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Articles

Synthesis of Well-Defined *N*-Heterocyclic Carbene Silver(I) Complexes

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A series of *N*-heterocyclic carbene (NHC)AgCl complexes [NHC = SIMes (**1**), IPr (**2**), SIPr (**3**), IPrMe (**4**), IMe (**5**), ICy (**6**), IAd (**7**), IsB (**8**), IDD (**9**), and TPh (**10**)] have been synthesized through reaction of the imidazolium chloride salts with Ag$_2$O or by direct metalation of the corresponding imidazol-2-ylidene carbene in the presence of AgCl. All silver(I) complexes [(SIMes)AgCl] (**11**), [(IPr)AgCl] (**12**), [(SIPr)AgCl] (**13**), [(IPrMe)AgCl] (**14**), [(IMe)AgCl] (**15**), [(ICy)AgCl] (**16**), [(IAd)AgCl] (**17**), [(IsB)AgCl] (**18**), [(IDD)AgCl] (**19**), and [(TPh)AgCl] (**20**) have been spectroscopically and structurally characterized. The structure of these silver complexes is dependent on the halide and the solvent used for the synthesis. Adjusting these parameters has led to the previously reported complex, [(IMes)$_2$Ag]$^+$[AgCl$_2$]$^-$ (**21**), and to a new silver complex, [(IMes)$_2$Ag]$^+_2$[Ag$_4$I$_6$]$^{2-}$ (**22**).

Introduction

It is now widely accepted that the saga of *N*-heterocyclic carbene (NHC) chemistry began in 1968 when Ölefe[1] and Wanzlick[2] successfully isolated the first chromium and mercury *N*-heterocyclic carbene complexes. In 1991, Arduengo's seminal discovery of a stable *N*-heterocyclic carbene[3] led to incredible activity and development in the coordination chemistry of NHCs. With better sigma donor ability than most phosphines, NHCs strongly bind and stabilize transition metals,[4] leading to a wide variety of well-defined catalytic systems. NHC complexes of late transition metals especially those of groups 8, 9, and 10 have been employed to catalyze Heck reactions,[5] cross-coupling reactions (such as the Suzuki−Miyaura reaction[6]), olefin metathesis,[7] and hydrogenation[8] reactions, among the most significant. From group 11, copper- and gold-NHCs are known to catalyze a more limited number of organic transformations,[9,10] but silver-NHC complexes have been reported recently to behave as efficient catalysts

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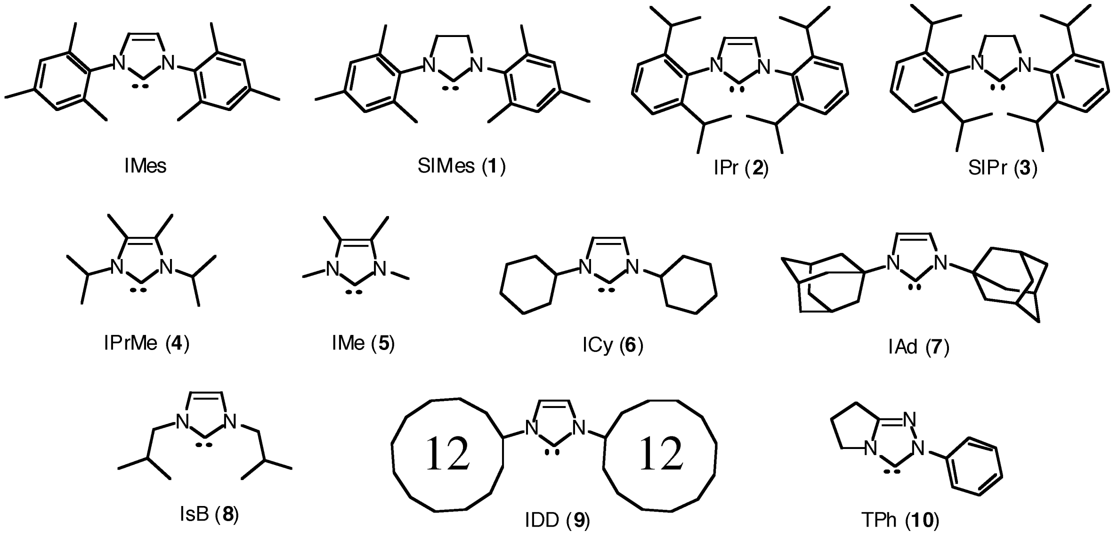

Figure 1. NHC ligands used in this study.

in transesterification reactions.[11] While tungsten-NHC complexes can be used as carbene transfer reagents,[12] silver-NHC compounds are the most popular complexes used for NHC transfer.[12,13] Their common use as transfer agents is due to their straightforward synthesis, usually circumventing the need for free NHC isolation, and the relative stability of the Ag-NHC complexes toward air and light.[12,15] NHC-silver complexes are known to adopt different architectures depending on the synthetic conditions employed. Most of the reported complexes are homoleptic with two carbene units bound to the silver in a linear fashion.[11−17] In the case of argentophilic interactions, some polymeric and bridged structures have been elucidated.[18,19] On the other hand, mono-carbene silver halides remain rare, with only a handful of reported examples.[20−22] We report here the synthesis of a series of two-coordinate NHC-silver(I) chloride complexes of general composition (NHC)AgCl. The NHC ligands used in the present study are shown in Figure 1 and are commonly used saturated and unsaturated ligands: (1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene) SIMes (**1**), (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) IPr (**2**), (1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene) SIPr (**3**), (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) IPrMe (**4**), (1,3,4,5-tetramethylimidazol-2-ylidene) IMe (**5**), (1,3-bis(cyclohexyl)imidazol-2-ylidene) ICy (**6**), (1,3-bis(adamantyl)imidazol-2-ylidene) IAd (**7**), (1,3-bis(isobutyl)imidazol-2-ylidene) IsB (**8**), and (1,3-bis(dodecyl)imidazol-2-ylidene) IDD (**9**), as well as the triazolium ligand (2,5,6,7-tetrahydro-2-phenyl-3H-pyrrolo[2,1-*c*]-1,2,4-triazol-3-ylidene) TPh (**10**). All new Ag(I)-NHC complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and X-ray diffraction.

Although the synthesis of the two-coordinate silver(I) chloride complex (IMes)AgCl[22] has been reported already, we noticed that the use of a more polar solvent favors the formation of $[(\text{IMes})_2\text{Ag}]^+[\text{AgCl}_2]^-$ (**21**). Finally, by studying the synthesis of (IMes)AgI in a polar solvent, we have obtained the unusual $[(\text{IMes})_2\text{Ag}]_2[\text{Ag}_4\text{I}_6]$ (**22**) complex.

Results and Discussion

Refluxing the imidazolium chloride salts SIMes·HCl (**1**), IPr·HCl (**2**), SI·Pr (**3**), ICy·HCl (**6**), IAd·HCl (**7**), IsB·HCl (**8**), and TPh·HCl (**10**) in dichloromethane (DCM) in the presence of a slight excess of Ag_2O yields complexes [(SIMes)AgCl] (**11**), [(IPr)AgCl] (**12**), [(SIPr)AgCl] (**13**), [(ICy)AgCl] (**16**), [(IAd)AgCl] (**17**), [(IsB)AgCl] (**18**), and [(TPh)AgCl] (**20**) according to eq 1:

$$2\text{NHC}\cdot\text{HCl} \xrightarrow[\text{Ag}_2\text{O}]{\text{DCM}} 2(\text{NHC})\text{AgCl} + \text{H}_2\text{O} \qquad (1)$$

Using the same conditions with the bulky salt IDD·HCl (**9**) leads to a mixture of 55% of the desired complex [(IDD)AgCl] (**19**) and 45% of the starting salt **9**. To increase the kinetics of the reaction, a solvent with a higher boiling point was selected, and after 12 h at reflux in THF, total conversion to **19** was obtained. It is noteworthy that contrary to the method described by Wang and Lin,[12] all syntheses can be carried out without exclusion of light with no deleterious effect on yields.

In anhydrous THF, under argon and in the dark, the free carbenes IPrMe (**4**) and IMe (**5**) are stirred overnight at room temperature in the presence of a slight excess of AgCl to yield complexes [(IPrMe)AgCl] (**14**) and

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Table 1. Chemical Shifts of the Carbenic Carbon in NMR for the (NHC)AgCl Complexes

complex	solvent[a]	δ (C−Ag) ppm	appearance of the signal	J^1($^{107-109}$Ag−^{13}C) Hz
(IMes)AgCl[22]	$CDCl_3$	185.0	doublet of doublets	270/234
(SIMes)AgCl (**11**)	$CDCl_3$	207.5	doublet of doublets	256/222
(IPr)AgCl (**12**)	$CDCl_3$	184.6	doublet of doublets	271/253
(SIPr)AgCl (**13**)	CD_2Cl_2	207.7	doublet of doublets	253/219
(IPrMe)AgCl] (**14**)	CD_2Cl_2	172.3	broad singlet	
(IMe)AgCl (**15**)	CD_2Cl_2	177.6	sharp singlet	
(ICy)AgCl (**16**)	$CDCl_3$	179.1	broad singlet	
(IAd)AgCl (**17**)	CD_2Cl_2	173.8	broad singlet	
(IsB)AgCl (**18**)	$CDCl_3$	179.8	sharp singlet	
(IDD)AgCl (**19**)	$CDCl_3$	177.8	broad doublet	unresolved
(TPh)AgCl (**20**)	$CDCl_3$	176.9	sharp singlet	

[a] Complexes partially soluble in $CDCl_3$ were fully solubilized in CD_2Cl_2.

[(IMe)AgCl] (**15**) and traces of metallic silver according to eq 2:[12]

$$\mathrm{NHC} \xrightarrow[\mathrm{THF}]{\mathrm{AgCl}} \mathrm{(NHC)AgCl} \qquad (2)$$

All complexes can be obtained in good yields in this manner with the notable exception of [(IMe)AgCl] (**15**). For this particular complex, and to a lesser extent for [(SIMes)AgCl] (**11**), the lower yields are due to the formation of a side-product. Separation of the desired complexes and the side-products is easily achieved by crystallization. Interestingly, when we examine the ^{1}H NMR spectrum of the side-products, we find similarities with spectra of [(IMe)$_2$Au]Cl and [(IMes)$_2$Au]Cl, two complexes that we have previously encountered while synthesizing a series of NHC gold(I) chloride complexes.[23] Usually homoleptic halide silver(I) carbene complexes have the formulation [Ag(NHC)$_2$]$^+$[AgX$_2$]$^-$,[11,12,15] and we propose the formulation [Ag(IMe)$_2$]$^+$[AgCl$_2$]$^-$ and [Ag(SIMes)$_2$]$^+$[AgCl$_2$]$^-$ for both side-products. While complexes **11**, **12**, **13**, **15**, **16**, and **20** display high stability toward light and air, complexes **14**, **17**, **18**, and **19** slowly decompose within a week to a month under air and light. Once again, ^{1}H NMR spectra of the decomposed products indicate a mixture of (NHC)AgCl and [Ag(NHC)$_2$]$^+$[AgX$_2$]$^-$.

The ^{1}H NMR spectra of complexes [(SIMes)AgCl] (**11**) and [(SIPr)AgCl] (**13**) give a single resonance at 4.00 and 4.07 ppm, respectively, for the saturated imidazole ring. [(IPrMe)AgCl] (**14**) and [(IMe)AgCl] (**15**) give a single high-field resonance at 2.16 and 2.12 ppm, respectively, for the methyl group on the unsaturated imidazole ring and the corresponding signal for the *N*-alkyl chains. [(IPr)AgCl] (**12**), [(ICy)AgCl] (**16**), [(IAd)AgCl] (**17**), [(IsB)AgCl] (**18**), and [(IDD)AgCl] (**19**) display a single resonance signal at low field between 6.95 and 7.21 ppm for the unsaturated imidazole ring and the corresponding signals for the *N*-aryl and *N*-alkyl chains. The ^{13}C NMR spectra give a low-field signal, attributed to the carbenic carbene at 207 ppm for both saturated complexes **11** and **13**, while unsaturated complexes **12** and **14**−**20** exhibit a signal between 173 and 185 ppm (Table 1). [(SIMes)AgCl] (**11**) gives a carbenic signal at 207.5 ppm as a doublet of doublets with an observable coupling between carbon and silver of $J^1(^{13}\mathrm{C}-^{109}\mathrm{Ag}) = 256$ Hz and $J^1(^{13}\mathrm{C}-^{107}\mathrm{Ag}) = 222$ Hz. [(SIPr)AgCl] (**13**) gives a signal at 207.7 ppm as a doublet of doublets with a coupling between silver and carbon ($J^1(^{13}\mathrm{C}-^{109}\mathrm{Ag}) = 271$ Hz and $J^1(^{13}\mathrm{C}-^{107}\mathrm{Ag}) = 253$ Hz). The similar values in chemical shift for **11** and **13** indicate no significant difference in the electronic donor properties existing for the saturated carbenes (SIMes and SIPr) in these silver systems. Nevertheless, both signals are 20 ppm downfield from that of the saturated complexes, confirming that saturated complexes exhibit a better electron-donating ability to the metal in the present system.[24] For the unsaturated NHCs, *N*,*N*-bis(alkyl)imidazolylidenes are generally considered better sigma donors than *N*,*N*-bis(aryl)-imidazolylidenes; however in the present silver(I) complexes, this trend is reversed. Surprisingly, (IPr)AgCl (**12**) and (IMes)AgCl[22] display the highest downfield signal for the unsaturated series. This signal appears at 184.6 ppm as a doublet of doublets with an observable coupling between carbon and silver of $J^1(^{13}\mathrm{C}-^{109}\mathrm{Ag}) = 253$ Hz and $J^1(^{13}\mathrm{C}-^{107}\mathrm{Ag}) = 219$ Hz. Usually complexes exhibiting strong coupling are known to exhibit no exchange or very slow exchange[12,24] (on the NMR time scale) of their carbene moieties with the silver centers and are poor carbene transfer agents for transmetalation.[25] This quasi-static behavior in solution might also be correlated to the downfield signal of the carbenic carbon, proving a stronger donation to the silver, and indicates a stronger Ag−C bond.[24] This stronger bond decreases the lability of the carbene moieties and inhibits the formation of [(NHC)$_2$Ag]$^+$, preventing the formation of an equilibrium between (NHC)AgCl and [(NHC)$_2$Ag]$^+$.[24] (IDD)AgCl (**19**) displays a broad doublet at 177.8 ppm, due to a weak coupling between carbon and silver, which is characteristic of a slightly faster exchange between IDD moieties and the silver centers. The upper field value of the signal shows that the IDD carbene does not exhibit strong donating abilities and the exchange should be faster.[24] We believe that this slow dynamic behavior is not due to electronic considerations but to the steric bulk of the dodecyl groups. Indeed, we have noticed that the formation of (IDD)-AgCl (**19**) was slower and under synthetic conditions required a higher reaction temperature, possibly due to the difficulty of the silver center to reach the carbenic center, which is protected by two large dodecyl groups. It is clear that having four dodecyl groups around the same silver center is very unlikely due to the overwhelming steric hindrance of such a situation. (IPrMe)-

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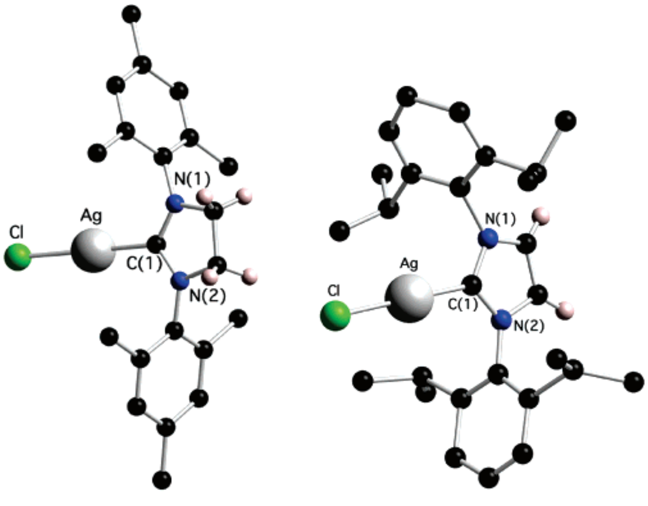
Table 2. Selected Bond Lengths and Angles for the (NHC)AgCl Complexes

complex	Ag–C (Å)	Ag–Cl (Å)	Ag⋯Ag (Å)	C–Ag–Cl (deg)
(SIMes)AgCl (**11**)	2.0832(19)	2.3358(5)		173.70(6)
(IPr)AgCl (**12**)	2.056(6)	2.316(17)		175.2(2)
(SIPr)AgCl (**13**)	2.081(9)	2.320(2)		173.3(2)
(IPrMe)AgCl (**14**)	2.087(3)	2.3184(8)		180.00(9)
(IMe)AgCl (**15**)	2.091(2)	2.3608(7)	3.0673(3)	172.56(7)
	2.077(2)	2.3382(7)		168.98(7)
	2.091(5)	2.3335(14)	3.0650(6)	170.06(15)
(ICy)AgCl (**16**)	2.075(6)	2.3290(15)	3.0181(6)	177.46(16)
	2.096(5)	2.3593(14)		166.27(16)
	2.085(5)	2.3293(14)		170.91(15)
(IAd)AgCl (**17**)	2.094(6)	21350(16)		176.08(14)
	2.073(17)	2.314(5)	3.108(2)	175.9(5)
(IsB)AgCl (**18**)	2.087(17)	2.332(5)	3.124(2)	178.7(5)
	2.060(19)	2.324(5)		178.1(6)
	2.067(18)	2.359(5)		176.9(5)
(IDD)AgCl (**19**)	2.067(4)	2.3200(9)		174.96(11)
(TPh)AgCl (**20**)	2.121(1)	2.4458(6)	3.0242(2)	150.34(6)
	2.105(2)	2.7978(6)	3.0752(2)	109.61(6)
	2.089(2)	2.4045(6)	Cl–Ag–Cl (deg)	C–Ag–C (deg)
		2.3753(6)	102.177(19)	169.51(9)
		2.8685(6)	96.159(18)	Ag–Ag–Ag (deg)
				147.295(7)

AgCl (**14**), (ICy)AgCl (**16**), and (IAd)AgCl (**17**) display signals at 172.3, 179.1, and 173.8 ppm, respectively, as broad singlets characteristic of a slow exchange between the carbene moieties and the silver centers.[17,24] This exchange is nevertheless faster than in the case of (IDD)AgCl (**19**). While the signal of (ICy)AgCl (**16**) is the most downfield (5 ppm from (IPr)AgCl (**12**)) and the IAd carbene leads to strong steric hindrance around the silver, the absence of coupling shows that these two parameters provide a small contribution, indicating a significantly slower exchange for these two complexes. (IMe)AgCl (**15**) and (IsB)AgCl (**18**) exhibit a ^{13}C NMR signal at 177.6 and 179.8 ppm, respectively, as two sharp singlets characteristic of a fast exchange of the carbene moieties[17,24] with the silver centers. This rapid equilibrium must be facilitated by the relatively small hindrance of both carbene moieties. The triazolium complex (TPh)AgCl (**20**) displays a ^{13}C NMR signal at 176.9 ppm, illustrating an average donating ability similar to the previously discussed unsaturated NHC-silver complexes. The signal is a sharp singlet, indicating a fast exchange of the triazolium moieties with the silver centers. The carbenic carbons of these new silver(I) complexes display resonances between 172 and 208 ppm, and these are good indicators of the donating properties of the carbene to silver. While some silver(I) carbene halide complexes are known to establish a dynamic equilibrium between (NHC)AgCl and $[(NHC)_2Ag]^+$,[12,17,24] a routine ^{13}C NMR can give specific indications about the rate of the exchange indicated by the pattern associated with the carbenic signal. For all complexes we have examined, steric and/or electronic factors lead to a wide range of exchange rates, as gauged by NMR signal positions and patterns.

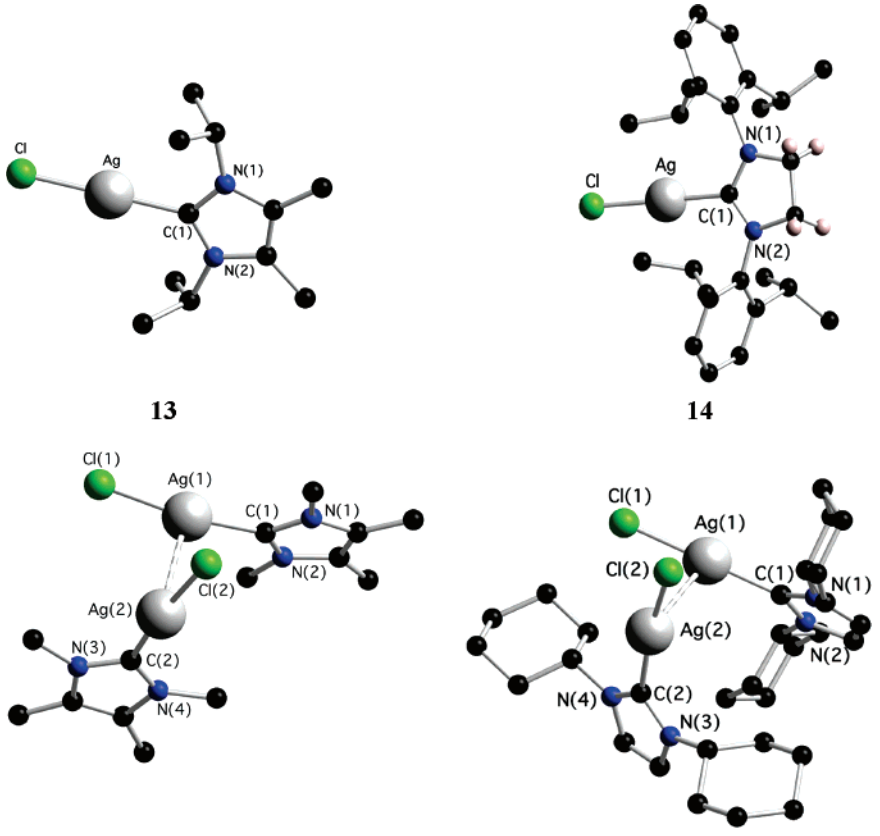
While NMR data give specific information about the complexes and their dynamic properties in solution, X-ray diffraction was used to unambiguously determine the structure of NHC-Ag-containing complexes in the solid state. Selected bond distances and bond angles are given in Table 2.

All complexes, with the exception of (TPh)AgCl (**20**), have a two-coordinate silver(I) atom in a close linear environment with a C–Ag–Cl bond close to 180°. All C–Ag bond distances are in the range 2.056–2.094 Å, which is in line with other silver bis- or mono-carbene complexes previously reported.[12,14,20,22,24,26] As expected, the silver–carbon bonds are longer than the gold–carbene bonds reported for analogous (NHC)Au(I)Cl complexes (bond lengths between 1.987 and 1.999 Å).[23] All Ag–Cl bond distances are between 2.332 and 2.360 Å, which is in the range of other silver(I) chloride complexes reported.[20,22] None of the C–Ag bond lengths are shortened with a simultaneous elongation of the Ag–Cl. The absence of a *trans*-effect for the complexes does not allow any comparisons of the electron-donating abilities for different carbene moieties. It is noteworthy that the shorter length of the Ag–C (2.057 Å) bond and the more downfield value of the carbenic signal (184.6 ppm) in (IPr)AgCl (**12**) hint at the better donating properties of the carbene IPr over other unsaturated carbene ligands. Complexes **11**, **12**, **13**, **14**, **17**, and **19** are monomeric with no evident argentophilic (Ag(I)⋯Ag(I)) interactions (Figures 1, 2, and 3). Indeed, all distances between silver(I) centers are greater than 3.44 Å, the sum of twice the van der Waals radius of Ag(I).[12] (IMe)AgCl (**15**) has two molecules in the asym-



11 **12**

Figure 2. Ball-and-stick representations of complexes (SIMes)AgCl (**11**) and (IPr)AgCl (**12**). Most hydrogen atoms have been omitted for clarity.



13 **14**

15 **16**

Figure 3. Ball-and-stick representations of complexes (SIPr)AgCl (**13**), (IPrMe)AgCl (**14**), (IMe)AgCl (**15**), and (ICy)AgCl (**16**). Most hydrogen atoms have been omitted for clarity.

metric unit and forms a dimer linked by argentophilic interactions with a Ag(I)···Ag(I) distance of 3.067 Å (Figure 2). (ICy)AgCl (**16**) and (IsB)AgCl (**18**) have four molecules in the asymmetric unit and display a dimeric structure with Ag(I)···Ag(I) distances between dimer centers longer than 3.44 Å.[12] For each dimer, two molecules of the complex are linked by argentophilic interactions with two Ag(I)···Ag(I) distances of 3.065 and 3.108 Å for (ICy)AgCl (**16**) and 3.108 and 3.124 Å for (IsB)AgCl (**18**) (Figure 3). (TPh)AgCl (**20**) has a unique structure where (TPh)AgCl coexists with $[(TPh)_2Ag]^+[AgCl_2]^-$ in the asymmetric unit. $[(TPh)_2Ag]^+$ is linked to (TPh)AgCl by an argentophilic interaction with a Ag(I)···Ag(I) distance of 3.042 Å to form a trimer. $[(TPh)_2Ag]^+$ is also linked to $[AgCl_2]^-$ by argentophilic interactions with a Ag(I)···Ag(I) distance of 3.075 Å, while $[AgCl_2]^-$ is linked to the silver and the chloride of (TPh)AgCl to form a bridge. In fact, the structure can also be envisaged as a polymer with each $[(TPh)_2Ag]^+$ unit bound by $[(TPh)Ag-(\mu Cl)_2-AgCl]^-$ units (Figures 4 and 5). It is interesting to note that in the bridged $[(TPh)Ag-(\mu Cl)_2-AgCl]^-$ moiety, even though there is no direct argentophilic interaction, a Ag(I)···Ag(I) distance of 3.510 Å can induce a preferential orientation in the packing of the structure.[19] For (TPh)AgCl, the Ag−C distance is slightly longer than others, with a value of 2.121 Å, but is reasonable if compared with the 2.772 Å of the silver(I) carbene described by Calano et al.[18] The two Ag−Cl bond distances of the bridge have values of 2.798 and 2.869 Å, which are marginally longer than the 2.535 Å value found for $[AgCl_2]^-$. The solid-state structure of (TPh)AgCl (**20**) confirms the sharp singlet found in ^{13}C NMR for the carbenic carbon, and it also justifies our expectations of a dynamic equilibrium between (TPh)AgCl and $[(TPh)_2Ag]^+[AgCl_2]^-$ in solution. For all complexes, no agostic interactions between silver−hydrogen or even silver−methyl groups have been observed as described in the silver(I) phosphine carborane complexes synthesized by Weller et al.,[27] with Ag−H and Ag−C(H_3) distances greater than 2.49 and 3.29 Å, respectively.[27]

To improve the yields of (NHC)AgCl complexes obtained, especially for (SIMes)AgCl (**11**) and (IMe)AgCl (**15**), the effect of the solvent polarity used in the synthesis was studied for the already well-defined (IMes)AgCl complex.[22] Three different solvents, chloroform, acetonitrile, and dimethyl sulfoxide, with a gradient of polarity, are used under similar experimental conditions. When NMR characterization of the crude reactions is carried out, a side-product is observed and its NMR spectrum is consistent with the previously reported bis-NHC $[(IMes)_2Ag]^+[AgCl_2]^-$ (**21**) complex.[11] After separation by crystallization, X-ray studies of the crystals grown confirmed that the side-product was

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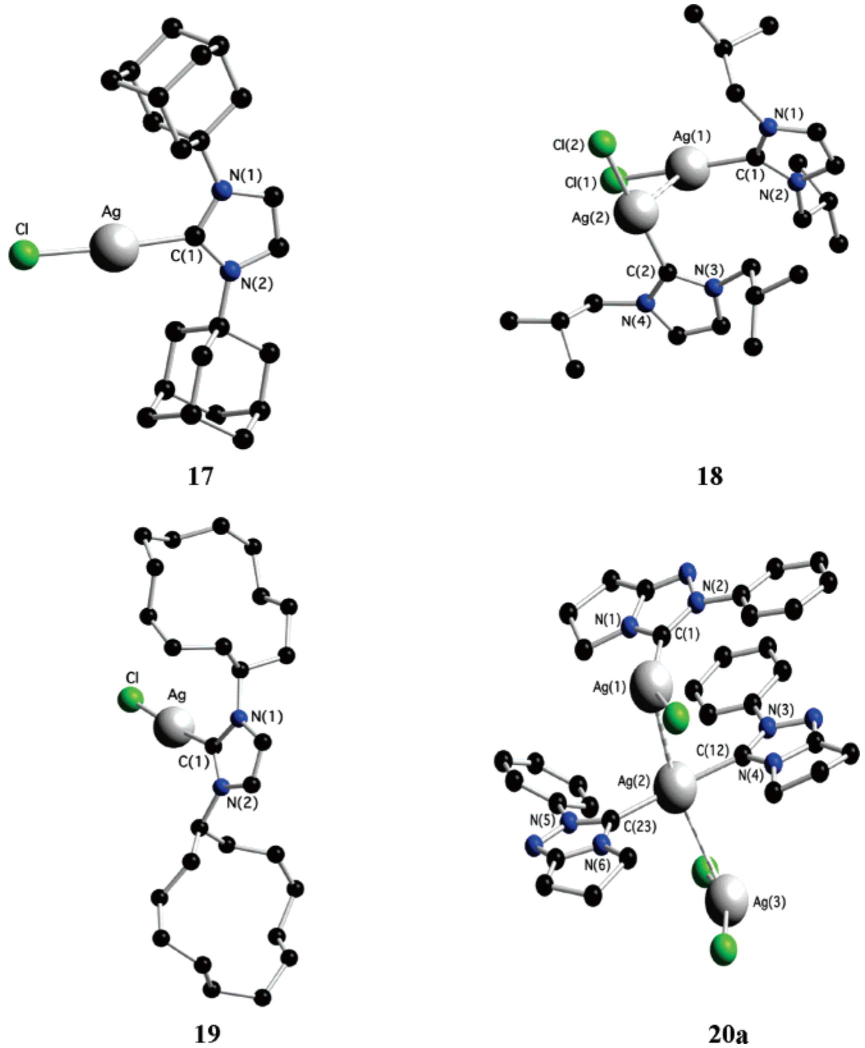
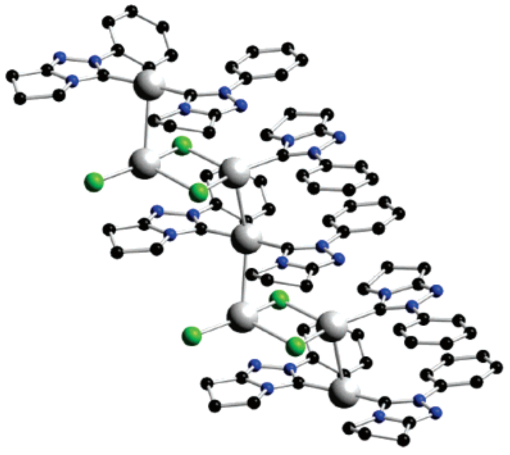


17 **18**

19 **20a**

Figure 4. Ball-and-stick representations of complexes (IAd)AgCl (**17**), (IsB)AgCl (**18**), (IDD)AgCl (**19**), and (TPh)AgCl as a trimer (**20a**). Hydrogen atoms have been omitted for clarity.



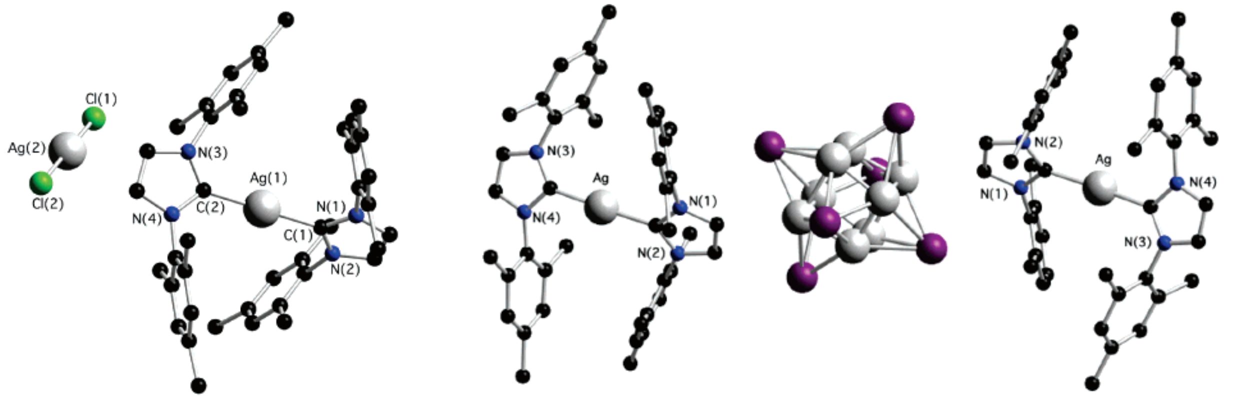
20b

Figure 5. Ball-and-stick representations of complex (TPh)AgCl as a bridged Ag−(μCl$_2$)−Ag polymer (**20b**). Hydrogen atoms have been omitted for clarity.

$[(IMes)_2Ag]^+[AgCl_2]^-$ (**21**) (Figure 6) and confirmed our hypothesis for the formation of $[(SIMes)_2Ag]^+[AgCl_2]^-$ and $[(IMe)_2Ag]^+[AgCl_2]^-$ as side-products from the syntheses of [(SIMes)AgCl] (**11**) and [(IMe)AgCl] (**15**). The three assays show that increasing the polarity of the solvent leads to an increase in the amount of bis-carbene complex formed (Table 3). It is reasonable to state that polar solvents must stabilize the ionic $[(IMes)_2Ag]^+$ form better than nonpolar solvents and might shift the equilibrium $\{(IMes)AgCl/[(IMes)_2Ag]^+\}$ toward the bis-NHC-Ag complex.

The ^{1}H NMR spectrum of **21** displays a single resonance at 7.23 ppm for the unsaturated imidazole ring and the corresponding signals for the *N*-mesityl groups.[11] The ^{13}C NMR spectrum does not exhibit any signal between 160 and 200 ppm, an observation also made by Hedrick et al.[11] Solid-state structural data showed a two-coordinate silver(I) atom in a linear environment with a C−Ag−C angle of 180°. The Ag−C bond distances are 2.066 and 2.084 Å, while both Ag−Cl bond distances are 2.534 Å (Table 4). All these values are in good agreement with the other bis-carbene complexes previously reported.[12,14,26] There is one cation $[(IMes)_2Ag]^+$ and one anion $[AgCl_2]^-$ present in the asymmetric unit. This complex is monomeric with no argentophilic interactions and no Ag−(μCl$_2$)−Ag bridging present, with the minimal Ag(I)···Ag(I) distance being 6.397 Å (Figure 6).

We also attempted to synthesize the complex (IMes)-AgI in acetonitrile to investigate the effect of the halide and the solvent polarity on the structure of the complex. We anticipated a mixture of mono- and bis-carbene. The



21 **22**

Figure 6. Ball-and-stick representations of complexes $[(IMes)_2Ag]^+[AgCl_2]^-$ (**21**) and $[(IMes)_2Ag]^+{}_2[Ag_4I_6]^{2-}$ (**22**). Hydrogen atoms have been omitted for clarity.

Table 3. Product Distribution of $[(IMes)_2Ag]^+[AgCl_2]^-$ and (IMes)AgCl

solvent (dielectric constant)[28]	$[Ag(IMes)_2]^+[AgCl_2]^-$	(IMes)AgCl
chloroform (4.2)	15%	85%
acetonitrile (37.5)	25%	75%
dimethyl sulfoxide (46.7)	34%	66%

^{1}H NMR and the ^{13}C NMR spectra of the reaction crude matched those of $[(IMes)_2Ag]^+[AgCl_2]^-$ (**21**), leading us to conclude that only the bis-NHC complex **22** is formed in acetonitrile. The fact that Zhang et al. have reported a polymeric mono-carbene silver(I) iodide, without any trace of bis-carbene, in nonpolar dichloromethane[19] leads us to believe that polarity of the solvent must be the dominating factor in directing the structure adopted by an iodide silver complex between mono- and bis-carbene. X-ray studies confirm that the silver(I) atom is surrounded by two carbon atoms in near linear environment with a C−Ag−C bond angle of 180°. There are two $[(IMes)_2Ag]^+$ cations and one $[Ag_4I_6]^{2-}$ anion in the asymmetric unit, leading to a $[(IMes)_2Ag]_2[Ag_4I_6]$ formulation for **22**. This complex is monomeric with no argentophilic interactions (Figure 5). The most surprising feature comes from the massive octahedral anion $[Ag_4I_6]^{2-}$ cluster. Inside this cage, the Ag(I)···Ag(I) distances are between 2.0915 and 3.1453 Å with half of the possible coordination site occupied by the silver anion and the Ag−I distances are between 2.7052 and 2.8507 Å (Table 4). The structure is centrosymmetric, with an inversion center located at the origin of the octahedron. This remarkable structure is the first silver halide complex reported with a general formula of $[(NHC)_2Ag]^+{}_2[Ag_4X_6]^{2-}$.

Conclusion

We report the synthesis of 10 new silver monocarbene complexes. Their straightforward synthesis can be accomplished by simple reaction of an imidazolium chloride salt with silver oxide or by reaction of a free NHC with silver chloride. The NMR and crystallographic data do not permit unambiguous determinations of electronic differences between the various NHC-Ag moieties as a function of NHC. We have observed a dynamic equilibrium between (NHC)AgCl and $[(NHC)_2Ag]^+[AgCl_2]^-$ species in solution, as gauged by a simple analysis of the ^{13}C NMR spectrum. It has also been observed that (TPh)AgCl (**20**) exhibits both forms (mono and bis carbene) in the solid state. In addition, by increasing the solvent polarity, formation of the bis-NHC complex can be favored. This trend looks more pronounced with the more easily polarizable iodide than with the harder chloride, allowing the synthesis of the first $[(NHC)_2Ag]^+{}_2[Ag_4X_6]^{2-}$ (**22**) complex. Determination of catalytic activity of this new series of well-defined silver-NHC complexes in a number of organic transformations is presently underway.

Experimental Section

General Considerations. All reactions using an imidazolium salt as starting material were carried out in aerobic condition. All reactions using a free carbene as starting material were carried out using standard Schlenk techniques under an atmosphere of dry argon or in a MBraun glovebox containing dry argon and less than 1 ppm oxygen. Anhydrous solvents were either distilled from appropriate drying agents or purchased from Aldrich and degassed prior to use by purging with dry argon and kept over molecular sieves.

Solvents for NMR spectroscopy were degassed with argon and dried over molecular sieves. NMR spectra were collected on a 400 MHz Varian Gemini spectrometer. Elemental analyses were performed by Robertson Microlit Labs. Carbene ligands **1**−**10** were synthesized following literature procedures.[29,30]

Synthesis of (SIMes)AgCl (11). A 50 mL flask was charged with SIMes·HCl (750 mg, 2.19 mmol) and 15 mL of dichloromethane. To this solution was added silver(I) oxide (583 mg, 2.52 mmol). The resulting solution was refluxed for 12 h, then filtered over Celite, and the filtrate was reduced to 10 mL. The solution was cooled to 0 °C, and heptane was slowly added until white crystals appeared. The solid was filtered, washed with pentane (10 mL), and dried under vacuum. Yield: 699 mg (71%). ^{1}H NMR ($CDCl_3$): δ (ppm) 6.95 (s, 4H, C*H*-aromatic), 4.00 (s, 4H, C*H$_2$*-imidazole), 2.30 (s, 12H, C*H$_3$*), 2.29 (s, 6H, C*H$_3$*). ^{13}C NMR (CD_2Cl_2): δ (ppm) 207.5 (dd, $J^1(^{109}Ag, ^{13}C) = 256$ Hz, $J^1(^{107}Ag, ^{13}C) = 222$ Hz, *C*-carbene), 139.0 (s, *C*H-aromatic), 135.7 (s, *C*H-aromatic), 135.3 (s, *C*H-aromatic), 130.0 (s, *C*H-aromatic), 51.3 (s, *C*H$_2$-imidazole), 21.2 (s, *C*H$_3$), 18.1 (s, *C*H$_3$). Anal. Calcd for $C_{21}H_{26}N_2AgCl$ (450.77): C, 55.96; H, 5.77; N, 6.21. Found: C, 56.27; H, 5.94; N, 6.08.

Synthesis of (IPr)AgCl (12). A 50 mL flask was charged with IPr·HCl (1 g, 2.35 mmol) and 15 mL of dichloromethane. To this solution was added silver(I) oxide (328 mg, 1.41 mmol). The resulting solution was stirred at room temperature for 12 h, then filtered over Celite, and the filtrate was reduced to 10 mL. Pentane (30 mL) was added to the solution to precipitate a white solid. The solid was washed further with pentane (3 × 10 mL) and dried under vacuum to afford a white powder. Yield: 2.160 g (88%). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.50 (m, 2H, C*H*-aromatic), 7.30 (m, 4H, C*H*-aromatic), 7.21 (s, 2H,

Table 4. Selected Bond Lengths and Angles for [(IMes)$_2$Ag]$^+{}_2$ Complexes

complex	Ag–C (Å)	Ag–Cl/Ag–I (Å)	C–Ag–C (deg)
[(IMes)$_2$Ag]$^+$[AgCl$_2$]$^-$ (**21**)	2.066(5) 2.084(5)	2.534(5)	180.000(1)
[(IMes)$_2$Ag]$^+{}_2$[Ag$_4$I$_6$]$^{2-}$ (**22**)	2.079(5) 2.082(5)	2.7556(14)–2.7774(14) 2.8121(14)–2.7212(12) 2.7468(12)–2.7751(13) 2.7157(13)–2.7627(14) 2.8507(14)–2.7025(14) 2.7175(14)–2.8397(14) 2.7052(14)–2.7627(14)	172.5(2)

C*H*-imidazole), 2.54 (septet, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 1.28 (d, *J* = 6.8 Hz, 12H, CH (C*H*$_3$)$_2$), 1.22 (d, *J* = 6.8 Hz, 12H, CH (C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$): δ (ppm) 184.6 (dd, J^1(^{109}Ag, ^{13}C) = 271 Hz, J^1(^{107}Ag, ^{13}C) = 235 Hz, *C*-carbene), 145.6 (s, *C*H-aromatic), 130.8 (s, *C*H-aromatic), 124.4 (s, *C*H-aromatic), 123.7 (s, *C*H-aromatic), 123.6 (s, *C*H-imidazole), 28.7 (s, *C*H (CH$_3$)$_2$), 24.7 (s, CH (*C*H$_3$)$_2$), 24.0 (s, CH (*C*H$_3$)$_2$). Anal. Calcd for $C_{27}H_{36}N_2AgCl$ (531.59): C, 61.00; H, 6.77; N, 5.27. Found: C, 61.20; H, 7.05; N, 5.22.

Synthesis of (SIPr)AgCl (13). A 50 mL flask was charged with SIPr·HCl (1 g, 2.60 mmol) and 15 mL of dichloromethane, to which was added silver(I) oxide (356 mg, 1.61 mmol). The resulting solution was stirred at room temperature for 12 h, then filtered over Celite, and the filtrate was reduced to 10 mL. Pentane (30 mL) was added to immediately precipitate a white solid. The solid was further washed with pentane (3 × 10 mL) and dried under vacuum to afford a white powder. Yield: 1.019 g (74%). ^{1}H NMR (CDCl$_3$): δ (ppm) 7.41 (m, 2H, C*H*-aromatic), 7.25 (m, 4H, C*H*-aromatic), 4.07 (s, 4H, C*H*$_2$-imidazole), 3.06 (septet, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 1.35 (d, *J* = 6.8 Hz, 12H, CH (C*H*$_3$)$_2$), 1.35 (d, *J* = 6.8 Hz, 12H, CH (C*H*$_3$)$_2$). ^{13}C NMR (CD$_2$Cl$_2$): δ (ppm) 207.7 (dd, J^1(^{109}Ag, ^{13}C) = 253 Hz, J^1(^{107}Ag, ^{13}C = 219 Hz, *C*-carbene), 147.0 (s, *C*H-aromatic), 134.9 (s, *C*H-aromatic), 130.1 (s, *C*H-aromatic), 124.8 (s, *C*H-aromatic), 54.1 (s, *C*H$_2$-imidazole), 29.0 (s, *C*H (CH$_3$)$_2$), 25.3 (s, CH (*C*H$_3$)$_2$), 24.0 (s, CH (*C*H$_3$)$_2$). Anal. Calcd for $C_{27}H_{38}N_2AgCl$ (533.59): C, 60.77; H, 7.12; N, 5.25. Found: C, 60.64; H, 7.38; N, 5.04.

Synthesis of (IPrMe)AgCl (14). In a glovebox, a 50 mL Schenk flask was charged with 120 mg (0.66 mmol) of IPrMe and 10 mL of THF, and then 143 mg (0.14 mmol) of silver(I) chloride was added. The resulting solution was kept in the dark and stirred at room temperature for 12 h. The remaining steps were then carried out in air. The solution was filtered over Celite and the filtrate reduced to 10 mL. Pentane (30 mL) was added to the solution, resulting in an immediate precipitation of a white solid. The solid was further washed with pentane (2 × 10 mL) and dried under vacuum, to afford a white powder. Yield: 63 mg (71%). ^{1}H NMR (CDCl$_3$): δ (ppm) 4.55 (septet, *J* = 6.9 Hz, 2H, NC*H*-isopropyl), 2.16 (s, 6H, C*H*$_3$-imidazole), 1.56 (d, *J* = 6.9 Hz, 12H, CH (C*H*$_3$)$_2$). ^{13}C NMR (CD$_2$Cl$_2$): δ (ppm) 172.3 (s, *C*-carbene), 124.9 (s, *C*H-imidazole), 51.5 (s, *C*H (CH$_3$)$_2$), 23.9 (s, CH (*C*H$_3$)$_2$), 9.5 (s, *C*H$_3$-imidazole). Anal. Calcd for $C_{11}H_{20}N_2AgCl$ (323.43): C, 40.85; H, 6.18; N, 8.66. Found: C, 40.96; H, 5.92; N, 8.57.

Synthesis of (IMe)AgCl (15). In a glovebox, a 50 mL Schenk flask was charged with 100 mg (0.81 mmol) of IMe and 10 mL of THF, and then 230 mg (0.16 mmol) of silver(I) chloride was added. The resulting solution was kept in the dark and stirred at room temperature for 12 h. The remaining steps were then carried out in air. The solution was cooled to −78 °C and rapidly filtered over Celite. The Celite was rinsed first with cold THF. The clear green solution obtained was discarded. Then the Celite was washed with 10 mL of dichloromethane, resulting in a bright yellow solution. Heptane was slowly added until the appearance of yellow clear crystals. The solids were filtered off, rinsed with pentane, and dried under vacuum. Yield: 80 mg (28%). ^{1}H NMR (CDCl$_3$): δ (ppm) 3.65 (s, 6H, NC*H*$_3$), 2.12 (s, 6H, C*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$): δ (ppm) 177.5 (s, *C*-carbene), 125.8 (s, *C*H-imidazole), 36.5 (s, *C*H$_3$), 9.2 (s, *C*H$_3$). Anal. Calcd for $C_7H_{12}N_2AgCl$ (267.69): C, 31.43; H, 4.48; N, 10.46. Found: C, 31.21; H, 4.38; N, 10.19.

Synthesis of (ICy)AgCl (16). A method of preparation similar to that used for compound (SIMes)AgCl (**11**) gave a white solid. Yield: 754 mg (72%). ^{1}H NMR (CDCl$_3$): δ (ppm) 6.98 (s, 2H, C*H*-imidazole), 4.22 (m, 2H, NC*H*-cyclohexyl), 2.02 (m, 4H, C*H*$_2$), 1.87 (m, 4H, C*H*$_2$), 1.74 (m, 2H, C*H*$_2$), 1.58 (m, 4H, C*H*$_2$), 1.43 (m, 4H, C*H*$_2$), 1.19 (m, 2H, C*H*). ^{13}C NMR (CDCl$_3$): δ (ppm) 179.1 (br s, *C*-carbene), 119.9 (s, *C*H-imidazole), 63.9 (s, N*C*H-cyclohexyl), 36.6 (s, *C*H$_2$), 27.5 (s, *C*H$_2$), 27.2 (s, *C*H$_2$). Anal. Calcd for $C_{15}H_{24}N_2AgCl$ (375.42): C, 47.99; H, 6.39; N, 7.46. Found: C, 48.17; H, 6.56; N, 7.40.

Synthesis of (IAd)AgCl (17). A 50 mL flask was charged with IAd·HCl (300 mg, 0.81 mmol) and 10 mL of dichloromethane, to which was added silver(I) oxide (112 mg, 0.48 mmol). The resulting solution was refluxed for 12 h, then filtered over Celite, and the filtrate was reduced to 5 mL. The solution was cooled to 0 °C, and pentane was slowly added until the appearance of white crystals. The solid was filtered off, washed with pentane (3 × 5 mL), and dried under vacuum to afford a white powder. Yield: 699 mg (71%). ^{1}H NMR (CD$_2$Cl$_2$): δ (ppm) 7.19 (s, 2H, C*H*-imidazole), 2.35–22 (br m, 20H, adamantyl), 1.75 (m, 10H, C*H*$_2$-adamantyl). ^{13}C NMR (CD$_2$Cl$_2$): δ (ppm) 173.8 (br s, *C*-carbene), 116.3 (s, *C*H-imidazole), 58.2 (s, N*C*H-adamantyl), 44.9 (s, *C*H$_2$), 36.0 (s, *C*H$_2$), 30.2 (s, *C*H$_2$). Anal. Calcd for $C_{23}H_{32}N_2AgCl$ (478.92): C, 57.68; H, 6.68; N, 5.85. Found: C, 57.88; H, 6.82; N, 5.59.

Synthesis of (IsB)AgCl (18). A method of preparation similar to that used for compound (SIMes)AgCl (**11**) gave a white solid. Yield: 838 mg (75%). ^{1}H NMR (CDCl$_3$): δ (ppm) 6.95 (s, 2H, *C*H-imidazole), 3.88 (d, *J* = 7.3 Hz, 4H, *CH*$_2$), 2.12 (m, 2H, *CH*), 0.91 (d, *J* = 6.3 Hz, 12H, *CH*$_3$). ^{13}C NMR (CDCl$_3$): δ (ppm) 179.3 (s, *C*-carbene), 121.6 (s, *C*H-imidazole), 53.4 (s, *C*H$_2$), 30.5 (s, *C*H), 20.0 (s, *C*H$_3$). Anal. Calcd for $C_{11}H_{20}N_2AgCl$ (323.39): C, 40.85; H, 6.18; N, 8.66. Found: C, 41.12; H, 6.34; N, 8.60.

Synthesis of (IDD)AgCl (19). A 50 mL flask was charged with IDD·HCl (500 mg, 1.15 mmol) and 10 mL of THF, to which was added silver(I) oxide (305 mg, 1.32 mmol). The resulting solution was stirred at reflux for 16 h, then filtered over Celite, and the filtrate was reduced to 5 mL. The solution was cooled to −40 °C, and cold pentane was slowly added until the appearance of a white precipitate. The solid was filtered off, washed with cold pentane (10 mL), and dried under vacuum. Yield: 415 mg (67%). ^{1}H NMR (CDCl$_3$): δ (ppm) 6.96 (s, 2H, C*H*-imidazole), 4.52 (m, 2H, NC*H*-cyclododecyl), 2.04 (m, 4H, C*H*$_2$), 1.69 (m, 4H, C*H*$_2$), 1.55–1.27 (m, 36H, C*H*$_2$). ^{13}C NMR (CDCl$_3$): (ppm) δ 177.8 (br d, *C*-carbene), 118.6 (s, *C*H-imidazole), 59.0 (s, N*C*H-cyclododecyl), 31.7 (s, *C*H$_2$), 23.8 (s, *C*H$_2$), 23.7 (s, *C*H$_2$), 23.6 (s, *C*H$_2$), 23.5 (s, *C*H$_2$), 21.8 (s, *C*H$_2$). Anal. Calcd for $C_{27}H_{48}N_2AgCl$ (543.43): C, 59.67; H, 8.83; N, 5.15. Found: C, 59.46; H, 8.71; N, 4.94.

Synthesis of (TPh)AgCl (20). A method of preparation similar to that used for compound (IPr)AgCl (**12**) gave a white solid. Yield: 590 mg (82%). ^{1}H NMR (CDCl$_3$): δ (ppm) 7.79 (m, 2H, C*H*-aromatic), 7.41 (m, 3H, C*H*-aromatic), 4.39 (m, C*H*$_2$-pyrrolidine), 3.10 (m, 2H, C*H*$_2$-pyrrolidine), 2.73 (m, 2H, C*H*$_2$-pyrrolidine). ^{13}C NMR (CDCl$_3$): δ (ppm) 176.9 (s, *C*-

carbene), 160.7 (s, N*C*═N), 140.1 (s, N*C*-aromatic), 129.5 (s, *C*H-aromatic), 129.0 (s, *C*H-aromatic), 122.9 (s, *C*H-aromatic), 46.6 (s, C*C*HN-pyrrolidine), 26.1 (s, *C*H$_2$-pyrrolidine), 21.5 (s, *C*H$_2$-pyrrolidine). Anal. Calcd for $C_{11}H_{11}N_3AgCl$ (329.43): C, 40.10; H, 3.34; N, 12.75. Found: C, 40.51; H, 3.13; N, 12.51.

Synthesis of $[(IMes)_2Ag]^+[AgCl_2]^-$ (21). A 50 mL flask was charged with IMes·HCl (340 mg, 0.99 mmol) and 10 mL of acetonitrile, to which was added silver(I) oxide (120 mg, 0.50 mmol). The resulting solution was refluxed for 24 h, then filtered over Celite, and the filtrate was reduced to 5 mL. The solution was left to crystallize, and brown pale crystals were obtained. Yield: 750 mg (85%). ^{1}H NMR (CD_3CN): δ (ppm) 7.23 (s, 2H, C*H*$_2$-imidazole), 6.97 (s, 4H, C*H*-aromatic), 2.42 (s, 6H, C*H*$_3$), 1.71 (s, 12H, C*H*$_3$). ^{13}C NMR (CD_3CN): δ (ppm) 140.2 (s, *C*H-aromatic), 135.9 (s, *C*H-aromatic), 135.5 (s, *C*H-aromatic), 129.8 (s, *C*H-aromatic), 123.9 (s, *C*H-imidazole), 21.1 (s, C*H*$_3$), 17.3 (s, C*H*$_3$). Anal. Calcd for $C_{42}H_{48}N_4Ag_2Cl_2$ (894.96): C, 56.33; H, 5.40; N, 6.26. Found: C, 55.88; H, 5.65; N, 6.49. HRMS: $[(IMes)_2Ag]$ $[AgCl_2]$: Calcd (cation) 717.29304 and experimentally measured 717.3080.

Synthesis of $[Ag(IMes)_2]^+{}_2[Ag_4I_6]^{2-}$ (22). A method of preparation similar to that used for compound $[(IMes)_2Ag]^+$-$[AgCl_2]^-$ (**21**) gave pale brown crystals. Yield: 299 mg (23%). ^{1}H NMR (CD_3CN): δ (ppm) 7.23 (s, 2H, C*H*$_2$-imidazole), 6.97 (s, 4H, C*H*-aromatic), 2.42 (s, 6H, C*H*$_3$), 1.71 (s, 12H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ (ppm) 140.1 (s, *C*H-aromatic), 135.9 (s, *C*H-aromatic), 135.5 (s, *C*H-aromatic), 129.8 (s, *C*H-aromatic), 124.0 (s, *C*H-imidazole), 21.1 (s, C*H*$_3$), 17.3 (s, C*H*$_3$). Anal. Calcd for $C_{84}H_{96}N_8Ag_6I_8$ (2625.46): C, 39.41; H, 3.68; N, 4.27. Found: C, 39.59; H, 3.98; N, 4.56. HRMS: $[(IMes)_2Ag]_2[Ag_4I_6]$: Calcd (cation) is 717.29304 and measured 717.2941.

Crystallographic information files (CIF) of complexes **11**−**22** have been deposited with the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K., and can be obtained on request free of charge, by quoting the publication citation and deposition numbers 279034−279044 for complexes **11**−**21** and 279130 for complex **22**.

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Supporting Information Available: Crystallographic information files (CIF) of complexes **11**−**22**. A discussion of the disorder associated with the anion $[Ag_4I_6]^{2-}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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