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Synthesis and characterization of variable-valent imidorhenium species. A family of imidorhenium(VI) amide complexes and their imidorhenium(V) imine precursors related by oxygen atom transfer

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Abstract

The synthesis of imidorhenium(V) $[\text{Re}(\text{NAr})\text{Cl}_3(\text{L})]$ complexes is reported. Their reaction with dilute HNO_3 furnishes $[\text{Re}(\text{NAr})\text{Cl}_3(\text{L}')]^+$ species incorporating monoionized iminoamide ligands (the ligands are abbreviated as L and L' respectively). The iminoamide complexes exhibit sextet EPR spectra in CH_2Cl_2 solution at room temperature. They are electroactive in MeCN solution and to display two quasi reversible responses near 0.2 and 1.6 V which can be attributed to $\text{Re}^{\text{V}} \rightarrow \text{Re}^{\text{VI}}$ and $\text{Re}^{\text{VI}} \rightarrow \text{Re}^{\text{VII}}$ oxidations respectively. One of the $[\text{Re}(\text{NAr})\text{Cl}_3(\text{L})]$ complexes has been structurally characterized. The *trans* influence of the amide nitrogen considerably lengthens the Re–N bond lying *trans* to the imido group. The triply bonded ReN–C moiety is linear.

Introduction

Conjugated nitrogen-donor ligands, such as α -diimines [1], are of abiding interest in transition metal chemistry. Recent studies have concerned matters such as unusual compound types [2], coordinated radical anions [3], redox-promoted transformations [4], polymerization catalysis [5] as well as photophysical and photochemical phenomena [6]. The present work originated from our previous interest in the rhenium chemistry of conjugated nitrogen-donor ligands [7–12]. In the case of α -diimines, the studies reported so far from different laboratories have been mostly confined to tricarbonyl species incorporating monovalent rhenium [13–15]. We therefore targeted the development and study of a new class of complexes designed to meet our objectives. We report here the synthesis of diimine complexes containing the $\text{Re}^{\text{V}}\text{NAr}$ moiety and their imine \rightarrow amide transformation which is of potential interest as a synthetic tool. We have used this reaction to prepare a family of iminoacetamide complexes incorporating the rare arylimide motif of hexavalent rhenium, $\text{Re}^{\text{VI}}\text{NAr}$. The synthesis and spectra of the imine and amide complexes along with a structure of an imine complex are reported.

Experimental

Materials

$[\text{Re}(\text{NAr})\text{Cl}_3(\text{PPh}_3)_2]$ [16] and the α -diimines (L) [17] were prepared by reported methods. For electrochemical

work HPLC grade MeCN (Spectrochem, India) was used. All other chemicals and solvents were of reagent grade and were used as received without further purification. Silica gel (60–120 mesh) from S.D. Fine Chem. Ltd. (India) was used for column chromatography.

Physical measurements

UV–Vis spectral measurements were made with a Shimadzu UV-1601 PC spectrophotometer. IR spectra were measured with Nicolet Magna IR 750 series II and Perkin-Elmer L-0100 spectrophotometers. EPR spectra were recorded on a Varian E-109C X-band spectrometer. Magnetic susceptibilities were measured on a PAR 155 vibrating sample magnetometer. A Perkin-Elmer 2400 Series II elemental analyzer was used for microanalyses (C, H, N). Electrochemical measurements were performed under N_2 using a CH 620A electrochemical analyzer, with a Pt working electrode. The supporting electrolyte was tetraethylammonium perchlorate (TEAP) and the potentials are referenced to the saturated calomel electrode (SCE) without junction correction.

Synthesis of $[\text{Re}(\text{NAr})\text{Cl}_3(\text{L})]$, (1) complexes

The three complexes were synthesized by the same general procedure based on the reaction of $[\text{Re}(\text{NAr})\text{Cl}_3(\text{PPh}_3)_2]$ with α -diimine in benzene. Details are given here for a representative case.

Preparation of $[\text{Re}(\text{NAr})\text{Cl}_3(\text{L}3)]$

To a suspension of $[\text{Re}(\text{NAr})\text{Cl}_3(\text{PPh}_3)_2]$ (100 mg, 0.106 mmol) in PhMe (25 cm^3) was added 32 mg

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(0.106 mmol) of L3. The resulting mixture was heated to reflux for 30 min producing a reddish pink solution. The reaction mixture was then cooled and the solvent was removed under reduced pressure. The solid mass thus obtained was repeatedly washed with *n*-hexane to remove the liberated PPh₃. The residue was dissolved in CH₂Cl₂ (10 cm³) and subjected to column chromatography on a silica gel column (10 × 1 cm, 60–120 mesh) prepared with PhMe. A reddish pink band was eluted with a PhMe-MeCN (25:1) mixture. Solvent removal from the eluate under reduced pressure afforded the imido complex which was dried in vacuum. Yield: 75%. (Found: C, 36.6; H, 2.5; N, 5.7; C₂₂H₁₈N₃Cl₆Re calcd.: C, 36.5; H, 2.5; N, 5.8%). ¹H NMR (δ (J, Hz) CDCl₃): 2.40 and 4.67 (C(13)-Me, s and C(14)-Me, s); 6.90–7.48 (aromatic multiplet).

Preparation of [Re(NAr)Cl₃(L1)]

[Re(NAr)Cl₃(PPh₃)₂] (100 mg, 0.110 mmol) and L1 (26 mg, 0.110 mmol) were employed. Yield: 70%. (Found: C, 42.7; H, 3.5; N, 6.7; C₂₂H₂₁N₃Cl₃Re calcd.: C, 42.6; H, 3.4; N, 6.8%). ¹H NMR (δ (J, Hz) CDCl₃): 2.37 and 4.55 (C(13)-Me, s and C(14)-Me, s); 6.26–7.49 (aromatic multiplet).

Preparation of [Re(NAr)Cl₃(L2)]

[Re(NAr)Cl₃(PPh₃)₂] (100 mg, 0.107 mmol) and L2 (28 mg, 0.107 mmol) were employed. Yield: 76%. (Found: C, 45.4; H, 4.2; N, 6.3; C₂₅H₂₇N₃Cl₃Re calcd.: C, 45.3; H, 4.1; N, 6.3%). ¹H NMR (δ (J, Hz) CDCl₃): 2.33 and 4.56 (C(13)-Me, s and C(14)-Me, s); 6.77–7.25 (aromatic multiplet).

Preparation of [Re(NAr)Cl₃(L')], (2) complexes

These complexes were synthesized in *ca.* 60% yield by the same general method based on the reaction of [Re(NAr)Cl₃(L)] with dilute HNO₃ in MeCN solution. Details are given for a representative case.

Preparation of [Re(NC₆H₅)Cl₃(L1')]

[Re(NC₆H₅)Cl₃(L1)] (100 mg, 0.161 mmol) was dissolved in MeCN (20 cm³) and 0.5 N HNO₃ (2 cm³) was added. The solution was stirred for 3 h at room temperature during which time it turned brown. Solvent evaporation under reduced pressure afforded a dark solid which was repeatedly washed with H₂O. The product was then dried in vacuum over P₄O₁₀. Yield: 60%. (Found: C, 41.1; H, 2.8; N, 6.9; C₂₁H₁₈N₃Cl₃ORe calcd.: C, 40.6; H, 2.9; N, 6.8%).

Preparation of [Re(NC₆H₄Me)Cl₃(L2')]

Yield: 62%. (Found: C, 43.5; H, 3.5; N, 6.4; C₂₄H₂₄N₃Cl₃ORe calcd.: C, 43.5; H, 3.6; N, 6.3%).

Table 1. X-ray crystallographic data for [Re(NC₆H₅)Cl₃(L1)]·H₂O

Empirical formula	C ₂₂ H ₂₃ Cl ₃ N ₃ ORe
fw	637.98
Crystal system, space group	Rhombohedral, R3
<i>a</i> , Å	22.390(11)
<i>b</i> , Å	22.390(11)
<i>c</i> , Å	13.213(4)
α, deg	90
β, deg	90
γ, deg	120
<i>V</i> , Å ³	5737(5)
<i>Z</i>	9
<i>T</i> , K	293
<i>d</i> _{calcd.} mg/m ³	1.662
μ, mm ⁻¹	5.098
<i>R</i> ₁ ^a (<i>wR</i> ₂ ^b)	0.0359(0.0930)

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

Preparation of [Re(NC₆H₄Cl)Cl₃(L3')]

Yield: 58%. (Found: C, 34.9; H, 2.2; N, 5.7; C₂₁H₁₅N₃Cl₆ORe calcd.: C, 34.8; H, 2.1; N, 5.8%).

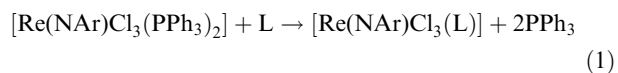
X-ray structure determination

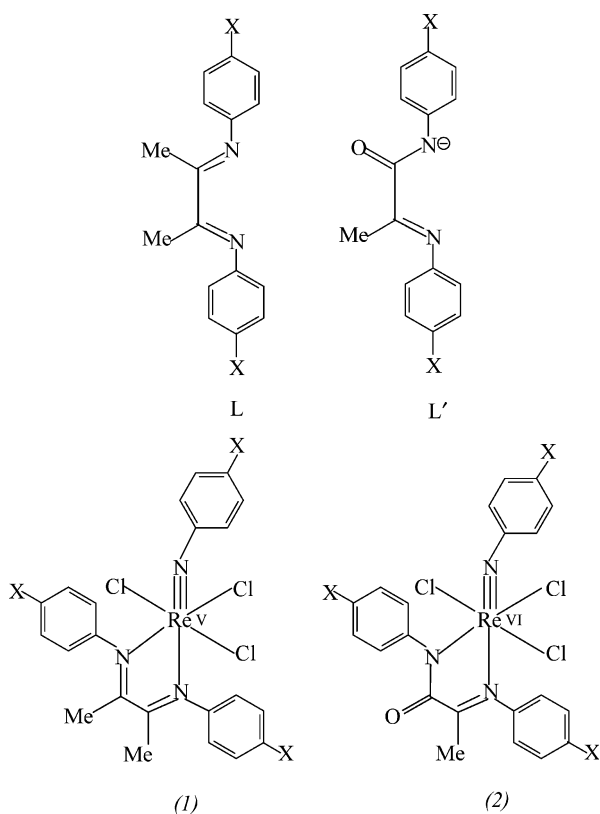
Single crystals of [Re(NC₆H₅)Cl₃(L1)] were grown by slow diffusion of hexane into CH₂Cl₂ solution. A suitable single crystal was mounted on the tip of a quartz tube and then attached to the goniometer head. X-ray diffraction data were collected on a Nicolet R3m/V four-circle diffractometer with graphite monochromated Mo-*K*α radiation (λ = 0.71073 Å) by ω-scan technique in the 2θ range 3–47°. The data were corrected for Lorentz-polarization and absorption. The structure was determined by the Patterson method and refined with SHELXTL V5.03 [18]. Non-H atoms were refined with anisotropic displacement parameters and the H atoms were added in calculated positions and refined isotropically. A summary of the crystallographic data for the structure is given in Table 1.

Results and discussion

The Re^V(NAr) complexes and their structure

The α-diimine ligands employed in the present work are abbreviated as L1(X = H), L2(X = Me) and L3(X = Cl) (general abbreviation, L). The Ar group in Re^V(NAr) is of type C₆H₄X(p). The three complexes of type [Re^V(NC₆H₄X)Cl₃(L)], (1), were synthesized from the [Re(NAr)Cl₃(PPh₃)₂] precursors in boiling PhMe, Equation (1).





We have succeeded in obtaining single crystals of $[\text{Re}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1})]$ and its X-ray structure has been determined. A perspective view of the molecule is shown in Figure 1 and selected bond parameters are listed in Table 2.

The coordination sphere is a distorted octahedron and the ReCl_3 fragment is meridional. The Cl1, Cl2,

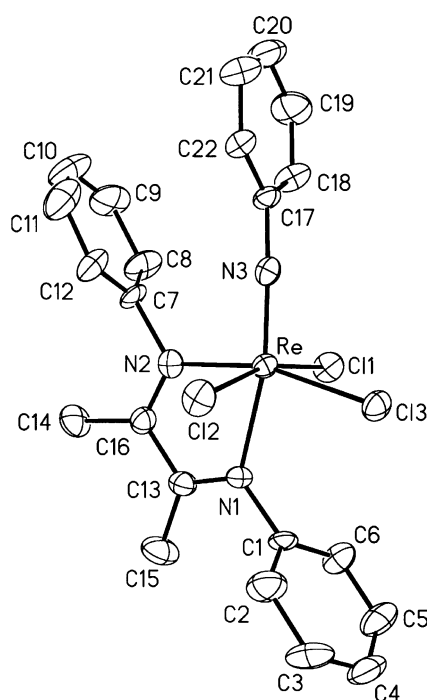


Fig. 1. Perspective view and atom labeling scheme for $[\text{Re}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1})]$. The non-H atoms are shown with 30% thermal probability ellipsoids. H atoms are omitted for clarity.

Table 2. Selected bond lengths (\AA) and bond angles ($^\circ$) for $[\text{Re}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1})] \cdot \text{H}_2\text{O}$

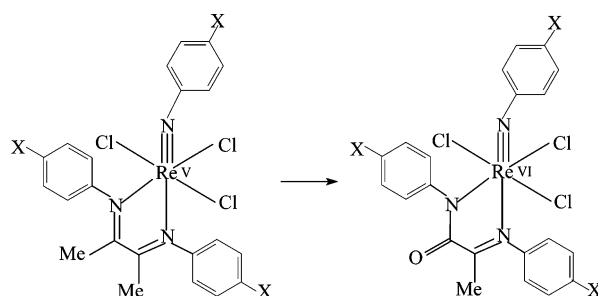
Bond lengths			
Re–N3	1.711(9)	Re–Cl1	2.369(3)
Re–N1	2.177(8)	Re–Cl2	2.352(3)
Re–N2	2.017(9)	Re–Cl3	2.335(3)
Bond angles			
N3–Re–N2	92.2(4)	N3–Re–N1	163.7(4)
N2–Re–N1	72.5(3)	N3–Re–Cl3	104.0(3)
N2–Re–Cl3	163.8(3)	N1–Re–Cl3	91.3(2)
N3–Re–Cl2	101.6(3)	N2–Re–Cl2	90.1(2)
N1–Re–Cl2	84.3(2)	Cl3–Re–Cl2	86.91(11)
N3–Re–Cl1	92.4(3)	N2–Re–Cl1	91.8(2)
N1–Re–Cl1	82.9(2)	Cl3–Re–Cl1	87.40(11)
Cl2–Re–Cl1	165.86(11)		

Cl3 and N2 atoms define the good equatorial plane with a mean deviation of *ca.* 0.01 \AA . The metal atom is displaced from this plane by *ca.* 0.29 \AA towards the N3 atom. The chelate ring in the molecule is planar with a mean deviation of 0.01 \AA . The two pendent phenyl rings make different dihedral angles (85.4° and 78.6°) with the chelate ring.

The Re–N3 distance, 1.711(9) \AA is close to the idealized $\text{Re} \equiv \text{N}$ bond length of 1.69 \AA [19]. The Re–N3–Cl17 angle is 166.6°, close to linearity. The Re–N1 bond lying trans to the imido group is 0.16 \AA longer than the Re–N2 bond trans to a chloride ligand. This is attributed to the trans effect of the NPh group.

Metal and ligand oxidation : characterization of the $\text{Re}^{\text{VI}}(\text{NAr})$ products

The $[\text{Re}^{\text{V}}(\text{NAr})\text{Cl}_3(\text{L})]$ complexes were found to react smoothly with dilute HNO_3 in MeCN at room temperature furnishing brown $[\text{Re}^{\text{VI}}(\text{NAr})\text{Cl}_3(\text{L}')]_2$ (2) complexes in moderate yield. Here **L'** [**L1'** (**X** = H), **L2'** (**X** = Me), **L3'** (**X** = Cl)] is the monoionized iminoacetamide ligand.



The type (2) complexes did not afford single crystals but their spectroscopic and magnetic properties taken collectively with those of related structurally characterized complexes [8] are fully consistent with the proposed structure (2).

The magnetic moments of (2) lie in the range 1.49–1.52 μB at room temperature. The moments are smaller than the spin-only value ($S = 1/2$) due to spin-orbit coupling [20]. In CH_2Cl_2 solution the complexes display well-resolved six line ($I = 5/2$) EPR spectra due

to hyperfine interactions with ^{185}Re (37.07%) and ^{187}Re (62.93%) which have nearly equal nuclear moments. The separation between the adjacent lines increases with increasing magnetic moment (H) due to second-order effects [21]. Center-field g values and the average hyperfine splittings (A) are listed in Table 3 and a representative EPR spectrum is shown in Figure 2.

Selected IR and UV–visible bands are collected in Table 4. The meridional ReCl_3 fragment can in principle give rise to three Re–Cl stretches of which at least two are observed in every type (2) complex. Two amide bands are observed in the ranges $1560\text{--}1568\text{ cm}^{-1}$ and

$1620\text{--}1624\text{ cm}^{-1}$. The type (2) complexes display a relatively weak absorption band near 500 nm in the visible region.

The precursor complexes of type (1) are known to display a $\text{Re}^{\text{VI}}/\text{Re}^{\text{V}}$ couple near 1.0 V, the oxidized complex being unstable [22]. In contrast the anionic amide ligand once stabilizes the hexavalent state and complexes (2) display quasi reversible $\text{Re}^{\text{VI}}/\text{Re}^{\text{V}}$ as well as $\text{Re}^{\text{VII}}/\text{Re}^{\text{VI}}$ couples near 0.2 and 1.6 V, respectively (Table 5). A representative voltammogram of a type (2) species is shown in Figure 3.

The decrease in $\text{Re}^{\text{VI}}/\text{Re}^{\text{V}}$ reduction potential by *ca.* 0.8 V highlights the preference of the amide ligand for the higher oxidation state of the metal.

Table 3. EPR spectral data at 300 K in CH_2Cl_2 solution

Compound	g^a	A^b
$[\text{Re}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1}')]]$	1.877	481
$[\text{Re}(\text{NC}_6\text{H}_4\text{Me})\text{Cl}_3(\text{L2}')]$	1.895	482
$[\text{Re}(\text{NC}_6\text{H}_4\text{Cl})\text{Cl}_3(\text{L3}')]$	1.901	481

^aAt center field.

^bAverage values.

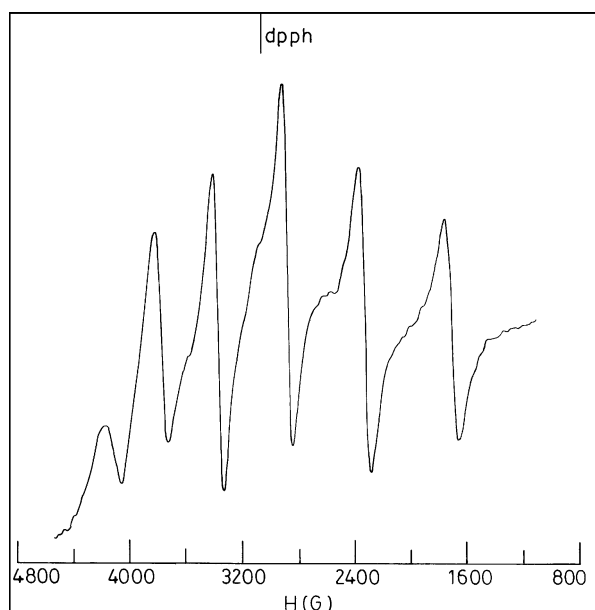


Fig. 2. ESR spectrum of $[\text{Re}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1}')]]$ in CH_2Cl_2 solution at 300 K. The instrument settings are: power, 30 dB; modulation, 100 KHz; sweep center, 3200 G.

Table 5. Cyclic voltammetric reduction potential data^a (300 K)

Complexes	$E_{1/2}$, V(ΔE_p^b , mV)	
	$\text{Re}^{\text{VI}}/\text{Re}^{\text{V}}$	$\text{Re}^{\text{VII}}/\text{Re}^{\text{VI}}$
$[\text{Re}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1})]$	0.93(70)	
$[\text{Re}(\text{NC}_6\text{H}_4\text{Me})\text{Cl}_3(\text{L2})]$	0.93(70)	
$[\text{Re}(\text{NC}_6\text{H}_4\text{Cl})\text{Cl}_3(\text{L3})]$	1.07(80)	
$[\text{Re}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1}')]]$	0.20(70)	1.56(100)
$[\text{Re}(\text{NC}_6\text{H}_4\text{Me})\text{Cl}_3(\text{L2}')]$	0.19(60)	1.54(100)
$[\text{Re}(\text{NC}_6\text{H}_4\text{Cl})\text{Cl}_3(\text{L3}')]$	0.22(70)	1.58(100)

^aSolvent is MeCN.

^b ΔE_p is peak-to-peak separation.

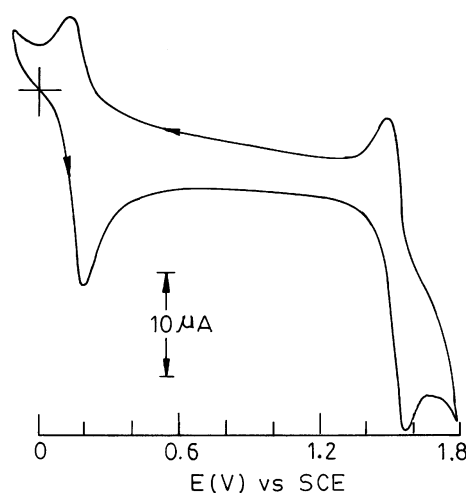


Fig. 3. Cyclic voltammogram of $[\text{Re}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1}')]]$ in MeCN solution at 300 K.

Table 4. UV–vis and IR spectral data

Complexes	UV–vis data ^a	IR data ^c (cm^{-1})		
	λ_{max} , (nm) (ϵ^b , $\text{M}^{-1}\text{cm}^{-1}$)	$\nu_{\text{Re–Cl}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=O}}$
$[\text{Re}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1})]$	345(8400), 517(4300), 740(720)	300, 315, 335	1485	
$[\text{Re}(\text{NC}_6\text{H}_4\text{Me})\text{Cl}_3(\text{L2})]$	340(9500), 515(5000), 750(1450)	300, 317, 334	1505, 1592	
$[\text{Re}(\text{NC}_6\text{H}_4\text{Cl})\text{Cl}_3(\text{L3})]$	346(8650), 521(4750), 750(1500)	320, 340	1491, 1595	
$[\text{Re}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1}')]]$	370(6000), 512(900)	305, 320, 335	1560	1620
$[\text{Re}(\text{NC}_6\text{H}_4\text{Me})\text{Cl}_3(\text{L2}')]$	372(5500), 510(1200)	310, 326	1565	1624
$[\text{Re}(\text{NC}_6\text{H}_4\text{Cl})\text{Cl}_3(\text{L3}')]$	378(5460), 519(920)	325, 340	1568	1622

^aSolvent is CH_2Cl_2 .

^bExtinction coefficient.

^cIn KBr disk.

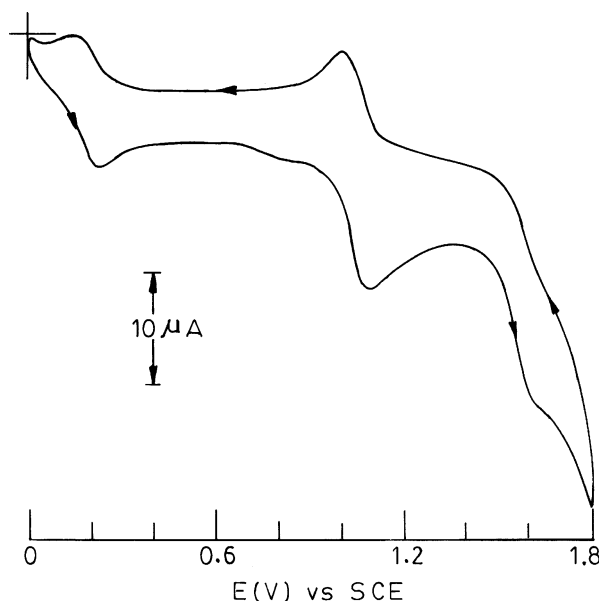


Fig. 4. Cyclic voltammogram (in MeCN solution) of the product obtained after solvent removal following the reaction of $[\text{Re}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1})]^+$ with H_2O at 300 K.

Nature of the imine \rightarrow amide oxidation

This oxidation is also achievable electrochemically. Upon exhaustive one-electron coulometry of $[\text{Re}^{\text{V}}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1})]$ at 1.2 V in dry MeCN the corresponding cation $[\text{Re}^{\text{VI}}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1})]^+$ is obtained in solution. Its cyclic voltammetry (initial scan cathodic) is virtually superimposable on that of the parent complex (initial scan anodic). However, upon making the solvent moist the hexavalent complex gets transformed to the amide complex $[\text{Re}^{\text{VI}}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1}')]^+$, also regenerating a substantial part of the parent complex. The residue obtained after solvent removal affords a cyclic voltammogram (Figure 4) in which $[\text{Re}^{\text{VI}}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1}')]^+$ and $[\text{Re}^{\text{V}}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1})]$ are in a 1:2 ratio. This can be rationalized by assuming that a H_2O molecule adds to the more polarized imine function with a shorter Re–N length (see the structure of $[\text{Re}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1})]$) furnishing the α -hydroxylamine intermediate, which can then react via an induced electron transfer route [23] finally affording $[\text{Re}^{\text{VI}}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1}')]^+$.

Conclusions

Imidorhenium(V) complexes bearing monoionized iminoamide ligands have been synthesized *via* metal promoted ligand oxidation of the corresponding imidorhenium(V) species incorporating diazabutadiene. Further studies on such rhenium mediated imine \rightarrow amide oxidations are in progress.

Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data

Centre (CCDC), CCDC No. 249244 for the complex $[\text{Re}(\text{NC}_6\text{H}_5)\text{Cl}_3(\text{L1})]$. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or website: <http://www.ccdc.cam.ac.uk>).

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