Preparation of Chiral Amine Carbonyl Chromium(0) Complexes with [(Norbornadiene)Cr$(CO)_4$] as the Complexation Reagent

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A number of chiral amines were prepared and used as ligands in carbonylchromium(0) complexes. Included are monoamines, chelating diamines and methionine methyl ester. For their complexation (norbornadiene)tetracarbonylchromium(0) was found to allow complexation in high, sometimes quantitative yields in boiling THF (65 °C). The amine complexes prepared could be used as complexation reagents for arenes in up to 81% yield in the presence of boron trifluoride–diethyl ether adduct if THF was used as the solvent. Significant chirality transfer from the chiral complexation reagents to the chiral arene complexes was, however, not observed.

Introduction

Complexes such as (carbene)pentacarbonylchromium(0), (alkene)pentacarbonylchromium(0), (diene)tetracarbonylchromium(0), and (arene)tricarbonylchromium(0) are important classes of carbonyl chromium(0) complexes. Many of these are used in organometallic and preparative organic chemistry, as well as in materials science and other fields. Most prominent for organic chemistry are Fischer-type carbene complexes and arene complexes.[1−20]

Because of electronic and steric effects due to the highly electron-withdrawing and sterically bulky tricarbonylchromium(0) fragment, (arene)tricarbonylchromium(0) complexes allow interesting reactions which are not observed for the uncomplexed arene. Semmelhack has elegantly summarized the key properties of tricarbonylchromium complexes in a figure published in 1976, which can now be found in many organometallic chemistry textbooks.[20] Important features are: the enhanced acidity of the protons at the aromatic ring as well as of those in benzylic positions, facilitation of nucleophilic attack at the arene ring, and enhanced rates of solvolysis in benzylic positions. In addition to these consequences of the electron-withdrawing nature of the $Cr(CO)_3$ group, the steric bulk of the tricarbonylchromium fragment usually makes reagents attack selectively at the face of the arene opposite to the $Cr(CO)_3$ group. An important additional aspect is the decrease in symmetry upon complexation of an arene to a metal, making complexes of prochiral arenes chiral. In combination with the selective attack at the face opposite to the metal this allows for stereoselective syntheses of chiral aromatic compounds.[4,10,11,13,14,21]

There are a number of complexation reagents known for the formation of (arene)tricarbonylchromium(0) complexes. In addition to $Cr(CO)_6$, these include tricarbonyl(naphthalene)chromium(0)[22] and reagents of the general formula $L_3Cr(CO)_3$. In these reagents L is usually an electroneutral, two-electron ligand, e.g. ammonia, pyridine, acetonitrile or propionitrile.

Here we describe the syntheses of a number of enantiomerically pure chiral amine carbonyl chromium(0) complexes. We regard such complexes as possible chiral complexation reagents for the formation of nonracemic (arene)tricarbonylchromium(0) complexes with prochiral arene ligands.[23]

As well as by simple complexation of enantiomerically pure ligands, enantiomerically pure chiral (arene)tricarbonylchromium(0) complexes have been obtained by diverse methods of resolution of racemic mixtures,[24] by diastereoselective complexation of enantiomerically pure chiral arenes,[25−27] and by enantioselective deprotonation and subsequent electrophilic attack at prochiral arene complexes using a chiral amide base.[28−37] The idea which inspired us in this context is based on the use of complexation reagents $L^*_3Cr(CO)_3$ or $L^*_2Cr(CO)_4$ with enantiomerically pure chiral ligands L*. The mechanism of their replacement by an arene is presumably a stepwise one involving intermediates like (η^2-arene)$L^*_2Cr(CO)_3$ or (η^4-arene)$L^*Cr(CO)_3$. With a prochiral arene, these intermediates should be formed as mixtures of diastereomers. The face of complexation is defined with the first complexation step and will not change after this first step. If these diastereomers are sufficiently different, the transition states of their formation, as well as those of the following steps, will also be different in energy. This should lead to the preferred formation of one of the enantiomers of the final, planar chiral arene complex. The ligands L*, liberated in the course of the reaction, could be recycled. In the optimum case, they could be used only in catalytic amounts and be reintroduced into the cycle after their liberation. It should be mentioned that related techniques have been used in the synthesis of planar chiral complexes of iron and ruthenium.[38−40]

To allow the selectivity of complexation reactions to be tested by NMR, they were performed using chiral arenes bearing asymmetric carbon atoms at some distance from

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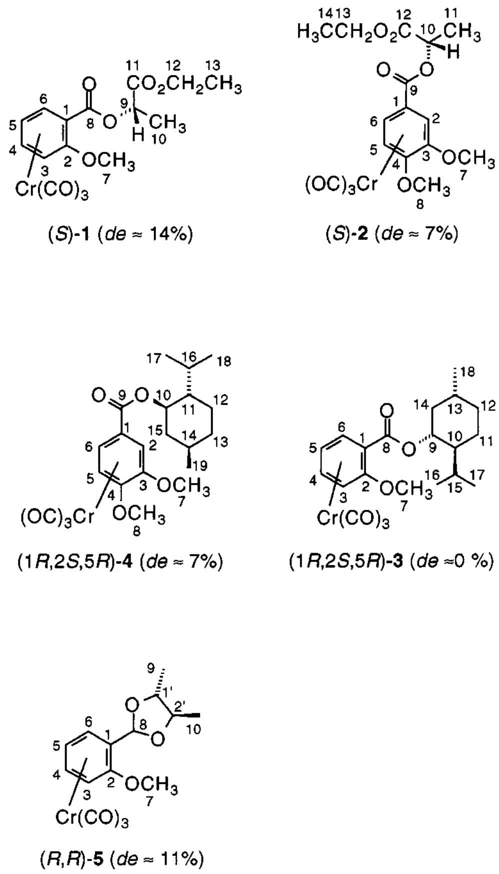


(*S*)-**1** (*de* ≈ 14%) (*S*)-**2** (*de* ≈ 7%)

(1*R*,2*S*,5*R*)-**4** (*de* ≈ 7%) (1*R*,2*S*,5*R*)-**3** (*de* ≈0 %)

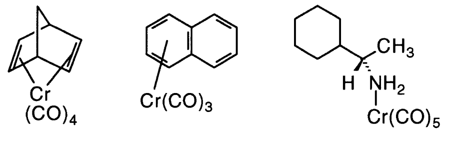
(*R*,*R*)-**5** (*de* ≈ 11%)

Scheme 1

the prochiral arene fragment. Before evaluating the desired complexation with chiral reagents, it was necessary to check the diastereoselectivity obtained by using an achiral complexation reagent. Therefore some chiral arenes were coordinated to $Cr(CO)_3$ to give arene complexes **1−5**[41] in 43−54% yield (Scheme 1).

In all cases the determination of the *de* was possible by inspection of the ^{1}H and ^{13}C NMR spectra. This makes all these complexes suitable for the detection of effects of chiral complexation reagents, where the diastereoselectivity observed with $Cr(CO)_6$ has to be taken into account.

Next, a complexation reagent for the amine ligands, allowing complexation under mild reaction conditions in good yield, had to be found. In our hands, tetracarbonyl(norbornadiene)chromium(0) (**6**) was found to be particularly useful for this purpose, as this reagent allows complexation of a variety of ligands at comparatively low temperature, namely in boiling THF (65 °C). Tetracarbonyl(norbornadiene)chromium(0) was first prepared by Werner by treatment of norbornadiene with $Cr(CO)_6$.[42,43] Although the authors showed its feasibility as a complexation reagent, it has not very often been used as such. To check its quality, we tried the complexation of naphthalene and obtained tricarbonyl(naphthalene)chromium(0) (**7**) in 80% yield by heating naphthalene and **6** in THF at 65 °C. Kündig had obtained **7** (Scheme 2), which is also used as a complexation reagent under mild reaction conditions, in a mixture of dibutyl ether and THF (100:1) at 138−142 °C in 80% yield.[22]

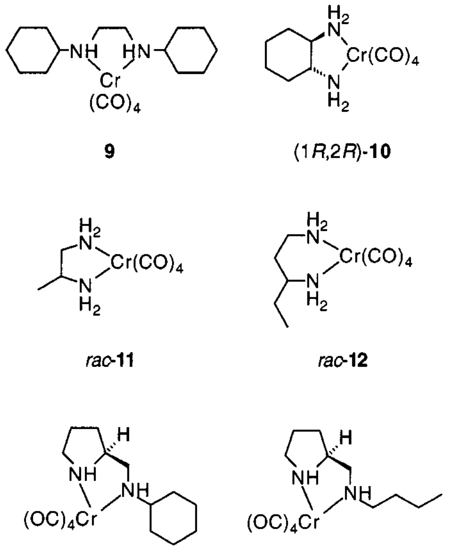


6 **7** (*S*)-**8**

Scheme 2

When **6** was dissolved in an approximately 9-fold excess of (*S*)-1-cyclohexylethylamine[44,45] and stirred in the dark for 18 h at 20 °C, enantiomerically pure monoaminepentacarbonylchromium complex (*S*)-**8** was obtained in 43% yield. The formation of aminepentacarbonylchromium complexes as side products had been observed by Werner.[43] Here, however, this reaction has become the main reaction path. The comparatively high yield indicates that carbonyl ligand exchange reactions between the participating chromium complexes play an important role, in addition to the desired complexation of the amine ligand.

While attempts to prepare complexes with monoamines were less successful, some complexes with diamines were obtained in high yields. In a first test, achiral (*N,N'*-dicyclohexyl)-1,2-ethanediamine[46,47] was coordinated to chromium by heating the diamine and **6** in THF at reflux for 30 min to give complex **9** in almost quantitative yield (Scheme 3).



9 (1*R*,2*R*)-**10**

rac-**11** *rac*-**12**

(*S*)-**13** (*S*)-**14**

Scheme 3

When, as according to Cotton,[48] a 15-fold excess of a mixture of *cis*- and racemic *trans*-1,2-diaminocyclohexane (1:3.5) was heated with $Cr(CO)_6$ without solvent at 120 °C for 4 h, a 90% yield of *rac*-*trans*-(1,2-diaminocyclohexane)tetracarbonylchromium(0) (*rac*-**10**) was obtained. Presumably for steric reasons, no *cis*-1,2-diaminocyclohexane complex was observed. However, as this method is unsuitable economically for enantiomerically pure ligands, (1*R*,2*R*)-1,2-diaminocyclohexane was complexed using tricarbonyl(norbornadiene)chromium(0) (**6**). Heating an equimolar mixture of enantiomerically pure diamine and **6** in THF for 30 min at 65 °C resulted in an almost quantitative yield of (1*R*,2*R*)-**10**.

Compounds *rac*-**11**[49] and *rac*-**12** (Scheme 3) were each obtained in 98% yield using the Cotton method.[48] Attempts to coordinate (−)-sparteine met with failure either with $Cr(CO)_6$ or with **6**, presumably for steric reasons.

Enantiomerically pure diamines can be obtained by the reduction of amino acid amides with $LiAlH_4$.[50] Thus, condensation of diethyl glutamate with cyclohexylamine (89%), followed by reduction with $LiAlH_4$ (66%)[51,52] and complexation with **6** (87%), afforded the enantiomerically pure tetracarbonylchromium complex (*S*)-**13**. In the complex the amine nitrogen atoms are asymmetric, because their lone electron pairs are no longer available for an inversion of their configuration. Remarkably, (*S*)-**13** was formed in diastereomerically pure form.

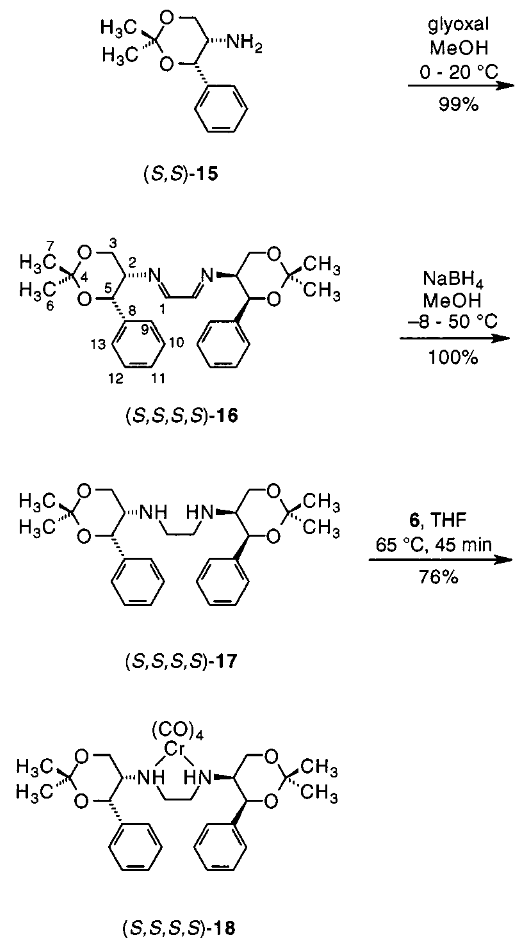
In a similar way, enantiomerically pure diamine complex (*S*)-**14** was prepared as a single diastereomer in 95% yield by reduction of the known[51] (*S*)-2-[(butylamino)carbonyl]-5-oxopyrrolidine (66%), followed by complexation with **6**.

Another route to chiral diamines is the reduction of the corresponding diazadienes, which are obtained by condensation of amine precursors with glyoxal (Scheme 4). (+)-(4*S*,5*S*)-5-Amino-2,2-dimethyl-4-phenyl-1,3-dioxane[53] [(*S*,*S*)-**15**], a side product in the synthesis of chloroamphenicol, was condensed with glyoxal in methanol in 99% yield to give diazadiene (*S*,*S*,*S*,*S*)-**16**. Quantitative reduction with sodium borohydride afforded chiral diamine (*S*,*S*,*S*,*S*)-**17**, which was coordinated at chromium by heating with **6** in THF to give complex (*S*,*S*,*S*,*S*)-**18** in 76% yield.

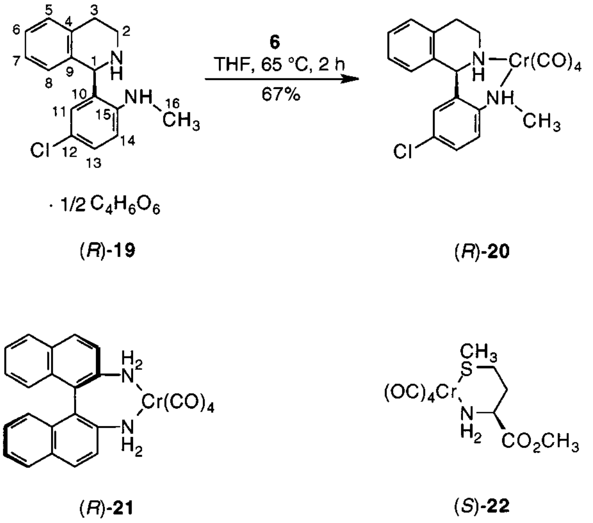
Isoquinoline derivative (*R*)-**19** (Scheme 5) is commercially available as its tartrate and has been used by Vedejs as a chiral proton source for the enantioselective protonation of prochiral amide enolates.[54] Complexation with **11** over 2 h gave complex (*R*)-**20** in 67% yield, beside minor amounts of (arene)tricarbonylchromium(0) complexes which were not identified.

Binaphthyl derivatives, especially BINAP, are successfully used in many asymmetric catalytic reactions.[55−59] Here, (*R*)-2,2′-diamino-1,1′-binaphthyl [(*R*)-DABN] was coordinated to the tetracarbonylchromium fragment using **6** for the complexation. The [(*R*)-DABN] complex (*R*)-**21** was obtained in 70% yield as a yellow, highly air-sensitive solid. As side products, some (arene)tricarbonylchromium complexes were separated by column chromatography. These were not completely characterized.

The results show that, with **6** as the complexation reagent, complexes of 1,2-, 1,3- and even 1,4-diamines can be obtained in good yields under comparatively mild reaction conditions.



Scheme 4



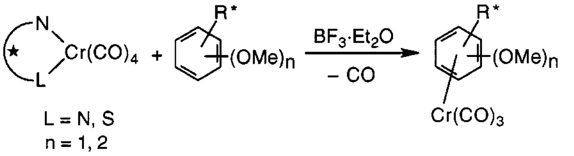
Scheme 5

As an example of a chiral heterobidendate ligand, L-methionine methyl ester[60] was included. Complexation was achieved in 49% yield with $Cr(CO)_6$. Chromium complex (*S*)-**22** was obtained as an orange, moderately air-stable, crystalline solid. Remarkably, the corresponding reaction of L-cysteine methyl ester did not work, either with $Cr(CO)_6$ or with **6**. Possibly, steric reasons account for this, as the covalent radius of sulfur is much larger than that of nitrogen. In addition, sulfur is a weaker ligand than nitrogen, so that the situation with L-cysteine methyl ester is very different from that of 1,2-diamine ligands.[61]

After the preparation of a number of chiral amine chromium(0) complexes, their suitability as complexation reagents had to be tested. When complexes **1−5** are prepared by reaction of the chiral ligands with a chiral complexation reagent, double stereodifferentiation[62] cannot formally be excluded. However, as the centers of chirality in the ligands and the aromatic system to be coordinated are rather far away from each other, double stereodifferentiation would not be expected to be important in these cases. Any significant influence of double stereodifferentiation would be uncovered by experiments with racemic material.

Triaminetricarbonylchromium(0) complexes have been known as complexation reagents for some time. The decomplexation of three ligands with complexation of just one supports the reaction entropically. While triamminetricarbonylchromium rather easily releases its ammonia ligands, which evaporate from the reaction mixture,[63−65] the corresponding reaction with substituted amine ligands, in order to be irreversible, requires the presence of Lewis acids to bind the liberated amine.[66] When a (diamine)tetracarbonylchromium(0) complex is used as a complexation reagent those factors should not be as important as with triaminetricarbonylchromium(0) complexes. However, the decomplexation of one of the carbonyl ligands and its evaporation out of the reaction mixture should make the reaction irreversible.

Here, it was found that some of the diamine complexes prepared allow complexation of arenes in the presence of trifluoroborane−diethyl ether adduct in THF at 65 °C in good yields (Scheme 6). Results are summarized in Table 1. For comparison, Table 2 summarizes the results obtained with $Cr(CO)_6$ as the complexation reagent.



Scheme 6. Complexation of arenes with amine carbonyl chromium complexes

The results clearly demonstrate the importance of the solvent THF. Only when this coordinating solvent at 65 °C was used were acceptable yields of complexes achieved. Entries 16 and 17 show that lower yields can also be obtained in TBME (*tert*-butyl methyl ether) at 55 °C. A comparison with the results in Table 2 shows that, when THF is used, the yields are somewhat higher even at reaction temperatures more than 50 °C lower. This indicates that amine carbonyl chromium(0) complexes are suitable complexation reagents for arenes. However, the diastereomeric excesses (*de* determined by NMR signal integration) achieved are the same as those obtained with $Cr(CO)_6$ within experimental error. This, and the preference for THF as the solvent,[22,67,68] suggests that the complexations performed starting from the amine complexes proceed by replacement of the amine by THF prior to the complexation of the arene. Thus, intermediates lacking chiral information, like $[(THF)_2Cr(CO)_4]$ and $[(THF)_3Cr(CO)_3]$, are likely to be involved. In order to obtain significant *de*s, the use of ligands other than amines as sources of the chiral information must therefore be considered.

Table 1. Complexation of chiral arenes with chiral amine carbonyl chromium complexes (TBME = *tert*-butyl methyl ether, MCH = methylcyclohexane)

Entry	Reagent	Product	Solvent	Temp. [°C]	Yield [%]	*de*
1	*rac*-**10**	**1**	THF	65	50	5
2	*rac*-**11**	**1**	THF	65	50	9
3	*rac*-**12**	**1**	THF	65	54	6
4	(1*R*,2*R*)-**10**	**1**	THF	65	53	10
5	(1*R*,2*R*)-**10**	**3**	THF	65	63	1
6	(*S*)-**14**	**3**	THF	65	25	6
7	(*S*)-**13**	**5**	THF	65	0	-
8	*rac*-**12**	**3**	$CHCl_3$	61	0	-
9	*rac*-**12**	**3**	TBME	55	8	5
10	(*S*)-**14**	**3**	MeCN	81	0	-
11	(*S*)-**14**	**3**	Bu_2O	70	0	-
12	(*S*)-**14**	**3**	MCH	70	0	-
13	(*S*)-**22**	**1**	THF	65	35	6
14	(*S*)-**22**	**1**	Et_2O	34	0	-
15	(*S*)-**22**	**3**	THF	65	77	4
16	(*S*)-**22**	**4**	TBME	55	19	6
17	(*S*)-**22**	**3**	TBME	55	29	2
18	(*S*)-**22**	**5**	THF	65	0	-

Table 2. Complexation of chiral arenes with hexacarbonylchromium

Entry	Product	Solvent	Temp. [°C]	Yield [%]	*de*
1	**1**	Bu_2O/THF (10:1)	117−120	48	14
2	**2**	Bu_2O/THF (10:1)	117−120	43	7
3	**3**	Bu_2O/THF (10:1)	117−120	54	0
4	**4**	Bu_2O/THF (10:1)	117−120	46	6
5	**5**	Bu_2O/THF (10:1)	117−120	46	11

Experimental Section

General: All operations were performed in flame-dried reaction vessels under an argon atmosphere using standard Schlenk techniques. Halogen-free solvents were distilled from sodium-potassium alloy/benzophenone. Dichloromethane was distilled from calcium chloride. − ^1H NMR: Bruker WP 80 (80 MHz), WP 200 SY (200.1 MHz), AM 400 (400.1 MHz). ^{13}C NMR: Bruker WP 200 SY (50.3 MHz), AM 400 (100.1 MHz). Signal multiplicities were determined using APT and DEPT techniques, + or − indicating positive or negative signal phase. Chemical shifts refer to $\delta_{TMS} = 0$ or to residual solvent signals.[69,70] For clarity, atom numbering is given in the formulas of the ligands and is used accordingly for their complexes. ^{31}P NMR: Bruker WP 200 (81.3 MHz) and AM 400 (161.9 MHz), ^1H decoupling, external standard 85% H_3PO_4. − IR: Bruker ISS 25, Perkin−Elmer FT-IR 580 and 1710. − MS: Finnigan MAT 112, 312 at 70 eV. FAB spectra were obtained using *o*-nitrobenzyl alcohol as the matrix and cesium as the ion source with Fisons VG autospec. − HRMS: Finnigan MAT 312, Fisons VG Autospec, peak matching with PFK. − Combustion analyses: Heraeus CHN Rapid. − Melting points (uncorr.) were determined in sealed glass tubes with an apparatus according to Dr. Tottoli. − Optical rotation: Perkin−Elmer polarimeter 241. − Column chromatography: Silica gel (J. T. Baker, 40 µm) was degassed by heating it with a heat gun at reduced pressure followed by putting it under normal pressure with argon. This sequence was repeated five times. Separations were performed by flash chromatography.[71]

Procedure for the Synthesis of Chiral Substituted Benzoic Acid Esters (Procedure 1): The acid chloride in diethyl ether was added dropwise to the enantiomerically pure alcohol (1 equiv.) and pyridine (1.5 equiv.) in diethyl ether at 0 °C. After the addition the mixture was allowed to warm to 20 °C and was then heated at reflux for 48 h. Then the mixture was poured into a threefold volume of ice water and acidified by addition of 1 N hydrochloric acid. The suspension was extracted four times with diethyl ether (50 mL each). The collected organic layers were dried over $MgSO_4$. After solvent removal at reduced pressure, some anhydride (side product) was removed by column chromatography.

Procedure for the Synthesis of (Arene)tricarbonylchromium(0) Complexes by Complexation with $Cr(CO)_6$ (Procedure 2): A mixture of the arene (1 equiv.) and hexacarbonylchromium (1.1 equiv.) in dibutyl ether/THF (10:1) was heated at reflux (117−120 °C) until no more uncomplexed arene could be detected (TLC control). After cooling to 25 °C, the solvent was removed at reduced pressure, and the product was purified by column chromatography.

(1*S*)-1-Ethoxycarbonylethyl 2-Methoxybenzoate: Procedure 1; 2-methoxybenzoic acid chloride (17.1 g, 100 mmol) in diethyl ether (50 mL), ethyl (*S*)-2-hydroxypropanoate (9.75 mL, 11.8 g, 100 mmol), pyridine (11.6 mL) in diethyl ether (100 mL). Column chromatography (SiO_2, diethyl ether/petroleum ether 1:1, length 20 cm, ø 5 cm) and solvent removal gave 20.5 g (80 mmol, 80%) of (1*S*)-1-ethoxycarbonylethyl 2-methoxybenzoate as a colorless oil. − IR (cap. film): $\tilde{\nu}$ = 3076 cm^{-1} (w), 2984 (m), 2940 (m), 2908 (m), 2840 (m, OCH_3), 1732 (s, br, ester C=O), 1600 (s), 1544 (m), 1492 (s), 1464 (s), 1436 (m), 1380 (m), 1348 (m), 1284 (s), 1252 (s), 1204 (s), 1164 (m), 1128 (s), 1096 (s), 1076 (s), 1048 (s), 1020 (s), 856 (m), 756 (s), 708 (m), 660 (m). − ^1H NMR (200.1 MHz, $[D_6]$acetone): δ = 1.25 (t, $^3J_{13\text{-}12}$ = 6.6 Hz, 3 H, 13-H), 1.56 (d, $^3J_{10\text{-}9}$ = 7 Hz, 3 H, 10-H), 3.88 (s, 3 H, 7-H), 4.2 (2q, 2 H, 12-H), 5.2 (q, 1 H, 9-H), 6.98−7.83 (ABCD line system, 4 H, 3-H, 4-H, 5-H, 6-H). − ^{13}C NMR (50.3 MHz, $[D_6]$acetone, APT): δ = 14.4 (−, C-13), 17.2 (−, C-10), 56.2 (−, C-7), 61.5 (+, C-12), 69.6 (−, C-9), 113.3 (−, C-3, C-4, C-5 or C-6), 120.7 (+, C-1), 120.8 (−, C-3, C-4, C-5 or C-6), 132.1 (−, C-3, C-4, C-5 or C-6), 134.5 (−, C-3, C-4, C-5, C-6), 160.0 (+, C-2), 165.6 (+, C-11), 171.3 (+, C-8). − MS (70 eV, 25 °C): *m/z* (%) = 253 (1) $[M^+ + 1]$, 252 (6) $[M^+]$, 207 (2), 136 (10), 135 (100) $[M^+ -$ ethyl lactate], 120 (3), 106 (7), 92 (10), 77 (22). − HRMS ($C_{13}H_{16}O_5$): calcd. 252.0998; found 252.0998. − $C_{13}H_{16}O_5$ (252.26): calcd. C 61.90, H 6.39; found C 60.98, H 6.37. − $[\alpha]_D^{20}$ = +3.0 (*c* = 1, Et_2O).

Tricarbonyl[η^6-(1*S*)-1-ethoxycarbonylethyl 2-methoxybenzoate]chromium(0) [(*S*)-1]: Procedure 2; (1*S*)-1-ethoxycarbonylethyl 2-methoxybenzoate (1.0 g, 3.9 mmol), $Cr(CO)_6$ (1.0 g, 4.5 mmol) in dibutyl ether (100 mL) and THF (10 mL). The solution was heated at reflux for 36 h with formation of a brown suspension. Column chromatography (SiO_2, diethyl ether/petroleum ether 1:4 → 1:1, length 30 cm, ø 2.5 cm) and solvent removal gave 720 mg [1.86 mmol, 48%, *de* ≈ 14%, purity ca. 95% (NMR)] of (*S*)-**1** as a viscous orange-red oil. − IR ($CHCl_3$): $\tilde{\nu}$ = 3098 cm^{-1} (w), 2960 (w), 2936 (w), 1980 (s, CO), 1912 (s, br, CO), 1728 (m, br, ester−C=O), 1524 (w), 1464 (m), 1416 (w), 1288 (m), 1228 (m), 1180 (m), 1096 (m), 1012 (m), 624 (m). − ^1H NMR (200.1 MHz, $[D_6]$acetone): δ = 1.22 (2t, $^3J_{13\text{-}12}$ = 6.8 Hz, 3 H, 13-H), 1.53 (2d, $^3J_{10\text{-}9}$ = 7 Hz, 3 H, 10-H), 3.85 (2s, 3 H, 7-H), 4.22 (4q, 2 H, 12-H), 5.11−6.44 (ABCD line system, 4 H, 3-H, 4-H, 5-H, 6-H), 5.17 (q, 1 H, 9-H). Double set of signals due to diastereomers. − ^{13}C NMR (100.6 MHz, $[D_6]$acetone, APT): δ = 14.3 + 14.4 (−, C-13), 17.1 + 17.2 (−, C-10), 56.85 + 56.86 (−, C-7), 61.7 + 61.8 (+, C-12), 70.3 + 70.4 (−, C 9), 75.4 + 75.6 (−, C-3, C-4, C-5 or C-6), 83.2 + 83.5 (+, C-1), 85.6 + 85.7 (−, C-3, C-4, C-5 or C-6), 97.9 + 98.0 (−, C-3, C-4, C-5 or C-6), 98.9 + 99.1 (−, C-3, C-4, C-5 or C-6), 145.6 + 145.8 (+, C-2), 164.0 + 164.1 (+, C-11), 170.8 + 170.9 (+, C-8), 232.8 + 232.9 (+, CO). Double set of signals due to diastereomers. − MS (70 eV, 160 °C): *m/z* (%) = 389 (2) $[M^+ + 1]$, 388 (4) $[M^+]$, 387 (1) $[M^+ - 1]$, 331 (1) $[M^+ - 2CO - 1]$, 304 (3) $[M^+ - 3CO]$, 303 (7) $[M^+ - 3CO - 1]$, 252 (24) $[M^+ - 3CO - Cr]$, 207 (8), 160 (35), 136 (50), 135 (100) $[M^+ - Cr - 3CO -$ ethyl lactate], 134 (60), 120 (14), 105 (47), 92 (54), 77 (63).

(1*S*)-1-Ethoxycarbonylethyl 3,4-Dimethoxybenzoate: Procedure 1; 3,4-dimethoxybenzoic acid chloride (4.01 g, 20 mmol) in diethyl ether (50 mL), ethyl (*S*)-2-hydroxypropanoate (2.27 mL, 2.36 g, 20 mmol) and pyridine (2.4 mL, 20 mmol) in diethyl ether (20 mL). Column chromatography (SiO_2, diethyl ether/petroleum ether 1:1, length 25 cm, ø 3.5 cm) and solvent removal gave 5.21 g (18.5 mmol, 92%) of (1*S*)-1-ethoxycarbonylethyl 3,4-dimethoxybenzoate as a light brownish solid, m.p. 67 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3076 cm^{-1} (m), 2984 (m), 2968 (m), 2940 (m), 2912 (m), 2840 (m, OCH_3), 1748 (s, ester C=O), 1712 (s, ester C=O), 1600 (s), 1516 (s), 1464 (s), 1420 (s), 1380 (m), 1352 (m), 1272 (s), 1228 (s), 1176 (s), 1136 (s), 1112 (s), 1024 (s), 948 (m), 876 (m). − ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.28 (t, $^3J_{14\text{-}13}$ = 7.2 Hz, 3 H, 14-H), 1.62 (d, $^3J_{11\text{-}10}$ = 7 Hz, 3 H, 11-H), 3.92 (s, 3 H, 7-H or 8-H), 3.93 (s, 3 H, 8-H or 7-H), 4.2 (q, $^3J_{13\text{-}14}$ = 7.2 Hz, 2 H, 13-H), 5.3 (q, $^3J_{10\text{-}11}$ = 7 Hz, 1 H, 10-H), 6.9 (d, $^3J_{5\text{-}6}$ = 8.6 Hz, 1 H, 5-H), 7.6 (d, $^4J_{2\text{-}6}$ = 1.8 Hz, 1 H, 2-H), 7.7 (dd, $^3J_{6\text{-}5}$ = 8.6 Hz, $^4J_{2\text{-}6}$ = 1.8 Hz, 1 H, 6-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 14.7 (CH_3, C-14), 17.6 (CH_3, C-11), 56.5 (CH_3, C-7 or C-8), 56.6 (CH_3, C-8 or C-7), 61.9 (CH_2, C-13), 69.6 (CH, C-10), 110.8 (CH, C-2, C-5 or C-6), 112.7 (CH, C-2, C-5 or C-6), 122.5 (C_q, C-1), 124.6 (CH, C-2, C-5 or C-6), 149.2 (C_q, C-3 or C-4), 153.8 (C_q, C-3 or C-4), 166.3 (C_q, C-12), 171.5 (C_q, C-9). − MS (70 eV, 60 °C): *m/z* (%) = 283 (5) $[M^+ + 1]$, 282 (29) $[M^+]$, 237 (3), 210 (2), 166 (11), 165 (100) $[M^+ -$ ethyl lactate], 149 (2), 137 (5), 122 (3), 107 (3), 91 (5), 79 (5), 77 (5). − HRMS ($C_{13}H_{16}O_5$): calcd. 281.110339; found 281.110474. − $C_{14}H_{18}O_6$ (282.29): calcd. C 59.57, H 6.43; found C 59.15, H 6.41. − $[\alpha]_D^{20}$ = +22.6 (*c* = 1, Et_2O).

Tricarbonyl[η^6-(1*S*)-1-ethoxycarbonylethyl 3,4-dimethoxybenzoate]chromium(0) [(1*S*)-2]: Procedure 2; (1*S*)-1-ethoxycarbonylethyl 3,4-dimethoxybenzoate (282 mg, 1.00 mmol) and $Cr(CO)_6$ (300 mg, 1.36 mmol) in dibutyl ether (75 mL) and THF (8 mL). The solution was heated at reflux for 26 h with formation of a yellow suspension. Column chromatography (SiO_2, diethyl ether/petroleum ether 1:3 → 1:1, length 40 cm, ø 2 cm) and solvent removal gave 180 mg [0.43 mmol, 43%, *de* ≈ 7%, purity ca. 95% (NMR)] of (1*S*)-**2**, mixture of diastereomers, as a viscous orange oil. − IR ($CHCl_3$): $\tilde{\nu}$ = 3040 cm^{-1} (w), 2984 (w), 2940 (w), 1976 (s, CO), 1904 (s, br, CO), 1724 (m, br, ester−C=O), 1540 (w), 1512 (w), 1488 (m), 1384 (w), 1312 (w), 1264 (s), 1222 (m), 1196 (m), 1180 (m), 1108 (m), 1016 (w). − ^1H NMR (400.1 MHz, $[D_6]$acetone): δ = 1.25 (t, $^3J_{14\text{-}13}$ = 7.1 Hz, 3 H, 14-H), 1.55 (2d, $^3J_{11\text{-}10}$ = 7 Hz, 3 H, 11-H), 3.88 (4s, 6 H, 7-H, 8-H), 4.2 (2q, $^3J_{13\text{-}14}$ = 7.1 Hz, 2 H, 13-H), 5.2 (2q, $^3J_{10\text{-}11}$ = 7 Hz, 1 H, 10-H), 5.8 (2d, $^3J_{5\text{-}6}$ = 6.6 Hz, 1 H, 5-H or 6-H), 6.15 (2d, $^3J_{5\text{-}6}$ = 6.6 Hz, 1 H, 6-H or 5-H), 6.24 (s, br, 1 H, 2-H). Double set of signals due to diastereomers. − ^{13}C NMR (100.6 MHz, $[D_6]$acetone, DEPT): δ = 14.29 + 14.30 (CH_3, C-14), 16.05 + 16.08 (CH_3, C-11), 56.13 + 56.18 (CH_3, C-7 or C-8), 56.98

+ 57.03 (CH_3, C-7 or C-8), 60.82 + 60.84 (CH_2, C-13), 69.64 + 69.76 (CH, C-10), 75.63 + 75.89 (CH, C-2, C-5 or C-6), 80.36 + 80.92 (CH, C-2, C-5 or C-6), 83.84 + 83.85 (C_q, C-1), 90.91 + 91.06 (CH, C-2, C-5 or C-6), 130.21 + 130.40 (C_q, C-3 or C-4), 137.18 + 137.24 (C_q, C-3 or C-4), 164.26 + 164.31 (C_q, C-12), 169.53 + 169.54 (C_q, C-9), 232.07 + 232.09 (C_q, CO). − MS (70 eV, 90 °C): *m*/*z* (%) = 418 (1) [M^+], 334 (3) [$M^+ - 3CO$], 306 (2), 283 (4), 282 (27) [$M^+ - 3CO - Cr$], 278 (4), 237 (3), 219 (4), 166 (9), 165 (100) [M^+ − Cr − 3CO − ethyl lactate], 137 (5), 122 (3), 107 (3), 92 (3), 79 (6), 52 (3) [^{52}Cr]. − HRMS ($C_{17}H_{18}CrO_9$): calcd. 418.035592; found 418.035126.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2-Methoxybenzoate:[72,73] Procedure 1; 2-methoxybenzoic acid chloride (3.41 g, 20 mmol) in diethyl ether (15 mL), (−)-menthol (3.12 g, 20 mmol) and pyridine (2.4 mL, 30 mmol) in diethyl ether (20 mL). Column chromatography (SiO_2, diethyl ether/petroleum ether 1:2, length 30 cm, ø 3.5 cm) and solvent removal gave 5.45 g (18.8 mmol, 94%) of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-methoxybenzoate as colorless needles, m.p. 42 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3028 cm^{-1} (w), 2952 (s), 2916 (s), 2864 (m), 1728 (s, ester C=O), 1596 (s), 1492 (s), 1452 (s), 1384 (m), 1368 (m), 1332 (m), 1280 (s), 1256 (s), 1180 (m), 1164 (m), 1136 (m), 1084 (s, C−O), 1016 (s), 960 (m), 756 (s), 712 (m), 660 (m). − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.81 (d, $^3J_{18\text{-}13}$ = 7 Hz, 3 H, 18-H), 0.91 (d, $^3J_{16/17\text{-}15}$ = 6.4 Hz, 3 H, 16-H or 17-H), 0.92 (d, $^3J_{17/16\text{-}15}$ = 7 Hz, 3 H, 17-H or 16-H), 1.10 (m, 3 H), 1.52 (m, 2 H), 1.71 (m, 2 H), 2.12 (m, 2 H), 3.88 (s, 3 H, 7-H), 4.92 (ddd, $^3J_{9\text{-eq-}14}$ = 4.3 Hz, $^3J_{9\text{-ax-}14}$ = 10.9 Hz, $^3J_{9\text{-}10}$ = 10.9 Hz, 1 H, 9-H), 6.96−7.75 (ABCD system, 4 H, 3-H, 4-H, 5-H, 6-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 16.1 (CH_3, C-16 or C-17), 20.8 (CH_3, C-17 or C-16), 21.9 (CH_3, C-18), 23.2 (CH_2, C-11), 26.0 (CH, C-15), 31.4 (CH, C-13), 34.2 (CH_2, C-12), 40.8 (CH_2, C-14), 47.1 (CH, C-10), 55.8 (CH_3, C-7), 74.5 (CH, C-9), 111.9 (CH, C-3, C-4, C-5 or C-6), 120.0 (CH, C-3, C-4, C-5 or C-6), 121.0 (C_q, C-1), 131.1 (CH, C-3, C-4, C-5 or C-6), 133.0 (CH, C-3, C-4, C-5 or C-6), 158.9 (C_q, C-2), 165.8 (C_q, C-8). − MS (70 eV, 20 °C): *m*/*z* (%) = 291 (4) [$M^+ + 1$], 290 (11) [M^+], 275 (2) [$M^+ - CH_3$], 235 (3), 177 (3), 154 (29), 153 (53), 152 (35), 139 (35), 138 (50), 136 (35), 135 (100) [$C_6H_4OCH_3CO^+$], 123 (39), 120 (18), 109 (29), 105 (32), 95 (57), 92 (34), 83 (36), 82 (37), 81 (43), 78 (42). − HRMS ($C_{18}H_{26}O_3$): calcd. 290.188195; found 290.188568. − $C_{18}H_{26}O_3$ (290.19): calcd. C 74.45, H 9.02; found C 74.37, H 9.06. − $[\alpha]_D^{20}$ = −48 (*c* = 1, Et_2O).

(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl 2-Methoxybenzoate: As described above, using (+)-menthol. − $[\alpha]_D^{20}$ = +46.1 (*c* = 1, Et_2O).

(1*R*,2*S*,5*R*)-Tricarbonyl[η^6-(2-isopropyl-5-methyl)cyclohexyl 2-methoxybenzoate]chromium(0) [(1*R*,2*S*,5*R*)-3]: Procedure 2; (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-methoxybenzoate (650 mg, 2.42 mmol), $Cr(CO)_6$ (600 mg, 2.73 mmol) in dibutyl ether (60 mL) and THF (6 mL). The solution was heated at reflux for 43 h with formation of an orange suspension. Column chromatography (SiO_2, diethyl ether/petroleum ether 1:2 → 1:1, length 35 cm, ø 3.5 cm) and solvent removal gave 560 mg (1.32 mmol, 54%, *de* ≈ 0%) of (1*R*,2*S*,5*R*)-**3** as a mixture of diastereomers. − IR ($CHCl_3$): $\tilde{\nu}$ = 3096 cm^{-1} (w), 2956 (m), 2928 (m), 2872 (w), 1980 (s, CO), 1908 (s, br, CO), 1716 (m, br, ester−C=O), 1524 (w), 1464 (m), 1416 (w), 1292 (m), 1256 (m), 1180 (w), 1120 (m), 1080 (m), 1012 (w). − MS (70 eV, 110 °C): *m*/*z* (%) = 426 (1) [M^+], 370 (2) [$M^+ - CO$], 343 (4) [$M^+ + 1 - 2CO$], 342 (9) [$M^+ - 2CO$], 290 (1) [$M^+ - 3CO - Cr$], 242 (5), 204 (16), 158 (19), 153 (25), 138 (40), 135 (100) [$C_6H_4OCH_3CO^+$], 123 (32), 95 (93), 81 (84). − HRMS ($C_{21}H_{26}CrO_6$): calcd. 426.113449; found 426.113586. − $C_{21}H_{26}CrO_6$ (426.42): calcd. C 59.15, H 6.15; found C 58.28, H 6.16.

The diastereomers were separated by column chromatography (SiO_2, diethyl ether/petroleum ether 1:4 → 1:1, length 120 cm, ø 3.5 cm).

Fraction I: R_f = 0.50 (diethyl ether/petroleum ether 2:1), orange solid, m.p. 140 °C (dec.). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 0.80 (d, $^3J_{18\text{-}13}$ = 7 Hz, 3 H, 18-H), 0.89 (m, 1 H), 0.91 (d, $^3J_{16/17\text{-}15}$ = 6.4 Hz, 3 H, 16-H or 17-H), 0.93 (d, $^3J_{17/16\text{-}15}$ = 7 Hz, 3 H, 17-H or 16-H), 1.1 (m, 2 H), 1.51 (m, 2 H), 1.73 (m, 2 H), 2.12 (m, 2 H), 3.87 (s, 3 H, 7-H), 4.85 (m, 1 H), 5.21−6.35 (ABCD system, 4 H, 3-H, 4-H, 5-H, 6-H). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT): δ = 15.4 (CH_3, C-16 or C-17), 20.2 (CH_3, C-16 or C-17), 21.4 (CH_3, C-18), 22.7 (CH_2, C-11), 25.5 (CH, C-15), 31.1 (CH, C-13), 33.9 (CH_2, C-12), 40.5 (CH_2, C-14), 47.1 (CH, C-10), 55.8 (CH_3, C-7), 74.5 (CH, C-9), 74.9 (CH, C-3, C-4, C-5 or C-6), 84.66 (C_q, C-1), 84.67 (CH, C-3, C-4, C-5 or C-6), 97.1 (CH, C-3, C-4, C-5 or C-6), 98.2 (CH, C-3, C-4, C-5 or C-6), 144.7 (C_q, C-2), 163.7 (C_q, C-8), 232.0 (C_q, CO).

Fraction II: R_f = 0.48 (diethyl ether/petroleum ether 2:1), orange solid, m.p. 143 °C (dec.). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 0.80 (d, $^3J_{18\text{-}13}$ = 7 Hz, 3 H, 18-H), 0.89 (m, 1 H), 0.91 (d, $^3J_{16/17\text{-}15}$ = 6.4 Hz, 3 H, 16-H or 17-H), 0.93 (d, $^3J_{17/16\text{-}15}$ = 7 Hz, 3 H, 17-H or 16-H), 1.1 (m, 2 H), 1.51 (m, 2 H), 1.73 (m, 2 H), 2.12 (m, 2 H), 3.86 (s, 3 H, 7-H), 4.85 (m, 1 H), 5.21−6.35 (ABCD line system, 4 H, 3-H, 4-H, 5-H, 6-H). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 15.3 (CH_3, C-16 or C-17), 20.2 (CH_3, C-16 or C-17), 21.3 (CH_3, C-18), 22.6 (CH_2, C-11), 25.7 (CH, C-15), 31.1 (CH, C-13), 33.9 (CH_2, C-12), 40.4 (CH_2, C-14), 47.0 (CH, C-10), 55.7 (CH_3, C-7), 74.41 (CH, C-3, C-4, C-5 or C-6), 74.42 (CH, C-9), 84.60 (C_q, C-1), 84.61 (CH, C-3, C-4, C-5 or C-6), 96.9 (CH, C-3, C-4, C-5 or C-6), 97.8 (CH, C-3, C-4, C-5 or C-6), 144.6 (C_q, C-2), 163.1 (C_q, C-8), 232.0 (C_q, CO).

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 3,4-Dimethoxybenzoate: Procedure 1; 3,4-dimethoxybenzoyl chloride (4.01 g, 20 mmol) in diethyl ether (35 mL), (−)-menthol (3.12 g, 20 mmol) and pyridine (2.4 mL, 30 mmol) in diethyl ether (20 mL). Column chromatography (SiO_2, diethyl ether/petroleum ether 2:3, length 25 cm, ø 3.5 cm) and solvent removal gave 6.08 g, 19.0 mmol, 95%) of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3,4-dimethoxybenzoate, colorless oil. − IR ($CHCl_3$): $\tilde{\nu}$ = 3028 cm^{-1} (w), 2960 (s), 2936 (m), 2872 (m), 1700 (s, ester C=O), 1600 (m), 1512 (s), 1464 (s), 1420 (m), 1344 (m), 1292 (s), 1288 (s), 1228 (m), 1176 (m), 1132 (m), 1112 (m), 1024 (m), 980 (m), 964 (m), 880 (m). − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.8 (d, $^3J_{18\text{-}13}$ = 6.8 Hz, 3 H, 19-H), 0.91 (d, $^3J_{17/18\text{-}16}$ = 7 Hz, 3 H, 17-H or 18-H), 0.92 (d, $^3J_{17/18\text{-}16}$ = 6.5 Hz, 3 H, 17-H or 18-H), 1.1 (m, 3 H), 1.55 (m, 2 H), 1.74 (m, 2 H), 1.95 (m, 1 H), 2.12 (m, 1 H), 3.94 (s, br, 6 H, 7-H, 8-H), 4.92 (ddd, $^3J_{10\text{-eq-}15}$ = 4.4 Hz, $^3J_{10\text{-ax-}15}$ = 10.8 Hz, $^3J_{10\text{-}11}$ = 10.8 Hz, 1 H, 10-H), 6.9 (d, $^3J_{5\text{-}6}$ = 8.5 Hz, 1 H, 5-H), 7.6 (d, $^4J_{2\text{-}6}$ = 1.9 Hz, 1 H, 2-H), 7.7 (dd, $^3J_{6\text{-}5}$ = 8.5 Hz, $^4J_{2\text{-}6}$ = 1.9 Hz, 1 H, 6-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 16.7 (CH_3, C-17 or C-18), 20.7 (CH_3, C-17 or C-18), 22.1 (CH_3, C-19), 23.8 (CH_2, C-12), 26.6 (CH, C-16), 31.5 (CH, C-14), 34.4 (CH_2, C-13), 41.1 (CH_2, C-15), 47.3 (CH, C-11), 56.0 (CH_3, C-7 or C-8), 56.01 (CH_3, C-7 or C-8), 74.6 (CH, C-10), 110.2 (CH, C-2, C-5 or C-6), 112.1 (CH, C-2, C-5 or C-6), 123.44 (C_q, C-1), 123.46 (CH, C-2, C-5 or C-6), 148.6 (C_q, C-3 or C-4), 152.8 (C_q, C-3 or C-4), 165.9 (C_q, C-9). − MS (70 eV, 70 °C): *m*/*z* (%) = 320 (3) [M^+], 319 (9) [$M^+ - 1$], 183 (13), 182 (100) [$C_6H_3(OCH_3)_2CO_2H^+$], 165 (27), 138 (13), 123 (13), 109 (5), 95 (31), 81 (27), 71 (28). − HRMS ($C_{19}H_{28}O_4$):

calcd. 320.198760; found 320.198792. − $C_{19}H_{28}O_4$ (320.43): calcd. C 71.22, H 8.81; found C 71.48, H 9.10. − $[\alpha]_D^{20}$ = −72.9, (*c* = 1, Et_2O).

(1*R*,2*S*,5*R*)-Tricarbonyl[η^6-(2-isopropyl-5-methyl)cyclohexyl 3,4-dimethoxybenzoate]chromium(0) [(1*R*,2*S*,5*R*)-4]: Procedure 2; (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3,4-dimethoxybenzoate (200 mg, 0.625 mmol), $Cr(CO)_6$ (220 mg, 1.00 mmol) in dibutyl ether (50 mL) and THF (5 mL). The solution was heated at reflux for 18 h with formation of an orange suspension. Column chromatography (SiO_2, diethyl ether/petroleum ether 1:2 → 1:1, length 20 cm, ø 2.5 cm) and solvent removal gave 130 mg [0.29 mmol, 46%, *de* ≈ 6% (NMR)] of (1*R*,2*S*,5*R*)-**4** as a viscous orange oil. − IR ($CHCl_3$): $\tilde{\nu}$ = 3096 cm^{-1} (w), 2960 (m), 2928 (m), 2872 (w), 1972 (s, CO), 1904 (s, br, CO), 1708 (m, br, ester-C=O), 1604 (m), 1536 (w), 1512 (w), 1488 (m), 1464 (m), 1384 (m), 1288 (m), 1280 (m), 1236 (m), 1180 (w), 1104 (m), 1020 (m). − ^1H NMR (400.1 MHz, $[D_6]$acetone): δ = 0.79 (2d, $^3J_{13\text{-}18}$ = 6.7 Hz, 3 H, 19-H), 0.9 (m, 1 H), 0.91 (d, $^3J_{17/16\text{-}18}$ = 7 Hz, 3 H, 17-H or 18-H), 0.92 (d, $^3J_{17/16\text{-}18}$ = 6.5 Hz, 3 H, 17-H or 18-H), 1.1 (m, 2 H), 1.55 (m, 2 H), 1.72 (m, 2 H), 1.98 (m, 1 H), 2.12 (m, 1 H), 3.85 (2s, 3 H, 7-H or 8-H), 3.87 (2s, 3 H, 7-H or 8-H), 4.85 (m, 1 H, 10-H), 5.72 (m, 1 H, 5-H), 6.08 (m, 1 H, 2-H), 6.19 (m, 1 H). Double set of signals due to diastereomers. − ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 15.6 (CH_3, C-17 or C-18), 20.02 + 20.03 (CH_3, C-17 or C-18), 21.3 (CH_3, C-19), 22.9 (CH_2, C-12), 25.94 + 25.95 (CH, C-16), 31.11 + 31.14 (CH, C-14), 33.83 + 33.85 (CH_2, C-13), 40.3 + 40.5 (CH_2, C-15), 46.9 + 47.2 (CH, C-11), 56.1 + 56.2 (CH_3, C-7 or C-8), 56.9 + 57.1 (CH_3, C-7 or C-8), 75.15 + 75.29 (CH, C-10), 75.5 + 76.3 (CH, C-2, C-5 or C-6), 80.4 (C_q, C-1), 85.1 + 85.4 (CH, C-2, C-5 or C-6), 90.8 + 90.9 (CH, C-2, C-5 or C-6), 130.3 + 130.8 (C_q, C-3 or C-4), 137.0 + 137.2 (C_q, C-3 or C-4), 164.19 + 164.21 (C_q, C-9), 232.14 + 232.36 (C_q, CO). − MS (70 eV, 120 °C): *m*/*z* (%) = 456 (2) [M^+], 455 (4) [$M^+ - 1$], 401 (3), 400 (8) [$M^+ - 2CO$], 373 (17), 372 (52) [$M^+ - 3CO$], 324 (5), 319 (4) [$M^+ - 3CO - Cr - 1$], 235 (21), 234 (100) [$M^+ - 3CO$ − menthyl], 233 (14), 206 (6), 189 (18), 182 (61), 165 (48), 129 (7), 95 (13), 81 (10), 77 (8), 52 (33) [^{52}Cr]. − HRMS ($C_{22}H_{28}CrO_7$): calcd. 456.124013; found 456.123077. − $C_{22}H_{28}CrO_7$ (456.45): calcd. C 57.89, H 6.18; found C 57.88, H 6.38.

1-[(1′*R*,2′*R*)-1′,2′-Dimethylethylenedioxy]methyl-2-methoxybenzene: 2-Methoxybenzaldehyde (7.39 g, 55.0 mmol), (2*R*,3*R*)-butane-2,3-diol (5 mL, 55.0 mmol) and *p*-toluenesulfonic acid (70 mg, 0.4 mmol) in benzene (20 mL) were heated at reflux for six days with azeotropic water removal. After cooling to room temperature the mixture was washed twice with aqueous sodium hydroxide solution (each 0.1 N, 20 mL), then with water (50 mL). After drying of the organic layer over K_2CO_3 and solvent removal at reduced pressure, a red-brown oil was obtained and purified by column chromatography (SiO_2, diethyl ether/petroleum ether 1:2, length 50 cm, ø 2 cm) to give 8.02 g (38.5 mmol, 70%) of 1-[(1′*R*.2′*R*)-1′,2′-dimethylethylenedioxy]methyl-2-methoxybenzene as a colorless oil. − IR ($CHCl_3$): $\tilde{\nu}$ = 3061 cm^{-1} (w), 3000 (m), 2972 (m), 2932 (m), 2884 (m), 2840 (w), 1604 (m, arom. C=C), 1492 (m, arom. C=C), 1464 (m), 1380 (m), 1284 (m), 1244 (s), 1088 (s, acetal C−O), 980 (acetal C−O), 940 (w), 908 (w). − ^1H NMR (200.1 MHz, $CDCl_3$): δ = 1.32 (2d, $^3J_{9\text{-}1'}$ = 5.4 Hz, 3 H, 9-H or 10-H), 1.38 (2d, $^3J_{10\text{-}2'}$ = 5.4 Hz, 3 H, 10-H or 9-H), 3.79 (m, 2 H, 1′-H, 2′-H), 3.86 (s, 3 H, 7-H), 6.32 (s, 1 H, 8-H), 6.86−7.57 (ABCD system, 4 H, 3-H, 4-H, 5-H, 6-H). − ^{13}C NMR (50.3 MHz, $[D_6]$acetone, APT): δ = 17.0 (−, C-9 or C-10), 17.4 (−, C-10 or C-9), 55.7 (−, C-7), 78.8 (−, C-1′ or C-2′), 80.7 (−, C-2′ or C-1′), 98.2 (−, C-8), 111.5 (−, C-3, C-4, C-5 or C-6), 120.9 (−, C-3, C-4, C-5 or C-6), 127.95 (−, C-3, C-4, C-5 or C-6),127.96 (+, C-1), 130.8 (−, C-3, C-4, C-5 or C-6), 158.6 (+, C-2). − MS (70 eV, 25 °C): *m*/*z* (%) = 209 (3) [$M^+ + 1$], 208 (62) [M^+], 193 (4), 177 (17) [$M^+ - OCH_3$], 135 (100) [$M^+ - C_4H_9O$], 121 (26), 119 (27), 108 (81), 92 (33), 91 (69), 77 (71). − HRMS ($C_{12}H_{16}O_3$): calcd. 208.1099; found 208.1100. − $[\alpha]_D^{20}$ = −12.2; $[\alpha]_{546}^{20}$ = −15.0; $[\alpha]_{436}^{20}$ = −28.4; $[\alpha]_{365}^{20}$ = −49.8 (*c* = 1, Et_2O).

Tricarbonyl{η^6-1-[(1′*R*,2′*R*)-1′,2′-dimethylethylenedioxy]methyl-2-methoxybenzene}chromium(0) [(*R*,*R*)-5]:[41] Procedure 2; 1-[(1′*R*,2′*R*)-1′,2′-dimethylethylenedioxy]methyl-2-methoxybenzene [(*R*,*R*)-**9**] (1.04 g, 5.0 mmol), $Cr(CO)_6$ (1.2 g, 5.5 mmol) in dibutyl ether (100 mL) and THF (10 mL). The solution was heated at reflux for 20 h with formation of a yellow suspension. Column chromatography (SiO_2 diethyl ether/petroleum ether 1:3 → 1:1, length 30 cm, ø 3.5 cm) and solvent removal gave 791 mg [0.23 mmol, 46%, *de* ≈ 11% (NMR)] of (*R*,*R*)-**5** as a mixture of diastereomers as a yellow oil.[41]

Procedure for the Preparation of (η^6-Arene)tricarbonylchromium Complexes with Tetracarbonyl(η^4-norbornadiene)chromium(0) (6) (Procedure 3):[42,43] The arene (1 equiv.) and **6** (1 equiv.) in THF were heated at reflux until no more **6** could be detected by TLC. Liberated norbornadiene was removed from the reaction mixture by a continuous flow of argon gas. After removal of the solvent and residual norbornadiene at reduced pressure the product was purified by column chromatography.

Tricarbonyl(η^6-naphthalene)chromium(0) (7):[22] Procedure 3; compound **6** (100 mg, 0.39 mmol) and naphthalene (50 mg, 0.39 mmol) in THF (50 mL) were heated at reflux for 72 h. Column chromatography (SiO_2, TBME/petroleum ether 1:5 → 1:3, length 20 cm, ø 2 cm) and solvent removal gave 82 mg (0.31 mmol, 80%) of **7** as a brick-red solid.[22,68]

Pentacarbonyl[(*S*)-1-cyclohexylethylamine]chromium(0) [(*S*)-8]: Compound **6** (275 mg, 1.07 mmol) in (*S*)-1-cyclohexylethylamine[44,45] (1.3 mL, 1.13 g, 8.89 mmol) was stirred for 18 h in the dark at 20 °C. Diethyl ether (20 mL) was added in four portions, causing precipitation of a fine yellow solid which, due to its instability, could not be characterized. After filtration through a P4 frit and solvent removal at reduced pressure a yellow oil was obtained. It was purified by column chromatography (SiO_2, diethyl ether/petroleum ether 1:1, length 30 cm, ø 2.5 cm) to give (*S*)-**8** (147 mg, 0.46 mmol, 43%) as a yellow crystalline solid (m.p. 105 °C, dec.). − IR (KBr): $\tilde{\nu}$ = 3340 cm^{-1} (m, amine), 3296 (w, amine), 2936 (m), 2856 (s), 2064 (m, CO), 1984 (m, CO), 1950 (m, CO), 1924 (s, CO), 1888 (s, CO), 1872 (s, CO), 1584 (m), 1084 (m), 1020 (m), 800 (m), 656 (m). − ^1H NMR (200.1 MHz, $[D_6]$acetone): δ = 0.85−1.82 (m, 14 H, 8-H, 1-H, 2-H, 3-H, 4-H, 5-H, 6-H), 2.38 (m, 1 H, 7-H), 2.62−3.04 (br, 2 H, amine). − ^{13}C NMR (50.3 MHz, $[D_6]$acetone, APT): δ = 17.3 (−, C-8), 26.9 (+, C-2 or C-3, C-4, C-5 or C-6), 27.09 (+, C-2 or C-3, C-4, C-5 or C-6), 27.13 (+, C-2 or C-3, C-4, C-5 or C-6), 27.4 (+, C-2 or C-3, C-4, C-5 or C-6), 45.2 (−, C-1), 61.1 (−, C-7), 215.6 (+, CO_{ax}), 215.9 (+, $4CO_{eq}$). − MS (70 eV, 70 °C): *m*/*z* (%) = 319 (2) [M^+], 318 (5) [$M^+ - 1$], 291 (3) [$M^+ - CO$], 263 (2) [$M^+ - 2CO$], 235 (2) [$M^+ - 3CO$], 208 (3), 207 (9) [$M^+ - 4CO$], 180 (13), 179 (64) [$M^+ - 5CO$], 156 (4), 127 (3) [amine], 126 (7), 120 (8), 106 (100), 95 (20), 79 (38), 77 (30), 52 (46) [^{52}Cr]. − $C_{13}H_{17}CrNO_5$ (320.43): calcd. C 48.91, H 5.37, N 4.39; found C 47.61, H 5.28, N 4.30. − $[\alpha]_D^{20}$ = −14.8 (*c* = 1, acetone).

Preparation of Diaminetetracarbonylchromium(0) Chelate Complexes From Liquid Diamines without Solvent (Procedure 4): Hexacarbonylchromium was suspended in the liquid diamine and heated at 120 °C in the dark, the mixture becoming orange-red. After cooling to 20 °C, ethanol was added, and unchanged hexacarbonylchromium filtered off with a P3 frit. After washing several times with ethanol the crude product was precipitated by addition of water. For complete crystallization the filtrate was stored for 24 h at 5 °C, then the crystals were filtered off with a P4 frit. The solid was washed with water and dried on the frit at 0.01 mbar. The product was washed from the frit with acetone and isolated as a yellow powder after removal of the acetone at reduced pressure.

Preparation of Chelate Diaminetetracarbonylchromium(0) Complexes with Tetracarbonyl(norbornadiene)chromium(0) (6) (Procedure 5): The amine (1 equiv.) and compound **6** (1 equiv.) in THF were heated at reflux until no more **6** could be detected by TLC. The reaction progress was indicated by a color change from orange-yellow to yellow. After solvent removal at reduced pressure the crude product was isolated either by crystallization (see Procedure 4) or by column chromatography.

(*N,N'*-Dicyclohexyl)-1,2-ethanediamine:[46,47] Sodium tetrahydridoborate (2.66 g, 70.0 mmol) was added to (*N,N'*-dicyclohexyl)-1,2-ethanediimine[74,75] (6.6 g, 30.0 mmol) in anhydrous methanol (50 mL) and heated for 3 h at 50 °C. After solvent removal at reduced pressure the residue was taken up with water (100 mL). The mixture was extracted three times with MTBE (each 50 mL), and the collected organic layers were dried over Na_2SO_4. After filtration and solvent removal at reduced pressure 6.6 g (29.5 mmol, 98%) of (*N,N'*-dicyclohexyl)-1,2-ethanediamine was obtained as a colorless solid (m.p. 86 °C). − IR (KBr): $\tilde{\nu}$ = 3388 cm^{-1} (m, amine), 3276 (s, amine), 2924 (s), 2852 (s), 2808 (m), 1492 (m), 1452 (s), 1376 (m), 1224 (m), 1144 (m), 1124 (s), 904 (m), 860 (m), 840 (m). − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.01−1.92 (m, 22 H, 3-H, 4-H, 5-H, 6-H, 7-H, amine), 2.39 (m, 2 H, 2-H), 2.73 (s, 4 H, 1-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 25.7 (CH_2, C-5), 26.8 [CH_2, C-4(6)], 34.3 [CH_2, C-3(7)], 47.7 (CH_2, C-1), 57.6 (CH, C-2). − MS (70 eV, 20 °C): *m/z* (%) = 225 (4) [M^+ + 1], 224 (20) [M^+], 223 (6), 191 (7), 136 (7), 126 (5), 113 (22), 112 (100), 83 (8), 69 (11). − HRMS ($C_{14}H_{28}N_2$): calcd. 224.225249; found 224.227325.

Tetracarbonyl[(*N,N'*-dicyclohexyl)-1,2-ethanediamine]chromium(0) (9): Procedure 5; (*N,N'*-dicyclohexyl)-1,2-ethanediamine[46,47] (220 mg, 0.98 mmol) and **6** (250 mg, 0.98 mmol) in THF (50 mL) was heated at reflux for 30 min. Crystallization (60 mL of ethanol, 50 mL of water) gave 375 mg (0.97 mmol, 99%) of **9** as a yellow powder (m.p. 143 °C). − IR (KBr): $\tilde{\nu}$ = 3280 cm^{-1} (m, amine), 2932 (s), 2860 (m), 2004 (s, CO), 1876 (s, CO), 1844 (s, CO), 1784 (s, CO), 1452 (m), 1264 (m), 1092 (m), 1060 (m), 960 (m), 696 (m), 656 (m). − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.09−2.90 (m, 26 H, 1-H, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H), 3.96 (s, br, 2 H, amine). − ^{13}C NMR (100.6 MHz, $CDCl_3$, APT): δ = 25.2 (+, C-5), 25.5 (+, C-4 or C-6), 25.6 (+, C-4 or C-6), 30.8 (+, C-3 or C-7), 31.6 (+, C-3 or C-7), 47.9 (+, C-1), 62.6 (−, C-2), 215.9 (+, CO_{ax}), 227.1 (+, CO_{eq}). − MS-FAB: *m/z* (%) = 388 (10) [M^+], 304 (56) [M^+ − 3CO], 276 (44) [M^+ − 4CO], 225 (60) [M^+ − 4CO − Cr + 1]. $C_{18}H_{28}CrN_2O_4$ (388.43): calcd. C 55.66, H 7.27, N 7.21; found C 53.67, H 7.57, N 6.99.

***rac*-(*trans*-1,2-Diaminocyclohexane)tetracarbonylchromium(0) [*rac*-10]:** Procedure 4; hexacarbonylchromium(0) (2.4 g, 10.9 mmol) and 20 mL of a mixture of *cis*- and *trans*-1,2-diaminocyclohexane (*cis/trans* = 1:3.5) were heated at 120 °C for 18 h in the dark. Crystallization (20 mL of ethanol, 100 mL of water) gave 2.73 g (9.81 mmol, 90%) of *rac*-**10** as a yellow powder (m.p. 165 °C, dec.). − IR (KBr): $\tilde{\nu}$ = 3356 cm^{-1} (m, amine), 3300 (m, amine), 2932 (m), 2860 (w), 2004 (m, CO), 1876 (s, CO), 1848 (s, CO), 1784 (s, CO), 1592 (m), 1024 (m), 700 (w), 672 (m), 644 (m). − ^{1}H NMR (200.1 MHz, [D_6]acetone): δ = 1.10−1.79 [m, 8 H, 3(6)-H, 4(5)-H], 2.74−3.09 (br, 4 H, amine), 3.42 [m, 2 H, 1(2)-H]. − ^{13}C NMR (50.3 MHz, [D_6]acetone, APT): δ = 25.5 [+, C-4(5)], 35.8 [+, C-3(6)], 59.4 [−, C-1(2)], 216.9 (+, CO_{ax}), 228.1 (+, CO_{eq}). − MS-FAB: *m/z* (%) = 278 (11) [M^+], 250 (3) [M^+ − CO], 222 (4) [M^+ − 2CO], 207 (4), 194 (5) [M^+ − 3CO], 167 (5), 166 (6) [M^+ − 4CO], 165 (5), 152 (9), 150 (6) [M^+ − 4CO − NH_2], 149 (9), 136 (68) [$Cr(CO)_3{}^+$], 108 (19) [$Cr(CO)_2{}^+$]. − $C_{10}H_{14}CrN_2O_4$ (278.23): calcd. C 43.17, H 5.07, N 10.07; found C 43.15, H 5.09, N 8.78.

(1*R*,2*R*)-(*trans*-1,2-Diaminocyclohexane)tetracarbonylchromium(0) [(1*R*,2*R*)-10]: Procedure 5; (1*R*,2*R*-)-*trans*-1,2-diaminocyclohexane (200 mg, 1.75 mmol) and **6** (446 mg, 1.74 mmol) in THF (30 mL) were heated at reflux for 30 min. Crystallization (15 mL of ethanol, 50 mL of water) gave 481 mg (1.73 mmol, 99%) of (1*R*,2*R*)-**10** as a yellow powder. − $[\alpha]_D^{20}$ = +34 (*c* = 0.5, acetone).

***rac*-(1,2-Diaminopropane)tetracarbonylchromium(0) (*rac*-11):**[49] Procedure 4; hexacarbonylchromium(0) (1.7 g, 7.7 mmol) and *rac*-1,2-diaminopropane (15 mL, 180 mmol) were heated at 120 °C for 14 h in the dark. Crystallization (20 mL of ethanol, 50 mL of water) gave 1.81 g (7.6 mmol, 98%) of *rac*-**11**, yellow powder (m.p. 195 °C, dec.). − IR (KBr): $\tilde{\nu}$ = 3372 cm^{-1} (m, amine), 3352 (m, amine), 3316 (m, amine), 3296 (m, amine), 2980 (w), 2940 (w), 2880 (w), 2012 (m, CO), 1916 (s, CO), 1868 (s, CO), 1844 (s, CO), 1772 (s, CO), 1592 (m), 1460 (m), 1136 (m), 1048 (m), 1016 (m), 700 (w), 676 (m), 644 (m). − ^{1}H NMR (200.1 MHz, [D_6]acetone): δ = 1.22 (d, 3 H, 3-H), 2.58−3.04 (br, 4 H, amine), 3.32 (br, 2 H, 1-H), 3.48 (br, 1 H, 2-H). − ^{13}C NMR (50.3 MHz, [D_6]acetone, APT): δ = 19.7 (−, C-3), 50.4 (+, C-1), 52.3 (−, C-2), 216.71 (+, CO_{ax}), 216.77 (+, CO_{ax}), 227.78 (+, CO_{eq}), 227.88 (+, CO_{eq}). − MS-FAB: *m/z* (%) = 238 (15) [M^+], 210 (10) [M^+ − CO], 154 (22) [M^+ − 3CO]. − $C_7H_{10}CrN_2O_4$ (238.16): calcd. C 35.30, H 4.23, N 11.76; found C 35.52, H 4.48, N 10.38.

***rac*-(1,3-Diaminopentane)tetracarbonylchromium(0) (*rac*-12):** Procedure 4; hexacarbonylchromium(0) (2.2 g, 10.0 mmol) and *rac*-1,3-diaminopentane (5 mL, 125.0 mmol) were heated at 120 °C for 15 h in the dark. Crystallization (20 mL of ethanol, 70 mL of water) gave 2.61 g (9.8 mmol, 98%) of *rac*-**12** as a yellow powder (m.p. 213 °C, dec.). − IR (KBr): $\tilde{\nu}$ = 3408 cm^{-1} (m, amine), 3344 (m, amine), 3300 (m, amine), 3280 (m, amine), 2936 (m), 2884 (m), 2004 (s, CO), 1908 (s, CO), 1858 (s, CO), 1846 (s, CO), 1792 (s, CO), 1588 (m), 1464 (m), 1152 (m), 1068 (m), 1016 (m), 700 (w), 660 (m), 640 (m), 460 (m). − ^{1}H NMR (200.1 MHz, [D_6]acetone): δ = 0.91 (t, $^{3}J_{5\text{-}4}$ = 7.8 Hz, 3 H, 5-H), 1.06−1.89 (m, br, 4 H, 2-H, 4-H), 2.34−2.78 (br, 4 H, amine), 2.88−3.19 (br, 2 H, 1-H), 3.19−3.38 (br, 1 H, 3-H). − ^{13}C NMR (50.3 MHz, [D_6]acetone, APT): δ = 10.0 (−, C-5), 33.6 (+, C-4), 34.4 (+, C-2), 47.4 (+, C-1), 60.2 (−, C-3), 216.0 (+, CO_{ax}), 216.9 (+, CO_{ax}), 225.9 (+, CO_{eq}), 226.3 (+, CO_{eq}). − MS (70 eV, 130 °C): *m/z* (%) = 267 (2) [M^+ + 1], 266 (3) [M^+], 238 (2) [M^+ − CO], 210 (4) [M^+ − 2CO], 182 (2) [M^+ − 3CO], 155 (4), 154 (15) [M^+ − 4CO], 145 (5), 121 (7), 108 (5), 86 (7), 85 (100) [amine − NH_3], 73 (38). − $C_9H_{14}CrN_2O_4$ (266.21): calcd. C 40.61, H 5.30, N 10.51; found C 40.88, H 5.44, N 9.92.

Tetracarbonyl{[(*S*)-2-cyclohexylaminomethyl]pyrrolidine}chromium(0) [(*S*)-13]: Procedure 5; (*S*)-aminocyclohexylmethyl)pyrrolidine[52] (213 mg, 1.17 mmol) and **11** (300 mg, 1.17 mmol) in THF (50 mL) were heated at reflux for 30 min. Column chromatography (SiO_2 diethyl ether/petroleum ether 1:2 → 1:0, length 35 cm, ø 3.5 cm) and solvent removal gave 350 mg (1.01 mmol, 87%) of (*S*)-**13** as a yellow solid (m.p. 138 °C, dec.). − IR (KBr): $\tilde{\nu}$ = 3296 cm^{-1} (m, amine), 3272 (w, amine), 2924 (m), 2852 (m), 2004 (m, CO), 1892 (s, CO), 1848 (s, CO), 1808 (s, CO), 1788 (s, CO), 1452 (m), 1260 (w), 1076 (w), 1016 (w), 940 (w), 804 (w), 696 (w), 656 (m), 636 (w), 456 (w). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 0.86−2.10 (m, 14 H, 2-H, 3-H, 7-H, 8-H, 9. H, 10-H, 11-H), 2.31 (m, 1 H, 6-H), 2.64−2.88 (m, 3 H, 1-H, 4-H), 3.28−3.41 (m, 2 H, 5-H), 3.80 (br, 1 H, amine), 4.55 (br, 1 H, amine). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT): δ = 24.9 (CH$_2$, C-9), 25.2 (CH$_2$, C-8 or C-10), 25.5 (CH$_2$, C-8 or C-10), 27.1 (CH$_2$, C-7 or C-11), 27.4 (CH$_2$, C-7 or C-11), 31.0 (CH$_2$, C-3), 31.2 (CH$_2$, C-2), 53.9 (CH, C-4), 55.5 (CH, C-5), 59.6 (CH, C-6), 62.2 (CH, C-1), 214.4 (C$_q$, CO$_{ax}$), 216.6 (C$_q$, CO$_{ax}$), 226.5 (C$_q$, CO$_{eq}$), 227.6 (C$_q$, CO$_{eq}$). − MS (70 eV, 220 °C): *m/z* (%) = 346 (2) [M$^+$], 262 (1) [M$^+$ − 3CO], 235 (14), 234 (40) [M$^+$ − 4CO], 149 (15), 112 (24), 98 (6), 83 (11), 70 (100) [C$_4$H$_8$N$^+$]. − MS-FAB: *m/z* (%) = 346 (35) [M$^+$], 290 (33) [M$^+$ − 2CO], 262 (94) [M$^+$ − 3CO], 234 (36) [M$^+$ − 4CO]. − HRMS ($C_{15}H_{22}CrN_2O_4$): calcd. 346.098467; found 346.098694. − $C_{15}H_{22}CrN_2O_4$ (346.34): calcd. C 52.02, H 6.40, N 8.09; found C 52.60, H 6.71, N 7.46. − $[\alpha]_D^{20} = +10$ (*c* = 0.1, acetone).

(*S*)-2-Butylaminomethyl)pyrrolidine: (*S*)-2-(Butylaminocarbonyl)-5-oxopyrrolidine[51] (2.71 g, 14.73 mmol) in THF (35 mL) was added dropwise over 5 h to a cold (0 °C) suspension of lithium aluminium hydride (1.52 g, 40 mmol) in THF (40 mL). After complete addition the mixture was heated at reflux for 3 h. After cooling to 0 °C excess lithium aluminium hydride was carefully hydrolyzed by addition of a saturated aqueous solution of sodium sulfate. The mixture was extracted 12 times with diethyl ether (each 50 mL), and the collected organic layers were dried over MgSO$_4$. After filtration and solvent removal at reduced pressure the crude product was purified by fractional distillation at 0.05 mbar to give 1.65 g (10.58 mmol, 72%) of (*S*)-2-butylaminomethyl)pyrrolidine as a clear, light- and air-sensitive liquid (b.p. 46 °C, 0.05 mbar). − IR (cap. film): $\tilde{\nu}$ = 3296 cm^{-1} (br, m, amine), 2956 (s), 2928 (s), 2868 (s), 2816 (m), 1600 (w), 1556 (m), 1456 (s), 1404 (s), 1372 (s), 1328 (s), 1132 (m), 812 (m). − ^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 0.91 (t, $^3J_{8\text{-}9}$ = 7.2 Hz, 3 H, 9-H), 1.32−1.91 (m, 8 H, 2-H, 3-H, 7-H, 8-H), 1.55 (br, 2 H, amine), 2.50−2.61 (m, 4 H, 4-H, 6-H), 2.86−2.94 (m, 2 H, 5-H), 3.2 (m, 1 H, 1-H). − ^{13}C NMR (100.6 MHz, CDCl$_3$, APT): δ = 14.6 (−, C-9), 21.1 (+, C-8), 26.3 (+, C-2 or C-3 or C-7), 30.4 (+, C-2 or C-3 or C-7), 32.9 (+, C-2 or C-3 or C-7), 47.13 (+, C-6), 50.6 (+, C-4), 56.1 (+, C-5), 59.0 (−, C-1). − MS (70 eV, 20 °C): *m/z* (%) = 157 (3) [M$^+$ + 1], 156 (3) [M$^+$], 113 (8), 88 (9), 87 (9), 86 (89), 85 (15), 84 (15), 71 (40), 70 (100) [C$_4$H$_8$N$^+$]. − HRMS ($C_9H_{20}N_2$): calcd. 156.162649; found 156.162354. − $[\alpha]_D^{20} = +124.7$ (*c* = 0.43, acetone).

[((*S*)-2-Butylaminomethyl)pyrrolidine]tetracarbonylchromium(0) [(*S*)-14]: Procedure 5; (*S*)-2-butylaminomethyl)pyrrolidine (0.73 g, 4.68 mmol) and **6** (1.118 g, 4.61 mmol) in THF (50 mL) were heated at reflux for 60 min. Column chromatography (SiO$_2$, diethyl ether/petroleum ether 1:2 → 1:0, length 35 cm, ø 3.5 cm) and solvent removal gave 1.40 g (4.38 mmol, 95%) of (*S*)-**14**, yellow solid (m.p. 113 °C, dec.). − IR (KBr): $\tilde{\nu}$ = 3412 cm^{-1} (m, amine), 3304 (m, amine), 2956 (m), 2928 (m), 2872 (m), 2000 (s, CO), 1916 (s, CO), 1868 (s, CO), 1836 (s, CO), 1804 (s, CO), 1772 (s, CO), 1616 (w), 1456 (m), 1376 (w), 1124 (w), 1076 (w), 1032 (w), 916 (w), 656 (m), 636 (m). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 0.92 (t, $^3J_{8\text{-}9}$ = 7.2 Hz, 3 H, 9-H), 1.19−2.10 (m, 9 H), 2.62−3.13 (m, 4 H), 3.24−3.41 (m, 2 H), 3.87 (br, 1 H, amine), 4.48 (br, 1 H, amine). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 12.9 (−, C-9), 19.5 (+, C-8), 26.65 (+, C-2 or C-3 or C-7), 26.66 (+, C-2 or C-3 or C-7), 30.3 (+, C-2 or C-3 or C-7), 54.9 (+, C-6), 55.1 (+, C-4), 56.7 (+, C-5), 60.5 (−, C-1), 214.2 (+, CO$_{ax}$), 215.9 (+, CO$_{ax}$), 225.9 (+, CO$_{eq}$), 227.3 (+, CO$_{eq}$). − MS (70 eV, 170 °C): *m/z* (%) = 209 (2), 208 (8) [M$^+$ − 4CO], 135 (2), 123 (3), 86 (11), 70 (100) [C$_4$H$_8$N$^+$], 52 (3) [^{52}Cr$^+$]. − HRMS ($C_9H_{20}CrN_2$): calcd. 208.103159; found 208.102539 − $[\alpha]_D^{20} = -108$ (*c* = 0.5, acetone).

Diazadiene(*S,S,S,S*)-16: A 30% aqueous solution of glyoxal (10.67 mL, 50.0 mmol) was added dropwise at 0 °C to a stirred solution of (+)-(4*S*,5*S*)-5-amino-2,2-dimethyl-4-phenyl-1,3-dioxane [(*S,S*)-**15**][53] (20.7 g, 100.0 mmol) in methanol (50 mL). After complete addition the mixture was warmed to 20 °C and stirred at this temperature for 2 h with formation of a beige suspension. The precipitate was isolated by filtration and washed three times with cold methanol (25 mL each) and then dried at 0.01 mbar. Partial solvent evaporation from the mother liquor caused more product to precipitate. Overall 21.45 g (49.4 mmol, 99%) of (*S,S,S,S*)-**16** was isolated as a colorless powder (m.p. 208 °C, dec.). − IR (CHCl$_3$): $\tilde{\nu}$ = 3064 cm^{-1} (w), 2996 (s), 2944 (m), 2872 (m), 1624 (m, imine), 1496 (w), 1452 (m), 1380 (s), 1268 (s), 1236 (s), 1196 (s), 1168 (s), 1124 (s), 1088 (s), 1056 (m, C−O), 1028 (m, C−O), 980 (m), 956 (m), 888 (m), 848 (s), 568 (m), 528 (m). − ^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 1.58 (s, 6 H, 6-H or 7-H), 1.60 (s, 6 H, 7-H or 6-H), 3.31 (ddd, $^3J_{2\text{-}5}$ = 2.1 Hz, $^3J_{2\text{-}5}$ = 2.8 Hz, $^3J_{2\text{-}3}$ = 2.4 Hz, 2 H, 2-H), 3.78 (dd, $^3J_{5\text{-}2}$ = 2.1 Hz, $^2J_{5\text{-}5}$ = 12.1 Hz, 2 H, 5-H), 4.34 (dd, $^3J_{5\text{-}2}$ = 2.8 Hz, $^2J_{5\text{-}5}$ = 12.1 Hz, 2 H, 5-H), 5.23 (d, $^3J_{3\text{-}2}$ = 2.4 Hz, 2 H, 3-H), 7.08−7.22 (m, 10 H, 9-H, 10-H, 11-H, 12-H, 13-H), 7.45 (s, 2 H, 1-H). − ^{13}C NMR (100.6 MHz, CDCl$_3$, DEPT): δ = 19.9 (CH$_3$, C-6 or C-7), 29.8 (CH$_3$, C-7 or C-6), 65.7 (CH$_2$, C-5), 68.3 (CH, C-2), 74.2 (CH, C-3), 100.2 (C$_q$, C-4), 126.8 [CH, C-10(12)], 127.9 (CH, C-11), 128.6 [CH, C-9(13)], 138.8 (C$_q$, C-8), 164.0 (CH, C-1). − MS (70 eV, 150 °C): *m/z* (%) = 438 (1) [M$^+$ + 2], 437 (4) [M$^+$ + 1], 436 (11) [M$^+$], 421 (6) [M$^+$ − CH$_3$], 378 (2) [M$^+$ − (CH$_3$)$_2$CO], 348 (4) [M$^+$ − (CH$_3$)$_2$COOCH$_2$], 301 (19), 300 (96) [M$^+$ − (CH$_3$)$_2$CO − C$_6$H$_6$], 299 (6), 273 (21), 272 (98) [M$^+$ − (CH$_3$)$_2$COOCH$_2$ − C$_6$H$_6$], 183 (8), 136 (14), 134 (8), 133 (31), 130 (9), 115 (8), 109 (18), 108 (100) [C$_6$H$_5$CH$_2$OH$^+$], 107 (77), 105 (43), 103 (17), 95 (7), 91 (19) [C$_6$H$_5$CH$_2$$^+$], 82 (19), 81 (15), 77 (25) [C$_6$H$_5$$^+$]. − HRMS ($C_{26}H_{32}N_2O_4$): calcd. 436.236208; found 436.234406. − $C_{26}H_{32}N_2O_4$ (436.55): calcd. C 71.54, H 7.39, N 6.42; found C 71.45, H 7.34, N 6.37. − $[\alpha]_D^{20} = +112.6$ (*c* = 1, acetone).

Diamine (*S,S,S,S*)-17: All operations were performed under argon in the dark. Sodium tetrahydridoborate (0.44 g, 12.0 mmol) was added to a stirred solution of (*S,S,S,S*)-**16** (2.18 g, 5.0 mmol) in anhydrous methanol (25 mL) at −8 °C. After complete addition the mixture was heated at 50 °C for 3 h. The solvent was then removed at reduced pressure, and the residue was taken up with water (50 mL). The aqueous layer was extracted four times with TBME (each 50 mL), the collected organic layers were dried over sodium sulfate, and after filtration the solvent was removed at reduced pressure to give 2.2 g (5.0 mmol, 100%) of (*S,S,S,S*)-**17** as a colorless oil. − IR (CHCl$_3$): $\tilde{\nu}$ = 3312 cm^{-1} (w, amine), 3064 (w), 2996 (s), 2940 (m), 2868 (m), 1496 (m), 1448 (m), 1380 (s), 1264 (m), 1232 (s), 1196 (s), 1168 (m), 1148 (m), 1072 (s), 1028 (m), 984 (m), 844 (s). − ^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 1.49 (s, 6 H, 6-H or 7-H), 1.51 (s, 6 H, 7-H or 6-H), 1.93 (m, 2 H, 1-H), 2.0 (s, br, 2 H, amine), 2.35 (m, 2 H, 1-H), 2.52 (m, 2 H, 2-H), 3.81 (dd, $^3J_{5\text{-}2}$ = 2.0 Hz, $^2J_{5\text{-}5}$ = 12.0 Hz, 2 H, 5-H), 3.99 (dd, $^3J_{5\text{-}2}$ = 2.0 Hz, $^2J_{5\text{-}5}$ = 12.0 Hz, 2 H, 5-H), 5.04 (d, $^3J_{3\text{-}2}$ = 2.0 Hz, 2 H, 3-H), 7.22−7.36 (m, 10 H, 9-H, 10-H, 11-H, 12-H, 13-H). − ^{13}C NMR (100.6 MHz, CDCl$_3$, DEPT): δ = 18.8 (CH$_3$, C-6 or C-7), 29.6 (CH$_3$, C-7 or C-6), 47.5 (CH$_2$, C-1), 55.2 (CH, C-2), 63.6 (CH$_2$, C-5), 73.4 (CH, C-3), 99.1 (C$_q$, C-4), 125.9 (CH, C-11), 127.1 [CH, C-10(12)], 128.0 [CH, C-9(13)], 139.7 ($\mathrm{C_q}$, C-8). − MS (70 eV, 100 °C): *m*/*z* (%) = 440 (3) [$\mathrm{M^+}$], 425 (29) [$\mathrm{M^+ - CH_3}$], 382 (3) [$\mathrm{M^+ - (CH_3)_2CO}$], 367 (4), 293 (31), 277 (29), 261 (7), 233 (16), 220 (100), 208 (11), 176 (8), 162 (37), 144 (21), 132 (74), 117 (26), 108 (13) [$\mathrm{C_6H_5CH_2OH^+}$], 97 (64), 91 (30) [$\mathrm{C_6H_5CH_2^+}$], 84 (25), 77 (12) [$\mathrm{C_6H_5^+}$], 69 (33). − HRMS ($\mathrm{C_{26}H_{36}N_2O_4}$): calcd. 440.267508; found 440.263519. − $[\alpha]^{20}_{\mathrm{D}}$ = +70.8 (*c* = 0.6, THF).

Diamine Complex (*S,S,S,S*)-18: Procedure 5; compound (*S,S,S,S*)-**17** (200 mg, 0.45 mmol) and **6** (110 mg, 0.43 mmol) in THF (50 mL) were heated at reflux for 45 min. Column chromatography ($\mathrm{SiO_2}$, TBME /petroleum ether 1:3 → 1:1, length 35 cm, ø 2.5 cm) and solvent removal gave 198 mg (0.33 mmol, 76%) of (*S,S,S,S*)-**18** as a yellow, air-sensitive solid (m.p. 103 °C, dec.). − IR (KBr): $\tilde{\nu}$ = 3264 $\mathrm{cm^{-1}}$ (m, amine), 3006 (w), 2992 (m), 2944 (m), 2876 (w), 2004 (s, CO), 1864 (s, CO), 1824 (s, CO), 1496 (w), 1472 (m), 1448 (m), 1244 (m), 1204 (s), 1096 (m), 952 (m), 856 (m), 740 (m), 700 (m). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.41 (s, 6 H, 6-H or 7-H), 1.57 (s, 6 H, 7-H or 6-H), 3.0 (s, br, 2 H, amine), 3.15 (m, 2 H, 1-H), 3.28 (m, 2 H, 1-H), 3.29 (m, 2 H, 2-H), 4.20 (d, $^2J_{5\text{-}5}$ = 13.4 Hz, 2 H, 5-H), 4.46 (dd, $^3J_{5\text{-}2}$ = 2.1 Hz, $^2J_{5\text{-}5}$ = 13.4 Hz, 2 H, 5-H), 5.49 (d, $^3J_{3\text{-}2}$ = 2.7 Hz, 2 H, 3-H), 7.42−7.50 (m, 10 H, 9-H, 10-H, 11-H, 12-H, 13-H). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 17.9 (−, C-6 or C-7), 26.3 (−, C-7 or C-6), 49.7 (+, C-1), 56.6 (−, C-2), 59.1 (+, C-5), 73.2 (−, C-3), 98.9 (+, C-4), 124.9 [−, C-10(12)], 128.0 (−, C-11), 129.2 [−, C-9(13)], 137.7 (+, C-8), 214.5 (+, $\mathrm{CO_{ax}}$), 225.6 (+, $\mathrm{CO_{eq}}$). − MS (70 eV, 140 °C): *m*/*z* (%) = 493 (7) [$\mathrm{M^+ - 4CO + 1}$], 492 (16) [$\mathrm{M^+ - 4CO}$], 426 (10), 425 (25), 382 (4), 367 (6), 337 (5), 293 (28), 277 (34), 261 (8), 233 (16), 220 (100), 208 (9), 176 (6), 163 (32), 144 (15), 132 (58), 117 (16), 97 (43), 91 (22) [$\mathrm{C_6H_5CH_2^+}$], 84 (20), 77 (10) [$\mathrm{C_6H_5^+}$], 69 (17), 52 (6) [$\mathrm{^{52}Cr}$]. − MS-FAB: *m*/*z* (%) = 492 (94) [$\mathrm{M^+ - 4CO}$]. − HRMS ($\mathrm{C_{26}H_{36}N_2O_4Cr}$): calcd. 492.208018; found 492.206757. − $\mathrm{C_{30}H_{36}CrN_2O_8}$ (604.62): calcd. C 59.60, H 6.00, N 4.63; found C 57.86, H 6.11, N 4.49. − $[\alpha]^{20}_{\mathrm{D}}$ = +91.6 (*c* = 0.225, acetone).

Tetracarbonyl{(*R*)-1-[5-chloro-2-(methylamino)phenyl]-1,2,3,4-tetrahydroisoquinoline}chromium(0) (*R*)-20: Procedure 5; (*R*)-1-[5-chloro-2-(methylamino)phenyl]-1,2,3,4-tetrahydroisoquinoline tartrate [(*R*)-**19**, Aldrich] (348 mg, 1.0 mmol), compound **6** (230 mg, 0.9 mmol), and triethylamine (2 mL, 1.45 g, 14.0 mmol) in THF (50 mL) were heated at reflux for 2 h. Column chromatography ($\mathrm{SiO_2}$, TBME/petroleum ether 1:1 → 1:0, length 40 cm, ø 2.5 cm) and solvent removal gave 263 mg (0.6 mmol, 67%) of (*R*)-**20** as an orange, air-sensitive solid (m.p. 85 °C, dec.). − IR (KBr): $\tilde{\nu}$ = 3298 $\mathrm{cm^{-1}}$ (w, amine), 3260 (w, amine), 3004 (w), 2976 (w), 2928 (w), 2012 (m, CO), 1980 (m, CO), 1896 (s, CO), 1872 (s, CO), 1828 (s, CO), 1488 (m), 1228 (m), 1076 (w), 896 (w). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 2.45−3.29 (m, 9 H, 2-H, 3-H, 16-H, amine), 5.15 (s, br, 1 H, 1-H), 6.38−7.42 (m, 7 H, 5-H, 6-H, 7-H, 8-H, 11-H, 13-H, 14-H). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone, APT): δ = 27.8 (+, C-3), 40.0 (−, C-16), 46.8 (+, C-2), 54.2 (−, C-1), 114.9 (−, C-14), 125.8 (−, C-5 or C-6 or C-7 or C-8 or C-11 or C-13), 127.0 (+, C-4 or C-9 or C-10 or C-12), 127.5 (−, C-5 or C-6 or C-7 or C-8 or C-11 or C-13), 127.7 (−, C-5 or C-6 or C-7 or C-8 or C-11 or C-13), 128.9 (−, C-5 or C-6 or C-7 or C-8 or C-11 or C-13), 129.3 (−, C-5 or C-6 or C-7 or C-8 or C-11 or C-13), 129.9 (−, C-5 or C-6 or C-7 or C-8 or C-11 or C-13), 133.26 (+, C-4 or C-9 or C-10 or C-12), 133.28 (+, C-4 or C-9 or C-10 or C-12), 135.0 (+, C-4 or C-9 or C-10 or C-12), 213.0 (+, $\mathrm{CO_{ax}}$), 213.6 (+, $\mathrm{CO_{ax}}$), 226.0 (+, $\mathrm{CO_{eq}}$), 226.7 (+, $\mathrm{CO_{eq}}$). − MS-FAB: *m*/*z* (%) = 438 (19) [$\mathrm{M^+}$], 410 (11) [$\mathrm{M^+ - CO}$], 354 (100) [$\mathrm{M^+ - 3CO}$], 326 (62) [$\mathrm{M^+ - 4CO}$], 274 (40) [$\mathrm{M^+ - 4CO - {}^{52}Cr}$]. − $\mathrm{C_{20}H_{17}ClCrN_2O_4}$ (436.81): calcd. C 54.99, H 3.92, N 6.41; found C 55.26, H 4.49, N 6.10. − $[\alpha]^{20}_{\mathrm{D}}$ = −152.0 (*c* = 0.1, acetone).

[(*R*)-2,2′-Diamino-1,1′binaphthyl]tetracarbonylchromium [(*R*)-21]: Procedure 5; (*R*)-2,2′-diamino-1,1′binaphthyl [(*R*)-DABN, Aldrich] (750 mg, 2.64 mmol) and compound **6** (650 mg, 2.5 mmol) were heated at reflux for 2 h. Column chromatography ($\mathrm{SiO_2}$, TBME/petroleum ether 1:5 → 1:2, length 30 cm, ø 3.5 cm) and solvent removal gave 79 mg (1.77 mmol, 70%) of (*R*)-**21**, yellow, very air-sensitive solid (m.p. 83 °C, dec.). − IR (KBr): $\tilde{\nu}$ = 3380 $\mathrm{cm^{-1}}$ (s, br, amine), 3052 (m), 2960 (m), 2064 (w), 1980 (m, CO), 1932 (s, CO), 1888 (s, CO), 1820 (m, CO), 1620 (s), 1508 (m), 1472 (w), 1432 (w), 1380 (m), 1348 (w), 1096 (m), 1024 (m), 816 (s). − ^{1}H NMR (400.1 MHz, [D$_6$]benzene): δ = 3.07 (s, br, 4 H, amine), 6.67−7.72 (m, 12 H, 3-H, 4-H, 6-H, 7-H, 8-H, 9-H). − ^{13}C NMR (100.6 MHz, [D$_6$]benzene, APT): δ = 113.3 (+, C-5) 119.1 (−, C-3), 123.3 (−, C-4 or C-6 or C-7 or C-8 or C-9), 125.3 (−, C-4 or C-6 or C-7 or C-8 or C-9), 127.9 (−, C-4 or C-6 or C-7 or C-8 or C-9), 129.2 (−, C-4 or C-6 or C-7 or C-8 or C-9), 129.6 (+, C-1 or C-10), 130.2 (−, C-4 or C-6 or C-7 or C-8 or C-9), 135.2 (+, C-1 or C-10), 144.0 (+, C-2), 217.0 (+, $\mathrm{CO_{ax}}$), 233.5 (+, $\mathrm{CO_{eq}}$). − MS-FAB: *m*/*z* (%) = 448 (10) [$\mathrm{M^+}$], 420 (9) [$\mathrm{M^+ - CO}$], 364 (22) [$\mathrm{M^+ - 3CO}$], 336 (59) [$\mathrm{M^+ - 4CO}$], 284 (100) [$\mathrm{M^+ - 4CO - Cr}$]. − $[\alpha]^{20}_{\mathrm{D}}$ = +97.4 (*c* = 1, THF).

Tetracarbonyl[L-methionine methyl ester]chromium(0) [(*R*)-22]: Triethylamine (1.9 mL, 13.5 mmol) was added to hexacarbonylchromium(0) (700 mg, 3.18 mmol) and L-methionine methyl ester hydrochloride (450 mg, 2.25 mmol) in THF (50 mL). The mixture was heated at reflux for 40 h, the color changing from colorless to yellow and then orange. Column chromatography ($\mathrm{SiO_2}$, diethyl ether/petroleum ether 1:2 → 1:0, length 30 cm, ø 3.5 cm) and solvent removal gave 362 mg (1.10 mmol, 49%) of (*R*)-**22** as an orange, crystalline solid (m.p. 141 °C, dec.). − IR (KBr): $\tilde{\nu}$ = 3348 $\mathrm{cm^{-1}}$ (m, amine), 3288 (m, amine), 2956 (w), 2920 (w), 2068 (w), 2008 (s, CO), 1872 (s, CO), 1832 (s, CO), 1724 (s, ester), 1652 (m), 1608 (m), 1256 (m), 1229 (m), 1084 (m), 1032 (m), 584 (m), 456 (m). − ^{1}H NMR (200.1 MHz, [D$_6$]acetone): δ = 2.44 (s, 3 H, 4-H), 2.66−2.85 (m, 4 H, 2-H, 3-H), 3.12−3.46 (m, 3 H, 1-H, amine), 3.64 (s, 3 H, 6-H). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT): δ = 22.4 ($\mathrm{CH_3}$, C-4), 27.7 ($\mathrm{CH_2}$, C-3), 36.3 ($\mathrm{CH_2}$, C-2), 51.5 ($\mathrm{CH_3}$, C-6), 59.2 (CH, C-1), 173.0 ($\mathrm{C_q}$, C-5), 215.3 ($\mathrm{C_q}$, $\mathrm{CO_{ax}}$), 215.9 ($\mathrm{C_q}$, $\mathrm{CO_{ax}}$), 224.6 ($\mathrm{C_q}$, $\mathrm{CO_{eq}}$), 225.1 ($\mathrm{C_q}$, $\mathrm{CO_{eq}}$). − MS (70 eV, 160 °C): *m*/*z* (%) = 327 (1) [$\mathrm{M^+}$], 326 (4) [$\mathrm{M^+ - 1}$], 298 (2) [$\mathrm{M^+ - 1 - CO}$], 243 (5) [$\mathrm{M^+ - 3CO}$], 221 (16), 220 (33), 215 (21) [$\mathrm{M^+ - 4CO}$], 192 (11), 164 (13) [$\mathrm{Cr(CO_4)^+}$], 163 (38) [$\mathrm{M^+ - Cr - 4CO}$], 146 (20), 132 (10) [$\mathrm{M^+ - Cr - 4CO - OCH_3}$], 131 (36), 115 (41), 108 (37) [$\mathrm{Cr(CO_2)^+}$], 103 (55) [$\mathrm{M^+ - Cr - 4CO - CO_2CH_3 - H}$], 80 (51) [$\mathrm{CrCO^+}$], 61 (100) [$\mathrm{CH_3SCH_2^+}$], 52 (57) [$\mathrm{^{52}Cr^+}$]. − MS-FAB: *m*/*z* (%) = 327 (24) [$\mathrm{M^+}$], 311 (13) [$\mathrm{M^+ - NH_2}$], 299 (14) [$\mathrm{M^+ - CO}$], 271 (2) [$\mathrm{M^+ - 2CO}$], 243 (41) [$\mathrm{M^+ - 3CO}$], 215 (14) [$\mathrm{M^+ - 4CO}$]. − HRMS ($\mathrm{C_{10}H_{13}CrNO_6S}$): calcd. 326.986869; found 326.986542. − $\mathrm{C_{10}H_{13}CrNO_6S}$ (326.99): calcd. C 36.70, H 4.00; found C 36.44, H 4.05. − $[\alpha]^{20}_{\mathrm{D}}$ = −5.4 (*c* = 0.5, acetone).

Procedure for the Complexation of Arenes with Chelating Diamine Tetracarbonylchromium(0) Complexes: The diamine tetracarbonylchromium(0) chelate complex (1 equiv.) and the arene (2 equiv.) were suspended or dissolved in the solvent (see Table 1) and stirred in the dark. Boron trifluoride−diethyl ether adduct (8 equiv.) was added dropwise, and the mixture was heated at the temperature given in Table 1 until no more diamine tetracarbonylchromium(0) complex could be detected by TLC (12−24 h). The reaction progress was indicated by a color change from orange-red to yellow. The mixture was cooled to 0 °C, and excess boron trifluoride−diethyl ether adduct was hydrolyzed with water. After extraction of the aqueous layer with diethyl ether the collected organic layers were dried over $MgSO_4$. The crude product was purified by column chromatography, and *de* was determined by NMR spectroscopy. Results are summarized in Table 1.

Procedure for the Complexation of Arenes with Tetracarbonyl(L-methionine methyl ester)chromium(0) [(*S*)-22]: A suspension of (*S*)-**22** (1 equiv.) and the arene (2 equiv.) in the appropriate solvent (see Table 1) was stirred in the dark. Boron trifluoride−diethyl ether adduct (6 equiv.) was added dropwise, and the mixture was heated at the temperature given in Table 1, until no more (*S*)-**22** was detected by TLC (10−20 h). The mixture was then cooled to 0 °C, and the excess boron trifluoride−diethyl ether adduct was hydrolyzed with water. After extraction of the aqueous layer with diethyl ether the collected organic layers were dried over $MgSO_4$. The crude product was purified by column chromatography, and *de* determined by NMR spectroscopy. Results are summarized in Table 1.

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