Oxidative addition of mono and bis(carbene) complexes derived from imidazolyl and thiazolyl gold(I) compounds

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Abstract

A series of cationic imidazolinylidene and thiazolinylidene gold(III) complexes was synthesized by the oxidative addition of halogens to the corresponding bis(carbene) gold(I) compounds. Similar reactions with the thiazolyl-derived mono(carbene) gold(I) complex only give mono(carbene) halogold(I) compounds. Quantum mechanical calculations employing the GAUSSIAN92 series of programs at the DFT/HF (hybrid density functional theory) level were carried out for the model complexes [Au(CNHCH=CHNH)₂Cl₂]⁺ and [Au(CNHCH=CHNH)₂]⁺ and compared to the molecular structure of the imidazolinylidene gold(III) compound [Au(CNMeCH=CHNMe)₂Cl₂][CF₃SO₃] as well as an analogous gold(I) complex. © 1997 Elsevier Science S.A.

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1. Introduction

Oxidative addition of gold(I) acyclic carbene complexes is the most important route to the formation of gold(III) carbene complexes [1–5]. Neutral mono(carbene) complexes and cationic bis(carbene) complexes have been used in such reactions. We have recently reported a rather simple method involving sequential transmetallation and protonation or alkylation for the synthesis of cyclic azole-derived carbene (or azolinylidene) compounds [6,7]. In this paper, the attempted oxidation of some of these complexes is described. We extended the previous approach of Bonati [1,2] and Laguna [2,4] for acyclic carbene complexes by using Cl₂, Br₂ as well as I₂ as oxidants and in the process discovered: (i) the unusual spontaneous decomposition of certain gold(III) compounds; (ii) that certain mono(carbene) types are unstable towards such oxidative additions; (iii) that unexpected ¹³C chemical shifts of the carbene carbon atoms in the gold(III) complexes are exhibited.

In addition, an X-ray structural study of the cationic chloro(imidazolinylidene) gold(III) compound, [Au(CNMeCH=CHNMe)₂Cl₂][CF₃SO₃], was undertaken, and quantum mechanical calculations employing the GAUSSIAN92 series of programs [8] at the DFT/HF (hybrid density functional theory) level were carried out for the model complexes [Au(CNHCH=CHNH)₂Cl₂]⁺ and [Au(CNHCH=CHNH)₂]⁺, and compared with the X-ray data. The principal aim of this theoretical study was to evaluate whether DFT calculations can play a useful role in the determination of the structures and bond distances of larger organogold compounds. Such applications of more advanced calculations are of particular interest to us and will also be the theme of future papers.

2. Results and discussion

The analytical and physical data for all the new compounds described are presented in Table 1, while ¹H NMR and ¹³C-{¹H} NMR spectroscopic results appear in Tables 2 and 3 respectively. The counterion CF₃SO₃ is not shown in the schemes.

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Table 1
Analytical and physical data

Complex	Yield(%)	M.p. (°C)	Colour	Analysis (%)		
				C	U	N
1a	90	219–220	Colourless	21.6(21.7)	2.8(2.7)	9.2(9.2)
1b	63	217–218	Light yellow	18.7(18.9)	2.2(2.3)	8.1(8.0)
1c	84	200–201	Orange	16.4(16.7)	1.9(2.0)	6.8(7.0)
2a	68	176 (decomp.)	Colourless	18.6(18.6)	2.0(2.1)	9.8(9.6)
2b	65	169 (decomp.)	Light yellow	16.0(16.1)	1.6(1.8)	8.5(8.4)
2c	89	197 (decomp.)	Orange	14.2(14.2)	1.5(1.3)	7.2(7.3)
3a	73	152–154	Yellow	17.5(17.6)	1.6(1.6)	4.5(4.6)
3b	68	172–174	Orange	15.1(15.4)	1.4(1.4)	4.1(4.0)
3c	32	197 (decomp.)	Red	11.4(11.4)	1.0(1.2)	3.3(3.3)
4a	64	83–85	Yellow	17.4(17.6)	1.6(1.5)	4.5(4.6)
4b	57	91–93	Orange	15.4(15.4)	1.2(1.4)	4.1(4.0)
4c	27	179 (decomp.)	Red	11.2(11.4)	1.1(1.2)	3.4(3.3)
5a	64	187–189	Yellow	20.7(20.5)	2.0(2.2)	4.3(4.4)
5b	52	174–176	Orange	17.9(18.0)	1.9(1.9)	3.8(3.8)
5c	41	230 (decomp.)	Red	13.9(13.7)	1.7(1.6)	3.2(3.3)
7a	52	183–184	Yellow	14.6(14.5)	1.5(1.5)	4.0(4.2)
7b	38	166–169	Orange	12.6(12.8)	1.4(1.3)	4.1(4.2)
10	48	115–118	Yellow	12.0(11.9)	1.4(1.3)	3.6(3.5)

2.1. Oxidative addition of bis(carbene) gold(I) complexes

The gold(III) imidazolinylidene and thiazolinylidene complexes 1a–c, 2a–c, 3a–b, 4a–b and 5a–b (Scheme 1) were prepared by the simple addition of halogens to the corresponding gold(I) bis(carbene) compounds 1–5

[6]. In contrast, however, the reactions of bis(thiazolinylidene) compounds with iodine, only produced mono(carbene) iodogold(I) compounds. These reactions are believed to involve initial formation of the gold(III) bis(carbene) complexes which then quickly and spontaneously undergo reductive elimination to form the carbene (iodo)gold compounds 3c–5c (and probably the

Table 2
^{1}H NMR data

Complex	H^4	H^5	NCMe	NH	NMe
1	7.14(4H, s)	7.14(4H, s)	–	–	3.98(12H, s)
1a	7.66(4H, s)	7.66(4H, s)	–	–	4.13(12H, s)
1b	7.67(4H, s)	7.67(4H, s)	–	–	4.07(12H, s)
1c	7.69(4H, s)	7.69(4H, s)	–	–	3.95(12H, s)
2	7.44(2H, d, J = 1.9)	7.36(2H, d, J = 1.9)	–	12.02(2H, br s)	3.94(6H, s)
2a	7.63(4H, s)	7.63(4H, s)	–	12.54(2H, br s)	4.11(6H, s)
2b	7.66(2H, d, J = 2.0)	7.64(2H, d, J = 1.9)	–	12.38(2H, br s)	4.05(6H, s)
2c	7.66(2H, d, J = 2.0)	7.63(2H, d, J = 1.9)	–	12.27(2H, br s)	3.94(6H, s)
3	8.54(2H, d, J = 4.2)	8.15(2H, d, J = 4.2)	–	–	4.42(3H, s)
3a	8.54(2H, d, J = 3.7)	8.40(2H, d, J = 3.7)	–	–	4.55(6H, s)
3b	8.55(2H, d, J = 3.7)	8.42(2H, d, J = 3.7)	–	–	4.50(6H, s)
3c	8.53(1H, d, J = 3.7)	8.42(1H, d, J = 3.7)	–	–	4.38(3H, s)
4	–	7.02(2H, s)	2.43(6H, s)	12.42(2H, br s)	–
4a	–	7.92(2H, s)	2.67(6H, s)	6.50(2H, br s)	–
4b	–	7.95(2H, s)	2.68(6H, s)	–	–
4c	–	7.38(1H, s)	2.61(3H, s)	8.50(1H, br s)	–
5	–	7.73(2H, s)	2.61(6H, s)	–	4.33(6H, s)
5a	–	8.01(2H, s)	2.71(6H, s)	–	4.42(6H, s)
5b	–	7.96(2H, s)	2.60(6H, s)	–	4.41(6H, s)
5c	–	8.05(1H, s)	2.74(3H, s)	–	4.25(3H, s)
7	–	7.08(2H, s)	2.43(6H, s)	13.40(1H, br s)	–
7a	–	7.64(1H, s)	2.57(3H, s)	13.30(1H, br s)	–
7b	–	7.44(1H, s)	2.63(3H, s)	13.20(1H, br s)	–
10	–	7.98(1H, s)	2.67(3H, s)	13.6(1H, br s)	–

Table 3
^{13}C NMR data

Complex	C²	C⁴	C⁵	CMe	NMe
1	185.7	123.9	123.9	–	38.1
1a	154.5	126.1	126.1		37.8
1b	154.1	126.4	126.4	–	38.1
1c	145.6	126.7	126.7		38.3
2	182.8	123.0	119.8	–	38.0
2a	160.6	125.3	121.6	–	37.5
2b	150.6	125.5	122.1	–	37.9
2c	144.1	125.6	122.4	–	38.3
3	206.9	140.2	125.9	–	44.9
3a	182.6	141.2	128.5	–	44.2
3b	178.9	141.3	129.0	–	45.6
3c	185.2	141.3	129.7	–	45.6
4	205.7	144.9	117.1	13.2	–
4a	179.6	148.1	121.9	13.5	–
4b	177.5	147.1	122.9	13.3	–
4c	189.7	146.3	121.2	13.4	–
5	207.0	148.7	121.4	14.2	43.8
5a	182.0	149.6	123.7	14.2	42.6
5b	168.6	149.2	123.9	14.3	43.7
5c	171.2	119.7	125.1	14.0	43.9
7	205.6	144.6	117.3	13.0	–
7a	192.6	145.1	117.6	13.2	–
7b	174.3	145.8	121.9	13.8	–
10	167.8	147.2	122.4	13.6	–

organic compounds 6, which were not isolated). Although cleavage of a Au–C bond has been observed during some oxidative addition reactions, the addition of halogens to gold(I) carbene complexes generally occurs with retention of this bond [9].

In a typical procedure the gold(I) carbene complexes are dissolved in methylene chloride, cooled to −20 or −40°C and treated with chlorine, bromine or iodine to give clear yellow, orange or red solutions after work-up. The crystals obtained upon cooling the filtrates are thermally stable in air at room temperature and are soluble in tetrahydrofuran, acetone and dichloromethane. Crystals of complex 1a were suitable for an X-ray crystallographic investigation and the results obtained together with those obtained from a theoretical study of the simple analogue $[AuCl_2(\overline{CNHCH=CHNH})_2]^+$ are discussed later.

The ^{1}H NMR data (Table 2) of the cationic gold(III) complexes 1a–c, 2a–c, 3a–b, 4a–b and 5a–b show that, as expected, almost all the resonances are shifted downfield with respect to the corresponding signals for the cationic gold(I) compounds 1–5 (that are included in the table for comparison). This can be ascribed to the larger electronegativity of the halogen atoms. The exceptions are the NMe protons of the imidazolinylidene compound 2c, formed by oxidative addition of iodine, the H⁴ protons of the thiazolinylidene compounds 3a and 3b (in which the shifts are virtually the same as the in the initial gold(I) compound 3), and the NH protons (the chemical shifts of which are concentration and solvent dependent). The chemical shifts of the H⁴, H⁵
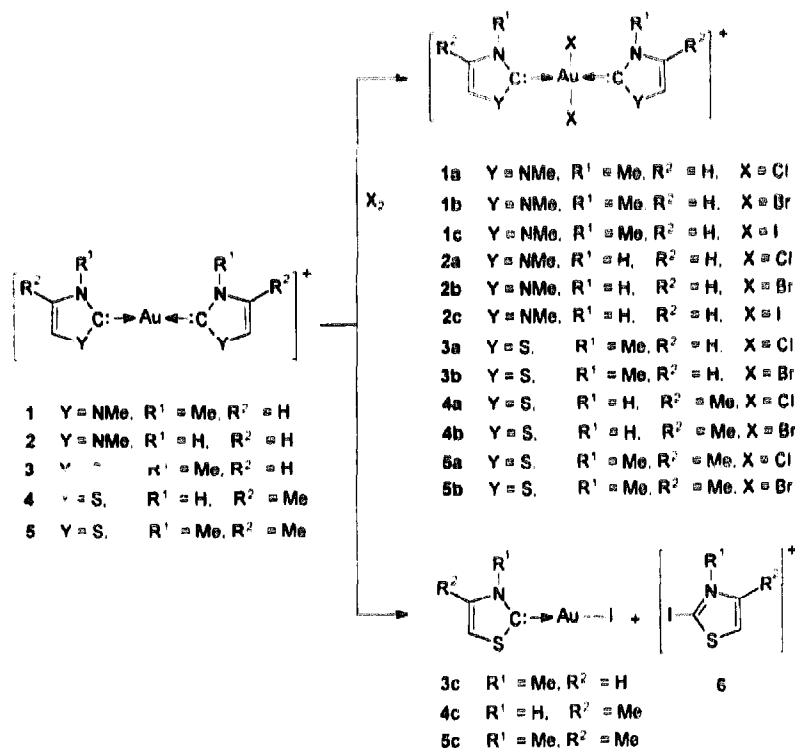
Scheme 1.

and NCMe protons of the mono(carbene) iodogold(I) compounds 3c–5c are also shifted downfield with respect to those in the corresponding precursor bis(carbene) gold(I) complexes 3–5. This occurs in spite of the overall change in charge from cationic to neutral and could suggest that the iodine has an electron withdrawing effect (σ) in this case. These results contrast with those for the analogous copper(I) imidazolinylidene and thiazolinylidene complexes in which both the protons and carbons of the neutral mono(carbene)iodo compounds and cationic bis(carbene) complexes have similar chemical shifts [10].

The carbene carbons in the new gold(III) complexes (Table 3) resonate between δ 144.1 and 182.6 and unexpectedly appear Δδ 22.2–38.7 ppm upfield from those observed for the analogous gold(I) bis(carbene) complexes 1–5. The acyclic gold(III) carbene compound [{(p-MeC₆H₄NH)(EtO)C}₂AuI₂]⁺ exhibits an even larger upfield shift of Δδ 44.8 ppm relative to its gold(I) counterpart [11]. We have observed that the formation of azolyl-derived carbene complexes of gold [6,7,12,13], copper [10,14,15], silver [16], tungsten [17] and iron [18–20] are accompanied by a large downfield shift of the coordinated carbon resonance [21,22]. The shifts of the coordinated carbons in the halogold(III) and halogold(I) compounds lie far upfield from these resonances which suggests that the halogens affect the "carbene character" of these compounds. In contrast, the chemical shifts of the Cᵛ, Cˣ and CMe carbons in the new gold(III) compounds all lie downfield relative to those in the precursor gold(I) compounds. The largest shift observed is for the Cˣ carbon of complex 4b which is shifted 5.8 ppm downfield relative to the corresponding carbon in the bis(carbene) gold(I) compound 4. An explanation for the 'anomalous' behaviour of the gold(III) coordinated carbene carbon, is still lacking.

Molecular ions were only observed in the mass spec-

tra of the gold(III) chloro(imidazolinylidene) complex 1a and the chloro(4-methylthiazolinylidene) complex 4a. The fragmentation of complex 1a occurs either via the reductive elimination of Cl₂, or the loss of a chlorine and an organic ligand fragment followed by loss of the remaining chlorine. Similar patterns were also observed in the mass spectra of the other new gold(III) compounds. In contrast, the molecular ion peak was observed in the mass spectra of all the new gold(I) compounds 3c–5c. Their fragmentation patterns indicate the loss of iodine followed by dimerization of the thiazolinylidene ligands.

2.2. Oxidative addition of mono(carbene) gold(I) complexes

The reaction of the mono(carbene) gold(I) compound 7 with halogens at −40°C in methylene chloride afforded, after work-up and crystallization, the mono(carbene) halogold(I) compounds 7a–b and 4c as well as the 2-halothiazole compounds 9a–c (Scheme 2). It is clear from the products obtained that instant reductive elimination of the intermediately formed bis-(carbene) gold(III) compound 8 occurred to form gold(I) complexes and organic compounds. In the case of oxidative addition of Cl₂, an additional trichlorogold(III) compound 10 was also isolated from the reaction mixture. This formation occurs since an excess of Cl₂ gas was bubbled into the reaction mixture. The NMR spectra indicate the presence of the 2-halothiazole compounds 9a–c. An alternative route towards the preparation of complex 10 involves the addition of [AuCl₃(tht)] to one equivalent of 4-methylthiazolyllithium followed by direct protonation with CF₃SO₃H.

The chemical shifts of all the protons in the mono(carbene) halogold(I) compounds 7a–b and 4c are shifted downfield relative to the corresponding protons in the precursor mono(carbene) gold(I) compound 7.

7a X = Cl   9a X = Cl
7b X = Br   9b X = Br
7c X = I   9c X = I
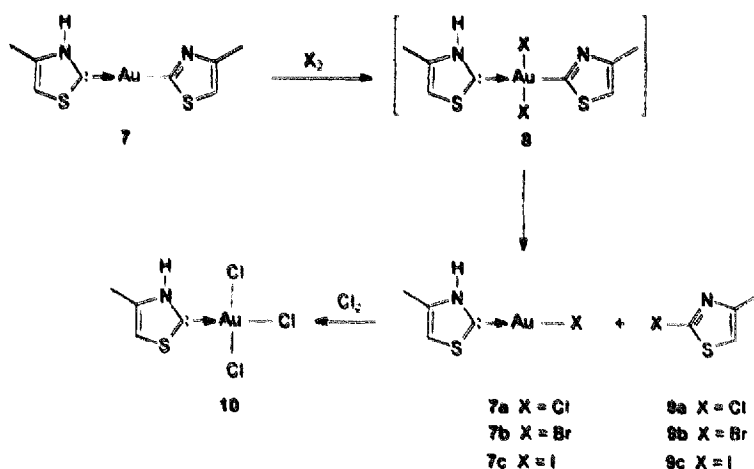
Scheme 2.

Furthermore, the H^5 proton of the chloro compound **7a** lies further downfield than that of the bromo compound **7b** which in turn lies further downfield than that of the iodo compound **4c**. This follows the trend of decreasing electronegativities of the halogens (Cl > Br > I). A similar downfield shift is observed for the protons of the trichloro(thiazolinylidene) complex **10** compared to those in the mono(carbene) complex **7a**.

The NMR resonances of the carbene carbon atoms in the mono(carbene) halogold(I) compounds **7a–b** and **4c** occur at δ 192.6, 174.3 and 189.7 respectively and are shifted $\Delta\delta$ 13.0, $\Delta\delta$ 31.3 and $\Delta\delta$ 15.9 ppm upfield from the resonance position of the corresponding carbon in the precursor mono(carbene) gold(I) compound **7**. The remaining carbon atoms in the new halogold compounds are all shifted downfield relative to the corresponding carbons in the precursor compound. The ^{13}C–$\{^1H\}$ NMR data for the trichloro compound **10** show that the carbene carbon resonates at δ 167.8 and that it is shifted $\Delta\delta$ 24.8 ppm upfield with respect to the corresponding carbon in the monochloro compound **7a**. This suggests, once again, that gold coordinated carbon atoms are "anomalously" effected by the addition of halogen atoms to the gold.

Molecular ions were observed in the mass spectra of complexes **7a–b** at m/z 331 and 376 and both their fragmentation patterns parallel that of the gold(I)iodo complex **4c**. The mass spectrum of complex **10** exhibits a weak peak for the molecular ion at m/z 401 and it

fragments by systematically loosing chloride atoms. Dimerization of the 4-thiazolinylidene ligand and chlorination of 4-methylthiazole were also observed in the mass spectrometer.

2.3. Structure of $[Au(\overline{CNMeCH=CHN}Me_2Cl_2[CF_3-SO_3]$ 1a

The molecular structure, anisotropic thermal ellipsoids and atom numbering scheme of the chloro(imidazolinylidene) gold(III) compound **1a** is shown in Fig. 1. Selected bond lengths and angles are presented in Table 4 and the atom coordinates in Table 5. The structures of two independent cations were determined.

In the cations, the coordination around the gold(III) atom is square planar and the chemically equivalent ligands are trans to one another. The imidazolinylidene ligands in both the cations are planar (maximum deviation from the least-squares plane are 0.015(20) Å and 0.030(21) Å) and the ligands situated trans to the gold atoms are coplanar as required by symmetry. In both cations, the coordination plane and the best plane through the heterocyclic ligands form an angle of 67.57(27)° or 66.03(27)° and, therefore, do not lie completely perpendicular to each other. The deviation from the expected perpendicular arrangement is probably due to crystal packing effects. However, this was not obvious from a packing diagram.

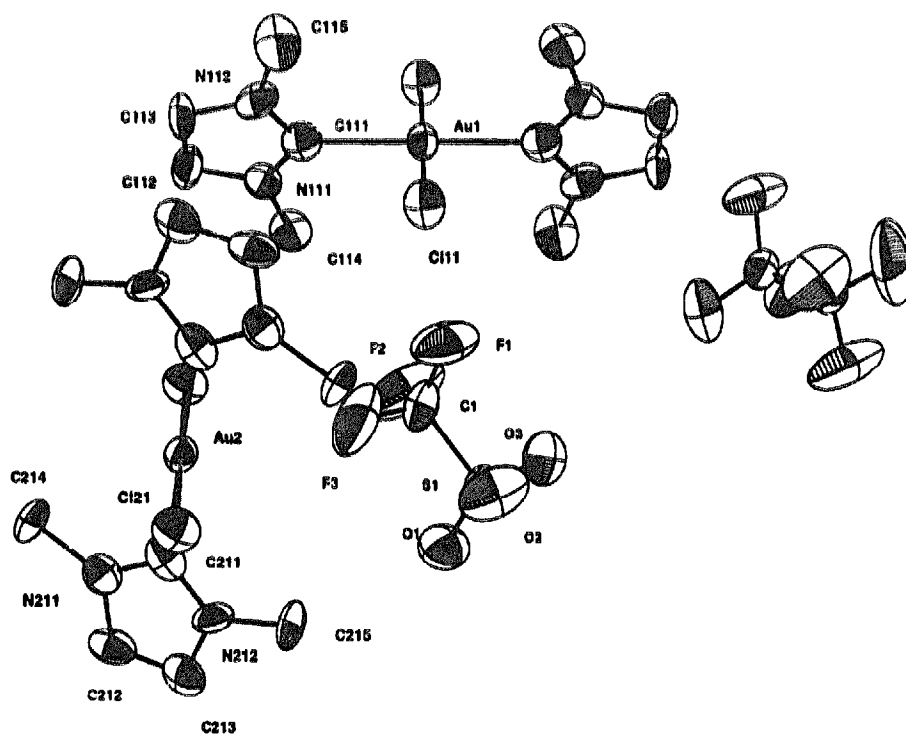The Au–C(sp^2) bonds of 2.13(2) and 2.07(2) Å are

Fig. 1. The molecular structure of the two independent cations and the anion of complex **1a**. The thermal ellipsoids are drawn at 50% probability limit. The cations contain centrosymmetric symmetry.

in agreement with those found in other gold(I) and gold(III) complexes, e.g. [Au(p-MeC$_6$H$_4$NH)$_2$I$_2$]ClO$_4$ ·(C$_2$H$_5$)$_2$O (2.07(2) and 2.09(2) Å) [23];
[Au(CNMeCH=CHNMe){CNMeCH=CHNH}][CF$_3$SO$_3$] (1.99(1) and 2.00(2) Å) [24] and [Au-{CNMeCH=CHS}$_2$][CF$_3$SO$_3$] [2.06(2) and 2.01(2)] [25]. Very little π back donation is believed to occur in complex 1a and indeed in all gold(I), silver(I), copper(I) and palladium(II) azolinylidene complexes [11,26,27]. This is supported by the 2.023(7) Å Au–C formal single bond length found in the gold(III) compound [AuMe$_2$(tmp)]NO$_3$ · H$_2$O (tmp = tri-2-pyridylmethane) [28].

The C$_{carbene}$–N distances, with an average length of 1.30(2) Å, are normal and compare well with similar separations in, for example, [Au(p-MeC$_6$H$_4$NH)$_2$-I$_2$]ClO$_4$ · (C$_2$H$_5$)$_2$O (1.29(2)–1.35(2) Å) [23] and [Au-{CNMeCH=CHN Me}{CNMeCH=CHN H}][CF$_3$SO$_3$] (average 1.34(2) Å) [24]. These bond lengths also show more double bond (1.29 Å) than single bond (1.47 Å) character. No intermolecular Au · · · Au interactions were observed within this compound.

2.4. Theoretical study

The results of the calculated B3LYP/LANL2DZ and BHANH/LANL2DZ geometry optimizations for the model compounds [Au{CNHCH=CHN H}$_2$Cl$_2$]$^+$ (11), [Au{CNHCH=CHNH}$_2$]$^+$ (12) and [CNHCH=CHN H] (14) as well as the experimental bond distances of analogous compounds [Au(CNMeCH=CHN Me)$_2$Cl$_2$]$^+$

Table 4
Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex 1a

Au(1)–Cl(1)	2.285(4)	Au(2)–Cl(2)	2.282(4)
Au(1)–C(11)	2.13(2)	Au(2)–C(21)	2.07(2)
N(11)–C(11)	1.30(2)	N(21)–C(21)	1.37(2)
N(11)–C(12)	1.40(2)	N(21)–C(22)	1.39(2)
N(12)–C(11)	1.30(2)	N(22)–C(21)	1.31(2)
N(12)–C(13)	1.40(2)	N(22)–C(23)	1.39(2)
C(12)–C(13)	1.39(3)	C(22)–C(23)	1.40(3)
C(1)–F(1)	1.29(2)	C(1)–F(2)	1.31(3)
C(1)–F(3)	1.29(2)	C(1)–S(1)	1.78(?)
S(1)–O(1)	1.42(1)	S(1)–O(2)	1.41(1)
S(1)–O(3)	1.41(2)		
Cl(1)–Au(1)–C(11)	89.1(4)	Cl(2)–Au(2)–C(21)	88.7(4)
Cl(1)–Au(1)–Cl(1)'	180.0(2)	Cl(2)–Au(2)–Cl(2)'	180.0(2)
Cl(11)–Au(1)–C(11)'	180.0(6)	C(21)–Au(2)–C(21)'	180.0(4)
C(11)–N(11)–C(12)	109(1)	C(21)–N(21)–C(22)	108(1)
C(11)–N(12)–C(13)	109(1)	C(21)–N(22)–C(23)	112(1)
Au(1)–C(11)–N(11)	123(1)	Au(2)–C(21)–N(21)	124(1)
Au(1)–C(11)–N(12)	125(1)	Au(2)–C(21)–N(22)	128(1)
N(11)–C(11)–N(12)	111(1)	N(21)–C(21)–N(22)	108(1)
N(11)–C(12)–C(13)	105(1)	N(21)–C(22)–C(23)	107(1)
N(12)–C(13)–C(12)	106(1)	N(22)–C(23)–C(22)	104(1)

Table 5
Fractional coordinates and equivalent thermal factors for 1a

Atom	x	y	z	U_{eq}
Au(1)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0358(3)
Cl(1)	0.4255(1)	0.4073(5)	9.4182(2)	0.053(2)
N(11)	0.5450(4)	0.368(1)	0.3626(7)	0.042(5)
N(12)	0.5489(5)	0.622(2)	0.3628(7)	0.048(5)
C(11)	0.5350(5)	0.497(2)	0.3979(9)	0.046(7)
C(12)	0.5673(6)	0.408(2)	0.2974(9)	0.050(7)
C(13)	0.5707(6)	0.573(2)	0.2986(9)	0.053(7)
C(14)	0.5345(6)	0.199(2)	0.382(1)	0.053(7)
C(15)	0.5440(7)	0.793(2)	0.383(1)	0.070(8)
Au(2)	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{2}$	0.0369(3)
Cl(2)	0.3234(2)	0.8458(5)	0.5833(2)	0.055(2)
N(21)	0.2953(4)	0.441(2)	0.4527(7)	0.049(5)
N(22)	0.2925(5)	0.438(2)	0.5797(7)	0.045(5)
C(21)	0.2822(6)	0.525(2)	0.514(1)	0.048(7)
C(22)	0.3149(6)	0.295(2)	0.483(1)	0.051(7)
C(23)	0.3133(6)	0.292(2)	0.566(1)	0.053(7)
C(24)	0.2875(6)	0.490(2)	0.3626(8)	0.057(7)
C(25)	0.2844(6)	0.487(2)	0.6612(8)	0.060(7)
C(1)	0.3923(7)	0.913(2)	0.3828(9)	0.057(8)
F(1)	0.4214(7)	1.007(2)	0.4330(7)	0.138(7)
F(2)	0.3543(6)	0.877(2)	0.4171(8)	0.172(9)
F(3)	0.4175(5)	0.782(1)	0.3828(7)	0.114(6)
S(1)	0.3684(2)	0.9962(5)	0.2846(2)	0.050(2)
O(1)	0.3384(5)	0.870(2)	0.2419(7)	0.102(6)
O(2)	0.3401(5)	1.131(2)	0.2988(7)	0.090(6)
O(3)	0.4150(5)	1.025(2)	0.2597(8)	0.097(7)

(1a), [Au{CNMeCH=CHN Me}{CNMeCH=CHNH}]$^+$ (13) [24] and [CN(Ad)CH=CHN(Ad)] (15) [29] (Ad = adamantyl) are summarized in Table 6.

The theoretical data are generally in good agreement with experimental values. The predicted Au–C$_{carbene}$ interatomic distances of 2.051 and 2.042 Å for the Au(III) and Au(I) compounds 11 and 12 are in reasonable agreement with the experimental values of 2.10(2) and 2.00(2) Å for complexes 1a and 13 respectively. These bonds are slightly elongated compared to the Au=CH$_2^+$ cation (B3LYP, 1.916 Å; MRCI, 1.889 Å) [30]. The theoretically predicted and experimental values of the Au–C$_{carbene}$ bond distances are similar for both the (III) and (I) oxidation states of gold. The heterocyclic ligand substructure in the Au(III) and Au(I) complexes compares, well to the free singlet carbene (C$_3$N$_2$H$_4$) 14, in which Hueckel aromaticity is reflected in the fact that the individual bonds are longer than regular double bonds and shorter than corresponding single bonds. This is consistent with a delocalized π system. The individual C$_{carbene}$–N bonds are slightly shortened upon coordination to gold, indicating that a somewhat stronger participation of the nitrogen lone pair in the ring-π-bonds is required due to the electrophilic character of the Au ion. These calculated bond lengths are longer than those obtained by X-ray methods. The predicted Au–Cl bonds of the Au(III) complex

Table 6
Comparison of selected bond lengths (Å) and angles (°) from X-ray data [a] and B3LYP/LANL2DZ and BHANH/LANL2DZ geometry optimizations [b] of Au(III) and Au(I) carbene complexes and the analogous free carbene compounds

Complex	Au(III)		Au(I)		Free carbene	
	calc. [Au$^+$Cl$_3$(C$_3$N$_2$H$_4$)$_2$]. 11	exp. [AuCl$_3$(C$_5$N$_2$H$_7$)$_2$]$^-$ 1a	calc. [Au$^+$(C$_3$N$_2$H$_3$)$_2$]. 12	exp. [Au(C$_3$N$_2$H$_6$)(C$_5$N$_2$H$_8$)]$^+$. 13	calc. [C$_3$N$_2$H$_4$]. 14	exp. [C$_{13}$N$_2$H$_{17}$]. 15
Au–C$_{carbene}$	2.051 2.012	2.10(2)	2.042 2.011	2.00(2)	–	–
Au–Cl	2.425 2.356	2.29(4)	–	–	–	–
C$_{carbene}$–N	1.361 1.338	1.32(2)	1.371 1.348	1.34(2)	1.395 1.369	1.37(2)
N–C	1.407 1.384	1.40(2)	1.403 1.383	1.37(2)	1.411 1.390	1.384(2)
C–C	1.373 1.355	1.40(3)	1.373 1.355	1.34(2)	1.371 1.353	1.338(3)
Au–C$_{carbene}$–N	127.5 127.3	125(1)	128.2 127.9	127.9(9)	–	–
C$_{carbene}$–N–C	112.2 110.9	109(1)	111.9 111.8	112.3(1)	114.3 113.9	112.2(2)
N–C$_{carbene}$–N	105.1 105.9	110(1)	103.6 104.0	103.5(1)	100.0 100.6	102.2(2)
N–C–C	108.3 108.3	106(1)	106.2 106.2	106(1)	105.7 105.8	106.7(2)
C$_{carbene}$–Au–Cl	90.0 90.0	88.9(4)	–	–	–	–
Total energy (hartree)	−617.577690 −613.575365	–	−587.697070 −583.975055	–	−226.134286 −224.492585	–
BDE Au–Cl (kcal/mol)	27.7 35.0	–	–	–	–	–
BDE Au–C (kcal/mol)	94.3 113.2	–	88.7 103.1	–	–	–

[a] Average bond distance is given.
[b] B3LYP/LANL2DZ (upper number) and BHANH/LANL2DZ (lower value).

11 are longer than the experimental values. This is reflected in the rather small BDE (bond dissociation energy) of 27.7 kcal/mol (averaged for both bonds) for the Au–Cl bond. A BDE of about 60 kcal/mol is expected for isolated AuCl [31]. A larger basis set with diffuse functions would be needed to achieve further improvement of the description. Contrary to the results obtained from the X-ray crystallographic study of the Au(III) complex **1a** (vide supra), the optimized structure of the model complex **11** is also planar but possesses D_{2d} symmetry. The structure in which the two halides have been rotated to give a torsional angle of 67.57(27)° or 66.03(27)° (as in the crystals) was calculated to be 7 kcal/mol higher in energy.

3. Experimental

3.1. General

All reactions involving organometallic reagents were performed under an atmosphere of nitrogen using standard vacuum-line and Schlenk techniques. Melting points were determined on a standardized Buchi 535 apparatus. Mass spectra (electron impact) were recorded on a Finnigan Mat 8200 instrument at ~ 70 eV (1.12 × 10⁻¹⁷ J) and NMR spectra on a Varian 200 FT spectrometer. Elemental analyses were carried out by the Division of Energy Technology, Council for Scientific and Industrial Research, Pretoria. South Africa.

The following starting materials were prepared according to published procedures:
[Au(CNR¹CR²=CHY)₂][CF₃SO₃] (**1**. Y = NMe. R¹ = Me. R² = H; **2**. Y = NMe. R¹ = H. R² = H; **3**. Y = S. R¹ = Me. R² = H; **4**. Y = S. R¹ = H. R² = Me; **5**. Y = S. R¹ = Me. R² = Me) and [Au(CNHCMe=CHS)-(C=NCMe=CHS)] **7** [6,7]. CF₃SO₃H was purchased from Aldrich and η-butyllithium from Merck. Tetrahydrofuran (thf) and diethyl ether were distilled under nitrogen from sodium diphenylketyl and CH₂Cl₂, hexane and pentane from CaH₂.

3.2. Preparation of [AuX₂(CNR¹CR²=CHY)]-[CF₃SO₃] (**1a**. Y = NMe. R¹ = Me. R² = H. X = Cl; **2a**, Y = NMe. R¹ = H. R² = H; X = Cl. **3a**, Y = S. R¹ = Me. R² = H. X = Cl; **4a**, Y = S. R¹ = H. R² = Me. X = Cl; **5a**. Y = S. R¹ = Me. R² = Me. X = Cl)

A typical preparation (complex **1a**) was carried out as follows: Cl₂ gas was bubbled through a solution of the gold(I) carbene complex.
[Au(CNMeCH=CHNMe)₂][CF₃SO₃] **1** (0.14 g. 0.4 mmol) in CH₂Cl₂ (30 cm³) at −40°C for 10 min. The mixture was stirred at −40°C for 30 min before allowing it to slowly warm up to room temperature. The

solvent was removed under vacuum and the residue washed several times with diethyl ether. redissolved in acetone and filtered through Celite. Concentration of the yellow filtrate and cooling to − 20°C afforded colourless crystals of complex **1a**.

Complexes **2a**, **3a**, **4a** and **5a** were prepared similarly using the appropriate starting material However, complexes **3a**, **4a** and **5a** were redissolved in CH₂Cl₂ (30 cm³) before crystallization.

3.3. Preparation of [AuX₂(CNR¹CR²=CHY)₂]-[CF₃SO₃] (**1b**. Y = NMe. R¹ = Me. R² = H. X = Br; **2b**. Y = NMe. R¹ = H. R² = H; X = Br. **3b**. Y = S. R¹ = Me. R² = H. X = Br; **4b**. Y = S. R¹ = H. R² = Me. X = Br; **5b**. Y = S. R¹ = Me. R² = Me. X = Br)

A typical preparation (complex **1b**) involves the slow dropwise addition of a solution of Br₂ (0.05 g, 0.3 mmol) in CH₂Cl₂ (15 cm³) to a solution of the gold(I) carbene complex, [Au(CNMeCH=CHN Me)₂][CF₃SO₃] **1** (0.11 g, 0.3 mmol) in CH₂Cl₂ (30 cm³) at −40°C. The mixture was stirred at − 40°C for 30 min before allowing it to slowly warm up to room temperature. The solvent was removed under vacuum and the residue washed several times with diethyl ether. redissolved in CH₂Cl₂ and filtered through Celite. Concentration of the orange filtrate and cooling to − 20°C afforded light yellow. cubic crystals of complex **1b**.

Complexes **2b**, **3b**, **4b** and **5b** were prepared similarly using the appropriate starting material.

3.4. Preparation of [AuX₂(CNR¹CR²=CHY)₂][CF₃-SO₃] (**1c**. Y = NMe. R¹ = Me. R² = H. X = I; **2c**. Y = NMe. R¹ = H. R² = H; X = I)

A typical preparation (complex **1c**) involves the slow dropwise addition of a solution of I₂ (0.05 g. 0.19 mmol) in CH₂Cl₂ (15 cm³) to a solution of the gold(I) carbene complex. [Au(CNMeCH=CHNMe)₂][CF₃SO₃] **1** (0.07 g. 0.19 mmol) in CH₂Cl₂ (30 cm³) at − 30°C. The mixture was stirred at − 30°C for 30 min before allowing it to slowly warm up to room temperature. The solvent was removed under vacuum and the residue washed several times with diethyl ether. redissolved in CH₂Cl₂ and filtered through Celite. Concentration of the orange filtrate and cooling to − 20°C afforded orange. cubic crystals of complex **1c**. Complex **2c** was obtained similarly.

3.5. Preparation of [Au(CNR¹CR²=CHS)] (**3c**. R¹ = Me. R² = H; **4c**. R¹ = H. R² = Me; **5c**. R¹ = Me. R² = Me)

A typical preparation (complex **3c**) involves the slow dropwise addition of a solution of I₂ (0.25 g. 1.00

mmol) in CH_2Cl_2 (10 cm^3) to a solution of the gold(I) carbene complex, [Au{CNMeCH=CHS}$_2$][CF$_3$SO$_3$] 3 (0.54 g, 1.00 mmol) in CH_2Cl_2 (30 cm^3) at $-40°C$. The mixture was stirred at $-30°C$ for 30 min before allowing it to slowly warm up to room temperature. The reaction mixture was allowed to stir for a further 30 min at room temperature before the solvent was removed under vacuum. The residue washed several times with pentane and diethyl ether, redissolved in CH_2Cl_2 and filtered through Celite. Concentration of the red filtrate and cooling to $-20°C$ afforded red crystals of complex 3c.

3.6. Preparation of [AuX{CNHCMe=CHS}] (7a, X = Cl; 7b, X = Br, 4c, X = I) and [AuCl$_3${CNHCMe=CHS}] 10

Cl$_2$ gas was bubbled through a solution of the mono-carbene complex [Au{CNHCMe=CHS}-{C=NCMe=CHS}] 7 (0.79 g, 2.0 mmol) in CH_2Cl_2 (30 cm^3) at $-40°C$ for 5 min. The yellow mixture was stirred at $-40°C$ for 30 min before allowing it to slowly warm up to room temperature. The reaction mixture was allowed to stir for a further 30 min at room temperature before it was stripped of solvent in vacuo. The residue was washed several times with pentane and diethyl ether, redissolved in CH_2Cl_2 and filtered through Celite. Concentration of the red filtrate and cooling to $-20°C$ afforded yellow crystals of complex 7a and 10. Complex 7b was prepared similarly to 7a, from a solution of Br$_2$ in CH_2Cl_2 (20 cm^3), whereas complex 4c was prepared from a solution of I$_2$ in CH_2Cl_2 (30 cm^3).

3.7. Preparation of [AuCl$_3${CNHCMe=CHS}] 10

A solution of 4-methylthiazole (0.09 g, 1.0 mmol) in thf(tetrahydrofuran) was cooled to $-78°C$ and treated with n-butyllithium (1.6 mol dm^{-3}, 0.63 cm^3, 1.0 mmol). The solution was stirred at this temperature for 30 min before [AuCl$_3$(tht)] (0.39 g, 1.0 mmol) were added in small portions. The mixture was stirred for one hour at $-78°C$ before the addition of HCF$_3$SO$_3$. The mixture was stirred a further hour before allowing it to slowly warm up to room temperature over a period of one hour. The solvent was removed under vacuum and the yellow residue washed several times with pentane and diethyl ether, redissolved in CH_2Cl_2 and filtered through Celite. Concentration of the red filtrate and cooling to $-20°C$ afforded yellow crystals of complex 10.

3.8. Crystal structure determination

Details of the crystal data and data collection for [Au{CNMeCH=CHNMe}$_2$Cl$_2$][CF$_3$SO$_3$] 1a are given in

Table 7
Crystal data, collection and refinement details for complex 1a

formula	AuC$_{11}$H$_{16}$F$_3$N$_4$O$_3$S
crystal size (mm)	0.25×0.18×0.10
crystal system	monoclinic
space group	C2/c
a (Å)	26.5507(26)
b (Å)	8.4334(8)
c (Å)	16.8565(19)
α (deg)	90
β (deg)	102.791(8)
γ (deg)	90
Z	8
V (Å^3)	3680.7(7)
d$_c$ (g m^{-3})	2.199
μ (mm^{-1})	8.48
radiation	MoKα(0.71073 Å)
temperature (°C)	22
diffractometer	Enraf-Nonius CAD 4
scan type	ω–2θ
scan range, θ (deg)	2 ≤ θ ≤ 20
hkl ranges	-25 to 25, -4 to 8, -16 to 16
maximum scan rate (deg min^{-1})	5.5
maximum scan time per reflection (s)	60
absorption corrections	Gaussian integration from crystal shape
reflections measured	4228
unique reflections used to refine	1533
parameters refined, refinement on F^2	229
goodness off it all	5.181
R(F), wR(F^2) ^{a}	0.037, 0.087

^{a} $R(F) = \Sigma(|F_o| - |F_c|)\Sigma|F_o|$; $wR(F^2) = [\Sigma w(|F_o^2| - |F_c^2|)^2]/\Sigma w|F_o^2|^2]^{1/2}$; $w = 1/\sigma^2$.

Table 7. Unit cell dimensions were obtained by a least-squares fit of the diffraction angles of 25 reflections. The data were collected on a Enraf-Nonius CAD4 diffraction at 22°C. The position of the gold atoms were determined from a Patterson map. The cell volume required 8 formula units in the cell. Contrary to expectation, this requirement was not satisfied by placing one formula unit in a general position but two independent cationic units on two separate centres of symmetry. Gold atoms were, therefore, placed in the special positions at Wyckoff sites a and c i.e. at positions ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) and ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{2}$), and as a result the molecular structure of two independent cations (with internal i symmetry) were determined. The anion was placed in a general position i.e. with no internal symmetry. Refinement was carried out by full-matrix least-squares methods (XTAL 3.4) [32]. No hydrogen atoms could be observed in difference maps and were thus not included. Anisotropic thermal parameters were used for all atoms. The effects of anomalous dispersion were taken into account in the refinement. A complete list of bond lengths and a table of thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

3.9. Computational details

A series of theoretical calculations have been performed utilizing the GAUSSIAN92 series of programs [8]. The inial geometries were obtained at the Hartree–Fock level employing a minimal basis set and accompanied by the relativistically derived effective core potential (ECP) [33] accounting for the mass velocity and Darwin terms (LANL1MB). This level of approximation, however, suffers from both the small basis set and the missing correlation energy. In subsequent calculations we consecutively improved the computational level extending the basis set to double zeta and using the smaller core ECP (LANL2DZ). For heavy atom containing systems this basis does reasonably well at reasonable computational costs [34]. In order to account for the correlation energy we employed different density functional theory (DFT) schemes and finally decided to perform the calculations using the hybrid HF/DFT namely Beckes Half-and-Half (BHANDH) and Becke3LYP (B3LYP) methods [35,36]. These functionals were proven for other gold containing compounds to give structures and relative energies in close agreement with the much more sophisticated ab initio method [37–39]. In the geometry optimization procedure we used analytical energy gradients and restricted the systems to C_{3v} symmetry.

Acknowledgements

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