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Stereoselective Synthesis of (η^6-Arene)Cr(CO)$_3$ Complexes Possessing a Chiral Center at the Benzylic Position

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Directed diastereoselective chromium complexation of *m*-methoxybenzyl alcohol derivatives was achieved by the temporary introduction of a sterically bulky Me_3Si group at either ortho position of the hydroxyalkyl group. The benzylic acetoxy group of the complexes was substituted by the reaction with some nucleophiles to lead to carbon–carbon bond formation products with stereochemical retention.

(η^6-Arene)tricarbonylchromium complexes have characteristic properties due to the strong electron-withdrawing ability and steric bulkiness of Cr(CO)$_3$ group, and significant applications in organic synthesis have been developed.[1] Direct chromium complexation of ortho- or meta-substituted aromatic compounds possessing a chiral center at the side chain such as **1** usually affords a diastereomeric mixture of chromium complexes. Stereoselective synthesis of diastereomeric chromium complexes having electron-withdrawing groups such as nitriles at the side chain is very important for the stereoselective synthesis of substituted fused or spiro compounds via an intramolecular nucleophilic substitution to the complexed arene ring by stabilized carbanions.[2] The (arene)Cr(CO)$_3$ unit can perform a dual purpose in stabilizing both carbanions[3] and carbonium ions[4] at the benzylic position. Thus, the Cr(CO)$_3$ group may act as an electron sink or the metal may donate electrons into vacant orbitals. Carbon–carbon bond formation via the Cr(CO)$_3$-stabilized carbonium ions was recently achieved by reaction of the benzylic acetoxyl group of the complexes with some nucleophiles.[5,6] Furthermore, this SN_1-type carbon–carbon formation would be expected to proceed with stereochemical retention at the benzylic position.[7] Therefore, stereoselective synthesis of the chromium complexes of ortho- or meta-substituted benzyl alcohol derivatives is required for the stereoselective preparation of the complexes having various functional groups at the side chain. Herein is reported the stereoselective synthesis of chromium com-

Scheme I

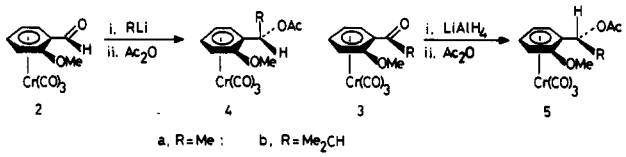

Table I

complex	nucleophiles	ratio of **4** and **5**	yield (%)
2	MeLi	98:2	66
2	Me_2CHLi	99:1	41
3a	$LiAlH_4$	2:98	74
3b	$LiAlH_4$	1:99	84

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(2) Semmelhack, M. F.; Harrison, J. J.; Thebtaranonth, Y. *J. Org. Chem.* **1979**, *44*, 3275. Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Thebtaranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* **1981**, *23*, 3957 and references cited therein.

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(4) (a) Cais, M. *Organomet. Chem. Rev.* **1966**, *1*, 435. (b) Haynes, L.; Pettit, R. *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1975; Vol. 5. (c) Acampora, M.; Ceccon, A.; Farra, M. D.; Giacometti, G. *J. Chem. Soc., Perkin Trans. 2* **1977**, 483.

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(7) Top, S.; Jaouen, G.; McGlinchey, M. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1110. Stereochemical retention in carbon–carbon bond formation via Cr(CO)$_3$-stabilized benzylic carbonium ions was confirmed by the following experiment. Complexation of (*S*)-*o*-methoxyphenethyl alcohol ($[\alpha]_D$ −70°) with Cr(CO)$_6$ gave predominantly (*S,S*)-chromium complex ($[\alpha]_D$ −188°), which was converted into (*R*)-3-(*o*-methoxyphenyl)-*n*-butyric acid ($[\alpha]_D$ −16°) by the following reaction sequences; (1) Ac_2O/pyr, (2) $CH_2{=}CHCH_2SiMe_3/BF_3{\cdot}OEt_2$, (3) *h*$\nu$-$O_2$, (4) $KMnO_4/NaIO_4$. The absolute stereochemistry at the benzylic position of the starting alcohol and final acid compounds is same configuration.

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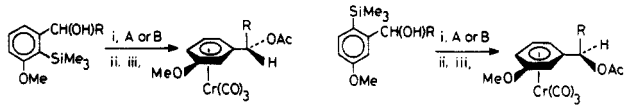
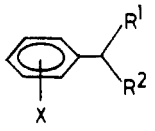
Scheme II[a]



a, R=Me : b=Me$_2$CH

[a] (i) (A) $Cr(CO)_6$ or (B) (naphthalene)$Cr(CO)_3$; (ii) n-$Bu_4N^+F^-$; (iii) Ac_2O/pyridine.

plexes of acyclic benzyl alcohol derivatives and the key chromium complexes required for synthesis of acorenone and acorenone B.



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Results and Discussion

Stereoselective Synthesis of Chromium Complexes of Substituted Benzylic Acetoxyl Compounds. Each diastereomer of the benzylic acetoxyl chromium complexes of *o*-methoxy compounds was prepared by modifications of known methods[8] (Scheme I).

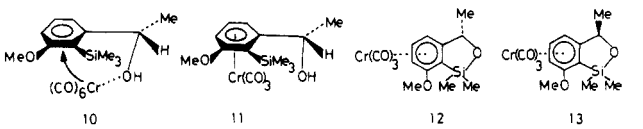
However, this stereoselective synthesis of each diastereomer of the benzylic hydroxyl complexes was applied only to the chromium complexes having the electron-donating group at the ortho position of the carbonyl group.[9] The synthesis of each diastereomeric chromium complex of meta-substituted benzyl alcohol derivatives was achieved by the direct complexation of the benzyl alcohol derivatives in which the sterically bulky and easily removable trimethylsilyl group was temporarily introduced at either ortho position of the hydroxyalkyl group (Scheme II). The reaction of 2-trimethylsilyl compound **6a**[10] with 1 equiv of $Cr(CO)_6$ in butyl ether, heptane, and THF (10:1:1) at 130 °C for 15–20 h under usual conditions, followed by de-trimethylsilylation and acetylation, gave predominantly[11] *S*,S** chromium complex **8a** (mp 88 °C). On the other hand, 6-trimethylsilyl compound **7a**[10] afforded the other diastereomeric complex *S*,R** isomer **9a** (mp 65 °C) under the same reaction sequences. Both complexes **8a** and **9a** are distinguishable from ^{1}H NMR spectra. Similarly, isopropyl compound **7b** was converted into the corresponding *S*,R** complex **9b**. This direct complexation to the arene nucleus may result from the same side[12] as the benzylic hydroxyl group via an interaction of chromium and hydroxy oxygen atom such as intermediate **10**, in which alkyl group should be placed away from the sterically bulky *o*-trimethylsilyl group by the steric repulsion.

Table II

compd	chromium reagent	ratio of 8 and 9	yield (%)
6a	A	98:2	69
7a	A	5:95	66
7b	A	4:96	77
6a	B	100:0	97
6b	B	100:0	88
7a	B	2:98	82
7b	B	0:100	85

However, the products and ratio of this direct complexation depend on the reaction conditions. Thus, reaction of excess of $Cr(CO)_6$ with **6a** for 2 days gave a mixture of *endo*- and *exo*-methyl cyclic siloxane chromium complexes **12** and **13** (**12**:**13** = 3:2) in 88% yield. The methyl signal at the benzylic position of less polar complex **13** appeared at a higher field (δ 1.45) than corresponding signal of the molar polar compound **12** (δ 1.60). Usually, exo complexes of the cyclic compounds show higher chemical shift and higher mobility on chromatography than the corresponding endo isomer.[13] The stereochemistry at the benzylic position of the complexes **12** and **13** could be confirmed by the following transformation. The complex **12** was converted to the *S*,S** chromium complex **8a** by treatment with n-$Bu_4N^+F^-$ and subsequently with acetic anhydride in pyridine. The isomeric complex **13** gave the corresponding *S*,R** chromium complex **9a** by the same sequences. Similarly, **6b** and **7a** afforded the corresponding cyclic chromium complexes as a mixture of *endo*- and *exo*-alkyl substitution product at the benzylic position in various ratio with excess of $Cr(CO)_6$ under the severe reaction conditions. Also, the treatment of **11** with $Cr(CO)_6$ for 2 days at 130 °C gave the same mixture of **12** and **13**. The formation of diastereomeric mixture of the cyclic compounds **12** and **13** under these conditions results from the following reaction path in which initially formed complexation product **11** was converted to the *endo*-methyl complex **12** by an intramolecular attack of the benzylic alkoxide anion to the silyl group with an excess of $Cr(CO)_6$ and then the *endo*-methyl complex **12** was equilibrated to the *exo*-methyl complex **13** under thermal conditions.[14] It is interesting that the silicone–methyl bond was selectively cleaved.

In order to get better stereoselectivity of this reaction, kinetic complexation under milder condition would be necessary. Thus, the compound **6a** was reacted with tricarbonyl(naphthalene)chromium[15] in ether containing THF at 70 °C for 4 h, giving exclusively the *S*,S** chromium complex **8a** in better yield and selectivity (Table II). The more bulky isopropyl derivative **6b** gave only **8b** without any diastereomeric contamination. Similarly, this arene exchange reaction of the regioisomeric trimethylsilyl compounds **7a** and **7b** gave the other diastereomeric complexes, *S*,R** isomer, **9a** and **9b** with higher selectivity and yield.



10 11 12 13

Carbon–Carbon Bond Formation via $Cr(CO)_3$-Stabilized Carbonium Ions. (Arene)$Cr(CO)_3$ systems sta-

(8) (a) Meyer, A.; Dabard, R. *J. Organomet. Chem.* **1972**, *36*, C38. (b) Besancon, J.; Tirouflet, J.; Card, A.; Dausausoy, Y. *Ibid.* **1973**, *59*, 267. (c) Solladie-Cavallo, A.; Suffert, J. *Tetrahedron Lett.* **1984**, *25*, 1897; *Synthesis* **1985**, 659 and references cited therein.

(9) The reaction of Grignard reagents or alkyllithiums with (*m*-methoxybenzaldehyde)chromium complex gave no diastereoselectivity as suggested in ref 8a. See also ref 8c.

(10) These compounds were obtained by the reaction of alkyllithiums with the corresponding aldehydes. 2-(Trimethylsilyl)-3-methoxybenzaldehyde was prepared by the literature method; Comins, D. L.; Brown, J. D. *J. Org. Chem.* **1984**, *49*, 1078. 3-Methoxy-6-(trimethylsilyl)benzaldehyde was synthesized from 3-methoxy-6-bromobenzaldehyde by the usual method.

(11) The diastereomeric ratio was determined by ^{1}H NMR spectra of the crude products.

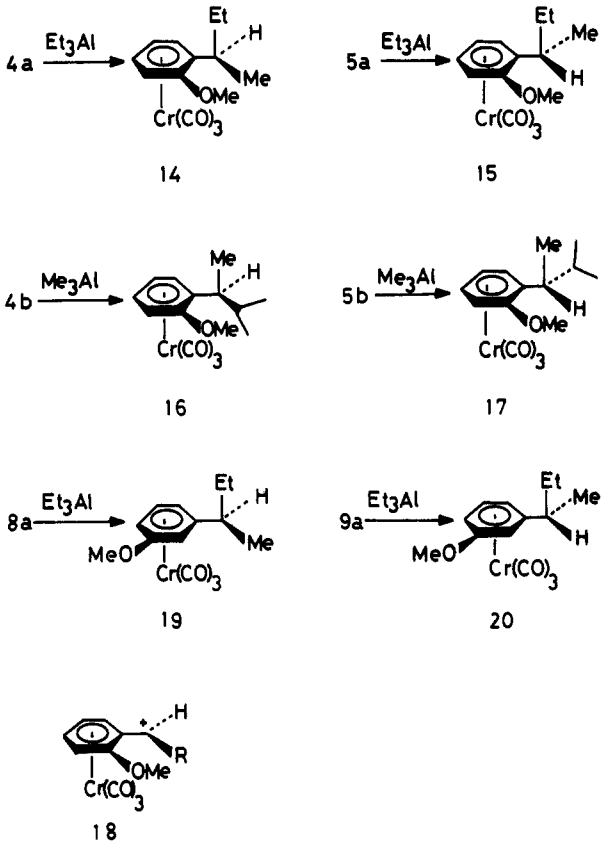
(12) Gracey, D. E. F.; Jackson, W. R.; Jennings, W. B.; Mitchell, T. R. B. *J. Chem. Soc. B* **1969**, 1204.

(13) Brocard, J.; Lebibi, J.; Couturier, D. *J. Chem. Soc., Chem. Commun.* **1981**, 1246. Gracey, D. E. F.; Jackson, W. R.; Jennings, W. B.; Rennison, S. C.; Spratt, R. *J. Chem. Soc. B* **1969**, 1210 and ref 12.

(14) Gracey, D. E. F.; Jackson, W. R.; McMullen, C. H.; Thompson, N. J. *J. Chem. Soc. B* **1969**, 1197.

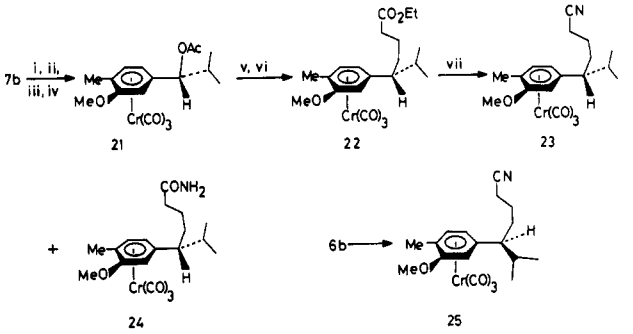
(15) Kündig, E. P.; Perret, C.; Spichinger, S. J. *J. Organomet. Chem.* **1985**, *286*, 183.

Scheme III



bilize both α-carbanions and α-carbonium ions. The synthetic utility of stabilization of α-carbonium ions in carbon–carbon bond formation is little known in comparison with the $Cr(CO)_3$-stabilized α-carbanions. Recently, Reetz and co-worker reported that enol silyl ethers react with benzylic acetoxy chromium complexes in the presence of Lewis acid to afford carbon–carbon coupling products.[5] Also, trialkylaluminums,[6a] diethylzinc,[6a] allyltrimethylsilanes, and electron-rich aromatics[6b] were used as nucleophiles for carbon–carbon bond formation. These SN_1-type carbon–carbon bond forming reactions could be expected to proceed with stereochemical retention.[7] The results of reaction of acyclic benzylic acetoxy complexes with some nucleophiles are summarized in Scheme III. The *S*,S** complex **4a** was reacted with trimethylaluminum to give one diastereomeric chromium complex **14** in 89% yield. On the other hand, reaction of the isomeric *S*,R** complex **5a** with triethylaluminum afforded the other diastereomeric complex **15** without formation of any diastereomeric isomers. Similarly, isopropyl complexes **4b** and **5b** were reacted with trimethylaluminum to give stereospecifically **16** and **17**, respectively, in 53% and 74% yield. The carbonium ion **18** derived from the complex **4b** by departure of the *exo*-acetoxy group was attacked from exo side to give **16**, in spite of severe steric interaction between methoxy and isopropyl groups in **18**. The low yield for the formation of **16** from **4b** may be attributed to this steric interaction. Similarly, *m*-methoxy complexes **8a** and **9a** gave stereospecifically **19** and **20** by the reaction with triethylaluminum, respectively. Also, allyl trimethylsilane instead of trialkyl-aluminums gave stereospecifically carbon–carbon coupling products in good yield by the reaction with the complexes **4**, **5**, **8**, and **9** in the presence of Lewis acid.

This stereospecific carbon–carbon bond formation was applied to the synthesis of natural spirosesquiterpenoids as follows. After complexation with tricarbonyl(naphthalene)chromium and subsequent de-trimethylsilylation of **7b**, 4-methylated chromium complex **21** was obtained in 78% overall yield without regioisomeric methylated complexes via a directed lithiation,[16] quenching with 1 equiv of MeI, and subsequent acetylation. The compound **21** was treated with ethyl 2-(trimethylsilyl)-3-butenoate[17] in the presence of boron trifluoride etherate and hydrogenated with PtO_2 to afford one diastereomeric chromium complex **22** in 66% yield. Treatment of **22** with dimethylaluminum amide[18] in refluxing xylene gave the nitrile complex **23** in 45% yield accompanied by 20% yield of amide complex **24**, which was converted to complex **23** by the repeated reaction with dimethylaluminum amide. The compound **23** has already been converted to acorenone B by Semmelhack and Yamashita.[19] Similarly, regioisomeric trimethylsilyl compound **6b** gave the other diastereomeric complex **25**, key intermediate to acorenone, in 15% overall yield by the same reaction sequences.



(i) (naphthalene)$Cr(CO)_3$; (ii) *n*-$Bu_4N^+F^-$; (iii) *n*-BuLi/TMEDA, then 1 equiv of MeI/HMPA; (iv) Ac_2O/pyridine; (v) CH_2=$CHCH(SiMe_3)CO_2Et/BF_3{\cdot}OEt_2$; (vi) PtO_2/H_2; (vii) Me_2AlNH_2

Experimental Section

All melting points are uncorrected and were determined on a Yanagimoto Model MPJ-2 micro melting point apparatus. IR spectra were recorded in $CHCl_3$ solution on a JASCO Model A-100 spectrometer, and ^1H NMR spectra were measured in $CDCl_3$ solution on Hitachi 90H, JEOL FX-100, and GX-400 spectrometers. Mass spectra were determined with a JEOL D-300 mass spectrometer. Elemental analyses were performed on a Perkin-Elmer Model 240 automatic analyzer. NMR chemical shifts are given in parts per million downfield from Me_4Si, and coupling constants are given in hertz.

(*S*,S)-Tricarbonyl(α-methyl-*o*-methoxybenzyl acetate)chromium (4a).** To a solution of **2** (424 mg, 1.57 mmol) in dry ether (30 mL) was added MeLi (2 mL, 1.57 N in ether, 2.6 mmol) at −78 °C under argon and the mixture was warmed to 0 °C for 2 h. After addition of water, the reaction mixture was extracted with ether, and the organic extract was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The resulting oily product was treated with acetic anhydride (0.5 mL) and (*N,N*-dimethylamino)pyridine (30 mg) in pyridine (5 mL) at 0 °C for 4 h. After being quenched with water, the mixture was extracted with ether. The extract was washed with cold dilute HCl and saturated $NaHCO_3$, dried over $MgSO_4$, and rotary evaporated. The resulting oil was purified by SiO_2 chromatography with ether–petroleum ether. Recrystallization from ether–hexane gave **4a** (344 mg, 66%): mp 122 °C; ^1H NMR 1.45 (3 H, d, J = 6), 2.15 (3 H, s), 3.75 (3 H, s), 4.82 (1 H, t, J = 6), 4.95

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(17) Albaugh-Robertson, P.; Katzenellenbogen, J. A. *J. Org. Chem.* **1983**, *48*, 5288.
(18) Wood, J. L.; Khatri, N. A.; Weinreb, S. M. *Tetrahedron Lett.* **1979**, 4907.
(19) Semmelhack, M. F.; Yamashita, A. *J. Am. Chem. Soc.* **1980**, *102*, 5924.

(1 H, d, J = 6), 5.47 (1 H, t, J = 6), 5.97 (1 H, q, J = 6); IR 1960, 1880, 1720 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O_6Cr$: C, 50.92; H, 4.27. Found: C, 50.97; H, 4.29.

(S*,R*)-Tricarbonyl(α-methyl-o-methoxybenzyl acetate)chromium (5a). To a mixture of $LiAlH_4$ (60 mg, 1.57 mmol) in dry ether (10 mL) was added a solution of tricarbonyl(o-methoxyacetophenone)chromium (404 mg, 1.41 mmol) in dry ether (10 mL) at 0 °C under argon. After being stirred for 30 min, the mixture was quenched with water and worked up as usual. The resulting oily product was acetylated under the same reaction conditions described above to give **5a** (345 mg, 74%): mp 75 °C; ^1H NMR 1.56 (3 H, d, J = 6), 2.06 (3 H, s), 4.80 (1 H, t, J = 7), 4.96 (1 H, d, J = 7), 5.55 (1 H, dd, J = 1, 7), 5.79 (1 H, dd, J = 1, 7), 5.93 (1 H, q, J = 6); IR 1960, 1880, 1720 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O_6Cr$: C, 50.92; H, 4.27. Found: C, 50.93; H, 4.27.

Isopropyl derivatives **4b** and **5b** were obtained by the same method.

(S*,S*)-Tricarbonyl(α-isopropyl-o-methoxybenzyl acetate)chromium (4b): yield 41%; mp 80 °C; ^1H NMR 0.92 (6 H, d, J = 7), 2.20 (3 H, s), 1.94–2.32 (1 H, m), 3.86 (3 H, s), 4.80 (1 H, t, J = 7), 4.94 (1 H, d, J = 7), 5.52 (1 H, t, J = 7), 5.69 (1 H, d, J = 7), 5.98 (1 H, d, J = 7); IR 1960, 1875, 1720 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_6$: C, 53.63; H, 5.06. Found: C, 53.73; H, 5.13.

(S*,R*)-Tricarbonyl(α-isopropyl-o-methoxybenzyl acetate)chromium (5b): yield 84%; mp 118 °C; ^1H NMR 0.94 (3 H, d, J = 6), 1.04 (3 H, d, J = 6), 2.14 (3 H, s), 2.03–2.24 (1 H, m), 4.77 (1 H, t, J = 6), 4.96 (1 H, d, J = 6), 5.36 (1 H, d, J = 6), 5.59 (1 H, t, J = 6), 5.72 (1 H, d, J = 6); IR 1965, 1880, 1720 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_6Cr$: C, 53.63; H, 5.06. Found: C, 53.71; H, 5.09.

(S*,S*)-Tricarbonyl(α-methyl-m-methoxybenzyl acetate)chromium (8a). 2-(Trimethylsilyl)-3-methoxy-α-methylbenzyl alcohol (**6a**) (224 mg, 1 mmol), tricarbonyl(naphthalene)chromium (320 mg, 1.2 mmol), THF (160 μL), and ether (6 mL) were placed in a Carius tube and heated at 70 °C for 4 h according to the literature method.[15] After evaporation of the organic solvents, the residue was purified by SiO_2 chromatography with ether–petroleum ether to give (S*,S*)-tricarbonyl(2-(trimethylsilyl)-3-methoxy-α-methylbenzyl alcohol)chromium (11) (250 mg): mp 127 °C; ^1H NMR 0.38 (9 H, s), 1.42 (3 H, d, J = 6), 1.97 (br s), 3.69 (3 H, s), 4.90 (1 H, br s), 4.99 (1 H, d, J = 7), 5.15 (1 H, d, J = 7), 5.75 (1 H, t, J = 7). Anal. Calcd for $C_{15}H_{20}O_5SiCr$: C, 49.99; H, 5.59. Found: C, 49.82; H, 5.65. The above complex 11 (214 mg, 0.59 mmol) in THF (2 mL) was treated with n-$Bu_4N^+F^-$ (1.8 mL, 0.4 M in THF, 0.72 mmol) at 0 °C for 4 h under argon. After addition of water, the reaction mixture was extracted with ether and worked up as usual to give (S*,S*)-tricarbonyl(3-methoxy-α-methylbenzyl alcohol)chromium (162 mg): mp 66 °C; ^1H NMR 1.50 (3 H, d, J = 7), 2.16 (1 H, d, J = 5), 3.68 (3 H, s), 4.40–4.73 (1 H, br), 4.95–5.16 (3 H, m), 5.56 (1 H, t, J = 6). Anal. Calcd for $C_{12}H_{12}O_5Cr$: C, 50.01; H, 4.20. Found: C, 49.63; H, 4.25. The above resulting complex (158 mg, 0.55 mmol) was acetylated with pyridine (3 mL), N,N-dimethylamino)pyridine (7 mg), and acetic anhydride (1 mL) by the above-mentioned procedure to give **8a** (172 mg): mp 88 °C; ^1H NMR 1.56 (3 H, d, J = 6), 2.11 (3 H, s), 3.71 (3 H, s), 5.00–5.15 (3 H, m), 5.56 (1 H, t, J = 7), 5.64 (1 H, q, J = 6); IR 1965, 1880, 1730 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O_6Cr$: C, 50.92; H, 4.27. Found: C, 50.85; H, 4.28.

The complexes **8b**, **9a**, and **9b** were synthesized by the same reaction sequences.

(S*,R*)-Tricarbonyl(α-methyl-m-methoxybenzyl acetate)chromium (9a): mp 65 °C; ^1H NMR 1.55 (3 H, d, J = 6.5), 2.13 (3 H, s), 3.74 (3 H, s), 4.86 (1 H, d, J = 7), 5.12 (1 H, d, J = 7), 5.25 (1 H, br s), 5.54 (1 H, t, J = 7), 5.65 (1 H, q, J = 6.5); IR 1970, 1880, 1720 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O_6Cr$: C, 50.92; H, 4.27. Found: C, 51.07; H, 4.26.

(S*,S*)-Tricarbonyl(α-isopropyl-m-methoxybenzyl acetate)chromium (8b): mp 109 °C; ^1H NMR 0.91 (6 H, d, J = 7), 1.80–2.20 (1 H, m), 2.11 (3 H, s), 3.66 (3 H, s), 4.85–5.15 (3 H, m), 5.30–5.60 (2 H, m); IR 1960, 1860, 1725 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_6Cr$: C, 53.63; H, 5.06. Found: C, 53.64; H, 5.08.

(S*,R*)-Tricarbonyl(α-isopropyl-m-methoxybenzyl acetate)chromium (9b); mp 95 °C; ^1H NMR 0.90 (3 H, d, J = 7), 0.93 (3 H, d, J = 7), 1.80–2.20 (1 H, m), 2.15 (3 H, s), 3.69 (3 H, s), 4.76 (1 H, d, J = 7), 5.04 (1 H, dd, J = 2, 7), 5.18 (1 H, d, J = 2), 5.39 (1 H, d, J = 7), 5.40 (1 H, t, J = 7). Anal. Calcd for $C_{16}H_{18}O_6Cr$: C, 53.63; H, 5.06. Found: C, 53.87; H, 5.19.

Reaction of 6a with Excess $Cr(CO)_6$ To Give 12 and 13. A mixture of 2-(trimethylsilyl)-3-methoxyphenethyl alcohol (200 mg, 0.89 mmol) and $Cr(CO)_6$ (440 mg, 2 mmol) in butyl ether (20 mL), heptane (2 mL), and THF (2 mL) was heated at 130–140 °C for 50 h under nitrogen. The yellow solution was allowed to cool, and the precipitate was filtered. After evaporation of the filtrate in vacuo, a crude product was purified by SiO_2 chromatography with ether–petroleum ether. First to elute was the *exo*-methyl complex **13** (109 mg): mp 172 °C; ^1H NMR 0.42 (3 H, s), 0.58 (3 H, s), 1.45 (3 H, d, J = 7), 3.70 (3 H, s), 4.75 (1 H, d, J = 6), 4.83 (1 H, d, J = 6), 5.12 (1 H, q, J = 7), 5.67 (1 H, t, J = 6); IR 1960, 1885 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_5SiCr$: C, 48.83; H, 4.68. Found: C, 48.73; H, 4.70. Second eluate afforded *endo*-methyl complex **12** (163 mg): mp 147 °C; ^1H NMR 0.37 (3 H, s), 0.60 (3 H, s), 1.60 (3 H, d, J = 7), 3.70 (3 H, s), 4.78 (1 H, d, J = 6.5), 4.90 (1 H, d, J = 6.5), 5.12 (1 H, q, J = 7), 5.59 (1 H, t, J = 6.5); IR 1965, 1890 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_5SiCr$: C, 48.83; H, 4.68. Found: C, 48.74; H, 4.71.

(S*,S*)-Tricarbonyl(1-methyl-1-(o-methoxyphenyl)propane)chromium (14). To a solution of the complex **4a** (100 mg, 0.3 mmol) in dry CH_2Cl_2 (6 mL) was added Et_3Al (1.2 mL, 1.0 M in hexane, 1.2 mmol) at −78 °C under argon. The mixture was warmed to 0 °C for 3 h, quenched with dilute cold HCl, and extracted with methylene chloride. The extract was washed with saturated $NaHCO_3$ and brine and dried over $MgSO_4$. Evaporation of the solvent and purification by SiO_2 chromatography gave **14** (81 mg, 89%): mp 84 °C; ^1H NMR 1.04 (3 H, t, J = 7), 1.18 (3 H, d, J = 7), 1.28–1.83 (2 H, m), 2.48–2.80 (1 H, m), 3.73 (3 H, s), 4.84 (1 H, t, J = 7), 4.97 (1 H, d, J = 7), 5.36–5.55 (2 H, m); IR 1960, 1870 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_4Cr$: C, 56.00; H, 5.37. Found: C, 55.75; H, 5.33.

The other complexes **5a**, **4b**, **5b**, **8a**, and **9a** were reacted with trialkylaluminums under the same conditions.

(S*,R*)-Tricarbonyl(1-methyl-1-(o-methoxyphenyl)propane)chromium (15): yield 86% mp 61 °C; ^1H NMR 0.88 (3 H, t, J = 7), 1.22 (3 H, d, J = 7), 1.32–1.66 (2 H, m), 2.78–3.12 (1 H, m), 3.70 (3 H, s), 4.84 (1 H, t, J = 7), 4.95 (1 H, d, J = 7), 5.36–5.50 (2 H, m); IR 1960, 1870 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_4Cr$: C, 56.00; H, 5.37. Found: C, 55.79; H, 5.36.

(S*,R*)-Tricarbonyl(1,2-dimethyl-1-(o-methoxyphenyl)propane)chromium (16): mp 73 °C; ^1H NMR 0.82 (3 H, d, J = 6.5), 0.90 (3 H, d, J = 6.5), 1.17 (3 H, d, J = 7), 1.60–1.98 (1 H, m), 2.88–3.16 (1 H, m), 3.85 (3 H, s), 4.88 (1 H, t, J = 6), 4.96 (1 H, d, J = 6), 5.40–5.52 (2 H, m); IR 1950, 1860 cm^{-1}. Anal. Calcd for $C_{15}H_{18}O_4Cr$: C, 57.32; H, 5.77. Found: C, 57.26; H, 5.81.

(S*,S*)-Tricarbonyl(1,2-dimethyl-1-(o-methoxyphenyl)propane)chromium (17): mp 36 °C; ^1H NMR 0.84 (3 H, d, J = 7), 0.96 (3 H, d, J = 7), 1.29 (3 H, d, J = 7), 1.90 (1 H, m), 2.12 (1 H, q, J = 7), 3.75 (3 H, s), 4.78 (1 H, t, J = 6), 4.99 (1 H, d, J = 6), 5.47–5.60 (2 H, m); IR 1950, 1860 cm^{-1}. Anal. Calcd for $C_{15}H_{18}O_4Cr$: C, 57.32; H, 5.77. Found: C, 57.37; H, 5.79.

(S*,S*)-Tricarbonyl(1-methyl-1-(m-methoxyphenyl)propane)chromium (19): yellow liquid (99% yield); ^1H NMR 0.93 (3 H, t, J = 7), 1.25 (3 H, d, J = 7), 1.30–1.80 (1 H, m), 2.28–2.60 (1 H, m), 3.68 (3 H, s), 4.75 (1 H, d, J = 7), 4.95 (1 H, d, J = 7), 5.05 (1 H, s); IR 1960, 1880 cm^{-1}; MS, m/e 300, 244, 216, 164, 136.

(S*,R*)-Tricarbonyl(1-methyl-1-(m-methoxyphenyl)propane)chromium (20): yield 88%; mp 46 °C; ^1H NMR 0.94 (3 H, t, J = 7), 1.21 (3 H, d, J = 7), 1.30–1.80 (2 H, m), 2.25–2.55 (1 H, m), 3.65 (3 H, s), 4.75 (1 H, d, J = 6), 4.90–5.10 (2 H, m), 5.48 (1 H, t, J = 6); IR 1960, 1880 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_4Cr$: C, 56.00; H, 5.37. Found: C, 55.91; H, 5.39.

Preparation of 21. To a solution of (S*,R*)-tricarbonyl(α-isopropyl-m-methoxybenzyl alcohol)chromium (800 mg, 2.52 mmol) prepared from **7b** and TMEDA (1.2 mL, 7.95 mmol) in dry THF (20 mL) was added n-BuLi (4.8 mL, 1.6 M in hexane, 7.68 mmol) at −78 °C under argon. After being stirred for 4 h, a mixture of MeI (0.16 mL, 2.57 mmol) and HMPA (1.4 mL, 8.05 mmol) was added to the reaction mixture, and the mixture was warmed to 0 °C for 4 h. Usual workup gave 720 mg (86%) of (S*,R*)-tricarbonyl(α-isopropyl-3-methoxy-4-methylbenzyl alcohol)chromium: yellow oil; ^1H NMR 0.95 (6 H, d, J = 7), 1.55–2.00 (1 H, m), 2.11 (3 H, s), 2.28 (1 H, d, J = 3), 3.74 (3 H, s), 4.00–4.25

(1 H, m), 4.74 (1 H, d, J = 6), 5.32–5.60 (2 H, m); IR 3600, 1950, 1860 cm^{-1}; MS, m/e 330, 312, 274, 246. The above complex (1.35 g, 4.07 mmol) was acetylated with acetic anhydride (3 mL) and (*N,N*-dimethylamino)pyridine (200 mg) in pyridine (20 mL) under the above-mentioned condition. Usual workup gave the complex **21** (1.44 g, 95%): mp 76 °C; ^1H NMR 0.87 (3 H, d, J = 7), 0.92 (3 H, d, J = 7), 1.70–2.30 (1 H, m), 2.11 (3 H, s), 2.15 (3 H, s), 3.71 (3 H, s), 4.86 (1 H, d, J = 7), 5.10–5.45 (3 H, m); IR 1960, 1870, 1730 cm^{-1}. Anal. Calcd for $C_{17}H_{20}O_6Cr$: C, 54.84; H, 5.41. Found: C, 54.85, H, 5.45.

Preparation of 22 from 21. To a solution of the complex **21** (850 mg, 2.28 mmol) and ethyl 2-(trimethylsilyl)-3-butenoate (2.2 g, 11.8 mmol) in dry CH_2Cl_2 (50 mL) was added boron trifluoride (1.8 mL, 6.9 mmol) at −78 °C under argon. The mixture was stirred at 0 °C for 2 h and warmed to room temperature for 2 h. After addition of water, the reaction mixture was extracted with methylene chloride. The extract was washed with saturated $NaHCO_3$ and brine and dried over $MgSO_4$. Evaporation in vacuo and purification by SiO_2 chromatography gave the coupling product as yellow oil (643 mg, 66%): ^1H NMR 0.85 (3 H, d, J = 7), 0.97 (3 H, d, J = 7), 1.30 (3 H, t, J = 7), 1.80–2.20 (1 H, m), 2.13 (3 H, s), 2.30–2.75 (3 H, m), 3.76 (3 H, s), 4.17 (2 H, q, J = 7), 4.82 (1 H, d, J = 6.5), 4.99 (1 H, br s), 5.38 (1 H, d, J = 6.5), 5.89 (1 H, d, J = 16), 6.78–7.15 (1 H, m); IR 1950, 1860, 1700 cm^{-1}; MS, m/e 426, 342. A mixture of the above coupling product (500 mg, 1.17 mmol) and PtO_2 (20 mg) in ethyl acetate (15 mL) was stirred at room temperature under a hydrogen atmosphere for 4 h. Filtration, evaporation, and purification by SiO_2 chromatography gave the complex **22** (485 mg, 97%): mp 80 °C; ^1H NMR 0.82 (3 H, d, J = 7), 0.92 (3 H, d, J = 7), 1.26 (3 H, t, J = 7), 1.50–2.00 (4 H, m), 2.11 (3 H, s), 2.10–2.55 (4 H, m), 3.78 (3 H, s), 4.11 (2 H, q, J = 7), 4.82 (1 H, d, J = 6.5), 5.08 (1 H, br s), 5.37 (1 H, d, J = 6.5). Anal. Calcd for $C_{21}H_{28}O_6Cr$: C, 58.87; H, 6.59. Found: C, 58.88; H, 6.70.

Reaction of 22 with Me_2AlNH_2 To Give Complex 23. Dimethylaluminum amide was prepared from Me_3Al (8.0 mL, 19% in hexane, 14 mmol) in dry CH_2Cl_2 (6.0 mL) and anhydrous NH_3 (10 mL) according to the literature method.[18] A solution of the compound **22** (130 mg, 0.31 mmol) in dry xylene (5.0 mL) was added to the dimethylaluminum amide prepared above, and the reaction mixture was refluxed for 4 h under argon. After being quenched with MeOH, the mixture was extracted with ether, and the extract was washed with dilute HCl and brine and dried over $MgSO_4$. Evaporation in vacuo and purification by SiO_2 chromatography gave the nitrile complex **23** (53 mg, 45%) as first fraction: mp 92 °C; ^1H NMR 0.86 (3 H, d, J = 7), 0.95 (3 H, d, J = 7), 1.70–2.00 (5 H, m), 2.11 (3 H, s), 2.25–2.60 (3 H, m), 3.77 (3 H, s), 4.80 (1 H, d, J = 7), 5.01 (1 H, br s), 5.38 (1 H, d, J = 7); IR 2250, 1950, 1850 cm^{-1}. Anal. Calcd for $C_{19}H_{23}O_4NCr$: C, 59.84; H, 6.08; N, 3.69. Found: C, 59.83; H, 6.15; N, 3.63. The second fraction gave the amide complex **24** (25 mg, 20%): ^1H NMR 0.80 (3 H, d, J = 7), 0.95 (3 H, d, J = 7), 1.40–2.40 (8 H, m), 2.10 (3 H, s), 3.75 (3 H, s), 4.82 (1 H, d, J = 7), 5.09 (1 H, br s), 5.34 (1 H, d, J = 7), 5.15–5.50 (2 H, br); IR 3200–3400, 1960, 1860, 1670 cm^{-1}; MS, m/e 315 (M^+ − 3CO), 263 (M^+ − $Cr(CO)_3$), 220, 161. The amide complex **24** was converted to the nitrile complex in 47% yield under the above-mentioned procedure.

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Circular Dichroism of Linearly Conjugated Chromophores

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A series of chiral four to eight π-electron systems of planar linearly conjugated systems has been prepared, and their chiroptical properties have been determined. The effect of changes in both configuration and conformation on the circular dichroism spectra of these molecules is discussed.

Substantial research efforts have been devoted toward the understanding of the chiroptical properties of conjugated dienes and enones. Homoannular *cisoid* dienes constitute a group of dienes with an inherently chiral chromophore for which an empirical diene chirality rule has been proposed.[1] A similar empirical rule has been advanced for skewed *transoid* dienes.[2] Alternatively, allylic axial bonds have been proposed to control long-wavelength π–π^* Cotton effect of dienes and enones[3-5] and a diene quadrant rule was postulated to account for the rotatory contributions of the diene and the axial allylic substituents.[6] Recently these different proposals were combined into an empirical-theoretical model of a helical 1,3-cyclohexiadiene chromophore.[7]

There are numerous optically active natural products which contain planar (or nearly planar) polyunsaturated conjugated chromophores. Examples of which are the triene chromophore in leukotrienes (**1a**), the polyene chromophore in optically active carotenoids (**1b**), and the conjugated carbonyl chromophore in the trichothecenes (**1c**) and the macrolide antibiotics (**1d**).

With the exception of the carotenoids[8] there has been only a paucity of effort directed toward the understanding of the chiroptical effects of these types of chromophores

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