DOI: 10.1002/ejic.200700672

Synthesis, Reactivity, X-ray Crystal Structures and Electrochemical Behaviour of Water-Soluble [Tris(pyrazolyl)borato]ruthenium(II) Complexes of 1,3,5-Triaza-7-phosphaadamantane (PTA)

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Keywords: Electrochemistry / Water-soluble complexes / Pyrazolylborates / Ruthenium / N ligands

A series of chloridoruthenium(II) complexes bearing the tripodal ligand tris(pyrazolyl)borate (Tp), the water-soluble cage phosphane 1,3,5-triaza-7-phosphaadamantane (PTA) and its *N*-boranyl adduct PTA(BH_3), together with PPh_3, have been synthesised. The corresponding monohydrido complexes have also been obtained by treating the chlorides with NaOMe. The X-ray crystal structures of [TpRuCl(PTA)(PPh_3)] (**2**) and [TpRuCl$(PTA)_2$] (**3**) are also described. Cyclic voltammetry (CV) studies in MeCN and dmso generally show reversible $Ru^{II/III}$ oxidation waves and the values of $E_{1/2}^{ox}$ reflect the electron-donating character of the ligands [Tp (each arm) > PTA > PTA(BH_3)], whose Lever electrochemical parameter (E_L) has been estimated for the first time.

Introduction

Whereas the chemistry of (cyclopentadienido)- and (pentamethylcyclopentadienido)ruthenium derivatives has been covered in the literature both broadly and in more detail,[1] less attention has been devoted to the corresponding hydrotris(pyrazolyl)borate (Tp) complexes, which have thus received increasing attention in recent years.[2] TpRu complexes containing a variety of co-ligands, particularly N-donors such as diamines, MeCN, pyridine, cycloocta-1,5-diene (cod) and hemilabile phosphanylamine ligands, were first reported about a decade ago,[3,4] the main interest residing in the application of such compounds as active catalysts for the dimerisation of terminal acetylenes or the coupling of phenylacetylene with benzoic acid or allyl alcohols.[4a,5] Tertiary phosphanes have also been used as co-ligands,[6] and complexes such as [TpRuX$(PPh_3)_2$] (X = Cl or H)[6a,6e,6h] and [TpRu(MeCN)$(PPh_3)_2$]BF_4[6e] have been shown to be quite efficient catalyst precursors for such reactions.[5,6e,7] Recent intriguing applications of TpRu complexes have been reported by Gunnoe and co-workers and include the use of [TpRuX$(PMe_3)_2$] (X = non-dative heteroatomic ligands such as OH, OMe, OPh or NHPh) for the catalytic H/D exchange between water and deuterated arenes,[8] and the spectacular catalytic hydroarylation of α-alkenes promoted by [TpRuPh(CO)(MeCN)] to give alkylarenes with good preference for the linear isomers over the branched ones.[9] Extension of this hydroarylation protocol to multiple C–X (X = O, S) bonds has also been demonstrated.[10] The hydration of nitriles to amides catalysed by the hydride [TpRuH(PPh_3)(MeCN)] has also been reported and is considered to be assisted by formation of an Ru–H···H–OH dihydrogen-bonding interaction in the transition state, which lowers the reaction barrier for the hydration step.[11]

The coordination properties of the Tp anion and substituted derivatives have been described in detail by Trofimenko, who has discussed their analogies and differences with cyclopentadienido ligands.[2,12] A good example of this is the comparison between [TpRuCl$(PPh_3)_2$] and [CpRuCl$(PPh_3)_2$],[13] where the higher reactivity of the former towards ligand substitution has been ascribed to both the higher nucleophilicity imparted to the metal atom by Tp, which labilises the Ru–Cl bond, and the higher steric constraint caused by the bulkier tris(pyrazolyl) framework. Another aspect of this class of tripodal ligands, which is recognized as being beneficial in their catalytic application, is their hemilability and the consequent easy change of hapticity from κ^3- to κ^2-coordination.[14]

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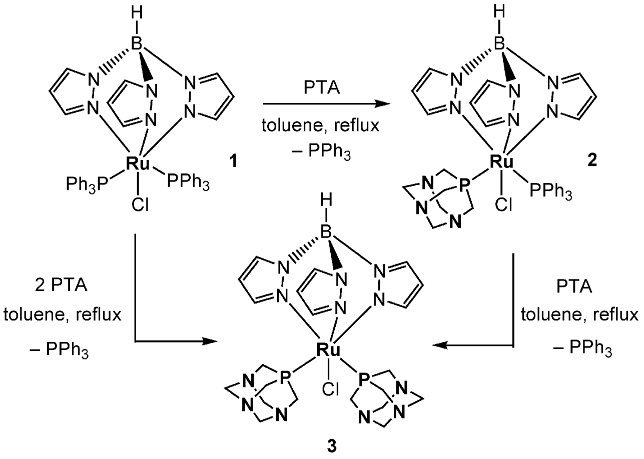
We have been interested for some years in the organometallic reactivity and application in catalysis of water-soluble phosphanes such as 1,3,5-triaza-7-phosphaadamantane (PTA),[15] and we recently communicated the synthesis of its *N*-BH_3 adduct [PTA(BH_3)].[16] To the best of our knowledge, no examples of TpRu complexes bearing monodentate water-soluble phosphanes are known in the literature.[17] Herein we describe the synthesis of a series of novel $TpRu^{II}$ chlorido and hydrido complexes bearing various combinations of PTA, PTA(BH_3) and PPh_3 as ancillary ligands, together with the X-ray crystal structure determinations of selected complexes. The cyclic voltammetric behaviour of the TpRu complexes is also reported as it provides interesting information on the donor abilities of the ligands.

Results and Discussion

Synthesis and Characterisation of TpRu Complexes with PTA and PTA(BH_3)

The novel [tris(pyrazolyl)borato]ruthenium(II) complexes [TpRuCl(PTA)(PPh_3)] (**2**) and [TpRuCl$(PTA)_2$] (**3**) were prepared in good yields by treating [TpRuCl$(PPh_3)_2$] with PTA in refluxing toluene in the molar ratio 1:1 or 1:2, respectively. Alternatively, compound **3** can be synthesised by treating **2** with PTA in refluxing toluene (Scheme 1).

A similar reaction with the *N*-boranyl adduct of PTA [PTA(BH_3)] gives the complexes [TpRuCl(PPh_3){PTA(BH_3)}] (**4**) and [TpRuCl{PTA$(BH_3)_2$}] (**5**). Alternatively, the TpRu complexes **4** and **5**, which contain the boronated PTA ligand, may be prepared in a straightforward manner by direct boronation of **2** and **3** in thf with excess BH_3·thf at room temperature. Whereas the reaction proceeds smoothly for **2** in a 1:1 ratio to give compound **4** in good yield, an excess of BH_3·thf has to be added to **3** in order to obtain **5** (Scheme 2) as the only product of the reaction (see below).

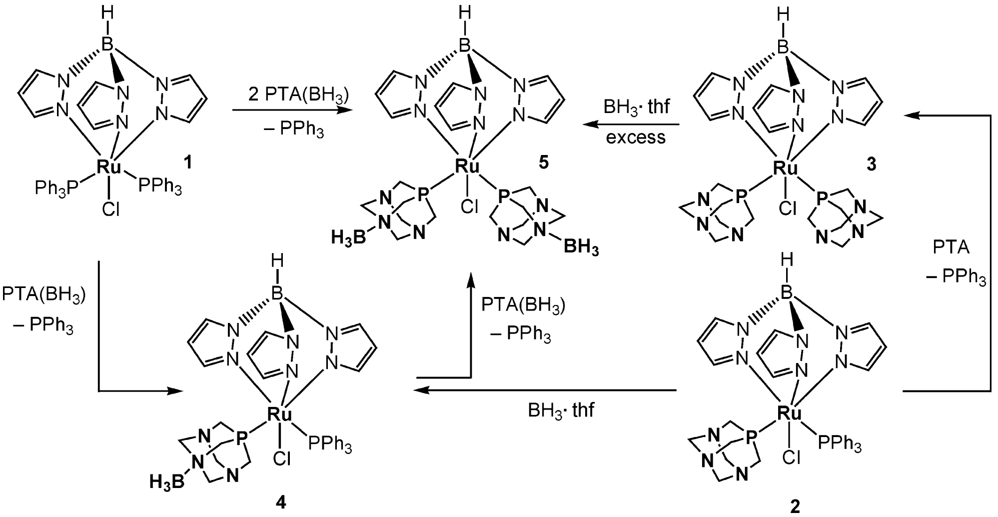


Scheme 1.

Whilst monitoring the reaction of **3** with increasing amounts of BH_3·thf by $^{31}P\{^1H\}$ NMR spectroscopy, we observed, in addition to the signals corresponding to complex **5**, the appearance of two new doublets (δ = –18.4 and –29.6 ppm, $^2J_{P,P}$ = 35.7 Hz), which progressively disappear as the singlet due to **5** increases in intensity. Although we did not attempt to isolate the complex first formed from **3**, the two doublets may be reasonably attributed to the formation of the intermediate mixed species [TpRuCl(PTA){PTA(BH_3)}] (**5′**).

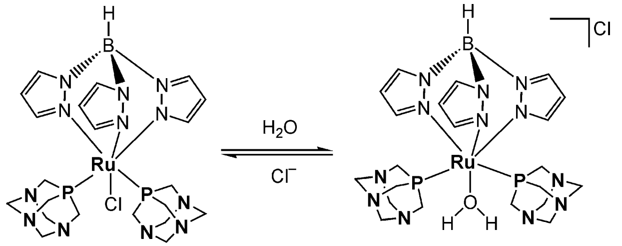
Monitoring of the reaction between **2** (or **3**) and excess BH_3·thf by $^{31}P\{^1H\}$ NMR spectroscopy in situ does not provide evidence for the formation of boronated species other than **5**. The absence of NMR signals ascribable to ruthenium complexes containing polyboronated ligands [PTA$(BH_3)_x$, x = 2, 3][16a] raises the question as to whether the *N*,*N*-diboronated PTA skeleton may still represent a valid P-type ligand for metal coordination.

Good analytical data were obtained for all complexes **2**–**5**, which were isolated as fairly air-stable yellow solids. Their solubility in common solvents depends strongly on



Scheme 2.

the nature of the phosphanes contained in the complexes. Thus, **2** is soluble in most common polar organic solvents but only slightly soluble in water ($S_{25°C}$ = 2.1 mg mL^{-1}), whereas replacement of the second PPh_3 ligand by PTA makes **3** water-soluble ($S_{25°C}$ = 18 mg mL^{-1}). Solutions of **3** in D_2O are stable at room temperature for several days, as indicated by the corresponding $^{31}P\{^1H\}$ NMR spectrum, which displays a singlet at δ = –26.1 ppm that remains unchanged. A new, slightly deshielded singlet slowly appears at δ = –24.0 ppm upon heating to 60 °C, and these two signals reach comparable intensities at this temperature after 6 d. This new signal may be safely attributed to aquation of the chlorido derivative to give the cationic aquo complex $[TpRu(H_2O)(PTA)_2]Cl$ (**3′**) (Scheme 3). Ligand substitution in related Ru(PTA) complexes, such as the antitumour compounds $[(\eta^6\text{-arene})RuCl_2(PTA)]$[18] and the corresponding Cp analogue, $[CpRuCl(PTA)(PPh_3)]$,[19] has also been reported. Quantitative formation of the same aquo cation takes place at 60 °C upon mixing D_2O solutions of $TlPF_6$ and **3** (NMR-tube experiment). No attempt was made to isolate the aquo complex in the solid state.



Scheme 3.

Boronation of PTA decreases the solubility of the complexes, making **4** sparingly soluble in halogenated solvents and acetone and insoluble in water. Complex **5**, which bears two boronated $PTA(BH_3)$ ligands, is practically insoluble in common organic solvents except dmso.

All complexes were fully characterised by elemental analysis and conventional spectroscopic techniques (IR and NMR) and, in the case of compounds **2** and **3**, crystals suitable for an X-ray analysis were obtained (see below). The IR spectra of compounds **2**–**5** show the characteristic ν_{BH} band of the Tp ligand at 2475–2508 cm^{-1}. Complexes **4** and **5** also exhibit three absorptions between 2267 and 2376 cm^{-1} due to the stretching modes of the *N*-coordinated borane (BH_3) unit. The ^1H NMR spectra of compounds **2**–**5** confirm the presence of the Tp ligand, showing the characteristic signals of the pyrazolyl protons in the range δ = 5.68–8.17 ppm. As expected, the complexity of the Tp signal depends on the degree of symmetry of the molecule due to homo- or heterophosphane substitution, and the same trend was observed in the ^{13}C NMR spectra, which were fully assigned (see Experimental Section) with the help of $^1H,^{13}C$-HSQC and DEPT-135 NMR experiments.

The $^{31}P\{^1H\}$ NMR spectrum of **2** shows two doublets at δ = –34.2 and 46.9 ppm ($^2J_{P,P}$ = 33.1 Hz) corresponding to the phosphorus resonances of PTA and PPh_3, respectively. Compound **3** presents a singlet at δ = –28 ppm corresponding to the P nuclei of both PTA ligands. Compounds **4** and **5** give a similar pattern, with two doublets at δ = –25.3 and 44.0 ppm ($^2J_{P,P}$ = 32.6 Hz) for compound **4** and a singlet at δ = –19.5 ppm for compound **5**, which is shifted downfield due to the influence of the BH_3 group. The presence of an N_{PTA}-coordinated borane unit is further confirmed by broad signals in the ^1H NMR spectra between δ = 0.74 and 1.54 ppm that integrate for three (**4**) or six protons (**5**), respectively.

Single-Crystal X-ray Structure Determination for Complexes 2 and 3

Suitable crystals of **2** and **3** were grown from dilute toluene solutions. Selected bond lengths and angles are summarised in Table 1, while thermal ellipsoid representations of the solid-state structures of one of the molecules in the asymmetric unit of $[TpRuCl(PTA)(PPh_3)]$ (**2**) and $[TpRuCl(PTA)_2]$ (**3**), along with the atomic numbering schemes, are depicted in Figures 1 and 2, respectively.

Table 1. Selected bond lengths [Å] and angles [°] for **2** and **3**.[a]

3		**2**		
			Molecule 1	Molecule 2
Ru–N(13)	2.100(4)	Ru–N_{Tp}	2.098(7)	2.087(7)
Ru–N(11^i)	2.148(3)	Ru–N_{Tp}	2.121(7)	2.110(7)
Ru–N(11)	2.148(3)	Ru–N_{Tp}	2.131(7)	2.149(7)
Ru–P	2.2676(10)	Ru–P_{PTA}	2.288(2)	2.288(2)
Ru–P^i	2.2675(10)	Ru–P	2.326(2)	2.332(2)
Ru–Cl	2.4186(16)	Ru–Cl	2.422(2)	2.418(2)
N–C_{PTA} (av.)	1.464(6)	N–C_{PTA} (av.)	1.466(9)	1.465(9)
P–C_{PTA} (av.)	1.846(4)	P–C_{PTA} (av.)	1.851(8)	1.843(8)
N(11^i)–Ru–N(11)	81.24(17)	N_{Tp}–Ru–N_{Tp}	81.0(2)	81.2(3)
N(13)–Ru–N(11^i)	88.37(11)	N_{Tp}–Ru–N_{Tp}	88.4(2)	88.3(3)
N(13)–Ru–N(11)	88.37(11)	N_{Tp}–Ru–N_{Tp}	86.9(2)	86.4(2)
N(13)–Ru–P	92.22(8)	N_{Tp}–Ru–P_{PTA}	88.52(17)	88.81(17)
N(11^i)–Ru–P	90.26(9)	N_{Tp}–Ru–P_{PTA}	89.40(18)	89.04(18)
N(11)–Ru–P	171.47(9)	N_{Tp}–Ru–P_{PTA}	170.03(18)	170.0(2)
N(13)–Ru–P^i	92.22(8)	N_{Tp}–Ru–P	94.44(17)	94.08(18)
N(11^i)–Ru–P^i	171.47(9)	N_{Tp}–Ru–P	172.60(19)	173.10(18)
N(11)–Ru–P^i	90.26(9)	N_{Tp}–Ru–P	91.80(18)	91.95(19)
P–Ru–P^i	98.22(5)	P_{PTA}–Ru–P	97.89(8)	97.85(8)
N(13)–Ru–Cl	174.57(12)	N_{Tp}–Ru–Cl	172.45(17)	172.01(18)
N(11^i)–Ru–Cl	87.51(8)	N_{Tp}–Ru–Cl	89.79(19)	85.68(19)
N(11)–Ru–Cl	87.51(8)	N_{Tp}–Ru–Cl	85.53(19)	89.5(2)
P–Ru–Cl	91.34(3)	P_{PTA}–Ru–Cl	92.04(8)	91.99(8)
P^i–Ru–Cl	91.34(3)	P–Ru–Cl	92.94(8)	93.69(8)

[a] Symmetry transformations used to generate equivalent atoms: i: *x*, 3/2 – *y*, *z*.

In keeping with the solution characterisation, both compounds consist of discrete molecules where the ruthenium(II) ion exhibits a distorted octahedral geometry with three contiguous coordination positions occupied by the κ^3-*N*,*N′*,*N′′* tridentate Tp ligand. One chlorido ligand and two mutually *cis*- oriented phosphane ligands (two *P*-bonded PTA ligands for **3** and one *P*-bonded PTA and one triphenylphosphane ligand for **2**) complete the coordination polyhedron around the ruthenium atom. The nitrogen-donor atoms of the Tp ligand occupy one of the faces of the octahedron, with the shorter Ru–N bond corresponding

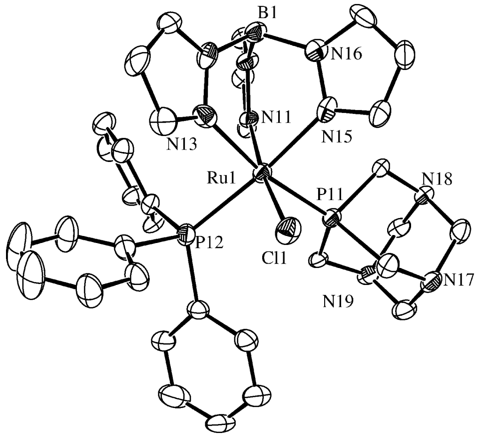


Figure 1. ORTEP view and atom-numbering scheme for **2**, showing thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

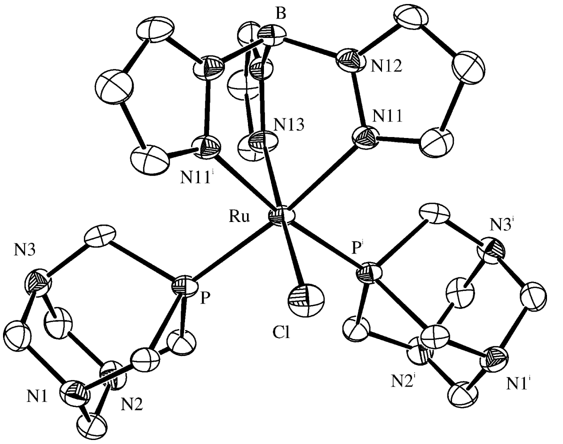


Figure 2. ORTEP view and atom-numbering scheme for **3**, showing thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

to that *trans* to the chlorido ligand. The Ru–N bonds *trans* to phosphorus atoms in **3** are identical on symmetry grounds and differ by 0.01 and 0.03 Å in the two molecules of **2**. These values are analogous to those found for other Tp–Ru^{II} complexes.[20]

The average Ru–Cl bond length (2.42 Å) is similar to previously published values.[4d,6a,6b,7,21] The Ru–P_{PTA} bond lengths in **3** and **2** are 2.267(1) and 2.288(2) Å, respectively, and are similar to those found for other PTA complexes with ruthenium.[19,21a,22] The angles around the metal atom deviate by less than 4° from the theoretical value of 90° except in two cases. One of these is the P–Ru–P angle, which opens to 98.22(5)° in **3** and 97.87(8)° in **2** despite the fact that the cone angle of PPh_3 (approx. 147°) is larger than that of PTA (approx. 102°).[15,22b,23] The other exception involves the N–Ru–N chelate angles of the Tp ligand in the same plane as the phosphorus atoms, which are narrower as a consequence of the variation of the P–Ru–P angles and have values of 81.24(17)° for **3** and 81.1(2)° (av.) for **2**. The *trans* angles diverge from the theoretical value of 180° due to the chelate requirements of the Tp ligand and the steric effects of the phosphane ligands already discussed for the *cis* angles. Thus, the N–Ru–Cl angles have values of between 172.0(1) and 174.6(1)° and the P–Ru–N angles range from 172.0(2) to 173.1(2)°.

Electrochemical Studies

Electrochemical studies on the present TpRu complexes were carried out to collect information about the donor properties of PTA and its *N*-boranyl adduct. The electrochemical behaviour of $[TpRuCl(PPh_3)_2]$ (**1**) was also investigated in order to compare these properties with triphenylphosphane. In spite of the increasing amount of attention being paid to this class of water-soluble ligands,[15] electrochemical studies on their coordination complexes have rarely been carried out and, to the best of our knowledge, are limited to Darensbourg's analysis of electrocatalysed H_2 production by models of iron hydrogenases incorporating PTA and electrophilically activated PTA analogues[24] and to a recent study on (cyclopentadienido)-ruthenium complexes related to the present TpRu species by online electrochemistry and electrospray mass spectrometry (EC/ESI-MS).[25]

The electrochemical behaviour of ruthenium(II) complexes **1**–**5** was studied in MeCN and dmso. Cyclic voltammetry (CV) in 0.2 M $[Bu_4N][BF_4]$ at a Pt disc electrode in both solvents shows a reversible, one-electron oxidation wave assigned to the $Ru^{II} \rightarrow Ru^{III}$ oxidation (wave I, at the half-wave oxidation potential values, ${}^{I}E_{1/2}{}^{ox}$, given in Table 2). Hence, it concerns the $Ru^{II/III}$ redox couple, as has been commonly recognized[26–30] for other $Ru^{II/III}$ complexes and also for the complexes [CpRuCl(L)(L′)] (L = PTA, PPh_3).[25] The occurrence of a one-electron oxidation was confirmed by exhaustive controlled potential electrolysis (CPE) in MeCN at a potential slightly anodic to that of the peak potential, which led to the consumption of nearly 1 F per mol of complex, with conversion of the oxidation wave to the corresponding reduction one at the same half-wave redox potential.

Table 2. Cyclic voltammetric data for the ruthenium complexes **1**–**5**.[a]

Complex	MeCN		dmso	
	${}^{I}E_{1/2}{}^{ox}$	${}^{II}E_p{}^{ox}$, ${}^{III}E_p{}^{ox}$	${}^{I}E_{1/2}{}^{ox}$	${}^{II}E_p{}^{ox}$
$[TpRuCl(PPh_3)_2]$ (**1**)	0.70[b]	1.98[c]	0.74	1.11
$[TpRuCl(PPh_3)(PTA)]$ (**2**)	0.70	1.26[d]	0.70	1.13[e]
$[TpRuCl(PTA)_2]$ (**3**)	0.66	1.23[f]	0.61	1.14
$[TpRuCl(PPh_3)\{PTA(BH_3)\}]$ (**4**)	0.80	1.75, 1.87[g]	0.77	–
$[TpRuCl\{PTA(BH_3)\}_2]$ (**5**)	0.89[h]	1.15, 1.23[g]	0.79	1.14

[a] Potentials in V (±0.02) vs. SCE, measured at 0.2 $V s^{-1}$. [b] The reversible oxidation wave with a lower current intensity observed at $E_{1/2}{}^{ox}$ = 1.00 V is ascribed to $[(\kappa^2\text{-Tp})RuCl(MeCN)(PPh_3)_2]$. [c] Upon scan reversal, a cathodic reversible wave is detected at 1.26 V. [d] Upon scan reversal, a cathodic reversible wave is detected at 0.89 V. [e] Upon scan reversal, a cathodic reversible wave is detected at 0.85 V. [f] Upon scan reversal, a cathodic reversible wave is detected at 1.03 V. [g] Poorly defined. [h] The reversible oxidation wave with a lower current intensity observed at $E_{1/2}{}^{ox}$ = 0.75 V is assigned to $[TpRuCl(MeCN)\{PTA(BH_3)\}]$.

A low-intensity reversible oxidation wave was also observed at a slightly higher or lower $E_{1/2}{}^{ox}$ value with respect to wave I for complexes [TpRuCl(PPh$_3$)$_2$] (**1**; Figure 3) and [TpRuCl{PTA(BH$_3$)}$_2$] (**5**), respectively, in MeCN. This additional process was assigned to oxidation of the complexes generated in situ by partial ligand displacement by MeCN, which should result in the formation of the acetonitrile adducts [(κ^2-Tp)RuCl(MeCN)(PPh$_3$)$_2$] or [TpRuCl(MeCN){PTA(BH$_3$)}] (see below). This partial ligand displacement appears to occur more extensively in dmso since wave I of the complexes in this solvent usually exhibits a much lower peak current intensity and CPE involves a charge consumption much lower than 1 F per mol of complex. This behaviour can be explained by considering the replacement of one of the coordinating arms of κ^3-Tp (thus becoming κ^2-Tp) by dmso (see below) and formation of complexes that exhibit oxidation potentials about 0.4 V above those of the starting complexes (wave I). In fact, a second irreversible oxidation wave (wave II) with a higher current intensity than that of wave I is observed close to the solvent/electrolyte discharge in dmso at an $E_p{}^{ox}$ value that is 0.35–0.53 V more anodic than that of ${}^{I}E_{1/2}{}^{ox}$ (Table 2). This second oxidation wave could also involve a ligand-centred oxidation since free PTA presents an irreversible oxidation wave at 1.05 V vs. SCE.

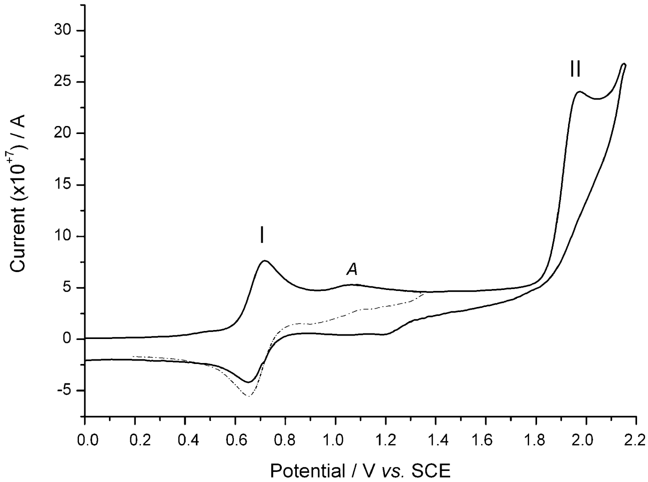


Figure 3. Cyclic voltammograms of [TpRuCl(PPh$_3$)$_2$] (**1**) (0.7 mM) in 0.2 M [Bu$_4$N][BF$_4$]/MeCN at a platinum disc (d = 0.5 mm) working electrode and at a scan rate of 0.2 V s^{-1}. Wave A is assigned to [(κ^2-Tp)RuCl(MeCN)(PPh$_3$)$_2$] (see text). The dotted line represents the cathodic scan following the oxidation waves I and A.

In the cyclic voltammograms in MeCN wave I is also followed at a higher potential by a second (and in a couple of cases also by a third) irreversible oxidation wave (Table 2) which is also believed to be ligand- rather than metal-centred. In fact, the Ru$^{III/IV}$ redox potential would be expected (see below) at a much higher potential (> 2.4 V vs. SCE) and, for example, the potassium salt of Tp in MeCN exhibits irreversible oxidation waves at 1.61 and 1.96 V. Such oxidation waves were not investigated further.

The values of the Ru$^{II/III}$ oxidation potential (${}^{I}E_{1/2}{}^{ox}$) of our complexes should reflect the electron-donor character of the ligands, which thus can be ordered as follows: PTA > PPh$_3$ > PTA(BH$_3$). This character can even be measured by applying the redox potential parametrisation approach proposed by Lever[26] for octahedral complexes, based on the linear relationship [Equation (1)] in which the redox potential of a complex (in V vs. NHE) is related to electrochemical parameters determined by the ligands and the metal redox centre. In this equation ΣE_L is the sum of the values of the E_L ligand parameter for all the ligands and S_M and I_M are the slope and intercept, respectively (dependent upon the metal, redox couple, spin state and stereochemistry).

$$E_{1/2}{}^{ox} = S_M \cdot (\Sigma E_L) + I_M \quad (1)$$

Application of Equation (1) to the complexes under study (with the ${}^{I}E_{1/2}{}^{ox}$ oxidation potentials converted to V vs. NHE) with known values of I_M (0.04 V vs. NHE) and S_M (0.97) for the Ru^{II}/Ru^{III} redox centre, as well as E_L for the Cl$^-$ and PPh$_3$ ligands (–0.24 and 0.39, respectively)[26] allowed us to tentatively estimate, for the first time, the E_L parameter for Tp (in complex **1**), PTA (in complexes **2** and **3**) and its *N*-boranyl adduct, PTA(BH$_3$) (in complexes **4** and **5**) as an average of two (for Tp) or four (for the other ligands) values for each ligand (measured in both MeCN and dmso). The estimated E_L values (Table 3) are as follows: 0.14 V (for each coordinated arm of Tp), 0.34 (PTA) and 0.45 [PTA(BH$_3$)] V vs. NHE. This order confirms the ordering above for the net electron-donor ability of such ligands on the basis of the oxidation potentials of their complexes.

Table 3. E_L ligand parameter values estimated in this study.[a]

Ligand	E_L [V] vs. NHE
Tp	014[b]
PTA	0.34
PTA(BH$_3$)	0.45

[a] From Lever's equation [Equation (1)]. [b] Per ligating pyrazolyl arm.

Remarkably, Tp appears to be a net electron-donor similar to HCpz$_3$ [hydrotris(pyrazolyl)methane], for which an identical E_L value has been estimated.[31] However, each pyrazolyl arm of Tp is a slightly weaker electron donor than pyrazole itself (E_L = 0.20 V vs. NHE). Application of Equation (1), using the estimated E_L values, to the above-mentioned unassigned low-intensity oxidation waves at 1.00 and 0.77 V vs. SCE (in MeCN solutions of complexes **1** and **5**), allowed us to tentatively identify the corresponding complexes as [(κ^2-Tp)RuCl(MeCN)(PPh$_3$)$_2$] and [TpRuCl(MeCN){PTA(BH$_3$)}], which have predicted $E_{1/2}{}^{ox}$ values of 0.96 and 0.74 V, respectively. The former complex is derived from displacement of one pyrazolyl arm of Tp in **1** by MeCN, whereas the latter complex results from substitution of one PTA(BH$_3$) ligand by acetonitrile.

Since *S*-bonded dmso (E_L = 0.57 V)[32] behaves as a considerably weaker net electron-donor than each ligating arm of Tp (E_L = 0.14 V as estimated above) and the corresponding ΔE_L difference is 0.43 V, coordinative displacement of one pyrazolyl group of Tp (conversion from a tri- to a dihapto ligand) by dmso would result in an increase of the oxidation potential of the complex by a value of 0.43 S_M [Equation (1)], i.e. 0.42 V. This difference is comparable to those observed between the oxidation potentials of the second and first waves (Table 2) in dmso (ΔE^{ox} in the 0.35–0.53 V range), thereby suggesting the occurrence of such a displacement reaction. This implies that the oxidation waves observed at potentials higher than those of wave I ($Ru^{II/III}$ redox pair) should not be assigned to the $Ru^{III/IV}$ oxidation. Indeed, the estimated $Ru^{III/IV}$ oxidation potentials (approx. 2.4 V vs. SCE), by application of a proposed version of Lever's relationship in which $S_M = 1.03$ and $I_M = 1.68$ V vs. NHE,[28] are much higher than the experimentally measured ones.

Synthesis and Characterisation of Water-Soluble TpRu Hydrides

The hydrido[tris(pyrazolyl)borato]ruthenium(II) complex [TpRuH(PPh$_3$)(PTA)] (**6**) was prepared by chloride metathesis upon treatment of **2** with an excess of NaOMe in MeOH at room temperature. Attempts to prepare this hydride according to the more standard method[33] using NaBH$_4$ as hydride source failed due to partial boronation of PTA. Similarly, the reaction of **2** with LiHBEt$_3$ or LiAlH$_4$ did not afford reproducible results and generally resulted in extensive decomposition. Attempts to prepare the bis(PTA) hydride [TpRuH(PTA)$_2$] (**7**) by using NaOMe or similar reagents proved unsuccessful, although treatment of complex **6** with PTA in refluxing toluene was an excellent method to prepare **7**. Further reaction of **6** with BH$_3$·thf provides a straightforward method to synthesise the new PTA-boronated hydrido complex [TpRuH(PPh$_3$){PTA-(BH$_3$)}] (**8**). A summary of these reactions is shown in Scheme 4.

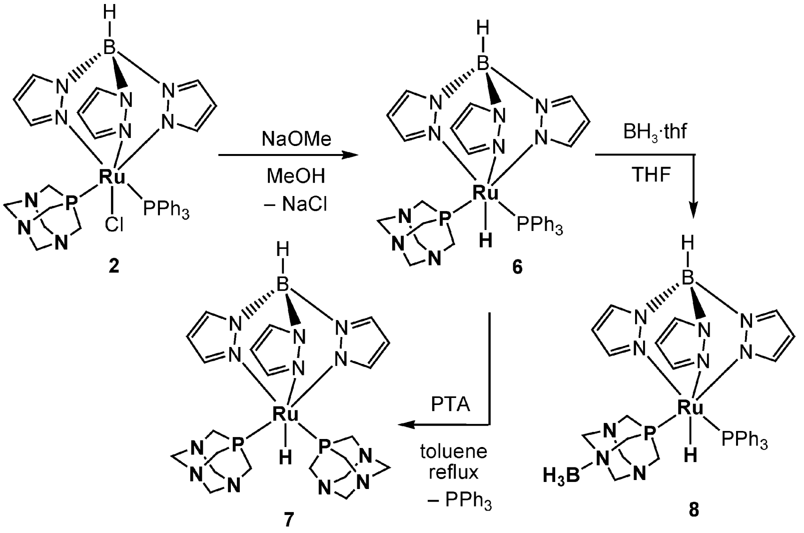
The hydrides **6**–**8**, which were isolated as pale-yellow solids in moderate yields, decompose slowly in air; thus, they were stored under argon. The complexes are soluble in halogenated solvents but slowly revert to the corresponding chloro complexes. The IR spectra of all hydride compounds, apart from the characteristic ν_{BH} band of the Tp ligand (2456–2464 cm^{-1}), show a medium-intensity absorption at 1920–1940 cm^{-1} attributed to ν_{RuH}.

The ^{1}H NMR spectra of compounds **6**–**8** confirm the presence of the Tp ligand by showing the characteristic signals of the pyrazole hydrogen atoms of the Tp group. Again, the number of these signals reflects the number of identical co-ligands attached to the metal centre. The ^{1}H NMR spectra of complexes **6** and **8** show a high-field-shifted doublet of doublets, each centred at $\delta \approx -14$ ppm, due to coupling to two different phosphorus atoms, which is highly diagnostic for the presence of a terminal hydrido ligand, whereas complex **7** displays a triplet at $\delta \approx -16$ ppm corresponding to the single hydrido ligand coupled to the two magnetically equivalent PTA P atoms ($^2J_{P,H} = 30.6$ Hz). A triplet with similar NMR parameters has been reported for the related hydride [CpRuH(PTA)$_2$] ($\delta = -14.46$ ppm, $^2J_{P,H} = 36.0$ Hz).[21a,22d]

In agreement with the proposed formulation, the ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra of hydrides **6**–**8** show similar patterns to the chlorido complexes and do not require additional comment.

Interestingly, while the solubility of the mixed PTA/PPh$_3$ hydride **6** in water is rather modest ($S_{25\,°C} = 2.0$ mg mL^{-1}), the bis(PTA) hydride **7** is readily soluble in water ($S_{25\,°C} = 21$ mg mL^{-1}), where it does not decompose even upon standing at room temperature for a week.

Water-soluble transition metal hydrides are still uncommon species[34] despite the increased attention recently paid to catalytic applications in water or aqueous biphasic systems and the growing interest in synthesising metal hydrides that combine good water solubility with thermal robustness and tolerance to highly polar substrates. As **6** seems to fulfil these latter requirements, it appears to be a good candidate for further studies and applications in aqueous-phase hydrogenation catalysis. Current work in our laboratories is



Scheme 4.

aimed at investigating the scope of **6** in catalysis and at preparing new water-soluble transition metal hydrides based on PTA and related systems.

Conclusions

A series of chloridoruthenium(II) complexes bearing the anionic tripodal tris(pyrazolyl)borato (Tp) ligand and the water-soluble cage phosphane PTA, or its boronated version PTA(BH_3), have been synthesised and characterised by spectroscopic methods and X-ray diffraction analysis of selected complexes {[TpRuCl(PTA)(PPh_3)] and [TpRuCl($PTA)_2$]}. Electrochemical CV studies have indicated the occurrence of partial κ^3 to κ^2 dechelation of Tp in some cases, and have allowed us to measure the values of $E_{1/2}{}^{\mathrm{ox}}$, which reflect the electron-donor character of the ligands [Tp (each arm) > PTA > PPh_3 > PTA(BH_3)]; the Lever electrochemical parameter E_L has also been estimated for the first time (except for PPh_3).

A series of TpRu hydrides containing PTA and PTA(BH_3) have been prepared and characterised. The hydride [TpRuH($PTA)_2$], which has been prepared in good yield, shows good solubility in water and high thermal stability. Further studies are in progress to determine the activities of the complexes obtained as hydrogenation catalysts in aqueous and biphasic systems and to evaluate their biological activity towards selected cell lines and their role in medicinal chemistry.[35]

Experimental Section

General Methods: All experimental manipulations were carried out under argon using standard Schlenk techniques. Once isolated, the complexes were found to be relatively stable in air, but were stored for precaution under an inert gas. All solvents were purified by conventional procedures[36] and distilled prior to use. The ligands PTA,[37] PTA(BH_3),[16a] KTp[12a] and the complex [TpRuCl($PPh_3)_2$][6a] (**1**) were prepared according to published methods. Other reagents were purchased from commercial sources in the highest available purity and used as received. IR spectra (KBr disc) were recorded with a Bruker Vector IFS 28 FT spectrophotometer. NMR spectra [^{1}H, ^{31}P(^{1}H), ^{13}C(^{1}H)] were obtained at room temperature (25 °C) with a Bruker ARX-400 spectrometer operating at frequencies of 400, 161 and 100 MHz, respectively; the spectra were recorded in $CDCl_3$, [D_6]dmso, D_2O or CD_2Cl_2 solution using the solvent as internal reference. ^{1}H and ^{13}C{^{1}H} NMR signals are referenced to internal TMS and those of ^{31}P{^{1}H} to 85% H_3PO_4; downfield shifts (δ in ppm) are considered positive. The ^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HSQC 2D-NMR experiments were performed with the same instrument using standard programs and processing routines. Microanalyses were carried out with a Fisons EA-1108 elemental analyzer.

Synthesis of [TpRuCl(PTA)(PPh_3)] (2): Solid PTA (180 mg, 1.14 mmol) was added to a stirred suspension of [TpRuCl($PPh_3)_2$] (**1**; 1000 mg, 1.14 mmol) in 20 mL of toluene, and the reaction mixture was refluxed for 40 min. The resultant yellow solution was filtered through Celite while hot to remove impurities. The yellow filtrate was reduced under vacuum to about 3 mL, and a yellow microcrystalline solid was precipitated upon addition of diethyl ether (5 mL). This precipitate was collected on a sintered glass frit and washed with diethyl ether (3 × 10 mL) before being dried in vacuo. Yield: 740 mg (84%). $S_{25\,°\mathrm{C}}$ = 2.1 mg mL^{-1}. $C_{33}H_{37}BClN_9P_2Ru$ (769.0): calcd. C 51.54, H 4.85, N 16.39; found C 51.50, H 4.87, N 16.35. IR (KBr pellet): ν_{BH} = 2475 cm^{-1} (w). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.88 (m, 6 H, $\mathrm{PC}H_2\mathrm{N}$), 4.20–4.46 (m, $\mathrm{NC}H_2\mathrm{N}$, 6 H), 5.68 [t, $^3J_{\mathrm{H,H}}$ = 2.3 Hz, 1 H, $\mathrm{HB(C_3}H_3\mathrm{N_2)_3}$], 5.77 [td, $^3J_{\mathrm{H,H}}$ = 2.2, $^5J_{\mathrm{H,P}}$ = 1.0 Hz, 1 H, $\mathrm{HB(C_3}H_3\mathrm{N_2)_3}$], 5.98 [d, $^3J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, $\mathrm{HB(C_3}H_3\mathrm{N_2)_3}$], 6.21 [td, $^3J_{\mathrm{H,H}}$ = 2.2, $^5J_{\mathrm{H,P}}$ = 1.0 Hz, 1 H, $\mathrm{HB(C_3}H_3\mathrm{N_2)_3}$], 6.62 [d, $^3J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, $\mathrm{HB(C_3}H_3\mathrm{N_2)_3}$], 7.22–7.30 (m, 3 H, $\mathrm{P}Ph_3$), 7.30–7.37 (m, 6 H, $\mathrm{P}Ph_3$), 7.52–7.63 [m, 6 H, $\mathrm{P}Ph_3$, 3 H, $\mathrm{HB(C_3}H_3\mathrm{N_2)_3}$], 8.17 [d, $^3J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, $\mathrm{HB(C_3}H_3\mathrm{N_2)_3}$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 51.9 (d, $^1J_{\mathrm{C,P}}$ = 13.4 Hz, $\mathrm{P}C\mathrm{H_2N}$), 73.4 (d, $^3J_{\mathrm{C,P}}$ = 5.6 Hz, $\mathrm{N}C\mathrm{H_2N}$), 105.2 [d, $^4J_{\mathrm{C,P}}$ = 2.1 Hz, $\mathrm{HB(}C_3\mathrm{H_3N_2)_3}$], 105.7 [d, $^4J_{\mathrm{C,P}}$ = 2.1 Hz, $\mathrm{HB(}C_3\mathrm{H_3N_2)_3}$], 105.8 [s, $\mathrm{HB(}C_3\mathrm{H_3N_2)_3}$], 127.5–130.0 ($C$ PPh_3), 133.4–136.6 (C PPh_3), 135.3 [s, $\mathrm{HB(}C_3\mathrm{H_3N_2)_3}$], 135.5 [s, $\mathrm{HB(}C_3\mathrm{H_3N_2)_3}$], 135.9 [s, $\mathrm{HB(}C_3\mathrm{H_3N_2)_3}$], 143.5 [s, $\mathrm{HB(}C_3\mathrm{H_3N_2)_3}$], 144.2 [s, $\mathrm{HB(}C_3\mathrm{H_3N_2)_3}$], 146.6 [s, $\mathrm{HB(}C_3\mathrm{H_3N_2)_3}$] ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 161 MHz): δ = –34.2 (d, $^2J_{\mathrm{P,P}}$ = 33.1 Hz, P_{PTA}), 46.9 (d, $^2J_{\mathrm{P,P}}$ = 33.1 Hz, $P_{\mathrm{PPh_3}}$) ppm.

Synthesis of [TpRuCl($PTA)_2$] (3). Method A: Solid PTA (90 mg, 0.57 mmol) was added to a stirred suspension of **1** (200 mg, 0.23 mmol) in 10 mL of toluene, and the reaction mixture was refluxed for 4 h. The resulting yellow precipitate was filtered and washed with diethyl ether (3 × 5 mL) and ethanol (3 × 5 mL) before being dried in vacuo. Yield: 128 mg (84%). **Method B:** Solid PTA was added (20 mg, 0.13 mmol) to a yellow solution of **2** (100 mg, 0.13 mmol) in hot toluene (10 mL), and the reaction mixture was stirred and refluxed for 3 h. The resulting yellow precipitate was filtered and washed with diethyl ether (3 × 5 mL) and ethanol (3 × 5 mL) before being dried in vacuo. Yield: 71 mg (83%). $S_{25\,°\mathrm{C}}$ = 18 mg mL^{-1}. $C_{21}H_{34}BClN_{12}P_2Ru$ (663.87): calcd. C 37.99, H 5.16, N 25.32; found C 37.96, H 5.19, N 25.21. IR [KBr pellets]: ν_{BH} 2508 cm^{-1} (w). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.13 (s, 12 H, $\mathrm{PC}H_2\mathrm{N}$), 4.44, 4.54 (AB system, $^2J_{\mathrm{AB}}$ = 14.0 Hz, 12 H, $\mathrm{NC}H_2\mathrm{N}$), 6.19 [br., $^3J_{\mathrm{H,H}}$ = 2.4 Hz, 3 H, $\mathrm{HB(C_3}H_3\mathrm{N_2)_3}$], 7.13 [d, $^3J_{\mathrm{H,H}}$ = 1.5 Hz, 1 H, $\mathrm{HB(C_3}H_3\mathrm{N_2)_3}$], 7.62 [d, $^3J_{\mathrm{H,H}}$ = 2.1 Hz, 2 H, $\mathrm{HB(C_3}H_3\mathrm{N_2)_3}$], 7.72 [d, $^3J_{\mathrm{H,H}}$ = 2.3 Hz, 1 H, $\mathrm{HB(C_3}H_3\mathrm{N_2)_3}$], 7.92 [d, $^3J_{\mathrm{H,H}}$ = 1.7 Hz, 2 H, $\mathrm{HB(C_3}H_3\mathrm{N_2)_3}$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 53.9 (d, $^1J_{\mathrm{C,P}}$ = 7.1 Hz, $\mathrm{P}C\mathrm{H_2N}$), 73.4 (d, $^3J_{\mathrm{C,P}}$ = 3.2 Hz, $\mathrm{N}C\mathrm{H_2N}$), 105.8, 106.3, 135.4, 136.7, 143.2, 146.9 [all s, $\mathrm{HB(}C_3\mathrm{H_3N_2)_3}$] ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 161 MHz): δ = –28.3 ppm (s); (D_2O, 161 MHz): δ = –26.1 ppm (s).

Synthesis of [TpRuCl(PPh_3){PTA(BH_3)}] (4). Method A: Solid PTA(BH_3) (97 mg, 0.57 mmol) was added to a stirred suspension of **1** (500 mg, 0.57 mmol) in 15 mL of toluene, and the reaction mixture was gently refluxed for 40 min. The yellow solution was filtered through Celite while hot, and the yellow filtrate was concentrated under vacuum to about 4 mL. Addition of diethyl ether (5 mL) gave **4** as a yellow microcrystalline solid, which was filtered and washed with diethyl ether (3 × 10 mL) before being dried in vacuo. Yield: 295 mg (66%). **Method B:** BH_3·thf was added with a syringe (0.4 mL, 0.4 mmol) to a suspension of **2** (300 mg, 0.39 mmol) in 20 mL of thf. The yellowish mixture was stirred at room temperature for 1 h before being filtered through Celite. The filtrate was concentrated under vacuum to about 4 mL, and diethyl ether (5 mL) was added to give a yellow solid, which was washed with diethyl ether (3 × 5 mL) and ethanol (3 × 5 mL) before being dried in vacuo. Yield: 262 mg (86%). $C_{33}H_{40}B_2ClN_9P_2Ru$ (782.83): calcd. C 50.63, H 5.15, N 16.10; found C 50.59, H 5.21, N 16.03. IR (KBr pellet): $\nu_{\mathrm{BH(Tp)}}$ = 2478 cm^{-1} (m); $\nu_{\mathrm{BH\{PTA(BH_3)\}}}$ = 2364 (s), 2314 (m), 2267 (m). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.90–1.44

(br., 3 H, BH_3), 3.35–4.50 (m, 12 H, C$H_{2\{\mathrm{PTA(BH_3)}\}}$), 5.78 [br. s, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 5.80 [br. s, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 6.21 [br. s, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 6.63 [br. s, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 7.21–7.50 (m, 15 H, P$Ph_3$), 7.62 [br. s, 2 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 7.65 [d, $^3J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 8.09 [br. s, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$] ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ = 49.1 (d, $^1J_{\mathrm{C,P}}$ = 15.5 Hz, PCH$_2$N), 49.7 (d, $^1J_{\mathrm{C,P}}$ = 14.8 Hz, PCH$_2$N), 55.2 (d, $^1J_{\mathrm{C,P}}$ = 10.6 Hz, PCH$_2$N), 71.1 (d, $^3J_{\mathrm{C,P}}$ = 5.6 Hz, NCH$_2$N), 77.7 (NCH$_2$N; partially masked by the CDCl$_3$ resonance), 105.6 [d, $^4J_{\mathrm{C,P}}$ = 2.1 Hz, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 105.8 [d, $^4J_{\mathrm{C,P}}$ = 2.1 Hz, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 106.3 [s, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 128.0–135.0 ($C$ PPh$_3$), 135.7 [s, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 135.8 [s, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 136.4 [s, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 143.8 [s, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 144.3 [s, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 147.0 [s, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$] ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, 161 MHz): δ = –25.34 (d, $^2J_{\mathrm{P,P}}$ = 32.6 Hz, $\mathrm{P_{PTA(BH_3)}}$), 43.98 (d, $^2J_{\mathrm{P,P}}$ = 32.6 Hz, $\mathrm{P_{PPh_3}}$) ppm.

Synthesis of [TpRuCl{PTA(BH$_3$)}$_2$] (5). Method A: Solid PTA(BH$_3$) (49 mg, 0.29 mmol) was added to a stirred suspension of **1** (100 mg, 0.11 mmol) in 10 mL of toluene, and the mixture was heated to reflux for 4 h. Workup as described above gave a yellow precipitate, which was collected by filtration through a sintered glass frit and washed with diethyl ether (3 × 5 mL) before being dried in vacuo. Yield: 50 mg (57%). **Method B:** 3 equiv. of BH$_3$·thf (0.4 mL, 0.4 mmol) was added with a syringe to a yellow suspension of **3** (100 mg, 0.15 mmol) in thf (15 mL) whilst stirring. The mixture was stirred at room temperature for 1 h. After removing the volatiles in vacuo, the resulting yellowish solid was washed with diethyl ether (3 × 5 mL) and dried in vacuo. Yield: 81 mg (75%). $\mathrm{C_{21}H_{40}B_3ClN_{12}P_2Ru}$ (721.5): calcd. C 36.47, H 5.83, N 24.31; found C 36.25, H 5.85, N 24.39. IR (KBr pellet): $\nu_{\mathrm{BH(Tp)}}$ = 2482 cm^{-1} (m); $\nu_{\mathrm{BH\{PTA(BH_3)\}}}$ = 2376 (s), 2318 (m), 2275 (m). ^{1}H NMR ([D$_6$]dmso, 400 MHz): δ = 0.74–1.54 (br., 6 H, BH_3), 3.29–4.46 (m, 24 H, C$H_{2\{\mathrm{PTA(BH_3)}\}}$), 6.29 [d, $^3J_{\mathrm{H,H}}$ = 2.3 Hz, 3 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 7.53 [d, $^3J_{\mathrm{H,H}}$ = 1.5 Hz, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 7.86 [d, $^3J_{\mathrm{H,H}}$ = 2.2 Hz, 2 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 7.94 [br. s, 3H HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$] ppm. ^{13}C{^{1}H} NMR ([D$_6$]dmso, 100 MHz): δ = 49.5 (d, $^1J_{\mathrm{C,P}}$ = 7.4 Hz, PCH$_2$N), 55.2 (d, $^1J_{\mathrm{C,P}}$ = 6.4 Hz, PCH$_2$N), 69.4 (br. s, NCH$_2$N), 76.4 (br. s, NCH$_2$N), 105.6 (s, 2 C), 106.9 (s, 1 C), 135.5 (s, 2 C), 137.0 (s, 2 C), 143.3 (s, 1 C), 148.0 [s, 1 C, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$] ppm. ^{31}P{^{1}H} NMR ([D$_6$]dmso, 161 MHz): δ = –19.5 ppm (s).

Synthesis of [TpRuH(PPh$_3$)(PTA)] (6): Solid **2** (200 mg, 0.26 mmol) was added in small portions to a vigorously stirred solution of sodium methoxide prepared by dissolving sodium (30 mg, 1.3 mmol) in 40 mL of methanol, and the reaction mixture was stirred at room temperature for 1.5 h. The mixture was then filtered through Celite to give a yellow solution, which was reduced under vacuum and worked up as above. The yellow solid obtained was washed with ethanol (3 × 5 mL). Yield (90 mg, 47%). $S_{25\,^\circ\mathrm{C}}$ = 2.0 mg mL^{-1}. $\mathrm{C_{33}H_{38}BN_9P_2Ru}$ (734.55): calcd. C 53.96, H 5.21, N 17.16; found C 53.92, H 5.18, N 17.05. IR (KBr pellet): ν_{BH} = 2456 cm^{-1} (m); ν_{RuH} = 1920 (w). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = –14.89 (dd, $^2J_{\mathrm{H,P}}$ = 31.2, $^2J_{\mathrm{H,P}}$ = 25.4 Hz, 1 H, RuH), 3.35–3.70 (m, 6 H, PCH_2N), 4.00–4.31 (m, NCH_2N, 6 H), 5.55 [t, $^3J_{\mathrm{H,H}}$ = 1.9 Hz, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 6.10 [t, $^3J_{\mathrm{H,H}}$ = 1.9 Hz, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 6.15 [t, $^3J_{\mathrm{H,H}}$ = 1.90 Hz, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 6.37 [br. s, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 7.16–7.41 [m, 15 H, P$Ph_3$, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 7.51 [d, $^3J_{\mathrm{H,H}}$ = 2.2 Hz, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 7.61 [d, $^3J_{\mathrm{H,H}}$ = 2.2 Hz, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 7.76 [s, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 7.83 [d, $^3J_{\mathrm{H,H}}$ = 2.2 Hz, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$] ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100 MHz): δ = 55.6 (d, $^1J_{\mathrm{C,P}}$ = 13.4 Hz, PCH$_2$N), 73.3 (d, $^3J_{\mathrm{C,P}}$ = 5.6 Hz, NCH$_2$N), 104.5 [d, $^4J_{\mathrm{C,P}}$ = 2.1 Hz, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 104.9 [d, $^4J_{\mathrm{C,P}}$ = 2.1 Hz, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 105.2 [s, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 127.4–134.7 ($C$ PPh$_3$), 134.8 [s, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 135.1 [s, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 135.3 [s, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 144.7 [s, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 145.4 [s, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 147.5 [d, $^4J_{\mathrm{C,P}}$ = 2.8 Hz, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$] ppm. ^{31}P{^{1}H} NMR (CDCl$_2$, 161 MHz): δ = –24.4 (d, $^2J_{\mathrm{P,P}}$ = 34.7 Hz, $\mathrm{P_{PTA}}$), 69.5 (d, $^2J_{\mathrm{P,P}}$ = 34.7 Hz, $\mathrm{P_{PPh_3}}$) ppm.

Synthesis of [TpRuH(PTA)$_2$] (7): Solid PTA (32 mg, 0.20 mmol) was added to a solution of **6** (150 mg, 0.20 mmol) in 10 mL of warm toluene, and the mixture was refluxed for 2 h before being filtered through Celite while hot. Workup of the yellow filtered solution as described above gave the hydride **7** as a yellow precipitate, which was collected by filtration through a sintered glass frit and washed with diethyl ether (3 × 5 mL) and ethanol (3 × 5 mL) before being dried in vacuo. Yield: 40 mg (40%). $S_{25\,^\circ\mathrm{C}}$ = 21 mg mL^{-1}. $\mathrm{C_{21}H_{35}BN_{12}P_2Ru}$ (629.42): calcd. C 40.07, H 5.60, N 26.70; found C 39.92, H 5.55, N 26.63. IR (KBr pellet): ν_{BH} = 2464 cm^{-1} (w); ν_{RuH} = 1866 (w). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = –15.96 (t, $^2J_{\mathrm{P,H}}$ = 30.6 Hz, 1 H, RuH), 3.75, 3.89 (AB system, $^2J_{\mathrm{AB}}$ = 15.0 Hz, 12 H, PCH_2N), 4.31, 4.40 (AB system, $^2J_{\mathrm{AB}}$ = 13.0 Hz, 12 H, NCH_2N), 6.08 [br. s, 2 H, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 6.26 [br. s, 1 H, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 7.53 [br. s, 1 H, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 7.57 [br. s, 2 H, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 7.63 [br. s, 2 H, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$], 7.75 [br. s, 1 H, HB($C_3\mathrm{H}_3\mathrm{N}_2$)$_3$] ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 161 MHz): δ = –16.8 (s) ppm.

Synthesis of [TpRuH(PPh$_3$){[PTA(BH$_3$)}] (8): A slight excess of BH$_3$·thf (0.2 mL, 0.2 mmol) was added with a syringe to a yellow suspension of **6** (100 mg, 0.14 mmol) in 10 mL of thf and the mixture was stirred at room temperature for 1 h. The resulting solution was filtered through Celite to remove impurities and the filtrate was concentrated to dryness under vacuum. The yellow solid obtained was washed with diethyl ether (3 × 5 mL) and ethanol (3 × 5 mL) before being dried under vacuum. Yield: 58 mg (55%). $\mathrm{C_{33}H_{41}B_2N_9P_2Ru}$ (748.39): calcd. C 57.96, H 5.52, N 16.84; found C 57.89, H 5.62, N 16.79. IR (KBr pellet): $\nu_{\mathrm{BH(Tp)}}$ = 2464 cm^{-1} (w); $\nu_{\mathrm{BH\{PTA(BH_3)\}}}$ = 2368 (m), 2319 (m), 2271 (w); ν_{RuH} = 1940 (m). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = –14.58 (dd, $^2J_{\mathrm{H,P}}$ = 32.5, $^2J_{\mathrm{H,P}}$ = 24.6 Hz, 1 H, RuH), 0.60–1.59 (br., 3 H, BH_3), 3.03–4.17 (m, 12 H, CH_2), 5.58 [br. s, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 6.11 [br. s, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 6.19 [br. s, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 6.40 [br. s, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 7.15–7.40 [m, 15 H, P$Ph_3$, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 7.53 [d, $^3J_{\mathrm{H,H}}$ = 2.0 Hz, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 7.63 [d, $^3J_{\mathrm{H,H}}$ = 2.0 Hz, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 7.71 [br. s, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$], 7.87 [d, $^3J_{\mathrm{H,H}}$ = 2.0 Hz, 1 H, HB($\mathrm{C}_3H_3\mathrm{N}_2$)$_3$] ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 161 MHz): δ = –15.7 (d, $^2J_{\mathrm{P,P}}$ = 35.6 Hz, $\mathrm{P_{PTA(BH_3)}}$), 68.6 (d, $^2J_{\mathrm{P,P}}$ = 35.6 Hz, $\mathrm{P_{PPh_3}}$) ppm.

Electrochemical Studies: The electrochemical experiments were performed with an EG&G PAR 273A potentiostat/galvanostat connected to a computer through a GPIB interface. Cyclic voltammograms were obtained for 0.2 M solutions of [Bu$_4$N][BF$_4$] in MeCN or dmso at a platinum disc working electrode (0.5 mm diameter) probed by a Luggin capillary connected to a silver wire pseudo-reference electrode; a Pt auxiliary electrode was also employed. Controlled-potential electrolyses (CPE) were carried out in electrolyte solutions with the above-mentioned composition in a two-compartment, three-electrode cell separated by a glass frit and equipped with platinum gauze working and counter electrodes. A Luggin capillary, probing the working electrode, was connected to a silver wire pseudo-reference electrode. The CPE experiments were monitored regularly by cyclic voltammetry (CV), thus assuring that no significant potential drift occurred during the electrolyses. The electrochemical experiments were performed under N$_2$ at room temperature. The potentials of the complexes were measured by CV in the presence of the couple [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ as the internal standard ($E_{1/2}^{\mathrm{ox}}$ = 0.45 V vs. SCE both in MeCN and dmso)[38] and the

Table 4. Crystal data and structure refinement.

	2	3
Empirical formula	$C_{66}H_{74}B_2Cl_2N_{18}P_4Ru_2$	$C_{21}H_{34}BClN_{12}P_2Ru$
Formula mass	1537.97	663.87
Temperature [K]	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	*Pnma*
a [Å]	10.1826(11)	19.135(2)
b [Å]	20.161(2)	15.873(2)
c [Å]	22.728(3)	10.7859(13)
α [°]	95.022(2)	90
β [°]	101.080(2)	90
γ [°]	90.104(3)	90
V [Å^3]	4560.5(9)	3275.9(7)
Z	2	4
$D_{\text{calcd.}}$ [Mg m^{-3}]	1.120	1.346
Absorption coefficient [mm^{-1}]	0.502	0.689
F(000)	1576	1360
Crystal size [mm]	$0.25 \times 0.45 \times 0.48$	$0.48 \times 0.47 \times 0.35$
θ range for data collection [°]	1.30–28.09	2.13–28.01
Index ranges	$-11 \le h \le 13$; $-22 \le k \le 26$; $-29 \le l \le 29$	$-24 \le \mathrm{h} \le 22$; $-13 \le \mathrm{k} \le 20$; $-14 \le \mathrm{l} \le 14$
Reflections collected	22493	16403
Independent reflections	16330 [R(int) = 0.0701]	3907 [R(int) = 0.0644]
Reflections observed [$I > 2\sigma(I)$]	6854	2754
Data completeness	0.734	0.953
Absorption correction	SADABS	SADABS
Max/min transmission	1.0000/0.8263	1.000/0.604
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	16330/0/847	3907/0/184
Goodness-of-fit on F^2	0.842	1.012
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0737 wR_2 = 0.1496	R_1 = 0.0524 wR_2 = 0.1302
R indices (all data)	R_1 = 0.1376 wR_2 = 0.1785	R_1 = 0.0779 wR_2 = 0.1370
Largest diff. peak/hole [e Å^{-3}]	1.333/–1.846	1.105/–1.218

redox potential values are normally quoted relative to the SCE. However, for the application of the Lever equation [Equation (1)] they were converted to V vs. NHE by adding 0.245 V.

Crystallographic Studies: Data were collected with a Siemens Smart CCD area-detector diffractometer with graphite-monochromated Mo-K_α radiation. Absorption correction was carried out using SADABS.[39] The crystallographic calculations were performed with the Oscail program.[40] The structures were solved by Patterson methods and refined by a full-matrix least-squares procedure based on F^2.[41] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. In both cases the Squeeze program[42] was used to correct the reflection data for diffuse scattering due to disordered solvent. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from the International Tables for X-ray Crystallography.[43] Further details of crystal data and structural refinement are given in Table 4. CCDC-651193 (**2**) and -651192 (**3**) 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.

Acknowledgments

The authors would like to thank the EC for promoting this scientific activity through the FP6 Research Training Network AQUACHEM (contract MCRTN-2003-503864). Thanks are also expressed to "Firenze Hydrolab", a project sponsored by a Ente Cassa di Risparmio di Firenze, and to the Fundação para a Ciência e a Tecnologia (Portugal) and its POCI 2010 programme (FEDER funded), for financial support. S. B. thanks the Xunta de Galicia for a Parga Pondal contract. M. R.-R. thanks the Xunta de Galicia for a postgraduate grant.

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[1] a) R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 2nd ed., J. Wiley, New York, **1994**; b) G. O. Spessard, G. L. Miessler, *Organometallic Chemistry*, Prentice-Hall, Upper Saddle River, NJ, **1997**.

[2] S. Trofimenko, *Chem. Rev.* **1993**, *93*, 943–980, and references cited therein.

[3] C. Slugovc, R. Schmid, K. Kirchner, *Coord. Chem. Rev.* **1999**, *185/186*, 109–126.

[4] a) C. Gemel, G. Trimmel, C. Slugovc, S. Kremel, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1996**, *15*, 3998–4004; b) C. Gemel, P. Wiede, K. Mereiter, V. N. Sapunov, R. Schmid, K. Kirchner, *J. Chem. Soc. Dalton Trans.* **1996**, 4071–4076; c) G. Trimmel, C. Slugovc, P. Wiede, K. Mereiter, V. N. Sapunov, R. Schmid, K. Kirchner, *Inorg. Chem.* **1997**, *36*, 1076–1083; d) C. Slugovc, P. Wiede, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1997**, *16*, 2768–2769; e) F. A. Jalón, A. Otero, A. Rodríguez, *J. Chem. Soc. Dalton Trans.* **1995**, 1629–1633.

[5] C. Slugovc, D. Doberer, C. Gemel, R. Schmid, K. Kirchner, B. Winkler, F. Stelzer, *Monatsh. Chem.* **1998**, *129*, 221–233.

[6] a) N. W. Alcock, I. D. Burns, K. S. Claire, A. F. Hill, *Inorg. Chem.* **1992**, *31*, 2906–2908; b) C. Gemel, G. Kickelbick, R. Schmid, K. Kirchner, *J. Chem. Soc. Dalton Trans.* **1997**, 2113–2117; c) C. Slugovc, V. Sapunov, P. Wiede, K. Mereiter, R. Schmid, K. Kirchner, *J. Chem. Soc. Dalton Trans.* **1997**, 4209–4216; d) N.-Y. Sun, S. J. Simpson, *J. Organomet. Chem.* **1992**, *434*, 341–349; e) W.-C. Chan, C.-P. Lau, Y.-Z. Chen, Y.-Q. Fang, S.-M. Ng, G. Jia, *Organometallics* **1997**, *16*, 34–44; f)

M. A. Halcrow, B. Chaudret, S. Trofimenko, *J. Chem. Soc. Chem. Commun.* **1993**, 465–467; g) B. Moreno, S. Sabo-Etienne, B. Chaudret, A. Rodríguez-Fernández, F. A. Jalón, S. Trofimenko, *J. Am. Chem. Soc.* **1995**, *117*, 7441–7451; h) M. Jiménez-Tenorio, M. A. Jiménez Tenorio, M. C. Puerta, P. Valerga, *Inorg. Chim. Acta* **1997**, *259*, 77–84.

[7] C. Slugovc, K. Mereiter, E. Zobetz, R. Schmid, K. Kirchner, *Organometallics* **1996**, *15*, 5275–5277.

[8] Y. Feng, M. Lail, K. A. Barakat, T. R. Cundari, T. B. Gunnoe, J. L. Petersen, *J. Am. Chem. Soc.* **2005**, *127*, 14174–14175.

[9] a) M. Lail, B. N. Arrowood, T. B. Gunnoe, *J. Am. Chem. Soc.* **2003**, *125*, 7506–7507; b) K. A. Pittard, J. P. Lee, T. R. Cundari, T. B. Gunnoe, J. L. Petersen, *Organometallics* **2004**, *23*, 5514–5523; c) M. Lail, C. M. Bell, D. Conner, T. R. Cundari, T. B. Gunnoe, J. L. Petersen, *Organometallics* **2004**, *23*, 5007–5020; d) N. A. Foley, M. Lail, T. B. Gunnoe, T. R. Cundari, J. L. Petersen, *J. Am. Chem. Soc.* **2007**, *129*, 6765–6781.

[10] J. P. Lee, K. A. Pittard, T. R. Cundari, T. B. Gunnoe, J. L. Petersen, *Organometallics* **2006**, *25*, 1500–1510.

[11] W. K. Fung, X. Huang, M. L. Man, S. M. Ng, M. Y. Hung, Z. Lin, C. P. Lau, *J. Am. Chem. Soc.* **2003**, *125*, 11539–11544.

[12] a) S. Trofimenko, *J. Am. Chem. Soc.* **1966**, *88*, 1842–1844; b) S. Trofimenko, *J. Am. Chem. Soc.* **1967**, *89*, 3904–3905; c) S. Trofimenko, *Chem. Rev.* **1972**, *72*, 497–509.

[13] For reviews on the chemistry of [CpRuCl(PPh_3)$_2$] and derivatives, see: a) M. A. Bennett, K. Khan, E. Wenger, *Comprehensive Organometallic Chemistry II*, vol. 7 (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**; b) S. G. Davies, J. P. McNally, A. J. Smallridge, *Adv. Organomet. Chem.* **1990**, *30*, 1–76.

[14] See, for example: E. Clot, O. Eisenstein, W. D. Jones, *Proc. Natl. Acad. Sci.* **2007**, *104*, 6939–6944.

[15] A. D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza, M. Peruzzini, *Coord. Chem. Rev.* **2004**, *248*, 955–993.

[16] a) S. Bolaño, A. Albinati, J. Bravo, L. Gonsalvi, M. Peruzzini, *Inorg. Chem. Commun.* **2006**, *4*, 360–363; b) *N*-boronation of PTA has also been reported by Frost et al.: B. J. Frost, C. A. Mebi, P. J. Gingrich, *Eur. J. Inorg. Chem.* **2006**, 1182–1189.

[17] Water-soluble complexes of the related tripodal tris(pyrazolyl) methanesulfonate ligand (SO_3Cpz_3) are known. See, for example: E. C. Alegria, L. M. Martins, M. Haukka, A. J. Pombeiro, *Dalton Trans.* **2006**, 4954–4961.

[18] C. Scolaro, A. Bergamo, L. Brescacin, R. Delfino, M. Cocchietto, G. Laurenczy, T. J. Geldbach, G. Sava, P. J. Dyson, *J. Med. Chem.* **2005**, *48*, 4161–4171.

[19] C. Lidrissi, A. Romerosa, M. Saoud, M. Serrano-Ruiz, L. Gonsalvi, M. Peruzzini, *Angew. Chem. Int. Ed.* **2005**, *44*, 2568–2572.

[20] See, for example: G. Albertin, S. Antoniutti, M. Bortoluzzi, J. Castro-Fojo, S. García-Fontán, *Inorg. Chem.* **2004**, *43*, 4511–4522, and references cited therein.

[21] a) D. N. Akbayeva, L. Gonsalvi, W. Oberhauser, M. Peruzzini, F. Vizza, P. Brueggeller, A. Romerosa, G. Sava, A. Bergamo, *Chem. Commun.* **2003**, 264–265; b) B. Buriez, I. D. Burns, A. F. Hill, A. J. P. White, D. J. Williams, J. D. E. T. Wilton-Ely, *Organometallics* **1999**, *18*, 1504–1516; c) C. Slugovc, K. Mauthner, M. Kacetl, K. Mereiter, R. Schmid, K. Kirchner, *Chem. Eur. J.* **1998**, *4*, 2043–2050; d) C. Slugovc, V. N. Sapunov, P. Wiede, K. Mereiter, R. Schmid, K. Kirchner, *J. Chem. Soc. Dalton Trans.* **1997**, 4209–4216; e) D. C. Wilson, J. H. Nelson, *J. Organomet. Chem.* **2003**, *682*, 272–289; f) S. Hartmann, R. F. Winter, B. M. Brunner, B. Sarkar, A. Knodler, I. Hartenbach, *Eur. J. Inorg. Chem.* **2003**, 876–891; g) S. Pavlik, C. Gemel, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, *J. Organomet. Chem.* **2001**, *617/618*, 301–310; h) S. Pavlik, K. Mereiter, M. Puchberger, K. Kirchner, *J. Organomet. Chem.* **2005**, *690*, 5497–5507; i) S. Pavlik, K. Mereiter, M. Puchberger, K. Kirchner, *Organometallics* **2005**, *24*, 3561–3575; j) S. Pavlik, M. Puchberger, K. Mereiter, K. Kirchner, *Eur. J. Inorg. Chem.* **2006**, 4137–4142; k) Y. Takahashi, M. Akita, S. Hikichi, Y. Moro-oka, *Inorg. Chem.* **1998**, *37*, 3186–3194.

[22] a) C. A. Mebi, R. P. Nair, B. J. Frost, *Organometallics* **2007**, *26*, 429–438; b) A. Romerosa, T. Campos-Malpartida, C. Lidrissi, M. Saoud, M. Serrano-Ruiz, M. Peruzzini, J. A. Garrido-Cárdenas, F. García-Maroto, *Inorg. Chem.* **2006**, *45*, 1289–1298; c) C. A. Mebi, B. J. Frost, *Organometallics* **2005**, *242*, 339–346; d) B. J. Frost, C. A. Mebi, *Organometallics* **2004**, *23*, 5317–5323; e) S. Bolaño, L. Gonsalvi, F. Zanobini, F. Vizza, V. Bertolasi, A. Romerosa, M. Peruzzini, *J. Mol. Catal. A* **2004**, *224*, 61–70; f) A. Romerosa, M. Saoud, T. Campos-Malpartida, C. Lidrissi, M. Serrano-Ruiz, M. Peruzzini, J. A. Garrido, F. García-Maroto, *Eur. J. Inorg. Chem.* **2007**, 2803–2812.

[23] C. A. Tolman, *J. Am. Chem. Soc.* **1970**, *92*, 2956–2965.

[24] R. Mejia-Rodriguez, D. Chong, J. H. Reibenspies, M. P. Soriaga, M. Y. Darensbourg, *J. Am. Chem. Soc.* **2004**, *126*, 12004–12014.

[25] V. Gutkin, J. Gun, P. V. Prikhodchenko, O. Lev, L. Gonsalvi, M. Peruzzini, A. Romerosa, T. Campos Malpartida, C. Lidrissi, *J. Electrochem. Soc.* **2007**, *154*, F7–F15.

[26] A. B. P. Lever, *Inorg. Chem.* **1990**, *29*, 1271–1285.

[27] N. A. Bokach, M. Haukka, P. Hirva, M. F. C. Guedes da Silva, V. Yu. Kukushkin, A. J. L. Pombeiro, *J. Organomet. Chem.* **2006**, *691*, 2368–2377.

[28] E. Reisner, V. B. Arion, A. Eichinger, N. Kandler, G. Geister, A. J. L. Pombeiro, B. K. Keppler, *Inorg. Chem.* **2005**, *44*, 6704–6716.

[29] E. Reisner, V. B. Arion, M. F. C. Guedes da Silva, R. Lichtenecker, A. Eichinger, B. K. Keppler, V. Yu. Kukushkin, A. J. L. Pombeiro, *Inorg. Chem.* **2004**, *43*, 7083–7093.

[30] A. J. L. Pombeiro, *Eur. J. Inorg. Chem.* **2007**, 1473–1482.

[31] E. C. B. Alegria, L. M. D. R. S. Martins, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *J. Organomet. Chem.* **2005**, *690*, 1947–1958.

[32] M. F. C. Guedes da Silva, A. J. L. Pombeiro, S. Geremia, E. Zangrando, M. Calligaris, A. V. Zinchenko, V. Yu. Kukushkin, *J. Chem. Soc. Dalton Trans.* **2000**, 1363–1371.

[33] See, for example: a) M. Jiménez-Tenorio, M. D. Palacios, M. C. Puerta, P. Valerga, *Organometallics* **2005**, *24*, 3088–3098; b) M. A. Jiménez Tenorio, M. Jiménez Tenorio, M. C. Puerta, P. Valerga, *J. Chem. Soc. Dalton Trans.* **1998**, 3601–3607.

[34] a) S. Ogo, N. Makihara, Y. Kaneko, Y. Watanabe, *Organometallics* **2001**, *20*, 49034910; b) T. Abura, S. Ogo, Y. Watanabe, S. Fukuzumi, *J. Am. Chem. Soc.* **2003**, *125*, 4149–4154.

[35] For application of PTA complexes in medicinal chemistry, see: a) W. H. Ang, P. J. Dyson, *Eur. J. Inorg. Chem.* **2006**, 4003–4018; b) A. Dorcier, W. H. Ang, S. Bolaño, L. Gonsalvi, L. Juillerat-Jeannerat, G. Laurenczy, M. Peruzzini, A. D. Phillips, F. Zanobini, P. J. Dyson, *Organometallics* **2006**, *25*, 4090–4096 and references cited therein.

[36] D. D. Perrin, W. Armarego, *Purification of Laboratory Chemicals*, 3rd ed. Butterworth and Heinemann, Oxford, **1988**.

[37] a) D. J. Daigle, A. B. Pepperman, G. Boudreaux, *J. Heterocycl. Chem.* **1974**, *11*, 1085–1086; b) D. J. Daigle, *Inorg. Synth.* **1998**, *32*, 40–45.

[38] A. J. L. Pombeiro, M. F. C. Guedes da Silva, M. A. N. D. A. Lemos, *Coord. Chem. Rev.* **2001**, *219–221*, 53–80.

[39] G. M. Sheldrick, *SADABS: An empirical absorption correction program for area detector data*, University of Göttingen, Germany, **1996**.

[40] P. McArdle, *J. Appl. Crystallogr.* **1995**, *28*, 65–67.

[41] G. M. Sheldrick, *SHELX-97: A program for the solution and refinement of crystal structures*, University of Göttingen, Germany, **1997**.

[42] A. L. Spek, *Acta Crystallogr., Sect A* **1990**, *46*, C34–C36.

[43] *International Tables for X-ray Crystallography*, Kluwer, Dordrecht, **1992**, vol. C.

Received: June 29, 2007