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## Synthesis and Characterization of a Biferrocene with a Fulvalene Ligand Fused into a Cis Conformation: X-ray Structure of *N,N*-Dimethyl-2,5''-(2-azoniapropane-1,3-diyl)biferrocene Pentaide

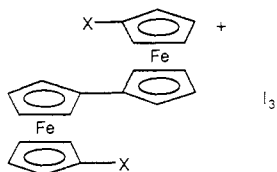
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The preparation and characterization of the first side-by-side fused biferrocenes are reported. 2,5''-Bis(dimethylamino)methylbiferrocene was used to prepare *N,N*-dimethyl-2,5''-(2-azoniapropane-1,3-diyl)biferrocene iodide (**12**). Reaction of **12** with I<sub>2</sub> in solution gives the analogous pentaide salt *N,N*-dimethyl-2,5''-(2-azoniapropane-1,3-diyl)biferrocene pentaide (**17**). Reaction of **12** with LiBH(sec-Bu)<sub>3</sub> gives the nonsalt fused biferrocene *N*-methyl-2,5''-(2-azoniapropane-1,3-diyl)biferrocene (**13**). Results from the X-ray structure of **17** show that this I<sub>3</sub><sup>-</sup> salt crystallizes in the orthorhombic space group *Pbca* with eight formula units in a cell having the dimensions *a* = 16.087 (6) Å, *b* = 17.796 (6) Å, and *c* = 20.839 (10) Å. Discrete I<sub>3</sub><sup>-</sup> anions and Fe<sup>II</sup><sub>2</sub> ammonium cations are present. The fulvalene ligand has a -CH<sub>2</sub>-N(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>- moiety fused between the 2- and 5''-positions. H...H contacts in the cation lead to a 38.4° dihedral angle in the fulvalene ligand. The cation can be described as two ferrocene moieties fused together in a side-by-side fashion with Fe...Fe = 4.571 (3) Å. <sup>57</sup>Fe Mössbauer data for **12**, **13**, and **17** show that these molecules are Fe<sup>II</sup><sub>2</sub> compounds. The Fe<sup>II</sup><sub>2</sub> cations in **12** and **13** are not easily oxidized. Complex **13** in CH<sub>3</sub>CN shows two one-electron reversible oxidation waves at 252 and 616 mV vs Ag/AgCl. The separation between the two waves in **13** is greater than that reported for the two waves for ferrocene in CH<sub>3</sub>CN. Chemical oxidation of **13** with I<sub>2</sub>, DDQ, or ferrocenium hexafluorophosphate in solution gives an I<sub>3</sub><sup>-</sup>, DDQH<sup>+</sup>, or PF<sub>6</sub><sup>-</sup> salt that is not an Fe<sup>II</sup>Fe<sup>III</sup> complex but is apparently an Fe<sup>II</sup><sub>2</sub> carbocation where there is a net hydride abstraction from the -CH<sub>2</sub>-NH(CH<sub>3</sub>)-CH<sub>2</sub>- bridge to form the carbocation.

### Introduction

The study of intramolecular electron transfer in mixed-valence complexes<sup>3</sup> has given insight into the factors that affect rates of electron transfer in solution redox processes, solid-state materials,<sup>4</sup> and biological electron-transport chains.<sup>5</sup> In the case of mixed-valence biferrocenium salts such as **1-8** the solid-state envi-



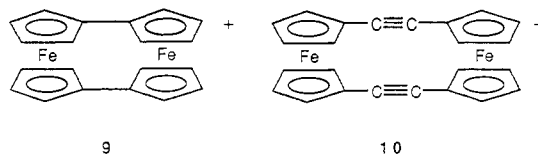
- |           |   |
|-----------|---|
| 1, X = I  | 5, X = -CH <sub>2</sub> CH <sub>3</sub>                                 |
| 2, X = Br | 6, X = -CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>                 |
| 3, X = Cl | 7, X = -CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> |
| 4, X = H  | 8, X = -CH <sub>2</sub> Ph  |

ronment has been shown to play a crucial role in determining the rate of intramolecular electron transfer.<sup>6</sup> For all of the complexes **1-8** there is a barrier for electron transfer, as indicated by IR spectra that show the presence of both Fe<sup>II</sup> and Fe<sup>III</sup> ions.<sup>6a</sup>

Complexes **1** and **2** transfer electrons at a rate greater than  $\sim 10^{10}$  s<sup>-1</sup> not only at 300 K but also at 4.2 K.<sup>6b,c</sup> The X-ray structures of these two complexes show that there is a C<sub>2</sub> axis relating the two iron ions in a cation. This results in a double-well potential-energy surface for the ground state of the cations in **1** and **2** where both vibronic states of the cation, Fe<sup>II</sup>Fe<sup>III</sup> and Fe<sup>III</sup>Fe<sup>II</sup>, are at the same energy. Fast electron/nuclear tunneling is facilitated. On the other hand, the cation in **3** has inequivalent iron ions as a result of the solid-state environment.<sup>6b,c</sup> The two vibronic states of the cation in **3** are at different zero-point energies. This considerably reduces the probability of tunneling, and the rate of transfer in **3** is less than  $\sim 10^7$  s<sup>-1</sup> at 340 K. Converting from a rate  $> \sim 10^{10}$  s<sup>-1</sup> for **1** and **2** at 4.2 K to a rate  $< \sim 10^7$  s<sup>-1</sup> for **3** at 340 K is an immense change in rates.

The situation in **4-8** is even more fascinating. At temperatures below  $\sim 200$  K these complexes show both an Fe<sup>II</sup> and Fe<sup>III</sup> doublet in their Mössbauer spectra.<sup>6d</sup> At higher temperatures these spectra show only one average-valence doublet. However, the temperature dependencies of the spectra are not simple. There is not evidence of line broadening at intermediate temperatures; that is, the rate of the process causing the change in these spectra is at all temperatures faster than the Mössbauer technique can sense ( $> \sim 10^8$  s<sup>-1</sup>). In the case of biferrocenium triiodide (**4**) a phase transition has been shown to be involved.<sup>6e,f</sup> In view of the appreciable intercation interactions occurring in stacks in these salts it is likely that it is the onset of some lattice disturbance such as solitons<sup>7</sup> that causes the change in the effective rate of intramolecular electron transfer.

In addition to changing the solid-state environment to probe the factors affecting electron transfer, the architecture of the mixed-valence biferrocenium cation can be modified. Complexes **9**<sup>8</sup> and **10**<sup>6a,9</sup> have delocalized electronic structures. In terms of



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- (1) University of Illinois.  
 (2) University of California at San Diego.  
 (3) For recent reviews, see: (a) Day, P. *Int. Rev. Phys. Chem.* **1981**, *1*, 149. (b) Brown, D. B., Ed. *Mixed-Valence Compounds, Theory and Applications in Chemistry, Physics, Geology and Biology*; Reidel Publishing Co.: Boston, MA, 1980. (c) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1-73. (d) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107-129.  
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 (6) (a) Kramer, J. A.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 3330. (b) Dong, T.-Y.; Cohn, M. J.; Hendrickson, D. N.; Pierpont, C. G. *J. Am. Chem. Soc.* **1985**, *107*, 4777. (c) Dong, T.-Y.; Hendrickson, D. N.; Pierpont, C. G.; Moore, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 963. (d) Dong, T.-Y.; Hendrickson, D. N.; Iwai, K.; Cohn, M. J.; Rheingold, A. L.; Sano, H.; Motoyama, I.; Nakashima, S. *J. Am. Chem. Soc.* **1985**, *107*, 7996. (e) Sorai, M.; Nishimori, A.; Hendrickson, D. N.; Dong, T.-Y.; Cohn, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 4266. (f) Kambara, T.; Hendrickson, D. N.; Dong, T.-Y.; Cohn, M. J. *J. Chem. Phys.* **1987**, *86*, 2362. (g) Dong, T.-Y.; Kambara, T.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1986**, *108*, 5857. (h) Dong, T.-Y.; Kambara, T.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1986**, *108*, 4423. (i) Sinha, U.; Lowery, M. D.; Ley, W. W.; Drickamer, H. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 2471. (j) Hendrickson, D. N.; Oh, S. M.; Dong, T.-Y.; Moore, M. F. *Comments Inorg. Chem.* **1985**, *4*, 329.

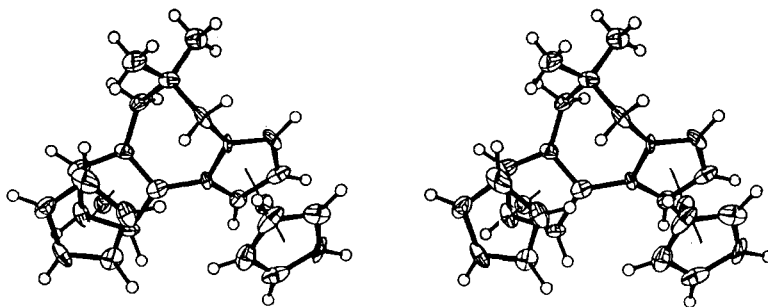
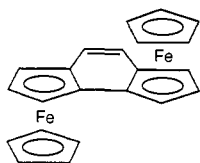


Figure 1. Stereoview of the  $\text{Fe}^{\text{II}}_2$  cation in *N,N*-dimethyl-2,5''-(2-azoniapropane-1,3-diyl)biferrocene pentaiodide (**17**).

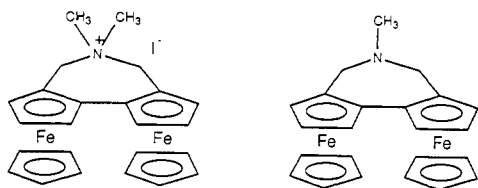
the PKS vibronic model<sup>10</sup> for mixed-valence complexes this means that the electronic coupling ( $\epsilon$ ) between orbitals on the  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  moieties, as propagated either by direct overlap of d orbitals or by the orbitals of the bridge, is so large that there is no potential-energy barrier for electron transfer. The single unpaired electron is in a molecular orbital that has equal contributions from both iron ions. The electronic coupling  $\epsilon$  in complexes **1–8** must be much smaller than in complexes **9** and **10**. In complexes **1–8** the fulvalene ligand is planar with the iron ions on opposite sides of this ligand and  $\text{Fe}\cdots\text{Fe} \approx 5.1 \text{ \AA}$ . Five different biferrocenes have been reported<sup>11–13</sup> where the trans conformation as pictured for **1–8** is held rigid by a bridge between the 2,2'-positions of the  $\eta^5, \eta^5$ -fulvalene ligand. A mixed-valence salt has been described for only one of these five trans-conformation fused biferrocenes. Iijima et al.<sup>13a</sup> reported the preparation of *trans*-( $\mu$ -*as*-indacene)bis(cyclopentadienyliron) (**11**) and the  $\text{I}_3^- \cdot 0.5\text{I}_2$  mix-



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ed-valence salt of **11**. The rate of electron transfer becomes faster than the <sup>57</sup>Fe Mössbauer time scale for this salt in the 100–200 K range.<sup>13b</sup>

In this paper we report the preparation and characterization of the first fused biferrocenes that have cis conformation, complexes **12** and **13**. The single-crystal X-ray structure of the  $\text{I}_5^-$  salt of the ammonium cation **12** is given.



12

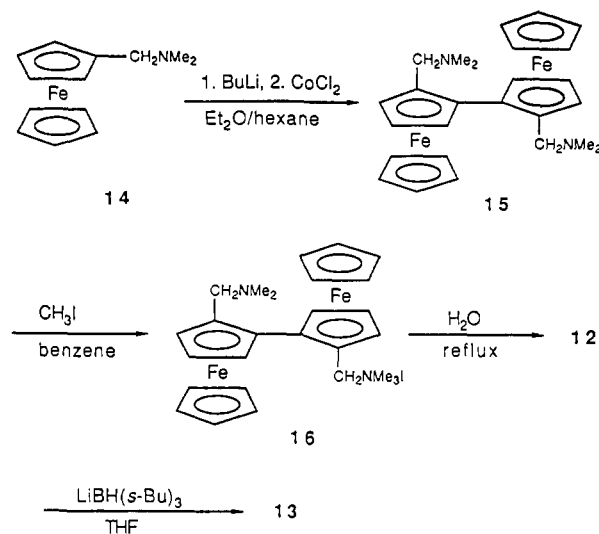
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## Results and Discussion

**Compound Preparation.** The fused biferrocenes **12** and **13** were

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- (12) Davison, A.; Rudie, A. W. *J. Organomet. Chem.* **1979**, *169*, 69.
- (13) (a) Iijima, S.; Motoyama, I.; Sano, H. *Chem. Lett.* **1979**, 1349. (b) Iijima, S.; Motoyama, I.; Sano, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3180.

## Scheme I

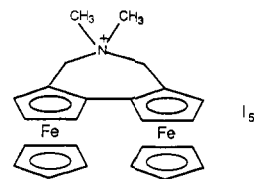


synthesized as indicated in Scheme I.

((Dimethylamino)methyl)biferrocene was lithiated with *n*-BuLi to give 2-lithio((dimethylamino)methyl)ferrocene, which upon reaction with  $\text{CoCl}_2$  gave 2,5''-bis((dimethylamino)methyl)biferrocene (**15**). When the monomethiodide of **15** (i.e., **16**) was heated in water, biferrocene **12** was obtained in high yield. This  $\text{Fe}^{\text{II}}_2$  compound has a fused structure wherein there is a cis conformation of the biferrocene, in contrast to the trans conformation of previously reported<sup>11–13</sup> fused biferrocenes. The amine moiety in **16** strongly competes with other nucleophiles to form the cation **12**. When **16** was treated with 2%–50% NaOH solution, only the ammonium cation **12** was obtained. Even in 15% acetic acid solution where **3** is protonated, the cation **12** was still the only product formed. The failure to cleave the seven-membered ring of cation **12** in aqueous NaOH demonstrates that cation **12** is stable to attack by nucleophiles.

It is known<sup>14</sup> that a tetraalkylammonium iodide with at least one methyl substituent will give a trialkylamine by treatment with  $\text{LiBHET}_3$ . In our case,  $\text{LiBH}(\text{sec-Bu})_3$  was used as a hydride source. The cyclic amine **13** was formed smoothly in good yield.

Compound **12** when dissolved in a variety of solvents has a pronounced tendency to form polyiodides upon the addition of  $\text{I}_2$  to the solution. This is a common behavior of organic ammonium halides. A triiodide salt of the cation of **12** (**19**) and a pentaiodide salt (**17**) were obtained as microcrystalline solids by



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**Table I.** Crystal and Experimental Data for *N,N*-Dimethyl-2,5''-(2-azoniapropane-1,3-diyl)biferrocene Pentaiodide (17)

formula	C <sub>24</sub> H <sub>26</sub> NFe <sub>2</sub> I <sub>5</sub>
cryst system	orthorhombic
space group	<i>Pbca</i>
<i>a</i> , Å	16.087 (6)
<i>b</i> , Å	17.796 (6)
<i>c</i> , Å	20.839 (10)
<i>V</i> , Å <sup>3</sup>	5966 (4)
<i>Z</i>	8
<i>d</i> (calc), g/cm <sup>3</sup>	2.393
radiation (Mo Kα) λ, Å	0.710 73 (graphite monochromator)
μ, cm <sup>-1</sup>	61.11
2θ limit, deg (octants)	46 (+ <i>h</i> , + <i>k</i> , + <i>l</i> ), 7 (± <i>h</i> , ± <i>k</i> , ± <i>l</i> )
no. of intensities (no. of unique intensities, <i>R</i> <sub>1</sub> )	5195 (4169, 0.016)
no. of intensities > 2.58σ( <i>I</i> )	2090
<i>R</i>	0.052
<i>R</i> <sub>w</sub> <sup>a</sup>	0.056

$$^a w = 1/(\sigma^2(F_o) + pF_o^2); p = 0.02.$$

**Table II.** Positional Parameters for *N,N*-Dimethyl-2,5''-(2-azoniapropane-1,3-diyl)biferrocene Pentaiodide (17)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
I(1)	0.0375 (1)	0.7537 (1)	0.32932 (8)
I(2)	0.16146 (8)	0.72070 (7)	0.24150 (7)
I(3)	0.2910 (1)	0.69212 (9)	0.13482 (9)
I(4)	0.34073 (9)	0.85812 (9)	0.11842 (8)
I(5)	0.3863 (1)	1.0080 (1)	0.1004 (1)
Fe(1)	0.1950 (2)	0.4836 (1)	0.3830 (1)
Fe(2)	0.0555 (2)	0.2633 (1)	0.4162 (1)
N	-0.0425 (8)	0.4771 (9)	0.3358 (8)
C(1)	0.209 (1)	0.493 (1)	0.283 (1)
C(2)	0.269 (1)	0.538 (1)	0.316 (1)
C(3)	0.317 (1)	0.490 (1)	0.356 (1)
C(4)	0.288 (1)	0.416 (1)	0.346 (1)
C(5)	0.223 (1)	0.417 (1)	0.304 (1)
C(6)	0.076 (1)	0.507 (1)	0.4150 (9)
C(7)	0.134 (1)	0.565 (1)	0.4336 (9)
C(8)	0.197 (1)	0.534 (1)	0.4701 (10)
C(9)	0.1797 (10)	0.4537 (9)	0.4780 (9)
C(10)	0.103 (1)	0.436 (1)	0.4419 (9)
C(11)	0.0485 (9)	0.3734 (9)	0.4457 (9)
C(12)	-0.010 (1)	0.3586 (9)	0.3966 (8)
C(13)	-0.062 (1)	0.304 (1)	0.4169 (10)
C(14)	-0.035 (1)	0.282 (1)	0.4800 (10)
C(15)	0.033 (1)	0.3246 (10)	0.4964 (9)
C(16)	0.055 (1)	0.170 (1)	0.359 (1)
C(17)	0.084 (1)	0.1522 (9)	0.421 (1)
C(18)	0.155 (1)	0.197 (1)	0.433 (1)
C(19)	0.170 (1)	0.240 (1)	0.381 (1)
C(20)	0.110 (2)	0.224 (1)	0.334 (1)
C(21)	-0.010 (1)	0.5205 (9)	0.3933 (8)
C(22)	-0.006 (1)	0.3979 (9)	0.3341 (9)
C(23)	-0.018 (1)	0.521 (1)	0.2770 (9)
C(24)	-0.1338 (1)	0.473 (1)	0.3401 (9)

adding the stoichiometric amount of iodine to a solution of **12**. In the case of these I<sub>3</sub><sup>-</sup> and I<sub>5</sub><sup>-</sup> salts the two iron ions have not been oxidized; the cation in both cases has an Fe<sup>II</sup><sub>2</sub> constitution (vide infra).

**X-ray Structure of *N,N*-Dimethyl-2,5''-(2-azoniapropane-1,3-diyl)biferrocene Pentaiodide (17).** Compound **17** crystallizes at 299 K in the orthorhombic space group *Pbca*. Table I summarizes the crystallography details. Tables II and III list the positional parameters and selected bond distances and angles, respectively.

Discrete I<sub>5</sub><sup>-</sup> anions and Fe<sup>II</sup><sub>2</sub> cations are present. No crystallographic symmetry is imposed on either the cation or the anion. A stereoview of the molecular structure of the Fe<sup>II</sup><sub>2</sub> cation is shown in Figure 1. Overall this biferrocene cation can be described as two ferrocene moieties fused together in a side-by-side fashion, where the dihedral angle between the two ferrocene moieties is approximately 40°. The side-by-side positioning of the two ferrocene units leads to interactions between protons on the two

**Table III.** Interatomic Dimensions for *N,N*-Dimethyl-2,5''-(2-azoniapropane-1,3-diyl)biferrocene Pentaiodide (17)

Distances (Å)			
C(1)–C(2)	1.43 (3)	C(16)–C(17)	1.40 (4)
C(2)–C(3)	1.41 (3)	C(17)–C(18)	1.42 (3)
C(3)–C(4)	1.42 (3)	C(18)–C(19)	1.35 (3)
C(4)–C(5)	1.37 (3)	C(19)–C(20)	1.40 (4)
C(5)–C(1)	1.44 (3)	C(20)–C(16)	1.40 (3)
C(6)–C(7)	1.44 (3)	C(11)–C(12)	1.42 (2)
C(7)–C(8)	1.38 (3)	C(12)–C(13)	1.35 (2)
C(8)–C(9)	1.46 (2)	C(13)–C(14)	1.44 (3)
C(9)–C(10)	1.47 (2)	C(14)–C(15)	1.37 (3)
C(10)–C(6)	1.45 (3)	C(15)–C(11)	1.39 (3)
Fe(1)–C(1)	2.10 (2)	Fe(2)–C(16)	2.04 (2)
Fe(1)–C(2)	2.08 (2)	Fe(2)–C(17)	2.03 (2)
Fe(1)–C(3)	2.04 (2)	Fe(2)–C(18)	2.01 (2)
Fe(1)–C(4)	2.07 (2)	Fe(2)–C(19)	2.03 (2)
Fe(1)–C(5)	2.08 (2)	Fe(2)–C(20)	2.05 (3)
Fe(1)–C(6)	2.07 (2)	Fe(2)–C(11)	2.06 (2)
Fe(1)–C(7)	2.04 (2)	Fe(2)–C(12)	2.04 (2)
Fe(1)–C(8)	2.03 (2)	Fe(2)–C(13)	2.03 (2)
Fe(1)–C(9)	2.07 (2)	Fe(2)–C(14)	2.00 (2)
Fe(1)–C(10)	2.09 (2)	Fe(2)–C(15)	2.03 (2)
C(6)–C(21)	1.48 (2)	C(12)–C(22)	1.48 (2)
C(21)–N	1.52 (2)	C(22)–N	1.53 (2)
C(23)–N	1.50 (2)	C(24)–N	1.47 (2)
C(10)–C(11)	1.43 (2)	I(1)–I(2)	2.770 (2)
I(2)–I(3)	3.089 (2)	I(3)–I(4)	3.080 (2)
I(4)–I(5)	2.791 (3)	Fe(1)⋯Fe(2)	4.571 (3)

Angles (deg)			
C(1)–C(2)–C(3)	108 (2)	C(16)–C(17)–C(18)	107 (2)
C(2)–C(3)–C(4)	107 (2)	C(17)–C(18)–C(19)	109 (2)
C(3)–C(4)–C(5)	109 (2)	C(18)–C(19)–C(20)	108 (2)
C(4)–C(5)–C(1)	109 (2)	C(19)–C(20)–C(16)	108 (2)
C(5)–C(1)–C(2)	106 (2)	C(20)–C(16)–C(17)	107 (2)
C(6)–C(7)–C(8)	110 (2)	C(11)–C(12)–C(13)	109 (2)
C(7)–C(8)–C(9)	108 (2)	C(12)–C(13)–C(14)	107 (2)
C(8)–C(9)–C(10)	108 (1)	C(13)–C(14)–C(15)	109 (2)
C(9)–C(10)–C(6)	106 (1)	C(14)–C(15)–C(11)	108 (2)
C(10)–C(6)–C(7)	109 (2)	C(15)–C(11)–C(12)	108 (1)
C(6)–C(10)–C(11)	121 (2)	C(10)–C(11)–C(12)	121 (2)
C(11)–C(12)–C(22)	121 (1)	C(12)–C(22)–N	114 (1)
C(22)–N–C(21)	111 (1)	N–C(21)–C(6)	119 (1)
C(21)–C(6)–C(10)	123 (2)	C(21)–N–C(23)	107 (1)
C(21)–N–C(24)	109 (1)	C(22)–N–C(23)	111 (1)
C(22)–N–C(24)	110 (1)	C(23)–N–C(24)	109 (1)
I(1)–I(2)–I(3)	174.95 (7)	I(2)–I(3)–I(4)	95.57 (6)
I(3)–I(4)–I(5)	178.64 (9)		

Angles between Planes (deg) <sup>a</sup>			
Cp(1)–Cp(2)	8.29	Cp(1)–Cp(3)	141.55
Cp(1)–Cp(4)	41.30	Cp(2)–Cp(3)	141.64
Cp(2)–Cp(4)	40.93	Cp(3)–Cp(4)	177.00

<sup>a</sup> Cp(1): C(1)–C(5). Cp(2): C(6)–C(10). Cp(3): C(11)–C(15). Cp(4): C(16)–C(20).

unsubstituted cyclopentadienyl ligands, and this leads to a twisted structure. The fulvalenide ligand is twisted with a dihedral angle between ring 2 (C(6)–C(10)) and ring 3 (C(11)–C(15)) of 38.4°, which is even larger than seen<sup>15</sup> for the dihedral angle in [1,1]-ferrocenophanes. The central C–C bond distance in the fulvalenide ligand, i.e., C(10)–C(11), is 1.43 (2) Å, which is slightly shorter than that (1.48 Å)<sup>16</sup> in biferrocene. The short C(10)–C(11) bond distance may result from a conjugation between the two ferrocene moieties in **17** that is greater than in biferrocene, but this seems unlikely.

Cyclopentadienyl ring 1 (C(1)–C(5)) and ring 2 associated with Fe(1) are not parallel; the dihedral angle between them is equal to 8.3°, which is the largest inclination angle observed for biferrocene compounds. The dihedral angle between ring 3 and ring 4 (C(16)–C(20)) bonded to Fe<sub>2</sub> is smaller (3.0°).

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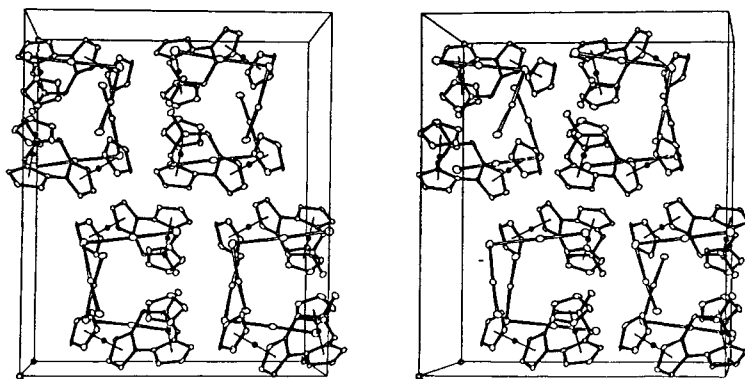


Figure 2. Stereoview of the packing of  $I_5^-$  anions and  $Fe^{II}_2$  cations in *N,N*-dimethyl-2,5''-(2-azoniapropane-1,3-diyl)biferrocene pentaiodide (**17**).

The twist in the fulvalenide ligand effectively eliminates strong contacts between the two unsubstituted cyclopentadienyl rings. The *N*-methyl carbon atom C(23), however, is less than 2.4 Å from the ring 1 plane and less than 3.7 Å from atom C(1). Considering the van der Waals radius for a methyl group and the half-thickness of an aromatic ring,<sup>17</sup> this repulsive contact apparently determines the large inclination angle between rings 1 and 2 and, in conjunction with the tetrahedral geometry of the ammonium bridge, influences the torsional distortion (38.4°) of the fulvalenide ligand. On the basis of bond lengths and planarity, distortion of this ligand appears to cause a partial isolation of multiple C–C bonds in ring 3, which shortens the length of the C(10)–C(11) bond. The repulsion between ring 1 and the bridge atom C(23) also forces the distance between Fe(1) and the ring 1 plane (1.69 Å) to be greater than that in ferrocene (1.65 Å) and curiously close to the value of the  $Fe^{III}$ –ring distance in the ferrocenium cation (1.69 Å).<sup>18b</sup>

The Fe...Fe distance in this compound is 4.57 (3) Å, which is shorter than the ~5.1 Å observed<sup>6</sup> for the biferrocenium salts **1**–**8**. It is a distance close to the Fe...Fe distance of ~4.6 Å in unoxidized [1,1]ferrocenophane and its derivatives.<sup>19</sup> However, the Fe...Fe distance in **17** is much longer than that of the other "side-by-side" molecules, e.g., bis(fulvalene)diiron has an Fe...Fe distance of 3.98 Å.<sup>20</sup>

The pentaiodide anion has a normal V-shaped array in which two iodine molecules are bonded to the central iodide ion. All of the I–I bond distances are within the normal range for a  $I_5^-$  anion.<sup>21</sup>

The packing of the  $I_5^-$  anions and  $Fe^{II}_2$  cations in the unit cell is illustrated in Figure 2. It is evident that the crystal lattice is composed of interwoven layers of biferrocene cations and  $I_5^-$  anions aligned normal to the *c* axis.

**Physical Properties of Complexes 12, 13, and 17.** <sup>1</sup>H NMR spectra were run for solutions of **12**, **13**, and **17**. Chemical shift data are summarized in the Experimental Section. The two protons on each of the CH<sub>2</sub> moieties in the bridge exhibit different peaks, caused by the different chemical environments for these two protons. The coupling constant (13 Hz) between the two *gem* protons on each CH<sub>2</sub> moiety is normal for a methylene group. The observation that in the <sup>1</sup>H NMR spectrum for either **12**, **13**, or **17** there is only a single resonance for all 10 protons on the two unsubstituted Cp rings indicates that in solution each of these fused biferrocenes is fluxional with a rapid intramolecular conformational equilibrium averaging the magnetic environments of all 10 protons. In the solid-state structure of **17** the two unsubstituted Cp rings are inequivalent.

Table IV. <sup>57</sup>Fe Mössbauer Fitting Parameters<sup>a</sup>

compd	<i>T</i> , K	$\Delta E_Q$ , mm/s	$\delta$ , <sup>b</sup> mm/s	$\Gamma$ , <sup>c</sup> mm/s	
<b>14</b>	110	2.288 (2)	0.499 (1)	0.147 (1)	0.136 (1)
<b>13</b>	110	2.435 (3)	0.498 (1)	0.161 (2)	0.165 (2)
<b>17</b>	110	2.446 (6)	0.499 (3)	0.151 (6)	0.146 (5)
<b>19</b>	110	2.349 (2)	0.488 (1)	0.159 (2)	0.158 (2)
	300	2.279 (6)	0.494 (3)	0.144 (6)	0.142 (6)
<b>20</b>	110	2.446 (27)	0.499 (13)	0.151 (25)	0.146 (24)
<b>21</b>	110	2.322 (2)	0.500 (1)	0.164 (2)	0.165 (2)
	295	2.332 (4)	0.492 (2)	0.134 (4)	0.133 (3)

<sup>a</sup> Estimated standard deviations in the least significant figures are given in parentheses. <sup>b</sup> Isomer shifts relative to iron metal at room temperature. <sup>c</sup> Full width at half-height taken from the least-squares fitting program. The width for the line at more negative velocity is listed first for each doublet.

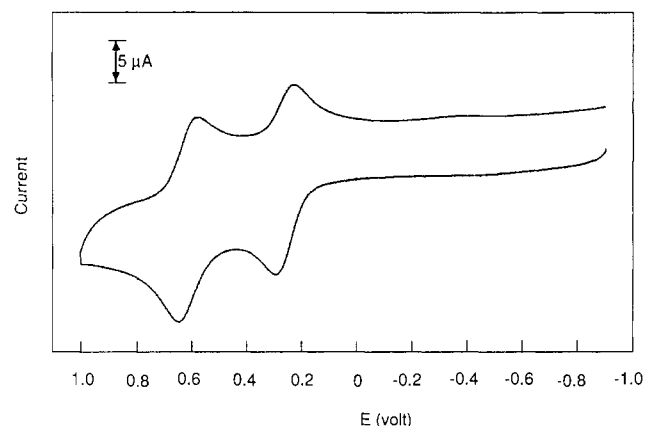


Figure 3. Cyclic voltammogram for *N*-methyl-2,5''-(2-azapropane-1,3-diyl)biferrocene in CH<sub>3</sub>CN. Potentials are shown relative to an Ag/AgCl reference electrode.

<sup>57</sup>Fe Mössbauer spectra were run at 110 K for complexes **12**, **13**, and **17**. In all three cases one quadrupole-split doublet is observed. Each spectrum was least-squares fit to Lorentzian line shapes. The resulting fitting parameters are given in Table IV. It is clear from these parameters that all three of these complexes contain only  $Fe^{II}$  metallocene units. That is, the cation in **17** is a  $Fe^{II}_2$  cation.

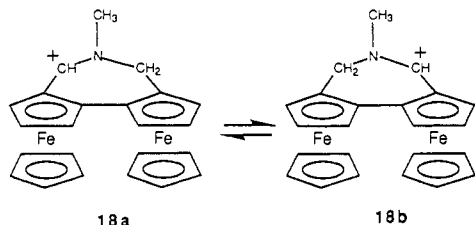
Cyclic voltammetry experiments were carried on complexes **12**, **13**, and **17**. The iodide complex **12** and pentaiodide complex **17** failed to give any CV wave in the range –900 to +1500 mV vs Ag/AgCl. The failure to see oxidation waves for the  $Fe^{II}$  metallocene moieties in these two complexes is very likely due to the fact that  $I^-$  (or  $I_3^-$ ) is being oxidized first and interferes with the metallocene oxidation. The uncharged amine-bridged biferrocene **13** was found to exhibit two successive reversible one-electron oxidation waves (see Figure 3), yielding first the mixed-valence  $Fe^{II}Fe^{III}$  and then the dioxidized  $Fe^{III}_2$  complex. The difference between the oxidative and reductive peak potentials for each of these two waves is ~60 mV, which indicates reversibility. The half-wave potentials are 252 and 616 mV vs Ag/AgCl electrode

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in  $\text{CH}_3\text{CN}$ . This gives a separation between the two waves of 364 mV for **13**. Biferrocene in  $\text{CH}_3\text{CN}$  is reported<sup>22</sup> to have waves at 240 and 555 mV vs Ag/AgCl, which gives a separation of 315 mV. Ferrocene in  $\text{CH}_3\text{CN}$  gives a wave at 310 mV vs Ag/AgCl.<sup>22</sup> It is interesting that the fused biferrocene complex **13** has a larger wave separation than biferrocene even though the fulvalenide ligand in **13** is very likely not planar.

**Oxidation of Complex 13.** Attempts to oxidize complex **13** chemically led to salts. When **13** was treated in benzene with iodine in a ratio of 1:1.5, a microcrystalline product (**19**) was obtained with a composition  $[\text{13}]\text{I}_3^-$ . Mössbauer spectra at 110 and 300 K both reveal only one doublet with quadrupole splittings of 2.35 and 2.28 mm/s, respectively. These values are only slightly smaller than the value for **13** at 110 K (2.44 mm/s). This indicates that the Fe atoms in this triiodide product remain in the oxidation state of  $\text{Fe}^{\text{II}}$ . When the stronger oxidizing agent 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) is used, the same result obtains: the ferrocene center remains unoxidized in a compound (**20**) with a biferrocene:DDQ ratio of 1:1.

Surprisingly, a product with a biferrocene: $\text{PF}_6^-$  ratio of 1:1 was formed when **13** was treated with ferrocenium hexafluorophosphate in benzene to give **21**. Mössbauer spectra run at 110 and 295 K (see Table IV) both show that only  $\text{Fe}^{\text{II}}$  is present in this salt. It is relevant to note that previously we reported the  $^{57}\text{Fe}$  Mössbauer spectra of  $[\text{1,12-dimethyl[1,1]-ferrocenophanium(2+)}](\text{DDQH}^-)_2$  at 300 and 4.2 K each show one quadrupole-split doublet with  $\Delta E = \sim 2.17$  mm/s.<sup>8e</sup> It is possible that an  $\text{Fe}^{\text{III}}$  site in ferrocenium salt could have a large quadrupole splitting. All of the microanalysis data for the oxidation products from **13** indicate that a 1+ charge is added somewhere to compound **13**. There are two possibilities: (1) one of the Fe centers does get oxidized, and the mixed-valence salt formed is detrapped on the Mössbauer time scale and has a large quadrupole splitting; (2) the bridge linking the two ferrocene subunits in **13** is oxidized. All three of these salts are barely soluble in organic solvents such as benzene, methylene chloride, and acetone. A  $^1\text{H}$  NMR spectrum obtained from a saturated solution of the triiodide salt in acetone- $d_6$  showed that all the resonance peaks move to downfield, compared to those for **13** with the methyl and unsubstituted Cp resonances at 3.87 and 4.47 ppm, respectively. The change of chemical shift upon oxidation of **13** is not the same on different parts of the molecule: the protons on unsubstituted Cp rings change only a very little amount compared with a large shift for the methyl protons. Therefore, it is likely the side chain is oxidized rather than the Fe center in complex **13**. That is, a carbocation is formed at one of the carbon atoms in the bridge as a result of an oxidation followed by a hydrogen atom abstraction. Furthermore, the  $^1\text{H}$  NMR results indicative that there is a rapid tautomeric equilibrium established, viz.



The stabilization of carbocations by ferrocene moieties is well documented.<sup>23</sup>

IR spectra for the three oxidation products of **13** also indicate that the iron atoms remain in the  $\text{Fe}^{\text{II}}$  oxidation state. The perpendicular cyclopentadienyl C-H bending modes for  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  metallocenes occur in different ranges: 805–815  $\text{cm}^{-1}$  for  $\text{Fe}^{\text{II}}$  and 840–850  $\text{cm}^{-1}$  for  $\text{Fe}^{\text{III}}$ .<sup>24</sup> KBr pellet IR spectra for **12**,

**13**, and **17** show one peak in this region at 816, 818, and 826  $\text{cm}^{-1}$ , respectively. The triiodide salt of **17** has an absorption band at 827  $\text{cm}^{-1}$ , the  $\text{DDQH}^-$  salt a band at 824  $\text{cm}^{-1}$ , and the  $\text{PF}_6^-$  salt a band at 811  $\text{cm}^{-1}$ . It is therefore clear that the ferrocene moieties are not involved in the chemical oxidation process.

### Experimental Section

**Physical Measurements.** Infrared spectra were recorded on an IBM Model 32 FTIR spectrometer.  $^1\text{H}$  NMR spectra were obtained on either a Varian XL-200 (200 MHz) or a General Electric QE-300 (300 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra were obtained on a CH-5 mass spectrometer. Cyclic voltammograms were obtained by using a BAS Model 100 electrochemical analyzer.  $^{57}\text{Fe}$  Mössbauer spectra were collected with a constant-acceleration spectrometer that has been described before.<sup>25</sup> Least-squares fitting of the powder sample Mössbauer spectra with Lorentzian lines was carried out by using a modified version of a previously reported<sup>26</sup> computer program. Elemental analyses were performed in the Microanalytical Laboratory of the School of Chemical Sciences.

**Compound Preparation.** 2,5''-Bis((dimethylamino)methyl)biferrocene (**15**) and its monomethyliodide **16** were prepared by a literature procedure.<sup>11,27</sup>

**N,N-Dimethyl-2,5''-(2-azoniapropane-1,3-diyl)biferrocene Iodide Hydrate (12).** Three different methods (a, b, and c) can be used to prepare **12**. (a) A suspension of 3.13 g (5.0 mmol) of **16** in 150 mL of water was heated to reflux until the evolution of trimethylamine ceased (45 min). The red solution was filtered while hot. After slowly cooling to room temperature, 2.52 g (4.3 mmol) of **12** was obtained (86%), which was pure enough for the next reaction. Pure samples of **12** can be obtained by recrystallization from water; mp > 250 °C, but darkened above 200 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.33 (s, 3 H), 4.01 (s, 3 H), 4.05 (d, 2 H,  $J = 13$  Hz), 4.37 (m, 2 H), 4.42 (s, 10 H), 4.52 (m, 4 H), 5.25 (d, 2 H,  $J = 13$  Hz). IR (KBr): 3430, 3069, 1460, 1408, 1107, 997, 909, 878, 643, 816, 500, 478, 469  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{28}\text{Fe}_2\text{INO}$ : C, 49.27; H, 4.82; Fe, 19.09; I, 21.69; N, 2.39. Found: C, 49.24; H, 4.79; Fe, 19.05; I, 21.64; N, 2.42.

(b) A suspension of 626 mg (1.0 mmol) of **16** in 30 mL of 10% NaOH was heated to reflux for 45 min. After cooling to room temperature, the mixture was filtered. The solid was recrystallized from  $\text{H}_2\text{O}$  to give 483 mg of pure **12** (82%). This sample was confirmed by its  $^1\text{H}$  NMR spectrum. Treatment of **16** with either 2% or 50% NaOH solutions affords the same result.

(c) A 626-mg sample (1.0 mmol) of **16** was dissolved in 30 mL of 15% acetic acid. This solution was heated to reflux for 2 h under argon. After the solution cooled, saturated  $\text{NaHCO}_3$  solution was added to neutralize the acid. The resulting precipitate was filtered and recrystallized from  $\text{H}_2\text{O}$  to give 502 mg (86%) of **12**.

**N-Methyl-2,5''-(2-azoniapropane-1,3-diyl)biferrocene (13).** To a suspension of 1.76 g (3.0 mmol) of **12** in 30 mL of dry THF was added 12.0 mL (12.0 mmol) of 1 N solution of  $\text{LiBH}(\text{sec-Bu})_3$  under argon. The mixture was refluxed for 5 h. After the homogeneous reaction mixture was cooled to 0 °C, 1.0 mL of water was added to decompose the extra hydride. The organic solvent was evaporated under vacuum, and the residue was extracted with 20 mL of diethyl ether. The ether solution was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and chromatographed on neutral alumina with benzene. A 0.92-g amount (72%) of **13** was obtained. Recrystallization from ether-hexane provided pure product; mp 140.5–141.5 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.26 (s, 3 H), 3.43 (d, 2 H,  $J = 13$  Hz), 4.08 (m, 4 H), 4.27 (m, 2 H), 4.34 (s, 10 H), 4.37 (d, 2 H,  $J = 13$  Hz). IR (KBr): 3087, 2934, 2780, 1456, 1367, 1304, 1254, 1107, 997, 887, 818, 482  $\text{cm}^{-1}$ . Mass spectrum:  $m/z$  425 (100%). Anal. Calcd for  $\text{C}_{23}\text{H}_{23}\text{Fe}_2\text{N}$ : C, 64.98; H, 5.45; Fe, 26.27; N, 3.29. Found: C, 65.28; H, 5.63; Fe, 26.04; N, 3.30.

**N,N-Dimethyl-2,5''-(2-azoniapropane-1,3-diyl)biferrocene Triiodide (19).** A solution of 51 mg (0.20 mmol) of iodine in 10 mL of benzene was added dropwise to a stirred solution of 117 mg (0.20 mmol) of **12** in 20 mL of benzene. A dark brown crystalline product formed immediately. Anal. Calcd for  $\text{C}_{24}\text{H}_{26}\text{Fe}_2\text{I}_3\text{N}$ : C, 35.12; H, 3.19; Fe, 13.61; N, 1.71. Found: C, 34.99; H, 3.34; Fe, 13.77; N, 1.66.

**N,N-Dimethyl-2,5''-(2-azoniapropane-1,3-diyl)biferrocene Pentaiodide (17).** A 127-mg amount (0.50 mmol) of iodine in 10 mL of benzene was added dropwise to 117 mg (0.20 mmol) of **12** in 15 mL of  $\text{CH}_2\text{Cl}_2$  with stirring. After 1 h, the dark red crystalline product was collected by

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filtration. IR (KBr): 1456, 1406, 1105, 997, 905, 826, 475  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{26}\text{Fe}_2\text{I}_3\text{N}$ : C, 26.82; H, 2.44; Fe, 10.39; I, 59.04; N, 1.30. Found: C, 26.83; H, 2.47; Fe, 10.42; I, 59.00; N, 1.26. Crystals suitable for X-ray diffraction were obtained by layering a  $\text{CH}_2\text{Cl}_2$  solution of 17 with benzene that contained a small amount of iodine.

**Reaction of *N*-Methyl-2,5''-(2-azapropene-1,3-diyl)biferrocene (13) with Iodine.** To a solution of 85 mg (0.20 mmol) of 13 in 20 mL of benzene was added dropwise 76 mg (0.30 mmol) of iodine in 10 mL of benzene. A dark brown crystalline compound was obtained (121 mg, 75%). Anal. Calcd for  $\text{C}_{23}\text{H}_{23}\text{Fe}_2\text{I}_3\text{N}$ : C, 34.28; H, 2.88; Fe, 13.86; I, 47.24; N, 1.74. Found: C, 34.55; H, 2.88; Fe, 13.77; I, 47.05; N, 1.73.

**Reaction of *N*-Methyl-2,5''-(2-azapropene-1,3-diyl)biferrocene (13) with DDQ.** A solution of 45 mg of 2,3-dichloro-5,6-dicyanoquinone (DDQ) in 10 mL of benzene was added dropwise to a stirred solution of 85 mg (0.20 mmol) of 13 in 20 mL of benzene. A dark brown crystalline compound which has the formula  $13\text{-DDQ}\cdot\text{H}_2\text{O}\cdot\frac{1}{2}\text{C}_6\text{H}_6$ , was obtained. Anal. Calcd for  $\text{C}_{34}\text{H}_{28}\text{Cl}_2\text{Fe}_2\text{N}_3\text{O}_3$ : C, 57.58; H, 3.98; Cl, 10.00; Fe, 15.75; N, 5.92. Found: C, 57.15; H, 4.07; Cl, 10.28; Fe, 15.66; N, 6.01.

**Reaction of *N*-Methyl-2,5''-(2-azapropene-1,3-diyl)biferrocene (13) with Ferrocenium Hexafluorophosphate.** To a suspension of 50 mg (0.15 mmol) of ferrocenium hexafluorophosphate in 30 mL of benzene was added 85 mg (0.20 mmol) of 13. The mixture was stirred for 24 h and then filtered. The solid was washed with benzene and air dried. A 87-mg amount (93%) of reaction product, which has the formula  $[13]\text{PF}_6\cdot\text{H}_2\text{O}\cdot\frac{1}{2}\text{C}_6\text{H}_6$ , was obtained. Anal. Calcd for  $\text{C}_{26}\text{H}_{28}\text{F}_6\text{Fe}_2\text{P}$ : C, 49.79; H, 4.50; Fe, 17.81; N, 2.23. Found: C, 50.38; H, 4.60; Fe, 17.52; N, 2.10.

**Crystal Measurements and Structure Determination for Complex 17.** The dark, opaque, prismatic crystal used for data collection had well-

developed faces ( $0.2 \times 0.4 \times 0.4$  mm). The crystal was mounted by using epoxy to a thin glass fiber with the (230) scattering planes roughly normal to the spindle axis. A Syntex P2<sub>1</sub> automated four-circle diffractometer was used to collect intensities at 299 K. Corrections were made for Lorentz and polarization effects, anomalous dispersion, and crystal decomposition (total decay, 53%). A numerical correction for absorption was applied where the maximum and minimum transmission factors were 0.210 and 0.065, respectively. Additional experimental details are given in Table I.

The structure was solved by direct methods (SHELXS-86). Correct positions for the iodine iron atoms were deduced from an *E* map. Subsequent least-squares difference Fourier calculations gave positions for the remaining non-hydrogen atoms. Hydrogen atoms were included as fixed contributors in "idealized" positions. In the final cycle of least squares, anisotropic thermal coefficients were refined for the non-hydrogen atoms and a group isotropic thermal parameters was varied for the hydrogen atoms. Successful convergence was indicated by the maximum shift/error for the last cycle. The highest residual electron density in the final difference Fourier map was found in the vicinity of the iodine atoms. A final analysis of variance between observed and calculated structure factors showed a slight inverse dependence on  $\sin \theta$ . The final atomic positional parameters are given in Table II.

**Acknowledgment.** We are grateful for partial funding from National Institutes of Health Grant HL 13652 (D.N.H.).

**Supplementary Material Available:** Tables of calculated hydrogen positions, planes, and thermal parameters (4 pages); a table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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## Reactivity of $(i\text{-C}_3\text{H}_7)_2\text{GaBr}$ with $\text{C}_2\text{H}_5\text{SH}$ and $\text{C}_2\text{H}_5\text{SeH}$ . Synthesis of $i\text{-C}_3\text{H}_7(\text{Br})\text{GaEC}_2\text{H}_5$ ( $\text{E} = \text{S}, \text{Se}$ )

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The synthesis of the Lewis acid-base adducts  $(i\text{-C}_3\text{H}_7)_2\text{GaBr}\cdot\text{HEC}_2\text{H}_5$  ( $\text{E} = \text{S}, \text{Se}$ ) is reported. The thermal treatment of these adducts to give isopropyl(ethylchalcogenolato)gallium bromides was demonstrated. All new compounds were characterized by physical methods ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and IR spectroscopy and DTA).

In comparison with the trialkylgallanes, the reactivity of dialkylgallium halides toward H-acidic compounds has received scant attention. With the exception of the well-investigated chemistry of the  $(\text{CH}_3)_2\text{Ga}^+$  moiety in aqueous solution,<sup>1</sup> there is not much information available on the chemistry in organic solvents of compounds containing this fragment.<sup>2</sup> This fact may be due to the enormously reduced reactivity of the gallium-carbon bond in such dialkylgallium compounds in general.<sup>3</sup> In this connection it has been elucidated very clearly that reactions of  $(\text{CH}_3)_2\text{GaSR}$  with HSR' result in an exchange of the thiolate group and thus in the formation of  $(\text{CH}_3)_2\text{GaSR}'$  if HSR' is more volatile than HSR'.<sup>4</sup> Therefore, it seems worthwhile to us to

investigate the reactions of  $(i\text{-C}_3\text{H}_7)_2\text{GaBr}$  with chalcogenols, such as  $\text{HSC}_2\text{H}_5$  and  $\text{HSeC}_2\text{H}_5$ , respectively, with respect to the reactivity of the gallium-carbon, gallium-bromine, and gallium-chalcogen bonds.

### Experimental Section

All experiments were performed under an atmosphere of dry nitrogen or, if necessary, argon in freshly distilled solvents.  $\text{GaBr}_3$ ,<sup>5</sup>  $(i\text{-C}_3\text{H}_7)_3\text{Ga}$ ,<sup>6</sup> and  $i\text{-C}_3\text{H}_7\text{Li}^+$  were prepared by published procedures.  $^1\text{H}$  NMR spectra were recorded on a JEOL FX 90Q spectrometer. Benzene- $d_6$  ( $\delta = 7.75$ ) was used as solvent, and all chemical shifts are reported with respect to  $\text{Me}_4\text{Si}$ .  $^{13}\text{C}$  NMR spectra were obtained on a JEOL FX 90Q instrument and are reported in ppm. IR spectra were recorded as Nujol mulls or films between CsI plates on a Perkin-Elmer 283 instrument, osmometric molecular weight determinations in benzene solution on a Knauer vapor-phase osmometer; melting- and decomposition points are uncorrected and obtained on a Du Pont 990 thermal analyzer. C and H microanalyses were performed on a Carlo Erba 1106 instrument;  $\text{Ga}^8$  and  $\text{Br}^9$

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