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Ag(I) N-Heterocyclic Carbene Complexes: Synthesis, Structure, and Application

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1. Introduction

Öfele and Wanzlick first pioneered the metalation of imidazol-2-ylidenes, better known as N-heterocyclic carbenes (NHCs), from imidazolium salts in 1968.[1,2] Lappert and co-workers followed this work with the investigation of N-heterocyclic carbene complexes synthesized from electron-rich olefins.[3,4] However, it was not until the isolation of the first free carbene by Arduengo, in 1991, that significant interest was given to the area.[5] Since then the complexation chemistry of these new ligands has become a major area of research.[6−10] This new class of ligand has shown to equal, if not exceed, phosphines in their ability to bind to a variety of metals.

Complexes of N-heterocyclic carbenes with virtually every transition metal and many main group elements have been reported.[1−10] N-Heterocyclic carbenes bind to both hard and soft metals making it a very versatile ligand system. NHCs bond to metals primarily through σ donation of the carbene lone pair to the metal. The bonding of the carbene was believed to have been purely σ donation in nature; however, recent evidence suggests that some degree of back-donation may occur.[11,12] The bond strength of N-heterocyclic carbenes, as mentioned earlier, has been shown to rival phosphines. Due to this bonding

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Jered Garrison was born in Marion, OH, in 1978. He received his B.S. degree in chemistry at Miami University in 2000. In the fall of 2000, he began the chemistry graduate program at the University of Akron under the direction of Professor Wiley Youngs. During his time in the Youngs' lab, he focused on the metalation chemistry involving N-heterocyclic carbenes and alkynes. He earned his Ph.D. in the summer of 2005. Currently, he is located at the University of Missouri in Columbia, MO, where he is conducting postdoctoral research involving radiopharmaceuticals under the direction of Professor Silvia Jurisson and Professor Timothy Hoffman.

Wiley Youngs is originally from northern New York State. He received a B.A. in Psychology from the State University of New York at Albany and returned to school to take undergraduate courses in chemistry at SUNY Potsdam and Clarkson University. He received a Ph.D. degree in 1980 under the supervision of Prof. Melvyn R.Churchill at SUNY Buffalo. After a postdoctoral fellowship with Prof. James A. Ibers at Northwestern University, he joined the faculty at Case Western Reserve University in 1983. In 1990, he moved to the University of Akron. His research interests include cyclynes, metal alkynes, N-heterocyclic carbenes, silver antimicrobials, metal-based cancer drugs, and fuel cell membranes.

strength, synthesizing N-heterocyclic carbene analogues of phosphine catalysts and studying their catalytic activity has received a great deal of interest.[7,8,13,14]

The first structurally characterized silver NHC complex was made by using a free carbene and a silver salt.[15] However, generation of the free carbene has been problematic for some NHC systems. This led to the discovery, by several research groups, of silver bases with which silver NHCs could be synthesized from imidazolium salts in-situ. In 1997, Bertrand and colleagues reported the synthesis of a silver NHC from triazolium salts using silver acetate.[16] Lin and Wang, in 1998, reported the syntheses of silver NHCs using Ag_2O.[17] Danopoulos and colleagues reported the syntheses of silver NHC complexes using Ag_2CO_3 in 2000.[18] These procedures, particularly Lin's, allowed N-heterocyclic carbene complexes of silver to be readily available and have led to a diverse area of research. Silver N-heterocyclic carbene complexes have played an important role in the development of other metal−carbene systems. Transmetalation reactions using silver carbenes have been reported for a wide variety of transition metals: Au(I), Cu(I), Cu(II), Ni(II), Pd(II), Pt(II), Rh(I), Rh(III), Ir(I), Ir(III), Ru(II), Ru(III), and Ru(IV). Recent reviews dealing with silver N-heterocyclic carbenes have been published by Arnold[19] and Lin and Vasam.[20]

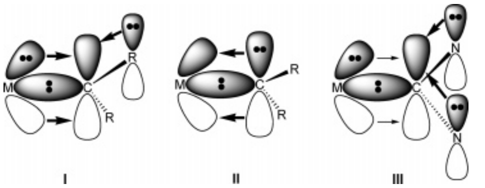


Figure 1. Orbital diagrams of a Fischer (**I**), Schrock (**II**), and N-heterocyclic (**III**) carbene.

Silver is a metal that has historically been used to maintain human health. Silver metal has been used by many early civilizations in the purification of drinking water. Throughout the 18th century and up to today, ionic silver compounds have been used as antimicrobial agents. Physicians still use silver salts in wound dressings to prevent infections.[21] The killing power of the silver ions per cell has been shown to be between $10^{-5}-10^{-7}$ ions.[22] The drawback of the current silver antimicrobial agents is that they do not kill over a sustained period of time. The slow release of silver ions from silver N-heterocyclic carbene complexes could obtain a slow release of silver ions into the wound and better prevent infection and promote healing.

This review will focus on the syntheses and uses of silver N-heterocyclic carbenes up to June 30, 2005. The review is subdivided into five categories: (1) background on the bonding of N-heterocyclic carbenes with an emphasis on specifically how they bond to silver(I), (2) syntheses of silver NHCs, (3) structural motifs of silver NHCs, (4) spectral properties of NHCs, and (5) uses of silver NHCs as transfer reagents, as possible antimicrobial agents, and as catalysts. The authors of this review have made compilations of the characteristic properties of all silver NHCs to date (silver−carbene bond lengths and angles, as well as the ^{13}C NMR resonances for the carbene carbons).

2. Background

2.1. Types of Carbenes

To facilitate the discussion of silver N-heterocyclic carbene complexes, a brief review of Fischer and Schrock carbenes and how they relate to NHCs is in order.[23] The molecular orbital diagrams in Figure 1 depict the bonding of Fischer (**I**) and Schrock (**II**) carbenes. Fischer carbenes σ bond to the metal but have an empty p orbital in which to accept electron density. At least one substituent group for Fischer

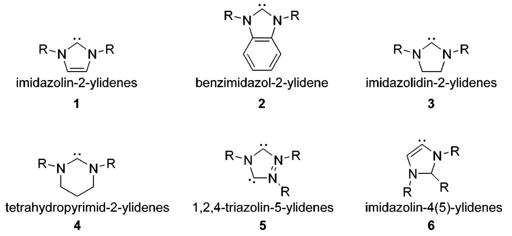


Figure 2. Types of NHCs.

carbenes is able to act as a good π-donor. The empty p orbital of the Fischer carbene is stabilized by significant π contribution from both the substituent(s) and the metal. The need for good π-back-donation from the metal to the empty p orbital of the carbene is critical. Fischer carbene complexes of metals that are poor π-donors, early transition/high oxidation state metals, have been shown to be unstable. On the other hand, complexes of late transition/low oxidation state metals tend to be significantly more stable.

Schrock carbenes tend to bind well with early transition metals with high oxidation states. Better π-donation from the filled p orbital to the d_π orbital of the metal can be achieved if the d-orbitals are empty thereby reducing electron repulsion in the overlapping orbitals. The repulsive effects inhibit the strength of the π-donation and overall lead to the destabilization of the metal Schrock carbene bond. Good substituents for Schrock carbenes are groups that are not π-donors, such as alkyl groups.

N-Heterocyclic carbene complexes (**III**) are also depicted in Figure 1. The stability of an NHC is largely due to the π-donation from the p orbitals of the adjacent nitrogen atoms to the empty p orbital of the carbene. A more detailed review of the electronic properties of N-heterocyclic carbenes can be found in two excellent reviews.[6,7] NHCs have been found to be excellent σ-donors to metals. It was first thought that this was the principle mode in which the carbene bonded to metals. Back-donation from the metal to the ligand was believed to be "negligible". However, recent theoretical and structural evidence has suggested that π-back-donation plays a larger role than previously thought. The degree of back-donation is dependent upon the metal in question. Whereas the degree of π-back-donation may be in question, there is a general consensus that it is smaller than the π-back-donation of Fischer carbenes.

2.2. Types of N-Heterocyclic Carbenes

Several types of N-heterocyclic carbenes have been used to complex silver (Figure 2). Imidazolin-2-ylidene (**1**), the first type of NHC to be complexed to silver, is an imidazole ring with substituents at the nitrogen atoms (1,3-position) and the singlet carbene located at the 2-position.[15] Benzimidazol-2-ylidenes (**2**), derivatives of **1**, have a benzene ring fused to the backbone of the imidazole ring.[17] Imidazolidin-2-ylidenes (**3**) are similar to **1** except that the backbone of the ring (4,5-position) is saturated thereby making the NHC more electron-rich.[24] Tetrahydropyrimid-2-ylidenes (**4**), six-membered saturated ring systems, are an extension of complexes such as **3**.[25,26]

1,2,4-Triazolin-5-ylidenes (**5**) are composed of a five-membered ring with three nitrogen atoms (1,2,4-positions) and the carbenes located at the 3- and 5-positions. Interestingly, the carbons in the 3,5 positions of **5** can both serve as potential carbene donors allowing **5** to bond to more than one metal.[16,27] Imidazolin-4(5)-ylidenes (**6**), also referred to as abnormal carbenes, have been reported where the carbene carbon bonds to the metal in the 4(5)-position, instead of the 2-position.[28]

2.3. Theoretical Calculations of Group 11 N-Heterocyclic Carbenes

Several theoretical studies have been done involving N-heterocyclic carbene complexes of group 11 metals.[11,12,29] Bond strengths of group 11 NHC complexes follow the pattern Au > Cu > Ag. While the silver NHC bonds were calculated to be relatively the weakest, the overall strength of the silver NHC bond is quite strong. An analysis of the bonding, by Frenking and co-workers, revealed the population of the relevant orbitals in the group 11 NHC complexes. This analysis is consistent with the bonding orbitals of the Ag(I) being a hybridization of the filled d_{z^2} orbital and the empty s orbital. This is rationalized as Coulombic repulsion from the lone pair of the NHC forcing the d_{z^2} and s orbitals to hybridize.[29] An analysis of similar systems, by Meyer and colleagues, has led to the same conclusion.[11]

Frenking also suggested that the M–carbene bonds for M = Cu, Ag, and Au were mostly ionic in nature with covalent interactions being nonnegligible. Analyses of NHC carbenes of both silver NHC halide complexes and silver N-heterocyclic biscarbenes by Ziegler and Rauk's energy decomposition schemes suggested that the bonds are mostly electrostatic in nature, with orbital interactions making a smaller contribution.[12] The stabilization energy from the orbital interactions using this method was found to be approximately 70% coming from σ interactions and 30% from π interactions. The calculated π interactions suggest a fairly high degree of π-back-donation for the silver NHC systems. However, π-back-donation for other similar silver carbene systems was found to be approximately half that of the previous value.[11]

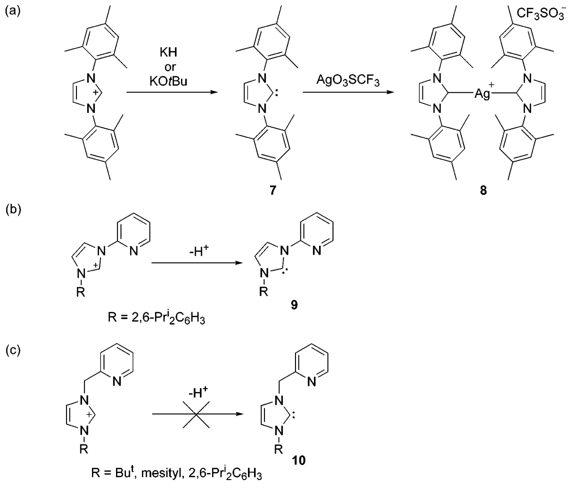
The π-donation of the nitrogen atoms to the empty p orbital increases upon complexation to group 11 metals. This is due to the donation of electron density from the carbene to the metal. The carbene therefore draws more electron density to itself by increasing the amount of electron density withdrawn from the lone pairs of the adjacent nitrogen atoms. Structural evidence also supports this theoretical view by comparison of the carbene–nitrogen bond distances of the complex vs the free carbene.[5,15]

3. Synthesis of Ag(I) N-Heterocyclic Carbenes

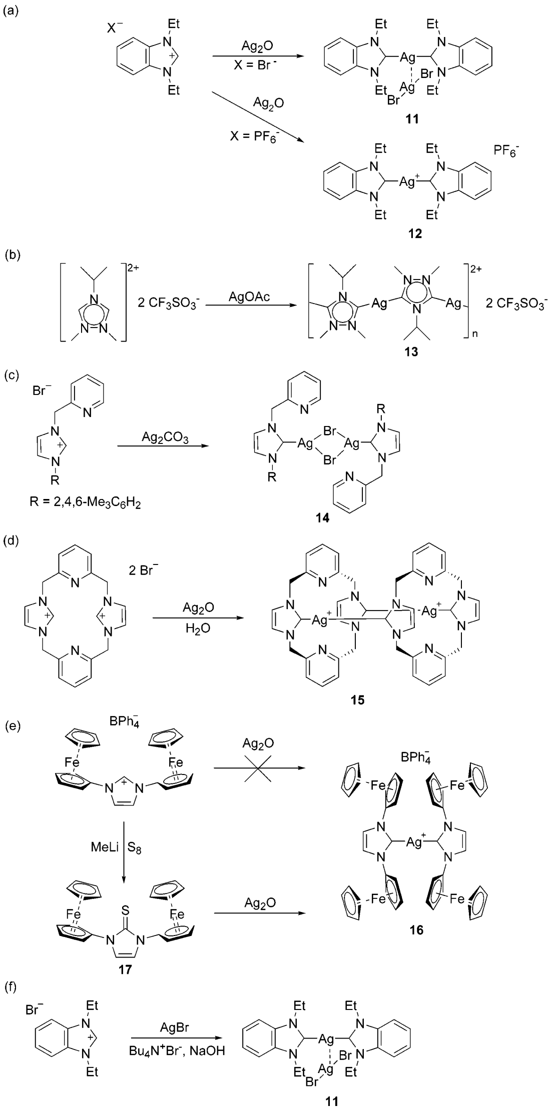
3.1. Free Carbene Route

Silver complexes of N-heterocyclic carbenes have been prepared from imidazolium salts in mainly four ways: (1) preparation of the free carbene and subsequent reaction with a silver salt,[15,30–33] (2) in-situ

Scheme 1



Scheme 2



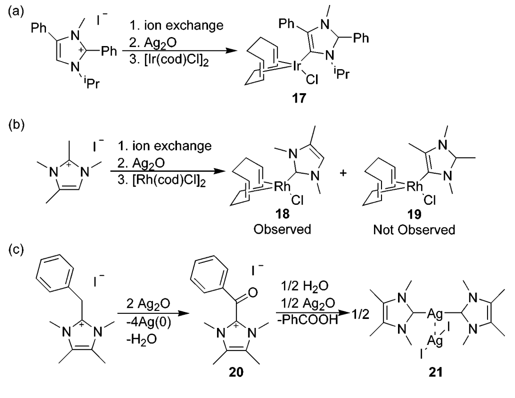
reaction of imidazolium salts with basic silver reagents,[11,16−18,25−28,34−100] (3) in-situ reaction of imidazolium salts with a base in the presence of a silver salt,[17] and (4) transmetalation from a tungsten NHC to silver.[24] The first reported synthesis of an N-heterocyclic carbene silver complex, Scheme 1a, was accomplished by deprotonation of the imidazolium salt to make the free carbene **7** and subsequent reaction of **7** with silver triflate to yield **8**.[15] Synthesis of **7** was novel due to the stability of the N-heterocyclic carbene and its potential use as a new class of ligand. The free carbene **7** could be isolated in high yield and stored for long periods of time. Several silver N-heterocyclic carbene complexes have been synthesized using this method.[15,30−33] While this procedure has been used for the syntheses of a wide variety of metal complexes, the conditions required to generate the free carbene (usually bases such as KH or KO*t*Bu) can lead to deprotonation of other acidic protons in the ligand. This deprotonation can lead to decomposition, particularly in ligands where methylene groups are α to the nitrogen atoms on the N-heterocyclic carbene.[27,30,31,37,45,46,79] Scheme 1b,c demonstrates the relative instability of the methylene-linked ligands vs the direct linkages. In Scheme 1b, the pyridine-linked imidazolium salt is deprotonated to produce the free carbene **9**, which has been complexed to various metals. However, the deprotonation of the methylene-linked imidazolium salt does not proceed smoothly to the free carbene **10** but instead decomposes (Scheme 1c).

3.2. Silver Base Route

Deprotonation by use of a silver base has been the most widely used method in the syntheses of N-heterocylic carbene complexes of silver. This procedure can be accomplished using a variety of silver bases such as Ag_2O, AgOAc, and Ag_2CO_3. Lin and co-workers reported a procedure, Scheme 2a, using Ag_2O to form silver complexes of 1,3-diethylbenzimidazol-2-ylidene, **11** and **12**.[17] Other bases such as AgOAc and Ag_2CO_3 have also been used to synthesize silver N-heterocyclic carbenes with success. The use of AgOAc, reported by Bertrand and colleagues, produced the first silver N-heterocyclic carbene polymer **13** (Scheme 2b).[16,27] Danapolous and co-workers reported the synthesis of a series of N-heterocyclic carbene complexes, such as **14**, using Ag_2CO_3 as a metalation agent for the imidazolium salts (Scheme 2c).[18] This use of Ag_2CO_3 has been employed by others.[51] However, reaction times using Ag_2CO_3 were reported to be longer than reaction times using Ag_2O.[18]

Silver oxide is the most commonly used of the metal bases.[11,17,18,25,26,28,34−100] Reactions can be easily monitored by the uptake of the insoluble silver oxide. A wide variety of solvents have been used with Ag_2O in the synthesis of silver NHCs, such as CH_2Cl_2, 1,2-dichloroethane, DMSO, acetone, methanol, acetonitrile, DMF, and water. In addition to these pure solvents, a number of solvent mixtures have been used as well. The fact that N-heterocyclic carbene complexes, such as **15**, can be made in water suggests that the deprotonation and subsequent metalation is a concerted process (Scheme 2d).[52,71,72] Whereas most of the metalation reactions involving imidazolium salts and silver oxide proceed at room temperature, Tulloch and co-workers found that silver oxide reactions with bulky imidazolium salts often require refluxing.[18] The need for refluxing suggests that

Scheme 3



steric bulk around the imidazolium cation affects the ability of the silver oxide to effectively deprotonate the imidazolium salt. Several groups have used 4 Å molecular sieves in the syntheses of silver NHCs.[18,47,53,59,60,62,84,85,97] It has been reported that the presence of sieves increases the speed of the reaction as well as the purity of some products.

The kinetics of the reaction of silver oxide with imidazolium salts have been shown to differ depending on the number of imidazolium cations.[18] Moieties with one imidazolium ring have been observed to react faster with silver oxide than those ligands that possess two or more imidazolium cations. The functional groups of the imidazolium salts have also been shown to affect the reactivity of the imidazolium salt toward metalation agents such as silver oxide.[34,93] Bildstein and co-workers found that when ferrocenyl groups were placed α to the imidazolium cation, Scheme 2e, the synthesis of silver complex **16** using silver oxide was unsuccessful.[34] The reduced acidity due to the ferrocenyl groups is believed to be the primary reason for the reduced reactivity toward silver oxide. They found that by synthesizing the thiourea derivative **17** from the imidazolium salt, using methyllithium and elemental sulfur, they could obtain the silver N-heterocyclic carbene complex **16** using silver oxide.

Abnormal NHCs have also been synthesized by use of silver oxide. An example of this is depicted in Scheme 3a.[28] The imidazolium salt in Scheme 3a has a phenyl blocking group on the 2-position of the imidazolium ring. Reaction of the imidazolium salt with silver oxide forces the deprotonation of the 4-position forming the abnormal silver NHC complex. Subsequent transmetalation with $[Ir(cod)Cl]_2$ gives the abnormal iridium NHC complex, **17**. Continuing their study into the abnormal binding of the 4(5)-position of NHCs, they explored the metalation chemistry of the imidazolium salt in Scheme 3b.[74] The imidazolium salt has all positions of the ring blocked by methyl groups with the exception of the 4(5)-position. Blocking the other positions was expected to allow the ring to bind only through the 4(5)-position. However, treatment of the imidazolium salt with silver oxide followed by transmetalation with $[Rh(cod)Cl]_2$ yielded the rhodium NHC complex **18** (C2 product) instead of the expected complex **19** (C4-(5) product).

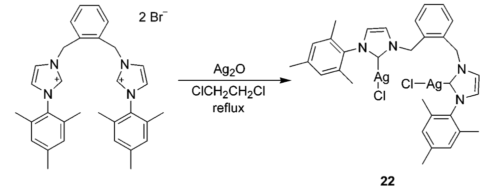
The unexpected C−C cleavage of the methyl at the 2-postion of the imidazolium ring in Scheme 3b prompted Crabtree and co-workers to investigate the mechanism of this C−C bond cleavage.[74] In their investigation, they prepared a series of imidazolium salts that were substituted with methyl groups at all positions of the ring except the 2-position. At the 2-position, several blocking groups such as methyl, ethyl, isopropyl, and benzyl were used to investigate the cleavage process. The imidazolium salt in Scheme 3c is the benzyl derivative of the substituted imidazolium salts. Treatment of the imidazolium salt with silver oxide gave a half of an equivalent of the silver NHC complex **21**, along with 4 equiv of silver metal and 1 equiv of benzoic acid. Crabtree and colleagues hypothesize that the 4 equiv of silver metal is obtained upon oxidation of imidazolium salt in Scheme 3c to the 2-benzoyl imidazolium salt **20**. Compound **20** undergoes hydrolysis to yield the unprotected imidazolium salt (C2−H) and benzoic acid. The unprotected imidazolium salt then reacts with additional silver oxide to yield the silver NHC complex **21**. The oxidative cleavage of the C−C bond was also found to occur for the methyl and ethyl derivatives of the imidazolium salt in Scheme 3c. However, isopropyl and phenyl derivatives do not undergo oxidative cleavage (inactivity of C2−Ph derivatives demonstrated in Scheme 3a). Presumably the isopropyl and phenyl derivatives do not undergo oxidative cleavage due to the their inability to oxidize to the ketone and undergo hydrolysis.

3.3. Base in the Presence of a Silver Salt and Transmetalation to Silver N-Heterocyclic Carbenes

An alternative method in the syntheses of silver N-heterocyclic carbene complexes is the deprotonation of the imidazolium cation in the presence of a silver salt. Lin and Wang reported a method using a basic phase transfer catalyst to synthesize **11** from the benzimidazolium salt in the presence of AgBr, Scheme 2f.[17] This procedure yields the same products as the silver oxide route, Scheme 2a. Although this procedure was successful for Lin and Wang, others have attempted to use this method to synthesize silver NHC complexes of other imidazolium salts without success.[18]

Liu and co-workers reported the transmetalation from tungsten(0) NHC complexes to silver (complexes **84**−**86**, these complexes are depicted in Figure 33 and are discussed in section 5.1).[24,102,103] Although these complexes were not isolated and structurally characterized, spectroscopic evidence indicates that the transformation was achieved. Interestingly, the silver NHC complexes generated from this method were found to be moisture sensitive. This is not characteristic for silver NHC complexes. Exposure of these silver NHCs to air leads to rapid decomposition to the imidazolinium salt. The formation of silver NHC by transmetalation from other metal centers (Mo(0), Cr(0), Pd(II), Rh(I), Pt(II)) has been suggested, but spectroscopic or structural evidence has not been reported to substantiate this assertion.[101,102] These methods of synthesizing silver NHCs have largely been abandoned due to the success of silver oxide.

Scheme 4



3.4. Salt Metathesis, Halogeno Anions, AgX Staircases, and Anion Exchanges

Halogen exchange reactions have been found to occur when N-heterocyclic carbene complexes are synthesized in chlorinated solvents. Danopoulos and co-workers reported halide exchange when synthesizing silver complexes in 1,2-dichloroethane or methylene chloride.[18] The extent of the salt metathesis differed depending upon the reaction conditions and the imidazolium salt used. An example of the halide exchange is depicted in Scheme 4. The diimidazolium salt undergoes salt methathesis in refluxing 1,2-dichloroethane to yield the silver NHC complex **22** with chloride as the coordinating counteranion. Lin and co-workers reported the salt metathesis of imidazolium iodide salts with chloride from methylene chloride during the synthesis of silver NHC complexes.[49] Interestingly, the exchange of bromide for chloride does not occur under the same conditions. The mechanism of the halogen exchange has not been reported, but it seems likely that silver must be present for this exchange process to proceed. It is noteworthy, that many researchers have reported the synthesis of silver NHCs using similar conditions without the occurrence of salt metathesis.

During the syntheses of the silver NHC complexes, a wide variety of halide−silver coordination chemistry can take place, Figure 3. Anionic halogeno complexes of silver ($[Ag_mX_n]^{(n-m)-}$ where $n > m$) can form, which act as the counterion for the charged silver NHC cation.[17,18,48,49,55,67,68,78,92] The larger anionic halogeno anions (larger than $AgBr_2^-$) are typically noted to have limited solubility in organic solvents.[67] The formation of halogeno complexes is dependent upon several factors: solvent, the countercation, halide, etc.[103] Complex **23** in Figure 3 is an example of the formation of a halogeno anion counterbalancing the silver NHC cation.[67] In this example, the anionic silver−halide cluster does not interact with the silver NHC complex. The relative stabilities of the halogeno complexes are $I^- > Br^- > Cl^-$. This is reflected in the silver NHC literature with halogeno complexes of iodide and bromide being more abundant than halogeno chloride complexes.

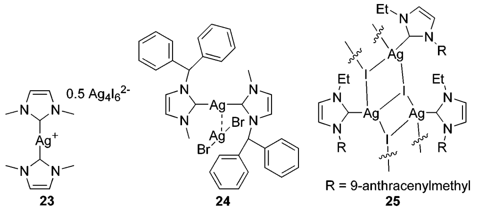


Figure 3. Examples of silver−silver and silver−halide interactions in the solid state.

In many instances, halogeno complexes form neutral compounds in the solid state through silver−silver interactions with the silver NHC complex. Complex **24** is a typical example of this type of interaction.[68] An exception to this was reported by Danapolous and co-workers in which the halogeno complexes were coordinated to an available donor group instead of through a silver−silver interaction.[18] It is unknown whether the silver−silver interaction remains in solution. However, given that complexes such as **24** with halogeno anions of type $AgBr_2^-$ are readily soluble in common organic solvents, it is likely these interactions persist in solution.

The formation of silver−halide "staircases" can also take place during the synthesis of silver NHCs.[49,54,67] These silver−halide staircases form two-dimensional architectures in the solid state on the basis of bridging halides. Complex **25** is an example of a typical staircase structure in which the silver NHCs are bridged by iodides to other silver NHCs.[54] A more detailed discussion of halogeno complexes and silver−halide staircases will be explored in the structural section.

Mixtures of halogeno and halide anions of silver NHCs have been reported.[43,64] To reduce the complications due to inorganic halogeno complexes and cluster formations, anion exchange of the imidazolium halide salt for a noncoordinating anion has been widely employed. After the anion exchange, the synthesis of the silver NHC usually proceeds cleanly to one product. Anion exchange of the halide after the synthesis of the silver NHC complex has also been performed, using reagents such as $AgBF_4$, to obtain clean products without the complexities of the halide.[44,64,66,72−74,78,104] Imidazolium salts with noncoordinating anions can be easier to isolate and work with than their halide counterparts due to the imidazolium halide's hygroscopic nature. Using noncoordinating imidazolium salts and halide sources, such as, Bu_4NCl, is an alternate way of producing silver−halide NHC complexes that avoids working with halide imidazolium salts.[25,49]

4. Structural Diversity of Ag(I) N-Heterocyclic Carbenes

The structural characterization of N-heterocyclic carbene complexes of silver has led to very complex bonding motifs in the solid state, especially in complexes with halide anions. During the compilation of the structural section in this review, it became apparent that the discussion of the structural motifs of NHCs could be divided and addressed in several different manners. It was decided to divide the structural section into two main areas, mono-NHC (one NHC per ligand) and multi-NHC (more than one NHC per ligand) complexes, mono-NHC complexes being the most prominent in the literature. An effort was made to cross-reference the applicable motifs of both sections (mono-NHC and multi-NHC complexes).

Complexes of silver with noncoordinating anions exist as biscarbene salts with the cationic silver bound by two carbene moieties and the noncoordinating anion balancing out the charge (C_2−Ag),

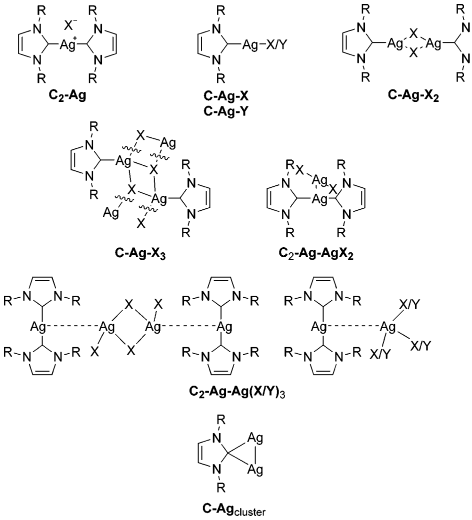


Figure 4. Bonding motifs of silver N-heterocyclic carbenes. X = halide and Y = non-halide.

Figure 4. Coordinating anions, mainly halides, have led to diverse bonding motifs in silver NHC chemistry. These bonding motifs have been characterized in five forms in the solid state: coordinating (C−Ag−X/Y), bridging (C−Ag−X_2), staircase (C−Ag−X_3), halogeno counterion of type $[AgX_2]^-$ (C_2−Ag−AgX_2), halogeno counterions of type $[Ag_2X_4]^{2-}$, and silver NHCs with silver−silver interactions that are stabilized by three donor groups. Silver NHC complexes with halogeno anions of type $[Ag_2X_4]^{2-}$ and complexes with silver−silver interactions stabilized by three donor groups have been placed in the same category, C_2−Ag−Ag$(X/Y)_3$, due to the structural similarities of these two groups. There is also a bonding motif in which NHCs are bonded to two silver cations of a cationic silver cluster (C−$Ag_{cluster}$). The discussion in this section will be divided into mono-NHC and multi-NHC complexes of silver(I). To discuss the general properties of each bonding motif, the discussion will be divided further into the categories given in Figure 4. The only exception to this is the C−$Ag_{cluster}$ motif; this bonding mode will be discussed separately.

During this structural discussion of silver NHC complexes, d^{10}−d^{10} interactions must be considered. The existence of metal(I)−metal(I) interactions of the coinage metals is widely acknowledged, particularly for gold. Gold has been shown to form complexes with particularly strong aurophillic interactions due to relativistic effects.[105] The strength of the d^{10}−d^{10} interactions for metal(I)−metal(I) systems is weaker than covalent bonds, but stronger than London dispersion forces. Qualitative estimates of the strength of these closed shell metal interactions are approximately equal to hydrogen bonding. Given this, it is not surprising that argentophillic interactions play a key role in the formation of many diverse silver(I)−silver(I) architectures in the solid state.

To proceed with the structural discussion, a decision must be made as to what is a significant silver(I)−silver(I) interaction and what is to be considered a contact. The metal−metal distance in metallic silver is 2.88 Å,[106] while the sum of the van der Waals radii for silver(0) is 3.44 Å.[107] These two values can be used as two extremes on a scale for determination of strong and weak interactions. Strong interactions are likely to be <3.0 Å, while weaker intereactions will be >3.3 Å. To discuss discrete molecules, it was decided to treat all silver(I)−silver(I) distances less than 3.3 Å as strong enough to merit depiction as bonds in all drawings and figures. Those interactions greater than 3.3 Å are omitted from the depictions. It is not the intent to give the impression that these “cutoffs” are based on evidence that silver(I)−silver(I) interactions greater than 3.3 Å are irrelevant. These assumptions are made only to simplify the discussion of the structural section.

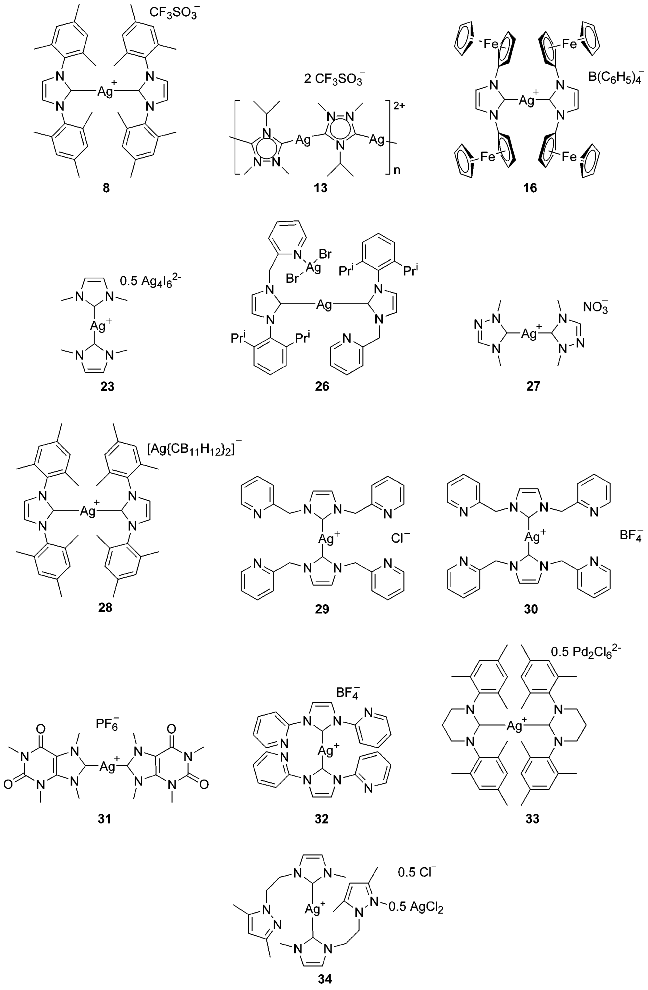


Figure 5. Mono-NHC biscarbenes with noncoordinating anions (C_2−Ag).

4.1. Mono-N-Heterocyclic Carbene Complexes of Silver

4.1.1. Mono-N-Heterocyclic Carbene Complexes of Silver with Noncoordinating Anions (C_2–Ag)

Mono-N-heterocyclic carbene complexes of silver with noncoordinating anions exist as biscarbenes in the solid state. All structurally characterized mono-NHC complexes of silver to date are given in Figure 5 (multi-NHC complexes of silver with noncoordinating anions are addressed in section 4.2.1). Examples of this structural motif, **8**, **13**, and **16**, are shown in Figure 6. The syntheses and relevant crystallographic data of these complexes are given in Scheme 2a,b,e

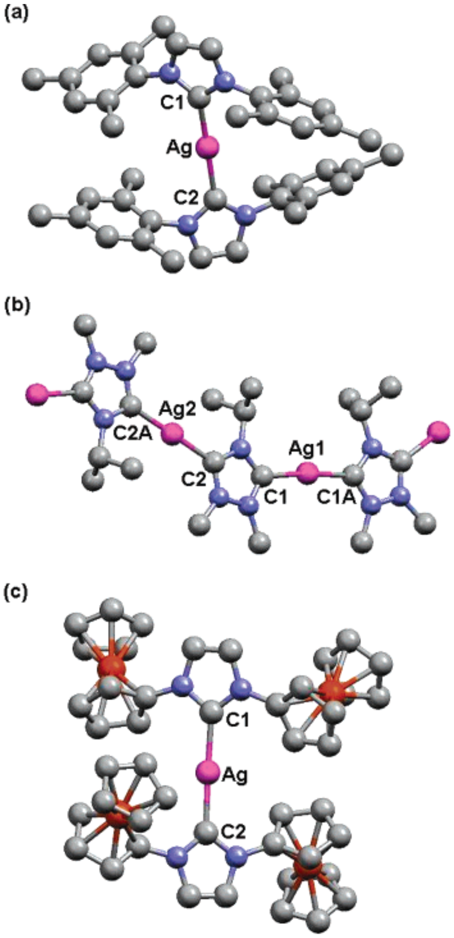


Figure 6. Molecular structures of the cationic portions of **8** (a), **13** (b), and **16** (c).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 8, 13, and 16[a]

compound	**8**[15]	**13**[16]	**16**[34]
Bond Lengths			
C1−Ag	2.067(4)	2.086(4)	2.092(4)
C2−Ag	2.078(4)	2.090(4)	2.082(4)
Bond Angles			
C−Ag−C	176.3(2)	174.7(2)/180	176.8(2)
Planes Calculation			
NHC ring/NHC ring	39.7	2.6/0.0	38.3

[a] The bond distances and angles were gathered from CIF files obtained from the Cambridge Structural Database (CSD). When values could not be obtained from the CSD, the values cited in the literature were used. Planes calculations were done using XP from the SHELXTL suite.

and Table 1. In complex **8**, the silver cation is coordinated to two NHCs. The silver−carbene bond distances are 2.067(4) and 2.078(4) Å for C1−Ag and C2−Ag, respectively.[15] The C1−Ag−C2 bond angle is close to linearity with an angle of 176.3(2)°.

The two NHC ligands in complex **8** are twisted with respect to one another. Planes calculations reveal an angle of 39.7° relative to the positions of the two NHC rings. The molecular structure of complex **16** is similar to **8** in that the molecule is a biscarbene in the solid state and the NHCs are N-functionalized with bulky groups, in this case ferrocenyl groups.[34] In a manner similar to complex **8**, the NHC rings of complex **16** are rotated 38.3° with respect to one another.

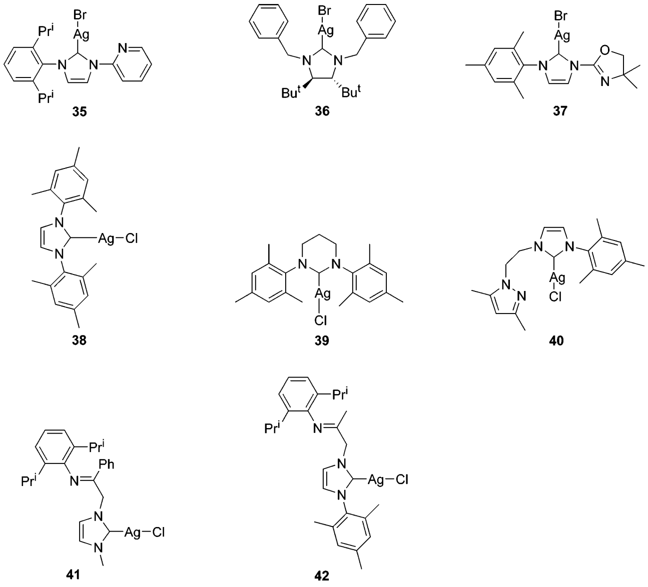


Figure 7. Silver N-heterocyclic carbenes with coordinating halides (C−Ag−X).

Complex **13** is unique in that the ligand is a single 1,2,4-triazolin-2-ylidene ring but is bound to two different metal centers.[16] The placement of this complex here in this review was debatable, but it was ultimately placed in the section because the ligand was composed of only one ring. Complex **13** is polymeric in the solid state with silver−carbene bond distances of 2.086(4) Å for C1−Ag1 and 2.090(4) Å for C2−Ag2. The silver−carbene bond angles are 174.7(2)° and 180° for C1−Ag1−C1A and C2−Ag2−C2A, respectively. Planes calculations of the NHC rings in complex **13** reveal a very different situation from that of **8** and **16**. The torsion angles between the two NHC rings is 2.6° for the NHC rings bonding to Ag1 and perfectly planar for the NHC rings bonding to Ag2. Comparison of **13** with **8** and **16** suggests that substituents in complexes **8** and **16** result in the rotation of the NHC rings to alleviate steric collisions. Complex **13** does not have the steric constraints and therefore is able to form the planar polymeric system.

4.1.2. Mono-N-Heterocyclic Carbene Complexes of Silver with One Coordinating Anion (C–Ag–X and C–Ag–Y)

Silver N-heterocyclic carbene complexes with singly coordinating anions are neutral with silver linearly bound to both a carbene moiety and an anion, usually a halide. Figure 7 gives all structurally characterized mono-NHC complexes of silver with coordinating halides to date (multi-NHC complexes of silver with coordinating halides are addressed in section 4.2.2). Complexes **35**, **36**, and **37** are examples of this type, and the molecular structures of these complexes are depicted in Figure 8a−c. The syntheses and relevant structural information of these complexes are given in Scheme 5a−c and Table 2. The silver−carbene bond distances for these complexes are 2.075(7), 2.09(2), and 2.093(4) Å for **35**, **36**, and **37**, respectively.[18,41,45] The Ag−Br bond distances for these

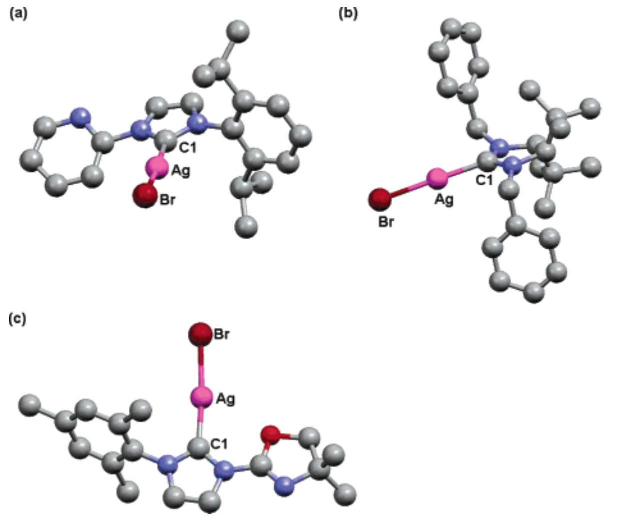


Figure 8. Molecular structures of **35** (a), **36** (b), and **37** (c).

Scheme 5

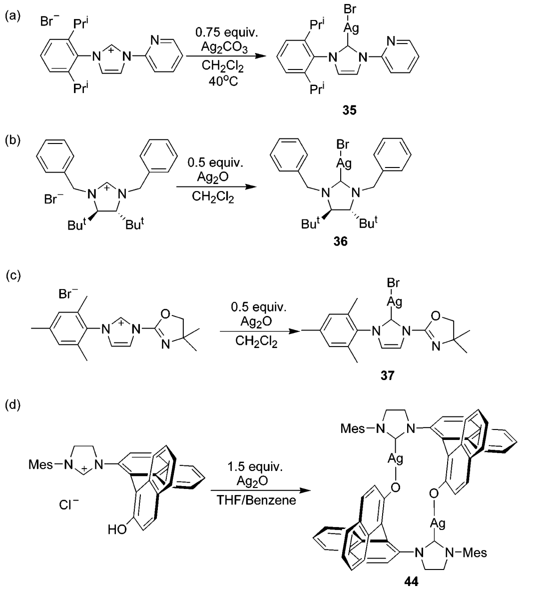


Table 2. Selected Bond Lengths (Å) and Angles (deg) for 35, 36, 37, and 44[a]

compound	**35**[18]	**36**[41]	**37**[45]	**44**[84]
		Bond Lengths		
C−Ag	2.075(7)	2.09(2)	2.093(4)	2.073(4)/2.071(3)
Ag−X	2.421(1)	2.401(3)	2.4303(6)	
Ag−O				2.129(3)/2.120(3)
		Bond Angles		
C−Ag−Br	176.1(2)	175.2(5)	169.4(1)	
C−Ag−O				174.7(1)/172.6(1)

[a] All values were gathered from CIF files obtained from the Cambridge Structural Database (CSD). When values could not be obtained from the CSD, the values cited in the literature were used.

complexes are consistent with distances ranging from 2.401(3)−2.4303(6) Å. The C1−Ag−Br bond angles are slightly bent with angles ranging from 169.4(1)°−176.1(2)°.

Structurally characterized silver NHC complexes with coordinating anions other than halides are relatively rare, Figure 9.[33,84,97] Complex **44** was synthesized from the imidazolium salt using 1.5 equiv of Ag_2O, Scheme 5d. The molecular structure of **44** is depicted in Figure 10, and the structural information for this complex is given in Table 2. Complex **44** was structurally characterized as the dimer in the solid state with each silver cation coordinating to an NHC as well as a phenoxide anion.[84] The silver−carbene bond distances are 2.073(4) (C1−Ag1) and 2.071(3) Å (C2−Ag2) with angles of 174.7(1)° and 172.6(1)° for C1−Ag−O2 and C2−Ag2−O1, respectively. The Ag1−Ag2 interaction is 3.2660(7) Å.

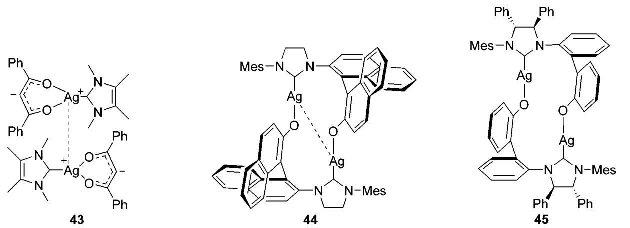


Figure 9. Silver N-heterocyclic carbenes with coordinating anions other than halides (C−Ag−Y).

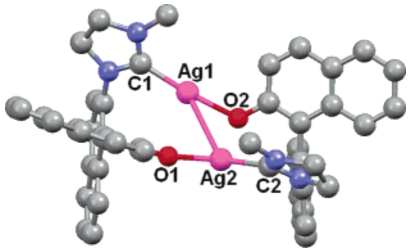


Figure 10. Molecular structures of complex **44**. Mesityl groups with the exception of the meso carbon were removed for clarity.

4.1.3. Mono-N-Heterocyclic Carbene Complexes of Silver with Bridging Halides (C–Ag–X_2)

Bridging halide complexes exist as neutral dimers with two silver cations each bound by a carbene moiety. The two silver NHC cations are connected by two bridging halides. In Figure 11 are all currently structurally characterized examples of mono-NHC complexes of this type (multi-NHC complexes of silver with bridging anions are addressed in section 4.2.3.) Complexes **14**, **48**, and **51** are depicted in Figure 12a−c, and the syntheses of these complexes are given in Scheme 6a−c. A compilation of all relevant bond distances and angles for these structures is given in Table 3. In complex **14**, the silver−carbene bond distances are 2.07(2) Å.[18] The Ag_2Br_2 cluster of **14** is planar with the bromides asymmetrically bound to the silver cations. The silver−bromide distances are 2.373(4) and 2.952(4) Å for Ag−Br and Ag−BrA, respectively. The bond angle for C1−Ag−Br is 162.5(5)°, whereas the C1−Ag−BrA angle is 94.6(5)°. Complex **51** has a similar arrangement to that of complex **14**.[85] The silver−carbene distance of **51** is 2.102(6) Å. The Ag_2Br_2 cluster's bond distances and angles are consistent with those of **14**.

The molecular structure of complex **48** is similar to those of **14** and **51** in that a Ag_2I_2 cluster is bridging two silver NHCs; however, in this case the silver−halide cluster is not planar but forms a

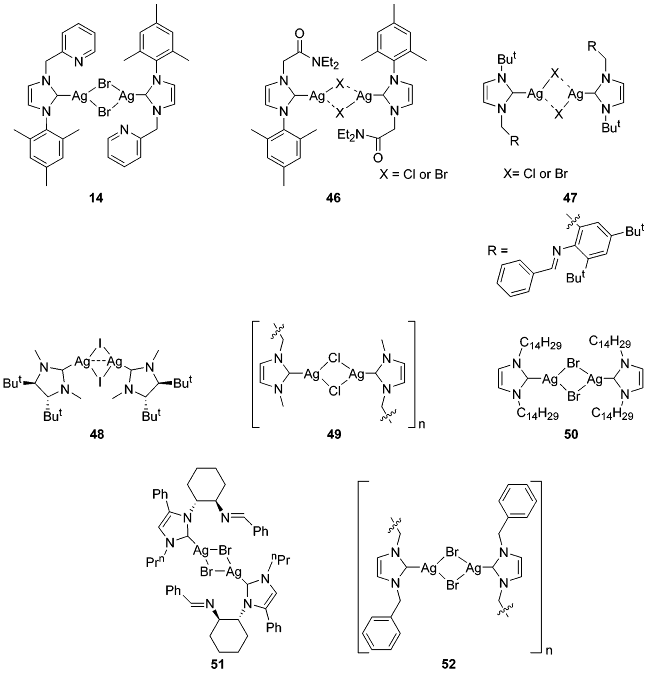


Figure 11. Silver N-heterocyclic carbenes with bridging halides (C−Ag−X_2).

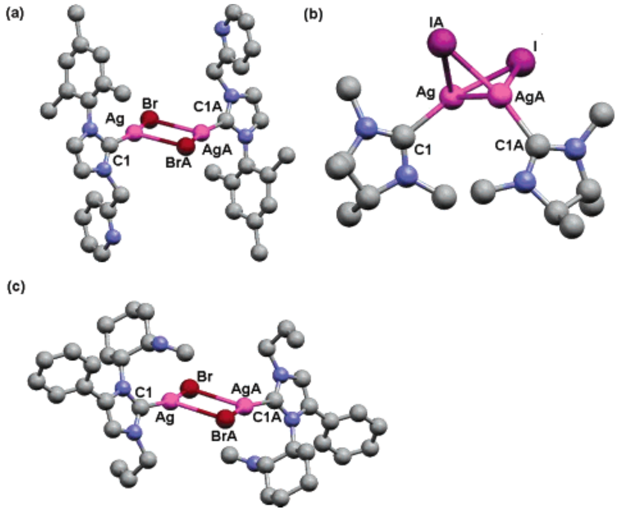


Figure 12. Molecular structures of silver NHC complexes **14** (a), **48** (b), and **51** (c). In compound **48**, the methyl groups of the *tert*-butyls were removed for clarity. In complex **51**, the phenyl groups of the imine were removed for clarity.

"butterfly" configuration.[41] The silver−carbene bond distances are 2.120(8) Å. The silver−iodide bonding is asymmetric with distances of 2.6251(8) and 3.337 Å for Ag−I and Ag−IA, respectively. The Ag_2I_2 cluster "butterfly" formation allows for a close silver−silver interaction between Ag and AgA (3.020(1)Å). Presumably, this is due to the low steric bulk of the N-functionalized methyl groups allowing the two NHC rings to be bent toward one another.

Scheme 6

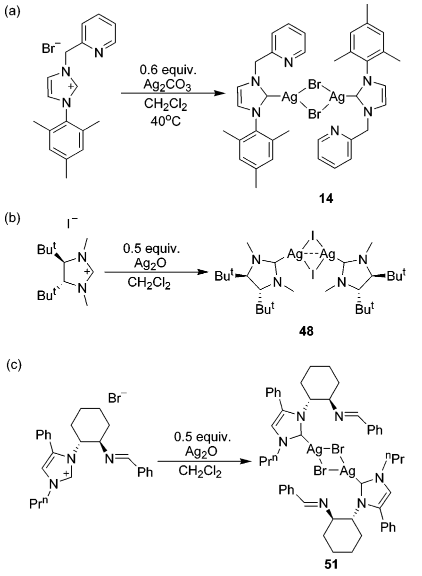


Table 3. Selected Bond Lengths (Å) and Angles (deg) for 14, 48, and 51[a]

compound	14[18]	48[41]	51[85]
	Bond Lengths		
C1−Ag	2.07(2)	2.120(8)	2.102(6)
Ag−X	2.373(4)	2.6251(8)	2.4778(8)
Ag−XA	2.952(4)	3.337[b]	3.0338(9)
Ag−AgA		3.020(1)	
	Bond Angles		
C1−Ag−X	162.5(5)	166.3(2)	159.1(2)
C1−Ag−XA	94.6(5)	101.2[b]	101.6(1)
Ag−X−AgA	77.6[b]	59.4[b]	80.66(2)
X−Ag−XA	102.4(2)	90.5[b]	99.34(2)

[a] All values were gathered from CIF files obtained from the Cambridge Structural Database (CSD). When values could not be obtained from the CSD, the values cited in the literature were used. [b] Value was not reported; the value was determined using atomic coordinates with Mercury 1.2.1

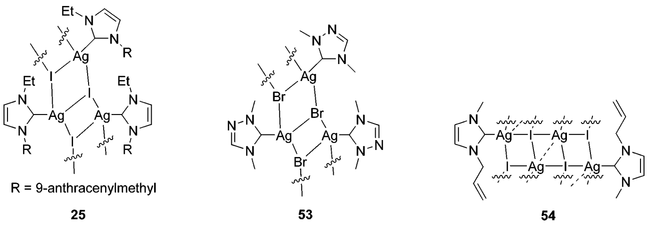


Figure 13. Silver NHC halide staircases (C−Ag−X_3).

4.1.4. Formation of Silver "Staircases" Using Mono-N-Heterocyclic Carbenes (C–Ag–X₃)

All structurally characterized complexes of silver NHC halide staircases are given in Figure 13. The molecular structures of **53**, **25,** and **54** are depicted in Figure 14a−c. Relevant structural information and syntheses for **53**, **25,** and **54** are given in Table 4 and Scheme 7a−c. The silver cations in complexes **53**, **25**, and **54** are tetracoordinate, bound by one N-heterocyclic carbene and three bridging halides. The NHC rings for these complexes form a slip stacked arrangement with NHC ring−NHC ring distances of 3.62 (**53**), 3.572 (**25**), and 3.32 Å (**54**). The silver−carbene bond distances (C1−Ag) are 2.131(5), 2.182(7), and 2.161(9) Å for **53**, **25**, and **54**, respectively.

Complexes **53** and **25** are similar to complex **14**, in that the repeating unit consists of a Ag_2X_2 cluster. The bonding distances between the silver cation and the bromides in complex **53** are asymmetric with Ag−BrA being the closest (2.6581(8) Å).[49] The remaining

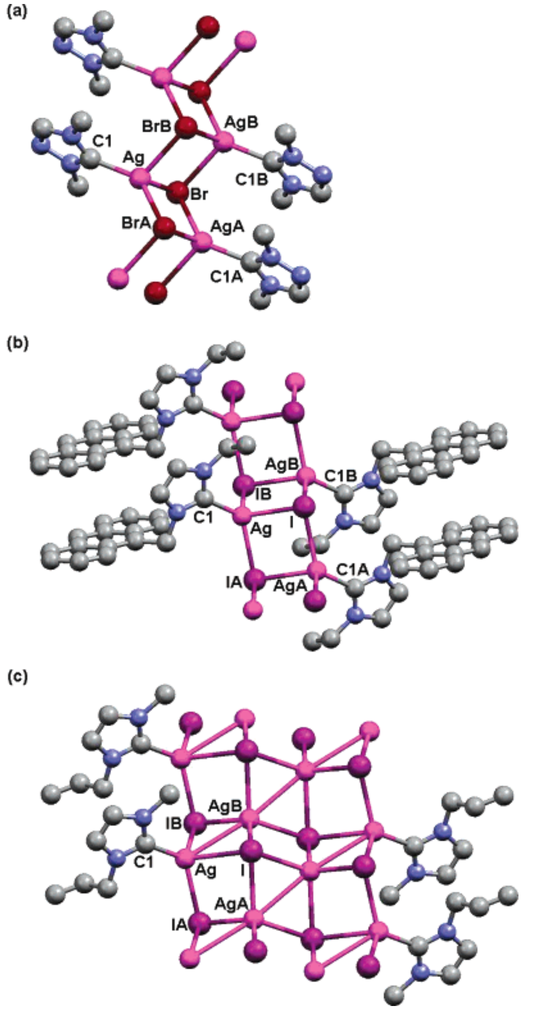


Figure 14. Molecular structures of **53** (a), **25** (b), and **54** (c).

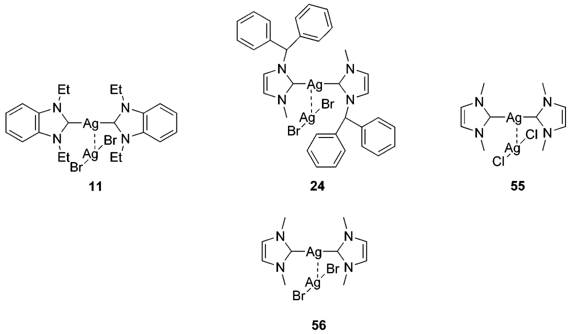


Figure 15. Silver N-heterocyclic carbenes with halogeno counteranions of type $[AgX_2]^-$ (C_2−Ag−AgX_2).

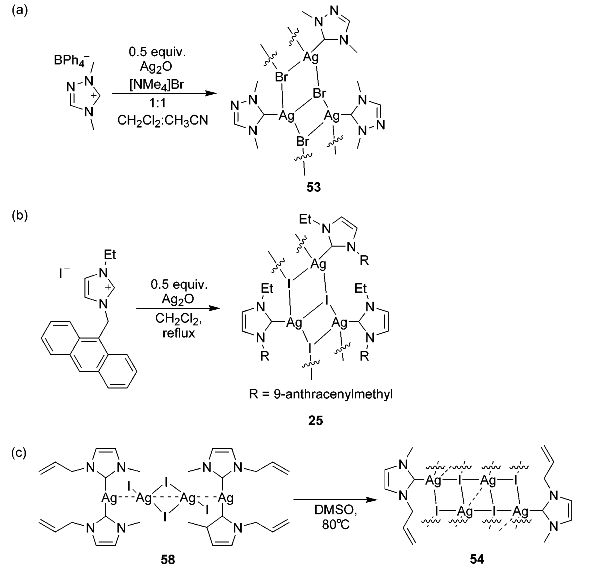
two silver−bromide distances are ~0.2 Å longer. The Ag−I staircase for complex **25** is similar to that of **53**; however, the Ag−I bond lengths for **25** are slightly longer than those for **53**, as expected, with distances ranging from 2.872(1)−3.010(2) Å.[54] Complex **54** is an extended analogue of complexes **53** and **25**.[67] In this staircase complex, the repeating Ag−I unit consist of a Ag_4I_4 cluster. The Ag−I distances range from 2.872(2)−3.233(3) Å. Interestingly, the synthesis of complex **54** is based upon rearrangement of silver NHC complex **58** upon heating in DMSO (complex **58** will be discussed later).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 53, 25, and 54[a]

compound	**53**[49]	**25**[54]	**54**[67]
	Bond Lengths		
C1−Ag	2.131(5)	2.182(7)	2.161(9)
Ag−X	2.8658(8)	3.010(2)	3.233(3)
Ag−XA	2.6581(8)	2.872(1)	2.872(2)
Ag−XB	2.8467(8)	2.921(1)	2.922(2)
Ag−AgB			3.217(2)
	Bond Angles		
C1−Ag−X	111.5(1)	111.7(2)	107.8(3)
C1−Ag−XA	135.0(1)	125.9(2)	126.1(3)
C1−Ag−XB	112.9(2)	111.8(2)	117.5(3)
Ag−X−AgA	80.68(2)	87.32(3)	77.49(4)
Ag−X−AgB	84.58(2)	71.65(3)	63.35(3)
Ag−XA−AgB	95.20(2)	104.22(4)	101.24(7)
X−Ag−XA	99.32(2)	92.68(3)	93.87(4)
X−Ag−XB	95.42(2)	108.35(3)	106.71(4)
XA−Ag−XB	95.20(2)	104.22(4)	101.24(7)

[a] All values were gathered from CIF files obtained from the Cambridge Structural Database (CSD). When values could not be obtained from the CSD, the values cited in the literature were used.

Scheme 7



4.1.5. Mono-N-Heterocyclic Carbene Complexes of Silver with Halegeno Anions of Type $[AgX_2]^-$ (C_2–Ag–AgX_2)

Structures have been reported in the literature in which silver NHC cations are charge balanced with halogeno anions of type $[AgX_2]^-$, Figure 15. Two examples of this type are complexes **11** and **55** depicted in Figures 16a and 17a, respectively. The syntheses of these complexes are given in Scheme 8a,b. In most halogeno silver NHC complexes, the silver cation is bound by two carbene moieties with the halogeno anion (in this case $[AgX_2]^-$) forming a silver−silver interaction perpendicular to the plane of the silver biscarbene.

The molecular structures of **11** and **55** are similar. The bond distances and angles for these structures are given in Table 5. The silver−carbene bond distances for complex **11** are 2.07(3) and 2.05(3) for C1−Ag1 and C2−Ag1, respectively.[17] The silver−carbene bond distances for **55** are 2.096(6) Å.[49] The carbene−silver−carbene bond angles are 176(1)°

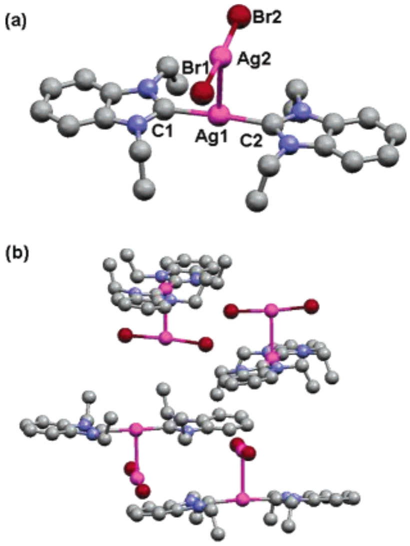


Figure 16. Molecular structure (a) and packing diagram (b) of complex **11**.

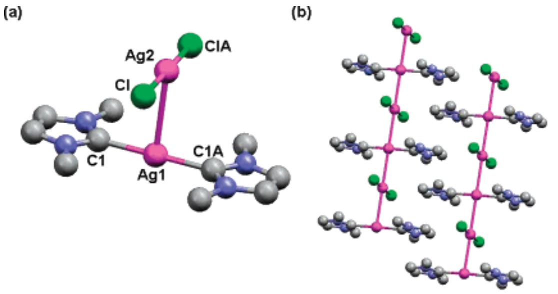
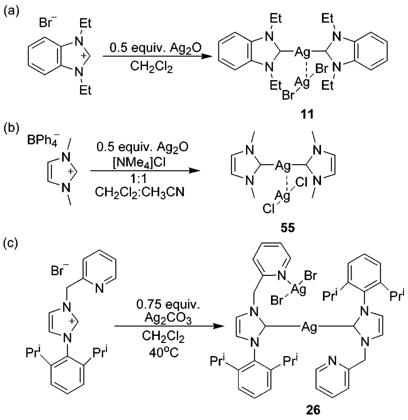


Figure 17. Molecular structure (a) and packing diagram (b) of complex **55**.

Scheme 8



(C1–Ag–C2) for **11** and 180° (C1–Ag–C1A) for **55**. The Ag1–Ag2 interaction is closer for complex **11** (2.954(4) Å) than for complex **55** (3.188(2) Å). The halide–silver–halide angle for the halogeno anion is 175.1(2)° and 180° for **11** and **55**, respectively. While the structures of these compounds are very similar, they adopt a totally different packing arrangement. Complex **11** consists of individual halogeno silver NHC units, which are depicted in the packing diagram in Figure 16b. The packing diagram of complex **55** (Figure 17b) shows a polymeric array of halogeno silver NHC units with each silver cation (Ag1) interacting with two halogeno anions, one above and the other below the plane of the silver NHC complex.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 11, 55, and 26[a]

compound	**11**[17]	**55**[49]	**26**[18]
		Bond Lengths	
C–Ag	2.07(3)/2.05(3)	2.096(6)	2.069(5)/2.074(5)
Ag1–Ag2	2.954(4)	3.188(2)	
Ag2–X	2.448(4)/2.448(4)	2.335(2)	2.491((1)/2.509(1)
N1–Ag2			2.467(4)
		Bond Angles	
C–Ag1–C	176(1)	180	175.9(2)
C–Ag1–Ag2	92.9(8)/91.2(8)	90	
X–Ag2–X	175.1(2)	180	154.5(1)
Ag1–Ag2–X	97.3(1)/87.5(1)	90	
N1–Ag2–X			108.8(1)/95.8(1)

[a] All values were gathered from CIF files obtained from the Cambridge Structural Database (CSD). When values could not be obtained from the CSD, the values cited in the literature were used.

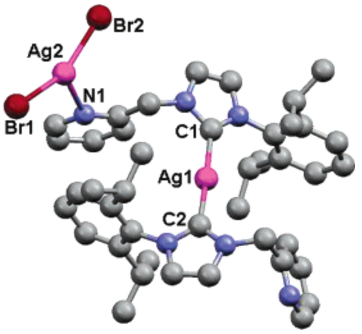


Figure 18. Molecular structure of complex **26**.

As stated previously most halogeno silver NHC complexes contain a silver–silver interaction. However, two reports have been published in the literature in which the halogeno anion is coordinated to a donor group instead of a silver cation.[18,98] Tulloch and co-workers reported the synthesis (Scheme 8c) and structure of **26**, depicted in Figure 18, where the silver-containing halogeno anion is coordinated to a pyridine ring.[18] The silver–carbene distances (Table 5) are 2.069(5) and 2.074(5) Å for C1–Ag1 and C2–Ag1, respectively. The distance from the pyridine to the halogeno anion is 2.467(4) Å (N1–Ag2). The halogeno anion deviates significantly from linearity, compared to complexes **11** and **55** with a Br1–Ag2–Br2 bond angle of 154.5(1)°.

4.1.6. Mono-N-Heterocyclic Carbene Complexes of Silver with Halogeno Anions of Type $[Ag_2X_4]^{2-}$ and Mono-N-Heterocyclic Carbene Complexes of Silver with Silver–Silver Interactions Stabilized by Three Donor Groups (C_2–Ag–Ag(X/Y)$_3$)

The three structurally characterized mono-NHC complexes of silver biscarbenes coordinating to halogeno anions of type $[Ag_2X_4]^{2-}$ are given in Figure 19 (multi-NHC complexes of silver with halogeno anions of type $[Ag_2X_4]^{2-}$ are addressed in section 4.2.3.). The molecular structures of complexes **57** and **58**, given in Figure 20a,b, are examples of this type of bonding motif. Bond distances and angles for these structures are given in Table 6. The syntheses of these complexes are summarized in Scheme 9a,b. Interestingly, in complex **57**, solvent effects seem to play a role in the synthesis of the solid-state motif.

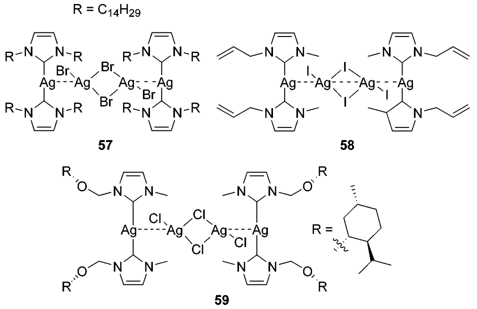


Figure 19. Biscarbene complexes of silver coordinating to halogeno counteranions of type $[Ag_2X_4]^{2-}$ (C_2–Ag–Ag–(X/Y)$_3$).

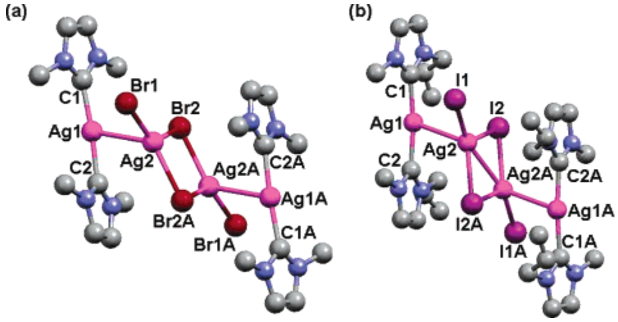


Figure 20. Molecular structures of **57** (a) and **58** (b). Alkyl substituents of complex **57** were removed for clarity.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 57 and 58^a

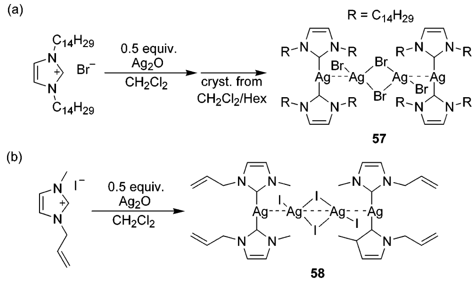
compound	**57**[48]	**58**[67]
	Bond Lengths	
C–Ag	2.094(5)/2.14(1)	2.103(9)/2.081(9)
Ag1–Ag2	3.007(2)	3.042(1)
Ag2–X1	2.531(2)	2.720(1)
Ag2–X2	2.681(2)	2.784(2)
Ag2–X2A	2.658(2)	2.831(2)
Ag2–Ag2A	3.436^b	2.964(2)
	Bond Angles	
C–Ag1–C	174.6(7)	172.8(3)
C–Ag1–Ag2	111.1(4)/70.7(4)	106.9(2)/76.1(3)
Ag1–Ag2–X1	86.96(6)	92.48(4)
Ag1–Ag2–X2	77.81(5)	80.50(3)
Ag1–Ag2–X2A	125.65(6)	120.36(4)
Ag2–X2–Ag2A	80.10(6)	63.72(3)
X1–Ag2–X2	129.32(6)	122.14(4)
X1–Ag2–X2A	127.30(7)	116.46(4)
X2–Ag2–X2A	99.90(6)	116.28(3)

^{a} All values were gathered from CIF files obtained from the Cambridge Structural Database (CSD). When values could not be obtained from the CSD, the values cited in the literature were used. ^{b} Value was not reported; the value was determined using atomic coordinates with Mercury 1.2.1

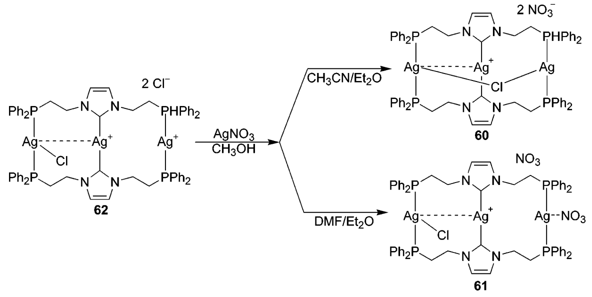
Complexes **57** and **50** could be obtained from the same silver NHC sample by simply changing the solvent from which the silver NHC was crystallized.[48]

The silver–carbene distances for these complexes are 2.094(5) and 2.14(1) Å for **57** and 2.103(9) and 2.081(9) Å for **58**.[48,67] The silver biscarbene–silver cluster interactions (Ag1–Ag2) are 3.007(2) and 3.042(1) Å for **57** and **58**, respectively. The only notable difference in the two structures is within the Ag_2X_2 cluster. In complex **57**, the Ag2–Ag2A distance is a long 3.436 Å, whereas in complex **58** the distance is 2.964(2) Å. The reason for the difference is not clear.

Scheme 9



Scheme 10



Lee and co-workers recently reported two compounds that are consistent with the C_2–Ag–Ag–(X/Y)$_3$ motif. Two of the coordinating ligands to Ag2 are phosphines instead of halides (Figure 21).[104] These two compounds are another example in which crystallization solvents play a role in determining the solid-state structure of silver NHC complexes. These two compounds were synthesized from the same material by the anion exchange of silver NHC complex **62** with silver nitrate, Scheme 10. The crystallization of the resulting silver NHC complex leads to the isolation of either complex **60** or **61** depending on the solvents used. The molecular structure and the structural data for both compounds are given in Figure 22 and Table 7, respectively. Crystals of complex **60** were grown from acetonitrile and ether. The silver–carbene bond distances are 2.12(1) and

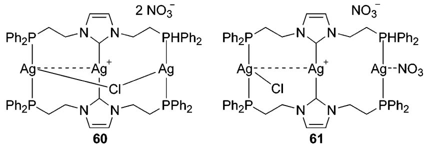


Figure 21. Biscarbene complexes of silver with silver–silver interaction stabilized by three donor groups (C_2–Ag–Ag(X/Y)$_3$).

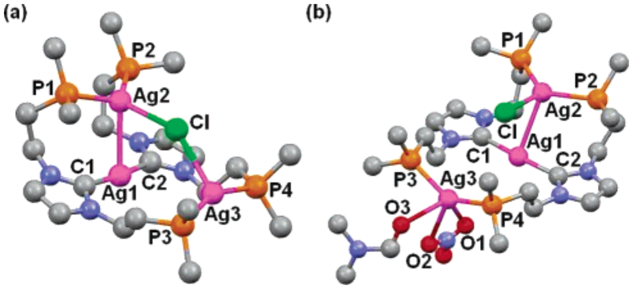


Figure 22. Molecular structures of **60** (a) and **61** (b). The phenyl groups were removed, except the meso carbon, for clarity.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for 60 and 61[a]

compound	**60**[104]	**61**[104]
	Bond Lengths	
C−Ag	2.12(1)/2.10(1)	2.110(5)/2.110(5)
Ag1−Ag2	2.928(1)	3.059(2)
Ag2−Cl	2.664(3)	2.528 (2)
Ag3−Cl	2.798(4)	
Ag2−(P1/P2)	2.472(4)/2.466(4)	2.457(2)/2.443(2)
Ag3−(P3/P4)	2.421(4)/2,418(4)	2.428(2)/2.419(2)
Ag3−(O1/O2)		2.658/2.701
Ag3−O3		2.624
	Bond Angles	
C−Ag1−C	173.7(5)	173.1(2)
C−Ag1−Ag2	86.3(3)/91.2(3)	91.0(1)/88.8(1)
Ag1−Ag2−(P1/P2)	106.10(9)/100.72(9)	102.32(5)/104.67(5)
Ag1−Ag2−Cl	76.27(9)	69.47(6)
P1−Ag2−P2	124.1(1)	122.16(6)
P3−Ag3−P4	154.2(1)	139.62(6)
Ag2−Cl−Ag3	145.5(2)	

[a] All values were gathered from CIF files obtained from the Cambridge Structural Database (CSD). When values could not be obtained from the CSD, the values cited in the literature were used.

2.10(1) Å for C1−Ag1 and C2−Ag2, respectively. The Ag1−Ag2 interaction (2.928(1) Å) is consistent with the silver−silver interactions of halogeno silver NHC complexes. The chloride bridges the two silver cations with Ag2−Cl and Ag3−Cl distances of 2.664(3) and 2.798(4) Å, respectively. Complex **61** was grown from a DMF and ether solution. The bonding with respect to the silver NHC portion of complex **60** is similar to that of complex **61**. The silver−carbene distances are both 2.110(5) Å. Unlike complex **60**, in complex **61** the chloride is coordinated to only one silver cation (Ag−Cl = 2.528(2) Å). The remaining Ag3 cation is bound by the two phospines and is weakly coordinated to a nitrate anion as well as a DMF molecule. The Ag−O1, Ag−O2, and Ag−O3 bond distances are 2.658, 2.701, and 2.624 Å, respectively. Apparently, the weakly coordinating DMF molecule is enough to stabilize the Ag3 cation and selectively form complex **61** vs complex **60**.

4.2. Multi-N-Heterocyclic Carbene Complexes of Silver

4.2.1. Multi-N-Heterocyclic Carbene Complexes of Silver with Noncoordinating Anions (C_2–Ag)

All structures of multi-NHC complexes of silver with noncoordinating anions are depicted in Figure 23 (mono-NHC complexes of silver with noncoordinating anions are addressed in section 4.1.1). Complexes **15**, **65**, and **69**, depicted in Figure 24, are examples of typical multidentate silver NHC structures with noncoordinating anions. The syntheses of these complexes and relevant bond distances and angles are given in Scheme 11a−c and Table 8. In complex **15**, the two pyridine-linked cyclophanes have silver−carbene bond distances of 2.085(2) and 2.087(2) Å for C1−Ag and C2−Ag, respectively.[38] The C1−Ag−C2 bond angle deviates from linearity with an angle of 171.55(9)°. Complex **65**, a ligand composed of three NHCs, forms a dimeric complex similar to that of **15**.[55] The silver−carbene distances for **65** are

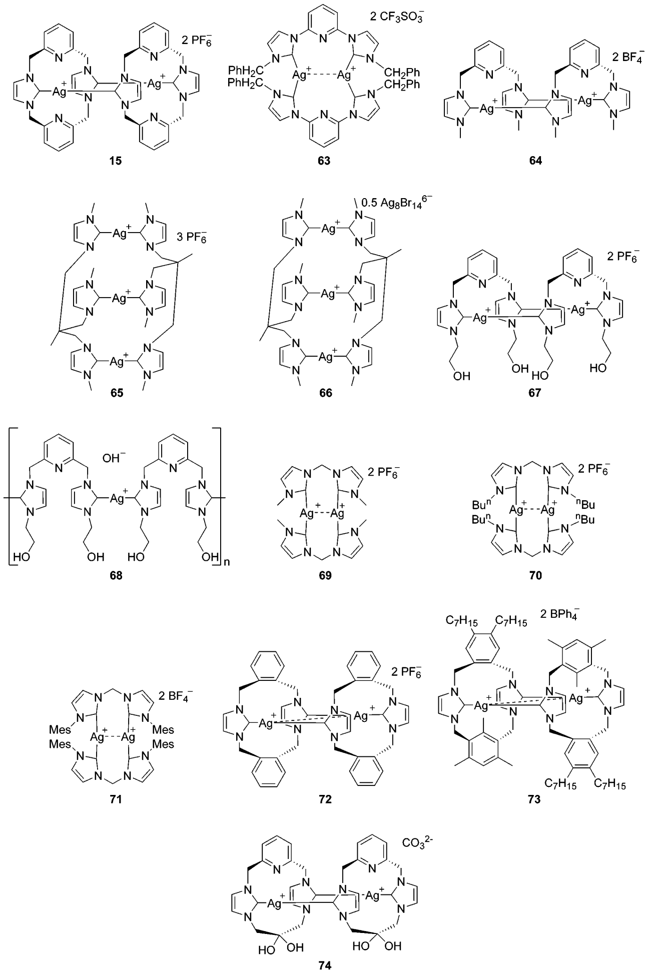


Figure 23. Multi-NHC ligands with noncoordinating anions (C_2−Ag).

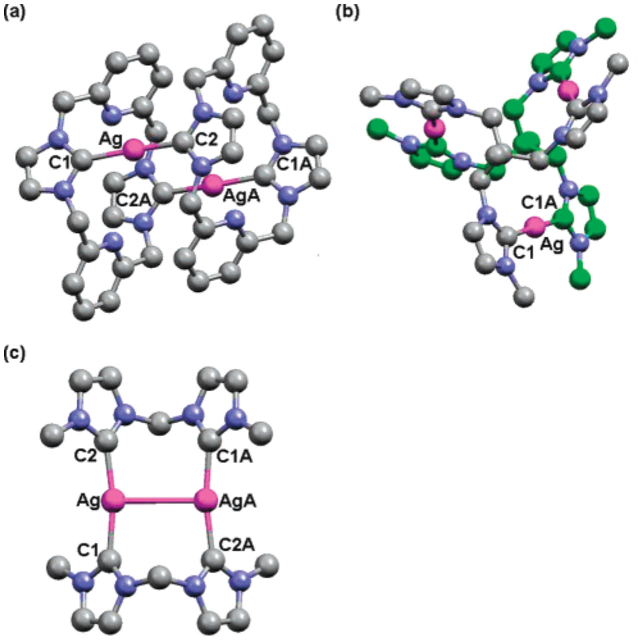


Figure 24. Molecular structures of the cationic portions of complexes **15** (a), **65** (b), and **69** (c). In complex **65**, the carbons of one of the tripodal NHC ligands are displayed green for clarity.

2.081(2) Å, while the carbene−silver−carbene bond angles are close to linearity with angles of 178.6(1)°.

Scheme 11

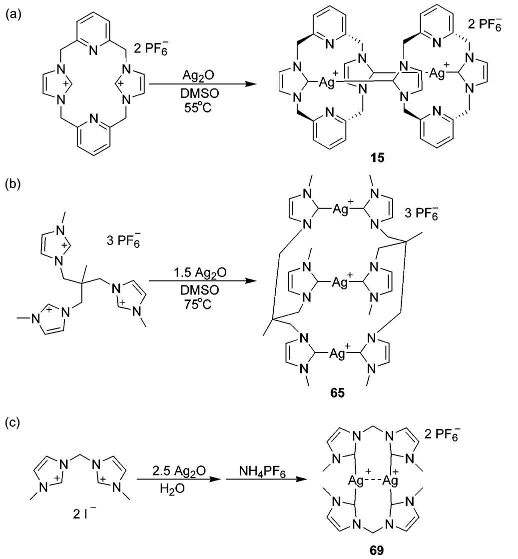


Table 8. Selected Bond Lengths (Å) and Angles (deg) for 15, 65, and 69[a]

compound	**15**[38]	**65**[55]	**69**[72]
	Bond Lengths		
C−Ag1	2.085(2)/2.087(2)	2.081(2)	2.096(5)/2.098(5)
Ag−AgA			3.2258(7)
	Bond Angles		
C−Ag−C	171.55(9)	178.6(1)	169.4(2)

[a] All values were gathered from CIF files obtained from the Cambridge Structural Database (CSD). When values could not be obtained from the CSD, the values cited in the literature were used.

The ligand in complex **69** has two NHC rings linked together by a methylene group.[72] The silver−carbene bond distances are 2.096(5) and 2.098(5) Å for C1−Ag and C2−Ag, respectively. The C1−Ag−C2 bond angle is more acute (169.4(2)°) compared to **15** and **65**. A silver−silver interaction is also present (Ag−AgA = 3.2258(7) Å), which is not present in complexes **15** and **65**. Whether the acute bond angle and silver−silver interaction are due to a need for the silver cations to interact or a consequence of ligand constraint is not clear. However, it seems likely that ligand constraints do play some role in the bonding of these systems.

4.2.2. Multi-N-Heterocyclic Carbene Complexes of Silver with Coordinating Anions (C–Ag–X)

Multidentate silver NHC complexes have also been structurally characterized with coordinating halide anions (Figure 25; mono-NHC complexes of silver with singly coordinating anions are addressed in section 4.1.2). Examples of these, complexes **75** and **76**, are depicted in Figure 26a,b. The syntheses and structural data for these complexes are given in Scheme 12a,b and Table 9. Complex **75** has a silver−carbene bond distance of 2.06(1) Å for C1−Ag and a Ag−Cl bond distance of 2.315(4) Å.[56] The bond angle for C1−Ag−Cl in complex **75** is 170.2(4)°. There is also a silver−silver interaction of 3.269(2) Å (Ag−AgA). Complex **76** is similar to that of complex **75** with silver−carbene and silver−chloride distances of 2.068(3) and 2.3187(8) Å, respectively.[46] However, the bond angle for complex **76** is closer to linearity than that of **75** with an angle of 176.25(8)°. This is presumably attributed to the absence of a silver−silver interaction in complex **76**.

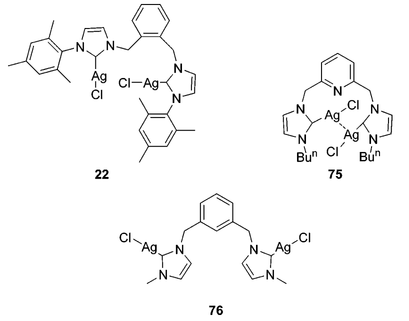


Figure 25. Multi-NHC ligands with coordinating halides (C−Ag−X).

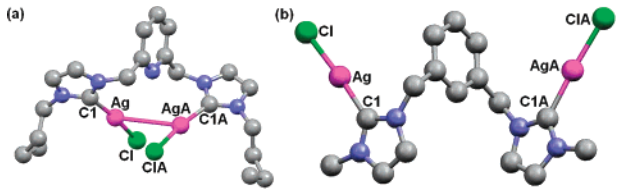


Figure 26. Molecular structures of complexes **75** (a) and **76** (b).

Scheme 12

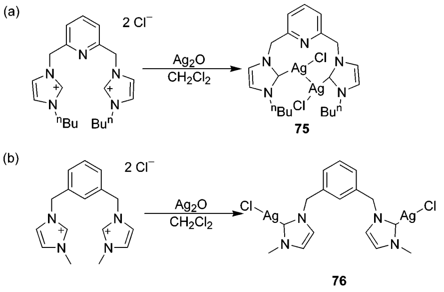


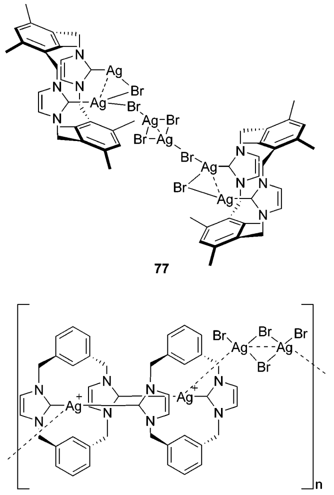
Table 9. Selected Bond Lengths (Å) and Angles (deg) for 75 and 76[a]

compound	**75**[56]	**76**[46]
	Bond Lengths	
C1−Ag	2.06(1)	2.068(3)
Ag−Cl	2.315(4)	2.3187(8)
Ag−AgA	3.269(2)	
	Bond Angles	
C1−Ag−Cl	170.2(4)	176.25(8)

[a] All values were gathered from CIF files obtained from the Cambridge Structural Database (CSD). When values could not be obtained from the CSD, the values cited in the literature were used.

4.2.3. Multi-N-Heterocyclic Carbene Complexes of Silver with Bridging Halides and Halogeno Anions (C_2–Ag–X_2 and C_2–Ag–Ag$(X/Y)_3$)

Complex bonding motifs are not limited to only mono-NHC complexes (Figure 27; mono-NHC complexes of silver with bridging halides and halogeno anions of type $[Ag_2X_4]^{2-}$ are addressed in sections 4.1.3 and 4.1.6, respectively); complexes **77** and **78** are examples of this and are depicted in Figures 28



77

78

Figure 27. Multi-NHC complexes of bridging halides (C_2–Ag–X_2) (**77**) and halogeno anions (C_2–Ag–Ag(X/Y)$_3$) (**78**).

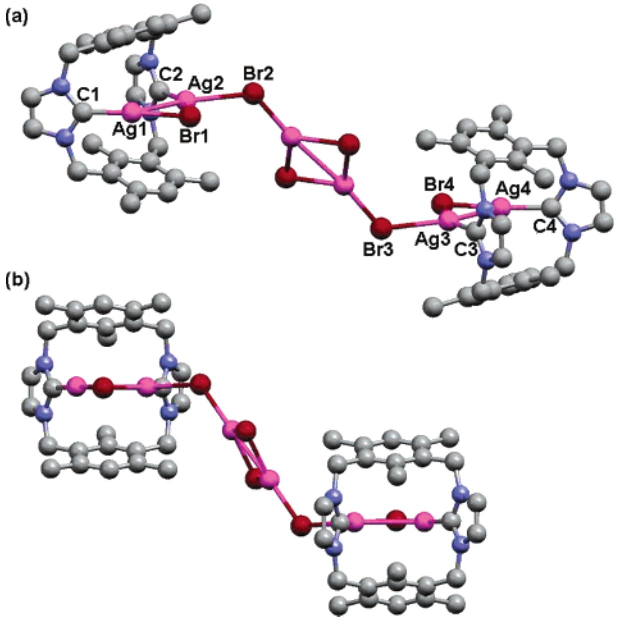


Figure 28. Molecular structure of complex **77** (a) from the side and (b) from the back.

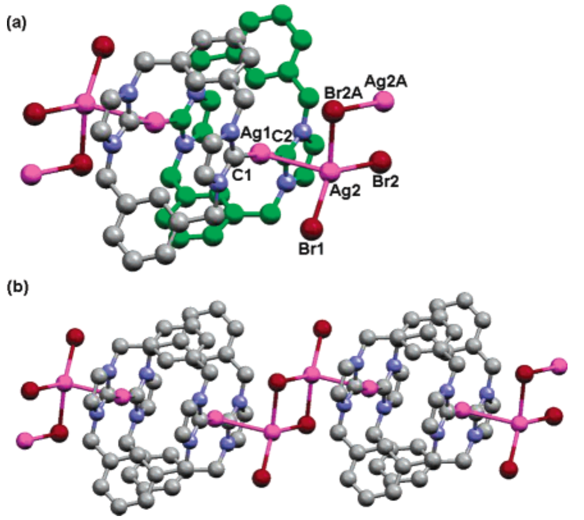
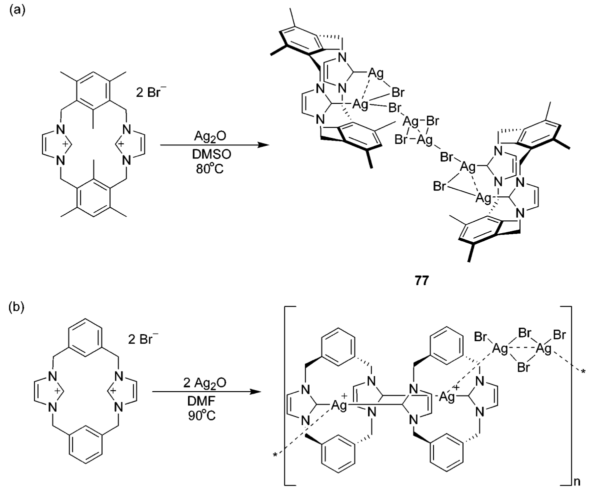


Figure 29. Molecular structure (a) and packing diagram (b) of complex **78**. In panel a, the carbons of one of the cyclophanes are displayed green for clarity.

Scheme 13



77

78

and 29, respectively.[78] The syntheses and relevant structural information for these complexes are summarized in Scheme 13 and Table 10. Complex **77**, in the solid state, has a unique bonding arrangement with each NHC of the cyclophane having a different bonding mode. This stands in stark contrast to the mulitidentate cyclophanes with noncoordinating anions (examples, **15**, **65**, and **69**). The bonding mode for Ag1 and Ag4 resembles the bonding arrangement of a silver NHC coordinating halide complex; both silver cations are coordinated with one NHC and one halide (Br1 and Br4, respectively). The silver–carbene–halide bond angles are consistent with this picture with C1–Ag1–Br1 and C4–Ag4–Br4 bond angles of 176.5(5)° and 175.5(6)°, respectively. The bonding of Ag2 and Ag3 resembles a bridging arrangement with the silver cations coordinated to one NHC and two bromides (Br1 and Br2 for Ag2 and Br3 and Br4 for Ag3). The bromides Br2 and Br3 are coordinated to a Ag_2Br_2 cluster that links the two cyclophanes.

The silver–carbene bond lengths of complex **77** are influenced by the bonding mode of the silver cations. The silver–carbene bond distance for the coordinating halide bonding arrangement C1–Ag1 and C4–Ag4 are 2.07(2) and 2.10(2) Å, respectively, whereas the silver cations with a bridging arrangement, C2–Ag2 and C3–Ag3, are longer with distances of 2.15(2) and 2.14(2) Å, respectively. Each cyclophane complex has a silver–silver interaction; the Ag1–Ag2 and Ag3–Ag4 distances are 3.003(3) and 2.996(2) Å, respectively.

Complex **78** is polymeric in the solid state with a bonding mode similar to the mono-NHC complexes **57** and **58** (depicted in Figure 20). The silver biscarbene (C1–Ag1–C2) is coordinated to an anionic silver cluster, Ag_2Br_4, through a silver–silver interaction. The silver–carbene bond distances are 2.089(4) and 2.095(4) Å for C1–Ag and C2–Ag, respectively. The silver–silver interaction (Ag1–Ag2) is 2.8999(4) Å.

Table 10. Selected Bond Lengths (Å) and Angles (deg) for 77 and 78[a]

compound	**77**[78]		**78**[78]
	Bond Lengths		
C1−Ag1/C4−Ag4	2.07(2)/2.10(2)	C−Ag	2.089(4)/2.095(4)
C2−Ag2/C2−Ag3	2.15(2)/2.14(2)	Ag1−Ag2	2.8999(4)
Ag1−Ag2/Ag3−Ag4	3.003(3)/2.996(2)	Ag2−X1	2.5154(6)
Ag1−X1/Ag4−X4	2.449(3)/2.450(3)	Ag2−X2	2.6525(6)
Ag2−X1/Ag3−X4	2.623(3)/2.634(3)	Ag2−X2A	2.6527(6)
Ag2−X2/Ag3−X3	2.837(3)/2.821(3)	Ag2−Ag2A	3.5981(5)
	Bond Angles		
C1−Ag1−Br1/C4−Ag4−Br4	176.5(5)/175.5(6)	C−Ag1−C	174.8(1)
C2−Ag2−Br1/C3−Ag3−Br4	153.1(6)/153.5(6)	C−Ag1−Ag2	69.7[b]/110.2[b]
C2−Ag2−Br2/C3−Ag3−Br3	107.7(6)/109.9(6)	Ag1−Ag2−X1	89.95[b]
C1−Ag1−Ag2/C4−Ag4−Ag3	125.0(6)/127.2(6)	Ag1−Ag2−X2	126.87[b]
C2−Ag2−Ag1/C3−Ag3−Ag4	102.1(6)/102.4(6)	Ag1−Ag2−X2A	82.68[b]
		Ag2−X2−Ag2A	85.41(2)
		X1−Ag2−X2	123.82(2)
		X1−Ag2−X2A	135.22(2)
		X2−Ag2−X2A	94.59(2)

[a] All values were gathered from CIF files obtained from the Cambridge Structural Database (CSD). When values could not be obtained from the CSD, the values cited in the literature were used. [b] Value was not reported; the value was determined using atomic coordinates with Mercury 1.2.1.

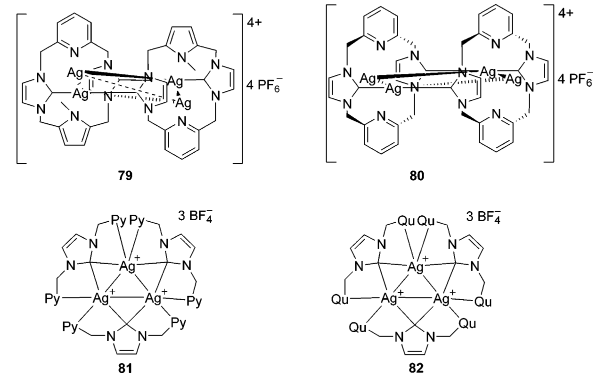
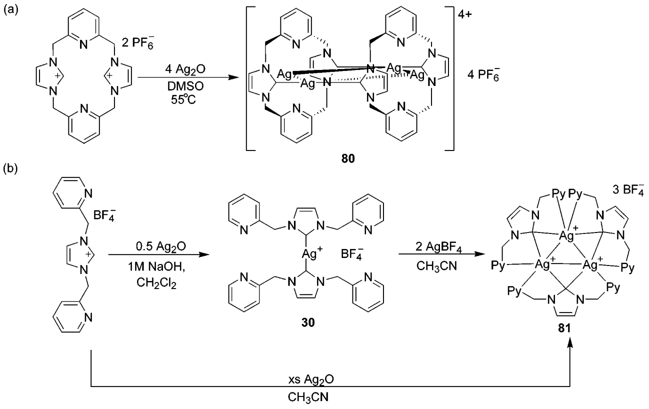


Figure 30. Cationic silver clusters stabilized by N-heterocyclic carbenes (C−Ag$_{\text{cluster}}$).

Scheme 14



4.3. Silver Clusters Stabilized by N-Heterocyclic Carbenes (C−Ag$_{\text{cluster}}$)

Interestingly, several NHC ligands have been reported to stabilize cationic silver clusters. All structures to date of silver clusters stabilized by NHCs are given in Figure 30. Complexes **80** and **81** will be used in this discussion as examples of this type of bonding motif. The syntheses, molecular structures, and relevant structural information can be found in Scheme 14a,b, Figures 31 and 32, and Table 11, respectively.

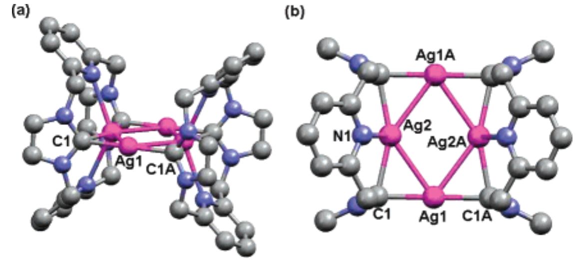


Figure 31. Complex **80** (a) viewed from the side of the molecular structure of the cationic portion and (b) viewed from the top looking down at the stabilized cationic silver cluster.

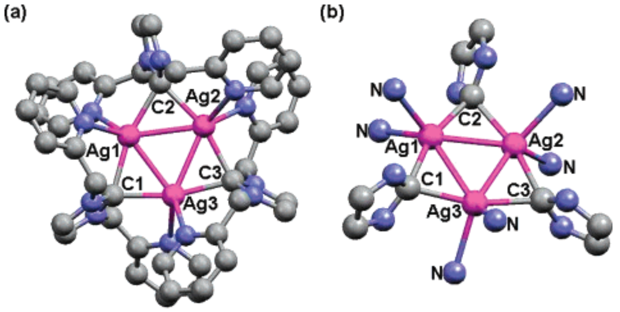


Figure 32. Complex **81** (a) viewed from the top of the molecular structure of the cationic portion and (b) viewed with the carbon atoms removed, except those of the NHC ring, for clarity.

Complex **80** is a tetranuclear silver cluster stabilized by the same ligand as complex **15** (Figure 24a).[52] The addition of excess Ag_2O to the reaction mixture produces complex **80** with complex **15** presumably being an intermediate in the reaction pathway. The tetranuclear silver cluster is planar with a Ag1−Ag2 bond distance of 2.8513(7) Å and a cross-ring distance (nonbonding) of 3.346(2) Å for Ag2−Ag2A. The bond angles for Ag1−Ag2−Ag1A and Ag2−Ag1−Ag2A are 108.14(3)° and 71.86(3)°, respectively. The silver−carbene bond distances are 2.136(5) Å, a considerable increase compared to that of complex **15** (2.085(2) and 2.087(2) Å). The carbene (C1) shows a considerable interaction with Ag2 with a C1−Ag2 bond distance

Table 11. Selected Bond Lengths (Å) and Angles (deg) for 80 and 81[a]

compound	**80**[52]	**81**[66]
	Bond Lengths	
C−Ag1	2.136(5)	2.255(8)/2.261(8)
C−Ag2	2.348(5)	2.266(7)/2.257(8)
C−Ag3		2.223(8)/2.237(7)
$N_{Pyridine}$−Ag1		2.406(7)/2.379(6)
$N_{Pyridine}$−Ag2	2.675(5)	2.409(7)/2.379(6)
$N_{Pyridine}$−Ag3		2.416(7)/2.361(7)
Ag1−Ag2	2.8513(7)	2.7718(9)
Ag2−Ag3		2.725(1)
Ag1−Ag3		2.7688(9)
	Bond Angles	
C−Ag−C	179.6(3)/157.3(3)	162.8(3)/163.7(3)/166.0(3)
Ag−C−Ag	78.8(2)	75.6(2)/74.9(3)/76.0(2)

[a] All values were gathered from CIF files obtained from the Cambridge Structural Database (CSD). When values could not be obtained from the CSD, the values cited in the literature were used.

of 2.348(5) Å. The suggestion of an interaction is justified by the tilt of the NHC rings toward the Ag2 and Ag2A cations. The silver cations, Ag2 and Ag2A, are also stabilized by the four pyridines of the cyclophanes. The N1−Ag2 bond distances are 2.675(5) Å, a rather long interaction.

Complex **81**, reported by Catalano and Malwitz, is an interesting trinuclear silver cluster that is stabilized by three NHCs and six pyridine rings.[66] The complex can be synthesized in one of two ways: reaction of the imidazolium salt with one-half equivalent of Ag_2O to form the intermediate complex **30**, which then rearranges with addition of $AgBF_4$ to form **81**, or reaction of the imidazolium salt with excess Ag_2O to form **81** directly. The trinuclear cluster contains silver bonding distances that range from 2.725(1) to 2.7718(9) Å and bond angles ranging from 58.92(2)° to 60.60(2)°. While complex **81** is similar to **80** in that the carbene interacts with two silver cations, it differs with respect to the degree of this interaction. Complex **80** bonds to the silver cations asymmetrically with the NHC interacting more strongly with one silver cation than the other. Complex **81** has NHC bonding interactions that are symmetric with all silver−carbene distances being nearly equal. The silver−carbene bond distances for complex **81** range from 2.223(8) to 2.266(7) Å.

4.4. General Trends

Reliably predicting the solid-state structure of silver NHCs is often difficult, particularly if the counteranion is a halide. If the counteranion is a noncoordinating anion, the resulting silver complex is likely to be a silver biscarbene (C_2−Ag). For halide complexes, a number of factors come in to play in determining the ultimate outcome in the solid state, such as the particular halide, sterics and flexibility of the ligand, additional donor groups of the ligand, argentophillic interactions, silver−halide interactions, and solvent interactions. With the number of factors to consider, it is no surprise that predicting the solid-state structure of the silver NHC complex cannot reliably be determined until the complex has been crystallographically characterized.

The silver−carbene bond distance remains fairly constant despite the diversity of the silver NHC bonding motifs. Silver carbene distances range from 2.056(7) to 2.516(6) Å with an average of 2.12(1) Å. A compilation of silver−carbene bond distances are given in Table 12, according to each bonding motif discussed. The silver biscarbenes with noncoordinating anions (C_2−Ag) have been structurally characterized with silver−carbene bond distances ranging from 2.06(1) to 2.117(5) Å with an average bond length of 2.087(5) Å. The silver−carbene bond lengths for the silver NHC complexes with coordinated halides (C−Ag−X) are slightly shorter with an average distance of 2.077(8) Å. There are few silver NHC complexes of the motif type C−Ag−$Y_{non-halide}$ in the literature, but to date, these complexes seem consistent with other silver NHC complexes (average bond length 2.074(7) Å). Silver NHC complexes with halogeno anions of type $[AgX_2]^-$ (C_2−Ag−AgX_2) are similar to the above motifs with an average silver−carbene bonding distance of 2.08(1) Å.

Whereas there is a slight difference in the bond length in the four aforementioned bonding motifs, there is certainly a trend of longer silver−carbene bonds in silver NHCs with the C_2−Ag−Ag$(X/Y)_3$ motif, bridging halides (C−Ag−X_2), silver−halide staircases (C−Ag−X_3), and stabilized clusters (C−$Ag_{cluster}$). Silver NHC complexes of type C_2−Ag−Ag$(X/Y)_3$ have an average bond length of 2.104(5) Å, a significant increase over the silver NHC complexes with halogeno anions of type $[AgX_2]^-$. The C−Ag−X_2 and C−Ag−X_3 motifs have average bond lengths of 2.103(9) Å and 2.158(7) Å, respectively. Although there are only a few reported NHC silver clusters, it can be seen that the silver−carbene bond distances of this type (average 2.259(9) Å) tend to be longer than other silver NHC complexes.

A compilation of all silver NHC bond angles, with the exception of the C−Ag−X_2 and C−Ag−X_3 motifs, is given in Table 13. The C_2−Ag, C_2−Ag−AgX_2, and C_2−Ag−Ag$(X/Y)_3$ bonding motifs have approximately the same average bond angles of 173.8(2)°, 177.0(6)°, and 173.5(5)°, respectively. Silver NHCs with coordinating halide anions (C−Ag−X) have bond angles that range from 163.3(2)° to perfectly linear with an average of 174.0(2)°. The bond angles of the C−$Ag_{cluster}$ motif are more acute with an average angle of 162.9(3)°. The reason for the deviation is understandable given that the carbenes in these systems are shared with more than one silver cation.

5. Spectral Characterization

5.1. NMR

The great majority of silver N-heterocyclic carbene complexes have been characterized by ^1H and ^{13}C NMR. In Figure 33 are the silver NHC complexes that have been characterized by ^{13}C NMR but not crystallographically. Although the solid-state structure of silver NHCs, revealed by X-ray diffraction studies, gives an abundance of structural information, in many cases, it is unlikely that the solid-state motifs survive in solution. One would presume that

Table 12. Silver−Carbene Bond Lengths (Å)[a]

Bond Lengths							
compd	C_2−Ag	compd	C−Ag−X	compd	C−Ag−X_2	comp	C−Ag−X_3
8[15]	2.067(4)/2.078(4)	**22**[18]	2.061(7)/2.092(8)	**14**[18]	2.07(2)	**25**[54]	2.182(7)
13[16]	2.086(4)/2.090(4)	**35**[18]	2.075(7)	**46**[18]	2.099(3)	**53**[49]	2.131(5)
15[38]	2.085(2)/2.087(2)	**36**[41]	2.09(2)	**47**[18]	2.098(2)	**54**[67]	2.161(9)
16[34]	2.082(4)/2.092(4)	**37**[45]	2.093(4)	**48**[41]	2.120(8)		
23[67]	2.088(7)/2.091(7)	**38**[57]	2.056(7)	**49**[49]	2.11(1)		
26[18]	2.069(5)/2.074(5)	**39**[25]	2.095(3)	**50**[48]	2.094(5)		
27[49]	2.089(3)/2.092(3)	**40**[98]	2.083(4)	**51**[85]	2.102(6)		
28[32]	2.069(6)/2.070(5)	**41**[99]	2.087(3)	**52**[93]	2.093(8)		
29[66]	2.082(6)/2.083(6)	**42**[99]	2.086(3)	**77**[78]	2.14(2)/2.15(2)		
30[66]	2.093(4)	**75**[56]	2.06(1)				
31[71]	2.068(4)	**76**[46]	2.068(3)				
32[76]	2.106(6)/2.117(5)	**77**[78]	2.10(2)/2.07(2)				
33[25]	2.101(3)/2.097(3)						
34[98]	2.09(1)/2.09(1)						
63[30,31]	2.087(4)/2.080(4)						
64[44]	2.088(4)/2.093(4)						
65[55]	2.081(2)						
66[55]	2.095(8)/2.102(9)						
66[55]	2.105(9)/2.114(9)						
66[55]	2.09(1)/2.095(9)						
67[70]	2.070(9)/2.091(9)						
67[70]	2.064(9)/2.074(8)						
68[70]	2.11(1)/2.06(1)						
69[72]	2.096(5)/2.098(5)						
70[72]	2.083(5)/2.088(5)						
70[72]	2.083(5)/2.085(5)						
70[72]	2.089(5)/2.091(5)						
70[72]	2.088(5)/2.091(5)						
71[73]	2.095(2)/2.093(2)						
72[78]	2.095(3)/2.093(3)						
73[78]	2.088(3)0.2.087(4)						
74[89]	2.079(4)/2.086(4)						
74[89]	2.074(4)/2.079(4)						
avg	2.087(5)		2.077(8)		2.103(9)		2.158(7)

compd	C_2−Ag−AgX_2	compd	C_2−Ag−Ag$(X/Y)_3$	compd	C−$Ag_{cluster}$	compd	C−Ag−$Y_{non-halide}$
11[17]	2.07(3)/2.05(3)	**57**[48]	2.094(5)/2.14(1)	**79**[39]	2.148(5)/2.149(6)	**43**[33]	2.09(1)
24[68]	2.083(4)	**58**[67]	2.103(9)/2.081(9)	**79**[39]	2.412(5)/2.516(6)	**44**[84]	2.073(4)/2.071(4)
55[49]	2.096(6)	**59**[92]	2.09(2)/2.10(2)	**80**[52]	2.136(5)/2.348(5)	**45**[97]	2.069(9)
56[49]	2.084(5)	**60**[104]	2.12(1)/2.10(1)	**81**[66]	2.255(8)/2.261(8)		
		61[104]	2.110(5)/2.110(5)	**81**[66]	2.266(7)/2.257(8)		
		78[78]	2.095(4)/2.089(4)	**81**[66]	2.223(8)/2.237(7)		
				82[76]	2.23(2)		
avg	2.08(1)		2.104(5)		2.259(9)		2.074(7)

[a] All values were gathered from CIF files obtained from the Cambridge Structural Database (CSD). When values could not be obtained from the CSD, the values cited in the literature were used. The total number of silver−carbene bonds of each molecule were used when the average values for each field were determined.

this would be especially true for silver NHC complexes based upon weakly coordinating motifs.

While tracking the progress of a metalation reaction can be easily accomplished by analysis of the imidazolium proton using ^{1}H NMR, deuterium exchange with protic NMR solvents is a concern. Decomposition of an NHC complex in a protic deuterated solvent would lead to the synthesis of the deuterated imidazolium salt. The absence of the imidazolium proton in this case could lead to a mistaken interpretation of the ^{1}H spectra. For this reason, ^{13}C NMR spectra tend to be more definitive as well as to reveal more information of the nature of silver NHC bonding in solution.

Table 14 gives all of the carbene resonances and coupling constants (if observed) for all silver NHC complexes at the time of this publication. The resonance values of the carbene complexes to silver ($C_{carbene}$) fall over a wide range, δ 213.7−163.2. Silver has two naturally occurring isotopes, ^{107}Ag and ^{109}Ag, with a percent abundance of 51.839(7)% and 48.161(7)%, respectively. Both of these isotopes are NMR active, and each has a nuclear spin of $^1/_2$. Given this information, one would expect a complex splitting pattern for the $C_{carbene}$ (doublet of doublets) based upon the coupling constants of each silver isotope. Carbene coupling to silver is observed in a few complexes, but the majority show no splitting pattern. In the complexes that do exhibit coupling, the coupling has been reported to extend, up to four bonds away, to the backbone of the NHC rings. The coupling constants for the $C_{carbene}$ bonding to ^{107}Ag and ^{109}Ag range from 180 to 234 Hz and 204 to 270 Hz, respectively. In the case that no splitting is observed, the $C_{carbene}$ resonance is found to be very sharp or broad singlet. Also, a significant number of

Table 13. Silver–Carbene Bond Angles (deg)[a]

			Bond Angles				
compd	C_2–Ag	compd	C–Ag–X	compd	C_2–Ag–AgX_2	compd	C_2–Ag–Ag(X/Y)$_3$
8[15]	176.3(2)	**22**[18]	177.4(2)/163.3(2)	**11**[17]	176(1)	**57**[48]	174.6(7)
13[16]	174.7(2)/180	**35**[18]	176.1(2)	**24**[68]	171.8(2)	**58**[67]	172.8(3)
15[38]	171.55(9)	**36**[41]	175.2(5)	**55**[49]	180	**59**[92]	168.7(7)
16[34]	176.8(2)	**37**[45]	169.4(1)	**56**[49]	180	**60**[104]	173.7(5)
23[67]	170.6(3)	**38**[57]	180			**61**[104]	173.1(2)
26[18]	175.9(2)	**39**[25]	176.62(8)			**78**[78]	174.8(1)
27[49]	176.5(1)	**40**[98]	171.7(1)				
28[32]	174.3(2)	**41**[99]	172.63(7)				
29[66]	175.0(2)	**42**[99]	176.31(9)				
30[66]	180	**75**[56]	170.2(4)				
31[71]	171.4(3)	**76**[46]	176.25(8)				
32[76]	176.8(2)	**77**[78]	175.5(6)/176.5(5)				
33[25]	178.3(1)						
34[98]	179.5(4)						
63[30,31]	165.5(2)						
64[44]	176.78(9)						
65[55]	178.6(1)						
66[55]	175.0(3)/171.2(3)						
66[55]	177.6(4)						
67[70]	175.7(4)/174.6(3)						
68[70]	174.7(4)						
69[72]	169.4(2)						
70[72]	171.3(2)/169.7(2)						
70[72]	173.4(2)/166.8(2)						
71[73]	173.50(9)						
72[78]	176.3(1)						
73[78]	164.7(1)						
74[89]	175.2 (1)/170.6(2)						
avg	173.8(2)		174.0(2)		177.0(6)		173.5(5)

compd	C–Ag$_{cluster}$	compd	C–Ag–Y$_{non-halide}$
79[39]	176.2(2)/136.7(2)	**44**[84]	174.7(1)/172.6(1)
80[52]	179.6(3)/157.3(3)	**45**[97]	175.3(3)
81[66]	162.8(3)/163.7(3)		
81[66]	166.0(3)		
82[76]	162.8(6)		
avg	162.9(3)		174.2(2)

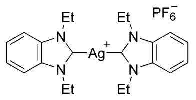
[a] All values were gathered from CIF files obtained from the Cambridge Structural Database (CSD). When values could not be obtained from the CSD, the values cited in the literature were used. The total number of silver–carbene angles of each molecule were used when the average values for each field were determined.

silver NHC complexes were reported with no observable carbene resonances.

The appearance of $C_{carbene}$ resonances for some silver NHC complexes are found to be concentration dependent; dilute samples give sharper signals than concentrated samples.[18] However, concentration effects do not account for the lack of coupling or the appearance of sharp single peaks for $C_{carbene}$ resonances. Lin and co-workers speculated that the absence of a splitting pattern is due to the fluxional behavior of silver NHC complexes on the NMR time scale.[17] A plausible fluxional behavior for halogeno silver NHC complexes, proposed by Lin, is illustrated in Scheme 15. According to this explanation, silver NHCs that are static or have dynamic behaviors that are slow on the NMR time scale will show $C_{carbene}$ coupling to silver. As the dynamic behavior increases on the NMR time scale, the $C_{carbene}$ resonance will become broader and eventually coalesce into a sharp singlet. While Lin and Wang gave an example of a possible mechanism for the dynamic behavior of halogeno silver NHCs, it is certainly reasonable, from the lack of coupling constants for other bonding arrangements, that silver NHCs of other bonding motifs could undergo similar dynamic behaviors in solution. The addition of chloride has been reported to slow this dynamic behavior in solution.[16]

Observation of the coupling of the $C_{carbene}$ to silver seems to indicate a static conformation for silver NHC complexes relative to the NMR time scale. However, if this assertion is true, it is still uncertain whether this static conformation persists indefinitely or the dynamic behavior is relatively slow compared to the NMR time scale. Also, the absence of an observable resonance for the $C_{carbene}$ of some silver NHCs is unclear. However, the dynamic behavior as well as the poor relaxation of the quaternary $C_{carbene}$ of silver NHCs could be significant factors contributing to the absence of the $C_{carbene}$ resonance.

Silver NHC complexes involving interactions with cationic silver clusters (i.e., **79** and **81** in Figure 30) have unusual coupling patterns that fall outside those reported for other silver NHC complexes. The reported coupling constants for **79** are 220 and 47 Hz.[39] The coupling constant value of 47 Hz falls far short of any reported NHC complex; it seems more likely that this splitting pattern is due to the bonding motif of this particular complex. The carbene in the silver complex interacts with two different silvers cations, one in a σ-bonding fashion and the other in a π-bonding interaction. The coupling constant of 220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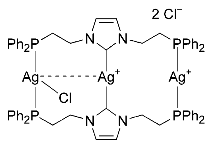
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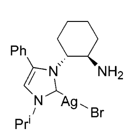
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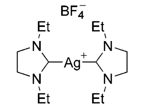
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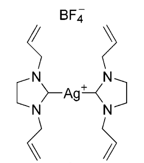
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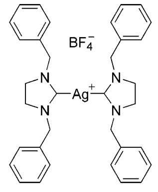
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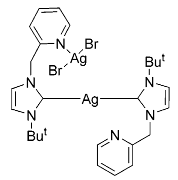
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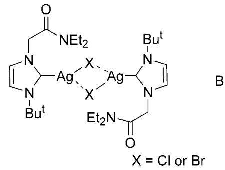

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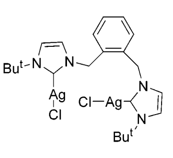
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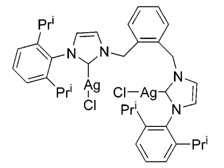
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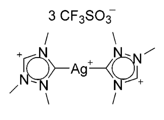
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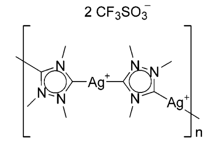
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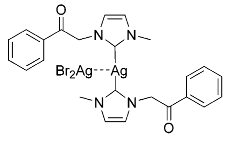
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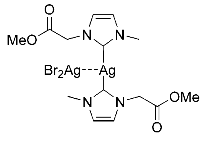
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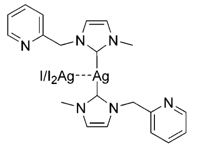
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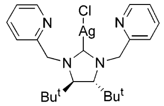
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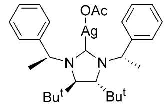
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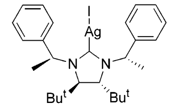
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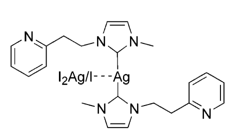
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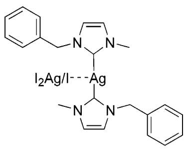
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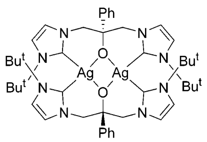
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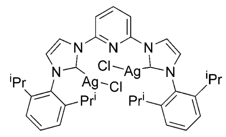
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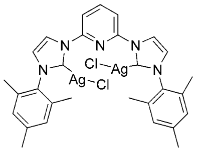
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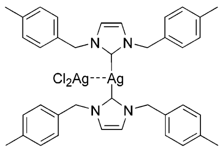
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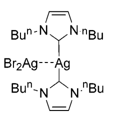
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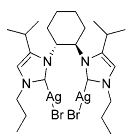
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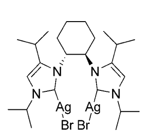
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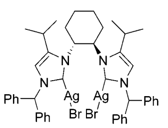
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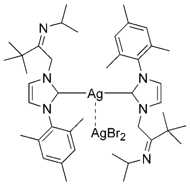
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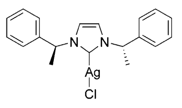
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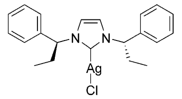
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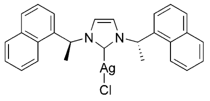
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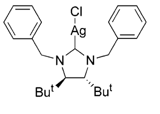
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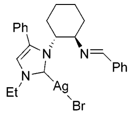
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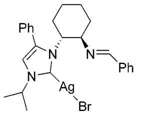
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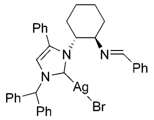
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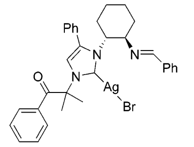
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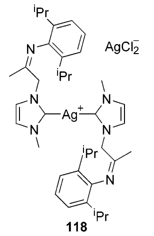
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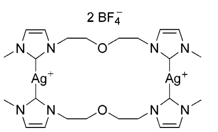
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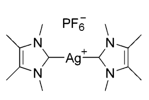
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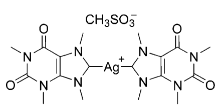
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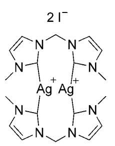
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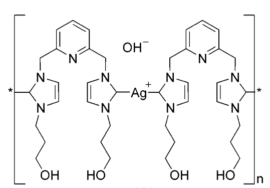
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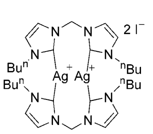
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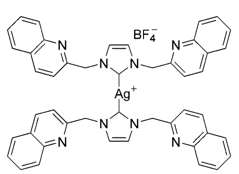
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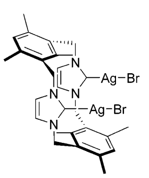
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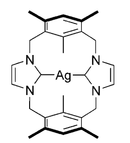
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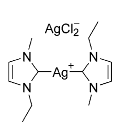
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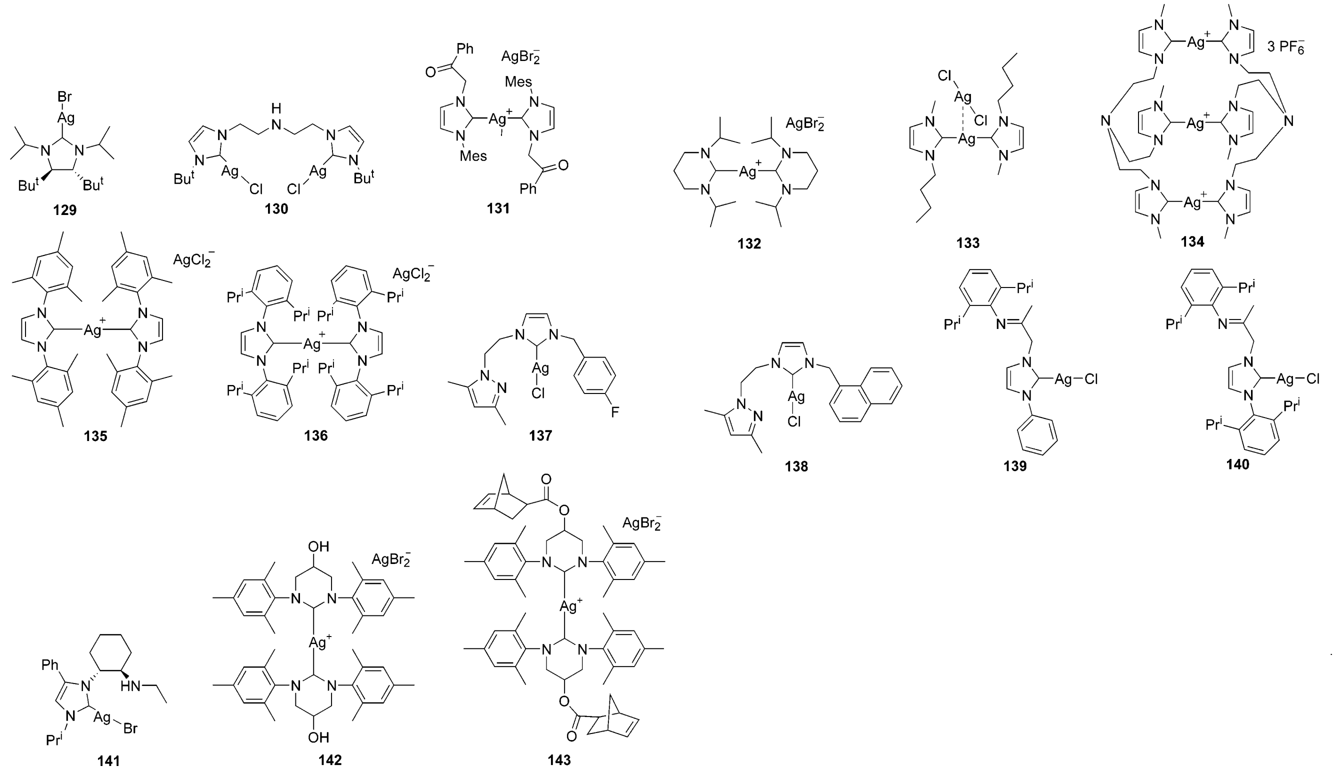


Figure 33. Silver NHC complexes that have ^{13}C NMR spectra but have not been structurally characterized. Connectivity is based upon the publishing author's depiction. When no depiction was given the authors of this review give a reasonable depiction.

Hz is consistent with a carbene σ-bonding interactionwith silver. The constant of 47 Hz was tentatively assigned as a π-bonding interaction between the p-orbital of the carbene and the other silver cation. However, given the complexes published by Catalano and co-workers, **81** and **82**, the interactions of complex **79** could be seen as simply three-center two-electron bonds. Complex coupling patterns with respect to the $C_{carbene}$ were also reported for complex **81**.[66]

The complexes for which ^{109}Ag NMR spectra have been collected are listed at the bottom of Table 14. The ^{109}Ag resonances of silver N-heterocyclic carbene complexes have a range from δ 597 to 727. In complexes **8** and **16**, the ^{109}Ag NMR reveals ^4J coupling of the silver cation to the protons on the backbone of the NHCs.[15,34] This coupling is not observed in complex **38**, probably due to the anisotropic effect of the chloride coordinated to the silver.[57] Solid-state studies of the ^{13}C and ^{109}Ag nuclei were also reported for complex **38**.

5.2. Mass Spectrometry

Silver N-heterocyclic carbenes have been studied using a variety of mass spectrometric techniques: electrospray ionization mass spectrometry (ES-MS), fast atom bombardment mass spectrometry (FAB-MS), liquid secondary ion mass spectrometry (LSI-MS), etc. The usefulness of these techniques for the characterization of silver N-heterocyclic carbene complexes has been shown to be relatively poor. However, examination of the mass spectra of structurally characterized complexes has led to several interesting observations. The following discussion will be divided according to the ionization technique used. Each section will focus on examples that are representative of that area and have been structurally characterized.

5.2.1. Electrospray Ionization Mass Spectrometry

Several groups have performed ES-MS on silver N-heterocyclic carbenes.[18,34,38,47,59,62,63,71,72,74,82,85,89,92,99,104] Danopoulos and colleagues were the first to report a series of silver NHCs analyzed by ES-MS.[18] In this work, they found that silver NHCs with solid-state motifs of C−Ag−X and C−Ag−X$_2$ formed biscarbenes (C$_2$−Ag) in the gas phase. Examples of this are given in Scheme 16a−c. Complexes **35** and **14**, according to results of electrospray mass spectrometry, form biscarbenes and acetonitrile complexes in the gas phase. Interestingly, only the biscarbene of complex **22** is reported under the ES-MS sampling conditions. Reports of other silver NHC complexes analyzed from coordinating solvents, such as acetonitrile, also do not mention silver NHC solvent complexes in the gas phase.[34,38,85] Whether these features were not present in the spectra, deemed not relevant to report, or simply not examined in detail is unclear. It is worthy to note that the decomposition of silver NHC complexes and observation of the corresponding imidazolium salts has been reported using ES-MS.[85]

Complex **15** (Scheme 16d), as mentioned earlier, is isolated as a dimer in the solid state with the silver cations bridging the two cyclophanes.[38] Analysis of the isotopic pattern of the silver complex from the ES-MS spectra showed the presence of the monomeric biscarbene instead of the dimer in the gas phase. However, not all silver NHCs deviate from the solid-state structure in the gas phase. Complex **69**

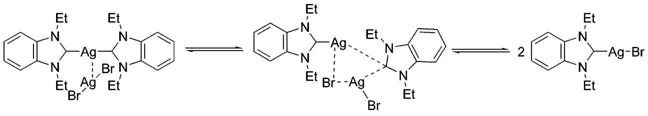
Table 14. Resonances for Silver NHCs

compd	δ $C_{carbene}$ (J in Hz)	compd	δ $C_{carbene}$ (J in Hz)
8[15]	183.6[e] ($^1J_{^{107}\mathrm{Ag}} = 188.0$; $^1J_{^{109}\mathrm{Ag}} = 208.6$)	**88**[18]	179.0[a,j]
11[17]	188.9[b,j]	**89**[18]	179.6[a,j]
12[17]	188[b] ($^1J_{^{107}\mathrm{Ag}} = 180$; $^1J_{^{109}\mathrm{Ag}} = 204$)	**90**[18]	*a,k*
13[16]	182.9[d,j]	**91**[27]	189.2[d,j]
14[18]	173.9[a,j]	**92**[27]	185.0[d,j]
15[38]	183[b,j]	**93**[37]	182.2[b,j]
16[34]	180.6[c] ($^1J_{^{107}\mathrm{Ag}} = 189$; $^1J_{^{109}\mathrm{Ag}} = 219$)	**94**[37]	182.0[b,j]
22[18]	*a,k*	**95**[37]	182.2[b,j]
24[68]	183.0[c,j]	**96**[41]	197.2[i,j]
25[54]	179.5[b,j]	**97**[41]	194.6[i] ($^1J_{^{107}\mathrm{Ag}} = 232$; $^1J_{^{109}\mathrm{Ag}} = 268$)
26[18]	*a,k*	**98**[41]	*b,k*
28[32]	183.6[c] ($^1J_{^{107}\mathrm{Ag}} = 180$; $^1J_{^{109}\mathrm{Ag}} = 208$)	**99**[43]	180.9[b,j]
30[66]	182.3[a,j]	**100**[43]	181.9[b,j]
31[71]	186.6[b,j]	**101**[47]	180.6[a,j]
32[76]	182.7[d,j]	**102**[53]	174.5[a,j]
33[25]	205.8[c] ($^1J_{^{107}\mathrm{Ag}} = 174$; $^1J_{^{109}\mathrm{Ag}} = 201$)	**103**[53]	174.5[a,j]
34[98]	180.5[a,j]	**104**[58]	*a,k*
35[18]	*a,k*	**105**[58]	180.6[a,j]
36[41]	206[a,j]	**106**[59]	*a,k*
37[45]	186.2[c,j]	**107**[59]	178.7[a] ($^1J_{^{107}\mathrm{Ag}} = 230$; $^1J_{^{109}\mathrm{Ag}} = 265$)
38[57]	185[c] ($^1J_{^{107}\mathrm{Ag}} = 234$; $^1J_{^{109}\mathrm{Ag}} = 270$)	**108**[59]	*a,k*
39[25]	205.9[c] ($^1J_{^{107}\mathrm{Ag}} = 228$; $^1J_{^{109}\mathrm{Ag}} = 260$)	**109**[60]	*a,k*
40[98]	*a,k*	**110**[61]	*a,k*
42[99]	*a,k*	**111**[61]	*a,k*
43[33]	179.4[c,j]	**112**[61]	*a,k*
44[84]	166.1[c,j]	**113**[61]	*a,k*
45[97]	234.0[a] ($^1J_{^{107}\mathrm{Ag}} = 232.7$; $^1J_{^{109}\mathrm{Ag}} = 268.4$)	**114**[62]	181.1[f,j]
46[18]	167[a,j]	**115**[62]	180.6[f,j]
47[18]	163.2[a,j]	**116**[62]	181.7[h,j]
48[41]	213.7[b,j]	**117**[62]	178.0[d,j]
51[85]	180.9[f,j]	**118**[63]	183.8 [f,j]
59[92]	180.9[a]	**119**[64]	*b,k*
60/61[104]	*a,k*	**120**[74]	177.6[b,j]
62[77,104]	*b,k*	**121**[71]	187.1[g,j]
63[30,31]	186.8[b] ($^1J_{^{107}\mathrm{Ag}} = 186.6$; $^1J_{^{109}\mathrm{Ag}} = 216.1$)	**122**[72]	*g,k*
64[44]	180.9[b,j]	**123**[70]	181[g,j]
65[55]	182.5[b,j]	**124**[72]	*g,k*
66[55]	182.1[b,j]	**125**[76]	*d,k*
67[70]	*b,k*	**126**[78]	178.3[b,j]
68[70]	181.1[b,j]	**127**[78]	*b,k*
69[72]	196.0[b,j]	**128**[80]	179.8[a,j]
70[72]	196.3[b,j]	**129**[81]	*a,k*
71[73]	180.9[b] ($^1J_{^{107}\mathrm{Ag}} = 182$; $^1J_{^{109}\mathrm{Ag}} = 210$)	**130**[82]	178.0[a,j]
72[78]	183.9[b] ($^1J_{^{107}\mathrm{Ag}} = 181$; $^1J_{^{109}\mathrm{Ag}} = 210$)	**131**[83]	185.0[a,j]
73[78]	180.0[b] ($1J_{^{107}\mathrm{Ag}} = 182$; $^1J_{^{109}\mathrm{Ag}} = 212$)	**132**[26]	*a,k*
74[89]	184.9[b] ($^1J_{\mathrm{C-Ag}} = 211$)	**133**[88]	179.6[c,j]
75[56]	179.8[a,j]	**134**[69]	179.4[b,j]
78[78]	181.1[b] ($^1J_{^{107}\mathrm{Ag}} = 180$; $^1J_{^{109}\mathrm{Ag}} = 208$)	**135**[95]	*a,k*
79[39]	163.2[b] ($^1J_{\mathrm{C}\sigma-\mathrm{Ag}} = 220$; $^1J_{\mathrm{C}\pi-\mathrm{Ag}} = 47$)	**136**[95]	*a,k*
80[52]	164[b,j]	**137**[98]	184.5[a,j]
81[66]	175.4[d] (multiple couplings)	**138**[98]	180.6[a,j]
82[76]	*d,k*	**139**[99]	182.5[f,j]
83[85]	177.4[d,j]	**140**[99]	*a,k*
84[24]	202.5[a] ($^1J_{^{107}\mathrm{Ag}} = 168$; $^1J_{^{109}\mathrm{Ag}} = 192$)	**141**[18]	*a,k*
85[24]	204.2[a] ($^1J_{^{107}\mathrm{Ag}} = 169$; $^1J_{^{109}\mathrm{Ag}} = 194$)	**142**[86]	*a,k*
86[24]	204.0[a] ($^1J_{^{107}\mathrm{Ag}} = 170$; $^1J_{^{109}\mathrm{Ag}} = 196$)	**143**[86]	*a,k*
87[18]	178.6[a,j]		
^{109}Ag			

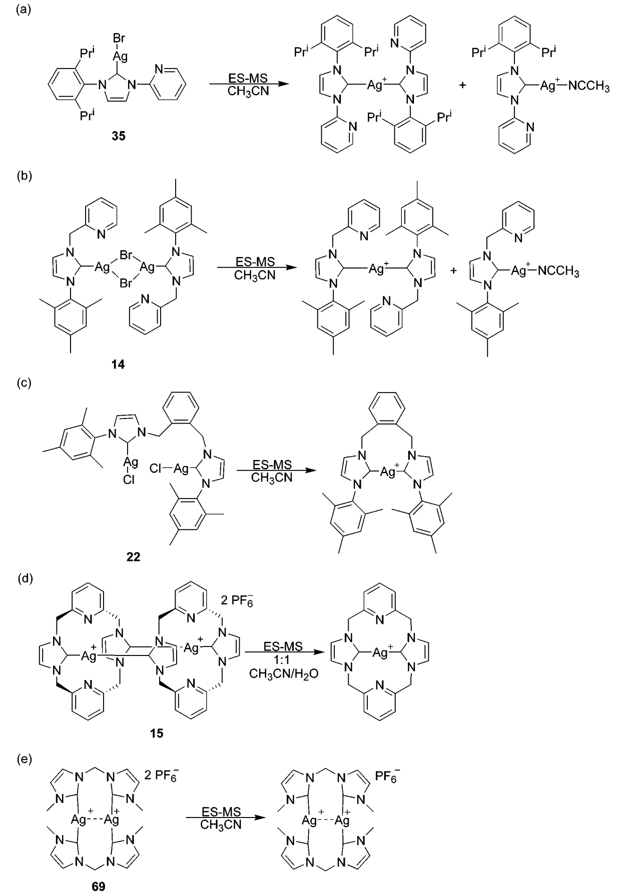
compd	δ $AgC_{carbene}$
8[15]	642.4[e] ($^4J_{\mathrm{AgH}} = 1.7$)
16[34]	727[c] ($^4J_{\mathrm{AgH}} = 1.6$)
38[57]	597[c]

[a] $CDCl_3$. [b] d_6-DMSO. [c] CD_2Cl_2. [d] CD_3CN. [e] d_5-Pyridine. [f] C_6D_6. [g] D_2O. [h] d_6-Acetone. [i] Solvent not specified. [j] No observed or reported coupling constants. [k] Not observed.

Scheme 15. Proposed Fluxional Behavior of Halogeno Silver NHC Complex 11



Scheme 16



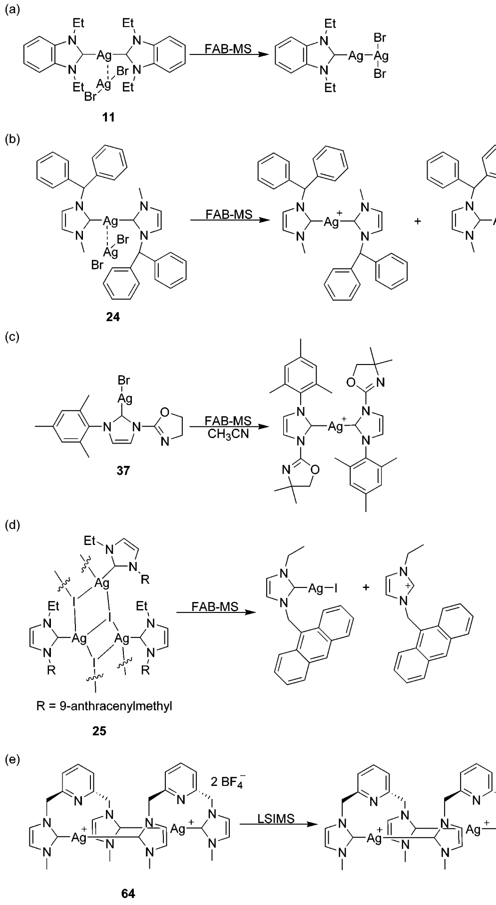
was structurally characterized in the solid state as a dimer.[72] Analysis of **69** by ES-MS, Scheme 16e, gave a peak corresponding to the dimer minus one hexaflurophosphate anion.

From the few silver NHC complexes that have been both structurally characterized and analyzed by ES-MS, it seems that silver NHC complexes of various motifs in the solid state often rearrange to form biscarbene complexes in the gas phase, whereas the complexes that are already biscarbenes in the solid state due to noncoordinating anions are readily observed in the gas phase as biscarbenes. Whether these rearrangements are associated with the solution dynamic behavior suggested for silver NHCs or occur only under ES-MS sampling conditions is unclear.

5.2.2. Fast Atom Bombardment and Liquid Secondary Ion Mass Spectrometry

The uses of FAB-MS and LSI-MS to analyze silver NHCs have also been reported.[17,25,26,30,31,44,45,54,59,60,64,68,71,86,93] Structurally characterized silver NHC halogeno complexes were first examined in the gas phase by Lin and co-workers.[17] They found that complex **11** (Scheme 17a) loses an

Scheme 17

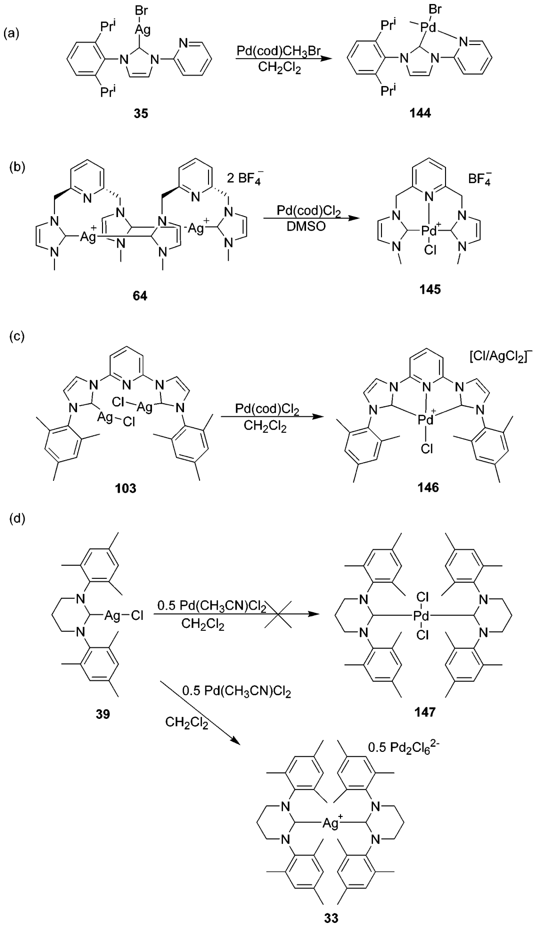


NHC moiety but retains the halogeno coordination in the gas phase. However, analysis of another halogeno complex **24** by FAB-MS, Scheme 17b, led to the observation of the biscarbene, the monocarbene, and the corresponding imidazolium salt.[68] Observation of a halogeno interaction in the gas phase for complex **24** was not reported.

Similar to ES-MS, the FAB-MS spectra of the coordinating silver halide NHC complex **37** revealed the existence of the biscarbene in the gas phase, Scheme 17c.[45] FAB-MS of the silver−iodide staircase **25** (C−Ag−X$_3$) shows the monomeric C−Ag−I complex, as well as the corresponding imidazolium cation, in the gas phase, Scheme 17d.[54] Interestingly, the analysis of complex **64** by LSI-MS is contrary to that of complex **15** by ES-MS. Cavell and colleagues reported that complex **64** exists as the dimer in the gas phase, Scheme 17e.[44] The reason for the existence of **15** as a monomer and **64** as a dimer in the gas phase is not clear. It could be attributed to the ionization technique; however, evidence thus far is far from conclusive.

Many of the problems with ES-MS also apply for FAB-MS and LSI-MS. There are relatively few compounds that have been both structurally characterized in the solid state and analyzed by FAB-MS or LSI-MS. Whether solution dynamics or the ionization technique is responsible for the observed rearrangements of silver NHCs in the gas phase is not clear.

Scheme 18



6. Uses of Ag(I) N-Heterocyclic Carbenes

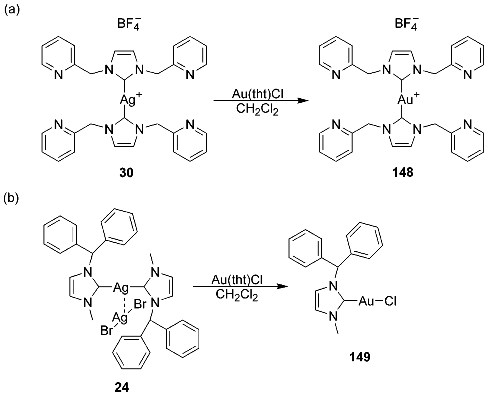
6.1. Transfer Chemistry

For many, the syntheses of silver NHC complexes are used only for the purpose of transferring to other metal systems. Some NHC complexes can be made directly from the imidazolium salt by deprotonation, using a strong base, and subsequent reaction with the desired metal. However, many ligands fail to metalate due to degradation under the harsh conditions required. Silver NHC complexes have proven themselves to be very adept at transferring to a variety of other metals: Au(I), Cu(I), Cu(II), Ni(II), Pd(II), Pt(II) Rh(I), Rh(III), Ir(I), Ir(III), Ru(II), Ru(III), and Ru(IV). Transmetalation reactions can be carried out under aerobic conditions and in the presence of water. However, there has been one reported instance where transmetalation would only proceed under an inert atmosphere.[11] The relative ease with which silver NHC complexes can be synthesized and transferred is an attractive alternative to reactions involving anaerobic conditions.

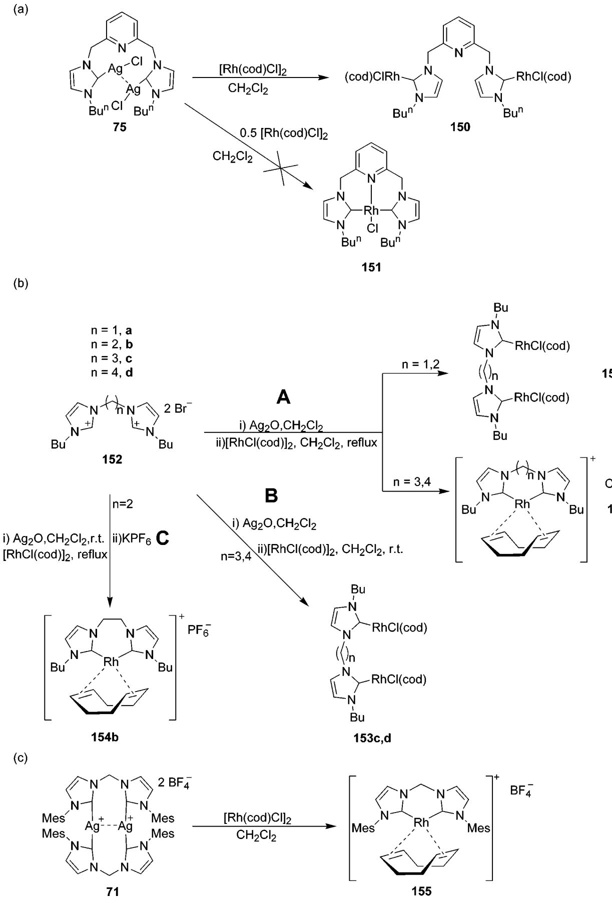
The metal to which silver NHCs are most widely transferred is palladium. A variety of palladium reagents have been used for transfer to NHCs: Pd(cod)Cl$_2$,[43,45,53,63,99,108] Pd(cod)Br$_2$,[108] Pd(cod)CH$_3$Br,[108] Pd(cod)CH$_3$Cl,[37,43,44,63,108] PdCl$_2$,[77,93,98] [Pd(allyl)Cl]$_2$[81,83] PdCl$_2$(CH$_3$CN)$_2$,[17,25,26,36,37,42−44,59,60,62,82,85,109] and PdCl$_2$(PhCN)$_2$.[43,56] Typical transmetalation reactions are depicted in Scheme 18a,b. Complex **35** can be transferred to palladium using Pd(cod)CH$_3$Br in CH$_2$Cl$_2$. The resulting complex, **144**, is square planar with the palladium bound by the NHC and the pyridine of the ligand.[108] The bidentate silver NHC complex **64** reacts with Pd(cod)Cl$_2$ in DMSO to form monomeric complex **145** with palladium bound by two NHC rings and the pyridine ring from the ligand. Cavell and co-workers have also accomplished the transmetalation of complex **64** from the imidazolium salt using a one-pot reaction.[44] Danapoulos and colleagues have observed the presence of halide/halogeno anion mixtures in isolated products.[53] In Scheme 18c, the transfer of complex **103** to **146** gives an example of the synthesis of mixed anions upon transmetalation. An alternative method to form palladium NHC complexes is to use the metal base Pd(OAc)$_2$. This route is synthetically appealing because the reactions can be accomplished in the presence of water and oxygen. However, Bellemin-Laponnaz, Gade, and co-workers reported that use of Pd(OAc)$_2$ failed to yield the desired palladium NHC complex from the imidazolium salt.[45] Due to the failure of Pd(OAc)$_2$ in this instance, they subsequently attempted to synthesize the palladium NHC by transmetalation. The transmetalation to the palladium NHC from the silver NHC complex proved successful.

It has also been noted that the transmetalation from silver to palladium does not always proceed.[25,81,98] NHCs with saturated backbones have been shown to be relatively poor transmetalation reagents when compared to NHCs with unsaturated backbones. Herrmann and co-workers showed that complex **39** when reacted with Pd(CH$_3$CN)$_2$Cl$_2$ does not form the expected product complex **147**, Scheme 18d. The Pd(CH$_3$CN)$_2$Cl$_2$ instead acts as a chloride scavenger and results in the formation of a $Pd_2Cl_6^{2-}$ anion and a silver biscarbene, **33**.[25] This work was reported to refute published reports of transmetalation of very similar systems.[26,86] The rationale for the relative inactivity of the saturated NHCs toward transmetalation vs the effortless transmetalation of unsaturated NHCs is the stronger donation of the saturated NHCs to the metal center. Stronger donation from the NHC to the silver has been suggested to inhibit the lability of the silver−carbene bond thereby hindering transmetalation. However, given that complex **132** undergoes transmetalation to palladium under the same conditions in which **39** failed, it seems likely that sterics play some role in the failure of **39** to transfer. Roland and co-workers have found that successful transmetalation of saturated NHC silver complexes is also dependent upon the palladium source used.[81] They found that transfer of complexes **98** and **129** to palladium would not proceed using Pd(CH$_3$CN)$_2$Cl$_2$ in either refluxing CH$_2$Cl$_2$ or CH$_3$CN. However, the use of [Pd(allyl)Cl]$_2$ with **98** and **129** gave the desired products within minutes at room temperature.

Scheme 19



Scheme 20



The transmetalation of silver NHCs to gold has been accomplished using gold reagents, Au[S(CH$_3$)$_2$]Cl[11,17,35,90,94,96,110] and Au(tht)Cl[68,76] (tht = tetrahydrothiophene). Gold transfers are usually accomplished in CH$_2$Cl$_2$ at room temperature and proceed to completion in a few hours. Examples of silver transmetalations to gold are given in Scheme 19a,b. Complex **30** reacts with Au(tht)Cl to give the gold(I) biscarbene complex **148**,[76] while complex **24** reacts with Au(tht)Cl to give the gold(I) halide complex **149**.[68] Gold biscarbene complexes (C$_2$−Au) and gold halide complexes (C−Au−X) can be synthesized depending on the anion involved. A noncoordinating anion favors the formation of the gold biscarbene complex, while halides favor an NHC gold halide arrangement.

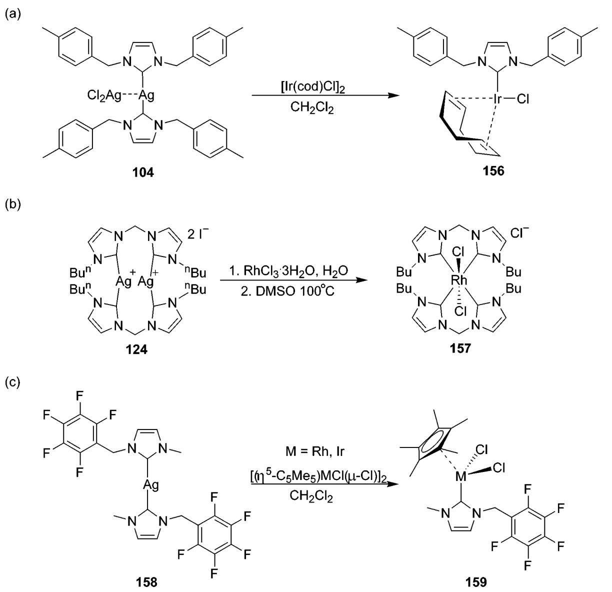
The syntheses of rhodium NHC complexes have also been accomplished using transmetalation reagents: [Rh(cod)Cl]$_2$[56,58,71,73,75,87,91,111] and [Rh(cod)(THF)$_2$]BF$_4$.[60] Complex **75** reacts with [Rh(cod)Cl]$_2$ in CH$_2$Cl$_2$, Scheme 20a, to form rhodium NHC complex **150** in which there is one rhodium atom per

NHC ring.[56] Attempts to obtain the biscarbene **151** by addition of one-half an equivalent of the rhodium reagent to complex **75** did not produce the bidentate complex **151**. It instead yielded complex **150** and unreacted starting material, **75**. This reaction is interesting when compared with similar transmetalation chemistry involving palladium, such as complex **64**, Scheme 18b, with Pd(cod)Cl_2 to give the bidentate complex **145**. It is often difficult to predict the outcome of a transmetalation reaction. Factors such as the sterics and flexibility of the imidazolium ligand, discussed below, as well as reaction conditions, are key determinants in the ultimate outcome of the transmetalation reaction.

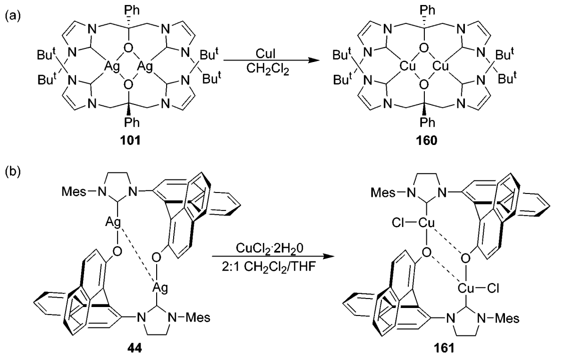
Crabtree and colleagues reported a study of the coordination chemistry of bidentate NHCs with different linker lengths upon transmetalation from silver to rhodium.[75] Scheme 20b gives a summary of their results. Imidazolium salts **152a**−**d** react with Ag_2O and undergo transmetalation with $[Rh(cod)Cl]_2$ using conditions A−C. Transfer from silver to rhodium in refluxing CH_2Cl_2, condition A, produces bis-monodentate complexes **153a**,**b** ($n = 1,2$) and bidentate complexes **154c**,**d** ($n = 3,4$). Under these conditions, it seems that the coordination of these bidentate NHCs is dependent on the alkyl linkers. Ligands with linker lengths of $n = 1,2$ favor the formation of bis-monodentate rhodium complexes, while $n = 3,4$ favor the formation of the bidentate systems. Interestingly the transmetalation was found to be temperature dependent. Transfer of silver complexes of **152c**,**d** at room temperature, condition B, yields the bis-monodentate rhodium complexes **153c**,**d**. Efforts to convert the bis-monodentate complexes **153c**,**d** to the bidentate complexes **154c**,**d** by refluxing in CH_2Cl_2 were unsuccessful. It was also noted that **152b** under condition C (one-pot reaction) underwent transfer to **154b**. Presumably this result is due to the presence of silver reagents and their ability to abstract a chloride from the bis-monodentate rhodium complex **153b**, thereby favoring the formation of **154b**. Although the linker length is an important factor in the coordination of bidentate NHCs such as **152a**−**d**, it is not the only one. Slaughter and co-workers report the transfer of the bidentate silver NHC complex **71** to the bidentate rhodium complex **155**, Scheme 20c. Complex **71** is similar to **152a** in that it consists of a methylene linker but with mesityl groups for substituents instead of butyl groups. From the work done with **152**, it would be expected that **71** would form a bis-monodentate complex upon transmetalation; however, this is not what is observed. Steric effects seem to play a role in determining the favored product.

Not surprisingly, transfer from silver NHCs to iridium NHCs have been explored using the analogous reagent, $[Ir(cod)Cl]_2$.[28,58,87] An example of a typical transfer is depicted in Scheme 21a. Complex **104** is combined with $[Ir(cod)Cl]_2$ in CH_2Cl_2 yielding complex **156**. Silver NHCs have also been transferred to rhodium(III) using $RhCl_3$·$3H_2O$.[72] Complex **124** is converted to a rhodium(III) NHC by addition of $RhCl_3$·$3H_2O$ in water, Scheme 21b. The resulting solid was then heated in DMSO to form complex **157**.

Scheme 21



Scheme 22

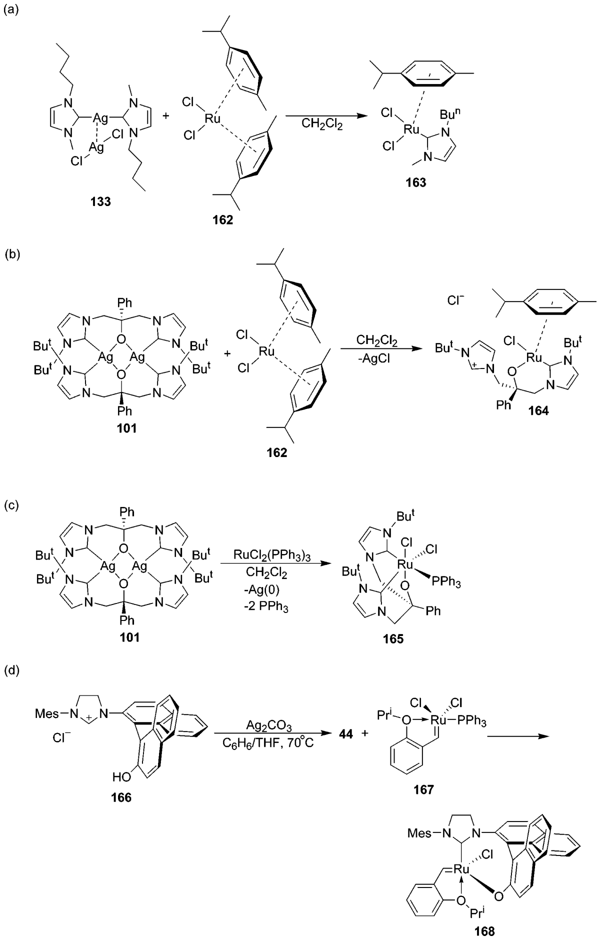


The use of $RhCl_3$·$3H_2O$ as a transfer agent is significant due to potential use of rhodium(III) complexes in radiopharmaceuticals. McGrandle and Saunders have recently reported the one-step transfer from silver to rhodium(III) and iridium(III) centers, Scheme 21c.[100] The silver complex **158** when combined with $[(\eta^5\text{-}C_5Me_5)MCl(\mu\text{-}Cl)]_2$ (where M = Rh or Ir) yields the trivalent metal complex **159** with one NHC, two chlorides, and a Cp ring as coordinating ligands.

Transmetalation from silver to copper has been reported by several researchers.[11,40,47,61,69,84,97] The transfer from silver to copper(I) was first structurally characterized by Arnold and co-workers.[47] Scheme 22a depicts an NHC transmetalation reaction from silver to copper(I). Complex **101** reacts with CuI in CH_2Cl_2 to produce a copper(I) NHC complex, **160**, in which two copper cations are bridging the two bidentate ligands. The copper atoms are also stabilized, as well as charge balanced, by the two alkoxide anions. Several copper(I) NHCs have been synthesized, using the free carbene route, and structurally characterized.[112−114] It is noteworthy, that the transmetalation method from silver to copper(I) NHCs has been reported to sometimes give different products than methods employing the use of free carbenes.[69]

Carbene transfer to copper(II) has been reported.[40,61,84,97] The purpose of the syntheses of most of the copper(II) carbene species was to study their

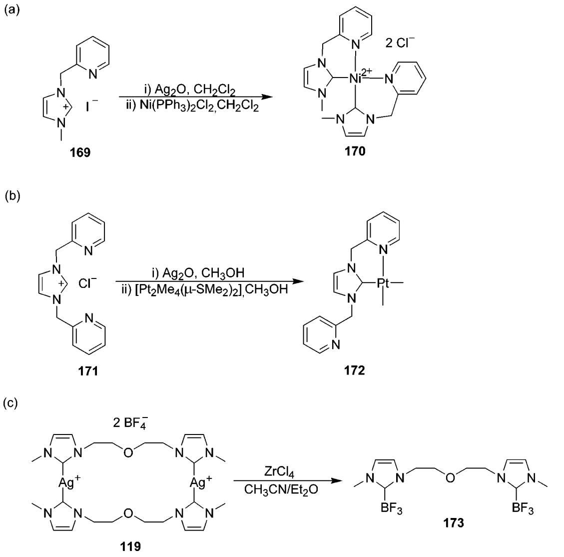
Scheme 23



potential catalytic application. In earlier work, the copper(II) NHC catalysts were not isolated or structurally characterized.[40,61] Although the authors of this work did not state whether they tried to isolate the copper(II) NHC species, it would not be surprising if this was very difficult given that there are few structures given in the Cambridge Structural Database that contain organometallic copper(II) complexes. However, recently two groups have reported examples of copper(II) NHC complexes.[84,97,115] Larsen and co-workers report the synthesis and structural characterization of an air stable NHC copper(II) complex. The reaction is depicted in Scheme 22b; complex **44** undergoes transmetalation with $CuCl_2 \cdot 2H_2O$ in a mixture of CH_2Cl_2 and THF to give complex **161**. Drawing from the hard/soft relationship, it would be expected that a copper(II) NHC species would be less stable than copper(I) complexes. However, given the stability of complexes such as **161** it seems that donors such as the alkoxides are crucial in the stability of copper(II) NHC complexes.

Recently, the transmetalation from silver to ruthenium(II),[88,104,116] ruthenium(III),[116] and ruthenium(IV)[51,97] has been reported. Depiction of the various reactions is given in Scheme 23a–d. Complex **133** underwent transmetalation with complex **162** in CH_2Cl_2 to yield the ruthenium(II) complex **163**.[88] Arnold and Scarisbrick have also reported the transfer to a ruthenium(II) center using complex **162**, Scheme 23b.[116] Combination of silver NHC complex **101** with **162** yielded the ruthenium(II) complex **164**. Interestingly, if the ruthenium reagent is changed to $RuCl_2(PPh_3)_3$, Scheme 23c, then the ruthenium(III) complex **165** is isolated. The oxidation of the ruthenium results in the reduction of silver(I) to silver(0) and the isolation of silver metal from the reaction vessel. Imidazolium salt **166**, Scheme 23d, undergoes deprotonation using Ag_2CO_3 as a silver base to presumably form complex **44**. Complex **44** undergoes reaction with the ruthenium(IV) source **167** to form the chiral ruthenium(IV) complex, **168**.[51]

Scheme 24



Transmetalations involving other d^8 metals have been reported; however, these transfers have not, as of yet, become widely used. Jin and colleagues reported the transfer from the silver complex of **169** to nickel(II) using $Ni(PPh_3)_2Cl_2$, Scheme 24a.[79] The nickel complex, **170**, was structurally characterized as a dimer with the NHCs in a cis conformation. Also, the use of $NiBr_2$(DME) (DME = 1,2-dimethoxyethane) as a transmetalation agent has recently been reported.[117] Using this reagent, a detailed study was performed on the dependence of the transmetalation product upon the steric restraints of the ligand. Also investigated was the transmetalation product's dependence on the molar ratios of the silver NHC complex with respect to the transmetalation agent. Puddephatt and co-workers have reported a platinum(II) NHC complex synthesized by transmetalation using $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$.[65] Imidazolium salt **171** is reacted with Ag_2O in CH_3OH to form the silver NHC complex, Scheme 24b. The silver complex was then reacted with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ at room temperature to yield the platinum complex **172**.

Cavell and colleagues have reported the transfer from silver to BF_3 by activation of a BF_4 anion.[64] Complex **119** was reacted with $ZrCl_4$ in a mixture of CH_3CN and Et_2O to form NHC–BF_3 adduct **173**, Scheme 24c. A proposed mechanism for the activation of the BF_4 anion was not given.

6.2. Pharmaceutical Application

Silver has been used as an agent to promote human heath in many different aspects: surgical needles, water purification, catheters, wound care, etc. Silver

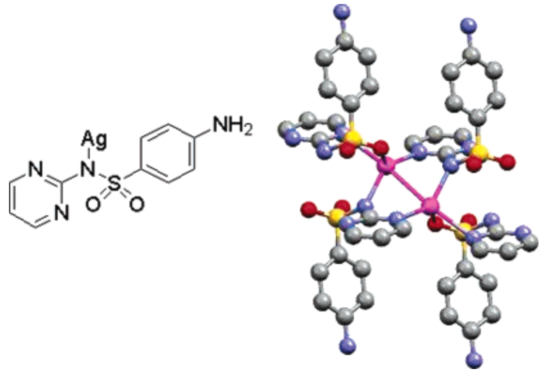


Figure 34. (a) Simplified structure of silver sulfadiazine and (b) solid-state structure of silver sulfadiazine(polymeric).

metal was used by many civilizations as an antimicrobial agent to purify drinking water. The use of silver compounds for medicinal use has been documented since the 17th century.[21,22,118,119] It is believed that the use of silver to cure ailments extends back to at least the middle ages but likely further into antiquity.

Silver nitrate has been used in the treatment of wounds and infectious diseases since before the discovery of bacteria. It has been widely used for nearly 200 years and is still in use today. During the 19th and 20th centuries, silver nitrate was used to minimize bacterial growth on burn patients. Since the 1880s and throughout the early 20th century dilute solutions of silver nitrate were dropped into newborn's eyes to prevent conjunctivitis as well as other bacterial infections.[120] In 1967, silver sulfadiazine was introduced and found to be a more effective and safer alternative to silver nitrate in the treatment of burn wounds. A simplified drawing and the solid-state structure of silver sulfadiazine is depicted in Figure 34.[121] Currently, silver sulfadiazine is the most widely used remedy in American burn centers. Several excellent reviews on the history and practical use of silver-based pharmaceuticals and antiseptic reagents have been published.[21,22,118,119,122]

Silver in its common forms have been found, in general, to be nontoxic to mammalian cells. Reagents such as silver sulfadiazine and silver nitrate when applied to a wound quickly kill bacteria, but their effects diminish relatively quickly due to wound exodus and other factors allowing the possibility for the wound to become infected. The discoloration of the skin from these silver compounds is also a major drawback to their widespread use. The search for a silver reagent that slowly releases silver into the wound and can be retained on the wound without discoloration thereby maintaining a constant source of antimicrobial agents to prevent infection is a subject of great interest in the medicinal community.

The synthesis of two silver N-heterocyclic carbene complexes, **68** and **123**, and investigation into their use as potential antimicrobial agents were recently reported.[70] It was found that both **68** and **123** released silver at a slower rate when compared to silver nitrate. The complexes were shown to be stable in deionized water. However, slow decomposition does occur when examined over a period of weeks. Although silver NHC complexes **68** and **123** decompose slowly in deionized water, the decomposition of the complexes was found to accelerate in saline solution. The accelerated decomposition is due to chloride anions in the saline solution extracting the silver cations from the silver NHC complexes. Typically in chemistry, interactions of silver cations and halide anions results in the formation of silver halide almost immediately, but due to the strong silver–NHC bond decomposition occurs slowly over time. The ultimate fate of the silver cation might not necessarily be AgCl. The formation of halogeno complexes with some water solubility can result in some circumstances. As mentioned earlier in the synthesis section, the formations of halogeno complexes are dependent on several factors.[103] The active species or distributions of bioavaliable active species that are responsible for the antimicrobial properties of these silver NHC complexes are not known.

Electrospun polymer mats have been investigated for several different applications, filters, protective clothing, wound dressing, drug delivery, solar cells, catalyst carriers, etc.[123,124] Recently, the encapsulation of the silver NHC complex **74** into an electrospun polymer mat has been reported.[89] The antimicrobial properties of this polymer mat were studied in detail. In this study, it was found that exposure of **74** to a humid environment caused the slow decomposition of the encapsulated silver NHC complex, which then deposited silver particles onto the polymer matrix. Transmission electron microscopy (TEM) images of the deposition of silver particles onto the polymer mat over time are depicted in Figure 35. The deposition of silver particles on the polymer presumably helps reduce the amount of deposition of silver species into the wound. The encapsulated silver NHC fiber mats were found to have better antimicrobial activity as well as a faster kill rate than either silver sulfadiazine or silver nitrate. It was also found that the bioavailability of the active silver species was increased by encapsulation of the silver NHC into the polymer mat.

When a pharmaceutical is designed, it is important to know the toxicity of all likely decomposition products. The likely decomposition pathway of silver NHC complexes is the release of cationic silver and the formation of the imidazolium salt. The drawback of complex **74** is that the corresponding imidazolium salt of complex **74** was found to be relatively toxic. The search for biologically benign imidazolium salts that can form NHC complexes to silver is being undertaken. A likely place to start is with xanthanine derivates that are commonly found in the body. The NHC ligand in complexes **31** and **121** is a derivative of a biologically benign xanthanine commonly referred to as caffeine.[71] It is likely that xanthanines such as this will be investigated for their pharmaceutical, as well as catalytic, potential in the years to come.

6.3. Catalysis

Catalytic study of silver NHC complexes has not yet received much attention. Peris, Fernandez, and co-workers were the first to study silver NHCs as

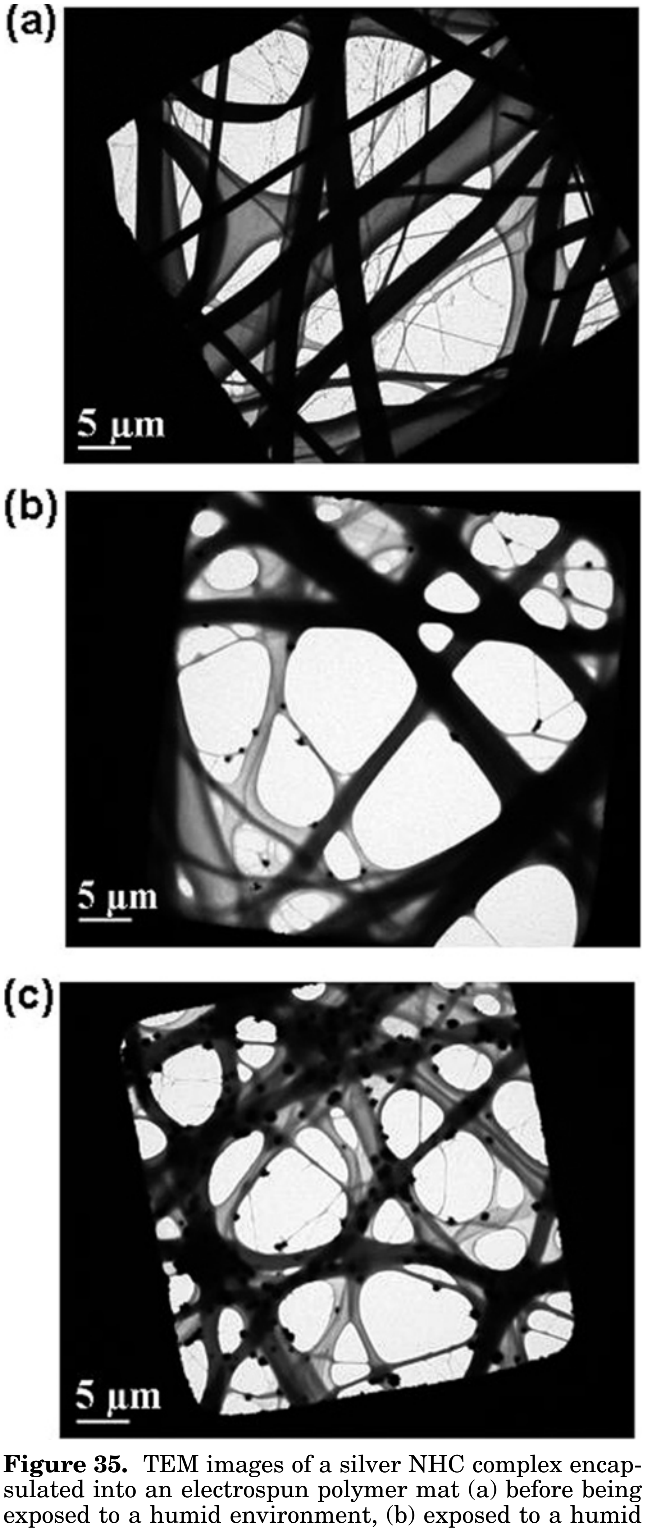
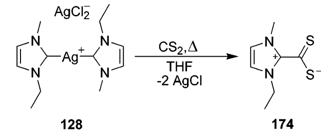


Figure 35. TEM images of a silver NHC complex encapsulated into an electrospun polymer mat (a) before being exposed to a humid environment, (b) exposed to a humid environment for 30 min, and (c) exposed to a humid environment for 65 h.

potential catalytic reagents.[92] They explored the use of complex **59** as a catalyst for diboration reactions with various terminal and internal alkenes. One of the problems with some metal systems used for diboration reactions is the selectivity of the hydroboration pathway over the diboration pathway. In their report, they found that complex **59** was very chemoselective for the formation of the diborane. The conversion rates for terminal alkenes were in general greater than those for internal alkenes. Electron donation from the substituents of the alkene increased the conversion rates of the diboration reaction. Interestingly, they found that increasing the temperature of the diboration reactions slows the conversion of the alkene to the diborane. Peris, Fernandez, and co-workers also reported that the use of other boranes inhibited the diboration process. The reason for this is not clear. Use of complex **59** for the diboration process by in-situ formation gave much lower yields than when complex **59** was isolated and then used. Further study of the catalytic process of silver NHCs is needed; however, discovering the active catalytic species of silver NHCs would not be trivial due to the dynamic nature of silver NHCs in solution.

Scheme 25



Waymouth, Hedrick and colleagues have recently studied silver NHCs for catalytic purposes.[80,95] They reported that silver NHCs **128** and **135** undergo thermolysis to produce free NHCs, which can then be used to catalyze the ring opening polymerization of L-lactide. The thermal stability of **128**, **135**, and **136** were studied by differential scanning calorimetry and thermogravimetric analysis. Complexes **135** and **136** were found to be stable below 250 °C; however, complex **128** showed thermal decomposition at a significantly lower temperature, 89.2 °C. The thermal decomposition of these silver NHCs was hypothesized to give free NHCs. The release of a small amount of free NHC was expected at elevated temperatures even for the thermally stable complexes **135** and **136**. To substantiate this hypothesis, they attempted to trap the free NHC by heating complex **128** in the presence of a trapping reagent, carbon disulfide (Scheme 25). The presence of the resulting zwitterion, **174**, was confirmed by NMR. With the generation of the free carbene confirmed, they then investigated the catalytic ability of the silver NHC complexes **128** and **135**. These complexes produced polymers with a narrow molecular weight distribution and no evidence of racemization.

7. Conclusions

N-Heterocyclic carbenes have received a great deal of attention within the last 15 years. They have been investigated for several purposes but are most prominent in the field of catalysis. The development of N-heterocyclic carbene complexes of silver has mainly come about by the discovery of the transmetalation from silver NHCs to other metal NHC systems. Silver N-heterocyclic carbenes, unlike other metal NHC systems, can be synthesized without the need for anaerobic conditions. The ease with which silver NHCs can be synthesized and undergo transmetalation has made it and continues to make it the most attractive route in the development of many metal NHC systems.

The structural study of silver NHCs has led to a diverse field of bonding motifs in the solid state. The silver−carbene interaction remains, in general, consistent from one bonding motif to another. The only exception to this is when the N-heterocyclic carbene bridges two silver cations. Argentophillic and silver−halide interactions play key roles in the formation of the structurally diverse silver NHC chemistry. The restraints of the ligand, sterics and flexibility (for multidentate ligands), are also factors that determine the outcome of the reaction. With further study will undoubtedly come other silver NHC motifs as well as further insight into the factors that control the formation of these novel systems.

The study of silver NHCs has since led to application of these complexes for practical use. Silver has had a long history in the promotion of human health. Silver NHCs are being explored for possible use as novel antimicrobial agents for wound healing. The stability of the silver−carbene bond allows for the slow release of silver from the embedded bandage into the wound, a major advantage over other silver antimicrobial agents. Silver NHCs are being investigated for their catalytic properties as well. However, more study needs to be done to establish the relevance of these potential catalysts.

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9. References

(1) Öfele, K. *J. Organomet. Chem.* **1968**, *12*, P42.
(2) Wanzlick, H.-W.; Schönherr, H.-J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 141.
(3) Lappert, M. F. *J. Organomet. Chem.* **1975**, *100*, 139.
(4) Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185.
(5) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.
(6) Bourissou, D.; Guerret, O.; François, P.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.
(7) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.
(8) Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.
(9) Korotkikh, N. I.; Shvaika, O. P.; Rayenko, G. F.; Kiselyov, A. V.; Knishevitsky, A. V.; Cowley, A. H.; Jones, J. N.; Macdonald, C. L. B. *ARKIVOC* **2005**, *8*, 10.
(10) Arduengo, A. J.; Tapu, D. In *Comprehensive Organic Functional Transformations II*; Katritzky, A. R., Taylar, R. J. K., Eds.; Elsevier: Oxford, U.K., 2005; p 1103.
(11) Hu, X.; Castro-Rodriguez, I.; Olsen, K.; Meyer, K. *Organometallics* **2004**, *23*, 755.
(12) Nemcsok, D.; Wichmann, K.; Frenking, G. *Organometallics* **2004**, *23*, 3640.
(13) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69.
(14) Jafarpour, L.; Nolan, S. P. *J. Organomet. Chem.* **2001**, *617−618*, 17.
(15) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405.
(16) Guerret, O.; Solé, S.; Gornitzka, H.; Teichert, M.; Trinquier, G.; Bertrand, G. *J. Am. Chem. Soc.* **1997**, *119*, 6668.
(17) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.
(18) Tulloch, A. A. D.; Danopoulos, A. A.; Winston, S.; Kleinhenz, S.; Eastham, G. *J. Chem. Soc., Dalton Trans.* **2000**, 4499.
(19) Arnold, P. L. *Heteroat. Chem.* **2002**, *13*, 534.
(20) Lin, I. J. B.; Vasam, C. S. *Comments Inorg. Chem.* **2004**, *25*, 75.
(21) Klasen, H. J. *Burns* **2000**, *26*, 131.
(22) Lansdown, A. B. G. *Br. J. Nurs.* **2004**, *13*, S6.
(23) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley & Sons: New York, 1999; pp 677−678.
(24) Ku, R.-Z.; Huang, J.-C.; Cho, J.-Y.; Kiang, F.-M.; Reddy, K. R.; Chen, Y.-C.; Lee, K.-J.; Lee, J.-H.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **1999**, *18*, 2145.
(25) Herrmann, W. A.; Schneider, S. K.; Öfele, K.; Sakamoto, M.; Herdtweck, E. *J. Organomet. Chem.* **2004**, *689*, 2441.
(26) Mayr, M.; Wurst, K.; Ongania, K.-H.; Buchmeiser, M. R. *Chem.−Eur. J.* **2004**, *10*, 1256.
(27) Guerret, O.; Solé, S.; Gornitzka, H.; Trinquier, G.; Bertrand, G. *J. Organomet. Chem.* **2000**, *600*, 112.
(28) Chianese, A. R.; Kovacevic, A.; Zeglis, B. M.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 2461.
(29) Boehme, C.; Frenking, G. *Organometallics* **1998**, *17*, 5801.
(30) Caballero, A.; Diez-Barra, E.; Jalón, F. A.; Merino, S.; Tejeda, J. *J. Organomet. Chem.* **2001**, *617−618*, 395.
(31) Caballero, A.; Diez-Barra, E.; Jalón, F. A.; Merino, S.; Rodriguez, A. M.; Tejeda, J. *J. Organomet. Chem.* **2001**, *627*, 263.
(32) Fox, M. A.; Mahon, M. F.; Patmore, N. J.; Weller, A. S. *Inorg. Chem.* **2002**, *41*, 4567.
(33) Chung, M. C. *Bull. Korean Chem. Soc.* **2002**, *23*, 921.
(34) Bildstein, B.; Malaun, M.; Kopacka, H.; Wurst, K.; Mitterböck, M.; Ongania, K.-H.; Opromolla, G.; Zanello, P. *Organometallics* **1999**, *18*, 4325.
(35) Wang, H. M. J.; Chen, C. Y. L.; Lin, I. J. B. *Organometallics* **1999**, *18*, 1216.
(36) Lee, C. K.; Chen, J. C. C.; Lee, K. M.; Liu, C. W.; Lin, I. J. B. *Chem. Mater.* **1999**, *11*, 1237.
(37) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741.
(38) Garrison, J. C.; Simons, R. S.; Talley, J. M.; Wesdemiotis, C.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2001**, *20*, 1276.
(39) Garrison, J. C.; Simons, R. S.; Kofron, W. G.; Tessier, C. A.; Youngs, W. J. *Chem. Commun.* **2001**, 1780.
(40) Pytkowicz, J.; Roland, S.; Mangeney, P. *Tetrahedron: Asymmetry* **2001**, *12*, 2087.
(41) Pytkowicz, J.; Roland, S.; Mangeney, P. *J. Organomet. Chem.* **2001**, *631*, 157.
(42) Nielsen, D. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **2001**, *20*, 995.
(43) Magill, A. M.; McGuinness, D. S.; Cavell, K. J.; Britovsek, G. J. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; White, A. H.; Skelton, B. W. *J. Organomet. Chem.* **2001**, *617−618*, 546.
(44) Nielsen, D. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2002**, *327*, 116.
(45) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Organometallics* **2002**, *21*, 5204.
(46) Chen, W.; Wu, B.; Matsumoto, K. *J. Organomet. Chem.* **2002**, *654*, 233.
(47) Arnold, P. L.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2002**, 2340.
(48) Lee, C. K.; Lee, K. M.; Lin, I. J. B. *Organometallics* **2002**, *21*, 10.
(49) Lee, K. M.; Wang, H. M. J.; Lin, I. J. B. *J. Chem. Soc., Dalton Trans.* **2002**, 2852.
(50) Perry, M. C.; Cui, X.; Burgess, K. *Tetrahedron: Asymmetry* **2002**, *13*, 1969.
(51) Van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954.
(52) Garrison, J. C.; Simons, R. S.; Tessier, C. A.; Youngs, W. J. *J. Organomet. Chem.* **2003**, *673*, 1.
(53) Danopoulos, A. A.; Tulloch, A. A. D.; Winston, S.; Eastham, G.; Hursthouse, M. B. *Dalton Trans.* **2003**, 1009.
(54) Liu, Q.-X.; Xu, F.-B.; Li, Q.-S.; Zeng, X.-S.; Leng, X.-B.; Chou, Y. L.; Zhang, Z.-Z. *Organometallics* **2003**, *22*, 309.
(55) Hu, X.; Tang, Y.; Gantzel, P.; Meyer, K. *Organometallics* **2003**, *22*, 612.
(56) Simons, R. S.; Custer, P.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2003**, *22*, 1979.
(57) Ramnial, T.; Abernethy, C. D.; Spicer, M. D.; McKenzie, I. D.; Gay, I. D.; Clyburne, J. A. C. *Inorg. Chem.* **2003**, *42*, 1391.
(58) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663.
(59) Bonnet, L. G.; Douthwaite, R. E.; Hodgson, R. *Organometallics* **2003**, *22*, 4384.
(60) Coleman, K. S.; Chamberlayne, H. T.; Turberville, S.; Green, M. L. H.; Cowley, A. R. *Dalton Trans.* **2003**, 2917.

(61) Alexakis, A.; Winn, C. L.; Guillen, F.; Pytkowicz, J.; Roland, S.; Mangeney, P. *Adv. Synth. Catal.* **2003**, *345*, 345.
(62) Bonnet, L. G.; Douthwaite, R. E.; Kariuki, B. M. *Organometallics* **2003**, *22*, 4187.
(63) Frøseth, M.; Dhindsa, A.; Røise, H.; Tilset, M. *Dalton Trans.* **2003**, 4516.
(64) Nielsen, D. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2003**, *352*, 143.
(65) Prokopchuk, E. M.; Puddephatt, R. J. *Organometallics* **2003**, *22*, 563.
(66) Catalano, V. J.; Malwitz, M. A. *Inorg. Chem.* **2003**, *42*, 5483.
(67) Chen, W.; Liu, F. *J. Organomet. Chem.* **2003**, *673*, 5.
(68) Schneider, S. K.; Herrmann, W. A.; Herdtweck, E. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2363.
(69) Hu, X.; Castro-Rodriguez, I.; Meyer, K. *J. Am, Chem. Soc.* **2003**, *125*, 12237.
(70) Melaiye, A.; Simons, R. S.; Milsted, A.; Pingitore, F.; Wesdemiotis, C.; Tessier, C. A.; Youngs, W. J. *J. Med. Chem.* **2004**, *47*, 973.
(71) Kascatan-Nebioglu, A.; Panzner, M. J.; Garrison, J. C.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2004**, *23*, 1928.
(72) Quezada, C. A.; Garrison, J. C.; Panzner, M. J.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2004**, *23*, 4846.
(73) Wanniarachchi, Y. A.; Khan, M. A.; Slaughter, L. M. *Organometallics* **2004**, *23*, 5881.
(74) Chianese, A. R.; Zeglis, B. M.; Crabtree, R. H. *Chem. Commun.* **2004**, 2176.
(75) Mata, J. A.; Chianese, A. R.; Miecznikowski, J. R.; Poyatos, M.; Peris, E.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 1253.
(76) Catalano, V. J.; Malwitz, M. A.; Etogo, A. O. *Inorg. Chem.* **2004**, *43*, 5714.
(77) Lee, H. M.; Zeng, J. Y.; Hu, C.-H.; Lee, M.-T. *Inorg. Chem.* **2004**, *43*, 6822.
(78) Baker, M. V.; Brown, D. H.; Haque, R. A.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2004**, 3756.
(79) Wang, X.; Liu, S.; Jin, G.-X. *Organometallics* **2004**, *23*, 6002.
(80) Sentman, A. C.; Csihony. S.; Nyce, G. W.; Waymouth, R. M.; Hedrick, J. L. *Polym. Prepr.* **2004**, *45*, 299.
(81) Roland, S.; Audouin, M.; Mangeney, P. *Organometallics* **2004**, *23*, 3075.
(82) Douthwaite, R. E.; Houghton, J.; Kariuki, B. M. *Chem. Commun.* **2004**, 698.
(83) Ketz, B. E.; Cole, A. P.; Waymouth, R. M. *Organometallics* **2004**, *23*, 2835.
(84) Larsen, A. O.; Leu, W.; Oberhuber, C. N.; Campbell, J. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2004**, *126*, 11130.
(85) Bonnet, L. G.; Douthwaite, R. E.; Hodgson, R.; Houghton, J.; Kariuki, B. M.; Simonovic, S. *Dalton Trans.* **2004**, 3528.
(86) Mayr, M.; Buchmeiser, M. R. *Macromol. Rapid Commun.* **2004**, *25*, 231.
(87) Mas-Marzá, E.; Poyatos, M.; Sanaú, M.; Peris, E. *Inorg. Chem.* **2004**, *43*, 2213.
(88) Csabai, P.; Joó, F. *Organometallics* **2004**, *23*, 5640.
(89) Melaiye, A.; Sun, Z.; Hindi, K.; Milsted, A.; Ely, D.; Reneker, D. H.; Tessier, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **2005**, *127*, 2285.
(90) Baker, M. V.; Barnard, P. J.; Brayshaw, S. K.; Hickey, J. L.; Skelton, B. W.; White, A. H. *Dalton* **2005**, 37.
(91) Evans, P. A.; Baum, E. W.; Fazal, A. N.; Pink, M. *Chem. Commun.* **2005**, 63.
(92) Ramírez, J.; Corberán, R.; Sanaú, M.; Peris, E.; Fernandez, E. *Chem. Commun.* **2005**, 3056.
(93) Chiu, P. L.; Chen, C. Y.; Zeng, J. Y.; Lu, C. Y.; Lee, H. M. *J. Organomet. Chem.* **2005**, *690*, 1682.
(94) Nieto-Oberhuber, C.; López, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178.
(95) Sentman, A. C.; Csihony, S.; Waymouth, R. M.; Hedrick, J. L. *J. Org. Chem.* **2005**, *70*, 2391.
(96) De Frémont, P.; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 2411.
(97) Van Veldhuizen, J. J.; Campbell, J. E.; Giudici, R. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 6877.
(98) Lee, H. M.; Chiu, P. L.; Hu, C.-H.; Lai, C.-L.; Chou, Y.-C. *J. Organomet. Chem.* **2005**, *690*, 403.
(99) Frøseth, M.; Netland, K. A.; Törnroos, K. W.; Dhindsa, A.; Tilset, M. *Dalton Trans.* **2005**, 1664.
(100) McGrandle, S.; Saunders, G. C. *J. Fluorine Chem.* **2005**, *126*, 451.
(101) Chen, H.-P.; Ku, R.-Z.; Liu, S. T. *J. Chin. Chem. Soc.* **2001**, *48*, 13.
(102) Liu, S.-T.; Reddy, K. R. *Chem. Soc. Rev.* **1999**, *28*, 315.
(103) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley & Sons: New York, 1999; pp 1089−1090.
(104) Chiu, P. L.; Lee, H. M. *Organometallics* **2005**, *24*, 1692.
(105) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.
(106) Emsley, J. *The Elements*, 3rd ed.; Oxford University Press: New York, 1998.
(107) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(108) Tulloch, A. A. D.; Winston, S.; Danopoulos, A. A.; Eastham, G.; Hursthouse, M. B. *Dalton* **2003**, 699.
(109) Pytkowicz, J.; Roland, S.; Mangeney, P.; Meyer, G.; Jutand, A. *J. Organomet. Chem.* **2003**, *678*, 166.
(110) Wang, H. M. J.; Vasam, C. S.; Tsai, T. Y. R.; Chen, S.-H.; Chang, A. H. H.; Lin, I. J. B. *Organometallics* **2005**, *24*, 486.
(111) Rivera, G.; Crabtree, R. H. *J. Mol. Catal. A: Chem.* **2004**, *222*, 59.
(112) Tulloch, A. A. D.; Danopoulos, A. A.; Kleinhenz, S.; Light, M. E.; Hursthouse, M. B.; Eastham, G. *Organometallics* **2001**, *20*, 2027.
(113) Hu, X.; Castro-Rodriguez, I.; Meyer, K. *Organometallics* **2003**, *22*, 3016.
(114) Kaur, H.; Zinn, F. K.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2004**, *23*, 1157.
(115) Arnold, P. L.; Rodden, M.; Davis, K. M.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2004**, 1612.
(116) Arnold, P. L.; Scarisbrick, A. C. *Orgaometallics* **2004**, *23*, 2519.
(117) Winston, S.; Stylianides, N.; Tulloch, A. A. D.; Wright, J. A.; Danopoulos, A. A. *Polyhedron* **2004**, *23*, 2813.
(118) Klasen, H. J. *Burns* **2000**, *26*, 117.
(119) Lansdown, A. B. G. *J. Wound Care* **2002**, *11*, 125.
(120) Bell, T. A.; Grayston, J. T.; Krohn, M. A.; Kronmal, R. A. *Pediatrics* **1993**, *92*, 755.
(121) Baenziger, N. C.; Struss, A. W. *Inorg. Chem.* **1976**, *15*, 1807.
(122) Melaiye, A.; Youngs, W. J. *Expert Opin. Ther. Pat.* **2005**, *15*, 125.
(123) Reneker, D. H.; Yarin, A. L.; Fong, H. Koombhongse, S. *J. Appl. Phys.* **2000**, *87*, 4531.
(124) Li, D.; Xia, Y. *Adv. Mater.* **2004**, *16*, 1151.

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