22837-81-6; (Z)-5k, 141171-98-4; (E)-5k, 93863-65-1; 8, 3506-84-1; 9, 70067-70-8; α11b, 141171-99-5; α12c, 141172-00-1; α13d, 141172-01-2; α14e, 141172-02-3; (E)-β14j, 3901-07-3; α15f, 3174-83-2; (E)-β15f, 770-36-5; α15h, 530-48-3; (E)-β15h, 103-30-0; α16l, 586-39-0; α17i, 141172-03-4; (E)-β17i, 141172-04-5; 18, 122-00-9; 19, 104-20-1; DPPF, 12150-46-8; DPPP, 6737-42-4; DPPB, 7688-25-7; DPPE, 1663-45-2; $CH_3CO_2H \cdot {}^1/_2Pd(II)$, 3375-31-3; 4-$CNC_6H_4OSO_2CF_3$, 66107-32-2; 3-$AcC_6H_4OSO_2CF_3$, 138313-22-1; 4-$MeOC_6H_4OSO_2CF_3$, 66107-29-7; $PhOSO_2CF_3$, 17763-67-6; 3-$NO_2C_6H_4OSO_2CF_3$, 32578-25-9; 3-$CNC_6H_4OSO_2CF_3$, 66152-74-7; 4-$MeC_6H_4OSO_2CF_3$, 29540-83-8; 3-$M3C_6H_4OSO_2CF_3$, 32578-31-7; Ph_3P, 603-35-0.

Supplementary Material Available: Complete characterization of compounds (E)-5h, 8, and α15f (1 page). Ordering information is given on any current masthead page.

Asymmetric Deprotonation and Complexation Reactions Mediated by Chiral Ketals as a Route to Ortho-Disubstituted (η^6-Arene)$Cr(CO)_3$ Complexes

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Received December 17, 1991

A series of chiral ketals derived from an aryl ketone or aldehyde and one of several C_2-symmetrical diols were converted to their corresponding (η^6-arene)$Cr(CO)_3$ complexes. The resultant 1,3-dioxolanes were trans substituted at C-4 and C-5 by groups CH_2X, where X = H (1), OCH_3 (2), or $N(CH_3)_2$ (3). Ortho deprotonation was attempted on complexes 1–3 using *tert*-butyllithium in THF solution to afford the corresponding lithio derivatives, which were treated with a variety of electrophiles ($MeOSO_2F$, TMSCl, $Ph_2C(O)$, Ph_2PCl). Although 1 gave a complex mixture of products, complexes 2 and 3 afforded good yields of disubstituted complexes (with the exception that the lithiated derivative of 3 did not undergo methylation when treated with $MeOSO_2F$). The stereoselectivity of the reactions was determined by NMR spectroscopy and found to be in the range of 3:1 for 2 and >9:1 for 3. The sense of diastereoselection were identified by chemical correlations (for compounds derived from 2) and by circular dichroism spectroscopy. Poor diastereoselection was obtained when this protocol was performed on the corresponding acetal ultimately derived from benzaldehyde and *N,N,N',N'*-tetramethyl-1,4-diamino-2,3-butanediol. In addition, a related series of ortho-disubstituted arenes bearing chiral ketal or acetal substituents in the benzylic position were subjected to complexation reactions with (naphthalene)$Cr(CO)_3$ in dibutyl ether. The best diastereoselectivity observed with this methodology was 48%, obtained with the acetal derived from *o*-tolualdehyde and *N,N,N',N'*-tetramethyltartramide.

Chromium arene complexes are valuable because they provide templates for the stereoselective elaboration of side chains and significantly modify the chemical reactivity of the attached arene.[1] The former results from the size of the chromium ligand and the tendency of side chains to adopt particular reactive conformations, whereas the electronic properties of the chromium facilitate either nucleophilic or electrophilic processes at the arene itself (mediated by deprotonation by or addition of organolithium reagents). A number of groups have established the particular utility of optically active η^6-arene chromium complexes for a variety of synthetic application.[2]

A bottleneck in the utilization of this chemistry by synthetic chemists has been the need for improved access to chiral complexes in optically active form. Traditionally, such materials have been obtained using resolution and recrystallization techniques;[2] recently reported variations on this theme include the kinetic resolution of η^6-arene chromium complexes bearing carbonyl-containing side chains using microbial techniques[3] or diastereomeric imine formation reactions.[4] More recently, diastereoselective deprotonation reactions of η^6-arene chromium complexes containing a chiral side chain have been utilized as a route to complexes having an element of planar dissymmetry.[5] These methods have ample precedent in ferrocene chemistry.[6] A complementary approach involves the stereoselective complexation of ortho-disubstituted benzene derivatives having a stereogenic center on one of the side chains; precomplexation with the chromium donor results in the diastereoselective delivery of the $Cr(CO)_3$ group to one of the diastereotopic faces of the arene unit.[1c,7] We have shown that the deprotonation/alkylation method can result in the formation of the opposite diastereomeric complex obtained in the complexation method.[5c]

These complementary methods are limited to substrates containing side chains which (1) are good promoters of ortho lithiation reactions or (2) effectively complex with chromium tricarbonyl donors and afford useful levels of selectivity in the arene complexation reactions. Additionally, (3) units employed in such methods must be nonreactive themselves to highly basic and nucleophilic organolithium species. It is also desirable that the aromatic

† Department of Medicinal Chemistry.

(1) Reviews: (a) Solladié-Cavallo, A. *Polyhedron* **1985**, *4*, 901–927. (b) Schlögl, K. *J. Organomet. Chem.* **1986**, *300*, 219–248. (c) Uemura, M. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI: Greenwich, CT, 1991; Vol. 2, pp 195–245.

(2) For review, see: Solladié-Cavallo, A. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI: Greenwich, 1989; Vol. 1; pp 99–133.

(3) (a) Gillois, J.; Buisson, D.; Azerad, R.; Jaouen, G. *J. Chem. Soc., Chem. Commun.* **1988**, 1224–1225. (b) Top, S.; Jaouen, G.; Gillois, J.; Baldoli, C.; Maiorana, S. *J. Chem. Soc., Chem. Commun.* **1988**, 1284–1285.

(4) (a) Davies, S. G.; Goodfellow, C. L. *Synlett* **1989**, 59–62. (b) Davies, S. G.; Goodfellow, C. L. *J. Chem. Soc., Perkin Trans. 1* **1989**, 192–194.

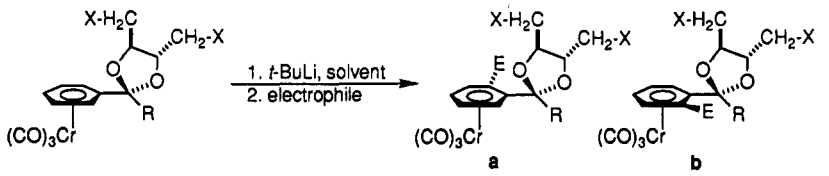
(5) (a) Blagg, J.; Davies, S. G.; Goodfellow, C. L.; Sutton, K. H. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1805–1811. (b) Heppert, J. A.; Thomas-Miller, M. E.; Milligan, M. L.; Vander Velde, D.; Aubé, J. *Organometallics* **1988**, *7*, 2581–2584. (c) Heppert, J. A.; Aubé, J.; Thomas-Miller, M. E.; Milligan, M. L.; Takusagawa, F. *Organometallics* **1990**, *9*, 727–739.

(6) For some examples, see: (a) Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5389–5393. (b) Pastor, S. D. *Tetrahedron* **1988**, *44*, 2883–2886.

(7) (a) Uemura, M.; Kobayashi, T.; Isobe, K.; Minami, T.; Hayashi, Y. *J. Org. Chem.* **1986**, *51*, 2859–2863. (b) Uemura, M.; Minami, T.; Hirotsu, K.; Hayashi, Y. *J. Org. Chem.* **1989**, *54*, 469–477.

0022-3263/92/1957-3563$03.00/0

Table I. Diastereoselective Deprotonation/Alkylation Reactions

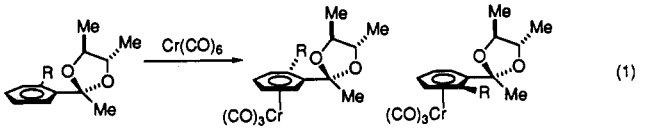


entry	starting material compd	R	X	solvent	electrophile	product compd	E	yield, %	a:b[a]
1	1[b]	CH_3	H	THF	CH_3SO_2F			nd[c]	
2	2	CH_3	OCH_3	THF	CH_3SO_2F	5	CH_3	79	75:25
3	2			Et_2O[d]	CH_3SO_2F	5		nd[e]	64:36
4	2			THF	$(CH_3)_3SiCl$	6	$Si(CH_3)_3$	82	78:22
5	2			THF	Ph_2PCl	7	PPh_2	74	79:21
6	3	CH_3	$N(CH_3)_2$	THF	$(CH_3)_3SiCl$	8	$Si(CH_3)_3$	62[f]	94:6
7	3			Et_2O[d]	$(CH_3)_3SiCl$	8		61	11:89
8	3			THF	Ph_2PCl	9	PPh_2	85	94:6
9	3			THF	$Ph_2C{=}O$	10	$C(OH)Ph_2$	80	98:2[g]
10	4	H	$N(CH_3)_2$	THF	$(CH_3)_3SiCl$	11	$Si(CH_3)_3$	64	56:44[h]

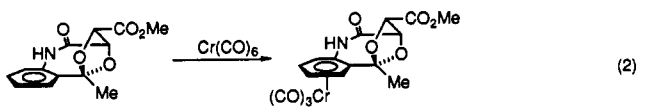
[a] Ratios determined by ^1H NMR integration of crude reaction mixtures (except where noted). Assignment of diastereomer stereochemical structures made by chemical correlation or circular dichroism studies; see text. [b] The enantiomer of 1 shown in Table I was used. [c] nd = not determined. Poor recovery of multiple products (not characterized). [d] A few drops of THF were added to solubilize lithiated intermediates. [e] Incomplete reaction. [f] In addition, 2',6'-disubstituted product was isolated in 21% yield. [g] Ratio determined after column chromatography. [h] Assignments may be reversed.

precursor be readily available in optically active form. We wished to determine whether chiral ketals or acetals, which are easily synthesized from C_2-symmetrical diols and aromatic ketones, could be used as directing groups in the synthesis of arene chromium complexes. Chiral ketals have been used to mediate a number of diastereoselective transformations, including cyclopropanation processes and various alkylation reactions.[8]

Two groups have attempted the stereoselective complexation of ortho-substituted aryl ketals with $Cr(CO)_6$. Solladié-Cavallo et al.[9] were unable to achieve greater than 20% de in the reactions of the ketal derived from (*S*,*S*)-(+)-butanediol (eq 1). In contrast, Levine and coworkers successfully accomplished the diastereoselective complexation of a more highly restricted complex in ca. 50:1 ratio (42% yield after recrystallization; eq 2).[10] In



(1)



(2)

related work, a chiral acetal derivative of (benzaldehyde)$Cr(CO)_3$ underwent a stereoselective methylation reaction at the benzylic position in a synthesis of (*R*)-*N*-acetyl-1-phenylethylamine.[11] Very recently, Green and co-workers reported the stereoselective deprotonation of arene chromium complexes bearing chiral acetal side chains.[12] Herein, we report the synthesis and asymmetric deprotonation chemistry of a series of η^6-arene chromium complexes bearing chiral ketal substituents as a complement to these previous approaches. We were particularly interested in assessing how the addition of coordinating groups on the ketal affects the selectivity of the ortho deprotonation reactions. The complexation behavior of some ketals derived from ortho-substituted arenes and the circular dichroism spectra of some of the products will also be discussed.

Results and Discussion

Diastereoselectivity of Deprotonation/Alkylation Reactions. A series of ketals and acetals systematically modified at ketal positions C-4 and C-5 were synthesized according to the standard routes summarized in Scheme I (see the Experimental Section for the preparations of 1–4 and the supplementary material for details of reaction sequences not directly involving chromium). Note that the chirality in each substrate is ultimately derived from diethyl tartrate, which is inexpensive and commercially available in either enantiomeric form.

The deprotonation/substitution reactions were carried out as previously reported.[5b,c] Thus, the substrate was deprotonated at −78 °C using *tert*-butyllithium as the base, followed by addition of the electrophile. When carried out in tetrahydrofuran (THF), the lithiation reactions afforded a homogeneous solution of metalated arene chromium complex, which could be quenched with a test electrophile. Although quenching of the anions derived from **3** or **4** with methanefluorosulfonate was problematic, possibly due to competing alkylation at the basic nitrogen ketal, other

(8) For some examples, see: (a) Mash, E. A.; Hemperly, S. B.; Nelson, K. A.; Heidt, P. C.; Van Deusen, S. *J. Org. Chem.* **1990**, *55*, 2045–2055. (b) Mash, E. A.; Hemperly, S. B. *J. Org. Chem.* **1990**, *55*, 2055–2060. (c) Alexakis, A.; Sedrani, P.; Mangeney, P.; Normant, J.-F. *Tetrahedron Lett.* **1988**, *29*, 4411–4414. (d) Alexakis, A.; Mangeney, P.; Ghribi, A.; Marek, I.; Sedrani, P.; Guir, C.; Normant, J.-F. *Pure Appl. Chem.* **1988**, *60*, 49–56. (e) Fujioka, H.; Yamamoto, H.; Kondo, H.; Annoura, H.; Kita, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1509–1511. (f) Isaki, M.; Nakamura, E. *J. Am. Chem. Soc.* **1990**, *112*, 7428–7430. (g) Jung, M. E.; Lew, W. *Tetrahedron Lett.* **1990**, *31*, 623–626. (h) Mash, E. A.; Hemperly, S. B.; Nelson, K. A.; Heidt, P. C.; Van Deusen, S. *J. Org. Chem.* **1990**, *55*, 2045–2055. (i) Eid, C. N., Jr.; Konopelski, J. P. *Tetrahedron Lett.* **1991**, *32*, 461–464. (j) Konopelski, J. P. *Tetrahedron Lett.* **1991**, *32*, 465–466. (k) Myers, A. G.; Harrington, P. M.; Kuo, E. Y. *J. Am. Chem. Soc.* **1991**, *113*, 694–695. (l) Boehler, M. A.; Konopelski, J. P. *Tetrahedron* **1991**, *47*, 4519–4538.

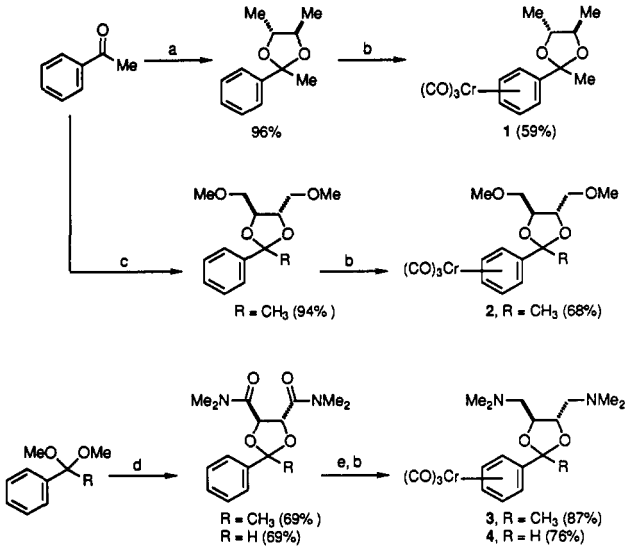
(9) Solladié-Cavallo, A.; Solladié, G.; Tsamo, E. *J. Org. Chem.* **1979**, *44*, 4189–4191.

(10) Stewart, K. R.; Levine, S. G.; Bordner, J. *J. Org. Chem.* **1984**, *49*, 4082–4084.

(11) Davies, S. G.; Newton, R. F.; Williams, J. M. J. *Tetrahedron Lett.* **1989**, *30*, 2967–2970.

(12) Kondo, Y.; Green, J. R.; Ho, J. *J. Org. Chem.* **1991**, *56*, 7199–7201.

Scheme I[a]



[a] Reagents: (a) (*R,R*)-butanediol, *p*-TsOH; (b) $Cr(CO)_6$; (c) (*S,S*)-2,3-bis(methoxymethyl)butanediol, *p*-TsOH; (d) *N,N,N',N'*-tetramethyltartramide, *p*-TsOH; (e) lithium aluminum hydride.

substitution reactions produced the expected arylation products. The results of these experiments are summarized in Table I.

Substrate **1** bearing the ketal derived from (*S,S*)-(+)-butanediol was found ineffective at promoting the ortho-deprotonation reaction. Thus, the NMR spectrum showed a number of produts formed in somewhat equivalent amounts; these materials were not further characterized. Substantial improvements were observed in ketals **2** and **3**, each bearing an additional ligating substituent. In most of these cases, the monosubstituted arene was isolated as the predominant product in the diastereomeric ratios shown (determined by ^1H NMR integration). For **2**, the ratios of ca. 3:1 resulted from attachment of the better coordinating methoxy substituent, whereas the ratios exceeded 9:1 where X = dimethylamino. In addition, an interesting solvent dependence was noted. When run in THF, the conversion **3** → **8** was highly selective, giving product of ≥92% de. When the reaction was carried out in diethyl ether (entry 7), the addition of butyllithium to **3** resulted in formation of a precipitate (presumably the lithiated arene) which could be dissolved upon the addition of a few drops of THF to the reaction mixture. Silylation of the lithium species prepared in this way gave a preponderance of **8b**, which was the minor isomer formed when the arene was lithiated in pure THF. A reduction in the **a**:**b** ratio was observed when this protocol was repeated on ketal **2** (cf. entries 2 and 3), but a reversal in the selectivity was not observed for this case. Although we have not systematically examined this phenomenon, possible explanations include a change in solvation or equilibration of the lithium species prior to addition of electrophile.[12]

Deprotonation of acetal **4** followed by silylation led to isolation of an approximately 1:1 ratio of diastereomers **11a,b**. The benzaldehyde-derived series was not further pursued, partially because of this disappointing result, but also because of the potential for competitive deprotonation at the benzylic position (this possibility was not rigorously investigated in the present case).[5c] Several other types of ketals with the potential to coordinate the base[13] were also

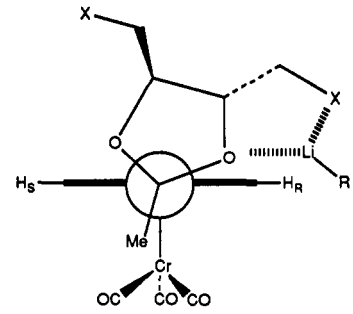


Figure 1. Proposed transition-state model for stereoselective lithiation reaction.

examined, e.g., those substituted at C-4 and C-5 by *N,N*-dimethylcarboxamide,[14] carbethoxy groups, or hydroxymethyl groups O-substituted by methoxymethyl ethers[5c,15] or *N,N*-dimethyl carbamate groups.[14] In no case were better than 2:1 ratios of diastereomers obtained. Finally, the conditions used for reactions of ketal **3** were modified by examining other bases (*n*- or *sec*-butyllithium) with various additives such as TMEDA and HMPA; again, inferior results were obtained.

A drawing of a proposed transition state leading to the observed stereoselectivities is shown in Figure 1. Since our results show that the dioxolane oxygen itself is a poor donor group (Table I, entry 1) and the magnitude of stereochemical induction increases with the Lewis basicity of the distal substituent, it is reasonable to propose that this is due to the formation of a bidentate complex between the ketal group and *t*-BuLi as shown. This effect, which may lead to a tighter transition state, is reminiscent of the greater ability of a benzylic methoxymethyl substituent to effect ortho deprotonation compared to a simple methyl ether.[5c] Due to the pseudo-C_2 symmetry of the ketal moiety, there exist two sites for such chelation in the substrate; however, it seems likely that only that site bearing a side arm syn to the arene ring can deliver the base to the reactive proton in an intramolecular process.[5,13] This sharply contrasts with the observations of the Mash group, who found that Simmons–Smith reagents preferentially undergo coordination to the lone pair trans to a bulky C-4/C-5 dioxolane substituent.[8a,b] In their work, then, it appears that the predominant donor atom is the oxygen in the dioxolane ring, since higher selectivities were found with dimethyl ketals relative to those containing additional coordinating groups.

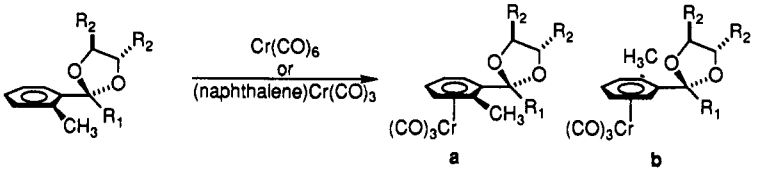
The observed direction of deprotonation requires that the mode of attack be at the *pro-R* proton as depicted. This requires a reactive rotamer in which the coordinated base is poised close to the arene ring. The most probable such rotamer is shown in Figure 1 and additionally places the methyl group in proximity to the chromium tricarbonyl moiety. Apparently the system experiences less steric congestion from the methyl group than would be engendered by alternative rotamers in which components of the ketal group are similarly placed. For example, the rotamer in which the CH_2X substituent trans to the arene eclipses the $Cr(CO)_3$ group would lead to delivery of the base to the *pro-S* proton and afford the diastereomeric product. This model accounts for the dependence of stereoselectivity on the nature of the distal substituent. However, the poor selectivity obtained with acetal **4** remains puzzling because the H substituent should experience less steric congestion with the $Cr(CO)_3$ group than the methyl group shown.

(13) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356–363.

(14) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879–933.

(15) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1–360.

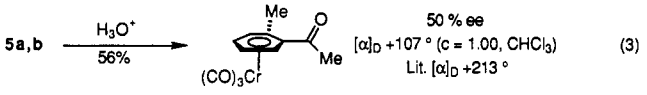
Table II. Complexation Reactions of 2'-Methyl Complexes



entry	starting material: compd	R_2	R_1	condns[a]	product: compd	yield, %	de,[b] %
1	12	CH_2OH	CH_3	A	19	77	6
2	12			B	19	nd[c]	38
3	13	CH_2OMe	CH_3	A	5	43	0
4	14	CO_2Et	CH_3	A	20	69	34
5	15	$CON(Me)_2$	CH_3	B	21	nd	15
6	16	$CON(Me)_2$	H	B	22	61	48
7	17	CH_2NMe_2	CH_3	B	23	nd	0
8	18	CH_2NMe_2	H	B	24	nd	14

[a] Conditions A: $Cr(CO)_6$ as chromium donor and $(n\text{-}Bu)_2O$/THF as solvent. Conditions B: (naphthalene)$Cr(CO)_3$ as chromium donor and THF as solvent. [b] de = diastereomeric excess. Ratios were determined by ^1H NMR integration of crude reaction mixtures. The major stereoisomer of compound **22** is **a** as shown (see text); the identity of the major product in the other entries was not determined. [c] nd = not determined.

Determination of Relative Stereochemistry. The relative stereochemistry of the major stereoisomer formed by the reaction of **2** was determined by removing the chiral ketal under acidic conditions as shown in eq 3. The rotation of the resultant ketone was compared with literature values to establish the absolute configuration of the major alkylation product to be that drawn as **a** (Table I).[16] Also, the magnitude of the rotation provided an additional check on our NMR assessment of the reaction stereoselectivity.



The stereostructures of compounds **8–10** could not be similarly assigned because the ketal group from dimethylamino-substituted ketals could not be removed under a variety of acid-catalyzed conditions (probably due to destabilization of the necessary cationic intermediate by the protonated amine moiety). We therefore resorted to circular dichroism (CD) spectroscopy as depicted in Figure 2. Neither the CD spectra of the ketal-containing ligands nor those of complexes **2** and **3** gave any appreciable Cotton effects over the wavelengths scanned (these spectra are reproduced in the supplementary material). Introduction of planar chirality via 2'-aryl substitution afforded distinctive spectra for both methoxy-substituted ketals (Figure 2, parts a and c) and their dimethylamino analogues (Figure 2, parts b and d), which strongly suggests that the two series are of the same absolute configuration. Although such data should always be interpreted with care,[2,16] the close correspondence of the curves with two sets of identical 2'-substituents is good evidence for our stereochemical assignments.

We did not carry out detailed stereochemical analysis of structures **11a,b** because of the poor ratio of products obtained by the deprotonation of acetal **4**.

Complexation of Prochiral Ketal Substrates. A series of ortho-substituted ketals was briefly examined with respect to complexations by two chromium tricarbonyl donors, $Cr(CO)_6$ or (η^6-naphthalene)$Cr(CO)_3$.[1c,7] The results are collected in Table II. Compounds **12–18** were prepared using standard methods (see the supplementary material).

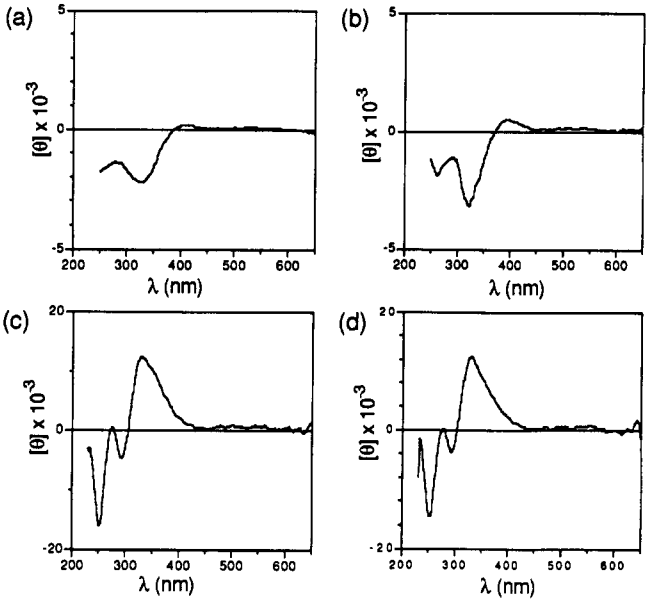


Figure 2. Circular dichroism spectra of 2'-substituted chromium arene complexes. Curves a and b correspond to the 2'-trimethylsilyl series for X = OMe and NMe_2, respectively: (a) Compound **6**. (b) Compound **8**. Curves c and d correspond to the 2'-diphenylphosphinyl series for X = OMe and NMe_2, respectively: (c) Compound **7**. (d) Compound **9**. See Table I for structures.

In short, complexation of the chiral ketals surveyed did not constitute a synthetically useful route to diastereomerically pure 2'-methylphenyl chromium complexes. In contrast to the situation with the deprotonation reactions described above, however, it is interesting to note that the most selective substrate was diamide-substituted *acetal* **16**, which gave substantially better selectivity than the corresponding ketal. The sense of stereoselection in this reaction afforded compound **22a**, as determined by hydrolysis to the corresponding known aldehyde.[16] We note that Uemura and co-workers obtained useful levels of selectivity in complexations using an achiral ketal containing an ortho substituent adorned with a stereogenic center.[7b] The results shown in Table II were sufficiently discouraging that we did not pursue this tack further.

Conclusion. The lithiation of chromium-complexed arenes containing side chains decorated with chiral ketal substituents has been carried out. Superior selectivities

(16) Meyer, A. *Ann. Chim. (Paris)* **1973**, *8*, 397–404.

have been obtained using the ketal bearing a dialkylamino substituent suitably disposed to provide an additional site for chelating the metal. In contrast, chiral complexation reactions were not found to be generally useful for the preparation of the title compounds.

Experimental Section

General. All reactions were carried out with the exclusion of air and moisture through modified Schlenk techniques. Although the organochromium compounds were generally stable in air for long periods in a crystalline state, many of the products were found to decompose in alkane solutions on exposure to air under laboratory light. Consequently, chromatographic and NMR spectrographic samples and metalation reactions were always protected from exposure to oxygen. Solvents were dried over sodium benzophenone ketyl except for di-*n*-butyl ether, which was dried over Na only. NMR solvents were dried over 5-Å molecular sieves and purged with dry nitrogen gas to remove oxygen. Chromatography was performed using either silica gel (230–400 mesh) under flash conditions or neutral alumina (150 mesh; deactivated with 20 mol % H_2O). Unless otherwise noted, all NMR measurements were carried out at ambient temperature in C_6D_6 solvent using a Varian XL-300 or a General Electric QE-300 at 300 (^{1}H), 75.6 (^{13}C), or 121.7 MHz (^{31}P). Unless otherwise noted all ^{13}C and ^{31}P NMR spectra were run under conditions of broad-band ^{1}H decoupling. ^{1}H NMR spectra were referenced against the residual ^{1}H impurity in benzene-d_6 or chloroform-d_1, ^{13}C NMR spectra against ^{13}C resonances of benzene-d_6 or chloroform-d_1, and ^{31}P NMR spectra against an external 70% H_3PO_4 sample. UV–vis absorbance spectra were measured on a Hewlett-Packard 8451A diode array spectrometer using a 1-cm cell, while circular dichroism spectra were taken on an Aviv spectrometer using a 0.1-cm cell. Optical rotation measurements were acquired at ambient temperature (25 °C) on a Perkin-Elmer Series 241 polarimeter using a 1-dm cell. The concentrations are reported in grams per decaliter. Mass spectra were obtained on a Ribermag MS 10 with direct insert source, and high-resolution mass spectra (HRMS) were acquired on a VG Analytical ZAB high-resolution mass spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY, or at the University of Kansas.

General Procedure for Preparation of Chromium Complexes: Tricarbonyl[η^6-(4*R*,5*R*)-2-phenyl-2,4,5-trimethyl-1,3-dioxolane]chromium(0) (1). To a 25-mL Schlenk flash was added (4*R*,5*R*)-2-phenyl-2,4,5-trimethyl-1,3-dioxolane (1.50 g, 7.80 mmol), $Cr(CO)_6$ (1.90 g, 8.58 mmol), *n*-Bu_2O (15 mL), and THF (1 mL). The mixture was refluxed for 72 h, cooled, and filtered to remove unreacted $Cr(CO)_6$. Removal of the solvent in vacuo followed by column chromatography (30% EtOAc/hex) yielded 1 (1.52 g, 4.63 mmol, 59%) as yellow crystals: $[\alpha]_D$ = −1.45 (*c* = 1.66, $CHCl_3$); ^{1}H NMR (500 MHz) δ 5.38 (d, 1 H, *J* = 6.5 Hz), 5.34 (d, 1 H, *J* = 6.5 Hz), 4.53 (t, 1 H, *J* = 6.2 Hz), 4.19 (t, 1 H, *J* = 6.0 Hz), 4.17 (t, 1 H, *J* = 6.0 Hz), 3.75 (dq, 1 H, *J* = 8.5, 6.1 Hz), 3.39 (dq, 1 H, *J* = 8.5, 6.0 Hz), 1.40 (s, 3 H), 1.10 (d, 3 H, *J* = 6.0 Hz), 0.98 (d, 3 H, *J* = 6.1 Hz); ^{13}C NMR δ 233.4, 114.5, 105.4, 95.3, 93.6, 88.2, 88.0, 79.3, 78.8, 29.7, 16.1, 15.4. MS *m*/*z* M^+ = 328; HRMS *m*/*z* calcd for $C_{15}H_{16}CrO_5$ M^+ 328.0398, found M^+ 328.0402. Anal. Calcd for $C_{15}H_{16}CrO_5$: C, 54.88; H, 4.91. Found: C, 55.21; H, 5.11.

Tricarbonyl[η^6-(4*S*,5*S*)-4,5-bis(methoxymethyl)-2-methyl-2-phenyl-1,3-dioxolane]chromium(0) (2). As described for 1, using (4*S*,5*S*)-2-methyl-2-phenyl-4,5-bis(methoxymethyl)-1,3-dioxolane (0.899 g, 3.56 mmol), $Cr(CO)_6$ (0.862 g, 3.90 mmol), *n*-Bu_2O (10 mL), and THF (1 mL). The mixture was refluxed for 72 h and worked up to afford 2 (0.939 g, 2.41 mmol, 68%) as a viscous yellow oil: UV (CH_2Cl_2) 230 nm (ε = 19 000), 250 (9600), 316 (12 000); CD (CH_2Cl_2, *c* = 0.940 g/L) 296 nm (Δε = −0.180); $[\alpha]_D$ = +4.83 (*c* = 5.2, $CHCl_3$); ^{1}H NMR δ 5.37 (d, 1 H, *J* = 6.4 Hz), 5.34 (d, 1 H, *J* = 6.4 Hz), 4.48 (t, 1 H, *J* = 6.2 Hz), 4.24 (t, 2 H, *J* = 6.3 Hz), 4.24–4.10 (m, 2 H), 3.55 (dd, 1 H, *J* = 10.2, 5.4 Hz), 3.45 (dd, 1 H, *J* = 10.2, 3.9 Hz), 3.37 (dd, 1 H, *J* = 10.5, 3.7 Hz), 3.28 (dd, 1 H, *J* = 10.5, 4.1 Hz), 3.11 (s, 3 H), 3.05 (s, 3 H), 1.49 (s, 3 H); ^{13}C NMR δ 233.4, 114.6, 107.2, 94.5, 93.1, 92.9, 88.6, 78.7, 78.0, 72.5, 72.2, 59.1, 58.8, 28.9. Anal. Calcd for $C_{17}H_{20}CrO_7$: C, 52.58; H, 5.19. Found: C, 52.66; H, 5.27.

Tricarbonyl[η^6-(4*S*,5*S*)-2-methyl-2-phenyl-4,5-bis((*N*,*N*-dimethylamino)methyl)-1,3-dioxolane]chromium(0) (3). As described for 1, using (4*S*,5*S*)-2-methyl-2-phenyl-4,5-bis((*N*,*N*-dimethylamino)methyl)-1,3-dioxolane (0.91 g, 3.3 mmol), $Cr(CO)_6$ (1.0 g, 4.5 mmol), *n*-Bu_2O (10 mL), and THF (1 mL). Concentration in vacuo followed by column chromatography (alumina, 80% EtOAc/hex) yielded 3 (1.21 g, 2.9 mmol, 88%) as a yellow oil: UV (CH_2Cl_2) 230 nm (ε = 18 000), 250 (8700), 318 (11 000); CD (CH_2Cl_2, *c* = 0.858 g/L) 305 nm (Δε = −0.240); $[\alpha]_D$ = −17.0 (*c* = 3.34, $CHCl_3$); ^{1}H NMR δ 5.38 (d, 1 H, *J* = 6.4 Hz), 5.35 (d, 1 H, *J* = 7.0 Hz), 4.52 (t, 1 H, *J* = 6.2 Hz), 4.22 (t, 2 H, *J* = 6.4 Hz), 4.06 (m, 2 H), 2.63 (dd, 1 H, *J* = 12.9, 6.3 Hz), 2.57 (dd, 1 H, *J* = 12.9, 4.0 Hz), 2.49 (dd, 1 H, *J* = 13.1, 4.1 Hz), 2.41 (dd, 1 H, *J* = 13.1, 5.4 Hz), 2.20 (s, 6 H), 2.19 (s, 6 H), 1.45 (s, 3 H); ^{13}C NMR δ 233.4, 114.7, 106.7, 95.0, 93.7, 93.3, 88.4, 88.3, 80.0, 79.9, 61.4, 61.1, 46.5, 46.4, 29.5. Anal. Calcd for $C_{19}H_{26}CrN_2O_5$: C, 55.07; H, 6.32. Found: C, 54.93; H, 6.11.

Tricarbonyl[η^6-(4*S*,5*S*)-4,5-bis((*N*,*N*-dimethylamino)-methyl)-2-phenyl-1,3-dioxolane]chromium(0) (4). As described for 1, using (4*S*,5*S*)-2-phenyl-4,5-bis((*N*,*N*-dimethylamino)methyl)-1,3-dioxolane (1.00 g, 3.78 mmol), $Cr(CO)_6$ (1.50 g, 6.82 mmol), *n*-Bu_2O (15 mL), and THF (1 mL). Column chromatography (alumina, 30% EtOAc/hex) yielded 4 (1.31 g, 3.27 mmol, 87%) as yellow crystals: $[\alpha]_D$ = −8.7 (*c* = 2.03, $CHCl_3$); ^{1}H NMR δ 5.37 (s, 1 H), 5.14 (d, 1 H, *J* = 6.8 Hz), 5.10 (d, 1 H, *J* = 4.7 Hz), 4.36 (m, 3 H), 4.30 (dt, 1 H, *J* = 6.9, 5.6 Hz), 3.96 (dt, 1 H, *J* = 6.9, 5.6 Hz), 2.45 (d, 2 H, *J* = 5.6 Hz), 2.33 (dd, 1 H, *J* = 13.2, 5.3 Hz), 2.30 (dd, 1 H, *J* = 13.2, 5.8 Hz), 2.14 (br s, 12 H); ^{13}C NMR δ 232.9, 107.7, 101.0, 92.8, 91.6, 91.5, 90.8, 80.6, 79.8, 61.4, 61.1, 46.4, 46.3. Anal. Calcd for $C_{18}H_{24}CrN_2O_5$: C, 54.00; H, 6.04; N, 7.00. Found: C, 54.14; H, 6.01; N, 6.58.

General Deprotonation/Alkylation Procedure: Tricarbonyl[η^6-(4*S*,5*S*)-4,5-bis(methoxymethyl)-2-methyl-2-(2′-methylphenyl)-1,3-dioxolane]chromium(0) (5). *t*-BuLi (2.2 mL, 3.71 mmol, 1.7 M solution in pentane) was added to a solution of 2 (1.106 g, 3.37 mmol) in THF (20 mL) kept at −78 °C. The mixture was stirred for 2.5 h at −78 °C followed by addition of $MeOSO_2F$ (0.33 mL, 4.08 mmol), stirred 1.5 h, and allowed to warm to room temperature. Removal of the solvent in vacuo produced a viscous brown oil which was purified by column chromatography (25% EtOAc/hex) to afford an inseparable mixture of **5a,b** (1.08 g, 2.68 mmol, 79%) as a viscous yellow oil: UV (CH_2Cl_2) 232 nm (ε = 16 000), 252 (8000), 318 (10 000); CD (CH_2Cl_2, *c* = 0.950 g/L) 262 nm (Δε = −0.264), 304 (+0.0518), 356 (−0.180); ^{1}H NMR (major diastereomer **5a**) δ 5.82 (d, 1 H, *J* = 6.4 Hz), 4.77 (t, 1 H, *J* = 6.1 Hz), 4.29 (t, 1 H, *J* = 6.6 Hz), 4.23 (d, 1 H, *J* = 6.4 Hz), 4.20–4.06 (m, 2 H), 3.58 (dd, 1 H, *J* = 10.2, 6.3 Hz), 3.41 (dd, 1 H, *J* = 10.2, 4.1 Hz), 3.39 (dd, 1 H, *J* = 10.7, 3.8 Hz), 3.29 (dd, 1 H, *J* = 10.7, 4.1 Hz), 3.10 (s, 3 H), 3.08 (s, 3 H), 2.12 (s, 3 H), 1.51 (s, 3 H); ^{13}C NMR (major diastereomer) δ 233.8, 113.4, 109.6, 107.8, 96.4, 95.2, 96.1, 86.8, 78.4, 77.3, 72.9, 71.9, 59.0, 58.9, 29.1, 19.7; ^{1}H NMR (minor diastereomer **5b**, diagnostic resonances only) δ 5.84 (d, 1 H, *J* = 6.9 Hz), 4.77 (t, 1 H, *J* = 6.0 Hz), 4.24–4.08 (m, 4 H), 3.63 (dd, 1 H, *J* = 10.2, 5.8 Hz), 3.49 (dd, 1 H, *J* = 10.2, 4.4 Hz), 3.12 (s, 3 H), 3.07 (s, 3 H), 2.12 (s, 3 H), 1.46 (s, 3 H); ^{13}C NMR (minor diastereomer) δ 233.4, 113.7, 109.5, 108.0, 96.5, 95.5, 91.7, 86.2, 78.6, 78.1, 72.7, 72.3, 60.0, 59.1, 28.8, 19.7. Anal. Calcd for $C_{18}H_{22}CrO_7$: C, 53.73; H, 5.51. Found: C, 53.90; H, 5.52.

Tricarbonyl[η^6-(4*S*,5*S*)-4,5-bis(methoxymethyl)-2-methyl-2-(2′-(trimethylsilyl)phenyl)-1,3-dioxolane]chromium(0) (6). As described for 5, using 2 (0.442 g, 1.14 mmol), *t*-BuLi (0.73 mL, 1.25 mmol, 1.7 M in pentane), and $ClSiMe_3$ (0.17 mL, 1.4 mmol). Column chromatography (10% EtOAc/hex) yielded an inseparable mixture of **6a,b** (0.427 g, 0.928 mmol, 82%) as a yellow oil: UV (CH_2Cl_2) 230 nm (ε = 14 000), 254 (6100), 320 (9300); CD (CH_2Cl_2, *c* = 0.970 g/L) 280 nm (Δε = −0.426), 325 (−0.678), 420 (+0.0552); ^{1}H NMR (major diastereomer **6a**) δ 5.23 (d, 1 H, *J* = 6.3 Hz), 5.09 (d, 1 H, *J* = 6.8 Hz), 4.85 (t, 1 H, *J* = 6.4 Hz), 4.36 (t, 1 H, *J* = 6.5 Hz), 4.31 (m, 1 H), 4.09 (m, 1 H), 3.71 (dd, 1 H, *J* = 9.9, 6.6 Hz), 3.48 (dd, 1 H, *J* = 10.0, 4.6 Hz), 3.28 (dd, 1 H, *J* = 10.5, 3.4 Hz), 3.20 (dd, 1 H, *J* = 10.6, 4.1 Hz), 3.10 (s, 3 H), 3.03 (s, 3 H), 1.45 (s, 3 H), 0.37 (s, 9 H); ^{13}C NMR (major diastereomer **6a**) δ 233.9, 125.2, 110.8, 108.3, 101.0, 94.8, 89.6, 89.1, 79.3, 76.6, 72.6, 72.5, 59.1, 58.0, 30.3, 2.28; ^{1}H NMR (minor diastereomer **6b**, diagnostic resonances only) δ 5.27 (d, 1

H, J = 6.8 Hz), 5.15 (d, 1 H, J = 6.7 Hz), 4.74 (t, 1 H, 6.3 Hz), 4.29 (t, 3 H), 4.02 (m, 1 H), 3.01 (s, 3 H), 2.99 (s, 3 H), 1.53 (s, 3 H), 0.42 (s, 9 H); ^{13}C NMR (minor diastereomer **6b**) δ 233.8, 124.8, 108.6, 99.9, 96.0, 90.9, 77.8, 76.6, 72.5, 72.3, 59.1, 58.6, 30.4, 2.05. Anal. Calcd for $C_{20}H_{28}CrO_7Si$: C, 52.16; H, 6.13. Found: C, 52.09; H, 6.16.

Tricarbonyl[η^6-(4*S*,5*S*)-4,5-bis(methoxymethyl)-2-(2′-(diphenylphosphino)phenyl)-2-methyl-1,3-dioxolane]chromium(0) (7). As described for **5**, using **2** (0.460 g, 1.54 mmol), *t*-BuLi (0.98 mL, 1.54 mmol, 1.57 M in pentane), and $ClPPh_2$ (0.28 mL, 1.54 mmol). Column chromatography (25% EtOAc/hex) yielded an inseparable mixture of **7a,b** (0.650 g, 1.13 mmol, 74%) as a foamy yellow solid: UV (CH_2Cl_2) 232 nm (ϵ = 20 000), 252 (12 000), 326 (8200); CD (CH_2Cl_2, c = 0.308 g/L) 251 nm ($\Delta\epsilon$ = −4.85), 276 (+0.174), 294 (−1.43), 331 (+3.80); ^{1}H NMR (500 MHz, major diastereomer **7a**) δ 7.64 (t, 2 H, J = 6.8 Hz), 7.39 (m, 2 H), 7.22–7.10 (m, 6 H), 5.64 (dd, 1 H, J = 5.9, 2.3 Hz), 4.67 (d, 1 H, J = 6.1 Hz), 4.49 (t, 1 H, J = 6.3 Hz), 4.40 (t, 1 H, J = 5.9 Hz), 4.08 (m, 1 H), 3.89 (dt, 1 H, J = 8.5, 5.5 Hz), 3.45 (dd, 1 H, J = 10.5, 3.5 Hz), 3.35 (dd, 1 H, J = 10.5, 5.0 Hz), 3.08 (s, 3 H), 2.97 (d, 2 H, J = 5.3 Hz), 2.91 (s, 3 H), 1.91 (s, 3 H); ^{13}C NMR (125.7 MHz, major diastereomer **7a**) δ 232.9, 138.2 (d, J = 11.3 Hz), 136.5 (d, J = 17.9 Hz), 135.2 (d, J = 20.8 Hz), 134.0 (d, J = 20.5 Hz), 129.5, 128.7, 128.5, 122.2 (d, J = 20.4 Hz), 109.2, 104.2 (d, J = 36.8 Hz), 96.3, 93.3, 92.2, 90.7, 79.6, 77.2, 72.4, 72.2, 59.0, 30.9 (d, J = 10.1 Hz); ^{31}P NMR (major diastereomer **7a**) δ −8.91 (s, PPh_2); ^{1}H NMR (500 MHz, diagnostic resonances, minor diastereomer **7b**) δ 7.64 (t, 2 H, J = 6.8 Hz), 7.33 (m, 2 H), 7.22–7.10 (m, 6 H), 5.88 (dd, 1 H, J = 6.4, 1.5 Hz), 4.63 (d, 1 H, J = 6.2 Hz), 2.99 (s, 3 H), 2.89 (s, 3 H), 2.66 (dd, 1 H, J = 10.2, 5.6 Hz), 2.58 (dd, 1 H, J = 10.2, 3.6 Hz), 2.19 (s, 3 H); ^{13}C NMR (125.7 MHz, major diastereomer **7b**) δ 232.6, 138.7 (d, J = 9.8 Hz), 136.2 (d, J = 16.7 Hz), 135.4 (d, J = 23.4 Hz), 133.3 (d, J = 21.2 Hz), 129.5, 128.7, 128.6, 122.8 (d, J = 20.0 Hz), 108.4 (d, J = 35.3 Hz), 95.9, 94.8, 93.9, 89.6, 78.6, 77.1, 72.1, 71.0, 58.7, 31.5 (d, J = 10.3 Hz); ^{31}P NMR (minor diastereomer **7b**) δ −9.21 (s); MS m/z (M + 1) 573; HRMS m/z calcd for $C_{29}H_{29}CrO_7P$ (M + 1) 573.1134, found (M + 1) 573.1119. Anal. Calcd for $C_{29}H_{29}CrO_7P$: C, 60.84; H, 5.11. Found: C, 60.79; H, 4.94.

Tricarbonyl[η^6-(4*S*,5*S*)-4,5-bis((*N*,*N*-dimethylamino)methyl)-2-methyl-2-(2′-(trimethylsilyl)phenyl)-1,3-dioxolane]chromium(0) (8). As described for **5**, using **3** (0.700 g, 1.69 mmol), *t*-BuLi (1.1 mL, 1.8 mmol, 1.67 M in pentane), and $ClSiMe_3$ (0.26 mL, 2.0 mmol). Column chromatography (alumina, 70%, EtOAc/hex) yielded an inseparable mixture of **8a,b** (0.510 g, 1.05 mmol, 62%) as a yellow waxy solid: UV (CH_2Cl_2) 230 nm (ϵ = 16 000), 255 (6600), 320 (9200); CD (CH_2Cl_2 c = 0.810 g/L) 263 nm ($\Delta\epsilon$ = −0.575), 294 (−0.341), 327 (−0.890), 394 (+0.152); ^{1}H NMR (major diastereomer **8a**) δ 5.18 (d, 2 H, J = 6.5 Hz), 4.79 (t, 1 H, J = 7.1 Hz), 4.33 (t, 1 H, J = 6.3 Hz), 4.10–4.08 (m, 2 H), 2.84 (dd, 1 H, J = 13.1, 6.5 Hz), 2.70 (dd, 1 H, J = 12.9, 3.2 Hz), 2.43 (dd, 1 H, J = 13.1, 4.7 Hz), 2.32 (dd, 1 H, J = 13.1, 4.6 Hz), 2.23 (s, 6 H), 2.07 (s, 6 H), 1.42 (s, 3 H), 0.41 (s, 9 H); ^{13}C NMR (major diastereomer **8a**) δ 233.9, 125.1, 96.2, 107.8, 100.4, 94.3, 90.0, 89.5, 79.7, 78.9, 62.3, 60.6, 46.6, 46.3, 30.9, 2.3; ^{1}H NMR (minor diastereomer **8b**) δ 5.45 (d, 1 H, J = 6.8 Hz), 5.08 (d, 1 H, J = 6.1 Hz), 4.72 (t, 1 H, J = 6.3 Hz), 4.42 (t, 1 H, J = 6.3 Hz), 4.09 (dt, 1 H), 3.97 (dt, 1 H), 2.58 (dd, 1 H, J = 12.7, 6.8 Hz), 2.43 (dd, 1 H, J = 12.9, 4.6 Hz), 2.36 (dd, 1 H, J = 12.9, 4.8 Hz), 2.32 (dd, 1 H, J = 12.7, 4.9 Hz), 2.14 (s, 6 H), 2.06 (s, 6 H), 1.59 (s, 3 H), 0.45 (s, 9 H); ^{13}C NMR (minor diastereomer **8b**) δ 233.8, 124.7, 98.1, 108.3, 98.9, 92.6, 92.0, 91.9, 79.4, 78.6, 61.9, 61.0, 46.6, 45.9, 31.2, 2.40. Anal. Calcd for $C_{22}H_{34}CrN_2O_5Si$: C, 54.30; H, 7.04; N, 5.87. Found: C, 54.69; H, 7.22; N, 5.57.

Use of Diethyl Ether as Solvent. The deprotonation/alkylation of **3** as described above was repeated using Et_2O as primary solvent with the addition of a very small amount of THF to dissolve the lithiated intermediate. The final product mixture gave **8a** and **8b** in a ratio of 11:89 and 61% yield.

Tricarbonyl[η^6-(4*S*,5*S*)-4,5-bis((*N*,*N*-dimethylamino)methyl)-2-(2′-(diphenylphosphino)phenyl)-2-methyl-1,3-dioxolane]chromium(0) (9). As described for **5**, using **3** (0.510 g, 1.23 mmol), *t*-BuLi (0.80 mL, 1.35 mmol, 1.7 M in pentanes), and $ClPPh_2$ (0.24 mL, 1.35 mmol). Column chromatography (alumina, 100% EtOAc) yielded an inseparable mixture of **9a,b** (0.63 g, 1.05 mmol, 85%): UV (CH_2Cl_2) 232 nm (ϵ 21 000), 256 (9600), 326 (6300); CD (CH_2Cl_2, c = 0.400 g/L) 252 nm ($\Delta\epsilon$ −4.40), 277 (+0.0548), 293 (−1.14), 330 (+3.80); $[\alpha]_D$ = +275.8 (c = 3.95, $CHCl_3$); ^{1}H NMR (major diastereomer **9a**) δ 7.61 (t, 2 H, J = 6.9 Hz), 7.36 (m, 2 H), 7.10–6.90 (m, 6), 5.58 (dd, 1 H, J = 5.7, 2.4 Hz), 4.64 (d, 1 H, J = 6.2 Hz), 4.43 (t, 1 H, J = 6.2 Hz), 4.34 (t, 1 H, J = 6.2 Hz), 4.14 (m, 1 H), 3.93 (dt, 1 H, J = 8.4, 5.8 Hz), 2.55 (dd, 1 H, J = 13.4, 5.2 Hz), 2.44 (dd, 1 H, J = 13.4, 5.2 Hz), 2.3–2.0 (m, 2 H), 2.22 (s, 6 H), 2.04 (s, 6 H), 1.73 (s, 3 H); ^{13}C NMR (major diastereomer **9a**) δ 233.1, 138.4 (d, J = 12.9 Hz), 136.7 (d, J = 19.2 Hz), 135.3 (d, J = 21.6 Hz), 134.3 (d, J = 21.4 Hz), 129.6, 128.9, 128.8, 128.6, 128.5, 122.3 (d, J = 19.4), 106.5 (d, J = 24.1 Hz), 95.9, 93.5, 92.5, 90.5, 80.9, 78.6, 61.2, 60.9, 46.9, 46.1, 31.1 (d, J = 8.0 Hz); ^{31}P NMR (major diastereomer **9a**) δ −8.32 ppm; ^{1}H NMR (diagnostic resonances, minor diastereomer **9b**) δ 7.61 (t, 2 H, J = 6.8 Hz), 7.35 (m, 2 H), 7.20–7.0 (m, 6 H), 5.89 (dd, 1 H, J = 6.3, 2.5 Hz), 4.47 (t, 1 H, J = 6.5 Hz), 4.35 (t, 1 H, J = 6.1 Hz), 4.07 (m, 1 H), 3.92 (dt, 1 H, J = 8.6, 5.6 Hz), 2.55–2.10 (m, 4 H), 2.14 (s, 6 H), 1.93 (s, 6 H), 1.73 (s, 3 H); ^{13}C NMR (diagnostic resonances, minor diastereomer **9b**) δ 233.4, 138.8 (d, J = 12.5 Hz), 136.4 (d, J = 12.5 Hz) 135.5 (d, J = 23.9 Hz), 133.4 (d, J = 20.7 Hz), 129.5, 128.8, 128.5, 123.4 (d, J = 19.6 Hz), 94.0, 93.7, 89.7, 79.6, 79.2, 61.6, 60.1, 31.7; ^{31}P NMR (minor diastereomer **9b**) δ −9.23 ppm; MS m/z (M + 1) 599; HRMS m/z calcd for $C_{31}H_{35}CrN_2O_5P$ (M + 1) 599.1767, found (M + 1) 599.1744.

Tricarbonyl[η^6-(4*S*,5*S*)-2-methyl-2-(2′-(diphenylhydroxymethyl)phenyl)-4,5-bis((*N*,*N*-dimethylamino)methyl)-1,3-dioxolane]chromium(0) (10). As described for **5**, using **3** (0.63 g, 1.5 mmol), *t*-BuLi (1.0 mL, 1.5 mmol, 1.57 M in pentane), $Ph_2C{=}O$ (0.28 g, 1.6 mmol), and degassed H_2O (2.0 mL). Column chromatography (alumina, 100% EtOAc) yielded an inseparable mixture of **10a,b** (0.72 g, 1.2 mmol, 80%) as a yellow foam: ^{1}H NMR (major diastereomer **10a**) δ 7.74 (d, 2 H, J = 7.50 Hz), 7.54 (s, 1 H), 7.46 (d, 2 H, J = 7.4), 7.15 (t, 2 H, J = 8.0 Hz), 7.08 (t, 2 H, J = 7.0 Hz), 7.03 (t, 2 H, J = 7.2 Hz), 5.42 (d, 1 H, J = 6.34), 4.48 (d, 1 H, J = 6.4 Hz), 4.48 (t, 1 H, J = 6.4 Hz), 4.34 (m, 1 H), 4.28 (t, 1 H, J = 6.4 Hz), 3.9 (m, 1 H), 2.51 (dd, 1 H, J = 13.1, 6.7 Hz), 2.39 (dd, 1 H, J = 13.0, 4.6 Hz), 2.29 (m, 2 H), 2.12 (s, 6 H), 2.13 (s, 6 H), 0.95 (s, 3 H); ^{13}C NMR (major diastereomer **10a**) δ 233.3, 147.6, 145.7, 129.3, 128.7, 128, 127.8, 127.6, 120.5, 114.7, 108.9, 95.8, 93.5, 91.4, 91.3, 81.5, 80.8, 77.4, 60.9, 60.6, 46.5, 46.3, 30.4; ^{1}H NMR (diagnostic resonances, minor diastereomer **10b**) δ 5.47 (d, 1 H, J = 6.6 Hz), 4.13 (m, 1 H); ^{13}C NMR (diagnostic resonances, minor diastereomer **10b**) δ 233.3, 146.0, 109.2, 79.8, 79.6, 78.4, 62.3, 61.6, 46.4, 46.2, 29.8. Anal. Calcd for $C_{32}H_{36}CrN_2O_6{\cdot}^1/_2H_2O$: C, 63.46; H, 6.16; N, 4.63. Found: C, 63.75; H, 6.08; N, 4.58.

Tricarbonyl[η^6-(4*S*,5*S*)-4,5-bis((*N*,*N*-dimethylamino)methyl)-2-(2′-(trimethylsilyl)phenyl)-1,3-dioxolane]chromium(0) (11). As described for **5**, using **4** (0.580 g, 1.45 mmol), *t*-BuLi (0.89 mL, 1.59 mmol, 1.3 M in cyclohexane), and $ClSiMe_3$ (0.21 mL, 1.75 mmol). An inseparable mixture of **11a,b** (0.439 g, 0.928 mmol, 64%) was yielded as a viscous oil: ^{1}H NMR (major diastereomer **11a**) δ 5.91 (s, 1 H), 5.42 (d, 1 H, J = 6.8 Hz), 4.93 (d, 1 H, J = 5.5 Hz), 4.79 (t, 1 H, J = 7.4 Hz), 4.33 (t, 1 H, J = 5.4 Hz), 4.06–3.88 (m, 2 H), 2.55–2.26 (m, 4 H), 2.17 (s, 6 H), 2.05 (s, 6 H), 0.333 (s, 9 H); ^{13}C NMR (major diastereomer **11a**) δ 233.3, 114.7, 102.5, 100.8, 99.6, 98.4, 94.4, 90.6, 88.6, 80.4, 80.2, 61.4, 61.1, 46.6, 46.3, 46.2, 0.611; ^{1}H NMR (minor diastereomer **11b**) δ 5.88 (s, 1 H), 5.57 (d, 1 H, J = 6.3 Hz), 4.94 (d, 1 H, J = 5.5 Hz), 4.82 (t, 1 H, J = 7.4 Hz), 4.37 (t, 1 H, J = 5.5 Hz), 4.06–3.88 (m, 2 H), 2.55–2.26 (m, 4 H), 2.13 (s, 6 H), 2.06 (s, 6 H), 0.36 (s, 9 H); ^{13}C NMR (minor diastereomer **11b**) δ 233.3, 113.9, 102.0, 100.6, 99.4, 98.6, 94.2, 90.8, 88.9, 80.3, 79.6, 61.2, 61.0, 46.4, 46.1, 46.0, 0.708. Anal. Calcd for $C_{21}H_{32}CrN_2O_5Si$: C, 53.37; H, 6.82. Found: C, 53.10; H, 6.82.

Acidic Removal of Ketal. Tricarbonyl(η^6-2′-methylacetophenone)chromium(0). To a 25-mL Schlenk flask was added a THF solution of crude **5** (0.373 g, 0.927 mmol) followed by 50% H_2SO_4 (2.5 mL). After being stirred for 25 h, the resulting orange solution was extracted into $CHCl_3$. Column chromatography (30% EtOAc/hex) resulted in the isolation of the title compound[16] (0.141 g, 0.522 mmol, 56%) as an orange solid: $[\alpha]_D$ = +107 (c = 1.0, $CHCl_3$) [lit.[16] for the *R* enantiomer $[\alpha]_D$ = +213 (c = 1.05, $CHCl_3$)]; ^{1}H NMR δ 4.86 (d, 1 H, J = 6.7 Hz), 4.55 (t, 1 H, J = 6.7 Hz), 4.04 (t, 1 H, J = 6.7 Hz), 4.02 (d, 1 H, J = 6.7 Hz), 2.10 (s, 3 H), 1.90 (s, 3 H).

Tricarbonyl[η^6-(4*S*,5*S*)-4,5-bis(hydroxymethyl)-2-methyl-2-(2′-methylphenyl)-1,3-dioxolane]chromium(0) (19). As for 1, using 12[17] (0.271 g, 1.41 mmol), $Cr(CO)_6$ (0.275 g, 1.25 mmol), *n*-Bu_2O (15 mL), and THF (1 mL). 19 (0.329 g, 0.879 mmol, 77%) was yielded as a yellow oil. The synthesis was repeated using (naphth)$Cr(CO)_3$ (1.00 g, 3.82 mmol), 12 (0.455 g, 1.91 mmol), and THF (10 mL): ^{1}H NMR (major diastereomer) δ 5.72 (d, 1 H, J = 5.8 Hz), 4.67 (t, 1 H, J = 5.9 Hz), 4.16 (t, 1 H, J = 6.6 Hz), 4.08 (d, 1 H, J = 6.5 Hz), 3.97 (m, 1 H), 3.92–3.82 (m, 1 H), 3.70–3.61 (m, 2 H), 3.47 (d, 2 H, J = 4.4 Hz), 2.01 (s, 3 H), 1.32 (s, 3 H); ^{13}C NMR (major diastereomer) δ 233.9, 113.2, 109.4, 107.4, 96.8, 95.5, 91.5, 86.7, 79.9, 79.8, 62.4, 62.2, 28.9, 19.6; ^{1}H NMR (minor diastereomer) δ 5.66 (d, 1 H, J = 6.3 Hz), 4.67 (t, 1 H, J = 5.9 Hz), 4.19 (t, 1 H, J = 6.4 Hz), 4.10 (d, 1 H, J = 6.3 Hz), 4.01–3.94 (m, 1 H), 3.92–3.82 (m, 1 H), 3.70–3.61 (m, 3 H), 3.47 (d, 2 H, J = 4.4 Hz), 2.02 (s, 3 H), 1.38 (s, 3 H); ^{13}C NMR (major diastereomer) δ 234.0, 112.7, 109.5, 107.6, 96.9, 95.2, 91.5, 86.2, 79.7, 79.0, 62.0, 61.7, 28.6, 19.7. Anal. Calcd for $C_{16}H_{18}CrO_7$: C, 51.34; H, 4.85. Found: C, 51.50; H, 5.07.

Complexation Route to Tricarbonyl[η^6-(4*S*,5*S*)-4,5-bis(methoxymethyl)-2-methyl-2-(2′-methylphenyl)-1,3-dioxolane]chromium(0) (5). As for 17, using 3 (0.950 g, 3.57 mmol), $Cr(CO)_6$ (0.864 g, 3.92 mmol), *n*-Bu_2O (15 mL), and THF (1 mL). 5 (0.610 g, 1.52 mmol, 43%) was yielded as a viscous yellow oil.

Tricarbonyl[η^6-(4*R*,5*R*)-4,5-bis(ethoxycarbonyl)-2-methyl-2-(2′-methylphenyl)-1,3-dioxolane]chromium(0) (20). As for 1, using 14[17] (0.300 g, 0.931 mmol), $Cr(CO)_6$ (0.225 g, 1.02 mmol), *n*-Bu_2O (15 mL), and THF (1 mL). An inseparable mixture of 20 (0.297 g, 0.648 mol, 69%) was yielded as an orange oil: ^{1}H NMR (major diastereomer) δ 5.80 (d, 1 H, J = 6.3 Hz), 4.97 (d, 1 H, J = 7.1 Hz), 4.86 (d, 1 H, J = 7.1 Hz), 4.60 (t, 1 H, J = 6.1 Hz), 4.17 (m, 1 H), 4.10 (m, 1 H), 3.92 (q, 2 H, J = 7.1 Hz), 3.85 (q, 2 H, J = 7.3 Hz), 2.10 (s, 3 H), 1.60 (s, 3 H), 0.92 (t, 3 H, J = 7.1 Hz), 0.85 (t, 3 H, J = 7.2 Hz); ^{13}C NMR (major diastereomer) δ 233.4, 168.8, 167.5, 112.0, 111.5, 109.0, 96.0, 95.2, 91.9, 86.4, 78.3, 77.3, 61.9, 28.8, 19.9, 13.9; ^{1}H NMR (diagnostic resonances, minor diastereomer) δ 5.90 (d, 1 H, J = 6.3 Hz), 5.07 (d, 1 H, J = 6.4 Hz), 4.79 (d, 1 H, J = 6.5 Hz), 4.60 (t, 1 H, J = 6.2 Hz), 4.17 (m, 1 H), 4.10 (m, 1 H), 3.74 (q, 2 H, J = 7.1 Hz), 2.12 (s, 3 H), 1.71 (s, 3 H), 0.85 (t, 3 H, J = 7.2 Hz), 0.80 (t, 3 H, J = 7.1 Hz); ^{13}C NMR (minor diastereomer) δ 233.3, 168.6, 167.9, 112.0, 111.5, 109.6, 96.5, 95.0, 91.7, 86.7, 77.9, 77.4, 61.8, 29.3, 19.9, 13.9. Anal. Calcd for $C_{20}H_{22}CrO_9$: C, 52.41; H, 4.84. Found: C, 52.98; H, 4.58.

Tricarbonyl[η^6-(4*R*,5*R*)-4,5-bis(*N*,*N*-dimethylcarbamoyl)-2-methyl-(2′-methylphenyl)-1,3-dioxolane]chromium(0) (21). As described for 1, using 15[17] (0.240 g, 0.784 mmol) and (naphth)$Cr(CO)_3$ (0.207 g, 0.784 mmol). Removal of solvent in vacuo yielded an inseparable mixture of 21 (0.210 g, 0.475 mmol, 61%) as a crude yellow oil: ^{1}H NMR (major diastereomer) δ 5.98 (s, 1 H), 5.68 (d, 1 H, J = 5.3 Hz), 5.63 (d, 1 H, J = 5.3 Hz), 4.53 (t, 1 H, J = 6.3 Hz), 4.24 (t, 1 H, J = 6.3 Hz), 4.13 (d, 1 H, J = 6.3 Hz), 2.66, 2.61, 2.54, 2.45 (s, 3 H), 1.88 (s, 3 H); ^{1}H NMR (minor diastereomer) δ 5.79 (s, 1 H), 5.69 (d, 1 H, J = 5.3 Hz), 5.65 (d, 1 H, J = 5.3 Hz), 5.56 (d, 1 H, J = 6.3 Hz), 4.52 (t, 1 H, J = 6.3 Hz), 4.26 (t, 1 H, J = 6.3 Hz), 4.13 (d, 1 H, J = 6.3 Hz), 2.67 (s, 3 H), 2.58 (s, 3 H), 2.52 (s, 3 H), 2.50 (s, 3 H), 1.80 (s, 3 H).

Tricarbonyl[η^6-(4*R*,5*R*)-4,5-bis(*N*,*N*-dimethylcarbamoyl)-2-(2′-methylphenyl)-1,3-dioxolane]chromium(0) (22). As described for 1, using 16[17] (0.240 g, 0.784 mmol) and (naphth)$Cr(CO)_3$ (0.207 g, 0.784 mmol). Removal of solvent in vacuo yielded an inseparable mixture of 22 (0.210 g, 0.475 mmol, 61%) as a crude yellow oil that was used in the synthesis of 22: ^{1}H NMR (major diastereomer) δ 5.98 (s, 1 H), 5.68 (d, 1 H, J = 5.3 Hz), 5.63 (d, 1 H, J = 5.3 Hz), 4.53 (t, 1 H, J = 6.3 Hz), 4.24 (t, 1 H, J = 6.3 Hz), 4.13 (d, 1 H, J = 6.3 Hz), 2.66, 2.61, 2.54, 2.45 (s, 3 H), 1.88 (s, 3 H); ^{1}H NMR (minor diastereomer) δ 5.79 (s, 1 H), 5.69 (d, 1 H, J = 5.3 Hz), 5.65 (d, 1 H, J = 5.3 Hz), 5.56 (d, 1 H, J = 6.3 Hz), 4.52 (t, 1 H, J = 6.3 Hz), 4.26 (t, 1 H, J = 6.3 Hz), 4.13 (d, 1 H, J = 6.3 Hz), 2.67 (s, 3 H), 2.58 (s, 3 H), 2.52 (s, 3 H), 2.50 (s, 3 H), 1.80 (s, 3 H).

Acid-Catalyzed Hydrolysis of 22: Tricarbonyl(η^6-*o*-tolualdehyde)chromium(0). To a 25-mL Schlenk flask was added a THF solution of crude 22 (0.340 g, 0.784 mmol) followed by 50% H_2SO_4 (1 mL). After stirring for 25 h, the resulting orange solution was extracted into $CHCl_3$. Column chromatography (15–30% EtOAc/hex) yielded the title compound[16] as an orange oil: ^{1}H NMR δ 9.14 (s, 1 H), 5.34 (d, 1 H, J = 6.3 Hz), 4.55 (t, 1 H, J = 5.8 Hz), 4.04 (t, 1 H, J = 6.4 Hz), 3.82 (d, 1 H, J = 6.3 Hz), 1.73 (s, 3 H); $[\alpha]_D$ (enantiomeric mixture) = +311 (c = 0.998, Cl_3) [lit.[16] $[\alpha]_D$ (*S* enantiomer) = +660 (c = 1.05, $CHCl_3$)].

Tricarbonyl[η^6-(4*S*,5*S*)-4,5-bis((*N*,*N*-dimethylamino)methyl)-2-methyl-2-(2′-methylphenyl)-1,3-dioxolane]chromium(0) (23). As described for 1, using 17[17] (1.0 g, 3.4 mmol), (naphth)$Cr(CO)_3$ (0.903 g, 3.42 mmol), and THF (15 mL). Column chromatography (35% EtOAc/hex) yielded an inseparable mixture of 23 (1.05 g, 2.45 mmol, 72%) as a viscous yellow oil: ^{1}H NMR (diastereomer 1) δ 5.88 (d, 1 H, J = 6.6 Hz), 4.68 (t, 1 H, J = 6.3 Hz), 4.20–3.97 (m, 4 H), 2.80–2.40 (m, 4 H), 2.20 (s, 6 H), 2.19 (s, 6 H), 2.12 (s, 3 H), 1.41 (s, 3 H); ^{13}C NMR (diastereomer 1) δ 233.9, 113.8, 109.5, 107.5, 95.3, 91.5, 86.0, 79.9, 79.3, 61.5, 61.2, 46.2, 29.1, 19.7; ^{1}H NMR (diastereomer 2) δ 5.88 (d, 1 H, J = 6.6 Hz), 4.68 (t, 1 H, J = 6.3 Hz), 4.20–3.97 (m, 4 H), 2.80–2.40 (m, 4 H), 2.20 (s, 6 H), 2.18 (s, 6 H), 2.13 (s, 3 H), 1.48 (s, 3 H); ^{13}C NMR (diastereomer 2) δ 233.9, 113.4, 109.7, 107.2, 96.7, 91.3, 86.5, 79.3, 78.9, 61.2, 60.8, 46.4, 29.5, 19.6. Anal. Calcd for $C_{20}H_{28}CrN_2O_5$: C, 56.07; H, 6.59; N, 6.54. Found: C, 56.31; H, 6.40; N, 6.40.

Tricarbonyl[η^6-(4*S*,5*S*)-4,5-bis((*N*,*N*-dimethylamino)methyl)-2-(2′-methylphenyl)-1,3-dioxolane]chromium(0) (24). As described for 1, using 18[17] (0.58 g, 2.1 mmol) and (naphth)$Cr(CO)_3$ (1.09 g, 4.1 mmol). Column chromatography (alumina, 35% EtOAc/hex) yielded an inseparable mixture of 24 (0.50 g, 1.2 mmol, 58%) as a viscous oil: ^{1}H NMR (major diastereomer) δ 5.65 (d, 1 H, J = 6.3 Hz), 5.63 (s, 1 H), 4.53 (t, 1 H, J = 6.3 Hz), 4.31 (t, 1 H, J = 6.3 Hz), 4.19 (d, 1 H, J = 6.3 Hz), 4.08 (m, 1 H), 3.95 (m, 1 H), 2.50–2.30 (m, 4 H), 1.92 (s, 3 H), 2.18, 2.09 (s, 3 H); ^{13}C NMR (major diastereomer) δ 233.3, 108.9, 105.1, 99.6, 94.3, 92.7, 92.6, 88.4, 80.5, 79.8, 61.5, 61.1, 46.5, 46.2, 18.0; ^{1}H NMR (minor diastereomer) δ 5.74 (d, 1 H, J = 6.3 Hz), 5.57 (s, 1 H), 4.56 (t, 1 H, J = 6.3 Hz), 4.31 (t, 1 H, J = 6.3 Hz), 4.19 (d, 1 H, J = 6.3 Hz), 4.08 (m, 1 H), 3.95 (m, 1 H), 2.50–2.30 (m, 4 H), 1.93 (s, 3 H), 2.16 (s, 3 H), 2.10 (s, 3 H); ^{13}C NMR (minor diastereomer) δ 233.3, 109.0, 105.5, 99.3, 94.5, 92.5, 88.0, 80.2, 79.7, 61.4, 61.2, 46.3, 18.0.

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Registry No. 1, 141376-14-9; 2, 141376-15-0; 3, 141376-16-1; 4, 141376-17-2; 5a, 141376-18-3; 5b, 141434-78-8; 6a, 141376-19-4; 6b, 141434-79-9; 7a, 141376-20-7; 7b, 141434-80-2; 8a, 141376-21-8; 8b, 141434-81-3; 9a, 141376-22-9; 9b, 141434-82-4; 10a, 141376-23-0; 10b, 141434-83-5; 11a, 141376-24-1; 11b, 141434-84-6; 12, 141376-03-6; 13, 141376-04-7; 14, 141376-05-8; 15, 141376-06-9; 16, 141376-07-0; 17, 141376-08-1; 18, 141376-09-2; 19a, 141376-25-2; 19b, 141434-85-7; 20a, 141376-26-3; 20b, 141434-86-8; 21a, 141376-27-4; 21b, 141434-87-9; 22a, 141376-28-5; 22b, 141434-88-0; 23a, 141376-29-6; 23b, 141434-89-1; 24a, 141376-30-9; 24b, 141434-90-4; i, 141434-77-7; ii, 141376-12-7; iii, 141376-10-5; iv, 141376-11-6; v, 141376-13-8; vi, 141123-77-5; $Cr(CO)_6$, 13007-92-6; tricarbonyl(η^6-2′-methylacetophenone)chromium(0), 36249-97-5; tricarbonyl(η^6-*o*-tolualdehyde)chromium(0), 32734-21-7; (*R*,*R*)-2,3-dihydroxybutane, 24347-58-8; acetophenone, 98-86-2;

(17) The reactants for this part of the study were prepared in exact analogy to the compounds shown in Scheme I. See the supplementary material for details.

(2S,3S)-1,4-dimethoxybutane-2,3-diol, 50622-10-1; acetophenone dimethyl acetal, 4316-35-2; (R,R)-N,N,N',N'-tetramethyltartamide, 26549-65-5; 2-methylacetophenone, 577-16-2; diethyl L-tartarate, 87-91-2; 2-methylacetophenone dimethyl acetal, 118719-92-9; o-tolualdehyde dimethyl acetal, 58378-32-8; tricarbonyl[η^6-(4S,5S)-4,5-bis[(N,N-dimethylamino)methyl]-2-methyl-2,6-bis-[2'-(trimethylsilyl)phenyl]-1,3-dioxolane]chromium(0), 141376-31-0.

Supplementary Material Available: Experimental details and spectral data for the preparation of the precursors to compounds 1–4, the preparation of compounds 12–18, and CD spectra of compounds 2, 3, and their immediate precursors (8 pages). This material is contained in many 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.

Rate-Determining Steps in Michael-Type Additions and E1cb Reactions in Aqueous Solution

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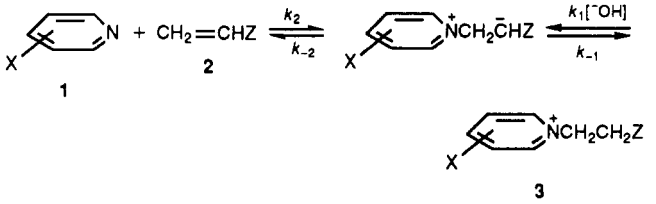
Rates of equilibration of a series of 10 substituted pyridines and five Michael acceptors (CH_2=CHZ, Z = CHO, $COCH_3$, SO_2CH_3, CN, and $CONH_2$) with the corresponding N(ZCH_2CH_2) pyridinium cations have been measured in aqueous solution at ionic strength 0.1 and 25 °C. Analysis of the dependence of the pseudo-first-order rate constants for equilibration as a function of acceptor concentration and of pH allows the evaluation of the second-order rate constants (k_{Nu}) for the nucleophilic attack of each of these pyridines upon each of these acceptors and also the second-order rate constants (k_{OH}) for the hydroxide ion catalyzed E1cb elimination reaction which is the microscopic reverse of each of these Michael-type addition reactions. Brønsted-type plots for each of these processes as a function of the basicity of the substituted pyridine are concave down for each of Z = CHO, $COCH_3$, and CN and are consistent with a change from rate-determining nucleophilic attack for the more basic pyridines to rate-determining protonation of the carbanionic intermediate by a water molecule for less basic pyridines and the corresponding microscopic reverse processes in the elimination reactions. The "break" in these Brønsted-type plots is shown to occur at a pyridine basicity that is a function of the Z-activating substituent. Brønsted β_{lg} and β_{nuc} are evaluated for each rate-determining step (wherever accessible); these two parameters are shown to pass through minima as a function of reactivity. β_{eq} is shown to be a simple linear function of reactivity (as log k_{Nu}) for nucleophilic addition to the acceptor species, although K_{eq} is relatively insensitive to the nature of the Z-activating substituent.

We have recently reported[1] that the rates of equilibration of acrylonitrile and a substituted pyridine with the corresponding *N*-(2-cyanoethyl)pyridinium cation (3, Z = CN) can be readily observed in aqueous solutions for many substituted pyridines (Scheme I).[2] For this Michael-type addition reaction[3] and its E1cb microscopic reverse, we demonstrated a change in rate-determining step as a function of pyridine basicity for pyridines having conjugate acids of pK_{BH} = 5.8. For pyridine nucleophiles of high basicity, rate-determining nucleophilic attack (k_2) was observed in the addition reactions; this assignment corresponds to rate-determining leaving group departure from the carbanionic intermediate (k_{-2}) in the elimination reaction. For weakly basic pyridines, deprotonation of 3 (Z = CN) (k_1) was found to be rate-determining for the elimination reaction, and consequently protonation (k_{-1}) of the carbanionic intermediate by a water molecule is rate-determining in the addition reaction in this case.

The wide range of basicities that is available for simple ring-substituted pyridines is crucial to the demonstration of such a change in the rate-determining step as a function of nucleophile (or nucleofuge) basicity. However, the particular reactivities that are associated with these pyridine nucleophiles (or nucleofuges) are also an important

Scheme I



factor in producing a change in the rate-determining step. In a subsequent study,[4] we demonstrated that a similar change in rate-determining step is apparent for the E1cb reactions of *N*-(2-(4-nitrophenyl)ethyl)pyridinium cations (3, Z = 4-$NO_2C_6H_4$) at pK_{BH} = 6.5, although no such change is observable[5] over a comparable range of nucleofuge basicities in the analogous elimination reactions of *N*-(2-(4-nitrophenyl)ethyl)quinuclidinium cations. This study[4] demonstrated that the ability to observe a change in rate-determining step, as well as the nucleofuge (or nucleophile) basicity at which this change occurs, may be a function of the nature of the carbanion-stabilizing group (i.e., activating group) (Z) as well as of the structure of the nucleofuge (nucleophile).

Electron-deficient monosubstituted alkenes 2 (acrylic acid derivatives, vinyl ketones, etc.) are commonly used as Michael acceptors in synthetic organic chemistry. While many reactivities of Michael acceptors toward nucleophilic addition reactions have been measured, the mechanistic

(1) Bunting, J. W.; Toth, A.; Heo, C. K. M.; Moors, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 8878.

(2) k_1 and k_{-1} of the current Scheme I are defined in the same way as these parameters in Scheme I of ref 1. k_2 and k_{-2} in the current work were defined as k_{Nu} and k_2, respectively, in ref 1. In the current report, k_{Nu} is defined as the observed second-order rate constant for the reaction of 1 with 2 (see eq 2).

(3) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 665.

(4) Bunting, J. W.; Kanter, J. P. *J. Am. Chem. Soc* **1991**, *113*, 6950.

(5) (a) Alunni, S.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 2052. (b) Keeffe, J. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 265.

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