Rhodium Mediated N−O Bond Formation

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Reaction of [Rh(phen)$_2$Cl$_2$]Cl (phen = 1,10-phenanthroline) with the ligand 3,5-bis(pyridin-2-yl)-1,2,4-triazole (Hbpt) in H_2O at pH 9 gives rise to the formation of a single stable compound. Single-crystal X-ray analysis of this material reveals that in the product obtained an oxygen atom has been inserted between the Rh(phen)$_2$ moiety and the triazole ring of the bpt ligand yielding a compound of the type [Rh(phen)$_2$(Obpt)](PF$_6$)$_2$·0.767CH$_3$CN·0.28H$_2$O. Insertion of oxygen in this manner has not been reported previously.

Introduction

A considerable amount of research has been dedicated to the study of ligand-bridged polynuclear transition metal complexes.[1] This particular class of complexes has been used as a basis for studying electron transfer processes with the aim of creating multicomponent systems (supramolecular systems) capable of effecting useful light- and/or redox-induced functions. Most of the initial systems developed incorporated ruthenium(II) polypyridine compounds, although systems incorporating other transition metals such as rhodium(III), osmium(II) and iridium(III) have also been investigated.[2−5]

We have recently started a systematic investigation into the photophysical properties of mixed ligand rhodium(III) complexes. These studies are aimed at achieving a better understanding of the way in which the excited states of rhodium(III) complexes are affected by the introduction of ligands other than polypyridyl ligands. In these studies the ligands investigated are based on substituted 1,2,4-triazole moieties. Through well-established synthetic routes both π accepting and σ donating groupings can be introduced and these triazole based ligands have been shown to promote interactions between metal centres in dinuclear structures via deprotonation of the triazole ring. As a result a wide range of both mononuclear and dinuclear complexes of ruthenium(II) and osmium(II) incorporating these ligands has been reported.[6] An additional interest in these ligands is due to their asymmetry, which allows for different coordination modes. Of particular interest are ligands such as 3,5-bis(pyridin-2-yl)-1,2,4-triazole (Hbpt) (for structure see Figure 1) for which mononuclear and dinuclear Ru^{II} and Os^{II} complexes have been reported.[5] Orthometallated Rh^{III} complexes with Hbpt and the related ligand 4-amino-3,5-bis(2-pyridyl)-4*H*-1,2,4-triazole (bptNH$_2$) have also been reported,[7−9] as have Rh^{I} complexes with the ligands Hbpt and bptNH$_2$.[10−11] In this paper we wish to report on a very unusual reaction product obtained when a rhodium(III) precursor is reacted with Hbpt. In the compound obtained an oxygen atom has inserted into the Rh^{III}-nitrogen bond. To the best of our knowledge this is the first time that such an insertion reaction has been observed.

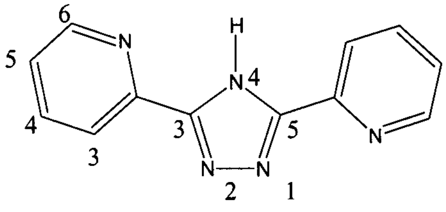

Figure 1. 3,5-bis(pyridin-2-yl)-1,2,4-triazole (Hbpt)

Results and Discussion

[Rh^{III} bis(1,10-phenanthroline)Cl$_2$]Cl was reacted with Hbpt in aqueous solution at pH 9. The product obtained was purified by column chromatography and precipitated

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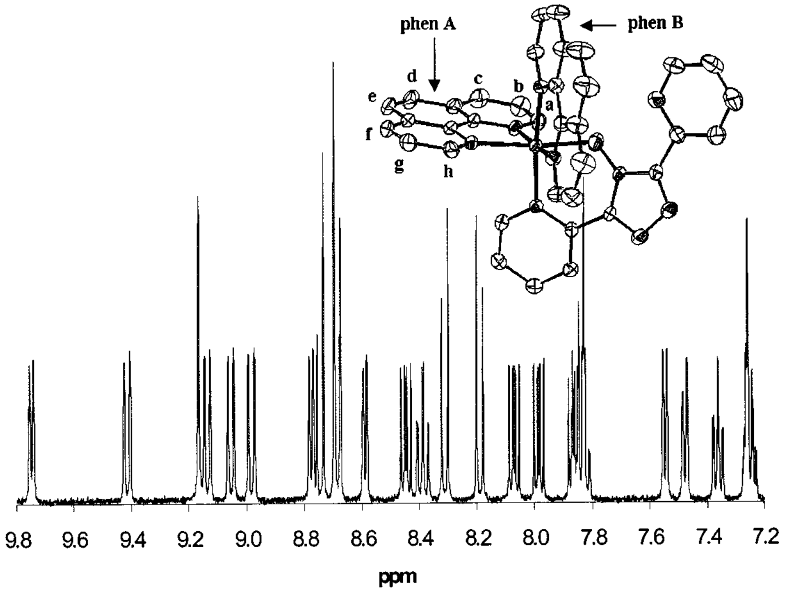

Figure 2. ^1H NMR spectrum $[Rh(phen)_2(Obpt)](PF_6)_2$ in [D_6]DMSO

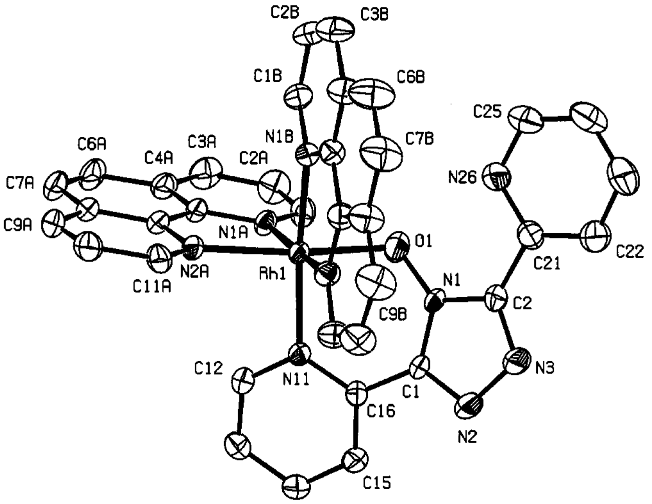

Figure 3. Molecular structure of the cation in $[Rh(phen)_2(Obpt)](PF_6)_2$; hydrogen atoms, counterions and the solvent molecules have been omitted for clarity

as a PF_6^- salt. NMR spectroscopy shows the presence of a single product (see Figure 2). Upon further recrystallisation of the product from acetonitrile/toluene (7:3) yellow needles were obtained. A single crystal X-ray investigation yielded the molecular structure, the cation of which is depicted in Figure 3. X-ray collection parameters are listed in Table 1 and selected bond lengths and angles are given in Table 2 and Table 3, respectively.

The most striking feature of the molecular structure is the presence of an oxygen atom between the metal centre and the triazole nitrogen atom. The rhodium centre is further surrounded by the two 1,10-phenanthroline ligands and the sixth coordination site is taken up by a pyridine ring of the bpt ligand. Two disordered PF_6^- counterions

Table 1. Crystallographic data for $[Rh(phen)_2(Obpt)](PF_6)_2\cdot 0.767CH_3CN\cdot 0.28H_2O$

Chem formula	$C_{36}H_{26}F_{12}N_9OP_2Rh\cdot 0.767CH_3CN\cdot 0.28H_2O$
Mol. wt.	1029.05
a (Å)	13.2334(12)
b (Å)	20.507(3)
c (Å)	16.0732(15)
β (°)	103.620(6)
Z	4
Volume (Å^3)	4239.3(8)
System, space group	monoclinic, $P2_1/m$
Crystal size	0.43 × 0.10 × 0.08
Temperature	297(2) K
F(000)	2059
Radiation, λ (Å)	Mo-K_α, 0.71073
D_{calcd}, g·cm^{-3}	1.612
Abs coeff, μ (mm^{-1})	0.577
Abs corr T (min, max)	0.791, 0.958
θ range for data collection	2 to 26°
Reflections collected	8528
Unique, $>2\sigma(I)$	8164, 5460
Parameters	709
Restraints	288
R (F_o)	0.062
R_w (F_o)	0.149
Residual electron density	+0.76, −0.68

Table 2. Selected bond lengths (Å) for $[Rh(phen)_2(Obpt)](PF_6)_2\cdot 0.767CH_3CN\cdot 0.28H_2O$

Rh1−O1	2.016(4)	Rh1−N11	2.086(5)
Rh1−N1A	2.034(4)	Rh1−N2A	2.105(4)
Rh1−N2B	2.035(5)	N1−O1	1.406(6)
Rh1−N1B	2.039(5)	N1−C1	1.342(7)
		N1−C2	1.372(7)

Table 3. Selected bond angles (°) for $[Rh(phen)_2(Obpt)](PF_6)_2 \cdot 0.767CH_3CN \cdot 0.28H_2O$

O1−Rh1−N1A	91.5(2)	N1A−Rh1−N2B	174.2(2)
O1−Rh1−N2A	171.4(2)	N1A−Rh1−N1B	93.6(2)
O1−Rh1−N1B	88.2(2)	N1B−Rh1−N2B	81.4(2)
O1−Rh1−N2B	91.4(2)	N1B−Rh1−N11	174.8(2)
O1−Rh1−N11	87.2(2)	N1−O1−Rh1	110.1(3)
Rh1−O1−N1−C1	56.3(6)		

and partial site occupancy acetonitrile (0.767) and water solvent molecules (0.28) complete the crystal structure (not depicted). The Rh−O bond length is 2.016(4) Å, in the range expected for Rh−O bond lengths. For example, in the diacetyl monooxime Rh^{III} complex reported by Moszner et. al., typical Rh−O bond lengths are 2.028Å and 2.023Å.[12] The N−O bond length is 1.406(6) Å and typical of an N−O single bond. The presence of the oxygen atom causes a substantial *trans* effect. The Rh−N distance *trans* to the oxygen atom is 2.105(4) Å, which is about 0.07 Å longer than the other three rhodium-nitrogen distances. A number of other rhodium polypyridyl crystal structures have been reported. Paul et al. have reported Rh−N bond lengths of 1.990(5), 2.059(5) and 2.036(5) Å in a rhodium(II) complex with the ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine and bond lengths of 2.027(10), 2.031(10), 2.083(9) and 2.071(9) Å were found by Brewer et al. in the case of the rhodium(III) complex with the ligand 2,3-bis(2-pyridyl)quinoxaline.[13,14] The X-ray structure of a ruthenium(II) complex with the ligand Hbpt has also been reported.[15]

The NMR spectrum shown in Figure 2 clearly indicates the presence of only one species, indicative of the absence of linkage isomers. This is in contrast with the behaviour of most common triazole complexes.[16,17] 2-D COSY spectroscopic techniques were used to assign the ^1H resonances where possible. The doublets observed at $\delta = 9.75$ and 9.42 can be attributed to the protons at positions **a** and **c** of the phenanthroline ring **A** respectively. These resonances are downfield with respect to the resonances observed for the equivalent protons in the $[Rh(phen)_3]^{3+}$ complex and this can be attributed to the influence of the oxygen in the rhodium complex.[18] The source of the singlet at $\delta = 9.17$ has yet to be determined. Deuteration of the $[Rh(phen)_2(Obpt)](PF_6)_2$ is currently being undertaken in order to unambiguously assign all of the resonances.

The emission spectrum obtained at 77 K in a 4:1 ethanol/methanol glass for $[Rh(phen)_2(Obpt)](PF_6)_2$ can be seen in Figure 4. This structured emission, with maxima at 453 nm, 482 nm and 513 nm, is typical of ligand-centred (LC) phosphorescence of rhodium(III) phenanthroline complexes.[19] This indicates that the lowest LC excited state in this heteroleptic complex lies on the phen ligands.

An insertion of oxygen, as observed in this case, has not been reported previously. The only slightly related compound reported in the literature is a Rh^I complex with the ligand $bptNH_2$.[11] In the complex [Rh(NHbpt)(diolefin)], where the diolefin is for example 2,2,2-octatriene, NMR spectroscopy and elemental analysis suggest that an isoelectronic Rh−NH−N-triazole bond is formed. The mechanism responsible for the formation of $[Rh(phen)_2(Obpt)](PF_6)_2$ can at present only be tentatively formulated. The fact that the reaction described here is carried out in basic solution may indicate that a rhodium hydroxy intermediate is formed by replacement of the chloride atom by water and subsequent deprotonation [Equation (1)]. Interaction between the OH group and the triazole ring may then result in the formation of the N−O bond. In order to account for the oxidative nature of this step, a likely mechanism is the formation of an intermediate Rh^I complex [Equation (2)] which is subsequently reoxidised by oxygen [Equation (3)]. The overall reaction would then amount to a rhodium-mediated oxidation of the ligand by molecular oxygen [Equation (4)].

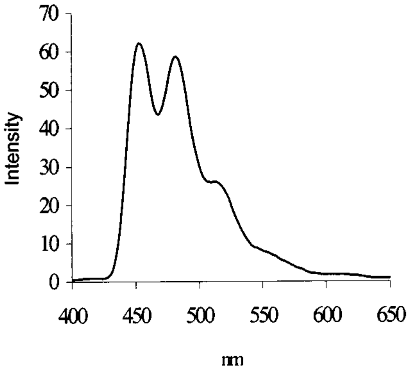

Figure 4. Emission spectra of $[Rh(phen)_2(Obpt)](PF_6)_2$ obtained in an ethanol/methanol 4:1 glass at 77 K

$$[Rh^{III}(phen)_2Cl_2]^+ + Hbpt + H_2O \rightarrow [Rh^{III}(phen)_2(OH)bpt]^+ + 2H^+ + 2Cl^- \quad (1)$$

$$[Rh^{III}(phen)_2(OH)bpt]^+ \rightarrow [Rh^I(phen)_2(Obpt)] + H^+ \quad (2)$$

$$[Rh^I(phen)_2(Obpt)] + 2H^+ + 1/2O_2 \rightarrow [Rh^{III}(phen)_2(Obpt)]^{2+} + H_2O \quad (3)$$

$$[Rh^{III}(phen)_2Cl_2]^+ + Hbpt + 1/2O_2 \rightarrow [Rh^{III}(phen)_2(Obpt)]^{2+} + 2Cl^- + H^+ \quad (4)$$

Interestingly no *N*-hydroxytriazoles have been reported in the literature. The formation of this N−O bond is therefore clearly dependent on the presence of the rhodium centre. Recently the formation of Rh^I−O−C bond via a Rh-hydroxy intermediate has been reported for the compound $[C_5(CH_3)_5]RhO(C_6F_4)CF_2]$.[20]

Conclusion

The reaction product reported upon reaction of $[Rh(phen)_2Cl_2]Cl$ and Hbpt is a very unusual one. In the complex obtained an oxygen atom has been inserted between the rhodium centre and the triazole ring. We are at present engaged in a systematic study of the interaction between rhodium polypyridyl centres and triazole type ligands. In this investigation we aim to further develop this chemistry and to determine the factors that control this unusual behaviour.

Experimental Section

Materials: Rhodium(III) chloride hydrate and 1,10-phenanthroline were purchased from Aldrich. [Rh(1,10-phenthroline)$_2$Cl$_2$]Cl and 3,5-bis(pyridin-2-yl)-1,2,4-triazole (Figure1) were prepared by previously reported procedures.[21,22]

Instrumentation: NMR spectra were obtained on a Bruker AC 400 MHz spectrometer. The peak positions are relative to TMS and the spectra were converted from their FID profiles using a Bruker WINNMR software package. Low temperature emission spectra were obtained at 77 K in a 4:1 ethanol/methanol glass using a Perkin−Elmer LS50B instrument. Elemental analysis on C, H and N was carried out at the Microanalytical Laboratory at University College Dublin (UCD) using an Exador analytical CE440.

Preparation of the Complex: Hbpt (0.3 mmol) was dissolved in H_2O at pH 9. [Rh(phen)$_2$Cl$_2$]Cl (0.1 mmol) was then added and the reaction mixture was refluxed for 8 hours. Purification was carried out using a Sephadex C-25 column. Unreacted ligand was removed with distilled water and the product was eluted using 0.1 M NaCl. The complex was precipitated by the addition of a saturated aqueous solution of NH_4PF_6 to the required fraction. Yield: 0.033 g, 32%. Crystals were obtained by recrystallisation from a minimum amount of acetonitrile/toluene (7:3). ^{1}H NMR spectroscopy was carried in [(CD$_3$)$_2$SO] and the resonances observed have been tentatively assigned as follows: **phenanthroline A:** δ = 9.75 (d, 1Ha), 8.45 (dd, 1Hb), 9.41 (d, 1Hc), 8.74 (d, 1Hd), 8.68 (d, 1He), 9.13 (d, 1Hf), 7.98 (dd, 1Hg), 8.59 (d, 1Hh); **phenanthroline B:** δ = 8.98 (d, 1Ha), 8.07 (dd, 1Hb), 8.78 (d, 1Hc), 8.31 (d, 1Hd), 8.19 (d, 1He); **bpt:** δ = 8.68 (d, 1H6), 8.39 (dd, 1H5), 7.36 (dd, 1H4), 7.48 (d, 1H3). It was not possible to assign the resonances at δ = 9.17 (s, 1 H), 9.05 (d, 1 H), 7.9−7.8 (m, 3 H), 7.55 (d, 1 H), 7.26 (m, 2 H) unambiguously. [Rh(phen)$_2$(Obpt)](PF$_6$)$_2$·H$_2$O: calcd. C 42.83, H 2.60, N 12.49; found C 42.24, H 2.63, N 12.97. It should be noted that the sample for elemental analysis was recrystallised from ethanol/water.

CCDC-168699 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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