*Journal of Organometallic Chemistry*, 102 (1975) 397—406


# CARBENE COMPLEXES FROM THE REACTION OF IONIC ISOCYANIDE COMPLEXES OF GOLD(I) WITH ALCOHOLS AND AMINES

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(Received June 30th, 1975)

## Summary

The synthesis and properties of several new types of carbene complexes, obtained by reaction of the ionic gold(I) isocyanide complexes, $[(RNC)_2Au]^+$, (R = *p*-$CH_3C_6H_4$, $C_6H_{11}$) with alcohols ROH (R = $CH_3$, $C_2H_5$) and amines RR'NH (R = H; R' = *p*-$FC_6H_4$, *p*-$CH_3C_6H_4$, $C_6H_5CH_2$, $CH_3$, $C_6H_{11}$, *o,o'*-$[(CH_3)_2CH]_2C_6H_3$; R = $CH_3$, R' = $C_6H_5$), are described.

Both bis-carbene $[(carbene)_2Au]^+$ and monocarbene $[(carbene)(RNC)Au]^+$ complexes can be obtained according to the nature of the parent complex and of the nucleophilic agent. As evidenced by their NMR spectra, the bis-carbene complexes are obtained as a mixture of geometrical isomers which in the case of $[\{(p\text{-}CH_3C_6H_4NH)(C_2H_5O)C\}_2Au]ClO_4$ were separated by fractional crystallization.

The carbene ligand can be easily displaced with triphenylphosphine yielding the mixed complexes $[(carbene)(PPh_3)Au]^+$; in the case of a diaminocarbene the displaced ligand rearranges to give the corresponding formamidine, HC(=NR)-NHR.

## Introduction

The reaction of isocyanide complexes with alcohols or amines to give carbene derivatives has been extensively investigated and carbene complexes of several metals are known [1]. Neutral carbene complexes of gold(I), previously described by us [2], were obtained through two different paths of reaction:

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$$RNC{\rightarrow}AuX + HY \rightarrow \{(RNH)(Y)C\}{\rightarrow}AuX \quad (1)$$

R = aromatic; Y = OR, NHR

$$[RN{=}C(OR')Au]_3 + HCl \rightarrow \{(RNH)(OR')C\}{\rightarrow}AuCl \quad (2)$$

R = aromatic, $CH_3$, $C_6H_{11}$; R′ = $CH_3$, $C_2H_5$

Path 1, i.e., conversion of the isocyanide to the carbene directly by attack of a nucleophile, is successful in some cases only and is very sensitive both to the nature of the coordinated isocyanide and of the nucleophilic agent. Path 2 is more generally useful, provided that the starting compound is available.

We have extended this reaction to the gold(I) ionic bis-isocyanide complexes, $[(RNC)_2Au]^+$, on the hypothesis that their reactivity towards nucleophiles should be enhanced and that, at least in some cases, such bis-carbene derivatives which contain only carbene ligands might be obtained. However; the reaction of the second coordinated isocyanide might be more difficult, indeed carbene ligands are generally considered to be poorer $\pi$-acceptors than isocyanides, so that, owing to increased $\pi$-bonding, in a mixed (isocyanide) gold carbene cation, nucleophilic attack might be more difficult than in a diisocyanide gold cation.

We have chosen therefore as substrates two ionic complexes having comparable steric hindrance around the gold atom but different electrophilic character, i.e. $[(p\text{-}CH_3C_6H_4NC)_2Au]^+$ and $[(C_6H_{11}NC)_2Au]^+$ [2b] and studied their reactivity with alcohols and with primary or secondary amines. A preliminary account of this work has appeared [3]; since then, other papers on gold(I) diamino-carbene complexes have been published [4].

## Results and discussion

By reaction of one of the parent complexes $[(RNC)_2Au]^+$, (R = $C_6H_{11}$, $p$-$CH_3$-$C_6H_4$) with both amines and alcohols, a carbene complex was obtained, i.e. in every case at least one of the coordinated ligands was found to be susceptible to the attack of the nucleophilic agent, according to reaction 3.

$$[(RNC)_2Au]^+ + n\ HY = [(RNC)_{2-n}\ \{(RNH)(Y)C\}_nAu]^+ \quad (3)$$

n = 1,2, Y = OR′, NHR′, NR′R″

Among the amines, only a very weak nucleophile, such as $p$-nitroaniline ($pK_a$ ~ 1), did not react under the same conditions.

The reaction with amines proceeded readily under very mild conditions, e.g. in $CHCl_3$ solution at room temperature, often in the presence of an excess of the amine, while the reaction with alcohols required more vigorous conditions, such as longer time of reaction and reflux. When the substrate was a bis-$p$-tolylisocyanide complex a bis-carbene derivative was obtained, according to reaction 4

$$[(p\text{-}CH_3C_6H_4NC)_2Au]^+\ [A]^- + YH \rightarrow [\{(p\text{-}CH_3C_6H_4NH)(Y)C\}_2Au]^+\ [A]^- \quad (4)$$

A = $ClO_4$, $BF_4$; Y = NHR, NRR′, OR

independently of the nature of the nucleophile. Actually, in this case, bis-carbene complexes were obtained even with alcohols or with amines with bulky substituents, such as $o,o'$-diisopropylaniline.

With the cyclohexylisocyanide derivative, $[(C_6H_{11}NC)_2Au]^+$, in every case but one, only one of the isocyanides was converted to the carbene and the mixed isocyanocarbene complexes were isolated (eqn. 5). A dicarbene was obtained

$$[(C_6H_{11}NC)_2Au]^+ + HY \rightarrow [\{(C_6H_{11}NH)(Y)C\}\ (C_6H_{11}NC)Au]^+ \qquad (5)$$

Y = OR, NHAr, NRAr

only in the case of $CH_3NH_2$. The general trend of the reaction can be summarized as follows:

(a) The ionic bis-isocyanide complexes are more reactive than the neutral complexes, as is shown by the conversion of the isocyanide to the carbene through direct attack (e.g. path 1) even in the case of a cycloaliphatic isocyanide. Indeed a positive charge on the gold compound helps the attack of the incoming agent.

(b) Aromatic isocyanides are more reactive than the cycloaliphatic ones and are attacked, within reasonable limits, independently of the nature of the nucleophile; that is, the attack on the cation is easier when an electron-withdrawing group, such as an aryl, replaces an aliphatic group; this effect had been already observed by us in the case of the (RNC)AuCl complexes [2b].

(c) Attack by amines is easier than that by alcohols: under suitable conditions, however, the latter compounds also react and both mono- and bis-carbene complexes can be obtained; indeed, an amine is a better nucleophile than an alcohol.

In order to evaluate the importance of steric effects in the substrate, it would have been of interest to compare the reactivity of the cyclohexyl derivative with that of the analogous methylisocyanide complexes, $[(CH_3NC)_2Au]^+$. Unfortunately we were unable to isolate the parent complexes: by reaction of $(CH_3)_2SAuCl$ with $CH_3NC$ and $NaClO_4$ (or $NaBF_4$) only very insoluble products were obtained, which analyzed for $(CH_3NC)_4Au_3Cl_2X$ (X = $ClO_4$, $BF_4$). Further investigations of their nature were prevented by their insolubility and formulae such as $2[(CH_3NC)_2Au^I][Au^ICl_2][X]$ can be only suggested on the basis of analytical, IR, and conductance data. No carbene derivative was obtained from them, possibly due to their high insolubility.

Molecular weight determinations of the carbene derivatives in chloroform solution show a certain degree of association in many cases: this result may be attributed to hydrogen bonding. Conductivity measurements (acetone solution) are in agreement with the behaviour of 1/1 electrolytes.

The infrared spectra of the bis-carbene complexes show all the adsorptions expected for the anion and for the carbene of this type i.e. $\nu$(NH) at ca. 3300 $cm^{-1}$ $\nu$(C=N) and $\delta$(NH) between 1600 and 1500 $cm^{-1}$, plus the strong, broad vibration around 1100 due to the uncoordinated anion. The isocyanide carbene complexes show, in addition, a sharp band of the coordinated isocyanide at 2250 $cm^{-1}$. It is notable that no significant decrease is observed in the value of $\nu$(C≡N) passing from the starting complex $[(RNC)_2Au]^+$ to the isocyanide carbene complex. Such a decrease has been reported in many cases and attributed to an increase of $\pi$-back-bonding from the metal to the isocyanide due to the strong $\sigma$-donor nature of this type of carbene [5].

The NMR spectra show, in several cases, in solution the presence of more than one isomer. This was expected and was reported for many other carbene complexes as a consequence of restricted rotation about the C—N or C—O bonds.

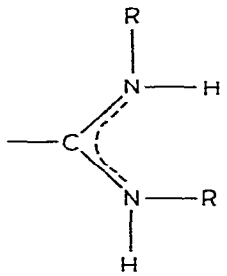
TABLE 1

FORMULAE, MOLECULAR FORMULAE, MELTING POINTS AND ANALYTICAL DATA OF THE COMPOUNDS IV-XIX

| Compound[a] | | Molecular formula | M.p. (°C) | Analytical data (Found (calcd.)) (%) | | | |
|---|---|---|---|---|---|---|---|
| | | | | C | H | N | Mol. wt.[b] (found (calcd.)) |
| IV | $[\{(ArNH)(p\text{-}FC_6H_4NH)C\}_2Au]ClO_4$ | $C_{28}H_{26}AuClF_2N_4O_4$ | 180 | 43.97 (44.70) | 3.33 (3.45) | 7.28 (7.44) | 1230 (752.5) |
| V | $[\{(ArNH)(p\text{-}CH_3C_6H_4NH)C\}_2Au]ClO_4$ | $C_{30}H_{32}AuClN_4O_4$ | 173(dec.) | 48.37 (48.40) | 4.27 (4.30) | 7.31 (7.52) | 1120 (744.5) |
| VI | $[\{(ArNH)(p\text{-}CH_3C_6H_4NH)C\}_2Au]BF_4$ | $C_{30}H_{32}AuBF_4N_4$ | >160(dec.) | 50.31 (49.20) | 4.51 (4.37) | 7.80 (7.65) | - (731.5) |
| VII | $[\{(ArNH)(C_6H_5CH_2NH)C\}_2Au]ClO_4$ | $C_{30}H_{32}AuClN_2O_4$ | > 60(dec.) | 49.20 (48.40) | 4.07 (4.30) | 7.36 (7.52) | 1270 (744.5) |
| VIII | $[\{(ArNH)(CH_3NH)C\}_2Au]ClO_4$ | $C_{18}H_{24}AuClN_4O_4$ | >130(dec.) | 36.40 36.33 (36.45) | 4.07 3.97 (4.05) | 9.47 9.27 (9.45) | - - (592.5) |
| IX | $[\{(ArNH)(C_6H_5NCH_3)C\}_2Au]ClO_4$ | $C_{30}H_{32}AuClN_4O_4$ | 202 | 48.00 (48.40) | 4.23 (4.30) | 7.48 (7.52) | - (744.5) |
| X | $[\{(ArNH)(o,o'[(CH_3)_2CH]_2C_6H_3NH)C\}_2Au]ClO_4$ | $C_{40}H_{52}AuClN_4O_4$ | 188 | 54.42 (54.30) | 5.70 (5.88) | 6.39 (6.33) | - (884.5) |
| XI | $[\{(ArNH)(C_6H_{11}NH)C\}_2Au]ClO_4$ | $C_{28}H_{40}AuClN_4O_4$ | >141(dec.) | 46.00 (46.10) | 5.53 (5.49) | 7.50 (7.69) | 1235 (728.5) |
| XII | $[\{(C_6H_{11}NH)(CH_3NH)C\}_2Au]ClO_4$ | $C_{16}H_{32}AuClN_4O_4$ | 165 | 34.12 (33.30) | 5.90 (5.55) | 9.63 (9.72) | - (576.5) |
| XIII | $[(C_6H_{11}NC)\{(C_6H_{11}NH)(ArNH)C\}Au]ClO_4$ | $C_{21}H_{31}AuClN_3O_4$ | >96(dec.) | 39.92 (40.55) | 4.97 (4.99) | 6.65 (6.76) | 730 (621.5) |
| XIV | $[(C_6H_{11}NC)\{(C_6H_{11}NH)(C_6H_5NCH_3)C\}Au]ClO_4$ | $C_{21}H_{31}AuClN_3O_4$ | >113(dec.) | 41.04 (40.55) | 4.90 (4.99) | 6.66 (6.76) | - (621.5) |
| XV | $[(Ph_3P)\{(ArNH)_2C\}Au]ClO_4$ | $C_{33}H_{31}AuClN_2O_4P$ | >170(dec.) | 49.72 (50.60) | 3.91 (3.96) | 3.35 (3.58) | - (782.5) |
| XVI | $[(C_6H_{11}NC)\{(C_6H_{11}NH)(CH_3O)C\}Au]ClO_4$ | $C_{15}H_{26}AuClN_2O_5$ | 100 | 32.71 (32.90) | 4.50 (4.76) | 5.01 (5.12) | 882 (546.5) |
| XVII | $[\{(ArNH)(CH_3O)C\}_2Au]ClO_4 \cdot 0.5\ CHCl_3$ | $C_{18.5}H_{22.5}AuCl_{2.5}N_2O_6$ | >85(dec.) | 33.76 (33.9) | 3.22 (3.45) | 4.35 (4.28) | - (654.3) |
| XVIII | $[\{(ArNH)(CH_3O)C\}_2Au]ClO_4$ | $C_{18}H_{22}AuClN_2O_6$ | | 36.35 (36.38) | 3.51 (3.70) | 4.62 (4.71) | (594.5) |
| XIXA | $[\{(ArNH)(C_2H_5O)C\}_2Au]ClO_4$ | $C_{20}H_{26}AuClN_2O_6$ | 185-186 | 38.49 (38.60) | 3.98 (4.17) | 4.55 (4.50) | 793 |
| XIXB | $[\{ArNH)(C_2H_5O)C\}_2Au]ClO_4$ | $C_{20}H_{26}AuClN_2O_6$ | 153 | 37.80 (38.60) | 4.06 (4.17) | 4.44 (4.50) | (622.5) |

[a] Ar is $p\text{-}CH_3C_6H_4$. [b] see text; in $CHCl_3$ ca. 1% w/w.

The spectra of the dicarbene derivatives are often very complicated since a great number of isomers is possible. Especially when bulky substituents are present, no assignment is possible and it is sometimes difficult to distinguish between the different isomers, owing to partial overlapping of the signals. Fischer's method [7] (homoallylic coupling) and comparison of the $J$ values, as was done for platinum complexes [6], are obviously not suitable in this case. Nevertheless, a few observations can be made on the spectra of the less complicated derivatives, such as $[Au\{C(NHC_6H_4CH_3)_2\}_2]^+ [A]^-$ ($A = ClO_4$, $BF_4$). Their spectra, besides the signals due to aromatic protons, show a signal (with a shoulder) at $\tau$ 7.75 ($p$-$CH_3$) and two signals due to the N—H, in a ratio ~1/10, suggesting that two isomers are present. It seems therefore that the predominant isomer is not in the configuration:



which would require two N—H signals in a ratio 1/1. This configuration, which would minimize steric interactions and is typical also of the *N,N'*-dimethylacetoamidinium ion $CH_3C(NHCH_3)_2^+$, was found in several carbenes of this type, both in solution [6] and in the solid state [8]. It is likely that in a less crowded molecule, as in the case of a bicoordinate metal, other configurations might be preferred.

Only two of the possible isomers are present in the solution of the alkoxoamino carbene $[\{(p\text{-}CH_3C_6H_4NH)(C_2H_5O)C\}_2Au]^+$; in this case the isomers can be separated by fractional crystallization. No conversion of one isomer to the other was observed (NMR spectra) up to the boiling point of the solvent ($CDCl_3$ or $CD_3CN$): clearly a high activation energy is involved in the rearrangement.

A reaction involving the carbene is its displacement by another ligand, a reaction which is often very difficult or does not occur at all (e.g. $[Pt(carbene)_4]^{2+}$ [9].

On the contrary, displacement from these gold(I) derivatives may be quite easy, even in very mild conditions. For example, by reaction of $[Au\{C(NHC_6H_4CH_3)_2\}_2]ClO_4$ with a neutral ligand, such as $Ph_3P$ in chloroform solution at ambient temperature, one of the carbene groups is readily released:

$$[Au\{C(NHC_6H_4CH_3)_2\}_2]ClO_4 + Ph_3P \rightarrow$$

$$[Ph_3P \rightarrow Au\{C(NHC_6H_4CH_3)_2\}]ClO_4 + HC(=NC_6H_4CH_3)NHC_6H_4CH_3$$

The formamidine resulting from the rearrangement of the carbene moiety was recovered from the solution and identified as such, or as a salt (picrate, perchlorate).

The same reaction on analogous derivatives has been reported to give rise to complete displacement of the carbene ligands [4], while here, the $[(Ph_3P)Au$-

(carbene)]$^+$ is stable even towards an excess of phosphine ligand.

The possibility of a rearrangement of the coordinate carbene to the isomeric formamidine complex, has been checked and excluded. Indeed, the formamidine complex can be isolated according to the reaction:

$$Ph_3P{\rightarrow}AuCl \xrightarrow[(2)\ HC(=NC_6H_4CH_3)NHC_6H_4CH_3]{(1)\ AgBF_4/CH_3OH} AgCl + [Ph_3P{\rightarrow}Au\{HC(=NC_6H_4CH_3)NHC_6H_4CH_3\}]BF_4$$

IR and NMR spectra distinguish between the isomeric cations, as previously suggested [10].

The bis-carbene complexes are also easily oxidized by halogens to the corresponding gold(III) carbene derivatives. Their synthesis and reactivity will be reported in detail elsewhere.

## Experimental

The elemental analyses were carried out by the microanalytical laboratory of this department and by Dr. Pascher's Mikroanalytisches Laboratorium (Bonn). Conductivity data were obtained at room temperature (20 ± 2°C), on a Philips Conductivity-meter. Molecular weight determinations were carried out at 37°C on a Mechrolab osmometer. Infrared spectra were recorded on Perkin—Elmer Mod. 137, 257, 457 spectrometers: $^1$H NMR spectra on a Varian NEVA-60 Mc with TMS as internal standard.

All the evaporations were carried out under reduced pressure using a water aspirator. Heating was accomplished through an oil bath.

The analytical data of the carbene complexes are collected in Table I. The NMR spectra are reported in the experimental section; chemical shift in $\tau$ units.

*Preparation of complexes*

The starting compounds, $[(p\text{-}CH_3C_6H_4NC)_2Au]ClO_4$ (I) and $[(C_6H_{11}NC)_2Au]ClO_4$ (II) were prepared as previously described [2b]. The compound $[(p\text{-}CH_3C_6H_4NC)_2Au]BF_4$ (III) was prepared as I, using $NaBF_4$ in place of $NaClO_4$.

*Reactions with amines*

*$[\{(p\text{-}CH_3C_6H_4NH)(p\text{-}FC_6H_4NH)C\}_2Au]ClO_4$ (IV).* To a solution of compound I (0.78 g) in $CHCl_3$ (50 ml), an excess of *p*-fluoroaniline (0.55 ml) was added and the mixture was stirred at room temperature under nitrogen for 12 hours. The white solid which formed was filtered off, recrystallized from $CH_2Cl_2$ (5 ml) and $Et_2O$ and dried in vacuo (0.54 g, yield 50%). NMR spectrum ($CDCl_3$): 7.69s ($CH_3$); 3.50-2.50m (Ar); 1.90 and 0.53 (NH) in a 1/4 ratio. ($CD_3COCD_3$): 7.76s ($CH_3$); 3.20-2.50m (Ar); -0.01s, broad (NH).

*$[\{(p\text{-}CH_3C_6H_4NH)_2C\}_2Au]ClO_4$ (V).* A solution of compound I (0.22 g) and $p\text{-}CH_3C_6H_4NH_2$ (0.05 g) in $CHCl_3$ (20 ml) was stirred at room temperature for 12 hours. The solution was evaporated to dryness and the oily residue was stirred under petroleum ether. The solid which formed was crystallized from $CHCl_3$ (5 ml) and $Et_2O$ to afford the analytical sample (0.12 g, 62%). IR (Nujol): 3280m, 3030vw, 2940s (br), 2860s, 1590m, 1545s (br), 1515s, 1470s, 1415w,

1380m, 1320m, 1300vw, 1280vw, 1230w, ~1090vs (br), 825s, 750w, 625m, 525s, 490w, 390vw. NMR spectrum ($CDCl_3$): 7.75s ($CH_3$); 3.30-2.25m (Ar); 1.90 and 0.63 (NH) (ca. 1/10).

*[{(p-$CH_3C_6H_4NH)_2C$}$_2$Au]$BF_4$ (VI).* Compound VI was prepared from III using the procedure described for complex V. NMR spectrum ($CDCl_3$): 7.74s ($CH_3$); 3.40-2.70m (Ar); 1.85 and 0.72 (NH) (ca. 1/10).

*[{(p-$CH_3C_6H_4NH$)($C_6H_5CH_2NH$)C}$_2$Au]$ClO_4$ (VII).* A solution of compound I (0.39 g) and 1.6 ml of $C_6H_5CH_2NH_2$ in $CHCl_3$ (20 ml) was stirred at room temperature for one hour. The solution was evaporated to dryness and the oil obtained was stirred alternatively with petroleum ether and diethyl ether. The crude product was dissolved in $CHCl_3$ and stirred overnight with charcoal. The pale yellow solution was filtered and evaporated to dryness; the resulting oil was stirred overnight under petroleum ether, to yield the solid analytical sample (0.27g, 50%). NMR spectrum ($CDCl_3$): 7.80s ($CH_3$); 5.57d (*J* 5cps)$CH_2$; 3.35-2.50m (Ar); ~1.85 br(NH—$CH_2$) and 0.53 (br) (NH) (ca. 1/1).

*[{(p-$CH_3C_6H_4NH$)($CH_3NH$)C}$_2$Au] $ClO_4$ (VIII).* A solution of compound I (0.61 g) and $CH_3NH_2$ (excess) in $CHCl_3$ (30 ml) was stirred at room temperature for 2 hours. From the solution, on evaporation to small volume, the complex (0.51 g, 75%) was obtained as white crystals, and washed twice with $Et_2O$. NMR spectrum ($CD_3COCD_3$): 7.72s (*p*-$CH_3$); 7.08-6.67m ($CH_3$); 3.17-2.50m (Ar); ~1.80 (br) (HN—$CH_2$); 0.58 (br) (NH).

*[{(p-$CH_3C_6H_4NH$)($C_6H_5NCH_3$)C}$_2$ Au] $ClO_4$ (IX).* A solution of compound I (0.66 g) and 0.27 ml of $C_6H_5NHCH_3$ was stirred at room temperature for two hours. The solution was evaporated to dryness and the oily residue was solidified under petroleum ether. The yellow crude product was washed with $CHCl_3$ to give the white analytical sample (0.38 g, 41%). NMR spectrum ($CD_3COCD_3$): 7.67s (*p*-$CH_3$); 6.50s ($CH_3$); 3.08-2.35m (Ar); 0.52 (br) (NH).

*[{(p-$CH_3C_6H_4NH$) (o,o'[$(CH_3)_2CH$]$_2C_6H_3NH$)C}$_2$ Au] $ClO_4$ (X).* A solution of compound I (0.55 g) and 0.75 ml (excess) of the amine in $CHCl_3$ (20 ml) was stirred at room temperature for 5 hours. The solution was evaporated to dryness and the oily residue was taken up with petroleum ether. The crude product crystallized from $CHCl_3/Et_2O$ (0.143 g, 15%). NMR spectrum ($CDCl_3$): 9.25d, 9.06d, 8.80d, 8.75d ($J \simeq 7$ cps) ($CH_3$), 7.72s (*p*-$CH_3$); 6.78 septet (CH); 3.24-2.42m (Ar); 1.35 (br), 0.43 (br) (NH) (ca. 1/9).

*[{(p-$CH_3C_6H_4NH$)($C_6H_{11}NH$)C}$_2$Au]$ClO_4$ (XI).* Compound I (0.46 g) and $C_6H_{11}NH_2$ (0.18 ml) were dissolved in $CHCl_3$ (20 ml) and stirred at room temperature for 5 hours. After evaporation to dryness, the oily residue was stirred under petroleum ether (several portions) for twelve hours and filtered (0.48 g, 73%). NMR spectrum ($CDCl_3$): 9.15-8.0 (br) ($CH_2$); 7.73s ($CH_3$): 6.5 (br) (CH); 3.16-2.67m (Ar); 2.0 d (br) ($J \simeq 8.5$ cps) ($NHC_6H_{11}$); 0.66 (br) (NH).

*[{($C_6H_{11}NH$)($CH_3NH$)C}$_2$Au]$ClO_4$ (XII).* To a solution of compound II (0.58 g) in $CHCl_3$ (10 ml), a solution of $CH_3NH_2$ in $CHCl_3$ was added (molar ratio 1/4). After one hour the white precipitate which had formed was filtered off, washed with $Et_2O$ and recrystallized from acetone—diethyl ether (0.255 g, 38%). NMR spectrum ($CD_3COCD_3$): ~9-7.8m (br) ($CH_2$); 7.19d, 7.15d, 6.80d, 6.76d ($J \simeq 5$ cps) ($CH_3$); ≃6.0 (br) (CH); 1.9-2.8 (br) (NH).

*[($C_6H_{11}NC$){($C_6H_{11}NH$)(p-$CH_3C_6H_4NH$)C}Au]$ClO_4$ (XIII).* A solution of compound II (0.69 g) and *p*-$CH_3C_6H_4NH_2$ (0.29 g) in $CHCl_3$ (40 ml) was stirred

overnight and then evaporated to dryness to give a yellow oil. The oil was taken up with petroleum ether and the crude product so obtained was crystallized twice from chloroform—petroleum ether. The white complex was filtered off and washed with $Et_2O$ (0.34 g, 41%). $\nu$(C≡N): 2250 $cm^{-1}$ (Nujol mull). NMR spectrum ($CDCl_3$): 9-7.8m (br) ($CH_2$); 7.66s ($CH_3$); 6.4-5.7m (br) (CH); 2.93-2.56m (Ar); 1.75d ($J \simeq 8$ cps) (HN—$C_6H_{11}$) and 0.47s NH (ca. 1 : 1).

*[($C_6H_{11}NC$){($C_6H_{11}NH$)($C_6H_5NCH_3$)C}Au]$ClO_4$ (XIV).* A solution of compound II (0.25 g) and *N*-methylaniline (0.11 ml) in $CHCl_3$ (20 ml) was stirred at room temperature for 12 hours. The solution was evaporated to dryness and the oily residue was taken up with petroleum ether. The white solid obtained was washed with several portions of petroleum ether under stirring (0.16 g, 52%). $\nu$(C≡N): 2260 $cm^{-1}$ (Nujol mull). NMR spectrum ($CDCl_3$): 9-7.7m (br) ($CH_2$); 6.53s, 6.25s ($CH_3$); ca. 6.1 (br) (CH); 2.65s (Ar); ca. 2.5 (br) (NH) (overlapping).

*Reactions with alcohols*

*[($C_6H_{11}NC$){($C_6H_{11}NH$)($CH_3O$)C}Au]$ClO_4$ (XVI).* Compound II (0.6 g) in methanol (30 ml) was refluxed under nitrogen for 90 hours. The solution was evaporated to dryness and the oily residue was stirred under petroleum ether. The crude product was crystallized twice from methanol—diethyl ether $\nu$(C≡N): 2260 $cm^{-1}$ (Nujol mull).

*[{(p-$CH_3C_6H_4NH$)($CH_3O$)C}$_2$Au] $ClO_4$ 0.5 $CHCl_3$ (XVII) and [{(p-$CH_3C_6H_4$-NH)($CH_3O$)C}$_2$Au] $ClO_4$ (XVIII).* Compound I (0.52 g) was dissolved in chloroform (5 ml) and methanol (20 ml) was added. The solution was refluxed gently for 72 hours under nitrogen. After evaporation to dryness of the filtered solution, the oil was solidified by stirring under petroleum ether. The crude product was crystallized from chloroform—diethyl ether to yield the analytical sample of compound XVII. The chloroform-free compound XVIII was prepared similarly, but in the absence of chloroform. The product precipitated upon concentration of the filtered solution; a second crop was obtained on further concentration in presence of diethyl ether.

Although an enrichment of one of the several possible isomers is obtained on fractional crystallization, no pure isomer (according to m.p. and NMR spectra) was separated. NMR spectrum ($CD_3COCD_3$): 7.65s (*p*-$CH_3$); 5.78, 5.76s, 5.51s, 5.49s ($OCH_3$); 2.5-3.0m (Ar); —1.07 (br), —1.55 (br) (NH). ($CDCl_3$): 7.63s (*p*-$CH_3$); 5.99s, 5.34s, 5.29s ($OCH_3$), 2.70s (Ar).

*[{(p-$CH_3C_6H_4NH$)($C_2H_5O$)C}$_2$Au]$ClO_4$ (XIXA and XIXB).* Compound I (2.0 g) was suspended in ethanol (50 ml) and refluxed under nitrogen for 96 hours. After filtering while hot (traces of gold), the solution was evaporated to about half its volume to afford the crystalline compound (XIXA), which was filtered and washed with diethyl ether to afford the analytical sample (0.25 g). The mother liquor was evaporated to 10 ml and filtered. The precipitate was discarded and the solution was evaporated to dryness. The residue was washed with diethyl ether and compound XIXB was filtered off (1.25 g). NMR spectrum ($CDCl_3$) isomer A: 8.54t ($J \simeq 7$ cps) ($CH_3$); 7.67s (*p*-$CH_3$); 5.20q ($CH_2$); 3.0-2.5m (Ar); —0.5 (NH). Isomer B: 8.74t ($J \simeq 7$cps) ($CH_3$); 7.67s (*p*-$CH_3$); 5.63q ($CH_2$); 3.0-2.5m (Ar); —0.1 (NH).

*Displacement reaction with $Ph_3P$*

To a solution of $[\{(p\text{-}CH_3C_6H_4NH)_2C\}_2Au]ClO_4$ (0.33 g) in $CHCl_3$ (20 ml) triphenylphosphine (0.12 g) (molar ratio 1/1) was added at room temperature. From the solution complex XV was precipitated with $Et_2O$ and crystallized from $CHCl_3/Et_2O$ (yield 90%). NMR spectrum ($CDCl_3$): 7.72s ($CH_3$); 3.08-2.33m (Ar); -0.3 br (NH). The solution was evaporated to dryness and the crude formamidine was crystallized from ethanol and identified by comparison with an authentic sample [10] (m.p., IR and NMR spectra) and as a picrate (Found: C, 55.3; H, 4.10; N, 15.8; $C_{21}H_{19}N_5O_7$ (mol. wt 453) calcd.: C, 55.6; H, 4.19; N, 15.45%). NMR spectrum ($CDCl_3$): 7.60s ($CH_3$); 2.70s (Ar); 1.81s (CH); 0.99s (CH) (picrate).

*Reactions with methylisocyanide*

(1) To a suspension of $(CH_3)_2SAuCl$ (0.68 g) in acetone (50 ml), methylisocyanide (0.38 ml) and then $NaClO_4 \cdot 2H_2O$ (0.5 g) were added; the mixture was stirred at ambient temperature one hour and the white precipitate was collected and washed several times with acetone (Found: C, 10.30; H, 1.09; N, 5.82%). The crude product was crystallized by extraction with $CH_2Cl_2$ in a Soxhlet apparatus; on cooling a white precipitate was obtained which was extracted again with acetone (250 ml). By concentration the analytical, white crystalline sample was obtained (0.14 g). (Found: C, 10.33; H, 1.26; N, 5.96, O, 7.09. $C_8H_{12}Au_3Cl_3N_4O_4$ (mol. wt. 925.5) (see text) calcd.: C, 10.38, H, 1.29, N, 6.04, O, 6.92%. $\Lambda$ (acetone, $7.5 \times 10^{-4}$ *M*): 174 $ohm^{-1}$ $cm^2$ $mol^{-1}$). IR (nujol): 2230 (C≡N), 1080vs, 625m ($ClO_4$), 330s (AuCl) $cm^{-1}$.

(2) The tetrafluoroborate was obtained and crystallized analogously using $NaBF_4$ in place of $NaClO_4$. (Found: C, 10.60, H, 1.21, N, 6.31, Au, 63.7. $C_8H_{12}Au_3BCl_2F_4N_4$ (mol. wt. 912.8) calcd.: C, 10.52; H, 1.31; N, 6.14; Au, 64.7%. $\Lambda$ (acetone 7 $10^{-4}$ *M*): 176 $ohm^{-1}$ $cm^2$ $mol^{-1}$) IR (nujol): 2290 (C≡N), 1050s (br), ($BF_4$), 335s $cm^{-1}$ (Au—Cl).

*Preparation of $[Ph_3P\rightarrow Au(p\text{-}CH_3C_6H_4N{=})HC(NHC_6H_4CH_3\text{-}p)]BF_4$*

To a suspension of $Ph_3PAuCl$ (0.72 g) in methanol (30 ml), 0.296 g of $AgBF_4$ were added. After a few minutes, the silver chloride was filtered off and formamidine (0.34 g) was added. The solution was filtered and evaporated to dryness; the oily residue was stirred with hexane and the pale yellow product was crystallized twice from $CH_2Cl_2/Et_2O$ to give the analytical sample (0.08 g, dec. 155°C). (Found: C, 51.5, H, 3.88, N, 3.83. $C_{33}H_{31}AuBF_4N_2P$ (mol. wt. 769.8) calcd.: C, 51.5, H, 4.01, N, 3.64%.) IR (Nujol mull); 3320m; 1625s; 1590s $cm^{-1}$. NMR spectrum ($CDCl_3$): 7.72 (br) ($CH_3$); 2.2-3.1m (Ar), 1.45s (CH), 0.65 (br) (NH).

## Acknowledgements

Financial support by CNR (Rome) is gratefully acknowledged.

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