

However in this case we found that *trans*-AIP quenched naphthalene fluorescence in both methanol and iso-octane at a rate close to the diffusion-controlled limit ($k_q = 1.14 \times 10^{10} \text{ sec}^{-1} M^{-1}$ in iso-octane) so that for $\text{azo} = 2 \times 10^{-2} M < 4\%$ of the excited singlet naphthalenes cross into their triplet manifold. *cis*-AIP and DBH also quenched the naphthalene fluorescence at a similar rate, and there was efficient induced decomposition of the DBH, $\Phi_{308}^{\text{naph}}(\text{dec}) = 1.0$. Bartlett and Engel¹⁶ have also recently observed the quenching of the fluorescence of aromatic compounds by azo compounds. Since the products and quantum yields for direct photolyses and the naphthalene-sensitized photolyses are so similar, it would appear that the latter is a case of singlet-singlet transfer.

Acknowledgments. I. I. A. and B. S. S. acknowledge support from the National Science Foundation under Undergraduate Research Participation Grant GY-4375 and College Faculty Summer Participation Grant GY-4111, respectively.

(16) P. D. Bartlett and P. S. Engel, *J. Am. Chem. Soc.*, **90**, 2960 (1968).

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The Preparation and Crystallographic Characterization of a Bridged Metallo-Carborane Complex Containing a Carbonium Ion Center: $(\text{B}_9\text{C}_2\text{H}_{10})_2\text{CoS}_2\text{CH}$

Sir:

In recent investigations of the chemistry of $(\text{B}_9\text{C}_2\text{H}_{11})_2\text{M}$ (M = transition metal) systems, we have attempted several Friedel-Crafts alkylations and have discovered a most unusual reaction, the product of which has been characterized by elemental analysis and a complete three-dimensional X-ray diffraction study.

When finely divided $\text{K}^+[(\text{B}_9\text{C}_2\text{H}_{11})_2\text{Co}]^-$ is stirred with several equivalents of aluminum chloride in carbon disulfide for 12 hr at room temperature, gas is evolved and the carbon disulfide acquires an orange color similar to that of the starting material. A fluffy yellow solid can be isolated in a highly variable yield from the filtered carbon disulfide solution. If a slow stream of hydrogen chloride is passed into the reaction mixture, however, the reaction time is halved, and a yield of 70% is consistently obtained.

Elemental analyses and a mass spectrometric molecular weight determination are consistent with the formulation of the complex as $(\text{B}_9\text{C}_2\text{H}_{10})_2\text{CoS}_2\text{CH}$. The ¹H nmr spectrum (acetone-*d*₆, 60 MHz) shows broad absorptions at δ 4.65 (4 H, cage C-H) and 11.5 (1 H, bridge C-H).

The molecular stereochemistry has been determined unambiguously by means of a single-crystal X-ray diffraction study.

When $(\text{B}_9\text{C}_2\text{H}_{10})_2\text{CoS}_2\text{CH}$ is extracted with hexane in a Soxhlet extractor, it crystallizes as bright orange

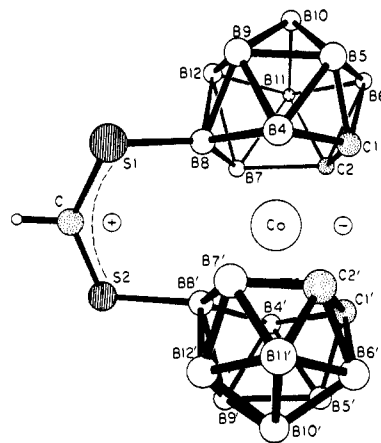


Figure 1. The $(\text{B}_9\text{C}_2\text{H}_{10})_2\text{CoS}_2\text{CH}$ molecule, projected onto the plane defined by Co, B(8), and B(8'). (Hydrogen atoms of the icosahedral cages are omitted for the sake of clarity.)

parallelepipeds in the noncentrosymmetric orthorhombic space group $\text{P}2_12_12_1$ (no. 19) with $a = 10.92$, $b = 13.17$, $c = 12.87 \text{ \AA}$, $V = 1852 \text{ \AA}^3$. The observed density, $\rho_{\text{obsd}} = 1.421 \pm 0.0006 \text{ g cm}^{-3}$, is in good agreement with the value calculated for $Z = 4$ ($\rho_{\text{calcd}} = 1.420 \text{ g cm}^{-3}$). A set of X-ray diffraction data complete to $\sin \theta = 0.42$ (Mo $\text{K}\alpha$ radiation) was collected with a 0.01° incrementing Buerger automated diffractometer, using a "stationary-background, ω -scan, stationary-background" counting sequence. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. Using anisotropic thermal parameters for all nonhydrogen atoms, refinement converged to a discrepancy index of $R_F = 7.88\%$ for the 1557 independent, nonzero reflections. All atoms, including each of the 21 hydrogen atoms, have been located unambiguously. No attempt was made to determine the absolute configurations of the molecule, but it should be noted that since the space group is nonpolar, bond distances will not be affected by ignoring the imaginary part of the cobalt and sulfur scattering factors.

The geometry of the $(\text{B}_9\text{C}_2\text{H}_{10})_2\text{CoS}_2\text{CH}$ molecule is shown in Figure 1. The cobalt atom is "sandwiched" between the two mutually staggered carborane moieties and is symmetrically bonded to all five atoms of each basal pentagon. Cobalt-boron distances range from 2.02 to 2.13 \AA (average 2.08 \AA), and cobalt-carbon distances vary from 2.04 to 2.06 \AA (average 2.05 \AA). [These values are in good agreement with the mean Co-B (or C) distance of 2.07 \AA in the disordered $\text{Cs}^+[(\text{B}_9\text{C}_2\text{H}_{11})_2\text{Co}]^-$.¹

The two icosahedra which share the cobalt atom as a common apex are further linked *via* an S-CH-S bridge which spans B(8) and B(8'), *i.e.*, the central of the three boron atoms in each of the basal pentagons. Individual bond lengths within this bridge (in \AA) are: B(8)-S(1) = 1.85 ± 0.02 , S(1)-C = 1.71 ± 0.02 , C-S(2) = 1.62 ± 0.02 , S(2)-B(8') = 1.90 ± 0.02 ; angles are [B(8)-S(1)-C] = $108 \pm 1^\circ$, [S(1)-C-S(2)] = $133 \pm 2^\circ$, and [C-S(2)-B(8')] = $109 \pm 1^\circ$. A comparison of the C-S(1) and C-S(2) distances shows

(1) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **6**, 1911 (1967).

them not to be significantly different at the 3σ level, and suggests that the S(1)-C-S(2) system is delocalized as shown in Figure 1.

Average distances within the icosahedral framework (B-B = 1.79 Å, B-C = 1.71 Å, C-C = 1.63 Å) are in good agreement with those found in such complexes as $(B_9C_2H_{11})Fe(\pi-C_5H_5)$,² $[B_9C_2H_{11}Re(CO)_3]^-$,³ and $[(B_9C_2H_{11})_2Cu]^{2-}$.⁴

Hydrolysis of $(B_9C_2H_{10})_2CoS_2CH$ can be accomplished by heating in alkaline 50% aqueous ethanol at the reflux temperature for 45 min. The fate of the bridge carbon (which presumably appears as formate ion) has not been specifically investigated. Addition of H_2O_2 and $(CH_3)_4N^+$ or Cs^+ precipitates the purple $[(B_9C_2H_{10})_2CoS_2]^-$ ion, which apparently contains a disulfide bridge linking the icosahedral cages.

Anal. Calcd for $C_4H_{20}B_{18}CoCsS_2$: C, 9.25; H, 3.88; B, 37.59; Co, 11.35; Cs, 25.60; S, 12.31. Found: C, 9.75; H, 4.03; B, 35.43; Co, 11.48; Cs, 26.59; S, 12.57. Average particle weight of $(CH_3)_4N^+$ salt by vapor pressure osmometer (acetonitrile): calcd, 230.1; found, 240. 1H nmr (acetone- d_6 , 60 MHz) of $(CH_3)_4N^+$ salt, δ 3.47 (12 H, $(CH_3)_4N^+$) and 4.04 (4 H, cage CH.)

Further details on this and other reactions of the $(B_9C_2H_{11})_2M$ complexes will appear in a future publication.

Acknowledgments. This research has been supported in part by the Office of Naval Research (M. F. H.), Advanced Research Projects Agency Contract SD-88 (M. R. C.), and National Science Foundation Grant GP-8077 (M. R. C.).

(2) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *J. Am. Chem. Soc.*, **87**, 3988 (1965).

(3) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **5**, 1189 (1966).

(4) R. M. Wing, *J. Am. Chem. Soc.*, **89**, 5599 (1967).

(5) Research Fellow of the Alfred P. Sloan Foundation, 1968-1970.

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Received November 1, 1968

Transannular π -Bond Activation by Sulfur toward Electrophilic Attack

Sir:

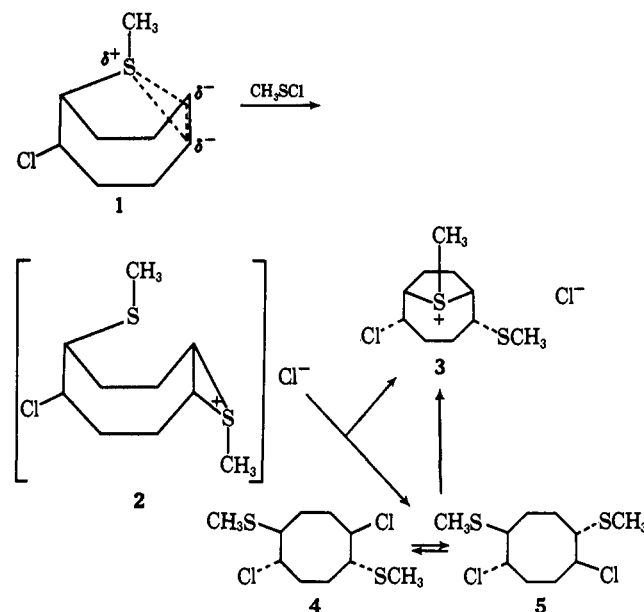
A unique case of transannular carbon-carbon bond formation during methanesulfonyl chloride addition to *cis,trans*-1,5-cyclodecadiene has been recently reported.¹ The interaction of a double bond with a cationic center across a ring is well established in this and other ring systems; however, such behavior with an episulfonium ion is unprecedented. It is particularly surprising in the case of the strongly bridging methylthio group since all evidence with such episulfonium ions points toward little charge being developed on carbon.²

(1) J. G. Traynham, G. R. Franzen, G. A. Knesel, and D. J. Northington, Jr., *J. Org. Chem.*, **32**, 3285 (1967).

(2) W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **88**, 2866 (1966); **90**, 2075 (1968).

During attempts to demonstrate a similar transannular carbon-carbon bond formation with 1,5-cyclooctadiene (COD) and methanesulfonyl chloride, an unexpected transannular π -bond activation by the methylthio group was detected which is the subject of the present communication.

Reaction of methanesulfonyl chloride with various amounts of COD ranging from equimolar to 10 *M* excess afforded about 80-90% of diadducts 3-5, and only 8-13% of monoadduct 1.³ This observation is in strong contrast to the highly selective monoadduct formation previously encountered with other dienes.⁴ The remarkable propensity for diadduct formation in the present case indicates a considerable activation of the remaining double bond in monoadduct⁵ 1 over those in COD toward the attack of sulfonyl chloride.



Apparently a transannular overlapping of the sulfur orbitals with the π bond as depicted in 1 is responsible for this increased nucleophilicity of the double bond. Inspection of a Dreiding model showed that in a twisted tub conformation the sulfur can come within bonding distance above the center of the π bond.

Addition of a second mole of methanesulfonyl chloride must then involve an intermediate such as the episulfonium ion 2. Ring opening of 2 by chloride in the well-documented *trans* manner⁵ would account for the oily diadduct(s) 4 and/or 5 formed in *ca.* 30% yield. More interestingly, intramolecular ring opening of episulfonium ion 2 by the methylthio group results in 2-chloro-5-methylthio-9-methyl-9-thiabicyclo[4.2.1]nonanesulfonium chloride (3), mp 175-177° dec, in *ca.* 50% yield. Mutual isomerization of the oily diadducts 4 and 5 through an episulfonium ion inter-

(3) All sulfonyl chloride additions during this study were conducted at -20 to -30° with *ca.* 50% methylene chloride solutions of the unsaturate.

(4) W. H. Mueller and P. E. Butler, *Chem. Commun.*, 646 (1966); *J. Org. Chem.*, **33**, 2642 (1968).

(5) The *trans* stereochemical relationship assumed for the monoadduct finds support in similar *trans* additions previously reported in ref 2 and other references cited therein.