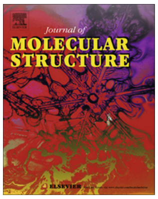
Journal of Molecular Structure 1053 (2013) 38–47

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc



Synthesis, structural characterization and properties of new *N*-heterocyclic carbene Ag(I) complexes

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HIGHLIGHTS

- *N*-heterocyclic Ag(I) carbene complexes have been prepared from imidazolium/benzimidazolium salts.
- Four of these compounds have been characterized by single crystal X-ray crystallography.
- In these crystal structures, supramolecular interactions are explored.
- One of these compounds exhibits solution emission at room temperature.

ARTICLE INFO

Article history:
Received 31 July 2013
Received in revised form 26 August 2013
Accepted 26 August 2013
Available online 31 August 2013

Keywords:
NHC–silver complexes
Structural elucidation
Supramolecular interactions
Spectroscopy

ABSTRACT

The syntheses and properties of new *N*-heterocyclic carbene complexes [{1-(2,3,5,6-tetra methyl benzyl)-3-benzylbimy}AgCl] (**2a**), [{1-(benzyl)-3-benzylbimy}$_2$Ag][BF$_4$] (**2b**), [{1-(benzyl)-3-butylbimy}AgBr]$_2$ (**2c**), [{1-(benzyl)-3-(4-nitro-benzyl)bimy}AgBr] (**2d**), [{1-(benzyl)-3-(4-bromo-benzyl)bimy}AgBr] (**2e**), [{1-(benzyl)-3-(4-nitro-benzyl)bimy}$_2$Ag][BF$_4$] (**2f**), [{1-(benzyl)-3-(4-bromo-benzyl)bimy}$_2$Ag][BF$_4$] (**2g**) (bimy = benzimidazol-2-ylidene), and [{1-(10-bromo-9-anthracenylmethyl)-3-butylimy}AgBr] (**2h**) (imy = imidazol-2-ylidene) have been described. Compounds **2a–2h** have been characterized by ^{1}H NMR-, UV–vis- LC/MS-spectral studies and elemental analysis. Compounds **2a–2c** and **2h** are unambiguously characterized by single crystal X-ray crystallography. Compound **2h** shows solution emission at room temperature.

1. Introduction

The most *N*-Heterocyclic carbenes (NHCs) are commonly derived from imidazolium/benzimidzolium salts. NHCs have attracted considerable attention because of their ability to coordinate very strongly to transition metals and main-group elements [1,2]. In 1968, Ofele and Wanzlick first pioneered the metalation of imidazol-2-ylidenes, that are popularly known as *N*-Heterocyclic carbenes [3,4]. NHCs (as ligands) are considered to be better σ donors (i.e., Lewis bases) than most phosphines [5]. NHCs, that are air-stable, are significantly simpler to synthesize. While some of these carbenes are isolable, some are less stable that can be generated in situ [6–11]. Transition metal-NHC complexes have received attention because of their applications in the areas of catalysis of organic reactions (most notably, the Heck and Suzuki C–C coupling reactions) [12–20], supramolecular- and materials-chemistry [21–23]. Silver–NHC complexes [24–30] are of special interest because of their ability to act as effective carbene transfer agent for the syntheses of Ni–, Pd–, Pt–, Cu–, Au–, Rh–, Ir– and Ru–carbene complexes; indeed, this route is one of the best method for the effective preparation of metal–carbene complexes [31,32]. In addition, silver carbene metal complexes are well noted as efficient fluorescent switches; they also exhibit biological activity and have been used as antimicrobial and antimitochondrial agents [33–40]. Herein we wish to report the syntheses of silver–NHC complexes [{1-(2,3,5,6-tetra methyl benzyl)-3-benzylbimy} AgCl] (**2a**), [{1-(benzyl)-3-benzylbimy}$_2$Ag][BF$_4$] (**2b**), [{1-(benzyl)-3-butylbimy}AgBr]$_2$ (**2c**), [{1-(benzyl)-3-(4-nitro-benzyl)bimy}AgBr] (**2d**), [{1-(benzyl)-3-(4-bromo-benzyl)bimy}AgBr] (**2e**), [{1-(benzyl)-3-(4-nitro-benzyl)bimy}$_2$Ag][BF$_4$] (**2f**), [{1-(benzyl)-3-(4-bromo-benzyl)bimy}$_2$Ag][BF$_4$] (**2g**) (bimy = benzimidazol-2-ylidene), and [{1-(10-bromo-9-anthracenylmethyl)-3-butylimy}AgBr] (**2h**). Among this **2a**–**2h**, the compounds **2a**, **2b**, **2c** and **2h** are characterized by single crystal X-ray structure analyses. All compounds **2a**–**2h** have been characterized by routine elemental analysis, UV–vis electronic absorption-, ^{1}H NMR-, and LC/MS-spectroscopic techniques.

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http://dx.doi.org/10.1016/j.molstruc.2013.08.051

2. Experimental section

2.1. Materials and physical measurements

All the chemicals for synthesis were commercially available and used as received. Benzimidazolium/imidazolium salts of bromide/tetrafluoroborate (**1a**–**1h**) were prepared according to literature procedure [41,42]. Syntheses of metal complexes were performed under light sensitive care. The general synthetic procedures are schematically shown in Scheme 1. Solvents were dried by standard procedures. Micro analytical (C, H, N) data were obtained with a FLASH EA 1112 Series CHNS Analyzer. ^{1}H NMR spectra of compounds were recorded on Bruker DRX-400 spectrometer using $Si(CH_3)_4$ [TMS] as an internal standard. Electronic absorption spectra of solutions were recorded on a Cary 100 Bio UV–vis spectrophotometer and emission spectra was recorded on spectrofluorimeter (Fluromax-4, Horiba Jobin Yvon).

2.2. Synthesis

Silver–NHC complexes are generally prepared in a one-pot reaction of an imidazolium/benzimidazolium salt with Ag_2O. In the present study, benzimidazolium/imidazolium halides (compounds **2a**–**2h**) were prepared according to Scheme 1 (characterization data of these compounds are mentioned in the section of Supplementary materials). The carbene compounds [{1-(2,3,5,6-tetra methyl benzyl)-3-benzylbimy}AgCl] (**2a**), [{1-(benzyl)-3-benzylbimy}$_2$Ag][BF_4] (**2b**), [{1-(benzyl)-3-butylbimy}AgBr]$_2$ (**2c**), [{1-(benzyl)-3-(4-nitro-benzyl)bimy}AgBr] (**2d**), [{1-(benzyl)-3-(4-bromo-benzyl)bimy}AgBr] (**2e**) and [{1-(10-bromo-9-anthracenylmethyl)-3-butylimy}AgBr] (**2h**) are prepared by the treatment of their corresponding benzimidazolium/imidazolium halides **1a**–**1e** and **1h** with Ag_2O in DCM at room temperature. Compounds of benzimidazolium halides **1d** and **1e** are converted to corresponding benzimidazolium tetrafluoroborate **1f** and **1g** respectively by an anionic exchange reaction with NH_4BF_4. The acetonitrile solutions of benzimidazolium tetrafluoroborates **1f** and **1g**, on refluxing with Ag_2O afford compounds [{1-(benzyl)-3-(4-nitro-benzyl)bimy}$_2$Ag][BF_4] (**2f**) and [{1-(benzyl)-3-(4-bromo-benzyl)bimy}$_2$Ag][BF_4] (**2g**) respectively as shown in Scheme 1. All these complexes **2a**–**2h** are stable in air but sensitive to sonication and higher temperature. In the preparation of **2a**–**2h** complexes, benzimidazolium/imidazolium halides/tetrafluoroborates are deprotonated in the presence of silver oxide. The ^{1}H NMR spectra of these carbene complexes **2a**–**2h** do not show a low-field signal within the range of 9.50–10.00 ppm, and the chemical shifts of other hydrogens are similar to those of benzimidazolium/imidazolium halide/tetrafluoroborate derivatives of **1a**–**1h**. The colorless, air-stable crystals of **2a–2c**, suitable for single X-ray crystallography, are obtained by slow diffusion of Et_2O into their respective CH_2Cl_2 soluttions, and single crystals of **2h** are otanied by diffusion of methanol into its 1,2-dichloroethane solution.

2.2.1. $[(C_{25}H_{26}N_2)AgCl]$ *(**2a**)*

3-Benzyl-1-(2,3,5,6-tetramethyl-benzyl)-3H-benzoimidazol-1-ium chloride (**1a**) (0.160 g, 0.3 mmol) and silver oxide (0.04 g, 0.15 mmol) were taken in CH_2Cl_2 (15 mL) and stirred at room temperature for 4 h. After completion of this reaction, it was filtered through Celite and solvent was concentrated to 3 mL by rotary evaporator and subsequently diethylether (2 mL) was added to give white solid. Yield: (0.08 g). ^{1}H NMR (400 MHz, δ ppm) (DMSO-d_6): 2.21 (m, 12H), 5.64 (d, 4H), 7.43 (m, 6H), 7.92 (m, 4H). ^{13}C NMR (DMSO-d_6): δ = 136.7, 135.9, 134.8, 133.5, 133.2, 129.2, 128.4, 127.4, 124.7, 124.4, 112.8, 112.5, 53.2, 47.2, 17.3. MS (ESI): *m/z* 496. Anal. Calc. for $C_{25}H_{26}N_2AgCl$: C 60.32, H 5.26, N 5.63. Found: C 60.55, H 5.21, N 5.97%.

2.2.2. $[(C_{21}H_{18}N_2)_2Ag][BF_4]$ *(**2b**)*

This complex was prepared in a manner analogous to that of **2a**. In this case, the reactants are: 1,3-dibenzylbenzimidazolium tetrafluoroborate (**1b**) (0.772 g, 2 mmol) and silver oxide (0.232 g, 1 mmol). Complex **2b** was obtained as a white powder. Yield: (0.54 g). ^{1}H NMR (400 MHz, δ ppm) (DMSO-d_6): 5.78 (s, 8H), 7.30 (m, 20H), 7.44 (s, 4H), 7.78 (s, 4H). ^{13}C NMR (DMSO-d_6): δ = 136.7, 134.0, 133.9, 129.2, 128.5, 127.7, 124.8, 112.9, 52.3. MS (ESI): *m/z*: 702 (M-H)$^+$. Anal. Calc. for $C_{42}H_{36}N_4AgBF_4$: C 63.74, H 4.58, N 7.08. Found: C 64.09, H 4.52, N 6.67%.

2.2.3. $[(C_{18}H_{20}N_2)AgBr]_{2.}$ *(**2c**)*

This complex was prepared in a manner analogous to that of **2a**. The starting precursors are: 3-benzyl-1-butyl-3-H-benzimidazol-1-ium bromide (**1c**) (0.373 g, 1 mmol) and silver oxide (0.116 g, 0.5 mmol). Complex **2c** was obtained as a white powder. Yield: (0.22 g). ^{1}H NMR (400 MHz, δ ppm) (DMSO-d_6): 0.91 (s, 6H), 1.34 (s, 4H), 1.87 (s, 4H), 4.53 (s, 4H), 5.78 (s, 4H), 7.43 (m, 14H), 7.75 (s, 2H), 7.89 (s, 2H). ^{13}C NMR (DMSO-d_6): δ = 136.8, 133.8, 133.7, 129.2, 129.0, 128.4, 127.7, 124.5, 121.5, 112.8, 112.7, 52.1, 48.9, 32.5, 19.9, 14.0. MS (ESI): *m/z*: 635 ([L_2Ag]$^+$, 100%). Anal. Calc. for $C_{36}H_{40}Ag_2Br_2N_4$: C 47.82, H 4.46, N 6.20. Found: C 47.49, H 4.39, N 6.67%.

2.2.4. $[(C_{21}H_{17}N_3O_2)AgBr]$ *(**2d**)*

This complex was prepared in a manner analogous to that of **2a**. In this case, the reactants are: 1-benzyl-3-(4-nitro-benzyl)benzimidazolium bromide (**1d**) (0.212 g, 0.5 mmol) and silver oxide (0.058 g, 0.25 mmol). Complex **2d** was obtained as a white powder. Yield: (0.124 g). ^{1}H NMR (400 MHz, δ ppm) (DMSO-d_6): 5.78 (d, 4H), 7.36 (m, 7H), 7.56 (d, 4H), 7.76 (s, 2H). ^{13}C NMR (DMSO-d_6): δ = 147.5, 144.3, 136.6, 134.0, 139.9, 129.3, 129.2, 128.7, 128.5, 127.5, 124.8, 124.3, 113.0, 112.7, 52.4, 51.5. MS (ESI): *m/z*: 529. Anal. Calc. for $C_{21}H_{17}N_3O_2AgBr$: C 47.49, H 3.23, N 7.91. Found: C 47.85, H 3.28, N 7.54%.

2.2.5. $[(C_{21}H_{17}N_2Br)AgBr]$ *(**2e**)*

This complex was prepared in a manner analogous to that of **2a**. In this case, the reactants are: 1-benzyl-3-(4-bromo-benzyl)benzimidazolium bromide (**1e)** (0.343 g, 0.74 mmol) and silver oxide (0.088 g, 0.37 mmol). Complex **2e** was obtained as a white powder. Yield: (0.144 g). ^{1}H NMR (400 MHz, δ ppm) (DMSO-d_6): 5.80 (s, 2H), 5.97 (s, 2H), 7.37 (m, 7H), 7.54 (d, 2H), 7.76 (m, 2H), 8.19 (d, 2H). ^{13}C NMR (DMSO-d_6): δ = 146.7, 144.3, 140.6, 136.7, 133.8, 132.2, 129.9, 129.3, 128.5, 127.8, 124.7, 112.8, 52.3, 51.6. MS (ESI): *m/z*: 562. Anal. Calc. for $C_{21}H_{17}N_2AgBr_2$: C 44.64, H 3.03, N 4.96. Found: C 44.35, H 3.09, N 5.38%.

2.2.6. $[(C_{21}H_{17}N_3O_2)_2Ag][BF_4]$ *(**2f**)*

1-Benzyl-3-(4-nitro-benzyl)benzimidazolium tetrafluoroborate (**1f**) (0.431 g, 1 mmol) and silver oxide (0.116 g, 0.5 mmol) were taken in acetonitrile (20 mL); the resulting reaction mixture was then refluxed for overnight. After cooling the solvent, it was filtered through Celite and solvnet was concentrated to 3 mL by rotary evaporator. Diethylether (3 mL) was added to give white product. Yield: (0.231 g). ^{1}H NMR (400 MHz, δ ppm) (DMSO-d_6): 5.76 (s, 4H), 5.92 (s, 4H), 7.28–7.39 (m, 14H), 7.49 (d, 4H), (7.70 (m, 4H), 8.12 (d, 4H). ^{13}C NMR (DMSO-d_6): δ = 144.6, 143.9, 137.3, 134.0, 130.1, 129.4, 129.0, 128.8, 128.1, 127.9, 127.7, 124.4, 124.3, 122.7, 121.9, 119.8, 111.1, 51.6, 47.9. MS (ESI): *m/z*: 793. Anal. Calc. for $C_{42}H_{34}N_6O_4AgBF_4$: C 57.23, H 3.89, N 9.53. Found: C 57.57, H 3.84, N 9.97%.

2.2.7. $[(C_{21}H_{17}N_2Br)_2Ag][BF_4]$ *(**2g**)*

This complex was prepared in a manner analogous to that of **2f**. The starting precursors are: 1-benzyl-3-(4-Bromo-benzyl)