Ligand- and Oxidation State-dependence of Structure in Triazenido-bridged Complexes with Face-to-face and Open-book Dirhodium Cores: MO Studies and the Crystal Structure of [Rh₂(µ-CO)(bipy)(dppm)(µ-RNNNR)₂][PF₆]₂·2CH₂Cl₂ (R = p-tolyl)†

Neil G. Connelly,[a] Till Einig,[a] Gabriel Garcia Herbosa,[a] Philippa M. Hopkins,[a] Carlo Mealli,[b] A. Guy Orpen[a] and Georgina M. Rosair[a]
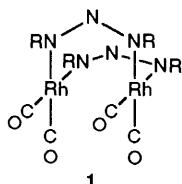
[a] *School of Chemistry, University of Bristol, Bristol BS8 1TS, UK*

[b] *Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, C.N.R., Via J. Nardi 49, I-50132 Firenze, Italy*

Treatment of [{Rh₂I(CO)(bipy)(µ-RNNNR)₂}₂][PF₆]₂ **2** with AgPF₆ and dppm gives [Rh₂(µ-CO)(bipy)(L–L)(µ-RNNNR)₂]²⁺ (**5**; L–L = dppm), X-ray and MO studies on which show that it may be viewed as an open-book [Rh₂]⁶⁺ core bridged by a 'ketonic' CO²⁻ ligand; this isomer is in equilibrium in solution with a face-to-face isomer in which the carbonyl ligand is terminally bound to one metal only, a related open-book to face-to-face conversion occurring on one-electron reduction of (**5**; L–L = dppe) to [Rh₂(CO)(bipy)(dppe-p)(µ-RNNNR)₂]⁺ **7**.

The systematic sequential substitution of the carbonyl ligands of the triazenido-bridged dirhodium complex [Rh₂(CO)₄(µ-RNNNR)₂] **1** has led to the isolation and characterisation of a three-membered redox series {containing [Rh₂]$^{z+}$ cores (z = 2–4)} in which the face-to-face geometry of the Rh₂L₈ unit seen in **1** is retained throughout.[1-3] As the oxidation level of the dimetal core is increased (from [Rh₂]²⁺ to [Rh₂]⁴⁺) an increase in the metal–metal bond order is observed, consistent with the stepwise depopulation of an orbital largely composed of the out-of-phase combination of the 4d$_{z^2}$ orbitals on the two rhodium atoms. We now describe a novel series of complexes wherein (*i*) the metal–metal bonded structure of the face-to-face [Rh₂]⁴⁺ core is converted into an 'open-book' geometry having an unusual 'ketonic' µ-carbonyl ligand bridging a dirhodium core with no metal–metal bond, and (*ii*) the 'open-book' structure is converted to a face-to-face [Rh₂]³⁺ configuration on one-electron reduction.

Treatment of [{Rh₂I(CO)(bipy)(µ-RNNNR)₂}₂][PF₆]₂ (**2**; Scheme 1) with AgPF₆ in acetonitrile yields AgI and brown [Rh(CO)L₂(bipy)(µ-RNNNR)₂][PF₆]₂ [**3**; L (solv) = MeCN, v(CO) 2093 cm⁻¹]. In acetonitrile; **3** (L = MeCN) undergoes decarbonylation, slowly at room temperature or rapidly under reflux, to give [Rh(NCMe)₃(bipy)(µ-RNNNR)₂][PF₆]₂ **4‡** in which all four carbonyl ligands of **1** have been substituted. Somewhat surprisingly the nitrile ligands of **4** are substitution-ally inert. However, the reaction of **2** with AgPF₆ in CH₂Cl₂ gives a reactive deep-green solution [v(CO) 2089 cm⁻¹] which probably contains **3** [L (solv) = CH₂Cl₂] and from which, on addition of L–L (L–L = bipy, dmbipy, phen or dppe),† dark green microcrystals are isolable in yields of 50–90%. Each of the new complexes **5** shows one carbonyl band in the IR spectrum (*ca.* 1750–1770 cm⁻¹) and a triplet resonance [*e.g.* L–L = phen, δ 181.6, *J*(¹³C¹⁰³Rh) 46 Hz] in the ¹³C NMR spectrum consistent with the unexpected and unprecedented (in the triazenide-bridged dirhodium system) presence of a

bridging carbonyl ligand. These data, together with those from the ¹H and ³¹P [for the dppe complex; δ 58.0, d, *J*(³¹P¹⁰³Rh) 127 Hz] spectra are consistent with a formula in which the two bridging triazenides are equivalent, namely [Rh₂(µ-CO)(bipy)(L–L)(µ-RNNNR)₂]²⁺ **5** (Scheme 1).

When a solution of **3** (L = CH₂Cl₂) was treated with the ligands L–LH **A–C** deprotonation at sulfur occurs and diamagnetic, brown [Rh₂]⁴⁺ complexes of the formula [Rh₂(CO)(bipy)(L–L)(µ-RNNNR)₂]⁺ are readily isolated in yields of 55–75%. For each of these complexes only one terminal carbonyl absorption is observed (*ca.* 2065–2070 cm⁻¹) and the NMR spectra are consistent with the axially bound face-to-face structure **6** in which L–L spans the axial site and one of the equatorial sites at one rhodium atom. The subtle dependence of structure on L–L is most clearly

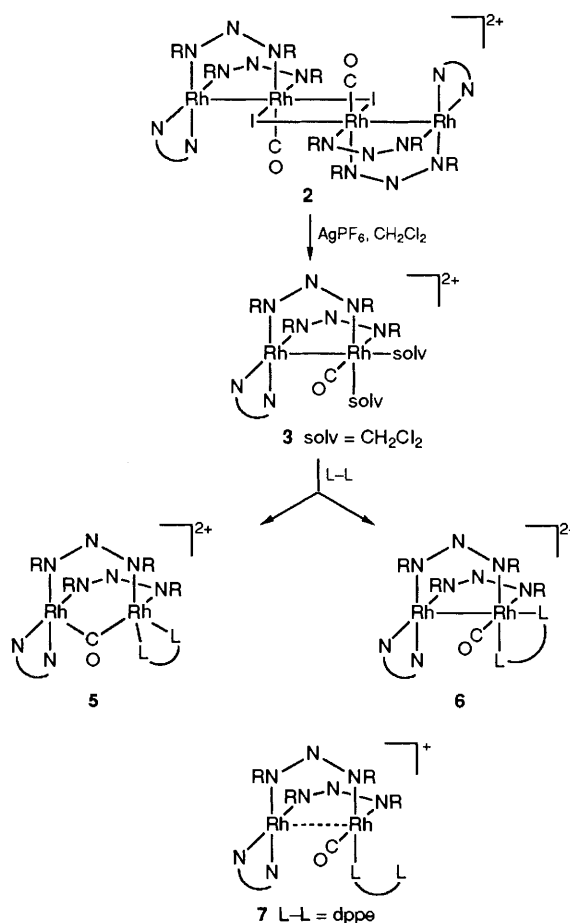**Scheme 1** N–N = bipy; R = p-tolyl

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† *Abbreviations used*: bipy = 2,2'-bipyridyl; dppm = bis(diphenyl-phosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dmbipy = 4,4'-dimethyl-2,2'-bipyridyl; phen = *o*-phenanthroline; thf = tetrahydrofuran.

‡ X-Ray studies on **4** show an unusual structure in which the third, axially coordinated nitrile ligand is bound to the rhodium(bipy) unit. {In all previous cases of [Rh₂(bipy)]⁴⁺ complexes with one axial ligand it is the rhodium not bound to bipy that carries the axial ligand}. A. G. Orpen and G. M. Rosair, unpublished results.
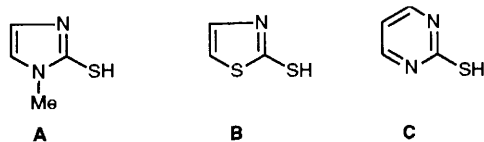
demonstrated by the reaction of 3 (L = CH₂Cl₂) with Ph₂PCH₂PPh₂ (dppm); the green crystalline product in Nujol shows one bridging carbonyl band (1756 cm⁻¹) but in solution both terminal (2070 cm⁻¹) and bridging (1758 cm⁻¹) carbonyl absorptions are observed. At room temperature, the ³¹P NMR spectrum shows only one broad signal at δ −32.8. At −80 °C, however, the spectrum shows a doublet signal [δ −23.6, J(³¹P¹⁰³Rh) 112.3 Hz], which may be assigned to a carbonyl-bridged isomer analogous to 5 (L–L = dppe), and doublet [δ −14.6, J(³¹P¹⁰³Rh) 95.2 Hz] and doublet of doublet signals [δ −91.6, J(³¹P¹⁰³Rh) ca. 40 and 80 Hz] (both of which are broadened by unresolved phosphorus coupling) which may be assigned respectively to the equatorial (coupled to one Rh atom), and axial (coupled to both Rh atoms, the second coupling via the trans-metal–metal bond) P atoms of a face-to-face isomer analogous to 6. The room temperature spectrum clearly shows there to be a rapid equilibrium between the two isomers 5 and 6 (L–L = dppm).

In order to confirm the structure proposed for the carbonyl-bridged isomer of 5 (L–L = dppm), a single-crystal X-ray analysis § was carried out on its bis-dichloromethane solvate. The molecular structure of the dication is shown in Fig. 1 and is of the form suggested on the basis of the spectroscopic evidence. The long metal–metal distance [3.179(2) Å] suggests little direct metal–metal bonding is present in 5 (L–L = dppm). The large angle at the bridging carbonyl [108.3(11)°] is in marked contrast to values observed in conventional Rh₂(μ-carbonyl) species (mean = 84.5°, standard deviation of distribution = 3.7°).[4] The local geometry at each of the rhodium atoms (ignoring the Rh···Rh vector) may be described as square pyramidal, with the Rh–C(1) interaction at the apex of the pyramid. Such geometries are well known in Rhᴵᴵᴵ acyl chemistry {as in e.g. [RhCl{C(O)Me}-(PMe₂Ph)₃]PF₆ in which the Rh–C–Me angle and ν(CO) are close to the corresponding values for 5 (L–L = dppm), at 112.2(4)° and 1720 cm⁻¹ respectively}.[5] In the light of these observations 5 (L–L = dppm) may be usefully viewed as a [Rh₂]⁶⁺ species with a ketonic bridging CO²⁻ ligand.

To evaluate this suggestion extended Hückel molecular orbital calculations[6] were carried out on models {[Rh₂H₄(CO)₅] in which hydride ligands replace triazenide ligands; Hückel parameters were taken from the literature[7]} for the dication of 5, (L–L = dppm) as both the carbonyl-bridged and unbridged isomers. In accord with the experimental evidence the calculated total energies for the two isomers are similar at reasonable geometries. The Rh···Rh overlap

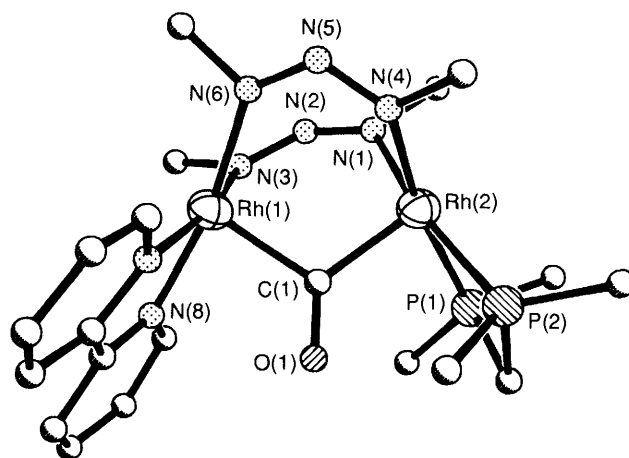**Fig. 1** Molecular geometry of the dication of 5 (L–L = dppm); phenyl and p-tolyl groups are represented by the ipso carbon atoms for clarity. Important molecular geometry parameters include: bond lengths (Å), Rh(1)···Rh(2) 3.179(2), Rh(1)–C(1) 1.992(22), Rh(2)–C(1) 1.929(20), C(1)–O(1) 1.192(26) Å; bond angles (°) Rh(1)–C(1)–Rh(2) 108.3(11), Rh(1)–C(1)–O(1) 122.2(14), Rh(2)–C(1)–O(1) 129.3(17).
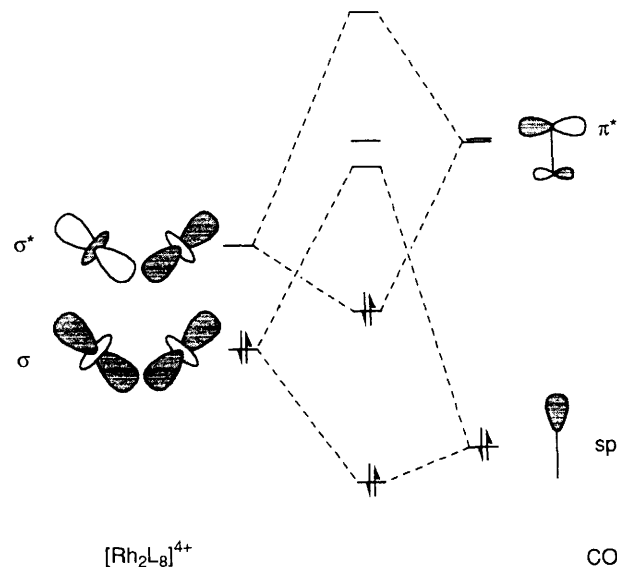
Fig. 2 Schematic interaction between the Rh₂L₈ unit and the bridging CO ligand

§ Crystal data for 5 (L–L = dppm)·2CH₂Cl₂: Rh₂P₄Cl₄F₁₂ON₈C₆₆H₆₀, M = 1680.8, monoclinic space group P2₁/n (No. 14), a = 15.013(5), b = 18.406(6), c = 27.991(8) Å, β = 103.85(5)°, V = 7510(4) Å³, Z = 4, Dc = 1.49 g cm⁻³, λ̄ = 0.71069 Å, μ = 8.1 cm⁻¹, F(000) = 3512, T = 295 K. Data were collected on a Nicolet P3m diffractometer for a unique portion of reciprocal space for 4 < 2θ < 45°. The structure was solved by heavy-atom methods and refined without positional constraints (except for C–H set to 0.96 Å) and with all ordered atoms heavier than carbon [and C(1) and C(2)] anisotropic by least-squares analysis (567 parameters) to R = 0.093 and S = 1.877 for 4677 unique, observed, absorption-corrected [I > 2σ(I)] intensity data. One of the two molecules of dichloromethane is highly disordered. The disorder and high mean-square displacement in the PF₆ anions led to relatively weak diffraction and the high R indices observed. Atomic coordinates, bond lengths, bond angles, and displacement parameters for 5 (L–L = dppm)·2CH₂Cl₂ have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

population for the bridged isomer is slightly negative (−0.051) indicating no Rh···Rh bonding (cf. 0.129 for the non-bridged isomer at the same Rh···Rh distance). The most important interactions between the Rh₂ unit and the μ-CO ligand are indicated in Fig. 2 The occupancy of both σ and σ* Rh···Rh orbitals arises because of the stabilisation of the latter by interaction with the in-plane CO π* orbital. As a consequence the Rh–Rh bond order is formally zero in the open-book, bridged isomer {and unity in the non-bridged face-to-face isomer, cf. isoelectronic [Rh₂(O₂CR)₄L] adducts}. The LUMOs are Rh–(μ-CO) antibonding in character and it is notable that the reduction of 5 leads to cleavage of a Rh–(μ-CO) bond, vide infra. In accord with the suggestion that the μ-CO has ketonic character there is a build-up of negative charge on the oxygen of this group (−0.98 e, cf. −0.76 for terminal carbonyls in the molecule). It is notable that in the crystal structure of 5 (L–L = dppm)·2CH₂Cl₂ the shortest intermolecular contact involving O(1) is a C–H···O hydrogen bond to an acidic hydrogen of the ordered dichloro-

methane molecule [$O(1)\cdots H(65B)$ 2.46 Å, $O(1)\cdots H(65B)$–C(65) 173°, $C(1)$–$O(1)\cdots H(65B)$ 167°], consistent with significant negative charge build-up at O(1). Perhaps the most realistic picture of the bonding in the bridged isomer of the dication of **5** (L–L = dppm) is somewhere between the extremes of a CO adduct of a $Rh_2L_8^{4+}$ unit and a CO^{2-} adduct of the $Rh_2L_8^{6+}$ unit.

The cyclic voltammogram of **5** (L–L = dppe) is unusual (by comparison with the face-to-face triazenide dirhodium complexes previously studied[1-3]) in showing two reduction waves at potentials (-0.20 and -0.53 V) which are readily chemically accessible. Thus, addition of one equivalent of $NaBH_4$ to **5** (L–L = dppe) in CH_2Cl_2 gave a brown solution from which brown crystals of [$Rh_2(CO)(bipy)(dppe)(\mu\text{-RNNNR})_2$]$^+$ **7** were readily isolated in 64% yield. The IR carbonyl (2018 cm^{-1}) and EPR spectra [room temperature, g_{av} = 2.182; 77 K (2:1 thf–CH_2Cl_2 glass), g_1 = 2.254, g_2 = 2.223, g_3 = 2.014, A_3(^{103}Rh) = 27.1, 8.0 G (hyperfine coupling to two inequivalent rhodium atoms; 1 G = 10^{-4} T)] of **7** were almost identical to those of [$Rh_2(CO)(bipy)(PPh_3)(\mu\text{-RNNNR})_2$]$^{+}$[3] showing that one-electron reduction of **5** (L–L = dppe) leads to (*i*) the regeneration of the 'normal' face-to-face structure associated with the [Rh_2]$^{3+}$ core and (*ii*) formation of a monodentate dppe ligand in accord with the observed preference for vacant axial sites in the lower oxidation levels of the dirhodium core.

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