

# Silver and Gold Complexes with Benzimidazolin-2-ylidene Ligands

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75<sup>th</sup> birthday

The dicarbene silver complexes **1a**, **b** of the type [Ag(NHC)<sub>2</sub>][AgBr<sub>2</sub>] (NHC = *N,N'*-dialkylbenzimidazolin-2-ylidene) have been prepared from the parent benzimidazolium salts by reaction with silver oxide. The silver complexes have been used for the transfer of the carbene ligand to gold(I) giving the gold complexes [AuCl(NHC)] **2a**, **b** in good yields. Crystals of **2a**, **b** have been obtained from chloroform/pentane solutions, and X-ray diffraction structure analyses revealed gold(I) atoms coordinated in a linear fashion by an NHC carbon atom and a chloro ligand.

**Key words:** *N*-Heterocyclic Carbene, Silver, Gold

## Introduction

Nowadays an enormous number of stable *N*-heterocyclic carbenes (NHCs) derived from different ring-sized heterocycles have been described [1]. Even larger is the number of transition metal complexes bearing NHC ligands. This trend is owed to the application of carbene complexes in various homogeneous catalytic reactions [2]. Such complexes normally exhibit an enhanced stability against air, heat and moisture compared to complexes derived from common phosphine ligands. The enhanced stability is the result of the superb  $\sigma$ -donor properties of the NHC donor leading to the formation of strong metal carbon bonds. In addition, a fine-tuning of the donor properties is possible by changing of the electronic parameters of the heterocyclic ring by a variation of the backbone of the heterocycle or the *N,N'*-substituents [3].

Most of the reported NHC complexes contain the ubiquitous imidazolin-2-ylidenes as carbene due to the easy and cheap access to this type of ligand [1]. The number of complexes with the benzimidazolin-2-ylidene ligands [1, 4] is, however, comparably small, although several procedures for the preparation of such complexes have been established. They can be obtained by reaction of a coordinatively unsaturated transition metal complex with free carbene ligands [4] or by cleavage of the C=C double bond of diben-

zotetraazafulvalenes [5]. A template-controlled reaction based on the intramolecular cyclization of metal-coordinated  $\beta$ -functionalized phenyl isocyanides has also been described [6]. The most facile route to benzimidazolin-2-ylidene complexes is the *in situ* deprotonation of a benzimidazolium salt in the presence of a suitable metal complex precursor. Suitable transition metal complexes with basic ligands for this procedure are [Pd(OAc)<sub>2</sub>] [7], [Ni(OAc)] [8] or [Ir( $\mu$ -OMe)(cod)]<sub>2</sub> [9]. These methods have been used for the preparation of carbene complexes bearing donor-functionalized [10] or pincer-type benzimidazolin-2-ylidene ligands [11]. In addition to these methods, Wang and Lin described the transfer of the benzimidazolin-2-ylidene ligand from the silver complex to gold(I) or palladium(II) [12]. Today, this carbene transfer reaction constitutes a standard procedure for the preparation of various NHC complexes without the need to isolate the free carbene ligand [13].

Recent years have seen a resurgence of interest in homogeneous reactions catalyzed by gold complexes [14], and in particular gold complexes bearing NHC ligands [15] played an important role. The preparation of silver(I) and gold(I) complexes bearing *N,N'*-dimethyl- and *N,N'*-diethyl-substituted benzimidazolin-2-ylidene ligands has been described [12, 16]. In our search for gold NHC complexes with superior solubility and different electronic properties

we prepared the derivatives with *N,N'*-di-*n*-propyl and *N,N'*-di-*n*-butyl substituents **2a** and **2b** and determined their molecular structures by X-ray diffraction.

## Results and Discussion

### Preparation of the silver(I) complexes

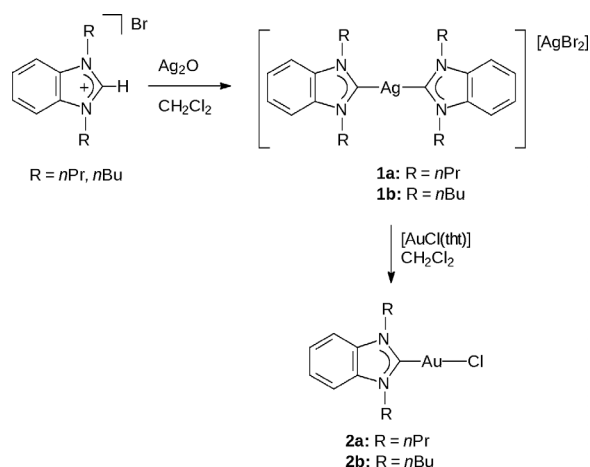
In analogy to the synthesis of silver NHC complexes described by Wang and Lin [12], the dicarbene silver complexes **1a**, **b** (Scheme 1) were prepared in good yields by reaction of the parent *N,N'*-dialkyl-substituted benzimidazolium salts [7, 17] with silver oxide in dichloromethane. The synthesis of silver complex **1b** with the *N,N'*-dibutylbenzimidazolin-2-ylidene ligand has already been described [18]. We repeated the synthesis by a slightly modified route to record the  $^{13}\text{C}$  NMR spectrum.

The characteristic downfield signal for the NCHN proton found in the  $^1\text{H}$  NMR spectra of the parent benzimidazolium salts [7, 18] around  $\delta \approx 11$  ppm is missing in the  $^1\text{H}$  NMR spectra of the silver complexes **1a**, **b**. The  $^{13}\text{C}$  NMR spectra of the dicarbene silver complexes reveal a resonance at  $\delta = 189.4$  ppm for the carbene carbon atoms of both compounds. This value is in good agreement with the carbene carbon resonance found for other silver complexes with benzimidazolin-2-ylidene ligands ( $\delta \approx 190$  ppm) [10a, 12, 13]. Mass spectra of the two complexes indicate that in both cases two carbene ligands are coordinated to one silver atom.

### Preparation of the gold(I) complexes

The silver complexes **1a**, **b** were used as carbene transfer reagents [12, 13] for the preparation of the gold complexes **2a**, **b** (Scheme 1). Treatment of **1a**, **b** with two equivalents of  $[\text{AuCl}(\text{tht})]$  (tht = tetrahydrothiophene) [19] gave the gold(I) complexes **2a**, **b** as colorless solids in good yields of about 90%.

The  $^{13}\text{C}$  NMR spectra exhibit signals at  $\delta = 178.3$  ppm (**2a**) and  $\delta = 177.4$  ppm (**2b**) for the carbene carbon atom which fall in the range observed previously for the C2 carbon atom of benzimidazolin-2-ylidene ligands coordinated to gold(I) ( $\delta = 175$ – $182$  ppm) [20]. Carbene transfer from silver(I) to gold(I) caused a high-field shift of the resonance for the carbene carbon atom of  $\Delta\delta \approx 12$  ppm compared to the parent silver complexes **1a**, **b** ( $\delta = 189.4$  ppm). The NMR resonances of the aromatic carbon atoms are not affected by the change of the metal center at the carbene carbon atom. The EI mass spectra of the



Scheme 1. Synthesis of complexes **1a**, **b** and **2a**, **b**.

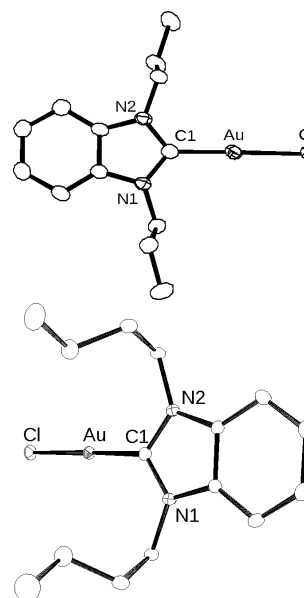


Fig. 1. Molecular structure of one of the crystallographically independent molecules in crystalline **2a** and molecular structure of **2b**. Hydrogen atoms are omitted for clarity; displacement ellipsoids are at 50% probability level.

gold complexes exhibit the peaks for the molecular ion (**2a**) $^+$ ,  $m/z = 434$ ; (**2b**) $^+$ ,  $m/z = 462$ ) as well as the peaks for the fragments [**2a** – Cl] $^+$  ( $m/z = 399$ ) and [**2b** – Cl] $^+$  ( $m/z = 427$ ) with the correct isotope pattern.

Crystals of **2a**, **b** suitable for X-ray diffraction studies have been obtained by slow diffusion of pentane into saturated chloroform solutions of the complexes **2a**, **b**, respectively. The asymmetric unit of **2a** contains two nearly identical independent molecules. Only one

Table 1. Selected bond lengths (Å) and angles (deg) for **2a** and **2b** with estimated standard deviations in parentheses.

	<b>2a</b>		<b>2b</b>
	Molecule A	Molecule B	
Distance			
Au–C <sub>carbene</sub>	1.969(6)	1.978(6)	1.982(3)
Au–Cl	2.3121(13)	2.2890(14)	2.2992(7)
Angle			
C <sub>carbene</sub> –Au–Cl	177.8(2)	178.4(2)	179.09(8)
N–C <sub>carbene</sub> –N	105.8(5)	107.3(5)	106.6(2)

of these molecules is depicted in Fig. 1 (top) together with the molecular structure of **2b** (bottom). Selected bond lengths and angles for **2a**, **b** are listed in Table 1.

Both molecular structures exhibit an almost linear coordination geometry at the gold atoms. The Au–C<sub>carbene</sub> bond lengths in **2a** (1.969(6) and 1.978(6) Å) and **2b** (1.982(3) Å) fall in the range observed previously for similar gold(I) carbene complexes with benzimidazolin-2-ylidene ligands [16, 20]. The same holds for the Au–Cl bond lengths (**2a** 2.3121(13) and 2.2890(14) Å, **2b** 2.2992(7) Å) [16, 20]. The C–Au–Cl bond angles (**2a** 177.8(2) and 178.4(2)°; **2b** 179.09(8)°) are close to linearity as expected for complexes with two-coordinated *d*<sup>10</sup> metal centers. The N–C–N angles at the carbene carbon atom in **2a** (105.8(5) and 107.3(5)°) and in **2b** (106.6(2)°) are in the range observed earlier for related transition metal complexes with benzimidazolin-2-ylidene ligands [7–12] and, as expected, they are larger than those observed in free benzimidazolin-2-ylidenes (≈ 104°) [1a].

No aurophilic interactions [21] have been observed for **2a** where intermolecular Au···Au distances are longer than 3.5 Å. Contrary to the situation found in **2a**, a short intermolecular Au–Au distance of 3.1566(4) Å has been observed for **2b**.

In conclusion, we have prepared silver dicarbene complexes which react with [AuCl(tht)] under carbene transfer to give the new gold(I) complexes **2a**, **b** in good yield. The molecular structures of **2a**, **b** exhibit no unusual features with the exception that aurophilic Au···Au interactions have been found for **2b** but not for **2a**. Further studies concerning the Au<sup>I</sup>→Au<sup>III</sup> oxidation in these gold(I) NHC complexes are in progress.

## Experimental Section

*N,N'*-Dipropyl- [8a], *N,N'*-dibutylbenzimidazolium bromide [17] and [AuCl(tht)] [19] were prepared according to described procedures. NMR spectra were recorded using Bruker Avance I 400 spectrometers. Mass spectra were obtained with MicroTof (Bruker Daltonics, Bremen) or Varian

MAT 212 spectrometers. Elemental analyses were obtained with a Vario EL III CHNS Elemental Analyzer at the Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster.

### General procedure for the synthesis of [bis-(*N,N'*-dialkylbenzimidazolin-2-ylidene)silver(I)] [dibromoargentate] (**1a**, **b**)

Samples of 0.6 mmol of an *N,N'*-dialkylbenzimidazolium bromide and 0.093 g (0.4 mmol) of silver oxide were suspended in dichloromethane (60 mL). The reaction mixture was stirred at ambient temperature for 12 h under exclusion of light. Then the reaction mixture was filtered through Celite, and the solvent was removed *in vacuo*. The residue was dissolved in dichloromethane (5 mL), and this solution was added dropwise to diethyl ether (200 mL). A colorless precipitate formed which was collected by filtration and dried *in vacuo*.

#### [Bis-(*N,N'*-dipropylbenzimidazolin-2-ylidene)silver(I)] [dibromoargentate] (**1a**)

Yield: 0.194 g (0.248 mmol, 83%). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>): δ = 7.49–7.46 (m, 4 H, Ar-H), 7.40–7.37 (m, 4 H, Ar-H), 4.39 (t, <sup>3</sup>J = 7.2 Hz, 8 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.92–1.85 (m, 8 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.97 (t, <sup>3</sup>J = 7.2 Hz, 12 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 189.4 (NCN), 133.8, 123.9, 111.5 (Ar-C), 51.0 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 23.7 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 11.5 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). – MS (MALDI): *m/z* = 513, 511 [M–AgBr<sub>2</sub>]<sup>+</sup>. – C<sub>26</sub>H<sub>36</sub>N<sub>4</sub>Ag<sub>2</sub>Br<sub>2</sub> (*M* = 780.1): calcd. C 40.03, H 4.65, N 7.18; found C 39.88, H 4.49, N 7.02.

#### [Bis-(*N,N'*-dibutylbenzimidazolin-2-ylidene)silver(I)] [dibromoargentate] (**1b**)

Yield: 0.216 g (0.258 mmol, 86%). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>): δ = 7.48–7.46 (m, 4 H, Ar-H), 7.40–7.37 (m, 4 H, Ar-H), 4.41 (t, <sup>3</sup>J = 7.2 Hz, 8 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.92–1.84 (m, 8 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.44–1.35 (m, 8 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.95 (t, <sup>3</sup>J = 7.2 Hz, 12 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 189.4 (NCN), 133.7, 123.9, 111.5 (Ar-C), 49.3 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 32.1 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 20.1 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.5 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). – MS (MALDI): *m/z* = 569, 567 [M–AgBr<sub>2</sub>]<sup>+</sup>. – C<sub>30</sub>H<sub>44</sub>N<sub>4</sub>Ag<sub>2</sub>Br<sub>2</sub> (*M* = 836.3): calcd. C 43.09, H 5.30, N 6.70; found C 42.89, H 5.17, N 6.56.

### General procedure for the synthesis of [(*N,N'*-dialkylbenzimidazolin-2-ylidene)gold(I) chloride] (**2a**, **b**)

A sample of 0.2 mmol of one of the silver dicarbene complexes **1a**, **b** and 0.128 g (0.4 mmol) of [AuCl(tht)] were

dissolved in dichloromethane (40 mL). The reaction mixture was stirred at ambient temperature under immediate formation of insoluble silver bromide. After 12 h the reaction mixture was filtered through Celite, and the solvent was removed *in vacuo*. The colorless residue was dissolved in dichloromethane (3 mL), and this solution was added dropwise to *n*-hexane (100 mL) causing formation of a colorless precipitate of the gold complexes. The precipitate was isolated by filtration and dried *in vacuo*. Crystals of **2a** and **2b** suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-pentane into saturated dichloromethane solutions of the gold complexes.

*[(N,N'-Dipropylbenzimidazolin-2-ylidene)gold(I) chloride] (2a)*

Yield: 0.153 g (0.352 mmol, 88 %). – <sup>1</sup>H NMR (400.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.56–7.50 (m, 2 H, Ar-H), 7.46–7.41 (m, 2 H, Ar-H), 4.44 (t, <sup>3</sup>J = 7.3 Hz, 4 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.99 (sext, <sup>3</sup>J = 7.3 Hz, 4 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.99 (t, <sup>3</sup>J = 7.3 Hz, 6 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). – <sup>13</sup>C NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 178.3 (NCN), 133.5, 124.6, 111.9 (Ar-C), 50.7 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 23.6 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 11.5 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). – MS (EI): *m/z* (%) = 434 (9.2) [M]<sup>+</sup>, 399 (27.1) [M–Cl]<sup>+</sup>. – C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>ClAu (*M* = 434.7): calcd. C 35.91, H 4.17, N 6.44; found C 35.69, H 3.99, N 6.33.

*[(N,N'-Dibutylbenzimidazolin-2-ylidene)gold(I) chloride] (2b)*

Yield: 0.168 g (0.365 mmol, 91 %). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>): δ = 7.48–7.43 (m, 2 H, Ar-H), 7.40–7.34 (m, 2 H, Ar-H), 4.40 (t, <sup>3</sup>J = 7.4 Hz, 4 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.90–1.80 (m, 4 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.41–1.29 (m, 4 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.89 (t, <sup>3</sup>J = 7.4 Hz, 6 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 177.4 (NCN), 132.8, 124.3, 111.4 (Ar-C), 48.5 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 31.8 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 19.8 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.5 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). – MS (EI): *m/z* (%) = 462 (3.3) [M]<sup>+</sup>, 427 (55.3) [M–Cl]<sup>+</sup>. – C<sub>15</sub>H<sub>22</sub>N<sub>4</sub>AuCl (*M* = 462.8): calcd. C 38.92, H 4.79, N 6.05; found C 39.07, H 4.57, N 5.83.

*X-Ray crystal structure determinations*

Suitable crystals of **2a** and **2b** were mounted on a Bruker AXS 2000 CCD diffractometer equipped with a rotating anode using MoK<sub>α</sub> radiation (λ = 0.71073 Å). Diffraction data were measured at 153(1) K in the range 3.8 ≤ 2θ ≤ 57.4° for **2a** and 3.8 ≤ 2θ ≤ 58.2° for **2b**. Structure solution [22] and refinement [23] were achieved with standard Patterson and Fourier techniques and full-matrix least-squares methods, respectively. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure models on calculated positions.

*Selected crystallographic details for 2a:* Formula C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>ClAu, *M* = 434.71, colorless crystal, 0.17 × 0.10 × 0.08 mm<sup>3</sup>, monoclinic, space group *P2<sub>1</sub>/c*, *Z* = 8, *a* = 12.3696(8), *b* = 13.5507(9), *c* = 17.0625(11) Å, β = 90.727(1)°, *V* = 2859.7(3) Å<sup>3</sup>, ρ<sub>calcd</sub> = 2.02 g cm<sup>-3</sup>, μ(MoK<sub>α</sub>) = 10.5 mm<sup>-1</sup>, empirical absorption correction (0.2695 ≤ *T* ≤ 0.4884), 30409 intensities collected (±*h*, ±*k*, ±*l*), 7396 independent (*R*<sub>int</sub> = 0.0506) and 5854 observed intensities [*I* ≥ 2σ(*I*)], 325 refined parameters, residuals for all data *R* = 0.0497, *wR*<sub>2</sub> = 0.0821. One *n*-propyl group is disordered.

*Selected crystallographic details for (2b):* Formula C<sub>15</sub>H<sub>22</sub>N<sub>2</sub>ClAu, *M* = 462.76, colorless crystal, 0.26 × 0.14 × 0.08 mm<sup>3</sup>, orthorhombic, space group *Pbcn*, *Z* = 8, *a* = 21.522(2), *b* = 8.7178(9), *c* = 17.055(2) Å, *V* = 3200.0(6) Å<sup>3</sup>, ρ<sub>calcd</sub> = 1.92 g cm<sup>-3</sup>, μ(MoK<sub>α</sub>) = 9.4 mm<sup>-1</sup>, empirical absorption correction (0.1773 ≤ *T* ≤ 0.4748), 33367 intensities collected (±*h*, ±*k*, ±*l*), 4305 independent (*R*<sub>int</sub> = 0.0324) and 3768 observed intensities [*I* ≥ 2σ(*I*)], 174 refined parameters, residuals for all data *R* = 0.0270, *wR*<sub>2</sub> = 0.0532.

CCDC 747965 (**2a**) and CCDC 747966 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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