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Transformations of Chiral (η^6-Arene)chromium Complexes in Organic Synthesis: Diastereoselective 1,4-Addition Reactions of Organocopper Reagents to (Ortho-substituted-phenyl (*E*)-enone)chromium Complexes

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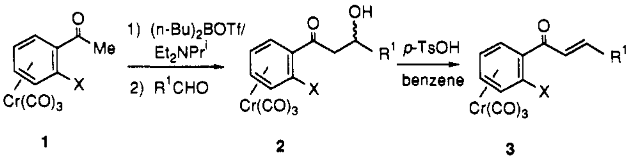
The conjugate addition of organocopper reagents to (*o*-alkoxyphenyl (*E*)-α,β-unsaturated enone)chromium complexes was observed to cause a dramatic reversal of diastereofacial selectivity, depending upon the organocopper reagents. The Gilman reagents attacked a *si* face at the β-position of the enone double bond in the (*o*-alkoxyphenyl α,β-enone)chromium complexes, while $RCu{\cdot}BF_3$ reagents attacked a *re* face at the β-carbon of the enone. The diastereoselective 1,4-conjugate addition to the (*o*-alkoxyphenyl enone)chromium complexes provides a new versatile method for remote stereocontrol at the 1,3,5-positions of the side chain in optically active forms. The conformations of *o*-methoxy complex **3** (X = OMe, R^1 = Me) and *o*-methyl complex **3** (X = Me, R^1 = Me) are different with respect to the benzylic carbonyl oxygen.

Introduction

One of the most exciting challenges in synthetic methodology is control of the stereochemistry in conformationally flexible 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 diastereoselection between adjacent carbon atoms (1,2-relationships).[1] However, general approaches to the stereoselective construction of remote chiral relationships in acyclic systems are few and have still been a challenging problem in organic synthesis. The conjugate addition of organocopper reagents to α,β-unsaturated enones and enoates is now a fundamental tool in carbon–carbon bond-forming processes.[2] Interest in these reactions has recently extended in the direction of stereoselectivity and the related subject of reaction mechanism. Accordingly, asymmetric versions have attracted widespread attention during the last few years, and valuable chiral auxiliary compounds have been developed for the highly asymmetric 1,4-addition reactions.[3]

(η^6-Arene)chromium complexes can exist in two enantiomeric forms when the phenyl ring is substituted with different substituents at the ortho or meta positions. Some of these chromium complexes could be easily obtained in the optically active forms via recrystallization[4] or column chromatography[5,6] of suitable diastereomers prepared by reaction with optically active resolution reagents. (η^6-Arene)chromium complexes have some characteristic properties due to the electronic effects and steric bulkiness of the $Cr(CO)_3$ group, and significant applications in organic synthesis have been developed.[7] Furthermore, the benzylic carbonyl group of the (*o*-alkoxyphenyl alkyl ketone)chromium complexes can be caused to react stereoselectively with nucleophiles such as alkyllithiums or hydride reagents to produce predominantly one diastereomeric (benzyl alcohol)chromium complex.[8] In addition, the resulting benzylic hydroxy or acetoxy groups of the chromium complexes can be substituted by some carbon nucleophiles in the presence of Lewis acids with stereochemical retention.[9] Therefore, our strategy of remote stereocontrol is based upon diastereoselective (or enan-

Scheme I. Preparation of (*o*-Substituted-phenyl (*E*)-enone)chromium Complexes



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[§] Rigaku Corp.

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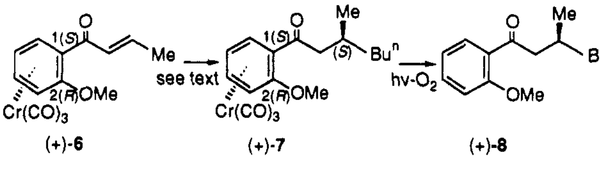
Scheme II



Scheme III

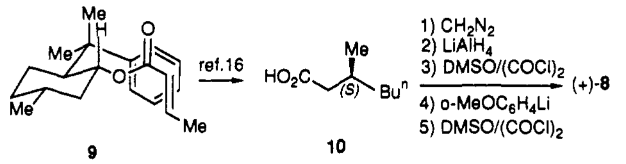
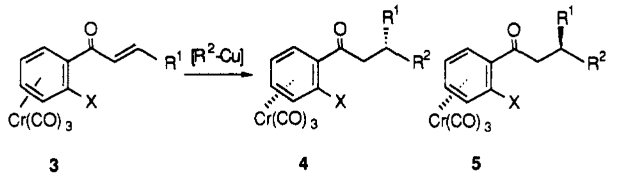


Table I. 1,4-Addition of Organocopper Reagents to (*E*)-Enone Complex 3



entry no.	complex	[R^2-Cu] reagent	4:5	yield, %
1	X = OMe, R^1 = Me	$Bu^n{}_2CuLi$	76:24	98
2	X = OMe, R^1 = Me	$Bu^nCu\cdot BF_3$	8:92	96
3	X = OMe, R^1 = Me	$Bu^n{}_2CuCNLi_2$	80:20	98
4	X = OMe, R^1 = Me	$Bu^nCuPBu_3\cdot BF_3$	50:50	97
5	X = OMe, R^1 = Me	$Bu^n{}_2CuLi/Me_3SiCl$	82:18	30[a]
6	X = OMe, R^1 = Bu^n	$MeCu\cdot BF_3$	10:90	88
7	X = OPr^i, R^1 = Me	$Bu^n{}_2CuLi$	92:8	93
8	X = OPr^i, R^1 = Me	$Bu^nCu\cdot BF_3$	48:52	94
9	X = Me, R^1 = Me	$Bu^n{}_2CuLi$	20:80	98
10	X = Me, R^1 = Me	$Bu^nCu\cdot BF_3$	3:97	85

[a] The major product is the recovered starting material (used with 5 equiv of Me_3SiCl according to the reported procedure[13]).

tioselective) synthesis of the chromium complexes of the *o*-alkoxyphenyl ketone compounds possessing the chiral center at the remote position of side chain. We report herein the diastereoselective 1,4-conjugate additions of organocopper reagents to (*o*-substituted phenyl (*E*)-enone)chromium complexes and a new approach to remote chiral induction utilizing (η^6-arene)chromium complexes as temporary templates to relay stereochemical information into conformationally flexible molecules.[10]

Results and Discussion

The requisite (*E*)-enone complexes 3 were easily accessible from the aldol condensation products[11] 2 of (*o*-substituted acetophenone)$Cr(CO)_3$ by dehydration with *p*-TsOH in refluxing benzene (Scheme I). The double-bond geometry of the product 3 was assigned as the (*E*)-enone on the basis of the observed coupling constant between the olefinic protons; *J* = 16.0 Hz for the complex 3 (R^1 = Me, X = OMe).

Reaction of the racemic ((*E*)-enone)chromium complex 3 (R^1 = Me, X = OMe) with $Bu^n{}_2CuLi$ in ether at -78 °C for 1 h gave a diastereomeric mixture of the 1,4-addition products of the Ar(1*S**,2*R**),3′(*R**) complex[12] 4 (R^1 = Me, R^2 = Bu^n, X - OMe) and Ar(1*S**,2*R**),3′(*S**) complex[12] 5 (R^1 = Me, R^2 = Bu^n, X = OMe) in a ratio of 76:24. The other reaction results are shown in Table I. Addition[13] of Me_3SiCl to the reaction mixture enhanced formation of the complex 4 slightly, but the yield of the addition products was low with recovery of the starting material (entry 5). On the other hand, $Bu^nCu\cdot BF_3$ reagent[14] afforded predominantly the corresponding diastereoisomeric 1,4-addition product 5 (X = OMe, R^1 = Me, R^2 = Bu^n) in a ratio of 92:8 (entry 2). The relative stereochemistry between the newly created stereogenic center and the $Cr(CO)_3$-complexed arene ring of the addition product 5 (R^1 = Me, R^2 = Bu^n, X = OMe) was determined as the Ar(1*S**,2*R**),3′(*S**) configuration by a comparison of optical rotation value as follows (Schemes II and III). Reaction of the Ar(1*S*,2*R*)-(+)-(*o*-methoxyphenyl (*E*)-1-propenyl ketone)chromium complex 6, derived from (*S*)-(+)-(*o*-methoxyacetophenone)chromium[15] ($[\alpha]_D^{25}$ = +464°, $CHCl_3$, *c* = 1.0) and propionaldehyde according to the procedure of Scheme I, with $Bu^nCu\cdot BF_3$ in either at -78 °C produced predominantly the 1,4-addition product 7 ($[\alpha]_D$ = +274°, $CHCl_3$) which was decomposed by an exposure to sunlight to give *o*-methoxyphenyl 2-methylhexyl ketone (*8*) with a positive sign of optical rotation ($[\alpha]_D$ = +19.4°, $CHCl_3$, *c* = 0.54). Meanwhile, an (*E*)-crotonic ester of (-)-8-phenylmenthol 9 derived from (+)-pulegone was converted to (-)-3-methylheptanoic acid (10) with the *S* configuration according to the literature method.[16] The compound 10 gave (+)-(*S*)-8 ($[\alpha]_D$ = +20.0°, $CHCl_3$, *c* = 0.65) by reaction sequences as shown in Scheme III. Therefore, the absolute configuration of the 1,4-addition product 7 obtained by reaction of Ar-(1*S*,2*R*)-enone complex 6 with $Bu^nCu\cdot BF_3$ possesses the *S* configuration at the newly created chiral center at the side chain. While the diastereoselectivity was low in the reaction of $Bu^n{}_2CuLi$ with the *o*-methoxy complex (entry 1), use of the corresponding sterically more bulky *o*-isopropoxy-substituted complex resulted in a marked increase in the selectivity under the same reaction conditions (entry 7). In addition, an alternation of R^1 and R^2 illustrates the possibility of directing the developing configuration at the C(*β*)-position as follows. Whereas reaction of $Bu^nCu\cdot BF_3$ with the butenone complex 3 (R^1 = Me, X = OMe) afforded predominantly the Ar(1*S**,2*R**),(*S**) complex 5 (R^1 = Me, R^2 = Bu^n, X = OMe) (entry 2), its epimeric Ar-(1*S**,2*R**),(*R**) complex 5 (R^1 = Bu^n, R^2 = Me, X = OMe)

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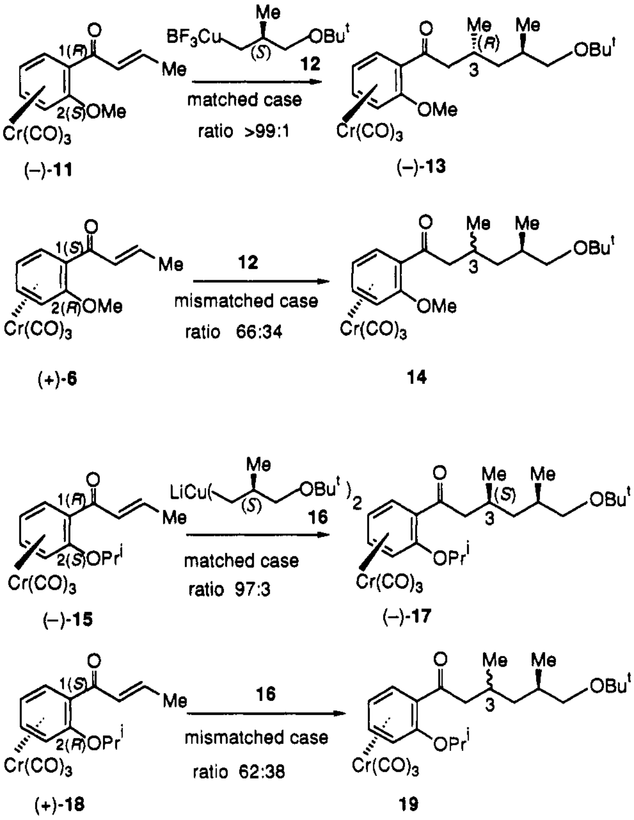
(15) Optically active (*o*-methoxyacetophenone)$Cr(CO)_3$ was easily prepared from optically active (*o*-methoxybenzaldehyde)$Cr(CO)_3$ by reaction of MeLi, followed by oxidation[21] of the benzylic hydroxy group with DMSO/Ac_2O. Optically active (*o*-methoxybenzaldehyde)$Cr(CO)_3$ was obtained by a resolution of diastereomers derived from the DL complex and L-valinol with column chromatography.[6]

(16) Oppolzer, W.; Loher, H. *Helv. Chim. Acta* **1981**, *64*, 2808.

Scheme IV. Double Stereoselection of 1,4-Conjugate Addition of Optically Active Organocopper Reagents with Chiral Complexes

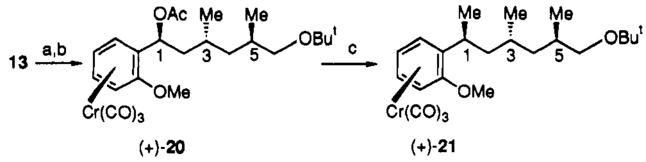


was formed by the addition of MeCu·BF$_3$ to the heptenone complex **3** (R^1 = Bu^n, X = OMe) (entry 6).

In general, Gilman reagents produced predominantly **4** in the 1,4-addition reaction to the *o*-alkoxy-substituted enone complexes, while RCu·BF$_3$ reagents gave mainly complexes **5**. With the *o*-isopropoxy-substituted complex, the diastereoselectivity in the conjugate addition with the Gilman reagents was superior than that of the *o*-methoxy-substituted complex due to the steric effect (Table 1, entry 7). Instead of the *o*-alkoxy substituents, the (*o*-methyl-substituted (*E*)-enone)chromium complex gave predominantly the Ar(1*S**,2*R**),(*S**) 1,4-addition complex **5** (R^1 = Me, R^2 = Bu^m, X = Me) by reactions with both Bu^n_2CuLi and BuCu·BF$_3$ reagents (entries 9 and 10). The stereochemistry at the newly created position was determined by a comparison of optical rotation values of the decomplexed compound of the 1,4-addition product derived from an optically active *o*-methyl-substituted complex and the corresponding authentic compound prepared from **10**, according to the same reaction sequences in the *o*-methoxy compound as mentioned above.

The diastereoselective 1,4-addition reactions of the organocopper reagents with the (*o*-alkoxyphenyl α,β-unsaturated enone)chromium complexes can be applied for 1,3,5-stereocontrol at the side chain in optically active forms as follows. Reaction of the (−)-Ar(1*R*,2*S*)-*o*-methoxy chromium complex **11** ($[\alpha]_D$ = −454°, CHCl$_3$, *c* = 0.07) with ((*S*)-2-methyl-3-*tert*-butoxypropyl)copper–boron trifluoride[17] (**12**) gave exclusively the addition product (−)-**13** with an *R* configuration at the C-3 position ($[\alpha]_D$ = −197°, CHCl$_3$, *c* = 0.095) in a ratio of >99:1 (Scheme IV). The newly created stereochemistry of the *R* configuration at the C-3 position of **13** can be assigned from the analogous reaction results with $Bu^nCu \cdot BF_3$ reagents. On the other hand, the corresponding (+)-Ar(1*S*,2*R*)-chromium complex **6** was reacted with the same *S* copper reagent **12** to give a diastereomeric mixture of **14** in the ratio 66:34. These results show that the former reaction is a matched case, while the latter combination is a mismatched pair. Similarly, (−)-Ar(1*R*,2*S*)-(*o*-isopropoxyphenyl-(*E*)-2-buten-1-one)Cr(CO)$_3$ (**15**) ($[\alpha]_D$ = −507°, CHCl$_3$, *c* = 0.09) was reacted with bis[(*S*)-2-methyl-3-butoxypropyl]cuprate (**16**) to provide the 3-(*S*) addition product **17** with >97% selectivity, but the corresponding (+)-Ar(1*S*,2*R*) chromium complex **18** afforded mismatched selectivity in the ratio 62:38 with the same (*S*)-diorganocuprate **16**. The addition product **13** can be easily converted to the 1,3-anti,3,5-anti trimethyl chromium complex (+)-**21** in 43% overall yield without any detectable epimers by the following method (Scheme V). A stereoselective reduction[8,9] of the benzylic ketone of the complex **13** followed by acetylation gave the (+)-1,3-anti chromium complex **20** in 81% yield. Treatment of complex **20** with Me$_3$Al produced the (+)-1,3-anti,3,5-anti trimethyl-substituted complex **21** with stereochemical retention[9] at the benzylic position. The results of such reaction sequences are useful tools for the stereoselective construction of a 1,3,5-pattern of alkyl substituents.

Scheme V. Stereoselective Synthesis of an Optically Active 1,3,5-Trimethyl Compound[a]



[a] (a) LiAlH$_4$; (b) Ac$_2$O/pyr (81% from **13**); (c) Me$_3$Al/CH$_2$Cl$_2$ (87%).

The observed π-face discrimination of the conjugate addition of the organocopper reagents would contribute to the conformations of the (*o*-substituted phenyl (*E*)-enone)chromium complexes. The X-ray crystallographic structures of [*o*-methoxyphenyl (*E*)-propenyl ketone]Cr(CO)$_3$ (**3**, X = OMe, R^1 = Me) and [*o*-methylphenyl (*E*)-propenyl ketone]Cr(CO)$_3$ (**3**, X = Me, R^1 = Me) are illustrated in Figures 1 and 2. The conformation of the benzylic carbonyl group of the *o*-methoxy-substituted complex exists in an anti form (OR/C=O) and s-cisoid ($C{=}O/C_\alpha{=}C_\beta$) structure, while the corresponding *o*-methyl-substituted complex is featured as a syn disposed (Me/C=C), s-cisoid conformation. The preferred anti disposed conformation of the *o*-methoxy complex is caused by an electronic effect of the OMe group and is consistent with those of the (*o*-methoxyacetophenone)- and (*o*-methoxypropiophenone)chromium complexes.[12c,18] The syn form in the *o*-methyl-substituted complex would contribute to a steric hindrance between the *o*-methyl and the propenyl groups. Indeed, the (*o*-methylacetophenone)chromium complex exists in a syn-disposed conformation, while the *o*-methylbenzaldehyde)chromium complex adopts the anti conformation.[12c] These conformations in solution are supported by the sign of the optical rotation of (*o*-substituted-phenyl ketone)chromium complexes. Ar(1*S*,2*R*)-[*o*-methoxyphenyl (*E*)-propenyl ke-

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[17] Optically active ((*S*)-2-methyl-3-*tert*-butoxypropyl)copper–boron trifluoride (**16**) was prepared via (*S*)-(+)-3-butoxy-2-methyl-1-bromopropane from methyl (*S*)-(+)-3-hydroxyisobutyrate: (a) Cohen, N. C.; Eichel, W. F.; Lopresti, R. J.; Neukom, C.; Saucy, G. *J. Org. Chem.* **1976**, *41*, 3505. (b) Nagaoka, H.; Kishi, Y. *Tetrahedron* **1981**, *37*, 3873 and references cited therein.

[18] Besançon, J.; Tirouflet, *J. Bull. Soc. Chim. Fr.* **1969**, 861. Besançon, J.; Tainturier, G.; Tirouflet, J. *Bull. Soc. Chim. Fr.* **1971**, 1804.

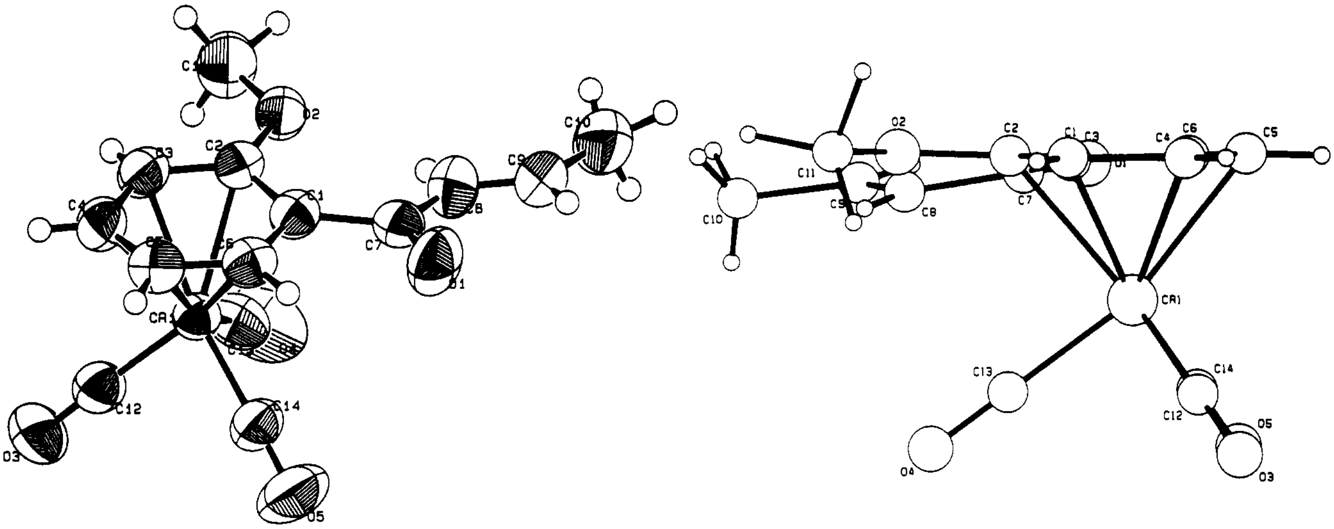

Figure 1. Molecular structure of (*E*)-(*o*-MeO-$C_6H_4COCH{=}CHMe)Cr(CO)_3$.

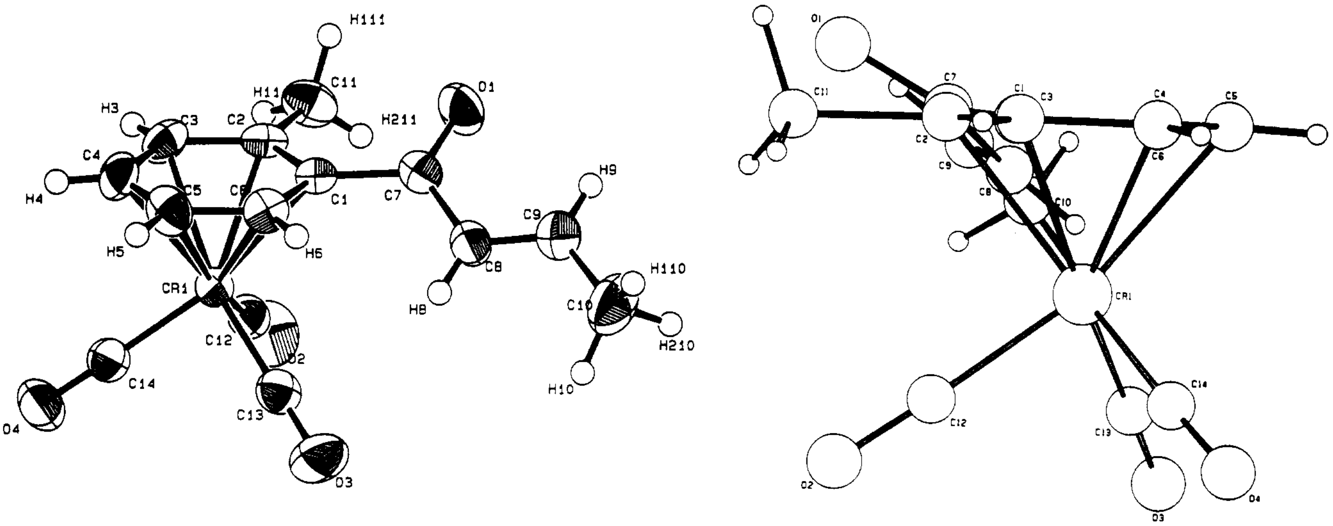

Figure 2. Molecular structure of (*E*)-(*o*-Me-$C_6H_4COCH{=}CHMe)Cr(CO)_3$.

tone]$Cr(CO)_3$ (**6**) shows a positive sign ($[\alpha]_D = +436°$, $CHCl_3$) associated with the anti disposed conformation, while the corresponding *o*-methyl-substituted complex with the same configuration, Ar(1*S*,2*R*), has a negative rotation ($[\alpha]_D = -92°$, $CHCl_3$) with the syn form.[12c] Interestingly, addition of 1 drop of boron trifluoride etherate to (−)-Ar(1*S*,2*R*)-[*o*-methylphenyl (*E*)-propenyl ketone]$Cr(CO)_3$ in chloroform solution effected a change to a positive optical rotation ($[\alpha]_D = +96°$), which might suggest that the syn-disposed conformation was converted to the anti form. However, no change of the optical rotation in the *o*-methoxy complex was observed by addition of boron trifluoride etherate.

The electron-donating methoxyl oxygen and its ipso carbon (C2) atoms in the plane of the arene are bent away from the $Cr(CO)_3$ group, while the electron-withdrawing carbonyl carbon (C7) and its ipso carbon (C1) atoms are bent toward the chromium group (Table V). These results are consistent with the previously reported results.[19] Similarly, the benzylic carbon and its ipso carbon atoms in the *o*-methyl complex are bent slightly toward the chromium group. The magnitude of the planar distortion in the *o*-Me complex is smaller than that of the *o*-MeO chromium complex. The benzylic carbonyl oxygen atom in the *o*-Me-substituted complexes is distal with respect to the chromium atom, and the double bonds of enone moieties in both complexes are proximal with respect to the $Cr(CO)_3$. The torsion angles O(1)–C(7)···C(1)–C(2), O(1)–C(7)···C(8)–C(9), and C(1)–C(7)···C(8)–C(9) in the *o*-Me complex are 30.3, 10.9, and −166.6°, respectively. With the *o*-MeO complex, the corresponding angles are 172.8, −11.2, and 167.2°. The deviation of the benzylic carbonyl from the arene plane in the *o*-Me complex is larger than that of the *o*-MeO complex. The dihedral angles between the arene plane and the enone plane are 8.74° in the *o*-MeO complex and 31.01° in the *o*-Me complex, respectively. Since the enone moiety in the *o*-methoxy complex is close to coplanar with the arene (Figure 1), the Gilman reagents attack the *si* face at the C_β position in the s-cisoid and anti-disposed conformation from exo side, giving the addition product **4**. With the *o*-Me complex, the C_β carbon and methyl group of the enone moiety are proximal to the $Cr(CO)_3$ group and one face of the double bond is partially blocked by the *o*-methyl substituent. Therefore, the Gilman reagents attack the *re* face at the β-position in the s-cisoid and syn-disposed form, giving the complex **5** as the major product. On the

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(19) Hunter, A. D.; Shilliday, L.; Scott-Furey, W.; Zaworotko, M. J. *Organometallics* **1992**, *11*, 1550 and references cited therein.

(20) We are indebted to a reviewer for the useful suggestion of transition-state structure in conjugated addition for an explanation of the diastereoselectivity.

(21) Levine, S. G.; Gopalakrishnan, B. *Tetrahedron Lett.* **1982**, *23*, 1239.

Table II. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compd	3 (X = OMe, R^1 = Me)	3 (X = Me, R^1 = Me)
empirical formula	$C_{14}H_{12}O_5Cr$	$C_{14}H_{12}O_4Cr$
fw	312.24	296.24
cryst color, habit	orange, prism	orange, plate
cryst dimens, mm	0.4 × 0.1 × 0.1	0.5 × 0.2 × 0.1
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
cell constants^a		
a, Å	10.863 (3)	7.804 (2)
b, Å	11.679 (4)	23.502 (4)
c, Å	11.250 (2)	8.120 (3)
β, deg	93.94 (2)	117.75 (2)
cell vol, Å^3	1424.5 (6)	1318.0 (7)
F(000)	640	608
Z	4	4
D_{calc}, g cm^{-3}	1.456	1.493
scan type	$\omega/2\theta$	$\omega/2\theta$
scan rate, deg/min in ω	8	12
scan width, deg	1.37 + 0.3 tan θ	1.26 + 0.3 tan θ
radiation	Cu Kα	Cu Kα
diffractometer	Rigaku AFC5R	Rigaku AFC5R
temp, °C	23	23
2θ range, deg	2–120	2–120
no. of unique rflns	2241	2030
no. of rflns obsd^b	1630	1596
R_{int}	0.039	0.021
transmissn range	0.82–1.35	0.82–1.32
structure determination	heavy-atom method	heavy-atom method
refinement	full-matrix least squares	full-matrix least squares
function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
weight	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
R	0.048	0.040
R_w	0.061	0.051
GOF	1.40	1.20
max shift/error	0.51	0.38
max peak in diff map, e/Å^3	0.23	0.27
min peak in diff map, e/Å^3	−0.37	−0.31

^{a} Least-squares refinement of $((\sin\theta)/\lambda)^2$ for 24 reflections ($\theta >$ 30.25). ^{b} $I > 1.5\sigma(I)$. Corrections: Lorentz–polarization and absorption (using program DIFABS: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158–166).

other hand, the reversal of diastereoselectivity in the reaction of RCu·BF_3 with the *o*-OMe complex would contribute to a change of the conformation. An alternative s-transoid and anti-disposed form could be postulated due to the steric effect of the coordination of the benzylic ketone with the Lewis acid, in which the *re* face at the C_β position is attacked, giving the complexes **5**. The diastereoselectivity in the reaction of the *o*-Me complex with RCu·BF_3 is curious. At this point, it cannot be determined whether the conformation (syn and s-cisoid) in the *o*-Me complex is unchanged or changed to the anti and s-transoid form as mentioned above, where both transition states produced the same complex **5**. Further investigations should be undertaken in order to find an explanation for a relationship of selectivities and conformations.

Experimental Section

All manipulations involving organometallics were carried out under an atmosphere of nitrogen or argon and using inert-gas/vacuum double-manifold techniques. $Cr(CO)_6$ was obtained from Strem Chemicals and used as received. Ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl immediately before use, and methylene chloride was distilled from P_2O_5. Diisopropylethylamine was distilled from CaH_2. Dibutylboron triflate (1.0 M in CH_2Cl_2) was purchased from Aldrich Chemical Co., Inc. ^1H NMR spectra were measured on Hitachi R-90 and JEOL GX-400 spectrometers. Chemical shifts are recorded in parts per million 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 JEOL D-300 and JEOL AX-500 spectrometers. Elemental analysis was performed on a Perkin-Elmer Model 240 elemental analyzer. All melting points were determined on a Yanagimoto MPJ-2 micro melting point apparatus and are uncorrected. Optical rotations were obtained on a JASCO DIP-370 automatic polarimeter at wavelength 589 nm (sodium D line) using a 1.0-decimeter cell with a total volume of 3 mL.

Preparation of [*o*-methoxyphenyl (*E*)-propenyl ketone]Cr(CO)$_3$ (3, X = OMe, R^1 = Me). A typical procedure for a dehydration of the aldol condensation products to give the (*E*)-enone complex is as follows. A solution of the aldol condensation product **2** (R^1 = Me: 200 mg, 0.6 mmol) and a catalytic amount of *p*-toluenesulfonic acid in benzene (5 mL) was refluxed for 30 min under nitrogen. The reaction mixture was poured into saturated aqueous $NaHCO_3$ and extracted with benzene. The extract was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on silica gel using hexane/ether as eluent to give the (*E*)-enone complex **3 (X = OMe, R^1 = Me)** as red crystals: yield 185 mg (93%); mp 78 °C; IR ($CHCl_3$) 1970, 1890, 1660 cm^{-1}; ^1H NMR

Table III. Atomic Coordinates and Equivalent Isotropic Temperature Factors (Å^2)

atom	*x*	*y*	*z*	B_{eq}^{a}	atom	*x*	*y*	*z*	B_{eq}^{a}
				(*E*)-(*o*-MeO-C_6H_4COCH=CHMe)Cr(CO)$_3$					
Cr	0.41445 (6)	0.19375 (6)	0.10629 (6)	3.99 (3)	C(5)	0.5869 (4)	0.2063 (4)	0.0129 (4)	5.0 (2)
O(1)	0.3222 (3)	0.3991 (3)	−0.1653 (3)	7.2 (2)	C(6)	0.4979 (4)	0.2736 (4)	−0.0432 (4)	4.7 (2)
O(2)	0.4153 (3)	0.4658 (3)	0.1928 (3)	5.4 (2)	C(7)	0.3313 (4)	0.4189 (4)	−0.0591 (4)	4.9 (2)
O(3)	0.4454 (4)	−0.0297 (3)	0.2314 (4)	7.7 (2)	C(8)	0.2478 (5)	0.4996 (5)	−0.0064 (5)	5.7 (2)
O(4)	0.2035 (4)	0.2462 (4)	0.2528 (4)	9.5 (3)	C(9)	0.1747 (5)	0.5663 (5)	−0.0693 (5)	6.1 (3)
O(5)	0.2457 (4)	0.0706 (4)	−0.0708 (4)	9.1 (2)	C(10)	0.0882 (7)	0.6528 (7)	−0.0253 (8)	8.2 (4)
C(1)	0.4337 (4)	0.3598 (4)	0.0155 (4)	4.3 (2)	C(11)	0.4465 (7)	0.4852 (6)	0.3174 (5)	7.4 (3)
C(2)	0.4694 (4)	0.3788 (4)	0.1369 (4)	4.4 (2)	C(12)	0.4346 (4)	0.0570 (4)	0.1843 (4)	5.2 (2)
C(3)	0.5570 (4)	0.3064 (4)	0.1963 (4)	4.8 (2)	C(13)	0.2848 (5)	0.2261 (4)	0.1968 (5)	5.7 (3)
C(4)	0.6148 (4)	0.2191 (4)	0.1360 (4)	5.0 (2)	C(14)	0.3109 (4)	0.1192 (4)	−0.0026 (4)	5.4 (2)
				(*E*)-(*o*-MeC_6H_4COCH=CHMe)Cr(CO)$_3$					
Cr	0.04195 (8)	0.14108 (2)	0.21625 (8)	2.50 (3)	C(6)	−0.1097 (7)	0.1392 (2)	−0.0886 (5)	3.0 (1)
O(1)	−0.5840 (4)	0.1426 (1)	−0.1245 (5)	4.6 (1)	C(7)	−0.4319 (6)	0.1191 (2)	−0.1013 (5)	3.2 (1)
O(2)	−0.0350 (5)	0.1337 (2)	0.5427 (4)	5.4 (2)	C(8)	−0.4306 (6)	0.0591 (2)	−0.1506 (6)	3.6 (2)
O(3)	0.0634 (5)	0.0142 (1)	0.2223 (5)	5.8 (2)	C(9)	−0.5896 (7)	0.0301 (2)	−0.2474 (6)	4.2 (2)
O(4)	0.4680 (4)	0.1452 (1)	0.4743 (4)	4.5 (1)	C(10)	−0.599 (1)	−0.0302 (2)	−0.3044 (9)	5.7 (2)
C(1)	−0.2479 (5)	0.1526 (1)	−0.0282 (5)	2.5 (1)	C(11)	−0.3456 (7)	0.2173 (2)	0.1702 (7)	4.1 (2)
C(2)	−0.2117 (5)	0.1996 (2)	0.0934 (5)	2.9 (1)	C(12)	−0.0040 (6)	0.1363 (2)	0.4184 (5)	3.3 (2)
C(3)	−0.0405 (6)	0.2312 (2)	0.1462 (6)	3.4 (2)	C(13)	0.0563 (6)	0.0634 (2)	0.2188 (5)	3.4 (2)
C(4)	0.0916 (6)	0.2168 (2)	0.0844 (6)	3.7 (2)	C(14)	0.3035 (6)	0.1432 (2)	0.3759 (5)	3.2 (1)
C(5)	0.0565 (6)	0.1706 (2)	−0.0365 (6)	3.7 (2)					

^{a} $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j$.

Table IV. Bond Distances (Å) and Selected Bond Angles (deg)

	(*E*)-(*o*-$MeOC_6H_4COCH{=}CHMe)Cr(CO)_3$		
Cr–C1	2.208 (5)	O4–C13	1.144 (6)
Cr–C2	2.262 (5)	O5–C14	1.158 (5)
Cr–C3	2.222 (5)	C1–C2	1.411 (6)
Cr–C4	2.200 (5)	C1–C6	1.414 (7)
Cr–C5	2.215 (5)	C1–C7	1.514 (6)
Cr–C6	2.175 (5)	C2–C3	1.407 (6)
Cr–C12	1.828 (5)	C3–C4	1.397 (7)
Cr–C13	1.834 (6)	C4–C5	1.406 (7)
Cr–C14	1.826 (5)	C5–C6	1.367 (7)
O1–C7	1.214 (5)	C7–C8	1.462 (7)
O2–C2	1.350 (5)	C8–C9	1.289 (7)
O2–C11	1.438 (6)	C9–C10	1.488 (9)
O3–C12	1.145 (6)		
Cr–C12–O3	178.5 (4)	O1–C7–C8	120.7 (4)
Cr–C13–O4	179.7 (5)	C1–C7–C8	121.5 (4)
Cr–C14–O5	179.1 (5)	C7–C8–C9	122.9 (5)
O2–C2–C1	118.0 (4)	C8–C9–C10	127.4 (6)
C2–C1–C7	127.4 (4)	C2–O2–C11	119.5 (4)
O1–C7–C1	117.8 (4)		
	(*E*)-(*o*-$MeC_6H_4COCH{=}CHMe)Cr(CO)_3$		
Cr–C1	2.225 (4)	O4–C14	1.155 (5)
Cr–C2	2.228 (4)	C1–C2	1.418 (5)
Cr–C3	2.209 (4)	C1–C6	1.413 (5)
Cr–C4	2.202 (4)	C1–C7	1.497 (5)
Cr–C5	2.219 (4)	C2–C3	1.409 (6)
Cr–C6	2.192 (4)	C2–C11	1.504 (6)
Cr–C12	1.840 (4)	C3–C4	1.382 (6)
Cr–C13	1.828 (4)	C4–C5	1.402 (6)
Cr–C14	1.840 (4)	C5–C6	1.377 (6)
O1–C7	1.217 (5)	C7–C8	1.467 (6)
O2–C12	1.143 (5)	C8–C9	1.311 (6)
O3–C13	1.159 (5)	C9–C10	1.480 (7)
Cr–C12–O2	179.0 (4)	O1–C7–C8	121.4 (4)
Cr–C13–O3	178.7 (4)	C1–C7–C8	119.1 (3)
Cr–C14–O4	178.8 (3)	C7–C8–C9	122.7 (4)
C1–C2–C11	123.5 (4)	C8–C9–C10	125.5 (5)
C2–C1–C7	121.9 (3)		
O1–C7–C1	119.5 (4)		

Table V. Least-Squares Planes

(*o*-$MeOC_6H_4COCH{=}CHMe)Cr(CO)_3$

atoms defining plane	dist, Å (esd)	additional atoms	dist, Å
	Plane 1		
C1	−0.0286 (0.0044)	Cr	−1.7146
C2	0.0293 (0.0044)	C12	−2.8275
C3	−0.0056 (0.0049)	C13	−2.7704
C4	−0.0263 (0.0049)	C14	−2.7691
C5	0.0285 (0.0051)	O2	0.0904
C6	0.0040 (0.0047)	C7	−0.1662
	Plane 2		
C2	0.0000		
O2	0.0000		
C11	0.0000		
	Plane 3		
C1	0.0024 (0.0044)		
C7	−0.0093 (0.0047)		
C8	0.0040 (0.0055)		
O1	0.0023 (0.0038)		
	Plane 4		
C7	0.0042 (0.0047)		
C8	−0.0050 (0.0054)		
C9	−0.0063 (0.0054)		
C10	0.0112 (0.0075)		

Dihedral Angles between Least-Squares Planes, deg

plane 2/plane 1	177.32	plane 3/plane 1	8.74
plane 3/plane 2	168.59	plane 4/plane 1	13.92
plane 4/plane 1	13.92	plane 4/plane 2	164.74
plane 4/plane 3	11.83		

(*o*-$MeC_6H_4COCH{=}CHMe)Cr(CO)_3$

atoms defining plane	dist, Å (esd)	additional atoms	dist, Å
	Plane 1		
C1	−0.0030 (0.0032)	Cr	−1.7130
C2	0.0023 (0.0033)	C12	−2.7898
C3	−0.0034 (0.0039)	C13	−2.8362
C4	0.0051 (0.0041)	C14	−2.7672
C5	−0.0064 (0.0041)	C7	0.0880
C6	0.0050 (0.0036)	C11	−0.0235
	Plane 2		
C1	0.0032 (0.0038)		
C7	−0.0133 (0.0042)		
C8	0.0053 (0.0048)		
O1	0.0041 (0.0038)		
	Plane 3		
C7	0.0032 (0.0046)		
C8	−0.0037 (0.0052)		
C9	−0.0053 (0.0057)		
C10	0.0091 (0.0077)		

Dihedral Angles between Least-Squares Planes, deg

plane 2/plane 1	31.01	plane 3/plane 1	141.25
plane 3/plane 2	167.76		

($CDCl_3$) δ 1.95 (3 H, dd, J = (6, 1), 3.80 (3 H, s), 4.90 (1 H, t, J = 7), 4.95 (1 H, d, J = 7), 5.70 (1 H, t, J = 7), 6.08 (1 H, dd, J = 1, 7), 6.75 (1 H, dd, J = 1, 16), 7.00 (H, dq, J = 16, 7). Anal. Calcd for $C_{14}H_{12}O_5Cr$: C, 53.85; H, 3.89. Found: C, 53.84; H, 3.89. Similarly, the corresponding optically active chromium complexes were obtained under the same conditions. Ar(1*R*,2*S*)-**15**: mp 68 °C; $[\alpha]_D^{20}$ = −454.0° ($CHCl_3$, *c* = 0.07). Ar(1*S*,2*R*)-**6**: mp 68 °C; $[\alpha]_D^{20}$ = +446.7° ($CHCl_3$, *c* = 0.07).

3 (X = Me, R^1 = Me): mp 102 °C; IR ($CHCl_3$) 1970, 1890, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.95 (3 H, dd, J = 7, 1), 2.30 (3 H, s), 5.00 (1 H, d, J = 7), 5.08 (1 H, t, J = 7), 5.52 (1 H, t, J = 7), 5.74 (1 H, d, J = 7), 6.50 (1 H, dd, J = 16, 1), 7.05 (1 H, dq, J = 16, 7). Anal. Calcd for $C_{14}H_{14}O_4Cr$: C, 56.76; H, 4.08. Found: C, 56.68; H, 4.08. Optically active complex Ar(1*S*,2*R*)-**3** (X = Me, R^1 = Me): mp 95 °C; $[\alpha]_D^{25}$; $[\alpha]_D^{25}$ = −91.9° ($CHCl_3$, *c* = 0.175).

3 (X = OPr^i, R^1 = Me): mp 67 °C; IR ($CHCl_3$) 1970, 1890, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (3 H, d, J = 7), 1.45 (3 H, d, J = 7), 1.95 (3 H, d, J = 6), 4.40 (1 H, dq, J = 7, 6), 4.90 (1 H, t, J = 7), 5.05 (1 H, d, J = 7), 5.70 (1 H, t, J = 7), 6.13 (1 H, d, J = 7), 6.85 (1 H, d, J = 16), 7.02 (1 H, dq, J = 16, 7). Anal. Calcd for $C_{16}H_{16}O_5Cr$: C, 56.47; H, 4.74. Found: C, 56.47; H, 4.74. Optically active complexes: Ar(1*R*,2*S*)-**19**, mp 93 °C, $[\alpha]_D^{25}$ = −506.9° ($CHCl_3$), *c* = 0.09); Ar(1*S*,2*R*)-**22**, mp 91 °C, $[\alpha]_D^{25}$ = +496.3° ($CHCl_3$, *c* = 0.09).

3 (X = OMe, R^1 = Bu^n): mp 68 °C; IR ($CHCl_3$) 1970, 1900, 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (3 H, t, J = 7), 0.95–2.40 (6 H, m), 3.80 (3 H, s), 4.89 (1 H, t, J = 7), 4.95 (1 H, d, J = 7), 5.70 (1 H, t, J = 7), 6.10 (1 H, d, J = 7), 6.72 (1 H, d, J = 16), 7.00 (1 H, dq, J = 16, 7). Anal. Calcd for $C_{17}H_{18}O_5Cr$: C, 57.63; H, 5.12. Found: C, 57.50; H, 5.13.

Preparation of 4 (X = OMe, R^1 = Me, R^2 = Bu^n): 1,4-Addition Reaction with Gilman Reagent. A typical procedure for 1,4-conjugate addition of Gilman reagents to the (*E*)-enone complexes is as follows. To a suspended mixture of CuI (76 mg, 0.4 mmol) in ether (2 mL) was added *n*-BuLi (0.5 mL, 1.6 M in hexane, 0.8 mmol) at −45 °C under argon, and the reaction mixture was stirred for 30 min. To the above black mixture was added a solution of the (*E*)-enone chromium complex **3** (X = OMe, R^1 = Me) (30 mg, 0.1 mmol) in ether (3 mL) at −78 °C; the mixture was stirred at −45 °C for 1 h. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ether. The extract was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on silica gel using ether/hexane as eluent to give a diastereomeric mixture of 1,4-addition products (34.5 mg, 97%) as red crystals. The ratio of diastereomers was determined by the area of doublet methyl (major product δ 1.08; minor product, δ 1.03) in the 400-MHz ^1H NMR of a C_6D_6 solution. Recrystallization of the crude compound from ether/hexane gave pure addition product

4 (X = OMe, R^1 = Me,R^2 = Bu^n): mp 65 °C; IR ($CHCl_3$) 1960, 1880, 1670 cm^{-1}; ^1H NMR (C_6D_6) δ 0.88 (3 H, t, *J* = 6.7), 1.08 (3 H, d, *J* = 6.7), 1.20–1.47 (6 H, m), 2.30–2.38 (1 H, m), 2.76 (1 H, dq, *J* = 7.1, 5.4), 2.84 (1 H, dq, *J* = 7.1, 6.5), 2.87 (3 H, s), 3.84 (1 H, d, *J* = 6.7), 3.95 (1 H, t, *J* = 6.7), 4.77 (1 H, dt, *J* = 6.7, 1.3), 6.04 (1 H, dd, *J* = 6.7, 1.5). Anal. Calcd for $C_{18}H_{22}O_5Cr$: C, 58.37; H, 5.99. Found: C, 58.24; H, 6.02.

Preparation of 5 (X = OMe, R^1 = Me, R^2 = Bu^n): 1,4-Addition Reaction with RCu·BF_3. A typical procedure of 1,4-conjugate addition with RCu·BF_3 reagents is as follows. To a suspended mixture of CuI (244 mg, 1.26 mmol) in ether (8 mL) was added Bu^nLi (0.8 mL, 1.6 M in hexane, 1.28 mmol) at −45 °C under argon, and the mixture was stirred for 30 min. Boron trifluoride etherate (0.16 mL, 1.28 mmol) was injected into the above mixture at −78 °C. After 5 min, a solution of (*E*)-enone chromium complex 3 (X = OMe, R^1 = Me) (100 mg, 0.32 mmol) in ether (2 mL) was added at the same temperature, and the reaction mixture was stirred for 1 h. The mixture was quenched with saturated aqueous NH_4Cl and extracted with ether. The extract was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on silica gel to afford 110 mg (93%) of a diastereomeric mixture of 1,4-addition products. The ratio was determined by the above-mentioned procedure. Recrystallization from ether/hexane gave pure **5 (X = OMe, R^1 = Me, R^2 = Bu^n)**: mp 60 °C; IR ($CHCl_3$) 1970, 1880, 1670 cm^{-1}; ^1H NMR (C_6D_6) δ 0.92 (3 H, d, *J* = 6.7), 1.02 (3 H, d, *J* = 6.7), 1.22–1.50 (6 H, m), 2.32–2.42 (1 H, m), 2.63 (1 H, dd, *J* = 6.7, 17.1), 2.87 (3 H, s), 2.98 (1 H, dd, *J* = 6.7, 16.5), 3.84 (1 H, d, *J* = 7.4), 3.96 (1 H, t, *J* = 6.2), 4.77 (1 H, t, *J* = 6.2), 6.04 (1 H, d, *J* = 6.7). Anal. Calcd for $C_{18}H_{22}O_5Cr$: C, 58.37; H, 5.99. Found: C, 58.18; H, 5.99. Optically active (+)-7 was obtained from (+)-enone 6 under the same conditions: $[\alpha]_D^{20}$ = +278.5° ($CHCl_3$, *c* = 0.57).

1,4-Conjugate addition of Gilman reagents and RCu·BF_3 reagents to enone complexes was carried out by the same procedure. The physical data of some representative compounds are as follows.

4 (X = OPr^i, R^1 = Me, R^2 = Bu^n): IR ($CHCl_3$) 1970, 1880, 1665, 1440 cm^{-1}; ^1H NMR (C_6D_6) δ 0.73 (3 H, d, *J* = 6.5), 0.89 (3 H, t, *J* = 6.5), 1.08 (3 H, d, *J* = 6.7), 1.10 (3 H, d, *J* = 6.7), 1.18–1.41 (6 H, m), 2.30–2.40 (1 H, m), 2.82 (1 H, dd, *J* = 4.9, 17.1), 2.91 (1 H, dd, *J* = 8.5, 17.1), 3.67 (1 H, m), 3.92–3.97 (2 H, m), 4.83 (1 H, t, *J* = 6.1), 6.08 (1 H, d, *J* = 6.7); MS *m/e* 398 (M^+), 342 (M^+ − 2CO), 314 (M^+ − 3CO); high-resolution mass calcd for $C_{20}H_{26}O_5Cr$ 398.1186, found 398.1194.

5 (X = Me, R^1 = Me, R^2 = Bu^n): IR ($CHCl_3$) 1970, 1880, 1680, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (3 H, t, *J* = 6.7), 0.97 (3 H, d, *J* = 6.2), 1.23–1.33 (6 H, m), 2.10–2.18 (1 H, m), 2.38 (3 H, s), 2.59 (1 H, dd, *J* = 7.9, 16.5), 2.71 (1 H, dd, *J* = 5.5, 11.5), 5.03 (1 H, d, *J* = 6.2), 5.13 (1 H, t, *J* = 6.2), 5.61 (1 H, t, *J* = 6.2), 5.88 (1 H, d, *J* = 7.0); MS *m/e* 354 (M^+), 270 (M^+ − 3CO); high-resolution mass calcd for $C_{18}H_{22}O_4Cr$ 354.0965, found 354.0949.

Preparation of (+)-(*S*)-*o*-Methoxyphenyl 2-Methylhexyl Ketone (8). A solution of (+)-7 ($[\alpha]_D$ = +278.5°, $CHCl_3$) (56 mg, 0.15 mmol), which was prepared from Ar(1*S*,2*R*)-(+)-6 with $Bu^nCu·BF_3$ in ether (30 mL), was exposed to sunlight for 1 h until the solution was changed from red to colorless. The precipitate was filtered off and washed with ether. The ether was evaporated and purified by silica gel chromatography with hexane/ether to afford 8 (29 mg, 80%); ^1H NMR ($CDCl_3$) δ 0.85 (3 H, t, *J* = 7), 0.88 (3 H, d, *J* = 7), 1.10–1.35 (6 H, m), 1.80–2.20 (1 H, m), 2.65 (1 H, dd, *J* = 7, 16), 2.90 (1 H, dd, *J* = 6, 16), 3.82 (3 H, s), 6.80–7.01 (2 H, m), 7.26–7.60 (2 H, m); $[\alpha]_D^{22}$ = +19.4° (*c* = 0.54, $CHCl_3$). (*S*)-10 was converted to (+)-8 by the standard method.

(−)-Ar(1*R*,2*S*)-Tricarbonyl[*o*-methoxyphenyl 2(*R*),4-(*R*)-dimethyl-5-*tert*-butoxypentyl ketone]chromium (13). To a suspended mixture of CuI (76 mg, 0.4 mmol) in ether (2 mL) was added 0.37 mL of (2-methyl-3-*tert*-butoxypropyl)lithium (1.08 M in ether, 0.4 mmol), which was prepared from lithium and (*S*)-2-methyl-3-*tert*-butoxy-1-bromopropane, at −45 °C under argon. The reaction mixture was stirred for 30 min, and boron trifluoride etherate (0.05 mL, 0.4 mmol) was added to the above suspended mixture at −78 °C. A solution of (*E*)-enone complex 11 (30 mg, 0.01 mmol) in ether (2 mL) was added to the reaction mixture at −78 °C and stirred for 1 h. The mixture was quenched with saturated aqueous sodium thiosulfite and extracted with ether. The extract was washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel chromatography with ether/hexane to afford 13 (37 mg, 86%) as an orange oil: ^1H NMR ($CDCl_3$) δ 0.91 (3 H, d, *J* = 6.7), 0.94 (3 H, d, *J* = 6.7), 1.05–1.15 (1 H, m). 1.17 (9 H, s), 1.20–1.30 (1 H, m), 2.30–2.38 (1 H, m), 2.71 (1 H, dd, *J* = 6.7, 16.5), 2.88 (1 H, dd, *J* = 6.7, 17.1), 3.07 (1 H, dd, *J* = 7.3, 8.6), 3.17 (1 H, dd, *J* = 6.1, 8.5), 3.85 (3 H, s), 4.92 (1 H, t, *J* = 6.1), 5.00 (1 H, d, *J* = 6.7), 5.78 (1 H, t, *J* = 6.1), 6.22 (1 H, d, *J* = 6.7); IR ($CHCl_3$) 1975, 1890, 1660, 1460 cm^{-1}; MS *m/e* 442 (M^+), 358 (M^+ − 3CO); high-resolution mass calcd for $C_{22}H_{30}O_6Cr$ 442.1447. Found 442.1444; $[\alpha]_D^{18}$ = −197° (*c* = 0.1, $CHCl_3$).

(−)-Ar(1*R*,2*S*)-Tricarbonyl[*o*-isopropoxyphenyl 2(*S*),4-(*R*)-dimethyl-5-*tert*-butoxypentyl ketone]chromium (17). To a suspended mixture of CuI (76 mg, 0.4 mmol) in ether (2 mL) was added 0.74 mL of ((*S*)-2-methyl-3-*tert*-butoxypropyl)lithium (1.08 M in ether, 0.8 mmol) at −45 °C under argon. The mixture was stirred for 30 min. A solution of (−)-(*E*)-Ar(1*R*,2*S*)-*o*-isopropoxy complex 15 (34 mg, 0.1 mmol) in ether (2 mL) was added to the reaction mixture at −78 °C and stirred for 1 h. The usual workup afforded (−)-17 (40 mg, 86%) as an orange oil: ^1H NMR ($CDCl_3$) δ 0.91 (3 H, d, *J* = 6.7), 0.93 (3 H, d, *J* = 6.7), 1.04–1.13 (1 H, m), 1.16 (9 H, m), 1.18–1.28 (1 H, m), 1.38 (3 H, d, *J* = 6.7), 1.48 (3 H, d, *J* = 6.7), 1.64–1.78 (1 H, m), 2.24–2.38 (1 H, m), 2.78 (1 H, dd, *J* = 6.7, 17.5), 2.90 (1 H, dd, *J* = 6.7, 17.5), 3.06 (1 H, dd, *J* = 6.7, 8.3), 3.16 (1 H, dd, *J* = 5.8, 8.7), 4.50 (1 H, dq, *J* = 6.7, 6.7), 4.92 (1 H, t, *J* = 6.1), 5.00 (1 H, d, *J* = 6.7), 5.78 (1 H, t, *J* = 6.1), 6.22 (1 H, d, *J* = 6.7); IR ($CHCl_3$) 1975, 1890, 1650, 1510, 1200 cm^{-1}; MS *m/e* 470 (M^+), 386 (M^+ − 3CO); high-resolution mass cald for $C_{24}H_{34}O_6Cr$ 470.1779, found 470.1780; $[\alpha]_D^{18}$ = −255° (*c* = 0.21, $CHCl_3$).

(+)-Ar(1*R*,2*S*)-Tricarbonyl[1-(*o*-methoxyphenyl)-1(*S*)-acetoxy-3(*R*),5(*R*)-dimethyl-6-*tert*-butoxyhexane]chromium (20). To a suspended mixture of $LiAlH_4$ (12 mg, 0.316 mmol) in ether (3 mL) was added a solution of the complex 13 (70 mg, 0.158 mmol) in ether (3 mL) at −78 °C under argon. After being stirred for 10 min at the same temperature, the mixture was quenched with saturated aqueous sodium sulfate and filtered off. The precipitate was washed with ether, and the filtrate was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was acetylated without purification under the usual conditions (acetic anhydride/pyridine, room temperature). Purification by silica gel chromatography with hexane/ether afforded 62.3 mg of 20 (81%): ^1H NMR ($CDCl_3$) δ 0.89 (3 H, d, *J* = 6.7), 0.94 (3 H, d, *J* = 6.7), 1.04–1.34 (2 H, m), 1.18 (9 H, s), 1.55–1.80 (3 H, m), 1.94 (1 H, t, *J* = 11.2), 2.08 (3 H, s), 3.06 (1 H, t, *J* = 7.8), 3.21 (1 H, dd, *J* = 6.0, 7.8), 3.78 (3 H, s), 4.80 (1 H, t, *J* = 6.0), 4.98 (1 H, d, *J* = 6.4), 5.58 (1 H, t, *J* = 6.4), 5.80 (1 H, d, *J* = 6.1), 5.95 (1 H, d, *J* = 9.9); IR ($CHCl_3$) 1960, 1870, 1720 cm^{-1}; MS *m/e* 486 (M^+), 402 (M^+ − 3CO); high-resolution mass calcd for $C_{24}H_{34}O_7Cr$ 486.1700, found 486.1705; $[\alpha]_D^{15}$ = +37.6° (*c* = 0.38, $CHCl_3$).

(+)-Ar(1*R*,2*S*)-Tricarbonyl[1-(*o*-methoxyphenyl)-1-(*S*),3(*R*),5(*R*)-trimethyl-6-*tert*-butoxyhexane]chromium (21). To a solution of the acetate complex 20 (14 mg, 0.029 mmol) in methylene chloride (2 mL) was added 0.1 mL of trimethylaluminum (1.5 M in hexane, 0.15 mmol) at −78 °C under argon, and the mixture was stirred for 30 min at the same temperature and then warmed to 0 °C over 1 h. The reaction mixture was quenched with water and extracted with methylene chloride. The extract was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel chromatography with hexane/ether to afford 11 mg (87%) of trimethyl complex 21: ^1H NMR ($CDCl_3$) δ 0.89 (3 H, d, *J* = 6.7), 0.91 (3 H, d, *J* = 6.7), 1.02–1.12 (1 H, m), 1.16 (3 H, d, *J* = 6.7), 1.18 (9 H, s), 1.20–1.80 (5 H, m), 2.88–2.98 (1 H, m), 3.06 (1 H, dd, *J* = 6.7, 8.3), 3.22 (1 H, dd, *J* = 6.7, 8.3), 3.75 (3 H, s), 4.86 (1 H, t, *J* = 6.7), 4.98 (1 H, d, *J* = 6.7), 5.44–5.49 (2 H, m); IR ($CHCl_3$) 1970, 1870 cm^{-1}; MS *m/e* 442 (M^+), 352 (M^+ − 3CO); high resolution mass calcd for $C_{23}H_{34}O_5Cr$ 442.1826, found 442.1801; $[\alpha]_D^{15}$ = +195° (*c* = 0.42, $CHCl_3$).

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Supplementary Material Available: Tables of hydrogen atom coordinates and B_{eq} values, anisotropic thermal parameters, bond angles, and torsion angles for two complexes, (*E*)-(MeO-$C_6H_4COCH{=}CHMe)Cr(CO)_3$ and (*E*)-(Me-$C_6H_4COCH{=}CHMe)Cr(CO)_3$, and ^1H NMR spectra (400 MHz) for compounds **13**, **17**, **20**, and **21** (18 pages). Ordering information is given on any current masthead page.

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Investigation of the Applicability of Molecular Mechanics (MMX) Calculations to a Conformational Investigation of Organometallic Compounds of the Types $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2R$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2C({=}O)R$, and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R$ (R = H, Alkyl, Acyl)

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The potential utility and applicability of a new molcular modeling program, MMX, to organotransition-metal chemistry is assessed by comparing calculated ligand rotation conformational energy profiles with relevant experimental data. To this end, both the identity of the lowest energy conformation and the enthalpy differences between the various conformations arising from alkyl or acyl ligand rotation in the flexible organometallic complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2R$ (R = H, Me, Ph, $C_6H_3(m\text{-}Me)_2$, Me_3Si) $(\eta^5\text{-}C_5H_5)Fe(CO)_2C(O)R'$ (R' = Me, Ph, $C_6H_3(m\text{-}Me)_2$), and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R''$ (R'' = H, Me, Et, CH_2Ph, CH_2SiMe_3, C(O)Me) are determined utilizing variable-temperature IR and NMR spectroscopy. For most of the compounds studied, the computed conformational energy profiles identify correctly the low-energy conformation, and provide surprisingly accurate estimates of the relative energies of the less stable conformations. The effects of electronic and entropic factors may complicate interpretations in a small number of cases, but the overall results seemingly validate the use of MMX to consider subtle steric effects on organometallic structural chemistry.

Molecular mechanics (MM) calculations have in recent years become a very valuable tool for rapid computation of the conformational energy profiles of a wide variety of types of molecules and complement the various quantum mechanical methodologies which are available.[1] Where comparisons with experimental data are possible, surprisingly accurate estimates of molecular properties are possible, and MM calculations are often the computational methodology of choice for the consideration of many medium-sized organic systems[2] and coordination[3] compounds.

With the development of many enantioselective organic reactions induced by chiral organotransition-metal compounds,[4] it would seem that MM calculations should be ideally suited for computational analyses of the factors involved in enantioselective steps, which are often believed to be strongly influenced by steric factors.[5] However, to date, very few such applications to organotransition-metal problems have been reported[5,6] and, of these, none has attempted to address closely the subtle energy differences which must of necessity be involved in many enantioselective processes (2–4 kcal mol^{-1}).[7] The parameterization

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