Tp* Rhenium(V) Oxo−Halide, −Hydride, −Alkyl, −Phenyl, and −Alkoxide Complexes: Syntheses and Oxidations

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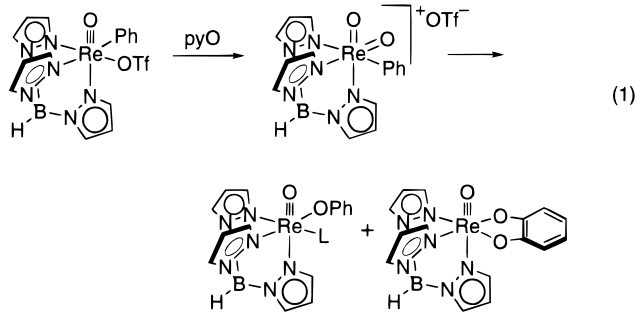
Rhenium−oxo complexes with the hydridotris(3,5-dimethyl-1-pyrazolyl)borate (Tp*) ligand are described. Halide complexes Tp*Re(O)X(Cl) (X = Cl, I) are prepared by treatment of Tp*Re(O)(OH)Cl with HX. Reaction of Tp*Re(O)Cl_2 (**3**) with 1 or 2 equiv of LiPh/$ZnCl_2$ or Et_2Zn produces the corresponding oxo−aryl and oxo−alkyl complexes Tp*Re(O)(Ph)Cl, Tp*Re(O)$(Ph)_2$, and Tp*Re(O)(Et)Cl. Alkoxide complexes Tp*Re(O)(OR)Cl and Tp*Re(O)$(OR)_2$ are prepared from **3** and ROH, PhOH, or catechol. Triflate complexes Tp*Re(O)X(OTf) (X = halide, H, Et, Ph, OEt, OPh) have been prepared by halide metathesis with AgOTf or by alkoxide metathesis with Me_3SiOTf. Hydride complexes Tp*Re(O)(H)X (X = Cl, H) are generated from the corresponding alkoxide complexes with BH_3·THF. Oxidation of Tp*Re(O)Ph(OTf) with Me_2SO gives a phenoxide complex, and oxidation of Tp*Re(O)Et(OTf) with pyridine *N*-oxide gives acetaldehyde. Both reactions are similar to oxidations of related Tp compounds. Tp*Re(O)H(OTf) is oxidized by either reagent to Tp*Re$(O)_3$, with liberation of H^+; such a hydride complex has not been accessible in the Tp system. The Tp* ligand imparts added stability to the rhenium(V) derivatives, making preparations easier. Steric constraints of the Tp* ligand are illustrated by the lack of phenyl and pyridine ligand rotation on the NMR time scale. The stability and crowding of the Tp* compounds inhibits reactions with oxygen atom donors so that heating is often required, and the resulting oxidations are more complex than for analogous Tp compounds.

Introduction

Selective oxidations are among the least explored and least understood areas of organometallic chemistry. While transition-metal complexes catalyze or mediate a number of organic oxidations, there is ample room for improvement and extension of these processes.[1] As one approach to this area, we have set out to generate strongly oxidizing organometallic complexes. Rhenium(V) oxo−alkyl and oxo−aryl complexes have been prepared using the hydridotris(1-pyrazolyl)borate or Tp ligand.[2] These compounds are relatively unreactive, but treatment with oxygen atom donors leads to oxidation of the organic ligands. The oxo−phenyl complex converts to phenoxide and catecholate complexes (eq 1; pyO = pyridine *N*-oxide). Related ethyl and ethoxide complexes



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form acetaldehyde. Rhenium(VII) dioxo cations [TpRe$(O)_2X]^+$ are the key reactive species in these reactions but have not been isolated.[2,3] They are quite oxidizing and electrophilic. Few cationic Re^{VII} complexes are known, despite the recent interest in Re^{VII}−oxo compounds.[4]

This report describes our preparations and studies of rhenium oxo complexes with the hydridotris(3,5-dimethyl-1-pyrazolyl)borate or Tp* ligand. Prior to these studies, Herrmann et al. had reported Tp*Re$(O)_3$ (**1**),

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Coe had generated Tp*Re(O)(OH)Cl (**2**) and Tp*Re(O)Cl_2 (**3**) (though not in high yields), and Santos et al. had explored rhenium chemistry with bis- and tetrakis-(1-pyrazolyl)borate ligands.[5] Gable and co-workers are also examining this system.[6] We moved from Tp to Tp* ligands, thinking that the more electron donating nature and increased size of Tp*[7,8] should provide additional stability and perhaps allow the isolation of rhenium(VII) cations. We have isolated Tp^*Re^{V} compounds that are not accessible in the Tp system, such as hydride[9] and fluoride[10] derivatives, but slow substitution reactions[11] have prevented the observation of Re^{VII} complexes.

Experimental Section

General Considerations. All experiments were performed under an inert atmosphere using standard vacuum line, Schlenk, and glovebox techniques, except where noted. Tp*Re(O)$_3$ (**1**), Tp*Re(O)(OH)Cl (**2**), and Tp*Re(O)Cl_2 (**3**) were synthesized by modifications of the published procedures.[5a,b] Solvents were degassed and dried according to standard procedures.[12] Deuterio solvents were purchased from Cambridge Isotope Laboratories. C_6D_6 was dried over sodium metal, and CD_2Cl_2 and $CDCl_3$ were dried over CaH_2. Reagents were obtained from Aldrich and used as received unless otherwise noted. Aqueous HF (48.5%), HCl (37%), and HBr (48%) were purchased from Baker. Aqueous HI (47%) was purchased from Aldrich. Et_3N was degassed, dried over CaH_2, and vacuum-transferred prior to use. Me_3SiCl was degassed and vacuum-transferred prior to use. Pyridine *N*-oxide was sublimed and stored under nitrogen. Acetaldehyde was dried over 4 Å molecular sieves. Me_2SO was dried over 4 Å molecular sieves. $Me_3SiOSiMe_3$ was dried over sodium metal and vacuum-transferred prior to use. Ethylene and propylene (Union Carbide) were used as received. Unless indicated otherwise, liquid chromatography was conducted using silica gel (grade 9385, 230−400 mesh; Merck).

NMR spectra were recorded on Bruker AC-200 (^{1}H, ^{19}F), DPX-200 (^{1}H, ^{13}C), and AM-499 (^{1}H) Fourier transform spectrometers. Spectra were recorded at ambient temperatures unless otherwise noted. ^{1}H and ^{13}C NMR spectra were referenced to residual protio solvent. IR spectra, reported in cm^{-1}, were recorded using a Perkin-Elmer 1600 FTIR spectrometer with samples prepared as Nujol mulls. Mass spectra were recorded with a Kratos Analytical mass spectrometer using direct injection and electron impact ionization unless otherwise indicated. Elemental analyses were performed by Canadian Microanalytical Services Ltd. or Atlantic Microlabs.

Tp*ReO$_3$ (1). A 250 mL flask was charged with Re_2O_7 (1.0 g, 2.06 mmol). THF (100 mL) and trifluoroacetic anhydride (1.2 mL, 8.1 mmol) were added by vacuum transfer at −78 °C. The resulting mixture was warmed to room temperature with stirring. The cream-colored suspension turned clear and colorless. The solution was again chilled to −78 °C, and KTp* (3.3 g, 10 mmol) was slowly added. The mixture was warmed to room temperature and stirred for 17 h. During this time the product precipitated. The resulting white solid was isolated by filtration and washed sequentially with H_2O, THF, and Et_2O. Drying in vacuo afforded Tp*ReO_3 (6.2 g, 73%) as a fine white powder which was spectroscopically identical with a sample prepared by the original procedure. ^{1}H NMR ($CDCl_3$): δ 5.89 (s, 3H, pz), 2.83, 2.35 (each s, 9H, pz-Me).

Tp*Re(O)(OH)Cl (2).[5b] Me_3SiCl (8.5 mL, 67 mmol) was added by vacuum transfer to a solution of **1** (2.84 g, 5.34 mmol) and PPh_3 (1.40 g, 5.34 mmol) in THF (100 mL). The resulting suspension was refluxed for 3 h. The volatiles were removed under reduced pressure, leaving a dark brown residue. The residue was washed with EtOH to remove Ph_3PO, affording a dark blue solid. Recrystallization from hexane/CH_2Cl_2 yielded a blue crystalline solid containing **2** (2.66 g, 90%) and **3** (0.14 g, 4.6%). This crude mixture can be used without further purification for the syntheses of **3**−**6**. Pure **2** was obtained by column chromatography on lipophilic Sephadex LH-20 with CH_2Cl_2. ^{1}H NMR ($CDCl_3$): δ 6.06 (s, 2H, pz), 5.63 (s, 1H, pz), 2.91, 2.81, 2.62, 2.59, 2.32, 2.20 (each s, 3H, pz-Me). IR: 2547 (ν_{BH}), 1547, 1418, 1377, 1203, 1075, 1045, 971 (ν_{ReO}), 864, 813, 787, 689, 640, 614. MS: *m*/*z* 552 (M^+).

Tp*Re(O)Cl_2 (3). Aqueous HCl (36.5−38%, 20 mL) was added to a solution of crude **2** (2.73 g, including 4.72 mmol of **2**) in 120 mL of CH_2Cl_2. The resulting mixture was stirred for 2 h at room temperature and then neutralized with saturated $NaHCO_3$ solution. The organic phase was separated and dried over $MgSO_4$, and the solvent was removed. Purification of the resulting residue by column chromatography using CH_2Cl_2 as the eluent followed by recrystallization from CH_2Cl_2/hexanes afforded 2.71 g of **3** (95%) as sky blue crystals. ^{1}H NMR ($CDCl_3$): δ 6.11 (s, 2H, pz), 5.69 (s, 1H, pz), 2.96, 2.67 (each s, 6H, pz-Me), 2.37, 2.22 (each s, 3H, pz-Me). IR: 2549 (ν_{BH}), 1544, 1418, 1204, 1073, 1040, 981 (ν_{ReO}), 861, 814, 786, 692, 644. MS: *m*/*z* 570 (M^+). Anal. Calcd for $C_{15}H_{22}BCl_2N_6ORe$: C, 31.59; H, 3.89; N, 14.74. Found: C, 31.54; H, 3.90; N, 14.63.

Tp*Re(O)(OH)OTf (4). A mixture of **2** (306 mg, 0.554 mmol), AgOTf (150 mg, 0.584 mmol), and C_6H_6 (30 mL) was stirred in the dark for 24 h. The suspension was filtered, and the volume was reduced to ∼3 mL. Pentane (10 mL) was added, and the resulting precipitate was isolated by filtration and washed with pentane to afford 225 mg of **4** (61%) as a blue solid. ^{1}H NMR ($CDCl_3$): δ 6.12, 6.06, 5.76 (each s, 1H, pz), 4.20 (br, 1H, Re−OH), 2.76, 2.68, 2.67, 2.57, 2.46, 2.24 (each s, 3H, pz-Me). ^{19}F NMR ($CDCl_3$): δ −0.284. IR: 3500 (ν_{OH}), 2557 (ν_{BH}), 1547, 1418, 1345, 1236, 1204, 1154, 1079, 1066, 1023, 975 (ν_{ReO}), 865, 814, 789, 692, 647. Anal. Calcd for $C_{16}H_{23}BF_3N_6O_5ReS$: C, 28.87; H, 3.48; N, 12.63. Found: C, 28.96; H, 3.51; N, 12.81.

Tp*Re(O)(Br)Cl (5). Aqueous HBr (47−49%, 1.5 mL) was added to a solution of **2** (81 mg, 0.147 mmol) in 20 mL of CH_2Cl_2, and the resulting mixture was stirred for 64 h at room temperature. Following the workup procedure for **3**, 86 mg of **5** (95%) was obtained as sky blue crystals. ^{1}H NMR ($CDCl_3$): δ 6.13, 6.09, 5.71 (each s, 1H, pz), 3.05, 2.95, 2.71, 2.67, 2.38, 2.23 (each s, 3H, pz-Me). IR: 2559 (ν_{BH}), 1542, 1410, 1363, 1201, 1068, 1042, 969 (ν_{ReO}), 910, 862, 814, 790, 688, 644. MS: *m*/*z* 614 (M^+). Anal. Calcd for $C_{15}H_{22}BBrClN_6ORe\cdot 0.25CH_2Cl_2$: C, 28.80; H, 3.57; N, 13.21. Found: C, 28.66; H, 3.55; N, 13.25.

Tp*Re(O)(I)Cl (6). Aqueous HI (3 mL) was added to a solution of crude **2** (450 mg, including 0.777 mmol of **2**) in 30 mL of CH_2Cl_2. The mixture was stirred for 10 min at room temperature and worked up as for **3**, yielding 458 mg (89%) of **6** as yellowish green crystals. ^{1}H NMR ($CDCl_3$): δ 6.16, 6.07, 5.71 (each s, 1H, pz), 3.17, 2.94, 2.77, 2.67, 2.38, 2.24 (each s, 3H, pz-Me). IR: 2559 (ν_{BH}), 1545, 1413, 1360, 1206, 1067, 1041,

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973 (ν_{ReO}), 861, 813, 791, 689, 642. MS: *m/z* 662 (M^+). Anal. Calcd for $C_{15}H_{22}BClIN_6ORe$: C, 27.23; H, 3.35; N, 12.70. Found: C, 27.38; H, 3.36; N, 12.58.

Tp*Re(O)(Cl)OTf (7). Me_3SiOTf (72 μL, 0.40 mmol) was added to a solution of Tp*Re(O)(F)Cl[10] (200 mg, 0.361 mmol) in CH_2Cl_2 (35 mL), and the solution was stirred for 45 min. Removal of the solvent under reduced pressure and washing with pentane afforded 240 mg of **7** (97%) as a sky blue powder. ^1H NMR ($CDCl_3$): δ 6.16, 6.12, 5.80 (each s, 1H, pz), 2.86, 2.83, 2.76, 2.64, 2.48, 2.26 (each s, 3H, pz-Me). ^{19}F NMR ($CDCl_3$): δ −0.28. IR: 2564 (ν_{BH}), 1543, 1418, 1355, 1236, 1198, 1157, 1078, 1070, 1048, 974 (ν_{ReO}), 956, 866, 824, 788, 736, 692, 635. MS: *m/z* 684 (M^+). Anal. Calcd for $C_{16}H_{22}BClF_3N_6O_4ReS$: C, 28.10; H, 3.24; N, 12.29. Found: C, 28.12; H, 3.33; N, 11.57.

Tp*Re(O)(Et)Cl (8). Et_2Zn in Et_2O (1.0 M × 0.18 mL, 0.18 mmol) was added to a solution of **3** (200 mg, 0.351 mmol) in C_6H_6 (150 mL), and the mixture was stirred for 2 h. The flask was opened to the air, and the solvent was removed under reduced pressure, leaving a brown residue. Purification by chromatography with toluene and recrystallization from CH_2Cl_2/hexanes yielded 166 mg of **8** (84%) as blue crystals. ^1H NMR ($CDCl_3$): δ 10.79, 4.37 (each dq, 1H, ReC*HH′*Me, *J* = 14.2, 7.2 Hz), 6.09, 6.01, 5.63 (each s, 1H, pz), 3.02, 2.83, 2.78, 2.52, 2.40, 2.22 (each s, 3H, pz-Me), 1.73 (t, 3H, $ReCH_2CH_3$, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$): δ 157.59, 155.65, 155.63 148.42, 146.09, 142.87, 108.82, 108.51, 108.05, 26.26, 24.84, 15.31, 15.15, 14.89, 12.52, 12.31, 12.27. IR: 2559 (ν_{BH}), 1544, 1420, 1365, 1201, 1069, 1043, 970 (ν_{ReO}), 879, 863, 813, 792, 690, 643. MS: *m/z* 564 (M^+). Anal. Calcd for $C_{17}H_{27}BClN_6ORe$: C, 36.21; H, 4.83; N, 14.90. Found: C, 36.43; H, 4.85; N, 14.79.

Tp*Re(O)(Et)$_2$ (9). Following the procedure for **8**, **3** (265 mg, 0.465 mmol), Et_2Zn in Et_2O (1.0 M × 0.51 mL, 0.51 mmol), and C_6H_6 (40 mL) were stirred for 1 h and worked up to give a 63 mg of **9** (24%). The procedure also gave 65 mg (25%) yield of **8**. ^1H NMR ($CDCl_3$): δ 10.24 (dq, 2H, ReC*HH′*Me, *J* = 14, 7.2 Hz), 6.03 (s, 2H, pz), 5.55 (s, 1H, pz), 4.93 (dq, 2H, ReCH*H′*Me, *J* = 14, 7.4 Hz), 2.83, 2.61 (each s, 6H, pz-Me), 2.35, 2.19 (each s, 3H, pz-Me), 1.70 (t, 6H, $ReCH_2CH_3$, *J* = 7.5 Hz). IR: 2543 (ν_{BH}), 1547, 1417, 1207, 1069, 1036, 1000 (ν_{ReO}), 858, 814, 782, 694, 648. CIMS: *m/z* 559 ($[M + 1]^+$). Anal. Calcd for $C_{19}H_{32}BN_6ORe$: C, 40.93; H, 5.79; N, 15.07. Found: C, 41.08; H, 5.65; N, 14.87.

Tp*Re(O)(Et)OTf (10). A mixture of **8** (169 mg, 0.300 mmol) and AgOTf (84.8 mg, 0.330 mmol) in C_6H_6 (12 mL) was stirred in the dark for 5 h and filtered. The volume was reduced by two-thirds. Pentane (30 mL) was vacuum-transferred into the flask, and a greenish blue solid was isolated by filtration. Purification by chromatography using toluene and recrystallization from toluene/pentane yielded 180 mg of **10** (89%). ^1H NMR ($CDCl_3$): δ 12.69, 3.90 (each dq, 1H, ReC*HH′*Me, *J* = 14.4, 7.2 Hz), 6.10, 6.01, 5.79 (each s, 1H, pz), 2.98, 2.84, 2.65, 2.52, 2.49, 2.28 (each s, 3H, pz-Me), 1.48 (t, 3H, $ReCH_2CH_3$, *J* = 7.2 Hz). ^{19}F NMR ($CDCl_3$): δ −0.42. IR: 2557 (ν_{BH}), 1538, 1347, 1307, 1237, 1198, 1159, 1076, 1065, 1045, 984, 973, 861, 812, 778, 689, 668. MS: *m/z* 678 (M^+). Anal. Calcd for $C_{18}H_{27}BF_3N_6O_4ReS$: C, 31.91; H, 4.02; N, 12.40. Found: C, 31.98; H, 3.95; N, 12.31.

Tp*Re(O)(Ph)Cl (11). PhMgCl in Et_2O (2.0 M × 0.10 mL, 0.20 mmol) was added to a solution of **3** (100 mg, 0.175 mmol) in toluene (100 mL). After stirring for 30 min, the flask was opened to the air and the volatiles were removed under reduced pressure, leaving a brown residue. The products were purified by chromatography using toluene to afford 70 mg of **11** (64%) as well as 26 mg of **12** (22%). ^1H NMR ($CDCl_3$): δ 7.85 (d, 1H, Ph, *J* = 7.6 Hz), 7.60 (dt, 1H, Ph, *J* = 1.2, 7.4 Hz), 7.27 (m, 1H, Ph), 6.89 (tt, 1H, Ph, *J* = 1.2, 7.4 Hz), 6.60 (d, 1H, Ph, *J* = 7.6 Hz), 6.10, 6.04, 5.57 (each s, 1H, pz), 3.08, 2.84, 2.60, 2.27, 2.03, 1.55 (each s, 3H, pz-Me). IR: 2544 (ν_{BH}), 1539, 1415, 1200, 1062, 1041, 969 (ν_{ReO}), 862, 815, 790, 733, 692, 645. MS: *m/z* 612 (M^+). Anal. Calcd for $C_{21}H_{27}BClN_6ORe$: C, 41.22; H, 4.45; N, 13.73. Found: C, 41.13; H, 4.42; N, 13.55.

Tp*Re(O)(Ph)$_2$ (12). PhMgCl in Et_2O (2.0 M × 1.0 mL, 2.0 mmol) was added to a −78 °C solution of **3** (495 mg, 0.868 mmol) in toluene (80 mL). The mixture was warmed to room temperature with stirring. After 5 h, a suspension of saturated NH_4Cl in EtOH (3 mL) was added. The solvent was evaporated under reduced pressure. The residue was extracted with toluene and purified by chromatography using toluene to afford 430 mg of **12** (75%) as blue crystals. ^1H NMR ($CDCl_3$): δ 7.83 (d, 2H, Ph, *J* = 7.6 Hz), 7.43, 7.13, 6.60 (each m, 2H, Ph), 6.08 (d, 2H, Ph, *J* = 7.8 Hz), 6.00 (s, 2H, pz), 5.53 (s, 1H, pz), 2.68, 1.98 (each s, 6H, pz-Me), 2.32, 1.07 (each s, 3H, pz-Me). ^{13}C NMR ($CDCl_3$): δ 155.77, 154.34, 153.98, 146.63, 144.58, 143.29, 140.34, 128.94, 125.39, 124.75, 108.59, 107.58, 16.42, 14.73, 12.94, 12.59. IR: 2544 (ν_{BH}), 1544, 1307, 1200, 1067, 1021, 990 (ν_{ReO}), 790. MS: *m/z* 654 (M^+). Anal. Calcd for $C_{27}H_{32}BN_6ORe$: C, 49.62; H, 4.93; N, 12.86. Found: C, 49.52; H, 4.91; N, 12.88.

Tp*Re(O)(Ph)OTf (13). A mixture of **11** (185 mg, 0.302 mmol) and AgOTf (81 mg, 0.32 mmol) in CH_2Cl_2 (30 mL) was stirred in the dark for 21 h. The solution was filtered, and the solvent was removed under reduced pressure. The residue was purified by chromatography with toluene to afford 144 mg of **13** (66%). ^1H NMR ($CDCl_3$): δ 7.62 (dt, 1H, Ph, *J* = 1.2, 7.4 Hz), 7.44 (d, 1H, Ph, *J* = 7.6 Hz), 7.22 (m, 1H, Ph), 6.66 (tt, 1H, Ph, *J* = 1.2, 7.3 Hz), 6.23 (d, 1H, Ph, *J* = 7.7 Hz), 6.12, 5.97, 5.75 (each s, 1H, pz), 2.94, 1.82 (each s, 6H, pz-Me), 2.62, 2.34 (each s, 3H, pz-Me). ^{19}F NMR (CD_2Cl_2): δ −0.485. IR: 2554 (ν_{BH}), 1544, 1342, 1232, 1205, 1186, 1158, 1067, 991, 969 (ν_{ReO}), 863, 812, 733, 696, 652, 617. MS: *m/z* 726 (M^+). Anal. Calcd for $C_{22}H_{27}BF_3N_6O_4ReS$: C, 36.42; H, 3.75; N, 11.58. Found: C, 36.49; H, 3.86; N, 11.48.

Tp*Re(O)(OMe)Cl (14). Complex **3** (1.02 g, 1.79 mmol), CH_3CN (50 mL), MeOH (2 mL), and Et_3N (14 mL, 0.10 mol) were placed in a 250 mL thick-walled glass bomb and stirred for 3 days at 75 °C, during which time the blue suspension gradually turned homogeneous. The bomb was opened to the air, and the volatiles were removed under reduced pressure. The residue was extracted with toluene and filtered through Celite. The solvent was removed under reduced pressure, and the resulting blue residue was purified by chromatography with toluene and recrystallized from CH_2Cl_2/hexanes to afford 0.89 g of **14** (88%) as blue crystals. ^1H NMR ($CDCl_3$): δ 6.04 (s, 2H, pz), 5.70 (s, 1H, pz), 5.46 (s, 3H, OMe), 2.83, 2.76, 2.63, 2.60, 2.45, 2.22 (each s, 3H, pz-Me). IR: 2545 (ν_{BH}), 1545, 1202, 1072, 1030, 953 (ν_{ReO}), 863, 814, 787, 692. MS: *m/z* 566 (M^+). Anal. Calcd for $C_{16}H_{25}BClN_6O_2Re$: C, 33.96; H, 4.45; N, 14.85. Found: C, 34.00; H, 4.40; N, 14.65.

Tp*Re(O)(OMe)$_2$ (15). MeOH (60 mL), **3** (1.00 g, 1.75 mmol), and Et_3N (12.5 mL, 89 mmol) were placed in a 250 mL thick-walled bomb and stirred for 6 days at 85 °C, during which time the blue suspension gradually turned homogeneous. The bomb was opened to the air, and the volatiles were removed under reduced pressure. The residue was extracted with toluene. The solvent was evaporated under reduced pressue, and the blue residue was purified by column chromatography using 10:1 CH_2Cl_2/EtOAc followed by recrystallization from CH_2Cl_2/hexanes to yield 0.95 g of **15** (96%) as blue crystals. ^1H NMR ($CDCl_3$): δ 6.00 (s, 2H, pz), 5.68 (s, 1H, pz), 4.69 (s, 6H, OMe), 2.69, 2.57 (each s, 6H, pz-Me), 2.42, 2.23 (each s, 3H, pz-Me). IR: 2539 (ν_{BH}), 1543, 1198, 1068, 1029, 943 (ν_{ReO}), 862, 812, 784, 692. MS: *m/z* 562 (M^+). Anal. Calcd for $C_{17}H_{28}BN_6O_3Re$: C, 36.37; H, 5.03; N, 14.97. Found: C, 36.34; H, 4.99; N, 14.82.

Tp*Re(O)(OEt)Cl (16). Tp*Re(O)Cl_2 (**3**; 25 mg, 0.044 mmol) was placed in a 25 mL bomb. NEt_3 (1.0 mL, 7.2 mmol) and EtOH (2.0 mL, 34 mmol) were added by vacuum transfer. The bomb was sealed and heated for 2 days. The volatiles were removed under reduced pressure, the residue was extracted

with toluene, and the extract was filtered through glass wool. The solvent was evaporated under reduced pressure, and the blue residue was purified by column chromatography using CH_2Cl_2 followed by recrystallization from C_6H_6/hexanes to yield 17 mg of **16** (67%) as blue crystals. ^{1}H NMR (C_6D_6): δ 7.00, 6.32 (each d of q, 2H, ReOC*HH*′CH$_3$, J_{HH} = 7, 12 Hz), 5.55, 5.45, 5.24 (each s 1H, pz), 2.97, 2.84, 2.56, 2.19, 2.14, 1.86 (each s, 3H, pz-Me), 1.58 (t, 34, OCH$_2$C*H*$_3$). ^{13}C NMR (C_6D_6): δ 158.5, 158.0, 156.1, 147.5, 146.4, 142.8, 108.9, 108.6, 107.9 (pz), 83.0 (ReO*C*H$_2$CH$_3$), 18.8 (ReOCH$_2$*C*H$_3$), 15.0, 14.8, 13.6, 12.4, 12.1, 12.0 (pz-Me). IR: 2547 (ν_{BH}), 1545, 1451, 1416, 1207, 1068, 1038, 956 (ν_{ReO}), 862, 816, 785, 642. MS: *m*/*z* 628 (M^+). Anal. Calcd for $C_{17}H_{27}BClN_6O_2Re$: C, 35.21; H, 4.69; N, 14.49. Found: C, 35.11; H, 4.51; N, 14.61.

Tp*Re(O)(OEt)OTf (17). A sealable NMR tube was charged with **16** (12 mg, 0.021 mmol), AgOTf (5.5 mg, 0.022 mmol), and C_6D_6 (1.1 mL). The solution immediately turned dark blue, and a purple precipitate was formed. ^{1}H NMR was consistent with the formation of **17**. ^{1}H NMR (C_6D_6): δ 5.38, 5.34, 5.29 (each s, 1H, pz), 4.95, 4.01 (each d of q, 2H, ReOC*HH*′CH$_3$, J_{HH} = 6, 11 Hz), 3.01, 2.75, 2.14, 2.06, 2.03, 1.81 (each s, 3H, pz-Me), 1.36 (t, 3H, ReOCH$_2$C*H*$_3$). ^{19}F NMR ($CDCl_3$): δ −0.48 (s).

Tp*Re(O)(OPh)Cl (18). Following the procedure for **14**, **3** (135 mg, 0.237 mmol), phenol (25 mg, 0.266 mmol), CH_3CN (30 mL), and Et_3N (0.5 mL, 3.6 mmol) were stirred for 3 days at 80 °C and worked up to afford 29 mg of **18** (20%). ^{1}H NMR ($CDCl_3$): δ 7.43 (t, 2H, Ph, J = 7.8 Hz), 6.87 (d, 2H, Ph, J = 8.0 Hz), 6.74 (t, 1H, Ph, J = 7.3 Hz), 6.09, 6.04, 5.72 (each s, 1H, pz), 2.84, 2.65, 2.63, 2.58, 2.31, 2.25 (each s, 3H, pz-Me). MS: *m*/*z* 628 (M^+). Anal. Calcd for $C_{21}H_{27}BClN_6O_2Re$: C, 40.17; H, 4.33; N, 13.38. Found: C, 40.49; H, 4.06; N, 13.41.

Tp*Re(O)(OPh)OTf (19). An NMR tube was charged with **18** (<5 mg), AgOTf (3.0 mg, 0.012 mmol), and CD_2Cl_2 (0.5 mL) and flame-sealed. After several hours at room temperature, ^{1}H NMR analysis revealed the formation of **19**. ^{1}H NMR (CD_2Cl_2): δ 7.07 (t, 2H, Ph, J = 8 Hz), 6.77 (t, 1H, Ph, J = 7 Hz), 5.90 (d, 2H, Ph, J = 8 Hz), 6.12, 5.96, 5.80 (each s, 1H, pz), 2.89, 2.80, 2.61, 2.77, 2.36, 1.90 (each s, 3H, pz-Me). ^{19}F NMR ($CDCl_3$): δ −0.32 (s).

Tp*Re(O)(O$_2$C$_6$H$_4$) (20). Catecholborane (1.0 M in THF × 0.50 mL, 0.50 mmol) was added to a 10 °C solution of **15** (100 mg, 0.178 mmol) in C_6H_6 (40 mL). The mixture was warmed to room temperature and stirred for 1 h, and a saturated aqueous $NaHCO_3$ solution (10 mL) was slowly added. The organic phase was separated, washed with H_2O (10 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting brown residue was purified by chromatography followed by recrystallization from CH_2Cl_2/hexane to yield 55 mg of **20** (51%), as well as a 31% yield of **24** (see below). ^{1}H NMR ($CDCl_3$): δ 7.13 (dd, 2H, C_6H_4, J = 5.7, 3.5 Hz), 6.78 (dd, 2H, C_6H_4, J = 5.7, 3.5 Hz), 6.04 (s, 2H, pz), 5.51 (s, 1H, pz), 2.74, 2.59 (each s, 6H, pz-Me), 2.18, 1.87 (each s, 3H, pz-Me). IR: 2542 (ν_{BH}), 1543, 1416, 1233, 1201, 1073, 1059, 1045, 987, 966 (ν_{ReO}), 862, 800, 783, 735, 692, 664. MS: *m*/*z* 608 (M^+).

Tp*Re(O)(S$_2$C$_6$H$_4$) (21). Following the procedure for **14**, **3** (200 mg, 0.351 mmol), 1,2-benzenedithiol (26 mg, 0.18 mmol), THF (50 mL), and Et_3N (0.3 mL, 2 mmol) were stirred for 1.5 h at 80 °C. Workup afforded 20 mg of **21** (9%) as reddish yellow crystals. ^{1}H NMR ($CDCl_3$): δ 7.91 (dd, 2H, J = 5.7, 3.5 Hz, C_6H_4), 7.06 (dd, 2H, J = 5.7, 3.5 Hz, C_6H_4), 6.05 (s, 2H, pz), 5.55 (s, 1H, pz), 2.86, 2.55 (each s, 6H, pz-Me), 2.20, 1.82 (each s, 3H, pz-Me). MS: *m*/*z* 640 (M^+).

Tp*Re(O)(H)Cl (22). BH_3·THF (1.0 M in THF × 1.23 mL, 1.23 mmol) was added to a −78 °C solution of **14** (632 mg, 1.12 mmol) in toluene (60 mL). The mixture was slowly warmed to −20 °C with stirring (ca. 1.5 h). A saturated aqueous $NaHCO_3$ solution (15 mL) was added, and the resulting slurry was warmed to room temperature with vigorous stirring. The toluene layer was separated and blue solids, contained in the water layer, were extracted with CH_2Cl_2 (2 × 10 mL). The organic phases were combined and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the blue residue was purified by chromatography using toluene. Recrystallization from CH_2Cl_2/hexane yielded 585 mg of **22** (97.4%) as blue crystals. ^{1}H NMR ($CDCl_3$): δ 8.64 (s, 1H, ReH), 6.13, 6.04, 5.58 (each s, 1H, pz), 3.06, 2.70, 2.61, 2.56, 2.48, 2.18 (each s, 3H, pz-Me). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.54, 155.89, 153.40, 148.69, 147.19, 143.54, 109.25, 107.55, 106.64, 16.95, 15.46, 15.40, 12.47, 12.46, 12.40. IR: 2550 (ν_{BH}), 1988 (ν_{ReH}), 1542, 1198, 1067, 992 (ν_{ReO}), 861, 813, 786, 687. MS: *m*/*z* 536 (M^+). Anal. Calcd for $C_{15}H_{23}BClN_6ORe$: C, 33.62; H, 4.33; N, 15.68. Found: C, 33.56; H, 4.31; N, 15.46.

Tp*Re(O)(H)OTf (23). A mixture of **22** (0.57 g, 1.06 mmol), AgOTf (286 mg, 1.11 mmol), CH_2Cl_2 (15 mL), and C_6H_6 (60 mL) was stirred for 24 h in the dark. The solution was filtered through Celite and then reduced to 10 mL by evaporation under reduced pressure. Pentane (30 mL) was added, and the resulting precipitate was isolated by filtration, washed with pentane, and dried in vacuo to afford 0.60 g of **23** (87%) as a blue powder. ^{1}H NMR ($CDCl_3$): δ 10.12 (s, 1H, ReH), 6.12, 6.06, 5.66 (each s, 1H, pz), 2.83, 2.76, 2.49, 2.22 (each s, 3H, pz-Me), 2.55 (s, 6H, pz-Me). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.24, 156.17, 154.28, 150.58, 147.81, 144.97, 109.18, 107.98, 107.05, 16.90, 15.41 (two carbons), 12.57, 12.47, 12.43. ^{19}F NMR ($CDCl_3$): δ 0.45 (s). IR: 2553 (ν_{BH}), 2058 (ν_{ReH}), 1542, 1415, 1355, 1234, 1202, 1179, 1150, 1076, 1064, 1034, 1010, 988, 956 (ν_{ReO}), 864, 819, 806, 794, 689. MS: *m*/*z* 650 (M^+). Anal. Calcd for $C_{16}H_{23}BF_3N_6O_4ReS$·0.5$CH_2Cl_2$: C, 28.64; H, 3.50; N, 12.15. Found: C, 28.87; H, 3.50; N, 12.31.

Tp*Re(O)(H)$_2$ (24). BH_3·THF (1.0 M in THF × 0.45 mL, 0.45 mmol) was added to a −78 °C solution of **15** (100 mg, 0.178 mmol) in toluene (70 mL). The mixture was gradually warmed to −30 °C with stirring (ca. 4 h). A saturated aqueous $NaHCO_3$ solution (10 mL) was added to the solution, and the mixture was warmed to room temperature with vigorous stirring. The toluene layer was separated, washed with H_2O (10 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting purple residue was purified by chromatography using toluene. Recrystallization from CH_2Cl_2/hexane yielded 79 mg of **24** (88%) as a purple powder. ^{1}H NMR ($CDCl_3$): δ 9.55 (s, 2H, ReH), 6.08 (s, 2H, pz), 5.49 (s, 1H, pz), 2.72 (s, 6H, pz-Me), 2.56 (s, 9H, pz-Me), 2.10 (s, 3H, pz-Me). IR: 2534 (ν_{BH}), 1969 (ν_{ReH}), 1539, 1197, 1179, 1067, 1002, 985 (ν_{ReO}), 910, 861, 815, 784, 690. MS: *m*/*z* 500 ([M − 2]$^+$). Anal. Calcd for $C_{15}H_{24}BN_6ORe$: C, 35.93; H, 4.82; N, 16.76. Found: C, 35.73; H, 4.64; N, 16.52.

Tp*ReH$_6$ (25). Catecholborane (1.0 M in THF × 1.50 mL, 1.50 mmol) was added at −78 °C to a solution of **15** (250 mg, 0.445 mol) in THF (50 mL). The solution was slowly warmed to room temperature and stirred (20 h). Saturated aqueous $NaHCO_3$ (10 mL) and benzene (10 mL) were added. The organic phase was separated, washed with H_2O (10 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting brown residue was purified by column chromatography using toluene as the eluent. Recrystallization from CH_2Cl_2/hexane afforded golden yellow crystals of **25** (100 mg, 46%). ^{1}H NMR ($CDCl_3$): δ 5.88 (s, 3H, pz), 2.44, 2.34 (each s, 9H, pz-Me), −3.04 (s, 6H, ReH). IR: 2530 (ν_{BH}), 2123, 2025 (ν_{ReH}), 1547, 1416, 1383, 1209, 1033, 984, 912, 883, 863, 813, 782, 729, 692; MS: *m*/*z* 484 (M^+ − 6). Anal. Calcd for $C_{15}H_{28}BN_6Re$: C, 36.81; H, 5.77; N, 17.17. Found: C, 35.92; H, 5.40; N, 16.25.

[Tp*Re(O)F(py)][OTf] (26). In an NMR tube, pyridine (1.0 μL, 12 μmol) was added to Tp*Re(O)(F)OTf [10] (2.0 mg, 3 μmol) in 0.4 mL of $CDCl_3$ at room temperature; **26** was formed quantitatively within 16 h. ^{1}H NMR ($CDCl_3$): δ 8.86 (d, 1H, J = 6 Hz, py), 8.43 (t, 1H, J = 7 Hz, py), 8.30 (d, 1H, J = 6 Hz, py), 8.21 (t, 1H, J = 7 Hz, py), 8.06 (t, 1H, J = 7 Hz, py), 6.33,

Table 1. Crystal and Structure Refinement Data for Tp*Re(O)(Ph)OTf (13)

empirical formula	$C_{22}H_{27}BF_3N_6O_4ReS$
fw	725.6
diffractometer	Enraf-Nonius CAD4
temp (K)	183
radiation, wavelength (Å)	Mo Kα ($\lambda = 0.710\ 73$)
cryst syst	monoclinic
space group	$P2_1/n$
unit cell dimens	
a (Å)	12.174(2)
b (Å)	17.524(3)
c (Å)	12.795(2)
β (deg)	106.88(2)
V (Å^3)	2612 (1)
Z	4
calcd density (Mg m^{-3})	1.845
abs coeff (mm^{-1})	4.795
F(000)	1424
cryst color, size (mm)	green, 0.12 × 0.20 × 0.28
2θ range for data collecn (deg)	2.0−50.0
limiting indices	$0 \le h \le 14$
	$-1 \le k \le 20$
	$-15 \le l \le 14$
no. of rflns collected	5145
no of indep rflns	4573 ($R_{int} = 0.027$)
abs cor	semiempirical
refinement method	full-matrix least squares
no. of data/restraints/params	4573/0/344
goodness of fit on F^2	1.06
final R indices ($I > 2\sigma(I)$) obsd	$R = 2.97\%$, $R_w = 3.75\%$
R indices (all data)	$R = 5.06\%$, $R_w = 4.17\%$
largest difference peak and hole (e Å^{-3})	1.52, −0.63

6.21, 5.75 (each s, 1H, pz), 2.81, 2.73, 2.70, 2.32, 2.29, 1.33 (each s, 3H, pz-Me).

[Tp*Re(O)Et(py)][OTf] (27). In an NMR tube, pyridine (1.0 μL, 12 μmol) was added to **10** (2.9 mg, 4.3 μmol) in 0.4 mL of $CDCl_3$ at room temperature; **27** was formed over 46 h at 80 °C. ^{1}H NMR ($CDCl_3$): δ 10.09, 4.25 (m, 1H, C*HH'*Me), 8.74 (d, 1H, $J = 6$, py), 8.22 (t, 1H, $J = 7$, py), 8.13 (t, 1H, $J = 7$, py), 8.05 (t, 1H, $J = 7$, py), 7.86 (d, 1H, $J = 6$), 6.22, 6.16, 5.83 (each s, 1H, pz), 2.93, 2.71, 2.64, 2.33, 2.07, 1.48 (each s, 3H, pz-Me), 1.53 (t, 3H, CH_2CH_3).

[Tp*Re(O)H(py)][OTf] (28). In an NMR tube, pyridine (4.4 μL, 54 μmol) was added to **23** (7.1 mg, 11 μmol) in 0.4 mL of $CDCl_3$ at room temperature; **28** was formed within 20 min. ^{1}H NMR ($CDCl_3$): δ 9.26 (d, 1H, $J = 6$, py), 9.10 (s, 1H, ReH), 8.15 (t, 1H, $J = 8$, py), 7.92 (m, 2H, py), 7.45 (d, 1H, $J = 6$, py), 6.25, 6.16, 5.67 (each s, 1H, pz), 2.74, 2.66, 2.58, 2.26, 2.15, 1.53 (each s, 3H, pz-Me).

X-ray Structural Determination of Tp*Re(O)(Ph)OTf (13). Layering pentane upon a solution of **13** in CH_2Cl_2 produced green prismatic 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). Data were refined using the SIEMENS version of SHELXL PC. A semiempirical absorption correction was applied, and the structure was solved from difference maps with refinement on the Re obtained from a Patterson method procedure. All hydrogens were placed with their idealized geometry, except for the boron hydrogen, which was located from the difference map.

Results

Syntheses. The procedure that forms $TpRe(O)Cl_2$ in high yield,[13] $KReO_4$ + KTp + HCl (aq) in ethanol, is ineffective with Tp* and other pyrazole−borate ligands. As reported by Herrmann and by Santos,[5] $Tp^*Re(O)_3$ (**1**) and related compounds are accessible from Re_2O_7, but half of the rhenium is lost as perrhenate. A more efficient procedure converts Re_2O_7 to $ReO_3(O_2CCF_3)$ with trifluoroacetic anhydride prior to treatment with KTp* (following ref 4a) and gives 75% yields of **1** on a 10 g scale (eq 2). Reduction of **1** with PPh_3 and Me_3SiCl

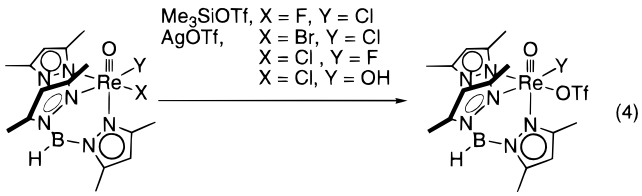
$$Re_2O_7 \xrightarrow[THF]{(CF_3CO)_2O} Re(O)_3(O_2CCF_3) \xrightarrow{KTp^*} \underset{\mathbf{1}}{Tp^*ReO_3} \qquad (2)$$

in refluxing THF, by the method of Coe,[5b] affords a mixture of Tp*Re(O)(OH)Cl (**2**) and a small amount of $Tp^*Re(O)Cl_2$ (**3**). We find that the compounds can be separated by column chromatography on silica gel (as can most of the compounds described here). If excess PPh_3 is employed, Tp*Re(O)(OH)Cl is formed as the only product. Treatment of the crude reaction mixture with aqueous HCl in CH_2Cl_2 gives $Tp^*Re(O)Cl_2$ in 95% overall yield based on Tp^*ReO_3 (eq 3).

$$\underset{\mathbf{1}}{Tp^*Re(O)_3} \xrightarrow[Me_3SiCl]{PPh_3} \underset{\mathbf{2}}{Tp^*Re(O)(OH)Cl} + \underset{\mathbf{3}}{Tp^*Re(O)Cl_2} \qquad (3)$$

$$\underset{\mathbf{2}}{Tp^*Re(O)(OH)Cl} \xrightarrow{HCl_{aq}} \underset{\mathbf{3}}{Tp^*Re(O)Cl_2}$$

Tp*Re(O)(OH)Cl (**2**) and $Tp^*Re(O)Cl_2$ (**3**) are excellent starting materials for a variety of rhenium(V) complexes. Treatment of **2** with concentrated aqueous HX (X = F, Br, I) gives the mixed halide compounds Tp*Re(O)(X)Cl in 89−95% yields. The fluoride complexes have been described elsewhere.[10] These complexes are all stable to air and temperature. Triflate complexes Tp*Re(O)Y(OTf) (Y = OH (**4**), F, Cl (**7**)) have been prepared either by metathesis of fluoride in Tp*Re(O)Y(F) using Me_3SiOTf or by exchange of heavier halides in Tp*Re(O)X(Y) with AgOTf (eq 4). The triflate ligands are



(4)

Y = OH (**4**), F, Cl (**7**)

coordinated to the metal center, as indicated by IR bands at 1350 cm^{-1} and ^{19}F NMR resonances several ppm downfield of ionic triflate.[14] The primary characterization of these compounds is by ^{1}H NMR. The C_s-symmetric $Tp^*Re(O)(X)_2$ complexes show pairs of methine, 3-Me, and 5-Me signals in a 2:1 ratio, while in Tp*Re(O)(X)(Y) complexes all the methine and methyl groups are inequivalent. IR spectra show BH stretches in the range 2570−2530 cm^{-1}, indicative of κ^3-Tp*

(13) (a) Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82*, 125−128. (b) Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091−4100.

(14) (a) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17−33. (b) See discussion in: Conry, R. R.; Mayer, J. M. *Organometallics* **1993**, *12*, 3179−3186 and references therein.

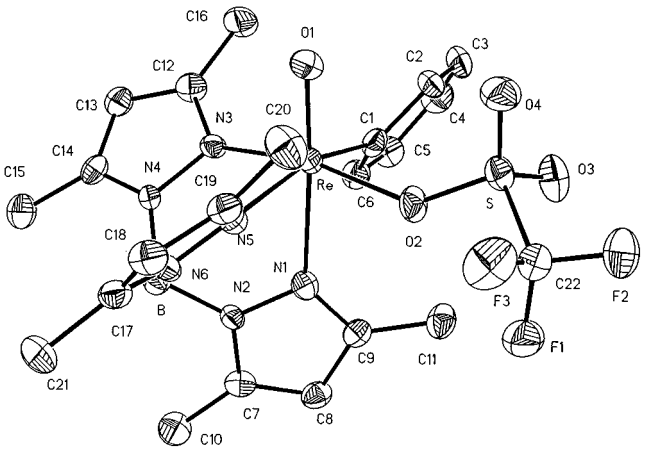


Figure 1.

ligands.[15] The characteristic strong Re≡O stretch (940−1000 cm^{-1}) occurs at higher frequencies (>980 cm^{-1}) in complexes containing good σ-donor ligands (H, Et, Ph), with lower values in complexes containing π-donor ligands (OR).

Reaction of **3** with 1.0 equiv of PhMgCl produces Tp*Re(O)Ph(Cl) (**11**; eq 5), while ≥2 equiv gives Tp*Re(O)Ph_2 (**12**). Similarly, **3** + Et_2Zn gives Tp*Re(O)Et(Cl)

$$\text{Tp}^{*}\text{Re(O)Cl}_2 \;(\mathbf{3}) \xrightarrow[\text{Et}_2\text{Zn}]{\text{PhMgCl or}} \text{Tp}^{*}\text{Re(O)(R)Cl}\quad \text{R = Et (}\mathbf{8}\text{), Ph (}\mathbf{11}\text{)} \qquad (5)$$

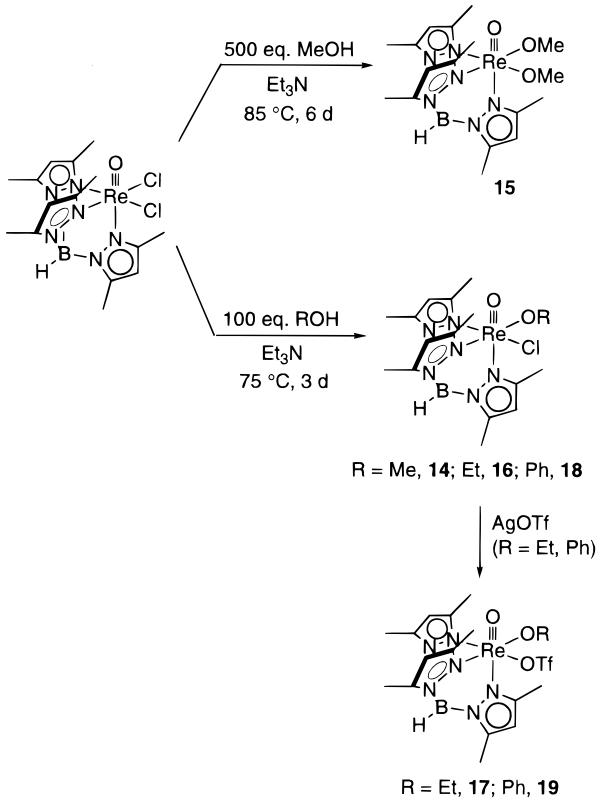
$$\xrightarrow[\text{- AgCl}]{\text{AgOTf}} \text{Tp}^{*}\text{Re(O)R(OTf)}\quad \text{R = Et (}\mathbf{10}\text{), Ph (}\mathbf{13}\text{)}$$

(**8**) with 0.5 equiv (eq 5), while 1.0 equiv (two ethyl groups per rhenium) gives a separable mixture of **8**, Tp*Re(O)$(Et)_2$ (**9**), and insoluble materials. Metatheses of **8** and **11** with AgOTf in benzene afford the triflate adducts Tp*Re(O)Et(OTf) (**10**) and Tp*Re(O)Ph(OTf) (**13**) as emerald green solids in good yields (eq 5). Complexes **8**, **9**, **11**, and **12** are air-stable while solutions of the triflate derivatives decompose over a period of hours of exposure to air. The ethyl and phenyl complexes show spectral characteristics similar to the those of the halides described above. The diastereotopic methylene hydrogens of the ethyl group of compound **8** possess strikingly separated chemical shifts, appearing at δ 10.79 and 4.37 in $CDCl_3$. The phenyl ligands in **11**−**13** show five separate ^1H NMR signals, indicating that phenyl rotation is slow on the NMR time scale. The X-ray crystal structure of **13** (Figure 1, Tables 1 and 2) shows the phenyl ligand interleaved between pyrazole rings. Complex **13** adopts a distorted-octahedral geometry with the rhenium atom displaced toward the oxo ligand, similar to other pyrazolylborate rhenium−oxo complexes.[2−5] The Re−O(1) distance of 1.675(4) Å is typical of a Re≡O triple bond.[16] The triflate ligand is covalently bound to the rhenium with a Re−OTf bond length of 2.099(4) Å.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Tp*Re(O)(Ph)OTf (13)

Re≡O(1)	1.675(4)	Re−C(1)	2.111(5)
Re−O(2)	2.099(5)	Re−N(1)	2.243(5)
S−O(2)	1.489(5)	Re−N(3)	2.041(5)
S−O(3)	1.428(4)	Re−N(5)	2.173(5)
S−O(4)	1.428(5)		
O(1)−Re−O(2)	96.7(2)	C(1)−Re−N(3)	87.8(2)
O(2)−Re−C(1)	93.3(2)	O(1)−Re−N(5)	94.3(2)
O(2)−Re−N(1)	83.2(2)	N(3)−Re−N(5)	89.0(2)
O(1)−Re−C(1)	103.1(2)	O(2)−Re−N(5)	86.1(2)
O(1)−Re−N(1)	173.3(2)	C(1)−Re−N(5)	162.5(2)
O(2)−Re−N(3)	167.3(2)		

Scheme 1



Alkoxide and aryloxide derivatives Tp*Re(O)(OR)Cl and Tp*Re(O)$(OR)_2$ (R = Me, Et, Ph) have been prepared by reaction of **3** with the corresponding alcohol and Et_3N (Scheme 1). Tp*Re(O)(OMe)Cl (**14**, 88%) is obtained as an air-stable purple solid upon heating acetonitrile solutions of **3** with 100 equiv of methanol and 10 equiv of Et_3N for 3 days at 75 °C.

The bis(alkoxide) derivatives are best formed using >500 equiv of alcohol and heating for 6 days. The mono- and bis(alkoxide) complexes can be chromatographically separated and purified. Related catecholate (**20**) and 1,2-benzenedithiolate (**21**) complexes are prepared similarly. Related Tp*Re(O)(diolate) complexes have been prepared by Gable directly from **1** using PPh_3 and the diol.[6] The triflate complexes Tp*Re(O)(OR)OTf (R = Et (**17**), Ph (**19**)) were prepared by stoichiometric treatment of Tp*Re(O)(OR)Cl with AgOTf. The bis(alkoxy) derivatives are air-stable in solution with no noticeable decomposition after several days, in contrast to alkoxide and related compounds with Tp or $B(pz)_4$ ligands.[5c,17] The alkoxy−halide complexes are slightly air-sensitive,

(15) (a) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121. See also: (b) Burns, I. D.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17*, 1552-7. (c) Northcutt, T. O.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 5148−5152.

(16) Mayer, J. M. *Inorg. Chem*. **1988**, *27*, 3899−3903.

(17) DuMez, D. D.; Mayer, J. M. *Inorg. Chem*. **1995**, *34*, 6396−6401.

while the solutions of the triflate derivatives rapidly decompose to **1** on exposure to air.

Hydride complexes are accessible from alkoxide complexes using borane reagents.[9] Treatment of Tp*Re(O)(OMe)Cl (**14**) with BH_3·THF gives Tp*Re(O)(H)Cl (**22**) in 97% optimized yield (eq 6). Reaction of **22** with AgOTf

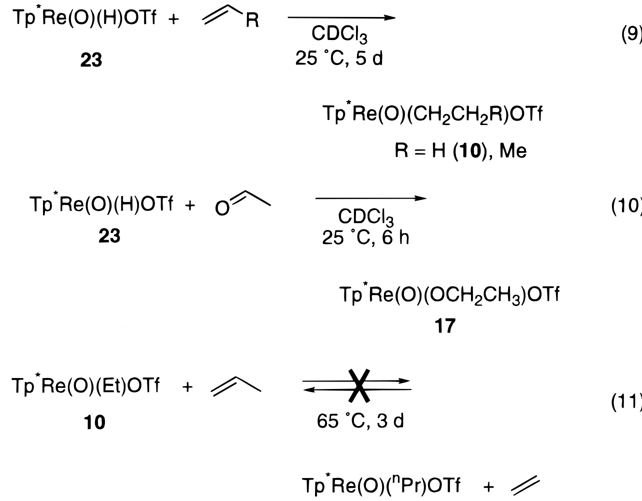
$$\underset{R = Me, Et}{Tp^*Re(O)(OR)Cl} \xrightarrow[\text{Toluene, -78 to -20 °C}]{1.1\ BH_3\bullet THF} \underset{\mathbf{22}}{Tp^*Re(O)(H)Cl} \xrightarrow{AgOTf} \underset{\mathbf{23}}{Tp^*Re(O)(H)OTf} \quad (6)$$

$$\underset{R = Me, Et}{Tp^*Re(O)(OR)_2} \xrightarrow[\text{toluene, -78 to -30 °C}]{2.5\ BH_3\bullet THF} \underset{\mathbf{24}}{Tp^*Re(O)H_2} \quad (7)$$

$$\underset{R = Me, Et}{Tp^*Re(O)(OR)_2} \xrightarrow[\text{THF, rt, 20 h}]{3.4\ BH_3\bullet THF} \underset{\mathbf{25}}{Tp^*ReH_6} \quad (8)$$

gives the hydrido−triflate complex Tp*Re(O)H(OTf) (**23**), an air-sensitive blue solid (eq 6). BH_3·THF similarly converts Tp*Re(O)(OMe)$_2$ (**15**) to the dihydride complex **24** (eq 7). Catecholborane plus **15** affords a mixture of **24** (31%) and the catecholate complex **20** (51%). Prolonged reactions of **15** and excess BH_3·THF afford Tp*ReH_6 (**25**) as the only isolable rhenium product (eq 8). The hexahydride can also be prepared by treatment of Tp*Re(O)Cl_2 with $LiAlH_4$ by a procedure analogous to the preparation of TpReH_6.[18] It is relatively air stable but highly acid sensitive. Its IR spectrum contains broad absorptions at ~2120 and 2025 cm^{-1}, similar to the ν(Re−H) values of 2111, 2042, and 2021 cm^{-1} reported for TpReH_6. The hydride ^1H NMR resonance appears at −3.04 ppm, ~0.5 ppm more upfield than the Tp derivative. The oxo−hydride complexes were characterized by standard methods, including downfield singlets for the hydride ligands in the ^1H NMR: δ 8.64 for **22**, δ 10.12 for **23**, and δ 9.55 for **24**. IR spectra of **22**−**24** show overlapping broad ν_{ReH} absorptions at ca. 1980 cm^{-1}. The X-ray crystal structure of Tp*Re(O)(H)OTf (**23**)[9] shows a pseudo-octahedral structure similar to the structure of **13**. The Re≡O and Re−OTf bond lengths are 1.665(5) and 2.086(4) Å.

Complexes **22**−**24** are not deprotonated by pyridine in CD_2Cl_2, indicating that the hydride ligands are not acidic. The hydrido−triflate **23** reacts with acetaldehyde, propylene, and ethylene by insertion to afford Tp*Re(O)(OEt)OTf (**17**), Tp*Re(O)(Pr)OTf, and Tp*Re(O)(Et)OTf (**10**), respectively (eqs 9 and 10). No reaction is observed with butadiene or with the larger alkenes cyclohexene and isobutene, nor (surprisingly) with allene, propyne, phenylacetylene, or hexafluoro-2-butyne. Despite the presence of potentially labile triflate ligands in **10** and Tp*Re(O)(Pr)OTf, we have observed no evidence for β-hydrogen elimination from the alkyl group. For instance, heating **10** with ~2−3 atm of propylene or Tp*Re(O)(^{n}Pr)OTf with ethylene at 65 °C for several days results in no incorporation or liberation of free olefin (eq 11). Heating $CDCl_3$ solutions of the hydride complexes for several days at 65 °C results in



$$Tp^*Re(O)(H)X \xrightarrow[CDCl_3]{\Delta} Tp^*Re(O)(Cl)X \quad (12)$$
$$X = Cl,\ \mathbf{22} \rightarrow \mathbf{3};\quad X = OTf,\ \mathbf{23} \rightarrow \mathbf{7}$$

hydride-for-chloride exchange: **23** is converted to Tp*Re(O)(Cl)OTf (**7**) and **22** forms **3** (eq 12).

Displacement Reactions of Tp*Re(O)X(OTf) Complexes. The triflate complexes Tp*Re(O)X(OTf) react with excess pyridine in $CDCl_3$ to generate the pyridine adducts [Tp*Re(O)(X)(py)][OTf] (eq 13). The adducts

$$Tp^*Re(O)(X)OTf \xrightarrow[CDCl_3]{pyridine} [Tp^*Re(O)(X)py]^+OTf^- \quad (13)$$
$$X = F, H, Et, Ph$$

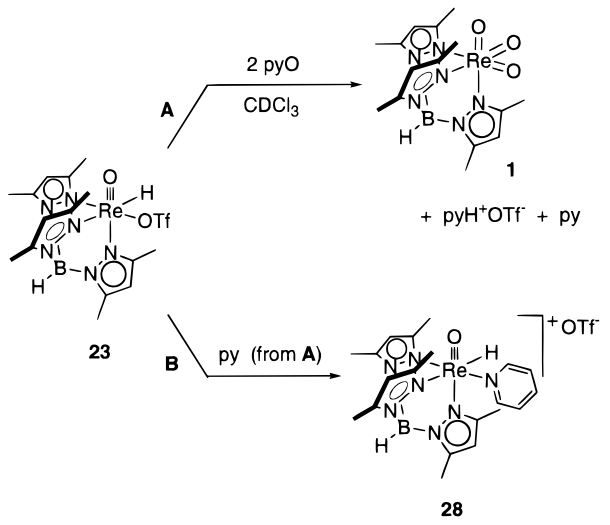
were identified by their ^1H NMR spectra. In each case there are five inequivalent pyridine protons, indicating that pyridine rotation is slow on the NMR time scale. This is analogous to the slow rotation of the isosteric phenyl ligands in **11**−**13**.

Triflate substitutions in the phenyl−triflate complex **13** and in related imido compounds have been shown to be associative in character and to follow bimolecular kinetics ($k_{13+py} = 2.6 \times 10^{-5}\ M^{-1}\ s^{-1}$ at 50 °C).[11] The relative rates of triflate displacement in Tp* compounds are as follows ($CDCl_3$, 40 mM py): Tp*Re(O)H(OTf) (**23**, minutes at 25 °C) > Tp*Re(O)F(OTf) ≅ Tp*Re(O)OEt(OTf) (**17**) > Tp*Re(O)Et(OTf) (**10**) > Tp*Re(O)Ph(OTf) (**13**, 1 week at 50 °C). This order follows the size of the sixth ligand (H → Ph) rather than any electronic effect. The reduction in rate as a result of increasing steric bulk of the ligand is consistent with the associative nature of the reaction. The pyridine adducts are robust: for instance not reacting with pyridine *N*-oxide (pyO) or Me_2SO (see below).

Oxidation of Tp*Re^V Oxo Complexes by Oxygen Atom Donors. The hydride complex Tp*Re(O)H(OTf) (**23**) reacts rapidly with pyridine *N*-oxide (pyO) in CD_2Cl_2 or $CDCl_3$ to afford Tp*Re(O)$_3$ (**1**), [Tp*Re(O)H(py)][OTf] (**28**), pyridine, and [pyH]OTf. No intermediates were detected in low-temperature experiments. In the initial stages **1** and py/[pyH]OTf are the sole products, and 2 equiv of pyO is consumed in the formation of **1** (Scheme 2, path **A**). As the pyridine is formed, it reacts competitively with **23** to give **28** and thus limits the yield of **1** in the oxidation (path **B**). The rate of path **A**

(18) Hamilton, D. G.; Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3198−3203.

Scheme 2



increases in the presence of larger concentrations of pyO, consistent with rate-limiting pyO displacement of triflate analogous to the pyridine reactions above. Similar competitive formation of pyridine complexes was observed for the related Tp complexes.[2a] Tp*Re(O)(H)Cl does not react with pyO over several days at ambient temperatures.

Oxidation of **23** by Me_2SO occurs over a few hours at room temperature to give **1**, Me_2S, and HOTf/Me_2SO as the major products. The NMR signals for "HOTf/Me_2SO" are the same as for a mixture of these compounds observed in the absence of the rhenium complexes. Over time **1** decays in the same manner as observed in independent reactions of **1** with HOTf. When the oxidation of Tp*Re(O)H(OTf) with Me_2SO is carried out in the presence of triphenylamine, $[Ph_3NH]OTf$ is formed and **1** does not decompose.

The hydroxo−triflate complex Tp*Re(O)(OH)OTf (**4**) reacts rapidly with pyO in $CDCl_3$ at room temperature to form **1**, pyridine, and [pyH]OTf. No intermediates are observed. Similarly, **4** reacts with Me_2SO at room temperature to give **1**, HOTf, and Me_2S within 15 min. Oxidation of Tp*Re(O)(OEt)OTf (**17**) with pyO occurs over 1 h, giving predominantly **1** and ethanol along with some [Tp*Re(O)(OEt)py]OTf and other products. Reaction of **17** with Me_2SO also gives **1** and ethanol as the major products, but in this case a small amount of acetaldehyde is observed at short reaction times and is consumed within 3 days. Treatment of the halide complexes Tp*Re(O)X(OTf) (X = F, Cl (**7**)) with pyO in CD_2Cl_2 forms pale green-yellow NMR-silent solutions. The fluoride reacts within 2 h; the chloride derivative reacts more slowly. The products have not been isolated or characterized. These reactions are most likely analogous to the pyO oxidation of the Tp derivative TpRe(O)Cl(OTf) to give the green, paramagnetic, and NMR-silent rhenium(VI) complex $TpRe(O)_2Cl$.[3]

The phenyl−triflate complex Tp*Re(O)Ph(OTf) (**13**) is oxidized by Me_2SO only upon heating. After 5 h at 80 °C in CD_2Cl_2, Tp*Re(O)(OPh)OTf, Me_2S, and Me_2SO_2 are observed (eq 14). The analogous reaction of the Tp−phenyl complex gives similar products, but at a much faster rate and via an observable $OSMe_2$ adduct.[2a] Oxidation of **13** with pyO at 25 °C gives a complex

$$\underset{\mathbf{13}}{Tp^*Re(O)(Ph)OTf} \xrightarrow[CD_2Cl_2,\ 80\ ^\circ C]{Me_2SO} \underset{\mathbf{19}}{Tp^*Re(O)(OPh)OTf} + Me_2S + Me_2SO_2 + ... \quad (14)$$

mixture of material, including a small amount of **1**. Surprisingly, no Tp*Re(O)(OPh)OTf or [Tp*Re(O)(OPh)-py]OTf could be identified in these reaction mixtures.

Treatment of the ethyl derivative Tp*Re(O)Et(OTf) (**10**) with ∼3 equiv of pyO in CD_2Cl_2, $CDCl_3$, or C_6D_6 results in slow formation of **1**, acetaldehyde, pyridine, and [pyH]OTf (eq 15). In the Tp case, acetaldehyde is

$$\underset{\mathbf{10}}{Tp^*Re(O)(Et)OTf} \xrightarrow[CD_2Cl_2]{pyO} \underset{\mathbf{1}}{Tp^*Re(O)_3} + MeCHO + py + [pyH]OTf + \underset{\mathbf{27}}{[Tp^*Re(O)(Et)py]OTf} + ... \quad (15)$$

quantitatively formed.[2b] As found for the hydrido−triflate **23**, the newly formed pyridine reacts with **10** to give [Tp*Re(O)Et(py)][OTf] (**27**), which is inert to further reaction with pyO. When a 5-fold excess of pyO is added, **10** is consumed ca. 5 times faster than when 1 equiv is used.

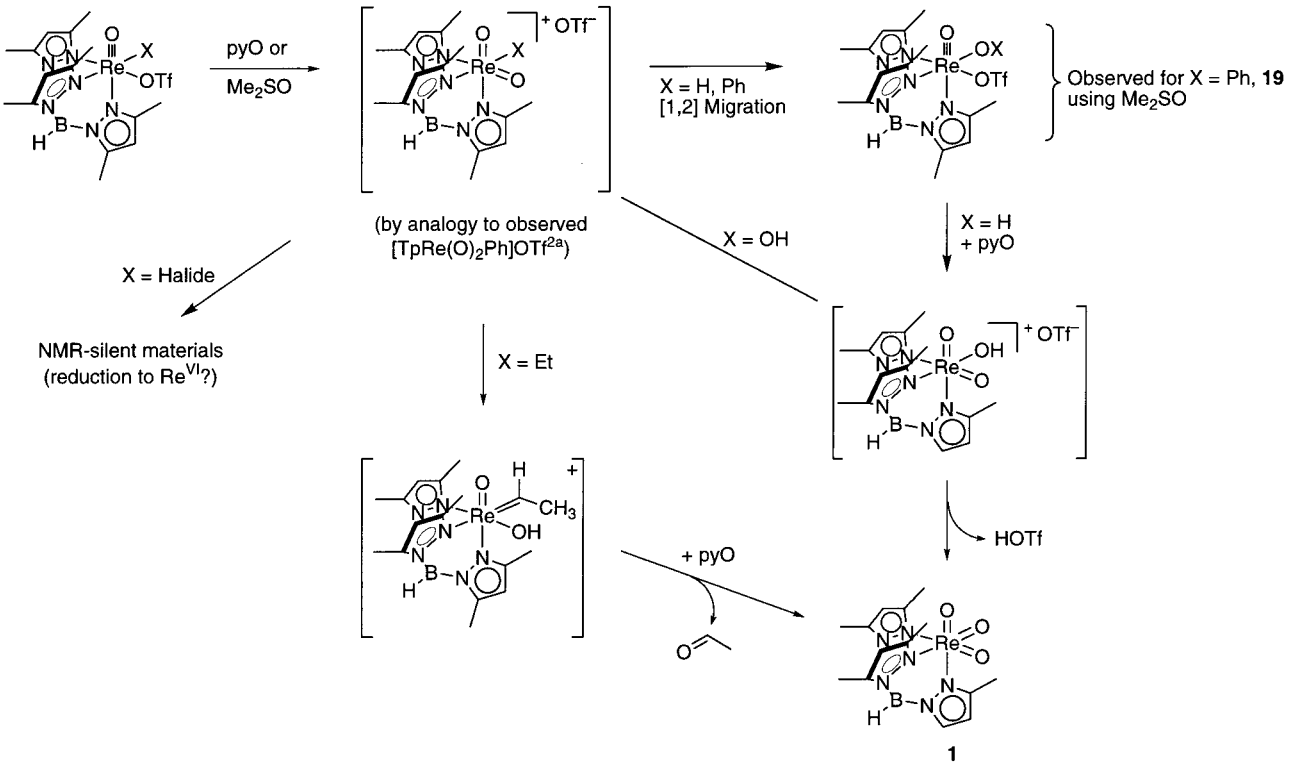
In contrast to the pyO reaction, oxidation of **10** with Me_2SO gives **1**, Me_2S, HOTf/Me_2SO, and new rhenium product(s). No acetaldehyde is observed. The generated **1** is slowly decomposed by the HOTf present (as in the oxidation of **23** by Me_2SO). The Me_2SO oxidation of **10** appears to be faster than oxidation by pyO and, unlike all of the other reactions of these Tp*−triflate complexes, the rate is unaffected by the concentration of Me_2SO. However, the reaction is irreproducible, perhaps suggesting involvement of a trace component in the reaction mixture. One of these reactions deposited small red crystals, which an X-ray structure determination suggested to be an ethylidyne complex. However, the data set was not of top quality (R_{int} = 10.3%), and our inability to obtain larger samples of this material makes its characterization uncertain.

Discussion

Stability of Tp* Compounds. $Tp^*Re(O)Cl_2$ (**3**) is a valuable starting material for the preparation of a variety of Tp*Re−oxo compounds. Alkyl, aryl, alkoxide, halide, hydride, and fluoride compounds are accessible in good yields. The Tp* compounds are considerably more stable than the analogous Tp derivatives. The Tp*−alkyl and −aryl triflate complexes can be handled in air indefinitely as solids and decompose only slowly in solution. The ethyl triflate complex (**10**) can be chromatographed on silica in air. In contrast, the Tp−rhenium−triflate compounds rapidly decompose on exposure to air. Tp*−hydride and −fluoride complexes are easily prepared, while many of the analogous Tp complexes have eluded efforts at isolation. To choose one example, the hydrido−triflate **23** is cleanly formed by metathesis of **22** with AgOTf, while reaction of TpRe(O)(H)Br with AgOTf results in disproportionation to $TpRe(O)Br_2$ rather than formation of [TpRe(O)(H)OTf].[19]

(19) Bennett, B. K.; Mayer, J. M. Unpublished results.

Scheme 3. General Mechanism for Oxidation of Tp*Re(O)(X)OTf (X = Halide, Et, Oh, H, OH)



We have had no success in many attempts to generate [TpRe(O)(H)OTf].

The greater stability of the Tp* complexes appears to be a result of the greater steric crowding in these molecules. The redox potentials of the Tp* complexes are only 110−180 mV more negative than those of the Tp complexes,[8] too small a difference to account for the substantial change in the observed chemistry. The steric crowding in the Tp* compounds is indicated by the lack of rotation of pyridine and phenyl ligands, an effect only seen for mesityl ligands in the Tp system.[2a] The crystal structure of **13** shows how the phenyl group interleaves between the pyrazole rings and their methyl substituents. The most dramatic effect of Tp* substitution is the slow rate of ligand substitution, estimated to be ca. 10^5 times slower than that of the Tp analogue.[11] This is the dominant reason for the higher—kinetic—stability of Tp* derivatives.

Oxidations of Tp*Re^V−Oxo Complexes. The oxidations of Tp*Re−oxo complexes in many ways parallel those of the analogous Tp compounds. Scheme 3 presents a generalized mechanism for reactions of pyO and Me_2SO with Tp$^{(*)}$Re(O)(X)OTf, for Tp$^{(*)}$ = Tp*, Tp and X = aryl, alkyl, hydride, hydroxide, alkoxide, halide. With the exception of the peculiar Me_2SO oxidation of Tp*Re(O)Et(OTf), each case appears to proceed by triflate substitution by the oxygen atom donor and generation of a rhenium(VII) dioxo cation, [Tp$^{(*)}$Re-$(O)_2X]^+$. Rates are accelerated by higher oxidant concentrations, consistent with rate-limiting triflate substitution. Our idea that dioxo cations with Tp* ligands would be more amenable to study was not correct. The slow associative ligand substitutions (described in more detail elsewhere[11]) mean that more forcing conditions are required to oxidize the Tp* compounds, which counteracts their proposed higher stability. In fact, oxidations in the Tp* system do not proceed nearly as cleanly as for the Tp compounds.

The fate of [Tp$^{(*)}$Re$(O)_2X]^+$ is very dependent on the nature of X. When X is a halide ligand and unreactive, NMR-silent material(s) are formed. Rhenium(VI), d^1 $TpReO_2X$ complexes have been isolated and characterized,[3] and the data in the Tp* system suggest similar products. Reduction of the unobserved [Tp$^{(*)}$Re$(O)_2X]^+$ is reasonable, given the high redox potential of [TpRe-$(O)_2Cl]^+$: $E_{1/2}$ = 0.93 V vs $Cp_2Fe^{+/0}$ in acetonitrile.[3] Reduction is less favored for the alkyl, aryl, and hydride derivatives because these species are likely to be weaker oxidants. Electrochemical studies of Tp$^{(*)}$Re(O)XY compounds show that substitution of chloride for ethyl or phenyl causes a reduction in the $Re^{VI/V}$ potential of 0.4 and 0.3 V, respectively.[8] When X = hydroxide (**4**), the putative [Tp*Re$(O)_2OH^+$] deprotonates to Tp*Re$(O)_3$ (**1**).[9] The trioxides are quite stable and common end products of the oxidation reactions. Independent experiments show that Tp$^{(*)}$Re$(O)_3$ species have very low basicities, consistent with the ability of [Tp*Re$(O)_2OH^+$] to protonate NPh_3.[9]

In complexes with an oxidizable X ligand, [Tp$^{(*)}$Re-$(O)_2X]^+$ decays by one of a number of pathways. Hydride and phenyl ligands appear to migrate to a neighboring oxo group, forming rhenium(V) phenoxide or hydroxide complexes. Such [1,2]-migrations have not been observed in other systems and have been ascribed to the electrophilicity of the oxo groups.[2] Phenoxide complexes are observed from both the Tp and Tp* compounds when Me_2SO is the oxidant. With pyO as the oxidant, TpRe-(O)(Ph)OTf is oxidized to both phenoxide and catecholate complexes. Such a further oxidation of the phenoxide complex may explain why Tp*Re(O)(Ph)OTf plus pyO gives a complex mixture of products, not including

Tp*Re(O)(OPh)OTf. The hydroxide complex **4** is not observed as a product in the oxidation of the hydride **23** because it is rapidly oxidized to **1** (see above).

Alkyl complexes are in general oxidized to $Tp^{(*)}Re(O)_3$ and aldehydes, as in the oxidation of Tp*Re(O)(Et)OTf (**10**) by pyO to give acetaldehyde (eq 15). It is not clear why the Me_2SO oxidation of **10** proceeds differently, or why the yield of acetaldehyde is lower for the Tp* compound. In the Tp system, alkyl group oxidation was shown to proceed by transfer of an α-hydrogen to an oxo group (Scheme 3),[2b] and **10** + pyO appears to proceed similarly. The alternative pathway of alkyl migration to oxo was ruled out in the Tp system by the observation of different products in alkyl vs alkoxide oxidations. By similar reasoning, the reaction of pyO with the ethyl complex **10** does not proceed through an ethoxide complex, as this reaction does not form Tp*Re(O)(OEt)OTf (**17**), [Tp*Re(O)(OEt)py]OTf, or the major organic product of **17** + pyO, ethanol. Me_2SO oxidizes **17** to give mostly ethanol, with little acetaldehyde, and the pyO oxidation shows exclusively ethanol. These contrast with the oxidation of the Tp analogue, which gives closer to equal amounts of the two products.[17] Perhaps further oxidation of acetaldehyde is competitive with alkoxide oxidation in the Tp* system, while it is only observed under more forcing conditions in the Tp system.

Acknowledgment. We are grateful for support from the U.S. National Science Foundation. Y.M. acknowledges a Fellowship from the Ministry of Education, Science, Sports, and Culture of Japan. We thank Dr. David Barnhart for assistance with X-ray crystallographic experiments and Dr. Martin Sadilek for mass spectrometric analyses.

Supporting Information Available: Text and tables giving X-ray crystallographic data for Tp*Re(O)(Ph)OTf (**13**). This material is available free of charge via the Internet at http://pubs.acs.org.

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