Articles

Tartrate-Derived Aryl Aldehyde Acetals in the Asymmetric Directed Metalation of Chromium Tricarbonyl Arene Complexes

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Received August 25, 1992 (Revised Manuscript Received July 12, 1993[•]*)*

A series of three chromium tricarbonyl benzaldehyde acetal complexes were prepared from benzaldehyde diethyl acetal and (+)-diethyl tartrate. These compounds were *ortho*-lithiated by a number of bases, and the diastereoselectivity of lithiation was determined by quenching of the resulting anions with Me_3SiCl. Complexes **1** and **2** were found to give moderate levels of diastereoselection, while the combination of complex **3** and 2.4 equiv of *n*-BuLi under equilibrating conditions gave an 86% de of silylated products. Other electrophiles gave slightly higher de's (88% to $\geq$94%), and all products derived from **3** were separable by column chromatography. Hydrolysis of the *ortho*-methylated product to the corresponding benzaldehyde complex (−)-**21** as well as X-ray structural analysis of the trimethylsilylated complex demonstrated that preferential *pro-R* deprotonation had occurred.

Introduction

The organic chemistry of (arene)tricarbonylchromium complexes has been the subject of much recent interest.[2] The reasons for this attention stem from the significant changes in chemistry from that of the uncomplexed arenes. Formation of these complexes results in a greater electrophilicity of the ring carbon atoms, greater acidity of both the ring and the benzylic hydrogens, and increased stability of the benzylic carbocations.

Perhaps the most significant potential effect of all in these complexes is the destruction of the σ plane of the benzene ring in arenes. Consequently, *ortho*- and *meta*-disubstituted (arene)tricarbonylchromium complexes (with different substituents) are chiral molecules. This fact, in concert with the ability of the chromium tricarbonyl function to effectively block one face of the ring, has led to a rapid increase in the use of chiral (arene)tricarbonylchromium complexes as intermediates[3] and as catalysts[4] for asymmetric synthesis.

To this point, the field has been hampered by the limited availability of enantiomerically enriched (arene)tricarbonylchromium complexes. Generally, preparation of enantiomerically enriched complexes of this type has been accomplished by classical or kinetic resolution of racemic mixtures. For example, a number of racemic acid and amine complexes have been resolved through crystallization of diastereomeric ammonium salts obtained with optically pure chiral amines or acids, respectively.[2a] Aryl aldehyde complexes have been resolved by the chromatographic separation of their diastereomeric semioxamazones prepared with (*S*)-(−)-5-(α-phenylethyl)semioxamazide,[2a] of imines prepared from L-valinol,[5] or of diastereomeric animals.[5c] Three groups have employed successful enzymatic[6a–d] or nonenzymatic[6e] kinetic resolution for preparation of enantiomerically enriched complexes, and in some cases, highly diastereoselective complexation of enantiomerically pure substrates has been successful.[5c,7] HPLC on chiral supports shows promise in the separation of racemic mixtures of these compounds.[8]

Recently, a limited number of methods based on directed ortho metalation have been employed for the preparation of enantiomerically enriched *ortho*-disubstituted (arene)-

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[•] Abstract published in *Advance ACS Abstracts*, October 1, 1993.

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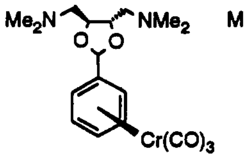
tricarbonylchromium complexes. Widdowson, for example, has demonstrated that some lithiated arene complexes undergo kinetic resolution in their reaction with enantiomerically pure oxazolidinones.[9] Additionally, it has been demonstrated by the Davies and Aubé/Heppert groups that α-phenethylethylamine- or ephedrine-derived substrates undergo highly diastereoselective ortho metalation;[10-12] unfortunately, the α-amino functional groups do not serve as readily removable chiral auxiliaries.

We were intrigued by the possibility of accomplishing asymmetric directed metalation of a monosubstituted arene–$Cr(CO)_3$ complex modified with a removable chiral auxiliary. Encouraged by the report of stereoselective methylations of benzylic carbocations,[13] we chose to investigate acetal auxiliaries derived from C_2-symmetric diols[14] as directed metalation groups, namely the diethyl tartrate-derived **1**–**3**, by virtue of the ready availability of both enantiomers of the chiral precursors and in anticipation of the ability to convert reaction products to the corresponding aryl aldehyde complexes. We have reported in preliminary form the highly diastereoselective metalation of substrate **3**[15] and wish to describe more fully our efforts in this area. After the appearance of our preliminary report, we became aware of the related work of the Aubé/Heppert group in the diastereoselective lithiation chemistry of acetophenone-derived ketals.[16]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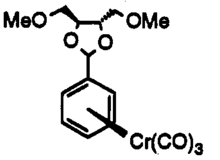
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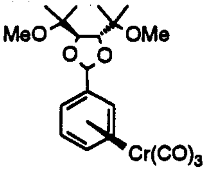
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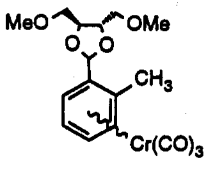
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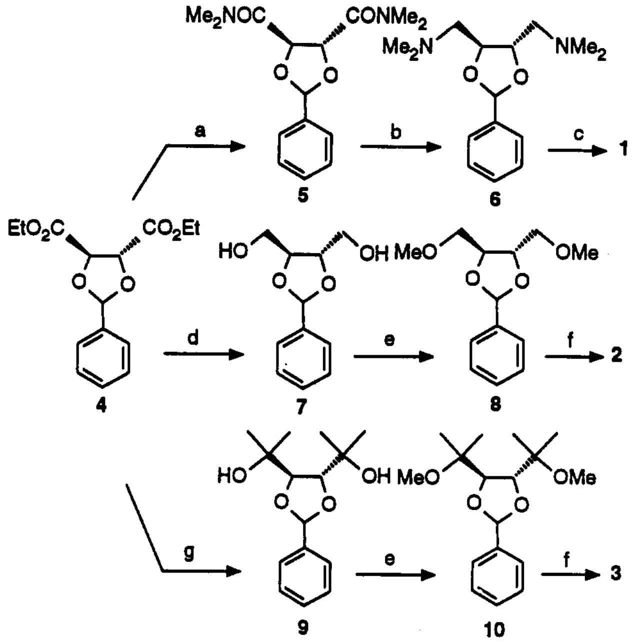
Results and Discussion

Substrate Preparation. The three 2-phenyldioxolane derivatives **1**–**3** were prepared from diester **4**, which was obtained from benzaldehyde and (+)-diethyl tartrate by a modification of the reported procedure (Scheme I).[17] Reduction of **4** with $LiAlH_4$[17] and subsequent methylation of the resultant diol **7** gave the bis(methoxymethyl) derivative **8**. The bis(dimethylamino) derivative **6** was synthesized by treatment of the dicarboxylate with dimethylamine to afford **5**, which could be reduced to **6** with sodium bis(2-methoxyethoxy)aluminum hydride. In our hands, the use of $LiAlH_4$ gave a mixture of products which were difficult to separate. Finally, the bis(1-methoxy-1-methylethyl) derivative **10** was prepared by treatment of the dicarboxylate with excess methylmagnesium iodide followed by methylation of diol **9** using a modification of the reported procedure.[18a]

Scheme I[a]



[a] Reagents: (a) Me_2NH; (b) $NaH_2Al(OCH_2CH_2OMe)$; (c) $Cr(CO)_6$ (2 equiv), $C_{10}H_8$ (0.5 equiv); (d) $LiAlH_4$; (e) NaH, MeI; (f) $Cr(CO)_6$; and (g) MeMgI.

Conversion of acetals **8** and **10** into their $Cr(CO)_3$ complexes could be accomplished under standard conditions ($Cr(CO)_6$/n-Bu_2O/THF/reflux).[19] In our hands, however, the bis[(dimethylamino)methyl] derivative **6** reacted sluggishly under these conditions to give modest yields of the $Cr(CO)_3$ complex. In view of the availability of (naphthalene)tricarbonylchromium as a mild complex-

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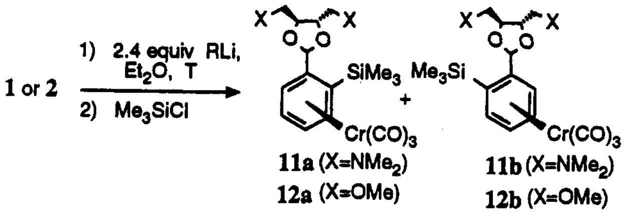
Table I. Lithiation of Complexes 1 and 2. Variation of Conditions



base	X	T (°C)	yield (%)	prod	a:b	de (%)
n-BuLi	NMe_2	−78	60	11	65:35	30
	(1)	−10	47		39:61	−22
t-BuLi		−78	64		64:36	28
		−20[a]	70		50:50	0
MeLi[b]		−78	60		47:53	−6
		−10[c]	53		72:28	44
n-BuLi	OMe	−78	70	12	87:13	74
	(2)	−30	57		56:44	12
t-buLi		−78	64		56:44	12
		−30	46		50:50	0
MeLi[b]		−78	7		50:50	0
		−30	32		59:41	18

[a] 1.2 equiv of *t*-BuLi. [b] Low halide concentration (1.4 M MeLi, 0.05 M in halide). [c] Slow addition of *n*-BuLi (2.4 equiv over 1.5 h).

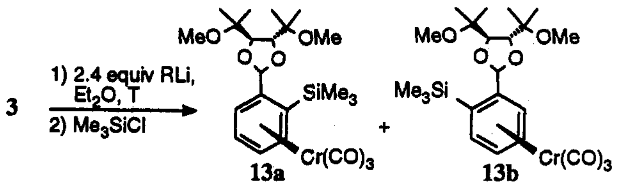
ing reagent,[20] naphthalene was added to the reaction mixture in expectation of in situ formation of (naphthalene)tricarbonylchromium. We were pleased to find that addition of 0.5 equiv of naphthalene to the standard complexation conditions resulted in the facile formation of 1 in 90% yield.

Lithiation of Complexes. For each of the acetals investigated, lithiation was attempted with each of MeLi, *n*-BuLi, and *t*-BuLi at two different temperatures, and the resulting carbanions were quenched with Me_3SiCl. The relative amount of lithiation at the *pro-R* versus *pro-S* site was determined by examination of the ^1H NMR spectra of the crude reaction products. It was rapidly discovered that diethyl ether was preferred to tetrahydrofuran (THF) as a reaction solvent; the use of THF resulted in much lower de's and, in some cases, multiple products. Finally, we were surprised to discover that with *n*-BuLi and MeLi, 1 equiv of base gave only trace amounts of deprotonation, whereas addition of a second equivalent resulted in complete deprotonation of the complexes. One equivalent of *t*-BuLi was normally sufficient for complete deprotonation.

Initially, we examined bis(dimethylamino) dioxolane 1 for deprotonation studies. Lithiation and quenching of the carbanion with Me_3SiCl afforded mixtures of **11a** and **11b**, which could be distinguished by their different chemical shifts for the hydrogen on the acetal carbon (δ 5.71 versus 5.73 for **11a** and **11b**, respectively) and for the trimethylsilyl hydrogens (δ 0.36 versus 0.37, respectively). Integration of these resonances was employed to determine the diastereomeric ratios (Table I).

Although **11a/b** could be formed in satisfactory yields, the observed diastereoselectivities were modest. In the best case, generation of the anion by slow addition of (2.4 equiv) MeLi at −10 °C resulted in a 44% de. Other base/temperature combinations gave significantly lower and, in two cases, inverted diastereoselection. The use of THF as a solvent led to de's of ~0 in all cases, and the use of a (1:1) hexane:diethyl ether mixture led to only small amounts of lithiation. In addition, **11a/b** could not be separated by silica gel chromatography.

Table II. Lithiation of 3. Variation of Conditions on Diastereoselectivity



base	T (°C)	yield (%)	**13a:13b**	de (%)
t-BuLi	−78	60	50:50	0
	−30	20	34:66	−32
MeLia[a]	−78	5	77:23	54
	−30	50	87:13	74
n-BuLi	−78	80	84:16	68
	−30	75	88:12	76
	−30[b]	90	93:7	86

[a] Low halide concentration (1.4 M MeLi, 0.05 M in halide). [b] Slow addition of *n*-BuLi (2.4 equiv over 1.5 h).

We next turned our attention to the lithiation of bis(methoxymethyl) derivative 2. Acetal 2 could be deprotonated by all three bases at −30 °C. At −78 °C, MeLi gave only a small amount of deprotonation, whereas the other two bases gave useful yields of deprotonation products. Attempts to lithiate 2 at higher temperatures (−15 °C), however, led to multiple products. The diastereoselectivities of lithiation were determined, after Me_3SiCl quenching by the different resonances of **12a** and **12b** for the acetal hydrogen (δ 5.84 versus 5.83 for **12a** and **12b**, respectively) and for the trimethylsilyl hydrogens (δ 0.37 versus 0.39 for **12a** and **12b**, respectively). With one exception, the diastereoselectivities of lithiation were uniformly poor (Table I). On the other hand, the use of 2.4 equiv of *n*-BuLi at −78 °C resulted in a 74% de of lithiation. Although we considered this de promising, we were unable to achieve chromatographic separation of **12a/b**. Due to this separation problem and our success in the use of other dioxolanes, we did not pursue the lithiation chemistry of 2 further.

In view of the lithiation chemistry of 2, we turned our attention to substituted dioxolane 3 as a substrate. Once again, 2 equiv of base was necessary for complete deprotonation of 3 (the use of 1.2 equiv of *n*-BuLi at −78 °C gave only approximately 20% conversion). The products of silylation of the lithiated species could be distinguished in the ^1H NMR spectrum of the crude product; the resonances for the acetal hydrogens (δ 6.01 for **13a** and δ 5.96 for **13b**) and the hydrogen atoms of the trimethylsilyl function (δ 0.35 for **13a** versus δ 0.39 for **13b**) were most convenient for the determination of the diastereomeric ratios (Table II).

Once again, *n*-BuLi proved to be the base of choice. At −78 °C, significant diastereoselection (68% de) took place.[21] Furthermore, and unlike dioxolane 2, diastereoselectivity improved with increased reaction temperature; conducting the reaction at −30 °C, with slow addition of base, resulted in a 93:7 ratio of **13a**:**13b**, or an 86% de. We were also pleased to find that silica gel chromatographic separation of **13a/b** was now quite facile. Furthermore, there was no

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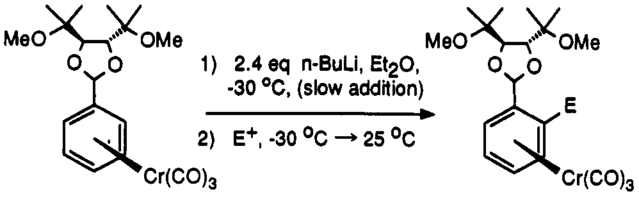
(21) The use of THF as a reaction solvent under analogous conditions led to several trimethylsilylated products, whose identities were not pursued. The addition of TMEDA had no perceptible effect on the reaction.

Table III. Electrophiles Incorporated in Lithiation of 3



3 **13 - 20**

electrophile	E	compd	yield (%)[a]	de (%)[b]
$ClSiMe_3$	$SiMe_3$	**13a**	77	86
MeI	Me	**14a**	62	92
		**15a**	67	92
$ClC(O)NEt_2$	$C(O)NEt_2$	**16a**	74	92
PhSSPh	PhS	**17a**	83	92
$ClSnBu_3$	$SnBu_3$	**18a**	73	91
$BrCH_2CH_2Br$	Br	**19a**	68	88
$ClPPh_2$	PPh_2	**20a**	69	≥94

[a] Yields of diastereomerically pure products. [b] Determined by ^1H NMR of the crude reaction mixtures.

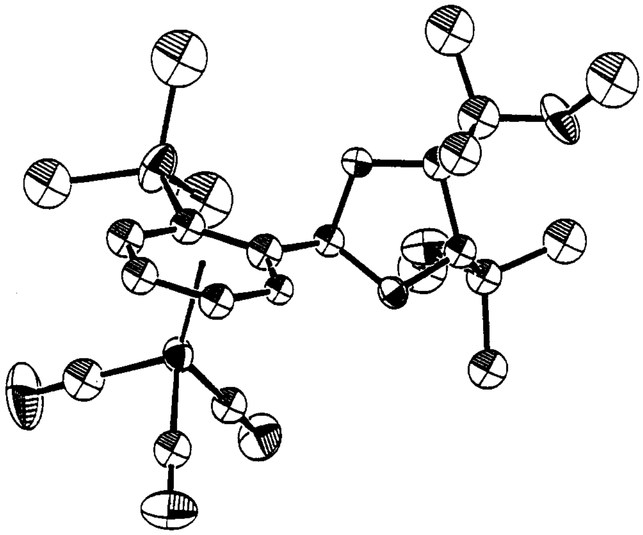
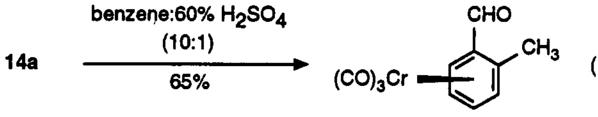


Figure 1. ORTEP drawing of **13a** based on X-ray coordinates.

evidence of products resulting from the deprotonation of the acetal hydrogen, which has been observed in related systems.[10b]

The reaction of the anion of **3** with several other electrophiles (MeI, $ClSnBu_3$, $ClPPh_2$, $BrCH_2CH_2Br$, allyl bromide, diethylcarbamyl chloride, and PhSSPh) was undertaken. In most of these cases (allyl bromide excepted), it was more convenient to compare the actual hydrogen resonance of the major diastereomer with that of the lowest field arene hydrogen of the minor diastereomer. Integration of these signals revealed diastereomeric excesses of 92% (**14a**, **15a**, **16a**, and **17a**), 91% (**18a**), and 88% (**19a**) (Table III). In the case of chlorodiphenylphosphine (**20a**), the minor diastereomer could not be detected in the ^1H NMR of the crude product; we estimate a ≥94% de for **20a**. In addition, we found that reactions of the anion with MeI (**14a**) and PhSSPh (**17a**) were relatively sluggish and that the addition of THF (one-half the diethyl ether volume) *after* the generation of the anion was complete enhanced the amount of electrophile incorporation without a noticeable compromise of the de. In all cases, the major diastereomer could be isolated in a pure state following silica gel chromatography. In the trimethylsilyl substitution case, a small amount (4%) of the minor diastereomer (**13b**) was also isolated.

Assignment of the direction of asymmetric induction was accomplished in two ways. The major trimethylsilyl-substituted product **13a** gave crystals suitable for X-ray structural analysis (Figure 1),[22] which revealed a 1*R*,2*S*-configuration at the chiral centers on the arene ring. Also, when the incorporated electrophile was MeI, the purified major diastereomer **14a** could be hydrolyzed (10:1 benzene: 60% aqueous H_2SO_4, 65% yield, 80% yield based on recovered starting material) to afford the known complex (−)-**21** (eq 1).[23] Both pieces of information indicate preferential abstraction of the *pro-R* proton. Hydrolysis of the acetal unit of the other lithiation products of **3** (**13a**, and **15a**–**20a**) proved to be less successful, as decomplexation of the tricarbonylchromium function became the dominant mode of reaction under several sets of conditions.



(-)-**21** (1)

The sense of asymmetric induction in the lithiation of **2** was established by incorporating iodomethane to give **22** (46% de, 74% yield), which underwent acetal hydrolysis to give (−)-**21** (43% yield, 52% ee after recrystallization), indicating preferential *pro-R* deprotonation. Similarities between the *ortho*-silylated complexes **12** and **13** were also evident in their ^1H NMR spectra in that the acetal hydrogen resonates farther downfield in the major isomer relative to that in the minor isomer; furthermore, the trimethylsilyl hydrogens in the major diastereomer of both **12** and **13** resonate further upfield. In addition, exchange of $CDCl_3$ for C_6D_6 as solvent results in a similar separation, in the same direction, of the acetal hydrogen resonances in both **12** and **13** (**12a**, δ 5.84 → 6.00; **12b**, δ 5.83 → 5.96; **13a**, 6.01 → 6.25; and **13b**, 5.96 → 6.20). Although the amine complexes **11a**/**b** do not successfully hydrolyze, they show analogous behavior in C_6D_6 (**11a**, δ 5.91 and **11b**, δ 5.88), and we therefore also assign **11a** as being the result of *pro-R* functionalization, in agreement with the published tentative assignment.[16]

Mechanistic Comments. The lithiation chemistry of **1**–**3** revealed several interesting properties which are worthy of further discussion. Aside from the high diastereoselectivity observed with the appropriate combination

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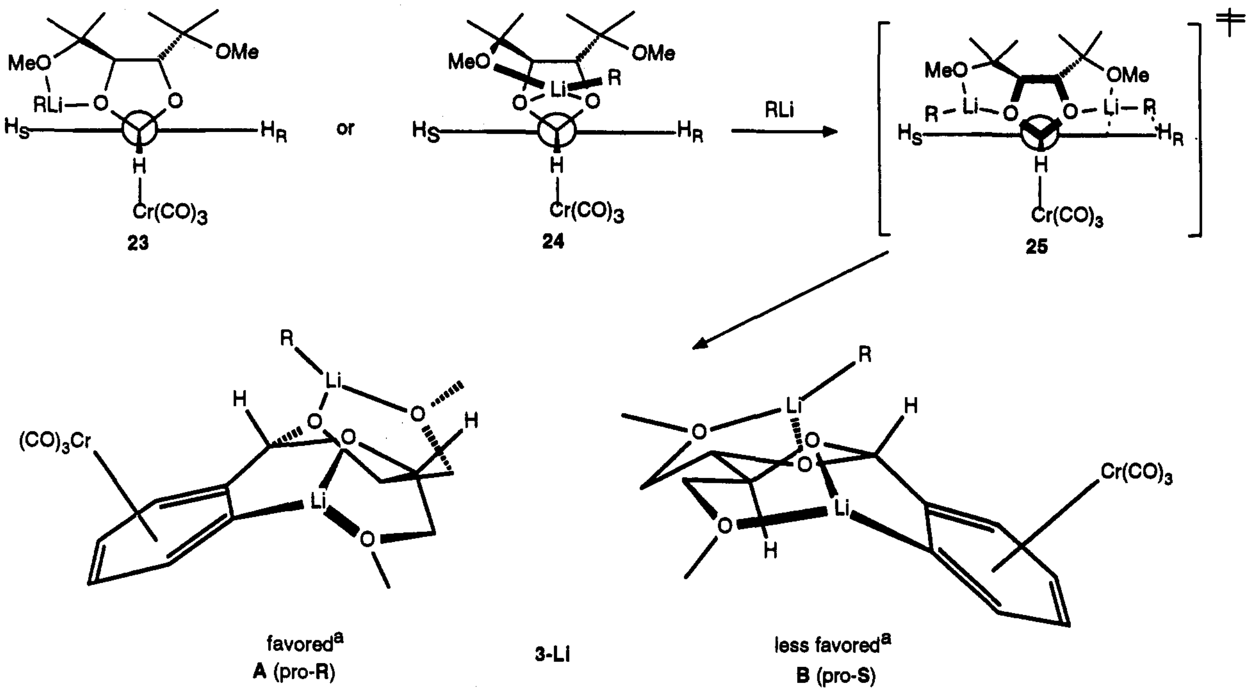
[22] Compound **13a** crystallized in the space group $P2_12_12_1$. The unit cell parameters were determined to be a = 11.868(4) Å, b = 19.528(7) Å, and c = 11.431(3) Å. The unit cell contains four asymmetric units of molecular formula $C_{23}H_{34}O_7SiCr$ in a volume of 2649(3) Å^3 which produces a calculated density of 1.260 g/cm^3. A total of 2673 reflections were recorded in the range $2\theta < 50°$ with a Rigaku AFC6S diffractometer using the θ–2θ scan routine and Mo Kα radiation (λ = 0.71069 Å). After Lorentz and polarization corrections and an empirical absorption correction, the structure was solved by the TEXSAN 9 package. The positions of all hydrogen atoms were calculated assuming a 0.95-Å C–H distance. The final agreement factors are R = 0.0644 and R_w = 0.0647 for 1039 unique, observed reflections [$|F_o| > 3\sigma(F_o)$] and 162 independent variables. The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

[23] (a) Solladié-Cavallo, A.; Solladié, G.; Tsamo, E. *J. Org. Chem.* 1979, *4*, 4189. The observed optical rotation, $[\alpha]^{26.5}{}_D$ −628° (c 0.25, $CHCl_3$), was slightly different from the literature value, $[\alpha]^{20}{}_D$ −664° (c 0.26, $CHCl_3$). However, the presence of the minor enantiomer was not detectable using $Eu(hfc)_3$, the shift reagent employed by Solladié-Cavallo for the determination of the optical purity for this compound. (b) Solladié-Cavallo, A.; Suffert, J. *Magn. Reson. Chem.* 1985, *23*, 739.

Scheme II[a]



[a] The fourth ligand at lithium and the *gem*-dimethyl groups are omitted for clarity.

of **3** and base, it is clear that 2 equiv of base are required for complete arene deprotonation. Furthermore, the results vary greatly with the choice of base.

In order to understand the lithiation process in more detail, a series of experiments were conducted in which the temperature for lithiation of **3** was changed during the reaction. Complex **3** was deprotonated at −78 °C with BuLi (2.4 equiv, slow addition), and after 1 h, one-half of the solution was quenched with Me_3SiCl at −78 °C. The remaining half was allowed to warm to −30 °C for 4.5 h and subsequently reacted with Me_3SiCl. Upon workup, the two fractions gave mixtures of **13a/b** in 80% de and 86% de, respectively. If this sequence was repeated with rapid addition of base, the de's were 68% (−78 °C) and 86% (−30 °C). Finally, if the anion generated at −78 °C with rapid addition of BuLi was treated with approximately 0.5 equiv of unreacted **3** (or if only 1.5 equiv of base was used), warmed to −30 °C for 4.5 h, and quenched with Me_3SiCl, an 86% de of **13a/b** was again realized. Yields of **13a** + **13b** were relatively consistent (75–85% based on recovered starting material) in each of these cases.

On the basis of the above, it is our belief that the results of rapid base addition to **3** at −78 °C are the consequence of kinetic lithiation and, that upon warming to −30 °C, the lithiated species equilibrates either with unreacted starting material or via an as yet undetected perlithiated species to give thermodynamic *ortho* lithiation more selectively at the *pro-R* site. The 80% de realized with slow base addition at −78 °C is the result of the partial equilibration of the lithiated species.

It is well established that any discussion of organolithium intermediates or transition states is complicated by the fact that alkyl- and aryllithiums are rarely monomeric in solution.[24] Nevertheless, we envision that there is a competition between the diastereomeric aryllithium species **A** and **B** (Scheme II), with the former having a *cis*-fused 5,5-ring system formed by the chelated lithium atom and the dioxolane ring as opposed to the *trans*-fused 5,5-system of the latter. Since a 6.0-kcal relative stabilization of the *cis* over the *trans* 5,5-fused ring system is known for the all-carbon framework,[25] **A** would be the preferred aryllithium. This corresponds to the abstraction of the *pro-R* hydrogen, which is in agreement with experiment. Although it is possible to create an alternative to **B** with a *cis*-fused 5,5-system, the lithium atom would not be able to approach the *pro-S* side of the ring. In this picture, it is possible to rationalize the superiority of the acetal in **3** as a chiral auxiliary relative to that in **1** or **2** in terms of the presence of the "*gem*-dimethyl effect",[26] which assists in the formation of **3-Li**. Lithiation intermediates derived from **1** may, in addition, have other competitive coordination modes due to the more highly basic nitrogen atoms present in the auxiliary.

The necessity for 2 equiv of alkyllithium for deprotonation is most likely due to the large number of ether oxygen atoms present in the acetal auxiliary and the probability that this auxiliary is able to coordinate the alkyllithium such that the base is held away from the *ortho*

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(24) For a list of references on alkyllithium aggregation, see: (a) Fraenkel, G.; Chow, A.; Winchester, W. R. *J. Am. Chem. Soc.* **1990**, *112*, 6190. For aryllithium aggregation studies, see: (b) Harder, S.; Boersma, J.; Brandsma, L.; van Heterten, A.; Kanters, J. A.; Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7802. (c) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

(25) Barrett, J. W.; Linstead, R. P. *J. Chem. Soc.* **1936**, 611.

(26) For a discussion of the "*gem*-dimethyl effect" and the related Thorpe–Ingold effect, see: Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Wiley-Interscience: New York, 1965; pp 191–192.

hydrogen atoms.[27] This phenomenon has been observed in other substrates for lithiation and particularly for substituted aryloxazolines.[28]

Comparison of our results with those of Aubé/Heppert,[16] while superficially very similar, reveals points which are more noteworthy for their differences. For example, there is likely a difference in the conformation of **3** and the dioxolanes of Aubé, at least for the ground state. The actual hydrogen in **3** is oriented roughly toward the chromium fragment, while for the Aubé/Heppert systems, the methyl group at C-2 of the dioxolane is most likely oriented *anti* to the chromium atom.[30] In addition, the two systems give maximum selectivity with very different solvent/base combinations, and *n*-BuLi/Et_2O combinations were not thoroughly investigated by the Kansas group. Finally, enhanced selectivity is realized in both cases by modifications which would be expected to assist in formation of a chelate ring with lithium; in the Aubé/Heppert system, a dimethylamino substituent on the dioxolane serves this purpose, whereas in our case, this is not particularly successful and, rather, geminal dimethyl groups serve this purpose.

In conclusion, we have shown that chiral acetal-substituted arene tricarbonylchromium complexes are capable of undergoing highly diastereoselective functionalization through directed metalation/electrophile incorporation. The choice of the appropriate acetal auxiliary enables complete separation of the minor diastereomeric impurities. Studies of the application of these compounds in asymmetric synthesis are in progress.

Experimental Section

General Data. Melting points were measured with a Thomas Hoover capillary melting point apparatus and are uncorrected. ^1H NMR spectra and ^{13}C NMR spectra were recorded in $CDCl_3$ (unless otherwise indicated) on a Brüker AC-300 spectrometer operated at 300 and 75 MHz, respectively. *J* values are given in hertz. Infrared spectra were recorded on a Nicolet 5DX FT-IR, using neat films on NaCl plates or using KBr pellets. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Mass spectra were acquired on a Finnegan 4000 mass spectrometer (EI mode). High-resolution mass spectra were obtained on a Kratos MS80 mass spectrometer by the staff of the Central Instruments Facility of Wayne State University.

MeLi, *n*-BuLi, and *t*-BuLi were obtained from Aldrich Chemical Co., Ltd. The titer of *n*-BuLi and *t*-BuLi was determined using 2,5-dimethoxybenzyl alcohol as standard;[31] the titer of MeLi was determined using diphenylacetic acid as standard.[32] Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl immediately prior to use. Column chromatography on silica gel (Merck, 0.04–0.063 mm) was performed according to the protocol of Still.[33]

(4*S*,5*S*)-[4,5-Bis((dimethylamino)methyl)-2-phenyl-1,3-dioxolane]tricarbonylchromium(0) (1). A mixture of dioxolane **6** (0.60 g, 2.27 mmol), $Cr(CO)_6$ (1.1 g, 5.0 mmol), naphthalene (0.14 g, 1.1 mmol), di-*n*-butyl ether (5 mL), and THF (1 mL) was heated to reflux for 48 h. After the mixture was cooled and filtered, the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography using $CHCl_3$:triethylamine (9:1) as the eluent to give **1** as a viscous yellow liquid (0.82 g, 90%): $[\alpha]^{26.5}{}_D$ −9.2° (*c* 6.55, $CHCl_3$) (lit.[16] −8.7°); IR (neat, NaCl) ν_{max} 1964, 1885 cm^{-1}; MS *m/e* (30 eV) 400 (M^+), 244 ($M^+ - 2CO$), 316 ($M^+ - 3CO$); HRMS *m/e* for $C_{18}H_{24}CrN_2O_5$ calcd (M^+) 400.1090, found 400.1094.

(4*R*,5*R*)-[4,5-Bis((dimethylamino)methyl)-2-(2′-(trimethylsilyl)phenyl)-1,3-dioxolane]tricarbonylchromium(0) (11a/b). To a solution of **1** (0.100 g, 0.25 mmol) in diethyl ether (Et_2O, 3 mL) cooled to −10 °C was added MeLi (0.60 mL of a 1.4 M Et_2O solution, 0.6 mmol) over a period of 1.5 h. The solution was stirred for 1 h, and Me_3SiCl (70 μL, 0.6 mmol) was added. The solution was stirred for 1 h at −10 °C and subsequently allowed to come to room temperature. The solvent was then removed under reduced pressure, and the residue was diluted with water and extracted with CH_2Cl_2. The CH_2Cl_2 layer was dried over $MgSO_4$ and concentrated under reduced pressure. Integration of the δ 5.71 (5.91 in C_6D_6) and δ 0.36 (0.33 in C_6D_6) resonances of **11a** and the δ 5.73 (5.88 in C_6D_6) and δ 0.37 (0.36 in C_6D_6) resonances of **11b** gave a 72:28 relative ratio. Purification by silica gel chromatography using chloroform:Et_3N (9:1) as the eluent gave an inseparable mixture of **11a/b**[16] (0.062 g, 53%) as a viscous oil.

(4*S*,5*S*)-[4,5-Bis(methoxymethyl)-2-phenyl-1,3-dioxolane]tricarbonylchromium(0) (2). A mixture of **8** (0.486 g, 2.04 mmol), $Cr(CO)_6$ (0.986 g, 4.47 mmol), di-*n*-butyl ether (5 mL), and THF (0.5 mL) was heated to reflux for 24 h. The mixture was cooled and filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether:ethyl acetate (5:1) as the eluent to afford **2** as a viscous yellow oil (0.582 g, 76%): $[\alpha]^{26.5}{}_D$ +14° (*c* 1.00, $CHCl_3$); IR (neat, NaCl) ν_{max} 1959, 1881 cm^{-1}; ^1H NMR δ 5.65 (s, 1H), 5.60–5.50 (m, 2H), 5.35–5.20 (m, 3H), 4.25–4.05 (m, 2H), 3.70–3.50 (m, 4H), 3.40 (s, 6H); ^{13}C NMR 232.2, 106.9, 101.6, 92.8, 91.5, 90.9, 78.4, 77.9, 72.43, 72.40, 59.45, 59.40; MS *m/e* (eV) 374 (M^+), 318 ($M^+ - 2CO$), 290 ($M^+ - 3CO$); HRMS *m/e* for $C_{16}H_{18}CrO_7$ calcd (M^+) 374.0458, found 374.0462.

(4*R*,5*R*)-[4,5-Bis(methoxymethyl)-2-(2′-(trimethylsilyl)phenyl)-1,3-dioxolane]tricarbonylchromium(0) (12a/b). To a solution of **2** (0.704 g, 0.188 mmol) in diethyl ether (3 mL) cooled to −78 °C was added *n*-BuLi (0.19 mL of a 2.36 M hexane solution, 0.45 mmol). The solution was stirred for 1 h, and Me_3SiCl (58 μL, 0.45 mmol) was added. The solution was stirred for 1 h at −78 °C and subsequently allowed to come to room temperature. Aqueous Na_2CO_3 (10 drops) followed by $MgSO_4$ was added, and the mixture was filtered and concentrated under reduced pressure. Integration of the δ 5.84 and 0.37 resonances of **12a** and the δ 5.83 and 0.39 resonances of **12b** in the ^1H NMR spectrum of the crude product gave a relative ratio of 87:13. Purification by silica gel chromatography using petroleum ether:ethyl acetate (5:1) as the eluent gave **12** (0.587 g, 70%) as a viscous oil: IR (NaCl) ν_{max} 1969, 1885 cm^{-1}; ^1H NMR for **12a** δ 5.84 (s, 1H), 5.56 (m, 1H), 5.56 (m, 1H), 5.42 (d, *J* = 6.4, 1H), 5.14 (m, 1H), 4.21 (m, 1H), 4.18 (m, 1H), 3.61 (m, 2H), 3.53 (m, 2H), 3.43 (s, 3H), 3.36 (s, 3H), 0.37 (s, 9H); for **12b** (diagnostic peaks only) δ 5.83 (s, 1H), 5.64 (d, *J* = 6.4), 3.40 (s, 3H), 0.39 (s, 9H); ^{13}C NMR for **12a** δ 232.8, 113.2, 101.3, 99.6, 98.6, 94.5, 90.4, 88.4, 78.2, 78.1, 72.9, 72.7, 59.6, 59.4, 0.5; for **12b** (diagnostic peaks only) δ 101.2, 99.5, 94.4, 90.6, 88.6, 78.0, 77.7, 72.5, 59.43, 59.27; MS *m/e* (50 eV) 446 (M^+), 362 ($M^+ - 3CO$); HRMS *m/e* for $C_{19}H_{26}CrO_7Si$ calcd (M^+) 446.0852, found 446.0860.

(4*R*,5*R*)-[4,5-Bis(1-methoxy-1-methylethyl)-2-phenyl-1,3-

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(27) A referee has suggested that the most accessible oxygen lone pairs are on the *pro-S* side of the acetal and that coordination of the first equivalent of alkyllithium (**23**) is there (and is unproductive). Alternatively, it may be possible for the acetal auxiliary of **3** to use three of the four oxygen atoms to coordinate the first equivalent of alkyllithium base in a tridentate manner (**24**) analogous to that of triamines such as *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMTDA).[29] In either case, addition fo a second equivalent of base could result in the use of the more appropriately situated acetal oxygen atoms to effect deprotonation of the arene ring (**25**).

(28) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 536 and references therein.

(29) For examples of triamines behaving as tridentate ligands toward alkyllithiums, see ref 24a and: (a) Fraenkel, G.; Winchester, W. R. *J. Am. Chem. Soc.* **1988**, *110*, 8720. (b) Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371. (c) Lappert, M. F.; Engelhardt, L. M.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1323. (d) Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Chem. Commun.* **1986**, 969. (e) Schumann, U.; Kopf, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 215; *Angew. Chem.* **1985**, *97*, 222.

(30) According to MMX (PC-MODEL) calculations.

(31) Winkle, M. R.; Lansinger, J. M.; Ronald, R. C. *J. Chem. Soc., Chem. Commun.* **1980**, 87.

(32) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

(33) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

dioxolane]tricarbonylchromium(0) (3). A mixture of **10** (1.47 g, 5 mmol), $Cr(CO)_6$ (2.20 g, 10 mmol), di-*n*-butyl ether (10 mL), and THF (1 mL) was heated to reflux for 24 h. The mixture was cooled and filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether:ethyl acetate (5:1) as the eluent. The resulting yellow solid was recrystallized from petroleum ether–Et_2O to afford **3** as yellow prisms (1.90 g, 88%): mp 81–83 °C; $[\alpha]^{26.5}_D$ −7.4° (*c* 0.81, $CHCl_3$); IR (KBr) ν_{max} 1968, 1887, 1870 cm^{-1}; ^{1}H NMR δ 5.69 (s, 1H), 5.60–5.55 (m, 2H), 5.30–5.25 (m, 3H), 4.18 (d, J = 3.5, 1H), 3.98 (d, J = 3.5, 1H), 3.22 (s, 3H), 3.19 (s, 3H), 1.28 (s, 3H), 1.17 (s, 3H), 1.15 (s, 3H), 1.12 (s, 3H); ^{13}C NMR 232.3, 107.2, 103.0, 92.4, 91.9, 91.4, 91.2, 84.9, 82.9, 77.2, 75.5, 49.2, 21.2, 20.9, 19.5; MS *m/e* (30 eV) 430 (M^+), 374 ($M^+ - 2CO$), 346 ($M^+ - 3CO$). Anal. Calcd for $C_{20}H_{26}CrO_7$: C, 55.81; H, 6.09. Found: C, 55.72; H, 6.13.

Conditions for the Lithiation of 3. To a solution of **3** (108 mg, 0.25 mmol) in dry Et_2O (4 mL) at −30 °C was added *n*-BuLi (0.32 mL of a 1.9 M solution in hexanes, 0.060 mmol) over a period of 1.5 h using a syringe pump. After addition, the solution was stirred at −30 °C for 3 h. Following addition of the electrophile (0.60 mmol), the solution was stirred for 1 h and allowed to warm to room temperature over 1 h. The solvent was removed under reduced pressure and the residue diluted with water and extracted with CH_2Cl_2. The CH_2Cl_2 layer was dried over $MgSO_4$ and concentrated under reduced pressure.

(1′*R*,2′*S*,4*R*,5*R*)-[4,5-Bis(1-methoxy-1-methylethyl)-2-(2′-(trimethylsilyl)phenyl)-1,3-dioxolane]tricarbonylchromium(0) (13a) and (1′*S*,2′*R*,4*R*,5*R*)-[4,5-Bis(1-methoxy-1-methylethyl)-2-(2′-(trimethylsilyl)phenyl)-1,3-dioxolane]tricarbonylchromium(0) (13b). Addition of chlorotrimethylsilane to a solution of lithiated **3** (0.25 mmol) followed by standard workup resulted in a crude product whose ^{1}H NMR spectrum revealed a resonance at δ 6.01 (**13a**) and δ 5.96 (**13b**) with a relative integral of 93:7. Purification by silica gel chromatography using petroleum ether:ethyl acetate (5:1) as the eluent gave sequentially **13a** (97 mg, 77%) and **13b** (5 mg, 4%).

13a: mp 164–165 °C (petroleum ether–Et_2O); $[\alpha]^{26.5}_D$ −25° (*c* 0.84, $CHCl_3$); IR (KBr) ν_{max} 1965, 1894, 1880 cm^{-1}; ^{1}H NMR δ 6.01 (s, 1H), 5.56 (d, J = 3.3, 2H), 5.41 (d, J = 6.4, 1H), 5.08 (m, 1H), 4.19 (d, J = 3.3, 1H), 3.94 (d, J = 3.3, 1H), 3.20 (s, 3H), 3.19 (s, 3H), 1.32 (s, 3H), 1.15 (s, 3H), 1.10 (s, 3H), 1.06 (s, 3H), 0.35 (s, 9H); ^{13}C NMR δ 233.1, 113.8, 101.6, 100.3, 98.8, 95.2, 89.9, 88.2, 84.8, 82.2, 77.7, 75.6, 49.6, 49.3, 22.5, 21.3, 21.2, 19.3, 0.52; MS *m/e* (30 eV) 502 (M^+), 446 ($M^+ - 2CO$), 418 ($M^+ - 3CO$). Anal. Calcd for $C_{23}H_{34}CrO_7Si$: C, 54.96; H, 6.82. Found: C, 54.82; H, 6.93.

13b: mp 162–164 °C (petroleum ether–Et_2O); $[\alpha]^{26.5}_D$ +44° (*c* 0.43, $CHCl_3$); IR (KBr) ν_{max} 1963, 1893, 1870 cm^{-1}; ^{1}H NMR δ 5.96 (s, 1H), 5.88 (d, J = 6.3, 1H), 5.50 (apparent t, J = 6.3, 1H), 5.28 (d, J = 6.3, 1H), 5.17 (apparent t, J = 6.3, 1H), 4.19 (d, J = 3.8, 1H), 3.98 (d, J = 3.8, 1H), 3.23 (s, 3H), 3.20 (s, 3H), 1.29 (s, 3H), 1.27 (s, 3H), 1.22 (s, 3H), 1.09 (s, 3H), 0.39 (s, 9H); ^{13}C NMR δ 233.0, 113.5, 102.3, 98.1, 94.0, 91.6, 90.6, 85.4, 82.9, 77.8 (in C_6D_6, obscured in $CDCl_3$), 75.8, 49.3, 49.0, 22.7, 21.6, 21.3, 20.0, 0.47; MS *m/e* (30 eV) 502 (M^+), 446 ($M^+ - 2CO$), 418 ($M^+ - 3CO$). Anal. Calcd for $C_{23}H_{34}CrO_7Si$: C, 54.96; H, 6.82. Found: C, 55.17; H, 6.86.

(1′*R*,2′*R*,4*R*,5*R*)-[4,5-Bis(1-methoxy-1-methylethyl)-2-(2′-methylphenyl)-1,3-dioxolane]tricarbonylchromium(0) (14a). Sequential addition of THF (9.5 mL) and iodomethane to a solution of lithiated **3** (1.21 mmol) followed by standard workup resulted in a crude product whose ^{1}H NMR spectrum revealed a resonance at δ 5.97 (**14a**) and δ 6.02 (**14b**) with a relative integral of 96:4. Purification by silica gel chromatography using petroleum ether:ethyl acetate (5:1) as the eluent followed by recrystallization from petroleum ether–Et_2O gave **14a** (335 mg, 62%) as yellow prisms: mp 84–86 °C; $[\alpha]^{26.5}_D$ −63.7° (*c* 2.29, $CHCl_3$); IR (NaCl) ν_{max} 1970, 1890, 1856 cm^{-1}; ^{1}H NMR δ 5.97 (s, 1H), 5.86 (d, J = 6.3, 1H), 5.32 (apparent t, J = 6.3, 1H), 5.15 (apparent t, J = 6.3, 1H), 5.09 (d, J = 6.3, 1H), 4.18 (d, J = 3.3, 1H), 3.99 (d, J = 3.3, 1H), 3.23 (s, 3H), 3.16 (s, 3H), 2.24 (s, 3H), 1.31 (s, 3H), 1.15 (s, 3H), 1.13 (s, 3H), 1.05 (s, 3H); ^{13}C NMR δ 233.0, 106.0, 100.5, 93.6, 93.4, 91.9, 89.3, 84.7, 82.5, 75.6, 49.43, 49.38, 22.1, 21.3, 21.0, 19.4, 18.2; MS *m/e* (40 eV) 444 (M^+), 388 ($M^+ - 2CO$), 360 ($M^+ - 3CO$). Anal. Calcd for $C_{21}H_{28}CrO_7$: C, 56.75; H, 6.35. Found: C, 56.56; H, 6.42.

(1′*R*,2′*S*,4*R*,5*R*)-[4,5-Bis(1-methoxy-1-methylethyl)-2-(2′-(2-propenyl)phenyl)-1,3-dioxolane]tricarbonylchromium(0) (15a). Addition of allyl bromide to a solution of lithiated **3** (0.271 mmol) followed by standard workup resulted in a crude product whose ^{1}H NMR spectrum revealed a resonance at δ 6.05 (**15a**) and δ 6.02 (**15b**) with a relative integral of 96:4. Purification by silica gel chromatography using petroleum ether:ethyl acetate (5:1) as the eluent followed by recrystallization from hexanes gave **15a** (73.8 mg, 67%) as yellow prisms: mp 114–115 °C; $[\alpha]^{26.5}_D$ +10° (*c* 0.481, $CHCl_3$); IR (NaCl) ν_{max} 1968, 1887 cm^{-1}; ^{1}H NMR δ 6.05 (s, 1H), 5.95 (m, 1H), 5.40 (dd, J = 1.1, 6.5, 1H), 5.34 (apparent dt, J = 1.1, 6.3, 1H), 5.23 (d, J = 6.4, 1H), 5.13–5.21 (m, 3H), 4.19 (d, J = 3.3, 1H), 4.01 (d, J = 3.3, 1H), 3.40 (d of $^1/_2$ABq, J = 6.5, 15.4, 1H), 3.24 (s, 3H), 3.19 (s, 3H), 3.19 (d of $^1/_2$ABq, J = 7.2, 15.4, 3H), 1.33 (s, 3H), 1.18 (s, 3H), 1.15 (s, 3H), 1.08 (s, 3H); ^{13}C NMR δ 232.8, 135.2, 118.0, 110.1, 106.1, 100.1, 92.9, 92.7, 91.2, 89.9, 84.7, 82.4, 75.5 (two resonances, accidental overlap), 49.4, 49.3, 35.5, 22.3, 21.2, 21.1, 19.3; MS *m/e* (25 eV) 470 (M^+), 386 ($M^+ - 3CO$). Anal. Calcd for $C_{23}H_{30}CrO_7$: C, 58.72; H, 6.43. Found: C, 58.91; H, 6.54.

(1′*R*,2′*S*,4*R*,5*R*)-[2-(2′-(*N*,*N*′-Diethylcarbamoyl)phenyl)-4,5-bis(1-methoxy-1-methylethyl)-1,3-dioxolane]tricarbonylchromium(0) (16a). Addition of diethylcarbamyl chloride to a solution of lithiated **3** (0.233 mmol) followed by standard workup resulted in a crude product whose ^{1}H NMR spectrum revealed a resonance at δ 5.89 (**16a**) and δ 5.99 (**16b**) with a relative integral of 96:4. Purification by silica gel chromatography using petroleum ether:ethyl acetate (5:1) as the eluent followed by recrystallization from hexanes gave **16a** (91.5 mg, 74%) as yellow prisms: mp 138–140 °C dec; $[\alpha]^{26.5}_D$ −111° (*c* 0.161, $CHCl_3$); IR (KBr) ν_{max} 1980, 1907, 1894, 1641 cm^{-1}; ^{1}H NMR δ 5.89 (s, 1H), 5.58 (dd, J = 6.5, 0.8, 1H), 5.41 (dd, J = 0.9, 6.2, 1H), 5.31 (apparent t, J = 6.4, 1H), 5.17 (apparent dt, J = 1.0, 6.2, 1H), 4.14 (d, J = 3.4, 1H), 4.01 (d, J = 3.4, 1H), 3.37 (m, 1H), 3.20 (s, 3H), 3.19 (s, 3H), 3.07 (m, 1H), 1.05–1.25 (m, 6H); ^{13}C NMR δ 231.5, 163.5, 112.0, 104.8, 100.3, 91.8, 90.6, 87.3, 85.5, 84.6, 82.6, 77.0, 75.4, 49.4, 49.2, 43.5, 39.7, 22.3, 21.4, 20.7, 19.4, 13.9, 11.9; MS *m/e* (25 eV) 529 (M^+), 445 ($M^+ - 3CO$). Anal. Calcd for $C_{25}H_{35}CrNO_8$: C, 56.70; H, 6.66; N, 2.65. Found: C, 56.50; H, 6.68; N, 2.62.

(1′*R*,2′*S*,4*R*,5*R*)-[4,5-Bis(1-methoxy-1-methylethyl)-2-(2′-(phenylthio)phenyl)-1,3-dioxolane]tricarbonylchromium(0) (17a). Addition of a solution of phenyl disulfide in THF (10 mL) to a solution of lithiated **3** (3.09 mmol) followed by standard workup resulted in a crude product whose ^{1}H NMR spectrum revealed a resonance at δ 6.34 (**17a**) and δ 6.12 (**17b**) with a relative integral of 96:4. Purification by silica gel chromatography using petroleum ether:ethyl acetate (5:1) as the eluent followed by recrystallization from hexanes gave **17a** (1.3796 g, 83%) as yellow prisms: mp 142–143 °C; $[\alpha]^{26.5}_D$ +245° (*c* 0.634, $CHCl_3$); IR (KBr) ν_{max} 1970, 1905 cm^{-1}; ^{1}H NMR δ 7.50–7.53 (m, 2H), 7.26–7.37 (m, 3H), 6.34 (s, 1H), 5.83 (dd, J = 1.6, 6.2, 1H), 5.19–5.28 (m, 2H), 5.13 (dd, J = 1.4, 6.3, 1H), 4.22 (d, J = 3.4, 1H), 4.06 (d, J = 3.4, 1H), 3.26 (s, 3H), 3.19 (s, 3H), 3.07 (m, 1H), 1.34 (s, 3H), 1.17 (s, 3H), 1.16 (s, 3H), 1.11 (s, 3H); ^{13}C NMR δ 231.9, 133.6, 132.8, 129.3, 128.3, 108.1, 107.7, 100.8, 95.3, 91.8, 90.3, 89.9, 84.6, 82.9, 77.2, 75.5, 49.44, 49.38, 22.2, 21.4, 20.9, 19.6; MS *m/e* (25 eV) 538 (M^+), 454 ($M^+ - 3CO$). Anal. Calcd for $C_{25}H_{35}CrNO_8$: C, 57.98; H, 5.61. Found: C, 58.18; H, 5.67.

(1′*R*,2′*R*,4*R*,5*R*)-[4,5-Bis(1-methoxy-1-methylethyl)-2-(2′-(tri-*n*-butylstannyl)phenyl)-1,3-dioxolane]tricarbonylchromium(0) (18a). Addition of tri-*n*-butylstannyl chloride to a solution of lithiated **3** (0.25 mmol) followed by standard workup resulted in a crude product whose ^{1}H NMR spectrum revealed a resonance at δ 5.65 (**18a**) and δ 5.93 (**18b**) with a relative integral of 95.5:4.5. Purification by silica gel chromatography using petroleum ether:ethyl acetate (9:1) as the eluent gave **18a** (132 mg, 73%) as a viscous yellow liquid: $[\alpha]^{26.5}_D$ +3.5° (*c* 2.01, $CHCl_3$); IR (neat, NaCl) ν_{max} 1964, 1888 cm^{-1}; ^{1}H NMR δ 5.65 (s, 1H), 5.57 (d, J = 6.1, 1H), 5.49 (apparent t, J = 6.1, 1H), 5.31 (d, J = 6.1, 1H), 5.10 (apparent t, J = 6.1, 1H), 4.16 (d, J = 3.3, 1H), 3.96 (d, J = 3.3, 1H), 3.20 (s, 3H), 3.18 (s, 3H), 1.60–1.50 (m, 6H), 1.40–1.25 (m, 10H), 1.22–1.0 (m, 14H), 0.95–0.85 (m, 9H); ^{13}C NMR δ 233.5, 114.3, 103.9, 101.5, 99.4, 94.6, 91.2, 89.5, 84.9, 82.3, 77.5 (in C_6D_6, obscured in $CDCl_3$), 75.5, 49.6, 49.4, 28.7, 27.4, 22.5, 21.2, 21.0, 18.9, 13.6, 11.4; MS *m/e* (70 eV) 720 (M^+, Sn^{120}), 465

($M^+ - 2CO - 3Bu$); HRMS *m/e* for $C_{32}H_{52}CrO_7Sn^{120}$ calcd (M^+) 720.2139, found 720.2148.

(1′*R*,2′*R*,4*R*,5*R*)-[2-(2′-Bromophenyl)-4,5-bis(1-methoxy-1-methylethyl)-1,3-dioxolane]tricarbonylchromium(0) (19a). Addition of dibromoethane to a solution of lithiated **3** (0.878 mmol) followed by standard workup resulted in a crude product whose ^1H NMR spectrum revealed a resonance at δ 6.03 (**19a**) and δ 6.11 (**19b**) with a relative integral of 94:6. Purification by silica gel chromatography using petroleum ether:ethyl acetate (9:1) as the eluent followed by recrystallization from petroleum ether–Et_2O gave **19a** (305 mg, 68%) as yellow prisms: mp 66–68 °C; $[\alpha]^{26.5}_D$ −57° (*c* 0.94, $CHCl_3$); IR (KBr) ν_{max} 1973, 1918, 1893 cm^{-1}; ^1H NMR δ 6.03 (s, 1H), 5.86 (d, *J* = 6.2, 1H), 5.48 (d, *J* = 6.2, 1H), 5.28 (apparent t, *J* = 6.2, 1H), 5.10 (apparent t, *J* = 6.2, 1H), 4.21 (d, *J* = 3.2, 1H), 4.04 (d, *J* = 3.2, 1H), 3.24 (s, 3H), 3.16 (s, 3H), 1.31 (s, 3H), 1.15 (s, 3H), 1.14 (s, 3H), 1.09 (s, 3H); ^{13}C NMR δ 231.3, 105.2, 102.3, 99.0, 94.4, 92.4, 91.4, 88.5, 84.7, 83.1, 77.2, 75.5, 49.4, 22.1, 21.4, 20.7, 19.7; MS *m/e* (40 eV) 508 (M^+), 452 ($M^+ - 2CO$), 424 ($M^+ - 3CO$). Anal. Calcd for $C_{20}H_{25}BrCrO_7$: C, 47.16; H, 4.95. Found: C, 47.16; H, 5.21.

(1′*R*,2′*S*,4*R*,5*R*)-[2-(2′-(Diphenylphosphino)phenyl)-4,5-bis(1-methoxy-1-methylethyl)-1,3-dioxolane]tricarbonylchromium(0) (20a). Addition of chlorodiphenylphosphine to a solution of lithiated **3** (0.25 mmol) was followed by standard workup. No peaks attributable to the product derived from deprotonation of the alternate *ortho* position could be observed in the ^1H NMR spectrum of the crude reaction product. Purification by silica gel chromatography using petroleum ether:ethyl acetate (9:1) as the eluent followed by recrystallization from petroleum ether–Et_2O gave **20a** (106 mg, 69%) as yellow prisms: mp 153–155 °C; $[\alpha]^{26.5}_D$ +166° (*c* 3.01, $CHCl_3$); IR (KBr) ν_{max} 1963, 1898, 1882 cm^{-1}; ^1H NMR δ 7.45–7.32 (m, 6H), 7.30–7.20 (m, 4H), 6.55 (d, *J* = 5.6, 1H), 5.66 (dd, *J* = 6.3, 1.5, 1H), 5.51 (apparent t, *J* = 6.3, 1H), 5.02 (apparent t, *J* = 6.3, 1H), 4.84 (d, *J* = 6.3, 1H), 3.95 (s, 2H), 3.23 (s, 3H), 3.05 (s, 3H), 1.30 (s, 3H), 1.14 (s, 3H), 0.85 (s, 3H), 0.76 (s, 3H); ^{13}C NMR δ 231.9, 135.1, 134.8, 133.5, 133.2, 129.6, 128.6, 128.4, 128.1, 113.5, 100.9, 100.7, 97.5, 93.9, 89.6, 87.5, 84.3, 82.8, 77.8 (in acetone-d_6, obscured in $CDCl_3$), 75.3, 49.5, 49.4, 22.1, 21.5, 21.1, 19.3; MS *m/e* (30 eV) 530 ($M^+ - 3CO$). Anal. Calcd for $C_{32}H_{35}CrO_7P$: C, 62.54; H, 5.74. Found: C, 62.33; H, 5.79.

(−)-(η^6-2-Methylbenzaldehyde)tricarbonylchromium(0) (−)-(21). A mixture of **14a** (67 mg, 0.15 mmol), 60% aqueous H_2SO_4 (0.5 mL), and benzene (5 mL) was stirred vigorously at room temperature for 48 h. The mixture was diluted with water and extracted with CH_2Cl_2. The CH_2Cl_2 layer was dried over $MgSO_4$ and concentrated under reduced pressure, and the resulting residue was purified by silica gel chromatography using petroleum ether:ethyl acetate (5:1) as the eluent to give sequentially **21** (25 mg, 65%) and starting **14a** (11 mg, 16% recovery). **21**: red needles; mp 98–99 °C (petroleum ether–Et_2O) (lit.[23] 99–100 °C); $[\alpha]^{26.5}_D$ −628° (*c* 0.25, $CHCl_3$) (lit.[23] $[\alpha]^{20}_D$ −664° (*c* 0.26, $CHCl_3$).

(4*R*,5*R*)-[4,5-Bis(methoxymethyl)-2-(2′-methylphenyl)-1,3-dioxolane]tricarbonylchromium(0) (22a/b). To a solution of lithiated **2** (0.83 mmol) at −78 °C was slowly added THF (7 mL) followed by MeI (290 mg, 0.20 mmol). The solution was stirred at −78 °C for 1 h and allowed to warm to room temperature over 1 h. The solvent was then removed under reduced pressure, and the residue was diluted with water and extracted with CH_2Cl_2. The CH_2Cl_2 layer was dried over $MgSO_4$ and concentrated under reduced pressure. Integration of the δ 5.82 resonance of **22a** and the δ 5.91 resonance of **22b** in the ^1H NMR spectrum of the crude product gave a relative ratio of 73:27. Purification by silica gel chromatography using petroleum ether:ethyl acetate (5:1) as the eluent gave **22** (237.2 mg, 74%) as a viscous oil: IR (NaCl) ν_{max} 1963, 1887, 1871 cm^{-1}; ^1H NMR for **22a** δ 5.82 (s, 1H), 5.85 (dd, *J* = 6.6, 1.1, 1H), 5.40 (apparent dt, *J* = 1.2, 6.3, 1H), 5.14 (apparent dt, *J* = 6.4, 0.9, 1H), 5.07 (d, *J* = 6.3, 1H), 4.19 (m, 1H), 4.13 (m, 1H), 3.61 (m, 2H), 3.64 (m, 2H), 3.56 (s, 3H), 3.38 (s, 3H), 2.27 (s, 3H); for **22b** (diagnostic peaks only) δ 5.91 (dd, *J* = 6.5, 0.9, 1H), 3.42 (s, 3H); ^{13}C NMR for **22a** δ 232.6, 108.9, 104.7, 100.2, 94.2, 92.6, 92.5, 88.5, 78.6, 77.7, 72.6, 72.4, 59.5, 59.3, 18.2; for **22b** (diagnostic peaks only) δ 109.0, 104.5, 99.9, 94.5, 92.7, 92.4, 88.2, 72.5, 72.2, 59.4, 18.1; MS *m/e* (70 eV) 388 (M^+), 304 ($M^+ - 3CO$); HRMS *m/e* for $C_{17}H_{20}CrO_7$ calcd (M^+) 388.0620, found 388.0614.

Hydrolysis of 22. A mixture of **22** (118 mg, 0.31 mmol), 60% aqueous H_2SO_4 (1.0 mL), and benzene (10 mL) was stirred vigorously at room temperature for 7 h. The mixture was diluted with water and extracted with CH_2Cl_2. The CH_2Cl_2 layer was dried over $MgSO_4$ and concentrated under reduced pressure, and the resulting residue was purified by silica gel chromatography using petroleum ether:ethyl acetate (5:1) as the eluent to give **8** (35 mg, 43%): $[\alpha]^{26.5}_D$ −350° (*c* 0.25, $CHCl_3$) (lit.[23] $[\alpha]^{20}_D$ −664° (*c* 0.26, $CHCl_3$)).

Acknowledgment. We are grateful for the Natural Sciences and Engineering Research Council (NSERC) of Canada for financial support. We also wish to thank the staff of the Central Instruments Facility of Wayne State University for the high-resolution mass spectral work.

Supplementary Material Available: Procedure for the preparation of **4–6** and **8–10** and copies of the NMR spectra of **2**, **12a/b**, **15a**, and **22a/b** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.