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SYNTHESIS OF RUTHENIUM-PALLADIUM AND RUTHENIUM-RHODIUM COMPLEXES LINKED BY PYRAZOLATE GROUPS AND CHLORINE ATOMS. CRYSTAL STRUCTURE OF $[(p\text{-cymene})ClRu(\mu\text{-}Cl)(\mu\text{-pz})Pd(C_8H_{11})]$

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Summary

The preparation of new heterobinuclear compounds of formula $[(p\text{-cymene})RuX_2(Pz)ML_2]$ (M = Pd, X = Cl, $L_2 = C_3H_5$, C_4H_7 or C_8H_{11}; Pz = pz *; M = Rh, X = Cl or I, L_2 = 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene, tfb, or bicyclo[2.2.1]heptadiene, nbd; Pz = pz or Mepz) is reported. One of the complexes, $[(p\text{-cymene})ClRu(\mu\text{-}Cl)(\mu\text{-pz})Pd(C_8H_{11})]$, has been characterized by single-crystal X-ray diffraction. The crystals are monoclinic, space group $P2_1/c$, with a 14.0044(10), b 14.9641(10), c 11.0456(5) Å, β 103.191(5)° and $Z = 4$. The structure has been refined to $R = 0.064$ for the 2850 observed reflexions with $I > 3\sigma(I)$. The coordination of the Pd atom to the C_8H_{11} ring system involves only three C atoms constituting a η^3-allyl group, at 2.147(17), 2.101(15) and 2.119(17) Å from the Pd atom. The Ru–Pd distance is 3.516(1) Å, the two atoms being bridged by a chlorine atom and a pyrazolate group; the other chlorine atom is terminal.

Introduction

Heteronuclear complexes are of particular interest because of the special features of the reactivity which might result from the presence of adjacent metals with

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

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different chemical properties [1]. Many such species containing bis(diphenyl-phosphino)methane or 2-(diphenylphosphino)pyridine as bridging ligands have been recently reported, mostly by Shaw, Balch, and coworkers [2,3]. In recent series of articles [4–8], we have shown that a variety of heteronuclear complexes that involve rhodium and other Group 8 metal atoms can be synthesized by use of azolate anions as bridging ligands. We describe here the synthesis and properties of a set of heterobridged complexes in which Ru^{II} to Pd^{II} or Rh^{I} centers are linked via bridging pyrazolate groups and chlorine atoms. A preliminary communication on the $[(p\text{-cymene})Ru(\mu\text{-Cl})_2(\mu\text{-pz})Rh(tfb)]$ complex has previously appeared [9].

Results and discussion

The procedure used for the synthesis of the heterobinuclear compounds reported here involves the initial bridging of the pyrazole ligand to ruthenium(II). A subsequent reaction with a second metal acetylacetonate complex gives the heterobinuclear compounds. Thus, the mononuclear $[(p\text{-cymene})RuCl_2(Hpz)]$ complex (Ia) (prepared by cleavage of the $[(p\text{-cymene})RuCl_2]_2$ dimer with the corresponding pyrazole) reacts with $[Pd(acac)L_2]$ (acac = acetylacetonate, $L_2 = C_3H_5$, C_4H_7 or C_8H_{11}) compounds to give $[(p\text{-cymene})ClRu(\mu\text{-Cl})(\mu\text{-pz})PdL_2]$ complexes ($L_2 = C_3H_5$ (II), C_4H_7 (III) or C_8H_{11} (IV)). The well-known tendency of the Pd^{II} ion (d^8) to form square-planar 16-electron complexes suggests that the two metals are bridged by a chlorine and a pyrazolate group, as recently found for the isoelectronic mixed-valence complex $[(C_5Me_5)ClRh(\mu\text{-Cl})(\mu\text{-pz})Rh(tfb)]$ [10]. Further support for the proposed double-bridged formulation comes from the X-ray crystal structure of complex IV (vide infra).

As expected, complex I abstracts the acetylacetonate group from [Rh(acac)(diolefin)] compounds to give heterobinuclear $[(p\text{-cymene})RuCl_2(pz)Rh(diolefin)]$ complexes (diolefin = tfb (V) or nbd (VI)). The reaction is faster for tfb than for nbd. For the 1,5-cyclooctadiene complex [Rh(acac)(cod)], containing the diolefin which has a lower π-acceptor ability than the others, the reaction is even slower, and no pure heterobinuclear complex was isolated.

Using the same synthetic route we prepared other related heterobimetallic compounds. Thus starting from $[(p\text{-cymene})RuX_2(HPz)]$ (X = Cl, HPz = HMepz (Ib); X = Cl, $HPz = HMe_2pz$ (Ic); X = I, HPz = Hpz (Id)) and treatment with [Rh(acac)(tfb)] gave the complexes VII (X = Cl, HPz = HMepz), VIII (X = Cl, $HPz = HMe_2pz$) and IX (X = I, HPz = Hpz) (eq. 1).

$$[(p\text{-cymene})RuX_2(HPz)] + [Rh(acac)(tfb)] \rightarrow [(p\text{-cymene})RuX_2(Pz)Rh(tfb)] \quad (1)$$

The structure of complex V (cf. ref 9) involves a triply-bridged arrangement, in contrast with the doubly-bridged arrangement observed for complex IV and $[(C_5Me_5)ClRh(\mu\text{-Cl})(\mu\text{-pz})Rh(tfb)]$ [10]. Particularly noteworthy for complex V is the high asymmetry of one of the chlorine bridges [9]. Although, similar triple-bridges are probably present in all the ruthenium(II)-rhodium(I) complexes reported in this paper, the possibility of a doubly-bridged formulation in some cases cannot be completely excluded.

TABLE 1

COLOUR, ANALYTICAL DATA, YIELDS, AND MOLECULAR WEIGHTS FOR THE HETERO-DINUCLEAR NEUTRAL COMPLEXES

Complex	Colour	Analyses (Found (calc.)(%))			Yield (%)	Mol. wt. ($CHCl_3$) Found (calc.)
		C	H	N		
II	Orange	42.9 (43.0)	4.9 (4.8)	5.0 (4.8)	60	633 (587)
III	Orange	36.8 (36.9)	4.2 (4.2)	5.4 (5.4)	59	556 (521)
IV	Orange	38.0 (38.3)	4.4 (4.5)	5.3 (5.3)	52	527 (535)
V	Orange	41.9 (42.7)	3.4 (3.3)	4.2 (4.0)	76	733 (702)
VI	Orange	41.2 (42.2)	4.5 (4.4)	4.6 (4.9)	67	576 (568)
VII	Orange	41.6 (43.5)	3.6 (3.5)	3.9 (3.9)	55	698 (716)
VIII	Orange	44.4 (44.4)	3.9 (3.7)	4.0 (3.8)	60	–
IX	Dark-red	33.8 (33.9)	2.4 (2.6)	3.4 (3.2)	74	885 (921)

Table 1 lists the analytical data, yields, and molecular weights for the new heterobimetallic complexes. Table 2 gives the ^1H NMR data for some selected heterobimetallic compounds.

Cationic complexes

A related cationic complex (X) containing the bridging pyrazolate group as well as the neutral pyrazole ligand can be prepared by treating the cationic complex $[(p\text{-cymene})RuCl(Hpz)_2]ClO_4$ (prepared "in situ" from $[(p\text{-cymene})RuCl_2]_2$, $AgClO_4$ and Hpz) with [Rh(acac)(tfb)] (eq. 2).

$$[(p\text{-cymene})RuCl(Hpz)_2]ClO_4 + Rh(acac)(tfb) \rightarrow$$

$$\underset{(X)}{[(p\text{-cymene})(Hpz)Ru(\mu\text{-}Cl)(\mu\text{-}pz)Rh(tfb)]ClO_4} + Hacac \qquad (2)$$

Interestingly, complex X reacts with sodium acetylacetonate to give a neutral complex XI, that presumably has the two pyrazolate groups as bridging ligands (eq. 3).

$$[(p\text{-cymene})(Hpz)RuCl(pz)Rh(tfb)]ClO_4 + Na(acac) \rightarrow$$

$$\underset{(XI)}{[(p\text{-cymene})RuCl(pz)_2Rh(tfb)]} + NaClO_4 + Hacac \qquad (3)$$

The reaction can be reversed; thus addition of a stoicheiometric amount of $HClO_4$ to the neutral complex XI, affords X.

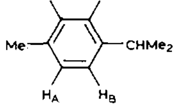
As mentioned above, we failed to obtain neutral heterobinuclear complexes using the diolefin 1,5-cyclooctadiene; in view of this, we explored a different route in an attempt to prepare a cationic heterobinuclear complex involving treatment of complex Ia with $[Rh(cod)(acetone)_x]ClO_4$. However, no formation of a heterobi-

TABLE 2

^{1}H NMR SPECTRA^a FOR SOME REPRESENTATIVE COMPOUNDS

Complex	H(3)/H(5)	H(4)	η^6-*p*-cymene	Others
II	7.78(d, 1H) 7.48(d, 1H)	6.20(t, 1H)	5.32 ^{b}(Δ(H_AH_B) 32, *J* 6) 2.90(sp, C*H*Me$_2$), 2.13 (s, CH_3) 1.25(d, 6H, CH_3 of CH*Me*$_2$, *J* 7)	–
III	7.87(d, 1H) 7.39(d, 1H)	6.24(t, 1H)	5.38(Δ(H_AH_B) 35, *J* 6) 2.90(sp, C*H*Me$_2$), 2.19(s, CH_3) 1.27(d, 6H, CH_3 of CH*Me*$_2$, *J* 7)	2.96(d, *J* 12) 3.92(d, *J* 6.7)
IV	7.84(d, 1H) 7.40(d, 1H)	6.23(t, 1H)	5.36(Δ(H_AH_B) 33, *J* 6) 2.90(sp, C*H*Me$_2$), 2.19)s, CH_3) 1.27(d, 6H, CH_3 of CH*Me*$_2$ *J* 7)	3.71(s, 2H) 2.82(s, 2H) 2.07(s, 3H, CH_3)
V	7.95(d, 1H) 6.51(d, 1H)	6.13(t, 1H)	5.42(Δ(H_AH_B) 36, *J* 5.7) 2.89(sp C*H*Me$_2$), 2.24(s, CH_3) 1.27(d, 6H, CH_3 of CH*Me*$_2$, *J* 6.7)	CH, 5.25(s, 2H) CH_2 3.36(s, 4H)
VI	7.87(d, 1H) 6.61(d, 1H)	6.12(t, 1H)	5.37(Δ(H_AH_B) 34, *J* 6) 2.85(sp, C*H*Me$_2$), 2.21(s, CH_3) 1.27(d, 6H, CH_3 of CH*Me*$_2$, *J* 7)	HC=C + CH 3.60 (s, 6H) CH_2 1.12(s, 2H)
IX	7.90(d, 1H) 6.45(d, 1H)	6.01(t, 1H)	5.37(Δ(H_AH_B) 39, *J* 6) 3.12(sp, C*H*Me$_2$), 2.44(s, CH_3) 1.28(d, 6H, CH_3 of CH*Me*$_2$, *J* 6.8)	CH, 5.23 (s, 2H) CH_2, 3.53(s, 4H)

[a] Spectra were determined at 200 MHz. Chemical shifts are in (ppm) relative to TMS; Δ and *J* in Hz. Apparency: s singlet, d doublet, t triplet, sp septriplet. [b] Midpoint of AB resonance is quoted. Labelling of *p*-cymene protons:



nuclear compound was observed; instead a redistribution reaction took place, to give $[RhCl(cod)]_2$ and [(*p*-cymene)Ru(μ-Cl)$_2$(μ-pz)Ru(*p*-cymene)]ClO_4 (XII). This last binuclear ruthenium compound has not been previously reported, and can be prepared directly by reaction of compound Ia with $AgClO_4$ in acetone.

Crystal structure

Figure 1 shows the molecular structure of the heterodinuclear complex [(η^6-*p*-cymene)ClRu(μ-Cl)(μ-pz)Pd(η^3-C_8H_{11})]. The main geometrical features of the complex are listed in Table 3.

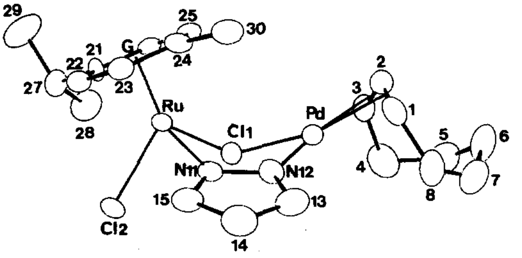


Fig. 1. A view of the structure of complex IV.

There is octahedral coordination about the Ru^{II} atom, with the *p*-cymene ligand occupying a *fac*-site. The intermetallic distance, 3.516(1) Å, is similar to that between Ru and Rh in [(*p*-cymene)Ru(μ-Cl)$_2$(μ-pz)Rh(tfb)] [9], in which two Cl bridging atoms are present. The Pd^{II} metal atom presents a square-planar coordination involving the Cl and the pz groups, and a η^3-allyl grouping from the conjugated dienyl system of the C_8H_{11} ring.

The Ru–Cl distances agree well with those corresponding to a Rh atom in a similar situation, [(C_5Me_5)ClRh(μ-Cl)(μ-pz)Rh(tfb)] [10], as do the Ru–N distances. However they are shorter than those in the above-mentioned ruthenium-rhodium complex [9], although the Ru–C(*p*-cymene) distances are similar, but shorter than those in [{(*p*-cymene)Ru}$_2$(μ-pz)$_2$(μ-OH)] [11].

The distances of the Pd atom from the atoms of the C_8H_{11} ring system (see Table 3) indicate that only C(1), C(2), C(3) are involved in the metal–ligand bonding [12], with the central carbon atom closer to the metal. The coordination plane through Cl(1), Pd, N(12) and that through C(2,3), Pd, C(1,2) (see Table 3) make an angle of 5.3(6)°, and the latter plane makes an angle of 57(2)° with that through the η^3-allyl group (C(1), C(2), C(3)), again in agreement with results reported by Churchill [12]. The C(7)–C(8), C(1)–C(2), and C(2)–C(3) bond lengths in the ring system reveals the unsaturated bond distribution, which, together with the metal bonding, pucker the ring into a conformation similar to that found by Churchill [12].

The *p*-cymene group presents similar features to those present in [{*p*-cymene)Ru}$_2$(μ-pz)$_2$(μ-OH)].

Experimental

C, H and N analyses were carried out with a Perkin–Elmer 240B microanalyzer. Infrared spectra were recorded on a Perkin–Elmer 599 spectrophotometer (range 4000–200 cm^{-1}) with Nujol mulls between polyethylene sheets, or in dichloromethane solutions between NaCl plates. ^1H NMR spectra were performed on $CDCl_3$ solutions at room temperature on a Varian XL 200 spectrophotometer (200 MHz) with $SiMe_4$ as internal standard. Molecular weights were determined with a Perkin–Elmer 115 osmometer.

The precursors [(*p*-cymene)$RuCl_2$]$_2$ [13], [Pd(C_8H_{11})Cl]$_2$ and [Pd(acac)(allyl)] [14], were prepared by published methods.

Synthesis of complexes [(p-cymene)RuCl$_2$(HPz)]; HPz = Hpz (Ia); HPz = HMepz (Ib); HPz = HMe$_2$pz (Ic)

A suspension of [(*p*-cymene)$RuCl_2$]$_2$ (183 mg, 0.3 mmol) and the appropriate pyrazole (0.6 mmol) in methanol was stirred at room temperature for 1 h, and the resulting orange solutions were concentrated under reduced pressure. Slow addition of diethyl ether gave precipitates of complexes Ia, Ib or Ic as orange microcrystals, which were filtered off, washed with diethyl ether, and vacuum-dried.

Ia: Found: C, 40.8; H, 4.9; N, 7.4. $C_{13}H_{18}N_2Cl_2Ru$ calc: C, 41.7; H, 4.9; N, 7.5%.
Ib: Found: C, 42.6; H, 5.1; N, 7.2. $C_{14}H_{20}N_2Cl_2Ru$ calc: C, 43.3; H, 5.1; N, 7.2%.
Ic: Found: C, 44.4; H, 5.1; N, 7.1%. $C_{15}H_{22}N_2Cl_2Ru$ calc: C, 44.8; H, 5.5; N, 7.0%.

Synthesis of [(η^6-p-cymene)RuI$_2$(Hpz)] (Id)

Potassium iodide (0.177 g, 1.068 mmol) was added to a solution of complex Ia (0.2 g, 0.534 mmol) in dichloromethane (30 ml). The mixture was stirred at room

TABLE 3

SELECTED PARAMETERS (Å AND °) [a]

Ru–Cl(1)	2.446(3)	Pd–Cl(1)	2.394(3)	Pd–N(12)	2.084(10)
Ru–Cl(2)	2.397(3)				
Ru–N(11)	2.080(8)	Pd–C(1)	2.119(17)	C(1)–C(2)	1.382(21)
Ru–G	1.661(10)	Pd–C(2)	2.101(15)	C(2)–C(3)	1.408(23)
		Pd–C(3)	2.147(17)	C(3)–C(4)	1.540(25)
Ru–C(21)	2.188(10)	Pd–C(4)	2.928(22)	C(4)–C(5)	1.519(38)
Ru–C(22)	2.162(11)	Pd–C(5)	4.157(26)	C(5)–C(6)	1.493(43)
Ru–C(23)	2.163(11)	Pd–C(6)	4.290(30)	C(6)–C(7)	1.470(48)
Ru–C(24)	2.197(11)	Pd–C(7)	3.851(23)	C(7)–C(8)	1.314(41)
Ru–C(25)	2.181(10)	Pd–C(8)	2.905(17)	C(8)–C(1)	1.482(23)
Ru–C(26)	2.189(9)				
Ru····Pd	3.516(1)	Ru–Cl(1)–Pd	93.1(1)		
Cl(1)–Ru–G	127.9(5)	N(12)–Pd–Cl(1)	90.1(3)		
Cl(2)–Ru–G	128.9(5)	N(12)–Pd–C(1,2)	120.6(6)		
N(11)–Ru–G	127.3(5)	N(12)–Pd–C(2,3)	156.5(6)		
N(11)–Ru–Cl(1)	85.8(3)	Cl(1)–Pd–C(1,2)	148.9(5)		
N(11)–Ru–Cl(2)	86.1(3)	Cl(1)–Pd–C(2,3)	113.3(5)		
Cl(1)–Ru–Cl(2)	86.3(1)	C(1,2)–Pd–C(2,3)	35.8(7)		
Ru–N(11)–N(12)	123.1(7)	Pd–N(12)–N(11)	118.9(7)		
Ru–Cl(1)–Pd–N(12)	42.6(3)	C(1)–C(2)–C(3)–C(4)	−40(3)		
Cl(1)–Pd–N(12)–N(11)	−26.3(7)	C(2)–C(3)–C(4)–C(5)	−58(2)		
Pd–N(12)–N(11)–Ru	−12.0(11)	C(3)–C(4)–C(5)–C(6)	53(3)		
N(12)–N(11)–Ru–Cl(1)	42.0(8)	C(4)–C(5)–C(6)–C(7)	50(3)		
N(11)–Ru–Cl(1)–Pd	−45.0(3)	C(5)–C(6)–C(7)–C(8)	−83(4)		
		C(6)–C(7)–C(8)–C(1)	−12(4)		
(Cl(1), Pd, N(12))–(C(2,3), Pd, C(1,2))	5.3(6)	C(7)–C(8)–C(1)–C(2)	34(3)		
(C(1), C(2), C(3))–C(2,3), Pd, C(1,2))	57(2)	C(8)–C(1)–C(2)–C(3)	44(3)		

[a] G stands for the centroid of the six-membered ring and C(1,2), C(2,3) for the midpoints of the C(1)–C(2) and C(2)–C(3) bonds. Within parentheses, the atoms indicate the planes definition.

temperature for 8 h, then filtered to remove the KCl. The solution was concentrated under reduced pressure, and slow addition of diethyl ether gave a dark-red solid which was filtered off, washed with diethyl ether, and vacuum-dried. (Found: C, 28.2; H, 3.2; N, 4.7. $C_{13}H_{18}N_2RuCl_2$ calc: C, 28.0; H, 3.2; N, 5.0%).

Synthesis of complexes II, III and IV

To dichloromethane solutions (30 ml) of [Pd(acac)(allyl)] (allyl = C_3H_5, C_4H_7 or C_8H_{11}) was added [(η^6-*p*-cymene)$RuCl_2$(Hpz)] (0.25 mmol). After 1 h stirring the

TABLE 4

DETAILS OF STRUCTURE DETERMINATION OF COMPOUND IV

Crystal data	
Formula	$C_{21}H_{28}Cl_2N_2RuPd$
Crystal habit	Prismatic, red
Crystal size (mm)	0.06 × 0.40 × 0.46
Symmetry	Monoclinic, $P2_1/c$
Unit cell determination	Least-squares fit from 98 reflexions ($\theta < 45°$)
Unit cell dimensions	14.0044(10), 14.9641(10), 11.0456(5) Å 90, 103.191(5), 90°
Packing: V (Å^3), Z	2253.7(3), 4
D_c (g cm^{-3}), M, F(000)	1.730, 586.84, 1168
μ (cm^{-1})	144.72
Experimental data	
Technique	Four circle diffractometer: Philips PW1100 Bisecting geometry Graphite oriented monochromator: Cu-K_α $w/2\theta$ scans, scan width: 1.5° Detector apertures 1 × 1, $u_p\theta_{max.}$ 65° 1 min/reflex.
Number of reflexions:	
Independent	3840
Observed	2850 ($3\sigma(I)$ criterion) 2 reflexions every 90 min Variation: no
Transmission factor	0.030–0.461
Solution and refinement	
Solution	Patterson
Refinement	Least-squares on F_{obs} with 1 block
Parameters:	
Number of variables	244 (H atoms fixed)
Degrees of freedom	2606
Ratio of freedom	11.7
H atoms	Difference synthesis
Final shift/error	0.02
w-scheme	Empirical as to give no trends in $\langle w\Delta^2F\rangle$ $\langle \lvert F_{obs}\rvert \rangle$ and $\langle \sin\theta/\lambda \rangle$
Max. thermal value	U_{22} (C(7)) = 0.25(3) Å^2
Final ΔF peaks	1.8 eÅ^{-3}
Final R and R_w	0.064, 0.085
Computer and programs	Vax 11/750, Xray76 [15]
Scattering factors	Int. Tables for X-Ray Crystallography [16]

solutions were evaporated under vacuum to ca. 1 ml and diethyl ether (15 ml) was added. The orange complexes II, III and IV which separated were filtered off, washed with diethyl ether, and air-dried.

Synthesis of complexes V–IX

To dichloromethane solutions (30 ml) of one of the complexes I (0.20 mmol) was added [Rh(acac)(diolefin)] (diolefin = tfb or nbd) (0.20 mmol). After 1 h stirring, the solutions were concentrated under reduced pressure. Addition of diethyl ether gave solids, which were filtered off, washed with diethyl ether, and vacuum-dried.

Synthesis of complex X

A suspension of [(*p*-cymene)RuCl$_2$]$_2$ (50 mg, 0.085 mmol) in acetone (30 ml) was treated with AgClO$_4$ (37 mg, 0.163 mmol) and Hpz (22 mg, 0.325 mmol). After 15 min stirring the AgCl was filtered off, and [Rh(acac)(tfb)] (70 mg, 0.163 mmol) was added to the solution. The mixture was stirred for 1 h and then concentrated to a small volume. Addition of diethyl ether gave a yellow solid, which was filtered off, washed with diethyl ether, and dried in vacuo (yield 70%). (Found: C, 40.4; H, 3.2; N, 6.8; complex X calc: C, 40.3; H, 3.3; N, 6.7%). Complex X is an electrolyte (1 :'1) in acetone.

TABLE 5

ATOMIC COORDINATES

Atom	*x/a*	*y/b*	*z/c*
Ru	0.44080(5)	0.37874(5)	0.18821(6)
Pd	0.21713(6)	0.28022(6)	0.20867(7)
Cl(1)	0.35965(18)	0.23410(17)	0.13976(24)
Cl(2)	0.47211(21)	0.37254(18)	−0.01611(22)
C(1)	0.0901(11)	0.2896(11)	0.2817(14)
C(2)	0.1522(10)	0.2247(12)	0.3450(12)
C(3)	0.1897(10)	0.1538(11)	0.2861(15)
C(4)	0.1315(18)	0.1009(14)	0.1736(20)
C(5)	0.0401(21)	0.0559(17)	0.1967(23)
C(6)	−0.0273(18)	0.1175(25)	0.2436(26)
C(7)	−0.0492(15)	0.1985(25)	0.1670(24)
C(8)	0.0057(12)	0.2705(20)	0.1769(21)
N(11)	0.3061(7)	0.4343(6)	0.1031(8)
N(12)	0.2198(7)	0.4031(7)	0.1207(9)
C(13)	0.1484(9)	0.4622(10)	0.0706(13)
C(14)	0.1922(11)	0.5343(9)	0.0228(13)
C(15)	0.2891(10)	0.5141(8)	0.0441(11)
C(21)	0.5958(7)	0.3703(7)	0.2830(10)
C(22)	0.5697(8)	0.4606(8)	0.2518(10)
C(23)	0.4911(9)	0.4997(8)	0.2903(10)
C(24)	0.4330(9)	0.4507(9)	0.3590(9)
C(25)	0.4607(8)	0.3610(8)	0.3884(9)
C(26)	0.5412(8)	0.3216(7)	0.3512(9)
C(27)	0.6827(8)	0.3284(9)	0.2421(13)
C(28)	0.6653(12)	0.2317(10)	0.2001(17)
C(29)	0.7732(12)	0.3375(15)	0.3440(21)
C(30)	0.3424(10)	0.4890(10)	0.3928(12)

Synthesis of complex XI

To an acetone solution (30 ml) of complex X (125 mg, 0.15 mmol) was added Na(acac) (18.3 mg, 0.15 mmol). The mixture was stirred for 1 h then evaporated to ca. 1 ml. Addition of diethyl ether (15 ml) gave a yellow solid which was filtered off, washed with methanol and diethyl ether, then dried in vacuo. (Found: C, 44.7; H, 3.1; N, 7.4; Mol. wt.: 727. Complex XI calc: C, 45.7; H, 3.5; N, 7.6%; Mol. wt.: 734).

Synthesis of complex XII

To a solution of [(*p*-cymene)RuCl$_2$(Hpz)] (Ia) (100 mg, 0.27 mmol) in acetone (30 ml) was added solid AgClO$_4$ (55.4 mg, 0.27 mmol). The mixture was stirred for 15 min then filtered, and the filtrate concentrated under reduced pressure. Addition of diethyl ether gave an orange solid which was filtered off, washed with diethyl ether, and dried in vacuo (yield, 52%). (Found: C, 38.9; H, 4.3; N, 4.0; Complex XII calc: C, 39.0; H, 4.4; N, 4.0%). Complex XII is an 1 : 1 electrolyte in acetone.

X-ray analysis

Details of the structure determination are given in Table 4. The final atomic coordinates for the non-hydrogen atoms appear in Table 5. Lists of anisotropic thermal factors, the hydrogen atom coordinates and observed and calculated structure factors are available from the authors on request.

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