Preparation and Crystal Structure of the Argentate Complex $[Li(tetrahydrofuran)_4][Ag\{C(SiMe_3)_3\}_2]$

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The product of the reaction between AgI and tris(trimethylsilyl)methyl-lithium in tetrahydrofuran (thf) has been shown by *X*-ray diffraction to be the ionic ate complex $[Li(thf)_4][Ag\{C(SiMe_3)_3\}_2]$; evidence is presented that this and the analogous ate complexes of lithium and copper retain their structures in solution.

No mononuclear σ-bonded organosilver compound has hitherto been structurally characterized, and even among multinuclear species structures have been determined only for the binuclear aryl complex $[\{2\text{-}(Me_3Si)_2CAgC_5H_4N\}_2]$,[1] the tetranuclear aryl-bridged complexes $[Ag(C_6H_2Me_3\text{-}2,4,6)]_4$[2] and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3CH_2NMe_2\text{-}2\text{-}Ag)]$,[3] and the polymeric alkynyl-bridged complex $[Ag(C{\equiv}CPh)_2{\cdot}Ag(PPh_3)_2]_n$.[4] We have now prepared the mononuclear dialkylsilver complex $[Li(thf)_4][Ag\{C(SiMe_3)_3\}_2]$ (thf = tetrahydrofuran) (**1a**) and determined its structure by *X*-ray diffraction. The complex is also the first structurally characterized lithium diorganoargentate; such compounds would normally be assumed, by analogy with the better known copper analogues, to be associated neutral, rather than ionic, species, and to involve bridging by the organic ligands between lithium and silver;[5] such structures are implied by n.m.r. studies for some lithium diarylsilver complexes in solution.[5,6] Complex (**1a**) is, in fact, isomorphous with the corresponding ionic ate derivatives, (**1b**) and (**1c**), of lithium[7] and copper,[8] respectively.

$[Li(thf)_4][M\{C(SiMe_3)_3\}_2]$
(**1a**) M = Ag
(**1b**) M = Li
(**1c**) M = Cu

In the preparation of (**1a**), a solution of $[Li(thf)_4][Li\{C(SiMe_3)_3\}_2]$ (13.7 mmol) in thf (80 cm^3) was added dropwise under argon to a stirred suspension of AgI (3.21 g, 13.7 mmol) in thf (20 cm^3) at −78 °C. After 1 h at −78 °C the mixture was brought to room temperature with stirring, then filtered, and the solvent was evaporated off under vacuum. A solution of the residue in toluene was kept at −10 °C, and gave several crops of long colourless needles of (**1a**) (70%), m.p. 65 °C (decomp.); ^1H n.m.r. δ $\{[^2H_8]$toluene$\}$ 0.57 (s, 27H), 1.19—1.82 (m, 8H), and 3.3—3.6 (m, 8H); ^{109}Ag n.m.r. {in toluene containing 10% $[^2H_8]$toluene, relative to external 2 M $AgNO_3$ in D_2O} δ +700 p.p.m.†

Crystal data: $C_{36}H_{86}AgLiO_4Si_6$, M = 866.4, triclinic, space group $P\bar{1}$, a = 9.426(1), b = 12.047(2), c = 23.331(3) Å, α = 94.49(2), β = 90.09(2), γ = 94.27(2)°, U = 2633.8 $Å^3$, Z = 2, D_c = 1.09 g cm^{-3}, $F(000)$ = 936. Monochromated Mo-K_α radiation, λ = 0.71069 A, μ = 5.4 cm^{-1}. R = 0.095, R' = 0.124 for 2857 unique reflections with $|F^2| > \sigma(F^2)$, measured on an Enraf-Nonius CAD-4 diffractometer in the range $2 < \theta < 18°$.‡

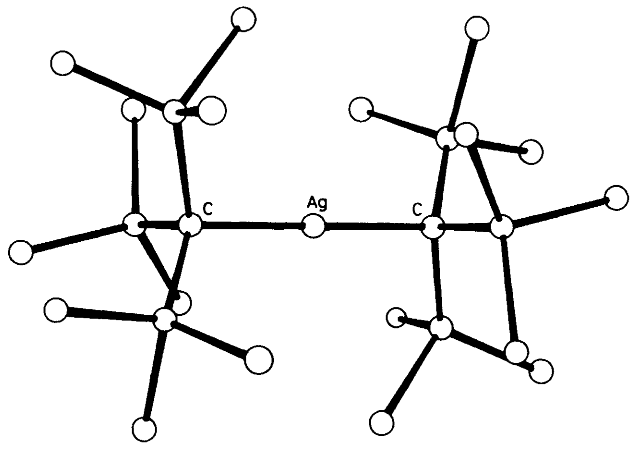

Figure 1. The structure of one of the anions of $[Li(thf)_4][Ag\{C(SiMe_3)_3\}_2]$.

As in (**1b**) and (**1c**), the unit cell contains two $[Li(thf)_4]$ cations related by an inversion centre, and two crystallographically independent $[M\{C(SiMe_3)_3\}_2]$ anions, each of which lies across an inversion centre, so that the anions are linear and the $C(SiMe_3)_3$ groups are staggered about the C–M–C direction (see Figure 1). The two anions have essentially similar geometries; the Ag–C bonds in the anions [2.162(7) and 2.198(7) Å, respectively] are very similar in length to those of the Li–C bonds in (**1b**) [2.16(1) and 2.20(1) Å],[7] and slightly longer than the Cu–C bonds in (**1c**) [2.03(1) and 2.07(1) Å].[8] The mean Ag–C bond length in (**1a**) [2.18(2) Å] is also close to those in the binuclear alkyl complex $[\{2\text{-}(Me_3Si)_2CAgC_5H_4N\}_2]$ [2.154(5) Å],[1] and the aryl-bridged tetranuclear complexes $[Ag(C_6H_2Me_3\text{-}2,4,6)]_4$ [2.20(3) Å][2] and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3CH_2NMe_2\text{-}2\text{-}Ag)]_4$ (2.17 Å)[3] but significantly larger than that of the shorter [2.040(13) Å] of the two Ag–C bonds in polymeric $[Ag(PPh_3)_2Ag(C{\equiv}CPh)_2]$, which contains unsymmetrical phenylethynyl bridges.[4]

The structural data for the anions are markedly better for (**1a**) than for (**1b**) and (**1c**), the R factor for (**1a**) being raised mainly by disorder in the cation. The strain in (**1a**) is relieved mainly by opening of the Me_3Si–C–$SiMe_3$ angles [mean 113.6(8)°] and closing of the Me–Si–Me angles [mean 104(2)°]. The central C–$SiMe_3$ bonds [mean 1.83(3) Å] are apparently shorter than the Si–Me bonds [mean 1.90(4) Å], as we suspected for (**1b**) and (**1c**);[8] this feature is presumably associated with the presence of the negative charge (*cf.* ref. 8), since all the neutral compounds containing the $(Me_3Si)_3C$ group for which structural details are available show the opposite effect: *e.g.* $Hg[C(SiMe_3)_3]_2$,[9] $(Me_3Si)_3CH$,[10] $(Me_3Si)_3CSiMe_2Ph$,[11] and $(Me_3Si)_3CB(Ph)[O(CH_2)_4C(SiMe_3)_3]$.[12]

The low solubilities of (**1a**—**c**) in toluene and heptane suggested that the ionic structures persisted in solution, and this was confirmed by Li n.m.r. spectroscopy. In all three cases solutions in $[^2H_8]$toluene gave sharp ^7Li resonances [(**1a**) −0.85, (**1b**) +0.88, (**1c**) −1.03 p.p.m.] close to that of the reference (2 M $LiNO_3$ in D_2O) and so corresponding to the

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† Throughout this article positive δ values denote shifts to low field of the reference.

‡ 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.

cation $[Li(thf)_4]^+$. For (**1b**) in thf solution the shift was 0.21 p.p.m. Because of the low solubility, the ^{7}Li resonance of the anion in (**1b**) could not be observed in toluene, but it appeared as a broad signal at 3.1 p.p.m. from solutions in thf. As the solution in thf was cooled, the ^{7}Li resonance broadened (ultimately becoming undetectable at −75 °C), as expected for a nucleus with a large quadrupole moment (-4.5×10^{-30} m^2) located in a position in which the electric field gradient tensor has large non-zero components. In contrast, for ^{6}Li, which has a smaller quadrupole moment (-8×10^{-32} m^2), the signal was sharper at room temperature and the broadening on cooling was negligible, so that the signal was still evident at −75 °C. (This provides a nice example of the advantage which can sometimes be gained by using a less receptive isotope which possesses a lower quadrupole moment.)

The appearance of the Li signal from the anion at lower field than that from the cation is at first sight surprising in view of the fact that the resonances from the anions are at higher field than those from the cations in $Li^+[Li(phthalocyanine)]^-$,[13] $[Na(crypt)]^+Na^-$ [crypt = $N\{(CH_2CH_2O)_2(CH_2)_2\}_3N$],[14] and $[Cs(18\text{-}C\text{-}6)_2]^+Cs^-$ [18-C-6 = $\overline{O\text{-}(CH_2CH_2O)_5CH_2CH_2}$],[15] but it is nicely consistent with the implications of *ab initio* calculations which indicate that the model anion $[LiMe_2]^-$ is best represented as containing positively charged lithium, *i.e.* as $[Me^-\ Li^+\ Me^-]$.[16]

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