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Application of chiral lithium amide base chemistry to the synthesis of planar chiral (arene)tricarbonylchromium(0) complexes

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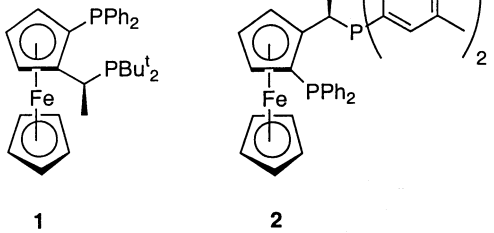
Abstract—Asymmetric functionalisation of tricarbonylchromium(0) complexes of benzyl alkyl ethers using a dilithiated chiral amide base is the key step in a short and versatile synthesis of planar chiral (arene)tricarbonylchromium(0) complexes. The synthesis of four complexes of potential use in asymmetric catalysis is described herein together with the first demonstration that the asymmetric functionalisation mediated by this chiral base may be used to introduce phosphine substituents.

1. Introduction

Ferrocene based planar chiral ligands feature heavily in any account of successful asymmetric catalysis.[1] Indeed the use of 'Josiphos'-type ligands in industrial asymmetric hydrogenation processes render them some of the most commercially successful enantioselective transition-metal catalyst ligands to date.[2,3] Thus the planar chiral diphosphine **1** is used for rhodium catalysed asymmetric hydrogenation of a tetrasubstituted alkene in the commercial scale production of (+)-biotin by Lonza AG, whilst the planar chiral diphosphine **2** is used for iridium catalysed asymmetric hydrogenation of an imine in the production process of the herbicide (*S*)-metolachlor by Novartis (Fig. 1).

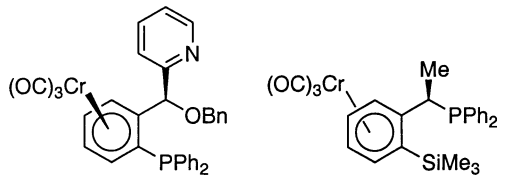
The potential of planar chiral ligands based on (arene)tricarbonylchromium(0) complexes in asymmetric catalysis has been recognised.[4] As a result there has been a significant increase in activity in this area in the last two to three years leading to the successful application of planar chiral (arene)tricarbonylchromium(0) complexes as catalyst ligands in a diverse range of reactions. Typical examples include the use of the planar chiral phosphine **3** as a ligand for the asymmetric rhodium catalysed hydroboration of styrenes[5] and the use of the planar chiral phosphine **4** as a ligand for the asymmetric palladium catalysed hydrovinylation of styrene with ethene (Fig. 2).[6] Progress, however, is limited by the relatively small number of 'resolution gateways' into the area, and it is acknowledged that although several synthetic strategies exist for the preparation of non-racemic planar chiral (arene)tricarbonylchromium(0) complexes, there is a need for more general approaches that allow the rapid and efficient preparation of a greater number of enantiomerically pure complexes.[4]

Non racemic chiral bases have been proven to be of significant use in the synthesis of a wide range of enantiomerically enriched organic molecules. Their use in the synthesis of organometallic reagents and catalysts, however, is still in its infancy. One of the first areas of organometallic chemistry to be examined in this context was the asymmetric functionalisation of tricarbonylchromium(0) complexes of arenes.[7] Application of chiral bases to aromatic functionalisation of these complexes was pioneered by



1 2

Figure 1.



3 4

Figure 2.

Keywords: chiral lithium amide base; planar chirality; (arene)tricarbonylchromium(0).

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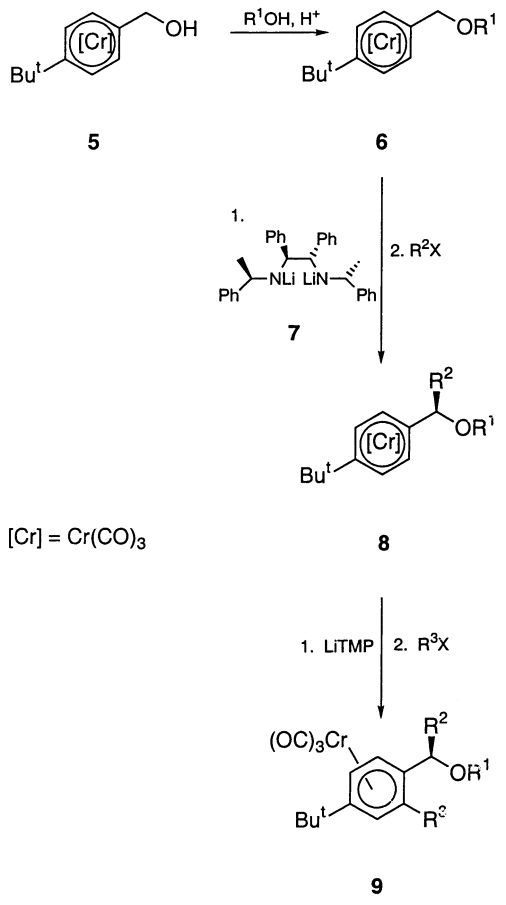


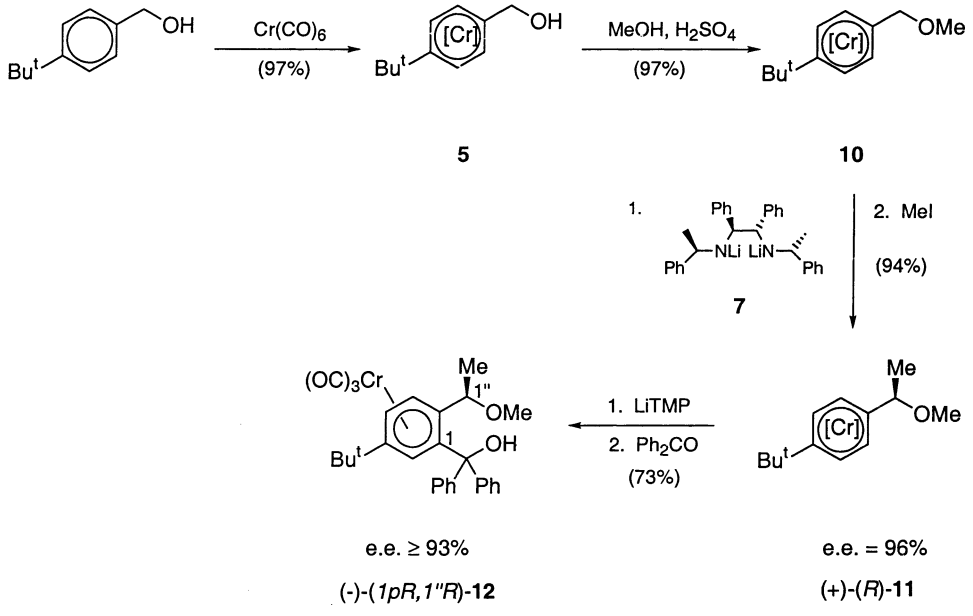
Scheme 1.

Simpkins, Kündig, Schmalz and Uemura in 1994–95,[7] whilst application of chiral bases to benzylic functionalisation was addressed by Gibson and Simpkins in 1996.[7] We have very recently combined chiral base chemistry developed within our group[7–9] with a highly selective ring deprotonation, also developed within our group,[10] to create a flexible approach to non-racemic planar chiral (arene)tricarbonylchromium(0) complexes (Scheme 1). Our synthesis starts with the reaction of readily synthesised tricarbonyl(4-*tert*-butylbenzyl alcohol)chromium(0) **5** with an alcohol under acid catalysis to give the ether complex **6**. Asymmetry is introduced into **6** by its treatment with the chiral base **7** (the diamine precursor of **7** is readily available from (*R*) and (*S*)-α-methylbenzylamine in two steps) and an electrophilic quench to give **8**. Finally a diastereoselective *ortho*-lithiation of **8** followed by an electrophilic quench gives the planar chiral complex **9**. We present in this paper a full account of the use of this method to synthesise four non-racemic planar chiral complexes that have potential as ligands in asymmetric catalysis. Our account includes the first description of the extension of the chiral base chemistry used to convert **6** into **8** to the incorporation of phosphine substituents.

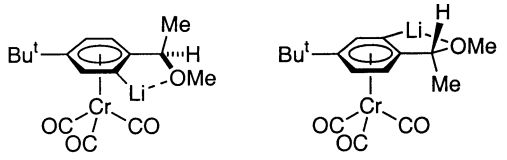
2. Results and discussion

Complex **5** was synthesised from commercially available 4-*tert*-butylbenzyl alcohol and hexacarbonylchromium(0). Thermolysis of a 1:1 mixture of these two components at 135°C in di-*n*-butyl ether and THF (10:1) for 48 h gave, after work-up, a 97% yield of the novel yellow crystalline tricarbonyl(4-*tert*-butylbenzyl alcohol)chromium(0) **5**. (It is of note that this reaction has been used to produce up to 25 mmol (7.55 g) of complex **5**.) Subsequent treatment of a methanolic solution of **5** with sulfuric acid gave novel tricarbonyl(1-methoxymethyl-4-*tert*-butylbenzene)chromium(0) **10** as yellow crystals in 97% yield. Although all the complexes described here are methyl ethers formed by the acidic methanol treatment described above, other ethers are readily synthesised by replacing methanol with the appropriate alcohol (Scheme 2).

Our preliminary studies had been carried out using iodomethane as the 'benzylic' electrophile R^2X and chlorotrimethylsilane as the 'ring' electrophile R^3X.[10] One of the



Scheme 2.



13a 13b

Figure 3.

aims of this study was to introduce *ortho* substituents onto the aromatic ring which would provide useful donor atoms to metals. Accordingly our first goal was to use benzophenone as the ring electrophile with a view to introducing a second oxygen donor atom.

Deprotonation of complex **10** was effected by stirring it with the non-racemic chiral lithium amide base **7** for 30 min at −78°C. Subsequent addition of iodomethane and stirring for a further 40 min at −78°C followed by work-up gave novel (+)-(*R*)-tricarbonyl[1-(1-methoxyethyl)-4-*tert*-butylbenzene)chromium(0), (+)-**11**, in 94% yield (Scheme 2). The enantiomeric excess of (+)-**11** was determined as 96% by HPLC analysis. (A sample of (±)-**11** was prepared for this analysis by reacting complex **10** with *tert*-butyllithium followed by an iodomethane quench (92% yield).) The absolute stereochemistry of (+)-**11** was assigned as *R* based on results obtained in our previous studies using chiral base **7** and benzyl ether complexes lacking the 4-*tert*-butyl substituent.[8]

Ring deprotonation of (+)-**11** was achieved by treatment of the complex with lithium tetramethylpiperidide (LiTMP) at −78°C for 1 h. Pleasingly, addition of benzophenone and stirring at −78°C, for 2 h and room temperature for 1 h, followed by work-up, gave novel (−)-(1*pR*,1″*R*)-tricarbonyl[2-(1-methoxyethyl)-5-*tert*-butyl(diphenylhydroxymethyl)benzene]chromium(0), (−)-**12**, in 73% yield. The enantiomeric excess of (−)-**12** was determined as ≥93% by HPLC analysis. (A sample of (±)-**12** was prepared for this analysis by reacting (±)-**11** with LiTMP followed by a benzophenone quench (93% yield).) Examination of the ^{1}H NMR spectrum of (−)-**12** [and (±)-**12**] revealed that only one diastereoisomer had been formed. The relative stereochemistry of this diastereoisomer was determined by X-ray crystallography of (±)-**12**[11] and found to be (1*pR*,1″*R*)(1*pS*,1″*S*). The absolute stereochemistry of (−)-**12** was thus assigned as (1*pR*,1″*R*).

The conversion of (+)-**11** to (−)-**12** is a highly selective reaction. The *para-tert*-butyl substituent shields the *meta* positions in complex (+)-**11** from lithiation, thus removing a serious problem encountered in systems lacking the *tert*-butyl substituent,[12–14] and the side-chain chirality introduced by the chiral lithium amide base directs substitution exclusively to one of the two diastereotopic *ortho* positions. This selectivity is accounted for by a model used to explain selective *ortho*-lithiation in tricarbonylchromium(0) complexes of α-methylbenzylamines.[12–14] Thus intermediate **13a** is lower in energy than intermediate **13b** in which there is an unfavourable interaction between the benzylic methyl and the tricarbonylchromium(0) rotor (Figs. 3 and 4).

Having ascertained that we could create planar chirality and simultaneously introduce an oxygen donor atom into our potential ligands, we turned our attention to the introduction of phosphine substituents.

Initially the methyl ether complex **10** was reacted with the chiral lithium amide base **7** followed by a benzyl bromide quench to generate the novel complex (+)-(*R*)-tricarbonyl[1-(1-methoxy-2-phenylethyl)-4-*tert*-butylbenzene]-chromium(0), (+)-**14** in 92% yield and 97% ee (determined by HPLC analysis using (±)-**14**). Treatment of (+)-**14** with LiTMP followed by a quench with chlorodiphenylphosphine gave the novel phosphine complex (−)-(1*pR*,1″*R*)-tricarbonyl[1-diphenylphosphine-2-(1-methoxy-2-phenylethyl)-5-*tert*-butylbenzene]chromium(0), (−)-**15** in 91% yield and 97% ee (determined by HPLC analysis using (±)-**15**) (Scheme 3). Similarly treatment of the chiral methyl ether complex (+)-**11** with LiTMP followed by chlorodiphenylphosphine gave the novel phosphine complex (−)-(1*pR*,1″*R*)-tricarbonyl[1-diphenylphosphine-2-(1-methoxyethyl)-5-*tert*-butylbenzene]chromium(0), (−)-**16** in 88% yield and 96% ee (determined by HPLC analysis using (±)-**16**) (Scheme 3).

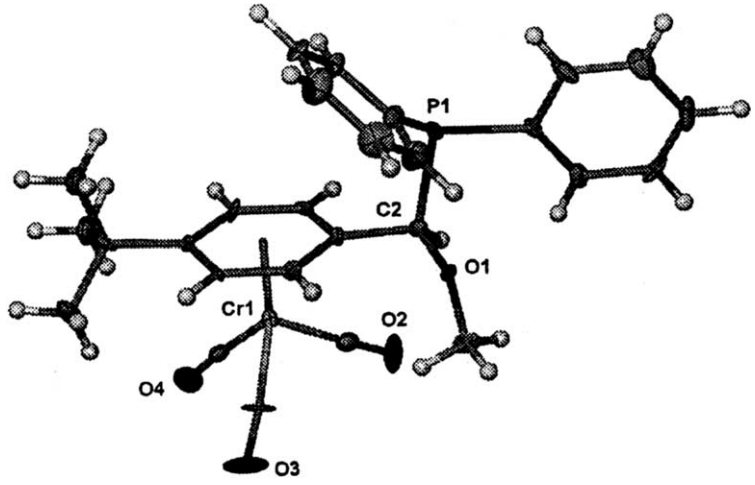
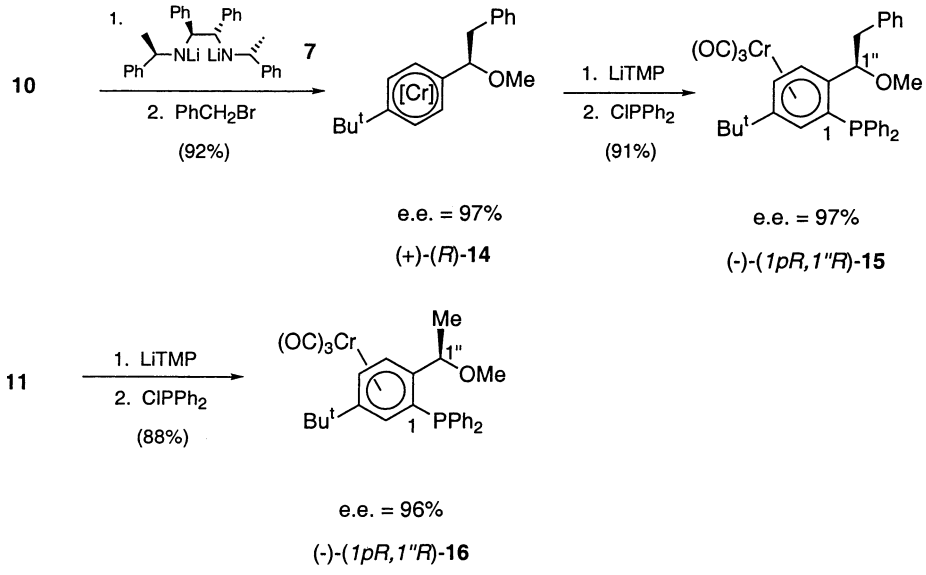


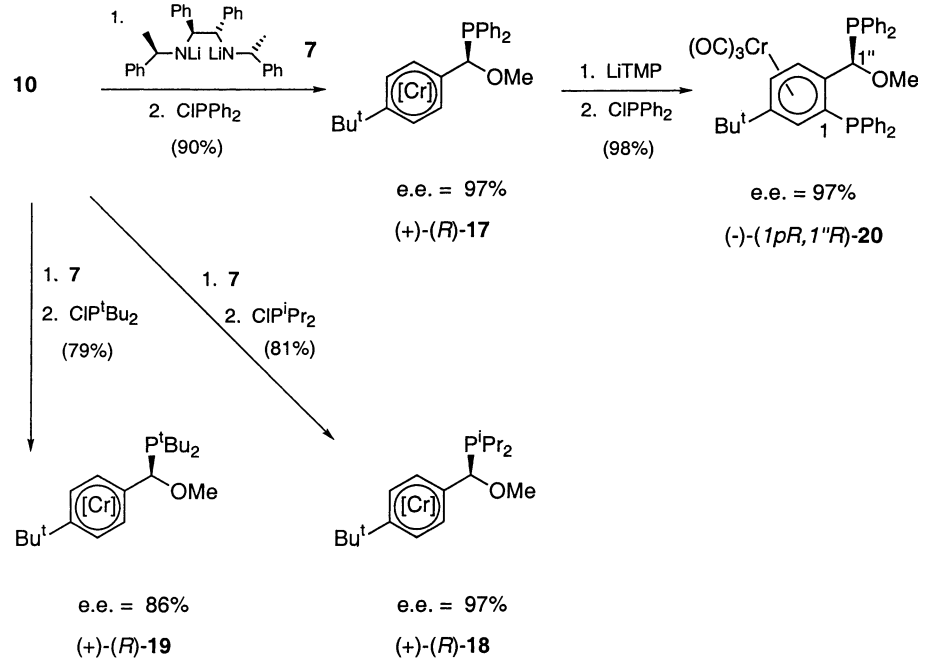
Figure 4. X-Ray crystallographic structure of (+)-tricarbonyl[1-(1-diphenylphosphine-1-methoxymethyl)-4-*tert*-butylbenzene]chromium(0), (+)-**17**.



Scheme 3.

Given the importance of diphosphine ligands in asymmetric catalysis, identification of a method of introducing a second phosphine substituent into the planar chiral complexes was as an important goal in this study. Our work to date on the asymmetric functionalisation of tricarbonylchromium(0) complexes of alkyl benzyl ethers using chiral lithium amide bases, had employed carbon, silicon and sulfur electrophiles; it was thus an opportune time to determine whether or not chiral lithium amide base chemistry could be used to introduce phosphine substituents. We were concerned not only about the level of reactivity between the benzylic anion and a phosphorus electrophile, but also about the level of stereoselectivity of the process and the stereochemical stability of the resulting product.

Accordingly complex **10** was treated with the chiral lithium amide base **7** followed by a chlorodiphenylphosphine quench (Scheme 4). Pleasingly work-up and analysis revealed that the desired and novel complex (+)-tricarbonyl[1-(1-diphenylphosphine-1-methoxymethyl)-4-*tert*-butylbenzene]chromium(0), (+)-**17** had been formed in 90% yield and 97% ee (determined by HPLC analysis using (±)-**17**). An X-ray crystallographic analysis of (+)-**17** (Fig. 1) revealed that its configuration was *R*, a stereochemical outcome consistent with our previous studies on related complexes.[8] Complex (+)-**17** crystallised in the chiral space group $P2_1$ and the asymmetric unit consisted of two independent molecules (consistent with other systems of this type that we have studied.[11]) Although



Scheme 4.

obtaining crystals proved difficult and the best samples consisted of small needles, the details of the molecular geometry are clear and unambiguous, and the absolute structure of the enantiomerically pure crystal studied was readily apparent from the Flack parameter. The stereochemical stability of (+)-**17** was probed by stirring the complex in THF for 24 h at room temperature. Subsequent HPLC analysis revealed that its enantiomeric purity was unchanged.

In order to ascertain whether or not other phosphine substituents could be introduced using the chiral lithium amide base chemistry, complex **10** was treated with base **7** followed by quenches with chlorodi(*iso*-propyl)phosphine and chlorodi(*tert*-butyl)phosphine. These gave the novel complexes (+)-tricarbonyl{1-[1-di(*iso*-propyl)phosphine-1-methoxymethyl]-4-*tert*-butylbenzene}chromium(0), (+)-**18** and (+)-tricarbonyl{1-[1-di(*tert*-butyl)phosphine-1-methoxymethyl]-4-*tert*-butylbenzene}chromium(0), (+)-**19** in 81 and 79% yield and 97 and 86% ee (determined by HPLC analysis using (±)-**18** and (±)-**19**) (Scheme 4). (The reduced enantiopurity of (+)-**19** is a reflection of the need to use a higher reaction temperature during the quench step to ensure a high chemical yield).

The first diphosphine in this series was synthesised by reaction of complex (+)-**17** with LiTMP followed by chlorodiphenylphosphine. This gave the novel diphosphine (−)-(1*pR*, 1″*R*)-tricarbonyl[1-diphenylphosphine-2-(1-diphenylphosphine-1-methoxymethyl)-5-*tert*-butylbenzene]-chromium(0), (−)-**20**, (−)-hasiphos, in 98% yield and 97% ee (as determined by HPLC analysis using (±)-**20**). The stereochemical stability of (−)-hasiphos was probed by stirring a THF solution of (−)-**20** at room temperature for 34 h. Subsequent HPLC analysis revealed that the enantiomeric purity of the complex was unchanged.

A comparison of the structures of (−)-**12**, (−)-**15**, (−)-**16** and (−)-**20** with the known planar chiral ligands **1**–**4** reveals that the complexes reported here have considerable potential as ligands for asymmetric catalysis. The work described in this paper demonstrates that these ligands, which all belong to the class of complex described by the general structure **9**, may be synthesised in high yield and high enantiomeric purity using an approach based on chiral lithium amide base chemistry.

3. Experimental

3.1. General

All reactions and manipulations involving organometallic compounds were performed under an inert atmosphere of dry nitrogen, using standard vacuum line and Schlenk tube techniques.[15] Reactions and operations involving (arene)tricarbonylchromium(0) complexes were protected from light. THF was distilled from sodium benzophenone ketyl. The concentration of alkyllithiums was determined by titration against diphenylacetic acid in THF.[16] Tetramethylpiperidine was purchased from Aldrich and stored without further purification over potassium hydroxide or alternatively it was distilled over CaH_2 and stored over potassium hydoxide. Chlorodiphenylphosphine was distilled prior to use. Flash column chromatography was performed using Merck silica gel 60 (230–400 mesh). All other reagents were used as obtained from commercial sources.

Melting points were recorded in open capillaries on a Büchi 510 melting point apparatus, and are uncorrected. IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrometer. NMR spectra were recorded at room temperature on Brüker AM 360, DRX 400 and DRX 500 instruments and *J* values are reported in Hz. Mass spectra were recorded on JEOL AX 505W and Kratos MS890MS spectrometers. Elemental analyses were performed by the University of North London microanalytical service. The amine precursor to chiral lithium amide base **7** was prepared according to a literature method.[17]

3.1.1. Tricarbonyl(4-*tert*-butylbenzyl alcohol)chromium(0) 5. A 250 mL round-bottomed flask fitted with a Liebig air condenser with a water condenser on top was charged with 4-*tert*-butylbenzyl alcohol (4.26 g, 26.0 mmol), hexacarbonylchromium(0) (5.71 g, 26.0 mmol), dry THF (15 mL) and dry di-*n*-butyl ether (155 mL). The suspension was thoroughly saturated with nitrogen, before being heated to 135°C and maintained under a slight nitrogen over pressure (ca. 50 mbar). After 48 h the orange reaction mixture was allowed to cool to room temperature and the solvent was removed in vacuo. Flash column chromatography (SiO_2; hexane/diethyl ether, 5:5–2:8) of the orange residue offered 7.55 g (97%) of complex **5** as yellow crystals. Mp: 100–101°C. IR (CH_2Cl_2, cm^{-1}): ν_{OH} 3603 (w), ν_{CO} 1963 (s), ν_{CO} 1885 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 1.29 (s, 9H, $(CH_3)_3C$), 1.97 (bs, 1H, OH), 4.49 (s, 2H, CH_2OH), 5.29 (d, J=6.5 Hz, 2H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}H$), 5.60 (d, J=6.5 Hz, 2H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}$H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.1 ($(CH_3)_3C$), 33.9 ($(CH_3)_3C$), 63.0 (COH), 89.0 (2C, $C_{Cr}H$), 92.8 (2C, $C_{Cr}H$), 111.8 ($C_{Cr}CH_2OH$), 122.2 (C_{Cr}(*t*-Bu)), 233.5 (C≡O). MS (EI): *m*/*z* (%) 300 (M^+, 46), 244 (M^+-2CO, 13), 216 (M^+-3CO, 100), 198 ($M^+-3CO-H_2O$, 32), 183 ($M^+-3CO-H_2O-CH_3$, 19), 147 ($M^+-Cr(CO)_3-OH$, 15). Anal. Calcd for $C_{14}H_{16}CrO_4$ (300.27): C, 56.00; H, 5.37. Found: C, 56.08; H, 5.29.

3.1.2. Tricarbonyl(1-methoxymethyl-4-*tert*-butylbenzene)-chromium(0) 10. Concentrated sulfuric acid (2.2 mL) was added dropwise to a solution of complex **5** (1.0 g, 3.33 mmol) in nitrogen saturated methanol (10 mL). The mixture was heated at 50°C for 3 h and stirred for a further 2 h at room temperature. To neutralise the reaction mixture saturated aqueous Na_2CO_3 (10 mL) was added carefully followed by the addition of diethyl ether (50 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether (3×50 cm^3). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure to give complex **10** as a yellow solid in high purity. Column chromatography (SiO_2; hexane/diethyl ether, 1:1) of this material gave 1.01 g (97%) of analytically pure complex **10** as a yellow crystalline solid. Mp: 44–45°C. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1964 (s), ν_{CO} 1885 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 1.28 (s, 9H, $(CH_3)_3C$), 3.46 (s, 3H, OCH_3), 4.18 (s, 2H, CH_2OCH_3), 5.25 (d, J=6.8 Hz, 2H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}H$), 5.57 (d, J=6.8 Hz, 2H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}$H). ^{13}C NMR (100 MHz, $CDCl_3$): δ

31.1 ($(CH_3)_3C$), 33.9 ($(CH_3)_3C$), 59.0 (CH_2OCH_3), 72.8 (CH_2OCH_3), 90.3 (2C, $C_{Cr}H$), 92.6 (2C, $C_{Cr}H$), 107.8 ($C_{Cr}CH_2OMe$), 121.8 (C_{Cr}(*t*-Bu)), 233.3 (C≡O). MS (EI): *m/z* (%) 314 (M^+, 25), 258 (M^+-2CO, 6), 230 (M^+-3CO, 46), 200 ($M^+-3CO-H_2CO$, 100), 178 ($M^+-Cr(CO)_3$, 12), 163 ($M^+-Cr(CO)_3-CH_3$, 42). Anal. Calcd for $C_{15}H_{18}CrO_4$ (314.30): C, 57.32; H, 5.77. Found: C, 57.38; H, 5.68.

3.1.3. (+)-(*R*)-Tricarbonyl[1-(1-methoxyethyl)-4-*tert*-butylbenzene]chromium(0) (+)-11. *n*-Butyllithium (2.78 mL, 1.58 M in hexane, 4.40 mmol) was added dropwise to a stirred solution of diamine **7**–H_2 (925 mg, 2.2 mmol) in THF (20 mL) at −78°C and the solution was allowed to reach room temperature over 30 min. The resulting deep pink solution of the chiral diamide **7** was then re-cooled to −78°C and a solution of heat gun-dried lithium chloride (93 mg, 2.2 mmol) in THF (10 mL) was added via a cannula. Stirring was continued for a further 5 min before a pre-cooled solution (−78°C) of complex **10** (629 mg, 2.2 mmol) in THF (8 mL) was added dropwise (ca. 3 min) via a short cannula. After stirring the orange solution at −78°C for 30 min, iodomethane (0.4 mL, 6.0 mmol) was added in one portion which resulted in a colour change of the solution to yellow. Stirring was continued for a further 40 min before methanol (1 mL) was added and the solvent removed in vacuo. Flash column chromatography (SiO_2; hexane/dichloromethane, 1:0–2:1) of the residue gave 615 mg (94%) of the title complex (+)-**11** as a yellow solid. Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 98:2, 0.6 mL/min, 330 nm); (*S*)-enantiomer t_r=10.4 min (minor); (*R*)-enantiomer t_r=11.0 min (major): 96% ee. $[\alpha]_D^{23}$=+40.1 (*c* 1.00, CH_2Cl_2). Mp: 67–68°C. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1962 (s), ν_{CO} 1882 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 1.29 (s, 9H, $(CH_3)_3C$), 1.45 (d, *J*=6.5 Hz, 3H, $CHCH_3$), 3.46 (s, 3H, OCH_3), 4.09 (q, *J*=6.5 Hz, 1H, $CHCH_3$), 5.20 (dd, *J*=6.8, 1.7 Hz, 1H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}H$), 5.42 (dd, *J*=6.8, 1.7 Hz, 1H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}H$), 5.49 (dd, *J*=6.9, 1.7 Hz, 1H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}H'$), 5.52 (dd, *J*=6.9, 1.7 Hz, 1H, C_{Cr}(*t*-Bu)$C_{Cr}H'C_{Cr}H'$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6 ($CHCH_3$), 31.1 ($(CH_3)_3C$), 33.9 ($(CH_3)_3C$), 57.3 (OCH_3), 76.6 ($CHCH_3$), 88.9 (C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}H$), 90.1 (C_{Cr}(*t*-Bu)$C_{Cr}HC'_{Cr}H$), 91.6 (2C, C_{Cr}(*t*-Bu)$C_{Cr}H$), 113.8 ($C_{Cr}CH$(Me)OMe), 122.7 (C_{Cr}(*t*-Bu)), 233.6 (C≡O). MS (EI): *m/z* (%) 328 (M^+, 13), 244 (M^+-3CO, 19), 212 ($M^+-3CO-CH_3OH$, 60), 192 ($M^+-Cr(CO)_3$, 10), 177 ($M^+-Cr(CO)_3-CH_3$, 100), 145 ($M^+-Cr(CO)_3-CH_3-CH_3OH$, 26). Anal. Calcd for $C_{16}H_{20}CrO_4$ (328.33): C, 58.53; H, 6.14. Found: C, 58.68; H, 6.24.

3.1.4. (±)-(*R*)(*S*)-Tricarbonyl[1-(1-methoxyethyl)-4-*tert*-butylbenzene]chromium(0) (±)-11. *t*-Butyllithium (0.72 mL, 1.64 M in hexane, 1.12 mmol) was added dropwise to a stirred solution of complex **10** (337 mg, 1.07 mmol) in THF (10 mL) at −78°C. The resulting deep orange solution was stirred for 1.5 h. Iodomethane (0.21 mL, 3.21 mmol) was added in one portion which resulted in a colour change of the solution to yellow. Stirring was continued at −78°C for a further 1.5 h before methanol was added and the solvent removed in vacuo. Flash column chromatography (SiO_2; hexane/diethyl ether, 9:1–1:1) of the residue gave 324 mg (92%) of the title complex (±)-**11** as a yellow solid. Mp: 79–80°C. All other data were identical to those obtained for (+)-**11**.

3.1.5. (−)-(1*pR*,1″*R*)-Tricarbonyl[2-(1-methoxyethyl)-5-*tert*-butyl-(diphenylhydroxymethyl)benzene]chromium(0) (−)-12. Methyllithium (0.37 mL, 1.49 M in diethyl ether, 0.55 mmol) was added dropwise to a stirred solution of tetramethylpiperidine (93 μL, 0.55 mmol) in THF (5 mL) at −78°C. The solution was allowed to reach room temperature and re-cooled to −78°C. Complex (+)-**11** (150 mg, 0.46 mmol) in THF (2 mL) was added via a cannula and the resulting orange solution was stirred for 1 h. A solution of benzophenone (255 mg, 1.4 mmol) in THF (5 mL) was added via a cannula and stirring was continued for a further 2 h at −78°C. The reaction vessel was removed from the acetone/dry ice bath and the reaction mixture stirred at room temperature for 1 h. Methanol was added and the solvent removed in vacuo. Flash column chromatography (SiO_2; hexane/diethyl ether, 10:0–5:5) of the residue gave 171 mg (73%) of the complex (−)-**12** as a yellow solid. Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 98:2, 0.4 mL/min, 330 nm); (*pR*,*R*)-enantiomer t_r=35.6 min (major); (*pS*,*S*)-enantiomer t_r=40.9 (minor): >93% ee. $[\alpha]_D^{21}$=−42.4 (*c* 0.75, CH_2Cl_2). Mp: 173–178°C. IR (Nujol, cm^{-1}): ν_{OH} 3386 (w), ν_{CO} 1953 (s), 1946 (m), 1879 (m), 1868 (s), 1860 (s). ^1H NMR (360 MHz, $CDCl_3$): δ 1.09 (s, 9H, $(CH_3)_3C$), 1.46 (d, *J*=6.3 Hz, 3H, CH_3CH), 2.47 (s, 3H, OCH_3), 3.64 (s, 1H, OH), 4.52 (q, *J*=6.3 Hz, 1H, CH_3CH), 4.72 (d, *J*=1.6 Hz, 1H, $C_{Cr}HC_{Cr}COH$), 5.55 (d, *J*=6.8 Hz, 1H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}H$), 5.60 (dd, *J*=6.8, 1.6 Hz, 1H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}H$), 7.32–7.41 (m, 10H, H_{ar}). ^{13}C NMR (90 MHz, $CDCl_3$): δ 22.0 (CH_3CH), 30.8 ($(CH_3)_3C$), 33.7 ($(CH_3)_3C$), 56.0 (OCH_3), 74.1 (CH_3CH), 81.5 (COH), 91.5 ($C_{Cr}H$), 92.1 ($C_{Cr}H$), 94.9 ($C_{Cr}H$), 117.6 (C_{Cr}), 117.7 (C_{Cr}), 121.1 (C_{Cr}), 127.5 (2C, $C_{ar}H$), 127.6 (2C, $C_{ar}H$), 127.8 ($C_{ar}H$), 128.1 (2C, $C_{ar}H$), 128.2 (2C, $C_{ar}H$), 128.5 ($C_{ar}H$), 144.2 (C_{ar}), 144.4 (C_{ar}), 233.6 (C≡O). MS (EI): *m/z* (%) 510 (M^+, 18), 426 (M^+-3CO, 100), 394 ($M^+-3CO-CH_3OH$, 62), 350 (27), 311 (37), 269 (50), 255 (53). Anal. Calcd for $C_{29}H_{30}CrO_5$ (510.55): C, 68.22; H, 5.92. Found: C, 68.21; H, 5.95.

3.1.6. (±)-(1*pR*,1″*R*)(1*pS*,1″*S*)-Tricarbonyl[2-(1-methoxyethyl)-5-*tert*-butyl-(diphenylhydroxymethyl)benzene]chromium(0) (±)-12. The procedure for the synthesis of the chiral complex (−)-**12** was followed. Methyllithium (1.31 mL, 1.76 M in diethyl ether, 2.3 mmol) was added dropwise at −78°C to a stirred solution of tetramethylpiperidine (0.39 mL, 2.3 mmol) in THF (20 mL). Complex (±)-**11** (657 mg, 2.0 mmol) in THF (8 mL) was added followed by the addition of benzophenone (1.26 g, 6.9 mmol) in THF (5 mL). Flash column chromatography of the residue gave 950 mg (93%) of complex (±)-**12** as a yellow solid. Mp: 158–159°C. All other data were identical to those obtained for (−)-**12**.

3.1.7. (+)-(*R*)-Tricarbonyl[1-(1-methoxy-2-phenylethyl)-4-*tert*-butylbenzene]chromium(0) (+)-14. *n*-Butyllithium (1.53 mL, 1.6 M in hexane, 2.45 mmol) was added dropwise to a stirred solution of diamine **7**–H_2 (515 mg, 1.22 mmol) in THF (12 mL) at −78°C and the solution was allowed to reach room temperature over 30 min. The resulting deep

pink solution of the chiral diamide **7** was then re-cooled to −78°C and a solution of heat gun-dried lithium chloride (52 mg, 1.22 mmol) in THF (8 mL) was added via a cannula. Stirring was continued for a further 5 min before a pre-cooled solution (−78°C) of complex **10** (350 mg, 1.11 mmol) in THF (5 mL) was added dropwise (ca. 2 min) via a short cannula. After stirring the orange solution at −78°C for 30 min, benzyl bromide (0.4 mL, 3.33 mmol) was added in one portion which resulted in a colour change of the solution to yellow. Stirring was continued for a further 50 min before methanol (1 mL) was added and the solvent removed in vacuo. Flash column chromatography (SiO_2; hexane/dichloromethane, 9:1–7:3) of the residue gave 412 mg (92%) of the title complex (+)-**14** as a yellow solid. Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 98:2, 0.3 mL/min, 330 nm); (*S*)-enantiomer t_r=28.6 min (minor); (*R*)-enantiomer t_r=29.8 min (major): 97% ee. $[\alpha]_D^{23}$=+33.4 (*c* 0.5, CH_2Cl_2). Mp: 86–89°C. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1962 (s), ν_{CO} 1882 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 1.29 (s, 9H, $(CH_3)_3C$), 2.94 (dd, *J*=13.8, 5.2 Hz, 1H, CHC*H*HPh), 3.04 (dd, *J*=13.8, 7.4 Hz, 1H, CHCH*H*Ph), 3.45 (s, 3H, OCH_3), 4.10 (dd, *J*=7.4, 5.2 Hz, 1H, C*H*CH_2Ph), 4.93 (dd, *J*=6.9, 1.7 Hz, 1H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}$*H*), 5.37 (dd, *J*=6.9, 1.7 Hz, 1H, C_{Cr}(*t*-Bu)C_{Cr}*H*C_{Cr}H), 5.40 (dd, *J*=6.9, 1.7 Hz, 1H, C_{Cr}(*t*-Bu)C_{Cr}H′C_{Cr}*H*′), 5.46 (dd, *J*=6.9, 1.7 Hz, 1H, C_{Cr}(*t*-Bu)C_{Cr}*H*′C_{Cr}H′), 7.12–7.14 (m, 2H, H_{ar}), 7.23–7.30 (m, 3H, H_{ar}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.0 ((*C*H_3)$_3$C), 33.9 ((CH$_3$)$_3$*C*), 44.1 (CH*C*H_2Ph), 58.6 (OCH_3), 82.0 (*C*HCH_2Ph), 88.6 (C_{Cr}H), 89.7 (C_{Cr}H), 90.8 (*C*$_{Cr}$H), 91.1 (*C*$_{Cr}$H), 112.2 (*C*$_{Cr}$CH(Bn)OMe), 123.1 (C_{Cr}(*t*-Bu)), 126.6 (C_{ar}H), 128.3 (2C, C_{ar}H), 129.7 (2C, C_{ar}H), 137.2 (C_{ar}), 233.6 (C≡O). MS (EI): *m/z* (%) 404 (M^+, 5), 320 (M^+−3CO, 50), 288 (M^+−3CO−CH_3OH, 12), 177 (M^+−Cr(CO)$_3$−C_7H_7, 100), 147 (M^+−Cr(CO)$_3$−C_7H_7−‴ CH_2O, 18). Anal. Calcd for $C_{22}H_{24}CrO_4$ (404.42): C, 65.34; H, 5.98. Found: C, 65.43; H, 6.08.

3.1.8. (±)-(*R*)(*S*)-Tricarbonyl[1-(1-methoxy-2-phenylethyl)-4-*tert*-butylbenzene]chromium(0) (±)-14. *t*-Butyllithium (1.46 mL, 1.68 M in hexane, 2.45 mmol) was added dropwise to a stirred solution of complex **10** (700 mg, 2.23 mmol) in THF (22 mL) at −78°C. The resulting deep orange solution was stirred for 1.5 h. Benzyl bromide (0.8 mL, 6.69 mmol) was added in one portion which resulted in a colour change of the solution to yellow. Stirring was continued at −78°C for a further 3 h before methanol (1 mL) was added and the solvent removed in vacuo. Flash column chromatography (SiO_2; hexane/diethyl ether, 9:1–1:1) of the residue offered 865 mg (96%) of the title complex (±)-**14** as a yellow solid. Mp: 85–86°C. All other data were identical to those obtained for (+)-**14**.

3.1.9. (−)-(1*pR*,1″*R*)-Tricarbonyl[1-diphenylphosphine-2-(1-methoxy-2-phenylethyl)-5-*tert*-butylbenzene]chromium(0) (−)-15. The procedure for the synthesis of the chiral complex (−)-**12** was followed. Methyllithium (0.40 mL, 1.57 M in diethyl ether, 0.63 mmol) was added dropwise at −78°C to a stirred solution of tetramethylpiperidine (0.11 mL, 0.63 mmol) in THF (8 mL). Complex (+)-**14** (212 mg, 0.52 mmol) in THF (5 mL) was added followed by the addition of chlorodiphenylphosphine (0.28 mL, 1.56 mmol). Flash column chromatography (SiO_2; hexane/diethyl ether, 95:5) of the residue gave 281 mg (91%) of complex (−)-**15** as a yellow solid. Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 99.6:0.4, 0.6 mL/min, 330 nm); (*pR*,*R*)-enantiomer t_r=16.2 min (major); (*pS*,*S*)-enantiomer t_r=22.1 min (minor): 97% ee. $[\alpha]_D^{20}$=−312 (*c* 0.75, CH_2Cl_2). Mp: 138–145°C. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1963 (s), ν_{CO} 1900 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 1.11 (s, 9H, $(CH_3)_3C$), 2.59 (s, 3H, OCH_3), 2.99 (dd, *J*=14.0, 10.0 Hz, 1H, CHC*H*HPh), 3.39 (dd, *J*=14.0, 2.7 Hz, 1H, CHCH*H*Ph), 4.94 (virt t, *J*=1.9 Hz, 1H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}PPh_2$), 5.06 (ddd, *J*=10.0, 5.9, 2.7 Hz, 1H, C*H*CH_2Ph), 5.50 (dd, *J*=6.8, 3.0 Hz, 1H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}$*H*), 5.59 (d, *J*=6.8 Hz, 1H, C_{Cr}(*t*-Bu)C_{Cr}*H*C_{Cr}H), 7.21–7.25 (m, 1H, H_{ar}), 7.30–7.41 (m, 14H, H_{ar}). ^{31}P NMR (162 MHz, $CDCl_3$): δ −13.1 ($C_{Cr}PPh_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.8 ((*C*H_3)$_3$C), 33.9 ((CH$_3$)$_3$*C*), 40.9 (CH*C*H_2Ph), 57.0 (OCH_3), 79.9 (d, *J*=18.2 Hz, *C*HCH_2Ph), 89.6 (d, *J*=4.5 Hz, C_{Cr}(*t*-Bu)*C*$_{Cr}HC_{Cr}PPh_2$), 91.4 (C_{Cr}(*t*-Bu)*C*$_{Cr}HC_{Cr}$H), 95.8 (d, *J*=2.8 Hz, C_{Cr}(*t*-Bu)C_{Cr}H*C*$_{Cr}$H), 102.7 (d, *J*=23.0 Hz, C_{Cr}(*t*-Bu)C_{Cr}H*C*$_{Cr}PPh_2$), 117.1 (d, *J*=21.2 Hz, *C*$_{Cr}$CH(Bn)OMe), 122.3 (C_{Cr}(*t*-Bu)), 126.4 (C_{Ph}H), 128.4 (2C, C_{Ph}H), 128.5 (d, *J*=7.0 Hz, 2C, C_{PPh}H), 128.6 (d, *J*=6.8 Hz, 2C, C_{PPh}H), 129.0 (C_{PPh}H), 129.4 (2C, C_{Ph}H), 129.7 (C_{PPh}H), 133.4 (d, *J*=19.6 Hz, 2C, C_{PPh}H), 134.3 (d, *J*=12.5 Hz, C_{PPh}), 134.7 (d, *J*=20.2 Hz, 2C, C_{PPh}H), 135.9 (d, *J*=9.0 Hz, C_{PPh}), 138.8 (C_{Ph}), 232.7 (C≡O). MS (EI): *m/z* (%) 588 (M^+, 5), 504 (M^+−3CO, 100), 472 (M^+−3CO−CH_3OH, 10), 452 (M^+−Cr(CO)$_3$, 6), 437 (M^+−Cr(CO)$_3$−CH_3, 29), 421 (M^+−Cr(CO)$_3$−P, 18). Anal. Calcd for $C_{34}H_{33}CrO_4P$ (588.60): C, 69.38; H, 5.65. Found: C, 69.32; H, 5.59.

3.1.10. (±)-(1*pR*,1″*R*)(1*pS*,1″*S*)-Tricarbonyl[1-diphenylphosphine-2-(1-methoxy-2-phenylethyl)-5-*tert*-butylbenzene]chromium(0) (±)-15. The procedure for the synthesis of the chiral complex (−)-**15** was followed. Methyllithium (0.57 mL, 1.57 M in diethyl ether, 0.9 mmol) was added dropwise at −78°C to a stirred solution of tetramethylpiperidine (0.16 mL, 0.9 mmol) in THF (11 mL). Complex (±)-**14** (303 mg, 0.75 mmol) in THF (5 mL) was added followed by the addition of chlorodiphenylphosphine (0.4 mL, 2.25 mmol). Flash column chromatography of the residue gave 382 mg (87%) of complex (±)-**15** as a yellow solid. Mp: 129–130°C. All other data were identical to those obtained for (−)-**15**.

3.1.11. (−)-(1*pR*,1″*R*)-Tricarbonyl[1-diphenylphosphine-2-(1-methoxyethyl)-5-*tert*-butylbenzene]chromium(0) (−)-16. Methyllithium (0.42 mL, 1.57 M in diethyl ether, 0.66 mmol) was added dropwise to a stirred solution of tetramethylpiperidine (0.11 mL, 0.66 mmol) in THF (8 mL) at −78°C. The solution was allowed to reach room temperature for 30 min and re-cooled to −78°C. Complex (+)-**11** (181 mg, 0.55 mmol) in THF (5 mL) was added via a cannula and the resulting orange solution was stirred for 1 h. Chlorodiphenylphosphine (0.22 mL, 1.65 mmol) was added in one portion which resulted in a colour change of the solution to yellow. Stirring was continued for a further 2 h at −78°C before the reaction vessel was removed from the acetone/dry ice bath and the reaction mixture stirred at room temperature for 1 h. Methanol (0.5 mL) was added and the solvent removed in vacuo. Flash column

chromatography (SiO_2; hexane/diethyl ether, 100:0–95:5) of the residue gave 248 mg (88%) of complex (−)-**16** as a yellow oil which solidified slowly on standing. Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 99.6:0.4, 0.6 mL/min, 330 nm); (*pS*,*S*)-enantiomer t_r=12.0 min (minor); (*pR*,*R*)-enantiomer t_r=13.3 min (major): 96% ee. $[\alpha]_D^{20}$=−356 (*c* 0.57, CH_2Cl_2). IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1963 (s), ν_{CO} 1900 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 1.09 (s, 9H, $(CH_3)_3C$), 1.47 (d, *J*=6.4 Hz, 3H, $CHCH_3$), 2.91 (s, 3H, OCH_3), 4.99 (virt t, *J*=1.9 Hz, 1H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}PPh_2$), 5.01 (q, *J*=6.5 Hz, 1H, $CHCH_3$), 5.32 (dd, *J*=6.8, 3.1 Hz, 1H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}H$), 5.62 (dd, *J*=6.8, 1.9 Hz, 1H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}H$), 7.36–7.40 (m, 10H, PPh_2). ^{31}P NMR (162 MHz, $CDCl_3$): δ −12.0 ($C_{Cr}PPh_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.7 ($CHCH_3$), 30.9 ($(CH_3)_3C$), 33.8 ($(CH_3)_3C$), 55.6 (OCH_3), 74.3 (d, *J*=19.5 Hz, $CHCH_3$), 87.2 (d, *J*=4.3 Hz, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}PPh_2$), 92.4 (C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}H$), 97.0 (d, *J*=3.0 Hz, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}H$), 102.6 (d, *J*=22.9 Hz, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}PPh_2$), 117.0 (d, *J*=21.3 Hz, $C_{Cr}CH(Me)OMe$), 121.5 (C_{Cr}(*t*-Bu)), 128.3 (d, *J*=7.2 Hz, 2C, $C_{ar}H$), 128.6 (d, *J*=7.1 Hz, 2C, $C_{ar}H$), 128.7 ($C_{ar}H$), 129.6 ($C_{ar}H$), 133.2 (d, *J*=20.1 Hz, 2C, $C_{ar}H$), 134.6 (d, *J*=10.7 Hz, C_{ar}), 134.7 (d, *J*=20.2 Hz, 2C, $C_{ar}H$), 136.3 (d, *J*=8.9 Hz, C_{ar}), 232.7 (C≡O). MS (EI): *m*/*z* (%) 512 (M^+, 13), 456 (M^+−2CO, 7), 428 (M^+−3CO, 100), 396 (M^+−3CO−CH_3OH, 32), 370 (M^+−3CO−C_3H_6O, 28), 345 (M^+−$Cr(CO)_3$−P, 10). Anal. Calcd for $C_{28}H_{29}CrO_4P$ (512.50): C, 65.62; H, 5.70. Found: C, 65.55; H, 5.64.

3.1.12. (±)-(1*pR*,1″*R*)(1*pS*,1″*S*)-Tricarbonyl[1-diphenylphosphine-2-(1-methoxyethyl)-5-*tert*-butylbenzene]chromium(0) (±)-16. The procedure for the synthesis of the chiral complex (−)-**16** was followed. Methyllithium (0.79 mL, 1.51 M in diethyl ether, 1.2 mmol) was added dropwise to a stirred solution of tetramethylpiperidine (0.21 mL, 1.2 mmol) in THF (12 mL) at −78°C. Complex (±)-**11** (328 mg, 1.0 mmol) in THF (5 mL) was added followed by the addition of chlorodiphenylphosphine (0.54 mL, 3.0 mmol). Flash column chromatography (SiO_2; hexane/diethyl ether, 100:0–95:5) of the residue gave 475 mg (93%) of complex (±)-**16** as a yellow solid. Mp: 95–96°C. All other data were identical to those obtained for (−)-**16**.

3.1.13. (+) (*R*)-Tricarbonyl[1-(1-diphenylphosphine-1-methoxymethyl)-4-*tert*-butyl-benzene]chromium(0) (+)-17. *n*-Butyllithium (1.33 mL, 1.84 M in hexane, 2.45 mmol) was added dropwise to a stirred solution of diamine **7**–H_2 (515 mg, 1.22 mmol) in THF (12 mL) at −78°C and the solution was allowed to reach room temperature over 30 min. The resulting deep pink solution of the chiral diamide **7** was then re-cooled to −78°C and a solution of heat gun-dried lithium chloride (52 mg, 1.22 mmol) in THF (8 mL) was added via a cannula. Stirring was continued for a further 5 min before a pre-cooled solution (−78°C) of complex **10** (350 mg, 1.11 mmol) in THF (5 mL) was added dropwise (ca. 2 min) via a short cannula. After stirring the orange solution at −78°C for 30 min, chlorodiphenylphosphine (0.6 mL, 3.33 mmol) was added in one portion which resulted in a colour change of the solution to yellow. Stirring was continued for a further 50 min before methanol (1 mL) was added and the solvent removed in vacuo. Flash column chromatography (SiO_2; hexane/dichloromethane, 10:0–7:3) of the residue gave 500 mg (90%) of the title complex (+)-**17** as a yellow solid. Enantiomeric excess was determined by HPLC analysis (Chiralcel AD, *n*-hexane/*i*-PrOH, 98:2, 0.6 mL/min, 330 nm); (*S*)-enantiomer t_r=13.5 min (minor); (*R*)-enantiomer t_r=18.0 min (major): 97% ee. $[\alpha]_D^{20}$=+66.1 (*c* 0.75, CH_2Cl_2). Mp: 143–144°C. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1960 (s), ν_{CO} 1882 (s). ^1H NMR (360 MHz, $CDCl_3$): δ 1.24 (s, 9H, $(CH_3)_3C$), 3.57 (s, 3H, OCH_3), 4.76 (d, *J*=4.0 Hz, 1H, $CHPPh_2$), 4.79 (d, *J*=7.0 Hz, 1H, $C_{Cr}H$), 5.14 (d, *J*=7.0 Hz, 1H, $C_{Cr}H$), 5.27 (s, 2H, $C_{Cr}H$), 7.28–7.39 (m, 8H, H_{ar}), 7.48–7.52 (m, 2H, H_{ar}). ^{31}P NMR (146 MHz, $CDCl_3$): δ 11.3 (PPh_2). ^{13}C NMR (90 MHz, $CDCl_3$): δ 30.8 ($(CH_3)_3C$), 33.8 ($(CH_3)_3C$), 60.0 (d, *J*=4.2 Hz, OCH_3), 83.2 (d, *J*=14.3 Hz, $CHPPh_2$), 89.5 (C_{Cr}(*t*-Bu)$C_{Cr}H$), 89.9 (C_{Cr}(*t*-Bu)$C'_{Cr}H$), 90.1 (d, *J*=3.6 Hz, $C_{Cr}HC_{Cr}CH(PPh_2)OMe$), 90.3 (d, *J*=6.3 Hz, $C'_{Cr}HC_{Cr}CH(PPh_2)OMe$), 108.9 (d, *J*=16.5 Hz, $C_{Cr}CH(PPh_2)OMe$), 123.9 (C_{Cr}(*t*-Bu)), 128.2 ($C_{ar}H$), 128.3 (2C, $C_{ar}H$), 128.4 ($C_{ar}H$), 129.3 (d, *J*=2.3 Hz, 2C, $C_{ar}H$), 133.5 (d, *J*=15.4 Hz, PC_{ar}), 133.9 (d, *J*=2.2 Hz, 2C, $C_{ar}H$), 134.1 (d, *J*=1.5 Hz, 2C, $C_{ar}H$), 134.5 (d, *J*=14.1 Hz, PC_{ar}), 233.7 (C≡O). MS (EI): *m*/*z* (%) 498 (M^+, 3), 470 (M^+−CO, 16), 442 (M^+−2CO, 9), 414 (M^+−3CO, 100), 384 (M^+−3CO−H_2CO, 38), 306 (M^+−3CO−C_6H_5P, 14), 257 (M^+−2CO−PPh_2, 6), 177 (M^+−$Cr(CO)_3$−PPh_2, 99). Anal. Calcd for $C_{27}H_{27}CrO_4P$ (498.48): C, 65.06; H, 4.46. Found: C, 64.97; H, 4.43.

Crystal data for (+)-**17**: $C_{27}H_{27}CrO_4P$, *M* 498.46 g mol^{-1}, monoclinic, space group $P2_1$, *a*=7.8107(4), *b*=26.3322(15), *c*=12.0494(6) Å, β=94.196(4)°, *U*=2471.6(2) $Å^3$, *Z*=4, μ=5.58 cm^{-1}, *T*=120 K, Reflections measured: 13,677, unique data: 8398 (R_{int}=0.140), parameters: 596, R_1 [$F^2>2\sigma(F^2)$] 0.1127, wR_2 (all data) 0.2227. Final Flack parameter: 0.02(4), indicating correct absolute structure despite the relatively poor overall precision of the data. Crystals were mounted on a thin glass fibre using silicon grease and cooled on the diffractometer to 100 K using an Oxford Cryostream low temperature attachment. Data were collected in wide-slicing mode using a Nonius ^{Kappa}CD diffractometer, with a detector to crystal distance of 30 mm. Crystals were indexed from five preliminary frames each of 2° width in φ using the Nonius Collect package.[18] The crystals proved to be extremely weakly diffracting with a large mosaic spread. Full data was collected using 0.9° φ and ω frames at a rate of 95 s deg^{-1}. Final unit cell dimensions and positional data were refined on the entire data set along with diffractometer constants to give the final unit cell parameters. Integration and scaling (DENZO, Scalepack[19]) resulted in data set corrected for Lorentz and polarisation effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. Structures were solved by direct methods (SHELXS-97[20]) and developed via alternating least squares cycles and difference Fourier synthesis (SHELXL-97[21]) with the aid of the XSeed interface.[22] The asymmetric unit was found to comprise of two independent molecules. All non-hydrogen atoms were modelled anisotropically. Hydrogen atoms were placed in calculated positions and allowed to ride on the atoms to which they were attached with an isotropic thermal parameter 1.2 times that of the parent atom (1.5 times for CH_3

groups). All calculations were carried out with either a Silicon Graphics Indy R5000 workstation or an IBM compatible PC. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 175591. Copies of the data can be obtained, free of charge, an application to CCDC, 12 Union Road, Cambridge CB IE2, UK [fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

3.1.14. (±)-(*R*)(*S*)-Tricarbonyl[1-(1-diphenylphosphine-1-methoxymethyl)-4-*tert*-butyl-benzene]chromium(0) (±)-17. *t*-Butyllithium (0.64 mL, 1.65 M in hexane, 1.05 mmol) was added dropwise to a stirred solution of complex **10** (300 mg, 0.95 mmol) in THF (10 mL) at −78°C. The resulting deep orange solution was stirred for 1.5 h. Chlorodiphenylphosphine (0.51 mL, 2.85 mmol) was added in one portion which resulted in a colour change of the solution to yellow. Stirring was continued at −78°C for a further 3 h before methanol (1 mL) was added and the solvent removed in vacuo. Flash column chromatography (SiO_2; hexane/diethyl ether, 1:0–4:1) of the residue offered 448 mg (95%) of the title complex (±)-**17** as a yellow solid. Mp: 122–123°C. All other data were identical to those obtained for (+)-**17**.

3.1.15. (+)-(*R*)-Tricarbonyl[1-(1-di-*iso*-propylphosphine-1-methoxymethyl)-4-*tert*-butylbenzene] chromium(0) (+)-18. *n*-Butyllithium (0.8 mL, 1.6 M in hexane, 1.27 mmol) was added dropwise to a stirred solution of diamine **7**–H_2 (268 mg, 0.64 mmol) in THF (5 mL) at −78°C and the solution was allowed to reach room temperature for 30 min. The resulting deep pink solution of the chiral diamide **7** was then re-cooled to −78°C and a solution of heat gun-dried lithium chloride (27 mg, 0.64 mmol) in THF (3 mL) was added via a cannula. Stirring was continued for a further 5 min before a pre-cooled solution (−78°C) of complex **10** (200 mg, 0.64 mmol) in THF (3 mL) was added dropwise (ca. 1 min) via a short cannula. After stirring the orange solution at −78°C for 30 min, chlorodi-*iso*-propylphosphine (0.2 mL, 1.27 mmol) was added in one portion which resulted in a colour change of the solution to yellow. Stirring was continued for a further 2 h before methanol (1 mL) was added and the solvent removed in vacuo. Flash column chromatography (SiO_2; hexane/dichloromethane, 10:0–7:3) of the residue gave 223 mg (81%) of the title complex (+)-**18** as a yellow solid. Enantiomeric excess was determined by HPLC analysis (Chiralcel AD, *n*-hexane/*i*-PrOH, 99.6:0.4, 0.6 mL/min, 330 nm); (*S*)-enantiomer t_r=9.0 min (minor); (*R*)-enantiomer t_r=9.4 min (major): 97% ee. $[\alpha]_D^{20}$=+109.4 (*c* 0.5, CH_2Cl_2). Mp: 110–112°C. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1959 (s), ν_{CO} 1881 (s). ^1H NMR (360 MHz, $CDCl_3$): δ 0.94 (dd, *J*=7.2, 2.2 Hz, 3H, CH_3), 0.98 (d, *J*=7.2 Hz, 3H, CH_3), 1.05 (dd, *J*=14.2, 7.1 Hz, 3H, CH_3), 1.10 (dd, *J*=12.2, 7.0 Hz, 3H, CH_3), 1.22 (s, 9H, $(CH_3)_3C$), 1.82–1.92 (m, 1H, C*H*$(CH_3)_2$), 2.01–2.10 (m, 1H, C*H*$(CH_3)_2$), 3.55 (s, 3H, OCH_3), 4.46 (d, *J*=4.5 Hz, 1H, CH(P*i*-Pr_2)OMe), 5.17 (d, *J*=6.8 Hz, 1H, $C_{Cr}H$), 5.46–5.52 (m, 3H, $C_{Cr}H$). ^{31}P NMR (146 MHz, $CDCl_3$): δ 37.2 ($P(CH(CH_3)_2)_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.2 (d, *J*=10.6 Hz, 2C, $CH(CH_3)_2$), 20.3 (d, *J*=16.0 Hz, $CH(CH_3)_2$), 21.1 (d, *J*=16.4 Hz, $CH(CH_3)_2$), 21.68 (d, *J*=14.6 Hz, $CH(CH_3)_2$), 21.72 (d, *J*=15.5 Hz, $CH(CH_3)_2$), 80.0 (d, *J*=28.0 Hz, CH(P*i*-Pr_2)OMe), 89.0 (d, *J*=1.9 Hz, $C_{Cr}HC_{Cr}CH$(P*i*-Pr_2)OMe), 89.2 (d, *J*=12.2 Hz, $C'_{Cr}HC_{Cr}CH$(P*i*-Pr_2)OMe), 91.3 (C_{Cr}(*t*-Bu)$C_{Cr}H$), 91.9 (C_{Cr}(*t*-Bu)$C'_{Cr}H$), 112.3 (d, *J*=15.1 Hz, $C_{Cr}CH$(P*i*-Pr_2)OMe), 123.0 (C_{Cr}(*t*-Bu)), 234.0 (C≡O). MS (FAB): *m/z* (%) 430 (M^+, 1), 402 (M^+−CO, 76), 374 (M^+−2CO, 65), 346 (M^+−3CO, 100), 316 (M^+−3CO−H_2CO, 12), 272 (M^+−3CO−P*i*-Pr_2, 27), 177 (M^+−$Cr(CO)_3$−P*i*-Pr_2, 90). Anal. Calcd for $C_{21}H_{31}CrO_4P$ (430.44): C, 58.60; H, 7.26. Found: C, 58.52; H, 7.25.

3.1.16. (±)-(*R*)(*S*)-Tricarbonyl[1-(1-di-*iso*-propylphosphine-1-methoxymethyl)-4-*tert*-butylbenzene] chromium(0) (±)-18. *t*-Butyllithium (0.50 mL, 1.54 M in pentane, 0.76 mmol) was added dropwise to a stirred solution of complex **10** (200 mg, 064 mmol) in THF (8 mL) at −30°C. The resulting deep orange solution was stirred for 1.5 h. Chlorodi-*iso*-propylphosphine (0.20 mL, 1.27 mmol) was added in one portion which resulted in a colour change of the solution to yellow. Stirring was continued at −30°C for a further 14 h before methanol was added and the solvent removed in vacuo. Flash column chromatography (SiO_2; hexane/dichloromethane, 10:0–7:3) of the residue offered 240 mg (88%) of the title complex (±)-**18** as a yellow solid. Mp: 100–102°C. All other data were identical to those obtained for (+)-**18**.

3.1.17. (+)-(*R*)-Tricarbonyl[1-(1-di-*t*-butylphosphine-methoxymethyl)-4-*tert*-butyl-benzene] chromium(0) (+)-19. *n*-Butyllithium (0.8 mL, 1.6 M in hexane, 1.27 mmol) was added dropwise to a stirred solution of diamine **7**–H_2 (268 mg, 0.64 mmol) in THF (5 mL) at −30°C and the solution was allowed to reach room temperature for 30 min. The resulting deep pink solution of the chiral diamide **7** was then re-cooled to −30°C and a solution of heat gun-dried lithium chloride (27 mg, 0.64 mmol) in THF (3 mL) was added via a cannula. Stirring was continued for a further 5 min before a pre-cooled solution (−30°C) of complex **10** (200 mg, 0.64 mmol) in THF (3 mL) was added dropwise (ca. 1 min) via a short cannula. After stirring the orange solution at −30°C for 30 min, chlorodi-*t*-butylphosphine (0.24 mL, 1.27 mmol) was added in one portion which resulted in a colour change of the solution to yellow. Stirring was continued for a further 6 h before methanol (1 mL) was added and the solvent removed in vacuo. Flash column chromatography (SiO_2; hexane/dichloromethane, 10:0–7:3) of the residue gave 231 mg (79%) of the title complex (+)-**19** as a yellow solid. Enantiomeric excess was determined by HPLC analysis (Chiralcel AD, *n*-hexane/*i*-PrOH, 98:2, 0.4 mL/min, 330 nm); (*S*)-enantiomer t_r=10.9 min (minor); (*R*)-enantiomer t_r=11.5 min (major): 86% ee. $[\alpha]_D^{20}$=+121 (*c* 0.5, CH_2Cl_2). Mp: 134–136°C. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1958 (s), ν_{CO} 1879 (s). ^1H NMR (360 MHz, $CDCl_3$): δ 1.08 (d, *J*=11.6 Hz, 9H, $PC(CH_3)_3$), 1.21 (s, 9H, $(CH_3)_3CC_{Cr}$), 1.25 (d, *J*=11.5 Hz, 9H, $PC(CH_3)_3$), 3.58 (s, 3H, OCH_3), 4.65 (s, 1H, CHP(OMe)), 5.20 (d, *J*=6.9 Hz, 1H, $C_{Cr}H$), 5.47–5.56 (m, 3H, $C_{Cr}H$). ^{31}P NMR (146 MHz, $CDCl_3$): δ 65.2 ($P(C(CH_3)_3)_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.3 (d, *J*=12.7 Hz, 3C, $PC(CH_3)_3$), 30.06 ($C_{Cr}C(CH_3)_3$), 30.1 (d, *J*=12.5 Hz, 3C, $PC(CH_3)_3$), 31.8 (d, *J*=21.4 Hz, 30.06 ($PC(CH_3)_3$), 32.8 ($C_{Cr}C(CH_3)_3$), 34.0 (d, *J*=25.1 Hz,

P*C*(CH_3)$_3$), 59.2 (OCH_3), 80.4 (d, J=36.5 Hz, CHP), 88.2 (d, J=2.5 Hz, $C_{Cr}HC_{Cr}CH$(P*t*-Bu$_2$)OMe), 88.9 (d, J=17.6 Hz, $C'_{Cr}HC_{Cr}CH$(P*t*-Bu$_2$)OMe), 90.2 (C_{Cr}(*t*-Bu)C_{Cr}H), 91.0 (C_{Cr}(*t*-Bu)C'_{Cr}H), 112.7 (d, J=22.6 Hz, $C_{Cr}CH$(P*t*-Bu$_2$)OMe), 121.7 ($C_{Cr}C(CH_3)_3$), 233.0 (C≡O). MS (FAB): *m*/*z* (%) 458 (M^+, 3), 430 (M^+-CO, 11), 402 (M^+-2CO, 36), 374 (M^+-3CO, 100), 344 ($M^+-3CO-H_2CO$, 2), 286 (M^+-3CO-P*t*-Bu, 4), 229 (M^+-3CO-P*t*-Bu$_2$, 25), 177 ($M^+-Cr(CO)_3-$P*t*-Bu$_2$, 94). Anal. Calcd for $C_{23}H_{35}CrO_4P$ (458.50): C, 60.25; H, 7.69. Found: C, 60.29; H, 7.61.

3.1.18. (±)-(*R*)(*S*)-Tricarbonyl[1-(1-di-*t*-butylphosphinomethoxymethyl)-4-*tert*-butyl-benzene] chromium(0) (±)-19. *t*-Butyllithium (0.5 mL, 1.54 M in hexane, 0.76 mmol) was added dropwise to a stirred solution of complex **10** (200 mg, 0.64 mmol) in THF (8 mL) at −30°C. The resulting deep orange solution was stirred for 1.5 h. Chlorodi-*t*-butylphosphine (0.24 mL, 1.27 mmol) was added in one portion which resulted in a colour change of the solution to yellow. Stirring was continued at −30°C for a further 15 h before methanol was added and the solvent removed in vacuo. Flash column chromatography (SiO_2; hexane/dichloromethane, 10:0–7:3) of the residue offered 225 mg (77%) of the title complex (±)-**19** as a yellow solid. Mp: 147–149°C. All other data were identical to those obtained for (+)-**19**.

3.1.19. (−)-(1*pR*,1″*R*)-Tricarbonyl[1-diphenylphosphine-2-(1-diphenylphosphine-1-methoxymethyl)-5-*tert*-butylbenzene]chromium(0) (−)-20. The procedure for the synthesis of the chiral complex (−)-**12** was followed. Methyllithium (0.51 mL, 1.65 M in diethyl ether, 0.84 mmol) was added dropwise at −78°C to a stirred solution of tetramethylpiperidine (0.15 mL, 0.84 mmol) in THF (12 mL). Complex (+)-**17** (350 mg, 0.7 mmol) in THF (5 mL) was added followed by the addition of chlorodiphenylphosphine (0.35 mL, 0.21 mmol). Flash column chromatography (SiO_2; hexane/diethyl ether, 10:0–5:5) of the residue gave 470 mg (98%) of complex (−)-**20** as a crystalline yellow solid. Enantiomeric excess was determined by HPLC analysis (Chiralcel AD, *n*-hexane/*i*-PrOH, 99:1, 0.6 mL/min, 330 nm); (*pS*,*S*)-enantiomer t_r=11.2 min (minor); (*pR*,*R*)-enantiomer t_r=14.0 min (major): 97% ee. $[\alpha]_D^{20}=-242$ (*c* 0.5, CH_2Cl_2). Mp: 78–80°C. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1964 (s), ν_{CO} 1893 (s). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.05 (s, 9H, $(CH_3)_3C$), 2.55 (s, 3H, OCH_3), 4.84 (s, 1H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}PPh_2$), 5.22 (ddd, J=6.8, 3.2, 2.3 Hz, 1H, $CHPPh_2$), 5.36 (dd, J=7.0, 1.0 Hz, 1H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}$H), 5.70 (dd, J=7.0, 4.6 Hz, 1H, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}$*H*), 7.25–7.28 (m, 1H, H_{ar}), 7.32 (dt, J=7.2, 1.5 Hz, 2H, H_{ar}), 7.37–7.49 (m, 15H, H_{ar}), 7.92 (dt, J=7.7, 1.7 Hz, 2H, H_{ar}). ^{31}P NMR (146 MHz, $CDCl_3$): δ −1.4 (d, J=10.1 Hz, $CHPPh_2$), −13.0 (d, J=10.1 Hz, $C_{Cr}PPh_2$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 30.8 ($(CH_3)_3C$), 33.8 ($(CH_3)_3C$), 59.0 (OCH_3), 82.6 (dd, J=31.1, 17.5 Hz, $CHPPh_2$), 91.0 (C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}$H), 93.4 (dd, J=13.2, 4.1 Hz, $C_{Cr}HC_{Cr}CH(PPh_2)OMe$), 95.1 (d, J=2.5 Hz, C_{Cr}(*t*-Bu)$C_{Cr}HC_{Cr}PPh_2$), 101.8 (d, J=4.6 Hz, $C_{Cr}CH(PPh_2)OMe$), 116.0 (dd, J=21.8, 16.1 Hz, $C_{Cr}PPh_2$), 122.0 (C_{Cr}(*t*-Bu)), 128.0 (C_{ar}H), 128.4 (d, J=5.8 Hz, 2C, C_{ar}H), 128.49 (d, J=5.8 Hz, 2C, C_{ar}H), 128.54 (2C, C_{ar}H), 128.6 (d, J=3.2 Hz, 2C, C_{ar}H), 129.1 (C_{ar}H), 129.7 (d, J=25.5 Hz, 2C, C_{ar}H), 132.2 (d, J=18.3 Hz, 2C, C_{ar}H), 133.4 (d, J=15.8 Hz, PC_{ar}), 133.6 (d, J=19.9 Hz, 2C, C_{ar}H), 134.4 (d, J=12.6 Hz, PC_{ar}), 134.6 (d, J=19.6 Hz, 2C, C_{ar}H), 136.0 (d, J=9.7 Hz, PC_{ar}), 136.5 (d, J=22.3 Hz, 2C, C_{ar}H), 137.6 (d, J=14.8 Hz, PC_{ar}), 232.5 (C≡O), 232.6 (2C, C≡O). MS (EI): *m*/*z* (%) 626 (M^+-2CO, 4), 598 (M^+-3CO, 29), 361 ($M^+-Cr(CO)_3-PPh_2$, 37), 91 (C_7H_7, 100). Anal. Calcd for $C_{39}H_{36}CrO_4P_2$ (682.65): C, 68.62; H, 5.32. Found: C, 68.69; H, 5.39.

3.1.20. (±)-(1*pR*,1″*R*)(1*pS*,1″*S*)-Tricarbonyl[1-diphenylphosphine-2-(1-diphenylphosphine-1-methoxymethyl)-5-*tert*-butylbenzene]chromium(0) (±)-20. The procedure for the synthesis of the chiral complex (−)-**20** was followed. Methyllithium (0.5 mL, 1.68 M in diethyl ether, 0.84 mmol) was added dropwise to a stirred solution of tetramethylpiperidine (0.14 mL, 0.84 mmol) in THF (9 mL) at −78°C. Complex (±)-**17** (350 mg, 0.70 mmol) in THF (5 mL) was added followed by the addition of chlorodiphenylphosphine (0.37 mL, 2.1 mmol). Flash column chromatography of the residue gave 410 mg (86%) of complex (±)-**18** as a yellow solid. Mp: 145–146°C. All other data were identical to those obtained for (−)-**20**.

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