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Preliminary communication

Bis(carbene) complexes of gold(I) and gold(III)

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SUMMARY

The preparation of $[(carbene)_2 Au]^+ClO_4^-$, $[(carbene)Au(C_6H_{11}NC)]^+ClO_4^-$ and of $[(carbene)_2 AuI_2]^+ClO_4^-$ is reported.

The addition of a nucleophile, such as an alcohol or an amine, to a coordinated isocyanide molecule yielding a carbene complex, *e.g.*

$$M{\leftarrow}CNR + H{-}Y \rightarrow M{\leftarrow}CY{-}NHR \quad (Y = OR, NHR)$$

is now well established[1,2]. Nevertheless, compounds with more than one carbene ligand are uncommon and those containing only carbene ligands are rare, *e.g.*[3] $[\{(MeNH)_2C\}_4Pt]^{2+}$ and[4] $[Hg\{C(OR)(NR_2)\}_2]^{2+}$.

The ionic, dicoordinated derivatives, $[(R{-}NC)_2 Au]^+$, obtained[5] during our investigations[5–10] on isocyanide complexes of gold, react with *p*-toluidine in chloroform at room temperature or with refluxing methanol (4 days) according to the following schemes:

$$[(Ar{-}NC)_2 Au]^+ClO_4^- + 2\ Ar{-}NH_2 \rightarrow [\{(Ar{-}NH)_2C\}_2 Au]^+ClO_4^- \qquad (I)$$

$$[(C_6H_{11}NC)_2 Au]^+ClO_4^- + Ar{-}NH_2 \rightarrow [(C_6H_{11}NC)AuC(NH{-}C_6H_{11})(NHAr)]^+ClO_4 \qquad (II)$$

$$[(Ar{-}NC)_2 Au]^+ClO_4^- + 2\ MeOH \rightarrow [\{(Ar{-}NH)(MeO)C\}_2 Au]^+ClO_4^- \qquad (III)$$

While coordinated aryl isocyanides allow the formation of bis(carbene) complexes, coordinated cyclohexyl isocyanide makes nucleophilic attack more difficult, so that, under

identical experimental conditions, only 1/1 addition takes place. The high reactivity of the ionic compounds is due to their positive charge which makes the cations better electrophiles than the neutral species[5].

Compound (I) is oxidized by halogens in chlorinated solvent, yielding compound (IV), readily purified by crystallization from dichloromethane/ethyl ether:

$$[\{(Ar{-}NH)_2C\}_2Au]^+ClO_4^- + I_2 \rightarrow [\{(Ar{-}NH)_2C\}_2AuI_2]^+ClO_4^-$$

(I) (IV)

Compound (IV) is the first carbene complex of gold(III), isoelectronic with platinum(II) for which carbene complexes are known[1,2,10]. Although the perchlorate contains two metal–carbon bonds and ligands with a formally divalent carbon, it is stable even in solution and melts without evident decomposition.

All the compounds* show the required ν(NH), δ(NH), and ν(C=N$^+$) bands at ca. 3240–3280 (broad), 1595–1600, and 1545–1575 cm^{-1}, plus the two absorptions required by a perchlorate ion having T_d symmetry, at ca. 1090 (broad and very strong) and 620 cm^{-1}. In addition, compound (II) shows a strong band due to coordinated $C_6H_{11}NC$ at 2254 cm^{-1}, a value quite similar to that observed in $[(R{-}NC)_2Au]^+ClO_4^-$.

The NMR spectra, recorded in $CDCl_3$ solution for compounds (I), (II), and (IV) are in agreement with the proposed formulae. In particular, the HN–Ar proton is found as a broad singlet between τ 0.06 and 0.50, while the NH proton adjacent to the cyclohexyl group is a broadened doublet at τ 1.74 having J 9 cps. For compound (III), the spectrum, recorded in $(CD_3)_2CO$, shows the required signals indicating the presence of two geometric isomers, one having a methoxyl signal at 5.78 and the other at 5.50.

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*Satisfactory elemental analyses were obtained for compounds (I)–(IV) inclusive.