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Ag(I) complexes of benzimidazol-2-ylidene ligands: a study of catalytic efficiency towards three-component coupling reactions

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Abstract: The *N*-heterocyclic carbene (NHC)–Ag(I) complexes **3a–c** were synthesized from benzimidazolium chlorides (**2a–c** = NHC.HCl), incorporating benzyl derivatives and a 2-methoxyethyl group (**a**: ³N = 2,4,6-trimethylbenzyl; **b**: ³N = 2,3,5,6-tetramethylbenzyl; **c**: ³N = pentamethylbenzyl). The compounds were characterized by spectroscopic and elemental analyses. The synthesized NHC–Ag(I) complexes (**3a–c**) were tested as catalysts for the catalytic three-component coupling reaction of aldehyde, alkyne, and amine to propargylamines in various solvents. All complexes were active catalysts for catalytic three-component coupling reactions with good yields under neat and mild conditions (after 4 h, yields of up to 94%).

Key words: *N*-heterocyclic carbene, benzimidazol-2-ylidene, coupling reaction, catalyst

1. Introduction

N-heterocyclic carbenes (NHCs) are cyclic constructions that are generally derived from deprotonation of imidazoli(ni)um, benzimidazolium, diazepinium, and pyrimidium salts. Since the isolation of the first free carbene by Arduengo,¹ transition metal carbene complexes have found wide application in organometallic chemistry.^{2–8} NHC–Ag(I) complexes have particular importance due to their structural variations and wide applications as operative NHC transfer agents in transmetalation reactions to make other NHC–metal complexes.^{9–15} The noticeable biological activity of NHC–silver complexes as anticancer and antimicrobial agents has been confirmed.^{16–22} In spite of carbene-free silver complexes having been used as catalysts in C–C and C–X (X: heteroatom) bond formation reactions,^{23–25} the availability of NHC–Ag(I) complexes in chemical catalysis remains limited, and only a few examples were published.^{26–36} In the course of our studies involving the use of benzyl substituted benzimidazol-2-ylidene ligands, we herein report the synthesis of a number of NHC–Ag(I) complexes and compare their catalytic activities in formation of propargylamines by means of the three-component coupling reaction with the present complexes.

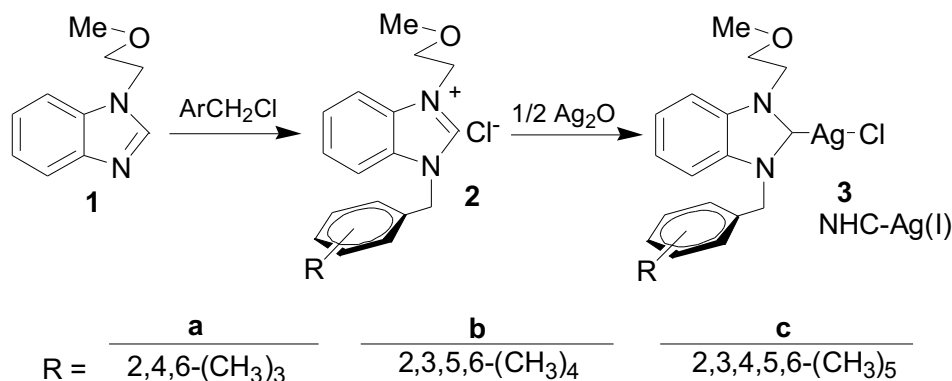
2. Results and discussion

2.1. Synthesis and characterization

The benzimidazolium salts to be used as carbene precursors, **2a–c**, were prepared by the published methods.^{37–46} These salts **2a–c** are colorless, air-stable solids. The NHC–Ag(I) complexes (**3a–c**) were prepared from

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the reaction of benzimidazolium salts with silver(I) oxide as white powders in 56%–82% yield, as shown in Scheme 1. The molecular and crystal structures of [1-(2-methoxyethyl)-3-(2,4,6-trimethylbenzyl)benzimidazol-2-ylidene]silver(I) chloride were previously characterized using X-ray diffraction by Özdemir and co-workers.⁴⁶ The benzimidazolium salts and silver complexes were determined from their characteristic spectroscopic data and elemental analyses. ¹³C and ¹H NMR chemical shifts were consistent with the proposed structures; in the ¹H NMR spectrum, the formation of NHC–Ag(I) complexes was determined by the absence of the resonance for C–H acidic protons around 9–11 ppm. In the ¹³C NMR spectrum, peaks for carbene carbons were not observed, which is consistent with the observation described in the literature. This observation was attributed to the fluxional behavior of the NHC–Ag(I) complexes.^{46–51}



Scheme 1. The synthesis of benzimidazolium salts **2a–c** and NHC–Ag(I) complexes **3a–c**.

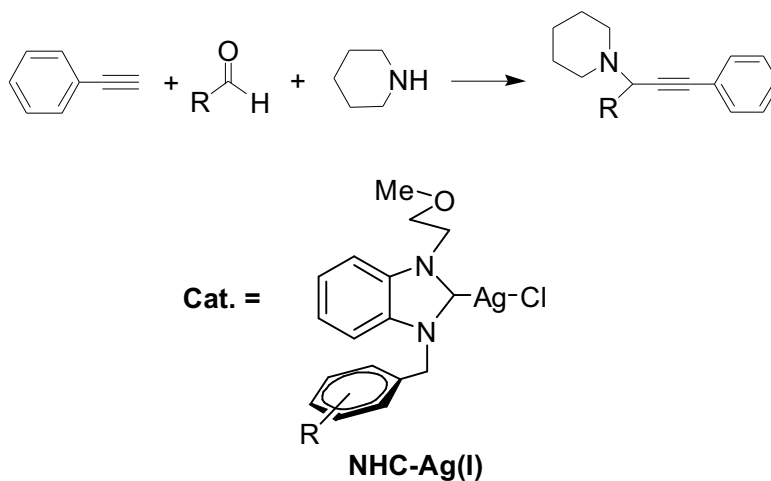
For the complexes of **3b** and **3c**, crystals could not be obtained despite the use of different solvent systems.

2.2. Catalytic activity of the NHC silver complexes

Recently, the formation of propargylamines by means of the three-component coupling reaction (Scheme 2) has attracted much attention, due to their importance in the construction of nitrogen-containing biologically active substances.⁵² The complexes of transition metals, especially silver, are known to show highly effective catalytic activity for this three-component coupling reaction.³⁴ However, only a limited number of NHC–Ag(I) complexes have been tested as catalysts,^{33–35} and generally these complexes were mononuclear NHC–Ag(I) complexes. Additionally, it was observed the monomeric NHC–Ag(I) complexes exhibit higher activity than the dimeric forms $\{[\text{Ag}(\text{NHC})\text{X}]_2\}$ and the ionic NHC–Ag(I) complexes.³⁵ However, the *m*-xyly bridging tetradentate cationic bis-NHCs silver complexes have been described by Cheng,³⁶ and it is interesting that, when these dinuclear complexes were used, the catalyst in the coupling reaction progressed remarkably faster.

Our work has demonstrated the preparation of monomeric (NHC)Ag–Cl **3a–c** and catalytic activities of the synthesized catalysts for the three-component coupling reaction of piperidine, *p*-formaldehyde, and phenylacetylene (model reaction). The results are summarized in the Table. When using the catalyst **3a** (3 mol%) for the three-component coupling reaction of benzaldehyde (entry 5) moderate yield was achieved. However, using the same molar ratio of this complex in the coupling of cyclohexanecarboxaldehyde or *p*-formaldehyde good catalytic activity was observed (entries 1 and 6). Alteration of the benzyl substituent of the NHC ligand did not have a strong influence on the catalytic performance of the derived complexes. A poor

result was observed when only Ag_2O was used as catalyst (Table, entry 4); moreover, when the reaction was repeated in the absence of any silver source, no desired product was detected.



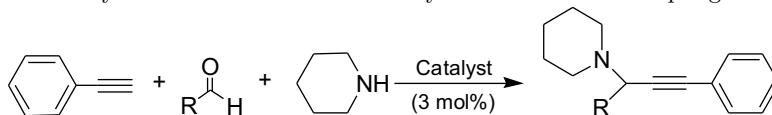
Scheme 2. Three-component coupling reaction.

The influence of solvents on the three-component coupling reaction using **3a** as catalyst was examined (Table, entries 6–13). Among the solvents in the Table, dioxane, CH_3CN , DMSO, and acetone were successful in the coupling reaction (Table, entries 5 and 7–9). DMF and toluene gave moderate yields of the desired products (Table, entries 10 and 11). Low yields were observed when the reactions were performed with water and ethanol (Table, entries 12 and 13). The three-component coupling reaction was also carried out under neat reaction conditions at $80\text{ }^\circ\text{C}$ and high yields of isolated product were obtained (Table, entries 14–19). These results indicate that the use of volatile solvents in the three-component coupling reactions could be avoided and thus it can be considered to provide an important contribution to reducing environmental pollution. A tentative mechanism for the three-component coupling reaction was suggested by Chao and co-workers:⁵³ 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.

3. Experimental

3.1. General considerations

All reactions and manipulations for the preparation of NHC ligands and their Ag(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. 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 the TÜBİTAK Microlab (Ankara, Turkey). Melting points was determined using an Electrothermal 9100 melting point detection apparatus. The unsymmetrical benzimidazolium chlorides to be used as carbene precursors (**2a–c**) were prepared according to a procedure slightly modified from the literature³¹ as depicted in Scheme 1. [1-(2-Methoxyethyl)-3-(2,4,6-trimethylbenzyl)benzimidazol-2-ylidene]silver(I) chloride, **3a**, was prepared according to the literature.⁴⁶

Table. Catalytic effect of NHC–silver catalyst and solvent on coupling reaction.^a

Entry	Aldehyde	Catalyst	Solvent	t/h	Yield (%) ^{b,c}
1	C ₆ H ₁₁ -CHO	3a	Dioxane	4	82
2	C ₆ H ₁₁ -CHO	3b	Dioxane	4	80
3	C ₆ H ₁₁ -CHO	3c	Dioxane	4	77
4	C ₆ H ₁₁ -CHO	Ag ₂ O	Dioxane	4	32
5	C ₆ H ₅ -CHO	3a	Dioxane	4	52
6	H-CHO	3a	Dioxane	4	84
7	H-CHO	3a	DMSO	4	80
8	H-CHO	3a	Acetone	4	78 ^d
9	H-CHO	3a	CH ₃ CN	4	79
10	H-CHO	3a	DMF	4	72
11	H-CHO	3a	PhMe	4	45
12	H-CHO	3a	H ₂ O	12	24 ^e
13	H-CHO	3a	EtOH	4	24 ^f
14	H-CHO	3a	Neat	4	94
15	C ₆ H ₁₁ -CHO	3a	Neat	4	88
16	C ₆ H ₅ -CHO	3a	Neat	4	67
17	<i>p</i> -CH ₃ C ₆ H ₄ -CHO	3a	Neat	4	70
18	<i>p</i> -OCH ₃ C ₆ H ₄ -CHO	3a	Neat	4	66
19	<i>p</i> -FC ₆ H ₄ -CHO	3a	Neat	4	68

^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.

^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.

3.2. Preparation of ligands

3.2.1. 1-(2-Methoxyethyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazolium chloride, 2b

1-(2-Methoxyethyl)benzimidazol (1.0 mmol) was dissolved in dried toluene (5.0 mL). 2,3,5,6-Tetramethyl benzyl chloride (1.1 mmol) was added to the solution and the mixture was refluxed for 6 h. The reaction mixture was then cooled to room temperature. Then *n*-hexane (10.0 mL) was added and the mixture was filtered. The solid was recrystallized from MeOH/Et₂O. Yield: 68%, mp: 198 °C. ¹H NMR (CDCl₃): δ = 9.81 (s, 1 H, NCHN), 7.96 (m, 1 H, Ar-H), 7.91 (m, 1 H, Ar-H), 7.60 (m, 1 H, Ar-H), 7.55 [s, 1 H, C₆H(CH₃)₄], 7.49 (m, 1 H, Ar-H), 5.76 [s, 2 H, CH₂C₆H(CH₃)₄], 4.91 (t, *J* = 2.4 Hz, 2 H, NCH₂CH₂OCH₃), 3.83 (t, *J* = 2.4 Hz, 2 H, NCH₂CH₂OCH₃), 3.25 (s, 3 H, NCH₂CH₂OCH₃), 2.24 [s, 6 H, *m*-C₆H(CH₃)₄], 2.22 [s, 6 H, *o*-C₆H(CH₃)₄] ppm. ¹³C NMR (CDCl₃): δ = 141.5 (NCHN), 135.0, 133.4, 133.7, 133.3, 131.8, 127.1, 127.4, 114.6, 113.2, 113.4 [Ar-C and C₆H(CH₃)₄], 69.9 (NCH₂CH₂OCH₃), 58.8 (NCH₂CH₂OCH₃), 47.8 (NCH₂CH₂OCH₃), 47.2 [NCH₂C₆H-(CH₃)₄], 20.5 [*m*-C₆H(CH₃)₄], 20.4 [*o*-C₆H(CH₃)₄] ppm.

3.2.2. 1-(2-Methoxyethyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolium chloride, 2c

This compound was prepared in the same manner as **2b** using 2,3,4,5,6-pentamethyl benzyl chloride (1.1 mmol) and 1-(2-methoxyethyl)benzimidazol, **1** (1.0 mmol). Yield: 62.0%, mp: 197-198 °C. ¹H NMR (CDCl₃): δ = 9.79 (s, 1 H, NCHN), 7.95 (m, 1 H, Ar-H), 7.64 (m, 1 H, Ar-H), 7.58 (m, 1 H, Ar-H), 7.54 (m, 1 H, Ar-H), 5.70 [s, 2 H, CH₂C₆(CH₃)₅], 4.90 (t, *J* = 2.4 Hz, 2 H, NCH₂CH₂OCH₃), 3.82 (t, *J* = 2.4 Hz, 2 H, NCH₂CH₂OCH₃), 3.24 (s, 3 H, NCH₂CH₂OCH₃), 2.25 [s, 3 H, *p*-C₆(CH₃)₅], 2.24 [s, 6 H, *m*-C₆(CH₃)₅], 2.22 [s, 6H, *o*-C₆(CH₃)₅] ppm. ¹³C NMR (CDCl₃): δ = 141.2 (NCHN) 137.8, 133.4, 133.6, 132.1, 131.6, 128.1, 127.3, 124.5 114.0, 113.2 [Ar-C and C₆(CH₃)₅], 69.9 (NCH₂CH₂OCH₃), 58.8 (NCH₂CH₂OCH₃), 47.7 (NCH₂CH₂OCH₃), 47.6 [NCH₂C₆-(CH₃)₅], 17.2 [*p*-C₆(CH₃)₅], 20.5 [*m*-C₆(CH₃)₅], 20.4 [*o*-C₆(CH₃)₅].

3.3. Preparation of silver-NHC complexes

Benzimidazolium chloride (1.0 mmol), activated molecular sieves (4 Å), and Ag₂O (0.5 mmol) in dichloromethane (15.0 mL) were stirred at 25 °C for 12 h in the dark, covered with aluminum foil under argon^{46,54} and filtered using Celite. The solvent was removed under vacuum. The residue was recrystallized from DCM /*n*-hexane.

3.3.1. [1-(2-Methoxyethyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazolin-2-ylidene]chloro silver(I), 3b

Yield: 74%, mp: 176–177 °C. Anal. Calc. for C₂₁H₂₆N₂OAgCl: C, 54.15; H, 5.63; N, 6.01. Found: C, 54.36; H, 5.54; N: 6.12. ¹H NMR (δ, CDCl₃) = 2.07 [s, 6H, CH₂C₆H(CH₃)₄-2,6]; 2.22 [s, 6H, CH₂C₆H(CH₃)₄-3,5]; 3.20 [s, 3H, CH₂CH₂OCH₃]; 3.69 [t, 2H, *J* = 5.1 Hz, CH₂CH₂OCH₃]; 4.45 [t, 2H, *J* = 5.1 Hz CH₂CH₂OCH₃]; 5.39 [s, 2H, CH₂C₆H(CH₃)₄-2,3,5,6]; 7.07 [s, 1H, CH₂C₆H(CH₃)₄-2,3,5,6]; 7.36 [m, 3H, NC₆H₄N]; 7.53 [d, 1H, *J* = 8.1 Hz, NC₆H₄N]. ¹³C NMR (CDCl₃): 16.2 [CH₂C₆H(CH₃)₄-2,6]; 20.8 [CH₂C₆H(CH₃)₄-3,5]; 47.3 [CH₂CH₂OCH₃]; 50.0 [CH₂C₆H(CH₃)₄-2,3,5,6]; 59.1 [CH₂CH₂OCH₃]; 72.2 [CH₂CH₂OCH₃]; 129.6, 133.3, 133.5, 134.2 [CH₂C₆H(CH₃)₄-2,3,5,6]; 111.1, 112.4, 124.1, 124.4, 134.6, 135.4 [NC₆H₄N]; the C₂ carbon was not observed.

3.3.2. [1-(2-Methoxyethyl)-3-(pentamethylbenzyl) benzimidazolin-2-ylidene]chloro silver(I), 3c

Yield: 56%, mp: 164–165 °C. Anal. Calc. for C₂₂H₂₈N₂OAgCl: C, 55.07; H, 5.88; N, 5.84. Found: C, 55.10; H, 5.92; N: 5.82. ¹H NMR (δ, CDCl₃) = 2.12 [s, 6H, CH₂C₆(CH₃)₅-2,6]; 2.21 [s, 6H, CH₂C₆(CH₃)₅-3,5]; 2.26 [s, 3H, CH₂C₆(CH₃)₅-4]; 3.19 [s, 3H, CH₂CH₂OCH₃]; 3.67 [t, 2H, *J* = 5.1 Hz, CH₂CH₂OCH₃]; 4.42 [t, 2H, *J* = 5.1 Hz CH₂CH₂OCH₃]; 5.39 [s, 2H, CH₂C₆(CH₃)₅-2,3,4,5,6]; 7.38 [m, 3H, NC₆H₄N]; 7.54 [d, 1H, *J* = 8.1 Hz, NC₆H₄N]. ¹³C NMR (CDCl₃): 17.1 [CH₂C₆(CH₃)₅-2,6]; 17.2 [CH₂C₆(CH₃)₅-3,5]; 17.4 [CH₂C₆(CH₃)₅-4]; 47.7 [CH₂CH₂OCH₃]; 50.1 [CH₂C₆(CH₃)₅-2,3,4,5,6]; 59.1 [CH₂CH₂OCH₃]; 72.2 [CH₂CH₂OCH₃]; 126.5, 133.0, 134.5, 137.3 [CH₂C₆(CH₃)₅-2,3,4,5,6]; 111.1, 112.3, 124.0 124.3, 134.3, 134.8 [NC₆H₄N]; the C₂ carbon was not observed.

4. Typical procedure of the three-component coupling reaction catalyzed by NHC-Ag(I) catalyst

In a typical procedure, a mixture 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 to 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 a 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 were removed under vacuum, the residue was purified by column chromatography on silica using ethyl acetate/hexane (1/2).

5. Conclusion

In summary, the facile synthesis and characterization of three mononuclear NHC-Ag(I) complexes (**3a–c**) derived from 1-(2-methoxyethyl)-3-(alkyl)benzimidazol-2-ylidene is reported. The preliminary catalytic study revealed that the silver complexes show good activity in a three-component coupling reaction under solvent-free reaction conditions. The efficiency slightly depends on the NHC ligand and decreases with the number of methyl groups on the benzyl substituent on the ^3N atom. Studies on the structural diversity of carbene precursors and the modification–efficiency relationship of NHC–Ag(I) complexes are continuing in our research lab.

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