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Preliminary communcation

THE MOLECULAR STRUCTURE OF A DICARBENOID COMPLEX OF GOLD(III), $[\{(p\text{-}MeC_6H_4NH)_2C\}_2AuI_2]ClO_4\cdot Et_2O$

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Summary

Bond lengths in the gold(III) cation *trans*-$[\{(p\text{-}MeC_6H_4NH)_2C\}_2AuI_2]^+$, determined by X-ray crystal structure analysis, indicate that the carbenoid ligands exert an appreciable *trans* influence on each other.

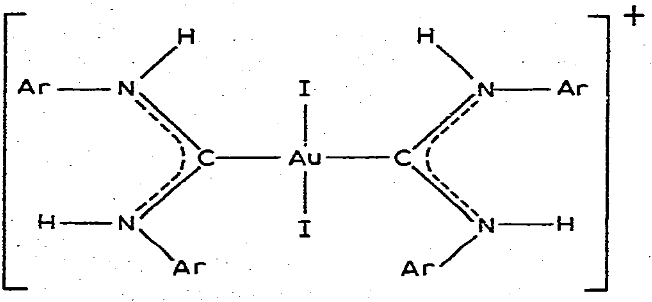
As a part of our studies of the structural properties and bonding in transition metal complexes containing carbon-donor ligands [1—3], we have carried out an X-ray crystal structure analysis of the title compound. The compound was prepared and characterised by Minghetti and Bonati and is believed to be the first carbenoid complex of gold(III) [4].

The crystals of $[\{(p\text{-}CH_3C_6H_4NH)_2C\}_2AuI_2]ClO_4\cdot(C_2H_5)_2O$ are monoclinic, space group $P2_1/c$. A unit cell of dimensions a 10.03, b 15.915, c 25.21 Å and β 101.63° contains four stoichiometric units. The intensities of 3521 independent reflexions, with $I \geqslant 3\sigma(I)$, were measured on a Hilger and Watts four-circle diffractometer. The structure was solved by the heavy atom method and refined by a least-squares treatment to $R = 0.054$ and $R' = 0.062$.

Crystals of the title compound are built of discrete gold(III) cations, perchlorate anions and diethyl ether molecules of solvation. The perchlorate ions display an almost ideal tetrahedral geometry.

In the cation, I, the coordination around the gold(III) atom is square planar and the chemically equivalent ligands are *trans* to one another. The metal atom and the α-amino hydrogen atoms in each $AuC(NHC_6H_4Me)_2$ fragment adopt a *cis,trans* configuration with respect to the C(carbenoid)—N bonds to which they are attached.

The carbenoid carbon atoms are coplanar with the atoms to which they are bonded, and these planes make dihedral angles of 75.7 and 81.4° with the coordination plane of the metal atom. The geometry around each carbenoid carbon atom is approximately trigonal, with the valency angles ranging from 112(1) to 127(1)°. The Au—C(carbenoid) distances [2.07(2) and 2.09(2) Å] are indicative of pure σ-bonding interactions (vide infra). However, the C(carbenoid)—N distances [1.29(2)—1.35(2) Å] reveal a high degree of multiple-bond character, and thus confirm the deductions based on the CN stretching frequency in I [4, 5]. Indeed, the analogous carbon—nitrogen distances in the organic amides are 1.35(2) Å, and those observed in other amino carbenoid metal complexes, of 1.31—1.34 Å, have been shown to correspond to a bond order of $\sim$1.7 [6]. It appears, therefore, that in this complex the coordinated carbene ligands are stabilised mainly by an intraligand interaction between the p_z orbital of the carbenoid carbon atom and the filled $2p$ orbitals of the α-nitrogen atoms. Hence, the metal—carbene bonding may be best described by Lewis structure I.



Ar = p-MeC$_6$H$_4$ (I)

The gold—carbon bond length data are still rather scarce and mostly of low or unstated accuracy. However, the formally single Au—C(phenyl) bond of 2.00(1) Å in *cis*-Au^{III}Cl$_2$Ph(SPr$_2$) [7] is significantly shorter (by 0.08 Å) than the Au—C(carbenoid) bonds in I. This may suggest that the carbenoid ligands in I exert a considerable *trans* influence on each other.

The Au—I bond lengths in I are 2.601(2) and 2.606(2) Å.

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