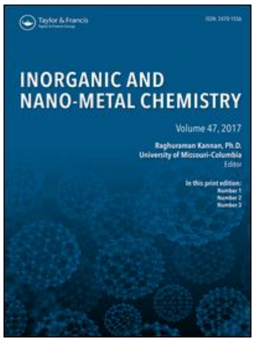

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Catalytic activity of *N*-heterocyclic carbene silver complexes derived from imidazole ligands

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ABSTRACT

The *N*-heterocyclic carbene (NHC)-silver(I) complexes, **3a–c** of the type (NHC)AgCl were prepared from 1-(methyl)-3-(alkyl)-imidazolium chlorides (**2a–c**) by the reactions with Ag_2O in dichloromethane as a solvent at room temperature. The complexes were characterized by elemental analyses and NMR spectroscopy. The catalytic activities of NHC-silver complexes were investigated in the three-component coupling reaction of aldehyde, alkyne, and amine to propargylamines.

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Catalysis; coupling; imidazole; *N*-heterocyclic carbene; silver(I)

Introduction

Imidazol-based *N*-heterocyclic carbenes (NHCs) have emerged as versatile ligational building blocks for a large variety of coordination compounds.[1] NHCs, which are strong σ-donors, have low π-acceptor ability, and transition metal carbene complexes obtained by using carbene precursors have had a wide application area in organometallic chemistry.[2] This development rests on the easy access to differently substituted NHCs, making them a good alternative to phosphines in the design of new organometallic catalysts.[2,3] The facile access to NHCs is complemented by the superior σ-donor properties of the carbene ligands compared to the most basic phosphines,[4] leading to a remarkable stability of the carbene complexes against air, moisture, heat, and oxidizing conditions.[2] Among various transition metal-carbene complexes, NHC-silver complexes have received special attention due to their structural diversity, wide application as effective carbene transfer agents in transmetalation reactions to make other NHC-metal complexes.[5] Also, the prominent biological activity of NHC-silver complexes as anticancer and antimicrobial agents has been confirmed.[6] As depicted in Scheme 1, different approaches such as (a) reaction of azolium salts with silver base, (b) reaction of free NHC with silver salts, and (c) reaction of azolium salts with silver salts under basic phase transfer conditions (PTC) have been used to prepare Ag(I)-NHCs. As early as 1993, Arduengo et al.[7] reported the first Ag(I)-NHC by the reaction of the Ag(I) salt with a free NHC. Later, Guerret et al.[8] reported that the reaction between triazolium triflate salt and a silver base such as Ag (OAc), yielded a polymeric Ag(I)-NHC. The reaction of another silver base, Ag_2O, with azolium salts to afford Ag (I)-NHCs was first reported in 1998 by Wang and Lin.[9]

The silver complexes have been extensively used to catalyze the formation of C-C and C-E (E: heteroatom) bonds,[10] the utility of Ag(I)-NHC complexes in chemical catalysis remains scarcely explored, and only a few examples were reported. In recent years, Ag(I)-NHC complexes have also been successfully used to catalyze the three-component coupling reaction of aldehyde, alkyne and amine to propargylamines.[11] In this paper, we report the catalytic activities of Ag(I)-NHC complexes based on 1-(methyl)-3-(alkyl)imidazole in the three-component coupling reaction.

Experimental

General considerations

All reactions and manipulations for the preparations of ligands and silver(I) complexes were carried out under argon in flame-dried glassware using standard Schlenk line techniques. Anhydrous solvents were either distilled from appropriate drying agents or purchased from Merck and degassed prior to use by purging with dry argon and kept over molecular sieves. 1-Methylimidazole (**1**) was purchased from Merck. All other reagents were commercially available and used as received. NMR spectra were recorded at 297 K on a Varian Mercury AS 400 NMR instrument at 400 MHz (^1H) and 100.56 MHz (^{13}C). Elemental analyses were performed by TUBITAK (Ankara, Turkey) Microlab. Melting points was determined using Electrothermal 9100 melting point detection apparatus.

General procedure for the preparation of ligands

The unsymmetrically N^1, N^3-substituted imidazolium salts (**2a–c**) can be prepared in analogy to published procedures according to a slightly modified procedure from the literature methods[12] depicted in Scheme 1. The benzyl chloride (10 mmol) and 1-methylimidazole (10 mmol) were stirred in DMF (15 mL) for 8 h at room temperature. Following

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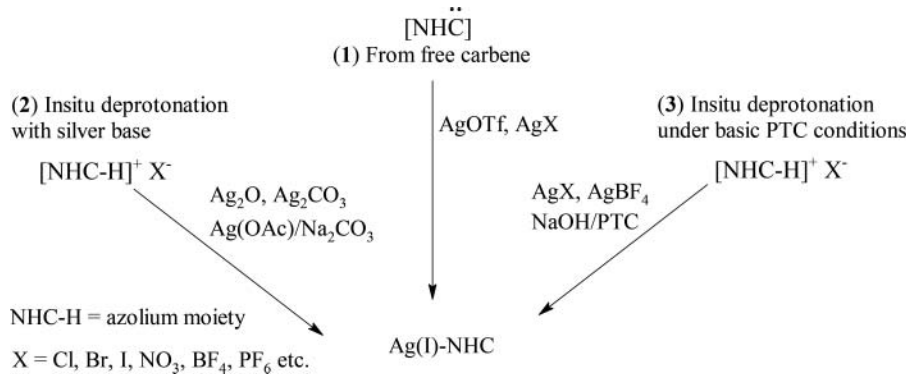


Scheme 1. Methods prescribed to prepare Ag(I)-NHCs.

the completion of the process DMF was removed. Diethyl ether was added, vigorously shaken, and then decantated. The white solid was recrystallized from ethanol/diethyl ether.

1-(methyl)-3-(2,4,6-trimethylbenzyl)imidazolium chloride, 2a

Yield: 76%, m.p.: 120°C. Anal. Calcd. for $C_{14}H_{19}N_2Cl$: C, 67.05; H, 7.64; N, 11.17. Found: C, 67.26; H, 7.72; N: 11.28. $\nu_{(CN)} = 1634\ cm^{-1}$. ^{1}HNMR ($\delta$, DMSO): 2.28 [s, 6H, $C_6H_2(CH_3)_3$]; 2.40 [s, 3H, $C_6H_2(CH_3)_3$]; 3.95 [s, 3H, NCH_3]; 5.56 [s, 2H, $NCH_2C_6H_2(CH_3)_3$]; 6.92 [d, 1H, J = 1.6 Hz, $NCHCHNCH_3$]; 7.04[s, 2H, $C_6H_2(CH_3)_3$]; 7.48 [d, 1H, J = 1.6 Hz, $NCHCHNCH_3$]; 9.14 [s, 1H, NCHN]. ^{13}C NMR (δ, DMSO): 20,0 [$C_6H_2(CH_3)_3$]; 21.4 [$C_6H_2(CH_3)_3$]; 37.0 [NCH_3]; 48.2 [$NCH_2C_6H_2(CH_3)_3$]; 121.0 [$NCHCHNCH_3$]; 124.8 [$NCHCHNCH_3$]; 125.7, 130.1, 137.3, 138.1 [$C_6H_2(CH_3)_3$]; 139.8 [NCHN].

1-(methyl)-3-(2,3,5,6-tetramethylbenzyl)imidazolium chloride, 2b

Yield: 64%, m.p.: 127°C. Anal. Calcd. for $C_{15}H_{21}N_2Cl$: C, 68.04; H, 7.99; N, 10.58. Found: C, 68.16; H, 8.12; N: 10.67. $\nu_{(CN)} = 1636\ cm^{-1}$. ^{1}HNMR ^{1}H NMR ($\delta$, DMSO): 2.23 [s, 6H, $C_6H(CH_3)_4$]; 2.29 [s, 6H, $C_6H(CH_3)_4$]; 3.94 [s, 3H, NCH_3]; 5.59 [s, 2H, $NCH_2C_6H(CH_3)_4$]; 6.86 [d, 1H, J = 1.6 Hz, NCHCHN]; 7.02 [s, 1H, $C_6H(CH_3)_4$]; 7.74 [d, 1H, J = 1.6 Hz, NCHCHN]; 9.12 [s, 1H, NCHN]. ^{13}C NMR (δ, DMSO): 16.0 [$C_6H(CH_3)_4$]; 20.8 [$C_6H(CH_3)_4$]; 37.1 [NCH_3]; 48.9 [$NCH_2C_6H(CH_3)_4$]; 121.3 [$NCHCHNCH_3$]; 123.2 [$NCHCHNCH_3$]; 128.2, 134.1, 134.4, 135.2 [$C_6H(CH_3)_4$]; 136.4 [NCHN].

1-(methyl)-3-(pentamethylbenzyl)imidazolium chloride, 2c

Yield: 65%, m.p.: 195°C. Anal. Calcd. for $C_{16}H_{23}N_2Cl$: C, 68.92; H, 8.31; N, 10.05. Found: C, 68.91; H, 8.24; N: 10.21. $\nu_{(CN)} = 1636\ cm^{-1}$. ^{1}H NMR ($\delta$, DMSO): 2.24 [s,6H, $C_6(CH_3)_5$]; 2.25 [s, 6H, $C_6(CH_3)_5$]; 2.27 [s, 3H, $C_6(CH_3)_5$]; 3.92 [s,3H, NCH_3]; 5.54 [s, 2H, $NCH_2C_6(CH_3)_5$]; 7.62 [d, 1H, J = 1.6 Hz, $NCHCHNCH_3$]; 7.74 [d, 1H, J = 1.6 Hz, $NCHCHNCH_3$]; 8.96 [s, 1H,NCHN]. ^{13}C NMR (δ, DMSO): 17.1 [$C_6(CH_3)_5$]; 17.3 [$C_6(CH_3)_5$]; 17.5 [$C_6(CH_3)_5$]; 37.2 [NCH_3]; 49.4 [$NCH_2C_6(CH_3)_5$]; 121.0 [$NCHCHNCH_3$]; 123.6 [$NCHCHNCH_3$]; 125.1, 133.2, 133.8, 136.4 [$C_6(CH_3)_5$]; 136.8 [NCHN].

General procedure for the preparation of Ag(I)-NHC complexes

A suspension of imidazolium salt (**2a–c**) and equivalent amount Ag_2O (1.0 mmol) in dichloromethane (15 mL) was stirred at room temperature for 10 h in the dark conditions and under argon[12,13] and filtered through celite. The solvent removed under vacuum. The crude product was recrystallized from dichloromethane/*n*-hexane.

Chloro-[1-(methyl)-3-(2,4,6-trimethylbenzyl)imidazol-2-yliden]silver(I), 3a

Yield: 63%; m.p.: 167°C. Anal. Calcd. for $C_{28}H_{36}N_4Cl_2Ag_2$: C, 47.02; H, 5.07; N, 7.83. Found: C, 47.46; H, 5.59; N: 7.92. $\nu_{(CN)} = 1636\ cm^{-1}$. ^{1}H NMR ($\delta$, $CDCl_3$): 2.26 [s, 12H, $C_6H_2(CH_3)_3$]; 2.31 [s, 6H, $C_6H_2(CH_3)_3$]; 3.86 [s, 6H, NCH_3]; 5.28 [s, 4H, $NCH_2C_6H_2(CH_3)_3$]; 6.57 [d, 2H, J = 4.0 Hz, $NCHCHNCH_3$]; 6.90 [d, 2H, J = 4.0 Hz, $NCHCHNCH_3$]; 7.01 [s, 4H, $C_6H_2(CH_3)_3$]. ^{13}C NMR (d, CDCl3): 20.4 [$C_6H_2(CH_3)_3$]; 21.3 [$C_6H_2(CH_3)_3$]; 39.2 [NCH_3]; 49.6 [$NCH_2C_6H_2(CH_3)_3$]; 120.1 [$NCHCHNCH_3$]; 122.0 [$NCHCHNCH_3$]; 127.8, 129.9, 138.1, 139.2 [Ar–C]; 182.6 [Ag–$C_{carbene}$].

Chloro-[1-(methyl)-3-(2,3,5,6-tetramethylbenzyl)imidazol-2-yliden]silver(I), 3b

Yield: %55; m.p.: 156°C. Anal. Calcd. for $C_{30}H_{40}N_4Cl_2Ag_2$: C, 48.48; H, 5.42; N, 7.54. Found: C, 48.82; H, 5.61; N: 7.75. $\nu_{(CN)} = 1634\ cm^{-1}$. ^{1}H NMR ($\delta$, $CDCl_3$): 2.16 [s, 12H, $C_6H(CH_3)_4$]; 2.25 [s, 12H, $C_6H(CH_3)_4$]; 3.91 [s, 6H, NCH_3]; 5.44 [s, 4H, $NCH_2C_6H(CH_3)_4$]; 6.55 [d, 2H, J = 4.0 Hz, $NCHCHNCH_3$]; 6.97 [d, 2H, J = 4.0 Hz, $NCHCHNCH_3$]; 7.06 [s, 2H, $C_6H(CH_3)_4$]. ^{13}C NMR (d, $CDCl_3$): 16.2 [$C_6H(CH_3)_4$]; 20.6 [$C_6H(CH_3)_4$]; 39.3 [NCH_3]; 50.5 [$NCH_2C_6H(CH_3)_4$]; 120.8 [$NCHCHNCH_3$]; 121.9 [$NCHCHNCH_3$]; 130.4, 132.9, 134.1, 134.7 [Ar–C]; 182.8 [Ag–$C_{carbene}$].

Chloro-[1-(methyl)-3-(pentamethylbenzyl)imidazol-2-yliden]silver(I), 3c

Yield: %60; m.p.: 147°C. Anal. Calcd. for $C_{32}H_{44}N_4Cl_2Ag_2$: C, 49.83; H, 5.75; N, 7.26. Found: C, 49.94; H, 5.92; N: 7.74. $\nu_{(CN)} = 1633\ cm^{-1}$. ^{1}H NMR ($\delta$, $CDCl_3$): 2.22 [s, 12H, $C_6(CH_3)_5$]; 2.28 [s, 12H, $C_6(CH_3)_5$]; 2.30 [s, 6H, $C_6(CH_3)_5$]; 3.84 [s, 6H, NCH_3]; 5.35 [s, 4H, $NCH_2C_6(CH_3)_5$]; 6.63 [d, 2H, J = 4.0 Hz, $NCHCHNCH_3$]; 6.90 [d, 2H, J = 4.0 Hz, $NCHCHNCH_3$]. ^{13}C

NMR (d, CDCl3): 17.1 [$C_6(CH_3)_5$]; 17.2 [$C_6(CH_3)_5$]; 17.5 [$C_6(CH_3)_5$]; 39.2 [NCH_3]; 50.7 [$NCH_2C_6(CH_3)_5$]; 120.3 [$NCHCHNCH_3$]; 121.9 [$NCHCHNCH_3$]; 127.6, 133.9, 133.8, 137.1 [Ar–C]; 182.1 [Ag–$C_{carbene}$].

General procedure for the Ag(I)-NHC catalyzed three-component coupling reaction

In a typical procedure, the mix of phenylacetylene (1.5 mmol, 164.7 μL), aldehyde (1.0 mmol), piperidine (1.2 mmol, 118.7 μL) and silver complex (3 mol%) was added in an oven-dried Schlenk tube (15 mL) with 1,4-dioxane (2.0 mL). The Schlenk tube was placed in a preheated oil bath (80°C). The mixture was stirred at 80°C for given time under an argon atmosphere. After the reaction was completed, the mixture was cooled to room temperature and diethyl ether was added. The organic portion was dried over $MgSO_4$ and filtered. After the volatile components in vacuum, the residue was purified by column chromatography on silica using ethyl acetate/hexane (1/2).

Results and discussion

Preparation of ligands

All the imidazolium salts as NHC precursors, **2a–c** were prepared similarly to the published procedures.[12] The synthesis of the imidazolium chlorides was achieved via one synthetic route (Scheme 2). The alkylation of 1-methylimidazole with alkyl chlorides produced unsymmetrical 1,3-dialkylimidazolium salts (**3a–c**). An important feature of the ligand precursors (**2**) is their facile preparation. Elemental analyses and NMR spectroscopic data confirmed the formation of **2**. In the ^1H NMR spectra of **2a–c**, the imidazolium protons appear at δ 9.14, 9.12, and 8.96 ppm, respectively. The ^{13}C NMR shift of the NCN sp^2 carbon atoms in **2a–c** appear between δ 139.8 and 136.8 ppm, respectively.

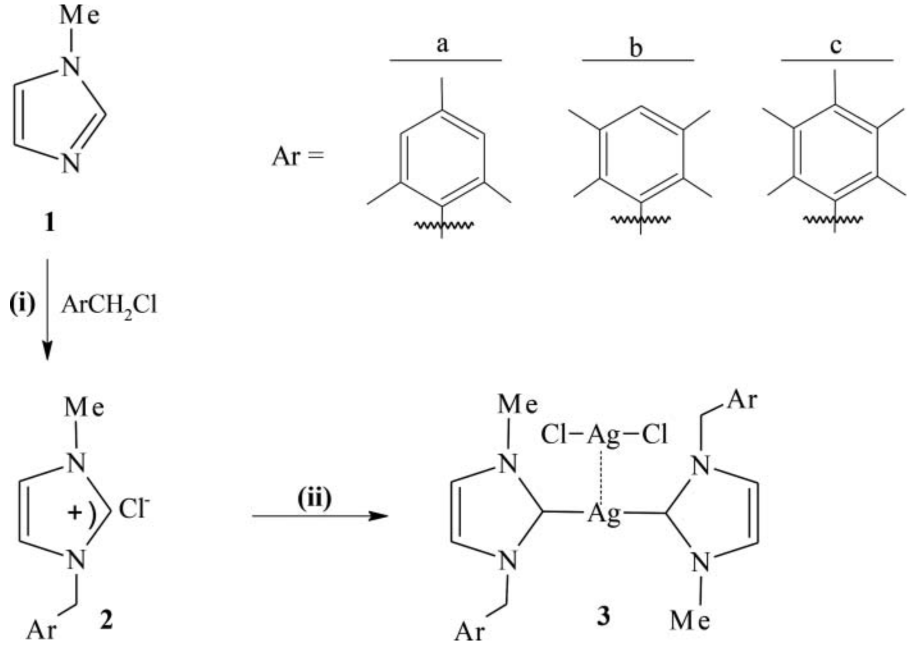
Preparation of silver(I)-NHC complexes

The silver complexes (**3a–c**) as shown in Scheme 2 were synthesized by the treatment of the imidazolium salts with silver(I) oxide as white powders in 55–63% yield. The imidazolium chlorides and Ag(I)-NHC complexes were determined from their characteristic spectroscopic data and elemental analyses. ^{13}C and ^1H NMR chemical shifts were consistent with the proposed structures; in the ^1H NMR spectrum, the absence of the resonance for the acidic proton (NC*H*N) around 8.9–9.2 ppm showed the formation of expected Ag(I)-NHC complexes. The ^{13}C NMR spectra, the resonance for carbene carbons in **3a–c** appear were showed at δ 182.6, 182.8, and 182.1 ppm, respectively, which was also mentioned in the literature.[12]

Catalytic activity of the silver(I)-NHC complexes

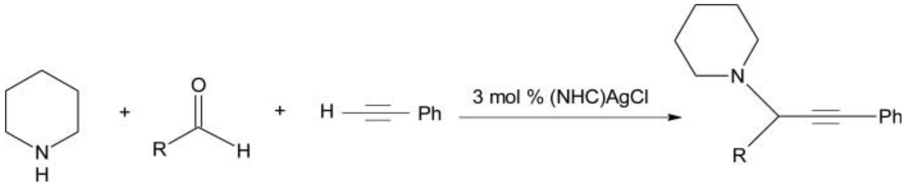
The three-component coupling reaction of alkyne, aldehyde, and amine catalyzed by transitions metals is useful approach to the preparation of propargylamines as key intermediates in the building of nitrogen-containing biologically active compounds.[14] Recent years have also seen that, the silver compounds exhibited highly effective catalytic activity for this three-component coupling reaction,[15] only several Ag-NHC systems performed as catalysts.[16–18]

We has demonstrated the synthesis of $[Ag(NHC)_2][AgCl_2]$, **3a–c** and catalytic activity in the three-component coupling reaction of piperidine, aldehyde and phenylacetylene (Table 1). Moderate yields were obtained when this complexes was used as the catalyst (3 mol%) for the coupling reaction. The **3a** complex showed low catalytic activity for the coupling of benzaldehyde. But, using this complex in the coupling of *p*-formaldeyhde was observed to high catalytic activity. Alteration the benzyl substituent of the NHC ligand has not shown a strong influence on the catalytic performance of the derived catalyst. However, as the number of methyl group decreases on the benzyl substituent, the



Scheme 2. Reagents and conditions: (i) DMF, 25°C; (ii) Ag_2O, CH_2Cl_2, 25°C.

Table 1. Catalytic activity of silver(I)-NHC complexes[a].



Entry	R	Solvent	Cat.	Yield (%)[bc]
1	H	Dioxane	3a	84
2	Cyclohexyl	Dioxane	3a	76
3	Cyclohexyl	Dioxane	3b	70
4	Cyclohexyl	Dioxane	3c	68
5	Phenyl	Dioxane	3a	12
6	H	Dioxane	Ag_2O	47
7	H	Dioxane	AgI	62
8	H	Acetone	3a	80[d]
9	H	DMSO	3a	82
10	H	H_2O	3a	13[e]
11	H	EtOH	3a	14[f]
12	H	Neat	3a	88
13	Cyclohexyl	Neat	3a	82
14	Phenyl	Neat	3a	27

[a] Reaction conditions: aldehyde (1.0 mmol), piperidine (1.2 mmol), phenylacetylene (1.5 mmol), NHC-Ag(I) catalyst (3 mol%), Dioxane (2.0 mL), 80°C, argon atmosphere, 8 h.
[b] Yield after purification by silica gel chromatography.
[c] Average of two runs.
[d] At 56°C.
[e] For 12 h.
[f] At 78°C.

efficiency slightly increases. The three-component coupling reaction was also carried out under neat reaction conditions at 80°C and high yields of isolated product could be obtained (Table 1, entries 12–14). These results indicate that the use of volatile solvents in the three-component coupling reactions could be avoided which is beneficial to reduce the environmental pollution. A tentative mechanism for three-component coupling reaction was suggested by Wei et al.[15]: initially by exchange of H of the C-H bond of alkyne and Ag(I) species a silver-acetylide and an iminium ion between aldehyde and amine forms. In the second step, the silver acetylide intermediate and the iminium ion generated in situ react to give the corresponding propargylamines and regenerate the silver(I) catalyst for further reactions.

Conclusion

We have shown that facile synthesis of three silver(I)-NHC complexes derived imidazolium from have been reported. Even though the complex **3a–c** bearing bromide ions are known in literature, the catalytic activities of this complex in the three-component coupling reaction have been studied in this report. Preliminary catalytic study revealed that the complexes moderate catalytic activity in three-component coupling reaction. The efficiency slightly depends on the NHC ligand and decreases as the number of methyl groups on the benzyl substituent on ^{3}N atom. Studies on the structural modification of NHC and the structure-activity relationship of catalysts are ongoing in our laboratory.

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