Pyridine-2-carboxamide complexes of arylimidorhenium(VI) derived from 2-pyridylmethyleneamine complexes of arylimidorhenium(V) *via* oxygen-atom transfer†

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Complexes of type $[\mathrm{Re^{V}L(NC_6H_4Y\text{-}\mathit{p})Cl_3}]$ (Y = H or Cl) have been synthesized where L is the Schiff base formed from pyridine-2-carbaldehyde and the aniline p-$\mathrm{XC_6H_4NH_2}$ (X = Me or Cl). Treatment with aqueous nitric acid in acetonitrile converts them into $[\mathrm{Re^{VI}L'(NC_6H_4Y\text{-}\mathit{p})Cl_3}]$, where L′ is a monoanionic pyridine-2-carboxamide. The latter complexes display hyperfine-split six-line solution EPR spectra at room temperature. The crystal structures of $[\mathrm{ReL(NC_6H_4Cl)Cl_3}]$ and $[\mathrm{ReL'(NC_6H_4Cl)Cl_3}]$ (X = Me in both cases) revealed the presence of severely distorted and meridionally configured $\mathrm{ReCl_3N_3}$ co-ordination spheres. The effective metal radius decreases only marginally upon metal oxidation and the imide fragment is approximately linear and triple bonded, Re≡N−C, in both cases. The rhenium(VI)–rhenium(V) reduction potentials in the two types of complex are ≈1.0 and ≈0.2 V respectively.

Rhenium-promoted oxygen-atom-transfer reactions[1] have received significant recent attention.[2–5] The usual type of transfer is from an oxo complex ‘Re^{i}O’ (i = metal valence) to an oxophilic substrate E, equation (1), where ‘Re^{i-2}’ is the reduced

$$\mathrm{Re^{\mathit{i}}O + E \longrightarrow Re^{\mathit{i}-2} + EO} \qquad (1)$$

rhenium product. We have shown that rhenium(III) complexes of 2-pyridylmethyleneamines **1** undergo an unusual oxygen-atom-transfer reaction in oxidizing aqueous environments affording rhenium(IV) pyridine-2-carboxamide species of type **2**.[6] The synthetic scope of this transformation is being further explored. Herein we report its utilization for making stable pyridine-2-carboxamide complexes incorporating the very rare arylimide motif of hexavalent rhenium. The precursors are the 2-pyridylmethyleneamine chelates of arylimidorhenium(V). The structure and properties of these arylimidorhenium-(V) and -(VI) families are described.

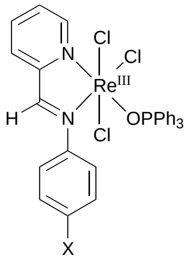
Results and Discussion

Synthesis

The aldimine complexes $[\mathrm{ReL(NC_6H_4Y)Cl_3}]$ **3** were synthesized in excellent yields by treating the phosphine oxide species[6] of type **1** with an excess of arylamine, p-$\mathrm{YC_6H_4NH_2}$, in boiling toluene, equation (2). The reaction involves a redistribution of the oxidation states of the metal and the phosphorus atom.

$$[\mathrm{Re^{III}L(OP^{V}Ph_3)Cl_3}] + p\text{-}\mathrm{YC_6H_4NH_2} \longrightarrow [\mathrm{Re^{V}L(NC_6H_4Y\text{-}\mathit{p})Cl_3}] + \mathrm{P^{III}Ph_3} + \mathrm{H_2O} \qquad (2)$$

Violet solutions of $[\mathrm{ReL(NC_6H_4Y)Cl_3}]$ treated with aqueous 0.5 mol dm^{-3} nitric acid in acetonitrile solution at room temperature rapidly change to brown and from the reaction mixture the carboxamide complexes $[\mathrm{ReL'(NC_6H_4Y)Cl_3}]$ **4** incorporating arylimidorhenium(VI) can be isolated in high yields. Authentic complexes of $\mathrm{Re^{VI}(NR)}$ (R = alkyl or aryl) are very rare[7–10] and no complex with R = aryl has so far been structurally characterized. The type **4** complexes are of special interest in this context.



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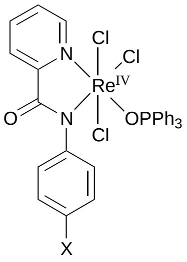

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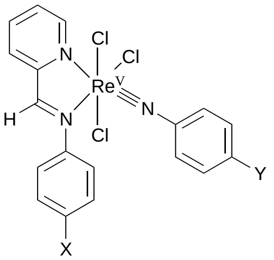

3a [ReL^1(NPh)Cl$_3$] (X = Me, Y = H)
3b [ReL^1(NC$_6$H$_4$Cl)Cl$_3$] (X = Me, Y = Cl)
3c [ReL^2(NC$_6$H$_4$Cl)Cl$_3$] (X = Cl, Y = Cl)

Rate studies on **1** ⟶ **2** and related aldimine ⟶ amide conversions in oxidizing aqueous environments have revealed that the rate-determining step is the addition of a molecule of water to the aldimine function polarized by one-electron metal oxidation.[6b,11,12] The water adduct undergoes induced electron transfer[13] associated with proton dissociation. It is logical to assume that a similar mechanism is applicable for the conversion **3** ⟶ **4**, the initial steps being the one-electron oxidation (by nitric acid) of **3** to $[\mathrm{Re^{VI}L(NC_6H_4Y)Cl_3}]^+$ (also accessible electrochemically, see below) and formation of its water adduct, **5**. The net transformation is as in equation (3). The three

$$[\mathrm{Re^{V}L(NC_6H_4Y)Cl_3}] + \mathrm{H_2O} \longrightarrow [\mathrm{Re^{VI}L'(NC_6H_4Y)Cl_3}] + 3\mathrm{e^-} + 3\mathrm{H^+} \qquad (3)$$

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† Dedicated to the memory of Professor Sir Geoffrey Wilkinson.

Non-SI units employed: $\mu_\mathrm{B} \approx 9.27 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.

Table 1 Electronic spectral[a] and IR[b] data at 298 K

Compound	UV/VIS λ_{max}/nm (ε/dm^{-3} mol^{-1} cm^{-1})	IR $\tilde{\nu}$/cm^{-1}
3a [ReL^1(NPh)Cl$_3$]	740 (1530), 540 (7310), 315 (10 500)	330, 1600
3b [ReL^1(NC$_6$H$_4$Cl)Cl$_3$]	740 (1460), 540 (7180), 325 (13 285)	325, 1595
3c [ReL^2(NC$_6$H$_4$Cl)Cl$_3$]	740 (1150), 545 (6125), 330 (10 210)	320, 1600
4a [ReL$^{1'}$(NPh)Cl$_3$]	530 (1930), 345 (14 605)	325, 1595, 1635
4b [ReL$^{1'}$(NC$_6$H$_4$Cl)Cl$_3$]	530 (2030), 360 (17 650)	310, 330, 1600, 1635
4c [ReL$^{2'}$(NC$_6$H$_4$Cl)Cl$_3$]	530 (2050), 360 (18 600)	320, 330, 1600, 1640

[a] The solvent is dichloromethane. [b] In KBr disc; ν(Re–Cl) 310–330, ν(C=N) 1595–1600, ν(C=O) 1595–1640 cm^{-1}.

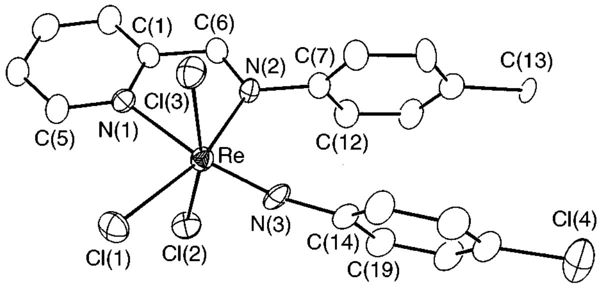
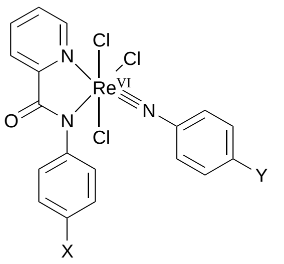


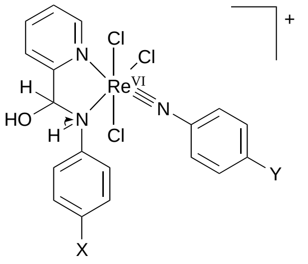
Fig. 1 An ORTEP[14] plot and atom labelling scheme for [ReL^1(NC$_6$H$_4$Cl-*p*)Cl$_3$] **3b**. All atoms are represented by their 30% thermal probability ellipsoids; H atoms are omitted for clarity



4a [ReL$^{1'}$(NPh)Cl$_3$] (X = Me, Y = H)

4b [ReL$^{1'}$(NC$_6$H$_4$Cl)Cl$_3$] (X = Me, Y = Cl)

4c [ReL$^{2'}$(NC$_6$H$_4$Cl)Cl$_3$] (X = Cl, Y = Cl)



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electrons are consumed by the external oxidant, nitric acid. The aldimine and amide complexes show one or two Re–Cl stretch(es) around 330 cm^{-1}, Table 1. The two strong amide bands of [ReL′(C$_6$H$_4$Y)Cl$_3$] and the C=N stretch of [ReL(C$_6$H$_4$Y)Cl$_3$] occur in the region 1590–1640 cm^{-1}. Characteristic electronic bands in the visible region are listed in Table 1.

Structures

The crystal structures of [ReL^1(NC$_6$H$_4$Cl)Cl$_3$] **3b** and [ReL$^{1'}$(NC$_6$H$_4$Cl)Cl$_3$] **4b** have been determined. Views of the molecules are shown in Figs. 1 and 2 and selected bond parameters are listed in Table 2. In both compounds the co-ordination geometry is distorted octahedral and the ReCl$_3$ fragment is meridionally spanning. The five-membered chelate ring along with the pyridine ring constitute an excellent plane in each case with mean deviation of ≈0.01 Å. The Cl(1), Cl(2), Cl(3) and N(2) atoms define virtually perfect planes from which the metal atom is displaced towards the imide nitrogen N(3) by 0.30 Å in **3b** and 0.28 Å in **4b**.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **3b** and **4b**

	3b	**4b**
Re–Cl(1)	2.357(4)	2.343(3)
Re–Cl(2)	2.392(4)	2.347(3)
Re–Cl(3)	2.359(3)	2.327(3)
Re–N(1)	2.224(8)	2.208(6)
Re–N(2)	2.033(8)	2.058(6)
Re–N(3)	1.697(8)	1.722(6)
N(2)–C(6)	1.302(13)	1.353(9)
C(6)–O	—	1.227(9)
Cl(1)–Re–Cl(2)	88.1(1)	88.7(1)
Cl(1)–Re–Cl(3)	87.8(1)	87.6(1)
Cl(2)–Re–Cl(3)	165.5(1)	166.1(1)
Cl(1)–Re–N(1)	90.0(2)	89.7(2)
Cl(2)–Re–N(1)	81.4(2)	81.8(2)
Cl(3)–Re–N(1)	84.7(2)	84.8(2)
Cl(1)–Re–N(2)	164.1(2)	165.0(2)
Cl(2)–Re–N(2)	92.0(2)	90.9(2)
Cl(3)–Re–N(2)	88.2(2)	89.3(2)
N(1)–Re–N(2)	74.3(3)	75.4(2)
Cl(1)–Re–N(3)	103.0(3)	102.1(2)
Cl(2)–Re–N(3)	96.0(3)	92.0(2)
Cl(3)–Re–N(3)	98.4(3)	101.9(2)
N(1)–Re–N(3)	166.7(4)	166.6(2)
N(2)–Re–N(3)	92.9(4)	92.9(3)
Re–N(3)–C(14)	168.4(7)	166.8(5)

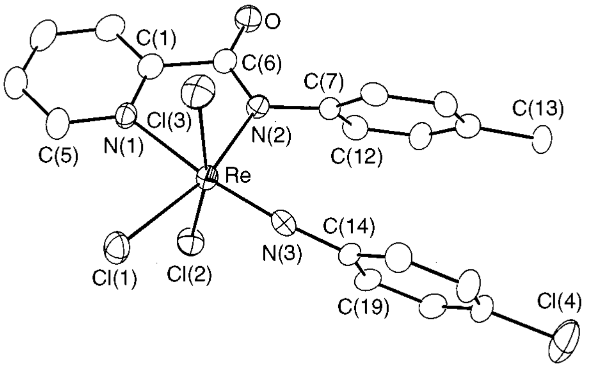

Fig. 2 An ORTEP plot and atom labelling scheme for [ReL$^{1'}$(NC$_6$H$_4$Cl-*p*)Cl$_3$] **4b**. Details as in Fig. 1

The amide group C(1)C(6)ON(2) in complex **4b** is planar with a mean deviation of 0.01 Å, the C(6)–O distance being 1.227(9) Å. The average Re–Cl length in **4b** is shorter than that in **3b** by ≈0.02 Å probably reflecting a small radial contraction between rhenium-(V) and -(VI). The Re–N(1) length in each complex is longer than the corresponding Re–N(2) length by ≈0.2 Å due to the *trans* influence of the imide nitrogen. The imide fragment Re–N(3)–C(14) is roughly linear in both complexes and the Re–N distance corresponds to triple bonding (ideal length Re^{V}≡NR ≈ 1.69 Å).[15]

Table 3 Cyclic voltammetric formal potentials[a] and EPR spectral data[b] at 298 K

Compound	$E_{\frac{1}{2}}$/V (ΔE_p/mV)	g[c]	A/G[d]
3a	0.96 (80)		
3b	1.04 (80)		
3c	1.08 (60)		
4a	0.14 (80), 1.50 (80)	1.906	484
4b	0.16 (80), 1.52 (80)	1.923	488
4c	0.23 (80), 1.63 (80)	1.917	492

[a] Solvent, acetonitrile; scan rate, 50 mV s^{-1}; $E_{\frac{1}{2}} = \frac{1}{2}(E_{pa} + E_{pc})$ where E_{pa} and E_{pc} are the anodic and cathodic peak potentials respectively; $\Delta E_p = E_{pc} - E_{pa}$. Reference electrode, SCE. The concerned couples are **3**$^+$–**3** (Re^{VI}–Re^{V}), **4**–**4**$^-$ (Re^{VI}–Re^{V}), **4**$^+$–**4** (Re^{VII}–Re^{VI}). [b] Solvent, dichloromethane–toluene (1:1). [c] At centre field. [d] Average values of hyperfine splitting.

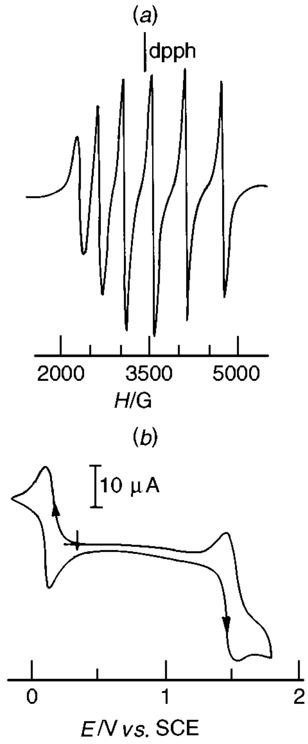

Fig. 3 (*a*) X-Band EPR spectrum of [ReL$^{1\prime}$(NC$_6$H$_4$Cl-*p*)Cl$_3$] in dichloromethane–toluene (1:1). Instrument settings: power 28 dB; modulation, 100 kHz; sweep centre, 3000 G; sweep time, 250 s, at 298 K; dpph = diphenylpicrylhydrazyl. (*b*) Cyclic voltammogram of a ≈10^{-3} mol dm^{-3} solution of [ReL$^{1\prime}$(NC$_6$H$_4$Cl-*p*)Cl$_3$] in acetonitrile (0.1 mol dm^{-3} NEt$_4$ClO$_4$) at a platinum electrode (scan rate, 50 mV s^{-1})

Only one other six-co-ordinated complex of Re^{VI}(NR), *viz*. [Re(NC$_2$Cl$_5$)Cl$_4$(POCl$_3$)] having a perhalogenated R group, has been structurally characterized.[9] The structures of two tetrahedral Re^{VI}(NR) species with a bulky R group (Bu^t) are also known.[10] Complex **4b** represents the first structurally characterized pseudo-octahedral Re^{VI}(NR) species in which a simple aryl function devoid of special electronic/steric features constitutes the R group. In the case of Re^{V}(NR) a few six-co-ordinated structures are known.[7,15–21]

EPR spectra of [ReL′(NC$_6$H$_4$Y)Cl$_3$]

The [Re^{V}L(NC$_6$H$_4$Y)Cl$_3$] complexes are diamagnetic (5d$_{xy}^2$). The bulk magnetic moments of [Re^{VI}L′(NC$_6$H$_4$Y)Cl$_3$] (5d$_{xy}^1$) are however significantly lower (1.4–1.5 μ_B, 298 K) than the spin-only value due to orbital coupling.[22,23]

The amide complexes display well resolved EPR lines in fluid solutions at room temperature which is relatively unusual for rhenium(VI) species.[18,23] The hyperfine structure consists of six lines ($I = \frac{5}{2}$ for ^{185}Re, 37.07% and ^{187}Re, 62.93%). The lines are unequally spaced reflecting second-order effects.[24] Centre-field *g* values and average hyperfine splittings are collected in Table 3 and a representative spectrum is shown in Fig. 3(*a*).

Reduction potentials

The aldimine and amide complexes display quasi-reversible one-electron voltammetric responses with peak-to-peak separations of ≈80 mV in acetonitrile solutions at a platinum electrode. Reduction potentials are listed in Table 3 and a representative voltammogram is shown in Fig. 3(*b*).

A single response occurs for [Re^{V}L(NC$_6$H$_4$Y)Cl$_3$] corresponding to the couple in equation (4). The reduction potential

$$[\mathrm{Re^{VI}L(NC_6H_4Y)Cl_3}]^+ + \mathrm{e}^- \rightleftharpoons [\mathrm{Re^{V}L(NC_6H_4Y)Cl_3}] \quad (4)$$

is ≈1.0 V *vs*. SCE and thus the one-electron oxidized complex which is crucial for the aldimine ⟶ amide conversion (see above) is accessible *via* nitric acid oxidation as well. The amide complexes [Re^{VI}L′(NC$_6$H$_4$Y)Cl$_3$] show two successive redox processes, equations (5) and (6).

$$[\mathrm{Re^{VII}L'(NC_6H_4Y)Cl_3}]^+ + \mathrm{e}^- \rightleftharpoons [\mathrm{Re^{VI}L'(NC_6H_4Y)Cl_3}] \quad (5)$$

$$[\mathrm{Re^{VI}L'(NC_6H_4Y)Cl_3}] + \mathrm{e}^- \rightleftharpoons [\mathrm{Re^{V}L'(NC_6H_4Y)Cl_3}]^- \quad (6)$$

The reduction potentials are subject to the usual Hammett effect (Table 3) of the X and Y substituents. The most remarkable feature is the depression of the rhenium(VI)–rhenium(V) couple by ≈0.8 V on going from [Re^{V}L(NC$_6$H$_4$Y)Cl$_3$] [equation (4)] to [Re^{VI}L′(NC$_6$H$_4$Y)Cl$_3$] [equation (6)]. In the redox sense the deprotonated amide function stabilizes the rhenium(VI) state to a great extent and this forms the basis of the stabilization of the arylimidorhenium(VI) motif upon co-ordination to pyridine-2-carboxamide. The stabilization is sufficient to make the rhenium(VII)–rhenium(VI) couple, equation (5), observable near 1.5 V.

Conclusion

It is demonstrated that the 2-pyridylmethyleneamine complexes [Re^{V}L(NC$_6$H$_4$Y-*p*)Cl$_3$] undergo facile oxygen-atom transfer in aqueous nitric acid affording the pyridine-2-carboxamide species [Re^{VI}L′(NC$_6$H$_4$Y-*p*)Cl$_3$] in excellent yields. Structural characterization of [Re^{V}L^1(NC$_6$H$_4$Cl)Cl$_3$] and [Re^{VI}L$^{1\prime}$(NC$_6$H$_4$Cl)Cl$_3$] has revealed the presence of nearly linear and triple bonded Re≡N–C fragments. The metal radius contracts only slightly upon metal oxidation. The amide ligand imparts remarkable redox stability to the rhenium(VI) state shifting the rhenium(VI)–rhenium(V) reduction potential to lower values by ≈0.8 V on going from the aldimine to the amide species. The latter display well resolved solution EPR spectra at room temperature.

Experimental

Materials

Complexes of type **1**[6] were prepared by reported methods. The purification and drying of dichloromethane and acetonitrile for synthesis as well as for electrochemical and spectral work were done as described.[25] Toluene was distilled over sodium before use. All other chemicals and solvents were of reagent grade and used as received.

Physical measurements

Spectra were recorded with the following equipment: electronic spectra, Hitachi 330 spectrophotometer; infrared spectra (KBr disc, 4000–300 cm^{-1}), Perkin-Elmer 783 spectrophotometer; X-band EPR spectra, Varian E-109C spectrometer (calibrant dpph, $g = 2.0037$). Electrochemical measurements were done by using a PAR model 370-4 electrochemistry system as described.[26] All experiments were performed at a platinum working electrode under a dinitrogen atmosphere, the supporting electrolyte being tetraethylammonium perchlorate. The potentials are referred to the saturated calomel electrode (SCE) and are uncorrected for the junction contribution. Magnetic susceptibilities were measured on a PAR-155 vibrating-sample magnetometer. Microanalyses were done using a Perkin-Elmer 240C elemental analyser. All compounds afforded satisfactory elemental analysis and only some representative instances will be cited.

Syntheses

$[Re^{V}L(NC_6H_4Y\text{-}p)Cl_3]$ 3. The complexes were prepared by the same general method. Details are given for **3b**. Yields were in the range 70–75%.

The complex $[ReL(OPPh_3)Cl_3]$ (100 mg, 0.13 mmol) was suspended in toluene (10 cm^3) and warmed to 60 °C. *p*-Chloroaniline (150 mg, 1.18 mmol) was added and the mixture refluxed for 2 h. The violet solution obtained was evaporated to dryness under reduced pressure and the resulting solid product dissolved in dichloromethane (5 cm^3) and subjected to chromatography on a silica gel column (20 × 1 cm; 60–120 mesh, BDH). The small yellow band which separated upon elution with benzene was rejected. The violet band that followed was eluted with benzene–acetonitrile (10:1). The required complex was obtained from the eluate as shiny dark microcrystals, by slow evaporation. Yield: 59 mg, 74% (Found: C, 39.2; H, 3.0; N, 7.2. Calc. for $C_{19}H_{17}Cl_3N_3Re$ **3a**: C, 39.35; H, 2.95; N, 7.25. Found: C, 37.25; H, 2.55; N, 6.90. Calc. for $C_{19}H_{16}Cl_4N_3Re$ **3b**: C, 37.15; H, 2.6; N, 6.85. Found: C, 35.15; H, 2.15; N, 6.55. Calc. for $C_{18}H_{13}Cl_5N_3Re$ **3c**: C, 34.05; H, 2.05; N, 6.6%).

$[Re^{VI}L'(NC_6H_4Y\text{-}p)Cl_3]$ 4. The same general method was used to synthesize complexes **4** from **3**. Details are given for **4b**. Yields varied in the range 80–85%.

The complex $[ReL^1(NC_6H_4Cl)Cl_3]$ (100 mg, 0.16 mmol) was dissolved in acetonitrile (20 cm^3) and 0.5 mol dm^{-3} aqueous nitric acid (0.2 cm^3) was added. The solution was stirred for 1 h during which time it turned brown. Solvent evaporation afforded a dark product which was repeatedly washed with water and dried *in vacuo* over P_4O_{10}. Yield: 84 mg, 82% (Found: C, 38.2; H, 2.75; N, 7.1. Calc. for $C_{19}H_{16}Cl_3N_3ORe$ **4a**: C, 38.35; H, 2.7; N, 7.05. Found: C, 36.3; H, 2.3; N, 6.6. Calc. for $C_{19}H_{15}Cl_4N_3ORe$ **4b**: C, 36.25; H, 2.4; N, 6.7. Found: C, 33.2; H, 2.0; N, 6.4. Calc. for $C_{18}H_{12}Cl_5N_3ORe$ **4c**: C, 33.25; H, 1.85; N, 6.45%).

Crystallography

Single crystals of complexes **3b** and **4b** were grown by slow diffusion of hexane into dichloromethane solutions of the respective complexes. Both crystals were dark coloured and similar procedures were used for both.

Cell parameters were determined by a least-squares fit of 30 machine-centred reflections ($2\theta = 15$–30°). Data were collected at 22 °C by the ω-scan technique in the range $3 \leqslant 2\theta \leqslant 50°$ on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å). Two check reflections after every 198 showed no intensity reduction. All data were corrected for Lorentz-polarization and absorption.[27] A total of 3885 (complex **3b**) and 4096 (**4b**) reflections were collected of which 3611 and 3716 were respectively unique; of these 2715 and 2685 were respectively taken as observed $[I > 3\sigma(I)]$ for structure solution and refinement. 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 procedures. All hydrogen atoms were included in calculated positions with fixed $U = 0.08$ Å^2. All calculations were done on a Micro VAX II computer using the SHELXTL PLUS program package[28] and crystal structure plots were drawn using ORTEP.[14] Significant crystal data are listed in Table 4.

Table 4 Crystal data for $[Re^{V}L^1(NC_6H_4Cl)Cl_3]$ **3b** and $[Re^{VI}L^{1\prime}(NC_6H_4Cl)Cl_3]$ **4b**

Complex	**3b**	**4b**
Formula	$C_{19}H_{16}Cl_4N_3Re$	$C_{19}H_{15}Cl_4N_3ORe$
M	614.3	629.3
Crystal size/mm	0.16 × 0.14 × 0.08	0.20 × 0.26 × 0.48
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	7.176(5)	13.286(7)
b/Å	11.929(6)	11.286(7)
c/Å	12.919(10)	13.500(7)
α/°	105.69(5)	—
β/°	97.85(6)	98.79(4)
γ/°	90.73(5)	—
U/Å^3	1054(1)	2100(2)
Z	2	4
D_c/g cm^{-3}	1.937	1.991
μ(Mo-Kα)/cm^{-1}	62.86	63.11
F(000)	588	1204
Transmission coefficient	0.6728/1.0000	0.5923/1.0000
Total reflections	3885	4096
Number unique reflections	3611	3716
Number observed reflections	2715	2685
g in $w = 1/[\sigma^2(\lvert F\rvert) + g\lvert F\rvert^2]$	0.0003	0.0002
Number refined parameters	244	253
R^a	0.044	0.033
R'^b	0.051	0.036
Goodness of fit	1.73	1.39
Maximum and mean Δ/σ	0.001, 0.000	0.000, 0.000
Data-to-parameter ratio	11.1:1	10.6:1
Maximum, minimum difference peaks/e Å^{-3}	1.38, −2.16	1.05, −1.01

^{a} $R = \Sigma\lvert F_o\rvert - \lvert F_c\rvert/\Sigma\lvert F_o\rvert$. ^{b} $R' = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/478.

Acknowledgements

We thank the Department of Science and Technology, Indian National Science Academy, and the Council of Scientific and Industrial Research, New Delhi for financial support. Affiliation with the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore is acknowledged.

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Received 23*rd January* 1997; *Paper* 7/00529F