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Di(μ-pyrazolate)bis(pentamethylcyclopentadienyl)rhodium Complexes. Molecular Structure of $[\{Rh(C_5Me_5)(pz)\}_2(\mu\text{-}pz)_2]$ (pz = pyrazolate)

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Abstract

Neutral and cationic complexes of the general formulae $[\{Rh(C_5Me_5)(Pz)\}_2(\mu\text{-}Pz)_2]$ and $[\{Rh(C_5Me_5)(HPz)\}_2(\mu\text{-}Pz)_2](ClO_4)_2$ were prepared, starting from the dinuclear tri-μ-hydroxo bridged complex $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]ClO_4$. The interconversion between these two types of structures in acidic or basic media were studied. The structure of the title complex was established by X-ray crystallography. The complex crystallizes in the space group $P2_1/n$ with cell dimensions of a = 13.4979(4), b = 10.1424(2), c = 11.7565(3) Å, β = 103.765(2)°. The compound has an internal crystallographic center of symmetry relating the two halves of the molecule. The two rhodium atoms are separated by 4.103(1) Å.

Introduction

There is an increasing interest in rhodium(I) complexes with pyrazole and pyrazolate-type ligands [1–11]. In these compounds the pyrazolate anions act either as *exo*-bidentate [1–3, 5–8, 11] or monodentate ligands [6–8]. On the other hand, the unusual formation of $[\{Rh(C_5Me_5)((CF_3)_2C_2N_3)\}_2(\mu\text{-}(CF_3)_2C_2N_3)(\mu\text{-}N_3)]$ by reaction of a dinuclear azido-cyclopentadienyl complex with hexafluorobut-2-yne has been reported [12]. This complex presents one bridging and two terminally-bonded azolate ligands.

We report now that structurally-related complexes with two identical bridging pyrazolate groups can be readily obtained by a direct and general route.

Results and Discussion

The reaction of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]ClO_4$ [13] with an excess of pyrazole (Hpz), 4-bromopyrazole (HBrpz) or indazole (Hidz) and potassium hydroxide (1/8/8 or 1/6/6) leads to the formation of neutral complexes with the formula $[\{Rh(C_5Me_5)(Pz)\}_2(\mu\text{-}Pz)_2]$ (Pz = pz (**I**), Brpz (**II**) or idz (**III**))*. Molecular weight measurements on complexes (**II**) and (**III**) support this formulation**, and although the measured molecular weight of the pyrazole complex is intermediate between a mononuclear or dinuclear formulation, an X-ray structural analysis of complex (**I**) confirms the presence of either *exo*-bidentate and monodentate pyrazolate groups in the solid state. Furthermore, the ^1H NMR spectrum of complex (**II**), in $CDCl_3$, shows resonances assignable to *exo*-bidentate (δ = 8.12 ppm (s, 4H)) and monodentate (δ = 7.68 ppm (s, 2H); 7.37 ppm (s, 2H)) pyrazolate ligands along with the attributable to the C_5Me_5 groups (δ = 1.03 ppm (s, 30H)).

Interestingly, the addition of perchloric acid to complexes (**II**) or (**III**) gives rise to the protonation of the monodentate pyrazolate ligand with formation of $[\{Rh(C_5Me_5)(HPz)\}_2(\mu\text{-}Pz)_2](ClO_4)_2$ (Pz = Brpz (**V**), idz (**VI**)). As expected, the acidic hydrogen atom of the coordinated pyrazole ligand can be removed with ease, *e.g.* addition of potassium hydroxide to complex (**V**) regenerates the neutral complex (**II**).

An alternative and more direct method of preparing the cationic $[\{Rh(C_5Me_5)(HPz)\}_2(\mu\text{-}Pz)_2](ClO_4)_2$ complexes involves the reaction of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]ClO_4$ with perchloric acid in the presence of an excess of the corresponding pyrazole ligand (Hpz (**IV**), HBrpz, Hidz, 3-methylpyrazole (HMepz) (**VII**), 3,5-dimethylpyrazole (HMe_2pz) (**VIII**)).

The IR spectra of the latter complexes present a ν(N–H) band at *ca.* 3.350 cm^{-1}, along with the expected absorptions due to the coordinated organic ligands and the uncoordinated perchlorate groups.

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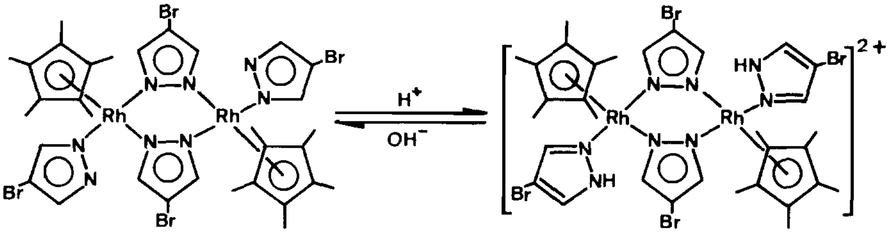
*A generic pyrazole is indicated by HPz and unsubstituted pyrazole ($C_3H_4N_2$) by Hpz.

Molecular weight measurements ($CHCl_3$). Complex (II**): Found, 1004; Requires $C_{32}H_{38}N_8Br_4Rh_2$, 1060. Complex (**III**): Found, 953; Requires, $C_{48}H_{50}N_8Rh_2$, 945.

0020-1693/85/$3.30



In this context it is convenient to recall that we have recently reported that the tri-μ-hydroxo complex $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]ClO_4$ reacted with pyrazole or 3-methylpyrazole to give triple-bridged complexes of the formula $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Pz)_2(\mu\text{-}OH)]ClO_4$. However, the di-$\mu$-hydroxo complex $[\{Rh(C_5Me_5)(HMe_2pz)\}_2(\mu\text{-}OH)_2](ClO_4)_2$ is obtained under similar conditions, when 3,5-dimethylpyrazole was used as ligand [13]. The latter complex reacts with excess of 3,5-dimethylpyrazole to give compound (VIII). Presumably this reaction involves the protonation of the hydroxo-bridges by the heterocyclic ligand and subsequent substitution by the 3,5-dimethylpyrazolate groups. As expected, complexes (IV) and (VII) are prepared from $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Pz)_2(\mu\text{-}OH)]ClO_4$ (Pz = pz, Mepz) by addition of the corresponding pyrazole in the presence of a stoichiometric amount of perchloric acid.

Conductivity studies in acetone at different concentrations on complexes (IV), (VII) and (VIII) ((V) and (VI) are not soluble enough) afford values of A in Onsager's equation of −1275, −1311 and −862 respectively, supporting their dinuclear nature [14, 15].

All attempts to prepare the triple pyrazolate bridged complexes $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Pz)_3]^+$ have been unsuccessful, although a related dinuclear complex of formula $[\{Mn(CO)_3\}_2(\mu\text{-}pz)_3]^-$ has been reported [16].

TABLE I. Crystal Structure Parameters.

$[\{Rh(C_5Me_5)(pz)\}_2(\mu\text{-}pz)_2]$	$C_{32}H_{42}N_8Rh_2$
Crystal System	Monoclinic
Space group	$P2_1/n$
a (Å)	13.4979(4)
b (Å)	10.1424(2)
c (Å)	11.7565(3)
β (°)	103.765(2)
U (Å)	1563.25(7)
Z	2
D_c (g cm^{-3})	1.582
$F(000)$	760
μ (cm^{-1})	90.054
Crystal size (mm)	0.352 × 0.224 × 0.056
$\theta_{max.}$ (°)	65
Reflections measured	2761
Unique data ($I > 3\sigma(I)$)	2680
Refined parameters	274
R^a	0.034
$R_w{}^b$	0.045

$^a R = \Sigma|\Delta|/\Sigma|F_o|$. $^b R_w = (\Sigma w\Delta^2/\Sigma wF_o{}^2)^{1/2}$, $\Delta = |F_o| - |F_c|$ (observed reflections only).

Molecular Structure of $[\{Rh(C_5Me_5)(pz)\}_2(\mu\text{-}pz)_2]$

The structure is illustrated in Fig. 1, with the atom labelling used given in Table III. Crystal data are given in Table I and selected geometrical parameters, with estimated standard deviations, are listed in Table II.

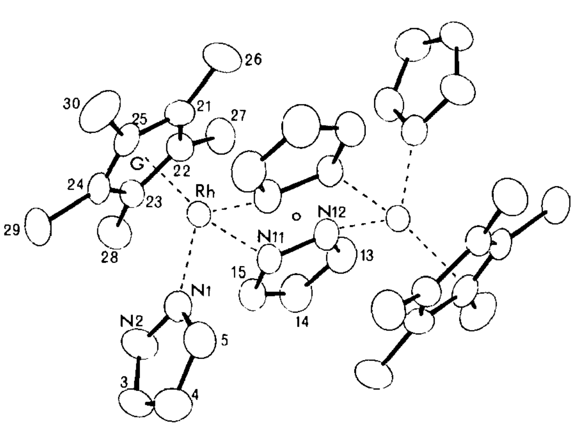


Fig. 1. A view of the complex showing the atomic numbering.

The compound has an internal crystallographic center of symmetry relating the two halves of the molecule. So the complex has two Rh atoms separated by 4.103(1) Å, excluding any significant metal–metal interaction [17]. Each Rh is octahedrally coordinated to three pyrazolate groups (two of them shared) and η^5-bonded to a C_5Me_5 ligand, which counts for three coordinating positions formally near to C23, to C25 and midway between C21 and C22. The mean Rh–C ring-distance is 2.181(2) Å, in the range of those found in C_5Me_5–Rh(III) complexes [18]. The distance of the metal atom to the least-square plane to the C_5Me_5 ring is 1.810(2) Å, equal to that to the centroid of the ring.

The two Rh in the complex are bridged by two pyrazolate groups (Rh–N11 2.102(3), Rh–N12 2.113(3) Å). These distances are in agreement with those found in $[\{Rh(C_5Me_5)((CF_3)_2C_2N_3)\}_2(\mu\text{-}(CF_3)_2C_2N_3)(\mu\text{-}N_3)]$ [12]. The Rh–N1 distance, in the monodentate pyrazolate ligand, is shorter (2.063(3) Å), and the coordination is less symmetric as N2–N1– Rh < C5–N1–Rh, while in the bridging pyrazolates these values are more alike. Moreover, this unshared ring seems to present some localization

TABLE II. Selected Bond Distances (Å), Bond Angles, Torsion Angles and Angles between Planes (°).

Rh–N1	2.063(3)	C3–C4	1.368(7)
Rh–N11	2.102(3)	C4–C5	1.365(6)
Rh–C21	2.186(4)	N11–N12	1.372(5)
Rh–C22	2.196(4)	N11–C15	1.345(5)
Rh–C23	2.164(4)	N12–C13	1.347(5)
Rh–C24	2.185(4)	C13–C14	1.380(7)
Rh–C25	2.175(4)	C14–C15	1.369(8)
Rh–N12(i)	2.113(3)	C21–C22	1.422(5)
Rh–G	1.810(2)	C21–C25	1.446(6)
N1–N2	1.351(5)	C22–C23	1.443(5)
N1–C5	1.335(6)	C23–C24	1.425(6)
N2–C3	1.333(5)	C24–C25	1.420(6)
N2–N1–Rh	119.5(2)	N1–Rh–N11	85.8(1)
C5–N1–Rh	131.4(3)	N1–Rh–N12(i)	90.9(1)
C15–N11–Rh	120.4(3)	N1–Rh–G	127.8(1)
N12–N11–Rh	124.5(2)	N11–Rh–N12(i)	91.2(1)
C13(i)–N12(i)–Rh	122.4(3)	N11–Rh–G	124.7(1)
N11(i)–N12(i)–Rh	121.1(2)	N12(i)–Rh–G	124.7(1)
C25–G–Rh–N1	79.4(2)	G–Rh–N1–N2	48.8(4)
C25–G–Rh–N11	−165.4(2)	G–Rh–N11–N12	84.9(3)
C25–G–Rh–N12(i)	−44.7(3)	G–Rh–N12(i)–N11(i)	−87.4(3)
N1, N2, C3, C4, C5		N11, N12, C13, C14, C15	69.0(2)
N1, N2, C3, C4, C5		C21, C22, C23, C24, C25	56.5(2)
N11, N12, C13, C14, C15		C21, C22, C23, C24, C25	15.4(2)

(i) and G stand for the symmetry operation −*x*, −*y*, 1 − *z* and for the centroid of the C_5Me_5 ring respectively.

TABLE III. Final Atomic Coordinates.

Atom	*x/a*	*y/b*	*z/c*
Rh	0.06551(2)	0.04628(2)	0.36454(2)
N1	0.2174(2)	0.0230(3)	0.4474(3)
N2	0.2838(3)	0.1218(4)	0.4441(4)
C3	0.3737(3)	0.0820(5)	0.5089(4)
C4	0.3665(4)	−0.0405(5)	0.5550(5)
C5	0.2667(4)	−0.0747(5)	0.5136(4)
N11	0.0526(2)	0.1461(3)	0.5170(3)
N12	−0.0291(2)	0.1352(3)	0.5671(3)
C13	−0.0364(4)	0.2513(4)	0.6202(4)
C14	0.0402(4)	0.3358(4)	0.6068(4)
C15	0.0940(4)	0.2664(4)	0.5417(4)
C21	−0.0648(3)	0.0401(4)	0.2131(4)
C22	−0.0484(3)	0.1731(4)	0.2511(3)
C23	0.0532(3)	0.2098(4)	0.2438(3)
C24	0.0962(3)	0.1005(4)	0.1963(3)
C25	0.0257(3)	−0.0058(4)	0.1798(3)
C26	−0.1611(4)	−0.0365(6)	0.2035(6)
C27	−0.1232(4)	0.2613(5)	0.2892(5)
C28	0.1007(4)	0.3438(5)	0.2650(5)
C29	0.1977(4)	0.1022(6)	0.1650(5)
C30	0.0381(5)	−0.1315(5)	0.1200(5)

in the bonds as N1–C5 and N2–C3 are shorter than the others. The length distribution in the shared rings is more even.

All pyrazolate rings are planar within precision but the C_5Me_5 rings are not, the atoms deviating in the range ±0.017(4) Å with the methyl groups within ±0.163(5) Å.

Experimental

Reactions were carried out under air. Solvents were distilled before use. C, H and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls. Molecular weights were measured in $CHCl_3$ with a Perkin-Elmer 115 osmometer. Conductivities were measured in acetone solutions with a Philips 9501/01 conductimeter. NMR spectra at 200 MHz were recorded on a Varian XL 200 spectrometer.

$[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]ClO_4$, $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Pz)_2(\mu\text{-}OH)]ClO_4$ (Pz = pz, Mepz) and $[\{Rh(C_5Me_5)(HMe_2pz)\}_2(\mu\text{-}OH)_2](ClO_4)_2$ were prepared as described elsewhere [13]. Since the methods used to prepare the compounds were very similar only typical procedures are given. The isolated compounds were identified by elemental analysis and conventional spectroscopic methods.

Preparation of the complex $[\{Rh(C_5Me_5)pz\}_2(\mu\text{-}pz)_2]$ *(I) from* $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]ClO_4$

To a solution of 100.0 mg (0.16 mmol) of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]ClO_4$ in methanol, Kpz (1.28 mmol) (obtained by stirring Hpz with a methanolic solution of KOH) was added. After 2 h stirring the mixture was vacuum-evaporated to dryness. The orange-yellow residue was extracted with dichloromethane and the resulting solution was concentrated under reduced pressure. The addition of diethylether led to the precipitation of the required complex. Yield (%): 55; Found: C, 50.8; H, 5.4; N, 14.7. $C_{32}H_{42}N_8Rh_2$ requires C, 51.6; H, 5.7; N, 15.0%.

Complexes **(II)** and **(III)** were similarly prepared. Yield (%): **(II)**, 68; **(III)**, 60.

Preparation of $[\{Rh(C_5Me_5)(Hpz)\}_2(\mu\text{-}pz)_2](ClO_4)_2$ *(IV) from* $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]ClO_4$

A mixture of 100.0 mg (0.16 mmol) of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]ClO_4$ Hpz (1.28 mmol) and an aqueous solution of $HClO_4$ (17.4 μl 60% w/w, 0.16 mmol) was refluxed in dichloromethane for 24 h. The resulting solution was concentrated under reduced pressure. Subsequent addition of diethylether led to the precipitation of the required complex as a yellow solid. Yield (%): 77; Found: C, 40.0; H, 4.5; N, 11.8. $C_{32}H_{44}N_8Cl_2O_8Rh_2$ requires C, 40.6; H, 4.7; N, 11.8%.

Complexes **(V)**, **(VI)**, **(VII)** and **(VIII)** were similarly prepared. Yield (%): **(V)**, 74; **(VI)**, 87; **(VII)**, 85.

Preparation of $[\{Rh(C_5Me_5)(HBrpz)\}_2(\mu\text{-}Brpz)_2](ClO_4)_2$ *(V) from* $[\{Rh(C_5Me_5)(Brpz)\}_2(\mu\text{-}Brpz)_2]$ *(II)*

To a solution of 63.6 mg (0.06 mmol) of $[\{Rh(C_5Me_5)(Brpz)\}_2(\mu\text{-}Brpz)_2]$ in dichloromethane, an aqueous solution of $HClO_4$ (13.0 μl 60% w/w, 0.12 mmol) was added which caused immediate precipitation. The resulting suspension was stirred for 16 h and the yellow microcrystalline solid was filtered off, washed with diethylether and air-dried. Yield (%): 73. Found: C, 30.1; H, 3.2; N, 9.0. $C_{32}H_{40}N_8Br_4Cl_2O_8Rh_2$ requires C, 30.5; H, 3.2; N, 8.9.

Reaction of $[\{Rh(C_5Me_5)(HBrpz)\}_2(\mu\text{-}Brpz)_2](ClO_4)_2$ *with Potassium Hydroxide*

A mixture of 37.8 mg (0.03 mmol) of $[\{Rh(C_5Me_5)(HBrpz)\}_2(\mu\text{-}Brpz)_2](ClO_4)_2$ and a methanolic solution of KOH (0.8 ml, 0.08 M, 0.06 mmol) was stirred for one h. The resulting solution was vacuum-evaporated to dryness and the residue was extracted with dichloromethane. The orange-yellow complex **(II)** was isolated by partial vacuum-evaporation and subsequent addition of diethylether. Yield (%): 53. Found: C, 36.1; H, 3.6; N, 10.6. $C_{32}H_{38}Br_4Rh_2$ requires C, 36.2; H, 3.6; N, 10.6.

Preparation of $[\{Rh(C_5Me_5)(HMe_2pz)\}_2(\mu\text{-}Me_2pz)_2](ClO_4)_2$ *(VIII) from* $[\{Rh(C_5Me_5)(HMe_2pz)\}_2(\mu\text{-}OH)_2](ClO_4)_2$

A mixture of 63.1 mg (0.07 mmol) of $[\{Rh(C_5Me_5)(HMe_2pz)\}_2(\mu\text{-}OH)_2](ClO_4)_2$ and 47.1 mg (0.49 mmol) of HMe_2pz was refluxed in dichloromethane for 24 h. The yellow complex was isolated by partial vacuum-evaporation and subsequent addition of diethylether. Yield (%): 90.

Preparation of $[\{Rh(C_5Me_5)(HPz)\}_2(\mu\text{-}Pz)_2](ClO_4)_2$ *(IV) from* $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Pz)_2(\mu\text{-}OH)]ClO_4$ *(Pz = pz, Mepz)*

A mixture of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)_2(\mu\text{-}OH)]ClO_4$ (0.05 mmol) Hpz (0.30 mmol) and an aqueous solution of $HClO_4$ (5.4 μl, 60% w/w, 0.05 mmol) was refluxed in dichloromethane for 24 h. The resulting solution was concentrated under reduced pressure and the addition of diethylether led to the precipitation of the required complex as a yellow solid. Yield (%): 75.

Complex **(VII)** was similarly prepared, starting from $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Mepz)_2(\mu\text{-}OH)]ClO_4$. Yield (%): 63.

Crystal Structure Determination

The main characteristics of the crystal analysis are presented in Table I. The sample, plate-like with a hexagonal basis, was analyzed on a Philips PW 1100 diffractometer with graphite monochromated CuK_α radiation. Unit cell parameters were refined from the 2θ values of 65 reflections ($\theta < 45°$).

Data were measured at one minute per reflection with $w/2\theta$ scan amplitude of 1.4 degrees. No decay in the sample was detected. The structure was solved by Patterson analysis and refined anisotropically by least-squares minimization of $w\Delta^2$, with $w = 1$ initially. In the final stages w's were chosen empirically to give no trends on $\langle w\Delta^2\rangle$ versus/F_0/or sin θ/λ. H-atoms from a F-synthesis were included isotropically in the refinement. The final F-map shows no electron density peaks greater than 0.68 $eÅ^{-3}$ near the Rh atom.

The X-Ray System was used [19] in all the calculations and the scattering factors were taken from the International Tables [20].

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