Au(I) and Au(III) complexes of a sterically bulky benzimidazole-derived *N*-heterocyclic carbene

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Abstract

The reaction of [AuCl(SMe$_2$)] with in situ generated [AgCl(^{i}Pr$_2$-bimy)] (^{i}Pr$_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene), which in turn was obtained by the reaction of Ag$_2$O with 1,3-diisopropylbenzimidazolium bromide (^{i}Pr$_2$-bimyH$^+$Br$^-$, **A**), afforded the mono-carbene Au(I) complex [AuCl(^{i}Pr$_2$-bimy)] (**1**). Subsequent reaction of **1** and the ligand precursor ^{i}Pr$_2$-bimyH$^+$BF$_4^-$, (**B**) in acetone in the presence of K$_2$CO$_3$ yielded the bis(carbene) complex [Au(^{i}Pr$_2$-bimy)$_2$]BF$_4$ (**2**) as a white powder in 80% yield. The oxidative addition of elemental iodine to complex **2** gave the bis(carbene) Au(III) complex *trans*-[AuI$_2$(^{i}Pr$_2$-bimy)$_2$]BF$_4$ (**3**) as an orange-red powder in 92% yield. All complexes **1**–**3** have been fully characterized by multinuclear NMR spectroscopies, ESI mass spectrometry, elemental analysis, and X-ray single crystal diffraction. Complexes **1** and **2** adopt a linear geometry around metal centers as expected for d^{10} metals. The geometry around the Au(III) metal center in **3** is essentially square-planar with two carbene ligands in *trans*-position to each other. Complex **3** shows absorption and photoluminescence properties owing to a ligand to metal charge transfer.
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Keywords: *N*-Heterocyclic carbene; Gold; Oxidative addition; Luminescent properties

1. Introduction

N-Heterocyclic carbenes (NHCs), initially considered curiosities, are nowadays common and powerful ligands in organometallic chemistry and catalysis owing to the ease of their preparation and their unique properties [1]. Especially group 10 transition metal complexes of NHCs have received great attention, while those of coinage metals remain relatively less explored, with the exception of Ag–NHC complexes [2]. The latter have been developed into very useful carbene transfer agents allowing for the preparation of various transition metal NHC complexes, which are otherwise only difficult to access. Au NHC complexes, although known for decades [3], have only recently made greater impact on NHC chemistry due to the potential application in medicinal chemistry and the resurgence of Au based catalysis. For example, Baker [4] and Çetin-

kaya [5] have reported antimitochondrial and antimicrobial activity exhibited by cationic bis(carbene) Au(I) complexes. Catalytic applications of Au(I) [6] and Au(III) [7] NHC complexes have also been reported recently in pioneering works of Herrmann and Nolan. Furthermore, Au complexes can also exhibit interesting photophysical properties, which have been attributed to aurophilic interactions [8,9]. In general, NHC chemistry is dominated by imidazole and imidazoline based carbene ligands. We have been interested in complexes of the relatively less explored benzimidazolin-2-ylidenes, which exhibit intermediate properties of the aforementioned two types [10]. In that respect, we have recently reported Pd(II) and Pt(II) complexes of the sterically bulky 1,3-diisopropylbenzimidazolin-2-ylidene ligand, which exhibited unusual anagostic (or preagostic) C–H···M interactions [11]. As a continuation, we herein report on the synthesis and structural characterization of an isoelectronic Au(III) complex of this unique ligand, which was obtained through oxidative addition to a suitable Au(I) carbene species. The absorption and

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emission properties of the first Au(III) benzimidazolin-2-ylidene complex is described as well.

2. Results and discussion

2.1. Synthesis and characterization

The synthesis of the desired Au(III)-bis(carbene) complex *trans*-[AuI$_2$(^{i}Pr$_2$-bimy)$_2$]BF$_4$ (**3**) has been achieved in 3 steps via oxidative addition of elemental iodine to suitable Au(I) precursors, and the reaction pathway is summarized in Scheme 1. Several protocols are available for the synthesis of Au(I) carbene complexes, namely cleavage of electron rich olefins [12], reactions of azolium salts or free NHCs with Au(I) precursors [13], carbene transfer from group 6 carbonyl complexes [14], and protonation or alkylation of gold azolyl complexes [15]. A facile and more general method involving a transmetallation reaction of Ag(I) carbene species with Au(I) precursors has been developed by Lin et al. [16]. Accordingly, we have obtained the complex [AuCl(^{i}Pr$_2$-bimy)] (**1**) [17] by treating [AuCl(SMe$_2$)] with in situ generated Ag–NHC species, which in turn have been prepared by mixing ligand precursor **A** and Ag$_2$O in a 2:1 molar ratio. An instant precipitation of AgBr indicated the successful carbene transfer onto Au(I) to form complex **1**.

Its ^{1}H and ^{13}C NMR spectra show the expected signals with the carbenoid carbon resonancing at 175.8 ppm. The signal for the isopropyl C–H proton (5.48 ppm), which has been reported to be involved in anagostic (or preagostic) C–H···M interactions to d^8 metal centers such as Pd(II) and Pt(II) [11] exhibits only a small downfield shift of $\Delta\delta = 0.27$ ppm compared to the salt precursor **A**. Since a large downfield shift (e.g. $\Delta\delta > 0.6$ ppm) is indicative of such C–H···M interactions, it is apparent that the d^{10} metal center in **1** does not favor these. Complex **1** has been further characterized by X-ray diffraction on single crystals

obtained by slow evaporation of a concentrated mixed toluene/CH$_2$Cl$_2$ solution. The molecular structure of **1** depicted in Fig. 1 confirms its identity as a linear monocarbene Au(I) complex with common Au–C$_{carbene}$ and Au–Cl bond lengths of 1.973(7) and 2.3053(15) Å, respectively. No aurophilic interactions have been observed in the solid state structure of complex **1**, which is most likely due to the steric bulk of the carbene ligand. Selected crystallographic data are summarized in Table 1.

Complex **1** was subsequently transformed into the bis(carbene) complex [Au(^{i}Pr$_2$-bimy)$_2$]BF$_4$ (**2**) by reacting with benzimidazolium salt ^{i}Pr$_2$-bimyH$^+$BF$_4^-$ (**B**) in the presence of K$_2$CO$_3$ in acetone. To obtain good yields of the bis(carbene) complex it is crucial that azolium salts with non-coordinating anions (here BF$_4^-$) are employed in this halo-substitution reaction [18]. When salt precursor **A** is used instead, a mixture of neutral mono- and cationic bis(carbene) Au(I) complexes was obtained. Complex **2** was isolated as a white powder in 80% yield. It is soluble in polar organic solvents and insoluble in non-polar solvents like diethyl ether, hexane and toluene. Noteworthy, this reaction can be conveniently carried out under aerobic conditions and no decomposition to metallic gold was observed. Compared to the ^{1}H NMR signals of **1**, those of complex **2** remain largely unaffected upon coordination of an additional NHC ligand. The septet for the isopropyl C–H protons is observed at 5.34 ppm, which is slightly shifted upfield by 0.14 ppm compared to **1**. This upfield-shift is indicative of a free rotation of the *N*-isopropyl group in the absence of C–H···M interactions. The resonance for the carbenoid carbon atoms at 187.4 ppm, on the other hand, is significantly downfield shifted by $\Delta\delta = 11.6$ ppm. This observation is in line with a lower Lewis acidity of the metal center due to the coordination of an additional strong σ-donor [19]. The formation of complex **2** was further supported by positive mode ESI mass spectrometry, which shows a base peak at
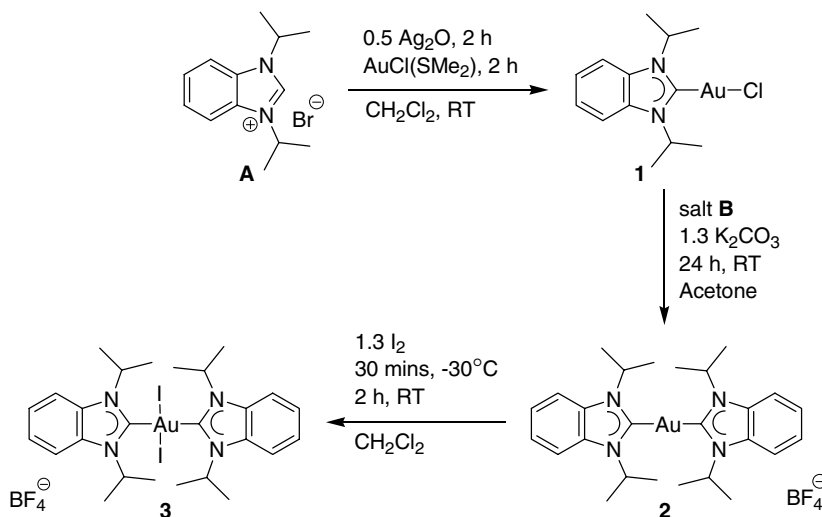
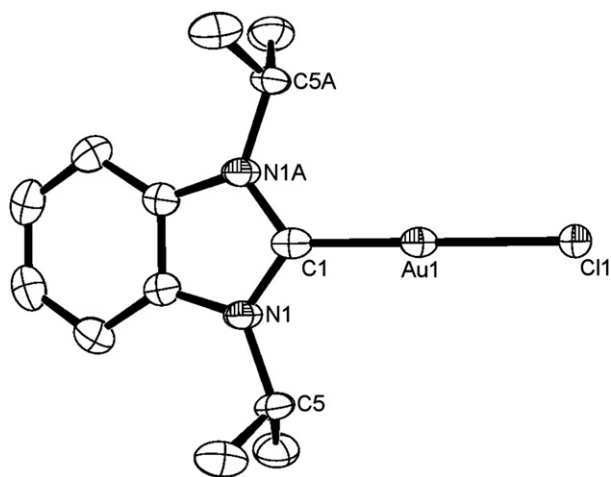Scheme 1. Synthesis of carbene complexes **1**–**3**.

Fig. 1. Molecular structure of **1** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au1–C1 1.973(7), Au1–Cl1 2.3053(15), C1–N1 1.357(6); C1–Au1–Cl1 179.77(19), N1–C1–N1A 106.9(6).

$m/z = 601$ corresponding to the $[M-BF_4]^+$ fragment. Single crystals of complex **2** were obtained by slow evaporation of a concentrated THF solution and subjected to X-ray diffraction analysis. The essentially linear structure (C1–Au1–C14: 175.62(14)°) of the complex-cation in **2** is depicted in Fig. 2. One of the isopropyl C–H protons is oriented away from the metal center corroborating the absence of any C–H···M interactions, which has also been found by ^{1}H NMR spectroscopy in solution. The Au1-C1

and Au1-C14 distances of 2.018 and 2.028 Å, respectively, are in good agreement with the previously reported values [18]. The two carbene planes are twisted out of coplanarity by an angle of ~26°. Similar to complex **1**, neither aurophilic nor notable π–π interactions were observed in the solid state structure of complex of **2**.

Generation of Au(III) carbene complexes by direct reaction of free carbenes with $AuCl_4$ have been reported to give mainly metallic gold along with the decomposition of the carbene and formation of Au(I) carbene complexes as a minor product [7]. This observation is not surprising since the Au(III) cation is known for its strong oxidizing nature [20]. A more convenient and milder pathway is the oxidative addition to more readily available Au(I)–NHC complexes [7,21]. Thus, the electron rich bis(carbene) complex **2** was treated with slight excess of elemental iodine to give trans-$[AuI_2(^iPr_2\text{-bimy})_2]BF_4$ (**3**) as a reddish-orange powder in 92% yield. This oxidative addition reaction is straightforward and does not require the exclusion of air and moisture. To our best knowledge, complex **3** is the first Au(III) benzimidazolin-2-ylidene complex. It is soluble in most common organic solvents with the exception of non-polar ones such as hexane, diethyl ether and toluene. The ^{1}H NMR spectrum shows a septet at 5.06 ppm for the C–H isopropyl protons, which is even more highfield than the corresponding signal in the salt precursor **A**, therefore ruling out any C–H···M anagostic interactions. Noteworthy, the latter have been commonly observed in isostructural and isoelectronic complexes of group 10

Table 1
Selected X-ray crystallographic data for complexes **1–3**

|	**1**	**2**	**3 · CH$_2$Cl$_2$**
Formula	$C_{13}H_{18}ClN_2Au$	$C_{26}H_{36}BF_4N_4Au$	$C_{27}H_{38}BCl_2F_4I_2N_4Au$
Formula weight	434.71	688.36	1027.09
Color, habit	Colorless, block	Colorless, block	Orange, rod
Crystal size (mm)	$0.32 \times 0.15 \times 0.10$	$0.30 \times 0.26 \times 0.10$	$0.40 \times 0.12 \times 0.10$
Temperature (K)	223(2)	223(2)	293(2)
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$Pnma$	$C2/c$	$Pmc2(1)$
a (Å)	12.2392(7)	39.7851(18)	10.7779(5)
b (Å)	10.5451(6)	12.6663(6)	11.2233(5)
c (Å)	10.8541(6)	11.6182(5)	15.3725(7)
α (°)	90	90	90
β (°)	90	104.6900(10)	90
γ (°)	90	90	90
V (Å^3)	1400.87(14)	5663.4(4)	1859.51(15)
Z	4	8	2
D_c (g cm^{-3})	2.061	1.615	1.834
Radiation used	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	10.673	5.242	5.802
θ range (°)	2.51–27.50	1.69–27.50	1.81–27.45
Unique data	9410	19,857	12,536
Maximum, minimum transmission	0.4150, 0.1314	0.6222, 0.3023	0.5946, 0.2049
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0275$, $wR_2 = 0.0741$	$R_1 = 0.0304$, $wR_2 = 0.0729$	$R_1 = 0.0343$, $wR_2 = 0.0872$
R indices (all data)	$R_1 = 0.0298$, $wR_2 = 0.0751$	$R_1 = 0.0402$, $wR_2 = 0.0764$	$R_1 = 0.0364$, $wR_2 = 0.0882$
Goodness-of-fit on F^2	1.130	1.045	1.081
Peak/hole (e Å^{-3})	2.198/−0.564	1.930/−0.649	2.109/−0.722
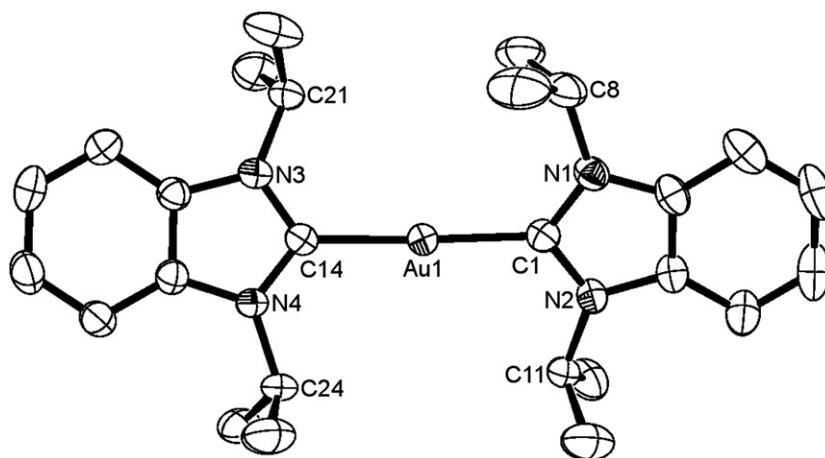
Fig. 2. Molecular structure of **2** showing 50% probability ellipsoids. Hydrogen atoms and BF_4^- anion have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au1–C1 2.018(4), Au1–C14 2.028(4), C1–N1 1.351(5), C1–N2 1.356(5), C14–N3 1.349(5), C14–N4 1.352(2); C1–Au1–C14 175.62(14), N1–C1–N2 106.5(3), N3–C14–N4 107.2(3).

metals bearing the same ligand [11]. The absence of such interactions in **3** is apparently due to its higher Lewis acidic metal center (higher oxidation state), which is also corroborated by an upfield shift of the signal for the carbenoid carbon to 150.9 ppm {176.5 ppm for Pt(II) and 180.0 ppm for Pd(II)}. However, this chemical shift is within the reported range for Au(III) carbene complexes of imidazolium analogues [7,21]. The formation of complex **3** is further supported by its ESI mass spectrum, which shows an isotopic envelope at $m/z = 849$ corresponding to the $[M-BF_4]^+$ fragment. The identity of **3** has finally been unambiguously confirmed by X-ray diffraction analysis on single crystals obtained from a concentrated dichloromethane solution. The molecular structure of the complex cation in **3** is shown in Fig. 3.

The coordination geometry around the four-coordinated Au(III) center is as expected square-planar with the two carbene ligands trans to each other. The C1–Au1–C8 and I1–Au1–I2 bonds are almost linear with angles 178.7(4)° and 179.37(3)°, respectively. The two carbene ring planes are exactly perpendicular to the AuC_2I_2 coordination plane with a dihedral angle of 90° due to symmetry. The Au–$C_{carbene}$ bonds of 2.048(9) Å, and the Au–I bonds of 2.6106(7) and 2.6017(6) Å, respectively, are non-exceptional and in good agreement with those found in other Au(III)–NHC complexes [7,21]. As observed for complex **1** and **2**, neither aurophilic nor π–π-interactions are observed.

2.2. Electronic properties

The electronic absorption spectra of complexes **1**–**3** were measured in dichloromethane solution. All complexes exhibit an intense absorption band at 230–290 nm, which is very similar in position and band shape to their carbene precursor **A**. Therefore, these bands can be assigned to π–π*
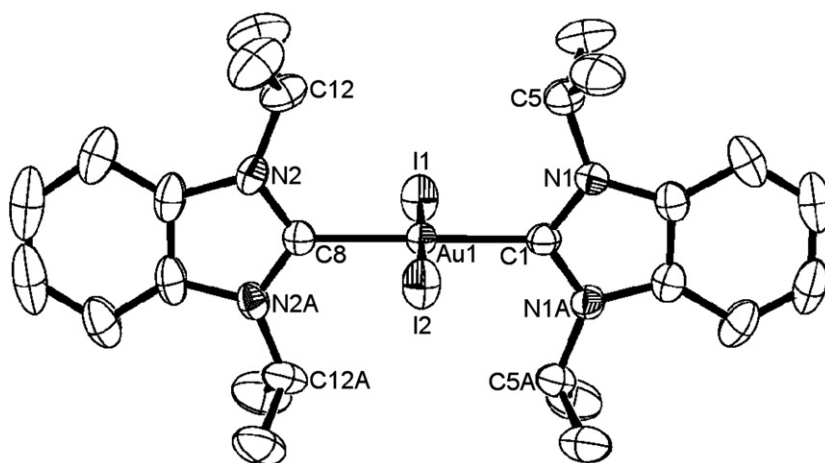

Fig. 3. Molecular structure of **3** · CH_2Cl_2 showing 50% probability ellipsoids. Hydrogen atoms, BF_4^- anion, and the solvent molecule have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au1–C1 2.048(9), Au1–C8 2.048(9), Au1–I1 2.6106(7), Au1–I2 2.6017(6), C1–N1 1.326(8), C8–N2 1.336(7); C1–Au1–C8 178.7(4), I1–Au1–I2 179.37(3), C1–Au1–I2 90.5(3), C1–Au1–I1 90.2(3), C8–Au1–I1 91.2(2), C8–Au1–I2 88.2(2).

aromatic intraligand transitions. In addition, complex **3** shows a slightly broad band at 365 nm with a molar absorption coefficient amounting to $\varepsilon = 9528 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ (Fig. 4). This band possibly arises from LMCT of the iodo ligands to the Au(III) metal center.

Furthermore, the three complexes were investigated for their luminescence properties. The solid state emission spectra were recorded at room temperature. Complex **1** and **2** do not show any luminescent behavior as there are no Au···Au interactions. Complex **3**, on the other hand, exhibits some luminescent properties even at room temperature despite the absence of any aurophilic interactions. Upon excitation at 390 nm, it displays an emission band at 580 nm (Fig. 5). Again this band is most likely to arise from charge transfer of the iodo ligands to the Au(III) metal center (LMCT). This is expected since iodo ligands are readily oxidizable and Au(III) is a strong oxidizing agent, which in turn satisfies the criteria for a charge transfer to occur [22].
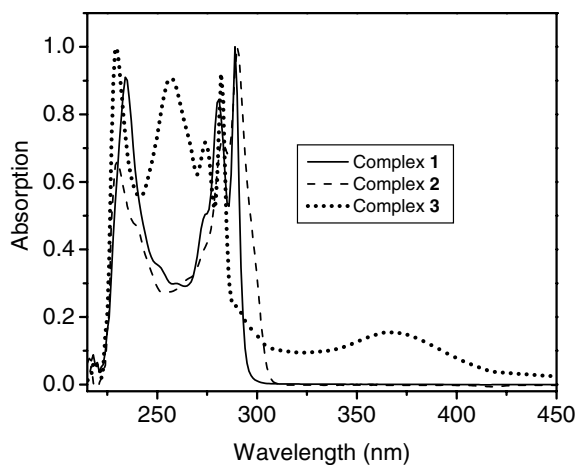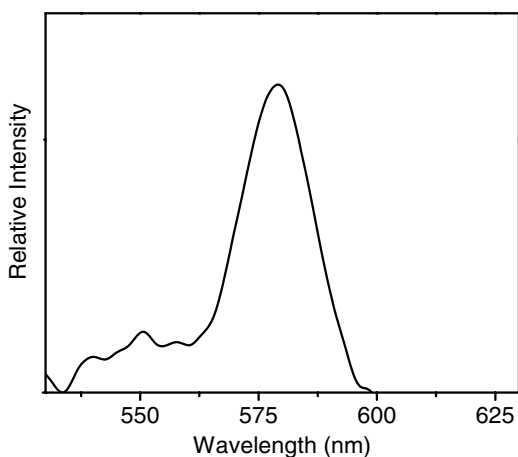

Fig. 4. Normalized absorption spectra of complexes **1**–**3**.

Fig. 5. Emission spectrum of complex **3** excited at 390 nm, measured in the solid state at room temperature.

3. Conclusion

In conclusion, we presented the synthesis and characterization of the novel bis(benzimidazolin-2-ylidene) Au(III) complex *trans*-[AuI$_2$(^{i}Pr$_2$-bimy)$_2$]BF$_4$ (**3**). The complex was synthesized straightforwardly in a 2-step approach through oxidative addition of I$_2$ to the bis(carbene) Au(I) complex [Au(^{i}Pr$_2$-bimy)$_2$]BF$_4$ (**2**), which in turn was obtained by halo substitution of neutral monocarbene Au(I) complex [AuCl(^{i}Pr$_2$-bimy)$_2$] (**1**). Complex **3** shows electronic absorption and photoluminescence behavior owing to a charge transfer from the iodo ligands to the Au(III) metal center. Research in our laboratory is underway to explore the catalytic activities of all these complexes.

4. Experimental

4.1. General considerations

If not indicated otherwise, all manipulations were carried out without taking precautions to exclude air and moisture. All solvents were used as received. All chemicals were used as received without further purification if not mentioned. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker ACF 300 and Bruker AMX 500 spectrometer. Mass spectra were measured using a Finnigan MAT LCQ (ESI) spectrometer. Elemental analyses were done on a Perkin–Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore. Salt **A** was synthesized by the reported procedure [11]. Salt **B** was obtained from **A** by anion exchange with excess NaBF$_4$ in acetone.

4.2. Synthesis of chloro(1,3-diisopropylbenzimidazolin-2-ylidene)gold(I) (1)

A mixture of Ag$_2$O (58 mg, 0.25 mmol) and 1,3-diisopropylbenzimidazolium bromide **A** (142 mg, 0.5 mmol) was stirred in CH$_2$Cl$_2$ (20 ml) at ambient temperature for 4 h. The reaction mixture was subsequently filtered over celite into a solution of [AuCl(SMe$_2$)] (147 mg, 0.5 mmol) in CH$_2$Cl$_2$ (10 ml), upon which AgBr precipitated instantly. The resulting suspension was stirred for an additional 2 h. Filtration over celite followed by removal of the solvent from the filtrate gave the product as a white powder (165 mg, 0.38 mmol, 76%). Crystals were obtained by slow evaporation of a concentrated mixed toluene/CH$_2$Cl$_2$ solution. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.63$ (dd, 2H, Ar–H), 7.35 (dd, 2H, Ar–H), 5.48 (m, ^3J(H,H) = 6.9 Hz, 2H, NCH(CH$_3$)$_2$), 1.71 (dd, ^3J(H,H) = 6.9 Hz, 12 H, CH$_3$). ^{13}C {^{1}H} NMR (76.90 MHz, CDCl$_3$): $\delta = 175.8$ (s, NCHN), 132.2 123.7, 112.9 (s, Ar–C), 54.2 (s, NCH(CH$_3$)$_2$), 21.5 (s, CH$_3$). Anal. Calc. for C$_{13}$H$_{18}$AuClN$_2$: C, 35.92; H, 4.17; N, 6.44. Found: C, 36.05; H, 4.20; N, 6.31%. MS (ESI): $m/z = 833$ [2M−Cl]$^+$.

4.3. Synthesis of bis(1,3-diisopropylbenzimidazolin-2-ylidene)gold(I) tetrafluoroborate (2)

K_2CO_3 (18 mg, 0.13 mmol) was added to the mixture of 1,3-diisopropylbenzimidazolium tetraflouroborate (**B**) (30 mg, 0.1 mmol) and complex **1** (44 mg, 0.1 mmol) in acetone (30 ml). The mixture was stirred for 24 h. The solvent was removed under reduced pressure. Dichloromethane (10 ml) was added to the residue and filtered through celite. The solvent was removed under reduced pressure and the residue was washed with ethylacetate (5 ml). A white powder (55 mg, 0.08 mmol, 80%) was obtained upon drying. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.74$ (dd, 4H, Ar–H), 7.45 (dd, 4H, Ar–H), 5.39 (m, ^3J(H,H) = 7.05 Hz, 4H, NCH(CH$_3$)$_2$), 1.85 (dd, ^3J(H,H) = 7.05 Hz, 24H, CH$_3$). ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): $\delta = 187.4$ (s, NCHN), 133.2, 125.4, 113.8 (s, Ar–C), 54.4 (s, NCH(CH$_3$)$_2$), 23.1 (s, CH$_3$). ^{19}F{^{1}H} NMR (282.37 MHz, CD$_2$Cl$_2$): -78.01 (s, ^{10}BF$_4$), -78.06 (s, ^{11}BF$_4$). Anal. Calc. for C$_{26}$H$_{36}$BF$_4$N$_4$Au: C, 45.37; H, 5.27; N, 8.14. Found: C 45.64, H 5.52, N 8.15%. MS (ESI): $m/z = 601.3$ [M−BF$_4$]$^+$.

4.4. Synthesis of trans-diiodo-bis(1,3-diisopropylbenzimidazolin-2-ylidene)gold(III) tetrafluoroborate (3)

Complex **2** (75 mg, 0.109 mmol) was dissolved in dichloromethane (20 ml) and elemental Iodine (35 mg, 0.140 mmol) dissolved in dichloromethane (10 ml) was added dropwise at $-30\,°C$. The resultant solution was stirred for 30 min at $-30\,°C$ and for another 2 h at ambient temperature. Evaporation of the solvent under reduced pressure yielded a reddish orange solid, which was washed several times with ether. The reddish orange solid was then dissolved in dichloromethane and filtered through celite. The solvent was removed under vacuum to get a red powder (94 mg, 0.099 mmol, 92%). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.89$ (dd, 4H, Ar–H), 7.54 (dd, 4H, Ar–H), 5.06 (m, ^3J(H,H) = 6.9 Hz, 4H, NCH(CH$_3$)$_2$), 1.91 (dd, ^3J(H,H) = 6.9 Hz, 24H, CH$_3$). ^{13}C{^{1}H} NMR (125.77 MHz, CD$_2$Cl$_2$): $\delta = 150.9$ (s, NCHN), 139.9, 125.3, 114.7 (s, Ar–C), 55.6 (s, NCH(CH$_3$)$_2$), 20.4 (s, CH$_3$). ^{19}F{^{1}H} NMR (282.37 MHz, CD$_2$Cl$_2$): -77.68 (s, ^{10}BF$_4$), -77.73 (s, ^{11}BF$_4$). Anal. Calc. for C$_{26}$H$_{36}$AuBF$_4$I$_2 \cdot 2$CH$_2$Cl$_2$: C, 30.24; H, 3.63; N, 5.04. Found: C, 30.55; H, 3.77; N, 5.05%. MS (ESI): $m/z = 854.9$ [M−BF$_4$]$^+$.

4.5. X-ray diffraction studies

Diffraction data for complexes **1**–**3** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 223(2) (**1**, **2**), and 293(2) K (**3**) using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected over the full sphere and were corrected for absorption. Structure solutions were found by the Patterson method. Structure refinement was carried out by full-matrix least-squares on F^2 using SHELXL-97 [23] with first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms. A summary of the most important crystallographic data is given in Table 1.

Acknowledgement

Appendix A. Supplementary material

CCDC 664618, 664619, and 664620 contain the supplementary crystallographic data for **1**, **2**, and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.11.003.

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