Neutral Isocyanide and Carbene Pentafluorophenyl Complexes of Gold(I) and Gold(III)

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The addition of isocyanide CNR (R = C_6H_5, t-C_4H_9 or cyclo-C_6H_{11}) to Au(tht)(C_6F_5) leads to the displacement of the neutral ligand and to the formation of Au(isocyanide)(C_6F_5). The only hitherto known isocyanide derivatives of gold(III), Au(isocyanide)(C_6F_5)X_2 (X = Cl, Br or I) and Au(CNC_6H_5)-(C_6F_5)$_2$Cl, have been prepared by oxidizing the obtained Au(isocyanide)(C_6F_5) with halogens or, respectively, Au(CNC_6H_5)Cl with [(C_6F_5)$_2$TlBr]$_2$.

Carbene gold(I) complexes, Au(carbene)(C_6F_5), have been prepared by adding alcohols ROH (R = CH_3, C_2H_5) or primary amines RNH_2 (R = CH_3, C_6H_5, C_6H_{11}, p-FC_6H_4, $C_6H_5CH_2$, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, $C_6H_5CH_2CH_2$) to the afore-mentioned gold(I) isocyanide derivatives. When oxidized with halogens they also give gold(III) complexes, Au-(carbene)(C_6F_5)X_2 (X = Br or I).

Introduction

Relatively little has so far been known of the chemistry of neutral isocyanide and carbene complexes of gold. Less than a dozen of gold(I) isocyanide compounds of the type Au(isocyanide)X (X = Cl, Br, I) have been described [1, 2] and no neutral gold(III) isocyanide derivative has yet been reported.

About twelve neutral carbene complexes of gold(I) of the type Au(carbene)X (X = Cl, I) are known [1–6] along with the single gold(III) derivative [7] Au($\overline{C}$–NH–(CH_2)_3–$\overline{O}$)Cl_3.

In the present paper we describe the preparation of a novel type of gold(I) "organo isocyanide" compounds Au(isocyanide)(C_6F_5) and that of the corresponding Au(carbene)(C_6F_5) derivatives, which have been obtained by reacting the former with alcohols and amines. Furthermore, the oxidative addition of halogens has led to the preparation of the first neutral isocyanide complexes of gold(III) of the general formula Au(isocyanide)(C_6F_5)X_2 (X = Cl, Br, I) and to a series of neutral carbene complexes of gold(III) of the type Au(carbene)(C_6F_5)X_2 (X = Br, I). A single compound of the type Au(CNC_6H_5)(C_6F_5)_2Cl

has been prepared by oxidizing Au(CNC_6H_5)Cl with [(C_6F_5)$_2$TlBr]$_2$.

Experimental

IR spectra were recorded (over the range 4000–200 cm⁻¹) on a Perkin Elmer 577 spectrophotometer using Nujol mulls between polyethylene sheets. ¹H n.m.r. spectra were recorded on a Perkin Elmer R12B at 60 MHz with Me_4Si as internal reference. C, H and N analyses were carried out with a Perkin Elmer 240 microanalyzer. Au was determined by ashing the samples in a crucible together with an aqueous solution of hydrazine.

The yields, analytical data and melting points of the prepared compounds are listed in Tables I, II and III; their IR and ¹H n.m.r. data are given in Tables IV, V and VI.

Preparation of (Phenylisocyanide)chlorogold(I)

Phenylisocyanide (1 mmol) was added to a dichloromethane (20 ml) solution of Au(tht)Cl [8] (0.32 g., 1 mmol). The solution was left standing for 5 min at room temperature, evaporated to dryness and the residue was recrystallized from dichloromethane–hexane (see Table I).

Preparation of (Isocyanide)(pentafluorophenyl)-gold(I)

A slight excess of isocyanide was added to an ether or dichloromethane solution of Au(tht)(C_6F_5) [8] and stirred for 1 h at room temperature. The evaporation of the solvent leads to a colourless oil, which was stirred with hexane for several hours. The resulting white solid was recrystallized from dichloromethane–hexane.

Oxidation with Bromobis(pentafluorophenyl)thallium(III)

A mixture of Au(CNC_6H_5)Cl (0.29 g., 0.91 mmol) and [(C_6F_5)$_2$TlBr]$_2$ in 30 ml of benzene was stirred for 1 1/2 h at reflux temperature. The precipitated TlBr was filtered off and the filtrate was evaporated

TABLE I. Isocyanide Complexes of Gold(I) and Gold(III).

No.	Complex[a]	Yield (%)	C	H	N	Au	M.p. (°C)
1	Au(CNPh)Cl	96	25.20 (25.05)	1.44 (1.50)	4.05 (4.17)	58.81 (58.69)	144(d)
2	Au(CNPh)(C$_6$F$_5$)	70	33.38 (33.42)	1.20 (1.07)	2.94 (2.99)	42.65 (42.16)	148(d)
3	Au(CNBu^t)(C$_6$F$_5$)	64	29.54 (29.14)	2.06 (2.06)	3.13 (3.21)	43.85 (44.06)	132(d)
4	Au(CNCy)(C$_6$F$_5$)	45	32.42 (32.99)	2.24 (2.34)	2.65 (2.95)	41.40 (41.62)	108(d)
5	Au(CNPh)(C$_6$F$_5$)$_2$Cl	34	33.23 (34.07)	0.92 (0.75)	2.01 (2.09)	28.02 (29.41)	192(d)
6	Au(CNPh)(C$_6$F$_5$)Br$_2$	71	25.15 (24.94)	0.86 (0.84)	2.11 (2.23)	31.17 (31.42)	134(d)
7	Au(CNBu^t)(C$_6$F$_5$)Cl$_2$	50	25.29 (25.50)	1.76 (1.75)	2.62 (2.70)	37.92 (38.02)	106(d)
8	Au(CNBu^t)(C$_6$F$_5$)Br$_2$	52	21.67 (21.27)	1.25 (1.49)	2.23 (2.31)	32.41 (32.45)	104(d)
9	Au(CNBu^t)(C$_6$F$_5$)I$_2$	80	18.64 (18.85)	1.16 (1.29)	1.92 (2.00)	27.63 (28.10)	116(d)
10	Au(CNCy)(C$_6$F$_5$)Cl$_2$	50	27.94 (28.69)	2.20 (2.03)	2.57 (2.57)	36.15 (36.20)	99
11	Au(CNCy)(C$_6$F$_5$)Br$_2$	30	24.93 (24.66)	1.61 (1.75)	2.16 (2.21)	30.99 (31.11)	105
12	Au(CNCy)(C$_6$F$_5$)I$_2$	66	21.48 (21.47)	1.39 (1.50)	1.81 (1.92)	27.05 (27.09)	100

[a]Ph = C$_6$H$_5$, Bu^t = t-C$_4$H$_9$, Cy = C$_6$H$_{11}$.

to dryness. The white crystals were repeatedly recrystallized from dichloromethane–hexane.

Oxidation with Halogens

Stoichiometric amounts of the halogen (Cl$_2$, Br$_2$ or I$_2$) were added to dichloromethane solutions of (isocyanide)(pentafluorophenyl)gold(I) and stirred for 2 h at room temperature. The solvent was evaporated and the residue was recrystallized from dichloromethane–hexane to give white (X = Cl), yellow (X = Br) or red (X = I) crystals, respectively.

Reactions with Amines

Amines were added (2:1) to dichloromethane or chloroform solutions of (isocyanide)(pentafluorophenyl)gold(I) and stirred at room temperature. The course of the reaction was controlled by periodic scans of the CN stretching region. In a few cases, where no reaction had taken place after 3 days' treatment at room temperature, the mixture was refluxed though with no positive result. Once the reaction was completed, the solvent was evaporated and the residue was, if necessary (when an oil was obtained), stirred with hexane. The resulting white solid was

recrystallized from dichloromethane–hexane (see Table II).

Reactions with Alcohols

A methanol or ethanol solution of (isocyanide)-(pentafluorophenyl)gold(I) was refluxed. As before, the course of the reaction was controlled by periodic scans of the CN stretching region. Once the reaction was completed a small quantity of precipitated gold was filtered off and the filtrate was evaporated to dryness. The residue was recrystallized from dichloromethane–hexane.

Preparation of (Carbene)(pentafluorophenyl)dihalogold(III)

A dichloromethane solution of equimolecular amounts of (carbene)(pentafluorophenyl)gold(I) and halogen was stirred for 2 h at room temperature. The evaporation of the solvent led frequently to an oil which was washed with hexane. The obtained solid was recrystallized from dichloromethane–hexane to yield orange coloured (X = Br) or red (X = I) crystals (see Table III).

Reactions with chlorine led to non-crystallizable oils.

TABLE II. Carbene Gold(I) Complexes of the General Formula $\begin{array}{c} R_1 \\ \diagdown \\ R_2 \diagup \end{array} C\text{--}Au\text{--}C_6F_5$.

No.	R_1	R_2	Reaction Time (h)	Yield (%)	C	H	N	Au	M.p. (°C)
13	C_6H_5NH	CH_3NH	5	84	34.34 (33.74)	2.17 (2.02)	5.66 (5.62)	38.57 (39.53)	115(d)
14	C_6H_5NH	C_6H_5NH	24	37	40.60 (40.72)	2.18 (2.15)	4.89 (5.00)	34.12 (35.15)	175(d)
15	C_6H_5NH	$C_6H_{11}NH$	30	55	40.85 (40.29)	3.14 (3.20)	4.95 (4.94)	34.47 (34.78)	176(d)
16	C_6H_5NH	$p\text{-}FC_6H_4NH$	48	56	39.03 (39.46)	1.93 (1.91)	4.67 (4.84)	33.20 (34.06)	165(d)
17	C_6H_5NH	$C_6H_5CH_2NH$	1	71	41.39 (41.75)	2.43 (2.62)	4.83 (4.86)	33.07 (34.31)	132(d)
18	C_6H_5NH	$p\text{-}CH_3C_6H_4NH$	8	60	40.73 (41.82)	2.36 (2.45)	4.77 (4.87)	33.12 (34.30)	182(d)
19	C_6H_5NH	$p\text{-}CH_3OC_6H_4NH$	96	47	39.27 (40.70)	2.16 (2.39)	4.56 (4.74)	32.27 (33.37)	172(d)
20	C_6H_5NH	$C_6H_5CH_2CH_2NH$	8	72	41.81 (42.86)	2.80 (2.74)	4.58 (4.76)	32.22 (33.48)	120(d)
21	$t\text{-}C_4H_9NH$	CH_3NH	72	44	30.34 (30.13)	2.86 (2.95)	5.56 (5.85)	41.32 (41.19)	112
22	$t\text{-}C_4H_9NH$	$C_6H_5CH_2NH$	96	45	39.90 (39.00)	3.51 (3.27)	5.16 (5.05)	35.36 (35.53)	100
23	$C_6H_{11}NH$	CH_3NH	3	61	33.17 (33.34)	2.94 (3.19)	5.45 (5.55)	38.75 (39.06)	98
24	$C_6H_{11}NH$	$t\text{-}C_4H_9NH$	96	36	37.14 (37.37)	3.99 (4.05)	5.07 (5.12)	35.72 (36.05)	130(d)
25	$C_6H_{11}NH$	$C_6H_{11}NH$	48	66	39.74 (39.86)	4.43 (4.22)	5.03 (4.89)	34.40 (34.41)	135
26	$C_6H_{11}NH$	$C_6H_5CH_2NH$	48	48	41.91 (41.38)	3.07 (3.47)	4.68 (4.82)	33.69 (33.94)	110
27	C_6H_5NH	CH_3O	48	41	34.37 (33.68)	1.92 (1.81)	2.95 (2.80)	38.18 (39.46)	95(d)
28	C_6H_5NH	CH_3CH_2O	12	37	35.91 (35.10)	2.35 (2.16)	2.90 (2.72)	37.13 (38.38)	78(d)
29	$C_6H_{11}NH$	CH_3O	72	25	33.25 (33.27)	3.06 (2.99)	2.83 (2.77)	38.75 (38.98)	132(d)

Results and Discussion

Isocyanide Complexes

We have used $Au(tht)(C_6F_5)$ as starting compound for the preparation of gold(I) isocyanide derivatives since its tetrahydrothiophen group (tht) can readily be replaced by anionic ligands [8] or by other neutral P- or As-donor groups [9]. The substitution reaction can also be accomplished with isocyanide, according to eq. (1):

$$RNC + Au(tht)(C_6F_5) \rightarrow Au(CNR)(C_6F_5) + (tht) \quad (1)$$
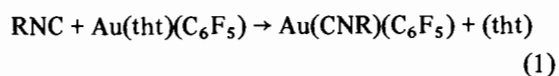
where R can be an aliphatic, a *cyclo*-aliphatic or an aromatic substituent.

The resulting compounds are air- and moisture-stable in the solid state, though when heated to their melting point they emit the characteristic smell of the free isocyanide. They are soluble in benzene, dichloromethane, chloroform and acetone, little soluble in ethanol and methanol and insoluble in hexane. They behave as non-conductors in acetone solution.

The reaction with halogens leads, according to eq. (2), to novel isocyanide complexes of gold(III).
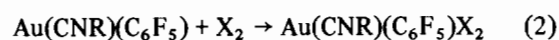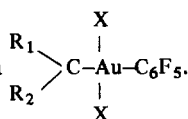
$$Au(CNR)(C_6F_5) + X_2 \rightarrow Au(CNR)(C_6F_5)X_2 \quad (2)$$

TABLE III. Carbene Gold(III) Complexes of the General Formula $\begin{matrix} R_1 \\ \\ R_2 \end{matrix} \searrow C-\overset{\overset{X}{|}}{\underset{\underset{X}{|}}{Au}}-C_6F_5.$

No.	R$_1$	R$_2$	X	Yield (%)	C	H	N	Au	M.p. (°C)
30	C$_6$H$_5$NH	CH$_3$O	Br	60	23.89 (25.51)	1.22 (1.37)	1.89 (2.12)	28.67 (29.89)	125(d)
31	C$_6$H$_5$NH	C$_6$H$_{11}$NH	Br	64	30.51 (31.42)	2.64 (2.49)	3.69 (3.85)	27.00 (27.12)	112(d)
32	C$_6$H$_5$NH	C$_6$H$_5$CH$_2$NH	Br	70	32.53 (32.72)	1.86 (1.90)	3.69 (3.81)	27.07 (26.83)	109(d)
33	C$_6$H$_5$NH	C$_6$H$_5$CH$_2$CH$_2$NH	Br	74	32.44 (33.71)	2.17 (2.15)	3.50 (3.74)	25.93 (26.33)	115(d)
34	t-C$_4$H$_9$NH	CH$_3$NH	Br	56	22.98 (22.58)	2.14 (2.21)	4.18 (4.39)	30.26 (30.87)	155
35	t-C$_4$H$_9$NH	CH$_3$NH	I	50	19.96 (19.68)	2.04 (1.92)	3.67 (3.82)	26.67 (26.91)	140
36	C$_6$H$_{11}$NH	C$_6$H$_{11}$NH	I	63	27.25 (27.62)	2.81 (2.92)	3.16 (3.39)	23.10 (23.84)	136
37	C$_6$H$_{11}$NH	C$_6$H$_5$CH$_2$NH	I	60	28.80 (28.79)	2.61 (2.41)	3.26 (3.35)	23.20 (23.61)	116

TABLE IV. I.r. Data for Isocyanide Complexes.

Complex	$\nu(C\equiv N)$	$\nu_{asym}(X-Au-X)$	$\nu_{sym}(X-Au-X)$
Au(CNPh)Cl	2230(s)		
Au(CNPh)(C$_6$F$_5$)	2212(s)		
Au(CNBu^t)(C$_6$F$_5$)	2225(vs)		
Au(CNCy)(C$_6$F$_5$)	2225(vs)		
Au(CNPh)(C$_6$F$_5$)$_2$Cl	2220(s)		
trans-Au(CNPh)(C$_6$F$_5$)Br$_2$	2260(s)	265(s)	230(m)
trans-Au(CNBu^t)(C$_6$F$_5$)Cl$_2$	2245(vs)	360(s)	a
trans-Au(CNBu^t)(C$_6$F$_5$)Br$_2$	2270(s)	260(m)	230(w)
Au(CNBu^t)(C$_6$F$_5$)I$_2$	2240(vs)		
trans-Au(CNCy)(C$_6$F$_5$)Cl$_2$	2300(s)	371(m)	332(m)
trans-Au(CNCy)(C$_6$F$_5$)Br$_2$	2280(s)	265(m)	230(m)
Au(CNCy)(C$_6$F$_5$)I$_2$	2280(s)		

^{a}The absorption is probably masked by $\nu_{asym}(X-Au-X)$.

The cleavage of the Au–C$_6$F$_5$ bond, which had been reported for the halogenation of other gold complexes [10], could not be observed in any case. The obtained compounds are also air- and moisture-stable. They are soluble in most organic solvents, but not in aliphatic hydrocarbons.

On the other hand, (phenylisocyanide)chlorogold-(I) can also be oxidized with bis(pentafluorophenyl)-thallium(III) bromide with transfer of the two pentafluorophenyl groups and precipitation of TlBr:

2Au(CNR)Cl + [(C$_6$F$_5$)$_2$TlBr]$_2$ →

          2Au(CNR)(C$_6$F$_5$)$_2$Cl + 2TlBr   (3)
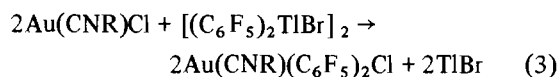
Moreover, the reaction with (tert-butylisocyanide)-chlorogold(I) gave a mixture of products which could not be resolved.

The stretching vibration $\nu(C\equiv N)$ of the free isocyanide is located in the 2200–2100 cm^{-1} region. $\Delta\nu$ (the diference between $\nu(C\equiv N)$ in the coordinated and in the free ligand) is generally >0 for complexes whose central atom is in a positive oxidation state, whilst it is negative or near nil for complexes of Cr(0), Ni(0), Co(0) and Pt(0) [1, 11]. As may be seen from Table IV, in the case of the described compounds $\Delta\nu$ is positive, the difference being larger for the gold(III) derivatives. This is in accordance with

TABLE V. I.r. and ¹H n.m.r. Data for the Carbene Complexes.

Complex	ν(NH)	δ(NH)	ν(CN)	Chemical Shifts
Au[C(NHC$_6$H$_5$)(NHCH$_3$)](C$_6$F$_5$)	3350w	1590m	1560s	1.6(NH), 2.6(C$_6$H$_5$), 7.1(CH$_3$)
Au[C(NHC$_6$H$_5$)$_2$](C$_6$F$_5$)	3325w	1595s	1540s	0.2(NH), 2.4(C$_6$H$_5$)
Au[C(NHC$_6$H$_5$)(NHC$_6$H$_{11}$)](C$_6$F$_5$)	3320m, 3190m	1595m	1550s	1.8(NH), 2.5(C$_6$H$_5$), 6.5(C$_6$H$_{11}$)
Au[C(NHC$_6$H$_5$)(p-NHC$_6$H$_4$F)](C$_6$F$_5$)	3340s, 3325s	1600m	1545vs	2.5(C$_6$H$_5$)
Au[C(NHC$_6$H$_5$)(NHCH$_2$C$_6$H$_5$)](C$_6$F$_5$)	3300w, 3190w	1600m	1560s	2(NH), 2.6(C$_6$H$_5$), 5.1(CH$_2$)
Au[C(NHC$_6$H$_5$)(p-NHC$_6$H$_4$CH$_3$)](C$_6$F$_5$)	3330s, 3320s	1600s	1545s	2.7(C$_6$H$_5$), 2.2(C$_6$H$_4$), 7.7(CH$_3$)
Au[C(NHC$_6$H$_5$)(p-NHC$_6$H$_4$OCH$_3$)](C$_6$F$_5$)	3320s	1600s	1540vs	2.6(C$_6$H$_5$), 6.3(OCH$_3$)
Au[C(NHC$_6$H$_5$)(NHCH$_2$CH$_2$C$_6$H$_5$)](C$_6$F$_5$)	3400m, 3350m	1590m	1555vs	1.7(NH), 2.7(C$_6$H$_5$), 6.0(CH$_2$N), 6.9(CH$_2$Ph)
Au[C(NHC$_4$H$_9$)(NHCH$_3$)](C$_6$F$_5$)	3410w, 3376w	1638m	1549s	7.25(CH$_3$), 8.35(C$_4$H$_9$)
Au[C(NHC$_4$H$_9$)(NHCH$_2$C$_6$H$_5$)](C$_6$F$_5$)	3345w, 3377w	1634m	1548s	
Au[C(NHC$_6$H$_{11}$)(NHCH$_3$)](C$_6$F$_5$)	3460m, 3380m	1632w	1555s	7.2(CH$_3$), 8.45(C$_6$H$_{11}$)
Au[C(NHC$_6$H$_{11}$)(NHC$_4$H$_9$)](C$_6$F$_5$)	3365m, 3270m	1610m	1545s	
Au[C(NHC$_6$H$_{11}$)$_2$](C$_6$F$_5$)	3280m	1630m	1555s	8.45(C$_6$H$_{11}$)
Au[C(NHC$_6$H$_{11}$)(NHCH$_2$C$_6$H$_5$)](C$_6$F$_5$)	3460m, 3370w	1639m	1545vs	2.7(C$_6$H$_5$), 5.75(CH$_2$), 8.65(C$_6$H$_{11}$)
Au[C(NHC$_6$H$_5$)(OCH$_3$)](C$_6$F$_5$)	3400w, 3340w	1600m	1540vs	
Au[C(NHC$_6$H$_5$)(OCH$_2$CH$_3$)](C$_6$F$_5$)	3400w, 3340w	1600m	1530s	
Au[C(NHC$_6$H$_{11}$)(OCH$_3$)](C$_6$F$_5$)	3340w	1635m	1551s	
Au[C(NHC$_6$H$_5$)(OCH$_3$)](C$_6$F$_5$)Br$_2$	3300w, 3260w	1600m	1570s	1.1(NH), 2.4(C$_6$H$_5$), 5.5(OCH$_3$)
Au[C(NHC$_6$H$_5$)(NHC$_6$H$_{11}$)](C$_6$F$_5$)Br$_2$	3290s	1600m	1570s	
Au[C(NHC$_6$H$_5$)(NHCH$_2$C$_6$H$_5$)](C$_6$F$_5$)Br$_2$	3210m	1605m	1560s	2.6(C$_6$H$_5$), 4.7(CH$_2$)
Au[C(NHC$_6$H$_5$)(NHCH$_2$CH$_2$C$_6$H$_5$)](C$_6$F$_5$)Br$_2$	3300w	1605w	1580s	
Au[C(NHC$_4$H$_9$)(NHCH$_3$)](C$_6$F$_5$)I$_2$	3371m, 3360m	1638m	1591vs	7.75(CH$_3$), 8.42(C$_4$H$_9$)
Au[C(NHC$_4$H$_9$)(NHCH$_3$)](C$_6$F$_5$)I$_2$	3369m, 3350m	1636m	1588vs	
Au[C(NHC$_6$H$_{11}$)$_2$](C$_6$F$_5$)I$_2$	3290m, 3278m	1635w	1585s	
Au[C(NHC$_6$H$_{11}$)(NHCH$_2$C$_6$H$_5$)](C$_6$F$_5$)I$_2$	3380m, 3280m	1640w	1576vs	8.45(C$_6$H$_{11}$)

the decreased ability of gold(III) compared with gold-(I) to lease electron density to the π^* ligand orbitals. The Au—X stretching vibrations confirm [12] that the dihalo-complexes are the *trans*-isomers (see Table IV).

Carbene Complexes

(Isocyanide)(pentafluorophenyl)gold(I) reacts with methanol or ethanol according to eq. (4):

$$Au(CNR)(C_6F_5) + R'OH \longrightarrow$$
$$Au[C(NHR)(OR')](C_6F_5) \quad (4)$$
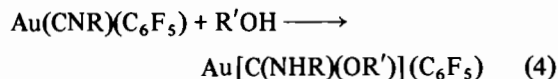
The resulting carbene derivatives are stable crystals, which are moderately soluble in organic solvents.

The process takes place readily whenever an electronwithdrawing substituent (such as the phenyl group) is attached to the isocyanide group. Nevertheless, the reaction of (*cyclo*-hexylisocyanide)(pentafluorophenyl)gold(I) proceeds only very slowly and affords low yields; no reaction could be observed with ethanol. The corresponding *tert*-butylisocyanide derivative does not react either with methanol or with ethanol, not even under more stringent conditions (in a closed tube at 100 °C). These negative results are, however, likely to be due to kinetic and not to thermodynamic reasons. Thus, Bonati and Minghetti [1] have established that some carbene complexes, which could not be synthesized by reacting an isocyanide derivative with alcohol, could be obtained by other routes.

The addition of amine to (isocyanide)(pentafluorophenyl)gold(I) derivatives, according to eq. (5), leads also to the formation of carbene. Reaction 5

$$Au(CNR)(C_6F_5) + R'NH_2 \longrightarrow$$
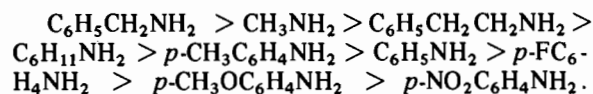$$Au[C(NHR)(NHR')](C_6F_5) \quad (5)$$
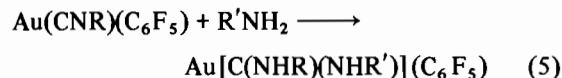
does readily take place in dichloromethane or chloroform solution at room temperature. As may be seen, the addition of amine proceeds under milder conditions than that of alcohols which is in accordance with the fact that amines are better nucleophiles than alcohols.

The phenylisocyanide derivative shows once more the highest reactivity; it reacts with all the tested

amines, except p-NO$_2$C$_6$H$_4$NH$_2$. The *cyclo*-hexylisocyanide derivative did not react with C$_6$H$_5$NH$_2$, p-FC$_6$H$_4$NH$_2$, p-CH$_3$OC$_6$H$_4$NH$_2$ and p-NO$_2$C$_6$H$_4$NH$_2$, whilst *tert*-butylisocyanide did not react with C$_6$H$_5$-NH$_2$, p-CH$_3$C$_6$H$_4$NH$_2$, t-C$_4$H$_9$NH$_2$, (C$_6$H$_5$)$_2$NH and p-NO$_2$C$_6$H$_4$NH$_2$.

From the time which each reaction takes to go to completion (see Table II) we may deduce that the aliphatic amines are more reactive than the aromatic ones, according to the following sequence:

$$C_6H_5CH_2NH_2 > CH_3NH_2 > C_6H_5CH_2CH_2NH_2 >$$
$$C_6H_{11}NH_2 > p\text{-}CH_3C_6H_4NH_2 > C_6H_5NH_2 > p\text{-}FC_6\text{-}$$
$$H_4NH_2 > p\text{-}CH_3OC_6H_4NH_2 > p\text{-}NO_2C_6H_4NH_2.$$

The oxidation with halogens (bromine and iodine) leads to dihalo-complexes of gold(III):

$$Au(carbene)(C_6F_5) + X_2 \longrightarrow$$
$$Au(carbene)(C_6F_5)X_2 \quad (6)$$
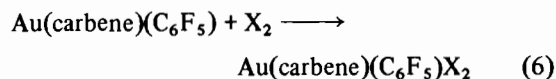
The treatment of Au(carbene)(C$_6$F$_5$) [carbene = C(NHC$_4$H$_9$)(NHCH$_3$) and C(NHC$_6$H$_{11}$)$_2$] with chlorine causes the cleavage of the Au—C$_6$F$_5$ bond and yields a mixture of products which could not be resolved. It does however not contain any pentafluorophenyl.

The obtained carbene derivatives are air- and moisture-stable solids which are moderately soluble in most organic solvents, but insoluble in hexane. Their acetone solutions are non-conducting.

The carbene complexes show an intense and frequently broad and asymmetric band at 1550 cm^{-1} (see Table V) which is assignable to a C—N stretching vibration with a bond order between 1 and 2. In the case of the gold(III) carbene this is slightly displaced towards higher energies. A bond order for the C—N bond higher than one points to the existence of several geometrical isomers, as has already been observed previously [6]. The ^{1}H n.m.r. spectra are actually more complex than those expected for single isomers; they generally show broad signals and in some cases it was not possible to assign those due to the NH resonance.

As may be seen from the Au—X stretching vibrations (listed in Table VI) the dibromocarbenegold(III) complexes are the *trans*-isomers.

TABLE VI. Stretching Vibrations ν(Au—X) for the Carbene Gold(III) Complexes.

Complex	ν_{asym}(X–Au–X)	ν_{sym}(X–Au–X)
Au[C(NHC$_6$H$_5$)(OCH$_3$)](C$_6$F$_5$)Br$_2$	265 (m)	230 (m)
Au[C(NHC$_6$H$_5$)(NHC$_6$H$_{11}$)](C$_6$F$_5$)Br$_2$	262 (m)	230 (m)
Au[C(NHC$_6$H$_5$)(NHCH$_2$C$_6$H$_5$)](C$_6$F$_5$)Br$_2$	265 (m)	228 (m)
Au[C(NHC$_6$H$_5$)(NHCH$_2$CH$_2$C$_6$H$_5$)](C$_6$F$_5$)Br$_2$	265 (m)	228 (w)
Au[C(NHC$_4$H$_9$)(NHCH$_3$)](C$_6$F$_5$)Br$_2$	260 (s)	225 (m)

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