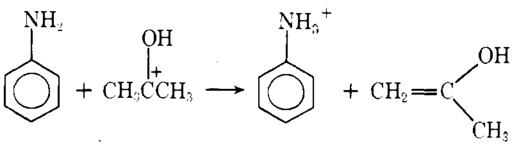
Table I. Observation by ICR Spectroscopy of Deuteron Abstraction from Carbon of Oxygen-Protonated Acetone

Abstracting base, B	Free energy of protonation of B relative to acetone,[a] kcal/mol	Is BD^+ observed?
$(CD_3)_2CO$	0.0[b,c]	No
THF[d]	2.5[b]	No
$(i\text{-}Pr)_2O$	9.1[e]	No
$(MeCO)_2CH_2$	10.7[f]	No
$(i\text{-}Pr)_2S$	13.0[f]	No
$C_6H_5NH_2$	13.9[e]	Yes
$HC{\equiv}CCH_2NH_2$	14.1[e]	Yes
$MeNH_2$	16.4[e]	Yes
$H_2C{=}CHCH_2NH_2$	18.8[e]	Yes
$EtNH_2$	19.1[e]	Yes

[a] Free energies for reactions, $BH^+ + (Me)_2CO \rightleftharpoons B + (Me)_2COH^+$. [b] Experimental data from J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, in press. [c] We have assumed a zero free energy for the reaction, $(CD_3)_2COH^+ + (CH_3)_2C{=}O \rightleftharpoons (CD_3)_2C{=}O + (CH_3)_2COH^+$. [d] Tetrahydrofuran. [e] Experimental data from R. W. Taft in "Proton Transfer Reactions," E. F. Caldin and V. Gold, Ed., Wiley-Halstead, New York, N.Y., 1975, p 31, with small corrections based on additional unpublished results. [f] Unpublished results of R. W. Taft.

abstraction from carbon, leading to formation of BD^+ and concurrently to acetone's enol tautomer. Therefore, by using a series of abstracting bases of known and increasing strength and by monitoring the onset of production of BD^+, it is possible to determine an approximate free energy of carbon deprotonation of acetone. Compared to the known free energy for oxygen deprotonation this yields a value for the heat of formation of the enol of acetone relative to that of its keto tautomer. Our data are displayed in Table I. Isopropyl sulfide (free energy of proton transfer, 13.0 kcal/mol greater than that of acetone) is the strongest base tested for which carbon dedeuteration is not observed. Aniline (free energy of proton transfer, 13.9 kcal/mol greater than that of acetone) does dedeuterate acetone from carbon as evidenced by the production of an ion of mass corresponding to molecular formula $C_6H_5NH_2D^+$. Deuterium incorporation due to reaction with fragment ions (i.e., those from isopropylthiol) is precluded by double-resonance experiments.[3] Specifically, the intensity of the resonance corresponding to an ion of mass BD^+ (for aniline and all stronger bases) was observed to decrease in response to ejection of protonated acetone from the system.

We conclude that proton transfer from protonated acetone to aniline is thermoneutral (i.e., that both the free energy and enthalpy for the process are 0 ± 2 kcal/mol).[4] It follows,



(1)

therefore, that the relative thermochemical stabilities of the keto and enol tautomers of acetone is approximately the same as the difference in free energies of protonation of aniline and acetone in the gas phase, or 13.9 ± 2 kcal/mol.[5] Such an estimate appears to be consistent with the lower limit of 8.2 kcal/mol established by Bell and Smith for the neat liquid.[1a] It seems to the present authors reasonable enough to suggest that specific hydrogen-bonding interactions between the enol of acetone and the solvent are of greater importance than those involving the keto tautomer. If for no other reason this is because a hydroxyl group can participate in three hydrogen bonds (acting once as a proton donor and twice in the capacity of an acceptor), whereas a carbonyl functionally can be involved in only two (in both, as a proton acceptor).[6]

Further experimental as well as theoretical studies are in progress. These are aimed both at elucidating the relative tautomer stabilities of other simple ketones and related systems, and at assessing the importance of solvation in dictating the direction of tautomeric equilibria.

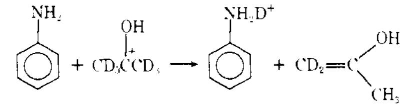
References and Notes

(1) (a) R. P. Bell and P. W. Smith, *J. Chem. Soc. B*, 241 (1977). (b) For a review, see S. Forsen and M. Nilsson in "The Chemistry of the Carbonyl Group," Part 2, S. Patai, Ed., Wiley-Interscience, New York, N.Y., 1970, p 157.

(2) For examples of the use of similar techniques in the elucidation of the thermodynamic stabilities of transient ions and neutral molecules, see (a) D. J. DeFrees, R. T. McIver, Jr., and W. J. Hehre, *J. Am. Chem. Soc.*, **99**, 3853 (1977); (b) D. J. DeFrees, W. J. Hehre, R. T. McIver, Jr. and D. H. McDaniel, *ibid.*, submitted for publication.

(3) Pulsed ion cyclotron resonance spectroscopy: (a) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 555 (1970); (b) J. D. Baldeschwieler and S. S. Woodgate, *Acc. Chem. Res.*, **4**, 114 (1971); (c) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Phys.*, **7**, 471 (1971).

(4) This requires the assumption that $\Delta G°$ and $\Delta H°$ for the process actually being dealt with experimentally (eq i) are identical with those of eq 1. It is expected that the maximum error introduced as a result of such an assumption is no greater than 0.5 kcal/mol.



(i)

(5) Two sources of error beyond those already discussed may be identified: (a) the finite resolution of the proton affinity scale, and (b) the likelihood that slightly endothermic proton transfer reactions as well as thermoneutral and exothermic processes will occur. We suspect that the quoted 2 kcal/mol error limit is large enough to take account of these uncertainties.

(6) Note also, that recent experimental[7a] and theoretical[7b] investigations have shown that hydrogen bonds to OH groups which act simultaneously as acceptors and donors are stronger than those involving sites which can function in only one of these capacities.

(7) (a) G. A. Jeffrey, M. E. Gress, and S. Takagi, *J. Am. Chem. Soc.*, **99**, 609 (1977); (b) Y.-C. Tse and M. D. Newton, *ibid.*, **99**, 611 (1977).

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Transition Metal Complexes of Novel Ring-Bridged Bis(η^5-cyclopentadienyl) Ligands. Their Synthesis, Chemistry, and Structural Characterization

Sir:

The availability of ligands which constrain two metals to remain in proximity and also allow, but do not require, the formation of a metal-metal bond should lead to a greater understanding of the chemistry of bimetallic systems. For example, the reactivity of organic molecules with metal cluster systems is under intense investigation;[1] however, the reactivity of intact bimetallic metal-metal bonded systems has not been examined as extensively. The metal-metal bond is frequently the most reactive part of the molecule leading to cleavage of the system and the generation of two independent monometallic systems. We wish to report some studies concerning ligands that produce bimetallic systems in which the metals are constrained to remain in proximity. The ligands are of the type $(C_5H_5)_2Z$ and principally three ligands have been examined: α,α'-dicyclopentadienyl-*m*-xylene (**1**), $[m\text{-}C_6H_4(CH_2C_5H_5)_2]$; 2,4-bis[cyclopentadienyldimethylsilyl]-2,4-dicarbacloso-heptaborane (7) (**2**), $[2,4\text{-}B_5H_5C_2[Si(CH_3)_2C_5H_5]_2]$; and dicyclopentadienyldimethylsilane (**3**), $[(CH_3)_2Si(C_5H_5)_2]$. The bridging segments $m\text{-}C_6H_4(CH_2)_2$, $[2,4\text{-}B_5H_5C_2[Si(CH_3)_2]_2]$, and $(CH_3)_2Si$ were selected for these ligands because they were expected to favor complexation of the cyclopentadienyl units to two metals as opposed to chelating to a single metal. Additionally, the flexibility of the bridging segments should allow a variety of intermetallic interactions.

Ligands **1** and **2** were prepared according to eq I and II:

$$m\text{-}C_6H_4(CH_2Br)_2 + 2NaC_5H_5 \xrightarrow{\text{THF}} m\text{-}C_6H_4(CH_2C_5H_5)_2 + 2NaBr \quad (I)$$

$$2,4\text{-}B_5H_5C_2[Si(CH_3)_2Cl]_2 + 2ClMgC_5H_5 \xrightarrow[\text{Et}_2\text{O}]{\text{C}_6\text{H}_6} 2,4\text{-}B_5H_5C_2[Si(CH_3)_2C_5H_5]_2 + 2MgCl_2 \quad (II)$$

Near quantitative yields of **1** can be obtained as a neat oil which rapidly polymerizes; however, it can be used without isolation in a reaction with sodium hydride to produce m-$C_6H_4(CH_2C_5H_4)_2{}^{2-}$ (**4**) which can be used effectively as a reagent. Substituted derivatives of **1** such as m-$C_6H_4(CH_2C_5H_4CH_3)_2$ can be prepared from tetrahydrofuran solutions of **4** and alkyl halides. These substituted derivatives are somewhat more stable and can be characterized spectrally.[2] Ligand **2** is prepared in over 80% yield and can be stored as a viscous oil.[3] The preparation of ligand **3** has been previously reported[4,5] and the ligand has recently been utilized to prepare monometallic complexes.[5]

In order to verify the tendency of **1, 2,** and **3** to form constrained bimetallic systems, reactions with several metal carbonyl derivatives were carried out to produce cyclopentadienyl metal carbonyl systems covalently linked through the cyclopentadienyl rings. For example, consider the reaction (eq III) of **4** with $M(CO)_6$ (M = Mo, W) to produce the m-$C_6H_4[CH_2C_5H_4M(CO)_3]_2{}^{2-}$ ions.[6]

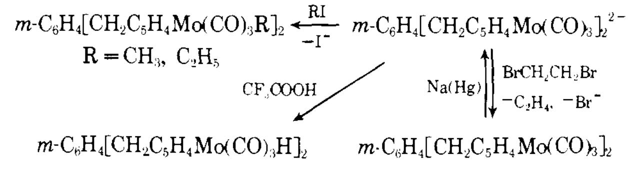
$$m\text{-}C_6H_4(CH_2C_5H_4)_2{}^{2-} + M(CO)_6 \xrightarrow[\Delta]{\text{THF}} m\text{-}C_6H_4[CH_2C_5H_4M(CO)_3]_2{}^{2-} + 6CO \quad (III)$$

$$M = \text{Mo, W}$$

These bimetallic dianions can be used to prepare linked bimetallic metal-hydride, metal-alkyl, and metal-metal bonded derivatives as shown in Scheme I utilizing the molybdenum system. Except in the case of m-$C_6H_4[CH_2C_5H_4M(CO)_3]_2$, where more bands are observed, the IR data are comparable to those observed in the corresponding unlinked analogues.[7] The NMR data in conjunction with the other characterization data confirm the bimetallic nature of the complexes. For example, the ^{1}H NMR spectrum of the m-$C_6H_4[CH_2C_5H_4Mo(CO)_3CH_3]_2$ complex contains the expected resonances from the hydrogen atoms on the benzene ring, the two cyclopentadiene rings, the two benzyl groups, and the two methyl groups in the expected ratios.

While **2** and **3** have been shown to react with $Mo(CO)_6$ and **3** with $Co_2(CO)_8$,[8] the best characterized reaction of **2** and **3** is with $Fe(CO)_5$. Refluxing iron pentacarbonyl with either **2** or **3** in xylene produces $(CH_3)_2Si[C_5H_4Fe(CO)_2]_2$ (**5**) and $2,4\text{-}B_5H_5C_2[Si(CH_3)_2C_5H_4Fe(CO)_2]_2$ (**6**), respectively, in about 40% yield.[9] Compounds **5** and **6** are examples of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ complexes in which the cyclopentadienyl rings are linked. Other derivatives of this type are known where the link between the rings is a substituted ethylene unit $\text{-}CRR_1CRR_1\text{-}$ (R = H, R_1 = $N(CH_3)_2$;[10a] $R = R_1 = CH_3$[10b]). Those derivatives, however, were generally prepared only in low yield from $Fe(CO)_5$ and substituted fulvenes; the ethylene link apparently was formed during the course of the complex formation.

Scheme I



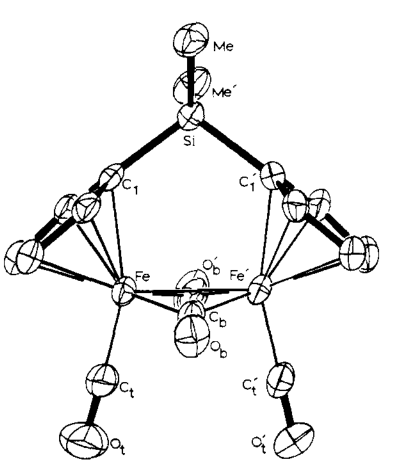


Figure 1. Perspective ORTEP drawing of the $(CH_3)_2Si[(\eta^5\text{-}C_5H_4)Fe(\mu\text{-}CO)(CO)]_2$ molecule, **5**. All atoms are represented by 50% probability thermal ellipsoids. Atoms of a given type labeled with and without a prime (′) are related to each other by the pseudo-C_2 axis which passes through Si and the midpoint of the Fe-Fe′ bond.

The results of a high-precision x-ray structural investigation for single crystals of **5** clearly demonstrate the ability of ligand **3** (and presumably **1** and **2**) to function as a bimetallic ligand in addition to its previously demonstrated ability[5b] to serve as a chelating ligand for a larger single metal atom.

Large well-shaped air-stable single crystals of **5**, obtained from evaporation of a hot toluene solution, are monoclinic, space group $P2_1/n$ (an alternate setting of $P2_1/c\text{-}C^5{}_{2h}$) with a = 11.683 (2) Å, b = 13.305 (2) Å, c = 10.836 (1) Å, β = 105.94 (1)°, and $Z = 4$ (ρ_{measd} = 1.667 g cm^{-3}; ρ_{calcd} = 1.681 g cm^{-3} for four $(CH_3)_2Si[(\eta^5\text{-}C_5H_4)Fe(\mu\text{-}CO)(CO)]_2$ units). Diffracted intensities were measured for 4858 independent reflections having $2\theta_{\text{Mo}K\bar{\alpha}} < 60.4°$ (the equivalent of 1.30 limiting Cu K$\bar{\alpha}$ spheres) on a computer-controlled Syntex P$\bar{1}$ autodiffractometer using Nb-filtered Mo K$\bar{\alpha}$ radiation and the θ–2θ scanning technique. The structural parameters[11] have been refined to convergence (R = 0.043 for 1658 independent reflections having $2\theta_{\text{Mo}K\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$) in cycles of unit-weighted full-matrix least-squares refinement which employed anisotropic thermal parameters for all nonhydrogen atoms.

The structural analysis reveals that the crystal is composed of discrete neutral dinuclear molecules of **5** (Figure 1) in which each iron atom achieves a filled valence shell electronic configuration by bonding to the other Fe atom through a two-electron single bond, to a terminal CO in a linear fashion, to two symmetrically bridging CO ligands, and to a single C_5 ring of the bridging bis(cyclopentadienyl)dimethylsilane ligand in a pentahapto fashion. Although the molecule possesses no rigorous crystallographic symmetry, it approximates rather closely C_{2v} site symmetry with the idealized C_2 axis passing through the Si atom and the midpoint of the Fe-Fe′ bond of Figure 1. The two mutually perpendicular mirror planes of a C_{2v} description for this molecule would ideally contain: Fe, Fe′, C_t, O_t, C'_t, O'_t, Si, C_1, and C'_1 in plane I; Si, Me, Me′, C_b, O_b, C'_b, and O'_b in plane II. The observed angle between the normals to the least-squares mean planes for these two groupings of atoms is 90.1°.

Bond lengths and angles for chemically equivalent atomic groupings, averaged in accord with approximate C_{2v} molecular symmetry, include: Fe–Fe′, 2.520 (1) Å;[12] Fe–C_t, 1.726 (9,3,3) Å,[12] Fe–C_b, 1.920 (7,6,12) Å;[12] Fe–C(cyclopentadienyl), 2.119 (7,10,22) Å; C–O, 1.176 (9,3,6) Å; cyclopentadienyl C–C, 1.422 (10,15,27) Å; Si–C(methyl), 1.862 (8,2,2) Å; Si–C(cyclopentadienyl), 1.876 (7,2,2) Å; Fe–C_b–Fe′, 82.0 (3,2,2)°;[12] C_b–Fe–C_b′, 95.5 (3,4,4)°; C_b–Fe–C_t, 90.4 (3,6,12)°; Fe–C_b–O_b, 138.9 (6,3,5)°; Fe–C_t–O_t, 177.9 (10,6,7)°; and C_t–Fe–Fe′, 103.2 (3,9,9)°. The similarity of these bonding parameters with those determined for *cis*-$[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)(CO)]_2$[13] (**7**) seems to indicate that the bridging Z group in ligand **3** has had little, if any, effect on the overall conformation of the $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)(CO)]_2$ grouping. Ligands **1** and **2** on the other hand contain considerably larger bridging groups which may well produce dramatic structural changes in similar pentahapto-bonded dinuclear complexes. Values of 105.7 (3)°, 114.4 (4)°, and 109.1 (3,8,14)° for the C_1–Si–C_1′, Me–Si–Me′, and four Me–Si–C_1 bond angles, respectively, indicate the presence of only small distortions from idealized tetrahedral geometry for the bridging silyl group in **5**. Both five-membered cyclopentadienyl rings are individually coplanar to within 0.01 Å and the four-atom $(Fe\text{–}C_b)_2$ grouping is folded away from the Si atom by 22.4° along the Fe–Fe′ bond. Assessment of the subtle but statistically significant structural differences between **5** and **7** which are produced by the dimethylsilyl bridge in **5** must await the results from least-squares refinement of a more sophisticated model (anisotropic nonhydrogen and isotropic hydrogen atoms) using the more complete data set (reflections with $2\theta_{\text{MoK}\bar{\alpha}} < 60.4°$).

The reactivity of **5** is somewhat different than its unbridged analogue **7**, since **5** is quite stable to air even in solution. Polarographic reduction of **5** apparently proceeds by steps ($E^0 = -1.54$; -2.20 V) to generate the $(CH_3)_2Si[C_5H_4Fe(CO)_2]_2{}^{2-}$ dianion while the unbridged system reduces in a two-electron step at −2.22 V.[14] Both **5** and **6** can be reduced to their respective bimetallic dianions by Na(Hg). These dianions can be used in reactions with alkyl halides to prepare derivatives of the type $(CH_3)_2Si[C_5H_4Fe(CO)_2R]_2$ and 2,4-$B_5H_5C_2[Si(CH_3)_2C_5H_4Fe(CO)_2R]_2$, where R = CH_3 and C_2H_5. The reaction of **5** with α,ω-alkyl dihalides gives $[(CH_3)_2Si[C_5H_4Fe(CO)_2]_2(CH_2)_n]_2$ for $n = 3, 4$, and 5.[15]

Ligands of the type reported here potentially allow the preparation of numerous linked $Z(\eta^5\text{-}C_5H_4ML_n)_2$ systems. Consequently the effect of a neighboring metal on the broad and diverse reactivity of $\eta^5\text{-}C_5H_5ML_n$ systems is open to examination. Further chemical and structural studies on metal derivatives of these ligands and those of similar type are currently underway.

Acknowledgment. Support of this research at both institutions by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We also thank the University of Nebraska Computing Center for a generous allocation of computer time.

References and Notes

(1) As examples, note (a) M. Tachikana, J. R. Shapley, R. C. Haltiwanger, and C. G. Pierpont, *J. Am. Chem. Soc.*, **98**, 4651 (1976); (b) M. G. Thomas, E. L. Muetterties, R. O. Day, and V. W. Day, *ibid.*, **98**, 4645 (1976). A study of a binuclear system recently has been reported by J. P. Collman, R. G. Finkle, P. L. Matlocle, R. Wahren, and J. I. Brauman, *ibid.*, **98**, 4687 (1976).

(2) For the *m*-$C_6H_4(CH_2C_5H_4CH_3)_2$ product: ^1H NMR ($CDCl_3$) δ 7.10 (m, 4 H, benzene), 6.23 (m, 4 H, vinylic cyclopentadiene), 3.70 (s, 4 H, benzyl), 3.00 (m, 4 H, allylic cyclopentadiene), 2.13 ppm (s, 6 H, methyl). Mass spectrum parent ion, $C_{20}H_{22}$, 262 amu. Apparently the isomers in which both the methyl group and the xylyl group substitute at the vinylic positions on the cyclopendiene rings predominate.

(3) The 2,4-$B_5H_5C_2[Si(CH_3)_2C_5H_5]_2$ product is isolated by alembic distillation at 120 °C and 10^{-4} Torr. ^1H NMR ($CDCl_3$) δ 6.50 (m, 8 H, vinylic cyclopentadiene), 3.00 (m, 2 H, allylic cyclopentadiene), 0.10 ppm (s, 12 H, methyl). Mass spectrum parent ion, $B_5C_{16}H_{27}Si_2$, 330 amu. We thank Dr. R. E. Williams of Chemical Systems Incorporated, Irvine, Calif., for a sample of 2,4-$B_5H_5C_2[Si(CH_3)_2Cl]_2$.

(4) K. C. Frisch, *J. Am. Chem. Soc.*, **75**, 6050 (1953).

(5) (a) H. Kopf and W. Kahl, *J. Organomet. Chem.*, **64**, 637 (1976); (b) C. A. Secaur, V. W. Day, R. D. Ernst, W. J. Kennelly, and T. J. Marks, *J. Am. Chem. Soc.*, **98**, 3713 (1976).

(6) M = Mo: IR (THF) ν_{CO} 1898, 1796, and 1741 cm^{-1}. M = W: IR (THF) ν_{CO} 1892, 1792, and 1736 cm^{-1}.

(7) *m*-$C_6H_4[CH_2C_5H_4Mo(CO)_3CH_3]_2$: mp 139–40 °C. Anal. Calcd: C, 50.17; H, 3.57; Mo, 30.83; O, 15.43. Found: C, 50.05; H, 3.94; Mo, 30.56; O, 15.45 (by difference). ^1H NMR ($CDCl_3$): δ 7.10 (m, 4 H, benzene), 5.16 (m, 8 H, cyclopentadienyl), 3.54 (s, 4 H, benzyl), 0.35 ppm (s, 6 H, methyl). IR (CH_2Cl_2) ν_{CO} 2018, 1926 cm^{-1}. *m*-$C_6H_4[CH_2C_5H_4Mo(CO)_3]_2$: ^1H NMR ($CDCl_3$) δ 7.08 (m, 4 H, benzene), 5.13 (m, 8 H, cyclopentadienyl), 3.65 ppm (s, 4 H, benzyl). IR ($CHCl_3$) ν_{CO} 2005, 1960, 1910, 1875 cm^{-1}. *m*-$C_6H_4[CH_2C_5H_4W(CO)_3CH_2CH_3]_2$ Anal. Calcd: C, 40.70; H, 3.18; W, 44.50; O, 11.62. Found: C, 40.08; H, 3.50; W, 44.43; O, 11.99 (by difference). The IR and ^1H NMR data are consistent with this formulation.

(8) $(CH_3)_2Si[C_5H_4Co(CO)_2]_2$: IR (hexane) ν_{CO} 2040, 1995 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.49 (s, 6 H, CH_3), 5.0.5.3 ppm (d, 8 H, cyclopentadienyl). Both **2** and **3** react with $Mo(CO)_6$ to yield apparent analogues of $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$ which are both very air and thermally unstable. Decomposition of the product made from **3** produces substantial quantities of $\eta^5\text{-}C_5H_5Mo(CO)_3CH_3$.

(9) Both **5** and **6** can be isolated by column chromatography on silica gel using benzene as the eluent. Recrystallization can be accomplished using toluene. **5** can also be purified by sublimation. $(CH_3)_2Si[C_5H_4Fe(CO)_2]_2$ Anal. Calcd: C, 46.86; H, 3.44; Fe, 27.24; Si, 6.85; O, 15.61. Found: C, 47.16; H, 3.34; Fe, 27.36; Si, 6.43; O, 15.71 (by difference). Mass spectrum parent ion, $C_{16}H_{14}Fe_2SiO_4$: 410 amu. IR ($CHCl_3$) ν_{CO} 1990, 1950, 1782 cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.1, 5.9 (dd, 8 H, cyclopentadienyl), 0.50 ppm (s, 6 H, CH_3). $B_5H_5C_2[Si(CH_3)_2C_5H_4Fe(CO)_2]_2$: IR (THF) ν_{CO} 2015, 1990, 1790 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.70 (s, 12 H, $SiCH_3$), 4.70, 5.00 ppm (dd, 8 H, cyclopentadienyl).

(10) (a) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 801 (1964); (b) E. Weiss and W. Hubel, *Chem. Ber.*, **95**, 1186 (1964).

(11) The two crystallographically independent iron atoms were located using direct methods (MULTAN) and the remaining nonhydrogen atoms of the totally general position asymmetric unit were located by standard difference Fourier techniques.

(12) The first number in parentheses following a given bond length or angle is the rms estimated standard deviation of an individual datum. The second and third numbers, when included, are the average and maximum deviations from the average value, respectively.

(13) R. F. Bryan, P. T. Green, M. J. Newlands, and D. S. Field, *J. Chem. Soc. A*, 3068 (1970).

(14) R. E. Dessy, P. M. Weissman, and R. L. Pohl, *J. Am. Chem. Soc.*, **80,** 5117 (1966).

(15) $(CH_3)_2Si[C_5H_4Fe(CO)_2CH_3]_2$: IR ($CDCl_3$) ν_{CO} 2025, 1990 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.20 (s, 6 H, $SiCH_3$), 0.6 (s, 6 H, $FeCH_3$), 4.90 ppm (s, 8 H, cyclopentadienyl). $[(CH_3)_2Si[C_5H_4Fe(CO)_2](CH_2)_5]_2$; mol wt [osmometry ($CHCl_3$)], Calcd: 960. Found: 946: IR (octane) ν_{CO} 2000, 1950 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.70 (s, 6 H, $SiCH_3$), 1.70 (m, 10 H, $(CH_2)_5$), 4.90 ppm (m, 8 H, cyclopentadienyl). $B_5H_5C_2[Si(CH_3)_2Fe(CO)_2CH_3]_2$: IR (THF) ν_{CO} 2010, 1960 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.05 (s, 6 H, $FeCH_3$), 0.20 (s, 12 H, $SiCH_3$), 4.00 ppm (s, 8 H, cyclopentadienyl).

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On the Extrinsic Circular Dichroism of J-Aggregate Species of Achiral Dyes

Sir:

Experimental observations of induced optical activity and enantiomeric resolutions continue to be of general scientific interest since Pasteur's resolution of hemihedral crystals of racemic sodium ammonium tartrate.[1] This special interest arises in part from the possibility that the novel observations may provide explanations for the prebiotic generation of optical