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Hydrido-oxo complexes of rhenium(V): synthesis, structure, spectroscopic properties, and reactions with acids and bases

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Dedicated to Professor Martin A. Bennett in recognition his many contributions to inorganic chemistry

Abstract

The reaction of $[ReH_4(\eta^2\text{-}H_2)(Cyttp)]X$ ($X = SbF_6$ (**1**(SbF_6)), OTf (**1**OTf)); Cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$, OTf = O_3SCF_3) with neat acetone at reflux temperature affords the dihydrido-oxo complex $[ReH_2(O)(Cyttp)]X$ ($X = SbF_6$ (**2**(SbF_6)), OTf (**2**(OTf))). The isotopomers $[ReH_2(^{18}O)(Cyttp)]SbF_6$ (**2**-$^{18}O(SbF_6)$), $[ReD_2(O)(Cyttp)]SbF_6$ (**2**-$d_2(SbF_6)$), and $[ReD_2(^{18}O)(Cyttp)]SbF_6$ (**2**-d_2,$^{18}O(SbF_6)$) were prepared, respectively, by treatment of **2**(SbF_6) with $H_2^{18}O$, D_2 under photolysis, and D_2 followed by $H_2^{18}O$. The structure of **2** (as **2**(SbF_6)·3/4MeOH) was determined by single-crystal X-ray diffraction analysis and shown to contain a meridionally-coordinated Cyttp and an oxo ligand approximately *cis* to each of the three phosphorus donor atoms (Re–O = 1.732(7) Å). The hydrido ligands were not located; however, their presence in the positions essentially *cis* and *trans* to the oxide in a severely distorted coordination octahedron of the metal is suggested by the elucidated molecular structure. The ^1H NMR signals at δ −1.04 (tt) and −12.62 (dtd) and the IR $\nu(ReH)$ absorptions at 2030 and 1716 cm^{-1} provide strong evidence for this assignment. The IR $\nu(Re^{16}O)$ band of **2**(SbF_6) at 923 cm^{-1} surprisingly shifts to 897 cm^{-1} in **2**-$d_2(SbF_6)$. Similarly, the $\nu(Re^{18}O)$ of **2**-$^{18}O(SbF_6)$ at 887 cm^{-1} moves to 854 cm^{-1} in **2**-d_2,$^{18}O(SbF_6)$. Changes are also observed for one of the $\delta(ReH)$ absorptions of **2**(SbF_6) at 817 cm^{-1}, which appears at 810 cm^{-1} in **2**-$^{18}O(SbF_6)$. A simple analysis of the $\nu(ReO)$ and δ(ReH or ReD) vibrational frequencies suggests that a resonance interaction occurs between the $\nu(ReO)$ and one of the $\delta(ReH)$ modes. Complex **2**(OTf) reacts at low temperature with KOH–pyridine to form $[Re(O)_2(py)(Cyttp)]OTf$, and with $Li[BEt_3H]$ in excess to give $ReH_5(Cyttp)$. Treatment of **2**(OTf) with aqueous HCl in benzene yields a green solid which is formulated as $[ReH_2(OH)Cl(Cyttp)]OTf$ from spectroscopic evidence.

Keywords: Rhenium complexes; Hydrido complexes; Oxo complexes; Isotopomers; IR spectra; Crystal structure

1. Introduction

Reports of new transition-metal hydrido-oxo complexes have been gradually appearing in the literature since 1976. Most of them have dealt with binuclear and polynuclear metal hydrido-oxo compounds, which are known for both homometallic and heterometallic systems, including Ta_2 [1], W_2 [2], Re_3 [3], Ru_3 [4–6], Re_4 [7], WRe [8], WRe_2 [9], W_2Re_2 [8a], $MnFe_3$ [10], $MoOs_3$ [11], and WOs_3 [12]. In practically all of these compounds, one or more hydride and a single oxide serve as bridging ligands (μ_2 for H; μ_2, μ_3 or μ_4 for O), and at least one metal center bonds to both hydride and oxide.

Compared to the foregoing, the number of known mononuclear transition-metal hydrido-oxo complexes is still very modest. In 1986 Bercaw and coworkers reported the synthesis of $Cp_2^*Ta(O)H$ ($Cp^* = \eta^5\text{-}C_5Me_5$) by reaction of $Cp_2^*Ta(CH_2)H$ with H_2O [13], and later Moïse et al. prepared the related $Cp_2'Ta(O)H$

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($Cp' = \eta^5$-C_5H_4Bu-t) from Cp'_2TaCl_2H [14a] or $[Cp'_2TaH_2]^+$ [14b] and hydroxide. The first hydrido-oxo complexes of rhenium, $Re(RC{\equiv}CR)_2(O)H$ (R = Me or Et), were obtained in 1989 by Mayer and coworkers via thermolysis of $Re(RC{\equiv}CR)_2(O)(O_2CH)$ [15a]. The analogous $Re(PhC{\equiv}CPh)_2(O)H$ resulted on treatment of $Re(PhC{\equiv}CPh)_2(O)I$ with $(n\text{-}Bu)_3SnH$ [15b]. Subsequently, it was demonstrated that $Re(EtC{\equiv}CEt)_3(OH)$ rearranges with loss of one $EtC{\equiv}CEt$ ligand also to yield $Re(EtC{\equiv}CEt)_2(O)H$ [16]. Other reported Re complexes are those of rhenium(V) and include TpRe(O)(H)Cl, $Tp^*Re(O)H_2$, Tp*Re(O)(H)Cl, and Tp*Re(O)(H)OTf (Tp = hydridotris(pyrazolyl)borate, Tp* = hydridotris-(3,5-dimethyl-1-pyrazolyl)borate, $OTf = O_3SCF_3$) [17], as well as $[ReH_2(O)(Cyttp)]^+$ and $[ReH(O)(F)(Cyttp)]^+$ ($Cyttp = PhP(CH_2CH_2CH_2PCy_2)_2$) [18,19].

Interest attaches to metal complexes with hydrido and oxo ligands because of their potential to transfer both of these atoms to various unsaturated substrates. In addition, the coupling of H and O ligands to generate OH is a transformation of current research interest and activity [16,17,20].

In this paper we report the synthesis, structure, spectroscopic properties, and reactions with acids and bases of the rhenium(V) complex $[ReH_2(O)(Cyttp)]^+$ (**2**). Later, related publications will deal with mechanism of formation of **2** from $[ReH_4(\eta^2\text{-}H_2)(Cyttp)]^+$ (**1**) and ketones [21] and with the transfer of the hydrido and oxo ligands of **2** to several unsaturated substrates [22]. A related study on $[ReH(O)(F)(Cyttp)]^+$ (**3**) and preliminary results on **2** have appeared in print [18,19].

2. Experimental

2.1. General procedures and measurements

Reactions and manipulations of air-sensitive compounds were conducted under an atmosphere of dry argon by use of standard procedures [23]. Solvents were dried [24], distilled under argon, and degassed before use. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. IR and NMR (^1H, ^2H, ^{19}F, and ^{31}P) spectra were obtained as described previously [25,26].

2.2. Materials

Reagents were procured from commercial sources and used as received, except as noted below. The complex $[ReH_4(\eta^2\text{-}H_2)Cyttp)]SbF_6$ (**1**(SbF_6), $Cyttp = PhP(CH_2CH_2CH_2PCy_2)_2$) was prepared according to the literature [27]. $[ReH_4(\eta^2\text{-}H_2)(Cytttp)]OTf$ (**1**(OTf), $OTf = O_3SCF_3$) was synthesized analogously from $ReH_5(Cyttp)$ [28] by using HOTf in place of $HSbF_6$.

2.3. Preparation of $[ReH_2(O)(Cyttp)]SbF_6$ *(**2**(SbF_6))*

A colorless solution of **1**(SbF_6) (1.0 g, 0.98 mmol) in 150 ml of acetone was maintained at reflux temperature (ca. 60 °C) for 12–15 h during which time it turned brown. The solution was allowed to cool to room temperature (r.t.) and was concentrated to approximately 5 ml under reduced pressure. Addition of 30 ml of Et_2O resulted in the formation of a light tan precipitate. The solid was collected on a filter frit, washed with a small amount of Et_2O, and dried under vacuum overnight. The yield of **2**(SbF_6) was 0.90 g (90%). IR (Nujol): ν(ReH) 2030 (w), 1716 (m) cm^{-1}, ν(ReO) 923 (m) cm^{-1}, δ(ReH) 845 (m), 817 (m) cm^{-1}, $\nu(SbF_6)$ 650 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, Cyttp signals not given): δ −1.04 (tt, $^2J_{HH} = {}^2J_{P_CH} = 5.0$ Hz (P_C = central P), $^2J_{P_WH} = 25.0$ Hz (P_W = wing P), 1 H, ReH), −12.62 (dtd, $^2J_{HH} = 5.0$ Hz, $^2J_{P_CH} = 57.5$ Hz, $^2J_{P_WH} = 35.0$ Hz, 1 H, ReH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 22.56 (d, $^2J_{P_CP_W} = 18.3$ Hz, P_W), 6.77 (t, $^2J_{P_CP_W} = 18.3$ Hz, P_C). *Anal.* Found: C, 42.19; H, 5.91. Calc. for $C_{36}H_{63}F_6OP_3ReSb$: C, 42.11; H, 6.18%.

2.4. Preparation of $[ReH_2(O)(Cyttp)]OTf$ *(**2**(OTf))*

The reaction between **1**(OTf) and acetone was carried out under the same conditions as that between **1**(SbF_6) and acetone, with essentially identical results. Spectroscopic properties of **2**(OTf) matched those given for **2**(SbF_6), except for the data characteristic of the anions.

2.5. Preparation of isotopomers of $[ReH_2(O)(Cyttp)]SbF_6$ *(**2**(SbF_6)*

2.5.1. Preparation of $[ReD_2(O)(Cyttp)]SbF_6$ *(**2**-d_2(SbF_6))*

A deoxygenated benzene solution (30 ml) of $[ReH_2(O)(Cyttp)]SbF_6$ (**2**(SbF_6)) (0.30 g, 0.29 mmol) in a Pyrex Schlenk flask was irradiated with a 450-W Hanovia medium-pressure Hg lamp at a distance of approximately 20 cm under a slow, continuous purge of D_2. After 30 min solvent was removed, and Et_2O (15 ml) was added to the light tan residue. The solid was filtered off, washed with Et_2O, and dried under vacuum overnight. Yield, 0.25 g (83%). IR (Nujol): ν(ReO) 897 (s) cm^{-1}, δ(ReD) 582 (w) cm^{-1}. ^2H NMR (acetone-d_6): δ −1.0 (t, ReD), −12.6 (dt, $^2J_{P_CD} = 8.5$ Hz, $^2J_{P_WD} = 5.6$ Hz, ReD). ^{31}P NMR (CD_2Cl_2): δ 23.0 (br s, P_W), 7.3 (br s, P_C).

2.5.2. Preparation of $[ReH_2(^{18}O)(Cyttp)]SbF_6$ *(**2**-^{18}O(SbF_6))*

A solution of $[ReH_2(O)(Cyttp)]SbF_6$ (**2**(SbF_6)) (0.20 g, 0.19 mmol) and excess $H_2^{18}O$ (0.25 ml, 13 mmol) in 30 ml of benzene was stirred for 10 h at r.t. The work-up was identical with that in Section 2.5.1. Yield, 0.18 g

(90%). IR (Nujol): ν(ReH) 2028 (w), 1737 (w), 1687 (w) cm^{-1}, $\nu(Re^{18}O)$ 887 (m) cm^{-1}, δ(ReH) 845 (m), 810 (m) cm^{-1}.

2.5.3. Preparation of $[ReD_2(^{18}O)(Cyttp)]SbF_6$ (**2**-d_2,$^{18}O(SbF_6)$)

The preparation was identical with that of $[ReH_2(^{18}O)(Cyttp)]SbF_6$ (**2**-$^{18}O(SbF_6)$) (Section 2.5.2), except that $[ReD_2(O)(Cyttp)]SbF_6$ (**2**-$d_2(SbF_6)$) was used in place of $[ReH_2(O)(Cyttp)]SbF_6$ (**2**(SbF_6)). IR (Nujol): $\nu(Re^{18}O)$ 854 (s) cm^{-1}, δ(ReD) 582 (w) cm^{-1}. ^{31}P NMR (CD_2Cl_2): δ 23.0 (br s, P_W), 7.3 (br s, P_C).

2.6. Reaction of $[ReH_2(O)(Cyttp)]OTf$ (**2**(OTf)) with KOH and pyridine

A solution of **2**(OTf) (0.062 g, 0.066 mmol) and pyridine (0.100 ml, 1.24 mmol) in 10 ml of CH_2Cl_2 was cooled to −78 °C and treated with KOH (0.010 g, 0.17 mmol). The contents were allowed to warm to r.t. with stirring over a 5-h period and then were concentrated to 2 ml under reduced pressure. Addition of Et_2O resulted in the formation of a yellow precipitate which was washed with 4 ml of H_2O and 5 ml of Et_2O and dried overnight. The yield of $[Re(O)_2(py)(Cyttp)]OTf$ was 0.067 g (85%). Selected spectroscopic data. IR (Nujol): ν(ReO) 817 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −21.9 (t, $^2J_{P_CP_W} = 17.3$ Hz, P_C), −26.1 (d, $^2J_{P_CP_W} = 17.3$ Hz, P_W). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −77.3 (referenced to internal $CFCl_3$, s, OTf^-). *Anal.* Found: C, 49.40; H, 6.28; N, 1.23. Calc. for $C_{42}H_{66}F_3NO_5P_3ReS$: C, 48.83; H, 6.44; N, 1.36%. Crystals suitable for X-ray diffraction analysis were grown from a CH_2Cl_2–hexane solution.

2.7. Reaction of $[ReH_2(O)(Cyttp)]OTf$ (**2**(OTf)) with aqueous HCl

A solution of **2**(OTf) (0.050 g, 0.053 mmol) in 5 ml of benzene was treated with 0.50 ml of 1.20 M aqueous HCl, and the contents were vigorously stirred for 30 min resulting in the formation of a yellow precipitate. The solid was filtered off, washed with benzene, and dried overnight. It turned from yellow to fluorescent green upon drying for 4 h under reduced pressure. The yield of $[ReH_2(OH)Cl(Cyttp)]OTf$ was 0.035 g (67%). Selected spectroscopic data. IR (Nujol): ν(OH) ~3280 (br) cm^{-1}, ν(ReH) 1617 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ −3.3 (br, 1 H, ReH), −7.9 (br m, 1 H, ReH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 29.3 (br, P_W), −3.4 (t, $^2J_{P_CP_W} = 15.4$ Hz, P_C). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −77.3 (referenced to internal $CFCl_3$, s, OTf^-).

2.8. Crystallographic analysis of $[ReH_2(O)(Cyttp)]SbF_6 \cdot 3/4MeOH$ (**2**$(SbF_6) \cdot 3/4MeOH$)

The crystal used for data collection was orange–red in color, clear, and multifaceted. Examination of the diffraction pattern at 223 K on a Rigaku AFC5S diffractometer revealed a monoclinic crystal system with systematic absences $h0l$, $h+l = 2n+1$, and $0k0$, $k = 2n+1$, which uniquely determine the space group as $P2_1/n$. The cell constants were obtained by a symmetry-restricted least-squares fit of the diffractometer setting angles for 25 reflections in the 2θ range 21–30° with Mo Kα radiation.

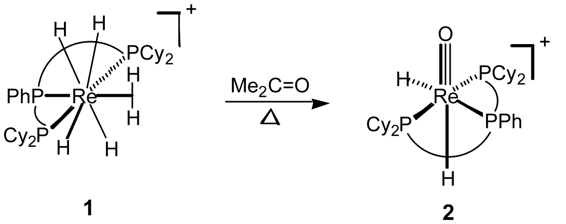
Data were collected by the ω scan method at 223 K. Six standard reflections were measured after every 150 reflections during data collection and indicated that a very small amount of crystal decomposition had occurred. On the average the intensities of the standards decreased by 3.4%. The data were corrected for Lorentz and polarization effects and for decay. A correction for absorption was made by the empirical ψ-scan method [29]. All calculations were done by the TEXSAN package of crystallographic programs [30].

The position of the Re atom was found from a Patterson map and used as a phasing model in the DIRDIF direct methods procedure [31]. Much of the Re complex and the SbF_6 anion were then located on the resulting electron density map. The remaining non-hydrogen atoms were subsequently located by standard Fourier methods. Full-matrix least-squares refinements based on F were performed in TEXSAN [30]. It eventually became apparent that there are three additional peaks near an inversion center and that they are not associated with the Re complex or the SbF_6 anion. These peaks are assumed to be part of a disordered solvent molecule. Since the crystals were grown from CH_2Cl_2–MeOH, and since the heights of these peaks are within a small range (2.3–3.3 e $Å^{-3}$), it is assumed that the disordered solvent molecule is methanol. All three peaks are labeled as carbon atoms (C(37), C(38), and C(39)) and given occupancy factors of 0.5. The interpretation of this model is as follows: 50% of the time a methanol molecule is located on an inversion center (C(39) and C(39)′ [related by the inversion center] for a total of two MeOH molecules in the unit cell), and 50% of the time a methanol molecule is located in a general position (C(38)) for a total of four MeOH's in the unit cell). The molecular formula is then an average of these two models and is given as $[ReH_2(O)(Cyttp)]SbF_6 \cdot 3/4MeOH$. The atoms involved in the disorder model are kept at the isotropic level of refinement. After anisotropic refinement the hydrogen atoms were included in the model as fixed contributions in their calculated positions with the assumptions C–H = 0.98 Å and $B(H) = 1.2 \cdot B(C_{eq})$. The two hydride ligands bonded to the Re atom are omitted from the model as they could not be located on a difference electron density map. The final refinement cycle yielded agreement indices of $R = 0.046$ and $R_w = 0.049$ for the 4979 reflections with $F_o^2 > 3\sigma(F_o^2)$ and the 445 variables. The maximum and minimum peaks of the final difference electron density map are 1.26 and -1.06 e Å^{-3}, with the maximum peak 0.92 Å from the Re atom. The next largest peaks in the map, from 0.91 to 1.20 e Å^{-3}, are in the vicinity of the disordered solvent molecule. Scattering factors for the non-hydrogen atoms, including terms for anomalous dispersion [32], and the scattering factors for the hydrogen atom [33], are from the literature. A summary of the crystal data and the details of the intensity data collection and refinement are provided in Table 1.

3. Results and discussion

3.1. Synthesis of [ReH$_2$(O)(Cyttp)]$^+$ (2) and its isotopomers

In the course of studies of reactions of rhenium(V) polyhydrido–phosphine complexes with ketones, we observed that prolonged treatment (12–15 h) of [ReH$_4$(η^2-H$_2$)(Cyttp)]SbF$_6$ (**1**(SbF$_6$)) with dry acetone at reflux temperature affords the dihydrido-oxo complex **2**(SbF$_6$) in 90% yield (Eq. (1)). Longer reaction times result in the formation of [ReH(O)(F)(Cyttp)]SbF$_6$ (**3**(SbF$_6$)) as well,



(1)

whereas use of acetone/benzene or acetone/toluene leads to the isolation of **3**(SbF$_6$) only [18,19]. To circumvent this substitution of fluoride for hydride, the counterion SbF$_6^-$ was replaced with OTf$^-$ later in our studies. The synthesis of **2**(OTf) was effected in two steps, viz. reaction of ReH$_5$(Cyttp) with HOTf and treatment of the product **1**(OTf) with acetone as described above for **1**(SbF$_6$).

Table 1
Summary of crystal data, data collection, and structure refinement parameters for [ReH$_2$(O)(Cyttp)]SbF$_6$·3/4MeOH (**2**(SbF$_6$)·3/4MeOH)

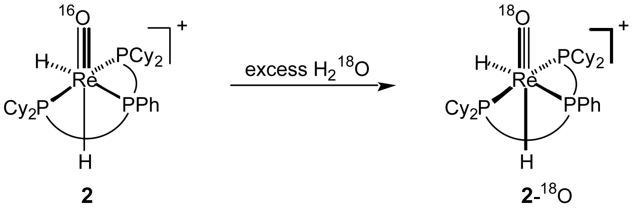
Empirical formula	$C_{36}H_{63}F_6OP_3ReSb \cdot 3/4CH_4O$
Formula weight	1050.80
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	13.517(2)
b (Å)	17.742(2)
c (Å)	18.162(2)
β (°)	102.95(1)
V (Å^3)	4244.6(9)
Z	4
D_{calc} (g cm^{-3})	1.64
Temperature (K)	223
Crystal size (mm^3)	0.12 × 0.19 × 0.23
Radiation	Mo Kα, graphite ($\lambda = 0.71069$ Å)
μ (cm^{-1})	38.2
2θ range (°)	4–55
Transmission factors	0.849–1.000
Data collected	$+h$, $+k$, $\pm l$
Unique data	10063
Unique data with $F_o^2 > 3\sigma(F_o^2)$	4979
Final no. of variables	445
$R(F)$ [a]	0.046
$R_w(F)$ [b]	0.049
Error in observation of unit weight (e)	1.23

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

Complex **2** was also obtained by using neat cyclohexanone or one of several other ketones in place of acetone. The apparent abstraction of oxygen from ketones by the metal center is precedented by similar behavior of WCl$_2$(PMePh$_2$)$_4$ [34]. These and related reactions of **1** will be considered in some detail in another paper dealing with mechanism of formation of **2** by use of organic carbonyl compounds [21].

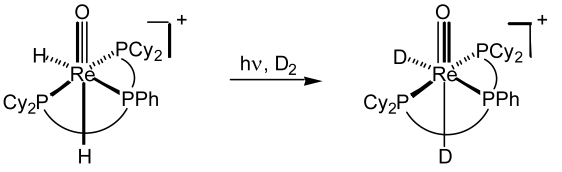
The product **2**(SbF$_6$) was isolated as a light tan solid that is stable to air in solution at ambient temperature for several days. It is soluble in CH$_2$Cl$_2$, acetone, THF, and benzene but essentially insoluble in Et$_2$O and MeOH. The triflate salt **2**(OTf) has similar solubility properties except that it dissolves in MeOH.

To aid in the studies of spectroscopic properties and reaction chemistry of **2**, the isotopomers [ReH$_2$(^{18}O)(Cyttp)]SbF$_6$ (**2**-^{18}O(SbF$_6$)), [ReD$_2$(O)(Cyttp)]SbF$_6$ (**2**-d_2(SbF$_6$)) and [ReD$_2$(^{18}O)(Cyttp)]SbF$_6$ (**2**-d_2,^{18}O(SbF$_6$)) were prepared from the unlabeled complex. The ^{18}O-containing isotopomer resulted on treatment of **2**(SbF$_6$) with a large excess of H$_2^{18}$O (Eq. (2)).



(2)

This reaction probably proceeds by nucleophilic attack of H$_2^{18}$O at the Re center and formation of a [ReH$_2$(^{16}OH)(^{18}OH)(Cyttp)]$^+$ intermediate. A similar mechanism has been proposed for the oxygen exchange in Cp$_2^*$WO and Cp$_2^*$Ta(O)H using H$_2^{18}$O [20,35]. Interestingly, use of D_2O in conjunction with **2**(SbF_6) does not lead to the formation of **2**-d_2(SbF_6). Again, this observation is similar to that of the absence of isotopic exchange for Cp^*_2WO and $Cp^*_2Ta(O)H$ on treatment with D_2O [20,35]. The deuterium-labeled isotopomer **2**-d_2(SbF_6) was, however, obtained by photolysis of a benzene solution of **2**(SbF_6) under an atmosphere of D_2 (Eq. (3)).



2 **2**-d_2 (3)

A monodeuterium product, **2**-d_1(SbF_6), could not be detected spectroscopically in that reaction. The double-labeled **2**-d_2,^{18}O(SbF_6) resulted from **2**-d_2(SbF_6) and $H_2^{18}O$.

3.2. Structural characterization of [ReH$_2$(O)(Cyttp)]-SbF$_6$ (2(SbF$_6$))

The structure of **2**(SbF_6) (as **2**(SbF_6)3/4MeOH), determined by X-ray diffraction techniques, consists of the complex cations **2** and the anions SbF_6^-. An ORTEP drawing of **2** is presented in Fig. 1, and selected bond distances and angles are given in Table 2.

The observed coordination environment around the Re center is comprised of the meridionally attached triphosphine Cyttp and one oxo ligand. The two hydrido ligands, implicated by the spectroscopic data (cf. Section 3.3), were not located. The meridional arrangement of the triphosphine around the metal is severely distorted, with the angles P(1)–Re–P(2), P(2)–Re–P(3), and P(1)–Re–P(3) being 92.0(1), 92.1(1), and 137.1(1)°, respectively. These bond angles may be contrasted with the much more octahedral ones found in another Cyttp complex, *cis*, *mer*-Ru(OTf)$_2$-(CO)(Cyttp), where P(1)–Ru–P(2), P(2)–Ru–P(3), and P(1)–Ru–P(3) are, respectively, 89.95(4), 92.09(4) and 177.87(4)° [36]. The distortion in the meridional arrangement of the Cyttp in **2** is most likely caused by the small size of the hydrido ligands, which appear to be positioned approximately *cis* and *trans* to the oxide. As expected, the phosphorus donors are displaced in these directions. The rhenium atom is located 0.795 Å out of the P_3 plane toward the oxo ligand. Such a displacement of the metal atom has been noted for octahedral rhenium Tp-oxo complexes [37]. This distortion in **2** is also reflected in the magnitude of the P–Re–O bond angles, 107.3(2)–111.1(3)°.

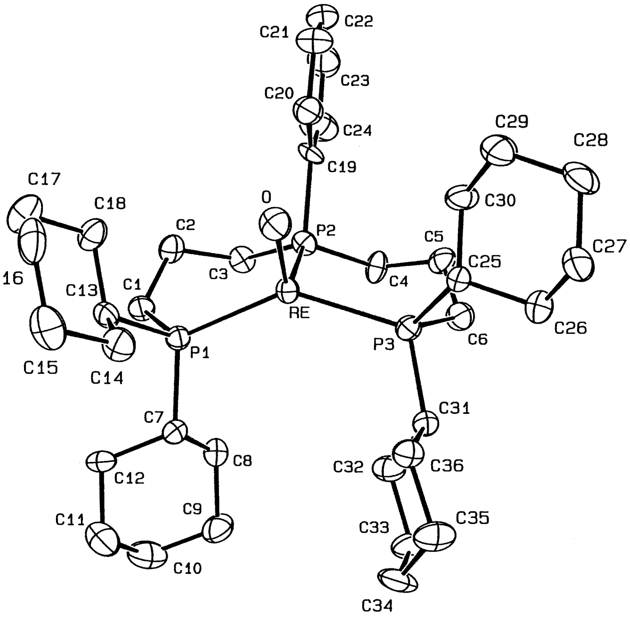


Fig. 1. Molecular structure of [ReH$_2$(O)(Cyttp)]$^+$ (**2**). Non-hydrogen atoms are drawn with 50% probability displacement ellipsoids. The two hydrogen atoms bonded to rhenium were not located. The other hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and bond angles (°) for [ReH$_2$(O)(Cyttp)]SbF$_6$·3/4MeOH (**2**(SbF_6)·3/4MeOH)

Bond lengths			
Re–P(1)	2.412 (3)	Re–P(3)	2.392(3)
Re–P(2)	2.380(3)	Re–O	1.732(7)
Bond angles			
P(1)–Re–P(2)	92.0(1)	P(1)–Re–O	110.8(2)
P(1)–Re–P(3)	137.1(1)	P(2)–Re–O	111.1(3)
P(2)–Re–P(3)	92.1(1)	P(3)–Re–O	107.3(2)

The bond distances Re–P(1) = 2.412(3), Re–P(2) = 2.380(3), and Re–P(3) = 2.392(3) Å (2.395 Å mean) are somewhat longer than the Re–P distances in ReH$_5$(Cyttp) (2.380 Å mean) but shorter than those in **1**(SbF_6) (2.435 Å mean) [27]. The Re–O bond distance of 1.732(7) Å is quite long for a monooxo complex of rhenium(V), with most of the reported bond lengths being less than 1.7 Å [37,38]. However, molecular orbital considerations suggest a Re≡O triple bond rather than a Re=O double bond for such a d^2 octahedral monooxo complex [38].

3.3. Spectroscopic properties of [ReH$_2$(O)(Cyttp)]-SbF$_6$ (2(SbF$_6$)) and its isotopomers

Selected ^1H, ^2H, and $^{31}P\{^1H\}$ NMR and IR data for **2**(SbF_6) and its isotopomers **2**-d_2(SbF_6), **2**-^{18}O(SbF_6), and **2**-d_2,^{18}O(SbF_6) are provided in Sections 2.3 and 2.5. The ^1H NMR spectrum of **2**(SbF_6) clearly reveals the presence of two inequivalent hydrido ligands with equal intensity resonances at δ −1.04 and −12.62. The signal at δ −1.04, assigned to the hydride approximately *trans* to the oxo ligand, occurs as a triplet of triplets by virtue of coupling with two equivalent wing-phosphorus (P_W)

nuclei ($^2J_{P_WH} = 25.0$ Hz) and because of equal coupling constants $^2J_{HH} = {}^2J_{P_CH} = 5.0$ Hz. The higher-field signal of the hydride '*cis*' to the oxide appears as a doublet of triplets of doublets, with splitting by the other hydride, two equivalent P_W nuclei ($^2J_{P_WH} = 35.0$ Hz), and the central-phosphorus (P_C) nucleus ($^2J_{P_CH} = 57.5$ Hz). The relatively small value of this $^2J_{P_CH}$ [39] suggests that the structure of **2** is distorted from a regular octahedron, as demonstrated by the X-ray diffraction analysis. The $^{31}P\{^1H\}$ NMR spectrum consists of a doublet at δ 22.56 and a triplet at δ 6.77 with $^2J_{P_CP_W} = 18.3$ Hz.

The isotopomer **2**-d_2(SbF_6) shows two high-field ^{2}H signals: a triplet ($^2J_{P_WD}$; $^2J_{DD}$ and $^2J_{P_CD}$ not discerned) at δ −1.0 and a doublet of triplets ($^2J_{P_CD}$ and $^2J_{P_WD}$, respectively) at δ −12.6 with expected coupling constants (cf. Section 2.5.1). Its $^{31}P\{^1H\}$ NMR spectrum is similar to that of **2**(SbF_6), but the signals are broad owing to unresolved phosphorus–deuterium coupling.

The presence of an oxo ligand in **2**(SbF_6), demonstrated by X-ray diffraction, is also indicated by the IR spectrum which shows a medium-intensity band at 923 cm^{-1}, assigned to ν(ReO). In the labeled **2**-^{18}O(SbF_6), this absorption occurs at 887 cm^{-1}, whereas the frequency predicted from the isotope mass effect is 877 cm^{-1}. Additionally, on going from **2** to **2**-^{18}O, the band at 817 cm^{-1}, assigned to one of the δ(ReH) modes, shifts to 810 cm^{-1}, and that at 1716 cm^{-1}, attributed to ν(ReH), splits into two weaker-intensity components at 1737 and 1687 cm^{-1}. These spectroscopic changes suggest occurrence of a resonance interaction between the ν(ReO) fundamental and one δ(ReH) mode.

Additional evidence for such an interaction is provided by the IR spectrum of the dideuterio complex **2**-d_2(SbF_6). Significantly, the ν(ReO) absorption of this isotopomer occurs at 897 cm^{-1}. Furthermore, the δ(ReH) bands of **2**(SbF_6) at 845 and 817 cm^{-1} disappear, and a new band replaces the former at 582 cm^{-1}, as calculated for δ(ReD). The other δ(ReD) absorption, predicted to occur at approximately 600 cm^{-1}, is probably hidden under the strong peak of ν((SbF_6) at 650 cm^{-1}. The two ν(ReH) bands of **2**(SbF_6) at 2030 and 1716 cm^{-1} are, as expected, absent in this spectrum; however, the corresponding ν(ReD) absorptions could not be identified because of numerous peaks in the 1450–1200 cm^{-1} region.

Finally, the isotopomer **2**-d_2,^{18}O(SbF_6) exhibits its ν(Re^{18}O) absorption at 854 cm^{-1}. This is the expected frequency for replacement of ^{16}O in **2**-d_2 with ^{18}O in **2**-d_2,^{18}O. Furthermore, the δ(ReD) band at 582 cm^{-1} for **2**-d_2(SbF_6) remains unchanged in this spectrum. Thus, there appears to be no resonance interaction between the vibrational modes involving oxygen (^{16}O or ^{18}O) and those involving deuterium.

The foregoing interactions of the vibrational modes are represented schematically in Fig. 2. Assuming that the shift of 26 cm^{-1} in ν(Re^{16}O) upon deuteriation of **2** represents the interaction energy of ν(Re^{16}O) and δ(ReH), the energy of the 'unperturbed' state of δ(ReH) can be calculated for the observed frequency. These calculated values are 871 and 843 cm^{-1} for the two bending modes observed for **2**(SbF_6) at 845 and 817 cm^{-1}, respectively. Although such an 'unperturbed' frequency of 871 cm^{-1} is closer to 897 cm^{-1} (i.e., 'unperturbed' ν(Re^{16}O), observed for **2**-d_2(SbF_6)), resonance interaction apparently occurs with the other, 843 cm^{-1} δ(ReH) mode, presumably due to symmetry. Similarly, the ν(Re^{18}O) band observed at 887 cm^{-1} for **2**-^{18}O(SbF_6) is shifted by 33 cm^{-1} to the expected ('unperturbed') value of 854 cm^{-1} in the double-labeled **2**-d_2,^{18}O. Thus, the energy of the 'unperturbed' state of δ(ReH) in **2**-^{18}O is calculated, using the interaction energy of 33 cm^{-1}, to be 843 cm^{-1}. This turns out to be identical with the δ(ReH) calculated for **2**. Finally, the splitting into two components of the lower energy ν(ReH) band of **2**-^{18}O(SbF_6) (vide supra) may be rationalized by Fermi resonance involving the first overtone of the 'unperturbed' ν(Re^{18}O) at 854 cm^{-1}.

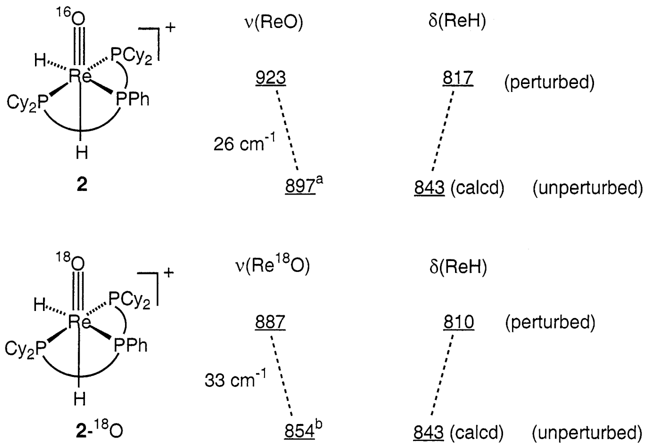


Fig. 2. Schematic representation of the interaction between ν(ReO) and δ(ReH). (a) From the spectrum of **2**-d_2. (b) From the spectrum of **2**-d_2,^{18}O.

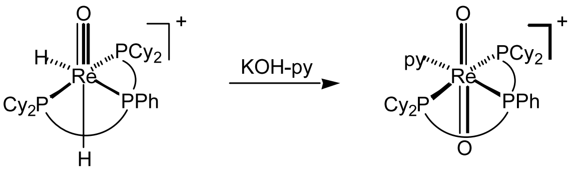
The above spectroscopic behavior has a precedent in the IR ν(CO) spectra of some metal hydrido–carbonyl complexes and their deuterio–carbonyl structural analogs. Vaska observed that on replacement of H with D in $IrH_2(CO)Cl(PPh_3)_2$ and *mer*-$OsH_2(CO)(PPh_3)_3$, inter alia, there was a shift in ν(CO) for the carbonyl *trans* to hydride, but not for that *cis* to hydride [40]. This shift was attributed to a resonance interaction between the vibrational states of ν(CO) and ν(MH) (but not ν(MD) because of a large energy difference) of the *trans* hydride. It is possible that in the present study resonance interaction, with the oxo ligand, also involves *trans* hydride.

The 'unperturbed' ν(ReO) of 897 cm^{-1} for **2**(SbF_6) is substantially lower than the ν(ReO) of 1006–1015 cm^{-1} for $[ReX(O)(F)(Cyttp)]^+$ (X = H (**3**), F, Cl, Br) [19]. It is also lower than ν(ReO) for rhenium(V) monooxo Tp* and Tp complexes, which include Tp*Re(O)(Cl)X (X = H, Cl, Br, I, OH, OTf, OMe, Et, Ph), TpRe(O)(X)Y (X = Cl, Y = OTf, Me; X = Br, Y = OTf, OEt; X = OTf, Y = OPh, Me), and a number of their close relatives. These complexes display ν(ReO) in the range 938–1002 cm^{-1} [17,37]. Four of them were shown by X-ray diffraction to possess Re–O bond lengths of 1.665(5), 1.667(9), 1.675(4), and 1.705(5) Å [17,37], all significantly shorter than that of 1.732(7) Å for **2**(SbF_6). Thus, both the IR and X-ray structural data indicate a lower Re–O multiple bond order in **2** than in the foregoing Tp* and Tp complexes. A possible reason for the observed difference may be related to the presence of five good electron-releasing phosphorus and hydrogen donors in **2**; this would enhance electron density at the rhenium center and therefore promote relative importance of Re=O over Re≡O through dispersal of negative charge onto oxygen.

3.4. *Reactions of [ReH$_2$(O)(Cyttp)]SbF$_6$ (**2**(SbF$_6$)) with acids and bases*

Reactions of **2** with acids and bases were examined in an attempt to learn about the nature of the hydrido and oxo ligands in this complex. For these studies, **2**(OTf) rather than **2**(SbF_6) was used as the substrate complex in order to circumvent possible participation of fluoride in substitution at rhenium.

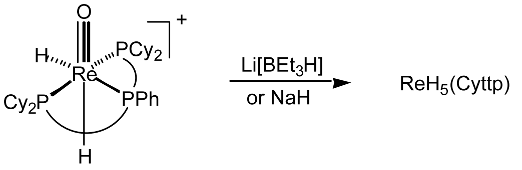
Attempted deprotonation of **2**(OTf) with the strong base NEt_3 or Proton Sponge ($C_{10}H_6(NMe_2)_2$) in the presence or absence of a potential ligand (MeCN, pyridine) resulted in no detectable reaction. In contrast, the small hydroxide ion reacted rapidly with **2**(OTf) at ambient temperature to afford a multitude of products, observable by $^{31}P\{^1H\}$ NMR spectroscopy. By running this reaction at −78 °C with warming to room temperature in the presence of pyridine, it was possible to isolate [Re(O)$_2$(py)(Cyttp)]OTf (**4**(OTf)) in very good yield (Eq. (4)).



2 **4** (4)

The product was characterized by elemental analysis, FAB mass spectrometry, and IR and NMR ($^{31}P\{^1H\}$, $^{19}F\{^1H\}$) spectroscopy. A complete X-ray diffraction study of **4**(OTf) was precluded by decomposition of the crystal during data collection. Nevertheless, limited acquired data support the *trans* arrangement of two oxo ligands and the *cis* orientation of pyridine to each oxygen. In the IR spectrum of **4**(OTf), ν(ReO) absorption is observed at 817 cm^{-1}, in agreement with Re=O bonding [37c]. The $^{31}P\{^1H\}$ NMR spectrum is consistent with a meridional attachment of Cyttp to Re, and the ^1H NMR spectrum shows one coordinated pyridine and the absence of hydrido ligands. The FAB mass spectrum exhibits a peak at *m/z* 806 which corresponds to the parent ion less one pyridine.

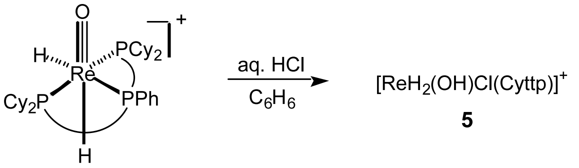
Treatment of **2**(OTf) with an excess of either Li[BEt$_3$H] or NaH affords known ReH$_5$(Cyttp) [28] (Eq. (5)). When only 1 equiv. of Li[BEt$_3$H] was employed, a multitude of products resulted.



2 (5)

They underwent conversion to ReH$_5$(Cyttp) upon addition of more Li[BEt$_3$H]. A reaction similar to the foregoing is the formation of Tp*ReH$_6$ from Tp*Re(O)(OR)$_2$ (R = Me or Et) and BH$_3$·THF [17b].

Complex **2**(OTf) underwent reaction with aqueous HCl in benzene to afford, after drying, a bright green solid which is formulated as [ReH$_2$(OH)Cl(Cyttp)]OTf (**5**(OTf)) (Eq. (6)) on the basis of spectroscopic evidence.



2 (6)

Accordingly, the $^{31}P\{^1H\}$ NMR spectrum shows signals for the two equivalent wing-phosphorus atoms and the central-phosphorus atom of Cyttp, and the ^1H NMR spectrum reveals two hydrido ligands at δ −3.3 and −7.9. The OH proton was not observed in the NMR spectrum; however, the IR spectrum shows a broad ν(OH) band centered around 3280 cm^{-1}. There are also a ν(ReH) absorption at 1617 cm^{-1} and a strong band at 281 cm^{-1}, which may be due to ν(ReCl) [41]. The complex readily changes color to pale yellow upon exposure to air and decomposes in solution. Satisfactory chemical analysis or FAB mass spectrum was not obtained.

Based on the foregoing spectroscopic data, protonation of **2**(OTf) appears to have occurred at the oxo ligand. Addition of proton to coordinated oxide is known for Re(EtC≡CEt)$_2$(O)H [15a].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC No. SIMCEW for **2**$(SbF_6)\cdot 3/4MeOH$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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