Regioselective Addition of Silylene on to [70]Fullerene

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[70]Fullerene reacts with photochemically generated bis(2,6-diisopropylphenyl)silylene to give the positionally isomeric 1:1 adducts as the isolable products.

Recent progress in the area of organic chemical derivatization of fullerenes by addition reactions continues to attract much attention.[1,2] Only very few discrete [70]fullerene derivatives, however, have been isolated and characterized[1,3] from the products of the addition of [Ir(CO)Cl(PPh$_3$)$_2$] to [70]fullerene[4] and the osmylation,[5] nucleophilic alkylations,[6,7] reduction[8] and cycloaddition[2c,9,10] of [70]fullerene. While all the positions in [60]fullerene are identical, five sets of carbon atoms (a–e in Fig. 1) and eight distinct types of C–C bonds are available in [70]fullerene.[6b] It can be anticipated that the different bonds will display different reactivities.[6b] In the addition of the iridium complex to [70]fullerene[4] thermodynamically controlled regiochemistry, in which attack at the double bond (a–b bond) at the poles is more favourable than that at other bonds, was observed. Moreover, Hawkins et al.[5] reported an analysis of the regiochemistry of the osmylation of [70]fullerene where the observed ratio of isomeric 1:1 adducts (2.1:1) demonstrates greater kinetic reactivity at sites of greater local curvature, rather than at sites of greater bond order. Here we report that the first regioselective addition of bis(2,6-diisopropylphenyl)silylene 1, as a reactive divalent species, onto [70]fullerene furnishes adduct 2. Addition at the a–b bond is more favourable than that at the c–c bond. On the basis of the LUMO electron densities at the positions a, b and c in [70]fullerene, this regioselectivity can be explained in terms of a HOMO(silylene)–LUMO([70]fullerene) interaction.

A toluene solution of [70]fullerene (3.3 × 10^{-3} mol dm^{-3}) and 2,2-bis(2,6-diisopropylphenyl)hexamethyltrisilane[2b] (3.3 × 10^{-3} mol dm^{-3}) as a silylene precursor was photolysed with a low-pressure mercury arc lamp to afford a thermally stable 1:1 adduct 2 in high yield (Scheme 1).† Adduct 2 contains two isomers of (Dip)$_2$SiC$_{70}$ (Dip = 2,6-diisopropylphenyl) which were separable by flash chromatography on silica gel. ^{1}H NMR spectra recorded before chromatography showed that the major (2a) and minor (2b) isomers were formed in a 2:1 ratio. No other isomer was detectable to a limit of 5%. FAB-MS of 2a (C$_{94}$H$_{34}$Si) displays a peak for 2a at 1190–1194 as well as a peak for [70]fullerene at 840–843 which arises from loss of 1. The UV–VIS absorption spectum of 2a is virtually identical to that of [70]fullerene except for the loss of the [70]fullerene bands at 333, 381 and 471 nm. The FAB-MS and UV–VIS spectra of 2 contain a number of unique features, but also suggest that 2 retains the essential electronic and structural character of [70]fullerene.

Silylene 1 adds to [60]fullerene at the 6-ring–6-ring junctions giving the corresponding silirane.[2b] Assuming that 1 also adds to [70]fullerene at 6–6 ring junctions, four (Dip)$_2$SiC$_{70}$ isomers are conceivable (Table 1). AM1 molecular orbital calculations[11] on the reaction of [70]fullerene with dihydrosilylene shows that the 6,6-adduct is more stable than the 5,6-adduct. In these four isomers, the silyl groups are positioned differently with respect to the mirror planes of [70]fullerene such that they each correspond to a characteristic number of symmetry-independent carbons and protons (Table 1). The ^{1}H NMR spectrum of 2a displays four methyl signals at δ 1.59, 1.35, 1.21 and 0.93, and
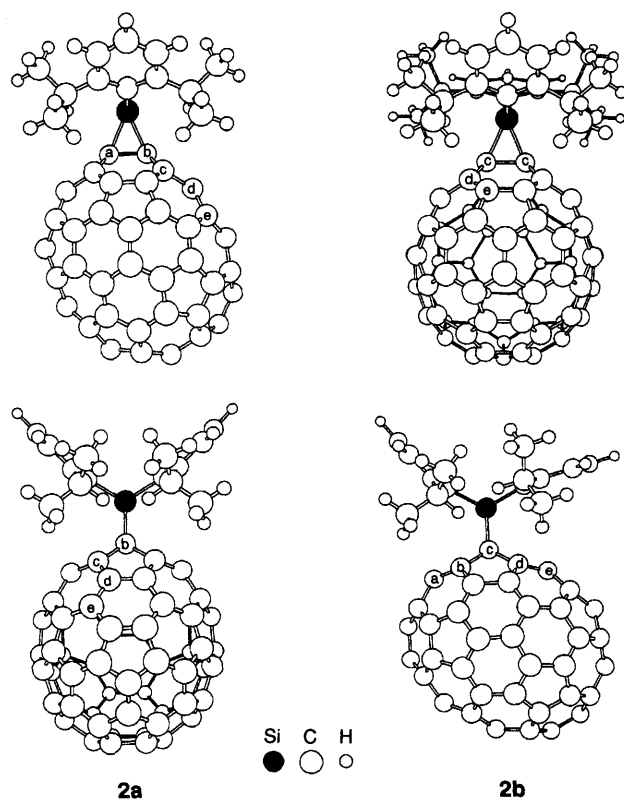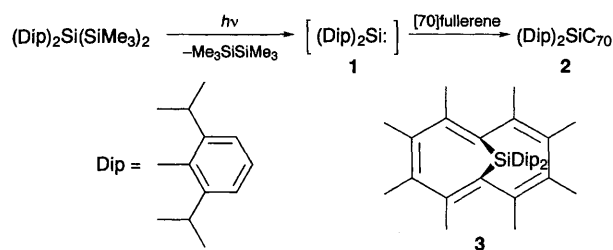

Fig. 1 Two views of the optimized C_s structures of 2a and 2b calculated with the AM1 method, including the labelling scheme

Scheme 1

Table 1 Number of independent protons and carbons in the 6–6 adduct of (Dip)$_2$SiC$_{70}$ 2

Isomer	Symmetry	CH	CH$_3$	sp^3 Carbon on [70]fullerene
2a	C_s	2	4	2
2b	C_s	2	4	1
a,b-	C_s	2	4	2
c,c-	C_s	2	4	1
d,e-	C_1	4	8	2
e,e-	C_{2v}	1	1	1

two methine signals at δ 3.81 and 3.60. Similarly, four methyl signals at δ 1.75, 1.47, 1.39 and 1.32, and two methine signals at δ 4.09 and 3.83 are observed in the ^{1}H NMR spectrum of **2b**. The ^{13}C NMR spectrum of **2a** shows two signals at δ 78.51 and 67.77 for the [70]fullerene skeleton which are attributed to the sp^3 fullerene carbons. 2D NMR measurements (HH COSY, CH COSY and CH COLOC NMR) were carried out to identify the signals. Comparing the NMR data for the two isomers, **2a** and **2b**, with the number of possible peaks for a,b-, c,c-, d,e- and e,e-isomers (Table 1), **2a** and **2b** correspond to a,b- and c,c-isomers, respectively. The C_s structures of **2a** and **2b** obtained by full geometry optimization at the AM1 level[11] are shown in Fig. 1.‡

The chemical shifts of the two carbon signals at δ 78.51 and 67.77, and the silicon signal at δ −83.70 are fully consistent with those expected for the silirane carbon atom and silicon atom in **2a** rather than in the isomeric silamethanoannulene **3a**.[2b] This experimental finding is also supported by AM1 calculations[11] on the reaction of [70]fullerene with **1** which shows that **3** is not located on the potential energy surface.

The kinetically controlled regioselectivity observed for the addition of silylene **1** to [70]fullerene agrees qualitatively with the AM1 calculations on [70]fullerene in that addition occurs at the a–b and c–c bonds with high bond orders.[2c,12] Remarkably, the major kinetic product of silylene addition is **2a** in which the silylene adds to the 6–6 ring junction at the a–b bond. The isomers do not equilibrate under the reaction conditions; silylation is kinetically controlled.

Products **2a** and **2b** are calculated to lie almost same in energy; **2a** and **2b** are formed with an exothermicity of 46.3 and 46.4 kcal mol^{-1} (1 cal = 4.184J). Moreover, the ratio of isomers **2a** and **2b** (2:1) is not correlated with the calculated bond orders for the respective bonds in [70]fullerene, 1.480 and 1.526.[2c] In contrast to the exothermicity for the addition of **1** to [70]fullerene and the bond orders, the magnitude of the LUMO electron densities of [70]fullerene at the HF/3-21G level§ agrees well with the observed regioselectivity. The LUMO electron densities at positions a, b and c [70]fullerene are 0.10, 0.05 and 0.05, respectively. Thus, the addition of silylene onto [70]fullerene takes place mainly at the a–b bond and to a lesser extent at the c–c bond, reflecting that the HOMO(silylene)–LUMO ([70]fullerene) interaction plays an important role in the reactivity of [70]fullerene.

In conclusion, spectroscopic analyses and theoretical investigations strongly support the addition at the a–b double bond at the poles is more favourable than that at the c–c bond, and the adducts have the silirane structure **2** and not the isomeric 1,6-silamethano[10]annulene structure **3**.

Footnotes

† $C_{70}\{(Dip)_2Si\}_2$ [FAB-MS, *m/z* 1540–1544 $(C_{70}\{(Dip)_2Si\}_2)$, 840–843([70]fullerene) was also obtained in 9% yield.

‡ Since the optimized C_1 structure of **2a** calculated with the AM1 method is lying only 2 kcal mol^{-1} lower than the C_s one, the NMR spectral data show C_s symmetry of **2a**.

§ Calculations were carried out using the GAUSSIAN 92 program.

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