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Synthesis and structural characterization of a silver complex of a mixed-donor N-heterocyclic carbene linked cyclophane†

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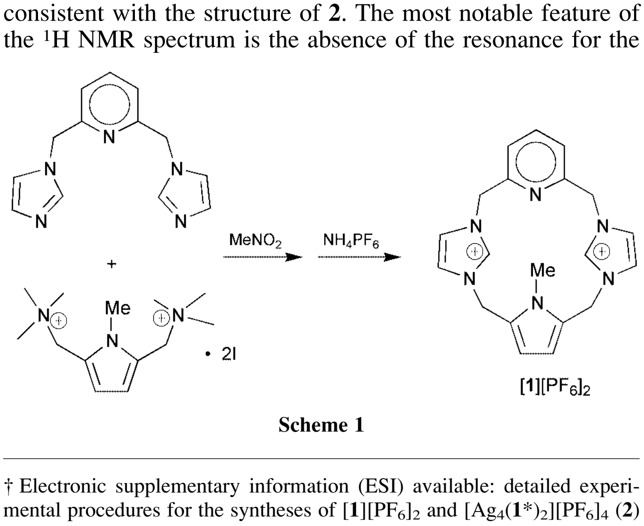
The synthesis of a dicationic imidazolium-linked cyclophane and a dimeric silver–N-heterocyclic carbene complex, that is the first silver complex with a N-heterocyclic carbene ligand involved in a π-bonding interaction, is reported.

Our group[1] and others[2] have been exploring the chemistry of silver complexes with mixed-donor N-heterocyclic carbene ligands. Bis(carbene)–Ag complexes with monodentate N-heterocyclic carbene ligands are all structurally similar, with two carbene moieties complexed to a Ag atom in a linear fashion.[3,4] The mixed-donor N-heterocyclic carbene ligands stabilize silver complexes that are quite varied. These complexes can have a combination of Ag–Ag, donor atom–Ag, and bis(carbene)–Ag interactions.

We report herein, the synthesis of the dicationic imidazolium-linked cyclophane **1** and the dimeric silver N-heterocyclic carbene complex $[Ag_4(\mathbf{1}^*)_2][PF_6]_4$ (**2**), where **1*** denotes deprotonated **1**, a bis-carbene-linked cyclophane.[5] Complex **2** is the first silver complex that has a N-heterocyclic carbene ligand involved in a π-bonding interaction. This novel situation facilitates the stabilization of a $[Ag_4]^{4+}$ cluster with four non-coordinating PF_6 anions.

The synthesis of cyclophane **1** is outlined in Scheme 1. The 3 + 1 condensation reaction of 2,6-bis(imidazolmethyl)pyridine[6] and 1-methyl-2,5-bis(trimethylaminomethyl)pyrrole diiodide[7] in nitromethane affords the cyclophane $\mathbf{1}[I]_2$. Treatment of an aqueous solution of $[\mathbf{1}][I]_2$ with ammonium hexafluorophosphate affords $[\mathbf{1}][PF_6]_2$. The ^1H and ^{13}C NMR spectra for $[\mathbf{1}][PF_6]_2$ are consistent with the proposed structure of **1**. The most notable features in the ^1H and ^{13}C NMR spectra are the resonances for the imidizolium protons at 8.6 ppm and the corresponding imidazolium carbons at 135.4 ppm. Cyclophane **1** in acetone generates $[\mathbf{1}][PF_6]^+$ ions at *m*/*z* 491.3 upon ESI-MS conditions (calculated *m*/*z* 491.2 for $C_{20}H_{22}N_6PF_6$).

Treatment of cyclophane $[\mathbf{1}][PF_6]_2$ with Ag_2O in DMSO at 55 °C affords the N-heterocyclic carbene complex $[Ag_4(\mathbf{1}^*)_2][PF_6]_4$ (**2**) (eqn. (1)). The ^1H and ^{13}C NMR data are consistent with the structure of **2**. The most notable feature of the ^1H NMR spectrum is the absence of the resonance for the imidazolium protons at 8.6 ppm. In the ^{13}C NMR spectrum for **2**, the carbene resonance appears as two doublets centered at 163.2 ppm ($^1J_{C_\sigma-Ag}$ = 220 Hz, $^1J_{C_\pi-Ag}$ = 47 Hz).[8] The chemical shift and the coupling pattern are consistent with two bonding interactions for the carbene moiety. The larger coupling of 220 Hz is consistent with a σ-bonding interaction between the carbene and a silver atom. Carbene–silver coupling constants have been reported in the range 204–220 Hz (^{109}Ag) and 180–189 Hz (^{107}Ag).[2b,3,4a,b] The smaller coupling of 47 Hz is unprecedented in silver–carbene chemistry, and we assign this value to an unconventional π-bonding interaction between the carbene and a neighboring silver atom. The assignment of each carbene interacting with two different silver atoms, *via* a σ-bonding and a π-bonding interaction, is consistent with the solid state structure for **2**.‡



Scheme 1

$$2\,[\mathbf{1}][PF_6]_2 + 4\,Ag_2O \longrightarrow \underset{\mathbf{2}}{[Ag_4(\mathbf{1}^*)_2][PF_6]_4} \qquad (1)$$

The structure of the tetracationic portion of **2** consists of a centrosymmetric dimer with four Ag cations (Fig. 1). The asymmetric unit consists of precisely half of the dimer leading to equivalent bond lengths and angles. With this in mind, we will confine our discussions to only the asymmetric portion of the molecule except in the cases where the inversion center produces additional non-redundant parameters. The four Ag atoms form a central planar core with two Ag cations bridging the Ag–Ag contacts between the other two. The Ag1–Ag1A cross-ring distance (2.9712(11) Å) is slightly longer than the bridging Ag1–Ag2 (2.7680(9) Å) and Ag1A–Ag2 (2.8077(16) Å) interactions. Each bridging Ag atom forms two bonding

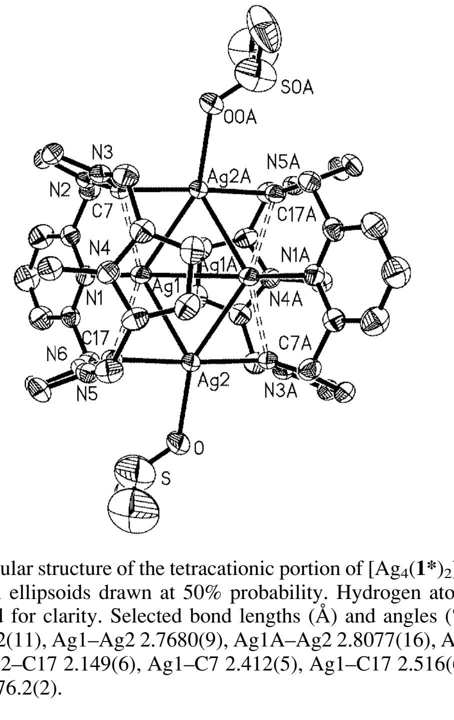


Fig. 1 Molecular structure of the tetracationic portion of $[Ag_4(\mathbf{1}^*)_2][PF_6]_4$ **2** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1–Ag1A 2.9712(11), Ag1–Ag2 2.7680(9), Ag1A–Ag2 2.8077(16), Ag2–C7A 2.148(6), Ag2–C17 2.149(6), Ag1–C7 2.412(5), Ag1–C17 2.516(6); C17–Ag2–C7A 176.2(2).

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† Electronic supplementary information (ESI) available: detailed experimental procedures for the syntheses of $[\mathbf{1}][PF_6]_2$ and $[Ag_4(\mathbf{1}^*)_2][PF_6]_4$ (**2**) and details of crystallography. See http://www.rsc.org/suppdata/cc/b1/b105751k

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interactions with the carbene ligands of two neighboring macrocycles at Ag2–C7A (2.148(6) Å) and Ag2–C17 (2.149(6) Å) bond distances and a nearly linear C17–Ag2–C7A (176.2(2)°) bond angle. These values are quite normal when compared to the same parameters reported for other silver–bis(carbene) complexes.[1,3,4a,b] In addition, each bridging Ag atom has a DMSO molecule coordinated to it with a Ag–O distance of 2.401(5) Å. The non-bridging Ag atoms are each coordinated to the pyridine nitrogen atoms of neighboring ligands at a Ag1A–N1A bond distance of 2.360(5) Å. An interesting feature of **2** is the manner in which each carbene ligand tilts inward toward the center of the molecule and interacts with the non-bridging Ag atoms at distances of Ag1–C7 (2.412(5) Å) and Ag1–C17 (2.516(6) Å). Bonding interactions of this type are unprecedented in N-heterocyclic carbene chemistry.[9] We assign this interaction as a π-carbene–silver bond. Our assignment is supported by previously reported silver–arene π-bonding interactions which lie in the range 2.43–2.61 Å.[10] The pyrrole portion of each macrocycle is positioned such that a π–Ag interaction could be envisioned; however, the shortest contact is 3.30 Å (Ag1–N4) and they vary from 3.30–3.89 Å.

Organosilver complexes having inner $[Ag_4]^{4+}$ clusters similar to **2** have been reported.[11] In fact, the structural similarity between **2**, $[Ag(C_6H_4CH_2NMe_2\text{-}2)]_4$ **3**[11a] and $[Ag(C_5H_3CH_2NMe_2\text{-}2)Fe(C_5H_5)]_4$ **4**[11e] is remarkable. For **3**, four Ag–Ag bonds that average 2.738(2) Å are each asymmetrically bridged by an anionic $^{-}C_6H_4CH_2NMe_2\text{-}2$ ligand forming two Ag–C bonds that average 2.155(13) and 2.381(13) Å, respectively. For **4**, four Ag–Ag bonds (2.740(2) Å) form a planar core with each of the Ag–Ag bonds symmetrically bridged by an anionic $(^{-}C_5H_3CH_2NMe_2\text{-}2)Fe(C_5H_5)$ ligand with Ag–C distances of 2.17(2) Å. The structural similarity between **2**, **3** and **4** can be explained in terms of the isoelectronic relationship between the anionic aryl ligands used for **3** and **4** and the N-heterocyclic carbene ligand.

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Notes and references

‡ *Crystal data* for $C_{22}H_{26}N_6Ag_2P_2F_{12}$ (**2**)·Me_2SO: M = 928.21, triclinic, space group $P\bar{1}$, a = 10.389(2), b = 11.272(2), c = 14.104(3) Å, α = 110.21(3), β = 96.34(3), γ = 102.46(3°), V = 1482.3(5) Å^3, Z = 2, D_c = 1.125 Mg m^{-3}, μ = 0.817 mm^{-1}, T = 200 K, Refinement for data with $I > 2\sigma(I)$ (5212 reflections, R_{int} = 0.0214) gave $R1(F)$ = 0.0444 and $wR2(F^2)$ = 0.1343 for all data.

See http://www.rsc.org/suppdata/cc/b1/b105751k/ for crystallographic data in CIF or other electronic format.

1 J. C. Garrison, R. S. Simons, J. M. Talley, C. Wesdemiotis, C. A. Tessier and W. J. Youngs, *Organometallics*, 2001, **20**, 1276.

2 (*a*) A. A. D. Tulloch, A. A. Danopoulos, S. Winston, S. Kleinhenz and G. Eastham, *J. Chem. Soc., Dalton Trans.*, 2000, 4499; (*b*) A. Caballero, E. Díez-Barra, F. A. Jalón, S. Merino and J. Tejeda, *J. Organomet. Chem.*, 2001, **617–618**, 395; (*c*) A. M. Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, A. H. White and B. W. Skelton, *J. Organomet. Chem.*, 2001, **617–618**, 546.

3 A. J. Arduengo III, H. V. R. Dias, J. C. Calabrese and F. Davidson, *Organometallics*, 1993, **12**, 3405.

4 (*a*) B. Bildstein, M. Malaun, H. Kopacka, K. Wurst, M. Mitterböck, K. Ongania, O. Giuliana and P. Zanello, *Organometallics*, 1999, **18**, 4325; (*b*) H. M. J. Wang and I. J. B. Lin, *Organometallics*, 1998, **17**, 972; (*c*) D. S. McGuinness and K. J. Cavell, *Organometallics*, 2000, **19**, 741.

5 N-Heterocyclic carbene-linked cyclophanes have only been observed in the gas phase: E. Alcalde, N. Mesquida and M. Vilaseca, *Rapid Commun. Mass Spectrom.*, 2000, **14**, 1443.

6 W. A. Herrmann, C. Kocher and L. Goossen, *US Pat.*, 6 025 496, 2000

7 I. T. Kim and R. L. Elsenbaumer, *Tetrahedron Lett.*, 1998, **39**, 1087.

8 ^{107}Ag and ^{109}Ag coupling constants for $^1J_{C\text{–}Ag}$ are within 10% of each other and were not resolvable for **2** due to broadening.

9 (*a*) D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39; (*b*) W. A. Herrmann and C. Köcher, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2162.

10 (*a*) H. C. Kang, A. W. Hanson, B. Eaton and V. Boekelheide, *J. Am. Chem. Soc.*, 1985, **107**, 1979; (*b*) P. F. Rodesiler, E. A. Hall Griffith and B. L. Amma, *J. Am. Chem. Soc.*, 1972, **94**, 761; (*c*) E. A. Hall Griffith and B. L. Amma, *J. Am. Chem. Soc.*, 1974, **96**, 5407; (*d*) E. A. Hall Griffith and B. L. Amma, *J. Am. Chem. Soc.*, 1974, **96**, 743; (*e*) I. F. Taylor, E. A. Hall and B. L. Amma, *J. Am. Chem. Soc.*, 1969, **91**, 5745; (*f*) H. G. Smith and R. E. Rundle, *J. Am. Chem. Soc.*, 1958, **80**, 5075.

11 (*a*) D. A. Edwards, R. M. Harker, M. F. Mahon and K. C. Molloy, *J. Chem. Soc., Dalton Trans.*, 1997, 3509; (*b*) E. M. Meyer, S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *Organometallics*, 1989, **8**, 1067; (*c*) S. Gambarotta, C. Floriani and A. Chiesi-Villa, *J. Chem. Soc., Chem. Commun.*, 1983, 1087; (*d*) P. M. Jeffries, S. R. Wilson and G. S. Girolami, *J. Organomet. Chem.*, 1993, **449**, 203; (*e*) A. N. Nesmeyanov, N. N. Sedova, Y. T. Struchkov, V. G. Adrianov, E. N. Stakheeva and V. A. Sazonova, *J. Organomet. Chem.*, 1978, **153**, 115.