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# Heterotopic silver–NHC complexes: from coordination polymers to supramolecular assemblies†

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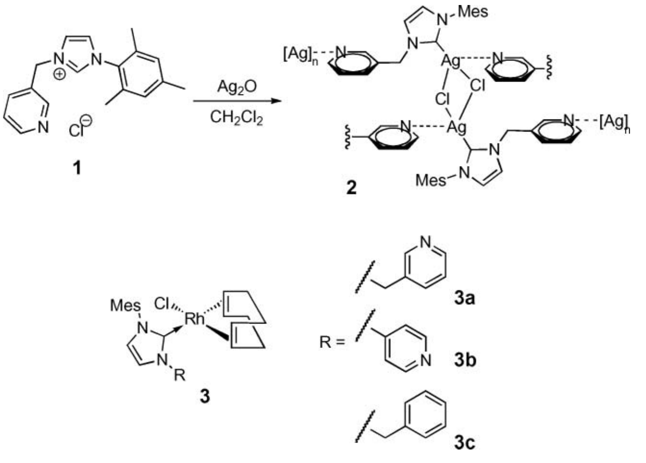
**New coordination polymers based on different combinations of silver atoms and pyridyl-substituted N-heterocyclic carbene moieties are described. The addition of Zn(II) templates leads to Ag–Zn supramolecular assemblies *via* selective $\text{Zn}\cdots\text{N}$ interactions; a process that can be reverted.**

Since they were first reported by Ölefe[1] and Wanzlick,[2] N-heterocyclic carbene (NHC) complexes have been extensively studied,[3] mainly after the isolation of the first stable NHC by Arduengo.[4] Due to their strong σ donor ability, their high air and moisture stability and their high affinity towards a wide range of transition metals, NHCs have been successfully applied in several homogeneous catalytic processes, such as olefin metathesis[5] and C–C cross-coupling reactions.[6] These properties also make NHC ligands particularly suitable for the incorporation into metal based supramolecular architectures,[7,8] but surprisingly NHCs have received only little attention in this area: rigid bis-NHC-based main-chain organometallic polymers have been described by Bielawski[9] and a few examples of silver coordination polymers.[10] These examples involve exclusively metal–heteroatom or metal–carbon interactions, but the combination of both has been less studied.[11] In this contribution we report a ditopic pyridyl-substituted NHC ligand that forms coordination polymers in the solid state and supramolecular complexes in solution with zinc(II)porphyrins. Whereas the NHC ligand remains coordinated to the silver atom, the pyridine coordinates to silver in the coordination polymer and to zinc in the assembly, leading to switchable supramolecular structures.



**Scheme 1** Synthesis of complexes **1–3**.

We designed a heterotopic NHC ligand that can not act as a bidentate ligand[12] and therefore should be a proper building block to produce larger well-defined supramolecular architectures. The NHC building block **1** (Scheme 1) is a modification of previously described[13] pyridyl-substituted imidazolium salts. Complex **1** contains a *meta*-pyridine instead of an *ortho*-pyridine, which prevents ligand coordination to metals in a chelating fashion. It has been previously used in the preparation of rhodium complex **3a** that has been applied, together with other related complexes **3** (Scheme 1), in "carbene polymerization" reactions.[14] In the current study, we focused our attention on the Ag compound **2**, used as a transfer agent[15] in the synthesis of **3**. Complex **2**, synthesized by the reaction of **1** with $Ag_2O$ (Scheme 1), was isolated and crystallized‡ from a dichloromethane–diethyl ether mixture and the solid state structure clearly showed the formation of a coordination polymer (Fig. 1). The *transoid* ligand conformation leads to an infinite one-dimensional double chain in which the ligand acts as a spacer between two Ag(I) atoms *via* the carbene and pyridyl donor groups in a "head-to-tail" orientation.[16] The parallel coordination polymers are connected *via* the silver atoms through two bridging chlorine atoms per silver-pair. In addition, there is a significant argentophilic attraction between Ag(I) atoms

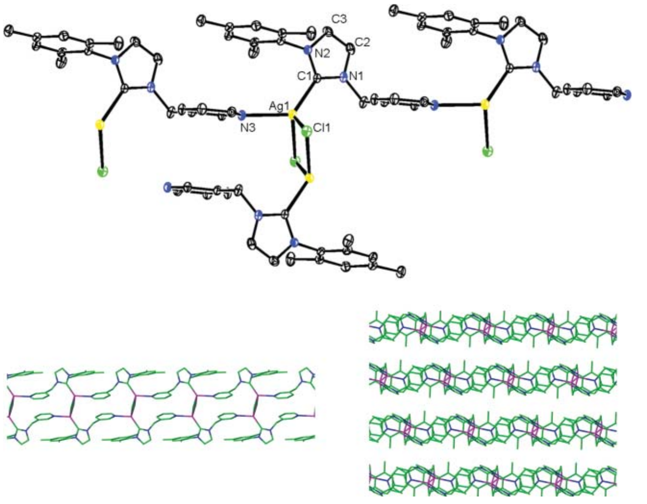


**Fig. 1** ORTEP diagram (top) of **2** with 50% probability ellipsoids and different perspectives of the polymeric chains (bottom). Hydrogen atoms are omitted for clarity.

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† Electronic supplementary information (ESI) available: Characterization of compounds **2**, **3**, **4**, **5A** and **5B**, GPC and UV-vis spectra of **2**, and UV-vis titration experiments for assemblies **5A** and **5B**. CCDC reference numbers 773279–773281. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c003352a

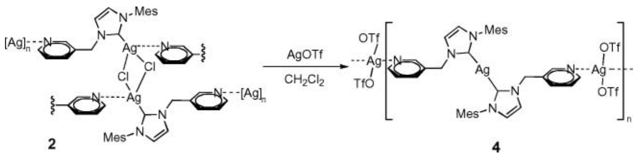
**Table 1** Selected bond lengths (Å) and angles (°)

| | 2 | 4 | 5A |
|---|---|---|---|
| Ag(1)–C(1) | 2.1322(13) | 2.081(3) | 2.071(3) |
| Ag(1)–Cl(1) | 2.6845(4) | | 2.3483(8) |
| Ag(2)–O(1) | — | 2.639(2) | — |
| Ag–N(3) | 2.3409(13) | 2.200(3) | — |
| Zn(1)–N(3) | — | — | 2.182(2) |
| C(1)–N(1) | 1.3572(19) | 1.348(3) | 1.348(4) |
| C(1)–N(2) | 1.3544(16) | 1.352(3) | 1.359(4) |
| C(2)–C(3) | 1.345(2) | 1.351(4) | 1.326(5) |
| C(1)–Ag(1)–Cl(1) | 111.80(3) | — | 166.46(9) |
| C(1)–Ag(1)–C(1′) | — | 177.15(10) | — |
| N(3)–Ag(2)–N(3′) | — | 151.28(8) | — |
| N(3)–Zn(1)–N(7) | — | | 93.21(8) |

as indicated by the distance Ag1–Ag1 of 3.0965(2) Å.[17] The Ag(I) atoms are in a distorted tetrahedral environment where the pyridine coordinates nearly perpendicularly to the plane formed by the Ag(I) and chlorine atoms (N–Ag1–Ag1: 100.74(3)°). The Ag1–C1 bond (2.1322(13) Å, Table 1) bisects the rest of the coordination sphere. Additional π–π stacking arrangement between pyridine rings (distance 3.532 Å) of adjacent polymers are also present. Although **2** is sparingly soluble in dichloromethane, the macrostructure is not retained in diluted solutions. According to $^1$H-NMR, GPC and UV/vis studies,[19] **2** dissociates into silver–NHC monomeric species.[10] Most strikingly, a band at 260 nm in the UV/vis absorption spectrum[19] is observed, which indicates that in diluted solutions of **2** the pyridine lone pair is not involved in coordinative bonds.[20]

Since the chloride plays an important role in the overall solid structure of **2**, we anticipated that the cationic derivatives would lead to different coordination polymers. The cationic form of **2** was simply accessible by a reaction of **2** with silver triflate (Scheme 2). The triflate salt (**4**) was crystallized‡ from a dichloromethane–diethyl ether mixture to yield crystals suitable for X-ray diffraction analysis. The solid state structure of **4** significantly differs from that of **2**. It also forms a 1D polymeric structure (Fig. 2) but it contains two different silver atoms. The polymers consist of alternating silver atoms, one surrounded by two NHC carbene ligands and the other by two pyridyl ligands. The structure contains Ag biscarbene cations which are balanced with Ag(OTf)$_2$ anions. The heterotopic NHC ligand acts as a linker between inequivalent and formally charged Ag(I) centres in a "head-to-head" orientation, that is, [Ag(I)]$^+$ selectively bonded to C and a formal [Ag(I)]$^-$ to N. It is noteworthy that the donor groups have relative *syn* orientation upon coordination to each Ag(I) ions, as can be observed in the disposition of Ag(carbene)$_2$$^+$ moieties with mesityl groups in close proximity (despite steric interactions). As a result, the Ag(NHC)$_2$$^+$ moieties adopt "loop" arrangements interconnected by Ag(OTf)$_2$ anions. The distances Ag1–C1 (2.081(3) Å) and Ag2–N3 (2.200(2) Å) are considerably shorter compared to those distances in **2** (Ag1–C1 2.1322(13) Å, Ag1–N3 2.3408(11) Å). The most interesting aspect of this structure is the presence of 2D undulating channels determined by the packing mode of the polymeric chain.[18] In a perpendicular view (*y*-axis), the Ag ions are aligned (Ag$^+$ ··· Ag$^-$ ··· Ag$^+$), matching with a $C_2$-symmetry axis, but the distances are too large (Ag1–Ag2 5.209 Å and 8.734 Å) to consider any argentophilic interaction. However, electrostatic interactions between ion pairs at this distance are still sufficiently large to significantly contribute to the solid state structure. In addition, some C ··· F, H ··· F and H ··· O intermolecular interactions (C2–F1 3.151 Å, H18A–F2 2.454 Å, O1–H4A 2.705 Å) involving triflate groups, that may be of importance, are observed.

The binding properties of this heterotopic NHC can also be applied in the design of heterometallic supramolecular architectures as it was found previously in the Rh assemblies with different Zn(II) templates.[14] This self-assembly approach has been applied by our group in homogeneous catalysis to make bidentate ligands[21–23] and to encapsulate metal complexes.[24] The above mentioned pyridine lability in **2** enables the construction of assemblies with Zn(II)–TPP (**A**) and Zn(II)–salphen (**B**). Thus, upon addition of the template to a solution of **2**, the pyridine coordinates selectively to Zn forming **5A** and **5B** in quantitative yields (Scheme 3). Despite the use of Ag–NHC as transfer agents and the existence of Zn–NHC complexes,[25] products derived from the coordination of carbene to Zn were not observed in these reactions. Assemblies **5A** and **5B** are stable both in solution and in the solid state and, interestingly, their solubilities are increased as compared to the poor solubility of **2**.[26] An X-ray diffraction study of a suitable crystal of **5A**‡ revealed the structure of the Zn(II)–TPP assembly based on Ag–NHC (Fig. 3).



**Scheme 2** Synthesis of compound **4**.

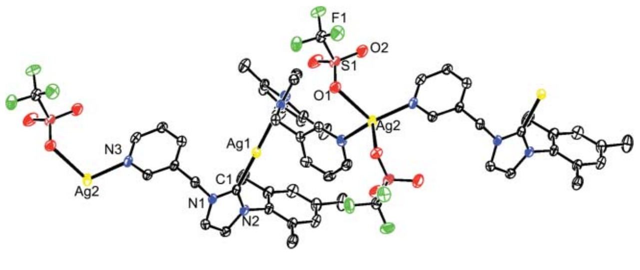


**Fig. 2** ORTEP diagram with 50% probability ellipsoids of **4**.[18] Hydrogen atoms are omitted for clarity.

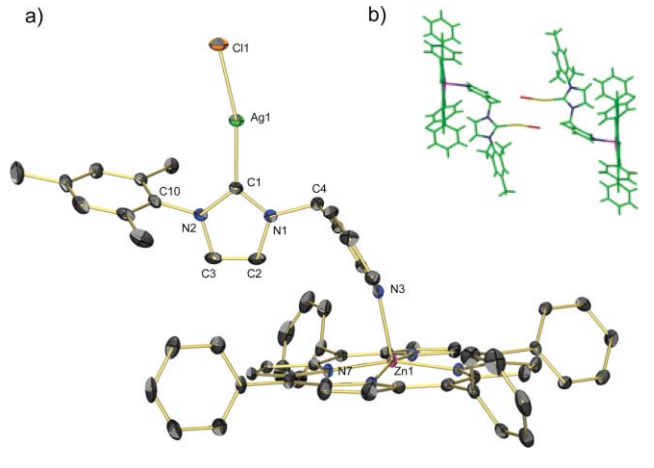
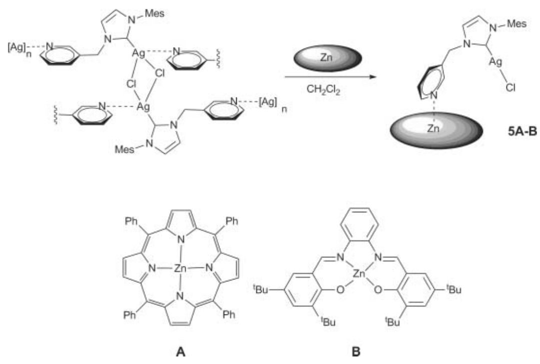


**Fig. 3** ORTEP view (a) of **5A** with 50% probability ellipsoids and perspective (b). Hydrogen atoms and solvent molecule are omitted for clarity.



**Scheme 3** Synthesis of assemblies **5A** and **5B**.

The molecule can be considered as a dimer connected by weak Ag···Cl interactions (3.041 Å) between heterometallic monomers (Fig. 3(b)), where the C(1)–Ag–Cl(1) angle (166.46(9)°) is slightly deviated from linearity. The pyridine coordinates to the Zn atom (Zn1–N3 2.182(2) Å) almost perpendicularly to the porphyrin plane ($N_{por}$–Zn1–N3: in the range 89–104°). Notably, the NHC *transoid* conformation maximizes the distance between Zn(II) and Ag(I) ions. To the best of our knowledge, this is the first X-ray structure of a supramolecular assembly of this type involving NHC ligands reported to date.

The assembly formation was further investigated by NMR and UV/vis.[19] As previously described with analogous pyridine–Zn(II) assemblies,[27] the complex induced shift of the *ortho*-pyridyl protons, observed in the $^1$H-NMR spectrum, is much higher in **5A** ($\Delta\delta = 5.0$ ppm) than in **5B** ($\Delta\delta = 0.2$ ppm). Apart from this, UV/vis titration experiments showed binding constants of $K_{ass} = 3.0 \times 10^3$ $M^{-1}$ for **5A**; and $K_{ass} = 6.5 \times 10^5$ $M^{-1}$ for **5B**. The magnitudes of the binding are similar to that reported on phosphine-assemblies[23a,c] and Rh–NHC complexes.[14]

Finally, it is worth mentioning that the dissolution of **5B** in a 5 : 1 mixture of dichloromethane–THF displayed a decrease of about two orders of magnitude in the binding constant ($K_{ass} = 7.4 \times 10^3$ $M^{-1}$). Furthermore, **2** completely precipitated out when **5B** was stirred in pure THF for few minutes. From the above mentioned experiments, it appears that addition of polar coordinating solvents weakens the Zn···N interactions and, finally, excess of coordinating solvents replaces Zn···N bond, reforming the Ag···N interaction, which leads to the precipitation of the insoluble polymer **2**.

In summary, we report a novel interesting building block to construct supramolecular architectures, based on non-chelating heterotopic NHC-pyridyl ligand. This ligand forms unique coordination polymers in combination with silver, providing materials with alternating metals arrays; $Ag^+$–$Ag^-$. The addition of Zn(II)–TPP to these complexes leads to pyridyl–zinc coordination, and as a consequence to well-defined soluble supramolecular assemblies. Changing the solvent makes this equilibrium reversible, facilitating the controlled interconversion between the various structures. Future studies include the application of these principles in material science and catalysis. Preliminary results show that the silver carbene complexes are active in several reactions, such as the copper-catalyzed Michael addition of $ZnEt_2$ to enones[28] or the 1,3-dipolar cycloaddition to imines for the synthesis of polysubstituted prolines.[29]

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## Notes and references

‡ Crystal data for **2**: $C_{18}H_{19}AgClN_3$, $M = 420.68$, triclinic, space group $P\bar{1}$, $a = 8.7708(2)$ Å, $b = 9.4691(2)$ Å, $c = 11.1568(3)$ Å, $\alpha = 86.174(2)°$, $\beta = 78.509(2)°$, $\gamma = 66.335(2)°$, $V = 831.57(4)$ Å$^3$, $Z = 2$, $T = 150$ K, $D_c = 1.680$ g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 13.75 cm$^{-1}$, Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å), $F(000) = 424.0$, $R_1 = 0.0153$, w$R_2 = 0.0393$. Crystal data for **4**: $C_{19}H_{19}AgF_3N_3O_3S$, $M = 534.30$, monoclinic, space group $C2/c$, $a = 19.9067(13)$ Å, $b = 13.9335(7)$ Å, $c = 15.7007(5)$ Å, $\beta = 103.914(4)°$, $V = 4227.1(4)$ Å$^3$, $Z = 8$, $T = 110$ K, $D_c = 1.679$ g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 11.04 cm$^{-1}$, Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å), $F(000) = 2144$, $R_1 = 0.0272$, w$R_2 = 0.0626$. Crystal data for **5A**: $2(C_{62}H_{47}AgClN_7Zn) + C_7H_8$, $M = 2289.65$, monoclinic, space group $P2_1/c$, $a = 10.8301(4)$ Å, $b = 21.1321(7)$ Å, $c = 24.3335(10)$ Å, $\beta = 101.511(2)°$, $V = 5457.0(4)$ Å$^3$, $Z = 2$, $T = 110$ K, $D_c = 1.393$ g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 8.96 cm$^{-1}$, Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å), $F(000) = 2348$, $R_1 = 0.0403$, w$R_2 = 0.0954$.

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