commonly used in these alkylations may play a similar role as indicated by the ^{119}Sn spectra of derivatives **9** and **10** in which, upon addition of 1 molar equiv of tetrabutylammonium bromide, similar broadening and upfield shift of the signals could be observed. No further experiments with other catalysts were carried out.

Experimental Section

General. ^{119}Sn NMR spectra were recorded on a Bruker WP-80 spectrometer (29 MHz) at 40 °C, with proton-noise decoupling under gated NOE supression, for ~0.25 M solutions in C_6D_6, under an argon atmosphere. The equivalent amount of NMI (calculated from the starting material) was directly added to the NMR sample. ^{13}C NMR spectra were obtained on a Varian XL-300 (75 MHz) spectrometer under proton-noise decoupling for the same solutions. The NMR samples were prepared as described below and directly analyzed without any previous purification. Assignment of signals was done by selective proton irradiation.[13] Chemical shifts values are given in ppm from internal C_6D_6 (128.0 ppm, ^{13}C) and Me_4Sn as external standard (^{119}Sn). The variable-temperature experiments were carried out for toluene solutions with external DMSO-d_6 (high temperature) or acetone-d_6 (low temperature).

Preparation of NMR Samples. (a) Mono-*O*-tributylstannyl Ethers 2 and 31. Compounds **1** and **30** (1.2 mmol) were separately refluxed with bis(tributyltin) oxide (0.62 mL, 1.2 mmol) in toluene (15 mL) under argon overnight with azeotropic removal of water, then evaporated, dissolved in C_6D_6, and filtered.

(b) Di-*O*-tributylstannyl Ethers 4, 12, 16, and 28. Diols **3**, **11**, **15**, and **27** (0.6 mmol) were separately treated with bis(tributyltin) oxide (0.62 mL, 1.2 mmol) for 18 h as in (a).

(c) Di-*O*-tributylstannyl Ethers 8 and 20 were prepared from diols **7** and **19** (0.6 mmol), respectively, by treatment with bis(tributyltin) oxide (0.93 mL, 1.8 mmol) for 48 h as in (a).

(d) Tri-*O*-tributylstannyl Ether 24 was prepared from triol **23** (0.6 mmol) by treatment with bis(tributyltin) oxide (0.93 mL, 1.8 mmol) for 48 h as in (a).

(e) Mixture of Stannylated Derivatives from Diol 3. From **3** (0.317 g, 1.8 mmol) and bis(tributyltin) oxide (0.31 mL, 0.6 mmol) in the above conditions for 24 h, a mixture of **3**, **4**, **5**, and **6** was obtained from which most of unreacted **3** could be separated by filtration. The final solution contained a 3:1:1.5 mixture of **4**, **5**, and **6**, respectively.

(f) Mixture of Stannylated Derivatives from Diol 7. From **7** (0.160 g, 0.6 mmol) and bis(tributyltin) oxide (0.31 mL, 0.6 mmol) refluxed overnight as above, a 2:1:2.5 mixture of **8**, **9**, and **10** was obtained. This mixture was refluxed overnight with more **7** (0.160 g, 0.6 mmol) to afford a new 1:3 mixture of **9** and **10** and unreacted **7**. An identical result was obtained when **7** (0.320 g, 1.2 mmol) was treated overnight with bis(tributyltin) oxide (0.31 mL, 0.6 mmol).

(g) Mixture of Stannylated Derivatives from Diol 11. From **11** (0.338 g, 1.2 mmol) and bis(tributyltin) oxide (0.31 mL, 0.6 mmol) refluxed overnight, a mixture of **11**, **12**, **13**, and **14** was obtained. Most of unreacted **11** could be separated by filtration to give a 4.5:1:4.5 mixture of **12**, **13**, and **14**.

(h) Mixture of Stannylated Derivatives from Diol 15. Treatment of **15** (0.338 g, 1.2 mmol) as in (g) gave a 2:1:1 mixture of **16**, **17**, and **18** and some unreacted **15**.

(i) Mixture of Stannylated Derivatives from Diol 19. Treatment of **19** (0.320 g, 1.2 mmol) as in (g) gave a 1:5:1 mixture of **20**, **21**, and **22** and some unreacted **19**.

(j) Mixture of Stannylated Derivatives from Triol 23. From **23** (0.194 g, 1.2 mmol) and bis(tributyltin) oxide (0.93 mL, 1.8 mmol) refluxed overnight, a 1:1:3 mixture of **24**, **25**, and **26** was obtained.

(k) Mixture of Stannylated Derivatives from Diol 27. Reaction of **27** (0.257 g, 1.2 mmol) with bis(tributyltin) oxide (0.31 mL, 0.6 mL) gave a 1:5 mixture of **28** and **29** and some starting **27**.

Acknowledgment. We thank the C.A.I.C.Y.T. and the C.S.I.C. for financial support, G. Corrales for excellent technical assistence, and Prof. A. Alemany for helpful advice.

Registry No. 1, 52579-97-2; 2, 117755-77-8; 3, 5540-31-8; 4, 117755-78-9; 5, 117755-79-0; 6, 117755-80-3; 7, 55287-63-3; 8, 117755-81-4; 9, 117755-82-5; 10, 117755-83-6; 11, 57701-27-6; 12, 77388-88-6; 13, 77388-87-5; 14, 77388-86-4; 15, 71117-37-8; 16, 117858-39-6; 17, 117755-84-7; 18, 117858-40-9; 19, 116836-98-7; 20, 117755-85-8; 21, 117755-86-9; 22, 117755-87-0; 23, 644-76-8; 24, 117755-88-1; 25, 117755-89-2; 26, 117755-90-5; 27, 492-70-6; 28, 117755-91-6; 29, 109482-27-1; 30, 109-86-4; 31, 117755-92-7; NMI, 616-47-7; ^{119}Sn, 14314-35-3; $(Bu_3Sn)_2O$, 56-35-9.

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[13] Birdsall, B.; Birdsall, N. J. M.; Feeney, J. *J. Chem. Soc., Chem. Commun.* 1972, 316–317.

1,5-Stereocontrol via (η^6-Arene)tricarbonylchromium Complexes

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1,5-Stereocontrol is achieved by diastereoselective $Cr(CO)_3$ complexation of *o*-alkoxyphenyl derivatives possessing a benzylic acetal and an allylic alcohol on the side chain, chirality transfer of the allylic alcohol system, and subsequent stereoselective conversion of the acetal to an alkyl substituent. The stereocontrolled ligand exchange reaction of (naphthalene)$Cr(CO)_3$ with the arene compounds **8** gives predominantly the (arene)chromium complexes **9**. The allylic acetate complexes **21** and **23** are reacted with sodium malonate in the presence of Pd(0) to afford the complexes **22** and **24** with a C-5 chiral center, by the stereo- and regioselective S_N2 type substitution. *O*-Methyl glycolate chromium complexes **26** and **28** are converted into the chirality transferred chromium complexes **27** and **29** by the enolate Claisen rearrangement. The benzylic acetal function of these chromium complexes with the chiral center at the C-5 position can also be transformed to the stereoisomeric methyl substituted function by the two series of reaction sequences.

Introduction

One of the most exciting challenges in synthetic methodology is control of stereochemistry in conformationally nonrigid systems. In recent years a number of efforts have been devoted to the exploration of stereoselective reactions in acyclic precursors, and various excellent methods have been developed for the diastereoselection between adjacent carbon atoms (1,2-relationships).[1] However, general approaches to the construction of remote chiral relationships

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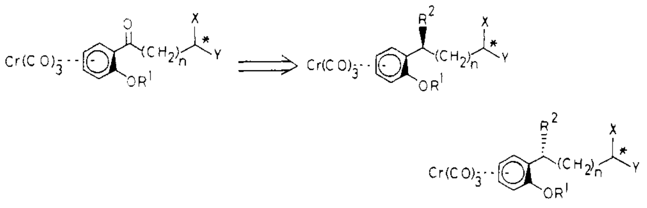
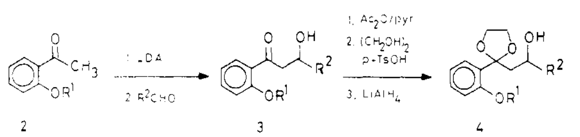
[1] A review: Heathcock, C. H. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3.

0022-3263/89/1954-0469$01.50/0 © 1989 American Chemical Society

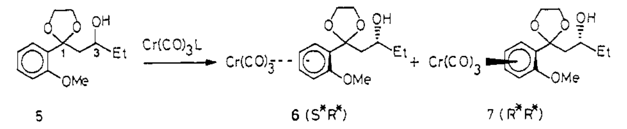
Scheme I



Scheme II



Scheme III



$Cr(CO)_3L$	reaction conditions	6:7	yield, %
$Cr(CO)_6$	butyl ether; heptane; THF (10:1:1); 140 °C; 24 h	55:45	75
$(naphthalene)Cr(CO)_3$	ethyl ether; 1 equiv of THF; 70 °C; 4 h	89:11	85

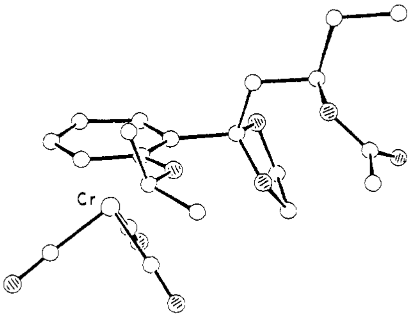


Figure 1. Crystal structure of acetate of 9 (R^1 = i-Pr, R^2 = Et, X = CH_2CH_2).

in acyclic systems are few and have still been a challenging problem in organic synthesis.[2] We report herein a new approach of 1,5-chiral induction based upon the utilization of (η^6-arene)chromium complexes as temporary templates to relay stereochemical information into conformationally flexible systems.

Chromium complexes of ortho- or meta-disubstituted arenes with a chiral center on the side chain can exist in two diastereomeric forms, and stereoselective synthesis of each diastereomeric chromium complex is an important subject in organic syntheses utilizing $(arene)Cr(CO)_3$ complexes. (η^6-Arene)tricarbonylchromium complexes have some characteristic properties due to the electronic effect and steric bulkiness of the $Cr(CO)_3$ group, and significant applications in organic synthesis have been developed.[3] The $Cr(CO)_3$ unit shows a dual behavior stabilizing both carbanions as an electron sink and carbocations as an electron donor. By utilization of the $Cr(CO)_3$-stabilized carbocations, the benzylic hydroxyl or acetoxyl group of the complexes could be substituted by some carbon nucleophiles in the presence of Lewis acids with stereochemical retention.[4] Furthermore, benzylic carbonyl group of (*o*-alkoxyphenyl alkyl ketones)$Cr(CO)_3$ complexes can be stereoselectively reacted with nucleophiles such as alkyllithiums or hydride reagents to produce single diastereomeric benzyl alcohol chromium complex.[4a,5] Therefore, our strategy of 1,5-stereoselection is based upon diastereoselective synthesis of the chromium complexes of *o*-alkoxyphenyl alkyl ketones bearing a chiral center at the C-5 position, and subsequent stereoselective conversion of the benzylic carbonyl group to the alkyl-substituted methine group in the chromium complexes (Scheme I).

Results and Discussion

Diastereoselective $Cr(CO)_3$ Complexation of Arene Compounds. We first examined the directed aldol condensation of (*o*-methoxyacetophenone)$Cr(CO)_3$ (1) with aldehydes to prepare the diastereomeric chromium complexes having a hydroxyl at C-3 position. However, treatment of the complex 1 with LDA in ether followed by addition of propionaldehyde gave no satisfactory results with respect to both yield (less than 10%) and diastereoselectivity (2:3 ratio). The low yield of the aldol condensation with the complex 1 would be attributed to the remarkable stabilization of $Cr(CO)_3$-complexed enolate anion due to the strong π acceptor of the CO ligand.[6]

Therefore, we next attempted diastereoselective $Cr(CO)_3$ complexation of arene compounds.[7] The starting compounds were prepared from *o*-alkoxyacetophenone by the sequence shown in Scheme II. Chromium complexation reaction of 3-hydroxy-1-(*o*-methoxyphenyl)pentan-1-one (3; R^1 = Me, R^2 = Et) was not successful with $Cr(CO)_6$ or $(naphthalene)Cr(CO)_3$. Usually, the $Cr(CO)_3$ complexation of *o*-alkoxyphenyl ketone derivatives was difficult. For instance, 8-methoxy-1-tetralone and 5,8-dimethoxy-1-tetralone afforded no corresponding (η^6-arene)chromium

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(2) Recent representative 1,5-stereocontrol: (a) Trost, B. M.; Klum, T. P. *J. Am. Chem. Soc.* **1981**, *103*, 1864–1865. (b) Heathcock, C. H.; Jarvi, E. J. *Tetrahedron Lett.* **1982**, *23*, 2825–2828. (c) Martinez, C. R.; Grieco, P. A.; Williams, E.; Kanai, K.; Srinivasan, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 1436–1438. (d) Fujiwara, J.; Fukutani, Y.; Hasegawa, M.; Maruoka, K.; Yamamoto, H. *Ibid.* **1984**, *106*, 5004–5005. (e) Schreiber, S. L.; Hulin, B. *Tetrahedron Lett.* **1986**, *27*, 4561–4564. (f) Heathcock, C. H.; Radel, P. A. *J. Org. Chem.* **1986**, *51*, 4322–4323. (g) Ibuka, T.; Nakano, T.; Nishii, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7420–7422. (h) Tomooka, K.; Okinaga, T.; Suzuki, K.; Tsuchihashi, G. *Tetrahedron Lett.* **1987**, *28*, 6335–6338. (i) Harada, T.; Hayashiya, T.; Wada, I.; Iwa-ake, N.; Oku, A. *J. Am. Chem. Soc.* **1987**, *109*, 527–532. (j) Takaya, H.; Ohta, T.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Inoue, S.; Kasahara, I.; Noyori, R. *Ibid.* **1987**, *109*, 1596–1598. (k) Heathcock, C. H.; Finkelstein, B. L.; Jarvi, E. T.; Radel, P. A.; Hadley, C. R. *J. Org. Chem.* **1988**, *53*, 1922–1942 and references cited therein.

(3) Reviews: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA 1987; p 920. (b) Pearson, A. J. *Metallo-Organic Chemistry*; John Wiley and Sons: New York, 1985; p 348. (c) Davies, S. G. *Organotransition Metal Chemistry, Application to Organic Synthesis*; Pergamon Press: Oxford, 1982. (d) Davies, R.; Kane-Maquire, L. A. P. Chromium Compounds with η^2-η^8 Carbon Ligands In *Comprehensive Organometallic Chemistry*; Wilkinsons, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, Chapter 26-2. (e) Kündig, E. P. *Pure Appl. Chem.* **1985**, *57*, 1855. (f) Semmelhack, M. F. *Ibid.* **1981**, *53*, 2379. (g) Jaouen, G. Arene Complexes in Organic Synthesis In *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, **1978**; Vol. 2, p 65.

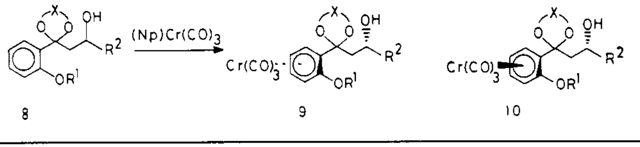
(4) (a) Uemura, M.; Kobayashi, T.; Isobe, K.; Minami, T.; Hayashi, Y. *J. Org. Chem.* **1986**, *51*, 2859–2863. (b) Uemura, M.; Kobayashi, T.; Hayashi, Y. *Synthesis* **1986**, 386–388. (c) Uemura, M.; Isobe, K.; Hayashi, Y. *Tetrahedron Lett.* **1985**, *26*, 767–770. (d) Reetz, M. T.; Sauerwald, M. *Ibid.* **1983**, *24*, 2837–2840.

(5) (a) Meyer, A.; Dabard, R. *J. Organomet. Chem.* **1972**, *36*, C38–42. (b) Besancon, J.; Tirouflet, J.; Card, A.; Dausausoy, Y. *Ibid.* **1973**, *59*, 267–279. (c) Solladie-Cavallo, A.; Suffere, J. *Tetrahedron Lett.* **1984**, *25*, 1897–1900. (d) *Synthesis* **1985**, 659–662 and references cited therein.

(6) Ph_3P or $(PhO)_3P$ chromium complexes obtained by photoligand-exchange reaction of the complex 1 gave the corresponding aldol products via lithium enolate in good yields, but unfortunately the selectivity of the condensation products appeared as 1:1 mixture.

(7) Preliminary communication of these diastereoselective complexation: Uemura, M.; Minami, T.; Hayashi, Y. *J. Am. Chem. Soc.* **1987**, *109*, 5277–5278.

Table I. Complexation of 8 with (Naphthalene)Cr(CO)$_3$



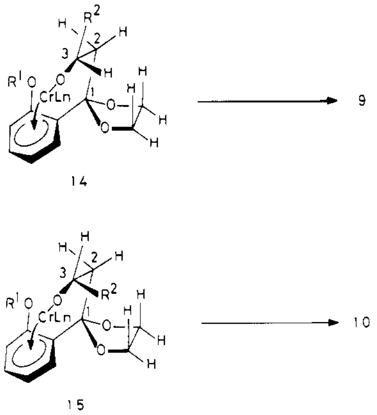
entry	R^1	R^2	X	9:10	yield, %
1	Me	Et	(CH$_2$)$_2$	89:11	85
2	Me	i-Pr	(CH$_2$)$_2$	96:4	89
3	Me	(*E*)-CH=CHMe	(CH$_2$)$_2$	92:8	73
4	Me	(*Z*)-CH=CHMe	(CH$_2$)$_2$	92:8	82
5	Me	(*E*)-C(Me)=CHMe	(CH$_2$)$_2$	98:2	85
6	Et	Et	(CH$_2$)$_2$	94:6	95
7	i-Pr	Et	(CH$_2$)$_2$	94:6	95
8	i-Pr	(*E*)-CH=CHMe	(CH$_2$)$_2$	94:6	80
9	Me	Et	(CH$_2$)$_3$	65:35	90
10	Me	Et	CH$_2$C(Me)$_2$CH$_2$	57:43	60

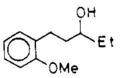
complexes by direct Cr(CO)$_3$ complexation reaction, while 5- or 7-methoxy-1-tetralones gave the corresponding arene complexes under the thermal conditions in good yields.[8] The failure of the direct chromium complexation in these type of ketones may be attributed to an intramolecular coordination of the chromium with two oxygen atoms of the benzylic ketone and *o*-methoxyl groups. This difficulty was overcome by protection of the carbonyl group. The thermal complexation of the acetal **5** with Cr(CO)$_6$ in butyl ether, heptane, and THF (10:1:1) at 130–140 °C for 24 h gave a mixture of easily separable diastereomers, *S**,*R** complex **6** and *R**,*R** complex **7** in a ratio of 55:45 (Scheme III).

Since this type of thermal complexation with Cr(CO)$_6$ reaches equilibrium during the long reaction time,[9] a kinetic complexation under milder conditions is expected to obtain higher diastereoselectivity. Kündig reported[10] the ligand transfer reaction from (naphthalene)tricarbonylchromium to another arene. The naphthalene–chromium bond is labile, and the naphthalene ligand undergoes facile slippage freeing a coordination site ($\eta^6 \rightarrow \eta^4$) for an incoming ligand. This path is accelerated by Lewis bases and donor solvents (e.g. THF), and the ligand transfer reaction to another arene via Cr(CO)$_3$ fragment proceeds at low temperature.

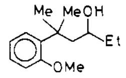
In fact, the treatment of **5** with (naphthalene)Cr(CO)$_3$ in ether containing 1 equiv of THF at 70 °C for 4 h in a sealed tube afforded predominantly *S**,*R** chromium complex **6** in a ratio of 89:11. The reaction results of the ligand transfer from (naphthalene)Cr(CO)$_3$ to the related substrates are summarized in Table I. The stereochemistry of the major complexation products was determined by X-ray crystallography (Figure 1). The diastereoselectivity of this ligand-exchange reaction increased with increasing steric bulkiness of both alkyl groups (R^1 and R^2). The ethylene acetal group at the benzylic position is important to get high selectivity as shown in the following results. In contrast to the ethylene acetal, the corresponding propylene acetal and dimethyl propylene acetal (entries 9, 10) afforded no good selectivity. The complexation of 1-(*o*-methoxyphenyl)pentan-3-ol (**11**) without an acetal function at the benzylic position resulted in low diastereoselectivity. However, *gem*-dimethyl compound **12** afforded high selectivity (92:8) to yield the corresponding *S**,*R** chromium complex predominantly. It may be concluded that the Thorpe–Ingold effect[11] is operative for the high diastereoselective chromium complexation. The hydroxyl group of the side chain also plays an important function for high selectivity. Thus, the corresponding acetate compound **13** gave a diastereomeric mixture in a ratio of only 65:35. From Table I, it is apparent that the selectivity of Cr(CO)$_3$ complexation in these types of arene compounds is independent of the presence/absence of a double bond at the C-4,5 position; that is, the chromium atom is not coordinated with the double bond on the complexation process. These results are contrasted with those of *o*-alkoxyphenyl compounds bearing a hydroxyl at C-1 and a double bond at the C-3,4 position on the side chain. For example, 1-(*o*-methoxyphenyl)-3-buten-1-ol afforded a 1:1 mixture of diastereomeric complexes under usual conditions, while 1-(*o*-methoxyphenyl)-1-butanol without the double bond gave exclusively the *S**,*S** chromium complex (92:8 ratio).

Scheme IV

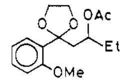




11 (ratio,65 : 35)



12 (ratio, 92 : 8)



13 (ratio, 65 : 35)

The high diastereoselective Cr(CO)$_3$ complexation on the ligand-exchange reaction summarized in Table I could be explained in the following manner (Scheme IV). The ligand-transfer reaction proceeded via an interaction of chromium with the hydroxyl[12] at C-3 in the transition state

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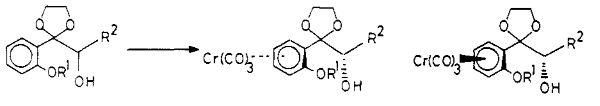
[8] (a) Uemura, M.; Nishikawa, N.; Take, K.; Ohnishi, M.; Hirotsu, K.; Higuchi, T.; Hayashi, Y. *J. Org. Chem.* **1983**, *48*, 2349–2356. (b) Uemura, M.; Minami, T.; Hayashi, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 1193–1194. (c) Uemura, M.; Isobe, K.; Hayashi, Y. *Chem. Lett.* **1985**, 91–94.

[9] Gracey, D. E. F.; Jackson, W. R.; McMullen, C. H.; Thompson, N. J. *J. Chem. Soc. B* **1969**, 1197–1203.

[10] (a) Kündig, E. P.; Perret, C.; Spichinger, S.; Bernardienelli, G. *J. Org. Chem.* **1985**, *286*, 183–200. (b) Kündig, E. P.; Desobry, V.; Grivet, C.; Rudolph, B.; Spichinger, S. *Organometallics* **1987**, *6*, 4505–4512.

[11] (a) DeTar, D. F.; Luthra, N. P. *J. Am. Chem. Soc.* **1980**, *102*, 4505–4512. (b) Exon, C.; Magnus, P. *Ibid.* **1983**, *105*, 2477–2478.

Table II. Complexation of 16 with (Naphthalene)Cr(CO)$_3$



16 17 18

entry	R^1	R^2	17:18	yield, %
1	Me	Me	85:15	80
2	Me	*n*-Bu	85:15	83
3	i-Pr	Me	92:8	88

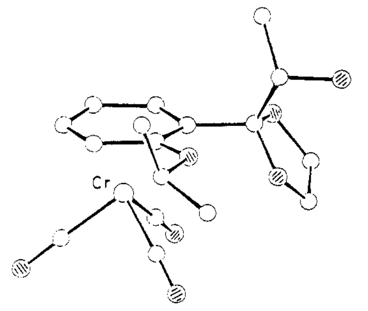
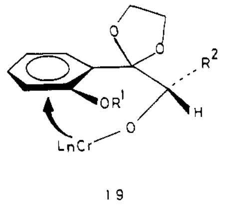


Figure 2. Crystal structure of 17 (R^1 = i-Pr, R^2 = Me).

14, in which the ethylene acetal (or *gem*-dimethyl) group is placed away from the *o*-alkoxyl group by a rotation around the C(1)–C(Ar) bond due to the steric reason, and the R^2 group is positioned to avoid a severe steric interaction with hydrogen atoms of the acetal. An alternative transition state 15, which leads to diastereomeric chromium complexes 10, meets with a significant steric interaction between R^2 and the hydrogen atoms of the acetal.

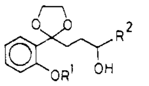
We next examined the diastereoselectivity of the ligand transfer reaction with the homologous arene compounds possessing a hydroxyl at the C-2 or the C-4 position. In the reaction with C-2 hydroxylated compounds 16,[13] *S**,*S** chromium complexes 17 were predominantly obtained (Table II). The stereochemistry was determined by X-ray crystallography of the major complexation product (Figure 2). The transition state 19 in this case is similar to those of ortho-substituted secondary benzyl alcohol derivatives, in which the complexation proceeds so that the steric interactions between *o*-alkoxyl and alkyl groups are minimized by the spacial arrangement of each group.



19

Arene compounds 20 with a hydroxyl at the C-4 position showed no diastereoselectivity on the ligand transfer complexation reaction (Table III). In this case, a longer distance between the hydroxyl and the acetal moiety lowered the steric limitation in the conformation of the alkyl group at the chiral center (C-4) on the side chain.

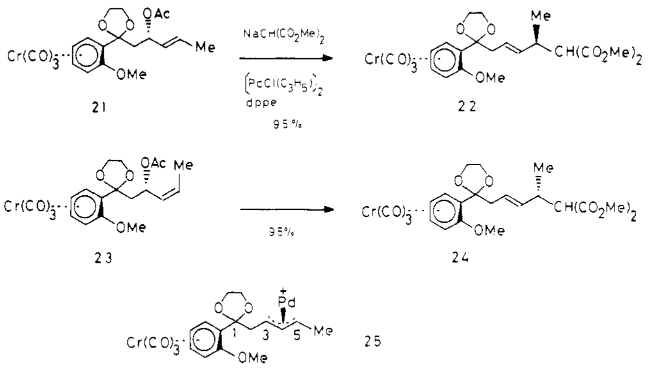
Table III. Complexation of 20 with (Naphthalene)Cr(CO)$_3$



20

entry	R^1	R^2	ratio of diastereomers	yield, %
1	Me	Et	50:50	75
2	Me	i-Pr	50:50	65
3	i-Pr	Et	50:50	60
4	i-Pr	i-Pr	56:44	70

Scheme V



Chirality Transfer on the Side Chain of (Arene)chromium Complexes. A saturated aliphatic moiety possessing methyl branches at the 1,5-positions is a common feature in acyclic natural products such as α-tocopherol[14] or insect pheromons.[15] For exploring the synthetic possibility of the 1,5-chiral system, we next turned our attention to an efficient diastereoselective chirality transfer from the C-3 to the C-5 position on the allylic alcohol chromium complexes, which were prepared stereoselectivity by a (naphthalene)chromium ligand-exchange reaction. For the effective chirality transfer, the Pd(0)catalyzed coupling reaction and the Claisen or related sigmatropic rearrangements occupy a prominent position among the available techniques for acyclic carbon–carbon bond formation by the homologation of a functionalized allylic system. The widespread application of the Pd(0) coupling reaction[16] or the Claisen rearrangement and its many variants[17] to the synthesis of both cyclic and acyclic targets can be attributed to the reliability of reported experimental procedures, the versatile disposition of the products with regard to further tranformation, and the predictable stereochemical outcome of the electrocyclic event.

(*E*)-Allyl acetate chromium complex 21 was reacted with sodium dimethylmalonate in the presence of 10 mol % of Pd(0) catalyst in THF at room temperature to give a single diastereomeric complex 22 in 95% yield without the formation of regio- and stereoisomeric coupling products. It

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[12] Complexation of 1-hydroxyindan with (trispyridine)Cr(CO)$_3$ in the presence of boron trifluoride etherate gave the endo hydroxy complex in very low yield, see ref 9.

[13] These compounds 16 were prepared by the following literature method: Cuvigny, T.; Larcheveque, M.; Normant, H. *Synthesis* **1978**, 857–858.

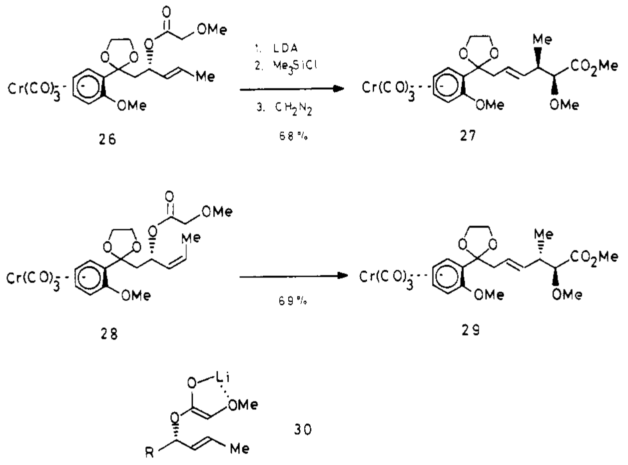
[14] (a) Chan, K.-K.; Cohen, N. C.; De Noble, J. P.; Specian, A. C., Jr.; Saucey, G. *J. Org. Chem.* **1976**, *41*, 3497–3505. (b) Schudel, P.; Mayer, H.; Isler, O. *Vitamines*; Sebrell, W. H., Jr., Harris, R. S., Eds.; Academic Press: New York, 1972; Vol. V, p 168.

[15] (a) Jewett, D. M.; Matsumura, F.; Coppel, H. C. *Science* **1976**, *192*, 51–53. (b) Suzuki, T. *Agric. Biol. Chem.* **1981**, *45*, 1357–1363. (c) Bystrom, S.; Hogberg, H.-E.; Norin, T. *Tetrahedron* **1981**, *37*, 2249–2254.

[16] Reviews: (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385–393. (b) Tsuji, J. *Organic Synthesis with Palladium Compound*; Springer-Verlag: New York, 1980. (c) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinsons, G., Stone, F. F. G., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 8, p 799. (d) Tsuji, J. *Pure Appl. Chem.* **1982**, *54*, 197.

[17] (a) Rhodes, S. J.; Raulines, N. R. *Org. React.* **1975**, *22*, 1. (b) Hill, R. K. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, Chapter 8. (c) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227–232.

Scheme VI

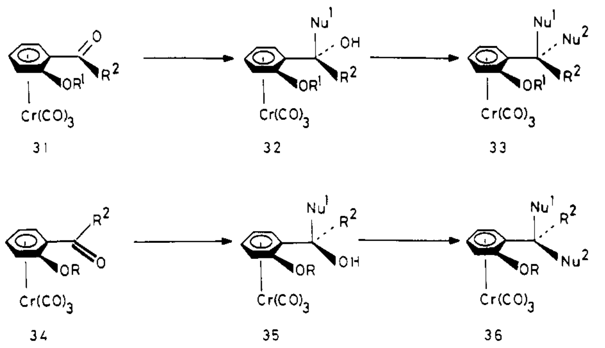


is particularly noteworthy for synthetic applications that the malonate anion attacked regioselectively at the distal carbon (C-5 position) to $Cr(CO)_3$-complexed arene on an intermediate π-allyl palladium complex **25**. This probably is due to steric and/or electronic effects of the chromium-complexed arene and ethylene acetal, and the stereochemical course of the substitution is with net retention.[16,18] Similarly, (*Z*)-allyl acetate chromium complex **23** produced a single coupling product **24** of complementary stereochemistry (5*S**) with an *E* double bond under the same reaction conditions (Scheme V).

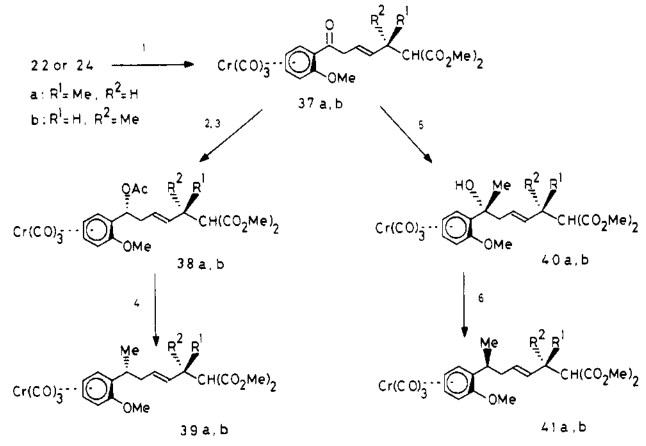
Next, the enolate Claisen rearrangement was examined for the chirality transfer reaction. While both the acetate chromium complexes **21** and **23** afforded no satisfactory rearrangement products, *O*-methyl glycolate resulted in the smooth rearrangement as follows.[19] Treatment of (*E*)-*O*-methyl glycolate chromium complex **26** with LDA in THF at -78 °C, followed by addition of trimethylsilyl chloride and subsequent warming to room temperature, gave a rearranged silyl ester, which was converted into a single 5,6-syn diastereomeric chromium complex **27** (Ar*S**,5*R**,6*S**) by the treatment with diazomethane in 68% overall yield. The formation of the vicinal syn diastereomer from (*E*)-*O*-methyl glycolate complex **26** was expected from the assumption that the intermediate enolate exists as a cyclic chelate geometry **30**, and the successive sigmatropic rearrangement proceeds via a chairlike six-center transition state.[19] On the other hand, starting from (*Z*)-olefin complex **28**, 5,6-anti complex **29** (Ar*S**,5*S**,6*S**) was obtained as a single rearrangement product under the same reaction conditions (Scheme VI). Extremely high diastereoselectivity in the enolate Claisen rearrangement would be attributed to a steric bulkiness of the $Cr(CO)_3$-complexed arene and acetal ring.

1,5-Stereocontrol by Stereoselective Alkylation of (Benzyl ketone)chromium Complexes. Since the stereoselective chirality transfer to the C-5 position on the side chain of (arene)chromium complexes was achieved, the next requirement for 1,5-stereocontrol is stereoselective conversion of the chromium-complexed benzylic acetal to an alkyl-substituted methine group. Reaction of the chromium complexes of *o*-alkoxyphenyl ketone derivatives with nucleophiles gives predominantly one diastereomer of benzyl alcohol chromium complex.[4a,5] Of the two conformers **31** and **34** of this type of complex, the former (**31**) is advantageous due to a dipole effect between the benzylic carbonyl and the *o*-alkoxy groups. Therefore, the chromium complex **32** was exclusively or predominantly obtained via an exo nucleophilic attack in the conformer **31**. Also, the resulting benzylic hydroxyl or acetoxyl group of this type of chromium complex could be easily substituted with various carbon nucleophiles in the presence (or absence) of Lewis acids via a $Cr(CO)_3$-stabilized carbocation with stereochemical retention (Scheme VII). Therefore, both diastereomers of the alkyl substituent at the benzylic position could be stereoselectively synthesized by a change of reaction order of two different nucleophiles (e.g., hydride and carbanions).

Scheme VII



Scheme VIII[a]



[a] Reagents: (1) Ph_3CBF_4; (2) $NaBH_4$; (3) Ac_2O/pyr; (4) Me_3Al; (5) MeLi; (6) $Et_3SiH/BF_3 \cdot OEt_2$.

Conversion of the benzylic acetal to the ketone group of the chromium complex **22** was carried out by an oxidative deacetalization[20] with trityl tetrafluoroborate to give β,γ-unsaturated ketone complex **37a** without isomerization of the double bond to the α,β-positions. Hydrolysis of the acetal under various acidic conditions afforded no satisfactory results. Reduction of the complex **37a** with $NaBH_4$ in MeOH at 0 °C followed by acetylation gave a single diastereomeric acetoxyl complex **38a**, which was converted into 1,5-*anti*-dimethyl chromium complex **39a** (*S**,*R**,*R**) by the treatment with trimethylaluminum in CH_2Cl_2 at -78 °C in 72% overall yield without contamination of the diastereoisomeric complexes. On the other hand, the reaction of the complex **37a** with methyllithium at -78 °C followed by an ionic hydrogenolysis with triethylsilane and boron trifluoride etherate afforded stereoselectively 1,5-*syn*-dimethyl complex **41a** (*S**,*S**,*R**). Both stereoisomeric

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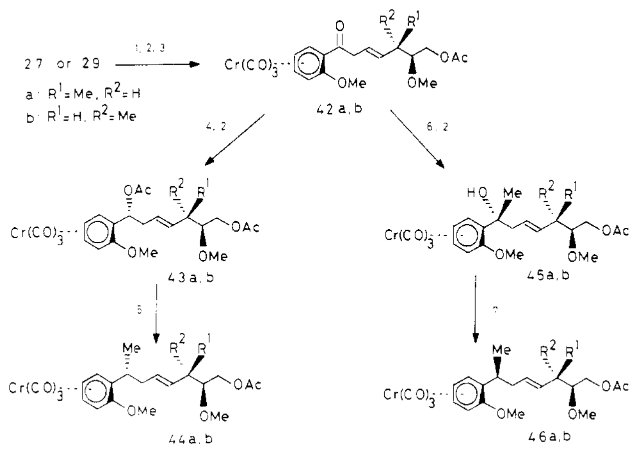
[18] Hayashi, T.; Yamamoto, A.; Hagihara, T. *J. Org. Chem.* **1986**, *51*, 723–727 and references cited therein.

[19] Gould, T. J.; Balestra, M.; Wittman, M. D.; Gary, J. A.; Rossano, L. T.; Kallmerten, J. *J. Org. Chem.* **1987**, *52*, 3889–3901 and references cited therein.

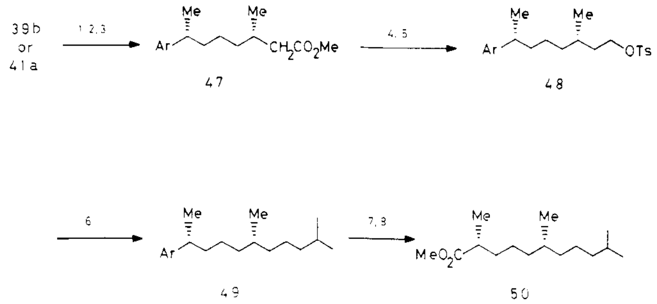
[20] Barton, D. H. R.; Magnus, P. D.; Smith, G.; Zurr, D. *J. Chem. Soc., Chem. Commun.* **1971**, 861–863.

Scheme IX[a]



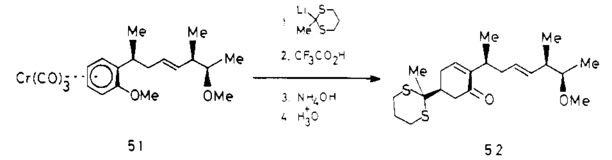
[a] Reagents: (1) $LiAlH_4$; (2) Ac_2O/pyr; (3) Ph_3CBF_4; (4) $NaBH_4$; (5) Me_3Al; (6) MeLi; (7) $Et_3SiH/BF_3{\cdot}OEt_2$.

Scheme X[a]



[a] Reagents: (1) $h\nu$-O_2; (2) H_2/Pd-C; (3) KOAc/DMSO; (4) $LiAlH_4$; (5) TsCl/pyr; (6) $(i\text{-}Bu)_2CuLi$; (7) $RuCl_3/NaIO_4$; (8) CH_2N_2.

Scheme XI



dimethyl compounds **39a** and **41a** are distinguishable in benzylic methyl signals of the ^1H NMR spectra. Similarly, the complex **37b** with a 5S^* configuration was stereoselectively converted into two diastereomeric dimethyl chromium complexes **39b** and **41b** via complexes **38b** and **40b**, respectively, by the same methods (Scheme VIII).

Likewise, the enolate Claisen rearrangement products, α-alkoxy ester chromium complexes **27** and **29**, can be applied to the stereoselective synthesis of acyclic systems containing 1,5,6-chiral centers by the stereoselective alkylation at the benzylic position. Methyl ester **27** with a 5,6-syn chromium complex was converted into acetoxymethyl derivative **42** prior to the modification of the benzylic acetal group (Scheme IX). The complex **27** afforded ketone chromium complex **42a** (S^*,R^*,S^*), which was further converted into 1,5-anti, 5,6-syn chromium complex **44a** in 53% overall yield by reduction, acetylation, and subsequent methylation. On the other hand, 1,5-syn, 5,6-syn chromium complex **46a** was obtained in 52% yield along with ca. 3–5% of diastereoisomeric complex **44a** by the treatment of the complex **42a** with MeLi and then with triethylsilane/boron trifluoride etherate. Instead of MeLi, the reaction of MeMgI with the complex **42a** gave a considerable amount of isomeric methyl derivative complex (ratio 3:2). The formation of stereoisomeric chromium complex with Grignard reagents would be due to a coordination of magnesium with both oxygen atoms of methoxyl and ketone groups in the conformer such as **34**. Similarly, 5,6-anti chromium complex **29** gave two diastereomeric chromium complexes **44b** and **46b** under the same reaction sequences.

These reaction schemes incorporate significant flexibility with regard to the stereochemistry of the remote centers, since a simple variation of allylic olefin geometry would result in an effective stereocontrol of the remote chiral centers bearing various alkyl substituents. The results of such reaction sequences are very useful for the construction of the 1,5-pattern of alkyl substituents, a relationship reminiscent of naturally occurring acyclic or macrocyclic systems such as the side chain of α-tocopherol. Thus, 1,5-*syn*-dimethyl chromium complexes **39b** and **41a** were derived to methyl 2(R^*),6(R^*),10-trimethylundecanoate (**50**) as follows. Demetalation by exposure to sunlight and subsequent hydrogenation of the double bond, followed by demethoxycarbonylation with KOAC/DMSO, afforded **47** in good yield. The compound **47** was converted to **48** by reduction with $LiAlH_4$ and following treatment with tosyl chloride. The tosylate **48** was reacted with lithium diisobutylcuprate to give **49**, which was oxidized with $RuCl_3/NaIO_4$[21] to afford **50** after diazomethane treatment in 54% yield (Scheme X).

Also, it has been well known that $Cr(CO)_3$-complexed anisole derivatives can be served as precursors of substituted cyclohexenone derivatives by nucleophilic addition to aromatic ring developed by Semmelhack and his group.[3,22] For example, chromium complex **51** was converted to cyclohexenone compound **52** by treatment of 2-lithio-2-methyl-1,3-dithian, subsequent protonation of resulting η^5-anionic chromium intermediate, demetalation, and final acidic hydrolysis, although the yield was not optimized (Scheme XI). The cyclohexenone compound **52** with four stereodefined chiral centers is useful for highly functionalized chiral acyclic systems. Further progress on this sequence will be presented elsewhere.

Experimental Section

^1H NMR and ^{13}C NMR spectra were measured on a Hitachi R-90 and a JEOL GX-400 spectrometer. All NMR spectra were recorded in $CDCl_3$ solvent with tetramethylsilane as an internal reference. Chemical shifts are recorded in parts per milion on the δ scale from tetramethylsilane, and coupling constants are given in hertz. IR spectra were determined on a JASCO A-100 spectrometer. Mass spectra were taken on a JEOL D-300 spectrometer. Elemental analysis was performed on a Perkin-Elmer Model 240 automatic elemental analyzer. All melting points are uncorrected and were determined on a Yanagimoto Model MPJ-2 micromelting point apparatus. Ether and THF were dried by distillation from sodium benzophenone ketyl before use, and methylene chloride was distilled from P_2O_5.

Preparation of (Naphthalene)Cr(CO)$_3$. A mixture of naphthalene (9.2 g, 72 mmol) and $Cr(CO)_6$ (8.4 g, 38 mmol) in dibutyl ether (240 mL) and THF (20 mL) was heated with stirring in 500-mL round-bottle flask fitted with a Liebig condenser (2.5 cm diameter, 60 cm length) at 150 °C for 20 h under a nitrogen atmosphere. After cooling to room temperature, solvents were removed in vacuo. The residue was dissolved with ether (300 mL), and the precipitate was removed by filtration. The red ether solution was evaporated in vacuo, and the crystalline residue was subjected to sublimation of naphthalene (70 °C, 5×10^{-2} mmHg) to leave red (naphthalene)$Cr(CO)_3$ (5.5 g, 55%). In most cases

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[21] Carlsen, P. H.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936–3938.

[22] Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Thebtaranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* **1981**, *37*, 3957–3965.

(Np)Cr(CO)$_3$ obtained by the above method was used in the ligand-exchange reaction without further purification.

Complexation of 2-(*o*-Methoxyphenyl)-2-(2-hydroxybut-4-yl)-1,3-dioxolane (5) with Cr(CO)$_6$ To Give Complexes 6 and 7. A mixture of **5** (1.33 g, 5.28 mmol) and Cr(CO)$_6$ (2.3 g, 10.45 mmol) in dibutyl ether (150 mL), heptane (15 mL), and THF (15 mL) was heated at 140 °C for 30 h under a nitrogen atmosphere. Solvents and excess of Cr(CO)$_6$ were removed in vacuo, the residue was dissolved with ether, and the precipitate was filtered off. The yellow ether solution was evaporated in vacuo, and the residue was purified by silica gel (30 g) chromatography with ether–petroleum ether. The first fraction gave S^*,R^* complex **6** as yellow crystals: 820 mg; mp 125 °C; IR (CHCl$_3$) 3550, 1970, 1890 cm^{-1}; ^{1}H NMR δ 0.88 (3 H, d, *J* = 7), 1.18–1.60 (2 H, m), 2.01–2.32 (2 H, m), 3.32 (1 H, s), 3.50–3.80 (1 H, m), 3.73 (3 H, s), 4.02–4.42 (4 H, m), 4.73 (1 H, t, *J* = 7), 4.93 (1 H, d, *J* = 7), 5.60 (1 H, t, *J* = 7), 5.95 (1 H, d, *J* = 7). Anal. Calcd for $C_{17}H_{20}O_7Cr$: C, 52.88; H, 5.19. Found: C, 52.72; H, 5.29. The second fraction afforded 700 mg of R^*,R^* complex **7**: mp 98 °C; IR (CHCl$_3$) 3550, 1965, 1890 cm^{-1}; ^{1}H NMR δ 0.93 (3 H, d, *J* = 7), 1.20–1.65 (2 H, m), 2.01–2.36 (2 H, m), 3.08 (1 H, s), 3.75 (3 H, s), 3.65–3.92 (1 H, m), 4.02–4.40 (4 H, m), 4.73 (1 H, t, *J* = 7), 4.94 (1 H, d, *J* = 7), 5.60 (1 H, t, *J* = 7), 5.95 (1 H, d, *J* = 7). Anal. Calcd for $C_{17}H_{20}O_7Cr$: C, 52.88; H, 5.19. Found: C, 52.63; H, 5.27.

Complexation of 5 with (Naphthalene)Cr(CO)$_3$. (Naphthalene)Cr(CO)$_3$ (1.15 g, 4.4 mmol) and **5** (1.0 g, 4.0 mmol) were placed in a heavy-wall glass tube equipped with a valve and gas inlet. After addition of ether (40 mL) and THF (0.36 mL, 4.4 mmol), the mixture was degassed by a freeze/pump/thaw cycle and then heated at 70 °C for 4 h in a closed system. Filtration, evaporation in vacuo, and SiO$_2$ chromatography gave a mixture of S^*,R^* complex **6** (1.08 g) and R^*,R^* complex **7** (0.13 g). The other chromium complexation products were synthesized analogously, and physical data of some representative major products were shown as follows. In some case, complexation products were identified as the corresponding acetate derivatives. **9 (R^1 = Me, R^2 = (*E*)-CH=CHMe, X = CH$_2$CH$_2$)**: mp 133 °C; IR (CHCl$_3$) 3550, 1965, 1890 cm^{-1}; ^{1}H NMR δ 1.62 (3 H, d, *J* = 7), 2.17 (2 H, d, *J* = 7), 3.28 (1 H, br s), 3.72 (3 H, s), 3.90–4.40 (5 H, m), 4.70 (1 H, t, *J* = 7), 4.89 (1 H, d, *J* = 7), 5.20–5.73 (2 H, m), 5.56 (1 H, t, *J* = 7), 5.93 (1 H, d, *J* = 7). Anal. Calcd for $C_{18}H_{20}O_7Cr$: C, 54.04; H, 5.04. Found: C, 54.00; H, 5.04. **9 (R^1 = Me, R^2 = (*Z*)-CH=CHMe, X = CH$_2$CH$_2$)**: mp 130 °C; IR (CHCl$_3$) 3540, 1970, 1890 cm^{-1}; ^{1}H NMR δ 1.55 (3 H, d, *J* = 7), 2.19 (2 H, m), 3.19 (1 H, br s), 3.72 (3 H, s), 3.95–4.43 (4 H, m), 4.50–4.70 (1 H, m), 4.70 (1 H, t, *J* = 7), 4.90 (1 H, d, *J* = 7), 5.20–5.50 (2 H, m), 5.57 (1 H, t, *J* = 7), 5.95 (1 H, dd, *J* = 1, 7). Anal. Calcd for $C_{18}H_{20}O_7Cr$: C, 54.04: H, 5.04. Found: C, 54.04; H, 5.02. **Acetate of 9 (R^1 = Et, R^2 = Et, X = CH$_2$CH$_2$)**: mp 70 °C; IR (CHCl$_3$) 1985, 1890, 1720 cm^{-1}; ^{1}H NMR δ 0.84 (3 H, t, *J* = 7), 1.43 (3 H, t, *J* = 7), 1.40–1.80 (2 H, m), 1.98 (3 H, s), 2.28 (1 H, d, *J* = 4), 2.35 (1 H, d, *J* = 1), 3.80–4.25 (6 H, m), 4.70 (1 H, t, *J* = 7), 4.86 (1 H, d, *J* = 7), 4.80–5.05 (1 H, m), 5.47 (1 H, t, *J* = 7), 5.95 (1 H, dd, *J* = 1, 7). Anal. Calcd for $C_{20}H_{24}O_8Cr$: C, 54.05; H, 5.44. Found: C, 54.12; H, 5.50. **Acetate of 9 (R^1 = CHMe$_2$, R^2 = Et, X = CH$_2$CH$_2$)**: mp 86 °C; IR (CHCl$_3$) 1970, 1895, 1720 cm^{-1}; ^{1}H NMR δ 0.83 (3 H, t, *J* = 7), 1.35 (3 H, d, *J* = 7), 1.44 (3 H, d, *J* = 7), 1.30–1.80 (2 H, m), 2.00 (3 H, s), 2.25 (1 H, d, *J* = 4), 2.30 (1 H, s), 3.90–4.40 (5 H, m), 4.65 (1 H, t, *J* = 7), 4.87 (1 H, d, *J* = 7), 4.85–5.05 (1 H, m), 5.55 (1 H, t, *J* = 7), 5.95 (1 H, d, *J* = 7). Anal. Calcd for $C_{21}H_{26}O_8Cr$: C, 55.02; H, 5.72. Found: C, 55.12; H, 5.78. **17 (R^1 = CHMe$_2$, R^2 = Me)**: mp 120 °C; IR (CHCl$_3$) 3500, 1960, 1897 cm^{-1}; ^{1}H NMR δ 1.05 (3 H, d, *J* = 7), 1.30 (3 H, d, *J* = 7), 1.37 (3 H, d, *J* = 7), 2.25 (1 H, d, *J* = 5), 3.95–4.48 (5 H, m), 4.65 (1 H, t, *J* = 7), 4.82 (1 H, d, *J* = 7), 5.56 (1 H, dt, *J* = 1, 7), 5.95 (1 H, dd, *J* = 1,7). Anal. Calcd for $C_{17}H_{20}O_7Cr$: C, 52.58; H, 5.19. Found: C, 52.53; H, 5.20. **Acetate of 17 (R^1 = Me, R^2 = *n*-Bu)**: mp 143 °C; IR (CHCl$_3$) 1970, 1900, 1735 cm^{-1}; ^{1}H NMR δ 0.78 (3 H, t, *J* = 7), 1.00–1.50 (4 H, m), 2.07 (3 H, s), 3.71 (3 H, s), 3.90–4.35 (4 H, m), 4.70 (1 H, t, *J* = 7), 4.86 (1 H, d, *J* = 7), 5.37 (1 H, dd, *J* = 4, 12), 5.55 (1 H, t, *J* = 7), 5.93 (1 H, dd, *J* = 1, 7). Anal. Calcd for $C_{20}H_{24}O_8Cr$: C, 54.05; H, 5.44. Found: C, 54.00; H, 5.51.

Acetylation of 9 (R^1 = Me, R^2 = (*E*)-CH=CHMe, X = CH$_2$CH$_2$) To Give Complex 21. A mixture of **9** (500 mg, 1.25 mmol), acetic anhydride (1 mL), and 4-(dimethylamino)pyridine (3 mg) in pyridine (5 mL) was stirred at room temperature for 2 h under nitrogen. The mixture was poured into cold ice-water and extracted with ether. Usual workup group 530 mg of **21** as yellow liquid: IR (CHCl$_3$) 1965, 1890, 1720 cm^{-1}; ^{1}H NMR δ 1.57 (3 H, d, *J* = 7), 1.97 (3 H, s), 2.32 (2 H, d, *J* = 6), 3.73 (3 H, s), 3.85–4.28 (4 H, m), 4.67 (1 H, t, *J* = 7), 4.87 (1 H, d, *J* = 7), 5.20–5.65 (3 H, m), 5.52 (1 H, t, *J* = 7), 5.90 (1 H, d, *J* = 7); MS, *m/e* 442 (M$^+$), 386 (M$^+$ − 2CO), 358 (M$^+$ − 3CO), 306 (M$^+$ − Cr(CO)$_3$). (*Z*)-Isomeric complex **23** was synthesized analogously: mp 97 °C; IR (CHCl$_3$) 1965, 1890, 1720 cm^{-1}; ^{1}H NMR δ 1.63 (3 H, d, *J* = 7), 1.98 (3 H, s), 2.36 (2 H, d, *J* = 6), 3.75 (3 H, s), 3.85–4.25 (4 H, m), 4.67 (1 H, t, *J* = 7), 4.80 (1 H, d, *J* = 7), 5.10–5.25 (3 H, m), 5.55 (1 H, t, *J* = 7), 5.95 (1 H, dd, *J* = 1, 7). Anal. Calcd for $C_{20}H_{22}O_8Cr$: C, 54.30; H, 5.01. Found: C, 54.31; H, 5.01.

Preparation of Complex 26. To a solution of chromium complex **9** (R^1 = Me, R^2 = (*E*)-CH=CHMe, X = CH$_2$CH$_2$) (500 mg, 1.25 mmol) and pyridine (10.3 mL) in THF (10 mL) at 0 °C was added a solution of methoxyacetyl chloride (200 mg, 1.84 mmol) in THF (10 mL) over 10 min under nitrogen. After stirring for 2 h the reaction mixture was diluted with ether and washed with dilute aqueous HCl, saturated aqueous NaHCO$_3$, and brine. The organic fraction was dried over MgSO$_4$, evaporated in vacuo, and chromatographed on silica gel (20 g) with 1:1 mixture of ether and petroleum ether to give 494 mg (85%) of **26**: IR (CHCl$_3$) 1960, 1890, 1740 cm^{-1}; ^{1}H NMR δ 1.60 (3 H, d, *J* = 6), 2.37 (2 H, d, *J* = 6), 3.41 (3 H, s), 3.75 (3 H, s), 3.95 (2 H, s), 3.90–4.30 (4 H, m), 4.70 (1 H, t, *J* = 7), 4.90 (1 H, d, *J* = 7), 5.34–5.80 (4 H, m), 5.92 (1 H, dd, *J* = 7); MS, *m/e* 472 (M$^+$), 416 (M$^+$ − 2CO), 388 (M$^+$ − 3CO). (*Z*)-Isomeric complex **28** was synthesized analogously: yield 84%; IR (CHCl$_3$) 1980, 1890, 1740 cm^{-1}; ^{1}H NMR δ 1.63 (3 H, d, *J* = 6), 2.36 (1 H, s), 2.43 (1 H, d, *J* = 2), 3.42 (3 H, s), 3.74 (3 H, s), 3.93 (2 H, s), 3.95–4.30 (4 H, m), 4.70 (1 H, t, *J* = 7), 4.90 (1 H, d, *J* = 7), 5.15–5.90 (3 H, m), 5.95 (1 H, dd, *J* = 1, 7); MS, *m/e* 472, 444, 416, 388.

Coupling of Complex 21 with Sodium Malonate To Give Complex 22. Bis(μ-chloro)bis(π-allyl)dipalladium (23 mg, 0.063 mmol) and 1,2-bis(diphenylphosphino)ethane (50 mg, 0.13 mmol) were placed in a 50-mL two-necked flask equipped with a serum cap and a three-way stopcock. The flask was filled with argon after evacuation, and to it were added through the serum cap with a syringe 15 mL of THF and 550 mg (1.2 mmol) of **21**. The solution was stirred at 0 °C for 5 min, and a solution of sodium dimethyl malonate was added at 0 °C, which was prepared in another flask by addition of 263 mg (2.0 mmol) of dimethyl malonate to a suspension of 72 mg (1.5 mmol) of 50% sodium hydride in mineral oil in THF (8 mL) at 0 °C. The reaction mixture was kept stirring at room temperature for 14 h, hydrolyzed with water, and extracted with ether. The ether extracts were washed with water and brine, dried over MgSO$_4$, and evaporated under reduced pressure. Purification of the residue by silica gel (15 g) with ether–petroleum ether gave 600 mg (94%) of **22** as yellow liquid: IR (CHCl$_3$) 1965, 1885, 1725 cm^{-1}; ^{1}H NMR δ 0.98 (3 H, d, *J* = 7), 2.60–2.90 (3 H, m), 3.23 (1 H, d, *J* = 5), 3.70 (3 H, s), 3.72 (3 H, s), 3.79 (3 H, s), 3.90–4.30 (4 H, m), 4.70 (1 H, t, *J* = 7), 4.88 (1 H, d, *J* = 7), 5.30–5.45 (2 H, m), 5.85 (1 H, t, *J* = 7), 5.90 (1 H, dd, *J* = 1, 7); MS, *m/e* 514 (M$^+$), 430. Stereoisomeric complex **24** was synthesized analogously from **23**: yield 95%; IR (CHCl$_3$) 1965, 1890, 1730 cm^{-1}; ^{1}H NMR δ 1.03 (3 H, d, *J* = 6), 2.68 (H, d, *J* = 6), 2.88 (1 H, m), 3.23 (1 H, d, *J* = 8), 3.67 (3 H, s), 3.71 (3 H, s), 3.77 (3 H, s), 3.98–4.28 (4 H, m), 4.75 (1 H, t, *J* = 7), 4.90 (1 H, d, *J* = 7), 5.30–5.50 (2 H, m), 5.84 (1 H, t, *J* = 7), 5.96 (1 H, dd, *J* = 1, 7); MS, *m/e* 514, 430.

Enolate Claisen Rearrangement of 26 To Yield Complex 27. To a solution of ester complex **26** (500 mg, 1.06 mmol) in THF (12 mL) at −78 °C was added LDA [prepared from *n*-BuLi (1.6 M in hexane, 0.73 mL, 1.17 mmol) and diisopropylamine (0.17 mL, 1.17 mmol) in THF (8 mL)] at −78 °C over 30 s. The reaction mixture was stirred for 2 min, and trimethylsilyl chloride (0.40 mL, 3.1 mmol) was added at −78 °C for 10 min and then was allowed to warm to room temperature for 3 h. The mixture was acidified with 5% HCl and extracted with ether. The organic fractions were extracted with 5% aqueous NaOH. The aqueous solution was acidified with dilute HCl and extracted with ether. The ether solution was treated with an excess of diazomethane for 5 min, quenched with acetic acid, and then washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, evaporated in vacuo, and then chromatographed on silica gel (20g) with 1:1 mixture of ether and petroleum ether to give complex **27** (300 mg, 60%): mp 96 °C; IR ($CHCl_3$) 1965, 1890, 1740 cm^{-1}; ^{1}H NMR δ 0.95 (3 H, d, $J = 7$), 2.50 (1 H, m), 2.70 (2 H, m), 3.33 (3 H, s), 3.54 (1 H, d, $J = 6$), 3.70 (3 H, s), 3.77 (3 H, s), 3.90–4.30 (4 H, m), 4.70 (1 H, d, $J = 7$), 4.91 (1 H, d, $J = 7$), 5.30–5.45 (2 H, m), 5.57 (1 H, t, $J = 7$), 5.94 (1 H, dd, $J = 1, 7$); ^{13}C NMR δ 16.21, 40.83, 43.33, 52.80, 56.65, 59.14, 66.06, 66.29, 73.34, 83.26, 85.31, 96.11, 96.71, 102.11, 125.50, 135.91, 142.18, 172.82, 233.521. Anal. Calcd for $C_{22}H_{26}O_9Cr$: C, 54.32; H, 5.39. Found: C, 54.54; H, 5.50. Stereoisomeric rearrangement complex **29** was synthesized analogously from **28**: yield 69%; yellow liquid; IR ($CHCl_3$) 1965, 1890, 1740 cm^{-1}; ^{1}H NMR δ 1.02 (3 H, d, $J = 7$), 2.52 (1 H, m), 2.68 (2 H, d, $J = 6$), 3.30 (3 H, s), 3.53 (1 H, d, $J = 6$), 3.68 (3 H, s), 3.75 (3 H, s), 3.90–4.30 (4 H, m), 4.69 (1 H, d, $J = 7$), 4.90 (1 H, d, $J = 7$), 5.35–5.45 (2 H, m), 5.55 (1 H, t, $J = 7$), 5.93 (1 H, dd, $J = 1, 7$); ^{13}C NMR δ 17.31, 40.73, 43.36, 52.19, 56.55, 59.22, 66.13, 66.32, 73.41, 83.31, 85.64, 96.11, 102.29, 108.78, 125.36, 135.32, 142.27, 172.73, 233.52; MS, *m/e* 486 (M$^+$), 402, 370.

Oxidative Deacetalization of 22 To Give 37a. A mixture of acetal complex **22** (580 mg, 1.13 mmol) and trityl tetrafluoroborate (385 mg, 1.24 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 3 h under nitrogen. The reaction mixture was poured into saturated aqueous $NaHCO_3$ and extracted with methylene chloride. The extract was washed with brine and dried over $MgSO_4$. Evaporation in vacuo and silica gel (15 g) chromatography afforded ketone complex **37a** (480 mg, 80%) as a red liquid: IR ($CHCl_3$) 1980, 1900, 1720, 1670 cm^{-1}; ^{1}H NMR δ 1.07 (3 H, d, $J = 7$), 2.75–3.08 (1 H, m), 3.27 (1 H, d, $J = 8$), 3.53 (2 H, d, $J = 6$), 3.64 (3 H, s), 3.67 (3 H, s), 3.80 (3 H, s), 4.88 (1 H, t, $J = 6$), 4.98 (1 H, d, $J = 6$), 5.35–5.85 (2 H, m), 5.57 (1 H, t, $J = 6$), 6.14 (1 H, d, $J = 6$); MS, *m/e* 470 (M$^+$), 386 (M$^+$ - 3CO). Stereoisomeric ketone chromium complex **37b** was synthesized analogously: yield 70%; IR ($CHCl_3$) 1985, 1900, 1720, 1670 cm^{-1}; ^{1}H NMR δ 1.09 (3 H, d, $J = 7$), 2.80–3.20 (1 H, m), 3.28 (1 H, d, $J = 8$), 3.50–3.82 (2 H, m), 3.66 (3 H, s), 3.68 (3 H, s), 3.81 (3 H, s), 4.88 (1 H, t, $J = 6$), 5.00 (1 H, d, $J = 6$), 5.30–5.85 (2 H, m), 5.58 (1 H, t, $J = 6$), 6.15 (1 H, d, $J = 6$); MS, *m/e* 470, 386.

Preparation of 1,5-*anti*-Dimethyl Complex 39a from 37a. To a solution of $NaBH_4$ (85 mg, 2.23 mmol) in MeOH (2 mL) was added the ketone complex **37a** (110 mg, 0.23 mmol) in MeOH (6 mL) at 0 °C for 10 min under nitrogen. The mixture was quenched with acetone and evaporated in vacuo. The residue was dissolved with ether, and the ether solution was washed with water and brine. The organic fraction was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was acetylated with acetic anhydride (0.5 mL) and pyridine (1.0 mL) under usual conditions to give acetate complex **38a** (110 mg) as yellow liquid: ^{1}H NMR δ 1.08 (3 H, d, $J = 7$), 2.07 (3 H, s), 2.40–2.63 (2 H, m), 2.70–3.05 (1 H, m), 3.28 (1 H, d, $J = 8$), 3.69 (3 H, s), 3.72 (3 H, s), 3.78 (3 H, s), 4.76 (1 H, t, $J = 7$), 4.95 (1 H, d, $J = 7$), 5.40–5.90 (5 H, m). A solution of the acetate complex **38a** (110 mg, 0.21 mmol) in CH_2Cl_2 (5 mL) was added to 0.60 mL of Me_3Al (1.8 M in hexane, 1.08 mmol) at -78 °C under nitrogen. The reaction mixture was warmed to 0 °C for 2.5 h and quenched with water. The reaction mixture was extracted with CH_2Cl_2, and the extract was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was chromatographed on silica gel (5 g) with ether–petroleum ether to afford *anti* complex **39a** (80 mg, 80%): IR ($CHCl_3$) 1970, 1890, 1730 cm^{-1}; ^{1}H NMR δ 1.07 (3 H, d, $J = 7$), 1.10 (3 H, d, $J = 7$), 2.00–2.10 (1 H, m), 2.36–2.46 (1 H, m), 2.76–2.86 (1 H, m), 2.90–3.00 (1 H, m), 3.31 (1 H, d, $J = 8$), 3.70 (3 H, s), 3.72 (3 H, s), 3.73 (3 H, s), 4.85 (1 H, t, $J = 7$), 4.98 (1 H, d, $J = 7$), 5.40–5.60 (4 H, m); ^{13}C NMR δ 19.26, 21.82, 32.88, 38.07, 39.47, 52.92, 53.01, 56.39, 58.57, 74.33, 85.89, 94.12, 94.92, 109.56, 130.39, 134.29, 142.20, 169.37, 169.46, 234.19; MS, *m/e* 470 (M$^+$). *syn*-Dimethyl complex **39b** was synthesized analogously from **37b**: yield 70%; yellow liquid; IR ($CHCl_3$) 1970, 1890, 1730 cm^{-1}; ^{1}H NMR δ 1.09 (3 H, d, $J = 7$), 1.11 (3 H, d, $J = 7$), 2.00–2.18 (1 H, m), 2.35–2.42 (1 H, m), 2.75–2.85 (1 H, m), 2.88–2.98 (1 H, m), 3.30 (1 H, d, $J = 8$), 3.69 (3 H, s), 3.71 (3 H, s), 3.72 (3 H, s), 4.86 (1 H, t, $J = 7$), 5.00 (1 H, d, $J = 7$), 5.42–5.60 (4 H, m); ^{13}C NMR δ 19.10, 21.83, 32.99, 37.93, 39.33, 52.92, 52.98, 56.39, 58.45, 74.34, 85.93, 94.06, 94.75, 109.58, 130.07, 134.39, 142.11, 169.46, 234.18; MS, *m/e* 470.

Preparation of 1,5-*syn*-Dimethyl Complex 41a from 37a. To a solution of ketone complex **37a** (100 mg, 0.21 mmol) in ether (5 mL) was added 0.60 mL of MeLi (1.4 M in ether, 0.84 mmol) at -78 °C under nitrogen. The mixture was stirred for 2 h, quenched with water, and extracted with ether. The ether fraction was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. Silica gel (5 g) chromatography afforded 90 mg of complex **40a** as a yellow liquid: ^{1}H NMR δ 1.07 (3 H, d, $J = 7$), 1.43 (3 H, s), 2.18–3.05 (3 H, m), 3.17 (1 H, br s), 3.26 (1 H, d, $J = 8$), 3.69 (3 H, s), 3.70 (3 H, s), 3.77 (3 H, s), 4.76 (1 H, t, $J = 7$), 4.96 (1 H, d, $J = 7$), 5.35–5.65 (3 H, m), 5.91 (1 H, d, $J = 7$). To a solution of the methylated complex **40a** (130 mg, 0.27 mmol) and 0.17 mL of triethylsilane (1.06 mmol) in CH_2Cl_2 (3 mL) was added boron trifluoride etherate (0.1 mL) at -78 °C under nitrogen, and the mixture was warmed to 0 °C for 3 h and quenched with saturated aqueous $NaHCO_3$. The mixture was extracted with methylene chloride, and usual workup afforded 90 mg of **41a**: IR ($CHCl_3$) 1970, 1890, 1730 cm^{-1}; ^{1}H NMR δ 1.03 (3 H, d, $J = 7$), 1.15 (3 H, d, $J = 7$), 2.00–2.10 (1 H, m), 2.20–2.26 (1 H, m), 2.80–2.88 (1 H, m), 3.05–3.12 (1 H, m), 3.28 (1 H, d, $J = 8$), 3.65 (3 H, s), 3.68 (6 H, s), 4.83 (1 H, t, $J = 7$), 4.93 (1 H, d, $J = 7$), 5.25–5.50 (4 H, m); ^{13}C NMR δ 18.84, 19.20, 31.64, 37.96, 41.02, 52.84, 52.93, 56.41, 58.39, 74.24, 85.87, 94.20, 107.97, 129.06, 134.68, 142.34, 169.35, 169.37, 234.21; MS, *m/e* 470. Another stereoisomeric complex **41b** was synthesized analogously: IR ($CHCl_3$) 1970, 1890, 1730 cm^{-1}; ^{1}H NMR δ 1.00 (3 H, d, $J = 7$), 1.15 (3 H, d, $J = 7$), 2.05–2.10 (1 H, m), 2.17–2.25 (1 H, m), 2.80–2.90 (1 H, m), 3.02–3.10 (1 H, m), 3.20 (1 H, d, $J = 8$), 3.63 (3 H, s), 3.68 (6 H, s), 4.83 (1 H, t, $J = 7$), 4.94 (1 H, d, $J = 7$), 5.25–5.50 (4 H, m); ^{13}C NMR δ 19.16, 19.20, 31.43, 37.88, 41.52, 52.90, 52.99, 56.38, 58.39, 74.15, 85.83, 94.21, 94.28, 108.16, 129.28, 134.48, 142.36, 169.24, 169.34, 234.19; MS, *m/e* 470.

Preparation of Complex 42a from 27. To a mixture of $LiAlH_4$ (30 mg, 0.79 mmol) in ether (5 mL) was added a solution of complex **27** (190 mg, 0.39 mmol) in ether (6 mL) at 0 °C under nitrogen, and the mixture was stirred for 2 h. The mixture was quenched with water, and usual workup gave an alcohol complex, which was acetylated with acetic anhydride (0.5 mL), 4-(dimethylamino)pyridine (3 mg) and pyridine (1.0 mL) to give the acetylated complex (160 mg, 82%): ^{1}H NMR δ 0.96 (3 H, d, $J = 7$), 2.05 (3 H, s), 2.20–3.20 (4 H, m), 3.37 (3 H, s), 3.77 (3 H, s), 3.80–4.30 (6 H, m), 4.72 (1 H, t, $J = 7$), 4.93 (1 H, d, $J = 7$), 5.30–5.42 (2 H, m), 5.58 (1 H, t, $J = 7$), 5.94 (1 H, dd, $J = 1, 7$). The above acetate complex (160 mg, 0.32 mmol) was treated with trityl tetrafluoroborate (130 mg, 0.39 mmol) to give ketone complex **42a** (100 mg, 70%) as a red liquid under the above-mentioned conditions: IR ($CHCl_3$) 1980, 1900, 1730, 1675 cm^{-1}; ^{1}H NMR δ 1.05 (3 H, d, $J = 7$), 2.05 (3 H, s), 2.30–2.60 (1 H, m), 3.05–3.30 (1 H, m), 3.40 (3 H, s), 3.56 (2 H, d, $J = 6$), 3.81 (3 H, s), 3.90–4.30 (2 H, m), 4.90 (1 H, t, $J = 7$), 5.00 (1 H, d, $J = 7$), 5.58 (1 H, d, $J = 7$), 5.60–5.90 (2 H, m), 6.15 (1 H, dd, $J = 1, 7$); MS, *m/e* 456 (M$^+$), 372 (M$^+$ - 3CO). Stereoisomeric complex **42b** was synthesized analogously from **29**: overall yield 63%; IR ($CHCl_3$) 1980, 1900, 1730, 1675 cm^{-1}; ^{1}H NMR δ 1.06 (3 H, d, $J = 7$), 2.04 (3 H, s), 2.30–2.60 (1 H, m), 3.15–3.35 (1 H, m), 3.40 (3 H, s), 3.66 (2 H, d, $J = 6$), 3.83 (3 H, s), 4.05 (2 H, d, $J = 7$), 4.88 (1 H, t, $J = 7$), 4.97 (1 H, d, $J = 7$), 5.45–5.80 (3 H, m), 6.15 (1 H, dd, $J = 1, 7$); MS, *m/e* 456, 372.

Preparation of Complexes 44 and 46. These four chromium complexes were synthesized by the above mentioned methods. **44a**: mp 66 °C; IR ($CHCl_3$) 1970, 1890, 1730 cm^{-1}; ^{1}H NMR δ 1.07 (3 H, d, $J = 7$), 1.16 (3 H, d, $J = 7$), 2.07 (3 H, s), 2.05–2.15 (1 H, m), 2.38–2.45 (2 H, m), 2.80–2.90 (1 H, m), 3.12–3.20 (1 H, m), 3.40 (3 H, s), 3.70 (3 H, s), 4.10 (2 H, ABX, $J_{AX} = 3$, $J_{BX} = 6$, $J_{AB} = 12$), 4.80 (1 H, t, $J = 7$), 4.94 (1 H, d, $J = 7$), 5.40–5.58 (4 H, m); ^{13}C NMR δ 16.97, 21.55, 22.04, 33.10, 39.20, 39.51, 56.29, 59.08, 65.14, 74.23, 83.58, 85.79, 94.02, 94.89, 109.43, 129.71, 134.42, 142.10, 171.62, 231.13. Anal. Calcd for $C_{22}H_{28}O_7Cr$: C, 57.89; H, 6.18. Found: C, 57.94; H, 6.22. **44b**: IR ($CHCl_3$) 1970, 1890, 1730 cm^{-1}; ^{1}H NMR δ 1.07 (3 H, d, $J = 7$), 1.16 (3 H, d, $J = 7$), 2.07 (3 H, s), 2.10–2.20 (1 H, m), 2.40–2.50 (2 H, m), 2.80–2.90 (1 H, m), 3.20–3.30 (1 H, m), 3.40 (3 H, s), 3.72 (3 H, s), 4.08 (2 H, ABX, $J_{AX} = 4$, $J_{BX} = 6$, $J_{AB} = 12$), 4.80 (1 H, t, $J = 7$), 4.95 (1 H, d, $J = 7$), 5.40–5.60 (4 H, m); ^{13}C NMR δ 16.58, 21.58, 22.05, 33.13, 38.91, 39.42, 56.31, 59.24, 65.32, 74.23, 83.34, 85.79, 93.86, 94.87, 109.49, 129.68, 134.08, 142.04, 172.23, 234.13; MS, *m/e* 456 (M^+), 372 ($M^+ - 3CO$). **46a**: IR ($CHCl_3$) 1970, 1890, 1730 cm^{-1}; ^1H NMR 0.98 (3 H, d, *J* = 7), 1.18 (3 H, d, *J* = 7), 2.03 (3 H, s), 2.07–2.17 (1 H, m), 2.20–2.30 (1 H, m), 2.30–2.42 (1 H, m), 3.08–3.18 (2 H, m), 3.38 (3 H, s), 3.36–3.42 (1 H, m), 3.70 (3 H, s), 3.98 (2 H, ABX, J_{AX} = 3, J_{BX} = 7, J_{AB} = 12), 4.80 (1 H, t, *J* = 7), 4.93 (1 H, d, *J* = 7), 5.25–5.45 (2 H, m), 5.45–5.56 (2 H, m); ^{13}C NMR δ 17.00, 19.36, 21.54, 31.64, 39.24, 41.50, 56.32, 59.09, 65.28, 74.10, 83.50, 85.70, 94.24, 108.09, 128.57, 134.70, 142.26, 171.56, 231.13; MS, *m/e* 456, 372. **46b**: IR ($CHCl_3$) 1970, 1890, 1730 cm^{-1}; ^1H NMR δ 0.98 (3 H, d, *J* = 7), 1.23 (3 H, d, *J* = 7), 2.07 (3 H, s), 2.10–2.30 (2 H, m), 2.35–2.42 (1 H, m), 3.05–3.15 (1 H, m), 3.18–3.25 (1 H, m), 3.40 (3 H, s), 3.70 (3 H, s), 4.00 (2 H, ABX, J_{AX} = 4, J_{BX} = 8, J_{AB} = 12), 4.84 (1 H, t, *J* = 7), 4.95 (1 H, d, *J* = 7), 5.28–5.42 (2 H, m), 5.45–5.55 (2 H, m); ^{13}C NMR δ 16.87, 19.36, 21.57, 31.43, 39.10, 41.64, 56.31, 59.38, 65.49, 74.02, 83.26, 85.74, 94.09, 94.24, 108.21, 128.73, 134.17, 142.30, 172.00, 234.16; MS, *m/e* 456, 372.

Preparation of 47. A yellow solution of the complex **39b** (680 mg, 1.43 mmol) in ether (70 mL) was exposed to sunlight until the yellow color turned to colorless. A precipitate was filtered off to give decomplexation product (400 mg). A mixture of above compound (400 mg) and 5% Pd/C in ethyl acetate (40 mL) was stirred at room temperature under 1 atm of hydrogen to give 400 mg of hydrogenated product: ^1H NMR δ 0.86 (3 H, d, *J* = 7), 1.16 (3 H, d, *J* = 7), 1.20–2.02 (7 H, m), 3.19 (1 H, d, *J* = 7), 3.05–3.20 (1 H, m), 3.66 (6 H, s), 3.76 (3 H, s), 6.70–7.24 (4 H, m). A mixture of hydrogenated product (400 mg, 1.19 mmol) and potassium acetate (240 mg, 2.45 mmol) in dry DMSO (15 mL) was heated at 135 °C for 2.5 h. The mixture was quenched with water and extracted with ether, and usual workup gave compound **47** (280 mg, 82%): IR ($CHCl_3$) 1730, 1600, 1590 cm^{-1}; ^1H NMR δ 0.86 (3 H, d, *J* = 7), 1.16 (3 H, d, *J* = 7), 1.20–2.31 (9 H, m), 3.15–3.22 (1 H, m), 3.60 (3 H, s), 3.77 (3 H, s), 6.85–7.20 (4 H, m); ^{13}C NMR δ 19.68, 21.00, 24.92, 30.24, 31.67, 36.79, 37.13, 41.68, 51.24, 55.34, 110.47, 120.57, 126.45, 126.70, 135.91, 156.98, 178.77; MS, *m/e* 278, 135.

Preparation of Tosylate 48. To a mixture of $LiAlH_4$ (55 mg, 1.45 mmol) in ether (15 mL) was added a solution of **47** (200 mg, 0.74 mmol) at 0 °C. The mixture was stirred for 1.5 h, and usual workup afforded 175 mg of alcohol. The above alcohol was reacted with tosyl chloride (200 mg, 1.1 mmol) in pyridine (4 mL) to give **48** (200 mg, 73%): ^1H NMR δ 0.73 (3 H, d, *J* = 7), 1.15 (3 H, d, *J* = 7), 1.10–1.70 (9 H, m), 2.40 (3 H, s), 2.95–3.20 (1 H, m), 3.73 (3 H, s), 4.00 (2 H, t, *J* = 7), 6.70–7.18 (4 H, m), 7.26 (2 H, d, *J* = 7), 7.72 (2 H, d, *J* = 7).

Preparation of 49. To a mixture of CuI (470 mg, 2.47 mmol) in ether (10 mL) was added 3.54 mL of i-BuLi (1.4 M in ether, 4.95 mmol) at -40 °C over 10 min under nitrogen. After being stirred for 10 min, a solution of **48** (200 mg, 0.50 mmol) in ether (10 mL) was added to the above mixture at -20 °C, and the reaction mixture was stirred for 3 h and then quenched with aqueous NH_4Cl. The mixture was extracted with ether, and usual workup afforded 135 mg (94%) of **49**: ^1H NMR δ 0.84 (9 H, d, *J* = 7), 0.95–1.70 (14 H, m), 3.00–3.25 (1 H, m), 3.76 (3 H, s), 6.70–7.20 (4 H, m).

Preparation of Methyl 2(*R),6(*R**),10-Trimethylundecanoate (50).** To a mixture of **49** (135 mg, 0.47 mmol) and sodium metaperiodate (2.0 g, 9.35 mmol) in water (15 mL), carbon tetrachloride (3 mL), and acetonitrile (3 mL) was added 15 mg of ruthenium trichloride hydrate, and the mixture was stirred vigorously for 16 h at room temperature and diluted with water. The mixture was extracted with CH_2Cl_2, and evaporated in vacuo. The residue was dissolved in ether and treated with diazomethane. Usual workup gave 67 mg (60%) of **50**: IR ($CHCl_3$) 1725, 1380, 1360 cm^{-1}; ^1H NMR δ 0.82 (3 H, d, *J* = 7), 0.85 (6 H, d, *J* = 7), 1.14 (3 H, d, *J* = 7), 1.00–1.70 (14 H, m), 2.42 (1 H, m), 3.72 (3 H, s); ^{13}C NMR δ 17.13, 19.63, 22.63, 22.72, 24.72, 24.78, 28.01, 32.65, 34.18, 36.91, 37.29, 39.37, 39.54, 51.41, 177.42; MS, *m/e* 242, 211, 157, 152.

Nucleophilic Addition to 51 To Give 52. To a solution of 2-methyl-1,3-dithian (150 mg, 1.12 mmol) in THF (4 mL) was added 0.70 mL of *n*-BuLi (1.6 M in hexane, 1.12 mmol) at -35 °C under nitrogen, and the mixture was stirred for 30 min and then cooled to -78 °C. To the above mixture was added 2 mL of HMPA and then a solution of complex **51** (150 mg, 0.38 mmol) in THF (4 mL), and the reaction mixture was stirred at 0 °C for 4 h. The mixture was cooled to -78 °C, and 0.29 mL of trifluoroacetic acid (3.7 mmol) was added to the above reaction mixture. After being stirred for 1 h at -78 °C , the mixture was poured into 10 mL of aqueous ammonia and further stirred for 1 h. The mixture was extracted with ether, and the extract was evaporated in vacuo. The residue was treated with dilute HCl, and usual workup afforded 15 mg of **52**: IR ($CHCl_3$) 1670 cm^{-1}; ^1H NMR δ 0.96 (3 H, d, *J* = 7), 0.99 (3 H, d, *J* = 7), 1.01 (3 H, d, *J* = 7), 1.60 (3 H, s), 1.80–3.20 (15 H, m), 3.31 (3 H, s), 5.30 (2 H, m), 6.65 (1 H, m); MS, exact mass calcd for $C_{21}H_{34}O_2S_2$ 382.1953, found 382.1976.

Use of α-Anilino Dienenitriles as Nucleophiles in Cycloadditions

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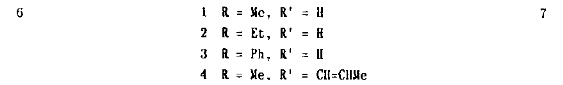
The α-anilino dienenitriles **1–5** were prepared. The dienes **1–3** reacted with dichlorocarbene and electrophiles containing electron-deficient double bonds such as maleic anhydride, benzoquinone, dimethyl acetylenedicarboxylate, tetracyanoethylene, and chlorosulfonyl isocyanate. The diarylmethylamines **8–10**, generated by cycloaddition of α-anilino dienenitriles and maleic anhydride, were successfully transformed into acridones **15–17**. Intramolecular cyclization of trienes **4** and **5** yielded the carbazoles and dihydro derivatives, accompanied by formation of 2-cyano-1-methylindole.

Introduction

Extensive study of α-amino nitriles has demonstrated their uses as precursors of α-amino acids[1] and as equivalents of acyl nucleophiles (C=O Umpolung).[2] The electron-withdrawing cyano group usually dominates over the electron-donating amino group in most of reactions. For example, the inductive effect of the cyano group causes the α-proton in α-(*N*,*N*-diethylamino)acetonitrile to become acidic enough for metalation with LDA.[3] The α-

Scheme I



6

7

1 R = Me, R' = H

2 R = Et, R' = H

3 R = Ph, R' = H

4 R = Me, R' = CH=CHMe

5 R = Ph, R' = CH=CHMe

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[2] Albright, J. D. *Tetrahedron* **1983**, *39*, 3207.

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