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Preparation of Pyrazole–Pyrazolate Half-Sandwich Complexes of Ruthenium and Osmium

Gabriele Albertin,*[a] Stefano Antoniutti,[a] Jesús Castro,[b] and Soledad García-Fontán[b]

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Pyrazole (HRpz) [MCl(η^6-*p*-cymene)(HRpz)L]BPh$_4$ (**1**–**8**) and imidazole (HIm) complexes [MCl(η^6-*p*-cymene)(HIm)L]BPh$_4$ (**9**–**10**) [M = Ru, Os; R = H, 3-Me, 3,5-Me$_2$; L = P(OEt)$_3$, PPh(OEt)$_2$, PPh$_2$OEt, CN*t*Bu] were prepared by allowing the dichloro compounds MCl$_2$(η^6-*p*-cymene)L to react with the appropriate azole in the presence of NaBPh$_4$. Treatment of the dichloro complexes with an excess of both pyrazole and NEt$_3$ yielded the pyrazole–pyrazolate derivatives [M(Rpz)(η^6-*p*-cymene)(HRpz)L]BPh$_4$ (**11**–**14**). Conversely, the reaction of carbonyl compounds RuCl$_2$(η^6-*p*-cymene)(CO) with pyrazole or imidazole yielded the bisazole complexes [MCl(η^6-*p*-cymene)(HRpz)$_2$]BPh$_4$ or [MCl(η^6-*p*-cymene)(HIm)$_2$]BPh$_4$ (**15**–**17**). The complexes were characterised spectroscopically (IR and ^{1}H, ^{13}C, ^{31}P NMR) and by X-ray crystal structure analysis [RuCl(η^6-*p*-cymene)(HRpz){PPh(OEt)$_2$}]BPh$_4$ (**1b**), [Ru(pz)(η^6-*p*-cymene)(HRpz){P(OEt)$_3$}]BPh$_4$ (**11a**) and [RuCl(η^6-*p*-cymene)(HRpz)$_2$]BPh$_4$ (**15**).

Introduction

The chemistry of transition metal complexes containing pyrazole (HRpz), pyrazolate (pz) and imidazole (HIm) as ligands has been extensively developed in the past few years and a number of complexes have been reported.[1–5] Interest in these studies stems from the potential of HRpz as a ligand, which may act as monodentate ligand, through its pyridinic nitrogen atom, or as either a monodentate or a bidentate bridging ligand, in a pz anion.[1–5] In addition, the possibility of using substituents on the heterocyclic ring may modify both steric and electronic properties of the HRpz ligand, giving rise to a rich and versatile chemistry.

However, the introduction of these ligands in the chemistry of half-sandwich arene complexes[6,7] is somewhat limited and, in the case of ruthenium and osmium, involves the preparation of oxine [M(η^6-*p*-cymene)(oxine)(Hazole)]$^+$ (M = Ru, Os) or amidine [Ru(η^6-*p*-cymene)L(3,5-HRR′pz)]$^{2+}$ (L = amidine) derivatives[8] containing HRpz as a ligand. These studies have been carried out in an attempt to prepare metal-based compounds with anticancer activity.[9] Heterodinuclear complexes of the type [(η^6-*p*-cymene)OsCl(μ-pz)$_2$M(COD)] (M = Rh, Ir; COD = 1,5-cyclooctadiene) as well as mono-[MCl$_2$(η^6-*p*-cymene)(HRpz)] and bispyrazole derivatives [MCl(η^6-*p*-cymene)(HRpz)$_2$]$^+$ (M = Ru, Os) are also known.[8b,10]

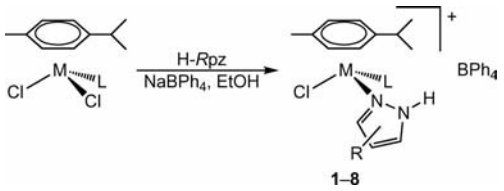
We are interested in the chemistry of half-sandwich arene complexes of Ru^{II} and Os^{II} and have recently reported the synthesis and reactivity of diazoalkane [MCl(N$_2$CAr1Ar2)(η^6-*p*-cymene)P]BPh$_4$, cyanoguanidine [M(η^6-*p*-cymene){NCN(H)C(NH$_2$)NH}P]$^+$ and imine complexes [M(η^6-*p*-cymene){HN=C(H)Ar}P]$^+$ of ruthenium and osmium stabilised by the half-sandwich fragment M(η^6-*p*-cymene)P (P = phosphite ligands).[11]

We have now extended these studies to include HRpz and HIm ligands, and here we report the synthesis and characterisation of some azole and of the first pyrazole–pyrazolate half-sandwich complexes of the iron triad.

Results and Discussion

Synthesis of Complexes

Dichloro complexes of ruthenium and osmium MCl$_2$(η^6-*p*-cymene)L, containing either phosphite or isocyanide as supporting ligands, react with the pyrazoles, HRpz, in the presence of NaBPh$_4$, to give the pyrazole complexes [MCl(η^6-*p*-cymene)(HRpz)L]BPh$_4$ (**1**–**8**), which were isolated as yellow solids and characterised (Scheme 1).

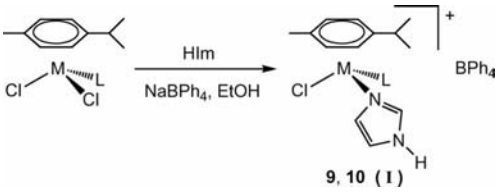


Scheme 1. M = Ru (**1**, **2**, **6**), Os (**3**–**5**, **7**, **8**); R = H (**1**, **3**, **6**, **7**), 3-Me (**2**, **4**, **8**), 3,5-Me$_2$ (**5**); L = P(OEt)$_3$ (**a**), PPh(OEt)$_2$ (**b**), PPh$_2$OEt (**c**) (**1**–**5**), CN*t*Bu (**6**–**8**).

[a] Dipartimento di Chimica, Università Ca' Foscari Venezia, Dorsoduro 2137, 30123 Venezia, Italy
[b] Departamento de Química Inorgánica, Universidade de Vigo, Facultade de Química, Edificio de Ciencias Experimentais, 36310 Vigo, Galicia, Spain

Crucial for successful synthesis was the use of ethanol containing $NaBPh_4$ as a solvent; the $NaBPh_4$ salt probably favours the substitution of the chloride ligand, allowing the separation of compounds **1**–**8** in good yield.

The results obtained with HRpz prompted us to extend our study to HIm to test whether related complexes could be prepared. The dichloro complexes $MCl_2(\eta^6$-*p*-cymene)P reacted with HIm in ethanol containing $NaBPh_4$ to yield the derivatives $[MCl(\eta^6$-*p*-cymene)(HIm)P]BPh_4 (**9** and **10**), which were isolated as BPh_4 salts and characterised (Scheme 2).



Scheme 2. M = Ru (**9**), Os (**10**); L = $P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**).

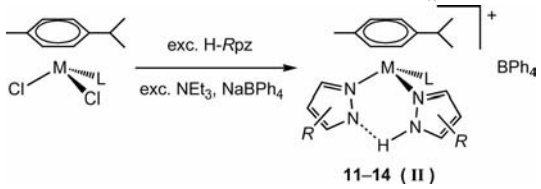
We also studied the reaction of the dichloro complexes $MCl_2(\eta^6$-*p*-cymene)L with a large excess of azole (HRpz and HIm) in an attempt to prepare bisazole derivatives $[M(\eta^6$-*p*-cymene)$(HRpz)_2L]^{2+}$ or $[M(\eta^6$-*p*-cymene$)(HIm)_2$-$L]^{2+}$. However, no bisazole complex was formed under any of the conditions studied, and **1**–**8** were the only complexes obtained. These species are therefore stable to substitution, since neither chloride, phosphite or isocyanide ligands could be substituted by an azole.

The acidic NH hydrogen atom of the coordinated pyrazole could be deprotonated in complexes **1**–**8** to give the related neutral species $MCl(\eta^6$-*p*-cymene)(pz)L containing a pz ligand. We therefore treated the HRpz complexes **1**–**8** with an excess of NEt_3 in an attempt to prepare the related neutral pz complexes. However, at room temperature, the reaction did not proceed, even after a long reaction time in the presence of a large excess of NEt_3, and the starting compounds **1**–**8** were recovered unchanged. Under reflux conditions, although some decomposition was observed, no pz complex was isolated.

$$[MCl(\eta^6\text{-}p\text{-cymene})(H\text{-}Rpz)L]^+ \xrightarrow{\text{exc. B}} MCl(\eta^6\text{-}p\text{-cymene})(Rpz)L$$

A different synthetic strategy was therefore used to prepare pz complexes, involving treatment of the dichloro complexes $MCl_2(\eta^6$-*p*-cymene)L with an excess of HRpz and a large excess of triethylamine in the presence of $NaBPh_4$. In a mixture of ethanol and dichloromethane, the reaction gave the new pyrazole–pyrazolate cations $[M(Rpz)(\eta^6$-*p*-cymene)$(HRpz)L]^+$ (**11**–**14**), which were isolated as BPh_4 salts and characterised (Scheme 3).

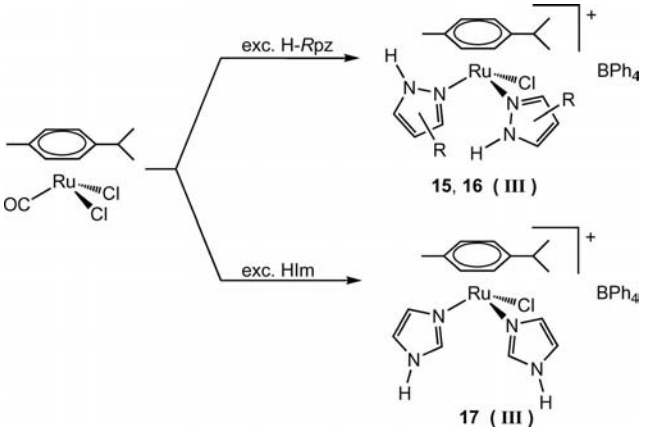
The reaction proceeded with substitution of both chloride ligands in the precursor $MCl_2(\eta^6$-*p*-cymene)L with concurrent deprotonation of one HRpz ligand, yielding unprecedented half-sandwich complexes **11**–**14** containing one HRpz and one Rpz molecule as ligands. Either the excess of azole, or the excess of base are needed to introduce two



Scheme 3. M = Ru (**11**), Os (**12**–**14**); R = H (**11, 12**, **14**), 3-Me (**13**); L = P (**11**–**13**) [$P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**)], $CNtBu$ (**14**).

Hpz units in the half-sandwich fragment which, after deprotonation of one NH hydrogen atom of HRpz, yields the final pyrazole–pyrazolate derivative.

The easy synthesis of half-sandwich azole complexes **1**–**14** with phosphite or isocyanide supporting ligands prompted us to extend our studies to the carbonyl precursors $MCl_2(\eta^6$-*p*-cymene)(CO). Results showed that the ruthenium complex $RuCl_2(\eta^6$-*p*-cymene)(CO) reacts with both Hpz and HIm to give bisazole complexes $[RuCl(\eta^6$-*p*-cymene$)(HRpz)_2]^+$ (**15** and **16**) and $[RuCl(\eta^6$-*p*-cymene)-$(HIm)_2]^+$ (**17**), which were isolated in good yield and characterised (Scheme 4).



Scheme 4. R = H (**15**), 3-Me (**16**).

In contrast to the related phosphite and isocyanide precursors, the reaction of $RuCl_2(\eta^6$-*p*-cymene)(CO) proceeds with the substitution, not only of one Cl^- ligand, but also of the CO group, yielding the bisazole complexes **15**–**17**. The reaction of the related osmium complex $OsCl_2(\eta^6$-*p*-cymene)(CO) with azoles was also studied, but only intractable mixtures of products were obtained.

Bispyrazole complexes of Ru and Os are known[8b,10] and were obtained from the reaction of a dinuclear complex $[MCl(\mu\text{-}Cl)(\eta^6$-*p*-cymene)] with an excess of HRpz. The use of carbonyl $RuCl_2(\eta^6$-*p*-cymene)(CO) as a precursor resulted in an alternative method for the synthesis of bisazole derivatives.

All azole complexes **1**–**17** were separated as yellow solids stable in air and in solution of polar organic solvents, in which they behave as 1:1 electrolytes.[12] Their formulation is supported by analytical and spectroscopic data (IR and ^1H, ^{13}C, ^{31}P NMR spectroscopy) and by X-ray crystal structure determinations of $[RuCl(\eta^6$-*p*-cymene)(HRpz)-$\{PPh(OEt)_2\}]BPh_4$ (**1b**), $[Ru(Rpz)(\eta^6$-*p*-cymene)(HRpz)-

$\{P(OEt)_3\}]BPh_4$ (**11a**) and $[RuCl(\eta^6\text{-}p\text{-cymene})(HRpz)_2]$-$BPh_4$ (**15**), whose ORTEP diagrams[13] are shown in Figures 1, 2 and 3, respectively.

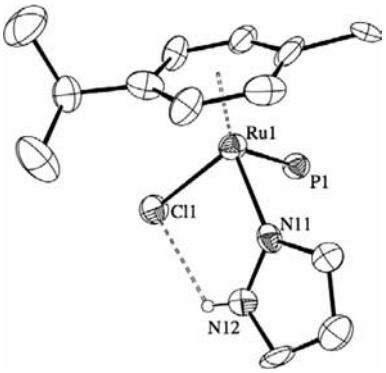


Figure 1. ORTEP view of one of the cations found in the asymmetric unit for complex **1b**, drawn at 30% probability level.

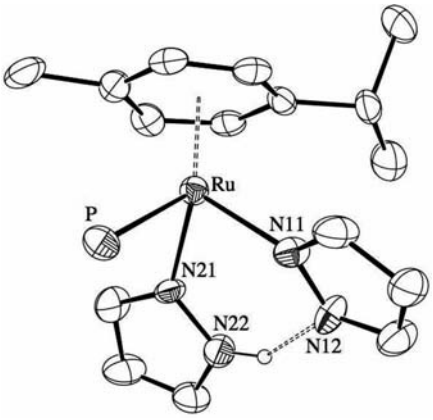


Figure 2. ORTEP view of the cation of complex **11a**, drawn at 30% probability level.

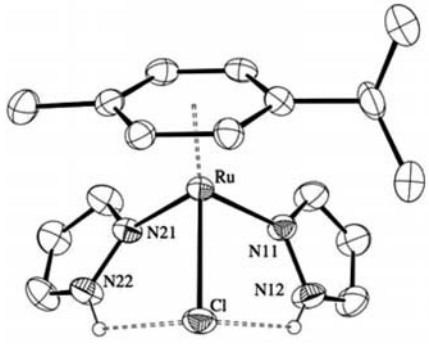
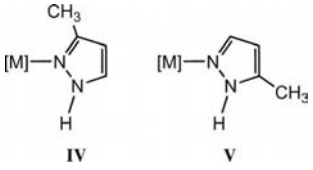


Figure 3. ORTEP view of the cation of complex **15**, drawn at 30% probability level.

The IR spectra of the HRpz complexes **1**–**8** show medium intensity bands at 3351–3238 cm^{-1}, attributed to the ν_{NH} of the HRpz ligand. A strong band at 2192–2174 cm^{-1} of the ν_{CN} of *t*Bu isocyanide is also observed in the isocyanide complexes **6**–**8**. However, the presence of the azole ligands is supported by ^1H NMR spectra, which show both a sloas [fc?>the NH of the HRpz unit, and signals between 7.50 and 5.91 ppm of the HRpz CH hydrogen atoms. A comparison of the chemical shift values of the NH group in our complexes with those of free HRpz also suggests iminic coordination of the azole, as observed in the solid state (Figure 1). The attribution of the signals of the HRpz ligand was supported by COSY experiments and by comparison with literature data.[3,14–17] The ^1H NMR spectra also contain signals of the *p*-cymene and phosphite or isocyanide supporting ligands, confirming the proposed formulation for the complexes. Lastly, the ^{13}C NMR spectra confirm the presence of the HRpz ligand, and heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple bond coherence (HMBC) experiments allow the attribution of the signals, as reported in the Exp. Section.

In contrast with the other HRpz complexes, the ^1H NMR spectra of the methylpyrazole derivatives **2a**, **2b** and **4b** show two signals for both NH protons at 11.55–10.84 ppm and the methyl substituents between 2.38 and 1.99 ppm. Two sharp singlets also appear in the $^{31}P\{^1H\}$ NMR spectra, suggesting the presence of two species, probably isomers. Both species present in **2a**, **2b** and **4b** may be complexes containing 3-Me-HRpz and 5-Me-HRpz, formed by the exchange of the nitrogen sites of the 3-methylpyrazole ligand. Isomerisation of pyrazole substituents on a metal centre has been observed previously,[14a,17a] and these precedents support the proposed formulation for our half-sandwich complexes **2a**, **2b** and **4b** (Scheme 5).



Scheme 5.

The IR spectra of HIm complexes **9** and **10** show a medium intensity band at 3336–3312 cm^{-1}, due to the ν_{NH} of the coordinated HIm group. ^1H NMR spectra confirm the presence of the azole ligand, showing a broad singlet at 8.25–8.00 ppm of the NH proton and three signals between 7.16 and 6.11 ppm of the CH hydrogen atom of the HIm group. Further support for the formulation proposed for complexes **9** and **10** came from ^{13}C NMR spectra, which, along with the signals of *p*-cymene, phosphite and BPh_4, showed three resonances between 140.3 and 117.9 ppm, attributed to the three HIm carbon atoms. $^{31}P\{^1H\}$ NMR spectra appear as sharp singlets fitting the proposed formulation for the complexes.

At room temperature, ^1H NMR spectra of **11**–**14** did not show any signal attributable to the NH proton of HRpz. However, when the sample temperature was lowered to –40 °C, a broad signal at 19.14–15.79 ppm appeared, which was assigned to the NH proton of HRpz involved in a N–H···N hydrogen bond. Classical inter- or intramolecular hydrogen bonds can shift the HRpz NH signal to higher frequencies,[3,4,10,14,17a] as observed for free HRpz involved in extensive intermolecular N–H···N interactions, and thus confirms the existence in solution of a type **II** geometry

(Scheme 3), with one HRpz and one Rpz ligand, as observed in the solid state (Figure 2). Beside the signals of the supporting phosphite or isocyanide ligands, the ^{1}H NMR spectra showed three resonances at 7.77–6.02 ppm attributed to the CH hydrogen atoms of HRpz. It is worth noting that only one set of signals for H3, H4 and H5 protons of the two HRpz groups were observed in the proton spectra, even at –80 °C, indicating that the two HRpz ligands sharing a hydrogen atom in a N–H···N arrangement were magnetically equivalent. The ^{13}C NMR spectra also show only one set of signals for the three C3, C4 and C5 carbon resonances of HRpz, fitting the proposed formulation for the pyrazole–pyrazolate derivatives.

The IR spectra of the bispyrazole complexes [RuCl(η^6-*p*-cymene)(HRpz)$_2$]BPh$_4$ (**15** and **16**) show two medium intensity bands at 3340–3261 cm^{-1}, attributed to the ν_{NH} of the two azole ligands. The ^{1}H NMR spectra show the characteristic broad signal of the NH of the HRpz at 11.08–10.53 ppm and related signals of the CH hydrogen atoms at 7.52–5.97 ppm, confirming the presence of HRpz ligands. Two singlets at δ = 2.17 and 2.13 ppm of the two methyl substituents of the HRpz in the ^{1}H NMR spectrum of **16** were also observed. The ^{13}C NMR spectra confirm the formulation proposed for complexes **15** and **16** showing both the signals of *p*-cymene and those of the three carbon resonances of azole groups at δ = 144.09–109.12 ppm. The IR spectra (ν_{NH} = 3304 cm^{-1}) and ^{1}H NMR spectra of complex **17** support the presence of the azole ligands in a type **III** geometry (Scheme 4), similar to those found in the solid state for the related HRpz complex **15**.

Table 1. Selected bond lengths [Å] and angles [°].

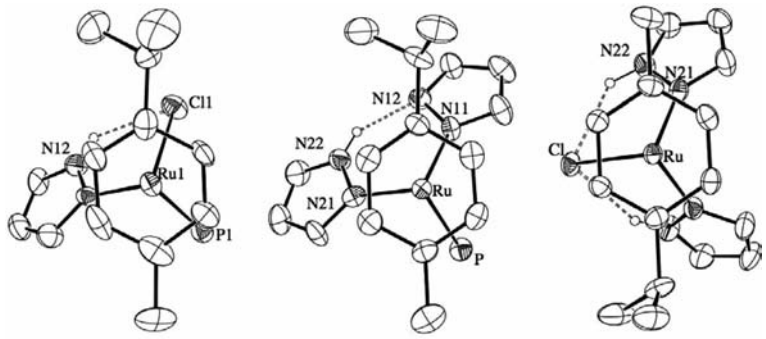
[a]	**1b**_mole 1	**1b**_mole 2	**11a**	**15**
Coordination bond lengths				
Ru–CT	1.7128(10)	1.7107(9)	1.7398(7)	1.6796(4)
Ru–P	2.296(4)	2.290(4)	2.260(2)	
Ru–Cl	2.404(3)	2.399(3)		2.4212(11)
Ru–N(1)	2.046(10)	2.067(10)	2.076(6)	2.112(4)
Ru–N(2)			2.093(7)	2.123(4)
Ru–C(1)	2.258(14)	2.286(12)	2.311(8)	2.201(4)
Ru–C(2)	2.242(14)	2.263(15)	2.183(8)	2.178(4)
Ru–C(3)	2.180(13)	2.158(17)	2.196(7)	2.170(4)
Ru–C(4)	2.247(13)	2.218(14)	2.230(8)	2.197(4)
Ru–C(5)	2.162(12)	2.149(14)	2.207(7)	2.174(4)
Ru–C(6)	2.193(12)	2.189(12)	2.259(7)	2.185(4)
Coordination bond angles				
N(1)–Ru–Cl	87.4(3)	87.7(2)		87.42(10)
N(2)–Ru–Cl				87.39(10)
N(1)–Ru–N(2)			90.6(3)	84.74(14)
N(1)–Ru–P	86.4(3)	86.8(3)	89.09(18)	
N(2)–Ru–P			86.51(18)	
P–Ru–Cl	84.37(13)	84.02(13)		
CT–Ru–N(1)	128.1(3)	127.1(2)	125.16(17)	128.77(10)
CT–Ru–N(2)			125.51(18)	128.78(10)
CT–Ru–P	129.97(10)	130.82(10)	127.82(7)	
CT–Ru–Cl	125.89(9)	125.80(9)		125.56(3)
Pyrazole bond angles				
C(13)–N(11)–N(12)	100.8(10)	102.6(10)	108.3(7)	104.3(4)
C(13)–N(11)–Ru	132.9(8)	132.1(8)	127.9(6)	131.4(3)
N(12)–N(11)–Ru	126.3(7)	125.3(7)	123.5(5)	124.2(3)
C(23)–N(21)–N(22)			105.1(8)	104.2(4)
C(23)–N(21)–Ru			130.2(7)	130.5(3)
N(22)–N(21)–Ru			124.5(6)	124.3(3)

[a] Labelling in coordination sphere of this table was standardised: N(1) and/or N(2) are the nitrogen donor atoms of the pyrazole or pyrazolate rings, and C(1) to C(6) are the carbons atoms of the *p*-cymene rings. CT represents the centroid of the benzene ring in the *p*-cymene ligand.

X-ray Crystal Structures

The structures of **1b**, **11a** and **15** consist of a tetraphenylborate anion and cation formed by a ruthenium atom η^6-coordinated to a *p*-cymene molecule, and to three donor atoms, leading to the formation of a "three-legged piano stool" structure. Of these ligands, one is anionic and the other two are neutral. For **1b**, the ligands forming the "legs" are an anionic chlorine atom, one P-donor diethoxyphenylphosphane ligand and a neutral N-donor HRpz ligand; for **11a**, the anionic ligand is a N-donor pz and the other two are a N-donor neutral HRpz ligand and a P-donor triethoxyphosphane; for **15**, the three ligands are one anionic chloride ligand and two neutral N-donor HRpz ligands. The geometry of the complexes is octahedral and marked by near 90° values for angles between "legs", as shown in Table 1. Expected angles between the centroid and the "legs" for the regular half-sandwich are 125.26°. The values found in **1b**, **11a** and **15** are close to this value, except for those of the phosphorus donor ligands, which are about 5° larger as a consequence of the expected cone angle of this kind of ligand.[18]

The average Ru–C$_{p\text{-cymene}}$ bond lengths are 2.212(1) Å for **1b** (average of two molecules), 2.184(4) Å for **15** and 2.231(8) Å for **11a**, with Ru–centroid arene ring distances of 1.712(1), 1.6796(4) and 1.7398(7) Å for **1b** (average of two molecules), **15** and **11a**, respectively. These values are consistent with distances reported for other *p*-cymene ruthenium(II). complexes.[11b,11c] The benzene ring of the *p*-cymene is more or less planar, with a root mean square (rms) deviation of 0.029 (average) for **1b**, 0.021 for **11a** and 0.005 for **15**. These differences are due the different *trans* influence of the ligands, with a large *trans* influence of the P donor ligand and a similar influence of the N and Cl donor ligands. Consequently, the large C–Ru bond lengths are those pseudo-*trans* to the P donor ligand in **1b** and **11a**. However, the orientation of the *p*-cymene ligand in three complexes is such that donor atoms in the "legs" may be considered staggered with the Ru–C bonds (see Figure 4) and this effect is consequently lowered. In **1b**, the phosphorus atom may be considered as *trans* to a carbon atom [labelled as C(22) and C(52) in each molecule], but in **11a** it is clearly *trans* to the C(1)–C(6) bond.



One of the cations **1b** **11a** **15**

Figure 4. View of the three cations through the Ru–centroid axis.

For **1b** and **11a**, the Ru–P bond lengths, 2.293(4) (average) and 2.260(2) Å, respectively, are comparable with those found in other related cationic arene ruthenium(II) compounds.[11b,11c] In **1b** and **15**, the Ru–Cl bond lengths, 2.402(3) (average) and 2.421(1) Å, respectively, are of the same order as in related cationic arene ruthenium(II) compounds.[11b,11c,19]

In compound **1b**, the Ru–N bond length is on average 2.06(1) Å − a very short value. To the best of our knowledge, it is the shortest value for a monodentate HRpz ligand bonded to a Ru^{II} atom.[20] A slightly longer value is found for nitrosyl Ru^{II} complexes,[21] $[RuCl_2(HRpz)_2(tmeda)]$[22] and $[Ru(p\text{-cymene})(pz)(HRpz)_2]^+$.[10d] The Ru–N bond lengths in **11a** are 2.076(6) Å for the anionic pz ligand and 2.093(7) Å for the neutral Hpz ligand, comparable with those mentioned in the literature.[19,22,23] The bond length for the anionic ligand is only about 0.02 Å shorter than with the neutral HRpz ligand. Since other electronic effects, such as the *trans* influence, are similar in both ligands, the small difference suggests some degree of exchange of the proton between the two ligands.[17a,24] A rather short intramolecular hydrogen bond between the two ligands is found, with an N–N distance of only 2.58(1) Å.[24b,14] In **15**, the Ru–N bond length is on average 2.118(4) Å, slightly longer than those found for **11b**, $[RuCl(p\text{-cymene})(Me_2Hpz)(PPh_2OH)]^+$[25] and $[Ru(p\text{-cymene})(pz)(HRpz)_2]^+$,[10d] but shorter than those found in neutral $[RuX_2(PPh_3)_2(HRpz)_2]$ ($X = Cl^-$, NCS^-).[19,23]

As reported previously,[17a] the two heterocyclic ligands form a dihedral angle of 20.3(4)°, partly due the intramolecular hydrogen bond, although the regularity of the coordination geometry is not affected, as the angle formed by the metal and the two cyclic ligands is 90.6(3)°. It is also worth noting that the geometrical parameters of both HRpz and pz ligands are similar, and the C–N–Ru and N–N–Ru bond angles do not show significant differences (see also supplementary crystallographic material).

In **1b**, the susbtituents of the phosphonite ligand are organised in such a way that the phenyl ring and the HRpz ligand are implicated in a π–π stacking interaction, with dihedral angles of 21.3(6) and 14.7(5)° and distances between centroids of 3.6831(4) and 3.4631(4) Å (see Figure 5). In addition, the HRpz ligand is implicated in an intramolecular hydrogen bond with the chloride bound to the same metal atom. The geometrical parameters for this interaction are listed in Table 2.

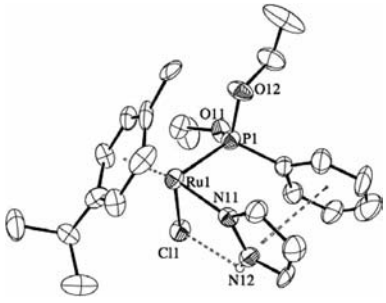


Figure 5. View of the π–π stacking in **1b**.

Table 2. Hydrogen bond lengths [Å] and angles [°].

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
1b				
N(12)–H(12)···Cl(1)	0.86	2.49	3.040(9)	122.3
N(22)–H(22A)···Cl(2)	0.86	2.49	3.043(10)	122.8
11a				
N(22)–H(2N)···N(12)	0.86	1.85	2.580(10)	141.0
15				
N(22)–H(2)···Cl	0.98(5)	2.41(5)	3.112(4)	128(4)
N(12)–H(1)···Cl	0.88(7)	2.38(7)	3.053(5)	134(6)
N(22)–H(2)···Cl^i	0.98(5)	2.60(5)	3.292(4)	128(3)
Symmetry operation, i: 1 –*x*, 1 –*y*, 1 –*z*				

In **15**, both HRpz ligands are almost perpendicular, with dihedral angles between best planes (rms of 0.002 for both) of 88.3(2)°. They are also interconnected through a pair of hydrogen bonds through the chlorine atom. This double bond contrasts with that found in the neutral rhenium(I) complex $[Re(CO)_3(HRpz)_2Br]$ with only one hydrogen interaction.[14] Also, the lack of this interaction in $[RuCl_2(HRpz)_2(tmeda)]$[22] and $[RuCl(\eta^6\text{-}C_6Me_6)(MeHRpz)_2]$[9] is surprising. In addition, in **15** one of the hydro-

gen bonds is bifurcated with a neighbouring cation resulting in the formation of a dimer (see Figure 6 and Table 2).

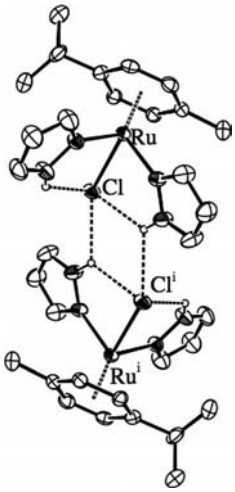


Figure 6. View of the superstructure of **15**.

Conclusions

In this paper, we report the reactivity of *p*-cymene complexes $MCl_2(\eta^6$-*p*-cymene)L, containing either phosphite, isocyanide or CO ligands, towards Hpz and HIm molecules, which allowed three different types of azole complexes to be obtained: HRpz $[MCl(\eta^6$-*p*-cymene)(HRpz)L]BPh_4 and HIm $[MCl(\eta^6$-*p*-cymene)(HIm)L]BPh_4 cations, unprecedented half-sandwich pyrazole–pyrazolate $[M(Rpz)(\eta^6$-*p*-cymene)(HRpz)L]BPh_4 derivatives and bisazole $[MCl(\eta^6$-*p*-cymene)$(HRpz)_2]BPh_4$ or $[MCl(\eta^6$-*p*-cymene)$(HIm)_2]BPh_4$ complexes. X-ray crystal structure determination for each of the three types of compounds also allowed interesting comparisons of the three half-sandwich *p*-cymene azole geometries. The evaluation of the Ru–N_{azole} bond length when ancillary ligands were excharged was remarkable. With chloride and $PPh(OEt)_2$, a very short Ru–N_{azole} bond length is observed. With $PPh(OEt)_2$ and an anionic pz ligand, there were two Ru–N bonds, longer than in preceding complexes and similar to each other, due to the exchange of the hydrogen atom. Lastly, with chloride and another neutral HRpz ligand, the Ru–N_{azole} bond lengths were longer, but within the range of literature values.[14]

Experimental Section

General: All synthetic work was carried out in an inert atmosphere (Ar, N_2) using standard Schlenk techniques or a vacuum atmosphere dry-box. All solvents were dried with appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. $RuCl_3 \cdot 3H_2O$ and OsO_4 were obtained from Pressure Chemical Co. (USA) Products and used as received. Phosphites, $PPh(OEt)_2$ and PPh_2OEt, were prepared by the method reported by Rabinowitz and Pellon.[26] $P(OEt)_3$ (Aldrich) was used as received. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded with a Perkin–Elmer Spectrum One FT-IR spectrophotometer. NMR spectra (^1H, ^{31}P, ^{13}C) were obtained with AC200 or AVANCE 300 Bruker spectrometers at temperatures between –80 and +30 °C, unless otherwise noted. ^1H and ^{13}C spectra are referenced to internal tetramethylsilane; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The COSY, HMQC and HMBC NMR experiments were performed using their standard programs. The SwaN-MR and iNMR software packages[27] were used to treat NMR spectroscopic data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C were measured with a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche of the University of Padua, Italy.

Synthesis of Complexes: Complexes $MCl_2(\eta^6$-*p*-cymene)L [L = $P(OEt)_3$, $PPh(OEt)_2$, PPh_2OEt], $MCl_2(\eta^6$-*p*-cymene)(CN*t*Bu) and $MCl_2(CO)(\eta^6$-*p*-cymene) (M = Ru, Os) were prepared following previously reported methods.[28]

$[MCl(\eta^6$-*p*-cymene)(HRpz)L]BPh_4 (1–5) [M = Ru (1, 2), Os (3–5); R = H (1, 3), 3-Me (2, 4), 3,5-Me_2 (5); L = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b), PPh_2OEt (c)]: In a 25 mL three-necked round-bottomed flask were placed the appropriate $MCl_2(\eta^6$-*p*-cymene)L complex (0.2 mmol), a slight excess of the appropriate HRpz (0.22 mmol), an excess of $NaBPh_4$ (0.3 mmol, 0.103 g) and ethanol (4 mL). The reaction mixture was stirred for 24 h and the yellow solid that separated was collected by filtration and recrystallised from CH_2Cl_2 and ethanol; yield 124 mg (75%) for **1a**, 123 mg (72%) for **1b**, 135 mg (76%) for **1c**, 126 mg (75%) for **2a**, 125 mg (72%) for **2b**, 137 mg (75%) for **3a**, 146 mg (77%) for **3b**, 142 mg (72%) for **4b**, 143 mg (76%) for **5a**.

1a: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3272 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 11.58 (br. s, 1 H, NH), 7.33–6.89 (m, 20 H, BPh_4), 7.50 (d, 1 H, H5 HRpz), 7.40 (d, 1 H, H3 HRpz), 6.45 (t, 1 H, H4 HRpz), 5.52, 5.46, 5.39, 5.21 (d, 4 H, Ph *p*-cym), 3.88, 3.80 (m, 6 H, CH_2), 2.68 (m, 1 H, CH *i*Pr), 2.08 (s, 3 H, CH_3 *p*-cym), 1.20 (t, 9 H, CH_3 phos), 1.18 (m, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 113.8 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, BPh_4), 146.4 (s, C3 HRpz), 132.5 (s, C5 HRpz), 116.9 (d, C1 *p*-cym), 109.3 (s, C4 HRpz), 105.3 (d, C4 *p*-cym), 90.56, 89.28 (d, C3 *p*-cym), 89.78, 88.06 (d, C2 *p*-cym), 63.9 (d, CH_2), 31.2 (s, CH *i*Pr), 22.1, 22.0 (s, CH_3 *i*Pr), 18.8 (s, CH_3 *p*-cym), 16.2 (d, CH_3 phos). Λ_M = 52.9 Ω^{-1} mol^{-1} cm^2. $C_{43}H_{53}BClN_2O_3PRu$ (824.20): calcd. C 62.66, H 6.48, Cl 4.30, N 3.40; found C 62.48, H 6.35, Cl 4.21, N 3.33.

1b: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3272 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 11.37 (br. s, 1 H, NH), 7.45–6.88 (m, 25 H, Ph), 6.28 (t, 1 H, H4 HRpz), 5.53, 5.45, 5.33, 5.17 (d, 4 H, Ph *p*-cym), 4.02, 3.90 (m, 4 H, CH_2), 2.69 (m, 1 H, CH *i*Pr), 2.01 (s, 3 H, CH_3 *p*-cym), 1.35 (m, 6 H, CH_3 *i*Pr), 1.17 (t, 6 H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 143.1 (s). Λ_M = 54.2 Ω^{-1} mol^{-1} cm^2. $C_{47}H_{53}BClN_2O_2PRu$ (856.24): calcd. C 65.93, H 6.24, Cl 4.14, N 3.27; found C 66.05, H 6.17, Cl 4.01, N 3.35.

1c: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3270 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 11.34 (br. s, 1 H, NH), 7.58–6.88 (m, 30 H, Ph), 7.25 (d, 1 H, H3 HRpz), 6.28 (t, 1 H, H4 HRpz), 5.49, 5.34, 5.16 (d, 4 H, Ph *p*-cym), 3.74, 3.70 (m, 2 H, CH_2), 2.68 (m, 1 H, CH *i*Pr), 2.08 (s, 3 H, CH_3 *p*-cym), 1.28 (t, 3 H, CH_3 phos), 1.19 (d, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 125.8 (s). Λ_M = 54.8 Ω^{-1} mol^{-1} cm^2. $C_{51}H_{53}BClN_2OPRu$ (888.29): calcd. C 68.96, H 6.01, Cl 3.99, N 3.15; found C 69.11, H 5.96, Cl 3.81, N 3.02.

2a: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3238 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 11.43, 11.25 (br. s, 1 H, NH), 7.55 (br., 1 H, H3 HRpz), 7.31–6.88 (m, 20 H, BPh_4), 7.27 (d, 1 H, H5 HRpz), 6.32, 6.22 (t, 1 H, H4 HRpz), 5.54, 5.47, 5.39, 5.23 (d, 4 H, Ph *p*-cym), 3.89, 3.82 (m, 6 H, CH_2), 2.68 (m, 1 H, CH *i*Pr), 2.33, 2.20 (s, 3 H, CH_3 HRpz), 2.15, 2.08 (s, 3 H, CH_3 *p*-cym), 1.22 (t, 9 H, CH_3 phos), 1.19 (m, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 115.1 (s); 113.7 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, Ph), 155.1, 143.5 (s, C5 HRpz), 147.3, 132.8 (s, C3 HRpz), 110.6 (d, C1 *p*-cym), 108.9 (d, C4 HRpz), 104.5 (d, C4 *p*-cym), 90.70, 89.52 (d, C3 *p*-cym), 89.84, 88.14 (d, C2 *p*-cym), 89.17, 89.15 (d, C2 HRpz), 88.59 (d, C3 HRpz), 87.56 (d, C2 HRpz), 63.9 (d, CH_2), 31.4, 31.3 (s, CH *i*Pr), 22.7, 22.6, 22.2, 22.1 (s, CH_3 *i*Pr), 18.8, 18.7 (s, CH_3 *p*-cym), 16.2 (d, CH_3 phos), 15.2, 11.2 (s, CH_3 HRpz). Λ_M = 51.6 $\Omega^{-1}mol^{-1}cm^2$. $C_{44}H_{55}BClN_2O_3PRu$ (838.23): calcd. C 63.05, H 6.61, Cl 4.23, N 3.34; found C 63.23, H 6.53, Cl 4.07, N 3.23.

2b: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3289 (m), 3261 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 11.26, 10.84 (br. s, 1 H, NH), 7.40–6.88 (m, 25 H, Ph), 7.12 (d, 1 H, H3 HRpz), 6.88 (d, 1 H, H5 HRpz), 6.04, 6.00 (t, 1 H, H4 HRpz), 5.56, 5.48, 5.33, 5.19 (d, 4 H, Ph *p*-cym), 4.08, 3.96, 3.87 (m, 4 H, CH_2), 2.73 (m, 1 H, CH *i*Pr), 2.20, 2.04 (s, 3 H, CH_3 *p*-cym), 2.19, 1.99 (s, 3 H, CH_3 HRpz), 1.39, 1.37 (t, 6 H, CH_3 phos), 1.20 (m, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 145.2 (s); 143.4 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, Ph), 153.7, 131.5 (s, C5 HRpz), 146.3, 142.5 (s, C3 HRpz), 120.5 (d, C1 *p*-cym), 109.0, 108.7 (s, C4 HRpz) 105.5, 102.6 (d, C4 *p*-cym), 90.7, 90.0, 89.2 (d, C3 *p*-cym), 89. 2, 86.5, 87.6, 87.3 (d, C2 *p*-cym), 65.2, 64.9 (d, CH_2), 31.4 (s, CH *i*Pr), 22.3, 21.9, 20.64 (s, CH_3 *i*Pr), 18.75, 18.60 (s, CH_3 *p*-cym), 16.2 (m, CH_3 phos), 15.9, 11.0 (s, 3-CH_3 and 5-CH_3 HRpz). Λ_M = 53.0 $\Omega^{-1}mol^{-1}cm^2$. $C_{48}H_{55}BClN_2O_2PRu$ (870.27): calcd. C 66.25, H 6.37, Cl 4.07, N 3.22; found C 66.39, H 6.44, Cl 4.24, N 3.07.

3a: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3351 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 11.79 (br. s, 1 H, NH), 7.78 (br., 1 H, H5 HRpz), 7.32–6.86 (m, 20 H, BPh_4), 6.44 (t, 1 H, H4 HRpz), 5.61, 5.56, 5.40, 5.32 (d, 4 H, Ph *p*-cym), 3.87, 3.80 (m, 6 H, CH_2), 2.61 (m, 1 H, CH *i*Pr), 2.19 (s, 3 H, CH_3 *p*-cym), 1.21, 1.19 (d, 6 H, CH_3 *i*Pr), 1.20 (t, 9 H, CH_3 phos); (–70 °C) 7.44 (br. s, H5 HRpz), 7.37 (br. s, H3 HRpz), 6.42 (br. s, H4 HRpz) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 70.1 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, BPh_4), 146.45 (s, C5 HRpz), 131.77 (s, C3 HRpz), 110.3 (d, C1 *p*-cym), 109.29 (s, C4 HRpz), 99.9 (d, C4 *p*-cym), 82.5, 80.35 (d, C2 *p*-cym), 81.40, 80.01 (d, C3 *p*-cym), 63.55 (d, CH_2), 31.03 (s, CH *i*Pr), 22.34, 22.18 (s, CH_3 *i*Pr), 18.57 (s, CH_3 *p*-cym), 16.16 (d, CH_3 phos). Λ_M = 49.7 $\Omega^{-1}mol^{-1}cm^2$. $C_{43}H_{53}BClN_2O_3OsP$ (913.36): calcd. C 56.55, H 5.85, Cl 3.88, N 3.07; found C 56.35, H 5.89, Cl 3.71, N 3.16.

3b: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3279 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 11.71 (br. s, 1 H, NH), 7.33–6.87 (m, 25 H, Ph), 7.21 (t, 1 H, H5 HRpz), 6.17 (t, 1 H, H4 HRpz), 5.59, 5.54, 5.36, 5.33 (d, 4 H, Ph *p*-cym), 4.02, 3.85 (m, 4 H, CH_2), 2.62 (m, 1 H, CH *i*Pr), 2.15 (s, 3 H, CH_3 *p*-cym), 1.36, 1.34 (t, 6 H, CH_3 phos), 1.19, 1.17 (d, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 98.8 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, Ph), 145.90 (s, C5 HRpz), 112.07 (d, C1 *p*-cym), 109.34 (d, C4 *p*-cym), 82.00, 80.33 (d, C2 *p*-cym), 80.95, 78.60 (d, C3 *p*-cym), 64.47, 64.36 (d, CH_2), 31.12 (s, CH *i*Pr), 22.40, 21.98 (s, CH_3 *i*Pr), 18.50 (s, CH_3 *p*-cym), 16.34, 16.14 (d, CH_3 phos). Λ_M = 52.4 $\Omega^{-1}mol^{-1}cm^2$. $C_{47}H_{53}BClN_2O_2OsP$ (945.40): calcd. C 59.71, H 5.65, Cl 3.75, N 2.96; found C 59.88, H 5.77, Cl 3.57, N 2.85.

4b: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3273, 3261 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 11.55, 11.22 (br. s, 1 H, NH), 7.32–6.86 (m, 25 H, Ph), 7.15, 7.06 (br., 1 H, H3 or H5 HRpz), 5.99, 5.91 (t, 1 H, H4 HRpz), 5.63, 5.56, 5.53, 5.37 (d, 4 H, Ph *p*-cym), 4.03, 3.85 (m, 4 H, CH_2), 2.67 (m, 1 H, CH *i*Pr), 2.39, 2.18 (s, 3 H, CH_3 *p*-cym), 2.14, 2.01 (s, 3 H, CH_3 HRpz), 1.38, 1.34 (t, 6 H, CH_3 phos), 1.08 (d, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 99.5, 98.9 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, Ph), 153.16, 141.80 [s, C3(CH_3) and C5(CH_3) HRpz], 146.54, 131.98 (C3 and C5), 116.90, 111.66 (d, C1 *p*-cym), 108.79, 108.73 (s, C4 HRpz), 99.98, 95.58 (d, C4 *p*-cym), 82.10, 79.22 (d, C2 *p*-cym), 80.80, 80.73, 80.13, 78.19 (d, C3 *p*-cym), 64.3 (m, CH_2), 31.40, 31.15 (s, CH *i*Pr), 22.51, 22.02, 20.59 (s, CH_3 *i*Pr), 18.73, 18.53 (s, CH_3 *p*-cym), 16.54, 11.01 (s, 3-CH_3 and 5-CH_3 HRpz), 16.2 (m, CH_3 phos). Λ_M = 51.9 $\Omega^{-1}mol^{-1}cm^2$. $C_{48}H_{55}BClN_2O_2OsP$ (959.43): calcd. C 60.09, H 5.78, Cl 3.70, N 2.92; found C 59.96, H 5.80, Cl 3.53, N 2.83.

5a: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3323 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 11.20 (br. s, 1 H, NH), 7.32–6.88 (m, 20 H, BPh_4), 6.10 (d, 1 H, H4 HRpz), 5.66, 5.62, 5.56, 5.45 (d, 4 H, Ph *p*-cym), 3.88, 3.77 (m, 6 H, CH_2), 2.56 (m, 1 H, CH *i*Pr), 2.34, 2.15 (s, 6 H, CH_3 HRpz), 2.28 (s, 3 H, CH_3 *p*-cym), 1.25, 1.16 (d, 6 H, CH_3 *i*Pr), 1.19 (t, 9 H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 71.39 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, BPh_4), 155.18 (s, C3 HRpz), 143.40 (s, C5 HRpz), 116.37 (d, C1 *p*-cym), 108.29 (s, C4 HRpz), 96.76 (d, C4 *p*-cym), 81.65, 80.17 (d, C2 *p*-cym), 80.87, 79.34 (d, C3 *p*-cym), 63.47 (d, CH_2), 31.09 (s, CH *i*Pr), 22.77, 22.75 (s, CH_3 *i*Pr), 21.10 (s, CH_3 *p*-cym), 16.11 (d, CH_3 phos), 15.83, 11.04 (s, CH_3 HRpz). Λ_M = 53.0 $\Omega^{-1}mol^{-1}cm^2$. $C_{45}H_{57}BClN_2O_3OsP$ (941.41): calcd. C 57.41, H 6.10, Cl 3.77, N 2.98; found C 57.28, H 6.16, Cl 3.59, N 2.95.

[MCl(η⁶-*p*-cymene)(HRpz)(CN*t*Bu)]BPh_4 (6–8) [M = Ru (6), Os (7, 8); R = H (6, 7), 3-Me (8)]: These complexes were prepared in the same way as the related phosphite derivatives **1**–**5** described above using $MCl_2(\eta^6$-*p*-cymene)(CN*t*Bu) as a precursor; yield 104 mg (70%) for **6**, 120 mg (72%) for **7**, 123 mg (73%) for **8**.

6: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3270 (m), $\tilde{\nu}_{CN}$ = 2192 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 11.55 (br. s, 1 H, NH), 7.50 (d, 1 H, H5 HRpz), 7.36–6.88 (m, 20 H, BPh_4), 7.32 (d, 1 H, H3 HRpz), 6.46 (t, 1 H, H4 HRpz), 5.46, 5.39, 5.29, 5.09 (d, 4 H, Ph *p*-cym), 2.63 (m, 1 H, CH *i*Pr), 1.97 (s, 3 H, CH_3 *p*-cym), 1.44 (s, 9 H, CH_3 *t*Bu), 1.25, 1.23 (d, 6 H, CH_3 *i*Pr) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, BPh_4), 145.7 (s, C3 HRpz), 132.9 (s, C5 HRpz), 111.5 (s, C1 *p*-cym), 109.35 (s, C4 HRpz), 109.09 (s, C4 *p*-cym), 89.67, 89.52 (s, C3 *p*-cym), 88.41, 87.94 (s, C2 *p*-cym), 60.1 (s, C *t*Bu), 31.9 (s, CH *i*Pr), 30.4 (s, CH_3 *t*Bu), 22.67, 22.35 (s, CH_3 *i*Pr), 18.9 (s, CH_3 *p*-cym). Λ_M = 54.5 $\Omega^{-1}mol^{-1}cm^2$. $C_{42}H_{47}BClN_3Ru$ (741.18): calcd. C 68.06, H 6.39, Cl 4.78, N 5.67; found C 67.88, H 6.46, Cl 4.66, N 5.54.

7: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3275 (m), $\tilde{\nu}_{CN}$ = 2187 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 11.80 (br. s, 1 H, NH), 7.50 (d, 1 H, H5 HRpz), 7.41 (br., 1 H, H3 HRpz), 7.35–6.86 (m, 20 H, BPh_4), 6.43 (t, 1 H, H4 HRpz), 5.62, 5.57, 5.43, 5.28 (d, 4 H, Ph *p*-cym), 2.61 (m, 1 H, CH *i*Pr), 2.07 (s, 3 H, CH_3 *p*-cym), 1.44 (s, 9 H, CH_3 *t*Bu), 1.24, 1.23 (d, 6 H, CH_3 *i*Pr) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, BPh_4), 145.93 (s, C3 HRpz), 132.10 (s, C5 HRpz), 109.52 (s, C4 HRpz), 104.32 (s, C1 *p*-cym), 103.29 (s, C4 *p*-cym), 82.15, 81.60 (s, C2 *p*-cym), 80.44, 80.41 (s, C3 *p*-cym), 59.78 (s, C *t*Bu), 31.89 (s, CH *i*Pr), 30.80 (s, CH_3 *t*Bu), 22.94, 22.48 (s, CH_3 *i*Pr), 18.63 (s, CH_3 *p*-cym) ppm. Λ_M = 52.7 $\Omega^{-1}mol^{-1}cm^2$. $C_{42}H_{47}BClN_3Os$ (830.34): calcd. C 60.75, H 5.71, Cl 4.27, N 5.06; found C 60.54, H 5.62, Cl 4.15, N 4.91.

8: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3334 (m), $\tilde{\nu}_{CN}$ = 2174 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 11.50 (br. s, 1 H, NH), 7.34–6.86 (m, 20 H, BPh_4), 7.27 (d, 1 H, H5 HRpz), 6.20 (d, 1 H, H4 HRpz), 5.63,

5.55, 5.45, 5.30 (d, 4 H, Ph *p*-cym), 2.61 (m, 1 H, CH *i*Pr), 2.36 (s, 3 H, CH_3 HRpz), 2.08 (s, 3 H, CH_3 *p*-cym), 1.44 (s, 9 H, CH_3 *t*Bu), 1.24 (d, 6 H, CH_3 *i*Pr) ppm. Λ_M = 51.2 $\Omega^{-1}mol^{-1}cm^2$. $C_{43}H_{49}BClN_3Os$ (844.36): calcd. C 61.17, H 5.85, Cl 4.20, N 4.98; found C 61.35, H 5.72, Cl 4.08, N 4.87.

[MCl(η⁶-*p*-cymene)(HIm)L]BPh₄ (9–10) [M = Ru (9), Os (10); L = P(OEt)₃ (a), PPh(OEt)₂ (b)]: These complexes were prepared according to the method used for **1**–**5** described above using HIm as a reagent; yield 128 mg (78%) for **9a**, 137 mg (80%) for **9b**, 140 mg (76%) for **10a**, 145 mg (77%) for **10b**.

9a: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3312 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 8.25 (br. s, 1 H, NH), 7.42–6.89 (m, 20 H, BPh_4), 6.38, 6.30, 6.18 (d, 3 H, CH HIm), 5.33, 5.13 (m, 4 H, Ph *p*-cym), 3.70 (m, 6 H, CH_2), 2.62 (m, 1 H, CH *i*Pr), 2.06 (s, 3 H, CH_3 *p*-cym), 1.19, 1.18 (t, 9 H, CH_3 phos), 0.98 (d, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 163.1 (s) ppm. Λ_M = 52.0 $\Omega^{-1}mol^{-1}cm^2$. $C_{43}H_{53}BClN_2O_3PRu$ (824.20): calcd. C 62.66, H 6.48, Cl 4.30, N 3.40; found C 62.47, H 6.56, Cl 4.19, N 3.26.

9b: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3322 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 8.13 (br. s, 1 H, NH), 7.39–6.89 (m, 25 H, Ph), 6.31 (d), 6.22 (s), 6.13 (d, 3 H, CH HIm), 5.21, 5.12 (d, 4 H, Ph *p*-cym), 3.80 (m, 4 H, CH_2), 2.52 (m, 1 H, CH *i*Pr), 2.00 (s, 3 H, CH_3 *p*-cym), 1.28 (t, 6 H, CH_3 phos), 0.90 (d, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 143.5 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–123 (m, BPh_4), 140.3, 131.3, 119.6 (s, CH HIm), 117.7 (d, C1 *p*-cym), 107.1 (d, C4 *p*-cym), 92.8 (d, C3 *p*-cym), 90.3 (d, C2 *p*-cym), 66.6 (d, CH_2), 31.2 (s, CH *i*Pr), 22.2, 22.0 (s, CH_3 *i*Pr), 18.1 (s, CH_3 *p*-cym), 16.4 (d, CH_3 phos) ppm. Λ_M = 53.8 $\Omega^{-1}mol^{-1}cm^2$. $C_{47}H_{53}BClN_2O_2PRu$ (856.24): calcd. C 65.93, H 6.24, Cl 4.14, N 3.27; found C 65.77, H 6.36, Cl 3.97, N 3.14.

10a: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3336 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 8.14 (br. s, 1 H, NH), 7.40–6.88 (m, 20 H, BPh_4), 7.16, 6.33 (s, 3 H, CH HIm), 5.52, 5.42, 5.28 (d, 4 H, Ph *p*-cym), 3.84, 3.73 (m, 6 H, CH_2), 2.55 (m, 1 H, CH *i*Pr), 2.16 (s, 3 H, CH_3 *p*-cym), 1.19 (d, 6 H, CH_3 *i*Pr), 1.18 (t, 9 H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, –60 °C): δ = 75.9 (s) ppm. Λ_M = 50.3 $\Omega^{-1}mol^{-1}cm^2$. $C_{43}H_{53}BClN_2O_3OsP$ (913.36): calcd. C 56.55, H 5.85, Cl 3.88, N 3.07; found C 56.74, H 5.69, Cl 3.75, N 2.96.

10b: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3321 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 8.00 (br. s, 1 H, NH), 7.40–6.91 (m, 25 H, Ph), 7.10, 6.73, 6.11 (s, 3 H, CH HIm), 5.54, 5.52, 5.37, 5.28 (d, 4 H, Ph *p*-cym), 4.05, 3.88, 3.70 (m, 4 H, CH_2), 2.53 (m, 1 H, CH *i*Pr), 2.16 (s, 3 H, CH_3 *p*-cym), 1.36, 1.30 (t, 6 H, CH_3 phos), 1.16, 1.14 (d, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 98.8 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, BPh_4), 138.88, 130.45, 117.90 (s, CH HIm), 110.50 (d, C1 *p*-cym), 97.70 (d, C4 *p*-cym), 81.60, 81.34 (d, C2 *p*-cym), 81.00, 78.40 (d, C3 *p*-cym), 64.35, 64.10 (d, CH_2), 30.85 (s, CH *i*Pr), 22.21, 22.15 (s, CH_3 *i*Pr), 18.36 (s, CH_3 *p*-cym), 16.24 (d, CH_3 phos) ppm. Λ_M = 55.4 $\Omega^{-1}mol^{-1}cm^2$. $C_{47}H_{53}BClN_2O_2OsP$ (945.40): calcd. C 59.71, H 5.65, Cl 3.75, N 2.96; found C 59.53, H 5.55, Cl 3.61, N 2.90.

[M(Rpz)(η⁶-*p*-cymene)(HRpz)L]BPh₄ (11–13) [M = Ru (11), Os (12, 13); R = H (11, 12), 3-Me (13); L = P(OEt)₃ (a), PPh(OEt)₂ (b)]: In a 25-mL three-necked round-bottomed flask were placed $MCl_2(\eta^6$-*p*-cymene)L (0.2 mmol), an excess of HRpz (0.9 mmol), an excess of $NaBPh_4$ (0.36 mmol, 0.12 g), ethanol (4 mL) and dichloromethane (8 mL). An excess of triethylamine (1.8 mmol, 0.25 mL) was added to the resulting solution, which was stirred at room temperature for 24 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (3 mL). A yellow solid slowly separated, which was collected by filtration and recrystallised from CH_2Cl_2 and ethanol; yield 115 mg (67%) for **11a**, 118 mg (66%) for **11b**, 124 mg (65%) for **12a**, 133 mg (68%) for **12b**, 135 mg (67%) for **13b**.

11a: ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.77 (d, 2 H, H5 HRpz/pz), 7.34 (d, 2 H, H3 HRpz/pz), 7.34–6.89 (m, 20 H, BPh_4), 6.39 (t, 2 H, H4 HRpz/pz), 5.47, 5.44 (d, 4 H, Ph *p*-cym), 3.55 (qnt, 6 H, CH_2), 2.22 (m, 1 H, CH *i*Pr), 2.01 (s, 3 H, CH_3 *p*-cym), 1.12 (t, 9 H, CH_3 phos), 1.08 (d, 6 H, CH_3 *i*Pr); [$(CD_3)_2CO$, –70 °C]: δ = 18.15 (s, 1 H, NH) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 115.8 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–121 (m, BPh_4), 145.7 (s, C3 HRpz/pz), 135.8 (s, C5 HRpz/pz), 107.7 (s, C4 HRpz/pz), 120.4 (d, C1 *p*-cym), 107.2 (d, C4 *p*-cym), 92.0 (d, C2 *p*-cym), 90.7 (d, C3 *p*-cym), 66.9 (d, CH_2), 31.4 (s, CH *i*Pr), 22.1 (s, CH_3 *i*Pr), 18.7 (s, CH_3 *p*-cym), 16.2 (d, CH_3 phos) ppm. Λ_M = 51.9 $\Omega^{-1}mol^{-1}cm^2$. $C_{46}H_{56}BN_4O_3PRu$ (855.82): calcd. C 64.56, H 6.60, N 6.55; found C 64.72, H 6.48, N 6.42.

11b: ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.38–6.53 (m, 25 H, Ph), 7.52 (d, 2 H, H5 HRpz/pz), 7.34 (d, 2 H, H3 HRpz/pz), 6.37 (t, 2 H, H4 HRpz/pz), 5.48, 5.42 (d, 4 H, Ph *p*-cym), 3.79 (m, 4 H, CH_2), 2.17 (m, 1 H, CH *i*Pr), 2.05 (s, 3 H, CH_3 *p*-cym), 1.31 (t, 6 H, CH_3 phos), 0.99 (d, 6 H, CH_3 *i*Pr); [$(CD_3)_2CO$, –70 °C]: δ = 18.38 (s, 1 H, NH), 7.63 (d, 2 H, H5 HRpz/pz), 7.54 (br. s, 2 H, H3 HRpz/pz), 7.30–6.75 (m, 25 H, Ph), 6.43 (m, 2 H, H4 HRpz/pz), 6.35, 6.06 (d, 4 H, Ph *p*-cym), 4.15 (m, 4 H, CH_2), 3.53 (m, 1 H, CH *i*Pr), 2.37 (s, 3 H, CH_3 *p*-cym), 1.38, 1.28 (t, 6 H, CH_3 phos), 0.92 (d, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 144.4 (s); [$(CD_3)_2CO$, –70 °C]: δ = 144.1 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–121 (m, BPh_4), 145.1 (s, C3 HRpz/pz), 132.1 (s, C5 HRpz/pz), 121.2 (s, C1 *p*-cym), 107.9 (s, C4 HRpz/pz), 105.9 (s, C4 *p*-cym), 92.4 (d, C2 *p*-cym), 89.8 (d, C3 *p*-cym), 66.1 (d, CH_2), 31.5 (s, CH *i*Pr), 22.0 (s, CH_3 *i*Pr), 18.6 (s, CH_3 *p*-cym), 16.5 (d, CH_3 phos). Λ_M = 52.5 $\Omega^{-1}mol^{-1}cm^2$. $C_{50}H_{56}BN_4O_2PRu$ (887.86): calcd. C 67.64, H 6.36, N 6.31; found C 67.75, H 6.47, N 6.18.

12a: ^1H NMR (CD_2Cl_2, –70 °C): δ = 18.84 (br. s, 1 H, NH), 7.64 (d, 2 H, H5 HRpz/pz), 7.43 (d, 2 H, H3 HRpz/pz), 7.43–6.86 (m, 20 H, BPh_4), 6.33 (t, 2 H, H4 HRpz/pz), 5.51, 5.47 (d, 4 H, Ph *p*-cym), 3.55 (q, 6 H, CH_2), 2.23 (m, 1 H, CH *i*Pr), 2.08 (s, 3 H, CH_3 *p*-cym), 1.11 (t, 9 H, CH_3 phos), 1.10 (d, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, –70 °C): δ = 71.23 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, BPh_4), 145.80 (s, C3 HRpz/pz), 134.96 (s, C5 HRpz/pz), 107.35 (s, C4 HRpz/pz), 112.8 (s, C1 *p*-cym), 101.1 (s, C4 *p*-cym), 83.34 (d, C2 *p*-cym), 82.33 (d, C3 *p*-cym), 63.40 (d, CH_2), 31.16 (s, CH *i*Pr), 22.21 (s, CH_3 *i*Pr), 18.42 (s, CH_3 *p*-cym), 16.12 (d, CH_3 phos) ppm. Λ_M = 53.9 $\Omega^{-1}mol^{-1}cm^2$. $C_{46}H_{56}BN_4O_3OsP$ (944.98): calcd. C 58.47, H 5.97, N 5.93; found C 58.30, H 5.84, N 5.78.

12b: ^1H NMR (CD_2Cl_2, –70 °C): δ = 18.74 (br. s, 1 H, NH), 7.44 (d, 2 H, H5 HRpz/pz), 7.41 (d, 2 H, H3 HRpz/pz), 7.40–6.89 (m, 25 H, Ph), 6.30 (t, 2 H, H4 HRpz/pz), 5.53, 5.46 (d, 4 H, Ph *p*-cym), 3.73 (m, 4 H, CH_2), 2.18 (m, 1 H, CH *i*Pr), 2.13 (s, 3 H, CH_3 *p*-cym), 1.28 (t, 6 H, CH_3 phos), 1.00 (d, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, –70 °C): δ = 96.4 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, BPh_4), 145.30 (s, C3 HRpz/pz), 134.50 (s, C5 HRpz/pz), 107.55 (s, C4 HRpz/pz), 113.70 (s, C1 *p*-cym), 98.50 (s, C4 *p*-cym), 83.64 (d, C2 *p*-cym), 81.23 (d, C3 *p*-cym), 65.42 (d, CH_2), 31.23 (s, CH *i*Pr), 22.11 (s, CH_3 *i*Pr), 18.40 (s, CH_3 *p*-cym), 16.40 (d, CH_3 phos) ppm. Λ_M = 52.1 $\Omega^{-1}mol^{-1}cm^2$. $C_{50}H_{56}BN_4O_2OsP$ (977.02): calcd. C 61.47, H 5.78, N 5.73; found C 61.63, H 5.59, N 5.65.

13b: ^1H NMR (CD_2Cl_2, –70 °C): δ = 19.14 (br. s, 1 H, NH), 7.33–6.86 (m, 25 H, Ph), 7.24 (d, 2 H, H5 HRpz/pz), 6.02 (d, 2 H, H4

HRpz/pz), 5.53, 5.47 (d, 4 H, Ph *p*-cym), 3.81 (m, 4 H, CH_2), 2.27 (m, 1 H, CH *i*Pr), 2.21 (s, 6 H, CH_3 HRpz/pz), 2.18 (s, 3 H, CH_3 *p*-cym), 1.30 (t, 6 H, CH_3 phos), 1.03 (d, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, –70 °C): δ = 96.5 (s) ppm. Λ_M = 51.9 $\Omega^{-1}mol^{-1}cm^2$. $C_{52}H_{60}BN_4O_2OsP$ (1005.07): calcd. C 62.14, H 6.02, N 5.57; found C 62.01, H 6.18, N 5.46.

[Os(Rpz)(η⁶-*p*-cymene)(HRpz)(CN*t*Bu)]BPh₄ (14): Complex **14** was prepared in the same way as **11**–**13** using $OsCl_2(\eta^6$-*p*-cymene)(CN*t*Bu) as a precursor; yield 118 mg (65%). IR (KBr pellet): $\tilde{\nu}_{CN}$ = 2170 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, –70 °C): δ = 15.79 (s, 1 H, NH), 7.60 (d, 2 H, H5 HRpz/pz), 7.38–6.86 (m, 20 H, BPh_4), 7.35 (d, 2 H, H3 HRpz/pz), 6.31 (t, 2 H, H4 HRpz/pz), 5.58, 5.41 (d, 4 H, Ph *p*-cym), 2.45 (m, 1 H, CH *i*Pr), 1.89 (s, 3 H, CH_3 *p*-cym), 1.45 (s, 9 H, CH_3 *t*Bu), 1.22 (d, 6 H, CH_3 *i*Pr) ppm. Λ_M = 54.6 $\Omega^{-1}mol^{-1}cm^2$. $C_{45}H_{50}BN_5Os$ (861.95): calcd. C 62.70, H 5.85, N 8.12; found C 62.57, H 5.80, N 8.01.

[RuCl(η⁶-*p*-cymene)(HRpz)₂]BPh₄ (15, 16) [R = H (15), 3-Me (16)]: In a 25 mL three-necked round-bottomed flask were placed $RuCl_2(CO)(\eta^6$-*p*-cymene) (0.10 g, 0.3 mmol), an excess of the appropriate HRpz (0.9 mmol), an excess of $NaBPh_4$ (0.6 mmol, 0.205 g), ethanol (3 mL) and dichloromethane (5 mL). The resulting solution was stirred for 20 h and then the solvent was removed under reduced pressure. The oil obtained was triturated with ethanol (2 mL) until a yellow solid separated, which was collected by filtration and crystallised from dichloromethane and ethanol; yield 164 mg (71%) for **15**, 164 mg (70%) for **16**.

15: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3334, 3306 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 11.08 (br., 2 H, NH), 7.52 (d, 2 H, H5 HRpz), 7.40–6.88 (m, 20 H, BPh_4), 7.38 (d, 2 H, H3 HRpz), 6.42 (t, 2 H, H4 HRpz), 5.50, 5.19 (d, 4 H, Ph *p*-cym), 2.44 (m, 1 H, CH *i*Pr), 1.69 (s, 3 H, CH_3 *p*-cym), 1.10 (d, 6 H, CH_3 *i*Pr) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, BPh_4), 144.09 (s, C5 HRpz), 131.84 (s, C3HRpz), 109.12 (s, C4 HRpz), 104.43 (s, C1 *p*-cym), 101.74 (s, C4 *p*-cym), 85.98 (d, C2 *p*-cym), 82.11 (d, C3 *p*-cym), 31.25 (s, CH *i*Pr), 22.22 (s, CH_3 *i*Pr), 18.35 (s, CH_3 *p*-cym) ppm. Λ_M = 50.5 $\Omega^{-1}mol^{-1}cm^2$. $C_{40}H_{42}BClN_4Ru$ (726.12): calcd. C 66.16, H 5.83, Cl 4.88, N 7.72; found C 66.01, H 5.69, Cl 4.76, N 7.61.

16: IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3350, 3261 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 10.53 (br. s, 2 H, NH), 7.31–6.86 (m, 20 H, BPh_4), 5.97 (s, 2 H, H4 HRpz), 5.94, 5.30 (d, 4 H, Ph *p*-cym), 2.71 (m, 1 H, CH *i*Pr), 2.17, 2.13 (s, 12 H, CH_3 HRpz), 1.57 (s, 3 H, CH_3 *p*-cym), 1.14 (d, 6 H, CH_3 *i*Pr) ppm. Λ_M = 53.3 $\Omega^{-1}mol^{-1}cm^2$. $C_{44}H_{50}BClN_4Ru$ (782.23): calcd. C 67.56, H 6.44, Cl 4.53, N 7.16; found C 67.69, H 6.52, Cl 4.38, N 7.10.

[RuCl(η⁶-*p*-cymene)(HIm)₂]BPh₄ (17): This complex was prepared following the method described above for **15** and **16** using HIm as a reagent; yield 155 mg (67%). IR (KBr pellet): $\tilde{\nu}_{NH}$ = 3304 (m, br) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 8.92 (br. s, 2 H, NH), 7.34–6.88 (m, 20 H, BPh_4), 7.08, 6.91, 6.68 (d, 6 H, CH HIm), 5.52, 5.23 (d, 4 H, Ph *p*-cym), 2.56 (m, 1 H, CH *i*Pr), 1.78 (s, 3 H, CH_3 *p*-cym), 1.14 (d, 6 H, CH_3 *i*Pr) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, Ph), 138.39, 130.10, 118.15 (s, CH HIm),

Table 3. Crystal data and structure refinement.

	1b	**11a**	**15**
Empirical formula	$C_{94}H_{106}B_2Cl_2N_4O_4P_2Ru_2$	$C_{46}H_{56}BN_4O_3PRu$	$C_{40}H_{42}BClN_4Ru$
Formula weight	1712.43	855.80	726.11
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	monoclinic	orthorhombic	triclinic
Space group	*Pc*	$P2_12_12_1$	$P\bar{1}$
Unit cell dimensions	*a* = 13.3727(16) Å	*a* = 10.840(2) Å	*a* = 9.9659(13) Å
	b = 9.4736(12) Å	*b* = 20.077(4) Å	*b* = 12.3667(17) Å
	c = 35.117(4) Å	*c* = 20.383(5) Å	*c* = 16.080(2) Å
	α = 90°	*α* = 90°	*α* = 104.137(2)°
	β = 102.330(4)°	*β* = 90°	*β* = 95.495(2)°
	γ = 90°	*γ* = 90°	*γ* = 106.743(3)°
Volume	4346.3(9) Å^3	4436.4(17) Å^3	1810.6(4) Å^3
Z	2	4	2
Density (calculated)	1.309 Mg/m^3	1.281 Mg/m^3	1.332 Mg/m^3
Absorption coefficient	0.498 mm^{-1}	0.432 mm^{-1}	0.540 mm^{-1}
F(000)	1784	1792	752
Crystal size	0.32 × 0.26 × 0.21 mm	0.37 × 0.15 × 0.12 mm	0.34 × 0.17 × 0.10 mm
Theta range for data collection	1.56 to 25.05°.	1.42 to 25.05°.	1.33 to 25.04°.
Index ranges	$-14 \le h \le 15$	$-9 \le h \le 12$	$-11 \le h \le 11$
	$-11 \le k \le 11$	$-23 \le k \le 23$	$-14 \le k \le 14$
	$-41 \le l \le 37$	$-24 \le l \le 23$	$-19 \le l \le 19$
Reflections collected	22119	19736	13641
Independent reflections	12129 [*R*(int) = 0.0895]	7235 [*R*(int) = 0.1121]	6313 [*R*(int) = 0.0475]
Reflections observed (> 2σ)	6457	4023	4356
Data completeness	0.994	0.968	0.987
Absorption correction		semiempirical from equivalents	
Max. and min. transmission	1.000 and 0.712	1.0000 and 0.6393	1.000 and 0.928
Refinement method		full-matrix least-squares on F^2	
Data/restraints/parameters	12129/2/1001	7235/0/511	6313/0/435
Goodness-of-fit on F^2	1.013	0.878	1.057
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0615 wR_2 = 0.1175	R_1 = 0.0580 wR_2 = 0.1078	R_1 = 0.0435 wR_2 = 0.0956
R indices (all data)	R_1 = 0.1534 wR_2 = 0.1552	R_1 = 0.1156 wR_2 = 0.1261	R_1 = 0.0801 wR_2 = 0.1114
Absolute structure parameter	0.02(4)	–0.08(5)	
Largest diff. peak and hole	0.524 and –0.799 e Å^{-3}	0.359 and –0.519 e Å^{-3}	0.546 and –0.365 e Å^{-3}

103.53 (s, C1 *p*-cym), 100.28 (s, C4 *p*-cym), 86.26 (s, C2 *p*-cym), 81.68 (s, C3 *p*-cym), 31.19 (s, CH *i*Pr), 22.36 (s, CH_3 *i*Pr), 18.28 (s, CH_3 *p*-cym) ppm. Λ_M = 52.6 Ω^{-1} mol^{-1} cm^2. $C_{40}H_{42}BClN_4Ru$ (726.12): calcd. C 66.16, H 5.83, Cl 4.88, N 7.72; found C 66.03, H 5.75, Cl 4.75, N 7.59.

X-ray Crystallography: Crystallographic data were collected with a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) and were corrected for Lorentz and polarisation effects. SMART software[29] was used for collection of data frames, indexing of reflections and determination of lattice parameters, SAINT[30] for integration of intensity of reflections and scaling, and SADABS[31] for empirical absorption correction. In the case of **1b**, study of the systematic absence prompted us to examine the noncentrosymmetric *Pc* space group and the related centrosymmetric *P*2/*c* space group. The *Pc* space group was finally used as well as two whole unit formulae in the asymmetric unit, due to small differences in the two molecules, and all attempts to find any symmetry relation to merge the two molecules was unsuccessful. For orthorhombic **11a** and triclinic **15**, the $P\bar{1}$ or $P2_12_12_1$ space groups were chosen, respectively. Structures were solved and refined with the Oscail program[32] by direct methods (**1b** and **11a**) or by Patterson methods (**15**) and refined by a full-matrix least-squares method based on F^2.[33] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters but, in the case of **15**, hydrogen atoms on the NH groups were found in the electron density map and refined with isotropic displacement parameters. In the case of **11a**, the presence of a HRpz ligand and a pz ligand in the coordination sphere made it difficult to decide which was the anionic and which the neutral ligand, because C–C or C–N bond parameters did not differ sufficiently to allow a decision to be taken. However, refinement of the occupancy factor of the two hypothesised positions provided an answer, and the hydrogen atom labelled as H(2N) was refined with isotropic displacement parameters. Details of crystal data and structural refinement are given in Table 3.

CCDC-785127 (for **1b**), -785128 (for **11a**), -785129 (for **15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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