Synthesis, Characterization and Molecular Structure of the Hydroperoxo Complex $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}pz)_3Rh(OOH)(dppe)][BF_4]$; Hpz = pyrazole, dppe = 1,2-bis(diphenylphosphino)ethane

Daniel Carmona,*[a] M. Pilar Lamata,[b] Joaquina Ferrer,[a] Javier Modrego,[a] Martin Perales,[a] Fernando J. Lahoz,[a] Reinaldo Atencio[a] and Luis A. Oro*[a]

[a] *Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., Pl. San Francisco s/n, 50009 Zaragoza, Spain*

[b] *Escuela Universitaria de Ingeniería Técnica Industrial, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., Corona de Aragón 35, 50009 Zaragoza, Spain*

The synthesis and structural characterization of the title hydroperoxide complex is described.

Transition-metal hydroperoxo complexes have recently attracted increasing interest. They are believed to be involved in the catalytic oxygenation of olefins,[1] as well as playing a role in several biochemical oxidation processes.[2] Work on stable hydroperoxo complexes has been limited to date. Strukul *et al.* have carried out extensive studies on hydroperoxo platinum complexes,[1b] but only three rhodium hydroperoxides have hitherto been reported, namely $K_2[Rh(OOH)(CN)_4(H_2O)]$,[3] *trans*-$[Rh(OOH)(OH)(NH_3)_4]^{+}$[4] and $[RhCl(OOH)(acac)(PPh_3)_2]$.[5] None of these latter complexes have been crystallographically characterized.

We are currently studying the reactivity of heteronuclear complexes, prepared using $[(\eta^5\text{-}C_5Me_5)Ir(pz)_2(Hpz)]$ **1**[6] as a building block. Thus, we have recently reported the synthesis of the binuclear IrRh complexes $[(\eta^5\text{-}C_5Me_5)(pz)Ir(\mu\text{-}pz)_2RhL_2]$ [L_2 = 1,5-cyclooctadiene **2**, $(CO)_2$ **3**, $(CO)(PPh_3)$ **4**, dppe **5**] and established that the protonation of **2**–**4** with aqueous HBF_4 takes place at one of the pyrazolate nitrogen atoms.[7] The metallo-ligand $[(\eta^5\text{-}C_5Me_5)Ir(pz)_3]^-$ can be considered as a metallic analogue of the tris(pyrazolyl)borates $RB(pz)_3^-$. Graham *et al.* reported that the dicarbonyl tris-(pyrazolyl)borate complexes $[M\{HM(dmpz)_3\}(CO)_2]$ (Hdmpz = 3,5-dimethylpyrazole; M = Rh, Ir) react differently with $HBF_4\cdot OEt_2$, depending on the metal. Thus, while the protonation of the rhodium complex takes place at one nitrogen affording the rhodium(I) derivative $[Rh\{\eta^2\text{-}HB(dmpz)_2(Hdmpz)\}(CO)_2][BF_4]$, the iridium complex is protonated at metal giving the iridium(III) hydride $[Ir\{\eta^3\text{-}HB(dmpz)_3\}(H)(CO)_2][BF_4]$.[8] We now report the synthesis and crystallographic characterization of the hydroperoxo complex $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}pz)_3Rh(OOH)(dppe)][BF_4]$ **6** prepared by protonation of **5** in the presence of dioxygen.

When $HBF_4\cdot OEt$ (1 equiv.) was slowly added to **5** in THF or acetone the original yellow suspension turned black. This black suspension has not been characterized,† but exposing the reaction mixture to air or pure oxygen results in its transformation into a yellow solution, from which a yellow solid spontaneously precipitates. The yellow solid was characterized as the hydroperoxo complex **6** (yield 71%) by analytical and spectroscopic means.‡ In particular, IR bands at 3490 [ν(OH)] and 823 [ν(OO)] cm^{-1} together with a broad ^1H NMR signal at δ 4.55 strongly suggested the presence of a hydroperoxo ligand.[2–4] The characteristic BF_4^- IR bands at *ca.* 1100 and 520 cm^{-1} confirmed the ionic nature of the complex. The change of the phosphorus chemical shift and $^1J(Rh\text{–}P)$ coupling constant from **5** (δ 70.2, 172.3 Hz)[7] to **6** (δ 52.5; 117.6 Hz) were indicative of oxidation of the rhodium atom from Rh^I to Rh^{III}.

In order to establish inequivocally the structure of complex **6**, and to obtain novel structural information about hydroperoxo ligands, a crystallographic study was undertaken.§ Fig. 1 shows the molecular structure of the complex. The molecule is binuclear with the two metallic centres triply bridged by three pyrazolate ligands, bonding through the nitrogen atoms. The iridium atom completes its pseudooctahedral coordination being bonded to a pentamethylcyclopentadienyl ring. The rhodium atom exhibits a slightly distorted octahedral coordination, linked to the phosphorus atoms of the chelating dppe ligand and one oxygen atom of the hydroperoxide ligand. The O–O distance [1.432(8) Å] and Rh–O–O angle [113.4(4)°] fall in the range reported for peroxocomplexes.[10] The O–O bond distance also compares well with that of the only other structurally characterized hydroperoxo complex reported, the dimolybdenum complex $[Hpy]_2[MoO(O_2)_2(OOH)]_2$ (py = pyridine) [1.458(10) Å].[11] An interesting feature of complex **6** is the existence of a triple pyrazolato bridge connecting the two transition metal atoms. This structural feature is usual in the chemistry of tris(pyrazolyl)borato transition-metal complexes,[12] but extremely rare in bi- or poly-nuclear pyrazolato-bridged transition-metal compounds.[13] In spite of the high *trans* influence invoked by peroxide ligands,[2] the three Rh–N distances are very similar.

Although we have not detected any intermediate in the transformation of **5** to **6**, protonation could occur either at rhodium or at one of the nitrogens of the pyrazolato ligands. Subsequent coordination of the free nitrogen or oxidative addition of the newly formed N–H bond, respectivley, will lead to the hexacoordinated hydrido-rhodium(III) species $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}pz)_3RhH(dppe)][BF_4]$. The nitrogen-rhodium bonds in this proposed hydride intermediate should be labile, allowing the coordination of dioxygen at rhodium

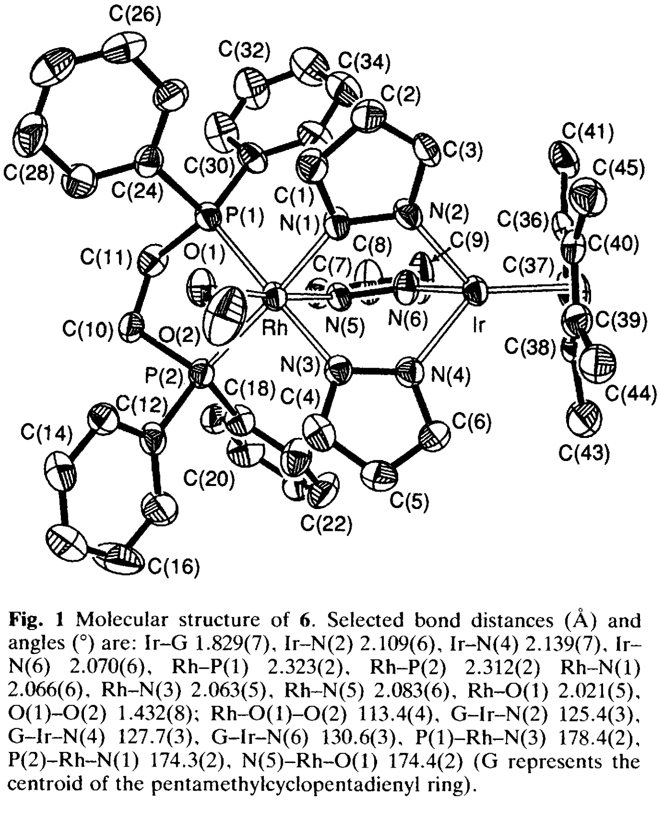

Fig. 1 Molecular structure of **6**. Selected bond distances (Å) and angles (°) are: Ir–G 1.829(7), Ir–N(2) 2.109(6), Ir–N(4) 2.139(7), Ir–N(6) 2.070(6), Rh–P(1) 2.323(2), Rh–P(2) 2.312(2) Rh–N(1) 2.066(6), Rh–N(3) 2.063(5), Rh–N(5) 2.083(6), Rh–O(1) 2.021(5), O(1)–O(2) 1.432(8); Rh–O(1)–O(2) 113.4(4), G–Ir–N(2) 125.4(3), G–Ir–N(4) 127.7(3), G–Ir–N(6) 130.6(3), P(1)–Rh–N(3) 178.4(2), P(2)–Rh–N(1) 174.3(2), N(5)–Rh–O(1) 174.4(2) (G represents the centroid of the pentamethylcyclopentadienyl ring).

centre.¶ Insertion of dioxygen into the Rh–H bond will afford the final product **6**.

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Footnotes

† The ^{1}H and ^{31}P NMR spectra of the black solution in CD_3COCD_3 from 200 to 273 K only revealed the presence of the starting complex **5** and increasing amounts (*ca.* 10% at 273 K) of the final product **6**.

‡ *Selected spectroscopic data* for **6**: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.74 (s, 15 H, C_5Me_5), 3.20 (m, 4 H, CH_2CH_2), 4.55 (br s, 1 H, OOH), 4.88 (br s, 1 H, 4-H pz), 5.38 (br s, 1 H, 3/5-H pz), 6.04 (br s, 2 H, 4-H pz), 7.85 (br s, 2 H, 3/5-H pz); $^{13}C\{^1H\}$ NMR (75.4 MHz) δ 145.4, 142.9, 141.8, 139.9 (C-3, C-5 pz), 106.3, 105.6 (C-4 pz), 89.5 (C_5Me_5), 10.6 (C_5Me_5); $^{31}P\{^1H\}$ NMR (121.4 MHz, H_3PO_4/D_2O 85% by mass) δ 52.5 [d, ^1J(Rh–P) 117.6 Hz]; IR (Nujol) ν/cm^{-1} 3490 (O–H), 823 (O–O), 1100, 520 (BF_4); FAB MS m/z (*m*-nitrobenzyl-alcohol) 1063 (M^+, 72%), 1030 (M^+ – OOH, 26), 963 (M^+ – OOH – pz, 100); satisfactory elemental analyses (C, H, N).

§ Four-circle Siemens AED diffractometer, graphite-monochromated Mo-Kα radiation. Complex **6** crystallizes in the monoclinic space group $P2_1/n$ with a = 11.996(1), b = 14.636(1), c = 25.538(4) Å, β = 102.23(1)°, V = 4382.0(9) Å^3, ρ_{calc} = 1.743, μ = 35.3 cm^{-1} and Z = 4. Data collection range $3 \leq 2\theta \leq 50°$, ω–2θ scan mode (T = 223 K), 8428 measured reflections, 5389 observed with $F \geq 4.0\sigma(F)$. Absorption correction based on psi-scan measurements.[9] Full anisotropic model (isotropic hydrogens), 561 parameters; R = 0.0393 and R_w = 0.0368. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ Facile tridentate–bidentate interconversions of the tris(pyrazolyl)-borate group have been proposed to be responsible for some chemical transformations of transition metal compounds containing this ligand.[14]

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