

Digold(I) Complexes Derived from 5,5'-Bibenzimidazolin-2-ylidene Ligands

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

The 5,5'-bibenzimidazolium dibromide salts **2** and **3** have been prepared by fourfold *N*-alkylation of 5,5'-bibenzimidazole (**2**: R = Pr; **3**: R = Bu). The diazolum salts were treated with silver oxide, and the *in situ*-formed silver complexes were subsequently reacted with [AuCl(SMe₂)] to give the dinuclear gold complexes **4** and **5**. The molecular structure of complex **5** has been determined by X-ray diffraction showing linearly coordinated gold(I) centers and, most likely due to steric crowding around the metal centers, no aurophilic interactions.

Key words: *N*-Heterocyclic Carbene, Gold, X-Ray Diffraction

Introduction

N-Heterocyclic carbenes (NHCs) are important ligands in transition metal complexes [1–3], and many of these complexes have found application as catalysts in various homogeneous catalytic transformations [4–6]. The NHC complexes normally exhibit a superior stability to moisture and air when compared to complexes bearing tertiary phosphines. This stability can be attributed to the superb σ -donor properties of the NHC ligand, which lead to strong metal-carbon bonds [1–3].

The unsaturated imidazolin-2-ylidenes are the most frequently used NHC ligands, while their benzannulated congeners, the benzimidazolin-2-ylidenes, have attracted less attention. Nevertheless, a number of procedures for the preparation of NHC complexes bearing benzimidazolin-2-ylidene ligands have been described. Such complexes are accessible by ligand substitution at a transition metal complex using a stable benzimidazolin-2-ylidene [7, 8]. Alternatively, coordinatively unsaturated transition metal complexes react with dibenzotetraazafulvalenes with cleavage of the olefinic C=C double bond and coordination of the free NHC to the transition metal [9, 10]. Both methods suffer from the limited availability of stable

benzimidazolin-2-ylidenes and the high reactivity of dibenzotetraazafulvalenes [9].

In analogy to the preparation of imidazolin-2-ylidene complexes, the most facile routes leading to complexes with benzimidazolin-2-ylidene ligands are the *in situ* deprotonation of benzimidazolium salts followed by coordination of the formed free NHC and the carbene transfer reaction using silver carbene complexes [3]. The *in situ* deprotonation is based on the reaction of a benzimidazolium salt with a suitable metal precursor possessing basic ligands such as Pd(OAc)₂ [11, 12] or [Ir(μ -OMe)(cod)]₂ [13, 14]. The carbene transfer reaction is based on the transfer of the carbene ligand from an NHC complex with a labile M–C_{NHC} bond, in particular silver NHC complexes, to another transition metal [15, 16].

In addition to these methods, the template-controlled intramolecular cyclization of coordinated β -functionalized phenyl isocyanides [17–20] as well as the oxidative addition of a C–X bond (X = Cl, I) of neutral benzimidazole derivatives to low-valent metal precursors [21–24] have recently been developed. The latter two methods lead to complexes bearing “protic” NHCs with an NH,NH- or NH,NR-substituted benzimidazolin-2-ylidene heterocycle which are useful precursors for multiple applications [25, 26].

Gold NHC complexes are routinely obtained by ligand transfer reactions [16], and these compounds have found application as catalysts for homogeneous transformations [27] and as metallodrugs [28, 29]. The successful application of gold NHC complexes in homogeneous catalysis is based on the rather inert Au–C_{NHC} bond in complexes of the type [Au(NHC)L]ⁿ⁺, which stays intact, while the ligand L can easily be substituted for halides [30] or nitrogen donors [31].

In our search for new gold NHC complexes with superior solubility and interesting electronic properties, we prepared rigid benzobiscarbene ligands and their digold complexes [32]. Here we describe the synthesis of digold complexes with the more flexible 5,5'-bibenzimidazolin-2-ylidene ligands.

Results and Discussion

Preparation of the bibenzimidazolium dibromide salts **2** and **3**

Compound 5,5'-bibenzimidazole (**1**) was obtained as described in the literature [33]. The *N,N',N'',N'''*-tetraalkyl-5,5'-bibenzimidazolium dibromide salts **2** (R = *n*-propyl) and **3** (R = *n*-butyl) were prepared by tetraalkylation of 5,5'-bibenzimidazole with *n*-propyl bromide or *n*-butyl bromide, respectively, following a previously described procedure [33]. Reaction of 5,5'-bibenzimidazole (**1**) with sodium hydride in toluene, followed by treatment of the reaction mixture with an alkyl bromide and finally ad-

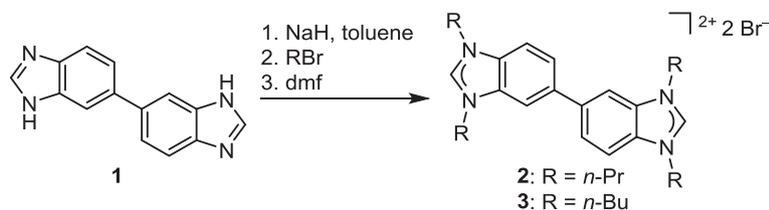
dition of DMF (Scheme 1) gave the *N,N',N'',N'''*-tetraalkyl-5,5'-bibenzimidazolium bromides **2** and **3** (R = *n*-butyl) in good yields.

NMR spectroscopic parameters for the bibenzimidazolium salt **3** were identical to those previously reported [33]. The bibenzimidazolium salt **2** was characterized by NMR spectroscopy and mass spectrometry. The ¹H NMR spectrum exhibits the resonance of the acidic NCHN protons at δ = 10.13 ppm, which is a value in good agreement with those reported for related bibenzimidazolium dibromides (δ = 10.05–10.29 ppm) [33]. The resonance for the NCHN carbon atoms was detected in the ¹³C{¹H} NMR spectrum at δ = 142.9 ppm and thus also falls in the expected range.

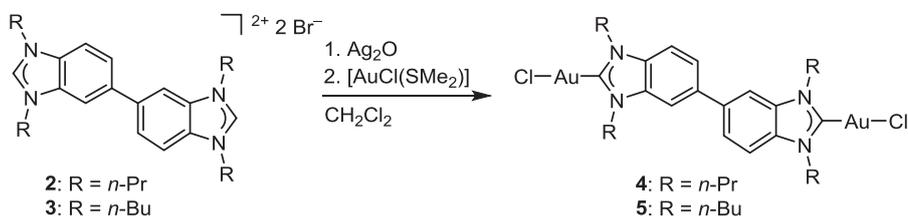
Preparation of the digold(I) complexes **4** and **5**

The synthesis of digold complexes of the 5,5'-bibenzimidazolin-2-ylidene ligands derived from **2** and **3** proceeded similarly to the preparation of digold complexes obtained from benzobis(imidazolium) salts [32] or gold complexes from benzimidazolium salts [30, 34, 35]. Treatment of the 5,5'-bibenzimidazolium salts **2** and **3** with silver oxide gave the silver NHC complexes, which were not isolated. The subsequent reaction of the silver complexes with [AuCl(SMe₂)] afforded the digold complexes **4** and **5** *via* transmetalation as colorless solids (Scheme 2) in good yields of 83–91%.

The formation of the digold complexes **4** and **5** could be inferred from NMR data of the com-



Scheme 1. Synthesis of the bibenzimidazolium dibromide salts **2** and **3**.



Scheme 2. Synthesis of the digold complexes **4** and **5**.

plexes as well as from their mass spectra. The ^1H NMR spectra of both complexes featured no resonance for the NCHN protons ($\delta \approx 10$ ppm) anymore, while the remainder of the resonances of the original bibenzimidazolium salts are still observed but slightly shifted. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of both complexes exhibit a resonance for the carbene carbon atoms at $\delta = 179.9$ ppm for **4** and at $\delta = 179.0$ ppm for **5**. Both resonances fall in the range previously observed for C_{NHC} carbon atoms in complexes of the type $[\text{AuCl}(\text{NHC})]$ (NHC = benzimidazolin-2-ylidene) ($\delta = 175.8$ – 178.8 ppm) [34, 35].

Crystals of composition $\mathbf{5} \cdot 2\text{CHCl}_3$ suitable for an X-ray diffraction study were obtained by slow diffusion of pentane into a saturated solution of **5** in chloroform. Complex **5** resides on a twofold axis bisecting the $\text{C6}–\text{C6}^*$ bond. The asymmetric unit contains $1/2$ formula unit. The chlorine atoms of the chloroform molecule in the asymmetric unit and the two terminal atoms of one butyl substituent are disordered.

The molecular structure of **5** is depicted in Fig. 1. The Au–C1 bond length measures $1.961(9)$ Å, and this value compares well with Au– C_{NHC} bond lengths found for benzimidazolin-2-ylidene gold(I) complexes [34, 35]. The Cl–Au–C1 bond angle ($177.5(2)^\circ$) is almost linear as expected. In addition, the N1–C1–N2 bond angle in **5** ($105.8(7)^\circ$) falls in the typical range for N1– C_{NHC} –N2 bond angles observed in related gold NHC complexes [32, 35]. The two central phenylene rings are not oriented in a coplanar fash-

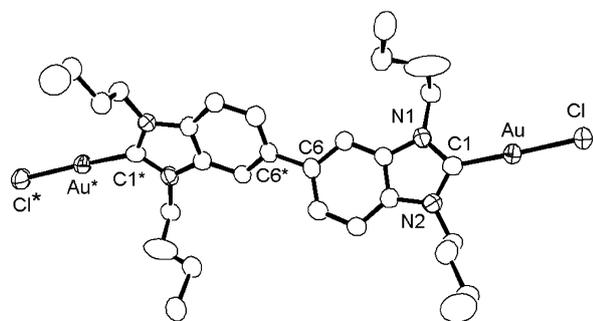


Fig. 1. Molecular structure of **5** in crystals of $\mathbf{5} \cdot 2\text{CHCl}_3$. Hydrogen atoms and solvent molecules are omitted for clarity, and only one set of positions for the disordered *N*-butyl substituent is shown. Displacement ellipsoids are at the 50% probability level. Starred atoms are related to those without an asterisk by a crystallographic twofold axis. Selected bond lengths (Å) and angles (deg): Au–C1 $1.961(9)$, Au–Cl $2.285(2)$, N1–C1 $1.363(11)$, N2–C1 $1.364(11)$; Cl–Au–C1 $177.5(2)$, N1–C1–N2 $105.8(7)$.

ion with a dihedral angle $\text{C7}–\text{C6}–\text{C6}^*–\text{C7}^*$ of 142.5° . This arrangement prevents any electronic communication between the two gold–NHC units.

Specific intra- or intermolecular bonding between gold(I) centers have been observed multiple times and have been described over the last 20 years in detail by the pioneering studies of the Schmidbauer group [36]. This type of "aurophilic interaction" can feature binding energies which occasionally may exceed those of strong hydrogen bonds. Complexes of the type $[\text{AuCl}(\text{NHC})]$ have also been shown to aggregate *via* aurophilic bonding into dimers or chains if the *N*-substituents are sufficiently small, but with larger *N*-substituents only mononuclear complexes have been observed. This latter situation appears to be valid for complex **5**, where no aurophilic interactions have been observed in the crystal structure.

Conclusion

Benzimidazolium salts can be easily prepared by fourfold *N*-alkylation of 5,5'-bibenzimidazole. These salts react with silver oxide followed by carbene transfer to $[\text{AuCl}(\text{SMe}_2)]$ to give digold NHC complexes. The $[5,5'-(N,N',N'',N''')\text{-tetraalkyl}]\text{bibenzimidazolin-2-ylidene}]\text{digold(I)}$ complexes feature a non-coplanar bridging biphenyl moiety, which prevents electronic communication between the metal centers. Aurophilic interactions are not observed for the digold complexes.

Experimental Section

The gold precursor $[\text{AuCl}(\text{SMe}_2)]$ was purchased by Sigma-Aldrich, while 5,5'-bibenzimidazole (**1**) and 5,5'-(*N,N',N'',N'''*-tetrabutyl)bibenzimidazolium dibromide (**3**) were prepared according to described procedures [33]. NMR spectra were recorded using Bruker Avance I 400 or Bruker Avance II 200 spectrometers. Mass spectra were obtained with MicroTof (Bruker Daltonics, Bremen) or Varian MAT 212 spectrometers.

Synthesis of 5,5'-(*N,N',N'',N'''*-tetrapropyl)bibenzimidazolium dibromide (**2**)

Compound **2** was prepared similar to the published procedure for the synthesis of the tetrabutylated analog **3** [33]. Compound **2** was prepared from 1.172 g of **1** (5.0 mmol), 0.180 g of NaH (4.5 mmol, 60% in mineral oil) and 1.229 g of *n*-propyl bromide (0.91 mL, 10 mmol) in a solvent mixture of toluene (40 mL) and dimethylformamide (30 mL). Yield: 2.65 g (4.7 mmol, 94%) of a beige powder. ^1H NMR

(400.1 MHz, [D₆]DMSO): δ = 10.13 (s, 2 H, NCHN), 8.77 (s br, 2 H, Ar-H), 8.29 (d, 3J = 8.8 Hz, 2 H, Ar-H), 8.21 (d, 3J = 8.8 Hz, 2 H, Ar-H), 4.67 (t, 3J = 7.1 Hz, 4 H, NCH₂CH₂CH₃), 4.56 (t, 3J = 7.1 Hz, 4 H, NCH₂CH₂CH₃), 2.05–1.93 (m, 8 H, NCH₂CH₂CH₃), 1.00–0.91 (m, 12 H, NCH₂CH₂CH₃) ppm. – ¹³C{¹H} NMR (100.6 MHz, [D₆]DMSO): δ = 142.9 (NCHN), 137.4, 131.9, 130.9, 126.2, 114.3, 112.5 (Ar-C), 48.2 (NCH₂CH₂CH₃), 22.11, 22.06 (NCH₂CH₂CH₃), 10.61, 10.58 (NCH₂CH₂CH₃) ppm. – MS (MALDI): m/z = 405 [M–2Br]⁺.

General synthesis of the [(5,5'-(N,N',N'',N''')-tetraalkyl)-bibenzimidazolin-2-ylidene]digold(I) dichlorides [4 and 5]

One of the bibenzimidazolium dibromides (0.125 mmol) was suspended together with Ag₂O (58 mg, 0.25 mmol) in dichloromethane (20 mL). The reaction mixture was stirred at ambient temperature for 2 h. Then [AuCl(SMe₂)] (74 mg, 0.25 mmol) was added to the reaction mixture, and stirring was continued for another 12 h. The reaction mixture was filtered through Celite, and the solvent was removed *in vacuo*. The resulting colorless powders can be recrystallized from a chloroform/hexane solvent mixture.

[(5,5'-(N,N',N'',N''')-Tetrapropyl)bibenzimidazolin-2-ylidene]digold(I) dichloride [4]

Yield: 87 mg (0.10 mmol, 83%). – ¹H NMR (400.1 MHz, CD₂Cl₂): δ = 7.71–7.66 (m, 4 H, Ar-H), 7.64–7.60 (m, 2 H, Ar-H), 4.60–4.48 (m, 8 H, NCH₂CH₂CH₃), 2.12–2.00 (m, 8 H, NCH₂CH₂CH₃), 1.03–1.00 (m, 12 H, NCH₂CH₂CH₃) ppm. – ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): δ = 179.9 (NCN), 138.2, 134.5, 133.5, 125.2, 112.7, 111.2 (Ar-C), 51.2, 51.1 (NCH₂CH₂CH₃), 24.08, 24.07 (NCH₂CH₂CH₃), 12.1, 12.0 (NCH₂CH₂CH₃) ppm. – MS (EI): m/z = 866 [M]⁺, 634 [M–AuCl]⁺.

[(5,5'-(N,N',N'',N''')-Tetraethyl)bibenzimidazolin-2-ylidene]digold(I) dichloride [5]

Yield: 105 mg (0.11 mmol, 91%). – ¹H NMR (200.1 MHz, CD₂Cl₂): δ = 7.77–7.60 (m, 6 H, Ar-H), 4.69–4.49

(m, 8 H, NCH₂CH₂CH₂CH₃), 2.13–1.91 (m, 8 H, NCH₂CH₂CH₂CH₃), 1.63–1.40 (m, 8 H, NCH₂CH₂CH₂CH₃), 1.08–0.99 (m, 12 H, NCH₂CH₂CH₂CH₃) ppm. – ¹³C{¹H} NMR (50.3 MHz, CD₂Cl₂): δ = 179.0 (NCN), 137.3, 133.6, 132.6, 124.2, 111.8, 110.1 (Ar-C), 48.7, 48.6 (NCH₂CH₂CH₂CH₃), 31.9 (NCH₂CH₂CH₂CH₃), 19.9 (NCH₂CH₂CH₂CH₃), 13.4 (NCH₂CH₂CH₂CH₃) ppm. – MS (EI): m/z = 922 [M]⁺, 689 [M–AuHCl]⁺.

X-Ray structure determination

A suitable crystal of 5 · 2CHCl₃ were mounted on a Bruker AXS 2000 CCD diffractometer equipped with a rotating anode. Diffraction data were collected at 153(2) K using MoK α radiation (λ = 0.71073 Å). Diffraction data were measured in the range $4.2 \leq 2\theta \leq 62.6^\circ$. Structure solution and refinement [37] were achieved with standard Patterson and Fourier techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure model on calculated positions.

Selected crystallographic details for 5 · 2CHCl₃: Empirical formula C₃₂H₄₄N₄Au₂Cl₈, M_r = 1166.28, colorless crystal, $0.10 \times 0.04 \times 0.03$ mm³, monoclinic, space group *C2/c*, Z = 4, a = 24.4179(11), b = 10.9662(5), c = 16.7051(7) Å, β = 116.4840(10)°, V = 4003.7(3) Å³, $\rho_{\text{calcd.}}$ = 1.93 g cm⁻³, μ = 7.9 mm⁻¹, empirical absorption correction ($0.506 \leq T \leq 0.798$), 24 352 intensities collected ($\pm h, \pm k, \pm l$), 6363 independent (R_{int} = 0.0504) and 3862 observed intensities [$I > 2 \sigma(I)$], 218 refined parameters, residuals for all data R = 0.0903, $wR2$ = 0.1674.

CCDC 1017539 contains 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.

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