PGSE NMR studies on RAPTA derivatives: Evidence for the formation of H-bonded dicationic species

ARTICLE *in* ORGANOMETALLICS · MARCH 2008

Impact Factor: 4.13 · DOI: 10.1021/om701131s

PGSE NMR Studies on RAPTA Derivatives: Evidence for the Formation of H-Bonded Dicationic Species

Sandra Bolaño,[†] Gianluca Ciancaleoni,[‡] Jorge Bravo,[†] Luca Gonsalvi,[§] Alceo Macchioni,*[,‡] and Maurizio Peruzzini[§]

Universidad de Vigo, Facultad de Química, Departamento de Quimica Inorgánica, 36310 Lagoas Marcosende, Vigo, Spain, Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto, 8, 06123 Perugia, Italy, and CNR-Istituto di Chimica dei Composti Organo Metallici (CNR-ICCOM), Via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy

Received November 12, 2007

*Summary: The self-aggregation tendency of RAPTA complexes {[Ru(η^6-p-cymene){PTA(-R)}Cl$_2$]X, R = H (**1**BPh_4 and **1**PF_6) and Me (**2**BPh_4 and **2**OTf), and [Ru(η^6-p-cymene)(PTA)$_2$Cl]X (**3**BPh_4 and **3**BF_4)} in acetone-d_6 was investigated by means of diffusion NMR spectroscopy. On increasing the concentration, the protonated species (**1**X) undergoes intercationic self-aggregation driven by hydrogen bonding that leads to the formation of $\mathbf{1}_2^{2+}$ dications and a small amount of $\mathbf{1}_2X^+$ ion triples.*

Although 1,3,5-triaza-7-phosphaadamantane (PTA) has been known since 1974,[1] its coordination chemistry has undergone a remarkable increase in interest in the last 15 years.[2] This renewed interest has been mainly due not only to the successful utilization of PTA−organometallic compounds as water-soluble catalysts[3] but also to their use as luminescent complexes[4] and promising anticancer agents.[5] Most of the distinctive features of PTA, including its high hydrosolubility and ability to form water-soluble transition-metal complexes, derive from its intrinsic tendency to establish hydrogen bonds via the three N-donor atoms residing in the lower rim of the adamantane skeleton. In fact, the N-functionality can act as either HB-acceptor[6] (HB = hydrogen bond) or, when protonated, HB-donor.[7] In this regard, direct involvement of the distal N-functionality in assisting both the hydrogenation reaction of benzylidene acetone[8] and the heterolytic splitting of a molecular dihydrogen ruthenium complex,[9] has been recently demonstrated.

Noncovalent interactions, occurring in the second coordination sphere of organometallic compounds, are generally recognized to play a relevant role in their reactivity and structure.[10] The occurrence of weak interactions in solution can be readily appreciated by NOE intermolecular[11] and diffusion[12] NMR studies or, even better, by taking advantage of the complementary information that these NMR methods allow us to obtain.[13] Although the current importance of transition-metal− PTA complexes is mostly ascribable to the establishment of weak interactions in polar solvents, to the best of our knowledge, no intermolecular study involving PTA−metal complexes in solution has been carried out.

Herein, we report the results of a PGSE (pulsed field gradient spin–echo)[14] NMR investigation on the self-aggregation properties of neutral and cationic arene ruthenium complexes bearing the PTA ligand and its protonated (PTA-H) and methylated derivatives (PTA-Me). The aim of this paper is to evaluate the tendency of such complexes to self-aggregate as a function of the chemical nature of the compound, possibly individualizing the weak interactions that are responsible for it. The establishment of several complex equilibria prevented us to carry out the study in water. Consequently, our analysis was conducted in acetone which, like water, is enough polar to minimize ion pairing. Additionally, acetone is an aprotic solvent, much less polar than water, thus allowing better evaluation of HB interactions.

* To whom correspondence should be addressed. Phone: +39 075 5855579. Fax: +39 075 5855598. Email: alceo@unipg.it.

[†] Universidad de Vigo.

[‡] Università di Perugia.

[§] CNR-ICCOM.

(1) Daigle, D. J.; Pepperman, A. B.; Vail, S. L. *J. Heterocycl. Chem.* **1974**, *11*, 407.

(2) Phillips, A. D.; Gonsalvi, L.; Romerosa, A.; Vizza, F.; Peruzzini, M. *Coord. Chem. Rev.* **2004**, *248*, 955.

(3) (a) Akbayeva, D. N.; Gonsalvi, L.; Oberhauser, W.; Peruzzini, M.; Vizza, F.; Brueggeller, P.; Romerosa, A.; Sava, G.; Bergamo, A. *Chem. Commun.* **2003**, 264. (b) Bolano, S.; Gonsalvi, L.; Zanobini, F.; Vizza, F.; Bertolasi, V.; Romerosa, A.; Peruzzini, M. *J. Mol. Catal. A* **2004**, *224*, 61. (c) Frost, B. J.; Mebi, C. A. *Organometallics* **2004**, *23*, 5317.

(4) (a) Assefa, Z.; McBurnett, B. G.; Staples, R. J.; Fackler, J. P.; Assman, B.; Angermaier, K.; Schmidbaur, H. *Inorg. Chem.* **1995**, *34*, 2490. (b) Assefa, Z.; McBurnett, B. G.; Staples, R. J.; Fackler, J. P.; John, P. *Inorg. Chem.* **1995**, *34*, 4965. (c) Forward, J. M.; Bohmann, D.; Fackler, J. P.; Staples, R. J. *Inorg. Chem.* **1995**, *34*, 6330.

(5) (a) Scolaro, C.; Chaplin, A. B.; Hartinger, C. G.; Bergamo, A.; Cocchietto, M.; Keppler, B. K.; Sava, G.; Dyson, P. J. *Dalton Trans.* **2007**, 5065. (b) Ang, W. H.; Daldini, E.; Juillerat-Jeanneret, L.; Dyson, P. J. *Inorg. Chem.* **2007**, *46*, 9048. (c) Dyson, P. J.; Ellis, D. J.; Laurenczy, G. *Adv. Synth. Catal.* **2003**, *345*, 211. (d) Allardyce, C. S.; Dyson, P. J.; Ellis, D. J.; Heath, S. L. *Chem. Commun.* **2001**, 1396. (e) Dyson, P. International Patent WO 02/40491 A1(2002).

(6) (a) Darensbourg, D. J.; Decuir, T. J.; Stafford, N. W.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H.; Kathó, A.; Joó, F. *Inorg. Chem.* **1997**, *36*, 4218. (b) Alyea, E. C.; Ferguson, G.; Kannan, S. *Chem. Commun.* **1998**, 345.

(7) Forward, J. M.; Assefa, Z.; Staples, R. J., Jr. *Inorg. Chem.* **1996**, *35*, 16.

(8) Mebi, C.; Frost, B. J. *Organometallics* **2005**, *24*, 2339.

(9) Rossin, A.; Gonsalvi, L.; Phillips, A. D.; Maresca, O.; Lledós, A.; Peruzzini, M. *Organometallics* **2007**, *26*, 3289.

(10) (a) Binotti, B.; Bellachioma, G.; Cardaci, G.; Carfagna, C.; Zuccaccia, C.; Macchioni, A. *Chem. Eur. J.* **2007**, *13*, 1570. (b) Macchioni, A *Chem. Rev.* **2005**, *105*, 2039. (c) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931.

(11) Macchioni, A. *Eur. J. Chem.* **2003**, 195 and references therein.

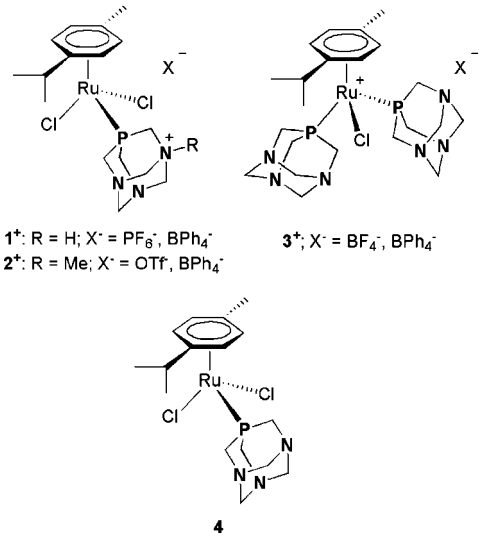
(12) (a) Zuccaccia, C.; Bellachioma, G.; Cardaci, G.; Macchioni, A. *Organometallics* **2000**, *19*, 4663. (b) Valentini, M.; Pregosin, P. S.; Ruegger, H. *Dalton* **2000**, *24*, 4507. (c) Bellachioma, G.; Ciancaleoni, G.; Zuccaccia, C.; Zuccaccia, D.; Macchioni, A. *Coord. Chem. Rev.*, doi: 10.1016/j.ccr.2007.12.016.

(13) Zuccaccia, D.; Bellachioma, G.; Cardaci, G.; Ciancaleoni, G.; Zuccaccia, C.; Clot, E.; Macchioni, A. *Organometallics* **2007**, *26*, 3930.

(14) (a) Hahn, E. L. *Phys. Rev.* **1950**, *80*, 580. (b) Stejskal, E. O.; Tanner, J. E *J. Chem. Phys.* **1965**, *42*, 288. (c) Stilbs, P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1987**, *19*, 1. (d) Price, W. S. *Concepts Magn. Reson.* **1997**, *9*, 299. (e) Price, W. S. *Concepts Magn. Reson.* **1998**, *10*, 197. (f) Johnson, C. S, Jr. *Prog. Nucl. Magn. Reson. Spectrosc.* **1999**, *34*, 203.

10.1021/om701131s CCC: $40.75
Publication on Web 03/14/2008

Scheme 1



Results and Discussion

Synthesis. Complexes [Ru(η^6-*p*-cymene){PTA(-H)}Cl_2]X (**1**X), [Ru(η^6-*p*-cymene){PTA(-Me)}Cl_2]X (**2**X), [Ru(η^6-*p*-cymene)(PTA)$_2$Cl]X (**3**X), and [Ru(η^6-*p*-cymene)(PTA)Cl_2] (**4**), shown in Scheme 1, were synthesized as detailed in the Experimental Section. In particular, complex **1**Cl was prepared by treating an aqueous solution of complex **4** with aqueous HCl (0.1 M) solution. **1**BPh_4 and **1**PF_6 were synthesized from **1**Cl through anion metathesis in methanol with an excess of $NaBPh_4$ and NH_4PF_6, respectively. **2**OTf was synthesized as described in the literature.[15] **2**BPh_4 was obtained as a yellow solid dissolving **2**OTf in methanol in the presence of a large excess of $NaBPh_4$. **3**Cl was synthesized by the reaction of [Ru_2(η^6-*p*-cymene)$_2Cl_2$(μ-Cl)$_2$] with 2 equiv of PTA in refluxing methanol. Anion metathesis reaction of **3**Cl with $NaBPh_4$ and halide removal using $AgBF_4$ gave **3**BPh_4 and **3**BF_4, respectively.

PGSE Measurements. The aggregation tendency of RAPTA complexes **1**−**4** (Scheme 1) in acetone-d_6 was studied by means of PGSE NMR experiments (Table 1). PGSE NMR[14] allows the translational self-diffusion coefficient (D_t) to be determined; the latter is related to the hydrodynamic radius (r_H) of the diffusing particle through to the Stokes–Einstein equation (1)

$$D_t = \frac{kT}{c\pi\eta r_H} \quad (1)$$

where k is the Boltzman constant, T is the temperature, c is a numerical factor, and η is the fluid viscosity. In order to obtain accurate hydrodynamic dimensions of the diffusing species, D_t data were treated as described in our recent paper.[16] The hydrodynamic volume (V_H) of the aggregates was determined by r_H assuming that they had a spherical shape. Finally, the aggregation number ($N^{+/-}$), defined as the ratio of experimental hydrodynamic volume of cation or anion and the hydrodynamic volume of the ion pair (V_H^{IP0}), was derived.[13,16]

$V_H^{IP0}$was considered equal to V_H^{+0} plus V_H^{-0}. While V_H^{-0} was known from previous studies [$V_H^{-0}(BPh_4^-)$ = 461 Å^3, $V_H^{-0}(PF_6^-)$ = 74 Å^3, $V_H^{-0}(BF_4^-)$ = 42 Å^3, $V_H^{-0}(OTf^-)$ = 72 Å^3],[13,17] V_H^{+0} and V_H^0(**4**) was experimentally determined from the PGSE measurements at the lowest concentrations. The results were as follows: V_H^{+0}(**1**$^+$) = 483 Å^3, in excellent agreement with its neutral isosteric analogous **4** (V_H^0 = 496 Å^3), V_H^{+0}(**2**$^+$) = 735 Å^3 and V_H^{+0}(**3**$^+$) = 796 Å^3 (entries 2, 25, 12, and 20, Table 1).

Table 1. Diffusion Coefficients ($10^{10}D_t^{+/-}$, m^2 s^{-1}), Average Hydrodynamic Volumes for Cations and Anions ($V_H^{+/-}$, Å^3), and Concentrations (C, mM) for 1X, 2X, and 3X Salts in Acetone-d_6 (ϵ_r = 20.56)

entry		D_t^+	D_t^-	V_H^+	V_H^-	N^+	N^-	C
1	**1**PF_6	12.0	22.0	834	217	1.5	0.4	4.7[a]
2		14.9	28.3	483	131	0.9	0.2	0.01
3	**1**BPh_4	9.20	11.9	1194	660	1.3	0.7	40
4		10.8	13.3	1003	546	1.0	0.6	13
5		12.4	14.4	739	527	0.8	0.5	2.4
6		14.7	15.0	517	487	0.5	0.5	0.47
7	**2**BPh_4	9.25	10.8	1188	800	1.0	0.7	65[a]
8		9.39	11.0	1072	720	0.9	0.6	51
9		10.8	12.6	937	638	0.8	0.5	23
10		11.5	13.5	826	552	0.7	0.5	9.9
11		12.5	14.5	724	508	0.6	0.4	1.1
12		12.2	14.8	735	469	0.6	0.4	0.1
13	**2**OTf	10.3	13.1	1023	569	1.3	0.7	49
14		11.7	14.5	865	517	1.1	0.7	27
15		11.8	16.6	792	342	1.0	0.4	8.7
16	**3**BPh_4	7.20	9.58	1161	579	0.9	0.5	24
17		9.64	12.5	1067	559	0.8	0.4	11
18		11.3	14.1	923	539	0.7	0.4	4.2
19		11.8	14.3	843	530	0.7	0.4	1.6
20		11.9	14.9	796	472	0.6	0.4	0.13
21	**3**BF_4	11.6	23.5	839	163	1.0	0.2	3.2[a]
22		11.8	28.4	800	118	0.9	0.1	0.44
23	**4**	13.4		579		1.2		16[a]
24		14.0		539		1.1		7.4
25		14.8		496		1.0		0.9

[a] Saturated solution.

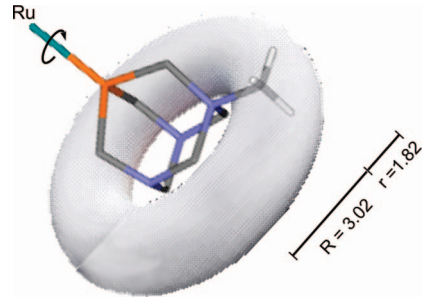


Figure 1. Schematic view of the PTAMe moiety derived from X-ray data reported in ref 15. The torus generated from the rapid rotation of the methylated PTA is outlined in gray; r and R are expressed in Å.

V_H^{+0}(**2**$^+$) appears to be larger than expected. In fact, the only chemical difference between **1**$^+$ and **2**$^+$ is the presence of the methyl group instead of the hydrogen atom that apparently does not justify a V_H^0 difference of 252 Å^3. Nevertheless, it has to be considered that, due to the rapid rotation of PTA around the Ru−P bond, the methyl group may occupy not only its intrinsic volume but also that of toroidal shape swept during its rotation. A simple calculation, carried out starting from the data in the solid state,[15] indicates that this volume amounts to V_{torus} = $2\pi^2Rr^2$ = 197.5 Å^3 (Figure 1). The sum V_H^0(**4**) + V_{torus} = 694 Å^3 is in agreement with the experimental hydrodynamic volume of **2**$^+$ (735 Å^3).

(15) Dorcier, A.; Dyson, P. J.; Gossens, C.; Rothlisberger, U.; Scopelliti, R.; Tavernelli, I. *Organometallics* **2005**, *24*, 2114.

(16) Macchioni, A.; Ciancaleoni, G.; Zuccaccia, C.; Zuccaccia, D. *Chem. Soc. Rev.* **2008**, *37*, 479 and references therein.

(17) Ciancaleoni, G.; Zuccaccia, C.; Zuccaccia, D.; Macchioni, A. *Organometallics* **2007**, *26*, 3624.

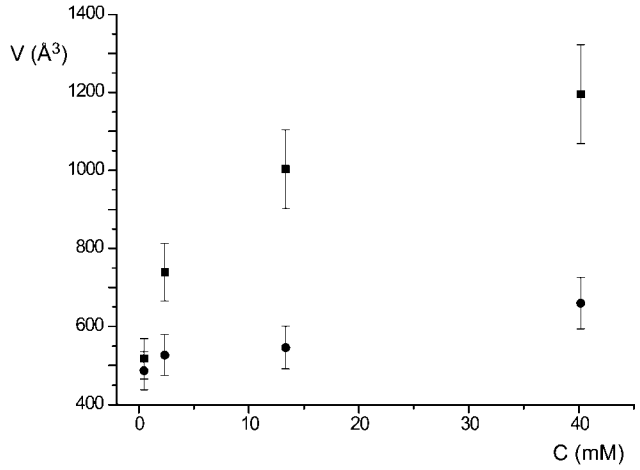


Figure 2. Dependence of the cationic and anionic average hydrodynamic volume (● = V^-, ■ = V^+) on the concentration of complex **1**BPh_4.

Aggregation of 1X. From PGSE data (Table 1, entries 1–6), it appears that at the lowest concentration values, **1**BPh_4 (entry 6), and **1**PF_6 (entry 2) are almost exclusively present as free ions. For both salts, $V_H{}^+$ and $V_H{}^-$ increase by increasing the concentration, but with different rates. Focusing on the most soluble **1**BPh_4 salt, $V_H{}^+$ and $V_H{}^-$ span from 517 and 487 Å^3 to 1190 and 660 Å^3, respectively, as the salt concentration increases (Figure 2). While the observed $V_H{}^-$ deviates little from $V_H{}^{-0}$, $V_H{}^+$ becomes more than 2-fold $V_H{}^{+0}$ (Figure 2). This data cannot be explained by the ion-pairing phenomenon alone that, in the actual case with anion and cation having about the same volumes, would always lead to equal $V_H{}^+$ and $V_H{}^-$. On the contrary, they suggest the formation of a substantial amount of $\mathbf{1}_2{}^+$ dications and a bit of $\mathbf{1}_2BPh_4{}^+$ ion triples. The latter are necessary to explain the observed value of $V_H{}^+$ that exceeds that of the dication (Table 1, entry 3). Also, **1**PF_6 has a great tendency to form dicationic species (Table 1, entry 1), but its low solubility precluded a complete study. It is reasonable to believe that the cation–cation aggregation is driven by the formation of hydrogen bonds between the good HB donor group (N-H$^+$) and one of the available HB acceptors (Cl and/or N).

Aggregation of 2X. In order to prove the effective influence of the aminic proton on the aggregative process, the RAPTA-methylated complex **2**BPh_4 was synthesized, where one of the nitrogen atoms of the PTA ligand bears a methyl group. **2**BPh_4 shows a marked decreased tendency to undergo cation–cation aggregation. The maximum $V_H{}^+$ value reached at the highest concentration (Table 1, entry 7) is the same than that of **1**BPh_4 (Table 1, entry 3), but this corresponds to a lower cationic aggregation since $V_H{}^{+0}$ for **2**BPh_4 is much higher, as seen before. In addition, the anion participates to the aggregation to a larger extent (Table 1). These results indicate, on one side, that the absence of the N-H hydrogen donor depresses the intercationic aggregation. On the other side, a certain tendency to ion pairing is observed for **2**BPh_4 that is probably favored by the peripheral location of the cationic charge. Changing the anion from $BPh_4{}^-$ to $CF_3SO_3{}^-$ does not lead to a significant modification of the aggregation tendency (entries 9 and 14 in Table 1). The growth of $V_H{}^-$ with the concentration is fast, according to the small $V_H{}^{-0}$ of triflate and its greater ability to form ion pairs with respect to tetraphenylborate. At the same time, the observation of $V_H{}^+$ values significantly higher than $V_H{}^{+0}$ with such a small counterion confirms that a certain amount of cation–cation aggregation has to occur. Since **2**CF_3SO_3 does not possess any HB donor and, consequently, has not the possibility to form HBs, it can be supposed that cation–cation aggregation occurs through the electrostatic interaction of the methylenic protons having a partial positive charge and the chlorine atom, as observed in the solid state for **2**Cl[15] (Figure 3).

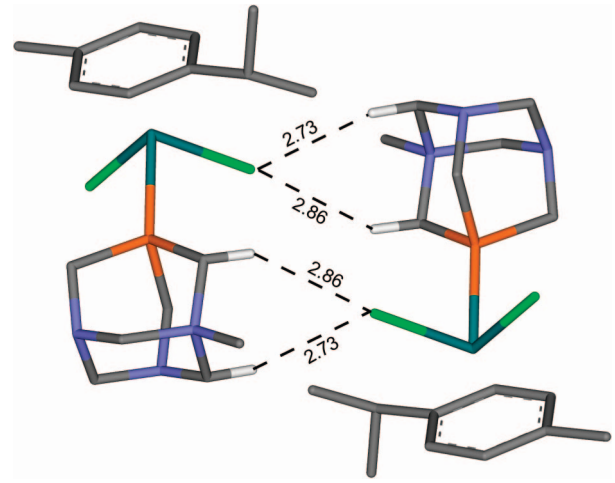


Figure 3. Noncovalent interactions (Å) present in the X-ray single-crystal structure of **2**Cl, reported by Dorcier et al.[15] Distances are expressed in angstroms, and all of the hydrogen atoms, except those involved in intermolecular interaction, are omitted for clarity.

Aggregation of 3X. In **3**X derivatives, the positive charge is formally centered on the metal. Consistently, a slightly smaller tendency to ion pairing is observed in **3**BPh_4 compared to **2**BPh_4 (entries 9 and 16 in Table 1). Instead, the tendency of **3**BPh_4 to form dications is a little higher than that of **2**BPh_4, but clearly lower than that of **1**BPh_4. It is not trivial to understand why **3**BPh_4 should have a higher tendency to form dications than **2**BPh_4. A possible explanation can be found by analyzing the solid-state structure of complex [CpRu(PTA){PTA(-H)}Cl]$PF_6 \cdot 3H_2O$[18] bearing two PTA ligands. Short intercationic contacts are present between the partial positively charged methylenic hydrogens belonging to the two PTA ligands and a chlorine atom (Figure 4). Such cooperative electrostatic interactions could be active also for **3**BPh_4 and persist in solution allowing the dication to be formed.

In conclusion, weak organometallic cation–cation interactions in solution have been previously documented in the literature. They were found in half-sandwich ruthenium(II) complexes bearing diamine (NH···Cl HB),[19] diimine (C−H···Cl electrostatic interaction),[13] 2,2′-dipyridylketone (O−H···O HB + π-π stacking),[20] 2-benzoylpyridine (π-π stacking),[21] and palladium phenantroline complexes (π-π stacking).[22] Despite this, only in the latter case multicationic aggregates were the predominant species in solution, while in other cases quadrupoles[13,19] or ion triples[20,21] were prevalently formed. Herein, we have shown that protonated RAPTA complexes have a remarkable tendency to form dications through intercationic HBs. The choice of acetone as solvent is crucial to highlight the formation of dications since it minimizes ion pairing.

(18) Mebi, C. A.; Frost, B. J. *Organometallics* **2005**, *24*, 2339.
(19) Zuccaccia, D.; Macchioni, A. *Organometallics* **2005**, *24*, 3476.
(20) Zuccaccia, D.; Foresti, E.; Pettirossi, S.; Sabatino, P.; Zuccaccia, C.; Macchioni, A. *Organometallics* **2007**, *26*, 6099.
(21) Zuccaccia, D.; Bellachioma, G.; Cardaci, G.; Zuccaccia, C.; Macchioni, A. *Dalton Trans.* **2006**, 1963.
(22) Macchioni, A.; Romani, A.; Zuccaccia, C.; Guglielmetti, G.; Querci, C. *Organometallics* **2003**, *22*, 1526.

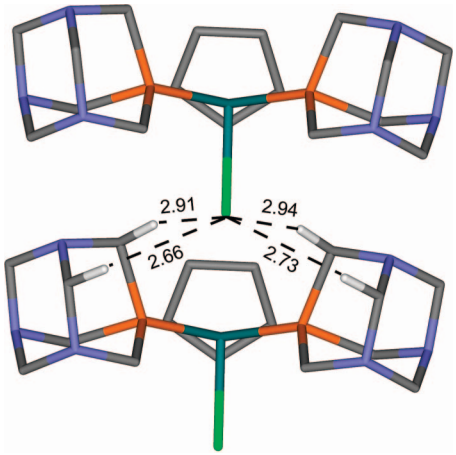


Figure 4. Noncovalent interactions (Å) present in the X-ray single-crystal structure of [CpRu (PTA)(PTAH)Cl]$PF_6 \cdot 3H_2O$.[18] Distances are expressed in angstroms. All of the solvent molecules and hydrogen atoms, apart from those involved in intermolecular interactions, are omitted for clarity.

Experimental Section

The PTA ligand and its derivatives[1] [$Ru_2(\eta^6$-*p*-cymene)$_2Cl_2(\mu$-Cl)$_2$],[23] [Ru(η^6-*p*-cymene)(PTA)Cl_2][24] (**4**), and [Ru(η^6-*p*-cymene)-(PTA)$_2$Cl]BF_4 (**3**BF_4)[25] were prepared according to the literature procedures. All other reagents were supplied by Aldrich and were used without further purification. The solvents were purified by conventional procedures.[26]

Synthesis of [Ru(η^6-*p*-cymene){PTA(-H)}Cl_2]X (1X), X = BPh_4, PF_6. Aqueous HCl (0.1 M, 2.2 mL) was added to a solution of [Ru(η^6-*p*-cymene)(PTA)Cl_2] (100 mg, 0.22 mmol) in water, at room temperature. After 30 min stirring, the solution was concentrated under reduced pressure and treated with a saturated solution of $NaBPh_4$ or $NaPF_6$ in methanol, giving immediately an orange solid (**1**BPh_4 or **1**PF_6, respectively). **1**BPh_4 (159.4 mg, 92.2%): ^{1}H NMR (acetone-d_6, 298 K) δ 7.35 (m, 8H, Ph), 6.94 (m, 8H, Ph), 6.79 (m, 4H, Ph), 5.86 (m, 4H, cymene), 5.16 (s, 6H, NCH_2), 4.58 (s, 6H, PCH_2), 2.74 (sept, 1H, J_{HH} = 6.9 Hz, CH), 2.04 (s, 3H, CH_3), 1.22 (d, 6H, J_{HH} = 6.85 Hz, CH_3); ^{31}P{^{1}H}NMR (acetone-d_6, 298 K) δ 22.1 (s). Anal. Calcd for $C_{40}H_{47}BCl_2N_3PRu$: C, 61.3; H, 6.05; N, 5.36. Found: C, 60.9; H, 6.13; N, 5.30. **1**PF_6 (118.3 mg, 88.2%): ^{1}H NMR (acetone-d_6, 298 K) δ 5.86 (m, 4H, cymene), 5.15 (s, 6H, NCH_2), 4.60(s, 6H, PCH_2), 2.73 (sept, 1H, J_{HH} = 7.0 Hz, CH), 2.05 (s, 3H, CH_3), 1.22 (d, 6H, J_{HH} = 6.84 Hz, CH_3); ^{19}F NMR (acetone-d_6, 298 K) δ –72.8 (d, J_{FP} = 707.9 Hz, PF_6); ^{31}P{^{1}H}NMR (acetone-d_6, 298 K) δ 22.1 (s), 140 (sept, J_{PF} = 707.9 Hz, PF_6).

Synthesis of [Ru(η^6-*p*-cymene){PTA(-Me)}Cl_2]X (2X), X = OTf, BPh_4. A mixture of [Ru(η^6-*p*-cymene)Cl_2]$_2$ (100 mg, 0.16 mmol) and [PTAMe]OTf (51.38 mg, 0.16 mmol) was refluxed in MeOH (20 mL) for 24 h. After evaporation of the solvent under reduced pressure, diethyl ether (30 mL) was added. The precipitated orange solid was filtered off and dried under vacuum. **2**OTf (92.7 mg, 92.3%): ^{1}H NMR (acetone-d_6, 298 K) δ 5.88 (m, 4H, cymene), 5.42−5.18 (m, 4H, NCH_2), 4.83–4.22 (m, 6 + 2 H, PCH_2+NCH_2), 3.11 (s, 3H, CH_3N), 2.72 (sept, 1H, J_{HH} = 6.9 Hz, CH), 2.04 (s, 3H, CH_3), 1.21 (d, 6H, J_{HH} = 6.98 Hz, CH_3); ^{19}F NMR (acetone-d_6, 298 K) δ −79.4 (s); ^{31}P{^{1}H}NMR (acetone-d_6, 298 K) δ –19.9 (s).

Metathesis reaction of **2**OTf with $NaBPh_4$ in MeOH gave the compound **2**BPh_4 (109.9 mg, 86.2%): ^{1}H NMR (acetone-d_6, 298 K) δ 7.36 (m, 8H, Ph), 6.94 (m, 8H, Ph), 6.70 (m, 4H, Ph), 5.84 (m, 4H, cymene), 5.32–5.13 (m, 4H, NCH_2), 4.84–4.22 (m, 6 + 2 H, PCH_2 + NCH_2), 3.11 (d, 3H, J_{HH} = 1.9, CH_3N), 2.73 (sept, 1H, J_{HH} = 7.1 Hz, CH), 2.04 (s, 3H, CH_3), 1.21 (d, 6H, J_{HH} = 6.90 Hz, CH_3).

Synthesis of [Ru(η^6-*p*-cymene)(PTA)$_2$Cl]X (3X), X = BPh_4, BF_4. A methanolic solution of [Ru(η^6-*p*-cymene)Cl_2]$_2$ (200 mg, 0.33 mmol) and PTA (206 mg, 1.32 mmol) was refluxed for 48 h. The mixture was cooled to room temperature, and the solvent was removed under reduced pressure to give a solid. The solid obtained was treated with a saturated solution of $NaBPh_4$ in MeOH, obtaining **3**BPh_4 (253 mg, 85.0%): ^{1}H NMR (acetone-d_6, 298 K) δ 7.35 (m, 8H, Ph), 6.94 (m, 8H, Ph), 6.79 (m, 4H, Ph), 6.54 (d, 2H, J_{HH} = 6.3 Hz, cymene), 6.36 (d, 2H, J_{HH} = 6.3 Hz, cymene), 4.74–4.56 (m, 12H, NCH_2), 4.56–4.38 (m, 12H, PCH_2), 2.70 (sept, 1H, J_{HH} = 6.8 Hz, CH), 2.18 (s, 3H, CH_3), 1.25 (d, 6H, J_{HH} = 6.90 Hz, CH_3). Anal. Calcd for $C_{46}H_{58}BClN_6P_2Ru$: C, 61.1; H, 6.46; N, 9.29. Found: C, 60.7; H, 6.60; N, 9.08.

A solution of **3**BPh_4 (80 mg, 0.088 mmol) in 20 mL of CH_2Cl_2 was treated with $AgBF_4$ (17.94 mg, 0.092 mmol). The white precipitate of $AgBPh_4$ was filtered off, and the solvent was removed under vacuum, giving the compound **3**BF_4: ^{1}H NMR (acetone-d_6, 298 K) δ 6.54 (d, 2H, J_{HH} = 6.4 Hz, cymene), 6.36 (d, 2H, J_{HH} = 6.3 Hz, cymene), 4.74–4.55 (m, 12H, NCH_2), 4.56–4.38 (m, 12H, PCH_2), 2.69 (sept, 1H, J_{HH} = 6.9 Hz, CH), 2.17 (s, 3H, CH_3), 1.25 (d, 6H, J_{HH} = 6.90 Hz, CH_3); ^{19}F NMR (acetone-d_6, 298 K) δ −151.84 ($^{10}BF_4^-$), −151.89 ($^{11}BF_4^-$).

PGSE NMR Measurements.[27] ^{1}H NMR measurements were performed by using the standard stimulated echo pulse sequence[27] on a Bruker AVANCE DRX 400 spectrometer equipped with a GREAT 1/10 gradient unit and a QNP probe with a Z-gradient coil at 296 K without spinning. The shape of the gradients was rectangular, their duration (δ) was 4–5 ms, and their strength (G) was varied during the experiments. All of the spectra were acquired using 32K points and a spectral width of 5000 (^{1}H) Hz and 18000 (^{19}F) Hz and processed with a line broadening of 1.0 (^{1}H) Hz and 1.5 (^{19}F) Hz. The semilogarithmic plots of ln (I/I_0) versus G^2 were fitted using a standard linear regression algorithm; the R factor was always higher than 0.99. Different values of Δ, "nt" (number of transients), and number of different gradient strengths (G) were used for different samples. The methodology for treating data was described previously.[19] The uncertainty in the measurements was estimated by determining the standard deviation of the slopes of the linear regression lines by performing experiments with different Δ values. The standard propagation of error analysis gave a standard deviation of approximately 3–4% in D_t and hydrodynamic radii and 10–15% in hydrodynamic volumes and aggregation numbers N.

Acknowledgment. We thank the DOW Chemical Co., the Ministero dell'Università e della Ricerca (MUR, Rome, Italy), and the Xunta de Galicia for support.

OM701131S

(23) Bennett, M. A.; Huang, T. N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74.
(24) Allardyce, C. S.; Dyson, P. J.; Ellis, D. J.; Heath, S. L. *Chem. Commun.* **2001**, 1396.
(25) Dyson, P. J.; Ellis, D. J.; Laurenczy, G. *Adv. Synth. Catal.* **2003**, *345*, 211.
(26) Perrin, D. D.; Armarego, W. *Purification of Laboratory Chemicals*, 3a ed.l Butterworth and Heinemann, Oxford, 1988.
(27) Valentini, M.; Rüegger, H.; Pregosin, P. S. *Helv. Chim. Acta* **2001**, *84*, 2833 and references therein.