Synthesis and Crystal Structure of the Silver(I) Alkyl Species, $[\{2\text{-}(Me_3Si)_2C(Ag)C_5H_4N\}_2]$, a Dimeric Compound Void of Electron-deficient Bonding

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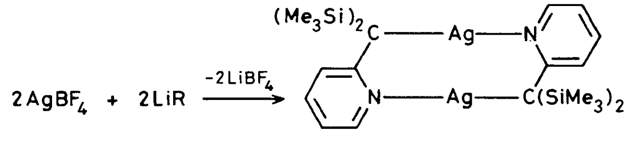
The silver(I) alkyl complex $[\{2\text{-}(Me_3Si)_2C(Ag)C_5H_4N\}_2]$, prepared by the reaction of the analogous lithium alkyl with $AgBF_4$ in tetrahydrofuran, is a binuclear complex in which the metal ion is not involved in electron-deficient bonding, being bound by a carbon atom at 2.154(5) Å and a nitrogen atom of a centrosymmetrically related ligand at 2.160(5) Å; the Ag ⋯ Ag′ separation is 2.654(1) Å.

Within the realm of silver(I) σ-bonded organometallic compounds, structural characterization of silver(I) alkyl species has been unsuccessful. The main problems have been the intrinsic instability of silver–carbon bonds and the formation of only sparingly soluble compounds.[1] We report the structure of the silver(I) alkyl compound $[\{2\text{-}(Me_3Si)_2C(Ag)C_5H_4N\}_2]$, which was prepared by a method similar to that recently devised for the copper(I) analogue.[2]

Noteworthy features of the molecule are that it is dimeric, contrasting with higher oligomers for other silver(I) σ-bonded complexes, and that the bonding is not electron deficient as is prevalent amongst silver aryl compounds.[3,4] The compound illustrates the potential of the ligand $2\text{-}(Me_3Si)_2\bar{C}C_5H_4N$ (R^-) in stabilizing unusual bonding configurations, a feature that was also established for the analogous lithium and copper(I) compounds.[2] These studies also allow metal(I) derivatives of R^- to be compared.

A stoicheiometric amount of LiR in thf (tetrahydrofuran) was added to a solution of $AgBF_4$ in thf at −78 °C. The solution was stirred for 30 min at room temperature, and the solvent was then removed *in vacuo*. Cooling a filtered pentane extract to −30 °C gave colourless prisms of the title compound. The compound slowly decomposes in solution at room temperature but is stable at −30 °C, whereas the solid is stable at room temperature for days. It is light-sensitive, a common feature of organosilver compounds. The nature of the compound was determined by *X*-ray structure analysis.†



The crystal is comprised of centrosymmetric dimers; a molecular projection with relevant bond distances and angles is shown in Figure 1. Other silver(I) σ-bonded aryl compounds are either tetrameric, with the ligands involved in three-centre two-electron bonding,[3,4] or polymeric with weak Ag-π interactions as in $[\{Ag(C{\equiv}CPh)PMe_3\}_n]$.[5]

The bonding in the complex is very similar to that observed in the corresponding dimeric copper(I) and lithium com-

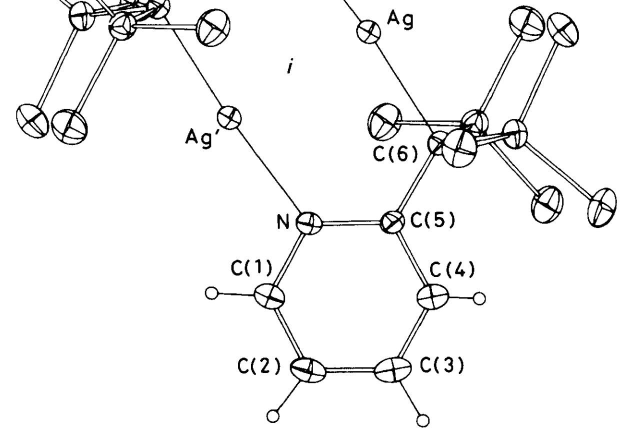


Figure 1. Molecular structure of $[\{2\text{-}(Me_3Si)_2C(Ag)C_5H_4N\}_2]$ showing 20% thermal ellipsoids for the non-hydrogen atoms; the projection is normal to the aromatic plane. Distances and angles defining the silver environment are Ag–C(6) 2.154(5), Ag–N′ 2.160(5), Ag–Ag′ 2.654(1) Å, C(6)–Ag–N′ 174.5(1), Ag′–Ag–C(6) 90.6(1), Ag′–Ag–N′ 84.8(1), Ag–N′–C(1′) 114.7(4), Ag–N′–C(5′) 125.9(4), Ag–C(6)–Si(1) 100.2(2), Ag–C(6)–Si(2) 99.4(2), Ag–C(6)–C(5) 116.4(3)°.

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† *Crystal data:* $C_{24}H_{44}Ag_2N_2Si_4$, orthorhombic, space group *Pcab*, $a = 16.318(9)$, $b = 16.115(1)$, $c = 12.033(6)$ Å, $Z = 4$. The structure was determined at 295 K, from 2183 'observed' reflections $[I > 3\sigma(I)]$ out of a total of 4532 (Mo-K_α radiation). R and R' values are respectively 0.039 and 0.048. 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.

plexes,[2] although it is noteworthy that it is not isostructural with either of them. The metal co-ordination is nearly linear; C(6)–Ag–N′ is 174.5(1)°, less than that of the copper(I) analogue, 178.0(5)°.[2] The Ag′–Ag–C(6) and Ag′–Ag–N′ angles, 90.6(1) and 84.8(1)°, may be compared with 90.4(1) and 91.6(1)° respectively for the copper(I) compound. These angles vary more in the lithium compound [66.1(2) and 104.4(3)°, with the C(6)–Li–N′ angle being 146.9(4)°], which has a step-like structure with the lithium atom residing out of the plane of one aromatic section by 1.21 Å; *cf.* the silver(I) and copper(I) compounds in which the aromatic rings and the metal atoms are nearly coplanar. The Ag ··· Ag′ distance is 2.654(1) Å, rather less than that found in [{Ag($C_6H_2Me_3$-2,4,6)}$_4$], 2.733(3) Å,[3] and [{Fe(η-C_5H_5)(η-$C_5H_3CH_2$-2-Ag)}$_4$], 2.740(2) Å, possibly short enough for some Ag–Ag bonding.[4] The geometrical variations compared to the copper(I) compound, in which the M ··· M′ distance is 2.412(1) Å, appear to be a consequence of incorporating a larger metal atom into the same planar system.

The Ag–C(6) distance, 2.154 Å, is shorter than in silver(I) aryl compounds: 2.20(3) Å in [{Ag($C_6H_2Me_3$-2,4,6)}$_4$][3] and 2.18(2) Å in the aforementioned ferrocenyl silver compound,[4] as would be expected as a consequence of the electron-deficient bonding in the latter, but is longer than in [{AgH (C≡CPh)PMe_3}$_3$] [2.04(1) Å].[5] The Ag–N′ distance, 2.160(5) Å, is surprisingly short, comparable with the value found in bis(2,6-dimethylpyridine)silver(I) perchlorate [2.166(4) Å].[6] It is noteworthy that the nitrogen functional group in the ferrocenyl silver compound is not bound to the silver centre.[4]

Stabilization of metal–carbon σ-bonds appears to be an important aspect of the chemistry of the ligand R^-, possibly due to the bulky trimethylsilyl groups preventing formation of R–R by a reductive elimination decomposition pathway, and/or attack on the metal centre by an incoming ligand (leading to a high activation barrier for attack), coupled with the functional group acting as a strong σ–π Lewis base.

We thank the Australian Research Grant Scheme for support.

Received, 26th January 1984; Com. 108

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