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New Pyrazolate-, Hydroxo- and Methoxo-bridged Complexes of Ruthenium(II)

Crystal Structure of $[\{Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)\}_2(pz)_2(OH)]BPh_4$

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As a continuation of our studies on binuclear rhodium(I) complexes with the pyrazolate ligand (pz^-) [1–3], we have recently prepared [4] some stable binuclear rhodium(III) complexes of formula $[\{Rh(C_5Me_5)\}_2(pz)_{3-x}(OR)_x]^+$ (R = Me, x = 2, R = H, x = 1)

In this context, we have initiated research studies on the synthesis of new isoelectronic ruthenium(II) complexes of the type $[\{Ru(arene)\}(pz)_{3-x}(OR)_x]^+$ Stephenson and coworkers [5, 6] have reported the preparation, properties and relative inertness towards several neutral Lewis bases of arene–ruthenium(II) complexes of formula $[\{Ru(arene)\}_2(OR)_3]^+$ (R = Me or H)

The tri-μ-hydroxo complexes $[\{Ru(arene)\}_2(OH)_3]^+$ [5] reacted with pyrazole (1 3 molar ratio) in refluxing acetone (5 h), to give binuclear complexes $[\{Ru(arene)\}_2(pz)_2(OH)]^+$ [arene = p-$MeC_6H_4CHMe_2$-(p-cymene) (**1**) or C_6Me_6 (**2**)], isolated as their BPh_4 salts * The IR spectra of (**1**) and (**2**) showed absorption bands at 3555 and 3595 cm^{-1} respectively, due to ν(OH) The X-ray structure determination of complex (**1**) (see below) completely substantiates the conclusion that both cations contain two bridging pyrazolate and one bridging hydroxo groups

The addition of pyrazole to $[\{Ru(arene)\}_2(OMe)_3]BPh_4$ (3 1) (arene = p-cymene** or C_6Me_6 [5]) in refluxing methanol (8 h) produced the $[\{Ru(arene)\}_2(pz)(OMe)_2]BPh_4$ (arene = p-cymene (**3**) or C_6Me_6 (**4**)) complexes Their IR spectra showed the presence of strong bands at 1050 (**3**) and 1040 cm^{-1} (**4**) attributed to ν(C–O) along with intense absorptions at 540 (**3**) and 525 cm^{-1} (**4**) (Ru–O–Ru) The ^1H NMR spectra of (**3**) and (**4**) revealed the usual [BPh_4^-] multiplets and the coordinated arene signals together with resonances at 8 02d (2H), 6 50t (1H) (pz^-) and 3 30s (6H) (OMe) (**3**) and 8 12d (2H), 6 50t (1H), (pz^-) and 2 65s (6H) (OMe) (**4**) in the required intensity ratios, supporting the proposed formulation

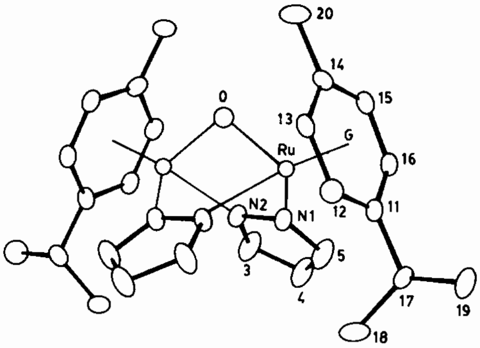

Fig 1 An ORTEP representation of complex (1), showing the atomic numbering The crystallographic two fold axis at (x, 0, 5/6) goes through the O atom and bisects the Ru–Ru' vector Selected bond distances and angles are Ru–O 2 088(2), Ru–N(1) 2 088(3), Ru–N(2') 2 084(3), Ru–G 1 690(1) Å, G–Ru–O/N(1)/N(2') 129 2(11)/130 8(1)/131 8(1), O–Ru–N(1)/N(2') 81 2(1)/81 0(1), N(1)–Ru–N-(2') 84 1(1)°, G being the centroid of the ring

Presumably all these complexes are formed by protonation of the hydroxo- or methoxo-bridges of the starting complexes by Hpz, to form aquo- or methanol-intermediates, which react with pz^- to give the isolated heterobridged compounds in high yields (80–95%)

The molecular structure of (**1**) has been established by X-ray diffraction on single crystals grown from CH_2Cl_2/Et_2O Crystal data for complex (**1**) Trigonal, space group $P3_121$, with $a = b =$ 10 0679(2), c = 37 2665(25) Å, V = 3271 3(2) $Å^3$, Z = 3, 2219 measured independent reflections, with 2091 observed ones ($I > 3\sigma(I)$) used in the refinement to give R = 0 019

The cation shows a crystallographic two fold axis and its more relevant crystallographic data are illustrated in Fig 1 The conformation about the Ru(II) atoms is that loosely referred to as a 'three legged piano stool' The Ru–C (ring) distances range between 2 183(4) and 2 219(4) Å and are comparable to those found for other related complexes [7, 8] The Ru–O bond distance is also analogous to that found in the related hydroxo-bridged complex $[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2(OH)_3]^+$ [9]

As expected, the overall geometry of the '$Ru(pz)_2(OH)Ru$' skeleton closely resembles that found for

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*Satisfactory elemental analyses were obtained for all new compounds

**This previously unreported complex was prepared by refluxing the corresponding tri-μ-hydroxo complex in methanol

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the related isoelectronic complex 'Rh(pz)$_2$(OH)Rh' [4] but the intermetallic distances are 3 5277(3) Å for the Ru complex and 3 488(1) Å for the Rh one

In summary, from the synthetic and structural data so far available there seems to exist a parallelism between the pyrazolate chemistry of the $\mathrm{Rh^{III}}$-($\mathrm{C_5Me_5}$) and $\mathrm{Ru^{II}}$(arene) moieties, although more vigorous reaction conditions are required for the synthesis of the Ru complexes Further work in this area is in progress

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