Highly Regioselective Benzylic Deprotonation of Some (η^6-Tetralin)- and (η^6-*trans*-Octahydroanthracene)$Cr(CO)_3$ Derivatives: Is the Regioselectivity Stereoelectronically Controlled?☆

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The regioselectivity of benzylic deprotonation of a number of conformationally restricted (arene)$Cr(CO)_3$ complexes has been examined in order to ascertain whether stereoelectronic effects play a role in such reactions. The complexes *rac*-**5**, *rac*-**6**, *rac*-**7**, *rac*-**8** and *rac*-**9** were diastereoselectively synthesized from the corresponding C_2-symmetric ligands (2,3-disubstituted *trans*-1,2,3,4-tetrahydronaphthalene and *trans*-1,2,3,4,4a,9,9a,10-octahydroanthracene derivatives). Due to the desymmetrization caused by the $Cr(CO)_3$ complexation, all four benzylic protons could be distinguished by ^1H NMR and were assigned in all cases by a combination of H,H-COSY spectra and the observation of H/D exchange at both *exo* positions (*tert*-BuOK/[D_6]DMSO). Deprotonation (*n*-butyllithium)/deuteration (D_2O or CF_3CO_2D) experiments revealed a very high, unforeseen regioselectivity in the cases of *rac*-**5** and *rac*-**7**, while the other substrates showed a low selectivity (*rac*-**6**) or could not be deuterated at all under these conditions (*rac*-**8**, *rac*-**9**). In the case of *rac*-**5**, the regioselectivity of the deprotonation was further confirmed by acylation (AcCl) or alkylation (MeI) of the lithiated intermediate. These results clearly rule out the notion that the regioselectivity is due to the preferred abstraction of pseudoaxially oriented benzylic hydrogen atoms. The crystal structures of *rac*-**1**, *rac*-**5** and *rac*-**7** suggest a possible link between the preferred conformation of the $Cr(CO)_3$ tripod and the regioselectivity of the benzylic deprotonation. In analogy to a commonly accepted picture often used to explain the regioselectivity of nucleophile additions to (arene)$Cr(CO)_3$ complexes, it was anticipated that those benzylic positions which are activated by an eclipsed CO ligand should be preferentially deprotonated (kinetically controlled). This (new) stereoelectronic model was corroborated by experiments using complexes *rac*-**60** and *rac*-**62**, which were regioselectively deprotonated at the predicted position. In summary, it has been shown for the first time that the preferred conformation of the $Cr(CO)_3$ tripod may have a directing influence on the regioselectivity of benzylic deprotonation in (arene)$Cr(CO)_3$ complexes, at least in conformationally unambiguous situations where no obvious electronic effects are operative.

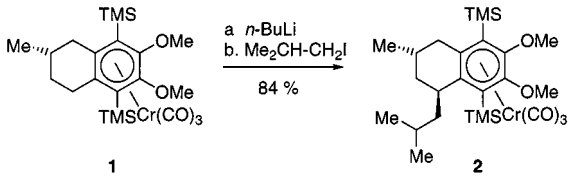
Introduction

(Arene)$Cr(CO)_3$ complexes represent a unique class of transition metal complexes, which are of considerable value for the synthesis of complex organic molecules[1]. One of the most useful effects of the $Cr(CO)_3$ fragment is the stabilization of negative charge in benzylic positions, which can be exploited for efficient benzylic deprotonation/alkylation reactions[2][3].

In the course of our program on the use of chiral (arene)$Cr(CO)_3$ complexes as building blocks for the total synthesis of bioactive compounds[4][5], we recently discovered that complex **1** is deprotonated by *n*-butyllithium in a highly regioselective fashion, permitting the regio- and diastereoselective preparation of benzylic alkylated products such as **2** (Scheme 1)[5].

While the regioselectivity of the benzylic deprotonation of (arene)$Cr(CO)_3$ complexes has hitherto been explained more or less exclusively in terms of electronic[1c][2][6] or complex-induced proximity effects[7], any rationalization of the high degree of regiocontrol during the deprotonation of **1** must be based on different concepts.

Scheme 1



1 **2**

The crystal structure of *rac*-**1** (see below) shows that the molecule preferentially adopts a half-chair conformation (**1′**; Figure 1). As a result, the two relevant benzylic *exo* hydrogen atoms, which have comparable steric environments, differ in that one (the one that is attacked by the base) adopts a pseudoaxial position, while the other is pseudoequatorially oriented. Therefore, it could not a priori be ruled out that the deprotonation step (leading to the anionic intermediate **3**) is stereoelectronically controlled[8].

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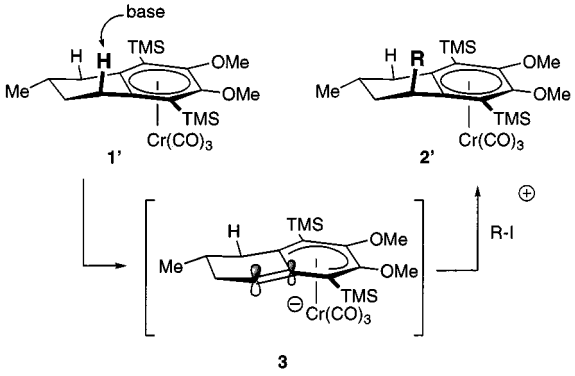
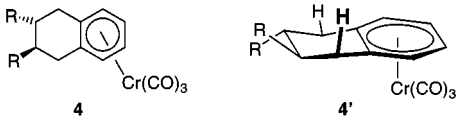
Figure 1. On the regio- and stereochemistry of the deprotonation/alkylation of complex **1**



In order to investigate whether such conformational or stereoelectronic effects do indeed play a role in the benzylic deprotonation of (arene)$Cr(CO)_3$ complexes, we decided to explore conformationally more rigid substrates of type **4** (Figure 2). Compared to **1**, these compounds should exhibit an even stronger preference for a half-chair conformation (**4′**)[9] and, as a result of the symmetry of such structures, the two benzylic positions are essentially electronically equivalent.

Figure 2. Preferred half-chair conformation of 2,3-disubstituted tetralin complexes of type **4**; the two benzylic *exo*-hydrogen atoms can be classified as pseudoaxial and pseudoequatorial, respectively



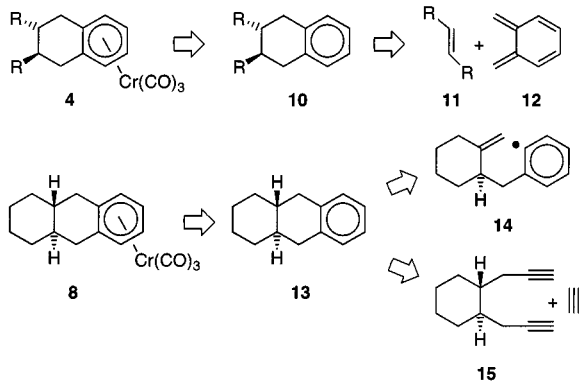
We report here on the synthesis and structural characterization of several (tetralin)- and (*trans*-octahydroanthracene)$Cr(CO)_3$ complexes (*rac*-**5**, *rac*-**6**, *rac*-**7**, *rac*-**8**, *rac*-**9**) as well as on investigations of their benzylic deprotonation. Furthermore, we present a modified mechanistic interpretation to explain the effects governing the regioselectivity of the benzylic deprotonation of such complexes.

Synthesis of the Complexes

Strategic Considerations

The syntheses of the various complexes were envisaged as being possible by the general routes outlined in Scheme 2. Retrosynthetically, the target compounds stem from C_2-symmetric ligands in each case. For the synthesis of 2,3-*trans*-disubstituted tetralin derivatives of type **10**, a Diels-Alder reaction of an (*E*)-configured dienophile **11** with an *o*-quinodimethane of type **12** was envisaged[10]. For the diastereoselective preparation of *trans*-octahydroanthracenes such as **13**[11], either a 6-*endo* cyclization of a radical intermediate of type **14**[12], or a metal-mediated [2+2+2]-cycloaddition (Vollhardt reaction)[13] employing the *trans*-bis(alkyne) **15** were considered. For the purposes of the anticipated deprotonation studies, it was sufficient to focus merely on synthetic methods that would furnish the target complexes in racemic form.

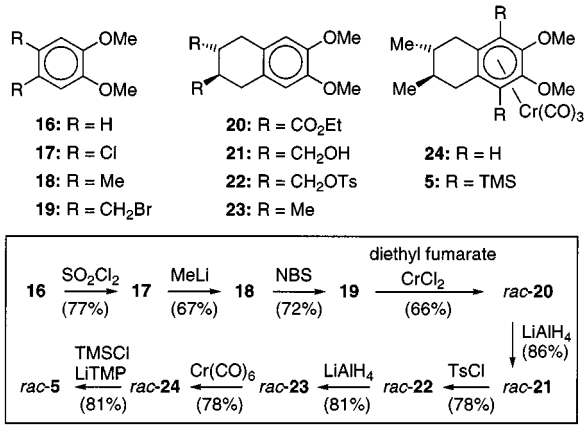
Scheme 2



Synthesis of *rac*-5

Compound **19**, the precursor of the dimethoxy-substituted *o*-quinodimethane, was prepared from veratrole (**16**) in three steps employing modified literature procedures[14]. The dichlorinated derivative **17** was converted to 4,5-dimethylveratrole (**18**) by reaction with methyllithium in diethyl ether[14a][14b]. Subsequent benzylic bromination of **18**[14c] with 2 equiv. of dry NBS in the presence of molecular sieves (4 Å) afforded **19** in 72% yield.

Scheme 3



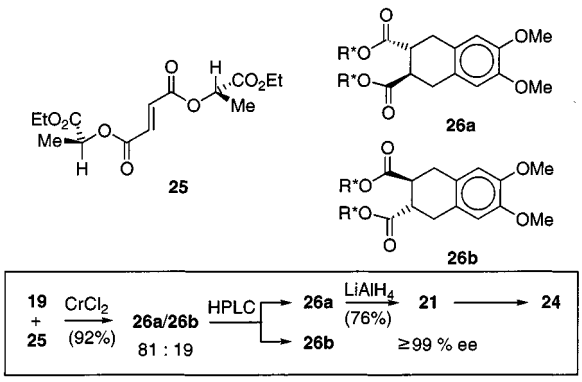
In situ generation of the *o*-quinodimethane from **19** by reductive debromination with $CrCl_2$ in THF[15] in the presence of diethyl fumarate at 0°C yielded the desired Diels-Alder product *rac*-**20** in 66% yield as the pure *trans* dia-

stereomer[16]. Reduction of *rac*-**20** with $LiAlH_4$ in diethyl ether (30°C, 0.5 h) afforded the diol *rac*-**21**. Deoxygenation of the diol *rac*-**21** was then achieved in 63% overall yield by $LiAlH_4$ reduction of the corresponding bis(tosylate) (*rac*-**22**)[17]. It proved to be important to carry out the ditosylation (*rac*-**21** → *rac*-**22**) at low temperature (0−4°C), otherwise the cyclic ether *rac*-**27** (see below) became the major product. Heating of *rac*-**22** with $Cr(CO)_6$ (1.1 equiv.) under standard conditions[18] (*n*-Bu_2O/THF; reflux) gave complex *rac*-**23** in 78% recrystallized yield. The introduction of the two trimethylsilyl substituents was finally accomplished in a one-pot procedure[5] using the reagent combination chlorotrimethylsilane/lithium tetramethylpiperidide[19] to afford the bis(silylated) complex *rac*-**5** in high yield. The crystal structure of *rac*-**5** is depicted in Figure 5.

Synthesis of Complex 24 (Nonracemic Series)

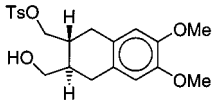
We also briefly investigated the Diels-Alder reaction of the **19**-derived *o*-quinodimethane employing chiral fumarates as dienophiles. While the use of dimenthyl fumarate[20] led only to a low selectivity (33% *de*; 92% yield), the lactic acid derivative **25** was found to be a much better chiral dienophile (Scheme 4)[21]. Thus, when **19** was treated with $CrCl_2$ in the presence of an excess of **25**, an 81:19 mixture of the two diastereomeric cycloaddition products **26a** and **26b** was obtained in high yield. After HPLC separation, the major diastereomer (**26a**) was converted by $LiAlH_4$ reduction to the optically active diol **21**, which was shown to be of ≥ 99% *ee* by means of HPLC on a chiral stationary phase[22]. It is remarkable that, compared to diethyl fumarate (see Scheme 3), the (more bulky) chiral fumarates generally gave much higher yields (>90%) in the Diels-Alder reactions. Following the procedures established for the racemic series, **21** was transformed to **24** (Scheme 4). The absolute and relative configuration of **24** was unequivocally established by means of a crystal structure analysis (see Figure 4), which (retrospectively) allowed assignment of the configurations of **26a** and **26b**.

Scheme 4



Synthesis of *rac*-6

The tetrahydrofuran derivative *rac*-**27**, which was initially obtained as an undesired side-product during the preparation of *rac*-**22** (see above), was isolated in 76% yield when *rac*-**21** was treated with *p*-TsCl in pyridine at 60°C, even when 3 equiv. of *p*-TsCl was used. Clearly, the S_N2-type cyclization of the monotosylated intermediate *rac*-**29** was faster than the second tosylation under these conditions[23].



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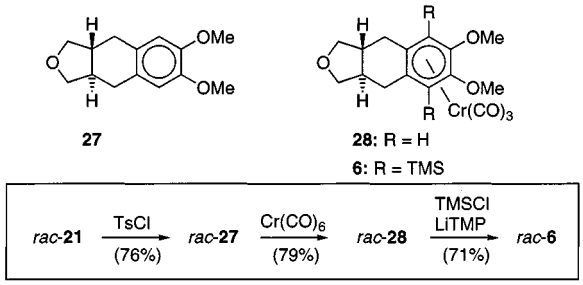
Since *rac*-**27** also represents a conformationally restricted tetralin derivative, it was converted to the corresponding $Cr(CO)_3$ complex *rac*-**28** (Scheme 5), which in turn was disilylated under the one-pot conditions described above to give *rac*-**6**.

Scheme 5

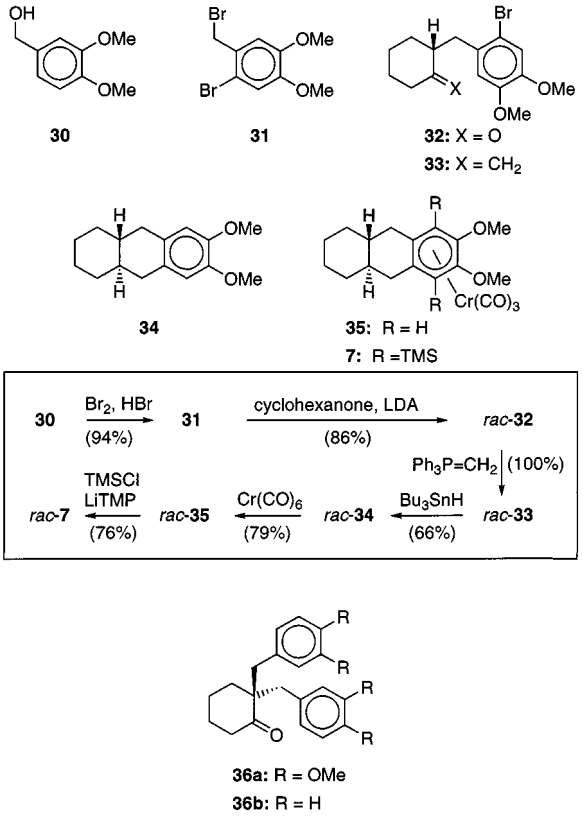


Synthesis of *rac*-7

The synthesis of *rac*-**7** (Scheme 6) was performed following the radical cyclization route outlined in Scheme 2. Starting from veratrum alcohol **30**, the dibromide **31** was prepared in high yield by treatment with bromine (1 equiv.) in benzene. Some hydrogen bromide was added to ensure completion of the reaction.

Alkylation of the enolate anion, prepared from **31** and cyclohexanone with LDA in THF, proceeded smoothly to give the ketone *rac*-**32** in high yield, together with small amounts of the doubly alkylated by-product **36a**, which could be easily separated by chromatography.

Scheme 6



36a: R = OMe
36b: R = H

Wittig methylenation of *rac*-**32** furnished the cyclization precursor *rac*-**33** in essentially quantitative yield. The crucial radical cyclization[24] of *rac*-**33** was performed in benzene, with slow addition of tributyltin hydride in the presence of AIBN. The *6-endo* cyclization product *rac*-**34** was obtained as the major product in 66% yield. Complexation of *rac*-**34** with $Cr(CO)_6$ (→ *rac*-**35**) followed by double silylation afforded *rac*-**7** in good overall yield (Scheme 6). X-ray crystal structure analysis (see Figure 6) of *rac*-**7** proved its relative configuration.

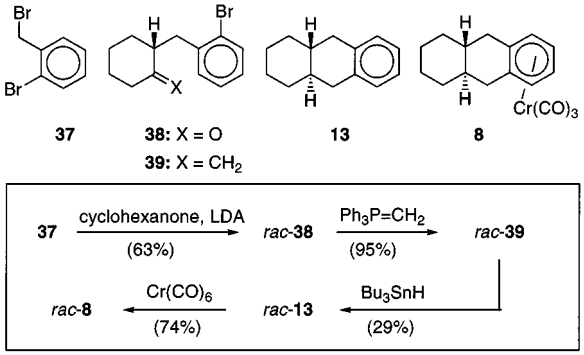
Synthesis of *rac*-8

The synthesis of the *trans*-octahydroanthracene ligand *rac*-**13** was accomplished following the same strategy. Alkylation of cyclohexanone (LDA, subsequent addition of the dibromide **37**, 3 h reflux in THF) afforded an 80:20 mixture of *rac*-**38** and the double-alkylation product **36b**, from which pure *rac*-**38** was isolated by kugelrohr distillation. Methylenation of *rac*-**38** to *rac*-**39** followed by radical cyclization afforded *rac*-**13** (Scheme 7)[12][25]. Subsequent complexation of *rac*-**13** with $Cr(CO)_6$ furnished *rac*-**8** in good yield (Scheme 7).

Synthesis of *rac*-9

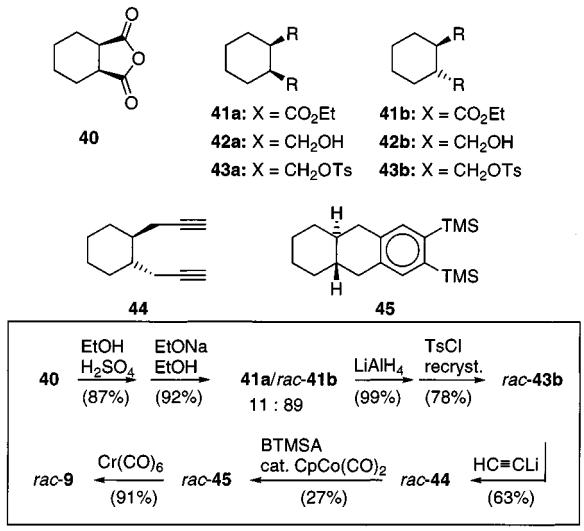
The *cis*-diester **41a**[26], obtained from hexahydrophthaloyl anhydride (**40**) in 87% yield, was converted to the *trans* isomer *rac*-**41b** by refluxing with ethanolic sodium ethoxide[27]. In contrast to a literature report[27], an inseparable mixture (*rac*-**41b**/**41a** = 89:11) was obtained rather

Scheme 7



than the pure *trans* product. Reduction with $LiAlH_4$ in diethyl ether quantitatively afforded the corresponding mixture of diols (*rac*-**42b**/**42a** = 89:11). Fortunately, tosylation with *p*-TsCl in pyridine and recrystallization of the crude product mixture led to the isolation of the essentially pure *trans*-ditosylate *rac*-**43b** in 78% yield. Conversion of *rac*-**43b** to the cyclization precursor, the dialkyne *rac*-**44**, was achieved by treatment with a 2 M solution of the lithium acetylide·ethylenediamine complex in DMSO at 8°C[28]. Vollhardt cyclization[13] employing *rac*-**44** and bis(trimethylsilyl)acetylene (BTMSA) in the presence of catalytic amounts of $CpCo(CO)_2$ afforded only a moderate yield of the C_2-symmetric ligand *rac*-**45**, which was finally converted to the desired complex *rac*-**9** in 91% yield (Scheme 8).

Scheme 8



Characterization of the Complexes

General Aspects

All complexes synthesized as described above were fully characterized by ^1H NMR, ^{13}C NMR, IR, MS and elemental analysis (see Experimental Section). All data were in accordance with the constitutional and (relative) configurational assignments implied in the structural formulae. In

particular, the fact that all benzylic hydrogen atoms were found to be non-equivalent in the ^{1}H-NMR spectra (see below) and that a full set of ^{13}C signals was observed in each case (see Experimental Section) immediately proves the *trans* configuration on grounds of symmetry.

X-ray Crystal Structure Investigations

The crystal structures of the complexes *rac*-**1** (Figure 3), **24** (Figure 4), *rac*-**5** (Figure 5) and *rac*-**7** (Figure 6) were determined[29] so as to reveal detailed information about configurational and conformational aspects.

The X-ray structure of complex *rac*-**1** (Figure 3) shows that the cyclohexene ring adopts a (slightly distorted) half-chair conformation with one homobenzylic ring carbon atom lying 0.32 Å below, and the other lying 0.50 Å above, the molecular plane defined by the arene ring. The methyl group on the cyclohexene ring is in a pseudoequatorial position. The benzene ring shows a slight deviation from planarity. The largest torsion angle in the benzene ring is 8.4°. The puckering of the benzene ring may be due to the presence of the bulky substituents. The Cr−C(ring) distances range from 2.228 to 2.273 Å. The benzene $Cr(CO)_3$ group has an eclipsed conformation.

The X-ray structure of complex **24** (Figure 4) shows two independent molecules with very similar conformations of the hydrocarbon ligand. The cyclohexene ring adopts a conformation between a twist-boat and an envelope form. The two methyl groups on the cyclohexene ring have pseudoequatorial orientations. One of the homobenzylic ring carbon atoms in molecule I lies 0.48 Å below and the other 0.26 Å above the molecular plane defined by the arene ring (0.54 Å and 0.26 Å for molecule II, respectively). The benzene ring shows only a very small deviation from planarity. The largest torsion angle in the benzene ring is 3.1° (molecule I) and −4.2° (molecule II). The Cr atom lies 1.75 Å below the plane of the benzene ring and the Cr−C(ring) distances range from 2.205 to 2.308 Å. The (benzene)$Cr(CO)_3$ group adopts an almost eclipsed conformation in both independent molecules which, however, differ in that the $Cr(CO)_3$ tripod is rotated through ca. 60°. The absolute configuration of **24** was established with the aid of anomalous scattering.

The X-ray structure of *rac*-**5** (Figure 5) shows a disorder, with two independent molecules in a ratio of ca. 60:40. In both molecules,which differ in the orientation of the $Cr(CO)_3$ tripod, the cyclohexene ring is in a half-chair conformation, with the methyl substituents in equatorial positions and with one homobenzylic ring carbon atom lying 0.42 (0.44) Å below and the other lying 0.36 (0.37) Å above the molecular plane defined by the arene ring. The benzene ring shows a slight deviation from planarity. The Cr−C(ring) distances range from 2.233 to 2.265 Å. As in the case of **24**, the benzene $Cr(CO)_3$ group has an eclipsed conformation in both independent molecules, but with different orientations (60° rotation).

The X-ray structure of *rac*-**7** (Figure 6) also shows two independent molecules with very similar conformations. As expected, the central cyclohexene ring has a twist-boat (half-chair) conformation and the saturated cyclohexane ring has a purely chair conformation. Interestingly, the benzene ring shows a significant deviation from planarity. The ring carbon atoms attached to the TMS groups deviate by about 0.07 Å from the plane of the other four ring atoms and are closer to the Cr Atom. The Cr−C(ring) distances range from 2.217(3) to 2.261(3) Å. The (benzene)$Cr(CO)_3$ group has an almost eclipsed conformation.

Figure 3. X-ray crystal structure of *rac*-**1**; only one enantiomer is depicted

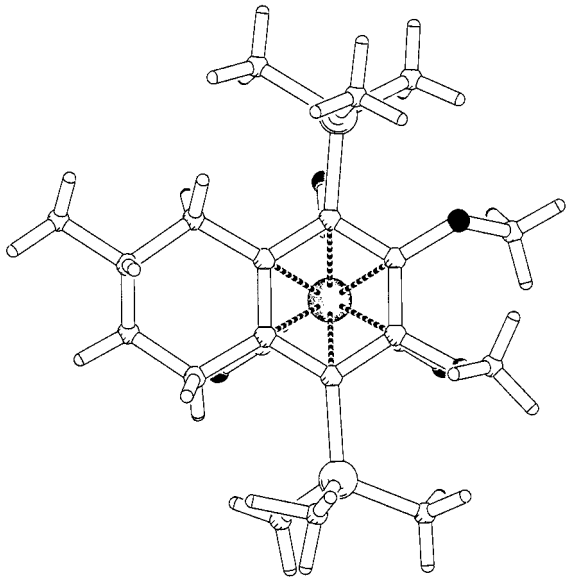
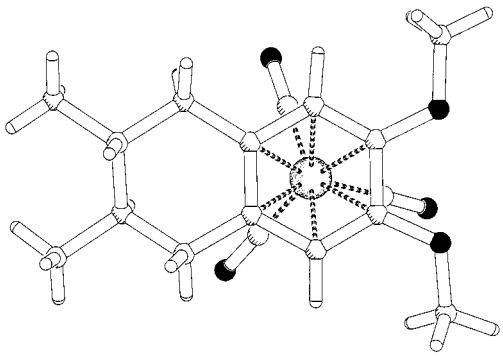


Figure 4. X-ray crystal structure of **24**; only one of two independent conformers is depicted



NMR-Spectroscopic Investigations

The ^{1}H-NMR and ^{13}C-NMR spectra of the various complexes (in $CDCl_3$) exhibit a number of interesting features. The signals for the benzylic hydrogen atoms are of particular interest. They all appear as double doublets (compare Figure 8) and are well separated in most cases − an important prerequisite for the unambiguous assignments necessary for the anticipated deprotonation/deuteration studies (see below).

As originally expected and confirmed by the crystal structures, the cyclohexene rings of the complexed ligands adopt half-chair conformations. Thus, the four dia-

Figure 5. X-ray crystal structure of *rac*-**5**; only one of two independent conformers and only one enantiomer is depicted

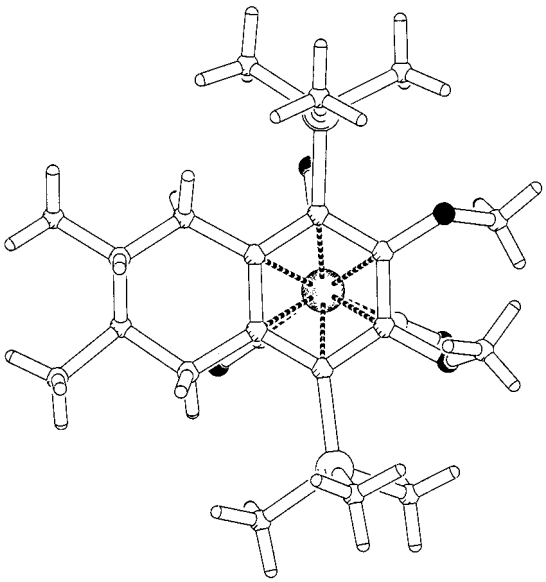
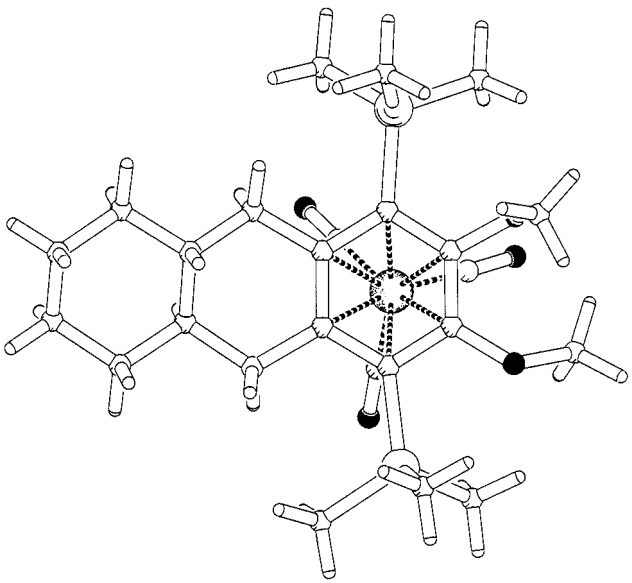


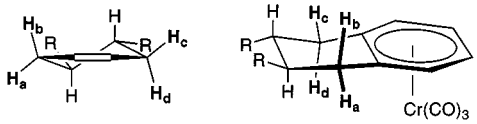
Figure 6. X-ray crystal structure of *rac*-**7**; only one enantiomer is depicted

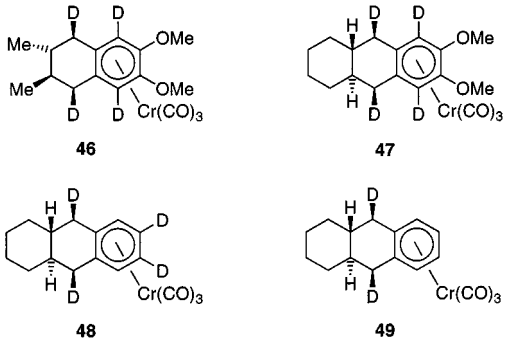


stereotopic benzylic protons may be classified as follows (Figure 7): *endo*-pseudoequatorial (H_a), *exo*-pseudoaxial (H_b), *exo*-pseudoequatorial (H_c) and *endo*-pseudoaxial (H_d).

By means of H,H-COSY spectra[30], it was possible to unambiguously designate the pairs of geminal hydrogen atoms (H_a,H_b; H_c,H_d) for all the complexes. Alternatively, the benzylic *exo*-hydrogen atoms could be identified in several cases by H/D exchange experiments with potassium *tert*-butoxide in [D_6]DMSO (1 h, 25°C). It has been established previously that only the *exo*-hydrogen atoms are substituted under these conditions[3c]. The results of these deuteration experiments are summarized in Table 1. It should be noted that the trimethylsilyl groups in *rac*-**5**, *rac*-**7** and *rac*-**9** were also displaced by deuterium under the reaction conditions (formation of *rac*-**46**, *rac*-**47** and *rac*-**48**). The degree of deuteration was determined in each case by means of ^{1}H-NMR spectroscopy. In addition, the formation of the multiply deuterated compounds was proven by mass spectrometry.

Figure 7. Labelling of the four diastereotopic benzylic hydrogen atoms of the (tetralin)$Cr(CO)_3$ complexes as used for the assignments of the NMR data (Table 2)





46 **47** **48** **49**

By combining the information obtained from both types of experiments (H,H-COSY and H/D exchange), a full assignment of all the benzylic hydrogen atoms in the complexes *rac*-**24**, *rac*-**35** and *rac*-**8** could readily be made. The assignments for the other complexes (*rac*-**5**, *rac*-**28**, *rac*-**6**, *rac*-**7** and *rac*-**9**) could then be deduced by means of analogy. The assignments and the relevant coupling constants of the benzylic resonances are summarized in Table 2.

The data presented in Table 2 highlights the close relationship between the following pairs of complexes: *rac*-**24**/*rac*-**35**, *rac*-**5**/*rac*-**7** and *rac*-**8**/*rac*-**9**. In all cases, the geminal coupling constants were measured as 16 ± 1 Hz. The vicinal coupling constants for the pseudoaxial hydrogen atoms (H_b and H_d) were found to be 11 ± 1 Hz, those for the pseudoequatorial hydrogen atoms (H_a and H_c) 5 ± 1 Hz. Apart from in the case of the hexahydronaphthofuran complexes *rac*-**28** and *rac*-**6**, the chemical shifts of the pseudoaxial hydrogen atoms (H_b and H_d) lie in the range δ = 2.1−2.4 and those for the pseudoequatorial hydrogen atoms (H_a and H_c) in the range δ = 2.5−2.8. The uncomplexed ligands show the corresponding signals at δ = 2.42 ± 0.03 (^3J = 9−12 Hz, pseudoaxial H) and at δ = 2.73 ± 0.05 (^3J = 4−5 Hz, pseudoequatorial H). These apparent similarities of the ^{1}H-NMR data reflect the very close structural relationship of the complexes and indicate that the complexation does not cause major conformational changes of the arene ligands. The ^{13}C-NMR data (see Experimental Section) also support this picture.

Deprotonation Studies

Having assigned the signals of the relevant benzylic protons, the regioselectivity of the deprotonation was deter-

Table 1. Results of the deuteration experiments[a]

Entry	Starting complex	Product[b]	Degree of deuteration[%][c] benzylic	aryl	Yield[d] [%]
1	*rac*-**5**	*rac*-**46** (*rac*-**24**-d4)	75 ± 15	85 ± 2	11
2	*rac*-**7**	*rac*-**47** (*rac*-**35**-d4)	> 97	92 ± 5	58
3	*rac*-**9**	*rac*-**48** (*rac*-**8**-d4)	70 ± 10	> 97	70
4	*rac*-**8**	*rac*-**49** (*rac*-**8**-d2)	> 97	–	98

[a] Results of the H/D exchange experiments with *t*BuOK/[D_6]DMSO. – [b] Major component of the crude product mixture according to TLC and ^{1}H NMR. – [c] Determined from the ^{1}H-NMR spectra. – [d] Non-optimized yield after chromatography and crystallization.

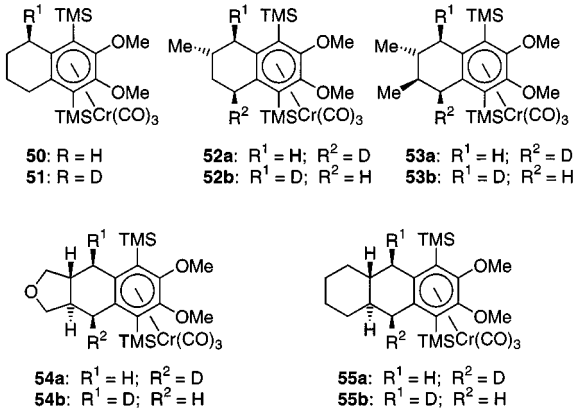
Table 2. NMR-spectroscopic assignments according to Figure 7[a]

Complex	$\delta(H_a)$	$\delta(H_b)$	$\delta(H_c)$	$\delta(H_d)$	$^2J(H_aH_b)$	$^2J(H_cH_d)$	$^3J(H_aH)$	$^3J(H_bH)$	$^3J(H_cH)$	$^3J(H_dH)$
rac-**24**	2.52	2.28	2.60	2.37	16.1	16.8	4.3	10.5	5.8	10.9
rac-**5**	2.79	2.13	2.55	2.35	16.3	16.1	4.8	10.5	4.9	11.6
rac-**28**	2.75	2.48	2.79	2.59	15.3	15.8	4.5	11.6	5.7	11.7
rac-**6**	3.02	2.30	2.79	2.53	15.2	15.6	4.7	11.3	5.0	12.1
rac-**35**	2.47	2.30	2.57	2.35	16.3	16.2	4.0	11.5	6.0	11.0
rac-**7**	2.80	2.09	2.53	2.31	16.2	16.0	5.5	11.0	5.5	11.0
rac-**8**	2.52	2.34	2.61	2.41	16.3	16.1	6.2	10.2	5.0	10.2
rac-**9**	2.52	2.34	2.60	2.40	17.0	17.0	5.5	12.0	6.0	11.0

[a] ^{1}H-NMR ($CDCl_3$) data for the benzylic hydrogens of the various complexes: chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. The uncertainty in the *J* values is estimated to be ± 0.5–1.0 Hz.

mined by lithiation of the various complexes (*rac*-**5**, *rac*-**6, rac**-**7**, *rac*-**8** and *rac*-**9**) followed by deuteration. Lithiation was carried out under conditions similar to those employed previously for the selective alkylation of **1** (see above). Preliminary experiments employing complexes *rac*-**1** and **50**[31] had shown that *n*-butyllithium in THF in the presence of hexamethyl phosphoric triamide (HMPA) as cosolvent represents a very suitable system[32]. In the absence of HMPA, significantly lower degrees of deuteration were observed.

In a typical experiment, the complex was dissolved in the solvent mixture (THF/HMPA, 10:1) and 1.5–3 equivalents of *n*-butyllithium was added. The development of a red color indicated the formation of a benzylic lithiated intermediate[3c]. Deuteration was then achieved by injecting D_2O or the more acidic D^+ source CF_3CO_2D. The latter had to be used in order to obtain a reasonably fast protonation of the anions derived from *rac*-**5** and *rac*-**7**, whereas the protonation of the anions derived from *rac*-**1** and **50** proceeded very rapidly, even with D_2O. After extractive work-up, the reisolated (deuterated) starting material was purified by chromatography and recrystallization. The degree and regioselectivity of the deuteration were then analyzed by means of ^{1}H-NMR spectroscopy[33] based on the assignments for the benzylic hydrogen atoms given above (Table 2). The purified deuterated samples were usually obtained in yields of 40–70%. In some experiments, losses were caused due to partial desilylation or decomplexation.



In particular, it should be noted that no suitable conditions were found for the deprotonation of complexes *rac*-**8** and *rac*-**9** with *n*-butyllithium. These compounds preferentially underwent desilylation (*rac*-**9**) or gave rise to a mixture of decomplexed substances after the usual work-up procedure (*rac*-**8**). In a preliminary experiment, it was shown that deprotonation of *rac*-**8** with *s*-butyllithium in THF at –100 °C occurs unselectively at the (less hindered) aryl positions, thus giving rise to a 1:1 mixture of the 6- and 7-methylated products upon treatment of the lithiated intermediates with methyl iodide.

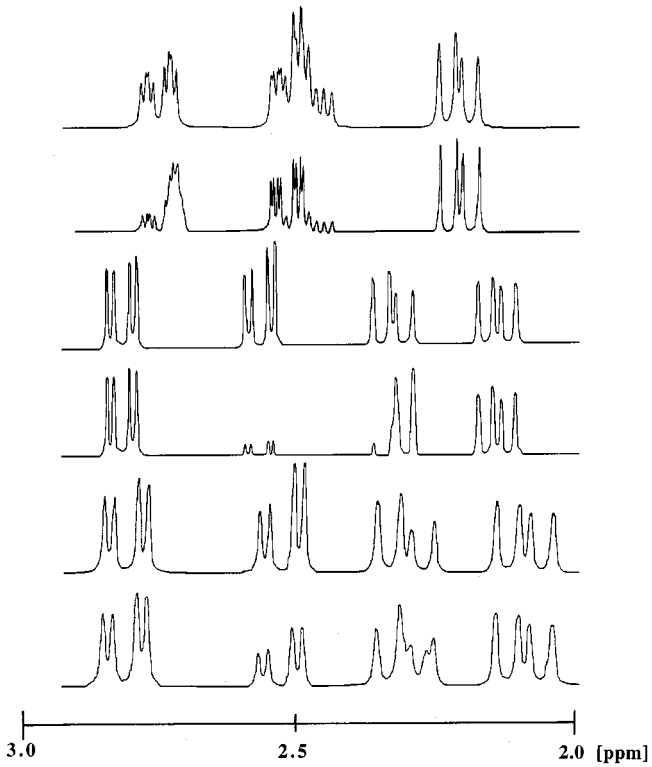
The results of the various deuteration experiments are summarized in Table 3. The most important results are as

Table 3. Selective benzylic deprotonation/deuteration experiments[a]

Entry	Starting complex	Product(s)[b]	Conditions[b]	Degree of deuteration [%]	Regioselectivity [c]
1	**50**	*rac*-**51**	B	95 ± 2	–
2	*rac*-**1**	*rac*-**52a** + *rac*-**52b**	C	85 ± 2	≥ 4:1
3	*rac*-**1**	*rac*-**52a**	B	90 ± 2	≥ 15:1
4	*rac*-**5**	*rac*-**53b**	A	65 ± 2	≥ 15:1
3	*rac*-**5**	*rac*-**53b**	C	50 ± 5	≥ 10:1
6	*rac*-**6**	*rac*-**54a** + *rac*-**54b**	C	90 ± 10[d]	≥ 1.5:1
7	*rac*-**7**	*rac*-**55b**	A	50 ± 2	≥ 15:1
8	*rac*-**53b** (65% D)	*rac*-**53b**	A	80 ± 2	≥ 15:1
9	*rac*-**53b** (65% D)	*rac*-**5**	A[e]	10	–
10	*rac*-**55b** (50% D)	*rac*-**55b**	A	90 ± 5	–[f]
11	*rac*-**55b** (50% D)	*rac*-**7**	A[e]	18	–

[a] Results of the deprotonation/deuteration experiments with *n*BuLi. – [b] A: 2 equiv. *n*BuLi; THF/HMPA, 10:1, −78°C → 25°C, 30 min, then CF_3COOD, −78°C → 25°C, 30 min; B: 1.5 equiv. *n*BuLi; THF/HMPA, 10:1, −70°C → 25°C, 15 min, then D_2O, 25°C, 15 min; C: 3 equiv. *n*BuLi; THF/HMPA, 10:1, 25°C, 30 min, then D_2O, 25°C, 30 min. – [c] Determined by means of ^{1}H-NMR spectroscopy on the assumption that a deviation ≥ 5% of the integrals of the benzylic hydrogen atoms must result from deuteration. – [d] In this case, the product mixture was completely desilylated with TBAF/SiO_2 before the degree of deuteration was determined. – [e] In this case, the lithiated intermediate was protonated by addition of CF_3COOH. – [f] According to the ^{1}H-NMR spectrum, ca. 15% of the high overall deuteration occurred at the C-4 position (*exo*-pseudoaxial).

Figure 8. ^{1}H-NMR signals ($CDCl_3$) of the benzylic protons for the following complexes (from top to bottom): *rac*-**1**, *rac*-**52a** (90% D), *rac*-**5**, *rac*-**53b** (80% D), *rac*-**7** and *rac*-**55b** (50% D)



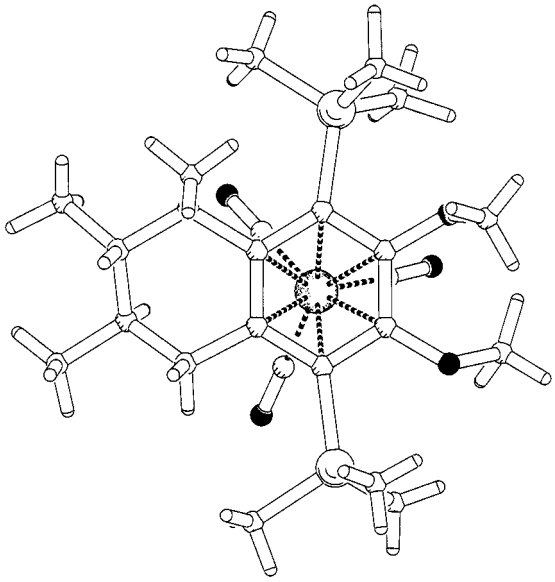
follows: (a) High regioselectivities were observed in the case of *rac*-**1**, *rac*-**5** and *rac*-**7** (see Table 3, entries 2–5, 7; see also Figure 8); (b) in contrast, *rac*-**6** showed only a very low regioselectivity (Table 3, entry 6); (c) the regioselectivity of the deprotonation of *rac*-**5** and *rac*-**7** indicates that the pseudoequatorial benzylic *exo*-hydrogen atoms were abstracted (formation of *rac*-**53b** and *rac*-**55b**), while the deprotonation of *rac*-**1** afforded selectively the *exo*-pseudoaxially deuterated product *rac*-**52a** as expected (see Scheme 1); (d) when the already deuterated complexes *rac*-**53b** and *rac*-**55b** were subjected to a second deprotonation/deuteration cycle, the degree of deuteration was further enhanced (Table 3, entries 8 and 10)[34]; (e) in accordance with the latter experiments, the corresponding deprotonation (dedeuteration)/protonation cycle (Table 3, entries 9 and 11) resulted mainly in the loss of the deuterium substitution (reversion to *rac*-**5** and *rac*-**7**). This also demonstrates that proton (or D^+) abstraction and reprotonation (redeuteration) occur at the same position[35].

In order to evaluate the synthetic potential of the aforementioned highly regioselective deprotonations, we also tried to trap the lithiated intermediates by alkylation and acylation. In the case of *rac*-**5**, treatment of the anion with methyl iodide or acetyl chloride afforded the products *rac*-**56** and *rac*-**57**, respectively, in good yields (Scheme 9). The relative configurations of these compounds were determined by means of ^{1}H-NMR spectroscopy and, in the case of *rac*-**56**, by X-ray crystallography as well (Figure 9)[36]. The results gave an independent proof that the benzylic deprotonation of *rac*-**5** occurs regioselectively at the pseudoequatorial position (H_c, see Figure 6), thereby corroborating the results of the deuteration studies described above. In contrast, the corresponding methylation and acetylation products derived from *rac*-**7** were found to be highly unstable and therefore of little synthetic value[37].

Discussion and Additional Experiments

The experimental results described in the previous section clearly show (for the cases of *rac*-**1**, *rac*-**5** and *rac*-**7**) that benzylic deprotonation of (arene)$Cr(CO)_3$ complexes can proceed with remarkably high regioselectivity, even if the position of the proton abstraction cannot a priori be predicted using the usual electronic arguments. Additionally, *our initial assumption that pseudoaxial benzylic hydrogen atoms are preferentially abstracted as a result of commonly invoked stereoelectronic factors*[8] *(see Introduction) has clearly been disproved* as, in contrast to the deprotonation

Figure 9. X-ray crystal structure of *rac*-**56**



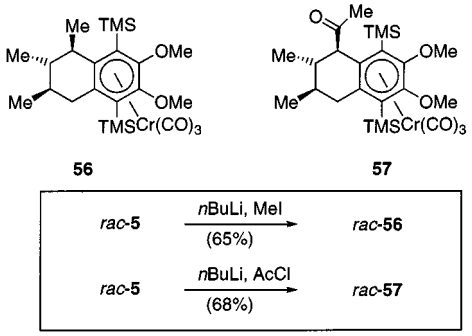
of *rac*-**1**, complexes *rac*-**5** and *rac*-**7** were selectively deprotonated at their pseudoequatorial positions.

The inspection of molecular models suggests an almost comparable steric environment at the competing benzylic positions in all cases. It is therefore unlikely that the complete reversal of the regioselectivity (changing from *rac*-**1** to *rac*-**5** or *rac*-**7**, respectively) is due to a simple steric effect.

At this point, we asked ourselves whether the conformation of the $Cr(CO)_3$ tripod could possibly have an influence on the regioselectivity of the benzylic deprotonation. Could such a previously unnoted or even cursorily excluded[38] effect be responsible for the observed selectivities?

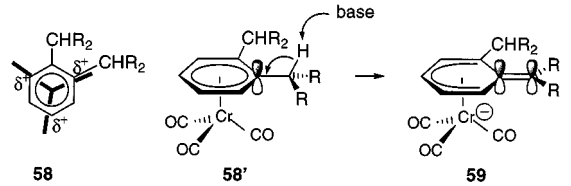
It is a broadly accepted hypothesis that the regioselectivity of kinetically controlled nucleophilic additions to (arene)chromium complexes is influenced by the preferred conformation of the $Cr(CO)_3$ tripod[1a]. This picture is based on the assumption that in the case of charge-controlled reactions, those arene carbon atoms that are eclipsed by a Cr−CO bond are preferentially attacked by a nucleophile due to the positive charge induced by the eclipsing CO ligand[39][40][41][42][43]. Analogous arguments have also been advanced in connection with regioselective ring lithiations of (arene)$Cr(CO)_3$ complexes[44].

Scheme 9



In a similar fashion, one could imagine that the (kinetic) acidity of a benzylic proton increases with an increasing positive partial charge at the adjacent arene center. Thus, if one of two competing benzylic positions is eclipsed by a CO ligand (substructure **58**), the proton abstraction at this center should be (stereoelectronically) favored (Figure 10).

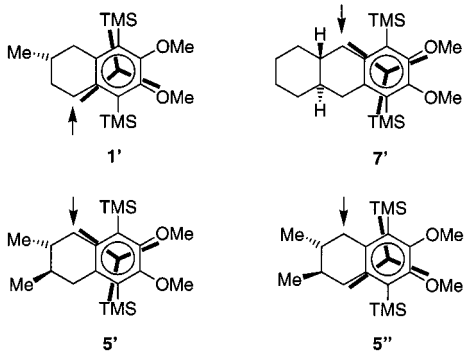
Figure 10. Explanation of the stereoelectronic effect resulting in the preferred deprotonation of those benzylic hydrogen atoms which are activated by an eclipsed CO ligand



The resulting anionic species (which is best represented by a formula of type **59**[45]) should also preferentially adopt an eclipsed conformation, since the deprotonated side-chain represents a strong donor substituent at the (arene)$Cr(CO)_3$ nucleus[46].

Further inspection of the crystal structures of the substrates *rac*-**1**, *rac*-**5** and *rac*-**7** (see above) revealed that in the case of *rac*-**1** and *rac*-**7**, the benzylic center at which the deprotonation preferentially takes place is indeed eclipsed by a CO ligand in the crystalline state (as indicated by the arrow in Figure 11). However, as mentioned above, the crystals of *rac*-**5** were found to contain two independent molecules with different conformations (**5′** and **5′′**), of which only one conformer (**5′**) reflected the observed regioselectivity of deprotonation (Figure 11).

Figure 11. Preferred conformation of the $Cr(CO)_3$ tripod (depicted by the bold lines) for complexes **1**, **7** and **5** as found in their crystal structures; the arrows mark those benzylic positions which were found to be preferentially attacked by *n*-BuLi

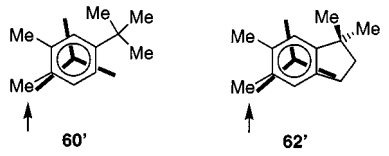


Of course, one can never unequivocally conclude a preferred conformation in solution from a crystal structure. More importantly, if the equilibration of the $Cr(CO)_3$ conformers[47] takes place rapidly compared to the deprotonation, the Curtin-Hammett principle[48] should apply and the regioselectivity would only be governed by the difference in energy between the competing transition states. Nevertheless, as mentioned above for nucleophile additions to (arene)$Cr(CO)_3$ complexes, the preferred conformation of the $Cr(CO)_3$ tripod may have an influence on the regioselectivity of attacking reagents. In such cases, the same fac-

tors determining the preferred ground state conformation also seem to be effective in the transition state and the most stable transition state is derived from the most stable ground state conformation (principle of least motion)[49]. In other words, the deprotonation is accompanied by a change of the overall electronic structure and the position of all atoms involved (delocalization). Therefore, the rate of proton transfer should be enhanced if the degree of structural and electronic reorganization is minimal[50].

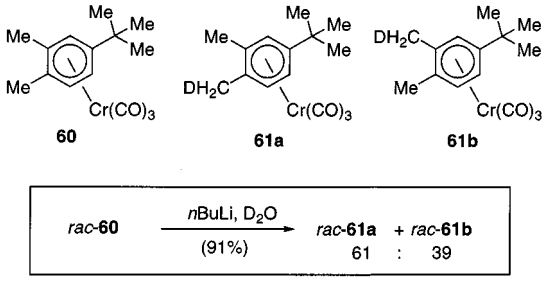
To probe the general applicability of this theory, we investigated the regioselectivity of the deprotonation/deuteration of complex *rac*-**60**[51] employing our tried and tested conditions (*n*-BuLi, D_2O). This substrate had previously been examined by Brocard[6d][38] under different conditions (*t*BuOK, DMSO, CH_2O), but no selectivity was observed. Due to the bulkiness of the *tert*-butyl group, *rac*-**60** should adopt the conformation depicted in formula **60′**. Accordingly, we would predict that the deprotonation should occur preferentially at the methyl group *para* to the *tert*-butyl substituent (as indicated by the arrow in Figure 12).

Figure 12. Lowest energy conformation of complexes **60** and **62**; the arrows mark those benzylic positions which are expected to be preferentially attacked by a base



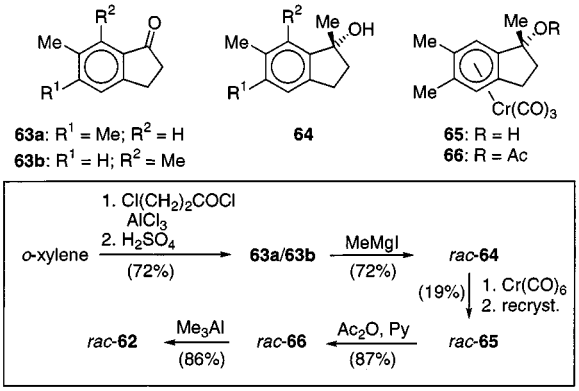
Indeed, when *rac*-**60** was first treated with *n*-butyllithium in THF at −78°C and then the resulting red solution was quenched with D_2O, a 61:39 mixture of the monodeuterated products *rac*-**61a** and *rac*-**61b** was isolated in high yield (Scheme 10)[52].

Scheme 10



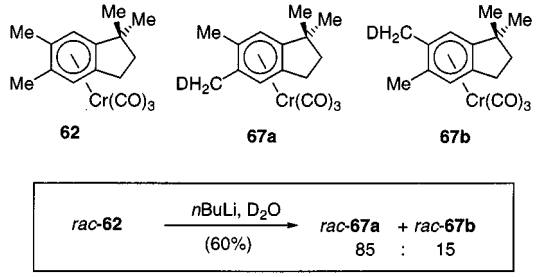
As a second probe of our hypothesis, we also studied complex *rac*-**62**, which was synthesized as indicated in Scheme 11. Thus, Friedel-Crafts acylation of *o*-xylene with 3-chloropropionic chloride and subsequent acid-catalyzed cyclization[53] afforded a 3:1 mixture of the indanones **63a**[54] and **63b**. After treatment with methylmagnesium iodide (→ *rac*-**64**) and (*endo*-selective)[55] complexation, the resulting mixture of regioisomeric indanol complexes was separated by fractional crystallization to furnish the pure regioisomer *rac*-**65**. *O*-Acetylation followed by treatment of the resulting acetate *rac*-**66** with trimethylaluminum[56] finally gave the desired complex *rac*-**62**.

Scheme 11



When *rac*-**62** was subjected to the proven deprotonation/deuteration conditions, the monodeuterated isomers *rac*-**67a** and *rac*-**67b** were formed in a ratio of 85:15 (Scheme 12). The assignments were unambiguously confirmed by NOE measurements. As in the case of *rac*-**60**, the regioselectivity of the benzylic deprotonation of *rac*-**62** can be understood in terms of a conformational picture (see Figure 12) and the assumption that the proton abstraction occurs predominantly at the methyl group that is activated by the eclipsing CO ligand.

Scheme 12



Conclusion

A series of conformationally restricted (arene)$Cr(CO)_3$ complexes has been synthesized and the regioselectivity of their benzylic deprotonation has been investigated. Our findings show that high regioselectivities can be obtained even in cases where no major electronic or steric effects are operative. The original assumption that pseudoaxially oriented hydrogen atoms are preferentially attacked by the base due to stereoelectronic reasons was clearly refuted by experiments employing (η^6-tetralin)- and (η^6-*trans*-octahydroanthracene)$Cr(CO)_3$ derivatives (*rac*-**5** and *rac*-**7**, respectively). On the other hand, experiments with the complexes *rac*-**60** and *rac*-**62** indicated that the conformation of the $Cr(CO)_3$ tripod exerts an influence on the regioselectivity.

Based on our current level of understanding, we wish to draw the following general picture: In the case of (arene)$Cr(CO)_3$ complexes with two competing benzylic positions, deprotonation occurs preferentially at that position

where the adjacent aryl center bears the greater positive partial charge. In the case of unambiguous electronic circumstances, the conformation of the $Cr(CO)_3$ tripod plays only a minor role[2][6], merely reflecting (and possibly amplifying) the polarization induced by the substituents. Should, however, the electronic effects not lead to a favorization of one position (e.g. due to a symmetric substitution pattern or the absence of polar substituents), the preferred conformation of the $Cr(CO)_3$ tripod may become important. In such cases, those benzylic positions which are eclipsed by a CO ligand in the lowest energy conformation are preferentially deprotonated (kinetic stereoelectronic effect).

It must be emphasized that this picture is as yet rather an empirical one and it would be interesting if it could be supported by quantum-chemical calculations and by more detailed structural information on the intermediates resulting from benzylic deprotonation of (arene)$Cr(CO)_3$ complexes. Investigations in this area are currently being performed in this laboratory.

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Experimental Section

General: Manipulations involving air-sensitive compounds were carried out under argon using Schlenk and syringe techniques. Anhydrous solvents were obtained by distillation from sodium benzophenone ketyl (THF and diethyl ether), from P_2O_5 (CCl_4), from CaH_2 (HMPA), or by filtration through ICN Alumina B Grade Super 1 (toluene and nBu_2O). Reagents (generally ≥ 98%) were used as received from Aldrich, Fluka, Merck, Acros and Chemetall without further purification, unless otherwise stated. The concentration of organolithium solutions was determined by titration with menthol in THF in the presence of 1,10-phenanthroline[57]. The organic solutions resulting from aqueous work-up were concentrated under reduced pressure using a rotary evaporator. All reactions were monitored by analytical thin-layer chromatography (TLC) using Merck silica gel 60 F 254 glass plates. The chromatograms were visualized with UV light or by staining with a cerium reagent (prepared by dissolving 2 g of phosphomolybdic acid and 1 g of cerium(IV) sulfate in a mixture of 10 ml conc. H_2SO_4 and 90 ml EtOH] followed by heating. Flash chromatography[58] was performed on silica gel 60 (230−400 mesh) from Merck. Preparative thin-layer chromatography (PTLC) was carried out using a chromatotron (Harrison Research Model 7924 T) on glass plates coated with 1−4 mm layers of silica gel containing gypsum (Merck PF 60 F 254). NMR spectra were recorded in $CDCl_3$ with Bruker instruments (AM 250, AM 270 or AM 400) using residual undeuterated solvent as an internal reference. The spectra are reported in ppm relative to tetramethylsilane using the following abbreviations to express the multiplicities: s = singlet; d = doublet; t = triplet; q = quadruplet; br = broad. ^{13}C chemical shifts were determined from ^1H-decoupled spectra, the number of protons bound directly to each carbon atom was determined employing the DEPT sequence[59] (q = CH_3; t = CH_2; d = CH; s = quaternary carbon atoms). Mass spectrometry was carried out at 70 eV using a Varian MAT 711 instrument. Infrared spectra were obtained using a Nicolet Magna FT-IR 750 instrument. Optical rotations were measured with a Perkin-Elmer 241 polarimeter, concentrations (*c*) are given in g/100 ml. Melting points were measured in open capillary tubes and are uncorrected.

1,2-Dichloro-4,5-dimethoxybenzene (**17**)[14a]: To 46 ml (0.36 mol) of veratrole (**16**), 66 ml (0.82 mol) of sulfuryl chloride was added dropwise over a period of 30 min. The mixture was stirred for 1 h at room temp. and, after fitting the flask with a reflux condenser, was heated to 80°C for 2 h. The reflux condenser was then replaced by a distillation set-up and the excess sulfuryl chloride was distilled off under reduced pressure (ca. 100 Torr). On cooling the mixture to room temp., a solid formed, which was washed with cold hexane (2 × 20 ml) and recrystallized from EtOH (30 ml) at 4°C yielding 57.70 g (77%) of **17** as colorless crystals, m.p. 82.5°C (ref.[14a]: m.p. 84°C). − R_f = 0.23 (hexane/EtOAc, 10:1). − IR (KBr): $\tilde{\nu}$ = 3003 (w), 2965 (w), 2937 (w), 2906 (w), 2836 (w), 1508 (m), 1432 (m), 1363 (m), 1260 (m), 1211 (m), 1179 (m), 1132 (m), 1027 (m), 920 (m), 840 (m), 794 (m), 678 (m), 1594 (w), 1337 (w), 1190 (w) cm^{-1}. − ^1H NMR (270 MHz): δ = 3.85 (s, 6 H), 6.91 (s, 2 H). − MS *m/z* (%): 208 (64), 206 [M^+] (98), 193 (32), 191 (50), 165 (8), 163 (13), 130 (8), 128 (25), 113 (12), 99 (16). − $C_8H_8Cl_2O_2$ (207.06): calcd. C 46.23, H 3.88; found C 46.46, H 3.99.

1,2-Dimethoxy-4,5-dimethylbenzene (**18**)[14b]: To a stirred solution of **17** (15 g, 72.2 mmol) in anhydrous diethyl ether (150 ml) was added methyllithium (100 ml, 160 mmol, 1.6 M in ether) at −20°C. The reaction flask was fitted with a reflux condenser and the temperature was allowed to rise to −7°C. At this point, an exothermic reaction took place, which was moderated by means of a suitably sized cooling bath. The cooling bath was then replaced by an oil bath and the brown solution was refluxed for 2 h. After cooling to 0°C, the reaction mixture was carefully quenched with 150 ml of water. The resulting mixture was extracted twice with diethyl ether, and the combined extracts were washed with 2 N HCl, saturated $NaHCO_3$ and brine, and dried with $MgSO_4$. The solvent was removed in vacuo and the dark-brown residue was kugelrohr-distilled (61°C, 0.6 Torr) yielding 8.08 g (67%) of **18** as a colorless oil, which solidified on standing; m.p. 42.5°C (ref.[14b]: m.p. 43°C). − R_f = 0.28 (hexane/EtOAc, 10:1). − IR (KBr): $\tilde{\nu}$ = 2999 (m), 2939 (m), 2846 (m), 1607 (m), 1519 (br), 1469 (s), 1394 (m), 1336 (s), 1266 (s), 1120 (br), 1105 (br), 997 (s), 854 (s), 828 (m), 732 (w) cm^{-1}. − ^1H NMR (270 MHz): δ = 2.20 (s, 6 H), 3.84 (s, 6 H), 6.67 (s, 2 H). − $C_{10}H_{14}O_2$ (166.22): calcd. C 72.26, H 8.49; found C 72.19, H 8.53.

1,2-Bis(bromomethyl)-4,5-dimethoxybenzene (**19**)[14c]: To a suspension of 3 g of powdered molecular sieves (4 Å) in 125 ml anhydrous CCl_4 was added **18** (5.0 g, 30.1 mmol), anhydrous NBS (10.76 g, 60.2 mmol) and AIBN (10 mg) and the mixture was refluxed for ca. 1 h whilst being irradiated with a 200-W lamp (Note: On completion of the reaction, the slightly reddish solution turns completely colorless). The mixture was then allowed to cool to room temp. and filtered successively through short pads of Celite and silica 60. After removing the solvent in vacuo, a slightly yellow oil was obtained, which crystallized spontaneously. Recrystallization from hexane/EtOAc (3:1) yielded 7.03 g (72%) of **19** as yellowish needles, m.p. 105°C (ref.[14c]: m.p. 109°C). − R_f = 0.27 (hexane/EtOAc, 4:1). − IR (KBr): $\tilde{\nu}$ = 3002 (w), 2954 (w), 2904 (w), 2828 (w), 1522 (s), 1460 (m), 1402 (w), 1357 (m), 1277 (s), 1239 (m), 1203 (s), 1127 (s), 1090 (m), 1032 (w), 1000 (m), 896 (w), 872 (m), 748 (m), 670 (w) cm^{-1}. − ^1H NMR (270 MHz): δ = 3.90 (s, 6 H),

4.63 (s, 4 H), 6.84 (s, 2 H). − MS; *m/z* (%): 324 [MH_2^+] (10), 323 [MH^+] (6), 245 (60), 243 (60), 231 (10), 229 (10), 165 (24), 163 [$MH^+ - 2Br$] (100), 149 (16), 121 (25). − $C_{10}H_{12}Br_2O_2$ (324.01): calcd. C 37.07, H 3.73; found C 36.58, H 3.66.

Diethyl (2RS,3RS)-6,7-Dimethoxy-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxyate (*rac*-**20**): A solution of **19** (6.48 g, 20 mmol) and 10 ml (62.8 mmol) of diethyl fumarate in 200 ml of anhydrous THF was cooled to 0°C. To this was added 6.8 g (55.4 mmol) of chromium(II) chloride (Merck, assay ca. 90%) to give a greenish suspension that rapidly turned purple. The mixture was kept at 0°C for 5 h, then the ice-bath was removed and the deep-purple solution was stirred at room temp. for 1 h; 50 ml H_2O was added and after 5 min the mixture was extracted with hexane/EtOAc (2:1, 3 × 100 ml). The combined organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed under reduced pressure and the remaining oil was crystallized from hexane/EtOAc (3:1) yielding 4.44 g (66%) of the Diels-Alder product *rac*-**20** as colorless crystals. An analytical sample was additionally purified by PTLC (hexane/EtOAc, 3:1), m.p. 80°C. − R_f = 0.29. − IR (KBr): $\tilde{\nu}$ = 2991 (m), 2963 (m), 2940 (m), 2920 (m), 2837 (m), 1728 (br, C=O), 1611 (s), 1518 (s), 1467 (s), 1378 (s), 1302 (s), 1247 (s), 1182 (s), 1116 (s), 1020 (s), 997 (s), 919 (m), 849 (s) cm^{-1}. − ^1H NMR (250 MHz): δ = 1.28 (t, *J* = 7.1 Hz, 6 H), 2.97 (m, 6 H), 3.84 (s, 6 H), 4.17 (q, *J* = 7.1 Hz, 4 H). − MS; *m/z* (%): 336 [M^+] (19), 291 (4), 262 (6), 189 (14), 115 (18), 100 (18), 57 (100). − $C_{18}H_{24}O_6$ (336.39): calcd. C 64.28, H 7.19; found C 64.17, H 7.12.

(2RS,3RS)-2,3-Bis(hydroxymethyl)-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (*rac*-**21**): 0.5 g (13.2 mmol) of $LiAlH_4$ was added in small amounts to a solution of 2.02 g (6 mmol) of *rac*-**20** in anhydrous diethyl ether over a period of 10 min. The suspension was heated to 30°C on a water bath for 40 min, cooled to 0°C, and then quenched by the dropwise addition of 10 ml EtOAc followed by 80 ml of 2 N HCl. The mixture was stirred until all the precipitated aluminates had dissolved and was then extracted with hexane/EtOAc (1:10, 6 × 50 ml) (Note: The resulting diol *rac*-**21** shows a surprisingly high solubility in water; longer reaction times lead to an increased formation of by-products). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, and dried with $MgSO_4$. The solvent was removed in vacuo and the colorless oil was crystallized from EtOAc yielding 1.28 g (86%) of the diol *rac*-**21** as colorless crystals, m.p. 135°C. − R_f = 0.23 (EtOAc). − IR (KBr): $\tilde{\nu}$ = 3481 (br, OH), 3386 (br, OH), 2906 (m), 2833 (C−H), 1517 (s), 1462 (m), 1353 (m), 1242 (s), 1219 (m), 1123 (s), 1098 (m), 1065 (m), 1027 (m), 988 (m), 895 (w), 849 (w), 745 (w) cm^{-1}. − ^1H NMR (270 MHz): δ = 1.83 (m, 2 H), 2.56 (dd, J_1 = 10.1 Hz, J_2 = 15.7 Hz, 2 H), 2.69 (dd, J_1 = 4.0 Hz, J_2 = 16.6 Hz, 2 H), 2.95 (br, 2 H, exchanges with D_2O), 3.65 (dd, J_1 = 6.3 Hz, J_2 = 10.9 Hz, 2 H), 3.78 (dd, J_1 = 3.3 Hz, J_2 = 10.9 Hz, 2 H), 3.83 (s, 6 H, OMe), 6.59 (s, 2 H). − MS; *m/z* (%): 252 [M^+] (100), 220 (20), 203 (75), 189 (14), 188 (15), 165 (25), 164 (32), 71 (30), 69 (41), 57 (88), 55 (70). − $C_{14}H_{20}O_4$ (252.31): calcd. C 66.65, H 7.79; found C 66.37, H 7.91.

(2RS,3RS)-6,7-Dimethoxy-2,3-bis(tosyloxymethyl)-1,2,3,4-tetrahydronaphthalene (*rac*-**22**): A stirred solution of 2.15 g (8.5 mmol) of diol *rac*-**21** in 25 ml of anhydrous pyridine was cooled to 0°C and 7.65 g (40 mmol) of *p*-toluenesulfonyl chloride was added within 5 min. The orange-red solution was stirred at this temperature for 1 h and then kept at 4°C for 24 h. The solution was then poured slowly into a vigorously stirred mixture of 100 ml conc. HCl, 100 g of ice and 200 ml of CH_2Cl_2, and stirring was continued while the mixture was allowed to warm to room temp. The layers were then separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 100 ml). The combined organic layers were washed with saturated aqueous $NaHCO_3$ and brine, and dried with $CaCl_2$. The solvent was removed under reduced pressure and 50 ml of EtOAc was added, whereupon 3.729 g (78%) of bis(tosylate) *rac*-**22** precipitated as a colorless crystalline powder, m.p. 150°C. − R_f = 0.27 (hexane/EtOAc, 1:1). − IR (KBr): $\tilde{\nu}$ = 3000 (w), 2939 (w), 2834 (w), 1597 (m), 1519 (s), 1468 (m), 1350 (s), 1248 (s), 1175 (s), 1100 (s), 950 (s), 868 (m), 835 (s), 779 (m), 665 (s) cm^{-1}. − ^1H NMR (270 MHz): δ = 2.04 (m, 2 H), 2.46 (s, 6 H), 2.52 (dd, J_1 = 7.2 Hz, J_2 = 16.4 Hz, 2 H), 2.68 (dd, J_1 = 4.5 Hz, J_2 = 16.6 Hz, 2 H), 3.81 (s, 6 H), 3.97 (d, *J* = 4.8 Hz, 4 H), 6.48 (s, 2 H), 7.35 (d, *J* = 8.1 Hz, 4 H), 7.76 (d, *J* = 8.3 Hz, 4 H). − MS; *m/z* (%): 560 [M^+] (22), 388 (4), 258 (4), 234 (4), 220 (4), 69 (60), 57 (100), 55 (88). − $C_{28}H_{32}O_8S_2$ (560.68): calcd. C 59.98, H 5.75; found C 59.84, H 5.70.

(2RS,3RS)-6,7-Dimethoxy-2,3-dimethyl-1,2,3,4-tetrahydronaphthalene (*rac*-**23**): 2.00 g (3.6 mmol) of the ditosylate *rac*-**22** was dissolved in 80 ml of anhydrous diethyl ether and 0.5 g of $LiAlH_4$ was added portionwise. The suspension was refluxed for 30 min, then allowed to cool to room temp., whereupon 10 ml of EtOAc was added dropwise, followed by 50 ml of 2 N HCl. The solution was stirred until all the precipitated aluminates had dissolved and was then extracted with hexane/EtOAc (2:1, 3 × 30 ml). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure and the colorless residue was purified by PTLC (4 mm layer SiO_2; hexane/EtOAc, 10:1) yielding 642 mg (81%) of *rac*-**23** as colorless, clear crystals, m.p. 82°C. − R_f = 0.25 (hexane/EtOAc, 10:1). − IR (KBr): $\tilde{\nu}$ = 2988 (m), 2955 (m), 2927 (m), 2880 (m), 2854 (m), 2832 (m), 1520 (s), 1465 (m), 1450 (m), 1247 (s), 1224 (s), 1112 (s), 1003 (m), 850 (m) cm^{-1}. − ^1H NMR (270 MHz): δ = 1.03 (d, *J* = 6.1 Hz, 6 H), 1.48 (m, 2 H), 2.39 (dd, J_1 = 10.4 Hz, J_2 = 15.7 Hz, 2 H), 2.73 (dd, J_1 = 3.4 Hz, J_2 = 16.8 Hz, 2 H), 3.83 (s, 6 H), 6.56 (s, 2 H). − ^{13}C NMR (62.7 MHz): δ = 19.5 (q), 35.4 (d), 38.0 (t), 55.6 (q), 111.4 (d), 128.7 (s), 146.9 (s). − MS; *m/z* (%): 221 (16), 220 [M^+] (100), 205 (12), 189 (8), 164 (65), 151 (8), 149 (7), 121 (7). − $C_{14}H_{20}O_4$ (252.31): calcd. C 76.33, H 9.15; found C 75.94, H 9.12.

(2RS,3RS,8aSR)-Tricarbonyl(η⁶-6,7-dimethoxy-2,3-dimethyl-1,2,3,4-tetrahydronaphthalene)chromium(0) (*rac*-**24**): A 50-ml Schlenk flask equipped with a reflux condenser and an Hg bubbler was flame-dried in vacuo and flushed with argon. All connections were made air-tight by using Teflon sleeves. After charging with 1.19 g (5.4 mmol) of the ligand *rac*-**23** and 1.24 g (5.6 mmol) of $Cr(CO)_6$, 25 ml of nBu_2O was added and the whole apparatus was evacuated and flushed with argon several times. After adding 2.5 ml of anhydrous THF, the solution was refluxed at 150°C (oil-bath temperature) for 20 h, protected from light for most of the time. The clear, yellow solution thus obtained was allowed to cool to room temp., the solvents were removed in vacuo, and the residue was dissolved in ca. 25 ml of EtOAc. The resulting solution was filtered through a 2-cm pad of silica, the solvent was removed under reduced pressure, and the residue (yellow oil) was crystallized from hexane/EtOAc (3:1) yielding 1.48 g (78%) of the chromium complex *rac*-**24** as yellow cubes, m.p. 167°C. − R_f = 0.3 (hexane/EtOAc, 3:1). − IR (KBr): $\tilde{\nu}$ = 2969 (w), 2912 (w), 2842 (w), 1942 (br, C=O), 1874 (br, C=O), 1848 (br, C=O), 1949 (m), 1428 (m), 1266 (m), 1235 (m), 1113 (m), 991 (m), 675 (m), 633 (all m) cm^{-1}. − ^1H NMR (250 MHz)[60]: δ = 1.00 (d, *J* = 3.1 Hz, 3 H), 1.02 (d, *J* = 3.1 Hz, 3 H), 1.36 (m, 1 H), 1.53 (m, 1 H), 2.29 (dd, J_1 = 22.1 Hz, J_2 = 10.7 Hz, 1 H), 2.36 (dd, J_1 = 22.8 Hz, J_2 = 10.9 Hz, 1 H), 2.53 (dd, J_1 = 21.7 Hz, J_2 = 4.4 Hz, 1 H), 2.59 (dd, J_1 = 20.9 Hz, J_2 = 3.9 Hz, 1 H), 3.74 (s, 3 H), 3.78 (s, 3 H), 5.15 (s, 1 H)

5.18 (s, 1 H). − ^{13}C NMR (63 MHz): δ = 18.8 (q), 34.1 (d), 35.0 (d), 36.0 (t), 37.5 (t), 56.9 (q), 57.1 (q), 78.3 (d), 78.8 (d), 101.9 (s), 103.6 (s), 132.2 (s), 132.3 (s), 234.0 (s). − MS; *m/z* (%): 357 (8), 356 [M$^+$] (24), 300 (15), 273 (54), 272 (100), 243 (25), 242 (90), 220 (10), 186 (23), 164 (8). − $C_{17}H_{20}CrO_5$ (356.34): calcd. C 57.30, H 5.66; found C 57.24, H 5.79.

(2RS,3RS,4aRS)-Tricarbonyl(η^6-6,7-dimethoxy-2,3-dimethyl-5,8-bis(trimethylsilyl)-1,2,3,4-tetrahydronaphthalene)chromium(0) (*rac*-**5**): To a solution of 1.247 g (3.5 mmol) of the chromium complex *rac*-**24** in 50 ml of anhydrous THF was added 3.26 g (30 mmol) of chlorotrimethylsilane and the mixture was cooled to −50°C. In a separate flask, a solution of 1.06 g (7.2 mmol) of 2,2,6,6-tetramethylpiperidine in 25 ml of anhydrous THF was cooled to −50°C and 4.5 ml of *n*-butyllithium (7.2 mmol, 1.6 M in hexane) was added. After 15 min, this (second) solution was added to the solution in the first flask by means of a transfer needle over a period of ca. 1 min. The reaction mixture was stirred for 15 min at −50°C and then for 3 h at room temp. After diluting with 50 ml of EtOAc, the organic solution was washed with 2 N HCl (2 × 50 ml), saturated aqueous $NaHCO_3$ and brine, and dried ($MgSO_4$). After removing the solvent, the remaining yellow oil was purified by PTLC (4-mm layer SiO_2; hexane/EtOAc, 10:1). The product was finally crystallized from hexane yielding 1.42 g (81%) of the disilylated complex *rac*-**5** as clear yellow prisms, m.p. 130°C. − R_f = 0.55 (hexane/EtOAc, 10:1). − IR (KBr): $\tilde{\nu}$ = 2982 (w), 2953 (w), 2900 (w, C−H), 1938 (s, C=O), 1876 (s, C=O), 1854 (s, C=O), 1249 (m), 1022 (m), 852 (m), 670 (m) cm^{-1}. − ^{1}H NMR (250 MHz)[60]: δ = 0.50 (pseudo s, 18 H), 0.96 (pseudo t, *J* = 6.2 Hz, 6 H), 1.25 (m, 1 H), 1.39 (m, 1 H), 2.13 (dd, J_1 = 16.1 Hz, J_2 = 10.5 Hz, 1 H), 2.35 (dd, J_1 = 16.3 Hz, J_2 = 11.6 Hz, 1 H), 2.55 (dd, J_1 = 16.3 Hz, J_2 = 4.9 Hz, 1 H), 2.79 (dd, J_1 = 16.1 Hz, J_2 = 4.8 Hz, 1 H), 3.71 (pseudo s, 6 H). − ^{13}C NMR (63 MHz): δ = 2.9 (q), 3.3 (q), 19.1 (q), 19.3 (q), 33.9 (d), 35.0 (d), 39.3 (t), 39.6 (t), 62.0 (q), 62.2 (q), 95.3 (s), 96.3 (s), 110.7 (s), 111.9 (s), 137.8 (s), 138.0 (s), 234.7 [s, Cr(CO)$_3$]. − ^{13}C NMR (63 MHz, [D$_8$]THF) δ = 3.2 (q), 3.4 (q), 19.2 (q), 19.4 (q), 34.9 (d), 35.9 (d), 40.2 (t), 40.5 (t), 62.1 (q), 62.4 (q), 95.9 (s), 96.9 (s), 111.5 (s), 112.6 (s), 138.7 (s), 139.0 (s), 235.4 [s, Cr(CO)$_3$]. − MS; *m/z* (%): 500 [M$^+$] (7), 444 (11), 417 (37), 416 (84), 258 (4), 220 (8), 57 (100), 55 (76). − $C_{23}H_{36}CrO_5Si_2$ (500.70): calcd. C 55.17, H 7.25; found C 54.99, H 7.12.

Bis[(1S)-1-ethoxycarbonylethyl] (2R,3R)-6,7-Dimethoxy-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate (**26a**) *and Bis-[(1S)-1-ethoxycarbonylethyl] (2S,3S)-6,7-Dimethoxy-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate* (**26b**): To a stirred solution of the dibromide **19** (2.43 g, 7.5 mmol) and bis[(*S*)-1-(ethoxycarbonyl)ethyl] fumarate (**25**) (6.01 g, 19 mmol) in 100 ml of dry THF, 2.46 g (20 mmol) of chromium(II) chloride (Merck, assay ca. 90%) was added at room temp. The greenish suspension turned purple within 0.5 h and was stirred for 4 h before 50 ml H_2O was added. After 5 min, the mixture was extracted with hexane/EtOAc, (2:1, 3 × 100 ml) and the combined organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed under reduced pressure and the remaining oil was purified by flash chromatography (hexane/EtOAc, 2:1) yielding 3.321 g (92%) of a mixture of the diastereomers **26a** and **26b**, besides 3.57 g (11 mmol) of recovered chiral fumarate **25**. The product mixture, which consisted of **26a** and **26b** in a ratio of 81:19 (by HPLC), 79:21 (by NMR), was separated by preparative HPLC (Waters Prep Pak Silica; hexane/dioxane, 4:1, 0.1 l/min).

Major Diastereomer **26a**: R_f = 0.23 (hexane/EtOAc, 2:1). − Anal. HPLC (MN Nuc 50−10; hexane/dioxane, 4:1; 2 ml/min; 254 nm): R_T = 5.05 min. − IR (KBr): $\tilde{\nu}$ = 2989 (w), 2940 (w), 2836 (w), 1739 (br, C=O), 1519 (s), 1451 (m), 1361 (m), 1248 (s), 1218 (s), 1177 (s), 1133 (s), 1116 (s), 1099 (s), 1050 (m) cm^{-1}. − ^{1}H NMR (270 MHz): δ = 1.28 (pseudo t, *J* = 7.2 Hz, 6 H), 1.52 (pseudo d, *J* = 7.1 Hz, 6 H), 2.90 (m, 2 H), 3.10 (m, 2 H), 3.24 (pseudo dd, J_1 = 6.9 Hz, J_2 = 2.9 Hz, 2 H), 3.83 (pseudo s, 6 H), 4.20 (pseudo q, *J* = 7.2 Hz, 4 H), 5.11 (pseudo q, *J* = 7.1 Hz, 2 H), 6.61 (pseudo s, 2 H). − $[\alpha]_D^{20}$ = −61, $[\alpha]_{578}$ = −63, $[\alpha]_{546}$ = −71, $[\alpha]_{436}$ = −119, $[\alpha]_{365}$ = −238, (*c* = 0.153 in $CHCl_3$). − $C_{24}H_{32}O_{10}$ (480.51): calcd. C 59.99, H 6.71; found C 59.77, H 6.84.

Minor Diastereomer **26b**: R_f = 0.23 (hexane/EtOAc, 2:1). − Anal. HPLC (MN Nuc 50−10; hexane/dioxane, 4:1; 2 ml/min; 254 nm): R_T = 5.53 min. − IR (KBr): $\tilde{\nu}$ = 2987 (w), 2939 (w), 2835 (w), 1743 (br, C=O), 1519 (s), 1451 (m), 1378 (m), 1247 (s), 1209 (s), 1177 (s), 1133 (s), 1115 (s), 1099 (s) cm^{-1}. − ^{1}H NMR (270 MHz): δ = 1.26 (pseudo t, *J* = 7.1 Hz, 6 H), 1.49 (pseudo d, *J* = 7.0 Hz, 6 H), 2.97 (m, 2 H), 3.12 (m, 2 H), 3.25 (m, 2 H), 3.83 (pseudo s, 6 H), 4.18 (pseudo q, 4 H), 5.09 (pseudo q, *J* = 7.0 Hz, 2 H), 6.58 (pseudo s, 2 H). − $[\alpha]_D^{20}$ = 16, $[\alpha]_{578}$ = 16, $[\alpha]_{546}$ = 19, $[\alpha]_{436}$ = 43, $[\alpha]_{365}$ = 100 (*c* = 0.319 in $CHCl_3$). − $C_{24}H_{32}O_{10}$ (480.51): calcd. C 59.99, H 6.71; found C 59.99, H 6.96.

(2R,3R)-2,3-Bis(hydroxymethyl)-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (**21**): To a solution of 0.48 g (1.1 mmol) of **26a** in 30 ml of dry diethyl ether was added 0.2 g (13.2 mmol) of $LiAlH_4$. The suspension was heated to reflux for 1 h, then cooled to 0°C, whereupon 10 ml of EtOAc was added dropwise, followed by 20 ml of 2 N HCl. The mixture was stirred until all the precipitated aluminates had dissolved and then extracted with hexane/EtOAc, (1:10, 5 × 25 ml) (Note: The resulting diol is rather soluble in water). The combined extracts were washed with saturated aqueous $NaHCO_3$ and brine, and dried with $MgSO_4$. The solvent was removed in vacuo and the resulting colorless oil was purified by PTLC (2-mm layer SiO_2; EtOAc) to yield 190 mg (76%) of diol **21** (> 99.4% *ee* according to HPLC), m.p. 135°C. − R_f = 0.23 (EtOAc). − Anal. HPLC (Daicel Chiralcel OJ, 0.7 ml/min, 254 nm): R_T (**21**) = 15.54 min; R_T (*ent*-**21**) = 14.10 min. − IR (KBr): $\tilde{\nu}$ = 3507 (br, OH), 3395 (br, OH), 2935 (m), 2908 (m), 2834 (m), 1611 (m), 1519 (s), 1460 (s), 1359 (m), 1254 (s), 1126 (s), 1063 (s), 998 (s) cm^{-1}. − ^{1}H NMR (270 MHz): δ = 1.82 (m, 2 H), 2.54 (dd, J_1 = 10.1 Hz, J_2 = 15.7 Hz, 2 H), 2.89 (dd, J_1 = 4.0 Hz, J_2 = 16.6 Hz, 2 H), 3.10 (br, 2 H, exchanges with D_2O), 3.64 (dd, J_1 = 6.3 Hz, J_2 = 10.9 Hz, 2 H), 3.78 (dd, J_1 = 3.3 Hz, J_2 = 10.9 Hz, 2 H), 3.83 (s, 6 H), 6.58 (s, 2 H). − $[\alpha]_D^{20}$ = −56, $[\alpha]_{578}$ = −58, $[\alpha]_{546}$ = −66, $[\alpha]_{436}$ = −122, $[\alpha]_{365}$ = −223 (*c* = 0.120 in $CHCl_3$). − MS; *m/z* (%): 252 [M$^+$] (100), 203 (98), 189 (17), 188 (18), 165 (46), 164 (26), 151 (13), 115 (13). − $C_{14}H_{20}O_4$ (252.31): calcd. C 66.65, H 7.79; found C 66.38, H 7.77.

(2R,3R)-6,7-Dimethoxy-2,3-bis(tosyloxymethyl)-1,2,3,4-tetrahydronaphthalene (**22**): 390 mg of the diol **21** was treated with 1.635 g (8.5 mmol) of *p*-TsCl in 10 ml of pyridine according to the procedure described above for the preparation of *rac*-**22**. Yield: 560 mg (67%) of the optically active ditosylate **22**. − M.p. 149°C. − R_f = 0.30 (hexane/EtOAc, 1:1). − IR (KBr): $\tilde{\nu}$ = 2998 (w), 2960 (w), 2901 (w), 2836 (w), 1515 (m), 1365 (s), 1176 (s), 968 (s), 853 (m), 553 (s) cm^{-1}. − ^{1}H NMR (270 MHz): δ = 2.05 (m, 2 H), 2.44 (s, 6 H), 2.53 (dd, J_1 = 7.2 Hz, J_2 = 16 Hz, 2 H), 2.67 (dd, J_1 = 5 Hz, J_2 = 17 Hz, 2 H), 3.81 (s, 6 H), 3.97 (d, *J* = 5 Hz, 4 H), 6.47 (s, 2 H), 7.35 (d, *J* = 8 Hz, 4 H), 7.76 (d, 4 H). − $[\alpha]_D^{20}$ = −14, $[\alpha]_{578}$ = −16, $[\alpha]_{546}$ = −19, $[\alpha]_{436}$ = −41, $[\alpha]_{365}$ = −73 (*c* = 0.494 in $CHCl_3$). − MS; *m/z* (%): 560 [M$^+$] (13), 430 (8), 388 (3), 272 (4), 234 (4), 233 (5), 217 (40), 216 (63), 204 (16), 203 (100), 201 (21), 189 (17), 188 (16), 58 (41). − HRMS: 560.1539 as calcd. for $C_{28}H_{32}O_8S_2$.

(2R,3R)-6,7-Dimethoxy-2,3-dimethyl-1,2,3,4-tetrahydronaphthalene (**23**): 841 mg (1.5 mmol) of the ditosylate **22** was treated with 240 mg (6.3 mmol) of $LiAlH_4$ in 50 ml of dry diethyl ether according to the procedure described above for the preparation of *rac*-**23**. Yield: 227 mg (69%) of **23** as colorless, clear crystals, m.p. 81°C. − R_f = 0.25 (hexane/EtOAc, 10:1). − IR (KBr): $\tilde{\nu}$ = 2998 (m), 2952 (m), 2933 (m), 2905 (m), 2882 (m), 2832 (m), 1518 (s), 1465 (m), 1249 (s), 1227 (s), 1114 (m) cm^{-1}. − ^1H NMR (270 MHz): δ = 1.03 (d, J = 6 Hz, 6 H), 1.49 (m, 2 H), 2.39 (dd, J_1 = 10 Hz, J_2 = 16 Hz, 2 H), 2.74 (dd, J_1 = 3.5 Hz, J_2 = 17 Hz, 2 H), 3.83 (s, 6 H), 6.56 (s, 2 H). − $[\alpha]_D^{20}$ = −105, $[\alpha]_{578}$ = −110, $[\alpha]_{546}$ = −126, $[\alpha]_{436}$ = −230, $[\alpha]_{365}$ = −408 (*c* = 0.805 in $CHCl_3$). − MS; *m/z* (%): 221 (16), 220 [M^+] (100), 205 (13), 189 (9), 164 (67), 69 (46), 57 (63), 55 (64). − HRMS: 220.1463 as calcd. for $C_{14}H_{20}O_4$.

(2R,3R,8aS)-Tricarbonyl(η⁶-6,7-dimethoxy-2,3-dimethyl-1,2,3,4-tetrahydronaphthalene)chromium(0) (**24**): 220 mg (1 mmol) of the ligand **23** was treated with 242 mg (1.1 mmol) of $Cr(CO)_6$ in 10 ml of dry nBu_2O and 1 ml of dry THF according to the procedure described above for the preparation of *rac*-**24**. Yield 260 mg (73%) of complex **24** as yellow cubes, m.p. 165°C. − R_f = 0.3 (hexane/EtOAc, 3:1). − IR (KBr): $\tilde{\nu}$ = 2969 (w), 2903 (w), 2842 (w), 1945 (br, C=O), 1869 (br, C=O), 1859 (br, C=O), 1495 (m), 1267 (w), 1113 (w) cm^{-1}. − NMR (400 MHz)[60]: δ = 1.01 (d, 3 H), 1.02 (d, 3 H), 1.38 (m, 1 H), 1.53 (m, 1 H), 2.28 (dd, J_1 = 16.2 Hz, J_2 = 10.6 Hz, 1 H), 2.37 (dd, J_1 = 16.9 Hz, J_2 = 10.8 Hz), 2.52 (dd, J_1 = 16.1 Hz, J_2 = 4.3 Hz, 1 H), 2.60 (dd, J_1 = 16.8 Hz, J_2 = 5.8 Hz, 1 H), 3.75 (s, 3 H), 3.78 (s, 3 H), 5.15 (s, 1 H), 5.18 (s, 1 H). − $[\alpha]_D^{20}$ = −95, $[\alpha]_{578}$ = −101, $[\alpha]_{546}$ = −122 (*c* = 0.485 in $CHCl_3$). − MS; *m/z* (%): 357 (5), 356 [M^+] (16), 300 (9), 273 (27), 272 (100), 243 (13), 242 (48), 220 (6), 186 (12), 164 (5), 149 (5). − $C_{17}H_{20}CrO_5$ (356.34): calcd. C 57.30, H 5.66; found C 57.44, H 5.51.

(3aRS,9aRS)-6,7-Dimethoxy-1,3,3a,4,9,9a-hexahydronaphtho[2,3-c]furan (*rac*-**27**): A solution of 760 mg (3 mmol) of the diol *rac*-**21** in 30 ml of $CHCl_3$ and 3 ml of pyridine was heated to 60°C and 1.720 g (9 mmol) of *p*-TsCl was added. Stirring was continued for 4 h at 60°C, then the mixture was cooled to 0°C and 30 ml of cold 2 N HCl was added. After 30 min, the layers were separated, the aqueous layer was extracted with $CHCl_3$ (2 × 30 ml), and the combined organic layers were washed with saturated $NaHCO_3$ and brine, and dried with $CaCl_2$ overnight. The solvent was removed under reduced pressure and the oily residue was purified by PTLC (3-mm layer SiO_2; hexane/EtOAc/CH_2Cl_2, 1:1:1) to yield 530 mg (76%) of the naphthofuran *rac*-**27** as colorless plates, m.p. 124°C. − R_f = 0.36 (hexane/EtOAc/CH_2Cl_2, 1:1:1). − IR (KBr): $\tilde{\nu}$ = 2937 (m), 2907 (m), 2854 (m), 2833 (m), 1684 (m), 1516 (s), 1239 (s), 1221 (s), 1094 (s), 988 (m), 902 (m) cm^{-1}. − ^1H NMR (270 MHz): δ = 2.04 (m, 2 H), 2.57 (dd, J_1 = 11.4 Hz, J_2 = 15. 6 Hz, 2 H), 2.93 (dd, J_1 = 15.6 Hz, J_2 = 4.1 Hz, 2 H), 3.48 (dd, J_1 = 7.9 Hz, J_2 = 10.2 Hz, 2 H), 3.85 (s, 6 H), 4.17 (pseudo t, J = 7.5 Hz, 2 H), 6.62 (s, 2 H). − ^{13}C NMR (63 MHz): δ = 31.7 (d), 42.5 (t), 55.8 (q), 72.6 (t), 112.2 (d), 127.6 (s), 147.2 (s). − $C_{14}H_{18}O_3$ (234.30): calcd. C 71.77, H 7.74; found C 71.75, H 7.76.

(3aRS,4aSR,9aRS)-Tricarbonyl{η⁶-6,7-dimethoxy-1,3,3a,4,9,9a-hexahydronaphtho[2,3-c]furan}chromium(0) (*rac*-**28**): As described above for the preparation of *rac*-**24**, 351 mg (1.5 mmol) of the ligand *rac*-**27** was heated with 350 mg (1.6 mmol) of $Cr(CO)_6$ in 10 ml nBu_2O and 1 ml THF for 20 h at 150°C (oil-bath temperature). The resulting cloudy yellow solution was cooled, the solvent was removed in vacuo, and the crystalline residue was taken up in 30 ml of EtOAc. The resulting solution was filtered through a 2-cm pad of silica, the solvent was evaporated once more, and the residue was recrystallized from hexane/EtOAc (1:1) to give 441 mg (79%) of the complex *rac*-**28** as small yellow crystals, m.p. 195°C. − R_f = 0.4 (EtOAc). − IR (KBr): $\tilde{\nu}$ = 2978 (m), 2939 (m), 2914 (m), 2850 (m), 1948 (br, C=O), 1874 (br, C=O), 1848 (br, C=O), 1496 (s), 1438 (s), 1289 (s), 1263 (s), 1236 (s), 1214 (s), 1096 (s), 978 (s), 673 (s), 629 (s) cm^{-1}. − ^1H NMR (270 MHz):[60] δ = 1.94 (m, 1 H), 2.14 (m, 1 H), 2.48 (dd, J_1 = 15.2 Hz, J_2 = 11.6 Hz, 1 H), 2.59 (dd, J_1 = 15.7 Hz, J_2 = 11.7 Hz, 1 H), 2.75 (dd, J_1 = 15.3 Hz, J_2 = 4.5 H, 1 H), 2.79 (dd, J_1 = 15.8 Hz, J_2 = 5.7 Hz, 1 H), 3.44 (pseudo d, J = 10.3 Hz, 1 H), 3.46 (pseudo d, J = 10.3 Hz, 1 H), 3.76 (s, 3 H), 3.80 (s, 3 H), 4.10 (pseudo t, J = 7.5 Hz, 1 H), 4.20 (pseudo t, J = 7.5 Hz, 1 H), 5.18 (s, 1 H), 5.21 (s, 1 H). − $C_{17}H_{18}CrO_6$ (370.32): calcd. C 55.14, H 4.93; found C 55.19, H 4.93.

(3aRS,4aSR,9aRS)-Tricarbonyl{η⁶-6,7-dimethoxy-5,8-bis(trimethylsilyl)-1,3,3a,4,9,9a-hexahydronaphtho[2,3-c]furan}chromium(0) (*rac*-**6**): To a solution of 185 mg (0.5 mmol) of the complex *rac*-**28** and 0.35 ml (2.5 mmol) of TMSCl in 10 ml of dry THF at −40°C, was added a solution of LiTMP [prepared separately from 0.19 ml (1.1 mmol) of 2,2,6,6-tetramethylpiperidine and 0.65 ml of *n*-butyllithium (1.04 mmol, 1.6 M in hexane) in 5 ml of dry THF], as described above for the preparation of *rac*-**5**. After 15 min at −40°C and 1 h at room temp., 30 ml of EtOAc was added and the mixture was washed with 2 N HCl (2 × 30 ml), saturated aqueous $NaHCO_3$ and brine. After drying and removal of the solvent, the remaining yellow oil was purified by flash chromatography (hexane/EtOAc, 3:1). The product was finally crystallized from hexane/EtOAc (3:1) yielding 182 mg (71%) of the disilylated complex *rac*-**6** as small yellow needles, m.p. 202°C. − R_f = 0.74 (EtOAc). − IR (KBr): $\tilde{\nu}$ = 2950 (w), 2899 (w), 2850 (w), 1944 (br, C=O), 1858 (br, C=O), 1362 (m), 1320 (m), 1250 (m), 1016 (m), 848 (m), 673 (m) cm^{-1}. − ^1H NMR (400 MHz):[60] δ = 0.46 and 0.47 (both s, 9 H), 1.79 (m, 1 H), 1.93 (m, 1 H), 2.30 (dd, J_1 = 15.2 Hz, J_2 = 11.3 Hz, 1 H), 2.53 (dd, J_1 = 15.6 Hz, J_2 = 12.1 Hz, 1 H), 2.79 (dd, J_1 = 15.6 Hz, J_2 = 5.0 Hz, 1 H), 3.02 (dd, J_1 = 15.2 Hz, J_2 = 4.7 Hz, 1 H), 3.37 (dd, J_1 = 10.4 Hz, J_2 = 7.5 Hz, 1 H), 3.40 (dd, J_1 = 10.4 Hz, J_2 = 7.5 Hz, 1 H), 3.73 (s, 3 H), 3.74 (s, 3 H), 4.09 (pseudo t, J = 7.5 Hz, 1 H), 4.15 (pseudo t, J = 7.5 Hz, 1 H). − $C_{23}H_{34}CrO_6Si_2$ (514.69): calcd. C 53.67, H 6.66; found C 53.49, H 6.51.

1-Bromo-2-(bromomethyl)-4,5-dimethoxybenzene (**31**): A solution of 5.05 g (30 mmol) of 3,4-dimethoxybenzyl alcohol (**30**) in 50 ml of dry benzene was cooled to 0°C and a solution of 1.60 ml (31 mmol) of Br_2 in 50 ml of dry benzene was added over a period of 20 min. Then, 5 ml of HBr (33% in AcOH) was added, the cooling bath was removed, and the red solution was stirred at ambient temperature for 30 min. The mixture was then sequentially washed with saturated aqueous $Na_2S_2O_3$ (50 ml), water (50 ml) and brine, and the organic solution was dried with $MgSO_4$. The solvent was removed under reduced pressure and the yellow, oily residue was crystallized from hexane/EtOAc (3:1) to yield 8.71 g (94%) of the dibromide **31** as thin, colorless needles, m.p. 81°C. − R_f = 0.35 (hexane/EtOAc, 3:1). − IR (CCl_4): $\tilde{\nu}$ = 3006 (w), 2959 (w), 2909 (w), 2841 (w), 1507 (s), 1464 (m), 1383 (m), 1262 (s), 1226 (s), 1210 (s), 1168 (s), 1036 (m) cm^{-1}. − ^1H NMR (270 MHz): δ = 3.87 (s, 3 H), 3.89 (s, 3 H), 4.59 (s, 2 H), 6.93 (s, 1 H), 7.02 (s, 1 H). − MS; *m/z* (%): 312 (7), 310 [M^+ + 2] (14), 308 [M^+] (6), 232 (20), 231 (99), 230 (20), 229 [MH^+ − Br] (100), 215 (5), 187 (7), 185 (9), 108 (13), 107 (17). − $C_9H_{10}Br_2O_2$ (309.99): calcd. C 34.77, H 3.25; found C 34.90, H 3.14.

(2RS)-2-(2′-Bromo-4′,5′-dimethoxybenzyl)cyclohexanone (*rac*-**32**): A stirred solution of diisopropylamine (4.65 ml, 33 mmol) in

100 ml anhydrous THF was cooled to −78°C and *n*-butyllithium (21 ml, 31.1 mmol, 1.48 M in hexane) was added by means of a syringe. After 20 min, a solution of cyclohexanone (4.7 ml, 36 mmol) in anhydrous THF (20 ml) was added slowly (over a period of ca. 30 min) and the resulting mixture was stirred for 10 min at −78°C. A solution of 9.3 g (30 mmol) of the dibromide **31** in anhydrous THF (50 ml) was then added over a period of 5 min, the temperature was allowed to rise, and stirring was continued for 3 h at 0°C and for 10 h at room temp. After quenching with 2 N HCl (100 ml), the mixture was extracted with EtOAc (3 × 100 ml). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, and dried with $MgSO_4$. After removing the solvent in vacuo, the resulting yellow oil was purified by flash chromatography (hexane/EtOAc, 5:1) yielding 8.48 g (86%) of the alkylation product *rac*-**32** as a colorless oil, which solidified upon standing within 48 h. In addition, 1.01 g of the dialkylated by-product **36a** was obtained. An analytical sample of *rac*-**32** was recrystallized from hexane/EtOAc (5:1); m.p. 72°C. − R_f = 0.16 (hexane/EtOAc, 5:1). − IR (CCl_4): $\tilde{\nu}$ = 3003 (w), 2936 (m), 2858 (w), 2839 (w), 1713 (s, C=O), 1580 (s), 1497 (s), 1260 (s), 1233 (s), 1165 (s) cm^{-1}. − ^{1}H NMR (270 MHz): δ = 1.40 (m, 1 H), 1.60 (m, 2 H), 1.82 (m, 1 H), 2.04 (m, 2 H), 2.32 (m, 1 H), 2.38 (m, 1 H), 2.48 (dd, J_1 = 7.5 Hz, J_2 = 19 Hz, 1 H), 2.63 (m, 1 H), 3.20 (dd, J_1 = 6 Hz, J_2 = 19 Hz, 1 H), 3.90 and 3.93 (both s, 3 H), 6.77 and 6.95 (both s, 1 H). − ^{13}C NMR (63 MHz): δ = 25.2 (t), 28.0 (t), 33.7 (t), 35.2 (t), 42.2 (t), 51.0 (d), 55.9 (q), 56.0 (q), 114.2 (d), 115.2 (d), 131.6 (s), 147.8 (s), 147.9 (s), 212.3 (s). − MS; *m/z* (%): 328 (12), 326 [M^+] (12), 248 (17), 247 (100), 231 (55), 229 (57), 151 (11). − $C_{15}H_{19}BrO_3$ (327.22): calcd. C 55.02, H 5.89; found C 55.06, H 5.85.

2,2-Bis(2′-bromo-4′,5′-dimethoxybenzyl)cyclohexanone (**36a**): ^{1}H NMR (270 MHz): δ = 1.74−2.06 (m, 6 H), 2.52 (m, 2 H), 3.23 (AB signal, 4 H), 3.80 (s, 6 H), 3.85 (s, 6 H), 6.70 (s, 2 H), 6.98 (s, 2 H).

(1′RS)-1-Bromo-4,5-dimethoxy-2-(2′-methylenecyclohexylmethyl)benzene (*rac*-**33**): A suspension of 18.7 g of methyltriphenylphosphonium bromide in 250 ml of anhydrous THF was cooled to −78°C and *n*-butyllithium (29 ml, 47 mmol, 1.6 M in hexane) was added by means of a syringe. The temperature was allowed to rise to −30°C over a period of 30 min. At this point, 11.45 g of *rac*-**32** was added, the cooling bath was replaced by an oil bath, and the orange solution was refluxed for 1 h. The cooled mixture was then washed with water (2 × 30 ml) and brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure and 100 ml of hexane was added to the residue, resulting in the precipitation of Ph_3PO. The solution was filtered through a pad of Celite and silica. The solvent was removed under reduced pressure yielding 11.35 g (> 99%) of the methylenated product *rac*-**33** as an essentially pure, slightly yellow oil, which crystallized within two weeks, m.p. 61°C. − R_f = 0.57 (hexane/EtOAc, 5:1). − IR (CCl_4): $\tilde{\nu}$ = 2934 (m, C−H), 3082 (w), 3002 (w), 2856 (w), 2839 (w), 1509 (s), 1496 (m), 1439 (m), 1219 (s), 1496, 1165 (m) cm^{-1}. − ^{1}H NMR (270 MHz): δ = 1.20 − 1.74 (m, 6 H), 2.08 (m, 1 H), 2.37 (m, 1 H), 2.66 (dd, J_1 = 5.5 Hz, J_2 = 14 Hz, 1 H), 3.00 (dd, J_1 = 9.5 Hz, J_2 = 14 Hz, 1 H), 5.60 (pseudo s, 1 H), 5.69 (pseudo s, 1 H), 6.66 (s, 1 H), 7.00 (s, 1 H). − ^{13}C NMR (63 MHz): δ = 24.6 (t), 28.6 (t), 32.7 (t), 35.3 (t), 38.4 (t), 43.3 (d), 56.0 (q), 56.1 (q), 105.8 (t), 113.8 (d), 114.6 (s), 115.4 (d), 132.5 (s), 147.7 (s), 148.0 (s), 152.3 (s). − MS; *m/z* (%): 326 (6), 324 [M^+] (7), 245 (32), 244 (24), 231 (98), 230 (100), 151 (6), 107 (6). − $C_{16}H_{21}BrO_2$ (325.25): calcd. C 59.09, H 6.51; found C 59.34, H 6.57.

(4aRS,9aRS)-6,7-Dimethoxy-1,2,3,4,4a,9,9a,10-octahydroanthracene (*rac*-**34**): To a refluxing solution of 1.63 g (5 mmol) of the olefin *rac*-**33** in 50 ml of dry benzene, a solution of 1.59 ml (5.2 mmol) of tributyltin hydride and 20 mg of azobis(isobutyronitrile) in 8 ml of dry benzene was added over a period of 5 h by means of a syringe pump. Refluxing was continued for 1 h, and then a solution of 5 g of KF in 20 ml of water was added to the cooled (room temp.) mixture. The resulting two-phase system was stirred vigorously overnight. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 30 ml). The combined organic layers were washed with water (2 ×) and brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure and the resulting colorless oil was purified by PTLC (4-mm layer SiO_2; hexane/CH_2Cl_2/EtOAc, 2:1:0.02). The product was finally crystallized from hexane to yield 810 mg (66%) of the cyclization product *rac*-**34** as clear, colorless prisms, m.p. 110°C. − R_f = 0.15 (hexane/CH_2Cl_2/EtOAc = 2:1:0.02). − IR (CCl_4): $\tilde{\nu}$ = 2998 (w), 2919 (m), 2854 (w), 2832 (w), 1518 (s), 1249 (m), 1224 (m), 1129 (w), 1112 (w) cm^{-1}. − ^{1}H NMR (270 MHz): δ = 1.06 (m, 2 H), 1.35 (m, 4 H), 1.84 (m, 4 H), 2.39 (dd, J_1 = 9 Hz, J_2 = 14.5 Hz, 2 H), 2.69 (dd, J_1 = 4.5 Hz, J_2 = 14.5 Hz, 2 H), 3.86 (s, 6 H), 6.56 (s, 2 H). − ^{13}C NMR (63 MHz): δ = 26.3 (t), 33.8 (t), 37.1 (t), 38.8 (d), 55.9 (q), 111.5 (d), 128.6 (s), 146.9 (s). − MS; *m/z* (%): 247 (18), 246 [M^+] (100), 231 (20), 229 (14), 206 (9), 164 (23), 151 (55), 149 (15), 57 (39), 55 (38). − HRMS: 246.1620 as calcd. for $C_{16}H_{22}O_2$.

(4aRS,8aSR,9aRS)-Tricarbonyl(η⁶-6,7-dimethoxy-1,2,3,4,4a,9,9a,10-octahydroanthracene)chromium(0) (*rac*-**35**): As described above for the preparation of *rac*-**24**, 1.06 g (4.3 mmol) of the ligand *rac*-**34** was heated with 0.99 g (4.5 mmol) of $Cr(CO)_6$ in 45 ml nBu_2O and 4.5 ml THF in a 100-ml Schlenk flask for 22 h at 150°C (oil-bath temperature). The resulting clear yellow solution was allowed to cool to room temp., whereupon a yellow precipitate formed. Cooling was continued in an ice bath for 1 h, and then the supernatant solution was carefully decanted off and the residue washed twice with cold diethyl ether. The yellow powder thus obtained was dried in vacuo to yield a first fraction of *rac*-**35**. The solvent of the decanted organic solution was removed in vacuo and the residue was purified by PTLC (1 mm SiO_2; hexane/EtOAc, 3:1). Recrystallization from EtOAc afforded 1.300 g (79%) of the complex *rac*-**35** as small yellow crystals, m.p. 201°C. − R_f = 0.38 (hexane/EtOAc, 10:1). − IR (KBr): $\tilde{\nu}$ = 2925 (w), 2854 (w), 1950 (s, C=O), 1874 (s, C=O), 1851 (s, C=O), 1495 (m) cm^{-1}. − ^{1}H NMR (270 MHz)[60]: δ = 0.96−1.54 (m, 6 H), 1.77 (pseudo dd, 4 H), 2.30 (dd, J_1 = 16 Hz, J_2 = 11.5 Hz, 1 H), 2.35 (dd, J_1 = 16 Hz, J_2 = 11 Hz, 1 H), 2.47 (dd, J_1 = 16.5 Hz, J_2 = 4 Hz, 1 H), 2.57 (dd, J_1 = 16.5 Hz, J_2 = 6 Hz, 1 H), 3.75 (s, 3 H), 3.79 (s, 3 H), 5.16 (s, 1 H), 5.20 (s, 1 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 25.8 (t), 26.0 (t), 33.1 (t), 34.7 (t), 36.4 (t), 37.2 (d), 38.2 (d), 57.0 (q), 57.1 (q), 78.3 (d), 79.0 (d), 101.7 (s), 103.4 (s), 132.2 (s), 132.3 (s), 234.1 (s). − MS; *m/z* (%): 382 [M^+] (16), 326 [M^+ − 2CO] (6), 299 (36), 298 [M^+ − 3CO] (100), 260 (15), 268 (56), 186 (6). − $C_{19}H_{22}CrO_5$ (382.38): calcd. C 59.68, H 5.80; found C 59.55, H 5.78.

(4aRS,8aSR,9aRS)-Tricarbonyl(η⁶-6,7-dimethoxy-5,8-bis(trimethylsilyl)-1,2,3,4,4a,9,9a,10-octahydroanthracene)chromium(0) (*rac*-**7**): To a solution of 3.06 g (8 mmol) of the complex *rac*-**35** and 10.1 ml (80 mmol) of TMSCl in 80 ml of anhydrous THF at −50°C, was added a solution of LiTMP [prepared separately from 2.85 ml (16.8 mmol) of 2,2,6,6-tetramethylpiperidine and 10.4 ml of *n*-butyllithium (16.6 mmol, 1.6 M in hexane) in 40 ml anhydrous THF], as described above for the preparation of *rac*-**5**. After 15 min at −50°C and 1 h at room temp., 50 ml of EtOAc was added and the mixture was washed with 2 N HCl (2 × 50 ml), saturated aqueous $NaHCO_3$ and brine. The dried ($MgSO_4$) solution was con-

centrated and the remaining yellow oil was purified by flash chromatography (hexane/EtOAc, 10:1). Crystallization of the product from hexane/EtOAc (10:1) yielded 3.21 g (76%) of the disilylated complex *rac*-**7** as dark-yellow cubes, m.p. 138°C. − R_f = 0.55 (hexane/EtOAc, 10:1). − IR (KBr): $\tilde{\nu}$ = 2984 (w), 2924 (w), 2904 (w), 2856 (w), 1957 (s), 1887 (s), 1361 (m), 1251 (m), 1020 (m), 857 (m) cm^{-1}. − ^1H NMR (270 MHz)[60]: δ = 0.46 (pseudo s, 18 H), 0.78−1.34 (m, 6 H), 1.78 (m, 4 H), 2.09 (dd, J_1 = 16 Hz, J_2 = 5.5 Hz, 1 H), 2.31 (dd, J_1 = 16 Hz, J_2 = 5.5 Hz, 1 H), 2.53 (dd, J_1 = 16 Hz, J_2 = 11 Hz, 1 H), 2.80 (dd, J_1 = 16.5 Hz, J_2 = 11 Hz, 1 H), 3.72 (pseudo s, 6 H). − ^{13}C NMR (63 MHz, $CDCl_3$) δ = 3.0 (q), 3.3 (q), 25.6 (t), 25.8 (t), 32.9 (t), 33.1 (t), 36.6 (t), 37.5 (t), 38.1 (t), 38.2 (d), 61.9 (q), 62.0 (q), 95.4 (d), 110.2 (s), 111.3 (s), 137.7 (s), 138.0 (s), 234.7 [s, $Cr(CO)_3$]. − MS; *m/z* (%): 526 (6), 470 [M^+ − 2CO] (13), 444 (18), 443 (42), 442 [M^+ − 3CO] (100). − $C_{25}H_{38}CrO_5Si_2$ (526.74): calcd. C 57.01, H 7.27; found C 57.03, H 7.31.

(2RS)-2-(2′-Bromobenzyl)cyclohexanone (*rac*-**38**): A stirred solution of 3.23 ml (33 mmol) of diisopropylamine in 100 ml of dry THF was cooled to −78°C and 13.8 ml (22 mmol) of a solution of *n*-butyllithium (1.6 M in hexane) was added by means of a syringe. After 10 min, a solution of 2.5 ml (25 mmol) of cyclohexanone in 10 ml of dry THF was added dropwise over a period of 20 min. The mixture was stirred for 1 h at −78°C and then transferred dropwise over a period of 1 h to a cold (0°C) stirred solution of α-bromobenzyl bromide (**37**) (5.0 g, 20 mmol) in 80 ml THF. The cooling bath was removed and the mixture was heated to reflux for 3 h. The cooled mixture was subsequently treated with 100 ml of 2 N HCl and extracted with EtOAc (3 × 100 ml). The combined organic extracts were washed with satd. aqueous $NaHCO_3$ and with brine, dried with $MgSO_4$, and the solvent was removed in vacuo. The crude product (yellow oil) consisted of *rac*-**38** contaminated with ca. 30% of the dialkylated product **36b** (NMR). Kugelrohr distillation (85°C, 0.5 Torr) afforded 4.23 g (63% yield) of the pure monoalkylated ketone *rac*-**38** as a colorless oil and 1.83 g (33%) of **36b** as a slightly yellow oil (130°C, 0.5 Torr); R_f = 0.33 (hexane/EtOAc, 10:1). − IR (ATR): $\tilde{\nu}$ = 3058 (w), 2932 (m), 2859 (w), 1708 (s, C=O), 1469 (m), 1444 (m), 1128 (w), 1021 (m), 745 (m) cm^{-1}. − ^1H NMR (400 MHz): δ = 1.42 (pseudo qd, 1 H), 1.54−1.73 (m, 2 H), 1.84 (m, 1 H), 2.00−2.12 (m, 2 H), 2.24 (pseudo dd, J_1 = 5.2 Hz, J_2 = 12.8 Hz, 1 H), 2.43 (m, 1 H), 2.55 (dd, J_1 = 8 Hz, J_2 = 16 Hz, 1 H), 2.65−2.75 (m, 1 H), 3.34 (dd, J_1 = 5.4 Hz, J_2 = 16.2 Hz, 1 H), 7.05 (pseudo td, J_1 = 2.5 Hz, J_2 = 8.5 Hz, 1 H), 7.18−7.27 (m, 2 H), 7.51 (pseudo d, J = 8 Hz, 1 H). − ^{13}C NMR (63 MHz): δ = 25.2 (t), 28.1 (t), 33.7 (t), 35.2 (t), 42.2 (t), 50.5 (d), 124.6 (s), 127.1 (d), 127.7 (d), 131.8 (d), 132.7 (d), 139.7 (s). − MS; *m/z* (%): 187 [M^+ − Br] (100), 171 (16), 169 (17), 119 (43), 107 (22), 69 (10). − HRMS: calcd. for $C_{13}H_{15}O$ (M − Br): 187.1123; found: 187.1118. − $C_{13}H_{15}BrO$ (267.17): calcd. C 58.44, H 5.66; found C 58.17, H 5.67.

2,2-Bis(2′-bromobenzyl)cyclohexanone (**36b**): ^1H NMR (270 MHz): δ = 1.63−1.88 (m, 6 H), 2.03−2.18 (m, 2 H), 3.18 (pseudo d, J = 13.9 Hz, 2 H), 3.33 (pseudo d, J = 14.0 Hz, 2 H), 7.06 (m, 2 H), 7.21 (m, 4 H), 7.55 (m, 2 H).

(1′RS)-1-Bromo-2-(2′-methylenecyclohexylmethyl)benzene (*rac*-**39**): To a stirred suspension of 9.0 g (25.3 mmol) of methyltriphenylphosphonium bromide in 100 ml of dry THF at −78°C, 13.9 ml (22.3 mmol) of a solution of *n*-butyllithium (1.6 M in hexane) was added by means of a syringe and the temperature was allowed to rise to −30°C over a period of 30 min. To the resulting orange solution was added 4.5 g (16.8 mmol) of *rac*-**38**, the cooling bath was replaced by an oil bath, and the mixture was heated to reflux for 2 h. The cooled mixture was then partitioned between water (50 ml) and EtOAc (50 ml) and the aqueous phase was extracted with further EtOAc (50 ml). The combined organic extracts were washed with brine, dried with $MgSO_4$, and the solvent was removed under reduced pressure. The residue was treated with 50 ml of hexane and filtered through a short pad of Celite (1 cm) and silica (1 cm). The solvent was removed under reduced pressure yielding 4.22 g (95%) of the methylenated product *rac*-**39** as a slightly yellow oil; R_f = 0.75 (hexane/EtOAc, 10:1). − IR (CCl_4): $\tilde{\nu}$ = 3067 (w), 2927 (s), 2853 (m), 1643 (m), 1469 (m), 1437 (m), 1023 (s), 882 (m), 745 (s) cm^{-1}. − ^1H NMR (270 MHz): δ = 1.18−1.76 (m, 6 H), 2.12 (m, 1 H), 2.32−2.59 (m, 2 H), 2.66 (dd, J_1 = 9.5 Hz, J_2 = 13 Hz, 1 H), 3.10 (dd, J_1 = 5.5 Hz, J_2 = 13 Hz, 1 H), 4.62 (pseudo s, 1 H), 4.74 (pseudo s, 1 H), 7.03 (pseudo dt, J_1 = 2 Hz, J_2 = 8 Hz, 1 H), 7.10−7.24 (m, 2 H), 7.54 (pseudo dd, J_1 = 1.5 Hz, J_2 = 9.5 Hz, 1 H). − ^{13}C NMR (63 MHz): δ = 24.6 (t), 28.7 (t), 32.8 (t), 35.3 (t), 38.8 (t), 42.8 (d), 105.9 (t), 124.9 (s), 127. 0 (d), 127.4 (d), 131.3 (d), 132.8 (d), 140.5 (s), 152.2 (s). − MS; *m/z* (%): 262 (20), 185 [M^+ − Br] (100), 171 (13), 169 (14), 129 (11), 117 (32), 95 (96), 94 (22), 79 (15), 67 (19). − $C_{14}H_{17}Br$ (265.19): calcd. C 63.41, H 6.46; found C 63.80, H 6.52.

(4aRS,9aRS)-1,2,3,4,4a,9,9a,10-Octahydroanthracene (*rac*-**13**)[12a]: To a refluxing solution of 3.7 g (14 mmol) of olefin *rac*-**39** in 75 ml of dry benzene, a solution of 4.77 ml (18 mmol) of tributyltin hydride and 20 mg of azobis(isobutyronitrile) in 5 ml of dry benzene was added over a period of 4 h by means of a syringe pump. Refluxing was continued for 30 min, and then a solution of 1 g of NH_4F in 40 ml of water was added to the cooled (room temp.) mixture. The resulting two-phase system was stirred vigorously overnight. After addition of 20 ml of 2 N HCl, the organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 ml). The combined organic layers were washed with water (2 ×) and brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure and the resulting colorless oil was purified by PTLC (4 mm layer SiO_2; hexane). The product was finally crystallized from hexane to yield 754 mg (29%) of the cyclized product *rac*-**13** as clear, colorless prisms, m.p. 64°C (ref.[12a]: 53°C). − R_f = 0.79 (hexane/EtOAc, 10:1).− IR (ATR): $\tilde{\nu}$ = 2917 (s), 2877 (m), 2846 (m), 2830 (m), 1493 (w), 1450 (w), 1421 (w), 945 (w), 742 (s) cm^{-1}. − ^1H NMR (400 MHz): δ = 1.06 (m, 2 H), 1.30−1.44 (m, 4 H), 1.78 (m, 4 H), 1.86 (d, J = 13 Hz, 2 H), 2.45 (dd, J_1 = 11 Hz, J_2 = 16 Hz, 2 H), 2.78 (dd, J_1 = 4 Hz, J_2 = 15.5 Hz, 2 H), 6.99 (m, 4 H). − ^{13}C NMR (63 MHz): δ = 26.3 (t), 33.8 (t), 37.4 (t), 38.7 (d), 125.3 (d), 128.6 (d), 136.9 (s). − MS; *m/z* (%): 186 [M^+] (100), 129 (22), 128 (19), 105 (20), 104 (48), 95 (21), 94 (17). − HRMS: 186.1409 as calcd. for $C_{14}H_{18}$. − $C_{14}H_{18}$ (186.30): calcd. C 90.25, H 9.75; found C 89.87, H 9.74.

(4aRS,8aSR,9aRS)-Tricarbonyl(η⁶-1,2,3,4,4a,9,9a,10-octahydroanthracene)chromium(0) (*rac*-**8**): As described above for the preparation of *rac*-**24**, 400 mg (2.2 mmol) of the ligand *rac*-**13** was heated with 0.55 g (2.5 mmol) of $Cr(CO)_6$ in 17 ml nBu_2O and 1.7 ml THF in a 100-ml Schlenk flask for 24 h at 150°C (oil-bath temperature). The resulting clear yellow solution was allowed to cool to room temp. and filtered through a short pad of silica. The solvent was removed in vacuo and the residue was purified by PTLC (4-mm layer SiO_2; hexane/EtOAc, 5:1) to yield 515 mg (74%) of *rac*-**8** as a light-yellow powder, m.p. 117°C. − R_f = 0.34 (hexane/EtOAc, 10:1). − IR (ATR): $\tilde{\nu}$ = 2922 (m), 2854 (w), 1948 (s), 1855 (s), 1459 (w), 1446 (w), 1430 (m), 667 (m) cm^{-1}. − ^1H NMR (400 MHz)[60]: δ = 1.05 (m, 2 H), 1.31 (m, 4 H), 1.77 (pseudo dd), 2.34 (dd, J_1 = 15.6 Hz, J_2 = 10 Hz, 1 H), 2.41 (dd, J_1 = 9.6 Hz, J_2 = 13.8 Hz, 1 H), 2.52 (dd, J_1 = 17 Hz, J_2 = 5 Hz, 1 H), 2.61 (dd, J_1 = 16.6 Hz, J_2 = 6.2 Hz, 1 H), 5.24 (m, 4 H). − ^{13}C NMR (63

MHz, $CDCl_3$): δ = 25.8 (t), 26.0 (t), 33.1 (t), 33.2 (t), 35.0 (t), 36.7 (t), 37.2 (d), 38.2 (d), 91.7 (d), 92.0 (d), 93.4 (s), 93.6 (s), 108.7 (s), 233.8 (s). − MS; *m/z* (%): 322 [M^+] (16), 266 (18), 238 (100), 52 (21). − HRMS: 322.0661 as calcd. for $C_{17}H_{18}CrO_3$. − $C_{17}H_{18}O_3Cr$ (322.32): calcd. C 62.70, H 5.63; found C 62.73, H 5.73.

Diethyl (1RS,2SR)-Cyclohexane-1,2-dicarboxylate (**41a**)[26]: To a solution of 51.4 g (0.33 mol) of *cis*-hexahydrophthaloyl anhydride (**40**) in 300 ml of dry EtOH was added 2.5 ml of conc. sulfuric acid and the mixture was refluxed for 5 h. After cooling to room temp., EtOAc (300 ml) was added and the mixture was sequentially washed with water (2 × 100 ml), saturated aqueous $NaHCO_3$ (100 ml), and brine. The aqueous extracts were back-extracted three times with 100 ml of EtOAc and the combined organic layers were dried with $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was distilled in vacuo (89°C, 0.5 Torr) through a 10-cm Vigreux column to yield 74.40 g (87%) of the *cis*-diester **41a** (containing ca. 1.5% of the *trans* isomer *rac*-**41b**), R_f = 0.15 (hexane/EtOAc, 10:1). − IR (CCl_4): ṽ = 2982 (w), 2938 (w), 2859 (w), 1793 (w, C=O), 1733 (s, C=O), 1245 (m), 1215 (m), 1180 (m) cm^{-1}. − ^1H NMR (270 MHz): δ = 1.24 (t, 6 H), 1.44 (m, 4 H), 1.77 (m, 2 H), 2.01 (m, 2 H), 2.79 (pseudo t, 2 H), 4.13 (q, *J* = 8 Hz, 4 H). − ^{13}C NMR (63 MHz): δ = 13.3 (q), 22.9 (t), 25.4 (t), 41.8 (d), 59.5 (t), 172.93 (s). − MS; *m/z* (%): 228 [M^+] (3), 183 (30), 154 (23), 109 (33), 95 (21), 81 (100).

Diethyl (1RS,2RS)-Cyclohexane-1,2-dicarboxylate (*rac*-**41b**)[26]: To a solution of 2.2 g (96 mmol) of sodium in 200 ml of dry EtOH was added 45.85 g (201 mmol) of the *cis*-diester **41a** and the mixture was refluxed for 5 h. After cooling to room temp., 200 ml of EtOAc was added and the mixture was washed with water (2 × 100 ml), 2 N HCl (100 ml), saturated aqueous $NaHCO_3$ (100 ml) and brine. The aqueous phases were re-extracted with EtOAc (3 × 100 ml) and the combined organic layers were dried with $MgSO_4$. The solvent was removed under reduced pressure and the residue was dried in vacuo yielding 42.30 g (92%) of *trans*-diester *rac*-**41b** (containing about 11% of the *cis*-diester according to NMR). − R_f = 0.15 (hexane/EtOAc, 10:1). − IR (CCl_4): ṽ = 2985 (w), 2938 (w), 2861 (w), 1733 (s, C=O), 1216 (s), 1178 (m) cm^{-1}. − ^1H NMR (270 MHz; only the signals of *rac*-**41b** are given): δ = 1.24 (t, *J* = 7 Hz, 6 H), 1.32 (m, 4 H), 1.79 (m, 2 H), 2.07 (pseudo d, 2 H), 2.59 (m, 2 H), 2.79 (pseudo t, 2 H), 4.12 (dq, J_1 = 8 Hz, J_2 = 4 Hz, 4 H). − ^{13}C NMR (63 MHz): δ = 14.0 (q), 25.1 (t), 28.8 (t), 44.8 (d), 60.3 (t), 175.0 (s). − MS; *m/z* (%): 228 [M^+] (2), 183 (47), 182 (27), 155 (25), 154 (50), 109 (37), 108 (33), 81 (100).

(1RS,2RS)-1,2-Bis(hydroxymethyl)cyclohexane (*rac*-**42b**)[27]: To a stirred suspension of 9.48 g (242 mmol) of $LiAlH_4$ in 150 ml of dry diethyl ether was added a solution of 23.05 g (101 mmol) of the mixture containing principally diester *rac*-**41b** (*rac*-**41b**/**41a** = 89:11) in 100 ml of dry diethyl ether, so that the mixture refluxed gently. After completion of the addition, refluxing was continued for 1 h. The cooled mixture was then quenched by the dropwise addition of 50 ml of EtOAc followed by 300 ml of 5 N HCl. Stirring was continued until most of the precipitate had dissolved. The layers were separated and the organic layer was washed with saturated aqueous $NaHCO_3$ and brine. The aqueous layers were re-extracted with EtOAc (5 × 50) and the combined organic layers were dried with $MgSO_4$. After removing the solvent under reduced pressure, 14.42 g (99%) of the diol mixture (*rac*-**42b**/**42a** = 89:11) was obtained, which crystallized spontaneously. An analytical sample was recrystallized from hexane/benzene (3:1) yielding colorless prisms of pure *rac*-**42b**, m.p. 55°C (ref.[27]: m.p. 57°C). − R_f = 0.35 (EtOAc). − IR (CCl_4): ṽ = 3272 (br, OH), 2925 (s), 2856 (m), 1061 (s), 1448 (m), 1030 (w), 966 (w) cm^{-1}. − ^1H NMR (270 MHz): δ = 1.07 (m, 2 H), 1.26 (m, 4 H), 1.63 (pseudo dd, 2 H), 1.86 (m, 2 H), 3.20 (br, 2 H, OH, exchanges with D_2O), 3.54 (pseudo dq, 4 H). − ^{13}C NMR (63 MHz): δ = 26.1 (t), 29.8 (t), 44.7 (d), 67.86 (t). − MS; *m/z* (%): 127 [$MH^+ - H_2O$] (68), 109 (42), 93 (70), 81 (100), 79 (47), 67 (88), 55 (36). − $C_8H_{15}O$ (127.21): calcd. C 66.63, H 11.18; found C 66.36 H 11.16.

(1RS,2RS)-1,2-Bis(tosyloxymethyl)cyclohexane (*rac*-**43b**)[27]: To a cold (0°C), stirred solution of 11.3 g (0.078 mol) of the diol *rac*-**42b** in 100 ml of dry pyridine, 60 g (0.315 mol) of *p*-TsCl was slowly added and stirring was continued for 1 h. The orange solution was kept at 4°C for 20 h, and then was poured slowly into a mixture consisting of conc. HCl (300 ml), ice (300 g) and CH_2Cl_2 (200 ml) under vigorous stirring. After 10 min, the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 100 ml). The combined organic layers were washed with saturated aqueous $NaHCO_3$ and brine, and dried with $CaCl_2$. The solvent was removed under reduced pressure to give an oily residue, which was crystallized from MeOH to yield 27.69 g (78%) of the ditosylate *rac*-**43b** as a pure diastereomer (the *cis* isomer **43a** could be not detected by either HPLC or NMR), m.p. 100°C (ref.[27]: m.p. 108°C). − R_f = 0.1 (hexane/EtOAc, 10:1); IR (CCl_4): ṽ = 2929 (w), 2859 (w), 1189 (s), 1178 (s), 1372 (m), 946 (m) cm^{-1}. − ^1H NMR (270 MHz): δ = 1.17 (m, 4 H), 1.63 (m, 6 H), 2.45 (s, 6 H), 3.87 (pseudo dq, 4 H), 7.37 (d, 4 H), 7.73 (d, *J* = 5 Hz, 4 H). − ^{13}C NMR (63 MHz): δ = 21.7 (q), 25.2 (t), 28.9 (t), 37.7 (d), 72.1 (t), 127.9 (d), 129.9 (d), 132.6 (s), 144.9 (s). − MS; *m/z* (%): 452 [M^+] (4), 281 (11), 280 (10), 155 (40), 125 (53), 109 (100), 91 (90), 67 (32), 65 (15). − $C_{22}H_{28}O_6S_2$ (452.58): calcd. C 58.39, H 6.24; found C 58.74, H 6.26.

(1RS,2RS)-1,2-Diprop-2′-ynylcyclohexane (*rac*-**44**): A solution of 9.83 g (107 mmol) of lithium acetylide ethylenediamine complex in 55 ml of dry DMSO was cooled to 8°C and 15.80 g (34.9 mmol) of the ditosylate *rac*-**43b** was added in small portions. Stirring was continued for 4.5 h and the temperature was allowed to rise to ambient. The dark-brown solution was then cooled to 8°C once more and 55 ml of water was added slowly, causing the mixture to foam. The mixture was subsequently extracted with hexane (4 × 50 ml) and the combined organic extracts were dried with $MgSO_4$. After removal of the solvent under reduced pressure, the crude product (4.8 g, ca. 90% pure) was kugelrohr-distilled (100°C, 0.1 Torr) to yield 3.65 g (63%) of the dialkyne *rac*-**44** as a colorless oil (Note: The product turns yellow quickly upon standing at room temp. but can be stored as a solid at −20°C), m.p. ca. 5−10°C. − R_f = 0.28 (hexane). − IR (CCl_4): ṽ = 3313 (m, C≡C−H), 2926 (m), 2857 (s), 1189 (s), 1178 (s), 1373 (m), 949 (m) cm^{-1}. − ^1H NMR (400 MHz): δ = 1.25 (m, 4 H), 1.45 (m, 2 H), 1.72 (m, 4 H), 1.95 (t, *J* = 3 Hz, 2 H), 2.27 (m, 4 H). − ^{13}C NMR (63 MHz): δ = 22.5 (t), 25.8 (t), 31.3 (t), 38.8 (d), 69.4 (s), 82.1 (d). − MS; *m/z* (%): 159 [$M^+ - 1$] (8), 145 (21), 131 (30), 117 (50), 105 (22), 104 (12), 95 (25), 93 (45), 91 (65), 81 (100), 79 (97), 77 (54), 67 (44), 55 (28). − HRMS as calcd. for $C_{12}H_{16}$: 159.1174.

(4aRS,9aRS)-6,7-Bis(trimethylsilyl)-1,2,3,4,4a,9,9a,10-octahydroanthracene (*rac*-**45**): A flame-dried Schlenk flask was fitted with a reflux condenser topped with an Hg bubbler. All joints were made air-tight using Teflon sleeves. The apparatus was flushed with argon and then charged with 1.143 g (8.7 mmol) of bis(trimethylsilyl)acetylene, 39 mg (0.2 mmol 10 mol-%) of dicarbonyl(cyclopentadienyl)cobalt[61] and 30 ml of dry octane. The apparatus was briefly evacuated and flushed with argon several times and then the mixture was heated to reflux (180°C oil-bath temperature). A separately prepared and degassed solution of 332 mg (2 mmol) of the dialkyne *rac*-**44**, 381 mg of bis(trimethylsilyl)acetylene and 39 mg

(0.2 mmol, 10 mol-%) of dicarbonyl(cyclopentadienyl)cobalt in 4.5 ml of octane was then added to the refluxing mixture by means of a syringe pump over a period of 11 h, under irradiation from a 200-W bulb. The resulting black solution was allowed to cool to room temp. and filtered through a short pad of Celite and silica. The solvent was removed under reduced pressure and the residue (black tar) was purified by PTLC (4-mm layer SiO_2; hexane). The product was crystallized from EtOAc/MeOH to yield 180 mg (27%) of *rac*-**45** as colorless plates (Note: Our attempts to run the reaction on a larger scale resulted in significantly lower yields); m.p. 74°C. − R_f = 0.65 (hexane). − IR (CCl_4): $\tilde{\nu}$ = 2920 (m), 2905 (m), 2951, 2877 (w), 2854 (w), 1249 (s), 854 (s), 839 (s) cm^{-1}. − ^1H NMR (270 MHz): δ = 0.36 (s, 18 H), 1.08 (m, 2 H), 1.37 (m, 4 H), 1.82 (pseudo dd, 4 H), 2.45 (dd, J_1 = 15.5 Hz, J_2 = 12 Hz, 2 H), 2.77 (dd, J_1 = 17 Hz, J_2 = 3.5 Hz, 2 H), 7.39 (s, 2 H). − ^{13}C NMR (63 MHz): δ = 2.0 (q), 26.3 (t), 29.7 (t), 37.3 (t), 38.8 (d), 136.1 (d), 136.6 (s), 142.3 (s). − MS; *m/z* (%): 330 [M^+] (29), 315 (100), 299 (84), 131 (6), 73 (14). − $C_{20}H_{34}Si_2$ (330.66): calcd. C 72.65, H 10.36; found C 72.57, H 1.37.

(4aRS,8aSR,9aRS)-Tricarbonyl[η⁶-6,7-bis(trimethylsilyl)-1,2,3,4,4a,9,9a,10-octahydroanthracene]chromium(0) (*rac*-**9**): As described above for the preparation of *rac*-**24**, 590 mg (1.8 mmol) of the ligand *rac*-**45** was heated with 440 mg (2.0 mmol) of $Cr(CO)_6$ in 20 ml nBu_2O and 2 ml of dry THF for 22 h at 150°C (oil-bath temperature). The clear, yellow solution thus obtained was allowed to cool to room temp. and filtered through a short pad of silica. The solvent was removed in vacuo and the residue was purified by PTLC (4-mm layer SiO_2; hexane/EtOAc, 10:1) to give 825 mg (91%) of *rac*-**9** as pale-yellow crystals, m.p. 162°C. − R_f = 0.31 (hexane). − IR (CCl_4): $\tilde{\nu}$ = 2924 (w), 2905 (w), 2856 (w), 1961 (s), 1891 (s), 1254 (m), 853 (m), 844 (m), 836 (m) cm^{-1}. − ^1H NMR (270 MHz)[60]: δ = 0.36 and 0.38 (both s, 9 H), 1.07 (m, 2 H), 1.36 (m, 4 H), 1.82 (pseudo dd, 4 H), 2.34 (dd, J_1 = 16.5 Hz, J_2 = 12 Hz, 2 H), 2.40 (dd, J_1 = 17 Hz, J_2 = 11 Hz, 2 H), 2.52 (dd, J_1 = 17.5 Hz, J_2 = 5.5 Hz, 2 H), 2.60 (dd, J_1 = 17 Hz, J_2 = 6 Hz, 2 H), 5.27 and 5.28 (both s, 1 H). − ^{13}C NMR (63 MHz): δ = 1.8 (q), 1.9 (q), 25.8 (t), 26.0 (t), 33.2 (t), 34.8 (t), 36.4 (t), 37.3 (d), 38.4 (d), 100.4 (d), 104.9 (s), 105.0 (s), 109.2 (s), 110.0 (s), 234.1 (s). − MS (*m/z*): 466 [M^+] (4), 382 [M^+ − 3CO] (100), 315 (13), 299 (12), 73 (6), 52 (6). − $C_{23}H_{34}CrO_3Si_2$ (466.69): calcd. C 59.16, H 7.34; found C 59.05, H 7.45.

General Procedure A: Deuteration of Cr(CO)₃ Complexes with tBuOK in [D₆]DMSO: In a small, flame-dried Schlenk flask, *t*BuOK (ca. 11 mg, 0.1 mmol) was dissolved under argon in 0.5 ml of dry [D_6]DMSO and 0.02−0.06 mmol of the respective chromium complex was added (for the exact amounts, see the individual experiments described below). The solution was stirred at room temp. for 1 h and then quenched with EtOAc (10 ml). The resulting mixture was transferred to a separatory funnel, washed with water (2 × 10 ml), and dried with $MgSO_4$. The solvent was removed in vacuo and the yellow residue was chromatographed on a 1-mm SiO_2 layer. The pure fractions of the major component were combined, the solvent was removed in vacuo, and the residue was characterized by ^1H NMR and MS.

*Preparation of rac-***46** *{(1RS,4SR)-1,4,5,8-[D₄]-rac-***24***}*: Complex *rac*-**5** (10 mg, 0.02 mmol) was treated with *t*BuOK/[D_6]DMSO as described above (General Procedure A) to afford 0.8 mg (11%) of the tetradeuterated complex *rac*-**46** as a yellow film. − ^1H NMR (270 MHz)[60]: δ = 1.00 (d, *J* = 3 Hz, 3 H), 1.02 (d, *J* = 3 Hz, 3 H), 1.38 (m, 1 H), 1.53 (m, 1 H), 2.29 (dd, J_1 = 22 Hz, J_2 = 11 Hz, 0.25 H), 2.37 (dd, J_1 = 23 Hz, J_2 = 11 Hz, 1 H), 2.52 (dd, J_1 = 21 Hz, J_2 = 4.5 Hz, 1 H), 2.60 (dd, J_1 = 20 Hz, J_2 = 5 Hz, 0.2 H), 3.75 (s, 3 H), 3.78 (s, 3 H), 5.15 (s, 0.16 H), 5.18 (s, 0.1 H). − MS; *m/z* (%): 360 [M^+] (22), 359 (12), 304 (8), 276 (100), 275 (55), 246 (55), 221 (52), 220 (51), 205 (45), 190 (18), 167 (29), 149 (74), 129 (18), 91 (36), 69 (32), 55 (34). − HRMS: calcd. for $C_{17}H_{16}D_4CrO_5$ 360.099; found 360.0993.

*Preparation of rac-***47** *{(9RS,10SR)-5,8,9,10-[D₄]-rac-***35***}*: Complex *rac*-**7** (20 mg, 0.036 mmol) was treated with *t*BuOK/[D_6]DMSO as described above (General Procedure A) to afford 8 mg (58%) of the tetradeuterated complex *rac*-**47** as a yellow film. − ^1H NMR (270 MHz)[60]: δ = 1.02 (m, 2 H), 1.30 (m, 4 H), 1.84 (pseudo dd, 4 H), 2.35 (d, J_1 = 12.2 Hz, 1 H), 2.45 (d, J_1 = 16.5 Hz, J_2 = 4 Hz, 1 H), 3.73 (s, 3 H), 3.77 (s, 3 H), 5.15 (s, 0.08 H), 5.19 (s, 0.08 H). − MS; *m/z* (%): 386 [M^+] (10), 330 (5), 302 (100), 272 (31), 250 (13), 43 (17). − HRMS: calcd. for $C_{19}H_{18}D_4CrO_5$ 386.1123; found 386.1118.

*Preparation of rac-***48** *{(9RS,10SR)-6,7,9,10-[D₄]-rac-***8***}*: Complex *rac*-**9** (20 mg, 0.043 mmol) was treated with *t*BuOK/[D_6]DMSO as described above (General Procedure A) to afford 14 mg (98%) of the tetradeuterated complex *rac*-**48** as a yellow film. − ^1H NMR (400 MHz)[60]: δ = 1.05 (m, 2 H), 1.31 (m, 4 H), 1.77 (pseudo dd, 4 H), 2.32 (d, *J* = 15.6 Hz, 0.3 H), 2.39 (d, *J* = 9.2 Hz, 1 H), 2.51 (pseudo d, J_1 = 17 Hz, $J \approx$ 3 Hz, 1 H), 2.61 (dd, J_1 = 16.3 Hz, J_2 = 5.8 Hz, 0.3 H, H-10), 5.24 (s, 2 H). − MS; *m/z* (%): 326 [M^+] (11), 243 (61), 241 (100), 240 (46), 151 (29), 150 (14), 52 (67). − HRMS: calcd. for $C_{17}H_{14}D_4CrO_3$ 326.0912; found 326.0920.

*Preparation of rac-***49** *{(9RS,10SR)-9,10-[D₂]-rac-***8***}*: Complex *rac*-**8** (20 mg, 0.062 mmol) was treated with *t*BuOK/[D_6]DMSO as described above (General Procedure A) to afford 14 mg (70%) of the dideuterated complex *rac*-**49** as a yellow film. − ^1H NMR (400 MHz)[60]: δ = 1.05 (m, 2 H), 1.31 (m, 4 H), 1.77 (pseudo dd, 4 H), 2.39 (d, *J* = 9.8 Hz, 1 H), 2.52 (pseudo s, 1 H), 5.24 (m, 4 H). − MS; *m/z* (%): 325 (11), 324 [M^+] (12), 269 (6), 268 (6), 241 (95), 240 (100), 189 (10), 188 (12), 120 (12), 107 (12), 52 (54). − HRMS: calcd. for $C_{17}H_{16}D_2CrO_3$ 324.0786; found 324.0780.

General Procedure B: Deprotonation of Cr(CO)₃ Complexes with n-Butyllithium and Deuteration with D₂O: A flame-dried 25-ml Schlenk flask was charged under argon with the respective chromium complex (0.08−0.1 mmol; for the exact amounts, see the individual experiments described below) and 5 ml of dry THF and 0.5 ml of dry HMPA were added. Then, *n*-butyllithium (190 µl, 0.3 mmol, 1.6 M in *n*-hexane) was injected into the stirred yellow solution at room temp. The solution usually turned red within 5 min, indicating the formation of a benzylic anion. After 30 min, D_2O (200 µl, 10 mmol) was injected and stirring was continued for at least another 30 min. The mixture was then diluted with EtOAc (30 ml), transferred to a separatory funnel, washed with 2 N HCl (2 × 20 ml), saturated aqueous $NaHCO_3$ (20 ml) and brine (20 ml), and dried with $MgSO_4$. The solvent was removed in vacuo and the yellow residue was purified by PTLC (for the exact conditions, see the preparations of the nondeuterated compounds) to furnish the deuterated samples in yields of 45−70%. Prior to the determination of the degree of deuteration by ^1H-NMR spectroscopy, the samples were further purified by recrystallization.

General Procedure C: Deprotonation of Cr(CO)₃ Complexes with n-Butyllithium and Deuteration with CF₃CO₂D: A flame-dried 25-ml Schlenk flask was charged under argon with the respective chromium complex (0.08−0.1 mmol; for the exact amounts, see the individual experiments described below) and 10 ml of dry THF and 1 ml of dry HMPA were added. The yellow solution was cooled to −78°C and *n*-butyllithium (120 µl, 0.2 mmol, 1.6 M in *n*-hexane) was injected with stirring. The mixture was allowed to warm to

room temp., whereupon its color changed to red within 10−20 min. After stirring for 30 min, the mixture was cooled to −78°C once more and CF_3CO_2D (77 µl, 1 mmol) was injected. The solution reverted to its original color within a few seconds and stirring was continued for a further 20 min. The mixture was then diluted with EtOAc (30 ml) and worked up as described in General Procedure B. The deuterated samples, obtained in yields of 50−75%, were further purified by recrystallization prior to determination of the degrees of deuteration by ^{1}H NMR.

Deprotonation/Deuteration of **50**: A solution of complex **50** (236.3 mg, 0.5 mmol) in 10 ml of dry THF and 1 ml of HMPA was cooled to −50°C and *n*-butyllithium (0.4 ml, 0.64 mmol, 1.6 M in hexane) was added by means of a syringe. Stirring was continued for 2 h at 0°C, and then the mixture was quenched with D_2O (0.5 ml, 45 mmol), diluted with hexane, washed with water and brine, and dried with $MgSO_4$. Upon removal of the solvent in vacuo, the deuterated (95% D) complex *rac*-**51** was obtained (230 mg, 97%). − ^{1}H NMR (270 MHz): δ = 0.54 (s, 18 H), 1.50−1.75 (m, 4 H), 2.49 (m, 1.05 H), 2.68 (m, 2 H), 3.71 (s, 6 H).

Deprotonation/Deuteration of rac-**1**: A stirred solution of complex *rac*-**1** (41 mg, 0.08 mmol) in 1 ml of dry THF and 0.1 ml of HMPA was cooled to −70°C and *n*-butyllithium (0.08 ml, 0.13 mmol, 1.6 M in hexane) was added by means of a syringe. Stirring was continued for 5 min at −70°C and then for 15 min at room temp. The mixture was subsequently quenched with D_2O (0.5 ml, 45 mmol), diluted with hexane, washed with water and brine, and dried with $MgSO_4$. Upon removal of the solvent in vacuo, the deuterated (90% D) complex *rac*-**52a** was obtained (38 mg, 93%). − ^{1}H NMR (250 MHz)[60]: δ = 0.45 (s, 9 H), 0.47 (s, 9 H), 1.01 (d, J = 6.5 Hz, 3 H), 1.18−1.33 (m, 1 H), 1.50−1.58 (m, 1 H), 1.69−1.76 (m, 1 H), 2.24 (dd, J_1 = 16.0 Hz, J_2 = 11.7 Hz, 1 H), 2.52 (ddd, J_1 = 16.0 Hz, J_2 = 11.0 Hz, J_3 = 5.0 Hz, 0.1 H), 2.57 (dd, J_1 = 16.0 Hz, J_2 = 5 Hz, 1 H), 2.78 (ddd, J_1 = 16.3 Hz, J_2 = 5.2 Hz, J_3 = 3.6 Hz), 3.71 (pseudo s, 6 H). − In a separate experiment, complex *rac*-**1** (49 mg, 0.1 mmol) was deuterated following General Procedure B. In this case, the ^{1}H-NMR spectrum of the product showed it to be a mixture of *rac*-**52a** and *rac*-**52b** in a ratio of approx. 4:1 (85 ± 3% D).

Deprotonation/Deuteration of rac-**5**: Complex *rac*-**5** (50 mg, 0.1 mmol) was deuterated following General Procedure C, yielding *rac*-**53b** (35.5 mg, 71%, 65% D). − ^{1}H NMR (270 MHz)[60]: δ = 0.50 (pseudo s, 18 H), 0.96 (pseudo t, J = 6.2 Hz, 6 H), 1.25 (m, 1 H), 1.39 (m, 1 H), 2.13 (dd, J_1 = 16.1 Hz, J_2 = 10.1 Hz, 1 H), 2.35 (dd, J_1 = 16.0 Hz, J_2 = 11.9 Hz, 1 H), 2.58 (dd, J_1 = 16.3 Hz, J_2 = 5.0 Hz, 0.35 H), 2.82 (dd, J_1 = 16.1 Hz, J_2 = 4.9 Hz, 1 H), 3.74 (pseudo s, 6 H). In a separate experiment, complex *rac*-**5** (50 mg, 0.1 mmol) was deuterated following General Procedure B. In this case, the ^{1}H-NMR spectrum indicated the formation of *rac*-**53b** with only ca. 50% D incorporation. When a sample of *rac*-**53b** (50 mg, 0.1 mmol, 65% D) was subjected to a second deprotonation/deuteration cycle following General Procedure C, the degree of deuteration was enhanced to 80% D (yield: 36 mg, 72%). In contrast, when a sample of *rac*-**53b** (50 mg, 0.1 mmol, 65% D) was treated with *n*-butyllithium as described in General Procedure C, with subsequent quenching with CF_3CO_2H (instead of CF_3CO_2D), the isolated material *rac*-**5** (18 mg, 35%) was found to contain less than 10% D.

Deprotonation/Deuteration of rac-**6**: Complex *rac*-**6** (41 mg, 0.08 mmol) was deuterated following General Procedure B, yielding a mixture of *rac*-**54a** and *rac*-**54b** with an overall degree of deuteration of 90 ± 10% D according to the ^{1}H-NMR spectrum. Since the crude material contained significant amounts of desilylated byproducts it was completely desilylated by treatment with tetrabutylammonium fluoride/silica (2 equiv., THF, 1 h, 25°C). ^{1}H NMR (270 MHz)[60]: δ = 1.94 (m, 1 H), 2.14 (m, 1 H), 2.48 (dd, J_1 = 15.2 Hz, J_2 = 11.6 Hz, 0.6 H), 2.59 (dd, J_1 = 15.7 Hz, J_2 = 11.7 Hz, 1 H), 2.74 (dd, J_1 = 10.6 Hz, J_2 = 4.6 Hz, 1 H), 2.80 (dd, J_1 = 11.2 Hz, J_2 = 4.9 Hz, 0.5 H), 3.44 (pseudo d, J = 10.3 Hz, 1 H), 3.46 (pseudo d, J = 10.3 Hz), 3.76 (s, 3 H), 3.80 (s, 3 H), 4.10 (pseudo t, J = 7.5 Hz, 1 H), 4.20 (pseudo t, J = 7.5 Hz, 1 H), 5.18 (s, 1 H), 5.21 (s, 1 H).

Deprotonation/Deuteration of rac-**7**: Complex *rac*-**7** (53 mg, 0.1 mmol) was deuterated following General Procedure C, yielding *rac*-**55b** (26 mg, 50%, 50% D). − ^{1}H NMR (270 MHz)[60]: δ = 0.46 (pseudo s, 18 H), 0.94 (m, 2 H), 1.28 (m, 4 H), 1.78 (m, 4 H), 2.09 (dd, J_1 = 16.5 Hz, J_2 = 11 Hz, 1 H), 2.31 (dd, J_1 = 15.5 Hz, J_2 = 10.8 Hz, 1 H), 2.53 (dd, J_1 = 16 Hz, J_2 = 5.5 Hz, 0.5 H), 2.80 (dd, J_1 = 16.2 Hz, J_2 = 5.5 Hz, 1 H), 3.72 (pseudo s, 6 H). − When a sample of *rac*-**55b** (53 mg, 0.1 mmol, 50% D) was subjected to a second deprotonation/deuteration cycle following General Procedure C, the ^{1}H-NMR spectrum of the isolated material (25 mg, 48%) indicated that deuteration had occurred at both benzylic *exo* positions: 75% D at C-1 (pseudo-equatorial) and 15% at C-4 (pseudo-axial). When a sample of *rac*-**55b** (53 mg, 0.1 mmol, 50% D) was treated with *n*-butyllithium as described in General Procedure C, with subsequent quenching with CF_3CO_2H (instead of CF_3CO_2D), the isolated material *rac*-**7** (11 mg, 20%) contained less than 18% D. Additionally, 18 mg (40%) of a mixture of monosilylated compounds was isolated.

(1RS,2RS,3RS,4aRS)-Tricarbonyl[η^6-6,7-dimethoxy-1,2,3-trimethyl-5,8-bis(trimethylsilyl)-1,2,3,4-tetrahydronaphthalene]chromium(0) (*rac*-**56**): A solution of *rac*-**5** (200 mg, 0.4 mmol) in dry THF (40 ml) and dry HMPA (4 ml) was cooled to −78°C and *n*-butyllithium (0.5 ml, 0.8 mmol, 1.6 M in *n*-hexane) was added. The cooling bath was removed and the mixture was stirred for 30 min while being slowly warmed to room temp. After cooling to −50°C, methyl iodide (0.25 ml, 4 mmol) was injected. Stirring was continued for 1 h, then the mixture was diluted with EtOAc (100 ml) and washed sequentially with 2 N HCl (2 × 20 ml), saturated aqueous $NaHCO_3$ and water. After drying with $MgSO_4$, the solvent was removed in vacuo and the product was purified by PTLC (hexane) followed by crystallization from hexane/EtOAc (10:1) at −30°C to yield *rac*-**56** (143 mg, 65%) as dark-yellow cubes; m.p. 114°C. − R_f = 0.55 (hexane/EtOAc, 10:1). − IR (KBr): $\tilde{\nu}$ = 2955 (w), 2901 (w), 2873 (w), 1955 (s, C=O), 1885 (s, C=O), 1452 (w), 1360 (m), 1320 (m), 1251 (m), 1229 (s), 1017 (m), 856 (m) cm^{-1}. − ^{1}H NMR (270 MHz): δ = 0.45 (s, 9 H), 0.47 (s, 9 H), 0.91 (m, 1 H), 0.95 (d, J = 6.5 Hz, 3 H), 1.05 (d, J = 6.5 Hz, 3 H), 1.21 (d, J = 7.1 Hz, 3 H), 1.33 (m, 1 H), 1.88 (dd, J_1 = 15.2 Hz, J_2 = 11.4 Hz, 1 H), 2.49 (dd, J_1 = 15.2 Hz, J_2 = 3.1 Hz, 1 H), 2.65 (pseudo q, J = 6.9 Hz, 1 H), 3.77 (s, 3 H), 3.78 (s, 3 H). − MS; *m/z* (%): 514 [M$^+$] (6), 458 (9), 432 (17), 431 (43), 430 (100), 428 (7), 73 (10). − HRMS: 514.1663 as calcd. for $C_{24}H_{38}CrO_5Si_2$. − $C_{24}H_{38}CrO_5Si_2$ (514.73): calcd. C 56.00, H 7.44; found C 55.87, H 7.52.

(1RS,2RS,3RS,4aRS)-Tricarbonyl[η^6-1-acetyl-6,7-dimethoxy-2,3-dimethyl-5,8-bis(trimethylsilyl)-1,2,3,4-tetrahydronaphthalene]chromium(0) (*rac*-**57**): A solution of *rac*-**5** (200 mg, 0.4 mmol) in dry THF (40 ml) and dry HMPA (4 ml) was cooled to −78°C and *n*-butyllithium (0.5 ml, 0.8 mmol, 1.6 M in *n*-hexane) was added. The cooling bath was removed and the mixture was allowed to stir for 30 min while slowly warming to room temp. After cooling to −50°C, acetyl chloride (0.2 ml, 2.8 mmol) was injected. Stirring was continued for 30 min, then the mixture was

diluted with EtOAc (100 ml) and washed sequentially with 2 N HCl (2 × 20 ml), saturated aqueous $NaHCO_3$ and water. After drying with $MgSO_4$, the solvent was removed in vacuo and the product was purified by PTLC (hexane/EtOAc, 3:1) followed by crystallization from the same solvent mixture at −4°C to yield *rac*-**57** (143 mg, 68%) as dark-yellow cubes; m.p. 68°C. − R_f = 0.32 (hexane/EtOAc, 10:1). − IR (KBr): $\tilde{\nu}$ = 2950 (w), 1957 (s, C=O), 1888 (s, C=O), 1360 (w), 1334 (w), 1252 (w), 1025 (w), 857 (w) cm^{-1}. − ^1H NMR (270 MHz): δ = 0.42 (s, 9 H), 0.46 (s, 9 H), 0.99 (d, *J* = 6.5 Hz, 3 H), 1.25 (d, *J* = 6 Hz, 3 H), 1.34 (m, 1 H), 1.44 (m, 1 H), 1.89 (dd, J_1 = 11 Hz, J_2 = 15.5 Hz, 1 H), 2.06 (s, 3 H), 2.57 (dd, J_1 = 3.5 Hz, J_2 = 15.5 Hz, 1 H), 3.69 (d, *J* = 5.5 Hz, 1 H), 3.78 (s, 3 H), 3.79 (s, 3 H). − MS; *m/z* (%): 542 [M^+] (7), 461 (19), 460 (45), 459 (100), 363 (9), 221 (6), 73 (10). − HRMS: 542.1612 as calcd. for $C_{25}H_{38}CrO_6Si_2$. − $C_{24}H_{38}CrO_5Si_2$ (514.73): calcd. C 55.83, H 7.06; found C 56.06, H 6.70.

Deprotonation/Deuteration of rac-**60**: In a small, flame-dried Schlenk flask, a stirred solution of *rac*-**60** (20 mg, 0.07 mmol) in 0.5 ml of dry THF was cooled to −78°C and *n*-butyllithium (48 µl, 0.08 mmol, 1.6 M in hexane) was added. The solution was kept at −78°C for 10 min, whereupon it rapidly turned red. It was stirred at −50°C for 30 min, then 0.1 ml (5 mmol) of D_2O was added, and after 5 min the cooling bath was removed. The mixture was subsequently diluted with 20 ml of EtOAc, transferred to a separatory funnel, and washed sequentially with 2 N HCl (20 ml), saturated aqueous $NaHCO_3$ (20 ml) and brine (20 ml). After drying with Na_2SO_4, the solvent was removed in vacuo and the yellow residue was purified by PTLC (hexane/EtOAc, 10:1) yielding 18.4 mg (91%) of a mixture of the monodeuterated complexes *rac*-**61a**/*rac*-**61b** with an overall degree of deuteration of 80%. − ^1H NMR (400 MHz): δ = 1.27 (s, 9 H, *t*Bu), 2.16 (pseudo s, 5.2 H, Me), 5.19 (d, 1 H), 5.39 (d, 1 H), 5.47 (s, 1 H). − MS; *m/z* (%): 299 [M^+] (23), 243 (7), 216 (36), 215 (100), 148 (7), 120 (3), 52 (40). − HRMS: calcd. for $C_{15}H_{17}DO_3Cr$ 299.0724; found 299.0727. Since the determination of the *rac*-**61a**/*rac*-**61b** ratio was not possible at this stage, the mixture was completely decomplexed by exposure to sunlight and air (Et_2O, 4 h) to provide a 5:3 mixture of 4-*tert*-butyl-1-[D_3]methyl-2-methylbenzene and 4-*tert*-butyl-1-methyl-2-[D_3]-methylbenzene. − ^1H NMR (400 MHz): δ = 1.29 (s, 9 H, *t*Bu), 2.21−2.24 (m, 2.5 H, Me at C-1), 2.25−2.28 (m, 2.7 H, Me at C-2), 5.19 (d, 1 H), 5.39 (d, 1 H), 5.47 (s, 1 H); the assignment of the methyl groups was accomplished by NOE experiments.

5,6-Dimethylindan-1-one (*rac*-**63**): A 250-ml flask was charged with $AlCl_3$ (32 g, 0.24 mol) and 80 ml of 1,2-dichloroethane (DCE). After cooling to 0°C, a solution of 3-chloropropionyl chloride (20.2 ml, 0.21 mol) in 20 ml of DCE was added over a period of 10 min. The mixture was stirred for 10 min at this temperature, and then a solution of *o*-xylol (24.1 ml, 0.2 mol) in 25 ml of DCE was added dropwise over a period of 1 h. The reaction mixture was stirred for 90 min (0°C → 22°C), quenched under external cooling by the addition of water (50 ml), and extracted with *tert*-butyl methyl ether (3 × 100 ml). The organic extracts were washed with water, saturated aqueous $NaHCO_3$, and further water, and then dried with $MgSO_4$. The solvent was removed in vacuo and the residue was filtered through a pad of silica gel/Celite with hexane/EtOAc (3:1). Crystallization from the same solvent system afforded 36.7 g (93%) of 3-chloro-1-(3,4-dimethylphenyl)propan-1-one (brown needles). 25 g (127 mmol) of this material was dissolved in conc. H_2SO_4 (150 ml) and the stirred solution was heated to 90°C over a period of 30 min and maintained at this temperature for a further 45 min. The dark-red mixture was then cooled to room temp. and carefully poured onto ca. 800 g of crushed ice. After extraction with *tert*-butyl methyl ether, the organic solution was washed with water, saturated aqueous $NaHCO_3$ and brine, and dried with $MgSO_4$. The solvent was removed in vacuo and the residue was filtered through a pad of silica gel and Celite with hexane/EtOAc (5:1). Crystallization from hexane/EtOAc (5:1) finally afforded 16.3 g (80%) of a 3:1 mixture of *rac*-**63a**/*rac*-**63a** as pale-brown plates. − IR (ATR): $\tilde{\nu}$ = 3012 (w), 2978 (w), 2943 (w), 2925 (w), 1696 (s), 1614 (m), 1462 (w), 1446 (w), 875 (m) cm^{-1}. − ^1H NMR (400 MHz): δ = 2.30 (s, 3 H), 2.35 (s, 3 H), 2.63−2.72 (m, 2 H), 3.00−3.08 (m, 2 H), 7.25 (s, 1 H), 7.52 (s, 1 H). − ^{13}C NMR (67 MHz): δ = 19.7 (q), 20.7 (q), 25.3 (t), 36.4 (t), 124.0 (d), 127.3 (d), 135.2 (s), 136.1 (s), 144.8 (s), 153.3 (s), 206.9 (s). − MS; *m/z* (%): 160 [M^+] (100), 145 (6), 132 (38), 117 (54), 115 (18), 103 (8), 91 (10). − HRMS: calcd. for $C_{11}H_{12}O$ 160.08882; found 160.0889.

(1RS)-1,5,6-Trimethylindan-1-ol (*rac*-**64**): To Mg turnings (170 mg, 7 mmol) in 5 ml of dry diethyl ether, MeI (980 mg, 6.9 mmol) was slowly added at room temp. After 30 min, the stirred mixture was heated to reflux for 30 min, then cooled to 0°C, whereupon a solution of *rac*-**63a**/*rac*-**63b** (1.0 g, 6.2 mmol) in 5 ml of diethyl ether was added dropwise. Stirring was continued for 30 min at room temp. and then the mixture was heated to reflux for 1 h. After quenching with water, the mixture was diluted with EtOAc and washed with water and brine. After drying with Na_2SO_4, the solvent was removed in vacuo and the residue was purified by PTLC (hexane/EtOAc, 10:1) to give 784 mg (72%) of *rac*-**64** as an inseparable mixture of regioisomers (3:1 ratio). In addition, 185 mg (19%) of the corresponding H_2O elimination products were obtained. − IR (ATR): $\tilde{\nu}$ = 3395 (m), 2964 (m), 2925 (m), 1687 (m), 1451 (m), 1384 (m), 1313 (m), 1180 (m) cm^{-1}. − ^1H NMR (400 MHz): δ = 1.58 (s, 3 H), 1.90 (br s, 1 H), 2.16−2.22 (m, 2 H), 2.74−2.83 (m, 1 H), 2.93−3.03 (m, 1 H), 2.28 (m, 3 H), 2.29 (s, 3 H), 7.04 (s, 1 H), 7.16 (s, 1 H). − ^{13}C NMR (100 MHz): δ = 19.8 (q), 27.2 (q), 28.9 (t), 42.5 (t), 81.1 (s), 124.9 (d), 125.9 (d), 135.0 (s), 136.6 (s), 140.2 (s), 145.9 (s). − MS; *m/z* (%): 176 [M^+] (8), 161 [$M^+ - CH_3$] (100), 158 [$M^+ - H_2O$] (25), 143 (28), 128 (15), 119 (10), 115 (10). − HRMS: calcd. for $C_{12}H_{16}O$ 176.12012; found 176.1212.

(1RS,3aRS)-Tricarbonyl(η⁶-1,5,6-trimethylindan-1-ol)chromium(0) (*rac*-**65**): A mixture of *rac*-**64** (518 mg, 2.94 mmol), $Cr(CO)_6$ (970 mg, 4.41 mmol), anhydrous nBu_2O (16 ml) and dry THF (1.6 ml) was heated to reflux for 18 h according to the procedure described above for the preparation of *rac*-**24**. The crude product was purified by PTLC (hexane/EtOAc, 3:1) to give 560 mg (61%) of a mixture regioisomers (m.p. 107°C), from which a sample of pure *rac*-**65** (176 mg, 19%) was obtained by fractional recrystallization from hexane/EtOAc. − M.p. 129°C. − IR (ATR): $\tilde{\nu}$ = 3581 (w), 2970 (w), 2927 (w), 1948 (s, C=O), 1861 (s, C=O), 1452 (w), 1389 (w), 670 (w) cm^{-1}. − ^1H NMR (270 MHz): δ = 1.44 (s, 3 H), 1.83 (br s, 1 H), 1.95−2.15 (m, 2 H), 2.16 (s, 3 H), 2.20 (s, 3 H), 2.60−2.75 (m, 2 H), 5.23 (s, 1 H), 5.64 (s, 1 H). − ^{13}C NMR (67 MHz): δ = 19.0 (q), 19.1 (q), 27.0 (q), 27.7 (t), 41.6 (t), 79.3 (s), 90.2 (d), 91.6 (d), 104.9 (s), 110.0 (s), 113.1 (s), 119.7 (s), 233.9 (s). − MS; *m/z* (%): 312 [M^+] (32), 256 (10), 228 (26), 229 (26), 226 (100), 210 (66), 195 (6), 159 (92), 144 (20), 129 (30). − HRMS: calcd. for $C_{15}H_{16}CrO_4$ 312.04537; found 312.0455. − $C_{15}H_{16}CrO_4$ (312.29): calcd. C 57.68, H 5.17; found C 57.63, H 5.18.

(1RS,3aRS)-Tricarbonyl(η⁶-1-acetoxy-1,5,6-trimethylindane)chromium(0) (*rac*-**66**): A mixture of *rac*-**65** (171 mg, 0.55 mmol), a small amount of DMAP, Ac_2O (0.86 ml) and 4 ml of pyridine was stirred under the exclusion of light for 22 h. It was then diluted with hexane/EtOAc (2:1) and washed with 2 N HCl, saturated aqueous $NaHCO_3$ and brine. After drying with Na_2SO_4, the solvent was removed in vacuo and the residue was purified by PTLC (hexane/EtOAc, 3:1) to give 170 mg (87%) of *rac*-**66**, m.p. 112°C. − IR

(ATR): $\tilde{\nu}$ = 1951 (s, C=O), 1867 (s, C=O), 1738 (w), 1389 (w), 1244 (w), 674 (w), 666 (w) cm^{-1}. – ^1H NMR (400 MHz): δ = 1.65 (s, 3 H), 2.09 (s, 3 H), 2.14 (s, 3 H), 2.17 (s, 3 H), 2.10–2.20 (m, 2 H), 2.66–2.72 (m, 2 H), 5.21 (s, 1 H), 5.61 (s, 1 H). – ^{13}C NMR (100 MHz): δ = 18.9 (q), 19.0 (q), 21.4 (q), 24.4 (q), 28.3 (t), 38.5 (t), 86.1 (s), 89.6 (d), 91.2 (d), 105.0 (s), 119.1 (s), 111.5 (s), 115.7 (s), 179.2 (s), 233.9 (s). – MS; *m/z* (%): 354 [M^+] (4), 294 (2), 268 (100), 210 (24), 159 (60), 141 (22). – HRMS: calcd. for $C_{17}H_{18}CrO_5$ 354.05593; found 354.0567; $C_{17}H_{18}CrO_5$ (354.32): calcd. C 57.62, H 5.12; found C 57.70, H 5.25.

(3aRS)-Tricarbonyl(η^6-1,1,5,6-tetramethylindane)chromium(0) (*rac*-**62**): In a flame-dried Schlenk flask, a solution of *rac*-**66** (95 mg, 0.27 mmol) in 7 ml of CH_2Cl_2 was cooled to −78°C and Me_3Al (0.14 ml, 1 mmol) was added dropwise. The mixture was stirred for 30 min at −78°C and for 30 min at 0°C, and then hexane (25 ml) and saturated aqueous NH_4Cl were carefully added. After the addition of some EtOAc, the mixture was washed with 2 N HCl and with brine, and dried with Na_2SO_4. The solvent was removed in vacuo and the residue was purified by PTLC (hexane/EtOAc, 10:1) to give 72 mg (86%) of pure *rac*-**62**, m.p. 103°C. – IR (ATR): $\tilde{\nu}$ = 2958 (w), 2928 (w), 1933 (s, C=O), 1870 (m, C=O), 1852 (s, C=O), 1826 (w), 1459 (w), 1389 (w), 671 (w) cm^{-1}. – ^1H NMR (400 MHz): δ = 1.14 (s, 3 H), 1.36 (s, 3 H), 1.79 (dd, J_1 = 7.5 Hz, J_2 = 12.5 Hz, 1 H), 1.95 (ddd, J_1 = 8.5 Hz, J_2 = 11.0 Hz, J_3 = 12.5 Hz, 1 H), 2.13 (s, 3 H), 2.19 (s, 3 H), 2.57 (dd, J_1 = 8.5 Hz, J_2 = 15.5 Hz, 1 H), 2.81 (ddd, J_1 = 7.5 Hz, J_2 = 11.0 Hz, J_3 = 15.5 Hz, 1 H), 5.18 (s, 1 H), 5.43 (s, 1 H). – ^{13}C NMR (67 MHz): δ = 19.0 (q), 19.1 (q), 27.5 (q), 28.8 (t), 29.2 (q), 39.3 (t), 42.9 (s), 90.0 (d), 92.6 (d), 103.8 (s), 109.2 (s), 115.0 (s), 122.6 (s), 234.6 (s). – MS; *m/z* (%): 310 [M^+] (12), 254 (6), 226 (100), 210 (2), 159 (6), 144 (2), 129 (2). – HRMS calcd. for $C_{16}H_{18}CrO_3$ 310.06610; found 310.0666.

Deprotonation/Deuteration of rac-**62**: In a small, flame-dried Schlenk flask, a stirred solution of *rac*-**62** (20 mg, 0.065 mmol) in 1 ml of dry THF was cooled to −78°C and *n*-butyllithium (123 µl, 0.2 mmol, 1.6 M in hexane) was added. The solution was stirred at −78°C for 30 min, then at −50°C for 30 min, before 0.1 ml (5 mmol) of D_2O was added. After 5 min, the cooling bath was removed, the mixture was diluted with 20 ml of EtOAc, washed with brine, and dried with Na_2SO_4. The solvent was removed in vacuo and the residue was crystallized from hexane/EtOAc to give 12 mg (60%) of a mixture of the monodeuterated complexes *rac*-**67a**/*rac*-**67b** with an overall degree of deuteration of 76%. ^1H NMR (400 MHz): δ = 1.14 (s, 3 H), 1.37 (s, 3 H), 1.79 (dd, J_1 = 7.5 Hz, J_2 = 12.5 Hz, 1 H), 1.95 (ddd, J_1 = 8.5 Hz, J_2 = 11.0 Hz, J_3 = 12.5 Hz, 1 H), 2.13 (s, 3 H), 2.17 (pseudo t, 2 H, 1 D), 2.57 (dd, J_1 = 8.5 Hz, J_2 = 15.5 Hz, 1 H), 2.81 (ddd, J_1 = 7.5 Hz, J_2 = 11.0 Hz, J_3 = 15.5 Hz, 1 H), 5.18 (s, 1 H), 5.43 (s, 1 H). – MS; *m/z* (%): 311 [M^+] (10), 255 (6), 227 (100), 211 (2), 160 (10), 145 (2), 129 (4). – HRMS: calcd. for $C_{16}H_{17}DCrO_3$ 311.07239; found 311.0716. – The exact ratio of the isomers was determined to be 85:15 (*rac*-**67a**/*rac*-**67b**) by means of a 600-MHz ^1H-NMR spectrum.

☆ Dedicated to Professor *E. O. Fischer* on the occasion of his 80th birthday.

[1] For some selected recent reviews, see: [1a] M. F. Semmelhack in *Comprehensive Organometallic Chemistry II*, vol. 12 (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, pp. 979–1015. [1b] M. F. Semmelhack in *Comprehensive Organometallic Chemistry II*, vol. 12 (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, pp. 1017–1038. [1c] S. G. Davies, T. D. McCarthy in *Comprehensive Organometallic Chemistry II*, vol. 12 (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, pp. 1039–1070. [1d] L. S. Hegedus, *Transition Metals in the Synthesis of Complex Organic Molecules*, University Science Books, Mill Valley, **1994**, chapter 10.

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[34] The fact that no significant loss of regioselectivity was found in these experiments indicates that the inherent directing effect must be stronger than the primary kinetic isotope effect.
[35] A protonation at the chromium atom of the anionic intermediate, which would eventually have resulted in the formation of an *endo*-protonated complex could thereby be excluded.
[36] X-ray crystal structure analysis of *rac*-**56**: Enraf-Nonius CAD4 diffractometer, Cu-K_α radiation, $2\Theta_{max}$ = 120°, empirical absorption correction ψ scans). Structure determination with direct methods (SIR92). The H atoms were taken from difference Fourier synthesis and refined using isotropic thermal parameters. All other atoms were refined using anisotropic thermal parameters. $C_{24}H_{38}O_5CrSi_2$, monoclinic, space group $P2_1/a$, a = 13.557 (9) Å, b = 11.076 (2) Å, c = 19.411 (6) Å, β = 107.08 (4)°, V = 2786 (4) $Å^3$, Z = 4, $\rho_{calcd.}$ = 1.227 gcm^{-1}, μ = 45.1 cm^{-1}; 3974 independent reflections with $I > 0$ were used; R = 0.044, Rw = 0.043. The residual electron density was less than 0.24 $eÅ^{-3}$. Further details of the crystal structure investigations are available on request from the CCDC; for details see ref.[29d].
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