

Preliminary communication

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

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SUMMARY

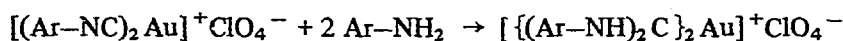
The preparation of $[(\text{carbene})_2\text{Au}]^+\text{ClO}_4^-$, $[(\text{carbene})\text{Au}(\text{C}_6\text{H}_{11}\text{NC})]^+\text{ClO}_4^-$ and of $[(\text{carbene})_2\text{AuI}_2]^+\text{ClO}_4^-$ is reported.

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



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 $[(\text{MeNH})_2\text{C}]_4\text{Pt}^{2+}$ and⁴ $[\text{Hg}\{\text{C}(\text{OR})(\text{NR}_2)\}_2]^{2+}$.

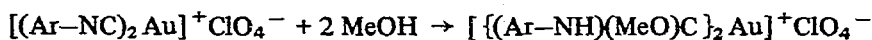
The ionic, dicoordinated derivatives, $[(\text{R}-\text{NC})_2\text{Au}]^+$, obtained⁵ during our investigations⁵⁻¹⁰ on isocyanide complexes of gold, react with *p*-toluidine in chloroform at room temperature or with refluxing methanol (4 days) according to the following schemes:



(I)



(II)

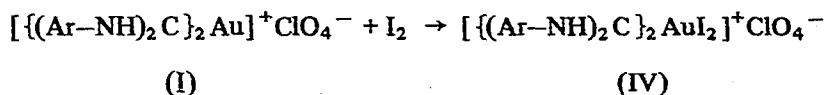


(III)

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 species⁵.

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



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 $\nu(NH)$, $\delta(NH)$, and $\nu(C=N^+)$ 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.

ACKNOWLEDGMENTS

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