Isocyanide and Carbene Complexes of Gold(I). The Stepwise Formation of Formamidines

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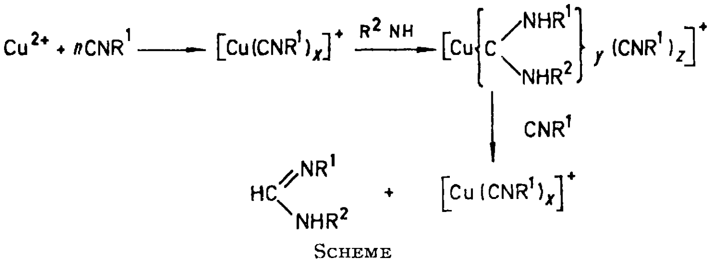
The syntheses of $Au(CNR^1)Cl$ and $[Au(CNR^1)_2]PF_6$ (R^1 = Bu^t or Pr^i) from $HAuCl_4,4H_2O$ and $[Bu^n_4N][AuCl_4]$, respectively, and CNR^1 in ethanol are described. These complexes react with primary and secondary amines giving $Au\{C(NHR^1)(NHR^2)\}(NH_2R^2)Cl$, $[Au\{C(NHR^1)(NHR^2)\}_2]PF_6$ and $[Au\{C(NHR^1)(NR_2^3)\}_2]PF_6$ ($R^1 = Bu^t$, $R^2 = Bu^t$, Pr^i or Bu^n; $R^1 = Pr^i$, $R^2 = Bu^t$ or Pr^i; $R^1 = Bu^t$, R^3 = Et or CH_2Ph; $R^1 = Pr^i$, R^3 = Et). Treatment of $[Au\{C(NHBu^t)[N(CH_2Ph)_2]\}_2]PF_6$ with PPh_3 afforded $[Au(PPh_3)_4]PF_6$ and the formamidine $CH(=NBu^t)$-$[N(CH_2Ph)_2]$, and of $[Au\{C(NHBu^t)_2\}_2]PF_6$ with $CNBu^t$, $[Au(CNBu^t)_2]PF_6$ and evidence for $CH(=NBu^t)$-$(NHBu^t)$.

THE 1,1-addition of primary and secondary amines to isocyanides, affording formamidines, is catalysed[1] by copper salts, and by $HAuCl_4,4H_2O$. It has been proposed[2] that the reaction mechanism involves the formation of a complex between the metal salt and isocyanide, with or without amine, and the amine then attacks the co-ordinated isocyanide giving a co-ordinated carbene species. The latter is then expelled from the metal ion by excess of CNR^1, or $R^2NH_2(R_2^1NH)$ giving, after a 1,2-hydrogen shift, the formamidine (Scheme)



SCHEME

Isocyanide complexes of copper(I) have been characterised,[3] but in the reactions with amines, no isolable and characterisable carbene complexes have been obtained. However, on treatment of $Cu\{CN(cyclo\text{-}C_6H_{11})\}Cl$ with piperidine (pipH), a species formulated[1] as $(CuCl)_2$-$\{CN(cyclo\text{-}C_6H_{11})\}_2(pipH)$ was isolated, but the nature of this compound has not been elucidated.

The apparent failure to obtain stable copper carbene complexes could be attributed to the lability of such species. In an effort to clarify the general reaction mechanism, by obtaining kinetically stable intermediates, we have investigated the related chemistry of gold(I) isocyanide complexes.

Isocyanide compounds of gold(I), $Au(CNR)X$ (R = cyclo-C_6H_{11}, aryl, or Bu^n; X = halide, CN, or

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[1] T. Saegusa, Y. Ho, S. Kobayashi, K. Hirota, and N. Yoshioka, *Bull. Chem. Soc. Japan*, 1969, **42**, 3310.

[2] A. Vogler, in 'Isonitrile Chemistry,' ed. I. Ugi, Academic Press, Inc. (London), Ltd., 1971, p. 217.

[3] L. Malatesta and F. Bonati, 'Isocyanide Complexes of Metals,' Wiley–Interscience, London, 1969, p. 38.

Ph) have been reported.[3] Reaction of $Au\{CN(p\text{-}MeC_6H_4)\}Cl$ with refluxing methanol during 2 days afforded[4] a mono-carbene species, $Au[C\{NH(p\text{-}MeC_6H_4)\}(OMe)]Cl$, and treatment of $Au(PPh_3)Cl$ with CNR and KOH in methanol gave[5] either $[Au\{C(=NC_6H_{11})(OMe)\}]_3$ or $Au(PPh_3)\{C(=NR)(OMe)\}$ (R = aryl). There is a brief description of a bis-carbene species, $[Au\{CN(Ph)CH_2CH_2NPh\}_2]^+$, obtained[6] by reaction of $Au(PPh_3)Cl$ with the 'electron rich' olefin $PhNCH_2CH_2N(Ph)C{=}CN(Ph)CH_2CH_2NPh$.

Here we describe the syntheses of t-butyl- and iso-propyl-isocyano- complexes of gold(I), their reactions with some primary and secondary amines, and the isolation of formamidines by reaction of gold-carbene complexes with PPh_3 or CNR.

EXPERIMENTAL

Conductivity data were obtained using a Phillips Conductivity meter with solutions at room temperature (20 ± 2°). I.r. and ^1H n.m.r. spectra were measured using Perkin-Elmer 457 and Varian HA100 or Perkin-Elmer R12A spectrometers, respectively. Vapour-phase chromatograms were obtained using a Pye model 105 intrument, using a 2½ ft column packed with OV17. The initial temperature of the column was 250 °C and the carrier gas N_2.

All reactions were carried out at room temperature, unless otherwise stated, and all yields are quoted with respect to the gold-containing precursor.

$Au(CNBu^t)Cl$.—A solution of $CNBu^t$ (0·53 g) in ethanol (5 ml) was added slowly with stirring to a solution of $HAuCl_4,4H_2O$ (2·7 g) in ethanol (35 ml). A yellow precipitate was formed which was filtered off, and treated (0·80 g) further with $CNBu^t$ (0·85 g) in ethanol (25 ml), when a colourless mixture was formed, which was stirred for 10 min. The solution became very pale blue and, on evaporation of the solvent *in vacuo* followed by recrystallisation of the residue from ethanol, afforded the *complex* as white needles (0·60 g, 29%).

$Au(CNPr^i)Cl$.—To a solution of $HAuCl_4,4H_2O$ (4·2 g) in ethanol (100 ml) was added $CNPr^i$ (1·8 g) slowly, and with stirring. A yellow precipitate formed which was filtered off (0·7 g). From the yellow mother liquor, on partial evaporation and cooling, the *complex* was obtained as white crystals (1·2 g, 39%). These could be recrystallised from ethanol–n-pentane.

$[Au(CNBu^t)_2]PF_6$.—To a suspension of $[Bu^n{}_4N][AuCl_4]$ (3·1 g) in ethanol (200 ml) was added, slowly and with stirring, $CNBu^t$ (3·4 g). The mixture became colourless, and NH_4PF_6 (0·82 g) was added, and stirring was continued for a further 10 min. The white precipitate which had formed was filtered off, washed with water and ethanol, and dried *in vacuo* (2·3 g, 67%). $[Au(CNPr^i)_2]PF_6$ was prepared similarly (36%).

$Au\{C(NHBu^t)_2\}(NH_2Bu^t)Cl$.—A suspension of $Au(CNBu^t)Cl$ (0·07 g) in NH_2Bu^t (excess) was stirred for 10 min. The white solid which formed was filtered off, washed with ether, and dried *in vacuo* (0·07 g, 70%). The solid became pale pink in a few hours, but could be satisfactorily recrystallised from acetone. The complex $Au\{C(NHPr^i)(NHBu^t)\}(NH_2Bu^t)Cl$ (60%) was prepared similarly (*M* osmometrically in acetone: calc. 448; found 495).

$[Au\{C(NHBu^t)_2\}_2]PF_6$.—A suspension of $[Au(CNBu^t)_2]PF_6$ (0·50 g) in NH_2Bu^t (4 ml) was stirred for 5 h. The white solid which formed was filtered off, washed with ether, and dried *in vacuo* (0·50 g, 78%).

$[Au\{C(NHPr^i)(NHBu^t)\}_2]PF_6$.—A suspension of $[Au(CNBu^t)_2]PF_6$ (0·50 g) in NH_2Pr^i (excess) was stirred for 2 h. Ethanol (10 ml) was then added, followed by n-pentane (30 ml). The white precipitate which had formed was then filtered off, washed with *n*-pentane, and dried *in vacuo* (0·24 g, 87%). The *complex* could also be obtained from $[Au(CNPr^i)_2]PF_6$ and NH_2Bu^t (61%). The compounds $[Au\{C(NHPr^i)_2\}_2]PF_6$ (70%), $[Au\{C(NHBu^t)(NEt_2)\}_2]PF_6$ (86%), $[Au\{C(NHPr^i)(NEt_2)\}_2]PF_6$ (72%), and $[Au\{C(NHBu^t)(NBu^n{}_2)\}_2]PF_6$ (quantit.) were prepared similarly using NH_2Pr^i, $NHEt_2$, and $NHBu_2{}^n$, respectively.

$[Au\{C(NHBu^t)[N(CH_2Ph)_2]\}_2]PF_6$.—A suspension of $[Au(CNBu^t)_2]PF_6$ (2·1 g) in $NH(CH_2Ph)_2$ (excess) was stirred for 20 h. To the solution was added n-pentane and a grey-white solid was precipitated. This was filtered off, washed with n-pentane, and dried *in vacuo* (yield 3·7 g, quantitative).

Reaction of $[Au\{C(NHBu^t)[N(CH_2Ph)_2]_2\}]PF_6$ *with* PPh_3: *Isolation of* $CH(=NBu^t)[N(CH_2Ph)_2]$.—To a stirred solution of PPh_3 (4·3 g) in ethanol (200 ml) was added $[Au\{C(NHBu^t)[N(CH_2Ph)_2]\}_2]PF_6$ (3·7 g). The stirring was maintained for 17 h, and the white precipitate of $[Au(PPh_3)_4]PF_6$ (5·2 g, 92%) was then filtered off, washed with n-pentane, and dried *in vacuo*. The filtrate was reduced *in vacuo*, and the oil so obtained distilled *in vacuo*. The oil which was collected (1·48 g, 64%) was characterised by v.p.c., coupled with i.r., n.m.r. spectroscopy, and mass spectrometry. The major component of the oil (>98%) was identified as $CH(=NBu^t)[N(CH_2Ph)_2]$, but the three minor components were not characterised.

Reaction of $[Au\{C(NHBu^t)_2\}_2]PF_6$ *with* $CNBu^t$.—To a suspension of $[Au\{C(NHBu^t)_2\}_2]PF_6$ (0·12 g) in ethanol (2 ml) was added, with stirring, an excess of $CNBu^t$ (*ca.* 0·35 g). After stirring for 24 h, the pinkish-white precipitate of $[Au(CNBu^t)_2]PF_6$ (0·07 g, 67%) was filtered off. Removal of the solvent from the filtrate afforded an oil which contained $CH(=NBu^t)(NHBu^t)$.

RESULTS AND DISCUSSION

Reaction of $HAuCl_4,4H_2O$ with CNR (R = Bu^t or Pr^i) in cold ethanol afforded, initially, a yellow solution, from which yellow solids could be obtained. Although elemental analytical results were inconclusive, it seems possible that these solids contain $Au(CNR)Cl_3$. Such species have been isolated[7] where R = $p\text{-}MeC_6H_4$ or $p\text{-}MeOC_6H_4$. Addition of further CNR, however, caused the formation of a colourless solution from which the white Au(CNR)Cl was isolated (elemental analyses, see Table).

Treatment of $[Bu^n{}_4N][AuCl_4]$ in cold ethanol with an excess of CNR gave, in the presence of $PF_6{}^-$, the new bis-isocyanide complexes, $[Au(CNR)_2]PF_6$ (R = Bu^t or Pr^i). We were unable to obtain species of the type $[Au(CNR)_4]^+$.

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Analytical, conductivity, and spectral data for gold(I) isocyanide and carbene complexes of formamides

	Elemental analyses (%)																
	Calcd.				Found					I.r. data (KBr discs; cm^{-1}				^{1}H n.m.r. data			
Complex	C	H	N	Cl	C	H	N	Cl	Λ[a]	$\nu_{NH,CH}$	$\nu_{C\equiv N}$	$\nu_{C=N}$	ν_{PF}	Solvent	τ	RA[h]	Assignments and remarks
Au(CNBu^t)Cl	19·0	2·9	4·4	11·3	19·3	3·2	4·2	11·4	4·0	2980s, 2950w, 2915w, 2890sh	2250vs, 2155vw			CDCl$_3$	8·42		t; $J_{NH}(J_N = 1)$
Au(CNPr^i)Cl	15·9	2·3	4·7	11·8	16·2	2·5	4·6	12·0	2·0	2980s, 2935m, 2865w	2240s, 2135sh			CDCl$_3$	5·90 8·50	1 6	Sept; C*H*Me$_2$($J_{HH} + J_{NH}$) dt; CH(C*H*$_3$)$_2$($J_{HH} + J_{NH}$)
[Au(CNBu^t)$_2$][PF$_6$]	23·6	3·6	5·5		23·7	3·7	5·7		98	2995w, 2950w, 2915w, 2880w	2260vs, 2220sh		830vs	(CD$_3$)$_2$SO	8·44		s
[Au(CNPr^i)$_2$][PF$_6$]	20·0	2·9	5·8		20·8	3·1	5·9		104	2999w, 2950w, 2908sh, 2885w	2265vs		835vs	(CD$_3$)$_2$SO	5·58 8·56	1 6	Sept; C*H*Me$_2$(J_{HH}) d; CH(C*H*$_3$)$_2$(J_{HH})
Au{C(NHBu^t)$_2$}(NH$_2$Bu^t)Cl	33·8	6·7	9·1	7·7	33·4	6·8	8·9	8·1	*b*	3235m, 3130m, 3065s, 2960s, 2915sh, 2870sh							
Au{C(NHPr^i)(NHBu^t)}-(NH$_2$Bu^t)Cl	32·2	6·5	9·4	7·9	32·5	6·5	8·9	8·6	7·0[c]	3220s, 3132m, 3065s, 2965s, 2927m, 2895 sh, 2847m		1597sh 1560vs		CDCl$_3$	8·47	2	C(C*H*$_3$)$_3$ of NHBu^t [i]
												1560vs		CDCl$_3$	8·80 8·47[j]	1 9	C(C*H*$_3$)$_3$ of NH$_2$Bu^t [i] s; C(C*H*$_3$)$_3$
[Au{C(NHBu^t)$_2$}$_2$][PF$_6$]	33·0	6·2	8·6		33·5	6·0	8·4		93	3340s, 3120w, 3065w, 2970s, 2935m, 2900sh, 2875w		1545sh, 1535vs	835vs	CDCl$_3$	1·85 8·57	1 9	brs; N*H* brs; C(C*H*$_3$)$_3$
														(CD$_3$)$_2$SO + D$_2$O	8·57		s; C(C*H*$_3$)$_3$
[Au{C(NHBu^t)(NHPr^i)}$_2$][PF$_6$]	30·7	5·8	8·9		30·9	5·8	9·0		90	3345s, 3220w, 3075w, 2965s, 2930m, 2910sh, 2875w 3335, 3295, 3080[d]		1560sh, 1550vs 1560sh, 1555[d]	845vs 845vs[d]	(CD$_3$)$_2$SO	2·20 5·88 8·53 8·80	~2 1 9 6	mult; N*H* mult; C*H*Me$_2$ s; C(C*H*$_3$)$_3$ d; CH(C*H*$_3$)$_3$(J_{HH})
[Au{C(NHPr^i)$_2$}$_2$][PF$_6$]	28·1	5·4	9·4		28·5	5·5	9·2		94	3415sh, 3345s, 3220vw, 3055w, 2970s, 2930sh, 2873w		1580sh, 1568vs, 1560sh	845vs				
[Au{C(NHBu^t)(NEt$_2$)}$_2$][PF$_6$]	33·0	6·2	8·6		33·0	6·2	8·8		89	3365s, 2975s, 2960sh, 2930m, 2895sh, 2870w		1560sh, 1545vs	830vs	(CD$_3$)$_2$SO	3·08 6·10 6·53 8·44 8·86	1 2 2 9 9	s; N*H* q; –CH$_2$– of Et group q; –CH$_2$– of Et group s; (C(C*H*$_3$)$_3$ dt; –CH$_3$ of Et groups
[Au{C(NHBu^t)[N(CH$_2$Ph)$_2$]}$_2$]-[PF$_6$]	50·6	5·4	6·2		50·7	5·4	6·4		85	3375m, 3085vw, 3065w, 3045w, 2973m, 2960m, 2920sh, 2870sh		1548vs	838vs	(CD$_3$)$_2$SO	2·72 4·86 5·34 8·61	11 2 2 9	m; N*H* and CH$_2$C$_6$*H*$_5$ s; –C*H*$_2$Ph s; –C*H*$_2$Ph s; C(C*H*$_3$)$_3$
[Au{C(NHBu^t)(NBu$^t_2$)}$_2$][PF$_6$]	40·7	7·4	7·3		41·3	7·3	7·7		85	3360m, 2960m, 2935m 2870w		1545vs	835vs	(CD$_3$)$_2$SO	3·15 6·17 6·58 8·44 8·60 9·10	1 2 2 23	s; N*H* brt brt protons of Bu^n group s; C(C*H*$_3$)$_3$ brmult; protons of Bu^n group asymm brt; C*H*$_3$of Bu^n group
[Au{C(NHPr^i)(NEt$_2$)}$_2$][PF$_6$]	30·7	5·8	8·9		30·9	5·6	8·8		93	3355m, 2970s, 2930m, 2870w		1558vs	849vs	(CD$_3$)$_2$SO	2·29 5·63 6·25 6·66 8·74 8·92 8·75 8·77	1 1 2 2 6 6 15	d; N*H* Sept; C*H*Me$_2$(J_{HH}) q; –CH$_2$– of Et group q; –CH$_2$– of Et group d; CH(C*H*$_3$)$_2$ brt; –CH$_3$ of Et groups d; CH(C*H*$_3$)$_3$(J_{HH}) s; C(C*H*$_3$)$_3$, prob. of NH$_2$Bu^t
[Au(PPh$_3$)$_4$][PF$_6$]	62·0	4·5			62·2	4·4			*b*	3350, 3287[d]		1562	850[d]				
CH(=NBu^t)[N(CH$_2$Ph)$_2$]	81·4	8·6	10·0		80·9	8·2	8·9		*b*	3080w, 3060w, 3000w, 2965s, 2930m, 2915m, 2860vw[e]		1639vs, 1605w[e]		(CD$_3$)$_2$SO	2·76 5·68 8·77	11 4 9	mult; C$_6$*H*$_5$ and C*H* s; CH$_2$Ph s; C(C*H*$_3$)$_3$
CH(–NBu^t)(NHBu^t)										3250s, 3050sh, 2960vs, 2940sh, 2890sh, 2780s, 2700m,[g]		1705vs, 1655vs 1568m 1550sh[g]	849m[g]				

[a] In Ω^{-1} cm^2 mol^{-1} in 10^{-14}M-MeNO$_2$ solution; for a 1:1 electrolyte, values should be in range 85—97 Ω^{-1} cm^2 mol^{-1}. [b] Not measured. [c] In acetone solution; non-conductor. [d] In the THF soln. [e] In CHCl$_3$ soln. [f] Impure product isolated after reaction between [Au{C(NHBu^t)$_2$}$_2$][PF$_6$] and CNBu^t in EtOH; [g] Liquid film. [h] Relative area. [i] NH proton resonances not detected. [j] C*H*Me$_2$ resonance not detected.

In both types of complex, ν_{CN} (see Table) was higher than the CN stretching frequency of the free isocyanide. This indicates that little $d \longrightarrow \pi^*$ donation occurs in these complexes. The complex ions, $[\mathrm{Au(CNR)_2}]^+$, are probably linear.

When $[\mathrm{Au(CNBu^t)_2}]\mathrm{PF_6}$ was suspended in $\mathrm{NH_2Bu^t}$, the bis-carbene complex $[\mathrm{Au\{C(NHBu^t)_2\}_2}]\mathrm{PF_6}$ was formed. A similar product was obtained from $[\mathrm{Au(CNPr^i)_2}]\mathrm{PF_6}$ and $\mathrm{NH_2Pr^i}$, and the mixed ligand species, $[\mathrm{Au\{C(NHBu^t)(NHPr^i)\}_2}]\mathrm{PF_6}$ was obtained either from $[\mathrm{Au(CNBu^t)_2}]^+$ and $\mathrm{NH_2Pr^i}$, or $[\mathrm{Au(CNPr^i)_2}]^+$ and $\mathrm{NH_2Bu^t}$. The i.r. spectra of these compounds showed ν_{NH} and $\nu_{\mathrm{C\overset{\cdots}{-}N}}$ bands which are characteristic of co-ordinated amino-carbenes,[8] and there was no evidence of $\nu_{\mathrm{C\equiv N}}$. The ^{1}H n.m.r. spectra (Table 3) of the symmetrical carbene species $[\mathrm{Au\{C(NHR)_2\}_2}]^+$ exhibited resonances due to R, and also resonances in the region $\tau = 2$. The latter could be assigned to the NH protons, and this was confirmed by treating $\mathrm{(CD_3)_2SO}$ solutions of $[\mathrm{Au\{C(NHBu^t)_2\}_2}]^+$ with $\mathrm{D_2O}$, when the N*H* resonance disappeared due to H/D exchange. The ^{1}H n.m.r. spectra of the species $[\mathrm{Au\{C(NHBu^t)(NHPr^i)\}_2}]^+$, prepared by both routes, were identical as expected.

Reaction of $[\mathrm{Au(CNBu^t)_2}]\mathrm{PF_6}$ with $\mathrm{NHEt_2}$ or $\mathrm{NH(CH_2Ph)_2}$ afforded the species $[\mathrm{Au\{C(NHBu^t)(NR_2)\}_2}]\mathrm{PF_6}$ ($\mathrm{R = Et}$ or $\mathrm{CH_2Ph}$). The ^{1}H n.m.r. spectra of these complexes exhibited singlet resonances due to the $\mathrm{Bu^t}$ protons, but the methylene resonances of the ethyl derivative occurred as *two* quartets, and the associated methyl proton signals appeared as a broad triplet; the methylene resonances of the benzyl derivative appeared as two singlets. This is caused by the restricted rotation about the $\mathrm{C\overset{\cdots}{-}N}$ bonds of the co-ordinated carbene, which leads to the inequivalence of the two R groups. Similar spectra were obtained from $[\mathrm{Au\{C(NHPr^i)(NEt_2)\}_2}]^+$ and $[\mathrm{Au\{C(NHBu^t)(NBu^n_2)\}_2}]^+$ (full resolution of the $\mathrm{Bu^n}$ signals was not achieved).

These complexes are among the few bis-carbene complexes. Other known bis-carbene complexes include $[\mathrm{Au\{\overline{CN(Ph)CH_2CH_2N}Ph\}_2}]^+$,[6] and some derivatives of $\mathrm{Hg^{II}}$.[9]*

Reaction of Au(CNR)Cl ($\mathrm{R = Bu^t}$ or $\mathrm{Pr^i}$) with $\mathrm{NH_2Bu^t}$ afforded species best formulated as $\mathrm{Au\{C(NHR)(NHBu^t)\}(NH_2Bu^t)Cl}$. The elemental analyses were not especially good, but could not be fitted to any other formulae reasonably consistent with our spectroscopic and other data. The i.r. spectra clearly indicated the presence of more NH stretching frequencies than would be expected for a simple carbene species $\mathrm{Au\{C(NHR)(NHBu^t)\}Cl}$. The ^{1}H n.m.r. spectra of these species exhibited resonances due to NH, R, and $\mathrm{Bu^t}$ protons. The compounds were non-electrolytes and monomeric and therefore *cannot* be $[\mathrm{Au\{C(NHR)(NHBu^t)\}(NH_2Bu^t)}]^+\mathrm{Cl^-}$, $[\mathrm{NH_3Bu^t}]^+[\mathrm{Au\{C({=}NR)(NHBu^t)\}Cl}]^-$, or $[\mathrm{Au\{C(NHR)(NHBu^t)\}(NH_2Bu^t)Cl}]_2$ (tetrahedral Au with bridging Cl). It is possible that the complexes contain three-co-ordinate gold(I), or that the excess $\mathrm{NH_2Bu^t}$ is hydrogen-bonded to the carbene moiety.

Treatment of $[\mathrm{Au\{C(NHBu^t)[N(CH_2Ph)_2]\}_2}]\mathrm{PF_6}$ with four equivalents of $\mathrm{PPh_3}$ in ethanol afforded, quantitatively, $[\mathrm{Au(PPh_3)_4}]\mathrm{PF_6}$. After removal of the phosphine complex, and work-up of the ethanolic residue, an oil, containing four components (v.p.c.), was isolated. The major fraction (98%) analysed elementally as $\mathrm{C_{19}H_{24}N_2}$, and had a molecular weight of 280. Its i.r. spectrum exhibited $\nu_{\mathrm{C=N}}$ and bands characteristic of $\mathrm{Bu^t}$ and benzyl groups, but *no* ν_{NH}. The ^{1}H n.m.r. spectrum exhibited resonances due to the $\mathrm{Bu^t}$ and $\mathrm{-CH_2-}$ groups; no NH resonances were detected and the spectrum was unchanged on addition of $\mathrm{D_2O}$. On the basis of these data, we propose that the structure of this compound is $\mathrm{CH({=}NBu^t)N(CH_2Ph)_2}$ (the CH resonance apparently coincides with the $\mathrm{C_6H_5}$ signals). Although the minor components of this reaction were not characterised, it seems probable from ^{1}H n.m.r. spectral studies that at least one of them may be $\mathrm{NH(CH_2Ph)_2}$; an NH and additional $\mathrm{-CH_2-}$ signals could be detected in the spectrum of the unpurified ethanolic solution obtained after removal of $[\mathrm{Au(PPh_3)_4}]\mathrm{PF_6}$.

In the reaction of $[\mathrm{Au\{C(NHBu^t)_2\}_2}]\mathrm{PF_6}$ with an excess of $\mathrm{CNBu^t}$ in ethanol, $[\mathrm{Au(CNBu^t)_2}]\mathrm{PF_6}$ was obtained. The i.r. spectral data obtained from the ethanolic residue were consistent with the formation of some $\mathrm{CH({=}NBu^t)(NHBu^t)}$, although there may have been some unchanged carbene complex present.

The sequence of reactions described above confirms the mechanistic suggestions in the Scheme. In the light of our results we suggest that the species described[1] as $\mathrm{[(CuCl)_2(CNC_6H_{11})_2(C_5H_{10}NH)}$ could be reformulated as $[\mathrm{Cu(CNC_6H_{11})\{C(NHC_6H_{11})(NC_5H_{10})\}}]^+[\mathrm{CuCl_2}]^-$.

No reaction was observed between $[\mathrm{Au(CNR)_2}]^+$ and methanol or ethanol on prolonged standing, or gentle reflux; prolonged heating of $[\mathrm{Au(CNR)_2}]^+$ with alcohols in sealed tubes at 60—100° led to dealkylation of the isocyanide and formation of $[\mathrm{Au(CN)}]_n$.

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* *Note added in proof:* The bis-carbene complexes $[\mathrm{Au\{C(NHMe)(NMeR')\}_2}]^+$, $\mathrm{R' = H}$ or Me, and $[\mathrm{Au\{C(NHC_6H_{11})[N(CH_2)_5]\}_2}]^+$, together with $[\mathrm{Au(CNC_6H_{11})_2}]^+$, have been briefly described recently; J. E. Parks and A. L. Balch, *J. Organometallic Chem.*, 1973, **57**, C103.

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