Synthesis and Reactions of Rhenium(V) Oxo−Hydride Complexes

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Summary: *Tp*ReO(H)Cl, TpRe(O)H(Cl), and Tp*ReO(H)$_2$ have been prepared by alkoxide-for-hydride metathesis using BH$_3$·THF. The triflate derivative Tp*Re(O)H(OTf) inserts olefins and is oxidized by oxygen-atom transfer reagents to give HOTf and Tp*ReO$_3$, likely by a pathway involving hydride migration to an oxo ligand (Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate; triflate = OTf = OSO$_2$CF$_3$).*

The chemistry of transition-metal oxo complexes has been receiving significant attention because of its importance in metal-mediated oxidation processes.[3] The organometallic chemistry of metal−oxo compounds holds the promise of novel and selective transformations. Complexes with both terminal oxo and hydride ligands are interesting both in combining the characteristic reactivity of the two ligands and also as they relate to the tautomeric hydroxide ligand, which is ubiquitous in aqueous and surface oxidation chemistry. Yet only three types of oxo−hydride compounds have been reported, and little information is available concerning their reactivity. Cp*$_2$Ta(O)H[4] and Re(O)H(RC≡CR)$_2$[5] are irreversibly formed by rearrangement of hydroxide complexes, and [Re(O)(H)$_2$Cyttp]$^+$ converts CO to a formate ligand.[6] Reported here are the synthesis, characterization, and reactivity of a new series of rhenium oxo−hydride complexes.

BH$_3$·THF in toluene at low temperatures was found to be effective for converting rhenium(V) oxo−alkoxide complexes to the corresponding oxo−hydride compounds. Thus, Tp*ReO(H)Cl (**1**, 97% yield) and Tp*ReO(H)$_2$ (**2**, 88%) are formed from Tp*ReO(OMe)Cl and Tp*ReO(OMe)$_2$, respectively (eq 1).[7,8] The Tp analogue TpReO(H)Cl (**1a**, 68%)[7] was similarly synthesized from TpReO(OEt)Cl[9] or in low yield by the reaction of ^{n}Bu$_3$-

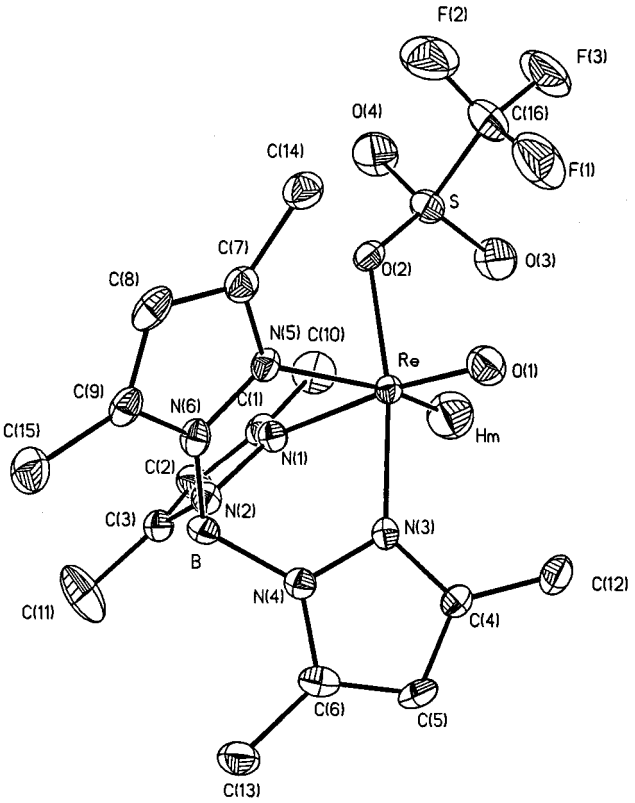

Figure 1.

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(3) Leading references: (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981. (b) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; John Wiley and Sons: New York, 1988. (c) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401−1449. (d) Watanabe, Y.; Groves, J. T. in *The Enzymes*, 3rd ed.; Academic Press: New York, 1992; Vol. 20, pp 405−452. (e) Herrmann, W. A.; Kühn, F. E. *Acc. Chem. Res.* **1997**, *30*, 169−180. (f) Abu-Omar, M. M.; Hansen, P. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 4966−4974 and references therein.

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(5) R = Me, Et, Ph. (a) Spaltenstein, E.; Erikson, T. K. G.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 617−623. (b) Tahmassebi, S. K.; McNeil, W. S.; Mayer, J. M. *Organometallics* **1997**, *16*, 5342−5353.

(6) Cyttp = (Cy$_2$PCH$_2$CH$_2$CH$_2$)$_2$PPh; [Re(O)H(F)Cyttp]$^+$ was also described. (a) Kim, Y.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 8600−8602. (b) Rende, D. E.; Kim, Y.; Beck, C. M.; Wojcicki, A. *Inorg. Chim. Acta* **1995**, *240*, 435−439.

(7) Full preparative, spectroscopic, and elemental analysis data are given in the Supporting Information. The preparation of **1** is typical: Anaerobically, a THF solution of BH$_3$·THF (1.0 M × 1.23 mL, 1.23 mmol) was added to a blue solution of Tp*ReO(OMe)Cl (632 mg, 1.12 mmol) in 60 mL of toluene at −28 °C. The mixture was stirred at −20 °C for 1.5 h. A saturated aqueous NaHCO$_3$ solution (15 mL) was added, and the resulting mixture was opened to the air and warmed to room temperature with vigorous stirring. The toluene layer was separated, and blue solids in the water layer were taken up with CH$_2$Cl$_2$ (10 mL × 2). The combined organic phases were dried over MgSO$_4$ and then evaporated under reduced pressure, leaving a blue residue, which was purified by chromatography on silica gel using toluene as the eluant, followed by recrystallization from CH$_2$Cl$_2$/hexane to yield Tp*ReO(H)Cl (585 mg, 97.4%) as blue crystals. ^{1}H NMR (CDCl$_3$): **1** 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); **1a** (C$_6$D$_6$): δ 8.31, 7.51, 7.49, 7.10, 6.96, 6.67 (each d, 1H, J = 2 Hz, pz), 6.85 (s, 1H, ReH), 5.69, 5.66, 5.27 (each t, 1H, J = 2 Hz, pz); **2** 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).

(8) (a) The methoxide complexes were prepared from Tp*Re(O)Cl$_2$ + MeOH + Et$_3$N: see Supporting Information. (b) Matano, Y.; Northcutt, T. O.; Brugman, J.; Mayer, J. M. Unpublished results. (c) Coe, B. J. *Polyhedron* **1992**, *11*, 1085−1091.

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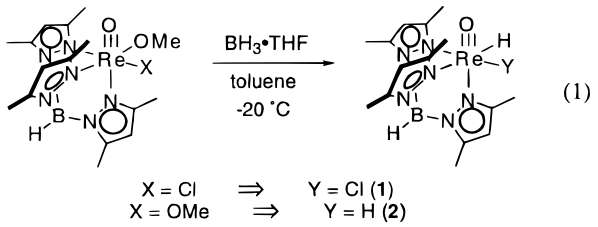


(1)

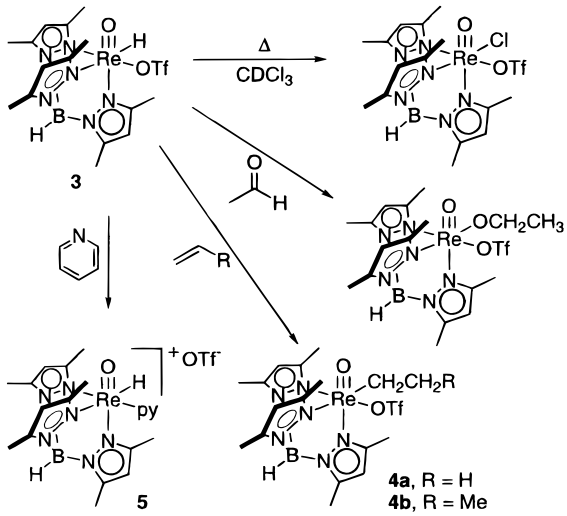
SnH with $TpReOCl_2$. Chloride **1** was converted to Tp*Re(O)H(OTf) (**3**) in 87% yield by metathesis with AgOTf in benzene/CH_2Cl_2.[10]

An X-ray diffraction analysis of **3** (Figure 1)[11] revealed that the rhenium center possesses a distorted octahedral coordination with a typical Re≡O bond length of 1.665(5) Å.[12] The hydride ligand was located in one of the octahedral sites and was refined (Re−H 1.69(8) Å; O(1)−Re−H 93(3)°). The Re−O(2) bond length of 2.086(4) Å indicates that the triflate is covalently attached to the rhenium atom, consistent with the solution structure as inferred from the ^{19}F NMR chemical shift of δ −0.24 ppm (in CD_2Cl_2 vs CF_3COOH).[13] The poor donation of the triflate ligand may be revealed in the Re−H stretching frequencies (IR, Nujol mull) at 1988, 1969, and 2058 cm^{-1} for **1**, **2**, and **3**, respectively. The hydride chemical shifts are quite downfield: δ 8.64 (**1**), 9.55 (**2**), and 10.12 (**3**) in $CDCl_3$.

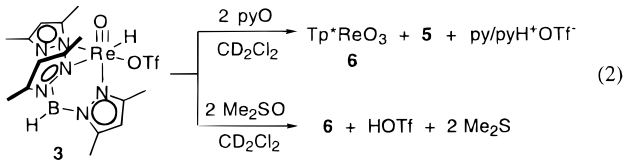
Complex **3** displays reactivity typical of a metal−hydride complex (Scheme 1). In $CDCl_3$ solution over several days at 65 °C, it undergoes hydride−chloride exchange forming Tp*ReO(Cl)OTf.[8b] Acetaldehyde reacts with **3** in $CDCl_3$ at room temperature to give Tp*ReO(OEt)OTf[8b] as the major initial product, indicating that **3** has some hydridic character. Reaction of **3** with excess ethylene in $CDCl_3$ or CD_2Cl_2 at room temperature gives Tp*ReO(Et)OTf (**4a**) in a quantitative NMR yield. Complex **4a** has been synthesized independently from Tp*ReO(Et)Cl and AgOTf. Propylene also inserts to give Tp*ReO(^{n}Pr)OTf (**4b**) in 95% NMR yield. Isobutene, 1,3-butadiene, and allene do not react with **3** over several days at 65 °C. The oxo−ethyl complex **4a** is recovered unchanged over 46 h at 80 °C in the presence or absence of propylene, and the propyl complex **4b** does not react with ethylene under similar conditions. β-hydrogen elimination is thus too endoergic to occur under these conditions.

The triflate ligand in **3** is readily displaced by pyridine (py) to form [Tp*Re(O)H(py)][OTf] (**5**) in a quantitative NMR yield (Scheme 1). No reaction was observed

Scheme 1



between pyridine (or ethylene) and **1**, indicating that the easily displaced triflate ligand is important for reactivity. Pyridine does not deprotonate either **3** or **5**, so the hydride ligands in these compounds are not very acidic. Reaction of **3** with the oxygen-atom donor pyridine *N*-oxide (pyO) in $CDCl_3$ or CD_2Cl_2 yields Tp^*ReO_3 (**6**),[8c] the pyridine adduct **5**, pyH^+OTf^-, and py over hours at room temperature (eq 2).[14] In the initial



(2)

stages of the reaction, **6** is the sole rhenium product, formed by consuming 2 equiv of pyO. Complex **5** is likely formed by the reaction of **3** with the pyridine generated during the oxidation. Me_2SO also oxidizes **3** to **6** at ambient temperature, also forming Me_2S and HOTf. Over time, **6** reacts further with the HOTf to generate a mixture of products. Reaction of **3** and Me_2SO in the presence of NPh_3 generates $HNPh_3^+$ (by ^1H NMR). The formation of HOTf and $HNPh_3^+$ ($pK_a \cong -5$ in H_2O[15]) shows that a strong protic acid is formed upon oxidation of **3**.

The mechanism of the oxidation reactions likely proceeds by initial oxygen-atom transfer to give a reactive rhenium(VII) dioxo cation, [Tp*Re(O)$_2$H][OTf] (**A** in Scheme 2), by analogy with previous studies on TpReO(X)OTf compounds (X = alkyl,[16] aryl,[13] alkoxy,[17] and halide[9c]). Intermediate **A** could then be deprotonated directly by NPh_3, py, or OTf^- (the lower pathway in Scheme 2), but it seems unlikely that **A** would be such a strong acid.[18] Significant acidity has not been observed in related rhenium hydrides, such as cationic **5** or the neutral rhenium(VII) tris(imido) hydride Re-

(9) (a) Tp = hydrotris(pyrazolyl)borate. (b) DuMez, D. D. Ph.D. Thesis, University of Washington, 1997. (c) DuMez, D. D.; Mayer, J. M. *Inorg. Chem.* **1998**, *37*, 445−453.

(10) On a vacuum line, a suspension of **1** (570 mg, 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 at room temperature shielded from light. Filtration, reduction of the filtrate to *ca.* 10 mL, and addition of pentane (30 mL) yielded 600 mg of **3** as a blue solid (87%). ^1H NMR ($CDCl_3$): δ 10.12 (s, 1H, ReH), 6.12, 6.06, 5.66 (each s, 1H, pz), 2.83, 2.76, 2.55, 2.55, 2.49, 2.22 (each s, 3H, pz-Me).

(11) Space group $P2_1/n$, a = 13.131(3) Å, b = 8.115(2) Å, c = 21.297(4) Å, β = 99.73(2)°, V = 2236(1) Å^3, Z = 4, D_c = 1.929 g cm^{-3}, T = 183 K; 3916 independent and 2955 observed reflections ($F > 4.0\sigma(F)$) refined to R = 2.97%, R_w = 4.02%, *GOF* = 0.88 on blue crystals. Selected bond lengths (Å) and angles (deg): Re−N(1) 2.251(5), Re−N(3) 2.055, Re−N(5) 2.119(5), O(1)−Re−O(2) 97.8(2), O(1)−Re−N(1) 172.7(2), O(1)−Re−N(3) 93.7(2), O(1)−Re−N(5) 106.2(2).

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

(13) Brown, S. N.; Mayer, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 12119−12133.

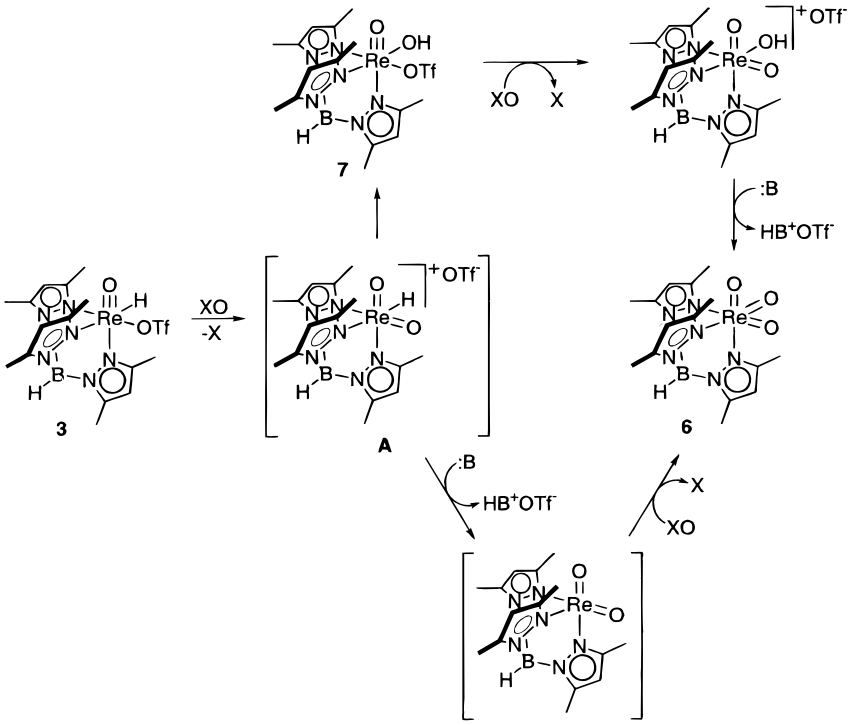
(14) In a typical procedure, **3** (6.8 mg, 10.5 μmol) and pyridine *N*-oxide (4.9 mg, 51.5 μmol), ca. 0.5 mL of $CDCl_3$ and $Me_3SiOSiMe_3$ (as an internal standard), were placed in an NMR tube, which was frozen and sealed with a torch.

(15) Arnett, E. M.; Quirk, R. P.; Burke, J. J. *J. Am. Chem. Soc.* **1970**, *92*, 1260−1266.

(16) DuMez, D. D.; Mayer, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 12416−12423.

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

Scheme 2. Mechanisms for Oxidation of Tp*Re(O)H(OTf) (3)



$(NAr)_3H$,[19] although neither of these would be expected to be as acidic as **A**. We favor a path involving rearrangement of the oxo−hydride **A** to the hydroxide complex Tp*ReO(OH)OTf (**7**) (the upper path in Scheme 2). Compound **7** has been prepared independently from Tp*ReO(OH)Cl and AgOTf.[20] It reacts with pyO and Me_2SO within minutes to give the same products as seen from **3**, presumably by oxidation to [Tp*Re$(O)_2OH^+OTf^-$], which converts to $Tp*ReO_3$ (**6**) and HOTf.[17] Thus, **7** is kinetically competent to be an intermediate in the oxidation of **3**.

The two pathways in Scheme 2 can be considered endmembers of a continuum of mechanisms between hydride migration and deprotonation assisted by base or the ion-paired triflate. There are no previous reports of an oxo−hydride to hydroxide rearrangement, but it is analogous to the oxo−phenyl to phenoxide transformation in the closely related $TpRe(O)_2Ph^+$ cation.[13] Zirconium and ruthenium hydrides have been converted to hydroxide ligands with N_2O, but oxo complexes are not likely intermediates.[21] The reverse reaction, hydroxide → oxo−hydride, has been reported in two other systems,[4,5b,22] and a likely example of imido−hydride → amide interconversion has been described.[19] The analogous hydride migration to oxo does not occur in the rhenium(V) complexes **1** and **1a**, as their hydride ligands do not exchange with D_2O.

In conclusion, rare examples of oxo−hydride complexes have been isolated, characterized, and shown to undergo typical hydride reactivity such as H/Cl exchange and insertion of olefins and acetaldehyde. Oxidation by oxygen-atom donors, however, transforms the hydride complex **3** into a strong acid, likely by a pathway involving migration of the hydride to an oxo ligand. Further investigations of such organometallic oxidation reactions are in progress.

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Supporting Information Available: Synthetic, spectroscopic, and analytical data for the new compounds and X-ray crystallographic data for compound **3** (10 pages). Ordering information is given on any currents masthead page.

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(18) The deprotonated form of **A**, "Tp*ReO_2" is apparently generated from **6** and PPh_3, and is converted to Tp*ReO(OH)Cl in the presence of Me_3SiCl/trace H_2O.[8] Tp*ReO(OH)OTf (**7**) shows no tendency to lose HOTf and form "Tp*ReO_2," even in the presence of Ph_3N.

(19) $[Re(NAr)_3]^-$ salts are quantitatively protonated by $[NEt_2H_2]OTf$ in THF: Williams, D. S.; Schrock, R. R. *Organometallics* **1993**, *12*, 1148−1160.

(20) Following the procedure for **3**,[10] Tp*ReO(OH)Cl[8c] (306 mg, 0.554 mmol) and AgOTf (150 mg, 0.584 mmol) in C_6H_6 (30 mL) gave 225 mg of blue **7** (61%). ^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) (ReO*H* not observed). ^{19}F NMR ($CDCl_3$): δ −0.28 (s). IR (Nujol mull): 3500 (νOH), 2557 (νBH), 1547, 1418, 1345, 1236, 1204, 1154, 1079, 1066, 1023, 975 (νReO), 865, 814, 789, 721, 692. 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.

(21) (a) Vaughan, G. A.; Rupert, P. B.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1987**, *109*, 5538. (b) Kaplan, A. W.; Bergman, R. G. *Organometallics* **1997**, *16*, 1106−8. (c) Grundy, K. R.; Laing, K. R.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1970**, 1500, reports apparent hydride-to-hydroxide oxidation with O_2.

(22) α-Elimination from a palladium hydroxide has been suggested: Blum, O.; Portnoy, M.; Milstein, D. *Abstracts of the XVth International Conference on Organometallic Chemistry*; Warsaw, Poland, 1992; P150.