Oxo Ligand Reactivity in the $[ReO_2L_4]^+$ Complex of 1-Methylimidazole. Preparation and Crystal Structures of Salts Containing the $ReOL_4^{3+}$ Core and Apical CH_3O^-, BF_3O^{2-}, and $(CH_3O)_2PO_2^-$ Groups

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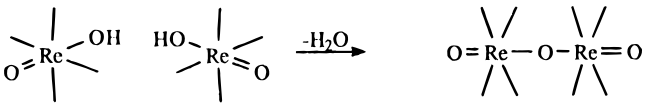
The oxo group of $[ReO_2(1\text{-MeIm})_4]^+$ can be methylated with excess methyl trifluoromethanesulfonate in CH_2Cl_2 under mild conditions, leading to $[ReO(OCH_3)(1\text{-MeIm})_4](CF_3SO_3)_2$, which is converted to the $B(C_6H_5)_4^-$ and PF_6^- salts. When the reaction is carried out in methanol in the presence of excess PF_6^-, the phosphate ester complex $[ReO\{OP(O)(OCH_3)_2\}(1\text{-MeIm})_4](PF_6)_2$ is isolated. $[ReO_2(1\text{-MeIm})_4]^+$ in the presence of acid, 2,2-dimethoxypropane, and excess BF_4^- transforms to the oxo−boron adduct $[ReO(OBF_3)(1\text{-MeIm})_4]^+$. The presence of the *trans*-O═Re−OR core was demonstrated by crystallographic studies on one compound of each type: $[ReO(OCH_3)(1\text{-MeIm})_4](PF_6)_2$, tetragonal, $P4/ncc$, $Z = 4$, $a = 13.022(3)$ Å, $c = 17.218(5)$ Å, $R = 0.0271$; $[ReO\{OP(O)(OCH_3)_2\}(1\text{-MeIm})_4](PF_6)_2$·toluene, monoclinic, $P2_1/c$, $Z = 4$, $a = 14.165(4)$ Å, $b = 13.052(6)$ Å, $c = 20.931(6)$ Å, $\beta = 95.83(2)°$, $R = 0.0373$; $[ReO(OBF_3)(1\text{-MeIm})_4](I_3)$, monoclinic, $P2_1/c$, $Z = 4$, $a = 13.373(4)$ Å, $b = 13.237(3)$ Å, $c = 16.689(6)$ Å, $\beta = 103.67(3)°$, $R = 0.0445$. The IR spectra show ν(Re═O) vibrations near 960 cm^{-1} in all cases. The solution UV−vis spectra of the CH_3O^- and BF_3O^{2-} compounds are similar to that of the parent oxo−hydroxo $[ReO(OH)(1\text{-MeIm})_4]^{2+}$ species, whereas the visible spectrum of the blue phosphate ester compound resembles that of the oxo−aquo $[ReO(OH_2)(1\text{-MeIm})_4]^{3+}$ ion. The compounds were also characterized by solution ^1H, ^{13}C, and ^{31}P NMR spectroscopy. This work confirms earlier conclusions that $ReO_2L_4^+$ units with good σ-donor imidazole ligands are more resistant to ligand loss than the pyridine analogues.

Introduction

In our previous paper,[1] we reported on the preparation and structural characterization of $[ReO_2L_4]^+$ salts with various imidazoles, which were found to form more readily than the pyridine analogues. The present paper deals with compounds which were obtained while trying to extend this initial work into two directions.

In mildly acidic solutions, decomposition of $[ReO_2L_4]^+$ takes place over a period of 1 h, as evidenced from large changes in the visible spectra. With 1-methylimidazole (1-MeIm), a decomposition product $[Re_3O_6(1\text{-MeIm})_{10}](BF_4)_3$ was isolated and shown by X-ray diffraction to consist of a linear μ-oxo trimer.[2] In order to determine if this trimer forms via a μ-oxo dimer of the type known for planar polydentate ligands,[3−5] attempts were made to prepare a $[Re_2O_3(1\text{-MeIm})_8]^{4+}$ dimer by the method used for the related cyanide complex $[Re_2O_3(CN)_8]^{4-}$, namely, by condensing two *trans*-$[ReO(OH)(CN)_4]^{2-}$ units (Scheme 1) under specific pH conditions.[6] However, the complicated decomposition process taking place in the same pH range made this approach impracticable. We turned to the method used to prepare halogenated dinuclear compounds

Scheme 1



$[Re_2O_3Cl_4L_4]$,[7] which consists of coupling two $ReO(OH)Cl_2L_2$ units produced in situ from $ReO(OR)Cl_2L_2$ and a controlled amount of water in a nonaqueous solvent. In the present case, coupling failed to take place between $[ReO(OH)L_4]^{2+}$ generated from $[ReO_2L_4]^+$ and 1 equiv of acid in methanol. Therefore, to assist water elimination, a water scavenger was introduced. However, instead of promoting the coupling reaction, attack on the BF_4^- counterion occurred, leading to a complex containing coordinated F_3BO^{2-}.

Our second target was the preparation of oxo-methylated compounds. A synthetic route to $[ReO(OCH_3)L_4]^{2+}$ complexes of pyridines was recently devised, and several such species were prepared and fully characterized.[8] Since our imidazole compounds are more basic than the pyridine analogues, the possibility was considered not only that monomethylated compounds could be obtained but that $[ReO(OR_2)L_4]^{3+}$ or $[ReO(ROH)L_4]^{3+}$ complexes could be accessed. Monomethylated $[ReO(OCH_3)(1\text{-MeIm})_4]^{2+}$ compounds showing the same violet color as $[ReO(OH)(1\text{-MeIm})_4]^{2+}$ were indeed obtained and under much milder conditions than reported for pyridines. However, the reactions in presence of PF_6^- raised particular problems: Two crystalline materials were isolated, with a blue color similar to that of $[ReO(OH_2)(1\text{-MeIm})_4]^{3+}$. They were initially believed to be $[ReO\{O(CH_3)_2\}L_4]^{3+}$ or $[ReO(CH_3OH)$-

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$L_4]^{3+}$, but one of them turned out to contain the standard $O{=}Re{-}OCH_3^{2+}$ core, while, in the other, the OCH_3 group has been replaced by a phosphate ester resulting from PF_6^- solvolysis.

Experimental Section

Materials and Physical Measurements. Methyl trifluoromethanesulfonate (methyl triflate), 2,2-dimethoxypropane (acetone dimethyl acetal), $NaBF_4$, NH_4PF_6, $NaB(C_6H_5)_4$ (all from Aldrich), and all other reactants and solvents (reagent grade) were used as received unless otherwise specified. *trans*-$[ReO_2(1\text{-MeIm})_4]I$ was prepared as described earlier.[1] Conversion to $[ReO_2(1\text{-MeIm})_4]BF_4$ was effected by metathesis with $NaBF_4$ in methanol. IR (CsI pellets) and electronic spectra were recorded on Perkin-Elmer 1750 FTIR and on UV−vis/NIR Varian/Cary-5E spectrophotometers, respectively. Solution ^1H and ^{13}C NMR spectra were run on a Varian VXR-300 or Bruker AMX-300 spectrometer. The residual solvent signal was used as internal reference: ^1H, δ(ppm): D_2O, 4.80; CD_3OD, 3.30; $(CD_3)_2CO$, 2.06. ^{13}C, δ(ppm): CD_3OD, 49.0; $(CD_3)_2CO$, 28.9. Solid-state ^{13}C CP-MAS spectra were obtained at 75.43 MHz with the Varian instrument (aromatic hexamethylbenzene carbons used as an external reference; δ 132.1 ppm). ^{31}P NMR spectra were run on a Bruker ARX-400 spectrometer and externally referenced to H_3PO_4 (δ 0.00 ppm). Elemental analyses were performed at the Laboratoire d'Analyse Élémentaire de l'Université de Montréal and the Guelph Chemical Laboratory, Guelph, Canada.

Preparative Work. $[ReO(OCH_3)(1\text{-MeIm})_4][B(C_6H_5)_4]_2$·Acetone. $[ReO_2(1\text{-MeIm})_4]I$ (0.48 g; 0.72 mmol) is added to CH_2Cl_2 (dried on molecular sieves and degassed, 20 mL) under argon. To the yellow suspension, a 25% molar excess of methyl trifluoromethanesulfonate (0.1 mL; 0.88 mmol) is added. The solution is stirred at room temperature under a stream of argon for 10 min, during which time all the solid dissolves and the solution turns burgundy red. The solvent is evaporated to dryness under vacuum. The bulk sample contains a 2:1 ratio of $[ReO(OCH_3)(1\text{-MeIm})_4]^{2+}$ and $[ReO_2(1\text{-MeIm})_4]^+$ (determined from ^1H NMR). The two species are separated by dissolving in a minimum volume of methanol, followed by addition of excess $NaBPh_4$ (0.55 g; 1.59 mmol) as a methanol solution (10 mL), inducing the precipitation of a peach solid, which is filtered off. This solid is twice purified by stirring in methanol, followed by decantation of the solution. The orange solution contains unreacted $[ReO_2(1\text{-MeIm})_4]^+$. The pure pink solid is obtained in 51% yield (0.44 g). IR (cm^{-1}): 960 (s), ν(Re═O). Visible spectrum (acetone; λ, nm, ϵ (M^{-1} cm^{-1})): 534 (171). ^1H NMR ($(CD_3)_2CO$; δ, ppm): $[ReO(OCH_3)(1\text{-MeIm})_4]^{2+}$, 8.00 (s, H2), 7.48 (t, 1.3 Hz, H5), 7.03 (t, 1.4 Hz, H4), 3.89 (s, N−CH_3), 3.75 (s, Re−OCH_3); BPh_4^-, 7.3 (m, H meta), 6.90 (t, 7.3 Hz, H ortho), 6.75 (t, 7.2 Hz, H para). ^{13}C CP-MAS (ppm): δ 139.5 (C2), 136.2 (BPh_4^-), 127.4 (C4), 126.5 (BPh_4^-), 122.7 (C5, BPh_4^-), 59.5 (Re−OCH_3), 31.6 and 34.1 (N−CH_3). Recrystallization of the pink solid in acetone gave a mixture of two crystalline forms. Elemental analysis performed on this sample indicated roughly one half acetone molecule per formula. Anal. Calcd for $C_{68}H_{73}B_2N_8O_3Re$: C, 64.91; H, 5.85; N, 8.91; B, 1.72. Found: C, 63.45; H, 5.41; N, 9.05; B, 1.65.

X-ray diffraction data were collected on a purple needle-shaped crystal of the acetone solvate $[ReO(OCH_3)(1\text{-MeIm})_4][B(C_6H_5)_4]_2$·acetone (tetragonal, *P*4/*ncc*, $Z = 4$, $a = 19.161(6)$ Å, $c = 16.747(9)$ Å). The structure was solved and refined down to $R1 = 0.056$. The $[ReO(OCH_3)(1\text{-MeIm})_4]^{2+}$ unit was found to lie on a crystallographic 4-fold axis, and the $B(C_6H_5)_4^-$ ion, on a 2-fold axis. The overall structure is well defined, but because of a superlattice problem, the esd's on light atoms positions are rather high and the structure is not described in detail in the present paper. The Re−OCH_3 carbon atom is disordered over four symmetry-equivalent positions off the 4-fold axis.

$[ReO(OCH_3)(1\text{-MeIm})_4](CF_3SO_3)_2$. The complex is prepared as described above using a larger excess (5−6 equiv) of methyl trifluoromethanesulfonate. The reaction mixture is stirred for 3 h, and a first crop of $[ReO(OCH_3)(1\text{-MeIm})_4](CF_3SO_3)_2$ is isolated by filtration. Addition of diethyl ether to the filtrate initiates the precipitation of a second fraction. Both fractions show identical spectroscopic properties and elemental analysis. Cumulative yield: 65−85%. IR (cm^{-1}): 962 (s), ν(Re═O). UV−vis (CH_3OH; λ, nm, ϵ (M^{-1} cm^{-1})): ∼208 (sh) (∼2.6×10^4), ∼236 (sh) (∼1.1×10^4), ∼270 (sh) (∼1.9×10^3), 534 (194). ^1H NMR (CD_3OD; δ, ppm): 7.84 (s, H2), 7.40 (t, 1.5 Hz, H5), 6.94 (t, 1.5 Hz, H4), 3.92 (s, N−CH_3), 3.70 (s, Re−OCH_3). ^{13}C NMR (CD_3OD; δ ppm): 122 (q, only two central lines visible, $J_{C-F} = 315$ Hz) (CF_3SO_3), 141.9 (C2), 130.2 (C4), 125.0 (C5), 59.0 (Re−OCH_3), 35.2 (N−CH_3). Anal. Calcd for $C_{19}H_{27}F_6N_8O_8ReS_2$: C, 26.54; H, 3.17; N, 13.03; S, 7.46. Found: C, 26.64; H, 3.03; N, 13.01; S, 7.30. When up to 50 equiv of methylating agent is used, as described in the literature for pyridines,[8] the same compound is isolated and dimethylation is not achieved.

A full set of X-ray diffraction data was collected on a crystal of $[ReO(OCH_3)(1\text{-MeIm})_4](CF_3SO_3)_2$ (monoclinic, $P2_1/c$, $Z = 2$, $a = 7.945(4)$ Å, $b = 18.695(9)$ Å, $c = 10.602(5)$ Å, $\beta = 96.30(4)°$), but the standard reflections showed some instability. The structure was solved, but could not be refined below $R1 = 0.076$. The overall features of the structure are well defined, but only the results of the more accurate study on the PF_6^- salt are discussed in this paper.

$[ReO(OCH_3)(1\text{-MeIm})_4](PF_6)_2$. $[ReO(OCH_3)(1\text{-MeIm})_4](CF_3SO_3)_2$ (0.0158 g, 0.0179 mmol) and NH_4PF_6 (0.0827 g, 0.507 mmol) are dissolved in acetone (∼3 mL), and ethanol (∼2 mL) is added. The purple solution is left to crystallize, and large royal blue crystals form overnight. IR (cm^{-1}): 958 (s), ν(Re═O). Yield, 0.0111 g (62%). Anal. Calcd for $C_{17}H_{27}F_{12}N_8O_2ReP_2$: C, 23.98; H, 3.20; N, 13.16. Found: C, 24.17; H, 3.15; N, 12.70.

$[ReO\{OP(O)(OCH_3)_2\}(1\text{-MeIm})_4](PF_6)_2$. A solution of $[ReO_2(1\text{-MeIm})_4]I$ (1.12 g, 1.66 mmol) in methanol (30 mL) is stirred under argon, and methyl trifluoromethanesulfonate (10 g, 61 mmol) is added. The solution instantaneously turns purple with frothing as some dimethyl ether is evolved. The mixture is stirred under a stream of argon for 5 min, until frothing subsides, and then sealed under argon and stirred overnight. The volume of the purple solution is then reduced to 5 mL, and excess NH_4PF_6 is added as a saturated methanol solution, followed by diethyl ether. The blue ether phase is decanted, two more extractions are effected, and the ether solution is evaporated to an oily residue, which is dried by pumping. The blue powder thus obtained is put through a second treatment with NH_4PF_6 (0.7 g) in methanol. The solution is evaporated, and the blue solid (0.92 g) is washed with CH_2Cl_2. The sample containing excess NH_4PF_6 is purified by dissolution in a 1:1 methanol−CH_2Cl_2 mixture, followed by addition of toluene. The blue solution is left to crystallize overnight, and deep blue needles (0.25 g, 15% yield) are obtained, which were used for the X-ray diffraction study. IR (cm^{-1}): 1250 (intensity gain), $\nu_{as}(PO_2)$; 1047 (s), ν(P═O); 972(s)/963(s), ν(Re═O); 842 (vs), 563 (m) (PF_6^-). UV−vis (CH_3OH; λ, nm, ϵ (M^{-1} cm^{-1})): ∼207 (sh) (∼6.5×10^3), ∼232 (sh) (∼2.2×10^3), ∼252 (sh) (∼1.7×10^3), ∼300 (br) (∼3.3×10^2), 614 (550). ^1H NMR (CD_3OD; δ, ppm): 7.94 (s, H2), 7.54 (t, 1.5 Hz, H5), 6.98 (t, 1.5 Hz, H4), 3.99 (s, N−CH_3), 3.47 (d, P−OCH_3, $^3J_{PH} = 11$ Hz). ^{13}C NMR (CD_3OD; δ, ppm): 144.4 (C2), 131.6 (C4), 125.8 (C5), 54.7 (P−OCH_3), 35.2 (N−CH_3). ^{31}P NMR (CD_3OD; δ, ppm): −144.9 (hept, $^2J_{PF} = 708$ Hz, PF_6^-), −1.5 (s, $(CH_3O)_2PO_2^-$). Fresh crystals contain 1 lattice toluene molecule per formula (see X-ray work). About half of the lattice toluene had been lost in the sample used for microanalysis. Anal. Calcd for $C_{21.5}H_{34}F_{12}N_8O_5P_3Re$: C, 25.90; H, 3.45. Found: C, 26.00; H, 3.38.

$[ReO(OBF_3)(1\text{-MeIm})_4](BF_4)$. A solution of $[ReO_2(1\text{-MeIm})_4](BF_4)$ (0.102 g, 0.162 mmol) in methanol (7 mL) is added to a solution of $NaBF_4$ (0.139 g, 1.27 mmol, 3.0 mL) in the same solvent, followed by tetrafluoroboric acid in methanol (0.43 mL of a 0.369 M solution). The solution is evaporated to half its initial volume, and dimethoxypropane (15 mL) is added. It becomes reddish-purple but returns to its purple color within a few minutes, while a gelatinous white precipitate forms. The purple solution is decanted after 30 min, and crystallization in the refrigerator gives purple plates contaminated by $NaBF_4$. Recrystallization in acetone/dimethoxypropane yields purple crystals. Yield: 0.042 g (37%). IR (cm^{-1}): 965 (m), ν(Re═O); 901 (s, br), ν(B−F). UV−vis (CH_3OH; λ, nm, ϵ (M^{-1} cm^{-1})): ∼207 (sh) (∼2.2×10^4), 245 (9.82×10^3), ∼280 (sh) (∼1.3×10^3), 536 (115). ^1H NMR (CD_3OD; δ, ppm): 7.82 (s, H2), 7.25 (t, 1.5 Hz, H5), 7.13 (t, 1.5 Hz, H4), 3.86 (s, N−CH_3). Anal. Calcd for $C_{16}H_{24}B_2F_7N_8O_2Re$: C, 27.40; H, 3.46; N, 15.98. Found: C, 27.30; H, 3.53; N, 16.12.

$[ReO(OBF_3)(1\text{-MeIm})_4](I_3)$ and $[ReO(OBF_3)(1\text{-MeIm})_4](BF_4)_{0.8}(I)_{0.2}$. Crystals of the triiodide salt used for the X-ray diffraction study were obtained during early attempts to prepare the above BF_4^- complex

Table 1. Crystallographic Data for the Three Structures

	$[ReO(OCH_3)(1\text{-}MeIm)_4](PF_6)_2$	$[ReO\{OP(O)(OCH_3)_2\}(1\text{-}MeIm)_4](PF_6)_2\cdot$toluene	$[ReO(OBF_3)(1\text{-}MeIm)_4](I_3)$
chem formula	$C_{17}H_{27}F_{12}N_8O_2P_2Re$	$C_{25}H_{38}F_{12}N_8O_5P_3Re$	$C_{16}H_{24}BF_3I_3N_8O_2Re$
fw	851.62	1037.75	995.15
a, Å	13.022(3)	14.165(4)	13.373(4)
b, Å	13.022(3)	13.052(6)	13.237(3)
c, Å	17.218(5)	20.931(6)	16.689(6)
β, deg		95.83(2)	103.67(3)
V, Å^3	2919.7(11)	3850(2)	2871(2)
Z	4	4	4
space group	*P*4/*ncc* (No. 130)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
temp, °C	21	−50	22
λ, Å	1.540 56	1.540 56	1.540 56
ρ_{calcd}, g/cm^3	1.937	1.790	2.303
μ, cm^{-1}	99.3	81.1	340.5
transm coeff	0.07−0.34	0.43−0.68	0.01−0.35
$R1$, $I > 2\sigma(I)$[a]	0.0271	0.0373	0.0445
wR^2, $I > 2\sigma(I)$[a]	0.0758	0.0853	0.0939

[a] $R1 = \sum(||F_o| - |F_c||)/\sum(|F_o|)$; $wR^2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

from $[ReO_2(1\text{-}MeIm)_4]I$. Details concerning this reaction are provided as Supporting Information. Two types of crystals were obtained during this preparation: a triiodide, whose crystal structure is described in this paper, showing a ν(Re═O) vibration mode at 934 cm^{-1}, and a mixed BF_4^-/I^- salt, for which the Re═O stretch is seen at 951 cm^{-1}. Both compounds show NMR spectra identical to that of the above BF_4^- salt. The composition of $[ReO(OBF_3)(1\text{-}MeIm)_4](BF_4)_{0.8}(I)_{0.2}$ was deduced from a crystal structure determination (triclinic, $P\bar{1}$, $Z = 4$, $a = 13.632(3)$ Å, $b = 13.761(3)$ Å, $c = 14.091(3)$ Å, $\alpha = 92.41(2)°$, $\beta = 102.44(2)°$, $\gamma = 102.41(2)°$) which is not reported in this paper. Counterion substitution and concomitant disorder were avoided by using the iodide-free BF_4^- salt as starting material.

Crystallographic Measurements and Structure Resolution. Crystallographic work was done on a Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Cu Kα radiation. Important crystallographic data are collected in Table 1. Details are available in the Supporting Information. In each case, the reduced cell was determined from rotation photographs and was transformed to the standard setting, if needed. The cell parameters were refined with 25 high-angle reflections. Intensity data were collected over the entire sphere ($2\theta_{max} = 140°$), corrected for absorption (NRCVAX package,[9] Gaussian integration from crystal faces), and averaged. The structures were solved and refined using the SHELXS-86[10] and SHELXL-93[11] programs. Heavy-atom positions were determined from a Patterson map. All non-hydrogen atoms were then located from successive ΔF maps. Hydrogen atoms were placed at idealized positions with an isotropic thermal parameter 20% (aromatic) or 50% (methyl) higher than the corresponding carbon atom. They were repositioned after each cycle. All non-hydrogen atoms were refined anisotropically. Atomic scattering factors were taken from the usual source.[12]

$[ReO(OCH_3)(1\text{-}MeIm)_4](PF_6)_2$. A deep blue crystal of dimensions (mm) 0.43 × 0.35 × 0.16 was used. The reduced cell indicated a tetragonal lattice and space group *P*4/*ncc* was unambiguously defined from the 4/*mmm* Laue symmetry and the systematic absences (*hk0*, $h + k$ odd; *0kl*, *l* odd; *hhl*, *l* odd). Data were measured in the entire sphere (17 948 reflections) and averaged to 1396 *hkl* reflections ($k \geq h$) ($R_{int} = 0.060$), of which 979 with $I > 2\sigma(I)$ were used for structure determination. The space group definition used is the one with the origin on $\bar{1}$. The $[ReO(OCH_3)(1\text{-}MeIm)_4]^{2+}$ cation sits on special position *4c*, the rhenium atom, the oxo ligand, and the methoxy group all lying on a 4-fold rotation axis. The two PF_6^- anions occupy special position *8f* (2-fold axis), where they are disordered over two orientations (50% occupancies). The P and one of the F atoms are common to both individuals, whereas the remaining positions are described as resolved half-atoms. The large thermal ellipsoids in PF_6^- indicate that thermal motion is extremely high or that extra unresolved orientations may exist for this anion. The final ΔF map shows a general background below ±0.4 e Å^{-3}.

$[ReO\{OP(O)(OCH_3)_2\}(1\text{-}MeIm)_4](PF_6)_2\cdot$Toluene. A blue needle of dimensions (mm) 0.47 × 0.08 × 0.05 was used to collect a whole sphere of reflections (24 362 measurements), which were averaged to two octants (6993 independent reflections, 5173 with $I > 2\sigma(I)$, $R_{int} = 0.039$). Space group $P2_1/c$ was unambiguously defined from the systematic absences (*h0l*, *l* odd; *0k0*, *k* odd). The complex cation and the two crystallographically independent PF_6^- anions in the asymmetric unit lie in general positions. The large thermal parameters of the fluorine atoms around P2 indicate disorder in this anion. All attempts to describe the disorder with two or three superimposed octahedra failed, and the unresolved model is retained. The lattice toluene molecule, which also shows disorder, is described with two orientations (50% occupancies), and the atomic positions were refined independently. Again, large thermal ellipsoids are indicative of further unresolved disorder in this area. The final ΔF map showed a general background below ±0.3 e Å^{-3}, with a few peaks of ±1.0 e Å^{-3} near Re or F atoms.

$[ReO(OBF_3)(1\text{-}MeIm)_4](I_3)$. A rust-colored platelet of dimensions (mm) 0.36 × 0.20 × 0.04 was used. The 20 461 reflections in the whole sphere were averaged to 5427 independent reflections ($R_{int} = 0.076$), of which 3470 with $I > 2\sigma(I)$ were used for the refinement. The space group $P2_1/c$ was uniquely determined from the systematic absences. Resolution and refinement were straightforward, no disorder being detected. The final ΔF map showed a few residuals of ±|1.0−2.0| e Å^{-3} near Re and I and a general background below ±0.4 e Å^{-3}.

Results

trans-$[ReO(OCH_3)(1\text{-}MeIm)_4]^{2+}$ was obtained as the triflate salt by reacting excess methyl triflate with *trans*-$[ReO_2(1\text{-}MeIm)_4]^+$. The counteranion was readily exchanged for PF_6^- or $B(C_6H_5)_4^-$. Two other types of compounds retaining the $ReO(1\text{-}MeIm)_4^{3+}$ core were prepared, in which the apical ligands are the trifluoro-oxoborate F_3BO^{2-} and a phosphate ester $(CH_3O)_2PO_2^-$, these apical ligands being produced by decomposition of the counteranion BF_4^- and PF_6^-, respectively.

Infrared Spectroscopy. For the three $[ReO(OCH_3)(1\text{-}MeIm)_4]^{2+}$ salts, the Re═O stretching mode appears as a strong band around 960 cm^{-1}, which corresponds to the range (955−975 cm^{-1}) reported for oxo−hydroxo[1] and oxo−methoxo[8,13] complexes. The presence of Re−OCH_3 in pyridine compounds has been detected from two modes:[8] a weak ν(Re−OCH_3) vibration at ∼750 cm^{-1}, observed in Raman, and a stronger ν(O-CH_3) vibration at 1120−1130 cm^{-1}, appearing in both the

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Raman and IR spectra. The latter mode has been identified in our IR spectra. The 1100−1200 cm^{-1} region is masked by many vibrations of the anions in the BPh_4^- salt, but the $CF_3SO_3^-$ salt shows only three bands. The very strong vibration at 1105 cm^{-1} is characteristic of 1-MeIm, while the one at 1165 cm^{-1} can be attributed to the anion $\nu(CF_3)$ mode.[14] The third band at 1140 cm^{-1} is assigned to the $\nu(O-CH_3)$ mode. This vibration occurs at 1130 cm^{-1} for the PF_6^- salt, where the anion does not interfere.

The spectrum of $[ReO(OBF_3)(1\text{-MeIm})_4](I_3)$ shows a very strong and broad system with maxima at 1030 and 1105 cm^{-1}, which we assign to $\nu(B-F)$ stretching in the F_3BO^{2-} unit. Very intense bands in the same region, including a strong component at 968 cm^{-1}, have been similarly assigned by Beck *et al*. for $(OC)_5Re(HOBF_3)$.[15,16] Our spectrum also displays a medium band at 935 cm^{-1}, which is not believed to have the same origin. It more likely originates from Re═O stretching, since this vibration in $[ReO(OCH_3)(1\text{-MeIm})_4]^{2+}$ occurs in the same region and no other suitable bands are available for this normally strong vibration down to 830 cm^{-1}. In the BF_4^- salt, the ν(Re═O) band is found at 965 cm^{-1}. A predominant $\nu(B-F)$ massif is present between 1000 and 1140 cm^{-1} for F_3BO^{2-} and BF_4^-, whereas an extra strong band at 901 cm^{-1} is due to uncoordinated BF_4^-, whose tetrahedral symmetry is lowered in the crystal.[17]

In $[ReO\{OP(O)(OCH_3)_2\}(1\text{-MeIm})_4](PF_6)_2$, the phosphate ester contributes to two well-defined features. A relatively strong band is observed at 1250 cm^{-1}, where the 1-MeIm ligand possesses only a weak vibration. Increased intensity is very likely due to P═O stretching in the nonmethylated PO_2 unit.[18,19] The strong feature at 1047 cm^{-1} is assigned to the $\nu(PO-CH_3)$ mode. A strong doublet at 963/972 cm^{-1} is due, at least in part, to ν(Re═O).

NMR Spectroscopy. The oxo-methyl signal for $[ReO(OCH_3)(1\text{-MeIm})_4]^{2+}$ is observed at 3.7 ppm (^{1}H) in methanol and at ∼59 ppm (^{13}C) in the same solvent or in the solid state. Reported values for related pyridine complexes are 3.7−4.3 ppm (^{1}H) and 58−59 ppm (^{13}C).[8]

The blue $[ReO\{OP(O)(OCH_3)_2\}(1\text{-MeIm})_4]^{2+}$ species is easily identified by ^{1}H NMR, the P-bonded methoxo groups appearing as a doublet with a $^3J_{PH}$ constant of 11 Hz: $^3J_{PH}$ couplings of 10.7 and 13.5 Hz have been found in Re(V) complexes with the related ligand $(CH_3O)_2PO^-$.[20]

Signals for coordinated imidazole were assigned as described earlier.[1] The ring protons appear at 7.73 (H2), 7.11 (H5), 7.10 (H4), and 3.71 (N−CH_3) in methanol for *trans*-$[ReO_2(1\text{-MeIm})_4]^+$.[1] The present complexes bearing a higher charge, the signals are generally displaced downfield from free 1-MeIm to a greater extent than for the singly charged $[ReO_2(1\text{-MeIm})_4]^+$ species. The proton whose chemical shift varies the most is H5, which moves downfield by 0.14, 0.29, and 0.43 ppm upon substitution of an oxo ligand by F_3BO^{2-}, $(OCH_3)_2PO_2^-$, and CH_3O^-, respectively. A similar pattern is observed for H2, although less markedly ($\Delta\delta$ = 0.09−0.21 ppm). The N-methyl groups also move downfield. The remaining ring proton H4 does not follow a standard trend: Its chemical shift varies from 0.03 ppm downfield to 0.16 ppm upfield compared to the dioxo precursor.

The ^{13}C spectra are not very sensitive to the nature of the apical ligand. C2 is the most affected carbon, appearing at 141.9 and 144.4 ppm (in CD_3OD) for the methoxo and the phosphate ester complexes, respectively. The δ value for *trans*-$[ReO_2(1\text{-MeIm})_4]^+$ in D_2O is 140.0.[1]

Electronic Spectroscopy. As noted earlier for the pyridine analogues, the UV−vis spectra of $[ReO(OH)(1\text{-MeIm})_4]^{2+}$ and $[ReO(OCH_3)(1\text{-MeIm})_4]^{2+}$ complexes are very similar.[8] The similarity is found here to extend to the F_3BO^{2-} complex. In the visible region, their d−d transitions occur near 535 nm with ϵ values of 100−200 M^{-1} cm^{-1} for the three types of compounds. In the UV region, the MLCT [$d_{xy} \rightarrow \pi_L^*$] band of $[ReO(OH)(1\text{-MeIm})_4]^{2+}$ is found below ∼240 nm in water, and a high-energy imidazole $\pi \rightarrow \pi_L^*$ absorption, below 225 nm. The methylated analogue has the MLCT transition at ∼236 nm (ϵ ∼1.1 × 10^4 M^{-1} cm^{-1}). The BF_3O^{2-} complex shows the MLCT band at 245 nm (ϵ ∼9.8 × 10^3 M^{-1} cm^{-1}), while the ligand-based $\pi \rightarrow \pi_L^*$ transition appears as a shoulder at ∼207 nm. Although the oxo−hydroxo, oxo−methoxo and oxo−oxoborato complexes all have very similar spectra in the visible, the MLCT region in the UV is quite different for the oxo−borate complex. The MLCT band of this compound is found shifted ∼10 nm to lower energies compared with the oxo−hydroxo and oxo−methoxo analogues, and the $\pi \rightarrow \pi_L^*$ band of the imidazole ligand moves to higher energy by ∼10 nm.

The d−d transition for the blue phosphate ester complex occurs at 614 nm (ϵ = 550 M^{-1} cm^{-1}). Both the position and the absorption coefficient are similar to those of the analogous oxo−aquo $[ReO(OH_2)(1\text{-MeIm})_4]^{3+}$ complex (624 nm, ∼450 M^{-1} cm^{-1}).[1]

Crystal Structures. X-ray diffraction work confirms the presence of a *trans*-$ReO(OR)L_4$ unit in the three cations (Figures 1−3). Selected bond lengths and angles are listed in Table 2.

Complexes of the type $[ReO(OR)L_4]^{n+}$ (R = H, CH_3, C_2H_5)[1,8,20,21,22] and $[ReO(OR)X_2L_2]$ (R = CH_3, C_2H_5; X = Cl, Br, I)[23] with N-donor and/or phosphine ligands usually exhibit rhenium−oxygen distances in the 1.64−1.73 Å range for the short high-order Re═O bond and 1.83−1.90 Å for the longer Re-OR bond,[21,23] although the latter has sometimes been reported to be much longer (∼2.00 Å).[21d,e] The high-order Re═O bond in $[ReO(OR)L_4]^+$ systems also tends to displace the *cis* ligands in the opposite direction, increasing the O═Re−L angle up to ∼94°.

$[ReO(OCH_3)(1\text{-MeIm})_4](PF_6)_2$. The $[ReO(OCH_3)(1\text{-MeIm})_4]^{2+}$ cation in this PF_6^- salt lies on a crystallographic 4-fold axis (Figure 1), making the O═Re−O−C unit perfectly linear and the four 1-MeIm ligands symmetry equivalent. The Re−N distance of 2.118(3) Å is normal. The Re═O1 and Re−

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Table 2. Selected bond lengths (Å) and angles (deg)

$[ReO(OCH_3)(1\text{-}MeIm)_4]^{2+}$		$[ReO\{OP(O)(OCH_3)_2\}(1\text{-}MeIm)_4]^{2+}$		$[ReO(OBF_3)(1\text{-}MeIm)_4]^{+}$	
Re−O(1)	1.701(6)	Re−O(1)	1.660(4)	Re−O(1)	1.697(7)
Re−O(2)	1.852(6)	Re−O(2)	1.988(4)	Re−O(2)	1.832(7)
Re−N(31)	2.118(3)	Re−N(31)	2.106(4)	Re−N(31)	2.126(7)
		Re−N(32)	2.099(4)	Re−N(32)	2.155(7)
		Re−N(33)	2.120(4)	Re−N(34)	2.120(7)
		Re−N(34)	2.102(4)	Re−N(33)	2.125(7)
O(2)−C(2)	1.433(8)	O(2)−P(1)	1.540(4)	O(2)−B(2)	1.450(13)
		P(1)−O(3)	1.452(4)	B(2)−F(21)	1.350(13)
		P(1)−O(4)	1.552(4)	B(2)−F(22)	1.388(13)
		P(1)−O(5)	1.560(5)	B(2)−F(23)	1.408(13)
		O(4)−C(4)	1.440(7)		
		O(5)−C(5)	1.395(8)		
O(1)−Re−O(2)	180.0	O(1)−Re−O(2)	178.8(2)	O(1)−Re−O(2)	179.3(3)
C(2)−O(2)−Re	180.0	P(1)−O(2)−Re	151.6(2)	B(2)−O(2)−Re	175.7(6)
O(1)−Re−N(31)	90.89(8)	O(1)−Re−N(31)	95.2(2)	O(1)−Re−N(31)	91.0(3)
		O(1)−Re−N(32)	94.0(2)	O(1)−Re−N(32)	91.2(3)
		O(1)−Re−N(33)	93.6(2)	O(1)−Re−N(34)	91.2(3)
		O(1)−Re−N(34)	95.7(2)	O(1)−Re−N(33)	90.4(3)
O(2)−Re−N(31)	89.11(8)	O(2)−Re−N(31)	85.7(2)	O(2)−Re−N(31)	89.2(3)
		O(2)−Re−N(32)	85.2(2)	O(2)−Re−N(32)	88.1(3)
		O(2)−Re−N(33)	85.5(2)	O(2)−Re−N(33)	89.4(3)
		O(2)−Re−N(34)	85.0(2)	O(2)−Re−N(34)	89.5(3)
N(31)−Re−N(31)[a]	89.86(9)	N(34)−Re−N(31)	89.7(2)	N(34)−Re−N(31)	89.3(3)
		N(32)−Re−N(31)	89.6(2)	N(31)−Re−N(32)	87.8(3)
		N(34)−Re−N(33)	89.1(2)	N(34)−Re−N(33)	91.0(3)
		N(33)−Re−N(32)	90.1(2)	N(33)−Re−N(32)	91.8(3)
N(31)−Re−N(31)[b]	178.21(15)	N(33)−Re−N(31)	171.2(2)	N(33)−Re−N(31)	178.6(3)
		N(34)−Re−N(32)	170.3(2)	N(34)−Re−N(32)	176.3(3)
C(21)−N(31)−Re	128.3(3)	C(41)−N(31)−Re	127.3(4)	C(21)−N(31)−Re	124.9(7)
		C(23)−N(33)−Re	126.1(4)	C(23)−N(33)−Re	127.4(7)
		C(21)−N(31)−Re	126.2(4)	C(41)−N(31)−Re	128.1(7)
		C(43)−N(33)−Re	127.6(4)	C(43)−N(33)−Re	127.3(6)
		C(22)−N(32)−Re	126.7(4)	C(22)−N(32)−Re	124.2(7)
		C(24)−N(34)−Re	124.5(4)	C(24)−N(34)−Re	126.9(7)
		C(42)−N(32)−Re	126.5(4)	C(42)−N(32)−Re	128.3(7)
		C(44)−N(34)−Re	128.5(4)	C(44)−N(34)−Re	128.0(7)
		O(3)−P(1)−O(2)	117.7(2)	F(21)−B(2)−F(22)	109.9(10)
		O(3)−P(1)−O(4)	114.0(3)	F(21)−B(2)−O(2)	112.0(10)
		O(2)−P(1)−O(4)	102.7(2)	F(21)−B(2)−F(23)	108.8(9)
		O(3)−P(1)−O(5)	108.4(3)	F(22)−B(2)−O(2)	110.1(8)
		O(2)−P(1)−O(5)	105.2(2)	F(22)−B(2)−F(23)	107.2(10)
		O(4)−P(1)−O(5)	108.3(3)	F(23)−B(2)−O(2)	108.7(9)
		C(4)−O(4)−P(1)	122.3(5)		
		C(5)−O(5)−P(1)	123.8(5)		

[a] $-y + 1/2, x, z$. [b] $-x + 1/2, -y + 1/2, z$.

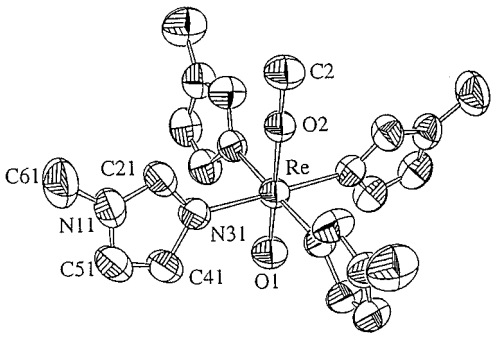

Figure 1. ORTEP drawing of the cation in $[ReO(OCH_3)(1\text{-}MeIm)_4](PF_6)_2$, showing the numbering scheme. Ellipsoids are drawn at a 50% probability level. Hydrogens are omitted.

O2 bond lengths (1.701(6) and 1.852(6) Å, respectively) lie in the middle of the ranges mentioned above. A survey of the structures containing O═Re−alkoxy units[21c,d,23a−d,24] reveals a very broad range of 143−176° for the Re−O−C angle. Therefore, the linear Re−O−CH_3 group found here seems to be atypical. Linearity probably results to some extent from packing forces, since the Re−O−C angles in the corresponding $CF_3SO_3^-$ and $B(C_6H_5)_4^-$ salts are 162.6° and 159.2°, respectively. Another particularity of the PF_6^- salt is the orientation of the 1-MeIm rings approximately parallel with the O═Re−OR axis: The O−Re−N−C torsion angle is 13.2(8)° and the C4 carbon is on the Re═O side in all cases (Table 3). There is a certain preference for this conformation in related pyridine and imidazole compounds,[1] but this trend is not followed by the $CF_3SO_3^-$ and $B(C_6H_5)_4^-$ salts, which have at least two rings at ∼45° from the O═Re−OR direction (Table 3). Mild steric constraint imposed by this parallel orientation undoubtedly contributes to keeping the O1═Re−N angle (90.89(8)°) much closer to 90° than in the oxo−hydroxo $[ReO(OH)(1,2\text{-}Me_2\text{-}Im)_4]^{2+}$ ion, where the imidazole ring is tilted at ∼45° from the O═Re−OH direction by the α-methyl groups and the O1═Re−N angles are increased to ∼94°.[1]

$[ReO(OBF_3)(1\text{-}MeIm)_4](I_3)$. Addition of the BF_3 Lewis acid

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Table 3. O1−Re−N3−C(α) Torsion Angles (deg) Describing Ring Orientation in Crystal Structures[a]

	ring 1	ring 2	ring 3	ring 4
$[ReO(OCH_3)(1\text{-MeIm})_4](PF_6)_2$	13.2(4) [C4]	13.2(4) [C4]	13.2(4) [C4]	13.2(4) [C4]
$[ReO(OCH_3)(1\text{-MeIm})_4](CF_3SO_3)_2$[b]	51.6(21) [C2]	−10.5(22) [C2]	−59.4(20) [C4]	9.2(22) [C4]
$[ReO(OCH_3)(1\text{-MeIm})_4](BPh_4)_2$[b]	41.7(7) [C2]	41.7(7) [C2]	41.7(7) [C2]	41.7(7) [C2]
$[ReO(OBF_3)(1\text{-MeIm})_4](I_3)$	3.1(7) [C4]	2.7(8) [C2]	4.0(8) [C2]	0.5(9) [C4]
$[ReO\{OP(O)(OCH_3)_2\}(1\text{-MeIm})_4](PF_6)_2$	−35.8(5) [C2]	−63.2(5) [C2]	−32.3(5) [C2]	−59.8(5) [C2]

[a] The four torsion angles are calculated with respect to the terminal high-order Re═O bond, and the α carbon is chosen so as to keep the angle in the $-90° \le \tau \le 90°$ range. The α carbon involved is identified in brackets. [b] Crystal structures determined as part of the present work but not described in detail (see Experimental Section).

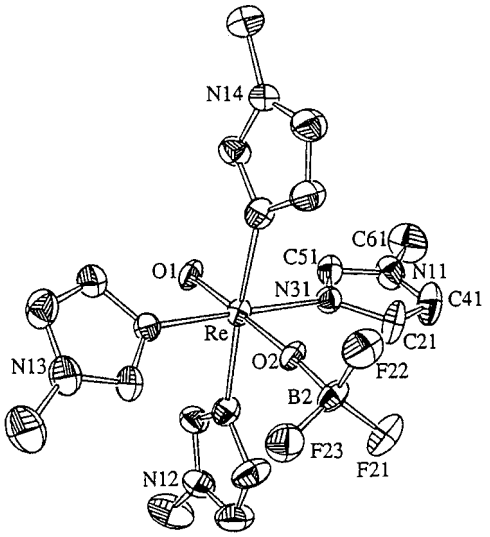

Figure 2. ORTEP drawing of the cation in $[ReO(OBF_3)(1\text{-MeIm})_4](I_3)$, showing the numbering scheme. Ellipsoids are drawn at a 30% probability level. Hydrogens are omitted.

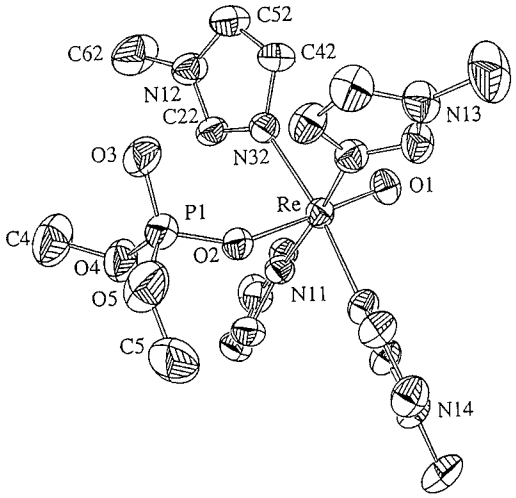

Figure 3. ORTEP drawing of the cation in $[ReO\{OP(O)(OCH_3)_2\}(1\text{-MeIm})_4](PF_6)_2$·toluene, showing the numbering scheme. Ellipsoids are drawn at a 50% probability level. Hydrogens are omitted.

to an oxo ligand of $[ReO_2(1\text{-MeIm})_4]^+$ deeply modifies the bond orders, so that $[ReO(OBF_3)(1\text{-MeIm})_4]^+$ (Figure 2) is best regarded as containing a F_3BO^{2-} ligand coordinated to the $[ReO(1\text{-MeIm})_4]^{3+}$ core. The Re═O1, Re−O2, and Re−N bond lengths (1.697, 1.832, and 2.131 (mean) Å, respectively) are not significantly different from those of $[ReO(OCH_3)(1\text{-MeIm})_4]^{2+}$ (Table 2). Linearity in the O1═Re−O2−B2 moiety is not imposed by symmetry, but the O1═Re−O2 (179.3(3)°) and Re−O2−B2 (175.7(6)°) angles are close to 180°. Linearity is again correlated with approximately parallel orientations of the 1-MeIm rings, which all make angles ≤4° with the O═Re−O axis (Table 3). The O1═Re−N angles are also remarkably close to 90° (90.2(3)−91.3(3)°).

No crystallographic work is available on complexes containing a unidentate F_3BO^{2-} ligand. In $(OC)_5Re(HOBF_3)$,[15] the B−O bond (1.476 Å) is similar to ours (1.450(13) Å), even though oxygen is protonated. In $[Rh_2(\mu\text{-}OBF_3)(CO)_2(\mu\text{-dppm})_2]$,[25] where oxygen is bridging, the B−O bond seems to be appreciably shorter (1.38(1) Å). Our compound should not be regarded as a simple BF_3 adduct, since the distances reported for typical BF_3·L adducts (L = CH_3OH, H_2O, $(C_6H_5)_3PO$, $(C_6H_5)_3AsO$, acrolein) are much greater (mean 1.526 Å, range 1.486−1.587 Å).[26] B−O bonding is probably more comparable with those of $CH_3OBF_3^-$ and $HOBF_3^-$, although the small size of the O-bonded group favors shorter B−O bonds (1.373 and 1.415 Å, respectively)[27] in the latter species. Our O−B−F and F−B−F angles (means 110.3 and 108.6°, respectively) and B−F distances (mean 1.382 Å) are normal, as are the I−I distances (2.900(2) and 2.907(2) Å) in the linear I_3^- ion.

$[ReO\{OP(O)(OCH_3)_2\}(1\text{-MeIm})_4](PF_6)_2$. The Re═O1 bond (1.660(4) Å) lies in the range for O═Re−OR species, but it is significantly shorter than those of the above compounds. This is consistent with greater Re═O bond order favored by the weaker *trans* Re−OP bond (1.988(4) Å), which is relatively long and above the expected range, although not as long as the Re−OH_2 distance (2.142(7) Å) in the oxo-aqua complex $[ReO(OH_2)(CN)_4]^-$.[28] The O═Re−O unit is almost linear (178.8(2)°), but this time, the Re−O−P angle is 151.6(2)°. The imidazole rings have adjusted to this situation, by avoiding orientations parallel to the O═Re−O axis (Table 3). Therefore, the factors preventing the displacement of the Re−N bonds away from the Re═O1 multiple bond are eliminated and the O1═Re−N angles increase to ∼94.5° as often observed. The only known structure of a rhenium complex with a coordinated OP group *trans* to an oxo ligand is the triphenylphosphine oxide complex $[ReO(OPPh_3)(catecholate)_2]^-$,[29] where coordination involves a phosphoryl oxygen. The O═Re−OP and Re−O−P angles are 178.5(3) and 172.5(5)°, respectively, whereas the multiple Re═O bond (1.576(8) Å) is very short and the Re−OP bond (2.232(6) Å) very long. In the present case, the phosphate diester ligand is coordinated via the O^- donor of the $(CH_3O)_2P(═O)O^-$ form. This is evidenced from the terminal P═O3 bond (1.452(4) Å) being much shorter than the P−ORe (1.540(4) Å) and P−OCH_3 (1.552(4), 1.560(5) Å) distances. These values compare well with those reported for complexes of a phosphite ester (1.488 and 1.595 Å, respectively).[20] Our

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P−O bonds are displaced away from the multiple P═O3 group: the O3−P−O angles are 117.7, 114.0 and 108.4°, compared with the remaining O−P−O angles of 102.7°, 105.2°, and 108.3°. The P atom has a similar environment in various $P(O)(OCH_3)_2(OR)$ compounds.[30]

Discussion

Methylation of the Oxo Ligand. Monomethylation of *trans*-$[ReO_2(1\text{-MeIm})_4]^+$ takes place under mild conditions. Iodomethane is not, as previously reported for pyridine compounds,[8] a strong enough agent to produce methylation to an appreciable extent, even with a large excess and long reaction times.

The $[ReO(OCH_3)(1\text{-MeIm})_4]X_2$ compounds (X = BPh_4^-, $CF_3SO_3^-$) are purple both in the solid state and in solution. In contrast, as a solid, the PF_6^- salt is blue like the phosphate ester complex and $[ReO(OH_2)(1\text{-MeIm})_4]^{3+}$, although, in solution, it is purple and shows the same UV−visible spectrum as the other salts. To explain these differences, the crystal structures of the three salts were compared and the following features were identified as potential factors: (i) The Re−O−CH_3 group is linear in the PF_6^- salt but bent in the others (159.2(9)°, $B(C_6H_5)_4^-$; 162.6(2)°, $CF_3SO_3^-$). (ii) The imidazole ligands are differently oriented (Table 3); they are all approximately coplanar with the O═Re−O direction in the PF_6^- salt, but at least some of them are rotated ∼45° from this direction in the other cases. (iii) Displacement of the Re−N bonds away from the Re═O bond is very small for the PF_6^- salt (O1−Re−N = 90.89(8)°) but appreciably greater for $B(C_6H_5)_4^-$ (92.5°) and $CF_3SO_3^-$ (92.8°). The structural particularities of the PF_6^- salt can be related to two electronic effects: The orientation of the imidazole rings parallel to the O═Re−O axis makes metal-to-ligand back-bonding possible via $d_{xy}-\pi^*$(imidazole) interactions, whereas the oxygen p orbitals of the linear sp-hybridized O−CH_3 group could participate to a different extent in the O═Re−O π system. However, it is not clear at this time how the metal-centered d−d transition would be affected by such effects.

Reaction of *trans*-$[ReO_2(1\text{-MeIm})_4]^+$ with BF_4^-. The oxo−boron complex $[ReO(OBF_3)(1\text{-MeIm})_4]^+$ was isolated from a methanol solution of $[ReO(OH)(1\text{-MeIm})_4]^{2+}$ and excess $NaBF_4$ in the presence of 2,2-dimethoxypropane. The same compound also formed, but less efficiently, in methanol by direct reaction of 6 equiv of $(Et_2O)BF_3$ with $[ReO_2(1\text{-MeIm})_4]^+$. In the latter case, after 24 h at room temperature, the ^{1}H NMR spectrum showed signals in a 1:3 ratio for the $[ReO(OBF_3)(1\text{-MeIm})_4]^+$ species and free ligand, which is protonated in the presence of the presumably acidic $(CH_3OH)BF_3$ adduct.[31,32]

Abstraction of F^- from BF_4^- by rhenium complexes has been reported previously for low oxidation states, and several compounds have been structurally characterized.[33] Very recently, the Re(V) compound $ReO(F)Cl_2(PPh_3)_2$ was obtained by reacting stoichiometric amounts of $(Et_2OH)BF_4$ with $ReO(OEt)Cl_2(PPh_3)_2$ in CH_2Cl_2.[34] This reaction likely proceeds via a coordinatively unsaturated species created by EtOH loss in the presence of acid. Since BF_4^- shows appreciable coordinating ability in poorly coordinating solvents,[17] a $ReO(FBF_3)Cl_2(PPh_3)_2$ intermediate probably forms, from which BF_3 is eventually lost. However, for the present dioxo compound, a coordination site cannot be opened readily unless imidazole is displaced, so that F^- is unlikely to be expelled via a similar process.

The $[(CO)_5Re(OBF_3)]^-$ ion containing the same F_3BO^{2-} ligand was identified in solution by Beck and co-workers.[15] It was obtained by acid dissociation of $(CO)_5Re(HOBF_3)$, which itself resulted from HF loss in solid $[(CO)_5Re(H_2O)](BF_4)$. Simple HF elimination does not occur here in methanol, since there is no sign of a reaction before dimethoxypropane is added as water quencher.

The role played by dimethoxypropane is not fully understood, but it is obviously not restricted to water quenching. The first step probably involves acidic proton transfer from $[ReO(OH)(1\text{-MeIm})_4]^{2+}$ to generate the $(CH_3)_2C^+OCH_3$ cation with CH_3OH elimination. The simplest mechanism would then involve F^- abstraction from BF_4^- and liberation of BF_3, probably as the $BF_3(CH_3OH)$ adduct, which would eventually add to the $[O═Re═O]^+$ core. An alternative pathway including greater participation of dimethoxypropane is suggested by recent results on adducts of the isoelectronic $[Re≡N]^{2+}$ unit, for which complexes containing $Re≡NBX_3$ groups (X = halogen) are known.[35] The red $[Re(NBPh_3)(Me_2PhP)(Et_2dtc)_2]$ compound (where Et_2dtc = diethyldithiocarbamato) is the only known complex of this type with an organic BR_3 unit. It is formed by reacting the nitride $[ReN(Me_2PhP)(Et_2dtc)_2]$ with HCl in acetone, followed by the addition of $NaBPh_4$.[36] The initial step is proposed to be the addition to the nitride group of the $(CH_3)_2C^+CH_2C(O)CH_3$ cation produced by acid condensation of acetone: The adduct was isolated and identified spectroscopically. The organic cation would then be displaced by Ph_3B generated by protolysis of Ph_4B^-. In acetone, the same reaction does not take place with our oxo complex, even when $[ReO(OH)(1\text{-MeIm})_4]^{2+}$ is left standing in the presence of excess acid. However, this result does not rule out a possible participation of the $(CH_3)_2C^+OCH_3$ ion derived from dimethoxypropane, playing a role similar to the condensed acetone carbocation. Thus, it is not clear whether F^- abstraction takes place in the bulk of the solution or with an oxo-coordinated $(CH_3)_2C^+OCH_3$ ion (assuming that such an adduct forms), but dimethoxypropane plays a determining part in this reaction. The preparation of the $[ReO(OBPh_3)(1\text{-MeIm})_4]^+$ analogue was attempted in methanol/dimethoxypropane, but the reaction was hampered by the total insolubility of the protonated salt $[ReO(OH)(1\text{-MeIm})_4](BPh_4)_2$.

Reaction of *trans*-$[ReO(OH)(1\text{-MeIm})_4]^{2+}$ or $[ReO(OCH_3)(1\text{-MeIm})_4]^{2+}$ with PF_6^-. The royal blue phosphate ester complex $[ReO\{OP(O)(OCH_3)_2\}(1\text{-MeIm})_4]^{2+}$ forms as the major product from a mixture of $[ReO_2(1\text{-MeIm})_4]^+$ and excess methyl triflate in methanol, to which PF_6^- is added. Initial reaction of methyl triflate with methanol leads to triflic acid, while some dimethyl ether is evolved. The equilibrium mixture, which is very acidic, should still contain strong methylating species like $(CH_3)_2OH^+$ and/or CH_3OH_2+. The violet color corresponds to either $[ReO(OH)(1\text{-MeIm})_4]^{2+}$ or, more likely, to $[ReO(OCH_3)(1\text{-MeIm})_4]^{2+}$, which once formed is more

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kinetically inert. There is no evidence for the presence of the bis-methylated species $[ReO\{O(CH_3)_2\}(1\text{-MeIm})_4]^{3+}$, since the solution retains its typical violet color. After addition of NH_4PF_6, the blue color develops during volume reduction, and workup yields a blue material, whose main constituent is the $[ReO\{OP(O)(OCH_3)_2\}(1\text{-MeIm})_4]^{2+}$ ion. This species, whose structure was eventually determined by X-ray diffraction, is identified from the ^1H NMR spectrum, in particular the characteristic ^{31}P-coupled doublet (J_{P-H} = 11 Hz) of the $(CH_3O)_2PO_2^-$ ligand. Several other weaker peaks are present, which were not identified, but no $[ReO(OCH_3)(1\text{-MeIm})_4]^{2+}$ remains, since the Re−OCH_3 signal at 3.70 ppm is absent. Pure $[ReO\{OP(O)(OCH_3)_2\}(1\text{-MeIm})_4](PF_6)_2$ was isolated from overnight recrystallization of the raw sample, but the other components could not be isolated.

Initial acid-promoted displacement[37] of F^- from PF_6^- is likely followed by relatively fast alcoholysis processes known to occur with PF_5,[38−41] generating various intermediate fluoro−oxo−alkoxo species and, finally, phosphate esters. The reaction does not reach the $PO(OCH_3)_3$ stage, probably because the third methoxy group is relative easy to displace.[42] The diester product, undoubtedly present as the acidic form $PO(OH)(OCH_3)_2$ under our conditions, displaces the CH_3O^- group from the Re−OCH_3 unit with elimination of CH_3OH.

Recrystallized $[ReO\{OP(O)(OCH_3)_2\}(1\text{-MeIm})_4](PF_6)_2$ in methanol is stable in a closed NMR tube. However, the raw product, although stable when kept away from moisture, changes into an unidentified green compound in moist conditions, whereas decomposition to a black material takes place after a few days in solution. This raw material is not very stable either in methanol solution. This may be due to hydrolysis of either the coordinated phosphate ester or other species generated earlier in the solvolytic process, which could be responsible for the long-term instability of the sample in the presence of water. Phosphates can show a wide variety of coordinating abilities, including a bridging role[43,44] in dinuclear complexes.

In order to verify the role of H^+ in the PF_6^- solvolysis, attempts were made to react PF_6^- under the conditions used to obtain the OBF_3^{2-} complex, since F^- displacement is known to take place. The protonated compound $[ReO(OH)(1\text{-MeIm})_4](PF_6)_2$ was reacted with excess NH_4PF_6 in a 2:1 mixture of methanol and dimethoxypropane. The only partially soluble starting material was allowed to react for 3 h, during which time the initial purple color was gradually lost, as well as all solubility. The resulting brown material showed IR bands neither at 950 cm^{-1} for a O═Re−OR system nor at 780 cm^{-1} for a dioxo compound. A broad IR band is present at 740 cm^{-1}, which could indicate the formation of a μ-oxo dimer. This remains to be confirmed, but it can be concluded that under these conditions, fluorine is definitely not appreciably displaced from PF_6^-.

Conclusion

This work confirms our previous observations that the *trans*-$ReO_2(1\text{-MeIm})_4$+ core with imidazole ligands is more resistant to ligand displacement than those of pyridines. $ReOCl_3(py)_2$, $ReO(OEt)I_2(py\text{-}X)_2$, and $ReO_2I(py\text{-}X)_2$ have been prepared from the corresponding $[ReO_2(py\text{-}X)_4]^+$ precursor (py-X = pyridine or substituted pyridine).[45] The related chemistry could not be developed under the same conditions with imidazoles, and attempts to prepare these species via other routes did not lead to ligand substitution. The 1-MeIm complex is also more resistant to ligand loss in aqueous solution than $[ReO_2(py)_4]^+$, which readily generates $[ReO_2(OH_2)(py)_3]^+$ in the absence of excess pyridine.[46] Apart from oxo protonation[1] and methylation,[8] few reports on the derivatization of *trans*-dioxo complexes with retention of the four N-donor ligands have been published. Oxo methylation of the imidazole compounds to $[ReO(OCH_3)L_4]^{2+}$ is found here to take place smoothly and efficiently, whereas the F_3BO^{2-} and $(CH_3O)_2PO_2^-$ complexes are obtained without imidazole loss. Clearly, the higher basicity of 1-MeIm improves the stability to the $[ReO_2L_4]^+$ unit, which provides a system on which the preparation of a broad range of $[ReO(OR)L_4]^{n+}$ complexes can be envisaged.

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Supporting Information Available: Figures showing ORTEP views of molecular packing and text describing the preparation of $[ReO(OBF_3)(1\text{-MeIm})_4](I_3)$ and $[ReO(OBF_3)(1\text{-MeIm})_4](I)_{0.2}(BF_4)_{0.8}$ (4 pages). X-ray crystallographic files, in CIF format, for complexes $[ReO(OCH_3)(1\text{-MeIm})_4](PF_6)_2$, $[ReO\{OP(O)(OCH_3)_2\}(1\text{-MeIm})_4](PF_6)_2$·toluene, and $[ReO(OBF_3)(1\text{-MeIm})_4](I_3)$ are available on the Internet only. Access and ordering information is given on any current masthead page.

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