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Synthesis, structure and reactivity of $[ReH_2(NR)(Cyttp)]^+$ (Cyttp = PhP(CH₂CH₂CH₂PCy₂)₂) complexes. Organoimido analogues of the oxo complex that transfers the elements of water to substrates

Mark W. Baize, Judith C. Gallucci, Andrew Wojcicki * Department of Chemistry, The Ohio State University, Columbus, OH 43210-1185, USA

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Abstract

The cationic organoimido-hydrido complexes $[ReH_2(NR)(Cyttp)]^+$ where $R=NC_6H_4Me_{-P}$ (2), Ph (3), Cy (4) and Cyttp= PhP(CH_2CH_2CH_2CP(y_2)_2 were synthesized by reaction of $[ReH_2(O)(Cyttp)]_{0,3}CG_1$ (1(T)) with the appropriate primary amine. Use of molecular sives promotes the formation of these rhenium products. 2-4 were shown by 'H NMR spectroscopy to contain two inequivalent, *cis* hydride ligands. An X-ray diffraction study of $2(PF_6)$ revealed the presence of distorted *mer*-Cyttp and the organoimido ligand *cis* to all three phosphorus atoms. The hydrido ligands were not located. Unlike its oxo-hydrido analogue, $1(SbF_6)$, 2(Tf) failed to react with CO or SO₂ under comparable, or even more forcing, conditions. However, with anhydrous HCl it afforded ReCl₃(Cyttp), and with NaBH₄, ReH₄(Cyttp).

Keywords: Crystal structures; Hydrido complexes; Imido complexes; Rhenium complexes

1. Introduction

We have recently reported the synthesis and characterization of an unusual ∞ -hydrido complex, $[ReH_2(O)-(Cytp)]^+$ (1, $Cytp = PhP(CH_2CH_2CP_2p_2)_2$), that transfers both oxygen and hydrogen to some unsaturated substrates, e.g. CO [1] (Eq. (1)) and RCN [2]. Double



transfer reactions involving different ligands are the basis of important organometallic catalytic processes, including hydroformylation [3]. In contrast, this type of chemistry has not been developed for complexes of transition metals in the higher oxidation states. Organoimido ligands, NR^{2-} , may be regarded as isoelectronic analogues of the oxo ligand, and imido and oxo complexes of similar constitution abound for a number of transition metals [4.5]. However, as with the oxo complexes [1,6], imido complexes that contain also hydrido ligands are still a rarity [5]. Rhenium(V), which forms a plethora of organoimido complexes, has yielded few imido-hydrido complexes: ReH(NR)Cl₂(PPh₃)₂ ($R = C_{eH_{A}}Me, C_{eH_{2}}O-Me-P$) [7], ReH(NR)₂(NpC₂Np) and ReH(NR)₂(PMe₂Ph)₂ ($R = C_{eH_{3}}(i-Pr)_{2-2.6}$, Np = neopentyl) [8]. None of these compounds has been reported to undergo transfer reactions of both imido and hydrido ligands.

In an attempt to extend ligand transfer chemistry to metal imido hydrides, we have synthesized a series of complexes $[ReH_2(NR)(Cytp)]^+$ where $R = C_6H_4Me_{\mathcal{P}}$ (2), Ph (3) and Cy (4). Reported here are the preparation and characterization of these compounds, including an X-ray structural analysis of $[ReH_2(NC_6H_4Me_{\mathcal{P}})(Cytp)]PF_6$ (2(PF₆)), and a preliminary study of their reactivity.

2. Experimental

2.1. General procedures and measurements

All reactions and sample manipulations were conducted under an atmosphere of argon by use of standard procedures

^{*} Corresponding author. Tel.: + 1-614-292 47 50; fax: + 1-614-292 16 85.

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[9]. Solvents were dried [10], distilled under argon, and degassed before use. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. NMR spectra were collected on a Bruker AM-250 or AC-300 spectrometer. Residual proton resonances in deuterated solvents were used as internal standards for the ¹HNMR spectra. ³¹P chemical shifts were referenced to external 85% H₃PO₄.

Reagents were obtained from various commercial sources and used as received. $[ReH_2(O)(Cytp)]O_3SCF_3(1(Tf))$ was prepared as reported in the literature [1].

2.2. Preparation of $[ReH_2(NC_6H_4Me-p)(Cyttp)]O_3SCF_3$ (2(Tf))

A mixture of freshly sublimed p-toluidine (1.0 g, 9.3 mmol), 1(Tf) (0.50 g, 0.53 mmol) and 4-Å molecular sieves (0.5 ml) was warmed to 60°C with a change of color to orange-red as the toluidine melted. Stirring at 60°C for 20 h resulted in the formation of a purple reaction mixture. Excess toluidine was sublimed (30°C/1 torr) onto a water-cooled cold finger, the residue was treated with 20 ml of CH₂Cl₂ and the mixture was filtered to remove the sieves. The solvent was removed from the filtrate under reduced pressure to leave a purple solid which was washed consecutively with 10 ml of 1:1 hexane/diethyl ether, 10 ml of diethyl ether and 10 ml of benzene. The product was recrystallized from a solution of CH₂Cl₂ (0.5 ml) and benzene (2 ml) layered with diethyl ether (5 ml). Purple-bronze crystals that formed were collected by filtration; yield 0.48 g (89%). ¹H NMR (acetoned₆): δ8.3-7.2 (m, Ph and C₆H₄), 3.4-0.6 (m, CH₂ and CH), 2.28 (s, Me), -3.77 (tt, ${}^{2}J_{PwH} = 28.4$ Hz, ${}^{2}J_{PcH} = 6.9$ Hz, $^{2}J_{HH} = 6.0 \text{ Hz}, trans(to \text{ N})-\text{H}), -8.65 (dtd, {}^{2}J_{PcH} = 48.7 \text{ Hz},$ ${}^{2}J_{PwH} = 32.3 \text{ Hz}, {}^{2}J_{HH} = 6.0 \text{ Hz}, cis(to \text{ N})-\text{H}). {}^{31}\text{P}\{{}^{1}\text{H}\} \text{ NMR}$ (acetone-d₆): δ 12.7 (d, ²J_{PcPw} = 19.0 Hz, wing Ps), 3.1 (t, ${}^{2}J_{PcPw} = 19.0$ Hz, central P). Anal. Calc. for C44H70F3NO3P3ReS: C, 51.35; H, 6.86; N, 1.36. Found: C, 51.45; H, 6.92; N, 1.42%.

2.3. Preparation of [ReH₂(NC₆H₄Me-p)(Cyttp)]PF₆ (2(PF₆))

To a solution of 2(Tf) in methyl alcohol was added 1 molar equivalent of NaBPh₄, also in methyl alcohol, resulting in the formation of a purple precipitate of $[ReH_2(NC_6H_4-Me_P)(Cyttp)]BPh_4$. This solid was dissolved in a minimum amount of CH₂Cl₂, and a solution of 1.05 molar equivalents of [Et₄N]PF₆ in CH₂Cl₂ was added with stirring to yield a white precipitate of [Et₄N]BPh₄. The mixture was filtered, the filtrate was evaporated to dryness and the residue was recrystallized similarly to 2(Tf). The anion exchange was confirmed by the absence of signals in the ¹¹B NMR spectrum of the product and the presence of a signal corresponding to PF₆⁻ in the ³¹P NMR spectrum [11].

2.4. Preparation of [ReH2(NPh)(Cyttp)]O3SCF3 (3(Tf))

A procedure analogous to that for 2(Tf) was followed starting with a reaction mixture of aniline (1.0 g, 10.8 mmol) and 1(Tf) (0.50 g, 0.53 mmol) containing 4-Å molecular sieves (0.5 ml). The mixture was heated for 24 h at 60°C. the sieves were removed by filtration and 5 ml of hexane was added to give a purple oil. The supernatant liquid was discarded and the oil was triturated with 10 ml of hexane to afford a purple solid. The solid was collected by filtration and washed first with 10 ml of diethyl ether and then 5 ml of benzene. Purple crystals were grown by slow diffusion of diethyl ether into a solution of the product in CH₂Cl₂/benzene; yield 0.50 g (92%). ¹H NMR (acetone-d₆): δ8.3-7.2 (m, Ph), 3.4–0.6 $(m, CH_2 \text{ and } CH)$, -3.82 $(tt, {}^2J_{PwH} = 27.5)$ Hz, ${}^{2}J_{PCH} = 6.7$ Hz, ${}^{2}J_{HH} = 6.0$ Hz, trans(to N)-H), -8.72 $(dtd, {}^{2}J_{PcH} = 47.8 \text{ Hz}, {}^{2}J_{PwH} = 32.5 \text{ Hz}, {}^{2}J_{HH} = 6.0 \text{ Hz}, cis(to$ N)-H). ${}^{31}P{}^{1}H{}$ NMR (acetone-d₆): $\delta 13.4$ (d, ${}^{2}J_{PcPw} = 19.4$ Hz, wing Ps), 2.5 (t, ${}^{2}J_{PcPw} = 19.4$ Hz, central P). Anal. Calc. for C43H68F3NO3P3ReS: C, 50.87; H, 6.75; N, 1.38. Found: C, 50.69; H, 6.75; N, 1.50%.

2.5. Preparation of [ReH2(NCy)(Cyttp)]O3SCF3 (4(Tf))

A solution of 1(Tf) (0.50 g, 0.53 mmol) in 2.0 ml of cyclohexylamine (1.7 g, 17 mmol) was maintained at 55°C for 3 h. A ³¹P{¹H} NMR spectrum of the reaction mixture showed signals at δ 15.1 (d) and 0.1 (t), 11.3 (d) and 10.4 (t) and -22.2 (br). The volatiles were removed under reduced pressure to leave an orange oil. The oil was dissolved in 2 ml of THF, and hexane was slowly added to give a pink precipitate. The solid was collected by filtration, washed with 5 ml of hexane, and dried under reduced pressure; yield 0.30 g (56%). ¹H NMR (acetone-d₀): δ 8.2 (m, Ph), 2.6–0.8 (m, CH₂ and CH), -4.0 (tt, ²J_{PwH}=28 Hz, ²J_{PcH}=7 Hz, ²J_{HH}=6 Hz, trans(to N)-H), -9.1 (dtd, ²J_{PcH}=50 Hz, ²J_{PwH}=33 Hz, ²J_{HH}=6 Hz, cis(to N)-H). ³¹P{¹H} MR (acetone-d₀): δ 15.5 (d, ²J_{PcEW}=19.5 Hz, wing Ps), 0.6 (t, ²J_{Pepw}=19.5 Hz, central P).

2.6. Reaction of [ReH₂(NC₆H₄Me-p)(Cyttp)]O₃SCF₃ (2(Tf)) with CO

Carbon monoxide was bubbled through a solution of 2(Tf)(20-25 mg, 0.019-0.024 mmol) in THF or acctone at 25-65°C for up to 12 h. No reaction was observed by ³¹P NMR spectroscopy.

Similar results were obtained by using $[ReH_2(NPh)-(Cyttp)]O_3SCF_3$ (3(Tf)) or $[ReH_2(NCy)(Cyttp)]O_3-SCF_3$ (4(Tf)) in place of 2(Tf).

2.7. Reaction of $[ReH_2(NC_6H_4Me-p)(Cyttp)]O_3SCF_3$ (2(Tf)) with SO₂

Gaseous SO₂ was bubbled through a solution of 2(Tf) (25 mg, 0.024 mmol) in THF at 25–60°C for 8 h. The reaction

was monitored by ³¹P NMR spectroscopy, and no change was observed in the spectrum.

2.8. Reaction of $[ReH_2(NC_6H_4Me-p)(Cyttp)]O_3SCF_3$ (2(Tf)) with $[Me_3O]BF_4$

A solution of 2(Tf) (20 mg, 0.019 mmol) in CH₂Cl₂ was treated with an excess of [Me₂O]BF₄, and the mixture was stirred for 4 h at room temperature. No reaction was observed by ³¹P NMR spectroscopy. The solution was then warmed to ~40°C. There was no change in the ³¹P NMR spectrum.

A similar result was obtained when $[Et_3O]BF_4$ was used in place of $[Me_3O]BF_4$.

2.9. Reaction of [ReH₂(NC₆H₄Me-p)(Cyttp)]O₃SCF₃ (2(Tf)) with HCl

A solution of anhydrous HCl in diethyl ether (0.2 ml, 1 M) was added to 50 mg (0.048 mmol) of 2(Tf) in 1 ml of THF. Immediately the purple color of the latter changed to green and, after 1 h of stirring, to yellow-brown. The volatiles were removed under reduced pressure to leave a yellow solid. This solid exhibited no ³¹P NMR signals, and gave a ¹H NMR spectrum identical with that reported for the paramagnetic ReCl₃(Cyttp) [12].

2.10. Reaction of $[ReH_2(NC_6H_4Me-p)(Cyttp)]O_3SCF_3$ (2(Tf)) with NaBH₄

A mixture of 2(Tf) (10 mg, 0.010 mmol) and NaBH₄ (10 mg, 0.26 mmol) in THF was stirred at 45°C for ~12 h. A ³¹P{¹H} NMR spectrum showed complete conversion to ReH₅(Cytp) (δ 24.2 (d, ²J_{PcPw} = 15.1 Hz), 1.8 (t, ²J_{PcPw} = 15.1 Hz)) [12].

2.11. Crystallographic analysis of [ReH₂(NC₆H₄Me-p)-(Cyttp)]PF₆ (2(PF₆))

Crystals of $2(PF_6)$ are dichroic: they appear purple from some directions and light brown from others. The data collection crystal was a rectangular rod in habit. Examination of the diffraction pattern on a Rigaku AFC5S diffractometer indicated a monoclinic crystal system. Based on the systematic absences, $0KO, k \neq 2n$, and $hOl, h + l \neq 2n$, the space group was uniquely determined as $P2_1/n$. Unit cell constants were obtained by a symmetry restricted least-squares fit of the setting angles for 25 reflections in the 2θ range $20-29^{\circ}$ with Mo K α radiation ($\lambda(K\alpha_1) = 0.70930$ Å). Six standard reflections were measured during data collection and showed a small uniform decrease in intensity. Data reduction was done with the teXsan package [13]. A linear decay correction was applied to the data based on an average decrease in intensity of 8.2%.

The structure was solved with the Patterson method in SHELXS-86 [14]. Phasing on the Re and three P atoms in DIRDIF [15] revealed all of the remaining non-hydrogen

Table 1	
Crystallographic data for [ReH2(NC4H4Me-p)(Cyttp)]PF4 (2(PF4)))

Formula	C43H70F6NP4Re
Formula weight	1025.13
Space group	P2,/n
2 (Å)	10.981(2)
ь (Å)	17.157(5)
c (Å)	24.613(2)
β(°)	95.49(1)
V (Å ³)	4616
z	4
D_{calc} (g cm ⁻³)	1.47
Crystal size (mm)	0.12×0.15×0.38
Radiation	Mo Ka with graphite monochromator
μ (cm ⁻¹)	28.27
Transmission factors	0.667-0.726
Temperature (°C)	24
20 limits (°)	4≤2θ≤50
Scan speed (° min ^{-ι} in ω)	4 with max. 6 scans reflection -1
Scan type	ω
Scan range (° in ω)	1.10
Background time/scan time	0.5
Data collected	$+h_{1}+k_{2}\pm l$
Unique data	8479
Unique data $(F_0^2 > 3\sigma(F_0^2))$	4672
No. variables	496
R(F) *	0.042
$R_{*}(F)^{b}$	0.038
Error in observation of unit weight	1.41

 ${}^{a}R(F) = \sum ||F_{o}| - |F_{c}||/\sum |F_{o}|.$

 ${}^{b}R_{w}(F) = [\sum w(|F_{o}| - |F_{c}|)^{2} / \sum wF_{o}^{2}]^{1/2}$ with $w = 1/\sigma^{2}(F_{o})$.

atoms. Full-matrix least-squares refinements based on F were performed in teXsan [13]; the function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. An analytical absorption correction was applied to the data [16]. The PF₆ group appears to be disordered as the B values for the fluorine atoms are large. It was not possible to model this disorder in terms of two discrete orientations, so only a single orientation is presented here. The hydrogen atoms bonded to carbon atoms are included in the model at calculated positions with C-H = 0.98 Å and fixed. The two hydrogen atoms bonded to Re were not located. The final refinement cycle was based on the 4672 intensities with $I > 3\sigma(I)$ and 496 variables and resulted in final agreement factors of R = 0.042 and $R_w = 0.038$. The final difference electron density map contains maximum and minimum peak heights of 0.67 and -0.65 e Å⁻³. Neutral atom scattering factors were used [17] and include terms for anomalous dispersion [18].

A summary of crystallographic details is provided in Table 1. Final positional and equivalent isotropic thermal parameters are given in Table 2.

3. Results and discussion

3.1. Synthesis

The complexes [ReH₂(NR)(Cyttp)]O₃SCF₃ (R = C₆H₄-Me-p (2(Tf)), Ph (3(Tf)), Cy (4(Tf))) were prepared by

Table 2 Positional and equivalent isotropic thermal parameters for $[ReH_2(NC_6-H_4Me_P)(Cyttp)]PF_6(2(PF_6))$

Atom	x	у	z	$B_{\rm eq}^{a}$ (Å ²)
Re	0.49490(4)	0.23517(2)	0.14030(2)	2.408(7)
P(1)	0.4723(2)	0.3750(1)	0.1464(1)	2.88(6)
P(2)	0.6884(2)	0.2499(1)	0.10447(9)	2.87(6)
P(3)	0.4640(2)	0.1099(1)	0.0965(1)	2.91(6)
P(4)	0.9824(4)	0.1733(2)	0.4139(1)	4.90(9)
F(1)	1.025(1)	0.1072(6)	0.4449(4)	14.9(4)
F(2)	1.0435(8)	0.1506(8)	0.3662(4)	15.6(4)
F(3)	0.8755(10)	0.1293(6)	0.3871(5)	14.8(4)
F(4)	0.916(1)	0.2420(6)	0.3811(4)	14.3(4)
F(5)	0.912(2)	0.1998(7)	0.4585(5)	25.9(7)
F(6)	1.073(1)	0.2269(8)	0.4326(6)	21.8(7)
N(1)	0.4858(6)	0.2116(4)	0.2096(3)	2.8(2)
C(I)	0.5817(9)	0.4398(5)	0.1184(4)	3.9(3)
C(2)	0.7141(10)	0.4129(6)	0.1176(4)	4.3(3)
C(3)	0.7263(9)	0.3443(6)	0.0772(4)	3.6(3)
C(4)	0.7222(8)	0.1858(6)	0.0487(4)	3.4(3)
C(5)	0.7063(9)	0.1003(6)	0.0613(4)	3.6(3)
C(6)	0.575(1)	0.0703(6)	0.0519(4)	4.7(3)
C(7)	0.4777(9)	0.4019(6)	0.2201(4)	3.2(2)
C(8)	0.6035(10)	0.3891(6)	0.2504(4)	4.4(3)
C(9)	0.602(1)	0.4016(7)	0.3114(4)	5.3(3)
C(10)	0.557(1)	0.4810(7)	0.3242(4)	5.7(4)
C(II)	0.431(1)	0.4958(6)	0.2937(5)	5.1(3)
C(12)	0.4342(9)	0.4849(6)	0.2322(4)	4.1(3)
C(13)	0.3276(8)	0.4162(5)	01155(4)	3.2(2)
C(14)	0.2159(9)	0.3893(6)	0.1437(4)	3.7(3)
C(15)	0 1007(10)	0 4328(7)	0 1209(5)	52(3)
C(16)	0.078(1)	0.4226(7)	0.0593(5)	5.7(4)
C(17)	0.189(1)	0 4452(7)	0.0308(5)	5.7(4)
C(18)	0.303(1)	0.4032(6)	0.0540(4)	4.4(3)
C(19)	0.8180(8)	0.2298(6)	0.1555(3)	3.1(2)
C(20)	0.9401(9)	0.2345(7)	0.1431(4)	4.3(3)
C(21)	1.0346(8)	0.2186(6)	0.1816(4)	4.2(3)
C(22)	1.0113(9)	0.1959(6)	0.2333(4)	3.9(3)
C(23)	0.8940(9)	0.1915(7)	0.2463(4)	4.4(3)
C(24)	0.7990(8)	0 2084(6)	0 2073(4)	34(2)
C(25)	0.3188(9)	0.0960(5)	0.0524(4)	3.4(3)
C(26)	0.2071(9)	0.1003(6)	0.0832(4)	4.0(3)
C(27)	0.093(1)	0.0825(7)	0.0462(5)	5.5(4)
C(28)	0.077(1)	0.1382(8)	-0.0017(5)	6.5(4)
C(29)	0.189(1)	0.1346(7)	-0.0331(4)	5.7(3)
C(30)	0.306(1)	0.1508(6)	0.0034(4)	4.5(3)
C(31)	0.4579(9)	0.0349(6)	0.1506(4)	3.6(3)
C(32)	0.5771(10)	0.0286(6)	0.1868(4)	4.3(3)
C(33)	0.564(1)	-0.0211(7)	0.2358(5)	5.7(4)
C(34)	0.523(1)	-0.1022(7)	0.2^02(5)	6.3(4)
C(35)	0.407(1)	-0.1018(7)	0.1808(6)	6.5(4)
C(36)	0.417(1)	-0.0468(7)	0.1321(5)	5.6(4)
C(37)	0.4656(9)	0.1997(6)	0.2642(4)	3.1(2)
C(38)	0.3532(9)	0.2070(8)	0.2808(4)	6.2(3)
C(39)	0.331(1)	0.1975(9)	0.3345(5)	7.3(4)
C(40)	0.425(1)	0.1800(7)	0.3734(4)	5.0(3)
C(41)	0.539(1)	0.1716(7)	0.3564(4)	5.4(4)
C(42)	0.5605(10)	0.1804(7)	0.3037(4)	5.2(3)
C(43)	0.402(1)	0.1711(8)	0.4332(5)	7.3(4)

* The form of the equivalent isotropic thermal parameter is: $B_{eq} = 8/3\pi^2 \Sigma_{c} \Sigma_{j} U_{ij} a_{i} * a_{j} * a_{i} \cdot a_{j}$.

reaction of $[ReH_2(O)(Cyttp)]O_3SCF_3$ (1(Tf)) with the appropriate primary amine (Eq. (2)).



This methodology of conversion of metal oxo complexes to the corresponding imido complexes was first reported by Chatt and Rowe [19] and has since been used as a general route to the latter [4,5]. In studying the reaction of 1(Tf) with *p*-toluidine we observed that the formation of 2(Tf) is promoted by the presence of molecular sieves in the reaction mixture. This effect may be attributed to the interaction of the sieves with water and the resultant shift of the equilibrium (Eq. (2)) position to the right. Both 2(Tf) and 3(Tf) were prepared cleanly and in high yield (89-92%) as purple crystalline solids by the application of this procedure. Complex 4(Tf) was obtained in moderate yield (56%) as a pink solid from 1(Tf) and the more basic cyclohexylamine without the use of molecular sieves. All three rhenium imido complexes are stable to air in acetone, THF, CH2Cl2 and CH3CN solution.

3.2. Characterization

The new rhenium organoimido complexes have been characterized by a combination of elemental analysis and/or ¹H and ³¹P NMR spectroscopy. The structure of $2(PF_6)$ was determined by X-ray diffraction techniques.

The ³¹P{¹H} NMR spectra of 2-4(Tf) each show a triplet and a doublet; these signals are assigned respectively to the central and the equivalent wing phosphorus atoms of the tridentate Cyttp ligand. In the ¹H NMR spectra, two signals with a 1:1 intensity ratio are observed upfield from TMS and are attributed to the presence of two inequivalent hydrides. The resonance at $\delta - 3.77$ to -4.0 in each spectrum appears as a triplet of triplets owing to similar coupling constants ²J_{HH} and ²J_{PeH} and a much larger coupling constant ²J_{PwH}, whereas the resonance at $\delta - 8.65$ to -9.1 is observed as a doublet of triplets of doublets, with ²J_{PCH} ~ 48 Hz, ²J_{PwH} ~ 32 Hz and $^{2}J_{HH} \sim 6$ Hz. Homonuclear decoupling experiments for 2(Tf) simplified the appearance of the lower-field signal to a triplet of doublets and of the higher-field signal to two overlapping triplets to confirm the aforementioned spin-spin coupling constant assignments. Based on the splitting pattern and the magnitude of J, the resonance at $\delta - 3.77$ to -4.0 is assigned

Table 3

to the hydride *trans* to NR (or *cis* to central P), whereas that at $\delta - 8.65$ to -9.1 is attributed to the hydride *cis* to NR (or *trans* to central P) in a distorted octahedral structure.

An X-ray diffraction study of $2(PF_6)$ confirmed the presence of a cationic complex of rhenium and the PF_6^- anion in the crystal. Only the coordination environment afforded the metal by the NC₆H₄Me-*p* and Cyttp ligands was observed; the two hydrides bonded to rhenium were not located. The structure of the cation 2 without the hydride ligands appears in Fig. 1, and selected bond distances and angles are provided in Table 3.

The geometry around the rhenium center of 2 in Fig. 1 is that of a distorted octahedron, with two *cis* ligands (viz., the hydrides *trans* to N(1) and *trans* to P(2), detected by ¹H NMR spectroscopy (vide supra)), conspicuously missing. The distortion occurs as the other donor atoms fill some of the space relinquished by the small hydrides. In this respect, the structure is similar to that of the rhenium oxo cation 1 in 1(SbE₂) [1].

The tridentate phosphine Cyttp adopts a distorted meridional arrangment about the metal, with the bond angles P(1)-Re–P(2) and P(2)-Re–P(3) being close to 90°, but with the angle P(1)-Re–P(3) of 154.23(9)° deviating considerably from 180°. The latter angle is, however, more obtuse than that found in $1(SbF_6)$ (137.1(1)°) [1]. The rhenium atom is not positioned in the P(1)P(2)P(3) plane, but is displaced from it by 0.51 Å towards N(1) (i.e. the fragment ReP(1)P(2)P(3) is pyramidal, not planar). In 1(ShF₆), the corresponding displacement is 0.80 Å towards the oxo ligand [1]. As it was stated earlier in the paper, these effects are thought to be steric in origin and may be attributed to the coordination of two small hydrides.

The imido nitrogen (N(1)) is tilted away from P(2) to give a rather obtuse P(2)-Re-N(1) bond angle of 121.0(2)°. The angles P(1)-Re-N(1) and P(3)-Re-N(1) are consid-



Fig. 1. ORTEP plot of 2 in 2(PFs). The non-hydrogen atoms are represented by 50% probability thermal ellipsoids, and the hydrogen atoms are omitted.

Selected bond distances	(Å)	and	angles	(°)	for	$\{\text{ReH}_2(\text{NC}_6\text{H}_4\text{Me}-p)\}$
(Cvttn) 1PE, (2(PE,))						

Re-P(1)	2.418(3)	Re-N(1)	1.766(7)			
Re-P(2)	2.391(2)	N(1)-C(37)	1.40(1)			
Re-P(3)	2.413(3)					
P(1)-Re-P(2)	91.03(8)	P(2)-Re-N(1)	121.0(2)			
P(1)-Re-P(3)	154.23(9)	P(3)-Re-N(1)	102.1(2)			
P(1)-Re-N(1)	98.7(2)	Re-N(1)-C(37)	172.4(7)			
P(2)-Re-P(3)	91.24(9)					

erably smaller: 98.7(2) and 102.1(2)°, respectively. Interestingly, in 1(SbF₆) the three P-Re-O bond angles are of comparable magnitude, with the P(2)-Re-O angle being smaller (111.1(3)°) and the P(1)-Re-O and P(3)-Re-O angles being larger (110.8(2) and 107.3(2)°) [1] than the corresponding P-Re-N angles in $2(PF_6)$. A possible cause for the relatively obtuse P(2)-Re-N(1) angle in $2(PF_6)$ may be the essential coplanarity of the phenyl rings on N(1) and P(2) (cf. Fig. 1), the dihedral angle between them being 11°. This larger angle keeps the two rings sufficiently apart.

The other important aspects of the structure relate to the bonding of the NC₆H₄Me-*p* ligand to the rhenium center. The Re–N(1) bond length of 1.766(7) Å may be compared with the corresponding distances in a number of octahedral rhenium(V) imido complexes containing at least one phosphine ligand [5]. These distances range from 1.685 to 1.75 Å, with the average value being 1.71–1.72 Å, i.e. slightly less than for $2(PF_6)$. However, the Re–N(1)–C(37) bond angle of $172.4(7)^\circ$ in $2(PF_6)$ is essentially identical with the average angle of $173-174^\circ$ found in the aforementioned rhenium imido complexes [5].

Imido-rhenium(V) bonding in octahedral complexes such as $Re(NPh)Cl_3(PPh_3)_2$ [20] has been described principally in terms of the resonance structure $Re \equiv NR$ which considers NR^{2-} to be a 6-electron donor [5]. The presence of an essentially linear ReNC moiety together with only a slightly longer Re-N bond distance suggest that a similar description is appropriate for 2. However, some contribution from a linear $M \equiv NR$ representation, with the NR^{2-} donating 4 electrons, may be important as well.

3.3. Reactivity

A preliminary study v/as undertaken to learn how the complexes $[ReH_2(NR)(Cyttp)]^+$ (2-4) compare in reactivity with the oxo complex $[ReH_2(O)(Cyttp)]^+$ (1).

Complex 1(SbF₆) undergoes facile reactions with CO to give the η^2 -formato-O,O' complex shown in Eq. (1), and with SO₂ to afford the 1:1 η^2 -sulfito-O,O' adduct [1]. In contrast, however, 2-4(Tf) were found to be inert toward CO even at temperatures up to 65°C. Furthermore, 2(Tf) failed to react with SO₂ in THF or acetone solution at 25– 60°C. The strongly electrophilic [Me₃O]BF₄ and [El₃O]BF₄ also did not react with 2(Tf) in CH₂Cl₂ solution. Complex 2(Tf) does, however, react with anhydrous HCl in diethyl ether to yield known [12] $\text{ReCl}_3(\text{Cyttp})$ (Eq. (3)).

$$[\operatorname{ReH}_{2}(\operatorname{NC}_{6}\operatorname{H}_{4}\operatorname{Me}_{p})(\operatorname{Cyttp})]^{+} + \operatorname{HCl} \rightarrow \operatorname{ReCl}_{3}(\operatorname{Cyttp}) \quad (3)$$

Reactions of metal oxo or imido complexes with hydrogen halides are known to proceed by protonation of the named ligand and substitution by halide ions, generally without change in the oxidation number of the metal [4]. However, in some cases, reduction of the metal has been observed, as it was in this study.

Treatment of 2(Tf) with NaBH₄ in THF solution afforded ReH₅(Cyttp) (Eq. (4)).

 $[\operatorname{ReH}_2(\operatorname{NC}_6H_4\operatorname{Me}_p)(\operatorname{Cyup})]^+ + \operatorname{NaBH}_4$

 $\rightarrow \text{ReH}_5(\text{Cyttp})$ (4)

This conversion is strictly analogous to that of 1(Tf) by LiBEt₃H or NaH also to give ReH₅(Cyttp) [2].

In summary, initial studies on reactions of the rhenium imido complexes 2-4 seem to indicate that these compounds are less reactive than their oxo relative 1. However, further investigations are necessary to understand the chemistry of these complexes.

4. Supplementary material

Hydrogen atom positional parameters, anisotropic thermal parameters, complete listings of bond distances and angles, and observed and calculated structure factors for $2(PF_6)$ are available on request from the authors.

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