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Synthesis and Characterization of Rhenium(VI) *cis*-Dioxo Complexes and Examination of Their Redox Chemistry

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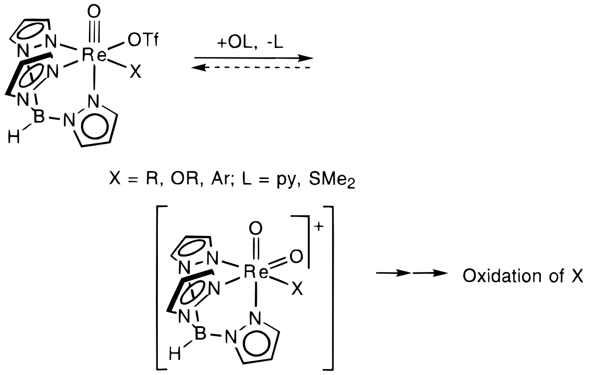
Reaction of rhenium(V)−oxo−halo−triflate complexes $(HB(pz)_3)ReO(X)OTf$ (**1**, X = Cl, Br, I) with 1 equiv of pyridine *N*-oxide forms rare d^1 rhenium(VI) *cis*-dioxo compounds $(HB(pz)_3)ReO_2X$ (**2**, X = Cl, Br, I). This reaction likely occurs by initial formation of the d^0 rhenium(VII) dioxo cation $(HB(pz)_3)ReO_2X^+$ by oxygen atom transfer, followed by a rapid one electron reduction. The chloride derivative **2a** has been characterized by an X-ray crystal structure. The d^1 dioxo compounds are fairly stable, disproportionating slowly to $(HB(pz)_3)ReO_3$ and $(HB(pz)_3)ReOX_2$. Electrochemical oxidations of $(HB(pz)_3)ReO_2X$ to Re(VII) cations are reversible and are at remarkably high potentials ($E_{1/2} = 0.93$ V vs $Cp_2Fe^{+/0}$ in acetonitrile for **2a**). When Me_2SO is used as the oxidant instead of pyridine *N*-oxide, the Re(V) adducts $[(HB(pz)_3)ReO(X)(OSMe_2)][OTf]$ (**5**) are formed by triflate displacement. These complexes reversibly lose SMe_2 (for **5a**, $k = 3.3(4) \times 10^{-6}$ s^{-1} at 297 K in CD_2Cl_2), as shown by isotope exchange experiments. The intermediate Re(VII) cations $(HB(pz)_3)ReO_2X^+$ oxidize Me_2S much faster than Me_2SO, indicating that they are highly electrophilic oxygen atom transfer reagents. Complexes **2**, however, are relatively unreactive materials. Crystallographic data for **2a**: $C_9H_{10}BClN_6O_2Re$; monoclinic, *Cc*; $a = 14.716(3)$, $b = 7.651(2)$, $c = 13.232(3)$ Å; $\beta = 110.61(3)$°; $Z = 4$.

Introduction

The chemistry of oxidizing metal centers is attracting increasing interest because of the importance of industrial and biochemical oxidation reactions.[1] Oxygen atom transfer is a popular method for the generation of reactive oxidants.[2] In the oxidations of the alkyl, alkoxide,[3] and aryl[4] complexes $(HB(pz)_3)ReO(X)OTf$ by oxygen atom donors, the active oxidants are d^0 rhenium(VII) dioxo cations $[(HB(pz)_3)ReO_2X]^+$ (eq 1; X = R, OR, Ar; $HB(pz)_3$ = hydrotris(1-pyrazolyl)borate; OTf = triflate, OSO_2CF_3). Such species have not yet been isolated, and direct observation has only been possible by low-temperature NMR for X = Ph.[4] Indirect evidence for these species comes from the rapid and reversible loss of Me_2S from the Me_2SO adducts $[(HB(pz)_3)ReO(X)(OSMe_2)]OTf$ ($k = 2.9(4)$ s^{-1} and $\Delta G° = +6.5$ kcal/mol at 25 °C for X = Ph[4]).

This report describes our efforts to prepare $[(HB(pz)_3)ReO_2(X)][OTf]$ complexes where the ancillary ligand X is a halide and not easily oxidized. A related d^0 rhenium bis(imido) cation, $[\{HB(3,5\text{-}Me_2pz)_3\}Re(N^tBu)_2Cl][PF_6]$, was reported in 1994 by Sundermeyer *et al.*[5] The oxidation of $(HB(pz)_3)ReO(Cl)OTf$ (**1a**)[6] with pyridine *N*-oxide (pyO), however, yields the d^1 complex $(HB(pz)_3)ReO_2Cl$ (**2a**) rather than the expected d^0 cation. The involvement of the d^0 cation in this and other reactions and its electrochemical generation from **2a** are discussed. The *cis*-dioxo structure of **2a** is rare for d^1 ions, and such compounds have been the subject of theoretical and biochemical discussions.[7] The only prior examples of *cis*-$Re^{VI}O_2$ complexes are the tetrahedral $Re(O)_2Ar_2$ (Ar = xylyl and mesityl).[8] *trans*-$Re^{VI}O_2$ derivatives are more common, often generated electrochemically from d^2 complexes.[9]



(1)

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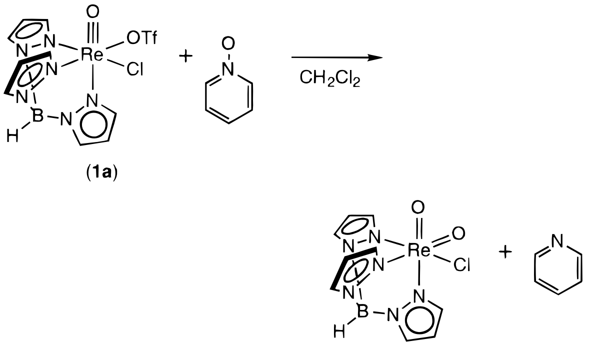
Results

Synthesis and Characterization of (HB(pz)$_3$)ReO$_2$X (X= Cl, Br, I). The reaction of (HB(pz)$_3$)ReO(Cl)OTf (**1a**) with 1 equiv of pyO in CH$_2$Cl$_2$ yields (HB(pz)$_3$)ReO$_2$Cl (**2a**) in good isolated yields (74%) (eq 2; in this report, compound numbers with "**a**" indicate chloride derivatives, "**b**" bromides, and "**c**" iodides). Addition of pyO to a solution of **1a** at room temperature results in immediate formation of a brown solution, which rapidly lightens in color. Within 5 min the reaction is complete and the solution is green, with a slight brown precipitate. The intermediate brown solution is rapidly formed even at −77 °C when CD$_2$Cl$_2$ is vacuum transferred into an NMR tube containing the two solid reactants. No new rhenium species are observed by ^{1}H NMR during low-temperature conversion of **1a** to **2a**.



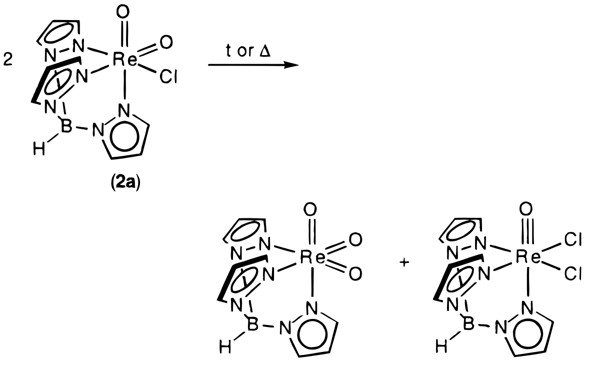
(**1a**)

(**2a**)

(2)

Isolation of **2a** is complicated by concurrent production of small amounts of (HB(pz)$_3$)ReO$_3$ (**3**),[10] typically 2−5% by ^{1}H NMR. Separation by recrystallization met with limited success due to similar solubilities of the two materials, and column chromatography is not valuable because of the reactivity of **2a** with alumina and silica gel. Purification was possible by HPLC, using a C$_8$ prep column with a water/acetonitrile mobile phase, but the slight water sensitivity of **2a** and the low capacity of this method rendered this impractical. Complex **2a** is essentially an air-stable material. It is sparingly soluble in benzene but has reasonable solubility in acetonitrile, chloroform, and methylene chloride. It slowly disproportionates as a solid or in solution to **3** and (HB(pz)$_3$)ReOCl$_2$ (**4a**) (eq 3). In CD$_2$Cl$_2$ solution under an inert atmosphere, disproportionation has a rough half-life of 3 d at 79 °C.

Compound **2a** has rhenium−oxo stretches at 912 and 823 cm^{-1} (symmetric and asymmetric, respectively), which are lower than those observed for a typical rhenium−oxo multiple bond (*e.g.*, 975 cm^{-1} for **4a** and 920 and 885 cm^{-1} for **3**). FAB-MS of **2a** showed a weak parent ion but was complicated by interactions with the 4-nitrobenzyl alcohol matrix; the parent ion was not observed using EI-MS. Compound **2a** has no discernible NMR spectrum,[11] as expected for a d^1 paramagnetic compound. The magnetic moment of **2a** is 1.6(3) μ_B at both 297 and 237 K, as determined by Evans method in CDCl$_3$. The value and temperature independence are what one would expect for an $S = {}^1/_2$ compound (spin only, 1.79 μ_B). No EPR spectrum of **2a** is observed at 296 K in CD$_2$Cl$_2$, and at 150 K a weak broad spectrum centered near $g = 2$ is obtained (Figure S1, Supporting Information). Difficulty in observing EPR spectra for d^1 dioxorhenium compounds has been previously noted;[12] molybdenum analogs have received much more attention.[13]



(**2a**)

(**3**)

(**4a**)

(3)

Initial identification of **2a** was difficult because of the lack of an NMR spectrum and the poor quality of the mass spectral data. The purity of **2a** is best indicated by the presence of a single B−H stretch and the absence of extra Re═O stretches in the IR spectrum. Alternative dimeric structures were considered, such as the rhenium(IV) bis(μ-oxo) and bis(μ-chloro) species (HB(pz)$_3$)ClRe(μ-O)$_2$ReCl(HB(pz)$_3$) and (HB(pz)$_3$)(O)Re(μ-Cl)$_2$Re(O)(HB(pz)$_3$). However, neither of these structures would give the observed widely spaced pair of symmetric and asymmetric O−Re−O stretching modes. Final confirmation of the formulation of **2a** came with the determination of the X-ray crystal structure.

Compound **2a** was crystallized as small emerald green rhombohedral crystals by vapor diffusion from CH$_2$Cl$_2$/Et$_2$O (Figure 1; Tables 1 and 2). The rhenium−oxo bond lengths of 1.797(11) and 1.741(10) Å, respectively, are slightly longer than typical Re−O triple bonds in monooxo complexes (1.69(3) Å) but comparable to the Re═O distances in *trans*-dioxo d^2 compounds (1.76 (2) Å).[7c,14,15] The d^1 tetrahedral ReO$_2$(Ar)$_2$ complexes have shorter Re═O distances [1.672(6)−1.688(5) Å].[8a,b] The oxo groups in **2** are *cis* with a O−Re−O bond angle of 107.1(4)°. There is a slight trans influence seen in the Re−N(pyrazole) distances: 2.107(8) Å *trans* to Cl vs 2.229(10) and 2.188(11) Å *trans* to O(1) and O(2). The other bond distances and angles involving the HB(pz)$_3$ ligand are typical;[16] the Re−

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(8) (a) Stavropoulos, P.; Edwards, P. G.; Behling, T.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 169−175. (b) Longly, C. J.; Savage, P. D.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Polyhedron* **1988**, *7*, 1079−1088. (c) ReO$_4^{2-}$ is observed as a transient in the aqueous pulse radiolysis of ReO$_4^-$: Libson, K.; Sullivan, J. C.; Mulac, W. A.; Gordon, S.; Deutsch, E. *Inorg. Chem.* **1989**, *28*, 375−7.

(9) Some examples: (a) Ram, M. S.; Skeens-Jones, L. M.; Johnson, C. S.; Zhang, X. L; Stern, C.; Yoon, D. L.; Selmarten, D.; Hupp, J. T. *J. Am. Chem. Soc.* **1995**, *117*, 1411−1421 and references therein. (b) Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1373. (c) Pipes, D.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 3256−3262. (e) Brewer, J. C.; Thorp, H. H.; Slagle, K. M.; Brudvig, G. W.; Gray, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 3171−3173.

(10) Degnan, I. A.; Herrmann, W. A.; Herdtweck, E. *Chem. Ber.* **1990**, *123*, 1347.

(11) Low, broad resonances are often observed in ^{1}H NMR spectra of samples containing **2** (at δ 13.3, 4.6, and 2.3 in CDCl$_3$), but these "peaks" neither move or sharpen significantly over a temperature range of 40 to −53 °C.

(12) Reference 9e and the following: Dirghangi, B. K.; Menon, M.; Banerjee, S.; Chakravorty, A. *Inorg. Chem.* **1997**, *37*, 3595−3601 and references therein.

(13) See, for instance, ref 7a and the following: (a) Xiao, Z; Bruck, M. A.; Doyle, C.; Enemark, J. H.; Grittni, C.; Gable, R. W.; Wedd, A. G.; Young, C. G. *Inorg. Chem.* **1995**, *34*, 5950−5962. (b) Gibson, J. F.; Lack, G. M.; Mertis, K.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1492. (c) Peng, G.; Nichols, J.; McCullough, E. A., Jr.; Spence, J. T. *Inorg. Chem.* **1994**, *33*, 2857−2864.

(14) Mayer, J. M. *Inorg. Chem.* **1988**, *27*, 3899.

(15) Trinka, T. M.; Parkin, G. *Polyhedron* **1997**, *16*, 1031−1045.

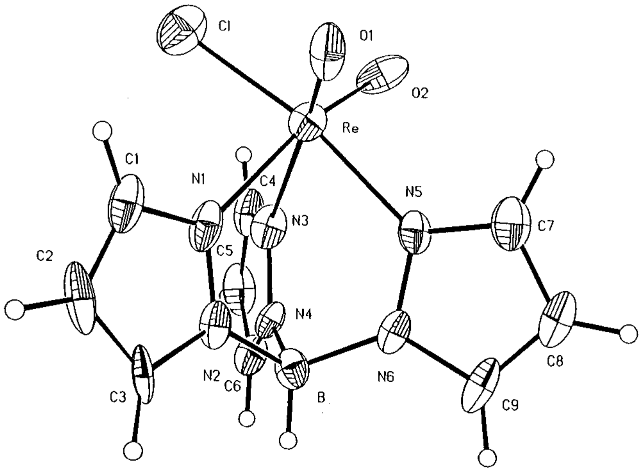


Figure 1. ORTEP drawing of $(HB(pz)_3)ReO_2Cl$ (**2a**).

Table 1. Crystallographic Data for $(HB(pz)_3)ReO_2Cl$ (**2a**)

empirical formula	$C_9H_{10}BClN_6O_2Re$
fw	466.7
cryst system, space group	monoclinic, *Cc*
cryst size (mm)	0.2 × 0.3 × 0.35
unit cell dimens	$a = 14.716(3)$ Å
	$b = 7.651(2)$ Å
	$c = 13.232(3)$ Å
	$\beta = 110.61(3)°$
V (Å^3)	1378.2(7)
Z	4
density (g/cm^3, calcd)	2.249
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)
monochromator	highly oriented graphite crystal
temp (°C)	−90
2θ range (deg)	2.0−50.0
index ranges	$-17 \le h \le 17, 0 \le k \le 8,$ $-15 \le l \le 15$
reflcns collcd	2397
indepdt reflcns	2397
obsd reflcns ($F > 4\sigma(F)$)	2354
abs coeff (cm^{-1})	0.0920
transm factors	0.948−0.389
no. of params	180
largest diff peak and hole (e Å^{-3})	6.4, −10.5
final R, R_w (obsd data)[a] (%)	4.81, 6.01
goodness of fit	1.10

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

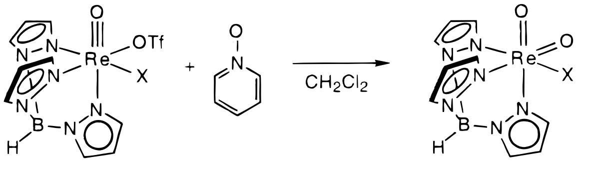
Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(HB(pz)_3)ReO_2(Cl)$ (**2a**)

Re−Cl	2.296 (4)	Re−O(1)	1.797 (11)
Re−N(1)	2.229 (10)	Re−O(2)	1.741 (10)
Re−N(3)	2.188 (11)	Re−N(5)	2.107 (8)
O(1)−Re−Cl	95.5(3)	O(2)−Re−Cl	92.6(3)
O(1)−Re−O(2)	107.1(4)	O(1)−Re−N(1)	86.9(4)
O(1)−Re−N(3)	163.6(4)	O(1)−Re−N(5)	92.5(5)
O(2)−Re−N(1)	164.8(4)	O(2)−Re−N(3)	88.7(4)
O(2)−Re−N(5)	91.2(4)		

Cl distance of 2.296(4) Å is slightly shorter than the 2.38(4) Å average for such bonds tabulated by Orpen *et al.*[17]

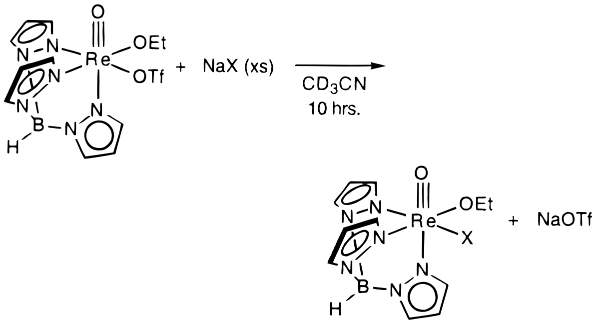
Structures of this type are often plagued by O/Cl disorder, both compositional and site disorders.[18] While small amounts of **3** and/or **4** might be present in the crystal (see eq 3 above), **2a** is clearly a discrete molecule rather than a mixture of these compounds on the basis of its IR spectrum, its lack of an NMR spectrum, its elution from an HPLC column, etc. A more likely problem is partial O/Cl site disorder about the $HB(pz)_3$ 3-fold axis, as found in the closely related structure of $(HB(pz)_3)Mo(O)Cl_2$.[19] Such a disorder could be the cause of the apparently long Re−O distances, the difference between the two Re−O bond lengths, the elongated thermal ellipsoids for the oxo groups, and the large residuals about the Re. While these issues suggest caution in the interpretation of the metrical data, the long Re−O bond lengths are consistent with the low Re−O stretching frequencies noted above.

The bromide and iodide analogs, $(HB(pz)_3)ReO_2Br$ (**2b**) and $(HB(pz)_3)ReO_2I$ (**2c**), have also been prepared from pyO oxidation of $(HB(pz)_3)ReO(X)OTf$ (X = Br, **1b**; I, **1c**; eq 4).

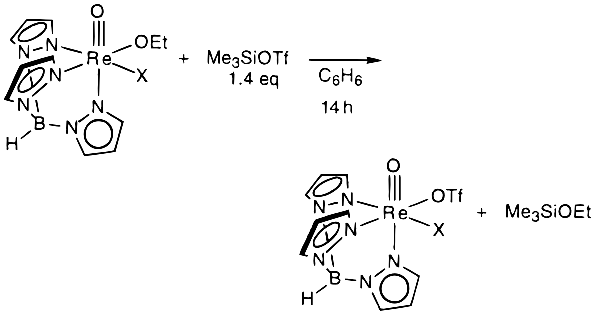


X = Br (**1b**), I (**1c**) X = Br (**2b**), I (**2c**) (4)

The halo−triflate compounds **1b**,**c** were prepared from $(HB(pz)_3)ReO(OEt)OTf$ as shown in eqs 5 and 6. Addition of an excess



(5)



(6)

X = Br (**1b**), I (**1c**)

of NaBr or NaI in acetonitrile gives the ethoxy−halide complexes $(HB(pz)_3)ReO(X)OEt$. Benzene solutions of these compounds are cleanly converted to **1b**,**c** on addition of 1 equiv of trimethylsilyl triflate (Me_3SiOTf). $(HB(pz)_3)ReO_2Br$ (**2b)** is isolated in 73% yield as a green solid with a small impurity of $(HB(pz)_3)ReO_3$. The disproportionation of **2b** occurs at roughly the same rate as for **2a**, giving rise to **3** and $(HB(pz)_3)ReOBr_2$ (**4b**) and another, as yet unidentified, diamagnetic product. The iodide analog **2c** is less stable than **2a** or **2b** and

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(16) Thomas, J. A.; Estes, G. W.; Elder, R. C.; Deutsch, E. *J. Am. Chem. Soc.* **1979**, *101*, 4581. References 3b, 4, 6, 25, and the following: Masui, C. S.; Mayer, J. M. *Inorg. Chim. Acta* **1996**, *251*, 325−333. Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1995**, *34*, 3560−3562.

(17) The value given is the mean Re−Cl distance (with standard deviation) for six-coordinate complexes in: Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−83 (Supplement).

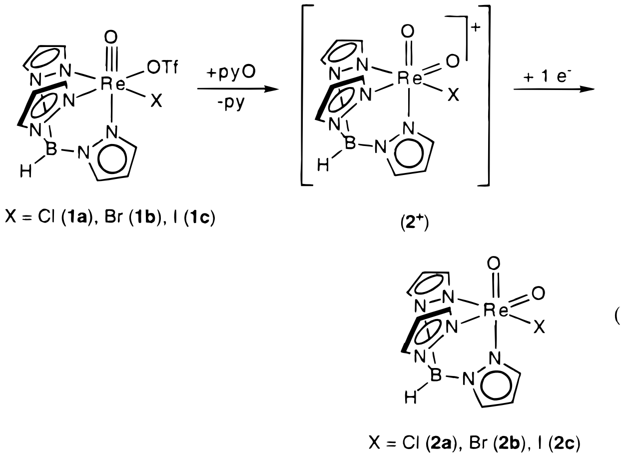
(18) Parkin, G. *Chem. Rev.* **1993**, *93*, 887; *Acc. Chem. Res.* **1992**, *25*, 455−460.

(19) Lincoln, S.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1594−1602.

is isolated in lower yield and purity. It visibly decomposes in CD_2Cl_2 forming I_2 and **3** within 30 min in the air. Slower decomposition is observed in the absence of air and in the solid state. Complexes **2b**,**c** are spectroscopically quite similar to **2a**, for instance with ν_{Re-O} values within 10 cm^{-1}. Complex **2b** has a magnetic moment of 1.5(3) μ_B by the Evans method in $CDCl_3$ at 297 K.

The cyclic voltammogram of **2a** in MeCN with a ferrocene standard (Figure 2) shows a quasi-reversible oxidation at $E_{1/2} = +0.93$ V vs $Cp_2Fe^{+/0}$. At scan rates of more than 100 mV/s, i_c/i_a approaches 1 and the peak separation (63 mV) is essentially that of $Cp_2Fe^{+/0}$ in the same solution (66 mV). At slower scan rates the return cathodic wave decreases. These data indicate that $\mathbf{2a}^+$ can be generated electrochemically but that it decomposes readily ($t_{1/2} < 10$ s). $\mathbf{2a}^+$ is an extremely strong oxidant, the potential quoted above being equivalent to +1.57 V vs NHE in MeCN.[20] The bromide analog **2b** behaves very similarly, with $E_{1/2} = +0.90$ V vs $Cp_2Fe^{+/0}$. Both **2a** and **2b** show irreversible reduction waves ($E_c = -0.67$ and -0.49 V vs $Cp_2Fe^{+/0}$, respectively), presumably involving reduction to Re(V).

Formation and Reactivity of (HB(pz)$_3$)ReO$_2$X. It is surprising that the halo−triflates **1** are oxidized by only one electron to **2** since pyridine *N*-oxide is a two-electron oxidant, an oxygen atom donor. Formation of $(HB(pz)_3)ReO_2X$ is likely to take place through initial oxygen atom donation to form the rhenium(VII) dioxo cations $(HB(pz)_3)ReO_2X^+$ ($\mathbf{2}^+$), which are then rapidly reduced by one electron to yield **2** (eq 7). The source of the reducing equivalent is most likely a rhenium compound, as aminium salts of comparable potential are reduced by (HB(pz)$_3$)ReO(Cl)X compounds. This would account for the lower than quantitative yield of **2** and the small amount of brown precipitate formed; no organic products other than pyridine are observed by NMR.



X = Cl (**1a**), Br (**1b**), I (**1c**)

($\mathbf{2}^+$)

X = Cl (**2a**), Br (**2b**), I (**2c**)

(7)

The need for a reductant can be shown by adding Cp_2Fe. When pyO was added to a solution of **1a** with 1.8 equiv Cp_2Fe in CD_2Cl_2, the reaction mixture turned the dark blue color of Cp_2Fe^+ within 5 min (eq 8). An IR spectrum indicated that **2a** was the only rhenium oxo product. The conversion of Cp_2Fe to Cp_2Fe^+ was monitored by ^1H NMR, comparing the shift and broadening of the ferrocene peak versus standard spectra of known Cp_2Fe/Cp_2Fe^+ ratios (at similar though not exactly the same concentrations). This indicated formation of 0.9(1) equiv of Cp_2Fe^+, based on the initial rhenium concentration.

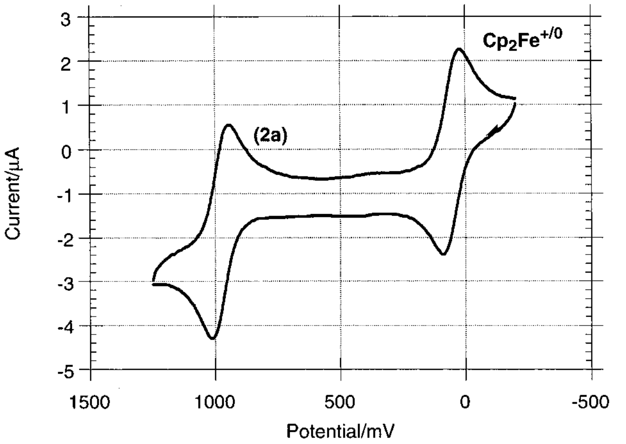
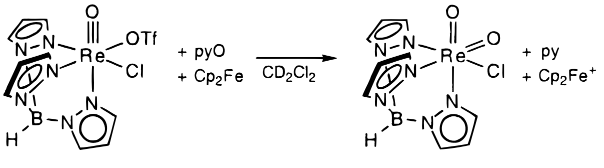


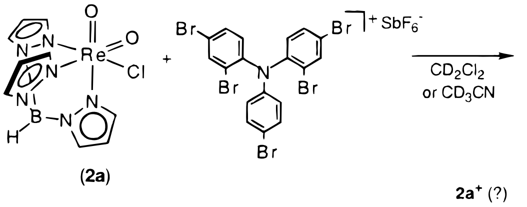
Figure 2. Cyclic voltammogram of $(HB(pz)_3)ReO_2Cl$ (**2a**) and ferrocene in MeCN, at a scan rate of 100 mV/s. The *x* scale is referenced to the quasireference electrode used.



(**1a**) (**2a**)

(8)

Converting **2a** to $\mathbf{2a}^+$ requires potent chemical oxidants because of the high potential for the Re(VII)/Re(VI) couple. Tris(bromophenyl)aminium salts have potentials of 0.4−1.36 V vs $Cp_2Fe^{+/0}$ depending on the amount of bromide substitution on the aryl rings.[21] The addition of 1.2 equiv of $[(2,4\text{-}Br_2H_3C_6)_2\text{-}(4\text{-}BrH_4C_6)N][SbF_6]$ ($E_{1/2} = +0.96$ V vs ferrocene in CH_3CN) to **2a** in CD_3CN or CD_2Cl_2 at ambient temperatures results in the slow formation of a new diamagnetic species, which in turn decomposes to a variety of unidentified rhenium products (eq 9). Monitoring the reaction in CD_3CN at −31 °C by NMR showed comparable yields and the same competitive decomposition. Similar reactivity was found with the more potent oxidant $[(2,4\text{-}Br_2H_3C_6)_3N][SbF_6]$ (+1.14 V) but not with the milder $[(4\text{-}BrC_6H_4)_3N][SbCl_6]$. ^1H NMR spectra of the new complex indicate a diamagnetic material with C_s symmetry, as would be expected for $\mathbf{2a}^+$.[22] Consistent with the formation of $\mathbf{2a}^+$ in reaction 9, oxidizing **2a** with 1.2 equiv of $[(2,4\text{-}Br_2H_3C_6)_2(4\text{-}BrH_4C_6)N][SbF_6]$ in the presence of 16 eq of SMe_2 in CD_2Cl_2 gives the Me_2SO adduct, $[(HB(pz)_3)ReO(Cl)(OSMe_2)]\text{-}[OTf]$ (**5a**, eq 10; see below). Complex **5a** is only observed in low yield apparently because it is unstable under these strongly oxidizing conditions, decomposing completely within the course of about 1 h. Complex **5a** is also formed when the milder



(**2a**)

$\mathbf{2a}^+$ (?) ⟶ (9)

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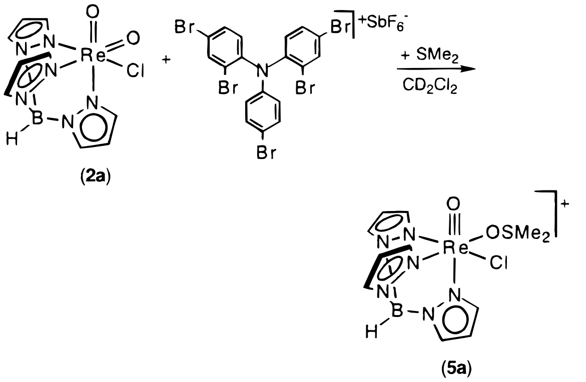
[20] Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877−910.

[21] Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577−585. Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* **1969**, 2719−2720.

[22] However, the related phenyl complex $[(HB(pz)_3)ReO_2(Ph)][OTf]$ showed averaging among the three pyrazole groups in low-temperature ^1H NMR spectra.[4]

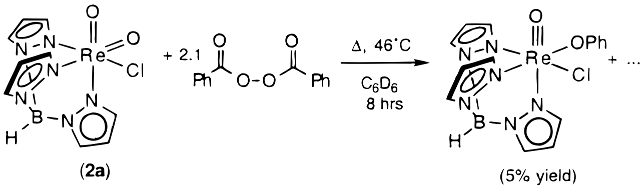


(10)

oxidant $[(4\text{-}BrC_6H_4)_3N][SbCl_6]$ is used, even though this reagent does not stoichiometrically oxidize **2a**.

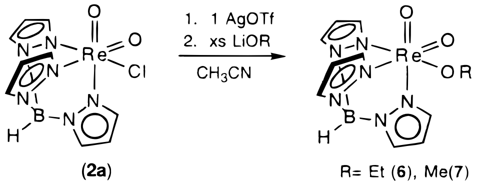
Complex **2a** is not particularly reactive, despite being an unusual d^1-dioxo complex. It is fairly stable in the air and only slightly water sensitive: H_2O-saturated methylene chloride solutions of **2a** decompose to a brownish solution over a 2 day period. As noted above, **2a** disproportionates to $(HB(pz)_3)ReOCl_2$ (**4a**) and $(HB(pz)_3)ReO_3$ (**3**). Reactions with acids are slow; for instance, addition of concentrated aqueous HCl to a CH_2Cl_2 solution of **2a** results in the eventual formation of **4a**. Bases, however, decompose **2a** quite rapidly. No reaction is observed between **2a** and Me_2S or olefins. NO_2 oxidizes **2a** in CD_2Cl_2 to **3**. A similar reaction is the reported oxidation of $ReO_2(mes)_2$ by NO_2 to give $ReO_3(mes)$ and ON(mes) (mes = mesityl).[23] As a side note, it is possible to form **2a** from $(HB(pz)_3)ReO(Cl)OTf$ (**1a**) and NH_4NO_3 in acetonitrile. When the reaction is carried out in a sealed NMR tube, the newly generated **2a** slowly converts to **3**, probably by continued reaction with NO_2 generated in the formation of **2a**. There is no apparent reaction of **2a** with NO or N_2O.

We have also briefly examined the ability of **2a** to act as a radical trap, which can be a facile reaction for oxidizing metal–oxo complexes.[24] Heating a dilute C_6D_6 solution of **2a** with 2.1 equiv of benzoyl peroxide, a source of phenyl radicals, gave ~5% yield of the phenoxide complex $(HB(pz)_3)ReO(Cl)OPh$ (eq 11). The product was confirmed by EI/MS and by spiking with an authentic sample.[25] Biphenyl, **4a**, and **3** were also formed in the reaction. While this is not an ideal test of the trapping ability of **2a**, as it is not very soluble in benzene and its disproportionation occurs on the same time scale as peroxide decomposition, the observation of the phenoxide product indicates that radical trapping can occur.



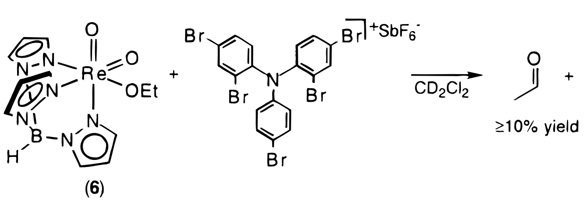
(11)

A number of attempts were made to exchange the chloride in **2a** for other ligands. Reactions with $ZnEt_2$, EtMgCl, and $ZnEt_2$/2 CuCl in either THF or benzene caused the reduction of **2a** to unknown rhenium products (visually resembling the reaction of **2a** with Cp_2Co). The most success was obtained for alkoxide compounds $(HB(pz)_3)ReO_2(OR)$ (R = Et, **6**, and Me, **7**), though these were obtained in low yield and only in impure form. The best method was the reaction of 1 equiv AgOTf with **2a**, followed by an excess of LiOR (eq 12). After multiple recrystallizations, the primary diamagnetic impurity in **6** and **7** was trioxide **3**. Compounds **6** and **7** were characterized by parent ions in the FAB-MS and by IR, with both showing Re–O stretches at about 907 and 814 cm^{-1}. Complexes **6** and **7** are slightly air sensitive and decompose on heating to **3** and unidentified rhenium products.

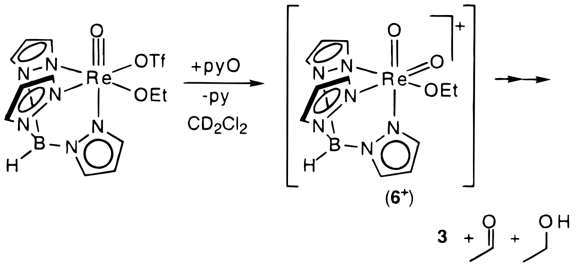


(12)

Oxidation of **6** with the aminium salt shown in eq 13 gives a small amount of acetaldehyde. The acetaldehyde is consumed under these conditions, so the amount formed must be larger than the ~10% yield observed by ^1H NMR using $(Me_3Si)_2O$ as an internal standard. Reaction of **6** with the aminium salt and pyridine *N*-oxide gives **3** and an apparently larger amount of acetaldehyde. One-electron oxidation of **6** should give the Re(VII) dioxo–ethoxide cation, $[(HB(pz)_3)ReO_2(OEt)]^+$ ($\mathbf{6}^+$), which has been proposed as a key intermediate in acetaldehyde formation from the rhenium(V) ethoxide $(HB(pz)_3)ReO(OEt)(OTf)$ and oxygen atom donors (eq 14).[3a] The independent oxidation of **6** is consistent with this proposed mechanism for alkoxide oxidation.



(13)



(14)

Reversible Formation of $[(HB(pz)_3)ReO_2X]^+$ from Me_2SO Adducts. Treatment of the halo triflate complexes $(HB(pz)_3)ReO(X)OTf$ (**1**) with Me_2SO yield the sulfoxide complexes $[(HB(pz)_3)Re(O)X(OSMe_2)]OTf$ (**5**; eq 15).[26] These complexes have been identified primarily by NMR, showing three inequivalent pyrazole rings and diastereotopic sulfoxide methyl groups. Analogous aryl[4] and alkoxy[3a] Me_2SO adducts are formed by similar triflate displacement reactions. Complexes **5** are reasonably stable, decomposing slowly at ambient temperatures to $(HB(pz)_3)ReO_3$ (**3**) and SMe_2.

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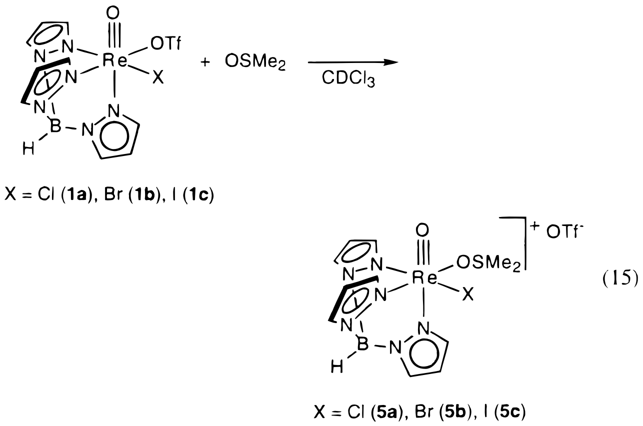
[23] McGilligan, B. S.; Arnald, J.; Wilkinson, G.; Hussain-Bates, B; Hursthouse, M. B. *J. Chem. Soc., Dalton. Trans.* **1990**, 2465–2475.

[24] For instance: (a) Steenken, S.; Neta, P. *J. Am. Chem. Soc.* **1982**, *104*, 1244–8. (b) Al-Sheikhly, M.; McLaughlin, W. L. *Radiat. Phys. Chem.* **1991**, *38*, 203–211. (c) Cook, G. K.; Mayer, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 1855–1868.

[25] Brown, S. N.; Mayer, J. M. *Organometallics* **1995**, *14*, 2951–2960.

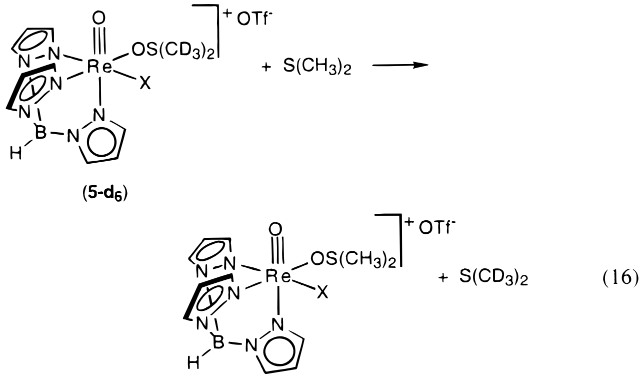
[26] The reaction of **1a** with Me_2SO to give **5a** is reported in ref 6.



X = Cl (**1a**), Br (**1b**), I (**1c**)

X = Cl (**5a**), Br (**5b**), I (**5c**)

Like the aryl and alkoxy derivatives, complexes **5** reversibly dissociate Me_2S from the bound Me_2SO ligand (eq 16). The exchange was demonstrated by preparing adducts with $OS(CD_3)_2$ and reacting them with ~60 equiv of $S(CH_3)_2$ [using a large excess to prevent significant back-incorporation of $S(CD_3)_2$]. The rates of exchange were determined by observing the slow increase in the protium concentration in the adduct by ^1H NMR. The kinetics are first order in rhenium complex and are assumed to be independent of the Me_2S concentration by analogy with the phenyl derivative.[4] The rate constants for Me_2S dissociation, k_{Me_2S}, are on the order of 10^5-10^6 times slower than those found earlier for the phenyl and ethoxy complexes (Table 3).



(**5-d$_6$**)

(**5**)

Complexes **5** also catalyze the disproportionation of Me_2SO to Me_2S and Me_2SO_2, slowly consuming the excess Me_2SO used in their synthesis (eq 17). In the presence of excess Me_2S, however, no sulfone is formed. This inhibition of disproportionation by Me_2S (as was first found[4] for $HB(pz)_3ReO(Ph)OSMe_2^+$) indicates that the mechanism of catalysis involves pre-equilibrium loss of Me_2S to form $\mathbf{2}^+$ (Scheme 1). The trapping of independently generated $\mathbf{2}^+$ by Me_2S is shown in eq 10. As discussed below, the relative rates of Me_2S and Me_2SO oxidation are a measure of the electrophilicity of the oxidant.

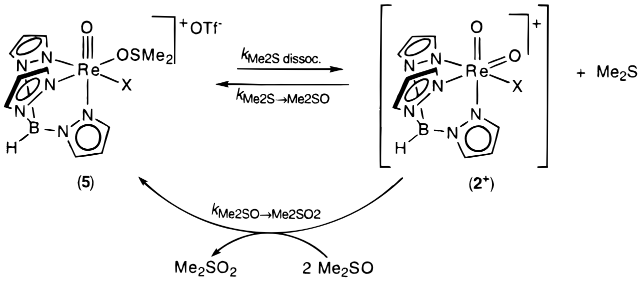
$$2\,Me_2SO \xrightarrow[\text{[(HBpz}_3\text{)Re(O)X(OSMe}_2\text{)]OTf}]{} Me_2S + Me_2SO_2 \qquad (17)$$

Table 3. Rate Constants for Me_2S Dissociation and Relative Rates of Me_2S and Me_2SO Oxidation[a]

compd	$k_{Me_2S\ dissoc}$ (s^{-1})[b]	$k_{Me_2S\to Me_2SO}/k_{Me_2SO\to Me_2SO_2}$ [c]
$[(HB(pz)_3)ReO(Cl)(OSMe_2)]^+$ (**4a**)	$3.3(4) \times 10^{-6}$	$>9 \times 10^2$
$[(HB(pz)_3)ReO(Br)(OSMe_2)]^+$ (**4b**)	$3.3(5) \times 10^{-6}$	$>1.1 \times 10^3$
$[(HB(pz)_3)ReO(I)(OSMe_2)]^+$ (**4c**)	$3.8(7) \times 10^{-5}$	d
$[(HB(pz)_3)ReO(Ph)(OSMe_2)]^+$	2.9(4)[e]	1.2×10^5 [e]
$[(HB(pz)_3)ReO(OEt)(OSMe_2)]^+$	8.2(6)[f]	8×10^4 [f]

[a] At 297 K in CD_2Cl_2. Rate constants as defined in Scheme 1. [b] By isotopic exchange and/or magnetization transfer. [c] See text. [d] Not determined. [e] Reference 4. [f] Reference 3a.

Scheme 1. Mechanism for Me_2S Exchange and Me_2SO Disproportionation



Discussion

The production of stable d^1 *cis*-dioxo complexes is surprising. The large majority of compounds with two terminal oxo ligands are d^0 and *cis*-octahedral or d^2 and *trans*-octahedral.[7c,e,27] In the *cis* configuration all three metal d_π orbitals (the t_{2g} orbitals) participate in π bonding with the oxo ligands, leaving no nonbonding orbitals to hold d electrons. The *trans* configuration leaves one nonbonding d orbital, d_{xy}, taking the O−M−O axis as *z*. The d electrons in d^1 or d^2 *cis*-dioxo octahedral complexes occupy an orbital with π-antibonding character, which accounts for the rarity of such compounds.[7,27] The d^1 case is nicely described in the recent report by Young and co-workers on $[LMoO_2X]^-$ compounds quite similar to **2**, including an X-ray structure of $[L'MoO_2(SPh)]^-$ [L = HB(3,5-Me_2pz)$_3$, HB(3-^{i}Pr-pz)$_3$; HB(3,5-$Me_2C_2N_3$)$_3$ = L′].[7a] There has been much interest in preparing such d^1 dioxo compounds as models for the EPR-active intermediates in molybdenum oxo-transferase enzymes. The metrical data for $[L'MoO_2(SPh)]^-$ include slightly long Mo=O distances of 1.742(9) Å (vs 1.700(6) Å average in the d^0 analog) and an open O−Mo−O angle of 112.1(4)°. These features were explained using EHMO calculations and an orbital model expanding on that outlined above. The metrical data are similar to those for **2a**, with Re−O = 1.797(11), 1.741(10) Å and <O−Re−O = 107.1(4). The stability of **2** and the molybdenum compounds is due in part to the requirement of facial coordination for the tripodal ligands used, inhibiting isomerization or dimerization.

The structural similarity between **2a** and the isoelectronic $[LMoO_2X]^-$ compounds does not extend to their chemical reactivity. The molybdenum compounds are quite basic and are strong reducing agents. The d^0/d^1 redox potential of [HB(3-^{i}Pr-pz)$_3$]MoO_2Cl, for instance, is −0.84 V vs $Cp_2Fe^{+/0}$ in MeCN.[28] This is a remarkable *1.77 V* different from the analogous $\mathbf{2a}^+/\mathbf{2a}$ redox potential. These molecules are identical except for the metal, the charge, and the isopropyl ligand substituents. There is an almost identical difference between the d^1/d^2 redox potentials of [HB(3,5-Me_2(pz)$_3$]$ReOCl_2^{+/o}$ ($E_{1/2}$

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[27] Mingos, D. M. P.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1987**, *109*, 5203−5208.

[28] Xiao, Z.; Bruck, M. A.; Doyle, C.; Enemark, J. H.; Grittini, C.; Gable, R. W.; Wedd, A. G.; Young, C. G. *Inorg. Chem.* **1995**, *34*, 5950.

$= +1.16$ V[29]) and $[HB(3,5\text{-}Me_2(pz)_3]MoOCl_2^{0/-}$ (-0.70 V).[30] Given the diagonal relationship between rhenium and molybdenum, much smaller differences would have been expected. The negative redox potential in the molybdenum complexes are not unusual or surprising. The unusual feature is the remarkably high potential of the $\mathbf{2a}^+/\mathbf{2a}$ couple, $+0.93$ vs $Cp_2Fe^{+/0}$ ($+1.57$ vs NHE). The related neutral trioxo complex, $(HB(pz)_3)ReO_3$ (**3**), is *2.4 V* less oxidizing than $\mathbf{2a}^+$, being reduced irreversibly at -1.49 V. The $\mathbf{2a}^+/\mathbf{2a}$ couple is one of the highest reversible potentials that we have found for an oxo complex. The origin of the high oxidation potential for $\mathbf{2a}^+$ must in part lie in its positive charge, a feature shared with "$[HB(3,5\text{-}Me_2(pz)_3]ReOCl_2^+$" but not found in **3** or $[HB(3\text{-}{}^iPr\text{-}pz)_3]MoO_2Cl$. Given the high potential, it is not surprising that the reactions of $(HB(pz)_3)Re(O)X(OTf)$ with pyridine *N*-oxide give **2** rather than $\mathbf{2}^+$ (eq 7 above)—something in the reaction mixture will give up an electron to $\mathbf{2}^+$.

The unobserved dioxo cations $\mathbf{2}^+$ are not only strong one-electron oxidants but also have electrophilic oxo ligands. This is according to the electrophilicity scale for oxygen atom donors developed by Adam, Di Furia, and others,[31] based on the relative rate constants for sulfoxide vs sulfide oxidation. For instance, basic H_2O_2 is nucleophilic and selectively oxidizes the electron poor sulfoxide sulfur ($>100{:}1$) while H_2O_2 in acidic solutions prefers to oxidize the more electron rich thioether ($\leq 1{:}4$). This ratio of rate constants can be estimated for $\mathbf{2a}^+$ and $\mathbf{2b}^+$ from the results above for the Me_2SO adducts **5a**,**b** (as described previously for $[(HB(pz)_3)Re(O)X(OSMe_2)][OTf]$ (X = Ph[4] or OEt[3a]). The rate of $Me_2S \rightarrow Me_2SO$ oxidation is, at equilibrium, equal to the rate of Me_2S dissociation from **5** (eq 18). Dividing this expression by the rate expression for $Me_2SO \rightarrow Me_2SO_2$ oxidation (eq 19) yields the ratio of rate constants for oxidation of Me_2S and Me_2SO by $\mathbf{2}^+$ (eq 20).

$$R_{Me_2S\ \text{dissociation}} = R_{Me_2S \rightarrow Me_2SO} = k_{Me_2S \rightarrow Me_2SO}[HB(pz)_3ReO_2X^+][Me_2S] \quad (18)$$

$$R_{Me_2SO \rightarrow Me_2SO_2} = k_{Me_2SO \rightarrow Me_2SO_2}[HB(pz)_3ReO_2X^+][Me_2SO] \quad (19)$$

$$\frac{k_{Me_2S \rightarrow Me_2SO}}{k_{Me_2SO \rightarrow Me_2SO_2}} = \frac{R_{Me_2S\ \text{dissociation}}[Me_2SO]}{R_{Me_2SO \rightarrow Me_2SO_2}[Me_2S]} \quad (20)$$

The rate of Me_2S dissociation was monitored by isotope exchange of bound $(CD_3)_2SO$ with excess $(CH_3)_2S$. Unfortunately, no sulfone is observed under these conditions due to the inhibition by the excess Me_2S. So only an upper limit for $R_{Me_2SO \rightarrow Me_2SO_2}$ can be obtained and, therefore, a lower limit to the electrophilicity measure (Table 3). Still, these limits are large numbers, on the order of 10^3, indicating that the oxo ligands of $\mathbf{2a}^+$ are highly electrophilic. From the slow formation of sulfone when only small amounts of Me_2S are present, an upper limit ca. 1000 times larger can be estimated. This places the dioxo halide cations $\mathbf{2a}^+$ in the same range as the previously measured phenyl and ethoxy derivatives (Table 3).

The rate constants for Me_2S dissociation, $k_{Me_2S\ \text{dissoc}}$, are 10^5–10^6 times slower than those found earlier for the phenyl and ethoxy complexes (Table 3). This is a dramatic effect of an ancillary ligand. It is interesting that the electrophilicities do not show a difference of this order. The ligand effect is likely due to SMe_2 loss being less thermodynamically favorable in the halide complexes because halide is a poorer donor to rhenium.[32] The phenyl ligand is a much better σ donor, leaving more electron density on Re. The Re−OEt σ bond is likely to be comparable to a Re−halide bond, but ethoxide is a much stronger π donor than Cl^- or Br^-. This π-donation likely provides significant stabilization for a Re(VII) complex, as the large majority of Re(VII) compounds have three or more strong π donor ligands (such as the very stable $HB(pz)_3ReO_3$, **3**).

Conclusions

Rare d^1 rhenium(VI) *cis*-dioxo compounds, $(HB(pz)_3)ReO_2X$ (**2**, X = Cl, Br, I), are formed on oxidation of d^2 $(HB(pz)_3)ReO(X)OTf$ (X = Cl, Br, I) by 1 equiv of pyridine *N*-oxide. This is a surprising result because pyridine *N*-oxide is a two-electron oxidant. The expected products, the rhenium(VII) dioxo cations $(HB(pz)_3)ReO_2X^+$, are likely formed but are readily reduced under the reaction conditions. Electrochemical studies of **2** show why this reduction is so facile: Reversible Re(VII)/Re(VI) couples are observed at 0.93 V (X = Cl) and 0.90 V (X = Br) vs $Cp_2Fe^{+/0}$ in acetonitrile. These are extremely high values (equivalent to ~1.5 V vs NHE) indicating that the rhenium(VII) dioxo cations are very oxidizing. The Re(VII)/Re(VI) couple in the related neutral trioxo complex, $(HB(pz)_3)ReO_3$, is *2.42 V* less oxidizing, and the isoelectronic d^0/d^1 potential for $[HB(3\text{-}{}^iPr\text{-}pz)_3]Mo(O)_2Cl$ is 1.8 V less oxidizing.[7a] The reactive cations $(HB(pz)_3)ReO_2X^+$ are also formed from reversible loss of Me_2S from the Me_2SO adducts $[(HB(pz)_3)ReO(X)(OSMe_2)][OTf]$. Under these conditions, the cations oxidize Me_2S much faster than Me_2SO, indicating that they are highly electrophilic oxygen atom transfer reagents. These results are consistent with previous mechanistic suggestions involving such cations as reactive intermediates. The electrophilic nature of $(HB(pz)_3)ReO_2X^+$ is likely due in part to their positive charge.

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. $(HB(pz)_3)ReOCl_2$,[33] $(HB(pz)_3)ReO(Cl)I$,[25] $(HB(pz)_3)ReO_3$,[10] $(HB(pz)_3)ReO(OEt)(OTf)$,[3a] and (bromoaryl)aminium salts (from tris(bromophenyl)amines and SbF_5)[21] were synthesized according to published procedures. Deutero solvents were purchased from Cambridge Isotope Laboratories. Other reagents were purchased from Aldrich and used as received unless otherwise noted.

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(29) Matano, Y.; Northcutt, T.; Mayer, J. M. Unpublished results.

(30) (a) Reported as -0.25 V vs Ag/AgCl,[30b] a reference that is 0.45 V cathodic of $Cp_2Fe^{+/0}$. (b) Cleland, W. E., Jr.; Barnhart, K. M.; Yamanouchi, K.; Collison, D.; Mabbs, F. E.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1987**, *26*, 1017−1025.

(31) (a) Adam, W.; Haas, W.; Lohray, B. B. *J. Am. Chem. Soc.* **1991**, *113*, 6202−6208 and references therein. (b) Ballistreri, F. P.; Tomaselli, G. A.; Toscono, R. M.; Conte, V.; Di Furia, F. *J. Am. Chem. Soc.* **1991**, *113*, 6209−6212. (c) As noted previously,[4] there is one caution on interpreting the relative rates of sulfide vs sulfoxide oxidation in this system. Me_2S oxidation gives a sulfoxide complex, while Me_2SO oxidation gives free Me_2SO_2; so there is an additional driving force for sulfide oxidation. Oxidation of Me_2S by $HB(pz)_3ReO_2(Ph)^+$ is very facile and has almost no enthalpic barrier, indicating an early transition state so the influence of the sulfoxide complex should be quite limited.

(32) In various transition metal systems with low d-electron counts, halide complexes are stronger oxidants than analogous alkoxide or hydrocarbyl compounds. See, for instance: Belmonte, P. A.; Own, Z.-Y. *J. Am. Chem. Soc.* **1984**, *106*, 7493−6.

(33) (a) Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82*, 125. (b) Degnan, I. A.; Behm, J.; Cook, M. R.; Herrmann, W. A. *Inorg. Chem.* **1991**, *30*, 2165. (c) Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091−4100.

NEt_3 and pyridine were degassed and dried over CaH_2 and then vacuum transferred prior to use. Pyridine *N*-oxide and dimethyl sulfone were sublimed and kept under nitrogen. Me_2SO was degassed and dried over 4 Å molecular sieves. Me_2S was degassed, dried over sodium, and vacuum transferred prior to use. $[Cp_2Fe][PF_6]$ was graciously provided by the Kovacs research group. Sodium halide salts were dried *in vacuo* at 120 °C. HCl, N_2O, NO_2, NO, and ethylene were purchased from Matheson.

NMR spectra were recorded on Bruker AC-200 (^{1}H, ^{13}C, ^{19}F), AF-300 (^{1}H, ^{13}C), and AM-499 (^{1}H) FT spectrometers, at ambient temperatures unless otherwise noted. Peaks in the ^{1}H and ^{13}C spectra were referenced to solvent resonances. ^{19}F spectra were referenced to neat $CF_3C(O)OH$. Low-temperature spectra utilized a Bruker B-VT 1000 temperature controller, calibrated with the ^{1}H chemical shifts for methanol.[34] Peak positions are reported in ppm, and coupling constants in Hz. The diamagnetic compounds show an ^{1}H NMR resonance for *H*B(pz)$_3$ at ∼4 ppm that is very broad (ca. 2 ppm wide) and barely perceptible above the baseline. The pyrazole protons always have a $J_{HH} = 2$ Hz which is not included in the spectral descriptions below. EPR spectra were taken on a Bruker B960 spectrometer in CH_2Cl_2 at a frequency of 9.34 GHz and power of 19.922 mW. IR spectra, reported below in cm^{-1}, were recorded using a Perkin-Elmer 1600 FTIR with samples prepared as Nujol mulls or evaporated films on NaCl plates. The pyrazole bands are relatively constant, and therefore, the following common bands are not repeated in each of the spectral lists below: 3112 (m), 1503 (m), 1409 (s), 1312 (s), 1212 (s), 1116 (s), 1072 (m), 1051 (vs), 987 (w), 762 (s), 715 (s), 657 (m), 615 (m). UV−vis measurements were recorded on a Hewlett Packard 8452A diode array spectrophotometer. Electron impact mass spectra were recorded using a Kratos Analytical mass spectrometer using a direct probe technique with samples packed into glass capillaries and heated typically to 100 °C. FAB-MS were performed on a VG 70 SEQ tandem hybrid instrument of EBqQ geometry, equipped with a standard saddle-field gun (Ion Tech ltd., Middlesex, U.K.) producing a beam of xenon atoms at 8 keV and 1 mA. Samples were applied to the FAB target in dichloromethane solutions. The matrix used was a 3-nitrobenzyl alcohol, and the spectra were taken in the positive ion mode.

Cyclic voltammetry was obtained in acetonitrile using a Bioanalytical Systems B/W 100 electrochemical analyzer with IR compensation. A Ag/$AgNO_3$ (0.1 M in CH_3CN) quasireference electrode, a platinum disk working electrode, and platinum wire auxiliary electrode were used. The electrolyte solution was 0.1 M Bu_4NPF_6 (triply recrystallized from ethanol) in CH_3CN, with sublimed ferrocene added as a reference standard. Elemental analyses were performed by Canadian Microanalytical Services Ltd.

Some reactions were performed in sealed NMR tubes. A general procedure for such reactions follows: 7.2 mg of (HB(pz)$_3$)ReO(Cl)-OTf (0.012 mmol) was placed in a sealable NMR tube. Me_2SO (1.3 μL) was added via syringe to the side of the tube, preventing contact with the rhenium complex. A needle valve was attached, and the apparatus was brought out of the glovebox and placed on a vacuum line. The Me_2SO was frozen by immersing the NMR tube in a dry ice/acetone bath. The NMR tube was evacuated, and ∼0.4 mL of $CDCl_3$ was vacuum transferred in. The tube was then sealed with a torch and the contents thawed and mixed.

(HB(pz)$_3$)ReO(Cl)(OTf) (1a).[6] A mixture of (HB(pz)$_3$)ReO(Cl)I (117 mg, 0.203 mmol), AgOTf (58 mg, 0.226 mmol, 1.1 equiv), and 25 mL of toluene in a round-bottom flask attached to a swivel-frit assembly was stirred for 2 d while being protected from light. The solution was filtered to give a yellow precipitate and a blue solution which was reduced *in vacuo* to 5 mL. Pentane (35 mL) was vacuum transferred onto the toluene solution at −78 °C and the flask allowed to warm to room temperature and stand for 7 h. The precipitated blue crystals were collected, washed with pentane, and dried *in vacuo*, giving 85 mg of **1a** (70%). ^{1}H NMR (δ): 6.11, 6.63, 6.64 (t, 1 H); 7.50, 7.70, 7.95 (d, 1 H); 8.05 (m, 3 H; three nearly superimposed pyrazole doublets). ^{13}C{^{1}H} NMR (δ): 107.0, 109.7, 110.1, 136.1, 139.9, 141.7, 146.9, 147.5, 149.0 (pz); *C*F$_3$SO$_3$ not observed. ^{19}F NMR: δ 1.23 (s). IR (Nujol mull) (cm^{-1}): 2540 (ν_{BH}); 1355, 1239, 1196, 1154 ($\nu_{CF_3SO_3}$); 989, 959 (ν_{ReO}); 674. Anal. Calcd for $C_{10}H_{10}BClF_3N_6O_4ReS$: C, 20.03; H, 1.68; N, 14.01. Found: C, 19.99; H, 1.71; N, 13.57.

(HB(pz)$_3$)ReO(Br)OEt. (HB(pz)$_3$)ReO(OEt)OTf (379 mg, 0.701 mmol) was placed in a 250 mL RB flask with excess NaBr (967 mg, 9.39 mmol, 13.4 equiv). CH_3CN (75 mL) was vacuum transferred in, and the solution was stirred for 14 h, giving a dull blue solution. The solvent was removed *in vacuo*, and CH_2Cl_2 (20 mL) was vacuum transferred in. The solution was purified by column chromatography (silica gel/CH_2Cl_2) in air, resulting in a vibrant blue solution. Removal of the solvent and recrystallization from CH_2Cl_2/pentane gave 253 mg (83% yield) of powder blue solid. ^{1}H NMR (C_6D_6; δ): 8.16, 7.09, 7.05, 6.70 (each d, 1H, pz); 7.66 (d, 2H, pz); 6.33, 6.15 (each d of q, 1H, $J_{HH'} = 7$ Hz, $J_{HH} = 3$ Hz, Re(OC*HH′*CH$_3$), 5.75, 5.71, 5.37 (each t, 1H, pz); 1.57 (t, 3H, $J_{HH} = 7$ Hz, Re(OCH$_2$C*H*$_3$)). ^{13}C{^{1}H} NMR ($CDCl_3$; δ): 148.2, 145.0, 144.9, 139.0, 137.5, 134.1, 108.5, 107.7, 106.0, and 84.3, 19.1 (O*C*H$_2$*C*H$_3$). IR (cm^{-1}): 2520 (w, ν_{BH}); 1181 (w); 1029 (s); 972 (s, ν_{ReO}). MS: *m/z* = 540 (M$^+$). Anal. Calcd for $C_{11}H_{15}BBrN_6O_2Re$: C, 24.46; H, 2.80; N, 15.56. Found: C, 24.64; H, 2.87; N, 15.54.

(HB(pz)$_3$)ReO(Br)OTf (1b). (HB(pz)$_3$)ReO(Br)OEt (102 mg, 0.188 mmol) was placed in a 100 mL RB flask with a stir bar and dissolved in benzene (10 mL). Me_3SiOTf (41.5 mL, 0.207 mmol, 1.1 equiv) was added via syringe. The solution was stirred for 16 h, and pentane (20 mL) was vacuum transferred in and allowed to slowly diffuse into solution. After cooling of the sample to −30 °C, 100 mg of blue **1b** (83% yield) was obtained on filtering and washing with 5 mL of benzene and 3 × 10 mL of pentane. ^{1}H NMR ($CDCl_3$; δ): 8.18, 8.07, 7.95, 7.86, 7.75, 7.42 (each 1d, 1H, pz), 6.58, 6.57, 6.06 (each t, 1H, pz). ^{13}C{^{1}H} NMR (CD_2Cl_2; δ): 150.2, 148.2, 147.4, 141.7, 139.6, 136.3, 110.6, 109.6, 107.4 (pz). ^{19}F NMR (CD_2Cl_2): −1.78 (s). IR (cm^{-1}): 2519 (w, ν_{BH}); 1346 (s, ν_{OTf}); 1231 (w, ν_{OTf}); 1186 (w, ν_{OTf}); 1161 (w, ν_{OTf}); 965 (s, ν_{ReO}); 917 (w); 639 (w). MS: *m/z* = 644 (M$^+$). Anal. Calcd for $C_{10}H_{10}BBrF_3N_6O_4ReS$: C, 18.64; H, 1.56; N, 13.04. Found: C, 18.76; H, 1.64; N, 13.08.

(HB(pz)$_3$)ReO(I)OEt. Following the procedure for the bromide analog, (HB(pz)$_3$)ReO(OEt)OTf (356 mg, 0.584 mmol) and NaI (1.42 g, 9.52 mmol, 16.3 equiv) gave 251 mg (73%) of blue-green product on addition of pentane to the CH_2Cl_2 solution. Chromatography was performed only when needed, with care to remove the compound from exposure to the air as soon as possible. ^{1}H NMR (CD_2Cl_2; δ): 8.35, 7.88, 7.82, 7.81, 7.77, 7.44 (each d, 1H, pz); 6.53, 6.47, 6.06 (each t, 1H, pz); 5.97 (q, 2H, 7 Hz, Re(OC*H*$_2$CH$_3$)); 1.44 (t, 3H, Re(OCH$_2$C*H*$_3$)). ^{13}C{^{1}H} NMR (CD_2Cl_2; δ): 150.0, 147.0, 145.0, 139.3, 138.2, 134.9, 108.6, 108.1, 106.3, 89.0 (O*C*H$_2$CH$_3$), 19.8 (OCH$_2$*C*H$_3$). IR (cm^{-1}): 2525 (w, ν_{BH}); 1183 (w); 1038 (s); 966 (s, ν_{ReO}). MS: *m/z* = 588 (M$^+$). Anal. Calcd for $C_{11}H_{15}BIN_6O_2Re$: C, 22.50; H, 2.57; N, 14.31. Found: C, 22.75; H, 2.59; N, 14.56.

(HB(pz)$_3$)ReO(I)OTf (1c). Following the procedure for the bromide analog, (HB(pz)$_3$)Re(O)I(OEt) (217 mg, 0.369 mmol) and Me_3SiOTf (0.10 mL, 0.517 mmol, 1.4 equiv) gave 229 mg of green **1c** (90% yield). ^{1}H NMR (C_6D_6; δ): 8.04, 7.91, 7.85, 6.83, 6.82, 6.52 (each d, 1H, pz), 5.60, 5.47, 5.19 (each t, 1H, pz). ^{13}C{^{1}H} NMR ($CDCl_3$; δ): 149.5, 148.9, 145.0, 140.9, 138.0, 135.8, 109.0, 108.3, 106.5 (pz). ^{19}F NMR (CD_2Cl_2; δ): −1.73 (s). IR (cm^{-1}): 2517 (w, ν_{BH}); 1345 (s, ν_{OTf}); 1231 (w, ν_{OTf}); 1174 (w, ν_{OTf}); 1152 (w, ν_{OTf}); 968 (s, ν_{ReO}); 648 (w). MS: *m/z* = 691 (M$^+$). Anal. Calcd for $C_{10}H_{10}BIF_3N_6O_4ReS$: C, 17.38 H, 1.46; N, 12.16. Found: C, 17.65; H, 1.57; N, 12.09.

(HB(pz)$_3$)ReO$_2$(Cl) (2a). A 250 mL RB flask was charged with a stir bar, 305 mg (0.509 mmol) of **1a**, 80 mL of CH_2Cl_2, and then pyO (51 mg, 0.536 mmol, 1.05 equiv). After 5 min of stirring, the flask was opened to the air and the solvent removed. The green residue was dissolved in MeCN and extracted once with hexanes. The MeCN layer was recovered and the solvent removed. The green residue was taken up in CH_2Cl_2 (20 mL) and extracted twice with water (2 × 10 mL). The CH_2Cl_2 layer was recovered and then filtered to remove any brown insoluble material which may have formed. The CH_2Cl_2 was removed *in vacuo*, and the residue was recrystallized with CH_2Cl_2/hexanes to give 175 mg (74% yield) of green **2a**. A good method for removing the small amount (typically <2%) of **3** has not been found. IR (cm^{-1}): 2507 (ν_{B-H}), 912 ($\nu_{Re=O,sym}$), 823 ($\nu_{Re=O,asym}$). FAB-MS:

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

m/*z* = 466 (M − 1^+). UV−vis [λ_{max}, nm (ϵ)]: 630 (15), 256 (4530). Anal. Calcd for $C_9H_{10}BClN_6O_2Re$: C, 23.17; H, 2.14; N, 18.01. Found: C, 23.48; H, 2.20; N, 17.12.

$(HB(pz)_3)ReO_2(Br)$ (2b). Following the procedure for **2a**, 151 mg of **1b** (0.234 mmol) and 25 mg of pyO (0.262 mmol, 1.12 equiv) gave 88 mg of green **2b** (73%) after recrystallization from CH_2Cl_2/hexanes. As with **2a**, the ∼5% impurity of **3** could not be separated. IR (cm^{-1}): 2518 (ν_{B-H}), 922 ($\nu_{Re=O,sym}$), 829 ($\nu_{Re=O,asym}$). FAB-MS: *m*/*z* = 511 (M^+). Anal. Calcd for $C_9H_{10}BBrN_6O_2Re$: C, 21.16; H, 1.96; N, 16.44. Found: C, 22.07; H, 2.05; N, 16.37.

$(HB(pz)_3)ReO_2(I)$ (2c). Following the procedure for **2a**, 98 mg of **1c** (0.142 mmol) and 15 mg of pyO (0.160 mmol, 1.12 equiv) gave 47 mg of green **2c** (about 50%) after recrystallization in the glovebox from CH_2Cl_2/hexanes. Isolated **2c** contains ∼15% **3** and ∼5% **4c** which could not be separated. IR (cm^{-1}): 2507 (ν_{B-H}), 912 ($\nu_{Re=O,sym}$), 823 ($\nu_{Re=O,asym}$). FAB-MS: *m*/*z* = 559 (M^+).

$[(HB(pz)_3)ReO(Cl)(OSMe_2)][OTf]$ (5a).[6] A sealable NMR tube was charged with 7.2 mg of **1a** (0.012 mmol), Me_2SO (1.3 μL, 0.015 mmol, 1.25 equiv), and 0.4 mL of CD_2Cl_2. The tube was sealed and the contents mixed, with the solution retaining a sky blue color. Solid samples of **5a** (and **5b**) can be obtained by slow crystallization from concentrated NMR-tube reactions containing 20−30 mg of **1a** (or **1b**). ^{1}H NMR (CD_2Cl_2; δ): 8.12, 7.50, 7.48 (each d, 1H, pz), 8.06−8.05 (overlapping d, 3H), 6.66, 6.62, 6.11 (each t, 1H, pz), 3.49, 3.46 (each s, 3H, $S(CH_3)CH'_3$). Similar procedures yield **5b**,**c**. For **5b**, ^{1}H NMR (CD_2Cl_2; δ): 8.16, 8.12, 8.05, 8.03, 7.53, 7.51 (each d, 1H, pz), 6.67, 6.61, 6.11 (each t, 1H, pz), 3.49, 3.47 (each s, 3H, $S(CH_3)CH'_3$). For **5c**, ^{1}H NMR (CD_2Cl_2; δ): 8.34, 8.12, 8.03, 8.01, 7.61, 7.52 (each d, 1H, pz), 6.66, 6.58, 6.10 (each t, 1H, pz), 3.48 (s, 6H, $S(CH_3)_2$).

$(HB(pz)_3)ReO_2(OEt)$ (6). A 100 mL RB flask was charged with a stir bar, 210 mg of **2a** (0.451 mmol), AgOTf (119 mg, 0.468 mmol, 1.04 equiv), and 40 mL of MeCN. The flask was wrapped in foil and the solution stirred for 4 h, resulting in a brown solution with a precipitate. The solution was filtered, LiOEt (140 mg, 2.69 mmol, 5.97 equiv) was added, and the mixture was allowed to stir for 4 h. After the solvent was removed *in vacuo*, the brown residue was taken up in CH_2Cl_2 (20 mL) and filtered. The solution was then fractionally recrystallized multiple times from CH_2Cl_2/hexanes, ultimately yielding 97 mg of a light brown-green solid (∼40% yield). IR (Nujol mull; cm^{-1}): 2497 (ν_{B-H}), 906 ($\nu_{Re=O,sym}$), 814 ($\nu_{Re=O,asym}$). FAB-MS: *m*/*z* = 477 (M^+).

$(HB(pz)_3)ReO_2(OMe)$ (7). Following the procedure for **6**, 102 mg of **2a** (0.219 mmol), 56 mg of AgOTf (0.220 mmol, 1 equiv), and 57 mg of LiOMe (1.50 mmol, 6.8 equiv) gave a brown solid after multiple fractional recrystallizations from benzene/pentane and CH_2Cl_2/pentane. The product contained no significant other rhenium oxo species by IR spectroscopy. IR (Nujol mull; cm^{-1}): 2495 (ν_{B-H}), 908 ($\nu_{Re=O,sym}$), 814 ($\nu_{Re=O,asym}$). FAB-MS: *m*/*z* = 462 (M − 1^+).

Exchange Kinetics for $[(HB(pz)_3)ReO(X)\{OS(CD_3)_2\}][OTf]$ (5a−c-d_6) and $S(CH_3)_2$. For each compound NMR tubes were prepared using ∼10 μmol of **5**, 1.2 equiv of $(CD_3)_2SO$, 0.5 μL of $(Me_3Si)_2O$, and 0.50 mL of CD_2Cl_2. On the vacuum line, ∼60 equiv of $(CH_3)_2S$ was vacuum transferred in using a gas addition bulb. The tube was sealed with a torch and the contents thawed and mixed. The ^{1}H NMR spectrum was taken periodically, and protio incorporation was noted. The maximum rates for Me_2SO oxidation to Me_2SO_2 under these conditions (using protio-Me_2SO) were estimated on the basis of the formation of less than 1% possible formation of Me_2SO_2 compared to the rhenium concentration in the time frame prior to large decomposition of the sulfoxide adduct species **5**.

X-ray Structure Determination of $(HB(pz)_3)ReO_2Cl$ (2a). Vapor diffusion of pentane to a solution of **2a** in CH_2Cl_2 at ca. 24 °C over 5 d deposited emerald green rhombohedral crystals. A crystal was glued to the tip of a glass fiber in air and data were collected on an Enraf-Nonius CAD4 diffractometer (Table 1). A semi-empirical (ψ-scan) absorption correction was applied and the structure was solved by direct methods using the SHELXTL PC program, with scattering factors and anomalous dispersion terms taken from the standard compilation.[35] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions. There was no evidence of the positional or compositional oxo/chloro disorder that is common for such molecules, though some disorder is difficult to rule out (see text). The final difference map contains large residuals close to the rhenium (+6.35 and −10.48 e Å^{-3}), perhaps reflecting deficiencies in the absorption correction.

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Supporting Information Available: Tables of data collection and refinement details, atom positional and thermal parameters, and bond distances and angles for the structure of $(HB(pz)_3)ReO_2Cl$ (**2a**) and a reproduction of the EPR spectrum of **2a** (9 pages). Ordering information is given on any current masthead page.

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(35) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974.