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Reactions of 1-Alkyl-3-phenylbenzimidazolium Salts with Ag_2O: The Formation of a Ring-Opening Formamide Derivative and a Ag Complex with an *N*-heterocyclic Carbene Ligand

Satoshi Sakaguchi *, Takashi Higashino, Yudai Tasaki, Ryo Ichihara and Tatsuo Yajima

Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan; k311104@kansai-u.ac.jp (R.I.); t.yajima@kansai-u.ac.jp (T.Y.)
* Correspondence: satoshi@kansai-u.ac.jp

Abstract: This study investigated the reactions of 1-alkyl-3-phenylbenzimidazolium salts with Ag_2O. It was found that the selectivity of the reaction products was influenced by the *N*-alkyl substituent on the azolium ring. For example, treating 1-methyl-3-phenylbenzimidazolium iodide (**2**) with Ag_2O for 24 h produced the ring-opening formamide derivative *N*-[2-(phenylamino)phenyl]-*N*-methylformamide (**2b**) in an 85% yield. In contrast, the reaction of 1-benzyl-3-phenylbenzimidazolium chloride (**3**) with Ag_2O under the same conditions yielded the corresponding *N*-heterocyclic carbene (NHC)–Ag complex (1-benzyl-3-phenylbenzimidazol-2-ylidene) silver(I) chloride (**3a**) in an 86% yield. Furthermore, the corresponding monodentate NHC–Au complex **2c** could be synthesized by allowing **2** to react with $AuCl(SMe_2)$ in the presence of Ag_2O.

Keywords: *N*-heterocyclic carbene; NHC–silver complexes; NHC–gold complex; hydrolysis; formamide

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1. Introduction

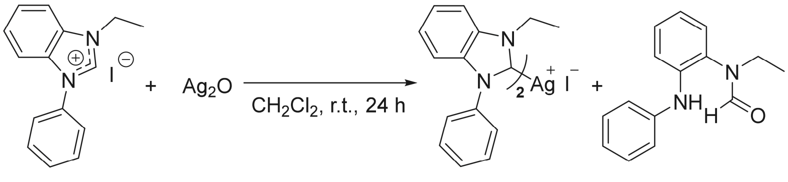
In recent years, *N*-heterocyclic carbenes (NHCs) have been widely used as ligands for metal catalysts because of their strong σ-donating ability [1–5]. Moreover, owing to the operational simplicity of their synthesis procedures, various *N*-substituents can be introduced into the side arms of NHCs. Consequently, these ligands are attracting rapidly increasing attention in the field of asymmetric catalysis [6–9]. To date, the most widely adopted method for the preparation of NHC species involves deprotonation at the C_2 position of an azolium salt with a Ag base to form an NHC–Ag complex [10–24]. This process can be accomplished using various Ag bases, such as Ag_2O, AgOAc, and Ag_2CO_3. In a pioneering study, Lin et al. introduced a procedure using Ag_2O to afford a Ag complex bearing 1,3-diethylbenzimidazol-2-ylidene [25–28]. Notably, NHC–Ag complexes play important roles as NHC transfer agents in the synthesis of numerous NHC–metal complexes (namely, the Ag_2O method), granting them extraordinary versatility. Thus, several applications employing NHC–Ag complexes to synthesize NHC–M (M = Group 8, 9, 10, and 11 elements) complexes via transmetalation have been documented [10–28].

Previously, we demonstrated the synthesis of a series of NHC–Pd(II) complexes derived from chiral hydroxyamide-functionalized benzimidazolium salts using the Ag_2O method [29,30]. Importantly, these NHC–Pd(II) complexes catalyzed asymmetric oxidative Heck-type reactions and asymmetric allylic alkylation (AAA) reactions [31–33]. Among these, in the Pd-catalyzed AAA reactions, we screened libraries of chiral NHC ligand precursors using an in situ-generated NHC–Pd(II) catalyst derived from chiral benzimidazolium salts via the Ag_2O method [33]. Consequently, we observed a reversal in enantioselectivity after changing the *N*-substituent from a methyl group to a phenyl group at the side arm of the chiral benzimidazolium ring. The intriguing observation that replacing the *N*-substituent on the chiral azolium ring with a aliphatic/aromatic group controlled the facial selection of the alkene substrate prompted us to study the reaction of a "simple" benzimidazolium salt with Ag_2O.

In this study, we discovered that the reaction of 1-ethyl-3-phenylbenzimidazolium iodide (**1**) with Ag_2O preferentially yielded the ring-opening formamide derivatives over the corresponding NHC–Ag complex. In the literature, Liu and Dai demonstrated that Ag_2O in CH_2Cl_2 promoted the hydrolysis of unsymmetrical pyridine-bridged pincer-type benzimidazolium halides, affording the corresponding ring-opening formamide derivatives [34–36]. However, to the best of our knowledge, the ring-opening reaction of a "simple" benzimidazolium salt with Ag_2O has not yet been reported. To address this, we focused on the ring-opening reaction of substituted benzimidazolium salts promoted by Ag_2O.

2. Results

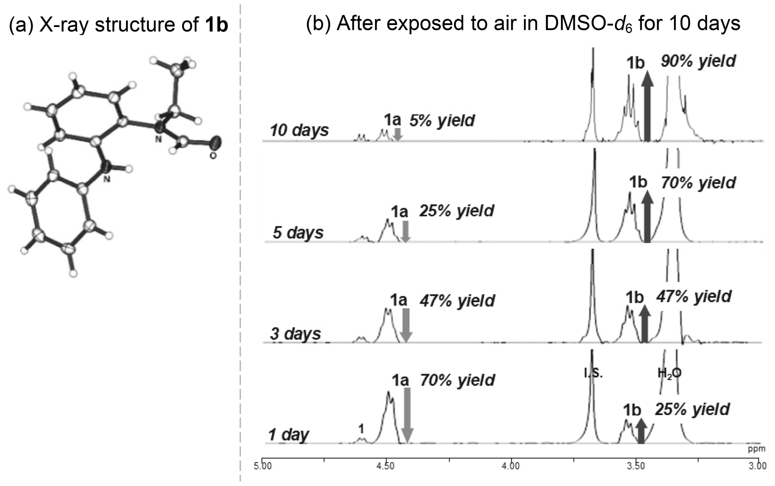
Based on our previously reported procedure for the preparation of the NHC–Ag complex, we initially performed the reaction of **1** with Ag_2O. Compound **1** (0.2 mmol) was allowed to react with Ag_2O (0.1 mmol) in CH_2Cl_2 (10 mL) at room temperature. As the reaction progressed, the black Ag_2O solid disappeared and a white precipitate was formed. After 24 h, the reaction produced bis(1-ethyl-3-phenylbenzimidazol-2-ylidene) silver(I) iodide (**1a**) and *N*-[2-(phenylamino)phenyl]-*N*-ethylformamide (**1b**) in 70% and 25% yields, respectively (Scheme 1, upper side). In the ^{13}C-NMR spectrum of the NHC–Ag complex **1a**, the carbene's carbon resonance was observed at δ 194.7 ppm, which is a characteristic of carbene metal complexes. On the other hand, the molecular structure of **1b** was established by single-crystal X-ray diffraction studies (Scheme 1a).



1 **1a** (70% yield) **1b** (25% yield)

(a) X-ray structure of **1b**

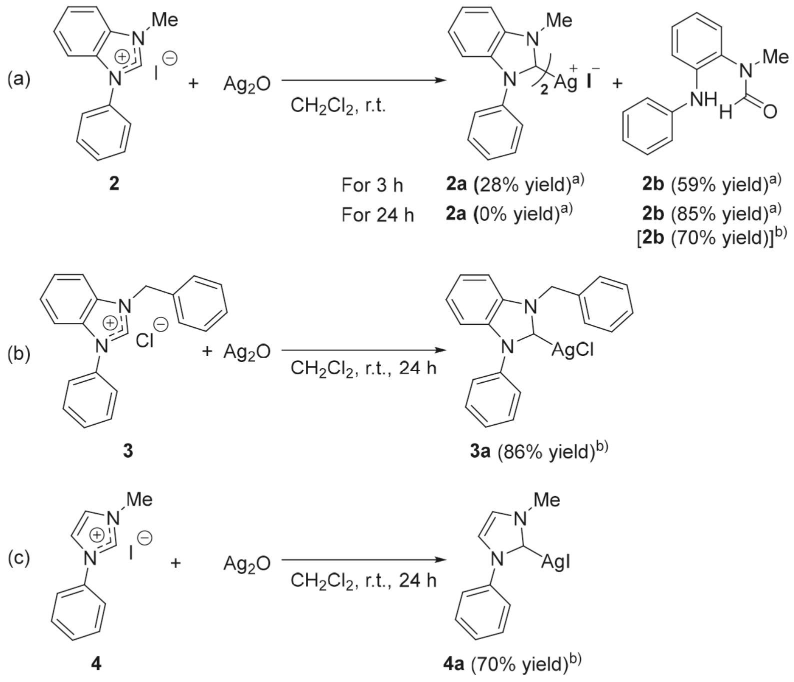
(b) After exposed to air in DMSO-d_6 for 10 days



Scheme 1. Reaction of **1** with Ag_2O.

After the reaction of **1** with Ag_2O for 24 h, we subjected the crude reaction mixture to ^{1}H-NMR analysis in DMSO-d_6 (Scheme 1b). On exposing the crude reaction mixture in the NMR tube to air at room temperature for several days, we observed a change in the product's composition. The initially clear solution of the crude mixture in DMSO-d_6 gradually transformed into a solution containing a white precipitate. The product yields monitored in the ^{1}H-NMR analysis were as follows (Scheme 1b; see also Supplementary Materials): **1a** (70% yield) and **1b** (25% yield) after 1 day; **1a** (47% yield) and **1b** (47% yield) after 3 days; **1a** (25% yield) and **1a** (70% yield) after 5 days; **1a** (5% yield) and **1b** (90% yield) after 10 days. These results suggest the decomposition of **1a** into **1b**. The underlying reaction pathway will be discussed later.

Furthermore, we examined three azolium salts bearing *N*-aliphatic and *N*-aromatic side arms (Scheme 2). 1-Methyl-3-phenylbenzimidazolium iodide (**2**) was allowed to react with Ag_2O in CH_2Cl_2 at room temperature for 3 h. This reaction preferentially afforded the corresponding ring-opening formamide derivative *N*-[2-(phenylamino)phenyl]-*N*-ethylformamide (**2b**) in a 59% yield over bis(1-methyl-3-phenylbenzimidazol-2-ylidene) silver(I) iodide (**2a**, 28% yield). Upon extending the reaction time to 24 h, **2b** was obtained as the sole product (Scheme 2a; refer to Supplementary Materials for details).



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[a] NMR yield using an internal standard method. [b] Isolated yield.

Scheme 2. Reactions of the selected azolium salts with Ag_2O.

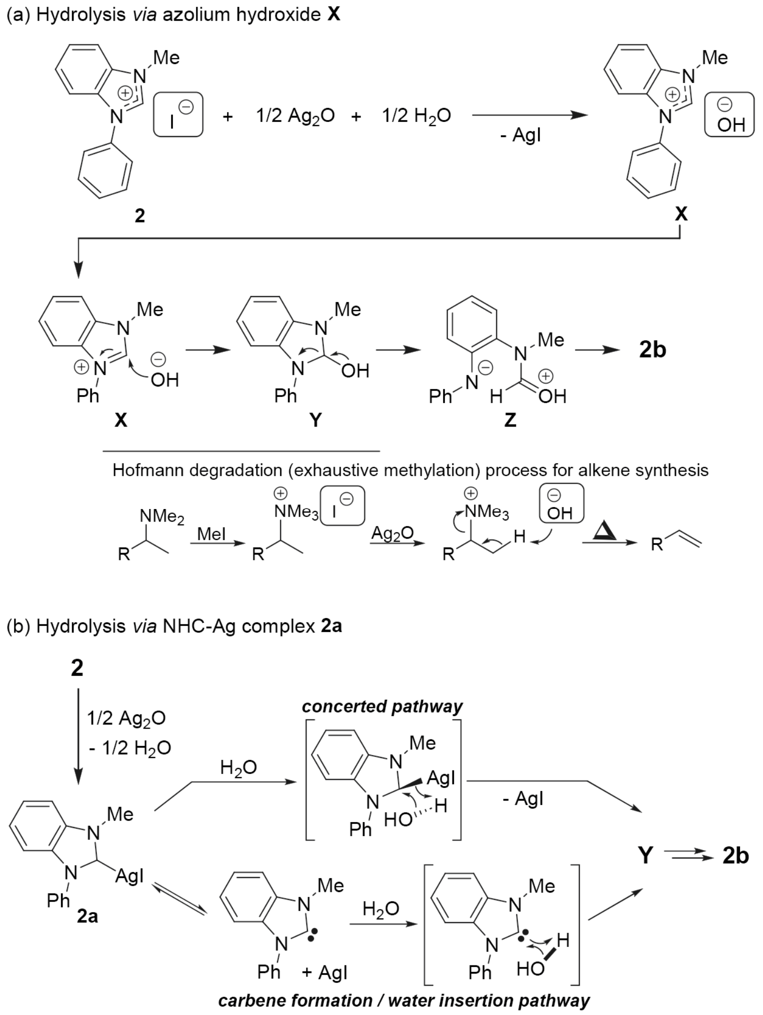
To date, various documents have focused on the reaction of **2** with Ag_2O in CH_2Cl_2 at room temperature, aimed at the synthesis of NHC–Ir complexes via transmetalation, which produces NHC–Ag complex **2a** as an intermediate [37–39]. However, these publications do not provide the characterization data for **2a**. In addition, they do not mention the formation of the ring-opening product **2b** in the foregoing reaction. Conversely, Pozharskii et al. demonstrated that the reaction of **2** with KNH_2 in liq. NH_3 at −70 °C for 2 h (Chichibabin reaction conditions) afforded **2b** in a 96% yield [40].

Next, the reaction of the *N*-benzyl-substituted benzimidazolium salt with Ag_2O was examined. Treating 1-benzyl-3-phenylbenzimidazolium chloride (**3**) with Ag_2O for 24 h yielded the corresponding NHC–Ag complex **3a** in an 86% yield (Scheme 2b). Gök and Akkoç have reported a similar observation; in their study, the corresponding NHC–Ag complex was synthesized by reacting 1-phenyl-3-(3,4,5-trimethoxybenzyl)benzimidazolium chloride with Ag_2O in CH_2Cl_2 [19,41].

Furthermore, on the other hand, previous reports indicate that treating 1-methyl-3-phenylimidazolium iodide (**4**) with Ag_2O affords the corresponding NHC–Ag complex **4a** [24,42,43]. Therefore, we attempted to reproduce this reaction in our laboratory. On treating **4** with Ag_2O in CH_2Cl_2, **4a** was obtained as a major product in a 70% yield (Scheme 2c). The formation of **4a** was confirmed by comparing its NMR spectra with those of a previously reported authentic sample. Thus, we concluded that the selectivity of the products in the reaction of azolium salt with Ag_2O depended on both the *N*-alkyl substituent of the azolium ring (methyl vs. benzyl) and the azolium skeleton.

3. Discussion

Li and Ollevier conducted a systematic study on the hydrolysis of an NHC–Ag complex derived from an imidazolinium salt to produce a formamide [44]. They reported that the NHC–Ag bearing a saturated backbone derived from the imidazolinium salt was easily hydrolyzed. They proposed that imidazolidinol was produced as an intermediate and later underwent rearrangement to afford a formamide in the hydrolysis reaction. By contrast, we demonstrated that the benzimidazolium salt **2** (or **1**) was hydrolyzed to formamide derivatives in the presence of Ag_2O. Plausible pathways are shown in Scheme 3.



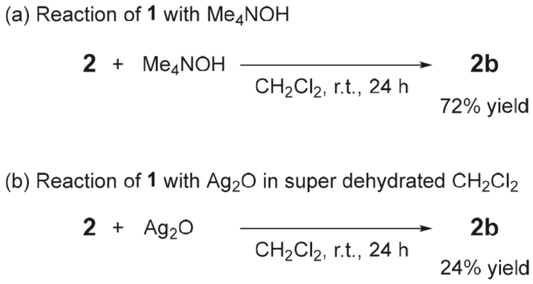
Scheme 3. Proposed pathways for the reaction of **2** with Ag_2O to form **2b**.

Although the reaction pathway for the reaction of **2** (or **1**) with Ag_2O remains unclear at this stage, the reaction might have proceeded via the formation of an azolium hydroxide and/or the NHC–Ag complex as an intermediate, as depicted in Scheme 3. First, the conversion of **2** into 1-methyl-3-phenylbenzimidazolium hydroxide (**X**) might have occurred through the action of Ag_2O and water (Scheme 3a).

Subsequently, the nucleophilic addition of an internal hydroxide to the azolium ring in the intermediate **X** led to the formation of adduct **Y**. Finally, **Y** undergoes rearrangement to form formamide derivative **2b** through intermediate **Z**. Notably, this anion-exchange (halide/hydroxide replacement) reaction is similar to the well-known Hofmann degradation (exhaustive methylation) for alkene synthesis (see Scheme 3a, lower side) [45].

On the contrary, the gradual decomposition of **1a** to **1b** observed in the reaction of **1** with Ag_2O, as depicted in Scheme 1a, implies the possibility of the hydrolysis of the NHC–Ag **1a** (or **2a**) intermediate to form the formamide derivative **1b** (or **2b**) (Scheme 3b). In this case, compound **2a** could have undergone direct hydrolyzation via the concerted addition of water and the elimination of AgI to generate imidazolidinol **Y**, which subsequently underwent a ring-opening reaction to form **2b** (concerted pathway). Alternatively, **2a** could have existed in equilibrium with free NHC and AgI. Here, note that free NHC formation from **X** via the intramolecular deprotonation of the azolium ring by hydroxide ions in **X** is also plausible. In this case, the subsequent incorporation of carbene into the O-H σ-bond of water would form **Y** (carbene formation/water insertion pathway). The latter pathway is similar to that proposed by Li and Ollevier [44].

To gain further insights into the reaction pathway, we investigated the reaction of **2** with tetramethylammonium hydroxide (Me_4NOH). We hypothesized that the counter-anion exchange between the iodide in **2** and the hydroxide in Me_4NOH would reversibly yield azolium hydroxide **X**. Indeed, treating **2** (0.2 mmol) with Me_4NOH (0.2 mmol) in CH_2Cl_2 (10 mL) at room temperature produced the formamide derivative **2b** in a 72% yield (Scheme 4a). This result suggests that halide/hydroxide replacement occurs in the reaction of **2** with Ag_2O to form **X**. Subsequently, intermediate **X** is converted into the ring-opening formamide **2b**, as depicted in Scheme 3a.

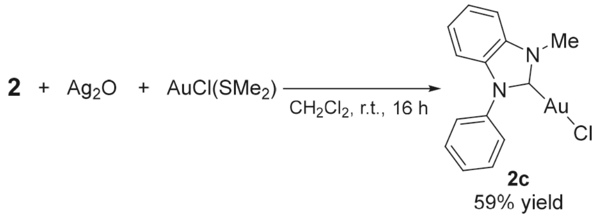

(a) Reaction of **1** with Me_4NOH

(b) Reaction of **1** with Ag_2O in super dehydrated CH_2Cl_2

Scheme 4. Mechanistic studies.

In addition, we hypothesized that the hydrolysis of Ag_2O in the presence of a trace amount of water would generate hydroxide ions (Scheme 3a). To confirm this assumption, we allowed **2** to react with Ag_2O in anhydride CH_2Cl_2. After sustaining this reaction for 24 h, the hydrolytic ring-opening product **2b** was obtained in a 24% yield (Scheme 4b). These results suggest that the reaction of **1** with Ag_2O proceeds though the formation of **X** as an intermediate, as depicted in Scheme 3a.

Finally, we investigated the synthesis of an NHC–metal complex from **2** using the Ag_2O method. First, we employed the "conventional Ag_2O technique". After treating **2** with Ag_2O in CH_2Cl_2 at room temperature, $AuCl(SMe_2)$ was added to the resulting mixture as a metal precursor. However, this reaction did not yield the desired NHC–Au complex but afforded the formamide derivative **2b** as a major product. This is attributed to the preferential formation of the ring-opening product over the corresponding NHC–Ag complex, as described above. Therefore, we hypothesized that, in the presence of three reactants, such as **2**, Ag_2O, and $AuCl(SMe_2)$, the NHC ligand-transfer reaction between the NHC–Ag complex and Au complex precursor would proceed smoothly to afford the corresponding AuCl(NHC) complex. As expected, this "coexistence Ag_2O technique" afforded the desired chloro(1-methyl-3-phenylbenzimidazol-2-ylidene)gold(I) (**2c**) in a 59% yield (Scheme 5). In a related study, Barnard et al. reported the synthesis of an NHC–Au complex from 1-methyl-3-phenylimidazolium iodide [24]. In addition, Togni and coworkers synthesized chloro(1-phenyl-3-trifluoromethylbenzimidazol-2-ylidene)gold(I) [46].



Scheme 5. Synthesis of NHC–Au(I) complex **2c**.

Complex **2c** was characterized by ^{1}H- and ^{13}C-NMR spectroscopies and elemental analysis. In the ^{13}C-NMR analysis of **2c**, the characteristic carbene carbon resonance at δ 178 ppm was evident. The successful preparation of NHC–Au complex **2c** implies that, once NHC–Ag complex **2a** is generated from the reaction of **2** with Ag_2O, transmetalation (NHC ligand-transfer reaction) proceeds smoothly, taking precedence over the hydrolysis reaction.

4. Materials and Methods

4.1. General Notes

All chemical reagents and solvents were obtained from commercial sources. Super-dehydrated dichloromethane was purchased from the Fujifilm Wako Pure Chemicals Corporation (Tokyo, Japan). Column chromatography was performed with silica gel 60 purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). ^{1}H-NMR spectra were recorded on a JEOL ECA400 (400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR) spectrometer. Chemical shifts were reported downfield from TMS (δ = 0 ppm) for ^{1}H-NMR. For ^{13}C-NMR, chemical shifts were reported on the scale relative to the solvent used as an internal reference. Elemental analyses were performed at Osaka University. Benzimidazolium salts, **1**–**4**, were synthesized according to the literature procedures.

1-Ethyl-3-phenylbenzimidazolium iodide (**1**) [47]: ^{1}H-NMR ($CDCl_3$): δ = 11.04 (s, 1H), 7.92–7.90 (m, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.76–7.62 (m, 6H), 4.95 (q, J = 7.2 Hz, 2H), 1.80 (t, J = 7.2 Hz, 3H); ^{1}H-NMR (DMSO-d_6): δ = 10.16 (s, 1H), 8.21 (d, J = 8.2 Hz, 1H), 7.86–7.68 (m, 8H), 4.61 (q, J = 7.2 Hz, 2H), 1.62 (t, J = 7.2 Hz, 3H); ^{13}C-NMR (DMSO-d_6): δ = 142.2, 133.1, 131.0, 131.0, 130.4, 130.3, 127.4, 126.8, 125.1, 113.9, 113.4, 42.4, 13.9. The NMR spectrum can be found in the Supplementary Materials.

1-Methyl-3-phenylbenzimidazolium iodide (**2**) [48–51]: ^{1}H-NMR (DMSO-d_6): δ = 10.13 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.85–7.71 (m, 8H), 4.17 (s, 3H); ^{13}C-NMR (DMSO-d_6): δ = 143.1, 133.2, 131.9, 130.9, 130.5, 127.4, 126.9, 125.1, 113.9, 113.3, 33.5. One of the aryl group ^{13}C NMR resonances was not observed. Mp.: 198.8–199.0 °C. The NMR spectrum can be found in the Supplementary Materials.

1-Benzyl-3-phenylbenzimidazolium chloride (**3**): ^{1}H-NMR (DMSO-d_6): δ = 10.88 (s, 1H), 8.06–7.67 (m, 11H), 7.43–7.34 (m, 3H), 5.95 (s, 2H). ^{13}C-NMR (DMSO-d_6): δ = 143.0, 133.8, 133.2, 131.3, 130.9, 130.5, 130.4, 128.9, 128.7, 128.6, 127.5, 127.0, 125.3, 114.3, 113.7, 50.1.

Anal. Calc. for $C_{20}H_{17}ClN_2$▪$0.3H_2O$: C, 73.64; H, 5.44; N, 8.59%; Found: C, 73.68; H, 5.20; N, 8.60%. Mp.: 229.9–230.2 °C. The NMR spectrum can be found in the Supplementary Materials.

1-Methyl-3-phenylimidazolium iodide (**4**) [52]: ^{1}H-NMR ($CDCl_3$): δ = 10.33 (s, 1H), 7.78–7.72 (m, 4H), 7.59–7.52 (m, 3H), 4.26 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 135.5, 134.2, 130.5, 130.3, 124.7, 122.1, 120.8, 37.6. The NMR spectrum can be found in the Supplementary Materials.

4.2. General Procedure for Reaction of Benzimidazolium Salt with Ag_2O to Give Ring-Opening Formamide Product

Benzimidazolium salt (0.2 mmol) and Ag_2O (0.1 mmol) were stirred in CH_2Cl_2 (10 mL) at room temperature for 24 h. After passing through a paper filter, the filtrate was dried in a rotary evaporator. The ring-opening formamide product from the residue was purified by column chromatography on silica gel, using AcOEt as an eluent.

N-[2-(Phenylamino)phenyl]-*N*-ethylformamide (**1b**): Mixture of two rotamers (85:15); Major: ^{1}H-NMR ($CDCl_3$): δ = 8.18 (s, 1H), 7.35–6.89 (m, 9H), 5.74 (br, 1H), 3.73 (q, *J* = 7.6 Hz, 2H), 1.15 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR ($CDCl_3$): δ = 163.4, 141.6, 140.9, 130.1, 129.4, 129.2, 128.0, 122.2, 120.3, 119.4, 116.6, 39.5, 12.7. ^{1}H-NMR (DMSO-d_6): δ = 8.04 (s, 1H), 7.28–6.80 (m, 9H), 3.53 (q, *J* = 7.6 Hz, 2H), 0.94 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (DMSO-d_6): δ = 162.5, 143.3, 140.2, 130.3, 130.2, 129.0, 128.6, 121.2, 120.1, 119.4, 117.4, 38.2, 12.4. Minor: ^{1}H-NMR ($CDCl_3$): δ = 8.37 (s, 1H), 7.43–6.88 (m, 9H), 5.82 (br, 1H), 3.71 (q, *J* = 7.6 Hz, 2H), 1.11 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR ($CDCl_3$): δ = 162.2, 143.3, 140.3, 128.5, 127.5, 122.2, 120.6, 120.2, 117.7, 45.4, 14.5. Two of the aryl group ^{13}C NMR resonances were not observed. ^{1}H-NMR (DMSO-d_6): δ = 8.24 (s, 1H), 7.28–6.80 (m, 10H), 3.53 (q, *J* = 7.6 Hz, 2H), 0.98 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (DMSO-d_6): δ = 163.2, 143.2, 140.0, 130.0, 129.0, 128.1, 127.9, 120.4, 120.3, 118.1, 118.0, 43.1, 14.3. Anal. Calc. for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66; Found, C, 75.03; H, 6.68; N, 11.66. Mp.: 119.5–119.8 °C. The NMR spectrum can be found in the Supplementary Materials. In addition, CCDC 2315032 contains the supplementary crystallographic data for **1b**. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/ (accessed on 19 December 2024).

N-[2-(Phenylamino)phenyl]-*N*-methylformamide (**2b**) [40]: Mixture of two rotamers (85:15); Major: ^{1}H-NMR ($CDCl_3$): δ = 8.23 (s, 1H), 7.34–7.22 (m, 5H), 7.12–6.91 (m, 4H), 5.69 (br, 1H), 3.20 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 163.7, 141.8, 140.4, 130.3, 129.3, 129.1, 128.6, 122.1, 120.7, 119.2, 117.2, 32.4. Minor: ^{1}H-NMR ($CDCl_3$): δ = 8.32 (s, 1H), 7.43–7.22 (m, 5H), 7.12–6.91 (m, 4H), 5.87 (br, 1H), 3.33 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 162.3, 143.2, 139.6, 130.4, 129.2, 128.4, 126.7, 122.2, 120.3, 117.8, 37.4. One of the aryl group ^{13}C NMR resonances was not observed. Anal. Calc. for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38; Found, C, 74.41; H, 6.08; N, 12.34. $\upsilon_{C=O}$ 1670 cm^{-1}, $\upsilon_{N\text{-}H}$ 3313 cm^{-1}. Mp.: 159.2–160.4 °C. The NMR spectrum can be found in the Supplementary Materials.

4.3. General Procedure for Reaction of Benzimidazolium Salt with Ag_2O to Give NHC–Ag Complex Product

Benzimidazolium salt (0.2 mmol) and Ag_2O (0.1 mmol) were stirred in CH_2Cl_2 (10 mL) at room temperature. After the reaction, a white precipitate was filtered with suction and washed with CH_2Cl_2 to form the desired silver complex.

Bis(1-ethyl-3-phenylbenzimidazol-2-ylidene) silver(I) iodide (**1a**): ^{1}H-NMR ($CDCl_3$): δ = 7.78–7.76 (m, 2H), 7.57–7.30 (m, 7H), 4.52 (q, *J* = 7.6 Hz, 2H), 1.48 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR ($CDCl_3$): δ = 194.7 ($C_{carbene}$), 138.4, 134.4, 133.4, 129.5, 128.6, 126.1, 123.8, 123.7, 111.8, 111.0, 44.2, 15.6. Anal. Calc. for $C_{30}H_{28}AgIN_4$▪$2.5CH_2Cl_2$▪$0.5H_2O$: C, 43.34; H, 3.81; N, 6.22. Found, C, 43.28; H, 3.46; N, 6.52. The NMR spectrum can be found in the Supplementary Materials.

Bis(1-methyl-3-phenylbenzimidazol-2-ylidene) silver(I) iodide (**2a**): ^{1}H-NMR (DMSO-d_6): δ = 7.88 (d, J = 8.2 Hz, 1H), 7.73–7.70 (m, 2H), 7.66–7.60 (m, 3H), 7.56–7.45 (m, 3H), 4.08 (s, 3H). Due to the poor solubility of **2a**, the measurement of ^{13}C-NMR failed. Anal. Calc. for $C_{28}H_{24}AgIN_4{\blacksquare}3CH_2Cl_2{\blacksquare}H_2O$: C, 40.29; H, 3.49; N, 6.06. Found, C, 40.09; H, 3.28; N, 6.48. The NMR spectrum can be found in the Supplementary Materials.

(1-Benzyl-3-phenylbenzimidazol-2-ylidene) silver(I) iodide (**3a**): ^{1}H-NMR (DMSO-d_6): δ = 7.88–7.30 (m, 14H), 5.78 (s, 2H). ^{13}C-NMR (DMSO-d_6): δ = 137.6, 135.9, 133.9, 133.1, 130.1, 129.4, 128.9, 128.2, 127.6, 126.2, 124.9, 124.7, 112.8, 112.2, 52.2. Carbene ^{13}C NMR resonance was not observed. Anal. Calc. for $C_{20}H_{16}AgClN_2$: C, 56.17; H, 3.77; N, 6.55%; Found: C, 56.14; H, 3.76; N, 6.65%. Mp.: 201.6–201.8 °C. The NMR spectrum can be found in the Supplementary Materials.

(1-Methyl-3-phenylimidazol-2-ylidene) silver(I) iodide (**4a**) [24]: ^{1}H-NMR (DMSO-d_6): δ = 7.84 (d, J = 1.2 Hz, 1H), 7.67 (d, J = 2.0 Hz, 1H), 7.67–6.65 (m, 2H), 7.49–7.48 (m, 3H), 3.86 (s, 3H); ^{13}C-NMR (DMSO-d_6): δ = 179.9 ($C_{carbene}$), 139.6, 129.6, 128.5, 124.0, 123.7, 122.1, 38.5. The NMR spectrum can be found in the Supplementary Materials.

4.4. Procedure for Preparation of NHC–Au Complex 2c

First, **2** (0.1 mmol, 34 mg), Ag_2O (0.05 mmol. 13 mg), and $AuCl(SMe_2)$ (0.11 mmol, 32 mg) were stirred in CH_2Cl_2 (2 mL) at room temperature for 16 h. After passing through a paper filter, the filtrate was dried in a rotary evaporator to give an orange liquid. The NHC–Au complex **2c** from the residue was purified by column chromatography on silica gel (hexane/EtOAc = 8/2) to afford 26 mg (0.59 mml) of **2c** as a yellow solid.

(1-Methyl-3-phenylbenzimidazol-2-ylidene) gold(I) chloride (**2c**): ^{1}H NMR ($CDCl_3$): δ = 7.64–7.54 (m, 6H), 7.50 (dt, J = 1.2 and 8.0 Hz, 1H), 7.42 (dt, J = 1.2 and 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 4.15 (s, 3H); ^{13}C NMR ($CDCl_3$): δ = 178.3 ($C_{carbene}$), 136.6, 134.0, 129.9, (129.9), 129.6, 126.6, 125.0, 124.9, 112.2, 111.2, 35.4; Anal. Calc. for $C_{14}H_{13}AuClN_2$: C, 38.16; H, 2.74; N, 6.36%; Found: C, 37.77; H, 2.86; N, 6.16%. The NMR spectrum can be found in the Supplementary Materials.

5. Conclusions

We investigated the selective formation of ring-opening formamide derivatives and Ag complexes bearing an NHC ligand in the reaction of 1-alkyl-3-phenylbenzimidazolium salts with Ag_2O. The selectivity of the products depended on both the *N*-alkyl substituent on the azolium ring (methyl vs. benzyl) and the azolium skeleton (benzimidazolium vs. imidazolium). Additional investigations of the reactions of various *N*-aryl substituted benzimidazolium salts with a Ag base, as well as the synthesis of various NHC–metal complexes using the "coexistence Ag_2O technique", are underway in our laboratory.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics13010018/s1, Experimental procedure; spectral data for substrates and products; NMR charts for substrates and products; ^{1}H-NMR of the crude reaction mixture after treating **1** with Ag_2O for 10 days; ^{1}H-NMR of the crude reaction mixture after treating **2** with Ag_2O for 24 h; ^{1}H-NMR of the crude reaction mixture after treating **2** with Ag_2O for 3 h.

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