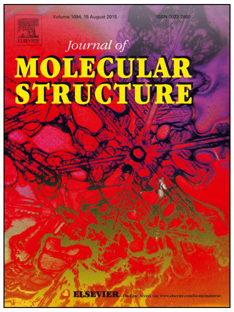

Dinuclear N-heterocyclic carbene silver complexes: Synthesis, luminescence and catalytic studies

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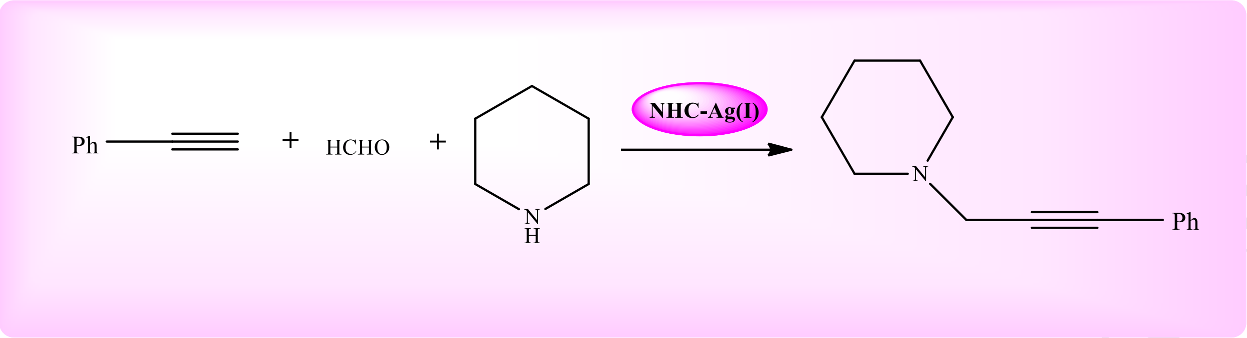
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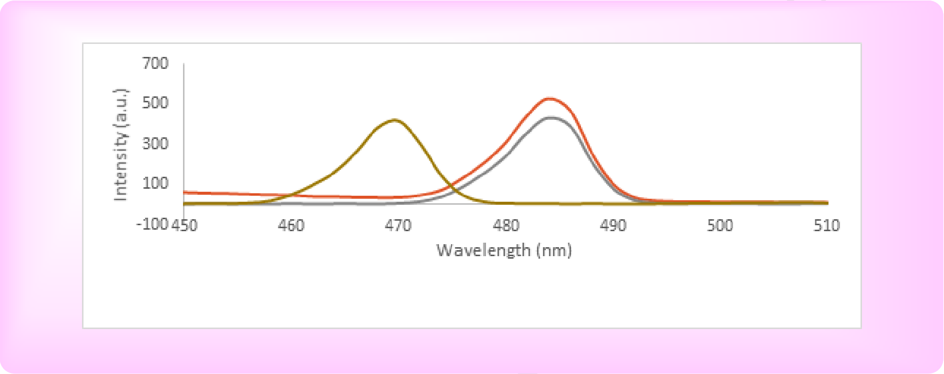
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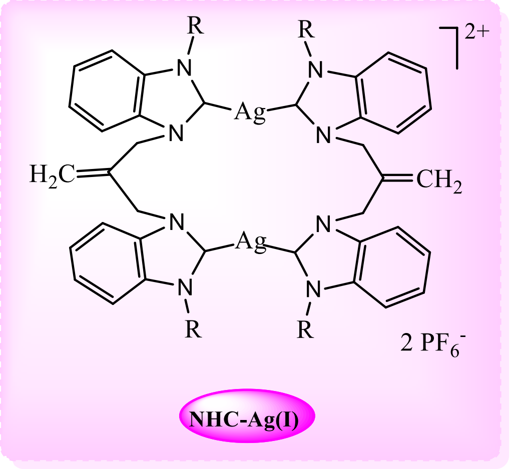
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Dinuclear N-heterocyclic carbene silver complexes: Synthesis, luminescence and catalytic studies

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Abstract

A new dibenzimidazole compound **(1)** and three dibenzimidazolium salts **(2a-2c)** were prepared. Reactions of these salts with silver(I) oxide in methanol led to dinuclear N-heterocyclic carbene silver complexes **(3a-3c)**. All of the compounds were characterized by ^{1}H NMR, ^{13}C NMR and elemental analyses. Molecular weights of the silver complexes were confirmed by MALDI-TOF mass spectrometry. Preliminary catalytic studies using all the silver complexes were performed on three-component coupling reaction of *p*-formaldehyde, piperidine and phenylacetylene. Complexes **3a** and **3c** exhibited good catalytic activities under neat conditions. The silver complexes showed luminescence properties in CH_3CN at room temperature.

Keywords: N-heterocyclic carbene, silver, luminescence, coupling reaction.

1. Introduction

N-heterocyclic carbene (NHC) ligands have drawn great interest in organometallic chemistry since the discovery of the first stable NHC in 1991 [1]. NHCs with strong σ-donating and weak π-accepting features are alternative to phosphines. They form stable metal complexes containing strong metal-carbon bonds [2].

Among the NHC-metal complexes, silver complexes have considerable importance. The first NHC-Ag(I) complex was isolated in 1993 by Arduengo et al. by the reaction of AgOTf and a free carbene [3] and since then many NHC silver complexes have been studied with increased attention. For synthesis, the most frequently used method has been deprotonation with a silver base such as Ag_2O, Ag_2CO_3 and AgOAc [4-6]. NHC-Ag(I) complexes have been widely used as sources of different metal complexes via transmetallation [7-14]. These compounds have antimicrobial and anticancer properties [15-

19]. Also, they have been studied as luminescent materials [20-23]. There have been limited number of reports related to the use of NHC-Ag(I) complexes in catalysis [24-32].

Herein, we report on the synthesis and characterization of three new dibenzimidazolium salts in which two NHC moieties are connected by 2-methylenepropane-1,3-diyl group and their dinuclear dicationic di(NHC) silver complexes. According to our knowledge, this bridging group which is analog of allyl has not been used for preparing dibenzimidazolium compounds yet. It is expected that this type of NHC precursors can generate effective catalysts. We also present luminescent properties and catalytic activities of Ag(I) complexes in three-component coupling reactions to give a propargylamine derivative.

2. Experimental

2.1. Reagents and Instruments

All reactions were carried out under open atmosphere unless stated otherwise. The reagents and the solvents were obtained from commercial suppliers and used as received. THF was distilled under argon over Na/K alloy. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Varian VNMRJ spectrometer. Elemental analyses were performed using a LECO-932 CHNS model analyzer. Molecular weights of the complexes were measured with Bruker Microflex LT MALDI-TOF mass spectrometer. Thermogravimetric analysis for **2c** was carried out with EXSTAR TG-DTA 7300 instrument.

2.2. Preparation of NHC precursors

2.2.1. 1,1′-(2-methylenepropane-1,3-diyl)dibenzimidazole (1)

Benzimidazole (1.182 g, 10 mmol) solution in dry THF (25 mL) was added to NaH (0.48 g, 12 mmol) in dry THF (5 mL) under argon atmosphere. The mixture was refluxed for 1h. After filtration, 1,1-bis(chloromethyl)ethylene (0.54 mL, 5 mmol) was added to the filtrate and it was refluxed for 24h. The mixture was filtrated and the solvent was removed. Water (100 mL) was added to the residue and it was extracted with CH_2Cl_2 (3x20 mL). After drying with Na_2SO_4, the solvent was removed and dibenzimidazole compound was recrystallized at CH_2Cl_2/hexane (1/4). Yield: 1.181 g, 82%. ^{1}H NMR ($CDCl_3$): $\delta = 7.82$ (d, 2H, J = 7.30 Hz, NCHN), 7.75 (s, 2H, Ar-H), 7.32-7.24 (m, 4H, Ar-H), 7.21-7.17 (m, 2H, Ar-H), 5.24 (s, 2H, $=CH_2$), 4.65 (s, 4H, NCH_2) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 144.13$, 143.30, 138.28, 133.80, 123.71, 122.91, 120.89, 118.28, 110.04, 47.59 ppm. Anal. Calc. for $C_{18}H_{16}N_4$: C, 74.96; H, 5.60; N, 19.43. Found: C, 74.62; H, 5.75; N, 19.45%.

2.2.2. 1,1′-dibenzyl-3,3′-(2-methylenepropane-1,3-diyl)dibenzimidazolium dibromide (2a)

1 (1 mmol) and benzyl bromide (2 mmol) were stirred in DMF (3 mL) at 80 °C for 24 h. The mixture was cooled to the room temperature. Et_2O (15 mL) was added and the mixture was filtered. The white solid was recrystallized from EtOH at room temperature. Yield: 89%. ^1H NMR (DMSO-d_6): δ = 10.11 (s, 2H, NCHN), 8.02-7.94 (m, 4H, Ar-H), 7.66-7.53 (m, 8H, Ar-H), 7.42-7.34 (m, 6H, Ar-H), 5.80 (s, 4H, NCH_2), 5.44 (s, 4H, NCH_2), 5.31 (s, 4H, $=CH_2$) ppm. ^{13}C NMR (DMSO-d_6): δ = 143.48, 136.42, 134.32, 131.71, 131.42, 129.42, 129.19, 128.88, 127.28, 127.21, 119.62, 114.55, 114.43, 50.46, 49.28 ppm. Anal. Calc. for $C_{32}H_{30}N_4Br_2$: C, 60.96; H, 4.81; N 8.89. Found: C, 61.61; H, 4.69; N, 9.08%.

2.2.3. 1,1′-di(3-methoxybenzyl)-3,3′-(2-methylenepropane-1,3-diyl)dibenzimidazolium dichloride (2b)

Compound **2b** was prepared similar to **2a** using 3-methoxybenzyl chloride. Yield: 80%. ^1H NMR (CD_3OD): δ = 9.86 (s, 2H, NCHN), 7.94-7.88 (m, 4H, Ar-H), 7.69-7.65 (m, 4H, Ar-H), 7.36-7.32 (m, 2H, Ar-H), 7.10-7.04 (m, 4H, Ar-H), 6.96 (dd, 2H, J = 9.16, 2.55 Hz, Ar-H), 5.72 (s, 4H, NCH_2), 5.47 (s, 4H, NCH_2), 5.32 (s, 2H, $=CH_2$), 3.78 (s, 6H, OCH_3) ppm. ^{13}C NMR (CD_3OD): δ = 160.44, 142.41, 135.75, 134.34, 131.64, 131.42, 130.20, 127.23, 127.15, 120.16, 118.89, 114.24, 113.94, 113.79, 113.47, 54.51, 50.74, 49.02 ppm. Anal. Calc. for $C_{34}H_{34}N_4O_2Cl_2$: C, 67.87; H, 5.71; N 9.32. Found: C, 68.46; H, 5.56; N, 9.60%.

2.2.4. 1,1′-di(4-methoxybenzyl)-3,3′-(2-methylenepropane-1,3-diyl)dibenzimidazolium dichloride (2c)

Compound **2c** was prepared similar to **2a** using 4-methoxybenzyl chloride. Yield: 95%. ^1H NMR (DMSO-d_6): δ = 10.51 (s, 2H, NCHN), 8.06-7.99 (m, 4H, Ar-H), 7.64-7.55 (m, 8H, Ar-H), 6.95-6.92 (m, 4H, Ar-H), 5.75 (s, 4H, NCH_2), 5.47 (s, 4H, NCH_2), 5.37 (s, 2H, $=CH_2$), 3.71 (s, 6H, OCH_3) ppm. ^{13}C NMR (DMSO-d_6): δ = 159.90, 143.52, 136.46, 131.69, 131.28, 130.71, 127.11, 127.08, 126.25, 120.27, 114.70, 114.60, 114.49, 55.64, 49.99, 49.17

ppm. Anal. Calc. for $C_{34}H_{34}N_4O_2Cl_2{\cdot}2.25H_2O$: C, 63.59; H, 6.06; N 8.73. Found: C, 63.57; H, 5.94; N, 8.62%. The presence of hydrate molecule was confirmed by TGA/DTA analysis.

2.3. General procedure for preparation of NHC silver complexes

Silver(I) oxide (2 mmol) was added to dibenzimidazolium salt (1 mmol) dissolved in MeOH (20 mL). The mixture was stirred at room temperature for 24 h in dark. The suspension was filtered through celite. NH_4PF_6 solution (2.5 mmol) in MeOH (10 mL) was added to the filtrate. The mixture was stirred at room temperature for 2 h in dark. After filtration, the solids were washed with MeOH (2x5 mL) and Et_2O (2x5 mL). The product was recrystallized from CH_3CN/Et_2O (1/3).

2.3.1. Bis[1,1′-dibenzyl-3,3′-(2-methylenepropane-1,3-diyl)dibenzimidazolin-2,2′-diylidene]disilver(I) bis(hexafluorophosphate) (3a)

Yield: 87%. ^{1}H NMR (DMSO-d$_6$): δ = 7.69-7.67 (m, 8H, Ar-H), 7.39-7.33 (m, 8H, Ar-H), 7.22-7.15 (m, 20H, Ar-H), 5.68 (s, 8H, NCH_2), 5.38 (s, 8H, NCH_2), 5.02 (s, 4H, $=CH_2$) ppm. ^{13}C NMR (DMSO-d$_6$): δ = 140.22, 136.40, 133.95, 133.59, 129.16, 128.45, 127.59, 124.89, 124.73, 112.92, 112.87, 52.33, 52.20 ppm. MALDI-TOF MS: $[M\text{-}PF_6]^+$ at m/z 1297.62. Anal. Calc. for $C_{64}H_{56}N_8Ag_2P_2F_{12}$: C, 53.27; H, 3.92; N, 7.77. Found: C, 52.85; H, 3.98; N, 7.03%.

2.3.2. Bis[1,1′-di(3-methoxybenzyl)-3,3′-(2-methylenepropane-1,3-diyl)dibenzimidazolin-2,2′-diylidene]disilver(I) bis(hexafluorophosphate) (3b)

Yield: 79%. ^{1}H NMR (DMSO-d$_6$): δ = 7.69-7.65 (m, 8H, Ar-H), 7.40-7.34 (m, 8H, Ar-H), 7.05 (t, 4H, J = 7.83 Hz, Ar-H), 6.79 (s, 4H, Ar-H), 6.74-6.69 (m, 8H, Ar-H), 5.62 (s, 8H, NCH_2), 5.36 (s, 8H, NCH_2), 4.97 (s, 4H, $=CH_2$), 3.56 (s, 12H, OCH_3) ppm. ^{13}C NMR (DMSO-d$_6$): δ = 159.77, 140.35, 137.86, 133.89, 133.65, 130.32, 124.90, 124.75, 119.42, 113.85, 113.18, 112.89, 55.36, 52.17, 52.04 ppm. MALDI-TOF MS: $[M\text{-}PF_6]^+$ at m/z 1418.04. Anal. Calc. for $C_{68}H_{64}N_8O_4Ag_2P_2F_{12}$: C, 52.25; H, 4.14; N, 7.17. Found: C, 52.45; H, 4.29; N, 7.17%.

2.3.3. Bis[1,1′-di(4-methoxybenzyl)-3,3′-(2-methylenepropane-1,3-diyl)dibenzimidazolin-2,2′-diylidene]disilver(I) bis(hexafluorophosphate) (3c)

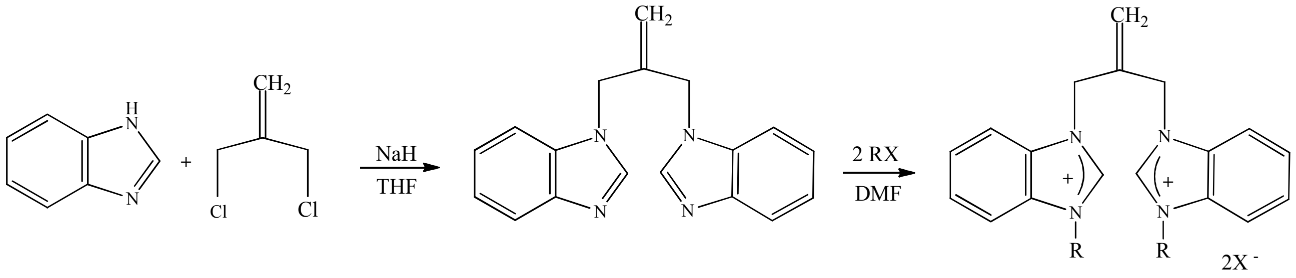
Yield: 76%. ^{1}H NMR (DMSO-d$_6$): δ = 7.65 (t, 8H, J = 6.26 Hz, Ar-H), 7.37-7.29 (m, 8H, Ar-H), 7.18 (d, 8H, J = 8.61 Hz, Ar-H), 6.68 (d, 8H, J = 9.00 Hz, Ar-H), 5.62 (s, 8H, NCH$_2$), 5.40 (s, 8H, NCH$_2$), 5.14 (s, 4H, =CH$_2$), 3.57 (s, 12H, OCH$_3$) ppm. ^{13}C NMR (DMSO-d$_6$): δ = 159.34, 133.89, 133.42, 129.14, 128.09, 124.75, 124.61, 114.45, 112.91, 112.81, 55.38, 52.41, 51.89 ppm. MALDI-TOF MS: [M-PF$_6$]$^+$ at m/z 1418.44. Anal. Calc. for $C_{68}H_{64}N_8O_4Ag_2P_2F_{12}$: C, 52.25; H, 4.14; N, 7.17. Found: C, 51.95; H, 3.79; N, 7.38%.

2.4. General procedure for the three-component coupling reaction

The mixture of *p*-formaldehyde (30 mg, 1 mmol), NHC-Ag(I) complex (3 mol%), phenylacetylene (168 μL, 1.5 mmol) and piperidine (120 μL, 1.2 mmol) in the solvent (2 mL) was stirred at 80 °C for 18h in dark. It was cooled to room temperature and Et$_2$O (20 mL) was added. Organic part was dried over MgSO$_4$. After filtration and removing the volatile components, propargylic amine compound was obtained by column chromatography on silica using EtOAc/hexane (1/3).

3. Results and Discussion

Preparation methods of 1,1′-(2-methylenepropane-1,3-diyl)dibenzimidazole **(1)** and the dibenzimidazolium salts **(2a-2c)** are shown in Scheme 1. Compound **1** was obtained by N-alkylation of benzimidazole with 1,1-bis(chloromethyl)ethylene in the presence of NaH in THF. Reaction of dibenzimidazole with benzyl halides gave the dibenzimidazolium salts **2a-c**. The salts are stable to air and moisture. Treatment of **2a-c** with 2 equiv. of Ag$_2$O in MeOH at room temperature and following the salt metathesis reaction of the formed NHC-Ag(I) bromide/chloride complexes with NH$_4$PF$_6$ in MeOH at room temperature produced hexafluorophosphate complexes (**3a-c)** (Scheme 2). These silver complexes are non-hygroscopic and air stable. They are soluble in CH$_3$CN, DMSO and DMF and insoluble in MeOH, Et$_2$O and hexane.

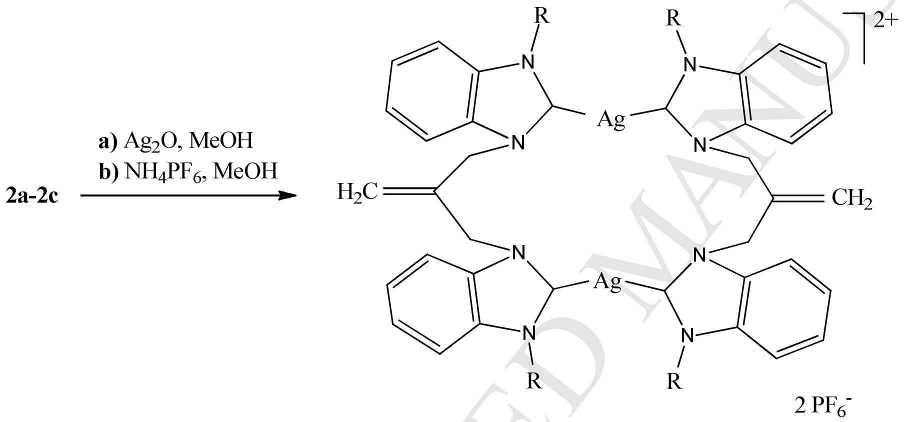


1

2a-2c

2a: R = $CH_2C_6H_5$; X = Br
2b: R = $CH_2C_6H_4OMe$-3; X = Cl
2c: R = $CH_2C_6H_4OMe$-4; X = Cl

Scheme 1. Synthesis of **1** and dibenzimidazolium salts **2a-2c**



3a-3c

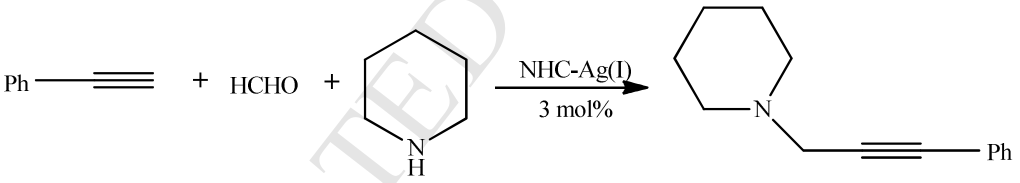
3a: R = $CH_2C_6H_5$
3b: R = $CH_2C_6H_4OMe$-3
3c: R = $CH_2C_6H_4OMe$-4

Scheme 2. Synthesis of dinuclear NHC-Ag(I) complexes **3a-3c**

The formulations of the all synthesized compounds were corroborated by elemental analysis method. ^{1}H and ^{13}C NMR signals were consistent with the expected structures. In the ^{1}H NMR spectra of the silver complexes **(3a-3c)**, extinction of the signals related to acidic C2 proton of the benzimidazolium salts **(2a-2c)** is an evidence of deprotonation. The signals for carbene carbon of the complexes were not observed in the ^{13}C NMR spectra. This unusual situation was ascribed to the fluxional behaviour of the complexes similarly for some NHC-Ag(I) complexes [33,34]. The molecular formulations of **3a-3c** were also established by MALDI-TOF mass spectroscopy. $[M\text{-}PF_6]^+$ signals were observed at 1297.62, 1418.04 and 1418.44, respectively.

Three-component coupling reactions of alkynes, aldehydes and amines (A^3-coupling) give propargylamines, significant compounds because of being a key intermediate in the construction of biologically active N-heterocycles. It is known that transition metal salts and complexes have been efficient catalysts for this reaction [35-40]. However, there have been a limited number of reports related to the catalytic applications of NHC-Ag(I) complexes in A^3-coupling reactions [41-47]. Herein, preliminary catalytic studies were carried out using phenylacetylene, piperidine and *p*-formaldehyde at 80 °C. The catalytic activity of **3a** was examined in different solvents (Table 1, entries 1-5). Moderate yields were obtained in acetone and CH_3CN. Good catalytic activity was observed with **3a** and **3c** under neat conditions (Table 1, entries 1 and 8). While **3a** and **3c** complexes bearing benzyl and 4-methoxybenzyl substituents on the NHC ligand showed almost similar activities (Table 1, entries 1,2,8,9), lower yields were obtained by **3b** complex containing 3-methoxybenzyl substituent (Table 1, entries 6,7). It was concluded that methoxy group occupying position 3 in compound **3b** caused to decrease in activity compared to **3a**. It was previously reported that decreasing of the number of the group on the NHC ligand led to lower catalytic efficiency [32].

Table 1. NHC-Ag(I) catalysed A^3-coupling reaction [a]



Entry	Catalyst	Solvent	Yield (%)[b,c]
1	**3a**	Neat	81
2	**3a**	CH_3CN	51
3	**3a**	Acetone	55
4	**3a**	DMF	25
5	**3a**	DMSO	30
6	**3b**	Neat	59
7	**3b**	CH_3CN	44
8	**3c**	Neat	83
9	**3c**	CH_3CN	50

[a] Reaction conditions: *p*-formaldehyde (1.0 mmol), piperidine (1.2 mmol), phenylacetylene (1.5 mmol), catalyst (3 mol %), solvent (2 mL), 18 h, 80 °C, in air.
[b] Isolated yields.
[c] Average of two runs.

The fluorescent emission spectra of complexes **3a, 3b** and **3c** were measured in CH_3CN at room temperature as shown in figure 1. The spectra obtained upon excitation at 240 nm exhibited maximum emission wavelengths at 484, 484 and 470 nm, respectively. d^{10}-d^{10} interactions of Ag(I) ions are thought to cause luminescence.

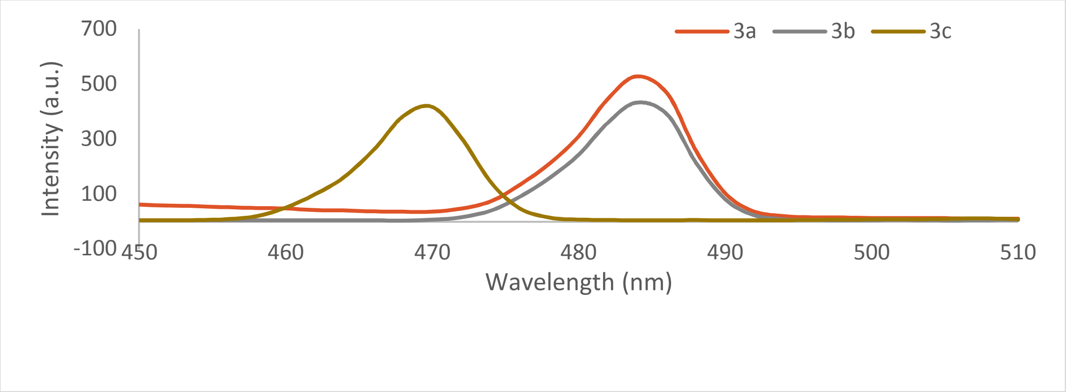


Figure 1. Emission spectra of complexes **3a-3c** (1.0 X 10^{-5} M in CH_3CN) at room temperature

4. Conclusions

In conclusion, we prepared three dinuclear NHC silver complexes derived from dibenzimidazol-2-ylidenes. Their structures were elucidated by ^1H NMR, ^{13}C NMR, elemental analysis and MALDI-TOF mass spectrometry. Preliminary catalytic studies disclosed that complexes **3a** and **3c** catalyzed three-component reaction of piperidine, phenylacetylene and *p*-formaldehyde with good yields under neat conditions. All the complexes were found to be luminescent in acetonitrile solutions at room temperature. Synthesis of new organometallic complexes obtained from these precursors and their catalytic studies are in progress.

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References

[1] A. J. Arduengo III, R. L. Harlow, M. Kline, A stable crystalline carbene, J. Am. Chem. Soc. 113 (1991) 361-363. https://doi.org/10.1021/ja00001a54.

[2] D. Pugh, A. A. Danopoulos, Metal complexes with ‘pincer’-type ligands incorporating N-heterocyclic carbene functionalities, Coord. Chem. Rev. 251 (2007) 610-641. https://doi.org/10.1016/j.ccr.2006.08.001.

[3] A. J. Arduengo III, H. V. R. Dias, J. C. Calabrese, F. Davidson, Homoleptic carbene-silver(I) and carbene-copper(I) complexes, Organometallics 12 (1993) 3405-3409. https://doi.org/10.1021/om00033a009.

[4] C. Xia, K. Yang, W. Sun, X. Lu, J. Xie, Silver(I), nickel(II) N-heterocyclic carbene complexes based on bidentate bis-imidazolium salt with a quinoxaline linker: syntheses, structures, and characterization, J. Coord. Chem. 70 (2017) 615-625. https://doi.org/10.1080/00958972.2016.1274401.

[5] S. Patil, K. Dietrich, A. Deally, B. Gleeson, H. Muller-Bunz, F. Paradisi, M. Tacke, Synthesis, Cytotoxicity and Antibacterial Studies of Novel Symmetrically and Nonsymmetrically 4□(Methoxycarbonyl)benzyl□Substituted N□Heterocyclic Carbene–Silver Acetate Complexes, Helvetica Chim. Acta 93 (2010) 2347-2364. https://doi.org/10.1002/hlca.201000310

[6] Y. Gok, S. Akkoc, O. Ozeroglu Celikal, I. Ozdemir, S. Gunal, E. Sayin, N-functionalized benzimidazol-2-ylidene silver complexes: synthesis, characterization, and antimicrobial studies, Turk. J. Chem. 37 (2013) 1007-1013. https://doi.org/10.3906/kim-1304-72.

[7] T. Nakamura, S. Ogushi, Y. Arikawa, K. Umakoshi, Preparations of a series of coinage metal complexes with pyridine-based bis(N-heterocyclic carbene) ligands including transmetalation to palladium complexes, J. Organomet. Chem. 803 (2016) 67-72. https://doi.org/10.1016/j.jorganchem.2015.12.006.

[8] E. A. Baquero, G. F. Silbestri, P. Gómez-Sal, J. C. Flores, E. Jesús, Sulfonated Water-Soluble N-Heterocyclic Carbene Silver(I) Complexes: Behavior in Aqueous Medium and as NHC-Transfer Agents to Platinum(II), Organometallics 32 (2013) 2814-2826. https://doi.org/10.1021/om400228s.

[9] J. Deng, H. Gao, F. Zhu, Q. Wu, Synthesis and Structure of Imine–N-Heterocyclic Carbene Palladium Complexes and Their Catalytic Behavior in Norbornene Polymerization, Organometallics 32 (2013) 4507-4515. https://doi.org/10.1021/om400268y.

[10] S. Hameury, P. Frémont, P.-A. R. Breuil, H. Olivier-Bourbigoub, P. Braunstein, Synthesis and characterization of oxygen-functionalised-NHC silver(I) complexes and NHC transmetallation to nickel(II), Dalton Trans. 43 (2014) 4700-4710. https://doi.org/10.1039/C3DT52773E.

[11] H. Iwasaki, Y. Teshima, Y. Yamada, R. Ishikawa, Y. Koga, K. Matsubara, Bimetallic Cu(I) complex with a pyridine-bridged bis(1,2,3-triazole-5-ylidene) ligand, Dalton Trans. 45 (2016) 5713-5719. https://doi.org/10.1039/C6DT00008H.

[12] M. Monticelli, C. Tubaro, M. Baron, M. Basato, P. Sgarbossa, C. Graiff, G. Accorsi, T.P. Pell, D. J. D. Wilsone, P. J. Barnard, Metal complexes with di(N-heterocyclic carbene) ligands bearing a rigid ortho-, meta or para-phenylene bridge, Dalton Trans. 45 (2016) 9540-9552. https://doi.org/10.1039/C6DT01129B.

[13] K. Y. Wan, A. J. Lough, R. H. Morris, Transition Metal Complexes of an (S,S)-1,2-Diphenylethylamine-Functionalized N-Heterocyclic Carbene: A New Member of the Asymmetric NHC Ligand Family, Organometallics 35 (2016) 1604-1612. https://doi.org/10.1021/acs.organomet.6b00031.

[14] E. Chardon, G. Dahm, G. Guichard, S. Bellemin-Laponnaz, Synthesis and structural characterization of alkyne-functionalized N-heterocyclic carbene complexes of ruthenium, palladium and rhodium, Inorg. Chim. Acta 467 (2017) 33-38. https://doi.org/10.1016/j.ica.2017.07.034.

[15] C. R. Shahini, G. Achar, S. Budagumpi, M. Tacke, S. A. Patil, Non–symmetrically p–nitrobenzyl–substituted N–heterocyclic carbene–silver(I) complexes as metallopharmaceutical agents, Appl. Organomet. Chem. 31 (2017) e3819. https://doi.org/10.1002/aoc.3819.

[16] R. A. Haque, S. Y. Choo, S. Budagumpi, A. A. Abdullah, M. B. K. Ahamed, A. M. S. A. Majid, Synthesis, crystal structures, characterization and biological studies of nitrile-functionalized silver(I) N-heterocyclic carbene complexes, Inorg. Chim. Acta 433 (2015) 35-44. https://doi.org/10.1016/j.ica.2015.04.023.

[17] M. O. Karatas, B. Olgundeniz, S. Gunal, I. Ozdemir B. Alici, E. Cetinkaya, Synthesis, characterization and antimicrobial activities of novel silver(I) complexes with coumarin substituted N-heterocyclic carbene ligands, Bioorg. Med. Chem. 24 (2016) 643-650. https://doi.org/10.1016/j.bmc.2015.12.032.

[18] M. A. Iqbal, M. I. Umar , R. A. Haque, M. B. K. Ahamed, M. Z. B. Asmawi, A. M. S. A. Majid, Macrophage and colon tumor cells as targets for a binuclear silver(I) N-heterocyclic carbene complex, an anti-inflammatory and apoptosis mediator, J. Inorg. Biochem. 146 (2015) 1-13. https://doi.org/10.1016/j.jinorgbio.2015.02.001.

[19] O. Sánchez, S. González, Á. R. Higuera-Padilla, Y. León, D. Coll, M. Fernández, P. Taylor, I. Urdanibia, H. R. Rangel, J. T. Ortega, W. Castro, M. C. Goite, Remarkable in vitro anti-HIV activity of new silver(I)– and gold(I)–N-heterocyclic carbene complexes. Synthesis, DNA binding and biological evaluation, Polyhedron 110 (2016) 14-23. https://doi.org/10.1016/j.poly.2016.02.012.

[20] H. J. H. Syu, J. Y. Z. Chiou, J.-C. Wang, I. J. B. Lin, Photoluminescence of self-assembled Ag(I) and Au(I) N-heterocyclic carbene complexes. Interplay the aurophilic, hydrogen bonding and hydrophobic interactions, RSC Adv. 7 (2017) 14611-14617. https://doi.org/10.1039/C6RA28294F.

[21] S. D. Adhikary, L. Jhulki, S. Seth, A. Kundu, V. Bertolasi, P. Mitra, A. Mahapatra, J. Dinda, Synthetic strategy of diflurophosphate-bridged bimetallic N-heterocyclic carbene complexes: Synthesis, structures and photoluminescence of picolyl-substituted alkylbenzimidazolylidene ligands, Inorg. Chim. Acta 384 (2012) 239-246. https://doi.org/10.1016/j.ica.2011.12.007.

[22] S. D. Adhikary, S. K. Seth, M. R. Senapati, J. Dinda, Binuclear luminescent silver(I) – N-heterocyclic carbene complex derived from 1-picolyl-3-pyrimidylbenzimidazoliumhexaflurophosphate, J. Mol. Structure 1042 (2013) 123-128. https://doi.org/10.1016/j.molstruc.2013.03.048.

[23] C.-X. Lin, X.-F. Kong, F.-B. Xu, Z.-Z. Zhang, Y. F. Yuan, Z. Dinuclear Macrocyclic Quinoline Bridged Mercury and Silver Bis(N□heterocyclic Carbene) Complexes: Synthesis, Structure, and Spectroscopic Studies, Anorg. Allg. Chem. 639 (2013) 881-885. https://doi.org/10.1002/zaac.201300067.

[24] H. Yoshida, I. Kageyuki, K. Takaki, Silver-Catalyzed Highly Regioselective Formal Hydroboration of Alkynes, Org. Lett. 16 (2014) 3512-3515. https://doi.org/10.1021/ol501465x.

[25] X. P. Fu, L. Liu, D. Wang, Y. J. Chen, C. J. Li, “On water”-promoted direct alkynylation of isatins catalyzed by NHC–silver complexes for the efficient synthesis of 3-hydroxy-3-ethynylindolin-2-ones, Green Chem. 13 (2011) 549-553. https://doi.org/10.1039/C0GC00807A.

[26] R. Kilincarslan, N.Sadic, B. Cetinkaya, Ag(I) complexes of benzimidazol-2-ylidene ligands: a study of catalytic e□ciency towards three-component coupling reactions, Turk. J. Chem. 40 (2016) 681-687. https://doi.org/10.3906/kim-1510-6.

[27] Q. Li, Y. F. Xie, B. C. Sun, J. Yang, H. B. Song, L. F. Tang, Synthesis of N-heterocyclic carbene silver and palladium complexes bearing bis(pyrazol-1-yl)methyl moieties, J. Organomet. Chem. 745-746 (2013) 106-114. https:// doi.org/10.1016/j.jorganchem.2013.07.055.

[28] M. K. Samantaray, V. Katiyar, D. Roy, K. Pang, H. Nanavati, R. Stephen, R. B. Sunoj, P. Ghosh, A Cationic (N□Heterocyclic carbene)silver Complex as Catalyst for Bulk Ring□Opening Polymerization of L□Lactides, Eur. J. Inorg. Chem. 2006 (2006) 2975-2984. https://doi.org/10.1002/ejic.200600209.

[29] S. Balcan, M. Balcan, B. Cetinkaya, Poly(l-lactide) initiated by silver N-heterocyclic carbene complexes: synthesis, characterization and properties, Polym. Bull. 70 (2013) 3475-3485. https://doi.org/10.1007/s00289-013-1034-9.

[30] Y. Fujii, J. Terao, N. Kambe, Silver-catalyzed carbomagnesiation of terminal aryl and silylalkynes and enynes in the presence of 1,2-dibromoethane, Chem. Commun. 0 (2009) 1115-1117. https://doi.org/10.1039/B820521C.

[31] Z. Tasci, A. Kunduracioglu, İ. Kani, B. Cetinkaya, A New Application Area for Ag□NHCs : CO_2 Fixation Catalyst, ChemCatChem. 4 (2012) 831-835. https://doi.org/10.1002/cctc.201100430.

[32] R. Kilincarslan, N.Sadic, Catalytic activity of N-heterocyclic carbene silver complexes derived from imidazole ligands, Inorg. and Nano-Metal Chem. 47 (2017) 462-466. https://doi.org/10.1080/15533174.2016.1186054.

[33] I. Ozdemir, E.O. Ozcan, S. Gunal, N. Gurbuz, Synthesis and Antimicrobial Activity of Novel Ag-N-Hetero-cyclic Carbene Complexes, Molecules 15 (2010) 2499-2508. https://doi.org/10.3390/molecules15042499.

[34] I. Ozdemir, N. Gurbuz, O. Dogan, S. Gunal, I. Ozdemir, Synthesis and antimicrobial activity of Ag(I)□N□heterocyclic carbene complexes derived from benzimidazol□2□ylidene, Appl. Organomet. Chem. 24 (2010) 758-762. https://doi.org/10.1002/aoc.1693.

[35] S. Sakaguchi, T. Kubo, Y. Ishii, A Three□Component Coupling Reaction of Aldehydes, Amines, and Alkynes, Angew. Chem. Int. Ed. 40 (2001) 2534-2536. https://doi.org/10.1002/1521-3773(20010702)40:13<2534::AID-ANIE2534>3.0.CO;2-2

[36] C. M. Wei, Z. G. Li, C. J. Li, The First Silver-Catalyzed Three-Component Coupling of Aldehyde, Alkyne, and Amine, Org. Lett. 5 (2003) 4473-4475. https://doi.org/10.1021/ol035781y.

[37] R. Manikandan, P. Anitha, P. Viswanathamurthi, J. G. Malecki, Palladium(II) pyridoxal thiosemicarbazone complexes as efficient and recyclable catalyst for the synthesis of propargylamines by a three□component coupling reactions in ionic liquids, Polyhedron 119 (2016) 300-306. https://doi.org/10.1016/j.poly.2016.09.005.

[38] S. Shabbir, Y. Lee, H. Rhee, Au(III) catalyst supported on a thermoresponsive hydrogel and its application to the A-3 coupling reaction in water, J. Catal. 322 (2015) 104-108. https://doi.org/10.1016/j.jcat.2014.11.009.

[39] D. S. Raghuvanshi, K. N. Singh, Highly Efficient Cadmium-Catalyzed Three-Component Coupling of an Aldehyde, Alkyne, and Amine via C-H Activation under Microwave Conditions, Synlett 3 (2011) 373-377. https://doi.org/10.1055/s-0030-1259323.

[40] L. Shi, Y. Q. Tu, M. Wang, F. M. Zhang, C. A. Fan, Microwave-Promoted Three-Component Coupling of Aldehyde, Alkyne, and Amine via C−H Activation Catalyzed by Copper in Water, Org. Lett. 6 (2004) 1001-1003. htpps://doi.org/10.1021/ol049936t.

[41] L. Rubio-Perez, M. Iglesias, J. Munarriz, V. Polo, J. J. Perez-Torrente, L. A. Oro, Efficient Rhodium□Catalyzed Multicomponent Reaction for the Synthesis of Novel Propargylamines, Chem. Eur. J. 21 (2015) 17701-17707. https://doi.org/10.1002/chem.201502993.

[42] R. Kilincarslan, A. Kunduracioglu, N. Sadic, Ag(I) Complexes Bearing N -heterocyclic Carbene Catalyzed Formation of Propargylamines by Three-component Coupling Reaction, Rev. Chim. 67 (2016), 2214-2216.

[43] Q. Li, X. Li, J. Yang, H.-B. Song, L.-F. Tang, Synthesis and structural characterization of N-heterocyclic carbene silver complexes derived from N-ferrocenylmethyl-N′-(pyridylmethyl)imidazolium iodides, Polyhedron 59 (2013) 29-37. https://doi.org/10.1016/j.poly.2013.04.032.

[44] C. H. Cheng, D. F. Chen, H. B. Song, L. F. Tang, Synthesis and catalytic activity of N-heterocyclic carbene silver complexes derived from 1-[2-(pyrazol-1-yl)phenyl]imidazole, J. Organomet. Chem. 726 (2013) 1-8. https://doi.org/10.1016/j.jorganchem.2012.12.008.

[45] P. Li, L. Wang, Y. Zhang, M. Wang, Highly efficient three-component (aldehyde–alkyne–amine) coupling reactions catalyzed by a reusable PS-supported NHC–Ag(I) under solvent-free reaction conditions, Tetrahedron Lett. 49 (2008**)** 6650-6654. https://doi.org/10.1016/j.tetlet.2008.09.026.

[46] M. T. Chen, B. Landers, O. Navarro, Well-defined (N-heterocyclic carbene)–Ag(I) complexes as catalysts for A^3 reactions, Org. Biomol. Chem. 10 (2012) 2206-2208. https://doi.org/10.1039/C2OB06900H.

[47] Y. Li, X. Chen, Y. Song, L. Fang, G. Zou, Well-defined N-heterocyclic carbene silver halides of 1-cyclohexyl-3-arylmethylimidazolylidenes: synthesis, structure and catalysis in A^3-reaction of aldehydes, amines and alkynes, Dalton Trans. 40 (2011) 2046-2052. https://doi.org /10.1039/C0DT01074J.

Highlights

- New N-heterocyclic carbene precursors and their dinuclear silver complexes were synthesized and characterized.
- Silver complexes were tested as catalysts in three-component coupling reaction of piperidine, p-formaldehyde and phenylacetylene.
- Silver complexes were observed to be luminescent.