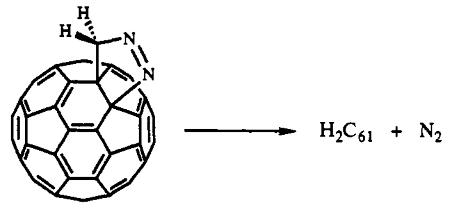
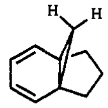
Scheme I



1

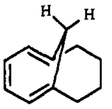
The ${}^1H$ NMR of the dihydrofulleroid shows *two* doublet peaks at 2.87 (H_A) and 6.35 (H_B) ppm in a 1:1 ratio. Spin decoupling revealed that the two sets of doublets ($J = 9.7$ Hz) are coupled. One hydrogen is remarkably deshielded relative to the other ($\Delta\delta = 3.48$ ppm). There are only a few cases reported where a $\Delta\delta > 3$ ppm was observed; of these, the most revealing is hydrocarbon **6**.[8] In the latter, the relevant high-field and low-field protons appear at 1.2 and 4.7 ppm, respectively, i.e., 1.67 and 1.65 ppm upfield relative to the corresponding fulleroid hydrogens. In the case of fulleroids, it was shown that aromatic protons which are directly above the "π" system of the 6-rings are drastically deshielded,[5] but a fulleroid with protons over a 5-ring has not yet been prepared; H_2C_{61} is the first case. Since aromatic ring currents cannot[9] exist in **6** and $\Delta\delta$ is the same as in the fulleroid, we conclude that, as is the case for C_{60},[10] there are no ring currents in the fulleroid spheroid.[9,11]

We propose structure **2** for H_2C_{61} on the basis of the above and the following: (i) The coupling constant of the methylene hydrogens is a good measure of the $C-CH_2-C$ angle, as shown for the following sequence of bridged cycloheptatrienes.[12]



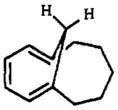
3

$J_{(H,H)} = 4.0$ Hz



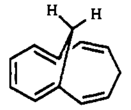
4

$J_{(H,H)} = 9.9$ Hz



5

$J_{(H,H)} = 11.3$ Hz



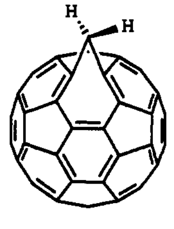
6

$J_{(H,H)} = 11$ Hz

$\delta(H) = 1.2$ ppm

$\delta(H) = 4.7$ ppm

(ii) The ${}^{13}C$ NMR spectrum of $H_2({}^{13}C)C_{60}$ prepared from (99%-${}^{13}C$) diazomethane shows a single peak at 38.85 ppm, which is in good agreement with that of methano[10]annulene (38.4 ppm), and 32 fulleroid resonances (135.15–149.25 ppm).[7,13] (iii) The coupling constants between the methylene carbon and its hydrogens are $J({}^{13}C,H_A) = 145.0$ and $J({}^{13}C,H_B) = 147.8$ Hz, respectively, and are typical for methano[10]annulenes.[14]



2

We have shown above that, contrary to all previous cases[5] reported for fulleroid synthesis, (1) the intermediate pyrazoline can be isolated and characterized; (2) the first step of the fulleroid synthesis is a dipolar addition across the reactive 6-ring–6-ring (pyracyclene)[15,16] junction; (3) thermal nitrogen loss occurs concomitantly with rearrangement (1,5-shift?); and (4) comparative ${}^1H$ NMR with a known bicyclic hydrocarbon incapable of sustaining an extended ring current indicates that there are no extended ring currents in the fulleroid "π" system.[9,11]

Acknowledgment. We thank the National Science Foundation for support through Grants DMR-88-20933, DMR-91-11097, and CHE-89-08323. Acknowledgment is made to Dr. Janet Cheetham for extraordinary help and the use of the UCSB-located, AMGEN Brucker AMX 500 spectrometer.

Supplementary Material Available: Complete spectroscopic characterization of pyrazoline **1** and fulleroid **2**, a cyclic voltammogram, a table of cyclic voltammetric data for C_{61} fulleroids, and a CHARMm computer modeling printout (14 pages). Ordering information is given on any current masthead page.

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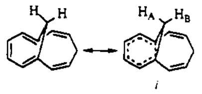
(8) Vogel, E. *Aromaticity*; Ollis, O. D., Ed.; The Chemical Society: London, 1967, Vol. 21, p 142.

(9) If there were a ring current in the "cyclohexatriene" moiety of **6** (see i), then proton H_A would have a chemical shift of 0 to −1 ppm. However, Robert Haddon (private communication; also: Haddon, R. C. *Tetrahedron* **1972**, *28*, 3613, 3635) mentioned a possible danger of using model chemical shifts (MCS) in analyzing ring currents.



i

(10) Haddon, R. C.; Schneemeyer, L. F.; Waszczak, J. V.; Glarum, S. H.; Tycko, R.; Dabbadh, G.; Kortan, A. R.; Muller, A. J.; Mujse, A. M.; Rosseinsky, M.; Zahurak, S. M.; Makhija, A. V.; Thiel, F. A.; Raghavachari, K.; Cockayne, E.; Elser, V. *Nature* **1991**, *350*, 46. Elser, V.; Haddon, R. C. *Nature* **1987**, *325*, 792.

(11) Another interpretation could be that two types of paramagnetic ring currents exist in fulleroids (and by extrapolation in fullerene C_{60}; Pasquarello, A.; Schlüter, M.; Haddon, R. C. *Science*, submitted; private communication and preprint). If that were the case, as well as on the basis of previous results, we would conclude that the ring currents of the 6-rings are deshielding and those of the 5-rings are shielding.

(12) Vogel, E.; Wiedemann, W.; Roth, H. D.; Eimer, J.; Günther, H. *Justus Liebigs Ann. Chem.* **1972**, *759*, 1.

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The First X-ray Structure of a 1,1-Di-Grignard Compound: Bis(bromomagnesio)bis(trimethylsilyl)methane

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Received May 21, 1992

As a part of our research aimed at new 1,1-di-Grignard reagents,[1,2] we have reported on the preparation of bis(bromomagnesio)bis(trimethylsilyl)methane (**1**);[3a] it was obtained in a

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(1) (a) Bertini, F.; Grasselli, P.; Zubiani, G.; Cainelli, G. *Tetrahedron* **1970**, *26*, 1281.

(2) (a) Van de Heisteeg, B. J. J.; Schat, G.; Tinga, M. A. G. M.; Akkerman, O. S.; Bickelhaupt, F. *Tetrahedron Lett.* **1986**, *27*, 6123. (b) Van de Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1986**, *308*, 1. (c) Van de Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1986**, *310*, C25. (d) Bickelhaupt, F. *Angew. Chem.* **1987**, *99*, 1020. (e) Bickelhaupt, F. *Pure Appl. Chem.* **1990**, *62*, 699.

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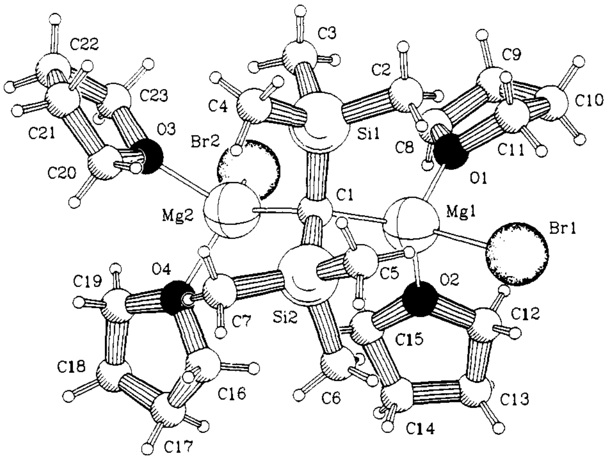

Figure 1. PLUTON drawing of **1** (molecule 1). Selected bond distances (Å) and angles (deg): Mg(1)–C(1), 2.10 (4); Mg(2)–C(1), 2.14 (4); Si(1)–C(1), 1.85 (4); Si(2)–C(1), 1.81 (4); Mg–O, 2.05 (3) (average); Mg(1)–C(1)–Mg(2), 112 (2); Si(1)–C(1)–Si(2), 113 (2); Mg(1)–C(1)–Si(1), 104 (2); Mg(1)–C(1)–Si(2), 107 (2); Mg(2)–C(1)–Si(1), 106 (2); Mg(2)–C(1)–Si(2), 115 (2); C(1)–Mg(1)–Br(1), 121 (1); C(1)–Mg(2)–Br(2), 122 (1); O–Mg–O, 93 (1) (average).

"classical" Grignard reaction from bis(trimethylsilyl)dibromomethane (**2**) with magnesium in diethyl ether and isolated by crystallization (40% yield). Somewhat unexpectedly, **1** turned out to be rather unreactive toward most electrophiles.[3]

In an attempt to better understand this unusual behavior, we undertook an X-ray structure determination of **1**. Crystals of **1** suitable for X-ray crystal structure determination were obtained from a saturated solution in THF/hexane (1:1) on cooling to +5 °C. The asymmetric unit of the orthorhombic unit cell contains two very similar molecules, one of which is shown in Figure 1.[4]

Anticipating **1** to be a crowded molecule and realizing that organomagnesium compounds tend to escape from congested situations by association to form bridged dimers or oligomers,[5] we were surprised to find *monomeric* units of **1** with *two* THF ligands per magnesium in the crystal; association measurements showed that the monomeric state is retained in THF solution. In view of this, the rather "normal" character of **1** noted at first sight was no lesser surprise: the central carbon atom is a slightly distorted tetrahedron with bond angles ranging from 104 (2)° to 116 (2)°, and the two magnesium atoms are tetracoordinated with unexceptional geometries.[5]

Closer examination reveals that all carbon–metal(loid) bonds are slightly shorter than usual. The (average) Mg–C bond distance is 2.12 (4) Å; in ether-coordinated Grignard reagents, Mg–C distances are normally about 2.15 Å.[5] Similarly, the (average) Si–C(1) bonds (1.83 (4) Å) are shorter than normal sp^3-hybridized Si–C bonds (1.88 Å). As **1** is a crowded molecule, we had, on the contrary, expected to find bond lengthening. Apparently, attachment of four electropositive groups to the central carbon leads to accumulation of negative charge at this carbon and thus to electrostatic strengthening and shortening of the highly polar bonds. This counteracts the steric crowding and contributes to the reduced reactivity of **1**.

The crowdedness of the molecule is an interesting feature. Intuitively, we had speculated[3] that steric hindrance by four bulky groups (two $SiMe_3$ groups and two $MgBr(THF)_2$ groups) is a major reason for the decreased reactivity of **1**. As can be seen in Figure 1, the central carbanionic carbon atom is indeed efficiently shielded against approach by large electrophiles.

Finally, we wish to point out that the structure **1** is the first experimentally determined compound carrying two strongly positive metal atoms at the same carbon atom (in addition to the two somewhat less positive silicons!). The only other two relevant structures are those of CD_2Li_2[6] and $Li_2[CH_2\{Al(CH_2SiMe_3)_3\}_2]$;[7] they have strongly different features because they are unsolvated and highly electron deficient, occurring either as a polymer or as an anionic complex with a hexacoordinated central carbon, respectively.

Acknowledgment. These investigations were supported in part (W.J.J.S., A.L.S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Advancement of Pure Research (NWO).

Supplementary Material Available: Tables of crystal data and details of the structure determination, final coordinates, and equivalent isotropic thermal parameters of the non-hydrogen atoms, hydrogen atom parameters, (an)isotropic thermal parameters, and bond distances and angles and PLUTON and ORTEP plots of the two molecules (17 pages). Ordering information is given on any current masthead page.

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[4] **Crystal data for 1**: $C_{23}H_{50}Br_2Mg_2O_4Si_2$, $M_r = 655.23$; colorless, block-shaped crystal (0.35 × 0.43 × 0.48 mm), orthorhombic, space group $Pc2_1b$, with $a = 11.225$ (1) Å, $b = 22.620$ (2) Å, $c = 26.844$ (2) Å, $V = 6816$ (1) Å^3, $Z = 8$, $d_{calcd} = 1.277$ g cm^{-3}, $F(000) = 2736$, μ(Mo Kα) = 24.8 cm^{-1}; 4916 independent reflections ($0.76 < \theta < 24.2°$, $\omega/2\theta$ scan, $T = 295$ K) were measured on an Enraf-Nonius CAD-4T/rotating anode diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The crystal reflected poorly and had rather broad reflection profiles. Data were corrected for Lorentz polarization effects, for a small linear increase (5%) of the intensity control reflections, and for absorption (DIFABS; correction range 0.411–1.324). The structure was solved by Patterson (SHELXS86) and difference Fourier techniques. The O(6) THF molecule was found to be disordered over two positions (50:50 ratio); all THF molecules show high thermal motion and were included in the full-matrix least-squares (SHELX76) refinement as rigid groups. Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. Br, Si, Mg, and O were refined with anisotropic thermal parameters, and carbon atoms were refined isotropically in view of the poor quality of the crystals and the limited number of observed reflections. Convergence was reached at $R = 0.072$, $wR = 0.080$, $w = 1/[\sigma^2(F) + 0.00071F^2]$ for 1652 reflections with $I > 2.5\sigma(I)$ and 304 parameters. A final difference Fourier map showed no residual density outside −0.38 and 0.49 e/Å^3. Geometrical details of the structure are provided as supplementary material.

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The Agglutination of Erythrocytes by Influenza Virus is Strongly Inhibited by Liposomes Incorporating an Analog of Sialyl Gangliosides[1]

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Received April 23, 1992

Infection of a mammalian cell by influenza virus begins with the recognition of sialic acid (SA) groups on the cell surface by a viral surface protein, hemagglutinin (HA). Although virus binds tightly to cells,[3] solubilized HA binds only weakly ($K_d \sim 2.5 \times 10^{-3}$ M) to methyl α-sialoside.[4] This qualitative difference in the strength of binding is the basis for the hypothesis that the binding of virus to cell is controlled by polyvalent interactions.[5]

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[1] This work is part of a collaboration with J. J. Skehel, J. R. Knowles, M. Karplus, and D. C. Wiley. Support provided by the NIH Grants GM 39589 and GM 30367.

[2] NSF Postdoctoral Fellow 1990–1992 (CHE-9002635).

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