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Synthesis and characterization of neutral and cationic diamino carbene complexes of gold(I)

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Abstract

Bis(1-methylimidazolyl)aurate compounds were prepared by reacting 1-methylimidazol-2-yllithium and 1-methylbenzimidazol-2-yllithium with [AuCl(THT)] (THT = tetrahydrothiophene). Protonation or alkylation of the aurates yielded bis(carbene) complexes of the type $[Au\{CNR^1CR^2=CR^3N(Me)\}_2]^+$ (R^1 = H or Me; R^2 = H, R^3 = H or $R^2R^3 = C_4H_4$). The reaction of 1-methylimidazol-2-yllithium with $[AuCl(PPh_3)]$ afforded the same bis(carbene) cation after protonation or alkylation. Mono(diamino)gold(I)carbene complexes resulted from the sequential reactions of 1-methylimidazol-2-yllithium with $[Au(C_6F_5)(THT)]$ or AuCN and CF_3SO_3Me or CF_3SO_3H. Complicating side-reactions such as homoleptic rearrangement and protonation on carbon rather than nitrogen were observed.

Keywords: Gold; Carbene; 1-Methylimidazole; 1-Methylbenzimidazole; Imidazolinylidene complexes

1. Introduction

The formation of metal carbene complexes via the well-known Fischer method [1] involving electrophilic addition to metal acyls, thioacyls or even imidoyls is not generally available for gold, since few of these precursor complex types are known in a useful form. A related route comprising the protonation and alkylation of aurate complexes, prepared from [AuCl(THT)] (THT = tetrahydrothiophene), $[AuCl(PPh_3)]$, $[Au(C_6F_5)(THT)]$ or [AuCN] and 2-lithiopyridine [2] or thiazol-2-yllithium [3] reagents, produces stable amino(organo)- and amino(thio)carbene complexes. Other known methods for the preparation of gold(I) carbene complexes include the addition of alcohols or amines to coordinated isocyanides [4–7], the cleavage of electron-rich olefins [8] and carbene transfer from tungsten pentacarbonyl complexes [9]. Burini and coworkers [10,11] prepared gold derivatives of imidazoles and unexpectedly obtained carbene complexes. The same authors later treated trimeric 1-benzyl-2-gold(I)imidazole with EtI or EtOOCCl and obtained mononuclear gold(I) carbene derivatives XAuCNRCH=CHNY (X = I or Cl; Y = Et or EtOOC) [11].

Copper(I) mono- [12] and bis(diamino)carbene [13] complexes were recently prepared in our laboratory by reacting 1-methylimidazol-2-yllithium with CuCl, CuI or CuO_3SCF_3 and alkylating with CF_3SO_3Me. This method was also used to prepare a pyrazolinylidene complex of copper(I) [13] in which the nucleophilic nitrogen that is alkylated to create the carbene complex is located γ to the metal-bonded carbon and not α as in the thiazolinylidene and imidazolinylidene compounds. The consecutive transmetalation–alkylation approach has now been extended to include the formation of gold(I) carbene complexes from 1-methylimidazol-2-yllithium reagents and [AuCl(THT)], $[AuCl(PPh_3)]$, AuCN or $[Au(C_6F_5)(THT)]$. The spontaneous rearrangement of certain products with mixed ligands to form homoleptic gold(I) compounds complicated some of the preparations. Attempts to prepare monoprotonated or monoalkylated compounds from di(imidazolyl)gold compounds, yielded dialkylated or diprotonated compounds as the major products. A mixed bis(carbene) complex $[Au\{CNHCH=CHN(Me)\}\{CN(Me)CH=CHN(Me)\}][CF_3SO_3]$ could, however, be isolated.

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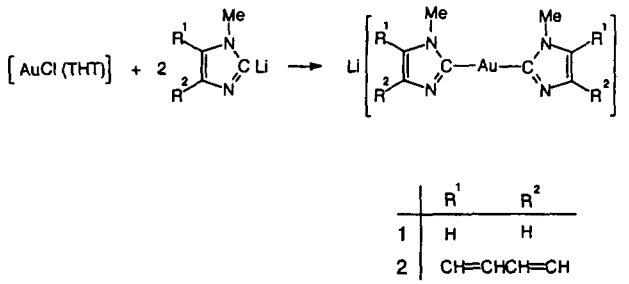


Scheme 1.

2. Results and discussion

The analytical and physical data for all the new compounds described are presented in Table 1 and the spectroscopic results appear in Table 2. The counter-ions $CF_3SO_3^-$ and Li^+ are not always shown in the schemes.

2.1. Synthesis and characterization of 1-methylimidazolylaurates

1-Methylimidazole and 1-methylbenzimidazole were lithiated at C^2 with BuLi at −40°C and −70°C respectively. The addition of half a molar amount of [AuCl(THT)] to a solution of the 1-methylimidazol-2-yllithium in THF (tetrahydrofuran) at −70°C produced the corresponding soluble aurate complexes **1** and **2** (Scheme 1) of which **1** was recrystallised from THF.

In the $^{13}C\{^1H\}$ NMR spectrum of complex **1**, [Au{C=NCH=CHN(Me)}$_2$]Li, the chemical shifts of the alkene carbons (δ 122.5 and 120.2 in CD_2Cl_2) show little change compared with 1-methylimidazole (δ 120.5 and δ 129.3 in CD_2Cl_2), while the coordinated carbon (C^2) resonates at δ 185.8, far upfield from the δ 138.2 value in the free imidazole despite the negative charge on the complex. This result implies a carbene character for the C^2 carbons of the 1-methylimidazolyl ligands in the aurate and, therefore, that the negative charge of the complex is located mainly on the Au and adjacent N atoms. The bis(thiazolyl)aurates have shown similar characteristics [3].

The mass spectrum of **1** does not exhibit a molecular ion. The fragments of compound **1** apparently recombine in the mass spectrometer to form the trimer [Au{C=NCH=CHN(Me)}]$_3$ and [Au{C=NCH=CHN(Me)}]$_n^+$ (n = 1, 2 or 3), the molecular and fragment ions thereof, as well as the [Au{C=NCH=CHN(Me)}$_2$]$^+$ ion could be identified in the spectrum. Various trimeric gold(I) imidazolyl compounds [10,11] are known.

Microcrystalline material of **1** is thermodynamically stable in air at room temperature for a limited period only and the compound is soluble in THF and CH_2Cl_2. The aurates **1** and **2** were not normally isolated but immediately after preparation used for further reactions.

2.2. Synthesis and characterization of bis(diaminocarbenes) complexes from [AuCl(THT)]

Protonation (with two molar amounts of CF_3SO_3H) or alkylation (with two molar amounts of CF_3SO_3Me) of the aurate complexes **1** and **2** yielded the stable bis(carbene) compounds **3–6** (Scheme 2).

One molar amount of CF_3SO_3H or CF_3SO_3Me also afforded the bis(carbene) compounds **3–6** probably via a homoleptic rearrangement (see Eq. (1), in which charges are omitted). In contrast, protonation or alkyla-

Table 1
Analytical and physical data

Complex	Yield (%)	M.p. (°C)	Colour	Analysis (%) [a]		
				C	H	N
1 [Au{(C=NCH=CHN(Me)}$_2$][Li]	84	144–145	Colourless	26.3(26.3)	2.7(2.8)	15.1(15.3)
3 [Au{CNHCH=CHN(Me)}$_2$][CF_3SO_3]	80	239–240	Colourless	21.0(21.2)	2.3(2.4)	10.7(10.9)
4 [Au{CNHC$_6$H$_4$N(Me)-*o*}$_2$][CF_3SO_3]	64	> 248(decomp.)	Yellow-green	33.6(33.5)	2.8(2.6)	9.1(9.2)
5 [Au{CN(Me)CH=CHN(Me)}$_2$][CF_3SO_3]	88	212–213	Colourless	24.3(24.5)	3.1(3.0)	5.3(5.2)
6 [Au{CN(Me)C$_6$H$_4$N(Me)-*o*}$_2$][CF_3SO_3]	30	265–270	Colourless	35.9(35.8)	3.2(3.2)	8.9(8.8)
7 [Au{CNHCH=CHN(Me)}{CN(Me)CH=CHN(Me)}][CF_3SO_3]	38	188–189	Colourless	22.9(22.9)	2.5(2.7)	10.6(10.7)
9 [Au(C_6F_5){CNHC$_6$H$_4$N(Me)-*o*}]	35	260(decomp.)	Colourless	33.8(33.9)	1.8(1.6)	5.6(5.7)
10 [Au(C_6F_5){CN(Me)CH=CHN(Me)}]	37	192–193	Colourless	28.6(28.7)	1.9(1.8)	6.1(6.1)
11 [Au(C_6F_5){CN(Me)C$_6$H$_4$N(Me)-*o*}]	43	250(decomp.)	Colourless	35.5(35.3)	2.1(2.0)	5.6(5.5)
12 [Au{N=CHN(Me)CH=CH}{CN(Me)CH=CHNH}][Au(C_6F_5)$_2$]	78	112–114	Colourless	26.9(26.9)	1.5(1.4)	6.4(6.3)
13 [Au(CN){CNHCH=CHN(Me)}]	30	160(decomp.)	Light yellow	19.8(19.7)	2.1(2.0)	13.6(13.8)
14 [Au(CN){CN(Me)CH=CHN(Me)}]	56	226(decomp.)	Colourless	22.8(22.6)	2.4(2.5)	13.2(13.2)

[a] Required values are given in parentheses.

tion (with one molar amount of CF_3SO_3H or CF_3SO_3Me) of the thiazolylaurates yielded neutral monocarbene complexes which could be further protonated or alkylated to give the corresponding cationic bis(carbene) complexes [3].

$$2[AuL^1(L^2)] \rightarrow [AuL^1_2] + [AuL^2_2] \quad (1)$$

We succeeded for the first time in isolating a mixed bis(carbene) complex (**7**) in pure form by successively alkylating and protonating the precursor 1-methylimidazolyl aurate complex **1** (Scheme 3). A mixture of compounds **5** and **7** was initially isolated from the reaction mixture and repeated recrystallization yielded complex **7**, containing both a secondary and a tertiary amino group.

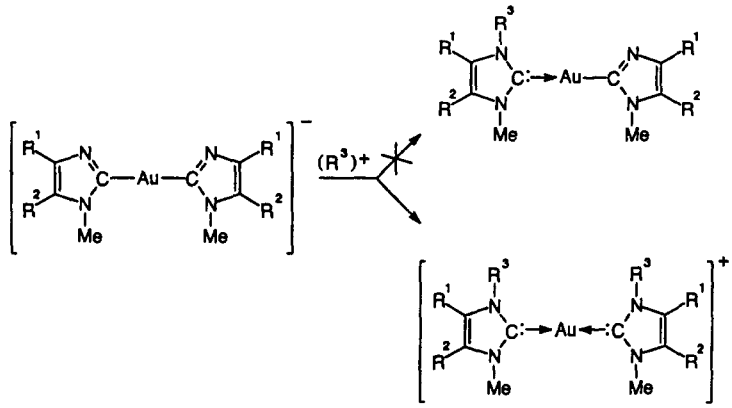
The X-ray crystal structure determination of **7** [14] shows an essentially linear complex with similar gold–carbon distances (Au–C = 1.99(1) Å for the carbene ligand formed by alkylation and Au–C = 2.00(2) Å for the one formed by protonation of the N atom). The two heterocyclic rings are identical in conformation and atom separations. No Au–Au contact occurs in the crystal.

The new compounds **3–7** are thermodynamically stable in air at room temperature, soluble in THF, CH_2Cl_2 and acetone, and have low solubilities in pen-

Table 2
Spectroscopic data

Complex		
1	δ_H [a]	7.08 (d, 2H, $J(H^4–H^5)$ 1.5, H^4), 6.98 (d, 2H, $J(H^5–H^4)$ 1.5, H^5), 3.79 (s, 6H, N–Me)
	δ_C [a]	185.8 (AuC), 122.5 (C^4), 120.2 (C^5), 36.8 (N–Me)
	m/z	834, $[Au\{C{=}NCH{=}CHN(Me)\}]_3^+$; 556, $[Au\{C{=}NCH{=}CHN(Me)\}]_2^+$; 359, $[Au\{C{=}NCH{=}CHN(Me)\}_2]^+$; 278, $[Au\{C{=}NCH{=}CHN(Me)\}]^+$
3	δ_H [b]	12.02 (br s, 2H, N–H), 7.44 (d, 2H, $J(H^4–H^5)$ 1.9, H^4), 7.37 (d, 2H, $J(H^5–H^4)$ 1.9, H^5), 3.94 (s, 6H, N–Me)
	δ_C [b]	182.8 (AuC), 123.0 (C^4), 119.8 (C^5), 38.0 (N–Me)
	m/z	361, $[Au\{CNHCH{=}CHN(Me)\}_2]^+$; 279, $[Au\{CNHCH{=}CHN(Me)\}]^+$
4	δ_H [a]	12.22 (br s, 2H, N–H), 7.49 (d, 2H, $J(H^4–H^5)$ 8.0, H^4), 7.12–7.33 (m, 4H, $2H^6$, $2H^5$), 6.79 (d, 2H, $J(H^6–H^7)$ 8.2, H^7), 3.66 (s, 6H, N–Me)
	δ_C [a]	189.3 (AuC), 133.2 and 132.5 (C^8, C^9), 124.9 and 124.6 (C^5, C^6), 112.9 (C^4), 110.8 (C^7), 34.8 (N = Me)
	m/z	461, $[Au\{CNHC_6H_4N(Me)\text{-}o\}_2]^+$, 329, $[Au\{CNHC_6H_4N(Me)\text{-}o\}]^+$
5	δ_H [b]	7.41 (s, 4H, $2H^4$, $2H^5$), 3.98 (s, 12H, N–Me)
	δ_C [b]	185.7 (AuC), 123.9 (C^4, C^5), 38.1 (N–Me)
	m/z	389, $[Au\{CN(Me)CH{=}CHN(Me)\}_2]^+$; 293, $[Au\{CN(Me)CH{=}CHN(Me)\}]^+$
6	δ_H [a]	7.64–7.59 (m, 4H, $2H^5$, $2H^6$), 7.58–7.53 (m, 4H, $2H^4$, $2H^7$), 4.17, (s, 12H, N–Me)
	δ_C [a]	191.3 (AuC), 134.4 (C^8, C^9), 125.5 (C^5, C^6), 111.9 (C^4, C^7), 35.5 (N–Me)
	m/z	490, $[Au\{CN(Me)C_6H_4N(Me)\text{-}o\}_2]^+$, 343, $[Au\{CN(Me)C_6H_4N(Me)\text{-}o\}]^+$
7	δ_H [b]	12.16 (br s, 2H, N–H), 7.54 (d, 1H, $J(H^4–H^5)$, 1.9, H^4), 7.45 (d, 1H, $J(H^5–H^4)$ 1.8, H^5), 7.41 (s, 2H, H^9, H^{10}), 4.02 (s, 3H, N^1–Me), 3.96 (s, 6H, N^6–Me, N^8–Me)
	δ_C [b]	185.3 (AuC^7), 183.0 (AuC^2), 123.9 (C^9, C^{10}), 123.2 (C^4), 120.0 (C^5), 38.0 (N^1–Me, N^8–Me)
	m/z	375, $[Au\{CN(Me)CH{=}CHN(Me)\}\{CNHCH{=}CHN(Me)\}]^+$; 293, $[Au\{CN(Me)CH{=}CHN(Me)\}]^+$; 279 $[Au\{CNHCH{=}CHN(Me)\}]$
9	δ_H [b]	12.46 (br s, H, N–H), 7.77–7.67 (m, 2H, H^5, H^6), 7.51–7.46 (m, 2H, H^4, H^7), 4.19 (s, 3H, N–Me)
	δ_C [b]	134.6 and 133.7 (C^8, C^9), 113.3 and 112.5 (C^4, C^7), 125.0 and 125.4 (C^6, C^5), 153.8–153.4, 148.1–147.8, 140.4–140.0, 135.1–133.6, (C_6F_5), 35.4 (N–Me)
	m/z	496, $[Au(C_6F_5)\{CNHC_6H_4N(Me)\text{-}o\}]^+$; 364, $[Au(C_6F_5)]$; 329, $[Au\{CNHC_6H_4N(Me)\text{-}o\}]^+$
10	δ_H [c]	7.04 (s, 2H, H^4, H^5), 3.82 (s, 6H, N–Me)
	δ_C [c]	189.5 (AuC), 123.4 (C^4, C^5), 38.7 (N–Me)
	m/z	460, $[Au(C_6F_5)\{CN(Me)CH{=}CHN(Me)\}]^+$; 364, $[Au(C_6F_5)]^+$; 293, $[Au\{CN(Me)CH{=}CHN(Me)\}]^+$
11	δ_H [b]	7.77–7.73 (m, 2H, H^5, H^6), 7.55–7.50 (m, 2H, H^4, H^7), 4.17 (s, 6H, N–Me)
	δ_C [a]	124.8 (C^6, C^5), 111.5 (C^4, C^7), 35.1 (N–Me)
	m/z	511, $[Au(C_6F_5)\{CN(Me)C_6H_4N(Me)\text{-}o\}]^+$; 344, $[Au\{CN(Me)C_6H_4N(Me)\text{-}o\}]^+$
12	δ_H [b]	12.32 (br s, 1H, N–H), 7.51 (s, 1H, H^7), 7.45 (d, H, $J(H^4–H^5)$ 1.9, H^4), 7.38 (d, 1H, $J(H^5–H^4)$ 1.7, H^5), 7.02 (s, 1H, H^{10}), 6,94 (s, 1H, H^9), 3.96 (s, 3H, N^1–Me), 3.71 (s, 3H, N^8–Me)
	δ_C [b]	185.7 (AuC), 134.7 (C^7), 129.7 (C^{10}), 122.6 (C^4), 119.3 (C^5, C^9), 37.8 (N^1–Me), 33.2 (N^8–Me), 152.1–152.5, 147.6–148.3, 140.2–139.8, 134.9–135.0 (C_6F_5)
	m/z	364, $[Au(C_6F_5)]^+$; 361, $[Au\{N{=}CHN(Me)CH{=}CH\}\{CNHCH{=}CHN(Me)\}]^+$; 279, $[Au\{CNHCH{=}CHN(Me)\}]^+$ or $[Au\{CH{=}NCH{=}CHN(Me)\}]^+$
13	δ_H [b]	12.05 (br s, 1H, NH), 7.52 (d, 1H, $J(H^4–H^5)$ 1.7, H^4), 7.44 (d, 1H, $J(H^5–H^4)$ 1.8, H^5), 4.00 (s, 3H, N–Me)
	δ_C [b]	182.8 (AuC), 123.2 (C^4), 119.9 (C^5), 38.1 (N–Me)
	m/z	223, $[Au(CN)]^+$; 164 $[\{CNHCH{=}CHN(Me)\}_2]^+$; 82, $[CNHCH{=}CHN(Me)]^+$
14	δ_H [b]	3.85 (s, 6H, N–Me), 7.34 (s, 2H, H^4, H^5)
	δ_C [b]	183,4 (AuC), 152.6 (CN), 123.7 (C^4, C^5), 38.1 (N–Me)
	m/z	319, $[Au(CN)\{CN(Me)CH{=}CHN(Me)\}]^+$; 293, $[Au\{CN(Me)CH{=}CHN(Me)\}]^+$; 223, $[Au(CN)]^+$

[a] Recorded in CD_2Cl_2. [b] Recorded in $(CD_3)_2CO$. [c] Recorded in a CD_2Cl_2 and $(CD_3)_2CO$ mixture.

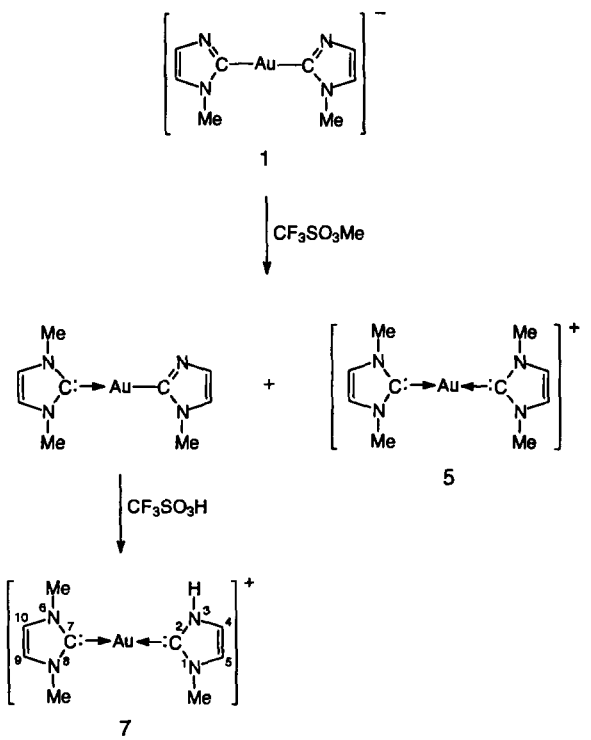


	R^1	R^2	R^3
3	H	H	H
4	CH=CHCH=CH		H
5	H	H	Me
6	CH=CHCH=CH		Me

Scheme 2.

tane, hexane and diethyl ether. The molecular ions of **3–7** were not observed in their mass spectra, but the cationic components $[Au(carbene\ ligand)_2]^+$ as well as the fragments $[Au(carbene\ ligand)]^+$ were always present.

The observation of N–H protons, at δ 12.02 and δ 12.22 in the ^1H NMR spectra of **3** and **4**, and N–Me proton signals that integrate for six protons, at δ 3.98 and δ 4.17 in the ^1H NMR spectra of **5** and **6**, confirmed the formation of carbene complexes. In the $^{13}C\{^1H\}$ NMR spectra of **3–6** the N–Me signals in the 1-methylimidazolinylidene compounds (**3**, δ 38.0; **5** δ 38.1) appear downfield from those in the 1-methylbenzimidazole-derived compounds (**4**, δ 34.8; **6**, δ 35.5). Mono- and bis(thiazolinylidene)gold(I) complexes do not display the same trend and the differences in the corresponding chemical shifts are less than 2 ppm [3]. The difference in the $^{13}C\{^1H\}$ NMR chemical shifts of the coordinated carbon atoms in the precursor aurate **1** (δ 185.8) and the carbene complexes **3** and **5** (δ 182.8 and 185.7) is insignificant. The signals for the carbene carbons in the imidazolinylidene complexes **3** and **5** appear 5–7 ppm upfield from those in the benzimidazolinylidene complexes **4** and **6** (189.3 for **4** and 191.3 for **6**). The same phenomenon was observed for (4-methylthiazolinylidene)gold(I) carbene and (benzothiazolinylidene)gold(I) carbene complexes [3]. The chemical shifts of C^4 and C^5 show virtually no change on conversion to the carbene. The small changes in the chemical shifts of C^2, C^4 and C^5 confirm that the electronic distribution in the framework of the aurates and corresponding carbene complexes is very similar. Interestingly, two different chemical shifts were observed for the two carbene carbon atoms in the unique mixed complex **7**. The resonances for the two cyclic ligands differ, and were assigned on the basis of the ^{13}C NMR spectra for compounds **3** and **5** which respectively contain the corresponding carbene ligands.



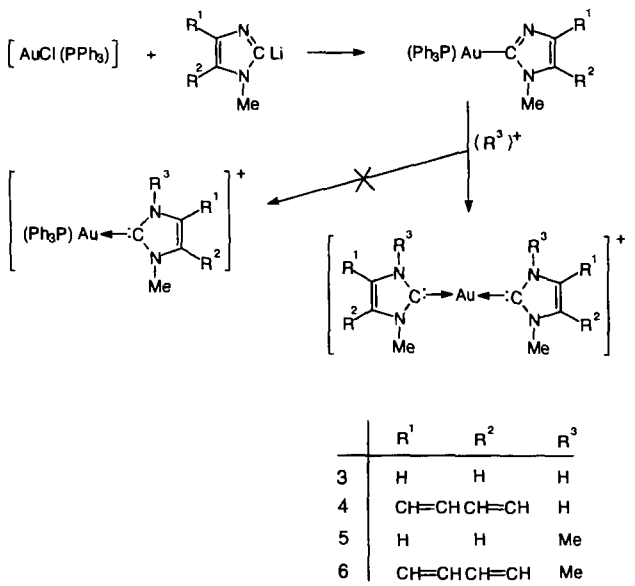
Scheme 3.

2.3. Bis(diamino)carbene complexes prepared from [AuCl(PPh$_3$)]

Only complexes **3–6** could be isolated from the final reaction mixtures during the attempted preparations of various mono(carbene) complexes from [AuCl(PPh$_3$)], lithiated 1-methylimidazole or 1-methylbenzimidazole and CF_3SO_3H or CF_3SO_3Me (Scheme 4). The transmetalations were carried out at low temperature. Burini and coworkers [10] have shown that stable trimeric *tris*[μ-(1-alkylimidazolato-N^3,C^2)tri-gold(I) complexes are formed when [AuCl(PPh$_3$)] is reacted with 1-alkyl-2-lithiumimidazole at room temperature. We therefore propose that at −70°C the neutral [Au(PPh$_3$)-{C=NCR^1=CR^{2}N(Me)] (R^1 = H, R^2 = H or R^{1}R^2 = C_4H_4) complexes form, and that protonation or alkylation at this low temperature then yields the cationic [Au(PPh$_3$){CN(R^1)CR^2=CR^{3}N(Me)}]$^+$ (R^1 = H or Me; R^2 = H and R^3 = H or R^{2}R^3 = C_4H_4) complexes which, however, undergo a homoleptic rearrangement (Eq. (1)) to furnish the bis(carbene) complexes. Protonation or alkylation of the trimers under comparable conditions do not afford bis(carbene) formation.

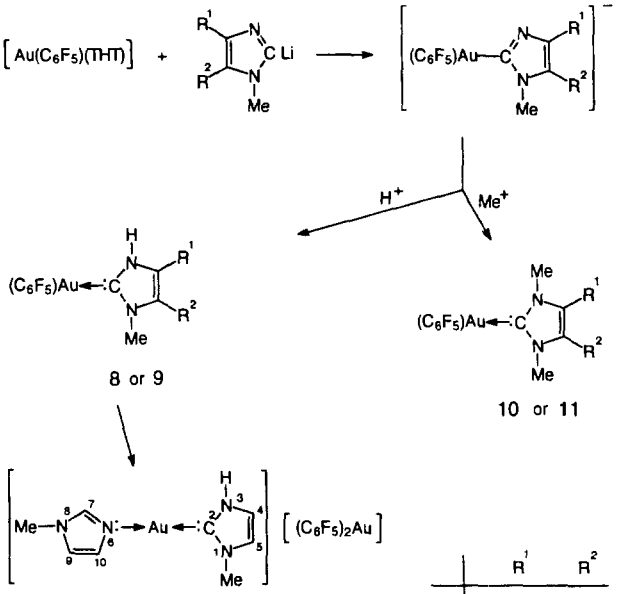
2.4. Synthesis and characterization of (diamino)carbene complexes prepared from [Au(C$_6$F$_5$)(THT)]

The reaction of [Au(C$_6$F$_5$)(THT)] with lithium 1-methylimidazol-2-yls and subsequent protonation or alkylation yielded carbene complexes **9**, **10**, **11** and **12** (Scheme 5). The aurates [(C$_6$F$_5$)Au{C=NCR^1=CR^{2}N(Me)}] (R^1 = H, R^2 = H or R^{1}R^2 = C_4H_4) were not isolated and acidification in the case of the (1-methylbenzimidazolyl)aurate yielded the neutral complex **9**



	R^1	R^2	R^3
3	H	H	H
4	CH=CHCH=CH		H
5	H	H	Me
6	CH=CHCH=CH		Me

Scheme 4.



	R^1	R^2
8	H	H
9	CH=CHCH=CH	
10	H	H
11	CH=CHCH=CH	

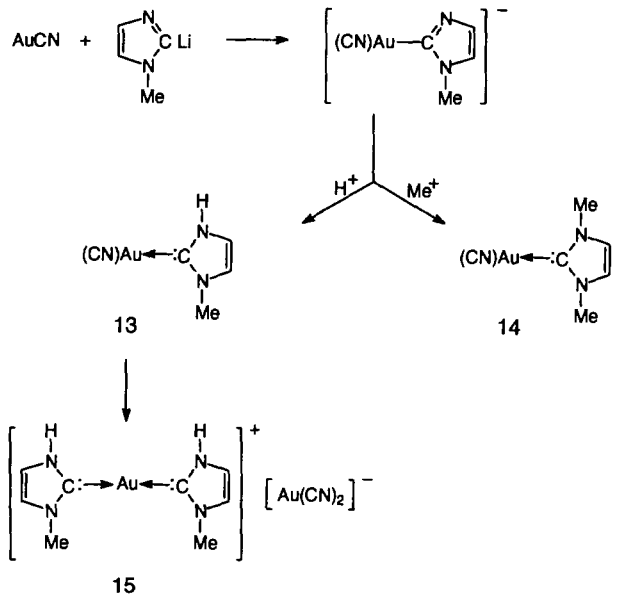
Scheme 5.

while (1-methylimidazolyl)aurate afforded the cationic complex **12**. Compound **12** contains an N-coordinated 1-methylimidazole ligand as well as a carbene ligand. We propose that a homoleptic rearrangement of **8** occurred in this instance, accompanied by a rapid proton migration from nitrogen to the initially coordinated carbon to give **12**.

Once again, the N–H protons in the ^{1}H NMR spectra of **9** (δ 12.46) and **12** (δ 12.32) and the six N–Me protons in the ^{1}H NMR spectra of **10** (δ 3.82) and **11** (δ 4.17) confirmed the formation of carbene compounds. The ^{13}C-{^{1}H} NMR chemical shifts of the N–Me groups display a similar trend as observed for the carbene complexes **3–6** (vide supra).

The structure assigned to **12** is based on its NMR spectra in acetone-d_6. The ^{1}H NMR spectrum shows the acidic proton H^7 at δ 7.51, the vinylic protons H^9 and H^{10} at δ 7.02 and δ 6.94 and the methyl group N^8–Me at δ 3.71. The carbene carbon appears at δ 185.7 and the two N–Me resonances at δ 37.8 (N^1–Me) and δ 33.2 (N^8–Me) in the ^{13}C-{^{1}H} NMR spectrum. The carbene carbon in **10** resonates at δ 189.5. Owing to the low solubility of complexes **9**, **10** and **11**, the weak signals for the C_6F_5 ligands in **10** and **11** and for the carbene carbons of **9** and **11**, could not be assigned with certainty.

Molecular ions were observed in the mass spectra of the neutral compounds **9**, **10** and **11**. The mass spectrum of complex **12** exhibited *m/z* values corresponding to its cation {Au{N=CHN(Me)CH=CH}{CNHCH=CHN-



Scheme 6.

(Me)}]$^+$ and fragments thereof, as well as an $[Au(C_6F_5)]^+$ fragment ion.

2.5. Synthesis and characterization of (diamino)carbenes prepared from AuCN

The plausible aurate complex $[Au(CN)\{\overline{C{=}NCH{=}CHN}(Me)\}]^-$, from reaction of AuCN and 1-methylimidazol-2-yllithium, yielded **13** and **14** on subsequent protonation (with CF_3SO_3H) or alkylation (with CF_3SO_3Me) (Scheme 6). Although compound **13** was isolated in crystalline form, it is unstable in solution and underwent a homoleptic rearrangement to afford the bis(carbene) complex **15**, which contains the same cation as **3**. This rearrangement is similar to that observed previously for neutral gold(I) complexes of the type R_3PAuCN (R = Ph, Me, Et, *i*-Pr or cyclohexyl) [15] which rearrange when in solution to give $[(R_3P)_2Au]^+$ and $[Au(CN)_2]^-$. The rearrangement of complex **13** was followed by ^1H NMR measured in acetone-d_6 every seventh consecutive day over a period of four weeks. The final equilibrium mixture contained the soluble species $Au(carbene)_2^+$, $Au(CN)_2^-$ and **13** in a ratio of 1.2 : 1 : 1 and the equilibrium constant in acetone-d_6 at 23°C for the equation **13** $\leftrightharpoons$ **15** + $Au(CN)_2^-$ was approximated as $K_c = 6.7 \times 10^{-1}$.

Carbene complex formation was confirmed by the N–H signal in the ^1H NMR spectrum of **13** (δ 12.05) and the N–Me signals in the ^1H NMR spectrum of **14** (δ 3.85). The carbene carbon signal in the $^{13}C\{^1H\}$ NMR spectrum of **14** was observed at δ 183.4, 6.1 ppm upfield from the corresponding one for **10**. The deshielding effect of the C_6F_5 group in **10** could be responsible for this effect. The very low intensity signal for the CN group could only be assigned in **14** (at δ 152.6). The molecular ion of **14** was observed in its mass spectrum and the fragment ions obtained for **13** also indicated its constitution. The IR spectra of complexes **13** and **14** showed strong ν(CN) vibrations (Nujol) at 2157 and 2166 cm^{-1} respectively.

3. Experimental

3.1. General

The compounds [AuCl(THT)] [16], $[AuCl(PPh_3)]$ [17], $[Au(C_6F_5)(THT)]$ [18] and AuCN [19] were prepared according to literature methods. Butyllithium (Merck), methyltrifluoromethane sulfonate (Aldrich), trifluoromethanesulfonic acid (Aldrich) and 1-methylimidazole (Fluka) were purchased and used without further purification. Benzimidazole (BDH) was used to prepare 1-methylbenzimidazole [20].

All reactions and manipulations were carried out under argon using standard Schlenk techniques. THF and diethyl ether were distilled under nitrogen from sodium diphenylketyl, pentane from sodium and CH_2Cl_2 from CaH_2.

Melting points were determined on a Büchi 535 apparatus. Mass spectra were recorded on a Finnigan Mat 8200 instrument (electron impact at 70 eV) and NMR spectra (^1H NMR at 200 MHz and $^{13}C\{^1H\}$ NMR at 50 MHz) on a VXR 200 FT spectrometer. Elemental analyses were carried out by the Division of Energy Technology, CSIR, Pretoria.

3.2. Preparation of $[Au\{\overline{C{=}NCH{=}CHN}(Me)\}_2]Li$ (1)

A solution of 1-methylimidazole (0.16 cm^3, 2.0 mmol) in 40 cm^3 THF was treated with BuLi in hexane (1.6 M, 1.25 cm^3, 2.0 mmol) at −40°C and stirred for 45 min. Small portions of [Au(THT)Cl] (0.30 g, 1.0 mmol) in THF (10 cm^3) were added slowly at −70°C. After stirring at −70°C for 2 h the mixture was allowed to warm to room temperature. If the mixture was used for further reactions at −70°C, it was stirred for only 1 h. Removal of the solvent under reduced pressure and washing with diethyl ether (3 × 20 cm^3) produced a white residue. Recrystallization from THF at −25°C afforded colourless crystals (yield 0.29 g).

3.3. Preparation of $[Au\{\overline{C{=}NC_6H_4N}(Me)\text{-}o\}_2]Li$ (2)

The analogous reaction at −70°C using 1-methylbenzimidazole (0.34 g, 2.6 mmol) in THF (40 cm^3), BuLi in hexane (1.6 M, 1.63 cm^3, 2.6 mmol) and [AuCl(THT)] (0.42 g, 1.3 mmol) in THF (10 cm^3) afforded a yellow solution of **2** that was used at −70°C for further reactions.

3.4. Preparation of $[Au\{\overline{CNHCH=CHN(Me)}\}_2][CF_3SO_3]$ (3)

The dropwise acidification of **1**, prepared from 1-methylimidazole (0.25 cm^3, 3.2 mmol) in 40 cm^3 THF, BuLi in hexane (1.6 M, 2.0 cm^3, 3.2 mmol) and [AuCl(THT)] (0.50 g, 1.6 mmol) in THF (10 cm^3), with CF_3SO_3H (0.29 cm^3, 3.2 mmol) at −70°C, afforded **3** after stirring for 30 min at −60°C. The reaction mixture was allowed to warm to room temperature and reduced to dryness under vacuum. The white residue was washed with a 1 : 1 mixture of pentane and diethyl ether (3 × 20 cm^3), extracted in 30 cm^3 CH_2Cl_2 and filtered through anhydrous $MgSO_4$. Concentration in vacuo to ca. 15 cm^3, layering with 10 cm^3 pentane and cooling to −25°C yielded colourless needles of **3** (yield 0.65 g).

3.5. Preparation of $[Au\{\overline{CNHC_6H_4N(Me)}\}_2\text{-}o][CF_3SO_3]$ (4)

Similarly the acidification of **2**, prepared from 1-methylbenzimidazole (0.34 g, 2.6 mmol) in THF (40 cm^3), BuLi in hexane (1.6 M, 1.63 cm^3, 2.6 mmol) and [AuCl(THT)] (0.41 g, 1.3 mmol) in THF (10 cm^3), with CF_3SO_3H (0.23 cm^3, 2.6 mmol), yielded **4**. The residue was washed with diethyl ether (3 × 20 cm^3) before extraction with CH_2Cl_2 (30 cm^3). Concentration in vacuo to ca. 15 cm^3 and cooling to −25°C produced yellow–green needles (yield 0.51 g).

3.6. Preparation of $[Au\{\overline{CN(Me)CH=CHN(Me)}\}_2][CF_3SO_3]$ (5)

The alkylation of **1**, prepared from 1-methylimidazole (0.24 cm^3, 3.0 mmol) in THF (40 cm^3), BuLi in hexane (1.6 M, 1.9 cm^3, 3.0 mmol) and [AuCl(THT)] (0.48 g, 1.5 mmol) in THF (10 cm^3), at −70°C with CF_3SO_3Me (0.33 cm^3, 3.0 mmol), produced colourless needles after work-up as described for **4**. The CH_2Cl_2 filtrate was layered with pentane (10 cm^3) for crystallization at −25°C (yield 0.71 g).

3.7. Preparation of $[Au\{\overline{CN(Me)C_6H_4N(Me)\text{-}o}\}_2][CF_3SO_3]$ (6)

Alkylation of the reaction mixture containing **2**, prepared from 1-methylbenzimidazole (0.34 g, 2.6 mmol) in THF (40 cm^3), BuLi in hexane (1.6 M, 1.63 cm^3, 2.6 mmol) and [AuCl(THT)] (0.42 g, 1.3 mmol) in THF (10 cm^3), with CF_3SO_3Me (0.29 cm^3, 2.6 mmol), afforded a mixture containing **6**. The filtrate was layered with diethyl ether (10 cm^3) after work-up as described for complex **4** and cooled to −25°C to obtain fine, colourless, needle-like crystals (yield, 0.25 g).

3.8. Preparation of $[Au\{\overline{CNHCH=CHN(Me)}\}\text{-}\{\overline{CN(Me)CH=CHN(Me)}\}][CF_3SO_3]$ (7)

After alkylation of **1**, prepared from 1-methylimidazole (0.17 cm^3, 2.2 mmol) in THF (40 cm^3), BuLi in hexane (1.6 M, 1.35 cm^3, 2.2 mmol) and [AuCl(THT)] (0.35 g, 1.1 mmol) in THF (10 cm^3), with CF_3SO_3Me (0.12 cm^3, 1.1 mol) at −70°C, the reaction mixture was stirred for 30 min at this temperature before the mixture was allowed to reach room temperature. Stirring at room temperature for 15 min was followed by cooling to −60°C and acidification with CF_3SO_3H (0.10 cm^3, 1.1 mmol). Purification of the products in the same way as for **4** produced a mixture of colourless needles of **5** and **7**. Vapour-diffusion recrystallization with acetone and pentane yielded pure crystals of **7** (yield 0.22 g).

3.9. Preparation of $[Au\{\overline{N=CHN(Me)CH=CH}\}\{\overline{CN(Me)CH=CHNH}\}][Au(C_6F_5)_2]$ (12)

Butyllithium in hexane (1.6 M, 0.85 cm^3, 1.4 mmol) was added to 1-methylimidazole (0.12 cm^3, 1.4 mmol) in THF (40 cm^3) at −40°C. The mixture was stirred for 45 min, $[Au(C_6F_5)(THT)]$ (0.61 g, 1.4 mmol) was added at −70°C and the reaction mixture was stirred for 2 h at this temperature. After adding CF_3SO_3H (0.13 cm^3, 1.3 mmol) dropwise, stirring for 30 min at −70°C and warming to room temperature the reaction mixture was worked-up in the same way as the mixture in **3**. Cubic crystals of **12** formed after a few days (yield 0.49 g).

3.10. Preparation of $[Au(C_6F_5)\{\overline{CNHC_6H_4N(Me)\text{-}o}\}]$ (9)

The analogous method at −70°C using 1-methylbenzimidazole (0.12 g, 0.9 mmol), BuLi in hexane (1.6 M, 0.57 cm^3, 0.9 mmol), $[Au(C_6F_5)(THT)]$ (0.41 g, 0.9 mmol) and CF_3SO_3H (0.8 cm^3, 0.9 mmol) afforded a white microcrystalline precipitate after isolation from the orange–brown mother liquor (yield 0.16 g). The residue was washed with pentane (3 × 30 cm^3) before extraction with CH_2Cl_2.

3.11. Preparation of $[Au(C_6F_5)\{\overline{CN(Me)CH=CHN(Me)}\}]$ (10)

Complex **10** was prepared according to the same procedure as **12** from 1-methylimidazole (0.10 cm^3, 1.3 mmol), BuLi in hexane (1.6 M, 0.81 cm^3, 1.3 mmol), $[Au(C_6F_5)(THT)]$ (0.58 g, 1.3 mmol) and CF_3SO_3Me (0.14 cm^3, 1.3 mmol). Colourless needle-like crystals were recrystallized from diethyl ether (yield 0.22 g).

3.12. Preparation of [Au(C_6F_5){$\overline{CN(Me)C_6H_4N(Me)\text{-}o}$}] (11)

The same method as for the preparation of **9** was employed to prepare **11** from 1-methylbenzimidazole (0.14 g, 1,0 mmol), BuLi in hexane (1.6 M, 0.65 cm^3, 1.0 mmol), [Au(C_6F_5)(THT)] (0.45 g, 1,0 mmol) and CF_3SO_3Me (0.12 cm^3, 1.0 mmol). A white microcrystalline precipitate was isolated from the orange–brown mother liquor (yield 0.22 g).

3.13. Preparation of [Au(CN){$\overline{CNHCH=CHN(Me)}$}] (13)

A solution of 1-methylimidazole (0.08 cm^3, 1.0 mmol) in THF (40 cm^3) was treated with BuLi in hexane (1.6 M, 0.63 cm^3, 1.0 mmol) at −40°C. The mixture was stirred for 45 min, AuCN (0.23 g, 1.0 mmol) was added and stirring continued for another hour at −40°C. The reaction mixture was warmed to room temperature and stirred for 12 h before the addition of CF_3SO_3H (0.09 cm^3, 1,0 mmol) at −40°C. After 30 min of stirring the reaction mixture was allowed to reach room temperature and reduced to dryness in vacuo. The white residue was washed with diethyl ether (3 × 20 cm^3) and extracted with acetone. The extract was filtered through anhydrous $MgSO_4$, the filtrate concentrated to ca. 10 cm^3 and layered with pentane (10 cm^3). Light yellow crystals formed at −25°C (yield 0.09 g).

3.14. Preparation of [Au(CN){$\overline{CN(Me)CH=CHN(Me)}$}] (14)

The analogous reaction using 1-methylimidazole (0.09 cm^3, 1.1 mmol), BuLi in hexane (1.6 M, 0.69 cm^3, 1.1 mmol), AuCN (0.25 g, 1.1 mmol) and CF_3SO_3Me (0.12 cm^3, 1.1 mmol) afforded **14**. The alkylating agent was added dropwise at −70°C. After stirring for 30 min at −70°C, the mixture was allowed to reach room temperature. The white residue was washed with diethyl ether (2 × 20 cm^3) and pentane (2 × 20 cm^3) before extraction with acetone (30 cm^3), filtration and concentration in vacuo to ca. 10 cm^3. Colourless cubic crystals formed at room temperature (yield 0.20 g).

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