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Reactions of symmetric *C*-imidazolylgold(I) leading to Au^I carbene complexes or mixed valence or Au^{III} imidazolyl derivatives. Crystal structure of [1-benzyl-3-(carboethoxy)imidazolin-2-yliden]chlorogold(I)

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Abstract

Reaction of trimeric 1-benzyl-2-gold(I)-imidazole, Au_3im_3 (im = [μ-(N^1-benzyl)imidazolato-N^3,C^2]) with X–Y reagents gives either gold(I) mononuclear carbene derivatives, $XAu\overline{CNRCH{=}CHN}Y$ (Y–X = Et–I or EtO(O=)C–Cl) or trinuclear mixed valence or gold(III) compounds. The gold(III) complexes, $[(X)(Y)Au]_3im_3$, are formed by addition of X–Y (benzoyl or *p*-tosyl chloride) or by reaction with thionyl chloride. With iodine and with Me_3SiI, $Au_3im_3I_2$ and $Au_3im_3I_4$, respectively, are formed. The crystal structure of $ClAu\overline{CN(CH_2Ph)CH{=}CHN}COOEt$ has been determined.

Introduction

Isolation of stable, trimeric organogold(I) compounds derived from heterocycles, such as $[(\mu\text{-Rim-}N^3,C^2)Au]_3$ (RimH = 1-benzyl- or 1-methylimidazole) [1], has allowed investigation of their behaviour in oxidative addition aimed at obtaining derivatives in which some or all of the three metal atoms have reached a higher oxidation number.

Oxidative addition to gold(I) compounds has long been known (for example, formation of dihalocyanoaurate(III) from halogen and $[Au(CN)_2]^-$) [2a], but it is not always a simple process, especially with alkylgold(I) derivatives [2b]. Furthermore, in this reaction the behaviour of polynuclear derivatives of gold(I) depends strongly on the bridging ligands: for example, trimeric derivatives of pyrazole (pzH), such as $[(\mu\text{-pz-}N,N')Au]_3$ [3], react with only one molecule of iodine to give a compound containing one Au^{III} and two Au^I coordination centres [4,5], while the trimeric derivative $[AuC(OMe){=}NMe]_3$ undergoes a stepwise addition with one, two, or three molecules of halogen [6].

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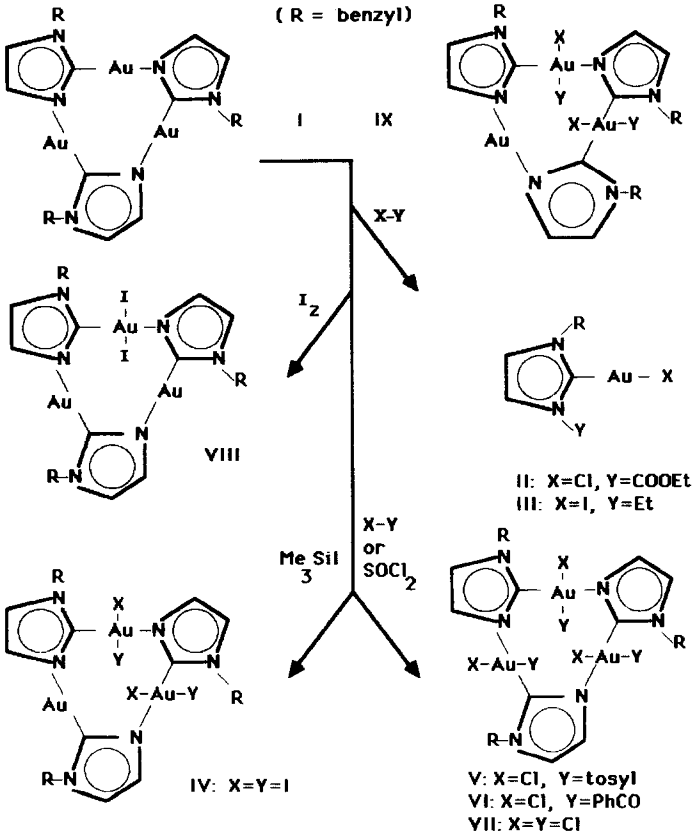
We thus decided to investigate the behaviour of another type of trimeric gold(I) compound, namely $[(\mu\text{-Rim-}N^3,C^2)\text{Au}]_3$ (I) (RimH = 1-benzylimidazole) [1], towards several reagents capable of bringing about oxidative addition. The results are reported in this paper together with the outcome of a single crystal X-ray structural study of one of the products.

Results and discussion

As shown in Scheme 1, interaction of the starting trimeric imidazolylgold(I) complex I with an X–Y reagent gave mononuclear or trinuclear compounds. In the first type of reaction, observed with ethyl chlorocarbonate or ethyl iodide, the mononuclear carbene complexes II and III were isolated rather than the expected trinuclear addition products. Clearly the Au–N bonds had been broken and the nine-membered ring destroyed while the formally covalent bond between gold and carbon had been replaced by a donor bond. In the second type of reaction a trinuclear compound, V–VII, IV, or VIII resulted, following 1 : 3, 1 : 2 or 1 : 1 addition, respectively.



Scheme 1.

Table 1

Analytical and other data [a]

Compound	Yield (%)	M.p. (°C)	Analyses (Found (calc.) (%))			Conditions [b] (crystalized from)
			C	H	N	
II	88	126–128	33.85 (33.74)	3.10 (3.04)	6.04 (6.05)	reflux, 24 h (EtOH)
III	87	99–101	28.38 (28.25)	2.82 (2.77)	5.46 (5.49)	reflux, 2 h (EtOH)
IV	62	178–80	22.72 (22.95)	1.89 (1.73)	5.13 (5.35)	0 °C, 6 h, N_2 (CH_2Cl_2/Et_2O)
V	26	150–152	37.49 (37.48)	2.98 (2.96)	5.08 (5.14)	reflux, 24 h (EtOH)
VI	88	155–157	41.24 (41.27)	2.84 (2.85)	5.58 (5.66)	reflux, 24 h (CH_2Cl_2/hexane)
VII	73	177–178	27.61 (28.25)	2.32 (2.13)	6.27 (6.59)	r.t., 15 min (CH_2Cl_2/Et_2O)
VIII	86	173–174	27.49 (27.37)	2.21 (2.07)	6.21 (6.38)	r.t., 10 min (CH_2Cl_2/Et_2O)

[a] Elemental analyses were carried out in our laboratory using a Carlo Erba 1106 instrument. [b] Solvent was dichloromethane in all cases except III where it was excess ethyl iodide.

All the compounds are stable when pure. They were identified from their elemental analyses (Table 1) and infrared and NMR data (Tables 2 and 3).

The identification of II and III as mononuclear carbene derivatives rather than trimeric addition products was established by use of various techniques but conclusive evidence was provided only by an X-ray single crystal structural study of complex II, as described below. The mass spectra of both of these compounds show

Table 2

^{1}H NMR spectral data [a]

No.	Aryl group	Imidazolyl group [b]	$PhCH_2$ [c]	Others
I	7.2–7.4m [5]	6.94d [1], 7.1d [1]	5.40 [2]	
I [h]	7.30–7.45m [5]	7.07d [1], 7.68d [1]	5.40 [2]	
II	7.35–7.45m [5]	6.96d [1], 7.60d [1]	5.51 [2]	4.50q [2], 1.62t [3] [d]
III	7.28–7.42m [5]	6.86d [1], 6.95d [1]	5.38 [2]	4.28q [2], 1.49t [3] [d]
IV	7.25–7.60m [5]	6.87d 6.90d 6.95d [1] 7.03d 7.05d 7.08d [1]	5.21, 5.37, 5.38 [2] [e]	
V	7.25–7.5m [7], 8.12s, 8.18s [2]	6.88d [1], 7.68d [1]	5.38 [2]	2.48s [3]
VI	7.33–7.48m [5], 7.52–7.6m [2], 7.75–7.85m [3]	7.02d [1], 7.68d [1]	5.49 [2]	
VII [h]	7.20–7.35m [5]	7.52d, 7.65d [2]	5.34 [f], 5.48 [2]	
VIII	7.25–7.55m [5]	6.88–7.94m [1], 7.01–7.12m [1]	5.25, 5.32, 5.40 [2]	

[a] NMR spectra were recorded on a Varian VXR-300 instrument. The solvent was $CDCl_3$ except where stated otherwise. [b] $J = 2.5$ Hz for doublets. [c] Always singlets. [d] Ethyl signals, $J = 7.5$ Hz. [e] Additional low intensity signals at 5.12s, 5.19s and 5.30s; see text. [f] Less intense signal. [g] DMSO solution.

Table 3

^{13}C NMR spectral data [a]

Compound	CH_2Ph	Imidazole and aromatic	Others
I [b]	51.90	120.19, 127.58, 127.62, 127.95, 128.51, 138.09, 167.22	
II	66.37	120.50, 120.95, 128.27, 129.15, 129.26, 133.84, 174.10	14.10, 56.69, 148.87
III	54.87	120.18, 120.26, 128.13, 128.76, 129.10, 135.06	16.50, 46.20
IV	53.78 53.88 54.32 55.12	120.44, 121.19, 122.01, 122.13, 123.00, 127.70, 128.10, 128.14, 128.40, 128.48, 128.53, 128.67 128.76, 128.89, 128.95, 129.02, 129.08, 129.16, 129.23, 129.41, 130.80, 131.38, 134.29, 136.64	
V	56.67	120.04, 120.67, 128.42, 129.30, 129.32, 129.62, 130.59, 132.85, 133.34, 147.71, 173.5	21.96
VI	56.53	120.77, 121.23, 128.34, 128.93, 129.20, 129.32, 130.85, 131.12, 133.84, 134.75, 174.87	128.21
VII [b]	52.73 53.44	119.30, 121.02, 122.17, 124.19, 127.43, 127.95, 128.17, 128.44, 128.70, 134.22, 134.80, 136.78, 165.18	
VIII	53.11 53.32 53.58	118.99, 120,22, 122.03, 127,37, 127.61, 127.75, 127.91, 128.47, 128.58, 128.74, 128.81, 128.92, 129.13, 131.21, 134.70, 137.13, 167.35	

[a] NMR spectra were recorded on a Varian VXR-300 instrument at 75 MHz in deuterated chloroform unless stated otherwise. [b] DMSO solution.

a parent ion corresponding to the monomer (*m/e* 462 and 510, respectively, but this may be due to thermal decomposition of a polynuclear complex under conditions needed for the vaporization. The ^{13}C spectra are also ambiguous: the C-2 signal of the imidazole ring, when detected (at 174.1 ppm for II in $CDCl_3$), lies at lower field than in the trimer I (167.2 ppm in DMSO), but is not comparable with the value found for another carbene complex of gold(I), namely 180.3 ppm for bis(1-benzylimidazolin-2-yliden)gold(I) chloride [1]) in DMSO.

The affinity of gold(I) for the heterocyclic carbene present in II is shown by the failure of an attempt to remove this ligand. Whereas with other carbene complexes of gold displacement is possible, and is followed by a rearrangement to a stable isomer, a formamidine [7], the ligand displaced by action of Ph_3P on III

$$(R{-}NH)_2C{-}AuCl + Ph_3P \rightleftharpoons R{-}NH{-}CH{=}NR + Ph_3PAuCl$$

enters into the coordination sphere of another gold atom to yield the bis(carbene)gold(I) chloride plus Ph_3PAuCl.

Oxidative addition was found to take place in the other cases studied here (III–VIII), but the results were variable and there is some evidence that the ring may be opened and closed again during some of the reactions. With iodine both a 1 : 1 and a 1 : 2 derivative can be formed; the 1 : 1 compound, VIII, was formed directly from the element (even if in excess), while the latter, IV, rather than the expected silicon-containing compound, was formed by the action of trimethyliodosilane. The 1 : 3 adducts were obtained by reaction with *p*-tosyl or benzoyl chloride (compounds V and VI, respectively) or thionyl chloride (compound VII).

For the 1 : 1 and 1 : 2 addition products (IV and VIII), the formulation as trinuclear compounds is based only on the analytical data (Table 1), since no molecular weight determinations were possible. All the polynuclear molecules reported here decompose in the mass spectrometer: the 1 : 1 and 1 : 2 iodine adducts decompose by an unidentified route, probably involving reactions of the fragments with iodine, the 1 : 3 adducts (V, VI and VII) under the same conditions regenerate the starting material, I (*m/e* 1062), thus confirming indirectly their trimeric nature.

The appearance in the NMR spectra (Table 2 and 3) of the 1 : 3 adducts V and VI of only one set of signals is consistent either with the presence of only one of the possible isomers which can result from three additions or with fluxional behaviour of the nine-membered ring. This second possibility is unlikely because in the other trinuclear compounds IV and VII the isomers are stable enough to be detected. These two compounds are the only products obtained by treatment of I with Me_3SiI or with thionyl chloride; during the reaction, which is unlikely to be a simple addition, the nine-membered ring of I may be broken and reformed; as a consequence an asymmetric isomer such as IX is formed in which the gold centres do not bear the same coordinating atoms: N_2, C_2 or NC. It is noteworthy that recent crystal structure determination carried out on an iridium(I) derivative of the same imidazolyl ligand, namely $[(OC)_2Ir(\mu\text{-1-benzyl-2-imidazolyl-}N^1,C^2]_2$, has shown [8] that the molecule is not symmetric and that the two coordination centres are different: one the two metals has a C_2N_2 environment, and the other a C_4 environment.

Structure determination

An ORTEP [9] representation of the molecule of the compound II with the numbering scheme is shown in Fig. 1. The interatomic distances and angles are listed in Table 4.

The crystal structure of II involves discrete molecules with no Au $\cdots$ Au interaction. The shortest intermolecular approaches between the molecule (x, y, z) and the equivalent ones, $x, y+1, z$; $x, y+1, z+1$; $x, y+1, z-1$; $-x+1, -y+1, -z+2$ are normal van der Waals contacts. The best planes, and the displacements of atoms from them, with the probability *P* that the moieties are non-planar, are given in

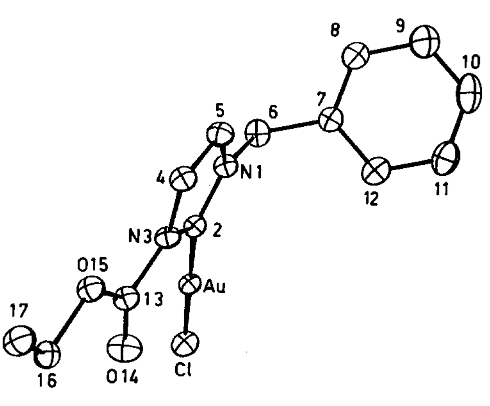


Fig. 1. ORTEP plot and atom numbering scheme. Thermal ellipsoids enclose 30% of the electron density. Hydrogen atoms are omitted for clarity.

Table 4

Bond lengths (Å) and angles (°) for non-hydrogen atoms

In the coordination sphere:			
Au–Cl	2.271(3)	Cl–Au–C(2)	179.9(3)
Au–C(2)	1.972(8)		
In the ligand:			
N(1)–C(2)	1.34(1)	C(9)–C(10)	1.37(3)
C(2)–N(3)	1.38(1)	C(10)–C(11)	1.36(2)
N(3)–C(4)	1.39(1)	C(11)–C(12)	1.37(2)
C(4)–C(5)	1.31(1)	C(12)–C(7)	1.38(2)
C(5)–N(1)	1.40(1)	C(13)–N(3)	1.42(1)
N(1)–C(6)	1.46(1)	C(13)–O(14)	1.18(1)
C(6)–C(7)	1.49(1)	C(13)–O(15)	1.32(1)
C(7)–C(8)	1.37(2)	O(15)–C(16)	1.48(1)
C(8)–C(9)	1.37(2)	C(16)–C(17)	1.51(2)
Au–C(2)–N(1)	127.5(6)	C(6)–C(7)–C(12)	121(1)
Au–C(2)–N(3)	128.1(6)	C(8)–C(7)–C(12)	119(1)
C(2)–N(1)–C(5)	110.6(8)	C(7)–C(8)–C(9)	121(1)
C(2)–N(1)–C(6)	126.3(8)	C(8)–C(9)–C(10)	119(1)
C(5)–N(1)–C(6)	123.1(8)	C(9)–C(10)–C(11)	121(1)
N(1)–C(2)–N(3)	104.5(7)	C(10)–C(11)–C(12)	119(1)
C(2)–N(3)–C(4)	110.0(7)	C(11)–C(12)–C(7)	121(1)
C(2)–N(3)–C(13)	123.8(7)	N(3)–C(13)–O(14)	123.7(9)
C(4)–N(3)–C(13)	126.2(8)	N(3)–C(13)–O(15)	109.0(7)
N(3)–C(4)–C(5)	107.1(8)	O(14)–C(13)–O(15)	127.3(9)
C(4)–C(5)–N(1)	107.9(9)	C(13)–O(15)–C(16)	115.6(7)
N(1)–C(6)–C(7)	112.6(8)	O(15)–C(16)–C(17)	107.2(8)
C(6)–C(7)–C(8)	120(1)		

Table 5. Both the imidazole ring and the N(3) C(13) O(14) O(15) group are planar, the maximum deviation being < 0.01 Å.

The Au^{I} atom is two-coordinate, in a linear arrangement with a Cl–Au–C(2) angle of 179.9(3)°; the Au–Cl and the Au–C bond lengths are 2.271(3) and 1.972(8) Å, respectively. The three atoms Au, C(6) and C(13) lie in the plane of the imidazole (deviation < 0.05 Å), showing that there is no difficulty in accommodating the substituents on the ring. This ring makes an angle of 12.65(3)° with the plane of the carboxylato group (i.e. N(3) C(13) O(14) O(15)), so that there is no conjugation between them; consequently the N(3)–C(13) length (1.42(1) Å) corresponds to a single bond.

Comparison between the Au–C distance found here (1.972(8) Å), where the carbene ligand is opposite to chlorine, and that in the linear bis carbene complex reported previously [1] (2.027(7) Å), shows that carbene ligands have a significant *trans*-influence, stronger than that of a chloride ligand. The same conclusion is indicated when the Au–Cl bond distance, 2.271(3), is compared with that of 2.257(4) Å reported for the salt [^{n}Bu$_4$][AuCl$_2$]$^-$ [10] and with those found in other linear gold(I) derivatives containing an L–Au–Cl arrangement, in which there are shorter or longer Au–Cl distances if L has a weaker or a stronger *trans*-influence; for example: 2.256(8) Å, (L = piperidine [11]), 2.262(3) Å (a metallated pyrazole [12]) or 2.279(3) Å, (L = Ph$_3$P [13]), 2.305(8) and 2.306(8) Å (L = Et$_3$P [14]).

Table 5

Planarity of molecular regions

Plane	Equation[a], χ^2, P	Atoms[b]	Displacements (Å)
I	$-0.6910X' + 0.4117Y' - 0.5941Z' + 9.0579 = 0$	N(1) *	0.000(8)
		C(2) *	−0.002(9)
		N(3) *	0.003(7)
	$\chi^2 = 0.61$ ($n = 2$) $P = 26.3\%$	C(4) *	−0.005(10)
		C(5) *	0.004(10)
		Au	0.0154(4)
		C(6)	−0.043(11)
		C(13)	−0.044(9)
II	$-0.6140X' + 0.6010Y' - 0.5117Z' + 6.7362 = 0$	N(3) *	0.000(7)
		C(13) *	−0.002(9)
		O(14) *	0.001(8)
	$\chi^2 = 0.064$ ($n = 1$) $P = 19.2\%$	O(15) *	0.000(7)
		C(2)	−0.277(8)
		C(4)	0.211(10)
		C(16)	0.119(11)

[a] Transformation matrix from triclinic X, Y, Z to orthogonal X', Y', Z' coordinates:

$$\begin{pmatrix} \sin\gamma & 0 & -\sin\alpha\cos\beta^* \\ \cos\gamma & 1 & \cos\alpha \\ 0 & 0 & \sin\alpha\sin\beta^* \end{pmatrix}$$

[b] Starred (*) atoms were included in the calculation of the plane.

Within the heterocycle, here and in the other carbene complex of gold [1], the internal angle at N(1) is equal to that at N(3) and that at C(4) is equal to that at C(5); moreover, the external angles at N(1), C(2) and N(3) are not very different, as if there were a symmetry axis passing through C(2) and bisecting the segment C(4)–C(5). As shown in Table 6 the values for the most significant distances or angles in the carbene ligands present in II correspond fairly well not only with those found in the bis(carbene)gold(I) cation [1] but also with those reported [15] for $[(OC)_5W\{\overline{CN(H)C(CO_2Et)C(O)N}Ph\}]^-$, an anion in which a differently substituted but still planar imidazolin-2-ylidene ligand is present.

Table 6

Comparison of molecular parameters inside the heterocycle

	II	[a,b]	[c]
Distance (Å)			
C–NR	1.34(1)	1.342(24)	1.382(8)
angles (°)			
M–C–NR	127.5(6)	129.5(20)	131.5(5)
N–C–N	104.5(7)	104.5(4)	102.5(5)
C2–N1–CH2	126.3(8)	123.2(7)	–
C5–N1–CH2	123.1(8)	125.4(10)	–

[a] Average values. [b] Bis(1-benzylimidazolin-2-yliden)gold(I) chloride [1].
[c] $[(OC)_5W\{\overline{CN(H)C(CO_2Et)C(O)N}Ph\}]^-$ [15].

X-Ray analysis

A suitable crystal of II was used for data collection. Accurate unit-cell dimensions were obtained by a least-squares fit of 2ϑ values for 25 reflections measured on a Philips PW1100 computer-controlled single-crystal diffractometer with graphite-monochromated Mo-K_α radiation at the Department of Organic Chemistry, University of Padua, Italy; the triclinic nature of the unit cell was confirmed by the use of the TRACER program [16]. The intensities of 3516 independent reflections were collected. The intensities of three standard reflections monitored showed no significant variation. The usual Lorentz and polarization factors and an empirical absorption correction [17], with minimum and maximum absorption factors of 1.0040 and 1.6176, were applied. An approximate absolute scale and a mean thermal factor of 3.98 Å^2 were determined by Wilson's method [18].

In all 3046 reflections having $I \geqslant 3\sigma(I)$, ($\sigma(I)$ based on counting statistics) were considered to have observable intensity and employed in the structure analysis. A summary of crystal data is given in Table 7.

Table 7

Crystal data, data collection, and refinement of the structure

Formula	$C_{13}H_{14}N_2O_2ClAu$
F.W.	462.69
Space group	$P\bar{1}$
Color	colorless
a, Å	14.950(2)
b, Å	7.374(1)
c, Å	6.878(1)
α, deg	92.62(1)
β, deg	103.11(1)
γ, deg	97.81(1)
V_c, Å^3	729.3(2)
Z	2
D_{calcd}, g cm^{-3}	2.11
Crystal size, mm	0.15×0.15×0.40
μ (Mo-K_α), cm^{-1}	106.0
Data collection instrument	Philips PW 1100
Radiation (monochromated)	Mo-K_α (λ = 0.7107 Å)
T of data collection, K	293
Scan mode	$\vartheta/2\vartheta$
Scan speed, deg s^{-1}	0.030
Scan width, deg	1.20
Data collection range (ϑ)	$2 \leqslant \vartheta \leqslant 28$
stds (measured every 180 min)	2 1 2, −2 −2 1, 3 1 −2
No. of unique reflections measured	3516 ($\pm h$, $\pm k$, l)
No. of data with $F_o^2 \geqslant 3\sigma(F_o^2)$	3046
No. of parameters refined	172
R [a] and R_w [b]	0.037, 0.039
Quality-of-fit indicator [c]	2.94

[a] $R = (\Sigma \| F_o | - k | F_c \|)/\Sigma | F_o |$. [b] $R_w = [\Sigma w(| F_o | - k | F_c |)^2/\Sigma w | F_o |^2]^{1/2}$; $w = \sigma^{-2}(| F_o |)$. [c] Quality-of-fit $= [\Sigma w(| F_o | - k | F_c |)^2/(N_{obs.} - N_{par.})]^{1/2}$.

Table 8

Final coordinates and equivalent isotropic thermal parameters (with esd's in parentheses)

Atom	x	y	z	B (Å^2)
Au	0.77448(3)	0.57346(5)	0.74133(5)	3.31(1)
Cl	0.7577(2)	0.3162(3)	0.5340(4)	5.09(8)
N(1)	0.7516(5)	0.8170(9)	1.0795(10)	3.5(2)
C(2)	0.7888(6)	0.7967(11)	0.9215(12)	3.1(2)
N(3)	0.8378(5)	0.9677(9)	0.9118(10)	3.4(2)
C(4)	0.8299(6)	1.0883(12)	1.0666(13)	3.7(3)
C(5)	0.7768(6)	0.9967(12)	1.1680(14)	4.0(3)
C(6)	0.6952(7)	0.6737(14)	1.1578(16)	4.5(3)
C(7)	0.6001(6)	0.7170(12)	1.1539(15)	4.0(3)
C(8)	0.5713(8)	0.7349(17)	1.3275(16)	5.9(4)
C(9)	0.4824(9)	0.7632(19)	1.3264(21)	7.4(5)
C(10)	0.4239(8)	0.7839(18)	1.1477(25)	7.1(5)
C(11)	0.4508(8)	0.7691(16)	0.9723(19)	6.0(4)
C(12)	0.5393(8)	0.7358(13)	0.9755(16)	4.9(4)
C(13)	0.8914(6)	1.0077(12)	0.7690(13)	3.7(3)
O(14)	0.8861(5)	0.9106(8)	0.6241(10)	5.7(3)
O(15)	0.9452(4)	1.1666(8)	0.8252(8)	4.1(2)
C(16)	0.9996(7)	1.2358(15)	0.6826(15)	4.3(3)
C(17)	1.0390(8)	1.4344(15)	0.7509(16)	4.8(4)

Structure determination and refinement

The structure was solved by standard Patterson and Fourier methods. The position of the unique gold atom was determined from a three-dimensional Patterson map. A difference electron density synthesis phased on the Au atom revealed the positions of all the non-hydrogen atoms. The full-matrix least-squares refinement [19] of the positional and first isotropic and later anisotropic thermal parameters of the non-hydrogen atoms reduced R to 0.053. The positions of the hydrogen atoms were then calculated from the geometry of the compound and checked on a three-dimensional difference Fourier map. The least-squares refinement, with the hydrogen atoms included in fixed positions with the same isotropic thermal parameters of the parent atoms, reduced R to 0.037 (R_w 0.039) after three cycles. In the early stages of the analysis the observed reflections were given unit weights; in the last three cycles a weight $w = \sigma^{-2}(|F_o|)$ was used.

The atomic scattering factors for the non-hydrogen atoms were taken from *International Tables* [20], and for hydrogen atoms those of Stewart [21] were used. The final atomic positional and isotropic equivalent thermal parameters are given in Table 8.

Tables of thermal parameters, of bond lengths and angles for hydrogen atoms, and a list of structure factors can be obtained from B.B.

Experimental

The reactions were monitored by thin layer chromatography on silica gel with a mixture of ethyl acetate and cyclohexane (20 : 80) as eluent; they were stopped when the starting compound I had disappeared. Each reaction was carried out at least twice under the conditions detailed in Table 1, and sometimes under different conditions which are not described because they led to either lower yields or to crude products prone to decomposition. The starting material was prepared as described previously [1]. A typical preparation is described below and essential additional details are in Table 1.

Tris[(μ-(N^1*-benzyl)imidazolato-*N^3,C^2*)(chloro)benzoyl)Au^{III}], VI*

A dichloromethane solution (10 mL) of I (100 mg; 94.1 mmol) and benzoyl chloride (463 mg; 329 mmol) was refluxed for 24 h and then evaporated to dryness; the residue was crystallized from dichloromethane/hexane to give an analytical sample of VI.

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