Diffusion NMR Studies on the Self-Aggregation of Ru-Arene CAP Complexes: Evidence for the Formation of H-Bonded Dicationic Species in Acetonitrile

Leonardo Sian,[†] Antonella Guerriero,*[,‡] Maurizio Peruzzini,[‡,§] Cristiano Zuccaccia,[†] Luca Gonsalvi,[‡] and Alceo Macchioni*[,†]

[†]Dipartimento di Chimica, Biologia e Biotecnologie and CIRCC, Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy

[‡]Consiglio Nazionale delle Ricerche (CNR), Istituto di Chimica dei Composti OrganoMetallici (ICCOM), Via Madonna del Piano 10, 50019 Sesto Fiorentino (Florence), Italy

[§]Consiglio Nazionale delle Ricerche (CNR), Dipartimento di Scienze Chimiche e Tecnologia dei Materiali (DSCTM), Via dei Taurini 19, 00185 Rome, Italy

S *Supporting Information*

ABSTRACT: The self-aggregation of neutral $[RuCl_2(\eta^6\text{-}p\text{-cymene})(CAP)]$ (**2**; p-cymene = 1-methyl-4-(propan-2-yl)-benzene) and ionic $[RuCl(\eta^6\text{-}p\text{-cymene})(L)(CAP)](PF_6)$ (**3**, L = CAP; **4**, L = MeCN) and $[RuCl_2(\eta^6\text{-}p\text{-cymene})(CAP\text{-}H)](BPh_4)$ (**5**; CAP-H = monoprotonated CAP) ruthenium-(II) arene complexes, bearing the water-soluble phosphine CAP (1,4,7-triaza-9-phosphatricyclo[5.3.2.1]tridecane), in aprotic polar solvents, was investigated by means of PGSE (pulsed field gradient spin−echo) diffusion NMR. In addition, the analogous neutral $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PTA)]$ (**1**) and monoprotonated $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PTA\text{-}H)](BPh_4)$ (**6**) PTA (1,3,5-triaza-7-phosphaadamantane) complexes were investigated in acetonitrile-$d_3$. Complexes **1**−**4** do not exhibit any tendency to self-aggregate in acetonitrile-d_3 and acetone-d_6. In contrast, **5** and **6** monoprotonated complexes undergo a peculiar self-aggregation process, involving almost exclusively the cation, leading to the main formation of dicationic species held together by intermolecular hydrogen bonds. This has been clearly demonstrated by ^1H diffusion NMR experiments, which allowed measurement of an average hydrodynamic volume for the cation that was more than double that expected, whereas that of the counterion is only slightly higher than that of the free anion. The trend of the aggregation number (N^+) as a function of the concentration of **5** and **6** was fitted using the equation of the equal K indefinite model of association, leading to $\Delta G°_{298\,K}$ = −3.1 and −3.0 kcal mol^{-1}, respectively, for the formation of H-bonded dications. The critical role played by the protonated −NH unit in establishing hydrogen bonding was further supported by the detection of **6**$^+$**2** dinuclear species in acetonitrile-d_3 solutions containing equimolar mixtures of **2** and **6**. The self-aggregation free energy of **2** ($\Delta G°_{298\,K}$ = −3.1 kcal mol^{-1}) and **6**$^+$ ($\Delta G°_{298\,K}$ = −2.9 kcal mol^{-1}) in such mixed solutions is practically identical with those of **5** and **6** in acetonitrile-d_3.

$\Delta G°(298\ K) = -3.1$ Kcal/mol in acetonitrile-d_3

Hydrogen Bonding
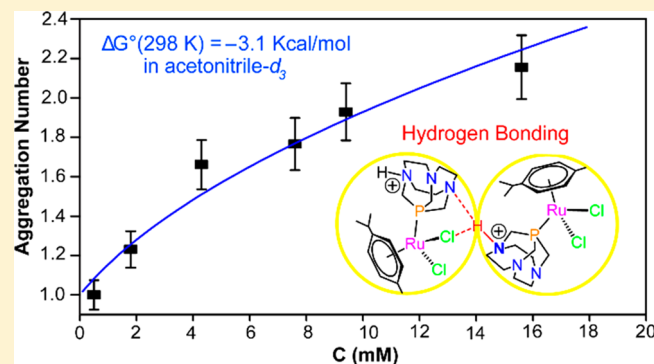
1. INTRODUCTION

Organometallic ruthenium complexes have attracted the attention of many research groups due to their great versatility and application in different fields such as catalysis, materials science, and biochemistry.[1,2] In particular, a widely used class of complexes is characterized by the presence of an η^6 metal-coordinated arene moiety and a piano-stool geometry, which endows the metal center with a wide range of applications.[3−5] Among the many stabilizing ligands, monodentate ligands containing P,N cages have been shown to give the complexes peculiar and tunable properties in terms of stability, reactivity, and solubility.[6] A well-known class of ruthenium(II) arene derivatives with these requisites, better known as RAPTA-type complexes (Chart 1),[7] is obtained in the presence of the cagelike aminophosphine PTA (1,3,5-triaza-7-phosphaadaman-

Chart 1. Sketches of RAPTA- and RACAP-Type Arene Derivatives
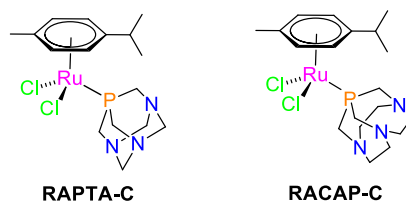
RAPTA-C   **RACAP-C**

tane),[8,9] and some of the corresponding complexes described in the literature were found to be active water-soluble catalysts in hydrogenation reactions[10] and very efficient anticancer agents.[11−13]

Recently, some of us reported the synthesis of ruthenium(II) *p*-cymene complexes bearing a higher homologue of PTA, namely 1,4,7-triaza-9-phosphatricyclo[5.3.2.1]tridecane ligand (CAP) (Chart 1), which showed interesting activities in homogeneous catalytic transfer hydrogenations[14] and in cytotoxicity studies against selected cancer cell lines.[15] Although CAP is structurally very similar to PTA, differing only in the presence of the nine-membered TACN (1,4,7-triazacyclononane) instead of triazacyclohexane in the lower rim of the cage, this modification brings about a different conformational behavior that is reflected in the reactivity and donor properties, in addition to unexpected NMR chemical shift values.[16,17] In contrast to the rigidity of the PTA ligand, CAP is characterized by a semiflexible cage with a fluxional geometry inversion driven by P⋯N and N⋯N intramolecular interactions, resulting in electron density accumulation at the center of the cage. Furthermore, the higher electron-donating ability of the phosphorus atom of CAP in comparison to PTA leads to a different reactivity toward oxidation, protonation, and methylation reactions of the free ligand.[16,17]

It is largely recognized that noncovalent interactions can play an important role in affecting the structure and reactivity of organometallic compounds.[18−21] NMR spectroscopy is considered the technique of choice to investigate the intermolecular interactions in solution, occurring in the second coordination sphere of organometallic complexes.[22−25] In particular, by combining NOE (nuclear Overhauser effect) and PGSE (pulsed field gradient spin−echo) NMR techniques, the formation and the nature of weak intermolecular interactions can be revealed.[26−28] The application of these techniques provided clear evidence for the formation of intermolecular adducts held together by ionic interactions,[29−31] hydrogen bonding,[32−35] halogen bonding,[36,37] π-stacking interactions,[38] and frustrated Lewis acid−base pairs,[39] whose structures were elucidated and correlated, in some cases, with their reactivity.[40−42]

It was demonstrated that the N functionalities in PTA complexes can be directly involved in intermolecular bond formation, acting as both HB acceptors[43,44] (HB = hydrogen bond) and HB donors on protonation.[45] Preliminary diffusion NMR studies indicate that RAPTA complexes can indeed undergo H-bonded driven self-aggregation in acetone.[46]

On the other hand, the behavior of RACAP derivatives toward self-aggregation is completely unexplored. In view of the important applications of RACAP complexes, we thought it of interest to assess such properties by diffusion NMR techniques and compare them to those of the analogous RAPTA complexes. A small library of Ru-CAP complexes (Chart 2), including the neutral RACAP-C (**2**), the ionic compounds $[RuCl(\eta^6\text{-}p\text{-cymene})(L)(CAP)](PF_6)$ (**3**, L = CAP; **4**, L = MeCN),[14,15] and the newly synthesized N-protonated derivative $[RuCl_2(\eta^6\text{-}p\text{-cymene})(CAP\text{-}H)](BPh_4)$ (**5**), was thus studied by diffusion NMR experiments and the results were compared to those obtained for RAPTA analogues (**1**, **6**). Due to the low stability of Ru-CAP complexes in acetone, which is usually the solvent of choice for these types of experiments on the basis of its polarity and aprotic nature, the experiments were carried out in acetonitrile-d_3. For comparison, $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PTA)]$ (**1**) and

Chart 2. Sketches of the Molecular Species Considered Herein

CAP   **1** (L = PTA)   **3** (L = CAP)
          2 (L = CAP)   **4** (L = MeCN)

5   **6**
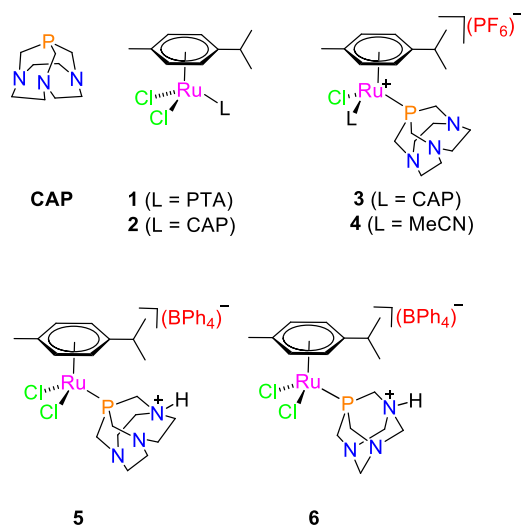
$[RuCl_2(\eta^6\text{-}p\text{-cymene})(PTA\text{-}H)](BPh_4)$ (**6**) were also investigated in acetonitrile-d_3. Interestingly, monoprotonated complexes **5** and **6** both exhibit a similar and marked tendency to form H-bonded dicationic species even in acetonitrile-d_3.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of Ruthenium Complexes. The synthesis of the cationic N-protonated complex $[RuCl_2(\eta^6\text{-}p\text{-cymene})(CAP\text{-}H)]Cl$ (**5**-Cl), the synthetic precursor of **5**, was at first attempted under the reaction conditions used to obtain the PTA analogue $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PTA\text{-}H)]Cl$:[46] i.e., by protonation of the neutral parent compound **2**[15] using a stoichiometric amount of aqueous HCl (0.1 M). By $^{31}P\{^1H\}$ NMR monitoring of the reaction at room temperature, incomplete conversion to **5**-Cl was observed, indicating that the chosen HCl concentration was not sufficient to obtain complete protonation. Thus, an excess (5 equiv) of HCl (1.0 M) was used. Under these conditions, complex **5**-Cl was obtained with complete conversion and was isolated after evaporation of water as a microcrystalline red powder. In contrast to the reactivity shown by the free ligand CAP, for which all three nitrogen atoms can be protonated under highly acidic conditions,[16] the protonation of the metal-coordinated phosphine seems to be less favored and, even in the presence of an excess of acid, only one nitrogen atom is protonated. **5**-Cl proved to be insoluble in chlorinated solvents and acetone but very soluble in water (S_{H_2O} = 74 g/L at 298 K). The $^{31}P\{^1H\}$ NMR spectrum of **5**-Cl in D_2O shows a singlet at 55.35 ppm, shifted slightly upfield in comparison to the neutral parent compound **2** (57.48 ppm in D_2O)[15] and in line with the values described for the ionic gold(I) CAP derivative $[(CAP\text{-}H_2)_3Au]^{7+}$ (50.99 ppm in D_2O).[16] In the corresponding ^1H NMR spectrum, the cage of the monoprotonated ligand $(CAP\text{-}H)^+$ maintains the same pattern of CAP, with a doublet centered at 4.02 ppm ($^2J_{HP}$ = 4.0 Hz) due to PCH_2N and a multiplet in the range 3.55−3.40 ppm due to N(CH_2)_2N of the lower rim, indicating a rapid proton exchange among all the N atoms. No substantial differences were noted in the $^{13}C\{^1H\}$ NMR spectrum with respect to **2**, with the exception of the signals due to carbon atoms of the cage at 50.29 ppm (d, $^1J_{CP}$ = 15.6 Hz) for PCH_2N

Table 1. Solvent, Concentration (C, mM), Average Self-Diffusion Coefficient ($D_t^{+/-}$, 10^{10} m^2 s^{-1}), Average Hydrodynamic Volume ($V_H^{+/-}$, Å^3), and Average Aggregation Number ($N^{+/-}$) of All Species at 298 K[a]

entry	species	solvent	C	D_t^+	D_t^-	V_H^+	V_H^-	N^+	N^-
1	CAP ($V_H^0 = 209$ Å^3)	acetone-d_6	8.0	22.9		220		1.05	
2		acetone-d_6	4.0	23.5		209		1.0	
3	1 ($V_H^0 = 483$ Å^3)	acetone-d_6[b]	16.0	13.4		579		1.20	
4		acetone-d_6[b]	7.4	14.0		539		1.10	
5		acetone-d_6[b]	0.9	14.8		496		1.00	
6		acetonitrile-d_3	7.5	14.5		536		1.11	
7		acetonitrile-d_3	3.0	14.9		508		1.05	
8		acetonitrile-d_3	0.8	15.2		490		1.02	
9	2 ($V_H^0 = 531$ Å^3)	acetone-d_6	3.1	15.1		534		1.01	
10		acetone-d_6	2.0	15.1		546		1.03	
11		acetone-d_6	0.6	15.1		541		1.02	
12		acetone-d_6	0.5	15.1		531		1.00	
13		acetonitrile-d_3	5.0	14.5		542		1.02	
14		acetonitrile-d_3	1.6	14.6		536		1.01	
15		acetonitrile-d_3	0.8	14.8		522		0.98	
16	3 ($V_H^0 = 918$ Å^3)	acetone-d_6	18.2	11.9	22.7	982	224	0.99	0.23
17		acetone-d_6	4.2	11.9	24.8	975	187	0.98	0.19
18		acetone-d_6	1.6	12.0	26.9	955	161	0.96	0.16
19		acetone-d_6	0.2	12.2	36.4	918	94	0.93	0.09
20	4 ($V_H^0 = 570$ Å^3)	acetone-d_6	11.4	13.7	25.0	687	185	1.07	0.29
21		acetone-d_6	4.0	13.7	24.9	689	177	1.07	0.28
22		acetone-d_6	0.45	14.8	28.1	570	148	0.89	0.23
23	5 ($V_H^{0+} = 546$ Å^3)	acetonitrile-d_3	15.6	10.7	13.7	1177	621	1.17	0.62
24		acetonitrile-d_3	9.4	11.4	14.0	1053	597	1.05	0.59
25		acetonitrile-d_3	7.6	11.5	14.0	964	590	0.96	0.59
26		acetonitrile-d_3	4.3	11.8	14.2	907	571	0.90	0.57
27		acetonitrile-d_3	1.8	13.3	14.5	672	547	0.67	0.54
28		acetonitrile-d_3	0.5	14.5	15.1	546	493	0.54	0.49
29	6 ($V_H^{0+} = 483$ Å^3)	acetone-d_6[b]	40	9.2	11.9	1194	660	1.3	0.7
30		acetone-d_6[b]	13	10.8	13.3	1003	546	1.0	0.6
31		acetone-d_6[b]	2.4	12.4	14.4	739	527	0.8	0.5
32		acetone-d_6[b]	0.47	14.7	15.0	517	487	0.5	0.5
33		acetonitrile-d_3	15.4	11.3	13.5	1017	647	1.08	0.69
34		acetonitrile-d_3	7.3	12.2	14.1	839	587	0.89	0.62
35		acetonitrile-d_3	1.0	14.5	15.2	548	483	0.58	0.51
36	5 ($V_H^{0+} = 546$ Å^3)	methanol-d_4/Acetonitrile-d_3	7.8	13.8	14.0	609	594	0.61	0.59
37		methanol-d_4/acetonitrile-d_3	1.7	14.4	14.0	555	595	0.55	0.59

[a]The standard propagation of error analysis provides an error of 3–4% on D_t and r_H values and 10–15% for V_H and N data. [b]Data from ref 46.

and 49.93 ppm (s) for N(CH$_2$)$_2$N, at variance with the pattern composed of a singlet at 51.10 ppm for N(CH$_2$)$_2$N and a doublet at 50.78 ppm for PCH$_2$N ($^1J_{CP}$ = 8.8 Hz) observed for **2**.[15] Further confirmation of the proposed formula of **5**-Cl was obtained by electrospray ionization mass spectrometry (ESI-MS) in acetonitrile, showing peaks at m/z 200.16 due to (CAP-H)$^+$ and at m/z 470.2 due to [RuCl(η^6-p-cymene)-(CAP)]$^+$, without patterns ascribable to bis-protonated CAP species.

The compound [RuCl$_2$(η^6-p-cymene)(CAP-H)](BPh$_4$) (**5**) was obtained as an orange solid by reacting **5**-Cl with a small excess of NaBPh$_4$ (1.6 equiv) in a EtOH/H$_2$O (16/1) mixture. Due to the presence of the hydrophobic anion, complex **5** is not soluble in water but it is soluble in DMSO, acetonitrile, and acetone. In the last solvent, **5** was observed to have little stability over time, with partial decomposition (ca. 30% based on ^{31}P{^{1}H} NMR) to unknown species after a few minutes of standing at room temperature. Complex **5** was characterized by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy in acetonitrile-d_3, showing a pattern similar to that of **5**-Cl. The counterion exchange from Cl$^-$ to BPh$_4^-$ was verified by the presence of three sets of signals in the ^{1}H NMR spectrum, in the range 7.27–6.85 ppm, integrating for 20 protons, in turn confirming the nature of **5** as a monoprotonated complex. The ^{13}C{^{1}H} NMR characterization was carried out in DMSO-d_6. Signals due to BPh$_4^-$ were detected as a quartet at 163.38 ppm ($^1J_{BC}$ = 49.3 Hz) due to

boron–carbon coupling and three singlets in the region 135.56−121.54 ppm.

To further validate the monocationic nature of **5**, conductivity measurements were also performed at room temperature. The conductivity of a solution of **5** in $CH_3CH_2NO_2$ (0.001 M) exhibited a value of 0.045 mS/cm, which is consistent with a monoprotonated species and similar to the value (0.065 mS/cm) obtained under the same conditions with the cationic complex **3**. For comparison, the complex $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PTA\text{-}H)](BPh_4)$ (**6**) was synthesized[46] and characterized in acetonitrile-d_3 by NMR spectroscopy. In this solvent, **6** shows a singlet at −25.56 ppm in $^{31}P\{^1H\}$ NMR spectrum, at a slightly shifted value in comparison to that observed in acetone-d_6 (−22.1 ppm). Other changes were observed in the ^1H NMR pattern, with PTA signals at δ_H 4.73 (s) and 4.29 ppm (s) due to NCH_2N and PCH_2N respectively, instead of the singlets at δ_H 5.16 and 4.58 ppm reported in acetone-d_6.

2.2. Diffusion PGSE NMR Measurements. Diffusion NMR spectroscopy is a powerful tool to detect the formation of supramolecular adducts in solution.[47−49] It is based on the measurement of the translational self-diffusion coefficient (D_t), which is related to the average hydrodynamic radius (r_H) of diffusing particles through the modified Stokes−Einstein equation (eq 1)

$$D_t = \frac{kT}{f_s c\pi\eta r_H} \tag{1}$$

where k is the Boltzmann constant, T is the temperature, f_s is the shape factor, c is a numerical factor, and η is the solution viscosity.[47,48] By assuming a spherical shape for the diffusing species, the experimental hydrodynamic volume (V_H) is obtained from r_H and, finally, the ratio between V_H and the volume associated with the single building block (V_H^0) provides an estimation of N (aggregation number).

For neutral complexes (**1**, **2**), V_H at the lowest concentration was assumed to be equal to V_H^0, whereas for the ionic complexes (**3**−**6**) the hydrodynamic volume of the ion pair (V_H^{IP0}) was considered as the sum of the volumes of the cation and anion (V_H^{0+} and $V_H^{0−}$, respectively). The $V_H^{0−}$ values are known from the literature ($V_H^{0−}(BPh_4^-) = 461$ Å^3 and $V_H^{0−}(PF_6^-) = 74$ Å^3),[30] while V_H^{0+} and V_H^0 volumes for CAP-based complexes were determined from low-concentration experiments, according to the literature.[50] The values of V_H^0 for complex **1** and V_H^{IP0} for species **6** are known from the literature.[46] The V_H^{0+} value of 546 Å^3 for **5** is in a good agreement with the value estimated for its corresponding neutral derivative **2** ($V_H^0 = 531$ Å^3), and the difference of 63 Å^3 in comparison to the homologue bearing the PTA ligand (**6**) is in line with the cage expansion due to the longer alkyl bridges in CAP. Moreover, replacment of one chlorine moiety with one CAP ligand as in the case of complex **3** leads to an increment of V_H^{0+} of about 370 Å^3, while the coordination of an acetonitrile molecule as in **4** is accompanied by an increment of only 24 Å^3.

Diffusion NMR spectroscopy was previously applied to study the self-aggregation behavior of Ru-arene RAPTA complexes in acetone-d_6.[46] For this reason, initial diffusion measurements were performed also for Ru-CAP complexes in acetone-d_6. However, due to the poor stability of Ru-CAP complexes in such a solvent, it was decided to use acetonitrile-d_3. This asked for a reinvestigation also of Ru-PTA complexes

in acetonitrile-d_3 for comparison. The results are summarized in Table 1.

Diffusion NMR measurements indicate that neutral complexes **1** ($N = 1.20/1.11$, entries 3−5 and 6−8 in Table 1) and **2** ($N = 1.03/1.02$, entries 9−12 and 13−15 in Table 1) do not show any tendency to self-aggregate in both acetone-d_6 and acetonitrile-d_3 (Table 1). At the same time, complexes **3** and **4** bearing PF_6^- are mostly present in solution as free ions, likely due to high relative permittivity of the used solvents. As a matter of fact, only a small increase in the V_H^+ and V_H^- values was observed by increasing the complex concentration (entries 16−19 and 20−22 in Table 1, respectively).

The self-aggregation tendency of **5** (Figure 1) and its PTA analogue **6** was studied in acetonitrile-d_3 ($\varepsilon_r = 37.5$), where
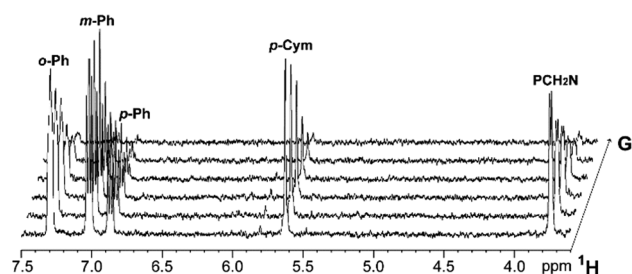

Figure 1. Attenuation of the intensity of NMR resonances of **5** as a function of applied gradient during a typical ^1H PGSE experiment in acetonitrile-d_3 at 298 K.

they exhibit a much higher stability (after 2 h, a period of time much longer than that of a typical PGSE experiment, only small signs of decomposition, amounting to less than 5% of the total concentration, were observed).

Complex **5** exhibits an increment of V_H^+ and V_H^- values as the concentration increases (from 0.5 to 15.6 mM), much more marked for V_H^+ (from 546 to 1177 Å^3, N^+ from 0.54 to 1.17) than for V_H^- (from 493 to 621 Å^3, N^- from 0.49 to 0.62) (Table 1 and Figure 2). Since the cation and the anion have almost the same hydrodynamic volume, $N^+ \approx N^- \approx 0.5$ is expected when free ions are mainly present in solution and somewhat higher and equal values approaching 1 when ion pairs become the dominant species. The observation of an unsymmetrical growth of N^+ and N^- with concentration, where N^- remains substantially constant (0.49−0.62), whereas N^+ increases from 0.54 up to 1.17, clearly indicates the formation of aggregates involving almost exclusively the cation.

An experimental trend similar to that of **5** was also observed for the PTA analogue **6** in acetonitrile-d_3, where the growth of N^+ is only slightly less accentuated, while the N^- versus C trends for the two complexes are very similar (Figure 2A and Table 1, entries 33−35). The aggregation tendency of the cations of **6** is slightly affected by solvent polarity in the expected way: in acetone-d_6 (Table 1, entries 29−32) the self-aggregation tendency is more accentuated than in the more polar solvent acetonitrile-d_3.[46] Overall, it can be stated that the self-aggregation motif of cations **5**$^+$ and **6**$^+$ in polar aprotic solvents, with relative permittivity up to 37.5, is the intercationic H bonding leading prevalently to dicationic + + species (and a small presence of + + − ion triples). In this respect, the presence of the N−H moiety is essential, since it acts as an HB donor to the two possible acceptors, i.e. Cl or N atoms, as described in our previous paper.[46] The key role played by the N−H moiety in the self-aggregation process is
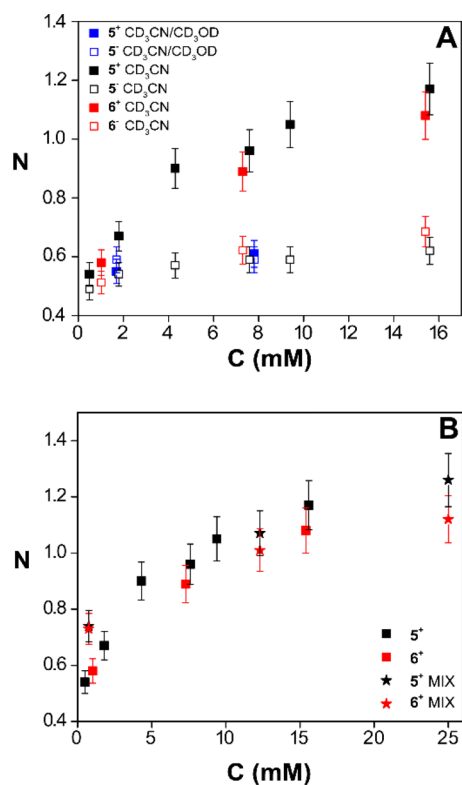
Figure 2. Trends of N^+ and N^- versus C for (A) complexes **5** and **6** in acetonitrile-d_3 and for **5** in a 50/50 acetonitrile-d_3/methanol-d_4 mixture at 298 K and (B) **5**$^+$ and **6**$^+$ in equimolar solutions of **5** and **6** in comparison to the independent aggregation trends of **5** and **6** in acetonitrile-d_3 at 298 K.

clearly indicated by the absence of any self-aggregation tendency of free ligand and the neutral complexes **1** and **2** and unprotonated complexes **3** and **4**.

In order to further confirm the role of hydrogen bonding, the aggregation tendency of complex **5** has been investigated in a 50/50 acetonitrile-d_3/methanol-d_4 mixture (Table 1, entries 36 and 37). Acetonitrile and methanol have similar relative permittivities, but the latter, being protic, should disfavor the intercationic H-bonding interactions. Consistently, under these experimental conditions, the aggregation tendency of cations is suppressed and N^+ and N^- values are substantially identical with those of N^- in pure acetonitrile-d_3 (Figure 2A). It is evident that the presence of a protic solvent, such as methanol, can interfere within the intermolecular interactions between the acceptor and donor moieties of cations, in line with previous results obtained for amino-acidate half-sandwich ruthenium(II) complexes in 2-propanol.[35]

Diffusion NMR experiments were also performed for equimolar mixtures of **5** and **6**, at different total ruthenium

concentrations in acetonitrile-d_3 at 298 K, in order to search for possible cation−cation recognition. The results are collected in Table 2. It is evident that the aggregation tendencies of cations **5**$^+$ and **6**$^+$ are both influenced by the presence of the other species. For example, at $[Ru]_{tot}$ = 12.3 mM the aggregation numbers of **5**$^+$ and **6**$^+$ are 1.07 and 1.01, respectively (Table 2, entry 2) and do not reflect their independent aggregation statuses at 6/7 mM solution, which are around 0.96 and 0.89, respectively (Table 1, entries 25 and 34, and Figure 2B). Instead the observed N^+ values for the **5**/**6** mixtures perfectly match with the general trends of N versus C (total) of **5** and **6** alone (Figure 2B). It is clear that there is not any sort of cation−cation recognition: the formation of mixed aggregates between **5**$^+$ and **6**$^+$ is as probable as that of the homoaggregates.

2.3. Determination of K and $\Delta G°_{298\,K}$. The thermodynamic parameters of the self-aggregation process were estimated by fitting the N versus C data with the equation of the *equal K* (EK) model of indefinite self-association.[30,51,48,52] The EK model assumes that the free energy ($\Delta G°_{298\,K}$) and equilibrium constants (K_e) of all associative steps of a monomer are ($K_1 = K_2 = ... = K_i = K_e$). Fittings for **5**$^+$ and **6**$^+$ are shown in Figure 3A, where N^+ values are derived by taking V_H^{0+} as the reference in order to correctly describe self-aggregation processes involving the cation as the monomer. The derived K_e values are very similar for both cations (Table 3), whereas the corresponding value of $\Delta G°_{298\,K}$ (ca. 3 kcal mol^{-1}) is consistent with the energy of an hydrogen bond in polar solvents.[35,53,54] The self-aggregation of **5**$^+$ and **6**$^+$ necessarily implies that the cations act as both HB donors and HB acceptors. Whereas the function of an HB-donor is exclusive of **5**$^+$ and **6**$^+$, among the studied species, neutral complexes **1** and **2** should act as even better HB acceptors than the cationic species because cation−cation repulsion interactions are avoided and a slightly higher basicity of N and Cl centers is expected.

For these reasons, the aggregation tendency of neutral species in the presence of a protonated complex was investigated as a function of the concentration, in acetonitrile-d_3 at 298 K (Table 4). The best cationic/neutral species combination was found in **6**$^+$/**2** species because (1) complex **6** exhibited an excellent stability in acetonitrile-d_3 and (2) the **6**$^+$/**1** mixture shows a single set of resonances in the ^{1}H NMR spectrum and only one resonance in the ^{31}P{^{1}H} NMR spectrum (at δ_P −32.1 ppm, while those of **1** and **6** fall at δ_P −36.3 and −25.6 ppm, respectively), suggesting a fast proton exchange on the chemical shift NMR time scale between the neutral and protonated species. In contrast, the ^{1}H NMR spectrum of **2** and **6**$^+$ mixtures showed two separate sets of resonances and offers the possibility to follow the signal attenuations of the individual species during PGSE experi-

Table 2. Average Self-Diffusion Coefficient ($D_t^{+/-}$, 10^{10} m^2 s^{-1}), Average Hydrodynamic Volume ($V_H^{+/-}$, Å^3), and Average Aggregation Number ($N^{+/-}$) for 5$^+$, 6$^+$, and BPh$_4^-$ in Acetonitrile-d_3 at 298 K as a Function of Total Ruthenium Concentration Obtained from the Mixture of Complexes 5 and 6^a

entry	C_{tot}	$D_t^+(5^+)$	$D_t^+(6^+)$	D_t^-	$V_H^+(5^+)$	$V_H^+(6^+)$	V_H^-	$N^+(5^+)$	$N^+(6^+)$	N^-
1	25.0	10.4	11.1	13.6	1265	1057	639	1.26	1.12	0.64
2	12.3	11.0	11.6	13.7	1077	951	622	1.07	1.01	0.62
3	0.76	12.7	13.2	14.6	747	687	538	0.74	0.73	0.53

^{a}The standard propagation of error analysis gives a standard deviation of 3-4% on D_t and r_H values and 10−15% for V_H and N data.
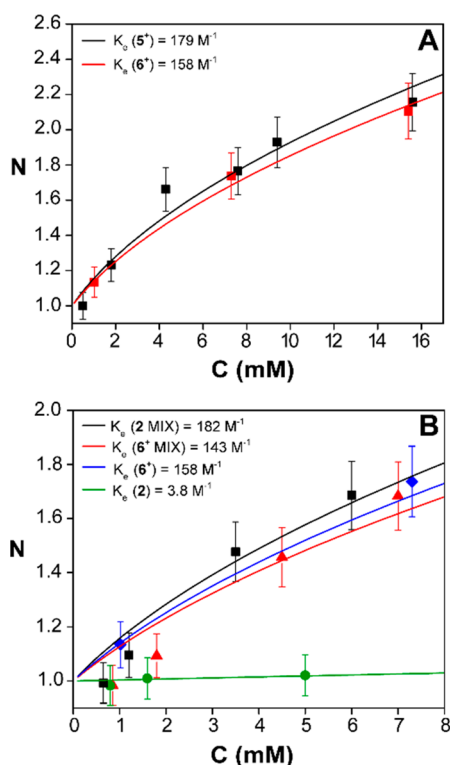
Figure 3. Fittings of N versus C experimental data (in acetonitrile-d_3 at 298 K) of (A) cations 5^+ (black squares and black line) and 6^+ (red squares and red line) and (B) **2** and 6^+ (black squares and red triangles, respectively) of a mixture of **2** and **6** (nominal concentrations) compared to the independent aggregation trends of **2** and 6^+ (green circles and blue diamonds, respectively) with the EK model.

Table 3. Equilibrium Constants (K_e, M^{-1}) and Corresponding Free Energy Values at 298 K ($\Delta G°$, kcal mol^{-1}) for 5^+, 6^+, and 2

	K_e	$\Delta G°_{298\,K}$
5^+	179 ± 31	−3.1 ± 0.7
6^+	158 ± 22	−3.0 ± 0.5
6^+ (mix)	143 ± 32	−2.9 ± 0.7
2 (mix)	182 ± 33	−3.1 ± 0.5

ments as a function of total ruthenium concentration. Experimental results are collected in Table 4.

At the highest concentration value, **2** exhibited V_H = 895 Å^3, which, divided by the volume of the single complex (531 Å^3), provided an aggregation number of 1.69 (entry 1 in Table 4 and Figure 3B). The latter value is much higher than that observed for the solution of **2** in acetonitrile-d_3 (N = 1.02 at

[**2**] = 5.0 mM, Table 1, entry 13), revealing that **2** is deeply involved in the formation of mixed aggregates with 6^+, reasonably acting as an HB acceptor. Clearly, the observed N^+ value for **6** is little affected by the presence of **2** (Table 1 entries 33−35, and Figure 3B), since it makes little difference having a dicationic dinuclear 6^+6^+ or a monocationic dinuclear 6^+2 species, from a hydrodynamic dimension point of view. Quantification of K and $\Delta G°_{298\,K}$ by fitting the N versus C trends consistently provides the same values, within the experimental error, as those obtained in experiments with **6** alone (Table 3). Attempts to detect intermolecular NOE contacts between **2** and 6^+ by means of NOESY NMR spectroscopy were unfortunately unsuccessful, probably due to the low maximum concentrations reachable for the species under observation (6.0 and 7.0 mM, respectively) and the extensive overlapping of diagnostic resonances associated with the p-cymene moiety. Nevertheless, all of the diffusion NMR results coherently point toward the critical role of HB intermolecular interactions in determining the self-aggregation of two cations or of a cation and a neutral species in acetonitrile-d_3.

CONCLUSIONS

The present study shows that protonated RACAP- and RAPTA-type complexes have a remarkable tendency to form dications through intercationic HBs (Chart 3a), also in a polar

Chart 3. Sketch of the Dinuclear Dicationic (a) and Monocationic (b) H-Bonded Species, as Deduced by Diffusion NMR Spectroscopy
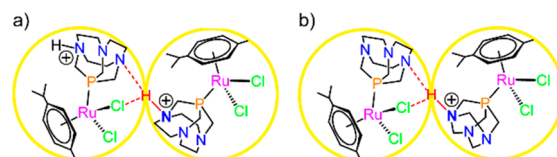
solvent such as acetonitrile. The self-aggregation free energy is small ($\Delta G°_{298\,K}$ = −3.0/−3.1 kcal mol^{-1}) and readily evaluable by diffusion NMR techniques. These indicate that the intercationic hydrogen bonding is not selective, in that mixed aggregates do form when both protonated RACAP and RAPTA complexes are contemporarily present in acetonitrile solution. At the same time, the propensity of such protonated species to act as HB donors was demonstrated also by the observation of dinuclear monocationic species between monoprotonated RAPTA and neutral RACAP species (Chart 3b).

Weak intercationic interactions have been previously observed in half-sandwich ruthenium(II) complexes,[50,29,32,55] mostly leading to ionic aggregates in which the anions are

Table 4. Average Self-Diffusion Coefficient ($D_t^{+/−}$, 10^{10} m^2 s^{-1}), Average Hydrodynamic Volume ($V_H^{+/−}$, Å^3), and Average Aggregation Number ($N^{+/−}$) for 2, 6^+, and BPh$_4^−$ in Acetonitrile-d_3 at 298 K as a Function of Total Ruthenium Concentration Obtained from a Mixture of Complexes 2 and 6^a

entry	C_{tot}	C(**2**)	C(**6**)	D_t(**2**)	D_t^+(6^+)	$D_t^−$	V_H(**2**)	V_H^+(6^+)	$V_H^−$	N(**2**)	N^+(6^+)	$N^−$
1	13.0	6.0	7.0	11.9	12.3	14.3	895	813	571	1.69	1.68	1.17
2	8.0	3.5	4.5	12.1	12.7	14.2	784	704	530	1.48	1.46	1.09
3	3.0	1.2	1.8	12.8	13.3	13.8	582	528	485	1.10	1.09	1.00
4	1.5	0.65	0.85	13.0	13.6	13.6	527	475	478	0.99	0.98	0.98

^{a}The standard propagation of error analysis gives a standard deviation of 3-4% on D_t and r_H values and 10−15% for V_H and N data.

directly involved, and in palladium phenanthroline complexes, exhibiting extended $\pi-\pi$ interactions.[38] To the best of our knowledge, this study represents the first case in which a purely dicationic species held together by HBs has been detected in acetonitrile, once again demonstrating that outer (or second coordination)-sphere interactions might be established even when they are rather unexpected.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00703.

> General methods and materials, synthetic details, selected NMR and ESI-MS spectra, and PGSE NMR experiments (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for A.G.: antonella.guerriero@iccom.cnr.it.
*E-mail for A.M.: alceo.macchioni@unipg.it.

ORCID Ⓘ

Cristiano Zuccaccia: 0000-0002-9835-2818
Luca Gonsalvi: 0000-0002-5996-6307
Alceo Macchioni: 0000-0001-7866-8332

Notes

The authors declare no competing financial interest.

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