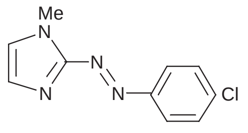
Synthesis and characterisation of a pair of azo anion radicals bonded to ruthenium(II)

Maya Shivakumar, Kausikisankar Pramanik, Prasanta Ghosh and Animesh Chakravorty*

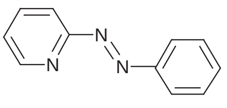
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India. E-mail: icac@iacs.ernet.in

The reactions of 1-methyl-2-(*p*-chlorophenylazo)imidazole (L^1) and 2-(phenylazo)pyridine (L^2) with $[Ru(H)(X)(CO)(PPh_3)_3]$ ($X = Cl, Br$) have afforded the green paramagnetic ($S = \frac{1}{2}$) and EPR-active ($g \approx 2.00$) title anion radical complexes $[Ru(L^{1\cdot-})(Cl)(CO)(PPh_3)_2]$ 1 and $[Ru(L^{2\cdot-})(Br)(CO)(PPh_3)_2]$ 2 in which the N–N bond lengths lie near 1.35 Å.

Familiar systems with nitrogen–nitrogen single and double bonds are hydrazines and azobenzenes. One-electron reduction[1–3] of the azo group can lead to a bond order of 1.5 due to population of the azo π^* orbital, but no such species have so far been isolated in pure form. Herein we describe the successful synthesis and structural characterisation of a pair of azo anion radicals bonded to bivalent ruthenium. The specific azo ligands used are the 2-(arylazo)heterocycles L^1 [3] and L^2 (general abbreviation, L).[4,5] The corresponding radical anions will be represented as $L^{1\cdot-}$ and $L^{2\cdot-}$ respectively.



L^1



L^2

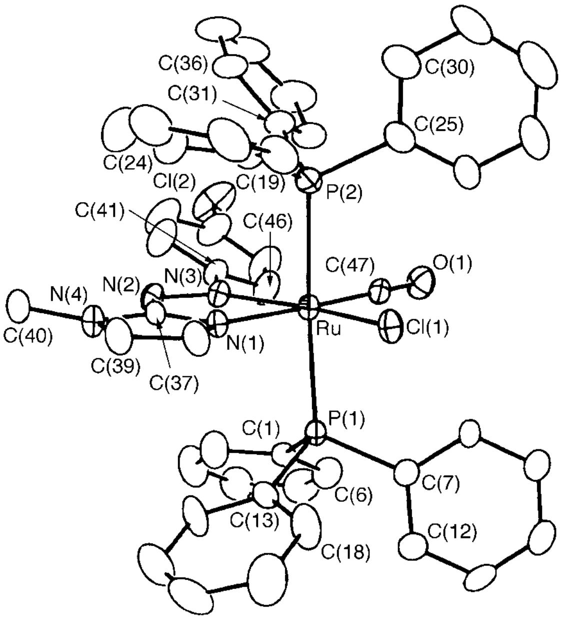


Fig. 1 ORTEP diagram of $[Ru(L^{1\cdot-})(Cl)(CO)(PPh_3)_2]$ **1** (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (°): Ru–Cl(1) 2.416(2), Ru–P(1) 2.385(2), Ru–P(2) 2.393(2), Ru–N(1) 2.093(6), Ru–N(3) 2.107(6), Ru–C(47) 1.854(8), N(2)–N(3) 1.369(8), O(1)–C(47) 1.116(8), P(1)–Ru–P(2) 175.25(8), Cl(1)–Ru–N(3) 162.6(2), N(1)–Ru–C(47) 175.8(3), N(1)–Ru–N(3) 76.0(2), Ru–C(47)–O(1) 179.5(8).

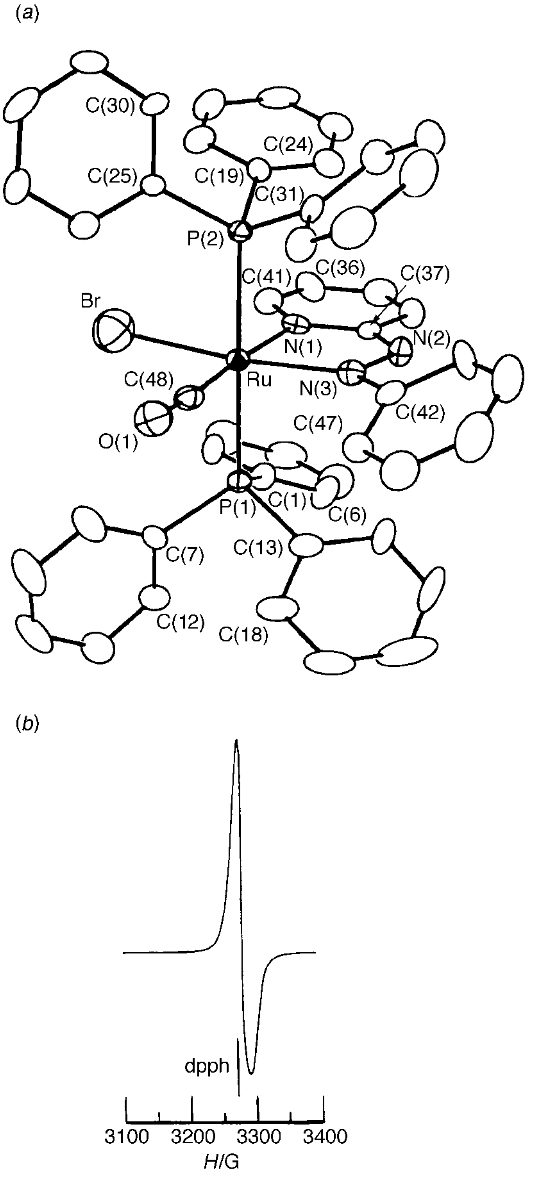


Fig. 2 (*a*) ORTEP diagram of $[Ru(L^{2\cdot-})(Br)(CO)(PPh_3)_2]$ **2** (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (°): Ru–Br 2.521(3), Ru–P(1) 2.415(4), Ru–P(2) 2.399(4), Ru–N(1) 2.111(13), Ru–N(3) 2.069(13), Ru–C(48) 1.843(17), N(2)–N(3) 1.341(17), O(1)–C(48) 1.125(18), P(1)–Ru–P(2) 176.3(2), Br–Ru–N(3) 168.8(3), N(1)–Ru–C(48) 175.5(6), N(1)–Ru–N(3) 76.3(5), Ru–C(48)–O(1) 175.3(14). (*b*) Powder EPR spectrum of **2** in the X-band (9.11 GHz) at 298 K. Instrument settings: power, 28 dB; modulation, 100 kHz; sweep center, 3200 G; sweep width, 1000 G; sweep time 240 s.

Addition of $[Ru(H)(Cl)(CO)(PPh_3)_3]$[6] (0.1 mmol) to a solution of L^1 (0.26 mmol) in dry benzene (10 ml) followed by heating to reflux for 1 h and subsequent cooling afforded the deep green crystalline complex $[Ru(L^{1\cdot-})(Cl)(CO)(PPh_3)_2]$ **1** in 85% yield (all operations were carried out in an oxygen free environment).† A similar reaction of L^2 with $[Ru(H)(Br)(CO)(PPh_3)_3]$ [6] in dry heptane furnished $[Ru(L^{2\cdot-})(Br)(CO)(PPh_3)_2]$ **2**.† The key to our success is the use of hydridic starting materials which provide the reducing equivalent that is necessary for anion radical generation, eqn. (1), *via* Ru–H bond cleavage.

$$[Ru(H)(X)(CO)(PPh_3)_3] + L \longrightarrow [Ru(L^{\cdot-})(X)(CO)(PPh_3)_2] + \tfrac{1}{2} H_2 + PPh_3 \quad (1)$$

The solid complexes which are quite stable in dry air behave as one-electron paramagnets (μ_{eff}: **1**, 1.80 μ_B and **2**, 1.78 μ_B) and display a single-line strong powder EPR signal (298 K) with g = 2.000 for **1** and g = 1.999 for **2**, the respective peak-to-peak line-widths being 9 G and 18 G. This is consistent with the azo anion radical description. The expected small ^{14}N hyperfine splitting is not resolved probably due to dominant anisotropic contributions.[2,7]

The X-ray structures‡ of **1** and **2** are shown in Fig. 1 and 2; Fig. 2 also displays the EPR spectrum of **2**. In each case the L ligand forms a planar five-membered chelate ring to which the *trans*-$Ru^{II}(PPh_3)_2$ fragment lies nearly orthogonally. The halide and carbon monoxide ligands are positioned *trans* to the azo and heterocyclic nitrogen atoms respectively. The N–N distances, 1.369(8) Å in **1** and 1.341(17) Å in **2**, are intermediate between those of double ($\approx$ 1.25 Å[8]) and single ($\approx$ 1.45 Å[9]) bonds as expected for the radical anion description.

Aerial oxidation of **1** and **2** in polar solvents gives $[Ru(L^1)(Cl)(CO)(PPh_3)_2]^+$ $\mathbf{1}^+$ and $[Ru(L^2)(Br)(CO)(PPh_3)_2]^+$ $\mathbf{2}^+$ which have been isolated as diamagnetic PF_6^- salts.† In dichloromethane solutions the $E_{\frac{1}{2}}$ values of the $\mathbf{1}^+/\mathbf{1}$ and $\mathbf{2}^+/\mathbf{2}$ couples are respectively −0.47 V and −0.39 V *vs.* SCE. Reversible coulometric recycling between **1** and $\mathbf{1}^+$ and between **2** and $\mathbf{2}^+$ can be repeatedly performed in an inert atmosphere. A wider application of our synthetic procedure for anion radical generation is under scrutiny.

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Notes and References

† Satisfactory elemental analyses were obtained. *Selected spectral data*: **1**, UV–VIS (C_6H_6): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 568 (5000), 507 (4500), 390 (16400); IR (KBr, cm^{-1}) 1287m (N=N), 1918s (C≡O). **2**, UV–VIS (C_6H_6): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 570 (2300), 540 (2200), 380 (7800); IR (KBr, cm^{-1}) 1288m (N=N), 1925s (C≡O). $\mathbf{1}^+PF_6^-$, UV–VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 524 (2940), 415 (12500), 294 (18500); IR (KBr, cm^{-1}) 1312m (N=N), 1945s (C≡O); δ_H ($CDCl_3$; 300 MHz), 7.05 (s, 1H), 6.91 (d, *J* 8.9, 2H), 6.66 (d, *J* 8.9, 2H), 6.32 (s, 1H), 4.13 (s, CH_3, 3H). $\mathbf{2}^+PF_6^-$, UV–VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 515 (1970), 450 (2070), 380 (6600); IR (KBr, cm^{-1}) 1320m (N=N), 1960s (C≡O); δ_H ($CDCl_3$; 300 MHz) 8.73 (d, *J* 7.8, 1H), 8.25 (t, *J* 7.9, 1H), 7.80 (d, *J* 5.4, 1H), 6.92 (t, *J* 8.1, 2H), 6.77 (t, *J* 6.0, 1H), 6.73 (d, *J* 8.4, 2H).

‡ *Crystal data* for **1**: $C_{47}H_{39}N_4OP_2Cl_2Ru$, M = 909.73, monoclinic, space group $P2_1/n$, a = 10.029(2), b = 33.984(7), c = 12.386(3) Å, β = 97.15(3)°, U = 4189(2) Å^3, Z = 4, μ = 0.620 mm^{-1}, total reflections collected 6866, unique reflections 6218, final R indices for 4109 observed [$I > 2\sigma(I)$] reflections: $R1$ = 0.0547, $wR2$ = 0.1015; **2**: $C_{48}H_{39}N_3OP_2BrRu$, M = 916.74, monoclinic, space group $P2_1/c$, a = 10.226(5), b = 17.443(7), c = 22.760(8) Å, β = 97.75(3)°, U = 4023(3) Å^3, Z = 4, μ = 1.506 mm^{-1}, total reflections collected 6186, unique reflections 5703, final R indices for 3402 observed [$I > 2\sigma(I)$] reflections: $R1$ = 0.1010, $wR2$ = 0.2591. All crystallographic measurements were performed using a Siemens R3m/V four-circle diffractometer and data were collected by the ω-scan method. The structures were solved by the Patterson heavy-atom method (SHELXTL-Ver. 5.03) and refined on F^2 by full matrix least squares using all unique data.[10] All nonhydrogen atoms for **1** and **2** are anisotropic with H-atoms included in calculated positions (riding model). Empirical absorption corrections for both cases were carried out on the basis of azimuthal scans.[11] One phenyl ring of $P(1)Ph_3$ and one of $P(2)Ph_3$ displayed two-fold disorder around C(13)–C(16) and C(31)–C(34) axes respectively in **1**. The crystal of **2** was relatively poorly diffracting and the peaks were broad. CCDC 182/977.

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