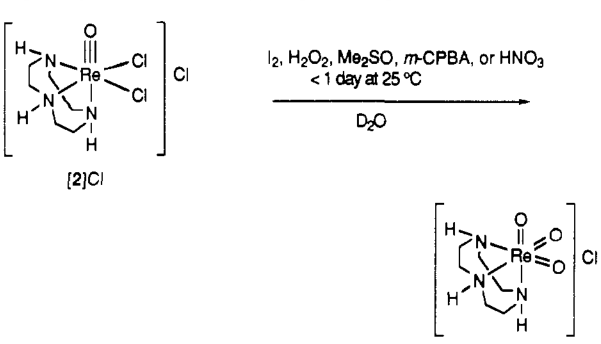
(2)

[2]Cl [3]Cl

Scheme I. Selected Oxygen Atom Transfer Reactions of Rhenium Me$_3$tacn Compounds



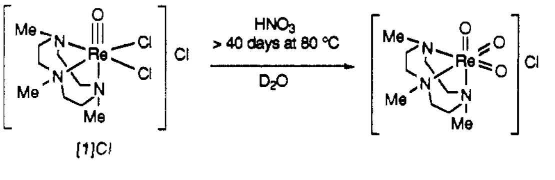
Interconversion of Rhenium(V) and Rhenium(VII) Oxo Complexes. The mixture of **2** and **3** isolated in reaction 2 is converted to a solution of solely **3** by the mild oxidizing agents I$_2$, *m*-CPBA, and Me$_2$SO within a day at ambient temperatures in deoxygenated D$_2$O (eq 3). Oxidation by Me$_2$SO in D$_2$O is faster in acid solution than in a sodium carbonate buffer (pH ≈ 10). Oxygen is a much less efficient oxidant, with the **2**/**3** mixture in D$_2$O requiring a week under an atmosphere of O$_2$ to convert to **3**.



(3)

[2]Cl [3]Cl

Surprisingly, compounds **1**, containing the Me$_3$tacn ligand, are not oxidized by O$_2$, I$_2$, *m*-CPBA, Me$_2$SO, or even H$_2$O$_2$. Oxidation of [**1**]Cl to the known trioxo complex[16] [Re(O)$_3$(Me$_3$tacn)]$^+$ has been observed only under forcing conditions: weeks in aqueous nitric acid at 80 °C (eq 4; Scheme I).



(4)

[1]Cl

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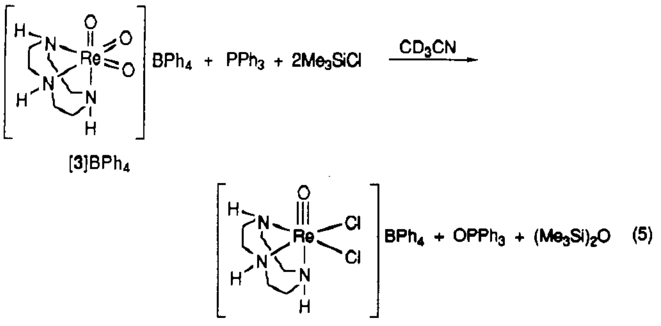
[18] (a) [ReOX$_2$(tacn)]X (X = Cl, Br, I), ref 16. (b) [ReOX$_2$(PPh$_3$)$_2$]ReO$_4$ (X = Cl, Br, I), Freni, M.; Guisto, D.; Romiti, P.; Minghetti, G. *Gazz. Chim. Ital.* **1969**, *99*, 286–289. (c) [ReOCl$_2$(tu)$_2$(H$_2$O)]Cl (tu = thiourea, H$_2$NCSNH$_2$), Lis, T. *Acta Crystallogr., Sect. B* **1976**, *32*, 2707–2709. (d) ReOCl(RSal) (RSal = OC$_6$H$_4$C(H)=NR and R = Me, Ph), Seeber, R.; Mazzocchin, G. A.; Mazzi, U.; Refosco, F.; Tisato, F. *Polyhedron* **1986**, *5*, 1975–1982. (e) [ReO(cyclam)(OH$_2$)]Cl$_3$ (cyclam = 1,4,8,11-tetraazacyclotetradecane), Parker, D.; Roy, P. S. *Inorg. Chim. Acta* **1988**, *148*, 251–253.

[19] (a) Rouchias, G. *Chem. Rev.* **1974**, *74*, 531–566. (b) See also ref 3, p 116.

[20] Spaltenstein, E.; Conry, R. R.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 8741–8742.

The rhenium(VII) compound [Re(O)$_3$(tacn)]BPh$_4$ ([**3**]BPh$_4$) transfers one oxygen to PPh$_3$ (even in the presence of excess PPh$_3$).[21] The intense violet rhenium product, which is likely to be [(tacn)$_2$Re$_2$(O)$_2$(μ-O)$_2$]$^{2+}$,[22] is reoxidized to [**3**]BPh$_4$ by O$_2$. Reduction of [**3**]BPh$_4$ with PPh$_3$ in the presence of excess Me$_3$SiCl yields [**2**]BPh$_4$, OPPh$_3$, and (Me$_3$Si)$_2$O (eq 5); Me$_3$SiCl alone does not react wtih [**3**]BPh$_4$. The weaker oxygen atom acceptors



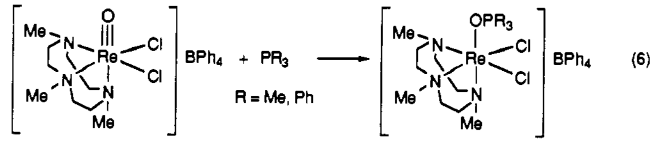
[**3**]BPh$_4$

(5)

[**2**]BPh$_4$

^{n}BuNC, AsPh$_3$, Me$_2$SO, and Me$_2$S do not reduce [**3**]BPh$_4$, although it does react with ^{n}BuNC in the presence of Me$_3$SiCl.[23] The methylated derivative [Re(O)$_3$(Me$_3$tacn)]BPh$_4$ is also reduced by PPh$_3$ and Me$_3$SiCl to give OPPh$_3$, but significant amounts of **1** are not observed.

Interconversion of Rhenium(V) and Rhenium(III) Complexes, Syntheses of [Re(L)Cl$_2$(Me$_3$tacn)]BPh$_4$. The rhenium(V) monooxo complex [**1**]BPh$_4$ transfers an oxygen atom to phosphines to form rhenium(III) phosphine oxide compounds (eq 6; Scheme I). With PPh$_3$, formation of orange-yellow **4** is complete in a day; using PMe$_3$, light pink **5** is formed within minutes. The weaker oxygen atom acceptors ^{n}BuNC, AsPh$_3$, Me$_2$SO, H$_2$, and Me$_2$S are unreactive with [**1**]BPh$_4$ over 2 weeks at ambient temperatures. With AsPh$_3$, no reaction was observed over 2 weeks at 80 °C.



(6)

[**1**]BPh$_4$

4 R=Ph
5 R=Me

The OPPh$_3$ ligand in **4** is easily replaced by acetonitrile or acetone (using the ligand as the solvent) and by pyridine or OPMe$_3$ (eq 7). In CH$_2$Cl$_2$, **4** decomposes completely over a period of a week to uncharacterized paramagnetic compound(s).[24] The acetone ligand in **7** is also labile, exchanging readily for pyridine or for CD$_3$CN or acetone-d_6 solvent. On the other hand, the OPMe$_3$ and pyridine ligands in **5** and **8** do not exchange with any of these ligands; **5** is stable in CH$_2$Cl$_2$.

$$\underset{\mathbf{4}}{[\mathrm{Re(OPPh_3)Cl_2(Me_3tacn)]BPh_4}} + \mathrm{L} \rightarrow [\mathrm{Re(L)Cl_2(Me_3tacn)]BPh_4} + \mathrm{OPPh_3} \quad (7)$$

$$\mathrm{L} = \mathrm{OPMe_3}\ (\mathbf{5}),\ \mathrm{CH_3CN}\ (\mathbf{6}),\ \mathrm{O{=}CMe_2}\ (\mathbf{7}),\ \mathrm{py}\ (\mathbf{8})$$

All of the rhenium(III) complexes are paramagnetic but exhibit sharp, shifted ^{1}H NMR spectra. This is a common (and useful) property of low-spin d^4 octahedral complexes of rhenium, osmium, tungsten, and other metals.[25] The spectra are consistent with C_s symmetry: for instance, **6** exhibits six methylene resonances for the Me$_3$tacn ligand, with chemical shifts from −10 to 24 ppm. Compounds **4**, **5**, **6**, and **8** all show parent ions M$^+$ in the FAB mass spectrum, but meaningful data could not be obtained for **7** because of its high air sensitivity. Strong IR bands at 1119 and 1085 cm^{-1} are assigned as P=O stretches in **4** and **5**.[26] Complex **7** has a C=O stretching band at 1609 cm^{-1}, indicating that the acetone is bound to rhenium in an η^1 fashion.[27]

The labile complexes **4** and **7** can be oxidized back to the rhenium(V) oxo complex **1** by oxygen atom transfer (e.g. eq 8; Scheme I); stoichiometric Me$_2$S is observed by ^{1}H NMR.

$$\underset{\mathbf{4},\,\mathbf{7}}{[\mathrm{Re(L)Cl_2(Me_3tacn)]BPh_4}} + \mathrm{Me_2SO} \rightarrow \underset{\mathbf{1}}{[\mathrm{Re(O)Cl_2(Me_3tacn)]BPh_4}} + \mathrm{Me_2S} + \mathrm{L} \quad (8)$$

However, compounds **5** and **6** are stable in Me$_2$SO-d_6 for over a month, presumably because the OPMe$_3$ and CH$_3$CN ligands are not labile. The chemistry of **4** is difficult to study because it reacts with the solvents it is soluble in. In CD$_2$Cl$_2$ (the best choice), **4** is oxidized by OAsPh$_3$, pyridine *N*-oxide, and Me$_3$NO to form small amounts of **1** and AsPh$_3$, py, or Me$_3$N competitively with decomposition. With N$_2$O, ^{t}BuOOH, H$_2$O, O$_2$, and Me$_2$SO$_2$, oxygen atom transfer is not observed before decomposition is complete.

The kinetics of two reactions of **4** have been studied: its oxidation to **1** in Me$_2$SO-d_6 and ligand substitution to form **6** in CD$_3$CN. Both follow first-order kinetics. On the basis of rate constants determined over the temperature range 21–65 °C, ΔH^* and ΔS^* were determined to be 26 ± 3 kcal/mol and 4 ± 9 eu for the oxidation of **4** and 24 ± 3 kcal/mol and −2 ± 9 eu for ligand substitution. The rate of conversion of **4** to **1** is essentially the same in Me$_2$SO-d_6 and 1:3 Me$_2$SO-d_6:CD$_2$Cl$_2$. In fact essentially all of the reactions of **4** occur at qualitatively the same rate, with a half-life of about a day at ambient temperatures.[28]

The chemistry of the acetone complex **7** can be explored more broadly than that of **4** because it is stable in acetone solution. Compound **7** is cleanly oxidized to **1** (eq 8) by Me$_2$SO, pyridine *N*-oxide, OAsPh$_3$, O$_2$, ^{n}BuNCO, ethylene oxide, and N$_2$O with the formation of 1 equiv of the reduced substrate (Me$_2$S, py, AsPh$_3$, etc.). H$_2$O and Me$_2$SO$_2$ are, however, unreactive at ambient temperatures (and upon heating yield brown insolubles and/or paramagnetic products). The oxidation of **7** to **1** by the rhenium(VII) tacn complex [**3**]BPh$_4$ is not facile, with only a small amount of **1** visible by NMR after 3 weeks; the reduction product of **3** has not been identified. Unlike the chemistry of **4**, the rates of reactions of **7** are dependent on the identity and the concentration of the reagent. For instance, the half-life for oxidation by Me$_2$SO is days with a 1–2 equiv but only hours with a large excess. Under comparable conditions, more rapid oxidation is observed with OAsPh$_3$ than with Me$_2$SO.

Discussion

The oxidations of the rhenium(III) complexes **4** and **7** are apparently[2] the first examples of simple oxygen atom transfer to rhenium.[29] Oxidation of rhenium(III) appears to require an open

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(21) This contrasts with the reported lack of reaction of PPh$_3$ with [Re(O)$_3$(tacn)]Cl.[16]

(22) (a) [(tacn)$_2$Re$_2$(O)$_2$(μ-O)$_2$]$^{2+}$ has been recently prepared by Wieghardt: Böhm, V. G.; Wieghardt, K.; Nuber, B.; Weiss, J. *Angew. Chem.* in press. (b) This reaction is analogous to the reduction of Cp*Re(O)$_3$ by PPh$_3$, yielding Cp$_2$*Re$_2$(O)$_2$(μ-O)$_2$: Herrmann, W. A.; Serrano, R.; Küsthardt, U.; Ziegler, M. L.; Guggolz, E.; Zahn, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 515–517; Herrmann, W. A.; Herdtweck, E.; Flöel, M.; Kulpe, J.; Küsthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165–1182.

(23) The reduction of [**3**]BPh$_4$ by ^{n}BuNC and Me$_3$SiCl is complicated by the reaction of Me$_3$SiCl with the ^{n}BuNCO formed. What is observed by NMR is the product of the reaction of ^{n}BuNCO with Me$_3$SiCl. It is possible that this further reaction provides the driving force for reduction.

(24) Other Re(III) compounds such as ReCl$_3$(CH$_3$CN)(PPh$_3$)$_2$ are readily oxidized by halocarbons to give Re(IV) complexes.[17b]

(25) (a) Chatt, J.; Leigh, G. J.; Mingos, D. M. P. *J. Chem. Soc. A* **1969**, 1674–1680. (b) Randall, E. W.; Shaw, D. *J. Chem. Soc. A* **1969**, 2867–2872. (c) Rossi, R.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R.; Toniolo, L. *J. Chem. Soc., Dalton Trans* **1982**, 1949–1952. (d) Randall, E. W.; Shaw, D. *Mol. Phys.* **1965**, *10*, 41.

(26) Free OPPh$_3$ 1190 cm^{-1}; OPMe$_3$ 1170 cm^{-1}; the usual shift upon coordination is about 30–150 cm^{-1} to lower frequency. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; 4th ed.; Wiley: New York, 1986.

(27) For example the ν(C=O) of the η^1-acetone in [Cp$_2$V(O=CMe$_2$)]$^+$ occurs at 1660 cm^{-1} (Gambarotta, S.; Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 1173–1178) while the ν(C=O) of the η^2-acetone in WCl$_2$(O=CMe$_2$)$_2$(PMePh$_2$)$_2$ appears at 1230 cm^{-1}, ref 35.

(28) Decomposition of **4b** in CD$_2$Cl$_2$ is a factor of 2 or 3 slower.

Table I

oxygen atom transfer couple		bond strength[a]	direction of reaction	
			Re(V) → Re(III)	Re(III) → Re(V)
Me_3PO	Me_3P	138[b]	✓	
Ph_3PO	Ph_3P	127	✓	
H_2O	H_2	118	no reaction	
Me_2SO_2	Me_2SO	112	no reaction	
^nBuNCO	^nBuNC	110[c]		✓
Ph_3AsO	Ph_3As	103[d]		✓
CH_3OH	CH_4	90	no reaction	
Me_2SO	Me_2S	87		✓
$\overline{CH_2CH_2O}$	CH_2CH_2	85		✓
py-O	py	72[e]		✓
N_2O	N_2	40		✓

[a] Bond strengths from ref 2 or as otherwise noted. [b] Assumed to be the same as for $^nPr_3PO$: Chernick, C. L.; Pedley, J. B.; Skinner, H. A. *J. Chem. Soc.* **1956**, 1401. [c] Assumed to be the same as for MeNCO, ref 2. [d] Reference 38. [e] py-O = pyridine *N*-oxide; py = pyridine. Shaofeng, L.; Pilcher, G. *J. Chem. Thermodyn.* **1988**, *20*, 463.

coordination site, as the compounds that can be oxidized, **4** and **7**, are those with labile ligands while **5**, **6**, and **8** are inert to both ligand substitution and oxidation. In the reactions of **4**, loss of $OPPh_3$ appears to be the rate-determining step: the reactions are first order, the activation parameters for substitution and oxidation are identical (within experimental error), and oxidation proceeds at essentially the same rate in neat Me_2SO and 1:3 Me_2SO/CH_2Cl_2. This implies that in the oxygen atom transfer reactions the coordinatively unsaturated intermediate (A in eq 9) is rapidly trapped by the oxidant (e.g. Me_2SO). The fact that an adduct such as B is not observed indicates tht the actual oxygen atom transfer step must be facile.

$$\underset{\mathbf{4}}{[Re(OPPh_3)Cl_2(Me_3tacn)]^+} \xrightarrow[-OPPh_3]{} \underset{\mathrm{A}}{[ReCl_2(Me_3\text{-}tacn)]^+} \xrightarrow[+OX]{fast} \underset{\mathrm{B}}{[Re(OX)Cl_2(Me_3tacn)]^+} \rightarrow \underset{\mathbf{1}}{[Re(O)Cl_2(Me_3tacn)]^+} + X \quad (9)$$

The reduction of $[\mathbf{1}]BPh_4$ by phosphines is one of the most facile reported phosphine reductions of rhenium(V) oxo complexes.[11,17a,19a,30] Deoxygenation of rhenium(V) does not appear to require an open coordination site, in contrast to the oxidation of rhenium(III). Rather, phosphine appears to attack directly at the oxo ligand to form a phosphine oxide complex, as has been suggested in other systems.[31] This is simply the reverse of the last step in eq 9.

The oxygen atom transfer reactions that interconvert rhenium(V) and rhenium(III) in general follow a consistent pattern: an oxygen atom is transferred from rhenium to substrate when the X–O bond strength is greater than 127 kcal/mol (X = PPh_3 or PMe_3) and reactions proceed in the reverse direction when the bond strength is less than 110 kcal/mol (X = ^nBuNC, $AsPh_3$, Me_2S, N_2), as summarized in Table I. This is consistent with the thermodynamic oxygen atom transfer reactivity scale developed by Holm.[2] Reagents of intermediate oxygen atom donor strength, Me_2SO_2 and H_2O, have not been observed to oxidize Re(III) or reduce Re(V). An exception to this pattern is the lack of reaction of methanol, an unusual substrate for oxygen atom transfer (although we have observed deoxygenation of methanol by $WCl_2(PMePh_2)_4$[32]). The inertness of compounds **5**, **6**, and **8** to oxidation even by potent oxygen atom donors is due to the kinetic barrier to ligand loss, as discussed above.

Scheme II. Thermochemical Cycles Used To Estimate the Rhenium–Oxo Bond Strength in $[Re(O)Cl_2(Me_3tacn)]^+$

A)

$$\begin{tikzcd}
{[Re(O)Cl_2(Me_3\text{-}tacn)]^+ + PPh_3} \arrow[r, "\Delta G < 0"] \arrow[d, "D(Re{\equiv}O)"'] & {[Re(OPPh_3)Cl_2(Me_3\text{-}tacn)]^+} \\
{[ReCl_2(Me_3\text{-}tacn)]^+ + [O] + PPh_3} \arrow[r, "-\Delta H(P{=}O)"] & {[ReCl_2(Me_3\text{-}tacn)]^+ + OPPh_3} \arrow[u, "-\Delta H(Re\text{-}OPPh_3)"]
\end{tikzcd}$$

$$D(Re{\equiv}O) - \Delta H(Re\text{-}OPPh_3) - \Delta H(P{=}O) \equiv \Delta G$$

$$D(Re{\equiv}O) - 22\ kcal/mol - 127\ kcal/mol < 0$$

$$\boxed{D(Re{\equiv}O) < 149\ kcal/mole}$$

B)

$$\begin{tikzcd}
{[Re(O{=}CMe_2)Cl_2(Me_3\text{-}tacn)]^+ + {}^nBuNCO} \arrow[r, "\Delta G < 0"] \arrow[d, "\Delta H(Re\text{-}O{=}CMe_2)"'] & {[Re(O)Cl_2(Me_3\text{-}tacn)]^+ + O{=}CMe_2 + {}^nBuNC} \\
{[ReCl_2(Me_3\text{-}tacn)]^+ + O{=}CMe_2 + {}^nBuNCO} \arrow[r, "\Delta H(C{=}O)"] & {[ReCl_2(Me_3\text{-}tacn)]^+ + O{=}CMe_2 + {}^nBuNC + [O]} \arrow[u, "-D(Re{\equiv}O)"]
\end{tikzcd}$$

$$\Delta H(Re\text{-}O{=}CMe_2) + \Delta H(C{=}O) - D(Re{\equiv}O) \equiv \Delta G$$

$$22\ kcal/mol + 110\ kcal/mol - D(Re{\equiv}O) < 0$$

$$\boxed{D(Re{\equiv}O) > 132\ kcal/mole}$$

By use of simple thermochemical cycles (Scheme II), the observed reactions can provide an estimate of the rhenium–oxo bond strength in **1**. Cycle A dissects the reaction of **1** with PPh_3 into three parts, the Re≡O, Ph_3P=O, and Re–$OPPh_3$ bond strengths. The Re–$OPPh_3$ bond strength is roughly 22 kcal/mol, based on the kinetic barrier to dissociation of $OPPh_3$ from **4** (25 kcal/mol) and a typical barrier to recoordination of 3 kcal/mol.[33] With $D(Ph_3P{=}O)$ = 127 kcal/mol, $D(Re{\equiv}O)$ is <149 kcal/mol. Similar arguments based on the oxidation of **7** by ^nBuNCO (cycle B) suggest that $D(Re{\equiv}O)$ >132 kcal/mol. The rhenium–acetone bond strength needed in cycle B is taken to be larger than the Re–$OPPh_3$ bond strength since acetone displaces $OPPh_3$ (eq 3). *Thus 132 kcal/mol < D(Re≡O) < 149 kcal/mol, or D(Re≡O) = 141 ± 9 kcal/mol.* It should be noted that these calculations ignore entropic contributions to ΔG; since there are more particles on the Re(V) side versus the Re(III) side of Scheme II, the inclusion of entropy should give a lower estimate of the bond strength.[34]

The Re≡O bond strength of roughly 141 kcal/mol in **1** is probably weaker than the W≡O bond in $W(O)Cl_2(PMePh_2)_3$, which we have estimated to be >138 kcal/mol by a similar cycle.[35] This is consistent with the observation that **1** will transfer its oxygen to phosphines but the tungsten compound will not. These approximate oxo bond strengths derived by thermochemical cycles are close to known gas-phase values: the average bond strengths for WO_3 and OsO_4 are 150 and 127 kcal/mol.[36] These values

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(29) Oxidation of $ReCl_3(CH_3CN)(PPh_3)_2$ with O_2 yields $Re(O)Cl_3(OPPh_3)PPh_3$,[17a] which could be viewed as an oxygen atom transfer reaction.

(30) (a) Abrams, M. J.; Davison, A.; Jones, A. G *Inorg. Chim. Acta* **1984**, *82*, 125–128. (b) Duatti, A.; Rossi, R.; Marchi, A.; Magon, L.; Roncari, E.; Mazzi, U. *Transition Met. Chem.* **1981**, *6*, 360–364. (c) Rowbottom, J. F.; Wilkinson, G.; *J. Chem. Soc., Dalton Trans.* **1972**, 826–830. (d) Chatt, J.; Leigh, G. J.; Mingos, D. M. P.; Paske, R. J. *J. Chem. Soc. A* **1968**, 2636–2641. (e) Sanders, J. R. *J. Chem. Soc. A* **1971**, 2991–2995. (Parts c–e and ref 17a are all of $ReOX_3(PPh_3)_2$ with differing X and PR_3.) (f) Gunz, H. P.; Leigh, G. J. *J. Chem. Soc. A* **1971**, 2229–2233.

(31) Newton, W. E.; Watt, G. D.; McDonald, J. W. In *Proceedings of the 3rd International Conference on the Chemistry and Uses of Molybdenum*; Barry, H. F., Mitchell, P. C. H., Eds.; Climax Molybdenum: Ann Arbor, MI, 1979; p 259. Topich, J.; Lyon, J. T., III *Polyhedron* **1984**, *3*, 55–60 and 61–65. Reynolds, M. S.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 3057–3062, and ref 2. The observation that external phosphine is oxidized by $[Ru(O)(PR_3)(bipy)_2]^{2+}$ but not the coordinated phosphine indicates direct attack of phosphine at oxygen rather than initial coordination to the metal center: Marmion, M. E.; Takeuchi, K. J. *J. Am. Chem. Soc.* **1986**, *108*, 510–511; **1988**, *110*, 1472–1480.

(32) Jang, S.; Atagi, L. M.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 6413.

(33) (a) Halpern, J. *Polyhedron* **1988**, *7*, 1483–1490. (b) Koenig, T. W.; Hay, B. P.; Finke, R. G. *Polyhedron* **1988**, *7*, 1499–1516.

(34) The entropic contribution to ΔG can be very crudely estimated to be on the order of 10 kcal/mol, using values in Fersht, A. *Enzyme Structure and Mechanism*; Freeman: New York, 1985; p 61.

(35) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298–2308.

are all substantially larger than the calorimetrically determined value for the first Mo=O bond dissociation energy in $Mo(O)_2(Et_2dtc)_2$ of 96 ± 3 kcal/mol.[37] The molybdenum value seems low, in comparison with the average D(Mo=O) in MoO_3 (g) of 141 kcal/mol[36] and given that $Mo(O)(Et_2dtc)_2$ will quantitatively deoxygenate Ph_3AsO for which $D(As{=}O) = 103 \pm 7$.[38,39]

It is interesting to note that Me_2SO will oxidize both Re(III) (7) and Re(V) ([**2**]Cl) and that PPh_3 will reduce both Re(VII) ([**3**]BPh_4) and Re(V) ([**1**]BPh_4). This contrasts with molybdenum oxo systems such as $Mo(O)_2dtc_2$ in which PPh_3 will reduce Mo(VI) but not Mo(IV).[2] Similarly, $WCl_2(PMePh_2)_4$ appears to be a much more avid oxygen atom acceptor than $W(O)Cl_2(PMePh_2)_3$.[40] Reaction 3 cannot, however, be used to estimate a bond strength in the rhenium(VII) species because [**2**]Cl → [**3**]Cl requires both an oxygen atom and an oxide ion. Similarly, [**3**]Cl → [**2**]Cl requires both an oxygen atom acceptor and a Lewis or protic acid to accept an oxide ion. (Of course, the rhenium itself can act as the acid with the formation of dimers or clusters.) In essence, the redox stoichiometry (two electron change) does not match the oxo stoichiometry (monooxo $\rightleftharpoons$ trioxo). This may be the reason why [**3**]Cl is reduced by ^nBuNC only in the presence of Me_3SiCl as a Lewis acid.[23] The noncomplementarity of oxygen and electron stoichiometry is a common occurrence in oxo chemistry and is a reason for the often complex mechanisms observed.[41]

The oxidation of [**1**]Cl to Re(VII) by aqueous nitric acid requires more than 40 days at 80 °C, while [**2**]Cl is oxidized within an hour at 25 °C. This dramatic difference in the ease of oxidation is difficult to understand because the metal complexes differ only in that **1** has the Me_3tacn ligand and **2** has tacn. The driving force for oxidation should be similar for the two compounds, indicating a kinetic effect. The oxidation of [**1**]Cl is accelerated by the presence of Ag^+, suggesting chloride dissociation, although the faster rate for the complex of the smaller ligand (tacn vs Me_3tacn) is not typical of dissociative processes. A conjugate base mechanism involving deprotonation of an N–H proton (common in cobalt(III) chemistry[42]) is ruled out by the observation that the oxidation of [**2**]Cl is faster in acid than in base. The tacn N–H groups might enhance the rate by directing the solvent water to assist in Cl^- dissociation, as suggested in other cobalt ammine chemistry.[42] It is also possible that oxygen atom transfer to [**2**]Cl is associative in character, which is prevented by the larger Me_3tacn ligand in [**1**]Cl. Further studies are in progress to probe the influence of ancillary ligands on the kinetics and thermodynamics of oxygen atom transfer.

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(36) Glidewell, C. *Inorg. Chim. Acta* **1977**, *24*, 149–157. E.g. for WO_3 (in kcal/mol): $D(O_2W{-}O) = 143$; $D(OW{-}O) = 147$; $D(W{-}O) = 161$. The average binding energy of an oxygen atom in Re_2O_7 is 150 kcal/mol, calculated by dividing $\Delta H°$ for $Re_2O_7(g) \rightarrow 2Re(g) + 7O(g)$ by seven, but this is not a meaningful value because there are six multiple bonds and two single bonds in Re_2O_7.

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

(38) (a) Barnes, D. S.; Burkinshaw, P. M.; Mortimer, C. T. *Thermochim. Acta* **1988**, *131*, 107–113. (b) D(As–O) has also been determined to be 106 ± 6 by Tsvetkov, V. G.; Aleksandrov, Y. A.; Glushakova, V. N.; Skorodumova, N. A., Kol'yakova, G. M. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1980**, *50*, 198–201.

(39) The discrepancy between D(Mo=O) and D(As=O) has been noted by Holm,[2] who suggested that the arsenic–oxygen bond strength might be in error. However, the second determination of $D(Ph_3As{=}O)^{38a}$ and the gas phase value for MoO_3 suggest that the actual molybdenum value may lie toward the high end of the reported error range.

(40) Su, F.-M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Polyhedron* **1989**, *8*, 1261–1277. See also ref 35.

(41) Beattie, J. K.; Haight, G. P., Jr. *Prog. Inorg. Chem.* **1972**, *17*, 93–145.

(42) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967; pp 134–135 (solvent assisted dissociation); and pp 415–416 (conjugate base mechanism).

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^1H NOE and Ligand Field Studies of Copper–Cobalt Superoxide Dismutase with Anions

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The ^1H NOE's on bovine erythrocyte $Cu(II)_2Co(II)_2$ superoxide dismutase in the presence of saturating amounts of azide have been measured and compared with those in the absence of azide. The interproton distances involving the histidines coordinated to copper(II) are quite similar. Efforts are made to minimize the errors in distances in order to obtain a reliable picture of the reciprocal positions of the above histidines. The conclusion that the histidine positions do not change upon anion binding is extended to the cases of CN^-, NCO^-, NCS^-, and F^-. Within this frame the essential disappearance of the hyperfine coupling between the protons of histidine-48 and the unpaired electron on copper(II) upon azide binding and the large variations of circular dichroism spectra are accounted for on the basis of an angular overlap treatment. The same model is used to discuss the spectral variations occurring in the cyanide and cyanate derivatives. It is proposed that the copper–nitrogen (His-48) distance increases upon anion binding as a result of a movement of the copper ion. The fluoride and thiocyanate derivatives are included in the present general model.

Introduction

Steady-state ^1H nuclear Overhauser effects (NOE) in paramagnetic metalloproteins can nowdays be measured,[1-3] and they potentially provide structural information in solution. We have measured ^1H NOE's on copper–cobalt superoxide dismutase (Cu_2Co_2SOD) and successfully related the X-ray interproton distances with those obtained from ^1H NMR spectroscopy.[4] The main result was the full assignment of the hyperfine-shifted signals in the ^1H NMR spectra, which, when performed through the analysis of T_1 and T_2 data,[5] could lead to some misassignment.

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