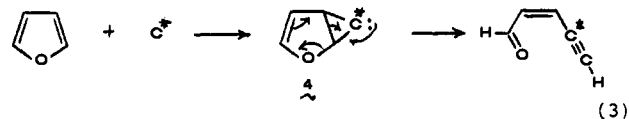


Figure 1.

carbon could be the major pathway in this system.

An alternate mode of attack is initial addition of carbon to one of the double bonds of furan to generate a cyclopropylidene intermediate **4**. The intermediacy of cyclopropylidenes has been well documented in the reaction of carbon with simple alkenes.<sup>6-8</sup> The cyclopropylidene, precluded in this system from normal rearrangement to a cumulene, could ring open as shown in eq 3.

As indicated in both eq 2 and 3, the two mechanisms for the formation of **2** may be differentiated through the use of labeled carbon atoms. In order to do this, we synthesized **1**-<sup>13</sup>C. The synthesis of the carbon-13-labeled diazo compound was accomplished using our previously reported procedure for the carbon-14-containing compound.<sup>4</sup> Authentic **2** was prepared according to the procedure of Schechter and Hoffmann<sup>5</sup> and its <sup>13</sup>C NMR measured.



Although the spectrum of **2** prepared by tosylhydrozone-lithium salt pyrolysis is complicated by the presence of a small amount of the trans isomer, we were able to assign the spectrum of *cis*-**2** as follows: C<sub>1</sub>, 191.2; C<sub>2</sub>, 139.6; C<sub>3</sub>, 127.0; C<sub>4</sub>, 88.9; C<sub>5</sub>, 77.5 ppm. The assignment of the C<sub>5</sub> resonance was confirmed by an observed *J*(<sup>13</sup>C-H) of 254.8 Hz, a typical value for terminal alkyne carbons.<sup>9</sup> When carbon-13 atoms were allowed to react with furan, the spectrum of the product showed only peaks corresponding to carbons 4 and 5. Since the yield of **2** is small, carbons which are not labeled do not appear in the spectrum. Hence, we conclude that <sup>13</sup>C atoms react with furan to generate **2** which is labeled at carbons 4 and 5. The ratio of peak height of C<sub>4</sub>:C<sub>5</sub> = 1.33 in the labeled sample as compared to C<sub>4</sub>:C<sub>5</sub> = 0.262 in the unlabeled sample allows us to calculate that **2** is 83.5% labeled at C<sub>4</sub>. Thus only a small amount of **2** arises by a C-H insertion, while the remainder probably results from addition to the double bond followed by the rearrangement shown in eq 3.

The fact that carbon atoms do not deoxygenate furan is not surprising when one considers that the furan HOMO ( $\pi_3$ ) has no electron density on oxygen.<sup>10</sup> However,  $\pi_3$  is of the proper symmetry to interact with the empty  $\pi$  orbital of atomic carbon to lower the energy of the transition state for addition to the double bond as shown in Figure 1a.

Attack of atomic carbon on an ether in which the HOMO is the nonbonding orbital on oxygen involves the HOMO-LUMO interaction in Figure 1b which favors attack on oxygen. Thus THF and other simple ethers are attacked by carbon atoms on oxygen.<sup>2</sup>

Reaction of carbenes, which also have an empty  $\pi$  orbital, with ethers appears to follow the same pattern. Thus methylene

reacts with THF to give significant quantities of products resulting from attack on oxygen.<sup>11</sup> Furan, however, gives only products of addition to the double bond and of C-H insertion.<sup>12</sup> The rearrangement shown in eq 2 may be compared with that observed when substituted carbenes are added to furans to produce, either directly<sup>13</sup> or upon heating<sup>14</sup> substituted 2,4-pentadienals.

It is anticipated that the use of <sup>13</sup>C atoms in conjunction with <sup>13</sup>C NMR will allow the detection of other rearrangements of energetic species similar to that reported here.

**Acknowledgment.** Financial support by the National Science Foundation through Grant No. MPS 75-05405 and by the Research Corporation is gratefully acknowledged.

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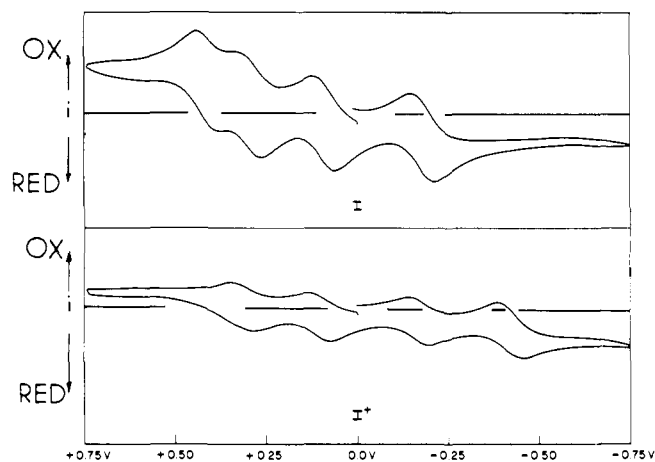
Received November 20, 1978

## Ferricenyl(III)tris(ferrocenyl(II))borate. Synthesis, Electrochemistry, and Molecular Structure of an Unusual Mixed-Valence Zwitterion

Sir:

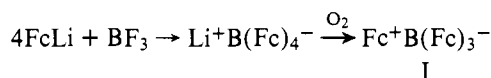
We report here our discovery of a novel mixed-valence ferrocene compound, namely, ferricenyl(III)tris(ferrocenyl(II))borate zwitterion (**I**) and our studies on its electrochemical, spectral, and structural characteristics. An X-ray crystallographic investigation of **I** has revealed its unique molecular structural features and furnishes valuable information about its electron-transfer processes. Compound **I** consists of three ferrocenyl(II) and one ferricenyl(III) moieties covalently attached to a tetravalent boron atom, hence the formal description of the complex as a zwitterion. In contrast to mixed-valence biferrocenes with  $\pi$ -bonding bridges<sup>1</sup> through which intervalence charge transfer takes place, it was anticipated that there would be little or no charge transfer through a coordinatively saturated<sup>2a</sup> boron atom. However, data presented below suggest that **I** acts as a mixed-valence system.

The reaction of an excess ferrocenyllithium, FcLi where Fc = dicyclopentadienyliron, with tri-*n*-butylborane or BF<sub>3</sub> af-

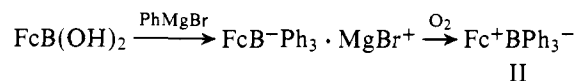


**Figure 1.** Cyclovoltamograms of  $\text{Fc}_4\text{B}$  (I) and  $\text{Fc}_4\text{B}^+$  ( $\text{I}^+$ ). The following experimental conditions obtain for both: solvent  $\text{CH}_2\text{Cl}_2$ , electrolyte  $(n\text{-Bu})_4\text{N}^+\text{BF}_4^-$ , SCE electrode as reference.

fords red tris(ferrocenyl)borane,<sup>2b</sup> mp 162–163 °C, and zwitterion I as a black, crude powder. Zwitterion I was recrystallized from  $\text{CH}_2\text{Cl}_2$ /hexane to yield black crystals. Elemental analysis for C, H, and Fe agreed well with our postulated formula  $\text{Fc}_4\text{B}$ . The overall synthesis may be represented as follows:



A similar compound, (triphenyl)(ferricenyl)borate zwitterion (II) has been reported to form from the air oxidation of (triphenyl)(ferrocenyl)borate.<sup>3</sup>



Compound II, while similar to I, lacks the interesting mixed-valence properties reported herein.

For example, I shows an electronic absorption spectrum consisting not only of bands assignable to a ferrocenyl moiety (273 nm ( $\epsilon$  40 000), 295 (24 000)) and to a ferricenyl group (480 nm ( $\epsilon$  1350), 665 (900)), but also a very broad band (900–2200 nm ( $\epsilon$  300)) with a maximum near 2200 nm. Absorptions in this spectral region have been commonly assigned as intervalence, electron-transfer transitions.<sup>1,4</sup>

Cyclovoltametry of I (Figure 1) reveals four reversible oxidation potentials at  $-0.18$ ,  $0.09$ ,  $0.29$ , and  $0.41$  V. The negative oxidation potential suggests that there is a ferricenium moiety in I. Furthermore, the positive oxidation potentials are rather low when compared with values for ferrocene or  $\pi$ -bridged ferrocene derivatives.

Complex I was quantitatively converted to its monovalent cation by a controlled current oxidation (1 F/mol), and the

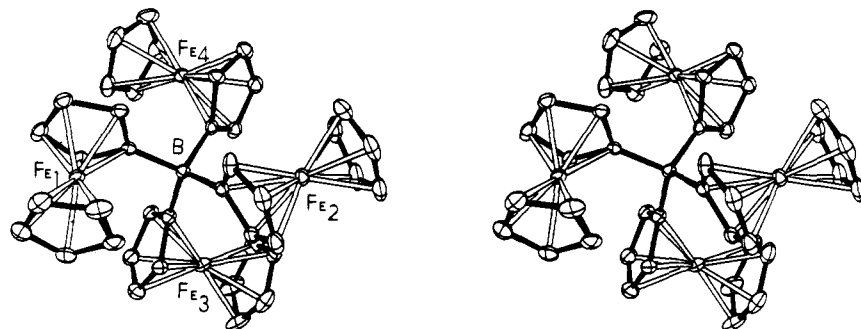
absorption spectrum of  $\text{I}^+$  was taken in  $\text{CH}_2\text{Cl}_2$ . The intervalence band in  $\text{I}^+$  is slightly narrower than that of I itself and at a somewhat higher excitation energy (1800 nm ( $\epsilon$  230–240)). The monocation was also obtained by chemical oxidation employing benzoquinone and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . Cyclovoltametry of  $\text{I}^+$  (Figure 1) shows two negative oxidation potentials for the two ferricenyl moieties ( $-0.42$  and  $-0.17$  V) and two positive oxidation potentials for the two ferrocenyl moieties (0.1 and 0.31 V).

It was decided that a molecular structure determination could aid in our understanding of the electrochemical and spectral properties of I. Crystal data for I are as follows:  $a = 17.224$  (3),  $b = 11.444$  (2),  $c = 15.547$  (3) Å;  $\beta = 94.50$  (1)°;  $V = 3055.0$  Å<sup>3</sup>;  $Z = 4$ ; space group  $P2_1/n$  (monoclinic). Intensity data for 4720 independent reflections were collected employing Mo  $K\alpha$  radiation and the  $\theta$ - $2\theta$  scan technique. The data were corrected for the usual geometric factors as well as absorption effects. The structure has been refined by full-matrix least-squares to an  $R_F$  value (anisotropic refinement of the nonhydrogen atoms) of 0.057.

The overall conformational properties of I are presented in Figure 2. While the complex is not required to possess any crystallographic symmetry, qualitatively, some elements of tetrahedral symmetry can be noted in Figure 2. In particular, the complex has a nearly threefold axis normal to the plane defined by Fe(1), Fe(2), and Fe(4). Thus one of the Fc units, that labeled Fe(3) in Figure 2, is sterically distinct. Quite surprisingly, this stereochemically distinct Fc group does not coincide with the electronically unique Fc moiety. Focusing on the centroid-to-centroid (c-t-c) distance between the two cyclopentadienyl rings in each Fc group, a clear trend is obtained. These distances in the groups defined by iron atoms 1, 2, and 3 range from 3.291 to 3.320 Å. Similar distances are observed in ferrocene<sup>5</sup> and several other ferrocenyl<sup>6</sup> derivatives. It has, however, been found that in several ferricenium salts this distance expands to  $\sim 3.4$  Å.<sup>7</sup> The observed c-t-c distance of 3.428 Å for Fe(4) seems to establish this as the ferricenyl moiety. Other parameters within the complex are in agreement with this interpretation.

In summary, then, the ferricenyl(tris(ferrocenyl))borate zwitterion contains one sterically distinct Fc group and one electronically unique Fc moiety and they are not coincident. Moreover, the presence of an intervalence electronic transition, as well as electrochemical data, establishes this inner salt as a mixed-valence system. The intervalence charge-transfer mechanism in I is probably different from the common through-bond electron transfer in  $\pi$ -bonded biferrrocene complexes. We suggest that the electron-transfer mechanism in I may proceed via a through-space mechanism.

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**Figure 2.** A stereoview of the molecular conformation of the ferricenyl(III)tris(ferrocenyl(II))borate inner salt.

Professor Richard Holm and the Stanford Chemistry Department for their hospitality during a portion of the 1977-1978 academic year.

**Supplementary Material Available:** Final atomic positional parameters as well as a listing of observed and calculated structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

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## Hydrogenation of Small Molecules by Transition Metal Cluster Hydrides. Reaction of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with Carbon Disulfide

Sir:

The hydrogenation of small molecules by transition metal cluster hydrides is presently an area of intense study.<sup>1</sup> In connection with our studies on the hydrogenation abilities of  $\text{H}_2\text{Os}_3(\text{CO})_{10}$ ,<sup>1d</sup> we have investigated its reaction with carbon disulfide. Here we report that we have found an unusual di-cluster reaction in which two triosmium clusters cooperatively attack and reduce a single molecule of carbon disulfide.

Over a period of 34 hr a solution of  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  in refluxing  $\text{CS}_2$  solvent slowly changes color from purple to yellow. This is accompanied by the formation of a brown precipitate. From the solution we have isolated<sup>2</sup> (21% yield) a yellow compound which we have analyzed as  $\text{H}_2\text{CS}_2[\text{HOs}_3(\text{CO})_{10}]_2$  on the basis of IR,<sup>3</sup> <sup>1</sup>H NMR, and X-ray crystallographic analyses.<sup>4</sup> The molecular structure is shown in Figure 1. Two regular  $\text{HOs}_3(\text{CO})_{10}$  groupings are bridged by an S-CH<sub>2</sub>-S ligand.<sup>5,6</sup> Each sulfur atom bridges two osmium atoms in separate cluster units. The S( $\mu$ -H)Os<sub>3</sub>(CO)<sub>10</sub> units are structurally similar to those observed in related monocluster systems.<sup>7</sup> Although the hydrogen atoms were not observed crystallographically, the presence of two hydrogen atoms on the carbon atom of the S-CH<sub>2</sub>-S bridge is indicated by the following considerations. The <sup>1</sup>H NMR spectrum shows only two resonances which are at  $\delta$  2.92 and -17.46 ppm with relative intensities of ~1:1. We assign the latter to a combination

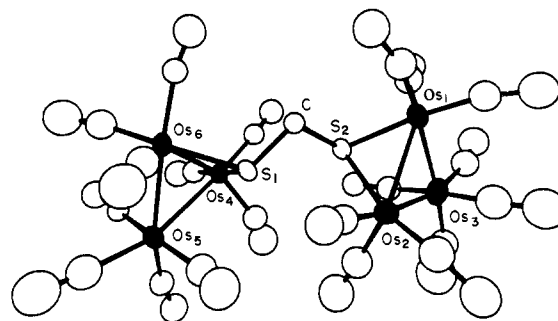


Figure 1. ORTEP diagram of  $(\text{H}_2\text{CS}_2)[(\text{H})\text{Os}_3(\text{CO})_{10}]_2$  showing 50% probability ellipsoids.

of equivalent bridging hydride ligands (one from each cluster) and the former to a methylene group. An alternative formulation as a dithioformate is considered most unlikely since the proton shifts in these ligands lie in the very characteristic region  $\delta$  10.0-15.0 ppm.<sup>8</sup> Structural considerations also support the formulation as a *gem*-dithiamethylene group. The C-S distances of 1.82 (2) and 1.86 (2) Å are similar to the distances 1.81-1.82 Å found in both monothia-<sup>9</sup> and *gem*-dithiaalkanes<sup>10</sup> and the 1.89 (4) Å found for the compound  $(\mu\text{-H})(\mu\text{-SC}_2\text{H}_5)\text{Os}_3(\text{CO})_{10}$ .<sup>7b</sup> In contrast the C-S distances in dithioformate ligands are considerably shorter and lie in the range 1.64-1.68 Å.<sup>11,12</sup>

The ligand behavior of carbon disulfide has been demonstrated in numerous metal complexes.<sup>14</sup> Carbon disulfide reacts with mononuclear metal hydrides to produce complexes containing chelating dithioformate ligands.<sup>8,11,15</sup> Our reaction shows that the cluster reduction proceeds one step farther to a  $\text{CH}_2\text{S}_2^{2-}$  unit which might be viewed as a precursor of dithioacetal. The reason for this is presently unclear, but may center on the tendency of sulfur atoms to favor bridging positions across two metal atoms. The greater reducing effects produced by the bridging environment may promote reduction reactions beyond the dithioformate stage. Efforts to produce still further reduction of the  $\text{CH}_2\text{S}_2$  unit are currently in progress.

**Acknowledgment.** Support of this research under Contract No. ER-78-S-02-4900 from the Office of Basic Energy Sciences, U.S. Department of Energy, is gratefully acknowledged. We thank Engelhard Industries for a gift of osmium tetroxide.

**Supplementary Material:** Fractional atomic coordinates (1 page). Ordering information is given on any current masthead page.

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- (2) The compound was isolated by column chromatography over  $\text{Al}_2\text{O}_3$ -6%  $\text{H}_2\text{O}$  with benzene solvent.
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- (4) Crystal data:  $a = 10.067$  (9),  $b = 13.240$  (7),  $c = 13.794$  (5) Å;  $\alpha = 84.59$  (3)°,  $\beta = 75.45$  (4)°,  $\gamma = 88.23$  (6)°; space group  $P\bar{1}$ ;  $Z = 2$ . Diffraction data were collected on an Enraf-Nonius CAD-4 automatic diffractometer; 3780 reflections ( $F^2 \geq 3.0\sigma(F^2)$ ) were used in the structure solution and refinement. The structure was solved by the heavy-atom method. All programs used were those of the Enraf-Nonius structure determination program library. Current values of the residuals are  $R = 0.051$  and  $R_w = 0.061$ .
- (5) Selected bond distances (angstroms): Os(1)-Os(2) = 2.867 (1), Os(1)-Os(3) = 2.872 (1), Os(2)-Os(3) = 2.854 (1), Os(4)-Os(5) = 2.875 (1), Os(4)-Os(6) = 2.871 (1), Os(5)-Os(6) = 2.875 (1), Os(1)-S(2) = 2.403 (4), Os(2)-S(2) = 2.414 (4), Os(4)-S(1) = 2.411 (4), Os(6)-S(1) = 2.419 (4), C-S(1) = 1.86(2), C-S(2) = 1.82(2).
- (6) Selected bond angles (degrees): Os(3)-Os(1)-Os(2) = 59.65 (2), Os(1)-Os(2)-Os(3) = 60.27 (3), Os(1)-Os(3)-Os(2) = 60.08 (2), Os(5)-Os(4)-Os(6) = 60.04 (2), Os(4)-Os(5)-Os(6) = 59.92 (2), Os(4)-Os(6)-Os(5) = 60.04 (2), Os(1)-S(2)-Os(2) = 73.0 (1), Os(4)-S(1)-Os(6) = 73.0 (1), Os(1)-S(2)-C = 110.2 (5), Os(2)-S(2)-S(2)-C = 110.0 (5), Os(4)-S(1)-C = 112.4 (5), Os(6)-S(1)-C = 114.4 (5), S(1)-C-S(2) = 105.3 (8).
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