Morgan and Tobe[4] have proposed that substitution of bromide in [PtBr(QAS)]$^+$ proceeds via a four-coordinate intermediate formed by the equilibrium dissociation of an equatorial arsenic group. The lack of a large difference in rate between substitution of chloride in [NiCl(QAS)] by cyanide and thiocyanate appears to be consistent with the Tobe mechanism. However, these results, combined with the apparent sluggishness of the nickel(II) complex, could also be consistent with either a dissociative interchange mechanism or attack of a square-pyramidal intermediate formed in a rate-determining intramolecular rearrangement.

**Acknowledgment.** We are grateful to the Graduate Office of Mississippi State University for support of this project and to Dr. Andrew Stefani of the University of Mississippi for use of the Durrum stopped-flow spectrophotometer.

**Registry No.** [NiCl(QAS)]$^+$, 48244-56-0; [Ni(CN)(QAS)]ClO$_4$, 14238-93-8; NCS$^-$, 302-04-5; CN$^-$, 57-12-5.

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## Carbene Complexes of Gold(III) and Reactions of the Coordinated Ligand

Giovanni Minghetti,*[1a] Flavio Bonati,[1b] and Guido Banditelli[1a]

Since the preliminary reports by Schoellkopf[2] and Badley,[3] many papers have been published on the addition of nucleophiles, such as alcohols and amines, to coordinated isocyanides affording carbene ligands with two heteroatoms directly bonded to the carbenoid carbon atom; the available results in this area have been reviewed recently.[4] Although examples of complexes of metals in high or relatively high oxidation states are not unknown (e.g., Rh(III)[5] and Pt(IV)[6]), difficulties in the preparation prevented an extensive development in this direction and most of the known carbenoid derivatives have metal ions in a low oxidation state (Hg(II), Pt(II), Pd(II), Mn(I), Fe(II), Ru(II), Rh(I), Au(I)).[4]

Here we report the syntheses of some ionic bis(carbene) complexes of gold(III), obtained by oxidation with halogens of the corresponding gold(I) derivatives. In the latter, the displacement of the coordinated carbene has been shown to be very easy,[7] so it seemed interesting to investigate also this aspect of the reactivity of these new derivatives with the aim of establishing the influence of the different oxidation state of the metal.

Following our preliminary communication,[8] the existence of other carbenoid complexes of gold(III) has been reported.[9]

**Experimental Section**

**Preparation of the Complexes.** The preparations of the starting gold(I) carbene complexes [{(p-CH$_3$C$_6$H$_4$NH)$_2$C}$_2$Au]ClO$_4$(or BF$_4$), [{(p-CH$_3$C$_6$H$_4$NH)(C$_2$H$_5$O)C}$_2$Au]ClO$_4$, and [{(C$_6$H$_{11}$NH)(CH$_3$NH)C}$_2$Au]ClO$_4$ were carried out as reported elsewhere.[8,14] The gold(III) complexes I and IV–VIII were obtained according to the following general procedure.

The gold(I) complex (ca. 0.5 g) was dissolved in CHCl$_3$ (ca. 30 ml), and iodine in CHCl$_3$ solution (ca. 10$^{-2}$ M) was added in a 1:1 molar ratio. The resulting red solution was evaporated to dryness and the oily residue was stirred under petroleum ether to give the orange crude product. The crude products (ca. >80% yield) were crystallized from CH$_2$Cl$_2$ (5 ml) and diethyl ether (15 ml) to give the analytical sample; only complex VI was analyzed as a crude solid.

Reactions with water afford the following three compounds.

**(a) $N,N'$-Di-p-tolylurea.** Compound I (0.6 g, 0.56 mmol) was dissolved in acetone (40 ml), water was added (40 ml), and the solution was kept under vigorous stirring at room temperature. In a short time (ca. 1 h) the red complex II was formed; after stirring of the suspension A overnight, the red complex disappeared, the solution B became white and strongly acidic, and a white precipitate was formed. The precipitate (0.11 g, 0.46 mmol, 41% on nitrogen) was filtered, crystallized from hot ethanol, and identified as $N,N'$-di-p-tolylurea through its melting point, ir spectrum, and elemental analyses. The solution B was concentrated under vacuum at room temperature to half-volume, extracted with CH$_2$Cl$_2$ (*caution!* saturated solutions of HClO$_4$ in CH$_2$Cl$_2$ are reported to be highly explosive[10]), and evaporated to dryness; an oily residue was obtained, which solidified under petroleum ether, yielding [{(ArNH)$_2$C}$_2$Au]I, IX, which decomposed on attempted crystallization. In a separate experiment the suspension A was filtered and compound II was isolated and characterized; on pumping (0.01 Torr) to constant weight, II gave III, which was not obtained on pumping I.

From complex I or IV, $N,N'$-di-p-tolylurea was obtained also if the reaction was carried out in strictly deoxygenated solvents and by using acetonitrile or methanol in place of acetone. In methanol, however, refluxing was necessary to accomplish the reaction.

**(b) $N$-Methyl-$N'$-p-tolylurea.** Compound VI (0.55 g, 0.65 mmol) was dissolved in acetone (20 ml) and water (20 ml) was added. After stirring of the mixture 9 days at room temperature, the solution was acidic and nearly colorless while a gold mirror formed. The solution was filtered and concentrated to afford a pale yellow crude product (0.18 g, 0.11 mmol, 85% on the starting complex) which was crystallized from ethanol–water and identified as $N$-methyl-$N'$-p-tolylurea through its melting point, elemental analyses, and ir and NMR spectra.

**(c) $N$-p-Tolylurethane.** Complex VII (0.57 g, 0.65 mmol) was dissolved in acetone (80 ml), and water (80 ml) was added. Immediately, a red precipitate was formed; after 2 days of stirring, the red precipitate disappeared, the solution was nearly colorless and acidic, and a yellow oil separated plus traces of gold. The oil was extracted with CH$_2$Cl$_2$, dried over Na$_2$SO$_4$, and then evaporated to dryness. The oily residue was solidified under petroleum ether (several portions) to afford {(ArNH)(C$_2$H$_5$O)C}AuI, X. The petroleum ether solution was evaporated to dryness to give an oily residue; ir and NMR spectra gave evidence of the presence of a mixture. The oily residue was extracted with CCl$_4$, evaporated to dryness, extracted with cyclohexane, and evaporated again to yield a sticky oily material, identified as $N$-p-tolylurethane by ir and NMR spectra.

**Reactions with Water in the Presence of LiCl (or NaCl).** Compound I (0.68 g, 0.62 mmol) was dissolved in acetone (20 ml); water (20 ml) and a large excess of LiCl (or NaCl) were added and the solution was stirred overnight. A white precipitate was filtered and crystallized from CHCl$_3$–Et$_2$O to afford the white, crystalline, analytical sample of [{(ArNH)$_2$C}$_2$Au]Cl, XI.

**Reactions of Compounds I and IV with Triphenylphosphine. (a) In Acetone.** Compound I (or IV) (0.75 g) was dissolved in acetone and Ph$_3$P was added (molar ratio 1:4). In a few minutes, the solution became colorless, and a white, crystalline product was formed (0.53 g, 0.62 mmol, 88%) which was filtered and crystallized from CHCl$_3$–petroleum ether affording (Ph$_3$P)$_2$AuI, XII. The filtered solution was evaporated to a small volume, filtered, and then evaporated to dryness. The residue was taken up with CHCl$_3$ and

Table I. Analytical Data

| No. | Compd[a] | %C Calcd | %C Found | %H Calcd | %H Found | %N Calcd | %N Found |
|---|---|---|---|---|---|---|---|
| I | [{(ArNH)$_2$C}$_2$AuI$_2$]ClO$_4$·(C$_2$H$_5$)$_2$O | 38.0 | 37.53 | 3.91 | 3.67 | 5.22 | 5.20 |
| II | [{(ArNH)$_2$C}$_2$AuI$_2$]ClO$_4$·(CH$_3$)$_2$CO | 37.50 | 37.93 | 3.60 | 3.76 | 5.30 | 5.02 |
| III | [{(ArNH)$_2$C}$_2$AuI$_2$]ClO$_4$ | 36.07 | 36.11 | 3.20 | 3.12 | 5.61 | 5.66 |
| IV | [{(ArNH)$_2$C}$_2$AuI$_2$]BF$_4$·0.75(C$_2$H$_5$)$_2$O | 38.0 | 38.09 | 3.79 | 3.89 | 5.37 | 5.14 |
| V | [{(ArNH)$_2$C}$_2$AuBr$_2$]ClO$_4$·0.5(C$_2$H$_5$)$_2$O | 40.8 | 41.10 | 3.93 | 3.75 | 5.95 | 6.01 |
| VI | [{(ArNH)(CH$_3$NH)C}$_2$AuI$_2$]ClO$_4$ | 25.5 | 26.13 | 2.84 | 2.98 | 6.62 | 6.51 |
| VII | [{(ArNH)(C$_2$H$_5$O)C}$_2$AuI$_2$]ClO$_4$ | 27.4 | 27.75 | 2.97 | 2.90 | 3.19 | 3.16 |
| VIII | [{(C$_6$H$_{11}$NH)(CH$_3$NH)C}$_2$AuI$_2$]ClO$_4$ | 23.1 | 23.18 | 3.85 | 3.69 | 6.75 | 6.51 |
| IX | [{(ArNH)$_2$C}$_2$AuI]I | 46.7 | 47.60 | 4.15 | 4.10 | 7.25 | 7.23 |
| X | {(ArNH)(C$_2$H$_5$O)C}AuI | 24.6 | 25.62 | 2.67 | 2.81 | 2.87 | 2.93 |
| XI | [{(ArNH)$_2$C}$_2$Au]Cl | 52.85 | 52.69 | 4.71 | 4.79 | 8.24 | 8.18 |
| XII | (Ph$_3$P)$_2$AuI | 50.9 | 50.69 | 3.84 | 3.49 | 0.00 | |
| XIII | [HC(NHAr)$_2$][(Ph$_3$P)$_2$AuI$_2$][b] | 51.0 | 51.61 | 3.91 | 3.72 | 2.33 | 2.42 |

[a] Ar is p-CH$_3$C$_6$H$_4$. [b] Percent Au: calcd, 15.4; found, 16.4. Percent I: calcd, 21.5; found, 21.15.

**Scheme I[a]**
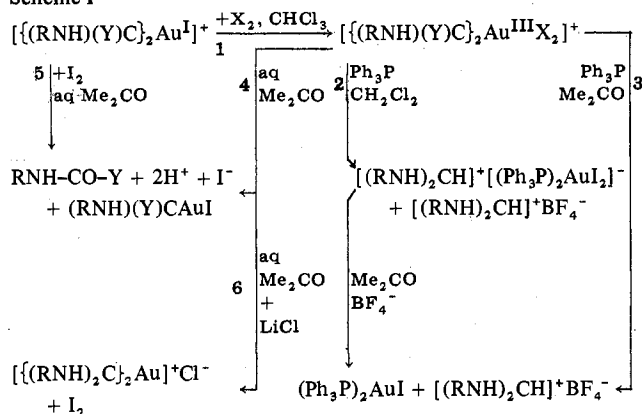


[a] Y = OEt or RNH; X = Br, I.

petroleum ether was added. The white precipitate which formed was filtered, recrystallized in the same way, and identified as [HC(NHC$_6$H$_4$CH$_3$-p)$_2$]ClO$_4$(or BF$_4$) by comparison with an authentic sample.[11]

**(b) In Dichloromethane.** To compound I (or IV) (0.20 g, 0.19 mmol) in CH$_2$Cl$_2$ (ca. 30 ml), triphenylphosphine (0.60 g, 2.99 mmol, excess) was added; the solution became colorless in a few minutes and a white precipitate (0.21 g, 0.175 mmol) was obtained by addition of Et$_2$O. The white precipitate was crystallized twice from CH$_2$Cl$_2$–Et$_2$O to give the analytical sample of [HC(NHAr)$_2$]$^+$-[(Ph$_3$P)$_2$AuI$_2$]$^-$, XIII. The solution from the reaction of compound IV was evaporated; the oily residue was solidified under petroleum ether and crystallized from CH$_2$Cl$_2$–petroleum ether to give [HC-(NHC$_6$H$_4$CH$_3$p)$_2$]BF$_4$. Compound XIII is unstable in acetone where it gives (Ph$_3$P)$_2$AuI; in the presence of NaBF$_4$, also the amidinium tetrafluoroborate was recovered.

See Table I for analytical data.

**Results and Discussion**

The reactions were carried out as described in Scheme I. The new gold(III) complexes of the type [(carbene)$_2$AuX$_2$]$^+$A$^-$, where carbene is (p-CH$_3$C$_6$H$_4$NH)$_2$C, (p-CH$_3$C$_6$H$_4$NH)(CH$_3$NH)C, (p-CH$_3$C$_6$H$_4$NH)(C$_2$H$_5$O)C, or (C$_6$H$_{11}$NH)(CH$_3$NH)C, X is Br or I, and A is ClO$_4$ or BF$_4$, were obtained as well-formed crystals by oxidation of the corresponding gold(I) derivatives with halogen (pattern 1). No by-product was observed. In several cases, analytical and spectral data show that they contain molecules of solvents, such as diethyl ether or acetone, which could not always be removed by pumping under vacuum.

By comparison, although halogen addition is sterically possible on the [(ArNC)$_2$Au]$^+$ cations, these do not add iodine, in agreement with the belief that this type of reaction is favored by the presence of σ-donor ligands.[12] Mixed complexes such as [(carbene)Au(Ph$_3$P)]$^+$ reacted with iodine in ill-defined

stoichiometric ratios, so that no pure compound is isolated.

According to a preliminary report of the x-ray crystal structure analysis of complex I by Manojlovic-Muir,[13] the iodine atoms are trans to one another and the complex may be best described by
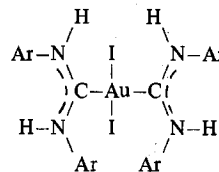


The Au–C distances 2.07 (2) and 2.09 (2) Å are reported as indicative of pure σ-bonding interactions.[13]

While the infrared spectra are very similar to those of the corresponding gold(I) bis(carbene),[14] the NMR spectra (Table II), which are in full agreement with the proposed formulas, show in several complexes (I–V) two NH signals in a 1:1 ratio, so it is likely that only one isomer is present in solution and that the carbene is in the amphi configuration, found, for complex I, also in the solid state.[13]

A characteristic feature of the reactivity of the bis(carbene) complexes of gold(I) is the very easy displacement in solution of the unstable carbene, according, e.g., to the reaction[14]

[{(ArNH)$_2$C}$_2$Au]$^+$ + Ph$_3$P = [{(ArNH)$_2$C}Au(PPh$_3$)]$^+$
    + HC(=NAr)NHAr
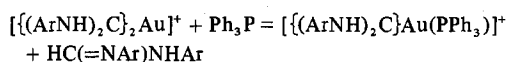
By reaction of triphenylphosphine with a gold(III) complex, I, in acetone solution, displacement of both the carbenes occurs while gold(III) is reduced to gold(I), affording the species (Ph$_3$P)$_2$AuI, XII, according to reaction 3 (Scheme I). Complex XII, which is monomeric in chloroform and is not an electrolyte in acetone solution, might be an authentic example of three-coordinate gold(I) derivative, of the type recently found by x-ray analysis for (Ph$_3$P)$_2$AuCl.[15] The displaced carbene was not isolated as the free N,N'-di-p-tolylformamidine but, conveniently, as the perchlorate [HC(NHAr)$_2$]ClO$_4$.

If the reaction with Ph$_3$P is carried out in CH$_2$Cl$_2$ (reaction 2) in place of acetone, a compound, XIII, is obtained for which a formula such as [HC(NHAr)$_2$]$^+$[(Ph$_3$P)$_2$AuI$_2$]$^-$ is suggested. The compound is unstable in acetone solution affording again (Ph$_3$P)$_2$AuI, XII, and [HC(NHAr)$_2$]$^+$, isolated as tetrafluoroborate.

Of particular interest was the behavior of the complex in solution in the presence of water; indeed, in these very mild conditions the oxidation of the metal-bonded carbene to the corresponding carbonyl compounds was achieved (reaction 5).

While the gold(III) carbene complexes appear to be stable in acetone solution, by addition of water a red intermediate

**Table II.** Properties and ¹H NMR Data of the New Complexes[a]

| No. | Compd[b] | Mp, °C | Color | Chem shifts,[c] $\tau$ |
|-----|----------|--------|-------|--------------------|
| I | [{(ArNH)₂C}₂AuI₂]ClO₄·(C₂H₅)₂O | 133 | Orange-red | 8.82 t, CH₃ ($J \simeq 7$ Hz); 7.61 s, $p$-CH₃; 6.52 q, CH₂; 3.2–2.5 m, Ar; 2.17 and 0.07 s, NH (1:1) |
| II | [{(ArNH)₂C}₂AuI₂]ClO₄·(CH₃)₂CO | 110 dec | Red | 7.88 s, CH₃; 7.65 s, $p$-CH₃; 3.25–2.65 m, Ar; 2.20 s, br, and −0.82 br, NH (1:1) |
| III | [{(ArNH)₂C}₂AuI₂]ClO₄[d] | 124 | Red | 7.63 s, $p$-CH₃; 3.16–2.5 m, Ar; 2.21 s and −0.17 s, NH (1:1) |
| IV | [{(ArNH)₂C}₂AuI₂]BF₄·0.75(C₂H₅)₂O | 116 | Orange-red | 8.85 t, CH₃ ($J \simeq 7$ Hz); 7.65 s, $p$-CH₃; 6.58 q, CH₂; 3.3–2.7 m, Ar; 2.20 br and 0.3, NH (1:1) |
| V | [{(ArNH)₂C}₂AuBr₂]ClO₄·0.5(C₂H₅)₂O | 135 dec | Yellow | 8.82 t, CH₃; 7.62 s, $p$-CH₃; 6.53 q, CH₂; 3.2–2.5 m, Ar; 2.06 s and 0.0 s, NH (1:1) |
| VI | [{(ArNH)(CH₃NH)C}₂AuI₂]ClO₄ | 131 | Yellow | 7.68 s and 7.63 s, $p$-CH₃; 7.41 d, 6.85 d, 6.78 d ($J \simeq 5$ Hz), CH₃; 3.4–2.1 m, Ar; 1.85, $H$N–CH₃; 1.25, NH |
| VII | [{(ArNH)(C₂H₅O)C}₂AuI₂]ClO₄[e] | 162 dec | Orange-red | 8.48 t, ($J \simeq 7$ Hz), CH₃; 7.71 s, $p$-CH₃; 5.33 q, CH₂; 2.86 s, Ar |
| VIII | [{(C₆H₁₁NH)(CH₃NH)C}₂AuI₂]ClO₄[f] | 160 dec | Orange-red | 9.0–7.6 m, br, CH₂; 6.96 d, 6.89 d, 6.83 d ($J \simeq 5$ Hz), CH₃; 6.22 br, CH; 2.7–1.6 br, NH |
| IX | [{(ArNH)₂C}₂Au]I[g,h] | | Pale yellow | |
| X | {(ArNH)(C₂H₅O)C}AuI[g] | 75 dec | Pale yellow | |
| XI | [{(ArNH)₂C}₂Au]Cl[i] | 185 | White | 7.77 s, $p$-CH₃; 3.34–2.66 m, Ar; −0.88 s, NH |
| XII | (Ph₃P)₂AuI[j] | 225 | White | |
| XIII | [HC(NHAr)₂][(Ph₃P)₂AuI₂] | 198 | White | 7.67 s, $p$-CH₃; 3.0–2.2, Ar; 1.36 s, CH |

[a] All the complexes gave satisfactory elementary analyses. [b] Ar is $p$-CH₃C₆H₄. [c] CDCl₃ solution, unless otherwise indicated, at 40 °C; integration always supported the formulas assigned. Key: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. [d] Molecular weight in CHCl₃: calcd, 998; found, 1090. [e] Only slightly soluble in CDCl₃. [f] NMR spectrum recorded in acetone. [g] Decomposes on attempted crystallization. [h] Λ 90 ohm⁻¹ cm² mol⁻¹ (acetone, 3 × 10⁻⁴ M). [i] Λ 106 ohm⁻¹ cm² mol⁻¹ (acetone, 5 × 10⁻⁴ M). [j] Molecular weight in CHCl₃: calcd, 848; found, 830. Compound is not an electrolyte in acetone.

compound was isolated at first and was identified as the less soluble acetone solvate, II. On prolonged stirring at room temperature the solution became colorless and strongly acidic, and the N,N'-disubstituted ureas (or N-substituted urethane, respectively) were formed according to reaction 4. The oxygen atom involved in the reaction cannot come from acetone, atmospheric dioxygen, or the perchlorate anion because the carbonyl compound was formed even when the reaction was carried out with a different anion (BF₄⁻) or in the absence of dioxygen or in a different solvent (acetonitrile or methanol). Workup of the solution allowed a small amount of a gold(I) carbene complex to be isolated, although the latter appears to be quite unstable in the very acidic solution and extensive decomposition to gold occurs; furthermore, the yield in ureas showed that only one of the carbenes can be oxidized in these conditions. In conclusion, the overall process may be described by reaction 4, which implies that the gold(III) complex is the oxidizing agent. Other, but secondary, processes such as the reduction to metallic gold or the action of dioxygen (e.g., indirectly through oxidation of I⁻ to iodine) cannot be completely ruled out when the reaction is carried out in the presence of air. Indeed, in the case of complex VI, for instance, the oxidation of both carbenes was obtained according to the yield of urea when the solution was stirred in air for 9 days. However, in any case the presence of orange-red gold(III) species is required; no reaction was observed with gold(I) complexes in aqueous acetone, while oxidation to urea was achieved in the presence of stoichiometric amount of iodine (reaction 5).

The gold(III) complex I (or its homologues II–IV) is a potentially oxidizing agent toward either the carbene ligand, as reported above, or the iodine ion. Indeed, in the presence of excess sodium or lithium chloride iodine is formed while the carbene ligand is not attacked and is found in the compound [(carbene)₂Au]⁺Cl⁻, which is insoluble (reaction 6).

Oxidation of a coordinated carbene in mild conditions is very unusual although oxidation by dioxygen in boiling hexane has been reported by Fischer.[16] In other cases the same result

required an addition of rather strong oxidizing agents such as cerium(IV)[17] or pyridine N-oxide.[18]

**Registry No.** [{(ArNH)₂C}₂AuI₂]ClO₄, 58919-37-2; [{(ArNH)₂C}₂AuI₂]BF₄, 58919-38-3; [{(ArNH)₂C}₂AuBr₂]ClO₄, 58919-40-7; [{(ArNH)(CH₃NH)C}₂AuI₂]ClO₄, 58919-42-9; [{(ArNH)(C₂H₅O)C}₂AuI₂]ClO₄, 58919-44-1; [{(C₆H₁₁NH)(CH₃NH)C}₂AuI₂]ClO₄, 58919-46-3; [{(ArNH)₂C}₂Au]I, 58919-47-4; {(ArNH)(C₂H₅O)C}AuI, 58866-17-4; [{(ArNH)₂C}₂Au]Cl, 58919-48-5; (Ph₃P)₂AuI, 21209-81-4; [HC(NHAr)₂][(Ph₃P)₂AuI₂], 58919-50-9; [{($p$-CH₃C₆H₄NH)₂C}₂Au]ClO₄, 42187-59-7; [{($p$-CH₃C₆H₄NH)₂C}₂Au]BF₄, 58320-41-5; [{($p$-CH₃C₆H₄NH)-(C₂H₅O)C}₂Au]ClO₄, 58299-90-4; [{(C₆H₁₁NH)(CH₃NH)C}₂-Au]ClO₄, 58299-94-8.

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