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Inorganica Chimica Acta 240 (1995) 435–439

Inorganica Chimica Acta

Fluoro–hydrido–oxo and other fluoro–oxo complexes of rhenium(V) containing a triphosphine ligand ☆

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Received 16 February 1995; revised 15 May 1995

Abstract

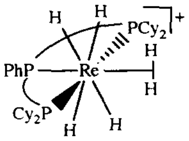
The fluoro–hydrido–oxo complex $[Re(F)(H)(O)Cyttp]^+$ (**3**, Cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$) was prepared in high yield from $[Re(H_2)H_4Cyttp]SbF_6$ (**1**(SbF_6)), $NaSbF_6$ and acetone in toluene at reflux. Reaction chemistry of **3** has been studied and, where appropriate, compared with that of the related dihydrido–oxo complex $[ReH_2(O)Cyttp]^+$ (**2**). Unlike **2**, which readily reacts with both CO and SO_2, **3** was found to be inert to these reagents under comparable conditions. However, **3**(SbF_6) reacts with $NaSbF_6$ at elevated temperature to afford the difluoro–oxo complex $[ReF_2(O)Cyttp]^+$ (**4**). **4** undergoes fluoride substitution by Cl^- or Br^- to yield $[Re(X)(F)(O)Cyttp]^+$ (X = Cl (**5**), Br (**6**)). **5** can also be obtained by treatment of **6**(BPh_4) with LiCl. All of these complexes contain *mer*-Cyttp, and **3**–**6** contain *trans* fluoride and oxide ligands as inferred from spectroscopic data.

Keywords: Ligand substitution; Rhenium complexes; Hydrido complexes; Fluoro complexes; Oxo complexes

1. Introduction

Transition-metal hydrido–oxo complexes are rare chemical species [1]. Yet considerable interest attaches to such compounds because of the possibility of effecting transfer of both hydrogen and oxygen to an unsaturated substrate.

It was reported from this laboratory [2] that reaction of $[Re(H_2)H_4Cyttp]SbF_6$ (**1**(SbF_6), Cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$) with acetone at reflux for 12–15 h affords the dihydrido–oxo complex $[ReH_2(O)Cyttp]SbF_6$ (**2**(SbF_6)). Longer reaction times result in the formation of $[Re(F)(H)(O)Cyttp]SbF_6$ (**3**(SbF_6)) as well, whereas use of acetone/benzene at reflux leads to the formation of **3** only. Since metal fluoro–hydrido complexes are rare [3], and since metal fluoro–hydrido–oxo complexes are, to our knowledge, unknown, we have endeavored to study the chemistry of **3** to compare it with that of the structurally related **2**.



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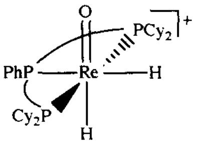

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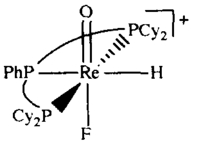

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Reported in this paper is a high-yield synthesis of complex **3** as well as its reaction chemistry, including ligand substitution.

2. Experimental

2.1. General procedures and measurements

All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of Ar using standard procedures [4]. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. IR, NMR (^1H, ^{31}P and ^{19}F) and FAB-MS were obtained as previously described [5].

All solvents were purified by use of the appropriate drying agents and distillation under an Ar atmosphere prior to use

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☆ This paper is dedicated to Professor Fred Basolo on the occasion of his 75th birthday.

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0020-1693/95/$09.50
SSDI 0020-1693(95)04565-Q

[6]. Distilled H_2O was purged with Ar for 45 min prior to use.

Reagents were obtained from commercial sources and used as received. A literature procedure was used to synthesize $[Re(H_2)H_4Cyttp]SbF_6$ [7].

2.2. *Synthesis of $[Re(F)(H)(O)Cyttp]SbF_6$ (3(SbF_6))*

A solution of $[Re(H_2)H_4Cyttp]SbF_6$ (1.77 g, 1.74 mmol) and excess $NaSbF_6$ (1.05 g, 4.06 mmol) in a mixture of acetone (20 ml, 15.8 g, 272 mmol) and toluene (40 ml) was maintained at reflux for 17 h. The volume of the solution was reduced in vacuo to ~5 ml, and 30 ml of Et_2O were added to give a white precipitate. The solid was collected on a filter frit, washed with 20 ml of H_2O and 4 ml of Et_2O, and dried under vacuum overnight. Yield 1.66 g (91%). IR (Nujol): ν(ReH) 1945 (m), ν(ReO) 1015 (m) cm^{-1}. MS (FAB), ^{187}Re isotope: m/z 809 (M^+), 726 (M^+ −Cy) *Anal.* Calc. for $C_{36}H_{62}F_7OP_3ReSb$: C, 41.39; H, 5.98; F, 12.73. Found: C, 41.38; H, 5.87; F, 12.59%.

2.3. *Synthesis of $[ReF_2(O)Cyttp]BPh_4$ (4(BPh_4))*

A solution of $[Re(F)(H)(O)Cyttp]SbF_6$ (0.498 g, 0.477 mmol) and $NaSbF_6$ (0.125 g, 0.483 mmol) in a mixture of acetone (2.5 ml) and toluene (2 ml) was transferred to a heavy-walled glass flask fitted with a Kontes valve teflon stopcock. The glass flask was placed in a sand bath at 149 °C and heated for 62 h. The volatiles were removed, and 15 ml of H_2O were added at room temperature to give a purple solid. The resultant solid was thoroughly washed with more H_2O (30 ml) to remove any remaining impurities. The solid was then dissolved in 75 ml of MeOH, and 260 mg (0.760 mmol) of $NaBPh_4$ were added. The resultant green precipitate was collected on a filter frit, washed with 15 ml of MeOH, and dried under vacuum overnight. Yield 378 mg (69%). IR (Nujol): ν(ReO) 1010 (m) cm^{-1}. MS (FAB), ^{187}Re isotope: m/z 827 (M^+), 808 (M^+ −F), 744 (M^+ −Cy).

2.4. *Synthesis of $[Re(Cl)(F)(O)Cyttp]BPh_4$ (5(BPh_4))*

A solution of $[ReF_2(O)Cyttp]BPh_4$ (200 mg, 0.175 mmol) and excess LiCl (96.4 mg, 2.27 mmol) in THF (3 ml) was stirred overnight. The volume of the solution was reduced in vacuo to ~0.5 ml, and 4 ml of Et_2O were added. The resultant light green solid was filtered off, washed with 4 ml of H_2O and 4 ml of Et_2O, and dried under vacuum overnight. Yield 180 mg (89%). IR (Nujol): ν(ReO) 1006 (m) cm^{-1}. MS (FAB), ^{187}Re and ^{35}Cl isotopes: m/z 843 (M^+), 808 (M^+ −Cl), 760 (M^+ −Cy).

2.5. *Synthesis of $[Re(Br)(F)(O)Cyttp]BPh_4$ (6(BPh_4))*

A solution of $[ReF_2(O)Cyttp]BPh_4$ (200 mg, 0.175 mmol) and excess LiBr (196 mg, 2.27 mmol) in THF (3 ml) was stirred overnight. The volume of the solution was reduced in vacuo to ~0.5 ml, and 4 ml of Et_2O were added. The resultant light green solid was filtered off, washed with 4 ml of H_2O and 4 ml of Et_2O, and dried under vacuum overnight. Yield 105 mg (49.9%). IR (Nujol): ν(ReO) 1006 (m) cm^{-1}. MS (FAB), ^{187}Re and ^{79}Br isotopes: m/z 887 (M^+), 808 (M^+ −Br), 804 (M^+ −Cy).

2.6. *Reaction of $[Re(F)(H)(O)Cyttp]SbF_6$ (3(SbF_6)) with NaH, LiCl or LiBr*

A solution of $[Re(F)(H)(O)Cyttp]SbF_6$ (30 mg, 0.028 mmol) and excess NaH, LiCl or LiBr (2.27 mmol) in THF (2 ml) was stirred overnight at room temperature. No reaction was observed by ^{31}P NMR spectroscopy.

2.7. *Reaction of $[Re(F)(H)(O)Cyttp]SbF_6$ (3(SbF_6)) with CO or SO_2*

Gaseous CO or SO_2 was bubbled through a solution of $[Re(F)(H)(O)Cyttp]SbF_6$ (30 mg, 0.028 mmol) in acetone (1 ml) for 1 h at room temperature. No reaction was observed by ^{31}P NMR spectroscopy.

2.8. *Reaction of $[ReF_2(O)Cyttp]BPh_4$ (5(BPh_4)) with NaH*

A solution of $[ReF_2(O)Cyttp]BPh_4$ (30 mg, 0.026 mmol) and NaH (10 mg, 0.41 mmol) in THF (3 ml) was stirred overnight at room temperature. No reaction was observed by ^{31}P NMR spectroscopy.

2.9. *Reaction of $[Re(Br)(F)(O)Cyttp]BPh_4$ (6(BPh_4)) with LiCl*

A solution of $[Re(Br)(F)(O)Cyttp]BPh_4$ (30 mg, 0.026 mmol) and excess LiCl (96 mg, 2.3 mmol) in THF (3 ml) was stirred at room temperature. The reaction was monitored by ^{31}P NMR and showed only $[Re(Cl)(F)(O)Cyttp]BPh_4$ after two weeks.

2.10. *Reaction of $[Re(Br)(F)(O)Cyttp]BPh_4$ (6(BPh_4)) with LiF*

A solution of $[Re(Br)(F)(O)Cyttp]BPh_4$ (30 mg, 0.026 mmol) and excess LiF (59 mg, 2.3 mmol) in THF (3 ml) was stirred for two weeks at room temperature. No reaction was observed by ^{31}P NMR spectroscopy.

2.11. *Reaction of $[Re(Cl)(F)(O)Cyttp]BPh_4$ (5(BPh_4)) with LiBr or LiF*

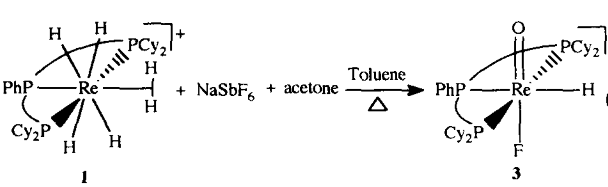
A solution of $[Re(Cl)(F)(O)Cyttp]BPh_4$ (30 mg, 0.026 mmol) and excess LiBr or LiF (2.3 mmol) in THF (3 ml) was stirred for two weeks at room temperature. No reaction was observed by ^{31}P NMR spectroscopy.

3. Results and discussion

3.1. Preparation and characterization of [Re(F)(H)(O)Cyttp]SbF$_6$ (3(SbF$_6$))

When a solution of **1**(SbF$_6$) in 1:1 acetone/benzene was maintained at reflux temperature, complex **3** was observed by ^{31}P NMR spectroscopy. The formation of **3** was preceded by the appearance of **2** in the spectrum. Similar replacement of hydride by fluoride from the complex fluoro anion BF$_4^-$ or PF$_6^-$ has been observed in other systems [3]. Prolonged reflux times resulted in the complete conversion to **3**, which was isolated as **3**(SbF$_6$) in moderate yield ($\leqslant$65%).

To enhance the yield of **3**(SbF$_6$), the foregoing reaction was run with added excess NaSbF$_6$. It was thought that the extra SbF$_6^-$ would be the source of reacting fluoride, thus leaving sufficient SbF$_6^-$ intact to function as the counterion for **3**. Accordingly, under these conditions in acetone/toluene at reflux temperature (Eq. (1)), a much higher isolated yield of **3**(SbF$_6$) (91%) was realized.



(1)

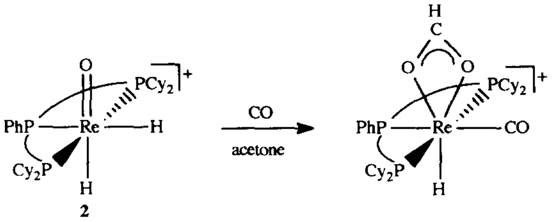
The chemical composition of **3**(SbF$_6$) was established by elemental analysis and FAB-MS, which showed the parent peak of **3** at *m/z* 809 (^{187}Re isotope). No fragmentation peaks corresponding to ($M^+ - $F) and ($M^+ - $O) were observed.

The structure of **3** is readily discerned from spectroscopic data, and various chemical shifts and coupling constants are provided in Table 1. Thus, the ^{31}P{H} NMR spectrum shows a doublet of doublets at δ 15.3 ($J_{PF} = 115.2$ Hz, $J_{PP} = 19.8$ Hz) for the wing phosphorus atoms (P$_w$) and a doublet of triplets at δ −6.5 ($J_{PF} = 64.8$ Hz, $J_{PP} = 19.8$ Hz) for the central phosphorus atom (P$_c$); the equivalence of the P$_w$ atoms implicates meridional coordination of Cyttp. An unusually low-field hydride resonance at δ 12.16 in the ^{1}H NMR spectrum appears as a doublet of quartets. Low-field positions of metal hydride resonances have been previously noted for other complexes [8]. Heteronuclear decoupling experiments simplified the signal at δ 12.16 to a doublet of triplets (^{1}H{^{19}F} NMR: $J_{PcH} = 71.4$ Hz, $J_{PwH} = 17.4$ Hz) and a doublet (^{1}H{^{31}P} NMR: $J_{FH} = 16.5$ Hz). The relative values of these coupling constants point to the hydride being positioned *trans* to the central phosphorus [9]. This is further supported by the selective decoupling of the central and wing phosphorus atoms which gives a quartet, owing to the similar values of J_{PwH} and J_{FH}, and a doublet of doublets, respectively, as expected. The ^{19}F NMR spectrum of **3**(SbF$_6$) exhibits an ReF resonance at δ −227.3 as a multiplet; upon proton decoupling, this signal simplifies to a triplet of doublets ($J_{PwF} = 115.2$ Hz, $J_{PcF} = 64.8$ Hz). The small value of J_{FH} (16.5 Hz, from the ^{1}H NMR spectrum) indicates a *cis* orientation of the fluoride and hydride ligands. The IR spectrum of **3**(SbF$_6$) shows an absorption band at 1015 cm^{-1}, which is assigned to ν(ReO).

Thus, from spectroscopic evidence, the inferred structure of **3** is related to that of **2** by replacement of the hydride *trans* to the oxide in the latter by fluoride.

3.2. Reactivity of [Re(F)(H)(O)Cyttp]SbF$_6$ (3(SbF$_6$))

As previously reported [2], **2**(SbF$_6$) readily reacts with CO and SO$_2$. With CO, a formate complex is obtained by transfer of one hydride and oxygen to the substrate (Eq. (2)).



(2)

Since the formate ligand in the product would appear to contain the hydrogen that was *cis* to the oxide in **2**, we examined the reaction between **3**(SbF$_6$) and CO with the expectation that a similar behavior involving the *cis*-O,H ligands would be observed. However, no reaction was observed under comparable experimental conditions. The lack of reactivity of **3** toward CO may be ascribed to a higher rhenium-to-

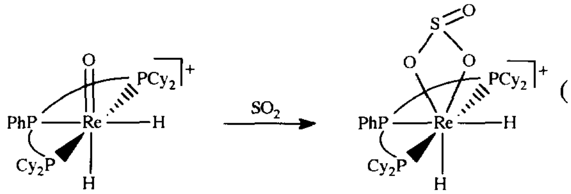
Table 1
Selected NMR data for complexes **2**–**6** [a]

Complex	δ (ppm)			J (Hz)			Miscellaneous δ (ppm) and J (Hz)
	P$_w$	P$_c$	(Re)F	P$_w$P$_c$	P$_w$F	P$_c$F	
2(SbF$_6$) [2]	22.56	6.77		18.3			*cis*-H (δ −12.64): $J_{PwH} = 35.0$, $J_{PcH} = 57.5$ *trans*-H (δ −1.04): $J_{PwH} = 25.0$, $J_{PcH} = 5.0$
3(SbF$_6$)	15.3	−6.51	−227.3	19.8	115.2	64.8	H (δ 12.16): $J_{PwH} = 17.4$, $J_{PcH} = 71.4$, $J_{FH} = 16.5$
4(BPh$_4$)	3.33	−20.60	−129.7	16.0	27	125	$J_{FF} = 94$
			−143.3		94	55	
5(BPh$_4$)	−3.58	−23.82	−140.1	18.1	88.8	58.3	
6(BPh$_4$)	−6.95	−26.00	−141.0	18.2	84.7	57.7	

[a] Spectra were obtained in acetone-d$_6$

oxygen bond order in **3** than in **2**. Accordingly, ν(ReO) occurs at 1015 cm^{-1} for **3**(SbF_6), but at 923 cm^{-1} for **2**(SbF_6) [2] [2]. This higher bond order would have two consequences on the reactivity of **3** with CO. First, an Re≡O triple bond would render **3** an 18-electron complex, thus precluding facile coordination of CO to the metal. Second, the developed formal positive charge on the oxygen upon going from Re=O to Re≡O [3] would make it more difficult to generate a [2+1] adduct with CO of the type $\overline{\text{Re}\overline{\text{O}}\text{C}}\text{O}$. Such a CO_2 complex is thought to be a precursor of the formate product [2].

Complex **2**(SbF_6) reacts with SO_2 to afford the sulfito product shown in Eq. (3). Again, the higher positive charge on the oxygen atom of **3** compared to **2** would make the addition of the electrophilic sulfur atom of SO_2 less favorable.

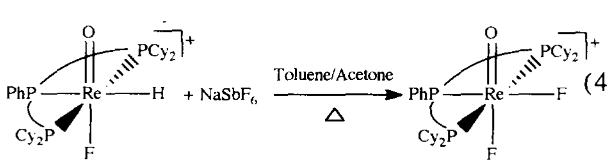


2

(3)

Having observed no transfer of H or O in **3** to the substrates CO and SO_2, we turned our attention to ligand substitution. In an attempt to regenerate **2**, **3**(SbF_6) was treated with NaH in THF at room temperature; however, no reaction was observed in 12 h. Attempts to replace fluoride with chloride or bromide also proved unsuccessful.

Since one hydride in **2** can be replaced with fluoride to generate **3**, we thought that under more forcing conditions the remaining hydride, *cis* to the oxide, might also be substituted. Accordingly, reaction of **3**(SbF_6) with $NaSbF_6$ was conducted at 149 °C for 62 h and resulted in the formation of $[ReF_2(O)Cyttp]^+$ (**4**) (Eq. (4)), which was isolated in 69% yield as **4**(BPh_4). The green solid product showed a FAB-MS peak at m/z 809 ($M^+ - F$). In the IR spectrum, a medium-intensity absorption was observed at 1010 cm^{-1} due to ν(ReO).



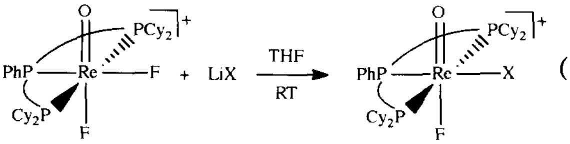
3 **4**

(4)

The structure of **4** was readily elucidated from spectroscopic data (Table 1). The appearance of two signals at δ −129.7 and −143.3, each a doublet of doublets of triplets, in the $^{19}F\{^1H\}$ NMR spectrum of **4**(BPh_4) implicates a *cis*-F_2 structure. The values of selected coupling constants are provided in Table 1. The resonance at δ −129.7 is characterized by a large J_{P_cF} (125 Hz) and a small J_{P_wF} (27 Hz), consistent with the fluoride being *trans* to P_c. Similar J_{PF} values have been reported for square-planar platinum fluoro-phosphine complexes [11]. The $^{31}P\{^1H\}$ NMR spectrum shows two resonances at δ 3.39 (ddd) and −20.60 (ddt). The presence of two $^{31}P\{^1H\}$ NMR signals as well as two $^{19}F\{^1H\}$ NMR signals reveals meridional coordination of Cyttp and, therefore, defines the structure of **4** as being analogous to that of **2**.

3.3. Reactivity of [ReF$_2$(O)Cyttp]BPh$_4$ (4(BPh$_4$))

Owing to the limited observed reactivity of **3**, it was of interest to ascertain whether the presence of an additional fluoride ligand in **4** would enhance the scope of substitution chemistry. In this vein, reactions were tried between **4**(BPh_4) and each of NaH, LiCl and LiBr in THF at room temperature for 12 h. Whereas NaH did not react, use of LiCl and LiBr led to the replacement of one fluoride in **4** by chloride and bromide, respectively, to afford complexes **5**(BPh_4) (X=Cl) and **6**(BPh_4) (X=Br) (Eq. (5)).

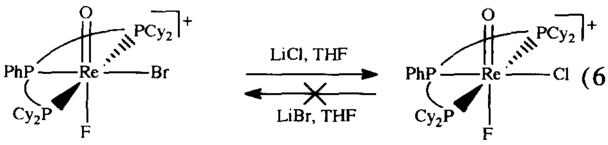


4 **5** (X = Cl), **6** (X = Br)

(5)

On the basis of their spectroscopic properties (see Table 1), these complexes are assigned structures derived from that of **4** by substitution of chloride or bromide for the *cis* (to the oxide) fluoride. The positions of the fluoride and chloride or bromide are proposed by comparison of the J_{PF} values of **5** and **6** with those of **3** and **4**. Therefore, the structures of **3**, **5** and **6** are all related by the *trans* orientation of fluoride and oxide ligands. Assuming that this is a thermodynamic effect, the *trans* disposition of F and O may result from the strong π-donor properties of the oxide, which would favor the bonding of the very electronegative (hard) fluoride rather than the more polarizable (softer) hydride, chloride or bromide opposite to it. Although fluoride is the best π donor of the halides [3], the values of ν(ReO) for **3**–**6** suggest that, in these complexes, it does not favorably compete with the *trans* oxide for the empty π orbitals of Re [12].

Complex **6**(BPh_4) can be converted to **5**(BPh_4) by prolonged treatment with LiCl in THF at room temperature (Eq. (6)).



6 **5**

(6)

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[2] These values represent the *observed* ν(ReO) frequencies. For **2**(SbF_6), the ν(ReO) mode couples with a vibrational mode of lower frequency, probably one of the δ(ReH) modes. Hence the true, *unperturbed* ν(ReO) mode has an energy lower than 923 cm^{-1} [10]. We do not know whether any coupling occurs between the ν(ReO) or δ(ReH) modes in **3**(SbF_6). Such a coupling would also make the *unperturbed* ν(ReO) frequency lower than that observed; however, it would not change the relative values of ν(ReO) for **2**(SbF_6) and **3**(SbF_6).

[3] The development of positive charge on the oxygen is also predicted by the electron-withdrawing properties of fluorine.

However, the attempted conversion of **6** to **4** by use of LiF under comparable conditions afforded no reaction. Also, no reaction was observed when **5**(BPh_4) was treated with LiBr or LiF under similar conditions. Thus, the affinity of X^- for the site *cis* to the oxide ligand follows the order $Cl^- > Br^- > F^-$. The relative lability of fluoride in this series contrasts with its observed inertness when positioned *trans* to the oxide.

Acknowledgements

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the ACS, for support of this research. D.E.R. thanks the US Department of Education for a fellowship under the NNF program and Amoco for a graduate fellowship.

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