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Ekkehardt Hahn, Mareike Jahnke, Tania Pape. Synthesis and Characterization of Gold(I) and Gold(III) Complexes Derived from Benzimidazolin-2-ylidene Ligands. *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2010, 636 (13-14), pp.2309. <10.1002/zaac.201000234>. <hal-00599880>

HAL Id: hal-00599880

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Submitted on 11 Jun 2011

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Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.201000234.R1
Wiley - Manuscript type:	Article
Date Submitted by the Author:	01-Jul-2010
Complete List of Authors:	Hahn, Ekkehardt; Westfaelische Wilhelms-Universitaet Muenster, Institut fuer Anorganische Chemie Jahnke, Mareike; Westfaelische Wilhelms-Universitaet Muenster, Institut fuer Anorganische Chemie Pape, Tania; Westfaelische Wilhelms-Universitaet Muenster, Institut fuer Anorganische Chemie
Keywords:	N-Heterocyclic Carbene, Gold, Oxidation, Molecular Structure



ARTICLE

DOI: 10.1002/zaac.200((will be filled in by the editorial staff))

Synthesis and Characterization of Gold(I) and Gold(III) Complexes Derived from Benzimidazolin-2-ylidene Ligands

Mareike C. Jahnke,^[a] Tania Pape,^[a] and F. Ekkehardt Hahn^{*,[a]}*In memory of Prof. Dr. Herbert Schumann***Keywords:** N-Heterocyclic Carbene; Gold; Oxidation, Molecular Structures

Substitution of the chloro ligand in (*N,N'*-dialkylbenzimidazolin-2-ylidene)gold(I) chlorides (alkyl = methyl, ethyl, propyl, butyl) succeeded by treatment of the gold chloride complexes with lithium bromide in acetone leading to the gold complexes of the type [AuBr(L)] **1–4**. Furthermore, the Au–C_{carbene} bond in complexes **1–4** is inert towards a change of the oxidation state of the metal

center. Complexes **1–4** have been oxidized chemically with elemental bromine leading to the gold(III) carbene complexes of the type [AuBr₃(L)] **5–8**. The molecular structures of the gold(I) complexes **1, 2** and **4** exhibiting a linear topology are presented together with the two molecular structures of the square-planar gold(III) complexes **6** and **8**.

Introduction

Today, N-heterocyclic carbenes (NHCs) are well established ligands in organometallic chemistry [1]. This development rests on the easy access to differently substituted NHCs making them a good alternative to phosphines in the design of new organometallic catalysts [1, 2]. The facile access to NHCs is complemented by the superior σ -donor properties of the carbene ligands compared to the most basic phosphines [3] leading to a remarkable stability of the carbene complexes against air, moisture, heat and oxidizing conditions [1]. Recently, poly-NHC ligands have also been used as building blocks for metallosupramolecular structures. Linear di- [4] as well as tri- or tetra-NHC ligands [5] have been employed for the generation of molecular rectangles or cylindrical molecules which provide cavities suitable as host for guest molecules during a catalytic reaction [6].

A large portion of all known NHC complexes contain a group 9 or 10 transition metal [2a, 7] or ruthenium [8] as the metal center. In addition, many silver carbene complexes [9] have been prepared after Wang and Lin [10] reported in 1998 the very useful carbene transfer reaction utilizing silver NHC complexes. Today, this carbene transfer reaction has developed into a versatile and well established procedure for the synthesis of transition metal NHC complexes [9].

Gold NHC complexes have only recently attracted interest, although the preparation of such complexes has been reported as early as 1998 [10]. This development supports the recent resurgence of interest in gold catalyzed reactions [11] which in turn has initiated a search for new gold NHC complexes [12]. Today gold NHC complexes are used as pharmaceuticals [13], in photophysical devices [14], and as catalysts for selected transformations in homogeneous catalysis [15].

The inertness of the Au–C_{NHC} bond during substitution reactions at linear [AuX(NHC)] complexes was noted by Wang and Lin as early as 1999 [16]. Ligand X in complexes of the type [AuX(NHC)] can be substituted for halides [16, 17], nitrogen- [18, 19] and phosphorous-donors [4a, 19] or even hydroxide [20]. It has also been shown, that the Au–C_{carbene} bond is not affected if gold(I) NHC complexes bearing unsaturated imidazolin-2-ylidene or saturated imidazolidin-2-ylidene ligands are oxidized with bromine [21] or chlorine [22] to give gold(III) complexes of the type [AuX₃(L)] (L = imidazolin-2-ylidene or imidazolidin-2-ylidene; X = Br, Cl).

Most known gold NHC complexes bear the ubiquitous unsaturated imidazolin-2-ylidenes as carbene ligands, while there are only a few examples for gold complexes bearing benzimidazolin-2-ylidenes [10, 16, 20a-b, 23, 24]. We have been interested in the synthesis and properties of transition metal complexes with benzimidazolin-2-ylidenes for several years [25]. Recently we reported the synthesis and some characteristic properties of gold(I) complexes of the type [AuCl(L)] bearing *N,N'*-dipropyl- or *N,N'*-dibutyl-substituted benzimidazolin-2-ylidene ligands [26].

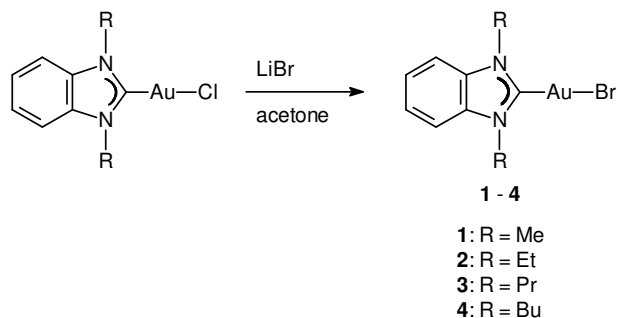
Here we describe the synthesis of gold(I) complexes with *N,N'*-dialkylated benzimidazolin-2-ylidene ligands and their oxidation with elemental bromine to the gold(III) complexes. The molecular structures of linear gold(I) NHC complexes will be discussed together with the molecular structures of square-planar gold(III) complexes.

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Results and Discussion

Gold(I) complexes of the type [AuCl(NHC)] (Scheme 1) were prepared as described [16, 26]. The oxidation of these gold(I) chloride complexes with bromine would lead to a mixture of complexes with bromo and chloro ligands. We therefore performed a halide exchange by treatment of the gold(I) chloride complexes with a tenfold excess of lithium bromide in acetone (Scheme 1) following the procedure described by Nolan et al. [21]. The gold(I) bromide complexes **1–4** were obtained in good yields (86–98%) after purification. Although the synthesis of complexes **1** and **2** has already been reported [16], we have listed them here, since we are providing additional analytical data.



Scheme 1. Synthesis of the gold(I) bromide complexes **1–4** by substitution of the chloro ligand.

The ^{13}C NMR spectra of gold complexes **1–4** exhibit the resonance for the carbene carbon atom in the narrow range of δ 180.5–181.2. Compared to the resonances of the carbene carbon atoms of the parent gold(I) chloride complexes (δ 178–179) [26] a slight downfield shift ($\Delta\delta$ 2–3) was observed upon the halide exchange, while all other resonances in the ^1H and ^{13}C NMR spectra remain nearly unchanged. Crystals of **1**, **2** and **4**, which were suitable for X-ray diffraction studies, have been obtained by slow diffusion of diethyl ether into dichloromethane solutions of the individual complexes. The molecular structures of complexes **1**, **2** and **4** are depicted in Figures 1 and 2 and selected bond parameters are listed in Table 1.

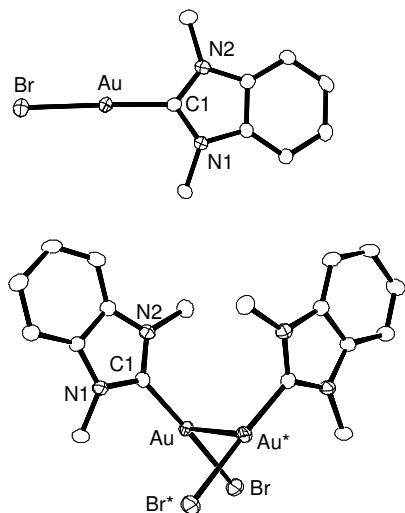


Figure 1. Molecular structure of the gold(I) complexes **1** (top) and drawing of the dinuclear species formed by Au...Au interactions (bottom). Ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

Complexes **1** and **4** reside on general positions in the unit cell, while complex **2** resides on a twofold axis passing through atoms Br, Au and C1. As expected, complexes **1**, **2**, and **4** exhibit a linear coordination geometry. Two molecules of **1** form a dinuclear species via intermolecular Au...Au interactions [27] (Au...Au 3.1179(3) Å, Figure 1, bottom). A similar aurophilic interaction (Au...Au 3.1216(4) Å) was found for **4** but not for **2**.

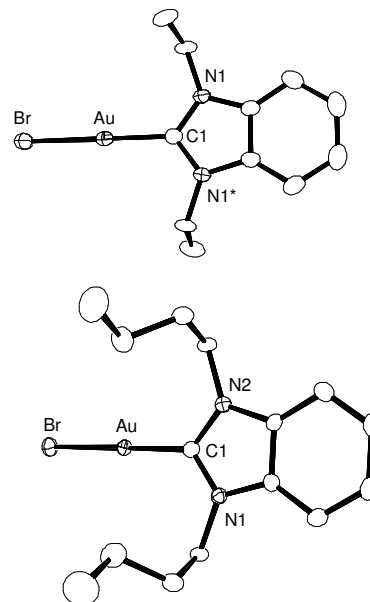


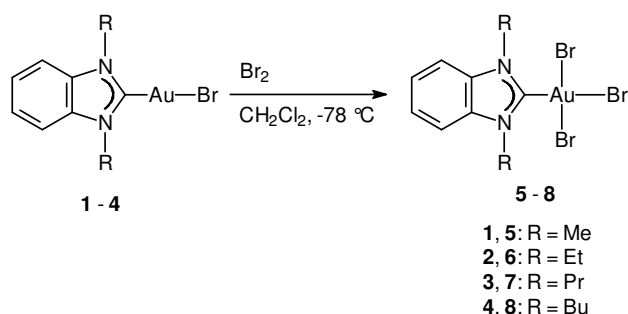
Figure 2. Molecular structures of the gold(I) complexes **2** (top) and **4** (bottom). Atoms Au, Br, and C1 of complex **2** lie on a crystallographic twofold axis. Ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

The Au–C bond lengths in **1** (1.982(3) Å), **2** (1.989(5) Å) and **4** (1.994(3) Å) are nearly identical to the Au–C separations in the parent monocarbene gold(I) chloride complexes of the type [AuCl(L)] with L = benzimidazol-2-ylidene (Au–C 1.969(6)–2.01(3) Å) [16, 23, 26]. These bond distances are also very close in magnitude to the values observed for Au–C bonds found in complexes of the type [AuBr(imidazol-2-ylidene)] (1.975 Å) [21]. The Au–Br bond lengths in **1**, **2**, and **4** also fall in the range previously observed for complexes of the type [AuBr(NHC)] [21]. As expected and previously observed for the parent [AuCl(NHC)] complexes [16, 23, 26], complexes **1**, **2**, and **4** exhibit an almost linear C–Au–Br bond. The N–C_{carbene}–N bond angles in the gold(I) complexes are slightly enlarged in comparison to the free benzimidazol-2-ylidenes (N–C_{carbene}–N \approx 104°) [28].

Table 1. Selected bond lengths (Å) and angles (deg) in complexes **1**, **2**, and **4**.

Compounds	1	2	4
Bond lengths			
Au–C1	1.982(3)	1.989(5)	1.994(3)
Au–Br	2.4083(4)	2.3910(7)	2.4065(4)
N1–C1	1.352(4)	1.345(4)	1.343(4)
N2–C1	1.354(4)	–	1.360(4)
Au...Au*	3.1179(3)	–	3.1216(4)
Bond angles			
C1–Au–Br	177.75(10)	180.0	179.30(9)
N1–C1–N2/	106.3(3)	107.5(4)	106.8(3)
N1–C1–N1*			

Reaction of the gold complexes **1–4** with elemental bromine in dichloromethane gave the orange gold(III) complexes of the type $[\text{AuBr}_3(\text{NHC})]$ **5–8** with NHC = *N,N*-dialkylated benzimidazolin-2-ylidene ligands in good yields (82–89 %, Scheme 2). The ^{13}C NMR spectra of the gold(III) complexes **5–8** show the resonances of the carbene carbon atoms in the range of δ 146.6–149.7. These values represent an upfield shift ($\Delta\delta$ 31–35) of the $\text{C}_{\text{carbene}}$ resonance upon oxidation of gold(I) to gold(III). This strong upfield shift is surprising when compared to the downfield shift of $\Delta\delta$ 1–2 observed for the carbon atoms of the aromatic ring upon the gold(I)→gold(III) oxidation. The resonances observed for $\text{C}_{\text{carbene}}$ in **5–8**, however, resemble the values found for the N–CH–N resonances in the parent benzimidazolium salts (δ 141–144) [25a–c, 25e]. The upfield shift of the $\text{C}_{\text{carbene}}$ resonance upon the gold(I)→gold(III) oxidation has been observed for related $[\text{AuX}_3(\text{NHC})]$ complexes bearing imidazolin-2-ylidene or imidazolidin-2-ylidene ligands [21, 22, 29] and some authors have tried to explain this observation with the higher Lewis acidity of gold(III) in comparison to gold(I) [21].



Scheme 2. Oxidation of the gold(I) complexes **1–4** with bromine to give the gold(III) complexes **5–8**.

Crystals of **6** and **8** suitable for X-ray diffraction studies have been obtained by slow diffusion of diethyl ether into dmf (**6**) or dichloromethane (**8**) solutions, respectively, of the complexes. Complex **8** crystallized as $\text{8}\cdot 0.5\text{CH}_2\text{Cl}_2$ with two formula units in the asymmetric unit. The two molecules of **8** in the asymmetric unit exhibit essentially identical metric parameters. Only one of these molecules is depicted in Figure 2 together with the molecular structure of **6**. Selected bond parameters are summarized in Table 2.

The gold(III) complexes **6** and **8** feature the expected square-planar coordination geometry. The Au–C bonds in **6** (2.003(4) Å) and in the two molecules in $\text{8}\cdot 0.5\text{CH}_2\text{Cl}_2$ (2.009(4) Å) are similar in lengths to the equivalent bond distances observed in gold(III) complexes of the type $[\text{AuBr}_3(\text{NHC})]$ (NHC = imidazolin-2-ylidene or imidazolidin-2-ylidene) (Au–C 2.002(6)–2.052(6) Å) [21, 29]. The Au–C distances are very similar in the gold(I) (**1**, **4**) and the gold(III) complexes **6** and **8**. The oxidation state of the gold atom apparently bears no significance for the Au–C bond lengths. Due to the *trans* effect of the carbene donor the Au–Br_{*trans*} bonds in **6** (2.4465(4) Å) and $\text{8}\cdot 0.5\text{CH}_2\text{Cl}_2$ (2.4521(5) Å and 2.4519(5) Å) are longer than the Au–Br_{*cis*} bonds (2.4107(5)–2.4276(4) Å). These parameters match the equivalent values observed for related gold(III) monocarbene complexes [21, 29]. The Au–Br_{*trans*} bond distances in **6** and $\text{8}\cdot 0.5\text{CH}_2\text{Cl}_2$ are significantly longer

than the Au–Br distances in **1** (2.4083(4) Å), **2** (2.3910(7) Å), and **4** (2.4065(4) Å) (Table 1).

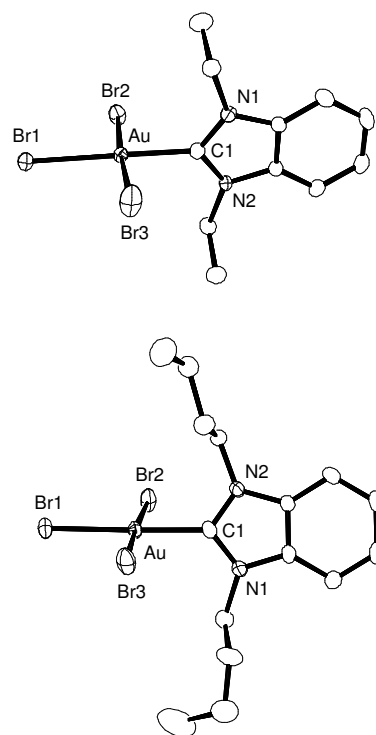


Figure 3. Molecular structures of the gold(III) complexes **6** (top) and **8** in $\text{8}\cdot 0.5\text{CH}_2\text{Cl}_2$ (bottom). Ellipsoids are drawn at the 50 % probability level and hydrogen atoms have been omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (deg) for **6** and $\text{8}\cdot 0.5\text{CH}_2\text{Cl}_2$.

Compounds	6	8 ·0.5CH ₂ Cl ₂	
		molecule A	molecule B
Bond lengths			
Au1–C1/	2.003(4)	2.009(4)	2.009(4)
Au2–C21			
Au1–Br3/	2.4107(5)	2.4256(5)	2.4159(5)
Au2–Br23			
Au1–Br2/	2.4276(4)	2.4109(5)	2.4224(5)
Au2–Br22			
Au1–Br1/	2.4465(4)	2.4521(5)	2.4519(5)
Au2–Br21			
N1–C1/	1.348(4)	1.344(5)	1.339(6)
N21–C21			
N2–C1/	1.346(4)	1.345(5)	1.343(6)
N22–C21			
Bond angles			
C1–Au1–Br1/	179.01(10)	178.62(12)	179.82(14)
C21–Au2–Br21			
Br3–Au1–Br2/	176.43(2)	176.34(2)	175.25(2)
Br23–Au2–Br22			
C1–Au1–Br3/	87.67(10)	88.71(12)	87.51(12)
C21–Au2–Br23			
C1–Au1–Br2/	88.82(10)	87.79(12)	88.01(12)
C21–Au2–Br22			
N1–C1–N2/	108.8(3)	108.7(4)	109.1(4)
N21–C21–N22			

The bond angles in **6** and **8**-0.5CH₂Cl₂ deviate only slightly from the perfect square-planar geometry. The N–C_{carbene}–N bond angles in **6** (108.8(3)°) and **8**-0.5CH₂Cl₂ (108.7(4)° and 109.1(4)°) are slightly larger than the equivalent angles in the parent gold(I) complexes (Table 1).

Conclusions

The synthesis of gold(I) complexes of the type [AuBr(L)] and of gold(III) complexes of the type [AuBr₃(L)] with L = benzimidazolin-2-ylidene ligands has been described. The gold(I) carbene complexes were obtained from [AuCl(L)] complexes by halide exchange with lithium bromide and the gold(III) complexes have been obtained by oxidation of [AuBr(L)] complexes with elemental bromine. The spectroscopic data for the new gold(I) and gold(III) complexes are in good agreement with equivalent data for related complexes bearing the related imidazolin-2-ylidene and imidazolidin-2-ylidene ligands. The same is true for the metric parameters of the linear complexes of the type [AuBr(L)] and the square-planar complexes of the type [AuBr₃(L)].

Experimental Section

All operations were carried out in an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and were freshly distilled prior to use. The (*N,N'*-dialkylbenzimidazolin-2-ylidene)gold(I) chlorides were prepared using published procedures [16, 26]. NMR spectra were recorded on a Bruker Avance I 400 (400 MHz) spectrometer. EI mass spectra were measured on a Varian MAT 212 instrument.

General Procedure for the Synthesis of the (*N,N'*-Dialkylbenzimidazolin-2-ylidene)gold(I) Bromides (1–4): A mixture of the (*N,N'*-dialkylbenzimidazolin-2-ylidene)gold(I) chloride (0.3 mmol) and a tenfold excess of lithium bromide (0.261 g, 3.0 mmol) were dissolved in acetone (10 mL). The reaction mixture was stirred for 24h at ambient temperature. The solvent was removed *in vacuo* and the bright yellow residue was dissolved in dichloromethane (30 mL). The solution was dried with magnesium sulfate, filtrated and the solvent was removed *in vacuo*. The gold(I) complexes were purified by column chromatography (silica gel, dichloromethane), dried *in vacuo* and were finally obtained as a colorless solid.

(*N,N'*-Dimethylbenzimidazolin-2-ylidene)gold(I) Bromide (1): Yield: 0.109 g, 85.7 %. ¹H NMR (400.0 MHz, CD₂Cl₂): δ = 7.52–7.44 (m, 4 H, Ar-H), 4.03 (s, 6 H, NCH₃). ¹³C NMR (100.6 MHz, CD₂Cl₂): δ = 133.1, 124.6, 111.3 (Ar-C), 34.8 (NCH₃). The resonance of the carbene carbon atom was not detected. MS (EI, 20 eV, 190 °C): *m/z* = 424, 422 (M⁺), 343 (M⁺ – Br).

(*N,N'*-Diethylbenzimidazolin-2-ylidene)gold(I) Bromide (2): Yield: 0.124 g, 91.3 %. ¹H NMR (400.0 MHz, CDCl₃): δ = 7.51–7.46 (m, 2 H, Ar-H), 7.45–7.40 (m, 2 H, Ar-H), 4.52 (q, ³J = 7.4 Hz, 4 H, NCH₂CH₃), 1.54 (t, ³J = 7.4 Hz, 6 H, NCH₂CH₃). ¹³C NMR (100.6 MHz, CDCl₃): δ = 180.5 (NCN), 132.7, 124.5, 111.4 (Ar-C), 43.8 (NCH₂CH₃), 15.4 (NCH₂CH₃). MS (EI, 20 eV, 200 °C): *m/z* = 452, 450 (M⁺), 371 (M⁺ – Br).

(*N,N'*-Dipropylbenzimidazolin-2-ylidene)gold(I) Bromide (3): Yield: 0.136 g, 94.9 %. ¹H NMR (400.0 MHz, CD₂Cl₂): δ = 7.50–7.45 (m, 2 H, Ar-H), 7.43–7.39 (m, 2 H, Ar-H), 4.41 (t, ³J = 7.3 Hz,

4 H, NCH₂CH₂CH₃), 1.98 (sext, ³J = 7.3 Hz, 4 H, NCH₂CH₂CH₃), 0.99 (t, ³J = 7.3 Hz, 6 H, NCH₂CH₂CH₃). ¹³C NMR (100.6 MHz, CD₂Cl₂): δ = 181.2 (NCN), 133.1, 124.4, 111.5 (Ar-C), 50.2 (NCH₂CH₂CH₃), 23.3 (NCH₂CH₂CH₃), 11.3 (NCH₂CH₂CH₃). MS (EI, 20 eV, 120 °C): *m/z* = 480, 478 (M⁺), 399 (M⁺ – Br).

(*N,N'*-Dibutylbenzimidazolin-2-ylidene)gold(I) Bromide (4): Yield: 0.149 g, 97.6 %. ¹H NMR (400.0 MHz, CDCl₃): δ = 7.49–7.45 (m, 2 H, Ar-H), 7.43–7.39 (m, 2 H, Ar-H), 4.47 (t, ³J = 7.4 Hz, 4 H, NCH₂CH₂CH₂CH₃), 1.93–1.89 (m, 4 H, NCH₂CH₂CH₂CH₃), 1.45–1.38 (m, 4 H, NCH₂CH₂CH₂CH₃), 0.96 (t, ³J = 7.4 Hz, 6 H, NCH₂CH₂CH₂CH₃). ¹³C NMR (100.6 MHz, CDCl₃): δ = 181.1 (NCN), 133.0, 124.4, 111.5 (Ar-C), 48.6 (NCH₂CH₂CH₂CH₃), 32.0 (NCH₂CH₂CH₂CH₃), 20.0 (NCH₂CH₂CH₂CH₃), 13.7 (NCH₂CH₂CH₂CH₃). MS (EI, 20 eV, 160 °C): *m/z* = 508, 506 (M⁺), 427 (M⁺ – Br).

General Procedure for the Synthesis of the (*N,N'*-Dialkylbenzimidazolin-2-ylidene)gold(III) Tribromides (5–8): A (*N,N'*-dialkylbenzimidazolin-2-ylidene)gold(I) bromide **1–4** (0.25 mmol) was dissolved in dichloromethane (10 mL). This colorless solution was cooled down to –78 °C, and an excess of bromine (0.03 ml, 0.6 mmol) was added to the solution of the gold(I) complex. The orange solution obtained was stirred for 2 h at –78 °C. Then the solvent was removed *in vacuo*. The orange residue was dissolved in dichloromethane (5 mL) and dried again *in vacuo* in order to remove unreacted bromine. This procedure was repeated once more. Finally, the residue was dissolved in dichloromethane (2 mL) and this solution was added to pentane (100 mL). The precipitate obtained was isolated by filtration and dried *in vacuo*.

(*N,N'*-Dimethylbenzimidazolin-2-ylidene)gold(III) Tribromide (5): Yield: 0.125 g, 85.7 %. ¹H NMR (400.0 MHz, CD₂Cl₂): δ = 7.62–7.54 (m, 4 H, Ar-H), 4.11 (s, 6 H, NCH₃). ¹³C NMR (100.6 MHz, CD₂Cl₂): δ = 146.8 (NCN), 134.3, 125.8, 111.6 (Ar-C), 34.8 (NCH₃). MS (EI, 20 eV, 160 °C): *m/z* = 424, 422 (M⁺ – 2Br), 343 (M⁺ – 3Br).

(*N,N'*-Diethylbenzimidazolin-2-ylidene)gold(III) Tribromide (6): Yield: 0.125 g, 82.1 %. ¹H NMR (400.0 MHz, [D₆]DMSO): δ = 7.83–7.76 (m, 2 H, Ar-H), 7.64–7.48 (m, 2 H, Ar-H), 4.49 (q, ³J = 7.4 Hz, 4 H, NCH₂CH₃), 1.46 (t, ³J = 7.4 Hz, 6 H, NCH₂CH₃). ¹³C NMR (100.6 MHz, [D₆]DMSO): δ = 133.4, 125.5, 112.3 (Ar-C), 43.5 (NCH₂CH₃), 15.2 (NCH₂CH₃). The resonance of the carbene carbon signal was not detected. MS (EI, 20 eV, 200 °C): *m/z* = 452, 450 (M⁺ – 2Br), 371 (M⁺ – 3Br).

(*N,N'*-Dipropylbenzimidazolin-2-ylidene)gold(III) Tribromide (7): Yield: 0.143 g, 89.4 %. ¹H NMR (400.0 MHz, [D₆]DMSO): δ = 8.05–7.99 (m, 2 H, Ar-H), 7.59–7.54 (m, 2 H, Ar-H), 4.55 (t, ³J = 7.6 Hz, 4 H, NCH₂CH₂CH₃), 2.03 (sext, ³J = 7.4 Hz, 4 H, NCH₂CH₂CH₃), 0.98 (t, ³J = 7.4 Hz, 6 H, NCH₂CH₂CH₃). ¹³C NMR (100.6 MHz, [D₆]DMSO): δ = 146.6 (NCN), 133.5, 125.4, 112.8 (Ar-C), 49.3 (NCH₂CH₂CH₃), 22.0 (NCH₂CH₂CH₃), 10.8 (NCH₂CH₂CH₃). MS (EI, 20 eV, 230 °C): *m/z* = 640, 638 (M⁺), 480, 478 (M⁺ – 2Br), 399 (M⁺ – 3Br).

(*N,N'*-Dibutylbenzimidazolin-2-ylidene)gold(III) Tribromide (8): Yield: 0.141 g, 84.3 %. ¹H NMR (400.0 MHz, CDCl₃): δ = 7.64–7.48 (m, 4 H, Ar-H), 4.94 (t, ³J = 7.9 Hz, 4 H, NCH₂CH₂CH₂CH₃), 2.06 (quint, ³J = 7.7 Hz, 4 H, NCH₂CH₂CH₂CH₃), 4.48 (sext, ³J = 7.4 Hz, 4 H, NCH₂CH₂CH₂CH₃), 1.00 (t, ³J = 7.3 Hz, 6 H, NCH₂CH₂CH₂CH₃). ¹³C NMR (100.6 MHz, CDCl₃): δ = 149.7 (NCN), 133.9, 125.5, 112.1 (Ar-C), 48.5 (NCH₂CH₂CH₂CH₃), 30.9 (NCH₂CH₂CH₂CH₃),

20.1 (NCH₂CH₂CH₂CH₃), 13.6 (NCH₂CH₂CH₂CH₃). MS (EI, 20 eV, 220 °C): *m/z* = 668, 666 (M⁺), 506 (M⁺ – 2Br), 426 (M⁺ – 3Br).

X-ray Diffraction Studies: Diffraction data for **1**, **2**, **4**, **6**, and **8**·0.5CH₂Cl₂ were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 153(2) K. Data were collected over the full sphere and were corrected for absorption. Data reduction was performed with the Bruker SMART [30] program package. For further crystal data details see Table 3. Structures solutions were found with the SHELXS-97 [31] package using the heavy-atom method and were refined with SHELXL-97 [32] against *F*² using first isotropic and later anisotropic thermal

parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models at calculated positions and their thermal parameters were fixed to 1.3 U_{eqv} of the parent atom. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-778476 (**1**), CCDC-778477 (**2**), CCDC-778478 (**4**), CCDC-778479 (**6**), and CCDC-778480 (**8**·0.5CH₂Cl₂). Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336033; www.ccdc.cam.ac.uk./data/request/cif].

Table 3. Summary of crystallographic data for **1**, **2**, **4**, **6** and **8**·0.5CH₂Cl₂.

parameter	1	2	4	6	8 ·0.5CH ₂ Cl ₂
formula	C ₉ H ₁₀ N ₂ AuBr	C ₁₁ H ₁₄ N ₂ AuBr	C ₁₅ H ₂₂ N ₂ AuBr	C ₁₁ H ₁₄ N ₂ AuBr ₃	C _{15.5} H ₂₃ N ₂ AuBr ₃ Cl
<i>M</i> _r	423.07	451.12	507.22	610.94	709.51
cryst size /mm ³	0.06 × 0.03 × 0.02	0.38 × 0.12 × 0.08	0.26 × 0.09 × 0.05	0.07 × 0.04 × 0.03	0.20 × 0.11 × 0.09
<i>a</i> /Å	20.6153(13)	10.458(2)	21.535(2)	8.7669(7)	16.9406(9)
<i>b</i> /Å	8.6171(6)	16.433(3)	8.8488(9)	10.7992(9)	14.9643(8)
<i>c</i> /Å	13.6594(9)	7.1908(13)	17.179(2)	16.3334(13)	17.3520(10)
α /°	90	90	90	90	90
β /°	124.1020(10)	94.513(3)	90	102.4610(10)	111.8540(10)
γ /°	90	90	90	90	90
<i>V</i> /Å ³	2009.2(2)	1232.0(4)	3273.6(6)	1509.9(2)	4082.7(4)
<i>Z</i>	8	4	8	4	8
space group	<i>C2/c</i>	<i>C2/c</i>	<i>Pbcn</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>D</i> _{calcd} /g·cm ⁻³	2.797	2.432	2.058	2.687	2.309
μ /mm ⁻¹	18.574 (Mo-K _α)	15.154 (Mo-K _α)	11.419 (Mo-K _α)	17.663 (Mo-K _α)	13.209 (Mo-K _α)
2 θ range /°	4.8–63.7	4.6–60.0	3.8–60.0	4.6–61.0	2.6–58.0
data collected	12150	7023	36226	17968	44454
unique data, <i>R</i> _{int}	3278, 0.0292	1798, 0.0422	4781, 0.0480	4603, 0.0358	10858, 0.0386
obsd data [<i>I</i> ≥ 2 σ (<i>I</i>)]	2806	1660	4244	3954	8202
<i>R</i> (all data)	0.0311	0.0256	0.0301	0.0331	0.0485
w <i>R</i> (all data)	0.0463	0.0558	0.0568	0.0535	0.0817
no. of variables	120	71	174	156	410
peak/hole /e ⁻ Å ³	0.935/–1.026	1.915/–1.835	0.603/–2.239	1.231/–1.463	1.822/–2.119

Acknowledgement

Financial support by the Deutsche Forschungsgemeinschaft (SFB 858 and IRTG 1444) is gratefully acknowledged.

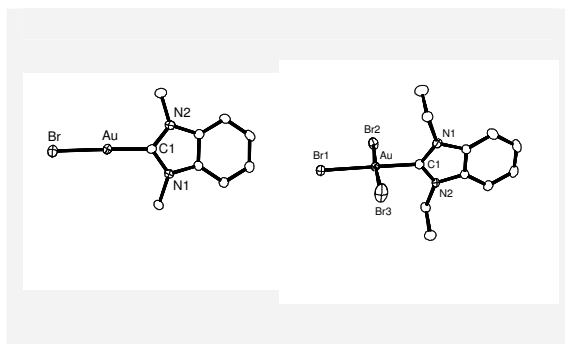
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