Fluoride Reactions with Hydrotris(pyrazolyl)borate Rhenium Oxo Complexes: Re−F vs B−F Bond Formation

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Rhenium−oxo−fluoride complexes are readily prepared using hydrotris(3,5-dimethyl-1-pyrazolyl)borate [HB-(3,5-$Me_2pz)_3^-$, Tp*] as a supporting ligand. For instance, treatment of Tp*Re(O)(OH)Cl with concentrated aqueous HF cleanly forms the chloro−fluoride complex Tp*Re(O)(F)Cl. Related fluoro−iodide, fluoro−triflate, and difluoride complexes are also described. In contrast, a variety of reactions of analogous compounds with the unsubstituted hydrotris(1-pyrazolyl)borate ligand [HB$(pz)_3^-$, Tp] have failed to produce fluoro complexes. Extended refluxing of TpRe(O)I_2 with an excess of NaF in acetonitrile in the air gives a modest yield of an unusual rhenium μ-pyrazolyl μ-oxo dimer, {[κ^2-H(F)Bpz$_2$]Re(O)}$_2$(μ-pz)$_2$(μ-O) (**5**) (pz = pyrazolyl). The X-ray crystal structure of **5** shows that one pyrazolyl of each Tp ligand has been substituted for fluoride. The different reactivity of the Tp and Tp* complexes is apparently due to the greater steric protection of the boron afforded by the Tp* ligand. Crystallographic data for **5**: monoclinic; space group *Cc*; $a = 19.103(4)$ Å, $b = 10.482(2)$ Å, $c = 14.240(3)$ Å, $\beta = 114.82(3)°$; $Z = 4$; $R = 3.73\%$, R_w (observed data) = 4.73%; GOF = 1.20.

Introduction

Transition metal fluoride complexes are often more difficult to prepare than those of the other halides.[3,4] This report describes efforts to prepare rhenium−oxo−fluoride complexes with hydrotris(pyrazolyl)borate (scorpionate) ligands: the parent hydrotris(1-pyrazolyl)borate, HB$(pz)_3^-$ (Tp), and the 3,5-dimethyl derivative, hydrotris(3,5-dimethyl-1-pyrazolyl)borate, HB$(Me_2pz)_3^-$ (Tp*). In studies of oxidizing rhenium compounds, rhenium(VII) dioxo cations of the form [TpRe(O)$_2$X]$^+$ have been implicated as reactive intermediates, but have thus far eluded isolation.[5,6] For instance, oxygen atom transfer to the rhenium(V) chloro−triflate complex TpRe(O)Cl(OTf) by pyridine *N*-oxide gives the rhenium(VI) species TpRe(O)$_2$Cl via the unobserved intermediate [TpRe(O)$_2$Cl]$^+$.[6c] Given the ability of fluoride to stabilize high oxidation state complexes, we set out to prepare rhenium(V) oxo−fluorides that could be oxidized to Re(VII). Preparation of fluoride complexes containing the Tp* ligands is straightforward, but is surprisingly problematic with Tp ligands. In one attempt to prepare a rhenium fluoride by reaction of a rhenium iodide complex with NaF, we instead isolated an unusual rhenium dimer, {[H(F)Bpz$_2$]Re(O)}$_2$(μ-pz)$_2$(μ-O) (**5**). Fluorination takes place at boron rather than at rhenium, with cleavage of a boron−pyrazolyl bond. The Tp ligand had proven to be robust in almost all other reactions involving such rhenium−oxo complexes. Cleavage of boron−pyrazolyl bonds is not uncommon in Tp chemistry,[7] and it may be particularly problematic for fluoride because of the strength of B−F bonds. Kläui et al. have commented on the scarcity of Tp−metal−fluoride complexes and have noted the decomposition of HB(3-Ph-pz)$_3^-$ by KF.[8]

Experimental Section

General Considerations. All experiments were performed under an inert atmosphere using standard vacuum, Schlenk, and glovebox techniques, except where noted. Solvents were degassed and dried according to standard procedures.[9] Tp*Re(O)$_3$,[10] Tp*Re(O)(OH)Cl,[10,11] and TpRe(O)I_2[12] were synthesized according to published procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratories. C_6D_6 was dried over sodium metal; CD_2Cl_2 and $CDCl_3$ were dried over CaH_2. Aqueous HF (48.5%) was purchased from Baker. Other reagents were obtained from Aldrich and used as received unless otherwise noted.

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. All spectra were recorded at ambient temperatures unless otherwise noted. Peaks in the ^{1}H spectra were referenced to solvent resonances. ^{19}F spectra were referenced to neat CF_3COOH. Peak positions are reported in ppm and coupling constants in Hz. IR spectra, reported below in cm^{-1}, were recorded using a Perkin-Elmer 1600 FTIR with samples prepared as evaporated films on NaCl plates. Electron impact mass spectra (EIMS) were performed on a Kratos Analytical mass spectrometer using a direct probe technique. FAB-MS were obtained on a VG 70 SEQ tandem hybrid instrument of EBqQ geometry, equipped with a standard

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saddle-field gun (Ion Tech Ltd., Middlesex, U.K.) producing a beam of xenon atoms at 8 keV and 1 mA. Samples were applied to the FAB target in dichloromethane solutions. The matrix used was a 3-nitrobenzyl alcohol, and the spectra were taken in the positive ion mode. Elemental analyses were performed by Canadian Microanalytical Services Ltd.

Tp*Re(O)(F)Cl (1). Crude Tp*Re(O)(OH)Cl (110 mg, including 0.190 mmol of Tp*Re(O)(OH)Cl and 0.009 mmol of Tp*Re(O)Cl_2) was dissolved in 10 mL of CH_2Cl_2 in a 100 mL polyethylene flask. Into this solution was added aqueous HF (48.5%, 1 mL), and the resulting mixture was stirred for 1 h at room temperature. The solution was neutralized with a saturated $NaHCO_3$ solution, and the organic phase was separated from the mixture. The CH_2Cl_2 solution was dried over $MgSO_4$ and evaporated under reduced pressure to leave a blue residue, which was purified by column chromatography on silica gel with CH_2Cl_2 as the eluent. Recrystallization from hexane/CH_2Cl_2 yielded Tp*Re(O)(F)Cl (95 mg, 90%) as sky blue crystals. ^{1}H NMR ($CDCl_3$): δ 6.12, 6.06, 5.70 (each s, 1H, pz), 2.97, 2.74, 2.68, 2.62, 2.43, 2.22 (each s, 3H, pz-Me). ^{19}F NMR ($CDCl_3$): δ 47.55. IR: 2554 (ν_{BH}), 1539, 1195, 1072, 969 (ν_{ReO}), 862, 815, 790, 687. EIMS: $m/z = 554$ (M^+). Anal. Calcd for $C_{15}H_{22}BClFN_6ORe$: C, 32.53; H, 4.00; N, 15.17. Found: C, 32.34; H, 3.89; N, 14.77.

Tp*Re(O)F_2 (2). A mixture of Tp*Re(O)$_3$ (266 mg, 0.501 mmol), Ph_3P (144 mg, 0.549 mmol), and CH_2Cl_2 (40 mL) was stirred for 23 h at room temperature, yielding a greenish brown solution. The solution was then poured into a 100 mL polyethylene flask, and aqueous HF (48.5%, 3 mL) was added. After 10 min of stirring at room temperature, the reaction mixture was neutralized by addition of saturated aqueous $NaHCO_3$ solution. The dark blue organic layer was dried over $MgSO_4$ and evaporated under reduced pressure to leave a brown residue, which turned blue on washing with EtOH. This material was purified by column chromatography on silica gel with CH_2Cl_2 as the eluent. Recrystallization from hexane/CH_2Cl_2 yielded Tp*Re(O)F_2 (217 mg, 81%) as sky blue crystals. ^{1}H NMR ($CDCl_3$): δ 6.07 (s, 2H, pz), 5.68 (s, 1H, pz), 2.77, 2.64 (each s, 6H, pz-Me), 2.49, 2.21 (each s, 3H, pz-Me). ^{19}F NMR ($CDCl_3$): δ 36.40. IR: 2554 (ν_{BH}), 1544, 1195, 1072, 974 (ν_{ReO}), 867, 815; EIMS: $m/z = 538$ (M^+).

Tp*Re(O)F(OTf) (3). Tp*Re(O)F_2 (260 mg, 0.484 mmol) was placed in a 100 mL round bottom flask, and CH_2Cl_2 (50 mL) was vacuum transferred in. To the blue suspension was added Me_3SiOTf (96 μL, 0.53 mmol), and the resulting solution was stirred for 2 h at room temperature. Evaporation of the volatiles under reduced pressure left blue solids, which were recrystallized from CH_2Cl_2/pentane to afford analytically pure Tp*Re(O)F(OTf) as sky blue crystals (300 mg, 93%). ^{1}H NMR ($CDCl_3$): δ 6.12 (s, 2H, pz), 5.77 (s, 1H, pz), 2.86, 2.66, 2.62, 2.59, 2.54, 2.25 (each s, 3H, pz-Me). IR: 2565 (ν_{BH}), 1545, 1419, 1354, 1236, 1196, 1155, 1080, 976, 950 (ν_{ReO}), 906, 866, 814, 790, 722, 690, 640, 631. EIMS: $m/z = 668$ (M^+). Anal. Calcd for $C_{16}H_{22}BF_4N_6O_4ReS$: C, 28.79; H, 3.32; N, 12.59. Found: C, 29.10; H, 3.56; N, 12.30.

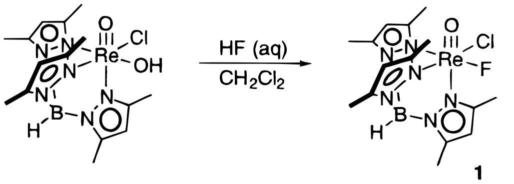
Tp*Re(O)(F)I (4). Tp*Re(O)F_2 (260 mg, 0.484 mmol) was placed in a 100 mL round bottom flask with a stir bar, and CH_2Cl_2 (40 mL) was vacuum transferred in. Me_3SiOTf (96 μL, 0.53 mmol) was added at room temperature, and the resulting blue solution was stirred for 30 min. Evaporation of the volatiles under reduced pressure left a blue residue, to which was added NaI (370 mg, 2.50 mmol). CH_2Cl_2 (20 mL) and CH_3CN (30 mL) were subsequently vacuum transferred into the flask, and the resulting mixture was stirred for 3 days at room temperature. Evaporation of the volatiles under reduced pressure left a residue, which was taken up with toluene. The toluene-soluble products were purified by column chromatography (three times) on silica gel with toluene as the eluent, affording Tp*Re(O)(F)I (50 mg, 16%) as yellow crystals. ^{1}H NMR ($CDCl_3$): δ 6.16, 6.01, 5.72 (each s, 1H, pz), 3.19, 2.77, 2.72, 2.61, 2.45, 2.25 (each s, 3H, pz). ^{19}F NMR ($CDCl_3$): δ 44.03. IR: 2554 (ν_{BH}), 1544, 1308, 1195, 1072, 974 (ν_{ReO}), 908, 862, 815, 790, 687. EIMS: $m/z = 646$ (M^+). Anal. Calcd for $C_{15}H_{22}BFIN_6ORe$: C, 27.92; H, 3.44; N, 13.02. Found: C, 28.27; H, 3.53; N, 12.91.

{[H(F)Bpz$_2$]Re(O)}$_2$(μ-pz)$_2$(μ-O) (5). TpRe(O)I_2 (315 mg, 0.538 mmol) and NaF (502 mg, 7.21 mmol, 13.4 equiv) were refluxed in acetonitrile (200 mL) in air. After 19 days the solvent was removed, and the brown residue was taken up in toluene and filtered. The solution was purified by column chromatography (silica gel/toluene), giving TpRe(O)I_2 (41%) and a deep blue fraction. This fraction was recovered and recrystallized from methylene chloride/hexanes to give 40.4 mg of **5** (17% yield; 29% based on converted TpRe(O)I_2). ^{1}H NMR ($CDCl_3$): δ 8.01 (br t, $J_{HH} \cong J_{FH} \cong 2$ Hz, 2H), 7.91, 7.67, 7.62, 7.23 (each d, $J_{HH} = 2$ Hz, 2H), 7.17 (br t, $J_{HH} \cong J_{FH} \cong 2$ Hz, 2H), 6.49, 6.39, 6.38 (each t, $J_{HH} = 2$ Hz, 2H). ^{19}F NMR ($CDCl_3$): δ -84.3, -122.3. IR: 3119 (w), 2931 (w), 2425 (w, ν_{B-H}), 1551 (w), 1488 (w), 1439 (w), 1402 (s), 1303 (m), 1210 (m), 1145 (s), 1103 (w), 1060 (s), 965 (m, $\nu_{Re=O}$), 767 (w), 737 (w) 688 (w), 675 (w), 642 (m). FAB-MS: $m/z = 883$ (M $-$ 1). Anal. Calcd for $C_{18}H_{20}B_2F_2N_{12}O_3Re_2$: C, 24.44; H, 2.28; N, 19.00. Found: C, 24.69; H, 2.32; N, 19.28.

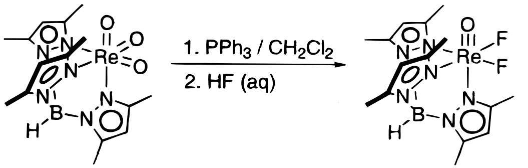
X-ray Structure Determination of {[H(F)Bpz$_2$]Re(O)}$_2$(μ-pz)$_2$(μ-O) (5). Slow diffusion of pentane layered on a solution of **5** in toluene at ~10 °C deposited dark blue rhombohedral crystals. A crystal was glued to the tip of a glass fiber in air, and data were collected on an Enraf-Nonius CAD4 diffractometer (Table 1). A semiempirical absorption correction was applied, and the structure was solved by direct methods using the SHELXTL PC program. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions. Disorder was modeled assuming 50% occupancy of fluorine in each of the two positions on each boron.

Results and Discussion

Reduction of Tp*Re(O)$_3$ with PPh_3 in the presence of Me_3SiCl gives the rhenium oxo−hydroxo−chloride complex Tp*Re(O)(OH)Cl contaminated with a small amount of Tp*Re(O)Cl_2.[10,11] Treatment of Tp*Re(O)(OH)Cl with 48.5% aqueous HF gives marine blue Tp*Re(O)(F)Cl (**1**) in 90% yield (eq 1). Similar reactions with aqueous HCl, HBr, or HI give the analogous Tp*Re(O)(X)Cl compounds.[11] The difluoride, Tp*Re(O)F_2 (**2**), is prepared by reacting Tp*Re(O)$_3$ with PPh_3 for 1 day in the absence of halide, followed by the addition of 48.5% aqueous HF under a nitrogen atmosphere (eq 2). [Tp*Re(O)$_2$] and its dimer [{Tp*Re(O)}$_2$(μ-O)$_2$] are reasonable intermediates in this reaction, by analogy with related pyrazolyl−borate and Cp* chemistry,[13] though to our knowledge they have not been isolated.



1 (1)



2 (2)

One fluoride ligand in **2** can be removed with Me_3SiOTf to yield Tp*Re(O)F(OTf) (**3**; eq 3). The analogous reaction with **1** also selectively removes fluoride over chloride, giving the known Tp*Re(O)Cl(OTf)[11] (eq 4). Treatment of **2** with Me_3SiI gives low yields of the fluoro−iodide complex Tp*Re(O)(F)I

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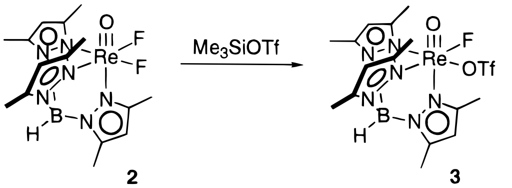
Table 1. Crystallographic Data for $\{[H(F)Bpz_2]Re(O)\}_2(\mu\text{-pz})_2(\mu\text{-O})$ (**5**)

$C_{18}H_{20}B_2N_{12}O_3Re_2$	fw, 884.5
$a = 19.103(4)$ Å	space group, *Cc*
$b = 10.482(2)$ Å	$T = -90$ °C
$c = 14.240(3)$ Å	$\lambda = 0.71073$ Å
$\beta = 114.82(3)°$	$\rho_{calcd} = 2.265$ g cm^{-3}
$\mu = 9.41$ cm^{-1}	$R(F_o)^a = 3.73\%$
$V = 2588.1(13)$ Å^3	$R_w(F_o)^b = 4.73\%$
$Z = 4$	GOF = 1.20

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w\,|F_o|^2]^{1/2}$.

(**4**), which is better prepared by substitution of the triflate ligand in **3** with NaI (eq 5).



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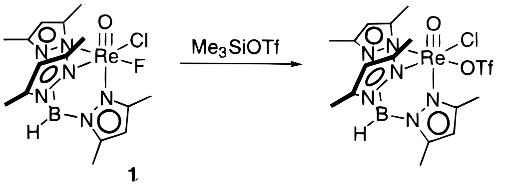

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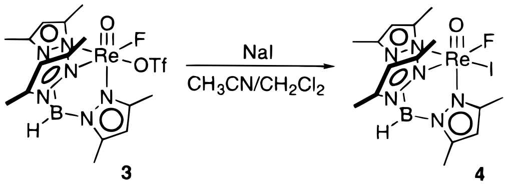


(5)

Dihalide complexes **1**, **2**, and **4** were purified by column chromatography on silica gel followed by recrystallization. The solubility of the fluoride complexes **1** and **2** is much lower than that of other Tp*Re(O)(X)Cl complexes with X = Cl, Br, I. Complex **2** is not soluble in hexane, benzene, or CH_3CN and is only slightly soluble in CH_2Cl_2 and $CHCl_3$. All of the halide complexes are air-stable and thermally stable. The fluoro–triflate **3** is slightly air-sensitive as a solid and is more soluble in CH_2Cl_2 and $CHCl_3$. ^1H NMR spectra of **1**, **3**, and **4** show three inequivalent pyrazolyl groups, while **2** shows a 2:1 ratio of pyrazolyls, consistent with its C_s symmetry. The B–H stretching mode appears at about 2560 cm^{-1} in all four compounds, consistent with a κ^3-coordination mode.[14]

In contrast to the straightforward preparations of oxo–fluoride complexes with the Tp* ligand, all efforts to prepare oxo–fluorides with the parent Tp ligand have been unsuccessful. While TpRe(O)Cl$_2$ is easily prepared from KReO$_4$, KTp, and aqueous HCl,[15] no fluorides are obtained from related reactions using HF. TpRe(O)(OR)Cl and TpRe(O)(OR)$_2$ are converted in high yield to TpRe(O)Cl$_2$ using aqueous HCl (analogous to eq 1 above),[6a] but reactions of 47% aqueous HF with TpRe(O)(OEt)$_2$, TpRe(O)(OMe)$_2$, TpRe(O)(O^{i}Pr)$_2$, and TpRe(O)(OEt)Cl result in decomposition of the rhenium species to unidentified products. There is no reaction between 47% HF and the rhenium alkyl compounds TpRe(O)(Et)Cl and TpRe(O)(Et)I in acetone. Similarly, no reaction was observed on treating TpRe(O)(OEt)$_2$ with benzoyl fluoride, PhC(O)F. Substitution of triflate in Tp–rhenium–triflate complexes by various fluoride sources was not successful, though such reactions are facile with other halides.[6]

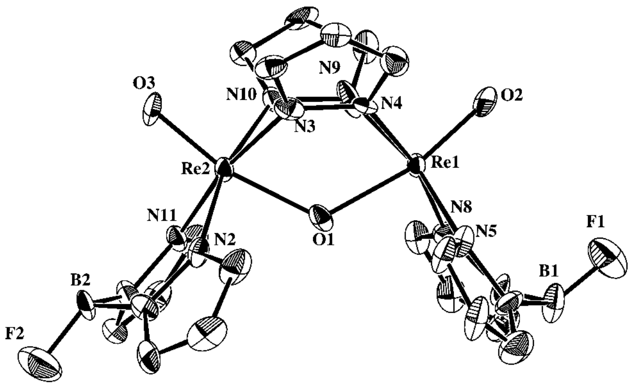
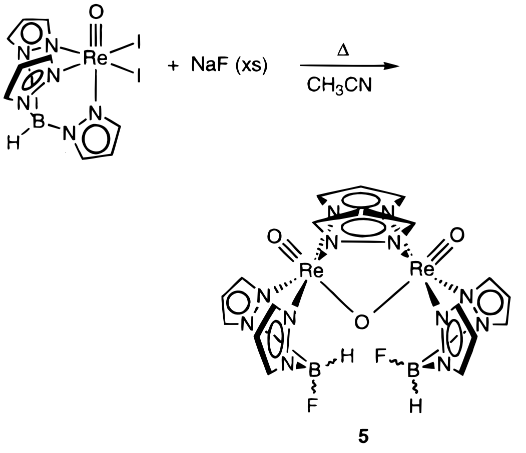


Figure 1. ORTEP drawing of the X-ray structure of $\{[H(F)Bpz_2]Re(O)\}_2(\mu\text{-pz})_2(\mu\text{-O})$ (**5**).

Halide metathesis is readily accomplished by refluxing TpRe(O)Cl$_2$ and excess NaBr or NaI in acetonitrile.[16] However, reactions of TpRe(O)Cl$_2$ with NaF or AgF did not give significant characterizable or chromatographable products. Refluxing the diiodide TpRe(O)I$_2$ with an excess of NaF in acetonitrile in the air for 19 days gave a pyrazolyl- and oxo-bridged rhenium dimer, $\{[H(F)Bpz_2]Re(O)\}_2(\mu\text{-pz})_2(\mu\text{-O})$ (**5**), in 17% yield (eq 6). Starting material was recovered in 41% yield, so the yield of **5** is 29% based on consumed TpReOI$_2$. Reacting TpReOI$_2$ with NaF in the absence of air did not form **5**, but produced two unidentified products. Partial decomposition was observed on refluxing pure TpRe(O)I$_2$ in acetonitrile for 10 days.



(6)

Compound **5** crystallized as long, dark blue rhombohedral crystals, and its structure was solved by X-ray diffraction (Figure 1). Crystallographic details are presented in Table 1, and a selection of bond distances and angles are given in Table 2. The molecule has a rough "C" shape with pseudo- (noncrys-

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $\{[H(F)Bpz_2]Re(O)\}_2(\mu\text{-}pz)_2(\mu\text{-}O)$ (**5**)

Re(1)−O(2)	1.654(12)	Re(1)−O(1)	1.925(11)
Re(1)−N(4)	2.113(15)	Re(1)−N(9)	2.115(19)
Re(1)−N(5)	2.046(15)	Re(1)−N(8)	2.089(14)
Re(2)−O(3)	1.687(14)	Re(2)−O(1)	1.932(12)
Re(2)−N(3)	2.102(12)	Re(2)−N(10)	2.126(13)
Re(2)−N(2)	2.082(14)	Re(2)−N(11)	2.101(12)
B(1)−N(6)	1.517(26)	B(1)−N(7)	1.555(24)
O(2)−Re(1)−O(1)	166.2(7)	O(2)−Re(1)−N(4)	90.4(6)
O(1)−Re(1)−N(4)	80.6(5)	O(2)−Re(1)−N(9)	90.2(6)
O(1)−Re(1)−N(9)	78.9(5)	N(4)−Re(1)−N(9)	87.0(7)
O(2)−Re(1)−N(5)	100.7(6)	O(1)−Re(1)−N(5)	90.0(5)
N(4)−Re(1)−N(5)	91.2(6)	N(9)−Re(1)−N(5)	168.9(6)
O(2)−Re(1)−N(8)	100.2(6)	O(1)−Re(1)−N(8)	88.4(5)
N(4)−Re(1)−N(8)	169.0(5)	N(9)−Re(1)−N(8)	89.8(7)
N(5)−Re(1)−N(8)	90.0(6)	O(3)−Re(2)−O(1)	166.8(5)
Re(1)−O(1)−Re(2)	124.2(7)	N(6)−B(1)−N(7)	110.8(16)

tallographic) C_{2v} symmetry. Each of the two rhenium centers has a coordination geometry typical of rhenium(V) oxo complexes,[17,18] with short Re−O multiple bond distances and O≡Re−N(pz) angles larger than 90°. The triply bridged structure of **5** is unusual and leads to an acute Re−O−Re bond angle of 124.2(7)°. O═Re−O−Re═O dimers are most often linear at the bridging oxygen,[17,19] although there are some examples of di-μ-oxo compounds with fairly acute angles.[20] As expected, the Re−O distances to the bridging oxygen, 1.925(11) and 1.932(12) Å, are much longer than the multiple-bond distances of 1.654(12) and 1.687(14) Å.

The most interesting feature of **5** is that one pyrazolyl group of each Tp ligand has been replaced with fluoride, forming κ^2-(H)(F)B(pz)$_2^-$ ligands. This (or a similar reaction) is likely the source of the bridging pyrazolyl ligands. The fluorine and hydrogen atoms are disordered in the structure, with the fluorine atoms either syn or anti with respect to the nearby terminal oxo ligand. The structure was solved by placing a fluorine at half occupancy in each of the four possible positions; for clarity, the figure shows only one of the two possible fluorine positions at each boron (the syn-anti isomer is drawn). The average B−F bond distance in **5** is 1.32(3) Å, consistent with the average bond length of 1.365(5) Å in $F_2B(\mu\text{-}pz)_2BF_2$.[21]

The FAB mass spectrum of **5** shows a cluster at $m/z = 883$ corresponding to $(M - 1)^+$ for the dinuclear complex. The B−H stretch in the IR spectrum occurs at 2425 cm^{-1}, about 100 cm^{-1} lower than is typical for κ^3-Tp complexes such as TpRe(O)X(Y).[5,6,10−12] Lower ν(BH) values typically indicate lower Tp hapticity,[14] but the influence of the fluorine is hard to anticipate.

The ^{1}H NMR spectrum of **5** shows nine resonances: three triplets, four doublets, and two broadened triplets. These are assigned to the three different types of pyrazolyl groups: three resonances for *syn*-B(H)F(pz)$_2^-$ ligands, three slightly shifted peaks for B(H)F(pz)$_2^-$ ligands with the anti orientation, and three resonances for the bridging pyrazolyls. ^{1}H NMR spectra of pyrazolyls are almost invariably doublet/triplet/doublet patterns, but in one of these sets there are broad triplets instead of doublets (the coupling patterns were confirmed by a COSY spectrum). The triplets are apparently a result of long-range coupling to fluorine ($J_{FH} \cong 2$ Hz) although this coupling was not observed in the ^{19}F NMR spectrum. The ^{19}F NMR spectrum shows two upfield resonances (δ −84.3, −122.3 in CDCl$_3$, referenced to external CF$_3$COOH), assigned as syn and anti fluorines. The spectra can be interpreted assuming that **5** is a single isomer in which one fluorine is syn and the other is anti (as drawn in Figure 1). But the NMR and X-ray data are also consistent with **5** being a roughly statistical mixture of three isomers—syn-anti, syn-syn, and anti-anti—if it is assumed that the chemical shifts of half of the molecule are not influenced by the orientation of the distant B(H)F(pz)$_2^-$ ligand.

The upfield ^{19}F signals in **5** are quite distant from the downfield peaks observed for the Tp* rhenium fluorides (δ 35−50). The pattern of pyrazolyl triplets and doublets in the ^{1}H NMR spectrum of **5** is different from what is normally seen for TpRe(O)X(Y) compounds. Similar upfield fluorine resonances and unusual triplet/doublet patterns were often observed in the products of other fluorination attempts, suggesting the formation of similar products.

Conclusions

It is straightforward to introduce fluoride ligand(s) into rhenium−oxo complexes with hydrotris(3,5-dimethyl-1-pyrazolyl)borate (Tp*) ligands, and the resulting complexes are quite stable. In contrast, we have been unable to prepare rhenium−oxo−fluoride complexes with the less sterically demanding hydrotris(pyrazolyl)borate (Tp) ligand. Refluxing TpRe(O)I$_2$ and NaF in acetonitrile yields an unusual dinuclear derivative in which fluoride has substituted for pyrazolyl to give κ^2-(H)(F)B(pz)$_2^-$ ligands. Fluorination of the boron of the Tp ligand was unexpected, but should not be surprising given the strength of B−F bonds. Pyrazolyl displacement reactions may be inhibited for the Tp* compounds by the increased steric bulk of the 3,5-dimethylpyrazolyl groups. The environment about the boron is quite crowded when there are substituents in the 5-position.[7] Our results are consistent with the report by Kläui et al. that HB(3-Ph-pz)$_3^-$ is decomposed by fluoride but 5-methyl derivatives, HB(3-R, 5-Me-pz)$_3^-$, are more robust.[8]

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Supporting Information Available: X-ray crystallographic files for $\{[\kappa^2\text{-}H(F)Bpz_2]Re(O)\}_2(\mu\text{-}pz)_2(\mu\text{-}O)$ (**5**). This material is available free of charge via the Internet at http://pubs.acs.org.

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