Anion complexation *via* C–H···X interactions using a palladacyclic receptor†

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Received (in Cambridge, UK) 31st January 2008, Accepted 20th March 2008
First published as an Advance Article on the web 23rd April 2008
DOI: 10.1039/b801823e

A novel organometallic receptor binds anions in solution and in the solid state, with complexes stabilised through a series of C–H···X interactions, as evidenced by ^{1}H NMR spectroscopy, X-ray crystallography and computational models.

Although the C–H···X hydrogen bond (where X is any acceptor atom) is generally accepted as an important weak interaction in the solid state,[1] there are relatively few examples of synthetic supramolecular host–guest complexes that are stabilized by such interactions in solution.[2–4] While some of these complexes involve a combination of various H-bonding interactions,[3] others have the C–H···X interaction as the sole H-bonding motif,[4] with the majority of these multiply charged imidazolium systems.[4c,d] Here we report a novel anion receptor incorporating a cationic organometallic palladacycle and present evidence for it binding various anions in solution *via* concerted C–H···X hydrogen bonding interactions.

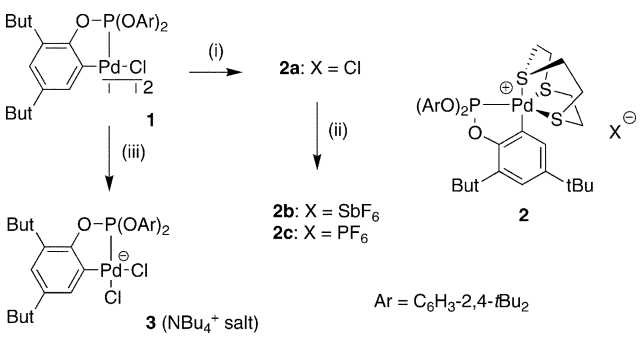
As part of our interest in five-coordinate palladium(II) complexes with orthometallated triaryl phosphite ligands, and the effect that this coordination mode has on the bonding of the cyclometallated ligand,[5] the palladacycle **1** was treated with two equivalents of the macrocycle 1,4,7-trithiacyclononane ([9]aneS_3) in dichloromethane. This led to the formation of the chloride salt of five-coordinate palladacycle **2**, complex **2a**, in good yield. The chloride counter-anion can be readily replaced by SbF_6^- or PF_6^- by salt metathesis to give complexes **2b** and **2c** (Scheme 1).

The crystal structure of complex **2b**‡ (see ESI†) shows the five-coordinate palladium cation interacting with the SbF_6 counter-anion through a series of C–H···F interactions from the methylene protons on the [9]aneS_3 ligand.

The ^{31}P NMR spectra of the complexes in $CDCl_3$ reveal that the P-donors are in essentially identical environments in all three cations (δ(^{31}P) 132.1, 131.8 and 130.8 for **2a–c**, respectively) and the corresponding ^{1}H NMR spectra show two signals for the methylene protons associated with the coordinated [9]aneS_3 ligand (*e.g.* **2b**: 2.60 ppm and 2.98 ppm), each integrating to six protons. The upfield and downfield environments observed in each case correspond to the *exo* and *endo* protons of the [9]aneS_3 ring, respectively (confirmed by NOE experiments) with the apparent equivalence of all the protons in each environment due to rapid interchange of the S-donor sites.

One important difference observed between the spectra of the complexes in $CDCl_3$ is that whereas the signals for both the *exo* and *endo* [9]aneS_3 protons of **2b** match those of **2c** (*i.e.* **2c**: 2.59 ppm and 2.97 ppm, respectively), in the case of **2a**, the *endo* proton signal is shifted significantly downfield (2.51 ppm and 3.62 ppm, respectively). This suggests that only in the chloride complex is there a pronounced interaction in solution between the anion and cation, with the chloride small enough to be located in the cavity formed by the metal-bound [9]aneS_3 ring. Further support for such an interaction was garnered by examining the effect of adding aliquots of $Bu_4N^+Cl^-$ to a solution of **2b** in $CDCl_3$ (*ca.* 20 mM), which induced a significant downfield shift in the *endo* proton signal, until with a slight excess of guest, the NMR spectrum resembled that of **2a**. A similar effect was found upon the addition of Bu_4NBr or Bu_4NI to **2b**. Job plots confirmed the binding stoichiometry as 1 : 1 (Fig. 1).

These data are consistent with the formation of a 1 : 1 complex between the cationic complex **2**§ and halide guests, **Hal**$^-$, with each anion situated in the cavity formed by the



Scheme 1 *Reagents and conditions*: (i) [9]aneS_3, CH_2Cl_2, r.t., 1 h; (ii) $AgSbF_6$ or NH_4PF_6, CH_2Cl_2, r.t., 1 h; (iii) Bu_4NCl, CH_2Cl_2 r.t., 1 h.

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† Electronic supplementary information (ESI) available: Experimental procedures, X-ray data for complexes **2b** and **2d**, NMR binding data and vapour pressure osmometry experiments. CCDC 662914 and 662915. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b801823e

Pd-bound macrocycle (Scheme 2) and acting as an H-bond acceptor to the six *endo* protons of the [9]aneS$_3$ ligand.¶

The titration experiments indicated that the binding strength followed the trend $Cl^- > Br^- > I^-$. A slight dissociation of the macrocycle from the chloride complex in $CDCl_3$ (*vide infra*) precluded the accurate determination of its binding constant in this solvent. However, this effect was much less marked for bromide and was not observable with iodide, allowing a binding constant with I^- to be determined as $K = 2.2 \times 10^3\ M^{-1}$ (±10%) (see ESI†).

The partial dissociation of the chloride complex **2a** in $CDCl_3$ was revealed by the appearance of signals for free [9]aneS$_3$, with the ratio of free to coordinated ligand at 25 °C approximately 15 : 85 ([**2a**] = 38 mM). Furthermore, the ^{31}P NMR spectrum of this solution showed an additional small singlet at 124.0 ppm, corresponding to the complex **3**, which could also be made directly from **1** (Scheme 1). However in the presence of a slight excess (1.25 equiv.) of [9]aneS$_3$, **2a** was observed as the sole phosphorus containing species in solution. The extent of dissociation was also increased slightly by dilution and by changing the solvent to CD_3CN. These findings indicate that **2a** is in equilibrium with species **2** and **3** in solution, as shown below in Scheme 3.

Complex **2d**, which consists of cation **2** and its counter-anion **3**, could be made in excellent yield by the addition of one equivalent of [9]aneS$_3$ to the dimer **1** in benzene. Whereas in $CDCl_3$, the complex is dissociated to some extent, its ^1H NMR spectrum in C_6D_6 ([**2d**] = 28 mM) gives rise to one set of signals, with the *endo* proton signal shifted downfield compared to **2b** in the same solvent (3.51 ppm *vs.* 2.66 ppm, respectively). This data is consistent with a strong pairing interaction between **2** and **3** in this solvent. As anticipated, its crystal structure‡ consists of an H-bonded complex between **2** and **3**, but with two identical units of each species in the unit cell, assembled in a tetrameric array (Fig. 2).

The two metal-bound chlorides on each molecule of **3** are oriented towards a proximate [9]aneS$_3$ ligand of one of the five-coordinate cations. Each chloride forms three hydrogen bonds with separate *endo* hydrogens on this ligand, while both chlorides in the same complex form close contacts with one *endo* hydrogen of the more remote [9]aneS$_3$. The fact that the close contacts occur with only the *endo* protons is consistent

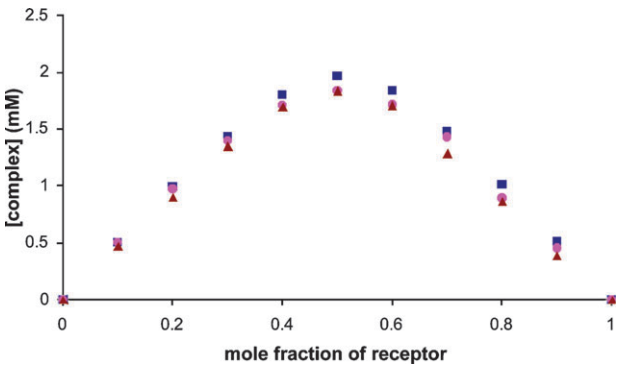
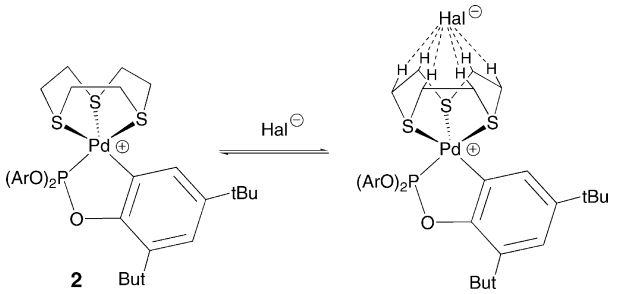


Fig. 1 ^1H NMR Job plots in $CDCl_3$ for **2b** and Bu_4NBr (total conc. = 5.17 mM, blue squares), Bu_4NI (total conc. = 5.07 mM, pink circles) and Bu_4NCl (total conc. = 4.75 mM, brown triangles).

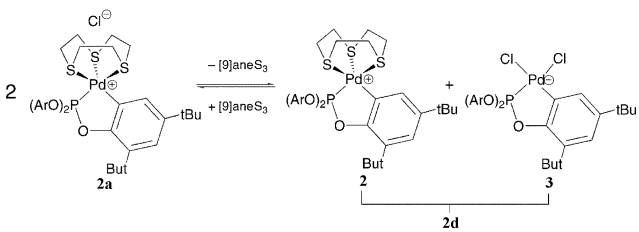


Scheme 2 Complexation of halide ions, **Hal**$^-$ by cation **2** (initial counter-ion is SbF_6, complex **2b**).

with the observation from the NMR studies that only the signal from these protons is affected by complexation. The range of Cl···H distances in **2d** (2.55–2.95 Å) fall within the sum of the van der Waals radii and can be considered as weak hydrogen bonds.[1] The extent of aggregation of complex **2d** in solution was investigated by vapour pressure osmometry (see ESI†) in benzene solution, which indicates that in solution, it is the ion-pair dimer that predominates in solution, rather than the tetramer.

In order to test whether the close Cl···H contacts in the X-ray structure of **2d** were indeed genuine interactions rather than a consequence of crystal packing, the core complex (*i.e.* a dimer with the two uncoordinated aryl groups and the two *t*Bu groups on the coordinated aryl of each ion replaced with hydrogens) was optimised using the Guassian03 program,[6] LANL2DZ[7] basis and MPW1PW91[8] functional. The resulting complex retained the close contacts between chloride and the *endo* C–H protons, with three such contacts being less than 2.5 Å, which in fact are closer than those observed in the X-ray structure.‖ Alternative arrangements of the anion **3** with respect to cation **2** that would rely on through space interactions alone were then optimised. However even though shorter Pd–Pd and Pd–Cl distances were observed in some cases, all complexes optimised with a higher energy overall. Thus it would appear that there is an attractive interaction local to the close C–H···Cl contacts that helps to stabilise the complex **2d**. Although these contacts fall comfortably within the sum of the van der Waals radii, the calculated change in C–H bond length in **2d** compared to **2** alone is very small (increasing by an average of 0.002 Å for each of the three sub 2.5 Å contacts), which is consistent with C–H···X H-bonding interactions being relatively weak.

In summary, these studies indicate that the new cationic palladium-containing thiacrown species **2** is able to complex various anions in solution, which appear to be mediated by C–H···X H-bonds. Complexation of either free halides



Scheme 3 Equilibrium between complexes **2a** and **2d** in solution.

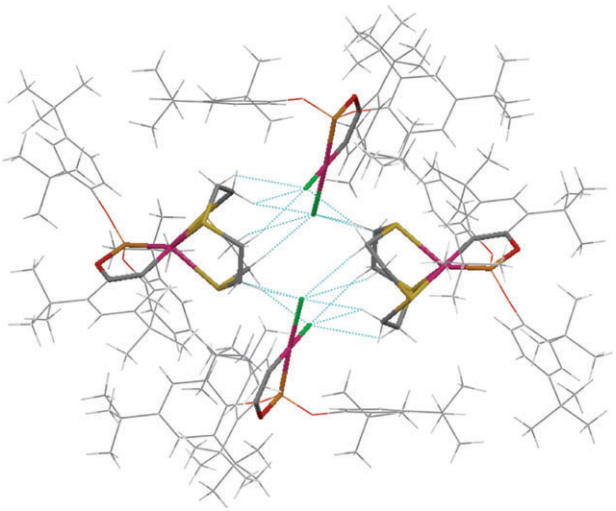


Fig. 2 Crystal structure of complex **2d** showing the tetranuclear motif supported by hydrogen bonds between chlorides and [9]aneS_3.

(*i.e.* Cl^- in **2a**), or metal-bound halides (in the form of the palladium dichloride complex **3**) can occur, and in the latter case, such an interaction is supported by crystallographic and modelling studies. It appears that the Pd(II) centre plays an important role in the anion binding process; firstly to pre-organize six of the methylene protons on the [9]aneS_3 ring in a convergent manner and secondly to render them sufficiently acidic (partially through the effect of the metal charge) so that they are effective H-bond donors in solution. We anticipate that the coordinated thiaazacrown motif has considerable promise in the development of novel H-bonding tectons and receptors for crystal engineering and supramolecular chemistry, respectively.

We thank the EPSRC for funding and for the provision of an Advanced Research Fellowship (R. B. B.), the RSC for the provision of the Sir Edward Frankland Fellowship (R. B. B.) and Johnson Matthey for the loan of palladium salts.

Notes and references

‡ *Crystal data*: Complex **2b**: $[C_{42}H_{68}O_3PPdS_3]SbF_6{\cdot}4C_6H_6$, λ = 0.71073 Å, space group $P\bar{1}$, a = 12.32(2), b = 12.719(13), c = 22.10(5) Å, α = 83.91(11), β = 79.8(2), γ = 78.56(8)°, V = 3332(10) Å^3, Z = 2, μ = 0.853 mm^{-1}, 73574 data were collected of which 15255 were independent. The structure was refined on F^2 to give $R1$ = 0.0757 ($F^2 > 2\sigma(F^2)$) and $wR2$ (all data) = 0.1868. CCDC 662914.
Complex **2d**: $[C_{42}H_{63}Cl_2O_3PPd][C_{48}H_{74}O_3PPdS_3]{\cdot}CD_3CN$, λ = 0.71073 Å, space group $P\bar{1}$, a = 15.297(4), b = 18.455(4), c = 19.724(7) Å, α = 108.554(19), β = 107.430(19), γ = 98.853(15)°, V = 4842(2) Å^3, Z = 2, μ = 0.572 mm^{-1}, 36518 data were collected of which 21041 were independent. The structure was refined on F^2 to give $R1$ = 0.0549 ($F^2 > 2\sigma(F^2)$) and $wR2$ (all data) = 0.1259. CCDC 662915.
§ A weak H-bonding interaction between the SbF_6 anion and receptor **2** in solution cannot be ruled out, although an NMR dilution experiment on **2b** (20 mM to 1 mM) in $CDCl_3$ gave no evidence for such an interaction.
¶ Signals for the NCH_2 protons of the Bu_4N^+ counter-cation also shifted slightly upfield upon complexation, presumably due to appreciable ion-pairing within the guest salt in this solvent. Studies with tetraphenylphosphonium halide salts, which are expected to be dissociated in solution to a greater extent, revealed very similar (but stronger) halide binding trends, but were hampered by solubility problems. For an in-depth discussion on the effect of counter-cations on anion binding, see ref. 9.
‖ The orientation of complex **3** with respect to the thiamacrocycle in **2** in the optimised structure of the dimer was found to be closer to perpendicular than that observed in the X-ray structure of the tetramer, reflecting the absence of packing effects present in the solid state, which would be similarly absent in solution.

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