ARTICLE

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Chiral base-mediated benzylic functionalisation of tricarbonylchromium(0) complexes of benzylamine derivatives

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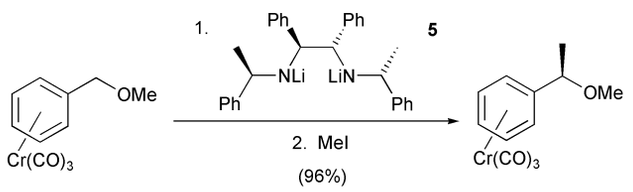
The novel complex (η^6-benzylamine)tricarbonylchromium(0) **11** was prepared in up to 66% yield by direct complexation with $Cr(CO)_6$ in refluxing 1,4-dioxane. Imine derivatives of this complex were readily deprotonated at the benzylic position by diamide **5**, and the resultant anions reacted regioselectively with electrophiles (Me_3SiCl or MeI) to give fairly good yields of products substituted at the benzylic carbon. Products of up to 87% e.e. were obtained in these reactions, with the highest enantioselectivity being derived from the *tert*-butyl-substituted imine complex **25**.

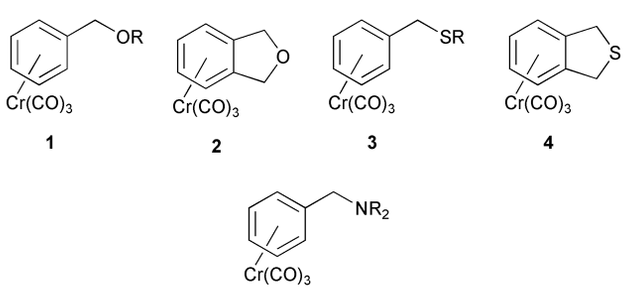
Asymmetric functionalisation of the benzylic position of tricarbonylchromium(0) complexes of acyclic and cyclic benzyl ethers **1** and **2** and thioethers **3** and **4** has been achieved using chiral bases.[1–6] In a typical example, chiral base **5**[7] was used to convert complex **6** into complex **7** in a yield of 96% and an enantiomeric excess of 97% (Scheme 1).[1] To date, however, the



6 **7** (97% ee)

Scheme 1

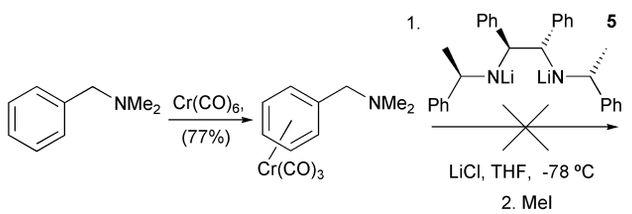
asymmetric functionalisation of nitrogen analogues of **1**–**4** using chiral bases has remained elusive. In order to address this issue, we initiated the study described below, the aim of which was to achieve asymmetric functionalisation of complexes of general structure **8**.



1 **2** **3** **4** **8**

Preliminary investigations

Our investigations began with a direct analogue of the oxygen and sulfur systems that had given rise to successful asymmetric benzylic functionalisations. The known *N*,*N*-dimethylbenzylamine complex **9**[8] was prepared by heating the ligand with $Cr(CO)_6$ in dibutyl ether–THF (Scheme 2). Treatment of this complex with diamide **5** under the same conditions used successfully with the ether substrates, followed by an iodomethane quench, gave only recovered starting material (81%). This result was consistent with a literature report that treatment



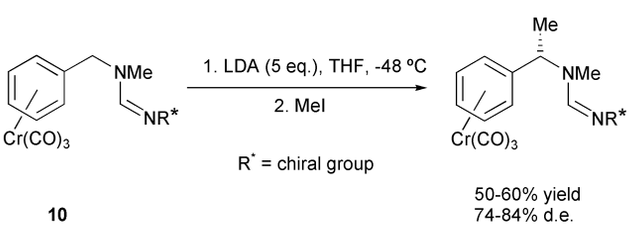
9

Scheme 2

of the tricarbonylchromium(0) complex of *N*-methylisoindoline with a monoamide chiral base did not result in clean metallation.[3]

Activated systems

It was decided that greater activation would be required for benzylic deprotonation at low temperature. A wide range of derivatives of purely organic amines have been employed to promote metallation on carbon adjacent to nitrogen, including imines, amides, carbamates, formamidines, nitrosamines and amine–borane complexes.[9,10] Davies achieved α-methylation of chiral formamidine derivatives of *N*-methylbenzylamine-$Cr(CO)_3$, **10**, using LDA as base at −48 °C (Scheme 3).[11]



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Scheme 3

Although good diastereomeric excesses were attained (74–84%), a disadvantage of using such formamidine derivatives for our purposes was that they are only applicable to functionalisation of a *secondary* amine, necessitating an additional alkyl group on nitrogen in addition to the benzyl group. It was considered to be of greater synthetic value if the parent benzylamine complex could be functionalised.

Synthesis of (benzylamine)tricarbonylchromium(0)

An obvious starting point for preparation of suitable derivatives of the benzylamine complex for benzylic deprotonation

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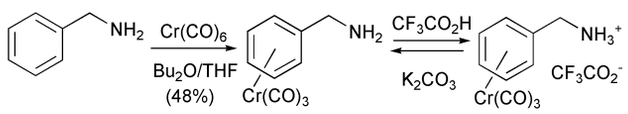
would be (benzylamine)tricarbonylchromium(0) itself. Surprisingly, however, this was unknown in the literature. Wary that this could have been due to difficulties in preparing the complex *via* the usual routes, benzylamine and $Cr(CO)_6$ were nonetheless heated under reflux in dibutyl ether–THF (10 : 1) for 48 h (Scheme 4). The crude reaction mixture contained a large



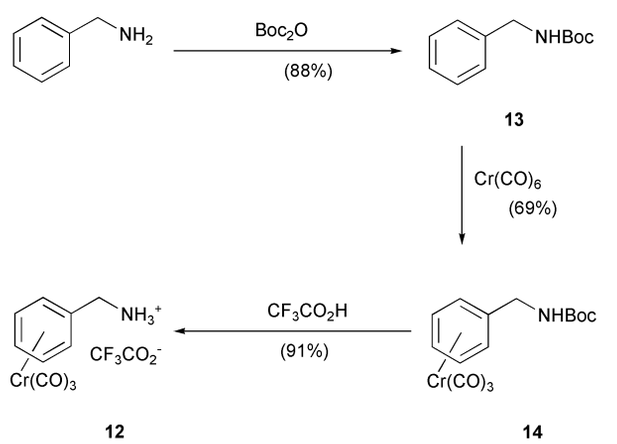
11 **12**

Scheme 4

amount of a dull yellow precipitate, in addition to a yellow solution. The solute was purified by column chromatography (elution with EtOH–CH_2Cl_2 mixtures was required owing to its high polarity) and shown to indeed be the novel benzylamine complex **11** by IR, ^{1}H NMR, ^{13}C NMR, MS and microanalysis.

The precipitate could not be identified, as it rapidly decomposed in the NMR solvents in which it was soluble (*e.g.* CD_3SOCD_3), although an IR spectrum indicated the presence of complexed carbonyl ligands (resonances at 1982 and 1876 cm^{-1}). Possibly this was a σ-complex (or mixture of such complexes), analogous to the tris(amine) complex $Cr(CO)_3(NH_3)_3$ which is often used as a complexing agent.[12] σ-Complex formation would be expected to be more likely for benzylamine compared to sterically more encumbered amines such as *N*,*N*-dimethylbenzylamine **9**. The quantity of precipitate produced was minimised using a large excess (12 equivalents) of benzylamine during complexation, giving complex **11** in up to 48% yield. The benzylamine complex was a yellow oil which darkened over several days storage under nitrogen. It was conveniently stockpiled as its trifluoroacetic acid salt **12**, from which the free amine could be regenerated by addition of aqueous K_2CO_3.

In view of the relatively low yields of benzylamine complex **11** obtained from this direct method, an alternative route was investigated. Benzylamine was Boc-protected and the product **13** complexed to tricarbonylchromium in 69% yield, by heating with $Cr(CO)_6$ (Scheme 5). Treatment of the *N*-Boc-benzylamine

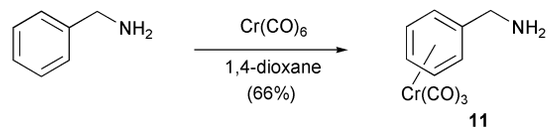


12 **14**

Scheme 5

complex **14** with trifluoroacetic acid in CH_2Cl_2 directly gave (η^6-benzylammonium)tricarbonylchromium(0) trifluoroacetate **12** in 91% yield (55% overall from benzylamine). Boc-protected benzylamine was identified by comparison of its mp and spectroscopic data with literature values,[13] whilst novel complex **14** was fully characterised by IR, ^{1}H NMR, ^{13}C NMR, MS and elemental analysis.

Finally, a direct complexation of benzylamine was attempted in 1,4-dioxane. It was hoped that the slightly stronger donor characteristics of this solvent relative to dibutyl ether–THF (10 : 1) would discourage σ-complex formation *via* the amine group. This indeed proved to be the most satisfactory route to (η^6-benzylamine)tricarbonylchromium(0) **11**, giving a 66% yield, with very little precipitate formation, using just 0.5 equivalents of benzylamine (Scheme 6).



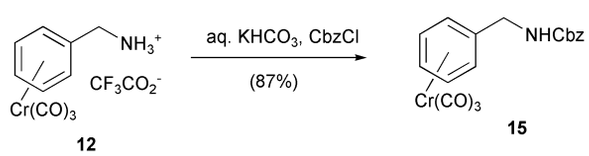
11

Scheme 6

Carbamate-activated systems

Schlosser has shown that treatment of uncomplexed *N*-Boc-benzylamine **13** with at least 2 equivalents of *sec*-butyllithium in THF at −50 °C results in lithiation on both nitrogen and the benzylic carbon.[14] Subsequent addition of carbon dioxide gave Boc-phenylglycine in 79% yield. Given that *N*-Boc-benzylamine complex **14** had already been prepared, this seemed a good initial candidate for benzylic lithiation using a chiral lithium amide base.

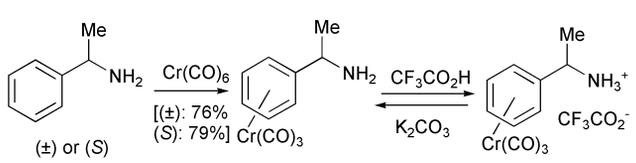
In addition to complex **14**, the *N*-Cbz-benzylamine complex **15** was targeted as an alternative substrate. This was synthesised in 87% yield by treatment of (η^6-benzylammonium)tricarbonylchromium(0) trifluoroacetate **12** with potassium hydrogencarbonate solution and benzyl chloroformate (Scheme 7).



12 **15**

Scheme 7

Anticipating the need to form a product for which the e.e. could be measured (and the absolute configuration readily established), 1-phenylethylamine complex **16**[15] was prepared by reacting the ligand with $Cr(CO)_6$. In contrast to benzylamine, complexation of 1-phenylethylamine did not produce large amounts of precipitate (presumably due to its more hindered amino group) and a good yield of complex **16** was obtained using either racemic or (*S*)-configured starting material (Scheme 8). Like benzylamine complex **11**, it was a yellow oil

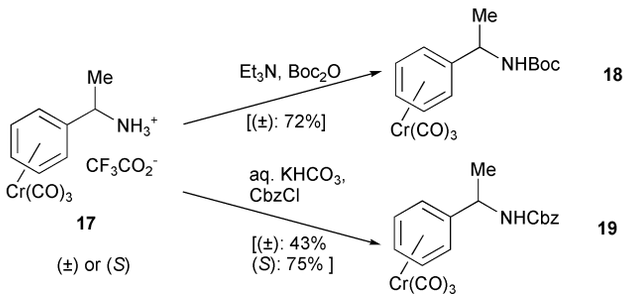


16 **17**

Scheme 8

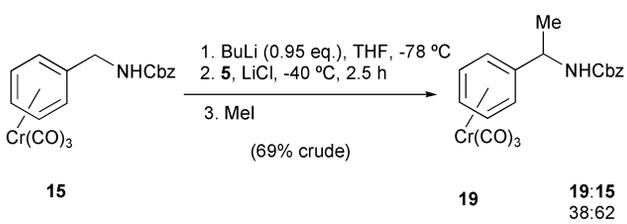
which darkened over a few days under nitrogen, but longer-term storage could be effected by conversion to the solid trifluoroacetic acid salt **17**.

Racemic (η^6-1-phenylethylammonium)tricarbonylchromium(0) trifluoroacetate **17** was converted to its *N*-Boc derivative **18** (the anticipated product of benzylic methylation of *N*-Boc-benzylamine complex **14**) by treatment with Boc_2O and triethylamine in methanol (Scheme 9). Attempts to separate the enantiomers of complex **18** by chiral HPLC, however, proved unsuccessful. Neither could complete separation of the enantiomers of the parent 1-phenylethylamine complex **16** be achieved by HPLC methods. Fortunately, chiral HPLC analysis did prove successful for the *N*-Cbz derivative **19**, which had been prepared from complex **17** using potassium hydrogencarbonate solution and benzyl chloroformate.



Scheme 9

Treatment of either *N*-Boc- or *N*-Cbz-benzylamine complex (**14** or **15** respectively) with 0.95 equivalents *n*-butyllithium (to deprotonate nitrogen), then diamide base **5** with LiCl in THF at −78 °C followed by a MeI quench gave no identifiable products other than starting material. A similar experiment (using complex **15**), but maintaining the reaction mixture at −40 °C after addition of the diamide **5**, produced an inseparable mixture of α-methylated complex **19** and starting material **15** (38 : 62), with only 69% overall recovery (Scheme 10). It was



Scheme 10

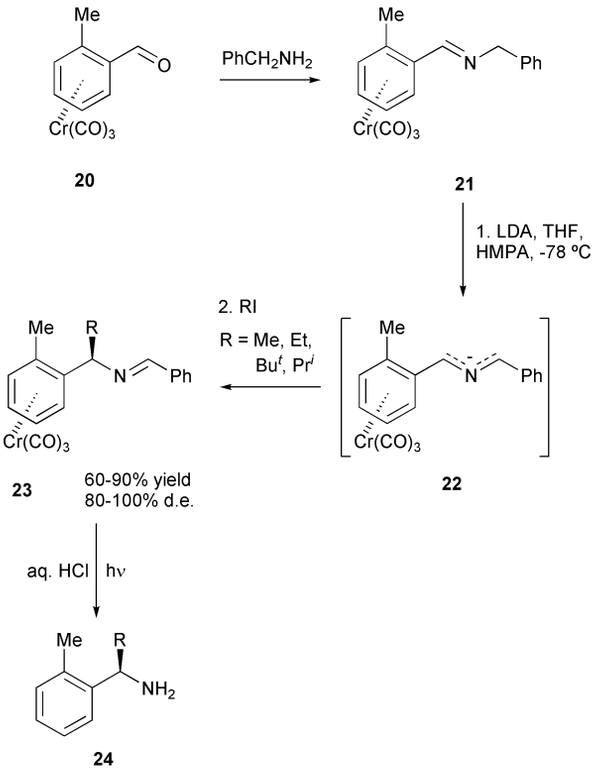
thus apparent that deprotonation at the benzylic position of carbamate complexes **14** and **15** by diamide **5** was relatively sluggish. Rather than pursuing this strategy further, our attention then turned to another class of substrate with greater activation of the benzylic protons.

Imine-activated systems

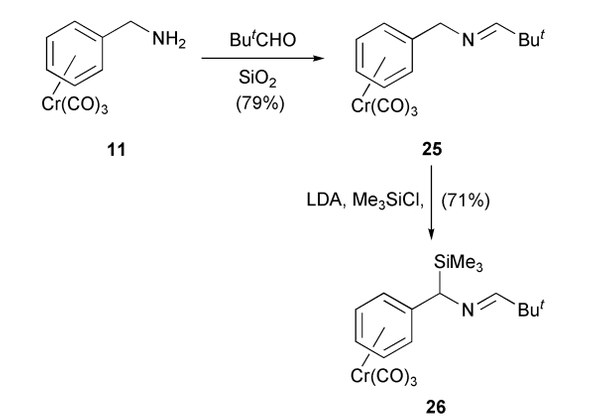
Deprotonation at the benzylic position of *N*-benzylimines may be accomplished using LDA in THF at −78 °C.[16] The 2-azaallyl anions thus formed react with electrophiles to give products of substitution α to nitrogen. Such a reaction was reported by Solladie-Cavallo for the complexed imine **21**, derived from *ortho*-methylbenzaldehyde complex **20** and benzylamine (Scheme 11).[17]

Although the deprotonation occurred adjacent to the (uncomplexed) phenyl group, alkylation of the intermediate delocalised anion **22** occurred predominantly α to the complexed arene. This regioselectivity was ascribed to either a greater charge density or a greater orbital coefficient at the observed alkylation site. Hydrolysis and decomplexation of the product **23** gave an α-alkyl benzylic amine **24**. Since high diastereoselectivities were achieved in the alkylation step, starting with optically pure *ortho*-methylbenzaldehyde complex **20** provided access to chiral benzylic amines **24** with high e.e. In view of these results, it seemed feasible that an imine derived from benzylamine complex **11** could be deprotonated at the benzylic position using a (chiral) lithium amide base, and that attack of an electrophile on the resultant 2-azaallyl anion would be regioselective for the carbon α to the complexed arene.

The novel imine complex **25** was prepared in 79% yield, on a 2 g scale, by stirring benzylamine complex **11** with trimethylacetaldehyde and silica gel at room temperature (Scheme 12). It was hoped that the *tert*-butyl-substituted 2-azaallyl anion derived from complex **25** would be less stabilised than an aryl-substituted analogue and hence exhibit greater reactivity and configurational stability. Treatment of complex **25** with LDA in



Scheme 11

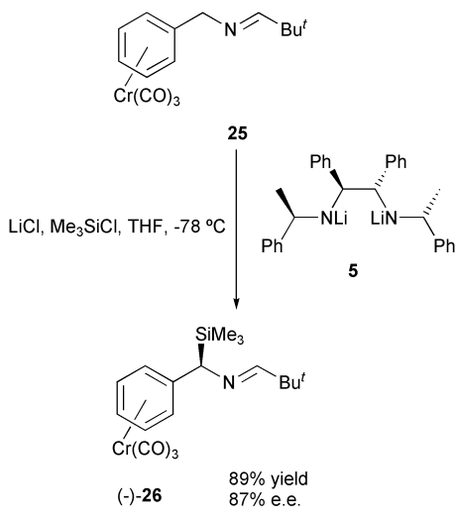


Scheme 12

THF at −78 °C, with an internal Me_3SiCl quench gave the novel silylated imine **26** in 71% yield. Complex **26** proved remarkably resistant to hydrolysis (presumably for steric reasons) with no reaction observed on stirring in 5% hydrochloric acid (r.t., 15 min), and purification by column chromatography on silica was possible. Furthermore, its enantiomers could be separated by chiral HPLC [Chiralcel OD-H, hexane–propan-2-ol (1999 : 1)]. Formation of complex **26** was thus a suitable method for probing asymmetric deprotonation of complex **25**.

Imine complex **25** was added to a solution of diamide **5**, LiCl and Me_3SiCl (*in situ* quench) in THF at −78 °C (Scheme 13). Silylated imine complex **26** was isolated in 89% yield, and with $[\alpha]_D^{25}$ −23 (c = 1, CH_2Cl_2). HPLC analysis of the product revealed the e.e. to be 87%—substantial asymmetric induction had been achieved.

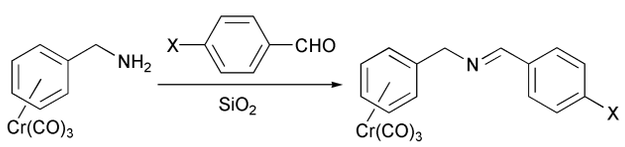
The effect of using an external quench of iodomethane was examined next. Benzylic methylation of the intermediate anion occurred readily at −78 °C, but the imine product was readily hydrolysed and unstable towards column chromatography, preventing direct measurement of the product e.e. A protocol was therefore developed for complete hydrolysis of the imine product followed by Cbz-derivatisation of the resultant 1-



Scheme 13

phenylethylamine complex to produce complex **19**, for which the e.e. could easily be measured by chiral HPLC (*vide supra*). This one-pot procedure was carried out using the crude product formed after deprotonation–methylation of the imine substrate. Imine hydrolysis was complete within 30 min using 6 M HCl–MeOH at room temperature, and Cbz-derivatisation was effected using benzyl chloroformate.

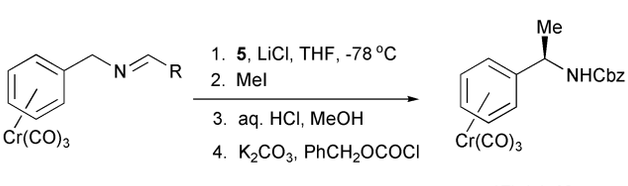
This method permitted use of substrates with an imine substituent other than *tert*-butyl. A series of novel aryl-substituted imine complexes **27**–**29** were prepared for this purpose by stirring benzylamine complex **11** with an arylaldehyde and silica gel at room temperature (Scheme 14).



Product	X	Yield(%)
27	H	81
28	NMe_2	61
29	NO_2	69

Scheme 14

Methylation of the *tert*-butyl-substituted imine **25** gave complex (+)-**19** in 69% overall yield with 81% e.e. (Scheme 15),

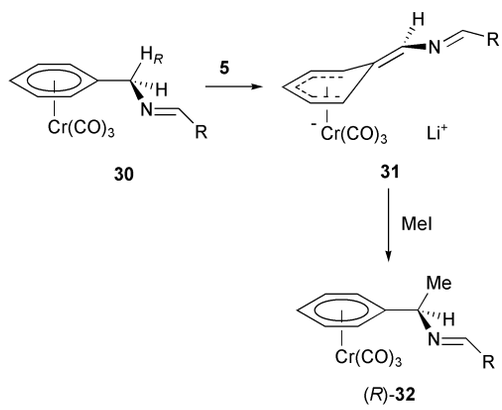


		Yield (%)	E.e. (%)
25	R = Bu^t	69	81
27	R = Ph	69	55
28	R = p-$C_6H_4NMe_2$	61	80
29	R - p-$C_6H_4NO_2$	0	-

Scheme 15

in reasonably good agreement with the e.e. obtained for silylation. As (*S*)-**19** had been prepared previously and was laevorotatory this product was clearly (*R*)-configured [the silylated complex (−)-**26** was tentatively assumed to be (*R*) based on this reasoning]. Phenyl-substituted imine **27** gave product (*R*)-(+)-**19** in 69% yield but only 55% e.e. The lower optical yield in this case may be related to the greater acidity of complex **27** or lower configurational stability of the more stabilised 2-azaallyl anion it forms. Thus, a better e.e. was obtained from the *para*-dimethylaminophenyl-substituted imine **28** (80% e.e., 61% yield), possibly due to the destabilising effect of the NMe_2 group on the intermediate anion. Attempted deprotonation of *para*-nitrophenyl-substituted imine **29**, on the other hand, resulted in complete decomposition of the complex.

Deprotonation of imine complexes **25**, **27** and **28** using diamide base **5** gave, in each case, (*R*)-**19**, the same product configuration as obtained in deprotonations of the acyclic ether complexes by this base.[1] A reaction pathway similar to that proposed for the ether complexes could therefore be operating. Selective removal of the pro-*R* benzylic proton [antiperiplanar to the tricarbonylchromium group] from the substrate **30** by base **5** would give a configurationally stable anion **31** (Scheme 16). Electrophilic attack would then occur stereoselectively from the *exo* face to give the (*R*)-configured product **32**.



Scheme 16

Experimental

General details

All reactions and manipulations involving organometallic compounds were performed under nitrogen using standard vacuum line and Schlenk tube techniques.[18] Reactions involving (arene)tricarbonylchromium(0) complexes were performed with the exclusion of light. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Diethyl ether was either distilled from sodium benzophenone ketyl or dried over sodium wire. 1,4-Dioxane and dichloromethane were distilled from calcium hydride. The concentrations of alkyllithiums were determined by titration against diphenylacetic acid in THF.[19] The precursor to diamide **5** was prepared according to a literature method.[7] All other reagents were used as obtained from commercial sources, unless otherwise stated.

Melting ponts were determined using either an Electrothermal IA9100 digital or Büchi 510 melting point apparatus, and are uncorrected. Melting points of organometallic compounds were determined in sealed capillaries under nitrogen. IR spectra were obtained on Perkin-Elmer 1710 or Mattson 5000 FTIR spectrometers. Elemental analyses were performed by Imperial College Microanalytical Service. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter with a 10 cm path length. Concentrations for optical rotation measurements are given in g/100 cm^3. NMR spectra were recorded at room temperature on JEOL GSX 270 (270 MHz ^1H, 67.9 MHz ^{13}C) or Bruker DRZ 300 (300 MHz ^1H, 75.4 MHz ^{13}C) instruments. ^1H NMR chemical shifts are referenced with respect to residual undeuterated solvent while ^{13}C NMR shifts are referenced with respect to deuterated solvent. Broadband ^1H decoupling was employed for ^{13}C NMR spectra. *J* values are given in Hz. Mass spectra were recorded on VG Micromass 7070E or Autospec-Q instruments at Imperial College, or a VG Mass Lab 12/250 instrument at EPSRC Mass Spectrometry Service, Swansea,

using EI or CI techniques. Analytical HPLC was carried out using a Unicam Crystal 200 pump with a Unicam Spectrea 100 uv-vis detector at Imperial College, or Waters 600E System Controller with a Waters 455 uv-vis detector at Associated Octel Company.

General procedure for complexation of arenes to tricarbonylchromium(0)

A round-bottomed flask fitted with an air condenser below a water condenser, connected in series (all joints B24), was charged with arene, hexacarbonylchromium(0), dibutyl ether and THF (Bu_2O : THF, 10 : 1). The mixture was thoroughly degassed and heated at reflux in the dark for 30–48 h (bath temp. approx. 140 °C). The resulting solution/suspension was cooled to room temperature, diluted with an equal volume of diethyl ether, filtered through a short pad of silica or Celite (elution with diethyl ether) and evaporated under reduced pressure. The residue was purified by column chromatography and/or recrystallisation.

(η^6-Benzyldimethylamine)tricarbonylchromium(0) 9[8]

Following the general procedure for complexation, benzyldimethylamine(2.00 g, 14.8 mmol), hexacarbonylchromium(0) (3.58 g, 16.2 mmol), dibutyl ether (60 cm^3) and THF (6 cm^3) were heated for 46 h, and the mixture filtered through Celite. Purification by flash column chromatography (SiO_2; EtOAc–Et_2O, 1 : 4) and recrystallisation from CH_2Cl_2–petroleum ether (bp 40–60 °C) gave the title complex **9** as a yellow crystalline solid (3.08 g, 11.3 mmol, 77%), mp 44.5–45.5 °C (lit.[8] mp 48–50 °C); δ_H (270 MHz; $CDCl_3$) 2.29 (6 H, s, CH_3), 3.14 (2 H, s, CH_2), 5.23–5.28 (1 H, m, Cr–CH_{para}), 5.30–5.32 (2 H, m, Cr–CH_{ortho}) and 5.36–5.41 (2 H, m, Cr–CH_{meta}); δ_C (67.9 MHz; $CDCl_3$) 45.2 (CH_3), 62.8 (CH_2), 91.3 (C_{para}), 93.2 and 93.8 (C_{ortho} and C_{meta}), 108.5 (C_{ipso}) and 232.8 (C≡O); *m*/*z* (EI) 271 (M^+, 77%), 215 (M − 2CO, 85), 187 (M − 3CO, 96) and 91 ($PhCH_2$, 100).

Attempted deprotonation of (η^6-benzyldimethylamine)-tricarbonylchromium(0) 9 using chiral lithium amide 5

A solution of lithium amide **5** was prepared by addition of BuLi (1.6 M in hexanes, 0.55 cm^3, 0.88 mmol) to a stirred solution of the diamine precursor to **5** (185 mg, 0.44 mmol) in THF (5 cm^3) at −78 °C, followed by warming to room temperature. The resulting pink solution was recooled to −78 °C and a solution of flame-dried LiCl (17 mg, 0.40 mmol) in THF (5 cm^3) was added *via* a cannula. To this was added a solution of complex **9** (108 mg, 0.40 mmol) in THF (5 cm^3) *via* a cannula over approximately 2 min. The solution was stirred at −78 °C for 1 h after which MeI (0.10 cm^3, 1.61 mmol) was added. After a further 1 h at −78 °C, MeOH was added, the mixture allowed to warm to room temperature and the solvents removed *in vacuo*. The residue was purified by flash chromatography (SiO_2; EtOAc–Et_2O, 1 : 4) which gave starting complex **9** (87 mg, 0.30 mmol, 81%). The ^{1}H NMR spectrum and TLC of the product were identical to those of authentic **9**.

Complexation of benzylamine to tricarbonylchromium in Bu_2O–THF to give complex 11

Following the general procedure for complexation, benzylamine (6.4 g, 60 mmol), hexacarbonylchromium(0) (1.10 g, 5.0 mmol), dibutyl ether (40 cm^3) and THF (4 cm^3) were heated for 48 h to give, after filtration through Celite and flash column chromatography (SiO_2; CH_2Cl_2–EtOH, 1 : 0 to 9 : 1), *(η^6-benzylamine)tricarbonylchromium(0)* **11** as a yellow oil (0.58 g, 2.4 mmol, 48%) (Found: C, 49.2; H, 3.5; N, 5.6. $C_{10}H_9CrNO_3$ requires C, 49.39; H, 3.73; N, 5.76%); ν_{max} (CH_2Cl_2)/cm^{-1} 1963s and 1890s (C≡O); δ_H (270 MHz; $CDCl_3$) 1.45 (2 H, br s, NH_2), 3.68 (2 H, s, CH_2), 5.23–5.28 (1 H, m, Cr–CH_{para}) and 5.39–5.43 (4 H, m, Cr–C$H_{ortho/meta}$); δ_C (67.9 MHz; $CDCl_3$) 44.8 (CH_2), 91.3 and 93.4 ($C_{ortho/meta/para}$), 114.2 (C_{ipso}) and 233.0 (C≡O); *m*/*z* (EI) 243 (M^+, 10%), 215 (M − CO, 3), 187 (M − 2CO, 8), 159 (M − 3CO, 72) and 52 (Cr, 100). Complex **11** darkened over several days storage under N_2 and was conveniently stockpiled as the trifluoroacetic acid salt. This was formed by addition of trifluoroacetic acid (1.1 equiv.) to a CH_2Cl_2 solution of the complex (0.2 M), followed by addition of an equal volume of diethyl ether to induce precipitation. The precipitate was filtered and washed with diethyl ether to give (η^6-benzylammonium)tricarbonylchromium(0) trifluoroacetate **12** as a yellow solid; δ_H (270 MHz; D_2O) 3.73 (2 H, s, CH_2) and 5.40–5.53 (5 H, m, Cr–CH). The free amine could be regenerated by addition of saturated aqueous K_2CO_3, extraction into diethyl ether and removal of the solvent *in vacuo*.

N-(*tert*-Butoxycarbonyl)benzylamine 13

A solution of benzylamine (5.36 g, 50 mmol) and di-*tert*-butyl dicarbonate (10.91 g, 50 mmol) in MeOH (25 cm^3) was stirred at room temperature for 2 h. The solvent was removed *in vacuo* and the residue recrystallised from petroleum ether (bp 40–60 °C) to give the title compound **13** as colourless needles (9.13 g, 44.1 mmol, 88%), mp 53.5–55 °C (lit.[13] mp 55.5–56.5 °C); ν_{max} (CH_2Cl_2)/cm^{-1} 3448m (NH), 1713s (C=O), 1505s and 1159s; δ_H (270 MHz; $CDCl_3$) 1.46 [9 H, s, C(CH_3)$_3$], 4.31 (2 H, d, *J*5.3, CH_2), 4.85 (1 H, br s, NH) and 7.23–7–36 (5 H, m, Ph).

[η^6-*N*-(*tert*-Butoxycarbonyl)benzylamine]tricarbonylchromium(0) 14

Following the general procedure for complexation, *N*-(*tert*-butoxycarbonyl)benzylamine **13** (4.15 g, 20.0 mmol), hexacarbonylchromium(0) (4.40 g, 20.0 mmol), dibutyl ether (80 cm^3) and THF (8 cm^3) were heated for 48 h, and the mixture filtered through Celite. Purification by flash column chromatography [SiO_2; CH_2Cl_2–petroleum ether (bp 40–60 °C), 7 : 3] and recrystallisation from diethyl ether–petroleum ether (bp 40–60 °C) gave the *title complex* **14** as a yellow crystalline solid (4.73 g, 13.8 mmol, 69%), mp 97–98 °C (Found: C, 52.4; H, 4.9; N, 4.15. $C_{15}H_{17}CrNO_5$ requires C, 52.48; H, 4.99; N, 4.08%); ν_{max} (CH_2Cl_2)/cm^{-1} 3449w (NH), 1969s and 1888s (C≡O) and 1714m (C=O); δ_H (270 MHz; $CDCl_3$) 1.47 [9 H, s, C(CH_3)], 4.10 (2 H, d, *J* 6.5, CH_2), 5.00 (1 H, br m, NH), 5.23–5.29 (3 H, m, Cr–C$H_{ortho/para}$) and 5.40 (2 H, dd, *J* 6.0, 6.0, Cr–CH_{meta}); δ_C (75.4 MHz; $CDCl_3$) 28.4 [C(CH_3)$_3$], 43.2 (CH_2), 80.4 [C(CH_3)$_3$], 91.2 (C_{ortho} or C_{meta}), 91.3 (C_{para}), 93.4 (C_{ortho} or C_{meta}), 110.3 (C_{ipso}), 156.0 (C=O) and 232.8 (C≡O); *m*/*z* (EI) 343 (M^+, 18%), 315 (M − CO, 18), 287 (M − 2CO, 50), 259 (M − 3CO, 85), 203 [M − 3CO − $(CH_3)_2$C=CH_2, 97] and 91 ($PhCH_2$, 100).

Boc deprotection of [η^6-*N*-(*tert*-butoxycarbonyl)benzylamine]-tricarbonylchromium(0) 14

A solution of complex **14** (3.43 g, 10.0 mmol) and trifluoroacetic acid (2.0 cm^3, 26 mmol) in CH_2Cl_2 (40 cm^3) was stirred at room temperature for 2 h. Diethyl ether (30 cm^3) was added and the resultant precipitate filtered and washed with further diethyl ether to give (η^6-benzylammonium)tricarbonylchromium(0) trifluoroacetate **12** as a yellow crystalline solid (3.25 g, 9.1 mmol, 91%). A sample of free amine, formed by addition of saturated aqueous K_2CO_3, extraction into diethyl ether and removal of the solvent *in vacuo*, had identical ^{1}H NMR and TLC data to those of authentic complex **12**.

Complexation of benzylamine to tricarbonylchromium in 1,4-dioxane to give complex 11

The general procedure for complexation was followed except 1,4-dioxane was used instead of dibutyl ether and THF, and the bath temperature was 110 °C. Thus, benzylamine (0.268 g,

2.50 mmol), hexacarbonylchromium(0) (1.10 g, 5.00 mmol) and 1,4-dioxane were heated for 48 h to give, after filtration through Celite and flash column chromatography (SiO_2; CH_2Cl_2–EtOH, 1 : 0 to 9 : 1), (η^6-benzylamine)tricarbonylchromium(0) **11** as a yellow oil (0.403 g, 1.66 mmol, 66%). The ^{1}H NMR and TLC data of the product were identical to those of authentic **11**.

[η^6-*N*-(Benzyloxycarbonyl)benzylamine]tricarbonylchromium(0) 15

(η^6-Benzylammonium)tricarbonylchromium(0) trifluoroacetate **12** (0.500 g, 1.40 mmol), saturated aqueous $KHCO_3$ (10 cm^3) and diethyl ether (10 cm^3) were stirred at room temperature for 10 min. Benzyl chloroformate (0.22 cm^3, 1.54 mmol) was added and stirring continued for 0.5 h. The layers were separated and the aqueous layer extracted with diethyl ether until no longer yellow. The combined organic phase was washed with brine (20 cm^3), dried (Na_2SO_4) and the solvent removed *in vacuo*. The residue was purified by flash chromatography [SiO_2; CH_2Cl_2–petroleum ether (bp 40–60 °C), 8 : 2] to give the *title complex* **15** as a yellow crystalline solid (0.461 g, 1.22 mmol, 87%), mp 105.5–107.5 °C (Found: C, 57.35; H, 4.1; N, 3.5. $C_{18}H_{15}CrNO_5$ requires C, 57.30; H, 4.01; N, 3.71%); ν_{max} (CH_2Cl_2)/cm^{-1} 3443w (NH), 1970s and 1895s (C≡O) and 1725m (C=O); δ_H (270 MHz; $CDCl_3$) 4.15 (2 H, d, *J* 6.5, NHCH_2), 5.15 (2 H, s, OCH_2), 5.20–5.40 (6 H, m, N*H* and Cr–C*H*) and 7.35–7.39 (5 H, m, Ph); δ_C (75.4 MHz; $CDCl_3$) 43.6 (*C*H$_2$NH), 67.2 (*C*H$_2$O), 91.3 and 93.2 (Cr–*C*$_{ortho/metal/para}$), 109.3 (Cr–*C*$_{ipso}$), 128.1 (Ph–*C*$_{ortho}$ or Ph–*C*$_{meta}$), 128.2 (Ph–*C*$_{para}$), 128.5 (Ph–*C*$_{ortho}$ or Ph–*C*$_{meta}$), 136.0 (Ph–*C*$_{ipso}$), 156.5 (*C*=O) and 232.6 (*C*≡O); *m*/*z* (EI) 377 (M$^+$, 0.2%), 321 (M − 2CO, 1), 293 (M − 3CO, 10), 185 (M − 3CO − PhCH$_2$O, 41), 157 (M − 3CO − PhCH$_2$OCO, 30) and 91 (PhCH$_2$, 100).

(±)-(η^6–1-Phenylethylamine)tricarbonylchromium(0) (±)-16 [15]

Following the general complexation procedure, (±)-1-phenylethylamine (0.60 g, 5.0 mmol), hexacarbonylchromium(0) (1.1 g, 5.0 mmol), dibutyl ether (30 cm^3) and THF (3 cm^3) were heated for 46 h to give, after filtration through Celite and flash column chromatography (SiO_2; CH_2Cl_2–EtOH, 1 : 0 to 19 : 1), the title complex (±)-**16** as a yellow oil (0.98 g, 3.8 mmol, 76%); ν_{max} (CH_2Cl_2)/cm^{-1} 1966s and 1888s (C≡O); δ_H (270 MHz; $CDCl_3$) 1.36 (3 H, d, *J* 6.7, C*H*$_3$), 1.50 (2 H, br s, N*H*$_2$), 3.84 (1 H, q, *J* 6.7, C*H*CH$_3$), 5.27–5.41 (4 H, m, Cr–C*H*), and 5.63 (1 H, d, *J* 6.5, Cr–C*H*$_{ortho}$); δ_C (75.4 MHz; $CDCl_3$) 26.0 (*C*H$_3$), 49.6 (*C*HCH$_3$), 90.0, 91.8, 92.1, 92.9 and 93.0 (*C*$_{ortho/metal/para}$), 119.0 (*C*$_{ipso}$) and 233.2 (*C*≡O); *m*/*z* (EI) 257 (M$^+$, 72%), 229 (M − CO, 20), 201 (M − 2CO, 53), 173 (M − 3CO, 91), 156 (M − 3CO − NH$_3$, 97) and 52 (Cr, 100). Complex **16** darkened over several days storage under N_2 and was conveniently stockpiled as the trifluoroacetic acid salt, formed by addition of trifluoroacetic acid (1.1 equiv.) to a CH_2Cl_2 solution of the complex (0.2 M), followed by addition of an equal volume of diethyl ether to induce precipitation. The precipitate was filtered and washed with diethyl ether to give (η^6-1-phenylethylammonium)tricarbonylchromium(0) trifluoroacetate **17** as a yellow solid; δ_H (270 MHz; CD_3SOCD_3) 1.53 (3 H, d, *J* 6.7, C*H*$_3$), 4.21 (1 H, q, *J* 6.7, C*H*CH$_3$), 5.74–5.80 (2 H, m, Cr–C*H*$_{meta}$), 5.84–5.89 (1 H, m, Cr–C*H*$_{para}$), (2 H, d, *J* 6, Cr–C*H*$_{ortho}$) and 8.44 (3 H, br s, N*H*$_3$). The free amine could be regenerated by addition of saturated aqueous K_2CO_3, extraction into diethyl ether and removal of the solvent *in vacuo*.

(*S*)-(+)-(η^6–1-Phenylethylamine)tricarbonylchromium(0) (*S*)-16

Following the procedure used for (±)-**16**, except using (*S*)-(−)-1-phenylethylamine instead of the racemate, complex (*S*)-**16** was isolated as a yellow oil (1.02 g, 3.97 mmol, 79%); $[\alpha]_D^{25}$ +20 (*c* = 1, CH_2Cl_2). The ^{1}H NMR and TLC data were identical to those of racemic complex **16**.

(±)-[η^6-*N*-(*tert*-Butoxycarbonyl)-1-phenylethylamine]tricarbonylchromium(0) (±)-18

A solution of (η^6-1-phenylethylammonium)tricarbonylchromium(0) trifluoroacetate **17** (36 mg, 0.10 mmol), di-*tert*-butyl dicarbonate (26 mg, 0.12 mmol) and triethylamine (20 µl, 0.14 mmol) in MeOH (1 cm^3) was stirred at room temperature for 2 h. The solvent was removed *in vacuo* and the residue purified by flash chromatography [SiO_2; CH_2Cl_2–petroleum ether (bp 40–60 °C), 6 : 4] and recrystallisation from diethyl ether–petroleum ether (bp 40–60 °C) to give the *title complex* (±)-**18** as a yellow solid (26 mg, 0.073 mmol, 72%), mp 79–81 °C; ν_{max} (CH_2Cl_2)/cm^{-1} 3447w (NH), 1970s and 1892s (C≡O) and 1708m (C=O); δ_H (270 MHz; $CDCl_3$) 1.46–1.48 [12 H, overlapping s and d, $J \approx 6$, C(CH_3)$_3$ and CHCH_3], 4.62–4.80 (2 H, br m, C*H*N*H*), 5.24–5.36 (3 H, m, Cr–C*H*), 5.40–5.44 (1 H, m, Cr–C*H*) and 5.47–5.50 (1 H, m, Cr–C*H*); δ_C (67.9 MHz; $CDCl_3$) 20.3 (CH*C*H$_3$), 28.3 [C(*C*H$_3$)$_3$], 47.6 (*C*HNH), 80.2 [*C*(CH$_3$)], 91.3, 91.4, 92.9 and 93.3 (*C*$_{ortho/metal/para}$), 114.0 (*C*$_{ipso}$), 155.1 (*C*=O) and 232.7 (*C*≡O); *m*/*z* (CI, NH$_3$) 375 [(M + NH$_4$)$^+$, 13%], 319 [M + NH$_4$ − (CH$_3$)$_2$C=CH$_2$, 28], 239 [M + NH$_4$ − Cr(CO)$_3$, 30] and 183 [M + NH$_4$ − Cr(CO)$_3$ − (CH$_3$)$_2$C=CH$_2$, 100] [Found: (M + NH$_4$)$^+$; 375.1023. $C_{16}H_{23}CrN_2O_5$ requires 375.1012].

(±)-[η^6-*N*-(Benzyloxycarbonyl)-1-phenylethylamine]tricarbonylchromium(0) 19

Racemic (η^6-1-Phenylethylammonium)tricarbonylchromium(0) trifluoroacetate **17** (36 mg, 0.10 mmol), saturated aqueous $KHCO_3$ (2 cm^3) and diethyl ether (2 cm^3) were stirred at room temperature for 10 min. Benzyl chloroformate (17 µl, 0.12 mmol) was added and stirring was continued for a further 0.5 h. The layers were separated and the aqueous layer extracted with diethyl ether until no longer yellow. The combined organic phase was dried (Na_2SO_4) and the solvent removed *in vacuo*. The residue was purified by flash chromatography [SiO_2; CH_2Cl_2–petroleum ether (bp 40–60 °C), 8 : 2] followed by recrystallisation from diethyl ether–petroleum ether (bp 40–60 °C) to give the *title complex* **19** as a yellow solid (17 mg, 0.043 mmol, 43%), mp 86–87 °C (Found: C, 58.05; H, 4.1; N, 3.5. $C_{19}H_{17}CrNO_5$ requires C, 58.31; H, 4.38; N, 3.58%); ν_{max} (CH_2Cl_2)/cm^{-1} 3432w (NH), 1970s and 1888s (C≡O) and 1716m (C=O); δ_H (270 MHz; $CDCl_3$) 1.49 (3 H, d, *J* 6.7, CHCH_3), 4.73 (1 H, br m, NHC*H*), 4.95–5.02 (1 H, s, N*H*), 5.07–5.18 (2 H, m, OCH_2), 5.25–5.30 (2 H, m, Cr–C*H*), 5.33–5.41 (2 H, Cr–C*H*), 5.47–5.50 (1 H, m, Cr–C*H*) and 7.29–7.40 (5 H, m, Ph); δ_C (67.9 MHz; $CDCl_3$) 20.2 (*C*H$_3$), 48.4 (*C*HNH), 67.2 (*C*H$_2$O), 91.3, 93.0 and 93.2 (Cr–*C*$_{ortho/metal/para}$), 113.2 (Cr–*C*$_{ipso}$), 128.2 (Ph–*C*$_{ortho}$ or Ph–*C*$_{meta}$), 128.3 (Ph–*C*$_{para}$), 128.6 (Ph–*C*$_{ortho}$ or Ph–*C*$_{meta}$), 136.1 (Ph–*C*$_{ipso}$), 155.7 (*C*=O) and 232.6 (*C*≡O); *m*/*z* (EI) 391 (M$^+$, 1%), 307 (M − 3CO, 15), 199 (M − 3CO − PhCH$_2$O, 61), 171 (M − 3CO − PhCH$_2$OCO, 20) and 105 (PhCHCH$_3$, 100).

(*S*)-(−)-[η^6-*N*-(Benzyloxycarbonyl)-1-phenylethylamine]-tricarbonylchromium(0) (*S*)-19

A similar procedure to that for (±)-**19** was followed using (*S*)-(η^6-1-phenylethylammonium)tricarbonylchromium(0) trifluoroacetate (*S*)-**17** (179 mg, 0.50 mmol), saturated aqueous $KHCO_3$ (5 cm^3) and diethyl ether (5 cm^3) and benzyl chloroformate (86 µl, 0.60 mmol) to give the *title complex* (*S*)-**19** as a yellow solid (147 mg, 0.376 mmol, 75%); $[\alpha]_D^{25}$ −30 (*c* = 1, CH_2Cl_2); ^{1}H NMR and TLC were identical to those of racemic complex **19**; HPLC: Chiralcel OD-H column; eluent propan-2-ol–hexane, 3 : 7; flow rate 1 cm^3 min^{-1}; detection 330 nm; (−)-**19** RT 13.8 min, (+)-**19** RT 16.8 min; e.e. ≥ 99%.

Attempted deprotonation of [η^6-*N*-(benzyloxycarbonyl)benzylamine]tricarbonylchromium(0) 15 using chiral lithium amide 5

A solution of lithium amide **5** was prepared by addition of BuLi (1.6 M in hexanes, 0.55 cm^3, 0.88 mmol) to a stirred

solution of the precursor chiral diamine (185 mg, 0.44 mmol) in THF (2 cm^3) at −78 °C, followed by warming to room temperature. The resulting pink solution was recooled to −78 °C and a solution of flame-dried LiCl (17 mg, 0.40 mmol) in THF (4 cm^3) was added *via* a cannula. A stirred solution of complex **15** (151 mg, 0.40 mmol) in THF (3 cm^3) at −78 °C was treated with BuLi (1.6 M in hexanes, 0.24 cm^3, 0.38 mmol) and the resultant solution added *via* a cannula to the lithium amide–LiCl solution at −40 °C over approximately 2 min. After 2.5 h at −40 °C, MeI (0.10 cm^3, 1.61 mmol) was added followed by, after a further 1 h at −40 °C, MeOH (1 cm^3). The mixture was allowed to warm to room temperature, the solvents removed *in vacuo* and the residue subjected to flash chromatography (SiO_2; toluene–diethyl ether, 50 : 1) to give an inseparable mixture of methylated complex **19** and starting complex **15** (107 mg) in 38 : 62 ratio, as determined by integration of the methyl signal for **19** and methylene signal for **15** in the ^1H NMR spectrum.

[η⁶-*N*-(2,2-Dimethylpropylidene)benzylamine]tricarbonylchromium(0) 25

A mixture of benzylamine complex **11** (1.75 g, 7.20 mmol), trimethylacetaldehyde (0.93 cm^3, 8.6 mmol) and silica gel (3 g) in CH_2Cl_2 (5 cm^3) was stirred for 0.5 h at room temperature. The slurry was transferred to a column with sintered glass fritt, with residual material transferred in diethyl ether. The column was eluted with diethyl ether, the solvents removed *in vacuo* and the residue recrystallised from petroleum ether (bp 40–60 °C) to give the *title complex* **25** as a yellow powder (1.78 g, 5.72 mmol, 79%), mp 62–62.5 °C (Found: C, 57.75; H, 5.45; N, 4.65. $C_{15}H_{17}CrNO_3$ requires C, 57.88; H, 5.50; N, 4.50%); ν_{max} (CH_2Cl_2)/cm^{-1} 1967s and 1890s (C≡O) and 1667m (C=N); δ_H (270 MHz; $CDCl_3$) 1.11 [9 H, s, C(CH_3)$_3$], 4.32 (2 H, d, *J* 1.2, CH_2), 5.22–5.26 (1 H, m, Cr–CH_{para}), 5.34–5.40 (4 H, m, Cr–$CH_{ortho/meta}$) and 7.67 (1 H, t, *J* 1.2, C*H*=N); δ_C (75.4 MHz; $CDCl_3$) 26.7 [C(CH_3)$_3$], 36.6 [*C*(CH_3)$_3$], 62.4 (CH_2), 91.5 (C_{para}), 92.1 and 93.0 (C_{ortho} and C_{meta}), 111.4 (C_{ipso}), 175.1 (H*C*=N) and 233.0 (*C*≡O); *m*/*z* (EI) 311 (M^+, 19%), 255 (M − 2CO, 45), 227 (M − 3CO, 85), 143 ($CrPhCH_2$, 96) and 135 [$CrNCC(CH_3)_3$, 100].

(±)-[η⁶-*N*-(2,2-Dimethylpropylidene)-α-(trimethylsilyl)benzylamine]tricarbonylchromium(0) (±)-26

LDA (1.47 M in cyclohexane, 0.33 cm^3, 0.49 mmol) was added to THF (5 cm^3) at −78 °C after which Me_3SiCl (0.10 cm^3, 0.8 mmol) was added, with stirring. A solution of complex **25** (125 mg, 0.40 mmol) in THF (5 cm^3) was added *via* a cannula. The resulting red solution was stirred for 0.5 h at −78 °C, MeOH (1 cm^3) was added, the mixture was allowed to warm to room temperature and the solvents removed *in vacuo*. The residue was subjected to column chromatography [SiO_2; diethyl ether–petroleum ether (bp 40–60 °C), 1 : 19] to give the *title complex* (±)-**26** as a yellow crystalline solid (109 mg, 0.285 mmol, 71%), mp 92–93 °C (Found: C, 56.3; H, 6.35; N, 3.65. $C_{18}H_{25}CrNO_3Si$ requires C, 56.38; H, 6.57; N, 3.65%); ν_{max} (CH_2Cl_2)/cm^{-1} 1962s and 1882s (C≡O) and 1660w (C=N); δ_H (300 MHz; $CDCl_3$) 0.00 [9 H, s, Si(CH_3)$_3$], 1.12 [9 H, s, C(CH_3)$_3$], 3.64 (1 H, s, C*H*$SiMe_3$), 5.09 (1 H, d, *J* 6.5, Cr–CH_{ortho}), 5.20 (1 H, m, Cr–CH_{meta}), 5.34 (1 H, m, Cr–CH_{para}), 5.42 (1 H, m, Cr–CH_{meta}), 5.76 (1 H, d, *J* 6.5, Cr–CH_{ortho}) and 7.51 (1 H, s, C*H*=N); δ_C (67.9 MHz; $CDCl_3$) −3.8 [Si(CH_3)$_3$], 27.0 [C(CH_3)$_3$], 36.6 [*C*(CH_3)$_3$], 67.2 (*C*H$SiMe_3$), 90.2, 90.3, 90.6, 92.9 and 93.5 ($C_{ortho/meta/para}$), 117.3 (C_{ipso}), 169.6 (H*C*=N) and 233.6 (*C*≡O); *m*/*z* (EI) 383 (M^+, 37%), 327 (M − 2CO, 17), 299 (M − 3CO, 82) and 135 [$CrNCC(CH_3)_3$, 100].

(−)-[η⁶-*N*-(2,2-Dimethylpropylidene)-α-(trimethylsilyl)benzylamine]tricarbonylchromium(0) (−)-26

BuLi (1.6 M in hexanes, 0.55 cm^3, 0.88 mmol) was added to a stirred solution of the diamine precursor to diamide **5** (185 mg, 0.44 mmol) in THF (6 cm^3) at −78 °C, and the mixture warmed to room temperature. The resulting pink solution was recooled to −78 °C and a solution of flame-dried LiCl (17 mg, 0.40 mmol) in THF (4 cm^3) was added *via* a cannula. Me_3SiCl (0.13 cm^3, 1.0 mmol) was added, followed by complex **25** (125 mg, 0.40 mmol) in THF (5 cm^3) and the resulting red solution was stirred at −78 °C for 0.5 h. MeOH (1 cm^3) was added, the mixture warmed to room temperature and the solvents removed *in vacuo*. The residue was subjected to column chromatography [SiO_2; diethyl ether–petroleum ether (bp 40–60 °C), 1 : 19] to give the *title complex* (−)-**26** as a yellow crystalline solid (137 mg, 0.357 mmol, 89%); $[a]_D^{25}$ −23 (*c* = 1, CH_2Cl_2); HPLC: Chiralcel OD-H column; eluent propan-2-ol–hexane, 1 : 1999; flow rate 1 cm^3 min^{-1}; detection 330 nm; (+)-**26** RT 10.4 min, (−)-**26** RT 11.4 min; e.e. 87%.

(η⁶-*N*-Benzylidenebenzylamine)tricarbonylchromium(0) 27

A mixture of benzylamine complex **11** (340 mg, 1.40 mmol), benzaldehyde (0.20 cm^3, 2.0 mmol) and silica gel (1 g) in CH_2Cl_2 (3 cm^3) was stirred for 0.5 h at room temperature. The slurry was transferred to a column with sintered glass fritt, with residual material transferred in diethyl ether. The column was eluted with diethyl ether, the solvents removed *in vacuo* and the residue recrystallised from diethyl ether–petroleum ether (bp 40–60 °C) to give the *title complex* **27** as yellow crystals (375 mg, 1.13 mmol, 81%), mp 87–88 °C (Found: C, 61.4; H, 3.65; N, 4.1. $C_{17}H_{13}CrNO_3$ requires C, 61.63; H, 3.96; N, 4.23%); ν_{max} (CH_2Cl_2)/cm^{-1} 1968s and 1889s (C≡O) and 1642m (C=N); δ_H (300 MHz; $CDCl_3$) 4.56 (2 H, s, CH_2), 5.24–5.28 (1 H, m, Cr–CH_{para}), 5.40–5.48 (4 H, m, Cr–$CH_{ortho/meta}$), 7.42–7.49 (3 H, m, Ph–$CH_{meta/para}$), 7.80–7.84 (2 H, m, Ph–CH_{ortho}) and 8.42 (1 H, s, C*H*=N); δ_C (75.4 MHz; $CDCl_3$) 63.0 (CH_2), 91.1 (Cr–C_{para}), 92.1 and 93.1 (Cr–C_{ortho} and Cr–C_{meta}), 110.6 (Cr–C_{ipso}), 128.4 and 128.6 (Ph–C_{ortho} and Ph–C_{meta}), 131.2 (Ph–C_{para}), 135.6 (Ph–C_{ipso}), 163.3 (H*C*=N) and 232.8 (*C*≡O); *m*/*z* (EI) 331 (M^+, 2%), 303 (M − CO, 3), 275 (M − 2CO, 11), 247 (M − 3CO, 47), 155 (CrNCPh, 47), 91 ($PhCH_2$, 63) and 52 (Cr, 100).

[η⁶-*N*-(4-Dimethylaminobenzylidene)benzylamine]tricarbonylchromium(0) 28

A mixture of benzylamine complex **11** (340 mg, 1.40 mmol), 4-dimethylaminobenzaldehyde (209 mg, 1.40 mmol) and silica gel (1 g) in CH_2Cl_2 (5 cm^3) was stirred for 1 h at room temperature. The slurry was transferred to a column with sintered glass fritt, with residual material transferred in diethyl ether. The column was eluted with diethyl ether, the solvents removed *in vacuo* and the residue recrystallised from diethyl ether–CH_2Cl_2 to give the *title complex* **28** as yellow plates (318 mg, 0.85 mmol, 61%), mp 109.5–110.5 °C (Found: C, 60.85; H, 4.65; N, 7.35. $C_{19}H_{18}CrN_2O_3$ requires C, 60.96; H, 4.85; N, 7.48%); ν_{max} (CH_2Cl_2)/cm^{-1} 1962s and 1888s (C≡O), 1636m and 1607s (C=N); δ_H (270 MHz; $CDCl_3$) 3.03 [6 H, s, N(CH_3)$_2$], 4.47 (2 H, s, CH_2), 5.20–5.25 (1 H, m, Cr–CH_{para}), 5.37–5.45 (4 H, m, Cr–$CH_{ortho/meta}$), 6.70 (2 H, d, *J* 8.9, Me_2NCCH), 7.65 (2 H, d, *J* 8.9, N=CHC*CH*) and 8.24 (1 H, s, C*H*=N); δ_C (67.9 MHz; $CDCl_3$) 40.1 [N(CH_3)$_2$], 63.2 (CH_2), 91.1 (Cr–C_{para}), 92.4 and 93.2 (Cr–C_{ortho} and Cr–C_{meta}), 111.5 (Me_2NCCH), 111.6 (Cr–C_{ipso}), 123.7 (N=CH*C*), 129.9 (N=CHC*C*H), 152.4 (Me_2NC), 163.3 (H*C*=N) and 233.0 (*C*≡O); *m*/*z* (EI) 374 (M^+, 4%), 318 (M − 2CO, 16), 290 (M − 3CO, 40), 198 [$CrNC(C_6H_4)NMe_2$, 58], 91 ($PhCH_2$, 100) and 52 (Cr, 79).

[η⁶-*N*-(4-Nitrobenzylidene)benzylamine]tricarbonylchromium(0) 29

A mixture of benzylamine complex **11** (340 mg, 1.40 mmol), 4-nitrobenzaldehyde (212 mg, 1.40 mmol) and silica gel (1 g) in CH_2Cl_2 (3 cm^3) was stirred for 1 h at room temperature. The

slurry was transferred to a column with sintered glass fritt, with residual material transferred in diethyl ether. The column was eluted with diethyl ether–CH_2Cl_2, 1 : 1, the solvents removed *in vacuo* and the residue recrystallised from diethyl ether–CH_2Cl_2 to give the *title complex* **29** as yellow-orange plates (363 mg, 0.965 mmol, 69%), mp 114.5–115.5 °C (Found: C, 53.95; H, 2.95; N, 7.2. $C_{17}H_{12}CrN_2O_5$ requires C, 54.26; H, 3.21; N, 7.44%); ν_{max} (CH_2Cl_2)/cm^{-1} 1968s and 1886s (C≡O), 1648w and 1603w (C=N), 1526m and 1347m (N–O); δ_H (300 MHz; $CDCl_3$) 4.63 (2 H, s, CH_2), 5.28–5.33 (1 H, m, Cr–CH_{para}), 5.40–5.48 (4 H, m, Cr–C$H_{ortholmeta}$), 7.98 (2 H, ABd, *J* 8.8, O_2NCCH), 8.31 (2 H, ABd, *J* 8.8, N=CHCCH) and 8.50 (1 H, s, CH=N); δ_C (67.9 MHz; $CDCl_3$) 63.0 (*C*H$_2$), 91.5 (Cr–C_{para}), 92.1 and 92.9 (Cr–C_{ortho} and Cr–C_{meta}), 109.7 (Cr–C_{ipso}), 123.9 (O_2NC*C*H), 129.1 (N=CHC*C*H), 141.0 (N=CH*C*), 149.3 (O_2N*C*), 161.0 (H*C*=N) and 232.8 (*C*≡O); *m*/*z* (EI) 376 (M$^+$, 1%), 320 (M − 2CO, 3), 292 (M − 3CO, 13), 240 [M − Cr(CO)$_3$, 24] and 91 (PhCH$_2$, 100).

General procedure for the synthesis of [η^6-*N*-(benzyloxycarbonyl)-1-phenylethylamine]tricarbonylchromium(0) 19 from *N*-benzylimine complexes using chiral lithium amide 5

BuLi (1.26–1.6 M in hexanes, 0.88 mmol) was added to a stirred solution of the chiral diamine precursor to **5** (185 mg, 0.44 mmol) in THF (6 cm^3) at −78 °C, and the mixture warmed to room temperature. The resulting pink solution was recooled to −78 °C and a solution of flame-dried LiCl (17 mg, 0.40 mmol) in THF (4 cm^3) was added *via* a cannula. The *N*-benzylimine complex (0.40 mmol) in THF (5 cm^3) was added *via* a cannula over approximately 2 min and the resulting deep orange to red solution stirred at −78 °C for 2 h. MeI (0.25 cm^3, 4.0 mmol) was added followed by, after 1 h, MeOH (1 cm^3). The mixture was warmed to room temperature, the solvents removed *in vacuo*, MeOH (10 cm^3) was added, followed by 6 M aqueous HCl (6 cm^3) and the mixture stirred until imine hydrolysis was complete by TLC. The mixture was cooled to 0 °C and saturated aqueous K_2CO_3 was added dropwise until the pH was above 9. Diethyl ether (5 cm^3) was added, followed by benzyl chloroformate (70 μl, 0.49 mmol) and the mixture stirred at room temperature for 0.5 h after which the layers were separated and the aqueous layer extracted with further diethyl ether until no longer yellow. The combined organic layers were dried (Na_2SO_4), the solvent removed *in vacuo* and the residue subjected to column chromatography (SiO_2; diethyl ether–toluene, 3 : 97). ^{1}H NMR and TLC were identical to those of authentic complex **19**.

Synthesis of complex (+)-19 from [η^6-*N*-(2,2-dimethylpropylidene)benzylamine]tricarbonylchromium(0) 25

The general procedure given above was followed using BuLi (1.6 M, 0.55 cm^3, 0.88 mmol) and complex **25** (125 mg, 0.40 mmol). Imine hydrolysis was complete within 0.5 h at room temperature. [η^6-*N*-(Benzyloxycarbonyl)-1-phenylethylamine]tricarbonylchromium(0) **19** was isolated as a yellow solid (108 mg, 0.276 mmol, 69%); $[a]_D^{25}$ +26 (c = 1, CH_2Cl_2); HPLC: as above for the direct synthesis of **19**; e.e. 81%.

Synthesis of complex (+)-19 from (η^6-*N*-benzylidenebenzylamine)tricarbonylchromium(0) 27

The procedure given above was followed using BuLi (1.26 M, 0.70 cm^3, 0.88 mmol) and complex **27** (133 mg, 0.40 mmol). Imine hydrolysis was complete within 0.5 h at room temperature. [η^6-*N*-(Benzyloxycarbonyl)-1-phenylethylamine]tricarbonylchromium(0) **19** was isolated as a yellow solid (108 mg, 0.276 mmol, 69%); $[a]_D^{25}$ +23 (c = 1, CH_2Cl_2); HPLC: as above for the direct synthesis of **19**; e.e. 55%.

Synthesis of complex (+)-19 from [η^6-*N*-(4-dimethylaminobenzylidene)benzylamine]tricarbonylchromium(0) 28

The procedure given above was followed using BuLi (1.26 M, 0.70 cm^3, 0.88 mmol) and complex **28** (150 mg, 0.40 mmol). Imine hydrolysis was complete within 1 h at room temperature. [η^6-*N*-(Benzyloxycarbonyl)-1-phenylethylamine]tricarbonylchromium(0) **19** was isolated as a yellow solid (96 mg, 0.245 mmol, 61%); $[a]_D^{26}$ +26 (c = 1, CH_2Cl_2); HPLC: as above for the direct synthesis of **19**; e.e. 80%.

Attempted deprotonation of [η^6-*N*-(4-nitrobenzylidene)benzylamine]tricarbonylchromium(0) 29 using chiral lithium amide 5

The procedure given above was initially followed using BuLi (1.6 M, 0.55 cm^3, 0.88 mmol) and complex **29** (150 mg, 0.40 mmol). On addition of the solution of complex **29** to the lithium amide–LiCl solution, the mixture became deep purple in colour with decomposition of the complex observed by TLC. The ^{1}H NMR spectrum (270 MHz; $CDCl_3$) of the purple residue obtained after addition of MeI, followed by MeOH and removal of the solvents *in vacuo*, revealed a complex mixture of products. In particular, no resonances ascribable to complexed arene ring protons (δ 5–6) were present.

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