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Review

# Preparation and application of N-heterocyclic carbene complexes of Ag(I)

Ivan J.B. Lin*, Chandra Sekhar Vasam

*Department of Chemistry, National Dong Hwa University, Shou-feng, Hualien 974, Taiwan*

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## Contents

## Abstract

The current status (up to 31 July 2006) of Ag(I)–NHCs (NHC = N-heterocyclic carbene) is presented with various NHC systems ranging from five membered to seven membered rings, including imidazolium, benzimidazolium, imidazolinium, triazolium, pyrimidinium, pyrazolium, seven-membered amidinium, and naphthimidazolium moieties, etc. It is our intention to provide an updated, and comprehensive review on the subject of Ag(I)–NHCs, which may further accelerate work on this topic. The main features of this review are to focus on (a) the ease and limitations in the synthesis of Ag(I)–NHCs, (b) the parameters influencing the solid state structures of Ag(I)–NHCs, and (c) the efficacy of Ag(I)–NHCs in transmetallation reactions. In particular, we would like to evaluate the widely adopted $Ag_2O$ technique in the preparation of Ag(I)–NHCs and the subsequent NHC transfer reactions, to afford other metal–NHCs.

*Keywords:* Silver(I) N-heterocyclic carbenes; Metal N-heterocyclic carbenes; Transfer of N-heterocyclic carbenes; Nano-silver

## 1. Introduction

In the past few years, N-heterocyclic carbenes (NHCs) have emerged as versatile ligational building blocks for a large variety of coordination compounds [1]. Earlier work considered NHCs as phosphine analogues, but the recent observations emphasized some differences in steric and electronic properties and thus their chemical behavior [2]. Since these ligands act as excellent strong σ-donors, they can produce stable metal–NHCs with strong metal–carbon bonds. For this reason, the metal–NHCs have been widely used as highly reactive and rather selective catalysts for numerous chemical transformations [3]. The utilization of metal–NHCs has also been useful in medicinal science applications [4]. Many research groups around the world are currently focusing on metal–NHC complexes.

Because of the usefulness of the metal–NHC complexes, many synthetic methods have been explored. According to the reports published on metal–NHCs, the most widely used preparation methods can be divided broadly into five types: (1) reaction of free NHCs with metal precursors [5], (2) reaction of electron-rich olefin dimers with organometallic fragments [6], (3) reaction of imidazolium salts with suitable basic transition metal salts [7], (4) reaction of azolium salts with metal precursors under basic phase transfer catalysis (PTC) con-

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*Abbreviations:* NHC, N-heterocyclic carbene; Me, methyl; Et, ethyl; $^i$Pr, isopropyl; $^n$Bu, *n*-butyl; $^t$Bu, tertiary butyl; Np, neopentyl; Mes, mesityl; Ph, phenyl; $PPh_3$, triphenylphosphine; cod, cyclooctadiene; 2,6-$^i$Pr$_2$-Ph, 2,6-diisopropylphenyl; Py, pyridyl; Pyrr, pyrrole; bn, benzyl; MeCN, acetonitrile; OTf, triflate; imy, imidazol-2-ylidene; bimy, benzimidazol-2-ylidene; tazy, triazol-2-ylidene; –CH(Ph)$_2$, diphenyl methyl; NP, nanoparticle; EA, elemental analysis; NMR, nuclear magnetic resonance

* Corresponding author. Tel.: +886 3 863 3599; fax: +886 3 863 3570.
*E-mail address:* ijblin@mail.ndhu.edu.tw (I.J.B. Lin).

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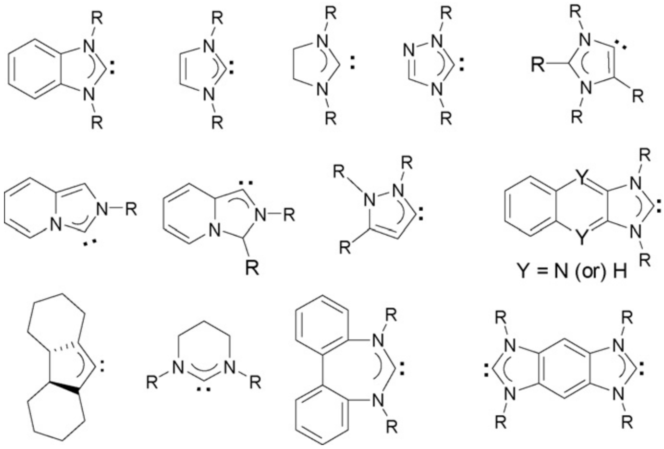
ditions [8], and (5) transmetallation with Ag(I)–NHCs [9a]. The last strategy is now well-established for the preparation of various transition metal–NHCs including Au(I) [9–17], Pd(II) [9a,18–39], Rh(I) [25,30,35,38–56], Rh(III) [41b,57], Ir(I) [40c,41,47,49,51,58,59], Ir(III) [41b,60,61], Cu(I) [62–64], Cu(II) [65–67], Ru(II) [56,68–72], Ru(III) [69], Ru(IV) [66a,73], Ni(II) [74,75], Pt(II) [26,31c,76], and proved to be a convenient method over other methods under certain conditions.

## 2. Aims and objectives

Metal–NHC chemistry has been reviewed by pioneers in the field. When Herrmann and Bertrand published excellent reviews in 2000 concerning the synthesis of metal–NHCs, few Ag(I)–NHCs were known [1,3b]. Indeed interest in the synthesis of Ag(I)–NHCs and their application in transmetallation reactions has only greatly increased in recent years. In this regard, we reviewed Ag(I)–NHCs in 2004 [77] providing general trends in Ag(I)–NHC chemistry. Arnold also had a mini review on Ag(I)–NHCs in 2002 [78]. Recently, Garrison and Youngs published a review on Ag(I)–NHCs in 2005 [79], focusing mainly on the structural parameters. We note that 62 papers dealing with Ag(I)–NHCs have been published since the Youngs' review.

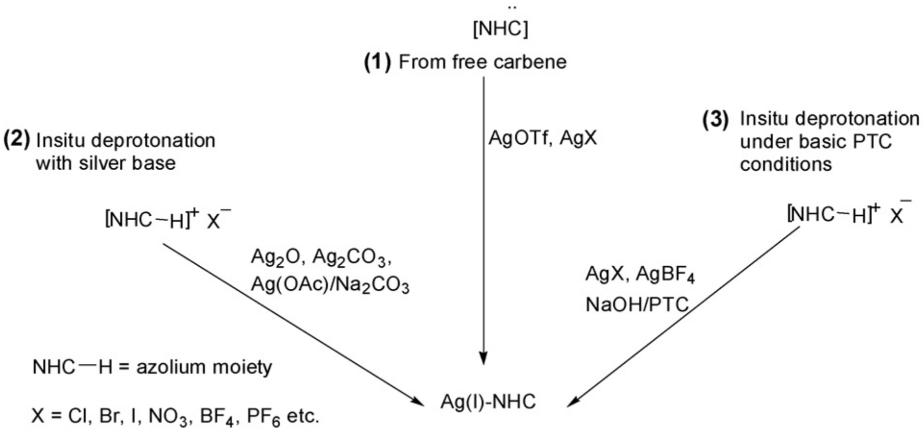
When we look at the present trends in the chemistry of metal–NHCs (up to 31 July 2006), the Ag(I)–NHCs comprise various NHC systems ranging from five membered to seven membered rings, including imidazolium, benzimidazolium, imidazolinium, triazolium, pyrazolium, quinoxaline and naphtho anellated imidazolium, imidazo[1,5-a]pyridine, bipiperidine and biisoquinoline derived imidazolium, bisimidazoliums with arene backbone, six-membered ring pyrimidinium, seven-membered ring amidinium moieties, etc. (Scheme 1). Therefore, it was our intention to provide an updated and comprehensive review on the subject of Ag(I)–NHCs, which may further accelerate work on this topic. The main features of this review were to evenly focus on (a) the ease and limitations in the synthesis of Ag(I)–NHCs, (b) the parameters influencing the solid state structures of Ag(I)–NHCs, and (c) the efficacy of transmetallation reaction by Ag(I)–NHCs. In particular, the authors would like to evaluate the widely applied $Ag_2O$ technique in the synthesis of Ag(I)–NHCs and their transmetallation efficiency to afford other important metal–NHCs.



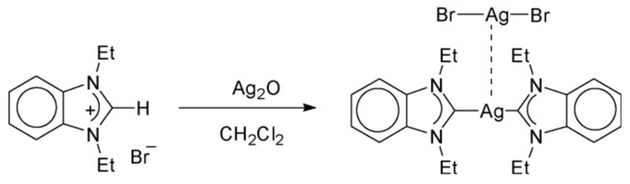
Scheme 1. Different NHC moieties explored so far in Ag(I) complexes.

## 3. Discussion

As depicted in Scheme 2, different approaches such as (1) reaction of azolium salts with silver base, (2) reaction of free NHC with silver salts, and (3) reaction of azolium salts with silver salts under basic PTC conditions, have been used to prepare Ag(I)–NHCs. As early as 1993, Arduengo reported the first Ag(I)–NHC by the reaction of Ag(I) salt with a free NHC [80]. Later, Bertrand in 1997, reported that the reaction between triazolium triflate salt and a silver base such as Ag(OAc) (OAc = acetate), yielded a polymeric Ag(I)–NHC [81]. The reaction of another silver base, $Ag_2O$, with azolium salts to afford Ag(I)–NHCs was first reported in 1998 by Lin and co-workers [9a]. This result was serendipitous. While using different bases for the deprotonation of azolium salts, in an attempt to synthesize Au(I)–NHCs, the employment of $Ag_2O$ as a mild base effectively produced the Au(I)–NHCs. This study implied the generation of Ag(I)–NHCs *in situ*, and their role as transmetallating agents to prepare other metal–NHCs. Based on this obser-



Scheme 2. Methods prescribed to prepare Ag(I)–NHCs.



Scheme 3. The first example of Ag(I)–NHC formed via $Ag_2O$ technique.

vation, efforts were initiated by Lin to isolate the Ag(I)–NHCs in the solid state.

In the very first approach, addition of *N*,*N*′-diethylbenzimidazolium bromide to $Ag_2O$ in $CH_2Cl_2$ at room temperature easily afforded the Ag(I)–NHC ([Ag]/[salt] = 1) via *in situ* deprotonation (Scheme 3) [9a]. The formation of Ag(I)–NHC was monitored by the gradual disappearance of the $Ag_2O$ suspension in the solution.

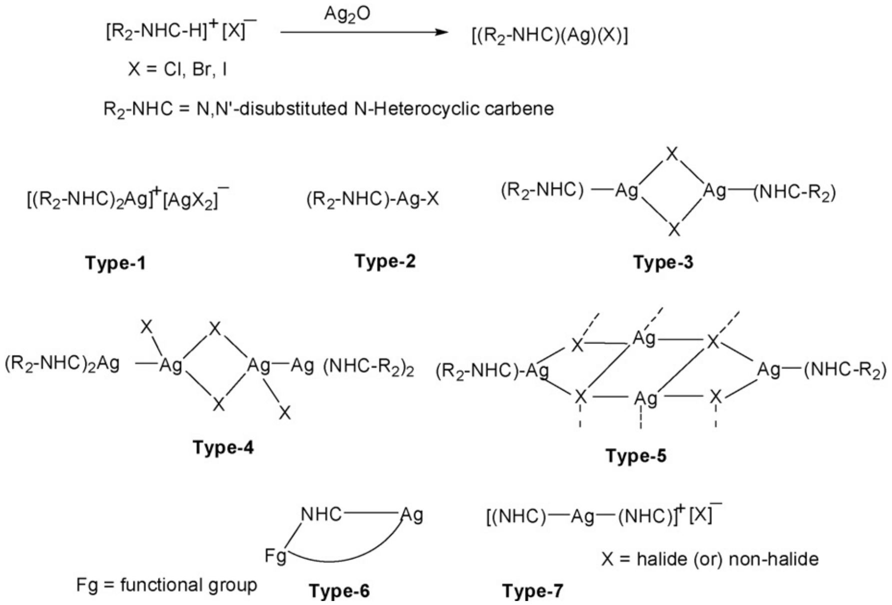
After this report, the $Ag_2O$ technique was regarded as a convenient strategy to prepare Ag(I)–NHCs. The special attributes of the $Ag_2O$ technique such as (a) reactions can be carried out in air, (b) solvent pre-treatments are not required, (c) no additional base is needed, (d) deprotonation usually takes place at $C^2$-carbene, and (e) the tolerance of $Ag_2O$ towards some active hydrogen atoms, were considered as some of the reasons to highlight this technique in metal–NHC chemistry. There are some reports of reactions being conducted in inert conditions without mentioning the reasons. Out of the 158 reports published until now on the preparation of Ag(I)–NHCs and their transmetallation, 142 deal with the $Ag_2O$ technique. The following content was divided into two major categories.

### 3.1. Formation of Ag(I)–NHCs

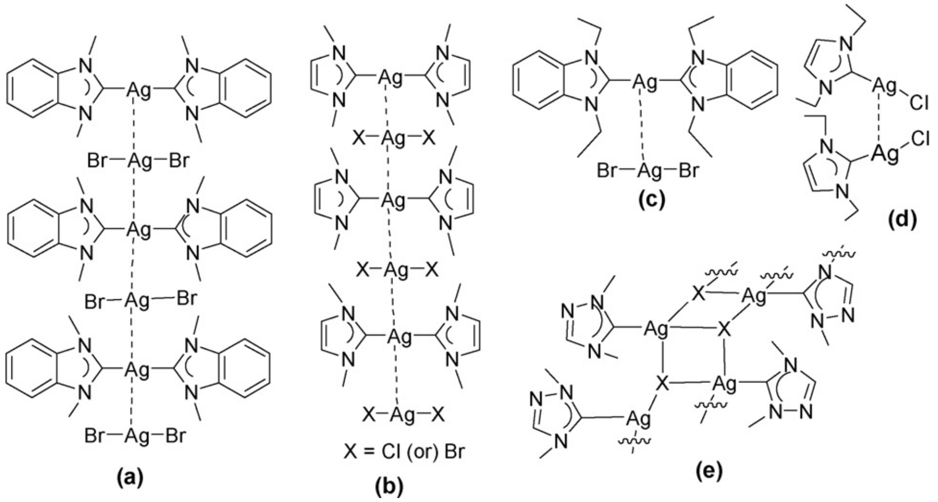
In this section, we will discuss first the reports on the $Ag_2O$ method and then discuss other methods. Due to their easy accessibility, a large number of mono-azolium halide salts (containing one azole ring) were employed to react with $Ag_2O$ to access Ag(I)–NHCs. In addition to mono-azolium salts, various bis-azolium and tris-azolium salts (containing two or three azole rings) with different linkers in pincer, cyclophane, and tripodal architectures were also investigated.

According to the available reports, mono-azolium halides can produce Ag(I)–NHCs of various ionic and neutral structures (types 1–7; Scheme 4) in the solid state. The salts with non-halide salts usually formed simple bis-carbene complexes (type-7; Scheme 4). The structures displayed by the Ag(I)–NHCs formed from bis- and poly-azolium salts will be discussed in later sections. These observations were based mainly on single crystal X-ray studies. Other techniques such as NMR and mass spectrometry were also used for the characterization of Ag(I)–NHCs. Nevertheless, fluxional behavior between the ionic and neutral complexes was observed in solution for most of the compounds.

The stoichiometric reaction of short chain azolium halides, i.e. (*N*,*N*′-$Me_2$ or *N*,*N*′-$Et_2$ substituted) benzimidazolium, imidazolium and triazolium chloride or bromides with $Ag_2O$ ([salt]/[metal] = 1) progressed smoothly in $CH_2Cl_2$ to produce either type-1 ion-pair complexes or type-2 and type-3 neutral complexes (Scheme 5a–e) [9a,9c,82]. The ion-pair Ag(I)–NHCs (Scheme 5a and b) based on *N*,*N*-dimethylbenzimidazolium and imidazolium moieties show extended Ag···Ag interactions due to the planar shape of the ligand. With the triazolium NHC moiety, each pair of neutral type-3 Ag(I)–NHC (Scheme 5e) further interacts with neighboring pairs by extended Ag···halide interactions, and form an infinite one-dimensional polymer, in which the Ag(I) adopts a tetrahedral geometry. Various *N*,*N*-dialkyl, *N*,*N*-diaryl and hetero-disubstituted *N*-alkyl, *N*′-aryl imidazolium chloride and bromide salts were also employed to react with $Ag_2O$, to afford normally the type-1 ionic or type-2 neutral complexes [10,16,83–86], but no extended Ag···Ag



Scheme 4. Common structures of Ag(I)–NHCs obtained from mono-azolium salts.



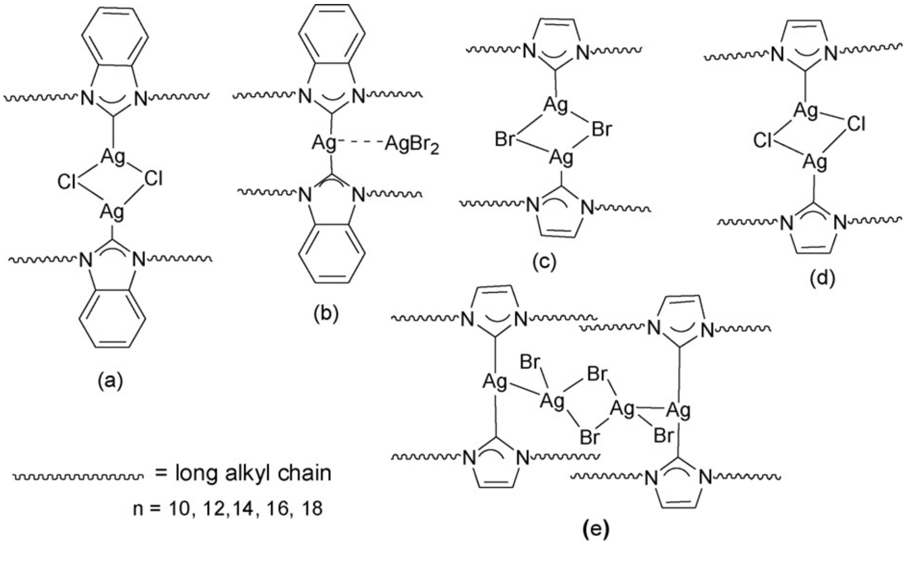
Scheme 5. Ag(I)–NHCs (a–e) obtained from short chain azolium halides via the $Ag_2O$ technique.

or Ag· · ·X interactions were observed in the reported crystal structures.

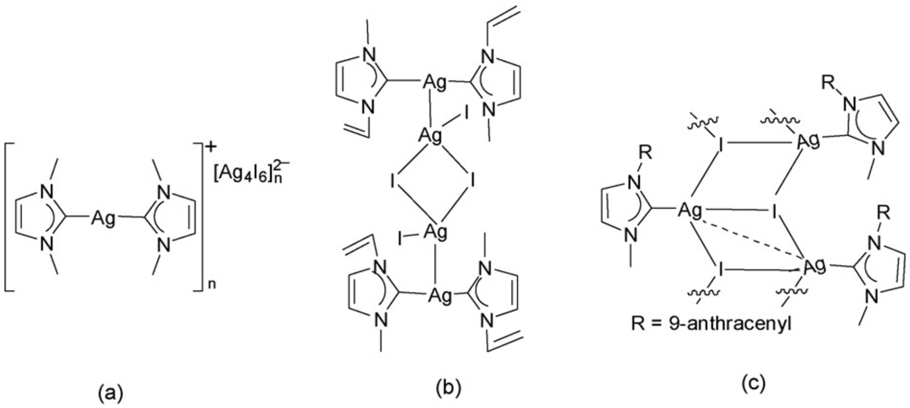
The reactions of long chain ($C_nH_{2n+1}$) azolium chloride and bromide salts ($n$ = 10, 12, 14, 16 and 18) with $Ag_2O$ were investigated (Scheme 6) [9c,82b]. For the chloride salts of benzimidazolium or imidazolium, recrystallization of the crude product from $CH_2Cl_2$/hexane gave chloride bridged type-3 neutral Ag(I)–NHC complexes (Scheme 6a and d). Under similar experimental conditions, the bromide salts of long chain benzimidazolium produced type-1 ion-pair complexes (Scheme 6b). The reaction of long chain bromide salts of imidazolium with $Ag_2O$ afforded a product with an empirical formula of [Ag(NHC)Br]. When this compound was crystallized from acetone, a type-3 complex (Scheme 6c) was obtained. However, upon crystallization from $CH_2Cl_2$/hexane, a type-4 complex (Scheme 6e) was isolated.

Extended Ag· · ·Ag interactions were not possible for the long-chain Ag(I)–NHCs, presumably, packing to obtain better chain–chain interactions were more important than Ag· · ·Ag interactions. Besides chain–chain interactions, both long chain and short chain Ag(I)–NHCs were stabilized by many secondary attraction forces such as extended hydrogen bonding and intermolecular Ag· · ·halide interactions. A structural comparison of both the short and long chain compounds according to the crystal structure analysis was provided in Schemes 5 and 6.

Actually, the long chain Ag(I)–NHCs were designed to study the possible formation of liquid crystals (LC); unfortunately none of them were mesomorphic, probably due to insufficient core–core interactions [9d,82b]. However, when mixed with their corresponding imidazolium salts they exhibited LC properties. Recent studies have projected this special type of organic–inorganic hybrids to serve as good single-source-precursors for silver nanomaterials [82b]. The stoichiometric reactions of azolium [$NO_3$], [$PF_6$], and [$BF_4$] salts produced simple bis-carbene complexes (type-7 as shown in Scheme 4) with or without basic PTC conditions [82b]. Usually the exclusion of light was not required in the $Ag_2O$ technique.



Scheme 6. Ag(I)–NHCs (a–e) obtained from long chain azolium halides.

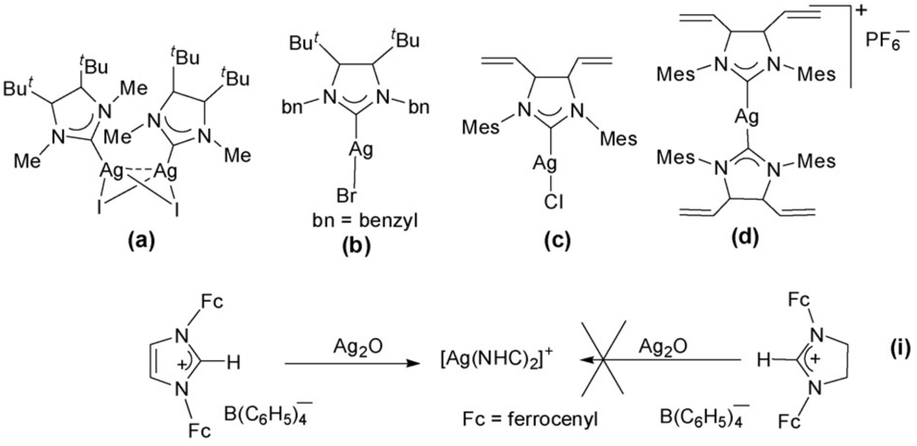


Scheme 7. Ag(I)–NHCs (a–c) obtained from imidazolium iodide salts.

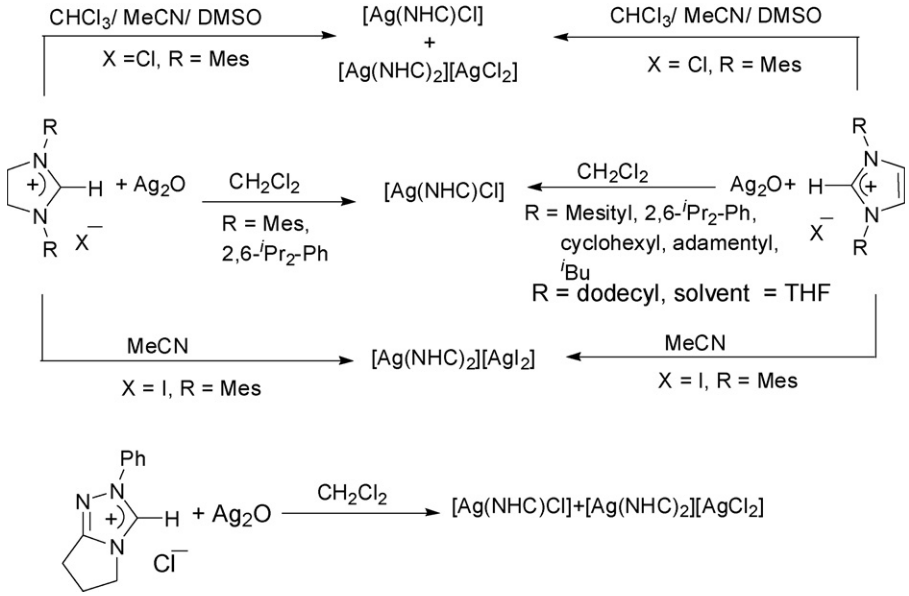
Iodide salts prefer to form ion-pair complexes with poly silver-iodide ion rather than neutral species [87]. The short chain *N*,*N*′-dimethylimidazolium iodide produces the type-1 ion-pair complex, Scheme 7a from DMSO (Scheme 7) [88]. The poly silver-iodide anion and the $[Ag(NHC)_2]^+$ cation were linked together by weak intermolecular Ag· · ·I interactions in the crystal packing. Replacing one methyl side arm with an allyl group led to the formation of a type-4 tetranuclear complex (Scheme 7b) upon recrystallization from DMSO [88]. However, the use of *N*-Me,*N*′-anthracenyl substituted imidazolium salt produced an iodide bridged type-5 neutral Ag(I)–NHC (Scheme 7c) in $CH_2Cl_2$ (Scheme 7) [89]. Despite the above observations, the interaction of *N*,*N*′-dimethyl-benzimidazolium or imidazolium iodides with $Ag_2O$ in $CH_2Cl_2$ produced Ag(I)–NHC at room temperature with chloride anion instead of iodide [82a,90]. Under similar conditions no metathesis of bromide by chloride occurred. The chlorinated solvent may be the source of the chloride. Liu used the same imidazolium iodide but isolated the final Ag(I)–NHC as $[Ag(Me_2\text{-imy})_2][Ag_4I_6]$ from hot DMSO [88].

The interaction of $Ag_2O$ with several saturated imidazolinium salts [91–93] with simple N-substituents was also studied using different solvent system including water. Type-2 mononuclear or type-3 halide bridged dinuclear Ag(I)–NHCs were normally formed from imidazolinium halides, and type-7 $[Ag(NHC)_2]^+$ complexes from non-halide salts similar to those of unsaturated imidazolium analogues. Some of the representative drawings were given in Scheme 8. Notably, the non-planar $Ag_2I_2$ unit in compound Scheme 8a exhibited both Ag· · ·Ag and Ag· · ·I interactions [91]. In contrast to the preparations above, the failure of the reaction of ferrocenyl substituted imidazolinium salt with $Ag_2O$ was attributed to reduced acidity (Scheme 8i) [94]. However, the unsaturated imidazolium salt with ferrocenyl substituents successfully produced a bis-carbene of the type-7.

In a recent advance, Nolan and Clyburne emphasized the influence of halide ions and the solvent on the structural formulae of Ag(I)–NHCs [84]. The reaction of *N*,*N*′-dialkyl or diaryl substituted imidazolium and imidazolinium chloride salts with $Ag_2O$ in $CH_2Cl_2$ was shown to form type-2 neutral complexes (Scheme 9) as observed from a single crystal X-ray study. However, the triazolium salt produced a Ag(I)–NHC in $CH_2Cl_2$ with the coexistence of both ionic (type-1) and neutral forms (type-2) in the solid state (Scheme 9). An increase in the solvent polarity increased the population of ionic bis-carbene (type-1) (Scheme 9). This aspect was further indicated by the use of the *N*,*N*-dimesityl substituted iodide salt, where only the ionic bis-carbene of type-1 complexes were formed in highly polar MeCN as determined by $^{13}C$ NMR and single crystal X-ray



Scheme 8. Ag(I)–NHCs (a–d) with saturated back bone (top) and reactions of *N*-ferrocenyl susbstituted salts (down, Eq. (i)).



Scheme 9. The formation of Ag(I)–NHC-halides in polar and non-polar solvents.

study (Scheme 9). This was proposed to be due to the higher polarizability of iodide than chloride. Type-2 [(NHC)AgCl] is identical to that of Nolan's work were also reported by Hahn and co-workers [92].

When mono-azolium salts (both halide and non-halide) with functional groups at one or two N-side arms were employed to react with $Ag_2O$, the Ag(I)–NHCs were also isolated as type-1 ion-pair, type-2 mononuclear neutral complexes, type-3 halide bridged complexes, type-4 $Ag_2X_4^{2-}$ bridged tetranuclear complexes, and type-7 bis-carbene complexes as determined by crystal structure and spectroscopic analysis (Scheme 10) [13a,20a,b,22a,c,24c,25,26,31,33,44,55,70,95–101]. Some representative examples were given in Scheme 10. Normally the functional group was not bonded to the Ag(I), but in a few reports coordination of functional groups to Ag(I) were illustrated [55a,70,95,100] (Scheme 10).

The work by Cavell and co-workers has shown the non-stoichiometric $X^-/AgX_2^-$ anion in some Ag(I)–NHCs, upon using imidazolium halides [20]. In such cases, it was suggested that replacing the halide by non-halide ion can avoid the ambiguity [20,42]. Arnold reported that the reaction of alcohol functionalized imidazolium halides with $Ag_2O$ led to the deprotonation of both $C^2$–H and –OH protons and yielded the type-6 halide free Ag(I)–NHC–alkoxyl complexes (Scheme 11i and iii) [62,101]. However, this phenomenon depends on steric factors (Scheme 11, Eq. (ii)). These observations were described on the basis of EA and NMR data only. Further in this work, the formation of an amine coordinated Ag(I)–NHC with the imidazolium salt having an alkylammonium side arm (Scheme 11iv) [101], suggested that $Ag_2O$ was not sufficiently basic to deprotonate the secondary amine. Hoveyda and co-workers reported the preparation, crystal structure characterization and catalytic application of the halide free Ag(I)–NHC-phenoxyl complexes (Scheme 11v) [66a,b].

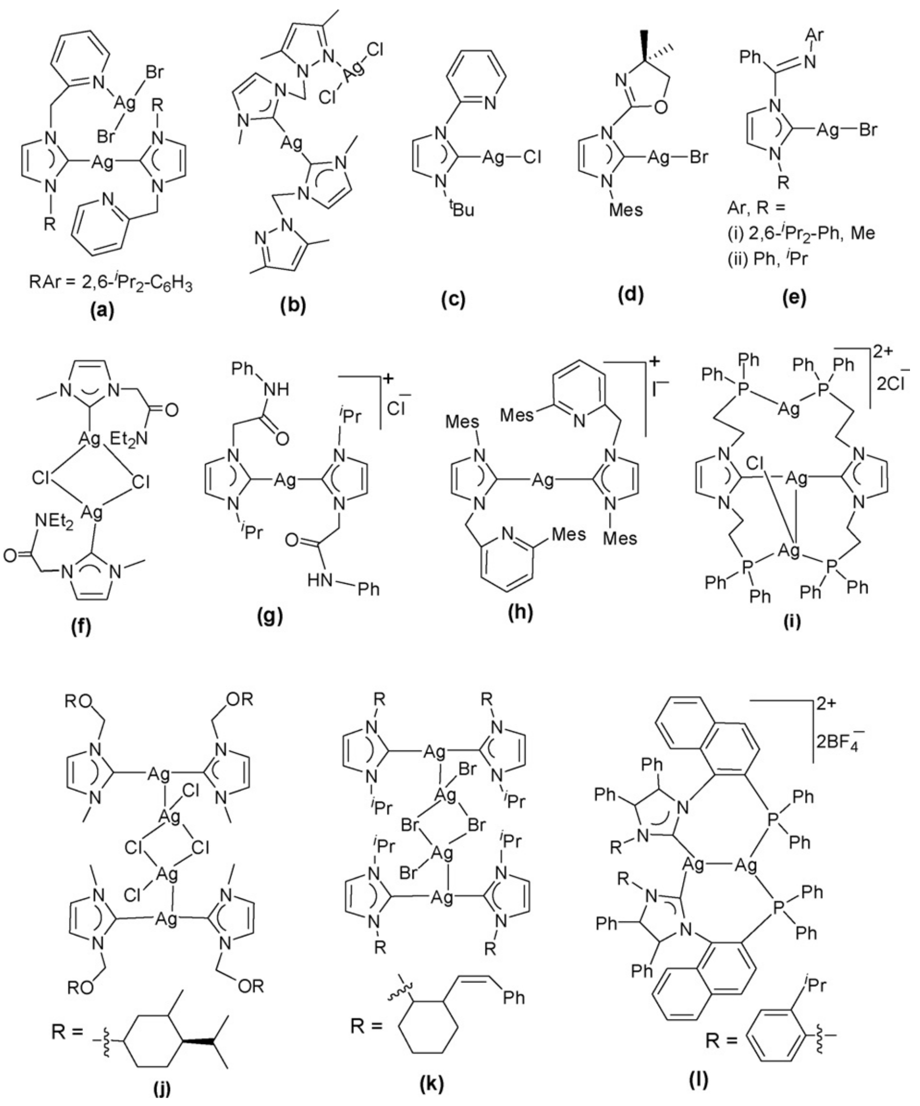
Several bis-imidazolium salts connected by a simple alkylenyl linker or by pyridyl, ether, and amine functional group linkers were designed to prepare Ag(I)–NHCs [15,20c,d,22b,d,23,27b,30,57,63,82a,90,101–105]. Bis-imidazolium salts with an arene backbone were also explored recently to afford Ag(I)–NHCs [48]. Structural drawings for some of the examples were given in Scheme 12. The use of halide salts produced either neutral or ionic Ag(I)–NHCs. Functional groups did not appear to play any role in the coordination.

Youngs and co-workers reported the first Ag(I)–NHC with antimicrobial properties (Scheme 13) [106]. Two neighboring bis-carbene units were bridged by Ag(I) to form a polymeric structure (Scheme 13a). Addition of $NH_4PF_6$ to this water-soluble polymer produced a water-insoluble discrete dinuclear Ag(I)–NHC (Scheme 13b).

Youngs and co-workers also pioneered the use of bis-imidazolium salts to prepare Ag(I)–NHC-cyclophanes (Scheme 14) [107]. Stoichiometric reactions (1:2) of imidazolium linked cyclophanes (Scheme 14a and b) with $Ag_2O$ produced dinuclear complexes (Scheme 14i), in which two Ag(I) ions bridged the NHC units of two different macrocyclic rings. The complex with *gem*-diol bridging functionality (from salt b, Scheme 14) was encapsulated to tecophilic fiber mats, to serve as a precursor for nanosilver, which exhibited excellent bacterial activity [107b].

Baker also isolated a variety of Ag(I)–NHC cyclophane complexes from salts given in Scheme 14c–f [108]. While the reactions of salts c and d and f with $Ag_2O$ easily afforded the dinuclear Ag(I)–NHCs in Eq. (i), reaction of salt e with $Ag_2O$ was very slow. The bromide ions of Ag(I)–NHCs obtained from salts d and f were replaced with $[PF_6]$ or $[BPh_4]$ to avoid the non-stoichiometric $Br^-/AgBr_2^-$ problem. EA and NMR data of the Ag(I)–NHC obtained from salt e were consistent with the formulation as neutral [Ag(NHC)Br], but single crystal study showed that a $Ag_2Br_2$ core was intercalated between two [Ag(NHC)Br] (Eq. (ii)).

Meyer and Periss designed tripodal-imidazolium salts with carbon or nitrogen anchors (Scheme 15a–c) to prepare



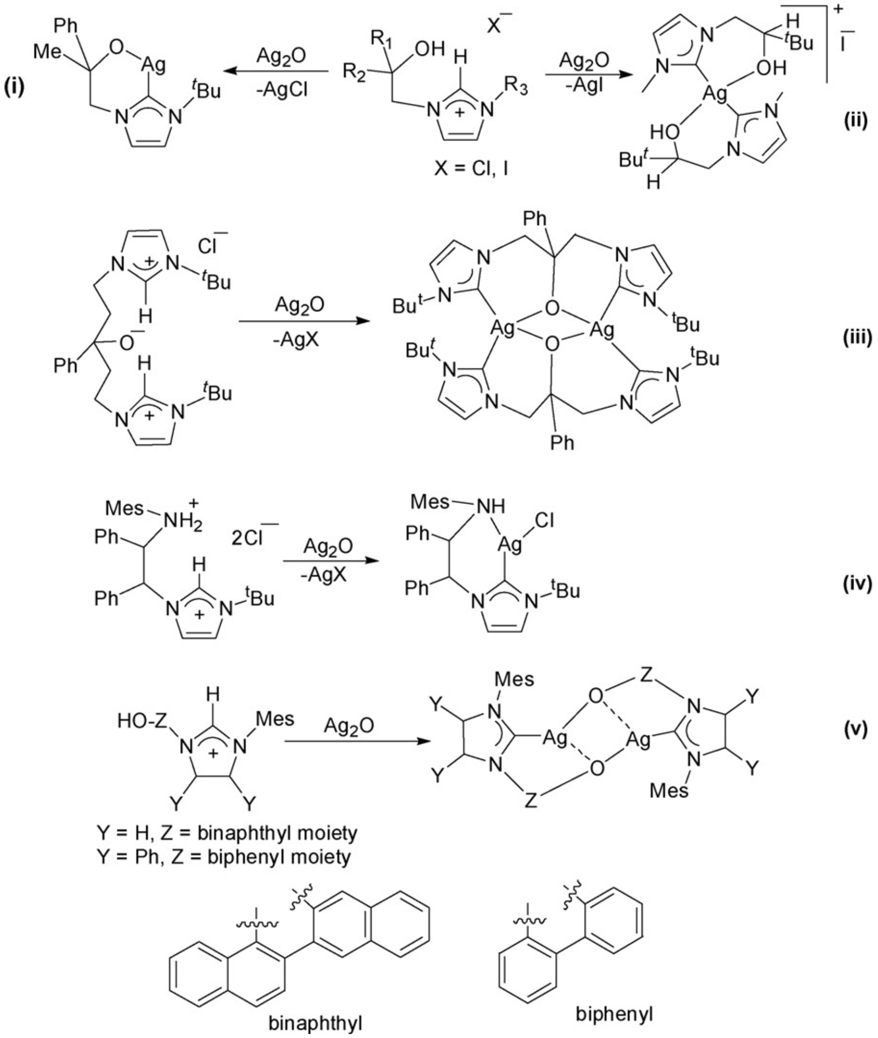
Scheme 10. Ag(I)–NHCs (a–h) with functional groups in the N-side arms.

Ag(I)–NHCs [41a,109]. The solid state structures of Ag(I)–NHCs (Scheme 15i) obtained from salts a and b showed that two tripodal NHCs were bridged by three Ag(I) ions via each of the three pendant arms to provide three units of bis-carbene Ag(I) complexes (Scheme 15) [109].

The synthesis conducted in the presence of excess $Ag_2O$ $[(Ag)/(salt) \geq 1]$ sometimes showed results different from that of the normal stoichiometric reactions $[(Ag)/(salt) \leq 1]$. This phenomenon was found to depend on the nature of the imidazolium salt and the solvent. Reports by Lin and co-workers [82b], Catalano et al. [13b,c,110], Youngs and co-workers [111,112] and Crabtreeand co-workers [40b,113] summarized this special type of observation. Lin noted that [82b] when excess $Ag_2O$ was used to react with *N*-methyl or ethyl substituted imidazolium halides $([Ag]/[salt] \geq 1.2)$ in $CH_2Cl_2$ for >18 h, the solution turned yellow, and a silver mirror together with brown powdery solid was coated on the reaction vessel. When the ratio of [Ag]/[salt] was $\leq 1.0$, no yellow solution nor silver mirror was observed. When long chain imidazolium halides react with excess $Ag_2O$, a yellow solution was observed but not the silver mirror nor the brown solid. The UV–vis spectrum of the yellow solution showed intense surface plasmon resonance (SPR) bands at ∼426 nm, suggesting the formation of nano-silver particles.

It appears that long chain imidazolium halides can stabilize AgNPs better than short chain imidazolium salts. The yellow colloidal AgNPs can be removed by activated carbon.

Catalano's work showed that when excess $Ag_2O$ reacts with imidazolium salts containing picolyl or quinolyl N-side arms $[(Ag)/(salt) = \sim 10]$, the homoleptic triangulo-$[Ag_3(\mu\text{-}NHC)_3]^{+3}$ complexes (Scheme 16a and b) are produced, with bridging μ2-carbenes and unusual Ag···Ag interactions (∼2.7 Å) [(Scheme 16) [13b,c,110], whereas, a simple $[Ag(NHC)_2]^+$ is obtained from the usual stochiometric reaction $[(Ag)/(salt) = 1]$. Identical compounds were obtained upon addition of $AgBF_4$ to the pre-formed $[Ag(NHC)_2]^+$ complexes in acetonitrile [110]. Youngs also reported a similar trinuclear complex (Scheme 16c) by using a similar imidazolium salt containing a terminal alkanol functionality [111], however, this time the ratio of [Ag]/[salt] was = 1.2.

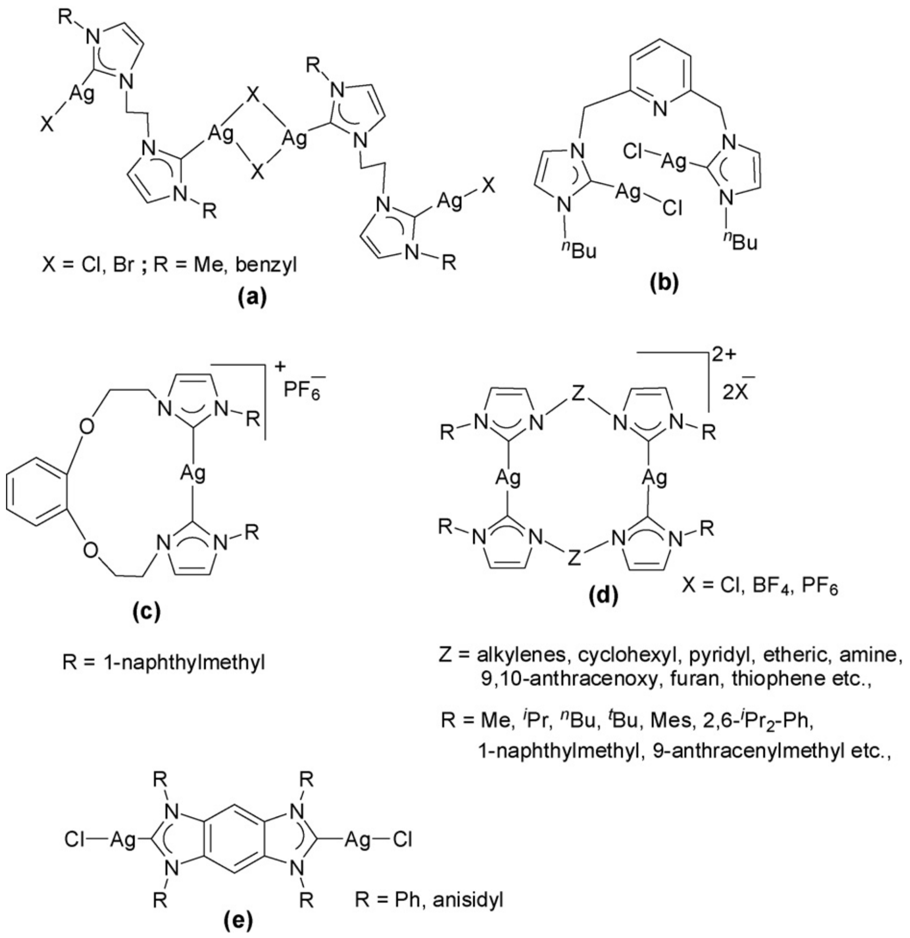


Scheme 11. Reactions (i–iv) of alcohol and ammonium functionalized imidazolium salts.

In the preparations of Ag(I)–NHC-cyclophane complexes (Scheme 17), Youngs demonstrated that a tetranuclear complex (Scheme 17a) was formed when four equivalents of $Ag_2O$ were treated with one equivalent of the $[PF_6]$ salt of imidazolium-cyclophane in DMSO [112a]. Under similar conditions, the bromide salt produced only a dinuclear compound (Scheme 17b) in water [112a]. These results indicated that the solubility of the products kinetically controlled the reaction. Crystal study revealed additional contacts (∼2.3–2.5 Å) between the non-bridging Ag and the NHCs. A similar tetranuclear complex was also obtained from pyridyl and pyrrole bridged imidazolium salt by utilizing excess of $Ag_2O$ [112b].

An unprecedented observation in the $Ag_2O$ technique was reported by Crabtree (Scheme 18) [40b,113]. When the imidazolium rings were occupied with substituents in all the positions (1–5 positions), those salts with methyl, benzyl and even ethyl substituents at the $C^2$-position (Scheme 18ii) produced normal $C^2$-bonded Ag(I)–NHCs by reaction with a four-fold excess of $Ag_2O$. Reaction of 1,2,3,4-tertramethyl imidazolium iodide with $Ag_2O$ also produced normal $C^2$-bonded Ag(I)–NHC. Metallic silver observed in these reactions suggested its role in the cleavage of the C–C bond at the $C^2$-position. However, C–C bond cleavage did not occur when the $C^2$-substituent was isopropyl. This different behavior was attributed to the steric effect caused by the $C^2$-substituent. It has been proposed that 2-carbonyl imidazolium species were intermediates in the above C–C bond cleavage reaction. To support this proposition, the reaction of 2-benzoylimidazolium salt was performed; indeed a normal Ag(I)–NHC was formed. This result provided a clue to the development of another potentially useful method that carbonyl-imidazolium species can be used as starting materials to prepare Ag(I)–NHC and other metal–NHCs (Scheme 18) [40b,113]. A report by Alcarazo et al. described the formation of abnormal Ag(I)–NHCs from 2-phenyl imidazo[1,5-a]pyridinium salt (Scheme 18, Eq. (iii)) [51].

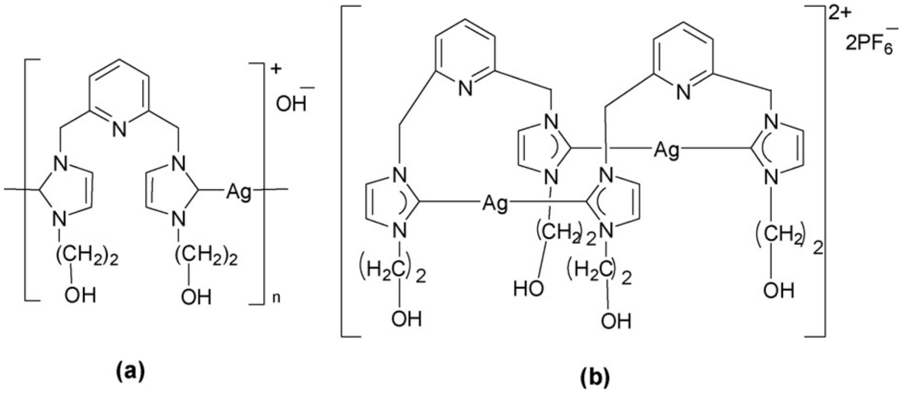
Very recently a report by Wang et al. reported that an iodide anchored trinuclear Ag(I)–NHC structure was obtained when a picolyl functionalized imidazolium iodide salt was reacted with 3 mol excess of $Ag_2O$ (Scheme 19) [21]. Previously, Cavell and co-workes reported an identical reaction [20a]; formation of an $[Ag(NHC)_2]^+$ with non-stoichiometric $I^-/AgI^{2-}$ anion was observed at 2:1 molar ratio of [imidazolium salt]/$[Ag_2O]$.



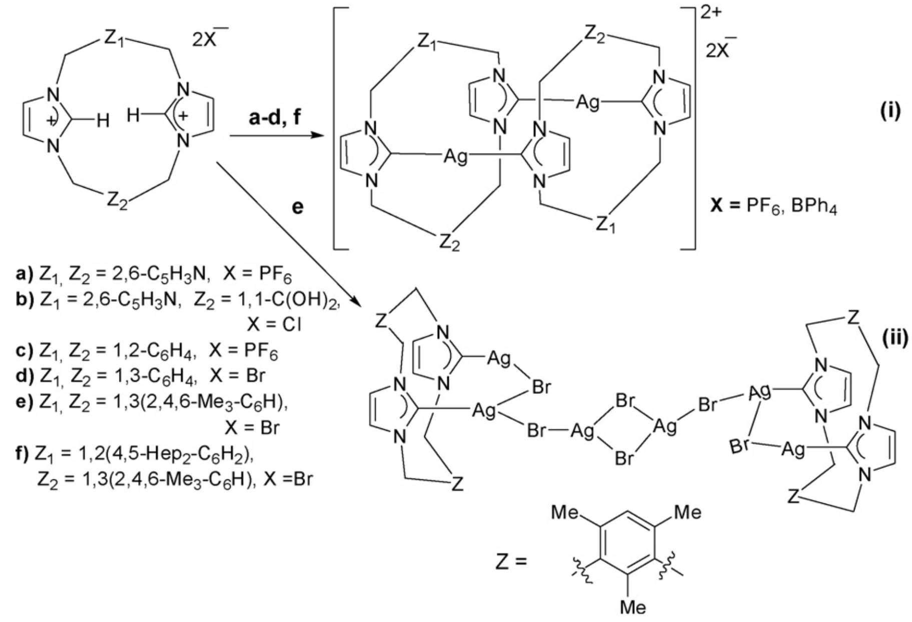
Scheme 12. Ag(I)–NHCs (a–e) obtained from bis-imidazolium salts.

Chiu et al. reported that when Ag(I) salts were added to a type-2 Ag(I)–NHC having an *N*-pyrazole and *N*′-aryl side-arm (Scheme 20a), a variety of Ag(I)–NHCs were obtained (Scheme 20) [114]. When the aryl was benzyl, the addition of $AgNO_3$ generated a coordination polymer $[Ag(NHC)(NO_3)]_n$ (Scheme 20b) in MeCN at room temperature. However, when aryl was *N*-naphthyl or fluorobenzyl, a metallomacrocycle (Scheme 20c) was obtained with the addition of $AgNO_3$ or $AgBF_4$. A simple bis-carbene with a *N*-fluorobenzyl substituent (Scheme 20d) was obtained upon the addition of $AgNO_3$ in refluxing methanol.

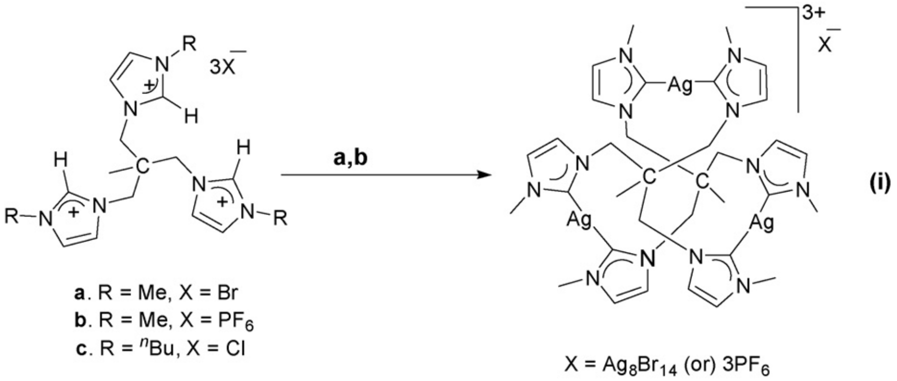
Ag(I)–NHC complexes with NHCs other than imidazol-2-ylidene carbene were also obtained via the $Ag_2O$ method. Buchmeiser and co-workers reported the first six-membered tetrahydropyrimidin-2-ylidene based Ag(I)–NHC from a tetrahydro-pyrimidinium bromide salt [38]. Herrmann et al. reported the first crystal structure of tetrahydropyrimidin-2-ylidene based Ag(I)–NHC (Scheme 21i) [115]. The large down



Scheme 13. polymeric (a) and dimeric (b) Ag(I)–NHC cyclophanes.



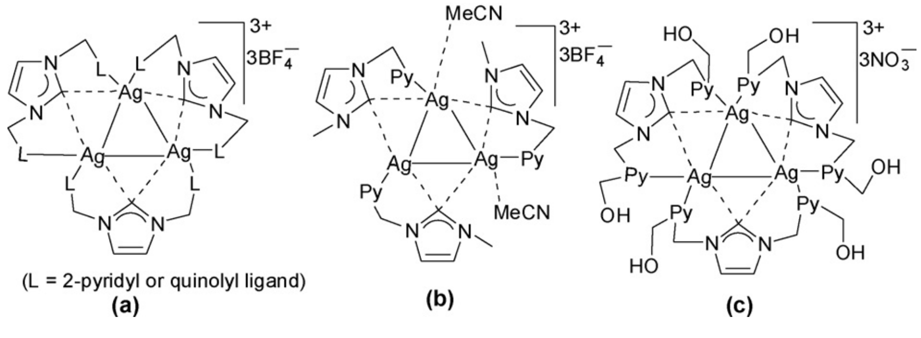
Scheme 14. Formation of Ag(I)–NHC cyclophane complexes with different bridging groups.



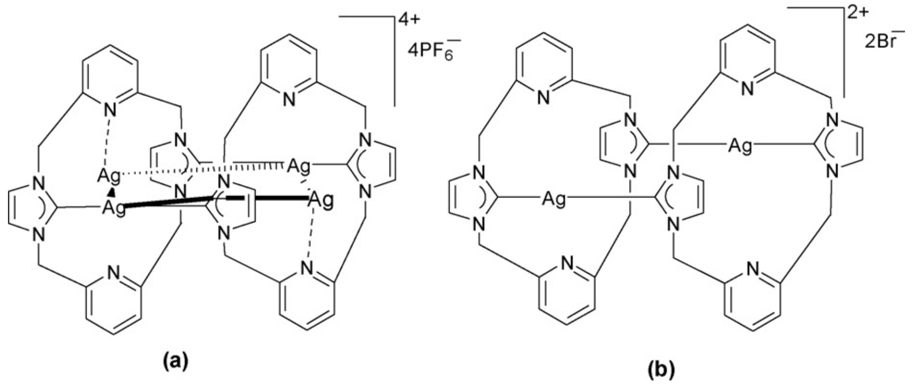
Scheme 15. Ag(I)–NHCs obtained from tripodal imidazolium salts.

field shift of the carbene-C resonance from that of the free salt was attributed to a strong Ag–C bond. Heinicke et al. reported that the reaction of electron deficient quinoxaline- and naphthyl-anellated salts with $Ag_2O$ produced neutral or bis-NHC complexes (Scheme 21ii and iii) [39,54]. Very recently, Herrmann et al. reported the formation of Ag(I)–NHCs from chiral imidazolium salts derived from 2,2′-bipyridine or from partially reduced biisoquinoline [49], but no characterization was provided.

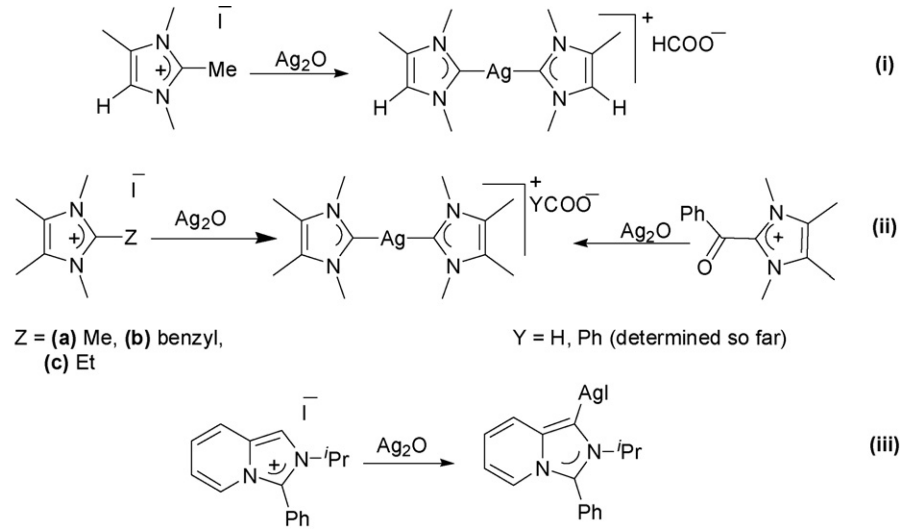
Other than the $Ag_2O$ technique, reactions of azolium salts with $Ag_2CO_3$, Ag(OAc), or with Ag(I) salts under PTC conditions or by transmetallation from other metal–NHCs were



Scheme 16. Homoleptic triangulo-$[(Ag_3\mu\text{-}NHC)_3]^{+3}$ complexes (a–c).

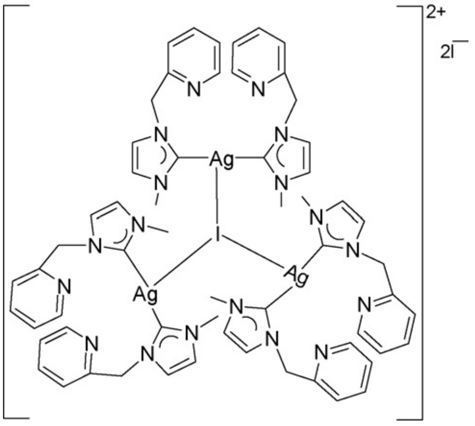


Scheme 17. Ag(I)–NHC cyclophanes (a and b) obtained with excess $Ag_2O$.

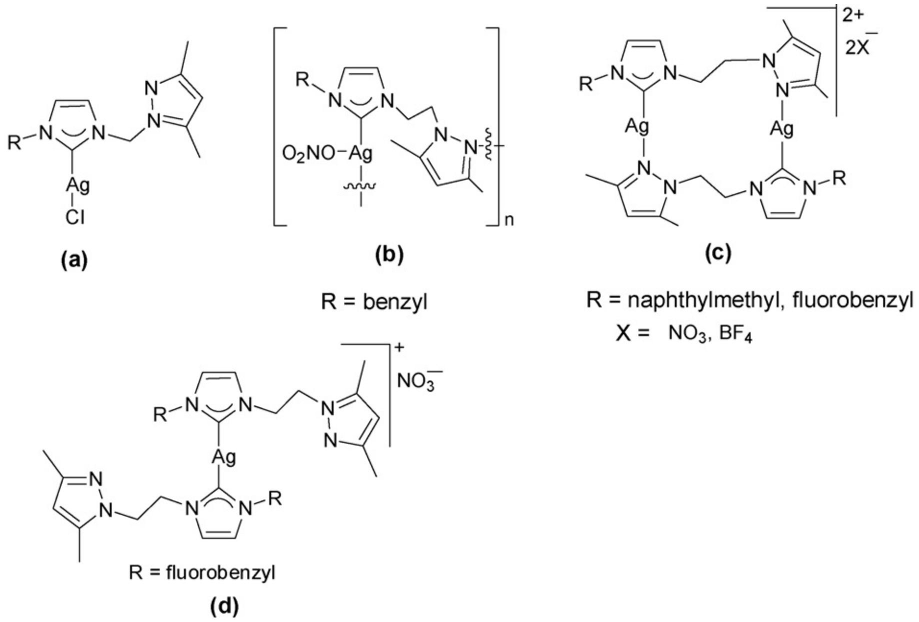


Scheme 18. Typical reactions of $Ag_2O$ with imidazolium salts having the substituents at the $C^2$-position.

also reported. Danopoulos' group observed that longer reaction times were needed when $Ag_2CO_3$ was used instead of $Ag_2O$ [95]. Recently, reports by Hoveyda and Gilbertson mentioned the validity of $Ag_2CO_3$ in the preparation of Ru–NHCs [56,73]. Charette explored the use of a combination of Ag(OAc) and $Na_2CO_3$ to prepare Ag(I)–NHCs from *N*-benzoylimidazolium ylide in refluxing THF (Scheme 22i) [67]. Formation of a dimeric structure linked through $C^2$-, N-atoms rather than $C^2$-, O-atoms was claimed to be due to the long Ag–C bond. When Stahl and co-workers tried to synthesize a Pd(II)–NHC from a seven-membered NHC ligand by the use of AgOAc, a type-2 Ag(I)–NHC was unexpectedly obtained (Scheme 22ii) [116]. Transfer of NHC from a putative Pd(II)–NHC to Ag(I) was anticipated. Buchmeiser and co-workers reported that six-membered tetrahydropyrimidin-2-ylidene complex of Rh(I) also transferred the NHC to Ag(I) upon reaction with excess $Ag(CF_3COO)$ (Scheme 22iii) [117]. Formation of a pyrazol-3-ylidene Ag(I), by the reaction of pyrazolium carboxylate with $Ag(CF_3SO_3)$ was described by Schmidt, based on mass spectroscopic data [118]. Earlier, Liu and co-workers reported that very unstable Ag(I)–NHCs based on a saturated imidazolinium moiety can be obtained by the transmetallation of $W^{III}$, $Mo^{III}$, $Cr^{III}$, $Pt^{II}$ and $Pd^{II}$–NHCs [119]. However, some of these Ag(I)–NHCs were stable enough to be isolated by the $Ag_2O$ technique [91]. The work by Lin and Catalano described the interaction of non basic Ag(I) salts with azolium salts under PTC/$OH^-$ conditions which also yielded Ag(I)–NHCs (Scheme 22iv and v) [9a,13b].



Scheme 19. Iodide anchored trinuclear Ag(I)–NHC.

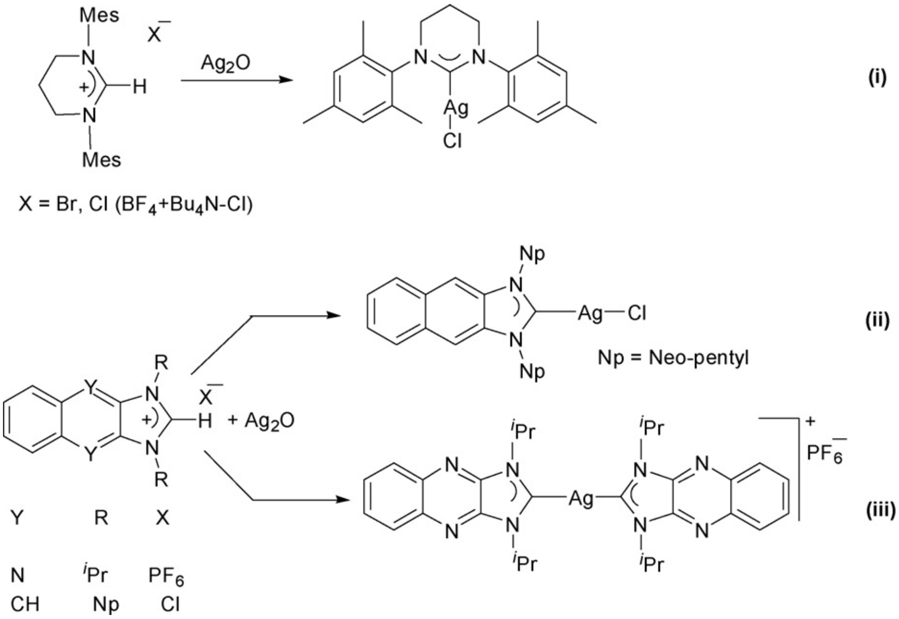


Scheme 20. Products (b–d) obtained from Ag(I)–NHCs (a) by the additions of Ag(I) salts.

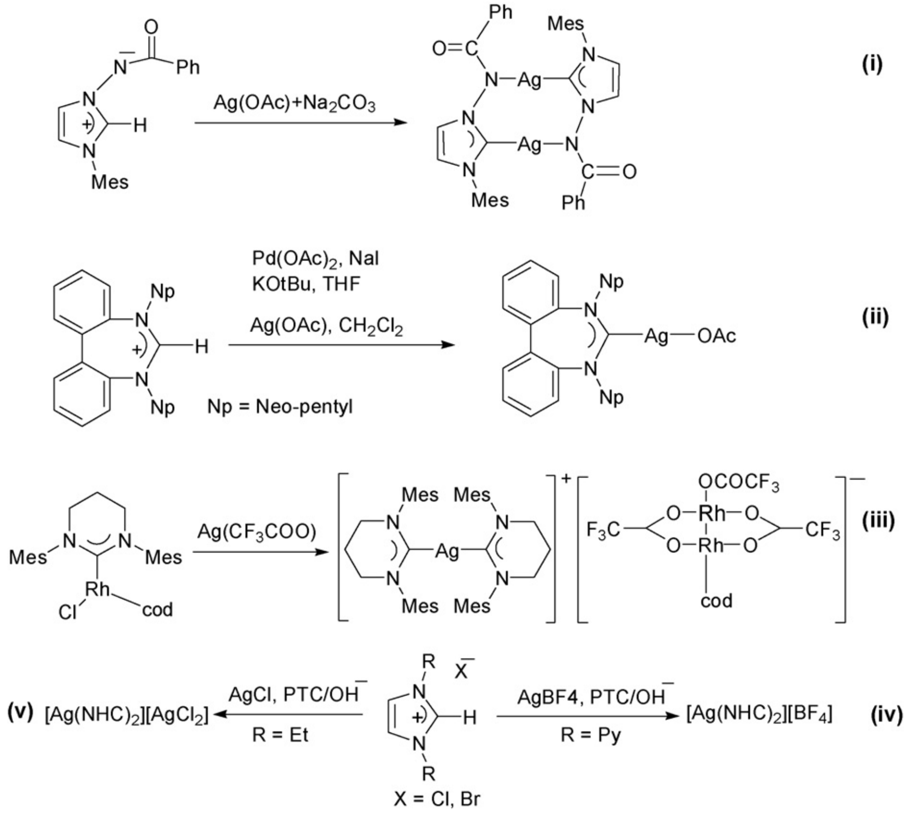
Regarding the implementation of Arduengo’s free NHC route, so far only three mono-NHCs (1,3-$Mes_2$-imy, 1,3,4,5-$Me_4$-imy, and 1,3-$^iPr_2$-4,5-$Me_2$-imy; imy = imidazol-2-ylidene), and one bis-NHC (1,1′-(pyridine-2,6-diyl)bis(3-benzyl-2,3-dihydro-1*H*-imidazole-2-ylidene) were employed to prepare Ag(I)–NHCs [80,84,120–122]. The use of mono-NHCs produced either type-2 neutral or type-7 bis carbene complexes depending on the Ag(I) precursor (Scheme 23i and ii). When a bis-carbene with pyridyl linker was used, an interesting double helical structure of Ag(I)–NHC [122] (Scheme 23iii), similar to that of reported Hg(II)–NHC [123] was found.

### 3.2. *Carbene transfer reactions of Ag(I)–NHCs*

In the present metal–NHC chemistry, Ag(I)–NHCs have proven popular mainly because of their role as NHC-transfer agents in the development of many other important metal–NHCs. Practical difficulties encountered in the synthesis of metal–NHCs by other methods [for example, Refs. 11,12,20,31,33,34,56,74,75] suggested that the $Ag_2O$ method was a good choice. Many authors suggested that active hydrogen atoms other than $C^2$–H can be protected effectively by this method. Although many studies have indicated that transmetal-

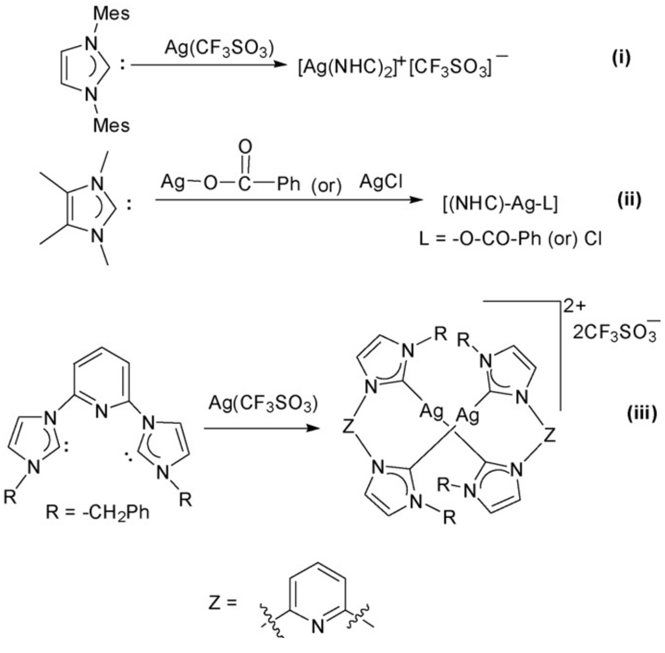


Scheme 21. The formation of Ag(I)–NHCs from pyrimidinium, naphtha- and quinoxaline imidazolium salts via the $Ag_2O$ technique.



Scheme 22. Preparation of Ag(I)–NHCs by different methods other than the $Ag_2O$ method.

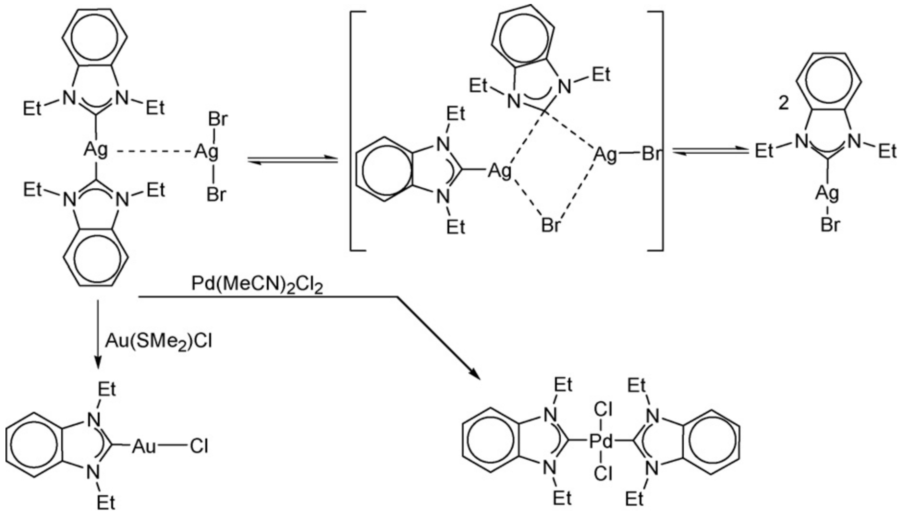
lation can be conducted in air, inert conditions were mentioned in few instances. The available literature revealed that NHC ligand transfers from Ag(I)–NHCs to various metal ions including Au(I), Pd(II), Cu(I), Cu(II), Ni(II), Pt(II), Ir(I), Ir(III), Rh(I), Rh(III), Ru(II), Ru(III) and Ru(IV) were successfully achieved. However, there were some limitations and unexpected products encountered in some studies, such as contamination of Ag-ions and the formation of unexpected metal–NHC geometries. Nevertheless, the transfer of NHC not only depended on the nature of Ag(I)–NHCs, but also on the nature of the receiving metal-precursors and the reaction conditions. The authors would like to review some of these problems.



Scheme 23. Ag(I)–NHCs via the free NHC route.

With the first successful transfer of NHC from an Ag(I)–NHC to Au(I) and Pd(II), the lack of $^{107,109}Ag$–$^{13}C$ coupling in the $^{13}C$ NMR spectrum and the labile nature of the Ag(I) complexes were proposed to be part of the reasons for the NHC migration (Scheme 24) [9a]. However, there was some evidence that Ag(I)–NHCs with non-fluxional Ag–C bonds were also able to transfer the NHCs [9a,42].

A literature survey revealed that the NHC transfer technique has most frequently been applied to the synthesis of Au(I), Pd(II) and Rh(I)–NHCs. Therefore, we will first focus on Au(I)–NHCs. Common methods used to synthesize Au(I)–NHCs [124] include: (a) cleavage of electron rich olefins with Au(I) sources, (b) direct reaction of Au(I) sources with azolium salts under PTC conditions, (c) direct reaction of Au(I) sources with preformed NHCs, (d) protonation or alkylation of gold azolyl compounds, and (e) transmetallation with Ag(I)–NHCs. Recent trends revealed that transmetallation has become popular. The reaction between an Ag(I)–NHC and gold precursors such as $Au(SMe_2)Cl$ or Au(tht)Cl, or $Au(PEt_3)Cl$ afforded Au(I)–NHC effectively. Lin generalized the preparation of various [Au(NHC)Cl] compounds (Scheme 25i), which can be used as good precursors to prepare Au(I)–NHC-core containing compounds [9a–c]. Herrmann and co-workers also



Scheme 24. Fluxional behavior of Ag(I)–NHCs and NHC transfer.

reported the easy synthesis of a neutral [Au(NHC)Cl] via transmetallation [10].

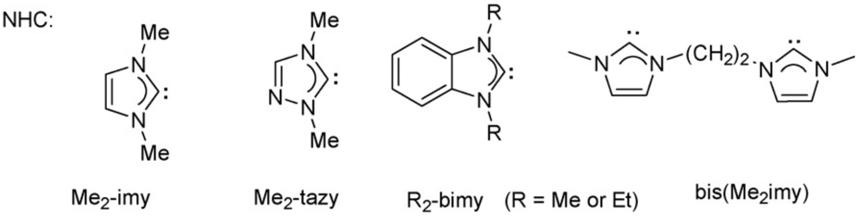
Recently, Nolan and co-workers described that in the preparation of certain neutral [Au(NHCs)Cl]s, the technique of transmetallation was superior to that of the free NHC method [11]. Baker et al. reported that in an attempt to isolate neutral [Au(NHC)Cl] by using the preformed NHC, a cationic Au(I)–NHC was obtained [12]; transmetallation easily controlled the formation of pure [Au(NHC)Cl]. It is noticeable that the use of imidazolium bromide in transmetallation to prepare [Au(NHC)Cl] may sometimes generate traces of [Au(NHC)Br]. If this is the case, the use of chloride salt may provide better quality [Au(NHC)Cl] [12]. Catalano et al. utilized pyridyl and picolyl substituted Ag(I)–NHCs to prepare Au(I)–NHCs, which served as excellent precursors to obtain a variety of polymeric gold compounds [13]. Meyer observed that the transmetallation of a tripodal Ag(I)–NHC afforded a tripodal Au(I)–NHC under inert conditions, but not in air (Scheme 26i) [14]. Zhang and co-workers reported that the transfer of ether bridged macrocyclic NHCs from dinuclear Ag(I)–NHCs gave Au(I)–NHCs smoothly under inert conditions (Scheme 26ii) [15]. With long *N*-alkyl chains, the ratio between the Ag to Au influenced the Au(I)–NHC formed; when the Ag/Au molar ratio was 2, a mixed $Ag_2Au_2$ compound (Scheme 26iii) was produced [9d], but with a molar ratio of 1, the reaction afforded only Au(I)–NHCs [90] (Scheme 26iv). Corberán et al. reported the preparation of *N*-methyl menthoxide and *N*-$^n$Bu substituted Au(I)–NHCs via transmetallation [16].

Regarding the synthesis of Pd(II)–NHCs, in addition to the transmetallation, other methods such as direct metallation of azolium salt with $Pd(OAc)_2$ or with Pd(II)-precursor in the presence of external base were also evaluated in some cases. The work by Cavell and co-workers [20], Tilset and co-workers [31], Gade and co-workers [33], and Shreev and co-workers [34] specified the failure of direct metallation to prepare Pd(II)–NHCs. Therefore transmetallation by Ag(I)–NHCs became of general interest.

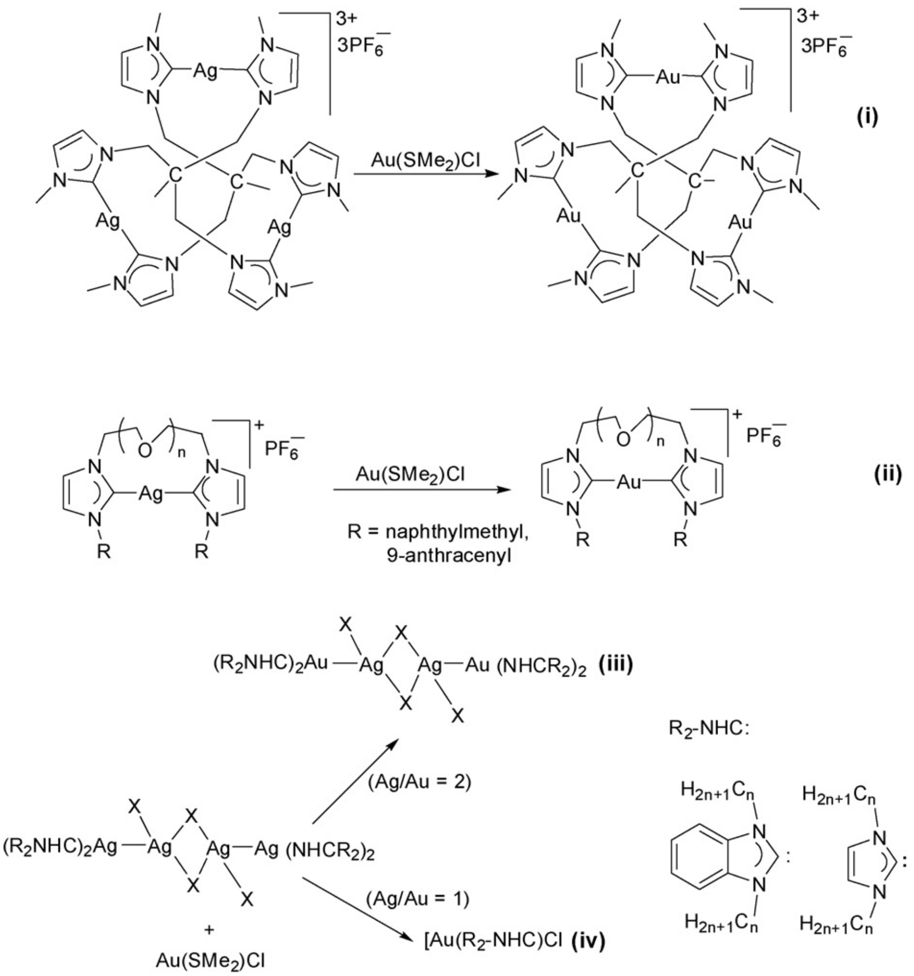
With non-functionalized NHCs (only with *N*-alkyl or *N*-aryl substituents), transmetallation normally produced simple $Pd(NHC)_2Cl_2$ complexes as shown in Scheme 24 [18,19]. Whereas, with functionalized NHCs, Pd(II)–NHCs of different structures were obtained, depending on the nature of the Pd(II) precursor, the reaction conditions, and stoichiometry of the reactants. For example, Cavell and co-workers showed that equimolar reactions between a picolyl substituted Ag(I)–NHC and $Pd(MeCN)_2Cl_2$ or PdMe(cod)Cl produced non-chelated Pd(II)–NHCs (Scheme 27i and ii) [20a]. A chelated mono-carbene complex, however, was obtained upon reaction

$$\mathrm{Au(SMe_2)Cl + [Ag(NHC)X] \longrightarrow [Au(NHC)Cl] + AgCl} \quad \textbf{(i)}$$

$$\mathrm{Au(SMe_2)Cl + [Ag(NHC)_2][PF_6] \longrightarrow [Au(NHC)_2][PF_6]} \quad \textbf{(ii)}$$



Scheme 25. Au(I)–NHCs of short alkyl chains from Lin's work.

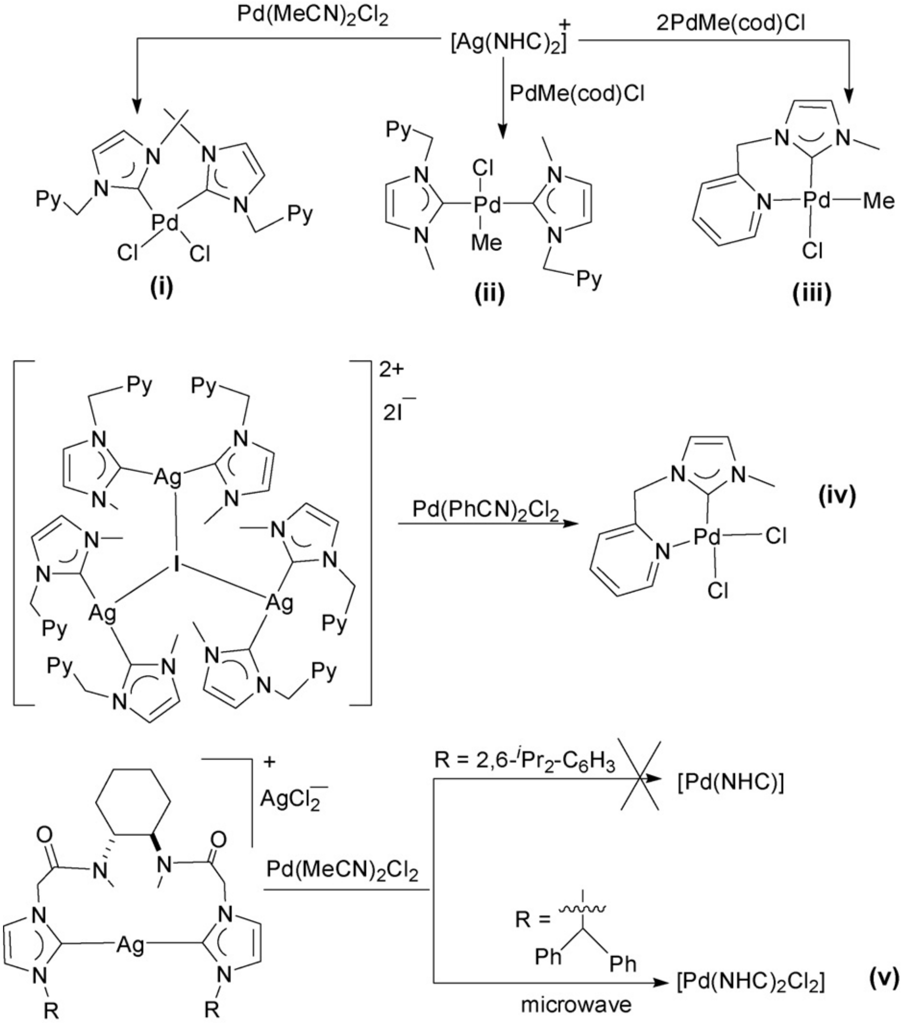


Scheme 26. The formation of mono and polynuclear Au(I)–NHCs by transmetallation.

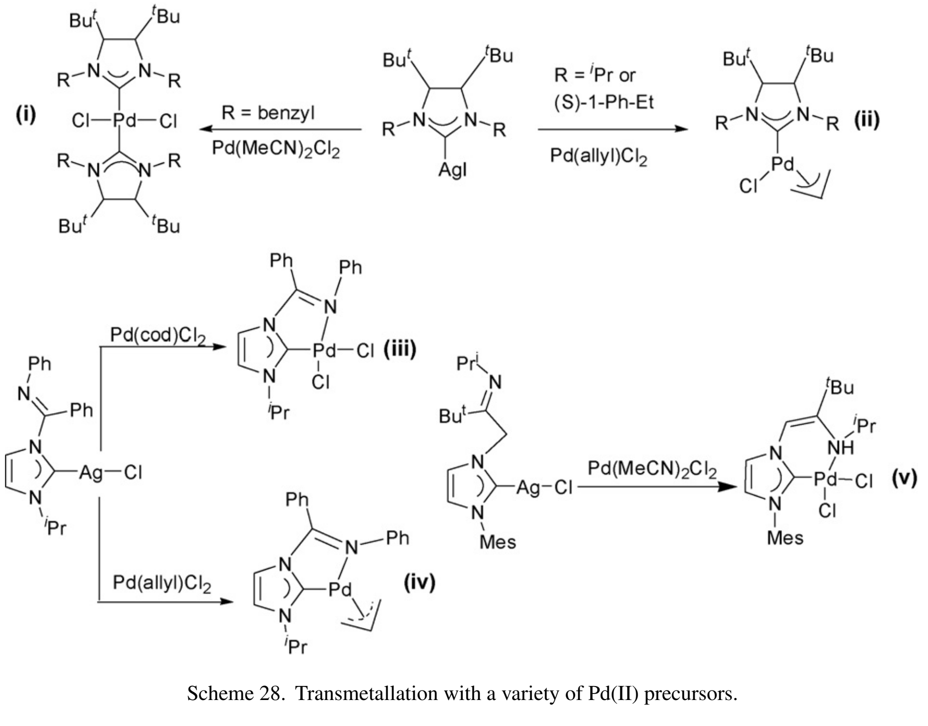
of Ag(I)–NHC with two equivalents of PdMe(cod)Cl (Scheme 27iii) [20a]. Wang et al. reported that the reaction of a trinuclear Ag(I)–NHC containing an *N*-picolyl sidearm with ∼3 M equivalents of $Pd(PhCN)_2Cl_2$ produced a chelated NHC complex (Scheme 27iv) [21]. Douthwaite also described the influence of reaction stoichiometry on the transfer reaction between a chiral dimeric Ag(I)–NHC and $Pd(MeCN)_2Cl_2$ [22c]. Burgess and colleagues described that some times the Ag(I)–NHCs with bulky N-substituents did not favor the NHC migration to Pd(II) (Scheme 27) [23]; in this situation, the use of microwave conditions was recommended (Scheme 27v). However, there was some evidence that NHCs with bulky N-substituents could still be transferred effectively to Pd(II) and different metal ions [for example, Ref. 22b,24,26,28,42–45,52,53,55,56]. Perhaps, the nature the of Pd(II) precursor used was a part of the reason.

The work by Mangeney and co-workers also demonstrated the influence of Pd(II) precursor in the NHC transfer process [24]. Ag(I)–NHCs with *N*-benzyl substituents transferred NHC smoothly to $Pd(MeCN)_2Cl_2$ (Scheme 28i) [24a], but not with N-$^{i}$Pr and *N*-(*S*)-1-phenylethyl substituents. In the latter case, reaction occurred when $Pd(allyl)Cl_2$ was used (Eq. (ii)) [24b]. Coleman and co-workers showed that the transfer of NHC from imine-functionalized Ag(I)–NHC to two different Pd(II) precursors produced chelated Pd(II)–NHCs (Scheme 28iii and iv) [25a]. Imine-functionalized Ag(I)–NHC with methylene-spacer produced a tautomerized Pd(II)–NHC (Scheme 28v) [25b]. In addition, several chelated Pd(II) complexes with achiral tridentate amino–NHC–amino [20b], achiral tridentate NHC–amino–NHC [22d], bidentate amino–NHC [24c] have been prepared easily via the carbene transfer technique.

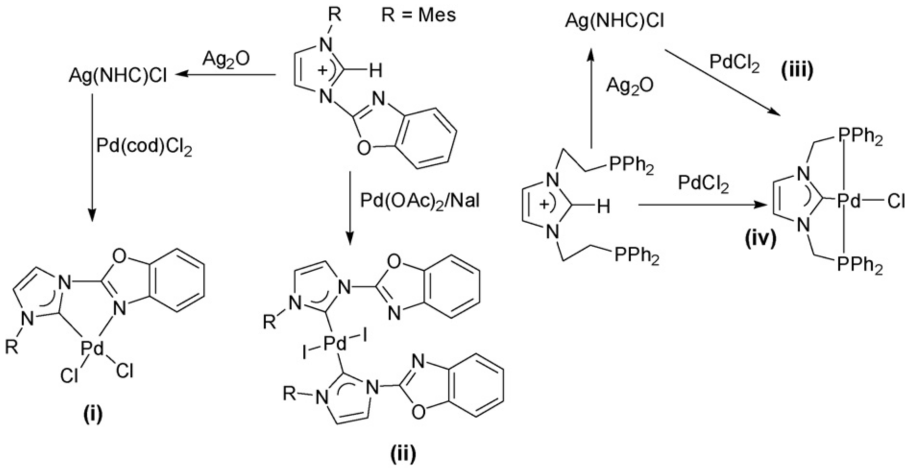
Poyatos et al. observed that the imidazolium salt with one *N*-oxazole side arm produced a chelated Pd(II)–NHC via transmetallation, and a non-chelated Pd(II)–NHC via direct-metallation (Scheme 29i and ii) [26]. The different halides used in the two reactions may cause the different chelation behaviors. Lee et al. reported that the imidazolium salt with two *N*-phosphine side arms formed only a chelated Pd(II)–NHC via either transmetallation or the direct-metallation with $PdCl_2$ (Scheme 29iii and iv) [27a]. Notably no base was added in the latter reaction; the high acidity of the salt along with the *N*-phosphine side arms suitable for chelation were proposed to be the reasons for the ease of $C^2$–H bond activation. Lee and co-workers also suggested the use of more polar solvents for a smooth progression of the transmetallation reactions [27b].



Scheme 27. The influence of reaction stoichiometry and bulkiness of the N-substituents in the preparation of Pd(II)–NHCs.



Scheme 28. Transmetallation with a variety of Pd(II) precursors.



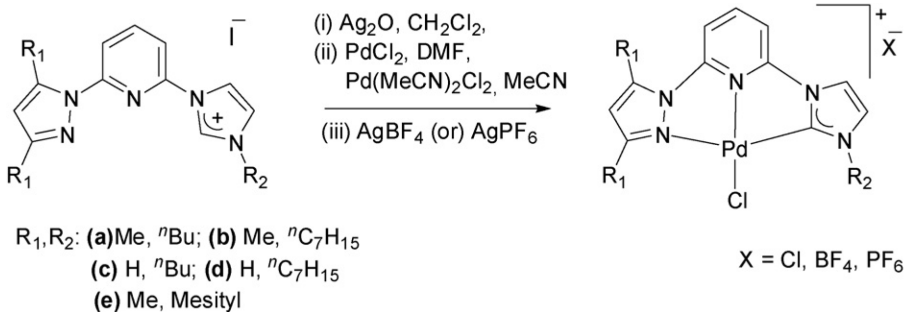
Scheme 29. Pd(II)–NHCs by transmetallation and direct metallation.

A Pd(II) complex consisting of a variety of unsymmetrical pyridyl supported pyrazolyl–NHC ligands was also obtained by the transmetallation method (Scheme 30) [28].

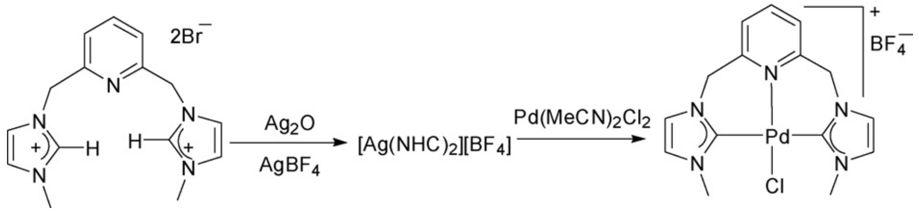
Danopoulos reported that the transfer of NHC from [Ag(NHC)halide] to Pd(II) was accompanied with the mixed anions Cl/$AgCl_2^-$ [29b,c]. In such a case, addition of $AgBF_4$ before the transmetallation produced pure Pd(II)–NHCs (Scheme 31) [20c].

In contrast to many reports which described carbene transfer from Ag(I)–NHCs to Pd(II) as being quite successful [18–39], work by Herrmann et al. showed that the intended carbene transfer of a six-membered NHC containing bulky mesityl N-substituents to Pd $(MeCN)_2Cl_2$ failed (Scheme 32i) [115]. The presence of a strong Ag–$C_{carbene}$ bond (as observed by the large down field shifts of the carbene-C resonance) was proposed to be a reason for the failure of NHC transfer. A similar result was observed by Buchmeiser and co-workers with the identical Ag(I)–NHC [38,125]. However, with N-$^i$Pr substituents, transmetallation was successful (Scheme 32ii) [38]. Hahn and co-workers reported that the transmetallation of a saturated five-membered imidazolin-2-ylidene with bulky *N*-mesityl and *N*-2,6-$^i$Pr$_2$–Ph substituents, to $PdI_2$ and [(*p*-cymene)RuCl(μ-Cl)]$_2$ failed (Scheme 32, iii) [92]. A seven-membered ring based NHC with two *N*-neo-pentyl substituents also did not undergo NHC transfer reaction (Scheme 32iv) [116]. When a bis-imidazolium salt linked by a highly electron withdrawing carbonyl group was used to react with $Ag_2O$ and $Pd(MeCN)_2Cl_2$ in a one pot reaction, a palladacyclobutan-3-one complex instead of a Pd(II)–NHC was produced (Scheme 32v), presumably due to the additional stabilization of the bonding mode in the former [126]. Despite that many imine-NHC functionalized Ag(I)–NHCs effectively produced the Pd(II)–NHCs, a recent report by Flahaut and co-workers reported the failure of the transfer of an imine-NHC to Pd(II) [24c]. Huynh et al. mentioned that when N-$^i$Pr substituted benzimidazolium salt was used, transmetallation gave a mixture of products with very low yields of Pd(II)–NHC [127]. This is quite unusual with simple azolium salts, but no experimental details were provided.

NHC transfer was also widely employed to form the Rh(I)–NHCs. In Crabtree's work, if the excess $Ag_2O$ was removed before the transmetallation reaction, the bis-imidazolium salts with short linkers ($n = 1$, 2) produced neutral non-chelated $[Rh(NHC)Cl]_2$ under refluxing conditions (Scheme 33i) [40a]. However, chelated ionic Rh(I)–NHCs were isolated from the salts with long linkers ($n = 3.4$) under similar reaction conditions in the presence of $KPF_6$ (Scheme 33ii). Chelated complexes as chloride salts were not characterized structurally due to decomposition. With the $n = 2$ linker, a chelated ionic Rh(I)–NHC was also formed in the presence of excess $Ag_2O$ and $KPF_6$ (Scheme 33ii) under refluxing conditions. On the other hand, non-chelated neutral Rh(I)–NHCs were produced if the transmetallation was performed at room temperature for $n$ values of 1–4 (Scheme 33i). Here it is noticeable that Viciano et al. were able to obtain chelated Ir(I)–NHCs at room temperature from the



Scheme 30. The formation of Pyridyl supported pyrazolyl-NHC Pd(II) complexes.



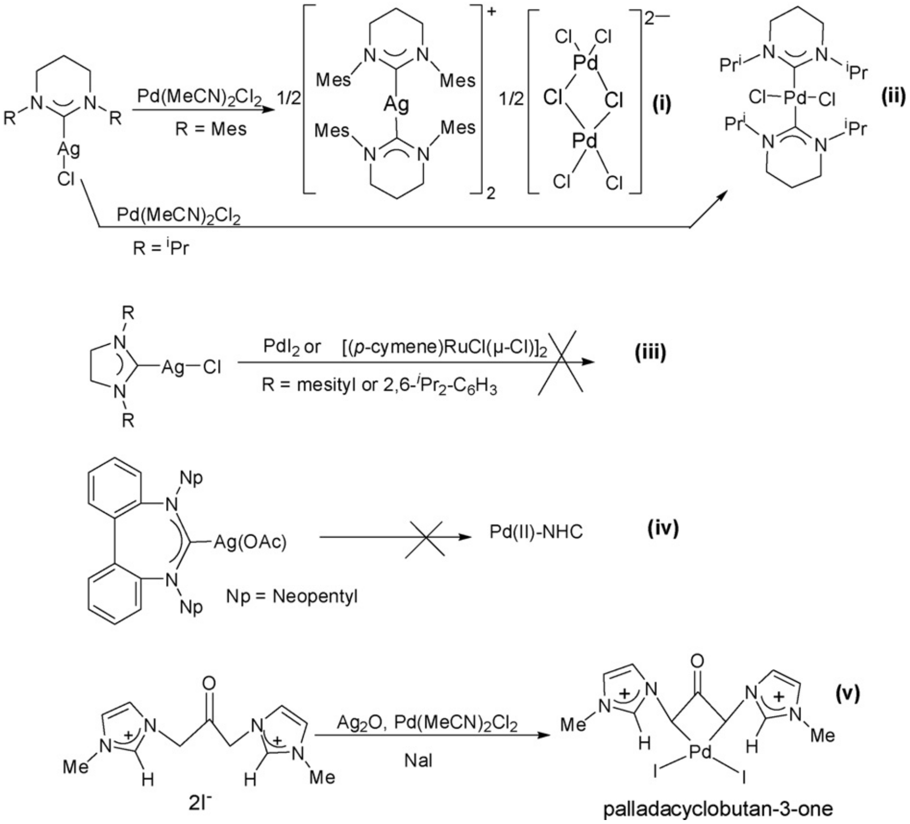
Scheme 31. Transmetallation by the use of $[Ag(NHC)_2][BF_4]$ complex.

bis-imidazolium salts with linkers of $n = 2–4$ [59a]. Youngs and co-workers also obtained a non-chelated dinuclear Rh(I)–NHC compound from dinuclear Ag(I)–NHC (Scheme 33iii) [30]; yet a chelated Pd(II)–NHC was formed from the same Ag(I)–NHC (Scheme 33iv). A report by Peris pointed out that a square planar but not tripodal Rh(I)–NHC or Ir(I)–NHC was obtained from the tripodal imidazolium salts (Scheme 33vi) [41a].

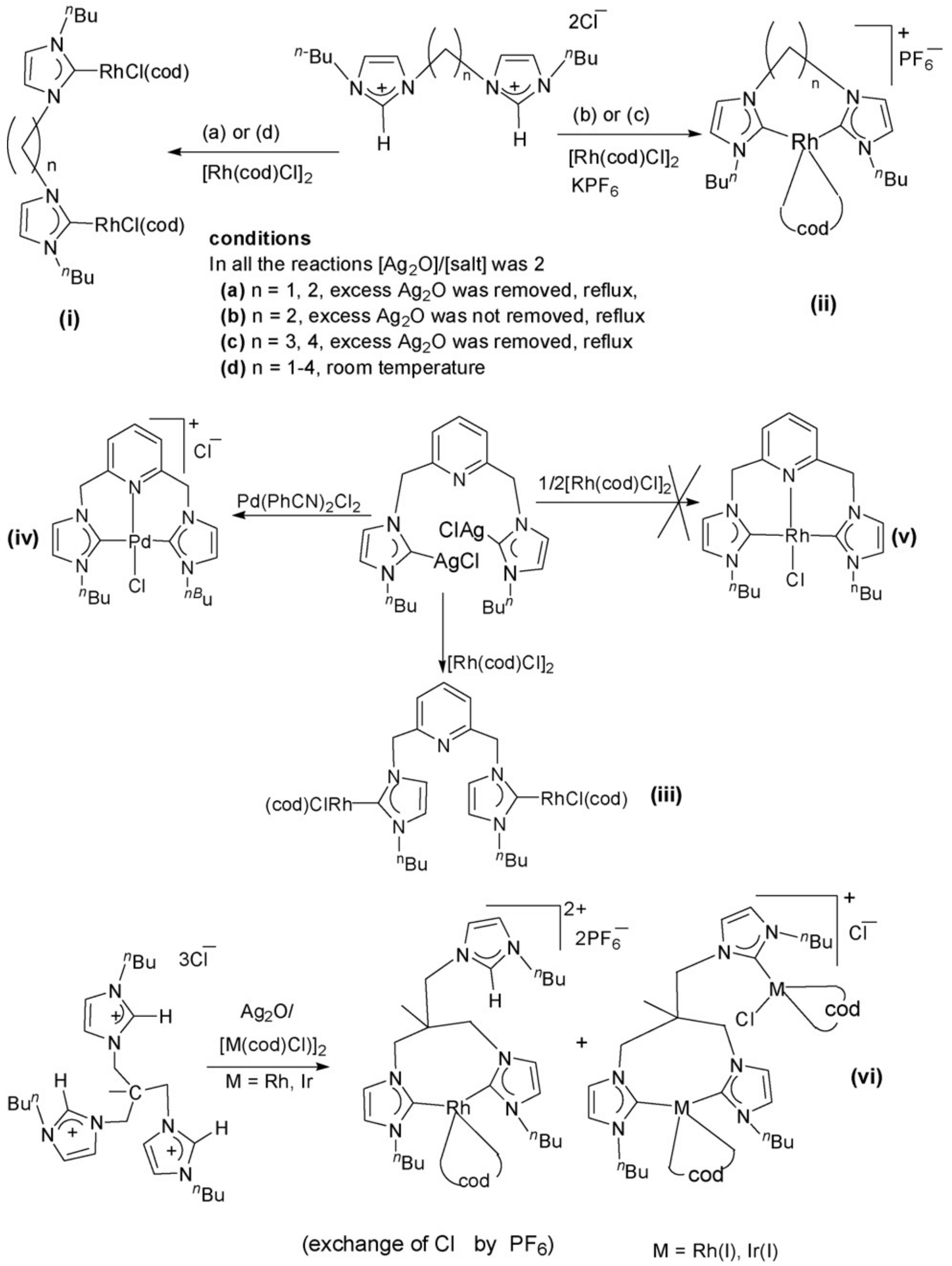
Slaughter demonstrated the use of a di-carbene complex, $[Ag(NHC)_2]_2[BF_4]_2$, to produce a chelated Rh(I)–NHC (Scheme 34) [42]. An important feature of this work was that NHCs with bulky *N*-mesityl substituents transferred effectively to Rh(I). As well, the reports by the groups of Tsuji and co-workers [43] and Liu and co-workers [44] also described the transfer of bulky NHCs such as dendrimer-NHC and *N*-pyridyl NHC to the Rh(I).

Youngs achieved NHC transfer from a dinuclear Ag(I)–NHC to radio active $^{105}$Rh(III) in hot DMSO (Scheme 35i) [57]. Peris and co-workers showed that the ratios between the pyridyl-substituted imidazolium salt and the metal-precursors (Rh(I) and Ir(I)) influenced the oxidation state of the metal ions in the final product [41b]. When the salt/M ratio was 1 (M = Rh, Ir), mono-NHC Rh(I) and Ir(I) complexes were shown to be formed via *in situ* Ag(I)–NHCs (Scheme 35ii). The coordination behavior of the pyridine side arm was uncertain in the mono-NHC complexes. On the other hand, when the salt/M ratio was 2, oxidation of the metal ions occurred to form chelated Rh(III) and Ir(III)–NHCs (Scheme 35iii). Ag(I) was proposed to oxidize the metal ions, since Ag(0) was observed. Arnold also came up with a similar observation with ruthenium ion [69]. However, a non-chelated neutral Ir(I)–NHC was formed from the 4,5-dichlorosubstituted imidazolium salt under similar conditions [59b].

In another approach, Youngs and co-workers demonstrated that a caffeine derived NHC was transferred efficiently from Ag(I)–NHC to Rh(I) in hot DMSO [45]. This attempt specified the possible use of biological sources to synthesize various transition metal–NHCs via the $Ag_2O$ technique. Coleman et al. reported that while an imino-NHC ligand was transferred to a



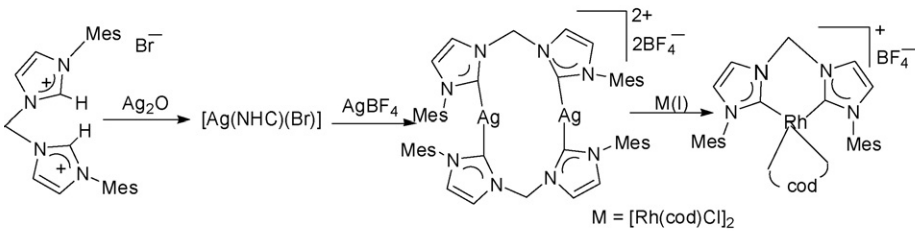
Scheme 32. Examples of some unsuccessful transmetallation reactions by Ag(I)–NHCs.



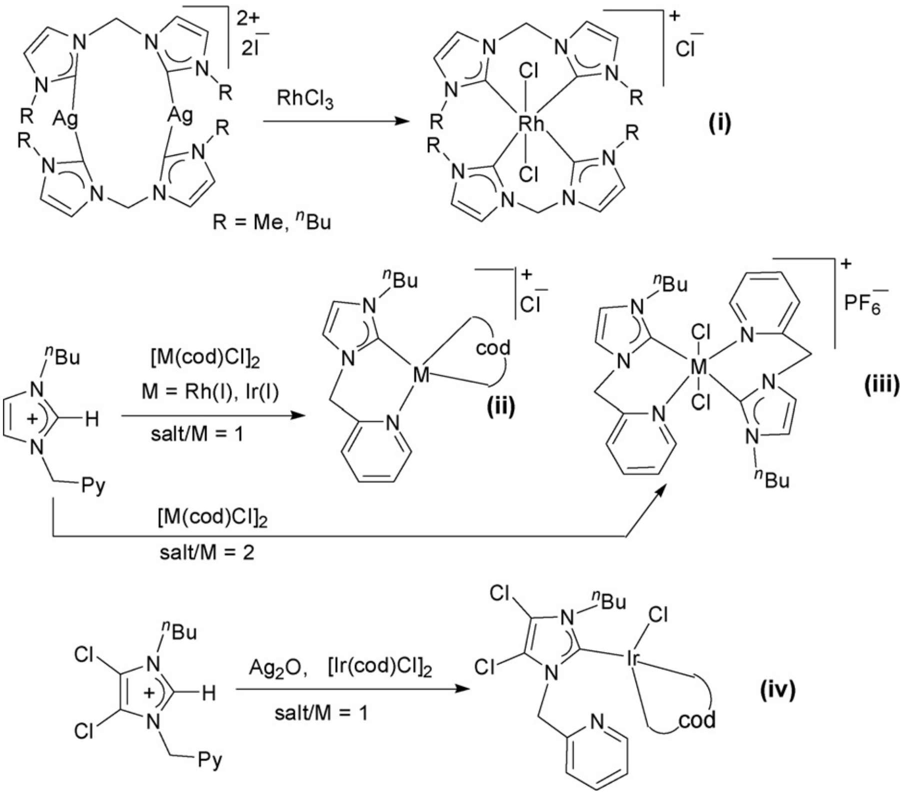
Scheme 33. The formation of Rh(I)–NHCs via the transmetallation reactions.

Rh(I) source in THF, tautomerization of the ligand was observed similar to that of the Pd(II)–NHC shown in Scheme 28 [25b].

Lee and co-workers described the NHC transfer from a phosphine functionalized trinuclear Ag(I)–NHC to Rh(I) producing a variety of rhodium complexes depending on the conditions (Scheme 36) [46]. The reaction between such an Ag(I)–NHC and $[Rh(cod)Cl]_2$ in dichloromethane, produced *cis*,*mer*-Rh(III)($PC^{NHC}P$)($CH_2Cl$)$Cl_2$ via oxidative addition of dichloromethane to the intermediate Rh(I)($PC^{NHC}P$)Cl complex (Scheme 36ii). In the absence of $CH_2Cl_2$, this reactive



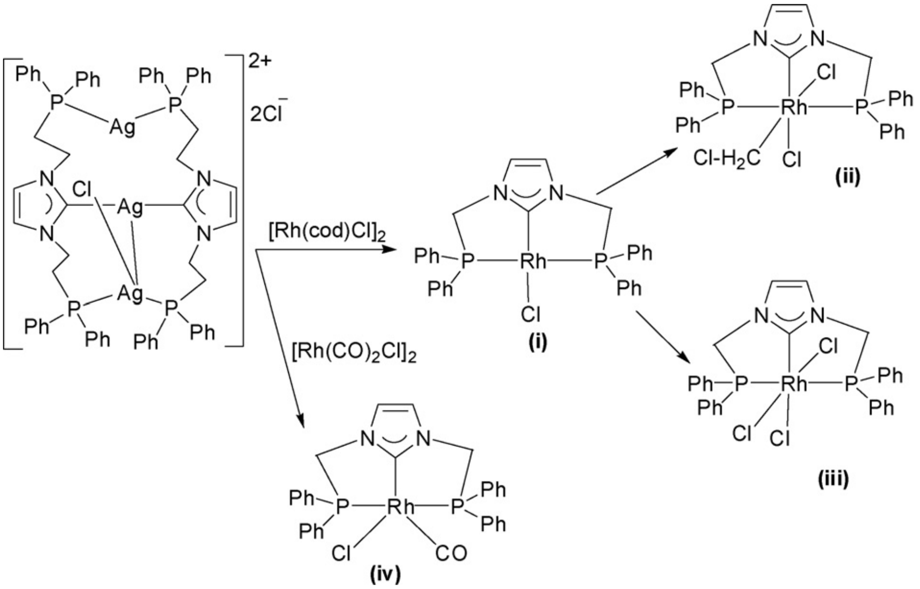
Scheme 34. The formation of chelated Rh(I)–NHC with methylene linkers.



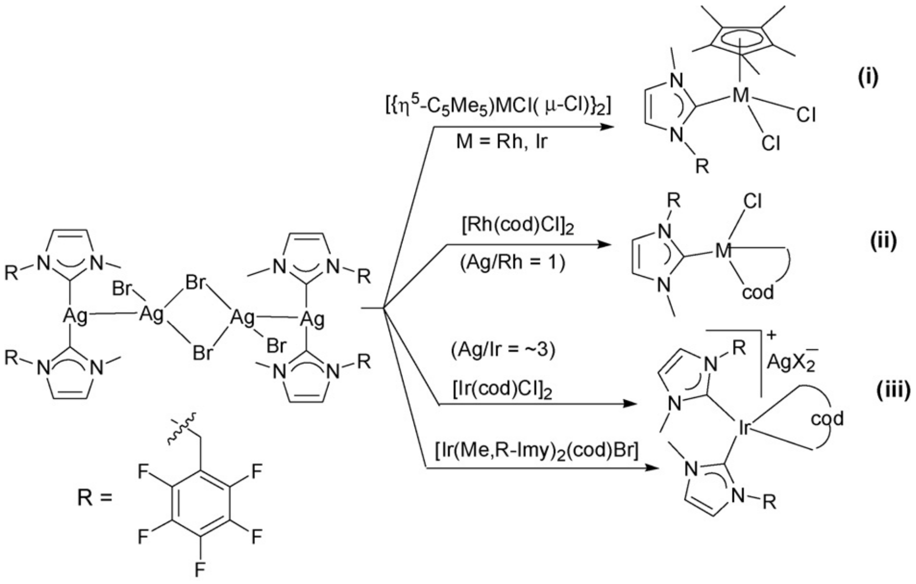
Scheme 35. The formation of Rh(III), Rh(I), Ir(I) and Ir(III)–NHCs.

Rh(I)(PC$^{NHC}$P)Cl intermediate was proposed to undergo oxidative degradation in DMF to afford *mer*-Rh(III)(PC$^{NHC}$P)Cl$_3$ complex (Scheme 36iii). A *mer*-Rh(I)(PC$^{NHC}$P)(CO)Cl), however, was obtained when [Rh(CO)$_2$Cl]$_2$ was employed (Scheme 36iv); in this case the Rh(I) center was proposed to be stabilized by the π-back bonding of the C≡O ligand.

Transfer of fluorinated NHC to different Rh(I) and Ir(I) reactants has been reported [47]. Saunders and co-worker [47a] showed that a half sandwich Rh(I)–NHC or Ir(I)–NHC complex was formed upon the reaction of Ag(I) fluorinated-NHC complex with [($\eta^5$-C$_5$Me$_5$)MCl(μ-Cl)$_2$] (M = Rh, Ir) in a 1:1 stoichiometry (Scheme 37i). While Whittlesey and co-workers [47b] employed the same Ag(I) fluorinated-NHC to react with [Rh(cod)Cl]$_2$ in a 1:1 stoichiometry to yield the analogous neutral Rh(I)–NHC (Scheme 37ii). An ionic bis-NHC complex of Ir(I) complex was obtained upon the reaction with [Ir(cod)Cl]$_2$



Scheme 36. Transmetallation reactions with different Rh(I) precursors.

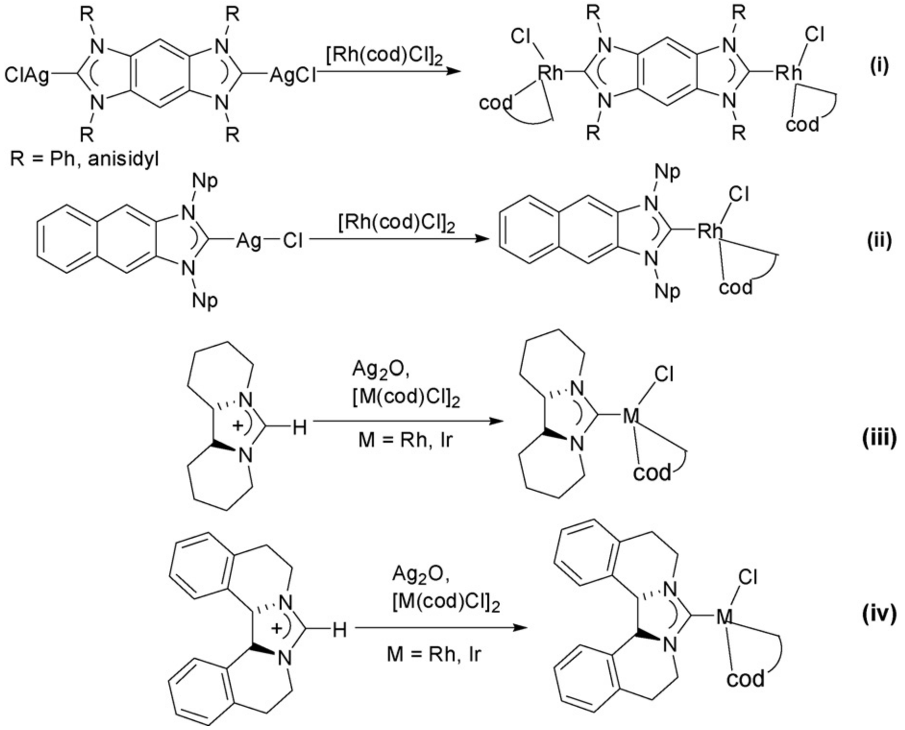


Scheme 37. The formation of fluorinated NHC–Rh(I) and Ir(I) complexes.

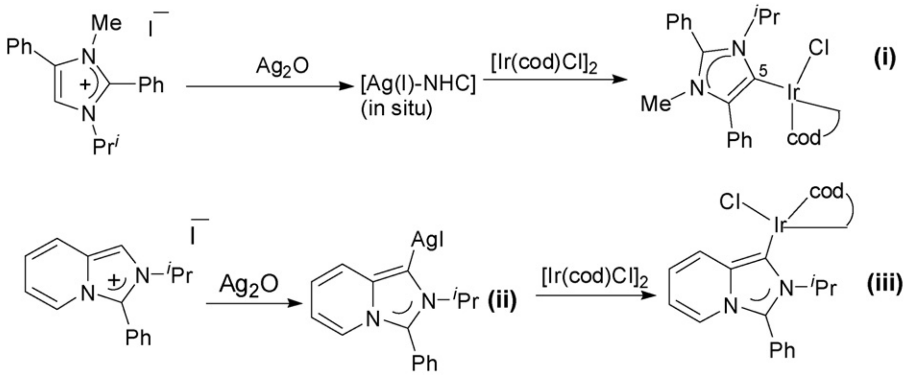
in a 3:1 stoichiometry (NHC/Ir = 3) at 70° (Scheme 37iii). This bis-NHC complex was also obtained by heating a neutral mono-NHC Ir(I) (prepared by another method) with the Ag(I)–NHC.

Rh(I) and Ir(I)–NHCs with NHCs other than simple imidazol-2-ylidene moieties were also prepared via transmetallation with Ag(I)–NHCs (Scheme 38). Bielawski used the transmetallation method to prepare a neutral dinuclear Rh(I)–NHC complex containing a bis-NHC with an arene backbone (Scheme 38i) [48]. Heinicke obtained the neutral mononuclear Rh(I)–NHC containing naphtha(2,3-*d*)imidazol-2-ylidene (Scheme 38ii) [39]. Herrmann et al. utilized chiral imidazolium salts derived from 2,2-bipiperidene and biisoquinoline to prepare Rh(I) and Ir(I)–NHCs via Ag(I)–NHCs formed *in situ* (Scheme 38iii and iv) [49]. The transfer of a saturated imidazolinium based NHCs to Rh(I) was reported by Hemchen and co-worker and Gilbertson and co-worker [55,56].

Crabtree made efforts to generalize the synthesis of abnormal $C^5$-bound Ir(I)–NHCs via the $Ag_2O$ technique [58]. The use of a 2-phenyl imidazolium salt generated an unstable $C^4$-bonded Ag(I) complex, which did not afford the Ir(I) complex



Scheme 38. The formation of Rh(I) and Ir(I)–NHCs other than simple imidazol-2-ylidene.



Scheme 39. The formation of abnormal Ir(I)–NHCs via abnormal Ag(I)–NHCs.

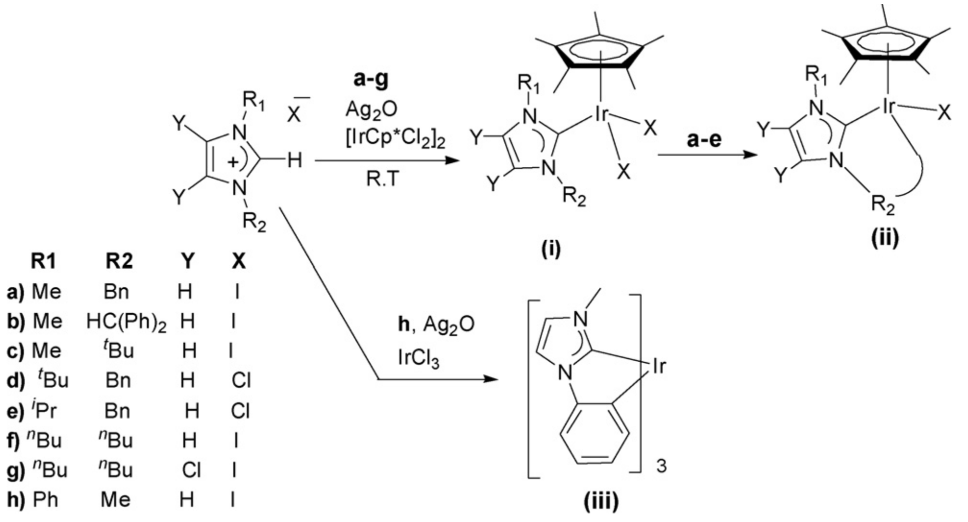
due to the more basic nature of the C$^4$-carbene. However, the salt designed with two blocking groups at both C$^2$- and C$^4$-positions such as 2,4-diphenyl imidazolium, reacted with Ag$_2$O and then [Ir(cod)Cl]$_2$ in a one pot reaction to give an abnormal C$^5$-bonded Ir(I) complex (Scheme 39i). However, an attempt to prepare abnormal C$^5$-bonded Rh(I)–NHC from 2,4-dimethyl imidazolium salt afforded only a normal C$^2$-bonded Rh(I)–NHC via C$^2$-bonded Ag(I)–NHC [40b], an indication of the influence of the substituent at the C$^2$-position. A report by Lasaletta also described the use of a C$^2$-blocked imidazo[1,5-a]pyridine iodide, an abnormal Ir(I)–NHC but not the Rh(I)–NHC was formed (Scheme 39ii) [51].

In view of the stability of organometallic complexes with NHC ligands, Peris utilized the Ag$_2$O technique to obtain stable Cp$^*$-Ir(III)–NHCs (Scheme 40) [60]. Cyclometallated products were obtained when salts (a–e) were used. However, the reactions of the salts (f and g) produced only the stable noncyclometallated complexes.

Thompson also reported the transfer of NHC to Ir(III) [61]. The reaction of a *N*-phenyl substituted imidazolium or benzimidazolium iodide salt with Ag$_2$O and IrCl$_3$ in refluxing ethoxyethane produced a mixed cyclometallated *fac*- and mer-Ir(III)-(NHC)$_3$ (Scheme 40iii) along with another product recognized as a μ-dichloro bridged cyclometallated dimer $[Ir(III)(Me,Ph\hat{N}HC)_2Cl]_2$. Treatment of this dimeric product with additional imidazolium salt in the presence of Ag$_2$O again produced the same mixed *fac*- and *mer*-Ir(III)-(NHC)$_3$.

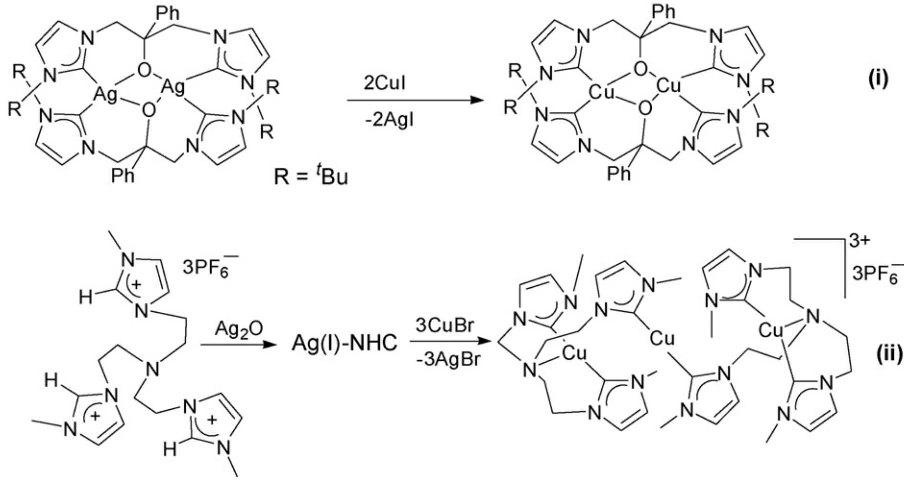
Arnold et al. highlighted the use of the transmetallation method to prepare Cu(I)–NHCs by a halide free neutral Ag(I) alkoxy–NHC complex [62]. A stable dinuclear Cu(I)–NHC, in which the Cu(I) ion was bound to two NHCs and two alkoxy groups was obtained (Scheme 41i). In reference to the bond strength of Cu(I)–NHC (319 kJ mol$^{-1}$), the Ag(I)–NHC bond was found to be weaker by approximately 63 kJ mol$^{-1}$, which was believed to be one reason for the facile transmetallation reactions [78]. Zhang and co-workers reported the isolation of a Cu(I)–NHC from crown ether linked Ag(I)–NHC in MeCN [63]. Meyer and co-workes described the transfer of NHC from carbon and nitrogen anchored tripodal Ag(I)–NHCs to Cu(I) [14,64]. The nitrogen anchored tripodal Cu(I)–NHC showed different geometries from those of free carbene route (Scheme 41ii) [64].

Manganey and co-workers explored the use of Ag$_2$O route for a number of Cu(II) catalyzed reactions; however, no structural characterization of Cu(II)–NHCs was provided [65]. This method gave better catalytic results than the direct utilization of



| | R1 | R2 | Y | X |
|---|---|---|---|---|
| **a)** | Me | Bn | H | I |
| **b)** | Me | HC(Ph)$_2$ | H | I |
| **c)** | Me | $^t$Bu | H | I |
| **d)** | $^t$Bu | Bn | H | Cl |
| **e)** | $^i$Pr | Bn | H | Cl |
| **f)** | $^n$Bu | $^n$Bu | H | I |
| **g)** | $^n$Bu | $^n$Bu | Cl | I |
| **h)** | Ph | Me | H | I |

Scheme 40. The formation of Cp$^*$Ir(III)–NHCs.

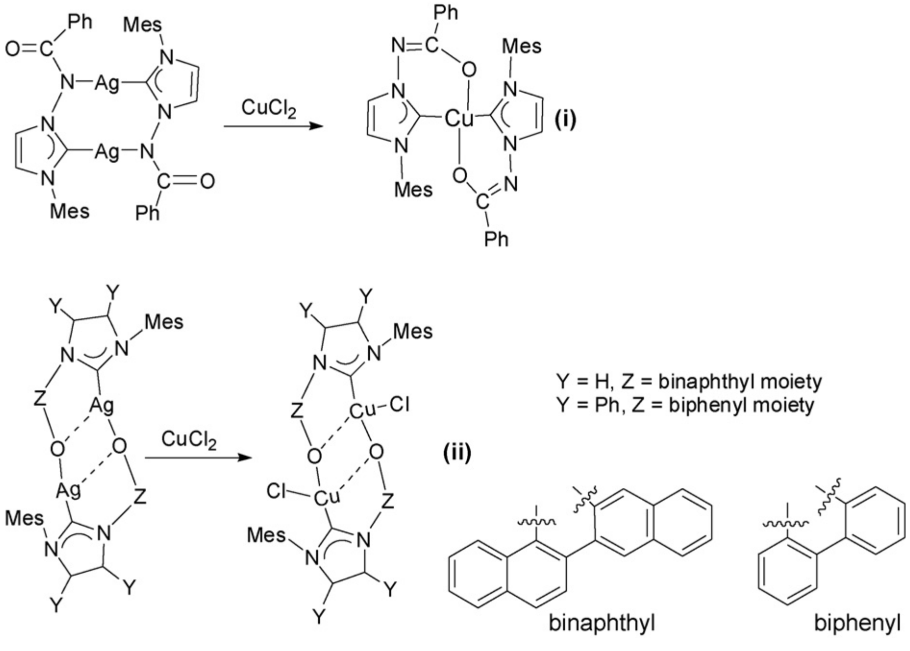


Scheme 41. The transfer of NHC to Cu(I).

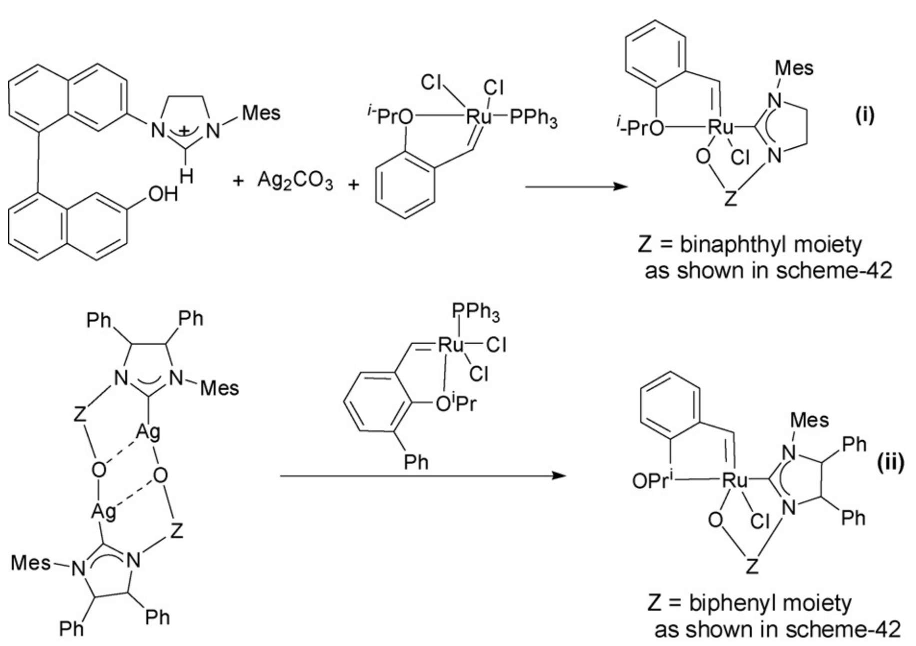
imidazolium salts as sources of NHCs. Recently, Hoveyda and co-workers [66] and Charette and co-workers [67] reported the preparation of Cu(II)–NHCs via transmetallation (Scheme 42i and ii). Interestingly, in Charette's work [67] the coordination mode of the side arm was changed from nitrogen to oxygen upon transmetallation.

Recently, the preparation of NHC complexes of ruthenium via transmetallation was reported. Hoveyda first reported the formation of a chiral mononuclear Ru(IV)–NHC via $Ag_2CO_3$ promoted transmetallation using a binaphthyl-alcohol functionalized imidazolinium salt as a precursor (Scheme 43i) [73]. Since some practical difficulties were observed with the above Ru(IV)–NHC in the olefin metathesis, a bi-phenyl-alcohol functionalized Ru(IV)–NHC was then designed via the $Ag_2O$ method [66a]; the dinuclear Ag(I)–NHC produced a mononuclear Ru(IV)–NHC (Scheme 43ii). Purification under inert conditions improved the yield of this Ru(IV)–NHC.

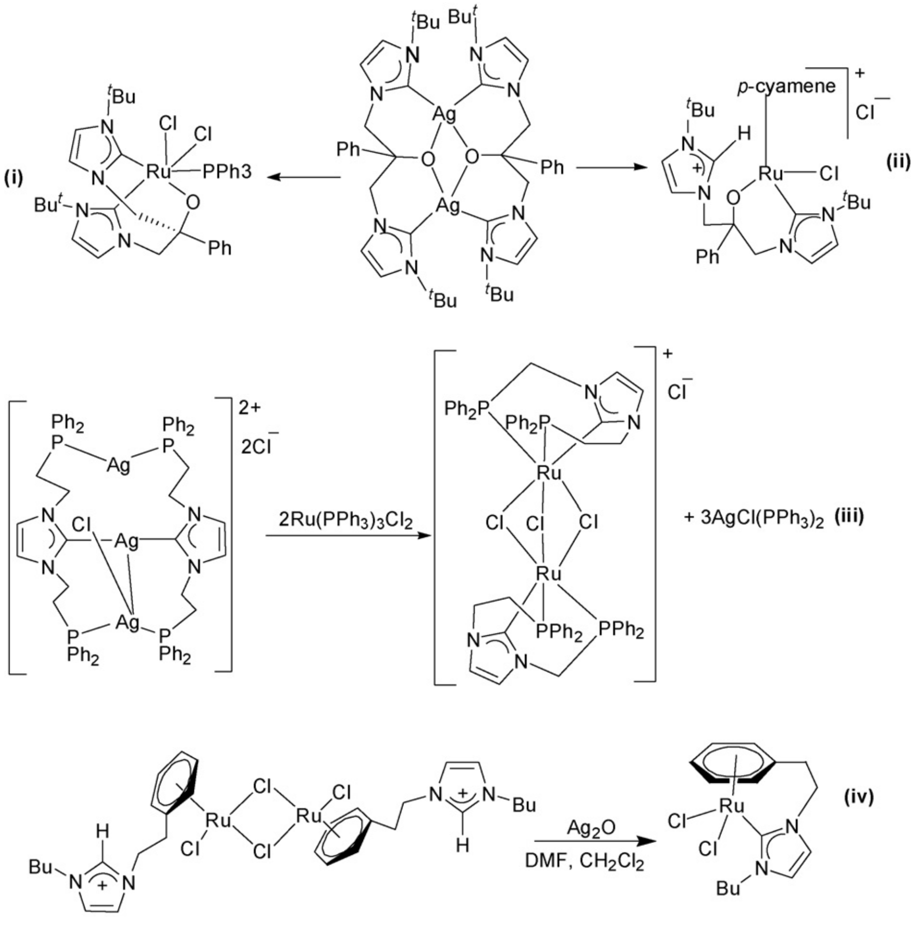
When Arnold et al. launched the transfer of NHC from Ag(I)–NHC-alkoxide to $RuCl_2(PPh_3)_3$, oxidation of Ru(II) to Ru(III) occurred along with the Ag(0) formation (Scheme 44i) [69]. When $[Ru(C_6H_4Me^iPr)Cl_2]_2$ was used, there was no change in oxidation state and Ru(II)–NHC with a dangling imidazolium was formed (Scheme 44ii). It was supposed that the oxidation potential of Ag(0)/Ag(I) in the Ag(I)–NHC-alkoxide complex may be large enough to oxidize Ru(II) in $[RuCl_2(PPh_3)_3]$, but not in $[Ru(p\text{-cymene})Cl_2]_2$. When Lee and co-worker conducted the transfer of NHC from a trinuclear Ag(I)–NHC to Ru $(PPh_3)_3Cl_2$, a Ru(II)–NHC but no Ru(III)–NHC was produced (Scheme 44iii) [70]. In a recent advance, Dyson and co-workers utilized the carbene transfer



Scheme 42. The transfer of NHC to Cu(II).

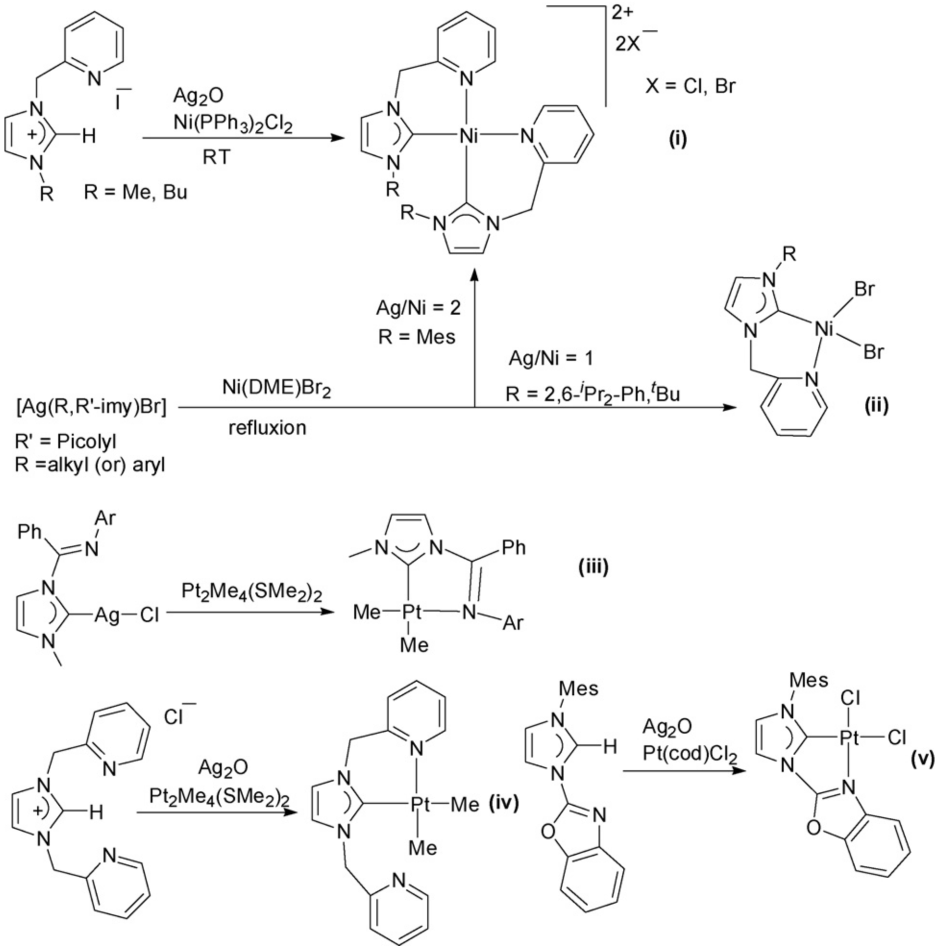


Scheme 43. The transfer of NHC to Ru(IV).



Due to the solubility problems, Ru(II) reactant was taken in DMF and $Ag_2O$ in $CH_2Cl_2$.

Scheme 44. The formation of Ru(II) and Ru(III)–NHCs.



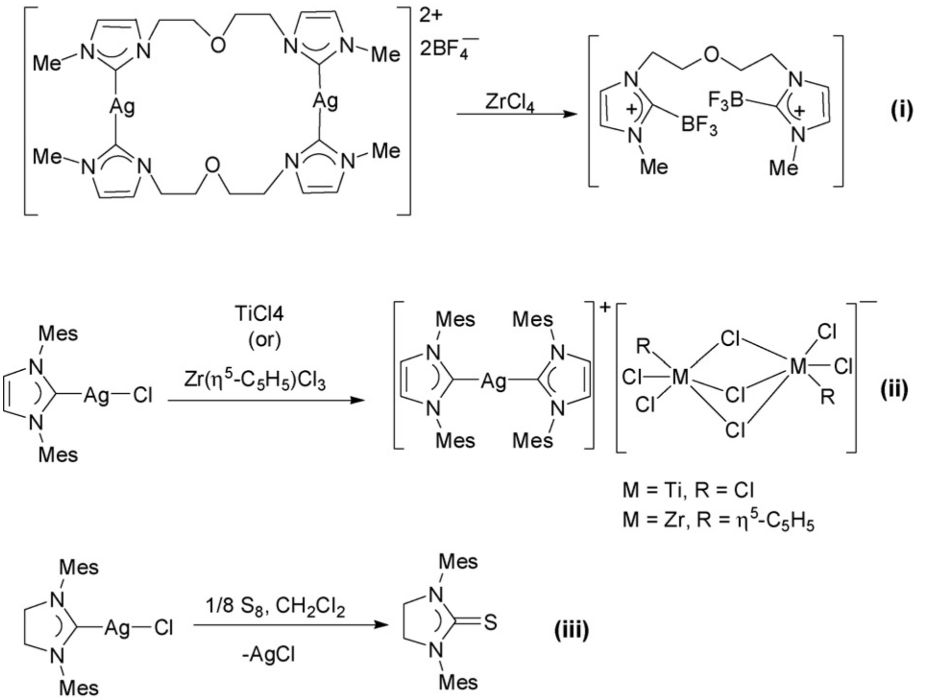
Scheme 45. The formation of Ni(II)–NHCs and Pt(II)–NHCs.

technique to prepare chelated the $\eta^6$-arene-NHC Ru(II) complex (Scheme 44iv) [71]. Xu and Gilbertson also reported the use of $Ag_2O$ and $Ag_2CO_3$ promoted NHC transfer reactions to Ru(II), in which peptide functionalized imidazolium salts were used [56].

Transfer of NHC from Ag(I)–NHC to other $d^8$ metal ions of Ni(II) [74,75] and Pt(II) [26,31c,76] was also investigated (Scheme 45). Jin and co-workers showed that the reaction of *N*-picolyl functionalized imidazolium iodide with $Ag_2O$ followed by $Ni(PPh_3)_2Cl_2$ in $CH_2Cl_2$ at room temperature provide a homoleptic chelated $[Ni(NHC)_2]^+$ (Scheme 44i) [74]. Danopoulos observed the formation of similar homoleptic $[Ni(NHC)_2]^+$ upon the interaction of two equivalents of preformed Ag(I)–NHCs containing *N*-picolyl side arms with $Ni(DME)Br_2$ (Scheme 44i) [75]. Under similar reaction conditions, the use of one equivalent of Ag(I)–NHC also formed a chelated neutral $[Ni(NHC)Br_2]$ (Scheme 44ii). Ag(I)–NHCs with *N*-pyridyl side arms also transferred the carbene to Ni(II). It appears that the efficiency of these reactions depends also on the nature of a second N-substituent on NHC.

The work of Tilset and co-workers [31c] and Puddephatt and co-worker [76] utilized the reaction of $Pt_2Me_4(SMe_2)_2$ with Ag(I)–NHCs to obtain Pt(II)–NHCs containing pyridyl or amine functionality (Scheme 44iii and iv). Poyatos et al. prepared an oxazole-carbene containing Pt(II)–NHC (Scheme 44v) [26].

It is notable that the transfer of NHC to group 4 metal ions did not occur. Cavell and co-workers reported that during the intended NHC transfer reaction between $[Ag(NHC)_2][BF_4]$ and $ZrCl_4$, an unusual activation of a B–F bond of $[BF_4]$ took place and formed a bis($NHC{:}BF_3$) (Scheme 46i) [104a]. This phenomenon indicated the non-innocent nature of $[BF_4]$ in the presence of nucleophilic NHCs under certain conditions. Hollmann et al. also observed that transmetallation between monomeric [Ag(NHC)Cl] and $TiCl_4$ or $Zr(\eta^5\text{-}C_5H_5)Cl_3$ produced the $[Ag(NHC)_2]^+$ cation and a group 4 metal-chloride anion (Scheme 46ii) [128]. The high chlorophilicity of these metal ions together with the large solvation/lattice enthalpy of the ionic products were proposed to be one reason for the preferred transfer of chloride than NHC. The saturated imidazolinium based Ag(I)–NHCs reported by Hahn and co-workers did not transfer the NHC to Pd(II) or Ru(II) but reacted with elemental sulfur to produce thio-carbonyl products [92] (Scheme 46iii).



Scheme 46. Transmetallation reactions with group 4 metal ions and elemental sulfur.

## 4. Conclusion

The present work revealed that the $Ag_2O$ technique has been the most popular method in the synthesis of Ag(I)–NHCs and in their subsequent uses as transmetallating agents. The $Ag_2O$ technique is tolerant of activated hydrogen atoms adjacent to functional groups. The use of normal azolium halide led to the formation of ionic or neutral Ag(I)–NHCs in the solid-state, depending on factors such as counter-ions, carbene cores, N-substituents and the crystallization conditions. A fluxional behavior between the ionic and neutral complexes was observed in solution for most of the compounds. The ionic or neutral compounds displayed structural diversity to give monomeric, dimeric and polymeric forms depending on the steric bulkiness around the Ag(I)–NHCs. In some instances non-stoichiometric $X^-/AgX^{2-}$ were reported; this happened because the $AgX^{2-}$ was in equilibrium with AgX(s) and $X^-$. This problem can be resolved if the halide ion was replaced by non-coordinating anions.

Depending on the nature of the imidazolium salts, the synthetic reactions conducted with excess $Ag_2O$ yielded interesting products. For example, the reaction of long *N*-alkyl chain containing imidazolium or benzimidazolium salts with excess $Ag_2O$ produced stable AgNPs in solution along with the AgNHCs. When *N*-pyridyl functionalized imidazolium salts reacted with excess $Ag_2O$, the triangulo-$[Ag_3(\mu\text{-NHC})_3]^{+3}$ complexes (Scheme 17a and b) with bridging $\mu^2$-carbenes and unusual $Ag\cdots Ag$ interactions were generated. Reaction of an imidazolium cyclophane with excess $Ag_2O$ gave a tetranuclear Ag(I)–NHC in DMSO and a dinuclear Ag(I)–NHC in water. The reaction of 2-methyl or 2-benzyl imidazolium salts with excess of $Ag_2O$ led to the oxidative cleavage of the C–C bond at $C^2$-position and formed the normal Ag(I)–NHCs in good yields. Addition of Ag(I) to the preformed Ag(I)–NHCs also directed the formation of Ag(I)–NHCs with diverse structures.

Ag(I)–NHCs played an important role as NHC transfer agents in the development of many metal–NHCs. So far transfers of NHC from Ag(I) to Ni(II), Pt(II), Pd(II), Cu(I), Cu(II), Au(I), Rh(I), Rh(III), Ir(I), Ir(III), Ru(II), Ru(III) and Ru(IV) have been reported. Some of the metal–NHCs can be prepared only by the transmetallation technique. The occurrence of transmetallation and nature of the transmetallated product depended not only on the Ag(I)–NHCs but also on the receiving metal-precursors and the reaction conditions. During the transfer of NHC to Ru(II) and Rh(I), oxidation of the metal ions was sometimes observed due to the high oxidation power of the Ag(I) or the halogenated solvents. In certain examples, the failure of transmetallation was proposed to be due to the strong Ag–C bond, bulky N-substituents or non-fluxional behavior. However, with similar features, examples of successful transfer of NHC were reported. The failure of NHC transfer from [Ag(NHC)halide] to group 4 metals was attributed to the high chlorophilicity of group 4 metal ions together with the large solvation/lattice enthalpy of the ionic products. The use of 2,4-blocked imidazolium salts with certain substituents resulted in the formation of either normal metal–NHCs or abnormal metal–NHCs.

Other than transmetallation, The use of Ag(I)–NHCs was also realized in homogeneous catalysis such as in the preparation of 1,2-bis(boronate) esters [16,97] and ring opening polymerization of lactides [85,98b], olefin polymerization [21], and as a source of free NHC in the copper catalyzed conjugate addition of diethylzinc to a variety of Michael acceptors [65]. More efforts are to be encouraged in this area to discover more applications. The liquid crystal properties of Ag(I)–NHCs may have material science application. Furthermore, the use of Ag(I)–NHCs as precursors for silver nanoparticles will certainly have an impact in medicinal, and applied sciences. The nature of these AgNPs, however, remains to be answered.

It is also interesting to mention theoretical calculations dealing with Ag(I)–NHCs, which provide insights into the nature of metal–NHC. The calculations reported by Mayer and co-workers [14] on the N–Me substituted tripodal Ag(I)–NHC and by Frenking and co-workers on unfunctionalized Ag(I)–NHC [129] showed non-negligible π-back bonding. However, calculations reported recently by Ghosh and co-workers concluded that functionalized NHCs are effective σ-donors [98].

## Acknowledgments

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