Journal of Organometallic Chemistry, 375 (1989) 147–160
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20070

Reactions of *C*-imidazolyllithium derivatives with Group Ib compounds: tris[μ-(1-alkylimidazolato-N^3,C^2)]tri-gold(I) and -silver(I). Crystal structure of bis(1-benzylimidazolin-2-yliden)gold(I) chloride

Flavio Bonati, Alfredo Burini *, Bianca Rosa Pietroni
Dipartimento di Scienze Chimiche dell'Università, 62032 Camerino (Italy)

and Bruna Bovio
Dipartimento di Chimica Generale dell' Università, viale Taramelli 12, 27100 Pavia (Italy)

(Received April 14th, 1989)

Abstract

Upon reaction of LMX (M = Au, X = Cl, L = PPh_3 or Me_2S; M = Ag, X = NO_3, L = Me_2S) with 1-R-2-lithiumimidazole the lithium is replaced by a noble metal to give the species $(1\text{-R-2-M-imidazole})_n$ (M = Au, R = methyl or benzyl, $n = 3$; M = Ag, R = benzyl). From Me_2SCuBr the compound bis(1-R-imidazol-2-yl) was obtained (R = methyl or benzyl). The unexpected formation during work up of $[Au(\overline{CN(CH_2Ph)CH{=}CHN}H)2]Cl$, a carbene derivative, was confirmed by an X-ray crystal structural study which showed the presence of two independent molecules where C–Au–C is 175.2(4) or 176.6(4)°, average Au–C is 2.027(7) Å, and there is an Au $\cdots$ Au interaction at 3.2630(5) Å.

Introduction

Organic compounds of gold(I) or of silver(I) are stable provided that a suitable ancillary ligand is available so that the metal can reach two-coordination, as in R_3PAuR, where R is alkyl or aryl. Nevertheless, an ancillary ligand is not always necessary and an organogold or organosilver compound, $[(X{-}Y)M]_n$ where M is Au or Ag, can be obtained if the organic group $[X{-}Y]^-$ contains a donor atom and its geometry is such as to allow the formation of oligomers or of polymers, e.g.: $[(X{-}Y)M]_3$ where (X–Y) is C(OR)=NR′ and M is Au [1] or Ag [2] or $[(X{-}Y)Au]_n$ where (X–Y) is C(NHR)=NR′ [3], respectively. In the case of gold the trimer was found to be reasonably stable and its existence was ascertained in the solid or gaseous phase as well as in solution [1]; it was therefore suggested that such an

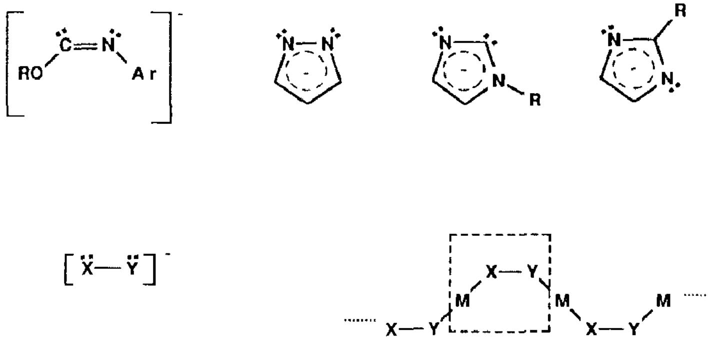


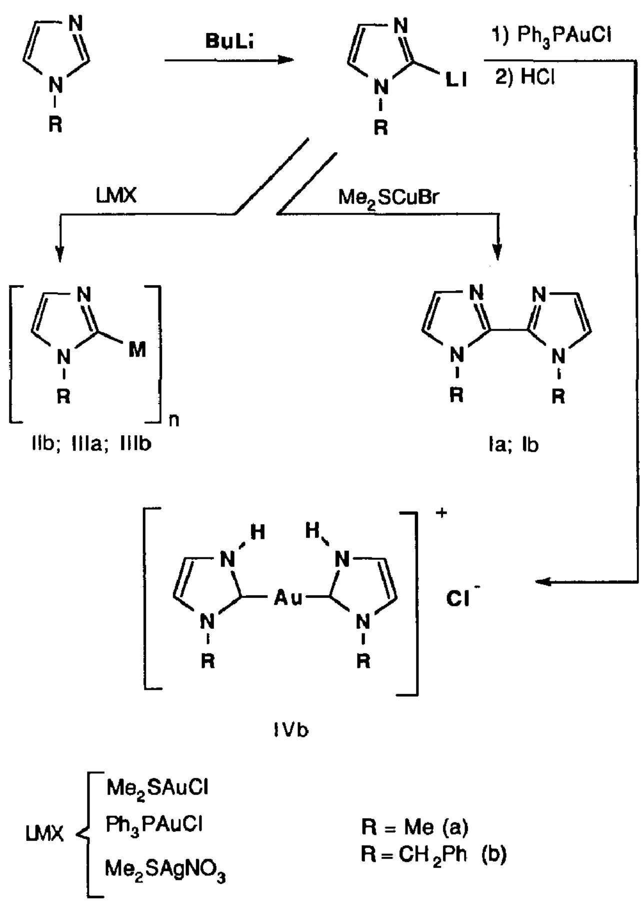
Fig. 1. Some of the exobidentate [X–Y]$^-$ ligands: (alkoxy)(arylimino)methyl, pyzolato-*N*,*N*′, imidazolato-N^3,C^2, and imidazolato-*N*,*N*′ (upper line) and polymer resulting upon coordination to M^+.

arrangement should be possible with other exobidentate (i.e. bidentate and bridging) mononegative anions, as in Fig. 1, although the existence of additional oligomers or polymers could not be excluded. The C(OR)=NR′ group can indeed be replaced by the pyrazolato-*N*,*N*′ ligand, affording comparable coordination oligomers, such as [Au(μ-pyrazolato-*N*,*N*′)]$_n$ [4a], where *n* may be 3 [4b] or more [4c]: compared with the C(OR)=NR′ group additional stability is provided here by the pseudo-aromatic ring. However, when the same group was replaced by another heteroaromatic ring, such an imidazolato-*N* ligand, no oligomeric but only monomeric (ligand)Au(imidazolato-*N*) or polymeric [Au(μ-imidazolato-*N*,*N*′)]$_n$ species were obtained [5].

In view of all these results, it was decided to try an imidazolato-N^3,C^2 as a mononegative and exobidentate ligand. This ligand is sterically and electronically comparable with a pyrazolato-*N*,*N*′; it is obtained less readily than this latter, but is likely to be a stronger donor, in the same way as with metal derivatives an alkyl is a better nucleophile than an amide. Besides, a *C*-derivative is expected to be a softer donor than a similar *N*-derivative, and its interaction with gold(I), a very soft acceptor [6], is expected to be favoured. Finally, an additional interest in studying the interaction between noble metals and imidazoles lies in the use of this class of heterocycles as corrosion inhibitors, as well as in the relevance of some of the resulting compounds in the anticorrosion mechanism [7].

Results and discussion

While a pyrazolato-*N* or an imidazolato-*N* can be easily made, for example from the heterocycle and alkali metal hydroxide in methanol, the preparation of a C^2-imidazolato requires deprotonation of an 1-substituted imidazole with an alkyllithium. The interaction of the 1-alkyl-2-lithium-imidazole, Li(imR) (see Scheme 1), with LAuCl (L = Me_2S or Ph_3P) gave the corresponding [Au(imR)]$_n$ compounds (IIIa, R = methyl; IIIb, R = benzyl) as air- and light-stable colourless solids; they were identified through analyses (Table 1), infrared spectra, and proton (Table 2) and ^{13}C NMR data (Table 3). It is remarkable that no LAu(imR) compound has been isolated, even for L = triphenylphosphine; on the other hand with azolato-*N* ligands, Ph_3PAu(pyrazolato-*N*) [4a] and several R_3PAu(imidazolato-*N*) [8,5] compounds have been isolated, the latter type being remarkably stable. The difference in behaviour of the *N*-aurated and *C*-aurated imidazoles is consistent with a bigger



Scheme 1

Table 1

Analytical and other data [a]

Compound	Yield (%)	M.p. (°C)	Analyses (Found (calc) (%))			MW (Found (calc))
			C	H	N	
Ia	14	105–107	58.89 (59.24)	6.12 (6.21)	34.77 (34.54)	
Ib	76	148–150	76.29 (76.41)	5.67 (5.77)	17.57 (17.82)	314 (314.39)
IIb	53	172–175	45.23 (45.31)	3.41 (3.42)	10.38 (10.57)	
IIIa	40	272–275 (dec.)	17.65 (17.28)	1.83 (1.81)	9.74 (10.07)	834 (834.19)
IIIb	54 [b]–89 [c]	240–242	34.54 (33.91)	2.58 (2.56)	7.64 (7.91)	1062 (1062.36)
IVb [d]	68	195–196 (dec.)	43.79 (43.77)	3.69 (3.67)	10.20 (10.21)	

[a] Elemental analyses were performed in our Microanalytical Laboratory (Carlo Erba 1106 elemental microanalyzer); for IVb complete elemental analyses were carried out by Mikroanalytisches Labor. Pascher, Bonn, Germany. Mass spectra were recorded on VG 7070 instrument. [b] Method A (see Experimental section). [c] Method B (see Experimental section). [d] Additional data: Found (calc) (%): Au, 36.00 (35.89); Cl, 6.31 (6.46).

Table 2

^{1}H NMR spectral data [a]

Compound	Aryl protons	Other protons
Ia	6.98 d [1]; 7.12 d [1]	4.02 s [3]
Ib	6.9–7.4 m [7]	5.73 s [2]
IIb	6.95 d [1]; 7.0 d [1]; 7.2–7.4 m [5]	5.28 s [2]
IIIa	6.96 d [1]; 7.15 d [1]	3.80 s [3]
IIIb	6.94 d [1]; 7.1 d [1]; 7.2–7.4 m [5]	5.40 s [2]
IVb	7.3–7.4 m [10]; 7.47 d [2]; 7.65 d [2]	5.41 s [4]; 13.17 s,br [2] [b]

[a] NMR spectra were recorded on a Varian VXR-300 instrument at 300 MHz. The solvent was DMSO for IVb, but for all the others $CDCl_3$ was used. The reference was external Me_4Si; s, singlet; d, doublet; m, multiplet; br, broad. [b] The signal disappears on deuteration.

difference in the *trans*-influence between triphenylphosphine and *C*-imidazolyl than that between the same ligand (or class of ligands) and *N*-imidazolyl.

The same reactions were carried out with silver(I) (see Scheme 1): compound IIb was obtained from Me_2SAgNO_3. With Me_2SCuBr a reaction was observed; a yellow insoluble intermediate was formed, but this was not isolated because it reacted, probably with adventitious oxygen, to give eventually a blue solution of copper(II) and a solid, identified as bis(1-R-imidazol-2-yl) (Ia, R = methyl; Ib R = benzyl). It should be noted that in the presence of imidazole oxygen oxidizes smoothly even massive metallic copper to polymeric $[Cu(im\text{-}N,N')_2]_n$ [7b].

The molecular weights of the gold compounds IIIa and IIIb were established by mass spectroscopy, and indicate a trimeric structure ($n = 3$): the presence of a heavier oligomer cannot be ruled out completely, but it would have to break down completely to the trimer in the mass spectrometer. The solubility of the gold and of the silver compounds rules out the formation of polymers; in addition the NMR evidence also rules out the simultaneous presence of different oligomers, for example of a trimer and a hexamer. In conclusion, a trimeric structure is likely for IIIa, IIIb (Fig. 2) and, by analogy, also for IIb, but the future isolation of other oligomers cannot be ruled out.

Table 3

^{13}C NMR spectral data [a]

Compound	CH_2	CH_3	C(2)	Other
Benzylimidazole [b]	49.44		137.78	119.56; 127.40; 127.65; 128.63; 128.70
Benzylimidazole [c,d]			137.4	119.7(C5); 129.7(C4)
Ib [b]	49.62		138.01	122.39; 127.01; 127.28; 127.89; 128.41; 137.52
IIb [c]	53.34		138.54	118.07; 127.47; 127.56; 128.36; 128.64; 129.89
IIIb [b]	51.90		167.22	120.19; 127.58; 127.62; 127.95; 128.51; 138.09
IVb [b]	53.39		180.33	119.52; 121.50; 127.50; 127.92; 128.63; 136.97
Methylimidazole [c,d]			137.6	129.3(C4); 119.7(C5)
Ia [b]		35.35	138.36	122.71; 127.74
IIIa [c]		35.47	167.21	121.00; 127.36

[a] NMR were recorded on a Varian VXR-300 instrument at 300 MHz. [b] The solvent used was DMSO. [c] The solvent used was $CDCl_3$. [d] M. Begtrup, J. Elguero et al., Magn. Res. Chem., 26 (1988) 134.

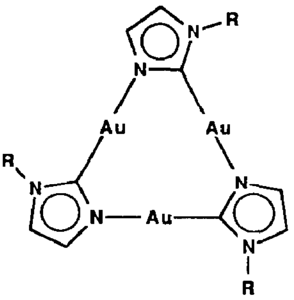


Fig. 2. IIIa, R = Me; IIIb, R = CH_2Ph.

In the ^{13}C NMR spectra (Table 3) of the gold compounds all the expected signals but one are found in approximately the same position as for the starting imidazole, imR, or the bis(1-R-imidazol-2-yl) compounds Ia and Ib. An exception involves the signal due to 2-C, which is displaced downfield by ca. 40 ppm compared with that from the corresponding metal-free imidazole. The observed displacement may be due to the presence of the metal or to the fact that the interaction between one Au(ImR-*N*) donor moiety and the neighbouring gold(I) acceptor is not fully represented by the classical formula **a** and that additional contribution from canonical structures such as **b**, **c**, or **d** in Fig. 3 must be considered; or, in other words, the said interaction is depicted by **e**.

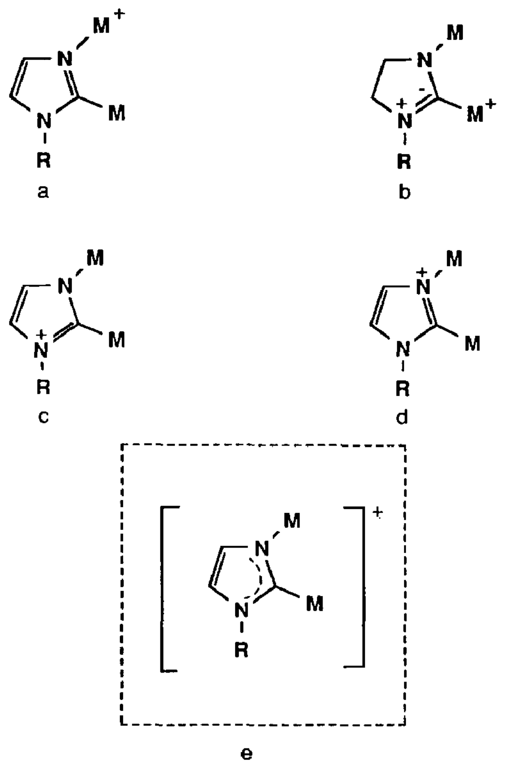


Fig. 3. Canonical structures (**a**–**d**) and resulting formulation for the $M(imR)M^+$ moiety.

Table 4

Bond lengths (Å) and angles (°) (with e.s.d.'s in parentheses)

AuA ··· AuB	3.2630(5)		
Molecule A			
In the coordination sphere			
Au–C(2)	2.01(1)	C(2)–Au–C(2′)	175.2(4)
Au–C(2′)	2.02(1)		
In the imidazolyl ligand			
N(1)–C(2)	1.42(1)	N(1′)–C(2′)	1.34(1)
C(2)–N(3)	1.28(2)	C(2′)–N(3′)	1.37(1)
N(3)–C(4)	1.40(1)	N(3′)–C(4′)	1.36(1)
N(3)–H(3)	0.95	N(3′)–H(3′)	0.95
C(4)–C(5)	1.41(2)	C(4′)–C(5′)	1.36(2)
C(5)–N(1)	1.33(1)	C(5′)–N(1′)	1.38(1)
N(1)–C(6)	1.48(1)	N(1′)–C(6′)	1.48(1)
C(6)–C(7)	1.47(1)	C(6′)–C(7′)	1.50(1)
C(2)–N(1)–C(5)	112.4(1.1)	C(2′)–N(1′)–C(5′)	111.0(8)
C(2)–N(1)–C(6)	123.2(8)	C(2′)–N(1′)–C(6′)	124.5(8)
C(5)–N(1)–C(6)	124.4(9)	C(5′)–N(1′)–C(6′)	124.4(7)
Au–C(2)–N(1)	123.7(9)	Au–C(2′)–N(1′)	131.7(8)
Au–C(2)–N(3)	132.0(9)	Au–C(2′)–N(3′)	124.2(7)
N(1)–C(2)–N(3)	104.0(9)	N(1′)–C(2′)–N(3′)	104.1(8)
C(2)–N(3)–C(4)	112.6(1.0)	C(2′)–N(3′)–C(4′)	112.2(8)
N(3)–C(4)–C(5)	105.7(1.1)	N(3′)–C(4′)–C(5′)	105.6(9)
C(4)–C(5)–N(1)	105.2(1.0)	C(4′)–C(5′)–N(1′)	107.1(8)
N(1)–C(6)–C(7)	112.6(8)	N(1′)–C(6′)–C(7′)	112.9(8)
C(6)–C(7)–C(8)	119.5(1.0)	C(6′)–C(7′)–C(8′)	121.7(1.0)
C(6)–C(7)–C(12)	121.2(9)	C(6′)–C(7′)–C(12′)	119.1(9)
Molecule B			
In the coordination sphere			
Au–C(2)	2.042(9)	C(2)–Au–C(2′)	176.6(4)
Au–C(2′)	2.031(9)		
In the imidazolyl ligand			
N(1)–C(2)	1.29(1)	N(1′)–C(2′)	1.34(1)
C(2)–N(3)	1.41(1)	C(2′)–N(3′)	1.36(1)
N(3)–C(4)	1.31(1)	N(3′)–C(4′)	1.36(1)
N(3)–H(3)	0.95	N(3′)–H(3′)	0.94
C(4)–C(5)	1.35(2)	C(4′)–C(5′)	1.35(2)
C(5)–N(1)	1.35(1)	C(5′)–N(1′)	1.35(1)
N(1)–C(6)	1.47(1)	N(1′)–C(6′)	1.50(1)
C(6)–C(7)	1.48(2)	C(6′)–C(7′)	1.48(2)
C(2)–N(1)–C(5)	111.2(9)	C(2′)–N(1′)–C(5′)	110.0(9)
C(2)–N(1)–C(6)	123.7(8)	C(2′)–N(1′)–C(6′)	121.3(8)
C(5)–N(1)–C(6)	125.0(9)	C(5′)–N(1′)–C(6′)	128.6(9)
Au–C(2)–N(1)	133.6(8)	Au–C(2′)–N(1′)	127.8(7)
Au–C(2)–N(3)	121.4(6)	Au–C(2′)–N(3′)	124.2(7)
N(1)–C(2)–N(3)	105.0(8)	N(1′)–C(2′)–N(3′)	104.6(8)
C(2)–N(3)–C(4)	109.2(8)	C(2′)–N(3′)–C(4′)	111.5(8)
N(3)–C(4)–C(5)	107.8(1.0)	N(3′)–C(4′)–C(5′)	104.9(1.0)
C(4)–C(5)–N(1)	106.7(9)	C(4′)–C(5′)–N(1′)	108.9(9)
N(1)–C(6)–C(7)	112.8(9)	N(1′)–C(6′)–C(7′)	111.5(9)
C(6)–C(7)–C(8)	118.8(1.0)	C(6′)–C(7′)–C(8′)	121.5(1.1)
C(6)–C(7)–C(12)	120.0(9)	C(6′)–C(7′)–C(12′)	119.2(1.0)

Table 4 (continued)

In hydrogen bridges			
Cl(1) · · · N(3′)A		3.133(8)	
Cl(1) · · · H(3′)A		2.20	
Cl(1) · · · H(3′)A · · · N(3′)A		168	
Cl(1) · · · N(3)B		3.144(8)	
Cl(1) · · · H(3)B		2.22	
Cl(1) · · · H(3)B · · · N(3)B		165	
Cl(2) · · · N(3)A		3.151(9)	
Cl(2) · · · H(3)A		2.20	
Cl(2) · · · H(3)A · · · N(3)A		177	
Cl(2) · · · N(3′)B		3.132(8)	
Cl(2) · · · H(3′)B		2.19	
Cl(2) · · · H(3′)B · · · N(3′)B		176	
In the phenyl rings			
(Weighted average of bond distances and endocyclic angles)			
C(7)–C(*ortho*)	1.395(6)	C(*ipso*)	119.7(5)
C(*ortho*)–C(*meta*)	1.395(7)	C(*ortho*)	119.9(4)
C(*meta*)–C(*para*)	1.392(9)	C(*meta*)	120.5(5)
		C(*para*)	119.2(9)

In one of our preparations, opening of tetrahydrofuran solvent occurred incidentally, with formation of a mixture of carboxylic acids, carbonyl compounds, and, in small yield, a solid identified as bis(1-benzylimidazolin-2-yliden)gold(I)chloride

Table 5

Average bond distances (Å) and angles (°) with their standard errors [a]

	N	x_m	σ_m	σ'_m
Au–C(2)	4	2.027	0.007	0.005
N(1)–C(2)	4	1.342	0.024	0.006
C(2)–N(3)	4	1.360	0.022	0.007
N(3)–C(4)	4	1.357	0.019	0.007
C(4)–C(5)	4	1.363	0.012	0.009
C(5)–N(1)	4	1.355	0.012	0.007
N(1)–C(6)	4	1.480	0.007	0.007
C(6)–C(7)	4	1.484	0.006	0.008
C(2)–Au–C(2′)	2	175.9	0.7	0.3
Au–C(2)–N(1)	4	129.5	2.0	0.4
Au–C(2)–N(3)	4	125.2	2.0	0.4
C(2)–N(1)–C(5)	4	111.1	0.4	0.5
N(1)–C(2)–N(3)	4	104.5	0.2	0.4
C(2)–N(3)–C(4)	4	111.3	0.8	0.4
N(3)–C(4)–C(5)	4	106.0	0.6	0.5
C(4)–C(5)–N(1)	4	107.0	0.7	0.4
C(2)–N(1)–C(6)	4	123.2	0.7	0.4
C(5)–N(1)–C(6)	4	125.4	1.0	0.4
N(1)–C(6)–C(7)	4	112.5	0.3	0.4
C(6)–C(7)–C(8)	4	120.3	0.7	0.5
C(6)–C(7)–C(12)	4	119.9	0.5	0.5

[a] All values were calculated from Ref. 9.

(IVb). This product was then obtained in good yield working up the reaction mixture in an acidic environment, as described in Experimental section. Compound IVb was characterized by complete elemental analysis, IR and NMR spectra, conductivity, and an X-ray crystal structure determination. The crystal contains two independent cations in which the gold shows approximately linear two-coordination, and the average Au–C distance is 2.027(7) Å; in each $(PhCH_2)NCAuCN(CH_2Ph)$ moiety the benzyl groups lie on opposite sides. The interatomic distances

Table 6

Planarity of molecular regions

Plane	Equation [a], χ^2, P	Atoms [b]	Displacements (Å)
Molecule A			
I	$0.2087X' + 0.1147Y' - 0.9712Z' + 3.5628 = 0$	N(1) *	−0.012(8)
		C(2) *	0.019(9)
		N(3) *	−0.013(8)
	$\chi^2 = 11.36$ ($n = 2$) $P > 99\%$	C(4) *	0.012(12)
		C(5) *	0.008(11)
		C(6)	−0.109(11)
		Au	0.2333(4)
II	$0.9013X' - 0.0229Y' - 0.4327Z' - 0.0648 = 0$	N(1′) *	−0.002(8)
		C(2′) *	0.005(11)
		N(3′) *	−0.002(9)
	$\chi^2 = 0.43$ ($n = 2$) $P = 19.2\%$	C(4′) *	0.000(11)
		C(5′) *	0.004(12)
		C(6′)	−0.086(10)
		Au	0.0770(4)
Molecule B			
III	$0.2401X' - 0.0864Y' - 0.9669Z' + 1.0615 = 0$	N(1) *	−0.001(8)
		C(2) *	0.000(8)
		N(3) *	0.001(8)
	$\chi^2 = 0.21$ ($n = 2$) $P = 9.8\%$	C(4) *	−0.004(12)
		C(5) *	0.003(11)
		C(6)	0.074(11)
		Au	0.0306(4)
IV	$0.8924X' + 0.0409Y' - 0.4493Z' - 3.4137 = 0$	N(1′) *	0.006(9)
		C(2′) *	−0.013(10)
		N(3′) *	0.008(8)
	$\chi^2 = 3.69$ ($n = 2$) $P = 83.4\%$	C(4′) *	−0.011(12)
		C(5′) *	−0.001(14)
		C(6′)	0.069(12)
		Au	−0.3391(4)

Interplanar angles (°)

I/II 52.7 III/IV 49.8

---

[a] Transformation matrix from monoclinic 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.

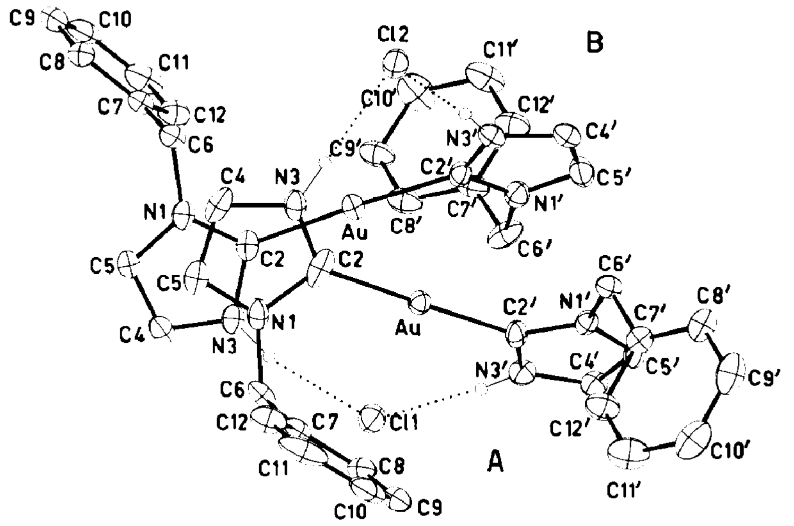


Fig. 4. ORTEP plot and numbering scheme of atoms. Thermal ellipsoids enclose 30% of electron density. Hydrogen atoms are omitted for clarity.

and bond angles in two independent molecules are listed in Table 4; the average values with their standard deviation are given in Table 5. An ORTEP [10] representation of the molecule with the numbering scheme is shown in Fig. 4. The cations have virtual C_2 symmetry but exhibit no real crystallographic symmetry, and all the atoms occupy general positions. The least-squares planes of the pentaatomic rings, the displacements of atoms from them, the χ^2 values with the probability P that the rings are non-planar and the angles between them, are given in Table 6. As shown in Table 7 the average values for the most significant distances or angles in our cation correspond fairly well with those reported by Fehlhammer [11] for the anion $[(CO)_5W\{\overline{CN(H)C(CO_2Et)C(O)N}Ph\}]^-$. A differently-substituted but equally planar imidazolin-2-ylidene ligand is present in both complexes, so that also the nature of the 2-C is the same in both, and, indeed, in the ^{13}C NMR spectrum of the tungsten or gold derivative the chemical shift for the 2-C atom is found approximately 30 ppm downfield of that for an imidazole.

Table 7

Comparison of some structural data relating to compound IV and to $[(OC)_5W\{\overline{CN(H)C(CO_2Et)C(O)N}Ph\}]^-$

	Au [a]	W [b]
Distances (Å)		
C–NH	1.360(22)	1.354(8)
C–NR	1.342(24)	1.382(8)
Angles(°)		
M–C–NH	125.2(2.0)	125.7(4)
M–C–NR	129.5(2.0)	131.5(5)
N–C–N	104.5(4)	102.5(5)

[a] Weighted average values. [b] From Ref. 11.

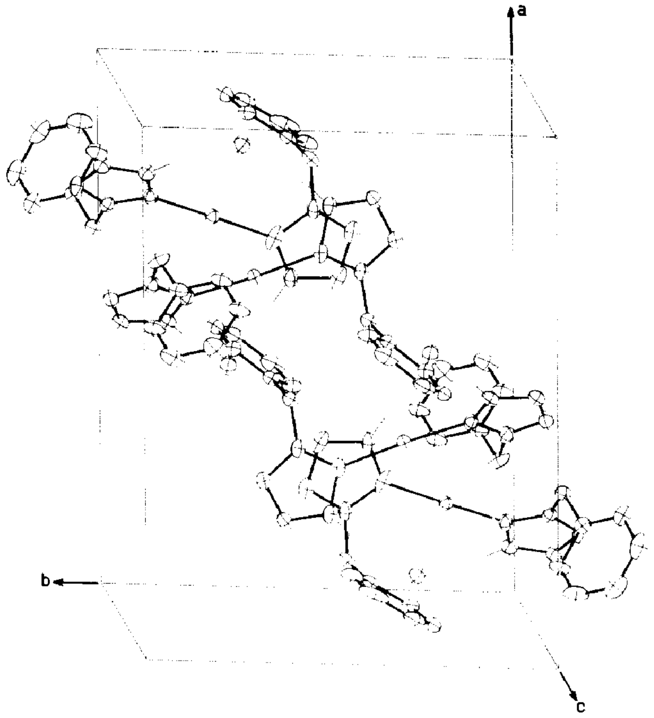


Fig. 5. Packing in the unit cell along *c*.

Interaction between gold atoms is possible and may be attractive [12a] or repulsive [12b]: here the Au(A)–Au(B) separation is 3.2630(5) Å, and the C–Au–C angles are 175.2(4) or 176.6(4)°. These values are quite similar to those found for Au $\cdots$ Au separations in the crystal of $[\mathrm{AuC(OEt){=}N}(p\text{-tolyl})]_3$ [1d], in which the presence of Au $\cdots$ Au interactions is shown by the asymmetry and non-planarity of the nine-membered ring; on the other hand, the similar nine-membered ring present in various $[\mathrm{Au}\{\mu\text{-}(\mathrm{pz}\text{-}N,N')\}]_3$ compounds (pzH = 3,5-bis(trifluoromethyl)- [4b] or 3,5-diphenylpyrazole [13a]), or in $\mathrm{Cl_2Au}[\{\mu\text{-}(\mathrm{pz}\text{-}N,N')\mathrm{Au}\}]_2$ [13b], is symmetric and planar, and the angles around gold are 180°, or very near to this value, because Au $\cdots$ Au intramolecular interactions are hindered by the substituents.

The two Cl^- ions join the two independent cations in a dimeric unit through four hydrogen bridges, whereas the shortest intermolecular approaches between this dimeric unit and the equivalent ones are normal Van der Waals contacts.

Experimental

The reactions were carried out under nitrogen and monitored by TLC (eluent 20 ethyl acetate/80 cyclohexane).

1-Alkyl-2-lithiumimidazole, Li(imR). To a solution of 1-alkyl-imidazole (2.5 mmol) in 10 ml of anhydrous freshly distilled tetrahydrofuran (THF) at −40°C was added the stoichiometric quantity of n-butyllithium (1.6 molar in hexane). After 1.5 h stirring the resulting solution was used.

Bis(1-alkyl-imidazol-2-yl), Ia (R = methyl) and Ib (R = benzyl). Solid dimethylsulphidebromidecopper(I) (0.52 g; 2.5 mmol) was added to a solution of Li(imR) at

0 ° C. After 2 h stirring at room temperature the solution was evaporated to dryness and the residue extracted with dichloromethane. The extract was washed with aqueous ammonia till the extract was colourless, then with water, dried over sodium sulphate and evaporated to dryness to leave an analytically pure sample.

1-Benzyl-2-silver-imidazole (IIb). Solid dimethylsulphidenitratosilver(I) (0.58 g; 2.5 mmol) was added to a solution at −40 ° C of Li(bzim). After 0.5 h stirring in the dark the brown suspension was evaporated to dryness and the residue extracted with benzene. An analytically pure sample was obtained by addition of hexane.

1-Alkyl-2-gold-imidazole, IIIa (R = methyl) and IIIb (R = benzyl).

(*Method A*). Solid triphenylphosphinechlorogold(I) (1.25 g; 2.5 mmol) was added to the solution of Li(imR) at −40 ° C. After 1 h stirring at room temperature, methanol (1 ml) was added and the solution evaporated to dryness. The residue was extracted with dichloromethane (15 ml), and the brown extract was washed with water until neutral, dried over sodium sulphate, and evaporated to dryness. The solid left was washed with hexane until no triphenylphosphine was detected in the washings. The analytical samples IIIa and IIIb were obtained by recrystallization from dichloromethane/hexane or by slow evaporation of a solution of the crude product in THF.

(*Method B*). The preparation was carried out in the same way as that described under method A above, but starting from dimethylsulphidechlorogold(I) (0.59 g; 2.34 mmol). The reaction was carried on for 15 min at −40 ° C.

Bis(1-benzylimidazolin-2-yliden)gold(I) chloride (IVb). Solid triphenylphosphinechlorogold(I) (1.25 g; 2.5 mmol) was added to the solution of Li(bzim) at −40 ° C. After 1 h stirring at room temperature, methanol (1 ml) was added and the solution evaporated to dryness. The residue was extracted with dichloromethane (15 ml) and the brown extract washed with aqueous hydrochloric acid (0.1 *N*; 3 × 50 ml). The pale yellow dichloromethane solution was dried over sodium sulphate and evaporated to dryness. The residual solid was stirred overnight with hexane, and then with THF at 50 ° C for 5 h, then filtered off and recrystallized from ethanol/diethyl ether to afford the analytical sample IVb, a crystal of which was taken for the X-ray structural determination.

Conductivity measurements were carried out at 25 ° C with a Philips GM 4249 bridge; the solvent was dimethyl sulfoxide, which had a specific conductivity of $2.17 \times 10^{-6}\ \Omega^{-1}$. A 1 mmolar solution 1 mmol had $\lambda = 53\ \mathrm{ohm}^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$.

X-ray analysis

The crystal used for the X-ray diffraction measured approximately 0.08 × 0.24 × 0.16 mm. Unit cell dimensions were derived from 25 measurements on a single crystal Philips PW1100 computer-controlled diffractometer with graphite-monochromated Mo-K_α radiation at the Dipartimento of Organic Chemistry, University of Padua (Italy) and by least-squares refinement of 2ϑ values; the triclinic cell was confirmed by the use of TRACER [14] The intensities were measured at room temperature with the $\vartheta/2\vartheta$ scan mode (scan width = 1.2°, scan speed = 0.030 deg s^{-1}) within the angular range $2 \leqslant \vartheta \leqslant 250°$. The intensities of three standard reflections were monitored every 180 min and showed no significant variation. Of the 7040 reflections collected, 5044 with $I \geqslant 3\sigma(I)$ were regarded as observed and used in the structure analysis. The intensities were corrected for Lorentz and polarization effects and for absorption [15], with minimum and maximum absorp-

Table 8. Final coordinates and equivalent isotropic thermal parameters for nonhydrogen atoms (with e.s.d.'s in parentheses)

Atom	x	y	z	B (Å^2)
Cl(1)	0.0381(2)	0.2448(2)	0.0627(3)	5.55(9)
Cl(2)	0.5176(2)	0.2573(2)	0.5141(3)	6.03(10)
Molecule A				
Au	0.22208(2)	0.20884(3)	0.39457(4)	3.58(1)
N(1)	0.2102(6)	0.4589(5)	0.4444(7)	4.6(3)
C(2)	0.2667(9)	0.3645(9)	0.4468(8)	6.0(5)
N(3)	0.3451(6)	0.4055(7)	0.4784(7)	4.7(3)
C(4)	0.3444(9)	0.5223(9)	0.4905(11)	6.0(5)
C(5)	0.2548(9)	0.5539(9)	0.4678(10)	5.6(4)
C(6)	0.1135(7)	0.4507(8)	0.4231(10)	4.9(4)
C(7)	0.0908(6)	0.4083(8)	0.5326(9)	4.4(3)
C(8)	0.0437(7)	0.3092(10)	0.5197(13)	6.1(5)
C(9)	0.0242(9)	0.2670(13)	0.6221(18)	7.7(6)
C(10)	0.0511(10)	0.3250(17)	0.7387(19)	9.2(8)
C(11)	0.0970(9)	0.4237(17)	0.7548(13)	8.8(7)
C(12)	0.1172(7)	0.4649(11)	0.6509(11)	6.1(4)
N(1′)	0.2014(5)	−0.0459(6)	0.3753(7)	3.8(2)
C(2′)	0.1790(7)	0.0551(8)	0.3281(10)	4.3(3)
N(3′)	0.1181(5)	0.0335(7)	0.2143(7)	4.3(3)
C(4′)	0.1034(7)	−0.0775(8)	0.1903(10)	4.7(4)
C(5′)	0.1567(8)	−0.1288(8)	0.2927(10)	5.1(4)
C(6′)	0.2618(6)	−0.0658(8)	0.5018(10)	4.4(3)
C(7′)	0.2143(7)	−0.1032(8)	0.5920(9)	4.5(3)
C(8′)	0.2447(8)	−0.1930(9)	0.6684(10)	5.5(4)
C(9′)	0.2003(12)	−0.2227(11)	0.7542(12)	7.8(6)
C(10′)	0.1228(11)	−0.1663(14)	0.7607(13)	7.8(6)
C(11′)	0.0946(9)	−0.0760(14)	0.6863(12)	7.7(6)
C(12′)	0.1360(8)	−0.0459(10)	0.5985(11)	6.1(5)
Molecule B				
Au	0.30093(2)	0.28469(3)	0.16945(4)	3.67(1)
N(1)	0.2814(6)	0.5390(6)	0.1417(7)	4.3(3)
C(2)	0.2476(7)	0.4413(7)	0.1393(8)	4.0(3)
N(3)	0.1553(5)	0.4598(6)	0.1060(7)	4.4(3)
C(4)	0.1387(7)	0.5664(9)	0.0907(11)	5.4(4)
C(5)	0.2172(8)	0.6187(8)	0.1119(11)	5.3(4)
C(6)	0.3767(7)	0.5585(8)	0.1655(11)	5.0(4)
C(7)	0.3994(6)	0.5936(8)	0.0520(10)	4.4(4)
C(8)	0.4543(7)	0.6853(9)	0.0625(13)	6.0(4)
C(9)	0.4802(8)	0.7151(11)	−0.0421(17)	6.9(6)
C(10)	0.4509(9)	0.6580(14)	−0.1575(15)	7.2(6)
C(11)	0.3952(9)	0.5654(14)	−0.1662(13)	7.5(6)
C(12)	0.3707(7)	0.5318(10)	−0.0594(11)	5.7(4)
N(1′)	0.3155(6)	0.0327(6)	0.1349(8)	4.7(3)
C(2′)	0.3473(6)	0.1261(7)	0.2018(9)	4.1(3)
N(3′)	0.4073(5)	0.0897(6)	0.3072(7)	4.2(3)
C(4′)	0.4107(7)	−0.0238(9)	0.3086(12)	5.2(4)
C(5′)	0.3529(9)	−0.0578(9)	0.1989(13)	6.0(5)
C(6′)	0.2499(8)	0.0374(10)	0.0066(10)	5.9(4)
C(7′)	0.2917(7)	0.0752(9)	−0.0875(9)	4.9(3)
C(8′)	0.2631(10)	0.1714(11)	−0.1537(11)	7.9(6)
C(9′)	0.3048(12)	0.2039(15)	−0.2409(18)	7.5(6)
C(10′)	0.3745(13)	0.1421(14)	−0.2633(11)	8.8(7)
C(11′)	0.4032(8)	0.0459(14)	−0.1971(14)	8.0(6)
C(12′)	0.3615(7)	0.0135(10)	−0.1099(11)	5.9(4)

tion factors of 1.0054 and 2.9340. An approximate absolute scale factor and a mean thermal parameter of 5.0133 Å^2 were determined by Wilson's method [16].

Crystal data. $C_{20}H_{20}N_4ClAu$. FW 548.87; triclinic, $a = 15.746(3)$, $b = 11.999(1)$, $c = 11.105(1)$ Å, $\alpha = 92.29(2)$, $\beta = 106.83(1)$, $\gamma = 88.77(2)°$; $V_c = 2006.6(4)$; $Z = 4$; $D_c = 1.82$ g cm^{-3}; $F(000) = 1056$; $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å; $\mu(\text{Mo-}K_\alpha) = 77.18$ cm^{-1}. Space group $P\bar{1}$.

Structure determination and refinement

The positions of two gold and two Cl atoms were obtained from a three-dimensional Patterson map, and refined, with isotropic thermal parameters, to $R = 0.149$, in three cycles of full-matrix least-squares. All the remaining non-hydrogen atoms were located from a three-dimensional difference Fourier synthesis phased on the Au and Cl. The full-matrix least-squares refinement of the positional and first isotropic and later anisotropic thermal parameters reduced R to 0.076. The positions of the hydrogen atoms calculated from the geometry of the compound and checked on a final difference Fourier map were not refined. Further refinement, with the hydrogen atoms included at fixed positions with the same isotropic thermal parameters of their bonded atoms, reduced R to 0.047 ($Rw = 0.050$). At all stages of the structure analysis, the observed reflections were given unit weights, since the use of weight $\sigma^{-2}(|F_o|)$ led to the same results but also to some nonpositive-definite thermal factors. The GOF value is 2.83 [$GOF = \Sigma\, w|\Delta F|^2/(NO - NV)$]. A final difference Fourier map showed maximum and minimum $\Delta\rho$ values 0.054 and -0.042 eÅ^{-3}, both close to the Au atoms. The atomic scattering factors for non-hydrogen atoms were taken from ref. 17 and those for hydrogen atoms from ref. 18. Anomalous dispersion effects were included in the scattering factors. The final atomic coordinates are given in Table 8. Tables of thermal parameters and a list of structure factors can be obtained from one of the authors (B. Bovio) on request.

Acknowledgments

We thank the "Ministero della Pubblica Istruzione" and the C.N.R. for financial support.

References

1 (a) G. Minghetti and F. Bonati, Angew. Chem., 84 (1972) 482; Angew. Chem., Int. Ed. Engl., 11 (1972) 429; (b) F. Bonati and G. Minghetti, Inorg. Chem., 13 (1974) 1600; (c) G. Minghetti and F. Bonati, Gazz. Chim. Ital., 102 (1972) 205; (d) A. Tiripicchio, M. Tiripicchio Camellini and G. Minghetti, J. Organomet. Chem., 171 (1979) 399; (e) M. Landi, L.F. Zerilli, G. Minghetti and G. Banditelli, Ann. Chim. (Rome), 64 (1974) 239.

2 (a) G. Minghetti, F. Bonati and M. Massobrio, J. Chem. Soc., Chem. Commun., (1973) 260; (b) G. Minghetti, F. Bonati and M. Massobrio, Inorg. Chem., 14 (1975) 1974.

3 F. Bonati and G. Minghetti, J. Organomet. Chem., 59 (1973) 403.

4 (a) F. Bonati, G. Minghetti and G. Banditelli, J. Chem. Soc., Chem. Commun., (1974) 88; (b) B. Bovio, F. Bonati and G. Banditelli, Inorg. Chim. Acta, 87 (1984) 25; (c) G. Banditelli, A.L. Bandini, F. Bonati, R.G. Goel and G. Minghetti, Gazz. Chim. Ital., 112 (1982) 539.

5 B. Bovio, F. Bonati, A. Burini and B.R. Pietroni, Z. Naturforsch. B, 39 (1984) 1747.

6 S. Ahrland and S. Balzamo, Inorg. Chim. Acta, 142 (1988) 285.

7 (a) G. Xue, Q. Dai and S. Jiang, J. Am. Chem. Soc., 110 (1988) 2393; (b) G. Xue, S. Jiang, X. Huang, G. Shi and B. Sun, J. Chem. Soc., Dalton Trans., (1988) 1487.

8 (a) F. Bonati, M. Felici, B.R. Pietroni and A. Burini, Gazz. Chim. Ital., 112 (1982) 5; (b) F. Bonati, A. Burini, M. Felici and B.R. Pietroni, Gazz. Chim. Ital., 113 (1983) 105; (c) F. Bonati, A. Burini, B.R. Pietroni, S. Calogero and F.E. Wagner, J. Organomet. Chem., 309 (1986) 363; (d) F. Bonati, A. Burini, B.R. Pietroni, E. Giorgini and B. Bovio, J. Organomet. Chem., 344 (1988) 119.

9 A. Domenicano, A. Vaciago and C.A. Coulson, Acta Crystallogr., B31 (1975) 221.

10 C.K. Johnson, ORTEP, Report ORNL-3793, Oak Ridge National Laboratory Tennessee, U.S.A. (1965).

11 W.P. Fehlhammer, A. Voelkl, U. Plaia and G. Beck, Chem. Ber., 120 (1987) 2031.

12 (a) P.K. Mehrotra and R. Hoffmann, Inorg. Chem., 17 (1978) 2187; (b) Y. Jiang, S. Alvarez and R. Hoffmann, Inorg. Chem., 24 (1985) 749; (c) H. Schmidbaur, W. Graf and G. Mueller, Angew. Chem. Int. Ed. Engl., 27 (1988) 417; (d) J. Vicente, M.T. Chicote, I. Saura-Llamas, P.G. Jones, K. Mayer-Baese and C.F. Erdbruegger, Organometallics, 7 (1988) 997.

13 (a) H.H. Murray, R.G. Raptis and J.P. Fackler Jr., Inorg. Chem., 27 (1988) 26; (b) M.N.I. Khan, S. Wang, D.D. Heinrich and J.P. Fackler Jr., Acta Crystallogr., Cryst. Struct. Commun., C44 (1988) 822.

14 S.L. Lawton, R.A. Jacobson, TRACER, a cell reduction program, Ames Laboratory, Iowa State University of Science and Technology, Ames, IA, (1965).

15 A.C.T. North, D.C. Phillips and F.C. Mathews, Acta Crystallogr., A24 (1968) 351.

16 A.J.C. Wilson, Nature, 150 (1942) 152.

17 International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, (1974).

18 R.F. Stewart, F.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.