A Thermally Stable and Soluble Arylsilver(I) Compound: Synthesis and Structure of Mesitylsilver(I)

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Mesitylsilver, $(AgMes)_4$ (Mes = 2,4,6-$Me_3C_6H_2$), is a thermally stable and soluble organometallic derivative of silver(I) having a centrosymmetric tetranuclear structure in the solid state.

Stable alkyl- and aryl-silver(I) derivatives remain rather exotic species in organometallic chemistry;[1] few have been synthesized and even fewer structurally characterized.[1,2] Their low solubility has prevented solid state characterization and molecular complexity determination in solution. Some of these reasons are probably responsible for the scarce utilization

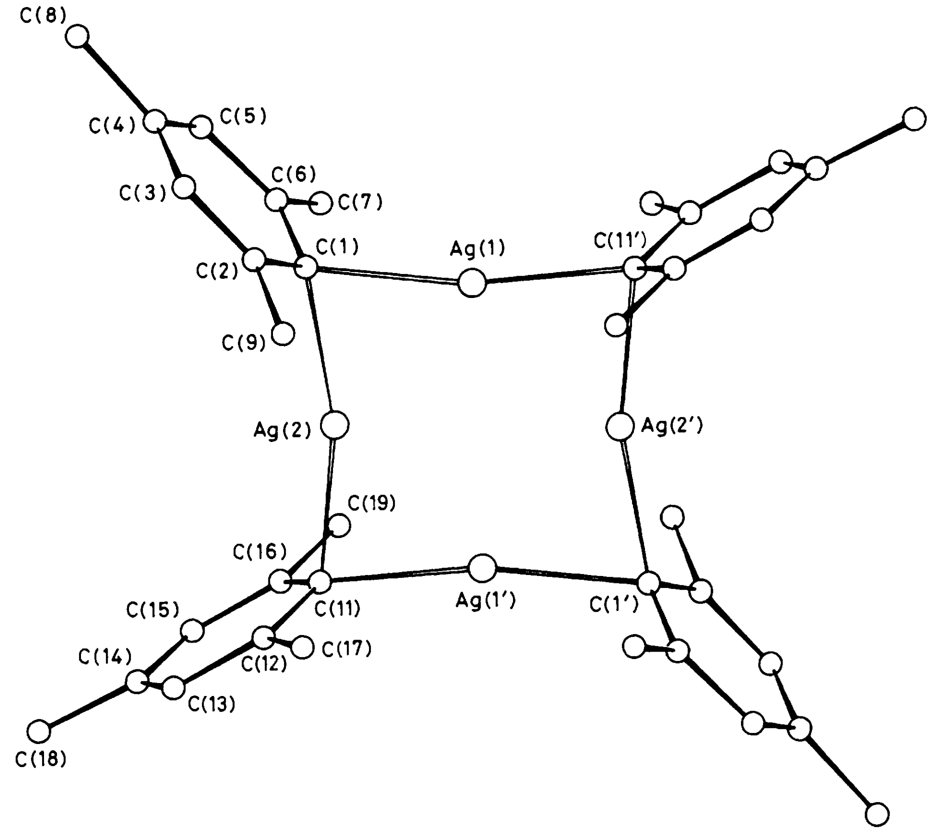

Figure 1. A view of the complex $[\mathrm{Ag(C_9H_{11})}]_4$. Bond distances (Å): Ag(1)–C(1), 2.22(3); Ag(1)–C(11'), 2.16(3); Ag(2)–C(1), 2.22(3); Ag(2)–C(11), 2.21(3); Ag(1)–Ag(2), 2.733(3). Bond angles (°): C(11')–Ag(1)–C(1), 169.0(9); Ag(1)–C(1)–Ag(2), 76.1(7); C(1)–Ag(2)–C(11), 165.2(8); Ag(2)–C(11)–Ag(1'), 78.1(7). The prime indicates a transformation of $(\bar{x}, \bar{y}, 1-z)$.

of organometallic compounds of silver in organic syntheses. Moreover, unconventional alkylating agents seem to be necessary for their synthesis.[2]

The present report deals with the synthesis and structural characterization of mesitylsilver, which is a thermally stable compound soluble in most common organic solvents. It was synthesised by a conventional method, following a recent procedure devised for mesitylcopper(I).[3]

A tetrahydrofuran (THF) suspension of AgCl was treated with the stoicheiometric amount of MesMgBr at −20 °C. The resulting suspension was stirred (20 h, room temp.) then dioxane was added to remove the magnesium salts. The filtered solution was evaporated and the residue recrystallized from toluene gave large shiny crystals of complex (**1**) in good yield (>60%) [equation (1)].†

$$4\ \mathrm{AgCl} + 4\mathrm{MesMgBr} \xrightarrow{-4\mathrm{MgClBr}} \underset{(\mathbf{1})}{\mathrm{Ag_4Mes_4}} \qquad (1)$$

$$\mathrm{Mes} = 2,4,6\text{-}\mathrm{Me_3C_6H_2}$$

Complex (**1**) is very soluble in organic solvents, it is light sensitive, and decomposes very rapidly in air. The tetrameric formulation (**1**) is based on the solid state structure determined by X-ray analysis. The molecular weight found by cryoscopy in benzene is 479, a value corresponding to a dinuclear entity (M.W. 454). Solution–solid state relationships are an intriguing problem in the organometallic chemistry of copper(I) and silver(I), because of inter- and intra-aggregate exchange, and solvent-dependent molecular complexity.[1]

Crystal data: $\mathrm{C_{36}H_{44}Ag_4}$, trigonal, space group $R\bar{3}$ (from structural analysis), $a = b = c = 18.395(3)$ Å, $\alpha = \beta = \gamma = 116.28(2)°$, $U = 3038(4)$ Å^3, $Z = 3$, $D_c = 1.49\ \mathrm{g\ cm^{-3}}$, $F(000) = 1344$, Mo-K_α radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-}K_\alpha) = 19.1\ \mathrm{cm^{-1}}$. The structure was solved by the heavy atom method and refined by full-matrix least-squares with anisotropic thermal parameters for nonhydrogen atoms. The hydrogen atoms, either located from a ΔF synthesis or put in calculated positions, were introduced in the least-squares refinement as fixed contributors ($U = 0.10$ Å^2). For 1966 unique observed structure amplitudes [$I > 3\sigma(I)$] collected at room temperature on a Philips PW 1100 diffractometer in the range $6 < 2\theta < 52°$ the current R is 0.062. Intensity data were corrected for absorption by a semi-empirical method.[4]‡

Crystals of complex (**1**) are made up of centrosymmetric tetrameric units $\mathrm{Ag_4Mes_4}$, in which the silver ion has a nearly linear co-ordination, the angles around Ag(1) and Ag(2) being 169.0(9) and 165.2(8)°, respectively. The aromatic ring is the bridging ligand. A picture of the structure along with the most relevant bond distances and angles is given in Figure 1. The mesityl group displays a bonding mode very similar to that observed in the corresponding copper(I) complexes $\mathrm{Cu_5Mes_5}$

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† Satisfactory analytical data were obtained; ^{1}H n.m.r. ($\mathrm{C_6D_6}$) δ 6.79 ($\mathrm{C_6H_2}$, m, 2H), 2.75 (o-Me, s, 6H), and 2.15 (p-Me, s, 3H).

‡ 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.

and $Cu_4Mes_4(C_4H_8S)_2$.[5] The $(Ag\text{–}C)_4$ framework is planar within experimental error, the total puckering amplitude being 0.01(1) Å.[6] The four independent Ag–C bond distances are not significantly different [mean value 2.20(3) Å] and the planar phenyl groups are nearly perpendicular to the eight-membered ring, the dihedral angles being 88.8(5) and 89.3(3)°, respectively. The most relevant structural comparison of (**1**) is with the structure of $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3CH_2NMe_2\text{-}2\text{-}Ag)]_4$,[7] in which the silver atom has nearly linear co-ordination geometry in a tetranuclear structure and the Ag–C bond distances [2.14(2) and 2.20(2) Å] are very close to those reported for complex (**1**). The Ag(1) - - - Ag(2) distance [2.733(3) Å] compares very well with the corresponding one in the ferrocenyl silver compound.[7] Complex (**1**) is an easily available starting material for studying silver–carbon σ-bond chemistry.

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