Enantiomerically Pure Axially Chiral Aminocarbene Complexes of Chromium

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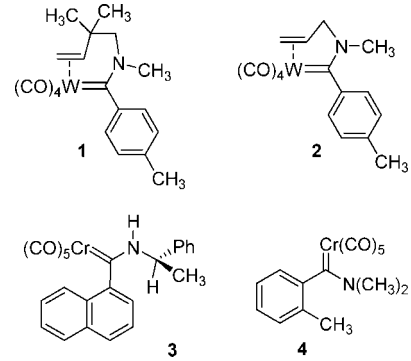
Aminocarbene complexes having a methyl group in the *ortho*-position to the aminocarbene moiety on the aromatic ring, (*S*)-pentacarbonyl[(*N,N*-dimethylamino)(3-methoxycarbonyl-2-methylphenyl)carbene]chromium(0) [**(*S*)-6**] and (*R*)-pentacarbonyl[(*N,N*-dimethylamino)(5-methoxycarbonyl-2-methylphenyl)carbene]chromium(0) [**(*R*)-7**], were prepared in enantiomerically pure form by the crystallization of diastereoisomeric esters with (*S*)-1-(1-naphthyl)ethanol. In the case of **(*S*)-6** the racemization barrier $\Delta G^{\ddagger}_{rac} = 121 \pm 0.5$ kJ·mol^{-1} was established. The substitution of *o*-methyl group with an isopropyl group virtually did not change the racemization barrier ($\Delta G^{\ddagger}_{rac} = 120.5 \pm 0.5$ kJ·mol^{-1}), while the introduction of an *o*-phenyl group led to substantial lowering of $\Delta G^{\ddagger}_{rac}$. Attempts to transfer chirality in thermal reactions of the complexes **(*S*)-6** and **(*R*)-7** with alkynes, palladium-catalyzed insertion into a C−H bond, and photochemical formation of β-lactams were unsuccessful.

Introduction

The rotation of an aromatic ring in alkoxy(aryl)- and amino(aryl)carbene complexes is hindered and the aromatic ring prefers to adopt the orthogonal orientation to the metal−carbene π-plane in the solid state.[1] In the case of chromium and tungsten aminocarbene complexes the predominantly orthogonal orientation of the aromatic ring was also proved in solution.[2] Casey found the energy barriers $\Delta G^{\ddagger}_{298}$ to the tolyl group rotation in tungsten carbene complexes **1** and **2** to be 17.0 kcal·mol^{-1} (71.1 kJ·mol^{-1}) and 11.5 kcal·mol^{-1} (48.1 kJ·mol^{-1}), respectively.[4] As a result of the hindered rotation, the complexes with a suitably substituted aromatic ring are axially chiral. E. O. Fischer observed this phenomenon already in 1976,[3] when he prepared chromium 1-naphthylaminocarbene complex **3** bearing an (*R*)-(+)-1-phenylethylamino group as a mixture of diastereoisomers. By repeated crystallizations he obtained a mixture of diastereoisomers with the "*E*" configuration on the carbene C−N bond enriched by one diastereoisomer to an 83:17 ratio. No attempts to establish the absolute configuration on the chiral axis of this compound were made at that time.

The existence of the rotational barrier was explained by steric reasons[4] or by the π-interaction of the aromatic ring with the carbene carbon atom.[5] We have recently shown that the rotational barrier in phenyl-substituted aminocarbene complexes of chromium is due to a balance between both steric and conjugation effects. Conjugation stabilizes the planar transition state during the rotation, but steric repulsion forces the phenyl ring out of the plane.[6] Therefore, electron-donating groups lower and electron-withdrawing groups raise the rotational barrier of the aryl ring in aryl-substituted aminocarbene complexes of chromium. We have also observed that the introduction of an *o*-methyl group on the benzene ring raises the rotational barrier substantially. This encouraged us to attempt the preparation of enantiomerically pure, axially chiral carbene complexes, in which the hindered rotation of the aromatic ring bound to the carbene carbon atom is the only source of chirality. Herein, we wish to report our results.



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(1) (a) For review see: Schubert, U. *Coord. Chem. Rev.* **1984**, *55*, 261. (b) $(CO)_5Cr{=}C(Ph)OCH_3$: Mills, O. S.; Redhouse, A. D *J. Chem. Soc. A* **1968**, 642. (c) $(CO)_5Cr{=}C(Ph)N(CH_3)_2$: Wang, C.-C.; Wang, Y.; Liu, H.-J.; Lin, K.-J.; Chou, L.-K.; Chan, K.-S *J. Phys. Chem. A* **1997**, *101*, 8887.
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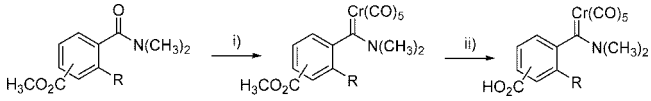
Scheme 1. Preparation of the *o*-Substituted Aminocarbene Complexes Bearing a Methoxycarbonyl Group, 5−8, and the Corresponding Carboxylic Acids 9−12[a]



[a] Reagents and conditions: (i) 1. $Na_2Cr(CO)_5$, THF; 2. $(CH_3)_3SiCl$. (ii) 1. NaOH, H_2O; 2. H_3PO_4.

Results and Discussion

Initially, the feasibility of the enantiomeric separation was tested on the simple chromium aminocarbene complex **4** by analytical HPLC on a Chiralcel OD-H column. The separation was successful, giving two peaks with retention times of 14.2 and 14.9 min (see the Experimental Section). For the chiral resolution on a preparative scale we chose to start with complexes functionalized by the methoxycarbonyl group, which can be readily hydrolyzed to free carboxylic acid and is stable under the conditions of carbene complex preparation from amides using Hegedus methodology ($Cr(CO)_5^{2-}/(CH_3)_3SiCl$).[7a–c] Four *o*-substituted aminocarbene complexes bearing a methoxycarbonyl group, **5**−**8**, and the corresponding carboxylic acids **9**−**12** were chosen as suitable candidates for the separation of enantiomers (Scheme 1, Table 1).

The chirality of esters **5**−**7** can be seen by the splitting of their ^1H NMR signals in the presence of $Eu(hfc)_3$. Whereas in the NMR spectrum of complex **5** only the $O-CH_3$ signal was split, complex **6** showed separate pairs of $Ph-CH_3$, $O-CH_3$, and both $N-CH_3$ signals. The NMR spectrum of complex **7** exhibited separation of $Ph-CH_3$, $O-CH_3$, and *Z* $N-CH_3$ signals. The chiral shift reagent $Eu(hfc)_3$ probably interacts with the carbonyl oxygen of the ester group and therefore can affect substituents close to the ester group, such as *ortho* and *meta* carbene moieties. Another method for the visualization of chirality, small-scale enantiomeric separation on a Chiralcel OD-H column, was successful for compounds **5** and **6** (9:1 hexane/2-propanol as mobile phase). Unfortunately, enantiomers of **7** and **8** proved to be inseparable by chromatography (chiral columns OD-H, AD, and OP were ineffective; only very slight separation was achieved with Chiralcel OJ with 4:1 hexane/2-propanol at 0.5 $mL \cdot min^{-1}$ for both compounds).

Although NMR spectra of acids **9**−**11** did not show any splitting of lines in the presence of $Eu(hfc)_3$, chiral analytical HPLC on the Chiralcel OD-H column separated enantiomers of **10** and **11** and partially also enantiomers of **9**. A large difference between retention times of enantiomers of **11** in analytical mode (Figure 1) enabled even injection of 20 mg (!) of racemic compound on a 250 × 4.6 mm column. This preparative resolution also enabled the determination of the racemization barrier of compound **11** by measuring the dependence of the ee on the time at elevated temperature. The estimated value of $\Delta G^{\ddagger}_{rac}$ is 113 ± 3 $kJ \cdot mol^{-1}$.

All attempts at resolving carboxylic acids **9**−**12** to single enantiomers by chiral amines were fruitless. Utilization of (*R*)-1-phenylethylamine, (*S*)-1,1′-binaphthyl-2,2′-diamine, (1*R*,2*R*)-diaminocyclohexane, (−)-ephedrine, cinchonidine, and brucine resulted in formation of viscous oils, which were extremely soluble in organic solvents and difficult to crystallize. Crystallization of(*R*)-1-phenylethylamine salts from acetone or 1-chlorobutane[8] (superior solvent for this crystallization) gave crystals with no enantiomeric enrichment at all.

To achieve the preparative resolution of the prepared compounds, we turned our attention back to methyl esters **5**−**7**. The stability of the carbene moiety in alkaline medium allowed the preparation of diastereoisomeric esters by the base-catalyzed transesterification of **5**−**7** with chiral alcohols. The transesterifications were conducted with (−)-menthol, 1-phenylethanol, and (*S*)-1-(1-naphthyl)ethanol at elevated temperature *in vacuo* using an excess of the chiral alcohol as a solvent. Whereas diastereoisomeric 1-phenylethyl esters were separable by preparative HPLC, (−)-menthyl esters were virtually inseparable. The best separation of individual diastereoisomers from their mixture was provided by the crystallization of (*S*)-1-(1-naphthyl)ethyl esters. Double crystallization of the (*S*)-1-(1-naphthyl)ethyl esters **13** and **14** from a mixture of THF, 2-propanol, and hexane gave pure diastereomers **(*S,S*)-13** and **(*R,S*)-14** (Scheme 2). The configurations on the chiral axes were assigned by single-crystal X-ray diffraction analyses (*S* in **(*S,S*)-13** and *R* in **(*R,S*)-14**; Figure 2). The selected bond distances and angles (Table 2) correspond with literature parameters of the chromium carbene complexes.[1c]

Transesterification of the single diastereomers **(*S,S*)-13** and **(*R,S*)-14** with methanol then provided the desired pure enantiomers **(*S*)-6** and **(*R*)-7** in good yield with optical purities of 98% and ≥95% ee (Figure 3, Scheme 2). The preparative resolution of **6** to enantiomers and their separability by chiral HPLC on an analytical scale also made possible the determination of the racemization barrier of compound **6**. From the dependence of the ee on the time at 90 °C in heptane the racemization half-life of 6.5 h and the racemization barrier of $\Delta G^{\ddagger}_{rac} = 121 \pm 0.5$ $kJ \cdot mol^{-1}$ were obtained.

Probably due to the steric demand of the carbene moiety, the transesterification reaction of 2-methoxycarbonylphenyl carbene complex **5** with (*S*)-1-(1-naphthyl)ethanol under the conditions analogous to the reactions of **6** and **7** did not proceed at all. Increased reaction temperature led only to decomposition of the starting material. An attempt to prepare the 1-(1-naphthyl)ethyl ester of *N,N*-dimethylphthalamic acid first was also not successful. In this case the conversion of mono-1-(1-naphthyl)ethyl phthalate to *N,N*-dimethylphthalamide failed.

With single enantiomers of methyl esters **(*S*)-6** and **(*R*)-7** in hand we tried to convert them to enantiomerically pure carboxylic acids **(*S*)-10** and **(*R*)-11**. Unfortunately, slow racemization during alkaline hydrolysis at 50 °C was observed. Together with complete retention of chirality during transesterification reactions this observation indicates slight lowering of the racemization barrier of carboxylates $\mathbf{10}^-$ and $\mathbf{11}^-$ in comparison with ester **6** and acid **11**. Such lowering of the rotational barrier can be rationally explained by the replacement of the carboxymethyl group with a more electron-releasing carboxylate anion.[6]

To explore the influence of the bulkiness of the substituent in *ortho* position to the carbene moiety on the racemization barrier, the *o*-phenyl (**15**) and *o*-isopropyl (**16**) complexes were prepared. However, we were not able to separate the enantiomers of carbene complex **16** using chiral HPLC. Therefore, the complex **17**, bearing a methoxycarbonyl group, was also prepared.

Small amounts of optically pure enantiomers of **15** for racemization experiments were obtained using preparative

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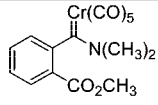
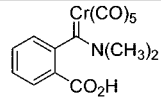
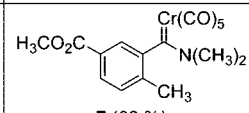
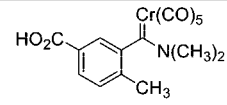
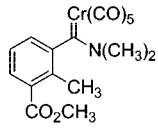
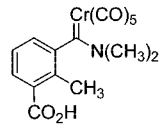
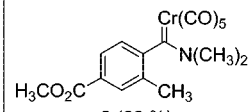
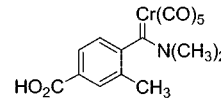
(10) Crystallographic data have been deposited with CCDC no. 649994, 649995, and 649996 for **(*S,S*)-13**, **(*R,S*)-14**, and **(*R,S*)-18**, respectively, and can be obtained free of charge from Cambridge Crystallographic Data Centre viawww.ccdc.cam.ac.uk/data_request/cif.

Table 1. Aminocarbene Complexes Bearing a Methoxycarbonyl Group and the Corresponding Carboxylic Acids Prepared According to Scheme 1

Carbene complex (Yield)	Carboxylic acid (Yield)	Carbene complex (Yield)	Carboxylic acid (Yield)
 **5** (36 %)	 **9** (96 %)	 **7** (68 %)	 **11** (94 %)
 **6** (64 %)	 **10** (91 %)	 **8** (60 %)	 **12** (85 %)

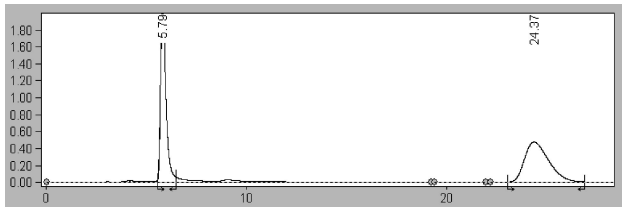
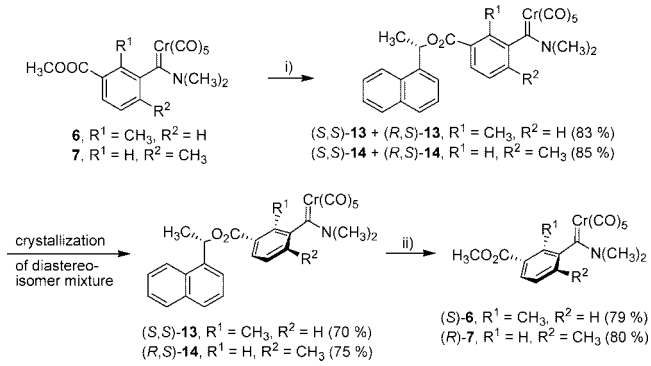


Figure 1. Chromatogram of racemic **11** (Chiralcel OD-H, 250 × 4.6 mm, mobile phase 0.5% acetic acid 4:1 hexane/2-propanol, flow rate 1 mL·min^{-1}, detection at 254 nm).

Scheme 2. Resolution of the Aminocarbene Complexes 6 and 7[a]



[a] Reagents and conditions: (i) (*S*)-1-(1-naphthyl)ethanol (7.7 equiv), Na (0.5 equiv); (ii) CH_3OH, Na (0.5 equiv).

HPLC. Pure **(*R*)-17** was obtained by the same methodology as was used for the preparation of **(R)-7** (Scheme 3). Also in this case the pure (*R*,*S*)-diastereoisomer was obtained by crystallization. Its structure was confirmed by X-ray analysis (Figure 2).

Carbene complex **15** fully racemized in heptane solution at 90 °C within several hours, showing that the racemization barrier of 2-phenyl complex **15** is much lower than that of 2-methyl complex **6**. On the other hand, the rate of racemization of 2-isopropylderivative **17** [$k_{rac} = 3.48 \times 10^{-5}$ s^{-1} and $\Delta G^{\ddagger}_{rac} = 120.5 \pm 0.5$ kJ·mol^{-1}] under the same conditions was approximately the same as in the case of 2-methylderivative **6**. The fact that the racemization barriers of the complexes **6** and **17** are virtually the same may point out that the rotation of the $N(CH_3)_2$ group out of the carbene ligand π-plane is involved in the racemization process.[11] The observed values of racemization barriers are in accordance with Fischer's value of at least 25 kcal·mol^{-1} for the rotation about the carbenecarbon−nitrogen bond in $(CO)_5Cr{=}C[N(CH_3)_2]CH_3$.[12] Similarly, Casey reported slow *E/Z*-isomerization of $(CO)_5W{=}C(4\text{-}CH_3C_6H_4)(NHCH_2CH{=}CH_2)$ at 80 °C.[13] It should also be pointed out that the *E/Z*-isomerization barrier in $(CO)_5Cr{=}C(2\text{-}CH_3C_6H_4)(NHCH_2CH{=}CH_2)$ is significantly higher in comparison with $(CO)_5Cr{=}C(C_6H_5)(NHCH_2CH{=}CH_2)$, suggesting that both processes—aryl ring rotation and *E/Z*-isomerization barrier—are dependent (note 16 in ref 6).

Figure 4 presents the CD spectra of resolved axially chiral complexes **(*S*)-6**, **(*R*)-7**, and **(*R*)-17** in dichloromethane. Generally, the spectra display intense dichroic absorption bands in the range 225–300 nm, while the CD activity in the region 325–425 nm is much lower. For **(*S*)-6**, **(*R*)-7**, and **(*R*)-17**, the same signs of the exciton couplets (230 nm, positive/250 nm, negative) correspond to the identical mutual position of methylcarboxylate and carbene functional groups. Furthermore, both **(*R*)-7** and **(*R*)-17** show negative Cotton effects (270–280 nm), whereas **(*S*)-6** has a positive Cotton effect in the same region.

We also examined the possibility of synthetic utilization of the obtained axially chiral carbene complexes. However, all attempts on chirality transfer of complexes **6** and **7** in previously described thermal reactions with alkynes,[14] palladium-catalyzed insertion into the C−H bond,[15] and photochemical reaction with imines[16] have failed.

Conclusions

The introduction of a methyl or isopropyl group to the *o*-position of chromium amino(phenyl)carbene complexes increases the rotational barrier of the aromatic ring to such an

(11) Preliminary *ab initio* calculations showed that both possibilities—passing of methyl around the $N(CH_3)_2$ group and around the $Cr(CO)_5$ group—are energetically comparable. Moreover, during the rotation the whole carbene substituent significantly lost its planarity and the plane of $N(CH_3)_2$ group became almost perpendicular to that of the carbene functionality. However, the IRC analysis of such transition states failed. Meca, L. Unpublished results.

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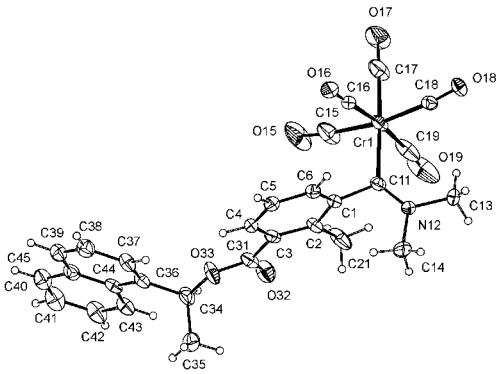
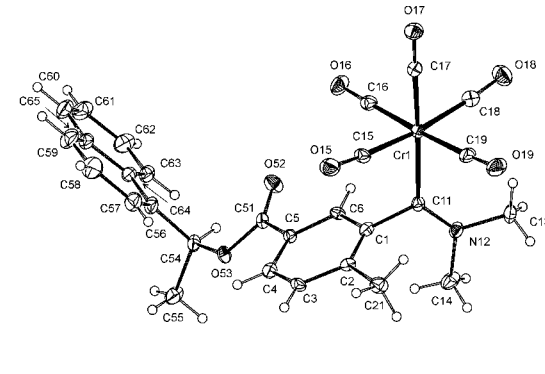
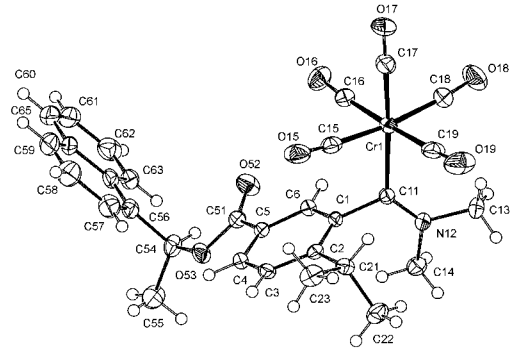


(*S,S*)-13



(*R,S*)-14

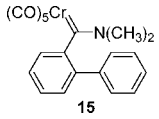


(*R,S*)-18

Figure 2. Overall view of **(*S,S*)-13**, **(*R,S*)-14**, and **(*R,S*)-18**. The displacement ellipsoids are drawn at the 50% probability level.[9,10]

Table 2. Selected Bond Lengths [Å] and Angles [deg] for (*S,S*)-13, (*R,S*)-14, and (*R,S*)-18

	(*S,S*)-13	(*R,S*)-14	(*R,S*)-18
Cr(1)−C(15)	1.894 (4)	1.924 (6)	1.913 (3)
Cr(1)−C(16)	1.882 (4)	1.924 (6)	1.901 (3)
Cr(1)−C(17)	1.867 (5)	1.864 (6)	1.863 (2)
Cr(1)−C(18)	1.888 (3)	1.886 (7)	1.907 (3)
Cr(1)−C(19)	1.888 (5)	1.900 (7)	1.901 (3)
Cr(1)−C(11)	2.128 (3)	2.137 (6)	2.142 (2)
C(11)−C(1)	1.500 (4)	1.504 (8)	1.508 (3)
C(11)−N(12)	1.302 (4)	1.324 (7)	1.301 (3)
Cr(1)−C(11)−C(1)	114.6 (2)	115.9 (4)	116.0 (2)
Cr(1)−C(11)−N(12)	130.5 (2)	130.7 (4)	130.8 (2)
C(11)−N(12)−C(13)	123.5 (3)	123.7 (5)	123.4 (2)
C(11)−N(12)−C(14)	124.3 (3)	124.5 (5)	126.2 (2)



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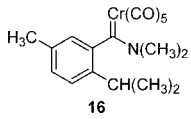

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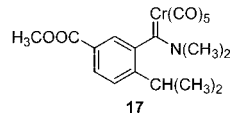

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extent that these complexes are axially chiral and can be resolved to enantiomers. The determined values of $\Delta G^{\ddagger}_{rac}$ for these complexes range from 113 to 121 kJ·mol^{-1} for acid **11** and esters **6** and **17**, whereas the rotational barrier of *o*-phenyl-derivative **15** is much lower.

Experimental Section

Melting points were determined on a Kofler block and are uncorrected. NMR spectra were measured on either a Varian Gemini 300 or a Bruker DRX 500 Avance spectrometer at 25 °C. Unambiguous assignment of NMR signals is based on $^{13}C\{^1H\}$, ^{13}C APT, COSY, and ^{13}C HMBC spectra. Infrared spectra were recorded on a Nicolet 740 instrument. UV–vis spectra were recorded on a Perkin-Elmer Lambda 25 spectrometer. CD spectra were recorded on a Jasco J-715 spectropolarimeter. Elemental analyses were carried out with a Perkin-Elmer 2400 instrument. Optical rotations were measured on an Autopol III automatic polarimeter (Rudolph Research, NJ). All experiments were carried out under argon. Tetrahydrofuran was distilled from benzophenone ketyl under Ar prior to use. (*S*)-1-(1-Naphthyl)ethanol, chromium hexacarbonyl, and chlorotrimethylsilane were purchased from commercial suppliers and were used without purification. Neutral aluminum oxide (Brockmann grade II−III) and silica gel were obtained from Merck. Unless stated otherwise, products were used in the crude state without further purification.

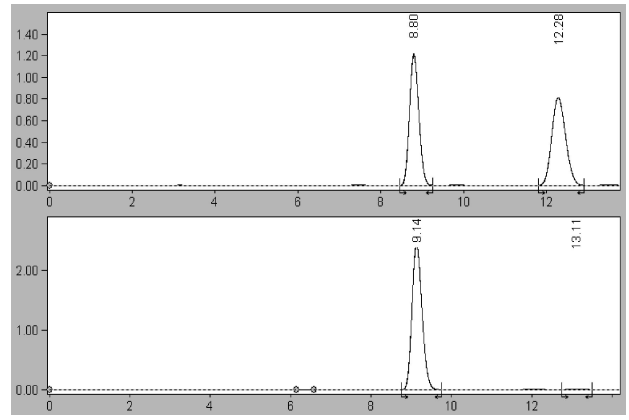
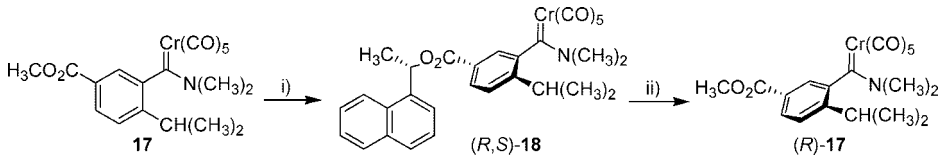


Figure 3. Chromatograms of racemic **6** and its pure enantiomer **(*S*)-6** (Chiralcel OD-H, 250 × 4.6 mm, mobile phase 9:1 hexane/2-propanol, flow rate 1 mL·min^{-1}, detection at 254 nm).

Crystal Structures. The yellow crystals of compounds **(*S,S*)-13**, **(R,S)-14**, and **(*R,S*)-18** were mounted on a glass fiber with epoxy cement and measured on a KappaCCD four-circle diffractometer with CCD area detector at 150(2) K, Mo Kα radiation.

Scheme 3. Resolution of the Aminocarbene Complex 17[a]



[a] Reagents and conditions: (i) 1. (*S*)-1-(1-naphthyl)ethanol (4.6 equiv), Na (0.9 equiv); 2. Crystallization of diastereoisomer a mixture, 68%. (ii) CH_3OH, Na (2 equiv), 69%.

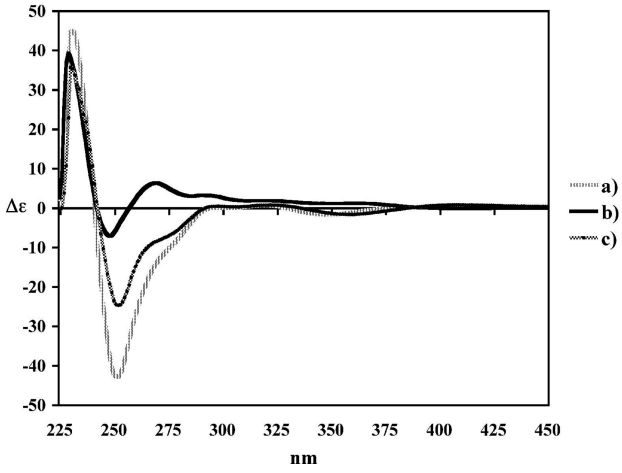


Figure 4. CD spectra of (a) **(*R*)-7**, (b) **(*S*)-6**, and (c) **(*R*)-17**.

The solutions were done with direct methods,[17] refinements were done by full-matrix least-squares based on F^2,[18] and the absorption was neglected. The hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $U_{iso}(H) = 1.2–1.5U_{eq}$(pivot atom).

The crystal of **(*R,S*)-18** was nonmerohedral twinned with volume ratio of the two parts of 0.926:0.074; the contribution of the second part was included in the refinement (twin matrix for *hkl* indices −1 0 0; 0 −1 0; 0.284 0 1). Two symmetrically independent molecules in the unit cell of **(*R,S*)-18** have almost identical geometry; maximal distance between atoms of molecules fitted one upon the other is 0.25 Å. Crystal data and results of structure refinement are summarized in Table 3.

Pentacarbonyl[(*N,N*-dimethylamino)(2-methylphenyl)methylene]chromium(0) (4). The same method as was used for the preparation of **6** starting from *N,N*,2-trimethylbenzamide (0.82 g, 5 mmol) furnished **4** (0.93 g, 55%) as yellow crystals. For elution of the product a hexane/dichloromethane mixture (3:1) was used instead of pure dichloromethane. Mp: >91 °C (methanol; dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.07 (s, 3H; Ph-C H_3), 3.04 (s, 3H; N−C H_3), 4.01 (s, 3H; N−C H_3), 6.71 (d, J = 7.7 Hz, 1H; Ph−*H*), 7.05−7.17 (m, 2H; Ph−*H*), 7.22 (t, J = 7.4 Hz, 1H; Ph−*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 276.5 (C═Cr), 223.2 (CO), 216.8 (CO), 151.6 (C−Ph), 130.6 (CH−Ph), 126.1 (CH−Ph), 126.0 (CH−Ph), 125.4 (C−Ph), 119.5 (CH−Ph), 51.0 (CH_3−N), 45.2 (CH_3−N), 18.8 (CH_3−Ph). IR ($CHCl_3$): ν 2055, 1972, 1930, 1533, 1400 cm^{-1}. Anal. Calcd (%) for $C_{15}H_{13}CrNO_5$: C 53.10, H 3.86, N 4.13. Found: C 53.37, H 3.94, N 4.11. The small-scale enantiomeric separation was performed using a Chiralcel OD-H column (250 × 4.6 mm, solvent 10% 2-propanol in hexane, flow 0.5 mL·min^{-1}, detection UV 254 nm). Under these conditions the separation gave two signals with retention times of 14.2 and 14.9 min.

Pentacarbonyl[(*N,N*-dimethylamino)(3-methoxycarbonyl-2-methylphenyl)carbene]chromium(0) (6). To a suspension of chromium hexacarbonyl (1.32 g, 6 mmol) in THF (30 mL) was added a solution of sodium naphthalenide prepared from sodium (0.36 g, 16 mmol) and naphthalene (2.04 g, 16 mmol) in THF (30 mL) at −78 °C via syringe. The reaction mixture was then allowed to warm to 0 °C, stirred at this temperature for 30 min, and cooled to −78 °C. Then 3-methoxycarbonyl-*N,N*,2-trimethylbenzamide (1.11 g, 5 mmol) in THF (5 mL) was added via syringe. The solution was allowed to warm to 0 °C, stirred for 30 min at 0 °C, and then cooled to −78 °C, and trimethylchlorosilane (1.5 mL, 12 mmol) was added via syringe. The solution was stirred at −78 °C for 30 min, then the cooling bath was removed, the mixture was stirred for additional 1 h without cooling, and neutral alumina (5 g) was added. THF was removed under reduced pressure, and the residue was dried under high vacuum to remove all solvents. Hexane (8 mL) was then added, and the suspension formed was transferred on the top of a column filled with silica gel (50 g). Naphthalene was eluted with hexane, and further elution with dichloromethane gave **6** as yellow crystals (1.27 g, 64%). Mp: 110 °C (methanol; dec). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.27 (s, 3H; Ph−C H_3), 3.05 (s, 3H; N−C H_3), 3.89 (s, 3H; O−C H_3), 4.03 (s, 3H; N−C H_3), 6.83 (d, J = 7.2 Hz, 1H; Ph−*H*), 7.30 (t, J = 7.7 Hz, 1H; Ph−*H*), 7.70 (d, J = 7.2 Hz, 1H; Ph−*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 276.2 (C═Cr), 223.0 (CO), 216.5 (CO), 167.7 (C═O), 152.6 (C−Ph), 131.1 (C−Ph), 128.2 (CH−Ph), 127.3 (C−Ph), 125.9 (CH−Ph), 123.3 (CH−Ph), 52.1 (CH_3−O), 51.2 (CH_3−N), 45.5 (CH_3−N), 17.3 (CH_3−Ph). ^{1}H NMR using Eu(hfc)$_3$ showed splitting of Ph−CH_3, O−CH_3, and both N−CH_3 signals. IR ($CHCl_3$): ν 2056, 1976, 1932, 1720, 1533, 1286 cm^{-1}. Anal. Calcd (%) for $C_{17}H_{15}CrNO_7$: C 51.39, H 3.81, N 3.53. Found: C 51.58, H 3.65, N 3.39. The small-scale enantiomeric separation was performed using a Chiralcel OD-H column (250 × 4.6 mm, solvent 10% 2-propanol in hexane, flow 1 mL·min^{-1}, detection UV 254 nm); the retention times were t_S = 8.8 and t_R = 12.3 min.

Pentacarbonyl[(*N,N*-dimethylamino)-(3-carboxy-2-methylphenyl)carbene]chromium(0) (10). Methyl ester **6** (199 mg; 0.5 mmol), powdered KOH (112 mg; 2 mmol), water (5 mL), THF (5 mL), and methanol (2 mL) were stirred under argon at 50 °C for 5 h (starting compound quantitatively disappeared during that time). Volatile solvents were then evaporated under vacuum, and nonacidic impurities were extracted with CH_2Cl_2. The pH of the mixture was adjusted to 1−2 with diluted H_3PO_4, and the product was extracted with diethyl ether. Extracts were dried over Na_2SO_4 and evaporated to afford **10** as yellow solid (174 mg; 91%). Mp: >110 °C (dec). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 2.20 (s, 3H; Ph−C H_3), 3.05 (s, 3H; N−C H_3), 3.99 (s, 3H; N−C H_3), 6.88 (d, J = 6.5 Hz, 1H; Ph−*H*), 7.36 (s, 1H; Ph−*H*), 7.61 (d, J = 6.5 Hz, 1H; Ph−*H*). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 266.5 (C═Cr), 223.6 (CO), 216.9 (CO), 168.8 (C═O), 152.7 (C−Ph), 132.3 (C−Ph), 127.7 (CH−Ph), 126.5 (C−Ph), 125.9 (CH−Ph), 122.9 (CH−Ph), 51.2 (CH_3−N), 45.6 (CH_3−N), 16.7 (CH_3−Ph). IR ($CHCl_3$): ν 3693, 2056, 1978, 1931, 1726, 1535, 1270 cm^{-1}. Anal. Calcd (%) for $C_{16}H_{13}CrNO_7$: C 50.14, H 3.42, N 3.65. Found: C 49.49, H 3.41, N 3.33. The small-scale enantiomeric separation was performed on a Chiralcel OD-H column (250 × 4.6 mm, solvent 0.5% acetic acid and

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(18) Sheldrick, G. M. *SHELXL97* University of Göttingen: Germany, 1997.

Table 3. Crystallographic Data and Results of Structure Refinement

	(*S,S*)-13	**(*R,S*)-14**	**(*R,S*)-18**
formula	$C_{28}H_{23}CrNO_7$	$C_{28}H_{23}CrNO_7$	$C_{30}H_{27}CrNO_7$
cryst syst	orthorhombic	orthorhombic	monoclinic
apace group [No.]	$P2_12_12_1$ [No. 19]	$P2_12_12$ [No. 18]	$P2_1$ [No. 4]
a [Å]	12.6930(2)	11.6900(1)	7.8806(1)
b [Å]	13.0310(2)	31.4720(2)	11.5719(2)
c [Å]	15.8080(3)	7.0070(7)	30.8273(5)
β [deg]			92.0770(9)
Z	4	4	4
V [Å^3]	2614.68(8)	2577.9(3)	2809.40(8)
D_x [g cm^{-3}]	1.365	1.385	1.337
cryst color	light yellow	light yellow	yellow
cryst size [mm]	0.10 × 0.10 × 0.45	0.10 × 0.18 × 0.40	0.10 × 0.25 × 0.40
cryst shape	bar	plate	prism
μ [mm^{-1}]	0.484	0.491	0.454
θ_{max} [deg]	27.5	27.5	27.5
range of h; k; l	−16,16; −16,16; −20,20	−14,15; −40,40; −9,9	−10,10; −15,15; −2,39
no. of measd reflns	41 157	16 390	25 673
no. of indep diffract. (R_{int}[a])	5995 (0.058)	5495 (0.070)	12 526 (0.040)
no. of obsd diffract. [$I > 2\sigma(I)$]	4782	5001	11 399
no. of params	339	338	714
w_1, w_2[b]	0.0820, 0.7917	0.0003, 15.9986	0.0345, 1.1872
absolut struct param (Flack)	0.01(2)	0.12(5)	−0.014(12)
R[c], wR for obsd diffract.	0.0498, 0.1281	0.0821, 0.1829	0.0375, 0.0835
R, wR for all data	0.0678, 0.1414	0.0904, 0.1877	0.0450, 0.0885
GOF[d]	1.02	1.10	1.05
residual electron density [e/Å^3]	−0.42, 0.83	−0.67, 0.85	−0.33, 0.28

[a] $R_{int} = \sum|F_o^2 - F_{o,mean}^2|/\sum F_o^2$. [b] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$. [c] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{1/2}$. [d] GOF $= [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$.

20% 2-propanol in hexane, flow 1 mL·min^{-1}, detection UV 254 nm); the retention times were $t_S = 6.7$ and $t_R = 10.3$ min.

Pentacarbonyl[(*N,N*-dimethylamino)(3-(*S*)-1′-(1-naphthyl)ethoxycarbonyl-2-methylphenyl)carbene]chromium(0) (13). (*S*)-1-(1-Naphthyl)ethanol (2.00 g, 11.6 mmol) and Na (18 mg, 0.78 mmol) were stirred under argon at 100 °C. After sodium has dissolved, finely powdered **6** (0.60 g, 1.51 mmol) was added at 70 °C. The light brown solution was stirred for 30 min at 70 °C and diminished pressure (1.5 kPa). The cold reaction mixture was dissolved in CH_2Cl_2 (2 mL) and subjected to column chromatography on silica gel (70 g). Elution with a hexane/dichloromethane mixture (1:1) provided **13** (0.67 g, 83%) as a yellow foam. Further elution with CH_2Cl_2 gave (*S*)-1-(1-naphthyl)ethanol (1.75 g), which was reused for the preparation of the next batch of the product. ^{1}H and ^{13}C NMR spectra showed the presence of **(*S,S*)-13** and **(*R,S*)-13** in equimolar amounts.

(*S*)-Pentacarbonyl[(*N,N*-dimethylamino)(3-(*S*)-1′-(1-naphthyl)ethoxycarbonyl-2-methylphenyl)carbene]chromium(0) ((*S,S*)-13). The above diastereomer mixture of **13** (0.6 g) was dissolved in hot THF (1 mL), then 2-propanol (0.5 mL) and hexane (5 mL) were added. After standing in a freezer for 2 h, crystals were filtered and washed with cold 2-propanol. Repeating of the crystallization procedure gave **(*S,S*)-13** as yellow crystals (0.21 g; 70%). ^{1}H NMR analysis of the mother liquor from the first crystallization revealed approximately 90% de of **(*R,S*)-13**. **(*S,S*)-13**: Mp >150 °C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.85 (d, $J = 6.6$ Hz, 3H; CH−CH_3), 2.24 (s, 3H; Ph−CH_3), 3.03 (s, 3H; N−CH_3), 4.01 (s, 3H; N−CH_3), 6.83 (d, $J = 6.9$ Hz, 1H; Ph−*H*), 6.88 (q, $J = 6.6$ Hz, 1H; C*H*−CH$_3$), 7.33 (t, $J = 7.7$ Hz, 1H; Ph−*H*), 7.45−7.59 (m, 3H; Np−*H*), 7.66 (d, $J = 6.9$ Hz, 1H; Ph−*H*), 7.76−7.91 (m, 3H; Np−*H*), 8.15 (d, $J = 8.3$ Hz, 1H; Np−*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 276.1 (C═Cr), 223.0 (CO), 216.5 (CO), 166.6 (C═O), 152.5 (C−Ph), 137.1 (C−Ar), 133.7 (C−Ar), 131.6 (C−Ar), 130.0 (C−Ar), 128.8 (CH−Ar), 128.4 (CH−Ar), 128.0 (CH−Ar), 127.1 (C−Ar), 126.3 (CH−Ar), 125.9 (CH−Ar), 125.6 (CH−Ar), 125.3 (CH−Ar), 123.2 (CH−Ar), 123.0 (CH−Ar), 122.9 (CH−Ar), 70.3 (CH−O), 51.1 (CH$_3$−N), 45.5 (CH$_3$−N), 22.0 (CH$_3$−C), 17.2 (CH$_3$−Ph). IR ($CHCl_3$): ν 2056, 1976, 1932, 1717 cm^{-1}. Anal. Calcd (%) for $C_{28}H_{23}CrNO_7$: C 62.57, H 4.31, N 2.61. Found: C 62.08, H 4.37, N, 2.53. **(*R,S*)-13** (approximately 90% de): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.86 (d, $J = 6.6$ Hz, 3H; CH−CH_3), 2.30 (s, 3H; Ph−CH_3), 3.00 (s, 3H; N−CH_3), 4.01 (s, 3H; N−CH_3), 6.83 (d, $J = 6.9$ Hz, 1H; Ph−*H*), 6.88 (q, $J = 6.6$ Hz, 1H; C*H*−CH$_3$), 7.31 (t, $J = 7.7$ Hz, 1H; Ph−*H*), 7.45−7.59 (m, 3H; Np−*H*), 7.68 (d, $J = 6.9$ Hz, 1H; Ph−*H*), 7.76−7.91 (m, 3H; Np−*H*), 8.20 (d, $J = 8.5$ Hz, 1H; Np−*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 276.0 (C═Cr), 223.0 (CO), 216.5 (CO), 166.4 (C═O), 152.6 (C−Ph), 137.3 (C−Ar), 133.7 (C−Ar), 131.3 (C−Ar), 130.0 (C−Ar), 128.8 (CH−Ar), 128.4 (CH−Ar), 128.2 (CH−Ar), 127.4 (C−Ar), 126.3 (CH−Ar), 125.9 (CH−Ar), 125.6 (CH−Ar), 125.3 (CH−Ar), 123.3 (CH−Ar), 123.0 (CH−Ar), 122.9 (CH−Ar), 70.4 (CH−O), 51.1 (CH$_3$−N), 45.5 (CH$_3$−N), 22.1 (CH$_3$−C), 17.3 (CH$_3$−Ph); IR ($CHCl_3$): ν 2056, 1976, 1932, 1717, 1533 cm^{-1}.

(*S*)-Pentacarbonyl[(*N,N*-dimethylamino)(3-methoxycarbonyl-2-methylphenyl)carbene]chromium(0) ((*S*)-6). The ester **(*S,S*)-13** (0.43 g, 0.8 mmol), THF (10 mL), methanol (40 mL), and Na (37 mg; 1.6 mmol) were stirred at 50 °C for 5 h. The light green solution was evaporated and the residue was dissolved in CH_2Cl_2 (1 mL) and subjected to column chromatography on silica gel (60 g). Elution with a hexane/dichloromethane mixture (1:2) provided **(*S*)-6** (0.25 g, 79%) as yellow crystals. Mp: >110 °C (dec). $[\alpha]_D$ +186.6 (c 1.085 in CH_2Cl_2). UV/vis (c 3.5 × 10^{-5} mol·dm^{-3}, CH_2Cl_2): 232 (33100), 357 nm (6200). CD (c 3.5 × 10^{-5} mol·dm^{-3}, CH_2Cl_2): 229 (39.4), 248 (−7.1), 269 (6.4), 319 (1.9), 361 (1.3), 410 nm (−0.1). Anal. Calcd (%) for $C_{17}H_{15}CrNO_7$: C 51.39, H 3.81, N 3.53. Found: C 51.32, H 3.84, N 3.41. Chiral chromatography on a Chiralcel OD-H column (250 × 4.6 mm, solvent 10% 2-propanol in hexane, flow 1 mL·min^{-1}, detection UV 254 nm) gave 98% ee for this product. The racemization barrier was determined in a small test tube connected with a stainless steel valve containing a rubber septum (NMR tube size) on its top. The apparatus was filled with a saturated solution of **(*S*)-6** in heptane under argon and placed in an oil bath at 90 °C. Samples were analyzed on Chiralcel OD-H column to give following results:

time (min)	0	40	85	130
ee (%)	92.7	85.8	79	74

from which $k = 2.98 \times 10^{-5}$ s^{-1} (calculated by the first-order rate equation $k = \sum t_i^{-2} \sum t_i \ln(ee_0/ee_i)$ with the ee_0 at time $t = 0$ and ee_i at t_i, respectively), and $\Delta G^{\ddagger}_{rac} = 121 \pm 0.5$ kJ·mol^{-1}.

Pentacarbonyl[(*N,N*-dimethylamino)(5-methoxycarbonyl-2-methylphenyl)carbene]chromium(0) (7). The same method as was used for the preparation of **6** starting from 5-methoxycarbonyl-*N,N*,2-trimethylbenzamide (1.11 g, 5 mmol) gave **7** as yellow crystals (1.35 g, 68%). Mp: >115 °C (methanol; dec). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.13 (s, 3H; Ph−C*H*$_3$), 3.05 (s, 3H; N−C*H*$_3$), 3.90 (s, 3H; O−C*H*$_3$), 4.03 (s, 3H; N−C*H*$_3$), 7.24 (d, $J = 8.0$ Hz, 1H; Ph−*H*), 7.41 (d, $J = 1.4$ Hz, 1H; Ph−*H*), 7.76 (dd, $J = 8.0$, 1.7 Hz, 1H; Ph−*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 275.8 (C═Cr), 222.9 (CO), 216.5 (CO), 166.4 (C═O), 151.2 (C−Ph), 131.0 (C−Ph), 130.9 (CH−Ph), 128.1 (C−Ph), 127.2 (CH−Ph), 120.9 (CH−Ph), 52.2 (CH_3−O), 51.1 (CH_3−N), 45.4 (CH_3−N), 19.0 (CH_3−Ph). ^{1}H NMR using Eu(hfc)$_3$ showed splitting of Ph−CH_3, O−CH_3, and N−CH_3 (in the position *Z* to chromium at 4.03 ppm) signals. IR ($CHCl_3$): ν 2056, 1976, 1932, 1720, 1605, 1533, 1438, 1299, 1264 cm^{-1}. Anal. Calcd (%) for $C_{17}H_{15}CrNO_7$: C 51.39, H 3.81, N 3.53. Found: C 51.47, H 3.72, N 3.33.

Pentacarbonyl[(*N,N*-dimethylamino)(5-carboxy-2-methylphenyl)carbene]chromium(0) (11). The same method as was used for the preparation of **10** starting from **7** (199 mg; 0.5 mmol) afforded yellow solid **11** (180 mg; 94%). Mp: >110 °C (dec). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 2.10 (s, 3H; Ph−C*H*$_3$), 3.05 (s, 3H; N−C*H*$_3$), 3.97 (s, 3H; N−C*H*$_3$), 7.34 (d, $J = 8.3$ Hz, 1H; Ph−*H*), 7.36 (s, 1H; Ph−*H*), 7.68 (d, $J = 7.7$ Hz, 1H; Ph−*H*). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 265.2 (C═Cr), 223.5 (CO), 216.9 (CO), 166.9 (C═O), 151.2 (C−Ph), 131.1 (C−Ph), 130.9 (CH−Ph), 128.6 (C−Ph), 126.9 (CH−Ph), 120.9 (CH−Ph), 51.1 (CH_3−N), 45.5 (CH_3−N), 18.4 (CH_3−Ph). IR ($CHCl_3$): ν 3693, 2055, 1931, 1886, 1677, 1604, 1539, 1267 cm^{-1}. Anal. Calcd (%) for $C_{16}H_{13}CrNO_7$: C 50.14, H 3.42, N 3.65. Found: C 49.19, H 3.57, N 3.26. The small-scale enantiomeric separation was performed on a Chiralcel OD-H column (250 × 4.6 mm, solvent 0.5% acetic acid and 20% 2-propanol in hexane, flow 1 mL·min^{-1}, detection UV 254 nm); the retention times were $t_R = 6$ min and $t_S = 25$ min). The determination of the racemization barrier was conducted in the same apparatus and under the same conditions as for compound **(*S*)-6**; heptane was substituted by diphenyl ether for solubility reasons. Unfortunately, after 1 h heating of the diphenyl ether solution strong decomposition was observed. Values of 66% ee at 0 min and 32% ee at 30 min then gave an estimation of $k_{rac} = 4 \times 10^{-4}$ s^{-1} and $\Delta G^{\ddagger}_{rac} = 113 \pm 3$ kJ·mol^{-1}.

Pentacarbonyl[(*N,N*-dimethylamino)(5-(*S*)-1′-(1-naphthyl)ethoxycarbonyl-2-methylphenyl)carbene]chromium(0) (14). The same method as was used for the preparation of the mixture of **(*S,S*)-13** + **(*R,S*)-13** starting from **7** (0.60 g, 1.51 mmol) gave **14** (0.67 g, 85%) as a yellow solid. ^{1}H and ^{13}C NMR spectra showed the presence of **(*R,S*)-14** and **(*S,S*)-14** in equimolar amounts.

(*R*)-Pentacarbonyl[(*N,N*-dimethylamino)(5-(*S*)-1′-(1-naphthyl)ethoxycarbonyl-2-methylphenyl)carbene]chromium(0) ((*R,S*)-14). The same method as was used for the preparation of **(*S,S*)-13** starting from **14** (0.6 g) with more THF (2 mL instead of 1 mL) gave **(*R,S*)-14** as yellow crystals (225 mg; 75%). ^{1}H NMR analysis of the mother liquor from the first crystallization revealed approximately 90% de of **(*S,S*)-14**. **(*R,S*)-14**: Mp >140 °C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.82 (d, $J = 6.6$ Hz, 3H; CH−C*H*$_3$), 2.12 (s, 3H; Ph−C*H*$_3$), 3.01 (s, 3H; N−C*H*$_3$), 4.01 (s, 3H; N−C*H*$_3$), 6.88 (q, $J = 6.6$ Hz, 1H; C*H*−CH_3), 7.25 (d, $J = 5.5$ Hz, 1H; Ar−*H*), 7.45−7.59 (m, 4H; Ar−*H*), 7.70 (d, $J = 7.2$ Hz, 1H; Ar−*H*), 7.81−7.92 (m, 3H; Ar−*H*), 8.21 (d, $J = 8.0$ Hz, 1H; Ar−*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 275.8 (C═Cr), 223.3 (CO), 216.8 (CO), 165.4 (C═O), 151.4 (C−Ph), 137.3 (C−Ar), 133.8 (C−Ar), 131.1 (C−Ar), 131.0 (CH−Ar), 130.3 (C−Ar), 128.6 (CH−Ar), 128.5 (C−Ar), 128.3 (CH−Ar), 127.6 (CH−Ar), 126.4 (CH−Ar), 125.7 (CH−Ar), 125.4 (CH−Ar), 123.5 (CH−Ar), 123.3 (CH−Ar), 121.1 (CH−Ar), 70.5 (CH−O), 51.0 (CH_3−N), 45.4 (CH_3−N), 21.8 (CH_3−C), 18.8 (CH_3−Ph). IR ($CHCl_3$): ν 2055, 1932, 1712, 1602 cm^{-1}. Anal. Calcd (%) for $C_{28}H_{23}CrNO_7$: C 62.57, H 4.31, N 2.61. Found: C 62.24, H 4.57, N 2.51. **(*S,S*)-14** (approximately 90% de): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.83 (d, $J = 6.6$ Hz, 3H; CH−C*H*$_3$), 2.13 (s, 3H; Ph−C*H*$_3$), 3.04 (s, 3H; N−C*H*$_3$), 4.03 (s, 3H; N−C*H*$_3$), 6.90 (q, $J = 6.6$ Hz, 1H; C*H*−CH_3), 7.25 (d, $J = 8.0$ Hz, 1H; Ph−*H*), 7.43−7.59 (m, 4H; Ar−*H*), 7.69 (d, $J = 6.9$ Hz, 1H; Ph−*H*), 7.77−7.92 (m, 3H; Ar−*H*), 8.18 (d, $J = 8.5$ Hz, 1H; Ar−*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 275.7 (C═Cr), 223.3 (CO), 216.8 (CO), 165.3 (C═O), 151.3 (C−Ph), 137.7 (C−Ar), 133.7 (C−Ar), 131.2 (C−Ar), 131.0 (CH−Ar), 130.0 (C−Ar), 128.9 (CH−Ar), 128.5 (C−Ar), 128.3 (CH−Ar), 127.5 (CH−Ar), 126.3 (CH−Ar), 125.6 (CH−Ar), 125.4 (CH−Ar), 123.0 (CH−Ar), 121.0 (CH−Ar), 70.2 (CH−O), 51.0 (CH_3−N), 45.4 (CH_3−N), 22.1 (CH_3−C), 18.8 (CH_3−Ph). IR ($CHCl_3$): ν 2055, 1932, 1713 cm^{-1}.

(*R*)-Pentacarbonyl[(*N,N*-dimethylamino)(5-methoxycarbonyl-2-methylphenyl)carbene]chromium(0) ((*R*)-7). The same method as was used for the preparation of **(*S*)-6** starting from **(*R,S*)-14** (199 mg; 0.8 mmol) afforded yellow crystals of **(*R*)-7** (254 mg; 80%). Mp: >115 °C (dec). $[\alpha]_D$ −95.6 (*c* 1.02 in CH_2Cl_2). UV/vis (*c* 2.7×10^{-5} mol·dm^{-3}, CH_2Cl_2): 238 (41900), 356 nm (6800). CD (*c* 2.7×10^{-5} mol·dm^{-3}, CH_2Cl_2): 231 (45.1), 251 (−42.8), 275 (−10.4), 318 (0.7), 348 (−1.7), 405 nm (0.2). Anal. Calcd (%) for $C_{17}H_{15}CrNO_7$: C 51.39, H 3.81, N 3.53. Found: C 51.36, H 3.84, N 3.42. ^{1}H NMR using Eu(hfc)$_3$ gave >95% ee for this product.

Pentacarbonyl[(*N,N*-dimethylamino)(2-methoxycarbonylphenyl)carbene]chromium(0) (5). The same method as was used for the preparation of **6** starting from 2-methoxycarbonyl-*N,N*-dimethylbenzamide (1.04 g, 5 mmol) gave **5** as yellow crystals (0.69 g, 36%). For elution of the product a hexane/dichloromethane mixture (1:1) was used instead of pure dichloromethane. Mp: 73−75 °C (methanol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.04 (s, 3H; N−C*H*$_3$), 3.87 (s, 3H; O−C*H*$_3$), 4.03 (s, 3H; N−C*H*$_3$), 6.71 (dd, $J = 7.7$, 0.8 Hz, 1H; Ph−*H*), 7.24 (dt, $J = 7.7$, 1.4 Hz, 1H; Ph−*H*), 7.56 (dt, $J = 7.7$, 1.4 Hz, 1H; Ph−*H*), 8.00 (dd, $J = 8.0$, 0.8 Hz, 1H; Ph−*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 270.8 (C═Cr), 223.2 (CO), 216.7 (CO), 166.0 (C═O), 152.6 (C−Ph), 132.8 (CH−Ph), 130.5 (CH−Ph), 125.8 (CH−Ph), 120.5 (CH−Ph), 119.7 (C−Ph), 52.5 (CH_3−O), 51.0 (CH_3−N), 45.8 (CH_3−N). ^{1}H NMR using Eu(hfc)$_3$ showed splitting of the O−CH_3 signal. IR ($CHCl_3$): ν 2055, 1969, 1929, 1713, 1542, 1277 cm^{-1}. Anal. Calcd (%) for $C_{16}H_{13}CrNO_7$: C 50.14, H 3.42, N 3.65. Found: C 50.55, H 3.57, N 3.55. The small-scale enantiomeric separation was performed on a Chiralcel OD-H column (250 × 4.6 mm, solvent 10% 2-propanol in hexane, flow 1 mL·min^{-1}, detection UV 254 nm); the retention times were 5.7 and 7.1 min.

Pentacarbonyl[(*N,N*-dimethylamino)(2-carboxyphenyl)carbene]chromium(0) (9). The same method as was used for the preparation of **10** starting from **5** (192 mg, 0.5 mmol) with prolonged heating time (16 h instead of 5 h) afforded yellow solid **9** (178 mg, 96%). Mp: >110 °C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.02 (s, 3H; N−C*H*$_3$), 3.97 (s, 3H; N−C*H*$_3$), 6.75 (d, $J = 7.7$ Hz, 1H; Ph−*H*), 7.29 (s, 1H; Ph−*H*), 7.63 (t, $J = 7.3$ Hz, 1H; Ph−*H*), 8.12 (s, 1H; Ph−*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 269.6 (C═Cr), 223.2 (CO), 216.9 (CO), 171.3 (C═O), 152.9 (C−Ph), 133.9 (CH−Ph), 131.5 (CH−Ph), 126.1 (CH−Ph), 120.7 (CH−Ph), 118.6 (C−Ph), 50.8 (CH_3−N), 45.9 (CH_3−N). IR ($CHCl_3$): ν 2055, 1973, 1928, 1682, 1546, 1402 cm^{-1}. Anal. Calcd (%) for $C_{15}H_{11}CrNO_7 \cdot 0.5H_2O$: C 47.63, H 3.20, N 3.70. Found: C 47.33,

H 3.20, N 3.59. The small-scale enantiomeric separation was performed on a Chiralcel OD-H column (250 × 4.6 mm, solvent 0.5% acetic acid and 20% 2-propanol in hexane, flow 1 mL·min^{-1}, detection UV 254 nm); the retention times were 5.0 and 5.2 min.

Pentacarbonyl[(*N,N*-dimethylamino)(2-biphenyl)carbene]chromium(0) (15). The same method as was used for the preparation of **6** starting from *N,N*-dimethylbiphenyl-2-carboxamide (0.90 g, 4 mmol) gave **15** as yellow crystals (1.01 g, 63%). For elution of the product a hexane/dichloromethane mixture (2:1) was used instead of pure dichloromethane. Mp: >110 °C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.15 (s, 3H; N−CH_3), 3.86 (s, 3H; N−CH_3), 6.86 (dm, J = 7.9 Hz, 1H; Ph−H), 7.23−7.43 (m, 8H; Ph−H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 277.1 (C═Cr), 223.5 (CO), 216.8 (CO), 150.9 (C−Ph), 140.1 (C−Ph), 131.5 (C−Ph), 131.0 (CH−Ph), 128.8 (CH−Ph), 128.3 (CH−Ph), 127.6 (CH−Ph), 127.4 (CH−Ph), 126.7 (CH−Ph), 120.4 (CH−Ph), 51.2 (CH_3−N), 46.7 (CH_3−N). IR ($CHCl_3$): ν 2055, 1975, 1929, 1533, 1402 cm^{-1}. Anal. Calcd (%) for $C_{20}H_{15}CrNO_5$: C 59.85, H 3.77, N 3.49. Found: C 59.73, H 3.79, N 3.40.

Pentacarbonyl[(*N,N*-dimethylamino)(2-isopropyl-5-methylphenyl)carbene]chromium(0) (16). The same method as was used for the preparation of **6** starting from 2-isopropyl-*N,N*,5-trimethylbenzamide (616 mg, 3 mmol) gave **16** as yellow crystals (197 mg, 17%; 51% to converted amide). For elution of the product a hexane/dichloromethane mixture (3:1) was used instead of pure dichloromethane. Further elution with a dichloromethane/methanol mixture (25:1) provided unreacted 2-isopropyl-*N,N*,5-trimethylbenzamide (410 mg). Mp: >90 °C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.12 (d, J = 6.7 Hz, 3H; CH−CH_3), 1.30 (d, J = 6.7 Hz, 3H; CH−CH_3), 2.31 (s, 3H; Ph−CH_3), 2.50 (sept, J = 6.7 Hz, 1H; −CH<), 3.10 (s, 3H; N−CH_3), 3.97 (s, 3H; N−CH_3), 6.49 (s, 1H; Ph−H), 6.99 (d, J = 8.0 Hz, 1H; Ph−H), 7.17 (d, J = 8.0 Hz, 1H; Ph−H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 278.4 (C═Cr), 223.7 (CO), 217.3 (CO), 151.2 (C−Ph), 135.6 (C−Ph), 133.5 (C−Ph), 127.5 (CH−Ph), 126.3 (CH−Ph), 119.9 (CH−Ph), 51.2 (CH_3−N), 46.4 (CH_3−N), 29.6 (>CH−), 24.8 (CH_3−C), 23.4 (CH_3−C), 21.1 (CH_3−Ph). IR ($CHCl_3$): ν 2054, 1974, 1929, 1531 cm^{-1}. Anal. Calcd (%) for $C_{18}H_{19}CrNO_5$: C 56.69, H 5.02, N 3.67. Found: C 56.15, H 5.15, N 3.45.

Pentacarbonyl[(*N,N*-dimethylamino)(2-isopropyl-5-methoxycarbonylphenyl)carbene]chromium(0) (17). The same method as was used for the preparation of **6** starting from 2-isopropyl-5-methoxycarbonyl-*N,N*-dimethylbenzamide (748 mg, 3 mmol) gave **17** as yellow crystals (435 mg, 34%; 89% to converted amide); for the final elution a hexane/dichloromethane mixture (1:1) was used. Further elution with a dichloromethane/methanol mixture (25:1) provided unreacted starting amide (0.46 g). Mp: >100 °C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.08 (d, J = 6.7 Hz, 3H; CH−CH_3), 1.28 (d, J = 6.7 Hz, 3H; CH−CH_3), 2.53 (sept, J = 6.7 Hz, 1H; −CH<), 3.04 (s, 3H; N−CH_3), 3.83 (s, 3H; O−CH_3), 3.94 (s, 3H; N−CH_3), 7.31 (d, J = 8.2 Hz, 1H; Ph−H), 7.33 (s, 1H; Ph−H), 7.77 (dd, J = 8.2, 1.8 Hz, 1H; Ph−H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 277.4 (C═Cr), 223.3 (CO), 216.9 (CO), 166.6 (C═O), 150.9 (C−Ph), 142.0 (C−Ph), 128.0 (C−Ph), 127.8 (CH−Ph), 126.8 (CH−Ph), 121.0 (CH−Ph), 52.2 (CH_3−O), 51.3 (CH_3−N), 46.7 (CH_3−N), 30.1 (>CH−), 24.5 (CH_3−C), 23.1 (CH_3−C). IR ($CHCl_3$): ν 2055, 1975, 1931, 1719, 1532, 1438, 1297, 1264, 1123 cm^{-1}. Anal. Calcd (%) for $C_{19}H_{19}CrNO_7$: C 53.65, H 4.50, N 3.29. Found: C 53.72, H 4.36, N 3.23. The small-scale enantiomeric separation was performed using a Chiralcel OD-H column (250 × 4.6 mm, solvent 10% 2-propanol in hexane, flow 1 mL·min^{-1}, detection UV 254 nm); the retention times were t_R = 7.7 and t_S = 21.5 min.

Pentacarbonyl[(*N,N*-dimethylamino)(2-isopropyl-5-(*S*)-1′-(1-naphthyl)ethoxycarbonylphenyl)carbene]chromium(0) (18). (*S*)-1-(1-Naphthyl)ethanol (667 mg, 3.9 mmol) and Na (18 mg, 0.78 mmol) were stirred under argon at 100 °C. After sodium has dissolved, finely powdered **17** (363 mg, 0.85 mmol) was added at 70 °C. The light brown solution was stirred for 2 h at 70 °C and diminished pressure (1.5 kPa). The cold reaction mixture was dissolved in CH_2Cl_2 (1 mL) and subjected to column chromatography on silica gel (30 g). Elution with a hexane/dichloromethane mixture (1:1) provided **18** (0.40 g; 83%) as a yellow foam. Further elution with CH_2Cl_2 gave (*S*)-1-(1-naphthyl)ethanol (0.47 g), which was reused for the preparation of the next batch of the product. ^{1}H and ^{13}C NMR spectra showed the presence of **(*R,S*)-18** and **(*S,S*)-18** in equimolar amounts.

(*R*)-Pentacarbonyl[(*N,N*-dimethylamino)(2-isopropyl-5-(*S*)-1′-(1-naphthyl)ethoxycarbonylphenyl)carbene]chromium(0) ((*R,S*)-18). The same method as was used for the preparation of **(*S,S*)-13** starting from **18** (0.36 g, 0.64 mmol) gave **(*R,S*)-18** as yellow crystals (148 mg, 82%). ^{1}H NMR analysis of the mother liquor from the first crystallization revealed approximately 90% de of **(*S,S*)-18**. **(*R,S*)-18**: Mp >150 °C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.16 (d, J = 6.7 Hz, 3H; CH−CH_3), 1.35 (d, J = 6.7 Hz, 3H; CH−CH_3), 1.82 (d, J = 6.5 Hz, 3H; O−CH−CH_3), 2.58 (sept, J = 6.7 Hz, 1H; −CH<), 3.07 (s, 3H; N−C H_3), 3.99 (s, 3H; N−CH_3), 6.88 (q, J = 6.5 Hz, 1H; CH−CH$_3$), 7.40 (d, J = 8.2 Hz, 1H; Ph−H), 7.46−7.60 (m, 4H; Ar−H), 7.70 (d, J = 6.7 Hz, 1H; Ar−H), 7.83 (d, J = 8.2 Hz, 1H; Ph−H), 7.87−7.95 (m, 2H; Ar−H), 8.20 (d, J = 8.2 Hz, 1H; Ar−H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 277.3 (C═Cr), 223.3 (CO), 217.0 (CO), 165.3 (C═O), 150.8 (C−Ph), 141.9 (C−Ph), 137.4 (C−Ar), 133.8 (C−Ar), 130.3 (C−Ar), 128.9 (CH−Ar), 128.5 (CH−Ar), 128.4 (C−Ar), 128.0 (CH−Ar), 126.8 (CH−Ar), 126.4 (CH−Ar), 125.7 (CH−Ar), 125.4 (CH−Ar), 123.5 (CH−Ar), 123.3 (CH−Ar), 121.1 (CH−Ar), 70.4 (CH−O), 51.3 (CH_3−N), 46.7 (CH_3−N), 30.1 (>CH−), 24.5 (CH_3−C), 23.1 (CH_3−C), 21.9 (CH_3−CH−O); IR ($CHCl_3$): ν 2055, 1974, 1931, 1713, 1533, 1292, 1263, 1112 cm^{-1}. Anal. Calcd (%) for $C_{30}H_{27}CrNO_7$: C 63.71, H 4.81, N 2.48. Found: C 64.11, H 5.07, N 2.33. **(*S,S*)-18** (approximately 90% de): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.16 (d, J = 6.7 Hz, 3H; CH−CH_3), 1.35 (d, J = 6.7 Hz, 3H; CH−CH_3), 1.83 (d, J = 6.5 Hz, 3H; O−CH−CH_3), 2.58 (sept, J = 6.7 Hz, 1H; −CH<), 3.10 (s, 3H; N−C H_3), 4.00 (s, 3H; N−CH_3), 6.89 (q, J = 6.5 Hz, 1H; CH−CH$_3$), 7.39 (d, J = 8.2 Hz, 1H; Ph−H), 7.43−7.59 (m, 4H; Ar−H), 7.68 (d, J = 7.0 Hz, 1H; Ar−H), 7.80 (d, J = 8.2 Hz, 1H; Ph−H), 7.85−7.95 (m, 2H; Ar−H), 8.18 (d, J = 8.2 Hz, 1H; Ar−H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 277.2 (C═Cr), 223.3 (CO), 217.0 (CO), 165.2 (C═O), 150.9 (C−Ph), 142.0 (C−Ph), 137.6 (C−Ar), 133.7 (C−Ar), 130.1 (C−Ar), 128.9 (CH−Ar), 128.4 (CH−Ar), 128.4 (C−Ar), 127.9 (CH−Ar), 126.8 (CH−Ar), 126.3 (CH−Ar), 125.6 (CH−Ar), 125.4 (CH−Ar), 123.1 (CH−Ar), 123.0 (CH−Ar), 121.0 (CH−Ar), 70.3 (CH−O), 51.3 (CH_3−N), 46.7 (CH_3−N), 30.1 (>CH−), 24.5 (CH_3−C), 23.1 (CH_3−C), 22.2 (CH_3−CH−O). IR ($CHCl_3$): ν 2055, 1974, 1931, 1713, 1534, 1402, 1292, 1263, 1113 cm^{-1}.

(*R*)-Pentacarbonyl[(*N,N*-dimethylamino)(2-isopropyl-5-methoxycarbonylphenyl)carbene]chromium(0) ((*R*)-17). The same method as was used for the preparation of **(*S*)-6** starting from **(*R,S*)-18** (125 mg, 0.22 mmol) afforded **(*R*)-17** (65 mg, 69%) as a yellow oil, which solidified upon several days in a freezer. Mp: 93 °C (dec). UV/vis (c 2.7 × 10^{-5} mol·dm^{-3}, CH_2Cl_2): 239 (34 800), 355 nm (5600). CD (c 2.7 × 10^{-5} mol·dm^{-3}, CH_2Cl_2): 230 (35.7), 252 (−24.6), 275 (−7.1), 322 (0.8), 360 (−1.6), 407 nm (0.9). Anal. Calcd (%) for $C_{19}H_{19}CrNO_7$: C 53.65, H 4.50, N 3.29. Found: C 54.03, H 4.64, N 3.24. Chiral chromatography on a Chiralcel OD-H column (250 × 4.6 mm, solvent 10% 2-propanol in hexane, flow 1 mL·min^{-1}, detection UV 254 nm) gave 99% ee for this product. The determination of the racemization barrier was conducted in the same apparatus and under the same conditions as for compound **(*S*)-6**. Samples were analyzed on a Chiralcel OD-H column to give the following results:

time (min)	0	40	80	120
ee (%)	97.4	90.5	82.2	75.7

from which $k_{rac} = 3.48 \times 10^{-5}$ s^{-1} and $\Delta G^{\ddagger}_{rac} = 120.5 \pm 0.5$ kJ·mol^{-1}.

Pentacarbonyl[(*N*,*N*-dimethylamino)(4-methoxycarbonyl-2-methylphenyl)carbene]chromium(0) (8). The same method as was used for the preparation of **6** starting from 4-methoxycarbonyl-*N*,*N*,2-trimethylbenzamide[19] (1.11 g, 5 mmol) gave the desired product (1.19 g, 60%) as yellow crystals. Mp: 115 °C (dec). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.12 (s, 3H, Ph−CH_3), 3.05 (s, 3H, N−CH_3), 3.91 (s, 3H, CO_2CH_3), 4.03 (s, 3H, N−CH_3), 6.79 (s, 1H, Ph−H), 7.90 (m, 2H, Ph−H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 276.0 (C═Cr), 223.1 (CO), 216.8 (CO), 166.6 (C═O), 154.9 (C−Ph), 132.4 (CH−Ph), 127.9 (C−Ph), 127.7 (CH−Ph), 125.9 (C−Ph), 119.8 (CH−Ph), 52.1 (CH_3−O), 51.0 (CH_3−N), 45.4 (CH_3−N), 18.6 (CH_3−Ph). IR ($CHCl_3$): ν 2055, 1974, 1932, 1716, 1296 cm^{-1}. Anal. Calcd (%) for $C_{17}H_{15}CrNO_7$: C 51.39, H 3.81, N 3.53. Found: C 50.97, H 3.66, N 3.42.

(19) The sample of 4-methoxycarbonyl-*N*,*N*,2-trimethylbenzamide was obtained from Dr. Patrik Pařík, University of Pardubice.

Pentacarbonyl[(*N*,*N*-dimethylamino)(4-carboxy-2-methylphenyl)carbene]chromium(0) (12). The same method as was used for the preparation of **10** starting from **8** (199 mg, 0.5 mmol) afforded the desired product (163 mg, 85%) as a yellow solid. Mp: decomposes without melting. IR ($CHCl_3$): ν 2055, 1973, 1930 cm^{-1}. Anal. Calcd (%) for $C_{16}H_{13}CrNO_7$: C 50.14, H 3.42, N 3.65. Found: C 49.96, H 3.26, N 3.37.

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Supporting Information Available: Crystallographic information files (CIF) for compounds **(*S*,*S*)-13**, **(*R*,*S*)-14**, and **(*R*,*S*)-18**; experimental details describing preparation of the amides used for the preparation of carbene complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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