

SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMISTRY OF PHENYLIMIDO-RHENIUM(V) COMPLEX OF 1,4,7-TRIAZACYCLONONANE (TACN)

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Abstract—The complex $[\text{Re}(\text{NPh})(\text{OH})(\text{PPh}_3)(\text{tacn})]^{2+}$ (**1**) was prepared by reacting $[\text{Re}(\text{NPh})\text{Cl}_3(\text{PPh}_3)_2]$ with tacn (tacn = 1,4,7-triazacyclononane) in CH_2Cl_2 and has been characterized by X-ray crystal analysis. The $\text{Re}\equiv\text{NPh}$ distance is 1.706(10) Å and the $\text{Re}-\text{N}-\text{Ph}$ angle is 170.2(9)°. In acetonitrile, the cyclic voltammogram of **1** shows an irreversible reduction wave at -0.77 V assignable to the reduction of rhenium(V) to rhenium(IV). Complex **1** catalyses alkene oxidation by PhIO.

High valent rhenium and ruthenium complexes having metal-ligand multiple bonds have been shown to exhibit interesting electrochemical and photochemical properties¹⁻³ and catalytic activities.^{4,5} Of particular interest to us are rhenium-imido complexes containing facially coordinating tridentate ligands such as 1,4,7-triazacyclononane (tacn) and its methylated derivatives (Me_3tacn). This paper describes the synthesis and properties of $[\text{Re}^{\text{V}}(\text{NPh})(\text{OH})(\text{PPh}_3)(\text{tacn})]^{2+}$. This complex has been found to mediate alkene oxidation by PhIO at room temperature.

EXPERIMENTAL

Materials

All preparations were performed using standard Schlenk or vacuum-line techniques. Dichloromethane (AR, Ajax) was distilled over calcium hydride under a nitrogen atmosphere. Organic substrates were purified by repeated distillation or recrystallization. 1,4,7-Triazacyclononane (tacn)

and $[\text{Re}^{\text{V}}(\text{NPh})\text{Cl}_3(\text{PPh}_3)_2]$ were prepared by published procedures.^{6,7}

*Preparation of $[\text{Re}^{\text{V}}(\text{NPh})(\text{OH})(\text{PPh}_3)(\text{tacn})]^{2+}$ (**1**).* A mixture of [rhenium(V)(NPh) $\text{Cl}_3(\text{PPh}_3)_2$] (0.2 g, 0.2 mmol) and tacn (0.05 g, 0.4 mmol) in dried CH_2Cl_2 (50 cm³) was stirred under nitrogen for 24 h and a green solution was obtained. The solution was evaporated to dryness and the residue was dissolved in water to give a green solution. Upon addition of excess LiClO_4 , a green solid precipitated. The solid was recrystallized by vapour diffusion of diethyl ether into an acetonitrile solution to give green crystals (yield 50%). Found: C, 39.5; H, 4.1; N, 6.1. Calculated for $\text{C}_{30}\text{H}_{36}\text{N}_4\text{Cl}_2\text{O}_9\text{PRe}$: C, 40.7; H, 4.1; N, 6.3. 270 MHz ¹H NMR (CD_3CN): 2.83 (m, 3H), 2.95–3.40 (m, 7H), 3.69, 3.95 (m, 1H each) CHH; 7.28, 7.83 (br, s, 1H each) NH; 7.36 (t, 2H), 7.76 (t, 1H) PhN; 7.39–7.66 (m, 18H) PPh_3 , PhN, NH; 11.37 (d, 1H) OH. ³¹P NMR (CD_3CN): 1.72(s), PPh_3 .

IR (Nujol mull): 1140 cm⁻¹ ($\nu_{\text{Re}\equiv\text{NPh}}$). UV-vis [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$): 259 (52870), 338 (22070).

Physical measurements. UV-vis absorption spectra were recorded in a Perkin-Elmer Lambda 19 spectrophotometer, IR spectra as Nujol mulls on a Nicolet 20FXC TF9IR spectrophotometer and ¹H NMR spectra on a JOEL 270 MHz FTNMR spectrometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) model

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175 universal programmer and a model 173 potentiostat. A Ag^+ -Ag reference electrode in acetonitrile was used.

GLC analyses were done on a Hewlett Packard model HP 5890 series II chromatography equipped with a flame ionization detector. Quantification of gas chromatographic components was performed on a Hewlett Packard HP 3393 series II integrator. Capillary column model HP 17 (phenyl methyl crosslink) was used to analyse the oxidation products.

Oxidation of alkene by iodosylbenzene catalysed by 1. In a typical experiment, a mixture of alkene (0.1 g) and $[\text{I}](\text{ClO}_4)_2$ (25 mg) in dichloromethane (10 cm^3) was stirred under a nitrogen atmosphere at room temperature. Iodosylbenzene (0.1 g) was added to the mixture, which was then stirred for 8–12 h. A blank containing the same amount of solvent, substrate and iodosylbenzene but without the metal catalyst was simultaneously stirred under the same conditions. After addition of internal standard, the aliquot was analysed by GLC, and the product yields were calculated based on the amount of iodobenzene formed.

X-ray structure determinations—crystal data. $[\text{Re}^{\text{V}}(\text{NPh})(\text{OH})(\text{PPh}_3)(\text{tacn})](\text{ClO}_4)_2 \cdot 0.5\text{Et}_2\text{O} \cdot 0.5\text{CH}_3\text{CN}$, $\text{C}_{33}\text{H}_{41}\text{N}_{4.5}\text{Cl}_2\text{O}_{9.5}\text{PRe}$, $M_r = 940.8$, space group, triclinic $P\bar{1}$, $a = 10.596(6)$, $b = 13.225(5)$, $c = 16.028(6)$ Å, $\alpha = 66.44(3)^\circ$, $\beta = 81.41(4)^\circ$, $\gamma = 69.54(4)^\circ$, $U = 1928.9(14)$ Å³, $Z = 2$, $D_c = 1.620 \text{ g cm}^{-3}$, μ (Mo- $K\alpha$) = 34.47 cm^{-1} , $F(000) = 941$.

Intensities were collected at 298 K on a Nonius CAD4 diffractometer with graphite-mo-chromatized Mo- $K\alpha$ radiation ($\gamma = 0.70930$ Å) using the $\theta/2\theta$ scan mode with $2\theta_{\text{max}} = 45^\circ$. Intensity data ($2\theta_{\text{max}} = 45^\circ$, $h = 10\text{--}11$, $k = 0\text{--}14$, $l = 15\text{--}17$) were corrected for Lorentz and polarization effects and empirical absorption. A total of 5021 independent reflections were measured of which 4170 reflections with $I_0 > 2.0\sigma(I_0)$ were used. The structure was solved by the Patterson method and refined by least squares. All data reduction and structure refinement were performed using the NRCC-SDP-VAX packages. The non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included at idealized positions with a fixed contribution. The final R_F and R_W values are 0.056 and 0.052, respectively. The goodness of fit is 2.76.

Selected bond distances and bond angles are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises coordinates, thermal parameters and remaining bond lengths and angles.

RESULTS AND DISCUSSION

High valent rhenium complexes of macrocyclic amines are not unprecedented in the literature. With tacn and its methylated derivatives, Wieghardt and co-workers had reported the synthesis and structure of $[\text{Re}(\text{tacn})\text{O}_3]^+$, $[\text{Re}(\text{Me}_3\text{tacn})\text{O}_3]^+$

Table 1. Selected bond distances (Å) and angles ($^\circ$) of $[\text{Re}^{\text{V}}(\text{NPh})(\text{OH})(\text{PPh}_3)(\text{tacn})]^+$

Re—P	2.434 (3)		
Re—O(1)	2.004 (7)		
Re—N(1)	1.706 (10)		
Re—N(2)	2.136 (10)		
Re—N(3)	2.203 (9)		
Re—N(4)	2.196 (10)		
P—Re—O(1)	90.59 (4)	N(2)—Re—N(4)	78.5 (4)
P—Re—N(1)	88.5 (3)	N(3)—Re—N(4)	74.2 (4)
P—Re—N(2)	165.8 (3)	Re—P—C(13)	111.9 (4)
P—Re—N(3)	91.2 (3)	Re—P—C(19)	112.9 (4)
P—Re—N(4)	105.4 (3)	Re—P—C(25)	116.5 (4)
O(1)—Re—N(1)	106.9 (4)	Re—N(1)—C(7)	170.2 (9)
O(1)—Re—N(2)	82.0 (3)	Re—N(2)—C(1)	110.8 (7)
O(1)—Re—N(3)	88.1 (3)	Re—N(2)—C(6)	114.2 (7)
O(1)—Re—N(4)	156.2 (4)	Re—N(3)—C(2)	112.9 (7)
N(1)—Re—N(2)	105.2 (4)	Re—N(3)—C(3)	110.6 (7)
N(1)—Re—N(3)	165.0 (4)	Re—N(4)—C(4)	116.2 (7)
N(1)—Re—N(4)	91.4 (4)	Re—N(4)—C(5)	103.5 (7)
N(2)—Re—N(3)	76.5 (3)		

(Me₃tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) and some monomeric and dimeric rhenium(V) complexes.^{8,9} In a previous study, the synthesis and X-ray structure of *trans*-[Re(NPh)(OH)(cyclam)]²⁺ was also reported.^{3a} In this work, compound **1** was prepared by reacting Re(NPh)Cl₃(PPh₃)₂ with tacn in CH₂Cl₂ under dry nitrogen. When oxygen was present during the reaction, the product yield was significantly reduced and a significant amount of [ReO₃(tacn)]⁺ was isolated as a perchlorate salt. [1](ClO₄)₂ is diamagnetic and is stable in water and acetonitrile at room temperature.

A perspective view of **1** is shown in Fig. 1. The structure features an interesting rhenium(V) complex having a phenylimido and a hydroxy group *cis* to each other. As expected, tacn facially coordinates to rhenium(V) with the N(3) atom *trans* to the phenylimido moiety. The Re≡NPh distance of 1.706(10) Å, is shorter than the related value of 1.731(9) Å in *trans*-[Re(NPh)(OH)(cyclam)]ClO₄₂^{3a} and of 1.740(6) Å in [Re(NPh)(bpy)₂(OEt)](PF₆)₂.^{1b} It is, however, similar to the Re≡N^tBu distance of 1.709(3) Å found in Re(N^tBu)Cl₂(η⁵-C₅Me₅)₂.¹⁰ The approximate linearity of the Re—N—Ph unit (170.2(9)°) indicates that the phenylimido group acts as a six-electron donor. The Re—N(tacn) distances are not equivalent. The Re—N(3) and Re—N(4) (bonds with the N atoms *trans* to a π-donor) have longer distance than that of Re—N(2) which is *trans* to PPh₃.

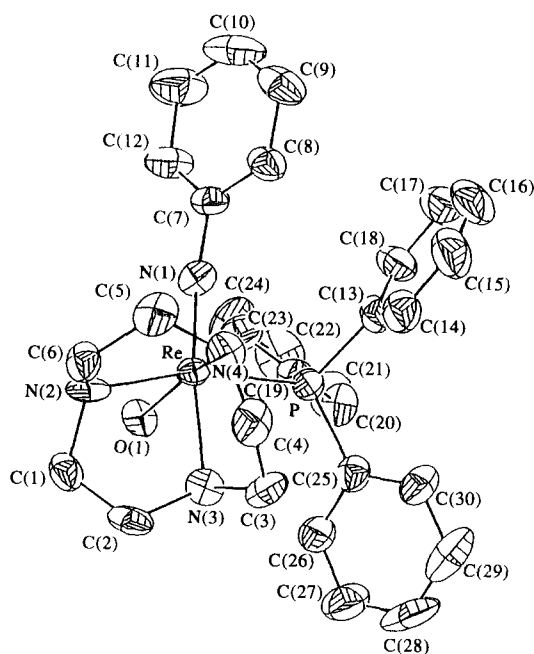


Fig. 1. A perspective view of the [Re(NPh)(OH)(PPh₃)(tacn)]²⁺ cation.

The Re—O(1) distance of 2.004(7) Å indicates some multiple bond character. The N(1)—O(1) angle of 106.9(4)° is smaller than the O—Re—O angle of 121.4(4)° in *cis*-[Re^V(bpy)py₂O₂]⁺¹¹ (py = pyridine).

The UV-vis absorption spectrum of **1** in acetonitrile shows two intense absorption peaks at 259 and 338 nm, which are due to dipole-allowed transitions because of their large ε_{max} values. It is interesting to note that the 338 nm band is similarly present in other Re^VN≡Ph complexes such as *trans*-[Re(dppe)₂(NPh)Cl]²⁺ (λ_{max} = 339 nm)^{1b} and *trans*-[Re(NPh)(OH)(cyclam)]²⁺ (λ_{max} = 308 nm).^{3b} The ¹H NMR spectrum for [Re(NPh)(OH)(PPh₃)(tacn)](ClO₄)₂ in CD₃CN indicates a C₁ symmetry for the cation. The result of D₂O exchange experiment indicated that the O—H and N—H protons are exchangeable. The cyclic voltammogram of [Re(NPh)(OH)(PPh₃)(tacn)]²⁺ in acetonitrile with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte shows two irreversible reduction waves at -0.77 V and -1.34 V *vs* SCE. With reference to previous electrochemical study on *trans*-[Re(NPh)(OH)(cyclam)]²⁺,^{3a} the former wave is tentatively assigned to the reduction of rhenium(V) to rhenium(IV). Upon oxidation, an irreversible wave at 1.0 V is found. An electrochemical study of [1](ClO₄)₂ in aqueous solution is hampered by its low solubility.

REACTIVITIES

The use of high valent rhenium complexes as catalysts for alkene oxidation have been reported.¹² In this work, [Re(NPh)(OH)(PPh₃)(tacn)]²⁺ was found to mediate oxidation of alkenes by iodobenzene and the results are summarized in Table 2. In each reaction studied, the total yield of organic products based on the amount of PhIO formed is < 50%. This has been found to be due to the disproportionation of PhIO to PhI and PhIO₂ catalysed by the rhenium complex. Figure 2 shows the time course of the PhIO oxidation of styrene catalysed by [Re(NPh)(OH)(PPh₃)(tacn)]²⁺. The reaction was slow, and no induction period was found. Styrene was oxidized to a mixture of styrene oxide and benzaldehyde (C=C cleavage product) in a ratio of 1:2. In the case of cyclohexene, 2-cyclohexen-1-one and 2-cyclohexen-1-ol were the predominant products. Cyclooctene was oxidized to give cyclooctene oxide only. Attempts to identify the active intermediate in these oxidation reactions failed. Addition of PhIO to an acetonitrile solution of [Re^V(NPh)(OH)(PPh₃)(tacn)]²⁺ gave no immediate spectral change. It is likely that in the catalytic oxidation reaction described above, the

Table 2. Results of $[\text{Re}(\text{NPh})(\text{OH})(\text{PPh}_3)(\text{tacn})](\text{ClO}_4)_2$ catalysed oxidation of alkenes by PhIO^a

Substrate	Solvent	Products	Turnover ^b
Styrene	Dichloromethane	Styrene oxide Benzaldehyde	11
Styrene	Acetonitrile	Benzaldehyde	Trace
Cyclohexene	Dichloromethane	Cyclohexene oxide 2-Cyclohexen-1-ol 2-Cyclohexen-1-one	8
Cyclooctene	Dichloromethane	Cyclooctene oxide	4

^a Conditions: alkene (0.1 g), PhIO (0.1 g), catalyst (25 mg); time 8 h; temperature 25°C.

^b The turnover values are based on the ratio of moles of oxidized products formed : moles of metal catalyst used.

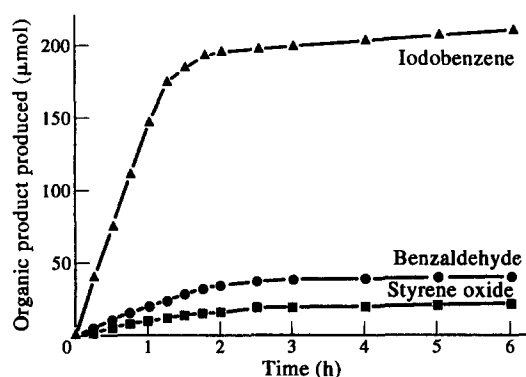


Fig. 2. Time dependence for the oxidation of styrene by iodobenzene catalysed by $[\text{Re}^{\text{V}}(\text{NPh})(\text{OH})(\text{PPh}_3)(\text{tacn})](\text{ClO}_4)_2$ in dichloromethane. Plot of amount of styrene oxide, benzaldehyde and iodobenzene vs reaction time.

complex functions as a Lewis acid catalyst which activates PhIO through a non-redox pathway. The activation of PhIO by non-redox active transition metal ions like copper(II) had been previously reported by VanAtta and co-workers.¹³

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