# C–H···π hydrogen bonding *vs*. anion complexation in rhodium(I) complexes of cyclotriveratrylene

Kirsty S. B. Hancock and Jonathan W. Steed*†

Department of Chemistry, King's College London, Strand, London, UK WC2R 2LS

The bimetallic rhodium(I) complex [{Rh(nbd)}₂(CTV)]-[BF₄]₂ exists as an infinite self-included chain in the solid state with intracavity CH···π interactions linking the inclusion polymer together; the analogous monometallic complex co-crystallises with the dinuclear species as an inclusion compound with acetone as the guest.

In the past decade the topic of supramolecular anion complexation has received ever increasing attention as a consequence of the relatively challenging and hitherto unexplored nature of the field.[1–5] This culminated last year in the publication of the first book dealing solely with the area.[6] The key to the production of useful anion hosts for applications in areas such as environmental and biochemical sensors, and in bulk waste remediation is the selectivity of the host for a given anionic guest (*e.g. in vivo* sensing of Cl⁻ [3] or monitoring the environmental levels of nutrients such as phosphates and nitrate[2,6]). Our initial approach to this problem has been based upon a simple consideration of electrostatic attraction of the anion to the site of greatest positive charge density on a host mediated by the steric requirements of this cationic binding pocket. The host is thus selective for anions possessing the most complementary size and symmetry match to the host binding pocket since it is these anions which are able to make the closest approach to the host positive charge. This simple concept has been demonstrated by the synthesis of organometallic hosts **1**[7,8] and **2**[9,10] in which the calix[4]arene[11]
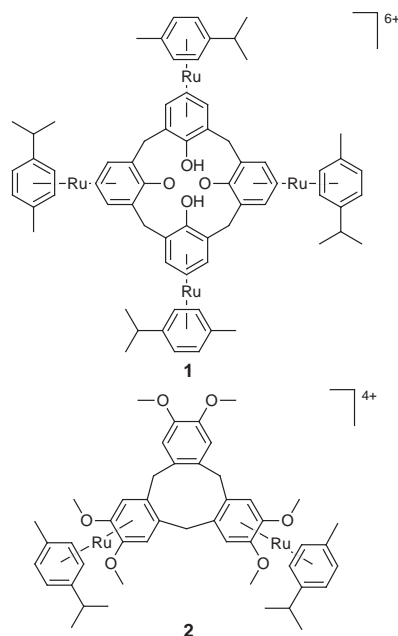

or cyclotriveratrylene (CTV)[12] cavities have been shown by X-ray crystallography to be occupied by tightly fitting anionic guests. In the case of host **1** the crystallographically demonstrated poor fit of I⁻ is borne out by ¹H NMR titration results in

solution which give binding constants in aqueous solution decreasing in the order Cl⁻ > Br⁻ > I⁻.[7] The selectivity of hosts such as **1** and **2** is reduced however, as a consequence of their multiply charged nature in as much as the host cavity is not the only site available for anion binding. Host **1** in particular binds up to five additional anions outside the host cavity. We now report preliminary results in a programme of research designed to reduce the overall host charge, in the anticipation of thus increasing host selectivity.

The synthesis of monocationic complexes of type '(arene)-Rh(diene)' [arene = benzene, xylenes, hexamethyl benzene *etc.*, diene = norbornadiene (nbd) or cyclooctadiene] was reported by Green and Kue in 1972[13] starting from the [Rh(diene)₂]⁺ **3** cations. Complexes of type **3** are relatively tedious to prepare, however, and we accordingly adopted the simpler procedure of direct reaction of [{Rh(nbd)Cl}₂] **4**[14] with CTV in CH₂Cl₂–acetone in the presence of 2 equiv. of Ag[BF₄]. After removal of precipitated AgCl this resulted in a clear yellow solution from which the complexes [Rh(η⁴-nbd)(η⁶-CTV)][BF₄] **5** and [{Rh(η⁴-nbd)}₂(η⁶ : η⁶-CTV)][BF₄]₂ **6** were obtained upon evaporation of the bulk of the solvent. Compounds were characterised by FABMS and ¹H NMR spectroscopy.

Crystals suitable for X-ray crystallography were prepared by slow diffusion of diethyl ether into an acetone solution of complex **6** over a period of *ca.* three weeks. Surprisingly, during the course of the crystal growth, partial solvolysis of **6** to give **5** occurred such that a co-crystallised product of formula [Rh(η⁴-nbd)(η⁶-CTV)][BF₄]·[{Rh(η⁴-nbd)}₂-(η⁶ : η⁶-CTV)][BF₄]₂·0.5 Me₂CO was eventually isolated. This fortuitous circumstance resulted in structure determinations (at −150 °C) for both **5** and **6** in the same experiment, Fig. 1.‡ Strikingly, the structure reveals that for **6**, in contrast to a wide range of bimetallic complexes related to the tetracation **2**,[10] the CTV cavity in **6** is not occupied by one of the BF₄⁻ anions. Instead **6** forms an inclusion polymer in which the norbornadiene ligand of one dicationic molecule engages in two short chelating, C–H···π hydrogen bonding interactions with the CTV carbon atoms C(3A) and C(4A) of the ring attached to Rh(1A); distances C(13A)···C(3A) 3.431(14), C(10A)···C(4A) 3.451(14), H(13A)···C(3A), 2.99, H(10A)···C(4A) 3.00 Å (C–H bond lengths normalised to 0.95 Å), Fig. 2. This may be compared to H···C distances in the range 2.73–3.05 Å recently reported for the organic system 2,3,7,8-tetraphenyl-1,9,10-anthyridine·toluene[15] in which there is much less steric hindrance at the arene (enabling a short C–H···π-centroid interaction), and falls well within the range associated with carbon acid hydrogen bonding interactions.[16,17] The observation of short intermolecular contacts alone does not however, necessarily mean an attractive intermolecular interaction. However, in this case the hydrogen bond acid–base complementarity between the donor and acceptor is clearly evident. Increased acidity of alkenes upon coordination to a metal centre arises from delocalisation of the metal positive charge, while it is the carbon atoms adjacent to the electron donating methoxy substituents which are the most electron rich on the CTV framework.

This result may be compared to the inclusion of iron(II) cations of type [Fe(arene)(Cp)]⁻¹ by free CTV recently
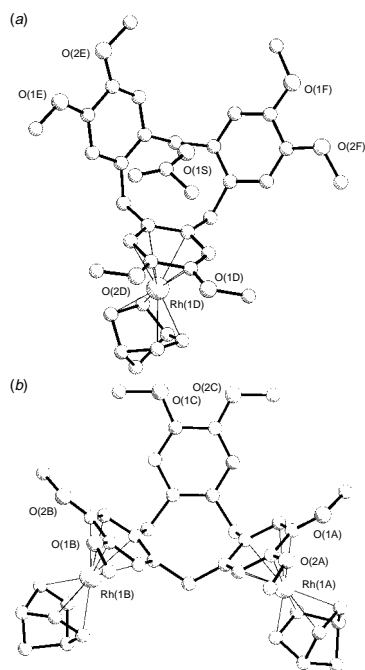
Fig. 1 (*a*) The monometallic and (*b*) bimetallic CTV based host complexes found in the structure of $[Rh(\eta^4\text{-nbd})(\eta^6\text{-CTV})][BF_4]\cdot[\{Rh(\eta^4\text{-nbd})\}_2(\eta^6:\eta^6\text{-CTV})][BF_4]_2\cdot0.5Me_2CO$
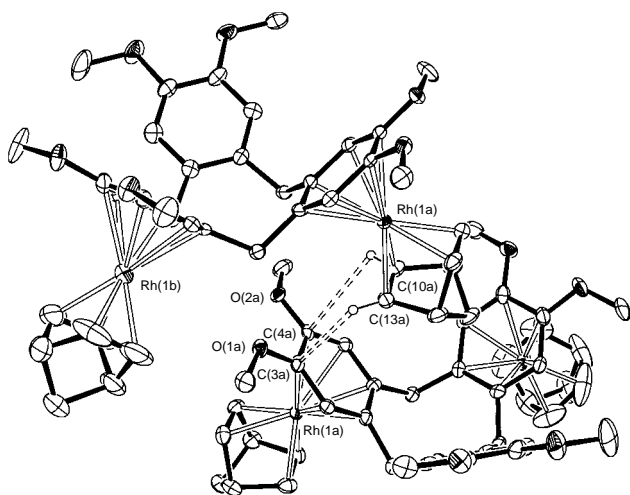
Fig. 2 C–H···π hydrogen bonding in the bimetallic complex **6**

reported by us,[18] in which shortest cyclopentadiene to CTV C···C contacts range from 3.44 to 3.59 Å depending on the identity of the arene. Curiously, however, in **6** it is the metallated ring attached to Rh(1A) which interacts with the C-acid guest. In contrast to compounds such as **2**, back bonding from the Rh^I centre will render the metalated CTV rings relatively electron rich, and it is presumably for this reason that intracavity anion binding is not observed in this case, in contrast to all other such systems with more than one metal centre.[2,7–10,19] However, the metallated ring should not be as electron rich as the free ring C(1C)–C(6C) and it seems that stacking of the anions external to the cavity around the two stacked Rh centres is maximised by the observed inclusion arrangement. This results in a short C(2A)–H···F(1A) contact; C(2A)···F(1A) 3.148(12) Å. Hence, it is clear that the electro-static forces between cations and anions and the chelating C–H···π hydrogen bonding interactions act synergically.

The structure of the co-crystallised molecule of **5** is of the solvent-inclusion type, with the CTV cavity being occupied by a partial molecule of acetone, the crystals apparently having undergone some desolvation even at the very low temperature of the experiment. The acetone is approximately parallel with the metallated ring C(1D)–C(6D) with guest–host contacts in the range 3.4–4.0 Å.

The fact that no intracavity anion inclusion by even the bimetallic host **6** is observed in the solid state correlates with its anion binding ability in solution. Addition of 10 mol equiv. of $[NBu^n_4]I$ to a sample of **6** in $(CD_3)_2CO$ resulted in no change whatsoever in its ^1H NMR spectrum. This contrasts to the tetracationic ruthenium species **2** in which a similar experiment results in chemical shift changes of 0.89 ppm for the protons of the CTV rings.[20] In an attempt to estimate the strength of the double C–H···π interaction in solution, the ^1H NMR spectrum of **6** was monitored at a variety of concentrations from 0.02 to 0.002 M. This did result in slight downfield shifts (*ca.* 0.1 ppm) for the resonances assigned to the protons of the CTV rings, suggesting some degree of self-association. However, similar changes were also noted upon addition of excess $[NBu^n_4][BF_4]$ and hence this is probably not representative of significant C–H···π interactions in solution.

Notes and References

1 K. T. Holman, J. L. Atwood and J. W. Steed, in *Advances in Supramolecular Chemistry, vol. 4*, ed. G. W. Gokel, JAI Press, London, 1997, pp. 287–331.
2 J. L. Atwood, K. T. Holman and J. W. Steed, *Chem. Commun.*, 1996, 1401.
3 P. D. Beer, *Chem. Commun.*, 1996, 689.
4 B. Dietrich, *Pure Appl. Chem.*, 1993, **65**, 1457.
5 M. M. G. Antonisse and D. N. Reinhoudt, *Chem. Commun.*, 1998, 443.
6 *Supramolecular Chemistry of Anions*, ed. A. Bianchi, K. Bowman-James and E. Garcia-Espana, Wiley–VCH, New York, 1997.
7 M. Staffilani, K. S. B. Hancock, J. W. Steed, K. T. Holman, J. L. Atwood, R. K. Juneja and R. S. Burkhalter, *J. Am. Chem. Soc.*, 1997, **119**, 6324.
8 J. W. Steed, R. K. Juneja and J. L. Atwood, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2456.
9 K. T. Holman, M. M. Halihan, J. W. Steed, S. S. Jurisson and J. L. Atwood, *J. Am. Chem. Soc.*, 1995, **117**, 7848.
10 A. B. Mitchell, J. W. Steed, K. T. Holman, M. M. Halihan, J. Montgomery, S. S. Jurisson, J. L. Atwood and R. S. Burkhalter, *J. Am. Chem. Soc.*, 1996, **118**, 9567.
11 C. D. Gutsche, *Calixarenes*, ed. J. F. Stoddart, Royal Society of Chemistry, Cambridge, 1989.
12 A. Collet, *Tetrahedron*, 1987, **43**, 5725.
13 M. Green and T. A. Kuc, *J. Chem. Soc., Dalton Trans.*, 1972, 832.
14 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 4735.
15 N. N. L. Madhavi, A. K. Katz, H. L. Carrell, A. Nangia and G. R. Desiraju, *Chem. Commun.*, 1997, 1953.
16 G. R. Desiraju, *Acc. Chem. Res.*, 1996, **29**, 441.
17 M. J. Zaworotko, *Chem. Soc. Rev.*, 1994, **23**, 283.
18 K. T. Holman, J. L. Atwood and J. W. Steed, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1736.
19 J. W. Steed, P. C. Junk, J. L. Atwood, M. J. Barnes, C. L. Raston and R. L. Burkhalter, *J. Am. Chem. Soc.*, 1994, **116**, 10 346.
20 M. Staffilani, G. Bonvicini, J. W. Steed, K. T. Holman, J. L. Atwood and M. R. J. Elsegood, *Organometallics*, 1998, **17**, 1732.