mals 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 $C_l$–Si–$C_l$′, Me–Si–Me′, and four Me–Si–$C_l$ 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 $\alpha,\omega$-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: $^1$H NMR ($CDCl_3$) $\delta$ 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. $^1$H NMR ($CDCl_3$) $\delta$ 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) $\nu_{CO}$ 1898, 1796, and 1741 cm$^{-1}$. M = W: IR (THF) $\nu_{CO}$ 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). $^1$H NMR ($CDCl_3$): $\delta$ 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 ($CH_2Cl_2$) $\nu_{CO}$ 2018, 1926 cm$^{-1}$. *m*-$C_6H_4[CH_2C_5H_4Mo(CO)_3]_2$: $^1$H NMR ($CDCl_3$) $\delta$ 7.08 (m, 4 H, benzene), 5.13 (m, 8 H, cyclopentadienyl), 3.65 ppm (s, 4 H, benzyl). IR ($CHCl_3$) $\nu_{CO}$ 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 $^1$H NMR data are consistent with this formulation.

(8) $(CH_3)_2Si[C_5H_4Co(CO)_2]_2$: IR (hexane) $\nu_{CO}$ 2040, 1995 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 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 ($CHCl_3$) $\nu_{CO}$ 1990, 1950, 1782 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$ 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) $\nu_{CO}$ 2015, 1990, 1790 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\nu_{CO}$ 2025, 1990 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 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) $\nu_{CO}$ 2000, 1950 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 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) $\nu_{CO}$ 2010, 1960 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$ 0.05 (s, 6 H, $FeCH_3$), 0.20 (s, 12 H, $SiCH_3$), 4.00 ppm (s, 8 H, cyclopentadienyl).

(16) Camille and Henry Dreyfus Teacher–Scholar.

**P. A. Wegner,* V. A. Uski, R. P. Kiester**
*Department of Chemistry,*
*California State University, Fullerton*
*Fullerton, California 92634*

**S. Dabestani, V. W. Day***[16]
*Department of Chemistry, University of Nebraska*
*Lincoln, Nebraska 68588*

*Received December 23, 1976*

---

## 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

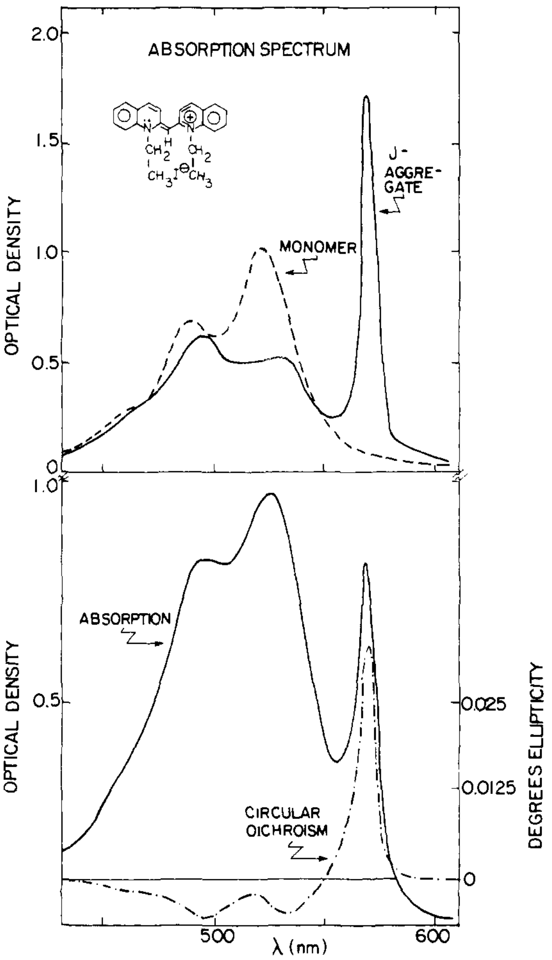


**Figure 1.** (Upper) Absorption spectra of monomeric (- - -) and J-aggregate (—) 1,1′-diethyl-2,2′-cyanine iodide (**1**) formed by the addition of 1 mL of a methanol solution of (**1**) [$3.0 \times 10^{-4}$ M] to 15 mL of water and 15 mL of 3 M aqueous NaCl, respectively (*l* 1 cm). (Lower) Absorption (—) and circular dichroism (- - -) spectra of **1** in an ethyl cellulose polymer film (5 wt %, ~20-μ film thickness).

activity.[2] Extrinsic optical activity has been observed for achiral molecules dissolved in chiral solvents,[3-5] in a chiral surfactant,[6] and in associated ion pairs.[7] The distinction of enantiomers by NMR in chiral solvents[8] and using chiral shift reagents[9] has also been reported. More recently extrinsic circular dichroism (CD) has been observed for achiral molecules oriented in macroscopic helical cholesteric mesophases.[10-14]

Since 1970 there have been two reports that CD was induced in 1,1′-diethyl-2,2′-cyanine iodide (**1**),[15] as well as in the chloride salt (**2**),[16] surprisingly by simple stirring of the solutions containing the potentially chiral dye J-aggregate.[17-19] Honda and Hada[15] also report that the CD sign induced in the aggregate absorption bands, which are quite distinct and red shifted from monomer absorption, is dependent on stirring direction. Since the general scientific and biological implications of such observations are numerous, we decided to investigate the details of the reported extrinsic CD of the J-aggregate forms of **1** and **2**. When attempting to reproduce the reports of the mechanical induction of CD in **1** and **2**, we experienced considerable difficulty. The J-aggregate was found to be a linearly dichroic (LD) microcrystalline species which could be simply filtered from solution, removing all apparent CD and J-aggregate absorption.

The observed signal ($\theta_{\text{obsd}}$) on a CD spectropolarimeter is due to a combination of CD ($\theta_{\text{real}}$) and LD[20-22] ($\theta_{\text{LD}}$) as described in eq 1.

$$\theta_{\text{obsd}} = \theta_{\text{real}} + \theta_{\text{LD}} \tag{1}$$

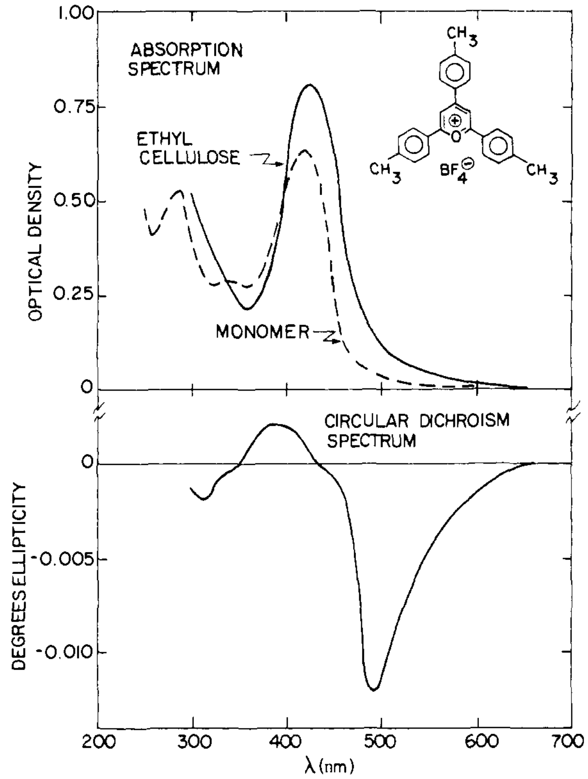


**Figure 2.** Absorption spectrum of tri(*p*-tolyl)pyrylium fluoroborate (**3**) in methanol (*c* $1.0 \times 10^5$ M, *l* 1 cm, (- - -)). Absorption and circular dichroism spectra of **3** in an ethyl cellulose polymer film (5 wt %, ~20-μ film thickness, (—)).

The *linear* contribution to the observed signal ($\theta_{\text{obsd}}$) on the Cary 61 spectropolarimeter can be eliminated by averaging signal intensities taken at cell rotation angles (normal to light beam) of 90° with respect to one another ($\theta_{\text{av}}$). Then the *circular* contribution ($\theta_{\text{real}}$) can be obtained by using the relationship shown in eq 2,

$$\theta_{\text{real}} = \tfrac{1}{3}[\theta_{\text{av}}(-30°, 60°) + \theta_{\text{av}}(0°, 90°) + \theta_{\text{av}}(30°, 120°)] \tag{2}$$

where $\theta_{\text{av}}$ for three sets of rotation angles is employed.[22] The separation of linear and circular dichroism is virtually impossible in fluid media, however, since the microcrystallites are free to rotate with respect to the cell.

To overcome this problem, **1** (5 wt %) was dissolved in an achiral polymer, a bis(phenol A) polycarbonate (Lexan),[23] and in a chiral polymer, ethyl cellulose,[24] using methylene chloride as the solvent to prepare the films. Owing to the limited solubility of **1** in the polymers, the J-aggregate species of **1** could be formed within the rigid polymer matrices. The absorption spectrum indicated the presence of monomer as well as J-aggregate.

When the achiral polymer was employed as the rigid matrix, the observed signals for the J-aggregate were very close to reported CD spectra produced by mechanical swirling.[15,16] However, the signals ($\theta_{\text{obsd}}$) were shown to be solely due to $\theta_{\text{LD}}$ through the use of eq 2. Our experimental observations indicate to us that the mechanical swirling results for J-aggregate species were due to a *linear* and not a *circular* dichroic effect. The time dependence of the J-aggregate CD signal for **1** reported by Bird[25] can now be rationalized as being due to changes in the linear dichroic effect relative to $\theta_{\text{real}}$ with time as the microcrystallities agglomerate. Nordén,[26] in an elegant spectroscopic investigation of the linear and circular dichroism of **1**, also suggests that the mechanical induction of CD reported by Honda and Hoda[15] may be due to instrumental sensitivity to LD from possibly nonhelical fibers.

However, when chiral ethyl cellulose was employed as the rigid matrix, CD ($\theta_{\mathrm{real}}$) was observed within the absorption bands of the J-aggregate species (see Figure 1). Figure 1 presents the absorption spectra of **1** as the monomer, the J-aggregate species, and the CD and absorption spectrum of mixture of J-aggregate and monomer in ethyl cellulose. The anisotropy factor ($g = \Delta A/A$) for the 572-nm band of the J-aggregate in ethyl cellulose was found to be $9.7 \times 10^{-4}$ (compared to $7.3 \times 10^{-3}$ for 1,1′-diethyl-2,2′-cyanine D-10-camphorsulfonate formed in achiral Lexan) and is indicative of a dissymmetric arrangement of chromophores.[27] We feel that the nucleation of enantiomeric crystallites in chiral polymers, which are optically transparent in the spectral region of interest, offers a general technique for probing the electronic nature of potentially chiral systems such as J-aggregates. This technique is similar to resolutions using single crystals of one enantiomer which have been shown to effect nucleation and crystallization of a second chiral substance.[28] Recent spectroscopic observations[29] on single crystals of **1** support our contention of the microcrystalline nature of J-aggregate species. Interest in extrinsic CD of achiral cationic dye species has been stimulated since 1961 by the report by Stryer and Blout that CD is induced in **1** by helical poly-α-L-glutamic acid.[30] Of the three models proposed to account for the observation of extrinsic CD in achiral dyes, our investigations support the tangential dye helix model where the rigid α helix serves simply as a nucleating site for the microcrystalline J-aggregate.

We have also extended the above technique to the investigation of J-aggregate formation in pyrylium dye salts by either incorporating the dye in ethyl cellulose at a concentration sufficient to encourage crystallization or by employing a D-10-camphorsulfonate counterion.

Figure 2 presents the absorption and CD spectrum of tri(*p*-tolyl)pyrylium fluoroborate (**3**),[31] as a typical example, in ethyl cellulose. Even though the absorption spectrum of **3** in ethyl cellulose does not clearly indicate the presence of the J-aggregate species the CD readily shows the J-aggregate absorption in a spectral region beyond the monomer absorption.

We conclude that the reports of CD within the electronic transitions of the J-aggregated species of **1**[30] and **2** induced by mechanical swirling are due to the artifact of linear dichroism. Also, we propose that rigid chiral polymer films be employed for such studies, since they allow one to distinguish between linear and circular dichroic effects. This technique also provides a chiral environment for the preferential nucleation of either D or L crystallites and may be generally applicable to probing the electronic structure of other enantiomeric microcrystalline species via their CD spectrum.

## References and Notes

(1) L. Pasteur, *Ann. Chim. Phys.*, (3) **24**, 442 (1848).
(2) G. Balavoine, A. Moradpour, and H. B. Kagan, *J. Am. Chem. Soc.*, **96**, 5152 (1974), and references cited therein.
(3) B. Bosnich, *J. Am. Chem. Soc.*, **89**, 6143 (1967).
(4) L. D. Hayward and R. N. Totty, *Chem. Commun.*, 676 (1969).
(5) L. D. Hayward and R. N. Totty, *Can. J. Chem.*, **49**, 624 (1971).
(6) T. Tachibana and K. Kuihara, *Naturwissenschaften*, **63**, 532 (1976).
(7) S. Takenaka, M. Sugiyama, and N. Tokura, *J. Chem. Soc., Perkins Trans. 2*, 555 (1976).
(8) W. H. Pirkle and S. D. Beare, *J. Am. Chem. Soc.*, **91**, 5150 (1969); **93**, 2817 (1971).
(9) M. D. McCreary, D. W. Lewis, D. L. Wernick, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 1038 (1974).
(10) F. D. Saeva and J. J. Wysocki, *J. Am. Chem. Soc.*, **93**, 5928 (1971).
(11) F. D. Saeva, *J. Am. Chem. Soc.*, **94**, 5135 (1972).
(12) F. D. Saeva, P. E. Sharpe, and G. R. Olin, *J. Am. Chem. Soc.*, **95**, 7656 (1973); **95**, 7660 (1973).
(13) F. D. Saeva and G. R. Olin, *J. Am. Chem. Soc.*, **95**, 7882 (1973).
(14) F. D. Saeva and G. R. Olin, *J. Am. Chem. Soc.*, **98**, 2709 (1976).
(15) C. Honda and H. Hada, *Tetrahedron Lett.*, **No. 3**, 177 (1976).
(16) R. A. Berg and B. A. Haxby, *Mol. Cryst. Liq. Cryst.*, **12**, 93 (1970).
(17) E. E. Jelley, *Nature (London)*, **138**, 1009 (1936).
(18) G. Scheibe, *Z. Angew. Chem.*, **49**, 563 (1936).
(19) S. F. Mason, *Proc. Chem. Soc. (London)*, 119 (1964).
(20) L. Velluz, M. Legrand, and M. Crosjean, "Optical Circular Dichroism", Academic Press, New York, N.Y., 1965.
(21) B. Nordn, *Chem. Scr.*, **8**, 46 (1975).
(22) M. J. B. Tunis-Schneider and M. F. Maestre, *J. Mol. Biol.*, **52**, 521 (1970).
(23) Bis(phenol A) polycarbonate (Lexan) of mol wt 13 000 was obtained from Aldrich Chemical Co.
(24) Ethyl cellulose (44.5–45.5 ethoxy content) was purchased from Polysciences, Inc.
(25) J. K. Maurius and G. R. Bird, *J. Phys. Chem.*, **76**, 2982 (1972).
(26) B. Nordén, *J. Phys. Chem.*, **81**, 151 (1977).
(27) S. F. Mason, *Chem. Phys. Lett.*, **32**, 201 (1975).
(28) Y. Iitaka, *Acta Crystallogr.*, **13**, 35 (1960); **14**, 1 (1961).
(29) A. P. Marchetti, C. D. Salzberg, and E. I. P. Walker, *Photogr. Sci. Eng.*, **20**, 107 (1976); *J. Chem. Phys.*, **64**, 4693 (1976), and references cited therein.
(30) L. Stryer and E. R. Blout, *J. Am. Chem. Soc.*, **83**, 1411 (1961).
(31) Tri(*p*-tolyl)pyrylium fluoroborate and 1,1′-diethyl-2,2′-cyanine iodide were purchased from Eastman Organic Chemicals, Rochester, N.Y.

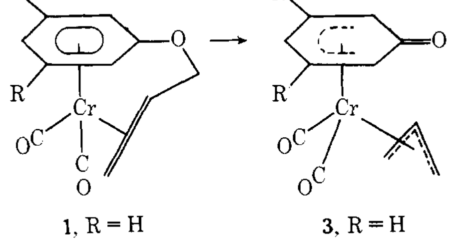
**F. D. Saeva,* G. R. Olin**
*Xerox Webster Research Center*
*Webster, New York 14580*

*Received April 22, 1977*

## Arene-Metal Complexes. 11.[1] Conversion of ($\eta^8$-Allyl phenyl ether)dicarbonylchromium to ($\pi$-Allyl)(6-oxocyclohexadienyl)dicarbonylchromium

*Sir:*

Treatment of ($\eta^8$-benzonorbornadiene)dicarbonylchromium with triphenylphosphine in benzene gives in good yield the corresponding (arene)(triphenylphosphine)dicarbonylchromium complex which results from displacement of the complexed carbon–carbon double bond by triphenylphosphine. However, when ($\eta^8$-allyl phenyl ether)dicarbonylchromium (**1**)[2] or the 3,5-dimethyl derivative **2**[3] was submitted to these reaction conditions,[4] the corresponding isomeric ($\pi$-allyl)(6-oxocyclohexadienyl)dicarbonylchromium complex, **3**[5] or **4**,[6] was obtained instead. Subsequently we established that the triphenylphosphine has no effect on this isomerization by observing that a solution of **1** in benzene at room temperature in the absence of any additional reagents isomerizes to **3**[7] at a rate comparable to that in the presence of triphenylphosphine. This reaction represents a novel route to $\pi$-allyl complexes, and **3** and **4** are unusual in as much as they are air-stable, moderately water-soluble, chromium(0) complexes possessing the 6-oxocyclohexadienyl ligand, an uncommon ligand which has only recently been reported to form $\pi$-complexes with metal ions.[8]



**1**, R = H
**2**, R = $CH_3$

**3**, R = H
**4**, R = $CH_3$

The anion form of the 6-oxocyclohexadienyl ligand is the phenoxide ion, which can also be thought of as a cyclopentadienide with a CO inserted between two carbon atoms. The stability of complexes **3** and **4** suggests that the preparation of numerous analogues of cyclopentadienide complexes which contain this ligand may be possible.

Our proposed structures for complexes **3** and **4** are supported by their NMR and IR data. The NMR spectrum of **4** is more easily analyzed since **4** possesses two methyl groups. The single