

## Reactions of (imidazol-2-ylidene)silver(I) chlorides with group 4 metal containing Lewis acids

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### Abstract

The reactivity of the monomeric *N*-heterocyclic carbene silver(I) complexes, 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene-silver(I) chloride ([Ag(IMes)Cl], **1**) and 1,3-bis-(4-bromo-2,6-dimethylphenyl)imidazol-2-ylidene-silver(I) chloride ([Ag(IMes<sup>Br</sup>)Cl], **2**), toward the group 4 metal containing Lewis acids, TiCl<sub>4</sub> and (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>3</sub>, in dichloromethane was investigated. Instead of the expected transfer of the *N*-heterocyclic carbene to the Lewis acidic metal centers with accompanying precipitation of AgCl, chloride transfer occurred leading to the formation of the salts, [Ag(IMes)<sub>2</sub>]<sup>+</sup>[(TiCl<sub>3</sub>)<sub>2</sub>(μ<sub>2</sub>-Cl)<sub>3</sub>]<sup>-</sup> (**3**) and [Ag(IMes<sup>Br</sup>)<sub>2</sub>]<sup>+</sup>[(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)ZrCl]<sub>2</sub>(μ<sub>2</sub>-Cl)<sub>3</sub><sup>-</sup> (**4**). The structure of the [Ag(IMes<sup>Br</sup>)<sub>2</sub>]<sup>+</sup> cation in **4** is significantly distorted in the solid state by interactions between the *para*-Br atoms of the IMes<sup>Br</sup> ligands and chloride ligands of the anions.

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### 1. Introduction

The importance of *N*-heterocyclic carbenes (NHCs) as ligands in organometallic chemistry continues to grow [1]. Interest has been driven, primarily, by the dramatic increases in both stability and reactivity achieved when NHCs are used to replace tertiary phosphine ligands in many of the transition-metal-based catalysts used for effecting carbon–carbon bond formation [2]. The significance of NHCs as ligands is not, however, restricted to these extensively studied systems that feature late transition metals, typically in low oxidation states. There has also been considerable recent interest in NHC complexes of early transition metals in high oxidation states [3]. In

these cases, coordination by the strongly electron-donating NHC imparts exceptional stability towards air and moisture to these otherwise highly air-sensitive systems. There is thus a need to develop simple and straightforward methodologies for the synthesis of NHC complexes featuring early transition metals.

The simplest approach for the synthesis of NHC-metal complexes has been direct combination of a metal containing Lewis acid (or suitable metal complex featuring a labile neutral ligand) with the free carbene [1]. Although NHC complexes of group 4 metals have been prepared by such direct combination [4], it has been demonstrated that the presence of any unreacted imidazolium halide, as an impurity in the NHC used, fatally compromises such syntheses [5]. We are, therefore, interested in developing alternate, less technically demanding, preparative routes to these complexes.

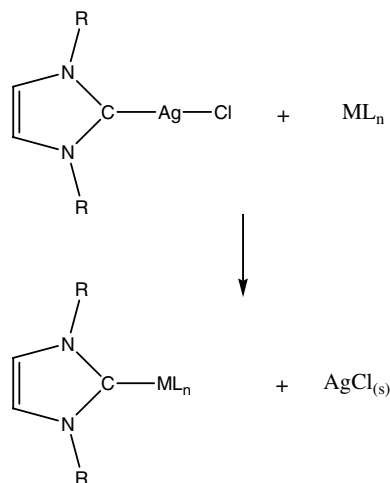
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NHC-silver(I) halide complexes represent an attractive class of NHC-transfer reagents, with potential for the desired transmetalation of NHC ligands to be accompanied by the thermodynamically favorable precipitation of solid silver(I) halide (Scheme 1) [6]. Silver(I) halide-NHC complexes are readily formed in high yield by the deprotonation of imidazolium halides using silver(I) oxide; a methodology that was first introduced by Wang and Lin in 1998 [6]. Since then a wide variety of NHC-silver(I) complexes have been prepared by this route [7]. As both the reactants and the NHC-silver(I) complexes formed are air and moisture stable (water is produced as a side product), this reaction represents a safe and easy entry point into NHC-metal chemistry. Accordingly, several research groups have begun to investigate the use of NHC-silver(I) complexes as NHC transfer reagents and have successfully prepared NHC complexes of several late transition metals by this method (namely: rhodium [8], iridium [8], palladium [9], and gold [6]).

We therefore decided to investigate the utility of NHC-silver(I) halides as reagents to facilitate NHC-transfer to early transition metals. The reactivity of the simple monomeric NHC-silver(I) chlorides: 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene:silver(I) chloride ([Ag(IMes)Cl], **1**) [10] and the structurally related 1,3-bis-(4-bromo-2,6-dimethylphenyl)imidazol-2-ylidene:silver(I) chloride ([Ag(IMes<sup>Br</sup>)Cl], **2**, Fig. 1), towards the strongly Lewis acidic group 4 transition metal containing compounds TiCl<sub>4</sub> and (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>3</sub> was studied.

## 2. Results and discussion

Dichloromethane solutions of the NHC-silver(I) chlorides, **1** and **2**, were added to solutions of TiCl<sub>4</sub> and (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>3</sub>, respectively. The reactions were



Scheme 1. The use of NHC silver(I) chlorides as NHC transfer agents.

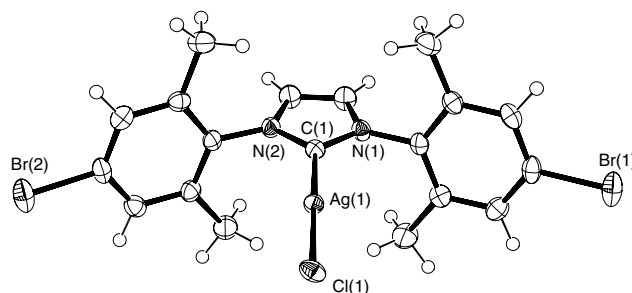
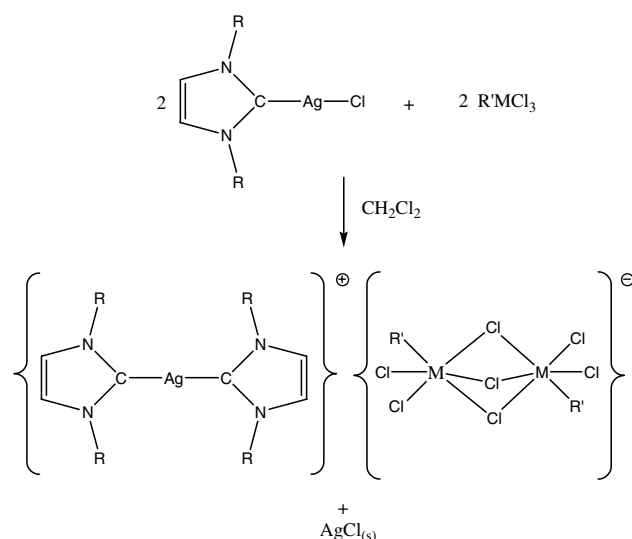


Fig. 1. X-ray crystal structure of **2**. Selected bond distances (Å) and angles (°): Ag(1)–C(1) = 2.064(3), Ag(1)–Cl(1) = 2.3197(6); Cl(1)–Ag(1)–C(1) = 179.38(7), Ag(1)–C(1)–N(1) = 127.32(19), Ag(1)–C(1)–N(2) = 128.31(18).

carried out in dichloromethane at room temperature under an atmosphere of dry nitrogen. In both cases a white precipitate of silver chloride formed on mixing of the reagents, which was separated by filtration. The products were obtained as crystalline solids on concentration and refrigeration of the filtrates. Instead of the anticipated transmetalation of the NHC ligand, chloride ion transfer occurred from the silver(I) ion to the d<sup>0</sup> early transition metal center to give the ionic compounds [Ag(IMes)<sub>2</sub>]<sup>+</sup>[(TiCl<sub>3</sub>)<sub>2</sub>(μ<sub>2</sub>-Cl)<sub>3</sub>]<sup>−</sup> (**3**) and [Ag(IMes<sup>Br</sup>)<sub>2</sub>]<sup>+</sup>[(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)ZrCl]<sub>2</sub>(μ<sub>2</sub>-Cl)<sub>3</sub>]<sup>−</sup> (**4**) as shown in Scheme 2. In the context of these reactions forming salts containing [Ag(NHC)<sub>2</sub>]<sup>+</sup> cations, it is interesting to note that an equilibrium between [Ag(NHC)X] and [Ag(NHC)<sub>2</sub>]<sup>+</sup>[AgX<sub>2</sub>]<sup>−</sup> exists for NHC complexes of silver(I) halides in polar solvents [11]. However, as NHC silver(I) chloride species have been successfully employed as NHC transfer reagents to late transition metals it is clear that it is the nature of the acceptor metal



Scheme 2. The reaction of NHC silver(I) chloride with group 4 metal containing Lewis acids reaction 1: R = 2,4,6-trimethylphenyl, M = Ti, R' = Cl. Reaction 2: R = 4-bromo-2,6-dimethylphenyl, M = Zr, R' = (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>).

complex which determines whether NHC or chloride transfer will occur. Presumably, in the case of these group 4 transition metal Lewis acids, the high chlorophilicity of the  $d^0$  metal center together with the large solvation/lattice enthalpy of the ionic products formed favor chloride transfer rather than the transmetallation of the NHC reported for the soft Lewis acidic, late transition metal centers.

The molecular structures of compounds **2**, **3** and **4** were determined by single-crystal X-ray diffraction. The solid-state molecular structure of **2** (Fig. 1) is, as expected, very similar to that observed for **1** [10] with an Ag–C<sub>carbene</sub> distance of 2.064(3) Å and an Ag–Cl distance of 2.314(2) Å. However, in contrast to the molecular packing of **1**, which is characterized by two equal Cl...H–C bonds (2.954 Å) symmetrically linking the chloride ligand of one molecule to the olefinic hydrogen atoms of the imidazole ring of an adjacent molecule to form a linear one dimensional head to tail chain, the packing of **2** is non-linear with asymmetric Cl...H–C lengths of 2.690 and 3.120 Å to the two olefinic hydrogen atoms of the imidazole ring of the neighboring molecule closest to the chloride ligand. In addition to these head to tail Cl...H–C hydrogen bonds, adjacent molecules of [Ag(IMes<sup>Br</sup>)Cl] are also linked via secondary long range Br...Ag...Br interactions (4.361 and 4.408 Å with a Br...Ag...Br angle of 173.96°), which give rise to a pseudo square-planar geometry at the silver ion center (Fig. 2) and assemble the molecules into a one dimensional ribbon.

Compound **3** exhibits an ionic structure, [Ag(IMes)<sub>2</sub>]<sup>+</sup>[(TiCl<sub>3</sub>)<sub>2</sub>(μ<sub>2</sub>-Cl)<sub>3</sub>]<sup>−</sup> (Fig. 3). The dicarbene silver cation, [Ag(IMes)<sub>2</sub>]<sup>+</sup>, was first prepared by Arduengo et al. [12] as the triflate salt by direct combination of the free carbene and silver(I) triflate. The important metrical parameters of the cation in **3** (Ag–C<sub>carbene</sub> distances of 2.064(2) and 2.068(2) and a C<sub>carbene</sub>–Ag–

C<sub>carbene</sub> angle of 176.57(8)) are very similar to the values reported for the triflate salt: Ag–C<sub>carbene</sub> distances of 2.067(4) and 2.078(4) and a C<sub>carbene</sub>–Ag–C<sub>carbene</sub> angle of 176.3(2)° [12]. The di-nuclear titanium chloride anion, [(TiCl<sub>3</sub>)<sub>2</sub>(μ<sub>2</sub>-Cl)<sub>3</sub>]<sup>−</sup>, consists of two titanium(IV) centers coordinated in a distorted octahedral manner by three terminal chloride ligands and three bridging μ<sub>2</sub>-chloride ligands. This anion was first observed by Floriani et al. [13] in the complex salt, [(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)TiCl<sub>3</sub>]<sup>+</sup>[(TiCl<sub>3</sub>)<sub>2</sub>(μ<sub>2</sub>-Cl)<sub>3</sub>]<sup>−</sup>, formed by the reaction of TiCl<sub>4</sub> with C<sub>6</sub>Me<sub>6</sub> in dichloromethane. The Ti–Cl bond distances observed in **3** (from 2.1980(7) to 2.2299(8) Å for the terminal chloride ligands and from 2.4476(7) to 2.5195(7) Å for the bridging chlorides) are similar to the values reported previously [13].

Compound **4** also exhibits an ionic structure, [Ag(IMes<sup>Br</sup>)<sub>2</sub>]<sup>+</sup>[(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>2</sub>]<sub>2</sub>(μ<sub>2</sub>-Cl)<sub>3</sub>]<sup>−</sup> (Fig. 4). The cation, [Ag(IMes<sup>Br</sup>)<sub>2</sub>]<sup>+</sup>, has very similar Ag–C<sub>carbene</sub> bond distances (2.068(3)) and a similar C<sub>carbene</sub>–Ag–C<sub>carbene</sub> bond angle (178.0(1)) to those observed for **3** (vide supra). However, in **4** the 4-bromo-2,6-dimethylphenyl groups of the two carbene ligands in [Ag(IMes<sup>Br</sup>)<sub>2</sub>]<sup>+</sup> adopt a more eclipsed configuration (with an N(1)–C(1)–C(1')–N(2') torsional angle of 30.20°) than the 2,4,6-trimethylphenyl ligands in **3** (with a corresponding N(1)–C(1)–C(22)–N(3) torsional angle of 67.09°). This significantly more eclipsed configuration is apparently driven by a close interaction between the *para*-bromine atoms of the ligand in the cation and the terminal chloride ligands of the anion (Br(1')–Cl(2) 3.507 Å and Br(2)–Cl(1) 3.314 Å). Such interactions have recently been discussed in some detail by Brammer et al. [14] who observed a number of instances of C–X...X'–M interactions. Our observation of close to linear C–Br...Cl angles (Cl(1)...Br(2)–C(15) = 163.44°; Cl(2)...Br(1')–C(7') = 159.62°) is in keeping with his results. It would appear that the magnitude of this inter-

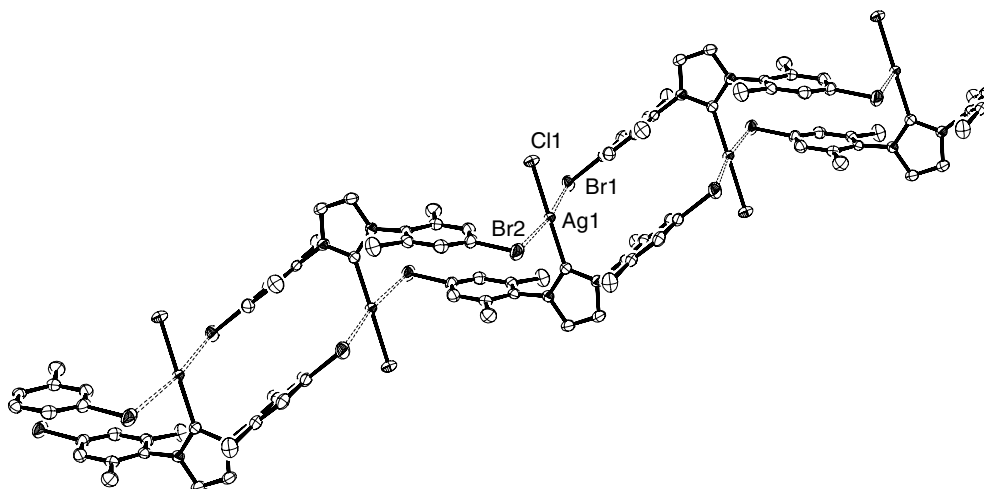


Fig. 2. Partial packing diagram of **2**, highlighting the long-range Ag–Br supramolecular interactions.

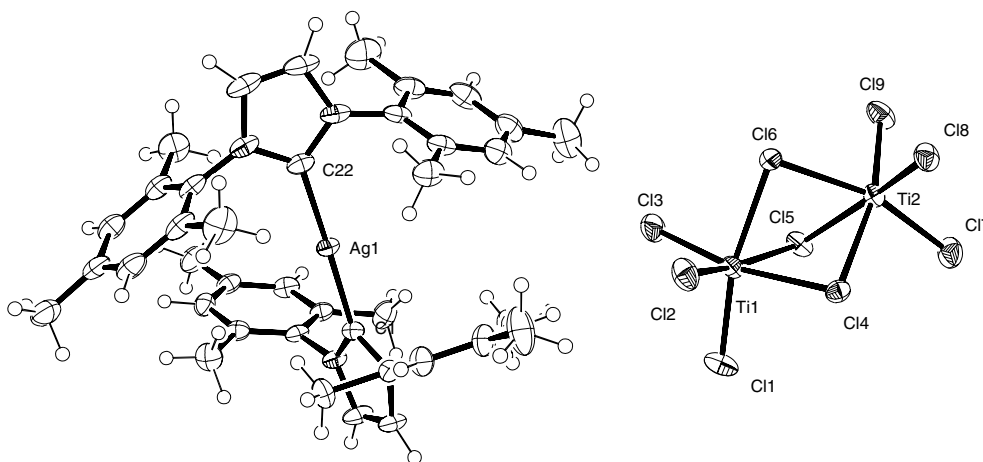


Fig. 3. X-ray crystal structure of **3**. Selected bond distances (Å) and angles (°): Ag(1)–C(1) = 2.068(2), Ag(1)–C(22) = 2.064(2), Ti(1)–Cl(1) = 2.2161(7), Ti(1)–Cl(2) = 2.2159(7), Ti(1)–Cl(3) = 2.2299(8), Ti(1)–Cl(4) = 2.4712(8), Ti(1)–Cl(5) = 2.4476(7), Ti(1)–Cl(6) = 2.5015(7), Ti(2)–Cl(4) = 2.5195(7), Ti(2)–Cl(5) = 2.4880(7), Ti(2)–Cl(6) = 2.4801(7), Ti(2)–Cl(7) = 2.2262(8), Ti(2)–Cl(8) = 2.1980(7), Ti(2)–Cl(9) = 2.2090(7), Ti(1) ... Ti(2) = 3.3964(6); C(1)–Ag(1)–C(22) = 176.57(8), Cl(1)–Ti(1)–Cl(2) = 98.54(3), Cl(2)–Ti(1)–Cl(3) = 97.89(3), Cl(1)–Ti(1)–Cl(3) = 97.61(3), Cl(2)–Ti(1)–Cl(5) = 165.86(3), Cl(1)–Ti(1)–Cl(5) = 92.13(3), Cl(3)–Ti(1)–Cl(5) = 89.79(3), Cl(2)–Ti(1)–Cl(4) = 91.15(3), Cl(1)–Ti(1)–Cl(4) = 91.18(3), Cl(3)–Ti(1)–Cl(4) = 166.28(3), Cl(5)–Ti(1)–Cl(4) = 79.33(2), Cl(2)–Ti(1)–Cl(6) = 89.42(3), Cl(1)–Ti(1)–Cl(6) = 167.26(3), Cl(3)–Ti(1)–Cl(6) = 91.07(3), Cl(5)–Ti(1)–Cl(6) = 78.53(2), Cl(4)–Ti(1)–Cl(6) = 78.67(2), Cl(8)–Ti(2)–Cl(9) = 98.92(3), Cl(8)–Ti(2)–Cl(7) = 99.05(3), Cl(9)–Ti(2)–Cl(7) = 99.26(3), Cl(8)–Ti(2)–Cl(6) = 91.32(3), Cl(9)–Ti(2)–Cl(6) = 91.77(3), Cl(7)–Ti(2)–Cl(6) = 163.44(3), Cl(8)–Ti(2)–Cl(5) = 166.12(3), Cl(9)–Ti(2)–Cl(5) = 90.54(2), Cl(7)–Ti(2)–Cl(5) = 89.34(3), Cl(6)–Ti(2)–Cl(5) = 78.18(2), Cl(8)–Ti(2)–Cl(4) = 91.43(2), Cl(9)–Ti(2)–Cl(4) = 165.76(3), Cl(7)–Ti(2)–Cl(4) = 88.65(3), Cl(6)–Ti(2)–Cl(4) = 78.16(2), Cl(5)–Ti(2)–Cl(4) = 77.65(2), Ti(1)–Cl(4)–Ti(2) = 85.77(2), Ti(1)–Cl(5)–Ti(2) = 86.96(2), Ti(1)–Cl(6)–Ti(2) = 85.97(2).

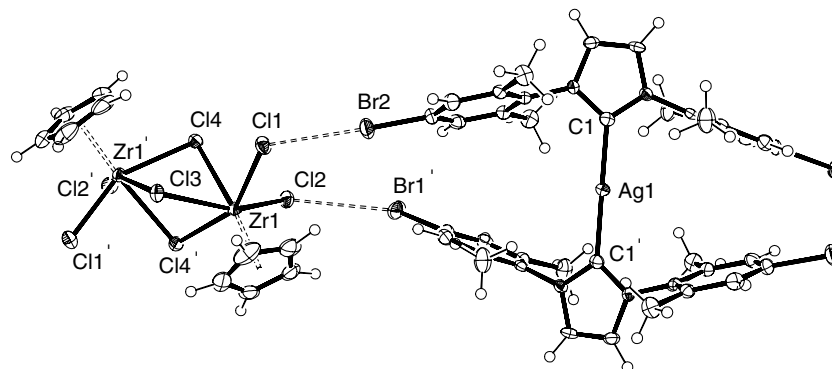


Fig. 4. X-ray crystal structure of **4** highlighting the inter-halogen interactions. Selected bond distances (Å) and angles (°): Ag(1)–C(1) = 2.068(3), Zr(1)–Cl(1) = 2.4507(9), Zr(1)–Cl(2) = 2.4496(9), Zr(1)–Cl(3) = 2.6334(9), Zr(1)–Cl(4) = 2.7347, Zr(1)–Cl(4') = 2.5675(9), Zr(1)–Cp(centroid) = 2.206; C(1)–Ag(1)–C(1') = 178.03(18), Cl(1)–Zr(1)–Cl(2) = 94.35(3), Cl(1)–Zr(1)–Cl(3) = 83.85(3), Cl(1)–Zr(1)–Cl(4) = 79.88(3), Cl(1)–Zr(1)–Cl(4') = 150.48(3), Cl(2)–Zr(1)–Cl(3) = 153.34(3), Cl(2)–Zr(1)–Cl(4) = 79.03(3), Cl(2)–Zr(1)–Cl(4') = 92.55(3), Cl(3)–Zr(1)–Cl(4) = 74.46(3), Cl(3)–Zr(1)–Cl(4') = 77.30(3), Cl(4)–Zr(1)–Cl(1') = 73.33(3), Zr(1)–Cl(3)–Zr(1') = 91.17(4), Zr(1)–Cl(4)–Zr(1') = 90.34(3).

action is sufficient to induce the considerable distortion observed in the  $[\text{Ag}(\text{NHC})_2]^+$  cation. Brammer has also suggested that these interactions are of potential value as “supramolecular synthons”, and this view is supported in this case, the inter-halogen interactions resulting in a 1-D polymeric array (Fig. 5). The anion,  $[\{(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2\}_2(\mu_2\text{-Cl})_3]^-$ , was first prepared by Dias et al. [15] as the counter ion of both the *N*-isopropyl-2-(*iso* propylamino)troponiminato tin(II) and germanium(II) [16] cations. Unlike the two previously reported examples, the anion  $[\{(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2\}_2(\mu_2\text{-Cl})_3]^-$  in **4** is disposed about a crystallographic

center of symmetry. Nevertheless, the metrical parameters are comparable to those previously reported [15,16].

### 3. Conclusion

While transmetalation from NHC-silver(I) halides has proven to be an effective method for the synthesis of late transition metal-NHC complexes, NHC-silver(I) chlorides do not act as NHC transfer reagents to Lewis acidic compounds containing  $d^0$  group 4 transition metals. The reaction with these highly chlorophilic metal

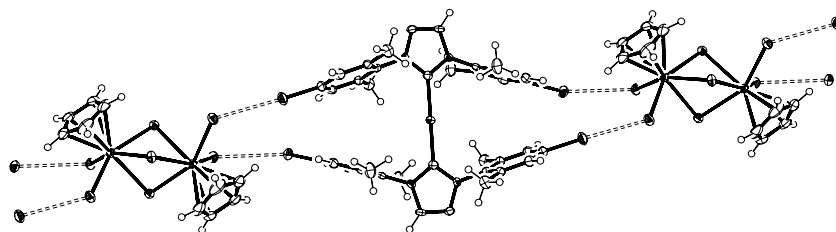


Fig. 5. Extended view of the polymeric chain in **4**.

complexes proceeds via chloride ligand transfer and results in the formation of ionic compounds containing dicarbene silver(I) cations and large di-nuclear group 4 metal chloride anions. The ease of formation and high stability of the large  $[(\text{IMes})_2\text{Ag}]^+$  cation suggests that NHC-silver(I) halides will prove useful reagents in the stabilization and crystallization of salts containing large anions.

## 4. Experimental

### 4.1. General data

The preparations of the imidazolium chlorides and the (imidazol-2-ylidene)silver(I) chlorides were performed in air using reagent grade solvents as received. The reactions involving  $\text{TiCl}_4$  and  $(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_3$  were performed under an atmosphere of dry argon in dichloromethane that was freshly distilled from calcium hydride under dry nitrogen. NMR spectra were recorded on a Bruker AMX400 spectrometer and are referenced via internal solvent resonances to TMS.

1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride and 1,3-bis-(4-bromo-2,6-dimethylphenyl)imidazolium chloride were prepared from stoichiometric amounts of *para*-formaldehyde, glyoxal, hydrochloric acid and the appropriate substituted aniline (2,4,6-trimethylaniline or 4-bromo-2,6-dimethylaniline) using a modification of the method given by Tilset et al. [17] (our preparations were carried out in air using solvents as received rather than the anhydrous and anaerobic conditions described in [15]). 1,3-Bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene silver(I) chloride (**1**) was prepared according to Ramnial et al. [10]. The transition metal containing compounds ( $\text{Ag}_2\text{O}$ ,  $\text{TiCl}_4$  and  $(\eta^5\text{-C}_5\text{H}_5)\text{-ZrCl}_3$ ) were purchased from Strem and used as received.

### 4.2. Preparation of 1,3-bis-(4-bromo-2,6-dimethylphenyl)imidazol-2-ylidene silver(I) chloride (**2**)

Excess  $\text{Ag}_2\text{O}$  (2.26 g; 9.80 mmol) was added to a solution of 1,3-bis(4-bromo-2,6-dimethylphenyl)imidazolium chloride (4.04 g; 8.50 mmol) in 100 mL dichloromethane. The mixture was heated at reflux for 18 h. After filtration

through Celite® the solvent was removed and the crude product dissolved in 100 mL tetrahydrofuran. The volume was reduced to 20 mL and the solution set aside for 48 h at  $-30^\circ\text{C}$ . The product formed as colorless crystals that were collected by filtration. Melting point:  $278\text{--}284^\circ\text{C}$ . Yield 3.36 g (67.7%). Anal. Found: C, 39.67; H, 2.95; N, 4.71. Calcd for  $\text{C}_{19}\text{H}_{18}\text{AgBr}_2\text{ClN}_2$ : C, 39.52; H, 3.14; N, 4.85.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.10 (s, 12H, *o*- $\text{CH}_3$ ), 7.18 (s, 2H,  $\text{C}=\text{CH}$ ), 7.39 (s, 4H, Ar-*H*).  $^{13}\text{C}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  17.8 (s, *o*- $\text{CH}_3$ ), 123.0 (s, Ar- $\text{C}_4$ ), 124.4 (s,  $\text{N}=\text{C}=\text{N}$ ), 132.2 (Ar- $\text{C}_{3,5}$ ), 134.8 (Ar- $\text{C}_1$ ), 135.4 (Ar- $\text{C}_{2,6}$ ).

### 4.3. Preparation of $[\text{Ag}(\text{IMes})_2]^+[(\text{TiCl}_3)_2(\mu_2\text{-Cl})_3]^-$ (**3**)

Titanium(IV) chloride (0.50 g, 2.63 mmol) was added to a solution of  $(\text{IMes})\text{AgCl}$  (1.14 g, 2.55 mmol) in dichloromethane (10 mL). On stirring at room temperature for 24 h, a white precipitate formed. The mixture was filtered through Celite® and the volume of solution reduced to 1 mL. After setting aside at  $-30^\circ\text{C}$  for 4 days, the product formed as yellow crystals, which were collected by filtration. Yield 1.15 g (83.2%). Anal. Found: C, 44.33; H 4.23, N 4.86. Calcd for  $\text{C}_{42}\text{H}_{48}\text{AgCl}_9\text{N}_4\text{Ti}$ : C, 44.58, H 4.27, N 4.95.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  2.12 (s, 24H, *o*- $\text{CH}_3$ ), 2.35 (s, 12H, *p*- $\text{CH}_3$ ), 7.20 (s, 8H, Ar-*H*), 8.29 (dd, 4H,  $\text{C}=\text{CH}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  17.3 (s, *o*- $\text{CH}_3$ ), 21.0 (s, *p*- $\text{CH}_3$ ), 125.2 (s,  $\text{N}=\text{C}=\text{N}$ ), 129.7 (s, Ar- $\text{C}_{3,5}$ ), 134.7 (s, Ar- $\text{C}_{2,6}$ ), 134.8 (s, Ar- $\text{C}_1$ ), 141.0 (s, Ar- $\text{C}_4$ ).

### 4.4. Preparation of $[\text{Ag}(\text{IMes}^{\text{Br}})_2]^+[\{(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2\}_2(\mu_2\text{-Cl})_3]^-$ (**4**)

A suspension of  $(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_3$  (1.00 g, 3.81 mmol) in dichloromethane (5 mL) was added to a solution of  $(\text{IMes}^{\text{Br}})\text{AgCl}$  (2.20 g, 3.81 mmol) in dichloromethane (10 mL). After stirring at room temperature for 24 h, the mixture was filtered through Celite® and the volume of solution reduced to 1 mL. On standing for a further 24 h at  $-30^\circ\text{C}$ , the product formed as colorless crystals. Yield 2.93 g (66.7%). Anal. Found: C, 37.18, H 3.14, N 4.00. Calcd for  $\text{C}_{48}\text{H}_{46}\text{AgBr}_4\text{Cl}_7\text{N}_4\text{Zr}_2$ : C 37.51, H 3.02,

Table 1  
Crystallographic data

	Complex 2	Complex 3	Complex 4
Empirical formula	C <sub>19</sub> H <sub>18</sub> Ag <sub>1</sub> Br <sub>2</sub> Cl <sub>1</sub> N <sub>2</sub>	C <sub>42</sub> H <sub>48</sub> Ag <sub>1</sub> Cl <sub>9</sub> N <sub>4</sub> Ti <sub>2</sub>	C <sub>48</sub> H <sub>46</sub> Ag <sub>1</sub> Br <sub>4</sub> Cl <sub>7</sub> N <sub>4</sub> Zr <sub>2</sub>
Formula weight	577.49	1131.56	1536.99
T (K)	123	123	123
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space Group	C2/c	P2 <sub>1</sub> /n	C2/c
a (Å)	29.5147(5)	19.1708(3)	25.8056(5)
b (Å)	8.3545(1)	14.4325(2)	14.4502(4)
c (Å)	17.2457(4)	20.6658(3)	17.5313(4)
β (°)	97.607(1)	116.551(1)	122.045(1)
Z	8	4	4
V (Å <sup>3</sup> )	4215.03	5114.84(13)	5541.3(2)
μ <sub>calc</sub> (mm <sup>-1</sup> )	4.879	1.187	3.978
F(0 0 0)	2240	2288	2992
Crystal dimensions (mm)	0.22 × 0.22 × 0.20	0.55 × 0.22 × 0.15	0.12 × 0.12 × 0.05
Color	Colorless	Yellow	Orange
Radiation	Mo Kα	Mo Kα	Mo Kα
No. reflections measured	23456	20579	12377
No. unique reflections	4822 (R <sub>int</sub> = 0.0360)	11459 (R <sub>int</sub> = 0.0706)	6347 (R <sub>int</sub> = 0.0562)
No. of parameters	231	535	303
R <sup>a</sup> (I > 2σ(I))	0.0264	0.0350	0.0373
R <sub>w</sub> <sup>b</sup> (all reflections)	0.0579	0.0712	0.0655
GOF	1.054	1.024	1.003

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b R_w = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]}{\sum [w(F_o^2)]} \right\}^{1/2}$$

N 3.65. The compound was insoluble in standard deuterated solvents and decomposed rapidly in DMSO; we were, therefore, unable to record NMR spectra.

#### 4.5. X-ray structure determinations

Crystallographic data for the complexes **2**, **3** and **4** are given in Table 1. Data were collected at 123 K on a Nonius Kappa-CCD diffractometer using graphite-monochromated Mo Kα radiation (0.710 73 Å). The structures were solved using direct methods (SHELXS-86) [18], and refined by full-matrix least squares on F<sup>2</sup> (SHELXL-93) [19]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms placed in calculated positions, riding on the parent atom. All calculations used the WinGX graphical interface [20].

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