The asymmetric synthesis of phosphorus- and sulfur-containing tricarbonyl(η^6-arene)chromium complexes using the chiral base approach

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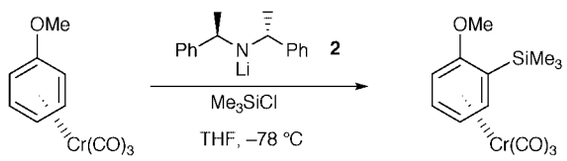
The use of a simple chiral lithium amide base **2** enables the asymmetric transformation of tricarbonyl-[η^6-(diphenylphosphinoyl)benzene]chromium(0) **12** into the corresponding *ortho*-silylated complex in up to 86% ee. A tin derivative was prepared similarly and was then used to prepare other derivatives *via* reduction to the corresponding phosphine, followed by transmetallation–electrophilic quench. In the case of tricarbonyl-(η^6-1,3-dihydroisobenzothiophene)chromium(0) the chiral base **2** was ineffective, and it was necessary to use a bis-lithium amide base **9** to effect asymmetric substitution in high ee (up to 95%). Decomplexation gave the corresponding chiral sulfides in highly enantiomerically enriched form. In all cases the absolute stereochemistry of the products was derived by conducting X-ray structure determinations on selected examples.

Introduction

The chiral base method has turned out to be a useful way of accessing certain types of non-racemic tricarbonyl(η^6-arene)-chromium complexes. A particularly important example is the reaction of the anisole complex **1** with the lithium amide base **2** to give the *ortho*-silylated complex **3** in about 90% enantiomeric excess, Scheme 1.[1]

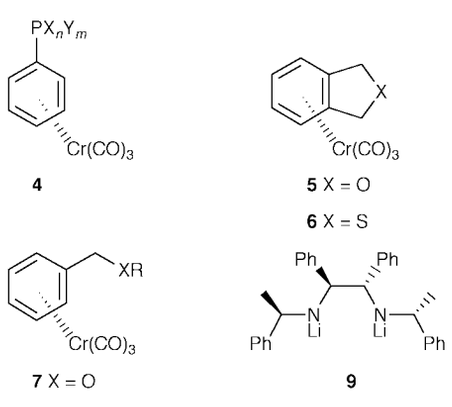


1 (+)-3

Scheme 1

Complex **3** prepared in this way has been utilised in studies of nucleophilic addition to chiral chromium complexes, and also in a total synthesis of (+)-ptilocaulin.[2,3]

Analogous chiral base reactions with other types of prochiral complexes were also examined, and an interest in enantiomerically enriched phosphines led us to examine complexes of general formula **4**.[4] Thus, it was hoped that a system in which the PX_nY_m group was a phosphine, phosphonate or phosphine oxide might furnish complexes with potential as chiral ligands for asymmetric catalysis.[5]



Our chiral base work also included benzylic metallation of complexes **5** and **6**,[6,7] an area of work also developed independently by Gibson and co-workers with the less conformationally constrained analogues **7** and **8**.[8] In both of these two studies it was found that the bis-lithium amide base **9** can sometimes provide excellent levels of enantioselectivity in situations where the simpler base **2** is inefficient.[9]

Aspects of this type of chiral base work have been described in detail previously;[10] the purpose of this paper is to provide full details of our studies of the phosphorus- and sulfur-containing complexes, **4** and **6** respectively.

Results and discussion

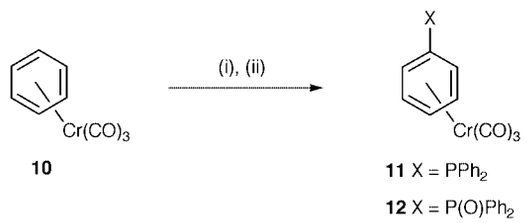
(i) Chemistry of phosphorus-containing systems 4

Our earlier study had shown that the type of transformation illustrated in Scheme 1 was also possible for prochiral complexes having various other substituents, including carbon, nitrogen and halogen types, but that the yields and levels of asymmetric induction were somewhat variable.[10] The presence of an oxygen-containing function, presumably to ensure efficient coordination of lithium appeared to be a prerequisite in order to secure at least workable levels of asymmetric induction.

This apparent requirement posed a problem when dealing with complexes having soft centres such as phosphorus or sulfur, and it was unclear if such systems would respond well under chiral base conditions. We decided to explore in detail complexes of general structure **4**, and after initial studies focused on the possibilities of using diphenylphosphine or the corresponding phosphine oxide as the substituent. A major factor which influenced our decision to study these systems was the possibility to devise an easy asymmetric synthesis of novel chiral phosphines, which might be useful ligands for asymmetric catalysis.

Neither of the desired complexes could be prepared by the usual protocol involving reaction of the appropriate arene with chromium hexacarbonyl.[11] This is an established problem in the phosphine series, where the ability of phosphine ligands to bind (*via* the phosphorus lone pair) to chromium is well

established.[12] In the case of triphenylphosphine oxide the oxidising potential of the ligand is presumably incompatible with the low valent chromium. We chose instead to prepare the required systems by lithiation of the parent benzene complex **10**, and reaction with appropriate phosphorus halides to give either phosphine or phosphine oxide products, **11** or **12**, respectively, Scheme 2.[13]



10

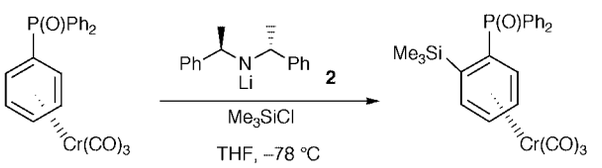
11 X = PPh_2

12 X = $P(O)Ph_2$

Scheme 2 *Reagents and conditions*: (i) ^{n}BuLi, THF, −78 °C to 0 °C; (ii) Ph_2PCl (64%) or $Ph_2P(O)Cl$ (68%).

Preliminary chiral base studies of the phosphine **11** were disappointing, producing mixtures of inseparable *meta*- and *para*-regioisomeric products. This behaviour seems somewhat similar to that seen with aniline complexes and, bearing in mind our previous experience with these systems, and the advantages of incorporating oxygen into the starting complex, we decided to move on to the phosphine oxide system.

Pleasingly, the reaction of phosphine oxide **12** with chiral base **2**, in the presence of Me_3SiCl (*in situ* quench) gave the desired *ortho*-silylated product (−)-**13** in good yield, and with an encouraging level of asymmetric induction (73% ee), Scheme 3.



12

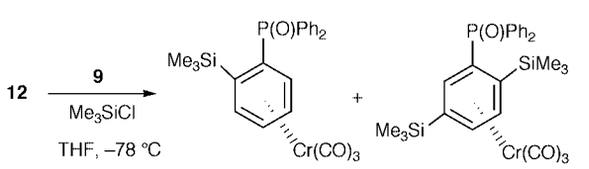
(–)-**13**

90%, 73% ee

Scheme 3

Crystallisation of a typical non-racemic sample of (−)-**13** from hexane allowed separation of the more highly crystalline racemate, leaving ≥50% yield of **13** in enantiomerically pure form. Further crystallisation from hexane then enabled an X-ray structure determination, which allowed the assignment of absolute configuration as shown in Fig. 1. Significantly, the sense of asymmetric induction in the reaction leading to **13** is opposite to that seen in our earlier work, *e.g.* in the synthesis of **3**, *vide infra*.

By reducing the reaction temperature to −100 °C it was possible to increase the ee of the product complex to 86%. However, other mono-lithium amide bases gave lower levels of induction, and this led us to attempt the metallation with bis-lithium amide base **9**. In this case we observed only small amounts of the anticipated mono-silylated complex (−)-**13**, the major product being the disilylated product (+)-**14**, with an ee of 82%, Scheme 4.



(–)-**13** (+)-**14**

Scheme 4

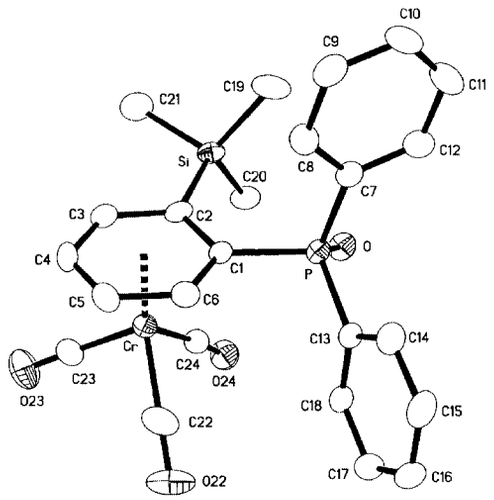
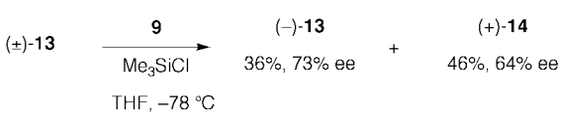


Fig. 1 Displacement ellipsoid plot for compound **13** [*T* 150 K, 50% probability, Flack parameter −0.04(4)].

At this stage the absolute configuration of the latter product was uncertain, but we were somewhat surprised that the mono-silylated product (−)-**13** produced by **9** should be of the same enantiomeric series as that produced by base **2**, since in the past these two bases had produced enantiocomplementary results. This observation, along with variable levels of observed ee for the small amounts of **13**, led us to believe that a kinetic resolution was responsible for the results with base **9**. This possible mechanism was subsequently demonstrated to be operative by exposure of *racemic* **13** to reaction with base **9** to give the expected products (−)-**13** and (+)-**14**, Scheme 5.

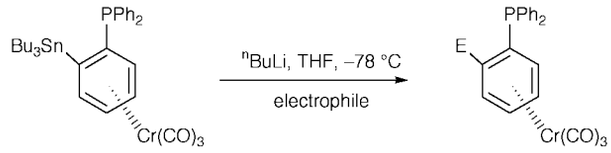


Scheme 5

The "product" **13** in the initial reaction, shown in Scheme 4, therefore represents an unreactive enantiomer in a stereodetermining step involving *meta*-silylation, and answers the concern that the reactions shown in Schemes 3 and 4 should not generate the same enantiomeric series. The potential of base **9** for over-silylation had not been a problem in earlier work, and we decided not to pursue this area further.

Surprisingly, when we attempted to carry out asymmetric substitution of **12** with electrophiles other than Me_3SiCl, such as MeI, D_2O, PhCHO, *etc*. no products were obtained, even in the presence of LiCl (one exception is Bu_3SnCl, which is discussed in detail later on). This result is perplexing, but mirrors a similar experience with a related metallation of a phosphinoyl-substituted ferrocene.[14] One possible explanation is that with Me_3SiCl there is a particularly strong interaction with the polarised oxygen of the P=O bond (the most extreme representation would be actual *O*-silylation), which activates the system towards metallation, and which is not possible with the other electrophiles.

With direct access to other substituted complexes denied our other options were to either substitute at the remaining *ortho*-position of **13** and then remove the silicon blocking group or attempt *ipso*-type replacement of the silicon group, for example using fluoride-mediated substitution reactions. Both of these avenues were explored, with little success. Complex **13** appears resistant to a second metallation using either alkyllithium or lithium amide bases, perhaps due to shielding of the remaining *ortho*-hydrogen by the phenyl groups of the phosphinoyl substituent. This effect is due to the conformation enforced on the phosphinoyl group due to the presence of the silicon substitu-



(–)-**20** **18**, **21** – **27**

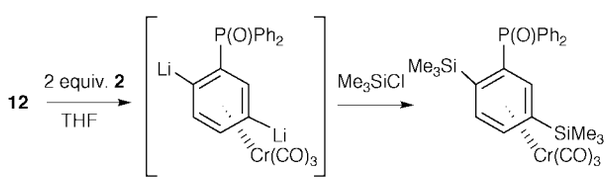
Table 1

Electrophile	Me_3SiCl	PhCHO	RCHO[a]	PhCOCl	MeI	EtI	BnBr	$(BrCF_2)_2$
Product[b]	**18**	**21**	**22**	**23**	**24**	**25**	**26**	**27**
Yield (%)	80	83	70	70	67	53	31	61

[a] R = cyclohexyl. [b] All (−)-isomers.

ent, as seen in the X-ray structure, Fig. 1. Fluoride mediated substitution of **13**, employing Bu_4NF or CsF,[15] gave the desired adduct only with PhCHO, and alternative electrophiles did not give good results. At this point the prospect of preparing varied chiral complexes *via* asymmetric metallation of **12** appeared somewhat bleak.

One further aspect of this work was confusing. Whereas bis-lithium amide base **9** was capable of metallating **13**, as shown in Scheme 5, we were unable to carry out this second metallation using other types of base, including **2**. However, if the starting complex was treated straightaway with excess **2**, then we did observe formation of (−)-**14**, Scheme 6.

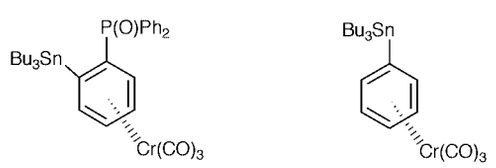


15 (–)-**14**

Scheme 6

These apparently contradictory results seem to indicate that (−)-**14**, formed using base **2**, cannot be formed *via* the intermediate mono-silylated complex **13**. We therefore propose that this reaction proceeds *via* an intermediate *dianion* **15**, as shown in Scheme 6, a type of intermediate previously demonstrated to be formed in the metallation of sulfinyl-substituted complexes.[16]

A breakthrough in our efforts to obtain further types of substituted complex was the finding that chiral base reaction of **12** with base **2** (at −100 °C) in the presence of Bu_3SnCl gave the *ortho*-stannylated complex **16** in excellent yield (98%). The use

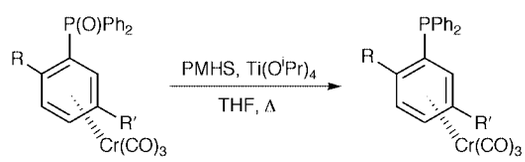


(–)-**16** **17**

of tin halides as *in situ* quenching agents for anions seems not to have been described explicitly before, and in this case the reagent presumably performs the crucial activation of the system towards metallation, as discussed above for Me_3SiCl. At this point the stannane product was assumed to have the same ee as the silylated chiral base product **13** (*ca.* 85% ee), but this could not be verified until further transformations had been carried out.

With stannane **16** in hand, obvious avenues to explore included transmetallation and cross-coupling reactions. However, reaction of **16** with ″BuLi resulted only in cleavage of the phosphinoyl group to give the simple stannylated complex **17**, and attempted Stille type reactions were also unsuccessful.

In order to progress this chemistry it was decided to reduce the phosphine oxide **16** to give the corresponding phosphine. This transformation was achieved using a mixture of polymethylhydrosiloxane and $Ti(OPr)_4$ in THF at reflux, Scheme 7.[17]



(±)-**13** (R = $SiMe_3$, R′ = H) (±)-**18** (R = $SiMe_3$, R′ = H) (74%)

(±)-**14** (R = R′ = $SiMe_3$) (±)-**19** (R = R′ = $SiMe_3$) (81%)

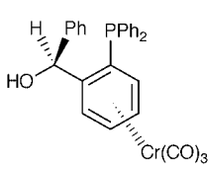
(–)-**16** (R = $SnBu_3$, R′ = H) (–)-**20** (R = $SnBu_3$, R′ = H) (93%)

Scheme 7

As shown, not only (−)-**16**, but also complexes **13** and **14** (as their racemates) were also cleanly reduced to the corresponding phosphines using this method.

A re-investigation of the transmetallation approach, this time with phosphine complex (−)-**20**, proved much more fruitful than with the corresponding phosphine oxide, Table 1.

The use of cyclohexanecarbaldehyde as quenching agent gave the desired adducts **22** as a 9:1 mixture of diastereomers, whereas the corresponding reaction with benzaldehyde gave only one detectable stereoisomeric product **21**. This latter com-



21

pound was shown to have the relative stereochemistry shown in Fig. 2 by X-ray structure determination,† and was assayed by HPLC and found to have an ee of 81%. We assume that this level of induction reflects that for the initial stannane intermediate (−)-**16**, and also the other products indicated in Table 1. This level of induction is in line with, but perhaps slightly lower than, that seen earlier in the generation of **13** under the same conditions.

The availability of stannylated complexes also suggested the possibility of Stille type couplings to give biaryl complexes. However, initial attempts in this area using complex **16** were not fruitful, and we turned instead to the use of the *ortho*-bromophosphine complex **27** in Suzuki cross-coupling reactions.

† This determination was carried out using racemic material.

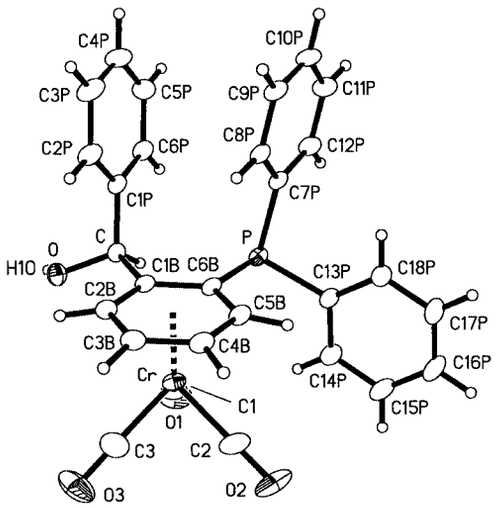


Fig. 2 Displacement ellipsoid plot for compound **21** [*T* 150 K, 50% probability].

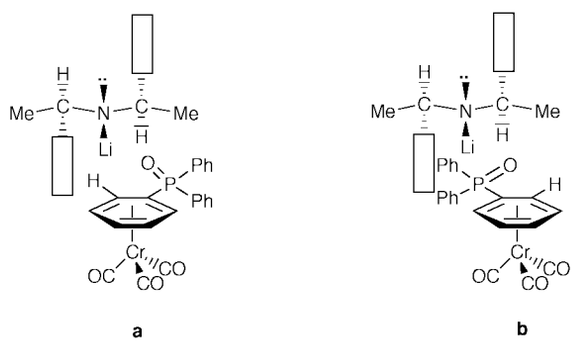
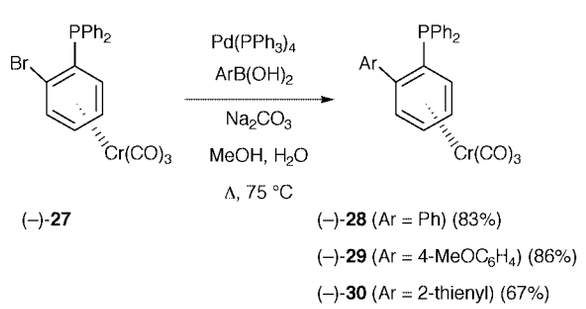


Fig. 3

Under usual Suzuki reaction conditions coupling of this substrate with typical arylboronic acids was achieved in high yield to give biaryl complexes **28**–**30**, Scheme 8.[18]

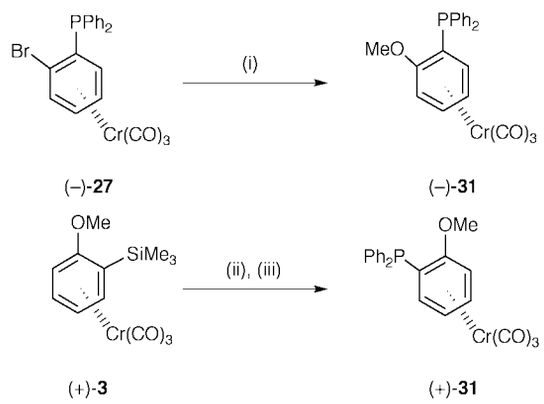


Scheme 8

This type of reaction sequence serves to generate product complexes not available by other means, for example by the transmetallation–electrophilic quench sequence, including the interesting thiophene derivative **30**.

To conclude this chiral base study of complex **12** we reconsidered the sense of enantioselectivity observed in the initial reaction with chiral base **2** and how this compares to our earlier work with anisole complex **1**. The present results with complex **12** conform to a naive model in which approach of the substrate to the chiral lithium amide occurs as shown in Fig. 3.

In Fig. 3a approach of the chromium complex to the chiral base occurs *via* an open quadrant, and coordination of the phosphine oxide to the lithiated base then allows removal of the ring hydrogen shown. In the case of removal of the enantiotopic hydrogen, shown in Fig. 3b, placing both the P=O and the hydrogen to be removed in the vicinity of the basic nitrogen results in steric clashes between a phenyl group on the base and those on the phosphorus atom. Although this model is simply a crude pictorial representation of the observed selectivity, it serves to explain a body of results involving enantioselective enolisation of cyclic ketones of varied structures, as well as deprotonation of certain other types of substrate.[19] In this regard, it is the reaction of complex **1** with base **2** that seems *not* to fit this simple model. Although we were in no doubt concerning the earlier results, this apparent disparity prompted us to correlate the anisole complex chemistry with the present work on phosphinoyl complex **12**. This was done as outlined in Scheme 9.



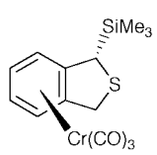
Scheme 9 *Reagents and conditions*: (i) NaOMe, 15-C-5, THF, Δ (61%); (ii) ^{n}BuLi, THF, Ph_2PCl (78%); (iii) TBAF, THF, −78 °C (95%).

Substitution of bromine in the complex (−)-**27** gave the *o*-methoxyphosphine complex (−)-**31**. This same compound could also be prepared starting with (+)-**3** by metallation and reaction with Ph_2PCl, followed by desilylation with tetrabutylammonium fluoride (TBAF). In this case the product was (+)-**31**, which was the expected outcome based on the original assignments.

The chemistry described above enables the synthesis of varied phosphorus-containing complexes in good enantiomeric excess. The crystallinity of many of these systems allows facile enantiomeric enrichment, thus allowing access to enantiomerically pure derivatives. Although we have been unable to explore this area further, the potential for these types of complex for asymmetric catalysis has been highlighted in a recent review by Bolm and Muniz.[5a]

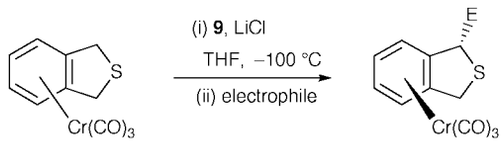
(ii) Chemistry of sulfur-containing system 6

The effective asymmetric substitution of complex **6** was demonstrated to require the use of bis-lithium amide **9** to achieve high enantiomeric excess, the use of the simpler base **2** giving products of only about 5% ee.[7] Initial reactions using base **9** in the presence of Me_3SiCl (*in situ* quench) gave the desired product **32** in 95% yield, and with an ee of 89%.



32

However, analogous reactions using base **9**, but with MeI as the electrophile, gave little or no product. As in our previous work,[10] this result was shown to be due to a salt in which LiCl, either generated from the Me_3SiCl or added deliberately, substantially accelerates the rate of metallation. In this case reaction with base **9** followed by D_2O quenching gave no deuterium incorporation, whereas the corresponding reaction including 0.5–1.0 equivalents of LiCl showed *ca.* 95% incorporation.



6 **33–38**

Table 2

Electrophile	Me_3SiCl	MeI	EtI	BnBr	Ph_2CO	allylBr	$ArCH_2Br$[a]
Product	**32**	**33**	**34**	**35**	**36**	**37**	**38**
Yield (%)	95	95	91	70	88	75	89
Ee (%)[b]	89	94	87[c]	n.d.[d]	95	n.d.[d]	95

[a] $ArCH_2Br$ = 2-(bromomethyl)naphthalene. [b] Determined by HPLC. [c] Sluggish alkylation at −78 °C may account for slightly lower ee. [d] Not determined (ee assay not readily established).

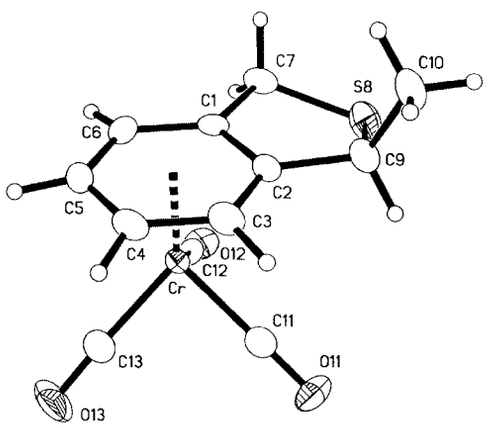


Fig. 4 Displacement ellipsoid plot for compound **33** [*T* 150 K, 50% probability, Flack parameter −0.02(2)].

Subsequently, by including LiCl into the reaction medium, we were able to conduct highly enantioselective metallations, and quench with a range of electrophiles, Table 2.

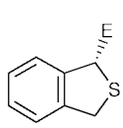
As shown, it was possible to determine the levels of ee for several of the products, these being good to excellent. The absolute stereochemistry of the products is based on an X-ray structure determination carried out on the methylated product **33** following recrystallisation, Fig. 4.

The sense of asymmetric induction is as expected from our previous work on the corresponding isobenzofuran complex **5**,[6] the bis-amide **9** giving opposite selectivity to the simpler amide **2** (both prepared from (*R*)-phenylethylamine). Interestingly, Gibson and co-workers observed a swap-over in the sense of absolute stereochemical outcome in the asymmetric synthesis of sulfur-containing complexes starting with **8** compared to ethers derived from **7**, using base **9**.[8] This unexpected observation is not duplicated in our results, presumably due to the additional conformational constraint imposed by incorporating the heteroatom into a ring structure.

Several further points relating to the chiral base reactions of this system are worthy of mention. Firstly, although the presence of LiCl is essential to promote metallation, it seems not to affect the enantioselectivity of the process; traces of product formed in the absence of salt were still of very high ee. Secondly, reactions can be conducted using the mono-lithium amide corresponding to **9**—*i.e.* the base generated when the diamine precursor is treated with only *one* equivalent of ″BuLi. In this case products are formed with comparable ee to when **9** is used, but in somewhat lower yields. This finding is in agreement with those of Gibson and co-workers, although in their system they found that even the yields of highly enriched products were not adversely affected by reducing the amount of ″BuLi used to one equivalent.[20]

Finally, we observed some variations in apparent rates of electrophilic quench, depending upon which type of base is used for the metallation. The best base for preparing racemic compounds (for ee assay) was ᵗBuLi, with other bases giving lower yields due to the formation of polysilylated by-products. Reaction with ᵗBuLi, followed by quenching with EtI or benzyl bromide, gave moderate yields of alkylated products (45–65%) after one hour at −100 °C, whereas analogous reactions using base **9** gave only traces of product. We attribute this effect to complexation of the intermediate anion with the monoanion corresponding to **9**—*i.e.* the anionic chromium complex forms a mixed aggregate with the mono-lithium amide, which reduces the rate of subsequent electrophilic quench. Another consequence of this effect is in the reaction with acetone. Using ᵗBuLi as the base gives 83% yield of the acetone adduct, whereas use of **9** gives only about 20% yield (although the ee is 99%!), presumably because the mixed aggregate is highly basic and promotes aldolisation of the acetone.

With some of the complexes, *i.e.* **32**, **33**, **36** and **38**, it was possible to improve the level of enantiomeric enrichment to >99% ee by recrystallisation. Finally, some of the complexes were exposed to light, in the presence of atmospheric oxygen, in order to effect demetallation and enable the isolation of the corresponding free sulfides **39**–**43** in highly enantiomerically enriched form.



39 E = Me (88%)
40 E = Et (70%)
41 E = Bn (84%)
42 E = allyl (79%)
43 E = 2-naphthylmethyl (86%)

Chiral sulfides have recently found use in a range of asymmetric transformations, including epoxidation, sulfenylation and cuprate addition reactions.[21–23] It is hoped that our new family of chiral sulfides, along with the respective chromium complexes, may open up new possibilities for the design of novel sulfur-containing reagents and catalysts.

Conclusion

The use of chiral lithium amide bases can provide an easy access to a wide range of chiral products in highly enantiomerically enriched form. In the present work we have sought to apply this strategy to some unusual tricarbonyl(η^6-arene)-chromium complexes containing phosphorus and sulfur. Hopefully the results will encourage others to use the chiral base method in the organometallic arena, and the types of chiral phosphine and sulfide that we have described here may yet prove to have applications in asymmetric catalysis.

Experimental

General details

Melting points were determined using a hot-stage melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded using a Perkin-Elmer 1600 Series FTIR spectrometer.

Mass spectra were recorded on an AEI MS-902 or VG Micromass 70E mass spectrometer, using electron impact ionisation (EI) or fast atom bombardment (FAB) using *m*-nitrobenzyl alcohol as the matrix. Microanalytical data were obtained on a Perkin-Elmer 240B elemental analyser. Optical rotations were recorded using a JASCO DIP370 digital polarimeter.

All NMR spectra were recorded on either a Bruker AM 250, JEOL FX 270, Bruker AM 400 or Bruker AM 500 spectrometer, with tetramethylsilane as internal standard. *J* values are recorded in Hz and assignments indicated for ^{13}C NMR were obtained with the aid of a DEPT sequence.

Flash column chromatography was performed using Fluka silica gel 60 (220–440 mesh). Analytical TLC was performed using MACHEREY-NAGEL Polygram® SIL G/UV$_{254}$ silica gel precoated plastic plates which were viewed under ultraviolet light and developed with basic potassium permanganate solution. Enantiomeric excesses were determined by high performance liquid chromatography (HPLC) using either Chiralcel OD or OJ columns at ambient temperatures. Detection was by UV at the stated wavelength and data was processed using an HP-3D Dos chemstation.

Organic solvents and reagents were dried by distillation from the appropriate drying agents. THF and Et_2O were distilled over sodium wire–benzophenone ketyl, methanol from magnesium methoxide and chlorotrimethylsilane from calcium hydride. Light petroleum refers to light petroleum (bp 40–60 °C) which was distilled prior to use. Unless otherwise stated, all other solvents and reagents were used as received from commercial suppliers.

Tricarbonyl[η^6-(diphenylphosphino)benzene]chromium(0)] 11 [13]

n-BuLi (3.5 ml of a 1.6 M solution in hexanes, 5.6 mmol) was added dropwise to a solution of tricarbonyl(η^6-benzene)-chromium(0) **10** (1.00 g, 4.7 mmol) in THF (25 ml) at −78 °C under an atmosphere of nitrogen. The reaction mixture was warmed to 0 °C and stirred for 0.25 h before being recooled to −78 °C. This solution was added dropwise by cannula to a solution of chlorodiphenylphosphine (1.70 ml, 9.47 mmol) in THF (10 ml) at −78 °C. Stirring was continued at −78 °C for an additional 1 h before the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (5 ml) and allowed to warm to room temperature. The reaction mixture was then extracted with ethyl acetate (2 × 30 ml), and the combined organic extracts were washed with water (50 ml), and brine (50 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Purification of the resulting yellow oil by flash column chromatography on silica gel (20% EtOAc–light petroleum) gave complex **11** as a yellow solid (1.0 g, 54%), mp 147–148 °C (lit.,[13] 146–147 °C); ν_{max} ($CHCl_3$)/cm^{-1} 1979 and 1897 (C=O); δ_H (250 MHz, $CDCl_3$) 5.18 (4H, m, CrC*H*), 5.44 (1H, m, CrC*H*), 7.39 (10H, m, Ar*H*); δ_C (68 MHz, $CDCl_3$) 91.9 (d, $J_{P\text{-}C}$ 5, 2Cr*C*H), 95.0 (Cr*C*H), 99.5 (d, $J_{P\text{-}C}$ 17, 2Cr*C*H), 104.0 (d, $J_{P\text{-}C}$ 20, Cr*C*), 130.0 (d, $J_{P\text{-}C}$ 7, ArCH), 130.7 (ArCH), 135.2 (d, $J_{P\text{-}C}$ 7, ArCH), 136.2 (d, $J_{P\text{-}C}$ 12, ArC) and 233.3 (3CO); *m*/*z* (EI) 398 (M$^+$, 3%), 314 [(M − 3CO)$^+$, 100%], 262 [(M − Cr(CO)$_3$)$^+$, 50%] and 183 [(M − Cr(CO)$_3$ − Ph)$^+$, 31%] (HRMS: found M$^+$, 398.0174. $C_{21}H_{15}O_3PCr$ requires *M*, 398.0164).

Tricarbonyl[η^6-(diphenylphosphinoyl)benzene]chromium(0) 12

n-BuLi (3.5 ml of a 1.6 M solution in hexanes, 5.6 mmol) was added dropwise to a solution of tricarbonyl(η^6-benzene)-chromium(0) (1.0 g, 4.7 mmol) in THF (25 ml) at −78 °C under an atmosphere of nitrogen. The reaction mixture was warmed to 0 °C and stirred for 0.25 h before being recooled to −78 °C. This solution was added dropwise by cannula to a solution of diphenylphosphinic chloride (1.70 ml, 8.91 mmol) in THF (10 ml) at −78 °C. Stirring was continued at −78 °C for an additional 1 h before the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (5 ml) and allowed to warm to room temperature. The reaction mixture was then extracted with ethyl acetate (2 × 30 ml), and the combined organic extracts were washed with water (50 ml) and brine (50 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Purification of the resulting yellow oil by flash column chromatography on silica (40% EtOAc–light petroleum) gave complex **12** as a yellow solid (1.21 g, 62%), mp 157–158 °C (Found: C, 61.07; H, 3.59. $C_{21}H_{15}O_4PCr$ requires C, 60.88; H, 3.65%); ν_{max} ($CHCl_3$)/cm^{-1} 1991 and 1934 (C≡O); δ_H (250 MHz, $CDCl_3$) 5.09 (2H, m, CrC*H*), 5.60–5.66 (3H, m, CrC*H*), 7.47–7.64 (6H, m, Ar*H*) and 7.70–7.79 (4H, m, Ar*H*); δ_C (68 MHz, $CDCl_3$), 87.4 [d, $J_{P\text{-}C}$ 9, 2Cr*C*H], 94.3 (d, $J_{P\text{-}C}$ 102, Cr*C*), 95.5 (Cr*C*H), 96.7 (d, $J_{P\text{-}C}$ 10, 2Cr*C*H), 128.4 (d, $J_{P\text{-}C}$ 12, 4Ar*C*H), 130.3 (2Ar*C*), 131.7 (d, $J_{P\text{-}C}$ 10, 4Ar*C*H), 132.4 (d, $J_{P\text{-}C}$ 3, 2Ar*C*H) and 230.3 (3CO); *m*/*z* (FAB) 415 [(M + H)$^+$, 20%], 358 [(M − 2CO)$^+$, 17%], 330 [(M − 3CO)$^+$, 100%] (HRMS: found [M + H]$^+$, 415.0236. Requires [*M* + *H*], 415.0191).

Synthesis of (2*S*)-tricarbonyl[η^6-(1-diphenylphosphinoyl-2-trimethylsilyl)benzene]chromium(0) 13 according to Scheme 3

A solution of the chiral base **2** (+LiCl) was prepared by addition of *n*-BuLi (3.9 ml of 1.6 M solution in hexanes, 6.2 mmol) to a solution of the appropriate chiral amine hydrochloride salt (758 mg, 2.90 mmol) in THF (30 ml) at −78 °C, under an atmosphere of nitrogen. The solution was warmed to room temperature and stirred for 0.25 h before being recooled to −78 °C, and Me_3SiCl (1.5 ml, 12 mmol) was added in one portion, followed by a solution of the chromium complex **12** (1.0 g, 2.4 mmol) in THF (3 ml). After stirring the solution at −78 °C for 0.5 h, saturated aqueous $NaHCO_3$ (5 ml) was added and the mixture was then allowed to warm to room temperature. The mixture was extracted with diethyl ether (30 ml), the organic extract was washed with dilute HCl (2 M, 30 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The resulting yellow oil was then purified by flash column chromatography on silica gel (25% EtOAc–light petroleum) to give the silylated complex **13** (1.05 g, 90%), mp 156–157 °C; $[\alpha]_D^{22}$ −203 (*c* 0.36 in $CHCl_3$) (Found: C, 59.29; H, 4.94. $C_{24}H_{23}O_4PSiCr$ requires C, 59.25; H, 4.77%); ν_{max} ($CHCl_3$)/cm^{-1} 1990, 1935 and 1872 (C≡O); δ_H (250 MHz, $CDCl_3$) 0.31 (9H, s, Si*Me*$_3$), 4.84 (1H, dd, $^3J_{P(O)\text{-}H}$ 10 and $^3J_{H\text{-}H}$ 6, CrC*H*), 5.27 (1H, dd, *J* 6, CrC*H*), 5.43 (1H, dd, *J* 6, CrC*H*), 5.55 (1H, d, *J* 6, CrC*H*) and 7.46–7.74 [10H, m, (Ar*H*)$_2$P]; δ_C (68 MHz, $CDCl_3$) 2.3 (Si(*C*H$_3$)$_3$), 91.4 (d, $J_{P\text{-}C}$ 11, Cr*C*H), 93.1 (Cr*C*H), 96.2 (d, $J_{P\text{-}C}$ 15, Cr*C*H), 98.7 (d, $J_{P\text{-}C}$ 11.00, Cr*C*H), 101.5 (d, $J_{P(O)\text{-}C}$ 104, Cr*C*), 105.8 (d, $J_{P\text{-}C}$ 15, Cr*C*), {(128.7, 128.9, 129.1), Ar*C*H}, 131.7 (d, $J_{P\text{-}C}$ 48, Ar*C*), {(132.2, 132.4, 132.5, 132.6, 132.8, 132.9, 133.1), Ar*C*H}, 134.0 (d, $J_{P\text{-}C}$ 102, Ar*C*) and 231.1 (3CO); *m*/*z* (FAB) 486 (M$^+$, 6%), 402 [(M − 3CO)$^+$, 48%] and 335 [(M − Cr(CO)$_3$ − CH$_3$)$^+$, 100%] (HRMS: found [M + H]$^+$, 487.0647. Requires [*M* + *H*], 487.0587).

The enantiomeric excess of **13** was determined to be 73% using a Chiralcel OD column with 99.5:0.5 hexane–isopropyl alcohol (IPA) as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention times 33.7 min (major) and 39.7 min (minor).

Synthesis of (2*S*)-tricarbonyl{η^6-[1-diphenylphosphinoyl-2,5-bis(trimethylsilyl)]benzene}chromium(0) 14 using 2 equiv. of chiral base 2 according to Scheme 6

A solution of chiral base **2** was prepared, as described above, using chiral amine hydrochloride salt (1.52 g, 5.80 mmol) and *n*-BuLi (8.3 ml of 1.6 M solution in hexanes, 13 mmol), in THF

(100 ml). To the resulting solution of the chiral base **2** (+LiCl) at −78 °C was added Me_3SiCl (4.0 ml, 31 mmol) in one portion, followed by a solution of the chromium complex **12** (1.20 g, 2.90 mmol) in THF (3 ml). After stirring the solution at −78 °C for 0.5 h, saturated aqueous $NaHCO_3$ (5 ml) was added and the mixture was allowed to warm to room temperature. The mixture was extracted with diethyl ether (2 × 30 ml), and the combined organic extracts were washed with dilute HCl (2 M, 2 × 30 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The resulting yellow oil was then purified by flash column chromatography on silica gel (10–25% EtOAc–light petroleum) to give the disilylated complex **14** as a yellow solid (1.33 g, 82%), mp 172 °C; $[a]_D^{22}$ −162 (*c* 1.0 in $CHCl_3$) (Found: C, 57.92; H, 5.65. $C_{27}H_{31}O_4PSi_2Cr$ requires C, 58.06; H, 5.60%); ν_{max} ($CHCl_3$)/cm^{-1} 1982 and 1923 (C≡O); δ_H (250 MHz, $CDCl_3$) 0.14 (9H, s, Si(C*H*$_3$)$_3$), 0.32 (9H, s, Si(C*H*$_3$)$_3$), 4.94 (1H, dd, $^3J_{P(O)-H}$ 10 and *J* 1, CrC*H*), 5.38 (1H, dd, *J* 6 and J_{P-H} 2, CrC*H*), 5.52 (1H, ddd, *J* 6, J_{P-H} 2 and *J* 1, CrC*H*) and 7.46–7.73 [10H, m, (Ar*H*)$_2$P]; δ_C (68 MHz, $CDCl_3$) −0.4 (Si(*C*H$_3$)$_3$), 3.0 (Si(*C*H$_3$)$_3$), 97.7 (d, *J* 10, Cr*C*H), 98.9 (d, *J* 7, Cr*C*), 100.0 (d, $J_{P(O)-C}$ 105, Cr*C*), 100.1 (Cr*C*H), 103.2 (d, *J* 13, Cr*C*H), 109.0 (d, *J* 15, Cr*C*), {(129.4, 129.5, 129.6, 129.7, 129.9), Ar*C*H}, {(133.1, 133.3, 133.3, 133.3, 133.5, 133.6), Ar*C*H}, 134.5 (d, $J_{P(O)-C}$ 101, Ar*C*) and 232.5 (3CO); *m*/*z* (FAB) 559 [(M + H)$^+$, 30%] (HRMS: found [M + H]$^+$, 559.0999. Requires [*M* + *H*], 559.0982).

The enantiomeric excess of **14** was found to be 79% using a Chiralcel OD column with 99.5:0.5 hexane–IPA as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention times 15.2 min (major) and 16.23 min (minor).

Synthesis of (2*R*)-tricarbonyl{η^6-[1-diphenylphosphinoyl-2,5-bis(trimethylsilyl)]benzene}chromium(0) 14 using chiral base 9 according to Scheme 4

A solution of the bis-lithium amide base **9** was prepared by addition of *n*-BuLi (0.40 ml of a 1.45 M solution in hexanes, 0.58 mmol) dropwise to a solution of the corresponding chiral diamine (0.12 g, 0.29 mmol) in THF (10 ml) at −78 °C under an atmosphere of nitrogen. The mixture was allowed to warm to room temperature and stirred for 0.25 h before it was recooled to −78 °C. Chlorotrimethylsilane (0.15 ml, 1.20 mmol) was added in one portion followed by complex **12** (0.10 g, 0.24 mmol) in THF (1 ml). The reaction mixture was allowed to stir at −78 °C for 0.5 h before saturated aqueous $NaHCO_3$ (3 ml) was added. After addition of EtOAc (5 ml), the organic layer was separated and washed with saturated aqueous $NaHCO_3$ (10 ml), brine (10 ml), and dried ($MgSO_4$). The organic extract was concentrated under reduced pressure and the resulting yellow residue was purified by flash column chromatography on silica gel (10–25% EtOAc–light petroleum) to give **14**, as a yellow solid (80 mg, 59%), mp 170 °C; $[a]_D^{20}$ 160 (*c* 0.64 in $CHCl_3$) and **13** as a yellow oil (8 mg, 7%); $[a]_D^{20}$ −119 (*c* 0.13 in $CHCl_3$). Both complexes were identified by their ^{1}H NMR spectra, which were identical to those described above. The ee of **14** was determined, as described above, to be 82%.

Synthesis of (2*S*)-tricarbonyl[η^6-(1-diphenylphosphinoyl-2-trimethylsilyl)benzene]chromium(0) 13 and (2*R*)-tricarbonyl-{η^6-[1-diphenylphosphinoyl-2,5-bis(trimethylsilyl)]benzene}-chromium(0) 14 *via* kinetic resolution of (±)-13 according to Scheme 5

A solution of chiral base **9** was prepared, as described above, using chiral diamine (43 mg, 0.10 mmol) and *n*-BuLi (0.13 ml of a 1.6 M solution in hexanes, 0.21 mmol) in THF (5 ml). The resulting solution of **9**, at −78 °C, was added dropwise by cannula to a solution of (±)-**13** (42 mg, 0.086 mmol) and chlorotrimethylsilane (0.05 ml, 0.43 mmol) in THF (5 ml) at −78 °C under an atmosphere of nitrogen. The reaction mixture was allowed to stir at −78 °C for 0.5 h before saturated aqueous $NaHCO_3$ (3 ml) was added. After addition of EtOAc (5 ml), the organic layer was separated and washed with saturated aqueous $NaHCO_3$ (10 ml), brine (10 ml), and dried ($MgSO_4$). The solvent was evaporated under reduced pressure and the resulting yellow residue was purified by flash column chromatography on silica gel (10–25% EtOAc–light petroleum) to give **14** as a yellow solid (22 mg, 46%), mp 171 °C; $[a]_D^{20}$ 110 (*c* 0.45 in $CHCl_3$) and **13** as a yellow oil (15 mg, 36%), $[a]_D^{20}$ −148 (*c* 0.72 in $CHCl_3$). Both complexes were identified by their ^{1}H NMR spectra, which were identical to those descibed above. The ee values for these samples of **14** and **13** were determined, as described above, to be 64% and 73% respectively.

(2*R*)-Tricarbonyl[η^6-(1-diphenylphosphinoyl-2-tributylstannyl)-benzene]chromium(0) 16

A solution of chiral base **2** was prepared, as described above, using chiral amine hydrochloride salt (473 mg, 1.81 mmol) and *n*-BuLi (2.25 ml, 1.6 M solution in hexanes, 3.60 mmol) in THF (15 ml). The resulting solution of chiral base **2** (+LiCl) was cooled to −100 °C, and a mixture of Bu_3SnCl (2.00 ml, 7.37 mmol) and complex **12** (624 mg, 1.51 mmol) in THF (5 ml), was added in one portion. After stirring at −100 °C for 0.5 h, saturated aqueous $NaHCO_3$ (5 ml) was added and the mixture was allowed to warm to room temperature. The mixture was extracted with diethyl ether (30 ml), and the organic extract was washed with dilute HCl (2 M, 30 ml) and stirred with aqueous ammonia (5% v/v, 100 ml) for 16 h. The organic layer was separated, dried ($MgSO_4$), and evaporated under reduced pressure. The resulting yellow oil was then purified by flash column chromatography on silica gel (20% EtOAc–light petroleum) to yield complex **16** as a yellow solid (1.03 g, 98%), mp 128 °C; $[a]_D^{22}$ −86 (*c* 2.4 in $CHCl_3$) (Found: C, 56.40; H, 6.04. $C_{33}H_{41}O_4PSnCr$ requires C, 56.35; H, 5.87%); ν_{max} ($CHCl_3$)/cm^{-1} 1974 and 1908 (C≡O); δ_H (250 MHz, $CDCl_3$) 0.85 (9H, t, *J* 7, Sn[(CH$_2$)$_3$-C*H*$_3$]$_3$), 1.09 (6H, m, Sn[(C*H*$_2$)$_3$CH$_3$]$_3$), 1.17–1.31 (6H, m, Sn-[(C*H*$_2$)$_3$CH$_3$]$_3$), 1.37–1.49 (6H, m, Sn[(C*H*$_2$)$_3$CH$_3$]), 5.08–5.14 (1H, m, CrC*H*), 5.18–5.24 (1H, m, CrC*H*), 5.40 (1H, d, *J* 6, CrC*H*), 5.46–5.53 (1H, m, CrC*H*) and 7.43–7.76 [10H, m, (Ar*H*)$_2$P]; δ_C (68 MHz, $CDCl_3$) 13.3 (3*C*H$_2$), 13.6 (3*C*H$_3$), 27.4 (3*C*H$_2$), 28.9 (3*C*H$_2$), 89.7 (d, J_{P-C} 11, Cr*C*H), 95.4 (Cr*C*H), 96.4 (d, J_{P-C} 16, Cr*C*H), 97.7 (d, J_{P-C} 13, Cr*C*H), 100.1 (d, J_{P-C} 110, Cr*C*), 107.7 (d, J_{P-C} 16, Cr*C*), {(128.2, 128.4, 128.6), Ar*C*H}, 130.8 (d, J_{P-C} 106, Ar*C*), {(131.7, 131.9, 132.2, 132.3, 132.5, 132.5), Ar*C*H}, 134.0 (ArC) and 231.3 (3CO); *m*/*z* (FAB) 703 (M$^+$, 1%), 647 [(M − Bu)$^+$, 100%] and 619 [(M − 3CO)$^+$, 7%] (HRMS: found [M − Bu]$^+$, 647.0405. Requires [*M* − *Bu*], 647.0465).

Reduction of phosphine oxides according to Scheme 7

(i) Preparation of tricarbonyl[η^6-(1-diphenylphosphino-2-trimethylsilyl)benzene]chromium(0) 18. To a mixture of complex **13** (0.11 g, 0.23 mmol) and polymethylhydrosiloxane (0.15 ml, 2.30 mmol of H equiv.) in THF (2 ml) was added Ti(O^{i}Pr)$_4$ (0.068 ml, 0.23 mmol) and the mixture was heated at reflux overnight. The reaction mixture was cooled to room temperature and diluted with THF (20 ml). NaOH solution (2 M, 100 ml) was added slowly with vigorous stirring and the mixture stirred for 8 h. The mixture was extracted with ethyl acetate (2 × 20 ml). The combined organic extracts were washed with dilute HCl (2 M, 10 ml), brine (2 × 20 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The product was purified by flash column chromatography on silica gel (10% EtOAc–light petroleum) to give complex **18** as a yellow crystalline solid (80 mg, 74%), mp 193 °C (Found: C, 60.94; H, 5.11. $C_{24}H_{23}O_3SiPCr$ requires C, 61.27; H, 4.93%); ν_{max} ($CHCl_3$)/cm^{-1} 1969 and 1902 (C≡O); δ_H (250 MHz, $CDCl_3$) 0.28 [9H, s, Si(C*H*$_3$)$_3$]; 4.71 (1H, ddd, *J* 6 and 2, CrC*H*), 5.27–5.39 (2H, m, CrC*H*), 5.44 (1H, ddd, *J* 6 and 2, CrC*H*) and 7.22–7.37 [10H, m, (Ar*H*)$_2$P]; δ_C (68 MHz, $CDCl_3$) 1.4 [Si(CH$_3$)$_3$], 92.0 (Cr*C*H),

93.4 (Cr*C*H), 95.6 (Cr*C*H), 99.4 (d, $J_{P\text{-}C}$ 12, Cr*C*H), 106.6 (d, $J_{P\text{-}C}$ 29, Cr*C*), 110.7 (d, $J_{P\text{-}C}$ 21, Cr*C*), {(128.5, 128.7, 128.9, 129.6, 133.2, 133.5), Ar*C*H}, 134.3 (d, $J_{P\text{-}C}$ 15, Ar*C*), {(134.6, 134.9), Ar*C*H}, 137.2 (d, $J_{P\text{-}C}$ 10, Ar*C*) and 232.4 (3CO); *m/z* (EI) 470 (M^+, 1%), 386 [$(M - 3CO)^+$, 100%] and 334 [$(M - 3CO - Cr)^+$, 32%] (HRMS: found M^+, 470.0587. Requires *M*, 470.0559).

(ii) Preparation of tricarbonyl{η⁶-[1-diphenylphosphino-2,5-bis(trimethylsilyl)]benzene}chromium(0) 19. To a mixture of complex **14** (0.10 g, 0.18 mmol) and polymethylhydrosiloxane (0.12 ml, 1.80 mmol of H equiv.) in THF (5 ml) was added $Ti(O^iPr)_4$ (0.053 ml, 0.18 mmol) and the mixture was heated at reflux overnight. The reaction mixture was cooled to room temperature and diluted with THF (20 ml). NaOH solution (2 M, 100 ml) was added slowly with vigorous stirring and the mixture stirred for 8 h. The mixture was extracted with ethyl acetate (3 × 20 ml). The combined organic extracts were washed with dilute HCl (2 M, 10 ml), brine (2 × 20 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The product was purified by flash column chromatography on silica gel (10% EtOAc–light petroleum) to give complex **19** as a yellow crystalline solid (79 mg, 81%), mp 164 °C; ν_{max} ($CHCl_3$)/cm^{-1} 1963 and 1900 (C≡O); δ_H (400 MHz, $CDCl_3$) 0.04 [9H, s, Si(CH_3)$_3$], 0.23 [9H, s, Si(CH_3)$_3$], 4.77 (1H, d, *J* 1, CrC*H*), 5.16 (1H, m, CrC*H*), 5.35 (1H, m, CrC*H*), 7.17 [3H, m, (Ar*H*)$_2$P] and 7.28 [7H, m, (Ar*H*)$_2$P]; δ_C (100 MHz, $CDCl_3$) −1.5 [Si(*C*H$_3$)$_3$], 1.3 [Si(*C*H$_3$)$_3$], 97.0 (d, $J_{P\text{-}C}$ 12, Cr*C*H), 98.8 (Cr*C*H), 99.6 (Cr*C*), 102.6 (Cr*C*H), 107.9 (d, $J_{P\text{-}C}$ 22, Cr*C*), 109.5 (d, $J_{P\text{-}C}$ 41, Cr*C*), {(128.5, 128.6, 128.7, 128.9, 129.6, 133.3, 133.5, 134.5, 134.7), Ar*C*H}, 135.3 (d, $J_{P\text{-}C}$ 14, Ar*C*), 137.6 (d, $J_{P\text{-}C}$ 11, Ar*C*) and 232.6 (3CO); *m/z* (FAB) 542 (M^+, 24%), 458 [$(M - 3CO)^+$, 100%] and 406 [$(M - 3CO - Cr)^+$, 14%] (HRMS: found M^+, 542.0950. Requires *M*, 542.0954).

(iii) Preparation of (2*R*)-tricarbonyl[η⁶-(1-diphenylphosphino-2-tributylstannyl)benzene]chromium(0) 20. To a mixture of complex (−)-**16** (0.10 g, 0.14 mmol) and polymethylhydrosiloxane (90 μl, 1.40 mmol of H equiv.) in THF (5 ml) was added $Ti(O^iPr)_4$ (42 μl, 0.14 mmol) and the mixture heated at reflux overnight. The reaction mixture was cooled to room temperature and diluted with THF (20 ml). NaOH solution (2 M, 100 ml) was added slowly with vigorous stirring and the mixture stirred for 8 h. The mixture was extracted with ethyl acetate (3 × 20 ml). The combined organic extracts were washed with dilute HCl (2 M, 10 ml), brine (2 × 20 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The product was purified by flash column chromatography on silica gel (10% EtOAc–light petroleum), to give complex **20** as a yellow crystalline solid (89 mg, 93%), mp 78 °C; $[a]_D^{22}$ −161 (*c* 0.85 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1964 and 1896 (C≡O); δ_H (250 MHz, $CDCl_3$) 0.85 (9H, t, *J* 7, Sn[(CH$_2$)$_3$CH_3]$_3$), 1.05 (6H, m, Sn[(CH_2)$_3$-CH$_3$]$_3$), 1.15–1.30 (6H, m, Sn[(CH_2)$_3$CH$_3$]$_3$), 1.36–1.46 (6H, m, Sn[(CH_2)$_3$CH$_3$]$_3$), 4.79–4.82 (1H, m, CrC*H*), 5.23–5.28 (2H, m, CrC*H*), 5.34–5.37 (1H, m, CrC*H*) and 7.24–7.36 [10H, m, (Ar*H*)$_2$P]; δ_C (68 MHz, $CDCl_3$) 12.3 (3*C*H$_2$), 13.6 (3*C*H$_2$), 27.3 (3*C*H$_2$), 28.9 (3*C*H$_3$), 92.2 (Cr*C*H), 94.2 (Cr*C*H), 97.1 (Cr*C*H), 100.0 (d, $J_{P\text{-}C}$ 17, Cr*C*H), 110.2 (d, $J_{P\text{-}C}$ 61, Cr*C*), 118.1 (d, $J_{P\text{-}C}$ 10, Cr*C*), {(128.4, 128.5, 128.5, 128.6, 129.0, 129.6, 133.2, 133.5, 134.3, 134.6), Ar*C*H}, 137.0 (d, $J_{P\text{-}C}$ 10, Ar*C*) and 232.7 (3CO); *m/z* (EI) 687 (M^+, 1%), 631 [$(M - 2CO)^+$, 23%] and 603 [$(M - 3CO)^+$, 2%].

Typical procedure for transmetallation–electrophilic quench to give chiral phosphine complexes in Table 1

(i) Preparation of (2*S*)-tricarbonyl[η⁶-(1-diphenylphosphino-2-trimethylsilyl)benzene]chromium(0) 18. *n*-BuLi (0.18 ml of a 1.55 M solution in hexane, 0.28 mmol) was added dropwise to a solution of complex (−)-**20** (98 mg, 0.14 mmol) in THF (10 ml) at −78 °C under an atmosphere of nitrogen. The reaction mixture was stirred at −78 °C for 0.5 h before addition of chlorotrimethylsilane (0.089 ml, 0.70 mmol) in one portion and the mixture was stirred at −78 °C for a further 0.25 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (1 ml), allowed to warm up to room temperature and extracted with ethyl acetate (3 × 10 ml). The combined organic extracts were washed with water (2 × 10 ml), dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The resulting yellow residue was purified by flash column chromatography on silica gel (5% EtOAc–light petroleum) to give complex **18** as a yellow solid (53 mg, 80%); $[a]_D^{24}$ −289 (*c* 0.40 in $CHCl_3$). The ^{1}H NMR spectrum of the product was identical to that described above.

(ii) Preparation of (1*S*,1′*S*)-tricarbonyl{η⁶-[1-diphenylphosphino-2-(1-hydroxy-1-phenylmethyl)]benzene}chromium(0) 21. The above typical protocol was followed using complex (−)-**20** (0.18 g). Flash column chromatography on silica gel (20% EtOAc–light petroleum) gave complex **21** as a yellow solid (109 mg, 83%), mp 167 °C; $[a]_D^{22}$ −206 (*c* 1.0 in $CHCl_3$) (Found: C, 66.49; H, 4.22. $C_{28}H_{21}O_4PCr$ requires C, 66.66; H, 4.20%); ν_{max} ($CHCl_3$)/cm^{-1} 1972 and 1904 (C≡O); δ_H (400 MHz, $CDCl_3$) 2.32 (1H, d, *J* 3, D_2O exch., CHO*H*), 4.86 (1H, d, *J* 6, CrC*H*), 5.13 (1H, dd, *J* 6 and 6, CrC*H*), 5.69 (1H, dd, *J* 6 and 6, CrC*H*), 5.89 (1H, dd, *J* 6 and *J* 3, CrC*H*), 6.57 (1H, dd, *J* 7 and *J* 3, C*H*OH), 6.86–6.97 (5H, m, Ar*H*), 7.04 (2H, m, Ar*H*), 7.15 (3H, m, Ar*H*) and 7.33–7.39 (5H, m, Ar*H*); δ_C (68 MHz, $CDCl_3$) 71.7 (d, *J* 26, *C*HOH), 86.7 (d, *J* 5, Cr*C*H), 90.0 (Cr*C*H), 94.9 (Cr*C*H), 98.2 (d, *J* 2, Cr*C*H), 100.8 (d, $J_{P\text{-}C}$ 26, Cr*C*), 121.5 (d, $J_{P\text{-}C}$ 21, Cr*C*), {(127.9, 128.0, 128.1, 128.2, 128.4, 128.6, 128.7), (Ar*C*H)$_2$P}, {(129.7, 132.6, 132.9), Ar*C*H}, 133.9 [d, $J_{P\text{-}C}$ 12, (Ar*C*)$_2$P], 134.4 [d, $J_{P\text{-}C}$ 7, (Ar*C*)$_2$P], {(134.6, 134.9), Ar*C*H}, 140.2 (Ar*C*) and 232.1 (3CO); *m/z* (EI) 504.5 [M^+, 6%], 448.5 [$(M - 2CO)^+$, 1%] and 420.4 [$(M - 3CO)^+$, 100%] (HRMS: found M^+, 504.05646. Requires *M*, 504.05826).

The enantiomeric excess of **21** was determined to be 81% using a Chiralcel OD column with 90 : 10 hexane–IPA as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention times 12.7 min (major) and 24.0 min (minor).

(iii) Preparation of (2*S*)-tricarbonyl{η⁶-[1-diphenylphosphino-2-(1-cyclohexyl-1-hydroxymethyl)]benzene}chromium(0) 22. The above typical protocol was followed using complex (−)-**20** (0.20 g), to give the product as a 9 : 1 mixture of diastereomers, as indicated by the ^{1}H NMR spectrum. The resulting yellow residue was purified by flash column chromatography on silica gel (20% EtOAc–light petroleum) to give the major stereoisomer of **22** as a yellow solid (103 mg, 70%), mp 186 °C; $[a]_D^{22}$ −257 (*c* 0.45 in $CHCl_3$) (Found: C, 65.56; H, 5.56. $C_{28}H_{27}O_4PCr$ requires C, 65.88; H, 5.33%); ν_{max} ($CHCl_3$)/cm^{-1} 3615 (OH), 1966 and 1904 (C≡O); δ_H (400 MHz, $CDCl_3$) 0.34–1.36 (11H, m, Cyhx), 1.74 (1H, d, *J* 4, D_2O exch., CHO*H*), 4.90 (1H, d, *J* 6, CrC*H*), 5.12 (1H, dd, *J* 6 and 6, CrC*H*), 5.34–5.41 (1H, m, CrC*H*), 5.50–5.53 (1H, m, C*H*OH), 5.60 (1H, dd, *J* 6, CrC*H*) and 7.38–7.42 [10H, m, (Ar*H*)$_2$P]; δ_C (68 MHz, $CDCl_3$) 23.6 (*C*H$_2$), 25.8 (*C*H$_2$), 26.0 (*C*H$_2$), 26.4 (*C*H$_2$), 30.4 (*C*H$_2$), 43.4 (*C*H$_2$), 72.8 (d, *J* 26, *C*H), 87.8 (d, *J* 5, Cr*C*H), 90.0 (Cr*C*H), 94.7 (Cr*C*H), 98.3 (d, *J* 2, Cr*C*H), 101.4 (d, *J* 24, Cr*C*), 122.2 (d, *J* 21, Cr*C*), {(128.6, 128.7, 128.9, 129.5, 129.6, 133.5, 133.8, 134.5, 134.8), (Ar*C*H)$_2$P}, 133.5 (d, $J_{P\text{-}C}$ 12, Ar*C*), 135.8 (d, $J_{P\text{-}C}$ 9, Ar*C*) and 232.3 (3CO); *m/z* (EI) 510 [M^+, 2.3%], 426 [$(M - 3CO)^+$, 100%] (HRMS: found M^+, 510.10719. Requires *M*, 510.10519). The minor diastereomer was not characterised.

(iv) Preparation of (2*S*)-tricarbonyl[η⁶-(1-diphenylphosphino-2-benzoyl)benzene]chromium(0) 23. The above typical protocol was followed using complex (−)-**20** (0.28 g). Flash column chromatography on silica gel (20% EtOAc–light petroleum) gave complex **23** as a red solid (144 mg, 70%), mp 157 °C; $[a]_D^{22}$

−66 (*c* 1.1 in $CHCl_3$) (Found: C, 66.82; H, 4.31. $C_{28}H_{19}O_4PCr$ requires C, 66.93; H, 3.81%); ν_{max} ($CHCl_3$)/cm^{-1} 1982, 1919 (C≡O) and 1694 (C=O); δ_H (400 MHz, $CDCl_3$) 4.90 (1H, d, *J* 6, CrC*H*), 5.30 (1H, ddd, *J* 6 and 1, CrC*H*), 5.43 (1H, dd, *J* 6, CrC*H*), 5.50 (1H, ddd, *J* 7, 2 and 1, CrC*H*), 7.25–7.46 [13H, m, ((Ar*H*)$_2$P + Ar*H*)] and 7.73 (2H, m, Ar*H*); δ_C (68 MHz, $CDCl_3$) 90.8 (Cr*C*H), 91.5 (Cr*C*H), 94.7 (d, $J_{P\text{-}C}$ 4, Cr*C*H), 96.0 (d, $J_{P\text{-}C}$ 2, Cr*C*H), 103.8 (d, $J_{P\text{-}C}$ 32, Cr*C*), 110.2 (d, $J_{P\text{-}C}$ 21, Cr*C*), {(128.2, 128.4, 128.5, 128.6, 128.7, 128.9, 129.5), (Ar*C*H)$_2$P}, {(132.9, 133.1, 133.5, 134.5, 134.9), Ar*C*H}, 135.0 (d, $J_{P\text{-}C}$ 17, Ar*C*), 136.3 (Ar*C*), 193.8 (C=O) and 230.7 (3CO); *m*/*z* (EI) 502.0 (M$^+$, 8%), 418.0 [(M − 3CO)$^+$, 90%)] (HRMS: found M$^+$, 502.0404. Requires *M*, 502.0426).

(v) Preparation of (2*S*)-tricarbonyl[η^6-(1-diphenylphosphino-2-methyl)benzene]chromium(0) 24. The above typical protocol was followed using complex (−)-**20** (0.25 g). Flash column chromatography on silica gel (20% EtOAc–light petroleum) gave complex **24** as a yellow solid (100 mg, 67%), mp 172 °C; $[a]_D^{22}$ −282 (*c* 0.93 in $CHCl_3$) (Found: C, 64.07; H, 4.18. $C_{22}H_{17}O_3PCr$ requires C, 64.07; H, 4.16%); ν_{max} ($CHCl_3$)/cm^{-1} 1968 and 1898 (C≡O); δ_H (400 MHz, $CDCl_3$) 2.27 (3H, s, CH_3), 4.76 (1H, d, *J* 6, CrC*H*), 4.99 (1H, dd, *J* 6 and 6, CrC*H*), 5.10 (1H, dd, *J* 6 and 6, CrC*H*), 5.47 (1H, dd, *J* 6 and 6, CrC*H*) and 7.31–7.38 [10H, m, (Ar*H*)$_2$P]; δ_C (68 MHz, $CDCl_3$) 20.0 [d, *J* 21, *C*H$_3$], 88.8 (Cr*C*H), 92.2 (d, *J* 4, Cr*C*H), 94.9 (Cr*C*H), 97.3 (Cr*C*H), 102.7 (d, *J* 20, Cr*C*), 114.5 (d, *J* 23, Cr*C*), {(128.7, 128.8, 128.8, 128.9, 129.3, 129.7, 133.1, 133.5, 134.5, 134.8), (Ar*C*H)$_2$P}, 133.3 (Ar*C*), 135.3 (d, $J_{P\text{-}C}$ 11, Ar*C*) and 232.6 (3CO); *m*/*z* (EI) 412.7 (M$^+$, 15%), 356.6 [(M − 2CO)$^+$, 1%)] and 328.6 [(M − 3CO)$^+$, 100%] (HRMS: found M$^+$, 412.0322. $C_{22}H_{17}O_3PCr$ requires *M*, 412.0320).

(vi) Preparation of (2*S*)-tricarbonyl[η^6-(1-diphenylphosphino-2-ethyl)benzene]chromium(0) 25. The above typical protocol was followed using complex (−)-**20** (0.17 g). Flash column chromatography on silica gel (20% EtOAc–light petroleum) gave complex **25** as a yellow oil (56 mg, 53%), $[a]_D^{25}$ −267 (*c* 1 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1952, 1916 and 1864 (C≡O); δ_H (400 MHz, $CDCl_3$) 0.97 (3H, dd, *J* 7 and 7, CH_3), 2.74 (1H, dq, J_{AB} 15 and *J* 7, CH*H*), 2.90 (1H, ddq, J_{AB} 15, *J* 7 and 4, C*H*H), 4.81 (1H, d, *J* 6, CrC*H*), 5.04 (1H, ddd, *J* 6 and 1, CrC*H*), 5.16 (1H, dd, *J* 6 and 3, CrC*H*), 5.53 (1H, dd, *J* 6, CrC*H*) and 7.41 [10H, m, (Ar*H*)$_2$P]; δ_C (100 MHz, $CDCl_3$) 14.2 (*C*H$_3$), 26.2 (d, $J_{P\text{-}C}$ 23, *C*H$_2$), 89.2 (Cr*C*H), 89.9 (Cr*C*H), 95.1 (Cr*C*H), 97.8 (Cr*C*H), 102.8 (d, $J_{P\text{-}C}$ 20, Cr*C*), 120.5 (d, $J_{P\text{-}C}$ 22, Cr*C*), 128.8 (Ar*C*H), {(129.4, 129.7, 133.6, 133.8), Ar*C*H}, 134.0 (d, $J_{P\text{-}C}$ 14, Ar*C*), {(134.6, 134.8), Ar*C*H}, 135.9 (d, $J_{P\text{-}C}$ 10, Ar*C*) and 232.6 (3CO); *m*/*z* (EI) 426 (M$^+$, 5%), 342 [(M − 3CO)$^+$, 100%]; (HRMS: found M$^+$, 426.0482. $C_{23}H_{19}O_3PCr$ requires *M*, 426.0477).

(vii) Preparation of (2*S*)-tricarbonyl[η^6-(1-diphenylphosphino-2-benzyl)benzene]chromium(0) 26. The above typical protocol was followed using complex (−)-**20** (0.27 g). Flash column chromatography on silica gel (20% EtOAc–light petroleum) gave complex **26** as a yellow solid (57 mg, 31%), mp 164 °C; $[a]_D^{25}$ −149 (*c* 0.75 in $CHCl_3$) (Found: C, 68.60; H, 4.27. $C_{28}H_{21}O_3PCr$ requires C, 68.84; H, 4.34%); ν_{max} ($CHCl_3$)/cm^{-1} 1966 and 1904 (C≡O); δ_H (250 MHz, $CDCl_3$) 4.10 (2H, s, PhCH_2), 4.80 (1H, d, *J* 6, CrC*H*), 4.89 (1H, dd, *J* 6 and 3, CrC*H*), 5.05 (1H, dd, *J* 6, CrC*H*), 5.43 (1H, dd, *J* 6, CrC*H*), 7.04–7.14 (5H, m, Ar*H*) and 7.24–7.39 [10H, m, (Ar*H*)$_2$P]; δ_C (68 MHz, $CDCl_3$) 39.0 (d, $J_{P\text{-}C}$ 22, PhCH_2), 90.2 (Cr*C*H), 92.3 (Cr*C*H), 94.9 (Cr*C*H), 98.0 (Cr*C*H), 103.2 (d, $J_{P\text{-}C}$ 21, Cr*C*), 118.5 (d, $J_{P\text{-}C}$ 22, Cr*C*), {(127.2, 128.9, 129.0, 129.1, 129.2, 129.6, 129.9, 130.1, 133.7, 134.0), Ar*C*H}, 134.4 (d, $J_{P\text{-}C}$ 10, Ar*C*), {(134.9, 135.2), Ar*C*H}, 137.5 (Ar*C*) and 232.9 (3CO); *m*/*z* (EI) 488 (M$^+$, 8%), 404 [(M − 3CO)$^+$, 100%] (HRMS: found M$^+$, 488.0627. $C_{28}H_{21}O_3PCr$ requires *M*, 488.0633).

(viii) Preparation of (2*R*)-tricarbonyl[η^6-(1-diphenylphosphino-2-bromo)benzene]chromium(0) 27. The above typical protocol was followed using complex (−)-**20** (0.38 g). Flash column chromatography on silica gel (10% EtOAc–light petroleum) gave complex **27** as a yellow solid (161 mg, 61%), mp 169 °C; $[a]_D^{22}$ −270 (*c* 0.52 in $CHCl_3$) (Found: C, 52.59; H, 2.79; Br, 16.63. $C_{21}H_{14}BrO_3PCr$ requires C, 52.85; H, 2.96; Br, 16.58%); ν_{max} ($CHCl_3$)/cm^{-1} 1980 and 1915 (C≡O); δ_H (400 MHz, $CDCl_3$) 4.75 (1H, dd, *J* 6 and 1, CrC*H*), 4.92 (1H, ddd, *J* 6, 6 and 1, CrC*H*), 5.43 (1H, dd, *J* 6 and 1, CrC*H*), 5.55 (1H, m, CrC*H*) and 7.41 (10H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 88.1 (Cr*C*H), 94.1 (Cr*C*H), 94.1 (Cr*C*H), 96.2 (Cr*C*H), 103.4 (d, $J_{P\text{-}C}$ 20, Cr*C*), 107.2 (d, $J_{P\text{-}C}$ 31, Cr*C*), {(128.9, 128.9, 129.0 129.0, 129.4, 130.1, 133.2, 133.4, 134.8, 135.0), (Ar*C*H)$_2$P}, 134.0 (d, $J_{P\text{-}C}$ 15, Ar*C*), 135.3 (d, $J_{P\text{-}C}$ 11, Ar*C*) and 231.3 (3CO); *m*/*z* (FAB) 479, 477 [(M + H)$^+$, 10%]; 422, 420 [(M − 2CO)$^+$, 14%]; 394, 392 [(M − 3CO)$^+$, 19%].

Suzuki couplings according to Scheme 8

(i) Preparation of (2*S*)-tricarbonyl[η^6-(1-diphenylphosphino-2-phenyl)benzene]chromium(0) 28. A mixture of complex (−)-**20** (100 mg, 0.21 mmol), benzeneboronic acid (51 mg, 0.42 mmol), sodium carbonate (44 mg, 0.42 mmol) and $Pd(PPh_3)_4$ (24 mg, 0.02 mmol) in methanol (4 ml) and water (0.4 ml) was degassed by three cycles of freeze–pump–thaw and stirred at 75 °C for 12 h under nitrogen. The reaction mixture was quenched with water and extracted with ethyl acetate (2 × 5 ml). The combined organic extracts were washed with aqueous NaOH (2 × 10 ml of 2 M solution), brine (20 ml), dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The yellow residue was purified by flash column chromatography on silica gel (10% EtOAc–light petroleum) to give complex **28** as a yellow solid (83 mg, 83%), mp 61 °C; $[a]_D^{20}$ −149 (*c* 0.42 in $CHCl_3$); ν_{max} ($CHCl_3$/cm^{-1}) 1970 and 1903 (C≡O); δ_H (400 MHz, $CDCl_3$) 4.84 (1H, d, *J* 6, CrC*H*), 5.27 (1H, dd, *J* 6 and 6, CrC*H*), 5.35 (1H, m, CrC*H*), 5.45 (1H, dd, *J* 6 and 6, CrC*H*) and 7.17–7.38 [15H, m, (Ar*H*)$_2$P + Ph]; δ_C (100 MHz, $CDCl_3$) 91.7 (Cr*C*H), 91.8 (Cr*C*H), 95.5 (Cr*C*H), 105.2 (d, $J_{P\text{-}C}$ 23, Cr*C*), 119.9 (d, $J_{P\text{-}C}$ 25, Cr*C*), {(127.8, 128.6, 128.7, 129.2, 129.5, 130.7, 133.7, 133.9, 134.7, 134.9), Ar*C*H}, 134.4 (d, *J* 15, Ar*C*), 136.2 (Ar*C*), 136.3 (d, *J* 10, Ar*C*) and 232.3 (3CO); *m*/*z* (FAB) 475 [(M + H)$^+$, 18%], 390 [(M − 3CO)$^+$, 100%] (HRMS: found M$^+$, 475.0548. $C_{27}H_{19}O_3PCr$ + H requires *M*, 475.0535).

(ii) Preparation of (2*S*)-tricarbonyl{η^6-[1-diphenylphosphino-2-(*p*-methoxyphenyl)]benzene}chromium(0) 29. A mixture of complex (−)-**20** (100 mg, 0.21 mmol), 4-methoxybenzeneboronic acid (64 mg, 0.42 mmol), sodium carbonate (44 mg, 0.42 mmol) and $Pd(PPh_3)_4$ (24 mg, 0.02 mmol) in methanol (4 ml) and water (0.4 ml) was degassed by three cycles of freeze–pump–thaw and stirred at 75 °C for 0.5 h under nitrogen. The reaction mixture was quenched with water and extracted with ethyl acetate (2 × 5 ml). The combined organic extracts were washed with aqueous NaOH (2 × 10 ml of 2 M solution), brine (20 ml) and dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The yellow residue was purified by flash column chromatography on silica gel (10% EtOAc–light petroleum) to give complex **29** as a yellow solid (91 mg, 86%), mp 68 °C; $[a]_D^{25}$ −91 (*c* 0.47 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1970 and 1903 (C≡O); δ_H (400 MHz, $CDCl_3$) 3.79 (3H, s, OCH_3), 4.87 (1H, d, *J* 6, CrC*H*), 5.25 (1H, dd, *J* 6 and 6, CrC*H*), 5.34 (1H, m, CrC*H*), 5.47 (1H, dd, *J* 6 and 6, CrC*H*), 6.73 (2H, d, *J* 8, *p*-Ar*H*), 7.17 (2H, d, *J* 8, *p*-Ar*H*) and 7.37 [10H, m, (Ar*H*)$_2$P]; δ_C (100 MHz, $CDCl_3$) 55.3 (OCH_3), 91.5 (Cr*C*H), 92.3 (Cr*C*H), 95.5 (Cr*C*H), 96.0 (Cr*C*H), 105.4 (d, $J_{P\text{-}C}$ 23, Cr*C*), 113.2 (Cr*C*H), 120.0 (d, $J_{P\text{-}C}$ 25, Cr*C*), {(120.1, 128.6, 128.7, 128.8, 129.2, 129.6, 132.0, 133.7, 133.9), Ar*C*H}, 134.6 (Ar*C*), {(134.8, 135.0), Ar*C*H}, 136.6 (d, $J_{P\text{-}C}$ 10, Ar*C*), 159.9 (Ar*C*)

and 232.5 (3CO); *m/z* (FAB) 505 [(M + H)$^+$, 5%], 420 [(M − 3CO)$^+$, 16%] (HRMS: found (M + H)$^+$, 505.0689. $C_{28}H_{21}O_4PCr$ + H requires (*M* + *H*), 505.0661).

(iii) Preparation of (2*S*)-tricarbonyl{η^6-[1-diphenylphosphino-2-(2-thienyl)]benzene}chromium(0) 30. A mixture of complex (−)-**20** (100 mg, 0.21 mmol), 2-thiopheneboronic acid (54 mg, 0.42 mmol), sodium carbonate (44 mg, 0.42 mmol) and $Pd(PPh_3)_4$ (24 mg, 0.02 mmol) in methanol (4 ml) and water (0.4 ml) was degassed by three cycles of freeze–pump–thaw and stirred at 75 °C for 24 h under nitrogen. Reaction mixture was quenched with water and extracted with ethyl acetate (2 × 5 ml). The combined organic extracts were washed with aqueous NaOH (2 × 10 ml of 2 M solution), brine (20 ml), dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The yellow residue was purified by flash column chromatography (10% EtOAc–light petroleum) to give complex **30** a yellow oil (67 mg, 67%), $[\alpha]_D^{22}$ −79 (*c* 0.25 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1973 and 1906 (C≡O); δ_H (400 MHz, $CDCl_3$) 4.81 (1H, d, *J* 6, CrC*H*), 5.22 (1H, ddd, *J* 6, 6 and 1, CrC*H*), 5.47 (1H, ddd, *J* 6, 6 and 1, CrC*H*), 5.52 (1H, m, CrC*H*), 6.86 (1H, dd, *J* 5 and 4, C*H*-thiophene), 6.93 (1H, m, C*H*-thiophene), 7.23 (1H, dd, *J* 5 and 1, C*H*-thiophene), 7.39 (9H, m, Ar*H*) and 7.58 (1H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 91.5 (Cr*C*H), 91.8 (Cr*C*H), 95.7 (Cr*C*H), 95.8 (Cr*C*H), 105.8 (d, $J_{P\text{-}C}$ 23, Cr*C*), 110.4 (d, $J_{P\text{-}C}$ 15, Cr*C*), {(126.8, 127.1, 130.3), *C*H-thiophene}, {(128.2, 128.7, 128.8, 128.9, 129.3, 129.7, 133.0, 133.6, 133.8, 134.8, 135.0), (Ar*C*H)$_2$P}, 134.4 (d, *J* 15, Ar*C*), 136.6 (d, *J* 10, Ar*C*), 138.2 (Ar*C*) and 232.1 (3CO); *m/z* (FAB) 481 [(M + H)$^+$, 3%] (HRMS: found [M + H]$^+$, 481.0134. $C_{25}H_{17}O_3PSCr$ requires [*M* + *H*], 481.0120).

Chemical correlation as in Scheme 9

(i) Preparation of (2*R*)-tricarbonyl[η^6-2-diphenylphosphinoanisole]chromium(0) 31 *via* nucleophilic substitution reaction. To a mixture of complex (−)-**27** (73 mg, 0.15 mmol) and sodium methoxide (41 mg, 0.77 mmol) in THF (5 ml) was added three drops of 15-crown-5. The mixture was refluxed for 12 h, cooled to room temperature and then water (3 ml) was added carefully. After addition of EtOAc (5 ml), the organic layer was separated, washed with water (5 ml), brine (20 ml) and dried ($MgSO_4$). The solvent was evaporated under reduced pressure and the resulting yellow residue was purified by flash column chromatography on silica gel (10% EtOAc–light petroleum) to give (−)-**31** as a yellow solid (40 mg, 61%), mp 109 °C; $[\alpha]_D^{24}$ −125 (*c* 0.81%, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1969 and 1898 (C≡O); δ_H (400 MHz, $CDCl_3$) 3.69 (3H, s, OCH_3), 4.74 (1H, dd, *J* 6 and 6, CrC*H*), 4.86 (1H, d, *J* 6, CrC*H*), 5.02 (1H, dd, *J* 6 and $J_{P\text{-}H}$ 3, CrC*H*), 5.59 (1H, dd, *J* 6 and 6, CrC*H*) and 7.32–7.40 (10H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 56.2 (O*C*H$_3$), 72.9 (Cr*C*H), 85.2 (Cr*C*H), 93.4 (d, $J_{P\text{-}C}$ 23, Cr*C*), 94.5 (Cr*C*H), 98.3 (Cr*C*H), {(128.6, 128.7, 128.8, 128.9, 129.1, 129.7, 133.0, 133.2), Ar*C*H}, 134.1 (d, $J_{P\text{-}C}$ 4, Ar*C*), {(134.8, 135.0), Ar*C*H}, 136.1 (d, $J_{P\text{-}C}$ 3, Ar*C*), 145.9 (d, $J_{P\text{-}C}$ 3, Cr*C*) and 232.5 (3CO); *m/z* (EI) 428 (M$^+$, 0.14%), 372 [(M − 2CO)$^+$, 8%], 344 [(M − 3CO)$^+$, 38%], 292 [(M − Cr(CO)$_3$)$^+$, 100%] (HRMS: found M$^+$, 428.0270. $C_{22}H_{17}O_4PCr$ requires *M*, 428.0270).

(ii) Preparation of (2*R*)-tricarbonyl(η^6-2-trimethylsilylanisole)chromium(0) 3.[10] A solution of the chiral base **2** (+LiCl) was prepared, as described above, by addition of *n*-BuLi (2.89 ml of a 1.55 M solution in hexanes, 4.48 mmol) to a solution of the corresponding chiral amine hydrochloride salt (0.59 g, 2.25 mmol) in THF (20 ml). The resulting solution of chiral base **2** (+LiCl) was then cooled to −100 °C and chlorotrimethylsilane (1.30 ml, 10.24 mmol) was added in one portion followed by a solution of anisole complex **1** (0.50 g, 2.04 mmol) in THF (2 ml). The reaction mixture was allowed to warm to −78 °C and stirred for 0.50 h. Saturated aqueous $NaHCO_3$ (10 ml) was added and the mixture was allowed to warm to room temperature. The organic layer was separated, washed with saturated aqueous $NaHCO_3$ (10 ml), HCl solution (2 M, 30 ml), brine (30 ml), dried ($MgSO_4$). The solvent was evaporated under reduced pressure and the resulting yellow oil was then purified by flash column chromatography on silica gel (5% EtOAc–light petroleum) to give firstly an unwanted doubly silylated by-product (tricarbonyl[η^6-2,6-bis(trimethylsilyl)-anisole]chromium(0) as a yellow solid (51 mg, 6%), mp 98–99 °C (lit.,[5] 84–85 °C); ν_{max} ($CHCl_3$)/cm^{-1} 1961, 1908 and 1872 (C≡O); δ_H (400 MHz, $CDCl_3$) 0.40 [18H, s, 2Si(CH_3)$_3$], 3.73 (3H, s, OCH_3), 4.82 (1H, t, *J* 6, CrC*H*) and 5.64 (2H, d, *J* 6, CrC*H*); δ_C (68 MHz, $CDCl_3$) 0.5 [2Si(*C*H$_3$)$_3$], 63.6 (O*C*H$_3$), 87.6 (Cr*C*H), 92.2 (2Cr*C*), 101.9 (2Cr*C*H), 153.0 (Cr*C*) and 233.6 (3CO); *m/z* (EI) 388 (M$^+$, 5%), 304 [(M − 3CO)$^+$, 41%], 252 [(M − Cr(CO)$_3$)$^+$, 20%] followed by the desired complex (+)-**3** as a yellow solid (540 mg, 84%), mp 110–111 °C (of a 99% ee sample) (lit.,[10] 78–79 °C); $[\alpha]_D^{23}$ 195 (*c* 0.21 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2958, 1965 and 1893; δ_H (400 MHz, $CDCl_3$) 0.32 (9H, s, Si(CH_3)$_3$), 3.74 (3H, s, OCH_3), 4.80 (1H, dd, *J* 6, CrC*H*), 4.99 (1H, d, *J* 6, CrC*H*), 5.59 (1H, dd, *J* 6 and *J* 1, CrC*H*) and 5.69 (1H, dd, *J* 6, CrC*H*); δ_C (100 MHz, $CDCl_3$) −0.5 [Si(*C*H$_3$)$_3$], 55.4 (O*C*H$_3$), 73.5 (Cr*C*H), 85.1 (Cr*C*H), 88.9 (Cr*C*), 95.9 (Cr*C*H), 101.8 (Cr*C*H), 147.5 (Cr*C*) and 233.7 (3CO); *m/z* (FAB) 316 (M$^+$, 62%), 260 [(M − 2CO)$^+$, 100%], 232 [(M − 3CO)$^+$, 68%] (HRMS: found M$^+$, 316.0237. $C_{13}H_{16}O_4SiPCr$ requires *M*, 316.0223).

The enantiomeric excess of this sample was shown to be 79% by use of a Chiralcel OJ column using 90 : 10 hexane–IPA as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention times 7.4 min (minor) and 10.2 min (major).

(iii) Phosphenylation of 3 *via ortho*-metallation and reaction with Ph_2PCl. *n*-BuLi (0.24 ml of a 1.55 M solution in hexanes, 0.37 mmol) was added dropwise to a solution of complex (+)-**3** (0.10 g, 0.32 mmol) in THF (10 ml) at −78 °C under an atmosphere of nitrogen. The mixture was stirred at −78 °C for 1 h before addition of chlorodiphenylphosphine (0.17 ml, 0.95 mmol) dropwise, and reaction mixture was then stirred at −78 °C for a further 1 h and then warmed to room temperature. Saturated aqueous $NaHCO_3$ (5 ml) was added in one portion. The organic layer was separated, washed with brine (20 ml), and dried ($MgSO_4$). The solvent was evaporated under reduced pressure, and the yellow residue was purified by flash column chromatography on silica gel (5% EtOAc–light petroleum) to give the desired phosphenylated complex as a yellow solid (0.12 g, 78%), mp 137 °C; $[\alpha]_D^{23}$ 234 (*c* 0.21 in $CHCl_3$) (Found: C, 60.22; H, 5.08. $C_{25}H_{25}O_4PSiCr$ requires C, 59.99; H, 5.03%); ν_{max} ($CHCl_3$)/cm^{-1} 1972 and 1904 (C≡O); δ_H (400 MHz, $CDCl_3$) 0.37 (9H, s, Si(CH_3)$_3$), 3.64 (3H, s, OCH_3), 4.76 (1H, dd, *J* 6, CrC*H*), 5.12 (1H, d, *J* 6, CrC*H*), 5.57 (1H, d, *J* 6, CrC*H*) and 7.41–7.48 [10H, m, (Ar*H*)$_2$P]; δ_C (100 MHz, $CDCl_3$) 0.2 [Si(*C*H$_3$)$_3$], 64.7 (O*C*H$_3$), 87.0 (Cr*C*H), 92.1 (Cr*C*), 96.4 (d, $J_{P\text{-}C}$ 26, Cr*C*), 99.2 (Cr*C*H), 100.4 (Cr*C*H), {(128.8, 128.8, 129.1, 129.8, 133.2, 133.4, 135.1, 135.29), Ar*C*H}, 134.7 (d, $J_{P\text{-}C}$ 13, Ar*C*), 137.4 (d, $J_{P\text{-}C}$ 12, Ar*C*), 151.2 (d, $J_{P\text{-}C}$ 18, Cr*C*) and 232.4 (3CO); *m/z* (EI) 500 (M$^+$, 3%), 416 [(M − 3CO)$^+$, 100%] (HRMS: found M$^+$, 500.0668. Requires *M*, 500.0665).

(iv) Preparation of (2*S*)-tricarbonyl(η^6-2-diphenylphosphinoanisole)chromium(0) (−)-31 by a desilylation reaction. To a stirred solution of the complex from (iii) above (87 mg, 0.17 mmol) in THF (10 ml) at −78 °C under an atmosphere of nitrogen, was added TBAF (0.17 ml of a 1.0 M solution in THF, 0.17 mmol) dropwise. After stirring the mixture at −78 °C for 0.5 h, saturated aqueous NH_4Cl (2.5 ml) was added and the reaction mixture was then warmed to room temperature. The mixture was extracted with CH_2Cl_2 (10 ml), the organic extract was washed with water (10 ml), brine (10 ml), dried ($MgSO_4$) and the solvent evaporated under reduced pres-

sure. The resulting yellow oil was purified by flash column chromatography on silica gel (10% EtOAc–light petroleum) to give (+)-**31** as a yellow solid (71 mg, 95%), $[a]_D^{23}$ 122 (*c* 1.1 in $CHCl_3$). The ^1H NMR spectrum of the product was identical to that described above for (−)-**31**.

Asymmetric substitution of complex 6 according to Table 2

(i) Preparation of (1*R*,3′*S*)-tricarbonyl[η⁶-1-trimethylsilyl-1,3-dihydroisobenzothiophene]chromium(0) 32 (Me_3SiCl *in situ* quench). A solution of the bis-lithium amide base **9** was prepared by addition of *n*-BuLi (0.55 ml of a 1.6 M solution in hexanes, 0.89 mmol) to a solution of the appropriate chiral diamine (186 mg, 0.44 mmol) in THF (10 ml) at −78 °C under an atmosphere of nitrogen. The solution was allowed to warm to room temperature with stirring and then recooled to −100 °C. Chlorotrimethylsilane (0.23 ml, 1.81 mmol) was added in one portion, followed by a solution of complex **6** (100 mg, 0.37 mmol) in THF (2 ml). The reaction mixture was stirred at this temperature for 1 h before MeOH (1 ml) was added with subsequent warming to room temperature. The solvents were removed under reduced pressure and the resulting yellow residue was purified by flash column chromatography on silica gel (10% EtOAc–light petroleum) to give complex **32** as a yellow solid (121 mg, 95%), mp 110 °C; $[a]_D^{23}$ −7 (*c* 0.62 in $CHCl_3$) (Found: C, 48.77; H, 4.62; S, 9.25. $C_{14}H_{16}O_3SCrSi$ requires C, 48.82; H, 4.68; S, 9.31%); ν_{max} ($CHCl_3$)/cm^{-1} 1968 and 1894 (C≡O); δ_H (400 MHz, $CDCl_3$) 0.13 (9H, s, Si*Me*$_3$), 3.40 (1H, d, $^4J_{H\text{-}H}$ 2, SC*H*), 3.81 (1H, d, J_{AB} 14, SC*H*H), 4.05 (1H, dd, J_{AB} 14 and $^4J_{H\text{-}H}$ 2, SCH*H*), 5.18 (1H, m, CrC*H*), 5.29 (2H, m, CrC*H*) and 5.48 (1H, d, *J* 6, CrC*H*); δ_C (68 MHz, $CDCl_3$) −3.1 [Si(*C*H$_3$)], 36.7 (*C*H$_2$), 39.9 (*C*H), 88.0 (Cr*C*H), 89.9 (Cr*C*H), 90.8 (Cr*C*H), 91.3 (Cr*C*H), 109.3 (Cr*C*), 117.0 (Cr*C*) and 232.8 (3CO); *m*/*z* (EI) 344 (M^+, 16%), 260 [$(M - 3CO)^+$, 44%] (HRMS: found M^+, 343.9992. requires *M*, 343.9994).

The enantiomeric excess of complex **32** was determined to be 89% using a Chiralcel OD column with 97.5:2.5 hexane–IPA as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention time 8.3 min (major) and 11.9 min (minor). Enantiomerically pure material (ee ≥99%) could be obtained by recrystallisation from ^{i}PrOH (85% recovery).

(ii) Preparation of complexes 33–38. *Typical procedure: (1S,3′S)-tricarbonyl(η⁶-1-methyl-1,3-dihydroisobenzothiophene)chromium(0) **33***. A solution of the bis-lithium amide base **9** was prepared by addition of *n*-BuLi (0.50 ml of a 1.6 M solution in hexanes, 0.80 mmol) to a solution of the appropriate chiral diamine (0.17 g, 0.40 mmol) in THF (10 ml) at −78 °C under an atmosphere of nitrogen. The solution was allowed to warm to room temperature with stirring and then cooled to −100 °C. To the resulting pink solution was added a solution of LiCl (7.7 mg, 0.18 mmol) in THF (5 ml) *via* a cannula, followed by a solution of complex **6** (100 mg, 0.37 mmol) in THF (10 ml) dropwise. The red solution was stirred at −100 °C for a further 1 h. Iodomethane (0.12 ml, 1.9 mmol) was added in one portion and the reaction mixture was allowed to warm to −78 °C and maintained at this temperature for a further 1 h. MeOH (1 ml) was added with subsequent warming to room temperature before the solvents were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (10–20% EtOAc–light petroleum) to give complex **33** as a yellow solid (100 mg, 95%), mp 118 °C; $[a]_D^{23}$ −110 (*c* 0.53 in $CHCl_3$) (Found: C, 50.63; H, 3.53. $C_{12}H_{10}O_3SCr$ requires C, 50.35; H, 3.52%); ν_{max} ($CHCl_3$)/cm^{-1} 1971 and 1897 (C≡O); δ_H (250 MHz, $CDCl_3$) 1.59 (3H, d, *J* 7, C*H*$_3$), 3.86 (1H, d, J_{AB} 14, SC*H*H), 4.24 (1H, d, J_{AB} 14, SCH*H*), 4.34 (1H, q, *J* 7, SC*H*), 5.26 (2H, m, CrC*H*) and 5.42–5.48 (2H, m, CrC*H*); δ_C (68 MHz, $CDCl_3$) 26.4 (*C*H$_3$), 35.8 (*C*H$_2$), 47.6 (*C*H), 89.7 (Cr*C*H), 90.3 (Cr*C*H), 91.4 (Cr*C*H), 91.6 (Cr*C*H), 111.0 (Cr*C*), 116.6 (Cr*C*) and 232.8 (3CO); *m*/*z* (EI) 286 (M^+, 24%), 202 [$(M - 3CO)^+$, 100%] (HRMS: found M^+, 285.9764. Requires *M*, 285.9756).

The enantiomeric excess of complex **33** was determined to be 94% using a Chiralcel OD column using 95:5, hexane–IPA as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention time 18.7 min (major) and 23.7 (minor).

Enantiomerically pure material {$[a]_D^{23}$ −117 (*c* 0.50 in $CHCl_3$), ee ≥99%} could be obtained by recrystallisation from ^{i}PrOH (89% recovery).

*Preparation of (1S,3′S)-tricarbonyl(η⁶-1-ethyl-1,3-dihydroisobenzothiophene)chromium(0) **34***. The above typical protocol was followed, using 0.30 g of **6**. Flash column chromatography on silica gel (15–25% EtOAc–light petroleum) gave complex **34** as a yellow solid (300 mg, 91%), mp 98 °C; $[a]_D^{23}$ −146 (*c* 0.3 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1971 and 1901 (C≡O); δ_H (250 MHz, $CDCl_3$) 1.03 (3H, t, *J* 7, C*H*$_3$), 1.58–1.98 (2H, m, C*H*$_2$), 3.80 (1H, d, J_{AB} 14, SC*H*H), 4.19 (2H, m, SCH*H* + SC*H*), 5.26 (2H, m, CrC*H*) and 5.45 (2H, m, CrC*H*); δ_C (68 MHz, $CDCl_3$) 12.2 (*C*H$_3$), 33.5 (*C*H$_2$), 36.5 (*C*H$_2$), 55.5 (*C*H), 90.4 (Cr*C*H), 90.7 (Cr*C*H), 91.7 (Cr*C*H), 92.2 (Cr*C*H), 111.9 (Cr*C*), 115.6 (Cr*C*) and 233.0 (3CO); *m*/*z* (FAB) 300 (M^+, 68%), 244 [$(M - 2CO)^+$, 65%], 216 [$(M - 3CO)^+$, 30%] (HRMS: found M^+, 299.9929. Requires *M*, 299.9912).

The enantiomeric excess of complex **34** was determined to be 87% using a Chiralcel OD column with 95:5, hexane–IPA as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention time 15.6 min (major) and 20.1 (minor).

*Preparation of (1S,3′S)-tricarbonyl(η⁶-1-benzyl-1,3-dihydroisobenzothiophene)chromium(0) **35***. The above typical protocol was followed, using 1.0 g of **6**. Flash column chromatography on silica gel (10–20% EtOAc–light petroleum) gave complex **35** as a yellow solid (932 mg, 70%), mp 90 °C; $[a]_D^{23}$ −177 (*c* 1.15 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1961 and 1876 (C≡O); δ_H (400 MHz, $CDCl_3$) 3.04–3.19 (2H, m, C*H*$_2$), 3.63 (1H, d, J_{AB} 14, SC*H*H), 3.81 (1H, d, J_{AB} 14, SCH*H*), 4.43 (1H, dd, *J* 7, 7, C*H*), 5.11–5.15 (2H, m, CrC*H*), 5.21–5.25 (1H, m, CrC*H*), 5.36 (1H, d, *J* 6, CrC*H*) and 7.11–7.28 (5H, m, Ar*H*); δ_C (68 MHz, $CDCl_3$) 35.5 (*C*H$_2$), 45.4 (*C*H$_2$), 53.6 (*C*H), 89.6 (Cr*C*H), 90.0 (Cr*C*H), 90.2 (Cr*C*H), 91.4 (Cr*C*H), 111.3 (Cr*C*), 113.7 (Cr*C*), 126.9 (Ar*C*H), 128.3 (Ar*C*H), 129.8 (Ar*C*H), 137.0 (Ar*C*) and 232.3 (3CO); *m*/*z* (EI) 362 (M^+, 4%), 278 [$(M - 3CO)^+$, 20%] and 135 [$(C_8H_7S)^+$, 100%] (HRMS: found M^+, 362.0061. $C_{15}H_{14}O_3SCr$ requires *M*, 362.0069).

*Preparation of (1S,3′S)-tricarbonyl[η⁶-1-(1-diphenyl-1-hydroxymethyl)-1,3-dihydroisobenzothiophene]chromium(0) **36***. The above typical protocol was followed, using 0.2 g of **6**. Flash column chromatography on silica gel (10–20% EtOAc–light petroleum) gave complex **36** as a yellow solid (290 mg, 88%), mp 158 °C; $[a]_D^{22}$ −118 (*c* 0.98 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 3528 (OH), 1963 and 1879 (C≡O); δ_H (400 MHz, $CDCl_3$) 3.15 (1H, s, D_2O exch., O*H*), 3.74 (1H, d, J_{AB} 14, SC*H*H), 4.09 (1H, d, J_{AB} 14, SCH*H*), 4.18 (1H, s, SC*H*), 4.79 (1H, dd, *J* 6, 6, CrC*H*), 5.23 (1H, dd, *J* 6, 6, CrC*H*), 5.32 (1H, d, *J* 2, CrC*H*), 5.37 (1H, d, *J* 6, CrC*H*), 7.26–7.37 (8H, m, Ar*H*) and 7.48 (2H, d, *J* 8, Ar*H*); δ_C (126 MHz, $CDCl_3$) 36.6 (*C*H$_2$), 62.9 (*C*H), 82.0 (*C*), 89.0 (Cr*C*H), 89.2 (Cr*C*H), 92.2 (Cr*C*H), 92.8 (Cr*C*H), 109.8 (Cr*C*), 113.1 (Cr*C*), 126.4 (Ar*C*H), 127.7 (Ar*C*H), 127.7 (Ar*C*H), 128.5 (Ar*C*H), 143.0 (Ar*C*), 146.1 (Ar*C*) and 232.5 (3CO); *m*/*z* (EI) 454 (M^+, 9%), 370 [$(M - 3CO)^+$, 56%] (HRMS: found M^+, 454.0309. Requires *M*, 454.0331).

The enantiomeric excess of complex **36** was determined to be 95% by using a Chiralcel OD column, with 95:5, hexane–IPA as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention time 15.5 min (major) and 27.5 (minor).

Enantiomerically pure material {$[a]_D^{22}$ −125 (*c* 0.98 in $CHCl_3$); ee ≥99%} could be obtained by recrystallisation from Et_2O–light petroleum (75% recovery).

*Preparation of (1S,3′S)-tricarbonyl(η⁶-1-allyl-1,3-dihydroisobenzothiophene)chromium(0) **37***. The above typical protocol

was followed, using 0.2 g of **6**. Flash column chromatography on silica gel (15–25% EtOAc–light petroleum) gave complex **37** as a yellow oil (173 mg, 75%), $[\alpha]_D^{23}$ −159 (*c* 4.3 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1960 and 1866 (C≡O); δ_H (400 MHz, $CDCl_3$) 2.61 (2H, m, CH_2), 3.80 (1H, d, J_{AB} 14, SC*H*H), 4.17 (1H, dd, J_{AB} 14 and $^4J_{H\text{-}H}$ 2, SCH*H*), 4.30 (1H, m, 2, SC*H*), 5.12 (2H, m, CrC*H*), 5.26 (2H, m, CrC*H*), 5.46 (2H, d, *J* 6, CH=CH_2) and 5.82 (1H, m, C*H*=CH_2); δ_C (100 MHz, $CDCl_3$) 35.8 (*C*H_2), 43.7 (*C*H_2), 52.3 (*C*H_2), 89.7 (Cr*C*H), 90.6 (Cr*C*H), 91.4 (Cr*C*H), 111.2 (Cr*C*), 114.0 (Cr*C*), 118.9 (*C*H_2), 133.8 (*C*H) and 232.3 (3CO); *m*/*z* (EI) 312 (M^+, 27%), 256 [$(M - 2CO)^+$, 14%], 228 [$(M - 3CO)^+$, 72%] (HRMS: found M^+, 311.9905. $C_{14}H_{12}O_3$SCr requires *M*, 311.9912).

Preparation of (1S,3′S)-tricarbonyl[η⁶-1-(2-naphthylmethyl)-1,3-dihydroisobenzothiophene]chromium(0) ***38***. The above typical protocol was followed, using 1.10 g of **6**. Flash column chromatography on silica gel (10–20% EtOAc–light petroleum) gave complex **38** as a yellow solid (1.48 g, 89%), mp 148 °C; $[\alpha]_D^{23}$ −250 (*c* 0.74 in $CHCl_3$) (Found: C, 63.90; H, 3.87. $C_{22}H_{16}O_3$SCr requires C, 64.07; H, 3.91%); ν_{max} ($CHCl_3$)/cm^{-1} 1971 and 1900 (C≡O); δ_H (400 MHz, $CDCl_3$) 3.23 (1H, dd, *J* 7 and J_{AB} 14, C*H*H), 3.32 (1H, dd, *J* 7 and J_{AB} 14, CHH_2), 3.63 (1H, d, J_{AB} 14, SC*H*H), 3.82 (1H, d, J_{AB} 14, SCH*H*), 4.54 (1H, dd, *J* 7, 7, SC*H*), 5.10 (2H, m, CrC*H*), 5.22 (1H, m, CrC*H*), 5.34 (1H, d, *J* 6, CrC*H*), 7.26 (1H, m, Ar*H*), 7.46 (2H, m, Ar*H*), 7.57 (1H, m, Ar*H*), 7.75 (2H, m, Ar*H*) and 7.82 (1H, m, Ar*H*); δ_C (68 MHz, $CDCl_3$) 35.5 (*C*H_2), 45.5 (*C*H_2), 53.6 (*C*H), 89.7 (Cr*C*H), 90.0 (Cr*C*H), 90.2 (Cr*C*H), 91.4 (Cr*C*H), 111.2 (Cr*C*), 113.7 (Cr*C*), 125.8 (Ar*C*H), {(126.2, 127.6, 127.6, 127.8, 127.9, 128.5), Ar*C*H}, 132.3 (Ar*C*), 133.2 (Ar*C*), 134.5 (Ar*C*) and 232.3 (3CO); *m*/*z* (EI) 412 (M^+, 10%), 328 [$(M - 3CO)^+$, 13%]; (HRMS: found M^+, 412.0229. Requires *M*, 412.0225).

The enantiomeric excess of complex **38** was determined to be 95% using a Chiralcel OD column, with 94 : 6 hexane–IPA as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention time 43.5 min (minor) and 50.4 min (major).

Enantiomerically pure material {$[\alpha]_D^{23}$ −264 (*c* 0.70 in $CHCl_3$), ee ≥99%} could be obtained by recrystallisation from ^{i}PrOH (76% recovery).

Demetallation of chromium complexes to give enantiomerically enriched sulfides 39–43

(i) Typical procedure: preparation of (1*S*)-1-methyl-1,3-dihydroisobenzothiophene 39.[24] A solution of enantiomerically pure complex **33** (24 mg, 0.08 mmol) in dichloromethane (10 ml) was exposed to sunlight for 12 h. After this time a green precipitate had formed. The solvent was removed under reduced pressure and the residue was dissolved in ethyl acetate (20 ml) and filtered through a pad of Celite. After removal of the solvent, the residue was purified by Kugelrohr distillation (85 °C/1 mbar) to give **39** as a colourless oil (11 mg, 88%), $[\alpha]_D^{23}$ −140 (*c* 0.012 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2962 and 2864; δ_H (400 MHz, $CDCl_3$) 1.63 (3H, d, *J* 7, CH_3), 4.19 (1H, d, J_{AB} 14, SC*H*H), 4.25 (1H, dd, J_{AB} 14, SCH*H*), 4.72 (1H, q, *J* 7, SC*H*) and 7.21 (4H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 24.3 (*C*H_3), 36.9 (*C*H_2), 48.2 (*C*H), 123.8 (Ar*C*H), 124.7 (Ar*C*H), 126.8 (Ar*C*H), 126.9 (Ar*C*H), 140.2 (Ar*C*) and 145.6 (Ar*C*); *m*/*z* (EI) 150 (M^+, 31%), 135 [$(M - CH_3)^+$, 100%] (HRMS: found M^+, 150.0507. C_9H_{10}S requires *M*, 150.0503).

(ii) Preparation of (1*S*)-1-ethyl-1,3-dihydroisobenzothiophene 40.[24] The general procedure was followed, using enantiomerically enriched complex **34** (17.2 mg). Purification by Kugelrohr distillation (60 °C/0.25 mbar) gave **40** as a colourless oil (7 mg, 70%) $[\alpha]_D^{23}$ −60 (*c* 0.33 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2964 and 2253; δ_H (400 MHz, $CDCl_3$) 1.03 (3H, t, *J* 7, CH_3), 1.79 (1H, m, C*H*HCH$_3$), 2.05 (1H, m, CH*H*CH$_3$), 4.19 (1H, d, J_{AB} 14, SCH*H*), 4.24 (1H, dd, J_{AB} 14, SC*H*H) 4.63 (1H, m, SC*H*) and 7.23 (4H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 11.7 (*C*H$_3$), 31.7 (*C*H_2), 36.8 (*C*H_2), 56.2 (*C*H), 124.2 (Ar*C*H), 124.8 (Ar*C*H), 126.8 (Ar*C*H), 126.9 (Ar*C*H), 140.6 (Ar*C*) and 144.3 (Ar*C*); *m* /*z* (EI) 164 (M^+, 10%), 135 [$(M - CH_2CH_3)^+$, 100%].

(iii) Preparation of (1*S*)-1-benzyl-1,3-dihydroisobenzothiophene 41. The general procedure was followed, using enantiomerically enriched complex **35** (0.39 g). Purification by Kugelrohr distillation (200 °C/1 mbar) gave **41** as a colourless oil (0.20 g, 84%); $[\alpha]_D^{23}$ −70 (*c* 0.5 in $CHCl_3$) (Found: C, 79.73; H, 6.33; S, 14.09. Requires C, 79.62; H, 6.24; S, 14.14%); ν_{max} ($CHCl_3$)/cm^{-1} 2906 and 1730; δ_H (400 MHz, $CDCl_3$) 3.03 (1H, dd, J_{AB} 14 and 9, CH*H*Ph), 3.34 (1H, dd, J_{AB} 14 and 5, C*H*HPh), 4.08 (2H, m, SCH_2), 4.91 (1H, m, SC*H*) and 7.21 (4H, m, Ar*H*); δ_C (68 MHz, $CDCl_3$) 36.5 (CH$_2$), 45.1 (*C*H$_2$), 55.3 (*C*H), 124.3 (Ar*C*H), 124.7 (Ar*C*H), 126.4 (Ar*C*H), 126.5 (Ar*C*H), 127.0 (Ar*C*H), 128.1 (Ar*C*H), 129.3 (Ar*C*H), 138.8 (Ar*C*), 140.7 (Ar*C*) and 143.5 (Ar*C*); *m*/*z* (EI) 226 (M^+, 1%), 135 [$(M - PhCH_2)^+$, 100%] (HRMS: found M^+, 226.0815. $C_{15}H_{14}$S requires *M*, 226.0816).

(iv) Preparation of (1*S*)-1-allyl-1,3-dihydroisobenzothiophene 42. The general procedure was followed, using enantiomerically enriched complex **37** (0.39 g). Purification by Kugelrohr distillation (100 °C/ 3 mbar) gave **42** as a colourless oil (22 mg, 79%) $[\alpha]_D^{23}$ −73 (*c* 1.18 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2902, 2253 and 1794; δ_H (400 MHz, $CDCl_3$) 2.54 (1H, m, CH*H*CH=CH$_2$), 2.79 (1H, m, C*H*HCH=CH$_2$), 4.17 (1H, d, J_{AB} 14, SC*H*H), 4.23 (1H, d, J_{AB} 14, SCH*H*), 4.72 (1H, m, SC*H*), 5.10 (2H, m, CH=CH_2), 5.86 (1H, m, C*H*=CH$_2$) and 7.22 (4H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 36.8 (*C*H_2), 42.9 (*C*H_2), 53.6 (*C*H), 117.4 (*C*H_2), 124.3 (Ar*C*H), 124.9 (Ar*C*H), 126.8 (Ar*C*H), 127.1 (Ar*C*H), 135.4 (*C*H), 140.7 (Ar*C*) and 143.7 (Ar*C*); *m*/*z* (EI) 176 (M^+, 0.2%), 135 [$(C_8H_7S)^+$, 43%] (HRMS: found M^+, 176.0643. $C_{11}H_{12}$S requires *M*, 176.0660).

(v) Preparation of (1*S*)-1-(2-naphthyl)-1,3-dihydroisobenzothiophene 43. The general procedure was followed, using enantiomerically pure complex **38** (0.10 g). Purification by flash column chromatography on silica gel (10% EtOAc–light petroleum) gave **43** as a white solid (58 mg, 86%), $[\alpha]_D^{23}$ −91 (*c* 0.23 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2906 and 1731; δ_H (400 MHz, $CDCl_3$) 3.19 (1H, dd, J_{AB} 14 and 9, CH_2), 3.50 (1H, dd, J_{AB} 14 and 5, CH_2), 4.08 (2H, m, SCH_2), 5.02 (1H, m, SC*H*), 7.20 (4H, m, Ar*H*), 7.44 (3H, m, Ar*H*), 7.64 (1H, s, Ar*H*) and 7.78 (3H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 36.7 (*C*H$_2$), 45.5 (*C*H$_2$), 55.5 (*C*H), 124.5 (Ar*C*H), {(125.0, 125.5, 126.0, 126.7, 127.2, 127.7, 127.8, 127.9, 128.0), Ar*C*H}, {(132.4, 133.5, 136.6, 140.9, 143.7), Ar*C*}; *m*/*z* (EI) 276 (M^+, 0.1%), 135 [$(C_8H_7S)^+$, 100%] (HRMS: found M^+, 276.0961. $C_{19}H_{16}$S requires *M*, 276.0973).

Crystal structure determination of 3‡

A crystal was mounted on a glass fibre and transferred into the cold stream of the diffractometer's low temperature device.

Crystal data. $C_{24}H_{23}CrO_4PSi$, $M = 486.5$, tetragonal, $a = 12.69(2)$, $c = 29.55(5)$ Å, $U = 4759(13)$ Å^3, $T = 150(2)$ K, space group $P4_12_12$ (No. 92), $Z = 8$, $D_c = 1.358$ g cm^{-3}, μ(Mo-Kα) = 0.625 mm^{-1}, 9031 reflections measured (including Friedel opposites), 4185 unique (R_{int} 0.123), 4185 used in all calculations. Final R_1 [3191 $F > 4\sigma(F)$] = 0.0536 and wR(all F^2) was 0.108. The Flack parameter refined to −0.04(4).[25]

Crystal structure determination of 21

A crystal was mounted on a glass fibre and transferred into the cold stream of the diffractometer's low temperature device.

‡ CCDC reference number 207/356. See http://www.rsc.org/suppdata/p1/1999/3177 for crystallographic files in .cif format.

Crystal data. $C_{28}H_{21}CrO_4P$, $M = 504.42$, triclinic, $a = 10.820(2)$, $b = 11.206(2)$, $c = 14.618(2)$ Å, $\alpha = 75.33(3)$, $\beta = 86.12(2)$, $\gamma = 78.60(2)°$, $U = 1680.5(5)$ Å^3, $T = 150(2)$ K, space group $P\bar{1}$ (No. 2), $Z = 2$, $D_c = 0.997$ g cm^{-3}, μ(Mo-Kα) = 0.411 mm^{-1}, 10515 reflections, 5907 unique (R_{int} 0.023), 5907 used in all calculations. Final R_1 [5017 $F > 4\sigma(F)$] = 0.0468 and wR(all F^2) was 0.115. The values for M, D_c and μ ignore the contents of an ill-defined solvent region which was modelled using the SQUEEZE option in PLATON98.[26]

Crystal structure determination of 33

A crystal was mounted on a glass fibre in a file of perfluoropolyether oil and transferred into the cold stream of the diffractometer's low temperature device.

Crystal data. $C_{12}H_{10}CrO_3S$, $M = 286.3$, monoclinic, $a = 6.581(6)$, $b = 8.758(9)$, $c = 10.333(8)$ Å, $\beta = 93.88(8)°$, $U = 594.2(7)$ Å^3, $T = 150(2)$ K, space group $P2_1$ (No. 4), $Z = 2$, $D_c = 1.600$ g cm^{-3}, μ(Mo-Kα) = 1.129 mm^{-1}, 2082 reflections measured (including Friedel opposites), 1971 unique (R_{int} 0.021), 1971 used in all calculations. Final R_1 [1952 $F > 4\sigma(F)$] = 0.0283 and wR(all F^2) was 0.0785. The Flack parameter refined to −0.02(2).[25]

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