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Oxygen Atom Transfer between Rhenium, Sulfur, and Phosphorus. Characterization and Reactivity of $Re(O)Cl_3(Me_2S)(OPPh_3)$ and $Re(O)Cl_3(CNCMe_3)_2$

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$Re(O)Cl_3(PPh_3)_2$ (I) reacts with Me_2SO to form $OPPh_3$ and $Re(O)Cl_3(Me_2S)(OPPh_3)$ (II), not "$Re(O)Cl_3(Me_2SO)(PPh_3)$" as had been previously reported. Compounds I and II are catalysts for oxygen atom transfer from Me_2SO to PPh_3. The mechanism of these oxygen atom transfer reactions has been studied with oxygen-18 labeling experiments. The rhenium oxo group does not appear to be involved; rather, the rhenium center acts as a Lewis acid activator for a Me_2SO ligand. The rhenium oxo group does, however, exchange oxygen atoms with $Me_2S^{18}O$, probably by a similar mechanism. Compound II is an excellent starting material for compounds of the form $Re(O)Cl_3L_2$, with L = isonitriles, phosphines, bipyridine, etc. The compounds $Re(O)Cl_3(CNR)_2$ (R = CMe_3 (IV), $CHMe_2$, C_6H_{11}) are rare examples of high-valent isonitrile complexes. An X-ray crystal structure of IV has been solved: space group $P2_1/c$, a = 6.003 (1) Å, b = 19.122 (3) Å, c = 14.625 (2) Å, β = 101.26 (1)°, Z = 4; the structure was refined to final residuals R = 0.020 and R_w = 0.023.

Oxidation/reduction reactions can be classified as either electron-transfer or atom-transfer processes, the latter being one type of inner-sphere electron-transfer reaction.[3] Atom-transfer reactions involving univalent groups have been intensively studied, but there is much less mechanistic understanding of reactions that involve transfer of a divalent group such as an oxygen atom.[4] Oxygen atom transfer plays a very important role in the redox chemistry of compounds with multiple bonds to oxygen, from metal–oxo complexes to non-metal oxides.[4-10] For instance, the reduction of perchlorate and perrhenate ions invariably occurs with loss of at least one oxo group, frequently by transfer to an oxygen atom acceptor such as a metal ion or a phosphine.[4-6] Oxygen atom transfer can also occur between two ligands coordinated to a metal center without involving a metal oxo group. Examples range from the oxidation of olefins, phosphines, and CO by coordinated nitro groups to the conversion of a metal–methylene complex to a formaldehyde compound by iodosylbenzene.[9] Oxygen atom transfer reactions have received renewed attention in the last few years because of their possible importance in biological systems such as the molybdoenzyme sulfite oxidase and the cytochrome P-450 enzymes.[7,11-13] Very reactive model systems for cytochrome P-450 and related enzymes have been generated by oxygen atom transfer to metalloporphyrins from iodosylbenzene, hypochlorite, or other species.[13] We have recently discovered a system in which oxygen atom transfer reactions between dimethyl sulfoxide, triphenylphosphine, and rhenium complexes seem to be particularly facile; this report includes mechanistic studies, syntheses of new compounds, and an X-ray structure determination.

Experimental Section

Syntheses were performed by using standard vacuum-line techniques except as indicated. Benzene, toluene, and triethylamine were purified by vacuum transfer from CaH_2, THF and diethyl ether were purified by vacuum transfer from Na/benzophenone, and methylene chloride was purified by vacuum transfer from Linde 4-Å sieves. Other solvents were reagent grade and were used without purification. With the exception of III and VIII, all of the rhenium(V) complexes prepared are stable to prolonged contact with air, and III can be handled in air for limited periods. NMR spectra were obtained on Varian CFT-20 or Bruker WM500 spectrometers. Chemical shifts (δ) are in ppm downfield from tetramethylsilane. IR spectra were obtained as Nujol mulls on a Perkin-Elmer 283 spectrophotometer and are reported in reciprocal centimeters. UV/vis spectra were recorded on a Hewlett-Packard 8450A spectrophotometer. Mass spectra were recorded on a Hewlett-Packard 5985 GC/MS system.

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Compounds I,[14] II,[15] III,[16] and $Me_2S^{18}O$ (usually 50% enrichment)[17] were prepared by literature methods. III was also prepared by starting from II as described below. Oxygen-18 enrichment of $OPPh_3$ was determined by mass spectral analysis comparing the relative abundance of m/e 277 and 279 after correcting m/e 279 by subtracting 6% of the relative abundance at m/e 277. ^{18}O enrichment of II was assessed qualitatively by IR spectroscopy, comparing the relative areas under the appropriate absorbances, or quantitatively by mass spectroscopy of $OPPh_3$ via eq 11 and 12; the error in these measurements is estimated to be ±5% (IR) and ±1% (MS). The values in eq 15 and 16 were determined by mass spectroscopy. Turnover numbers for catalytic reactions (eq 5 and 6) were measured by using NMR spectroscopy and are based on the total number of moles of rhenium.

$^{18}OPPh_3$. PPh_3 (0.302 g) was dissolved in 15 mL of CH_2Cl_2 under 1 atm of Cl_2 (Matheson) and stirred for 20 min. The Cl_2 and 5 mL of CH_2Cl_2 were removed, 15 mL of Et_2O was added, and 0.328 g of white Cl_2PPh_3 was filtered off. $H_2{}^{18}O$ (0.016 mL) in 2 mL of THF was added dropwise to a solution of Cl_2PPh_3 (0.234 g) in 30 mL of THF and 0.23 mL of Et_3N, and the reaction mixture was stirred for 1 h. Solvents were reduced to 15 mL and white Et_3NHCl was filtered off and washed with 5 mL of THF in the air. The combined filtrates were evaporated to dryness, yielding 0.154 g (78%) of white $^{18}OPPh_3$ (enrichment 86%).

Re(^{18}O)Cl$_3$(Me$_2$S)(OPPh$_3$). $Me_2S^{18}O$ (enrichment 50%) (0.035 mL) was added via syringe to a suspension of II (0.122 g) in 12 mL of toluene, and the mixture was stirred under 1 atm of HCl (Matheson) for 24 h. Filtration in the air and washing with acetone (1 × 2 mL) and Et_2O (1 × 10 mL) gave 0.105 g (86%) of light green powder with roughly 12% ^{18}O enrichment in the oxo ligand. Higher enrichments but lower yields were obtained in CH_2Cl_2 without HCl. IR: 992 cm^{-1} ($Re^{16}O$); 945 cm^{-1} ($Re^{18}O$).

Re(^{18}O)Cl$_3$(Me$_2$S)(^{18}OPPh$_3$). $Me_2S^{18}O$ (enrichment 50%) (0.1 mL) and I (1.05 g) were suspended in 80 mL benzene and stirred under 1 atm of HCl for 2 days. Filtration in the air and washing with Et_2O (2 × 10 mL) and acetone (1 × 5 mL) gave 0.657 g (80%) of light green powder. The product was predominantly ^{18}O enriched (45%) in the $OPPh_3$ ligand and slightly enriched in the rhenium oxo group (11%). IR: 1140 cm^{-1} ($P^{16}O$); 1062 cm^{-1} ($P^{18}O$).

Re(O)Cl$_3$(Me$_2$S)(^{18}OPPh$_3$). $^{18}OPPh_3$ (0.012 g) and II (0.053 g) were suspended in 12 mL of benzene and stirred under 1 atm of HCl for 3 days. Filtration in the air and washing with petroleum ether (2 × 3 mL) and acetone (3 × 3 mL) gave 0.030 g (57%) of light green powder. The product was roughly 49% ^{18}O enriched in the $OPPh_3$ ligand.

Re(O)Cl$_3$[P(*p*-Tol)$_3$]$_2$. A suspension of II (0.102 g) and P(p-Tol)$_3$ (*p*-Tol = *p*-tolyl) (0.120 g; Strem) in 8 mL of THF was stirred for 21 h. After removal of 4 mL of THF and addition of 3 mL of pentane, the solution was filtered, and the solids were washed with pentane (2 × 2 mL) and ethanol (1 × 5 mL). *Yield*: 0.124 g (86%) of yellow powder. ^1H NMR (CD_2Cl_2): δ 2.39 ($C_6H_4CH_3$), 7.24 (d, $^3J_{HH}$ = 8 Hz), 7.59 (m, $C_6H_4CH_3$). IR: 1197, 1092, 967 (ReO), 805 cm^{-1}.

Re(O)Cl$_3$(bpy).[16] A suspension of II (0.084 g) and 2,2′-bipyridine (0.024 g, Strem) in 10 mL of THF was stirred for 6 h. Filtration and washing with diethyl ether (3 × 5 mL) gave 0.049 g (77%) of yellow powder.

Re(O)Cl$_3$(PPh$_3$)(OPPh$_3$) (III).[16] A suspension of II (0.093 g) and LiCl (0.020 g) in 8 mL of THF was stirred until yellow, and then PPh_3 (0.037 g) was added and stirring was continued for 2 h. Removal of almost all of the solvent left a green slurry, which was recrystallized from CH_2Cl_2 and diethyl ether to yield 0.100 g (82%) of light green plates of III.

Re(O)Cl$_3$(CNCMe$_3$)$_2$ (IV). *tert*-Butyl isocyanide (0.25 g, Strem) was added to a suspension of II (0.30 g) in 5 mL of benzene. After the mixture was stirred for 3 h, 10 mL of hexane was added and the solids were filtered off. Recrystallization from methylene chloride/hexane gave 0.183 g (83%) of blue IV. Anal. Calcd for $C_{10}H_{18}Cl_3ON_2Re$: C, 25.30; H, 3.82; N, 5.90. Found: C, 25.51, 25.66; H, 3.91, 3.92; N, 5.81, 5.84. ^1H NMR (CD_2Cl_2): δ 1.74 (s). ^{13}C NMR (CD_2Cl_2): δ 108.7 (br, *C*N-*t*-Bu), −1.35 (s, CN*C*Me$_3$), 30.79 (q, $^1J_{CH}$ = 130 Hz, C(*C*H$_3$)). IR: 2239 s, 2226 s (CN), 1232, 1185, 976 s (ReO), 722, 318 cm^{-1}. UV/vis [λ_{max}, nm (ε)]: 590 (44), 262 (850).

Re(O)Cl$_3$(CNCHMe$_2$)$_2$ (V). V was prepared in the same way as IV above: II (0.50 g), 10 mL of benzene, and isopropyl isocyanide (0.25 g, Strem) gave 0.30 g (87%) of blue V. Anal. Calcd for $C_8H_{14}Cl_3ON_2Re$: C, 21.51; H, 3.16; N, 6.27. Found: C, 21.53; H, 3.33; N, 6.25. ^1H NMR (CD_2Cl_2): δ 5.17 (sept, $^3J_{HH}$ = 7 Hz, C*H*Me$_2$), 1.65 (d, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_2Cl_2): δ 109.2 (br, *C*N-*i*-Pr), 51.61 (d $^1J_{CH}$ = 143 Hz, *C*HMe$_2$), 23.69 (q, $^1J_{CH}$ = 130 Hz, CH(*C*H$_3$)$_2$). IR: 2248 s, 2235 s (CN), 1335, 1169, 1133, 1114 s, 985 s, (ReO), 904, 783, 722.

Re(O)Cl$_3$(CNC$_6$H$_{11}$)$_2$ (VI). Cyclohexyl isocyanide (0.092 g, Strem) was added to a suspension of 0.200 g of II in 10 mL of THF in a fume hood. After the mixture was stirred for 1 h, half of the solvent was removed and insoluble impurities were filtered off. Pentane was added, and the product was filtered off and washed with ether and petroleum ether to yield 0.094 g (58%) of blue powder (VI). Anal. Calcd for $ReOCl_3N_2C_{14}H_{22}$: C, 31.91; H, 4.21; N, 5.32. Found: C, 31.98; H, 4.05; N, 5.31. ^1H NMR ($CDCl_3$): δ 5.01 (m, C*H*(CH$_2$)$_5$), 2.07, 1.99, 1.87, 1.57 (m, CH(C*H*$_2$)$_5$). IR: 2245, 2230 s (CN), 1360, 1348, 1322, 1124, 980 s (ReO), 898, 780 cm^{-1}. UV/vis [λ_{max}, nm (ε)]: 582 (7), 264 (7000).

Re(O)Br$_3$(CNCMe$_3$)$_2$ (VII). Following the procedure for IV above, with Re(O)Br$_3$(Me$_2$S)OPPh$_3$ (0.203 g), CN-*t*-Bu (0.082 g, Aldrich), and 10 mL of benzene, gave, after recrystallization from THF/pentane, 0.119 g (75%) of a dark green product, VII. [Re(O)Br$_3$(Me$_2$S)OPPh$_3$ is formulated in this fashion (and not as "Re(O)Br$_3$(Me$_2$SO)PPh$_3$"[15]) because it is chemically and spectroscopically similar to II.] ^1H NMR ($CDCl_3$): δ 1.73. IR: 2240, 2235 s (CN), 1232, 1185, 990 s (ReO), 727, 239 cm^{-1}. UV/vis [λ_{max}, nm (ε)]: 606 (80), 305 (6100).

Re(O)Cl$_2$(OMe)(CNCMe$_3$)$_2$ (VIII). Compound IV (0.134 g) was dissolved in MeOH (11 mL) and stirred for 20 h. After removal of all but 4 mL of solvent, diethyl ether (5 mL) was added and the mixture was cooled. Filtration gave 0.013 g (13%) of red powdery VIII. ^1H NMR ($CDCl_3$): δ 3.48 (s, OC*H*$_3$), 1.72 (s, C(C*H*$_3$)$_3$). IR: 2240 s, 2222 s (CN), 1190, 1098, 948, 940 (ReO), 720.

ReCl$_3$(CNCMe$_3$)$_2$PPh$_3$. PPh_3 (0.10 g) was added to a solution of IV (0.10 g) in 3 mL of CH_2Cl_2. After the mixture was stirred for 1 h, hexane (14 mL) was added and the resulting yellow product filtered off. ^1H NMR (C_6D_6): δ 13.42 (dd, *J* = 13.7 Hz), 7.95 (td, *J* = 3.8 Hz), 7.61 (m, P(C$_6$H$_5$)$_3$), 9.11 (s, CNC(C*H*$_3$)$_3$), 7.24 (s CNC(C*H*$_3$)$_3$). IR: 2150 s, 2095 s (CN), 1158 s, 1116, 750 s, 689 cm^{-1}.

X-ray Structure of Re(O)Cl$_3$(CNCMe$_3$)$_2$ (IV). A blue crystal of $ReOCl_3(CNCMe_3)_2$ (IV), grown by slowly cooling a dichloromethane/hexane solution, was fixed in a glass capillary under dinitrogen atmosphere. The capillary was mounted on a Syntex P3 diffractometer and cooled to −100 °C. After the crystal was shown to be suitable (ω-scan average peak widths of 0.23° at half-height), the space group and the approximate cell parameters were determined. Final parameters, refined by using 50 computer-centered reflections from diverse regions of reciprocal space, are shown in Table I, as are other crystallographic data.

Intensity data were collected by using the ω-scan technique (variable scan range 4.0–10.0° min^{-1}; scan time = total background time; 1.0° scan range). To verify sample integrity, three standard reflections were monitored after each 200 reflections; no signal decomposition was observed. An empirical absorption correction, generated from the intensities of several reflections measured at 10° increments about the diffraction vector, was applied to the data. The data were processed with the use of counting statistics and a *p* value of 0.02 to derive standard deviations.[18]

Table I. Summary of X-ray Diffraction Data

complex	$Re(O)Cl_3(CNCMe_3)_2$ (IV)
formula	$C_{10}H_{18}Cl_3N_2ORe$
fw	474.83
space group	$P2_1/c$
a, Å	6.003 (1)
b, Å	19.122 (3)
c, Å	14.625 (2)
β, deg	101.26 (1)
V, Å^3	1646.5 (8)
Z	4
ρ_{calcd}, g cm^{-3}	1.915
cryst dimens, mm	0.30 × 0.33 × 0.45
temp, °C	−100
radiation	Mo Kα (0.710 69 Å) from graphite monochromator
μ, cm^{-1}	79.62
2θ limits, deg	4–55
transmissn factors	0.784–0.995; average 0.863
total no. of unique observns	4248
data $F_o^2 > 3\sigma(F_o)^2$	3055
final no. of variables	154
R	0.020
R_w	0.023
goodness of fit	1.40

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Table II. Positional Parameters and Standard Deviations for $Re(O)Cl_3(CNCMe_3)_2$ (IV)[a]

Atom	x	y	z	B(A2)
RE	0.23884(2)	0.13228(1)	0.20246(1)	1.432(2)
CL(1)	0.1064(2)	0.05922(5)	0.31743(7)	2.71(2)
CL(2)	0.0292(2)	0.22665(5)	0.24690(7)	2.56(2)
CL(3)	-0.0867(2)	0.10172(7)	0.09263(8)	3.11(2)
O	0.3977(5)	0.1726(2)	0.1365(2)	2.42(6)
N(1)	0.4545(6)	-0.0176(2)	0.1705(2)	2.12(7)
N(2)	0.6065(6)	0.1576(2)	0.3912(2)	2.06(6)
C(1)	0.3812(7)	0.0362(2)	0.1800(3)	1.91(7)
C(2)	0.4845(7)	0.1497(2)	0.3221(3)	1.83(7)
C(10)	0.5550(7)	-0.0873(2)	0.1717(3)	2.22(8)
C(11)	0.3608(9)	-0.1395(2)	0.1663(4)	3.4(1)
C(12)	0.6651(8)	-0.0935(3)	0.0868(4)	3.9(1)
C(13)	0.7232(9)	-0.0931(3)	0.2625(4)	4.2(1)
C(20)	0.7371(7)	0.1618(2)	0.4872(3)	2.14(8)
C(21)	0.9590(7)	0.1995(3)	0.4851(3)	3.0(1)
C(22)	0.5955(8)	0.2037(3)	0.5424(3)	3.7(1)
C(23)	0.778(1)	0.0871(3)	0.5210(4)	4.3(1)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Selected Bond Lengths (Å) and Angles (deg) in $Re(O)Cl_3(CNCMe_3)_2$ (IV)

Re–O	1.671 (2)	Re–Cl(1)	2.436 (1)
Re–C(1)	2.079 (3)	Re–Cl(2)	2.363 (1)
Re–C(2)	2.083 (3)	Re–Cl(3)	2.348 (1)
C(1)–N(1)	1.138 (4)	C(2)–N(2)	1.136 (4)
N(1)–C(10)	1.463 (4)	N(2)–C(20)	1.471 (4)
O–Re–Cl(1)	164.33 (9)	Cl(1)–Re–Cl(2)	89.13 (3)
O–Re–Cl(2)	101.62 (9)	Cl(1)–Re–Cl(3)	89.38 (4)
O–Re–Cl(3)	102.27 (9)	Cl(1)–Re–C(1)	78.56 (10)
O–Re–C(1)	91.0 (1)	Cl(1)–Re–C(2)	77.59 (9)
O–Re–C(2)	91.1 (1)	Cl(2)–Re–Cl(3)	87.79 (3)
Cl(3)–Re–C(1)	89.14 (9)	Cl(2)–Re–C(1)	167.35 (10)
Cl(3)–Re–C(2)	166.51 (10)	Cl(2)–Re–C(2)	88.52 (9)
C(1)–Re–C(2)	91.7 (1)		
Re–C(1)–N(1)	177.1 (3)	Re–C(2)–N(2)	174.7 (3)
C(1)–N(1)–C(10)	172.4 (3)	C(2)–N(2)–C(20)	170.8 (4)

The solution and refinement of the structure were carried out on a PDP-11 computer using local modification of the SDP-Plus program package supplied by the Enraf-Nonius Corp. The rhenium atom position was obtained in an origin-removed Patterson synthesis, and the remaining non-hydrogen atoms were located by the usual combination of Fourier synthesis and full-matrix least-squares refinements. In the refinements the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are respectively the observed and calculated structure amplitudes and where $w = 1/\sigma^2(F_o)$. The atomic scattering factors and anomalous dispersion terms were taken from the standard compilations.[19] All 18 hydrogen atoms were found, placed in idealized positions with a C–H distance of 0.95 Å, and included in subsequent refinements as fixed contributions (B_H = 4.0 Å^2). Positional and equivalent isotropic thermal parameters of the non-hydrogen atoms are listed in Table II; selected bond lengths and angles are given in Table III. Tables of anisotropic thermal parameters and idealized hydrogen atom positions (Tables V and VI) are available as supplementary material, as is a listing of observed and calculated structure factor amplitudes (Table VII). The final agreement indices, R and R_w, are shown in Table I, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$. The largest peak remaining in a final difference Fourier synthesis, corresponding to 0.72 e Å^{-3}, is associated with the metal atom.

(19) *International Tables of X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Tables 2-2B, 2.3.1.

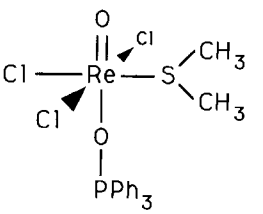


Figure 1. Line drawing of $Re(O)Cl_3(Me_2S)(OPPh_3)$ (II) based on a preliminary X-ray structural study.[20]

Results

The reaction of Me_2SO with $Re(O)Cl_3(PPh_3)_2$ (I)[14] in the presence of acid was originally reported to give a Me_2SO complex, "$Re(O)Cl_3(Me_2SO)(PPh_3)$".[15] However, a preliminary X-ray crystal structure of this material,[20] as well as its chemical and spectroscopic properties, shows it to be a complex containing dimethyl sulfide and triphenylphosphine oxide, $Re(O)Cl_3(Me_2S)(OPPh_3)$ (II; Figure 1, eq 1). Transfer of oxygen atoms

$$\underset{\text{I}}{Re(O)Cl_3(PPh_3)_2} + 2Me_2SO \xrightarrow[C_6H_6]{HCl} \underset{\text{II}}{Re(O)Cl_3(Me_2S)(OPPh_3)} + Me_2S + OPPh_3 \quad (1)$$

from Me_2SO to both of the PPh_3 ligands of I has occurred in the reaction, and therefore 2 equiv of Me_2SO per rhenium are required. The Me_2S and $OPPh_3$ byproducts have been identified by NMR and mass spectroscopy; no PPh_3 has been detected. The original synthesis of II required either aqueous hydrochloric acid or HCl gas, but we find that HCl is not needed if a stoichiometric amount of Me_2SO is used. However, yields of II are higher (95% vs. 75%) when HCl is present. Compound II is not formed by adding Me_2S and $OPPh_3$ to I.

The synthesis of II using oxygen-18 enriched Me_2SO (Me_2S^*O) yields a product isotopically enriched in both the oxo and triphenylphosphine ligands, although primarily in the latter (eq 2, see Experimental Section and below). Reaction of isolated II with Me_2S^*O results in exchange of ^{18}O only with the rhenium–oxo ligand (eq 3), a reaction that can be used to prepare specifically labeled II. Exchange occurs with or without added HCl and will also occur with $H_2{}^{18}O$/HCl. HCl seems to both solubilize II and catalyze the exchange so that it is faster than a competing reaction of II with Me_2SO that forms a mixture of products. The exchange reaction may be responsible for the partial enrichment of the oxo ligand found in reaction 2: II is probably formed unenriched at the oxo site and subsequently undergoes exchange with the excess Me_2S^*O present (see Discussion).

$$\underset{\text{I}}{Re(O)Cl_3(PPh_3)_2} + 2Me_2S^*O \rightarrow \underset{\text{II}}{Re(^*O)Cl_3(Me_2S)(^*OPPh_3)} \quad (2)$$

$$\underset{\text{II}}{Re(O)Cl_3(Me_2S)(OPPh_3)} + Me_2S^*O \rightarrow \underset{\text{II}}{Re(^*O)Cl_3(Me_2S)(OPPh_3)} \quad (3)$$

A double-label experiment indicates that a great deal of exchange occurs in these reactions: when $Re(^*O)Cl_3(Me_2S)(OPPh_3)$ is suspended in toluene with Me_2SO-d_6, complete scrambling of the isotopic labels is observed in the Me_2S and Me_2SO products (eq 4). The scrambling of the deuterium labels results from the

$$Re(^*O)Cl_3(Me_2S)OPPh_3 + Me_2SO\text{-}d_6 \xrightarrow[C_7H_8]{} Me_2SO\text{-}h_6,\text{-}d_6 + Me_2S^*O\text{-}h_6,\text{-}d_6 + Me_2S\text{-}h_6,\text{-}d_6 \quad (4)$$

(20) The diffraction data are not of sufficient quality to distinguish between space groups *Pnma* and *Pna*2_1. Preliminary structural refinement has been carried out in *Pnma* [a= 8.844 (7) Å, b = 14.273 (4) Å, c = 18.453 (4) Å, Z = 4] to final residuals R = 0.080, R_w = 0.074, and goodness-of-fit = 2.40. Stenkamp, R. E.; Bryan, J. C.; Mayer, J. M., work in progress.

exchange of oxygen between Me_2SO and Me_2S, which is efficiently catalyzed by II at ambient temperature (eq 5).

$$Me_2SO\text{-}d_6 + Me_2S \overset{II}{\rightleftharpoons} Me_2S\text{-}d_6 + Me_2SO \quad (5)$$

Compound II also catalyzes transfer of an oxygen atom from Me_2SO to PPh_3 (eq 6). $Re(O)Cl_3(PPh_3)_2$ (I) and $Re(O)Cl_3(PPh_3)(OPPh_3)$ (III)[16] also act as catalysts for this reaction. The catalytic reactions (eq 5 and 6) proceed rapidly in a variety of solvents including benzene, methylene chloride, and THF, with rates from roughly 0.3 to 3 turnover/min; the fastest reactions were observed in benzene with II as the catalyst. Me_2SO and PPh_3 are unreactive in these solvents in the absence of catalysts.[21]

$$Me_2SO + PPh_3 \xrightarrow{II} Me_2S + OPPh_3 \quad (6)$$

Monitoring reaction 6 in CH_2Cl_2 shows little change in the visible spectrum (350–800 nm) over the course of the reaction. The spectra all contain a broad weak band centered roughly at 715 nm, which is also observed in the spectra of pure I, II, and III (ϵ = 30–50). Catalytic activity seems to slowly decrease with time. The rhenium-containing material recovered from the catalytic reactions is not identical with II, but its spectroscopic data are consistent with mixtures of oxorhenium(V) trichloride complexes, $Re(O)Cl_3LL'$ (L, L' = PPh_3, $OPPh_3$, Me_2S). The recovered material is still an active catalyst, having roughly the same activity as the solution prior to isolation.

These exchange and catalytic reactions indicate that II is quite reactive despite its very limited solubility in common solvents. In chloroform and methylene chloride the Me_2S ligand is labile at ambient temperatures: complete equilibration of $Me_2S\text{-}h_6$ with $Re(O)Cl_3(Me_2S\text{-}d_6)(OPPh_3)$ requires only a few minutes, although the exchange is slow on the NMR time scale. The $OPPh_3$ ligand is less labile, with only partial exchange observed between $OPPh_3$ and $Re(O)Cl_3(Me_2S)(*OPPh_3)$ in methylene chloride in 1 h. This reaction has been used to prepare II specifically ^{18}O labeled in the triphenylphosphine oxide ligand (eq 7).

$$\underset{II}{Re(O)Cl_3(Me_2S)OPPh_3} + *OPPh_3 \rightarrow \underset{II}{Re(O)Cl_3(Me_2S)(*OPPh_3)} \quad (7)$$

Reactions of II with donor ligands usually lead to substitution of both Me_2S and $OPPh_3$: for instance PPh_3, P(*p*-Tol)$_3$, and bipyridine yield I, $Re(O)Cl_3[P(p\text{-}Tol)_3]_2$, and $Re(O)Cl_3(bpy)$,[16] respectively (eq 8). Reaction of $Re(*O)Cl_3(Me_2S)(OPPh_3)$ with

$$\underset{II}{Re(O)Cl_3(Me_2S)(OPPh_3)} + 2L \xrightarrow{THF} Re(O)Cl_3L_2 + Me_2S + OPPh_3 \quad (8)$$

$$L = PPh_3, P(p\text{-}Tol)_3;\ L_2 = bpy$$

PPh_3, P(p-Tol)$_3$, or bpy does not result in a measurable loss of the ^{18}O label from the rhenium oxo group. The reaction of II with tetraethylammonium chloride gives $[Et_4N]_2[Re(O)Cl_5]$[15] (eq 9).

$$\underset{II}{Re(O)Cl_3(Me_2S)(OPPh_3)} + 2Et_4NCl \xrightarrow{CH_2Cl_2} [Et_4N]_2[Re(O)Cl_5] + Me_2S + OPPh_3 \quad (9)$$

Reaction with LiCl in THF, however, gives a yellow solution believed to contain $[Re(O)Cl_4(OPPh_3)]^-$ by analogy with other $Re(O)X_4(L)^-$ salts[6a] and because the addition of PPh_3 gives III (eq 10).

$$\underset{II}{Re(O)Cl_3(Me_2S)(OPPh_3)} + LiCl \xrightarrow{THF} Li[Re(O)Cl_4(L)] + Me_2S$$

$$Li[Re(O)Cl_4(L)] \xrightarrow{PPh_3} \underset{III}{Re(O)Cl_3(PPh_3)(OPPh_3)} \quad (10)$$

(21) Slow reaction is observed in chloroform, if it has not been dried and degassed. This could be due to traces of HCl in the solvent.

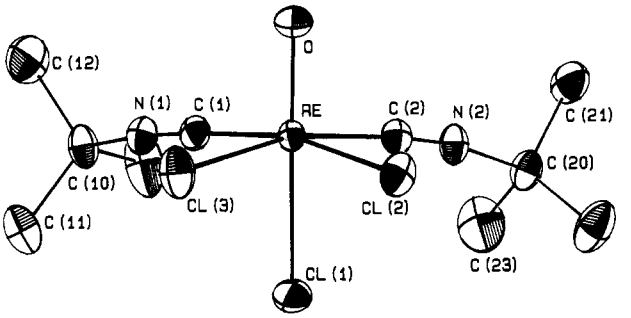


Figure 2. Perspective drawing of $Re(O)Cl_3(CNCMe_3)_2$ (IV). Hydrogen atoms have been omitted for clarity.

Isonitrile ligands will also displace the Me_2S and $OPPh_3$ ligands in II to form deep blue bis(isocyanide) complexes (eq 11). A

$$\underset{II}{Re(O)Cl_3(Me_2S)(OPPh_3)} + 2CNR \xrightarrow{THF} Re(O)Cl_3(CNR)_2 + Me_2S + OPPh_3 \quad (11)$$

R = CMe_3 (IV)
R = $CHMe_2$ (V)
R = c-C_6H_{11} (VI)

green bromide derivative, $Re(O)Br_3(CNCMe_3)_2$ (VII), has also been isolated, starting from $Re(O)Br_3(Me_2S)(OPPh_3)$.[15] The syntheses are successful for isonitriles with large alkyl substituents (*tert*-butyl, isopropyl, and cyclohexyl), but an unidentified mixture of products is obtained by using *n*-butyl isocyanide. The new compounds have been characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopies as well as analytical data; the X-ray crystal structure of IV has also been determined (Figure 2). Compounds IV–VII are among the few examples of high-valent isonitrile complexes, such as $[Mo(O)Cl(CNCMe_3)_4]^+$ and $Re(NC_6H_4Me)Cl_3(CNC_6H_{11})_2$.[22] Isonitrile ligands appear to bind most strongly to metals in low (0 to +2) oxidation states.[5,23]

Compound IV is insoluble in hydrocarbon solvents but very soluble in THF and chlorinated solvents. Unlike I–III, IV is rapidly reduced under mild conditions by triphenylphosphine to form $OPPh_3$ (eq 12). The paramagnetic rhenium(III) product

$$\underset{IV}{Re(O)Cl_3(CNCMe_3)_2} + 2PPh_3 \xrightarrow{THF} ReCl_3(CNCMe_3)_2(PPh_3) + OPPh_3 \quad (12)$$

has been tentatively identified as $ReCl_3(CNCMe_3)_2PPh_3$ by its ^1H NMR and IR spectra although it has not been isolated in pure form. The related reaction with $PMePh_2$ gives $OPMePh_2$ and diamagnetic $ReCl_3(CNCMe_3)_2(PMePh_2)_2$ (eq 13), identified by

$$\underset{IV}{Re(O)Cl_3(CNCMe_3)_2} + 3PMePh_2 \xrightarrow{THF} ReCl_3(CNCMe_3)_2(PMePh_2)_2 + OPMePh_2 \quad (13)$$

comparison with a sample prepared from $ReCl_3(PMePh_2)_3$ and $CNCMe_3$.[24] Reactions 11 and 12 have been used to measure the percent ^{18}O enrichment in II, by first converting II to IV and analyzing the $OPPh_3$ formed by mass spectroscopy and then reacting IV with PPh_3 to give a second batch of phosphine oxide. The first sample of $OPPh_3$ gives the enrichment of the phosphine oxide ligand in II; the second sample gives the enrichment of the oxo ligand.

Compound IV is inert to a variety of electrophiles and weak nucleophiles; no reaction is observed with dimethylamine, 2-propanol, norbornene, aqueous HCl (12 M), MeI, and $[Me_3O]BF_4$ under mild conditions. With more robust reagents such as HCl

(22) Novotny, M.; Lippard, S. J. *Inorg. Chem.* **1974**, *13*, 828–831. La Monica, G.; Cenini, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1145. Other high-valent isocyanide complexes: Freni, M.; Roniti, P. *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1973**, *55*, 708. Guy, J. T., Jr.; Bennett, D. W. *Inorg. Chim. Acta* **1985**, *96*, L83–L85. Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Nielson, A. J.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1983**, 2651–2656. Lam, C. T.; Lewis, D. L.; Lippard, S. J. *Inorg. Chem.* **1976**, *15*, 989–991.

(23) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209–310. Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193–233.

(24) Tulip, T. H., unpublished results.

in THF, triflic acid, LiMe, $ZnEt_2$, and NaOMe, reaction occurred but no characterizable product could be obtained. In methanol, IV is cleanly converted to a methoxy complex (VIII) (eq 14).

$$\underset{\text{IV}}{Re(O)Cl_3(CNCMe_3)_2} + MeOH \rightarrow \underset{\text{VIII}}{Re(O)(OMe)Cl_2(CNCMe_3)_2} + HCl \quad (14)$$

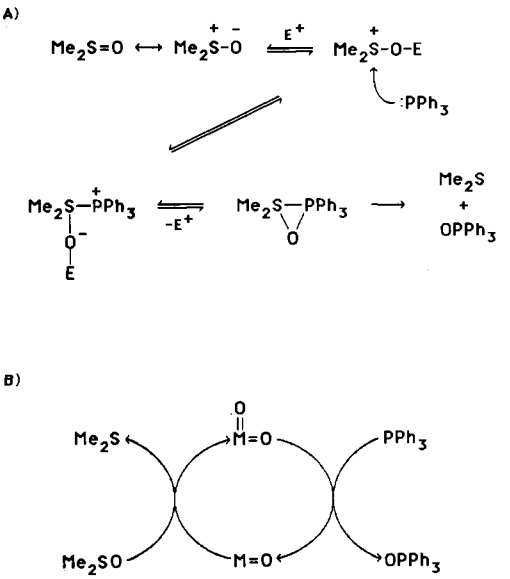
Spectroscopic data for VIII suggest a structure with trans oxo and methoxide ligands. Replacement of a halide ligand trans to an oxo group by an alkoxide is a common reaction for rhenium(V) oxo compounds, probably due to the strong trans labilizing power of the oxo ligand.[6a,25] The Re=O stretching frequency in VIII is significantly lower than that of IV (948, 940 cm^{-1} in VIII; 976 cm^{-1} in IV), due to competition between O and OMe ligands for π bonding with the rhenium. A band at 1098 cm^{-1} in the spectrum of VIII not found in spectra of IV is assigned to ν(C—O) of the methoxide ligand. The IR bands due to the isonitrile stretching modes are very similar for IV and VIII, indicating that the cis rearrangement of isonitrile ligands in IV is maintained in VIII.

X-ray Crystal Structure of $Re(O)Cl_3(CNCMe_3)_2$ (IV). The crystal structure of IV (like II[20]) contains isolated molecules with octahedral coordination about the rhenium center (Figure 2). Complex IV adopts a facial geometry with both isonitrile ligands cis to the oxo group, while II has meridonal stereochemistry with the Me_2S ligand cis to oxo. It is interesting to note that in oxo, imido, and nitrido compounds "soft" and/or π-acid ligands almost invariably lie cis to the multiply bonded ligand. This general rule appears to hold for isonitrile, carbonyl, olefin, acetylene, thioether, and often phosphine ligands.[18,22,25b,26-29] The origin of this effect seems to be the dominant electronic influence of the multiply bonded ligand, which forces the metal nonbonding d electrons to lie in the plane perpendicular to the M–O or M–N bond axis.[29] Thus the cis position is preferred for a π-acid ligand; the Lewis acidity of the metal center may be the most "soft" in this position as well.

The cis chloride ligands in IV are significantly bent away from the oxo group (∠ O–Re–Cl = 101.6, 102.3 (1)°), while the isonitrile ligands lie almost perpendicular to the metal–oxo bond (∠ O–Re–C = 91.0, 91.1 (1)°). This pattern, which is typical of oxo compounds,[6a,26,28] appears to be due both to the electronic factors described above and to sizable steric interactions with the oxo ligand.[30] The geometries of I, II, and IV are (not including the oxo ligand) meridonal–trans, meridonal–cis, and facial, suggesting that the arrangement of the halide ligands is not of great importance. The trans structure of I is probably the result of steric interactions between the triphenylphosphine ligands.[25a,27] The facile interconversion of compounds I, II, and IV (eq 1, 8, and 11) suggests that at some point in these reactions (presumably at a five-coordinate intermediate) there is a low barrier to changes in stereochemistry.

The rhenium–carbon bonds in IV (average 2.081 (3) Å) are among the longest reported for rhenium isonitrile complexes,[31] suggesting that π-back-bonding from the rhenium to the isonitrile ligands is not very extensive. This is supported by the high energy of the CN stretching modes in IV (2226, 2239 cm^{-1}).[32] The Re–O bond in IV (1.671 (2) Å) is typical of reported Re–O distances in monooxo compounds (1.63–1.71 Å);[29] it is quite short compared to the 1.35 Å covalent radius of rhenium.[33]

Scheme I



Discussion

Two basic classes of mechanisms have been proposed for reactions in which Me_2SO acts as an oxidant (Scheme I).[7,10,17] Most of these reactions are believed to involve nucleophilic attack at the sulfur atom of Me_2SO, which is promoted by a protic or Lewis acid catalyst. The acid binds to the oxygen atom, which is normally the most basic site of Me_2SO as indicated by its two resonance structures:

$$Me_2S{=}O \leftrightarrow Me_2S^+{-}O^-$$

Binding an electrophile to the oxygen favors the second resonance structure and therefore facilitates nucleophilic attack at the sulfur. These steps are well precedented in the oxidation of alcohols by sulfoxides.[10b,17] In the case of triphenylphosphine oxidation by Me_2SO, the phosphorus is proposed to initially bind to sulfur and then to migrate to the oxygen to form a three-membered ring, which finally collapses to products (Scheme IA).[10a]

Me_2SO oxidations mediated by transition-metal compounds, however, normally proceed via a different mechanism, involving a change in the oxidation state of the metal center (Scheme IB).[7] For example $Mo(O)_2(S_2CNR_2)_2$ and related compounds catalyze the oxidation of PPh_3 by Me_2SO in two steps: phosphine oxide is formed by oxygen atom transfer from molybdenum(VI) to phosphorus, and Me_2SO is reduced by oxygen atom transfer to Mo(IV).[7]

In the rhenium system described above, both stoichiometric and catalytic oxidation of PPh_3 by Me_2SO is observed. The mechanisms of these reactions have been examined by using oxygen-18 labeling experiments. Reaction of Me_2SO with ^{18}O-enriched I, $Re(^*O)Cl_3(PPh_3)_2$ (following eq 1), yields products with preferential enrichment in the rhenium oxo group (eq 15). Studies

$$\underset{\substack{29\% \\ \text{I}}}{Re(^*O)Cl_3(PPh_3)_2} + 2.2\,Me_2SO \rightarrow \underset{\substack{12\% \\ \text{II}}}{Re(^*O)Cl_3(Me_2S)(^*OPPh_3)} + \underset{6\%}{^*OPPh_3} + \underset{7\%}{OPPh_3} \quad (15)$$

(25) (a) Chatt, J.; Rowe, G. A. *J. Chem. Soc.* **1962**, 4019–4033. Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. *J. Chem. Soc.* **1964**, 1054–1066. (b) Lock, C. J. L.; Turner, G. *Can. J. Chem.* **1977**, *55*, 333–339. Ciani, G. F.; D'Alfonso, G.; Romiti, P. F.; Sironi, A.; Freni, M. *Inorg. Chim. Acta* **1983**, *72*, 29–37.
(26) Lock, C. J. L.; Wan, C. *Can. J. Chem.* **1975**, *53*, 1548–1553.
(27) Sergienko, V. S.; Porai-Koshits, M. A. *Koord. Khim.* **1982**, *8*, 251–257 and references therein.
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(29) Mayer, J. M.; Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 7454–7462 and references therein.
(30) Bright, D.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 703–709, 709–716.
(31) Albers, M. O.; Boeyens, J. C. A.; Coville, N. J.; Harris, G. W. *J. Organomet. Chem.* **1984**, *260*, 99–104. Chiu, K. W.; Howard, C. G.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 803–808. Anderson, L. B.; Barder, T. J.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 3629–3636.
(32) ν(CN) for gaseous CN-*t*-Bu has been reported as 2134 cm^{-1}: Green, J. A., II; Hoffman, P. T. In *Isonitrile Chemistry*; Ugi, I., Ed.; Academic: New York, 1971; pp 1–7.
(33) Huheey, J. E. *Inorganic Chemistry*; Harper & Row: New York, 1972; p 185.

of the catalytic reaction (eq 6) yield similar results (eq 16; the percentages indicate the amount of isotopic enrichment in each site).

$$\underset{29\%}{Re(*O)Cl_3(Me_2S)(OPPh_3)} + 3Me_2SO + 3PPh_3 \rightarrow \underset{\text{II}}{Re(*O)Cl_3(Me_2S)(*OPPh_3)} + 3Me_2S + 3*OPPh_3 \quad (16)$$

$$\underset{17\%}{\qquad} \qquad \underset{5\%}{\qquad} \qquad \underset{4\%}{\qquad}$$

The results indicate that the phosphine oxide formed does not draw its oxygen completely or statistically from the rhenium oxo group. The observation of a small amount of oxygen-18 in the phosphine oxide, however, suggests more than one process is occurring in these reactions. We believe that oxygen atom transfer to triphenylphosphine occurs directly from a Me_2SO ligand activated by the rhenium center, without the direct involvement of the rhenium oxo group (eq 17). The small amount of $^{18}OPPh_3$ is formed by the same mechanism from $Me_2S^{18}O$ (eq 19), which is produced by oxygen atom exchange between $Re(^{18}O)Cl_3(Me_2S)(OPPh_3)$ and Me_2SO (eq 18; see eq 3 above). The rhenium

$$\underset{\text{I}}{Re(^{18}O)Cl_3(PPh_3)_2} + Me_2SO \rightarrow \underset{\text{II}}{Re(^{18}O)Cl_3(Me_2S)(OPPh_3)} + OPPh_3 \quad (17)$$

$$\underset{\text{II}}{Re(^{18}O)Cl_3(Me_2S)(OPPh_3)} + Me_2SO \rightarrow \underset{\text{II}}{Re(O)Cl_3(Me_2S)(OPPh_3)} + Me_2S^{18}O \quad (18)$$

$$\underset{\text{I}}{Re(O)Cl_3(PPh_3)_2} + Me_2S^{18}O \rightarrow \underset{\text{II}}{Re(O)Cl_3(Me_2S)(^{18}OPPh_3)} + {}^{18}OPPh_3 \quad (19)$$

compounds seem to react as Lewis acid promoters of Me_2SO (path A of Scheme I) rather than as redox agents. A very similar mechanism can account for the catalysis of oxygen atom exchange between Me_2SO and Me_2S (eq 5).

The mechanistic results are unfortunately complicated by the fact that the reactions are not completely stoichiometric as written due to a number of side reactions. For instance II slowly reacts with Me_2SO at ambient temperatures to give Me_2S and a variety of other products; II is therefore not quantitatively recovered from the exchange or catalytic reactions (eq 3–6). The presence of HCl gas seems to partially inhibit this decomposition as well as labilize the $OPPh_3$ ligand and increase the solubility of II in benzene and toluene, leading overall to "cleaner" reactions. HCl does not qualitatively change the pattern of isotope labeling in the reactions (cf. eq 20; compare eq 15), but these results are not mechanistically very informative because HCl by itself is an effective catalyst for Me_2SO oxidation of PPh_3.[34]

$$\underset{29\%}{Re(*O)Cl_3(PPh_3)_2} + 2.2\,Me_2SO \xrightarrow[C_7H_8]{HCl} \underset{\text{II}}{Re(*O)Cl_3(Me_2S)(*OPPh_3)} + *OPPh_3 \quad (20)$$

$$\underset{\text{I}}{\qquad} \qquad \underset{23\%}{\qquad} \qquad \underset{4\%}{\qquad} \qquad \underset{2\%}{\qquad}$$

The exchange of oxygen atoms between II and Me_2SO (eq 3 and 18) probably also proceeds by a mechanism involving nucleophilic attack at sulfur, except that the nucleophile is a rhenium oxo group instead of an external phosphine. Oxo attack at sulfur leads to a four-membered ring that can cleave in the opposite fashion to exchange the oxygen atoms (eq 21). Intermolecular

$$L_nRe(*O)(OSMe_2) \rightleftharpoons L_nRe[*OS(O)Me_2] \rightleftharpoons L_nRe(O)(*OSMe_2) \quad (21)$$

attack of PPh_3 is faster than this intramolecular process due to the very low basicity of the Re=O group, as found in studies of other monooxorhenium compounds.[6,35]

The data do not conclusively rule out alternative mechanisms for this oxygen exchange reaction that involve a change in the oxidation state of the rhenium center (such as Scheme IB). However these are unlikely because of the difficulty of oxidizing or reducing II under the conditions of the reactions. For instance II is not reduced under mild conditions by Me_2S, PPh_3,[6] or isonitrile ligands. In addition Me_2SO does not readily oxidize the labile rhenium(III) compound $ReCl_3(NCMe)(PPh_3)_2$. The oxidation of rhenium(V) compounds normally requires strong oxidants and the presence of multiple π-donor ligands (as in the formation of the perrhenate ion).[6]

In contrast to the reactions of I and II, the reactions of IV with PPh_3 and $PMePh_2$ must occur by oxygen atom transfer from the rhenium oxo group to the phosphorus center. Compound IV is probably more easily reduced because of the presence of π-acid isonitrile ligands that stabilize lower valent compounds, although this is not an uncommon reaction for rhenium(V) oxo complexes.[6,16] The oxygen atom transfer appears to proceed without coordination of the phosphine to the rhenium center, since the reduction of IV (eq 12, 13) is faster than the dissociation of an isonitrile ligand, as measured by ligand exchange (eq 22).

$$Re(O)Cl_3(CNCMe_3)_2 + 2CNCHMe_2 \rightarrow Re(O)Cl_3(CNCHMe_2)_2 + 2CNCMe_3 \quad (22)$$

Takeuchi has recently reported an excellent demonstration that phosphine coordination is not required for oxygen atom transfer: ruthenium oxo complexes of the form $[Ru(O)(bpy)_2(PR_3)]^{2+}$ do not oxidize the bound phosphine but rapidly oxidize triphenylphosphine in solution.[36]

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Supplementary Material Available: Tables of bond lengths and angles (Table IV), non-hydrogen atom thermal parameters (Table V), and idealized hydrogen atom positions (Table VI) for IV (3 pages); a listing of observed and calculated structure factor amplitudes for $Re(O)Cl_3(CNCMe_3)_2$ (IV) (Table VII) (16 pages). Ordering information is given on any current masthead page.

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