C(β)–C(γ) bonds and the tendency toward coplanarity of the carbon portion of the ring. Reduction of the torsional angles about the C(β)–C(γ) bonds and concomitant relaxation of the planarity requirements for the C(α)–C(β) bonds are implied by structures **1a–c**. Unfortunately, a "donor–acceptor" type of conjugation involving the sulfur 3d orbitals does not lead to clear stereochemical predictions.[2,13] Orbital symmetry considerations indicate the availability of a suitable 3d orbital in a hypothetical planar molecule (Case I).[13] However, when the sulfone group is not coplanar with the rest of the molecule, another geometry is approached (Case II),[13] and delocalization into a different 3d orbital may be anticipated.[14] Independent evidence regarding the relative merits of the two types of conjugation is inconclusive,[1] and it may *not* be assumed that optimal delocalization requires a planar thiepin 1,1-dioxide ring. We finally note that nonbonded interactions and orbital rehybridization phenomena[6a] which cannot be quantitatively assessed also may influence the observed structure.

We feel that the preceding data are evidence for electron delocalization in thiepin 1,1-dioxide. Conclusions regarding the nature and extent of the effect must, however, be formed with consideration of the chemical properties of the molecule.[4]

Acknowledgment. We gratefully acknowledge the Committee on Research, University of California, the Computer Science Center, University of Maryland, and the Biochemistry Section, Walter Reed Army Medical Center, for financial support.

---

[13] H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

[14] The highest filled (donor) 1,3,5-hexatriene molecular orbital (ψ_3) has b_2 symmetry. It is, therefore, necessary that the available sulfur 3d orbital (acceptor) also have b_2 symmetry (Case I)[13] or that a compatible symmetry (a_1, as in Case II) be available. Carbon–sulfur orbital overlap in the latter case would be favored by as large an angle as possible between the C(α)–S–C(α′) and C(α)–C(β)–C(β′)–C(α′) planes.

Herman L. Ammon
Division of Natural Sciences
University of California, Santa Cruz, California 95060

Plato H. Watts, Jr., James M. Stewart
Department of Chemistry
University of Maryland, College Park, Maryland 20784

William L. Mock
Mellon Institute of Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Received April 1, 1968

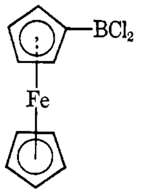
The Interaction of Diboron Tetrachloride with Ferrocene

Sir:

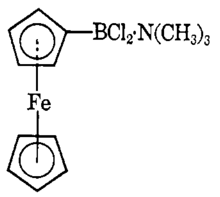
We wish to report the preparation of a new boron derivative of ferrocene, ferrocenyldichloroborane, from the reaction of diboron tetrachloride and ferrocene. The study of this reaction was undertaken as a part of our general investigation of the interactions of boron trihalides and diboron tetrahalides with organometallic compounds of the transition metals. Ferrocene readily forms a charge-transfer complex with tetracyanoethylene, a π acid.[1] Although the original work indicated that the tetracyanoethylene might be complexed with the iron, recent crystallographic studies have shown that the acid is bonded to the cyclopentadienyl rings.[2] Since it has been suggested that B_2Cl_4 acts as a π acid in its reactions with olefins,[3,4] it was of interest to investigate the possibility that B_2Cl_4 would interact with the ferrocene cyclopentadienyl rings as a π acid.

With hexane as the reaction medium, ferrocene and B_2Cl_4 were found to react readily at temperatures between −23 and 0°.[5,6] After approximately 2 days at 0°, the main reaction product, a red, crystalline solid, was separated from gray-green insoluble reaction products by extraction with hexane at 0°. The reaction products which were readily volatile at room temperature were distilled into a vacuum line (*vide infra*); unreacted ferrocene was removed by prolonged pumping at 10^{-6} mm and room temperature.

The infrared and ^{1}H nmr spectra of the red solid indicated that the substance was a monosubstituted ferrocene derivative. Ferrocene and its monosubstituted derivatives display characteristic absorption bands near 1000 and 1110 cm^{-1}.[7] While the presence of these bands is not conclusive proof of monosubstitution, they are very often indicative of derivatives of this type. We observed these bands at 1000 and 1107 cm^{-1}. In addition, bands assigned to B–Cl vibrations were observed at 887 (s) and 922 cm^{-1} (m). The ^{1}H nmr spectrum of the solid dissolved in benzene consisted of a pair of triplets at τ 5.57 and 5.65 (total relative intensity 4, J = 2 Hz) and a singlet at τ 6.08 (relative intensity 5). Characterization of the red material by complete elemental analysis was difficult due to problems in handling the air-sensitive, low-melting (33°) solid. However, a chloride analysis and a molecular weight determination indicated that the substance was $C_{10}H_{10}BCl_2Fe$.[8] It may be concluded from the spectral and analytical data that the red solid is ferrocenyldichloroborane (I). This new boron derivative of ferrocene was best characterized as the orange-yellow trimethylamine adduct II.[9] The solid amine complex was only slightly air-sensitive and was sublimable at 110–120° *in vacuo*. The complex exhibited an infrared



I



II

---

[1] M. Rosenblum, R. W. Fish, and C. Bennett, *J. Amer. Chem. Soc.*, **86**, 5166 (1964).

[2] E. Adman, M. Rosenblum, S. Sullivan, and T. N. Margulis, *ibid.*, **89**, 4540 (1967).

[3] R. W. Rudolph, *ibid.*, **89**, 4216 (1967).

[4] M. Zeldin, A. R. Gatti, and T. Wartik, *ibid.*, **89**, 4217 (1967).

[5] The reactions described in this communication were carried out in an all-glass *zweikugel*. Diboron tetrachloride and the appropriate solvents were distilled into the apparatus from a vacuum line. The reaction and extraction of soluble materials were carried out in this apparatus; solids were handled in a drybox.

[6] Diboron tetrafluoride does not react with ferrocene under similar conditions: W. J. Painter, unpublished results.

[7] M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Part I, John Wiley and Sons, Inc., New York, N. Y., 1965, p 38.

[8] *Anal.* Calcd for $C_{10}H_9BCl_2Fe$: Cl, 2.66; mol wt, 267. Found: Cl, 2.57; mol wt, 254 (by freezing point depression in benzene).

[9] *Anal.* Calcd for $C_{13}H_{18}BCl_2NFe$: C, 47.9; H, 5.57; B, 3.32; N, 4.30; Fe, 17.1; mol wt, 326. Found: C, 47.7; H, 5.66; B, 2.94; N, 4.33; Fe, 16.3; mol wt, 332 (by ebulliometry in benzene).

band assigned to N→B at 715 cm^{-1} in addition to bands assignable to B–Cl and the ferrocenyl group.

The most abundant volatile products from the preparative reaction were BCl_3 and H_2; traces of HCl and $HBCl_2$ were also observed. A representative reaction may now be written as

$$(\pi\text{-}C_5H_5)_2Fe + B_2Cl_4 \xrightarrow[60\ \text{hr}]{0°,\ \text{hexane}} 0.61(\text{I}) + 0.73BCl_3 + \\ 0.20H_2 + 0.03HCl + HBCl_2\ (\text{trace}) + \\ \text{unreacted ferrocene and unknown solids}$$

No unreacted B_2Cl_4 was detected; the fate of all of the boron is unknown at the present time. The presence of HCl may be accounted for by our observation that BCl_3 and ferrocene react slowly in hexane at 0° to produce observable amounts of HCl and I. The evolution of hydrogen in the course of the reaction is noteworthy.[10] Hydrogen is known to react very rapidly with B_2Cl_4 to produce dichloroborane which then disproportionates to BCl_3 and B_2H_6.[11] While we observed a trace of dichloroborane, no diborane was detected. Furthermore, in view of the rapidity of the H_2–B_2Cl_4 reaction, it is surprising that the evolved hydrogen is not removed by reaction with any B_2Cl_4 which has not yet reacted with ferrocene. A possible explanation for this apparent anomaly is that B_2Cl_4 does indeed form a π complex with ferrocene as the first step in the reaction; in this condition B_2Cl_4 may not react with hydrogen. The stabilization of B_2Cl_4 by π-donor molecules has previously been noted,[12] but it is not known whether the tetrahalide is thereby rendered stable to reaction with hydrogen. The probable sources of the volatile products, as they relate to the mechanism of the ferrocene–diboron tetrachloride reaction, are currently under investigation.

Several groups of workers have shown that there is a direct correlation between the oxidation potentials of substituted ferrocenes and the electron-withdrawing properties of the substituents.[13] In order to obtain information concerning the extent of electron withdrawal by the $-BCl_2\cdot N(CH_3)_3$ group, cyclic voltammetry studies were initiated. A reversible, one-electron oxidation of II in acetonitrile occurred at an $E_{1/2}$ of 0.45 V *vs.* sce; this is characteristic of the oxidation of a ferrocene to a ferricenium complex. Since we found ferrocene to have an oxidation potential ($E_{1/2}$) of 0.42 V, it is evident that the $-BCl_2\cdot N(CH_3)_3$ group has little or no effect on the oxidation potential. Of most interest in this brief study was the observation of two, partially reversible, one-electron reduction waves at $E_{1/2} = -0.24$ and -0.93 V for compound II. Ferrocene itself is not reduced at cathodic potentials of down to -2.0 V *vs.* sce. Thus, we tentatively suggest that the substituent is the site of the reduction, but this awaits experimental proof.

Only one previous study of the reactions of diboron tetrachloride with aromatic systems has been reported; naphthalene gave rise to an addition product, whereas a substitution reaction occurred with benzene to give phenyldichloroborane.[14] It might be noted that the rate of reaction of B_2Cl_4 with ferrocene is apparently greater than with benzene; a 60% yield of ferrocenyldichloroborane was obtained in 60 hr, while 36 days was required to produce approximately the same yield of phenyldichloroborane.

Ferrocenylboronic acid and organoferrocenylboronic acids are the only boron derivatives of ferrocene previously reported in the literature.[15,16] Since a dihaloboryl group possesses a more versatile chemistry than a dihydroxyboryl group, the synthesis of ferrocenyldichloroborane opens the possibility of more extensive investigations into the properties of borane groups attached to a metallocene.

Acknowledgments. We wish to thank Dr. M. Dale Hawley and Mr. James Lawless for the cyclic voltammetry data, and Professor Riley Schaeffer for helpful discussions. We also wish to thank the Research Corporation for partial support of this research.

---

(10) The hydrogen observed in these experiments apparently arises from the B_2Cl_4–ferrocene reaction and not from the hydrolysis of B–B bonds. Every precaution was taken to ensure the absence of water; furthermore, hydrogen was evolved in all 14 reactions attempted.

(11) R. J. Brotherton in "Progress in Boron Chemistry," Vol. 1, H. Steinberg and A. L. McCloskey, Ed., The Macmillan Co., New York, N. Y., 1964, p 42.

(12) J. Feeney, A. K. Holliday, and F. J. Marsden, *J. Chem. Soc.*, 356 (1961).

(13) D. W. Hall and C. D. Russell, *J. Amer. Chem. Soc.*, **89**, 2316 (1967).

(14) W. B. Fox and T. Wartik, *ibid.*, **83**, 498 (1961).

(15) G. Marr, R. E. Moore, and B. W. Rockett, *J. Chem. Soc., C*, 24 (1968), and references therein.

(16) We thank a referee for pointing out that H. Rosenberg and F. Hedberg reported on a number of boron derivatives of ferrocene at the Third International Symposium on Organometallic Chemistry, Munich, Germany, Aug 1967.

(17) National Science Foundation Trainee, 1965–1968.

John C. Kotz, Elroy W. Post[17]
Department of Chemistry
Kansas State University, Manhattan, Kansas 66502
Received May 5, 1968

Studies on the Synthesis of Dimeric Vinca Alkaloids[1]

Sir:

The dimeric Vinca alkaloids have stimulated considerable interest from both a chemical and a biological standpoint.[2] Our continued interests in this area[3] necessitated an investigation directed at the development of a reaction which would have potential application for syntheses of the dimeric systems.

In a previous communication[4] we reported the conversion of 4β-dihydrocleavamine (I, R = R′ = H; R″ = CH_2CH_3) into its ester derivative I (R = $COOCH_3$; R′ = H; R″ = CH_2CH_3) *via* a sequence which required, as its key step, the reaction of cyanide ion with the chloroindolenine II (R = R′ = H; R″ = CH_2CH_3) to provide an 18-cyanodihydrocleavamine. We now report our results which illustrate that such chloroindolenine intermediates are also important for the synthesis of dimeric compounds.

All of the dimeric alkaloids in this family contain a carbomethoxy group at $C_{18'}$ (see, for example, IV,

---

(1) Presented by J. P. Kutney at a Symposium on the Chemistry of Natural Products, University of West Indies, Kingston, Jamaica, Jan 2–5, 1968.

(2) For a recent review of the chemistry and biological properties in this family, see "Proceedings of the First Symposium of the European Cancer Chemotherapy Group," Excerpta Medica Foundation, New York, N. Y., 1966.

(3) J. P. Kutney, K. K. Chan, A. Failli, J. M. Fromson, C. Gletsos, and V. R. Nelson, *J. Am. Chem. Soc.*, **90**, 3891 (1968).

(4) J. P. Kutney, W. J. Cretney, P. Le Quesne, B. McKague, and E. Piers, *ibid.*, **88**, 4756 (1966).