Chiral base mediated asymmetric synthesis of tricarbonyl(η^6-arene)-chromium complexes

Richard A. Ewin,[a] Angus M. MacLeod,[b] David A. Price,[a] Nigel S. Simpkins*,[a] and Alan P. Watt[b]

[a] *Department of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, UK*
[b] *Merck Sharp and Dohme Research Laboratories, Terlings Park, Harlow, Essex CM20 2QR, UK*

Enantiomerically enriched tricarbonyl(η^6-arene)chromium complexes can be obtained in up to 94% ee from the enantioselective *ortho*-metallation reaction of certain symmetrically substituted complexes with Me_3SiCl, mediated by a chiral lithium amide base. The level of asymmetric induction depends upon the nature of the starting ring substituent(s) and, in the case of anisole-type complexes, a proton transfer reaction involving the chiral metallated intermediate and the neutral tricarbonyl(η^6-arene)chromium complex results in rapid racemisation in the absence of an *in situ* electrophilic quench. Non-racemic derivatives of a tricarbonyl(η^6-arene)chromium complex derived from 1,3-dihydroisobenzofuran are also prepared in up to 99% ee by chiral base deprotonation, and trends in the regioselectivity of metallation of this complex with a range of lithium amide bases are described.

Introduction

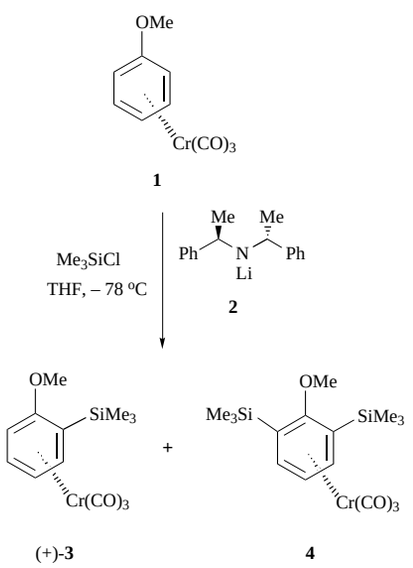
Tricarbonyl(η^6-arene)chromium complexes have emerged as important intermediates in organic synthesis, the presence of the transition metal facilitating regio- and stereo-selective substitution of positions on or adjacent to the aromatic ring.[1] Since unsymmetrically substituted complexes are chiral, a recent focus of attention has been the development of methods for the preparation of such complexes in non-racemic form. Until quite recently, the repertoire of such methods was rather limited, involving either resolution methods,[2] or the diastereoselective complexation of arenes bearing chiral auxiliaries.[3] Recently however, alternative asymmetric approaches to tricarbonyl(η^6-arene)chromium complexes have appeared, including diastereoselective metallation,[4] palladium-catalysed cross coupling reactions[5] and a range of others.[6]

Our own efforts in this area have focused on the possibility of a direct, asymmetric metallation of a prochiral complex by use of a chiral lithium amide base. Our preliminary publications in this area have demonstrated the validity of this approach,[7–9] and have been followed by closely related independent contributions from the groups of Kundig,[10] Schmalz,[11] Uemura[12] and Gibson.[13] Herein, we describe our work in this area in further detail, including chiral base reactions involving *ortho*-metallation and benzylic metallation of tricarbonyl(η^6-arene)-chromium complexes, aspects of anion racemisation and unusual regioselectivities in the metallation of a complex derived from 1,3-dihydroisobenzofuran.

Results and discussion

Asymmetric metallation of tricarbonyl(η^6-arene)chromium complexes

We anticipated a novel and direct approach to chiral, non-racemic tricarbonyl(η^6-arene)chromium complexes would be possible by treatment of a prochiral complex with an enantiomerically pure chiral lithium amide base.[14] For a monosubstituted system, a kinetically controlled discrimination between the two enantiotopic *ortho*-hydrogens available would lead directly to a non-racemic product after reaction with a suitable electrophile. The viability of this approach was demonstrated on treatment of the anisole complex **1** with the chiral base **2**, in the presence of Me_3SiCl [*in situ* quench (ISQ) conditions], which resulted in the formation of *ortho*-silylated complex (+)-**3** in 83% yield and 84% ee, along with minor amounts (*ca.* 4%) of the disilylated product **4** (Scheme 1).[7]

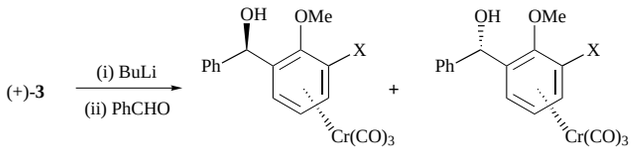


Scheme 1

It was also established that a single recrystallisation of enantiomerically enriched complex (+)-**3**, obtained as shown in Scheme 1, allowed the isolation of material of >97% ee in reasonable overall yield (*ca.* 50%).

The use of a slight excess of the chiral base (1.1 equiv.) under relatively dilute conditions (0.04 M) resulted in the maximum specific rotation observed for **3** and minimised the formation of **4**. Alternative protocols, involving the addition of Me_3SiCl to the reaction mixture subsequent to chiral base metallation (conventional external quench method), gave (+)-**3** with significantly lower levels of asymmetric induction, a phenomenon which was explored subsequently (*vide infra*). In order to estab-

lish the absolute configuration of (+)-**3**, we further transformed non-racemic material as indicated in Scheme 2.

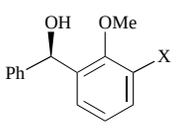


(+)-**5** X = $SiMe_3$ (+)-**6** X = $SiMe_3$
(–)-**7** X = H (–)-**8** X = H

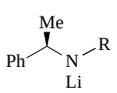
Scheme 2

Thus, *ortho*-lithiation of (+)-**3** at the remaining free site using BuLi, followed by addition of benzaldehyde, gave the two diastereoisomeric addition products (+)-**5** and (+)-**6** in yields of 50 and 44%, respectively. Both of these complexes were easily desilylated by treatment with Bu_4NF to give (−)-**7** (84%) and (−)-**8** (53%) respectively, and in addition, (+)-**5** was decomplexed by exposure to sunlight to give (+)-**9** (83%). Comparison of specific rotation data for (−)-**8**, prepared previously by the group of Davies, allowed assignment of the absolute configurations as shown.[15]

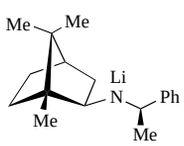
Both of the complexes (−)-**7** and (−)-**8** were also decomplexed to give the corresponding diaryl products (+)-**10** and (−)-**10**, having equal and opposite specific rotations at a level of 82% optical purity.



(+)-**9** X = $SiMe_3$
(+)-**10** X = H



11a R = Bn
11b R = Pr^i
11c R = cyclohexyl



12

An alternative and more direct approach for the preparation of aldehyde addition products from silylated complex (+)-**3** involved treatment of this compound with CsF–18-crown-6 in the presence of PhCHO.[16] This resulted in direct ipso-substitution of the silicon substituent, resulting in the formation of a mixture of (+)-**7** and (+)-**8**, isolated in 19 and 24% yield respectively, these complexes having specific rotations equal in magnitude, but opposite in sign, to those for their enantiomers prepared earlier according to Scheme 2. Thus, either enantiomeric series of benzaldehyde addition complexes can be accessed by this route.

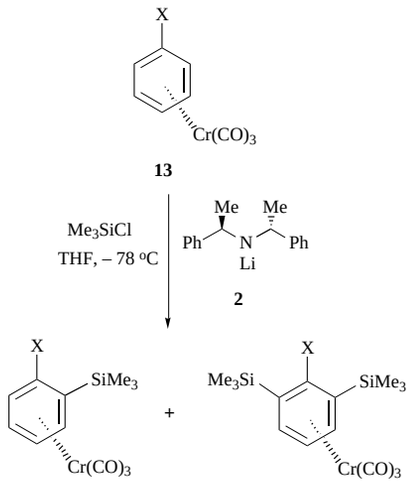
Before applying the new method to other complexes, we briefly examined the metallation of the anisole complex with the alternative chiral lithium amides **11** and **12** under the optimal Me_3SiCl ISQ conditions (Table 1). Since the results obtained were inferior to those with base **2**, we proceeded to use this lithium amide to effect the enantioselective metallation of a range of complexes **13a**–**h** (Table 2).

Comparison of the results for **13a** with those for anisole complex **1** shows that the change of *O*-alkyl group from methyl to ethyl has very little effect. However, changing to an isopropyl group (**13b**) results in a significant drop in chemical yield and a slight improvement in enantioselectivity. The use of a *tert*-butyl group (**13c**) completely halts the reaction, presumably because chelation of the lithium of the chiral base to the ether oxygen is precluded on steric grounds and without this interaction the reaction does not proceed. It was hoped that the additional metal coordination site present in the methoxymethyl ether **13d** would lead to improved selectivities with this complex, but in fact similar results to those seen with **1** were obtained. In the reactions of complexes **13a**, **13b** and **13d**, the desired mono-

Table 1 Enantioselective metallation of **1** with chiral lithium amide bases to give (+)-**3**

Chiral base	Yield (%)	Ee (%)
11a	67	59
11b	65	59
11c	73	54
12	59	25

Table 2 Enantioselective metallation of complexes **13** with chiral base **2** to give **14**

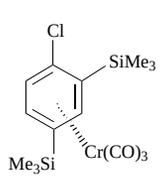


14 **15**

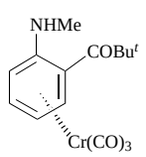
Compound	X	Yield (%)	Ee (%)
13a	OEt	82	81
13b	OPr^i	65	90
13c	OBu^t	0	—
13d	OCH_2OMe	76	80
13e	Cl	27	51
13f	F	57	16
13g	$CONPr^i_2$	87	48
13h	$N(Me)COBu^t$	65	44

silylated product complexes **14** were obtained cleanly, the disilylated complexes **15** being relatively minor by-products.

The substitution reactions of chlorobenzene complex **13e** under Me_3SiCl *in situ* quench conditions proved to be more difficult to control, with mixtures of polysilylated products being obtained when lithium diisopropylamide (LDA) was used as base. With chiral base **2** the reaction was a little improved, and we were able to isolate the desired product (+)-**14** in a modest 27% yield and 51% ee. In this case the 2,4-disilylated complex **16** proved to be a significant by-product and was isolated in optically active form (the ee was not determined).



16



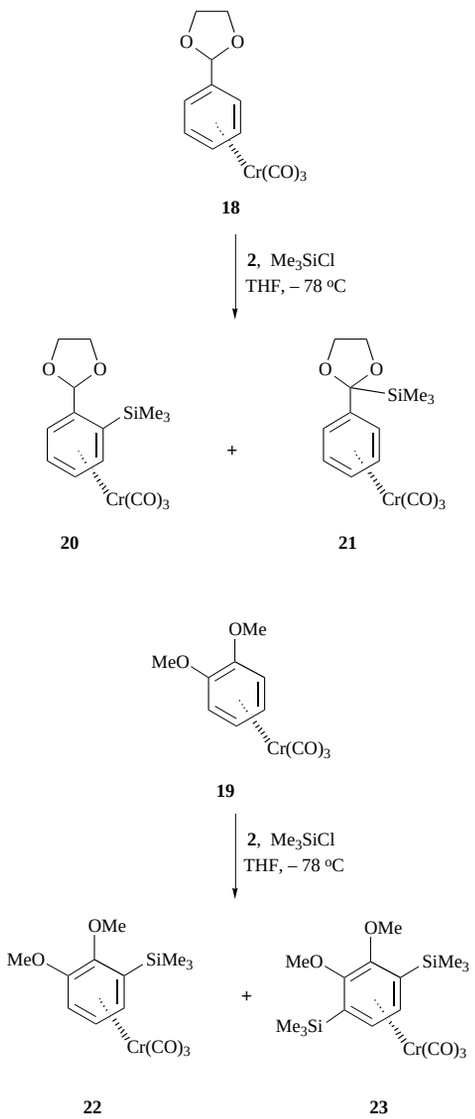
17

The silylation reactions of the fluoro and carboxamide derivatives **13f** and **13g** proved more straightforward, the desired products (−)-**14f** and (−)-**14g** being isolated in 57 and 87% yields, respectively. The metallation reaction of the amide **13g** was very smooth and, in contrast to most of the other

reactions, we were unable to isolate any polysilylated by-products.

Finally, having found that metallation of dimethylaniline complex with base **2** gave disappointing results (modest yields of *meta*-silylated products), we examined the reactions of amide derivative **13h**. In this case an acceptable yield but modest enantiomeric excess was achieved, with the reaction being notable for the formation of ketone by-product **17**, which could be suppressed by the use of increased amounts of Me_3SiCl (10 equiv.) compared to the standard procedure.

Two further systems were examined; the dioxolane derivative **18** and the veratrole complex **19** (Scheme 3). Under the usual



Scheme 3

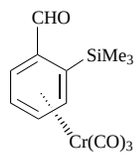
Me_3SiCl ISQ conditions the *ortho*-silylated dioxolane complex (+)-**20** was formed in 36% yield with an ee of 84% accompanied by **21**, the product of substitution at the benzylic position, in 34% yield. Hydrolysis of the acetal in complex **20**, by heating under reflux in wet acetone with pyridinium toluene-*p*-sulfonate (PPTS), gave the known aldehyde complex (+)-**24**, thus confirming our assignment of the absolute stereochemistry.[17]

In the case of the veratrole complex **19** the level of induction appeared somewhat better than observed with the other complexes, with ee levels of 92–95% being obtained on several runs. Typically, the desired product **22** was obtained in around 70%, accompanied by 10–12% of the unwanted disilylated complex **23**. Schmalz and Schellhaas also reported excellent selectivity in the asymmetric metallation of **19** using base **2** and described

Table 3 Variation of ee of **3** with metallation time under external quench conditions

t/min[a]	Ee (%)[b]
0.5	73
10	70
20	67
40	59
60	52
100	39
140	33
180	25

[a] Time between mixing of **1** and **2** and addition of Me_3SiCl. [b] Yield of (+)-**3** remains constant at *ca*. 84%.



24

similar results with a range of related complexes of potential value in synthesis.[11]

From the results outlined above, along with those described by other groups, it seems clear that coordination of the lithium amide to the ether functionality in the starting complex is important in achieving high levels of enantioselectivity. In other types of complex, the levels of regio- and enantio-control available are less useful to date, with carbonyl- or chlorine-containing systems giving mediocre results and the fluorobenzene complex giving a very low ee. Although the absolute sense of the asymmetric induction has been proved in the case of **3** and **20**, we have assigned the other results by analogy.

Anion equilibration in metallated anisole-type complexes

As mentioned above, in the metallation of anisole complex **1** best results were obtained by treatment of the complex with base **2** in the presence of Me_3SiCl (*in situ* quench conditions), which resulted in the formation of the desired *ortho*-silylated complex **3** in 83% yield and 84% ee. After some further experiments, two aspects of this metallation reaction were puzzling. Firstly, the Me_3SiCl ISQ procedure gave optimal asymmetric induction, whereas external quenching (EQ) with Me_3SiCl gave product **3** with an ee which decreased on increasing the metallation time allowed (Table 3).[8] Secondly, although the Me_3SiCl EQ protocol gave a non-racemic product in good chemical yield (albeit of reduced ee), the use of other electrophiles under identical conditions gave very low yields of racemic products.

Since chiral base reactions involving Me_3SiCl under either EQ or ISQ conditions gave good yields of product **3** after a reaction period of only 5 min (total time before quench with aqueous $NaHCO_3$) at −78 °C, we were perplexed by the very low yields of adducts (*ca*. 10%) with electrophiles such as PhCHO under the same conditions. A deuteriation study (Table 4) showed that the metallation of **1** by base **2** is actually rather slow, requiring about three hours to reach completion, thus making the high yields obtained after 5 min using Me_3SiCl seemingly anomalous.

A possible cause of this effect was thought to be LiCl, which is liberated on reaction of the metallated complex with Me_3SiCl, and which could then affect the rate of deprotonation.[18] To test this idea we carried out deuteriation experiments in the presence of added LiCl (0.5 equiv.) and found that metallation was complete within only 2 min. The high yields obtained with Me_3SiCl as the electrophile can therefore be rationalised, since the LiCl generated on reaction with Li·**1** allows subsequent rapid completion of the metallation (effectively under ISQ conditions). We attribute the modified reactivity of chiral lithium

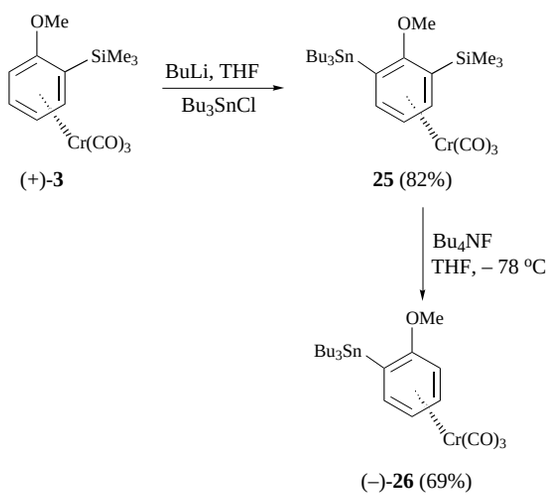
Table 4 Deuterium incorporation after reaction of **1** with **2** and quenching with D_2O

Metallation time/min	Deuterium incorporation (%)
5	28
30	55
60	72
120	93
180	97

amides in the presence of LiCl to the formation of a mixed lithium amide–lithium chloride aggregate.[19] In previous work this effect has been manifested in the form of improved levels of enantiomeric excess,[18] whereas in the present work it is clear that a dramatic increase in the rate of metallation is achieved.

At this point we could propose an explanation for the data in Table 3, namely, that in the absence of an *in situ* quench, an equilibration process was eroding the enantiomeric excess of Li·**1**.[20] This process could involve non-stereoselective proton transfer between Li·**1** and neutral **1**, or could also involve the chiral amine corresponding to **2**. Clearly, the shorter the initial period allowed before addition of Me_3SiCl, the less equilibration is possible, and the more the overall reaction approximates an *in situ* quench.

To substantiate this idea, we required access to samples of Li·**1** of known enantiomeric purity, which could then be tested for configurational stability under various reaction conditions. Reaction of a sample of (+)-**3** of 84% ee, as shown in Scheme 4,



(+)-**3** **25** (82%) (–)-**26** (69%)

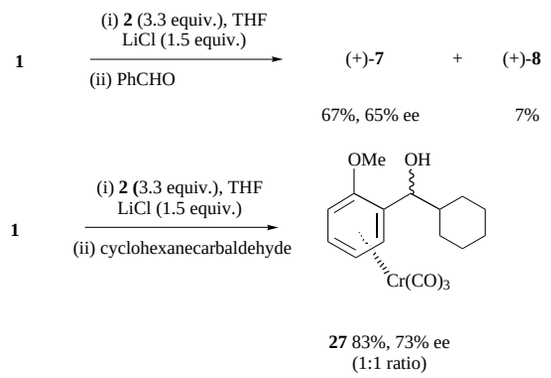
Scheme 4

allowed the preparation of the stannyl derivative (−)-**26** without loss of stereochemical integrity (*i.e.* **26** was shown by HPLC to have an ee of 83%).

Addition of a sample of (−)-**26** to a solution of BuLi in THF at −78 °C resulted in rapid transmetallation [monitored by thin layer chromatography (TLC)] to give the intermediate lithiated complex. After 1 h at −78 °C the mixture was quenched by addition of Me_3SiCl to give (−)-**3** with a specific rotation equal and opposite to that of the sample of (+)-**3** used to make the tin derivative (−)-**26**. This shows that under these conditions the intermediate Li·**1** is configurationally stable.

However, in similar reactions we added the neutral complex **1** (0.5 equiv.) to the intermediate Li·**1**, generated from (−)-**26** as described above, and found that subsequent quenching with Me_3SiCl after only 5 min gave racemic product **3**. These experiments clearly reveal the primary source of the racemisation process seen in the chiral base reactions under EQ conditions, which apparently involves non-stereoselective proton transfer between **1** and Li·**1**. We also examined the effect of adding the chiral secondary amine corresponding to **2** to solutions of the non-racemic lithiated anisole complex prepared from the tin derivative (−)-**26**. In this case (0.5 equiv. of amine) much slower equilibration of the organolithium was observed than when neutral complex **1** was added (only *ca*. 35% loss in ee over 2 h at −78 °C). We believe that the slow racemisation under these conditions is due to small amounts of neutral complex **1** being produced through protonation of some Li·**1** by the chiral amine.

Finally, we have used the above findings to devise modified deprotonation conditions which allow direct asymmetric transformation of complex **1** by use of electrophiles other than Me_3SiCl under EQ-type conditions. We reasoned that the racemisation process would be less likely if rapid metallation could be achieved on mixing **1** and base **2**, so that no (or little) free neutral **1** was available for proton transfer. The use of an excess of chiral base, in combination with LiCl (which had been demonstrated to dramatically accelerate metallation) seemed appropriate. The new protocol involved gradual addition (syringe pump, 15 min) of the complex **1** to an excess of **2** (3.3 equiv.) in the presence of LiCl (1.5 equiv.). Under these conditions we found that quenching the reaction mixture with PhCHO or cyclohexanecarbaldehyde gave the expected products as mixtures of diastereomers, with levels of ee approaching those available under ISQ conditions (Scheme 5).



Scheme 5

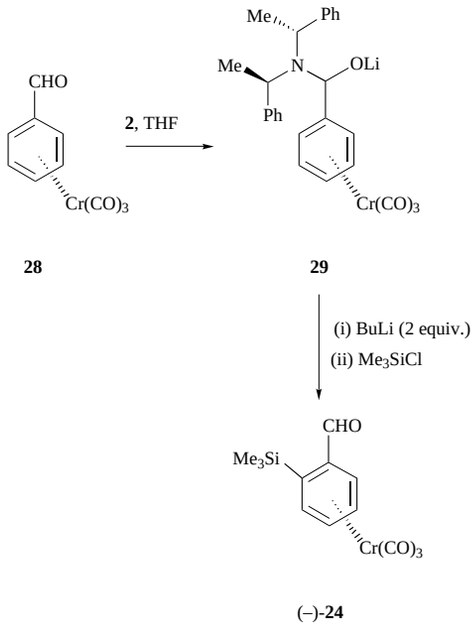
The erosion of enantiomeric excess observed in EQ-type reactions of complex **1**, compared to Me_3SiCl ISQ reactions, was also observed for other anisole-type complexes **13a**, **13b**, **13d** and **19**. However, some other complexes, including chlorobenzene complex **13e** and the acetal system **18**, did not undergo equilibration; in these cases electrophilic quenching after 1 h gave exactly the same enantiomeric excess as the ISQ procedure.

Enantioselective metallation *via* an intermediate α-amino alkoxide

An alternative approach to asymmetric metallation, which was briefly investigated, involved the formation of a chiral α-amino alkoxide by addition of the chiral lithium amide **2** to tricarbonyl(η^6-benzaldehyde)chromium **28**.[21] Subsequent *in situ* metallation, by addition of BuLi, and reaction with Me_3SiCl gave, after an acidic aqueous work-up, the aldehyde complex (−)-**24** in 84% ee (Scheme 6).

The product **24** was of opposite absolute configuration to that prepared earlier *via* asymmetric deprotonation of acetal **18**. The yield in this reaction could not be improved above the modest 38% achieved using 2 equiv. of BuLi, and our efforts to isolate the postulated intermediate α-amino alkoxide **29** by trapping with $Bu^tMe_2SiOSO_2CF_3$ or Bu^tPh_2SiCl were not successful.

Our results are closely related to those recently published by Alexakis *et al.*, involving the use of lithium amides derived from diamines to effect the type of transformation shown in Scheme 6.[22] Compared to our results, improved chemical yields were reported, although the enantioselectivity was not quite as good (up to 78% maximum). Significantly, this group



Scheme 6

established that the stereoselectivity in the formation of the additional stereocentre in an intermediate α-amino alkoxide, analogous to **29** (undefined in our case), was very good.

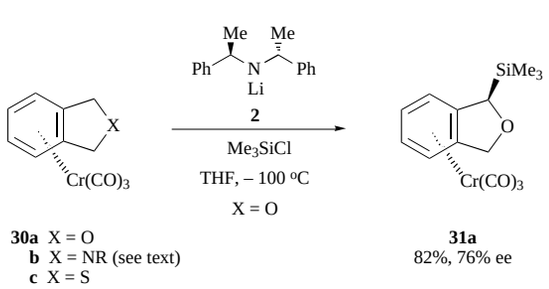
Enantioselective metallation of a complex from 1,3-dihydrobenzofuran

Since certain alkyl-substituted tricarbonyl(η^6-arene)chromium complexes have been shown to undergo facile deprotonation at the benzylic position, we became interested in establishing if the chiral base method could be applied to systems in which discrimination between enantiotopic benzylic hydrogens was the key step.[23] We were initially attracted to the series of complexes **30a**–**c** as systems for study. It was anticipated that the presence of a heteroatom in these systems (especially oxygen) would facilitate metallation, whilst the conformational constraint provided by the heterocyclic ring would enforce diastereoselective (*exo*) metallation.

Preliminary studies were not promising; the sulfur-containing system **30c** was easily prepared, but gave racemic products in reactions with base **2**. We had difficulty in preparing nitrogen compounds **30b** having an appropriate R group [*e.g. tert*-butoxycarbonyl (Boc)] for metallations, and other derivatives having R = Me or CH_2CH_2OMe did not undergo clean metallations.

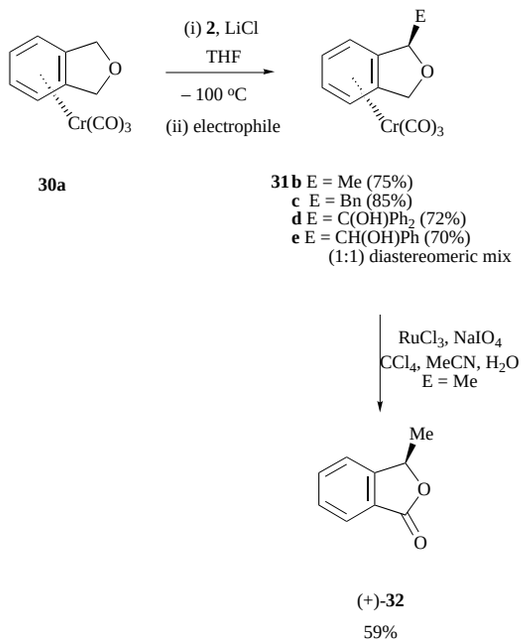
Attention was therefore focused on the isobenzofuran system **30a**, which had previously been shown to undergo efficient benzylic substitution on metallation with Bu^{t}Li, followed by electrophilic quench with alkyl halides.[24] We were pleased to find that treatment of **30a** with chiral base **2**, in the presence of Me_3SiCl, resulted in the formation of α-silylated product **31a** in 82% yield and 76% ee (Scheme 7).

Reactions with electrophiles other than Me_3SiCl initially



Scheme 7

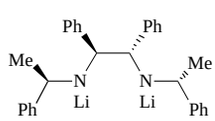
proved unrewarding and complex **30a** showed low levels of deuterium incorporation on treatment with base **2** followed by D_2O. As in the case of anisole complex **1**, this apparent inconsistency was traced to the influence of LiCl on the metallation reaction, which is generated only during the *in situ* reaction with Me_3SiCl. As we found previously, simply conducting the chiral base reactions in the presence of LiCl resulted in a dramatic acceleration of the metallation (complete deuterium incorporation after only 5 min at −78 °C), allowing enantioselective reaction with electrophiles other than Me_3SiCl. A convenient way of conducting such 'added salt' reactions is simply to treat the hydrochloride salt of the appropriate chiral amine with 2 equiv. of BuLi, thus generating the required mixture of LiCl and lithium amide *in situ*. In this way, reaction of **30a** with **2** at −100 °C, followed by addition of the appropriate electrophile (MeI, $PhCH_2Br$, PhCOPh or PhCHO) gave **31b**–**e** (Scheme 8).



Scheme 8

Each of the alkylated products was obtained at similar levels of enantiomeric excess as the silylated derivative **31a**, *i.e.* 75–80% ee. As shown, conversion of the methylated compound **31b** into the known lactone (+)-**32** was possible on treatment with RuO_4,[25] generated *in situ* according to the Sharpless protocol.[26] This served to assign the absolute configuration of **31b**, the other derivatives presumably belonging to the same enantiomeric series.

Contemporaneous studies in this area by the group of Gibson showed that the enantioselective benzylic functionalisation of (alkyl benzyl ether)tricarbonylchromium(0) complexes could be achieved using chiral base **33**,[13] which we had

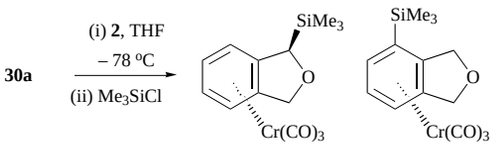


33

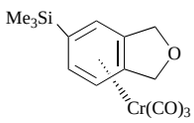
described previously.[27] The very high levels of enantioselectivity reported (≥99% ee) prompted us to re-examine the deprotonation of complex **30a** using this base.

Thus treatment of **30a** with the chiral lithium diamide **33** (formed from the corresponding vicinal diamine and 2 equiv. of BuLi) at −100 °C in the presence of 1 equiv. of LiCl, followed

Table 5 Regiochemical outcome of metallations of **30a**



31a **34**



35

		Ratio (%)[b] (% ee)		
Base	Total yield (%)[a]	**31a**	**34**	**35**
2	82	>95 (71)	Trace (NE)[d]	ND[c]
11a	74	90 (42)	10 (30)	ND[c]
11b	39	67 (70)	30 (NE)[d]	3
LDA	56	ND[c]	83	17
LTMP	67	80	16	4
BuLi	73	18	78	4
Bu^{t}Li	70	100	ND[c]	ND[c]

[a] Total yield of **31a**, **34** and **35**. [b] Refers to ratio in the crude mixture by HPLC. [c] ND = not detected. [d] NE = not established.

by addition of benzophenone, resulted in the formation of (−)-**31d** in 70% yield and in 99% ee. It therefore appears that very high levels of induction are available in certain metallations involving base **33**, and it may prove productive to re-examine some of the earlier, less selective reactions with this base.

During the studies described above we required a sample of racemic **31a** for HPLC analysis. To our surprise, reaction of **30a** with LDA in THF at −78 °C, followed by addition of Me_3SiCl, gave none of the desired **31a** but instead furnished mainly **34**, the product of *ortho*-lithiation. A detailed examination of the regiochemistry of the metallation of **30a** was then carried out, the results of which are shown in Table 5.

LDA proved to be the only lithium amide we tested that gave **34** as the major product, the chiral bases **11a** and **11b** giving mainly **31a**, but in lower enantioselectivity than **2**. Traces of the regioisomeric product **35** were also found in some mixtures, appreciable amounts of this compound appearing only when LDA was employed. The bulky amide lithium 2,2,6,6-tetramethylpiperidide (LTMP) gave contrasting results to LDA, the regiochemical result resembling those obtained with the chiral bases. We also found that BuLi gave mainly **34**, this result contrasting sharply with that obtained using Bu^{t}Li, which gave only **31a**.

In general it appears that bulkier bases (*e.g.* Bu^{t}Li and **2**) give metallation predominantly or exclusively at the benzylic position, whereas the less hindered bases (LDA and BuLi) metallate the aromatic nucleus. At present we regard all of the results described in Table 5 to be the result of kinetic control; unfortunately, the relative instability of the metallated derivatives of **30a** precluded warming of the solutions containing these species in order to probe possible equilibration pathways. The origins of the observed regioselectivities are not clear. Blagg *et al.*, observed a somewhat similar outcome on studying the metallation of a complex derived from α-methylbenzyl methyl ether.[28] As in our case, the use of Bu^{t}Li resulted in formation of a benzylic carbanion, whilst BuLi caused ring-metallation to predominate. These authors proposed that Bu^{t}Li 'removes the most acidic α-proton without appreciable co-ordination to oxygen', whilst efficient ether oxygen co-ordination seems to lead to regioselective *ortho*-metallation. That similar dichotomous behaviour should be observed in our system is rather remarkable, given the lack of conformational freedom of the benzylic oxygen and the associated lone pairs.

Conclusions

This study has demonstrated the applicability of chiral lithium amide base methodology to the asymmetric synthesis of a range of tricarbonyl(η^6-arene)chromium complexes. As yet we are unable to provide a rationale for the sense of asymmetric induction observed in the above reactions, or to fully explain the disparate levels of induction seen with the different complexes. However, from the examples tested, it appears that the asymmetric deprotonation works best when one or more oxygen atoms, particularly ether linkages, are present in the starting prochiral complex. The finding that useful levels of asymmetric induction can be obtained in metallations at ring positions and at benzylic positions of these complexes, using the very readily available base **2**, and that very high induction can be achieved in some reactions using the new base **33**, should stimulate further studies and applications in this area.

Experimental

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 (all complexes showed two absorptions at 1940–1990 and 1860–1930 cm^{-1} for the C≡O bond). Mass spectra were recorded on an AEI MS-902 or VG Micromass 70E mass spectrometer, using electron impact ionisation (EI). Microanalytical data were obtained on a Perkin-Elmer 240B elemental analyser. Optical rotations were recorded using a JASCO DIP-370 digital polarimeter. All NMR spectra were recorded on either a Bruker WP80, Bruker AM250, JEOL FX270, Bruker AM400 or Bruker DRX500 spectrometer, with tetramethylsilane as internal standard. *J* Values are recorded in Hz and multiplicities indicated for ^{13}C NMR were obtained using a DEPT sequence. Flash column chromatography was performed using Fluka silica gel 60 (220–440 mesh). Analytical thin layer chromatography (TLC) was performed using CAMLAB silica gel F_{254} precoated plastic plates which were viewed under ultraviolet light and developed with basic potassium permanganate solution. Enantiomeric excesses were evaluated using chiral stationary phase high perforance liquid chromatography (HPLC) columns at ambient temperature. Samples were dissolved at approximately 1 mg ml^{-1} in the solvent system and 5–10 μl was injected corresponding to 2.5–5 μg of each enantiomer on the column. Detection was by UV at the stated frequency and data was processed using an HP-3D DOS Chemstation. All retention times refer to the enantiomeric mixture obtained from the reaction with the chiral lithium amide **2** unless otherwise stated. Organic solvents and reagents were dried from the following as required: THF (sodium wire–benzophenone ketyl), EtOAc (anhydrous potassium carbonate), MeOH (magnesium methoxide), benzene, CH_2Cl_2 and chlorotrimethylsilane (calcium hydride). Unless otherwise stated all other reagents were used as received from commercial suppliers. All starting complexes were prepared according to standard procedures.[29]

General procedure for the enantioselective deprotonation of tricarbonyl(η^6-arene)chromium(0) complexes

In a typical enantioselective metallation reaction a solution of the chiral lithium amide **2** was prepared from the corresponding chiral amine (248 mg, 1.10 mmol) in THF (22 ml) at −78 °C, under an atmosphere of nitrogen, by addition of BuLi (0.69 ml of a 1.6 M solution in hexanes, 1.10 mmol), followed by warming to room temperature for 15 min. The resulting solution of the chiral base **2** was then cooled to −78 °C and Me_3SiCl (0.38

ml, 3.00 mmol) added in one portion. A solution of the chromium complex (1.00 mmol) in THF (3 ml), was then immediately added in one portion. After stirring the solution at −78 °C for 30 min, saturated aqueous $NaHCO_3$ (5 ml) was added and the reaction allowed to warm to room temperature. The reaction mixture was extracted with CH_2Cl_2 (40 ml), the organic extract was washed with water (15 ml) and dried ($MgSO_4$), and the solvent evaporated under reduced pressure. The resulting yellow oil was then purified by flash column chromatography on silica gel to give the silylated products.

(2*R*)-Tricarbonyl(η⁶-2-trimethylsilylanisole)chromium(0) (+)-3

The general procedure was followed using complex **1** and purification of the yellow oil by flash column chromatography (5% Et_2O–light petroleum) gave firstly *tricarbonyl*[η⁶-2,6-*bis*(*trimethylsilyl*)*anisole*]*chromium*(0) **4** as a yellow crystalline solid (18 mg, 4%), mp 84–85 °C (Found: C, 49.41; H, 6.28. $C_{16}H_{24}CrO_4Si_2$ requires C, 49.48; H, 6.18%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2951 (C–H), 1966, 1897, 1330 and 841; δ_H(250 MHz, $CDCl_3$) 0.39 [18 H, s, $Si(CH_3)_3$ × 2], 3.72 (3 H, s, OCH_3), 4.79 (1 H, t, *J* 6.2, Ar-*H*) and 5.62 (2 H, d, *J* 6.2, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 0.36 ($SiCH_3$), 63.6 (OCH_3), 87.5 [C(4)H], 92.0 [C(2 + 6)] and 101.8 [C(3 + 5)H] (no CO peak detected); *m*/*z* (EI) 388 (M^+, 7%), 332 (M−2CO, 5), 304 (M−3CO, 100) and 252 [M−Cr(CO)$_3$, 7], followed by the known complex (2*R*)-tricarbonyl[η⁶-2-(trimethylsilyl)anisole]chromium(0) (+)-**3**[30] as a yellow crystalline solid (264 mg, 83%), mp 79–80 °C, (lit.,[30] 71–73 °C); $[\alpha]_D^{29}$ +205 (*c* 1.10 in $CHCl_3$) (Found: C, 49.23; H, 5.20. $C_{13}H_{16}CrO_4Si$ requires C, 49.36; H, 5.06%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2953 (C–H), 1957, 1898, 1587 (Ar), 1503 (Ar) and 841 (C–H); δ_H(250 MHz, $CDCl_3$) 0.32 [9 H, s, $Si(CH_3)_3$], 3.74 (3 H, s, OCH_3), 4.78 (1 H, dd, *J* 6.1 and 6.1, Ar-*H*), 4.97 (1 H, d, *J* 6.1, Ar-*H*), 5.58 (1 H, d, *J* 6.1, Ar-H) and 5.66 (1 H, dd, *J* 6.1 and 6.1, Ar-*H*); δ_C(68 MHz, $CDCl_3$) −0.7 ($SiCH_3$), 55.3 (OCH_3), 73.4 [C(6)H], 85.1 [C(4)H], 88.8 [C(2)], 96.0 [C(5)H], 101.8 [C(3)H], 147.5 [C(1)] and 233.7 (CO); *m*/*z* (EI) 316 (M^+, 20%), 260 (M − 2CO, 11), 232 (M − 3CO, 100) and 217 (7).

Tricarbonyl(η⁶-α-phenyl-2-methoxy-3-trimethylsilylbenzyl alcohol)chromium(0) complexes (+)-5 and (+)-6

To a stirred solution of the complex (+)-**3** (316 mg, 1.00 mmol) in THF (15 ml) at −78 °C, under an atmosphere of nitrogen, was added BuLi (0.69 ml of a 1.6 M solution in hexanes, 1.10 mmol) dropwise. After 1 h stirring at −78 °C, benzaldehyde (0.30 ml, 3.00 mmol) was added in one portion and the reaction stirred for 1 h. Saturated aqueous NH_4Cl (5 ml) was then added and the reaction warmed to room temperature, the reaction mixture was extracted with CH_2Cl_2 (40 ml), the organic extract was washed with water (15 ml) and dried ($MgSO_4$) and the solvent evaporated under reduced pressure. Purification of the resulting yellow oil by flash column chromatography (15% Et_2O–light petroleum) gave firstly *tricarbonyl*(η⁶-α-*phenyl*-2-*methoxy*-3-*trimethylsilylbenzyl alcohol*)*chromium*(0) (+)-**6** as a yellow solid (186 mg, 44%), mp 152–155 °C; $[\alpha]_D^{29}$ +13 (*c* 1.40 in $CHCl_3$) (Found: C, 56.89; H, 5.16. $C_{20}H_{22}CrO_5Si$ requires C, 56.86; H, 5.25%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3588 (O–H), 1969, 1897, 1454, 1341 and 841; δ_H(250 MHz, $CDCl_3$) 0.39 [9 H, s, $Si(CH_3)_3$], 2.31 (1 H, d, *J* 2.8, D_2O exch., CHO*H*), 3.46 (3 H, s, OCH_3), 4.91 (1 H, dd, *J* 6.2 and 6.2, Ar-*H*), 5.53 (1 H, d, *J* 6.2, Ar-*H*), 5.86 (1 H, d, *J* 2.8, C*H*OH), 6.01 (1 H, d, *J* 6.2, Ar-*H*) and 7.36 (5 H, m, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 0.3 ($SiCH_3$), 63.6 (OCH_3), 69.4 (PhCHOH), 86.8 [C(5)H], 92.3 [C(3)], 94.6 [C(6)H], 100.7 [C(4)H], 107.8 [C(1)], 127.6 (Ph-CH), 128.5 (Ph-CH), 128.8 (Ph-CH), 141.3 [Ph-C or C(2)] and 146.6 [Ph-C or C(2)] (no CO peak detected); *m*/*z* (EI) 422 (M^+, 8%), 338 (M−3CO, 98), 305 (41), 165 (27), 73 ($SiMe_3$, 68) and 52 (Cr, 100), followed by *tricarbonyl*(η⁶-α-*phenyl*-2-*methoxy*-3-*trimethylsilylbenzyl alcohol*)*chromium*(0) (+)-**5** as a yellow solid (211 mg, 50%), mp 123–125 °C; $[\alpha]_D^{29}$ +28 (*c* 1.89 in $CHCl_3$) (Found: C, 57.20; H, 5.36. $C_{20}H_{22}CrO_5Si$ requires C, 56.86; H, 5.25%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3352 (O–H), 1965, 1898, 1454, 1343 and 841; δ_H(250 MHz, $CDCl_3$) 0.41 [9 H, s, $Si(CH_3)_3$], 2.52 (1 H, d, *J* 3.8, D_2O exch., CHO*H*), 3.95 (3 H, s, OCH_3), 4.74 (1 H, dd, *J* 6.2 and 6.2, Ar-*H*), 5.44 (1 H, d, *J* 6.2, Ar-*H*), 5.50 (1 H, d, *J* 6.2, Ar-*H*), 5.93 (1 H, d, *J* 3.8, C*H*OH) and 7.36 (5 H, m, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 0.3 ($SiCH_3$), 64.5 (OCH_3), 70.5 (PhCHOH), 86.2 [C(5)H], 91.6 [C(3)], 96.3 [C(6)H], 100.7 [C(4)H], 105.4 [C(1)], 126.6 (Ph-CH), 128.3 (Ph-CH), 128.4 (Ph-CH), 141.2 [Ph-C or C(2)] and 148.0 [Ph-C or C(2)] (no CO peak detected); *m*/*z* (EI) 422 (M^+, 7%), 338 (M − 3CO, 80), 305 (44), 239 (100), 165 (96) and 73 ($SiMe_3$, 92).

(*R*)-α-Phenyl-2-methoxy-3-trimethylsilylbenzyl alcohol (+)-9

A solution of the complex (+)-**5** (48 mg, 0.11 mmol) in Et_2O (5 ml) was left standing in sunlight for 48 h. After this time a green precipitate had formed; the precipitate was removed by filtration and the filtrate concentrated under reduced pressure. Purification of the resulting colourless oil by flash column chromatography (5% EtOAc–light petroleum) gave (R)-α-*phenyl*-2-*methoxy*-3-*trimethylsilylbenzyl alcohol* (+)-**9** as a colourless oil (28 mg, 87%); $[\alpha]_D^{29}$ +79 (*c* 0.56 in $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3591 (O–H), 1582, 1494, 1453, 1142, 1001, 893 and 840; δ_H(250 MHz, $CDCl_3$) 0.33 [9 H, s, $Si(CH_3)_3$], 2.75 (1 H, br s, CHO*H*), 3.69 (3 H, s, OCH_3), 6.18 (1 H, s, C*H*OH) and 7.12 (8 H, m, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 0.0 ($SiCH_3$), 63.1 (OCH_3), 71.2 (PhCHOH), 124.3 (Ph-CH), 126.6 (Ph-CH), 127.3 (Ph-CH), 128.3 (Ph-CH), 130.3 (Ph-CH), 133.2 [C(1 or 3)], 135.4 (Ph-CH), 136.0 [C(1 or 3)], 143.5 (Ph-C) and 163.1 [C(2)]; *m*/*z* (EI) 286 (M^+, 11%), 284 (31), 269 (M − OH, 64), 239 (95), 209 (M − Ph, 61), 165 (71), 105 (67) and 89 (100) (HRMS: found M^+, 286.1369. $C_{17}H_{22}O_2Si$ requires *M*, 286.1389).

Tricarbonyl(η⁶-α-phenyl-2-methoxybenzyl alcohol)chromium(0) (−)-7

To a stirred solution of the complex (+)-**5** (129 mg, 0.30 mmol) in THF (5 ml), at 0 °C in the dark, was added tetrabutylammonium fluoride (TBAF) (0.60 ml of a 1.0 M solution in THF, 0.60 mmol) dropwise. The reaction was warmed to room temperature for 2 h and then poured onto saturated aqueous NH_4Cl (20 ml). The reaction mixture was extracted with CH_2Cl_2 (30 ml), the organic extract was washed with water (10 ml) and dried ($MgSO_4$) and the solvent evaporated under reduced pressure. Purification of the yellow oil by flash column chromatography (60% Et_2O–light petroleum) gave *tricarbonyl*(η⁶-α-*phenyl*-2-*methoxybenzyl alcohol*)*chromium*(0) (−)-**7** as a yellow solid (88 mg, 84%), mp 159–160 °C; $[\alpha]_D^{29}$ −37 (*c* 1.02 in $CHCl_3$) (Found: C, 58.31; H, 3.97. $C_{17}H_{14}CrO_5$ requires C, 58.29; H, 4.03%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3586 (O–H), 1965, 1897, 1873 and 1463; δ_H(250 MHz, $CDCl_3$) 2.95 (1 H, d, *J* 3.9, CHO*H*), 3.86 (3 H, s, OCH_3), 4.71 (1 H, dd, *J* 6.2 and 6.2, Ar-*H*), 5.01 (2 H, d, *J* 6.2, Ar-*H*), 5.50 (1 H, dd, *J* 6.2 and 6.2, Ar-*H*), 5.98 (1 H, d, *J* 3.9, C*H*OH), 7.34 (3 H, m, Ar-*H*) and 7.56 (2 H, m, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 56.0 (OCH_3), 70.5 [PhCHOH or C(3)H], 72.7 [PhCHOH or C(3)H], 84.4 [C(5)H], 94.3 [C(4 or 6)H], 95.3 [C(4 or 6)H], 102.7 [C(1)], 126.9 (Ph-CH), 128.2 (Ph-CH), 128.3 (Ph-CH), 138.7 [Ph-C or C(2)] and 142.4 [Ph-C or C(2)] (no CO peak detected); *m*/*z* (EI) 350 (M^+, 14%), 294 (M − 2CO, 7), 266 (M − 3CO, 77), 197 [M − Cr(CO)$_3$ − OH, 31], 181 (52), 165 (44) and 91(100).

Tricarbonyl(η⁶-α-phenyl-2-methoxybenzyl alcohol)chromium(0) (−)-8

To a stirred solution of the complex (+)-**6** (131 mg, 0.31 mmol) in THF (5 ml), at 0 °C in the dark, was added TBAF (0.62 ml of a 1.0 M solution in THF, 0.62 mmol) dropwise. The reaction was warmed to room temperature for 2 h and then poured onto saturated aqueous NH_4Cl (20 ml). The reaction mixture was extracted with CH_2Cl_2 (30 ml), the organic extract was washed with water (10 ml) and dried ($MgSO_4$) and the solvent evapor-

ated under reduced pressure. Purification of the yellow oil by flash column chromatography (20% Et_2O–light petroleum) gave the known complex tricarbonyl(η^6-α-phenyl-2-methoxybenzyl alcohol)chromium(0) (−)-**8**[15] as a yellow solid (57 mg, 53%), mp 109–112 °C, (lit.,[15] 113–114 °C); $[\alpha]_D^{29}$ −118 (*c* 1.14 in $CHCl_3$) [lit.,[15] $[\alpha]_D^{24}$ −178 (*c* 1.46 in $CHCl_3$)] (Found: C, 58.38; H, 4.04. $C_{17}H_{14}CrO_5$ requires C, 58.29; H, 4.03%); ν_{max}($CHCl_3$)/cm^{-1} 1966, 1898, 1497 and 1451; δ_H(250 MHz, $CDCl_3$) 2.15 (1 H, br s, CHO*H*), 3.73 (3 H, s, OCH_3), 4.89 (1 H, dd, *J* 6.6 and 6.6, Ar-*H*), 4.98 (1 H, d, *J* 6.6, Ar-*H*), 5.48 (1 H, dd, *J* 6.6 and 6.6, Ar-*H*), 5.91 (1 H, s, C*H*OH), 5.99 (1 H, d, *J* 6.6, Ar-*H*) and 7.23 (5 H, m, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 56.0 (OCH_3), 68.6 [PhCHOH or C(3)H], 73.4 [PhCHOH or C(3)H], 85.3 [C(5)H], 92.5 [C(4 or 6)H], 94.1 [C(4 or 6)H], 105.1 [C(1)], 126.4 (Ph-CH), 128.1 (Ph-CH), 128.5 (Ph-CH), 141.3 [Ph-C or C(2)], 141.7 [Ph-C or C(2)] and 233.0 (CO); *m*/*z* (EI) 350 (M^+, 4%), 294 (M − 2CO, 8), 266 (M − 3CO, 49), 197 [M − $Cr(CO)_3$ − OH, 33], 181 (55), 165 (60) and 91(100).

(*R*)-α-Phenyl-2-methoxybenzyl alcohol (+)-10

A solution of the complex (−)-**7** (80 mg, 0.23 mmol) in Et_2O (8 ml) was left standing in sunlight for 48 h. After this time a green precipitate had formed; the precipitate was removed by filtration and the filtrate concentrated under reduced pressure. Purification of the resulting colourless oil by flash column chromatography (30% Et_2O–light petroleum) gave (R)-α-*phenyl*-2-*methoxybenzyl alcohol* (+)-**10** as a colourless oil (31 mg, 62%); $[\alpha]_D^{29}$ +28 (*c* 0.79 in $CHCl_3$) (Found: C, 78.19; H, 6.53. $C_{14}H_{14}O_2$ requires C, 78.48; H 6.59%); ν_{max}($CHCl_3$)/cm^{-1} 3558 (O–H), 2940 (C–H), 1601 (Ar), 1490, 1464, 1110 and 1003; δ_H(250 MHz, $CDCl_3$) 3.03 (1 H, d, *J* 5.5, CHO*H*), 3.83 (3 H, s, OCH_3), 6.05 (1 H, d, *J* 5.5, C*H*OH), 6.89 (2 H, m, Ar-*H*) and 7.22 (7 H, m, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 55.4 (OCH_3), 72.3 (PhCHOH), 110.7 [C(3)H], 120.8 (Ph-CH), 126.5 (Ph-CH), 127.1 (Ph-CH), 127.9 (Ph-CH), 128.1 (Ph-CH), 128.7 (Ph-CH), 131.8 [C(1)], 143.2 (Ph-C) and 156.7 [C(2)]; *m*/*z* (EI) 214 (M^+, 100%), 196 (M − H_2O, 81), 135 (73), 109 (72) and 77 (Ph, 83).

(*S*)-α-Phenyl-2-methoxybenzyl alcohol (−)-10

A solution of the complex (−)-**8** (57 mg, 0.16 mmol) in Et_2O (5 ml) was left standing in sunlight for 48 h. After this time a green precipitate had formed; the precipitate was removed by filtration and the filtrate concentrated under reduced pressure. Purification of the resulting colourless oil by flash column chromatography (30% Et_2O–light petroleum) gave the known compound (*S*)-α-phenyl-2-methoxybenzyl alcohol (−)-**10**[15] as a colourless oil (23 mg, 67%); $[\alpha]_D^{29}$ −28 (*c* 0.46 in $CHCl_3$) [lit.,[15] $[\alpha]_D^{20}$ −34 (*c* 1.2 in $CHCl_3$)]; ν_{max}($CHCl_3$/cm^{-1} 3591 (O–H), 2936 (C–H), 1601 (Ar), 1490, 1464, 1111 and 1005; δ_H(250 MHz, $CDCl_3$) 2.95 (1 H, d, *J* 5.5, CHO*H*), 3.83 (3 H, s, OCH_3), 6.05 (1 H, d, *J* 5.5, C*H*OH), 6.89 (2 H, m, Ar-*H*) and 7.22 (7 H, m, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 55.4 (OCH_3), 72.3 (PhCHOH), 110.7 [C(3)H], 120.8 (Ph-CH), 126.5 (Ph-CH), 127.1 (Ph-CH), 127.9 (Ph-CH), 128.1 (Ph-CH), 128.7 (Ph-CH), 131.8 [C(1)], 143.2 (Ph-C) and 156.7 [C(2)]; *m*/*z* (EI) 214 (M^+, 100%), 196 (M − H_2O, 45), 135 (36), 109 (38) and 77 (Ph, 43) (HRMS: found M^+, 214.1003. $C_{14}H_{14}O_2$ requires *M*, 214.0994).

Fluoride mediated synthesis of (2*R*)-tricarbonyl(η^6-α-phenyl-2-methoxybenzyl alcohol)chromium(0) (+)-7 and (+)-8

The CsF (248 mg, 1.63 mmol) was flame dried under vacuum and allowed to cool under a stream of nitrogen. To the dry solid was then added a solution of 18-crown-6 (32 mg, 0.12 mmol) in benzene (5 ml). Benzaldehyde (0.25 ml, 2.45 mmol) was then added in one portion followed by a solution of complex (+)-**3** (255 mg, 0.81 mmol) in benzene (1 ml) and the reaction stirred in the dark at room temperature, under nitrogen, for 12 h. The reaction mixture was poured onto saturated aqueous NH_4Cl (5 ml) and extracted with CH_2Cl_2 (20 ml), the organic extract was washed with water (5 ml) and dried ($MgSO_4$) and the solvent evaporated under reduced pressure. Purification of the yellow oil by flash column chromatography (20% Et_2O–light petroleum) gave tricarbonyl(η^6-α-phenyl-2-methoxybenzyl alcohol)-chromium(0) (+)-**8**[15] as a yellow solid (68 mg, 24%), $[\alpha]_D^{29}$ +125 (*c* 1.12 in $CHCl_3$) followed by tricarbonyl(η^6-α-phenyl-2-methoxybenzyl alcohol)chromium(0) (+)-**7** as a yellow solid (54 mg, 19%), $[\alpha]_D^{29}$ +37 (*c* 1.08 in $CHCl_3$).

(2*R*)-Tricarbonyl(η^6-1-ethoxy-2-trimethylsilylbenzene)-chromium(0) (+)-14a

The general procedure was followed using **13a** and purification of the yellow oil by flash column chromatography (10% Et_2O–light petroleum) gave *tricarbonyl*[η^6-1-*ethoxy*-2,b-*bis*(*trimethylsilyl*)*benzene*]*chromium*(0) **15a** as a yellow crystalline solid (24 mg, 6%), mp 106–108 °C (Found: C, 50.80; H, 6.86. $C_{17}H_{26}CrO_4Si_2$ requires C, 50.72; H, 6.51%); ν_{max}($CHCl_3$)/cm^{-1} 2955 (C–H), 1967, 1897, 1324 and 841; δ_H(250 MHz, $CDCl_3$) 0.38 [18 H, s, Si(CH_3)$_3$ × 2], 1.39 (3 H, t, *J* 7.0, CH_3CH_2), 3.80 (2 H, q, *J* 7.0, CH_3CH_2), 4.79 (1 H, t, *J* 6.2, Ar-*H*) and 5.63 (2 H, d, *J* 6.2, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 0.3 ($SiCH_3$), 15.0 (OCH_2CH_3), 71.9 (OCH_2), 87.6 [C(4)H], 92.1 [C(2 + 6)], 101.9 [C(3 + 5)H], 151.6 [C(1)] and 233.6 (CO); *m*/*z* (EI) 402 (M^+, 9%), 318 (M − 3CO, 100), 266 [M − $Cr(CO)_3$, 11], 207 (87) and 73 ($SiMe_3$, 33), followed by *tricarbonyl*(η^6-1-*ethoxy*-2-*trimethylsilylbenzene*)*chromium*(0) (+)-**14a** as a yellow crystalline solid (270 mg, 82%), mp 61–63 °C; $[\alpha]_D^{29}$ +135 (*c* 2.32 in $CHCl_3$) (Found: C, 50.68; H, 5.60. $C_{14}H_{18}CrO_4Si$ requires C, 50.91; H, 5.45%); ν_{max}($CHCl_3$)/cm^{-1} 1963, 1889 and 841; δ_H(250 MHz, $CDCl_3$) 0.33 [9 H, s, Si(CH_3)$_3$], 1.38 (3 H, t, *J* 7.0, CH_3CH_2), 3.89 (2 H, m, CH_3CH_2), 4.77 (1 H, dd, *J* 6.9 and 6.9, Ar-*H*), 4.94 (1 H, d, *J* 6.9, Ar-*H*), 5.57 (1 H, d, *J* 6.9, Ar-*H*) and 5.65 (1 H, dd, *J* 6.9 and 6.9, Ar-*H*); δ_C(68 MHz, $CDCl_3$) −0.7 ($SiCH_3$), 14.3 (OCH_2CH_3), 64.1 (OCH_2), 74.2 [C(6)H], 84.9 [C(4)H], 88.6 [C(2)], 96.2 [C(5)H], 102.0 [C(3)H], 146.9 [C(1)] and 233.8 (CO); *m*/*z* (EI) 330 (M^+, 35%), 274 (M − 2CO, 19), 246 (M − 3CO, 100), 201 (31) and 187 (34).

(2*R*)-Tricarbonyl(η^6-1-isopropoxy-2-trimethylsilylbenzene)-chromium(0) (+)-14b

The general procedure was followed using **13b** and purification of the yellow oil by flash column chromatography (20% Et_2O–light petroleum) gave *tricarbonyl*[η^6-1-*isopropoxy*-2,b-*bis*(*trimethylsilyl*)*benzene*]*chromium*(0) **15b** as a yellow crystalline solid (4 mg, 1%), mp 124–126 °C (Found: C, 52.37; H, 7.21. $C_{18}H_{28}CrO_4Si_2$ requires C, 51.90; H, 6.76%); ν_{max}($CHCl_3$)/cm^{-1} 2955 (C–H), 1967, 1897, 1602 (Ar), 1312 and 841; δ_H(250 MHz, $CDCl_3$) 0.40 [18 H, s, Si(CH_3)$_3$ × 2], 1.22 [6 H, d, *J* 6.2, CH(CH_3)$_2$], 4.55 [1 H, septet, *J* 6.2, C*H*(CH_3)$_2$], 4.75 (1 H, t, *J* 6.1, Ar-*H*) and 5.67 (2 H, d, *J* 6.1, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 0.6 ($SiCH_3$), 21.4 [OCH(CH_3)$_2$], 74.8 (OCH), 87.3 [C(4)H], 90.4 [C(2 + 6)], 102.2 [C(3 + 5)H], 153.0 [C(1)] and 233.8 (CO); *m*/*z* (EI) 416 (M^+, 8%), 332 (M − 3CO, 100), 273 (39), 257 (22) and 126 (11), followed by *tricarbonyl*(η^6-1-*isopropoxy*-2-*trimethylsilylbenzene*)*chromium*(0) (+)-**14b** as a yellow crystalline solid (224 mg, 65%), mp 64–66 °C; $[\alpha]_D^{29}$ +126 (*c* 2.22 in $CHCl_3$) (Found: C, 52.48; H, 5.98. $C_{15}H_{20}CrO_4Si$ requires C, 52.32; H, 5.81%); ν_{max}($CHCl_3$)/cm^{-1} 2952, 1958, 1897, 1510, 1408 and 841; δ_H(250 MHz, $CDCl_3$) 0.32 [9 H, s, Si(CH_3)$_3$], 1.31 [3 H, d, *J* 6.0, CH(CH_3)$_2$], 1.42 [3 H, d, *J* 6.0, CH(CH_3)$_2$], 4.36 [1 H, qq, *J* 6.0 and 6.0, C*H*(CH_3)$_2$], 4.76 (1 H, dd, *J* 6.1 and 6.1, Ar-*H*), 4.97 (1 H, d, *J* 6.1, Ar-*H*), 5.59 (1 H, d, *J* 6.1, Ar-*H*) and 5.66 (1 H, dd, *J* 6.1 and 6.1, Ar-*H*); δ_C(68 MHz, $CDCl_3$) −0.6 ($SiCH_3$), 21.6 [OCH(CH_3)], 22.2 [OCH(CH_3)], 71.1 (OCH), 75.0 [C(6)H], 84.5 [C(4)H], 88.3 [C(2)], 96.4 [C(5)H], 102.1 [C(3)H], 146.5 [C(1)] and 233.9 (CO); *m*/*z* (EI) 344 (M^+, 15%), 288 (M − 2CO, 10), 260 (M − 3CO, 100), 217 (9) and 187 (33).

(2*R*)-Tricarbonyl(η^6-1-methoxymethoxy-2-(trimethylsilyl-benzene)chromium(0) (+)-14d

The general procedure was followed using **13d** and purification

of the yellow oil by flash column chromatography (10% Et_2O–light petroleum) gave *tricarbonyl*[η^6-1-*methoxymethoxy*-2,3-*bis*(*trimethylsilyl*)*benzene*]*chromium*(0) **15d** as a yellow crystalline solid (25 mg, 6%), mp 105–107 °C (Found: C, 49.18; H, 6.42. $C_{17}H_{26}CrO_5Si_2$ requires C, 48.78; H, 6.26%); $\nu_{max}(CHCl_3)$/cm^{-1} 1968, 1899, 1330 and 842; δ_H(250 MHz, $CDCl_3$) 0.40 [18 H, s, Si(CH_3)$_3$ × 2], 3.54 (3 H, s, OCH_3), 4.79 (1 H, t, *J* 6.1, Ar-*H*), 4.96 (2 H, s, CH_2) and 5.65 (2 H, d, *J* 6.1, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 0.36 ($SiCH_3$), 57.8 (OCH_3), 87.6 [C(4)H], 92.5 [C(2 + 6)], 100.8 (OCH_2O), 101.9 [C(3 + 5)H] and 233.4 (CO); *m*/*z* (EI) 418 (M^+, 8%), 334 (M − 3CO, 100), 273 (M −3CO−OCH_2OCH_3, 22) and 163 [M − $Cr(CO)_3$ − CH_2OCH_3 − $SiCH_3$ − H, 19], followed by (2R)-*tricarbonyl*(η^6-1-*methoxymethoxy*-2-*trimethylsilylbenzene*)*chromium*(0) (+)-**14d** as a yellow crystalline solid (263 mg, 76%), mp 74–75 °C; $[\alpha]_D^{29}$ +184 (*c* 2.34 in $CHCl_3$) (Found: C, 48.94; H, 5.49. $C_{14}H_{18}CrO_5Si$ requires C, 48.55; H, 5.24%); $\nu_{max}(CHCl_3)$/cm^{-1} 1957, 1899, 1863, 975 (C–H) and 841 (C–H); δ_H(250 MHz, $CDCl_3$) 0.34 [9 H, s, Si(CH_3)$_3$], 3.49 (3 H, s, OCH_3), 4.78 (1 H, dd, *J* 6.1 and 6.1, Ar-*H*), 4.99 (1 H, d, *J* 7.1, CH_2), 5.17 (1 H, d, *J* 7.1, CH_2), 5.27 (1 H, d, *J* 6.1, Ar-*H*), 5.57 (1 H, d, *J* 6.1, Ar-*H*) and 5.63 (1 H, dd, *J* 6.1 and 6.1, Ar-*H*); δ_C(68 MHz, $CDCl_3$) −0.7 ($SiCH_3$), 56.8 (OCH_3), 77.3 [C(6)H], 85.3 [C(4)H], 88.9 [C(2)], 94.5 (OCH_2O), 96.1 [C(5)H], 101.4 [C(3)H], 145.1 [C(1)] and 233.6 (CO); *m*/*z* (EI) 346 (M^+, 11%), 262 (M − 3CO, 77), 201 (21), 165 (35) and 45 (CH_2OCH_3, 9).

(2*R*)-Tricarbonyl(η^6-1-chloro-2-trimethylsilylbenzene)-chromium(0) (+)-14e

The general procedure was followed using **13e** and purification of the yellow oil by flash column chromatography (2% Et_2O–light petroleum) gave firstly *tricarbonyl*[η^6-1-*chloro*-2,4-*bis*-(*trimethylsilyl*)*benzene*]*chromium*(0) (+)-**16** as a yellow crystalline solid (31 mg, 8%), mp 81–83 °C; $[\alpha]_D^{29}$ +18.5 (*c* 0.52 in $CHCl_3$) (Found: C, 46.05; H, 5.56; Cl, 9.14. $C_{15}H_{21}ClCrO_3Si_2$ requires C, 45.86; H, 5.35; Cl, 9.04%); $\nu_{max}(CHCl_3)$/cm^{-1} 1971, 1903, 1601 (Ar), 1296, 1140 and 842; δ_H(250 MHz, $CDCl_3$) 0.34 [9 H, s, Si(CH_3)$_3$], 0.44 [9 H, s, Si(CH_3)$_3$], 4.85 (1 H, d, *J* 6.2, Ar-*H*), 5.28 (1 H, s, Ar-*H*) and 5.45 (1 H, d, *J* 6.2, Ar-*H*); δ_C(100 MHz, $CDCl_3$) −1.6 ($SiCH_3$), −0.5 ($SiCH_3$), 91.6 [C(2)H], 95.9 [C(5)H], 98.3 [C(2)], 99.5 [C(3)H], 103.8 [C(4)], 120.1 [C(1)] and 232.3 (CO); *m*/*z* (EI) 392 (M^+, 13%), 264 (17), 236 (62), 221 (66) and 149 (100), followed by *tricarbonyl* [η^6-1-*chloro*-2,6-*bis*(*trimethylsilyl*)*benzene*]*chromium*(0) **15e** as a yellow crystalline solid (47 mg, 12%), mp 125–127 °C (Found: C, 45.98; H, 5.56; Cl, 8.92. $C_{15}H_{21}ClCrO_3Si_2$ requires C, 45.86; H, 5.35; Cl, 9.04%); $\nu_{max}(CHCl_3)$/cm^{-1} 2953 (C–H), 1974, 1906, 1352, 858 and 842; δ_H(250 MHz, $CDCl_3$) 0.42 [18 H, s, Si(CH_3)$_3$ × 2], 4.88 (1 H, t, *J* 6.0, Ar-*H*) and 5.65 (2 H, d, *J* 6.0, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 0.00 ($SiCH_3$), 86.5 [C(4)H], 97.6 [C(2 + 6)], 101.7 [C(3 + 5)H], 127.6 [C(1)] and 232.7 (CO); *m*/*z* (EI) 392 (M^+, 5%), 308 (M − 3CO, 28), 241 (29), 133 (61) and 73 ($SiCH_3$, 100), followed by (2R)-*tricarbonyl*(η^6-1-*chloro*-2-*trimethylsilylbenzene*)-*chromium*(0) (+)-**14e** as a yellow crystalline solid (85 mg, 27%), mp 82–84 °C; $[\alpha]_D^{29}$ +6.4 (*c* 0.82 in $CHCl_3$) (Found: C, 45.14; H, 4.04; Cl, 10.94. $C_{12}H_{13}ClCrO_3Si$ requires C, 44.93; H, 4.06; Cl, 11.07%); $\nu_{max}(CHCl_3)$/cm^{-1} 1977, 1900, 1342, 1102, 843 and 617; δ_H(250 MHz, $CDCl_3$) 0.43 [9 H, s, Si(CH_3)$_3$ × 2], 4.88 (1 H, dd, *J* 6.2 and 6.2, Ar-*H*), 5.32 (1 H, d, *J* 6.2, Ar-*H*), 5.51 (1 H, d, *J* 6.2, Ar-*H*) and 5.57 (1 H, dd, *J* 6.2 and 6.2, Ar-*H*); δ_C(100 MHz, $CDCl_3$) −0.3 ($SiCH_3$), 86.6 [C(4, 5 or 6)H], 90.9 [C(4, 5 or 6)H], 95.4 [C(4, 5 or 6)H], 97.6 [C(2)], 100.0 [C(3)H], 120.7 [C(1)] and 234.9 (CO); *m*/*z* (EI) 320 (M^+, 13%), 264 (M−2CO, 17), 236 (M − 3CO, 62), 221 (66) and 149 (100).

Tricarbonyl(η^6-1-fluoro-2-trimethylsilylbenzene)chromium(0) (−)-14f

The general procedure was followed and purification of the yellow oil by flash column chromatography (5% Et_2O–light petroleum) gave *tricarbonyl*[η^6-1-*fluoro*-2,6-*bis*(*trimethylsilyl*)-*benzene*]*chromium*(0) **15f** as a yellow crystalline solid (71 mg, 19%), mp 128–130 °C (Found: C, 48.08; H, 5.90. $C_{15}H_{21}CrFO_3Si_2$ requires C, 47.85; H, 5.62%); $\nu_{max}(CHCl_3)$/cm^{-1} 1973, 1900, 1601 (Ar), 1347 and 858; δ_H(250 MHz, $CDCl_3$) 0.36 [18 H, d, *J* 0.6, Si(CH_3)$_3$ × 2], 4.70 (1 H, td, *J* 6.0 and 5.1, Ar-*H*) and 5.56 (2 H, dd, *J* 6.0 and 3.5, Ar-*H*); δ_C(68 MHz, $CDCl_3$) −0.7 ($SiCH_3$), 86.3 [C(4)H], 86.5 [C(2 + 6), d, J_{CF} 34.0], 100.1 [C(3 + 5)H, d, J_{CF} 12.2], 152.7 [C(1), d, J_{CF} 253.9] and 232.9 (CO); *m*/*z* (EI) 376 (M^+, 12%), 292 (M − 3CO, 100), 277 (14), 133 (13) and 73 ($SiMe_3$, 42), followed by *tricarbonyl*(η^6-1-*fluoro*-2-*trimethylsilylbenzene*)*chromium*(0) (−)-**14f** as a yellow crystalline solid (173 mg, 57%), mp 56–57 °C; $[\alpha]_D^{29}$ −4.4 (*c* 0.86 in $CHCl_3$) (Found: C, 47.77; H, 4.47. $C_{12}H_{13}CrFO_3Si$ requires C, 47.36; H, 4.31%); $\nu_{max}(CHCl_3)$/cm^{-1} 1977, 1903, 1362, 1098 and 844; δ_H(250 MHz, $CDCl_3$) 0.39 [9 H, s, Si(CH_3)$_3$], 4.80 (1 H, m, Ar-*H*), 5.24 (1 H, m, Ar-*H*), 5.47 (1 H, m, Ar-*H*) and 5.63 (1 H, m, Ar-*H*); δ_C(68 MHz, $CDCl_3$) −0.7 ($SiCH_3$), 78.6 [C(6)H, d, J_{CF} 24.4], 86.0 [C(4)H], 88.1 [C(2), d, J_{CF} 20.0], 94.9 [C(5)H, d, J_{CF} 7.3], 98.7 [C(3)H, d, J_{CF} 11.0], 148.0 [C(1), d, J_{CF} 260.0] and 232.3 (CO); *m*/*z* (EI) 304 (M^+, 14%), 248 (M − 2CO, 13), 220 (M − 3CO, 79), 205 (14) and 52 (Cr, 100).

Tricarbonyl(η^6-2-trimethylsilyl-*N*,*N*-diisopropylbenzamide)-chromium(0) (−)-14g

The general procedure was followed using **13g** and purification of the yellow oil by flash column chromatography (20% Et_2O–light petroleum) gave *tricarbonyl*(η^6-2-*trimethylsilyl*-N,N-*diisopropylbenzamide*)*chromium*(0) (−)-**14g** as a yellow crystalline solid (359 mg, 87%), mp 128–130 °C; $[\alpha]_D^{29}$ −48 (*c* 1.80 in $CHCl_3$) (Found: C, 55.24; H, 6.76; N, 3.37. $C_{19}H_{27}CrNO_4Si$ requires C, 55.19; H, 6.58; N, 3.39%); $\nu_{max}(CHCl_3)$/cm^{-1} 1980, 1898, 1638 (C=ONPr$^i_2$), 1614 (Ar), 1320 and 841; δ_H(250 MHz, $CDCl_3$) 0.36 [9 H, s, Si(CH_3)$_3$], 1.24 [6 H, br s, CH(CH_3)$_2$], 1.48 [6 H, br s, CH(CH_3)$_2$], 3.45 [1 H, br s, CH(CH$_3$)$_2$], 4.52 [1 H, br s, CH(CH$_3$)$_2$], 5.23 (2 H, m, Ar-*H*), 5.38 (1 H, d, *J* 6.7, Ar-*H*) and 5.42 (1 H, d, *J* 6.7, Ar-*H*); δ_C(100 MHz, $CDCl_3$, 298 K) 0.4 ($SiCH_3$), 20.5 [br, NCH(*C*H$_3$)$_2$], 46.6 (N*C*HMe$_2$), 51.1 (N*C*HMe$_2$), 90.7 [C(3, 4, 5 or 6)H], 91.3 [C(3, 4, 5 or 6)H], 91.9 [C(3, 4, 5 or 6)H], 97.2 [C(3, 4, 5 or 6)H], 100.7 [C(1 or 2)], 116.7 [C(1 or 2)], 166.3 (NC=O) and 232.3 (CO); δ_C(100 MHz, $CDCl_3$, 333 K) 0.5 ($SiCH_3$), 20.7 [br, NCH(*C*H$_3$)$_2$], 20.8 [br, NCH(*C*H$_3$)$_2$], 49.3 (br, N*C*HMe$_2$), 90.8 [C(3, 4, 5 or 6)H], 91.0 [C(3, 4, 5 or 6)H], 91.9 [C(3, 4, 5 or 6)H], 97.1 [C(3, 4, 5 or 6)H], 101.1 [C(1 or 2)], 116.8 [C(1 or 2)], 166.4 (NC=O) and 232.3 (CO); *m*/*z* (EI) 357 (M^+ − 2CO, 9%), 329 (M − 3CO, 69), 262 (58), 218 (33) and 177 (100).

Tricarbonyl[η^6-*N*-methyl-2′-(trimethylsilyl)trimethylacetanilide]chromium(0) (+)-14h

The general procedure was followed using **13h**, except that 10 equiv. of Me_3SiCl were employed, and purification of the resulting orange oil by flash column chromatography (20% EtOAc–light petroleum) gave *tricarbonyl*(tert-*butyl* η^6-2-*methylaminobenzoate*)*chromium*(0) **17** as a low melting point red solid (13 mg, 8%) (Found: C, 55.14; H, 5.32; N, 4.25. $C_{15}H_{17}CrNO_4$ requires C, 55.05; H, 5.24; N, 4.28%); $\nu_{max}(CHCl_3)$/cm^{-1} 1967, 1898, 1636 (C=O), 1553 and 946; δ_H(270 MHz, $CDCl_3$) 1.11 [9 H, s, C(CH_3)$_3$], 2.45 [3 H, d, *J* 5.0, NH(CH_3)], 4.44 (1 H, d, *J* 6.6, Ar-*H*), 4.51 (1 H, dd, *J* 6.6 and 6.6, Ar-*H*), 5.51 (1 H, dd, *J* 6.6 and 6.6, Ar-*H*) and 6.02 (1 H, d, *J* 6.6, Ar-*H*); *m*/*z* (EI) 327 (M^+, 29%), 271 (M − 2CO, 20), 243 (M − 3CO, 57), 227 (46), 159 (100) and 134 (22), followed by *tricarbonyl*(η^6-N-*methyl*-2′-(*trimethylsilyl*)*trimethylacetanilide*)*chromium*(0) (+)-**14h** as a yellow crystalline solid (129 mg, 65%), mp 91–93 °C; $[\alpha]_D^{29}$ +1.2 (*c* 0.68 in $CHCl_3$) (Found: C, 54.38; H, 6.69; N, 3.63. $C_{18}H_{25}CrNO_4Si$ requires C, 54.12; H, 6.31; N, 3.51%); $\nu_{max}(CHCl_3)$/cm^{-1} 2954 (C–H), 1966, 1896, 1641 (NC=O), 1465, 1330, 1085 and 842; δ_H(400 MHz, $CDCl_3$) 0.32 [9 H, s, Si(CH_3)$_3$], 1.33 [9 H, s, C(CH_3)$_3$], 3.51 (3 H, s, NCH_3), 5.25 (2 H, m, Ar-*H*) and 5.42 (2 H, m, Ar-*H*); δ_C(68 MHz, $CDCl_3$) −0.4

($SiCH_3$), 27.9 [C(CH_3)$_3$], 39.7 [C(CH$_3$)$_3$], 42.8 (NCH_3), 91.4 [C(3, 4, 5 or 6)H], 93.8 [C(3, 4, 5 or 6)H], 94.2 [C(3, 4, 5 or 6)H], 95.3 [C(3, 4, 5 or 6)H], 104.6 [C(2)], 128.5 [C(1)], 180.0 (NC=O) and 232.6 (CO); *m*/*z* (EI) 343 (M^+ − 2CO, 10%), 315 (M − 3CO, 100), 248 (19), 229 (8), 190 (28) and 162 (8).

(2′*S*)-Tricarbonyl[η^6-2-(2′-trimethylsilylphenyl)-1,3-dioxolane]-chromium(0) (+)-20

The general procedure was followed using **18** and purification of the yellow oil by flash column chromatography (20% Et_2O–light petroleum) gave firstly *tricarbonyl*(η^6-2-*phenyl*-2-*trimethylsilyl*-1,3-*dioxolane*)*chromium*(0) **21** as a yellow crystalline solid (122 mg, 34%), mp 152–154 °C (Found: C, 50.51; H, 5.29. $C_{15}H_{18}CrO_5Si$ requires C, 50.27; H, 5.03%); ν_{max}($CHCl_3$)/cm^{-1} 2958 (C–H), 1968, 1895, 1601 (Ar) and 841; δ_H(80 MHz, $CDCl_3$) 0.04 [9 H, s, Si(CH_3)$_3$], 3.81 (2 H, m, CH_2), 4.26 (2 H, m, CH_2), 5.04 (2 H, m, Ar-*H*) and 5.43 (3 H, m, Ar-*H*); δ_C(68 MHz, $CDCl_3$) −4.4 ($SiCH_3$), 65.8 [O(CH_2)$_2$O], 88.4 [C(3′ + 5′, 4′ or 2′ + 6′)H], 92.9 [C(3′ + 5′, 4′ or 2′ + 6′)H], 95.3 [C(3′ + 5′, 4′ or 2′ + 6′)H], 108.0 [OCO or C(1′)], 112.8 [OCO or C(1′)] and 233.1 (CO); *m*/*z* (EI) 358 (M^+, 13%), 302 (M − 2CO, 45), 274 (M − 3CO, 72), 229 (34) and 149 (100), followed by (2′S)-*tricarbonyl*[η^6-2-(2′-*trimethylsilylphenyl*)-1,3-*dioxolane*]*chromium*(0) (+)-**20** as a yellow crystalline solid (129 mg, 36%), mp 55–58 °C; $[\alpha]_D^{29}$ +22 (*c* 1.33 in $CHCl_3$) (Found: C, 50.13; H, 5.21. $C_{15}H_{18}CrO_5Si$ requires C, 50.27; H, 5.03%); ν_{max}($CHCl_3$)/cm^{-1} 1970, 1899, 1109 and 842; δ_H(250 MHz, $CDCl_3$) 0.39 [9 H, s, Si(CH_3)$_3$], 4.01 (4 H, m, CH_2CH_2), 5.14 (1 H, ddd, *J* 6.2, 6.2 and 1.3, Ar-*H*), 5.43 (1 H, dd, *J* 6.2 and 1.3, Ar-*H*), 5.50 (2 H, m, Ar-*H*) and 5.72 (1 H, s, C*H*); δ_C(68 MHz, $CDCl_3$) 0.5 ($SiCH_3$), 65.4 (OCH_2), 65.8 (OCH_2), 88.0 [C(3′, 4′, 5′ or 6′)H], 90.5 [C(3′, 4′, 5′ or 6′)H], 94.5 [C(3′, 4′, 5′ or 6′)H], 98.4 [C(2′)], 99.8 [C(3′, 4′, 5′ or 6′)H], 101.1 (CH), 113.4 [C(1′)] and 232.6 (CO); *m*/*z* (EI) 358 (M^+, 20%), 274 (M−3CO, 57), 212 (39), 163 (100) and 126 (44).

Tricarbonyl(η^6-1,2-dimethoxy-3-trimethylsilylbenzene)-chromium(0) (+)-22

The general procedure was followed using complex **19** and purification of the yellow oil by flash column chromatography (20% CH_2Cl_2–light petroleum) gave firstly *tricarbonyl*[η^6-1,2-*dimethoxy*-3,6-*bis*(*trimethylsilyl*)*benzene*]*chromium*(0) **23** as a yellow crystalline solid (18%), mp 130–135 °C (Found: C, 49.19; H, 6.56. $C_{17}H_{26}CrO_5Si_2$ requires C, 48.78; H, 6.26%); ν_{max}-($CHCl_3$)/cm^{-1} 1959 and 1884; δ_H(400 MHz, $CDCl_3$) 0.37 [18 H, s, Si(CH_3)$_3$ × 2], 3.81 (6 H, s, OCH_3) and 4.98 (2 H, s, Ar-*H*); δ_C-(126 MHz, $CDCl_3$) −0.4 ($SiCH_3$), 62.67 (OCH_3), 94.70 [C(4 + 5)H], 97.66 [C(3 + 6)], 138.52 [C(1 +)] and 233.90 (CO); *m*/*z* (EI) 418 (M^+, 66%), 362 (M − 2CO, 11) and 334 (M − 3CO, 100) (HRMS: found M^+, 418.0734. $C_{17}H_{26}CrO_5Si_2$ requires *M*, 418.0724), followed by the known complex tricarbonyl(η^6-1,2-dimethoxy-3-trimethylsilylbenzene)chromium(0) (+)-**22**[11] as a yellow crystalline solid (69%), mp 75 °C; $[\alpha]_D^{20}$ +312 (*c* 0.28 in $CHCl_3$) [lit.,[11] $[\alpha]_D^{20}$ +308 (*c* 1 in $CHCl_3$)] (Found: C, 48.52; H, 5.24. $C_{14}H_{18}CrO_5Si$ requires C, 48.55; H, 5.24%); ν_{max}($CHCl_3$)/cm^{-1} 1954 and 1866; δ_H(400 MHz, $CDCl_3$) 0.35 [9 H, s, Si(CH_3)$_3$], 3.79 (3 H, s, OCH_3), 3.91 (3 H, s, OCH_3), 4.92 (1 H, d, *J* 6.1, Ar-*H*), 5.17 (1 H, dd, *J* 6.0 and 6.7, Ar-*H*) and 5.30 (1 H, d, *J* 6.6, Ar-*H*); δ_C(68 MHz, $CDCl_3$) −0.73 ($SiCH_3$), 56.55 (OCH_3), 63.56 (OCH_3), 78.42 [C(6)H], 89.63 [C(4 or 5)H], 91.90 [C(4 or 5)H], 98.24 [C(3)], 134.09 [C(1 or 2)], 135.76 [C(1 or 2)] and 233.94 (CO); *m*/*z* (EI) 210 [(M − Cr(CO)$_3$)$^+$, 66%], 195 (72) and 165 (100).

Hydrolysis of acetal (+)-20 to give (2*S*)-tricarbonyl(η^6-2-trimethylsilylbenzaldehyde)chromium(0) (+)-24

A solution of the complex (+)-**20** (108 mg, 0.30 mmol) and PPTS (23 mg, 0.09 mmol) in acetone (4 ml) and water (1 ml) was heated under reflux for 48 h. The reaction was allowed to cool to room temperature and poured onto saturated aqueous $NaHCO_3$ (10 ml). The reaction mixture was extracted with CH_2Cl_2 (20 ml), the organic extract was washed with water (5 ml) and dried ($MgSO_4$), and the solvent evaporated under reduced pressure. Purification of the red oil by flash column chromatography (10% Et_2O–light petroleum) gave the known complex (2*S*)-tricarbonyl(η^6-2-trimethylsilylbenzaldehyde)-chromium(0) (+)-**24**[17] as a low melting point red solid (64 mg, 68%); $[\alpha]_D^{29}$ +122 (*c* 0.08 in $CHCl_3$) [lit.,[17] $[\alpha]_D^{20}$ +146 (*c* 0.116 in $CHCl_3$)]; ν_{max}($CHCl_3$)/cm^{-1} 1984, 1921, 1691 (CHO), 1602 (Ar), 1096 and 843; δ_H(250 MHz, $CDCl_3$) 0.42 [9 H, s, Si(CH_3)$_3$], 5.42 (1 H, d, *J* 6.1, Ar-*H*), 5.49 (2 H, m, Ar-*H*), 5.79 (1 H, d, *J* 6.1, Ar-*H*) and 9.73 (1 H, s, C*H*O); δ_C(68 MHz, $CDCl_3$) 0.5 ($SiCH_3$), 92.3 [C(3, 4, 5, or 6)H], 93.1 [C(3, 4, 5, or 6)H], 93.7 [C(3, 4, 5, or 6)H], 97.4 [C(3, 4, 5, or 6)H], 100.2 [C(1 or 2)], 102.5 [C(1 or 2)], 190.8 (HC=O) and 230.9 (CO); *m*/*z* (EI) 314 (M^+, 10%), 258 (M − 2CO, 8), 230 (M − 3CO, 45), 163 (100), 126 (20) and 52 (41) (HRMS: found M^+, 314.0033. $C_{13}H_{14}CrO_4Si$ requires *M*, 314.0066).

Preparation of (2*R*)-tricarbonyl(η^6-2-trimethylsilylanisole)-chromium(0) (+)-3 using Me_3SiCl as an external electrophile

A solution of the chiral base **2** (1.10 mmol), prepared as described previously, was cooled to −78 °C and a solution of the chromium complex **1** (244 mg, 1.00 mmol) in THF (3 ml) was added dropwise. After stirring the solution at −78 °C for a predetermined metallation time, Me_3SiCl (0.38 ml, 3.00 ml) was added in one portion and the reaction stirred at −78 °C for 30 min. Saturated aqueous $NaHCO_3$ (5 ml) was then added and the reaction allowed to warm to room temperature. The reaction mixture was extracted with CH_2Cl_2 (40 ml), the organic extract was washed with water (15 ml) and dried ($MgSO_4$), and the solvent evaporated under reduced pressure. Purification of the resulting yellow oil by flash column chromatography (20% Et_2O–light petroleum) gave **4** as a yellow crystalline solid (17 mg, 4%) followed by (+)-**3** as a yellow crystalline solid (264 mg, 83%). The decrease in the level of asymmetric induction with increasing metallation time is summarised in Table 3.

Metallation study of tricarbonyl(η^6-anisole)chromium(0) 1 using D_2O

A solution of the chiral base **2** (1.10 mmol), prepared as described previously, was cooled to −78 °C and a solution of the chromium complex **1** (244 mg, 1.00 mmol) in THF (3 ml) added dropwise. After stirring the solution at −78 °C for a predetermined metallation time, D_2O (12 mmol, 0.22 ml) was added in one portion. The reaction was allowed to warm to room temperature and poured onto water (15 ml), the mixture was extracted with CH_2Cl_2 (40 ml), the organic extract was washed with water (15 ml) and dried ($MgSO_4$), and the solvent evaporated under reduced pressure. Purification of the resulting yellow oil by flash column chromatography (20% Et_2O–light petroleum) gave the deuteriated complex as a yellow solid; analysis of this material using ^{1}H NMR experiments enabled the deuterium incorporation to be calculated. The deuterium incorporation results are summarised in Table 4.

Metallation of tricarbonyl(η^6-anisole)chromium(0) 1 in the presence of added LiCl

A solution of the chiral base **2** (1.10 mmol), prepared as described previously, was cooled to −78 °C and LiCl (5.17 ml of a 0.097 M solution in THF, 0.50 mmol) was added in one portion. After 5 min stirring at −78 °C a solution of the chromium complex **1** (244 mg, 1.00 mmol) in THF (3 ml) was added dropwise. After stirring the solution at −78 °C for 2 min D_2O (12 mmol, 0.22 ml) was added in one portion. The reaction was allowed to warm to room temperature and poured onto water (15 ml), the reaction mixture was extracted with CH_2Cl_2 (40 ml), the organic extract was washed with water (15 ml) and dried ($MgSO_4$), and the solvent evaporated under reduced pressure. Purification of the resulting yellow oil by flash column

chromatography (20% Et_2O–light petroleum) gave the deuteriated complex as a yellow solid; analysis of this material using ^1H NMR experiments showed complete deuterium substitution for an *ortho*-proton.

(2*R*)-Tricarbonyl(η⁶-2-tributylstannyl-6-trimethylsilylanisole)-chromium(0) (+)-25

To a stirred solution of complex (+)-**3** (1.41 g, 4.47 mmol, 84% ee) in THF (25 ml) at −78 °C, under an atmosphere of nitrogen, was added BuLi (3.07 ml of a 1.6 M solution in hexanes, 4.92 mmol) dropwise. After stirring at −78 °C for 60 min Bu_3SnCl (3.64 ml, 13.41 mmol) was added dropwise. The reaction was warmed to room temperature for 60 min and then poured onto saturated aqueous $NaHCO_3$ (30 ml). The reaction mixture was extracted with CH_2Cl_2 (50 ml), the organic extract was washed with water (20 ml) and dried ($MgSO_4$), and the solvent evaporated under reduced pressure. Purification of the resulting yellow oil by flash column chromatography (2% Et_2O–light petroleum) gave (2R)-*tricarbonyl*(η⁶-2-*tributylstannyl*-6-*trimethylsilyl-anisole*)*chromium*(0) (+)-**25** as a yellow oil (2.22 g, 82%); $[\alpha]_D^{29}$ +45 (*c* 3.50 in $CHCl_3$) (Found: C, 49.57; H, 7.34. $C_{25}H_{42}CrO_4SiSn$ requires C, 49.60; H, 6.99%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1954, 1897, 1865, 1464, 1330, 1003 and 861; δ_H(250 MHz, $CDCl_3$) 0.37 [9 H, s, $Si(CH_3)_3$], 0.90 {9 H, t, *J* 7.2, $Sn[(CH_2)_3CH_3]_3$}, 1.16 {5 H, m, $Sn[(CH_2)_3CH_3]_3$}, 1.22 {8 H, m, $Sn[(CH_2)_3CH_3]_3$}, 1.54 {5 H, m, $Sn[(CH_2)_3CH_3]_3$}, 3.67 (3 H, s, OCH_3), 4.84 (1 H, dd, *J* 6.1 and 6.1, Ar-*H*) and 5.53 (2 H, m, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 0.1 ($SiCH_3$), 11.6 ($SnCH_2$), 13.6 [$Sn(CH_2)_3CH_3$], 27.2 ($SnCH_2CH_2$), 29.9 ($SnCH_2CH_2CH_2$), 62.5 (OCH_3), 88.9 [C(4)H], 91.2 [C(2 or 6)], 93.0 [C(2 or 6)], 101.4 [C(3 or 5)H], 103.5 [C(3 or 5)H], 152.4 [C(1)] and 234.0 (CO); *m*/*z* (EI) 606 [$M^+(C_{25}H_{42}CrO_4Si^{120}Sn)$, 7%], 464 (10), 462 (6), 413 (100), 411 (66), 409 (50), 267 (74), 265 (32) and 135 (86).

(2*R*)-Tricarbonyl(η⁶-2-tributylstannylanisole)chromium(0) (−)-26

To a stirred solution of the complex (+)-**25** (1.82 g, 3.00 mmol) in THF (10 ml) at −78 °C, under an atmosphere of nitrogen, was added Bu_4NF (2.73 ml of a 1.1 M solution in THF, 3.00 mmol) dropwise. After stirring at −78 °C for 10 min saturated aqueous NH_4Cl (2.5 ml) was added and the reaction warmed to room temperature. The reaction mixture was extracted with CH_2Cl_2 (20 ml), the organic extract was washed with water (10 ml) and dried ($MgSO_4$), and the solvent evaporated under reduced pressure. Purification of the resulting yellow oil by flash column chromatography (4% Et_2O–light petroleum) gave (2R)-*tricarbonyl*(η⁶-2-*tributylstannylanisole*)*chromium*(0) (−)-**26** as a yellow oil (1.11 g, 69%); $[\alpha]_D^{29}$ −96 (*c* 1.30 in $CHCl_3$) (Found: C, 50.08; H, 6.65. $C_{22}H_{34}CrO_4Sn$ requires C, 49.56; H, 6.43%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2923 (C–H), 2850, 1954, 1896, 1859, 1456 and 1007; δ_H(250 MHz, $CDCl_3$) 0.88 {9 H, t, *J* 7.2, $Sn[(CH_2)_3CH_3]_3$}, 1.08 {6 H, m, $Sn[(CH_2)_3CH_3]_3$}, 1.28 {6 H, m, $Sn[(CH_2)_3CH_3]_3$}, 1.50 {6 H, m, $Sn[(CH_2)_3CH_3]_3$}, 3.69 (3 H, s, OCH_3), 4.83 (1 H, dd, *J* 6.2 and 6.2, Ar-*H*), 5.01 (1 H, d, *J* 6.2, Ar-*H*), 5.50 (1 H, d, *J* 6.2, Ar-*H*) and 5.60 (1 H, dd, *J* 6.2 and 6.2, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 10.6 ($SnCH_2$), 13.6 [$Sn(CH_2)_3CH_3$], 27.2 ($SnCH_2CH_2$), 28.8 ($SnCH_2CH_2CH_2$), 55.2 (OCH_3), 74.5 [C(4)H], 86.8 [C(6)H], 89.5 [C(2)], 95.6 [C(5)H], 103.1 [C(3)H], 146.6 [C(1)] and 234.2 (CO); *m*/*z* (EI) 341 [$M^+(C_{22}H_{34}CrO_4{}^{120}Sn) - Cr(CO)_3 - Bu$, 100%), 339 (69), 337 (37), 227 (63), 225 (50), 223 (22), 197 (38) and 195 (27).

Preparation of (2*S*)-tricarbonyl(η⁶-2-trimethylsilylanisole)-chromium(0) (−)-3 *via* the transmetallation of (−)-26 and addition of Me_3SiCl

To a stirred solution of BuLi (0.12 ml of a 1.6 M solution in hexanes, 0.20 mmol) in THF (4 ml) at −78 °C, under an atmosphere of nitrogen, was added a solution of the complex (−)-**26** (96 mg, 0.18 mmol) in THF (0.5 ml) in one portion. After stirring at −78 °C for 60 min, Me_3SiCl (0.14 ml, 1.07 mmol) was added dropwise and the reaction stirred at −78 °C, for a further 30 min. Saturated aqueous $NaHCO_3$ (2 ml) was added and the reaction allowed to warm to room temperature. The reaction mixture was extracted with CH_2Cl_2 (15 ml), the organic extract was washed with water (5 ml) and dried ($MgSO_4$), and the solvent evaporated under reduced pressure. Purification of the resulting yellow oil by flash column chromatography (5% Et_2O–light petroleum) gave (−)-**3** as a yellow solid (48 mg, 85%); $[\alpha]_D^{29}$ −195 (*c* 0.61 in $CHCl_3$).

Preparation of tricarbonyl(η⁶-2-trimethylsilylanisole)-chromium(0) 3 *via* the transmetallation of (−)-26, equilibration with 1 and subsequent addition of Me_3SiCl

To a stirred solution of BuLi (0.14 ml of a 1.6 M solution in hexanes, 0.22 mmol) in THF (4 ml) at −78 °C, under an atmosphere of nitrogen, was added a solution of the complex (−)-**26** (105 mg, 0.20 mmol) in THF (0.5 ml) in one portion. After stirring at −78 °C for 3 min a solution of tricarbonyl-(η⁶-anisole)chromium(0) **1** (24 mg, 0.10 mmol) in THF (0.5 ml) was added. After 5 min Me_3SiCl (0.14 ml, 1.07 mmol) was added dropwise and the reaction stirred at −78 °C, for a further 30 min. Saturated aqueous $NaHCO_3$ (2 ml) was added and the reaction allowed to warm to room temperature. The reaction mixture was extracted with CH_2Cl_2 (15 ml), the organic extract was washed with water (5 ml) and dried ($MgSO_4$), and the solvent evaporated under reduced pressure. Purification of the resulting yellow oil by flash column chromatography (5% Et_2O–light petroleum) gave **3** as a yellow solid in very nearly racemic form (53 mg, 84%); $[\alpha]_D^{29}$ −0.80 (*c* 0.53 in $CHCl_3$).

Preparation of tricarbonyl(η⁶-2-trimethylsilylanisole)-chromium(0) 3 *via* the transmetallation of (−)-26, equilibration with chiral amine and subsequent addition of Me_3SiCl

To a stirred solution of BuLi (0.13 ml of a 1.6 M solution in hexanes, 0.20 mmol) in THF (4 ml) at −78 °C, under an atmosphere of nitrogen, was added a solution of the complex (−)-**26** (99 mg, 0.19 mmol) in THF (0.5 ml) in one portion. After stirring at −78 °C for 3 min a solution of the chiral amine corresponding to **2** (23 mg, 0.10 mmol) in THF (0.5 ml) was added. After a further 60 min Me_3SiCl (0.14 ml, 1.07 mmol) was added dropwise and the reaction stirred at −78 °C for a further 30 min. Saturated aqueous $NaHCO_3$ (2 ml) was added and the reaction allowed to warm to room temperature. The reaction mixture was extracted with CH_2Cl_2 (15 ml), the organic extract was washed with water (5 ml) and dried ($MgSO_4$), and the solvent evaporated under reduced pressure. Purification of the resulting yellow oil by flash column chromatography (5% Et_2O–light petroleum) gave **3** as a yellow solid (50 mg, 84%); $[\alpha]_D^{29}$ −144 (*c* 0.50 in $CHCl_3$).

Synthesis of (+)-7 and (+)-8 by metallation of 1 under LiCl modified conditions

A solution of the chiral base **2** (3.30 mmol), prepared as described above, was cooled to −78 °C and LiCl (10.61 ml of a 0.141 M solution in THF, 1.50 mmol) was added in one portion. After 5 min stirring at −78 °C a solution of the chromium complex **1** (244 mg, 1.00 mmol) in THF (5 ml) was added dropwise by syringe pump over 15 min. Once the addition was complete PhCHO (1.02 ml, 10 mmol) was added in one portion and the reaction mixture maintained at −78 °C for 30 min before addition of saturated aqueous NH_4Cl (5 ml) and subsequent warming to room temperature. The reaction mixture was extracted with CH_2Cl_2 (30 ml), the organic extract was washed with water (15 ml) and dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The resulting yellow oil was then purified by flash column chromatography (40% Et_2O–light petroleum) to give (+)-**8** as a yellow solid (24 mg, 7%); $[\alpha]_D^{29}$ +115 (*c* 0.48 in $CHCl_3$), followed by (+)-**7** as a yellow solid (234 mg, 67%); $[\alpha]_D^{29}$ +35 (*c* 2.34 in $CHCl_3$).

Tricarbonyl(η⁶-α-cyclohexyl-2-methoxybenzyl alcohol)-chromium(0) 27 by metallation of 1 under LiCl modified conditions

The reaction was performed under identical conditions to those described previously for the preparation of **7** and **8**. The yellow oil was purified by flash column chromatography (10% Et_2O–light petroleum) to give *tricarbonyl*(η⁶-α-*cyclohexyl*-2-*methoxybenzyl alcohol*)*chromium*(0) **27** as two diastereoisomers, the first as a yellow oil (145 mg, 41%); $[\alpha]_D^{29}$ +112 (*c* 0.94 in $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3585 (O–H), 2934 (C–H), 1966, 1901, 1243 and 735; δ_H(250 MHz, $CDCl_3$) 1.17 (5 H, m, CH_2), 1.57 (7 H, m, CH_2 and CHO*H*), 3.73 (3 H, s, OCH_3), 4.66 (1 H, m, C*H*OH), 4.94 (1 H, dd, *J* 6.2 and 6.2, Ar-*H*), 5.02 (1 H, d, *J* 6.2, Ar-*H*), 5.54 (1 H, dd, *J* 6.2 and 6.2, Ar-*H*) and 5.84 (1 H, d, *J* 6.2, Ar-*H*); δ_C(100 MHz, $CDCl_3$) 26.0 (CH_2), 26.3 (CH_2), 27.4 (CH_2), 29.3 (CH_2), 44.1 (CH), 55.7 (OCH_3), 70.2 [C(3)H or CHOH], 73.3 [C(3)H or CHOH], 85.3 [C(5)H], 93.2 [C(4 or 6)H], 94.1 [C(4 or 6)H], 105.5 [C(1)], 142.0 [C(2)] and 233.1 (CO); *m*/*z* (EI) 356 (M^+, 4%), 300 (M − 2CO, 12), 272 (M−3CO, 22), 250 (39), 235 (30), 220 (8), 137 (100) and 121 (97) (HRMS: found M^+, 356.0666. $C_{17}H_{20}CrO_5$ requires *M*, 356.0716), followed by the other diastereoisomer as a yellow oil (149 mg, 42%), $[\alpha]_D^{29}$ +164 (*c* 0.97 in $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 2931 (C–H), 1966, 1877, 1233 and 718; δ_H(250 MHz, $CDCl_3$) 1.19 (6 H, m, CH_2), 1.72 (6 H, m, CH_2 and CHO*H*), 2.63 (1 H, d, *J* 8.9, C*H*OH), 3.79 (3 H, s, OCH_3), 4.81 (1 H, dd, *J* 6.1 and 6.1, Ar-*H*), 5.03 (1 H, d, *J* 6.1, Ar-*H*) and 5.52 (2 H, m, Ar-*H*); δ_C(100 MHz, $CDCl_3$) 25.8 (CH_2), 26.0 (CH_2), 26.2 (CH_2), 29.6 (CH_2), 30.4 (CH_2), 43.0 (CH), 55.9 (OCH_3), 73.5 [C(3)H or CHOH], 78.4 [C(3)H or CHOH], 83.8 [C(5)H], 93.8 [C(4 or 6)H], 97.0 [C(4 or 6)H], 103.2 [C(1)] and 140.7 [C(2)]; *m*/*z* (EI) 356 (M^+, 5%), 300 (M − 2CO, 13), 272 (M − 3CO, 23), 250 (52), 137 (100) and 121 (59) (HRMS: found M^+, 356.0655. $C_{17}H_{20}CrO_5$ requires *M*, 356.0716).

Synthesis of (2*S*)-tricarbonyl(η⁶-2-trimethylsilylbenzaldehyde)-chromium(0) (−)-24 *via* an intermediate α-amino alkoxide

A solution of the chiral base **2** (1.00 mmol), prepared as described above, was cooled to −78 °C and a solution of the chromium complex **28** (242 mg, 1.00 mmol) in THF (2 ml) was added dropwise. After stirring the solution at −78 °C for 30 min, BuLi (1.25 ml of a 1.6 M solution in hexanes, 2.00 mmol) was added dropwise and the reaction stirred at −78 °C for 60 min, after which Me_3SiCl (0.38 ml, 3.00 mmol) was added in one portion. The reaction was warmed to room temperature and poured onto saturated aqueous NH_4Cl (5 ml) and extracted with CH_2Cl_2 (30 ml). The organic extracts were washed with water (10 ml) and dried ($MgSO_4$), and the solvent evaporated under reduced pressure. The resulting red oil was purified by flash column chromatography (10% Et_2O–light petroleum) to give (−)-**24** as a low melting point red solid (119 mg, 38%); $[\alpha]_D^{29}$ −118 (*c* 0.18 in $CHCl_3$) [lit.,[17] $[\alpha]_D^{18}$ −154 (*c* 1.14 in $CHCl_3$)].

General procedure for the deprotonation of tricarbonyl(η⁶-1,3-dihydroisobenzofuran)chromium(0) 30a with a lithium amide base

The lithium amide base was prepared by treatment of a solution of the corresponding amine in THF with BuLi at −78 °C. The mixture was warmed to room temperature and after 10 min recooled to −78 °C and Me_3SiCl added. A solution of complex **30a** in THF was then added and the reaction mixture stirred for 10 min before quenching by addition of MeOH (2 ml). The solvent was then evaporated under reduced pressure to give the silylated products *tricarbonyl*(η⁶-1-*trimethylsilyl*-1,3-*dihydroisobenzofuran*)*chromium*(0) **31a**, *tricarbonyl*(η⁶-4-*trimethylsilyl*-1,3-*dihydroisobenzofuran*)*chromium*(0) **34** and *tricarbonyl*(η⁶-5-*trimethylsilyl*-1,3-*dihydroisobenzofuran*)*chromium*(0) **35** in the ratios given in Table 5 (obtained from the crude material). The involatile residue was then subjected to flash chromatography on silica gel to give the isolated yields of monosilylated complexes.

Deprotonation of tricarbonyl(η⁶-1,3-dihydroisobenzofuran)-chromium(0) 30a with LDA

The general procedure was followed using diisopropylamine (128 mg, 1.26 mmol), BuLi (0.79 ml of a 1.6 M solution in hexanes, 1.26 mmol), Me_3SiCl (0.44 ml, 3.47 mmol) and complex **30a** (294 mg, 1.15 mmol). Purification of the yellow oil by flash column chromatography (15% EtOAc–light petroleum) gave an inseparable mixture of **34** and **35** as a yellow crystalline solid (182 mg, 56%), (mp 60 °C); $\nu_{max}(CHCl_3)/cm^{-1}$ 1968 and 1893; δ_H(400 MHz, $CDCl_3$) (for **34**) 0.35 [9 H, s, $Si(CH_3)_3$], 4.76–4.99 (4 H, m, H_2COCH_2), 5.13 (1 H, t, *J* 6.1, Ar-*H*), 5.32 (1 H, d, *J* 6.2, Ar-*H*) and 5.73 (1 H, d, *J* 6.2, Ar-*H*); (for **35**) 0.31 [9 H, s, $Si(CH_3)_3$], 4.76–4.99 (4 H, m, H_2COCH_2), 5.35 (2 H, m, Ar-*H*) and 5.64 (1 H, s, Ar-*H*); δ_C(100 MHz, $CDCl_3$) (for **34**) −0.71 ($SiCH_3$), 71.68 and 72.19 [C(1 + 3)H_2], 88.32 and 88.64 [C(6 + 7)H], 93.05 [C(4)], 98.13 [C(5)H], 107.41 [C(7a)], 115.28 [C(3a)] and 232.91 (CO); (for **35**) −1.09 ($SiCH_3$), 71.94 and 72.07 [C(1 + 3)H_2], 84.16 and 92.23 [C(4, 6 or 7)H], 97.06 [C(4, 6 or 7)H], 107.47 [C(7a)], 111.47 [C(3a)] and 238.54 (CO). *m*/*z* (EI) 328 (M^+, 22%), 272 (M − 2CO, 12) and 244 (M − 3CO, 100) (HRMS: found M^+, 328.0223. $C_{14}H_{16}CrO_4Si$ requires *M*, 328.0222).

Deprotonation of tricarbonyl(η⁶-1,3-dihydroisobenzofuran)-chromium(0) 30a with chiral base 2

The general procedure was followed using the corresponding amine (527 mg, 2.34 mmol) in THF (10 ml), BuLi (1.46 ml of a 1.6 M solution in hexanes, 2.34 mmol), Me_3SiCl (0.81 ml, 6.39 mmol) and complex **30a** (542 mg, 2.12 mmol) in THF (2 ml). The reaction was carried out at −100 °C. Purification of the yellow oil by flash column chromatography (10% EtOAc–light petroleum) gave **31a** as a yellow oil (571 mg, 82%), $[\alpha]_D^{20}$ +14.5 (*c* 2.44 in $CHCl_3$) (Found: C, 51.21; H, 4.91. $C_{14}H_{16}CrO_4Si$ requires C, 51.33; H, 4.88%); ν_{max}(film)/cm^{-1} 1970, 1893 and 1647 (Ar); δ_H(400 MHz, $CDCl_3$) 0.11 [9 H, s, $Si(CH_3)_3$], 4.77 (1 H, d, *J* 1.8, OC*H*$SiMe_3$), 4.88 (1 H, dd, *J* 12.0 and 1.8, CH*H*OCH-$SiMe_3$), 4.93 (1 H, d, *J* 12.0, C*H*HOCH$SiMe_3$), 5.18 (1 H, dd, *J* 6.2 and 6.2, Ar-*H*), 5.29 (1 H, dd, *J* 6.2 and 6.2, Ar-*H*), 5.34 (1 H, d, *J* 6.2, Ar-*H*) and 5.51 (1 H, d, *J* 6.2, Ar-*H*); δ_C(68 MHz, $CDCl_3$) −3.77 ($SiCH_3$), 72.18 [C(1)H], 78.96 [C(3)H_2], 83.92 [C(4, 5, 6 or 7)H], 86.52 [C(4, 5, 6 or 7)H], 90.01 [C(4, 5, 6 or 7)H], 91.61 [C(4, 5, 6 or 7)H], 107.80 [C(3a or 7a)], 114.97 [C(3a or 7a)] and 232.83 (CO); *m*/*z* 328 (M^+, 41%) and 272 (M − 2CO, 28), 244 (M − 3CO, 74).

Deprotonation of tricarbonyl(η⁶-1,3-dihydroisobenzofuran)-chromium(0) 30a with chiral base 11a

The general procedure was followed using the corresponding amine (256 mg, 1.21 mmol) in THF (5 ml), BuLi (0.76 ml of a 1.6 M solution in hexanes, 1.21 mmol), Me_3SiCl (0.42 ml, 3.31 mmol) and complex **30a** (282 mg, 1.10 mmol) in THF (1 ml). Purification of the yellow oil by flash column chromatography (10% EtOAc–light petroleum) gave **31a**, **34** and **35** as a yellow oil (266 mg, 74%).

Deprotonation of tricarbonyl(η⁶-1,3-dihydroisobenzofuran)-chromium(0) 30a with chiral base 11b

The general procedure was followed using the corresponding amine (70 mg, 0.43 mmol), BuLi (0.27 ml of a 1.6 M solution in hexanes, 0.43 mmol), Me_3SiCl (0.15 ml, 1.17 mmol) and complex **30a** (100 mg, 0.39 mmol). Purification of the yellow oil by flash column chromatography (10% EtOAc–light petroleum) gave **31a**, **34** and **35** as a yellow crystalline solid (50 mg, 39%).

Deprotonation of tricarbonyl(η⁶-1,3-dihydroisobenzofuran)-chromium(0) 30a with lithium tetramethylpiperidide

The lithium amide base was prepared by treatment of a solution of 2,2,6,6-tetramethylpiperidine (75 mg, 0.53 mmol) in

THF (5 ml) with BuLi (0.33 ml of a 1.6 M solution in hexanes, 0.53 mmol) at −78 °C. The mixture was warmed to room temperature and after 10 min recooled to −78 °C and a solution of complex **30a** (124 mg, 0.48 mmol) in THF (1 ml) was then added. The reaction mixture turned immediately red and Me_3SiCl (0.15 ml, 1.17 mmol) was added after 0.5 min. Stirring was continued for 10 min before quenching by addition of MeOH (2 ml). The solvent was then evaporated under reduced pressure to give the silylated products **31a**, **34** and **35** in the ratios given in Table 5. The involatile residue was then subjected to flash chromatography on silica gel (10% EtOAc–light petroleum) to give **31a**, **34** and **35** as a yellow solid (106 mg, 67%).

Deprotonation of tricarbonyl(η⁶-1,3-dihydroisobenzofuran)-chromium(0) 30a with BuLi

BuLi (0.68 ml of a 1.6 M solution in hexanes, 1.09 mmol) was added to a solution of the complex **30a** (255 mg, 1.00 mmol) in THF at −78 °C and the reaction stirred at −78 °C for 1 h. Me_3SiCl (0.38 ml, 2.98 mmol) was then added and the reaction mixture stirred for 10 min before quenching by addition of MeOH (2 ml). The solvent was then evaporated under reduced pressure to give the silylated products **31a**, **34** and **35** in the ratios given in Table 5. The involatile residue was then subjected to flash chromatography on silica gel (10% EtOAc–light petroleum) to give **31a**, **34** and **35** as a yellow solid (240 mg, 73%).

Deprotonation of tricarbonyl(η⁶-1,3-dihydroisobenzofuran)-chromium(0) 30a with Bu^{t}Li

Bu^{t}Li (0.29 ml of a 1.7 M solution in pentane, 0.49 mmol) was added to a solution of the complex **30a** (113 mg, 0.44 mmol) in THF at −78 °C and the reaction stirred at −78 °C for 5 min. Me_3SiCl (0.17 ml, 1.33 mmol) was then added and the reaction mixture stirred for 10 min before quenching by addition of MeOH (2 ml). The solvent was then evaporated under reduced pressure and the involatile residue subjected to flash chromatography on silica gel (10% EtOAc–light petroleum) to give the silylated product **31a** (102 mg, 70%).

Tricarbonyl(η⁶-1-methyl-1,3-dihydroisobenzofuran)chromium(0) (+)-31b

The chiral amide base **2** was prepared by addition of BuLi (3.14 ml of a 1.6 M solution in hexanes, 5.03 mmol) to a THF (30 ml) solution of the corresponding chiral amine hydrochloride (686 mg, 2.63 mmol) at −78 °C, followed by stirring at room temperature for 10 min. The reaction was recooled to −100 °C and a THF (2 ml) solution of complex **30a** (560 mg, 2.19 mmol) at −100 °C was added. After 5 min, MeI (1.36 ml, 21.88 mmol) was added and stirring was continued at −100 °C for 30 min, when the reaction was poured into Et_2O–1 M HCl [200 ml, 1:1 (v/v)]. The organic phase was then separated, washed with brine (100 ml) and dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The residue was purified by column chromatography (20% EtOAc–light petroleum) to give the known complex tricarbonyl(η⁶-1-methyl-1,3-dihydroisobenzofuran)chromium(0) (+)-**31b**[24] as a yellow oil (441 mg, 75%); $[\alpha]_D^{20}$ +35 (*c* 0.48, $CHCl_3$); ν_{max}(film)/cm^{-1} 1958, 1866; δ_H(250 MHz, $CDCl_3$) 1.44 (3 H, d, *J* 6.5, CH_3), 4.85 (1 H, d, *J* 12.2, C*H*HOCHMe), 4.99 (1 H, dd, *J* 12.3 and 1.8, CH*H*OCHMe), 5.16 (1 H, dq, *J* 6.5 and 1.8, OC*H*Me), 5.22–5.30 (2 H, m, Ar-*H*), 5.41–5.47 (1 H, m, Ar-*H*) and 5.48–5.52 (1 H, m, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 22.12 (CH_3), 70.51 [C(3)H_2], 79.14 [C(1)H], 85.93 [C(5 + 6)H], 90.91 [C(4 or 7)H], 91.02 [C(4 or 7)H], 109.04 [C(3a or 7a)], 113.27 [C(3a or 7a)] and 232.34 (CO); *m*/*z* 270 (M^+, 28%), 186 (M − 3CO, 63) and 119 (100) (HRMS: found M^+, 269.9991. $C_{12}H_{10}CrO_4$ requires *M*, 269.9984).

(*R*)-3-Methylphthalide (+)-32

Sodium periodate (1.426 g, 6.67 mmol) was added to a CCl_4–CH_3CN–H_2O (2:2:3, v/v) solution of complex **31b** (225 mg, 0.83 mmol) followed by $RuCl_3.H_2O$ (5 mg, 0.02 mmol) and the reaction stirred for 20 min. CH_2Cl_2 (10 ml) was then added and the organic layer separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 ml) and the combined organic extracts dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The residue was purified by column chromatography (30% EtOAc–light petroleum) to give the known compound (*R*)-3-methylphthalide (+)-**32**[25] as a clear oil (72 mg, 59%); $[\alpha]_D^{20}$ +34 (*c* 0.52, MeOH) [lit.,[25b] $[\alpha]_D^{24}$ −43.5 (*c* 0.51, MeOH)]; ν_{max}(film)/cm^{-1} 1760 (C=O); δ_H(400 MHz, $CDCl_3$) 1.64 (3 H, d, *J* 6.7, CH_3), 5.58 (1 H, q, *J* 6.7, C*H*OCO), 7.45 (1 H, dd, *J* 7.6 and 0.8, Ar-*H*), 7.53 (1 H, t, *J* 7.5, Ar-*H*), 7.69 (1 H, td, *J* 7.5 and 1.0, Ar-*H*) and 7.90 (1 H, d, *J* 7.7, Ar-*H*); δ_C(68 MHz, $CDCl_3$) 20.31 (CH_3), 77.68 [C(3)H], 121.49 [C(4, 5, 6 or 7)H], 125.57 [C(4, 5, 6 or 7)H], 128.99 [C(4, 5, 6 or 7)H], 133.98 [C(4, 5, 6 or 7)H], 151.11 [C(3a + 7a)] and 170.59 (C=O); *m*/*z* 148 (M^+, 22%), 133 (M − Me, 51) and 105 (99) (HRMS: found M^+ 148.0523. $C_9H_8O_2$ requires *M*, 148.0524).

Tricarbonyl(η⁶-1-benzyl-1,3-dihydroisobenzofuran)chromium(0) (+)-31c

The chiral amide base **2** was prepared by addition of BuLi (0.57 ml of a 1.6 M solution in hexanes, 0.91 mmol) to a THF (5 ml) solution of the corresponding chiral amine hydrochloride (123 mg, 0.47 mmol) at −78 °C, followed by stirring at room temperature for 10 min. The reaction was recooled to −100 °C and a THF (1 ml) solution of complex **30a** (100 mg, 0.39 mmol) at −100 °C was added. After 5 min, BnBr (0.14 ml, 1.17 mmol) was added and stirring was continued at −100 °C for 30 min, after which the reaction was poured into Et_2O–1 M HCl [40 ml, 1:1 (v/v)]. The organic phase was then separated, washed with brine (20 ml) and dried ($MgSO_4$), and the solvent evaporated under reduced pressure. The residue was purified by column chromatography (20% EtOAc–light petroleum) to give the known complex tricarbonyl(η⁶-1-benzyl-1,3-dihydroisobenzofuran)chromium(0) (+)-**31c**[24] as an orange oil (115 mg, 85%); $[\alpha]_D^{20}$ +109 (*c* 1.56 $CHCl_3$); ν_{max}(film)/cm^{-1} 1963 and 1876; δ_H(400 MHz, $CDCl_3$) 2.94 (1 H, dd, *J* 13.7 and 6.9, PhCH_2), 3.10 (1 H, dd, *J* 13.7 and 6.9, PhCH_2), 4.79 (2 H, s, CH_2OCH-CH_2Ph), 5.07 (1 H, d, *J* 6.3, Ar-*H*), 5.12 (1 H, t, *J* 6.2, OC*H*-CH_2Ph or Ar-*H*), 5.21 (1 H, t, *J* 6.2, OC*H*CH_2Ph or Ar-*H*), 5.24 (1 H, t, *J* 6.2, OC*H*CH_2Ph or Ar-*H*), 5.40 (1 H, d, *J* 6.3, Ar-*H*) and 7.07–7.33 (5 H, m, Ph-*H*); δ_C(68 MHz, $CDCl_3$) 42.41 (PhCH_2), 70.93 [C(3)H_2], 83.34, 85.66, 86.70, 90.44 and 91.41 [C(1 + 4 + 5 + 6 + 7)H], 109.40 and 111.09 [C(3a + 7a)], 126.88, 128.45 and 129.74 (Ph-CH), 135.72 (Ph-C) and 232.29 (CO); *m*/*z* 346 (M^+, 3%), 262 (M − 3CO, 17), 210 [M − Cr(CO)$_3$, 56] and 105 (100) (HRMS: found M^+, 346.0298. $C_{12}H_{10}CrO_4$ requires *M*, 346.0297).

Tricarbonyl[η⁶-1-(α-hydroxybenzyl)-1,3-dihydroisobenzofuran]-chromium(0) 31e

The chiral amide base **2** was prepared by addition of BuLi (0.57 ml of a 1.6 M solution in hexanes, 0.91 mmol) to a THF (5 ml) solution of the corresponding chiral amine hydrochloride (123 mg, 0.47 mmol) at −78 °C, followed by stirring at room temperature for 10 min. The reaction was recooled to −100 °C and a THF (1 ml) solution of complex **30a** (100 mg, 0.39 mmol) at −100 °C was added. After 5 min, PhCHO (0.12 ml, 0.78 mmol) was added and stirring was continued at −100 °C for 30 min, after which the reaction was poured into Et_2O–1 M HCl [40 ml, 1:1 (v/v)]. The organic phase was then separated, washed with brine and dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The residue was purified by column chromatography (CH_2Cl_2, then 50% EtOAc–CH_2Cl_2) to give *tricarbonyl*[η⁶-1-(α-*hydroxybenzyl*)-1,3-*dihydroisobenzofuran*)-*chromium*(0) **31e** as a yellow oil and an inseparable 1:1 mixture of diastereomers (98 mg, 70%); ν_{max}(film)/cm^{-1} 3407 (O–H), 1963 and 1878; δ_H(400 MHz, $CDCl_3$) 2.31 (0.5 H, d, *J* 4.0, O*H*), 2.75 (0.5 H, d, *J* 2.3, O*H*), 4.69 (0.5 H, dd, *J* 6.9 and 2.2, PhC*H*OH), 4.73–5.08 [5 H, m, CH_2OCHCH(OH)Ph, OC*H*-

CH(OH)Ph and 2Ar-*H*)], 5.17 (0.5 H, dd, *J* 4.6 and 2.1, PhC*H*OH), 5.23 (0.5 H, t, *J* 6.2, Ar-*H*), 5.25 (0.5 H, t, *J* 6.3, Ar-*H*), 5.39 (0.5 H, d, *J* 6.3, Ar-*H*), 5.44 (0.5 H, d, *J* 6.2, Ar-*H*), 7.17–7.60 (5 H, m, Ph-*H*); δ_C(68 MHz, $CDCl_3$) 71.18 and 72.53 [C(3)H_2], 75.98, 76.12, 85.18, 85.32, 86.58, 87.85, 88.03, 90.05, 90.17, 91.68 and 91.91 [C(1 + 4 + 5 + 6 + 7)H], 106.96, 107.33, 109.31 and 110.31 [C(3a + 7a)], 126.18, 127.62, 128.21, 128.54 and 128.77 (Ph-CH) and 232.06 and 232.27 (CO); *m*/*z* 362 (M^+, 5%), 278 (M − 3CO, 17) and 119 (30) (HRMS: found M^+, 362.0256. $C_{18}H_{14}CrO_5$ requires *M*, 362.0246).

Tricarbonyl(η⁶-1-hydroxydiphenylmethyl-1,3-dihydroisobenzofuran)chromium(0) (+)-31d

The chiral amide base **2** was prepared by addition of BuLi (0.57 ml of a 1.6 M solution in hexanes, 0.91 mmol) to a THF (5 ml) solution of the corresponding chiral amine hydrochloride (123 mg, 0.47 mmol) at −78 °C, followed by stirring at room temperature for 10 min. The reaction was recooled to −100 °C and a THF (1 ml) solution of complex **30a** (100 mg, 0.39 mmol) at −100 °C was added. After 5 min, a THF (1 ml) solution of Ph_2CO (214 mg, 1.17 mmol) was added and stirring was continued at −100 °C for 30 min, after which the reaction was poured into Et_2O–1 M HCl [40 ml, 1:1 (v/v)]. The organic phase was then separated, washed with brine and dried ($MgSO_4$), and the solvent evaporated under reduced pressure. The residue was purified by column chromatography (20% EtOAc–light petroleum) to give *tricarbonyl*(η⁶-1-*hydroxydiphenylmethyl*-1,3-*dihydroisobenzofuran*)*chromium*(0) (+)-**31d** as a yellow solid (123 mg, 72%), mp 172 °C; $[\alpha]_D^{20}$ +86 (*c* 2.46, $CHCl_3$) (Found: C, 65.54; H, 4.04. $C_{24}H_{18}CrO_5$ requires C, 65.75; H, 4.14%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3415, 1963 and 1877; δ_H(250 MHz, $CDCl_3$) 2.59 (1 H, s, O*H*), 4.37 (1 H, d, *J* 6.4, Ar-*H*), 4.90–4.95 [3 H, m, Ar-*H* and CH_2OCHC(OH)Ph_2], 5.23 (1 H, td, *J* 6.2 and 0.6, Ar-*H*), 5.38 (1 H, d, *J* 6.3, Ar-*H*), 5.97 [1 H, s, OC*H*C(OH)Ph_2] and 7.19–7.53 (10 H, m, Ph-*H*); δ_C(68 MHz, $CDCl_3$) 73.08 [C(3)H_2], 80.97 (Ph_2COH), 85.00, 87.26, 88.95, 89.90 and 92.38 [C(1 + 4 + 5 + 6 + 7)H], 107.80 and 110.76 [C(3a + 7a)], 126.45, 127.22, 127.63, 127.76, 128.21 and 128.50 (Ph-CH), 142.62 (Ph-C), 144.10 (Ph-C) and 232.42 (CO); *m*/*z* 438 (M^+, 5%), 354 (M − 3CO, 42) and 119 (14) (HRMS: found M^+, 438.0548. $C_{24}H_{18}CrO_5$ requires *M*, 438.0559).

Tricarbonyl(η⁶-1-hydroxydiphenylmethyl-1,3-dihydroisobenzofuran)chromium(0) (−)-31d

The chiral amide base **33** was prepared by addition of BuLi (0.54 ml of a 1.6 M solution in hexanes, 0.86 mmol) to a THF (5 ml) solution of the corresponding chiral amine (180 mg, 0.43 mmol) and flame dried LiCl (17 mg, 0.40 mmol) at −78 °C. The reaction was stirred at room temperature for 10 min and then recooled to −100 °C and a THF (1 ml) solution of complex **30a** (100 mg, 0.39 mmol) at −100 °C was added to it. After 5 min, a THF (1 ml) solution of Ph_2CO (214 mg, 1.17 mmol) was added and stirring was continued at −100 °C for 30 min, after which the reaction was poured into Et_2O–1 M HCl [40 ml, 1:1 (v/v)]. The organic phase was then separated, washed with brine and dried ($MgSO_4$), and the solvent evaporated under reduced pressure. The residue was purified by column chromatography (15% EtOAc–light petroleum) to give (−)-**31d** as a yellow solid (119 mg, 70%); $[\alpha]_D^{20}$ −104 (*c* 0.5, $CHCl_3$).

Chiral stationary phase HPLC data

Complex (+)-**3** separated on a Chiralcel OJ column using 90:10, hexane–EtOH as eluent. Flow rate 1.5 ml min^{-1}. Detection 324 nm. Retention times 4.35 min (minor) and 6.68 min (major).

Complex (+)-**7** separated on a Chiralpak AD column using 75:25, hexane–Pr^{i}OH as eluent. Flow rate 1.5 ml min^{-1}. Detection 320 nm. Retention times 9.11 min (major) and 13.26 min (minor).

Complex (+)-**14a** separated on a Chiralcel OJ column using 90:10, hexane–EtOH as eluent. Flow rate 1.5 ml min^{-1}. Detection 230 nm. Retention times 3.99 min (minor) and 4.66 min (major).

Complex (+)-**14b** separated on a Chiralcel OF column using 95:5, hexane–EtOH as eluent. Flow rate 1.5 ml min^{-1}. Detection 230 nm. Retention times 3.09 min (minor) and 4.42 min (major).

Complex (+)-**14d** separated on a Chiralcel OF column using 99:1, hexane–EtOH as eluent. Flow rate 1 ml min^{-1}. Detection 320 nm.

Complex (+)-**14e** separated on a Chiralcel OJ column using 95:5, hexane–EtOH as eluent. Flow rate 1.5 ml min^{-1}. Detection 324 nm. Retention times 3.96 min (minor) and 5.32 min (major).

Complex (+)-**14f** separated on a Chiralcel OJ column using 95:5, hexane–EtOH as eluent. Flow rate 1.5 ml min^{-1}. Detection 324 nm. Retention times 4.12 min (major) and 5.94 min (minor).

Complex (+)-**14g** separated on a Chiralcel OJ column using 95:5, hexane–EtOH as eluent. Flow rate 1.5 ml min^{-1}. Detection 324 nm. Retention times 2.77 min (major) and 3.24 min (minor).

Complex (+)-**14h** separated on a Chiralpak AD column using 85:15, pentane–Pr^{i}OH as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention times 8.58 min (minor) and 9.13 min (major).

Complex (+)-**20** separated on a Chiralcel OJ column using 95:5, hexane–EtOH as eluent. Flow rate 1.5 ml min^{-1}. Detection 324 nm. Retention times 9.18 min (minor) and 10.93 min (major).

Complex (+)-**22** separated on a Chiralcel OJ column using 98:2, hexane–Pr^{i}OH as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention times 11.53 min (minor) and 16.30 min (major).

Complex (+)-**24** separated on a Chiralcel AD column using 97:3 hexane–EtOH as eluent. Flow rate 1.5 ml min^{-1}. Detection 324 nm. Retention times 3.8 min (minor) and 4.1 min (major).

Complex (+)-**27** separated on a Chiralpak AD column using 85:15, hexane–Pr^{i}OH as eluent. Flow rate 1.5 ml min^{-1}. Detection 320 nm. Retention times 12.86 min (major) and 13.81 min (minor).

Complex (+)-**31a** separated on a Chiralpak AD column using 98:2, hexane–Pr^{i}OH as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention times 9.25 min (minor) and 10.64 min (major).

Complex (+)-**31b** separated on a Chiralcel OD column using 97:3, hexane–Pr^{i}OH as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention times 20.96 min (minor) and 25.06 min (major).

Complex (+)-**31c** separated on a Chiralcel OD column using 97:3, hexane–Pr^{i}OH as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention times 24.86 min (major) and 26.86 min (minor).

Complex **31d** separated on a Chiralcel OD column using 80:20, hexane–Pr^{i}OH as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention times 18.00 and 21.32 min (major) and 27.69 and 39.28 min (minor).

Complex (+)-**31e** separated on a Chiralcel OD column using 97:3, hexane–Pr^{i}OH as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention times 24.77 min (minor) and 36.03 min (major).

Complex **34** separated on a Chiralcel OD column using 97:3, hexane–Pr^{i}OH as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention times 25.64 min and 29.07 min (from the reaction with LDA).

Complex **35** separated on a Chiralcel OD column using 98:2, hexane–Pr^{i}OH as eluent. Flow rate 1 ml min^{-1}. Detection 256 nm. Retention times 17.18 and 18.35 min (from the reaction with LDA).

Acknowledgements

We are grateful to the Engineering and Physical Sciences Research Council (EPSRC) and Merck Sharp and Dohme (Terlings Park, Harlow, Essex, UK CM20 2QR) for support of D. A. P. under the CASE scheme, and we also acknowledge the EPSRC for a postdoctoral fellowship to R. A. E. The authors also thank Dr D. Widdowson for communication of some unpublished results.

References

1 For reviews, see: (*a*) F. J. McQuillin, D. G. Parker and G. R. Stephenson, *Transition Metal Organometallics for Organic Synthesis*, Cambridge University Press, 1991; (*b*) M. F. Semmelhack, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 4, p. 517; (*c*) M. F. Semmelhack, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Elsevier Science Ltd, Oxford, 1995, vol. 12, p. 1017; (*d*) S. G. Davies and T. D. McCarthy, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Elsevier Science Ltd, Oxford, 1995, vol. 12, p. 1039.

2 For examples, see (*a*) J-F. Carpentier, L. Pamart, L. Maciewjeski, Y. Castanet, J. Brocard and A. Mortreux, *Tetrahedron Lett.*, 1996, **37**, 167; (*b*) M. Uemura, H. Nishimura, S. Yamada, Y. Hayashi, K. Nakamura, K. Ishihara and A. Ohno, *Tetrahedron:Asymmetry*, 1994, **5**, 1673; (*c*) C. Baldoni, S. Maiorana, G. Carrea and S. Riva, *Tetrahedron:Asymmetry*, 1993, **4**, 767.

3 See: (*a*) H-G. Schmalz, B. Millies, J. W. Bats and G. Dürner, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 631; (*b*) M. Uemura, R. Miyake, K. Nakayama, M. Shiro and Y. Hayashi, *J. Org. Chem.*, 1993, **58**, 1238; (*c*) A. Alexakis, P. Mangeney, I. Marek, F. Rose-Munch, E. Rose, A. Semra and F. Robert, *J. Am. Chem. Soc.*, 1992, **114**, 8288; (*d*) A. Alexakis, T. Kanger, P. Mangeney, F. Rose-Munch, A. Perrotey and E. Rose, *Tetrahedron:Asymmetry*, 1995, **6**, 47.

4 (*a*) Y. Kondo, J. R. Green and J. Ho, *J. Org. Chem.*, 1991, **56**, 7199; (*b*) Y. Kondo, J. R. Green and J. Ho, *J. Org. Chem.*, 1991, **58**, 6182; (*c*) A. Alexakis, T. Kanger, P. Mangeney, F. Rose-Munch, A. Perrotey and E. Rose, *Tetrahedron:Asymmetry*, 1995, **6**, 47; (*d*) S. G. Davies and W. E. Hume, *J. Chem. Soc., Chem. Commun.*, 1995, 251; (*e*) S. G. Davies, T. Loveridge and J. M. Clough, *J. Chem. Soc., Chem. Commun.*, 1995, 817.

5 (*a*) M. Uemura, H. Nishimura and T. Hayashi, *Tetrahedron Lett.*, 1993, **34**, 107; (*b*) M. Uemura, H. Nishimura and T. Hayashi, *J. Organomet. Chem.*, 1994, **473**, 129.

6 See for examples (*a*) E. P. Kündig, R. Liu and A. Ripa, *Helv. Chim. Acta*, 1992, **75**, 2657; (*b*) R. P. Hsung and W. D. Wulff, *J. Am. Chem. Soc.*, 1994, **116**, 6449; (*c*) J. A. S. Howell, M. G. Palin, G. Jaouen, B. Malezieux, S. Top, J. M. Cense, J. Salaün, P. McArdle, D. Cunningham and M. O'Gara, *Tetrahedron:Asymmetry*, 1996, **7**, 95; (*d*) P. W. N. Christian, R. Gil, K. Muniz-Fernández, S. E. Thomas and A. T. Wierzchleyski, *J. Chem. Soc., Chem. Commun.*, 1994, 1569; (*e*) S. L. Griffiths, S. Perrio and S. E. Thomas, *Tetrahedron:Asymmetry*, 1994, **5**, 1847.

7 D. A. Price, N. S. Simpkins, A. M. MacLeod and A. P. Watt, *J. Org. Chem.*, 1994, **59**, 1961.

8 D. A. Price, N. S. Simpkins, A. M. MacLeod and A. P. Watt, *Tetrahedron Lett.*, 1994, **35**, 6159.

9 R. A. Ewin and N. S. Simpkins, *Synlett*, 1996, 317.

10 E. P. Kündig and A. Quattropani, *Tetrahedron Lett.*, 1994, **35**, 3497.

11 H-G. Schmalz and K. Schellhaas, *Tetrahedron Lett.*, 1995, **36**, 5515.

12 M. Uemura, Y. Hayashi and Y. Hayashi, *Tetrahedron:Asymmetry*, 1994, **5**, 1427.

13 E. L. M. Cowton, S. E. Gibson, M. J. Schneider and M. H. Smith, *Chem. Commun.*, 1996, 839.

14 (*a*) P. J. Cox and N. S. Simpkins, *Tetrahedron:Asymmetry*, 1991, **2**, 1; for more recent contributions, see: (*b*) N. J. Newcombe and N. S. Simpkins, *J. Chem. Soc., Chem. Commun.*, 1995, 831; (*c*) D. M. Hodgson and A. R. Gibbs, *Tetrahedron:Asymmetry*, 1996, **7**, 407; (*d*) D. I. MaGee, S. Setiadji and R. A. Martin, *Tetrahedron:Asymmetry*, 1995, **6**, 639; (*e*) D. Price and N. S. Simpkins, *Tetrahedron Lett.*, 1995, **36**, 6135.

15 L. A. Bromley, S. G. Davies and C. L. Goodfellow, *Tetrahedron: Asymmetry*, 1991, **2**, 139.

16 F. Effenburger and K. Schöllkopf, *Chem. Ber.*, 1985, **118**, 4356.

17 S. G. Davies and C. L. Goodfellow, *J. Chem. Soc., Perkin Trans. 1*, 1990, 393.

18 (*a*) B. J. Bunn, N. S. Simpkins, Z. Spavold and M. J. Crimmin, *J. Chem. Soc., Perkin Trans. 1*, 1993, 3113; (*b*) M. Majewski, R. Lazny and P. Nowak, *Tetrahedron Lett.*, 1995, **36**, 5465; (*c*) see also B. H. Lipshutz, M. R. Wood and C. W. Lindsley, *Tetrahedron Lett.*, 1995, **36**, 4385.

19 D. B. Collum, *Acc. Chem. Res.*, 1993, **26**, 227.

20 Equilibration in tricarbonyl(η^6-arene)chromium complexes has been observed previously, see for example ref. 4(*b*). See also E. P. Kundig, C. Grivet and S. Spichiger, *J. Organomet. Chem.*, 1987, **332**, C13; Dr D. Widdowson, personal communication.

21 D. L. Comins and J. D. Brown, *J. Org. Chem.*, 1984, **49**, 1079.

22 A. Alexakis, T. Kanger, P. Mangeney, F. Rose-Munch, A. Perrotey and E. Rose, *Tetrahedron:Asymmetry*, 1995, **6**, 2135.

23 (*a*) R. J. Card and W. S. Trahanovsky, *J. Org. Chem.*, 1980, **45**, 2560; (*b*) G. Jaouen, S. Top, A. Laconi, D. Couturier and J. Brocard, *J. Am. Chem. Soc.*, 1984, **106**, 2207; (*c*) M. F. Semmelhack, J. Bisaha and M. Czarny, *J. Am. Chem. Soc.*, 1979, **101**, 768; (*d*) G. Simonneaux and G. Jaouen, *Tetrahedron*, 1979, **35**, 2249; (*e*) M. C. Sénéchal-Tocquer, D. Sénéchal, J. Y. Le Bihan, D. Gentric and B. Caro, *Bull. Soc. Chim. Fr.*, 1992, **129**, 121.

24 S. J. Coote, S. G. Davies, D. Middlemiss and A. Naylor, *J. Organomet. Chem.*, 1989, **379**, 81.

25 (*a*) U. Nagai, T. Shishido, R. Chiba and H. Mitsuhashi, *Tetrahedron*, 1965, **21**, 1701; (*b*) H. Takahashi, T. Tsubuki and K. Higashiyama, *Chem. Pharm. Bull.*, 1991, 3136.

26 P. H. J. Carlsen, T. Katsuki, V. S. Martin and K. B. Sharpless, *J. Org. Chem.*, 1981, **46**, 3936.

27 K. Bambridge, M. J. Begley and N. S. Simpkins, *Tetrahedron Lett.*, 1994, **35**, 3391.

28 J. Blagg, S. G. Davies, C. L. Goodfellow and K. H. Sutton, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1805.

29 C. A. L. Mahaffy and P. L. Pauson, *Inorg. Synth.*, 1979, **19**, 154.

30 M. F. Semmelhack and A. Zask, *J. Am. Chem. Soc.*, 1983, **105**, 2034.

Paper 6/05812D
Received 20*th August* 1996
Accepted 8*th October* 1996