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Synthesis of Silver(I) and Gold(I) Complexes with Cyclic Tetra- and Hexacarbene Ligands

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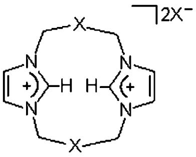
Cyclic polyimidazolium salts have been investigated with respect to their function as anion receptors and cyclophane-like tetraimidazolium tetracations have been shown to bind anions inside the ring cavity.[1] Cyclic polyimidazolium cations can also serve as precursors for N-heterocyclic carbenes (NHCs) and their complexes.[2] Complexes of cyclic di-NHC ligands have been generated from bisazolium cyclophanes like **A**. However, such dicarbene ligands coordinate in a *cis*-fashion to the metal center.[3] They act as classical bidentate ligands rather than encapsulating the metal in a manner typical for macrocyclic ligands. Only one cyclic tetradentate dicarbene ligand is known to form a saddle-shaped macrocyclic complex **B** with nickel(II).[4] We have described the first complex with a macrocyclic tetracarbene ligand **C**.[5] The rhenium complex of a tridentate, facially coordinated [11]ane-P$_2$C$^{\mathrm{NHC}}$ macrocycle has also been reported.[6]

Since the preparation of complex **C** in a metal-template controlled domino-reaction is cumbersome we became interested in the preparation of complexes with macrocyclic poly-NHC ligands from cyclic polyimidazolium cations. This approach has previously been applied successfully for the preparation of some mono (Pd$^{\mathrm{II}}$) and dinuclear (Cu$^{\mathrm{I}}$, Ag$^{\mathrm{I}}$) carbene complexes from the cyclic tetraimidazolium salt **D**.[7]

We became particularly interested in the lutidine-bridged tetraimidazolium salt H$_4$-**1**(Br$_4$)[8] which upon C^2 deprotonation would yield a potentially hexadentate ligand possessing two C$^{\mathrm{NHC}}$-N-C$^{\mathrm{NHC}}$ pincer-type binding sites. Here we describe the mono and dinuclear silver(I) complexes with the carbene ligands derived from H$_4$-**1**(Br)$_4$ and the transfer of the carbene ligand to yield the mono and dinuclear gold(I) complexes (Scheme 1). A slight modification in the synthesis protocol employed for the preparation of H$_4$-**1**(Br)$_4$ yields the cyclic hexaimidazolium salt H$_6$-**6**Br(BPh$_4$)$_5$ (Scheme 2). The preparation and molecular structure of the hexanuclear silver(I)-NHC complex derived from this ligand is also described.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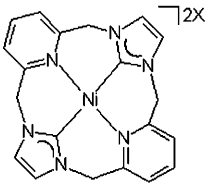
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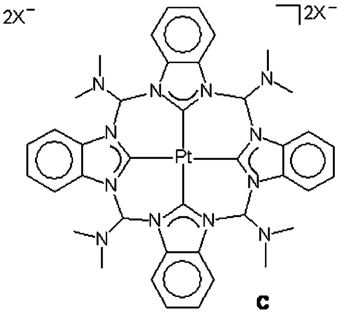
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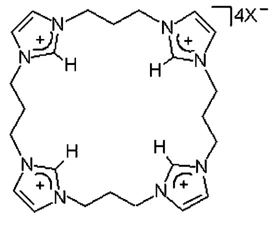
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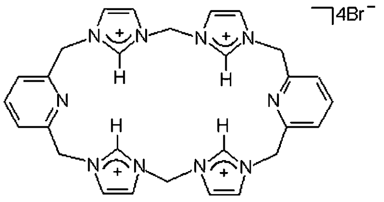
H$_4$-**1**(Br)$_4$

The tetraimidazolium salt H$_4$-**1**(Br)$_4$ is soluble in water.[8] Anion exchange gave the salt H$_4$-**1**(PF$_6$)$_4$, which is freely soluble in acetonitrile, but insoluble in water. The dinuclear silver(I) complexes [**2**](Br)$_2$ and [**2**](PF$_6$)$_2$ were prepared in a yield of about 60 % by the procedure described by Wang and Lin[9] from the salts H$_4$-**1**(Br)$_4$ or H$_4$-**1**(PF$_6$)$_4$, respectively, and two equivalents of Ag$_2$O (Scheme 1). The counterions in the salts of type H$_4$-**1**(X)$_4$ determine, which solvent had to be used for the preparation of the dinuclear silver complexes. Both the salt H$_4$-**1**(Br)$_4$ and the carbene complex[**2**](Br)$_2$ dissolve well in water and DMSO, whereas the hexafluorophosphate H$_4$-**1**(PF$_6$)$_4$ and [**2**](PF$_6$)$_2$ are only soluble in acetonitrile, DMF and acetone. The silver carbene complex [**2**]Br$_2$ is much less stable towards heat than

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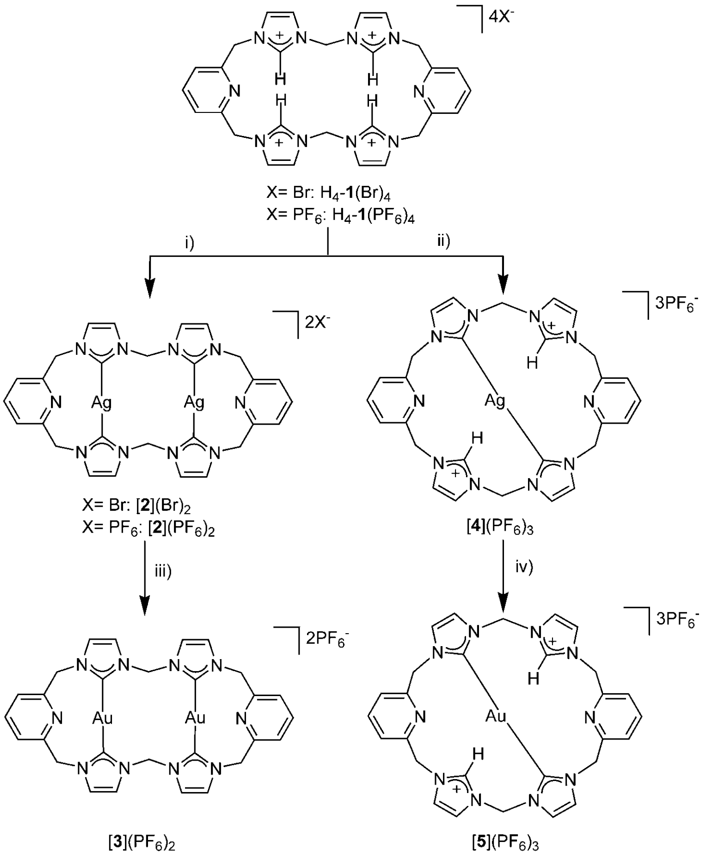
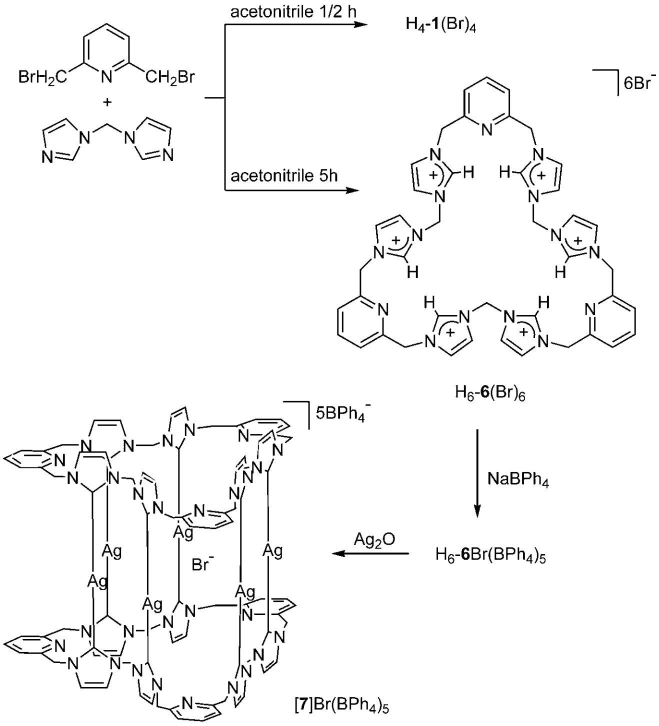


Scheme 1. Preparation of mono and dinuclear carbene complexes. i) H_4-**1**$(Br)_4$/2 Ag_2O/H_2O or H_4-**1**$(PF_6)_4$/2 Ag_2O/acetonitrile, ii) H_4-**1**$(PF_6)_4$/2 $AgPF_6$/NaH/acetonitrile, iii) 2 [AuCl(SMe$_2$)], −2 AgCl, −2 SMe$_2$, iv) [AuCl(SMe$_2$)], −AgCl, −SMe$_2$.

[**2**]$(PF_6)_2$. The decomposition of [**2**]$(Br)_2$ at temperatures above 50 °C leads to the formation of a silver mirror in the reaction vessel. The hexafluorophosphate salt [**2**]$(PF_6)_2$ can be manipulated in boiling acetonitrile without any noticeable decomposition. After workup both dinuclear silver carbene complexes were isolated as pale brown solids.

Formation the carbene complex [**2**]$(Br)_2$ was detected by ^{1}H NMR spectroscopy. The resonance of the imidazolium proton of H_4-**1**$(Br)_4$ disappears upon complex formation. In addition, the methylene resonances of the tetraimidazolium cation were detected as singlets, although these protons become diastereotopic in the carbene complex and give rise to a doublet for each proton (AA′ spin system). The imidazolium N-CH-N resonance of H_4-**1**$(X)_4$ ($\delta = 138$ ppm) is absent in the ^{13}C NMR spectrum of [**2**]$(Br)_2$ and the resonance for the carbene carbon atom was observed at $\delta = 181.3$ ppm. The ^{109}Ag NMR spectrum of [**2**]$(Br)_2$ shows a resonance at $\delta = 702$ ppm.

The salt [**2**]$(Br)_2$ could not be crystallized partly owing to its instability upon heating for solvent removal. The hexafluorophosphate salt [**2**]$(PF_6)_2$ crystallized from the reaction mixture upon addition of a small amount of DMSO as [**2**]$(PF_6)_2$·2 $AgPF_6$·6 DMSO. The X-ray analysis of these crystals shows the expected dinuclear silver tetracarbene complex (Figure 1, top). Compound [**2**]$(PF_6)_2$ co-crystallized with two equivalents of $AgPF_6$ and six equivalents DMSO (Figure 1, bottom). The complex dication [**2**]$^{2+}$ resides on a crystallographic twofold axis which bisects the Ag1–Ag1* vector. The two silver atoms are bound inside of the cavity of the macrocyclic tetracarbene ligand are each coordinated by two carbene donor groups. The co-crystallized silver atoms are connected to the cation [**2**]$^{2+}$ by Ag2−Ag1 and Ag2−$C_{carbene}$ interactions (Figure 1, bottom). They complete their coordination sphere by coordination of DMSO molecules. The Ag1−Ag1* (2.874(2) Å) and Ag1−Ag2 (2.705(2) Å) separations differ slightly in lengths.



Scheme 2. Synthesis of H_6-**6**$Br(BPh_4)_5$ and of the hexanuclear complex [**7**]$Br(BPh_4)_5$.

Transmetalation of [**2**]$(PF_6)_2$·2 $AgPF_6$ with [AuCl(SMe$_2$)] in acetonitrile yields after 3 h at ambient temperature exclusively the homodinuclear gold complex [**3**]$(PF_6)_2$ (Scheme 1) regardless of the amount of [AuCl(SMe)$_2$] used. The heterobimetallic Ag/Au complex was not observed. The maximum yield of [**3**]$(PF_6)_2$ (50 %) was obtained in the reaction of 1 equivalent of [**2**]$(PF_6)_2$ with 2.2 equivalents of [AuCl(SMe$_2$)]. Recrystallization of [**3**]$(PF_6)_2$ from acetonitrile/diethyl ether gave the dinuclear gold carbene complex as a white solid.

The NMR spectra of [**3**]$(PF_6)_2$ are similar to those of [**2**]$(Br)_2$ and exhibit the AA′spin system typical for the methylene protons upon complex formation. The resonance for the carbene carbon atom was observed at $\delta = 182.9$ ppm.

Attempts to synthesize a mononuclear silver carbene complex from the tetraimidazolium cation [**1**]$^{4+}$ were successful when a stoichiometric amount of $AgPF_6$ and an external base like NaH were used instead of Ag_2O. The mono-

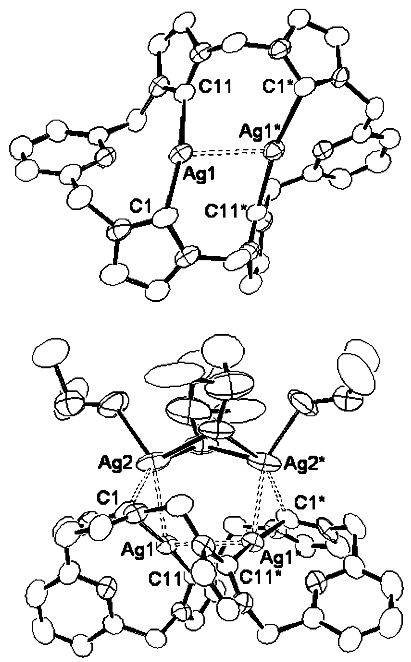


Figure 1. Molecular structure of $[\mathbf{2}]^{2+}$ (top) and $[\mathbf{2}]^{2+}\cdot 2Ag^{+}\cdot 4DMSO$ (bottom) in $[\mathbf{2}](PF_6)_2\cdot 2AgPF_6\cdot 6DMSO$. Selected bond lengths [Å] and angles [°]: Ag1–Ag1* 2.874(2), Ag1–Ag2 2.705(2), Ag1–C1 2.186(10), Ag1–C11 2.106(9), Ag2–C1 2.219(11); C1-Ag1-C11 169.9(4).

nuclear silver complex $[\mathbf{4}](PF_6)_3$ was obtained this way in 45% yield as a brownish solid (Scheme 1). The ^{1}H NMR spectrum of $[\mathbf{4}](PF_6)_3$ shows the signal for the remaining two imidazolium C^2 protons essentially unshifted relative to $\mathbf{1}](PF_6)_4$.[8] Only one triplet was observed at $\delta = 7.99$ ppm for the H_{para} protons of the pyridine ring indicating that $[\mathbf{4}]^{3+}$ possesses an inversion center in solution. The resonance for the carbene carbon atoms was found at $\delta = 183.7$ ppm in the ^{13}C NMR spectrum exhibiting the rare Ag–C coupling (dd, $^1J_{CAg(107)} = 184$ Hz, $^1J_{CAg(109)} = 212$ Hz).[11] The ^{109}Ag NMR spectrum shows the resonance for the silver atom at $\delta =$ 634 ppm.

An X-ray diffraction analysis with crystals of $[\mathbf{4}](PF_6)_3\cdot MeCN\cdot H_2O$ confirmed the conclusions drawn from the NMR spectra (Figure 2). The silver cation in $[\mathbf{4}]^{3+}$ is coordinated by two carbene carbon atoms, which are related by a pseudo-inversion center in an almost linear fashion (angle C1-Ag-C15 172.6(5)°). The Ag–C bond lengths are comparable (Ag–C1 2.077(11) Å, Ag–C15 2.057(11) Å) and fall in the range previously observed for similar silver-dicarbene complexes.[9–11]

The carbene ligand in $[\mathbf{4}]^{3+}$ can be transferred to gold(I) to yield the complex $[\mathbf{5}](PF_6)_3$ (Scheme 1). Similarly to the dinuclear silver and gold complexes $[\mathbf{2}]^{2+}$ and $[\mathbf{3}]^{2+}$ the mononuclear gold complex $[\mathbf{5}]^{3+}$ leads to better resolved NMR spectra than observed for the silver complex $[\mathbf{4}]^{3+}$. For example four resolved proton resonances have been observed for the methylene groups bridging the pyridine moiety to the ylidene and imidazolium nitrogen atoms, respectively.

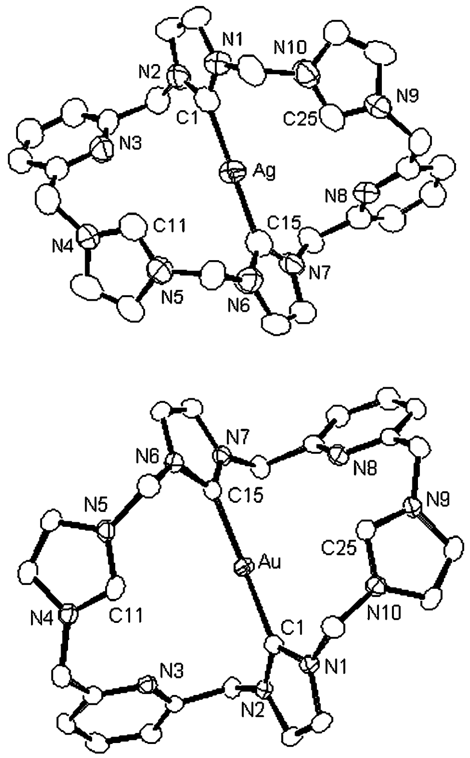


Figure 2. Molecular structure of $[\mathbf{4}]^{3+}$ in $[\mathbf{4}](PF_6)_3\cdot MeCN\cdot H_2O$ and $[\mathbf{5}]^{3+}$ in $[\mathbf{5}](PF_6)_3\cdot 2MeCN\cdot 0.5H_2O$. Selected bond lengths [Å] and angles [°] for $[\mathbf{4}]^{3+}$ and the $[\mathbf{5}]^{3+}$in square brackets: M–C1 2.077(11) [1.999(4)], M–C15 2.057(11) [2.007(4)], N1–C1 1.371(14) [1.356(5)], N2–C1 1.324(13) [1.344(5)], N4–C11 1.313(13) [1.320(5)], N5–C11 1.331(13) [1.330(5)], N6–C15 1.362(14) [1.355(5)], N7–C15 1.359(13) [1.340(5)], N9–C25 1.312(13) [1.311(5)], N10–C25 1.324(13) [1.327(5)]; C1-M-C15 172.6(5) [177.29(15)], N1-C1-N2 103.6(10) [104.1(3)], N4-C11-N5 109.6(10) [108.6(3)], N6-C15-N7 103.2(09) [104.4(3)], N9-C25-N10 108.4(10) [108.7(3)].

Crystals of composition $[\mathbf{5}](PF_6)_3\cdot 2MeCN\cdot 0.5H_2O$ were grown from an acetonitrile solution. The structure analysis (Figure 2) reveals, that the complex cations $[\mathbf{4}]^{3+}$ and $[\mathbf{5}]^{3+}$ are almost isostructural. The major difference are the generally shorter $M-C_{carbene}$ distances[12] in $[\mathbf{5}]^{3+}$ compared to $[\mathbf{4}]^{3+}$. The molecular structures of the cations $[\mathbf{4}]^{3+}$ and $[\mathbf{5}]^{3+}$ allow for a direct comparison of the bond parameters of coordinated imidazolin-2-ylidenes and their parent imidazolium moieties present in the same molecule.[13] Upon deprotonation of the imidazolium cation the N–C bond distances expand slightly and the N-C-N angle becomes more acute in accordance with theoretical predictions[14] and previous observations.[2]

Prolongation of the time used for the addition of 2,6-bis-(bromomethyl)pyridine to methylenediimidazol (both in acetonitrile) from 30 min to 5 h results in the formation of an approximately 1:1 mixture of H_4-$\mathbf{1}(Br)_4$ and H_6-$\mathbf{6}(Br)_6$ (Scheme 2). The hexaimidazolium salt leads to a resonance at $\delta \approx 10$ ppm for the proton bound to C^2 in the ^{1}H NMR spectrum (in [D$_6$] DMSO), while this proton is observed at $\delta \approx 11$ ppm in H_4-$\mathbf{1}(Br)_4$. The remaining proton chemical shifts are almost identical in H_4-$\mathbf{1}(Br)_4$ and H_6-$\mathbf{6}(Br)_6$. Separation of these two compounds is difficult, owing to their virtually identical solubility. Attempts to differentiate the solubility by the use of different counterions were only partially successful.

Attempts to exchange all six bromo counterions for tetraphenyl borato anions did not proceed to completion and gave the salt H_6-**6**Br$(BPh_4)_5$ most likely owed to the superb halogen-receptor properties of the hexaimidazolium salt. Anion exchange in H_6-**6**$(Br)_6$ with $NaBPh_4$ and subsequent reaction of the formed H_6-**6**Br$(BPh_4)_5$ with Ag_2O in acetonitrile at 50 °C for 8 h yielded the hexanuclear complex [**7**]Br$(BPh_4)_5$ as a pale brown solid (Scheme 2). Recrystallization from acetone gave [**7**]Br$(BPh_4)_5$ as colorless crystals in 10 % yield.

The X-ray structure analysis of the acetone solvate [**7**]Br$(BPh_4)_5\cdot 8\,C_3H_6O$ shows a sandwich like hexanuclear silver(I) complex. The silver atoms form a slightly distorted hexagon coordinated between the two hexacarbene ligands (Figure 3). Bond lengths and angles in the cation [**7**]Br^{5+} fall in the typical range observed previously for linear silver dicarbene complexes.[9,11] Like the hexaimidazolium salt the hexacarbene complex acts also as an anion receptor by encapsulating of a bromide in the center of the silver hexagon. The five additional tetraphenylborate anions show no remarkable contacts to the complex cation.

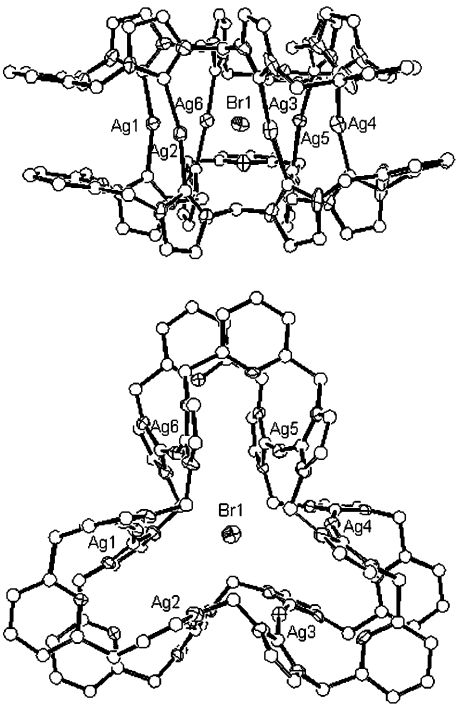


Figure 3. Molecular structure of the cation [**7**]Br^{5+} in [**7**]Br$(BPh_4)_5\cdot 8\,C_3H_6O$ viewed parallel (top) and perpendicular (bottom) to the Ag_6 hexagon. Selected bond lengths [Å] and angles [°]: range Ag–C 2.080(9)–2.112(8), range N–$C_{carbene}$ 1.333(9)–1.372(10), range Ag···Ag three short distance 3.2055/(8)–3.3348(8) and three longer distances 3.8221(9)–3.9540(8), range Ag···Br 3.4644(12)–3.7469(13); range C-Ag-C 161.4(3)–165.3(3) N-$C_{carbene}$-N 103.0(7)–105.1(8).

We have shown that cyclophane-like tetraimidazolium salts can be used for the preparation of mono and dinuclear silver carbene complexes with macrocyclic polycarbene ligands. Both the dinuclear and mononuclear silver complexes can be used in transmetalation reactions to produce the gold(I) complexes. A hexaimidazolium salt and its conversion into a hexacarbene ligand are also reported. Further work is directed towards the expansion of the bridge between the imidazolium units, which should allow to accommodate two square-planar metal centers in a double-pincer style coordination environment in the lutidine-bridged tetraimidazolium salts.

Experimental Section

Spectroscopic data for [2](Br)$_2$: ^{1}H NMR (200.1 MHz, [D_6]DMSO): δ = 7.94 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H, Ar-H_{para}), 7.77 (s, 4H, NC*H*=CHN), 7.62 (s, 4H, NCH=C*H*N), 7.57 (d, $^{3}J_{HH}$ = 7.7 Hz, 4H, Ar-H_{meta}), 7.12, (d, $^{2}J_{HH}$ = 14.2 Hz, 2H, NC*H*HN), 6.27 (d, $^{2}J_{HH}$ = 14.2 Hz, 2H, NCH*H*N), 5.46, (d, $^{2}J_{HH}$ = 14.2 Hz, 4H, CC*H*HN), 5.28 ppm (d, $^{2}J_{HH}$ = 14.2 Hz, 4H, CCH*H*N); ^{13}C{^{1}H} NMR (50.1 MHz, [D_6]DMSO): δ = 181.3 ($C_{carbene}$), 154.6 (Ar-C_{ipso}), 138.4 (Ar-C_{para}), 128.6 (N*C*=CN), 122.7 (Ar-C_{meta}), 121.7 (NC=*C*N), 63.8 (NCH_2N), 55.6 ppm (C*C*H_2N); MALDI-MS (positive ions): *m*/*z* (%): 611 (100) [**2**−Ag]$^+$, 797 (30) [**2**+Br]$^+$.

Data for [3](PF$_6$)$_2$: ^{1}H NMR (400.1 MHz, [D_7]DMF): δ = 8.20 (d, $^{3}J_{HH}$ = 2.0 Hz, 4H, NC*H*=CHN), 8.08 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H, Ar-H_{para}), 7.93 (d, $^{3}J_{HH}$ = 2.0 Hz, 4H, NCH=C*H*N), 7.82 (d, $^{3}J_{HH}$ = 7.6 Hz, 4H, Ar-H_{meta}), 7.21 (d, $^{2}J_{HH}$ = 14.0 Hz, 2H, NC*H*HN), 6.52 (d, $^{2}J_{HH}$ = 14.0 Hz, 2H, NCH*H*N), 5.80 (d, $^{2}J_{HH}$ = 13.3 Hz, 4H, CC*H*HN), 5.53 ppm (d, $^{2}J_{HH}$ = 13.3 Hz, 4H, CCH*H*N; ^{13}C{^{1}H} NMR (400.1 MHz, [D_7]DMF): δ = 182.9 ($C_{carbene}$), 155.3 (Ar-C_{ipso}), 141.0 (Ar-C_{para}), 126.9 (N*C*=CN), 125.7 (Ar-C_{meta}), 121.4 (NC=*C*N), 65.9 (NCH_2N), 57.5 ppm (C*C*H_2N); MALDI-MS (positive ions): *m*/*z* (%): 1041 (100) [**3**+PF_6]$^+$).

Data for [4](PF$_6$)$_3$: ^{1}H NMR (400.1 MHz, [D_7]DMF): δ = 9.78 (s, 2H, NCHN, imidazolium), 7.99 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H, Ar-H_{para}), 7.94 (s, 2H, NC*H*=CHN, ylidene), 7.91 (s, 4H, NC*H*=C*H*N, imidazolium), 7.66 (s, 2H, NCH=C*H*N, ylidene), 7.72, 7.62 (d, $^{3}J_{HH}$ = 7.7 Hz, 4H, Ar-H_{meta}), 6.76 (d, $^{2}J_{HH}$ = 14.2 Hz, 4H, NCH_2N), 5.73 ppm (d, $^{2}J_{HH}$ = 14.2 Hz, 8H, CCH_2N); ^{13}C{^{1}H} NMR (100.6 MHz, [D_7]DMF): δ = 183.7 (dd, $^{1}J_{CAg(107)}$ = 184 Hz, $^{1}J_{CAg(109)}$ = 212 Hz, $C_{carbene}$), 155.7 (Ar-C_{ipso}), 153.6 (Ar-C_{ipso}), 139.8 (Ar-C_{para}), 139.3 (NCHN, imidazolium), 125.9 (N*C*H=CHN, imidazolium), 124.9 (N*C*H=CHN, ylidene), 124.4 (Ar-C_{meta}), 123.5 (Ar-C_{meta}), 122.7 (NCH=*C*HN, ylidene), 122.4 (NCH=*C*HN, imidazolium), 62.5 (NCH_2N), 57.8 (C*C*H_2N, ylidene), 54.2 ppm (C*C*H_2N, imidazolium); MALDI-MS (positive ions): *m*/*z* (%): 901 (100) [**4**+2PF_6]$^+$; MALDI-MS (negative ions): *m*/*z* (%): 1192 (100) [**4**+H+4PF_6)].

Data for [5](PF$_6$)$_3$: ^{1}H NMR (400.1 MHz, [D_7]DMF): δ = 10.30 (s, 2H, NCHN, imidazolium), 8.11 (d, $^{3}J_{HH}$ = 2.0 Hz, 2H, NC*H*=CHN, ylidene), 8.03 (d, $^{3}J_{HH}$ = 2.0 Hz, 4H, NC*H*=C*H*N, imidazolium), 8.01 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H, Ar-H_{para}), 7.80 (d, $^{3}J_{HH}$ = 2.0 Hz, 2H, NCH=C*H*N, ylidene), 7.69, 7.63 (d, $^{3}J_{HH}$ = 7.5 Hz, 4H, Ar-H_{meta}), 7.48 (d, $^{2}J_{HH}$ = 13.3 Hz, 2H, NC*H*HN), 6.79 (d, $^{2}J_{HH}$ = 13.3 Hz, 2H, NCH*H*N), 5.83 (d, $^{2}J_{HH}$ = 15.8 Hz, 2H, CC*H*HN, N-imidazolium), 5.78 (d, $^{2}J_{HH}$ = 14.7 Hz, 2H, CC*H*HN, N-ylidene), 5.67 (d, $^{2}J_{HH}$ = 15.8 Hz, 2H, CCH*H*N, N-imidazolium), 5.51 ppm (d, $^{2}J_{HH}$ = 14.7 Hz, 2H, CCH*H*N, N-ylidene), ^{13}C{^{1}H} NMR (100.6 MHz, [D_7]DMF): δ = 186.6 ($C_{carbene}$), 155.7 (Ar-C_{ipso}), 153.3 (Ar-C_{ipso}), 140.5 (NCHN, imidazolium), 139.5 (Ar-C_{para}), 125.3 (N*C*H=CHN, imidazolium), 124.6 (N*C*H=CHN, ylidene), 123.8 (Ar-C_{meta}), 123.3 (Ar-C_{meta}), 122.5 (NCH=*C*HN, ylidene), 122.0 (NCH=*C*HN, imidazolium), 61.5 (NCH_2N), 56.2 (C*C*H_2N, ylidene), 53.8 ppm (C*C*H_2N, imidazolium); MALDI-MS (positive ions): *m*/*z* (%): 991 (100) [**5**+2PF_6]$^+$.

Crystal data for [2](PF$_6$)$_2\cdot$2 AgPF$_6\cdot$6 DMSO: $C_{40}H_{62}N_{10}Ag_4F_{24}O_6S_6$, M = 1982.72, monoclinic, $P2/n$, a = 13.955(6), b = 12.887(6), c = 19.000(9) Å, β = 90.991(11)°, V = 3416(3) Å^3, T = 153(2) K, λ = 0.71073 Å, Z = 2, μ =

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1.522 mm^{-1}, 23344 data measured, 5062 unique data, $R=0.0735$, $wR=0.18.23$ for 3990 contributing reflections $[I\geq 2\sigma(I)]$, refinement against $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions. [**4**]$(PF_6)_3$·$MeCN$·H_2O: $C_{30}H_{33}N_{11}AgF_{18}OP_3$, $M=1106.45$, monoclinic, $P2_1/n$, $a=8.631(2)$, $b=13.336(3)$, $c=37.317(9)$ Å, $\beta=90.442(14)°$, $V=4295(2)$ Å^3, $T=153(2)$ K, $\lambda=1.54178$ Å, $Z=4$, $\mu=5.935$ mm^{-1}, 22467 data measured, 6827 unique data, $R=0.0841$, $wR=0.21.29$ for 3318 contributing reflections $[I\geq 2\sigma(I)]$, refinement against $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions. [**5**]$(PF_6)_3$·2 MeCN·0.5 H_2O: $C_{32}H_{35}N_{12}AuF_{18}O_{0.5}P_3$, $M=1227.60$, monoclinic, $P2_1/n$, $a=8.5550(13)$, $b=13.224(2)$, $c=37.159(6)$ Å, $\beta=90.633(3)°$, $V=4203.5(11)$ Å^3, $T=153(2)$ K, $\lambda=0.71073$ Å, $Z=4$, $\mu=3.740$ mm^{-1}, 48243 data measured, 12324 unique data, $R=0.0412$, $wR=0.0888$ for 9377 contributing reflections $[I\geq 2\sigma(I)]$, refinement against $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions. [**7**]$Br(BPh_4)_5$·8 C_3H_6O: $C_{228}H_{226}N_{30}Ag_6B_5BrO_8$, $M=4295.57$, triclinic, $P\bar{1}$, $a=17.9810(6)$, $b=19.5407(7)$, $c=31.1327(12)$ Å, $\alpha=89.417(2)$, $\beta=88.514(2)$, $\gamma=76.024(2)°$, $V=10611.4(7)$ Å^3, $T=153(2)$ K, $\lambda=1.54178$ Å, $Z=2$, $\mu=5.079$ mm^{-1}, 62845 data measured, 35503 unique data, $R=0.0784$, $wR=0.2192$ for 23486 contributing reflections $[I\geq 2\sigma(I)]$, refinement against $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms except solvent molecules where one common isotropic thermal parameter was defined and hydrogen atoms on calculated positions.

CCDC-655903 ([**2**]$(PF_6)_2$·2 $AgPF_6$·6 DMSO), 655904 ([**4**]$(PF_6)_3$·MeCN·H_2O), 655905 ([**5**]$(PF_6)_3$·2 MeCN·0.5 H_2O) and 705373 ([**7**]$Br(BPh_4)_5$·8 C_3H_6O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: gold · macrocyclic ligands · polycarbenes · silver

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