Figure 1. Structure of $(3)\text{-}1,2\text{-}B_9C_2H_{11}Al(C_2H_5)$ in schematic form.

upon precipitation with trimethylammonium chloride, proved to be $(3)\text{-}1,2\text{-}B_9C_2H_{12}^{-}NH(CH_3)_3^{+}$.[9]

Treatment of II with anhydrous HCl regenerated $(3)\text{-}1,2\text{-}B_9C_2H_{13}$ in quantitative yield.

Addition of either I or II to $TiCl_4$ in heptane produced dark red solutions similar to those described by Ziegler using trialkylaluminums.[10] Subsequent exposure of these solutions to ethylene gas catalytically produced high-molecular-weight polyethylene at ambient temperature and pressure.

Finally, it was possible to thermally rearrange II by subliming the compound through a glass-wool-filled hot tube. Only starting material was recovered at 350°, but at 410° an 85% yield of pure $1,7\text{-}B_9C_2H_{11}\text{-}Al(C_2H_5)$ (V) was obtained, mp 100–102° (uncor) in a sealed capillary. Slow hydrolysis of V and precipitation with trimethylammonium chloride gave $(3)\text{-}1,7\text{-}B_9C_2H_{12}^{-}NH(CH_3)_3^{+}$.[9]

Compound II crystallizes in the centrosymmetric orthorhombic space group $Pnma$ (D_{2h}^{16}; No. 62) with $a = 16.304$, $b = 7.533$, $c = 9.398$ Å, $\rho_{calcd} = 1.084$ g cm^{-3} for mol wt 188.45 and $Z = 4$.[11] X-Ray diffraction data to $\sin \theta = 0.95$ (Cu Kα radiation, $\bar{\lambda}$ 1.5418 Å) were collected on a PAILRED diffractometer using a stationary-background, ω scan, stationary-background counting sequence and equiinclination Weissenberg geometry. All data were corrected for absorption ($\mu = 10.18$ cm^{-1}). The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. Using anisotropic thermal parameters for nonhydrogen atoms and (fixed) isotropic thermal parameters for icosahedral hydrogen atoms, the final discrepancy index was $R_F = 8.42\%$ for the 499 independent nonzero reflections.

The molecule (II) is bisected by a crystallographic mirror plane which passes through the aluminum atom and the carbon of the methylene group. The terminal

(9) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Amer. Chem. Soc.*, 90, 862 (1968).

(10) K. Ziegler, E. Holzkamp, H. Breil, and H. Martin, *Angew. Chem.*, 67, 541 (1955).

(11) Because of the great air sensitivity of the complex, the density was not measured.

carbon of the ethyl group is disordered about the crystallographic mirror plane.[12] As shown in Figure 1, the aluminum atom is bonded to the C_2B_3 face of the $B_9C_2H_{11}^{2-}$ ion, mean distances being Al–B = 2.137 ± 0.008 and Al–C = 2.173 ± 0.007 Å. The aluminum–ethyl σ-bond length is 1.930 ± 0.006 Å. Mean distances within the B_9C_2 icosahedron are: B–B = 1.777 ± 0.012, B–C = 1.697 ± 0.011, and C–C = 1.561 ± 0.009 Å. Boron–hydrogen distances range from 1.09 ± 0.07 to 1.33 ± 0.09, averaging 1.20 ± 0.08 Å; the (icosahedral carbon)–hydrogen bond is 0.80 ± 0.08 Å in length.[13]

Having demonstrated the structure of II and the most likely analogous structures of IV and V (1,7 carbon atoms in V) two interesting points remain; the structure of I (and III, by analogy) and the nature of the THF adduct of II reported earlier.[5] These problems are currently under investigation.

(12) Thermal parameters of all atoms in the structure are reasonable, thus militating against a possible redesignation of the molecule to the noncentrosymmetric space group $Pna2_1$. A plot of the distribution of X-ray intensities as a function of sin θ does not allow us to distinguish satisfactorily between the centrosymmetric or noncentrosymmetric alternatives; see E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Crystallogr.*, 3, 210 (1950).

(13) X-Ray diffraction experiments typically give abnormally low values to (light atom)–hydrogen bonds.

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(15) Alfred P. Sloan Research Fellow, 1968–1970.

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Reactions of Optically Active Heterohelicenes. Synthesis of an Optically Active Undecaheterohelicene

Sir:

The synthesis, resolution, and racemization of a number of heterohelicenes has recently been described.[1] We now wish to report the synthesis of an optically active undecaheterohelicene, starting from the partially resolved heptaheterohelicene I as outlined in Scheme I.[2] The compound I (15 mg, $[\alpha]^{25}_{436}$ +550° (CHCl$_3$), optical purity *ca.* 7.5%) was converted into the aldehyde II, which was coupled with the phosphonium salt III. The resulting alkene IV (8 mg, $[\alpha]^{25}_{578}$ +140° (CHCl$_3$) was irradiated for 3 hr in 120 ml of benzene in the presence of a trace of iodine using a Hanovia S 81 lamp. Evaporation of the solvent and column chromatography of the residue furnished 1.12 mg of the optically active undecaheterohelicene bis(naphtho[2,1-*b*]thieno)[1,2-*e*:1',2'-*e*']benzo[1,2-*b*:-4,3-*b*']bis-[1]benzothiopene (V),[3] $[\alpha]^{25}_{578}$ +214° (CHCl$_3$). The

(1) (a) H. Wynberg and M. B. Groen, *J. Amer. Chem. Soc.*, 90, 5339 (1968); (b) H. Wynberg and M. B. Groen, *Chem. Commun.*, 964 (1969).

(2) This reaction sequence was successfully carried out first with racemic I on a larger scale. Correct elemental analyses (C, H, and S) were obtained for the racemic forms of all products.
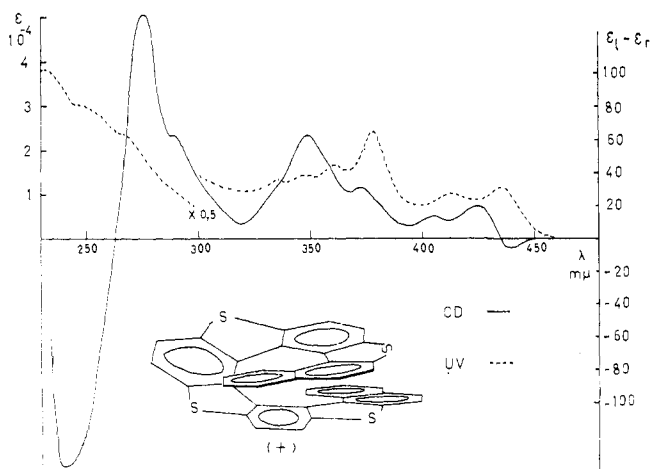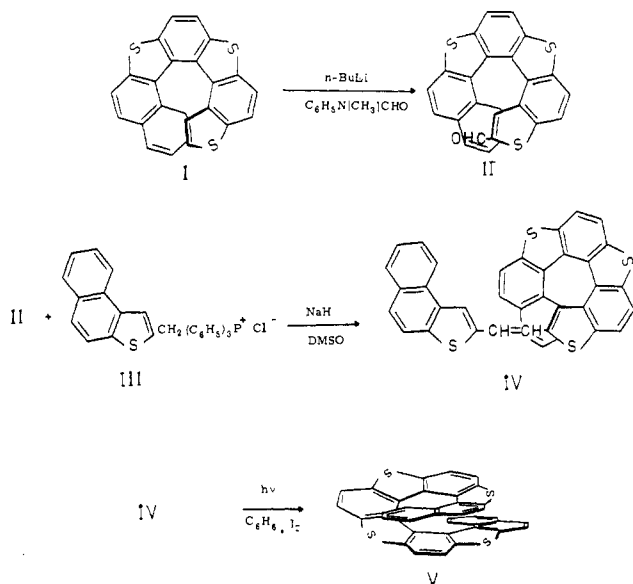
Figure 1. The uv spectrum (cyclohexane) and cd spectrum (methanol) of (+)-V.

Figure 2. The nmr spectrum (60 MHz) of V (2% in CDCl₃).

specific rotation of optically pure V should be at least +3600° at 546 mμ and +2900° at 578 mμ. The calculated molar rotations are $[\phi]^{25}_{546}$ 22,000° and $[\phi]^{25}_{578}$ 17,000 (in CHCl₃). The uv and cd spectra

of (+)-V are shown in Figure 1 and the nmr spectrum in Figure 2. The mass spectrum (70 eV) of V contained in addition to the strong M⁺ (m/e 602) and M²⁺ peaks (m/e 301) a prominent peak at m/e 368 (25% relative to the M⁺ peak) tentatively assigned to the planar ion VI. A metastable belonging to the fragmentation V⁺ → VI is present also in the spectrum at m/e 226.

VI
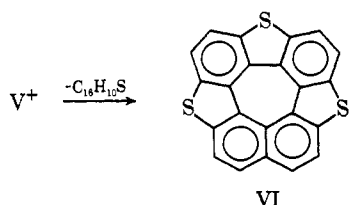
These data unambigously establish the structure of V. Martin has recorded the optical activity of heptahelicene,[4] and optically active octa- and nonahelicene[5]
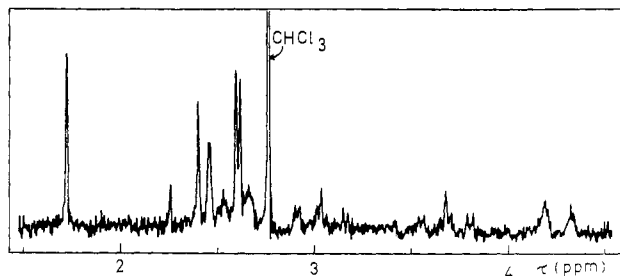
(3) The melting point of (±)-V was 368–370°.

have also been obtained in his Brussels laboratory. Of additional interest is the method we used to obtain optically active I. Instead of the crystal picking technique—which severely limits the scale of subsequent reactions—crystallization from optically active α-pinene, $[\alpha]^{25}$D −29.3° (neat), was successful. Thus 50-mg quantities of the heptaheterohelicene I were each dissolved in 10 ml of (−)-α-pinene with warming. The solutions were allowed to cool at room temperature or at −25°. The individual precipitates were each dissolved in 1.0 ml of chloroform and the optical rotations were measured in a 5-cm cell. The results are shown in Table I.

Table I

Recovd heteroheli-cene, mg	Condn of crystalln, °C	Measured rotation, α^{25}_{436}, deg	Specific rotation, $[\alpha]^{25}_{436}$, deg
7	−25 (4 days)	+3.60	+1000
13	−25 (1 day)	+2.43	+370
4	−25 (4 hr)	+4.27	+2400
16	+20 (1 day)	+0.27	+34

Repetition of these experiments using toluene–petroleum ether (1:1) or methylcyclohexane as solvent gave only optically inactive material, thus establishing that the optically active solvent has induced resolution.[6]

(4) R. H. Martin, M. Flammang-Barbieux, J. P. Cosyn, and M. Gelbcke, Tetrahedron Lett., 3507 (1968).

(5) Personal communication from Professor Martin.

(6) We have not established conclusively at this time whether this resolution is thermodynamic in nature or simply due to preferential seeding (kinetic) or a combination of both! Few authenticated cases are known where resolution by crystallization from an optically active solvent is truly thermodynamic in nature [see, e.g., D. R. Buss and T. Vermeulen, Ind. Eng. Chem., 60 (8), 12 (1968)].

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Base-Catalyzed Hydrogen–Deuterium Exchange in Diene–Iron Tricarbonyl Complexes

Sir:

We report that treatment of electronegatively substituted diene–iron tricarbonyl complexes with deuterated alcohols at 25° in the presence of base leads to hydrogen–deuterium exchange as in eq 1. Exchange is limited to those hydrogens α to the Z substituent. The position and extent of deuterium incorporation can be determined by nmr and mass spectrometry. The