$C_{61}Br_2$: A new synthesis of dibromomethanofullerene and mass spectrometric evidence of the carbon allotropes C_{121} and C_{122}

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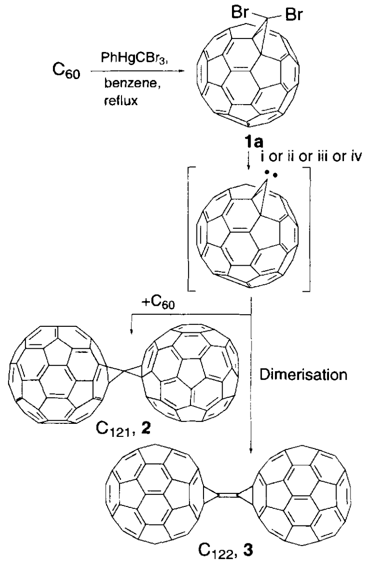
The new preparative synthesis and the characterisation of 1′,1′-dibromo-1,2-methano[60]fullerene 1a using a Seyferth reagent and the mass spectrometric evidence of the novel dumb-bell shaped molecular carbon allotropes C_{121} 2 and C_{122} 3 obtained *via* a proposed intermediate $C_{60}C$: carbene generated from 1a are reported.

In 1985 Kroto, Smalley and coworkers reported the mass spectroscopic detection of a novel unexpected carbon cluster, [60]fullerene (C_{60}).[1] Since then, great effort has been spent on synthesising and characterising new carbon clusters and derivatives of the fullerenes as well as on explaining their mechanism of formation.[2–7] Carbon nanotubes,[3] polymeric chains of C_{60},[4] dimeric clusters C_{2n-1} (n = 60, 70)[5] and derivatives of new carbon allotropes $C_{n(60+5)}$ starting from acetylene methanofullerenes[6] have been reported.

We considered that another route to new carbon allotropes with differently hybridised carbon atoms would be opened by the addition of methanofullerenecarbene, $C_{60}C$:, to C_{60} and its dimerisation, leading to the hitherto unknown carbon allotropes C_{121} and C_{122}. $C_{60}C$:, the first carbon allotrope with a carbene structure, should be accessible as an intermediate from dihalomethanofullerenes, dibromomethanofullerenes in particular.[7] Many miscellaneous syntheses are known to derivatise fullerenes[8] and also the syntheses of dihalomethanofullerenes have already been reported by Nogami and coworkers.[9]

Here we describe a new route to $C_{61}Br_2$ using a Seyferth reagent (Scheme 1).[10] By refluxing a mixture of 1 equiv. C_{60} and 0.9 equiv. $C_6H_5HgCBr_3$ in benzene followed by GPC–HPLC separation, we obtained $C_{61}Br_2$ in 54% yield. The higher bis- and tris-adducts are formed as by-products. Varying the quantity of Seyferth reagent used affects the product ratio of the mono : bis : tris : tetra : penta : hexaadducts, but it was not possible, however, to obtain only one single product. A one-step synthesis of a highly symmetrical hexaadduct as reported for a Diels–Alder reaction[11] did not succeed despite the use of an excess of Seyferth reagent.



Scheme 1 Synthesis of **1a** and investigated syntheses to **2** and **3** with calculated structures of C_{121} and C_{122} *via* a proposed $C_{60}C$: carbene. *Reagents and conditions*: i, toluene, $Fe(CO)_5$, 0 °C → reflux; ii, toluene, $h\nu$ 330 nm, 25 °C; iii, toluene, Cu, reflux; iv, toluene (or THF), Bu^nLi, −90 °C → reflux.

The monoadduct **1a** was completely characterised by ^{13}C NMR, UV–VIS spectroscopy MALDI-TOF-MS and DEI-MS. As expected, two signals for the cyclopropane ring [C(61) δ 32.9 C(1), C(2) δ 80.2] and 15 of the predicted 16 signals confirming the C_{2v} symmetry are observed in the ^{13}C NMR spectrum (two signals overlap).† In addition, the UV–VIS spectrum shows the typical methanofullerenes absorption at 425 nm. Detection of **1a** by DEI-MS is complicated owing to the low intensity of the signals for the molecular peak of **1a** and in most cases only the C_{60} signal is observed. With MALDI-TOF-MS, however, the molecular peak can be detected easily with 9-nitroanthracene as the matrix.[12] As can be concluded from the proposed [2 + 1]addition mechanism of $:CBr_2$ carbene to a C_{60} double bond, no 5,6-ring bridged isomers are formed. Higher bis and tris adducts were detected by MALDI-TOF-MS. An exact characterisation is not possible, because of the various isomers that can be formed (Fig. 1).[13]

Semiempirical PM3 calculations[14] on **1** indicate that the opened 5,6-ring bridged isomer **1b** should be 4.0 kcal mol^{-1} more stable than the closed 6,6-ring bridged isomer **1a** found experimentally. As observed for the corresponding $C_{61}H_2$,[15] attempts to thermally or photochemically isomerise **1a** to **1b** failed. Surprisingly, the opened 6,6-ring bridged isomer **1c** with a methano[10]annulene substructure[16a] is located as a local minimum on the potential energy surface and is only 6.6 kcal mol^{-1} less stable than **1a**. No other methanofullerene is predicted to form a stable opened 6,6-ring bridged isomer.[17,18] The calculated value is in the same range as that calculated for the valence tautomerisation of 1,6-methano[10]annulene and its bis-norcaradiene tautomer.[16]

The possibility of synthesising the carbon clusters C_{121} and C_{122} was investigated by various methods to form the $C_{60}C$: carbene.‡ Although no dimeric products have yet been isolated, signals of the expected masses 1452§ (C_{121}; MALDI-TOF-MS) and 1464§ (C_{122}; MALDI-TOF-MS and DEI-MS) were detected by mass spectrometric analysis of the crude reaction products (Fig. 2). The new clusters **2** and **3** can be detected after the Seyferth reaction, but for **3** the highest intensity in the MS

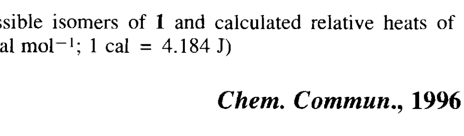


Fig. 1 Possible isomers of **1** and calculated relative heats of formation $\Delta_{f,rel}H$ (kcal mol^{-1}; 1 cal = 4.184 J)

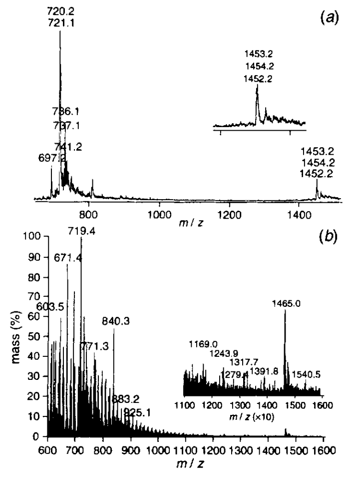


Fig. 2 (*a*) MALDI-TOF-MS after the Seyferth reaction and (*b*) DEI-MS after dimerisation with Bu^nLi

is observed after dimerisation of $C_{60}C$: in THF.‡ These findings imply that although the desired products are formed under the conditions used, they occur in such low quantities that all attempts to separate them failed. On the other hand, the possibility that **2** and **3** are formed under the mass spectrometric conditions cannot be excluded. A peak at *m/z* 1452 can also be detected in a solution of C_{60} and $C_{61}H_2$ synthesised using the Simmons–Smith reaction.[19,20]

The C_{2v} symmetry of **2** and the D_{2h} symmetry of **3** are proposed to be due to the reaction mechanism and to known cyclopropylidene and bicyclopropylidene substructures.[21] Semiempirical PM3 calculations[14] support these stable structures with calculated heats of formation per C atom that are nearly the same as that of C_{60} (C_{60}, 13.529; **2**, 13.518; **3** 13.659 kcal mol^{-1}). In accordance with observed X-ray structure of methanofullerenes,[22] the closed 6,6-ring bridged isomers of **2** and **3** with C_{2v} and D_{2h} symmetry, respectively, are stable.

This new synthesis with the Seyferth reagent is a versatile method for preparing methanofullerenes and it should be applicable to other halogen carbons, *e.g.* fluorocarbons ($C_{60}C_xF_{2x}$). The application to higher fullerenes could lead to a wide range of new carbon allotropes due to the regioisomers formed.

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Footnotes

† A solution of [60]fullerene (100 mg, 13.9 mmol) and $PhHgCBr_3$ (66 mg, 12.5 mmol) in benzene (200 ml) was heated under reflux for 6 h. After removal of the benzene, the residue in dry THF (500 ml) was heated under reflux for 10 min, filtered, and the solvent was removed by evaporation. The crude product was separated from [60]fullerene and its polyadducts by GPC–HPLC using trichloromethane as solvent. Yield 54% (according to $PhHgCBr_3$). Mp >250 °C. DEI-MS *m/z* (%): 891.8 (0.5, [M^+]), 720.0 (20, [$M^+ - CBr_2$]), 91.0 (100, [CBr^+]). MALDI-TOF-MS *m/z*: 892.0 (100, [M^-]), 720.1 (30, [$M^- - CBr_2$]). ^{13}C NMR (400 MHz, CS_2, ext. CD_3CN), δ: 32.9 [1 C, C(61)], 80.2 [2 C, C(1), C(2)], 139.7 (4 C), 141.7 (4 C), 142.6 (4 C), 142.8 (4 C), 143.3 (2 C), 143.6 (2 C), 143.7 (4 C), 143.9 (4 C), 144.2 (4 C), 144.8 (2 C), 145.1 (4 C), 145.2 (4 C), 145.3 (4 C), 145.8 (2 × 4 C), 145.9 (4 C). UV-VIS ($CHCl_3$), λ/nm: 334, 425, 492.

‡ Compounds **2** and **3** have been prepared by various methods.[23] The formation of an intermediate $C_{60}C$: is suggested and most probable, but nucleophilic attack of $C_{60}CBr^-$ followed by elimination of Br^- cannot be excluded.

§ The most abundant peaks are 1453 (C_{121}) and 1465 (C_{122}) because of the ^{13}C isotope.

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