sensitivity to LD from possibly nonhelical fibers.

However, when chiral ethyl cellulose was employed as the rigid matrix, CD (θ_{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 9.7×10^{-4} (compared to 7.3×10^{-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.

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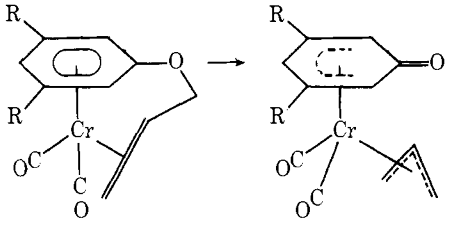
Arene–Metal Complexes. 11.[1] Conversion of (η^8-Allyl phenyl ether)dicarbonylchromium to (π-Allyl)(6-oxocyclohexadienyl)dicarbonylchromium

Sir:

Treatment of (η^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 (η^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 (π-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 π-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 π-complexes with metal ions.[8]



1, R = H
2, R = CH$_3$

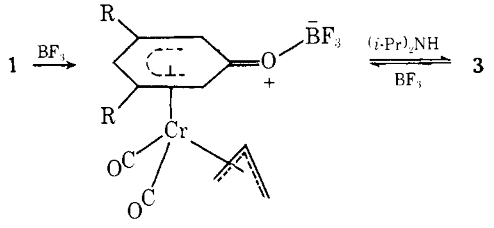
3, R = H
4, R = CH$_3$

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 signal for both methyl groups and the single signal for both ring hydrogen atoms that are adjacent to the ring carbonyl group are consistent with the plane of symmetry which our proposed structure for **4** possesses. Moreover, the NMR spectra of both **3** and **4** show A_2M_2X patterns which are very similar to those described for π-allyl moieties of other π-allyl complexes.[9] The IR spectra of both **3** and **4** show an absorption at 1600 cm^{-1} which is almost as intense as those due to the metal-bound carbonyl groups. For this reason our proposed structures for **3** and **4** are ones that possess a ring carbonyl group.

In the presence of triethylamine the isomerization of arene-chelate **2** to **4** still occurred but in the presence of carbon monoxide **2** was converted to the corresponding (arene)tricarbonylchromium complex.

Treatment of arene-chelate **1** with boron trifluoride etherate in benzene resulted in the immediate formation of the BF_3 adduct of **3** (**5**).[10] Complex **5** could be converted to **3** by treatment with diisopropylamine. In a separate experiment **5** was obtained by treatment of **3** with boron trifluoride etherate.



5

The NMR spectrum of **5** is similar to that of **3** except that the ring hydrogens of **5** are deshielded compared to those of **3**, most likely a result of the electron withdrawing characteristics of the BF_3 moiety.[11] In comparing the π-allyl portion of the NMR spectrum of **3** to that of adduct **5** the chemical shifts of H_M (which are cis to H_X) and H_X of **5** are lower field than those of **3**, but the chemical shift of H_A of **5** is about the same as that of **3**. If these shifts are due to through space effects then the orientation of the π-bound allyl group is such that H_X is pointing toward the complexed ring in each complex.

The basicity of the ring carbonyl group of complexes **3** and **4** is further indicated by the formation of a stable hydrochloride salt (**6**)[12] of **4** prepared by treating **4** with dry HCl in an ether-benzene mixture.

The 6-oxocyclohexadienyl ligand is the middle member of the series of unsaturated ketones which includes cyclopentadienone and cycloheptadienone, and in fact complexes **3** and **4** appear to possess some properties which are similar to those of (cyclopentadienone)tricarbonyliron (**7**)[13] and (cycloheptatrienone)tricarbonylchromium (**8**).[14] For example all of these complexes can be protonated by mineral acids forming stable salts. The ring carbonyl group of neither complex **4** nor **8** will undergo nucleophilic attack by *n*-butyllithium and neither **4** nor **8** can be alkylated with methyl iodide.

The mechanism for the cleavage reaction catalyzed by the Lewis acid boron trifluoride probably involves initial complexation of the BF_3 with the ether oxygen atom followed by cleavage of the oxygen allyl bond. Apparently in the absence of a Lewis acid cleavage of the oxygen allyl bond occurs spontaneously.

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(3) Compound **2:** mp 86–89 °C dec; IR (ether) 1924, 1869 cm^{-1}; NMR (C_6D_6) δ 5.08 (s, 1, *o*-ArH), 4.60–4.30 (m, 2, $-CH_2-$), 4.18 (s, 1, *o*-ArH), 3.70 (s, 1, *p*-ArH), 3.70–3.36 (m, 1, $-C\mathit{H}{=}CH_2$), 2.60 (d, J = 12.0 Hz, 1, *trans*-$CH{=}C\mathit{H}H$), 1.98 (s, 3, $-CH_3$), 1.88 (d, J = 9.0 Hz, 1, *cis*-$CH{=}C\mathit{H}H$), and 1.82 (s, 3, $-CH_3$); *m/e* (%) (70 eV) 271 (6.76), 270 (22.2), 242 (3.38), 214 (53.3), 173 (100), 122 (31.1); exact mass calcd for $C_{13}H_{14}CrO_3$: 270.0348, found: 270.0345 ± 0.0014.

(4) A solution of 0.91 mmol of **1**[2] and 0.76 mmol of triphenylphosphine in 10 mL of benzene was stirred under nitrogen at ambient temperatures for 93 h. The product mixture was rinsed into a separatory funnel with 50 mL of ether and the ethereal solution was extracted with two 50-mL portions of water. The solvent was removed from the combined, orange aqueous phase under reduced pressure providing an orange solid. This material was dissolved in 50 mL of benzene and the solution was dried and filtered and the solvent was removed under vacuum to give a 27% yield of **3**[5] as an orange crystalline solid.

(5) Compound **3:** mp 115 °C dec; IR ($CHCl_3$) 2875, 1972, 1909, 1582 cm^{-1}; IR (THF) 1957, 1899, 1597 cm^{-1}; NMR (acetone-d_6) δ 6.13–5.77 (m, 3), 4.73 (d, J = 7.0 Hz, 2, –CHCOCH–), 4.70–4.52 (m, 1, π-allyl X portion of A_2M_2X), 3.46 (d, J = 7.0 Hz, 2, π-allyl M_2 portion of A_2M_2X), and 1.39 (d, J = 12.0 Hz, 2, π-allyl A_2 portion of A_2M_2X). Anal. Calcd for $C_{11}H_{10}CrO_3$: C, 54.54; H, 4.17. Found: C, 54.19; H, 4.16.

(6) Compound **4:** mp 110 °C dec; IR ($CHCl_3$) 1960, 1897, 1573 cm^{-1}; IR (CCl_4) 1958, 1898, 1597 cm^{-1}; NMR (C_6D_6) δ 4.62 (s, 1), 4.60–4.32 (m, 1, π-allyl X portion of A_2M_2X), 4.19 (s, 2), 3.08 (d, J = 7.2 Hz, 2, π-allyl M_2 portion of A_2M_2X), 1.45 (s, 6, $-CH_3$), and 1.02 (d, J = 11.0 Hz, 2, π-allyl A_2 portion of A_2M_2X); *m/e* (%) (70 eV) 271 (7.68), 270 (18.0) 242 (11.8), 214 (78.0), 173 (100), 122 (98.0). Exact mass. Calcd for $C_{13}H_{14}CrO_3$: 270.03481, found: 270.03417 ± 0.00027. Anal. Calcd for $C_{13}H_{14}CrO_3$: C, 57.77; H, 5.23. Found: C, 57.69; H, 5.34.

(7) A solution of 0.091 mmol of **1** in 1.0 mL of benzene was purged with nitrogen and placed in the dark for 93 h. During this period changes were observed in the IR spectra corresponding to the gradual disappearance of 1 and formation of **3.** Workup provided a 43% yield of **3.**

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(10) Compound **5:** mp (dec) 140 °C dec; IR (THF) 1978, 1927, 1563 cm^{-1}; NMR (acetone-d_6) δ 6.90–6.50 (m, 2), 6.45–6.21 (m, 2), 5.96 (d, J = 6.5 Hz, 1, $-CHC{=}O$) 5.20–4.70 (m, 1, π-allyl X portion of A_2M_2X), 3.91 (d, J = 7.5 Hz, 2, π-allyl M_2 portion of A_2M_2X), and 1.36 (d, J = 10.0 Hz, 2, π-allyl A_2 portion of A_2M_2X). Anal. Calcd for $C_{11}H_{10}BCrF_3O_3$: C, 42.61; H, 3.26. Found: C, 39.30; H, 3.50.

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(12) Compound **6:** mp 148 °C dec; IR (KBr) 1976, 1922, 1551 cm^{-1}. Anal. Calcd for $C_{13}H_{15}ClCrO_3$: C, 50.90; H, 4.94; Cl, 11.56. Found: C, 50.68; H, 5.08; Cl, 11.56.

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Phototransposition of Carbon Atoms in Cyclopentadiene. Photoisomerization of Cyclopentadiene to Tricyclo[2.1.0.0^{2,5}]pentane

Sir:

Numerous five-membered heteroaromatic compounds are converted photochemically to ring-atom transposed isomers: indazole, for instance, is rearranged to benzimidazole;[1] 2-phenylthiophene gives 3-phenylthiophene;[2] and 3,5-diphenylisoxazole affords 2,5-diphenyloxazole.[3] Heteroatom-containing analogues of bicyclo[2.1.0]pent-2-ene and 3-vinylcyclopropene are the most commonly invoked intermediates responsible for these isomerizations; in some instances, such molecules have been detected and characterized.[4]

Phototransposition of carbon atoms has not been observed in the analogous hydrocarbon systems, for cyclopentadienes exhibit facile thermal[5] and photochemical[6] 1,5 shifts which would tend to obscure possible skeletal-atom permutations.

We have addressed this experimental problem through synthesis and photolysis of vicinal [$^{13}C_2$]cyclopentadiene: the phototransposition reaction does occur, and the previously