

Cofacial Metallocenes. Synthesis and Crystal Structure of 1,8-Diferrocenylnaphthalene

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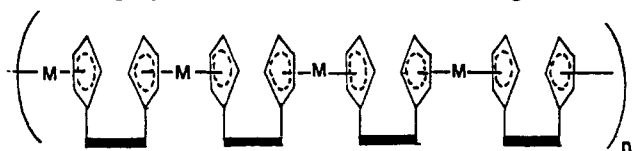
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The synthesis of 1,8-diferrocenylnaphthalene (**3**) is described. This substance is of interest as a model and potential precursor for columnar polymeric metallocenes in which cyclopentadienyl rings of adjacent metallocene nuclei are held proximate and cofacial. Although the molecule is very crowded, 1,8-diferrocenylnaphthalene may be made in high yield by coupling 1,8-diiodonaphthalene and ferrocenylzinc chloride in the presence of dichloro[1,1'-bis(diphenylphosphino)ferrocene]palladium(II) (Pd(dppf)Cl₂). An X-ray crystal structure determination of the compound shows the naphthalene ring and bonds from the peri-carbon atoms to the cyclopentadienyl rings to be highly distorted. The two substituted cyclopentadienyl rings are rotated by ~46° from a conformation which would place them perpendicular to the naphthalene ring. Cyclic voltammetry measurements, carried out on **3** in methylene chloride, show two reversible, one-electron waves at +0.013 and 0.208 V vs. a Ag/0.1 M AgNO₃ reference electrode. The monocation, derived by oxidation of **3** with silver tetrafluoroborate, exhibits an intervalence transfer band at 1600 nm (ϵ_{max} 200), not shown by the corresponding dication of **3**. A comparison of these properties with those of biferrocenyl, diferrocenylacetylene, and 1,4-diferrocenylbutadiyne suggests that **3**⁺ is best represented as a weakly interacting mixed-valence system.

Introduction

As part of a program directed toward the synthesis of highly conducting, columnar organometallic polymers,¹ we set out to design a polymeric mixed-valence metallocene system in which the monomeric units would be constrained to interact with one another through space, across their cyclopentadienyl ring surfaces. Although a large number of metallocene polymers are known,² none having this molecular configuration have been reported.³ In principle, a stacked polymer of this form, such as **I**, might be con-



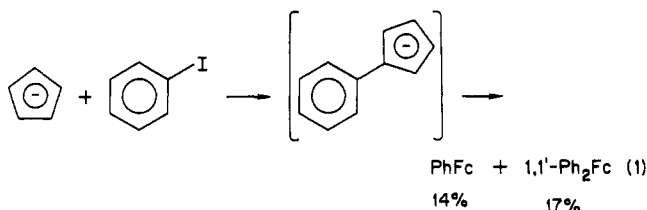
structed employing a relatively rigid, noninteracting hydrocarbon framework to support the individual metallocene nuclei. Providing the metallocene units are held face to face and at an internuclear distance of 4 Å or less, electron or hole conduction in a partially oxidized array of such a polymer might then occur through overlapping ring π orbitals. One such system that meets these requirements is based on *peri* substitution of naphthalene. This paper describes the synthesis and properties of the monomeric unit 1,8-diferrocenylnaphthalene (**3**) which may serve as a model for such polymeric systems. Moreover, the synthetic approach adopted for the synthesis of **3** should lend itself, through appropriate variants, to the synthesis of more highly aggregated structures and to elaboration of these to include transition metals other than iron.

Results and Discussion

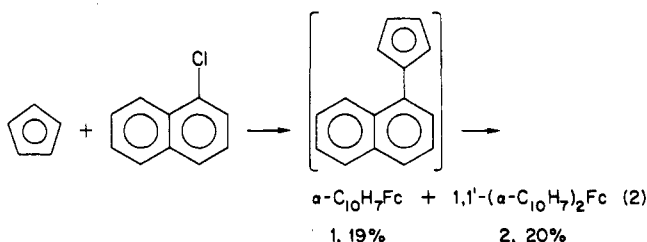
At the outset, two synthetic routes to **3** were considered. The first was based on the work of Bunnett and his co-

workers, who showed in a number of publications⁴ that coupling of stabilized anions with aryl halides, including hindered ones, could be achieved by a radical chain process initiated by electron transfer from the anion to the aryl halide. Such reactions, termed S_{RN}1 by Bunnett, have been carried out with a number of anions including fluorenyl and indenyl carbanions but not, apparently, with cyclopentadienyl anion.

We found that sodium cyclopentadienide, in liquid ammonia solution, reacted with iodobenzene to give the desired coupled product. This was not isolated but was transformed in situ by reaction with anhydrous ferrous chloride to a mixture of phenyl- and 1,1'-diphenylferrocene (eq 1). However, the yield of these products was low.



The yield of coupled product, α -naphthylferrocene (**1**) and 1,1'-di- α -naphthylferrocene (**2**), was also low when the reaction partner was 1-chloronaphthalene, and no significant improvement in yield could be achieved with 1-iodonaphthalene.



We turned, therefore, to an examination of an alternative approach to the synthesis of **3** involving the coupling of metallated ferrocenes with halonaphthalenes, mediated by transition-metal catalysts.⁵ A closely related coupling

(1) Torrance, J. B. *Acc. Chem. Res.* 1979, 12, 79. Carraher, C. E., Sheats, J. E., Pittman, C. U., Eds. "Organometallic Polymers"; Academic Press: New York, 1978. Seymour, R. B., Ed. "Conductive Polymers"; Plenum Press: New York, 1981.

(2) Neuse, E. W.; Rosenberg, H. "Metallocene Polymers"; Marcel Dekker: New York, 1970.

(3) Polymeric systems based on complexation of pairs of conjugated cyclopentadienyl anions have been discussed by Katz. See: Katz, T. J.; Pesti, J. *J. Am. Chem. Soc.* 1982, 104, 346 and references therein.

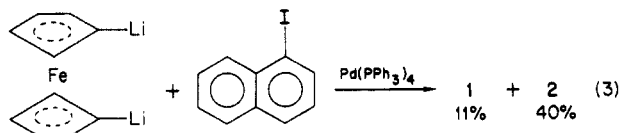
(4) Bunnett, J. F. *Acc. Chem. Res.* 1978, 11, 413.

Table I. Products Resulting from Reaction between 1,8-Dihalonaphthalenes and Monometalated Ferrocenes

entry	M	X	cat. ^a	yields, ^b %		
				6	1	3
1	Li	I	Pd(PPh ₃) ₄		14.1	trace
2	Li	I	Ni(PPh ₃) ₄		1.6	
3	MgBr	I	Ni(dppp)Cl ₂	50	49	
4	ZnCl	Br	Ni(PPh ₃) ₄	11	65	29
5	ZnCl	Br	Ni(dppp) ₂ ^d	10	23	52
6	ZnCl	Br	Ni(dppf) ₂ ^e		26	42
7	ZnCl	Br	Pd(PPh ₃) ₄			
8	ZnCl	Br	Pd(dppf)Cl ₂			25 (46) ^c
9	ZnCl	I	Pd(dppf)Cl ₂			58 (94) ^c

^a In general 5 molar % of catalyst, based on 1,8-dihalonaphthalene was used. ^b All yields are of isolated, purified products and are calculated on the basis of the amount of 1,8-dihalonaphthalene used. ^c Yield is based on the amount of 1,8-dihalonaphthalene consumed. ^d dppp = 1,3-(diphenylphosphino)propane. ^e dppf = 1,1'-bis(diphenylphosphino)ferrocene.

of 1,1'-dilithioferrocene with 1,1'-diiodoferrocene in the presence of cupric chloride to give a polyferrocenylene has recently been reported by Neuse and Bednarik.⁶ However, initial attempts to effect coupling of dilithioferrocene with 1,8-diiodonaphthalene under these conditions yielded only unreacted starting material. The use of Ni(II) or Pd(II) catalysts proved more successful. A model reaction, using 1,1'-dilithioferrocene and 1-iodonaphthalene in the presence of 5 molar % Pd(PPh₃)₄ gave a modest yield of the α -naphthylferrocenes 1 and 2, but the same reaction with Ni(PPh₃)₄ as catalyst failed to yield any appreciable amount of coupled product.



The sterically more demanding model reactions, involving the coupling of monometalated ferrocenes with 1,8-dihalonaphthalenes in the presence of various nickel and palladium catalysts, were next examined. These results are summarized in Table I.

With Pd(PPh₃)₄ as catalyst, lithioferrocene and 1,8-diiodonaphthalene gave only α -naphthylferrocene (1) in low yield together with a trace of the desired compound 3 (run 1). The use of Ni(PPh₃)₄ as catalyst in this reaction resulted in a significantly lower yield of 1 (run 2), and, while the replacement of lithioferrocene by the Grignard reagent led to an improvement in the yield of 1, no diferrocenylnaphthalene (3) was detected (run 3). Significantly, a substantial amount of naphthalene 3 was recovered from this reaction, indicating extensive metal halogen exchange

(5) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980. Noyori, R. In "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1, Chapter 2. Kozikowski, A. D.; Wetler, H. F. *Synthesis* 1976, 561. Felkin, H.; Swierczewski, G. *Tetrahedron* 1975, 31, 2735. Kumada, M. In "Organotransition Metal Chemistry"; Ishi, Y., Tsutsui, M., Ds.; Plenum Press: New York, 1975. Tamao, K.; Sumitoni, K.; Yoshihisa, K.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajuma, I.; Miriato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* 1976, 49, 1958.

(6) Neuse, E. W.; Bednarik, L. *Transition Met. Chem.* (Weinheim, Ger.) 1979, 4, 87.

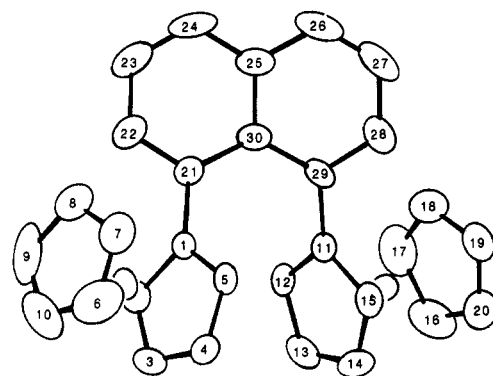


Figure 1. Molecular structure of 1,8-diferrocenylnaphthalene (50% boundary ellipses are shown).

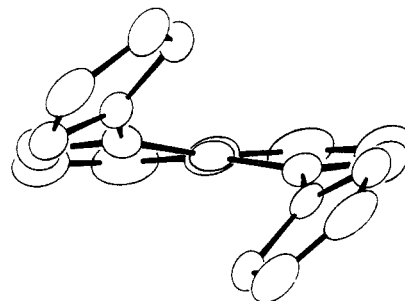


Figure 2. A view of the distorted naphthalene plane and 1,8-cyclopentadienyl rings.

competing with the coupling reaction. We therefore turned to an examination of the less reactive organozinc reagents, first employed in aryl coupling reactions by Negishi, King, and Okukado,⁷ and found that the yield of 3 was significantly improved. A number of catalysts were examined (runs 4-9), of which the best proved to be dichloro[1,1'-bis(diphenylphosphino)ferrocene]palladium Pd(dppf)Cl₂.⁸ This gave none of the products of halogen metal exchange (1 and 6) formed in the presence of other catalysts. The coupling reaction with Pd(dppf)Cl₂ proceeds at a lower rate

(7) Negishi, E.-I.; King, A. O.; Okukado, N. *J. Org. Chem.* 1977, 42, 1822.

(8) Hayashi, T.; Konishi, M.; Kumada, M. *Tetrahedron Lett.* 1979, 1871. The phosphine is available from Aldrich Chemical Co.

Table II. Cyclic Voltammetry Data^a

compd	$E_{1/2}(1)$	$E_{1/2}(2)$	solv	$\Delta E_{1/2}$
1-ferrocenylnaphthalene	0.088		CH ₃ CN	
1,8-diferrocenylnaphthalene	0.013	0.208	CH ₂ Cl ₂	0.195
	-0.038	0.112	CH ₃ CN	0.150
ferrocene	0.098 (0.100) ^b		CH ₂ Cl ₂	
biferrocenyl	0.015 (-0.005) ^b	0.354 (0.345) ^b	CH ₂ Cl ₂	0.339 0.350 ^b

^a Measurements were carried out by using either Bu₄NBF₄ in CH₂Cl₂ or Et₄NClO₄-CH₃CN as supporting electrolyte and a Ag/0.1 M AgNO₃ reference electrode at a scan rate of 50 or 100 mV s⁻¹. ^b Values are those reported in ref 9 and corrected for reference to SCE to Ag/0.1 M AgNO₃, +0.440 V vs. SCE.

Table III. Selected Distances (Å) and Angles (deg) for (C₁₀H₉Fe)₂C₁₀H₆^a

Bond Distances			
Fe(1)-C(1)	2.076 (3)	Fe(2)-C(11)	2.066 (3)
Fe(1)-C(2)	2.043 (3)	Fe(2)-C(12)	2.043 (3)
Fe(1)-C(3)	2.042 (4)	Fe(2)-C(13)	2.049 (4)
Fe(1)-C(4)	2.043 (4)	Fe(2)-C(14)	2.044 (4)
Fe(1)-C(5)	2.044 (3)	Fe(2)-C(15)	2.034 (3)
Fe(1)-C(6)	2.043 (4)	Fe(2)-C(16)	2.043 (4)
Fe(1)-C(7)	2.035 (4)	Fe(2)-C(17)	2.038 (4)
Fe(1)-C(8)	2.037 (4)	Fe(2)-C(18)	2.031 (4)
Fe(1)-C(9)	2.027 (5)	Fe(2)-C(19)	2.040 (4)
Fe(1)-C(10)	2.038 (5)	Fe(2)-C(20)	2.046 (5)
C(1)-C(21)	1.489 (5)	C(11)-C(29)	1.486 (5)
C(21)-C(22)	1.379 (5)	C(29)-C(28)	1.381 (5)
C(21)-C(30)	1.437 (4)	C(29)-C(30)	1.442 (4)
C(22)-C(23)	1.394 (6)	C(28)-C(27)	1.405 (6)
C(23)-C(24)	1.354 (6)	C(27)-C(26)	1.342 (7)
C(24)-C(25)	1.411 (6)	C(26)-C(25)	1.422 (6)
C(25)-C(30)	1.429 (5)		
C(1)-C(2)	1.431 (5)	C(11)-C(12)	1.416 (4)
C(2)-C(3)	1.422 (5)	C(12)-C(13)	1.416 (5)
C(3)-C(4)	1.406 (5)	C(13)-C(14)	1.401 (6)
C(4)-C(5)	1.415 (5)	C(14)-C(15)	1.401 (5)
C(1)-C(5)	1.420 (4)	C(11)-C(15)	1.425 (5)
C(6)-C(7)	1.383 (7)	C(16)-C(17)	1.463 (7)
C(7)-C(8)	1.391 (6)	C(17)-C(18)	1.394 (7)
C(8)-C(9)	1.422 (7)	C(18)-C(19)	1.375 (6)
C(9)-C(10)	1.398 (8)	C(19)-C(20)	1.375 (7)
C(6)-C(10)	1.382 (8)	C(16)-C(20)	1.375 (8)
Bond Angles			
C(1)-C(21)-C(22)	119.0 (3)	C(11)-C(29)-C(28)	119.3 (3)
C(1)-C(21)-C(30)	121.4 (3)	C(11)-C(29)-C(30)	121.7 (3)
C(22)-C(21)-C(30)	119.4 (3)	C(28)-C(29)-C(30)	118.7 (3)
C(21)-C(22)-C(23)	121.7 (3)	C(27)-C(28)-C(29)	121.7 (3)
C(22)-C(23)-C(24)	119.4 (4)	C(26)-C(27)-C(28)	120.0 (4)
C(23)-C(24)-C(25)	121.4 (4)	C(25)-C(26)-C(27)	121.4 (4)
C(24)-C(25)-C(26)	121.7 (4)	C(21)-C(30)-C(29)	125.3 (3)
C(24)-C(25)-C(30)	119.4 (3)	C(21)-C(30)-C(25)	116.9 (3)
C(26)-C(25)-C(30)	118.9 (3)	C(25)-C(30)-C(29)	117.8 (3)

^a Standard deviations in the least significant digit appear in parentheses.

Table IV. Comparison of Distortions in 1,8-phenyl- or 1,8-Dicyclopentadienyl-Substituted Naphthalenes

compound	rotatn of Ph or Cp from 90° orientatn, deg	interphenyl (or Cp) ring angle, deg	av displacement of α,β cations from naphthalene best plane, Å
1,8-diphenylnaphthalene (7)	23		$\pm 0.015, \pm 0.005$
5,6-diphenylacenaphthene (8)	33	26	$\pm 0.044, \pm 0.010$
1,4,5,8-tetraphenylnaphthalene (9)	32	34	$\pm 0.091, \pm 0.048$
1,8-diferrocenylnaphthalene (3)	46 (av)	29.1	$\pm 0.164, \pm 0.040$

than with other Ni or Pd catalysts, and with 1,8-dibromonaphthalene as substrate, both starting material as well as the half-coupled product 1-ferrocenyl-8-bromonaphthalene were recovered from the product mixture. With 1,8-diiodonaphthalene as reactant, 58% was converted to **3** and the yield of this product, corrected for recovered diiodonaphthalene, rose to an agreeable 94%.

Molecular Structure of 1,8-Diferrocenylnaphthalene. The compound is an orange solid, mp 275 °C dec. Its molecular structure is shown in Figure 1, which also gives the numbering scheme. The crystal structure

consists of loosely packed molecules, with no intermolecular C-C contacts <3.47 Å. This view and a partial view of the molecule viewed from the "edge" of the naphthalene best plane (Figure 2) indicate the severe steric crowding present in the molecule. Bond distances and angles are presented in Table III. Below we indicate the nature and magnitude of the distortions which arise from the crowding and compare these to *peri*-diphenylnaphthalenes.

(i) The two substituted cyclopentadienyl rings are positioned face-to-face and are rotated 47-45° from a conformation which would place them perpendicular to

Table V. Torsion Angles (deg) and Distances of Atoms from Naphthalene Mean Plane (Å)

Torsion Angles		Distances of Atoms from Naphthalene Mean Plane	
C(1)-C(21)-C(30)-C(29)	18.1	C(22)	0.042 (4)
C(1)-C(21)-C(22)-C(23)	170.6	C(23)	-0.157 (4)
C(1)-C(21)-C(30)-C(25)	-161.1	C(24)	-0.104 (4)
C(11)-C(29)-C(28)-C(27)	169.1	C(25)	0.005 (4)
C(11)-C(29)-C(30)-C(21)	20.2	C(26)	0.113 (4)
C(11)-C(29)-C(30)-C(25)	-160.5	C(27)	0.156 (4)
C(21)-C(22)-C(23)-C(24)	-6.1	C(28)	-0.037 (4)
C(21)-C(30)-C(25)-C(24)	-13.2	C(29)	-0.168 (3)
C(21)-C(30)-C(25)-C(26)	167.2	C(30)	-0.003 (3)
C(21)-C(30)-C(29)-C(28)	-166.2		
C(22)-C(21)-C(30)-C(25)	14.1		
C(22)-C(21)-C(30)-C(29)	-166.7		
C(22)-C(23)-C(24)-C(25)	6.9		
C(23)-C(22)-C(21)-C(30)	-4.8		
C(23)-C(24)-C(25)-C(26)	-177.5		
C(23)-C(24)-C(25)-C(30)	2.9		
C(24)-C(25)-C(26)-C(27)	-177.0		
C(24)-C(25)-C(30)-C(29)	167.5		
C(25)-C(26)-C(27)-C(28)	6.2		
C(25)-C(30)-C(29)-C(28)	13.0		
C(26)-C(25)-C(30)-C(29)	-12.1		
C(26)-C(27)-C(28)-C(29)	-5.2		
C(27)-C(26)-C(25)-C(30)	2.6		
C(27)-C(28)-C(29)-C(30)	-4.6		

the naphthalene best plane. The comparable values (Table IV) in 1,8-diphenylnaphthalene⁹ (7, 23°), 5,6-diphenylacenaphthene¹⁰ (8, 33°), and 1,4,5,8-tetraphenylnaphthalene¹¹ (9, 32°) are significantly smaller. The larger rotation in **3** would appear to occur in order to avoid severe nonbonded interactions between C(18)-C(28) and C(22)-C(8) and their associated H atoms. In this conformation the latter two C...C distances are 3.47 and 3.44 Å, respectively. This phenomenon is *not* a factor in the analogous di- and tetraphenyl compounds. For these molecules we thus expect steric strain to be relieved in part by other mechanisms.

(ii) Figure 3 shows distances and angles about the di-substituted naphthalene moiety (A) and important internal nonbonded contacts and deviations from the naphthalene best weighted least-squares plane (B). The parameters in Figure 3A and the nonbonded contacts in Figure 3B are remarkably similar to those observed for 1,8-diphenylnaphthalene. The dihedral angle between the 1- and 8-substituted cyclopentadienyl rings is 29.1°, slightly more than that observed for **8** (26°) but less than that observed for **9** (34°). Again, this mechanism cannot provide much relief of strain in the present case, as further splaying will increase the severity of the nonbonded interactions between C(18)-C(28), C(22)-C(8), and their associated hydrogen atoms.

(iii) There are two closely related types of distortion, which will relieve strain in this molecule—out-of-plane bending of the naphthalene to cyclopentadienyl bonds and distortion of the naphthalene moiety itself. Both of these distortions occur to a greater extent than heretofore observed in similar molecules (see Figure 3B and Table V). The out-of-plane distortions of C(1) and C(11) are ~0.07 Å greater than those observed in **9** while the naphthalene plane distortions are much greater than those previously observed (maximum of 0.091 Å in **9**). However, the distortions observed here fall within the ranges observed for (formally less comparable) overcrowded substituted naphthalenes.¹²

(iv) A final manifestation of steric strain in this molecule appears in the long Fe(1)-C(1) and Fe(2)-C(11) distances,

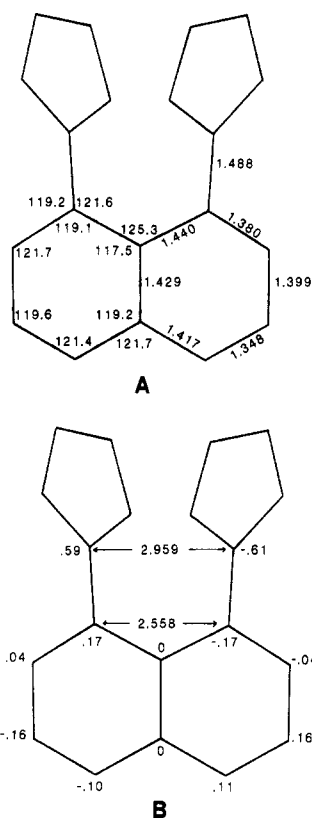


Figure 3. (A) Averaged parameters for 1,8-diferrocenylnaphthalene. (B) Deviations from naphthalene plane and contacts.

2.076 (3) and 2.066 (3) Å; further, the average angle subtended at iron by the cyclopentadienyl ring centers is 1.8°. Thus there appears to be little evidence for distortion of the ferrocene moieties via a ring tilt mechanism,¹³ despite the observation that the energy associated with such a distortion is low ($\nu_{\text{tilt}} \sim 400 \text{ cm}^{-1}$)¹⁴ and despite the fact that such distortion would reduce the severity of the C(18)-C(28) and C(22)-C(8) contacts.

NMR Spectra. The ¹³C and ¹H NMR spectra of 1,8-diferrocenylnaphthalene exhibit single resonances for each of the enantiomerically related carbon atoms of the substituted cyclopentadienyl rings and the protons bound to these centers. Such chemical shift equivalence requires rapid interconversion of enantiomeric molecules through exchange of out-of-plane distortions of the naphthalene rings. The low-temperature ¹H NMR spectrum of **3** taken

(9) Ogilvie, R. A. Ph.D. Thesis, Massachusetts Institute of Technology, 1971.

(10) Evrard, P. G.; Piret, P.; Van Meersehe, M. *Acta Crystallogr., Sect. B* **1972**, *B28*, 497.

(11) Clough, R. L.; Kung, W. J.; Marsh, R. E.; Roberts, J. D. *J. Org. Chem.* **1976**, *41*, 3603.

(12) Herbstein, F. H. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1661. Blount, J. F.; Cozzi, F.; Damewood, J. R., Jr.; Iroff, L. D.; Sjostrand, U.; Mislou, K. *J. Am. Chem. Soc.* **1980**, *102*, 99. Wong-Ng, W.; Nyburg, S. C.; Awwal, A.; Jankie, R.; Kresge, A. J. *Acta Crystallogr., Sect. B* **1982**, *38*, 559. Sim, G. A. *Ibid.* **1982**, *38*, 623.

(13) Hillman, M.; Nagy, A. G. *J. Organomet. Chem.* **1980**, *184*, 433.

(14) Lippincott, E. R.; Nelson, R. D. *Spectrochim. Acta* **1958**, *10*, 307.

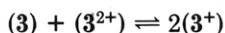
down to $-75\text{ }^\circ\text{C}$ failed to show any significant broadening of the two-proton resonance signal at δ 4.27, assigned to either H-2,5 or H-3,4 of the substituted cyclopentadienyl ring. If the chemical shift difference between exchanging diastereotopic protons is approximated by the chemical shift difference of H-2,5 and H-3,4 protons, then an exchange barrier somewhat less than 10 kcal/mol may be estimated for this process. Whatever the precise value of the exchange barrier, it must be substantially lower than that reported for 1,8-di-*tert*-butylnaphthalene of >24 kcal/mol,¹⁵ although the exchange process must involve a twisting motion of the ferrocene nuclei which forces the unsubstituted cyclopentadienyl rings to pass over C-2 and C-7 of the naphthalene ring. Moreover, the transition state for exchange must involve increased repulsive interactions of the substituted cyclopentadienyl rings.

Finally, a comparison of the chemical shift of protons in the substituted cyclopentadienyl ring of **3** with those in 1,1'-di- α -naphthylferrocene (**2**) shows the unusual shielding of these protons in **3** which may be attributed to ring currents of the cofacial cyclopentadienyl ring. Owing to these and their anticipated disparate effects on H-2,5 and H-3,4, it is not possible to assign these resonances with certainty.

Electrochemistry. Table II summarizes the cyclic voltammetry data obtained for **1** and **3**. Half-wave potentials were calculated from peak potentials, $E_{1/2} = (E_{pa} - E_{pc})/2$, and redox reactions show good reversibility for one-electron transfers with $E_{pa} - E_{pc}$ values in the range of 0.055–0.065 V. We also determined half-wave potentials for ferrocene and biferrocenyl for comparison. Although these latter redox reactions appeared to be quasireversible in methylene chloride, half-wave potentials agree with those reported in the literature.¹⁶

A comparison of the potentials for **1** and **3** shows that $\Delta E_{1/2}$ for **3** is derived almost as much from a decrease in the first oxidation potential for **3** compared to that for **1** as it is from an increase in the second oxidation potential for **3** compared with the potential for **1**. Similar observations pertain to the data for ferrocene and biferrocenyl, and it seems likely that these effects reflect some degree of electronic interaction either through the naphthalene ring or more directly through the π orbitals of the cofacial cyclopentadienyl rings in the neutral compound. The crystal structure of **3** would appear to allow either of these modes of electronic communication between the metal centers in **3** although the effective interaction of π orbitals on facing cyclopentadienyl rings may be small. In the monocation derived from **3**, both conjugation and electronic field effects are likely to be significant determinants of the second redox potential, but the relative importance of each of these is difficult to assess.

The magnitude of $\Delta E_{1/2}$ for **3** does not in itself provide definitive grounds for distinguishing between localized and delocalized mixed valence states, since as Taube¹⁷ has pointed out the equilibrium



depends on the thermodynamic properties of all the species in equilibrium and hence cannot be used as a measure of those of the monocation alone. This is well illustrated by $\Delta E_{1/2}$ values for biferrocene and [2.2]ferrocenophane-1,13-diyne which are very similar (0.350 and 0.355 V, re-

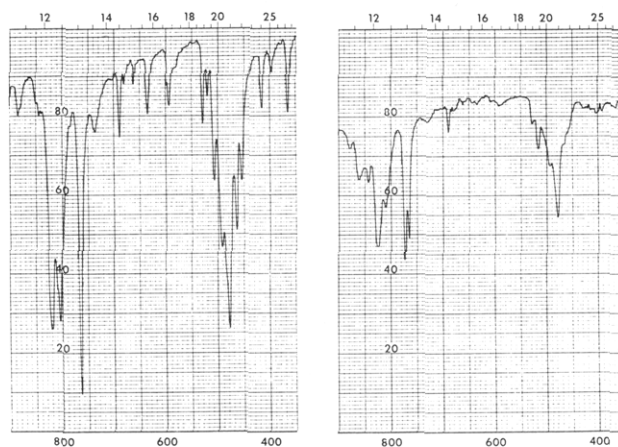


Figure 4. Infrared absorption spectra of (1,8-Fc₂C₁₀H₆) (A) and (1,8-Fc₂C₁₀H₆)(BF₄) (B).

spectively, in CH₂Cl₂),¹⁸ although the monocation of the first is best described, on the basis of Mössbauer, EPR, and magnetic susceptibility measurements as a localized mixed-valence species, while the diyne has been shown to be delocalized.¹⁹ Nevertheless we must note that, of the several other dinuclear compounds for which $\Delta E_{1/2}$ values in the range of 0.35–0.1 V have been determined, all give monocations that have localized charge. [0.0]-Ferrocenophane, the only other dinuclear ferrocene whose singly charged cation appears to be delocalized, has a value for $\Delta E_{1/2}$ of 0.590 V.

Infrared Spectra. As has been shown by Kramer and Hendrickson,¹⁹ absorptions in the infrared region are often of diagnostic value in assessing whether or not electron-transfer rates in mixed-valence salts are greater than 10^{12} s⁻¹. The C–H out-of-plane bending vibration found in ferrocene at 815 cm⁻¹ moves to 851 cm⁻¹ in the ferrocenium ion and is greatly attenuated in intensity. Ring–metal–ring stretching and tilting bands, found at 475 and 491 cm⁻¹ in ferrocene, are not perceptibly shifted in the cation but are greatly reduced in intensity. The monocation derived from [2.2]ferrocenophane-1,13-diyne, which is delocalized on the Mössbauer and EPR times scales, appears to be delocalized on the vibrational time scale as well, since its infrared spectrum shows a single C–H bending band at 831 cm⁻¹.

The infrared spectra of **3** and its monocation, taken as KBr pellets, are shown in the region of 900–400 cm⁻¹ in Figure 4. As can be seen, the intense doublet band centered at 810 cm⁻¹ in **3**, remains essentially unshifted in **3**⁺, and a new weak doublet assignable to C–H bending in the cationic nucleus is to be seen, centered at 850 cm⁻¹. Ring tilting and stretching modes, which give rise to a complex set of bands at 480 cm⁻¹ in **3**, remain unshifted in **3**⁺ but are greatly reduced in intensity. The very intense band at 765 cm⁻¹ in **3** which is split in **3**⁺ may be assigned to a C–H out-of-plane bending mode of the naphthalene nucleus. It too is unchanged in frequency. The weight of evidence from the infrared data suggests that the monocation derived from **3** is not delocalized on the vibrational time scale.

Electronic Spectra. Solutions of the mono- and dications derived from 1,8-diferrocenylnaphthalene (**3**) as well as α -naphthylferrocenium cation were prepared by

(15) Anderson, J. E.; Franck, R. W.; Mandella, W. L. *J. Am. Chem. Soc.* **1972**, *94*, 4608.

(16) LeVanda, C.; Bechgaard, K.; Cowan, D. O.; Rausch, M. D. *J. Am. Chem. Soc.* **1977**, *99*, 2964.

(17) Taube, H. *Ann. N. Y. Acad. Sci.* **1978**, *313*, 481. See also: Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 4393.

(18) LeVanda, C.; Bechgaard, K.; Cowan, D. O. *J. Org. Chem.* **1976**, *41*, 2700.

(19) Kramer, J. A.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 3330. LeVanda, C.; Bechgaard, K.; Cowan, D. O.; Mueller-Westerhoff, U. T.; Eilbrack, P.; Candela, G. A.; Collins, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 3181 and references therein.

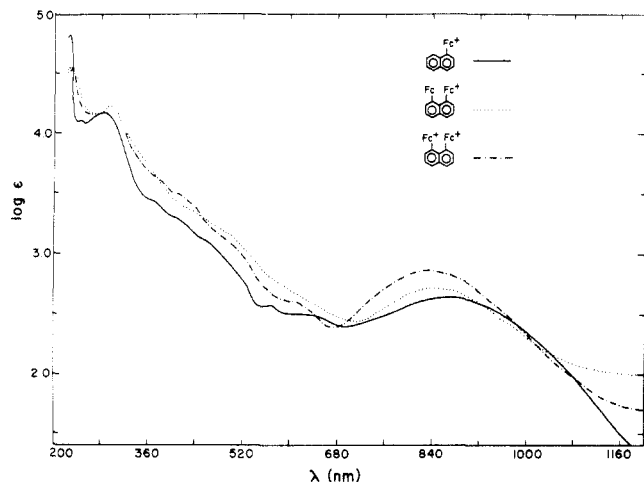


Figure 5. Absorption spectra of $(\alpha\text{-C}_{10}\text{H}_7\text{Fc})^+\text{BF}_4^-$ (—), $(1,8\text{-Fc}_2\text{C}_{10}\text{H}_6)(\text{BF}_4)^-$ (---), and $(1,8\text{-Fc}_2\text{C}_{10}\text{H}_6)(\text{BF}_4)_2$ (-.-).

oxidation of the ferrocenes with an equivalent amount of silver tetrafluoroborate in either methanol or methylene chloride solution. UV-visible spectra of these salts, taken in methanol, are shown in Figure 5. The difference between the first and second half-wave potentials for **3** is such that, at equilibrium, the singly oxidized species in solution is calculated from the Nernst equation to be more than 90% monocation. The absorption properties of all three cations do not differ appreciably throughout the UV and visible regions. The partially obscured band near 600 nm, present in the spectra of the monocations, as well as that of the dication, is probably related to the corresponding transition in ferrocenium cation itself, which has been assigned to a ligand to metal charge-transfer transition (${}^2E_{2g} \rightarrow {}^2E_{1u}$) by Prins.²⁰

The longer wavelength absorption near 850 nm represents a more highly delocalized transition associated with electronic interactions between the aryl and ferrocenium centers. Phenylferrocenium tetrafluoroborate exhibits an absorption band at 805 nm (ϵ 530), similar in energy and absorbance to that shown by the α -naphthylferrocenium ion, and it is of interest to note that the absorbance of the band is not markedly diminished in either the mono- or dications of **3**, notwithstanding the steric constraints, which precludes optimal interaction of the aryl and ferrocenyl groups in these cations. Instead there is an increase in the energy of this transition for 3^+ and 3^{2+} compared with that for 1^+ .

Of particular interest is the appearance of a broad intervalence band in the near infrared spectrum of 3^+ , which is absent in the spectrum of the dication 3^{2+} . This is shown in Figure 6. The integrated absorbance of this band has been shown by Hush²¹ and by Robin and Day²² to be an approximate measure of the delocalization parameter α , the mixing coefficient of donor and acceptor wave functions in the ground state. This treatment considers donor and acceptor sites as single centers, neglecting charge dispersal through metal-ligand interaction, as would certainly be important in the ferrocenium ion. It has nevertheless been used by Cowan and his group^{18,19} as an approximate measure of delocalization in a number of mixed-valence ferrocene systems. The value of α , which

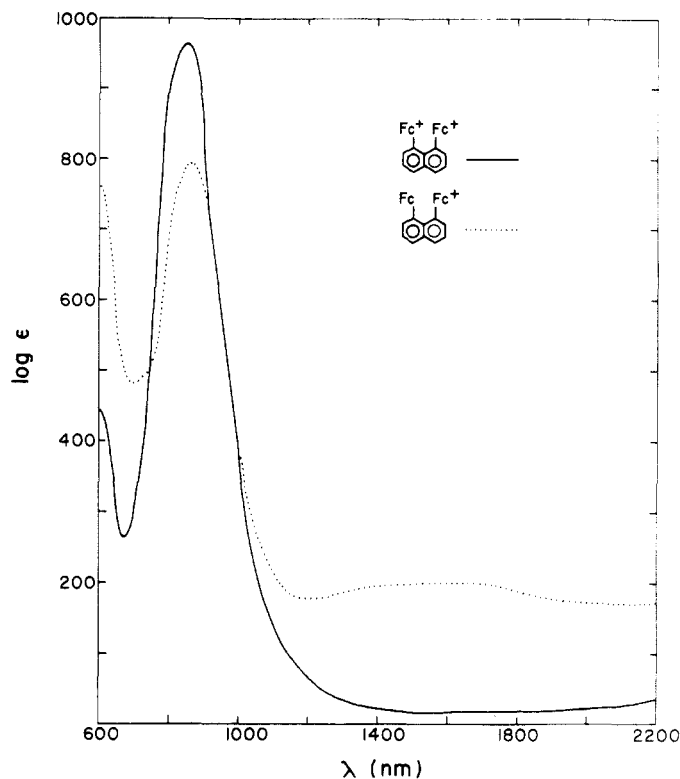


Figure 6. Near infrared absorption spectra of $(1,8\text{-Fc}_2\text{C}_{10}\text{H}_6)^+\text{BF}_4^-$ (---) and $(1,8\text{-Fc}_2\text{C}_{10}\text{H}_6)(\text{BF}_4)_2$ (—).

depends on $\Delta\nu_{1/2}$, the intervalence band half-width, is difficult to estimate for 3^+ , since this band is very broad and overlaps with the more intense absorption at 840 nm at its high-frequency end and with infrared absorptions at the other. However, a rough estimate of 4300 cm^{-1} for $\Delta\nu_{1/2}$ leads to a value of 0.03 for α and places this cation within the same class as biferrocenyl, diferrocenylacetylene, and 1,4-diferrocenylbutadiyne, for which values of α of 0.04–0.09 have been calculated. In accord with the results of the electrochemical studies and the infrared measurements, these calculations suggest that delocalization of charge in the ground state of 3^+ is small. Whether such delocalization results from classical "through-bond" conjugation, involving the naphthalene ring, or is in part derived from direct π -orbital interaction of the partially overlapping cofacial cyclopentadienyl rings is at present unknown. However, direct "through-space" interaction of metal centers, as has recently been suggested for some crowded tri- and tetraferrocene derivatives²³ would appear to be excluded by the structure of **3**.

We plan to examine the possibility of preparing transition-metal analogues of **3** and polymers based on structure **3** through coupling of 1,1'-dimetalated ferrocenes with 1,8-dihalonaphthalenes.

Experimental Section

Solvents were routinely dried by standard procedures and stored under nitrogen.

All the reactions and subsequent operations were performed under a nitrogen atmosphere.

Infrared spectra were recorded on Perkin-Elmer spectrophotometers, Models 457, 567, and 683. ${}^1\text{H}$ nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R-32 spectrometer (NSF GU 3852). ${}^{13}\text{C}$ nuclear magnetic resonance spectra were determined at 22.64 MHz with broad-band decoupling on a Bruker WH-90 spectrometer (NSF GU 3852, GP 37156). UV spectra were recorded on a Perkin-Elmer recording spectrophotometer Model 323. Mass spectra were recorded on a Hewlett-Packard GC/MS system, Model 5985.

(20) Prins, R. *J. Chem. Soc., Chem. Commun.* 1970, 280. Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* 1971, 93, 3603.

(21) Hush, N. S. *Prog. Inorg. Chem.* 1967, 8, 391.

(22) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* 1967, 10, 247.

(23) Delgado-Pena, F.; Talkam, D. R.; Cowan, D. O. *J. Organomet. Chem.* 1983, 253, C43.

Electrochemical Measurements. Methylene chloride and acetonitrile were each distilled from anhydrous P_2O_5 under a nitrogen atmosphere.

Cyclic voltammograms were obtained by using a Princeton Applied Research Model 173 potentiostat, a Model 175 universal programmer, and sweep-rate data were recorded on a Houston Instruments X-Y recorder. The working electrode, a platinum disk (IBM), and the reference, a $Ag/AgNO_3/CH_3CN$ electrode, were connected via a salt bridge containing $n-Bu_4NBF_4$ (0.2 M) in CH_2Cl_2 or Et_4NClO_4 (0.2 M) in CH_3CN . All electrochemical experiments were performed under argon. A 1:1 relationship of the anodic and cathodic peak current was observed in all measurements.

Melting points were determined under a nitrogen atmosphere on a Kofler hot stage and are uncorrected.

Elemental analyses were determined by either Galbraith Laboratories, Inc., Knoxville, TN, or Microlytics, South Deerfield, MS.

1,1'-Diphenylferrocene and Phenylferrocene. This reaction was performed in a three-neck round-bottom flask fitted with a solid CO_2 -acetone condenser and a magnetic stirrer. The reaction mixture was swept by a slow stream of dry nitrogen. Sodium metal (2.0 g, 87 mmol) was added to 250 mL of anhydrous liquid ammonia, and then ferric nitrate (ca. 0.01 g) was added to catalyze formation of $NaNH_2$. After the deep blue color had disappeared, 5.7 g (86 mmol) of freshly distilled cyclopentadiene was added slowly to give a yellowish green solution. After 45 min, iodobenzene (12.0 g, 58.8 mmol) was added to form a deep red solution. Sodium (2 g) was then added slowly and in small bits until the dark blue persisted, and the solution was stirred for 30 min. Anhydrous ferrous chloride (8.0 g, 63 mmol) was then added to the solution followed by THF (200 mL). Ammonia was allowed to evaporate, and the remaining solution was stirred overnight at room temperature. The reaction mixture was then filtered through Celite, and the filtrate was collected and evaporated on the rotary evaporator to dryness. The residue was redissolved in diethyl ether, washed with distilled water three times, dried over magnesium sulfate, and rotary evaporated to give a dark brown oil. This oil was chromatographed on neutral alumina (Activity II) with hexane to give 2.1 g (14%) of phenylferrocene, mp 114–115 °C (lit.²⁴ 113–114 °C), and 1.7 g (17%) of 1,1'-diphenylferrocene, mp 152.5–153.5 °C (lit.²⁴ 154–155 °C). These products were further characterized by their NMR spectra.

1,1'-Di- α -naphthylferrocene and α -Naphthylferrocene. These compounds were prepared following the previously described procedure using 1-chloronaphthalene (2.04 g, 12.5 mmol), sodium (0.70 g, 30 mmol), and cyclopentadiene (0.85 g, 13 mmol). The reaction yielded 1,1'-di- α -naphthylferrocene [mp 190 °C (lit.²⁶ mp 189–190 °C); 0.56 g (20.4%); 1H NMR ($CDCl_3$) δ 4.43 (b s, 4 ($H_{3,7}$ -Cp), 4.66 (b s, 4 ($H_{2,5}$ -Cp), 7.15–7.57 (m, 3 Ar), 7.67–7.97 (m, 3 Ar), 8.53 (d, 1, $J = 8$ Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 135.24, 133.68, 131.66, 128.28, 127.96, 127.63, 126.92, 125.82, 125.30, 125.04, 87.62, 71.77, 70.14; mass spectrum, m/e 438] and α -naphthylferrocene [0.36 g (18.5%), mp 92.5–93.5 °C (lit.²⁵ mp 96–97 °C)].

Coupling Reactions of Ferrocenyllithium and 1,8-Diiodonaphthalene Using $Pd(PPh_3)_4$ as Catalyst. Ferrocenyllithium was prepared from butyllithium in hexane (2.5 mL, 3.5 mmol) and bromoferrocene (0.79 g, 3.0 mmol) in 10 mL of hexane as described in the literature.²⁶ The reaction mixture was stirred at room temperature for 5 h during which an orange solid formed. Solvent was then removed by cannula, and the solid was taken up in 20 mL of THF. In a 100-mL three-neck round-bottom flask containing a magnetic stirring bar was placed 0.102 g (0.088 mmol) of $Pd(PPh_3)_4$, 0.40 g (1.1 mmol) of 1,8-diiodonaphthalene, and 15 mL of THF. This mixture was stirred for 30 min, followed by addition at 0 °C of the THF solution of the previously prepared ferrocenyllithium. After being stirred overnight at room temperature, the reaction mixture was quenched with 50 mL of 10% HCl and extracted with three 15-mL portions of ether. The combined ether extract was washed with water and dried over $MgSO_4$, and the solvent was removed on a rotary evaporator. Products were separated on preparative silica gel plates using 10%

methylene chloride in hexane to yield 14.1% of α -naphthylferrocene, mp 92.5–93.5 °C, and a trace of 1,8-diferrocenyl-naphthalene.

A similar reaction using $Ni(PPh_3)_4$ as catalyst was carried out and yielded only 1.6% of α -naphthylferrocene.

Another reaction using ferrocenyl magnesium bromide²⁷ (instead of ferrocenyllithium) and $Ni(dppp)Cl_2$ as catalyst was carried out in the same fashion. This yielded 49% of α -naphthylferrocene and 50% of naphthalene.

Coupling Reaction of Ferrocenylzinc Chloride and 1,8-Dibromonaphthalene Using Nickel Catalysts. Ferrocenylzinc chloride was prepared by adding 0.42 g (3.1 mmol) of anhydrous zinc chloride to 10 mL of a THF solution of ferrocenyllithium which was prepared from 0.79 g (3.0 mmol) of bromoferrocene by the previously described procedure. This mixture was stirred for 1 h at room temperature. In a 100-mL three-neck round-bottom flask, $Ni(PPh_3)_4$ was prepared in situ by adding 0.32 mL of a 1 M hexane solution of DIBAL-H to 10 mL of a THF solution of PPh_3 (0.18 g, 0.69 mmol) and $Ni(acac)_2$ (0.042 g, 0.16 mmol) at room temperature. The green color of $Ni(acac)_2$ disappeared upon addition of DIBAL-H and was replaced by a brick-red color. 1,8-Dibromonaphthalene (0.20 g, 0.70 mmol) was then added, and the mixture was stirred for 30 min at 0 °C. A solution of ferrocenylzinc chloride was then added, and stirring at 0 °C was continued for an additional hour. The solution was then warmed to room temperature and stirred overnight. The same separation procedure described previously was followed and yielded 11% of naphthalene, 65% of α -naphthylferrocene, and 29% of 1,8-diferrocenyl-naphthalene: mp 275 °C dec; 1H NMR ($CDCl_3$) δ 3.94 (s, 10, Cp), 4.27 (b s, 4, $H_{2,5}$ -Cp), 3.99 (b s, 4, $C_{3,4}$ -Cp), 7.65 (t, 2, $J = 8$ Hz, $H_{3,6}$ -Ar), 7.68 (d, 2, $J = 8$ Hz, $H_{2,7}$ -Ar), 7.89 (d, 2, $J = 8$ Hz, $H_{4,5}$ -Ar); ^{13}C NMR ($CDCl_3$) δ 66.51, 70.79 ($C_{2,5,3,4}$ -Cp), 69.49 (C_1 -Cp), 123.93, 126.73, 131.73, 136.60 (Ar); mass spectrum, m/e 496.

Anal. Calcd for $C_{30}H_{24}Fe_2$: C, 72.62; H, 4.87. Found: C, 72.61; H, 4.80.

A similar reaction using $Ni(dppf)_2$ (prepared in situ by reduction of $Ni(acac)_2$ using DIBAL-H in the presence of 2 equiv of $dppf$) as catalyst was carried out in the same manner as in the previous experiment. This yielded 26% of α -naphthylferrocene and 42% of 1,8-diferrocenyl-naphthalene.

Another reaction using $Ni(dppp)_2$ (prepared in situ by reduction of $Ni(dppp)Cl_2$ using DIBAL-H in the presence of 1 equiv of $dppp$) as catalyst was carried out as above and yielded 10% of naphthalene, 23% of α -naphthylferrocene, and 52% of 1,8-diferrocenyl-naphthalene.

Coupling Reaction of Ferrocenylzinc Chloride and 1,8-Dihalonaphthalene Using Palladium Catalysts. A 15-mL THF solution of ferrocenylzinc chloride prepared from 0.683 g (2.58 mmol) of bromoferrocene, as described earlier, was added to 10 mL of a THF solution of 1,8-dibromonaphthalene (0.16 g, 0.56 mmol) and $Pd(dppf)Cl_2$ (0.043 g, 0.059 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 3 h. This mixture was then heated under reflux for 1 h to ensure completion of the reaction. The same separation procedure described previously was followed and afforded 73 mg of 1,8-dibromonaphthalene, 70 mg of 1,8-diferrocenyl-naphthalene (46% based on consumed 1,8-dibromonaphthalene) and 49 mg of 1-bromo-8-ferrocenyl-naphthalene: 1H NMR ($CDCl_3$) δ 4.07 (s, 5, Cp), 4.21 (t, 2, $J = 1.5$ Hz, $C_{2,5}$ -Cp), 4.44 (t, 2, $J = 1.5$ Hz, $C_{3,4}$ -Cp), 7.10 (t, 1, $J = 7.5$ Hz, C_6 -Ar), 7.38 (t, 1 H, $J = 7.5$ Hz, C_3 -Ar), 7.54–7.77 (m, 3, $C_{4,5,7}$ -Ar), 8.32 (dd, 1, $J = 7.5, 1.2$ Hz, C_2 -Ar), mass spectrum, m/e 391.

Anal. Calcd for $C_{20}H_{15}BrFe$, C, 61.42; H, 3.87. Found: C, 61.08; H, 3.73.

A similar reaction using 0.40 g (1.5 mmol) of bromoferrocene, 0.028 g (0.038 mmol) of $Pd(dppf)Cl_2$, and 0.104 g (0.27 mmol) of 1,8-diiodonaphthalene as starting materials was carried out as above. This yielded 40 mg of recovered 1,8-diiodonaphthalene and 77 mg of 1,8-diferrocenyl-naphthalene (94% yield, based on 1,8-diiodonaphthalene consumed).

Oxidation of 1,8-Diferrocenyl-naphthalene with Silver Tetrafluoroborate. An acetonitrile solution (5 mL) of $AgBF_4$

(24) Pauson, P. L. *J. Am. Chem. Soc.* **1954**, *76*, 2187.

(25) Beckwith, L. J.; Leydon, R. *J. Aust. J. Chem.* **1966**, *19*, 1381.

(26) Hedberg, F. L.; Rosenberg, H. *Tetrahedron Lett.* **1969**, 4011.

(27) Kato, S.; Wakamatsu, M.; Mizuta, M. *J. Organomet. Chem.* **1974**, *78*, 405.

Table VI. Data for the X-ray Diffraction Study of 1,8-Diferrocenylnaphthalene

(A) Crystal Data at 21 (1) °C	
cryst system: monoclinic	Z = 4
space group: $P2_1/c$ [C_{2h}^5 ; No. 14]	cryst size: 0.10 × 0.21 × 0.59 mm
a = 17.134 (5) Å	fw 496.3
b = 10.195 (3) Å	$\rho_{\text{calcd}} = 1.529 \text{ g cm}^{-3}$
c = 12.351 (4) Å	$\rho_{\text{obsd}}^a = 1.53 (1) \text{ g cm}^{-3}$
$\beta = 92.20 (3)^\circ$	$\mu = 14.0 \text{ cm}^{-1} (\text{Mo K}\alpha)$
V = 2155.9 Å ³	

cell constant determination: 12 pairs of $\pm(hkl)$ and refined 2θ , ω , χ values in the range $23 < |2\theta| < 25^\circ$ ($\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$)

(B) Measurement of Intensity Data

radiation: Mo K α , graphite monochromator
 reflctns measd: $\pm h, +k, +l$ (to $2\theta = 46^\circ$)
 scan type, speed $\theta-2\theta$, 2.44-6.51°/min
 scan range: symmetrical, $(1.6 + \Delta(\alpha_2 - \alpha_1))^\circ$
 no. of reflctns measd: 3186; 3016 in unique set
 std reflctns: 400, 061, 336 measd after each 60 reflctns; variation $< \pm 3\sigma(I)$ for each
 abs correctn: empirical, normalized transmission factors 0.861-1.000
 statistical informatn:^b $R_s = 0.023$; $R_{\text{av}} = 0.018 (hk0)$

(C) Solution and Refinement (All 3016 Data Used in Refinement)

weighting of reflctns:^c $p = 0.035$
 soln: Patterson and difference-Fourier synthesis; nonroutine (see text)
 refinement:^d full-matrix least squares; anisotropic temperature factors for Fe, C atoms; H atoms fixed, treated as described elsewhere;^c $R = 0.059$; $R_w = 0.050$ ($R = 0.033$; $R_w = 0.045$ for 2157 data for which $|F_o| > 3.92\sigma(|F_o|)$)
 final difference-Fourier map: 0.48 e/Å near C(16) and C(17); 0.35 e/Å³ near Fe(1); other peaks random and $\leq 0.34 \text{ e/Å}^3$
 weighting scheme analysis: no systematic dependence on magnitude of $|F_o|$, $(\sin \theta)/\lambda$, or indices

^a Determined by neutral buoyancy in aqueous KI solution. ^b $R_s = \Sigma \sigma(|F_o|) / \Sigma |F_o|$; $R_{\text{av}} = [\Sigma |I - I_{\text{av}}| / \Sigma I]$. ^c Reference 28. ^d $R = \Sigma (||F_o| - |F_c||) / \Sigma |F_o|$, $R_w = \{\Sigma w[|F_o| - |F_c|]^2 / \Sigma w|F_o|^2\}^{1/2}$ and $\text{SDU} = \{\Sigma w[|F_o| - |F_c|]^2 / (m - n)\}$ where m (= 3016) is the number of observations and n (= 290) is the number of parameters.

Table VII. Atomic Coordinates for 1,8-Diferrocenylnaphthalene

atom	x	y	z
Fe(1)	0.43321 (3)	0.19670 (5)	-0.15891 (4)
Fe(2)	0.07153 (3)	0.20516 (5)	-0.36020 (4)
C(1)	0.3206 (2)	0.2707 (3)	-0.1772 (2)
C(2)	0.3251 (2)	0.1672 (3)	-0.0989 (3)
C(3)	0.3514 (2)	0.0517 (3)	-0.1508 (3)
C(4)	0.3642 (2)	0.0830 (4)	-0.2596 (3)
C(5)	0.3464 (2)	0.2173 (3)	-0.2758 (3)
C(6)	0.5470 (2)	0.1673 (5)	-0.1964 (3)
C(7)	0.5274 (2)	0.2981 (4)	-0.2095 (3)
C(8)	0.5043 (2)	0.3476 (4)	-0.1108 (4)
C(9)	0.5091 (3)	0.2428 (7)	-0.0348 (3)
C(10)	0.5363 (3)	0.1330 (5)	-0.0898 (3)
C(11)	0.1823 (2)	0.2793 (3)	-0.3281 (3)
C(12)	0.1549 (2)	0.2104 (3)	-0.2375 (2)
C(13)	0.1398 (2)	0.0788 (4)	-0.2688 (3)
C(14)	0.1560 (2)	0.0662 (4)	-0.3786 (3)
C(15)	0.1813 (2)	0.1884 (4)	-0.4158 (3)
C(16)	-0.0428 (2)	0.1476 (5)	-0.3639 (5)
C(17)	-0.0316 (2)	0.2695 (6)	-0.3027 (4)
C(18)	-0.0026 (2)	0.3601 (4)	-0.3755 (4)
C(19)	0.0042 (2)	0.3009 (4)	-0.4748 (3)
C(20)	-0.0204 (3)	0.1729 (5)	-0.4676 (4)
C(21)	0.2958 (2)	0.4090 (3)	-0.1604 (3)
C(22)	0.3219 (2)	0.4740 (4)	-0.0679 (3)
C(23)	0.3102 (2)	0.6083 (4)	-0.0548 (3)
C(24)	0.2789 (2)	0.6794 (4)	-0.1382 (4)
C(25)	0.2500 (2)	0.6187 (4)	-0.2343 (3)
C(26)	0.2198 (2)	0.6931 (4)	-0.3238 (4)
C(27)	0.1892 (2)	0.6347 (4)	-0.4130 (4)
C(28)	0.1795 (2)	0.4978 (4)	-0.4153 (3)
C(29)	0.2063 (2)	0.4192 (3)	-0.3308 (3)
C(30)	0.2504 (2)	0.4788 (3)	-0.2419 (2)

(15.0 mg, 0.077 mmol) was added to a solution of 1,8-diferrocenylnaphthalene (39.6 mg, 0.080 mmol) in 20 mL of CH₂Cl₂. The solution was concentrated in vacuo after being stirred for 0.5 h. Methanol was added, and the silver metal was removed by filtration and washed well with methanol. The solution was

made up to a volume of 100 mL, and aliquots were withdrawn and diluted as needed.

The same procedure, employing 2 molar equiv of AgBF₄, was used to prepare methanol solutions of the dication.

X-ray Structure Determination. Crystals of 3 were obtained by slow evaporation of a warm CH₂Cl₂ solution. Preliminary Weissenberg photographs exhibited systematic absences ($h0l$, l odd; $0k0$, k odd) and symmetry indicative of space group $P2_1/c$. Most operations were performed as described previously;²⁸ other operations are described below. Details of the structure analysis, in outline form, are given in Table VI. It was evident at an early stage that the structure was pseudosymmetric; the intensities of reflections for which $h + k \neq 2n$ were systematically very weak. Solution of the Patterson function gave Fe(1) at $\sim(0.43, 0.20, -0.15)$ and Fe(2) at $\sim(0.93, 0.70, -0.15)$, consistent with the observations above. Successful solution of the structure was not obtained until the *true* relative positions of the Fe atoms were obtained. The correct positions were established by trial-and-error manual movement of the relative (x_1, x_2) , (y_1, y_2) , and (z_1, z_2) pairs and comparison of the R values obtained. When the correct Fe positions were established, a difference Fourier synthesis revealed the positions of all C atoms. All data were corrected for secondary extinction by applying an empirical correction of the form $|F_o|_{\text{cor}} = |F_o|(1.0 + gI_o)$ where $g = 2.2 (2) \times 10^{-7}$. Atomic coordinates for all non-hydrogen atoms are given in Table VII.

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Registry No. 1, 1292-36-0; 1⁺BF₄⁻, 94161-78-1; 2, 12101-67-6; 3, 94161-70-3; 3⁺BF₄⁻, 94161-72-5; 3²⁺(BF₄)₂, 94161-74-7; 4 (M = Li), 1271-15-4; 4 (M = MgBr), 94161-75-8; 4 (M = ZnCl), 94161-76-9; 5 (X = I), 1730-04-7; 5 (X = Br), 17135-74-9; 6, 91-20-3; Pd(PPh₃)₄, 14221-01-3; Ni(dppp)Cl₂, 15629-92-2; Ni(PPh₃)₄, 15133-82-1; Ni(dppp)₂, 15629-49-9; Ni(dppf)₂, 94202-32-1; Pd(dppf)Cl₂, 72287-26-4; Ni(acac)₂, 3264-82-2; phenylferrocene,

1287-25-8; 1,1'-diphenylferrocene, 12098-13-4; cyclopentadiene, 542-92-7; iodobenzene, 591-50-4; ferrous chloride, 7758-94-3; 1-chloronaphthalene, 90-13-1; zinc chloride, 7646-85-7; bromoferrocene, 1273-73-0; 1,1-dilithioferrocene, 33272-09-2; 1-iodonaphthalene, 90-14-2.

Supplementary Material Available: Tables of (i) anisotropic thermal parameters, (ii) H atom positions, (iii) bond angles for cyclopentadienyl rings, and (iv) observed and calculated structure amplitudes (13 pages). Ordering information is given on any current masthead page.

Synthesis, Characterization, and Crystal and Molecular Structure of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3 \cdot \text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2 \cdot \text{Ga}(\text{CH}_2\text{SiMe}_3)_3$

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The complex $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3 \cdot \text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2 \cdot \text{Ga}(\text{CH}_2\text{SiMe}_3)_3$, prepared from $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$, has been fully characterized by analysis, standard spectroscopic methods, cryoscopic molecular weight measurements, and an X-ray structural study. The compound crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 9.911(4) \text{ \AA}$, $b = 16.427(6) \text{ \AA}$, $c = 14.770(6) \text{ \AA}$, $\beta = 90.43(4)^\circ$, and $Z = 2$ for $d_{\text{calcd}} = 1.08 \text{ g cm}^{-3}$. Full-matrix least-squares refinement led to a final R value of 0.075 for 1598 observed reflections. The molecule lies on a crystallographic inversion center. The geometry about the gallium atom is distorted tetrahedral with a Ga-C(av) distance of 1.99 [1] \AA and a Ga-N distance of 2.241 (9) \AA .

Introduction

The (trimethylsilyl)methyl group is considered to be a bulky substituent with larger steric effects than those of a methyl group. Consequently, the (trimethylsilyl)methyl group 3 derivatives $\text{M}(\text{CH}_2\text{SiMe}_3)_3$ ($\text{M} = \text{Al}, \text{Ga}, \text{In}$) are considered to be weaker Lewis acids than the corresponding methyl derivatives. For example, diethyl ether can be readily removed from the gallium² and indium³ derivatives, but the strong base NMe_3 forms stable complexes with all of these group 3 compounds. Diamines of the type $\text{Me}_2\text{N}(\text{CH}_2)_n\text{NMe}_2$ ($n = 2, 3$) react with MMe_3 ($\text{M} = \text{Al}, \text{Ga}, \text{In}$) to form 1:2 complexes⁴ $\text{Me}_3\text{M} \cdot \text{Me}_2\text{N}(\text{CH}_2)_n\text{NMe}_2 \cdot \text{MMe}_3$. Cryoscopic molecular weight measurements of these methyl complexes in benzene solution are consistent with monomeric behavior and little dissociation into 1:1 complexes and free Lewis acid. During the course of some of our investigations of the chemistry of $\text{M}(\text{CH}_2\text{SiMe}_3)_3$, $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ was reacted with a large excess of $\text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2$. The isolated product $(\text{Me}_3\text{SiCH}_2)_3\text{Ga} \cdot \text{Me}_2\text{NCH}_2\text{H}_4\text{NMe}_2 \cdot \text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ was fully characterized by analysis, standard spectroscopic methods, cryoscopic molecular weight measurements, and an X-ray structural study. This structural study represents only the second report of a structure of a neutral trialkylgallium-amine donor-acceptor complex and the first with an alkyl group other than methyl.

Experimental Section

The organogallium compounds described in this investigation were oxygen and moisture sensitive and were manipulated in a vacuum line or a purified argon atmosphere. The reagent $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ was synthesized by the literature procedure.² The ligand $\text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2$ (TMED) was dried over P_2O_5 and was vacuum distilled immediately prior to reaction. Infrared spectra were recorded in the range 4000–250 cm^{-1} by means of a Perkin-Elmer 683 spectrometer. The spectra were recorded as Nujol

mulls by using CsI plates. Bands due to mulling agents have been omitted. The ^1H NMR spectrum was recorded at 90 MHz and ambient temperature by using a Varian EM-390 spectrometer. Chemical shift data are reported in δ units (ppm) and are referenced to SiMe_4 as 0.00 and C_6H_6 as 7.13. Molecular weight measurements were obtained cryoscopically in benzene by using an instrument similar to that described by Shriver.⁵

Synthesis of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3 \cdot \text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2 \cdot \text{Ga}(\text{CH}_2\text{SiMe}_3)_3$. The title compound was prepared by vacuum distilling a large (tenfold) excess of $\text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2$ onto 0.785 g (2.37 mmol) of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ in a reaction tube equipped with a Teflon valve. After being warmed to room temperature, the reaction mixture was stirred for 5 h. The excess ligand was removed by vacuum distillation at room temperature to leave a viscous yellow liquid. This liquid was then heated to 45 $^\circ\text{C}$ under high vacuum, and colorless crystals were sublimed to the cooler portions of the tube. The crystals were isolated and resublimed at 45 $^\circ\text{C}$. The final product $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3 \cdot \text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2 \cdot \text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ (0.71 g, 0.912 mmol, 77.3%) was isolated as colorless crystals: mp 89–91 $^\circ\text{C}$, ^1H NMR (benzene, δ) +2.34 (s, 1.0, CH_2 -TMED), +1.88 (s, 2.9, Me-TMED), +0.20 (s, 11.4, $\text{Me}-\text{CH}_2\text{SiMe}_3$), -0.30 (s, 3.0, $\text{CH}_2-\text{CH}_2\text{SiMe}_3$); IR (Nujol, cm^{-1}) 1288 (w), 1252 (m), 1240 (s), 1162 (vw), 1128 (w), 1095 (vw), 1012 (m, sh), 999 (m), 982 (s), 960 (m), 945 (m), 860 (s, sh), 850 (s), 822 (vs), 783 (w), 748 (m), 721 (m), 677 (m), 610 (vw), 562 (w), 538 (w), 513 (m), 459 (vw); cryoscopic molecular weight, formula weight $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3 \cdot \text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2 \cdot \text{Ga}(\text{CH}_2\text{SiMe}_3)_3$, 778.9; molality (obsd mol wt) 0.0990 (549), 0.0687 (491), 0.0540 (452); hydrolysis, 0.0900 g (0.116 mmol) hydrolyzed in 6 M HCl for 48 h at 100 $^\circ\text{C}$ gave 0.697 mmol of SiMe_4 , calcd 0.696. (SiMe_4 from hydrolysis was purified by fractionation through two -78 $^\circ\text{C}$ traps and isolated at -196 $^\circ\text{C}$, and the quantity was determined by PVT measurements on the vacuum line.)

Collection of X-ray Diffraction Data and Solution of Structure for $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3 \cdot \text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2 \cdot \text{Ga}(\text{CH}_2\text{SiMe}_3)_3$. Single crystals of the air-sensitive compound were isolated by sublimation at 65 $^\circ\text{C}$ from an attempted reaction between $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ and LiH in $\text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2$ and were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin \theta/\lambda)^2)$ values for 15 reflections ($\theta > 20^\circ$) accurately centered on the diffractometer are given in Table I.

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(2) Beachley, O. T., Jr.; Simmons, R. G. *Inorg. Chem.* 1980, 19, 1021.

(3) Beachley, O. T., Jr.; Rusinko, R. N. *Inorg. Chem.* 1979, 18, 1966.

(4) Storr, A.; Thomas, B. S. *Can. J. Chem.* 1970, 48, 3687.

(5) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969; p 159.