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# Reactions of trimeric 1-benzyl-2-gold(I)imidazole leading to $Au^I$ carbene complexes. Crystal structure of [1-benzyl-3-benzoyl-imidazolin-2-yliden]chlorogold(I) †

Bruna Bovio

*Dipartimento di Chimica Generale dell'Università, viale Taramelli 12. 27100 Pavia (Italy)*

Alfredo Burini and Bianca Rosa Pietroni

*Dipartimento di Scienze Chimiche dell'Università, via S. Agostino 1, 62032 Camerino (Italy)*

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## Abstract

The crystal structure determination of a compound previously described as tris-[{$\mu$-($N^1$-benzyl)imidazolato-$N^3$,$C^2$}(chloro)benzoylgold(III)], which turned out to be a gold(I) mononuclear carbene derivative, has led to a reconsideration of the reactions of [$Au_3im_3$] (im = $\mu$-($N^1$-benzyl)imidazolato-$N^3$,$C^2$) with reagents X–Y. The mononuclear or trinuclear nature of other Au imidazolyl derivatives is discussed and the compounds obtained by reaction with X–Y = Cl–COOEt, I–Et or Cl–*p*-tosyl and chlorobenzoyl appear to be mononuclear, whereas those obtained by reaction with $Me_3SiI$, $SOCl_2$ or $I_2$ appear to be trinuclear mixed valence or gold(III) compounds.

## 1. Introduction

In a previous investigation [1] of the behaviour of the trimeric [$Au_3im_3$] (**I**) (im = [$\mu$-($N^1$-benzyl)imidazolato-$N^3$,$C^2$]) towards several X–Y reagents, a number of derivatives were obtained, which could be either gold(I) mononuclear carbene derivatives or trinuclear mixed valence or gold(III) compounds. Namely the reaction could be either an oxidative addition to gold(I) atoms without ring breaking or a cleavage of Au–N bonds of the trimeric [$Au_3im_3$] (**I**). We suppose that [$Au_3im_3$] undergoes oxidative addition with a reagent X–Y, leading to compounds **II**, **III**, **IV** (see Scheme 1); when the products of the oxidative addition are unstable, this may be followed by reductive elimination which breaks the trimer enneaatomic ring to give the carbene compounds **V**–**VIII**. It is known that organometallic compounds which readily undergo oxidative addition reactions may first be attacked at the metal by an electrophilic reagent X–Y and then undergo reductive elimination to give the final products [2].

During our further investigations in this field we obtained some crystals of the compound VII, previously described as a gold(III) trimeric compound [1].

X-ray structure analysis shows that VII is a gold(I) mononuclear carbene complex. On the basis of this new result the original reaction scheme has had to be revised (Scheme 1).

## 2. Results and discussion

The previous formulation of the compound **VII** was based on ambiguous C-2 $^{13}$C NMR and mass spectroscopy data [1], summarized in Table 1. The $^{13}$C NMR spectral data show that the resonance of the C-2 of the imidazole ring, when detected, is displaced downfield compared with that from the corresponding metal-free imidazole.

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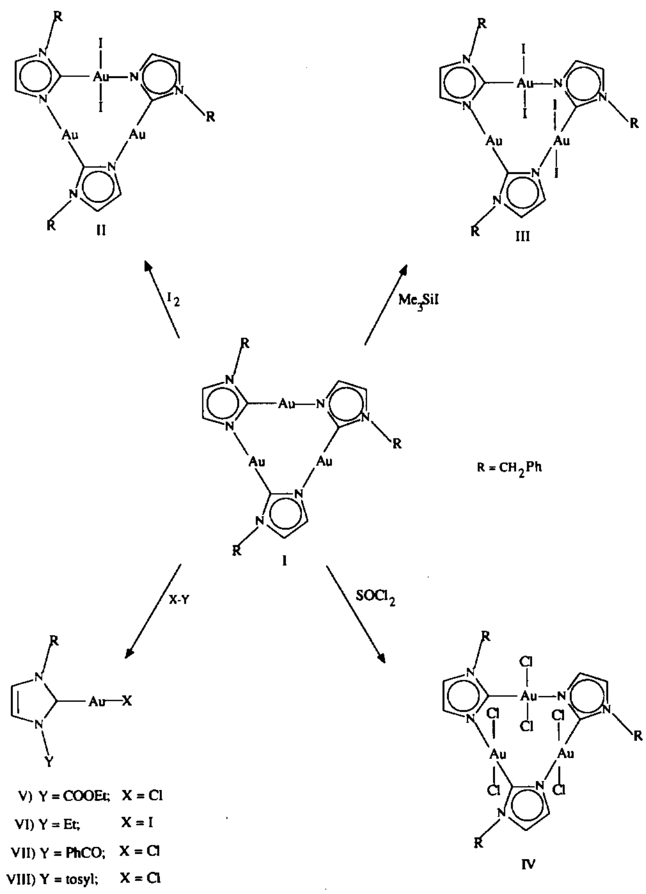
Correspondence to: Professor B. Bovio.

[†] This work began when Prof. Flavio Bonati was still alive and it is dedicated to his memory.



Scheme 1.

The C-2 signal in compound **VII** (at 174.87 ppm) lies *ca.* 7.6, 7.5, 9.7 ppm lower than in the trimeric compounds **I**, **II**, **IV**, respectively; *ca.* 5.5, 5.8 ppm higher than in other carbene complexes [Au(imH)$_2$Cl] [3] and **VI**, respectively; and almost in the same position as in the mononuclear carbene derivative **V**.

The C-2 signals of the trimeric and the mononuclear carbene compounds fall in a narrow spectral region and cannot therefore give conclusive information about the nature of **VII**; moreover, few examples are available for comparison. The mass spectra of the compounds **V** and **VI** show a parent ion corresponding to the monomer ($m/e$ 462 and 510, respectively) whereas compound **IV** shows a parent ion at 1062, leading us to suppose that **IV** decomposes in the mass spectrometer to regenerate **I** ($m/e$ 1062). The compound **VII** gives a signal at 1062, incorrectly interpreted as supporting the trimeric nature of this compound.

Since the X-ray crystal structure determination shows that **VII** is a monomeric gold(I) derivative, namely [1-benzyl-3-benzoyl-imidazolin-2-yliden]chlorogold(I), the mononuclear compounds **V** and **VI** exhibit a behaviour in the gas phase different from that of the mononuclear compound **VII**. In the mass spectrometer the monomeric carbene complexes **V** and **VI** do not decompose to regenerate the starting trimeric compound, whereas **VII** gives a fragment that does regenerate **I**. These considerations suggest that **VIII**, previously reported as a trinuclear derivative [1], might be a carbene gold(I) complex: in fact its $^{13}$C NMR spectrum shows the C-2 signal at 173.5 ppm, and the behaviour of **VII** and **VIII** in the gas phase is the same.

### 2.1. Structure determination

The monoclinic primitive cell has a volume $V_c$ 1606.5(7) Å$^3$. Assuming a reasonable density (*ca.* 2 g cm$^{-3}$), this cell contains four ($C_{17}H_{14}N_2OClAu$) units, not consistent with the earlier hypothesis of a trimeric compound ($C_{17}H_{14}N_2OClAu$)$_3$.

An ORTEP plot [5] of **VII** with the numbering scheme is given in Fig. 1.

The interatomic distances and angles are listed in Table 2. The crystal structure shows discrete molecules with a weak Au ··· Au interaction. The shortest intermolecular approaches between the molecule $x$, $y$, $z$ and the equivalent $-x$, $1/2+y$, $1/2-z$; $1-x$, $1/2+y$, $1/2-z$; $x$, $1/2-y$, $1/2+z$ and $1-x$, $1-y$, $1-z$

TABLE 1. $^{13}$C NMR and mass spectral data

| Compound | C-2 | $m/e$ | Reference |
|---|---|---|---|
| Benzylimidazole (im) | 137.78 [a] | – | 3 |
| | 137.4 [b] | | 4 |
| [Au$_3$im$_3$] (I) | 167.22 [a] | 1062 | 3 |
| [Au$_3$im$_3$I$_2$] (II) | 167.35 [b] | – | 1 |
| [Au$_3$im$_3$I$_4$] (III) | – | – | 1 |
| [Au$_3$im$_3$Cl$_6$] (IV) | 165.18 [a] | 1062 | 1 |
| [Auim(COOEt)Cl] (V) | 174.10 [b] | 462 | 1 |
| [AuimEtI] (VI) | 180.68 [b,c] | 510 | 1 |
| [Auim(COPh)Cl] (VII) | 174.87 [b] | 1062 | 1 |
| [AuimTosylCl] (VIII) | 173.5 [b] | 1062 | 1 |
| [Au(imH)$_2$Cl] | 180.33 [a] | – | 3 |

[a] Solvent DMSO. [b] Solvent CDCl$_3$. [c] Signal not observed previously.

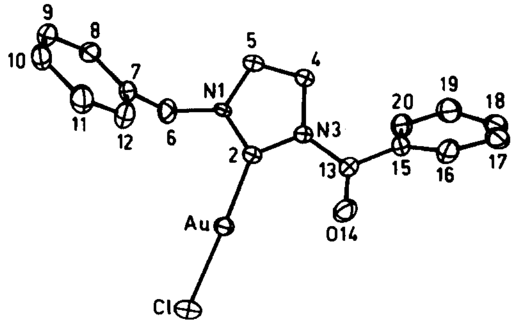


Fig. 1. ORTEP plot and numbering scheme of atoms. Thermal ellipsoids enclose 25% of the electron density. Hydrogen atoms are omitted for clarity.

TABLE 2. Interatomic distances (Å) and bond angles (°) (with e.s.d.'s in parentheses)

| | | | |
|---|---|---|---|
| Au($x$, $y$, $z$) ··· Au($1-x$, $1/2+y$, $1/2-z$) 3.4308(4) | | | |
| *In the coordination sphere:* | | | |
| Au–Cl | 2.286(2) | Cl–Au–C(2) | 176.8(3) |
| Au–C(2) | 1.97(1) | | |
| *In the ligand:* | | | |
| N(1)–C(2) | 1.33(1) | C(11)–C(12) | 1.38(1) |
| C(2)–N(3) | 1.38(1) | C(12)–C(7) | 1.37(1) |
| N(3)–C(4) | 1.420(7) | N(3)–C(13) | 1.408(8) |
| C(4)–C(5) | 1.332(9) | C(13)–O(14) | 1.202(9) |
| C(5)–N(1) | 1.396(8) | C(13)–C(15) | 1.486(9) |
| N(1)–C(6) | 1.481(8) | C(15)–C(16) | 1.39(1) |
| C(6)–C(7) | 1.53(1) | C(16)–C(17) | 1.38(1) |
| C(7)–C(8) | 1.38(1) | C(17)–C(18) | 1.39(2) |
| C(8)–C(9) | 1.38(1) | C(18)–C(19) | 1.38(2) |
| C(9)–C(10) | 1.37(1) | C(19)–C(20) | 1.39(1) |
| C(10)–C(11) | 1.38(1) | C(20)–C(15) | 1.38(1) |
| Au–C(2)–N(1) | 126.5(7) | C(8)–C(9)–C(10) | 119.9(7) |
| Au–C(2)–N(3) | 129.1(9) | C(9)–C(10)–C(11) | 119.9(8) |
| C(2)–N(1)–C(5) | 112.1(7) | C(10)–C(11)–C(12) | 120.0(9) |
| C(2)–N(1)–C(6) | 124.6(7) | C(11)–C(12)–C(7) | 121.0(8) |
| C(5)–N(1)–C(6) | 123.2(5) | N(3)–C(13)–O(14) | 120.4(6) |
| N(1)–C(2)–N(3) | 104.4(1.0) | N(3)–C(13)–C(15) | 116.5(6) |
| C(2)–N(3)–C(4) | 109.8(7) | O(14)–C(13)–C(15) | 123.1(6) |
| C(2)–N(3)–C(13) | 125.0(7) | C(13)–C(15)–C(16) | 117.5(7) |
| C(4)–N(3)–C(13) | 125.2(5) | C(13)–C(15)–C(20) | 121.3(7) |
| N(3)–C(4)–C(5) | 106.3(5) | C(16)–C(15)–C(20) | 120.8(7) |
| C(4)–C(5)–N(1) | 107.2(5) | C(15)–C(16)–C(17) | 120.2(1.0) |
| N(1)–C(6)–C(7) | 112.3(6) | C(16)–C(17)–C(18) | 118.9(1.0) |
| C(6)–C(7)–C(8) | 119.7(7) | C(17)–C(18)–C(19) | 121.6(9) |
| C(6)–C(7)–C(12) | 121.9(6) | C(18)–C(19)–C(20) | 119.1(1.1) |
| C(8)–C(7)–C(12) | 118.2(7) | C(19)–C(20)–C(15) | 119.4(9) |
| C(7)–C(8)–C(9) | 121.0(8) | | |

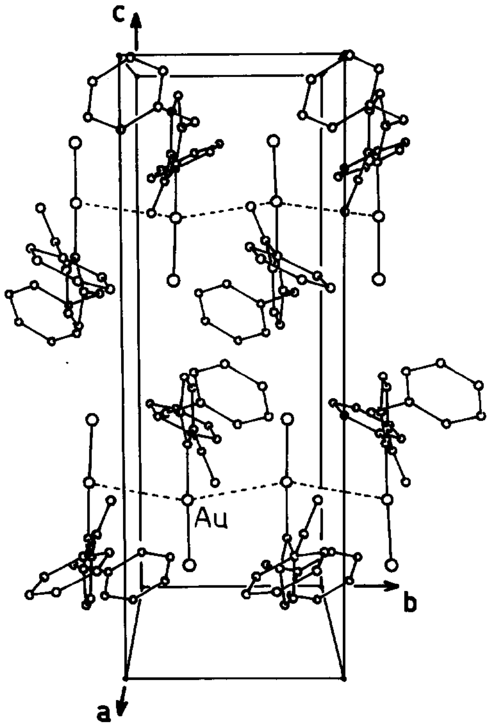


Fig. 2. Perspective packing diagram.

are normal van der Waals contacts. The molecule $x$, $y$, $z$ is in contact with the two adjacent ones $1-x$, $1/2+y$, $1/2-z$ and $1-x$, $-1/2+y$, $1/2-z$, through the $2_1$ axis, with Au ··· Au distances 3.4308(4) Å, thus giving a chain of molecules along the $b$ axis. The unit-cell packing given in Fig. 2, reveals quasi-one-dimensional linear chains with weak $Au^I \cdots Au^I$ interactions without halogen bridges such as those reported for $Au_2Cl_2C_{10}H_{16}N_2$ [6]. There are no interconnections between the Au atom chains through bridging ligands as in $[Au_2(tmb)_2Cl_2]$ [6] and no multi-dimensional $Au^I$ network. The Au ··· Au ··· Au angle is 152.857(9)°, compared with the value 163.66(4)° for $Au_2Cl_2C_{10}H_{16}N_2$ [6].

The best planes and the displacements of atoms from them, with the probability $P$ that the moieties are non-planar, are given in supplementary material. The Au atom is two-coordinate in a linear arrangement with a Cl–Au–C(2) angle 176.8(3)°. This distortion is attributable to the weak Au ··· Au interaction. The Au–Cl and Au–C bond lengths are 2.286(2) and 1.97(1) Å, respectively. The Au, C(6) and C(13) atoms are slightly displaced (−0.10, 0.17, and −0.01 Å) from the plane of the imidazole. The imidazole ring makes an angle of 25.3(4)° with the plane containing N(3)C(13)-O(14)C(15), the phenyl ring C(15)–C(20) makes an angle of 44.2(5)° with the plane N(3)C(13)O(14)-C(15),

TABLE 3. Comparison of some structural data in carbene ligands

| | **a** [a] [7] | **b** [b,c] [3] | **V** [1] | **VII** [This work] |
|---|---|---|---|---|
| *Distances (Å)* | | | | |
| M–C(2) | 2.242(7) | 2.027(7) | 1.972(8) | 1.97(1) |
| N(1)–C(2) | 1.382(8) | 1.34(2) | 1.34(1) | 1.33(1) |
| C(2)–N(3) | 1.354(8) | 1.36(2) | 1.38(1) | 1.38(1) |
| N(3)–C(4) | 1.403(8) | 1.36(2) | 1.39(1) | 1.420(7) |
| C(4)–C(5) | 1.414(9) | 1.36(1) | 1.31(1) | 1.332(9) |
| C(5)–N(1) | 1.408(9) | 1.35(1) | 1.40(1) | 1.396(8) |
| N(1)–C(6) | 1.440(8) | 1.48(1) | 1.46(1) | 1.481(8) |
| *Angles (°)* | | | | |
| M–C(2)–N(1) | 131.5(5) | 129.5(2.0) | 127.5(6) | 126.5(7) |
| M–C(2)–N(3) | 125.7(4) | 125.2(2.0) | 128.1(6) | 129.1(9) |
| N(1)–C(2)–N(3) | 102.5(5) | 104.5(4) | 104.5(7) | 104.4(1.0) |
| C(2)–N(3)–C(4) | 114.2(5) | 111.3(8) | 110.0(7) | 109.8(7) |
| N(3)–C(4)–C(5) | 105.2(5) | 106.0(6) | 107.1(8) | 106.3(5) |
| C(4)–C(5)–N(1) | 104.4(5) | 107.0(7) | 107.9(9) | 107.2(5) |
| C(5)–N(1)–C(2) | 113.6(5) | 111.1(5) | 110.6(8) | 112.1(7) |
| C(2)–N(1)–C(6) | 125.6(6) | 123.2(7) | 126.3(8) | 124.6(7) |
| C(5)–N(1)–C(6) | 120.8(5) | 125.4(1.0) | 123.1(8) | 123.2(5) |

[a] **a**: $[(CO)_5W\{CN(H)C(COOEt)C(O)NPh\}]^-$.
[b] **b**: $[Au\{CN(CH_2Ph)CH{=}CHNH\}_2]Cl$. [c] Weighted average values.

so that there is no conjugation between them. Consequently the N(3)–C(13) separation (1.408(8) Å) corresponds to a single bond.

The rather short Au–C (1.97(1) Å) and long Au–Cl (2.286(2) Å) distances found here confirm the significant *trans*-influence of the carbene ligands, already noted [1]. Table 3 gives a comparison of the most significant structural features in the carbene ligands.

Bond distances and angles in our compound **VII** correspond very well with those in the analogous compound **V**, whereas there are some significant differences from $[\mathrm{Au}\{\overline{\mathrm{CN(CH_2Ph)CH{=}CHNH}}\}_2]\mathrm{Cl}^-$ **b**, especially the longer Au–C(2) distance in **b**, due to the different *trans*-influences of carbene and chloride. The inverted relative values of the external angles Au–C(2)–N(1) and Au–C(2)–N(3) in **b**, are due to the different sizes of the substituent at N(3): H atom in **b** and COOEt or COPh in **V** and **VII**, respectively.

As for $[(\mathrm{CO})_5\mathrm{W}\{\overline{\mathrm{CNHC(COOEt)C(O)NPh}}\}]^-$ **a**, the angles inside the heterocycle compare quite well with those in compounds **b**, **V** and **VII** the only exception being the much larger C(2)–N(3)–C(4) angle in **a**. The external W–C(2)–N(1) and W–C(2)–N(3) angles are similar only to the corresponding angles in **b** because there is the same substituent on N(3). There is a greater difference between angles C(2)–N(1)–C(6) and C(5)–N(1)–C(6) in compound **a**, possibly attributable to the requirement of accommodating the CO ligands.

TABLE 4. Crystal data. Data collection, and refinement of the structure

| | |
|---|---|
| Formula | $C_{17}H_{14}N_2OClAu$ |
| Formula weight | 494.7 |
| Space group | $P2_1/c$ |
| Colour | colourless |
| $a$ (Å) | 12.847(2) |
| $b$ (Å) | 6.670(3) |
| $c$ (Å) | 18.819(1) |
| $\beta$ (°) | 94.998(8) |
| $V_c$ (Å$^3$) | 1606.5(7) |
| $Z$ | 4 |
| $D_{\mathrm{calc.}}$ (g cm$^{-3}$) | 2.05 |
| Crystal size (mm) | 0.14×0.35×0.70 |
| $\mu$(Mo K$\alpha$), (cm$^{-1}$) | 96.3 |
| Data collection instrument | Enraf-Nonius CAD4 |
| Radiation (monochromated) | Mo K$\alpha$ ($\lambda = 0.7107$ Å) |
| $T$ of data collection (K) | 293 |
| Scan mode | $\omega/2\theta$ |
| Data collection range | $2 < \theta < 30$ |
| no. of unique reflections measd. | 5170 ($h, k, \pm l$) |
| no. of data with $F_o^2 \geq 3\sigma(F_o^2)$ | 4003 |
| no. of parameters refined | 199 |
| $R^a$ and $R_w^b$ | 0.037, 0.040 |

[a] $R = (\Sigma \| F_o| - k|F_c\|)/\Sigma|F_o|$.
[b] $R_w = [\Sigma w(|F_o| - k|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

TABLE 5. Final coordinates and equivalent isotropic thermal parameters (with e.s.d.'s in parentheses)

| Atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| Au | 0.52286(2) | 0.27370(4) | 0.23667(1) | 3.001(6) |
| Cl | 0.5942(2) | 0.2837(3) | 0.1296(1) | 4.23(5) |
| N(1) | 0.5233(3) | 0.2400(10) | 0.3936(2) | 3.1(1) |
| C(2) | 0.4685(8) | 0.2727(18) | 0.3313(8) | 8.6(2) |
| N(3) | 0.3674(4) | 0.3020(8) | 0.3488(2) | 2.9(1) |
| C(4) | 0.3647(5) | 0.2955(11) | 0.4240(3) | 3.3(2) |
| C(5) | 0.4622(5) | 0.2600(14) | 0.4510(3) | 3.9(2) |
| C(6) | 0.6339(5) | 0.1746(11) | 0.4018(4) | 4.2(2) |
| C(7) | 0.7081(5) | 0.3451(12) | 0.4259(4) | 3.3(2) |
| C(8) | 0.7817(5) | 0.3165(14) | 0.4831(4) | 4.4(2) |
| C(9) | 0.8554(6) | 0.4614(17) | 0.5023(4) | 5.0(3) |
| C(10) | 0.8559(6) | 0.6367(16) | 0.4647(5) | 5.3(3) |
| C(11) | 0.7821(6) | 0.6689(15) | 0.4085(5) | 5.2(3) |
| C(12) | 0.7096(6) | 0.5229(13) | 0.3890(4) | 4.0(2) |
| C(13) | 0.2809(5) | 0.3401(11) | 0.2995(3) | 3.2(2) |
| O(14) | 0.2931(4) | 0.4092(10) | 0.2418(3) | 5.0(2) |
| C(15) | 0.1766(5) | 0.2883(13) | 0.3226(4) | 3.9(2) |
| C(16) | 0.0951(7) | 0.4206(16) | 0.3048(5) | 5.5(3) |
| C(17) | −0.0045(6) | 0.3749(21) | 0.3210(5) | 8.1(4) |
| C(18) | −0.0223(7) | 0.1923(25) | 0.3533(6) | 8.6(5) |
| C(19) | 0.0575(7) | 0.0567(21) | 0.3697(5) | 7.0(4) |
| C(20) | 0.1586(6) | 0.1061(14) | 0.3543(4) | 4.6(3) |

Bond distances in **a**, especially W–C(2), are longer than the corresponding values in **b**, **V** and **VII** (with the exceptions of the shorter C(2)–N(3) and N(1)–C(6) bonds), owing to the much stronger *trans*-influence of CO in compound **a**.

### 2.2. *X-Ray analysis*

A colourless prismatic crystal of approximate dimensions 0.14 × 0.35 × 0.70 mm was used for data collection. Accurate unit-cell parameters were obtained by a least-squares fit of $2\theta$ values for 25 reflections measured on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K$\alpha$ radiation at the Centro Grandi Strumenti dell'Università, Pavia, Italy. The monoclinic cell was confirmed by use of TRACER [8].

A summary of crystal data is given in Table 4. The intensities of 5170 independent reflections were collected at room temperature within the angular range $2 < \theta < 30$, using the $\omega/2\theta$ scan mode. The intensities of three standard reflections (6 −2 8, −4 1 −12, 8 −1 8) were monitored every 300 min, and showed no significant variation. The intensities were corrected for Lorentz and polarization effects and for absorption (minimum and maximum absorption factors 0.6517 and 0.9989) [9]. The structure factors were then placed on an approximate absolute scale by means of a Wilson plot [10]. A total of 4003 reflections having $I \geq 3\sigma(I)$ were considered to be observable and used in the structure analysis.

### *2.3. Structure determination and refinement*

The structure was solved by Patterson and Fourier methods and refined with Au, N, C, and O atoms anisotropic and hydrogen atoms at calculated positions with the $B_{iso}$ parameters of their bonded atoms, giving $R = 0.037$, $R_w = 0.040$. The average shift/e.s.d. ratio in the final refinement cycle was 0.79. At all stages of the structure analysis, the observed reflections were given unit weights. Attempts to use other weights, made at the end of the refinement, did not lead to better results. The maximum and minimum $\Delta\rho$ values on the final difference Fourier map were 0.58 and −0.46, both close to the Au atom. No extinction correction was applied.

The final atomic positional and isotropic equivalent thermal parameters are given in Table 5.

All calculations were carried out with the Enraf-Nonius SDP crystallographic computing package [11] and with local programs.

## 3. Experimental details

The reaction was monitored by thin layer chromatography on silica gel with a mixture of ethyl acetate and cyclohexane (50/50) as eluent; it was stopped when the starting compound **I** had disappeared. The starting compound **I** was prepared as described previously [3].

### *3.1. [1-Benzyl-3-benzoyl-imidazolin-2-yliden]chlorogold(I) (VII)*

A dichloromethane solution (10 ml) of **I** (0.19 mmol) and benzoyl chloride (0.66 mmol) was heated under reflux for 24 h and then evaporated to dryness; the crude product was washed with hexane and crystallized by slow evaporation of a benzene solution. White microcrystalline material was obtained after few days, yield 88%. A single crystal from this batch was used for the X-ray analysis.

Anal. Found: C, 41.24; H, 2.84; N, 5.58. $C_{17}H_{14}AuClN_2O$ calc.: C, 41.27; H, 2.85; N, 5.66%. $^1H$ NMR ($CDCl_3$) $\delta$ 7.85–7.75 m (3), 7.68 d (1), 7.6–7.52 m (2), 7.48–7.33 m (5), 7.02 d (1), 5.49 s (2). Solid state vibrational spectra in the range 500–200 $cm^{-1}$ [$\nu$(Au–Cl = 330 (IR), 329 $cm^{-1}$ (R); $\nu$(Au–C) = 465 (IR), 404 $cm^{-1}$ (R)].

## 4. Supplementary material available

Table of thermal parameters, positions of hydrogen atoms, table of mean planes, and a list of structure factors can be obtained from B.B. on request.

## Acknowledgments

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