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Metal−Metal Interactions in Weakly Coupled Mixed-Valence *E*- and *Z*-Diferrocenylethylene Complexes

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To study metal-to-metal interactions in mixed-valence states of two weakly coupling ferrocenyl groups assembled in E or Z conformation on an ethylenic double bond, *E*-1,2-dimethyldiferrocenylethylene (**1**), *Z*-1,2-dimethyldiferrocenylethylene (**2**), and 1,2-diferrocenylcyclohexene (**3**) were synthesized and structurally characterized. Crystals of **1** are triclinic, $P\bar{1}$, with $a = 7.494(9)$ Å, $b = 10.801(3)$ Å, $c = 11.971(2)$ Å, $\alpha = 102.17(2)°$, $\beta = 106.12(9)°$, $\gamma = 90.42(2)°$, $V = 907.8$ Å^3, and $Z = 2$. Crystals of **2** are monoclinic, $P2_1/c$, with $a = 13.601(8)$ Å, $b = 11.104(4)$ Å, $c = 13.732(1)$ Å, $\beta = 114.26(7)°$, $V = 1890.8(3)$ Å^3, and $Z = 4$. Crystals of **3** are orthorhombic, $P2_12_12_1$, with $a = 5.766(2)$ Å, $b = 13.090(1)$ Å, $c = 26.695(2)$ Å, $V = 2014.9(3)$ Å^3, and $Z = 4$. Intervalence transition spectra (IT) and electrochemical data have been determined and compared with those of diferrocenylbenzene (para, ortho, and meta). The comproportionation constants in nitrobenzene at 25 °C were found to be 490 and 813 for **1** and **3**, respectively. That of **2** was not measured because of the fact that **2**$^+$ isomerizes rapidly in all solvents tested, yielding nearly a racemic mixture of E and Z conformers. This finding helps to clear the paradoxical phenomenon between experimental results of mixed-valence complexes of *E*- and *Z*-1,2-bis(1′-ethyl-1-ferrocenyl)-1,2-dimethylethylene and theories. The stability of the mixed-valence species was discussed in terms of resonance delocalization, Coulomb repulsion energy, inductive effect, magnetic interaction, structural factors, and statistical factor. According to our analysis based on the Hush formalism, the contribution due to Coulomb repulsion energy dominates the overall stability of the mixed-valence state in **1**$^+$, **2**$^+$, and **3**$^+$. Stabilization that arises from resonance delocalization is only minor and contributes less than 4% to the overall stability, even in **3**$^+$ where linked C_p rings and the ethylenic plane are coplanar. In calculating the resonance contribution, crystallographic Fe−Fe distances of 7.44 Å (**1**) and 6.68 Å (**3**) were used for **1**$^+$, and **3**$^+$, respectively.

Introduction

It has been demonstrated that weakly coupled class II mixed-valence complexes of the three isomers of diferrocenylbenzene (para, ortho, and meta) show distinctively different spectroscopic data (position ν_{max}, extinction coefficient ϵ_{max}, half-bandwidth $\Delta\nu_{1/2}$ of the intervalence transitions) and comproportionation constants in acetonitrile.[1,2] In contrast, mixed-valence complexes of *E*- and *Z*-1,2-bis(1′-ethyl-1-ferrocenyl)-1,2-dimethylethylene exhibit identical spectroscopic and electrochemical results in dichloromethane.[3] Judging from Hush formalism,[4,5] the spectroscopic results of the latter are interesting because they imply that both isomers have the same oscillator strength (f), dipole strength (D), and transition dipole moment ($|M|$) and that the intermetallic distance (γ_{mm}) in the electronic coupling matrix (H_{AB}) is a through-bond instead of through-space as in mixed-valence complexes of diferrocenyl polyenes.[6] Moreover, the primary contributions to the stability of the mixed-valence species have been discussed[7−13] and summarized as[14]

$$\Delta G°_{tot} = \Delta G°_{r} + \Delta G°_{coul} + \Delta G°_{induc} + \Delta G°_{mag} + \Delta G°_{struc} + \Delta G°_{stat} \quad (1)$$

where $\Delta G°_r$, $\Delta G°_{coul}$, $\Delta G°_{induc}$, $\Delta G°_{mag}$, $\Delta G°_{struc}$, and $\Delta G°_{stat}$ are stabilization energies due to resonance delocalization, Coulomb repulsion energy, inductive effect, magnetic interaction, structural factors, and statistical factor, respectively. Among these factors, the contribution due to Coulomb repulsion energy is clearly through-space and will be expected to have different values for E and Z isomers. Then it is hard to rationalize the fact that *E*- and *Z*-1,2-bis(1′-ethyl-1-ferrocenyl)-1,2-dimethylethylene have exactly the same comproportionation constant. To clear the apparently paradoxical results that may be related to the solvent effect, the following mixed-valence complexes of *E*-1,2-dimethyldiferrocenylethylene (**1**), *Z*-1,2-dimethyldi-

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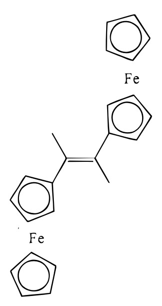
ferrocenylethylene (**2**), and the analogue of **2** with "fixed" conformation, 1,2-diferrocenylcyclohexene (**3**) were synthesized, characterized, and studied in a number of solvents.



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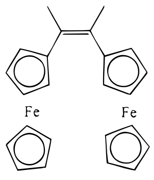

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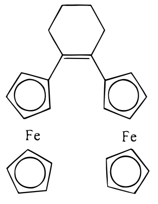

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Experimental Section

General Methods and Chemicals. All syntheses and manipulations were carried out using standard Schlenk techniques.[15] All yields reported refer to isolated material judged to be homogeneous by thin-layer chromatography and NMR spectroscopy. ^{1}H NMR spectra were obtained in $CDCl_3$ on a Bruker Aspect-3000 (300 MHz) spectrometer. All chemical shifts are in ppm, relative to δ(tetramethylsilane) = 0 ppm. Melting points were determined by differential scanning calorimetry (DSC), and results were obtained in an N_2 atmosphere on a Du Pont 910 differential scanning calorimeter. Solvents were dried according to established procedures[16] by distillation under N_2 from appropriate drying agents: benzene and tetrahydrofuran (THF) from sodium/benzophenone, acetonitrile from P_2O_5, methylene chloride from CaH_2. Chemicals were obtained from the following sources: $LiAlH_4$ from Merck, $CDCl_3$ from MSD, Al_2O_3 from Fluka, and the rest from Aldrich.

Preparation of *E*- and *Z*-Dimethyldiferrocenylethylene. **1** and **2** were synthesized via a low-valent titanium coupling method with some modification.[17-19] A solution of $TiCl_4$ (27 mmol) in THF (50 mL) was added to a suspension of $LiAlH_4$ (ca. 15 mmol) in THF (50 mL). The mixture was refluxed for 3 h, and then 2.0 g (8.8 mmol) of monoacetylferrocene[20] in 50 mL of THF was added. The resultant mixture was again refluxed for 3 h before it was brought to room temperature and chilled in an ice bath. To quench the reaction, saturated aqueous potassium carbonate solution (50 mL) was poured slowly into the flask. The solution was extracted thoroughly with $CHCl_3$, and the chloroform extract was concentrated and chromatographed (Al_2O_3) with 1:1 benzene/CH_2Cl_2 to get 1.0 g (54%) of crude products. Separation of **1** and **2** was made possible because of the fact that the E isomer is much less soluble in benzene. For **1**: orange, mp 218 °C. Anal. Calcd for $C_{24}H_{24}Fe_2$: C, 67.91; H, 5.70. Found: C, 68.24; H, 5.75. For **2**: orange, mp 188 °C. Anal. Calcd for $C_{24}H_{24}Fe_2$: C, 67.91; H, 5.70. Found: C, 68.19; H, 5.73.

Table 1. Summary of Crystallographic Data for 1,1-Diferrocenylethylene Complexes

compound	**1**[a]	**2**[b]	**3**[c]
empirical formula	$C_{24}H_{24}Fe_2$	$C_{24}H_{24}Fe_2$	$C_{26}H_{26}Fe_2$
fw	424.13	424.13	450.17
crystal system	triclinic	monoclinic	orthorhombic
temp, K	298	298	298
λ, Å	0.710 73	0.710 73	0.710 73
space group	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
a, Å	7.494(9)	13.601(8)	5.766(2)
b, Å	10.801(3)	11.104(4)	13.090(1)
c, Å	11.971(2)	13.732(1)	26.695(2)
α, deg	102.17(2)	90	90
β, deg	106.12(9)	114.26(7)	90
γ, deg	90.42(2)	90	90
V, Å^3	907.8(3)	1890.8(3)	2014.9(3)
Z	2	4	4
d_{calcd}, g cm^{-3}	1.552	1.490	1.484
μ, mm^{-1}	1.602	1.538	1.448
$R[F^2 > 2\sigma(F^2)]$[d]	0.0282	0.0423	0.0239
wR2(F^2)[e]	0.0994	0.114	0.0560

[a] **1** = *E*-1,2-dimethyldiferrocenylethylene. [b] **2** = *Z*-1,2-dimethyldiferrocenylethylene. [c] **3** = 1,2-diferrocenylcyclohexene. [d] $R = \sum||F_0| - |F_c||/[\sum|F_0|$. [e] $wR2(F^2) = \sum|w(F_0^2 - F_c^2)^2|/[\sum|w(F_0^2)^2|]^{1/2}$. $w = 1/[\sigma^2(F_0^2) + (0.1000P)^2]$, where $P = (\max(F_0^2,0) + 2F_c^2)/3$.

Table 2. Selected Bond Lengths (Å) and Dihedral Angles (deg) between Least-Square Planes in *E*-1,2-Dimethyldiferrocenylethylene (**1**), *Z*-1,2-Dimethyldiferrocenylethylene (**2**), and 1,2-Diferrocenylcyclohexene (**3**)

1	C1−C11	1.478(3)	C11−C12	1.517(3)
	C11−C11A	1.354(3)		
2	C1−C21	1.474(4)	C21−C22	1.353(4)
	C22−C11	1.465(4)		
3	C1−C21	1.475(3)	C21−C22	1.346(3)
	C22−C11	1.484(3)		

1	C1−C2−C3−C4−C5 and C1−C11−C11A−C1A	37.6(6)
2	C1−C2−C3−C4−C5 and C1−C21−C22−C11	42.1(4)
	C11−C12−C13−C14−C15 and C1−C21−C22−C11	42.6(2)
3	C1−C2−C3−C4−C5 and C1−C21−C22−C11	40.2(1)
	C11−C12−C13−C14−C15 and C1−C21−C22−C11	41.5(4)

Preparation of Adipoylferrocene ($FcCO(CH_2)_4COFc$, Fc = Ferrocene). To a stirred sludge of 2 g (15 mmol) of $AlCl_3$ and 1 mL of adipoyl chloride ($ClCO(CH_2)_4COCl$, 6.9 mmol) under nitrogen, 20 g (108 mmol) of ferrocene in 150 mL of CH_2Cl_2 was added 10 min later. The resultant mixture was stirred at room temperature for 12 h. and then 300 mL of 10% Na_2CO_3 was added to quench the reaction. The organic layer, washed three times each with 100 mL of saturated NaCl solution, was concentrated to 10 mL and charged to a Al_2O_3 column. By removal of excess ferrocene in the mixture with *n*-hexane, the desired compound was isolated as chromatographed with CH_2Cl_2; yield 2 g (59%), yellow, mp 143 °C. Anal. Calcd for $C_{26}H_{26}O_2Fe_2$: C, 64.76; H, 5.43. Found: C, 64.44; H, 5.37. ^{1}H NMR ($CDCl_3$): δ 1.80 (p, 2H), 2.78 (t, 2H), 4.20 (s, 5H), 4.50 (t, 2H), 4.80 (t, 2H). ^{13}C NMR ($CDCl_3$): δ 24.4, 39.6, 69.3, 69.7, 72.1, 79.1, 204.1.

Preparation of 1,2-Diferrocenylcyclohexene (3). A solution of $TiCl_4$ (27 mmol) in THF (50 mL) was added to a suspension of $LiAlH_4$ (ca. 15 mmol) in THF (50 mL). The mixture was refluxed for 3 h, and then 1 g (2.07 mmol) of adipoylferrocene in 100 mL of THF was added dropwise for 5 h. The resultant mixture was refluxed for another 30 min before it was brought to room temperature and chilled in an ice bath. To quench the reaction, 100 mL of 10% Na_2CO_3 solution was added. The solution was extracted thoroughly with CH_2Cl_2, and the extract was concentrated and chromatographed (Al_2O_3) with hexane; yield 500 mg (53%), yellow, mp 167 °C. Anal. Calcd for $C_{26}H_{26}Fe_2$: C, 69.37; H, 5.82. Found: C, 69.48; H, 5.66. ^{1}H NMR ($CDCl_3$): δ 1.77 (p, 2H), 2.47 (t, 2H), 3.94 (t, 2H), 4.08 (m, 7H). ^{13}C NMR ($CDCl_3$): δ 23.6, 32.3, 67.0, 68.9, 69.2, 89.9, 129.8.

X-ray Crystallography. Single crystals were obtained by slow diffusion of hexane into saturated benzene solution containing **1** or **2**, while that of **3** was obtained the same way with CH_2Cl_2 in lieu of benzene. Data were recorded on a Siemens R3m/V diffractometer equipped with a highly oriented graphite crystal monochromator (298 K, Mo Kα X-radiation λ = 0.717 03 Å). Cell parameters were determined from 25 accurately centered reflections in the range 0° ≤ 2θ ≤ 30°. Three standard reflections were monitored every 197 reflections during data collection, and no variation was observed The structure solutions were carried out using SHELXTL PC software[21] on a Siemens PCD-4H computer. The iron atom positions were determined by the Patterson method. Subsequent Fourier difference

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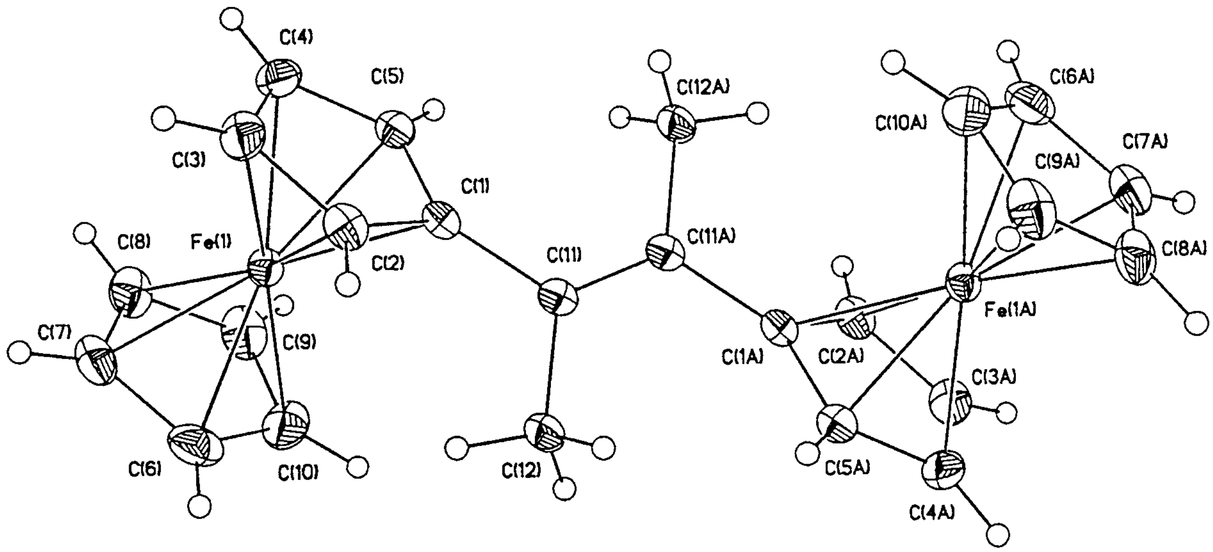

Figure 1. ORTEP drawing of *E*-1,2-dimethyldiferrocenylethylene (**1**) showing the atomic numbering scheme.

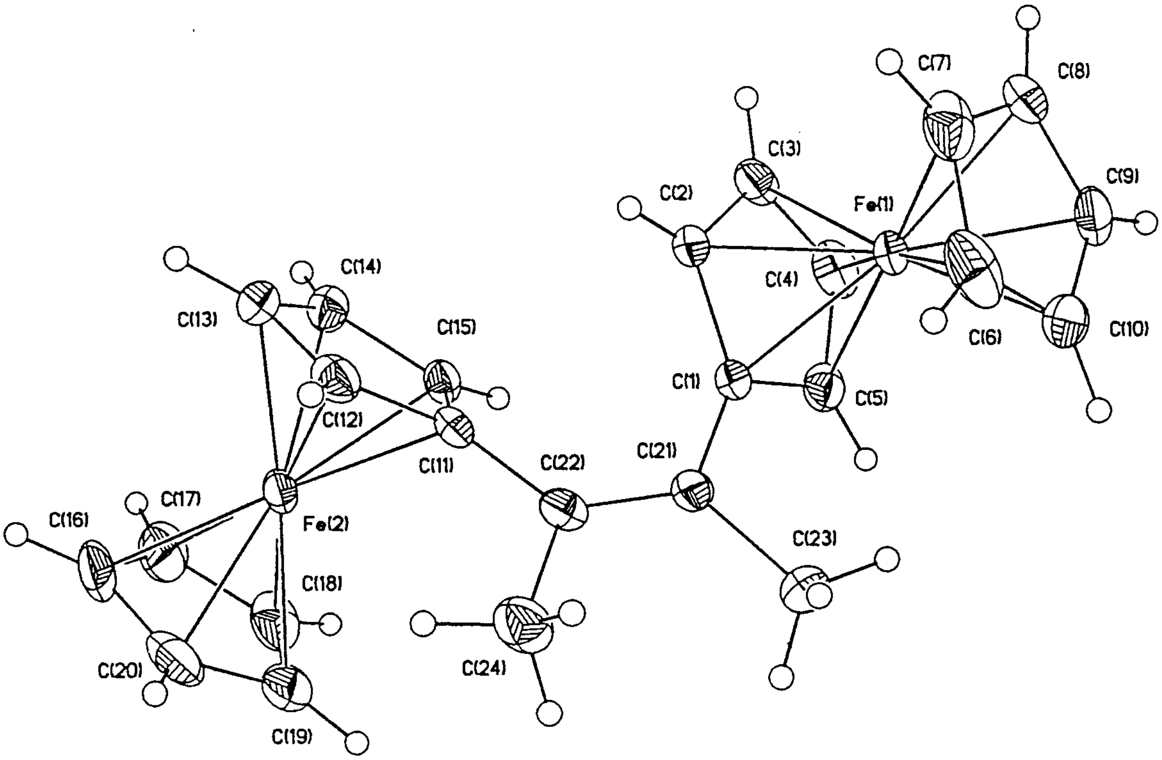

Figure 2. ORTEP drawing of *Z*-1,2-dimethyldiferrocenylethylene (**2**) showing the atomic numbering scheme.

syntheses revealed the positions of the other non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined using a riding model (C−H, 0.96 Å) with fixed thermal parameters ($U = 0.05$ Å^2). Crystal data and details associated with structure refinement are summarized in Table 1. The selected bond lengths and dihedral angles between the least-squares planes of **1**−**3** are given in Table 2.

Cyclic Voltammetry. Cyclic voltammetric experiments were carried out in nitrobenzene by using a Princeton Applied Research (PAR) model 273 electrochemistry system and a standard three-electrode configuration. The working electrode (Beckman No. 39273) was a platinum inlay electrode with a surface area of 0.28 cm^2. Its surface was polished to a mirror-bright finish with polishing alumina before each experiment. The auxiliary electrode was a Pt wire, and the reference electrode was a PAR-KO103 nonaqueous reference electrode, Ag/0.1 M $AgNO_3$ in CH_3CN, located inside a reference electrode bridge tube with a Vycor tip (PAR-K0065) to prevent contamination of the test solution by the reference electrode filling solution. Solutions were 1.0×10^{-3} to 5×10^{-4} M in the complex and 0.1 M in $(Bu_4N)PF_6$, and they were purged with N_2 for 15 min prior to each measurement. The scan rates were 200 mV/s. The $E_{1/2}°$ values were calculated from the average of the cathodic and anodic potentials. Under these conditions the $E_{1/2}°$ value of ferrocene is 125 mV.

NIR Measurements. Equimolar concentrations of the oxidant (ferrocenium tetrafluoroborate) and the reductant (**1**, **2**, or **3**) were allowed to react in a sidearmed flask containing nitrobenzene for 20 min. The resulting solution was transferred to a flow cell capped with a septum and connected to a temperature bath with the syringe technique. Metal-to-metal charge-transfer (IT) spectra were recorded on a Shimadzu 3101 spectrophotometer.

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(21) *SHELXTL PC for Siemens Crystallographic Research Systems*, release 5; Siemens Analytical X-ray Instruments Inc.: Madison, WI.

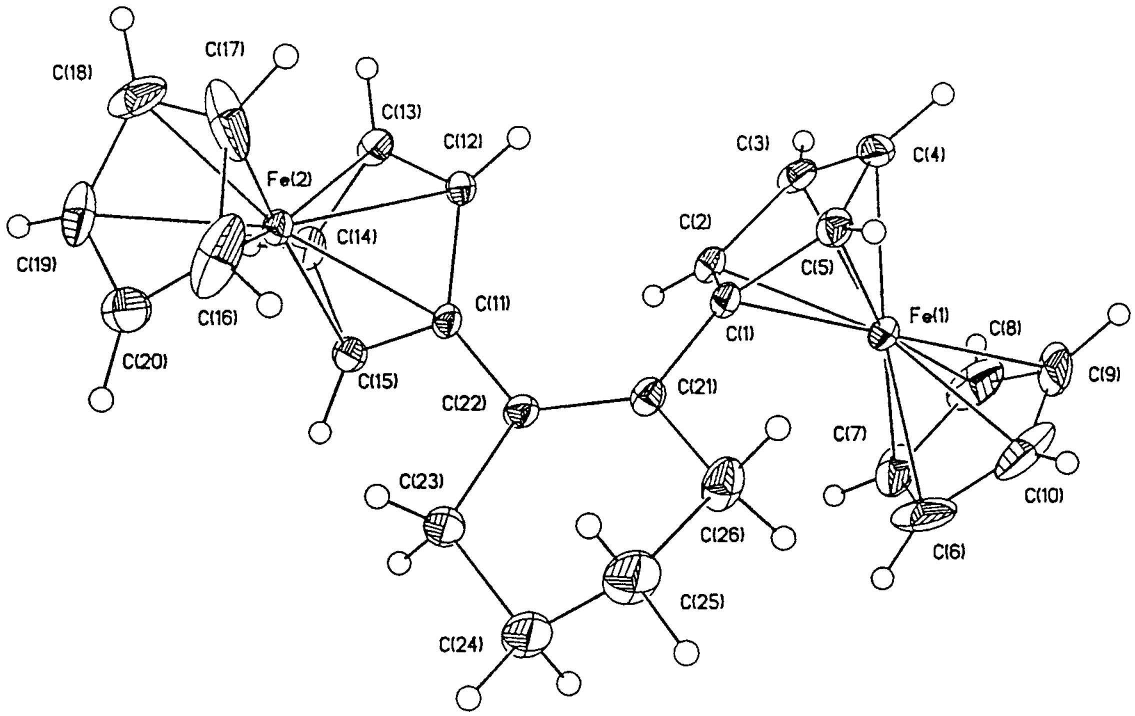

Figure 3. ORTEP drawing of 1,2-diferrocenylcyclohexene (**3**) showing the atomic numbering scheme.

Results and Discussion

Description of the Structures. Figure 1 shows an ORTEP drawing of **1** with the atomic numbering scheme. The E isomer crystallizes in the triclinic space group $P\bar{1}$ with two ferrocenyl units trans to each other. The free C_p rings are essentially planar in which all the carbon atoms are within 0.01 Å of their least-squares planes. The dihedral angle between the bridged C_p rings is 0°, and that between bridged C_p and the adjacent ethylenic plane C12−C11−C11A−C1A is 37.6°. The average Fe−C distance of 2.04 Å is consistent with that reported in the literature.[22] This structure results in an Fe−Fe distance of 7.445(0) Å.

Figure 2 shows an ORTEP drawing of **2** with the atomic numbering scheme. The Z isomer crystallizes in monoclinic space group $P2_1/c$ with two ferrocenyl units cis to each other. The dihedral angle between the bridged C_p rings is 46.7°, and that between bridged C_p and ethylenic plane C1−C21−C22−C11 is 42.1°. The average Fe−C distances associated with Fe1 and Fe2 are virtually identical with the slighter longer value of 2.06 Å in the E isomer. The ethylenic double bond has a length of 1.353(4) Å. This structure gives rise to an Fe−Fe distance of 6.680(8) Å.

Figure 3 shows an ORTEP drawing of **3** with the atomic numbering scheme. It crystallizes in the orthorhombic space group $P2_12_12_1$ with two ferrocenyl units cis to each other. Resembling closely that in **2**, the dihedral angle between the bridged C_p rings is 45.6° and that between C1−C2−C3−C4−C5 and ethylenic plane C1−C21−C22−C11 is 40.2°. The ethylenic double bond has a length of 1.346(3) Å. This structure gives rise to an Fe−Fe distance of 6.678(9) Å.

NMR. The ^{1}H NMR spectra of **1** and **2** are very similar, and the major difference is that all corresponding signals in **1** are downfield-shifted. A comparison is made with the corresponding data of **2** inside the bracket: methyl protons (s, 3H), δ 2.169 (2.047) ppm; free C_p (s, 5H), δ 4.272 (4.209) ppm; ortho protons on substituted C_p rings (t, 2H) centered at δ 4.372 (4.173) ppm; and meta protons (t, 2H) centered at 4.481 (4.158) ppm. In the course of NMR measurements we found that **1** and **2** isomerize noticeably in $CDCl_3$ even in the reduced [II−II] state as their ruthenium analogues.[23] The isomerization would be expected to proceed even faster in $\mathbf{1}^+$ and $\mathbf{2}^+$ with a possible radical cation transition state. To make sure near-IR measurements of $\mathbf{1}^+$ and $\mathbf{2}^+$ correspond to the expected conformation, all samples employed in near-IR runs were reduced by $Na_2S_2O_3$ and examined again via NMR. We found the isomerization is indeed fast enough to yield nearly a racemic mixture of E and Z isomers in CH_2Cl_2. Judging from the closeness of cathodic and anodic peak potentials in **1** and **2** ($E_{\mathrm{cathodic}}/E_{\mathrm{anodic}}$ in mV: −6/76, 164/250 for **1**; 6/90, 174/262 for **2**), we think the electrochemical results of *E*- and *Z*-1,2-bis(1′-ethyl-1-ferrocenyl)-1,2-dimethylethylene[3] are explainable and pose no threat to the Hush formalism either. Further experiments confirm that $\mathbf{2}^+$ isomerizes

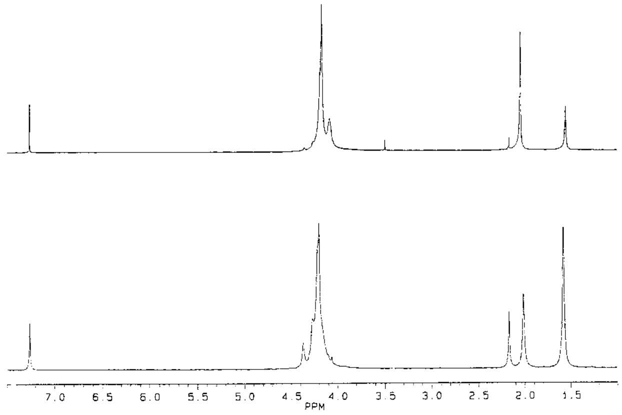

Figure 4. NMR spectrum of *Z*-1,2-dimethyldiferrocenylethylene (**2**) in $CDCl_3$ (top) and that of $\mathbf{2}^+$ after oxidation in CH_2Cl_2 and then reduction by $Na_2S_2O_3$ (bottom).

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Table 3. Spectroscopic Data of the Intervalence Transitions and Electronic Coupling Parameters for Mixed-Valence **1**, **2**, **3**, 1,2-Diferrocenylethene, Diferrocenylbenzene (Para, Ortho, Meta), and *E*- and *Z*-1,2-Bis(1′-ethyl-1-ferrocenyl)-1,2-dimethylethylene (E and Z, Respectively)[a]

compound	ν_{max}, cm^{-1}	ϵ_{max}, M^{-1} cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	f [f]	D,[f] Å	$\|M\|$,[f] Å esu	H_{AB},[f] cm^{-1}	α
$\mathbf{1}^+$	6020	460	3830	8.10×10^{-3}	0.35	1.69×10^{-10}	284	0.047
$\mathbf{2}^+$	*b*	*b*	*b*	*b*	*b*	*b*	*b*	*b*
$\mathbf{3}^+$	5951	340	3811	5.96×10^{-3}	0.30	1.46×10^{-10}	270	0.045
1,2-diferrocenylethne[c]	5714	1200	4300	2.37×10^{-2}	0.62	2.97×10^{-10}	473	0.083
1,2-diferrocenylethne[d]	4910	1340	4360	2.69×10^{-2}	0.71	1.15×10^{-10}	492	0.10
para[e]	7450	620	4906	1.40×10^{-2}	0.42	2.00×10^{-10}	347	0.046
ortho[e]	6540	91	6750	2.83×10^{-3}	0.20	9.59×10^{-11}	202	0.031
meta[e]	8290	46	4040	8.55×10^{-4}	0.097	4.68×10^{-11}	105	0.013
E[e]	5000	650	4600	1.38×10^{-2}	0.50	2.42×10^{-10}	337	0.067
Z[e]	5000	650	4600	1.38×10^{-2}	0.50	2.42×10^{-10}	375	0.067

[a] References 1 and 3. $\mathbf{1}^+$, $\mathbf{2}^+$, and $\mathbf{3}^+$ were measured in nitrobenzene, para in chloroform, ortho and meta in acetonitrile, and E and Z in dichloromethane. [b] Did not measure because of isomerization. [c] Reference 24, in CH_2Cl_2 containing 0.2 M Bu_4BF_4. [d] Reference 6, in CH_2Cl_2 containing 0.1 M Bu_4BF_4. [e] Values of *f*, *D*, and |*M*| were calculated from data in refs 1 and 3. [f] Calcd from $f = (4.6 \times 10^{-9})\epsilon_{max}\Delta\nu_{1/2}$, $D = [f/(1.085 \times 10^{-5}\,\nu_{max})]^{1/2}$, $|M| = (4.803 \times 10^{-10})D$, $H_{AB} = (2.05 \times 10^{-2})[\epsilon_{max}\Delta\nu_{1/2}\nu_{max}]^{1/2}/\gamma_{mm}$.

Table 4. Redox Potentials and Comproportionation Constants of **1**, **2**, **3**, 1,2-Diferrocenylethene, Diferrocenylbenzene (para, ortho, meta),[a] *E*- and *Z*-1,2-Bis(1′-ethyl-1-ferrocenyl)-1,2-dimethylethylene (E and Z, Respectively)[b] and Their Resonance and Nonresonance Contributions to Overall Free Energy Change in Mixed-Valence States[c]

compound	$(E_{1/2}°)_1$, mV	$(E_{1/2}°)_2$, mV	$\Delta E_{1/2}°$, mV	K_c [g]	$\Delta G°_r$,[g] cm^{-1}	$\Delta G°_{nr}$,[g] cm^{-1}
1	58	217	159	490	−26.8	−1257
2	48	218	170	752		
3	35	207	172	813	−24.5	−1364
1,2-diferrocenylethene[d]	*e*	*e*	*e*	*e*	*e*	*e*
1,2-diferrocenylethene[f]	290	460	170	752	−99	−1274
para[g]	386	490	104	60	−32.3	−816
ortho[g]	387	518	131	160	−12.5	−1039
meta[h]	398	488	90	35	−2.7	−734
E[h]	330	475	145	349	−45	−1168
Z[h]	325	475	150	349	−56	−1158

[a] Reference 1. [b] Reference 3. [c] The values of $E_{1/2}°$ of **1**, **2**, and **3** were measured against a PAR-KO103 nonaqueous reference electrode, Ag/0.1 M $AgNO_3$ in CH_3CN, located inside a reference electrode bridge tube with Vycor tip (PAR-K0065). These values are the average of the potentials for peak anodic and cathodic currents in the cyclic voltammograms recorded at 200 mV/s. The values of $E_{1/2}°$ of ortho and meta were measured in CH_3CN, while that of para was measured in $CHCl_3$. Values were with respect to SCE. The values of $E_{1/2}°$ of E and Z were measured in CH_2Cl_2. Values were with respect to SCE. [d] Reference 24. [e] Not available. [f] Reference 6. [g] Calcd from ref 13. [h] Values of $\Delta G°_r$ and $\Delta G°_{nr}$ were calculated from data in refs 1 and 3.

to $\mathbf{1}^+$ in other organic solvents such as CH_2Cl_2, CH_3Cl, benzonitrile, nitromethane, and nitrobenzene and that $\mathbf{1}^+$ would retain its conformation in nitromethane and nitrobenzene. For $\mathbf{3}^+$ the conformation in all solvents remains unchanged, which is ascribed to the steric hindrance of the cyclohexene. These observations are summarized in Figures 4 and 5.

NIR and Electronic Coupling Parameters. NIR data for the intervalence transitions (IT) were summarized in Table 3. Also included in the table were numerical values for the oscillator strength (*f*), dipole strength (*D*), transition dipole moment (|*M*|), and the electronic coupling matrix (H_{AB}). In carrying out the calculation, the through-space crystallographic Fe−Fe distances of 7.44 Å and 6.68 Å were used as the intermetallic distance (γ_{mm}) for **1** and **3**, respectively. The degree of ground-state delocalization in mixed-valence complexes $\mathbf{1}^+$ and $\mathbf{3}^+$ can be estimated by the square of the mixing coefficient α, $(H_{AB}/\nu_{max})^2$, as 0.224% and 0.207%, respectively. The delocalization is small, and $\mathbf{1}^+$ and $\mathbf{3}^+$ thus fall within the weakly coupling class II complex.[2] It is noteworthy that the values of H_{AB} obtained by Ribou et al. (492 cm^{-1})[6] and Cowan et al. (473 cm^{-1})[24] on 1,2-diferrocenylethylene are ca. 1.7 times larger than that of $\mathbf{1}^+$ (284 cm^{-1}). That the substitution by methyl groups decreases H_{AB} significantly is apparently attributed to α instead of ν_{max}. Without the steric hindrance between methyl protons and the ones on the adjacent C_p ring, 1,2-diferrocenylethene may sustain better coplanarity of the plane consisting of C_p rings and the ethylenic plane to enhance the resonance effect.

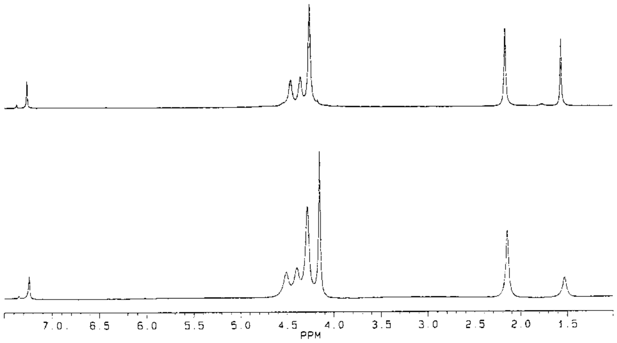

Figure 5. NMR spectrum of *E*-1,2-dimethyldiferrocenylethylene (**1**) in $CDCl_3$ (top) and that of $\mathbf{1}^+$ after oxidation in nitrobenzene and then reduction by $Na_2S_2O_3$ (bottom).

Stability of the Binuclear Complexes. 1−3 show reversible redox reactions at the Pt electrode in nitrobenzene containing 0.1 M $[n\text{-}Bu_4N]PF_6$ as the supporting electrolyte. Table 4 summarizes half-wave potentials ($E_{1/2}°$) of **1**−**3** and of some related complexes.[1,3] As can be seen in Table 4, $\Delta G°_r$ of $\mathbf{1}^+$ or $\mathbf{3}^+$ contributes less than 4% to the overall free energy change of the comproportionation equilibrium. Thus, the comproportionation constant K_c is largely determined by nonresonance contributions, i.e.,

$$\Delta G°_{nr} = \Delta G°_{coul} + \Delta G°_{induc} + \Delta G°_{mag} + \Delta G°_{struc} + \Delta G°_{stat} \quad (2)$$

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The statistical contribution $\Delta G°_{\mathrm{stat}}$ of $-290\ \mathrm{cm}^{-1}$ (36 mV) for identical, noninteracting metal ions is expected to decrease in systems with significant electronic interaction[25] and to remain essentially constant in the homologous series of **1**, **2**, and **3** and that of para, ortho, and meta.[1] The contribution due to structural changes, $\Delta G°_{\mathrm{struc}}$, namely, bond making and bond breaking to give changes in coordination number and geometry,[26−28] is considered to be equal within these two homologous series mentioned. The possible contribution due to magnetic interaction between metal centers in the III−III state via a superexchange[29,30] pathway is assumed to be as small as that of the dirutheniumpyrazine complex.[31] It should be noted that in the mixed-valence form of the binuclear ruthenium complex $[(\mathrm{NH_3})_5\mathrm{RuLRu}(\mathrm{NH_3})_5]^{5+}$ the major contribution to $\Delta G°_{\mathrm{tot}}$ is the $\Delta G°_{\mathrm{induc}}$ term. This term arises from two primary effects:[32] the decrease of the π-acid nature of the bridging ligand in the II−II dimer relative to the III−III dimer; the inductive effect of the coordinated Ru(III) on the bridging π^* orbital in the II−III dimer. It is expected that Ru(III) will lower the energy of the π^* orbital more efficiently than Ru(II), thus increasing the back-bonding interaction.[11] In contrast, the largest contribution to $\Delta G°_{\mathrm{tot}}$ in **1**−**3** seems to be the $\Delta G°_{\mathrm{coul}}$ term. The argument that Coulomb repulsion energy of the metal charges contributes most to the comproportionation constant is supported by the K_c value calculated by the following equation[33]

$$K_c = 4\exp\left(\frac{1}{D_s\gamma_{mm}k_bT}\right) = 4\exp\left(\frac{561}{D_s\gamma_{mm}}\right), \quad \text{at 298 K with } \gamma_{mm} \text{ in Å} \qquad (3)$$

where D_s is the dielectric constant of the material between the metal atoms separated by γ_{mm}. Using the crystallographic Fe−Fe distance of 7.44 Å of **1** as the intermetallic separation and applying eq 3, we conclude that $D_s = 15.7$. Applying $D_s = 15.7$ and the crystallographic Fe−Fe distance of 6.68 Å of **3**, we obtain $K_c = 842$, close enough to the value measured by cyclic voltammetry of $K_c = 813$. Judging from essentially the same crystallographic Fe−Fe distance and the dihedral twist between the linked C_p planes in **2** and **3**, we conclude $\Delta G°_{\mathrm{coul}}$ to be also the major contribution to K_c in **2**. It should be noted that calculation of the comproportionation constant using the macroscopic dielectric constant for the solvent, as in the case of Sutton and Taube,[7,32] falls far short of the experimental value.

Conclusion

The structure of **1** shows an almost planar $C_5H_4C{=}CC_5H_4$ moiety with an Fe−Fe distance of 7.44 Å, while structures of **2** and **3** have essentially the same dihedral twist angle between the two linked C_p rings (45.6° vs 46.7°) and the same Fe−Fe distance (6.68 Å). The mixed-valence ions of **1**−**3** belong to class II as evidenced by values of α^2 (<0.3%). The stability of the mixed-valence species is dominated by the Coulomb repulsion energy of nonresonance contributions.

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Supporting Information Available: Tables listing crystallographic data, atomic positional parameters, anisotropic thermal parameters, bond lengths and angles for *E*-1,2-dimethyldiferrocenylethylene (**1**), *Z*-1,2-dimethyldiferrocenylethylene (**2**), and 1,2-diferrocenylcyclohexene (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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