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Reactivity of cationic gold(I) carbene complexes toward oxidative addition of bromine

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ABSTRACT

We have synthesized and characterized several cationic complexes of gold(I) of the type $[Au(L_1)(L_2)]^+$ (L_1 = NHC, L_2 = DIC; L_1 = NHC, L_2 = NAC; L_1 = NAC, L_2 = DIC; L_1 = L_2 = NAC; NHC = N-heterocyclic carbene; NAC = N-acyclic carbene, DIC = 2,6-dimethylphenylisocyanide).

The complexes of type $[Au(NHC)(DIC)]^+$ react with a slight excess of Br_2 yielding the corresponding gold(III) species $[Au(NHC)(DIC)Br_2]^+$. The latter decompose with a rate that is modulated by the nature of the ancillary ligands. The oxidative addition of Br_2 to complexes of the type $[Au(NHC)(NAC)]^+$ and $[Au(L)(NAC)]^+$ (L = DIC, NAC) has been also carried out and the ensuing gold(III) derivatives $[Au(NHC)(NAC)Br_2]^+$ and $[Au(NAC)_2Br_2]^+$ are stable in solution whereas the complex $[Au(NAC)(DIC)Br_2]^+$ decomposes. Finally, on the basis of kinetic studies we have proposed propose a mechanism involving a fast pre-equilibrium forming an adduct containing the starting complex and Br_2 followed by a slow rearrangement of the latter to yield the final gold(III) derivatives.

1. Introduction

The increasing number of scientific reports in the last decade testifies the important role played by Au(I) and Au(III) complexes in biochemical and chemical research. The anti-arthritis and chemotherapeutic properties of the Au(I) derivatives bearing strong σ-donor ligands such as phophines and carbenes or those of the Au(III) complexes with poly-amines or poly-pyridines are well documented [1], whereas the catalytic activity of the gold complexes was studied mostly in the case of the Au(I) compounds [2]. As matter of fact, the Au(III) derivatives were investigated only for some selected species such as $[AuCl_4]^-$ [3], $[AuRCl_3]^-$, $[AuR_2Cl_2]^-$, $[AuRCl_2]_2$, $[AuR_2Cl]$ [4], or complexes stabilized by chelating ligands of the type N–X (X = N, O, C) [5].

Recently, Nolan addressed his attention to derivatives of the type $[Au(NHC)X_3]$ (NHC = N-heterocyclic carbenes, X = Cl^-, Br^-) which were obtained by oxidative addition of the appropriate halogen X_2 to neutral gold(I) complexes of the type [Au(NHC)X] [6]. (Table 1 SI) Furthermore, this kind of reaction was also studied in the case of phospine and isocyanide derivatives. Interestingly, the oxidative addition of halogens to complexes of the type $[Au(R_3P)X]$ (X = Br^-, I^-) is strongly influenced by the steric hindrance of the phosphine [7] whereas the reactivity of the isocyanide derivatives [Au(CNR)X] is principally modulated by the electronic characteristics of both the isocyanide and halogen, so that only the complex [Au(*t*–Bu–NC)Br_3] can be prepared and isolated [8].

The oxidative addition of neutral gold(I) substrates of the type [Au(L)(Ar)] (L = NHC [6c], CNR, NAC [9]; NAC = N-acyclic carbene) was also extensively studied and the ensuing reaction yielding the stable Au(III) derivatives $[Au(L)(Ar)X_2]$ represents a well known and established process. Notably, at least in one case the oxidative addition product [Au(IPr)(Me)I_2] (IPr = di-isopropylphenylimidazol-2-ylidene) undergoes a subsequent reaction to give the reductive elimination products MeI and [Au(IPr)I] [10].

On the other hand, investigations on cationic complexes are rather rare and only the synthesis of $[Au(NAC)_2I_2]^+$ [11], $[Au(NHC)_2I_2]^+$ (NHC = benzimidazole) [2] and $[Au(NHC)_2X_2]^+$ (X = Cl^-, Br^-,I^-; NHC = imidazole , thiazole) [12] from complexes of general formula $[Au(L)_2]^+$ (L = NAC, NHC) was reported.

We have recently reported a study of the reactions of cationic substrates of the type $[Au(NHC)(CNR)]^+$ (CNR = isocyanide) with secondary amines to give the corresponding

$[Au(NHC)(NAC)]^+$ complexes [13]. Therefore, we decided to study the reaction of the latter with Br_2 and compare the results with those emerging from the reaction of the related species $[Au(L)(L')]^+$ (L = NHC, NAC; L′ = NAC, 2,6-dimethylphenylisocyanide with the general purpose of investigating the almost unknown) reactivity of the cationic complexes of gold(I) toward oxidative addition.

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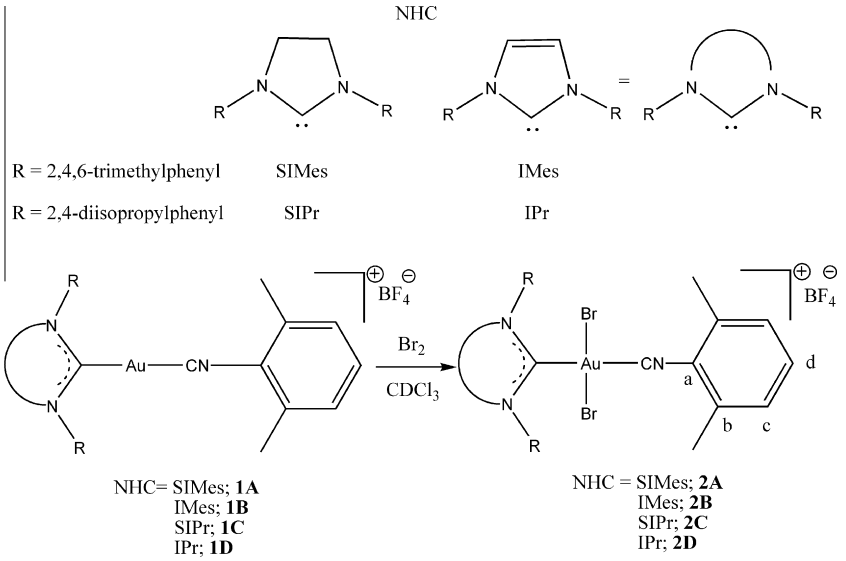


Scheme 1.

2. Results and discussion

2.1. Synthesis of the complexes [Au(NHC)(DIC)Br_2]BF_4

We have synthesized novel complexes of the type [Au(NHC)(DIC)Br_2]BF_4 (**2A**–**2D**) (DIC = 2,6-dimethylphenylisocyanide) by reacting the derivatives [Au(NHC)(DIC)]BF_4 [13] with a slight excess of Br_2 (1:1.1) at RT in $CDCl_3$ according to the reaction reported in Scheme 1.

Under NMR experimental conditions (see Section 4.3), the reaction goes to completion in several minutes. However, the reaction products **2** are quite unstable and decompose giving the complexes [Au(NHC)Br_3] (**3**), the organic derivative *N*-(2,6-dimethylphenyl)carboximidoyldibromide (Ar–N=CBr_2), colloidal gold and traces of unidentified species. However, the decomposition rate strongly depends on the nature of the ligands, thus **2A** and **2C** decompose in some hours (~5) whereas **2B** and **2D** are more stable and decompose within 24 h. Remarkably, addition of an excess of Br_2 to all the starting complexes **1** induces slow formation of the sole derivative **3** and the organic derivative *N*-(2,6-dimethylphenyl)carboximidoyldibromide and unidentified species (Scheme 2).

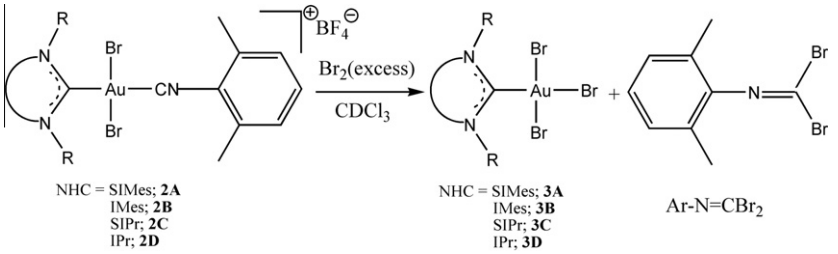
When compared with the ^{1}H NMR spectra of related species **1**, complexes **2** display a general deshielding of the coordinated isocyanide (H^d and CH_3) and of the imidazolium (CH) or imidazolinium (CH_2) proton (see Table 1). Notably, in the ^{13}C NMR spectra of complexes **2**, the carbene carbons display a marked up-field shift ($\Delta\delta$ ~30 ppm). Similar behaviour is detectable when Au(III) carbene derivatives are compared with their related Au(I) species, this fact being traceable back to the enhanced acidity of the metal centre [6,12].

Finally, complexes **2** exhibit the IR stretching frequency of the coordinated isocyanide at ca. 2260 cm^{-1} (stretching frequencies of free isocyanide and complexes **1** at ca. 2119 and 2200 cm^{-1}, respectively). Complexes **2** are also characterized by an intense LMCT transition band (AuBr) in the UV–Vis spectrum at ca. 340 nm [14] and by the lack of any luminescent property, at variance with complexes of type **1** emitting at 427 nm (λ^{exc} = 300 nm) in CH_2Cl_2.

2.2. Synthesis of the complexes [Au(NHC)(NAC)Br_2]BF_4; (NAC = C((NHC$_6$H$_3$(CH$_3$)$_2$)(NC$_5$H$_{10}$))

Complexes **4** were synthesized as reported in the published procedure [13] and react with a slight excess of bromine at RT in $CDCl_3$ to give gold(III) derivatives **5** (Scheme 3). Under NMR conditions, also this process is fast and quantitative and complexes **5** are stable even in the presence of an excess of bromine.

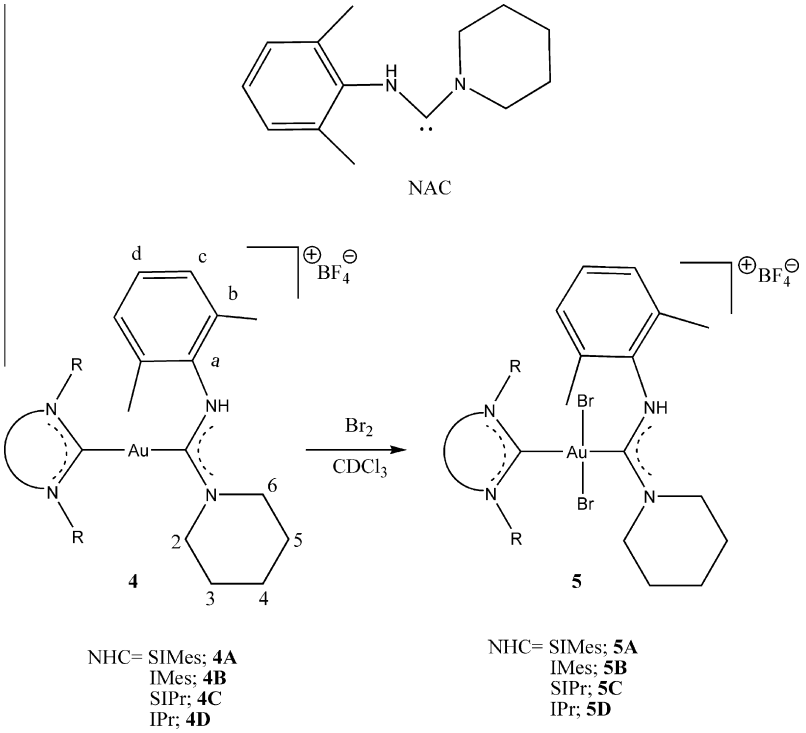
At variance with the Au(I) precursors **4**, complexes **5** display ^{1}H NMR spectra that seem to suggest a hindered rotation about both the Au–C bonds. This fact, which is probably due to the steric hindrance of the bromine atoms lying in the coordination plane, is testified by the doubling of the signals of the NHC protons. In particular, the *CH* protons of the imidazolium ring of complexes **5B** and **5D** resonate as two broad singlets whereas the CH_2 imidazolinium protons are detectable as an A_2B_2 system. Moreover, these signals display a slight but generalized down-field shift with respect to those of the starting complexes **4** and the protons of the



Scheme 2.

Table 1
Selected ^{1}H and ^{13}C signals for the complexes **1** and **2** at 298 K ($CDCl_3$).

	CH_3	CH	CH_2	$CH(CH_3)_2$	H^d	CH	CH_2	$CH(CH_3)_2$	C^a	C^d	NCN_{NHC}
1A	2.30	–	4.28	–	7.34	–	51.8	–	123.2	131.8	199.2
1B	2.34	7.46	–	–	7.35	124.8	–	–	123.2	131.7	177.4
1C	2.22	–	4.40	3.13	7.48	–	54.7	28.8	124.5	131.9	199.4
1D	2.27	7.63	–	2.54	7.36	125.9	–	28.8	*nd*	131.9	178.6
2A	2.32	–	4.52	–	7.41	–	53.4	–	121.9	131.7	165.3
2B	2.44	7.75	–	–	7.43	125.6	–	–	121.9	132.2	145.2
2C	2.39	–	4.64	3.37	7.49	–	56.0	29.2	121.8	132.0	167.0
2D	2.42	7.90	–	2.87	7.43	124.8	–	29.3	*nd*	131.9	147.7



Scheme 3.

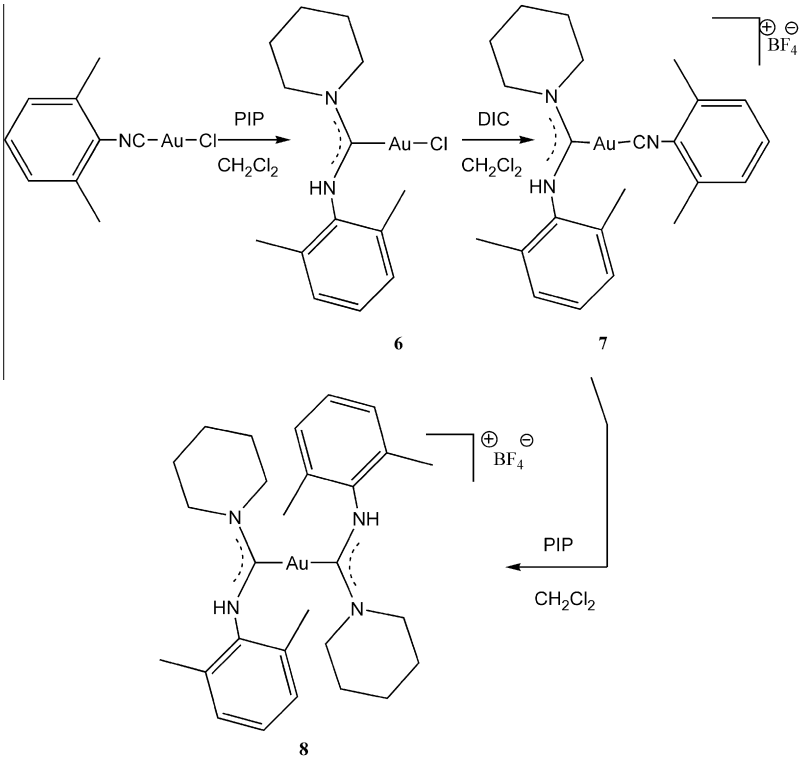
R substituents at NHC ligands (mesityl, di-isopropylphenyl) are usually split into two different groups of signals (see Table 2).

If the NAC part of the complexes is taken into consideration, the cross-peaks between the NH and H^6_{pip} protons of complexes **4** are observed in the NOESY spectrum. Similar behaviour is detected also in the case of the corresponding protons of complexes **5** suggesting that the *endo* configuration of the Au(III) derivatives is maintained [13]. The NHC and NAC carbene carbons resonate at higher field than those of the corresponding starting complexes **4** (see Table 2). Furthermore, it is worth noting that the well-defined

Table 2
Selected ^{1}H and ^{13}C signals at 298 K in $CDCl_3$ for the complexes **4** and **5**.

	CH	CH_2	$CH(CH_3)_2$	NH	H^2_{pip}	H^6_{pip}	CH	CH_2	$CH(CH_3)_2$	NCN_{NHC}	NCN_{NAC}
4A	–	3.92	–	7.84	3.44	3.48	–	50.9	–	207.4	201.2
4B	7.07	–	–	8.04	3.45	3.54	122.7	–	–	185.9	201.2
4C	–	4.02	2.90	7.78	2.93	3.43	–	53.7	28.7	207.9	200.6
4D	7.19	–	2.39	7.89	3.01	3.48	123.9	–	28.6	187.4	200.4
5A	–	4.07[a]	–	8.22	3.17	3.68	–	51.9	–	184.1	172.3
5B	7.09 7.13	–	–	8.62	3.36	3.83	124.6	–	–	*nd*	170.1
5C	–	4.23[a]	3.20 3.41	8.41	2.95	3.68	–	54.4 54.8	28.7 29.4	185.4	171.6
5D	7.23 7.33	–	2.70 2.88	8.37	3.07	3.71	124.1 124.5	–	28.7 29.3	159.0	170.9

[a] A_2B_2 system.



Scheme 4.

HMBC cross-peaks between the carbene carbon of NAC and the NH and H^2_{pip} protons of complexes **4** are noticed only in the case of **5C** and **5D** derivatives.

Finally, the ν_{NH} and ν_{CN} frequencies at ca. 3315 and 1550 cm^{-1} characterize the IR spectra of complexes **4**, whereas complexes **5** display the related stretching at 3280 and 1565 cm^{-1}, respectively. In the latter case the asymmetric stretching ν(AuBr) at ca. 265 cm^{-1} is diagnostic. At variance with complexes **4** which do not display any LMCT transition band and emit in CH_2Cl_2 at 397 nm (λ^{exc} = 280 nm, NHC = SIMes , SIPr), the UV–Vis spectra of complexes **5** are characterized by an LMCT absorption band in the UV–Vis spectrum at ca. 340 nm (AuBr) [14] and by the lack of any luminescent property.

2.3. Synthesis of the complexes [Au(L)(NAC)Br_2]BF_4 (L = DIC, NAC)

The synthesis of the gold(I) complexes [Au(L)(NAC)]BF_4 is carried out according to published protocols, as reported in Scheme 4 [13]. The nucleophilic attack of piperidine (PIP) on the complex [Au(DIC)Cl] [15] yields the [Au(NAC)Cl] (**6**) derivative. The latter can be reacted with DIC in the presence of $AgBF_4$ to give [Au(NAC)(DIC)]BF_4 (**7**) which undergoes a further piperidine attack in CH_2Cl_2 at RT yielding the compound [Au$(NAC)_2$] (**8**) (Scheme 4).

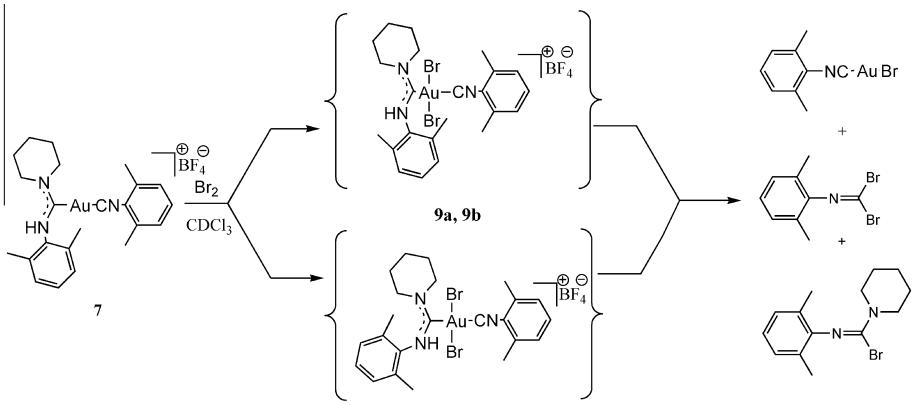
The ^{1}H NMR signals of the methyl and of the aromatic protons in complex **6** resonate at lower and at higher field, respectively, than those of the starting complex [Au(DIC)Cl] whereas the carbene carbon resonates at almost the same frequency as similar complexes [16]. When complex **7** is compared with complex **6**, the marked de-shielding of the N*H* proton is evident together with a less important down-field shift of the H^6_{pip} whereas the shielding of the H^2_{pip} signal is observed (Table 3). Notably, the cross peak between the N*H* and the H^6_{pip} signal in the NOESY spectrum suggest an *endo* configuration for the NAC fragment of complex **7** [13,17]. Moreover, the cross peaks between the carbene carbon and N*H* and H^2_{pip} protons are detected also in this case in the HMBC spectrum (see Supplementary material).

The ^{1}H NMR spectrum of complex **8,** notwithstanding its slight solubility in $CDCl_3$, is consistent with a symmetric structure in solution. The signals ascribable to CH_3, H^6_{pip}, H^2_{pip} and N*H* protons are all shifted up-field with respect to those of complex **7**. Unfortunately, the low solubility of complex **8** does not allow an adequate NOESY or HMBC investigation and hence the *endo-amphi* structure reported in Scheme 3 is merely hypothetical and based on steric

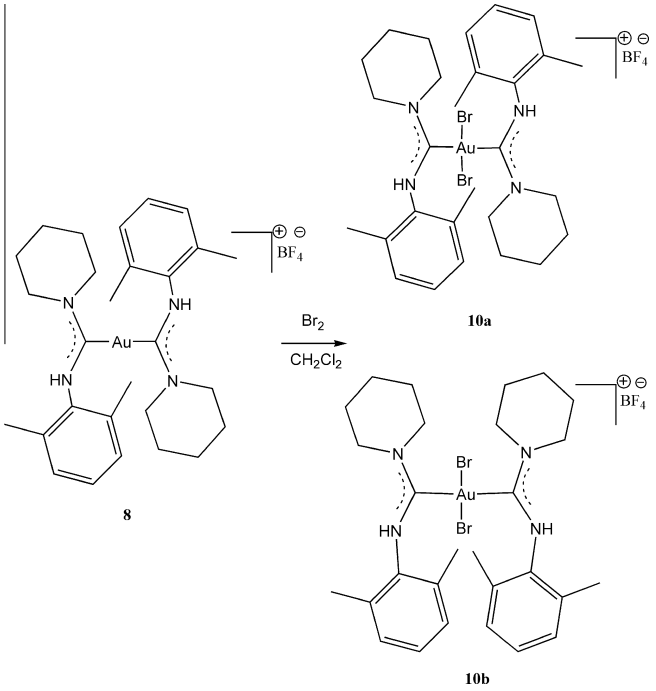
Table 3
Selected ^{1}H and ^{13}C carbene carbon signals at 298 K in $CDCl_3$ for the complexes [Au(NAC)Cl], [Au(NAC)L]BF_4, [Au(NAC)LBr_2]BF_4 (L = DIC, NAC), [Au(NAC) Br] and [Au(NAC)Br_3].

	NAC *CH*$_3$	DIC *CH*$_3$	H_p^2	H_p^6	NH	NCN
6	2.25	–	4.23	3.57	6.90	191.3
7	2.30	2.33	4.01	3.83	8.66	195.1
8	2.15	–	3.47	3.02	7.58	202.3
9	2.59/2.45	2.45/2.44	4.08/3.97	3.97/3.02	9.39/9.05	–
10[a]	2.44/2.39	–	3.95/3.65	3.06/2.94	7.89/8.29	–
[Au(NAC)Br]	2.26	–	4.25	3.56	6.83	–
[Au(NAC)Br_3][b]	2.47	–	4.13	3.18	7.43	–

[a] The insolubility of the complex and the partial overlapping of the signals do not allow the complete characterization.
[b] Sample not isolated.



Scheme 5.



Scheme 6.

considerations. Complex **8** is also formed in the stoichiometric reaction mixture yielding complex **7**. Reaction times longer than 5 min induce partial decomposition of **7** and the consequent formation of a slight quantity of **8**. Complex **8** displays a moderate up-field shift of C^6_{pip} and C^2_{pip} and a down-field shift (~7 ppm) of its carbene carbon with respect to complex **7**. On the contrary, such a signal is shifted up- field when compared with the complexes of type **5** (see Tables 2 and 3).

When a slight excess of Br_2 is added to complex **7** (1.1:1) under NMR experimental conditions, the subsequent fast reaction yields an equimolecular mixture of the *endo* and *exo* isomers **9a** and **9b**. Both isomers decompose and the complex [Au(DIC)Br], the organic derivatives *N*-(2,6-dimethylphenyl)-piperidine-1-carboximidoyl bromide (BrC(=N–Ar)C_5H_{10}N), and *N*-(2,6-dimethylphenylcarboximidoyldibromide (Ar–N=CBr_2) are detected in solution in ca. 30 min (see Scheme 5) [17].

The decomposition process does not yield the Au(I) carbene complex as was observed in the case of the oxidative addition of Br_2 on complexes **1**. Evidently, the NAC fragment imparts a reduced

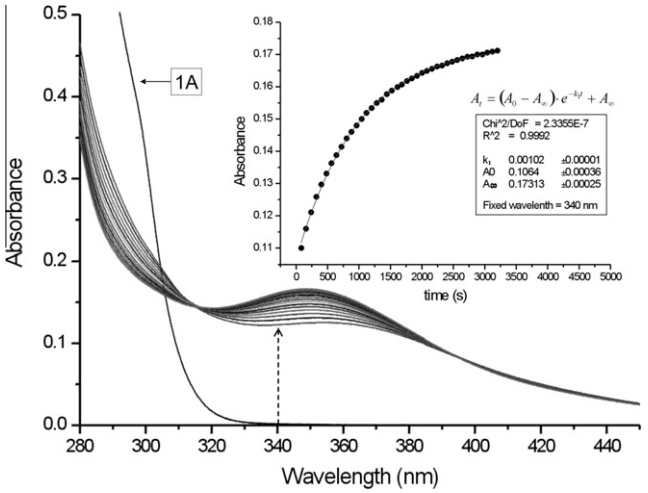


Fig. 1. Absorbance changes for the reaction **1A** + Br_2 → **2A** in $CHCl_3$ at 298 K ([**1A**] = 1×10^{-4} mol L^{-1}, [Br_2] = 8×10^{-5} mol L^{-1}) Top Insert: Non-linear regression analysis of absorbance vs. time (s) at fixed wavelength (340 nm; ε_{Br2} = 60).

stability to its derivative if compared with that of NHC analogs (*vide supra*). Such an experimental evidence might be supported by the instability of the independently synthesized complex [Au(NAC)Br_3] which rapidly decomposes into BrC(=N–Ar)C_5H_{10}N and $[AuBr_2]^-$.[1]

The ^{1}H NMR spectrum of the isomeric mixture of complexes **9a** and **9b** displays the deshielding of the N*H*, C*H*$_3$ DIC and C*H*$_3$ NAC protons. The H^6_{pip} and H^2_{pip} protons resonate at higher and lower field in the case of complex **9b** (*exo*) and **9a** (*endo*), respectively with respect to those of complex **7**. In particular, the H^6_{pip} of complex **9b** undergo an up-field shift of 0.8 ppm owing to the proximity of the aromatic ring.

The oxidative addition of a slight excess of Br_2 (1.1:1) to the complex **8** at RT in CH_2Cl_2 gives rapidly and quantitatively the complex **10** (Scheme 6).

Complex **10** might be present in solution as an equilibrium mixture of four different isomers, namely the *amphi* isomer (**10a**) and the *anti* isomer (**10b**) and the related *endo* and *exo* species. Despite the limited solubility of **10** in the usual NMR solvents and the con-

[1] Complex [Au(NAC)Br3] was prepared and characterized in situ (CDCl3) by oxidative addition of Br2 to the complex [Au(NAC)Br]. ^{1}H NMR ($CDCl_3$, T=298 K, ppm): δ 1.43, 1.67, 1.94 (H_{pip}^3, H_{pip}^4 and H_{pip}^5), 2.47 (s, 6H, CH_3^{Ar}), 3.18 (bs, 2H, H_{pip}^6), 4.13 (bt, 2H, H_{pip}^2, *J*= 4.5 Hz), 7.15 (d, 2H, H^c, *J*=7.5), 7.22 (t, 1H, H^d), 7.43 (bs, 1H, N*H*).

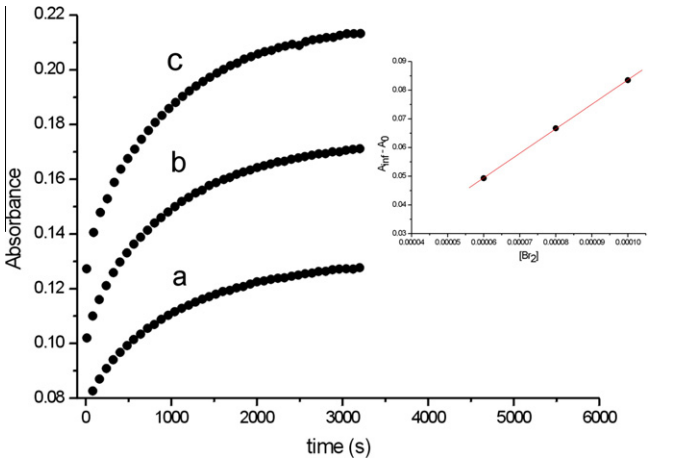


Fig. 2. Non-linear regression of absorbance vs. time (s) at fixed wavelength (340 nm) and 298 K for the reaction: **1A** + Br_2 → **2A**; ([**1A**] = 1×10^{-4} mol L^{-1}) (a) $[Br_2] = 6 \times 10^{-5}$ mol L^{-1}, $k_1 = 9.7 \times 10^{-4}$ s^{-1}; $A_\infty - A_0 = 4.93 \times 10^{-2}$ (b) $[Br_2] = 8 \times 10^{-5}$ mol L^{-1}, $k_1 = 1.02 \times 10^{-3}$ s^{-1}; $A_\infty - A_0 = 6.67 \times 10^{-2}$ (c) $[Br_2] = 1 \times 10^{-4}$ mol L^{-1}, $k_1 = 1.04 \times 10^{-3}$ s^{-1}; $A_\infty - A_0 = 8.35 \times 10^{-2}$. Top insert: linear dependence of $A_\infty - A_0$ on bromine concentration.

sequent poor quality of the spectra, we advance the hypothesis that the *exo* species is not present in solution since no marked shielding of the H^6_{pip} and H^2_{pip} protons is observed. On the other hand, the splitting of almost all the other signals suggests the presence in solution of two species which we identify as the *anti* and *amphi* isomers, although the similar complex $[Au((ArNH)_2C)_2I_2]$-ClO_4 is present in solution only in its *amphi* form [11a].

2.4. Kinetic measurements of the oxidative addition of Br_2 on complexes of type **1** and **4**

In order to avoid the side reactions promoted by the bromine in excess, we have carried out the oxidative addition of Br_2 to complexes **1** and **4** with a $[Br_2]$/[Complex] molar ratio less than or equal to unity. The reactions went smoothly to completion and in the case of complexes **1** the previously described subsequent slow rearrangement of the reaction products **2** into complexes of the type **3**, did not interfere with the measured reaction rate.

Moreover, as can be seen in Fig. 1, the reaction profile of the reaction between complex **1A** and Br_2 strongly suggests a fast pre-equilibrium process followed by a rate-determining reaction leading to a final spectrum that is coincident with that of an authentic sample of complex **2A**.

The dependence of the absorbance on time is better described by the following mono-exponential function:

$$A_t = (A_0 - A_\infty) \cdot e^{-k_1 t} + A_\infty$$

where A_0, A_t and A_∞ represent the absorbance immediately after Br_2 addition, the time dependent absorbance and the absorbance at the end of the reaction, respectively.

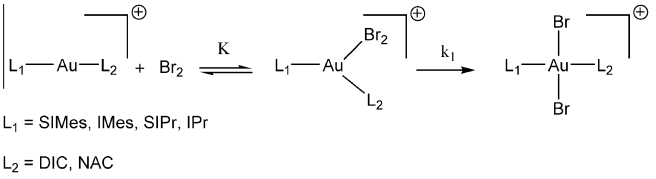
Moreover, the ensuing k_1 values for the reactions carried out in the presence of variable concentrations of bromine are virtually independent on the bromine concentration, whereas the $A_\infty - A_0$ differences are linearly dependent on the bromine concentrations, as can be seen in Fig. 2. Notably, owing to the low molar extinction coefficient of Br_2 at 340 nm ($\varepsilon_{Br2} = 60$) the change of absorbance due to the added and unreacted bromine should be negligible.

We observed similar behaviour for all the complexes studied and the k_1 values calculated by a non-linear regression of A_t vs. t data are reported in the following Table 4.

A reasonable mechanistic scheme taking into account the experimental evidence is described in Scheme 7.

Table 4
Calculated k_1 (s^{-1}).

Complex	$10^3 \times k_1$ (s^{-1})	Complex	$10^3 \times k_1$ (s^{-1})
1A	1.0 ± 0.1	4A	fast
1B	3.1 ± 0.1	4B	fast
1C	1.0 ± 0.1	4C	67 ± 2
1D	3.2 ± 0.1	4D	71 ± 2



Scheme 7.

In Scheme 7 the equilibrium reaction between the starting complex and the intermediate adduct **I** is thought to be fast and quantitative and is followed by a monomolecular rearrangement to the final species. It is noteworthy that intermediate adducts bearing *end-on* coordinated bromine were hypothesized by other authors in the oxidative addition of X_2 to complexes of the type $[Au(NHC)(CH_3)]$ ($X_2 = I_2$, Br_2, Cl_2) [10] and $[Pd(NN)(C_4(CN)_4)]$ ($X_2 = Br_2$) [18]. However, in our opinion an intermediate adduct involving an interaction between bromine and the isocyanide carbon cannot be ruled out *a priori*.

The first-order k_1 constants appear to be hardly influenced by the nature of the substituents of the carbene fragment whereas the electronic factors may have some importance. As a matter of fact, the stronger σ-donating ability of the NAC ligand as compared with that of the isocyanide renders the reaction rates of the oxidative process in complexes **4** almost two orders of magnitude higher than those of complexes of type **1**.

3. Conclusion

Following published procedures [13], we have synthesized the carbene complexes of gold(I) of the type $[Au(NHC)(L_2)]$ (L_2 = DIC (**1**); L_2 = NAC (**4**)) and also synthesized and characterized the novel species $[Au(NAC)(L_2)]$ (L_2 = DIC (**7**); L_2 = NAC (**8**)). We have studied the oxidative addition of bromine to complexes **1** and **4** to give the gold(III) derivatives **2** and **5**. The complexes of type **2** are rather unstable and decompose in solution to give the derivatives **3**, whereas complexes of type **5** were isolated in their pure form and fully characterized. The isomers **9a** and **9b** obtained from the oxidative addition of bromine to complex **7** are also unstable, whereas isomers **10a** and **10b** that were obtained from the di-NAC derivative **8**, are stable and slightly soluble complexes. The oxidative addition reaction was interpreted on the basis of a mechanism involving fast and complete formation of an intermediate adduct bearing one undissociated molecule of Br_2 which then rearranges to the reaction product *via* a first order monomolecular step.

4. Experimental

4.1. Solvents and reagents

CH_2Cl_2 was distilled over CaH_2 under inert atmosphere (Ar), $CHCl_3$ was distilled and stored over silver foil. All the other chemicals were commercially available grade products unless otherwise stated. The complexes $[Au(NHC)(DIC)](BF_4)$, $[Au(NHC)(NAC)](BF_4)$

(NHC = SIMes, IMes, SIPr, IPr; NAC = C((NHC$_6$H$_3$(CH$_3$)$_2$)(NC$_5$H$_{10}$)) and [Au(DIC)Cl] were prepared following literature procedures [13].

4.2. IR, NMR and UV–Vis measurements

The IR, ^{1}H, and ^{13}C{^{1}H} NMR spectra were recorded on a Perkin–Elmer Spectrum One spectrophotometer and on a Bruker 300 Avance spectrometer, respectively. The proton and carbon assignment was performed by ^{1}H–^{1}H COSY, ^{1}H–^{1}H NOESY, ^{1}H–^{13}C HMBC and ^{1}H–^{13}C HMQC experiments. UV–Vis spectra were taken on a Perkin–Elmer Lambda 40 spectrophotometer equipped with a Perkin–Elmer PTP6 (Peltier temperature programmer) apparatus.

4.3. Preliminary studies and kinetic measurements

All the oxidative additions were preliminarily analyzed by ^{1}H NMR technique by dissolving the complex under study [Au(NHC)(DIC)]BF$_4$, [Au(NHC)(NAC)]BF$_4$, [Au(DIC)(NAC)]BF$_4$ and [Au(NAC)$_2$]BF$_4$ in 0.6 mL of CDCl$_3$ ([complex]$_0 \approx 0.02$ mol dm^{-3}) at 298 K. An appropriate aliquot of a concentrated solution (0.25 mol dm^{-3}) of bromine was added ([Br$_2$]$_0 \approx 0.02$ mol dm^{-3}), and the reaction was followed to completion by monitoring the disappearance of the signals of the starting complex and the concomitant appearance of those of the Au(III) di-bromo complex.

A UV–Vis preliminary investigation was also carried out with the aim of determining the best wavelengths for spectrophotometric determination, corresponding to the widest change in absorbance. For this purpose, 3 mL of freshly distilled CHCl$_3$ solution of the complex under study ([complex]$_0 \approx 1 \times 10^{-4}$ mol dm^{-3}) was placed in a thermostated (298 K) cell compartment of the UV–Vis spectrophotometer, and aliquots of a concentrated solution of bromine were added ([Br$_2$]$_0 \approx$ [complex]$_0$). The absorbance change was monitored in the 250–500 nm wavelength range. The kinetics of the oxidative addition at fixed wavelength were recorded at $\lambda = 340$ nm in the [Br$_2$]$_0$ concentration range 6.0×10^{-5}–1.3×10^{-4} mol dm^{-3} by adding aliquots of a mother solution of bromine (0.01 mol dm^{-3}) to 3 mL of freshly distilled CHCl$_3$ solution of the complex under study ([complex]$_0 \approx 1 \times 10^{-4}$ mol dm^{-3}).

4.4. Synthesis of the complexes

4.4.1. [Au(SIMes)(DIC)Br$_2$]BF$_4$ (**2A**)

To a solution of [Au(SIMes)(DIC)]BF$_4$ (0.0087 g, $1.2 \cdot 10^{-2}$ mmol) placed in an NMR tube (CDCl$_3$, 0.6 mL), an aliquot (≈50 μL, 1.3×10^{-2} mmol) of a concentrated solution (0.25 mol dm^{-3}) of bromine in CDCl$_3$ was added. After checking the total conversion of the starting complex into the reaction product [Au(SIMes)(DIC)Br$_2$]BF$_4$, the solvent was evaporated and diethyl ether added. The yellow precipitate was filtered off through a gooch, washed with pentane and dried under vacuum. Partial formation of [Au(SIMes)Br$_3$] was observed. Yield: 72%. ^{1}H NMR (CDCl$_3$, T = 298 K, ppm): δ 2.32 (s, 6H, CH$_3^{DIC}$), 2.41 (s, 6H, CH$_3^{SIM}$), 2.53 (s, 12H, CH$_3^{SIM}$), 4.52 (s, 4H, CH_2) 6.98 (s, 4H, H^{SIM}), 7.19 (d, 2H, H^c, J = 7.5 Hz), 7.41 (t, 1H, H^d). ^{13}C{^{1}H} NMR (CDCl$_3$, T = 298 K, ppm): δ 18.3 (CH$_3^{DIC}$), 19.4 (CH$_3^{SIM}$), 21.0 (CH$_3^{SIM}$), 53.4 (CH_2), 121.9 (C^a), 128.8 (C^c), 130.1 (C$_{SIM}^3$ and C$_{SIM}^5$), 131.7 (C^d), 133.1 (C$_{SIM}^4$), 136.1 (C$_{SIM}^2$ and C$_{SIM}^6$), 137.8 (C^b), 140.2 (C$_{SIM}^1$), 165.3 (NCN$_{SIM}$). IR (CH$_2$Cl$_2$, cm^{-1}): ν 2922.8 (CH), 2263.7 (CN), 1606.7 (CN), 1524.3, 1462.6 (CC), 1064.2 (BF$_4$).

The following complexes were prepared under conditions similar to those of [Au(SIMes)(DIC)Br$_2$]BF$_4$ by using the appropriate [Au(NHC)(DIC)]BF$_4$ precursor. Partial formation of [Au(NHC)Br$_3$] was observed in all cases.

4.4.2. [Au(IMes)(DIC)Br$_2$]BF$_4$ (**2B**)

Yield: 78%, orange solid. ^{1}H NMR (CDCl$_3$, T = 298 K, ppm): δ 2.30 (s, 12H, CH$_3^{IM}$), 2.38 (s, 6H, CH$_3^{IM}$), 2.44 (s, 6H, CH$_3^{DIC}$), 7.06 (s, 4H, H^{IM}), (d, 2H, H^c, J = 7.5 Hz), 7.43 (t, 1H, H^d), 7.75 (s, 2H, –HC=CH–). ^{13}C{^{1}H} NMR (CDCl$_3$, T = 298 K, ppm): δ 18.4 (CH$_3^{DIC}$), 19.1, 21.1 (CH$_3^{IM}$), 121.9 (C^a), 125.6 (–HC=CH–), 128.9 (C^c), 130.0 (C$_{IM}^3$ and C$_{IM}^5$), 132.2 (C^d), 133.2 (C$_{IM}^4$), 135.1 (C$_{IM}^2$ and C$_{IM}^6$), 137.9 (C^b), 141.1 (C$_{IM}^1$), 145.2 (NCN$_{IM}$) not detected. IR (CH$_2$Cl$_2$, cm^{-1}): ν 2926.8 (CH), 2262.7 (CN), 1602.7 (CN), 1479.6, 1443.7 (CC), 1064.1 (BF$_4$).

4.4.3. [Au(SIPr)(DIC)Br$_2$]BF$_4$ (**2C**)

Yield: 69%, orange solid. ^{1}H NMR (CDCl$_3$, T = 298 K, ppm): δ 1.34 (d, 12H, CH$_3^{SIP}$, J = 6.9 Hz), 1.45 (d, 12H, CH$_3^{SIP}$), 2.39 (s, 6H, CH$_3^{DIC}$), 3.37 (sept, 4H, HC(CH$_3$)$_2$), 4.64 (s, 4H, CH_2), 7.20 (d, 2H, H^c, J = 7.5 Hz), 7.30 (d, 4H, H$_{SIP}^3$ and H$_{SIP}^5$, J = 7.5 Hz), 7.42 (t, 1H, H^d), 7.49 (t, 2H, H$_{SIP}^4$). ^{13}C{^{1}H} NMR (CDCl$_3$, T = 298 K, ppm): δ 18.3 (CH$_3^{DIC}$), 23.9, 27.2 (CH$_3^{SIP}$), 29.2 (HC(CH$_3$)$_2$), 56.0 (CH_2), 121.8 (C^a), 125.1 (C$_{SIP}^3$ and C$_{SIP}^5$), 128.9 (C^c), 131.1 (C$_{SIP}^4$), 132.0 (C^d), 133.2 (C$_{SIP}^1$), 137.7 (C^b), 147.1 (C$_{SIP}^2$ and C$_{SIP}^6$), 167.0 (NCN$_{SIP}$). IR (CH$_2$Cl$_2$, cm^{-1}): ν 2965.3, 2926.6 (CH), 2262.7 (CN), 1589.7 (CN), 1507.2, 1458.4 (CC), 1062.1 (BF$_4$).

4.4.4. [Au(IPr)(DIC)Br$_2$]BF$_4$ (**2D**)

Yield: 75%, orange oil. ^{1}H NMR (CDCl$_3$, T = 298 K, ppm): δ 1.22 (d, 12H, CH$_3^{IP}$, J = 6.60 Hz), 1.40 (d, 12H, CH$_3^{IP}$), 2.42 (s, 6H, CH$_3^{DIC}$), 2.87 (septet, 4H, –CH(CH$_3$)$_2$), 7.21 (d, 2H, H^c, J = 7.8 Hz), 7.39 (d, 4H, H$_{IP}^3$ and H$_{IP}^5$, J = 7.8 Hz), 7.43 (t, 1H, H^d), 7.60 (t, 2H, H$_{IP}^4$), 7.90 (s, 2H, –HC=CH–). ^{13}C{^{1}H} NMR (CDCl$_3$, T = 298 K, ppm): δ 18.3 (CH$_3^{DIC}$), 22.9, 26.6 (CH$_3^{IP}$), 29.3 (HC(CH$_3$)$_2$), (C^a) not detected, 124.8 (–HC=CH–), 128.0 (C^c), 128.9, 129.2 (C$_{IP}^3$ and C$_{IP}^5$), 131.9 (C^d), 132.0 (C$_{IP}^4$), 133.3 (C$_{IP}^1$), 137.9 (C^b), 146.1 (C$_{IP}^2$ and C$_{IP}^6$), 147.7 (NCN$_{IP}$). IR (CH$_2$Cl$_2$, cm^{-1}): ν 2969.3, 2931.6 (CH), 2264.7 (CN), 1589.8, 1556.8 (CN), 1458.5 (CC), 1060.1 (BF$_4$).

4.4.5. [Au(SIMes)(NAC)Br$_2$]BF$_4$ (**5A**)

To a solution of [Au(SIMes)(NAC)](BF$_4$) (0.0097 g, 1.2×10^{-2} mmol) placed in an NMR tube (CDCl$_3$, 0.6 mL) an aliquot (≈50 μL, 1.3×10^{-2} mmol) of a concentrated solution (0.25 mol dm^{-3}) of bromine in CDCl$_3$ was added. The yellow gold(-III) complex precipitated from the solution was filtered off over gooch, washed with pentane and dried under vacuum. Yield: 94%. ^{1}H NMR (CDCl$_3$, T = 298 K, ppm): δ 1.31 (bs, 2H, H$_{pip}^4$), 1.67 (bs, 4H, H$_{pip}^3$ and H$_{pip}^5$), 2.04 (s, 6H, CH$_3^{Ar}$), 2.16 (s, 6H, CH$_3^{SIM}$), 2.31 (s, 3H, CH$_3^{SIM}$), 2.43 (s, 3H, CH$_3^{SIM}$), 2.45 (s, 6H, CH$_3^{SIM}$), 3.17 (bt, 2H, H$_{pip}^2$, J = 5.4 Hz), 3.68 (bt, 2H, H$_{pip}^6$, J = 5.4 Hz), 4.07 (A$_2$B$_2$ system, 4H, H_2C–CH_2), 6.72 (d, 2H, H^c, J = 7.5 Hz), 6.85 (s, 2H, H$_{SIM}$), 6.93 (s, 2H, H$_{SIM}$), 7.02 (t, 1H, H^d), 8.22 (bs, 1H, NH). ^{13}C{^{1}H} NMR (CDCl$_3$, T = 298 K, ppm): δ 18.6 (CH$_3^{SIM}$), 19.3 (CH$_3^{SIM}$), 19.5 (CH$_3^{Ar}$), 20.6 (CH$_3^{SIM}$), 20.8 (CH$_3^{SIM}$), 23.41 (C$_{pip}^4$), 25.4, 25.7 (C$_{pip}^3$ and C$_{pip}^5$), 49.2 (C$_{pip}^6$), 51.9 (CH$_2$), 54.9 (C$_{pip}^2$), 128.4 (C^c), 129.6 (C^d), 130.2 (C$_{SIM}^3$ and C$_{SIM}^5$), 135.2 (C^b), 136.7 (C$_{SIM}^2$ and C$_{SIM}^6$), 136.9 (C$_{SIM}^4$), 139.0 (C^a), 139.8 (C$_{SIM}^1$), 172.3 (NCN$_{ACYCLIC}$), 184.1 (NCN$_{SIM}$). IR (KBr pellet, cm^{-1}): ν 3287.7 (NH), 2952.7, 2857.7 (CH), 1563.5 (CN), 1508.6 (CC), 1083.5 (BF$_4$). IR (polyethylene pellet, cm^{-1}): ν 266.6 (AuBr). *Anal.* Calc. for C$_{35}$H$_{46}$AuBr$_2$F$_4$N$_4$: C, 43.50; H, 4.80; N, 5.80. Found: C, 43.63; H, 4.72; N, 5.83%.

The following complexes were prepared under conditions similar to those of [Au(SIMes)(NAC)Br$_2$]BF$_4$ by using the appropriate [Au(NHC)(NAC)]BF$_4$ precursor.

4.4.6. [Au(IMes)(NAC)Br$_2$]BF$_4$ (**5B**)

Yield: 91.0%, yellow solid. ^{1}H NMR (CDCl$_3$, T = 298 K, ppm): δ 1.40 (bs, 2H, H$_{pip}^4$), 1.65 (bs, 2H, H$_{pip}^3$ or H$_{pip}^5$), 1.74 (bs, 2H, H$_{pip}^3$ or H$_{pip}^5$), 1.94 (s, 6H, CH$_3^{IM}$), 2.12 (s, 6H, CH$_3^{Ar}$), 2.24 (s, 6H, CH$_3^{IM}$), 2.38 (s, 3H, CH$_3^{IM}$), 2.49 (s, 3H, CH$_3^{IM}$), 3.36 (bt, 2H, H$_{pip}^2$,

J = 5.4 Hz), 3.83 (bt, 2H, H_{pip}^{6}, J = 5.4 Hz), 6.80 (d, 2H, H^{c}, J = 7.50), 6.93 (s, 2H, H^{IM}), 7.02 (s, 2H, H^{IM}), 7.09 (t, 1H, H^{d}), 7.09 (s, 1H, *HC*=CH), 7.13 (s, 1H, *HC* = CH), 8.62 (bs, 1H, N*H*). $^{13}C\{^{1}H\}$ NMR selected data ($CDCl_3$, T = 298 K, ppm): δ 18.4 (CH_3^{IM}), 19.0 (CH_3^{IM}), 19.6 (CH_3^{Ar}), 20.8 (CH_3^{IM}), 21.2 (CH_3^{IM}), 124.6 (–*C*H=*C*H–), 128.0 (C^{c}), 129.3, 130.3 (C_{IM}^{3} and C_{IM}^{5}), 170.1 ($NCN_{ACYCLIC}$). IR (KBr pellet, cm^{-1}): ν 3287.7 (NH), 2953.6, 2857.7 (CH), 1564.4 (CN), 1479.7, 1441.6 (CC), 1082.4 (BF_4). IR (polyethylene pellet, cm^{-1}): ν 265.6 (AuBr). *Anal.* Calc. for $C_{35}H_{44}AuBBr_2F_4N_4$: C, 43.59; H, 4.60; N, 5.81. Found: C, 43.74; H, 4.54; N, 5.92%.

4.4.7. [Au(SIPr)(NAC)Br$_2$]BF$_4$ (**5C**)

Yield: 94%, yellow solid. ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.16–1.21 (m, 18H, CH_3^{SIP}), 1.30 (bs, 2H, H^{4}_{pip}), 1.47 (d, 6H, CH_3^{SIP}), 1.54 (bs, 2H, H_{pip}^{3} or H_{pip}^{5}), 1.63 (bs, 2H, H_{pip}^{3} or H_{pip}^{5}), 2.08 (s, 6H, CH_3^{Ar}), 2.95 (bt, 2H, H^{2}_{pip}, J = 5.1 Hz), 3.20 (m, 2H, –*CH*$(CH_3)_2$), 3.41 (m, 2H, -*CH*$(CH_3)_2$), 3.68 (bs, 2H, H^{6}_{pip}), 4.23 (A_2B_2 system, 4H, H_2C-CH_2), 6.57 (d, 2H, H^{c}, J = 7.5 Hz), 6.78 (t, 1H, H^{d}), 7.13 (d, 2H, H_{SIP}^{3} or H_{SIP}^{5}, J = 7.5 Hz), 7.27 (d, 2H, H_{SIP}^{3} or H_{SIP}^{5}, J = 7.5 Hz), 7.45 (t, 2H, H_{SIP}^{4}), 8.41 (bs, 1H, N*H*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 19.7 (CH_3^{Ar}), 23.0, 23.4 (CH_3^{SIP}), 24.1 (C_{pip}^{4}), 25.5, 25.7 (C_{pip}^{3} and C_{pip}^{5}), 27.0, 27.75 (CH_3^{SIP}), 28.7, 29.4 (*HC*$(CH_3)_2$), 49.3 (C_{pip}^{6}), 54.7 (C_{pip}^{2}), 54.4, 54.8 (–*C*H$_2$–*C*H$_2$–), 124.3, 124.9 (C_{SIP}^{3} and C_{SIP}^{5}), 128.3 (C^{c}), 128.5 (C^{d}), 130.8 (C_{SIP}^{4}), 131.9, 132.23 (C_{SIP}^{1}), 133.9 (C^{a}), 136.6 (C^{b}), 146.4, 148.2 (C_{SIP}^{2} and C_{SIP}^{6}), 171.6 ($NCN_{ACYCLIC}$), 185.4 (NCN_{SIP}). IR (KBr pellet, cm^{-1}): ν 2964.7, 2857.8 (CH), 1568.6 (CN), 1492.7, 1457.7 (CC), 1082.6 (BF_4). IR (polyethylene pellet, cm^{-1}): ν (AuBr) not detected. *Anal.* Calc. for $C_{41}H_{58}AuBBr_2F_4N_4$: C, 46.88; H, 5.56; N, 5.33. Found: C, 46.75; H, 5.68; N, 5.21%.

4.4.8. [Au(IPr)(NAC)Br$_2$]BF$_4$ (**5D**)

Yield: 95%, yellow solid. ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.02 (d, 6H, CH_3^{IP}, J = 6.3 Hz), 1.09 (d, 6H, CH_3^{IP}), 1.17 (d, 6H, CH_3^{IP}), 1.28 (bs, 2H, H^{4}_{pip}), 1.39 (d, 6H, CH_3^{IP}), 1.57 (bs, 2H, H_{pip}^{3} or H_{pip}^{5}), 1.69 (bs, 2H, H_{pip}^{3} or H_{pip}^{5}), 2.12 (s, 6H, CH_3^{Ar}), 2.70 (m, 2H, –*CH*$(CH_3)_2$), 2.88 (m, 2H, –*CH*$(CH_3)_2$), 3.07 (bt, 2H, H^{2}_{pip}, J = 5.7 Hz), 3.71 (bt, 2H, H^{6}_{pip}, J = 5.7 Hz), 6.60 (d, 2H, H^{c}, J = 7.5 Hz), 6.82 (t, 1H, H^{d}), 7.20 (s, 2H, H_{IP}^{3} or H_{IP}^{5}, J = 7.5 Hz), 7.23 (s, 1H, *HC*=CH), 7.33 (s, 1H, *HC*=CH), 7.36 (s, 2H, H_{IP}^{3} or H_{IP}^{5}, J = 7.5 Hz), 7.55 (t, 2H, H_{IP}^{4}), 8.37 (bs, 1H, N*H*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 19.7 (CH_3^{Ar}), 22.2, 22.3 (CH_3^{IP}), 23.4, 25.5 (C_{pip}^{3} and C_{pip}^{5}), 25.7 (C_{pip}^{4}), 26.4, 27.0 (CH_3^{IP}), 28.7, 29.3 (*HC*$(CH_3)_2$), 49.1 (C_{pip}^{6}), 54.7 (C_{pip}^{2}), 124.1, 124.5 (–*C*H=*C*H–), 126.3 (C_{IP}^{3} and C_{IP}^{5}), 128.2 (C^{c}), 128.5 (C^{d}), 131.5 (C_{IP}^{4}), 132.0, 132.4 (C_{IP}^{1}), 134.0 (C^{a}), 136.7 (C^{b}), 145.3, 146.9 (C_{IP}^{2} and C_{IP}^{6}), 170.9 ($NCN_{ACYCLIC}$), 159.0 (NCN_{IP}). IR (KBr pellet, cm^{-1}): ν 3279.7 (NH), 2964.6, 2862.7 (CH), 1570.6 (CN), 1465.7, 1444.7 (CC), 1082.5, (BF_4). IR (polyethylene pellet, cm^{-1}): ν 263.6 (AuBr). *Anal.* Calc. for $C_{41}H_{56}AuBBr_2F_4N_4$: C, 46.97; H, 5.38; N, 5.34. Found: C, 46.82; H, 5.46; N, 5.49%.

4.4.9. [Au(NAC)Cl] (**6**)

0.14 mL (1.632 mmol) of pure piperidine was added to a stirred solution of [Au(DIC)Cl)] (0.340 g, 0.935 mmol) in 15 mL of CH_2Cl_2. After 15 min, the solution was treated with activated charcoal and filtered through Celite and the solvent removed under reduced pressure. A 1:1 mixture of Et_2O and *n*-hexane was added to the product, which was filtered off and washed with *n*-pentane (3 × 3 mL). The resulting solid was dried under vacuum. Yield: 92%, white solid. ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.74–1.79 (m, 6H, H_{pip}^{3}, H_{pip}^{4} and H_{pip}^{5}), 2.25 (s, 6H, CH_3^{Ar}), 3.57 (bt, 2H, H_{pip}^{6}, J = 6 Hz), 4.23 (bt, 2H, H_{pip}^{2}, J = 4.2 Hz), 6.90 (bs, 1H, N*H*), 7.10 (d, 2H, H^{c}, J = 7.50), 7.19 (t, 1H, H^{d}). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 18.8 (CH_3^{Ar}), 24.3, 25.8, 26.8 (C_{pip}^{3}, C_{pip}^{4} and C_{pip}^{5}), 45.5 (C_{pip}^{6}), 58.1 (C_{pip}^{2}), 128.4 (C^{c}), 128.5 (C^{d}), 136.2 (C^{b}), 137.0 (C^{a}), 191.3 ($NCN_{ACYCLIC}$). IR (KBr pellet, cm^{-1}): ν 3286.5 (NH), 2934.5, 2851.6 (CH), 1546.2 (CN), 1480.6, 1438.5 (CC). *Anal.* Calc. for $C_{14}H_{20}AuClN_2$: C, 37.47; H, 4.49; N, 6.24. Found: C, 37.57; H, 4.36; N, 6.33%.

4.4.10. [Au(NAC)Br]

To a stirred solution of [Au(NAC)Cl] (0.285 g, 0.636 mmol) in 50 mL of anhydrous acetone, LiBr (0.552 g, 6.365 mmol) was added. After 24 h, the solvent was evaporated and anhydrous CH_2Cl_2 added. The resulting suspension was treated with $MgSO_4$. After filtration over Millipore the resulting clear solution, concentrated under reduced pressure, yielded the crude product upon addition of Et_2O. The white residue was filtered off and washed with diethyl ether (3 × 3 mL). The resulting solid was dried under vacuum. Yield: 87%, white solid. ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.73–1.86 (m, 6H, H_{pip}^{3}, H_{pip}^{4} and H_{pip}^{5}), 2.26 (s, 6H, CH_3^{Ar}), 3.56 (bt, 2H, H_{pip}^{6}, J = 6 Hz), 4.25 (bt, 2H, H_{pip}^{2}, J = 4.7 Hz), 6.83 (bs, 1H, N*H*), 7.12 (d, 2H, H^{c}, J = 7.2), 7.20 (t, 1H, H^{d}). IR (KBr pellet, cm^{-1}): ν 3273.6 (NH), 2934.6, 2851.7 (CH), 1549.3 (CN), 1476.7, 1438.6 (CC). IR (polyethylene pellet, cm^{-1}): ν 261.0 (AuBr). *Anal.* Calc. for $C_{14}H_{20}AuBrN_2$: C, 34.09; H, 4.09; N, 5.68. Found: C, 34.19; H, 4.01; N, 5.58%.

4.4.11. [Au(DIC)(NAC)]BF$_4$ (**7**)

To a stirred solution of [Au(NAC)Cl] (0.200 g, 0.446 mmol) and DIC (0.07 g, 0.534 mmol) in CH_2Cl_2 (15 mL) solid $AgBF_4$ was added (0.096 g, 0.493 mmol). The reaction proceeds at room temperature with the concomitant precipitation of AgCl. After 15 min, the reaction mixture was treated with activated charcoal and filtered through Celite. The resulting clear solution, concentrated under reduced pressure, yielded the crude product upon addition of Et_2O. The white residue was filtered off and washed with Et_2O (3 × 3 mL) and *n*-pentane (3 × 3 mL). The resulting solid was dried under vacuum. Yield: 98%, white solid. ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.80 (m, 6H, H_{pip}^{3}, H_{pip}^{4} and H_{pip}^{5}), 2.30 (s, 6H, CH_3^{Ar}), 2.33 (s, 6H, CH_3^{DIC}), 3.83 (bt, 2H, H_{pip}^{6}, J = 5.7 Hz), 4.01 (bt, 2H, H_{pip}^{2}), 7.09 (d, 2H, H^{c}_{Ar}, J = 6.3 Hz), 7.16 (t, 1H, H^{d}_{Ar}), 7.17 (d, 2H, H^{c}_{DIC}, J = 7.5 Hz), 7.36 (t, 1H, H^{d}_{DIC}), 8.66 (bs, 1H, N*H*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 18.5 (CH_3^{DIC}), 18.7 (CH_3^{Ar}), 24.1, 25.8, 27.3 (C_{pip}^{3}, C_{pip}^{4} and C_{pip}^{5}), 46.5 (C_{pip}^{6}), 57.8 (C_{pip}^{2}), 128.1, 128.5 (C^{c}_{Ar}, C^{d}_{Ar}, C^{c}_{DIC}), 131.6 (C^{d}_{DIC}), 136.2, 137.1, 137.6 (C^{a}_{Ar}, C^{b}_{Ar}, C^{a}_{DIC}, C^{b}_{DIC}), 191.2 ($NCN_{ACYCLIC}$). IR (KBr pellet, cm^{-1}): ν 3298.2 (NH), 2932.4, 2862.6 (CH), 2216.2 (CN), 1569.5 (CN), 1479.4, 1439.4 (CC), 1076.4 (BF_4). *Anal.* Calc. for $C_{23}H_{29}AuBF_4N_3$: C, 43.76; H, 4.63; N, 6.66. Found: C, 43.66; H, 4.69; N, 6.78%.

4.4.12. [Au(NAC)$_2$]BF$_4$ (**8**)

0.047 mL (0.475 mmol) of pure piperidine was added to a stirred solution of [Au(DIC)(NAC)]BF_4 (0.2 g, 0.317 mmol) in 15 mL of CH_2Cl_2. After 15 min the solution was treated with activated charcoal and filtered through Celite and the solvent removed under reduced pressure. A 1:1 mixture of Et_2O and *n*-hexane was added to the product, which was filtered off and washed with *n*-pentane (3 × 3 mL). The resulting solid was dried under vacuum. Yield: 97%, white solid. ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.32 (bs, 4H, H_{pip}^{4}), 1.63 (bs, 8H, H_{pip}^{3} and H_{pip}^{5}), 2.15 (s, 12H, CH_3^{Ar}), 3.02 (bt, 4H, H_{pip}^{6}, J = 5.7 Hz), 3.47 (bt, 4H, H_{pip}^{2}), 7.05 (d, 4H, H^{c}, J = 6.6 Hz), 7.12 (t, 2H, H^{d}), 7.58 (bs, 2H, N*H*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 18.6 (CH_3^{Ar}), 24.1 (C_{pip}^{4}), 25.7, 27.1 (C_{pip}^{3} and C_{pip}^{5}), 42.3 (C_{pip}^{6}), 55.9 (C_{pip}^{2}), 127.9 (C^{d}), 128.1 (C^{c}), 136.8 (C^{b}), 137.6 (C^{a}), 202.2 ($NCN_{ACYCLIC}$). IR (KBr pellet, cm^{-1}): ν 3313.3 (NH), 2931.4, 2859.5 (CH), 1549.4 (CN), 1482.4, 1442.4 (CC), 1083.2 (BF_4). *Anal.* Calc. for $C_{28}H_{40}AuBF_4N_4$: C, 46.94; H, 5.63; N, 7.82. Found: C, 46.82; H, 5.73; N, 7.97%.

*4.4.13. [Au(NAC)$_2$Br$_2$]BF$_4$ (**10**)*

To a solution of [Au(NAC)$_2$]BF$_4$ (0.0086 g, $1.2\cdot10^{-2}$ mmol) in an NMR tube ($CDCl_3$, 0.6 mL) an aliquot (≈50 μL, 1.3×10^{-2} mmol) of a concentrated solution (0.25 mol dm^{-3}) of bromine in $CDCl_3$ was added. The yellow gold(III) compound which precipitated from the solution was filtered over a gooch, washed with pentane and dried under vacuum. Yield: 98%. IR (KBr pellet, cm^{-1}): *ν* 3289.6 (NH), 2944.5, 2857.6 (CH), 1569.2 (CN), 1471.6, 1444.5 (CC), 1084.4 (BF_4). IR (polyethylene pellet, cm^{-1}): *ν* 263.4 (AuBr). *Anal.* Calc. for $C_{28}H_{40}AuBBr_2F_4N_4$: C, 38.38; H, 4.60; N, 6.39. Found: C, 38.48; H, 4.46; N, 6.55%.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.05.020.

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