Pronounced Effects of Ring Tilting on the Intramolecular Electron-transfer Rate in Mixed-valence Polyalkyl-substituted Biferrocenium Cations

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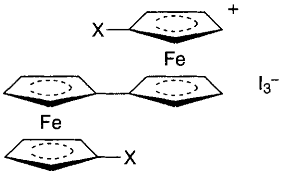
The results of X-Ray structural determinations, electrochemical measurements, near-IR, ^{57}Fe Mössbauer measurements, and an explanation of the influence of steric factors on the electron-transfer rates for a series of polyalkyl substituted mixed-valence biferrocenium triiodides are reported.

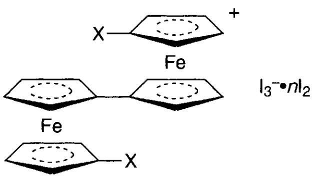
In recent years, the fundamental nature of electron transfer in the mixed-valence biferrocenium cations (**1–13**) and other systems in the solid state has begun to receive considerable attention. We undertook the present work in the hope that comparison of the molecular structures would improve our understanding of the factors that control the rate of intramolecular electron transfer in the solid state for a series of mixed-valence biferrocenium salts. In the solid state, the rate of electron transfer for a given mixed-valence cation is influenced by various structural factors and lattice dynamics,[1–5] including the electronic and vibronic coupling between two metal ions,[6–9] the nature of the counter ion,[10–12] and cation–anion interaction.[13] In this communication, we suggest that structural micromodifications in mixed-valence biferrocenium cations have certain important effects on the intramolecular electron-transfer rate. To study the influence of the structural effect, we have prepared a series of polyalkylbiferrocenium triiodide salts **14–19** and the corresponding neutral species **14′–19′**.† This is an important regime for study, since lattice dynamic effects are expected to be most pronounced for electron transfer.[1–5]

Compounds **14–19** give unusual temperature-dependent Mössbauer spectra (Table 1). At temperatures below 77 K they each show two doublets, one for the iron(II) and the other for the iron(III) site. Increasing the temperature in each case causes the two doublets to move together, eventually to become a single 'average-valence' doublet at temperature of 200, 295, 265, 125 and 200 K for **14**,[14,15] **15–17**,[14,15] and **19**, respectively. The Mössbauer results indicate that compounds **14–17** and **19** are delocalized on the Mössbauer timescale at 300 K. Only a single 'average-valence' doublet is seen. This does not happen for **18** where two doublets are observed in the 300 K Mössbauer spectrum. This pattern is expected for a mixed-valence cation which is valence-trapped on the timescale of Mössbauer technique (electron-transfer rate $\leqslant 10^7$ s^{-1}).[16,17] The IR spectra for mixed-valence **14–19** are seen to exhibit two C–H perpendicular bending bands, which may be readily assigned to Fe^{II} (≈ 815 cm^{-1}) and Fe^{III} (≈ 845 cm^{-1}) moieties. It is clear that compounds **14–19** are localized on the IR timescale.[16,17]

In common with most mixed-valence complexes,[6,7,18,19] compounds **14–19** in CH_2Cl_2 solution have an intervalence transition (IT) band at 4651 cm^{-1}, which is not present for the neutral compound or dioxidized ion. The value of α^2 is a direct measure of delocalization in the ground state.[20,21] As shown in Table 1, in all cases there is good evidence for localized valence.[22]



	X		X
1	H	**5**	I
2	Et	**6**	Br
3	Pr^n	**7**	Cl
4	Bu^n		



	X	*n*
8	CH_2Ph	0
9	C_6H_4I-*p*	0
10	C_6H_4Br-*p*	1
11	C_6H_4Cl-*p*	0
12	C_6H_4I-*o*	0
13	C_6H_4Br-*o*	0

From the rate constants illustrated in Table 1, the magnitudes of electron-transfer rate between the two Fe sites in **14–19** are nearly equivalent in solution. This observation is consistent with the electrochemical data. The corresponding neutral species **14′–19′** show two successive reversible one-electron oxidations to yield the mono- and then the di-cation. It has been shown that the peak-to-peak separation ($\Delta E_{1/2}$) can gauge the interaction between two Fe sites.[23,24] The separations between the two oxidation waves for the neutral compounds of **14–19** are 0.37,[15] 0.38, 0.36, 0.37,[15] 0.38 and 0.36, respectively. In other words, the magnitudes of the electronic interactions between the two Fe sites in **14–19** are nearly equivalent in solution. Of course, this is not consistent with the solid-state variable-temperature ^{57}Fe Mössbauer results.

Recently, there has been considerable progress made in understanding what factors control the rate of intramolecular electron transfer in the solid state for mixed-valence biferrocenium salts.[2,3,11–15,23–32] Hendrickson suggested[2,11,13,33] that what is affecting the Mössbauer spectrum and impacting a temperature dependence is the onset of lattice dynamics (a second-order phase transition). In Hendrickson's theoretical model,[13] the factors that are potentially important in controlling the rate of intramolecular electron transfer in a mixed-valence biferrocenium cation include the effective barrier for charge oscillation in the anion and the intermolecular cation–cation and cation–anion interactions. In our primary paper,[15] we found that there is a significant influence in the electron-transfer rate in the mixed-valence biferrocenium salt when the cyclopentadienyl (Cp) rings in each ferrocenyl moiety are tilted from the parallel geometry. Deviations of the Cp rings from the parallel position were found to correlate quite well with the critical temperature (T_c) of electronic delocalization–localization in biferrocenium salts. The Cp tilt angles in each ferrocenyl moiety for **1, 2, 17** and **5** are 0.3, 4.8, 5.9, and 15.6°, respectively while the corresponding T_c values on the Mössbauer timescale are 365, 275, 125 and < 4.2 K, respectively. However, there is still one important question that remains. Can the electronic effect of the substituent on the Cp ring be excluded? Thus, the binuclear mixed-valence compounds **14–19** are of use in understanding the steric effect of substituent on the rate of electron-transfer. We believe that the relatively minor perturbations of the tilt of the Cp ring can have a pronounced effect on the electronic structure and therefore rate of intramolecular electron transfer. The mixed-valence compounds **14–19** serves as a very sensitive probe of the microscopic structure. Hence, X-ray crystallographic studies of **14–19** were undertaken to help us to elucidate the geometric influences on the rates of intramolecular electron transfer in mixed-valence biferrocenium cations. The respective dihedral angles between the two least-squares planes of the Cp rings for a given ferrocenyl moiety in **15–19** are 3.9(5), 4.2(2), 5.9(2), 4(1) and 6.6(7) while the transition temperature (T_c) on the Mössbauer timescale are 295, 265, 125, > 300 and 200 K, respectively. We suggest that the difference in the rates of

Table 1 Physical properties of mixed-valence compounds **15**, **16**, **18** and **19** and neutral precursors

Mössbauer characteristics

Compound	T/K	$\Delta E_Q{}^a$	δ^b	Γ^c
15	300	1.158	0.445	0.504, 0.426
	290	1.521	0.454	0.454, 0.338
		0.850	0.462	0.439, 0.351
	280	1.624	0.462	0.366, 0.314
		0.747	0.455	0.413, 0.332
	80	1.938	0.526	0.284, 0.283
		0.582	0.525	0.343, 0.341
16	300	1.224	0.452	0.395, 0.419
	270	1.237	0.465	0.457, 0.478
	260	1.474	0.472	0.393, 0.421
		1.024	0.468	0.372, 0.377
	200	1.828	0.493	0.403, 0.430
		0.856	0.499	0.476, 0.425
	80	2.086	0.527	0.287, 0.299
		0.690	0.524	0.347, 0.336
18	300	1.832	0.455	0.267, 0.280
		0.627	0.450	0.368, 0.332
	80	2.029	0.528	0.252, 0.297
		0.554	0.529	0.346, 0.325
19	300	1.233	1.233	0.433, 0.446
	220	1.280	0.496	0.470, 0.506
	200	1.290	0.501	0.492, 0.515
	180	1.491	0.501	0.446, 0.480
		1.101	0.503	0.407, 0.426
	150	1.583	0.509	0.466, 0.478
		1.068	0.524	0.412, 0.420
	80	1.708	0.525	0.461, 0.465
		0.990	0.540	0.438, 0.441

Electrochemical data

Compound	$E_{1/2}{}^d$/V	$\Delta E_{1/2}{}^e$/V	Δ^f/mV	$I_c/I_a{}^g$
[Fe(η^5-C_5H_5)$_2$]	0.37		77	0.97
15′	0.13	0.38	70	0.93
	0.51		66	1.08
16′	0.23	0.36	68	0.93
	0.59		72	1.06
18′	0.14	0.38	65	0.94
	0.52		72	1.10
19′	0.25	0.36	89	0.90
	0.61		74	1.09

Crystal data

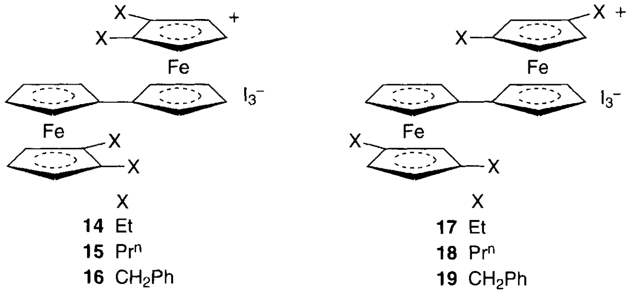
Compound	Fe–C^h/Å	Fe–Cp^i/Å	Stagger angle/°	Tilt angle^j/°
15	2.067(1)	1.671(6)	0.4(6)	3.9(5)
16	2.07(4)	1.675(2)	5.4(2)	4.2(2)
18	2.07(2)	1.67(1)	16.5(9)	4(1)
19	2.056(1)	1.6675(8)	3.5(5)	6.6(7)

Absorption maximum of IT band

Compound	$\nu_{max}{}^k$	$\varepsilon_{max}{}^l$	$\Delta\nu_{1/2(obs)}{}^m$	α^2	$10^{-12}K_{et}$
15	4651	1323	3044	0.0141	2.46
16	4651	1200	3128	0.0132	2.30
18	4651	1388	3128	0.0152	2.65
19	4651	1139	2976	0.0119	2.08

[a] Quadrupole splitting (in mm s^{-1}). [b] Isomer shift referred to iron foil (in mm s^{-1}). [c] Full width at half-height taken from the least-squares-fitting program. The width for the line at more positive velocity is listed first for the doublet. [d] All half-wave potentials are referred to the AgCl/Ag electrode. [e] Peak separation between two waves. [f] Peak-to-peak separation between the resolved reduction and oxidation wave maxima. [g] Peak-current ratio between cathode and anode. [h] The average distance of Fe–C. [i] The average distance between Fe atom and the least-squares planes of the Cp rings. [j] The dihedral angle between two least-squares Cp planes in each ferrocenyl unit. [k] Absorption maximum of IT band in cm^{-1}. [l] In dm^{-3} mol^{-1} cm^{-1}. [m] Full width at half-height in cm^{-1}.

electron transfer of **14**–**19** is a result of differences in the degree of tilting of the Cp rings from a parallel geometry. It has been reported that the interactions between cation and anion also play an important role in controlling the magnitude of electron-transfer rate. Therefore, we only make a comparison for mixed-valence compounds **1**–**3**, **5**, **15**–**17** and **19** in which the positioning of the triiodide anion relative to the fulvalenide ligand is perpendicular, rather than parallel to the fulvalenide ligand as found in **8** and **10**. Mixed-valence compounds **10** and **12** are also excluded from the comparison because of the strong van der Waals interaction between the halide substituent in the benzyl unit and triiodide anion. Under this condition, *i.e.* same type of steropacking arrangement, there is a correlation between the tilt angle and the rate of electron transfer in the series of biferrocenium triiodide salts (Fig. 1). The Cp rings in the cation are tilted by the hydrogen-bond networks between the substituents and I_3^- anions. The substituents in the series of biferrocenium cations modify the local structure of the ferrocenyl moiety. In the qualitative view, we suggest that there is an increased ($d_{x^2-y^2}$, d_{xy})-ring overlap as the rings tilt (Scheme 1). Hückel MO calculations for the series of cations are in progress. If our suggestion is correct, the HOMO–LUMO gap will decrease as the tilt angle increases and we wish to qualitatively describe the relationship between ring tilt and frontier orbital energy in the cation.



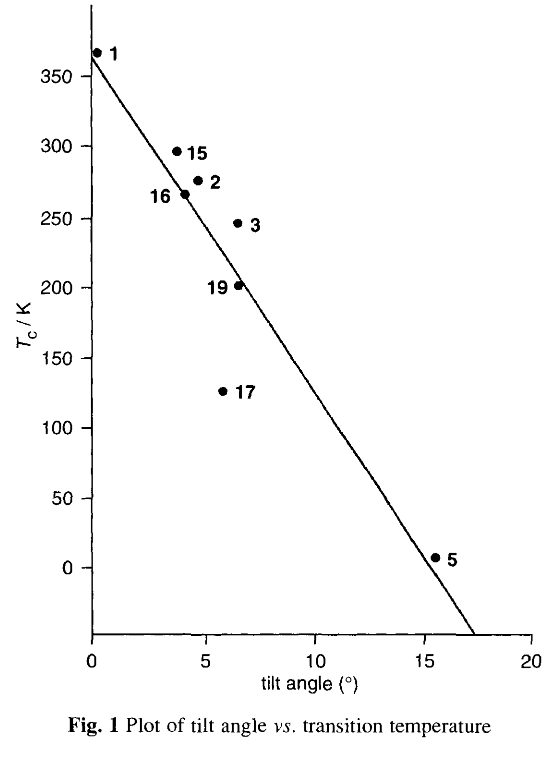
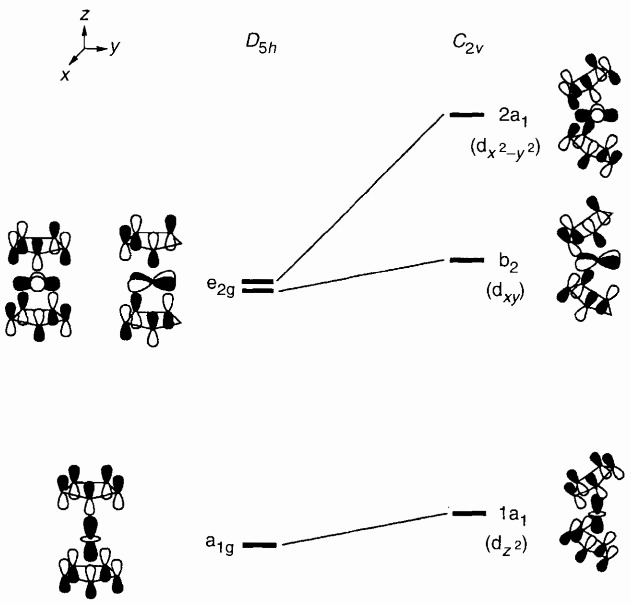


Fig. 1 Plot of tilt angle *vs.* transition temperature



Scheme 1

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Footnotes

† All new compounds gave satisfactory spectroscopic and analytical data. *Selected physical data*: **15′**, mp 77.2–78 °C; M$^+$, *m/z* 538; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.87 (t, 12H, CH$_3$), 1.36 (m, 8H, CH$_2$), 2.03 (m, 8H, CH$_2$), 3.83 (d, 2H, Cp), 3.88 (d, 4H, Cp), 4.12 (d, 4H, fulvalenide), 4.16 (d, 4H, fulvalenide). **16′**, mp 180.1–180.2 °C; M$^+$, *m/z* 731; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.46 (s, 8H, CH$_2$), 3.89 (s, 6H, Cp), 4.18 (s, 4H, fulvalenide), 4.26 (s, 4H, fulvalenide), 6.92 (d, 8H, *o*-benzyl), 7.10 (m, 12H, *m*- and *p*-benzyl). **18′**, mp 51.5–52.5 °C; M$^+$, *m/z* 538; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.86 (t, 12H, CH$_3$), 1.40 (m, 8H, CH$_2$), 2.04 (t, 8H, CH$_2$), 3.83 (s, 6H, Cp), 4.14 (t, 4H, fulvalenide), 4.24 (t, 4H, fulvalenide). **19′**, mp 152–153 °C; M$^+$, *m/z* 731; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.40 (s, 8H, CH$_2$), 3.86 (s, 6H, Cp), 4.12 (s, 4H, fulvalenide), 4.24 (s, 4H, fulvalenide), 7.09 (d, 8H, *o*-benzyl), 7.15 (d, 4H, *p*-benzyl), 7.22 (d, 8H, *m*-benzyl).

Crystal data for **15**: M = 919.08, triclinic, space group $P\bar{1}$, a = 8.764(1), b = 9.329(3), c = 11.240(3) Å, α = 103.08(3), β = 97.88(1), γ = 102.80(2)°, U = 855.8(4) Å^3, F(000) = 889.91, D_c = 1.783 g cm^{-3}, Z = 1, μ = 7.09 mm^{-1}, R = 0.038 and R_w = 0.045. **16**: M = 1111.26, triclinic, space group $P\bar{1}$, a = 9.307(2), b = 10.626(2), c = 10.965(1) Å, α = 76.82(1), β = 85.59(1), γ = 86.29(2)°, U = 1051.5(3) Å^3, F(000) = 985.89, D_c = 1.755 g cm^{-3}, Z = 1, μ = 5.79 mm^{-1}, R = 0.034 and R_w = 0.040. **18**: M = 919.08, monoclinic, space group $P21/n$, a = 13.647(4), b = 10.171(2), c = 13.929(4) Å, β = 116.390(2)°, F(000) = 1363.87, D_c = 1.762 g cm^{-3}, Z = 2, μ = 6.97 mm^{-1}, R = 0.067, R_w = 0.087. **19**: M = 1111.26, triclinic, space group $P\bar{1}$, a = 9.517(3), b = 10.688(3), c = 10.830(4) Å, α = 74.03(3) β = 79.81(3), γ = 89.53(3)°, U = 1041.4(6) Å^3, F(000) = 817.94, D_c = 1.772 g cm^{-3}, Z = 1, μ = 6.32 mm^{-1}, R = 0.057 and R_w = 0.069. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 M. J. Cohn, T.-Y. Dong, D. N. Hendrickson, S. J. Geib and A. L. Rheingold, *J. Chem. Soc., Chem. Commun.*, 1985, 1095.

2 T.-Y. Dong, D. N. Hendrickson, K. Iwai, M. J. Cohn, A. L. Rheingold, H. Sano, I. Motoyama and S. Nakashima, *J. Am. Chem. Soc.*, 1985, **107**, 7996.

3 S. Iijima, R. Saida, I. Motoyama and H. Sano, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1375.

4 S. Nakashima, M. Katada, I. Motoyama and H. Sano, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 2253.

5 M. Kai, M. Katada and H. Sano, *Chem. Lett.*, 1988, 1523.

6 T.-Y. Dong, T. Y. Lee, S. H. Lee, G. H. Lee and S. M. Peng, *Organometallics*, 1994, **13**, 2337.

7 T.-Y. Dong, T. J. Ke, S. M. Peng and S. K. Yeh, *Inorg. Chem.*, 1989, **28**, 2103.

8 T.-Y. Dong, M. Y. Hwang and Y. S. Wen, *J. Organomet. Chem.*, 1990, **391**, 377.

9 T.-Y. Dong, T. Y. Lee and H. M. Lin, *J. Organomet. Chem.*, 1992, **427**, 101.

10 T.-Y. Dong, C. C. Schei, T. L. Hsu, S. L. Lee and S. J. Li, *Inorg. Chem.*, 1991, **30**, 2457.

11 R. J. Webb, S. J. Geib, D. L. Staley, A. L. Rheingold and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1990, **112**, 5031; R. J. Webb, T.-Y. Dong, C. G. Pierpont, S. R. Boone, R. K. Chadha and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1991, **113**, 4806.

12 T.-Y. Dong, T. Kambara and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1986, **108**, 5857.

13 T. Kambara, D. N. Hendrickson, T.-Y. Dong and M. J. Cohn, *J. Chem. Phys.*, 1987, **86**, 2362.

14 T.-Y. Dong, C. K. Chang, C. H. Huang, Y. S. Wen, S. L. Lee, J. A. Chen, W. Y. Yeh and A. Yeh, *J. Chem. Soc., Chem. Commun.*, 1992, 526.

15 T.-Y. Dong, C. H. Huang, C. K. Chang, Y. S. Wen, S. L. Lee, J. A. Chen, W. Y. Yeh and A. Yeh, *J. Am. Chem. Soc.*, 1993, **115**, 6357.

16 W. H. Jr. Morrison and D. N. Hendrickson, *Inorg. Chem.*, 1975, **14**, 2331.

17 M. F. Moore, S. R. Wilson, M. J. Cohn, T.-Y. Dong, U. T. Mueller-Westerhoff and D. N. Hendrickson, *Inorg. Chem.*, 1985, **24**, 4559.

18 F. Delgado-Pena, D. R. Talham and D. O. Cowan, *J. Organomet. Chem.*, 1983, **253**, C43.

19 T.-Y. Dong and C. C. Schei, *J. Organomet Chem.*, 1993, **447**, 107.

20 *Mixed-valence Compounds, Theory and Applications in Chemistry, Physics, Geology and Biology*, ed. D. B. Brown, Reidel Publishing Co., Boston, MA, 1980.

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

22 P. Day, *Int. Rev. Phys. Chem.*, 1981, **1**, 149.

23 W. H. Morrison Jr., S. Krogsrud and D. N. Hendrickson, *Inorg. Chem.*, 1973, **12**, 1998.

24 C. LeVanda, K. Bechgaard, D. O. Cowan, U. T. Mueller-Westerhoff, P. Eilbracht, G. A. Candela and R. L. Collins, *J. Am. Chem. Soc.*, 1976, **98**, 3181; C. LeVanda, K. Bechgaard and D. O. Cowan, *J. Org. Chem.*, 1976, **41**, 2700; E. E. Bunel, P. Campos, J. Ruz, L. Valle, I. Chadwick, M. S. Ana, G. Gonzalez and J. M. Manriquez, *Organometallics*, 1988, **7**, 474; H. Atzkern, B. Huber, F. H. Köhler, G. Müller and R. Müller, *Organometallics*, 1991, **10**, 238; D. O. Cowan, P. Shu, F. L. Hedberg, M. Rossi and T. J. Kistenmacher, *J. Am. Chem. Soc.*, 1979, **101**, 1304; R. Chukwu, A. D. Hunter, B. D. Santarsiero, S. G. Bott, J. L. Atwood and J. Chassaignac, *Organometallics*, 1992, **11**, 589.

25 T.-Y. Dong and C. Y. Chou, *J. Chem. Soc., Chem. Commun.*, 1990, 1332.

26 T.-Y. Dong, C. C. Schei, M. Y. Hwang, T. Y. Lee, S. K. Yeh and Y. S. Wen, *Organometallics*, 1992, **11**, 573.

27 T.-Y. Dong, M. J. Cohn, D. N. Hendrickson and C. G. Pierpont, *J. Am. Chem. Soc.*, 1985, **107**, 4777.

28 T.-Y. Dong, D. N. Hendrickson, C. G. Pierpont and M. F. Moore, *J. Am. Chem. Soc.*, 1986, **108**, 963.

29 D. O. Cowan, R. L. Collins and F. Kaufman, *J. Phys. Chem.*, 1971, **75**, 2025.

30 D. O. Cowan, C. Levanda, J. Park and F. Kaufman, *Acc. Chem. Res.*, 1973, **6**, 1.

31 I. Motoyama, K. Suto, M. Katada and H. Sano, *Chem. Lett.*, 1983, 1215.

32 D. N. Hendrickson, S. M. Oh, T.-Y. Dong, T. Kambara, M. J. Cohn and M. F. Moore, *Comments Inorg. Chem.*, 1985, **4**, 329, and references therein.

33 M. Sorai, A. Nishimori, D. N. Hendrickson, T.-Y. Dong and M. J. Cohn, *J. Am. Chem. Soc.*, 1987, **109**, 4266.