

Note

# Coordination polymers of silver(I) with bis(*N*-heterocyclic carbene): Structural characterization and carbene transfer

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## Abstract

Reactions of the ethylene- and methylene-bridged bis(imidazolium) salts with an equivalent amount of silver oxide in dichloromethane at room temperature produced readily the silver NHC compounds  $[\text{Ag}_2\text{LBr}_2]$ . These compounds are partially soluble in DMF. The X-ray structure determination on **3d** ( $\text{L} = 1,1'$ -dibenzyl-3,3'-ethylenediimidazolin-2,2'-diylidene) reveals the formation of bromide bibridged  $(\text{Ag}_2\text{LBr}_2)_n$  chains and a unique supramolecular motif with weak  $\text{Ag} \cdots \text{Ag}$  interactions of 3.429 Å. Similar to monomeric silver(I) NHC complexes, the silver coordination polymers can also act as carbene transfer reagents for the formation of chelating palladium NHC complexes in excellent yields.

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*Keywords:* Coordination polymer; Silver NHC compounds; Palladium NHC complexes; X-ray determination

## 1. Introduction

Nucleophilic *N*-heterocyclic carbene (NHC) ligands have attracted considerable amount of research interests since the isolation of their free carbene and successful preparation of their transition metal complexes by Arduengo et al. in 90s [1]. NHC ligands are strong  $\sigma$ -donor with negligible  $\pi$ -accepting ability, and so they resemble donor phosphine ligands rather than the classical Fischer- or Schrock-type carbenes [2]. In contrast to metal phosphine complexes, they form metal complexes that have higher stability towards heat, moisture, and oxygen. Numerous publications related to their metal coordination chemistry and catalytic properties have been reported in the past 10 years [3].

The recent advance of employing silver(I) NHC complexes as carbene transfer reagent has attracted research interests for their preparations [4]. In particular, many

palladium(II) NHC complexes were prepared via the convenient silver carbene pathway [5]. Among the reported Ag(I) NHC complexes [5,6], some are also shown to have potential applications in material science [7]. For example, the recently reported [1-(9-anthracenylmethyl)-3-ethylimidazol-2-ylidene silver(I) iodide] [8a] and  $[(\text{pyCH}_2)_2\text{im}]_3\text{Ag}_3(\text{BF}_4)_3$  [8b] give strong luminescence. An interesting aspect of these two silver(I) NHC complexes is the aggregation of silver(I) centers by argentophilic attraction with  $\text{Ag} \cdots \text{Ag}$  separations shorter than the sum of their van der Waals radii. Although, the close-shell  $d^{10}$  argentophilic attraction is generally weaker than the  $\text{Au(I)} \cdots \text{Au(I)}$  interaction, termed aurophilic attraction [9], examples of Ag(I) associations have been observed [8,10,11].

We are engaged in projects of the applications of transition metal NHC complexes in homogenous catalysis [12]. In the course of preparation of palladium complexes with methylene- and ethylene-bridged bis(NHC) via the silver carbene protocol, we have isolated a series of silver(I) bis(NHC) coordination polymers. So far, only few examples of silver(I) NHC coordination

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polymers have been reported in the literature [8a,13]. The X-ray structural determination on one of the silver(I) bis(NHC) compounds reveals weak argentophilic attractions with Ag...Ag contacts of 3.429 Å. Despite the polymeric nature of these silver compounds in the solid state, the bridging bis(NHC) can still be displaced from the Ag(I) centers to form chelating palladium bis(NHC) complexes in excellent yields.

## 2. Experimental

### 2.1. General procedure

All reactions were performed under dry nitrogen using standard Schlenk technique. Solvents used were purified according to conventional methods.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker AV-300 spectrometer. Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer. Positive FAB mass spectra were recorded on a Finnigan/Thermo Quest MAT mass spectrometer with nitrobenzyl alcohol as the matrix. The bis(NHC) precursors **1** and **2** were synthesized according to the literature procedure [12a].

### 2.2. General procedure for the preparation of $[\text{Ag}_2\text{LBr}_2]$ (**3**)

A suspension of **1** (1.0 g) and an equivalent amount of  $\text{Ag}_2\text{O}$  in dichloromethane (50 mL) was stirred at room temperature for 2 h with exclusion of light. The color of the suspension gradually changed from black to white. The suspension was then filtered, washed with dichloromethane, and dried under vacuum to give a white solid.

### 2.3. $[\{1,1'\text{-di}(4\text{-methoxybenzyl})\text{-}3,3'\text{-ethylenediimidazolin-}2,2'\text{-diylidene}\}\text{disilver(I) dibromide}]$ (**3a**)

Yield: 1.2 g (83%). Anal. Calc. for  $\text{C}_{24}\text{H}_{26}\text{Ag}_2\text{Br}_2\text{N}_4\text{O}_2$ : C, 37.05; H, 3.37; N, 7.20. Found: C, 37.01; H, 3.31; N, 7.15%. m.p. 237–245 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  3.68 (s, 6H,  $\text{CH}_3$ ), 4.59 (s, 4H,  $\text{CH}_2$ ), 5.10 (s, 4H,  $\text{ArCH}_2$ ), 6.84 (d,  $^3J_{\text{HH}} = 8.3$  Hz, 4H,  $\text{Ar-H}$ ), 7.09 (d,  $^3J_{\text{HH}} = 8.3$  Hz, 4H,  $\text{Ar-H}$ ), 7.32 (s, 2H, imi-H), 7.39 (s, 2H, imi-H). FAB MS:  $m/z$  509.6  $[\text{AgL}]^+$ , 403.6  $[\text{L} + \text{H}]^+$ .

### 2.4. $[\{1,1'\text{-di}(3\text{-methoxybenzyl})\text{-}3,3'\text{-ethylenediimidazolin-}2,2'\text{-diylidene}\}\text{disilver(I) dibromide}]$ (**3b**)

Yield: 1.3 g (97%). Anal. Calc. for  $\text{C}_{24}\text{H}_{26}\text{Ag}_2\text{Br}_2\text{N}_4\text{O}_2$ : C, 37.05; H, 3.37; N, 7.20. Found: C, 36.70; H,

3.35; N, 7.03%. m.p. 223–226 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  3.67 (s, 6H,  $\text{CH}_3$ ), 4.57 (s, 4H,  $\text{CH}_2$ ), 5.12 (s, 4H,  $\text{ArCH}_2$ ), 6.83–6.83 (m, 6H,  $\text{Ar-H}$ , imi-H), 7.21–7.38 (m, 6H,  $\text{Ar-H}$ , imi-H). FAB MS: 509.6  $[\text{AgL}]^+$ , 403.6  $[\text{L} + \text{H}]^+$ .

### 2.5. $[\{1,1'\text{-di}(4\text{-fluorobenzyl})\text{-}3,3'\text{-ethylenediimidazolin-}2,2'\text{-diylidene}\}\text{disilver(I) dibromide}]$ (**3c**)

Yield: 1.3 g (92%). Anal. Calc. for  $\text{C}_{22}\text{H}_{20}\text{Ag}_2\text{Br}_2\text{F}_2\text{N}_4$ : C, 35.05; H, 2.67; N, 7.43. Found: C, 34.95; H, 2.93; N, 7.41%. m.p. 274–276 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  4.60 (s, 4H,  $\text{CH}_2$ ), 5.18 (s, 4H,  $\text{ArCH}_2$ ), 7.14 (br s, 8H,  $\text{Ar-H}$ ), 7.37 (s, 2H, imi-H), 7.47 (s, 2H, imi-H). FAB MS:  $m/z$  485.6  $[\text{AgL}]^+$ , 380.2  $[\text{L} + \text{H}]^+$ .

### 2.6. $[\{1,1'\text{-dibenzyl}\text{-}3,3'\text{-ethylenediimidazolin-}2,2'\text{-diylidene}\}\text{disilver(I) dibromide}]$ (**3d**)

Yield: 1.4 g (95%). Anal. Calc. for  $\text{C}_{22}\text{H}_{22}\text{Ag}_2\text{Br}_2\text{N}_4$ : C, 36.80; H, 3.09; N, 7.80. Found: C, 36.44; H, 3.04; N, 7.81%. m.p. 240–242 °C (dec.).  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  4.57 (s, 4H,  $\text{CH}_2$ ), 5.20 (s, 4H,  $\text{PhCH}_2$ ), 7.10–7.16 (br s, 4H,  $\text{Ph-H}$ ), 7.25–7.35 (m, 8H,  $\text{Ph-H}$ , imi-H), 7.40 (s, 2H, imi-H). FAB MS:  $m/z$  449.5  $[\text{AgL}]^+$ , 343.5  $[\text{L} + \text{H}]^+$ .

### 2.7. $[\{1,1'\text{-di}(1\text{-naphthalenemethyl})\text{-}3,3'\text{-ethylenediimidazolin-}2,2'\text{-diylidene}\}\text{disilver(I) dibromide}]$ (**3e**)

Yield: 1.3 g (97%). Anal. Calc. for  $\text{C}_{30}\text{H}_{26}\text{Ag}_2\text{Br}_2\text{N}_4$ : C, 44.04; H, 3.20; N, 6.85. Found: C, 43.95; H, 3.13; N, 6.80%. m.p. 250–252 °C (dec.).  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  4.60 (s, 2H,  $\text{CH}_2$ ), 5.62 (s, 2H,  $\text{ArCH}_2$ ), 5.5–6.0 (br s, 4H,  $\text{CH}_2$ ), 7.40–8.03 (m, 18H,  $\text{Ar-H}$ , imi-H). FAB MS:  $m/z$  549.6  $[\text{AgL}]^+$ , 442.2  $[\text{L} + \text{H}]^+$ .

### 2.8. $[\{1,1'\text{-dimethyl}\text{-}3,3'\text{-ethylenediimidazolin-}2,2'\text{-diylidene}\}\text{disilver(I) dibromide}]$ (**3f**)

Yield: 1.5 g (93%). Anal. Calc. for  $\text{C}_{10}\text{H}_{14}\text{Ag}_2\text{Br}_2\text{N}_4$ : C, 21.23; H, 2.49; N, 9.90. Found: C, 21.05; H, 2.42; N, 9.84%. m.p. 227–230 °C (dec.).  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  3.75 (s, 6H,  $\text{CH}_3$ ), 4.60 (s, 4H,  $\text{CH}_2$ ), 7.30 (s, 2H, imi-H), 7.38 (s, 2H, imi-H). FAB MS:  $m/z$  297.3  $[\text{AgL}]^+$ , 190.1  $[\text{L} + \text{H}]^+$ .

### 2.9. Preparation of $[\{1,1'\text{-dimethyl}\text{-}3,3'\text{-methylenediimidazolin-}2,2'\text{-diylidene}\}\text{disilver(I) dibromide}]$ (**4f**)

A suspension of **2f** (1.0 g) and an equivalent amount of  $\text{Ag}_2\text{O}$  in dichloromethane (50 mL) was stirred at room temperature for 3 d with exclusion of

light. The color of the suspension gradually changed from black to reddish brown. The suspension was then filtered, washed with dichloromethane, and dried under vacuum to give a light brown solid. Yield: 1.37 g (84%). Anal. Calc. for  $C_9H_{12}Ag_2Br_2N_4$ : C, 19.59; H, 2.19; N, 10.15. Found: C, 19.35; H, 2.27; N, 10.06%. m.p. 235–241 °C (dec.).  $^1H$  NMR (DMSO- $d_6$ ):  $\delta$  3.84 (s, 6H,  $CH_3$ ), 6.67 (s, 4H,  $CH_2$ ), 7.53 (s, 2H, imi-H), 7.89 (s, 2H, imi-H). FAB MS:  $m/z$  283.3  $[AgL]^+$ , 176.1  $[L + H]^+$ .

### 2.10. General procedure for the preparation of $PdLCl_2$ from silver carbene compounds

A suspension of 0.2 g of silver compounds **3** or **4f** and an equivalent amount of  $PdCl_2$  in DMF (5 mL) was stirred at 90 °C for 16 h. The color of the suspension gradually changed from white to grey. The solution was then filtered to remove the  $AgBr$  formed. The filtrate was reduced to ca. 1 mL. Upon addition of diethyl ether, a white solid was formed which was filtered and dried under vacuum. The spectroscopic data of compound **5a–5e** [12a] and **6f** [14] obtained were identical to those reported in the literature. Yield of **5a**: 0.15 g (100%); **5b**: 0.14 g (91%). **5c**: 0.15 g (100%); **5d**: 0.15 g (100%); **5e**: 0.12 g (81%); **6f**: 0.08 g (63%).

### 2.11. Structure determination of **3d**

Crystals suitable for X-ray diffraction were obtained by dissolving the compound (ca. 5 mg) in minimum amount of DMF (ca. 1 mL). After vigorous stirring and gentle warming, the solution was filtered and placed in a 2 mL vial which was then loosely capped and placed inside a 20 mL scintillation vial containing ca. 5 mL of diethyl ether. Crystals formed after the system stood undisturbed for 1–2 d.

Diffraction data were collected on a Bruker SMART CCD with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) at 273(2) K. The crystal data is summarized in Table 1. Calculations for the structures were performed using SHELXTL 5.1. Tables of neutral atom scattering factors,  $f'$  and  $f''$ , and absorption coefficient are from a standard source [15]. All atoms except hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using of a riding model. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 230179. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44 0 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

Table 1  
Crystallographic data for **3d**

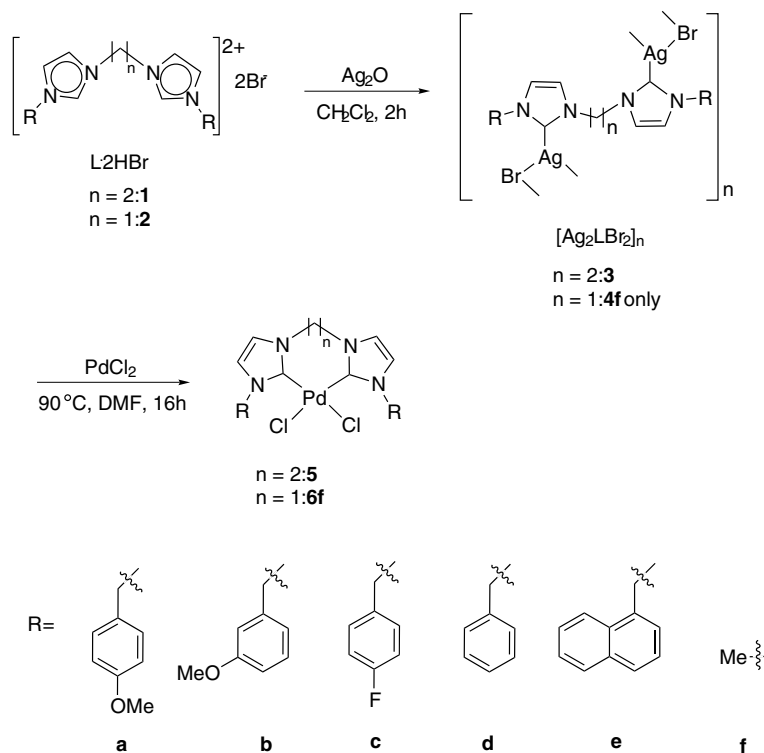
Empirical formula	$C_{11}H_{11}AgBrN_2$
Formula weight	359.00
Color and habit	Colorless prism
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
$a$ (Å)	6.2633(19)
$b$ (Å)	7.993(3)
$c$ (Å)	12.066(4)
$\alpha$ (°)	101.677(11)
$\beta$ (°)	95.702(10)
$\gamma$ (°)	92.604(7)
$V$ (Å <sup>3</sup> )	587.3(3)
$T$ (K)	273(2)
$Z$	2
$D_{calc}$ (mg/m <sup>3</sup> )	2.030
$\mu$ (mm <sup>-1</sup> )	5.085
Range of transm. factor	0.52–0.39
Number of unique data	2610
Number of parameters refined	136
$R_1$ [ $I > 2\sigma I$ ]	0.0531
$wR_2$ (all data)	0.1452
Residuals (e Å <sup>-3</sup> )	0.621, –0.626

## 3. Results and discussion

### 3.1. Preparation of silver complexes

The ethylene- and methylene-bridged bis(imidazolium) bromide **1** and **2** (shown in Scheme 1) were synthesized according to the literature procedure [12a]. As shown in Scheme 1, the new silver complexes of bis(NHC) **3a–3f** could be obtained readily in excellent yields (83–97%). The  $^1H$  NMR spectra of **3a–3f** show the absence of any signal at about  $\delta$  9.3 indicating the successful deprotonation of the carbenic protons in **1a–1f**. Like the ligand precursors **1a–1f**, the presence of only one set of resonance for the methylene and ethylene protons reflect the symmetric nature of **3a–3f**. All the resonance signals upon coordination with Ag metal are up-field shifted relative to those corresponding signals in **1a–1f**. As an example, the resonances observed at  $\delta$  4.74 and 5.33 for the ethylene and methylene protons in **1a** are up-field shifted to  $\delta$  4.59 and 5.10, respectively, in **3a**. These up-field shifts of resonances can be attributed to the electro-neutrality of **3a–3f** compared with the ionic nature of **1a–1f**.

We attempted the preparation of silver complexes with the methylene-bridged bis(imidazolium) bromides **2a–2f** following an analogous procedure. However, to our surprise, the reaction was highly dependent on the *N*-substitution of the imidazole rings. Numerous attempts were made but only with **2f** bearing *N*-methyl substitutions, we were able to obtain the corresponding silver compound **4f**. The light brown solid obtained was also stable in air and only sparingly soluble in high polar solvents. Similar to **3a–3f**, in its  $^1H$  NMR spectrum,



Scheme 1.

there is no resonance signal at  $\delta$  9.61 indicating the successful removal of the carbenic proton in **2f**. All of the resonances in **4f** are up-field shifted compared with that in **2f**. For example, the resonance signal observed for the methylene and methyl protons in **2f** are at  $\delta$  6.81 and 3.92 while those in **4f** appear at  $\delta$  6.67 and 3.84, respectively. Due to the limited solubility of **3a–3f** and **4f**, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were not obtained, but all the compounds give satisfactory elemental analysis. Positive fast-atom bombardment mass spectra (FAB-MS) of **3a–3f** in nitrobenzyl alcohol as the matrix show  $m/z$  peaks corresponding to  $[\text{AgL}]^+$  and  $[\text{L} + \text{H}]^+$ . Calculated isotopic distributions of the fragments were in good agreement with the observed spectra.

### 3.2. Molecular structure of **3d**

Due to the limited solubility of **3a–3f**, the recrystallization of the compounds was proven to be a challenge. Fortunately, in the case of **3d**, we were able to obtain crystals suitable for structural determination by thoroughly dissolving a small sample in DMF with slight warming, and then allowing slow diffusion of diethyl ether into the solution. Colorless prisms were produced in 1–2 d. Fig. 1(a) shows its molecular structure. The compound crystallized in the triclinic space group  $P\bar{1}$  with one half of  $[\text{Ag}_2\text{LBr}_2]$  in the asymmetric unit. The second half is generated by inversion through a center of symmetry. The two imidazole rings of the bis(NHC)

ligand arranges in an *anti* conformation and coordinates to two Ag(I) ions. Each Ag(I) also possesses a bridging bromide which coordinates to one another through the inversion-related Ag(I) center of the next molecule and hence link up the  $[\text{Ag}_2\text{LBr}_2]$  units into an extended one-dimensional ladder polymer. Each Ag(I) ion adopts a distorted trigonal planar coordination geometry with the sums of angles at the metal center being  $357.24^\circ$ . The Ag(1)–C(1) distance of 2.093(8) Å is in the usual range of known silver carbene complexes [6]. The two silver-bromide bonds of 2.6558(14) and 2.6808(13) Å are almost equal in length. Thus each  $\text{Ag}_2\text{Br}_2$  moiety forms a perfect rhombus with the sum of internal angles being  $360.00^\circ$ . The Ag(1)–Ag(1B) distance of 3.605 Å, which is longer than the sum of van der Waals radii of two Ag(I) centers of 3.44 Å [16], is non-bonding. Remarkably, Ag(I) ions in the polymer chain also stack about centers of symmetry to form an intriguing zigzag chain of argentophilic interactions (Fig. 1(c)). These weak  $\text{Ag}\cdots\text{Ag}$  contacts of 3.429 Å are shorter than those within the polymeric chains (3.605 Å) and close to the van der Waals limit. Examples of weak  $\text{Ag}\cdots\text{Ag}$  interactions with intermetallic distance from 3.40–3.60 Å are known [17]. The  $\text{Ag}\cdots\text{Ag}\cdots\text{Ag}$  angle is  $125.9^\circ$ . The fact that each Ag(I) ion is positioned out of the least-squares plane fit to the carbenic carbon and the two bridging bromide atoms (0.223 Å) towards the inversion-related Ag(I) center is clear evidence of the argentophilic attraction. In contrast, a similar polymeric

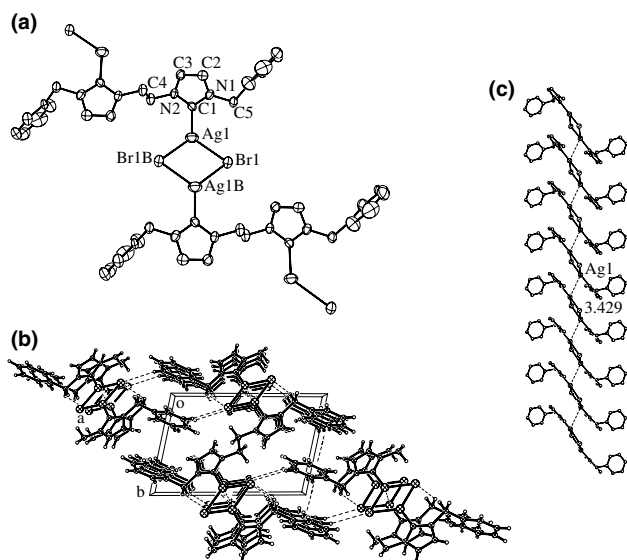


Fig. 1. (a) A perspective view of two molecules of **3d** which shows the bridging bromide portion. Thermal ellipsoids are depicted at 35% probability level for all non-hydrogen atoms. Selected bond distances (Å): Ag(1)–C(1), 2.093(8); Ag(1)–Br(1B), 2.6558(14); Ag(1)–Br(1), 2.6808(13); Selected bond angles (°): C(1)–Ag(1)–Br(1B), 132.6(2); C(1)–Ag(1)–Br(1), 129.6(2); Br(1B)–Ag(1)–Br(1), 95.02(4); Ag(1B)–Br(1)–Ag(1), 84.98(4); C(1)–N(1)–C(2), 111.2(7); C(3)–N(2)–C(1), 112.3(6); N(1)–C(1)–Ag(1), 128.8(6); N(2)–C(1)–Ag(1), 128.0(6); C(3)–C(2)–N(1), 106.9(8); C(2)–C(3)–N(2), 106.3(8). (b) A view along the *a*-axis. (c) A view along the *b*-axis of structure **3d** emphasizing the weak intermolecular Ag–Ag interactions. The distance is in Å amount. All hydrogen atoms are omitted for clarity.

structure of silver(I) bis(NHC) chloride with *N*-methyl substitutions [ $\text{Ag}_2(\text{Me}_2\text{-edimy})\text{Cl}_2$ ] was reported in which no argentophilic attraction was observed [13b]. In this structure, the corresponding Ag···Ag distance is significantly longer (3.725 Å) and the Ag(I) centers are coplanar with the least-squares plane fit to the carbene carbon and the two bridging chloride atoms (0.014 Å) [13b]. The Ag(1)–Br(1) distance of 2.6808(13) Å is within the typical range of 2.65–2.79 Å of known non-NHC silver bromide complexes [18]. However, the distance is long in comparison with other Ag(NHC)Br complexes. For example, the corresponding distance is 2.4980(7) Å in  $[\text{Ag}(\text{C}_{14}\text{H}_{29})_2\text{-imy}]\text{Br}_2$  [7a] and 2.491(1)–2.421(1) Å in the silver bromide complexes with *N*-functionalized/NHC reported by Danopoulos et al. [6a]

It is worthy to note that the silver bromide coordination polymers **3a–3f** and **4f** are totally insoluble in chlorinated solvents, whereas the closely related silver chloride compound was soluble in dichloromethane [13b].

### 3.3. Reaction of silver compounds with palladium dichloride

Monomeric silver NHC complexes were shown to be excellent carbene transfer reagents for the preparation of

transition metal NHC complexes [4]. A typical procedure involves the stirring of a silver carbene complex in dichloromethane with the presence of a suitable metal precursor. For the preparation of palladium carbene complexes,  $\text{PdCl}_2$  or its derivatives are used. We were interested to see if the silver(I) coordination polymers **3a–3f** and **4f** can also mediate the same carbene transfer ability. However, due to the limited solubility of **3a–3f** in dichloromethane, we switched to the more polar DMF (or DMSO) as solvent and found that a prolongation of heating a suspension of the silver compounds **3a–3e** and  $\text{PdCl}_2$  for 16 h produced the corresponding bidentate palladium ethylene-bridged bis(NHC) chloride complexes **5a–5e** in almost quantitative yield. Recently, we had successfully prepared the appropriate palladium complexes **5a–5e** employing the classical method of heating the corresponding imidazolium salts with palladium acetate [12a] while others obtained closely related palladium methyl complexes by reacting  $\text{Pd}(\text{bipy})\text{Me}_2$  with generated free carbene ligands [19]. This study shows that, compared with the palladium acetate and free carbene pathways, the preparation of palladium chloride complexes **5a–5e** via the silver bis(NHC) compounds **3a–3e** represent the method of choice as the yields in both preparation of the silver coordination polymers **5a–5e** and the subsequent NHC transfer reactions are almost quantitative. Also, the silver NHC compounds, unlike the free NHC ligands, are air-stable and hence, are considerably easier to handle. However, employing the same condition for the preparation of **5f** results in failure. The compound **5f** may be intrinsically unstable as our previous attempt with  $\text{Pd}(\text{OAc})_2$  protocol was also unsuccessful [12a]. In contrast, the methylene-bridged bis(carbene) analog **4f** cleanly reacts with palladium chloride to give **6f** in 63% of yield. The classical  $\text{Pd}(\text{OAc})_2$  pathway also produced **6f** with a slightly higher yield of 78% [14]. The result appears to show that it is desirable for silver complexes with the ethylene-linked bis(NHC) bearing large *N*-substituents, whereas small substituents are favored in methylene-linked analog.

## 4. Conclusions

A series of silver(I) ethylene-bridged bis(NHC) coordination polymers **3a–3f** have been successfully prepared by stirring a suspension of the corresponding bis(imidazolium) salts with silver oxide in dichloromethane. However, under the same condition, the analogous silver compounds with methylene-bridged bis(NHC) can only be obtained with the ligand bearing *N*-methyl substitutions. All the silver compounds obtained are only partially soluble in high polar solvent. We were able to obtain crystals and successfully determine the structure of **3d**, which reveals a unique supramolecular motif of



weak argentophilic interactions with Ag···Ag distances of 3.429 Å.

We have also successfully demonstrated for the first time that silver coordination polymers **3a–3e** and **4f** can successfully transfer, similar to many reported monomeric silver carbene complexes, their carbene moieties to palladium centers forming bidentate palladium bis(NHC) complexes in excellent yields.

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