Mono and Binuclear Gold Complexes with Diamine and Carbene Ligands

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The reaction of $NH_2(CH_2)_nNH_2$ *(n = 2 or 3) with* C_6F_5Autht *(tht = tetrahydrothiophen) or* $(C_6F_5)_m$*AuCNR (m = 1 or 3; R = Ph or* p*-tolyl (To)) leads to* $C_6F_5AuNH_2(CH_2)_nNH_2$ *or, respectively,* $(C_6F_5)_m$*AuC(NHR)[NH*$(CH_2)_nNH_2$*], which react with* $(C_6F_5)_m$*AuCNR to give binuclear carbene complexes of the types* $C_6F_5AuC(NHR)[NH(CH_2)_nNH_2]$*-*$AuC_6F_5$*,* $(C_6F_5)_m$*AuC(NHR)[NH*$(CH_2)_n$*NH](RHN)-*$CAuC_6F_5$ *or* $(C_6F_5)_3$*AuC(NHTo)[NH*$(CH_2)_n$*NH]-(ToHN)CAu*$(C_6F_5)_3$*.*

In XAutht (X = Cl or C_6F_5*) or* $O_3ClOAuPPh_3$ *the displacement of the tht or* $OClO_3$ *group by* C_6F_5*-*$AuNH_2(CH_2)_nNH_2$ *leads to the binuclear complexes* $C_6F_5AuNH_2(CH_2)_nNH_2AuX$ *or* $[C_6F_5AuNH_2$*-*$(CH_2)_2NH_2AuPPh_3]ClO_4$*.*

The reaction of cis*-*$[(C_6F_5)_2Au(OEt_2)_2]ClO_4$ *with diamine renders* cis*-*$[(C_6F_5)_2AuNH_2(CH_2)_n$*-*$NH_2]ClO_4$ *which react with CNPh to give carbene complexes of the type* $[(C_6F_5)_2AuNH_2(CH_2)_nNHC$*-(NHPh)]*$ClO_4$ *and* $\{(C_6F_5)_2AuC(NHPh)[NH(CH_2)_n$*-NH]C(NHPh)}*$ClO_4$*.*

Introduction

Few organo-gold complexes containing a neutral bidentate ligand – generally a diphosphine [1, 2] – are known. With diamines, compounds of the types $[R_2Au(L–L)]^+$ (L–L = $NH_2(CH_2)_2NH_2$ [3–6], α,α′-bipy, *o*-phen [7–9]; R = Me, Et, n-Pr, n-Bu; R_2 = Ph_4C_2), $Me_2XAu(L–L)$ (L–L = 2,7-dimethyl-1,8-naphthyridine [8]; X = Cl, Br, I, CN, SCN, SeCN), $Me_3Au(L–L)$ (L–L = $C_5H_6N_2$ [10]) along with the binuclear complexes $[(n\text{-}Pr)_2XAu]_2[NH_2(CH_2)_2NH_2]$ (X = Br, CN [11]) and $(Me_3Au)_2[NH_2(CH_2)_2NH_2]$ [10] have been reported. Moreover, it is known that the amines can act as nucleophiles towards goldisocyanide under formation of the corresponding carbenes [12–14]. This type of reaction had so far not been studied with the diamines $NH_2(CH_2)_nNH_2$, which owing to their two NH_2 groups should be able to form binuclear carbenes.

By using the precursors $C_6F_5AuNH_2(CH_2)_nNH_2$ and $(C_6F_5)_mAuC(NHR)[NH(CH_2)_nNH_2]$ [n = 2 or 3, m = 1 or 3; R = phenyl (Ph) or *p*-tolyl (To)], whose preparation is described in the present paper (except for the previously reported [15] complex with n = 2, m = 3, R = To) and which contain a free NH_2 group, and reacting them with other gold derivatives containing a readily displaceable ligand or with goldisocyanide we have been able to obtain new binuclear complexes.

Experimental

IR spectra were recorded (over the range 4000–200 cm^{-1}) on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets; conductivities were measured in 5×10^{-4} *M* acetone solution with a Philips 9501/01 conductimeter; moleculear weights were determined in approx. 10^{-3} *M* solution in $CHCl_3$ using the isopiestic method on a Perkin-Elmer mod. 115 apparatus. C, H and N analyses were carried out with a Perkin-Elmer 240 microanalyzer; Au was determined by ashing the samples with an aqueous solution of hydrazine.

The yields, analytical data and melting points of the novel complexes are collected in Table I. All the reactions were carried out at room temperature.

Preparation of the complexes $C_6F_5AuNH_2(CH_2)_n$*-*NH_2 *[n = 2 (1) or 3 (2)]*

To a solution of $C_6F_5Au(tht)$ (tht = tetrahydrothiophen) [16] (0.452 g, 1 mmol) in 20 ml of diethylether was added $NH_2(CH_2)_nNH_2$ (1 mmol) (n = 2 or 3) and stirred for 30 min. Evaporation to ~5 ml and addition of 20 ml of hexane led to the precipitation of the white complex (*1*) or, respectively, (*2*), which was recrystallized from dichloromethane-hexane.

$C_6F_5Au(4,4'\text{-}bipy)AuC_6F_5$ *(3)*

To a solution of C_6F_5Autht [16] (0.452 g, 1 mmol) in 20 ml of dichloromethane was added 4,4′-

TABLE I. Analytical Data for Complexes *1*–*32*.

Complex	Yield (%)	M.p. (°C)	Anal. found (calcd) (%)				Λ_M[a] (ohm^{-1} cm^2 mol^{-1})	Mol. wt.[b] found (calcd)
			C	H	N	Au		
1 $C_6F_5AuNH_2(CH_2)_2NH_2$	76	100(d)	23.15 (22.65)	2.05 (1.9)	7.2 (6.6)	45.95 (46.45)	1	466 (424)
2 $C_6F_5AuNH_2(CH_2)_3NH_2$	76	69	24.65 (24.65)	2.45 (2.3)	6.35 (6.4)	44.1 (44.95)	13	429 (438)
3 $C_6F_5Au(4,4'$-bipy$)AuC_6F_5$	76	150(d)	29.1 (29.9)	1.2 (0.9)	3.1 (3.15)	44.7 (44.5)	c	c
4 $[(C_6F_5)_2AuNH_2(CH_2)_2NH_2]ClO_4$	85	139(d)	24.6 (24.35)	1.2 (1.2)	4.2 (4.05)	29.35 (28.5)	131	–
5 $[(C_6F_5)_2AuNH_2(CH_2)_3NH_2]ClO_4$	82	189(d)	25.15 (25.55)	1.7 (1.45)	4.15 (4.0)	27.25 (27.95)	126	–
6 $C_6F_5AuC(NHPh)[NH(CH_2)_2NH_2]$	67	134(d)	33.9 (34.15)	2.3 (2.5)	8.0 (7.95)	36.85 (37.35)	5	595 (527)
7 $C_6F_5AuC(NHTo)[NH(CH_2)_2NH_2]$	83	135(d)	35.2 (35.5)	3.1 (2.8)	8.0 (7.75)	35.9 (36.4)	9	568 (541)
8 $C_6F_5AuC(NHPh)[NH(CH_2)_3NH_2]$	80	105(d)	36.35 (35.5)	2.9 (2.8)	7.8 (7.75)	35.8 (36.4)	6	560 (541)
9 $C_6F_5AuC(NHTo)[NH(CH_2)_3NH_2]$	75	128	37.0 (36.75)	3.3 (3.1)	8.35 (7.55)	34.9 (35.45)	20	567 (555)
10 $(C_6F_5)_3AuC(NHTo)[NH(CH_2)_3NH_2]$	68	165(d)	39.7 (39.15)	2.1 (1.95)	4.75 (4.7)	22.65 (22.15)	7	943 (889)
11 $[(C_6F_5)_2\overline{AuNH_2(CH_2)_2NHC}(NHPh)]ClO_4$	74	230(d)	31.0 (31.8)	1.9 (1.65)	5.0 (5.3)	25.1 (24.8)	111	–
12 $[(C_6F_5)_2\overline{AuNH_2(CH_2)_3NHC}(NHPh)]ClO_4$	78	165(d)	33.35 (32.7)	2.4 (1.9)	5.4 (5.2)	25.1 (24.4)	116	–
13 $[(C_6F_5)_2\overline{AuC(NHPh)[NH(CH_2)_2NH]C}(NHPh)]ClO_4$	40	240(d)	37.0 (37.5)	2.3 (2.0)	6.2 (6.25)	22.3 (22.0)	117	–
14 $[(C_6F_5)_2\overline{AuC(NHPh)[NH(CH_2)_3NH]C}(NHPh)]ClO_4$	50	160(d)	37.9 (38.25)	2.4 (2.2)	5.7 (6.15)	22.35 (21.6)	102	–
15 $C_6F_5AuNH_2(CH_2)_2NH_2AuCl$	80	132(d)	14.55 (14.65)	1.7 (1.25)	4.65 (4.25)	60.65 (60.0)	c	c
16 $C_6F_5AuNH_2(CH_2)_2NH_2AuC_6F_5$	65	105(d)	21.05 (21.35)	1.1 (1.0)	4.2 (3.55)	49.6 (50.0)	c	c
17 $C_6F_5AuNH_2(CH_2)_3NH_2AuCl$	51	120(d)	16.3 (16.1)	2.35 (1.5)	4.9 (4.2)	58.15 (58.8)	c	c
18 $C_6F_5AuNH_2(CH_2)_3NH_2AuC_6F_5$	65	140(d)	21.65 (22.45)	1.35 (1.25)	3.55 (3.5)	48.9 (49.1)	7	817 (802)
19 $[C_6F_5AuNH_2(CH_2)_2NH_2AuPPh_3]ClO_4$	64	130(d)	30.95 (31.75)	2.35 (2.35)	2.75 (2.85)	40.0 (40.1)	103	–

20 $C_6F_5AuC(NHPh)[NH(CH_2)_2NH_2]AuC_6F_5$	45	70(d)	29.15 (28.3)	1.85 (1.45)	4.7 (4.7)	43.85 (44.2)	4	844 (891)
21 $C_6F_5AuC(NHTo)[NH(CH_2)_2NH_2]AuC_6F_5$	46	160(d)	29.2 (29.2)	1.8 (1.65)	4.5 (4.65)	42.9 (43.5)	12	919 (905)
22 $C_6F_5AuC(NHPh)[NH(CH_2)_3NH_2]AuC_6F_5$	14	85(d)	28.6 (29.2)	1.65 (1.65)	4.75 (4.65)	44.0 (43.5)	9	952 (905)
23 $C_6F_5AuC(NHTo)[NH(CH_2)_3NH_2]AuC_6F_5$	49	180(d)	30.2 (30.05)	2.0 (1.85)	5.05 (4.55)	41.95 (42.85)	3	928 (919)
24 $C_6F_5AuC(NHPh)[NH(CH_2)_2NH](PhHN)CAuC_6F_5$	57	130(d)	33.2 (33.8)	1.8 (1.8)	5.6 (5.65)	40.1 (39.6)	1	^{c}
25 $C_6F_5AuC(NHTo)[NH(CH_2)_2NH](ToHN)CAuC_6F_5$	45	130(d)	35.9 (35.25)	2.3 (2.15)	5.95 (5.5)	37.8 (38.55)	8	960 (1022)
26 $C_6F_5AuC(NHPh)[NH(CH_2)_2NH](ToHN)CAuC_6F_5$	70	165(d)	34.75 (34.55)	2.0 (2.0)	5.25 (5.55)	39.6 (39.05)	3	949 (1008)
27 $C_6F_5AuC(NHTo)[NH(CH_2)_3NH](ToHN)CAuC_6F_5$	36	100(d)	36.6 (35.9)	2.5 (2.35)	5.5 (5.4)	37.6 (38.0)	8	1032 (1037)
28 $C_6F_5AuC(NHPh)[NH(CH_2)_2NH](ToHN)CAu(C_6F_5)_3$	62	170(d)	37.0 (36.7)	1.65 (1.5)	3.9 (4.15)	28.8 (29.35)	4	1237 (1342)
29 $C_6F_5AuC(NHTo)[NH(CH_2)_2NH](ToHN)CAu(C_6F_5)_3$	50	140(d)	37.0 (37.2)	1.8 (1.65)	4.9 (4.1)	28.75 (29.05)	2	1198 (1356)
30 $C_6F_5AuC(NHTo)[NH(CH_2)_3NH](ToHN)CAu(C_6F_5)_3$	40	140(d)	37.95 (37.7)	1.9 (1.75)	4.4 (4.1)	29.4 (28.75)	3	1257 (1371)
31 $(C_6F_5)_3AuC(NHTo)[NH(CH_2)_2NH](ToHN)CAu(C_6F_5)_3$	47	225(d)	38.35 (38.35)	1.5 (1.3)	3.7 (3.3)	22.7 (23.3)	12	1720 (1691)
32 $(C_6F_5)_3AuC(NHTo)[NH(CH_2)_3NH](ToHN)CAu(C_6F_5)_3$	50	155(d)	38.0 (38.75)	1.8 (1.4)	3.9 (3.3)	22.75 (23.1)	8	1587 (1705)

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[a] In acetone. [b] Chloroform. [c] Insoluble.

bipyridyl (0.078 g, 0.5 mmol). After 1 h stirring complex (*3*) was filtered off.

$[(C_6F_5)_2\ AuNH_2(CH_2)_nNH_2]ClO_4$ [n = 2 (4) or 3 (5)]

To a suspension of *cis*-$Bu_4N[(C_6F_5)_2AuCl_2]$ [17] (0.844 g, 1 mmol) in 25 ml of diethylether was added $AgClO_4$ (0.415 g, 2 mmol) and stirred for 90 min under exclusion of light. The precipitated AgCl and $[Bu_4N]ClO_4$ were removed. Addition of $NH_2(CH_2)_nNH_2$ (1 mmol) to the filtrate gave rise to the precipitation of the white complex (*4*) or, respectively (*5*), which was recrystallized from dichloromethane-hexane.

$C_6F_5AuC(NHR)[NH(CH_2)_nNH_2]$ [n = 2, R = Ph (6) or p-tolyl (To) (7); n = 3, R = Ph (8) or To (9)] and $(C_6F_5)_3AuC(NHTo)[NH(CH_2)_3NH_2]$ (10)

To a solution of C_6F_5AuCNR [14, 18] [R = Ph (0.467 g, 1 mmol) or To (0.481 g, 1 mmol)] or $(C_6F_5)_3Au(CNTo)$ [15] (0.815 g, 1 mmol) in 25 ml of dichloromethane was added $NH_2(CH_2)_nNH_2$ [n = 2 (0.134 ml, 2 mmol) or 3 (0.10 ml, 1.2 mmol)] and stirred for 1 h. Evaporation to ~8 ml and addition of hexane led to the precipitation of the white complexes (*6–10*), which were recrystallized from dichloromethane-hexane.

$[(C_6F_5)_2\overline{AuNH_2(CH_2)_nNHC}(NHPh)]ClO_4$ [n = 2 (11) or 3 (12)] and $[(C_6F_5)_2\overline{AuC(NHPh)\{NH(CH_2)_n\text{-}NH\}C}(NHPh)]ClO_4$ [n = 2 (13) or 3 (14)]

To a solution of (*4*) or (*5*) (0.2 mmol) in 15 ml of dichloromethane was added the stoichiometric amount of CNPh [19] and stirred until the ν(C≡N) vibration of the isocyanide could not any longer be detected in the solution (2 h, 3 h, 4 d or, respectively 4 d). Evaporation to ~5 ml and addition of hexane led to the white complexes (*11–14*) which were recrystallized from dichloromethane-hexane.

$C_6F_5AuNH_2(CH_2)_nNH_2AuX$ [n = 2, X = Cl (15) or C_6F_5 (16); n = 3 X = Cl (17) or C_6F_5 (18)]

To a solution of (*1*) or (*2*) (0.2 mmol) in 15 ml of dichloromethane was added XAutht [16] (0.2 mmol) and stirred for 30 min. Evaporation to *ca.* 8 ml and addition of hexane (20 ml) led to the white complexes (*15–18*).

$[C_6F_5AuNH_2(CH_2)_2NH_2AuPPh_3]ClO_4$ (19)

To a solution of $ClAuPPh_3$ (0.099 g, 0.2 mmol) in 15 ml of dichloromethane was added $AgClO_4$ (0.041 g, 0.2 mmol) and stirred for 2.5 h under exclusion of light. The formed AgCl was filtered off and (*1*) (0.085 g, 0.2 mmol) was added to the filtrate and stirred for 30 min. Evaporation to ~8 ml and addition of 20 ml of hexane led to the precipitation of the white complex (*19*).

$C_6F_5AuC(NHR)[NH(CH_2)_nNH_2]AuC_6F_5$ [n = 2, R = Ph (20) or To (21); n = 3, R = Ph (22) or To (23)] and $C_6F_5AuC(NHR)[NH(CH_2)_nNH](R'HN)CAuC_6F_5$ [n = 2, R = R' = Ph (24), To (25); R = Ph, R' = To (26); n = 3, R = R' = To (27)]

C_6F_5AuCNR [14, 18] (0.2 mmol) was added to a solution of 0.2 mmol of (*1*), (*2*), (*6*), (*7*) or (*9*) in 15 ml of dichloromethane and stirred until the ν(C≡N) vibration of isocyanide could no longer be observed in the samples of the solution (5–30 days). Evaporation to ~8 ml and addition of hexane led to the precipitation of the white complexes (*20–27*), which were recrystallized from dichloromethane-hexane.

$C_6F_5AuC(NHR)[NH(CH_2)_nNH](ToHN)CAu(C_6F_5)_3$ [n = 2, R = Ph (28), To (29); n = 3, R = To (30)]

To a solution of (*6*) or (*9*) (0.2 mmol) in 15 ml of dichloromethane was added $(C_6F_5)_3AuCNTo$ [15] (0.163 g, 0.2 mmol) and stirred for 30 min (n = 3, R = To) or, respectively, 7 h (n = 2, R = Ph). Evaporation to ~5 ml and addition of hexane led to the precipitation of the white complexes (*28*) or (*30*), which were recrystallized from dichloromethane-hexane.

Complexes (*29*) or (*30*) could also be obtained by starting from (*10*) or $(C_6F_5)_3AuC(NHTo)[NH(CH_2)_2NH_2]$ [15] (0.2 mmol) and $C_6F_5AuCNTo$ [14] (0.096 g, 0.2 mmol) and using the same work-up as before. Reaction time: 1 day (n = 3, R = To) or, respectively, 15 days (n = 2, R = To).

$(C_6F_5)_3AuC(NHTo)[NH(CH_2)_nNH](ToHN)CAu(C_6F_5)_3$ [n = 2 (31) or 3 (32)]

They were prepared by starting from (*10*) or $(C_6F_5)_3AuC(NHTo)[NH(CH_2)_2NH_2]$ [15] (0.2 mmol) and $(C_6F_5)_3AuCNTo$ [15] (0.163 g, 0.2 mmol) and using the same work-up as for complexes (*28–30*). Reaction time: 8 days (n = 2) or, respectively, 30 min (n = 3).

Results and Discussion

a) Starting Complexes

The displacement of tetrahydrothiophen (tht) in C_6F_5Autht by ethylene or propylenediamine leads to mononuclear complexes as represented in eqn. 1.

$$C_6F_5Autht + NH_2(CH_2)_nNH_2 \longrightarrow C_6F_5AuNH_2(CH_2)_nNH_2 + tht \qquad (1)$$

n = 2 (*1*) or 3 (*2*)

though in the case of 4,4′-bipyridyl (4,4′-bipy) the binuclear derivative $C_6F_5Au(4,4'\text{-bipy})Au(C_6F_5)$ (*3*) is obtained in every case, even when using an excess of the ligand (4,4′-bipy/Au = 1.2/1 molar ratio).

Complexes (*1–3*) are isolated as white air- and moisture-stable solids, which are non-conducting in acetone solution (see Table I). Since (*3*) is insoluble in organic solvents neither its conductivity nor its molecular weight could be determined.

Addition of $AgClO_4$ to suspensions of *cis*-$Bu_4N[(C_6F_5)_2AuCl_2]$ [17] in diethylether, followed by the elimination of the precipitated AgCl and $[Bu_4N]ClO_4$, renders solutions which are stable at room temperature and are supposed to contain *cis*-$[(C_6F_5)_2Au(OEt_2)_2]^+$. Addition of $NH_2(CH_2)_nNH_2$ allows the isolation of the corresponding cationic complexes (eqn. 2)

$$cis\text{-}Bu_4N[(C_6F_5)_2AuCl_2] +$$

$$+\ 2AgClO_4 \xrightarrow[-2AgCl,\ -[Bu_4N]ClO_4]{}$$

$$cis\text{-}[(C_6F_5)_2Au(OEt_2)_2]ClO_4 \xrightarrow{NH_2(CH_2)_nNH_2}$$

$$cis\text{-}[(C_6F_5)_2AuNH_2(CH_2)_nNH_2]ClO_4 \qquad (2)$$

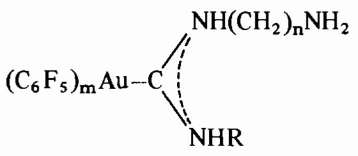
n = 2 (*4*) or 3 (*5*)

which are conducting in acetone solution (1:1 electrolytes) (Table I). Their IR spectra show two bands at 1090(s,br) and 625(s) cm^{-1} characteristic of the ClO_4 anion [20], along with two others in the 800 cm^{-1} region [815(s) and 805(s) cm^{-1}], which confirm the *cis*-configuration of the C_6F_5 groups [17].

b) Mononuclear Carbene Complexes

It is well known that amines react with gold-isocyanide to give the corresponding carbenes [12–14]. Similarly, diamines are able to use one of their $-NH_2$ groups as represented in eqn. 3

$$(C_6F_5)_mAuCNR + NH_2(CH_2)_nNH_2 \longrightarrow$$



$$(C_6F_5)_mAu{-}C\begin{cases}NH(CH_2)_nNH_2\\ NHR\end{cases} \qquad (3)$$

m = 1, n = 2, R = Ph (*6*) or *p*-tolyl (To) (*7*); n = 3, R = Ph (*8*) or To (*9*)
m = 3, n = 3, R = To (*10*)

The course of these reactions was monitored by IR spectroscopy until the C≡N stretching absorption due to the isocyanide could no longer be observed. The reaction is more rapid for the gold(III) (10 min) than for the gold(I) precursors (1 h), in agreement with the nucleophilic attack accepted for this type of reaction [12, 21].

The white complexes (*6–10*) are non-conducting in acetone and monomeric in chloroform. Their IR spectra are characterized by bands located at 3450–3200(m) {ν(NH)}, 1640–1615(s) {δ(NH)}, and 1580–1560(s) {ν(CN)} cm^{-1}.

Though in (*4*) and (*5*) the two NH_2 groups of the diamine should be coordinated to the gold centre, the complexes react with one or two moles of isocyanide (CNPh) to give cyclic carbenes, as may be seen from the equation (4) *(see next page)*.

The white complexes (*11–14*) are air- and moisture-stable at room temperature and conducting in acetone solution (1:1 electrolytes). Their IR spectra show absorptions at 3420–3180(m) {ν(NH)}, 1610(s) {δ(NH)}, 1590–1580 {ν(CN)}, 1100(s,br) and 628(m) (ClO_4^-) and 822(s) and 812(s) (due to two mutually *cis* C_6F_5 groups) cm^{-1}.

c) Binuclear Complexes

One of the amine groups of complexes (*1*) and (*2*) can further be coordinated to another gold centre by displacement of other weakly attached ligands (tht or $OClO_3$), as represented in eqns. (5) and (6)

$$C_6F_5AuNH_2(CH_2)_nNH_2 + XAutht \longrightarrow$$

$$C_6F_5AuNH_2(CH_2)_nNH_2AuX + tht \qquad (5)$$

n = 2, X = Cl (*15*) or C_6F_5 (*16*); n = 3, X = Cl (*17*) or C_6F_5 (*18*)

$$C_6F_5AuNH_2(CH_2)_2NH_2 + O_3ClOAuPPh_3 \longrightarrow$$

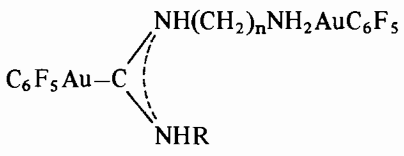
$$[C_6F_5AuNH_2(CH_2)_2NH_2AuPPh_3]ClO_4 \qquad (6)$$

(*19*)

Since (*15–17*) are only very little soluble in organic solvents neither their conductivities nor their molecular weights could be determined. (*18*) is non-conducting and monomeric in solution, whilst (*19*) behaves as a 1:1 electrolyte in acetone. The IR spectra of (*15*) and (*17*) show an absorption at 338(m) cm^{-1}, due to ν(Au–Cl).

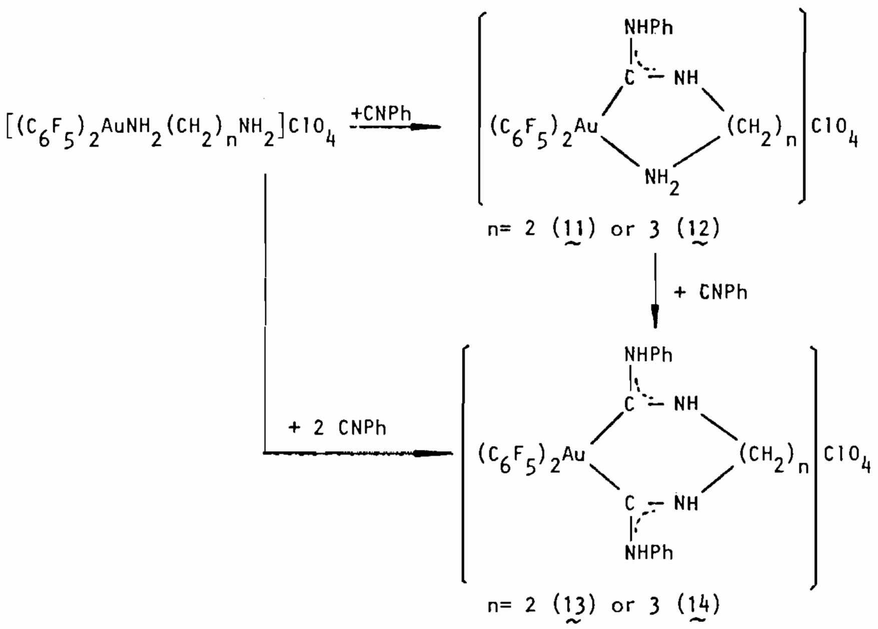
Complexes (*1*) and (*2*) react also with gold isocyanide to give binuclear carbenes (eqn. 7).

$$C_6F_5AuNH_2(CH_2)_nNH_2 + C_6F_5AuCNR \longrightarrow$$

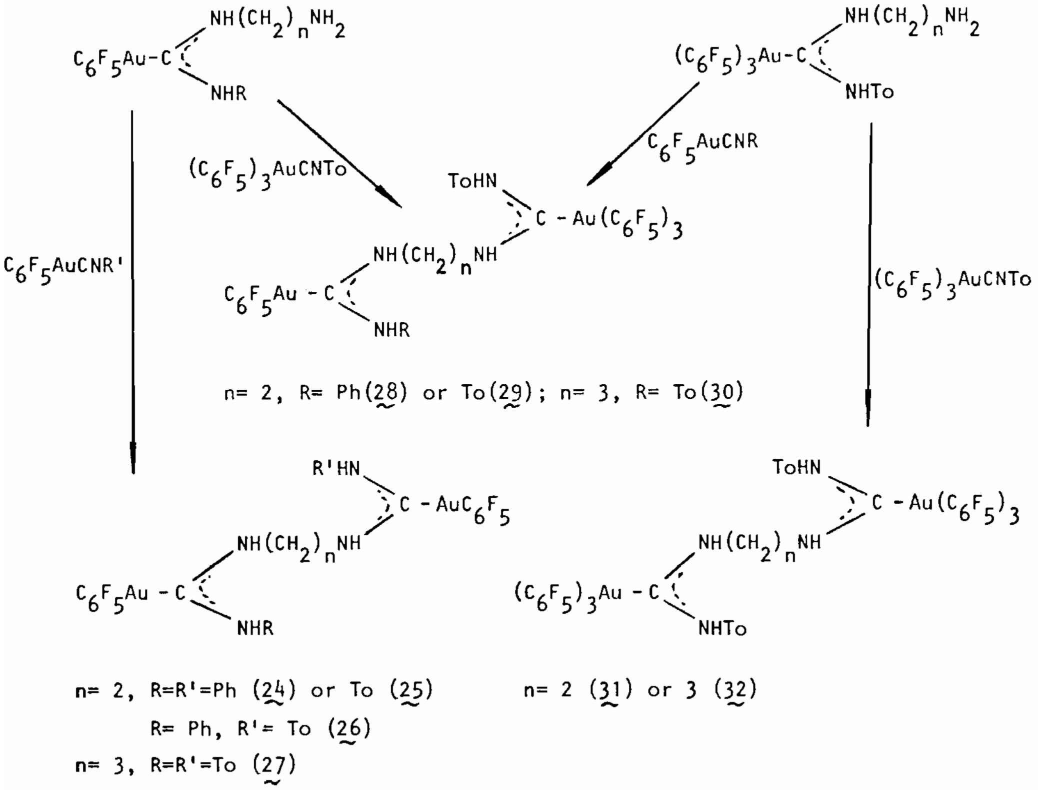


$$C_6F_5Au{-}C\begin{cases}NH(CH_2)_nNH_2AuC_6F_5\\ NHR\end{cases} \qquad (7)$$

n = 2, R = Ph (*20*) or To (*21*); n = 3, R = Ph (*22*) or To (*23*)



(4)



Scheme 1

Similar reactions take place by starting from complexes (*6–10*) or from the elsewhere described [15] $(C_6F_5)_3AuC(NHTo)[NH(CH_2)_2NH_2]$ all of which contain a free NH_2 group that can react with gold-isocyanide under the formation of double binuclear carbenes, as may be seen from Scheme I.

The reactions represented in eqn. 7 and Scheme 1 are quite slow, especially if the starting complex is a gold(I) isocyanide (it takes between 3 and 30 days until the isocyanide disappears entirely) and are a quicker (30 min to 1 day) for $(C_6F_5)_3AuCNTo$, except for the preparation of complex (*31*) (8 days).

Complexes (*20–32*) are white air- and moisture-stable solids; their conductivities and molecular weights being in good agreement with the proposed formulae. Their IR spectra show absorption bands in the 3400–3150(m) {ν(NH)}, 1610–1600(s) {δ(NH)} and 1600–1575(s) {ν(CN)} regions, characteristic of carbenes [18].

References

1 H. Schmidbaur, 'Organogold Compounds', Gmelin Handbuch der Anorganischen Chemie. Springer Verlag, Berlin (1980) p. 249, 252 and 255.

2 R. Usón, A. Laguna, M. Laguna, E. Fernandez, M. D. Villacampa, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc. Dalton,* 1679 (1983).

3 M. G. Miles, G. E. Glass and R. S. Tobias, *J. Am. Chem. Soc., 88,* 5738 (1966).

4 P. L. Kuch and R. S. Tobias, *J. Organometal. Chem., 122,* 429 (1976).

5 F. H. Brain and C. S. Gibson, *J. Chem. Soc.,* 762 (1939).

6 A. Burawoy, C. S. Gibson and S. Holt, *J. Chem. Soc.,* 1024 (1935).

7 M. E. Foss and C. S. Gibson, *J. Chem. Soc.,* 3063, 3075 (1949).

8 H. Schmidbaur and K. C. Dash, *J. Am. Chem. Soc., 95,* 4855 (1973).

9 R. Usón, J. Vicente and M. T. Chicote, *Inorg. Chim. Acta, 35,* L305 (1979).

10 H. Gilman and L. A. Woods, *J. Am. Chem. Soc., 70,* 550 (1943).

11 A. Burawoy and C. S. Gibson, *J. Chem. Soc.,* 219 and 1024 (1935).

12 F. Bonati and G. Minghetti, *Gazz. Chim. Ital., 103,* 373 (1973).

13 G. Minghetti, F. Bonati and G. Banditelli, *Inorg. Chem., 15,* 1718 (1976).

14 R. Usón, A. Laguna, J. Vicente, J. García and B. Bergareche, *J. Organometal. Chem., 173,* 349 (1979).

15 R. Usón, A. Laguna, M. Laguna, E. Fernández, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc. Dalton,* 1971 (1982).

16 R. Usón, A. Laguna and J. Vicente, *J. Chem. Soc., Chem. Commun.,* 353 (1976); *J. Organometal. Chem., 131,* 471 (1977).

17 R. Usón, A. Laguna, J. García and M. Laguna, *Inorg. Chim. Acta, 37,* 201 (1979).

18 R. Usón, A. Laguna, J. Vicente, J. García, B. Bergareche and P. Brun, *Inorg. Chim. Acta, 28,* 237 (1978).

19 I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer and K. Offermann, *Angew. Chem. Int. Ed., 4,* 472 (1965).

20 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.,* 3091 (1961).

21 B. Crociani, T. Boschi, M. Nicolini and U. Belluco, *Inorg. Chem., 11,* 1292 (1972).