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Synthesis and characterization of new imidorhenium(V) and imidorhenium(VI) complexes of pyridyltriazines and pyrazinyltriazine with halide coligands including rare iodide

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Abstract

The blue colored imido complexes [Re(NC₆H₄Cl)X₃(L)] have been synthesized by three methods: (i) reaction of [Re^VOX₃(L)] with *p*-ClC₆H₄NH₂, (ii) reaction of [Re^{III}(OPPh₃)X₃(L)] with *p*-ClC₆H₄NH₂ and (iii) reaction of [Re^VOX₃(PPh₃)₂] with L followed by the addition of *p*-ClC₆H₄NH₂ in boiling toluene. Here, X = Cl, Br, I and L are 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (L²) and its dimethyl (L¹) and pyrazinyl (L³) analogues. The [Re(NC₆H₄Cl)Cl₃(L¹)] (1a), [Re(NC₆H₄Cl)Cl₃(L²)] (1b), [Re(NC₆H₄Cl)Br₃(L²)] (1c), [Re(NC₆H₄Cl)I₃(L²)] (1d), [Re(NC₆H₄Cl)Cl₃(L³)] (1e), [Re(NC₆H₄Cl)Br₃(L³)] (1f), [Re(NC₆H₄Cl)Cl₃(L²)] (1g), complexes have been characterized electrochemically and spectroscopically. The X-ray structures of [Re(NC₆H₄Cl)Cl₃(L²)] and [Re(NC₆H₄Cl)I₃(L³)] reveal that the ReCl₃ fragment is meridionally disposed and that the L ligand is N,N-coordinated such that the pyridine/pyrazine nitrogen lies trans to the imide nitrogen. The feasibility of generating the rhenium(VI) congener of the imidorhenium(V) complex is also examined with the help of six-line EPR spectra at room temperature.

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1. Introduction

This work stems from our previous interest in the transition-metal chemistry of bipyridine-like ligands in general and pyridyltriazines and pyrazinyltriazine, in particular [1]. The richness of this chemistry in the cases of iron [2], ruthenium [3] and molybdenum [4] prompted us to explore parallel developments for the neighboring element rhenium. In the present work, the successful synthesis of rhenium(V) arylimides complexes of 5,6-dimethylpyridyltriazine, 5,6diphenylpyridyltriazine and 5,6-diphenylpyrazinyltriazine with various halide coligands is explored. The complexes have been isolated in the solid state and crystal structure

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determination has authenticated the presence of various halide coligands including rare iodide. The complexes displaying two bands in the visible region near 590 and 750 nm, are diamagnetic and show well defined ¹H NMR lines. They are electroactive in acetonitrile solution and exhibit a well defined Re^{VI}/Re^V couple near 1.0 V versus SCE. In general, the reduction potentials of pyrazinyltriazine complexes are greater than pyridyltriazine complexes reflecting the superior electron withdrawing ability of the pyrazinyl fragment [5]. Similarly, phenyl substituted triazine complexes are superior electron withdrawal than the corresponding methyl substituted ones. The feasibility of generating the rhenium(VI) congener of the imidorhenium(V) complex is examined with the help of electrochemical and EPR techniques [6]. The dianionic imido nitrogen in NAr²⁻ is formally isoelectronic with the oxo ligand and their rhenium(V) chemistry has received significant attention [7–9].

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2. Experimental

2.1. Materials

 $[ReOX_3(PPh_3)_2]$, $[ReOX_3(L)]$, $[Re(OPPh_3)X_3(L)]$ and L were prepared as reported methods [8]. *p*-Chloroaniline was purchased from Aldrich (USA) and used as obtained. For electrochemical work, HPLC grade acetonitrile was used. All other chemicals and solvents were of reagent grade and were used as received.

2.2. Physical measurements

UV-Vis spectra (CH₂Cl₂ solution), IR spectra (KBr disk), and ¹H NMR spectra (CDCl₃) were recorded on a Shimadzu UVPC 1601 spectrophotometer, a Nicolet Magna IR 750 Series II spectrometer, and a Bruker FT 300 MHz spectrometer, respectively. The numbering scheme used for ¹H NMR assignment is the same as in crystallography. Spin-spin structures are abbreviated as follows: s, singlet; d, doublet; t, triplet. Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 Series II elemental analyzer. EPR spectra were recorded on a Varian E-109C X-band spectrometer. Electrochemical measurements were performed under nitrogen atmosphere using a CH 620A electrochemical analyzer, with platinum working electrode. The supporting electrolyte was tetraethylammonium perchlorate (TEAP), and the potentials are referenced to the saturated calomel electrode (SCE) without junction correction. Mass spectra were measured with Q-TOF mass spectrometer (MeCN).



2.2.1. Synthesis of complexes

The X = Cl, Br imido complexes, i.e., **1a–c**, **1e** and **1f** were synthesized by the three general procedures and details are given in the case of one complex while the iodo species **1d** and **1g** are quite stable unlike their oxo precursors were isolated by procedure (iii) only. The details of syntheses and characterization of the compounds are given in the Supplementary material.

2.3. Crystal structure determination

Single crystals of the complexes $[Re(NC_6H_4Cl)Cl_3(L^2)]$. **1b** and $[\text{Re}(\text{NC}_6\text{H}_4\text{Cl})\text{I}_3(\text{L}^3)]$ (**1g**) were grown by slow diffusion of hexane into dichloromethane solutions of the respective compounds. Data were collected on a Nicolet R3m/V four-circle diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) by the ω -scan technique in the range $3^{\circ} \leq 2\theta < 47^{\circ}$ and $3^{\circ} \leq 2\theta < 50^{\circ}$, respectively, in the case of 1b and 1g complexes. All data were corrected for Lorentz-polarization and absorption [10]. The metal atoms were located from Patterson maps and the rest of the non-hydrogen atoms emerged from successive Fourier syntheses. The structures were then refined by full-matrix least-squares procedure on F^2 . All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions. Calculations were performed using the SHELXTL[™] V 5.03 program package [11].

2.4. $[Re(NC_6H_4Cl)Cl_3(L^2)]$ (1b)

Empirical formula $C_{52}H_{36}Cl_8N_{10}Re_2$, crystal system monoclinic; space group $P2_1/c$; a = 10.956(7) Å, b = 26.150(10) Å, c = 18.252(5) Å, $\beta = 93.38(4)^\circ$; V = 5220(4)Å³; Z = 4, 7634 unique reflections. Final residuals $R_1 = 0.0575$; $wR_2 = 0.1335$ $[I > 2\sigma(I)]$.

2.5. $[Re(NC_6H_4Cl)I_3(L^3)]$ (1g)

Empirical formula $C_{25}H_{17}CII_3N_6Re$, crystal system monoclinic; space group $P2_1/c$; a = 12.534(7) Å, b = 15.180(5) Å, c = 16.487(7) Å, $\beta = 112.00(4)^\circ$; V = 2909(2)Å³; Z = 4. 5584 unique reflections. Final residuals $R_1 = 0.0494$; $wR_2 = 0.1180 \ [I > 2\sigma(I)]$.

3. Results and discussion

3.1. Synthesis

Upon boiling $[ReOX_3(L)]$ with p-ClC₆H₄NH₂ in toluene a blue solution is formed and on work-up, this afforded blue colored imido complexes of type **1**. The reaction is stated in Eq. (1). Here, the Re^VO moiety acts as a base

$$[\operatorname{Re}^{\mathsf{V}}\operatorname{OX}_{3}(\mathrm{L})] + p\operatorname{-ClC}_{6}\operatorname{H}_{4}\operatorname{NH}_{2}$$

$$\rightarrow [\operatorname{Re}^{\mathsf{V}}(\operatorname{NC}_{6}\operatorname{H}_{4}\operatorname{Cl})\operatorname{X}_{3}(\mathrm{L})] + \operatorname{H}_{2}\operatorname{O}$$
(1)

and the oxo function is transferred formally as an oxide dianion which then combines with amine protons generating bound imide and free water. This is to be contrasted with the transfer of an oxygen atom from Re^{VO} to the oxophilic substrates [1].

It was observed that the same imido species could also be prepared by boiling $[Re^{III}(OPPh_3)X_3(L)]$ with *p*-ClC₆-H₄NH₂ in toluene in air. In effect the OPPh₃ ligand is replaced by NAr^{2-} and the metal oxidation state increases by two units [1].

It was subsequently observed that reaction between $[\text{Re}^{V}\text{OX}_{3}(\text{PPh}_{3})_{2}]$ and L in toluene followed by the addition of *p*-ClC₆H₄NH₂ afforded the imido complexes **1** in a onepot reaction. Another advantage of this procedure is that the X = I species could also be isolated. These iodo species are quite stable unlike their oxo precursors, $[\text{Re}^{V}\text{OI}_{3}(\text{L})]$, which could not be isolated. The methods by which the complexes of type **1** are synthesized are shown in Scheme 1.

3.2. Spectra and electrochemistry

The UV-Vis spectra of the imido complexes are qualitatively similar to those of the oxo precursors and are characterized by two bands in the visible region near 590 and 750 nm, precluding the possible observation of ligand field transitions of the type $d_{yy} \rightarrow d_{yz}$, d_{yz} [8]. Such transitions may be the origin of the two relatively weak bands observed in the visible spectrum of [Re(MeNH₂)₄- $(MeN)Cl]^{2+}$ [6]. The complexes are diamagnetic and display well resolved ¹H NMR lines in the aromatic region. The NMR data are given in the Supplementary material. The complexes are electroactive in acetonitrile solution and exhibit a well defined Re^{VI}/Re^V couple near 1.0 V versus SCE. In general, the potentials of the L^3 species are slightly higher than the corresponding L^2 species. Similarly, phenyl substituted L^2 complexes have superior electron withdrawing ability than the corresponding L^1 ligated ones. There is a relatively large decrease (by 0.6 V) in the reduction potential in going from $[ReOX_3(L)]$ to $[Re(NAr)X_3(L)]$, signifying a better stability of the Re^{VI} state under imide coordination [1,8,9].

3.3. Electrochemical oxidation of type 1 species

Blue colored type **1** complexes undergo one-electron oxidation electrochemically affording green colored 1^+ complexes at room temperature. 1^+ complexes are very unstable and spontaneously reduce to type **1** complexes. The representative case of **1e**, which forms relatively stable electrooxidized congener, will be considered. Constant potential coulometry of this complex at 1.15 V in dry acetonitrile furnished the cation $[\text{Re}^{\text{VI}}(\text{NC}_6\text{H}_4\text{Cl})\text{Cl}_3(\text{L}^3)]^+$ (Scheme 1) whose cyclic voltammogram (initial scan cathodic) is the same as that of the parent complex (initial scan anodic), Fig. 1. In order to confirm that **1e**⁺ contains oxi-



Fig. 1. Cyclic voltammogram of $[\text{Re}(\text{NC}_6\text{H}_4\text{Cl})\text{Cl}_3(\text{L}^3)]$ (1e) in acetonitrile solution at platinum working electrode (scan rate 100 mV s⁻¹).

dized metal, the X-band EPR spectra in dried acetonitrile were examined. The spectrum of $1e^+$ is shown in Fig. 2.

3.4. Structures

3.4.1. $[Re(NC_6 H_4 Cl)Cl_3 (L^2)]$ (1b)

The complex crystallizes with two metrically similar but crystallographically distinct molecules (Molecule 1 and



Fig. 2. X-band EPR spectrum of $[\text{Re}(\text{NC}_6\text{H}_4\text{Cl})\text{Cl}_3(\text{L}^3)]^+$, $\mathbf{1e}^+$ in acetonitrile solution (300 K). Instrument settings power, 30 dB; modulation, 100 KHz; sweep center, 3200 G, At center field g = 1.97, Average values A = 459 G.



Molecule 2) in the asymmetric unit. Perspective views of the molecules are shown in Fig. 3 and selected bond parameters are listed in Table 1.

In both the molecules, the distorted octahedral ReCl₃N₃ coordination sphere has meridional disposition for the chloride ligands. The heterocyclic ligand is N,N-coordinated and the pyridine nitrogen (N1/N1') lies trans to the imido nitrogen (N5/N5'). In Molecule 1, the equatorial atoms Cl1, Cl2, Cl3 and N2 constitute a good plane (mean deviation 0.01 Å) and the Re1 atom is displaced from this plane by 0.30 Å towards imido nitrogen N5. In Molecule 2, Cl1', Cl2', Cl3' and N2' define only a satisfactory plane (mean deviation 0.05 Å) from which Re1' atom is displaced by 0.32 Å. The mean deviations of the pyridine, triazine and chelate rings from the planarity are, respectively, 0.01, 0.05 and 0.02 Å in Molecule 1 and 0.01, 0.04 and 0.06 Å, respectively, in Molecule 2. When all three rings are taken together the corresponding mean deviations are 0.06 and 0.12 Å, respectively, for two molecules. Overall, Molecule 2 is slightly more distorted than Molecule 1.

The Re–N(imide) lengths Re1–N5, 1.720(12) Å and Re1'–N5', 1.717(11) Å are only slightly longer than the idealized triple bond value 1.69 Å, the corresponding double bond being 1.84 Å [12,13]. The Re1–N5–C21 fragment (Molecule 1) is significantly more linear than the Re1'– N5'–C21' fragment (Molecule 2), as can be seen from the angle subtended at the nitrogen atom – 170.0(10)° and 159.0(10)°, respectively. In hexacoordinated Re^V-imido species, the Re–N(imido) bond have been found to span the range 1.67–1.79 Å and the Re–N–C angle to span the range 160–180° [1,9,12–20].

3.4.2. $[Re(NC_6 H_4 Cl)I_3 (L^3)]$ (1g)

A molecular view of 1g is shown in Fig. 4 along with the atom numbering scheme. Selected bond parameters are listed in Table 2. In the meridional ReI_3N_3 coordination

Table 1

Selected bond distances (Å), angles (°) and their estimated standard deviations for $[Re(NC_6H_4Cl)Cl_3(L^2)]$

	Molecule 1	Molecule 2
Distance		
Re1-N1	2.235(11)	2.222(11)
Re1-N2	2.070(11)	2.061(11)
Re1-Cl1	2.355(4)	2.377(4)
Re1-Cl2	2.382(4)	2.386(4)
Re1-Cl3	2.389(4)	2.389(4)
Re1–N5	1.720(12)	1.717(11)
Angles		
N5-Re1-N2	90.7(5)	90.4(5)
N5-Re1-N1	165.1(5)	161.5(4)
N5-Re1-Cl1	104.4(4)	104.5(4)
N5-Re1-Cl3	98.3(4)	91.7(4)
N1-Re1-Cl1	90.5(3)	91.8(3)
N1-Re1-Cl2	84.0(3)	82.5(3)
N2-Re1-Cl2	90.6(3)	86.0(3)
N1-Re1-Cl3	81.5(3)	80.4(3)
N2-Re1-Cl3	89.2(3)	95.7(3)
Cl1-Re1-Cl3	88.39(14)	87.38(18)
Cl2-Re1-Cl3	164.93(14)	161.54(14)

N.B. The scheme of atom numbering of both the molecules is the same. The prime sign(')s as shown in the crystal structure of Molecule 2 (Fig. 3) are omitted from the table for clarity.

sphere the I1, I2, I3 and N2 atoms define a good plane with mean deviation 0.02 Å and the metal atom is displaced towards the N6 atom by 0.29 Å from the plane. Here, the pyrazine, triazine and chelate rings are all planar (mean deviation, <0.02 Å). The entire chelated ligand (metal included) excluding the phenyl rings makes a satisfactory plane with mean deviation 0.05 Å.

The Re–N6 length, 1.717(9) Å is again consistent with triple bonding. The *trans* influence of the triple bonds is reflected in lengthening of the Re–N1 bond compared to Re–N2 bond by ~ 0.17 Å. A similar lengthening due to *trans* influence also occurs in the structure of [Re-



Fig. 3. Molecular view and atom labeling scheme for Molecule 1 and Molecule 2 of $[Re(NC_6H_4Cl)Cl_3(L^2)]$ (1b). All non-hydrogen atoms are represented by 30% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity.



Fig. 4. Molecular view and atom labeling scheme for $[\text{Re}(\text{NC}_6\text{H}_4\text{Cl})-\text{I}_3(\text{L}^3)]$ (1g). All non-hydrogen atoms are represented by 30% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond distances (Å), angles (°) and their estimated standard deviations for $[\text{Re}(\text{NC}_6\text{H}_4\text{C})]_3(\text{L}^3)]$

L			
Distances			
Re–N1	2.258(9)	Re–N2	2.087(9)
Re–I1	2.711(2)	Re–I2	2.730(2)
Re–I3	2.735(2)	Re–N6	1.717(9)
Angles			
N6-Re-N2	91.5(4)	N6-Re-N1	164.6(4)
N6-Re-I1	101.5(3)	N6-Re-I2	99.2(3)
N6–Re–I3	94.0(3)	N2-Re-N1	73.2(3)
N2-Re-I1	166.5(2)	N1-Re-I1	93.7(2)
N1-Re-I2	83.2(2)	N2-Re-I2	91.5(3)
N1-Re-I3	83.6(2)	N2-Re-I3	86.1(3)
I1-Re-I3	89.34(5)	I2-Re-I3	166.70(3)
C20–N6–Re	168.5(9)		

 $(NC_6H_4Cl)Cl_3(L^2)$] (Table 1). In the lattice, a nonbonded $Cl \cdots I$ interaction 3.81(4) Å occurs between symmetry related molecules as depicted in Fig. 5.

4. Conclusion

The seven imido complexes of type $[\text{Re}^{V}(\text{NC}_{6}\text{H}_{4}\text{C}\text{l})$ -X₃(L)] (X = Cl, Br, I; and L = L¹-L³) have been synthesized and characterized. These display $\text{Re}^{VI}/\text{Re}^{V}$ couple near 1.0 V as compared to 1.6 V in $[\text{Re}^{V}\text{OX}_{3}(\text{L})]$ signifying a better stabilization of the rhenium(VI) state under imide coordination. The imido complexes are nearly reversible electrooxidized in solution to EPR-active congeners of the hexavalent metal.



Fig. 5. Nonbonded $Cl \cdots I$ contacts in $[Re(NC_6H_4Cl)I_3(L^3)]$ (1g).

X-ray structure determination of $[\text{Re}(\text{NC}_6\text{H}_4\text{Cl})\text{Cl}_3(\text{L}^2)]$ and $[\text{Re}(\text{NC}_6\text{H}_4\text{Cl})\text{I}_3(\text{L}^3)]$ has revealed Re = N(imide) triple bonding (distance ~ 1.72 Å) with consequent lengthening (by ~0.17 Å) of Re–N lying *trans* to the imide nitrogen and a shift of the metal atom towards the imide nitrogen away from the equatorial plane of the halide ligands. The structural characterization of rare iodo complexes of Re^{V}NAr is also interesting.

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Appendix A. Supplementary material

CCDC 624556 and 292213 contain the supplementary crystallographic data for **1b** and **1g**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.02.001.

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