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A small tris(imidazolium) cage forms an *N*-heterocyclic carbene complex with silver(I)†

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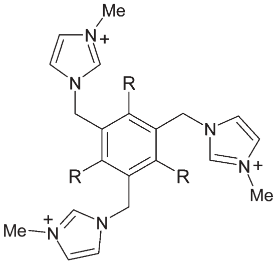
Received (in Austin, TX, USA) 8th June 2007, Accepted 6th July 2007
First published as an Advance Article on the web 7th August 2007
DOI: 10.1039/b708692j

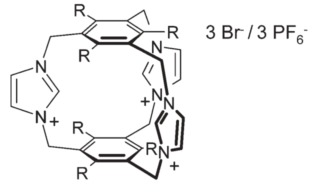
A small, sterically rigid tris(imidazolium) cyclophane reacts with Ag_2O to give an Ag(I) carbene complex in which one of the imidazolium moieties remains protonated.

There is currently tremendous interest in silver(I) complexes of *N*-heterocyclic carbenes (NHC), particularly as carbene transfer reagents.[1,2] While silver(I) carbene compounds were little known when metal NHC compounds were reviewed in 2000,[3] they have since been the subject of intense study, particularly given the tremendous interest in NHC ligands in catalysis,[4–8] the fundamentals of their chemistry compared with phosphines,[9,10] and the subject has recently been reviewed.[1,11] A number of recent reports have explored the chemistry of silver(I) NHC-based cyclophanes to give macrocyclic derivatives, showing interesting bonding modes and capable of complexing C_{60}, for example.[12–15] In general, however, the chemistry of imidazolium-bridged cyclophanes and the carbenes derived from them is relatively unexplored. Tripodal tris(imidazolium) compounds of type **1**, like many tripodal hexasubstituted benzene type ‘pinwheel’ compounds,[16–23] are known to act as excellent hosts for anions. A tripodal carbene derived from compounds of type **1** is also able to bind to thallium(I) but no transition metal complexes have been made.[24] Related to the tripodal **1** is the tris(imidazolium) cage compound **2a**. This extremely rigid [5.5.5]metacyclophane was first reported in 1999[25] and, while it has been suggested that it may act as an anion host,[26] Fabbrizzi and co-workers recently pointed out that there is insufficient free space within the compound to include an anion guest.[27] We reasoned that, while the inclusion properties of compounds of type **2** are limited, deprotonation of the compound should result in a novel, rigid NHC cage ligand capable of binding metal ions.

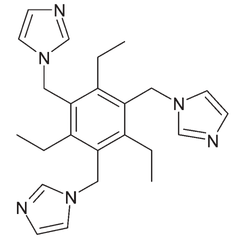
Reaction of 1,3,5-tribromomethyl-2,4,6-triethylbenzene[28] with imidazole proceeds smoothly to give the tris(imidazole) derivative **3**. Further reaction with 1,3,5-tribromomethyl-2,4,6-triethylbenzene gives the cage compound **2b** in good yield without the need for high dilution conditions. The ^1H NMR spectrum of this ligand (bromide salt) shows a singlet resonance in methanol-d_4 solution assigned to the imidazolium H2 protons at δ 5.80 ppm. This highly shielded chemical shift is indicative of the *endo* position of the H2 protons observed crystallographically,[25,26] and contrasts to values of *ca.* 8–8.5 ppm observed for compounds of type **1**.[27,29] Reaction of **2b** with Ag_2O yields the novel NHC complex $[Ag(\mathbf{2b}-2H)](PF_6)_2$ (**4**), after metathesis of the counterions with NH_4PF_6. Unlike the time-averaged D_{3h} symmetric precursor **2b**, compound **4** exhibits an ^1H NMR spectrum suggesting C_{2v} symmetry in methanol-d_4 solution. A resonance integrating for 1H is observed at 6.66 ppm, assigned to the single imidazolium H2 proton, and the methylene resonances assigned to Ha and Ha′ form a geminal AB quartet, suggesting a rigid, non-symmetrical conformation. The symmetry of the complex is lowered further in acetonitrile solution, with methylene resonances assigned to Hc and Hc′ being slightly inequivalent.



1
R = Me, Et, *n*-Bu



2a R = Me
2b R = Et



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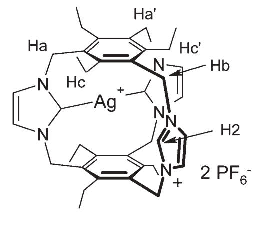

4

The $^{13}C\{^1H\}$ NMR spectrum of the complex also reflects its C_{2v} symmetry and exhibits two doublets assigned to the carbene carbon atoms centred on 178.0 ppm. Typical coupling constants of 186.5 and 215.5 Hz are observed to ^{107}Ag and ^{109}Ag, respectively.[12]

Complex **4** was characterised by X-ray crystallography,‡ which revealed a solid-state structure entirely consistent with the solution NMR spectroscopic data, Fig. 1. Ag–C distances of 2.085(9) and 2.118(10) Å are typical of related, less constrained complexes.[12] Also like related compounds, the C–Ag–C angle of 175.9(4)° is essentially linear and the complex exhibits near-perfect mirror symmetry, broken only by a slight rotation of the remaining imidazolium moiety perpendicular to the C–Ag–C axis. It is likely

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† Electronic supplementary information (ESI) available: Experimental details, structures of compounds **1**–**4** and crystal structure information for compound **1**. See DOI: 10.1039/b708692j

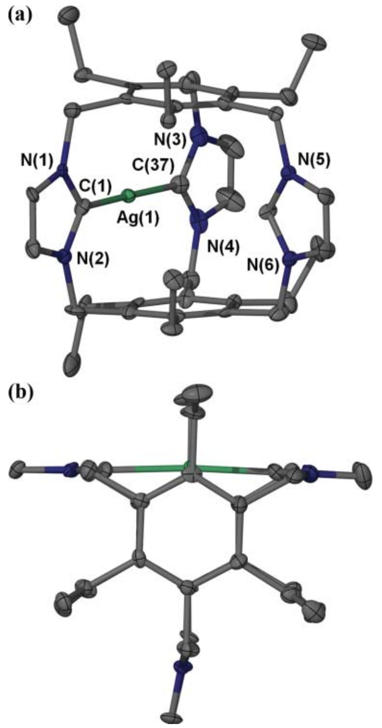

Fig. 1 Molecular structure (30% ellipsoids) of [Ag(**2b**−2H)]$(PF_6)_2$ (**4**), (a) side view and (b) view parallel to the molecular *pseudo*-mirror plane showing the rotation of the imidazolium moiety that breaks the *pseudo*-mirror symmetry. Selected bond lengths (Å): Ag(1)–C(1) 2.085(9), Ag(1)–C37 2.118(10). H atoms omitted for clarity.

that this tilt is responsible for the observation of inequivalent Hc and Hc′ resonances in acetonitrile, while it is averaged in methanol. The fact that this conformational characteristic is observable by NMR spectroscopy suggests that the complex is rigid and the close approach required between the imidazolium CH group and the Ag(I) centre is repulsive and hence increases the activation barrier for exchange. The requirement for linearity of the C–Ag–C axis (which is likely to have a strong directional preference as a result of both σ and π contributions to the bonding[30]) results in an expansion of the complex with the aromatic ring centroid separation increasing from 5.15 Å in the structure of **2a** to 5.31 Å. This is reflected in the downfield chemical shift of the imidazolium H2 proton relative to **2b**, although its endogeneous position at the edge of the metallocyclophane cavity is clear from the fact that the value of 6.66 ppm is still much more shielded than in complexes of type **1**.

While the structure of **2a** is known as the bromide salt, we sought to obtain crystals of **2b** for a direct comparison with **4**. We were able to crystallise **2b** serendipitously from an attempt to crystallise precursor **3** in the presence of $FeCl_3 \cdot 6H_2O$ and trace HBr from hot aqueous solution. This reaction resulted in the isolation of **2b** as the mixed bromide–tetrachloroferrate(III) salt, $\mathbf{2b}^{3+}Br^{-} \cdot 2[FeCl_4]^{-}$ (**5**). Salt **5** adopts a threefold symmetric cubic packing arrangement in the solid-state in the unusual, chiral space group $P2_13$, Fig. 2. The molecular structure of the **2b** cation is similar to that of the bromide salt of **2a**, albeit with an even shorter aromatic inter-centroid separation of 5.08 Å, however, the crystal packing arrangement is remarkable. Both the **2b** trication and the two independent $[FeCl_4]^{-}$ anions are situated upon crystallographic threefold axes with a single chloro ligand penetrating into the pocket generated by the ethyl substituents to give a very short anion–π interaction,[31–34] $Cl_3Fe–Cl \cdots \pi$(centroid) distance 3.424 Å. While this distance, which is approximately the sum of the van der Waals radii, is longer than the *ca.* 3.2 Å observed for chloride ion contacts to very electron deficient aromatic rings,[32,33] it is interesting in such a relatively electron rich arene. The packing along the threefold axes is thus a polar chain comprising $\mathbf{2b}^{3+} \cdots [FeCl_4]^{-} \cdots [FeCl_4]^{-} \cdots Br^{-} \cdots \mathbf{2b}^{3+} \cdots$ *etc.* The incorporation of the Br^{-} anion appears to allow the structure to avoid a mismatching interaction from the cyclophane aromatic ring to a triangular face of an $[FeCl_4]^{-}$ anion opposite the chloride ligand engaging in the anion–π interaction. In other words, bromide incorporation is necessary because, while the cation has non-crystallographic mirror symmetry perpendicular to the molecular and crystallographic threefold axis, the tetrahedral anion does not. This simultaneous high symmetry match (both the cation and anion possess threefold rotation axes) and frustration (one exhibits mirror symmetry but the other does not) suggests a possible strategy for the design of polar molecular crystals.

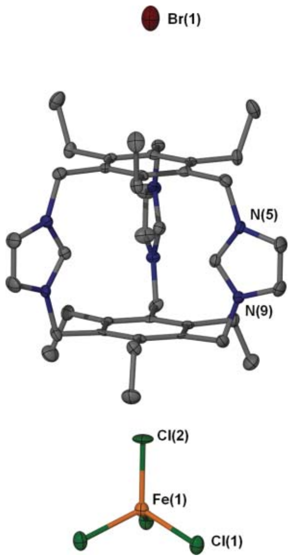

Fig. 2 View of cation **2b** with coaxial Br^{-} and $[FeCl_4]^{-}$ perpendicular to the crystallographic threefold axis. Note the penetration of Cl(2) into the cavity created by the ethyl groups (50% ellipsoids, H atoms omitted for clarity).

In conclusion we have shown that a small, threefold symmetric cyclophane forms an intra-cavity complex with Ag(I) in which the electronic requirements of the Ag–C bonding, coupled with the sterically constrained nature of the cage, result in reaction of only two of the three imidazolium moieties, even in the presence of two equivalents of Ag_2O. The resulting rigid NHC complex is stable to air and moisture and exhibits well-defined conformational properties. The Ag(I) complex may prove a useful transfer agent for this novel carbene/imidazolium ligand, which may have applications in catalysis and in crystal engineering. Work is currently in progress on further NHC complexes of benzene-anchored NHC ligands, including those of **2b**.

We gratefully thank the Leverhulme Trust and EPSRC for funding.

Notes and references

‡ Crystal data for **4**: $C_{39}H_{49}AgF_{12}N_6P_2$, $M = 999.65$, colourless plate, $0.20 \times 0.10 \times 0.10$ mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.4533(12)$, $b = 15.5863(15)$, $c = 22.8102(18)$ Å, $\beta = 112.441(4)°$, $V = 4092.2(6)$ Å^3, $Z = 4$, $D_c = 1.623$ g cm^{-3}, $F_{000} = 2040$, SMART 1 k, MoKα radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{max} = 58.4°$, 48483 reflections collected, 11030 unique ($R_{int} = 0.3042$). Final $GooF = 1.010$, $R1 = 0.1216$, w$R2 = 0.1720$, R indices based on 4288 reflections with $I > 2\sigma(I)$ (refinement on F^2), 557 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.664$ mm^{-1}. Crystal data for **5**: $C_{39}H_{51}BrCl_8Fe_2N_6$, $M = 1079.07$, orange triangular plate, $0.20 \times 0.20 \times 0.10$ mm^3, cubic, space group $P2_13$ (No. 198), $a = 16.6032(7)$, $V = 4576.9(3)$ Å^3, $Z = 4$, $D_c = 1.566$ g cm^{-3}, $F_{000} = 2200$, SMART 6 k, MoKα radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{max} = 58.3°$, 77681 reflections collected, 4143 unique ($R_{int} = 0.2321$). Final $GooF = 0.896$, $R1 = 0.0467$, w$R2 = 0.0910$, R indices based on 2350 reflections with $I > 2\sigma(I)$ (refinement on F^2), 171 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 2.010$ mm^{-1}. Absolute structure parameter = 0.048(15). CCDC 650053–650054. For crystallographic data in CIF format see DOI: 10.1039/b708692j

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