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Binuclear hydroxo-, methoxo-, and pyrazolate-bridged complexes of ruthenium(II). Molecular structure of $[\{(p\text{-cymene})Ru\}_2(\mu\text{-pz})(\mu\text{-OH})_2]BF_4$ (p-cymene = $p\text{-MeC}_6H_4CHMe_2$, pz = pyrazolate)

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Abstract

The tris(μ-hydroxo)diruthenium complexes $[\{(p\text{-cymene})Ru\}_2(\mu\text{-OH})_3]A$ (A = BPh_4, BF_4, or PF_6) react with pyrazole-type ligands (HLL) to give the bridged complexes $[\{(p\text{-cymene})Ru\}_2(\mu\text{-LL})(\mu\text{-OH})_2]A$ and/or $[\{(p\text{-cymene})Ru\}_2(\mu\text{-LL})_2(\mu\text{-OH})]A$, depending on the pyrazolate, counteranion and reaction conditions. The tris(μ-methoxo)diruthenium complexes $[\{(p\text{-cymene})Ru\}_2(\mu\text{-OMe})_3]A$ react in methanol with HLL to give the μ-pyrazolate compounds $[\{(p\text{-cymene})Ru\}_2(\mu\text{-LL})(\mu\text{-OMe})_2]A$. The bis($\mu$-pyrazolate)($\mu$-methoxo)complexes $[\{(p\text{-cymene})Ru\}_2(\mu\text{-pz})_2(\mu\text{-OMe})]A$ have also been prepared. The structure of $[\{(p\text{-cymene})Ru\}_2(\mu\text{-pz})(\mu\text{-OH})_2]BF_4$ was determined by X-ray diffraction methods. The complex consists of two (p-cymene)Ru moieties connected by one pyrazolate and two hydroxo-groups. The two ruthenium atoms are 3.2120(5) Å apart.

Introduction

Considerable interest has recently been shown in the coordination chemistry of pyrazolate type ligands [1]. We have recently reported the synthesis of binuclear pentamethylcyclopentadienyl-rhodium(III) [2–4] and iridium(III) [4] complexes containing pyrazolate or pyrazolate and methoxo- or hydroxo-bridging groups. Only the mono(μ-pyrazolate)bis(μ-methoxo)-bridged derivatives $[\{(C_5Me_5)M\}_2(\mu\text{-Pz})(\mu\text{-OMe})_2]^+$ or the bis(μ-pyrazolate)mono(μ-hydroxo)-bridged complexes $[\{(C_5Me_5)M\}_2(\mu\text{-Pz})_2(\mu\text{-OH})]^+$ (Pz = pyrazolate-type ligand, sometimes referred to as diazolate, M = Rh or Ir) can be isolated and characterized, although

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mono(μ-pyrazolate) complexes are detected as intermediates in the formation of the latter complexes [2–4].

Since the "Ru^{II}(arene)" unit is isoelectronic with the "$M^{III}(C_5Me_5)$" (M = Rh or Ir) moieties, we felt that they might form analogous complexes but perhaps with new stoicheiometries not observed in rhodium or iridium chemistry.

In the present paper we describe the reactivity of the dinuclear ruthenium complexes $[\{(p\text{-cymene})Ru\}_2(\mu\text{-OR})_3]A$ (R = H or Me; A = BPh_4, BF_4, or PF_6) with the pyrazole-type ligands HLL [HLL = pyrazole (Hpz), 3-methylpyrazole (Hmpz), 3,5-dimethylpyrazole (Hdmpz), or indazole(benzopyrazole) (Hidz)]. The crystal structure of the mono(μ-pyrazolate)bis(μ-hydroxo)complex $[\{(p\text{-cymene})Ru\}_2(\mu\text{-pz})(\mu\text{-OH})_2]BF_4$ is also reported.

When this work was in progress, the preparation by a different route of the related μ-hydroxo(benzene) derivatives $[\{(\eta^6\text{-benzene})Ru\}_2(\mu\text{-pz})(\mu\text{-OH})]Cl$ and $[\{(\eta^6\text{-benzene})Ru\}_2(\mu\text{-pz})_2(\mu\text{-OH})]Cl$ was reported [5].

Part of this work has been previously communicated [6].

Results and discussion

Hydroxo complexes

The tris(μ-hydroxo)-complexes $[\{(p\text{-cymene})Ru\}_2(\mu\text{-OH})_3]A$ (A = BPh_4, BF_4, PF_6) [7] react with equimolecular amounts of 3,5-dimethylpyrazole (Hdmpz) to give air-stable solids of formula $[\{(p\text{-cymene})Ru\}_2(\mu\text{-dmpz})(\mu\text{-OH})_2]A$ [A = BPh_4 (IIIa), BF_4 (IIIb), or PF_6 (IIIc)], as shown in eq. 1.

$$[\{(p\text{-cymene})Ru\}_2(\mu\text{-OH})_3]A + Hdmpz \rightarrow [\{(p\text{-cymene})Ru\}_2(\mu\text{-dmpz})(\mu\text{-OH})_2]A + H_2O \quad (1)$$

The complex of pyrazole itself $[\{(p\text{-cymene})Ru\}_2(\mu\text{-pz})(\mu\text{-OH})_2]BF_4$ (Ib) was similarly prepared, but treatment of the tris(μ-hydroxo) complexes with pyrazole (Hpz) (BPh_4 or PF_6 salts), or 3-methylpyrazole (Hmpz) or indazole (Hidz) in 1/1 molar ratio affords mixtures of the mono-μ- and the bis(μ-diazolate) complexes $[\{(p\text{-cymene})Ru\}_2(\mu\text{-LL})(\mu\text{-OH})_2]A$ [LL = pz, A = BPh_4 (Ia) or PF_6 (Ic); LL = mpz, A = BPh_4 (IIa), BF_4 (IIb) or PF_6 (IIc); LL = idz; A = BPh_4 (IVa), BF_4 (IVb), or PF_6 (IVc)] and $[\{(p\text{-cymene})Ru\}_2(\mu\text{-LL})_2(\mu\text{-OH})]A$ [LL = pz; A = BPh_4 (Va) or PF_6 (Vc); LL = mpz, A = BPh_4 (VIa), BF_4 (VIb), or PF_6 (VIc); LL = idz, A = BPh_4 (VIIIa), BF_4 (VIIIb), or PF_6 (VIIIc)].

The formation of these mixtures can be accounted for if the rate of formation of $[\{(p\text{-cymene})Ru\}_2(\mu\text{-LL})(\mu\text{-OH})_2]^+$ from the corresponding tris(μ-hydroxo)complex is slower than the rate of formation of the bis(μ-diazolate) complexes $[\{(p\text{-cymene})Ru\}_2(\mu\text{-LL})_2(\mu\text{-OH})]^+$ from the corresponding mono(μ-diazolate) compounds.

The mono(μ-diazolate) compounds Ia, Ic, II and IV could not be separated from the mixtures but pure samples of the bis(μ-diazolate) complexes Va, Vc, VI and VIII have been prepared by adding an excess of the corresponding diazolate to the mixtures, or carrying out reaction 1 in 1/5 molar ratio. The homologous pyrazolate complex $[\{(p\text{-cymene})Ru\}_2(\mu\text{-pz})_2(\mu\text{-OH})]BF_4$ (Vb) has also been prepared by this method.

Table 1

Analytical results, yields, and IR [a] data for the new μ-hydroxo-complexes

Complex	Analysis, found (calc.) (%)			Yield (%)	ν(O–H) (cm^{-1})
	C	H	N		
$[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-pz})(\mu\text{-OH})_2]\mathrm{BF}_4$ (Ib)	42.3	5.5	4.0	61	3565
	(42.0)	(5.1)	(4.3)		
$[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-dmpz})(\mu\text{-OH})_2]\mathrm{BPh}_4$ (IIIa)	64.2	6.5	3.0	50	3555
	(64.1)	(6.3)	(3.05)		
$[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-dmpz})(\mu\text{-OH})_2]\mathrm{BF}_4$ (IIIb)	43.4	5.5	4.15	61	3540
	(43.8)	(5.4)	(4.1)		
$[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-dmpz})(\mu\text{-OH})_2]\mathrm{PF}_6$ (IIIc)	40.8	5.3	3.9	77	3590
	(40.3)	(5.0)	(3.8)		
$[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-pz})_2(\mu\text{-OH})]\mathrm{BPh}_4$ (Va)	62.8	6.0	5.7	91	3575
	(64.0)	(5.9)	(6.0)		
$[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-pz})_2(\mu\text{-OH})]\mathrm{BF}_4$ (Vb)	44.1	5.1	7.9	63	3570
	(44.2)	(5.0)	(7.9)		
$[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-pz})_2(\mu\text{-OH})]\mathrm{PF}_6$ (Vc)	40.9	4.2	7.5	77	3610
	(40.8)	(4.6)	(7.3)		
$[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-mpz})_2(\mu\text{-OH})]\mathrm{BPh}_4$ (VIa)	64.1	6.3	6.0	65	3550
	(64.45)	(6.1)	(5.8)		
$[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-mpz})_2(\mu\text{-OH})]\mathrm{BF}_4$ (VIb)	45.9	5.6	7.45	58	3520
	(45.7)	(5.3)	(7.6)		
$[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-mpz})_2(\mu\text{-OH})]\mathrm{PF}_6$ (VIc)	42.7	4.7	7.15	67	3620
	(42.3)	(4.95)	(7.05)		
$[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-idz})_2(\mu\text{-OH})]\mathrm{BPh}_4$ (VIIIa)	66.4	5.7	5.45	61	3600
	(66.9)	(5.7)	(5.4)		
$[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-idz})_2(\mu\text{-OH})]\mathrm{BF}_4$ (VIIIb)	50.4	5.2	6.8	66	3590
	(50.5)	(4.9)	(6.9)		
$[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-idz})_2(\mu\text{-OH})]\mathrm{PF}_6$ (VIIIc)	47.15	4.7	6.3	66	3600
	(47.1)	(4.5)	(6.5)		

[a] Nujol mulls.

However, only mono(μ-diazolate) compounds could be prepared using 3,5-dimethylpyrazole. Only complexes III were recovered after heating the tris(μ-hydroxo) compounds $[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-OH})_3]A$ with five equivalents of Hdmpz in acetone under reflux during 24 h.

Table 1 lists analytical and IR data for the new complexes and Table 2 selected ^{1}H NMR data. The IR spectra show ν(OH) bands in the 3540–3620 cm^{-1} range, together with characteristic absorptions of the corresponding anion. The ^{1}H NMR spectra show the *p*-cymene, diazolate, and OH resonances with the expected relative intensities and multiplicities. Two different *p*-cymene ligands were observed for the mpz and idz monosubstituted derivatives II and IV.

There are two possible isomers for the cationic bis(μ-diazolate) complexes VI and VIII, due to the unsymmetrical substitution of the bridging diazolates, denoted by A and B in Fig. 1. The ^{1}H NMR data show that the two isomers of VIb and VIIIa, VIIIb, VIIIc are formed in a 1/1 ratio, whereas the two isomers of complexes VIa and VIc are formed in the ratio A : B :: 2 : 1. The ^{1}H NMR spectra of the B isomers show two AB systems and two doublets, assigned to the aromatic and the diasterotopic isopropyl methyl protons of the *p*-cymene ligand, respectively [8,9].

Table 2

Relevant ^1H NMR data [a,b] for the new μ-hydroxo-complexes.

Complex	*p*-Cymene [c]			Diazolate [c]						OH
	Me	^iPr	H_A/H_B	$H_{3/5}$	H_4	$Me_{3/5}$	H^1/H^4	H^2/H^3	H^5	
Ia	1.91s	1.12d, 2.55sp $^3J(HH) = 6.8$	4.74, 5.04 $J(AB) = 5.95$	7.91d $^3J(HH) = 1.7$	6.40t					0.18s
Ib	2.07s	1.11d, 2.50sp $^3J(HH) = 6.9$	5.32, 5.55 $J(AB) = 6.0$	8.00d $^3J(HH) = 2.1$	6.40t					3.46s
Ic	2.04s	1.10d, 2.50sp $^3J(HH) = 6.8$	5.31, 5.56 $J(AB) = 6.0$	8.02d $^3J(HH)2.2$	6.42t					4.74s
IIa	1.84s	1.08d, 2.5–2.6sp $^3J(HH) = 8.7$	4.79, 5.06 $J(AB) = 5.9$	7.82bs	6.16bs	2.54s				0.42s
	1.95s	1.12d $^3J(HH) = 8.5$	4.94, 5.24 $J(AB) = 5.9$							
IIb	2.02s	1.12d, 2.5–2.6sp $^3J(HH) = 6.8$	5.3–5.8	7.94bs	6.18bs	2.60s				3.51s
	2.07s	1.13d $^3J(HH) = 6.9$								
IIc	2.01s	1.13d, 2.5–2.6sp $^3J(HH) = 6.9$	5.33, 5.55 $J(AB) = 5.9$	7.97d $^3J(HH) = 2.1$	6.19d	2.61s				2.58s
	2.06s	1.13d $^3J(HH) = 6.9$	5.57, 5.81 $J(AB) = 5.9$							
IIIa	1.88s	1.11d, 2.40sp $^3J(HH) = 6.8$	5.07, 5.34 $J(AB) = 5.95$		6.00s	2.49s				0.30s
IIIb	2.02s	1.15d, 2.50sp $^3J(HH) = 6.8$	5.63, 5.83 $J(AB) = 5.9$		6.00s	2.55s				3.32s
IIIc	2.01s	1.14d, 2.55sp $^3J(HH) = 7.0$	5.59, 5.82 $J(AB) = 5.7$		6.02s	2.55s				2.32s
IVa	1.87s	1.05d, 2.5–2.6sp $^3J(HH) = 6.8$	5.17, 5.41 $J(AB) = 5.8$				7.76pd [d]	7.36pt [d]	8.48s	0.67s
	1.93s	1.11d $^3J(HH) = 7.0$	4.80, 5.10 $J(AB) = 6.0$							
IVb	2.01s	1.09d, 2.5–2.6sp $^3J(HH) = 8.8$	5.43, 5.67 $J(AB) = 5.8$				7.74pd 7.77pd	7.15pt 7.37pt	8.63s	3.72s

	2.10s	1.13d ^3J(HH) = 8.7	5.75, 5.95 J(AB) = 5.7							
IVc	1.99s	1.08d, 2.5–2.6sp ^3J(HH) = 6.8	5.43, 5.67 J(AB) = 6.0				7.7pd	7.15pt 7.38pt	8.67s	2.79s
	2.083s	1.13d ^3J(HH) = 7.0	5.73, 5.95 J(AB) = 6.0							
Va[e]	2.24s	1.22d, 2.80sp ^3J(HH) = 6.9	5.42, 5.74 J(AB) = 6.3	7.98d ^3J(HH) = 2.2	6.17t					3.95s
Vb	2.21s	1.13d, 2.72sp ^3J(HH) = 6.8	5.32, 5.48 J(AB) = 6.1	7.66d ^3J(HH) = 2.1	6.12t					3.96s
Vc	2.18s	1.12d, 2.75sp ^3J(HH) = 6.8	5.30, 5.47 J(AB) = 6.1	7.67d ^3J(HH) = 2.2	6.13t					2.89s
VIa	1.98s	1.03d, 2.6–2.7sp ^3J(HH) = 6.8	4.7–5.4	[d]	5.98bs	2.02s				[f]
	2.25s	1.04d ^3J(HH) = 6.8								
	2.31s	1.13d ^3J(HH) = 6.9 1.17d ^3J(HH) = 6.9								
VIb	2.16s	1.05d, 2.5–2.7sp ^3J(HH) = 5.6	5.3–5.9	7.48d ^3J(HH) = 1.6	5.82bs	2.20s				4.14s
	2.19s	1.08d ^3J(HH) = 6.6		7.57d ^3J(HH) = 1.5		2.36s				4.22s
	2.25s	1.15d ^3J(HH) = 7.6 1.19d ^3J(HH) = 7.6								
VIc	2.17s	1.06d, 2.5–2.7sp ^3J(HH) = 6.8	5.3–5.9	7.49d ^3J(HH) = 2.0	5.82bs	2.35bs				3.16s
	2.20s	1.07d ^3J(HH) = 6.9		7.59d ^3J(HH) = 1.95						3.26s
	2.25s	1.12d ^3J(HH) = 6.9 1.19d ^3J(HH) = 7.3								

Table 2 (continued)

Complex	*p*-Cymene [c]			Diazolate [c]						OH
	Me	^{i}Pr	H_A/H_B	$H_{3/5}$	H_4	$Me_{3/5}$	H^1/H^4	H^2/H^3	H^5	
VIIIa	2.05s	0.93d, 2.2–2.8sp $^3J(HH) = 6.8$	4.8–5.8				[d]	[d]	8.17s	[f]
	2.11bs	0.93d $^3J(HH) = 7.3$ 1.15d $^3J(HH) = 6.6$ 1.17d $^3J(HH) = 6.8$							8.27s	
VIIIb	2.19s	0.97d, 2.4–3.0sp $^3J(HH) = 6.9$	5.5–6.2				7.53pd	6.89pt 7.14pt	8.22s 8.30s	4.70s 4.74s
	2.26s	0.98d $^3J(HH) = 6.8$								
	2.30s	1.17d $^3J(HH) = 6.9$ 1.18d $^3J(HH) = 6.8$								
VIIIc	2.17s	0.96d, 2.5–2.7sp $^3J(HH) = 6.8$	5.5–6.2				7.50pd	6.89pt 7.15pt	8.32s 8.34s	3.55s
	2.23s	0.98d $^3J(HH) = 6.8$								
	2.26s									

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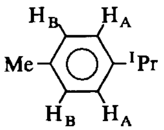
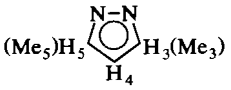
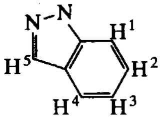
[a] Measured in $CDCl_3$ at room temperature unless otherwise stated; chemical shifts relative to $SiMe_4$ as external standard; *J* in Hz. [b] Abbreviations: s, singlet; d, doublet; pd, pseudodoublet; pt, pseudotriplet; sp, septet; bs, broad singlet. [c] Labelling of the *p*-cymene, pyrazolate, and indazolate protons:







[d] Obscured by the BPh_4 protons. [e] In CD_3COCD_3. [f] Not observed.

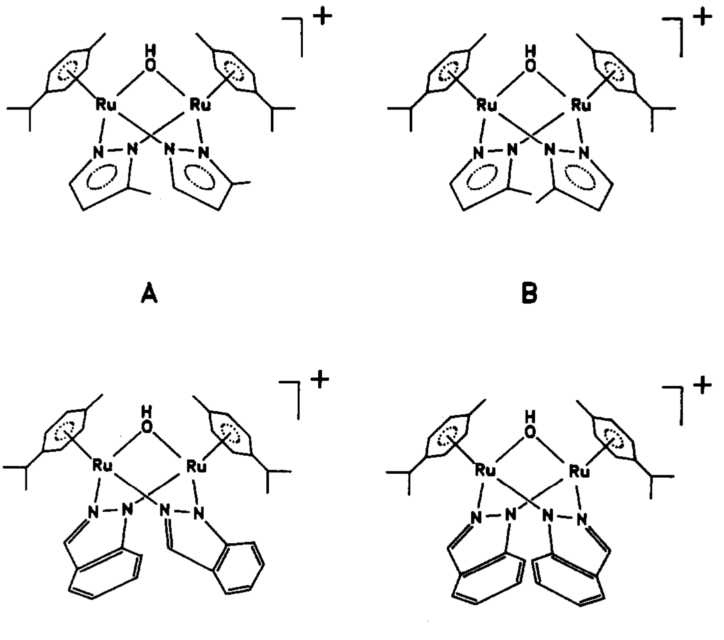
Methoxo-complexes

The tris(μ-methoxo)-complexes [{(p-cymene)Ru}$_2$(μ-OMe)$_3$]A (A = BPh_4, BF_4, PF_6) [7] react with diazoles, HLL, in methanol to give the mono(μ-diazolate) compounds [{(p-cymene)Ru}$_2$(μ-LL)(μ-OMe)$_2$]A, as shown in eq. 2.

$$[\{(p\text{-cymene})Ru\}_2(\mu\text{-OMe})_3]A + HLL \longrightarrow [\{(p\text{-cymene})Ru\}_2(\mu\text{-LL})(\mu\text{-OMe})_2]A + MeOH \quad (2)$$

A LL	BPh_4	BF_4	PF_6
pz	IXa	IXb	IXc
mpz	Xa	Xb	Xc
dmpz	XIa	XIb	XIc
idz	XIIa	XIIb	XIIc

The rate of formation of these complexes depends on both the diazole and the anion. Thus, although the dmpz derivative XIb could be isolated in 70% yield after stirring a 1 : 1 mixture of [{(p-cymene)Ru}$_2$(μ-OMe)$_3$]BF_4 and Hdmpz at room temperature for 24 h, it was necessary to heat under reflux during 24 h a 1 : 1 mixture in solution of the corresponding PF_6 salt and Hdmpz to obtain an 80% conversion to XIc. Furthermore, after 24 h of reflux, a solution of the tris(μ-methoxo)tetraphenylborate and Hdmpz in 1 : 5 molar ratio gives inseparable mix-



A B

Fig. 1. Schematic representation of the two isomers for the cations of complexes VI and VIII.

tures of the starting complex and XIa in molar ratio 1:3, judged by ^{1}H NMR measurements. The tetrafluoroborate and hexafluorophosphate salts IXb, IXc, Xb, Xc, XIIc were prepared in higher than 70% isolated yield at room temperature from 1:1 solutions of the tris(μ-methoxo) complex and HLL after 1 h. Again, the rate of formation of the homologous BPh$_4$ salts is slower. Thus, similar yields of the complexes IXa, Xa, and XIIa were obtained after heating under reflux solutions of [{(p-cymeme)Ru}$_2$(μ-OMe)$_3$]BPh$_4$ and the corresponding HLL (1:1) during 12 h (Hpz) or 24 h (Hmpz and Hidz).

We have not been able to obtain the tetrafluoroborate complex [{(p-cymene)Ru}$_2$(μ-mpz)(μ-OMe)$_2$]BF$_4$ pure, because it was always contaminated by the bis(μ-hydroxo)-compound [{(p-cymene)Ru}$_2$(μ-mpz)(μ-OH)$_2$]BF$_4$ (IIb) (5%), probably formed by hydrolysis (see below).

The bis(μ-pyrazolate)(μ-methoxo)-complexes [{(p-cymene)Ru}$_2$(μ-pz)$_2$(μ-OMe)]A [A = BF$_4$ (XIIIb) or PF$_6$ (XIIIc)] were obtained by treating in methanol the appropriate tris(μ-methoxo)-complex with Hpz (1:5) at room temperature during 4 h (XIIIb) or by heating it under reflux during 24 h (XIIIc) (eq. 3). Only 20% conversion of the related tetraphenylborate complex [{(p-cymeme)Ru}$_2$(μ-pz)$_2$(μ-OMe)]BPh$_4$ was achieved under the latter conditions.

Table 3

Analytical results, and yields for the new μ-methoxo-complexes

Complex	Analysis, found (calc.)(%)			Yield (%)
	C	H	N	
[{(p-cymene)Ru}$_2$(μ-pz)(μ-OMe)$_2$]BPh$_4$ (IXa)	63.7	6.7	2.7	86
	(64.0)	(6.25)	(3.0)	
[{(p-cymene)Ru}$_2$(μ-pz)(μ-OMe)$_2$]BF$_4$ (IXb)	43.5	5.55	4.1	72
	(43.7)	(5.6)	(4.1)	
{{(p-cymene)Ru}$_2$(μ-pz)(μ-OMe)$_2$]PF$_6$ (IXc)	40.6	5.3	4.15	86
	(40.4)	(5.0)	(3.8)	
[{(p-cymene)Ru}$_2$(μ-mpz)(μ-OMe)$_2$]BPh$_4$ (Xa)	63.9	6.9	3.0	57
	(64.4)	(6.4)	(3.0)	
[{(p-cymene)Ru}$_2$(μ-mpz)(μ-OMe)$_2$]PF$_6$ (Xc)	41.2	5.3	3.5	80
	(41.3)	(5.2)	(3.7)	
[{(p-cymene)Ru}$_2$(μ-dmpz)(μ-OMe)$_2$]BF$_4$ (XIb)	45.4	5.9	4.3	70
	(45.4)	(5.8)	(4.0)	
[{(p-cymene)Ru}$_2$(μ-dmpz)(μ-OMe)$_2$]PF$_6$ (XIc)	41.8	5.4	3.2	80
	(42.1)	(5.4)	(3.6)	
[{(p-cymene)Ru}$_2$(μ-idz)(μ-OMe)$_2$]BPh$_4$ (XIIa)	65.1	6.4	2.9	70
	(64.75)	(6.05)	(2.85)	
[{(p-cymene)Ru}$_2$(μ-idz)(μ-OMe)$_2$]BF$_4$ (XIIb)	47.1	5.45	3.9	58
	(47.3)	(5.3)	(3.8)	
[{(p-cymene)Ru}$_2$(μ-idz)(μ-OMe)$_2$]PF$_6$ (XIIc)	44.1	5.2	3.5	73
	(43.9)	(4.95)	(3.53)	
[{(p-cymene)Ru}$_2$(μ-pz)$_2$(μ-OMe)]BF$_4$ (XIIIb)	44.9	5.4	7.6	66
	(45.3)	(4.4)	(7.8)	
[{(p-cymene)Ru}$_2$(μ-pz)$_2$(μ-OMe)]PF$_6$ (XIIIc)	41.1	5.1	7.1	87
	(41.6)	(4.8)	(7.2)	

$$[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-OMe})_3]\mathrm{A} + 2\mathrm{Hpz} \rightarrow$$

$$[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-pz})_2(\mu\text{-OMe})]\mathrm{A} + 2\mathrm{MeOH} \qquad (3)$$

$$\mathrm{A} = \mathrm{BF_4}\ (\mathrm{XIIIb}),\ \mathrm{PF_6}\ (\mathrm{XIIIc})$$

Attempts to prepare the tetrafluoroborate salts of the bis(μ-diazolate)(μ-methoxo)-complexes (diazolate = mpz, idz) yielded the bis(μ-diazolate)(μ-hydroxo) complexes VIb and VIIIb. The methoxo complexes may be formed but could hydrolyse with traces of water in the solvent.

We have prepared only (μ-3,5-dimethylpyrazolate)methoxo-complexes and did not observe di-μ-bridged derivatives for this pyrazolate ligand.

Table 3 lists the analytical data for the new μ-methoxo-complexes and Table 4 shows selected ^{1}H NMR data consistent with the proposed formulations.

Crystal structure of $[\{(\eta^6\text{-p-cymene})\mathrm{Ru}\}_2(\mu\text{-pz})(\mu\text{-OH})_2]\mathrm{BF_4}$ *(Ib)*

Fig. 2 shows a view of the cation of the complex, together with the atom labelling used. Atomic positional parameters and selected bond lengths and angles are presented in Tables 5 and 6, respectively. The cation consists of two ruthenium atoms bridged by a pyrazolate and two hydroxo-groups. The pseudo-octahedral coordination of the ruthenium atoms is completed by an η^6 p-cymene ring. The separation between the two ruthenium atoms, 3.2120(5) Å, falls between that reported for the tris(μ-hydroxo)benzene and mesitylene complexes $[\{(\eta^6\text{-arene})\mathrm{Ru}\}_2(\mu\text{-OH})_3]^+$ [arene = benzene [10] (Ru–Ru = 2.9812(7) Å), mesitylene [11] (Ru–Ru = 2.989(3) Å)] and that reported for the bis(μ-pyrazolate)(μ-hydroxo)p-cymene derivative [6] $[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-pz})_2(\mu\text{-OH})]^+$ [Ru–Ru = 3.5277(3) Å]. Consistent with this, the average bond angle of oxygen for the bridging hydroxo-group in Ib, 100.6(2)°, is greater than those in the tris(μ-hydroxo)-compounds [91.5(1)° and 90.9(4)° for the benzene [10] and mesitylene [11] derivatives, respectively].

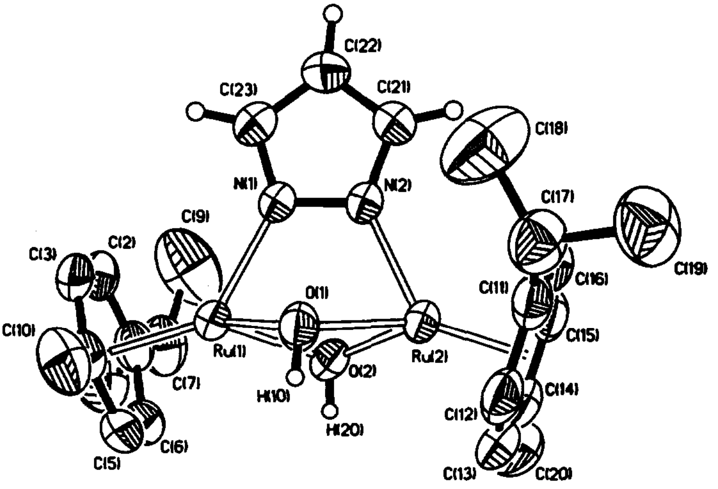


Fig. 2. Molecular structure of the cation $[\{(p\text{-cymene})\mathrm{Ru}\}_2(\mu\text{-pz})(\mu\text{-OH})_2]^+$. Hydrogen atoms of the p-cymene ligand have been omitted for clarity.

Table 4

Relevant ^{1}H NMR data [a,b] for the new μ-methoxo- complexes

Complex	*p*-Cymene [c]			Diazolate [c]						OMe
	Me	^{i}Pr	H_A/H_B	$H_{3/5}$	H_4	$Me_{3/5}$	H^1/H^4	H^2/H^3	H^5	
IXa	2.05s	1.26d, 2.65sp ^3J(HH) = 6.8	4.75, 4.89 J(AB) = 5.9	8.00d ^3J(HH) = 1.5		6.49t				3.39s
IXb	2.25s	1.31d, 2.82sp ^3J(HH) = 6.9	5.18, 5.25 J(AB) = 6.1	8.17d ^3J(HH) = 2.2		6.47t				3.50s
IXc [d]	2.29s	1.33d, 2.90sp ^3J(HH) = 6.8	5.45, 5.59 J(AB) = 6.0	8.44d ^3J(HH) = 2.0		6.50t				3.63s
Xa	2.01s	1.20d, 2.5–2.7sp ^3J(HH) = 6.8	5.07, 5.31 J(AB) = 5.9	7.94d ^3J(HH) = 1.8	2.61s	6.24d				3.11s
	2.03s	1.30d ^3J(HH) = 6.8	4.78, 4.90 J(AB) = 5.9							
Xb	2.21s	1.25d, 2.5–2.7sp ^3J(HH) = 6.9	5.43, 5.63 J(AB) = 5.4	8.10d ^3J(HH) = 2.0	2.71s	6.24d				3.31s
	2.23s	1.35d ^3J(HH) = 6.9	5.17, 5.21 J(AB) = 5.4							
Xc	2.19s	1.24d, 2.75sp ^3J(HH) = 6.8	5.38, 5.59 J(AB) = 6.1	8.09d ^3J(HH) = 1.9	2.70s	6.23d				3.29s
	2.21s	1.34d, 2.75sp ^3J(HH) = 6.9	5.14, 5.20 J(AB) = 6.1							
XIa	1.99s	1.23d, 2.55sp ^3J(HH) = 6.9	5.15, 5.29 J(AB) = 6.0		2.56s	6.04s				2.93s

XIb	2.18s	1.26d, 2.60sp ^3J(HH) = 6.9	5.47, 5.59 J(AB) = 6.1		2.64s	6.03s				3.09s
XIc	2.16s	1.26d, 2.70sp ^3J(HH) = 6.8	5.45, 5.57 J(AB) = 6.1		2.63s	6.03s				3.07s
XIIa	2.04s	1.21d, 2.6–2.9sp ^3J(HH) = 6.8	5.17, 5.35 J(AB) = 6.2				7.91sd	7.21st	8.60s	3.16s
	2.11s	1.28d ^3J(HH) = 6.8	4.79, 4.93 J(AB) = 6.2				7.85sd	[e]		
XIIb	2.30s	1.26d, 2.8–3.0sp ^3J(HH) = 6.8	5.50, 5.66 J(AB) = 6.0				7.99sd	7.43st	8.85s	3.39s
	2.30s	1.34d ^3J(HH) = 6.8	5.32, 5.36 J(AB) = 6.2				7.87sd	7.18st		
XIIc	2.28s	1.25d, 2.80sp ^3J(HH) = 6.9	5.48, 5.64 J(AB) = 6.3				7.99sd	7.44st	8.82s	3.37s
	2.28s	1.34d, 2.80sp ^3J(HH) = 6.9	5.26, 5.34 J(AB) = 6.2				7.87sd	7.18st		
XIIIa	1.99s	1.06d, 2.65sp ^3J(HH) = 6.8	4.74, 4.94 J(AB) = 5.9	7.52d ^3J(HH) = 1.5		6.12t				4.26s
XIIIb	2.22s	1.13d, 2.83sp ^3J(HH) = 6.8	5.30, 5.39 J(AB) = 5.9	7.69d ^3J(HH) = 2.1		6.14t				4.70s
XIIIc [d]	2.26s	1.15d, 2.90sp ^3J(HH) = 6.8	5.58, 5.79 J(AB) = 6.2	7.99 ^3J(HH) = 2.2		6.16t				4.74s

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[a] Measured in $CDCl_3$ at room temperature unless otherwise stated; chemical shifts relative to $SiMe_4$ as external standard; J in Hz. [b] Abbreviations; s, singlet; d, doublet; sp, septet; bs, broad singlet. [c] The labelling of *p*-cymene, pyrazolate and indazolate protons is the same as in Table 2. [d] In CD_3COCD_3. [e] Obscured by the BPh_4 protons.

Table 5

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for the complex $[\{(p\text{-cymene})Ru\}_2(\mu\text{-pz})(\mu\text{-OH})_2]BF_4$ (Ib)

Atom	*x*	*y*	*z*	U_{eq}
Ru(1) [a]	81509(3)	31573(2)	48298(2)	415(1)
Ru(2) [a]	69114(3)	32943(2)	64806(2)	425(1)
F(1)	4404(4)	2706(4)	4467(4)	177(3)
F(2)	3684(6)	4076(4)	4806(3)	180(3)
F(3)	3159(6)	3475(3)	3674(2)	177(3)
F(4)	2508(4)	2772(5)	4661(3)	189(3)
O(1)	7782(3)	4159(2)	5682(2)	48(1)
O(2)	6752(3)	2525(2)	5451(2)	49(1)
N(1)	9214(3)	2628(2)	5779(2)	45(1)
N(2)	8671(3)	2664(2)	6474(2)	44(1)
B	3485(6)	3258(5)	4391(3)	67(2)
C(1)	8096(5)	2210(3)	3835(2)	59(2)
C(2)	9331(4)	2540(4)	3989(2)	60(2)
C(3)	9611(4)	3513(4)	4044(2)	57(2)
C(4)	8657(4)	4208(3)	3961(2)	56(2)
C(5)	7407(4)	3882(4)	3791(2)	56(2)
C(6)	7141(4)	2915(4)	3730(2)	57(2)
C(7)	7703(6)	1164(4)	3814(3)	81(2)
C(8)	7524(6)	829(4)	2994(3)	95(3)
C(9)	8562(8)	543(5)	4299(4)	133(4)
C(10)	8920(5)	5252(3)	4074(3)	74(2)
C(11)	6785(4)	4210(3)	7505(3)	56(2)
C(12)	5852(4)	4457(3)	6928(3)	60(2)
C(13)	5001(4)	3787(3)	6592(3)	60(2)
C(14)	5075(4)	2825(4)	6835(3)	60(2)
C(15)	6003(4)	2557(3)	7412(2)	56(2)
C(16)	6848(4)	3245(3)	7729(3)	57(2)
C(17)	7680(5)	4946(4)	7855(3)	72(2)
C(18)	9028(6)	4644(5)	7832(5)	124(3)
C(19)	7336(6)	5192(5)	8671(3)	98(3)
C(20)	4209(5)	2091(4)	6466(3)	85(2)
C(21)	9466(4)	2279(3)	7010(2)	55(2)
C(22)	10536(4)	1986(3)	6662(3)	62(2)
C(23)	10338(4)	2227(3)	5895(3)	55(2)
H(10) [b]	7297(43)	4587(35)	5544(26)	66(16)
H(20) [b]	6085(41)	2664(31)	5242(25)	52(14)

[a] Atom coordinates for these atoms are expressed $\times 10^5$ and $U_{eq} \times 10^4$. [b] These two hydrogen atoms were refined as free isotropic atoms.

The Ru–O bond distances [average 2.087(4) Å] are comparable to those found in the related complexes $[\{(\eta^6\text{-arene})Ru\}_2(\mu\text{-OH})_3]^+$ [arene = benzene 2.079(3) Å [9], mesitylene 2.098(10) Å [5]] and $[\{(p\text{-cymene})Ru\}_2(\mu\text{-pz})_2(\mu\text{-OH})]^+$ 2.088(2) Å. The Ru–N distances (2.078 Å, average) fall between those found in the related mono(μ-pyrazolate)(μ-chloro)-complex $[\{(\eta^6\text{-benzene})Ru\}_2(\mu\text{-pz})(\mu\text{-Cl})_2]Cl$ (2.067 Å) [5] and in the bis(μ-pyrazolate) compounds $[\{(\eta^6\text{-benzene})Ru\}_2(\mu\text{-pz})_2(\mu\text{-Cl})]Cl$ [5] and $[\{(\eta^6\text{-}p\text{-cymene})Ru\}_2(\mu\text{-pz})_2(\mu\text{-OH})]BPh_4$ [6], 2.087 and 2.086 Å, respectively. However, the differences are not significant. Several short intermolecular distances between hydrogen atoms of the ligands and fluorines of the anion are

Table 6

Selected bond distances (Å) and angles (°) for the complex $[\{(p\text{-cymene})Ru\}_2(\mu\text{-pz})(\mu\text{-OH})_2]BF_4$ (Ib)

Ru(1)–O(1)	2.090(3)	Ru(2)–O(1)	2.094(3)
Ru(1)–O(2)	2.085(3)	Ru(2)–O(2)	2.078(3)
Ru(1)–N(1)	2.077(3)	Ru(2)–N(2)	2.078(3)
Ru(1)–C(1)	2.170(4)	Ru(2)–C(11)	2.198(4)
Ru(1)–C(2)	2.156(5)	Ru(2)–C(12)	2.156(5)
Ru(1)–C(3)	2.181(4)	Ru(2)–C(13)	2.172(4)
Ru(1)–C(4)	2.194(4)	Ru(2)–C(14)	2.188(5)
Ru(1)–C(5)	2.173(4)	Ru(2)–C(15)	2.184(5)
Ru(1)–C(6)	2.157(4)	Ru(2)–C(16)	2.159(4)
O(1)–H(10)	0.82(5)	O(2)–H(20)	0.80(4)
N(1)–N(2)	1.361(4)	C(21)–C(22)	1.383(6)
N(1)–C(23)	1.331(5)	C(22)–C(23)	1.371(6)
N(2)–C(21)	1.336(5)		
C(1)–C(2)	1.409(7)	C(11)–C(12)	1.412(6)
C(1)–C(6)	1.426(7)	C(11)–C(16)	1.411(6)
C(1)–C(7)	1.531(7)	C(11)–C(17)	1.511(7)
C(2)–C(3)	1.404(7)	C(12)–C(13)	1.411(7)
C(3)–C(4)	1.413(7)	C(13)–C(14)	1.417(7)
C(4)–C(5)	1.426(6)	C(14)–C(15)	1.416(6)
C(4)–C(10)	1.507(7)	C(14)–C(20)	1.504(7)
C(5)–C(6)	1.392(7)	C(15)–C(16)	1.413(6)
C(7)–C(8)	1.493(8)	C(17)–C(18)	1.504(8)
C(7)–C(9)	1.490(9)	C(17)–C(19)	1.514(8)
O(1)–Ru(1)–O(2)	76.0(1)	O(1)–Ru(2)–O(2)	76.0(1)
O(1)–Ru(1)–N(1)	78.7(1)	O(1)–Ru(2)–N(2)	79.0(1)
O(1)–Ru(1)–G(1) [a]	134.6(1)	O(1)–Ru(2)–G(2) [a]	133.3(1)
O(2)–Ru(1)–N(1)	79.4(1)	O(2)–Ru(2)–N(2)	78.7(1)
O(2)–Ru(1)–G(1) [a]	132.1(1)	O(2)–Ru(2)–G(2) [a]	133.1(1)
N(1)–Ru(1)–G(1) [a]	133.4(1)	N(2)–Ru(2)–G(2) [a]	133.9(1)
Ru(1)–O(1)–Ru(2)	100.3(1)	Ru(1)–O(2)–Ru(2)	101.0(1)
Ru(1)–O(1)–H(10)	116.0(3)	Ru(2)–O(1)–H(10)	109.0(3)
Ru(1)–O(2)–H(20)	108.0(3)	Ru(2)–O(2)–H(20)	107.0(3)
Ru(1)–N(1)–N(2)	116.1(2)	N(1)–N(2)–C(21)	108.1(3)
Ru(1)–N(1)–C(23)	136.0(3)	N(2)–C(21)–C(22)	109.1(4)
N(2)–N(1)–C(23)	107.9(3)	C(21)–C(22)–C(23)	105.0(4)
Ru(2)–N(2)–N(1)	116.7(2)	N(1)–C(23)–C(22)	109.9(4)
Ru(2)–N(2)–C(21)	135.1(3)		

[a] G(1) and G(2) represent the centroids of the p-cymene rings C(1)–C(6) and C(11)–C(16), respectively.

observed. Among them, two clear hydrogen bonds [O(2)–H(20) ··· F(1) and O(1)–H(10) ··· F(2′); O(2) ··· F(1) 2.959(6) Å and O(1) ··· F(2′) 3.031(6) Å] maintain together two symmetry-related cations through two bridging BF_4^- anions, forming a tetranuclear structure (see Figure 3, in which both cations and anions are related by a symmetry centre; transformation $1-x$, $1-y$, $1-z$).

Although from a structural point of view the interactions O–H ··· F are evident, there is no significant differences between the ν(OH) frequencies (Nujol mulls) observed for Ib and its BPh_4 analogue Ia (Table 1).

Experimental

C, H, and N analyses were carried out with a Perkin–Elmer 240B microanalyser. IR spectra were recorded on a Perkin–Elmer 577 spectrophotometer (range 4000–200 cm^{-1}) using Nujol mulls between polyethylene sheets. ^{1}H NMR spectra were recorded on a Varian XL 200 spectrometer. Solvents were dried and distilled before use.

Preparation of $[\{(p\text{-cymene})Ru\}_2(\mu\text{-dmpz})(\mu\text{-OH})_2]A$ $[A = BPh_4$ *(IIIa)*, BF_4 *(IIIb)*, *or* PF_6 *(IIIc)*$]$

A mixture of $[\{(p\text{-cymene})Ru\}_2(\mu\text{-OH})_3]A$ (0.15 mmol) and stoicheiometric amounts of Hdmpz was heated under reflux in acetone (30 cm^3) for 24 h. The mixture was filtered where necessary and the solutions were concentrated under reduced pressure. Addition of diethyl ether led to the precipitation of yellow complexes which were filtered off, washed with diethyl ether and air-dried. These compounds were also prepared under the same conditions, but using an excess of the diazole (1/5 molar ratio).

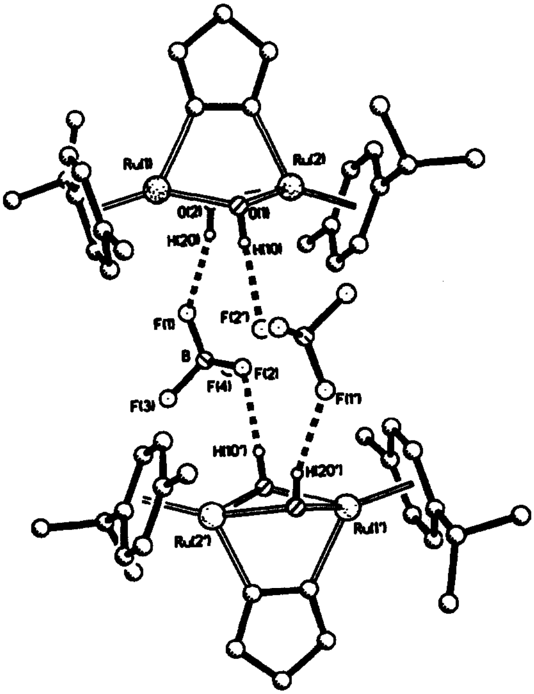

Fig. 3. Bridging of the BF_4^- anions between pairs of dinuclear cations through hydrogen-bonding interactions.

Preparation of [{(p-cymene)Ru}$_2$(μ-LL)$_2$(μ-OH)]A [LL = pz; A = BPh$_4$ (Va), BF$_4$ (Vb), PF$_6$ (Vc). LL = mpz; A = BPh$_4$ (VIa), BF$_4$ (VIb), PF$_6$ (VIc). LL = idz; A = BPh$_4$ (VIIIa), BF$_4$ (VIIIb), or PF$_6$ (VIIIc)

A mixture of {[(*p*-cymene)Ru}$_2$(μ-OH)$_3$]A (0.15 mmol) and the corresponding HLL ligand (0.75 mmol) was heated under reflux in acetone (30 cm^3) for 20 h. The mixture was filtered if necessary and the solutions were concentrated under reduced pressure. Addition of diethyl ether led to the precipitation of yellow complexes, which were filtered off, washed with diethyl ether and air-dried.

Reactions under milder conditions (1/1 molar ratio, room temperature) led to mixtures of the mono(μ-pyrazolate) complexes and the bis(μ-pyrazolate) compounds, excepting when LL = pz and A = BF$_4$, when pure [{(*p*-cymene)Ru}$_2$(μ-pz)(μ-OH)$_2$]BF$_4$ was isolated.

Complexes Va,c, VI and VIII could be prepared from mixtures of the mono(μ-pyrazolate) and the bis(μ-pyrazolate) complexes obtained as above by heating them under reflux in acetone with excess of the corresponding HLL ligand during 20 h.

Preparation of [{(p-cymene)Ru}$_2$(μ-LL)(μ-OMe)$_2$]A [LL = pz; A = BPh$_4$ (IXa), BF$_4$ (IXb), or PF$_6$ (IXc). LL = mpz; A = BPh$_4$ (Xa), BF$_4$ (Xb), or PF$_6$ (Xc). LL = dmpz; A = BPh$_4$ (XIa), BF$_4$ (XIb), or PF$_6$ (XIc). LL = idz; A = BPh$_4$ (XIIa), BF$_4$ (XIIb), or PF$_6$ (XIIc)

A mixture of [{(*p*-cymene)Ru}$_2$(μ-OMe)$_3$]A (0.14 mmol) and stoicheiometric amounts of the corresponding HLL ligand in methanol (30 cm^3) was stirred for 1 h. The mixture was filtered as necessary and the solutions were concentrated under reduced pressure. Addition of diethyl ether led to the precipitation of yellow complexes which were filtered off, washed with diethyl ether, and air dried. The complex [{(*p*-cymene)Ru}$_2$(μ-mpz)(μ-OMe)$_2$]BF$_4$ (Xb) as prepared, contained *ca.* 5% of the hydroxo-compound [{(*p*-cymene)Ru}$_2$(μ-mpz)(μ-OH)$_2$]BF$_4$ (IIa).

Complex XIb was prepared as above, but the reaction time was 24 hours.

Complexes IXa, Xa, XIIa, and XIc were similarly prepared, with reflux times of 12 h (IXa) or 24 h (Xa, XIc, and XIIa).

The treatment of [{(*p*-cymene)Ru}$_2$(μ-OMe)$_3$]BPh$_4$ with Hdmpz in 1/5 molar ratio at reflux temperature during 24 h affords 3 : 1 mixtures of [{(*p*-cymene)Ru}$_2$(μ-OMe)$_3$]BPh$_4$ and [{(*p*-cymene)Ru}$_2$(μ-dmpz)(μ-OMe)$_2$]BPh$_4$ (XIa).

Preparation of [{(p-cymene)Ru}$_2$(μ-pz)$_2$(μ-OMe)]A [A = BF$_4$ (XIIIb) or PF$_6$ (XIIIc)]

A mixture of [{(*p*-cymene)Ru}$_2$(μ-OMe)$_3$]A (0.15 mmol) and Hpz (0.75 mmol) was heated under reflux in methanol (30 cm^3) for 4 h (XIIIb) or 24 h (XIIIc). The resulting solutions were concentrated under reduced pressure. Addition of diethyl ether led to the precipitation of yellow complexes which were filtered off, washed with diethyl ether, and air-dried.

Starting from [{(*p*-cymene)Ru}$_2$(μ-OMe)$_3$]BPh$_4$ a 4:1 mixture of IXa and [{(*p*-cymene)Ru}$_2$(μ-pz)$_2$(μ-OMe)]BPh$_4$ (XIIIa) was obtained, operating as above (24 h reflux).

*Crystal data for [{(*p*-cymene)Ru}$_2$(μ-pz)(μ-OH)$_2$]BF$_4$ (Ib)*

$C_{23}H_{33}BF_4N_2O_2Ru_2$, $M = 658.47$, monoclinic, space group $P\ 2_1/n$, $a = 10.6739(4)$, $b = 14.0705(5)$, $c = 17.2521(6)$ Å, $\beta = 93.185(4)°$, $V = 2587.0(2)$ Å^3, $Z = 4$, $D_c = 1.691$ Mg·m^{-3}, $F(000) = 1320$, λ(Mo-K_α) = 0.71069 Å, $\mu = 11.95$ cm^{-1}, $T = 20°$C.

Data collection and reduction. A Siemens AED-2 diffractometer with monochromated Mo-K_α radiation was used. An orange prismatic block 0.165 × 0.173 × 0.515 nm was mounted on a glass fibre. 5040 intensities were registered to $2\theta_{max} = 50°$. Averaging equivalents gave 4344 unique reflections, of which 3700 with $F \geqslant 5.0\sigma(F)$ were used for all calculations (program system SHELX76) [12]. Cell constants were refined from setting angles of 58 reflections in the range 2θ 20–35°. An absorption correction was applied using the ψ-scan method [13] (transmissions 0.725–0.777).

Structure solution and refinement. The structure was solved by Patterson and extended by difference syntheses. All atoms were refined anisotropically. Hydrogen atoms were localized in several difference Fourier maps and included in the final structure factor calculations using a riding model. The final R value was 0.0302, with $R_w = 0.0397$. The weighting scheme was $w^{-1} = \sigma^2(F) + gF^2$, with $g = 0.000135$; 316 parameters; maximum $\Delta/\sigma < 0.002$, maximum $\Delta\rho$ 0.50 e Å^{-3}. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. [14]. Final atomic coordinates are given in Table 5.

Additional material available from the authors comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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