A Homoleptic Arylgold(I) Complex: Synthesis and Structure of Pentanuclear Mesitylgold(I)

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The mesitylgold(I) complex, $(AuMes)_5$ (Mes = $2,4,6\text{-}Me_3C_6H_2$), which has a five pointed star shape, was synthesized by the reaction of AuCOCl with a tetrahydrofuran solution of MesMgBr: the Au–C bond distances range from 2.12(2) to 2.20(2) Å.

The isolation and structural characterization of homoleptic alkyl- and aryl-gold(I) compounds have been unsuccessful so far,[1] and they were believed to be unstable. The Au–C bond in gold(I) complexes may be stabilized by the presence of ancillary ligands around the metal or donor atoms on the organic moiety.[1]

The present report deals with the synthesis and structural characterization of mesitylgold(I), which is a fairly thermally

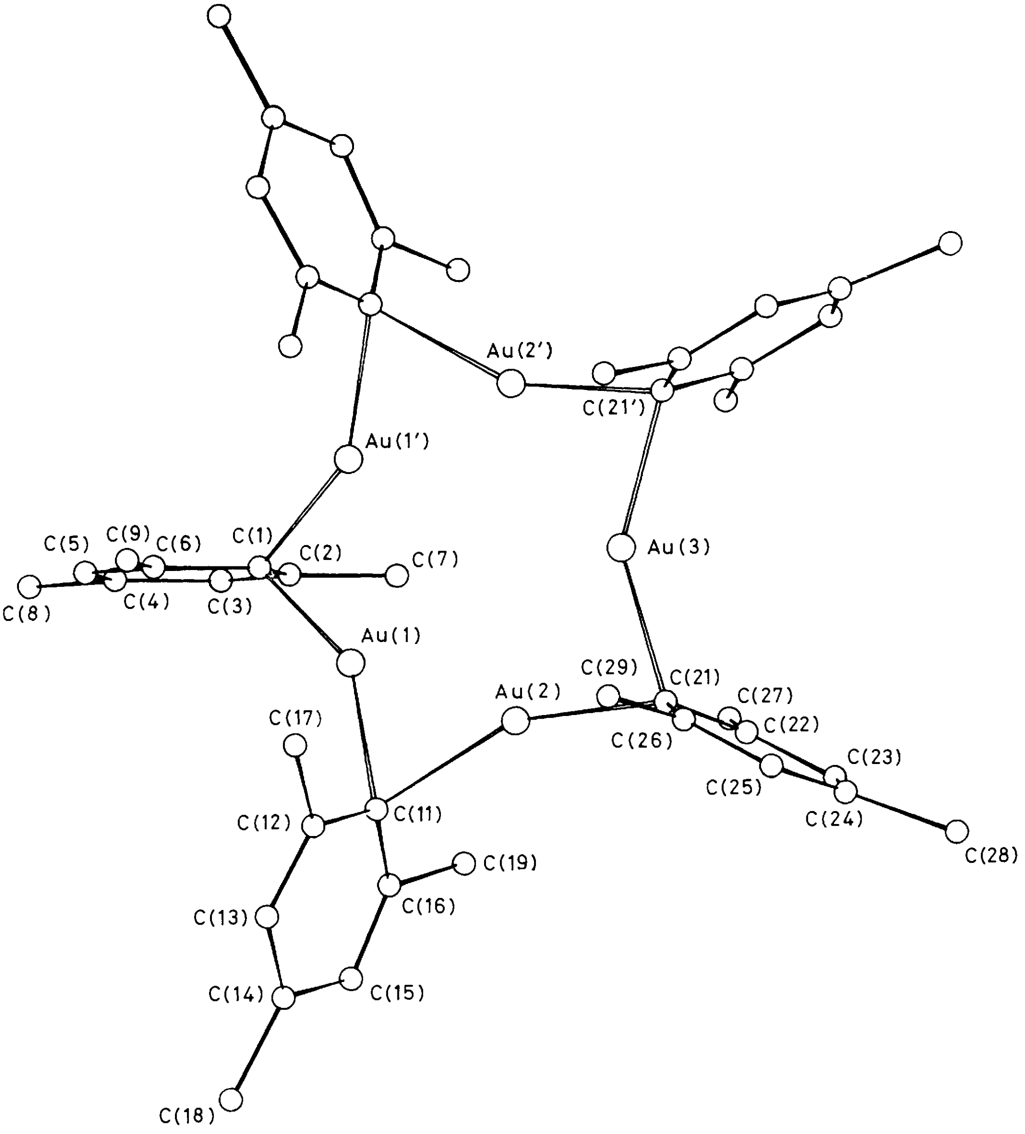

Figure 1. A view of the complex molecule $(AuMes)_5$. Bond distances: Au(1)–C(1) 2.13(3), Au(1)–C(11) 2.20(2), Au(2)–C(11) 2.19(2), Au(2)–C(21) 2.12(2), Au(3)–C(21) 2.18(2) Å. Bond angles: C(1)–Au(1)–C(11) 150.4(6), C(11)–Au(2)–C(21) 152.9(8), C(21)–Au(3)–C(21′) 148.3(7), Au(1)–C(1)–Au(1′) 78.2(1), Au(1)–C(11)–Au(2) 75.9(7), Au(2)–C(21)–Au(3) 78.1(8)°. Prime indicates a transformation of (x, $\frac{1}{2}-y$, z).

stable organometallic compound soluble in the most common organic solvents. It was prepared using a conventional method, following a recent procedure devised for mesitylcopper(I)[2,3] and mesitylsilver(I).[4] The present results allow us to draw a comparison between the homoleptic mesityl derivatives of all metals of group IB.

A tetrahydrofuran (thf) solution of AuCOCl[5] was treated with the stoicheiometric amount of MesMgBr (Mes = 2,4,6-$Me_3C_6H_2$) at −50 °C. Carbon monoxide was lost during the Grignard addition. The resulting suspension was stirred overnight at room temperature and dioxane added to remove the magnesium salts. The filtered solution was carefully concentrated and cooled at 0 °C. The mesitylgold complex (**1**) was obtained as cubic yellow crystals containing two thf molecules of crystallization *per* pentameric unit.† Complex (**1**) can be

$$5\ AuCOCl + 5\ MesMgBr \xrightarrow[-MgBrCl]{-CO} (AuMes)_5$$

(**1**)

recrystallized from hot thf, though slight decomposition can occur. Its solubility in hydrocarbon solvents, *e.g.* toluene, is fairly good. The structure of (**1**) was elucidated by an *X*-ray analysis.

Crystal data: $C_{53}H_{71}Au_5O_2$, orthorhombic, space group *Pnma*, $a = 21.864(10)$, $b = 27.188(11)$, $c = 8.951(5)$ Å, $U = 5321(4)$ Å^3, $Z = 4$, $D_c = 2.15$ g cm^{-3}, $F(000) = 3200$ e, Mo-K_α radiation ($\lambda = 0.71069$ Å), μ(Mo-K_α) = 137.5 cm^{-1}. The structure was solved by the heavy atom method (Patterson and Fourier techniques) and refined by full-matrix least-squares anisotropically only for the gold atoms. The *X*-ray analysis revealed the presence of disordered thf molecules of crystallization in a complex to thf molar ratio of 1:2. All calculations were carried out using the SHELX-76 program.

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† Satisfactory analytical data have been obtained for the solid dried *in vacuo* to remove the solvent; ^1H n.m.r. (C_6D_6) δ 6.81 (Ph, m, 2H), 3.01 (o-Me, s, 6H), and 1.90 (p-Me, s, 3H).

For 2023 unique observed structure amplitudes $[I > 3\sigma(I)]$ collected at room temperature on a Philips PW 1100 diffractometer in the range $6 < 2\theta < 47°$ the current R is 0.054. A correction for absorption was applied.‡

The structure of (**1**) consists of ten-membered rings of alternate gold and carbon atoms (Figure 1) which form a five-pointed star-shaped skeleton, similar to that found for $(CuMes)_5$.[5] The molecule has a C_m crystallographic symmetry with the mirror plane containing Au(3) and the mesityl ligand C(1)—C(9). Therefore the four atoms Au(1), Au(2), Au(1′), and Au(2′) define a plane from which Au(3), C(1), C(11), and C(21) are displaced by 0.321(1), 0.40(4), −0.46(3), and 0.46(3) Å, respectively. The polynuclear ring is puckered, the total puckering amplitude[6] being 0.93(3) Å. The mesitylene ring planes are nearly perpendicular to the mean plane through the polynuclear ring, the dihedral angles they form varying from 85.8(5) to 89.7(5)°. All the Au–C bond distances are very close ranging from 2.12(2) to 2.20(2) Å, while C–Au–C and Au–C–Au bond angles range from 148.3(7) to 152.9(8) and from 75.9(7) to 78.2(1)°, respectively.

$$[(\eta^5\text{-}C_5H_5)Fe\{\eta^5\text{-}C_5H_4(AuPPh_3)_2\}]^+$$

(**2**)

$$[Au_2\{\mu\text{-}(CH_2)_2PEt_2\}_2]$$

(**3**)

The Au–C bond distances are very close to those found in complex (**2**),[7] where two gold(I) ions are bridged by an aromatic carbon at 2.15 and 2.28 Å. The Au–C bond distances are substantially independent of the bonding mode displayed by the C-donor ligands; they are 2.062(8) and 2.041(9) in $[Au(C_6F_5)_2]^-$,[8] 2.050(4) in $[Au\{2,6\text{-}(MeO)_2C_6H_3\}(PPh_3)]$,[9] and 2.09(3) and 2.10(3) Å in complex (**3**).[10] The C–Au–C angle values in complex (**1**) suggest a significant deviation from the linear stereochemistry preferred by Au^I and normally encountered, *i.e.* in all the related complexes mentioned above. Such a bending of the C–Au–C unit seems to be attributable to an Au^I–Au^I bond, whose distances range from 2.692(4) to 2.710(3) Å in complex (**1**). Gold–gold distances are 2.77 in complex (**2**) and 3.023(1) Å in complex (**3**).

This is the first synthetic and structural report of a homoleptic alkyl- or aryl-gold(I) complex. We must emphasize that the mesityl ligand seems to induce an unusual stabilization of the metal–carbon bond in Cu^I, Ag^I, and Au^I complexes. The three metals of the group 1B form very similar cyclic structures with very close structural parameters in $(CuMes)_5$,[3] $(CuMes)_4$-(tetrahydrothiophene)$_2$,[3] and $(AgMes)_4$.[4]

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.