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COMPLEXES OF RHENIUM(V) WITH AMINOACETOPHENONES AND THEIR REACTIONS WITH SOME BIDENTATE LIGANDS

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ABSTRACT. Complexes of rhenium(V) with 2-, 3- and 4-aminoacetophenone (H_2aap) have been synthesized. The reaction of *trans*-$ReOCl_3(PPh_3)_2$ with 2-H_2aap in benzene yielded the imido complex [Re(2-aap)$Cl_3(PPh_3)$], in which the oxo oxygen and one of the PPh_3 groups were substituted by the dianionic imido nitrogen and the neutral ketonic oxygen, respectively. With 3- and 4-H_2aap the imido complexes *trans*-[Re(aap)$Cl_3(PPh_3)_2$] were isolated. The monodentate coordination mode of these latter two ligands was authenticated by the X-ray crystal structure of *trans*-[Re(3-aap)$Cl_3(PPh_3)_2$]; crystals are triclinic, *P1*, with a = 10.567(5), b = 11.989(6), c = 18.739(8) Å, α = 74.82(4)°, β = 75.27(4)°, γ = 73.15(4)°, U = 2152(2) Å^3, Z = 2, R = 0.0469. The further reaction of [Re(3-aap)$Cl_3(PPh_3)_2$] with the bidentate ligands 2-aminophenol and 8-hydroxyquinoline (HL) led to the isolation of complexes of the type [Re(3-aap)$Cl_2(PPh_3)$(L)]. However, with 1,2-diaminobenzene (H_2dab), the 3-aap imido moiety was displaced by the imido group {$N(C_6H_4)NH_2$}, to give the complex *trans*-[Re(dab)$Cl_3(PPh_3)_2$].

KEY WORDS: Complexes of rhenium(V), Aminoacetophenone, Imido complex, Bidentate ligands, 2-Aminophenol, 8-Hydroxyquinoline

INTRODUCTION

There is currently a renewed interest in transition-metal imido chemistry, mainly due to its application in the synthesis of various nitrogen hetrocycles [1, 2] and in catalysis such as the hydro-amination of alkynes and cyclo-addition reactions with unsaturated organic substrates [3, 4].

Our involvement in rhenium(V)-imido complexes stems from the possible therapeutic applications of rhenium radiopharmaceuticals in nuclear medicine[5, 6]. The attractive nuclear properties of the ^{186}Re and ^{188}Re isotopes make them useful as potential radiotherapeutic agents for the treatment of malignant tumours of the skeleton, liver and kidneys and other organs in the pelvic cavity [7]. We believe that the incorporation of the Re=N-R core into a complex would allow the modification of the organic substituent R to manipulate the biodistribution of the radiopharmaceutical. In addition, the incorporation of functional groups in the organic moiety R may facilitate the linking of the rhenium(V) imido complex to biologically relevant molecules.

In this study, we have treated 2-, 3- and 4-aminoacetophenone (I, H_2aap) with *trans*-$ReOCl_3(PPh_3)_2$ to give the rhenium(V)-imido complexes Re(=N-R)$Cl_3(PPh_3)_2$ (II). The presence of the acetophenone entity in complexes II would enable the possible reaction of the coordinated imide with other amines, for example, to produce coordinated Schiff bases anchored through the imido nitrogen of aap^{2-}. Replacement of the Cl^- and PPh_3 coligands may then result in a large number of complexes whose biodistribution can be fine-tuned by imido substituents and ancillary ligands. This report deals with the synthesis of complexes II, and their reactions with 2-aminophenol (H_2amp), 8-hydroxyquinoline (Hquin) and 1,2-diaminobenzene (H_2dab).

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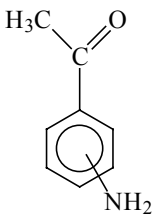

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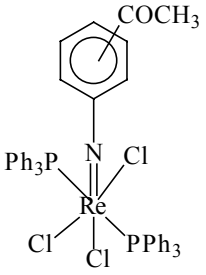


II

EXPERIMENTAL

Reagents

Trans-$ReOCl_3(PPh_3)_2$ was synthesized by a published procedure [8]. Solvents were reagent grade and were purified and dried before use. All other reagents were obtained commercially, and their purity was checked by ^1H NMR spectroscopy and melting point determination.

Physical measurements

The scientific instrumentation used was the same as reported elsewhere [9]. IR spectra were obtained in KBr discs and ^1H NMR spectra in $(CD_3)_2SO$, unless stated otherwise. Electronic spectra were all obtained in acetonitrile, and data are given as λ_{max}/nm with extinction coefficients (in units $M^{-1}cm^{-1}$) in parentheses. Elemental analyses for carbon, hydrogen and nitrogen were done by the Chemistry Department, University of the Western Cape, Cape Town. Crystal data were measured at room temperature on a Nicolet R3m/V diffractometer.

Synthesis

*[Re(2-aap)Cl$_3$(PPh$_3$)] (**1**)*. In a volume of 20 cm^3 of benzene, 103 mg (123 μmol) of *trans*-$ReOCl_3(PPh_3)_2$ and 26 mg (192 μmol) of 2-aminoacetophenone (2-H_2aap) were heated under reflux conditions for 21 h. After heating was discontinued and the solution cooled to room temperature, an olive green precipitate was obtained. The precipitate was filtered, washed with benzene and diethyl ether and dried under vacuum. Yield = 41%, m.p.= 220 °C(dec). Anal. calcd. for $C_{26}H_{22}NOCl_3PRe$ (mol. wt.= 688.0 g/mol): C, 45.39; H, 3.22; N, 2.04%. Found: C, 45.48; H, 3.20; N, 2.06. Infrared data: ν(C=O) 1495(m); ν(P-C) 1435(s); ν(Re/N-) 1095(m); ν(Re-Cl) 320(m), 288(m). NMR data δ_H: 2.66 (s, 3H, C*H*$_3$); 7.03 (d, 1H, *H*^{3}); 7.16 (t, 1H, *H*^{4}); 7.73 (t, 1H, *H*^{6}); 7.48-7.65 (m, 16H, *H*^{5} and P*Ph*$_3$). UV-Vis: 482(sh); 365(5520); 258(2360).

*[Re(3-aap)Cl$_3$(PPh$_3$)$_2$] (**2**)*. A solution of 108 mg (130 μmol) of *trans*-$ReOCl_3(PPh_3)_2$ and 27 mg (200 μmol) of 3-aminoacetophenone (3-H_2aap) in 20 cm^3 of benzene was heated under reflux for 17 h, resulting in a green solution. After heating was discontinued, the solvent was removed on the rotavaporator, and the green residue dissolved in 25 cm^3 of acetone. The resultant solution was filtered, and allowed to evaporate at room temperature yielding green crystals, which were filtered off, washed with ethanol, and dried under vacuum. Yield = 84%, m.p. = 185 °C. Anal. calcd. for $C_{44}H_{37}NOCl_3PRe$ (mol.wt. = 950.30 g/mol): C, 55.61; H, 3.92; N, 1.47%. Found: C, 55.79; H, 3.84; N, 1.50%. Infrared data: ν(C=O) 1687(s); ν(Re/N-) 1089(m); ν(Re-Cl) 315(m),

298(m). NMR data δ_H ($CDCl_3$): 2.27 (s, 3H, CH_3); 6.82 (t, 1H, H^5); 6.96 (d, 1H, H^6); 7.10 (s, 1H, H^2); 7.16 (m, 15H, PPh_3); 7.71-7.77 (m, 15H, PPh_3); 7.95 (d, 1H, H^4). UV-Vis: 402 (3210); 331 (9570); 259 (40200).

*[Re(4-aap)Cl_3(PPh_3)$_2$] (**3**)*. A mixture of 105 mg (126μmol) of *trans*-$ReOCl_3(PPh_3)_2$ and 26 mg (195 μmol) of 4-aminoacetophenone in 20 cm^3 of benzene was heated under reflux for 17 h. The same procedure as for complex **2** was followed, yielding yellow-brown crystals which were filtered off, washed with ethanol and dried under vacuum. Yield = 64%, m.p. = 199 °C. Anal. calcd. for $C_{44}H_{37}NOCl_3PRe$ (mol. wt. = 950.30 g/mol): C, 55.61; H, 3.92; N, 1.47%. Found: C, 55.63; H, 3.86; N, 1.48%. Infrared data: ν(C=O) 1685(s); ν(Re/N-) 1091 (m); ν(Re-Cl) 322(m), 301(m). NMR data δ_H($CDCl_3$): 2.54 (s, 3H, CH_3); 6.80 (d, 1H, H^3 and H^5); 7.19 (m, 15H, PPh_3); 7.28 (d, 1H, H^2 and H^6); 7.69-7.75 (m, 15H, PPh_3). UV-Vis: 411 (2300); 340 (13900); 262 (39800).

*[Re(3-aap)Cl_2(PPh_3)(Hamp)] (**5**)*. A mixture of 67mg (70 μmol) of complex **2** and 17 mg (154 μmol) of 2-aminophenol (H_2amp) in 18 cm^3 of benzene was heated under reflux for 2.5 h and then cooled to room temperature. The yellow-green precipitate obtained was filtered, washed with benzene and diethyl ether, and dried under vacuum. Yield = 63%, m.p. = 180 °C(dec). Anal. calcd. for $C_{32}H_{28}N_2O_2Cl_2PRe$ (mol. wt. = 760.69 g/mol): C, 50.52; H, 3.71; N, 3.68%. Found: C, 50.63; H, 3.76; N, 4.00%. Infrared data: ν(NH_2) 3215(m), 3174(m); ν(C=O) 1681(s); δ(NH_2) 1603(m); ν(P-C) 1485(s); ν(Re/N-) 1095(m); ν(C-O) 1279(m); ν(ReN) 438(m); ν(Re-Cl) 318(m). NMR data δ_H: 2.48 (s, 3H, CH_3); 6.20 (d, 1H, $H^{6'}$ of Hamp); 6.57 (t, 1H, $H^{5'}$ of Hamp); 6.91 (t, 1H, H^5 of 3-aap); 7.41 (m, 15H, PPh_3); 7.63 (m, 4H, H^2 and H^6 of 3-aap, and $H^{3'}$ and $H^{4'}$ of Hamp); 8.14 (d, 1H, H^4 of 3-aap); 8.65 (br s, 2H, NH_2). UV-Vis: 420 (3890); 312 (13000); 293 (13500).

*[Re(3-aap)Cl_2(PPh_3)(quin)] (**6**)*. A mixture of 83 mg (87 μmol) of complex **2** and 19 mg (131 μmol) of 8-hydroxyquinoline in 20 cm^3 of ethanol was heated under reflux for 20 h. After heating was discontinued, the solution was cooled to room temperature and a golden brown precipitate was isolated. The product was washed with ethanol and diethyl ether and dried. Yield = 57%, m.p. = 197 °C(dec). Anal. calcd. for $C_{35}H_{28}N_2O_2Cl_2PRe$ (mol. wt. = 796.69 g/mol): C, 52.77; H, 3.54; N, 3.52%. Found: C, 52.67; H, 3.79; N, 3.41%. Infrared data: ν(C=O) 1692(s); ν(C=N) 1576(s); ν(Re/N-) 1095(m); ν(Re-N) 448(m); ν(Re-O) 353(m); ν(Re-Cl) 319(m). NMR data δ_H: 2.48 (s, 3H, CH_3 of 3-aap); 6.75 (d, 1H, $H^{3'}$ of quin); 7.48 – 7.57 (m, 2H, $H^{1'}$ and $H^{6'}$ of quin); 7.42 (m, 10H); 7.59 – 7.69 (m, 8H); 7.77 (t, 1H, H^5 of 3-aap); 8.10 (s, 1H, H^2 of 3-aap); 8.29 (d, 1H, H^6 of 3-aap); 8.38 (d, 1H, H^4 of 3-aap). UV-Vis: 591 (390); 384 (9050); 320(sh); 255 (41400).

*[Re(1,2-dab)Cl_3(PPh_3)$_2$] (**7**)*. To a volume of 25 cm^3 of ethanol was added a mass of 89 mg (94 μmol) of complex **2** and 12 mg (111 μmol) of 1,2-diaminobenzene (H_2dab). The resultant solution was heated under reflux for 4 h. After allowing the solution to cool to room temperature, a bright red precipitate was obtained. Yield = 60%, m.p. = 191 °C(dec). Anal. calcd. for $C_{42}H_{36}N_2Cl_3P_2Re$ (mol. wt. = 923.3 g/mol): C, 54.64; H, 3.93; N, 3.03%. Found: C, 54.41; H, 3.90; N, 2.96%. Infrared data: ν(NH_2) 3395(m), 3311(m); δ(NH_2) 1625(s); ν(C-N) 1306(s), 1256(s); ν(Re/N-) 1091(s); ν(P-C) 1434(s); ν(Re-Cl) 315(m), 295(m). NMR data δ_H: 4.39 (br s, 2H, NH_2); 6.84 (m, 2H, H^1 and H^4); 6.96 (m, 2H, H^5 and H^6); 7.44-7.63 (m, 30H, PPh_3)). UV-Vis (DMF): 482 (3290); 372 (1790); 325 (2900); 266 (14800).

Crystallography

The recrystallization of complex **2** from acetone yielded green crystals suitable for structure analysis. Details of the crystal data, measurements of intensities and data processing are summarized in Table 1. The bond lengths and angles for complex **2** are listed in Table 2. The hydrogen atom coordinates, isotropic displacement parameters, and the anisotropic displacement coefficients are available as supplementary data from the authors.

Table 1. Crystal data and structure refinement.

Empirical formula	$C_{45.50}H_{40}Cl_3NO_{1.50}P_2Re$
Formula weight	979.28
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	*a* = 10.567(5) Å alpha = 74.82(4)°
	b = 11.989(6) Å beta = 75.27(4)°
	c = 18.739(8) Å gamma = 73.15(4)°
Volume, Z	2152(2) $Å^3$, 2
Density (calculated)	1.512 mg/m^3
Absorption coefficient	3.121 mm^{-1}
F(000)	976
Crystal size	0.5 x 0.3 x 0.1 mm
θ range for data collection	2.30 to 25.05°
Limiting indices	$0 < h < 12$, $-13 < k < 14$, $-21 < l < 22$
Reflections collected	7586
Independent reflections	7586 (R_{int} = 0.0000)
Absorption correction	Psi-scans
Max. and min. transmission	0.980 and 0.327
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7554 / 0 / 356
Goodness-of-fit on F^2	1.065
Final R indices [I>2σ(I)]	R1 = 0.0469, wR2 = 0.1226
R indices (all data)	R1 = 0.0517, wR2 = 0.1549

Table 2. Selected bond distances (Å) and angles (°) in $[Re(3\text{-aap})Cl_3(PPh_3)_2]$•½ Me_2CO.

	Molecule **A**	Molecule **B**
Re-Cl(1)	2.395(9)	2.440(8)
Re-Cl(2)	2.424(8)	2.408(8)
Re-Cl(3)	2.420(7)	2.362(7)
Re-P(1)	2.491(8)	2.483(7)
Re-P(2)	2.502(7)	2.490(8)
Re-N(1)	1.74(2)	1.73(2)
N(1)-Re-Cl(1)	87.9(6)	88.8(4)
N(1)-Re-Cl(2)	96.3(4)	95.5(4)
N(1)-Re-Cl(3)	174.7(4)	174.5(4)
N(1)-Re-P(1)	89.9(4)	90.7(4)
N(1)-Re-P(2)	96.0(4)	94.2(4)
Cl(1)-Re-Cl(2)	175.1(4)	174.7(3)
P(1)-Re-P(2)	173.3(3)	172.9(3)
Re-N(1)-C(1)	177(2)	179(2)

Data collection and processing, structure analysis and refinement

The complex appears to have a centre of symmetry which was removed by the presence of a solvent molecule. Refinement was attempted using $P\bar{1}$, but the *P1* space group produced a better fit of the data.

Data were corrected for Lorentz, polarization and absorption effects. The structures were solved by heavy atom methods and refined using the SHELXTL/PC [10] and SHELXL-93 [11] suite of programs. The refinement was performed using weighted full-matrix least squares on F^2. In the final least-squares cycle, the non-hydrogen atoms were refined anisotropically.

Of the 7586 reflections that were collected, 7117 were unique with $I \geq 2\sigma(I)$. The final *R* factor was 0.047, *wR*2 = 0.123 and the goodness of fit = 1.065 for all observed reflections.

RESULTS AND DISCUSSION

Reactions of trans-$ReOCl_3(PPh_3)_2$ with H_2aap

The reaction of *trans*-$ReOCl_3(PPh_3)_2$ with 2-aminoacetophenone (2-H_2aap) in boiling benzene yielded an olive-green precipitate of the complex [Re(2-aap)$Cl_3(PPh_3)$] (**1**). The analysis of this product reveals that the ligand coordinates as a bidentate *N,O*-donor chelate, through the dianionic deprotonated imido nitrogen and the neutral acetophenone oxygen atom. The same reaction with the ligands 3- and 4-aminoacetophenone resulted in complexes of the type *trans*-[Re(n-aap)$Cl_3(PPh_3)_2$] in very good yields. The complex *trans*-[Re(3-aap)$Cl_3(PPh_3)_2$] (**2**) was isolated as green crystals and *trans*-[Re(4-aap)$Cl_3(PPh_3)_2$](**3**) as golden-brown crystals. In **2** and **3** the ligands coordinate as dianionic monodentate nitrogen-donors resulting in rhenium(V)-imido complexes.

In the IR spectrum of **1**, the Re=N- stretching frequency appears as a medium band at 1095 cm^{-1}, which falls within the range (1000-1200 cm^{-1}) normally observed for rhenium(V)-imido complexes [12]. The absence of the NH_2 stretch vibration, which appears as two sharp bands at 3464 and 3342 cm^{-1} in the free ligand, supports the coordinated mode of 2-aap. The band attributable to ν(C=O) has shifted dramatically to 1495 cm^{-1} from 1645 cm^{-1} in the free ligand, indicating coordination of the ketonic oxygen to rhenium(V). The Re-Cl stretching frequencies are assigned to the two bands of medium intensities at 320 and 288 cm^{-1}, with the latter band due to the chloride coordinated *trans* to the imido group.

In the ^{1}H NMR spectrum of **1** a singlet at δ2.66 ppm is assigned to the methyl protons of 2-aap (at 2.37 ppm in the free ligand). The doublet at 7.03 ppm is assigned to the proton H^3, and the two triplets at 7.16 and 7.73 to H^4 and H^5, respectively. A multiplet at 7.48-7.65 ppm integrates for 16 protons and is attributed to H^6 and the protons of the triphenylphosphine group. The IR spectra of **2** and **3** display Re=N- stretching frequencies at 1089 and 1091 cm^{-1} respectively. The ν(C=O) of **2** and **3** are observed as strong bonds at 1687 and 1685 cm^{-1}, with the Re-Cl stretches at 315 and 298 cm^{-1} for **2**, and at 322 and 301 cm^{-1} for **3**.

The proton spectra (in $CDCl_3$) of **2** and **3** display the methyl protons at δ 2.27 and 2.54 ppm, respectively. The signal of proton H^5 in **2** appears as a triplet at 6.82 ppm, with the two doublets at 6.95 and 7.96 ppm being assigned to H^6 and H^4, respectively. A singlet at 7.10 ppm is attributed to H^2. The two multiplets observed at 7.16 and 7.71-7.77 ppm are the result of the presence of the two PPh_3 groups in **2** (at 7.19 and 7.69-7.75 ppm for **3**). The spectrum of **3** reveals two doublets at 6.80 and 7.28 ppm, each integrating for two protons. The former is assigned to H^2 and H^6, and the latter to H^3 and H^5.

Complex **1** is soluble in acetonitrile, dichloromethane, chloroform, acetone and ethanol, in which it gives a yellow-green solution. Complexes **2** and **3** are insoluble in ethanol, but soluble

in the other solvents. The complexes are diamagnetic (no paramagnetic broadening observed in the ^{1}H NMR spectra) and stable for long periods in solution and in the solid state.

Crystal structure of [Re(3-aap)$Cl_3(PPh_3)_2$•½Me_2CO]

The structure of complex **2** is shown in Figure 1. The monomeric neutral octahedral complex is formally a rhenium(V) species with the phenylimido unit formally a dianionic ligand. The asymmetric unit consists of two complexes **A** and **B** together with one molecule of Me_2CO. The phenylimido ligand is roughly perpendicular to the mean equatorial plane (dihedral angle of 87.9° in **A** and 87.3° in **B**). **A** and **B** are superimposable and the metric parameters do not differ by more than two esd's. For example, the Re-N(1)-C(1) angle is 174.7(4)° and 174.5(4)° in **A** and **B**, respectively.

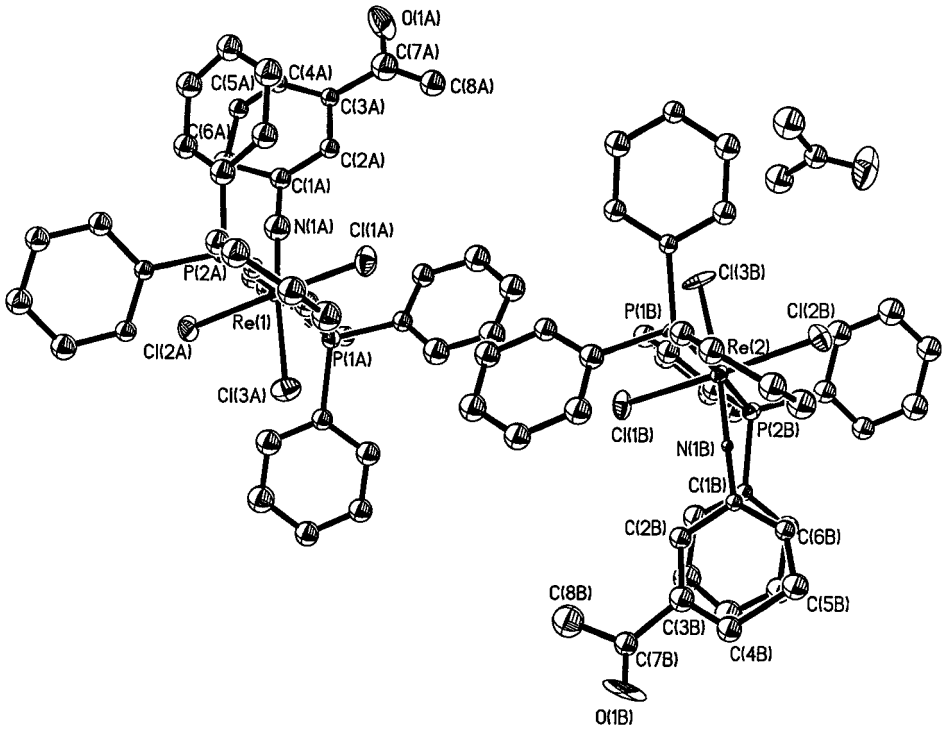


Figure 1. The ORTEP diagram of the structure of *trans*-[Re(3-aap)$Cl_3(PPh_3)_2$] depicting the atom labelling scheme and 40% thermal ellipsoids probability.

These values, as well as the bond lengths, agree well with those reported for other rhenium(V) phenylimido octahedral complexes [13-16]. In both **A** and **B** the Re(V) ion is displaced from the mean equatorial plane Cl(1)P(1)Cl(2)P(2) by 0.10 Å towards N(1).

The crystal structure of [Re(4-aap)$Cl_3(PEt_2Ph)_2$] (**4**) has previously been reported [17], and it was synthesized by reacting the substituted aniline with $ReOCl_3(PEt_2Ph)_2$ in benzene [18]. The Cl_{trans}-Re-NR bond angle of **4** is given as 175.02(17)°, which is similar to that [174.7(4)°] of **2**. Data for the two complexes are given in Table 3. Although the Re-Cl bond lengths correspond well, the Re-P bond lengths of **4** are shorter than those of **2**, suggesting that there is less steric

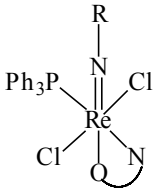
hindrance amongst the ligands in the complex containing PEt_2Ph as the phosphine ligand. The Re=N- bond length of **2** is also significantly longer than that in **4**, mainly due to steric crowding around the Re(V) centre in **2**. However, it compares well with distances of 1.740(6) and 1.735(5) Å found for this bond in $[Re(NPh)(bipy)_2(OEt)](PF_6)_2$ and $[Re(NPh)(o\text{-bpy})(OEt)](PF_6)_2$ (bpy = 1,2-bis(2,2'-bipyridyl-6-yl)ethane) [15, 16].

Table 3. A comparison of relevant bond lengths in the complexes $[Re(3\text{-aap})Cl_3(PPh_3)_2]$ and $[Re(4\text{-aap})Cl_3(PEt_2Ph)_2]$.

Complex	Re=N-	Re-Cl_{trans}	Re-Cl_{cis}	Re-P
$Re(3\text{-aap})Cl_3(PPh_3)_2$	1.74(2)	2.420(7)	2.410(9)	2.497(8)
$Re(4\text{-aap})Cl_3(PEt_2Ph)_2$	1.69(1)	2.410(3)	2.416(3)	2.459(4)

*Reactions of **2** with H_2amp and Hquin*

The reaction of **2** with 2-aminophenol and 8-hydroxyquinoline led to the substitution of chloride and triphenylphosphine to give the complexes $[Re(3\text{-aap})Cl_2(PPh_3)(L)]$ (L = Hamp (**5**), quin (**6**)). In these complexes the ligands Hamp and quin behave as monoanionic *N,O*-donor chelates, coordinating through the anionic phenolic oxygen and the neutral amino (in **5**) and pyridine (in **6**) nitrogen atoms. Experimental evidence suggests that the anionic oxygen-donor atoms of Hamp and quin are coordinated *trans* to the imido nitrogen of 3-aap:



The IR spectra of **5** and **6** clearly show the presence of the ligands Hamp and quin. The Re=N- stretching frequency appears at 1095 cm^{-1} in both complexes, and the carbonyl stretching frequencies ν(C=O) of 3-aap are seen at 1681 and 1692 cm^{-1} in **5** and **6**, respectively. The coordinated amino group in **5** gives rise to two medium bands at 3215 and 3174 cm^{-1} (ν(NH)). The presence of only one band at 318 cm^{-1} (ν(Re-Cl)) for both **5** and **6** indicates that the chlorides are in equivalent positions, i.e. *trans* to each other.

In the proton NMR spectrum of **5**, the protons of the NH_2 group of Hamp appear as a broad singlet at δ8.65 ppm (at 4.38 ppm in the free ligand), indicating coordination through the neutral nitrogen. Assignment of all the other signals for **5** and **6** are given in the Experimental section, and there are no unusual features.

Both complexes are diamagnetic (no paramagnetic broadening in the ^1H NMR spectra), and they are soluble and stable in DMF, acetonitrile, acetone and dichloro-methane.

Reaction of 2 with H_2dab

The reaction of 1,2-diaminobenzene (H_2dab) with **2** in ethanol did not lead to the displacement of either the chloride or phosphine ligands, but led to the substitution of the imido-coordinated 3-aap to give the product $[Re(dab)Cl_3(PPh_3)_2]$(**7**).

In the IR spectrum of **7** the sharp band at 1091 cm^{-1} indicates the presence of the Re=N- moiety originating from the coordinated dab^{2-}. The ν(C=O) of 3-aap at 1687 cm^{-1} in **2** is absent in the spectrum of **7**. Two peaks at 3395 and 3311 (ν(NH)) show the presence of the

uncoordinated NH_2 group of dab^{2-}, while the presence of two equivalent chlorides *cis* to the imido group and one in the *trans* position is indicated by two peaks at 315 and 295 cm^{-1} respectively. In fact, the IR, ^1H NMR and UV-Vis spectra and melting point of **7** are identical to that of $[Re(dab)Cl_3(PPh_3)_2]$, which was reported earlier in the literature [19].

The displacement of 3-aap from **2** by dab^{2-} to form **7** is surprising. Instead of coordinating as a bidentate *N,N*-donor, or condensing with the ketonic oxygen to form a coordinated Schiff base, the ligand dab^{2-} bonds in the imido form. One plausible explanation could be the greater stability of **7** relative to **2**. The acetyl group of 3-aap is electron withdrawing, making the amino group a weaker electron-donor. Thus, in the imido form, the ligand dab^{2-} is preferred to $3\text{-}aap^{2-}$ by the high oxidation state Re(V).

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