

# Chemistry of tricarbonylrhenium(I) chelates of azopyrimidines, azoimidazoles and anion radicals thereof<sup>☆</sup>

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## Abstract

The azopyrimidine and azoimidazole ligands (general abbreviations, RL) used in the present work are 2-(*p*-R-C<sub>6</sub>H<sub>4</sub>NN)C<sub>4</sub>H<sub>3</sub>N<sub>2</sub>, RL<sub>pm</sub> (R = H, Cl) and 2-(*p*-R-C<sub>6</sub>H<sub>4</sub>NN)-1-(Me)C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>, RL<sub>im</sub> (R = Me, Cl), respectively. The reaction of Re(CO)<sub>5</sub>Cl with a slight excess of RL in boiling benzene has furnished blue–violet complexes of type Re(CO)<sub>3</sub>Cl(RL) which have been spectrally characterized. In Re(CO)<sub>3</sub>Cl(HL<sub>pm</sub>) and Re(CO)<sub>3</sub>Cl(CIL<sub>im</sub>) the Re–N<sup>h</sup>, Re–N<sup>a</sup> distances are 2.173(6), 2.136(6) Å and 2.150(5), 2.166(5) Å, respectively (N<sup>h</sup> and N<sup>a</sup> are heterocyclic and azo N atoms, respectively). Their N–N lengths (1.271(8), 1.281(7) Å) implicate relatively weak Re-azo( $\pi^*$ ) back-bonding. In the lattice of Re(CO)<sub>3</sub>Cl(HL<sub>pm</sub>), pair-wise C–H $\cdots$ O hydrogen bonding between symmetry related molecules is present (C $\cdots$ O; 3.264(9) Å, H $\cdots$ O; 2.460(10) Å; C–H $\cdots$ O; 130.6(5)°). The lattice of Re(CO)<sub>3</sub>Cl(CIL<sub>im</sub>) also consists of centrosymmetric dimers held by aromatic  $\pi$ – $\pi$  stacking between parallelly placed pendant aryl rings (centroid $\cdots$ centroid distance, 3.781(9) Å). Extended Hückel calculations reveal that the LUMO of Re(CO)<sub>3</sub>Cl(RL) is  $\sim$ 60% azo in character. One-electron quasireversible electrochemical reduction occurs near –0.1 and –0.4 V vs. SCE in the cases of Re(CO)<sub>3</sub>Cl(RL<sub>pm</sub>) and Re(CO)<sub>3</sub>Cl(RL<sub>im</sub>), respectively. The redox orbital is believed to be to the above noted LUMO. Electrogenerated Re(CO)<sub>3</sub>Cl(RL $^{\cdot-}$ ) underwent spontaneous solvolytic chloride displacement in MeCN furnishing Re(CO)<sub>3</sub>(MeCN)(RL $^{\cdot-}$ ) which has been isolated. The latter in turn reacted with imidazole and triphenyl phosphine furnishing Re(CO)<sub>3</sub>(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)(RL $^{\cdot-}$ ) and Re(CO)<sub>3</sub>(PPh<sub>3</sub>)(RL $^{\cdot-}$ ), respectively. The pattern of carbonyl stretching frequencies of these radical anion complexes is similar to that of Re(CO)<sub>3</sub>Cl(RL) but for shifts to lower frequencies by 10–40 cm<sup>-1</sup>. All the three radical anion systems are one-electron paramagnets (1.7–1.8  $\mu_B$ ). The unpaired electron is primarily localized in a predominantly azo- $\pi^*$  orbital. A small metal contribution (<sup>185, 187</sup>Re, *I* = 5/2) is present and both Re(CO)<sub>3</sub>(MeCN)(RL $^{\cdot-}$ ) and Re(CO)<sub>3</sub>(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)(RL $^{\cdot-}$ ) display six-line EPR spectra (*A*  $\sim$  28 G). The line shapes and intensities are characteristic of the presence of *g*-strain. In the case of Re(CO)<sub>3</sub>(PPh<sub>3</sub>)(RL $^{\cdot-}$ ) seven nearly equispaced lines are observed due to virtually equal coupling with metal and <sup>31</sup>P (*I* = 1/2) nuclei. The *g* values of the radical species span the range 2.0033–2.0066. © 2004 Elsevier B.V. All rights reserved.

**Keywords:** Tricarbonylrhenium(I) chelates; Azoligands and radical anions thereof; Azopyrimidines and azoimidazoles

## 1. Introduction

In combination with appropriate coligands, azoheterocycles have been shown from this laboratory to act as versatile ligands suited for stable binding of all oxidation states of rhenium in the interval +1 to +5 [1–4]. In the

particular case of the monovalent state, homoleptic stabilization requires tris chelation thus satisfying the large back-bonding demand of the 5d<sup>6</sup> ion via multiple d( $\pi$ Re)–p( $\pi^*$ azo) interactions [4]. On the other hand, in the presence of a strong  $\pi$ -accepting coligand, bis/mono chelation of azoheterocycles to rhenium(I) should be feasible. In this context the Re<sup>I</sup>(CO)<sub>3</sub> moiety would be a good choice and indeed its monochelates with 2,2'-azobispyridine [5] and 2-(phenylazo)pyridine [6] have been structurally characterized. We also note that Re<sup>I</sup>(CO)<sub>3</sub> complexes are of general interest in terms of their potential photophysical [7] and radiopharmaceutical [8] properties.

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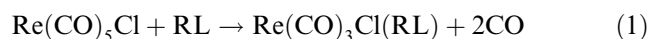
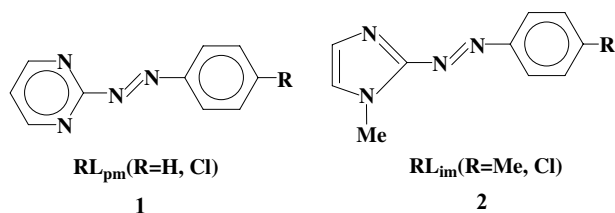
E-mail address: [icac@mahendra.iacs.res.in](mailto:icac@mahendra.iacs.res.in) (A. Chakravorty).

In the present work we explore the  $\text{Re}(\text{CO})_3$  chemistry of azopyrimidine and azoimidazole ligands (RL). The synthesis and structure of species of type  $\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}(\text{RL})$  are reported. Reductive halide elimination in the presence of neutral monodentate donors (D) have furnished radical anion organometallics of type  $\text{Re}^{\text{I}}(\text{CO})_3(\text{D})(\text{RL}^{\cdot-})$  which have been isolated and characterized.

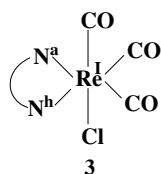
## 2. Results and discussion

### 2.1. Synthesis and characterization of $\text{Re}(\text{CO})_3\text{Cl}(\text{RL})$

The azoheterocycles (general abbreviation RL) used in the present work are 2-(arylo)pyrimidine ( $\text{RL}_{\text{pm}}$ ), **1** and 2-(arylo)-1-methylimidazole ( $\text{RL}_{\text{im}}$ ), **2**. The reaction, Eq. (1), of  $\text{Re}(\text{CO})_5\text{Cl}$  with slight excess of RL proceeds smoothly in boiling



benzene furnishing blue–violet crystalline complexes of composition  $\text{Re}(\text{CO})_3\text{Cl}(\text{RL})$  belonging to the coordination type **3** ( $\text{N}^{\text{a}}$  and  $\text{N}^{\text{h}}$  are azo and heterocyclic N atom, respectively) in excellent yields.



Spectral characterization data of the diamagnetic (idealized  $t_{2g}^6$ ) complexes are collected in Section 3. In  $^1\text{H}$  NMR, well resolved lines corresponding to RL protons are observed. The complexes are characterized by a moderately intense band near 550 nm in  $\text{Re}(\text{CO})_3\text{Cl}(\text{RL}_{\text{pm}})$  and near 510 nm in  $\text{Re}(\text{CO})_3\text{Cl}(\text{RL}_{\text{im}})$ . The band is assigned to MLCT transition of the idealized type  $t_{2g}(\text{Re}) \rightarrow \pi^*(\text{azo})$ . The observed band energy order  $\text{Re}(\text{CO})_3\text{Cl}(\text{RL}_{\text{pm}}) < \text{Re}(\text{CO})_3\text{Cl}(\text{RL}_{\text{im}})$  is consistent with the more negative reduction potential of the azo group in the latter species (vide infra). In IR three strong and sharp CO stretching frequencies are resolved near 2025, 1930 and  $1900\text{ cm}^{-1}$  (Table 1) in the case of  $\text{Re}(\text{CO})_3\text{Cl}(\text{RL}_{\text{im}})$ . However in  $\text{Re}(\text{CO})_3\text{Cl}(\text{RL}_{\text{pm}})$  only two strong bands occur near 2025 and  $1925\text{ cm}^{-1}$  (Table 1). The latter band is broader and more intense than the former and is believed to incorporate two unresolved components.

Table 1  
Carbonyl stretching frequencies<sup>a</sup>

Complexes	$\nu_{\text{CO}}\text{ cm}^{-1}$
$\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$	2032 <sup>s</sup> 1924 <sup>s,br</sup>
$\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{pm}})$	2022 <sup>s</sup> 1928 <sup>s,br</sup>
$\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$	2026 <sup>s</sup> 1931 <sup>s</sup> 1902 <sup>s</sup>
$\text{Re}(\text{CO})_3\text{Cl}(\text{MeL}_{\text{im}})$	2023 <sup>s</sup> 1934 <sup>s</sup> 1899 <sup>s</sup>
$\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})(\text{CIL}_{\text{pm}}^-)$	2010 <sup>s</sup> 1888 <sup>s,br</sup>
$\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})(\text{CIL}_{\text{im}}^-)$	2020 <sup>s</sup> 1924 <sup>s</sup> 1880 <sup>sh</sup>
$\text{Re}(\text{CO})_3(\text{PPh}_3)(\text{CIL}_{\text{pm}}^-)$	2010 <sup>s</sup> 1900 <sup>s,br</sup>
$\text{Re}(\text{CO})_3(\text{PPh}_3)(\text{CIL}_{\text{im}}^-)$	2010 <sup>s</sup> 1898 <sup>s,br</sup>
$\text{Re}(\text{CO})_3(\text{C}_3\text{H}_4\text{N}_2)(\text{CIL}_{\text{pm}}^-)$	2005 <sup>s</sup> 1890 <sup>s,br</sup>
$\text{Re}(\text{CO})_3(\text{C}_3\text{H}_4\text{N}_2)(\text{CIL}_{\text{im}}^-)$	2021 <sup>s</sup> 1925 <sup>sh</sup> 1901 <sup>s,br</sup>

<sup>a</sup> In KBr disc. <sup>s</sup> Strong peak, <sup>s,br</sup> Strong and broad, <sup>sh</sup> Shoulder.

### 2.2. Structure

The X-ray structures of  $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$  and  $\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$  have been accurately determined. Molecular views are shown in Figs. 1 and 2 and selected bond parameters are listed in Tables 2 and 3. In the distorted octahedral  $\text{ReC}_3\text{N}_2\text{Cl}$  coordination sphere the three carbon monoxide ligands are facially disposed to maximize Re–CO back-bonding. In  $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$ , the  $\text{Re}(\text{HL}_{\text{pm}})$  fragment excluding the pendant phenyl ring constitutes a good plane (mean deviation 0.03 Å) and the C11O1 and C12O2 molecules also lie on this plane which makes a dihedral angle of  $37.1^\circ$  with the pendant phenyl ring. The behaviour of  $\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$  is very similar; the dihedral angle between the corresponding plane and the pendant chlorophenyl group is  $45.1^\circ$ .

The structure of  $\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$  provides an opportunity to observe the effect of rhenium oxidation states on metal–ligand bond lengths via comparison with  $\text{Re}^{\text{II}}\text{Cl}_2(\text{MeL}_{\text{im}})_2$  [4a] and  $\text{Re}^{\text{III}}\text{Cl}_3(\text{OPPh}_3)(\text{CIL}_{\text{im}})$  [2a]. The average Re–N(imidazole), Re–N(azo) and Re–Cl lengths are 2.052(8), 2.003(8) and 2.389(3) Å, respectively in  $\text{Re}^{\text{II}}\text{Cl}_2(\text{MeL}_{\text{im}})_2$  and 1.999(14), 1.978(15) and 2.356(6) Å, respectively in  $\text{Re}^{\text{III}}\text{Cl}_3(\text{OPPh}_3)(\text{CIL}_{\text{im}})$ . Upon comparing with the lengths 2.150(5), 2.166(5) and

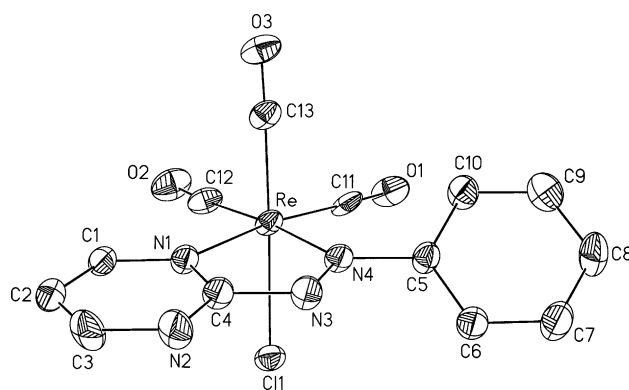


Fig. 1. Perspective view and atom-labeling scheme for  $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$ .

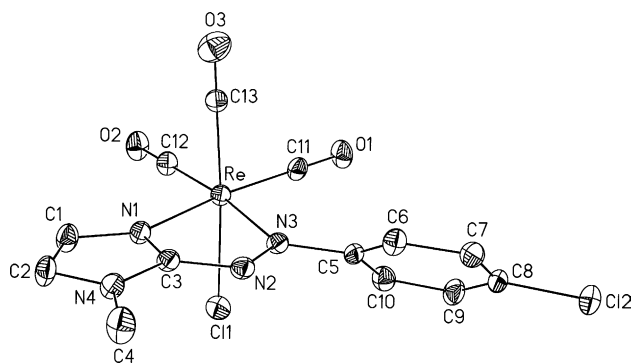


Fig. 2. Perspective view and atom-labeling scheme for  $\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$ .

2.449(2) Å, respectively in  $\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$ , the progressive contraction of the metal radius upon oxidation is neatly revealed. Between  $\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$  and  $\text{Re}^{\text{III}}\text{Cl}_3(\text{OPPh}_3)(\text{CIL}_{\text{im}})$  the above three distances decrease by as much as 0.1–0.2 Å. A similar bond length

Table 2

Selected bond parameters (bond lengths in Å; bond angles in °) for  $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$

Bond lengths			
Re–N(1)	2.173(6)	O(1)–C(11)	1.167(10)
Re–Cl(1)	2.467(2)	O(2)–C(12)	1.150(10)
Re–N(4)	2.136(6)	O(3)–C(13)	1.128(9)
Re–C(11)	1.916(8)	N(3)–N(4)	1.271(8)
Re–C(12)	1.920(8)	H(1)···O(3)	2.460(10)
Re–C(13)	1.923(8)	C(1)···O(3)	3.264(9)
Bond angles			
N(1)–Re–Cl(1)	83.0(2)	Cl(1)–Re–C(13)	177.1(2)
N(1)–Re–N(4)	73.0(2)	N(4)–Re–C(11)	98.3(3)
N(1)–Re–C(11)	170.6(2)	N(4)–Re–C(12)	173.6(3)
N(1)–Re–C(12)	101.0(3)	N(4)–Re–C(13)	94.9(3)
N(1)–Re–C(13)	94.1(3)	C(11)–Re–C(12)	87.5(4)
Cl(1)–Re–N(4)	83.8(2)	C(11)–Re–C(13)	90.1(3)
Cl(1)–Re–C(11)	92.6(2)	C(12)–Re–C(13)	87.7(3)
Cl(1)–Re–C(12)	93.3(2)	C(1)–H(1)···O(3)	130.6(5)

Table 3

Selected bond parameters (bond lengths in Å; bond angles in °) for  $\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$

Bond lengths			
Re–N(1)	2.150(5)	Re–C(13)	1.972(8)
Re–Cl(1)	2.449(2)	O(1)–C(11)	1.138(8)
Re–N(3)	2.166(5)	O(2)–C(12)	1.138(8)
Re–C(11)	1.916(7)	O(3)–C(13)	1.052(9)
Re–C(12)	1.917(7)	N(2)–N(3)	1.281(7)
Bond angles			
N(1)–Re–Cl(1)	86.4(2)	Cl(1)–Re–C(13)	175.8(2)
N(1)–Re–N(3)	73.0(2)	N(3)–Re–C(11)	96.5(2)
N(1)–Re–C(11)	169.5(2)	N(3)–Re–C(12)	173.3(2)
N(1)–Re–C(12)	101.0(2)	N(3)–Re–C(13)	93.8(2)
N(1)–Re–C(13)	89.5(2)	C(11)–Re–C(12)	89.5(3)
Cl(1)–Re–N(3)	85.8(2)	C(11)–Re–C(13)	89.9(3)
Cl(1)–Re–C(11)	94.2(2)	C(12)–Re–C(13)	89.2(3)
Cl(1)–Re–C(12)	90.7(2)		

trend is observed between  $\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$  and  $\text{Re}^{\text{III}}\text{Cl}_3(\text{OPPh}_3)(\text{HL}_{\text{pm}})$  [3]. In contrast to the Re–N and Re–Cl distances, the azo N–N length (1.27–1.28 Å) in the present  $\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}(\text{RL})$  complexes are significantly shorter than those (1.32–1.34 Å) [2a,3,4a] in the bivalent and trivalent complexes noted above.

This happens because in  $\text{Re}(\text{CO})_3\text{Cl}(\text{RL})$  the CO ligand act as a strong back-bonder, reducing the demand for Re–azo back-bonding.

Significant non-covalent interactions characterize both the lattices. In the case of  $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$  where all the H atoms were directly located in difference Fourier maps, C(1)–H(1)···O(3) hydrogen bonding between symmetry related molecules generate centrosymmetric pairs as depicted in Fig. 3(a). The relevant bond parameters (Table 2) are well within the acceptable ranges for such hydrogen bonding: C···O, 3.0–3.5 Å; H···O, 2.3–3.0 Å and C–H···O, 100–180° [9]. The lattice of  $\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$  also consists of dimers which incorporate aromatic  $\pi$ – $\pi$  stacking of the pendant aryl rings (Fig. 3(b)). The perpendicular distance between the two parallel six-membered rings is 3.598(9) Å, the offset angle [10] being 17.9(6)°. The distance between the centroids of the two rings is 3.781(9) Å. The  $\pi$ – $\pi$  stacking is associated with a Cl(2)···O(3) contact of length 3.188(7) Å which is slightly shorter than the Van der waals sum of ~3.3 Å.

Extended Hückel calculations on  $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$  using crystallographic coordinates reveals that the

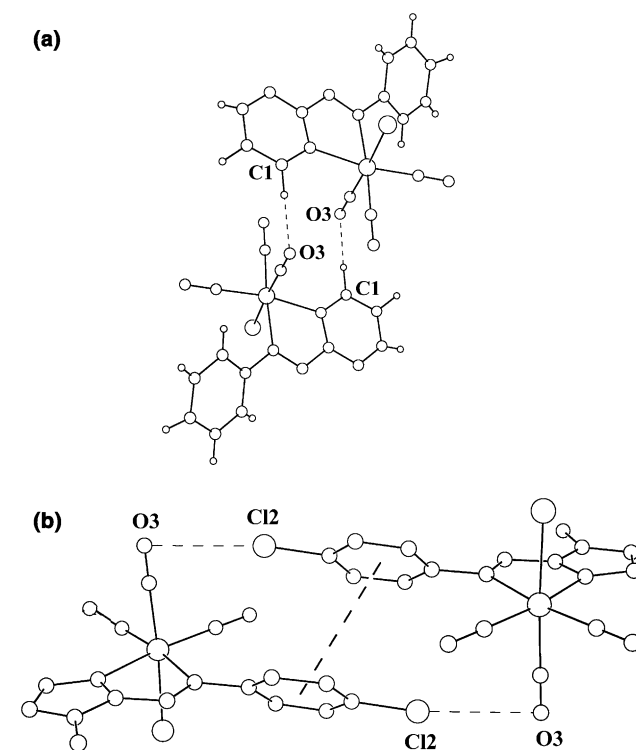
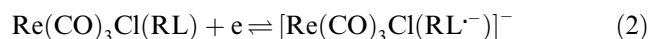


Fig. 3. Lattice interactions in (a)  $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$  and (b)  $\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$ .

LUMO is mostly localized on the  $HL_{pm}$  ligand, the major contributor (61%) being the azo function; the LUMO in  $Re(CO)_3Cl(CIL_{im})$  is of similar nature with 57% azo contribution. For further details see Section 3.

### 2.2.1. One-electron reduction: isolation of radical anion species

In acetonitrile solution the complexes display a quasireversible one-electron cyclic voltammetric response near  $-0.1$  V in the case of  $Re(CO)_3Cl(RL_{pm})$  and near  $-0.4$  V vs. SCE in the case of  $Re(CO)_3Cl(RL_{im})$ . The redox orbital is believed to be the LUMO noted above. The added electron is thus localized in the RL ligand, primarily in the azo function. Reduction potential data for the couple of Eq. (2) are listed in the Section 3.



The  $RL_{im}$  ligand is more difficultly reducible than  $RL_{pm}$  and this is also reflected in the trend of MLCT band energies, vide supra. In addition to the above couple, the complexes also display irreversible metal oxidation at positive potentials. The observed electrochemical pattern of the  $Re(CO)_3Cl(RL)$  species is qualitatively similar to those of 2-(aryloxy)pyridine [6] and 2,2'-azobispyridine [5] chelates. Reduced species of the latter chelate, generated in solution, have been characterized by EPR and other spectral data [11].

The  $Re(CO)_3Cl(RL\cdot^-)$  species generated coulometrically could not be isolated in pure form. However upon leaving them in acetonitrile solution chloride dissociation occurs furnishing  $Re(CO)_3(MeCN)(RL\cdot^-)$  species which have been successfully isolated. Treatment of  $Re(CO)_3(MeCN)(RL\cdot^-)$  with triphenyl phosphine or imidazole in dichloromethane solution has afforded  $Re(CO)_3(D)(RL\cdot^-)$  ( $D = PPh_3, C_3H_4N_2$ ). These radical complexes are red to brown in colour and are nonconducting in solution. In the solid state these are stable for many hours. In IR the  $D = MeCN$  and  $D = C_3H_4N_2$  species respectively display  $\nu_{C\equiv N}$  and  $\nu_{N-H}$  stretches near 2230 and 2985  $cm^{-1}$ . A quasireversible cyclic voltammetric response due to coordinated  $RL\cdot^-$  occurs at a potentials close to that of the parent chloro complex consistent with localization of the redox process on the RL ligand.

Table 4  
EPR spectral data in dichloromethane solution and bulk magnetic moments in solid state at 298 K

Complexes	<i>g</i>	<i>A</i> (G)	$\mu_{eff}, \mu_B$
$Re(CO)_3(CH_3CN)(CIL_{pm}^{\cdot-})$	2.0066	27.25	1.81
$Re(CO)_3(CH_3CN)(CIL_{im}^{\cdot-})$	2.0029	27.25	1.80
$Re(CO)_3(PPh_3)(CIL_{pm}^{\cdot-})$	2.0037	40.42	1.79
$Re(CO)_3(PPh_3)(CIL_{im}^{\cdot-})$	2.0033	39.17	1.77
$Re(CO)_3(C_3H_4N_2)(CIL_{pm}^{\cdot-})$	2.0058	29.25	1.75
$Re(C_3)(C_3H_4N_2)(CIL_{im}^{\cdot-})$	2.0039	28.75	1.74

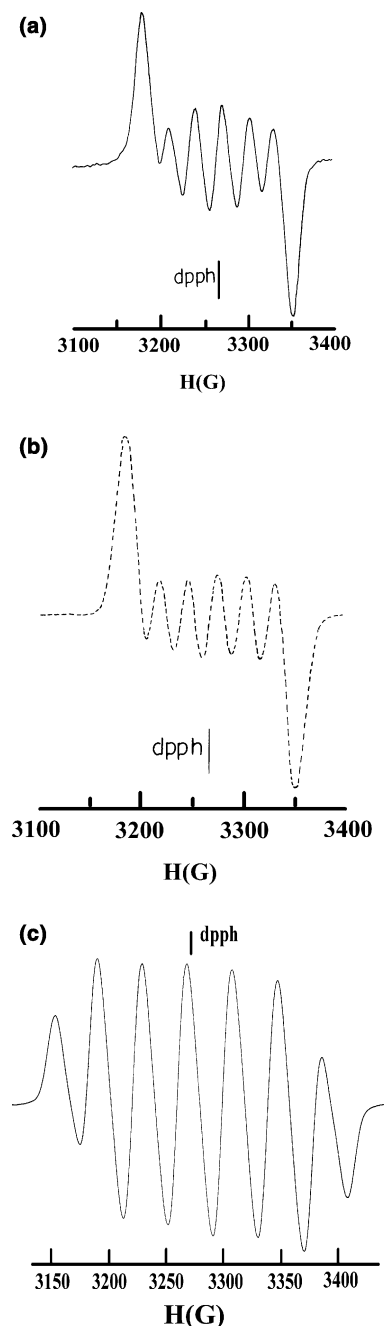


Fig. 4. X-band EPR spectrum of (a)  $Re(CO)_3(C_3H_4N_2)(CIL_{im}^{\cdot-})$ , (b)  $Re(CO)_3(C_3H_4N_2)(CIL_{im}^{\cdot-})$  simulated and (c)  $Re(CO)_3(PPh_3)(CIL_{pm}^{\cdot-})$ . Solvent used is dichloromethane (298 K) and instrument settings are power, 30 dB; modulation, 100 kHz; sweep center, 3200 G; sweep width, 500 G.

The pattern of carbonyl stretching frequencies in the radical chelates is closely similar to that of the parent  $Re(CO)_3Cl(RL)$  species but for shifts to lower frequencies by 10–40  $cm^{-1}$  (Table 1). The shift is consistent with radical anion formation which logically augments  $Re-CO$  back-bonding. Selected spectral and magnetic properties of six representative radical species are collected in Table 4. Their magnetic moments (1.7–1.8  $\mu_B$ )

corresponds to  $S = 1/2$ . In dichloromethane solution both  $\text{Re}(\text{CO})_3(\text{MeCN})(\text{RL}^{\cdot-})$  and  $\text{Re}(\text{CO})_3(\text{C}_3\text{H}_4\text{N}_2)(\text{RL}^{\cdot-})$  display six-line EPR spectra due to the presence of a small metal contribution ( $^{185}\text{Re}$  and  $^{187}\text{Re}$ ,  $I = 5/2$  for both) to the spin-bearing orbital ( $A \sim 28$  G). The unusual line shape and intensities which have been simulated (Fig. 4(a) and (b)) arise from  $g$ -strain [12]. No nitrogen hyperfine structure is resolved in the spectra; it is known that  $^{14}\text{N}$  coupling constant in azo- $\pi^*$  radicals is small and difficult to observe [11,13]. Like monovalent rhenium, bivalent ruthenium has  $d^6$  configuration and structure determination of  $\text{Ru}(\text{CO})\text{Cl}(\text{PPh}_3)_2(\text{CIL}_{\text{im}}^{\cdot-})$  [14] and related species has indeed revealed the presence of long N–N bonds corresponding to population of azo- $\pi^*$  orbitals [15]. However solution EPR studies failed to reveal nitrogen hyperfine structures [14,15] as in the case of the present azoheterocycle anion radical chelates of rhenium(I).

In the case of  $\text{Re}(\text{CO})_3(\text{PPh}_3)(\text{RL}^{\cdot-})$  the coupling with metal is somewhat stronger ( $A \sim 40$  G) and seven nearly equispaced lines (Fig. 4(c)) are observed corresponding to virtually equal coupling with  $^{185,187}\text{Re}$  ( $I = 5/2$ ) and  $^{31}\text{P}$  ( $I = 1/2$ ). This situation has been previously observed in diazabutadiene organometallics [16]. The  $g$ -values in all radical species examined by us are only slightly higher than the free-electron value of 2.0023.

### 3. Experimental

#### 3.1. Materials

Ligands of type 2-(aryloxy)pyrimidine [17] and 2-(aryloxy)-1-methyl-imidazole [18] were prepared by reported methods. Pentacarbonyl chlororhenium(I), triphenyl phosphine and imidazole were purchased from Aldrich (USA). The purification and drying of dichloromethane and acetonitrile for synthesis as well as for electrochemical and spectral work were done as before [19]. Benzene was distilled over sodium before use. All other chemicals and solvents were of analytical grade and were used as received.

#### 3.2. Physical measurements

Electronic and IR spectra were recorded with a Shimadzu UV-1601PC spectrophotometer and a Nicolet Magna IR series II spectrometer, respectively.  $^1\text{H}$  NMR spectra were obtained using a Bruker 300 MHz FT NMR spectrometer. The numbering scheme used for  $^1\text{H}$  NMR is the same as in crystallography. Spin–spin structures are abbreviated as: s, singlet; d, doublet; t, triplet; m, multiplet. EPR spectra were recorded on a

PAR 155 vibrating-sample magnetometer. Microanalyses (C, H, N) were performed using a Perkin–Elmer 240C elemental analyzer. Solution electrical conductivity was measured in acetone with a Phillips PR 9500 bridge by using a platinized electrode (cell constant of 1.05). The electrochemical measurements were performed at a platinum electrode under nitrogen atmosphere in acetonitrile solution by using a model 620A electrochemical analyzer of CHI Instruments. The supporting electrolyte was tetraethylammonium perchlorate and potentials are referenced to the saturated calomel electrode (SCE).

#### 3.3. Synthesis of the complexes, $\text{Re}(\text{CO})_3\text{Cl}(\text{RL})$

The  $\text{Re}(\text{CO})_3\text{Cl}(\text{RL})$  complexes were synthesized in excellent yield ( $\sim 85\%$ ) by reacting  $\text{Re}(\text{CO})_5\text{Cl}$  in boiling benzene with slight excess of the RL ligand. Details of a representative case are given below. The other compounds were prepared analogously.

##### 3.3.1. $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$

$\text{HL}_{\text{pm}}$  (31 mg, 0.168 mmol) was added to a hot solution of  $\text{Re}(\text{CO})_5\text{Cl}$  (50 mg, 0.138 mmol) in 40 ml benzene. On subsequent heating to reflux for 3 h the solution colour changed from light yellow to blue–violet. The solvent was then evaporated under reduced pressure and the residue washed thoroughly with hexane for the removal of excess ligand. It was dried, and then recrystallized from a dichloromethane/hexane (1:3) mixture affording a crystalline product which was dried in vacuo over fused calcium chloride. Yield: 56 mg (83%). Anal. Found: C, 31.81; H, 1.68; N, 11.46. Calc. for  $\text{C}_{13}\text{H}_8\text{N}_4\text{O}_3\text{ClRe}$ : C, 31.87; H, 1.65; N, 11.44%. UV–Vis ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 544 (2870); 386 (7210).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , J/Hz): 9.28 (d, 1H, H(1),  $J_{12}$  4.71,  $J_{13}$  2.28), 7.72 (dd, 1H, H(2),  $J_{21}$  4.71,  $J_{23}$  5.56), 9.23 (d, 1H, H(3),  $J_{32}$  5.56,  $J_{31}$  2.28), 8.07 (d, 2H, H(6), H(10),  $J$  9.12), 7.61 (complex multiplet, 3H, H(7), H(8), H(9)).  $E_{\text{pa}}(\text{Re}^{\text{II}}/\text{Re}^{\text{I}})$  couple): 1.60 V,  $E_{1/2}(\text{HL}_{\text{pm}}^{\cdot-})/(\text{HL}_{\text{pm}})$ :  $-0.13$  V ( $\Delta E_{\text{p}} = 70$  mV).

##### 3.3.2. $\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{pm}})$

$\text{Re}(\text{CO})_5\text{Cl}$  (50 mg, 0.138 mmol) and  $\text{CIL}_{\text{pm}}$  (36 mg, 0.165 mmol) were employed. Yield: 61 mg (84%). Anal. Found: C, 29.72; H, 1.36; N, 10.73. Calc. for  $\text{C}_{13}\text{H}_7\text{N}_4\text{O}_3\text{Cl}_2\text{Re}$ : C, 29.78; H, 1.35; N, 10.69%. UV–Vis ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 552 (3850); 393 (9480).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , J/Hz): 9.29 (d, 1H, H(1),  $J_{12}$  4.56,  $J_{13}$  2.22), 7.65 (dd, 1H, H(2),  $J_{21}$  4.56,  $J_{23}$  5.53), 9.23 (d, 1H, H(3),  $J_{32}$  5.53,  $J_{31}$  2.22), 8.04 (d, 2H, H(6), H(10),  $J$  8.82), 7.62 (d, 2H, H(7), H(9),  $J$  8.85).  $E_{\text{pa}}(\text{Re}^{\text{II}}/\text{Re}^{\text{I}})$  couple): 1.70 V,  $E_{1/2}(\text{CIL}_{\text{pm}}^{\cdot-})/(\text{CIL}_{\text{pm}})$ :  $-0.12$  V ( $\Delta E_{\text{p}} = 80$  mV).

##### 3.3.3. $\text{Re}(\text{CO})_3\text{Cl}(\text{MeL}_{\text{im}})$

$\text{Re}(\text{CO})_5\text{Cl}$  (50 mg, 0.138 mmol) and  $\text{MeL}_{\text{im}}$  (33 mg, 0.165 mmol) were used. Yield: 59 mg (84%). Anal.

Found: C, 33.29; H, 2.43; N, 11.09. Calc. for  $C_{14}H_{12}N_4O_3ClRe$ : C, 33.24; H, 2.39; N, 11.07%. UV–Vis ( $CH_2Cl_2$ ,  $\lambda_{max}$  (nm) ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ): 496 (4790); 427 (11740).  $^1H$  NMR ( $CDCl_3$ ,  $\delta$ , J/Hz): 7.89 (d, 2H, H(6), H(10),  $J$  8.49), 7.56 (d, 1H, H(1), ill resolved), 7.40 (d, 1H, H(2), ill resolved), 7.35 (d, 2H, H(7), H(9),  $J$  8.31), 4.20 (s, 3H, N–Me), 2.48 (s, 3H, 8–Me).  $E_{pa}(Re^{II}/Re^I$  couple): 1.41 V,  $E_{1/2}(MeL_{im}^+)/(MeL_{im}^-)$ :  $-0.43$  V ( $\Delta E_p = 85$  mV).

### 3.3.4. $Re(CO)_3Cl(CIL_{im})$

$Re(CO)_5Cl$  (50 mg, 0.138 mmol) and  $CIL_{im}$  (37 mg, 0.168 mmol) were employed. Yield: 62 mg (86%). Anal. Found: C, 29.63; H, 1.75; N, 10.67. Calc. for  $C_{13}H_9N_4O_3Cl_2Re$ : C, 29.66; H, 1.72; N, 10.64%. UV–Vis ( $CH_2Cl_2$ ,  $\lambda_{max}$  (nm) ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ): 515 (3820); 410 (10240).  $^1H$  NMR ( $CDCl_3$ ,  $\delta$ , J/Hz): 7.91 (d, 2H, H(6), H(10),  $J$  8.91), 7.60 (d, 1H, H(1),  $J$  1.08), 7.54 (d, 2H, H(7), H(9),  $J$  8.91), 7.45 (d, 1H, H(2), ill resolved), 4.22 (s, 3H, N–Me).  $E_{pa}(Re^{II}/Re^I$  couple): 1.45 V,  $E_{1/2}(CIL_{im}^+)/(CIL_{im}^-)$ :  $-0.41$  V ( $\Delta E_p = 80$  mV).

### 3.4. Synthesis of the complexes $Re(CO)_3(CH_3CN)(RL^-)$

Constant potential coulometry of  $Re(CO)_3Cl(RL)$  at a potential of  $\sim 200$  mV lower than  $E_{1/2}$  in dry acetonitrile solution furnished the required radical species. Details are given here for a representative case.

#### 3.4.1. $Re(CO)_3(CH_3CN)(CIL_{pm}^-)$

$Re(CO)_3Cl(CIL_{pm})$  (50 mg, 0.095 mmol) was taken in 30 ml dry acetonitrile. To this solution 40 mg of TEAP was added and it was subjected to exhaustive electrolysis at  $-0.33$  V and the reduced solution was left to stand for 5 h during which time the colour became red. The solvent was then evaporated under reduced pressure and the residue was dissolved in benzene (excess TEAP remains insoluble). The filtered solution was stripped of solvent under reduced pressure, and the red solid complex thus obtained was dried in vacuo. Yield: 37 mg (73%). Anal. Found: C, 34.04; H, 1.95; N, 13.28. Calc. for  $C_{15}H_{10}N_5O_3ClRe$ : C, 34.00; H, 1.90; N, 13.22%. UV–Vis ( $CH_2Cl_2$ ,  $\lambda_{max}$  (nm) ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ): 527 (2970); 377 (10,860). IR (KBr,  $cm^{-1}$ ): 2231 ( $\nu_{C\equiv N}$ ).  $E_{pa}(Re^{II}/Re^I$  couple): 1.67 V,  $E_{1/2}(CIL_{pm}^+)/(CIL_{pm}^-)$ :  $-0.13$  V ( $\Delta E_p = 70$  mV).

#### 3.4.2. $Re(CO)_3(CH_3CN)(CIL_{im}^-)$

$Re(CO)_3Cl(CIL_{im})$  (50 mg, 0.095 mmol) was employed. Yield: 36 mg (71%). Anal. Found: C, 33.82; H, 2.29; N, 13.21. Calc. for  $C_{15}H_{12}N_5O_3ClRe$ : C, 33.87; H, 2.27; N, 13.17%. UV–Vis ( $CH_2Cl_2$ ,  $\lambda_{max}$  (nm) ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ): 544 (2960); 382 (9930). IR (KBr,  $cm^{-1}$ ):

2229 ( $\nu_{C\equiv N}$ ).  $E_{pa}(Re^{II}/Re^I$  couple): 1.45 V,  $E_{1/2}(CIL_{im}^+)/(CIL_{im}^-)$ :  $-0.45$  V ( $\Delta E_p = 80$  mV).

### 3.5. Synthesis of the complexes, $Re(CO)_3(D)(RL^-)$

The  $Re(CO)_3(D)(RL^-)$  complexes were synthesized in excellent yield ( $\sim 75\%$ ) by reacting  $Re(CO)_3(CH_3CN)(RL^-)$  in dichloromethane at room temperature with slight excess of D. Details of a representative case are given below. The other compounds are prepared analogously.

#### 3.5.1. $Re(CO)_3(PPh_3)(CIL_{pm}^-)$

To a stirred red solution of  $Re(CO)_3(CH_3CN)(CIL_{pm}^-)$  (50 mg, 0.094 mmol) in dry dichloromethane (25 ml) was added 32 mg (0.122 mmol) of  $PPh_3$ . The mixture was stirred for 1 h when the colour of the solution changed from red to brown. The solvent was then removed under reduced pressure and the brown solid thus obtained was washed thoroughly with hexane and finally dried in vacuo. Yield: 53 mg (75%). Anal. Found: C, 49.62; H, 3.00; N, 7.49. Calc. for  $C_{31}H_{22}N_4O_3PClRe$ : C, 49.57; H, 2.95; N, 7.46%. UV–Vis ( $CH_2Cl_2$ ,  $\lambda_{max}$  (nm) ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ): 537 (3490); 369 (11430); 263 (15420).  $E_{pa}(Re^{II}/Re^I$  couple): 1.72 V,  $E_{1/2}(CIL_{pm}^+)/(CIL_{pm}^-)$ :  $-0.12$  V ( $\Delta E_p = 100$  mV).

#### 3.5.2. $Re(CO)_3(PPh_3)(CIL_{im}^-)$

$Re(CO)_3(CH_3CN)(CIL_{im}^-)$  (50 mg, 0.094 mmol) and 32 mg  $PPh_3$  (0.122 mmol) were used. Yield: 55 mg (78%). Anal. Found: C, 49.39; H, 3.25; N, 7.48. Calc. for  $C_{31}H_{24}N_4O_3ClPRe$ : C, 49.43; H, 3.21; N, 7.44%. UV–Vis ( $CH_2Cl_2$ ,  $\lambda_{max}$  (nm) ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ): 547 (2950); 377 (9260); 267 (12010).  $E_{pa}(Re^{II}/Re^I$  couple): 1.48 V,  $E_{1/2}(CIL_{im}^+)/(CIL_{im}^-)$ :  $-0.41$  V ( $\Delta E_p = 80$  mV).

#### 3.5.3. $Re(CO)_3(C_3H_4N_2)(CIL_{pm}^-)$

$Re(CO)_3(CH_3CN)(CIL_{pm}^-)$  (50 mg, 0.094 mmol) and 8 mg imidazole (0.118 mmol) were employed. Yield: 39 mg (74%). Anal. Found: C, 34.44; H, 2.04; N, 15.03. Calc. for  $C_{16}H_{11}N_6O_3ClRe$ : C, 34.50; H, 1.99; N, 15.09%. UV–Vis ( $CH_2Cl_2$ ,  $\lambda_{max}$  (nm) ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ): 548 (3380); 374 (5850); 312 (10620). IR (KBr,  $cm^{-1}$ ): 2985 ( $\nu_{N-H}$ ).  $E_{pa}(Re^{II}/Re^I$  couple): 1.65 V,  $E_{1/2}(CIL_{pm}^+)/(CIL_{pm}^-)$ :  $-0.16$  V ( $\Delta E_p = 80$  mV).

#### 3.5.4. $Re(CO)_3(C_3H_4N_2)(CIL_{im}^-)$

$Re(CO)_3(CH_3CN)(CIL_{im}^-)$  (50 mg, 0.094 mmol) and 8 mg imidazole (0.118 mmol) were used. Yield: 40 mg (76%). Anal. Found: C, 34.32; H, 2.39; N, 15.08. Calc. for  $C_{16}H_{13}N_6O_3ClRe$ : C, 34.38; H, 2.34; N, 15.03%. UV–Vis ( $CH_2Cl_2$ ,  $\lambda_{max}$  (nm) ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ): 561 (3450); 380 (5780); 314 (11140). IR (KBr,  $cm^{-1}$ ): 2988 ( $\nu_{N-H}$ ).  $E_{pa}(Re^{II}/Re^I$  couple): 1.44 V,  $E_{1/2}(CIL_{im}^+)/(CIL_{im}^-)$ :  $-0.47$  V ( $\Delta E_p = 80$  mV).

Table 5  
Crystal data for  $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$  and  $\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$

Complexes	$\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$	$\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$
Empirical formula	$\text{C}_{13}\text{H}_8\text{ClN}_4\text{O}_3\text{Re}$	$\text{C}_{13}\text{H}_9\text{Cl}_2\text{N}_4\text{O}_3\text{Re}$
Formula weight	489.88	526.34
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2/c$
$a$ (Å)	8.4010(7)	14.365(3)
$b$ (Å)	9.0220(9)	7.496(2)
$c$ (Å)	10.7310(7)	14.546(3)
$\alpha$ (°)	92.380(7)	–
$\beta$ (°)	106.232(6)	96.15(3)
$\gamma$ (°)	89.878(8)	–
$V$ (Å <sup>3</sup> )	780.21(11)	1557.3(5)
$Z$	2	4
$\mu$ (Mo $K_\alpha$ ) (mm <sup>-1</sup> )	7.974	8.164
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	2.085	2.245
Total reflections	2631	16926
Independent reflections ( $R_{\text{int}}$ )	2631 (0.0000)	3640 (0.0561)
$R_1^a, wR_2^b [I > 2\sigma(I)]$	0.0373, 0.0909	0.0438, 0.1039

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

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

### 3.6. Molecular orbital calculation

Extended Hückel calculations and orbital plots were performed using the ICON software package developed by Hoffmann and others [20]. Experimental atomic coordinates of  $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$  and  $\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$  were used in the calculations. In the case of  $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$  significant contributors to the LUMO are azo (61%), phenyl ring (14%), pyrimidinyl ring (13%), carbonyl (6%) and metal (2%). In the case of  $\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$  the contributors are azo (57%), chlorophenyl ring (7%), imidazolyl ring (24%), carbonyl (1%), metal (2%).

### 3.7. X-ray structure determination

Single crystals of  $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$  ( $0.40 \times 0.35 \times 0.30$  mm<sup>3</sup>) and  $\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$  ( $0.35 \times 0.30 \times 0.30$  mm<sup>3</sup>) were grown by slow diffusion of hexane into dichloromethane solutions at room temperature. Cell parameters were determined by a least-squares fit of 30 machine-centred reflections ( $2\theta = 14\text{--}28^\circ$ ). Data were collected by the  $\omega$ -scan technique on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo  $K_\alpha$  radiation ( $\lambda = 0.71073$  Å). Two check reflections measured after every 198 reflections showed no significant intensity reduction in any case. All data were corrected for Lorentz polarisation effects and an empirical absorption correction [21] was done on the basis of azimuthal scan of six reflections for the crystals.

The metal atom was located from Patterson maps and the rest of the non-hydrogen atoms emerged from successive Fourier syntheses. The structures were refined by full matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of  $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$  were located and refined isotropi-

cally, but for  $\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$  hydrogen atoms were added at calculated positions. Calculations were performed using the SHELXTL, version 5.03 [22] programme package. Significant crystal data are listed in Table 5.

## 4. Conclusion

Blue–violet complexes of type  $\text{Re}(\text{CO})_3\text{Cl}(\text{RL})$  have been synthesized and the structures of  $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$  and  $\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$  determined. Consistent with contraction of metal radius upon oxidation, the Re–N distances within the  $\text{Re}(\text{RL})$  fragment decrease considerably in going from  $\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}(\text{RL})$  to  $\text{Re}^{\text{III}}\text{Cl}_3(\text{OPPh}_3)(\text{RL})$ . Strong Re–CO back-bonding makes the N–N length in the former significantly shorter than that in the later. The crystal lattices of  $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$  and  $\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$  incorporate intermolecular interactions: C–H $\cdots$ O hydrogen bonding in the former and aromatic  $\pi$ – $\pi$  stacking in the latter. The LUMO of  $\text{Re}(\text{CO})_3\text{Cl}(\text{RL})$  is predominately azo- $\pi^*$  in character and coulometric reduction in the presence of ligands has afforded the one-electron paramagnetic ( $S = 1/2$ ) radical anion species  $\text{Re}(\text{CO})_3(\text{MeCN})(\text{RL}^{\cdot-})$ ,  $\text{Re}(\text{CO})_3(\text{C}_3\text{H}_4\text{N}_2)(\text{RL}^{\cdot-})$  and  $\text{Re}(\text{CO})_3(\text{PPh}_3)(\text{RL}^{\cdot-})$  in pure form. Their solution EPR spectra have revealed that the unpaired electron is primarily localized on the azoheterocycle ligand. A small metal contribution is present.

## 5. Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC nos. 230074 and 230075 corresponding to  $\text{Re}(\text{CO})_3\text{Cl}(\text{HL}_{\text{pm}})$  and  $\text{Re}(\text{CO})_3\text{Cl}(\text{CIL}_{\text{im}})$ , respectively. 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; email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or <http://www.ccdc.cam.ac.uk>).

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