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

Mareike C. Jahnke, Christian Schulte to Brinke and F. Ekkehardt Hahn
Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 30, D-48149 Münster, Germany
Reprint requests to Prof. Dr. F. E. Hahn. Fax: +49 251 8333108. E-mail: fehahn@uni-muenster.de
Received August 14, 2014

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 diazolium 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-ylidenenes 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 C2–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 \([\text{Au}(\text{NHC})_L]^n\), 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 \(N,N',N''\)-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 addition of DMF (Scheme 1) gave the \(N,N',N''\)-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 \(^1\)H NMR spectrum exhibits the resonance of the acidic NCHN protons at \(\delta = 10.13\) ppm, which is a value in good agreement with those reported for related bibenzimidazolium dibromides (\(\delta = 10.05 – 10.29\) ppm) [33]. The resonance for the NCHN carbon atoms was detected in the \(^{13}\)C\{\(^1\)H\} NMR spectrum at \(\delta = 142.9\) 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′-bibenzimidazol-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 \([\text{AuCl}(\text{SMe}_2)]\) 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-
plexes as well as from their mass spectra. The $^1$H 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 $^{13}$C($^1$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$_{\text{NHC}}$ carbon atoms in complexes of the type [AuCl(NHC)] (NHC = benzimidazol-2-ylidene) ($\delta = 175.8 – 178.8$ ppm) [34, 35].

Crystals of composition 5·2CHCl$_3$ 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 C6–C6$^*$ bond. The asymmetric unit contains $\frac{1}{2}$ 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$_{\text{NHC}}$ bond lengths found for benzimidazol-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$_{\text{NHC}}$–N2 bond angles observed in related gold NHC complexes [32, 35]. The two central phenylene rings are not oriented in a coplanar fashion with a dihedral angle C7–C6–C6$^*$–C7$^*$ of 142.5$^\circ$. 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 Schmidbaur group [36]. This type of "aurophilic interaction" can feature binding energies which occasionally may exceed those of strong hydrogen bonds. Complexes of the type [AuCl(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**

Bibenzimidazolium salts can be easily prepared by fourfold N-alkylation of 5,5′-bibenzimidazole. These salts react with silver oxide followed by carbene transfer to [AuCl(SMe$_2$)] to give digold NHC complexes. The [5,5′-(N,N′,N″,N‴-tetraalkyl)bibenzimidazol-2-ylidene]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 [AuCl(SMe$_2$)] was purchased by Sigma-Aldrich, while 5,5′-bibenzimidazole (1) and 5,5′-(N,N′,N″,N‴-tetraalkyl)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 tetrabutyalted 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. – $^1$H NMR
(400.1 MHz, [D$_6$]DMSO): $\delta = 10.13 \; (s, \; 2 \; H, \; NCHCN), \; 8.77 \; (s \; br, \; 2 \; H, \; Ar-H), \; 8.29 \; (d, \; J = 8.8 \; Hz, \; 2 \; H, \; Ar-H), \; 8.21 \; (d, \; J = 8.8 \; Hz, \; 2 \; H, \; Ar-H), \; 4.67 \; (t, \; J = 7.1 \; Hz, \; 4 \; H, \; NCH$_2$CH$_2$CH$_3$), \; 4.56 \; (t, \; J = 7.1 \; Hz, \; 4 \; H, \; NCH$_2$CH$_2$CH$_3$), \; 2.05–1.93 \; (m, \; 8 \; H, \; NCH$_2$CH$_2$CH$_3$), \; 1.00–0.91 \; (m, \; 12 \; H, \; NCH$_2$CH$_2$CH$_3$) ppm. – $^{13}$C $\{^1$H$\}$ NMR (100.6 MHz, [D$_6$]DMSO): $\delta = 142.9 \; (NCHCN), \; 137.4, \; 131.9, \; 130.9, \; 126.2, \; 114.3, \; 112.5 \; (Ar-C), \; 48.2 \; (NCH$_2$CH$_2$CH$_3$), \; 22.1, \; 22.06 \; (NCH$_2$CH$_2$CH$_3$), \; 10.61, \; 10.58 \; (NCH$_2$CH$_2$CH$_3$) ppm. – MS (MALDI): $m/z = 405 [M–2Br]^+$.

General synthesis of the \(\{5,5^{\prime}-(N,N^\prime,N,N^{\prime\prime},N^{\prime\prime\prime}$-tetraalkyl-bibenzimidazol-2-ylidene)digold(I) dichlorides\) 4 and 5

One of the bibenzimidazolium dibromides (0.125 mmol) was suspended together with Ag$_2$O (58 mg, 0.25 mmol) in dichloromethane (20 mL). The reaction mixture was stirred at ambient temperature for 2 h. Then [AuCl(SMe$_2$)]$_2$ (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.

\(\{5,5^{\prime}-(N,N^\prime,N,N^{\prime\prime},N^{\prime\prime\prime}$-Tetrapropyl-bibenzimidazol-2-ylidene)digold(I) dichlorides\) 4

Yield: 87 mg (0.10 mmol, 83%). 1$^H$ NMR (400.1 MHz, CD$_2$Cl$_2$): $\delta = 7.71–7.66 \; (m, \; 4 \; H, \; Ar-H), \; 7.64–7.60 \; (m, \; 2 \; H, \; Ar-H), \; 4.60–4.48 \; (m, \; 8 \; H, \; NCH$_2$CH$_2$CH$_3$), \; 2.12–2.00 \; (m, \; 8 \; H, \; NCH$_2$CH$_2$CH$_3$), \; 1.03–1.00 \; (m, \; 12 \; H, \; NCH$_2$CH$_2$CH$_3$) ppm. – $^{13}$C $\{^1$H$\}$ NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta = 179.9 \; (NCCN), \; 138.2, \; 134.5, \; 133.5, \; 125.2, \; 112.7, \; 111.2 \; (Ar-C), \; 51.2, \; 51.1 \; (NCH$_2$CH$_2$CH$_3$), \; 24.08, \; 24.07 \; (NCH$_2$CH$_2$CH$_3$), \; 12.1, \; 12.0 \; (NCH$_2$CH$_2$CH$_3$) ppm. – MS (EI): $m/z = 866 [M]^+$, 634 [M–AuCl]$^+$.

\(\{5,5^{\prime}-(N,N^\prime,N,N^{\prime\prime},N^{\prime\prime\prime}$-Tetraethyl-bibenzimidazol-2-ylidene)digold(I) dichlorides\) 5

Yield: 105 mg (0.11 mmol, 91%). 1$^H$ NMR (200.1 MHz, CD$_2$Cl$_2$): $\delta = 7.77–7.60 \; (m, \; 6 \; H, \; Ar-H), \; 4.69–4.49 \; (m, \; 8 \; H, \; NCH$_2$CH$_2$CH$_2$CH$_3$), \; 2.13–1.91 \; (m, \; 8 \; H, \; NCH$_2$CH$_2$CH$_2$CH$_3$), \; 1.63–1.40 \; (m, \; 8 \; H, \; NCH$_2$CH$_2$CH$_2$CH$_3$), \; 1.08–0.99 \; (m, \; 12 \; H, \; NCH$_2$CH$_2$CH$_2$CH$_3$) ppm. – $^{13}$C $\{^1$H$\}$ NMR (50.3 MHz, CD$_2$Cl$_2$): $\delta = 179.0 \; (NCN), \; 137.3, \; 133.6, \; 132.6, \; 124.2, \; 111.8, \; 110.1 \; (Ar-C), \; 48.7, \; 48.6 \; (NCH$_2$CH$_2$CH$_2$CH$_3$), \; 31.9 \; (NCH$_2$CH$_2$CH$_2$CH$_3$), \; 19.9 \; (NCH$_2$CH$_2$CH$_2$CH$_3$), \; 13.4 \; (NCH$_2$CH$_2$CH$_2$CH$_3$) ppm. – MS (EI): $m/z = 922 [M]^+$, 689 [M–AuHCl]$^+$.

X-Ray structure determination

A suitable crystal of 5-2CHCl$_3$ was mounted on a Bruker AXS 2000 CCD diffractometer equipped with a rotating anode. Diffraction data were collected at 153(2) K using MoK$\alpha$ radiation ($\lambda = 0.71073 \; \text{ Å}$). 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 5-2CHCl$_3$:

Empirical formula C$_{36}$H$_{44}$N$_4$Au$_2$Cl$_6$, $M_r = 1166.28$, colorless crystal, 0.10 $\times$ 0.04 $\times$ 0.03 mm$^3$, monoclinic, space group $C2/c$, $Z = 4$, $a = 24.4179(11)$, $b = 10.9662(5)$, $c = 16.7051(7) \; \text{Å}$, $\beta = 116.4840(10)^\circ$, $V = 4003.7(3) \; \text{Å}^3$, $\rho_{calc} = 1.93 \; \text{g cm}^{-3}$, $\mu = 7.9 \; \text{mm}^{-1}$, empirical absorption correction (0.506 $\leq 2\theta \leq 0.798$), 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.

Acknowledgement

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

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