Characterization of mono(carbene) and bis(carbene) complexes of gold(I) derived from lithiated pyridine

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Abstract

The carbene complexes $[\mathrm{Au}(\overline{\mathrm{CNHCH{=}CHCH{=}C}}\mathrm{H})\mathrm{Cl}]$ (2) and $[\mathrm{Au}(\overline{\mathrm{CN(R)CH{=}CHCH{=}C}}\mathrm{H})_2]\mathrm{X}]$ (R = H, X = Cl (4)) (R = Me, X = $\mathrm{CF_3SO_3}$ (5)) are formed when the products of the reactions between [Au(THT)Cl] (THT = tetrahydrothiophene) and 2-lithiopyridine are acidified with HCl or alkylated with $\mathrm{CF_3SO_3Me}$. Compound 4 crystallizes with two molecules of H_2O. The complex is monomeric and interacts with the water molecules and the chloride ion through a complex network of hydrogen bonds.

Key words: Gold; Carbene; Pyridine

1. Introduction

The ease with which neutral and cationic mono(amino-thio) and bis(amino-thio) carbene complexes of gold(I) can be prepared [1,2], by either protonation or alkylation of stable aurates obtained from gold(I) halides and lithiated thiazoles, prompted us to investigate the reaction of [Au(THT)Cl] (THT = tetrahydrothiophene) with 2-lithiopyridine in an attempt to prepare new amino-organo carbene complexes of gold(I).

Although various methods for the preparation of gold complexes containing bis(amino) [3-5], amino-alkoxy [4,5], and amino-thio [1,2] carbenes are known, the synthesis of amino-organo carbene complexes of gold(I) has been restricted to carbene transfer reactions involving pre-formed tungsten carbene complexes and $\mathrm{HAuCl_4}$ [6].

We describe below the preparation of bis(amino-organo) carbene complexes obtained by the protonation or alkylation of the anionic ('ate') complex $\mathrm{Li}[\mathrm{Au}(\overline{\mathrm{CNCH{=}CHCH{=}C}}\mathrm{H})_2]$ (1), as well as a facile route to a mono(carbene)chlorogold compound. The X-ray crystal structure of the protonated bis(carbene) complex $[\mathrm{Au}(\overline{\mathrm{CNHCH{=}CHCH{=}C}}\mathrm{H})_2]\mathrm{Cl}$ (4) is also described.

2. Results and discussion

2.1. Synthesis and characterization

Whereas treatment of [Au(THT)Cl] with two equivalents of 2-lithiopyridine in tetrahydrofuran (THF) gave a pale-yellow solution, presumably containing the aurate 1 (Scheme 1), use of one equivalent of metallated pyridine caused precipitation of a colourless insoluble compound with an elemental analysis consistent with its formulation as the 2-pyridyl polymer $[\{\mathrm{Au}(\overline{\mathrm{CNCH{=}CHCH{=}C}}\mathrm{H}\}_n]$ (2) ($n \geqslant 3$) [7].

Compound 2 has previously been prepared, by a different method, by Jutzi and Hensler [8], while Bonati *et al.* [9] used mass spectroscopy data as a basis for proposing trimeric structures for the related compounds derived from 1-R-2-lithioimidazole (R = Me or $\mathrm{CH_2Ph}$). Although yellow single crystals of 2 were obtained from $\mathrm{CH_2Cl_2}$–pentane mixtures, attempts to characterize this compound by means of X-ray diffraction methods were unsuccessful owing to crystal decomposition at room temperature.

Addition of HCl in diethyl ether to a stirred suspension of 2 in $\mathrm{CH_2Cl_2}$ gave the soluble neutral chloro(pyridinylidene) complex $[\mathrm{Au}(\overline{\mathrm{CNHCH{=}CHCH{=}C}}\mathrm{H})\mathrm{Cl}]$ (3). The ^{1}H (NMR) spectrum for 3 clearly shows the presence of an N–H resonance at 14.6 ppm and the ^{13}C NMR spectrum reveals a carbene resonance at 197.1 ppm (Table 1).

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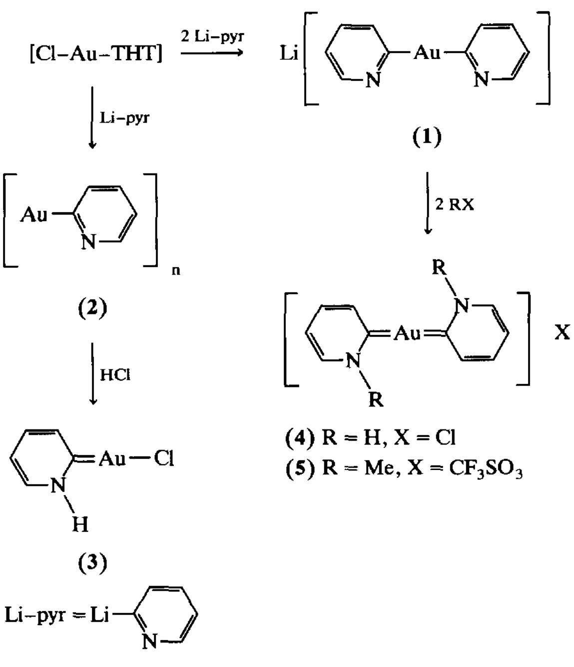

Scheme 1.

Because of the presence of a reactive Au–Cl bond in [Au(CNHCH=CHCH=CH)Cl] (3), the use of this compound as a starting point for the preparation of other organo gold compounds containing a gold–carbene fragment is currently under investigation.

The aurate Li[Au(CNCH=CHCH=CH)$_2$] (1), which was not isolated, is readily protonated with HCl or alkylated with CF_3SO_3Me to give the bis(carbene) complexes [Au(CNHCH=CHCH=CH)$_2$]Cl (4) and [Au(CN(Me)CH=CHCH=CH)$_2$][CF_3SO_3] (5) respectively. Interestingly, and in similar fashion to that reported for bis(carbene) gold complexes derived from imidazoles [9], only bis(carbene) complexes were obtained from 1 irrespective of whether one or two molar equivalents of acid or alkylating agent was used. This behaviour contrasts with that found for thiazolyl 'ate' complexes of gold(I), which yield both mono(carbene) and bis(carbene) compounds [1,2].

The cationic complexes 4 and 5 exhibit carbene resonances in the ^{13}C NMR spectrum at 196.2 ppm ($CDCl_3$) and 201.3 ppm ($(CD_3)_2CO$) respectively (Table 1). Like complex 3, both 4 and 5 gave mass spectra strongly, indicating the presence of CH(CH)$_3$NC=CN(CH)$_3$CH$^+$ ions, but no molecular ions were observed.

All the new compounds are only sparingly soluble in organic solvents of low polarity, such as hexane or diethyl ether but more soluble in more highly polar solvents such as $CHCl_3$, CH_2Cl_2, THF and acetone.

2.2. X-Ray crystal structure of 4

The molecular structure, atom numbering scheme and hydrogen bonding network of [Au(CNHCH=CH-CH=CH)$_2$]Cl·$2H_2O$ (4) is shown in Fig. 1. Selected bond lengths and angles are presented in Table 2, and the atom coordinates in Table 3.

Single crystals of [Au(CNHCH=CHCH=CH)$_2$]Cl (4) were obtained by recrystallization from CH_2Cl_2 at −20°C. Although several attempts were made to grow larger crystals, only small crystals of 4 were obtained.

The crystal structure of 4 reveals a linear cationic bis(carbene) complex with a C(11)–Au–C(21) bond angle of 179.6(9)°, in which the two planar ring systems (largest deviation from best plane 0.02(3) Å) are twisted by 29(1)° with respect to each other. The structure also reveals the presence of a complex network of hydrogen bonds that extends throughout the crystal lattice. The two water molecules (O(1) and O(2)) are hydrogen bonded to each other and to the chloride counter-ion (Cl). The chloride ion is also hydrogen bonded to the proton on N(1), while one of the water molecules (O(2)) is hydrogen bonded to the proton on N(2). The

TABLE 1. Spectroscopic data for complexes 3–5

Compound	NMR [a], δ (ppm)		MS [b]	
	^1H	$^{13}C\{^1H\}$	m/z	Assignment
3	14.6 (br s, 1H, NH), 8.4–7.2 (m, 4H, cyclo-C_5H_4N)	197.1 (Au=C), 139.5, 138.9, 138.7, 120.8 (N(CH)$_4$)	276 156	AuCNHCH=CHCH=CH$^+$ CH(CH)$_3$NC=CN(CH)$_3$CH$^+$
4	13.1 (br s, 1H, NH), 8.3–6.9 (m, 4H, cyclo-C_5H_4N)	192.6 (Au=C), 138.9, 138.3, 138.0, 120.2 (N(CH)$_4$)	276 156	AuCNHCH=CHCH=CH$^+$ CH(CH)$_3$NC=CN(CH)$_3$CH$^+$
5 [c]	8.8–7.1 (m, 4H, cyclo-C_5H_4N), 4.62 (s, 3H, Me)	201.3 (Au=C), 145.7, 139.9, 139.0, 123.9 (N(CH)$_4$)	156	CH(CH)$_3$NC=CN(CH)$_3$CH$^+$

[a] Recorded at 298 K in $CDCl_3$ unless otherwise indicated.
[b] Electron impact at 70 eV.
[c] NMR spectra recorded in acetone-d_6.

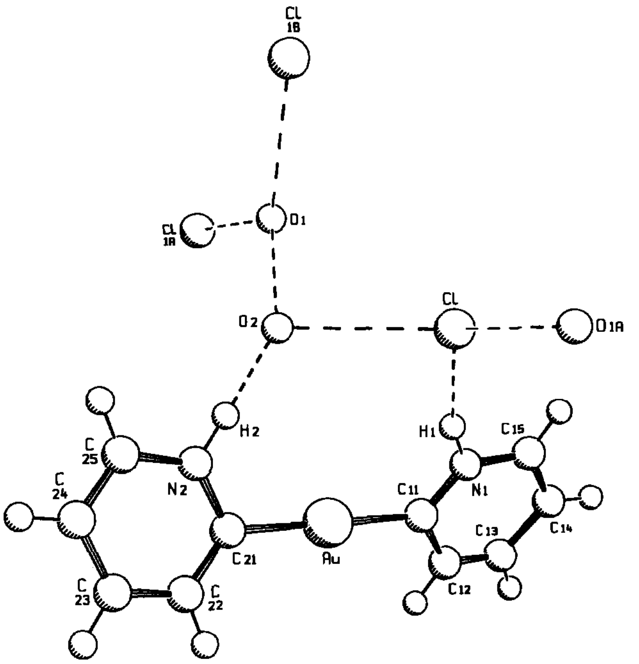

Fig. 1. Perspective drawing of $[\mathrm{Au}(\overline{\mathrm{CNHCH{=}CHCH{=}C}}\mathrm{H})_2]\mathrm{Cl}\cdot 2\mathrm{H_2O}$ (**4**) showing the waters of crystallization (O(1) and O(2)) and the chloride counter-ion (Cl). The hydrogen bonds are shown as broken lines. $\mathrm{Cl(1)^A}$ and $\mathrm{Cl(1)^B}$ refer to the chloride ions at positions $(x, 1+y, z)$ and $(\frac{1}{2}-x, \frac{1}{2}+y, z)$ respectively, while $\mathrm{O(1)^A}$ indicates the oxygen of the water at $(x, y-1, z)$.

remaining water molecule (O(1)) is only hydrogen bonded to the chloride ions and the second water molecule (O(2)) and shows no interaction with the coordinated ligands.

TABLE 2. Selected bond lengths (Å) and angles (°) in **4**

Au–C(11)	2.03(2)	Au–C(21)	2.02(2)
N(1)–C(11)	1.27(3)	N(2)–C(21)	1.39(3)
C(11)–C(12)	1.42(3)	C(21)–C(22)	1.39(3)
C(11)–Au–C(21)	179(1)		
Au–C(11)–N(1)	120(1)	Au–C(21)–N(2)	115(1)
Au–C(11)–C(12)	122(1)	Au–C(21)–C(22)	128(1)
N(1)–C(11)–C(12)	118(1)	N(2)–C(21)–C(22)	115(1)
Hydrogen bonds [a]			
Cl–N(1)	3.18(2)		
Cl–O(2)	3.14(2)	$\mathrm{O(1)–Cl(1)^A}$	3.18(2)
$\mathrm{Cl–O(1)^A}$	3.18(2)	$\mathrm{O(1)–Cl(1)^B}$	3.21(1)
O(1)–O(2)	2.78(2)	O(2)–N(2)	2.83(2)

[a] $\mathrm{Cl(1)^A}$ at $(x, 1+y, z)$; $\mathrm{Cl(1)^B}$ at $(\frac{1}{2}-x, \frac{1}{2}+y, z)$; $\mathrm{O(1)^A}$ at $(x, y-1, z)$.

TABLE 3. Fractional coordinates and equivalent thermal factors for **4**

Atom	x	y	z	U_{eq} [a] (Å^2)
Au	0.28815(8)	0.7794(1)	0.65862(3)	0.0476(3) [b]
N(1)	0.312(2)	0.644(2)	0.5679(6)	0.037(6)
C(11)	0.243(2)	0.695(3)	0.5986(6)	0.040(7)
C(12)	0.130(2)	0.683(3)	0.5836(8)	0.047(8)
C(13)	0.101(2)	0.635(4)	0.5429(8)	0.062(9)
C(14)	0.181(2)	0.575(4)	0.5094(8)	0.061(9)
C(15)	0.292(2)	0.586(3)	0.5244(7)	0.047(7)
N(2)	0.443(2)	0.930(3)	0.7228(7)	0.051(7)
C(21)	0.334(2)	0.864(3)	0.7190(7)	0.045(8)
C(22)	0.285(2)	0.840(3)	0.7604(7)	0.044(7)
C(23)	0.335(2)	0.884(4)	0.8009(9)	0.063(9)
C(24)	0.443(2)	0.962(4)	0.8026(8)	0.057(9)
C(25)	0.496(3)	0.984(4)	0.7629(8)	0.05(1)
Cl	0.5733(5)	0.6098(9)	0.5788(2)	0.039(2) [b]
O(1)	0.668(1)	1.205(2)	0.5897(5)	0.052(5)
O(2)	0.586(1)	0.937(2)	0.6474(5)	0.049(5)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

[b] Anisotropically refined; see Section 3.

The absence of Au ··· Au interactions in **4** can be ascribed to the extensive intermolecular hydrogen bonding, which precludes the formation of any interactions between the respective gold atoms. The absence of Au ··· Au interactions, together with the apparently shorter Au–C (carbene) bond lengths (Au–C(11), 1.97(2) Å; Au–C(21), 1.98(2) Å), is in contrast with their presence in the cationic bis(carbene) complexes $[\mathrm{Au}(\overline{\mathrm{CNHC(Me){=}CHS}})_2]_2[\mathrm{ZnCl_4}]$ [2] and $[\mathrm{Au}(\overline{\mathrm{CN(CH_2Ph)CH{=}CHNH}})_2]\mathrm{Cl}$ [9], in which the Au ··· Au non-bonded distances are 3.329(3) and 3.2630(5) Å and the average Au–C (carbene) bond lengths are 2.03(4) and 2.027(7) Å respectively. However, as with **4**, a relatively short Au–C (carbene) bond length of 1.961(9) Å has been observed in the neutral mono(carbene) complex $[\mathrm{Au}(\overline{\mathrm{CN(Me)C(Me){=}CHS}})(\mathrm{C_6F_5})]$ [1].

3. Experimental details

3.1. General

2-Bromopyridine and $\mathrm{CF_3SO_3Me}$ were purchased from Aldrich and BuLi in hexane from Merck. [Au(THT)Cl] was prepared by a published method [10]. The solution of HCl in ether was made by slowly treating Analar $\mathrm{H_2SO_4}$ (Merck) with NaCl and allowing the gaseous HCl formed to bubble through ether.

All reactions and manipulations were carried out under dinitrogen by using standard Schlenk techniques. Melting points were determined on a Büchi 535 apparatus and are corrected. Mass spectra (electron impact) were recorded on a Finnigan Mat 8200 instrument and NMR spectra on a Varian VXR 200 FT spectrometer. Elemental analyses were carried out by the CSIR (Pretoria) and by the Mikroanalytische Labor Pascher (Bonn).

3.2. Preparation of pyridylgold(I) [{Au(CNCH=CH-CH=CH)}$_n$] ($n \geqslant 3$) (2)

A solution of 2-bromopyridine (0.38 g, 4.8 mmol) in 20 cm^3 of THF was treated with BuLi in hexane (1.3 M, 3.7 cm^3, 4.8 mmol) at −50°C for 1 h, and then [Au(THT)Cl] (1.5 g, 4.8 mmol) was added slowly in small portions. After stirring at −50°C for 2 h, the mixture was allowed to warm to room temperature (22°C) over a period of 3 h, during which a yellow precipitate was formed. After removal of the solvent under reduced pressure the yellow residue was washed with CH_2Cl_2 (4×30 cm^3) and dried under vacuum. The yellow hygroscopic material decomposes above 120°C (yield, 3.4 g (85%)). Anal. Found: C, 21.8; H, 1.5; N, 5.4. AuC_5H_4N calc.: C, 21.9; H, 1.5; N, 5.7%.

3.3. Preparation of [Au(CNHCH=CHCH=CH)Cl] (3)

Addition of $HCl \cdot Et_2O$ (3.8 M, 1.1 cm^3, 4.2 mmol) to a stirred suspension of [{Au(CNCH=CHCH=CH)}$_n$] ($n \geqslant 3$) (**2**) (1.1 g, 4.0 mmol; as monomer) in CH_2Cl_2 (20 cm^3) gave a clear solution. A green microcrystalline solid was obtained by keeping the solution at −30°C overnight (yield, 0.95 g (76.2%); Mp. 179–180°C). Anal. Found: C, 19.5; H, 1.6; N, 4.4. Calc.: C, 19.3; H, 1.6; N, 4.5%.

3.4. Preparation of [Au(CNHCH=CHCH=CH)$_2$]Cl (4)

A THF solution of lithiopyridine (*ca.* 4.8 mmol) was prepared at −50°C as described for **2**, [Au(THT)Cl] (0.77 g, 2.4 mmol) was slowly added and the mixture stirred at this temperature for 1 h. The temperature was then raised to −10°C and a solution of HCl in ether (1.3 M, 4.0 cm^3, 5.2 mmol) was added dropwise. The mixture was allowed to warm to room temperature during 1 h, and the solvent was then removed under vacuum. The solid residue was dissolved in CH_2Cl_2 (20 cm^3) and the solution filtered through anhydrous $MgSO_4$. After concentration of the solution to 8 cm^3 and addition of pentane (5 cm^3), the solution was cooled to −20°C, yielding **4** as a yellow microcrystalline solid. Larger crystals of **4**, which were used in the X-ray study, were obtained by recrystallization from CH_2Cl_2 at −20°C (yield, 0.78 g (76%); m.p., 195–196°C). Anal. Found: C, 27.8; H, 3.3; N, 6.5. Calc. (for two H_2O molecules of crystallization): C, 28.2; H, 3.3; N, 6.6%.

3.5. Preparation of [Au(CN(Me)CH=CHCH=CH)$_2$]-[CF_3SO_3] (5)

The same procedure described for **4** was followed but with CF_3SO_3Me in place of HCl. Compound **5** was obtained as a yellow microcrystalline solid from CH_2Cl_2 solutions at −20°C. Crystals suitable for X-ray diffraction could not be obtained (yield, 0.87 g (68%); m.p., 127–129°C). Anal. Found: C, 29.6; H, 2.5; N, 5.4. Calc.: C, 29.3; H, 2.7; N, 5.3%.

TABLE 4. Crystal data, collection and refinement details for **4**

Formula	$C_{10}H_{10}N_2AuCl \cdot 2H_2O$
Molecular weight	424.64
Crystal size (mm × mm × mm)	0.050 × 0.075 × 0.085
Colour	Light green
Crystal system	Orthorhombic
Space group	*Pbca*
a (Å)	12.0509(7)
b (Å)	7.2907(15)
c (Å)	29.761(4)
Z	8
Volume U (Å^3)	2614.8(6)
D_c (g cm^{-3})	2.157
Radiation	Mo Kα
λ (Å)	0.71073
μ (cm^{-1})	11.8
T (°C)	22
F(000)	1560
Scan type $\omega:2\theta$	1:1
Scan range θ (°)	2–25
Scan angle (°)	$0.5 + 0.35 \tan \theta$
Zone collected	
h	0, +9
k	0, +15
l	0, +38
Maximum scan rate (° min^{-1})	16.48
Maximum scan time (s per reflection)	90
Aperture size (mm)	1.3
Reflections measured	2304
Unique reflections used	1234, $I > 3\sigma(I)$
Decay (%)	None
Parameters refined	75
Maximum positional shift (estimated standard deviation)	0.20 (average 0.04)
Residual electron density (electrons Å^{-3})	
Maximum	2.5
Minimum	−2.9
R	0.085
R_w	0.043

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

3.6. Crystal structure determination

Details of the crystal data and data collection parameters for [Au(CNHCH=CHCH=CH)$_2$]Cl (**4**) are given in Table 4. Unit cell dimensions were obtained by a least-squares fit of the diffraction angles of 25 reflections. The data were collected on an Enraf–Nonius CAD4 diffractometer at 22°C. The position of the gold atom was determined from a Patterson synthesis (SHELX-86) [11]. Subsequent refinement was carried out by full-matrix least-squares methods (XTAL 3.2) [12]. Atomic scattering factors were taken from the literature [13]. Application of either empirical or analytical absorption corrections to the data set did not improve the structure but led to increased R values. The structure was therefore refined with data uncorrected for absorption effects; these effects were, however, small because of the small crystal selected for the data collection. Anisotropic thermal parameters were used for only the gold and chloride atoms, since use of anisotropic thermal parameters for the remaining non-hydrogen atoms did not lead to significant improvement in the R values or the precision of the bond lengths and angles. The hydrogen atoms were placed in calculated positions and refined with a common isotropic temperature factor ($U_{iso} = 0.038$ Å^2). The low precision in the bond lengths and angles is ascribed to the very small size of the crystal used, which resulted in the large number of unobserved reflections. The effects of anomalous dispersion were taken into account in the refinement.

A complete list of bond lengths and angles and a table of thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

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