

# Synthesis and Reactions of Rhenium(V) Oxo–Hydride Complexes

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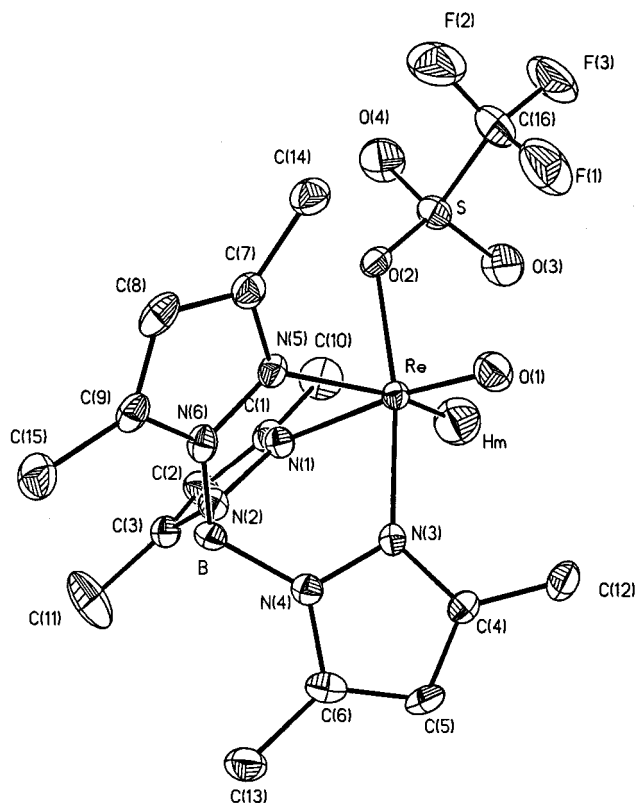
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**Summary:**  $Tp^*ReO(H)Cl$ ,  $TpRe(O)H(Cl)$ , and  $Tp^*ReO(H)_2$  have been prepared by alkoxide-for-hydride metathesis using  $BH_3 \cdot THF$ . The triflate derivative  $Tp^*Re(O)H(OTf)$  inserts olefins and is oxidized by oxygen-atom transfer 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 =  $OTf = OSO_2CF_3$ ).

The chemistry of transition-metal oxo complexes has been receiving significant attention because of its importance in metal-mediated oxidation processes.<sup>3</sup> 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.  $Cp^*_2Ta(O)H^4$  and  $Re(O)H(RC \equiv CR)_2^5$  are irreversibly formed by rearrangement of hydroxide complexes, and  $[Re(O)(H)_2Cytpt]^+$  converts CO to a formate ligand.<sup>6</sup> Reported here are the synthesis, characterization, and reactivity of a new series of rhenium oxo–hydride complexes.

$BH_3 \cdot THF$  in toluene at low temperatures was found to be effective for converting rhenium(V) oxo–alkoxide complexes to the corresponding oxo–hydride com-



**Figure 1.**

pounds. 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).<sup>7,8</sup> The Tp analogue  $TpReO(H)Cl$  (**1a**, 68%)<sup>7</sup> was similarly synthesized from  $TpReO(OEt)Cl$ <sup>9</sup> or in low yield by the reaction of  $^nBu_3-$

(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  $BH_3 \cdot THF$  (1.0 M  $\times$  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  $-28^\circ C$ . The mixture was stirred at  $-20^\circ C$  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  $CH_2Cl_2$  (10 mL  $\times$  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  $CH_2Cl_2$ /hexane to yield  $Tp^*ReO(H)Cl$  (585 mg, 97.4%) as blue crystals.  $^1H$  NMR ( $CDCl_3$ ): **1**  $\delta$  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** ( $C_6D_6$ ):  $\delta$  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**  $\delta$  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  $Tp^*Re(O)Cl_2 + MeOH + Et_3N$ ; 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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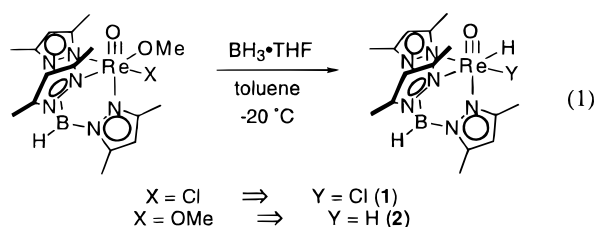
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(3) Leading references: (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981. (b) Nugent, W. A.; Mayer, J. M. *Metal–Ligand Multiple Bonds*; John Wiley and Sons: New York, 1988. (c) Holm, 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.

(4)  $Cp^* = C_5Me_5$ . (a) van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347–5349. (b) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21–39. (c) Parkin, G.; van Asselt, A.; Leahy, D. J.; Whinnery, L.; Hua, N. G.; Quan, R. W.; Henling, L. M.; Schaefer, W. P.; Santarsiero, B. D.; Bercaw, J. E. *Inorg. Chem.* **1992**, *31*, 82–85.

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(6)  $Cytpt = (C_2H_5PCH_2CH_2CH_2)_2PPh$ ;  $[Re(O)H(F)Cytpt]^+$  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.

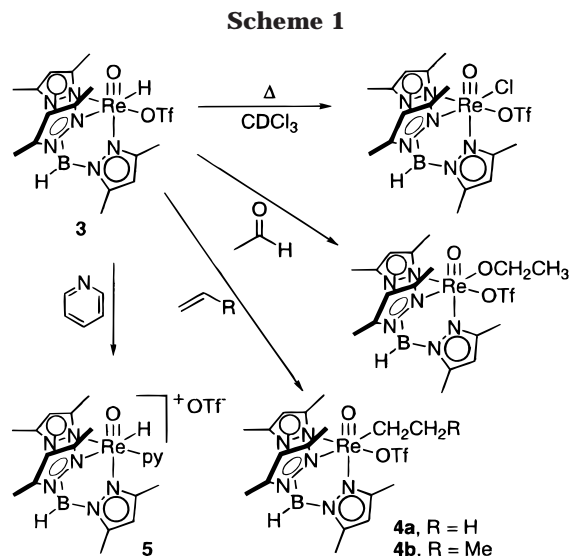


SnH with  $\text{Tp}^*\text{ReOCl}_2$ . Chloride **1** was converted to  $\text{Tp}^*\text{Re}(\text{O})\text{H}(\text{OTf})$  (**3**) in 87% yield by metathesis with  $\text{AgOTf}$  in benzene/ $\text{CH}_2\text{Cl}_2$ .<sup>10</sup>

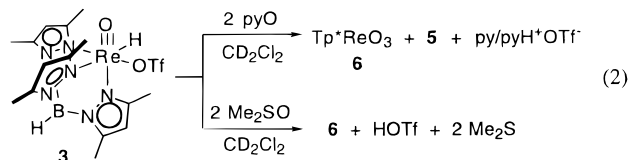
An X-ray diffraction analysis of **3** (Figure 1)<sup>11</sup> revealed that the rhenium center possesses a distorted octahedral coordination with a typical  $\text{Re}=\text{O}$  bond length of 1.665–(5) Å.<sup>12</sup> The hydride ligand was located in one of the octahedral sites and was refined ( $\text{Re}-\text{H}$  1.69(8) Å;  $\text{O}(1)-\text{Re}-\text{H}$  93(3)°). The  $\text{Re}-\text{O}(2)$  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  $^{19}\text{F}$  NMR chemical shift of  $\delta -0.24$  ppm (in  $\text{CD}_2\text{Cl}_2$  vs  $\text{CF}_3\text{COOH}$ ).<sup>13</sup> The poor donation of the triflate ligand may be revealed in the  $\text{Re}-\text{H}$  stretching frequencies (IR, Nujol mull) at 1988, 1969, and 2058  $\text{cm}^{-1}$  for **1**, **2**, and **3**, respectively. The hydride chemical shifts are quite downfield:  $\delta$  8.64 (**1**), 9.55 (**2**), and 10.12 (**3**) in  $\text{CDCl}_3$ .

Complex **3** displays reactivity typical of a metal–hydride complex (Scheme 1). In  $\text{CDCl}_3$  solution over several days at 65 °C, it undergoes hydride–chloride exchange forming  $\text{Tp}^*\text{ReO}(\text{Cl})\text{OTf}$ .<sup>8b</sup> Acetaldehyde reacts with **3** in  $\text{CDCl}_3$  at room temperature to give  $\text{Tp}^*\text{ReO}(\text{OEt})\text{OTf}$ <sup>8b</sup> as the major initial product, indicating that **3** has some hydridic character. Reaction of **3** with excess ethylene in  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  at room temperature gives  $\text{Tp}^*\text{ReO}(\text{Et})\text{OTf}$  (**4a**) in a quantitative NMR yield. Complex **4a** has been synthesized independently from  $\text{Tp}^*\text{ReO}(\text{Et})\text{Cl}$  and  $\text{AgOTf}$ . Propylene also inserts to give  $\text{Tp}^*\text{ReO}(\text{Pr})\text{OTf}$  (**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.  $\beta$ -hydrogen elimination is thus too endoergic to occur under these conditions.

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



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  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  yields  $\text{Tp}^*\text{ReO}_3$  (**6**),<sup>8c</sup> the pyridine adduct **5**,  $\text{pyH}^+\text{OTf}^-$ , and py over hours at room temperature (eq 2).<sup>14</sup> In the initial



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.  $\text{Me}_2\text{SO}$  also oxidizes **3** to **6** at ambient temperature, also forming  $\text{Me}_2\text{S}$  and  $\text{HOTf}$ . Over time, **6** reacts further with the  $\text{HOTf}$  to generate a mixture of products. Reaction of **3** and  $\text{Me}_2\text{SO}$  in the presence of  $\text{NPh}_3$  generates  $\text{HNPh}_3^+$  (by  $^1\text{H}$  NMR). The formation of  $\text{HOTf}$  and  $\text{HNPh}_3^+$  ( $\text{p}K_a \approx -5$  in  $\text{H}_2\text{O}$ )<sup>15</sup> 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,  $[\text{Tp}^*\text{Re}(\text{O})_2\text{H}][\text{OTf}]$  (**A** in Scheme 2), by analogy with previous studies on  $\text{Tp}^*\text{ReO}(\text{X})\text{OTf}$  compounds ( $\text{X} = \text{alkyl}$ ,<sup>16</sup> aryl,<sup>13</sup> alkoxy,<sup>17</sup> and halide<sup>9c</sup>). Intermediate **A** could then be deprotonated directly by  $\text{NPh}_3$ , py, or  $\text{OTf}^-$  (the lower pathway in Scheme 2), but it seems unlikely that **A** would be such a strong acid.<sup>18</sup> Significant acidity has not been observed in related rhenium hydrides, such as cationic **5** or the neutral rhenium(VII) tris(imido) hydride  $\text{Re}(\text{O})\text{H}(\text{O})\text{OTf}$ .

(14) In a typical procedure, **3** (6.8 mg, 10.5  $\mu\text{mol}$ ) and pyridine *N*-oxide (4.9 mg, 51.5  $\mu\text{mol}$ ), ca. 0.5 mL of  $\text{CDCl}_3$  and  $\text{Me}_3\text{SiOSiMe}_3$  (as an internal standard), were placed in an NMR tube, which was frozen and sealed with a torch.

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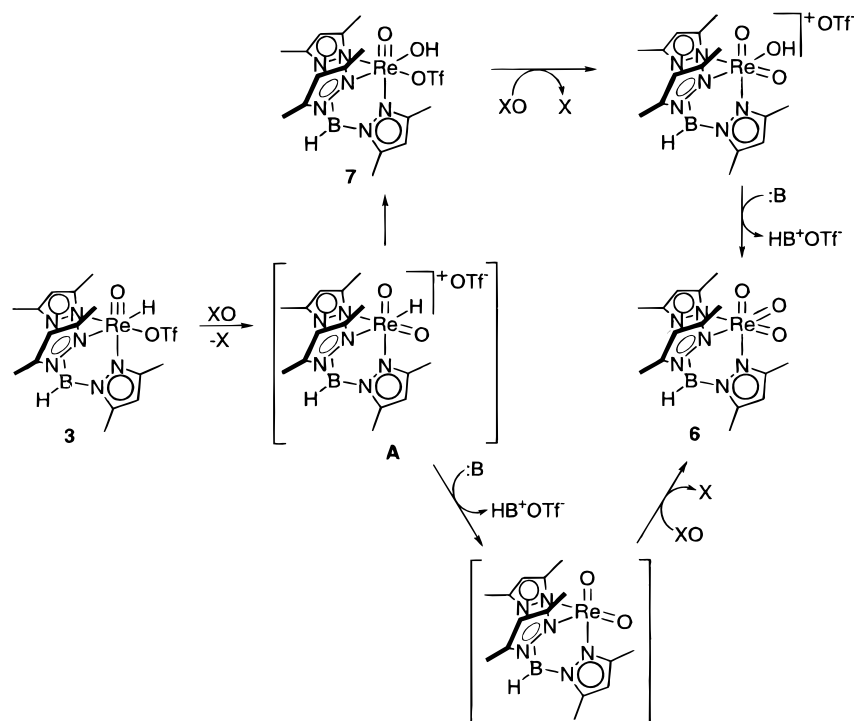
(9) (a) Tp = hydrotris(pyrazolyl)borate. (b) DuMez, D. D. Ph.D. Thesis, University of Washington, 1997. (c) DuMez, D. D.; Mayer, J. M. *Inorg. Chem.* **1998**, *37*, 445–453.

(10) On a vacuum line, a suspension of **1** (570 mg, 1.06 mmol),  $\text{AgOTf}$  (286 mg, 1.11 mmol),  $\text{CH}_2\text{Cl}_2$  (15 mL), and  $\text{C}_6\text{H}_6$  (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%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  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,  $\beta = 99.73(2)^\circ$ ,  $V = 2236(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.929$  g  $\text{cm}^{-3}$ ,  $T = 183$  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):  $\text{Re}-\text{N}(1)$  2.251(5),  $\text{Re}-\text{N}(3)$  2.055,  $\text{Re}-\text{N}(5)$  2.119(5),  $\text{O}(1)-\text{Re}-\text{O}(2)$  97.8(2),  $\text{O}(1)-\text{Re}-\text{N}(1)$  172.7(2),  $\text{O}(1)-\text{Re}-\text{N}(3)$  93.7(2),  $\text{O}(1)-\text{Re}-\text{N}(5)$  106.2(2).

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Scheme 2. Mechanisms for Oxidation of  $\text{Tp}^*\text{Re}(\text{O})\text{H}(\text{OTf})$  (**3**)

( $\text{NAr}$ )<sub>3</sub>H,<sup>19</sup> 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  $\text{Tp}^*\text{ReO}(\text{OH})\text{OTf}$  (**7**) (the upper path in Scheme 2). Compound **7** has been prepared independently from  $\text{Tp}^*\text{ReO}(\text{OH})\text{Cl}$  and  $\text{AgOTf}$ .<sup>20</sup> It reacts with  $\text{pyO}$  and  $\text{Me}_2\text{SO}$  within minutes to give the same products as seen from **3**, presumably by oxidation to  $[\text{Tp}^*\text{Re}(\text{O})_2\text{OH}^+\text{OTf}^-]$ , which converts to  $\text{Tp}^*\text{ReO}_3$  (**6**) and  $\text{HOTf}$ .<sup>17</sup> Thus, **7** is kinetically competent to be an intermediate in the oxidation of **3**.

The two pathways in Scheme 2 can be considered end-members 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  $\text{TpRe}(\text{O})_2\text{Ph}^+$  cation.<sup>13</sup> Zirconium and ruthenium hydrides have been converted to hydroxide ligands with  $\text{N}_2\text{O}$ , but oxo complexes are not likely intermediates.<sup>21</sup> The reverse reaction, hydroxide  $\rightarrow$  oxo–hydride, has been reported in two other systems,<sup>4,5b,22</sup> and a likely example of imido–hydride  $\rightarrow$  amide interconversion has been described.<sup>19</sup> The analo-

gous hydride migration to oxo does not occur in the rhenium(V) complexes **1** and **1a**, as their hydride ligands do not exchange with  $\text{D}_2\text{O}$ .

In conclusion, rare examples of oxo–hydride complexes have been isolated, characterized, and shown to undergo typical hydride reactivity such as  $\text{H}/\text{Cl}$  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.

**Acknowledgment.** The National Science Foundation is acknowledged for generous financial support. We thank Dr. David Barnhart for his assistance with the X-ray crystallography, Drs. James Roe and Martin Sadilek for their assistance with the MS measurements, and Drs. Darin D. DuMez and Brian Bennett for their assistance and comments. Y.M. acknowledges a Fellowship from the Ministry of Education, Science, Sports, and Culture, Japan.

**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 current masthead page.

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(18) The deprotonated form of **A**, " $\text{Tp}^*\text{ReO}_2$ " is apparently generated from **6** and  $\text{PPh}_3$ , and is converted to  $\text{Tp}^*\text{ReO}(\text{OH})\text{Cl}$  in the presence of  $\text{Me}_3\text{SiCl}/\text{trace H}_2\text{O}$ .<sup>8</sup>  $\text{Tp}^*\text{ReO}(\text{OH})\text{OTf}$  (**7**) shows no tendency to lose  $\text{HOTf}$  and form " $\text{Tp}^*\text{ReO}_2$ ," even in the presence of  $\text{Ph}_3\text{N}$ .

(19)  $[\text{Re}(\text{NAr})_3]^+$  salts are quantitatively protonated by  $[\text{NET}_2\text{H}_2]^+\text{OTf}^-$  in THF: Williams, D. S.; Schrock, R. R. *Organometallics* **1993**, *12*, 1148–1160.

(20) Following the procedure for **3**,<sup>10</sup>  $\text{Tp}^*\text{ReO}(\text{OH})\text{Cl}$  (306 mg, 0.554 mmol) and  $\text{AgOTf}$  (150 mg, 0.584 mmol) in  $\text{C}_6\text{H}_6$  (30 mL) gave 225 mg of blue **7** (61%). <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  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) (ReOH not observed). <sup>19</sup>F NMR ( $\text{CDCl}_3$ ):  $\delta$  –0.28 (s). IR (Nujol mull): 3500 ( $\nu\text{OH}$ ), 2557 ( $\nu\text{BH}$ ), 1547, 1418, 1345, 1236, 1204, 1154, 1079, 1066, 1023, 975 ( $\nu\text{ReO}$ ), 865, 814, 789, 721, 692. Anal. Calcd for  $\text{C}_{16}\text{H}_{23}\text{BF}_3\text{N}_6\text{O}_3\text{ReS}$ : 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  $\text{O}_2$ .

(22)  $\alpha$ -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.