DOI: 10.1002/ejoc.200600018

Synthesis of An Enantioenriched C_2-Symmetric Molecule by a Chiral-Base-Mediated Kinetic Resolution of an (Arene)tricarbonylchromium(0) Complex

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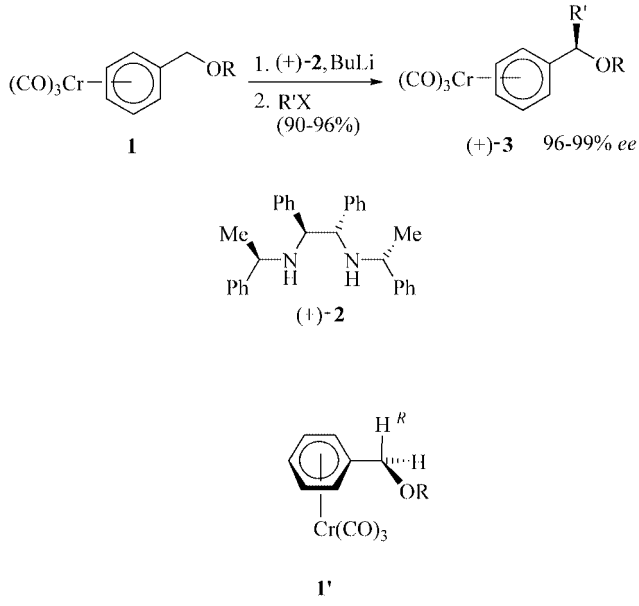
Keywords: (Arene)tricarbonylchromium(0) complex / Asymmetric synthesis / C_2 Symmetry / Chiral base / Conformational control / Kinetic resolution

Trimethylsilyl substituents have been used to control the conformational preferences of a 1,2-disubstituted (arene)tricarbonylchromium(0) complex. The kinetic resolution of the mono-methyl derivative (±)-**11** using a chiral base/iodomethane quench sequence led to the synthesis of the enantioenriched C_2-symmetric bis-ether (+)-**13**.

Introduction

The creation of new ligand motifs underpins the design of more active, economic and environmentally friendly new catalysts for use in synthetic chemistry. Ligands that are C_2-symmetric have proven to be very successful in this arena, delivering highly enantioselective catalysts based on a wide variety of transition metals.[1] Examples of widely used C_2 ligands include bis-alcohols, such as 1,1′-bi-2-naphthol (binol)[2] and the α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanols (taddols),[3] bis-phosphanes such as 2,3-*O*-isopropylidene-1,4-bis(diphenylphosphanyl)butane-2,3-diol (diop)[4] and 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl (binap),[5] and bis-oxazolines such as pybox.[6]

Tricarbonylchromium(0) complexes of arenes continue to receive widespread attention.[7] Some time ago we discovered a chiral-base-mediated reaction that efficiently generated a single chiral centre.[8] We showed that tricarbonylchromium(0) complexes of alkyl benzyl ethers such as **1** react with *n*-butyllithium/chiral bis-amine **2** and an electrophile to give the chiral ether complexes **3** in high yield and enantiomeric excess (Scheme 1). Working with the (+)-(*R*,*S*,*S*,*R*) enantiomer of the bis-amine, derived from (*R*)-α-methylbenzylamine,[9] gives the (*R*) configuration at the new stereocentre, presumably because of the preference of the base to abstract the pro-*R* benzylic hydrogen. It is anticipated that the abstraction takes place whilst the benzylic hydrogen is antiperiplanar to the arene centroid–chromium axis (see structure **1′**) to maximise the orbital overlap in the transition state, and that alkylation proceeds with retention of configuration, two well-established features of the chemistry of (arene)tricarbonylchromium(0) complexes.[10]



Scheme 1.

More recently, as part of a study of the use of this reaction to create two or three chiral centres in one pot, we examined the reactivity of the bis-ether **4**.[11] The reaction of complex **4** with one equivalent of the bis-amine (+)-**2** and two equivalents of *n*-butyllithium followed by quenching with iodomethane gave a single mono-methylated species (+)-**5** that was isolated in 99% yield and shown to have an enantiomeric excess of 99% by HPLC analysis (Scheme 2).[11] The relative and absolute stereochemistry of (+)-**5** was confirmed by X-ray crystallography.[12] The reaction of (+)-**5** with one equivalent of the bis-amine (+)-**2** and two equivalents of *n*-butyllithium followed by quenching with iodomethane subsequently gave the *meso* complex **6** in

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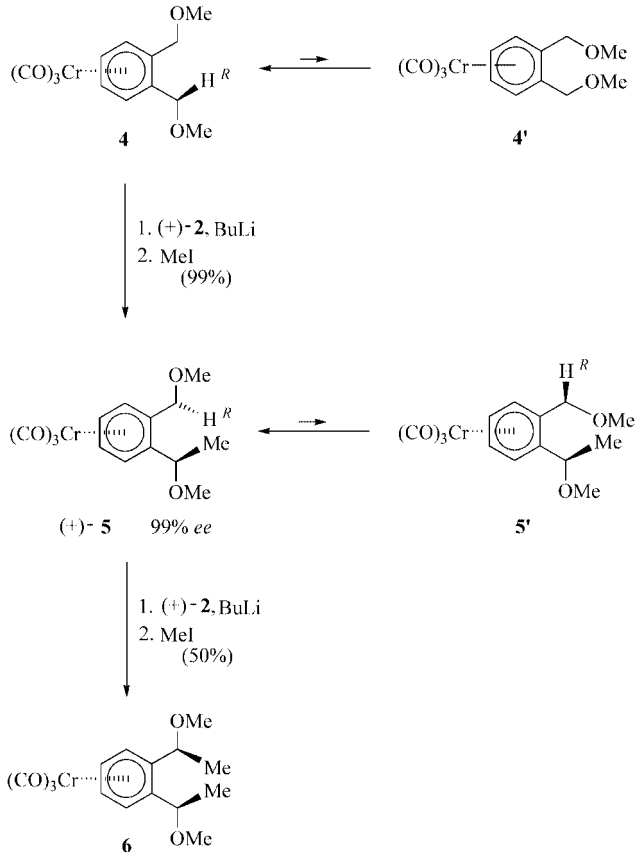
50% yield.[13] The stereochemistry of **6** was also confirmed by X-ray crystallography.[12]



Scheme 2.

The results of the two reactions depicted in Scheme 2 are explained as follows. The bis-ether complex **4** prefers to adopt conformations in which steric interactions between the two methoxy groups are minimised (e.g. conformation **4** rather than e.g. conformation **4′**). The chiral base then abstracts the only pro-*R* hydrogen, which can readily adopt an antiperiplanar relationship to the arene centroid–chromium axis (i.e. the hydrogen highlighted on structure **4**); methylation then occurs with retention of the configuration to give (+)-**5**. In order to generate a dimethylated product that is C_2-symmetric after removal of the chromium unit, the remaining pro-*R* hydrogen of **5** must be removed in the second reaction. The examination of the conformations **5** and **5′** reveals a problem: in conformation **5**, in which the interactions between the *ortho* substituents are minimised, the pro-*R* hydrogen is pointing towards the tricarbonylchromium(0) unit and is thus difficult to access for steric reasons; whilst in conformation **5′**, although the pro-*R* hydrogen can adopt the favourable antiperiplanar relationship to the chromium, the interactions between the *ortho* substituents are less favourable. The result of the second reaction reveals that in this case the conformational preferences of the substrate over-ride the preferences of the chiral base, and the pro-*S* hydrogen of **5** is abstracted, albeit inefficiently, to give the undesired *meso* complex **6**.

In order to generate a product that will provide a C_2-symmetric molecule after decomplexation, the pro-*R* hydrogen that lies buried in the tricarbonylchromium(0) unit in complex (+)-**5**, must be accessed and replaced with an electrophile. Figure 1 illustrates two approaches to this challenge. In the first, represented by structure **7**, the *ortho* substituents are tethered together to mimic the higher energy conformation **4′** (Scheme 2), whilst in the second, represented by structure **8**, bulky substituents are introduced to give the same effect. The methylation of the conformationally constrained derivatives **7** and **8** using the (+)-(*R*,*S*,*S*,*R*)-chiral base should give the mono-methylated complexes **9** and **10** by abstraction of the only pro-*R* hydrogen essentially antiperiplanar to the chromium in each substrate. Release of the conformational constraints imposed by either the tether or the bulky substituents should give the mono-

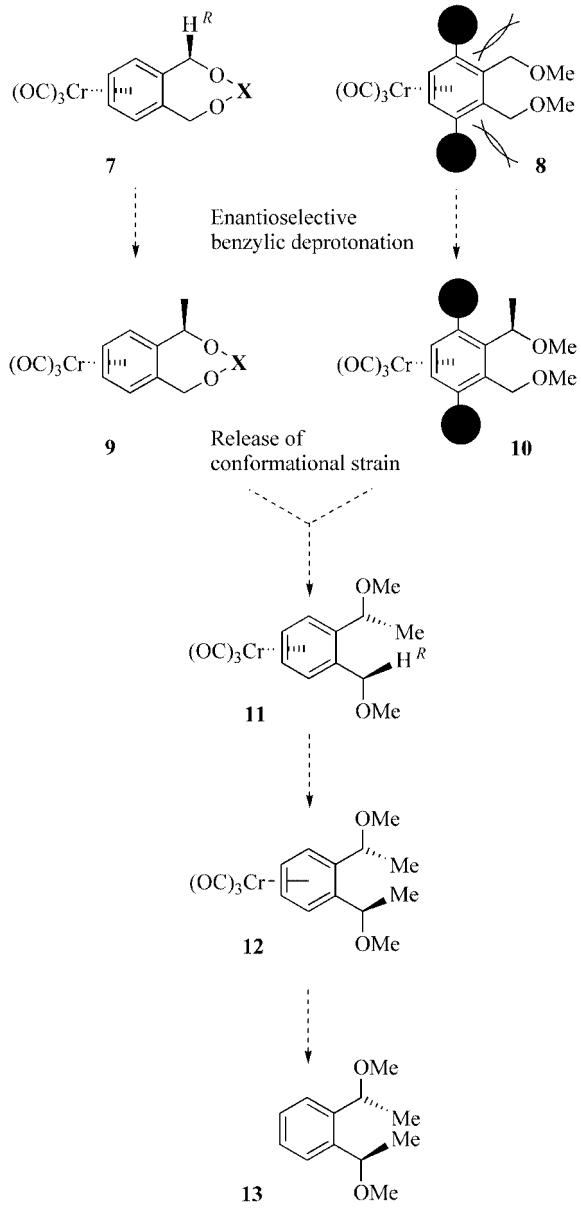
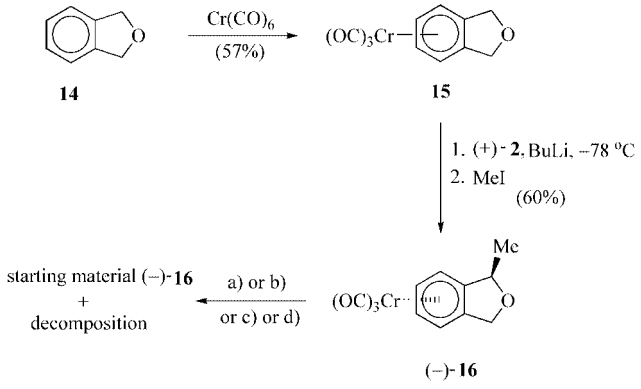


Figure 1. Two approaches to conformational control in tricarbonylchromium(0) complexes of *ortho*-substituted arenes.

methylated complex **11**, that can now access a conformation in which steric interactions between the *ortho* substituents are minimised, and the remaining pro-*R* hydrogen is placed antiperiplanar to the chromium. Deprotonation with the (+)-(*R*,*S*,*S*,*R*)-chiral base should then lead to the bis-methylated product **12**, which on decomplexation should afford the desired C_2 symmetry, depicted here in the bis-ether **13**. This paper describes a study designed to examine the feasibility of both of these approaches.

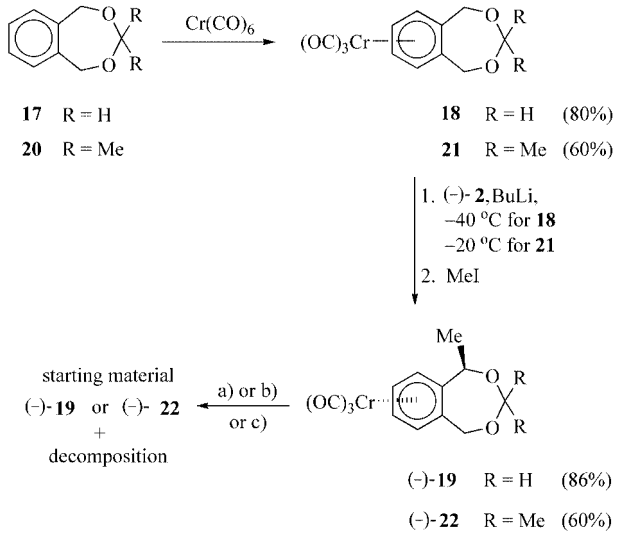
Results and Discussion

Initially, the phthalan derivative **15** was chosen to test the viability of the tethering approach. Thermolysis of commercially available 1,3-dihydroisobenzofuran **14** with hexacarbonylchromium(0), and subsequent treatment of the complex **15** with the chiral bis-amine (+)-**2** and *n*-butyllithium, followed by an iodomethane quench provided a sample of the mono-methylated complex (–)-**16** (Scheme 3).[14–16] Release of the conformational constraint in (–)-**16** was now necessary to facilitate the removal of the remaining pro-*R* benzylic hydrogen by the chiral base. Unfortunately, all attempts to open the five-membered ring resulted in either the return of starting material or a complex mixture of decomposition products, a result consistent with previous attempts to open the cyclic ether (±)-**16** with acidic methanol.[14]



Scheme 3. Et_2OBF_3 (1.1 equiv.), MeOH, 75 °C, 16 h; b) Et_2O–BF_3 (1.1 equiv.), NaOMe (1 equiv.), DCM, 50 °C, 16 h; c) H_2SO_4 (50% in water), room temp., 16 h; d) HBF_4 (54% in diethyl ether) MeOH, room temp. 16 h.

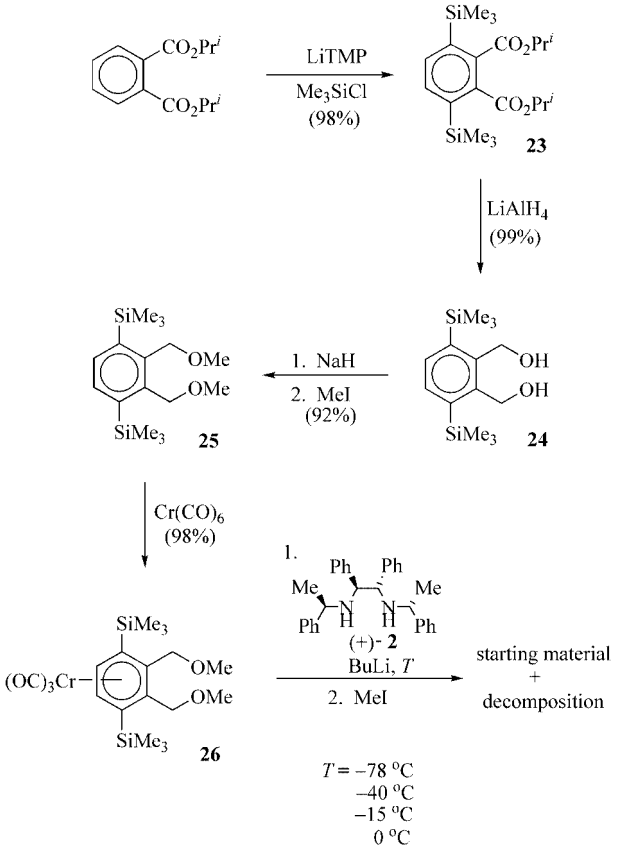
In order to try to facilitate the ring-opening step, it was decided to examine an acetal embedded in a larger ring, the cleavage of which is well documented under acidic conditions.[17] Thermolysis of 1,3-dioxa-5,6-benzocycloheptene (**17**)[18] with hexacarbonylchromium(0) delivered the novel complex **18** in 80% yield (Scheme 4). The methylation to give (–)-**19** proceeded smoothly, once it had been recognised that **18** required a higher temperature than **15** for the chiral base step (–40 °C rather than –78 °C). Attempts to cleave the ring in (–)-**19**, however, proved fruitless. A final attempt to employ the tethering strategy was made using the dimethyl ketal, 2,2-dimethyl-1,3-dioxa-5,6-benzocycloheptene (**20**),[18,19] as it is recognised that dimethyl ketals are more readily cleaved under acidic conditions than their corresponding methylene acetals.[17] The thermolysis of the ketal **20** with hexacarbonylchromium(0) proceeded smoothly to give the novel complex **21**, which was readily alkylated, providing it was treated with the chiral base at –20 °C. Interestingly, deprotonation gets steadily more difficult in the series of the substrates **15**, **18**, **21**. This is perhaps a reflection of the tendency of complexes **18** and **21** to adopt conformations that minimise steric interactions between the acetal/ketal group and the tricarbonylchromium(0) unit; such conformations make it harder for the pro-*R* benzylic hydrogen on the *exo* face of the molecule to adopt an antiperiplanar relationship to the arene centroid–chromium axis. With complex (–)-**22** in hand, a range of acidic conditions were used to try to open the ketal but, once again, only starting material and/or decomposition products were obtained.



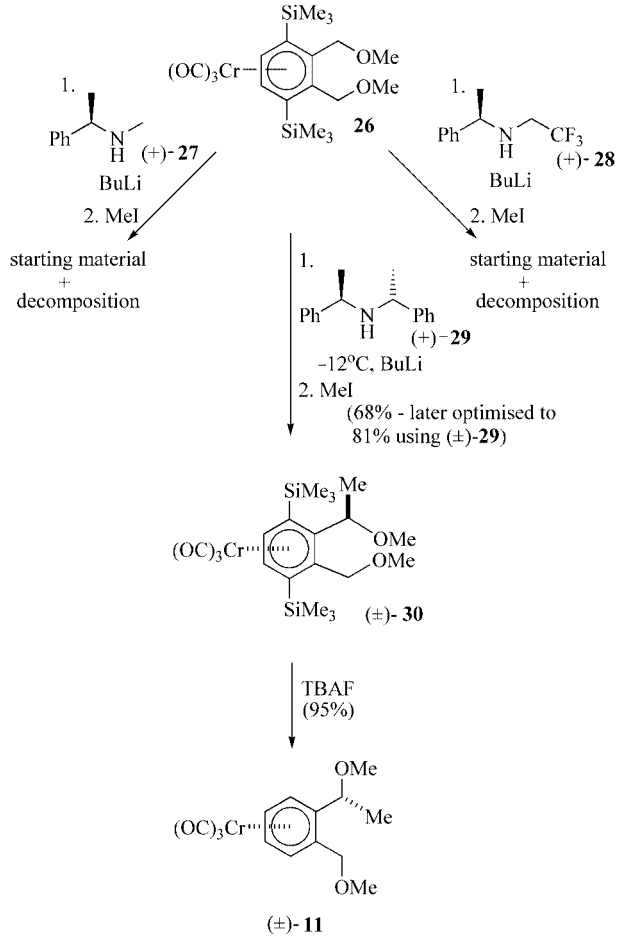
Scheme 4. A) HCl (2.7 N), MeOH, room temp., 16 h; b) HBF_4 (54% in diethyl ether), MeOH/H_2O, room temp., 16 h; c) HCl (6 N), 1,4-dioxane, room temp., 16 h.

In view of the difficulties experienced in opening the ether (–)-**16**, acetal (–)-**19** and ketal (–)-**22**, a new approach to access both pro-*R* benzylic hydrogen atoms was adopted. The trimethylsilyl groups were selected to act as sterically demanding groups designed to favour the conformation depicted by structure **8** (Figure 1).[20] The desired bis-ether **25** (Scheme 5) was synthesised efficiently in multigram quantities from commercially available diisopropyl phthalate through *ortho*-lithiation/silylation[21] to give **23**, reduction of the esters with lithium aluminium hydride to give **24** and a subsequent methylation. The bis-ether **25** reacted smoothly with hexacarbonylchromium(0) to give the novel tricarbonylchromium(0) complex **26** as a yellow, crystalline air-stable solid in 98% yield.

Methylation of complex **26**, which represents the key transformation of structure **8** to structure **10** in Figure 1, was then examined. Initial reactions involved the chiral bis-amide derived from (+)-(*R*,*S*,*S*,*R*)-**2**, but utilising a range of temperatures between –78 °C and 0 °C disappointingly failed to provide the desired mono-methylated product



Scheme 5.



Scheme 6.

(Scheme 5). Reasoning that the size of both the chiral bis-amide and the flanking trimethylsilyl groups rendered them unreactive with each other, the attention turned to smaller chiral amides. The mono-amides derived from the commercially available amine (+)-**27** and the trifluoro amine (+)-**28**, synthesised by a literature procedure,[22] were each added to the bis-ether complex **26**, but both proved ineffective under a range of conditions (Scheme 6). In contrast, the mono-amide derived from (+)-bis(α-methylbenzyl)amine (**29**), used at –12 °C, delivered the mono-methylated complex **30** in 81% yield. To facilitate the stereochemical analysis of this product, its trimethylsilyl substituents were removed using tetrabutylammonium fluoride. Comparison of the NMR spectra of **11** with those of **5** (Scheme 2) revealed that they were indeed diastereoisomers, i.e. our strategy of using bulky flanking groups to control the conformation of the adjacent benzyl ethers had worked, and we had succeeded in removing and replacing the previously inaccessible benzylic pro-*R* hydrogen. Our excitement proved to be short-lived, however, as HPLC analysis of **11** revealed that it was racemic, an outcome that may be a result of the relatively high temperature needed for the deprotonation.

At this point our strategy for accessing the C_2-symmetric molecule **13** (Figure 1) was modified. As alkylation using the mono-amide **29** was chemically efficient,[23] it was decided to attempt a kinetic resolution of racemic **11**. It was anticipated that due to the preference of the chiral bis-amide derived from (+)-**2** to remove an antiperiplanar pro-*R* hydrogen, the enantiomer of racemic **11** already bearing an *R* chiral centre would react more readily than the corresponding *S* enantiomer (Figure 2).

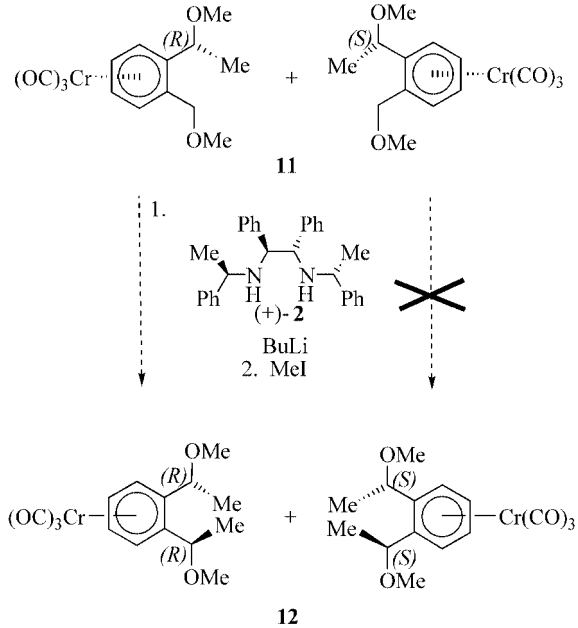
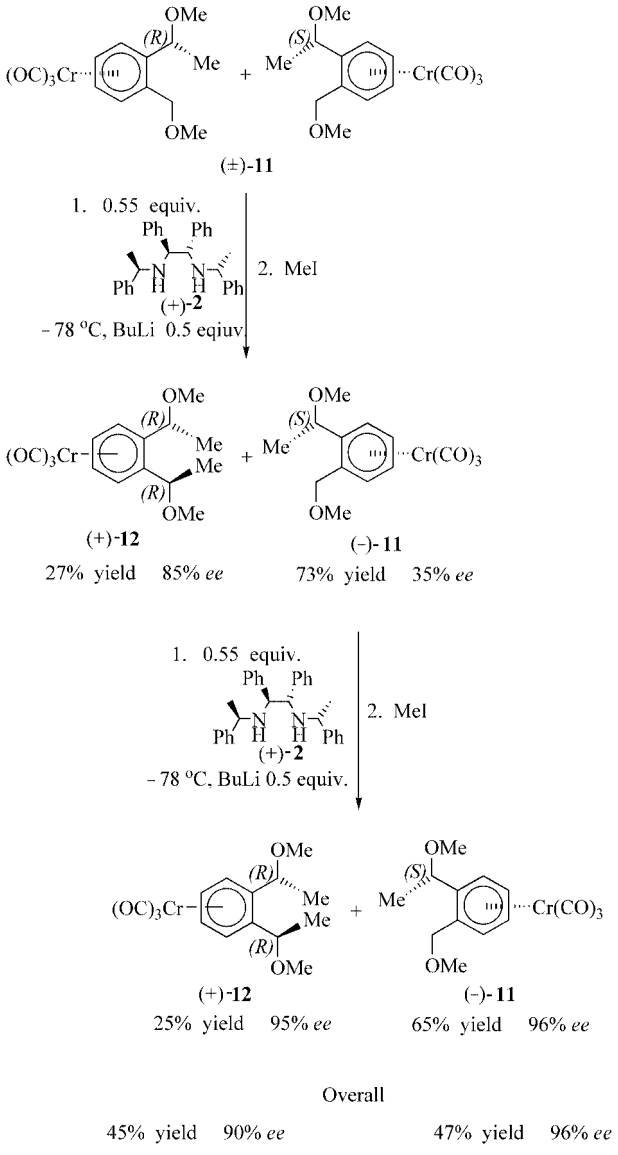


Figure 2. The proposed kinetic resolution of **11**.

After examining a range of different reaction conditions, nearly complete resolution was achieved in a two-step procedure. Treatment of (±)-**11** with 0.55 equivalents of the bis-amine and 0.5 equivalent of *n*-butyllithium at –78 °C for 45 min followed by an iodomethane quench gave a 27% yield of the bis-methylated product (+)-**12** of 85% enantiomeric excess, together with unreacted mono-methylated (–)-**11** in 73% yield and 35% *ee* by HPLC analysis (Scheme 7). Subjecting the latter material to the same reaction conditions gave a second sample of (+)-**12** [25% yield (in the second reaction), 95% *ee*] and enhanced the enrichment of (–)-**11** to 96% *ee* (65% yield in the second reaction). Overall it had proved possible to obtain a 45% yield of the bis-methylated (+)-**12** of 90% *ee*, and a 47% yield of the mono-methylated (–)-**11** of 96% *ee*.



Scheme 7.

In an attempt to enhance the enantiopurity of (+)-**12**, a sample of (+)-**12** of 94% *ee* (obtained during the optimisation of the kinetic resolution procedure) was crystallised from cold hexane. HPLC analysis revealed an enantioenrichment of the mother liquor (98% *ee*), and an enantiodepletion of the crystals (71% *ee*). In a separate experiment a batch of (+)-**12** of 84% *ee* gave a small sample of crystals that were suitable for X-ray analysis. This analysis confirmed the predicted relative stereochemistry of **12** (Figure 3), but was unable to confirm our prediction of the absolute stereochemistry, as the crystal examined proved to be racemic, a result consistent with the observation of enantiodepletion on crystallisation. Nevertheless, the preference of the bis-amide derived from (*R*)-α-methylbenzylamine to abstract the pro-*R* benzylic hydrogen is sufficiently well documented in our earlier work[8,11,24] for us to be confident that the two stereocentres of (+)-**12** are indeed *R*.

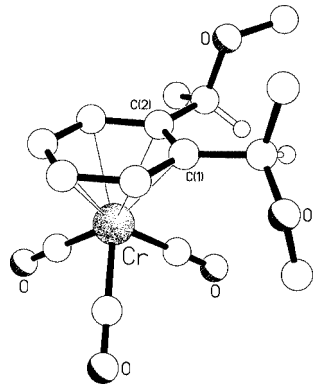
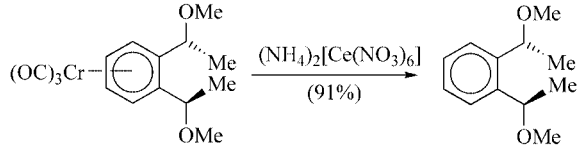


Figure 3. The molecular structure of **12**.

Finally the oxidative removal of the tricarbonylchromium(0) unit using ceric ammonium nitrate cleanly gave the target C_2-symmetric compound (+)-**13** (Scheme 8)[25] thus demonstrating with a model electrophile that controlling the conformational preferences of *ortho*-substituted benzylic ethers provides a route to enantioenriched C_2-symmetric products.



Scheme 8.

Conclusion

Two approaches to controll the conformational preferences of *ortho*-substituted benzylic ethers have been examined, and the approach that relied on non-covalent interactions proved successful. Although the steric demands of the trimethylsilyl groups proved to be a liability as well as an asset in this chemistry, due to the size of the chiral bases used, this approach to controll conformations to generate C_2-symmetry after decomplexation should find use in reactions of 1,2-disubstituted (arene)tricarbonylchromium(0)

complexes that rely on smaller reagents. The kinetic resolution of **11** using the chiral base worked well, and it is anticipated that introduction of functionalised electrophiles into this chemistry will provide a range of C_2-symmetric ligands for use in asymmetric catalysis.

Experimental Section

General: All reactions were performed under dry nitrogen using standard vacuum line and Schlenk tube techniques.[26] Reactions involving the use of (arene)tricarbonylchromium(0) complexes were protected from sunlight. Tetrahydrofuran was distilled from sodium benzophenone ketyl and used immediately. The concentrations of alkyllithiums were determined by titration against diphenylacetic acid in tetrahydrofuran.[27] Chiral bis-amine (+)-**2**,[9] the benzofuranchromium(0) complex **15**,[14] acetal **17**,[18,28] ketal **18**[18,19] and the chiral amine (+)-**28**[22] were prepared according to the corresponding literature procedure. All remaining chemicals were used as purchased from commercial sources. Thin layer chromatography was performed on Merck silica gel glass plates (60 F_{254}) using UV light (254 nm) as visualizing agent and/or vanillin or potassium permanganate and heat as developing agents. Flash column chromatography was performed with BDH silica gel (330–70 μm particle size). Melting points were recorded in open capillaries with a Buchi 510 melting point apparatus and are uncorrected. Optical rotations were recorded with a Perkin–Elmer 241 Polarimeter using a 1-dm path length and concentrations are given as g mL^{-1}. IR spectra were recorded with a Perkin–Elmer 1600 FT-IR spectrometer. NMR spectra were recorded at room temperature with Bruker AC 300F instruments in $CDCl_3$. *J* values are reported in Hz and chemical shifts in ppm. Mass spectra were recorded with Micromass Platform II and Micromass AutoSpec-Q spectrometers. Analytical HPLC was performed with a Unicam Crystal 200 pump, a Unicam 100 UV/Vis Detector and a Daicel Chiralcel AS column (25 cm × 0.46 cm). Elemental analyses were performed by the London Metropolitan University microanalytical service.

General Experimental for the Preparation of Chiral Bis-amide from (+)-2: *n*-Butyllithium (2.50 M in hexanes) (2.2*n* mmol) was added dropwise to a stirred solution of the bis-amine (+)-**2** (1.1*n* mmol) in dry tetrahydrofuran (12.0*n* mL) at –78 °C under nitrogen. The solution was then warmed to room temperature over a period of 30 min. The resulting deep red solution was recooled to –78 °C, and a solution of heat-gun-dried lithium chloride (1.1*n* mmol) in tetrahydrofuran (4.0*n* mL) was added dropwise through a cannula and the reaction mixture was stirred for a further 5 min.

Benzofuran Chromium(0) Complex (–)-16: A precooled (–78 °C) solution of complex **15** (1.0*n* mmol) in tetrahydrofuran (8.0*n* mL) was introduced dropwise through a short cannula to the reaction mixture containing the chiral bis-amide obtained as described above. After stirring the orange solution at –78 °C for a period of 10 min, iodomethane (10.0*n* mmol) was added in one portion, which resulted in a colour change of the solution to yellow. The reaction mixture was then stirred for 4 h at –78 °C before methanol (1.0*n* mL) was added and the solvent removed in vacuo. Purification of the residue by flash column chromatography (silica gel; hexane/ethyl acetate, 10:0 → 9:1) afforded (–)-**16** as a yellow oil (0.063 g, 60%). R_f = 0.26 (silica gel; hexane/ethyl acetate, 4:1). $[\alpha]_D^{20}$ = –8.6 (*c* = 0.007 in $CHCl_3$). IR (neat): $\tilde{\nu}_{max}$ = 1970, 1880 cm^{-1} (C≡O). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45 (d, *J* = 6.5 Hz, 3 H, CHC*H*$_3$), 4.86 (d, *J* = 12.5 Hz, 1 H, C*H*H), 5.00 (d, *J* = 12.5 Hz, 1 H, CH*H*), 5.17 (q, *J* = 6.5 Hz, 1 H, C*H*CH$_3$), 5.25–5.51 (m, 4 H, C$_{Cr}$*H* × 4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.7 (CH*C*H$_3$), 69.5 (*C*H$_2$), 78.1 (*C*HCH$_3$), 84.5, 89.9, 90.7 and 91.8 (*C*$_{Cr}$H), 109.5 and 110.7 (*C*$_{Ar}$), 232.8 (*C*≡O × 3) ppm. MS (EI): *m*/*z* (%) = 270 (42) [M$^+$], 186 (90) [M$^+$ – 3 CO], 52 (100) [Cr].

Acetal Chromium(0) Complex 18: A 100-mL round-bottomed flask containing a stirrer bar and fitted with a reflux condenser was placed under nitrogen and charged with 1,3-dioxa-5,6-benzocycloheptene (**17**, 1.00 g, 6.65 mmol), hexacarbonylchromium(0) (1.61 g, 7.32 mmol), dry tetrahydrofuran (5 mL) and dry di-*n*-butyl ether (50 mL). The suspension was thoroughly saturated with nitrogen, before it was heated to 135 °C and maintained under nitrogen at the same temperature for 48 h. The yellow reaction mixture was then cooled to room temperature and the solvent was removed in vacuo. Purification of the crude products by flash column chromatography (silica gel; hexane/ethyl acetate, 9:1 to 3:1) afforded **18** as a yellow crystalline solid (1.52 g, 80%). R_f = 0.29 (silica gel; hexane/ethyl acetate, 3:1); m.p. 170–172 °C. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 1970, 1891 cm^{-1} (C≡O). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.62 (d, *J* = 14.0 Hz, 2 H, ArC*H*H × 2), 4.73 (d, *J* = 14.0 Hz, 2 H, ArC*H*H × 2), 4.92 (d, *J* = 5.0 Hz, 1 H, OCH*H*O), 5.03 (d, *J* = 5.0 Hz, 1 H, OC*H*HO), 5.28 (s, 4 H, C$_{Cr}$*H* × 4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 70.5 (Ar*C*H$_2$ × 2), 90.8 and 91.8 (*C*$_{Cr}$H × 2), 94.6 (O*C*H$_2$O), 98.4 and 109.5 (*C*$_{Cr}$), 232.3 (*C*≡O × 3) ppm. MS (EI): *m*/*z* (%) = 286 (28) [M$^+$], 202 (57) [M$^+$ – 3 CO], 52 (100) [Cr]. $C_{12}H_{10}CrO_5$ (286.20): calcd. C 50.35, H 3.52; found C 50.41, H 3.49.

Acetal Chromium(0) Complex (–)-19: A precooled (–40 °C) solution of complex **18** (1.0*n* mmol) in tetrahydrofuran (8.0*n* mL) was introduced dropwise through a short cannula to the reaction mixture containing the chiral bis-amide obtained as described above. After stirring the orange solution at –40 °C for a period of 45 min, iodomethane (10.0*n* mmol) was added in one portion, which resulted in a colour change of the solution to yellow. The reaction mixture was then stirred for 1.5 h at –40 °C before methanol (1.0*n* mL) was added and the solvent removed in vacuo. Purification of the residue by flash column chromatography (silica gel; hexane/ethyl acetate, 10:0 to 8.5:1.5) afforded (–)-**19** as a yellow oil (0.360 g, 86%). R_f = 0.32 (silica gel; hexane/ethyl acetate, 3:1). $[\alpha]_D^{20}$ = –29.3 (*c* = 0.001 in $CHCl_3$). IR (neat): $\tilde{\nu}_{max}$ = 1968, 1891 cm^{-1} (C≡O). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.55 (d, *J* = 6.5 Hz, 3 H, CHC*H*$_3$), 4.56 (d, *J* = 14.0 Hz, 1 H, ArC*H*H), 4.80 (d, *J* = 14.0 Hz, 1 H, ArCH*H*), 4.93 (q, *J* = 6.5 Hz, 1 H, C*H*CH$_3$), 5.00 (d, *J* = 6.0 Hz, 1 H, OCH*H*O), 5.18 (d, *J* = 6.0 Hz, 1 H, OC*H*HO), 5.28–5.37 (m, 4 H, C$_{Cr}$*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.2 (*C*H$_3$), 71.8 (Ar*C*H$_2$), 76.6 (*C*HCH$_3$), 90.0, 91.0, 91.3 and 92.9 (*C*$_{Cr}$H), 98.6 (OCH$_2$O) 109.5 and 112.7 (*C*$_{Cr}$), 232.3 (*C*≡O × 3) ppm. MS (CI): *m*/*z* (%) = 318 (100) [M + NH$_4^+$], 301 (99) [M + H$^+$], 271 (22) [M$^+$ – OCH$_2$ + H$^+$]. $C_{13}H_{12}CrO_5$ (300.19): calcd. C 52.00, H 4.02; found C 51.96, H 3.96.

Ketal Chromium(0) Complex 21: A 100-mL round-bottomed flask containing a stirrer bar and fitted with a reflux condenser was placed under nitrogen and charged with 2,2-dimethyl-1,3-dioxa-5,6-benzocycloheptene (**20**, 0.550 g, 3.23 mmol), hexacarbonylchromium(0) (0.782 g, 3.55 mmol), dry tetrahydrofuran (3 mL) and dry di-*n*-butyl ether (25 mL). The suspension was thoroughly saturated with nitrogen, before it was heated to 135 °C and maintained under an inert atmosphere at the same temperature for 48 h. The yellow reaction mixture was then cooled to room temperature and the solvent was removed in vacuo. Purification of the crude products by flash column chromatography (silica gel; hexane/ethyl acetate, 9:1 to 3:1) afforded **21** as a yellow crystalline solid (0.610 g, 60%). R_f = 0.43 (silica gel; hexane/ethyl acetate, 3:1); m.p. 100–102 °C. IR

(CH_2Cl_2): $\tilde{\nu}_{max}$ = 1967, 1889 cm^{-1} (C≡O). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.51 (s, 6 H, CH_3×2), 4.66 (s, 4 H, CH_2×2), 5.24 (s, 4 H, $C_{Cr}H$×4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.6 (CH_3×2), 63.3 (CH_2×2), 90.7 and 90.8 (C_{Cr}H×2), 102.7 [$C(CH_3)_2$], 109.8 (C_{Cr}×2), 232.8 (C≡O×3) ppm. MS (CI): *m*/*z* (%) = 332 (4) [M + NH_4^+], 314 (6) [M^+], 257 (100) [M^+ – $OC(CH_3)_2$ + H^+]. $C_{14}H_{14}CrO_5$ (314.29): calcd. C 53.50, H 4.49; found C 53.60, H 4.45.

Ketal Chromium(0) Complex (–)-22: A precooled (–20 °C) solution of complex **21** (1.0*n* mmol) in tetrahydrofuran (8.0*n* mL) was introduced dropwise through a short cannula to the reaction mixture containing the chiral bis-amide obtained as described above. After stirring the orange solution at –20 °C for a period of 45 min, iodomethane (10.0*n* mmol) was added in one portion, which resulted in a colour change of the solution to yellow. The reaction mixture was then stirred for 2 h at –20 °C before methanol (0.8 mL) was added and the solvent removed in vacuo. Purification of the residue by flash column chromatography (silica gel; hexane/ethyl acetate, 10:0 to 9:1) afforded (–)-**22** as a yellow solid (0.140 g, 60%). R_f = 0.41 (silica gel; hexane/ethyl acetate, 4:1); m.p. 100–102 °C. $[\alpha]_D^{20}$ = –20.7 (*c* = 0.001 in $CHCl_3$). IR (neat): $\tilde{\nu}_{max}$ = 1967, 1887 cm^{-1} (C≡O). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.48 (d, *J* = 6.5 Hz, 3 H, CHCH_3), 1.51 (s, 6 H, CH_3×2), 4.26 (d, *J* = 15.0 Hz, 1 H, C*H*H), 5.04 (d, *J* = 15.0 Hz, 1 H, CH*H*), 5.13 (q, *J* = 6.5 Hz, 1 H, C*H*CH$_3$), 5.23–5.31 (m, 4 H, $C_{Cr}H$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.0 (*C*H$_3$), 24.1 and 24.3 [C(*C*H$_3$)$_2$], 63.9 (*C*H$_2$), 66.2 (*C*HCH$_3$), 90.1, 91.2, 91.3 and 91.8 (C_{Cr}H), 102.4 [$C(CH_3)_2$], 111.7 and 112.1 (C_{Cr}), 232.8 (*C*≡O×3) ppm. MS (CI): *m*/*z* (%) = 332 (58) [M + NH_4^+], 328 (45) [M^+], 271 (100) [M – $OC(CH_3)_2$ + H^+]. $C_{15}H_{16}CrO_5$ (328.27): calcd. C 54.88, H 4.91; found C 54.76, H 4.84.

Bis-ester 23: Methyllithium (12.2 mL, 1.6 M in hexanes, 19.5 mmol) was added dropwise to a stirred solution of tetramethylpiperidine (3.31 mL, 19.5 mmol) in dry tetrahydrofuran (95 mL) at –78 °C under nitrogen. The solution was then warmed to 0 °C over a period of 30 min. The resulting light yellow solution was recooled to –78 °C and trimethylsilyl chloride (10.7 mL, 84.9 mmol) was added followed by diisopropyl phthalate (2.0 mL, 8.49 mmol). The solution was kept at –78 °C for 20 min and then slowly warmed to room temperature. The reaction mixture was left stirring at the same temperature for 1 h before methanol (5 mL) was added and the solvent evaporated under vacuum. Purification of the crude products by flash column chromatography (silica gel; hexane/ethyl acetate, 4:1) afforded **23** as a white solid (3.30 g, 98%). R_f = 0.8 (silica gel; hexane/ethyl acetate, 4:1); m.p. 84–86 °C. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 1722 (C=O), 1265 cm^{-1} (Si–CH_3). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.31 [s, 18 H, Si(CH_3)$_3$×2], 1.40 (d, *J* = 6.0 Hz, 12 H, CHCH_3×4), 5.18–5.24 (m, 2 H, CH_3CHCH_3×2), 7.62 (s, 2 H, $C_{Ar}H$×2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.7 [Si(*C*H$_3$)$_3$×2], 21.8 (CH*C*H$_3$×4), 69.4 (*C*HCH$_3$×2), 135.2 (C_{Ar}H×2), 137.9 (C_{Ar}×2), 139.2 (C_{Ar}Si×2), 169.8 (*C*=OOCH×2) ppm. MS (CI): *m*/*z* (%) = 412 (83) [M + NH_4^+], 335 (100) [M^+ – OCH(CH$_3$)$_2$], 277 (23) [M^+ – 2 OCH(CH$_3$)$_2$]. $C_{20}H_{34}O_4Si_2$ (394.65): calcd. C 60.86, H 8.68; found C 60.94, H 8.69.

Bis-alcohol 24: A 500-mL flask containing a magnetic stirrer was placed under an inert atmosphere and charged with lithium aluminium hydride (1.93 g, 50.7 mmol). Tetrahydrofuran (80 mL) was added through a syringe. The suspension was vigorously stirred and then cooled to 0 °C before a solution of the phthalate **23** (10.0 g, 25.3 mmol) in tetrahydrofuran (80 mL) was introduced through a cannula over a period of 10 min. After the addition was complete a condenser was fitted and the reaction heated at reflux for 16 h before being cooled to room temperature. Upon cooling, a saturated solution of potassium (L)-tartrate (70 mL) was carefully added. The organic layer was separated and the aqueous layer extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$) and evaporated under reduced pressure. The volatiles were removed in vacuo to give **24** as a white solid (7.10 g, 99%). R_f = 0.34 (silica gel; hexane/ethyl acetate, 4:1); m.p. 125–127 °C. IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 3424 (OH), 1265 cm^{-1} (Si–CH_3). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.43 [s, 18 H, Si(CH_3)$_3$×2], 4.86 (s, 4 H, CH_2×2), 7.56 (s, 2 H, $C_{Ar}H$×2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.7 [Si(*C*H$_3$)$_3$×2], 62.9 (*C*H$_2$×2), 134.1 (C_{Ar}H×2), 142.1 (C_{Ar}×2), 145.2 (C_{Ar}Si×2) ppm. MS (CI): *m*/*z* (%) = 300 (81) [M + NH_4^+], 282 (100) [M^+], 265 (62) [M^+ – H_2O]. $C_{14}H_{26}O_2Si_2$ (282.50): calcd. C 59.51, H 9.27; found C 59.47, H 9.27.

Bis-ether 25: To a stirred suspension of sodium hydride (60% dispersion in mineral oil) (1.47 g, 36.8 mmol), previously washed with pentane (30 mL), in tetrahydrofuran (60 mL), was added thorugh a cannula a solution of the bis-alcohol **24** (4.15 g, 14.7 mmol), in dry tetrahydrofuran (22 mL). The reaction mixture was stirred for 1 h at 0 °C, before iodomethane (4.59 mL, 73.8 mmol) was added thorugh a syringe. Stirring was continued at room temperature for 18 h. A saturated aqueous solution of ammonium chloride (40 mL) was then added, the organic layer was separated and the aqueous layer extracted with diethyl ether (3 × 60 mL). The combined organic layers were washed with brine (30 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Flash column chromatography (silica gel; hexane/ethyl acetate, 10:0 to 9:1) of the crude product afforded **25** as a white solid (4.22 g, 92%). R_f = 0.60 (silica gel; hexane/ethyl acetate, 9:1); m.p. 62–64 °C. IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1265 cm^{-1} (Si–CH_3). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.37 [s, 18 H, Si(CH_3)$_3$×2], 3.49 (s, 6 H, OCH_3×2), 4.61 (s, 4 H, CH_2×2), 7.52 (s, 2 H, $C_{Ar}H$×2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.6 [Si(*C*H$_3$)$_3$×2], 58.4 (O*C*H$_3$×2), 71.8 (*C*H$_2$×2), 134.1 (C_{Ar}H×2), 141.9 (C_{Ar}×2), 142.1 (C_{Ar}Si×2) ppm. MS (CI): *m*/*z* (%) = 328 (38) [M + NH_4^+], 311 (24) [M + H^+], 279 (100) [M^+ – 2 OH + 3 H^+]. $C_{16}H_{30}O_2Si_2$ (310.57): calcd. C 61.88, H 9.73; found C 61.84, H 9.82.

Chromium(0) Complex 26: A 250-mL round-bottomed flask containing a stirrer bar and fitted with a reflux condenser was placed under nitrogen and charged with the bis-ether **25** (1.90 g, 6.12 mmol), hexacarbonylchromium(0) (1.48 g, 6.73 mmol), dry tetrahydrofuran (6.0 mL) and dry di-*n*-butyl ether (61.0 mL). The suspension was thoroughly saturated with nitrogen, before it was heated to 135 °C and maintained under nitrogen at the same temperature for 24 h. The yellow reaction mixture was then cooled to room temperature and the solvent was removed in vacuo. Filtration of the crude product through celite afforded **26** as a yellow crystalline solid (2.68 g, 98%). R_f = 0.56 (silica gel; hexane/ethyl acetate, 4:1); m.p. 108–110 °C. IR (neat): $\tilde{\nu}_{max}$ = 1962, 1889 cm^{-1} (C≡O). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.39 [s, 18 H, Si(CH_3)$_3$×2], 3.43 (s, 6 H, OCH_3×2), 4.19 (s, 4 H, CH_2×2), 5.31 (s, 2 H, $C_{Ar}H$×2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.6 [Si(*C*H$_3$)$_3$×2], 58.8 (O*C*H$_3$×2), 70.3 (*C*H$_2$×2), 98.1 (C_{Ar}H×2), 103.3 (C_{Ar}×2), 111.1 (C_{Ar}Si×2), 232.9 (*C*≡O×3) ppm. MS (EI): *m*/*z* (%) = 446 (13) [M^+], 362 (72) [M^+ – 3 CO], 300 (100) [M^+ – 2 Si(*C*H$_3$)$_3$]. $C_{19}H_{30}CrO_5Si_2$ (446.60): calcd. C 51.09, H 6.77; found C 50.95, H 6.68.

Chromium(0) Complex (±)-30: *n*-Butyllithium (0.59 mL, 2.5 M in hexanes, 1.48 mmol) was added dropwise to a stirred solution of (±)-bis-α-methybenzylamine (**29**, 0.34 mL, 1.48 mmol), in dry tetrahydrofuran (10 mL) at –78 °C. The solution was then warmed

to room temperature over a period of 30 min. The resulting light yellow solution of the chiral amide was re-cooled to –12 °C and a solution of heat-gun-dried lithium chloride (0.063 g, 1.48 mmol) in tetrahydrofuran (10 mL) was added through a cannula. Stirring was continued for a further 5 min before a pre-cooled solution (–12 °C) of complex **26** (0.600 g, 1.34 mmol) in tetrahydrofuran (14 mL) was introduced dropwise through a short cannula. After stirring the orange solution at –12 °C for 1.5 h, iodomethane (0.83 mL, 13.4 mmol) was added in one portion leading to a colour change of the solution to yellow. Stirring was continued for a further 1.5 h before the reaction was quenched with methanol (0.5 mL) and the solvent removed in vacuo. Flash column chromatography (silica gel; hexane/ethyl acetate, 10:0 to 9.7:0.3) of the residue afforded (±)-**30** as a yellow solid (0.498 g, 81%). R_f = 0.63 (silica gel; hexane/ethyl acetate, 9.6:0.4); m.p. 98–100 °C. IR (neat): $\tilde{\nu}_{max}$ = 1959, 1886 cm^{-1} (C≡O). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.40 [s, 9 H, Si(CH_3)$_3$], 0.41 [s, 9 H, Si(CH_3)$_3$], 1.53 (d, J = 6.5 Hz, 3 H, CHCH_3), 3.41 (s, 3 H, OCH_3), 3.42 (s, 3 H, OCH_3), 4.12 (d, J = 11.0 Hz, 1 H, CHH), 4.59 (d, J = 11.0 Hz, 1 H, CHH), 5.17 (d, J = 6.5 Hz, 1 H, $C_{Ar}H$), 5.47 (d, J = 6.5 Hz, 1 H, $C_{Ar}H$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.9, 1.5 [Si(CH_3)$_3$], 22.3 (CHCH$_3$), 57.1 and 58.2 (OCH$_3$), 70.2 (CH$_2$), 76.6 (CHCH$_3$), 96.1 and 101.4 (C_{Ar}H), 110.5 and 119.1 (C_{Ar}), 133.8 and 134.0 (C_{Ar}Si), 233.3 (C≡O × 3) ppm. MS (EI): m/z (%) = 460 (9) [M$^+$], 376 (47) [M$^+$ – 3 CO], 314 (100) [M$^+$ – 2 Si(CH_3)$_3$]. $C_{20}H_{32}CrO_5Si_2$ (460.63): calcd. C 52.14, H 7.00; found C 52.17, H 6.97.

Chromium(0) Complex (±)-11: To a solution of complex (±)-**30** (0.080 g, 0.17 mmol) at room temperature in tetrahydrofuran (14 mL) was added dropwise under nitrogen a solution of tetra-*n*-butylammonium fluoride (0.69 mL, 1.0 M in tetrahydrofuran, 0.69 mmol). The reaction mixture was stirred for 15 min and saturated ammonium chloride (28 mL) was added. The mixture was extracted with dichloromethane (3 × 30 mL), the organic extracts were combined, washed with brine (50 mL), dried with magnesium sulfate and then concentrated in vacuo. Purification of the crude product by flash column chromatography (silica gel; hexane/ethyl acetate, 4:1) afforded (±)-**11** as a yellow solid (0.051 g, 95%). R_f = 0.28 (silica gel; hexane/ethyl acetate, 4:1); m.p. 35–38 °C. IR (neat): $\tilde{\nu}_{max}$ = 1967, 1886 cm^{-1} (C≡O). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.53 (d, J = 6.5 Hz, 3 H, CHCH_3), 3.33 (s, 3 H, OCH$_3$), 3.50 (s, 3 H, OCH$_3$), 4.12 (d, J = 12.0 Hz, 1 H, CHHOCH$_3$), 4.29 (q, J = 6.5 Hz, 1 H, CHCH$_3$), 4.54 (d, J = 12.0 Hz, 1 H, CHHOCH$_3$), 5.22–5.27 (m, 1 H, $C_{Cr}H$), 5.40 (d, J = 6.0 Hz, 1 H, $C_{Cr}H$), 5.47–5.51 (m, 1 H, $C_{Cr}H$), 5.64 (d, J = 6.0 Hz, 1 H, $C_{Cr}H$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8 (CHCH$_3$), 56.4 and 59.1 (OCH$_3$), 70.5 (CH$_2$OCH$_3$), 73.9 (CHCH$_3$), 89.5, 90.5, 93.2 and 94.2 (C_{Cr}H), 108.2 and 110.6 (C_{Cr}), 232.7 (C≡O × 3) ppm. MS (EI): m/z (%) = 316 (38) [M$^+$], 232 (74) [M$^+$ – 3 CO], 172 (86) [M$^+$ – 3 CO – 2 OCH$_3$], 52 (100) [Cr]. $C_{14}H_{16}CrO_5$ (316.26): calcd. C 53.16, H 5.09; found C 53.19, H 5.09.

Chromium(0) Complexes (–)-11 and (+)-12: *n*-Butyllithium (0.39 mL, 1.6 M in hexanes, 0.63 mmol) was added dropwise to a stirred solution of the bis-amine (+)-**2** (0.292 g, 0.69 mmol) in dry tetrahydrofuran (10 mL) at –78 °C under nitrogen. The solution was then warmed to room temperature over a period of 30 min. The resulting deep red solution was recooled to –78 °C and a solution of heat gun dried lithium chloride (0.027 g, 0.63 mmol) in tetrahydrofuran (10 mL) was added dropwise through a cannula. The reaction mixture was stirred for a further 5 min before a precooled (–78 °C) solution of complex (±)-**11** (0.400 g, 1.26 mmol) in tetrahydrofuran (11 mL) was introduced dropwise through a short cannula. After stirring the orange solution at –78 °C for a period of 45 min, iodomethane (0.39 mL, 6.32 mmol) was added in one portion, which resulted in a colour change of the solution to yellow. The reaction mixture was then stirred for 60 min at –78 °C before methanol (0.5 mL) was added and the solvent removed in vacuo. Purification of the residue by flash column chromatography (silica gel; hexane/ethyl acetate, 10:0 to 4:1) afforded complex (+)-**12** as a yellow solid (0.112 g, 27%) and complex (–)-**11** as a yellow solid (0.304 g, 73%). Enantiomeric excess for (+)-**12** was determined by HPLC analysis (Chiralcel AS, hexane/2-propanol, 99.5:0.5, 0.25 mL min^{-1}, 330 nm); (*S*,*S*)-enantiomer t_r = 39.60 min (minor); (*R*,*R*)-enantiomer t_r = 42.20 min (major): 85% *ee*. Enantiomeric excess for (–)-**11** was determined by HPLC analysis (Chiralcel AS, hexane/2-propanol, 99.5:0.5, 0.25 mL min^{-1}, 330 nm); (*R*)-enantiomer t_r = 59.36 min (minor); (*S*)-enantiomer t_r = 62.75 min (major): 35% *ee*.

Complex (–)-**11** was further reacted as follows: *n*-butyllithium (0.26 mL, 1.6 M in hexanes, 0.42 mmol) was added dropwise to a stirred solution of the bis-amine (+)-**2** (0.194 g, 0.46 mmol) in dry tetrahydrofuran (8 mL) at –78 °C under nitrogen. The solution was then warmed to room temperature over a period of 30 min. The resulting deep red solution was recooled to –78 °C and a solution of heat gun dried lithium chloride (0.018 g, 0.42 mmol) in tetrahydrofuran (5 mL) was added dropwise through a cannula. The reaction mixture was stirred for a further 5 min before a precooled (–78 °C) solution of the complex (–)-**11** (35% *ee*, from the above reaction) (0.266 g, 0.84 mmol) in tetrahydrofuran (8 mL) was introduced dropwise through a short cannula. After stirring the orange solution at –78 °C for a period of 45 min, iodomethane (0.26 mL, 4.20 mmol) was added in one portion, which resulted in a colour change of the solution to yellow. The reaction mixture was then stirred for 60 min at –78 °C before methanol (0.5 mL) was added and the solvent removed in vacuo. Purification of the residue by flash column chromatography (silica gel; hexane/ethyl acetate, 10:0 to 4:1) afforded the complex (+)-**12** as a yellow solid (0.072 g, 25%) and the complex (–)-**11** as a yellow solid (0.172 g, 65%).

Data for (–)-11: Enantiomeric excess was determined by HPLC analysis (Chiralcel AS, hexane/2-propanol, 99.5:0.5, 0.25 mL min^{-1}, 330 nm); (*S*)-enantiomer t_r = 59.36 min (minor); (*R*)-enantiomer t_r = 62.75 min (major): 96% *ee*. R_f = 0.28 (silica gel; hexane/ethyl acetate, 4:1); m.p. 36–37 °C. $[a]_D^{20}$ = –72.8 (c = 0.001 in $CHCl_3$). All data were identical to those obtained for (±)-**11**.

Data for (+)-12: Enantiomeric excess was determined by HPLC analysis (Chiralcel AS, hexane/2-propanol, 99.5:0.5, 0.25 mL min^{-1}, 330 nm); (*S*,*S*)-enantiomer t_r = 39.60 min (minor); (*R*,*R*)-enantiomer t_r = 42.20 min (major): 95% *ee*. R_f = 0.28 (silica gel; hexane/ethyl acetate, 4:1); m.p. 40–42 °C. $[a]_D^{20}$ = +84.2 (c = 0.001 in $CHCl_3$). IR (neat): $\tilde{\nu}_{max}$ = 1961, 1876 cm^{-1} (C≡O). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48 (d, J = 6.0 Hz, 3 H, CHCH_3), 1.52 (d, J = 6.0 Hz, 3 H, CHCH_3), 3.36 (s, 3 H, OCH_3), 3.53 (s, 3 H, OCH_3), 4.25 (q, J = 6.0, 1 H, CHCH$_3$), 4.35(q, J = 6.0, 1 H, CHCH$_3$), 5.34–5.30 (m, 1 H, $C_{Cr}H$), 5.51–5.43 (m, 2 H, $C_{Cr}H$ × 2), 5.57–5.55 (m, 1 H, $C_{Cr}H$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.5 and 23.8 (CHCH$_3$), 55.9 and 57.7 (OCH$_3$), 73.3 and 73.8 (CHCH$_3$), 88.5, 90.9, 91.1 and 93.1 (C_{Cr}H), 108.5 and 115.9 (C_{Cr}), 232.9 (C≡O × 3). MS (EI): m/z (%) = 330 (14) [M$^+$], 274 (20) [M$^+$ – 2 CO], 246 (59) [M$^+$ – 3 CO], 182 (100) [M$^+$ – 2 OCH$_3$]. $C_{15}H_{18}CrO_5$ (330.29): calcd. C 54.54, H 5.49; found C 54.67, H 5.57.

Bis-ether (+)-13: Ceric ammonium nitrate (0.329 g, 0.60 mmol) was added to a solution of complex (+)-**12** (0.100 g, 0.30 mmol) in methanol (7 mL). The resulting mixture was stirred at room temperature for 15 min. The reaction mixture was then concentrated in vacuo to afford the crude product which was purified by flash

column chromatography (silica gel; hexane/diethyl ether, 4:1) to afford (+)-**13** as a colourless oil (0.053 g, 91%). R_f = 0.75 (silica gel; hexane/diethyl ether, 4:1). $[\alpha]_D^{20}$ = +151.7 (c = 0.001 in $CHCl_3$). IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 1214 cm^{-1} (C–O–C). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.47 (d, J = 6.5 Hz, 6 H, $CHCH_3 \times 2$), 3.23 (s, 6 H, $OCH_3 \times 2$), 4.65 (q, J = 6.5 Hz, 2 H, $CHCH_3 \times 2$), 7.29–7.32 (m, 2 H, $C_{Ar}H \times 2$), 7.43–7.46 (m, 2 H, $C_{Ar}H \times 2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.6 ($CHCH_3 \times 2$), 56.3 ($OCH_3 \times 2$), 75.4 ($CHCH_3 \times 2$), 125.7 and 127.7 ($C_{Ar}H \times 2$), 140.8 ($C_{Ar} \times 2$) ppm. MS (CI): m/z (%) = 212 (73) [M + NH_4^+], 195 (48) [M + H^+], 163 (100) [M^+ – OCH_3]. HMRS (CI) for $C_{12}H_{18}O_2$ [M + H^+] calcd. 195.1389, found 195.1384.

X-ray Crystallography of (±)-12: Crystal data for (±)-**12**: $C_{15}H_{18}CrO_5$; M = 330.29; crystal system: triclinic, $P\bar{1}$; cell dimension: a = 8.5604(7), b = 8. 6953(8), c = 11.7914(11) Å, α = 72.248(8), β = 79.510(7), γ = 67.390(8)°; V = 769.56(12) $Å^3$; Z = 2; $D_{calcd.}$ = 1.425 g/cm^{-3}; μ(Cu-K_α) = 6.284 mm^{-1}; F(100) = 344; T = 173(2) K; pale yellow prisms; crystal dimensions: 0.07 × 0.07 × 0.06 mm^3; θ range 3.95 to 71.01°; hkl limits: –9,10/–10,10/–13,14; number of data measured: 6883; number of data with $F > 4\sigma(F)$: 2774; number of variables 190; goodness-of-fit on F^2: 1.056; R_1 = 0.0348; R_w = 0.0921; largest diff. peak: 0.344 e·$Å^{-3}$.

CCDC-282315 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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Received: January 10, 2006
Published Online: February 9, 2006

