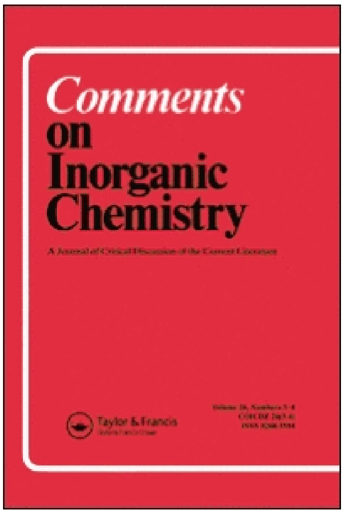

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SILVER(I) N-HETEROCYCLIC CARBENES

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SILVER(I) N-HETEROCYCLIC CARBENES

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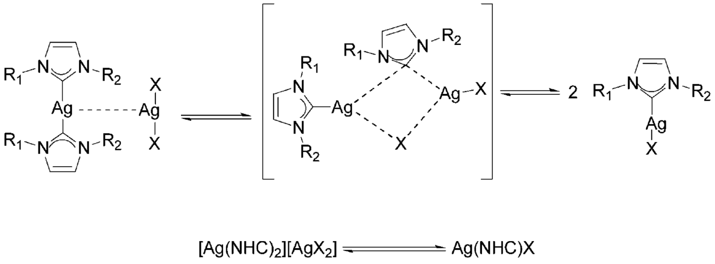
This review presents a detailed overview on the synthesis of Ag^I–NHCs and their role as carbene transferring agents as an easy access to various important transition metal-NHC complexes. The nature of NHC ligands, counter anions and solvents are recognized as key factors in the determination of Ag^I–NHCs and their derivatives. The lack of $Ag–C_{carbene}$ bond coupling in various Ag^I–NHCs suggests the lability of $Ag–C_{carbene}$ bond, which appears to be an appropriate reason in the transfer of carbene. It has been suggested by various authors that carbene transfer from Ag^I–NHCs is particularly useful when the carbene N-functionality contains base sensitive functional groups or acidic hydrogen. Importantly Ag^I–NHCs are less air sensitive than the free carbenes and are easy to synthesize. These properties allow them to be handled easily in further operations. Apart from the carbene transferring property, the nature of $Ag–C_{carbene}$ bond, the influence of NHC on the Ag...Ag contacts and the molecular aggregation to generate novel structural motifs and supramolecular assemblies have also been emphasized.



$[Ag(NHC)_2][AgX_2] \rightleftharpoons Ag(NHC)X$

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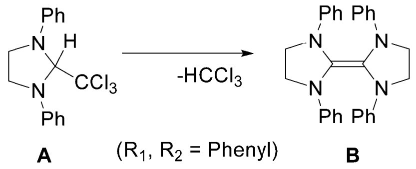
1. INTRODUCTION

1.1. Pre-phase

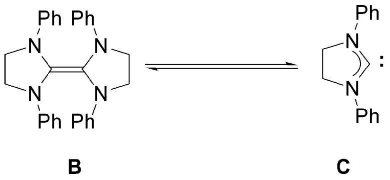
Imidazole–based N-heterocyclic carbenes (NHCs) are a type of cyclic carbenes in which the carbene carbon possessing two nonbonding electrons is stabilized by two adjacent amino groups. NHCs have had a remarkable impact on inorganic and organometallic chemistry. The fundamental electronic and steric properties of the NHCs determine their behavior of ligation. In view of this fact, research has been pursued for long time during the 1970s and 1980s to isolate free and stable NHCs. In this period, NHCs had been characterized in metal complexes not as ligands.

1.2. Past Events

In the chronological order of NHCs, the concept of stable NHCs was first proposed by Wanzlick in his prolific work in the early 1960s. It was predicted that the presence of an amino substituent would increase the stability of NHCs. An initial attempt to synthesize a saturated diamino carbene from **A** failed. Rather, the reaction afforded an enetetramine **B** instead [eqn. (1)].[1]

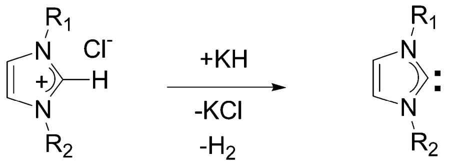


(1)



(2)

Based on the chemical nature of **B**, Wanzlick postulated that the diamino carbene **C** can be formed as an intermediate during the formation of **B** and proposed that equilibrium exists between **C** and **B** [eqn. (2)]. Denk et al. have provided some supportive evidence in favor of Wanzlick's equilibrium.[2] Later, other experimental evidence was forwarded by the research groups of Hann and Lemal, in which the equilibrium between benzimidazolium carbene and the corresponding enetetramine was affected by steric and thermodynamic factors.[3] Based on these results, Herrmann stated that Wanzlick's equilibrium exists between stable carbenes and the corresponding eneteramines and that the equilibrium depends on several factors.[4] Wanzlick, again in 1970, noticed that deprotonation of an imidazolium salt by potassium tertiary butoxide yielded an imidazol-2-ylidene, which, however, was trapped but not isolated.[5] Nevertheless his contributions in the chemistry of NHCs stimulated much related research. In 1991, using a similar technique, Arduengo et al. isolated and characterized the first stable imidazol-2-ylidene carbene **E** from **D** [eqn. (3)].[6]

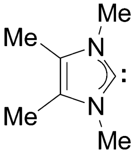


(3)

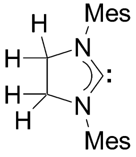
R_1, R_2 = adamentyl

D **E**

Earlier, the steric bulk and "aromaticity" of Arduengo's compound were assumed to be necessary for the isolation of a stable carbene. But the need for bulky substituents and aromaticity was refuted by Arduengo with his successful isolation of a carbene with only methyl substituents on the heterocycle **F** and a carbene with a saturated backbone **G**.[7]

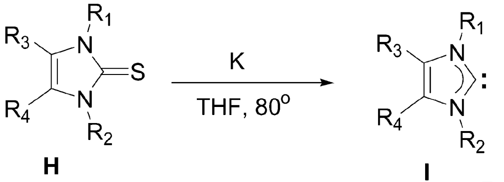


F



G (Mes = mesityl)

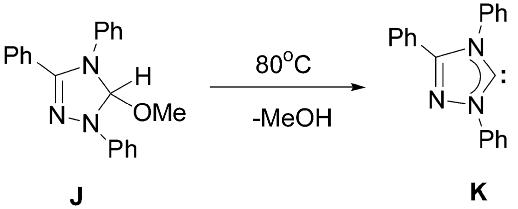
In this continuation, Kuhn et al. developed a new synthetic route to obtain alkyl substituted NHC **I** from **H** [eqn. (4)],[8] and Enders et al. synthesized a triazole carbene **K**, which became the first commercially available carbene obtained from **J** [eqn. (5)].[9]



(4)

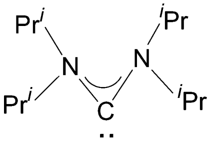
H **I**

R_1, R_2 = Me (or) Et (or) iso-Propyl
R_3, R_4 = Me



(5)

Later, Alder in 1996, with his successful synthesis of $C(N{-}iPr_2)_2$ (**L**), suggested that a cyclic system is not essential for the stabilization of carbene.[10]



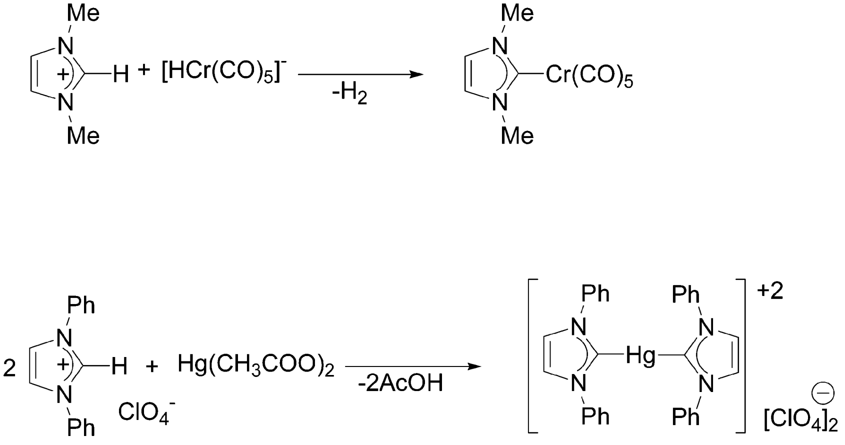
L

Adopting these principles, several other stable aminocarbenes have been synthesized. Overall, it is observed that one amino substituent is capable of stabilizing the carbene if the other substituent is a heteroatom such as S, O and even appropriate aryl groups.[11] The synthesis and properties of NHCs have been reviewed several times and will not be discussed in detail here.[12]

1.3. General Aspects in Coordination Chemistry

NHCs are recognized as very basic and very strong nucleophiles, which makes them excellent donors that form strong bonds to metal centers. In this regard, NHCs have become one of the most useful classes of ligands in organometallic chemistry since their first appearance. The very first information on the coordination of NHCs to metal centers was reported independently by Wanzlick and Ofele in 1968 from their pioneering work on the synthesis of chromium and mercury carbenes (Scheme 1).[13]

The chronology of metal-NHCs was then extended by Lappert.[14] Although many synthetic strategies of metal complexes of NHCs appeared in the literature, the renaissance of these complexes started only after the isolation of NHCs in free and stable form. Since their electronic and steric properties are liable to ample modification, several NHCs along with additional donor sites have been designed to obtain metal



Scheme 1. Synthesis of the first transition metal complexes of NHCs.

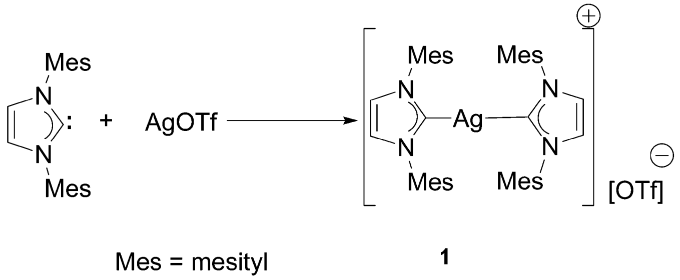
complexes of diverse structures and different properties.[12,15] Studies have shown that the Lewis basicity of NHCs is comparable to that of tertiary phosphines. Therefore many NHCs form strong bonds toward metal ions.[16] Furthermore, the use of metal-NHC complexes as catalysts in many chemical transformations is superior to the use of metal-phosphine complexes. This is because the deactivation of metal-phosphine catalysts due to the degradation of phosphine by P–C bond cleavage and orthometalation does not occur with the metal-NHC complexes.[17] The successful application of Ru^{I}–NHCs in the olefin metathesis reactions and Pd^{II}–NHCs in the cross coupling reactions almost revolutionized the area of catalysis.[12,18] The applications of transition metal complexes of NHCs as catalysts are well known in many reactions; specific processes include: Heck and Suzuki coupling, amide arylation, hydrosilation, olefin metathesis, cross coupling, Sonogashira coupling, aryl amination, C–H activation, ethylene–CO copolymerization, Stille coupling, Kumada coupling, hydrogenation, hydroformylation and many more [See the Ref. 18a and cross references therein].

Among the transition metal-NHCs, there is a growing interest in Silver(I)–NHCs (Ag^{I}–NHCs) due to simpler synthetic strategies, stability, fascinating structural diversity and most importantly they have been recognized as effective carbene group transfer agents in the synthesis of many structurally and catalytically important transition metal NHCs. The use of carbene transfer technique from Ag^{I}–NHCs works well for the metal ions of Au^{I}, Pd^{II}, Pt^{II}, Rh^{I}, Ru^{II}, Ru^{III}, Ir^{I}, and Cu^{I}. In light of these considerations, we report an overview of the recent works on Ag^{I}–NHC complexes regarding their synthesis, structure, bonding and reactivity.

2. SYNTHESIS AND PROPERTIES OF Ag^{I}-NHC COMPLEXES

2.1. By the Use of Free Carbene

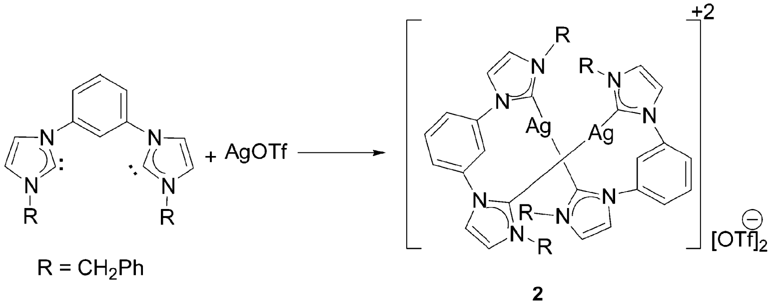
The first example of an Ag^{I}–NHC complex was reported in 1993 by Arduengo.[19] Reaction of a free form of NHC (N,N′-dimesityl substituted) with silver triflate in THF afforded Ag^{I}–NHC complex **1** [eqn. (6)].



1

(6)

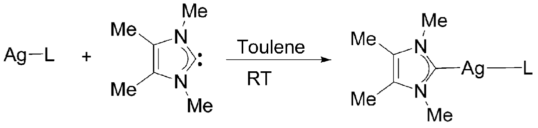
This technique was applied only in a few instances. In one instance, a pyridyl bridged biscarbene, which was stable only at 0°C, reacted with silver triflate to form a stable double helical complex **2** [eqn. (7)].[20] Attempts to stabilize the free carbene at room temperature were unsuccessful.



2

(7)

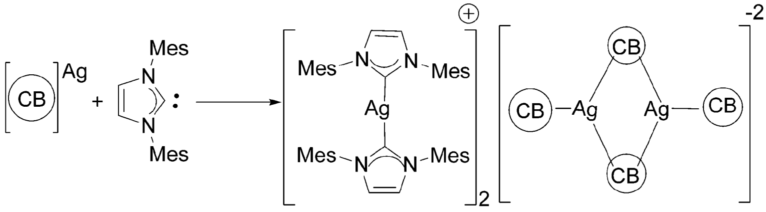
In another instance, reaction of 1,3,4,5-tetramethyl substituted carbene with silver-phenylacetonate in THF at room temperature gave a mononuclear silver complex **3** [eqn. (8)].[21]



(8)

3.L = (monodentate phenyl acetonato-)
4.L = (bidentate 1,3 diphenyl-1,3-propanedionato-)

The same carbene was also treated with silver(1,3-diphenyl-1,3-propanedionate) and formed a similar mononuclear Ag^I–NHC **4**.[22] Reaction of dimesityl-NHC with Ag^I salt of carborane anion gave an ion pair **5** [eqn. (9)].[23]



(9)

CB = carborane

5

Most of the free carbenes generated are air–, moisture–, and temperature–sensitive. This method, therefore, is hampered by the tedious precautions required to synthesize free carbenes. Furthermore, when an imidazolium salt is subjected to deprotonation by such strong base there is a possibility of decomposition of the carbene.

2.2. By in situ Deprotonation

To overcome the difficulties arising in the employing of free and stable carbenes, in 1998 our group described a very convenient method to synthesize Ag^I–NHCs.[24a] Simply by mixing an imidazolium salt with Ag_2O afforded a complex of Ag^I–NHC. This method featured several advantages.

1) **deprotonation normally occurs at C^2-carbene**
2) **air does not have to be excluded**
3) **solvent pretreatments are not necessary**
4) **no other strong bases are needed.**

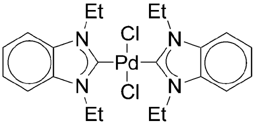
This technique provides high yields of Ag^I–NHCs, and is easy to operate. We have also demonstrated for the first time that these complexes are good precursors for the synthesis of other transition-metal-carbene complexes through carbene transfer phenomenon. Many other research groups have been advancing the success of this technique to synthesize Ag^I–NHCs, and the access of other interesting transition metal complexes. The synthesis and use of Ag^I–NHCs is particularly effective when the N-functionality of NHC contains base sensitive groups or more than one acidic hydrogen. We have also noted that the use of Ag(OAc) or Ag_2CO_3 instead of Ag_2O is limited to a few reports. From the available literature we divided the Ag^I–NHCs in to the following three classes to present a comprehensive discussion on the synthesis, structure and reactivity:

1) **Ag^I–NHCs containing alkyl or aryl N-substituents**
2) **Ag^I–NHCs containing additional donor atoms in N-substituents**
3) **Ag^I–NHCs containing chiral NHCs.**

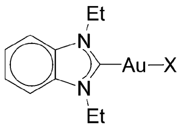
2.2.1. Ag^I–NHCs containing alkyl or aryl N-substituents. The first experimental success was obtained by the reaction of a bromide salt of **Ia** with Ag_2O suspended in CH_2Cl_2 (Scheme 2).[24a] The reaction proceeded smoothly to afford $[Ag(Et_2\text{-bimy})_2][AgBr_2]$ (**6,** Et_2-bimy stands for N,N′-diethyl benzimidazol-2-ylidene) as indicated by the gradual disappearance of the Ag_2O suspension.

Crystal structure of **6** shows that the molecular cation, which has two linearly coordinated carbenes, associates with $[AgBr_2]^-$ to form an ion pair through weak Ag. . .Ag interaction. To have a compound free of $[AgBr_2]^-$ anion, reaction of the $[PF_6]^-$ salt (**Ib**) with Ag_2O under basic PTC conditions produced $[Ag(Et_2\text{-Bimy})_2]PF_6$ (**7**). The lack of ^{13}C-$^{107,\ 109}Ag$ couplings in the ^{13}C-NMR spectrum of compound **6** reveals the labile nature of the Ag-$C_{carbene}$ bond and suggests an equilibrium (Scheme 3) between $[Ag(Et_2\text{-bimy})_2][AgBr_2]$ and $[Ag(Et_2\text{-bimy})Br]$ in solution.

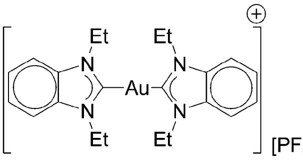
In view of this fluxional behavior it was considered that these Ag^I NHCs would be efficient carbene transfer agents and this technique was successfully applied to synthesize the Pd^{II}–NHC **6a** and Au^INHCs **6b** and **7a**.[24a]



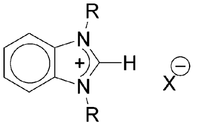
6a



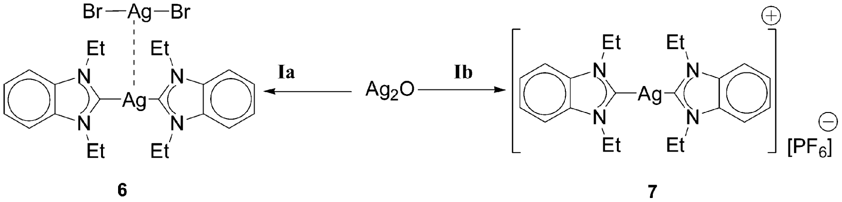
6b



7a



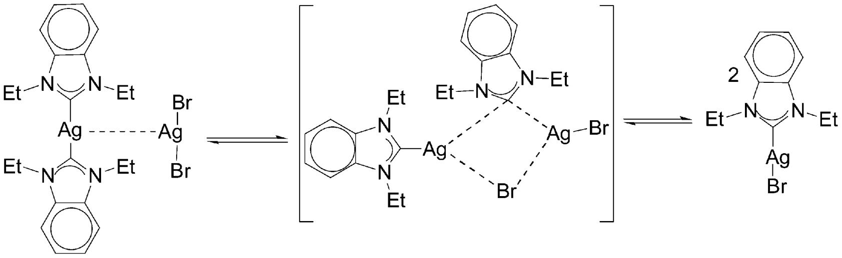
I **a.** R_1, R_2 = ethyl, X = Br
b. R_1, R_2 = ethyl, X = $[PF_6]$
c. R_1, R_2 = methyl, X = Br



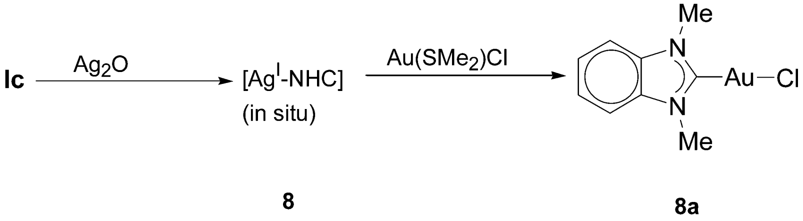
Scheme 2. Synthesis of Silver(I) benzimidazol-2-ylidene carbene by in situ deprotonation.

Another major advantage observed from this carbene transfer technique is that the silver halide precipitate can be reused to regenerate the silver carbene complex under phase transfer conditions. Thus, silver(I) is, in a sense, a catalyst for the synthesis of other metal-carbene complexes. Further, the Ag^I–NHC **8** of **Ic**, generated in situ was used to synthesize Au^I-NHC of the type **8a** (Scheme 4).[24b]

After the initial reports on silver-benzimidazol-2-ylidene carbene, most of the other carbenes being studied are imidazol-2-ylidene carbene. Ag^I complexes with a few other NHC systems are also reported. It appears that the formation of Ag^I–NHCs is influenced by the nature of N-substituents as well as the counter ions associated with it.



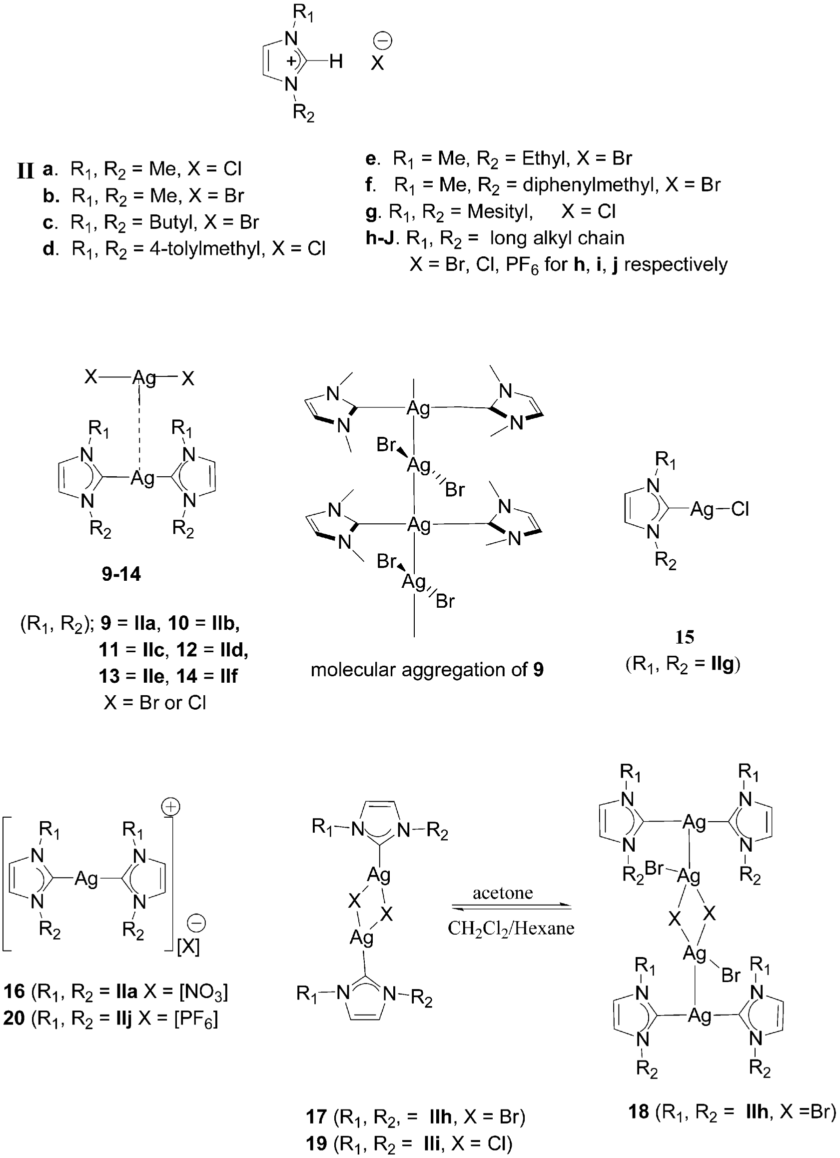
Scheme 3. A proposed equilibrium between $[Ag(Et_2\text{-bimy})_2][AgBr_2]$ and $Ag(Et_2\text{-bimy})Br$.



Scheme 4. Synthesis of Au^I-NHC from in situ generated Ag^I-NHC of Ic.

Imidazolium chloride and bromide salts **IIa–f** containing simple short chain alkyl or aryl N-substituents reacted with Ag_2O to give Ag^I–NHCs **9–14**, respectively, with ion-pair formulation similar to that of **6** (Scheme 5a).[25] The exception is **IIg**, which gave a relatively rare example of a monomeric Ag^I–NHC **15**.[26] Presumably the bulky mesityl groups disfavor the formation of silver biscarbene cation. Crystallographic studies show that compounds **9** and **10** are polymers consisting of alternating cations and anions aggregated through Ag^I...Ag^I attractions. The presence of polymeric Ag...Ag chains is evidenced by their luminous properties. Compound **16** was obtained from the equimolar reaction of $AgNO_3$ with **9** in acetonitrile.[25a]

On the other hand, lamellar dinuclear and tetranuclear Ag^I–NHCs **17** and **18** were obtained from the reaction of bromide salt (**IIi**) containing long alkyl side arms (i.e. liquid crystalline imidazolium salts) (Scheme 5a).[27] Compound **17** was isolated by the recrystallization of the crude product from acetone, whereas **18** was isolated from CH_2Cl_2/hexane. Transformation between **17** and **18** was observed. In **17** the two neutral Ag(NHC)Br units associate through intermolecular Ag...Br interactions and in **18** the $[Ag_2Br_4]_2^-$ anion is intercalated between two $[Ag(NHC)_2]^+$ cations with weak Ag(cation)...Ag(anion) attraction. With chloride salt **IIi**, a dinuclear Ag^I–NHC **19** was isolated from CH_2Cl_2/hexane, whose structure was similar to the bromo compound **17**.[28] When bromo and chloro benzimidazolium salts of **IIIa** and **IIIb** were employed in the reaction, a different formulation was again observed (Scheme 5b). For the chloride salt a monomeric complex **21** was obtained, whereas for the bromide salt an ion pair formulation **22** similar to that of **6** was observed.[28] With $[PF_6]^-$ counter ion of **IIj** and **IIIc**, both imidazolium and benzimidazolium salts produced the normal biscarbene complexes **20** and **23**,[28] whose basic crystal structures



II a. R_1, R_2 = Me, X = Cl
b. R_1, R_2 = Me, X = Br
c. R_1, R_2 = Butyl, X = Br
d. R_1, R_2 = 4-tolylmethyl, X = Cl
e. R_1 = Me, R_2 = Ethyl, X = Br
f. R_1 = Me, R_2 = diphenylmethyl, X = Br
g. R_1, R_2 = Mesityl, X = Cl
h-J. R_1, R_2 = long alkyl chain
X = Br, Cl, PF_6 for **h**, **i**, **j** respectively

9-14

(R_1, R_2); **9** = **IIa**, **10** = **IIb**,
11 = **IIc**, **12** = **IId**,
13 = **IIe**, **14** = **IIf**
X = Br or Cl

molecular aggregation of **9**

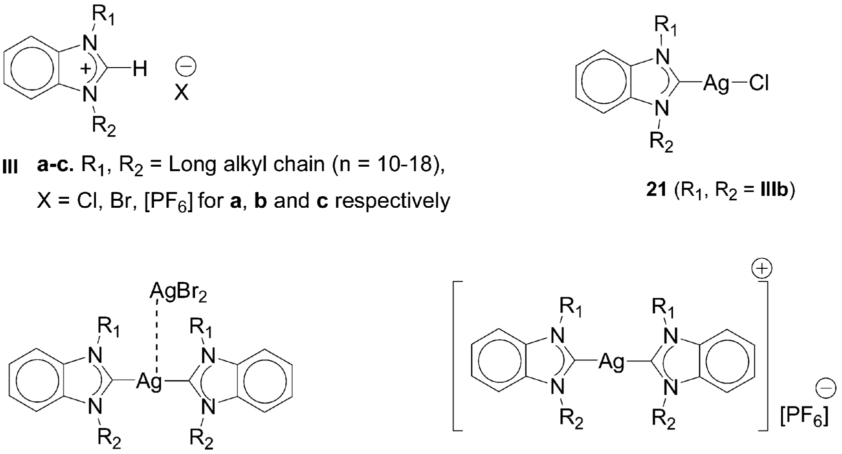
15
(R_1, R_2 = **IIg**)

16 (R_1, R_2 = **IIa** X = [NO_3]
20 (R_1, R_2 = **IIj** X = [PF_6]

17 (R_1, R_2, = **IIh**, X = Br)
19 (R_1, R_2 = **IIi**, X = Cl)

18 (R_1, R_2 = **IIh**, X =Br)

Scheme 5a. Structural diversity in Ag^I-NHCs with respect to the chain length of N-substituents of imidazol-2-ylidene.



III **a-c.** R_1, R_2 = Long alkyl chain (n = 10-18), X = Cl, Br, $[PF_6]$ for **a**, **b** and **c** respectively

21 (R_1, R_2 = **IIIb**)

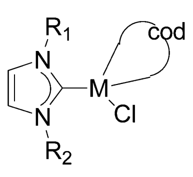
22 (R_1, R_2 = IIIa)

23 (R_1, R_2 = IIIc)

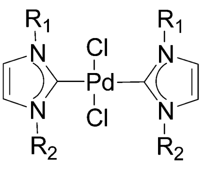
Scheme 5b. Ag^I-NHCs of benzimazol-2-ylidene with long alkyl chain N-substituents.

are similar to the other biscarbene complexes of **16** and **7**, respectively (Scheme 5a and 5b).

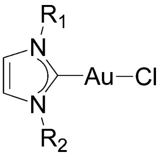
The Ag^I–NHCs of **11–14** were tested for their carbene transfer efficiency. The mononuclear Rh^I–NHC **11a** and Ir^I–NHCs **12a** were easily produced by the transfer of carbenes from **11** and **12**, respectively, in CH_2Cl_2 at room temperature.[25b] However, an attempt to synthesize a biscarbene complex of Ir^I was unsuccessful. For the other d^8 metal ions, a Pd^{II}–NHC **13a** was obtained from **13** and a mononuclear Au^I–NHC complex **14a** was obtained from **14**. [25c,d]



11a, M = Rh
12a, M = Ir
(cod = cyclooctadiene)



13a

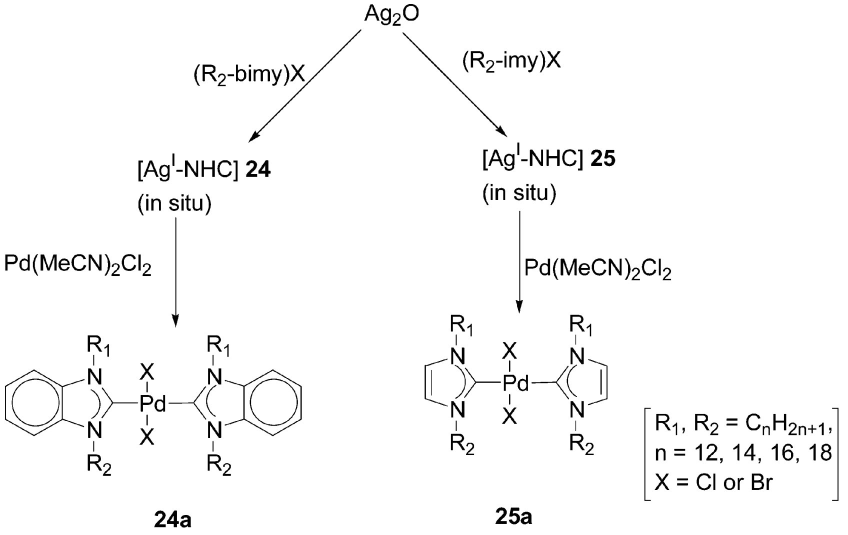


14a

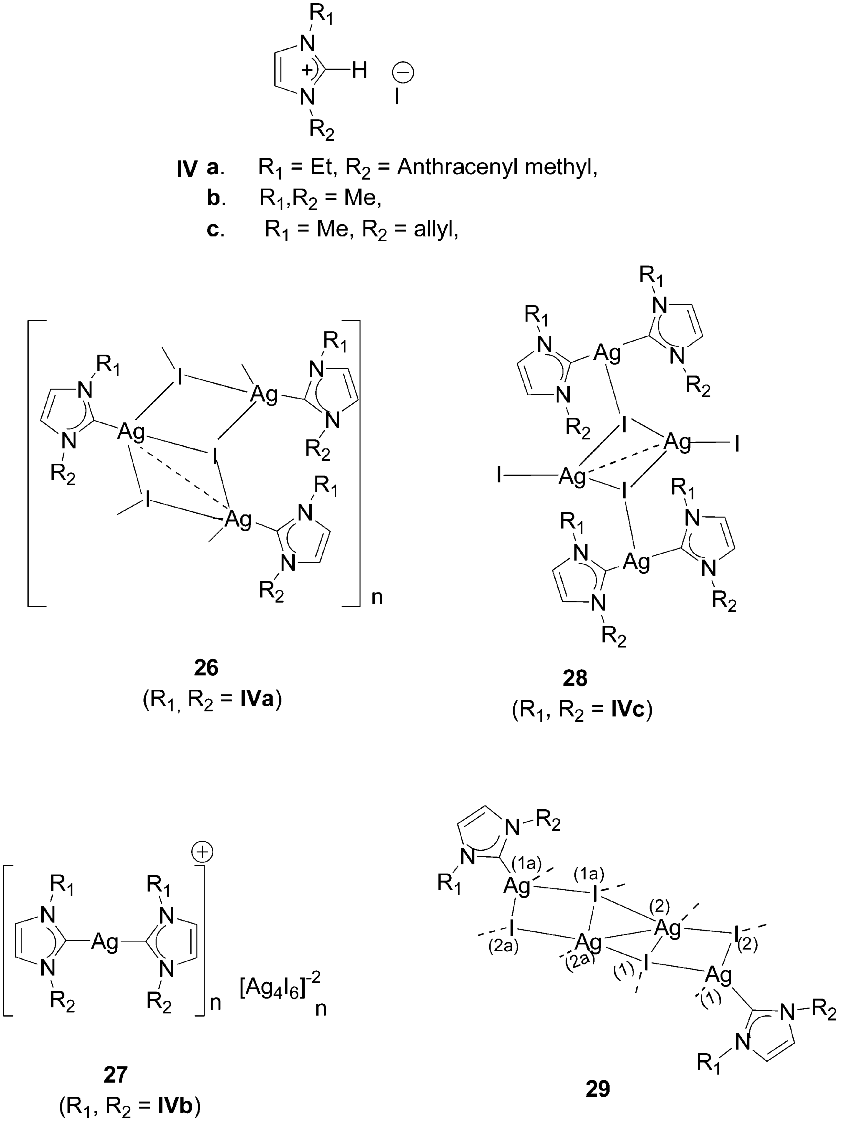
On the other hand, the carbene transfer technique used to synthesize Au^I-NHCs with long-chain arms from compound **17** or **18** has afforded a heteronuclear (Ag_2Au_2) compound.[27] This result differs from those with short chain arms. Note that, instead of using the Ag-carbene transfer technique, liquid crystalline Au^I-carbene complexes were best prepared by the reaction of Au^I with imidazolium salts under PTC conditions.[29] Structure of the heteronuclear Ag_2Au_2 compound is similar to the tetranuclear compound **18**.

Ag^I–NHCs (**24** and **25**) of benzimidazolium and imidazolium halides (chloride or bromide), armed with long alkyl chains ($n = 10, 12, 14, 16$), generated in situ were used to produce the first thermally stable liquid crystalline Pd^{II}–NHCs, *trans*-$Pd((C_nH_{2n+1})_2\text{-bimy})_2X_2$ (type **24a**) and $Pd((C_nH_{2n+1})_2\text{-imy})_2X_2$ (type **25a**) ($n = 10, 12, 14, 16$; Bimy = benzimidazol-2-ylidene, Imy = imidazol-2-ylidene) (Scheme 6).[30]

Despite the fact that there a large number of Ag^I–NHCs (in this category) being synthesized by employing chloride or bromide salts, only a few compounds with iodide salts have been prepared. In this respect, a luminescent Ag^I–NHC **26**, a stair polymer, has been synthesized from **IVa** (Scheme 7).[31] In **26**, each silver atom is coordinated by a carbene carbon and three bridging iodides and possesses a distorted-tetrahedral configuration, whereas each bridging iodide is capped to three silver atoms in a trigonal-pyramidal arrangement.



Scheme 6. The first liquid crystalline Pd^{II}-NHCs from benzimidazolium and imidazolium salts containing long alkyl chain N-substituents.



IV a. R_1 = Et, R_2 = Anthracenyl methyl,
b. R_1,R_2 = Me,
c. R_1 = Me, R_2 = allyl,

26
(R_1, R_2 = **IVa**)

28
(R_1, R_2 = **IVc**)

27
(R_1, R_2 = **IVb**)

29

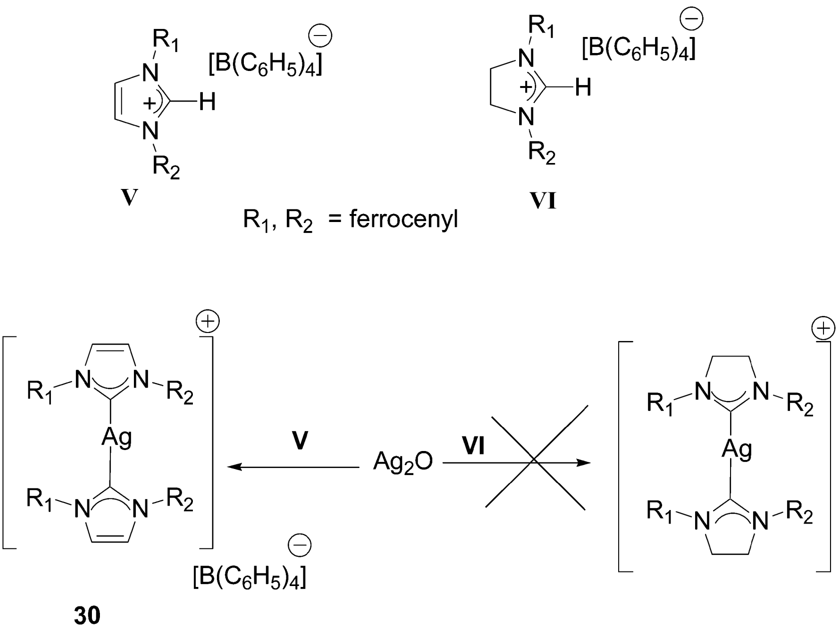
Scheme 7. Formation of Ag^I-NHCs from imidazolium iodide salts.

The formation of polymeric compounds **27** and **28** from **IVb** and **IVc** also indicates the influence of iodide ion on the tendency of nucleation (Scheme 7).[32] In **27**, the cations of $Ag(NHC)_2{}^+$and anions of one dimensional $[Ag_4I_6]^{-2}$ are held together by Ag^I...I interactions to form a two–dimensional polymer. With replacement of one methyl side arm with an allyl group, a tetranuclear complex **28** was obtained. Upon dissolution of **28** in hot DMSO, a new coordination polymer **29**, possessing an infinite ribbon stair structure, was generated.

In a different consideration, interaction of an N, N′-diferrocenyl imidazolium salt **V** with Ag_2O afforded complex **30** (Scheme 8).[33] Under similar conditions, results with saturated backbone of **VI** suggested that the oxide might be too weak a base to perform the deprotonation reaction to give the expected product.

Despite the fact that imidazole–based Ag^I–NHCs are well documented, Ag^I–NHCs based on triazole, which has an additional nitrogen atom in the ring, have received little attention.

To this end, the first example of Ag^I–NHC with triazolium-carbene (triazol-2-ylidene denoted as tazy) was synthesized by Bertrand in 1997 using Wanzlick's strategy.[34] Reaction of one equivalent of silver(I) acetate with dicationic triazole heterocycle (**VIIa**) in refluxing THF yielded a biscarbene complex **31** (Scheme 9). Under the same reaction



Scheme 8. Reaction of Ag_2O with ferrocenyl substituted imidazolium and imidazolinium salts.

conditions, interaction between 2 equivalents of silver(I) acetate with **VIIa** and **VIIb** produced the first polymeric $Ag^{I}-NHC$ complexes of **32** and **33**, respectively. A single crystal structural study reveals that **33** is a one-dimensional polymer, in which all the rings are coplanar.

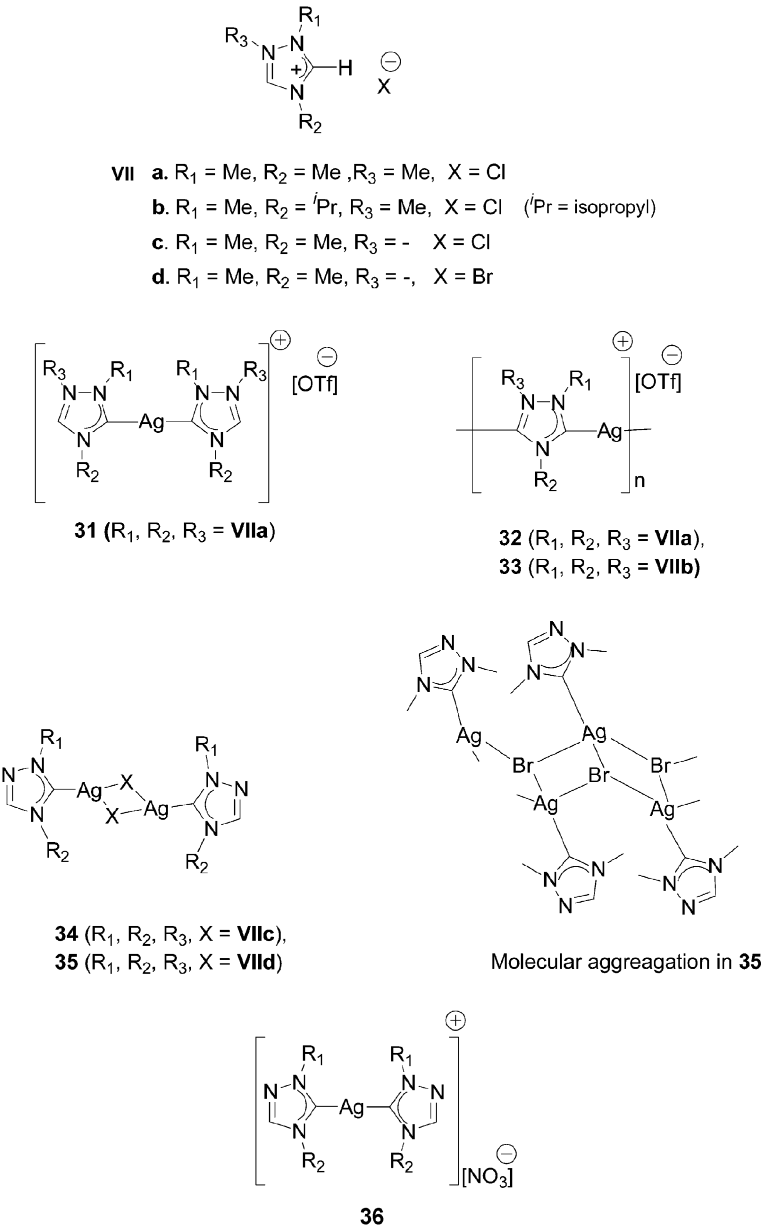
Later, the halide bridged $Ag^{I}-NHCs$ **34** and **35** were synthesized from the reaction of chloro or bromo triazolium salts **VIIc–d** (Scheme 9).[25a] Crystal structure of the bromo compound shows that the Ag^{I} center adopts a tetrahedral geometry by coordinating with one tazy and three bridging μ_3-Br ligands. It thus forms an infinite one–dimensional polymer. Compound **34** was further reacted with $AgNO_3$ in MeCN to produce a mononuclear biscarbene compound **36**.[25a] The nitrate ion forms CH...O hydrogen bonds, rather than coordinates to the Ag^{I} center.

Considering bisimidazolium salts, reaction of ethylene bridged salt **VIIIa** with Ag_2O in CH_2Cl_2 yielded a dicarbene complex **37** (Scheme 10).[25a] This dicarbene complex further associates with neighboring molecules through bridging chloride to form an extended 1-D ladder polymer. Carbene transfer from **37** to Au^{I} resulted in an isostructure of dicarbene complex **37a**.[28]

In situ generation of Ag^{I} NHCs **38–41** through the reaction of **VIIIb–e** with Ag_2O, followed by carbene transfer to $[Rh(cod)Cl]_2$, gave various results (Scheme 10).[35] If the transfer of carbene was carried out under refluxing conditions and excess Ag_2O was removed, bisimidazolium salts with linkers of $n = 1$ and 2 gave dirhodium carbene complexes **38a** and **39a**, whereas with linkers of $n = 3$ and 4 produced mononuclear chelating complexes **40a** and **41a**. If the carbene transfer was carried out in the presence of Ag_2O, a chelating complex was also obtained with the linker of $n = 2$. However, if the reaction was carried out at room temperature, only dirhodium carbene complexes **38b–41b** were obtained, irrespective of the linker length. Attempts to convert these bridging carbene complexes to chelated complexes were unsuccessful.

Reactions of bulky bisimidazolium bromide salts **IXa–d** with Ag_2O in refluxing dichloroethane generated the neutral monomeric $Ag^{I}-NHCs$ NHCs of **42–45**, in which metathesis of bromide by chloride occurred in the reaction (Scheme 11).[36] Reaction between **43** and $Pd(cod)Cl_2$ gave two compounds of identical stoichiometry: a cyclic dimer and a monomeric species (**43a–b**). Reaction of **IXd** with Ag_2O was claimed to give a very poor yield of the product.[37]

Results from Buchmeiser et al. showed that Ag_2O even reacted with less acidic NHC precursors **Xa–d** (Scheme 12).[38] $Ag^{I}-NHCs$ of **46–49**



VII **a**. R_1 = Me, R_2 = Me ,R_3 = Me, X = Cl
b. R_1 = Me, R_2 = ^{i}Pr, R_3 = Me, X = Cl (^{i}Pr = isopropyl)
c. R_1 = Me, R_2 = Me, R_3 = - X = Cl
d. R_1 = Me, R_2 = Me, R_3 = -, X = Br

31 (R_1, R_2, R_3 = **VIIa**)

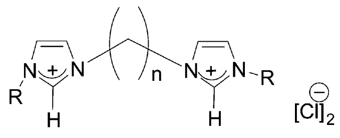
32 (R_1, R_2, R_3 = **VIIa**),
33 (R_1, R_2, R_3 = **VIIb**)

34 (R_1, R_2, R_3, X = **VIIc**),
35 (R_1, R_2, R_3, X = **VIId**)

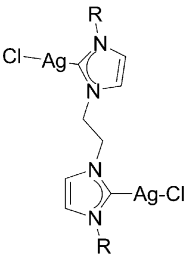
Molecular aggreagation in **35**

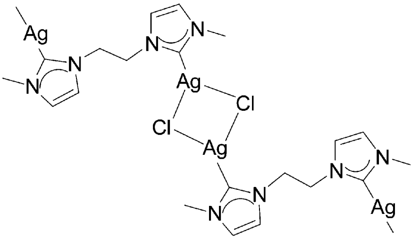
36

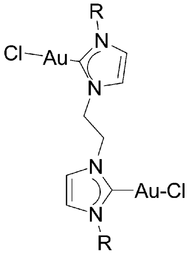
Scheme 9. Formation Ag^{I}-NHCs with triazolium carbenes (triazol-2-ylidene).



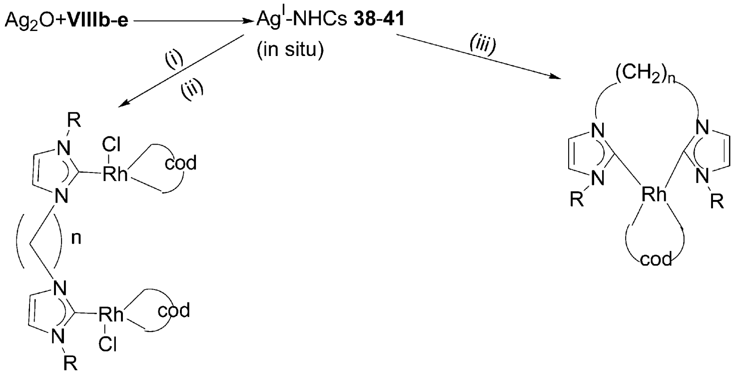
VIII a. R = Me, n = 2, X = Cl
b-e. R = n-Bu, X = Br
n = 1,2,3,4 for **b**,**c**,**d**,**e** respectively







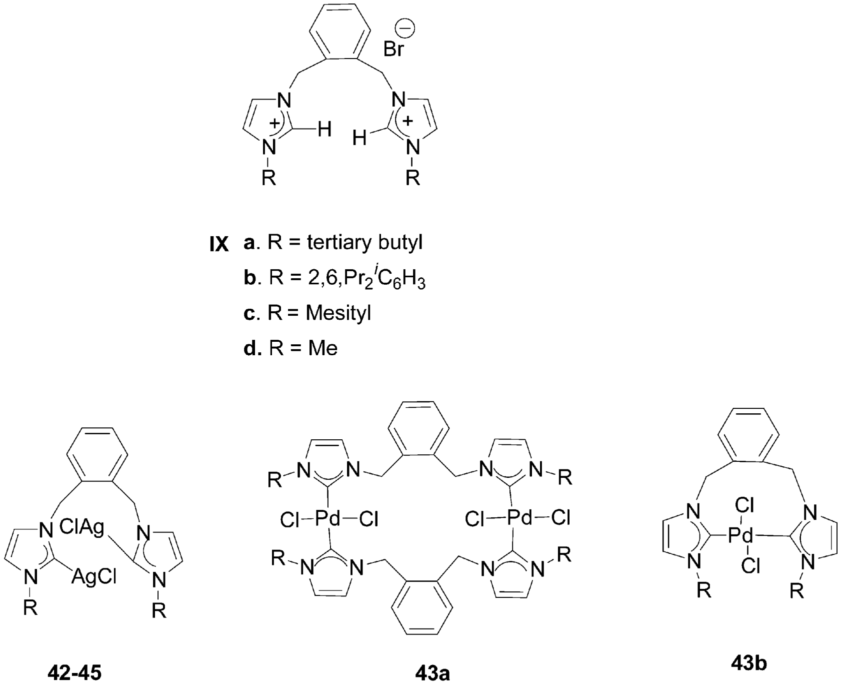
37 (R, X, n = **VIIIa**) molecular aggregation in compound-**37** **37a**



38a, **39a** and **38b-41b** **40a**,**41a**

(i) **VIIIb**-c, **38** and **39**, refluxion
(ii) **VIIIb-e**, **38-41**, room temperature
(iii) **VIIId-e**, **40** and **41**, refluxion

Scheme 10. Formation of Ag^I-NHCs and their subsequent transition metal derivatives from bisimidazolium salts with alkyl linkers.



IX **a**. R = tertiary butyl
b. R = 2,6,$Pr_2^iC_6H_3$
c. R = Mesityl
d. R = Me

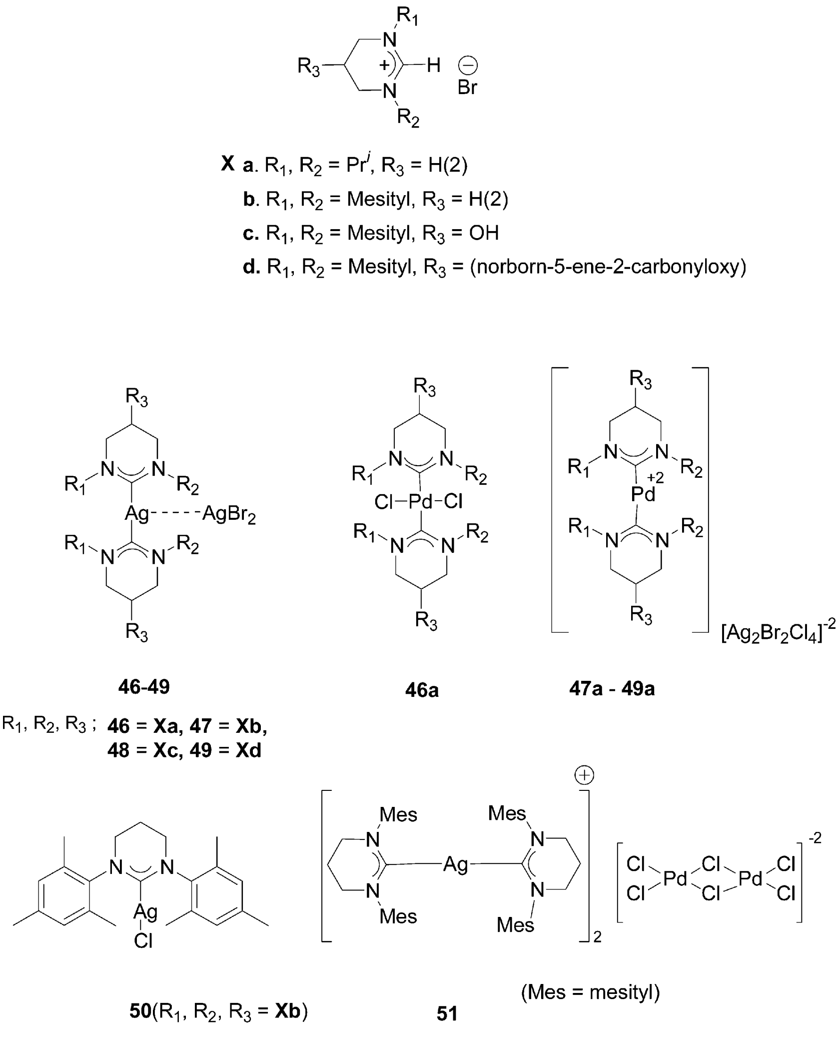
42-45 **43a** **43b**

R; **42** = **IXa**, **43** = **IXb**
44 = **IXc**, **45** = **IXd**

Scheme 11. Ag^I-NHCs and their Pd^{II}-NHCs formed from bulky bisimidazolium salts with aryl linker.

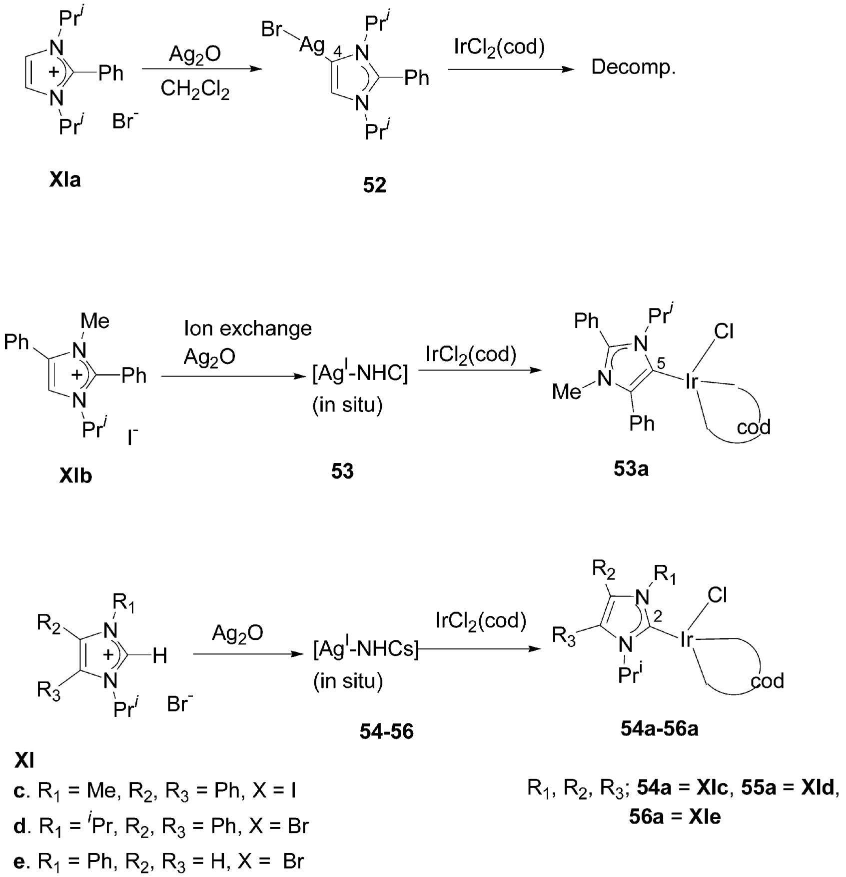
were obtained from this symmetrically disubstituted pyrimidinium bromide salts. Upon carbene transfer from compounds **46–49** to $PdCl_2(CH_3CN)_2$, isolation of the complexes **46a–49a** was claimed.

On the contrary, Herrmann's group showed that the reaction between **Xb** and Ag_2O generated the monomeric Ag^I–NHC **50** (Scheme 12), which was confirmed from the X-ray crystal work.[39] More importantly, they concluded that the reaction between the monomeric **50** and $Pd(MeCN)_2Cl_2$ gave a compound (**51**) with two Ag^I–NHC cations and a $[Pd_2Cl_6]^{-2}$ anion, instead of the desired Pd^{II}–NHC **47a** reported by Buchmeiser. The reasons that compound **50** cannot act as a carbene transfer agent have been proposed to be due to the stronger sigma bond formed between silver and pyrimid-2-ylidene and also steric reasons.



Scheme 12. Ag^I-NHCs formed from pyrimidinium salts and their derivatives.

In a recent advance, Crabtree's group described the use of Ag^I–NHC to afford abnormal C^5-bonded Ir^I–NHC complexes (Scheme 13).[40] Initial attempts through blocking the C^2-center of the imidazolium salt **XIa** gave an unstable C^4-bonded Ag^I complex of **52**, which failed to produce the corresponding Ir^I complex due to the more basic nature of the C^4-position. Upon blocking both the C^2- and C^4-positions, reaction of



XIa **52**

XIb **53** **53a**

54-56 **54a-56a**

XI

c. R_1 = Me, R_2, R_3 = Ph, X = I

d. R_1 = ^{i}Pr, R_2, R_3 = Ph, X = Br

e. R_1 = Ph, R_2, R_3 = H, X = Br

R_1, R_2, R_3; **54a** = **XIc**, **55a** = **XId**, **56a** = **XIe**

Scheme 13. Abnormal C^5-bonded Ir^I-NHCs and normal C^2-bonded Ir^I-NHCs from Ag^I-NHCs.

XIb with Ag_2O followed by $IrCl_2$(cod) gave an abnormal C^5-bonded Ir^I complex **53a** in a one pot reaction, presumably through the in situ formation of Ag^I–NHC **53**. C^2-bonded Ir^I complexes **54a–56a** were also synthesized by using the established procedures from the in situ generated Ag^I–NHCs **54–56**.

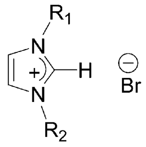
2.2.2. Ag^{I}NHCs containing additional donor atoms in N-substituents. NHCs with additional donor groups have attracted considerable interest in coordination chemistry as a basis for new hybrid ligand platforms, which can exhibit unusual reactivity. Reports on the phenomenon of these classes of Ag^I–NHCs formation and their subsequent transition metal derivatives in this context are best divided in to three kinds:

a) **Ag^Icomplexes with monoNHCs containing additional donor atoms**
b) **Ag^I complexes with bisNHCs bridged by additional donor atom**
c) **Ag^I complexes with polyNHC motifs containing carbon or nitrogen anchors.**

a) **Ag^I complexes with monoNHCs Containing Additional Donor Atoms**: Synthesis and structural characterization of Ag^I–NHCs with additional donor atoms were demonstrated by the groups of Danopoulos and Cavell in 2000.[36a,41] In Danopoulos' research, a variety of protocols of Ag^I–NHCs (**57–66**) have been established from the reactions of imidazolium bromide salts **XIIa–j** with Ag_2O or Ag_2CO_3 (Scheme 14).[36a] Usually the reactions proceeded faster in refluxing dichloromethane or dichloroethane. Addition of molecular sieves has been claimed to improve the purity of the complexes, presumably by absorbing the water generated. Under these conditions, neutral complexes **57–63** and **66** were obtained from**XIIa–g** and **j,** and ion pairs **64** and **65** were obtained from **XIIh-I**, respectively. Metathesis of bromide by chloride occurred in the chlorinated solvents. Introduction of additional substituents on pyridine ring has no significant effect on the structural parameters. The halide bridged neutral complexes have shown weak Ag...Ag interactions. Generation of Ag^I–NHCs from the AgCl under phase transfer condition was not successful.

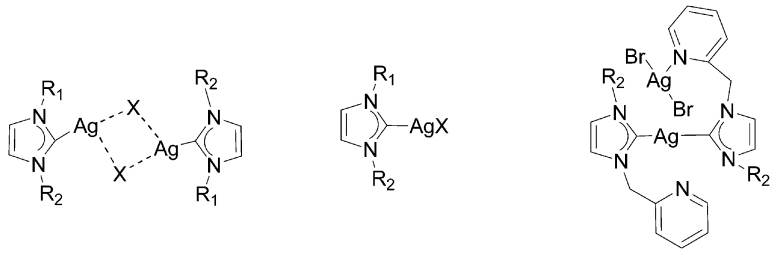
Compound **57**, which consists of a methoxy functionality, produced a mixture of mono and dicarbene complexes **57a** and **57b** through the reaction with $PdCl_2$(cod),[42] whereas the carboamyl group functionalized compound **59** produced a single Pd^{II} NHC **59a** with trans carbenes. There is no evidence of carbonyl oxygen atom participation in bonding in the Ag^I–NHCs of **57–59** and their Pd^{II}–NHCs **57a** and **59a**. Compounds **62**, **63**, **65** and **66**, which contain pyridyl functionality, were reacted with Pd(cod)(Me)Br to produce the chelated mononuclear Pd^{II}–NHCs **62a**, **63a**, **65a** and **66a**, respectively.[42] In these Pd^{II}–NHCs, the carbene moiety is trans to the bromide, whereas the pyridine is trans to the methyl group.

Cavell's research group described the synthesis of Ag^I–NHCs (**67–70**) from the precursors **XIIIa–e** (Scheme 15).[41,37] It is noticeable that while using bromide salts (**XIIIa–b**) gave a regular ion-pair compounds **67** and **68**, the use of iodide salts (**XIIIc–d**) gave products



XII

R_1 (donor group)	**R_2**
a) methoxymethyl,	2,6-diisopropylphenyl
b) diethylcarbamoylmethyl	tertiary butyl
c) diethylcarbamoylmethyl	mesityl
d) 2-benzylideneamino 3,5-di-tert-butylbenzyl	teriary butyl
e) pyridyl	tertiarybutyl
f) pyridyl	2,6-diisopropylphenyl
g) substituted pyridyl	2,6-diisopropylphenyl
h) picolyl	tertiary butyl
i) picolyl	2,6-diisopropylphenyl
j) picolyl	mesityl

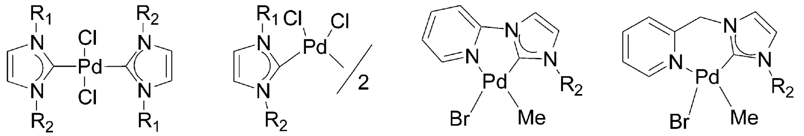


57-59, 66 **60-63** **64, 65**

R_1, R_2; **57 = XIIa**, **58 = XIIb**, **59 = XIIc**, **66 = XIIj**

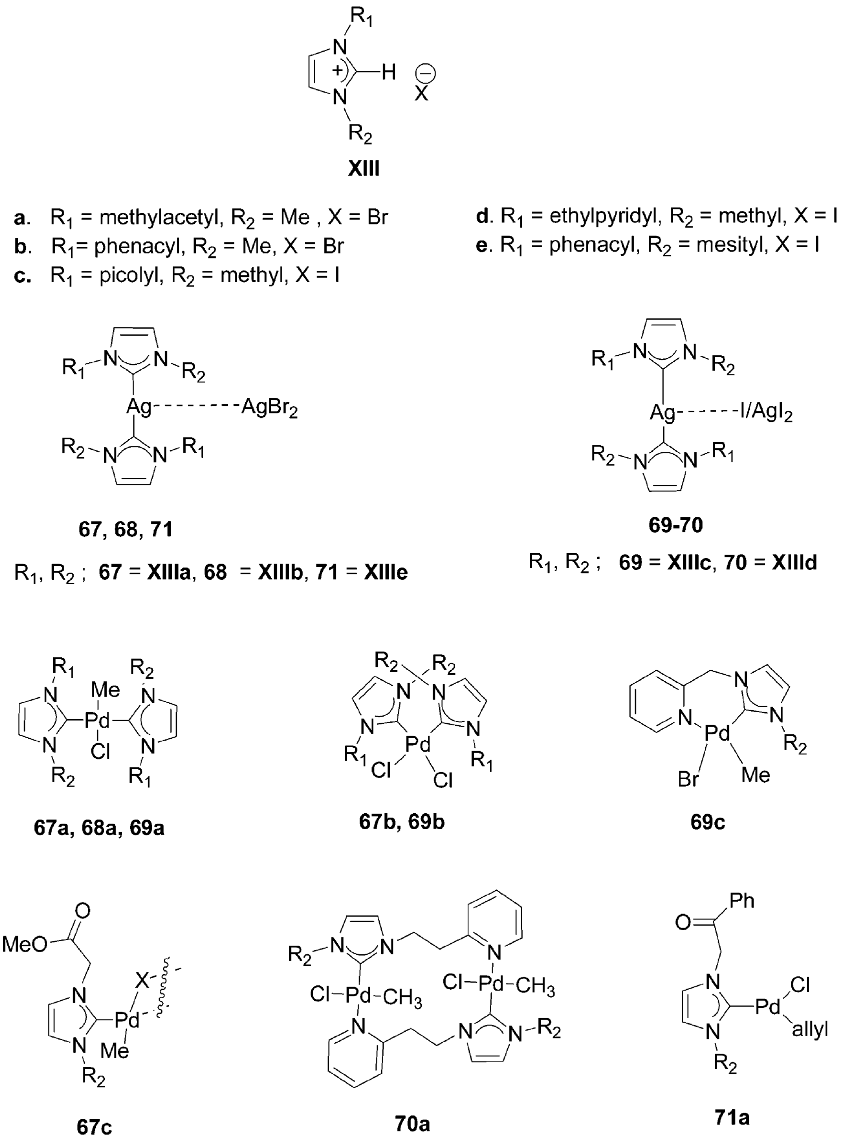
R_1, R_2; **60 = XIId**, **61 = XIIe**, **62 = XIIf**, **63 = XIIg**

R_1, R_2; **64 = XIIh**, **65 = XIIi**



57a, 59a **57b** **62a,63a** **65a, 66a**

Scheme 14. Ag^I-NHCs and the corresponding Pd^{II}-NHC derivatives with varied N-functionalities.



XIII

a. R_1 = methylacetyl, R_2 = Me , X = Br
b. R_1= phenacyl, R_2 = Me, X = Br
c. R_1 = picolyl, R_2 = methyl, X = I
d. R_1 = ethylpyridyl, R_2 = methyl, X = I
e. R_1 = phenacyl, R_2 = mesityl, X = I

67, 68, 71

R_1, R_2 ; **67 = XIIIa, 68 = XIIIb, 71 = XIIIe**

69-70

R_1, R_2 ; **69 = XIIIc, 70 = XIIId**

67a, 68a, 69a

67b, 69b

69c

67c

70a

71a

Scheme 15. Formation of Ag^I-NHCs as ion-pairs with varied N-functionalities and the corresponding Pd^{II}-NHC derivatives.

69 and **70** with mixed I^- and AgI_2^-. Despite their structural diversity, these Ag^I–NHCs are all efficient carbene transferring agents. Compound **71**, an analogue of compound **68** was prepared from **XIIIe**, reported recently by Waymouth's group.[43]

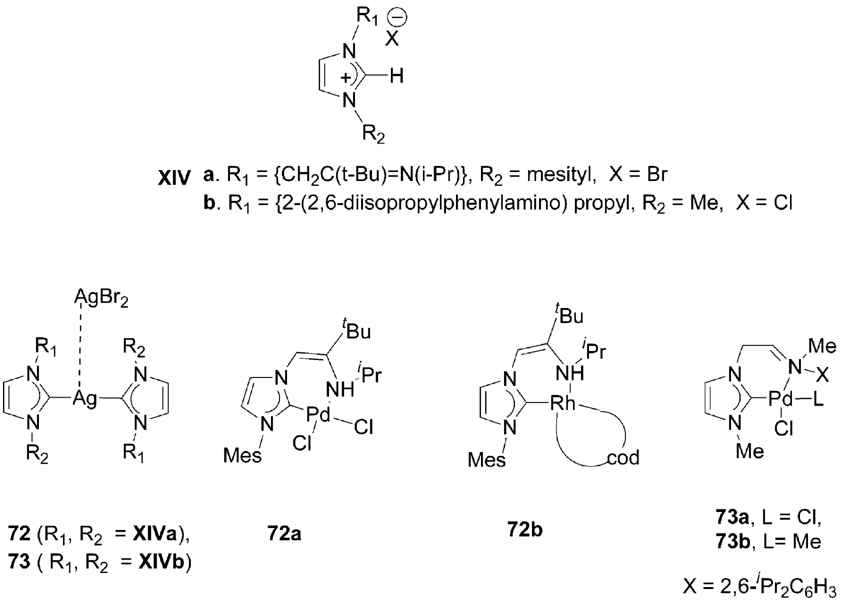
The transfer of carbene from compounds **67–71** to Pd^{II} center indicated that the products isolated were determined by factors such as the nature of donor group, the Pd^{II} precursor, and the stoichiometric ratios of NHC/Pd (Scheme 15). The carbonyl oxygen in the NHCs also does not participate in the coordination of Pd^{II} compounds. When the Pd^{II} precursor was PdMeCl(cod) and with an equal molar of NHC/Pd, trans bis-carbene complexes **67a–69a** were isolated. When the precursor was $PdCl_2(MeCN)_2$, complexes **67b** and **69b** of cis form were obtained. Chelated Pd^{II} monomer **69c** was obtained upon reaction of PdMeCl(cod) with **69** in a 2:1 ratio. Under similar conditions an increase in the spacer length by two carbons, as in **70**, produced a 14 membered metallocyclic ring compound **70a**. When compound **67** was reacted with PdMeCl(cod) in a 2:1 molar ratio, two dimeric isomers of **67c**, which are in equilibrium (not shown) with a chelated mononuclear species, were resulted at 0°C. When compound **71** was reacted with $[Pd(allyl)Cl_2]$, a mononuclear Pd^{II}–NHC **71a** was produced.[43]

Based on the success obtained by Danopoulos' and Cavell's groups, other Ag^I complexes of single NHC with additional donor atoms have also been reported.

Reaction of the bromide salt (**XIVa**), a first non-cyclic imino-NHC precursor, with Ag_2O in refluxing CH_2Cl_2 gave a regular ion-pair complex **72** (Scheme 16).[44] The imine-chloride salt (**XIVb**) also produced a similar ion-pair **73** by simply stirring in CH_2Cl_2.[45] ^1H-NMR study of compound **72** reveals the possible existence of ZZ and EZ isomers and not EE isomer due to the steric crowding of such systems. The non–bonding nature of the imine functional group in compound **73** was confirmed by the observation of two $\nu_{C=N}$ absorptions at higher frequencies (1685 and 1665 cm^{-1}) in the IR spectrum.

Interaction of **72** with $[PdCl_2(MeCN)_2]$ in CH_2Cl_2 and $[Rh(cod)(THF)_2][BF_4]$ in THF gave the enamine complexes **72a** and **72b**, respectively, via tautomerization. Reaction of compound **73** with Pd(cod)ClX (X = Cl, or Me) in cold CH_2Cl_2 produced **73a** and **73b**.

Catalano et al. highlighted the influence of different bifunctionalized NHC precursors **XVa–e** on homonuclear (Ag^I–Ag^I) and heteronuclear (Ag^I–Au^I) interactions (Scheme 17).[46] Reaction between the chloride



XIV **a**. R_1 = {CH_2C(t-Bu)=N(i-Pr)}, R_2 = mesityl, X = Br
b. R_1 = {2-(2,6-diisopropylphenylamino) propyl, R_2 = Me, X = Cl

72 (R_1, R_2 = **XIVa**),
73 (R_1, R_2 = **XIVb**)

72a

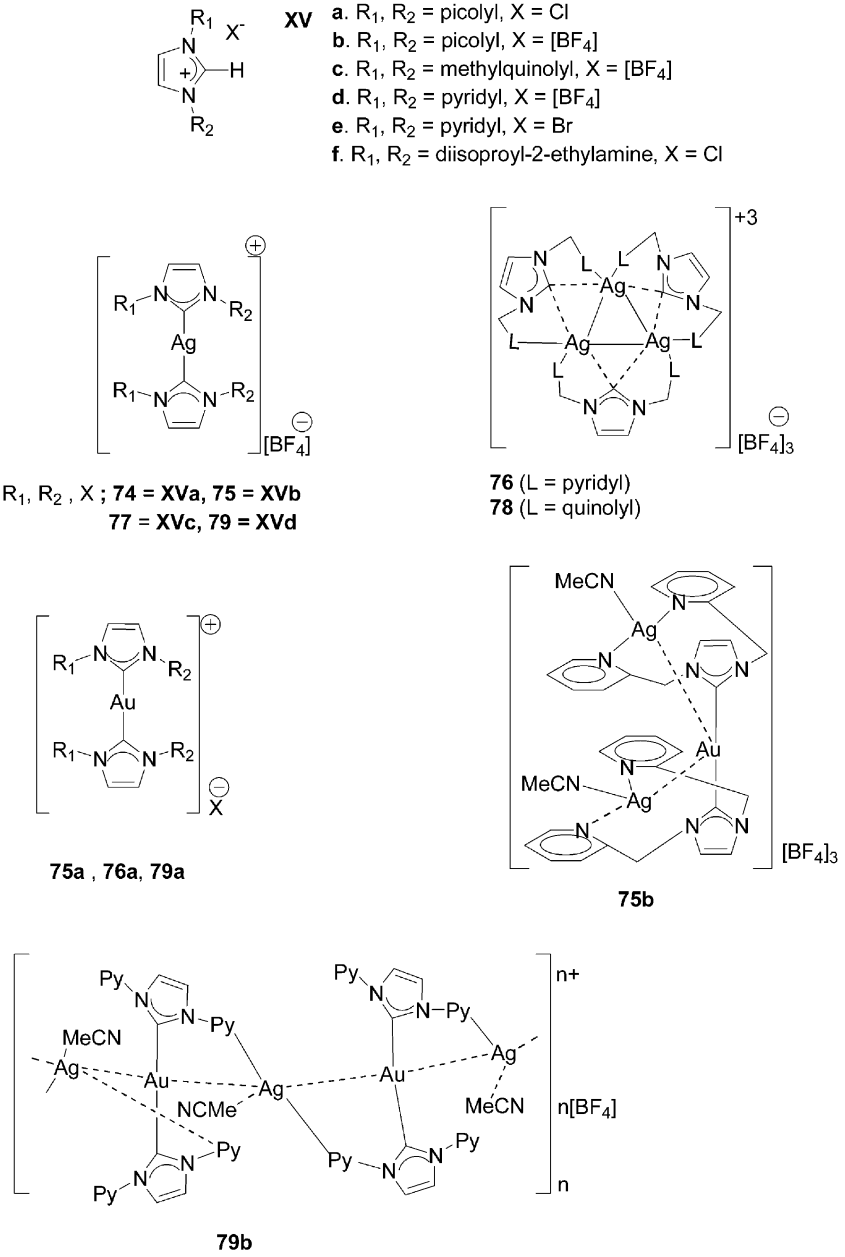
72b

73a, L = Cl,
73b, L= Me

X = 2,6-$^i Pr_2C_6H_3$

Scheme 16. Formation of Ag^I–NHCs and their transiton metal derivatives with imino-carbene precursors.

salt **XVa** and Ag_2O in CH_2Cl_2, with or without PTC conditions, led to the formation of complex **74**. Complex **75** was synthesized under PTC conditions from the $[BF_4]^-$ salt of **XVb** or alternatively by exchanging chloride ion from **74** in CH_2Cl_2. Crystal structure of **74** showed that the two imidazole rings are slightly canted, consequently the picolyl side arms are turned back and permit shorter intermolecular Ag…Ag interactions (~3.6Å), whereas in **75** the imidazole rings are virtually coplanar and thus result in longer Ag…Ag separations. Addition of excess $AgBF_4$ to the complex **75** in acetonitrile produced a homoleptic triangulo-$[(\mu\text{-}NHC)_3Ag_3]^{+3}$ complex **76** with bridging μ2-carbenes and unusual Ag…Ag interactions (~2.7 Å).[46a] In **76**, the carbene ligands are perpendicular to the trigonal Ag_3 face and the two pyridine arms coordinate to the Ag(I) centers, one above and one below the Ag_3 plane. Carbene transfer from **75** to Au(tht)Cl gave the isostructural Au^I complex **75a** in CH_2Cl_2. Addition of $AgBF_4$ to **75a** in MeCN yielded the trimetallic compound **75b**, in which the newly incorporated Ag^I centers are coordinated with two pyridyl side arms of NHC fragment and also with one solvent molecule. In this connection, compound **75b** possesses weak argentophilic-aurophilic



XV

a. R_1, R_2 = picolyl, X = Cl
b. R_1, R_2 = picolyl, X = $[BF_4]$
c. R_1, R_2 = methylquinolyl, X = $[BF_4]$
d. R_1, R_2 = pyridyl, X = $[BF_4]$
e. R_1, R_2 = pyridyl, X = Br
f. R_1, R_2 = diisoproyl-2-ethylamine, X = Cl

R_1, R_2 , X ; **74 = XVa, 75 = XVb**
77 = **XVc, 79 = XVd**

76 (L = pyridyl)
78 (L = quinolyl)

75a , **76a**, **79a**

75b

79b

Scheme 17. Homoleptic and Heteroleptic of Ag^I-NHCs from bifunctionalized Imidazolium salts.

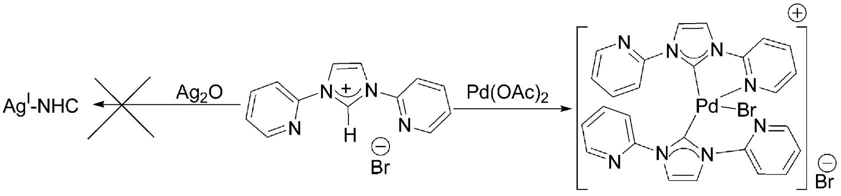
(Ag^I...Au^I ~ 3.25Å) and argentophilic (Ag^I...Ag^I ~ 3.43Å) interactions as determined from the X-ray crystal study.[46b] Using imidazolium salt **XVc** as a carbene precursor, results similar to that of **XVb** were obtained. The structures of the monometallic compound **77** and the trimetallic compound **78** resemble those of **75** and **76**, respectively.[46b]

Compounds **79** and **79a** analogous to **75** and **75a** were isolated from **XVd**, which has two directly linked pyridyl groups.[46b] The $M-C_{carbene}$ bond lengths in **79** are longer than those in **79a** in accordance with Schmidbaur's observation.[47] Reaction of **79a** with $AgBF_4$ did not provide the corresponding trimetallic compound, rather an unusual helical structured heteronuclear polymer **79b** was obtained, possibly due to the rigidity of the NHC. In **79b**, one of the two pyridyl groups on opposing NHCs of an Au^I–NHC fragment are coordinating to the two alternate Ag^I centers and making a polymer.[46b] The Ag^I...Au^I separations (~2.8,2.9 Å) in **79b** are shorter than those in **75b** (~3.2 Å). The photoluminescent properties seem to be tuned by ligands.

Attempts to synthesize an Ag^I–NHC from **XVe** failed. The interaction of halide salts with Ag_2O may be different from that of tetrafluoborate salt **XVd**. That is why the targeted Pd^{II}–NHCs have been prepared from the reaction of the dipyridyl imidazolium salts with $Pd(OAc)_2$ (Scheme 18).[48]

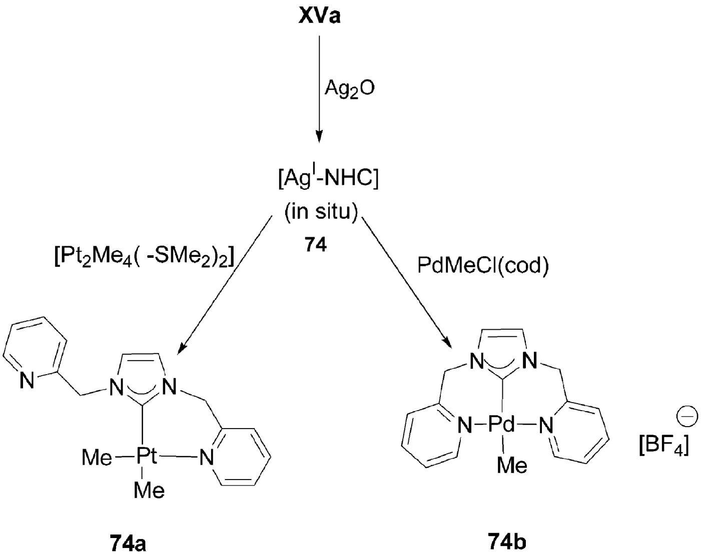
Further, the Ag^I–NHC **74** generated in situ from **XVa** (Scheme 19) was used as a carbene source during the synthesis of Pt^{II}–NHC **74a**,[49] and Pd^{II}–NHC **74b**.[37] Elemental analysis of **74a** reveals the presence of AgCl fragment, but the nature of bonding is uncertain.

The synthesis of **80a** by using the in situ generated Ag^I–NHC **80** of **XVc** led to decomposition. This was proposed to be due to the weaker donor ability of the amine group as compared to the pyridyl group,[37] such that reductive elimination of the methyl group with the carbene in cis position occurred (Scheme 20). Whereas the usage of $PdCl_2(NCPh)_2$

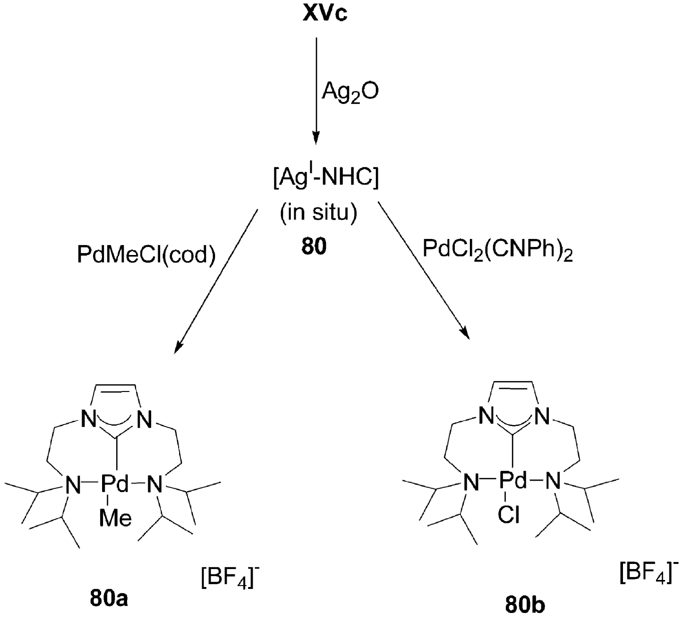


XVe

Scheme 18. Synthesis of Pd^{II} complexes of pyridyl carbene.



Scheme 19. Formation of Pt^{II}–NHC and Pd^{II}–NHC with difunctionalized ligand via carbene transfer from Ag^{I}–NHCs.



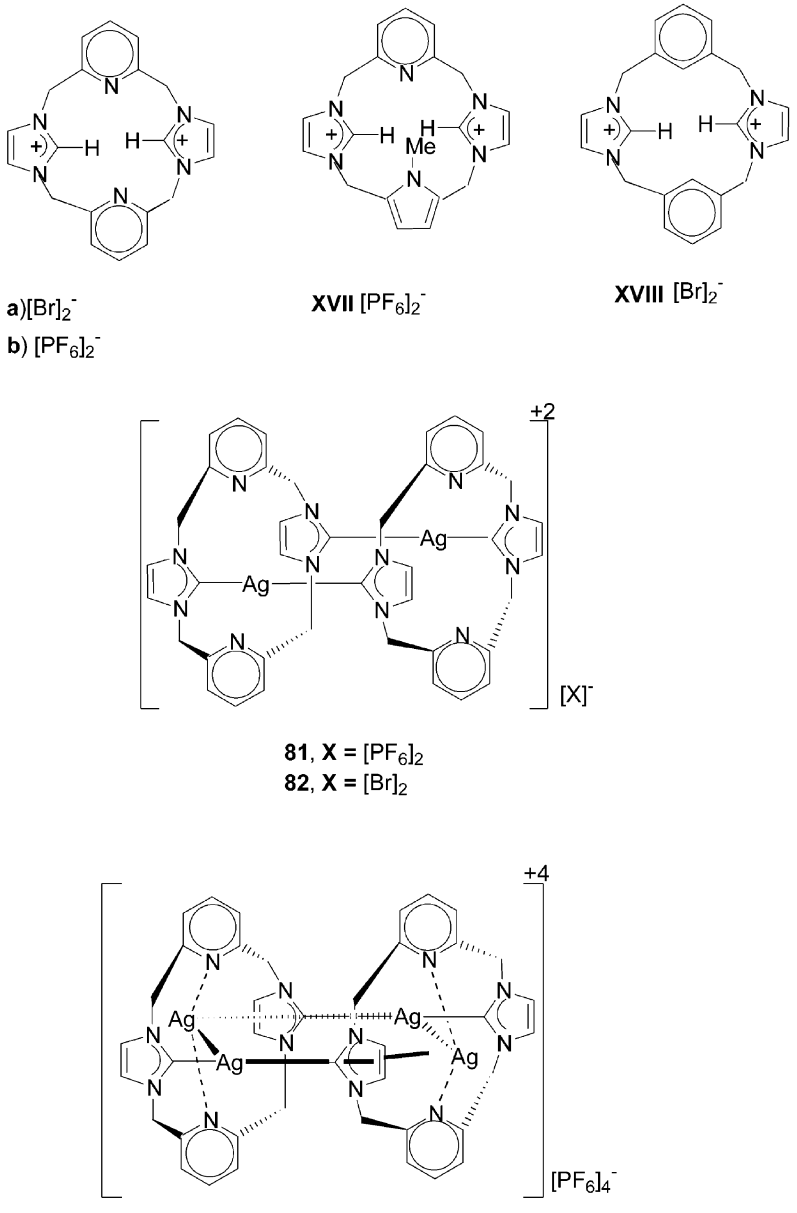
Scheme 20. Formation of Pd^{II}-NHC of isopropylamine linked carbene from Ag^{I}–NHC.

precursor instead of PdMeCl(cod) followed by the addition of $AgBF_4$ in a one pot reaction resulted in a stable complex **80b**, presumably the halogen atom is not prone to reductive coupling with carbene.

b) **Ag^I complexes with bisNHCs Bridged by Additional Donor Atoms**: NHCs bridged with donor groups (through N or O atoms) have been reported as a useful ligand to afford more stable metal-NHC complexes. In this context, dicationic imidazolium-linked cyclophane represents one of the unusual and new class of NHC-precursors and may have tremendous promise in molecular recognition and host-guest chemistry.

Towards this end, Ag^I–NHC linked cyclophane complexes **81–84** were reported for the first time by Youngs' group (Scheme 21).[50–52] Formulation of these compounds depends on the stoichiometries of the reactants and the solvent. Complex **81**, in which two NHC linked cyclophane rings bridged by two Ag^I centers were obtained from the reaction of **XVIa** with Ag_2O in a molar ratio of 2:1 in hot DMSO.[50] Mass spectroscopic information suggests a monomeric structure in the solid state. Compound **82**, the first Ag^I–NHC synthesized in water, was obtained from the reaction of bromo precursor **XVIb** with Ag_2O using a 4:1 molar ratio.[51] With the same stoichiometry, **XVa** produced a tetranuclear complex **83** in hot DMSO.[51] And thus it has been concluded that the reaction is kinetically controlled by solvent in terms of solubility factor. A similar tetranuclear Ag^I–NHC linked cyclophane **84** with a pyridine and pyrrole bridge was synthesized from **XVII**.[52]

It is notable that the ^{13}C-NMR spectrum of **84** displayed two doublet signals for the C^2-carbene, and the determined coupling constants 220 and 47 Hz were claimed for two types of bonding interactions.[52] Unconventional π-bonding interaction between carbene and neighboring non-bridging silver atom was clearly seen in the crystal study of both **83** and **84**. The central planar core of the complex is constructed by two NHC coordinated Ag^I centers and also by two pyridine coordinated Ag^I centers. The Ag-$C_{carbene}$ distances are similar to that of **81**. In this continuation, additional bonding contacts between the NHC and pyridine coordinated Ag^I centers were also observed around $\sim$2.3–2.5Å, which were found to be very similar to those reported for silver-arene π-bonding interactions. And thus it was postulated that these are π-bonding interactions and described as a η^1-carbene silver bond.[53] Further, the distance between a NHC–Ag^I and the adjacent pyridine-Ag^I was observed in the close range with elemental Ag about 2.89 Å. Information



XVI a) $[Br]_2^-$
b) $[PF_6]_2^-$

XVII $[PF_6]_2^-$

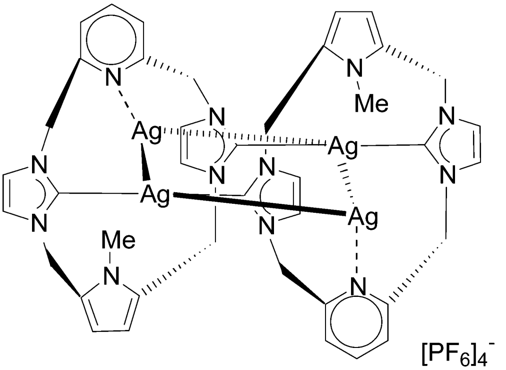
XVIII $[Br]_2^-$

81, X = $[PF_6]_2$
82, X = $[Br]_2$

83

Scheme 21. Formation of NHC linked Cyclophane complexes of Ag^I from Dicationic Imidazolium salts.

on the interaction of benzene bridged cyclophane **XVIII** with Ag_2O has revealed the poor performance of the reaction (not shown).[37]

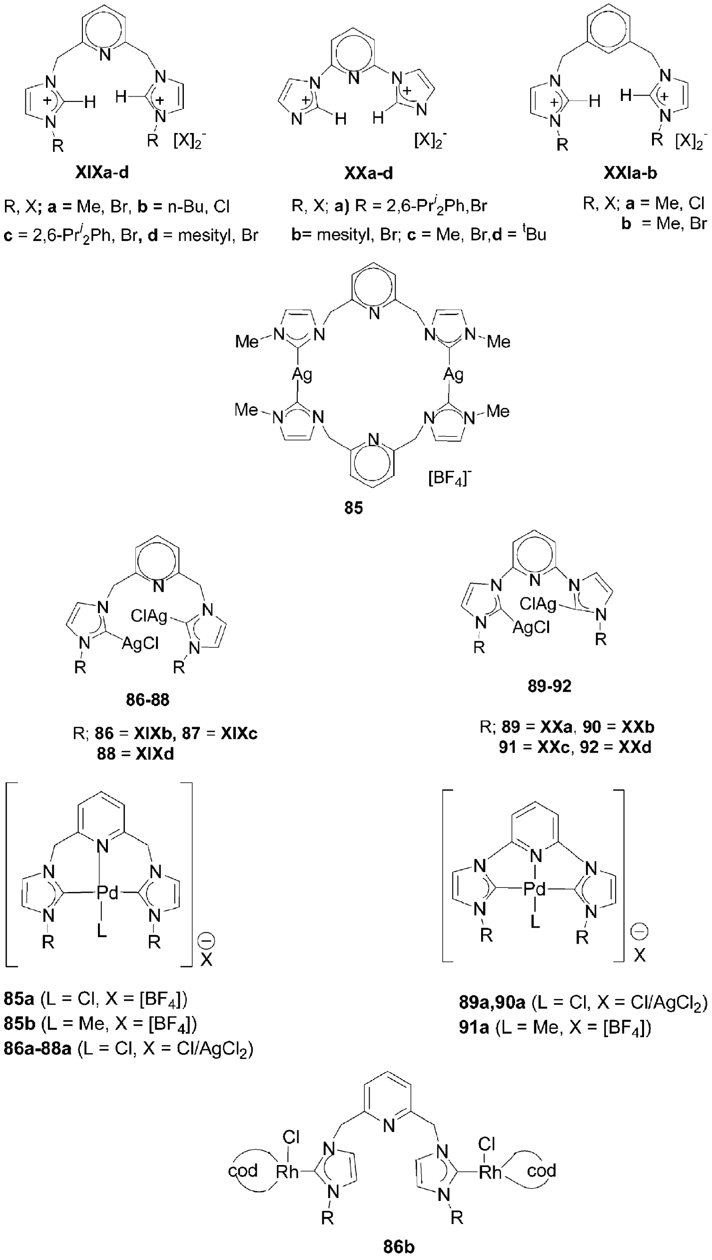


84

Bisimidazolium salts with single bridging unit have also been demonstrated to have varieties of bonding fashions with Ag^I metal center (Scheme 22).

Equimolar reaction between **XIXa** and Ag_2O initially produced an Ag^I–NHC with improportionate stoichiometry, which then treated with $AgBF_4$ to obtain a cyclic dicarbene complex **85** (Scheme 22).[54] The two independent Me-imy rings are appreciably tilted with respect to the central Ag_2C_4 plane.

On the contrary, reactions of Ag_2O with **XIXb–d** and **XXa–b** afforded monomers **86–90** respectively.[36b,54b,55] Crystal structure of **86** shows a noncyclic molecule in which each carbene is coordinated to a separate AgX fragment. The failure of **86** to form metallomacrocyclic-NHC was suggested to be due to the steric requirement of the butyl group.[55] However, **86** possesses intramolecular Ag...Ag interactions with a nearest contact about 2.37Å. All these Ag^I–NHCs (**85–90**) transferred the carbene efficiently to the Pd^{II}center to obtain **85a–90a** (Scheme 22). On the other hand, the Pd^{II}–NHC **91a** was synthesized via Ag^I–NHC **91** generated in situ from **XXc**.[54b] The nature of the Pd^{II} precursor determines the fourth coordinating position. The Ag^I–NHC of the type **92** was also synthesized from **XXd**, but the targeted carbene transfer to PdMeCl(cod) produced only the reductive elimination product 2,6-bis(2-methyl-3-tert-butylimidazolium-1-yl)pyridine.[54b] The use of **86** was further promoted to synthesize the dirhodium NHC **86b** by the reaction with $[Rh(cod)Cl]_2$.[55]



XIXa-d

R, X; **a** = Me, Br, **b** = n-Bu, Cl

c = 2,6-Pr^i_2Ph, Br, **d** = mesityl, Br

XXa-d

R, X; **a)** R = 2,6-Pr^i_2Ph,Br

b= mesityl, Br; **c** = Me, Br,**d** = ^{t}Bu

XXIa-b

R, X; **a** = Me, Cl

b = Me, Br

85

86-88

R; **86** = **XIXb**, **87** = **XIXc**

88 = **XIXd**

89-92

R; **89** = **XXa**, **90** = **XXb**

91 = **XXc**, **92** = **XXd**

85a (L = Cl, X = $[BF_4]$)

85b (L = Me, X = $[BF_4]$)

86a-88a (L = Cl, X = $Cl/AgCl_2$)

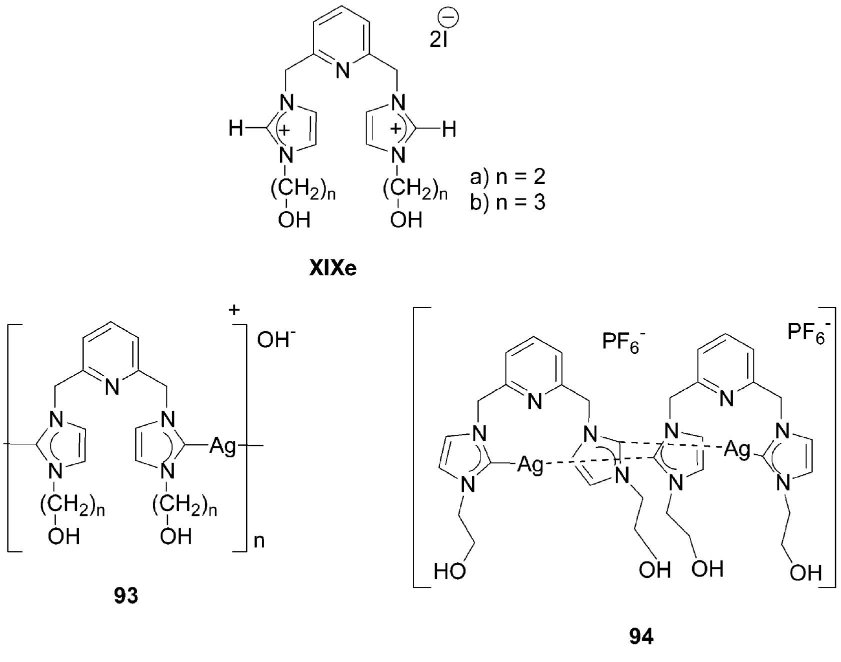
89a,90a (L = Cl, X = $Cl/AgCl_2$)

91a (L = Me, X = $[BF_4]$)

86b

Scheme 22. Ag^I-NHCs and their Pd^{II}, Rh^I-NHC derivatives formed with bisimidazolium salts.

Terminal N-functionality with an alkanol group as shown in **XIXe** was employed to synthesize Ag^I NHCs of **93** and **94** (Scheme 23).[56] Compound **93** is a water-soluble Ag^I–NHC adopts a one dimensional polymeric structure in the solid. However, in solution and gas phase it exists as a monomer. Reaction of **93** with aqueous NH_4PF_6 yielded a water-insoluble dimmer **94**. The choice of anion has a pronounced effect on the structures adopted and consequently on their solubility. Owing to its water-solublity nature, **93** demonstrated its use as the first Ag^I–NHCs containing antimicrobial agent.



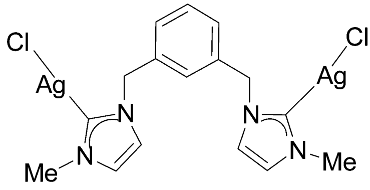
XIXe

93

94

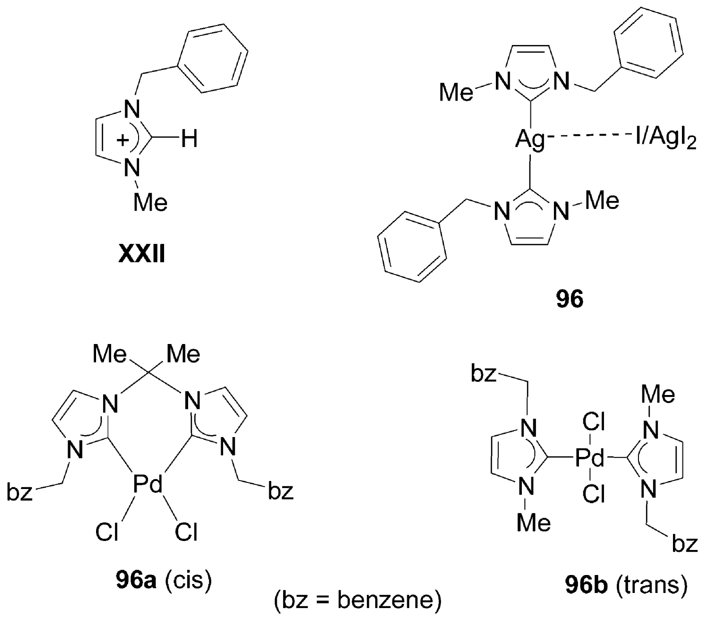
Scheme 23. Ag^I-NHCs formed with Alkanol N-substituents.

The bisimidazolium salt **XXI** differs from **XIX**, in that the bridging pyridine was replaced by bridging benzene (Scheme 22). Reaction of Ag_2O with **XXIa** produced **95**.[57] Crystal structure of **95** shows that the two imidazolium ring planes are approximately perpendicular to the phenyl ring and consequently the molecule exhibits a chair–like conformation, which results in very weak intermolecular Ag…Ag distances of ~4 Å and Ag…Cl contacts of ~3.6 Å and consequently a 3-D network.



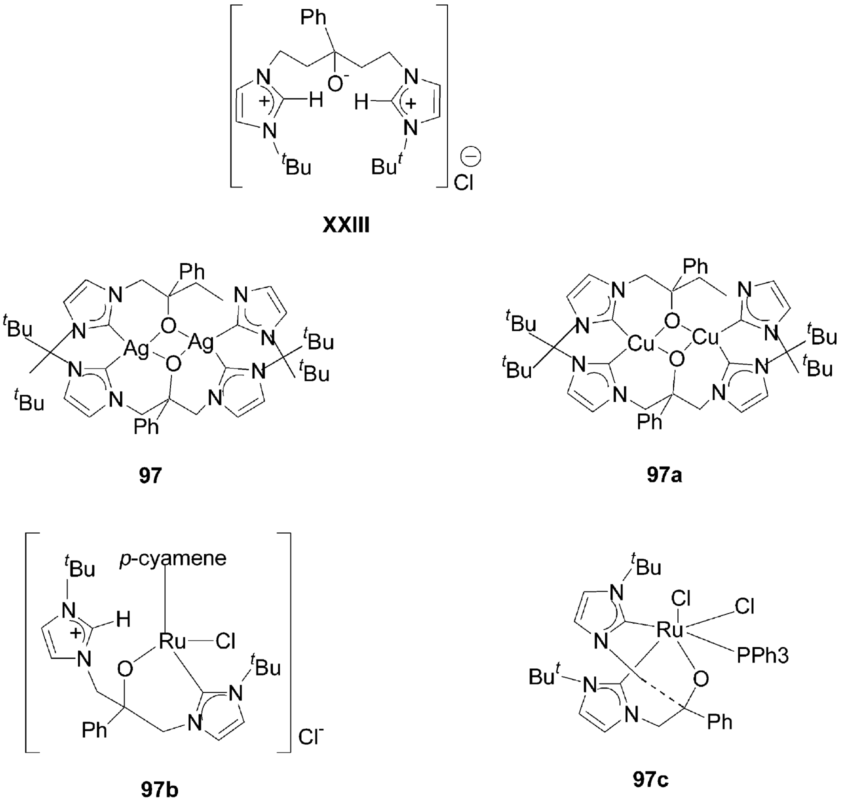
95

When the bromide salt **XXIb** was used, the yield of the product was very low (not shown).[37] The Ag^I–NHCs of the type **95** seems to serve as useful precursors to derive other transition metal-NHCs with C^C^C pincer modeling. However C^C^C pincer type NHC complexes with Pd^{II} have already been synthesized by other methods.[36b,58] On the other hand, when the Ag^I–NHC of the type **96** derived from **XXII** containing benzene in the N-terminated chain, its interaction with $Pd(MeCN)_2Cl_2$ gave cis complex **96a** and with Pd(Me)Cl(cod) provided a trans complex **96b** reveals that benzene in N-terminated chain may not act as a hemilabile group (Scheme 24).[37]



Scheme 24. Ag^I–NHC and its Pd^{II}–NHC derivatives with benzyl side arm.

The first neutral and halide free Ag^{I}–NHC **97**, which has an anionic NHC-based ligand with alkoxy functional group was obtained from **XXIII** (Scheme 25).[59] While simple Ag^{I}–NHCs did not react with copper halides, carbene transfer reaction between compound **97** and CuI has proceeded effectively in CH_2Cl_2 to produce dimeric Cu^{I}–NHC **97a**.



XXIII

97

97a

97b

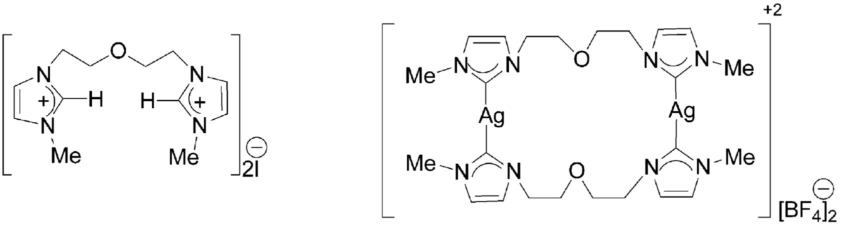
97c

Scheme 25. Formation of halide free Ag^{I}–NHC and its Cu^{I}, Ru^{I}, Ru^{III}–NHC derivatives.

The use of **97** was further promoted to obtain novel ruthenium carbenes (Scheme 25).[60] When **97** was reacted with $[Ru(p\text{-cymene})Cl_2]_2$ in dichloromethane, produced a Ru^{II}–NHC **97b**, having a bounded NHC and free imidazolium cation. The same reaction in THF also gave **97b**. On the other hand, reaction of **97** with $[RuCl_2(PPh_3)_3]$ led to the oxidation of Ru^{II} center and produced a first stable trivalent Ru^{III}–NHC

97c leaving behind the silver metal precipitate. It was reasoned that the oxidation potential of Ag^{I} to Ag^{0} in **97** is high enough to oxidize the Ru^{II} in $[RuCl_2(PPh_3)_3]$, but not enough in $[Ru(p\text{-cymene})Cl_2]_2$.[61]

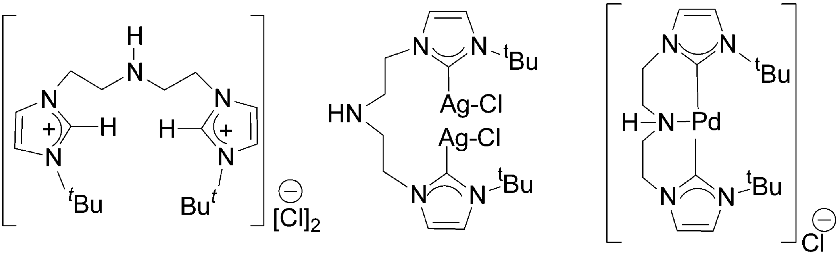
In the series of bridging carbene complexes, Ag^{I}–NHC containing an etheric bridge has also been synthesized (Scheme 26).[62] Reaction of the iodide salt **XXIV** with Ag_2O followed by the addition of $AgBF_4$ resulted in **98**. Information from NMR and mass spectra suggests a dinuclear species.



XXIV **98**

Scheme 26. Ag^{I}–NHC formed with ether bridged bisimidazolium salt.

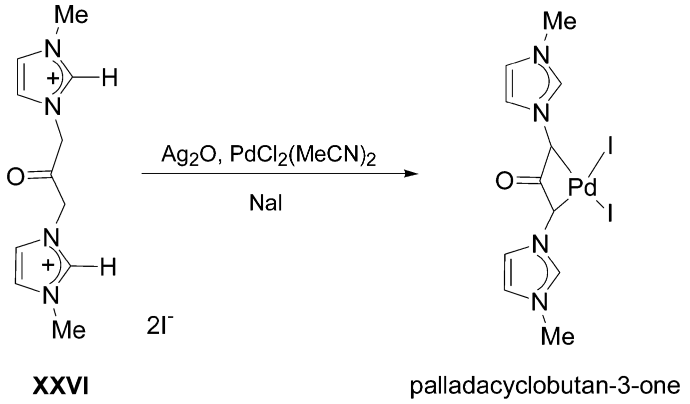
Very recently, the use of a biscarbene precursor **XXV**, which has a secondary amine linker, was also explored via Ag^{I}–NHC route (Scheme 27).[63] The dicarbene complex **99** obtained in CH_2Cl_2 underwent carbene transfer reaction with $PdCl_2(MeCN)_2$ to afford **99a**, the first example of NHC-metal complex with a secondary amine.



XXV **99** **99a**

Scheme 27. Pd^{II}–NHC, the first example of NHC-metal complex with a secondary amine.

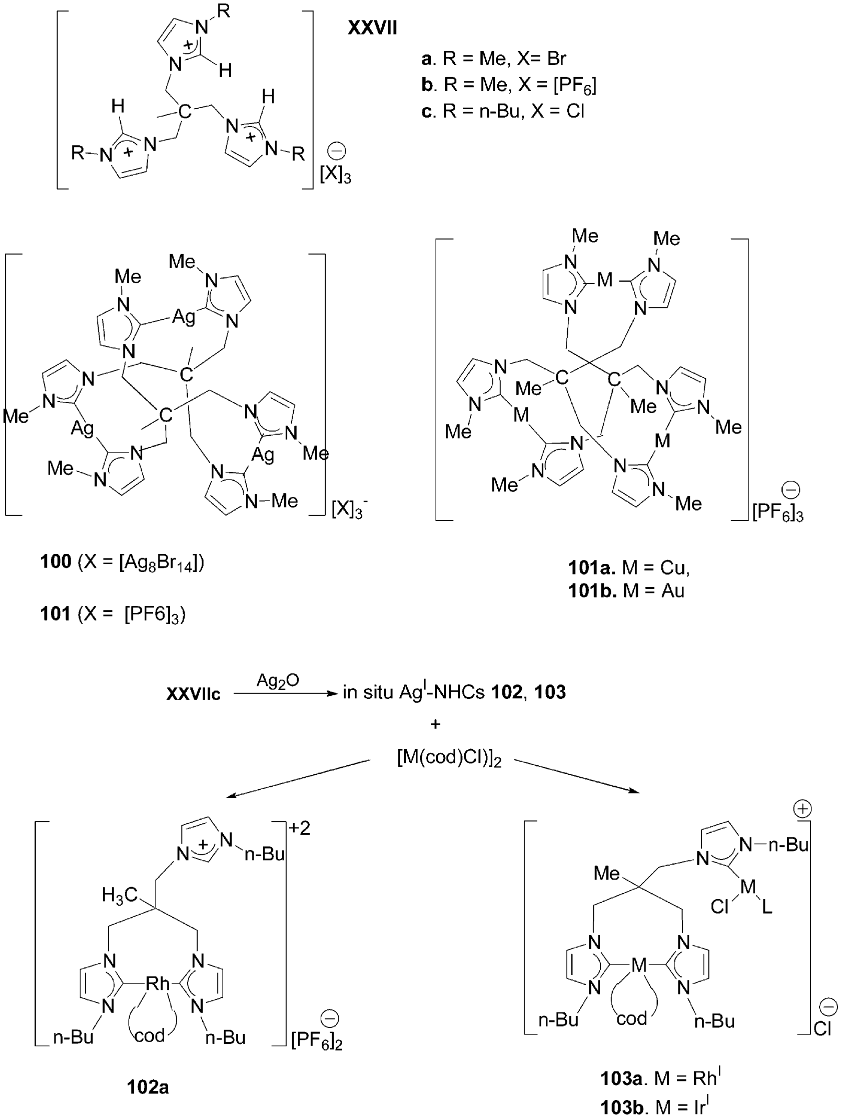
However, when the dicationic imidazolium salt **XXVI** is bridged by a highly electron withdrawing carbonyl group, its interaction with $PdCl_2(MeCN)_2$ in the presence of Ag_2O led to the deprotonation at the more acidic methylene groups and produced the palladacyclobutan-3-one instead of a Pd^{II}–NHC [eqn. (10)].[64]



(10)

c) Ag^Icomplexes with PolyNHC Motifs Containing Carbon or Nitrogen Anchors: In comparison with the biscarbenes (C^C), coordination compounds of polycarbenes are relatively rare.[65] To this end, imidazolium salts (neo pentane based) **XXVIIa-b**, a precursor for tripodal NHCs (tricarbene precursors) was reacted with Ag_2O to give complexes **100** and **101** from hot DMSO by Meyer's group (Scheme 28).[66, 67] In the solid state, compound **100** exists as an adduct of two cationic carbene complexes bridged by a cluster of silver bromide anion through two bridging bromides. Crystal structure of **101** showed that the three Ag^I centers are bridged by two tripodal NHC fragments via each of the three pendant arms.

In comparison to the free imidazolium ring, elongated C–N bonds and smaller $N{-}C_{carbene}{-}N$ angles in the complexed carbene supports the decrease in nitrogen-to-carbene π bonding and increase in p-character at C^2-center. Since this situation has arisen during the coordination with moderately electron rich Ag^+ center, thus Mayer anticipated the existence of non-negligible π-back donation to the carbene. DFT calculations of this compound (**101**) shows that there is a significant overlap of fully occupied metal d(xz) and d(yz) orbitals with partially empty π/π^* hybrid orbitals. The elongated C–N bond lengths are consistent with the values



100 ($X = [Ag_8Br_{14}]$)

101 ($X = [PF6]_3$)

101a. M = Cu,
101b. M = Au

102a

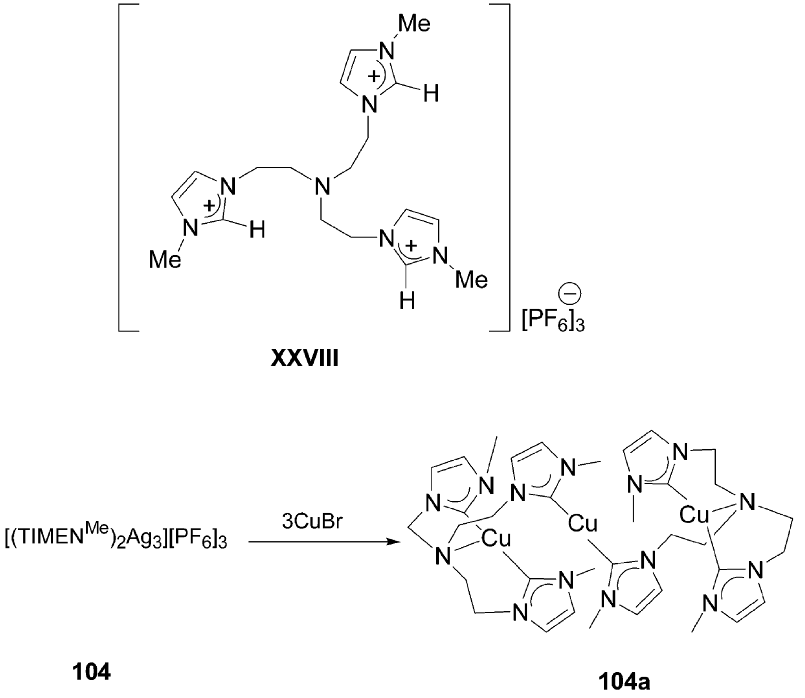
103a. M = Rh^I
103b. M = Ir^I

Scheme 28. Formation of Ag^I–NHCs with tricarbene ligands and their NHC derivatives with Cu^I, Au^I, Rh^I, Ir^I.

obtained by DFT study. This phenomenon has been further supported by comparing the structural parameters of three iso-structural biscarbene complexes $M(NHC)_2$ ($M = I^+$, Ag^+ and Ni^0).[19, 68]

Compound **101** was used to produce the iso-structural Cu^{I}–NHC **101a** and Au^{I}–NHC **101b** under dry N_2 atmosphere.[67] The same reactions in air produced imidazolium salts, suggesting that the reaction proceeded via free carbene intermediate as was observed during the synthesis of tungsten diamino carbene complex. In a recent article, the use of **XXVIIc** was described to produce the Rh^{I}–NHC **102a** and **103a** and Ir^{I}–NHCs**103b** from the in situ generated Ag^{I}–NHC **102** and **103**, respectively.[69] It appears that due to the steric factors, the ligand **XXVIIc** is unable to coordinate to the metal center in a tripodal fashion as **XXVIIa** in **101** or other analogous.

Replacement of carbon anchor by nitrogen into the tripodal-NHC system produced the first N-anchored tetradentate tricarbene ligand, which can serve as structural mimics of metal containing enzymes.[70] Reaction of this tetradenate ligand precursor **XXVIII** with Ag_2O produced a Ag^{I}–NHC **104**, isostructural to **101**, and was employed to prepare the Cu^{I}–NHC **104a** (Scheme 29).[70]



XXVIII

104

104a

Scheme 29. Ag^{I}-NHC and its Cu^{I}-NHC derivative from N-anchored tricarbene ligand.

2.2.3 Ag^I–NHCs Containing Chiral NHCs. Chiral transition metal complexes play a prominent role in metal catalyzed enantioselective synthesis and asymmetric reactions.[71] In this respect, Ag^I complexes formed with chiral NHC are recognized as useful starting materials to produce other chiral transition metal complex catalysts. Mangeney et al. proved that Ag_2O can interact selectively with the less acidic imidazolnium salts **XXIXa–f** to produce chiral imidazolin-2-ylidene based Ag^I–NHCs **105–116** (Scheme 30).[72, 73, 74] Note that using the imidazolinium salt with ferrocenyl substituent, Bieldstein was not able to obtain the corresponding Ag^I–NHC.[33] The ^{13}C-NMR signals observed above 200 ppm for some of these Ag-$C_{carbene}$ coordinations are higher than many other established work. However, in Herrmann work also the ^{13}C-NMR signals observed above 200 ppm for Ag^I–NHCs with pyrimidinium carbene and ascribed for highly strong Ag-$C_{carbene}$ coordination.[39] Crystal structure of compound **105**, a dimeric form bridged by iodides, represents a considerable variety in the family of Ag^I–NHCs NHCs and also in metal-NHCs. Crystal structure of compound **106** indicates a mononuclear species.

The Ag^I–NHCs of Mangeney's work behaved differently from the Herrmann's proposal during the carbene transfer.[39] Transmetallation between **106** and $PdCl_2(MeCN)_2$ occurred smoothly and produced **106a–b** at room temperature.[75] The same approach either with **107** or **110** did not give the desired products even under refluxing conditions.[73] Therefore $[Pd(allyl)Cl]_2$ was used as the palladium source, which gave **107a** and **110a,** correspondingly.[73] The Ag^I–NHCs **105** and **111–116** were used as source of NHC to produce imidazolin-2-ylidene copper complex catalysts during the enantioselective conjugate addition of dialkyl zinc to enones.[74,76] It was commented that the usage of Ag^I–NHCs gave better results than the imidazolium salts in the supplying of NHC and consequently the yield of catalytic reaction.

Bisimidazolium salts (**XXXa–f**) consist of diamide chiron bridge produced the Ag^I–NHCs **117–122** (Scheme 31).[77,71] Carbene transfer from compounds of **117–120** to $Pd(MeCN)_2Cl_2$, furnished the Pd^{II}–NHCs **117a–120a** at room temperature, but for the compound of **121** the compound **121a** was obtained under microwave conditions. Due to the bulkiness of R-group in compound **122**, the carbene transfer to Pd^{II} was unsuccessful.

Trans-1,2-diamino cyclohexane derived monoimidazolium imine bromides **XXXIa–d** and bisimidazolium bromides **XXXIIa–c** were used

XXIXa-f

105-116

R$_1$, R$_2$, X$^-$;

XXIXa = Me, I, **b** = benzyl, Br,

c = *i*-Pr, Br, **d** = Picolyl, Cl,

e = (S)-1-phenylethyl, (OAc),

f = (S)-1-phenylethyl, I,

g = (S)-1-phenylethyl, Cl,

h = (S)-1-phenylpropyl, Cl,

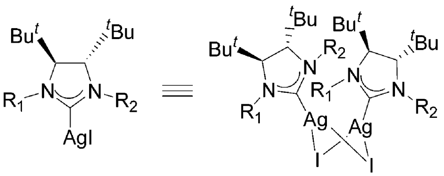
i = (S)-1-napthylethyl, Cl,

j = benzyl, Cl, **k** = methoxybenzyl, Cl

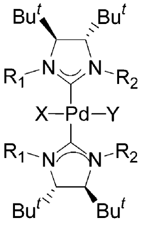
l = Me, Cl

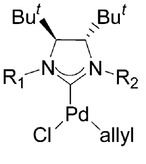
R$_1$, R$_2$;

105 = XXIXa, 106 = XXIXb,
107 = XXIXc, 108 = XXIXd,
109 = XXIXe, 110 = XXIXf
111 = XXIXg, 112 = XXIXh
113 = XXIXi, 114 = XXIXj
115 = XXIXk, 116= XXIXl



105

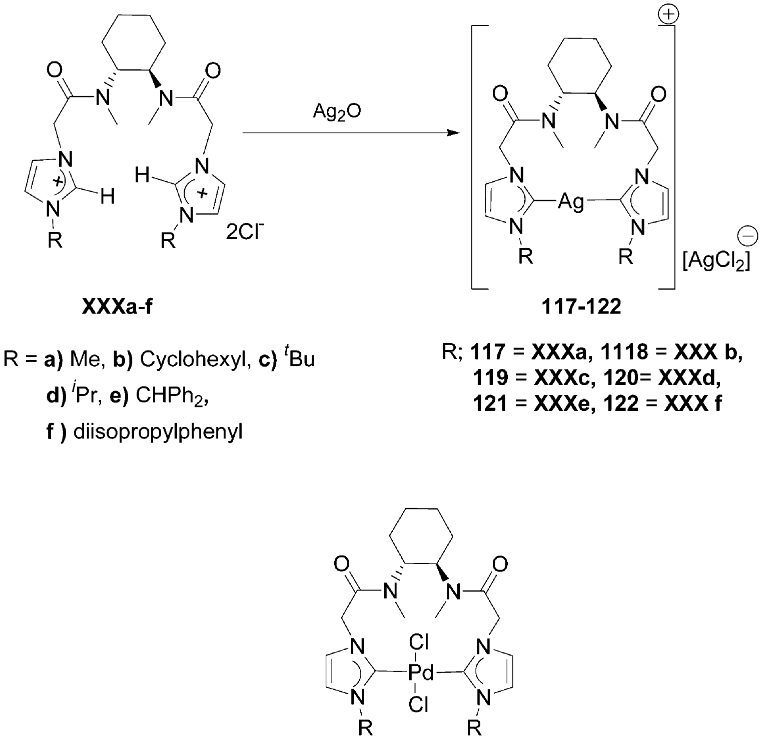




107a, 110a

106a. X = Y =Cl
106b. X = Br, Y = Cl

Scheme 30. Ag^{I}-NHCs and their Pd^{II}-NHC derivatives formed with chiral imidazolin-2-ylidene carbene ligands.



XXXa-f

R = **a)** Me, **b)** Cyclohexyl, **c)** ^{t}Bu
d) ^{i}Pr, **e)** CHPh$_2$,
f) diisopropylphenyl

117-122

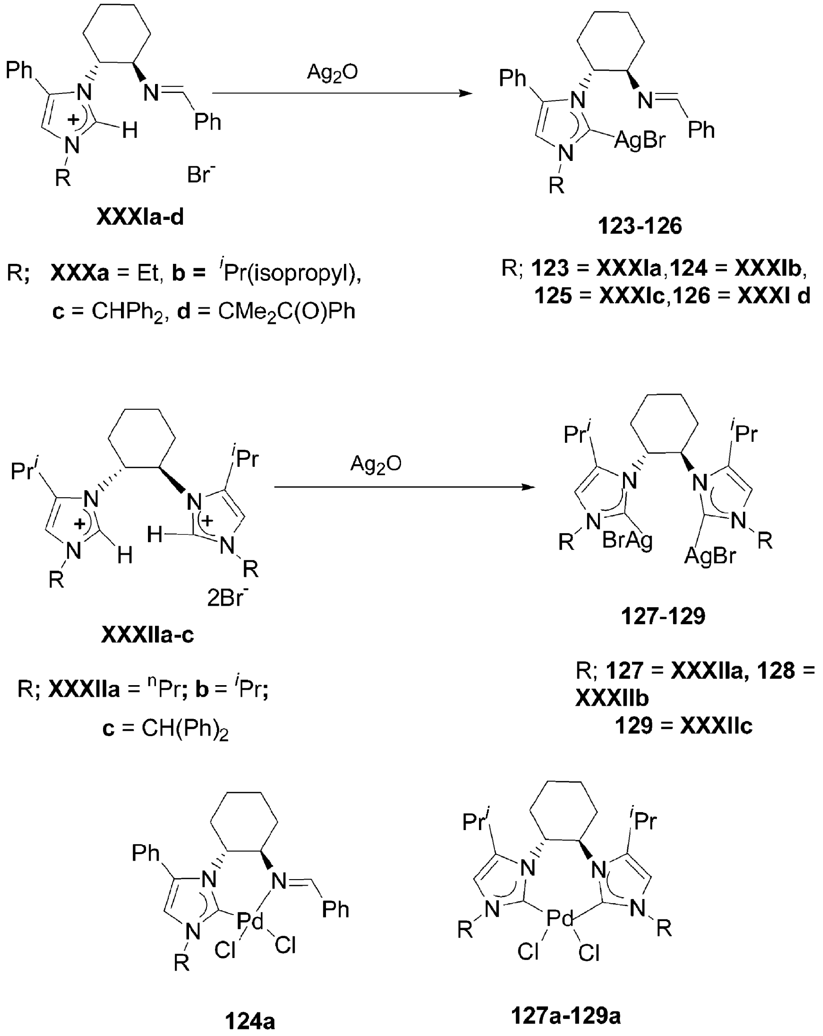
R; **117 = XXXa, 1118 = XXX b,**
119 = XXXc, 120= XXXd,
121 = XXXe, 122 = XXX f

117a-121a

Scheme 31. Ag^{I}-NHCs and their Pd^{II}-NHC derivatives formed with chiral diamide based NHC ligands.

to synthesize Ag^{I}–NHCs of constrained geometry (**123–129**) (Scheme 32).[78] Carbene transfer from **124** and **127–129** to PdCl$_2$(MeCN)$_2$ afforded the mononuclear complexes **124a** and **127a–129a** respectively in MeCN at 90°.

NHCs with chiral oxazoline linkage represent a new class of C^N donor ligands and form stable complexes with transition metals.[79] In this respect, Ag^{I}–NHC **130** has been synthesized from imidazolium bromide **XXXIII** (Scheme 33).[80] In the solid state **130** is a monomer in which the mesityl ring orients orthogonally to the imidazolium ring plane. The oxazoline N-atom is pointing away from the Ag^{I} center. Upon carbene transfer, chelated Pd^{II}–NHC **130a** has been generated at room temperature.



XXXIa-d

R; **XXXa** = Et, **b** = ^{i}Pr(isopropyl), **c** = CHPh$_2$, **d** = CMe$_2$C(O)Ph

123-126

R; **123** = **XXXIa**, **124** = **XXXIb**, **125** = **XXXIc**, **126** = **XXXI d**

XXXIIa-c

R; **XXXIIa** = ^{n}Pr; **b** = ^{i}Pr; **c** = CH(Ph)$_2$

127-129

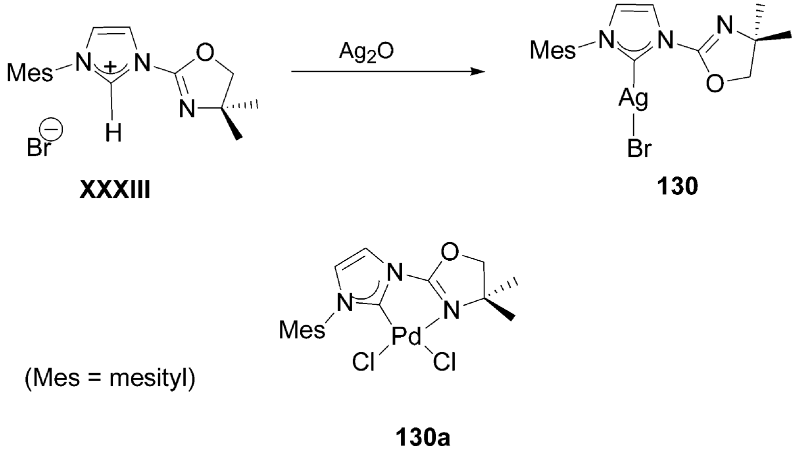
R; **127** = **XXXIIa**, **128** = **XXXIIb** **129** = **XXXIIc**

124a

127a-129a

Scheme 32. Ag^I-NHCs and their Pd^{II}-NHC derivatives formed with chiral-amine based NHC ligands.

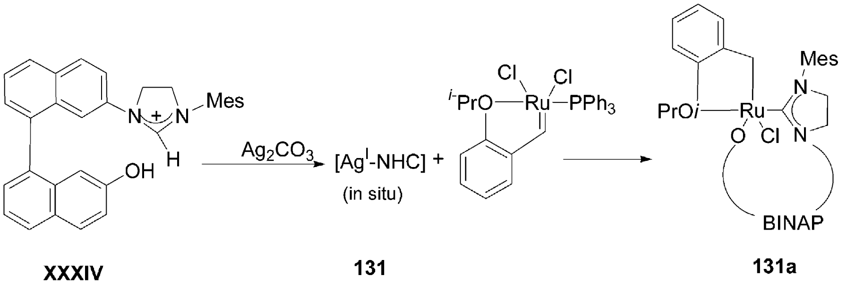
Hoveyda and his co-workers described the synthesis of a recyclable chiral Ru^{II}–NHC catalyst **131a** via the in situ generation of Ag^I–NHC **131** (Scheme 34).[81] In this one pot reaction, imidazolium salt **XXXIV** was interacted with Ag$_2$CO$_3$ followed by a Ru^{II} precursor and produced the compound **131a**.



XXXIII **130**

(Mes = mesityl) **130a**

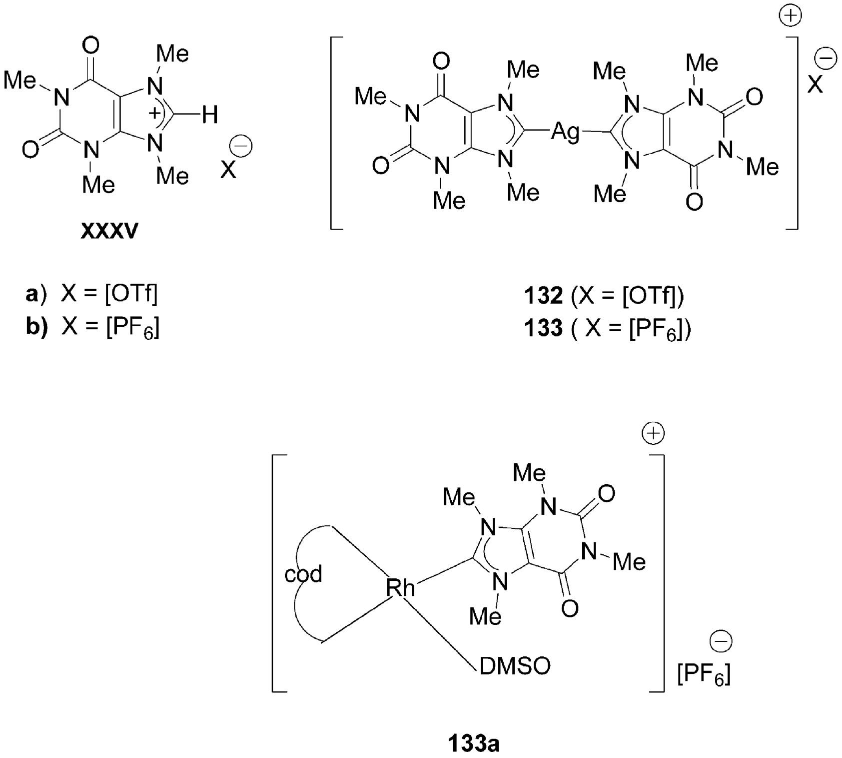
Scheme 33. Formation Ag^I–NHC and its Pd^{II}–NHC derivative with chiral oxazoline based NHC ligand.



XXXIV **131** **131a**

Scheme 34. Formation of Ru^{II}–NHC with chiral BINAP based NHC ligand via carbene transfer from Ag^I–NHC.

Special Cases. Metal ions, participation in enzymatic functions is well known. Metal complexes with biologically functionalized xanthine derivatives have been developed extensively over the last few decades. In this area, nitrogen–bounded Ag^I complexes are only familiar.[82] For the very first time, Youngs' group used caffeine derived from xanthine as a source to produce Ag^I–NHC complex (Scheme 35).[83] Reaction of methylated caffeine **XXXVa** and Ag_2O was conducted smoothly in water to produce **132**. Hot DMSO was used in the reaction of $[PF_6]^-$ salt of methylated caffeine **XXXVb** to afford **133**. Carbene transfer from **133** to $[Rh(cod)Cl]_2$ produced the Rh^I NHC **133a**.



XXXV

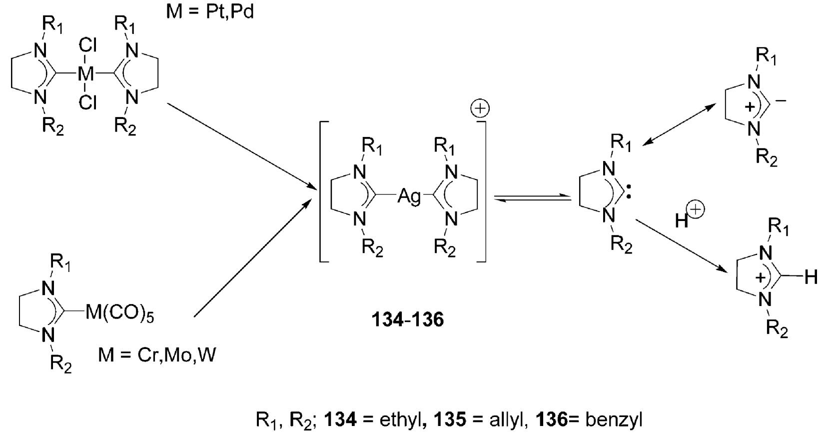
a) X = [OTf]
b) X = [PF$_6$]

132 (X = [OTf])
133 (X = [PF$_6$])

133a

Scheme 35. Formation of Ag^I–NHCs from caffeine derived imidazolium-carbene ligand precursors and the corresponding Rh^I–NHC derivative.

A contradictory result has been reported that the Ag^I–NHCs **134–136** can be obtained by the transfer of non-aromatic NHCs (imidazolin-2-ylidene) from W^{III} or Mo^{III} or Cr^{III} or Pt^{II} or Pd^{II}–NHC complexes (Scheme 36).[84] It was concluded that the Ag^I–NHCs obtained by this method are air-sensitive, decomposes immediately to the respective basic carbene and then turns immediately to imidazolinium salt by protonation. The above synthetic reaction is irreversible and stated that the Ag^I–NHCs synthesized by this method could not serve as carbene transfer agents due to the more basic nature of this imidazolin-2-ylidene. In contrary, stable Ag^I–NHCs with imidazolin-2-ylidene carbene has been synthesized by using Ag$_2$O technique,[71–74] and have been employed efficiently as carbene transfer agents to produce the Pd^{II}–NHCs and Cu^I–NHCs.



Scheme 36. Formation of Ag^I–NHCs from Group VI and X metal-NHCs.

3. CONCLUDING REMARKS

The literature survey on Ag^I–NHCs indicates that numerous Ag^I–NHCs have been reported within a very short period. Although the first Ag^I–NHC was reported in 1993, the major advancement in the literature has been observed only after the discovery of their carbene transfer ability to other catalytically important transition metals in 1998. It has been highlighted in the literature that the synthesis of Ag^I–NHCs through the in situ deprotonation of NHC precursors selectively at the C^2-position by Ag_2O, and their effective carbene transfer efficiency can provide a convenient way to overcome the difficulties arising from the use of strong base, regorous solvent pretreatment, anaerobic conditions and sophisticated glasswares to yield the free carbenes. The use of Ag_2CO_3 as an alternative to Ag_2O is limited to a few examples.

The electronic effects imposed on the structural modeling and properties of Ag^I–NHCs and other transition metal-NHCs have been studied by varying the N-substituents and counter anions of the imidazolium salts, the NHC precursors. Results with imidazolium halide salts showed that Ag^I–NHCs were isolated as ion-pairs $[Ag(NHC)_2][AgX_2]$ or monomeric neutral complexes [Ag(NHC)X]. A possible equilibrium has been proposed between ion-pair and neutral species in the solution. In few instances, the ion-pairs were formed with improportionate stoichiometries, but it had no effect on their carbene transfer efficiency. Synthetic reactions in chlorinated solvents have maintained the metathesis of iodide and bromide by chloride. The use of [BF_4] or [PF_6] or [NO_3] salts avoided the formation of ion-pairs and also improved the stability and solubility of the complexes.

The N-substituents have great influence on product formation. With simple short N-alkyl substituents the products isolated are markedly distinguishable from those containing long chain alkyl substituents. When N-substituents contain donor atoms as studied in section **2.2.1a** and **2.2.1b** [C^N^C, C^C^C type], the synthesis of Ag^I–NHCs provides an easy access to other metal-NHCs with hemilabile coordination. Ag^I complexes with cyclophane linked NHCs or tripodal-NHCs provide new molecular conformations. Ag^I–NHCs of these classes consisting of multidentate ligation may play a useful role in molecular recognition and host-guest chemistry. Complexes of chiral NHCs with Ag^I have also emerged as a useful source for the ready accessment of several Pd^{II}–NHCs, which are most useful for asymmetric catalysis. Such efforts with other transition metals are highly encouraging. Metal complexes of less acidic imidazolinium and pyrimidinium carbene were also accessed via the respective Ag^I–NHCs.

Structural variations of the Ag^I–NHC depends on the nature of the NHC and the Ag...X (halide or other counter ion) interactions. As observed in the literature, the Ag^I ion has high affinity for carbene carbon and exhibits linear or trigonal or tetrahedral coordination in Ag^I–NHCs. The ability of NHC ligands in the stabilization of silver clusters by supporting the short Ag–Ag separations (argentophilicity) is quite recognizable in making the supramolecular assemblies. However, when compared to the aurophilicity, studies concerning the influence of argentophilicity on the luminescent properties of Ag^I–NHCs are very rare. Crystal structures of Ag^I–NHCs **81–84**, **101** and **105** are observed to be quite novel in metal-NHC chemistry. Apart from the structure of complex cation in an ion-pair, the structure adopted by a silver halide [(Ag-X)n] complex depends on the size of the halide atoms, on the steric bulk of the ligand, and on the solvent from which it was isolated.

The lack of Ag–$C_{carbene}$ bond coupling in several Ag^I–NHCs indicates the lability of Ag–$C_{carbene}$ bond, which appears to be one of the reasons to realize their application as carbene transfer agents. Normally the carbene transfer is accompanied by the thermodynamically favorable precipitation of solid silver(I) halide. According to the very first report on carbene transfer reactions of Ag^I–NHCs (**6** and **7**), it was described that inert atmosphere is not necessary during the carbene migration from Ag^I–NHC to other transition metals. On the other hand, the transfer of carbene from Ag^I–NHC **98** to Cu^I–NHC **98a** had to be carried out under dry N_2 atmosphere. In the presence of air, imidazolium salts were produced. These results suggest that this specific reaction proceeded via free carbene intermediate as was observed during the synthesis of tungsten diamino carbene complex. The carbene transfer reaction needs further study to understand the detailed mechanism.

DFT calculations made on Ag^I complex (**98**) of tripodal-NHC support the existence of non-negligible π-back bonding. At this confluence it would be better to mention the theoretical calculations concept published by Frenking's group on the nature of metal-ligand bonding in coinage metal-NHCs. In the first report,[85] quantum mechanical ab initio calculations on bond lengths and energies of (NHC)CM(Cl) (CM = coinage metal) showed that the electrostatic attractions between the positively charged metal ion and the lone pair of the NHC contribute strong ionic character to the $M–C_{carbene}$ bond. The counter line diagram for molecular orbital interaction indicated little π-back bonding from the metal to the ligand. The calculated dissociation energies for the NHC complexes decrease in the order of Au > Cu > Ag. Recently the contributions of σ and π bonding orbitals to the $M–C_{carbene}$ in the coinage metal-NHCs (both mono and dicarbene) have been calculated using an EDA (energy decomposition analysis) method.[86] According to the EDA study, the covalent contribution is $<35\%$ of the total attractive interaction in the $M–C_{carbene}$ bonds and the out-of-plane π back bonding contributes $\sim 20\%$ to the total orbital interaction, which is not substantially smaller than that in Fischer carbene complexes.[87]

The ruthenium-NHC complexes are known as the most active catalysts for several chemical transformations. The Ag^I–NHC route now proved as one of the easy method to access the stable ruthenium-NHC complexes (**86b**, **86c** and **114a**) in both lower and higher oxidation states. Oxidation of phosphine based Ru^{II}–NHC **86b** to Ru^{III}–NHC **86c** by Ag^I–NHC **86** indicates the probability of deriving other metal-NHCs with higher oxidation states.

Manipulating the electronic parameters at C^2- and C^4- positions of simple imidazolium salts has produced the abnormal C^5-bonded Ir^I–NHCs via the transfer of carbene from the in situ generated C^5-bonded Ag^I–NHC. Since the C^5-bonded NHC is a very strong electron donor, efforts with other metal ions have to be promoted.

Apart from the carbene transfer efficiency, Ag^I–NHCs are going to gain relevance in medicinal applications. For example, Youngs' group reported the water-soluble pincer Ag^I–NHC as a novel antimicrobial agent. The isolation of Ag^I–NHC from caffeine, a xanthine derivative containing imidazole moiety, may explore the biological systems as a possible source to isolate a similar kind of metal-NHC systems.

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