Asymmetric Synthesis of Alpha Substituted Benzyl Alcohols *via* the Stereoselective Addition of Nucleophiles to Homochiral Tricarbonyl(η^6-*o*-trialkylsilylbenzaldehyde)chromium(0) Complexes

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The addition of nucleophiles to tricarbonyl(η^6-*o*-trialkylsilylbenzaldehyde)chromium(0) complexes proceeds with complementary diastereoselectivities in the presence or absence of strong Lewis acids. The ready availability of homochiral aldehyde complexes, *via* classical resolution with L-valinol, permits the synthesis of alpha substituted benzyl alcohols with high enantiomeric excesses.

The asymmetric synthesis of chiral alpha substituted benzyl alcohols *via* the stereoselective addition of nucleophiles to *ortho* substituted tricarbonyl(η^6-benzaldehyde)chromium(0) or tricarbonyl(η^6-acetophenone)chromium(0) complexes followed by decomplexation of the products, has been well reported.[1] A limitation of this approach to date has been the production of *ortho* substituted products. Asymmetric addition of dialkylzinc reagents to benzaldehyde *via* homochiral alkaloid[2] or amino alcohol[3] catalysis has been reported to give the corresponding alpha substituted benzyl alcohol derivatives in moderate to good enantiomeric excesses. However, the availability of suitable dialkylzinc reagents limits this approach. The use of trimethylsilyl group as a temporary protecting group in tricarbonyl(η^6-arene)chromium(0) chemistry has been well documented.[4] We wished to investigate the stereoselective addition of nucleophiles to homochiral tricarbonyl(η^6-*o*-trimethylsilylbenzaldehyde)chromium(0) (**1**) and homochiral tricarbonyl(η^6-*o*-tri-isopropylsilylbenzaldehyde)chromium(0) (**2**), where subsequent removal of the trialkylsilyl and tricarbonylchromium(0) groups would yield homochiral alpha substituted benzyl alcohols. Some of the results shown below have been previously communicated.[5]

Results and Discussion

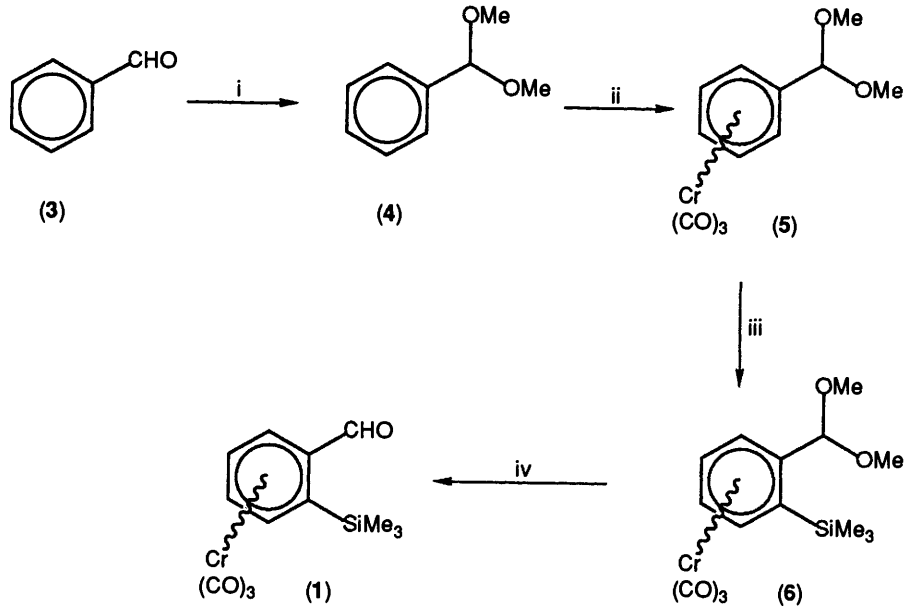
Racemic tricarbonyl(η^6-*o*-trimethylsilylbenzaldehyde)chromium(0) (**1**) was prepared in four steps starting from benzaldehyde (**3**). Treatment of the arene (**3**) with trimethyl orthoformate in the presence of a catalytic quantity of concentrated H_2SO_4 gave, after work-up and distillation, the corresponding dimethoxy acetal (**4**) in good yield.[6] The ^{1}H NMR spectrum of the arene (**4**) contained a six proton singlet (δ 3.35), characteristic of the two methoxy groups. Thermolysis of hexacarbonylchromium(0) with the arene (**4**) in a 10:1 mixture of dibutyl ether and tetrahydrofuran (THF), under an inert atmosphere of nitrogen, gave a yellow solution, which on subsequent work-up gave the corresponding tricarbonylchromium(0) complex (**5**) as yellow granules. The ^{1}H NMR spectrum of complex (**5**) contained the upfield proton multiplets of five contiguous complexed aromatic protons (δ 5.54–5.52, 5.38–5.34, 5.31–5.29) and a six-proton singlet (δ 3.39) characteristic of the dimethoxy acetal group.

Treatment of benzaldehyde acetals with alkyl-lithium reagents leads to regiospecific *ortho* metallation *via* chelation of the base with a benzylic oxygen.[7] The yield of this reaction can be enhanced by co-ordination of the arene to the tricarbonylchromium(0) group.[8] Thus, addition of butyl-lithium followed by chlorotrimethylsilane to a cooled (−78 °C) THF solution of complex (**5**) gave, on work-up and recrystallisation, yellow needles in good yield. The product was identified as the *o*-trimethylsilyl acetal (**6**) on the basis of the ^{1}H NMR spectrum, which contained three aromatic proton multiplets consistent with four contiguous protons (δ 5.61–5.59, 5.47–5.45, 5.20–5.15) and a nine-proton singlet (δ 0.37) characteristic of a trimethylsilyl group. A molecular ion *m/z* 360 (M^+) in the mass spectrum and a correct elemental microanalysis confirmed the identity of the complex.

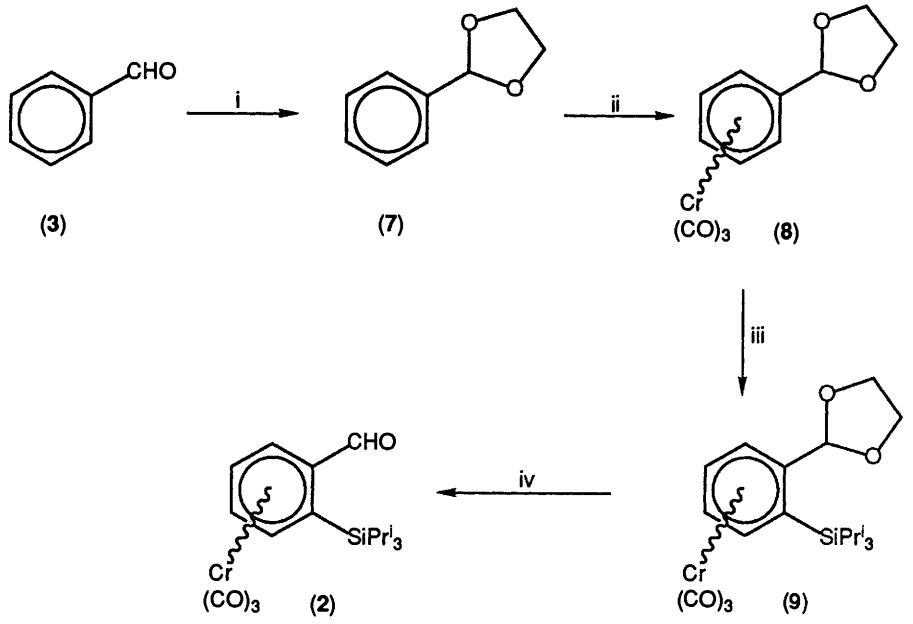
Subsequent prolonged (72 h) treatment of complex (**6**) with acidic, aqueous THF released tricarbonyl(η^6-*o*-trimethylsilylbenzaldehyde)chromium(0) (**1**) as a low melting point red solid in essentially quantitative yield (Scheme 1). The ^{1}H NMR spectrum of complex (**1**) was similar to that of complex (**6**) but with the loss of the two three-proton methoxy singlets (δ 3.53, 3.15) and a downfield shift of the benzylic proton (from δ 5.32 to 9.73). Presumably, the rate of hydrolysis of this acetal was slow due to the presence of the *ortho* trimethylsilyl group. Since loss of the benzylic methoxy groups occurs preferentially from conformations which place the leaving group antiperiplanar to the tricarbonylchromium(0) group, then hydrolysis may proceed at a relatively fast rate to the hemiacetal stage, but subsequent loss of the remaining methoxy group will presumably be slow due to the inability of the molecule to achieve conformations which place this group antiperiplanar to the tricarbonylchromium(0) group. Such conformations are inaccessible due to adverse steric interactions between the benzylic hydroxy group and the *ortho* silyl function.

Preparation of complex (**2**) followed a similar route, but using the ethane-1,2-diol derived acetal of benzaldehyde (**3**), since it was found that quenching the *ortho* lithiated acetal from complex (**5**) with chlorotri-isopropysilane proceeded in only very low yield. Benzaldehyde (**3**) was treated with ethane-1,2-diol and acid and heated in a Dean-Stark apparatus at reflux with benzene solvent. Distillation gave the required acetal (**7**) in good yield. The ^{1}H NMR spectrum of the product (**7**) contained a benzylic proton singlet (δ 5.85) and a four-proton multiplet (δ 4.21–4.02) characteristic of the dioxolane ring protons. Complexation of the acetal (**7**) under standard conditions gave, on work-up and recrystallisation, yellow plates in moderate yield, identified as tricarbonyl(η^6-2-phenyl-1,3-dioxolane)chromium(0) (**8**) on the basis of the upfield shifted aromatic proton signals in the ^{1}H NMR spectrum (from δ 7.55–7.39 to δ 5.58–5.54 and δ 5.37–5.29).

Regioselective silylation of complex (**8**), *via* a chelation controlled deprotonation *ortho* to the acetal substituent, was observed on treatment with butyl-lithium followed by chlorotri-isopropylsilane under standard alkylation conditions. The product was identified as the *o*-tri-isopropylsilylated compound (**9**) by ^{1}H NMR spectroscopy. The silyl group signals consisted



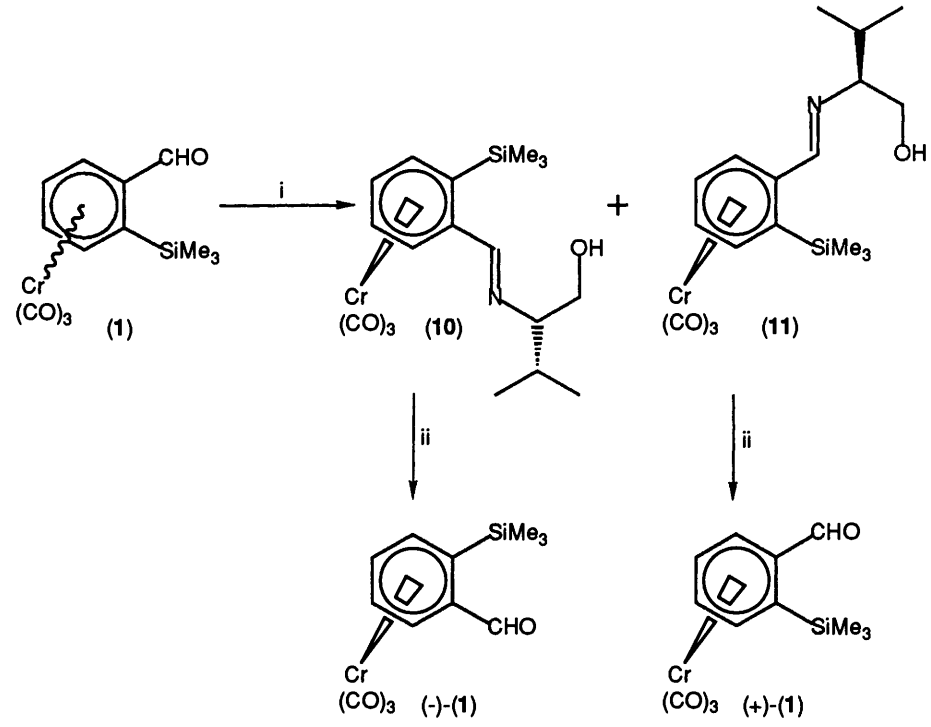
Scheme 1. *Reagents:* i, $H(COMe)_3$, H^+; ii, $Cr(CO)_6$, Bu_2O, THF, heat; iii, BuLi, THF, −78 °C; $SiMe_3Cl$, THF, −78 °C; iv, H_3O^+, THF.



Scheme 2. *Reagents:* i, $HOCH_2CH_2OH$, H^+; ii, $Cr(CO)_6$, Bu_2O, THF, heat; iii, BuLi, THF, −78 °C; $SiPr^i_3Cl$, THF, −78 °C; iv, H_3O^+, THF.

of a three-proton multiplet (δ 1.50–1.32) assigned as the protons alpha to silicon and two nine-proton doublets (δ 1.23, *J* 7.1 Hz, δ 1.18, *J* 7.1 Hz) characteristic of the diastereotopic methyl protons of the isopropyl groups. The two aromatic proton triplets (δ 5.72–5.66, 5.18–5.12) and two aromatic proton doublets (δ 5.54, 5.44–5.41) were characteristic of four contiguous protons, consistent with *ortho* functionalisation having occurred. Hydrolysis of complex (**9**) was achieved on treatment with acidic aqueous THF for 6 days. Again the slow rate of liberation of the free aldehyde (**2**) can be ascribed to the presence of the *ortho* silyl group (*vide supra*). Tricarbonyl(η^6-*o*-tri-isopropysilylbenzaldehyde)chromium(0) (**2**) was isolated as red needles in excellent yield (Scheme 2). The ^{1}H NMR spectrum of the product was similar to that of the acetal complex (**9**), but with the benzylic proton signal shifted downfield (from δ5.56 to 9.80) and loss of the dioxolane ring proton multiplet.

Treatment of tricarbonyl(η^6-*o*-trimethylsilylbenzaldehyde)-chromium(0) (**1**) with L-valinol in Et_2O containing 4 Å molecular sieves, gave an orange solution. Filtration through Celite and evaporation of the solvent left an orange oil which crystallised an addition of hexane.^{1}H NMR spectroscopy showed the solid to be a 50:50 mixture of the two imines (**10**) and (**11**) or their corresponding oxazolidines, with characteristic benzylic proton singlets (δ 8.24, 8.22). Chromatography (SiO_2) with Et_2O–Et_3N (10:1) as a basic eluant gave two fractions, which were separately evaporated and recrystallised from hexane to give orange needles. The ^{1}H NMR spectrum of fraction one contained a benzylic proton singlet (δ 8.24), two aromatic proton doublets (δ 6.10–6.07, 5.54–5.50), two aromatic proton triplets (δ 5.70–5.63, 5.31–5.25), and a nine-proton silyl singlet (δ 0.44). The ^{1}H NMR spectrum of fraction two contained a benzylic proton singlet (δ 8.22), two aromatic proton doublets (δ 5.98–5.95, 5.48–5.31), two aromatic proton



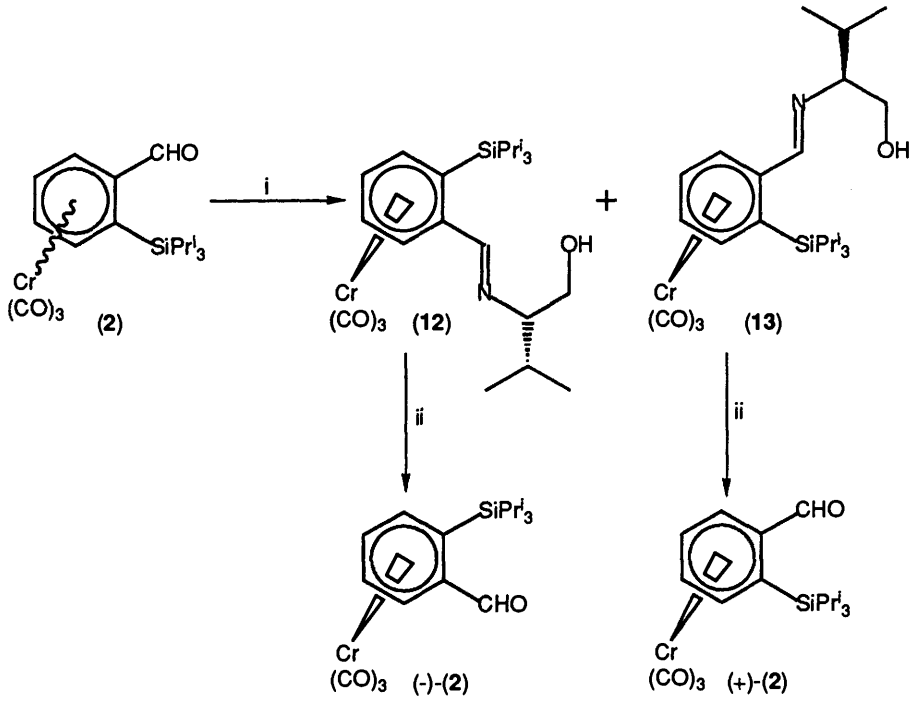
Scheme 3. *Reagents:* i, L-valinol, 4 Å molecular sieves, Et_2O; separate; ii, H_3O^+. THF

triplets (δ 5.66–5.59, 5.31–5.24) and a nine-proton silyl singlet (δ 0.43). Both products gave molecular ions *m/z* 399 (M^+) in their mass spectra. The two fractions were identified as imines (**10**) and (**11**) and not oxazolidines on the basis of their solution (CH_2Cl_2) IR C=N stretches at 1 632 cm^{-1} for fraction one and 1 640 cm^{-1} for fraction two.

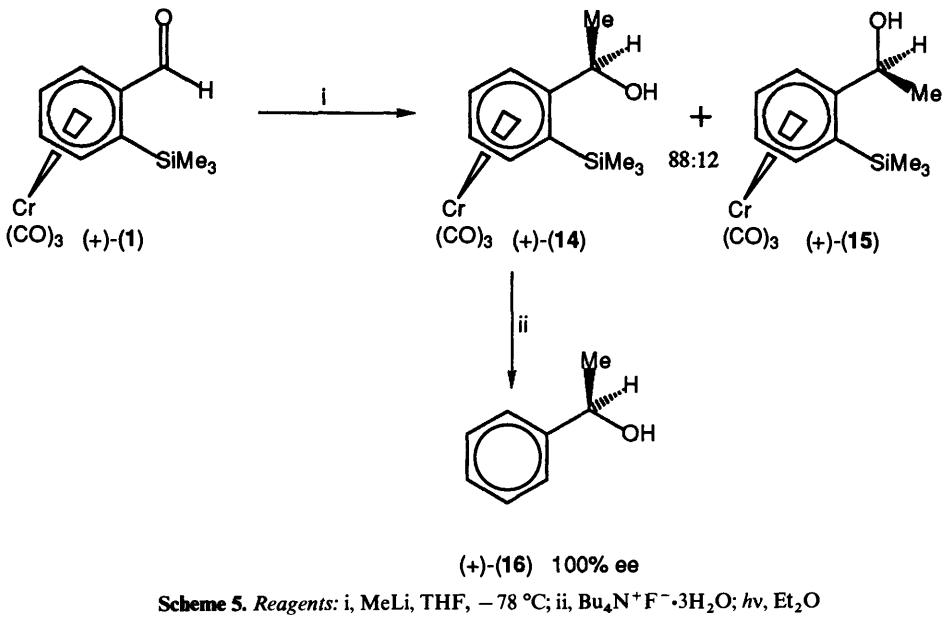
Hydrolysis of the first fraction in acidic aqueous THF gave a red oil, with a ^1H NMR spectrum identical with that of the racemic starting material (**1**). Optical rotation {$[\alpha]_D^{18}$ −154° (*c* 1 in $CHCl_3$)}, identified the product as (−)-tricarbonyl(η^6-*o*-trimethylsilylbenzaldehyde)chromium(0) (−)-(**1**). The presence of only a single compound, as detected by ^1H NMR spectroscopy, in fraction one prior to hydrolysis necessitates that the sample of (−)-(**1**) is homochiral. The absolute configuration of complex (−)-(**1**) was assigned by analogy with literature precedent.[9] Similarly hydrolysis of diastereoisomer (**11**) gave complex (+)-(**1**) {$[\alpha]_D^{20}$ +146° (*c* 0.1 in $CHCl_3$)}. Again the presence of only a single diastereoisomer as detected by ^1H NMR spectroscopy in fraction two prior to hydrolysis, necessitates that the sample of (+)-(**1**) is homochiral (Scheme 3).

The above methodology was extended to the resolution of tricarbonyl(η^6-*o*-tri-isopropylsilylbenzaldehyde)chromium(0) (**2**). Thus, treatment of racemic complex (**2**) with L-valinol in Et_2O containing 4 Å molecular sieves, gave an orange solution. Evaporation of an aliquot of the solution gave an orange oil. The ^1H NMR spectrum of the crude oil contained three sets of peaks in unequal ratios. The minor set of peaks was consistent with unchanged starting material (**2**). Chromatography (SiO_2) of the remainder of the mixture, with Et_2O–hexane–Et_3N (10:10:1) as eluant, gave three bands. The first fraction was identified as starting material (−)-(**2**) {$[\alpha]_D^{19}$ −384° (*c* 0.8 in $CHCl_3$)] by ^1H NMR spectroscopy. The optical activity of this fraction indicated that partial kinetic resolution had occurred, L-valinol reacting with (+)-(**2**) at a greater rate than with (−)-(**2**). The remaining two fractions were isolated separately and identified as the imines (**12**) and (**13**) and not oxazolidines by analogy with above. The ^1H NMR spectrum (C_6D_6) of the second fraction contained a benzylic proton singlet (δ 8.17), two aromatic proton doublets (δ 5.84–5.80, 5.13–5.10) and two aromatic proton triplets (δ 4.84–4.78, 4.34–4.28). The ^1H NMR spectrum (C_6D_6) of the third fraction contained a benzylic proton singlet (δ 8.21), two aromatic proton doublets (δ 5.82–5.78, 5.11–5.08) and two aromatic proton triplets (δ 4.86–4.80, 4.35–4.29). Acidic, aqueous THF hydrolysis of the second fraction gave compound (−)-(**2**) as a red solid, {$[\alpha]_D^{19}$ −485° (*c* 0.1 in $CHCl_3$)}, which must be homochiral due to the presence of only a single diastereoisomer at the imine stage prior to hydrolysis. Similarly, fraction three gave homochiral (+)-(**2**) as a red solid, {$[\alpha]_D^{21}$ +515° (*c* 0.1 in $CHCl_3$)}. The absolute configuration of (−)-(**2**) and (+)-(**2**) were assigned according to the literature precedent (Scheme 4).[9]

Treatment of (+)-tricarbonyl(η^6-*o*-trimethylsilylbenzaldehyde)chromium(0) (+)-(**1**) with MeLi in THF at −78 °C gave a yellow solution immediately. Work-up and chromatography gave the two 1-phenethanol derivatives (+)-(**14**) and (+)-(**15**) in a ratio of 88:12. The ^1H NMR spectrum of the major isomer (+)-(**14**) {$[\alpha]_D^{21}$ +20° (*c* 1 in $CHCl_3$)} incorporated a three-proton doublet (δ 1.56, *J* 6.5 Hz), a benzylic proton multiplet (δ 4.84–4.72) and a nine-proton silyl singlet (δ 0.41). A molecular ion *m/z* 330 (M^+) in the mass spectrum also confirmed the identity of the product. The ^1H NMR spectrum of the minor isomer (+)-(**15**) contained a three proton doublet (δ 1.48, *J* 6.3 Hz), a benzylic proton quartet (δ 4.82, *J* 6.3 Hz) and a nine-proton silyl singlet (δ 0.41). A molecular ion *m/z* 330 (M^+) in the mass spectrum also confirmed the identity of the product. Treatment of complex (+)-(**14**) with an excess of tetrabutylammonium fluoride trihydrate quantitatively desilylated the complex to give a yellow oil.[4] Standard decomplexation of the oil gave, following distillation, (+)-1-phenethanol as a clear oil (+)-(**16**) {$[\alpha]_D^{20}$ +51° (*c* 1 in $CHCl_3$), lit.,[10] $[\alpha]_D$ +39.5° (neat)} identified by comparison with an authentic sample. The absolute configuration of (+)-(**16**) was determined on the basis of the sign of the optical rotation-(+)-1-phenethanol has (*R*) stereochemistry.[10] Thus, the major isomer (+)-(**14**) produced on addition of MeLi to complex (+)-(**1**) must have the stereochemistry indicated below (Scheme 5).



Scheme 4. *Reagents:* i, L-valinol, 4 Å molecular sieves, Et_2O; separate; ii, H_3O^+, THF



Scheme 5. *Reagents:* i, MeLi, THF, −78 °C; ii, $Bu_4N^+F^-\cdot 3H_2O$; *hv*, Et_2O

Addition of MeMgI to racemic (**1**) in THF at −78° C gave a yellow solution, which on work-up gave a yellow oil. The ^1H NMR spectrum of the product contained two sets of peaks, which were consistent with an 17:83 mixture of complexes (**14**) and (**15**). The change in the stereoselectivity of addition from MeLi to MeMgI can be attributed to greater Lewis acidity of metal ion species in the Grignard reagent. Two types of addition can be envisaged, Lewis acid free and Lewis acid co-ordinated mechanisms (see Figures 1 and 2 respectively). In the Lewis acid free mechanism whilst the lowest energy conformer is (**18**), there will be an equilibrium population of conformer (**19**), possibly somewhat stabilised by a direct oxygen lone pair-silicon d-orbital interaction. Analysis of molecular models predicts that addition of the nucleophile to the carbonyl group will be much faster in conformer (**19**). In conformer (**18**) the preferred *ca.* 109° angle of attack of the nucleophile[11] is sterically hindered by the bulky trialkylsilyl group, whereas in conformer (**19**), the nucleophile can approach through free space. Thus, since the rate limiting step of this reaction is presumably the addition of the nucleophile and the equilibrium between the conformers is rapidly established, the major product will arise from addition to conformer (**19**) to give complex (**14**). This is in accord with the Curtin-Hammett principle.[12]

In the presence of strong Lewis acids, however, the first step of the reaction is co-ordination of the Lewis acid to the carbonyl oxygen. This drastically increases the size of the carbonyl group and thus conformer (**21**), Figure 2, is very strongly destabilised with respect to conformer (**20**). Consequently, the inaccessibility of conformer (**21**) means that the major product isomer will result from a slow addition of nucleophile to conformer (**20**), at

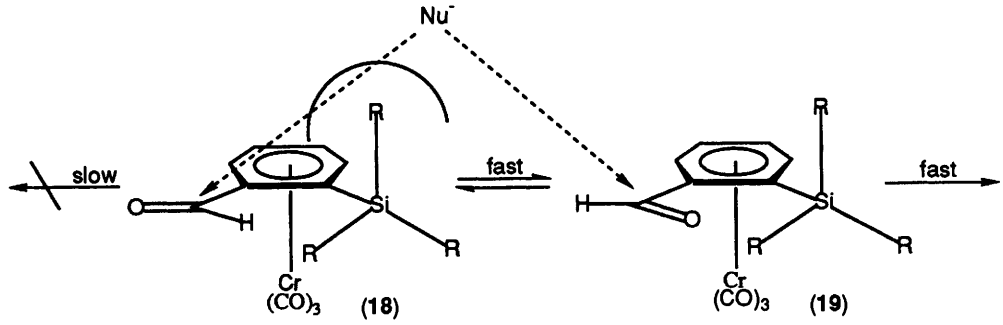


Figure 1. Lewis acid free mechanism for the addition of nucleophiles to tricarbonyl(η^6-*o*-trialkylsilylbenzaldehyde)chromium(0) complexes.

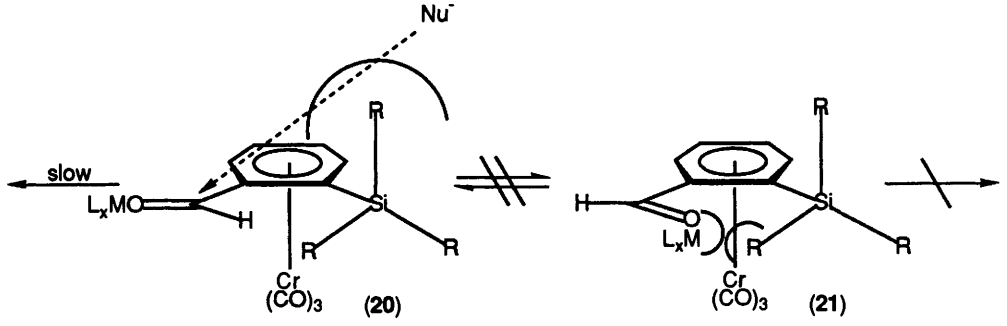
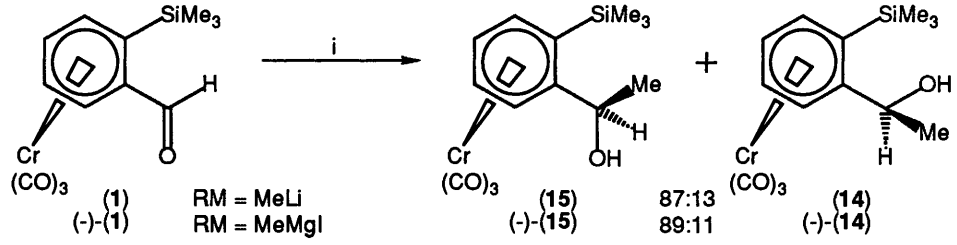


Figure 2. Lewis acid co-ordinated mechanism for the addition of nucleophiles to tricarbonyl(η^6-*o*-trialkylsilylbenzaldehyde)chromium(0) complexes.



Scheme 6. *Reagents:* i, $MgBr_2 \cdot OEt_2$, Et_2O; RM, Et_2O.

ca. 109° to the carbonyl group, to give complex (**15**). Alternatively, the Lewis acid co-ordinated species may have some chromium stabilised benzylic carbonium ion character with an exocyclic double bond to the benzylic carbon. The minimum energy trajectory of approach of nucleophiles onto this species would presumably not be at 109° to the carbonyl group, but antiperiplanar to the chromium-C_{ipso} bond and therefore not pass as close to the bulky silyl unit. The production of the minor diastereoisomers, complex (**15**) in the case of MeMgI and complex (**14**) in the case of MeLi addition, may result from the operation of both Lewis acid free and Lewis acid co-ordinated mechanisms to a greater or lesser extent.

If the two addition mechanisms to complex (**1**) depend entirely on the strength and concentration of Lewis acidic species, then addition of strong Lewis acids prior to the nucleophilic reagent should strongly favour the production of complex (**15**) over (**14**). Thus, pre-treatment of complex (**1**) in Et_2O with $MgBr_2 \cdot OEt_2$ (prepared from Mg and 1,2-dibromoethane in dry Et_2O),[13] gave a dark red solution, indicative of the formation of a strong Lewis acid co-ordinated species. Addition of MeLi [to pre-treated racemic (**1**)], or MeMgI [to pre-treated chiral (−)-(**1**)], at room temperature gave, on work-up, mixtures of complexes (**14**) and (**15**). In the case of MeLi addition the ratio of products (**14**) and (**15**) was 13:87, reflecting the expected changeover in selectivity and in the case of MeMgI addition the ratio was 11:89 (Scheme 6).

Mixtures of complexes (**14**) and (**15**) were separable by chromatography (Al_2O_3). Treatment of complex (−)-(**15**) with tetrabutylammonium fluoride trihydrate followed by oxidative decomplexation gave (*R*)-1-phenethanol (+)-(**16**) {$[\alpha]_D^{20}$ +56° (*c* 0.5 in $CHCl_3$), lit.,[10] $[\alpha]_D$ +39.5° (neat)} identified by comparison with an authentic sample. The enantiomeric purities of samples of (+)-(**16**) were checked by ^1H NMR spectroscopic analysis of their (*R*)-Mosher's esters[14] and found to be homochiral. [The (*R*)-Mosher's ester of racemic phenethanol (**16**) was prepared to confirm that no kinetic resolution in the esterification was occurring and that the diastereoisomeric esters of both (+)- and (−)-(**16**) were distinguishable by ^1H NMR spectroscopy.]

Another route through to complexes (**14**) and (**15**) was envisaged *via* a hydride reduction of tricarbonyl(η^6-*o*-trimethylsilylacetophenone)chromium(0) (**22**). In this complex the greater steric bulk of the α-methyl group over the carbonyl oxygen should favour conformations which place the carbonyl oxygen *syn* to the trimethylsilyl group. Use of hydride donors with weak Lewis acidic counterions such as Li^+ will presumably favour production of complex (**15**) over complex (**14**). Treatment of tricarbonyl(η^6-2-phenyl-2-methyl-1,3-dioxolane)-chromium(0) (**23**) with butyl-lithium followed by chlorotrimethylsilane gave the *ortho* silylated complex (**24**). The ^1H NMR spectrum of complex (**24**) contained two aromatic proton multiplets (δ 5.56–5.45, 5.28–5.20) integrating to four protons, a

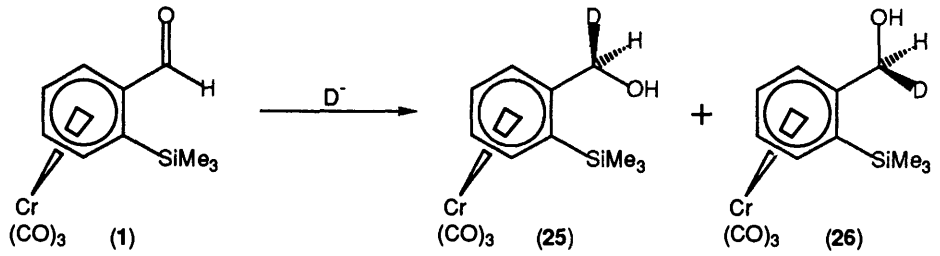
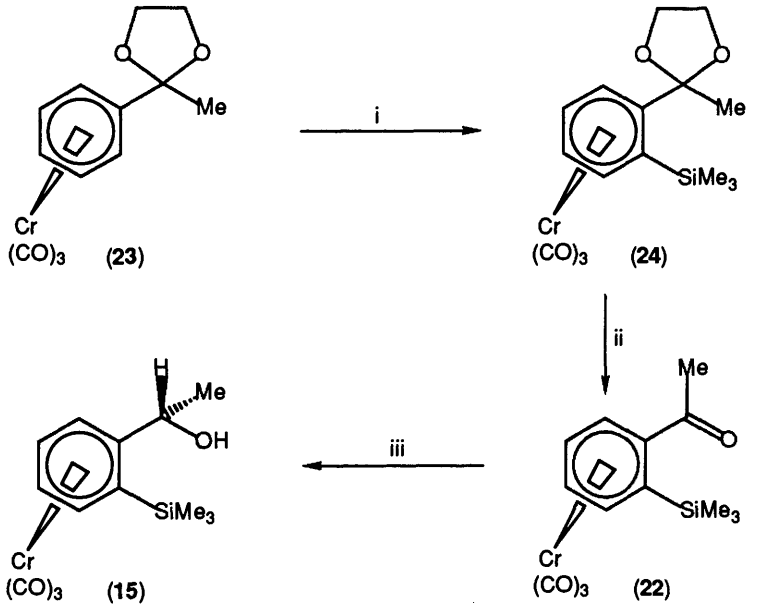


Table 1. Addition of deuteride to tricarbonyl(η^6-*o*-trimethylsilylbenzaldehyde)chromium(o) (1)

Entry	Reagent	Conditions	(25):(26)	Yield (%)
1	$LiEt_3BD$	THF, −78 °C	92:8	100%
2	$LiEt_3BD$	THF, −100 °C	92:8	98%
3	$LiEt_3BD$	CH_2Cl_2, −100 °C	75:25	99%
4	$LiEt_3BD$	Toluene, −91 °C	80:20	89%
5	$LiEt_3BD/MgBr_2{\cdot}OEt_2$	Et_2O, 20 °C	12:88	95%
6	$LiAlD_4$	THF, −78 °C	38:62	100%
7	$LiAlD_4/MgBr_2{\cdot}OEt_2$	Et_2O, 20 °C	4:96	72%



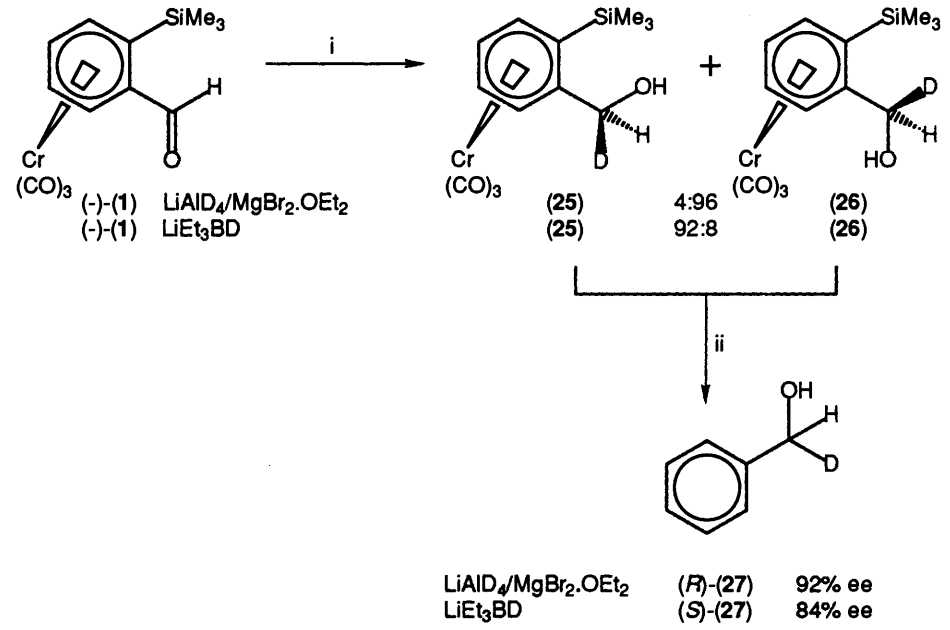
Scheme 7. *Reagents:* i, BuLi, THF, −78 °C; $SiMe_3Cl$, THF, −78 °C; ii, H_3O^+, THF; iii, $LiEt_3BH$, THF

four-proton multiplet (δ 4.16–4.00) characteristic of the dioxolane ring protons, a three-proton methyl singlet (δ 1.62), and a nine-proton silyl singlet (δ 0.40). Treatment of complex (**24**) with acidic, aqueous THF liberated the free acetophenone derivative (**22**). The ^1H NMR spectrum of complex (**22**) was similar to that of (**24**) but with the loss of the dioxolane ring proton multiplet and upfield shift of the methyl singlet (δ 2.49). Treatment of complex (**22**) with $LiEt_3BH$ in THF at −78 °C gave, on work-up, a single compound in good yield identified by ^1H NMR spectroscopy as complex (**15**) (Scheme 7). None of the benzylic epimer (**14**) was detected under these reaction conditions. This stereoselective addition is consistent with a Lewis acid free mechanism, involving *exo* attack of hydride at the carbonyl group in conformations which place the carbonyl oxygen and not the α-methyl group *syn* to the bulky *ortho* trimethylsilyl group.

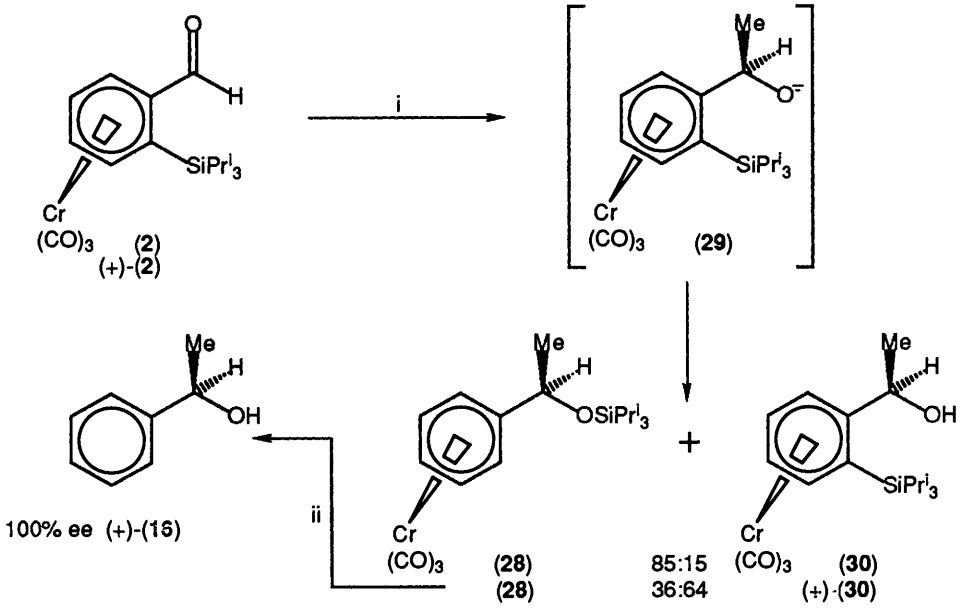
Addition of deuteride, from $LiEt_3BD$ and $LiAlD_4$, to racemic complex (**1**), with and without $MgBr_2{\cdot}OEt_2$ pre-treatment, was studied. The ratios of products (**25**) and (**26**) were determined using ^1H NMR spectroscopy (C_6D_6), by relative integration of the benzylic proton signals [(**25**), δ 4.06; (**26**), δ 3.88] and the results are summarised in Table 1 above.

Presumably $LiEt_3BD$ reacts primarily in the Lewis acid-free mode, whilst the reverse is true for $LiAlD_4$: this is consistent with the nature of the reagents. The reactions in Entries 1 and 7 of Table 1, were repeated on homochiral (−)-(**1**). The mixtures of diastereoisomers (**25**) and (**26**) were not separable and in both cases the mixture was desilylated with tetrabutylammonium fluoride trihydrate and oxidatively decomplexed to give α-deuteriobenzyl alcohol (**27**). The enantiomeric purities of both samples of (*R*)- and (*S*)-(**27**) were checked by ^1H NMR spectroscopic analysis of their (*R*)-Mosher's esters and found to range from 84% to 92% e.e., in accord with the observed d.e. of the products from the corresponding addition reactions (Scheme 8).

Since the rationale for the stereoselectivity observed in



Scheme 8. *Reagents:* i, D^-; ii, $Bu_4N^+F^-\cdot 3H_2O$; *hv*, O_2, Et_2O.



Scheme 9. *Reagents:* i, MeLi, THF, −78 °C; ii, $Bu_4N^+F^-\cdot 3H_2O$, *hv*, O_2, Et_2O.

the addition of nucleophiles to complex (**1**) depended upon the large steric bulk of the *o*-trimethylsilyl group, it may be predicted that increasing the size of the silyl group to tri-isopropylsilyl should increase the stereoselectivities observed. Addition of MeLi to a THF solution of racemic tricarbonyl-(η^6-*o*-tri-isopropylsilylbenzaldehyde)chromium(0) (**2**), gave on quenching with Pr^iOH and chromatography, two fractions in a ratio of 85:15. The ^1H NMR spectrum (C_6D_6) of fraction one contained two aromatic proton doublets (δ 5.07–5.03, 4.73–4.71), three aromatic protons with a benzylic proton multiplet (δ 4.45–4.35) and a three-proton methyl doublet (δ 1.17, *J* 6.3 Hz). The absence of an infrared hydroxy absorption band, low melting point (45–46 °C) and a correct elemental microanalysis confirmed the identity of the product as the *o*-tri-isopropylsilyl complex (**28**), presumably formed by a transfer of the silyl group from the aromatic ring to the benzylic oxygen within anion (**29**), generated after addition of the nucleophile. A similar migration in the reverse direction has been reported in the literature.[10] The second fraction was identified as the 1-phenethanol derivative (**30**) on the basis of its ^1H NMR spectrum which clearly indicated the presence of two aromatic proton triplets (δ 5.71–5.65, 5.25–5.19), two aromatic proton doublets (δ 5.53–5.50, 5.46–5.43), a methyl doublet (δ 1.59, *J* 6.3 Hz) and two silyl multiplets (δ 1.54–1.34, 1.26–1.18). Repeating the reaction on (+)-(**2**) but quenching with water at −78 °C to remove any phenethoxides before warming, followed by work-up and chromatography, gave complexes (**28**) and (+)-(**30**) $\{[\alpha]_D^{20}$ +129° (*c* 0.1 in $CHCl_3$)} as separate fractions in a ratio of 36:64. Desilylation of separate samples of compounds (**28**) and (+)-(**30**) with tetrabutylammonium fluoride trihydrate followed by standard decomplexation gave in both cases homochiral [by ^1H NMR spectroscopic analysis of the (*R*)-Mosher's ester derivatives], (*R*)-1-phenethanol (+)(**16**). This confirmed that the absolute configurations at the benzylic sites within complexes

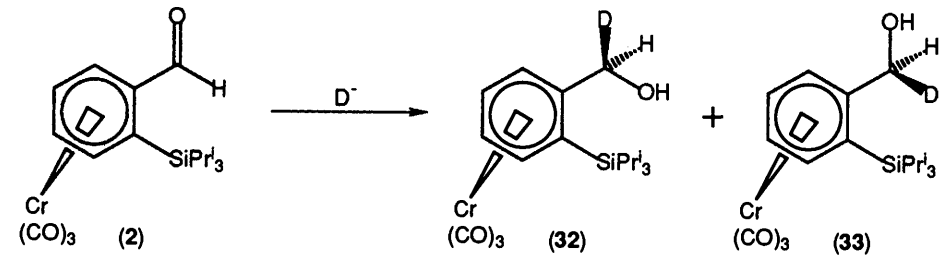
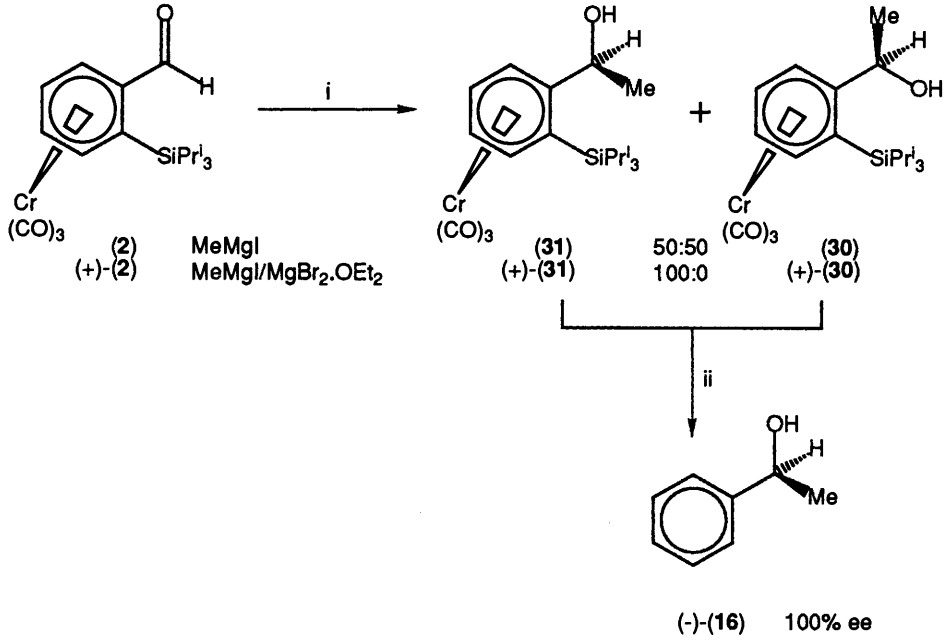


Table 2. Addition of deuteride to tricarbonyl(η^6-*o*-tri-isopropylsilylbenzaldehyde)chromium(0)

Entry	Reagent	Conditions	(32):(33)	Yield (%)
1	$LiEt_3BD$	THF, −78 °C	86:14	99
2	$LiEt_3BD/MgBr_2{\cdot}OEt_2$	Et_2O, 20 °C	12:88	92
3	$LiAlD_4$	THF, −78 °C	30:70	100
4	$LiAlD_4/MgBr_2{\cdot}OEt_2$	Et_2O, 20 °C	6:94	65



Scheme 10. *Reagents:* i, RM; ii, $Bu_4N^+F^-{\cdot}3H_2O$; *hν*, O_2, Et_2O.

(**28**) and (**30**) are the same and this is consistent with both complexes arising from the common intermediate oxygen anion (**29**). The stereochemistry of the products (**28**) and (**30**) is the same as that observed in the corresponding reaction using the trimethylsilyl analogue (**1**). This confirms the assignment of the absolute configuration of (+)-(**2**) as that shown below and is consistent with the literature precedent (Scheme 9).

Treatment of racemic complex (**2**) with MeMgI at −78 °C gave a mixture of products in a ratio of 50:50, identified by ^{1}H NMR spectroscopy as complex (**30**) and a new complex (**31**). Complex (**31**) had a similar spectrum to that of complex (**30**), clearly containing two aromatic proton triplets (δ 5.79–5.73, 5.22–5.15), two aromatic proton doublets (δ 5.55–5.51, 5.48–5.45) and a three-proton methyl doublet (δ 1.47, *J* 6.3 Hz). Compound (**31**) was assigned as the benzylic epimer of complex (**30**).

The increase in size of the silyl group has removed any selectivity in the Grignard addition reaction. Presumably the large silyl group sufficiently slows the rate of attack of nucleophile in conformer (**20**), Figure 2, so that products from the Lewis acid free pathway, Figure 1, are produced at an equivalent overall rate, despite the low concentration of unco-ordinated aldehyde. Repeating the reaction but with $MgBr_2{\cdot}OEt_2$ pre-treatment of complex (**2**) should ensure that there is no unco-ordinated aldehyde present and only a slow attack of nucleophile through conformer (**20**) of the Lewis acid co-ordinated pathway should be observed to give complex (**31**). Treatment of a crimson Et_2O solution of complex (+)-(**2**) with $MgBr_2{\cdot}OEt_2$ in Et_2O gave a dark red solution, which slowly turned yellow on addition of MeMgI. Work-up gave a single compound in essentially quantitative yield, identified by ^{1}H NMR spectroscopy as (+)-(**31**) $\{[\alpha]_D^{20}$ +79° (*c* 0.8 in $CHCl_3)\}$. Fluoride-mediated desilylation followed by standard decomplexation gave (*S*)-1-phenethanol (−)-(**16**), which was homochiral by ^{1}H NMR spectroscopic analysis of the (*R*)-Mosher's ester derivative (Scheme 10).

Addition of deuteride from $LiEt_3BD$ and $LiAlD_4$ to complex (**2**) with and without $MgBr_2{\cdot}OEt_2$ pre-treatment gave predictable results, Table 2, the diastereoisomers (**32**) and (**33**) being distinguishable from their ^{1}H NMR spectra. The ratios

observed are similar to those obtained from the corresponding additions to the trimethyl analogue (**1**), see Table 1.

The reaction in Entry 4 of Table 2 was repeated on homochiral (−)-(**2**). The 6:94 mixture of diastereoisomers (**32**) and (**33**) $\{[\alpha]_D^{18}$ −50° (*c* 0.7 in $CHCl_3$)} was desilylated with tetrabutylammonium fluoride trihydrate and decomplexed to give (*R*)-α-deuteriobenzyl alcohol (**27**) in 88% e.e., determined by ^1H NMR spectroscopy on the (*R*)-Mosher's ester derivative.

Conclusion.—Homochiral tricarbonyl(η⁶-*o*-trialkylsilylbenzaldehyde)chromium(0) complexes (**1**) and (**2**) are readily available *via* a classical separation and subsequent hydrolysis of the L-valinol derived imines. Addition of nucleophiles to these aldehyde complexes proceeds with complementary stereoselectivities in the presence or absence of strong Lewis acidic species. Subsequent fluoride mediated desilylation followed by oxidative decomplexation gives rise to alpha subsituted benzyl alcohols in high enantiomeric excesses. Either enantiomer of the alpha substituted benzyl alcohol complex can thus be prepared from either optical antipode of the aldehyde complex, and therefore, either enantiomer of the homochiral complexes (**1**) and (**2**) is formally equivalent to either enantiomer of a chiral benzaldehyde synthon.

Experimental

All reactions involving the preparation or utilisation of tricarbonyl(η⁶-arene)chromium(0) complexes were performed under an atmosphere of nitrogen.[16] All commercial reagents were purified according to standard techniques.[17] THF was distilled from sodium benzophenone ketyl under an atmosphere of nitrogen. Diethyl ether was peroxide free and dibutyl ether was dried over sodium and distilled under an atmosphere of nitrogen prior to use. Hexacarbonylchromium(0) was steam distilled prior to use. Butyl-lithium was used as a 1.6M solution in hexanes and methyl-lithium and methylmagnesium iodide were used as solutions in diethyl ether. Column chromatography was performed on Alumina (Grade V: Grade I, 10% H_2O deactivated) unless otherwise indicated.

M.p.s were obtained on a Kofler hot-stage apparatus and are uncorrected. IR spectra were obtained as solutions in dichloromethane and ^1H NMR spectra were obtained at 300 MHz unless otherwise stated. Mass spectra were obtained using In Beam Electron Impact or Chemical Ionisation techniques.

α,α-Dimethoxytoluene (**4**).[6]—Benzaldehyde (**3**) (35.0 g, 330 mmol) was added to trimethyl orthoformate (37.5 g, 354 mmol) and the mixture stirred. On addition of concentrated H_2SO_4 (2 drops) the solution rapidly darkened. After stirring (24 h), Na_2CO_3 (200 mg) was added and the mixture distilled to give α,α-dimethoxytoluene (**4**) as a clear, colourless oil (42.2 g, 84%), spectroscopically identical with a commerically available sample,[10] b.p. 90 °C (13 mmHg); δ($CDCl_3$) 7.50–7.34 (5 H, m, ArH), 5.42 [1 H, s, $ArCH(OR)_2$], and 3.35 (6 H, s, $ROCH_3$).

General Procedure for Preparation of Tricarbonyl(η⁶-arene)chromium(0) Complexes.—A deoxygenated mixture of Bu_2O–THF (10:1), arene, and hexacarbonylchromium(0) was heated at reflux until the formation of the first trace of green precipitate was observed. The cooled solution was then filtered through Celite and the solvent evaporated to give the crude complex.

Tricarbonyl(η⁶-α,α-dimethoxytoluene)chromium(0) (**5**).—Thermolysis of hexacarbonylchromium(0) (4.78 g, 21.7 mmol) with α,α-dimethoxytoluene (**4**) (3.00 g, 19.7 mmol) under standard conditions (110 ml solvent, 72 h) followed by work-up and column chromatography (Al_2O_3, Et_2O–light petroleum, 1:1), gave a yellow solid. Recrystallisation of this from CH_2Cl_2–light petroleum gave tricarbonyl(η⁶-α,α-dimethoxytoluene)(chromium(0) (**5**) as yellow granules (4.89 g, 86%), ν_{max} 2 828 (OCH_3) and 1 969 and 1 889br cm^{-1} (CO); δ($CDCl_3$) 5.54–5.52 (2 H, d, ArH), 5.38–5.34 (2 H, t, ArH), 5.31–5.29 (1 H, d, ArH), 5.12 [1 H, s, $ArCH(OR)_2$], and 3.39 (6 H, s, $ROCH_3$); *m/z* 288 (M^+).

General Procedure for Alkylation of Tricarbonyl(η⁶-arene)chromium(0) Complexes.—Butyl-lithium was added dropwise to a cooled (−78 °C) THF solution of the complex and the mixture stirred (−78 °C, 2 h). The alkyl halide was added and stirring continued (−78 °C, 2 h). Sufficient MeOH was slowly added to quench the reaction and the mixture was warmed (20 °C) and evaporated to give a residue containing the crude alkylated complex.

Tricarbonyl(η⁶-α,α-dimethoxy-o-trimethylsilyltoluene)chromium(0) (**6**).—Tricarbonyl(η⁶-α,α-dimethoxytoluene)chromium(0) (**5**) (2.50 g, 8.68 mmol) in THF (12 ml) was treated with butyl-lithium (1.65M; 5.79 ml, 9.55 mmol) and chlorotrimethylsilane (2.83 g, 26.1 mmol) under standard conditions. Work-up and column chromatography (Al_2O_3, Et_2O–light petroleum, 1:1) gave a red solid. Recrystallisation of this from CH_2Cl_2–light petroleum gave the title compound (**6**) as yellow needles (2.81 g, 90%), m.p. 86–87 °C (Found: C, 50.0; H, 5.8. $C_{15}H_{20}CrO_5Si$ requires C, 50.0; H, 5.6%); ν_{max} 2 825 (OCH_3) and 1 971, 1 965, and 1 890br cm^{-1} (CO); δ($CDCl_3$) 5.61–5.59 (2 H, m, ArH), 5.47–5.45 (1 H, d, ArH), 5.32 [1 H, s, $ArCH(OR)_2$], 5.20–5.15 (1 H, m, ArH), 3.53, 3.15 [6 H, 2 s, $ROCH_3$], and 0.37 [9 H, s, $ArSi(CH_3)_3$]; δ(C_6D_6) 5.30 [1 H, s, $ArCH(OR)_2$], 5.29–5.24, 4.93–4.89 (2 H, 2 d, ArH), 4.77–4.70, 4.29–4.23 (2 H, 2 t, ArH), 3.13, 2.72 (6 H, 2 s, $ROCH_3$) and 0.24 [9 H, s, $ArSi(CH_3)_3$]; *m/z* 360 (M^+).

Tricarbonyl(η⁶-o-trimethylsilylbenzaldehyde)chromium(0) (**1**).—Tricarbonyl(η⁶-α,α-dimethoxy-*o*-trimethylsilyltoluene)chromium(0) (**6**) (3.80 g, 10.6 mmol) was dissolved in THF (50 ml) and aqueous HCl (1M; 10 ml) added. The solution was stirred (72 h) and then concentrated. The aqueous residue was extracted with Et_2O (3 × 30 ml) and the organic extracts were combined, dried ($MgSO_4$), and evaporated to give a red oil. Column chromatography (Al_2O_3, Et_2O–light petroleum, 1:1) gave the title compound (**1**) as a low melting point red solid (3.34 g, 100%), ν_{max} 1 979, 1 905br (CO), and 1 705 and 1 688 cm^{-1} (C=O); δ($CDCl_3$) 9.73 (1 H, s, ArCHO), 5.81–5.78, 5.44–5.42 (2 H, 2d, ArH), 5.59–5.54, 5.53–5.49 (2 H, 2 t, ArH), 0.42 [9 H, s, $ArSi(CH_3)_3$]; δ(C_6D_6) 9.09 (1 H, s, ArCHO), 4.79–4.73, 4.48–4.41 (4 H, 2 m, ArH), 0.18 [9 H, s, $ArSi(CH_3)_3$]; *m/z* 314 (M^+).

2-Phenyl-1,3-dioxolane (**7**).—A mixture of benzaldehyde (**3**) (20.0 g, 189 mmol) and ethane-1,2-diol (12.0 g, 193 mmol) in benzene (250 ml), containing a catalytic quantity of *p*-TsOH·H_2O (1.90 g, 10.0 mmol), was heated at reflux in a Dean-Stark trap until water ceased to be evolved (6 h). Evaporation of the solvent followed by distillation of the crude oil gave 2-phenyl-1,3-dioxolane (**7**) as a clear, colourless oil (19.7 g, 69%); δ($CDCl_3$) 7.55–7.39 (5 H, m, ArH), 5.85 [1 H, s, $ArCH(OR)_2$], and 4.21–4.02 (4 H, m, OCH_2CH_2O).

Tricarbonyl(η⁶-2-phenyl-1,3-dioxolane)chromium(0) (**8**).—Thermolysis of hexacarbonylchromium(0) (7.33 g, 33.3 mmol) with 2-phenyl-1,3-dioxolane (**7**) (5.00 g, 33.3 mmol) under standard conditions (275 ml solvent, 72 h) followed by work-up and column chromatography (SiO_2, Et_2O) gave a yellow solid. Recrystallisation from Et_2O–hexane gave the title compound

(**8**) as yellow plates (4.51 g, 47%); δ($CDCl_3$) 5.58–5.54, 5.37–5.29 [6 H, 2 m, ArH, $ArCH(OR)_2$], and 4.19–4.11 and 4.09–4.01 (4 H, 2 m, OCH_2CH_2O).

Tricarbonyl[η⁶-2-(o-*tri-isopropylsilylphenyl*)-1,3-*dioxolane*]-*chromium*(0) (**9**).—Tricarbonyl(η⁶-2-phenyl-1,3-dioxolane)-chromium(0) (**8** (1.00 g, 3.50 mmol) in THF (10 ml) was treated with butyl-lithium (2.50M; 1.47 ml, 3.68 mmol) and chlorotri-isopropylsilane (1.35 g, 7.00 mmol) under standard conditions. Work-up and column chromatography (Al_2O_3, Et_2O–hexane, 1:3) gave a single compound as a yellow solid. Recrystallisation from Et_2O–light petroleum gave the title compound (**9**) as yellow needles (703 mg, 45%); δ($CDCl_3$) 5.72–5.66, 5.18–5.12 (2 H, 2 t, ArH), 5.56 [1 H, s, $ArCH(OR)_2$], 5.54, 5.51, 5.44–5.41 (2 H, 2 d, ArH), 4.19–3.95 (4 H, m, OCH_2CH_2O), 1.50–1.32 [3 H, m, $RCH(CH_3)_2$], and 1.23 and 1.18 [18 H, 2 d, J_1 7.1 Hz, J_2 7.1 Hz, $RCH(CH_3)_2$].

Tricarbonyl(η⁶-o-*tri-isopropylsilylbenzaldehyde*)*chromium*(0) (**2**).—Tricarbonyl[η⁶-2-(*o*-tri-isopropylsilylphenyl)-1,3-dioxolane]chromium(0) (**9**) (1.40 g, 3.17 mmol) was dissolved in THF (25 ml) and aqueous HCl (2.5M; 10 ml) added. The solution was stirred (6 days) and then evaporated to a red oil. Column chromatography (SiO_2, Et_2O–hexane, 1:3) followed by recrystallisation from hexane, gave the title compound (**2**) as red granules (1.20 g, 95%), m.p. 64–66 °C (Found: C, 57.0; H, 6.9. $C_{19}H_{26}CrO_4Si$ requires C, 57.3; H, 6.58%); ν_{max} 1 980, 1 910br (CO), and 1 699 cm^{-1} (C=O); δ($CDCl_3$) 9.80 (1 H, s, ArC*H*O), 5.79–5.76, and 5.57–5.54 (2 H, 2 d, ArH), 5.71–5.65 and 5.48–5.42 (2 H, 2 t, ArH), 1.52–1.34 [3 H, m, $RCH(CH_3)_2$], 1.19 and 1.17 [18 H, 2, d, J_1 7.1 Hz, J_2 7.1 Hz, $RCH(CH_3)_2$]; δ(C_6D_6) 9.57 (1 H, s, ArCHO), 5.20–5.16 and 4.96–4.92 (2 H, 2 d, ArH), 4.60–4.54 and 4.37–4.31 (2 H, 2 t, ArH), 1.14–0.99 [3 H, m, $RCH(CH_3)_2$], 0.94 and 0.93 [18 H, 2 d, J_1 6.4 Hz, J_2 6.4 Hz, $RCH(CH_3)_2$]; *m*/*z* 398 (M^+).

Classical Resolution of Tricarbonyl(η⁶-o-*trimethylsilylbenz-aldehyde*)*chromium*(0) (**1**).—L-Valinol (981 mg, 952 mmol) was added to an Et_2O (30 ml) solution of tricarbonyl(η⁶-*o*-trimethylsilylbenzaldehyde)chromium(0) (**1**) (2.99 g, 9.52 mmol) containing an excess of 4 Å molecular sieves (10 g). The mixture was stirred (18 h), filtered through Celite and evaporated to give an orange oil. Addition of hexane gave orange crystals. Column chromatography (SiO_2, Et_2O–Et_3N, 10:1) gave two fractions. Fraction one was crystallised from hexane to give the L-valinol derived imine of (−)-tricarbonyl(η⁶-*o*-trimethylsilyl-benzaldehyde)chromium(0) (−)-(**1**), complex (**10**) as orange needles (870 mg, 23%), m.p. 92—94 °C (Found: C, 53.9; H, 6.3; N, 3.3. $C_{18}H_{25}CrNO_4Si$ requires C, 54.1; H, 6.3; N, 3.5%); $[\alpha]_D^{19}$ −601° (*c* 1.11 in $CHCl_3$); ν_{max} 3 588 (OH), 1 968 and 1 892br (CO), and 1 632 cm^{-1} (C=N); δ($CDCl_3$) 8.24 (1 H, s, ArC*H*=NR), 6.10–6.07 and 5.54–5.50 (2 H, 2 d, ArH), 5.70–5.63, 5.31–5.25 (2 H, 2 t, ArH), 3.81–3.75 (2 H, m, RCH_2OH), 3.03–2.94 (1 H, m, RR^1CHN=CHAr), 1.99–1.85 [2 H, m, $RCH(CH_3)_2$, RO*H*], 0.96 and 0.88 [6 H, 2 d, J_1 6.8 Hz, J_2 6.7 Hz, $RCH(CH_3)_2$], and 0.44 [9 H, s, $ArSi(CH_3)_3$]; *m*/*z* 399 (M^+). Fraction two was crystallised from hexane to give the L-valinol derived imine of (+)-tricarbonyl(η⁶-*o*-trimethylsilylbenzalde-hyde)chromium(0) (+)-(**1**), complex (**11**) as orange needles (1.40 g, 37%), m.p. 96–97 °C (Found: C, 54.3; H, 6.5, N, 3.2. $C_{18}H_{25}CrNO_4Si$ requires C, 54.1; H, 6.3; N, 3.5%); $[\alpha]_D^{19}$ +4 455° (*c* 0.875 in $CHCl_3$); ν_{max} 1 974 and 1 899br (CO) and 1 640 cm^{-1} (C=N); δ($CDCl_3$) 8.22 (1 H, s, ArC*H*=NR), 5.98–5.95, 5.48—5.31 (2 H, 2 d, ArH), 5.66–5.59 and 5.31–5.24 (2 H, 2 t, ArH), 3.83–3.78 (2 H, m, RCH_2OH), 3.03–2.97 (1 H, m, RR^1CHN=CHAr), 1.99–1.85 [1 H, m, $RCH(CH_3)_2$], 1.46 (1 H, t, *J* 6.1 Hz, RCH_2OH), 0.98, 0.94 [6 H, 2 d, 7.7 Hz, J_2 7.0 Hz, $RCH(CH_3)_2$], and 0.43 (9 H, s, $ArSi(CH_3)_3$]; *m*/*z* 399 (M^+).

Complex (**10**) (399 mg, 1.00 mmol) was dissolved in THF (5 m) containing water (1 ml) and concentrated HCl (6 drops). After the mixture had been stirred for 2 h, evaporation of the solvent and column chromatography (SiO_2,Et_2O), gave the product as a red oil which was identified as (−)-tricarbonyl(η⁶-*o*-trimethylsilylbenzaldehyde)chromium(0) (−)-(**1**) (310 mg, 99%) by comparison with an authentic sample, $[\alpha]_D^{18}$ −154° (*c* 1.14 in $CHCl_3$). Complex (**11**) (399 mg, 1.00 mmol) was dissolved in THF (5 ml) containing water (1 ml) and concentrated HCl (6 drops). After the mixture had been stirred for 1.5 h, evaporation of the solvent and column chromatography (SiO_2, Et_2O) gave the product as a red oil which was identified as (+)-tricarbonyl(η⁶-*o*-trimethylsilylbenzalde-hyde)chromium(0) (+)-(**1**) (314 mg, 100%) by comparison with an authentic sample, $[\alpha]_D^{20}$ +146° (*c* 0.116 in $CHCl_3$).

Resolution of Tricarbonyl(η⁶-o-*tri-isopropylsilylbenzalde-hyde*)*chromium*(0) (**2**).—L-Valinol (142 mg, 138 mmol) was added to a Et_2O (10 ml) solution of tricarbonyl(η⁶-*o*-tri-isopropylsilylbenzaldehyde)chromium(0) (**2**) (550 mg, 1.38 mmol) containing an excess of 4 Å molecular sieves (10 g). The mixture was stirred (96 g), filtered through Celite, and evaporated to give an orange oil. Column chromatography (SiO_2, Et_2O–hexane–Et_3N, 10:10:1) gave three fractions. Fraction one was evaporated to afford a red solid which was identified as (−)-tricarbonyl(η⁶-*o*-tri-isopropylsilylbenzalde-hyde)chromium(0) (−)-(**2**) (77 mg, 14%) by comparison with an authentic racemic sample, $[\alpha]_D^{19}$ −384° (*c* 0.824 in $CHCl_3$). Fraction two was evaporated to give the L-valinol derived imine of (−)-tricarbonyl(η⁶-*o*-tri-isopropylsilylbenzaldehyde)chrom-ium(0) (−)-(**2**), complex (**12**) as a red oil (253 mg, 38%); δ(C_6D_6) 8.17 (1 H, s, ArCH=NR), 5.84–5.80 and 5.13–5.10 (2 H, 2 d, ArH), 4.84–4.78 and 4.34–4.28 (2 H, 2 t, ArH), 3.66–3.54 (2 H, m, RCH_2OH), 2.95–2.87 (1 H, m, RR^1CHN=CHAr), 1.84–1.68 [1 H, m, $RCH(CH_3)_2$], and 1.43–0.73 {27 H, m, $RCH(CH_3)_2$, $ArSi[CH(CH_3)_2]_3$}. Fraction three was evaporated to give the L-valinol derived imine of (+)-tricarbonyl(η⁶-*o*-tri-isopropyl-silylbenzaldehyde)chromium(0) (+)-(**2**), complex (**13**) as a red oil (293 mg, 44%); δ(C_6D_6) 8.21 (1 H, s, ArC*H*=NR), 5.82–5.78 and 5.11–5.08 (2 H, 2 d, ArH), 4.86–4.80 and 4.35–4.29 (2 H, 2 t, ArH), 3.55–3.51 (2 H, m, RCH_2OH), 2.87–2.78 (1 H, m, RCH_2OH), 2.41–2.30 (1 H, m, RR^1CHN=CHAr), 1.82–1.72 [1 H, m, $RCH(CH_3)_2$], and 1.39–0.78 {27 H, m, $RCH(CH_3)_2$, $ArSi[CH(CH_3)_2]_3$}.

Complex (**12**) (253 mg, 0.52 mmol) was dissolved in THF (5 ml) containing water (2 ml) and concentrated HCl (40 drops). After the mixture had been stirred for 5 h, evaporation of the solvent and column chromatography (Al_2O_3, Et_2O–hexane, 1:1), the product was isolated as a red solid and identified as (−)-tricarbonyl(η⁶-*o*-tri-isopropylsilylbenzaldehyde)chromium(0) (−)-(**2**) (166 mg, 80%), by comparison with an authentic racemic sample, $[\alpha]_D^{19}$ −485° (*c* 0.095 in $CHCl_3$). Complex (**13**) (293 mg, 0.61 mmol) was dissolved in THF (5 ml) containing water (1 ml) and concentrated HCl (0.5 ml). After the mixture had been stirred for 15 h, evaporation of the solvent and column chromatography (Al_2O_3, Et_2O–hexane, 1:1), the product was isolated as a red solid and identified as (+)-tricarbonyl(η⁶-*o*-tri-isopropylsilylbenzaldehyde)chromium(0) (+)-(**2**) (170 mg, 70%), by comparison with an authentic sample, $[\alpha]_D^{21}$ +515° (*c* 0.14 in $CHCl_3$).

General Procedure for Addition of Nucleophiles to Substituted Tricarbonyl(η⁶-*benzaldehyde*)*chromium*(0) *Complexes.*—A Et_2O or THF solution of the nucleophile was added dropwise to a cooled (−78 °C) THF solution of the complex and the mixture stirred (−78 °C, 1 h). Sufficient MeOH was slowly added to quench the reaction and the mixture warmed (20 °C) and evaporated to give a residue containing the crude product.

Addition of MeLi *to* (+)-*Tricarbonyl*(η^6-o-*trimethylsilylbenzaldehyde*)*chromium*(0) (+)-(**1**).—(+)-Tricarbonyl(η^6-*o*-trimethylsilylbenzaldehyde)chromium(0) (+)-(**1**) (157 mg, 0.50 mmol) in THF (10 ml) was treated with MeLi (1.4M; 0.71 ml, 0.99 mmol) under standard conditions. Column chromatography (Al_2O_3, Et_2O–light petroleum, 2:1) gave two product fractions in a ratio of 12:88. Fraction one, the minor isomer, was evaporated to give a yellow solid. Recrystallisation of this from CH_2Cl_2-light petroleum gave (SS)-*tricarbonyl*(η^6-o-*trimethylsilyl*-1-*phenethanol*)*chromium*(0) (+)-(**15**) as yellow needles (18 mg, 10%), m.p. 75 °C (Found: C, 50.8; H, 5.7. $C_{14}H_{18}CrOSi$ requires C, 50.9; H, 5.49%); $[\alpha]_D^{20}$ +36° (*c* 0.765 in $CHCl_3$); ν_{max} 1 968 and 1 888br (CO) and 1 607 cm^{-1} (arene ring); δ($CDCl_3$) 5.75–5.68 and 5.22–5.15 (2 H, 2 t, ArH), 5.52–5.47 (2 H, m, ArH) 4.82 [1 H, q, *J* 6.3 Hz, ArC*H*(OH)CH_3], 2.13 [1 H, s, br, ArCH(O*H*)CH_3], 1.48 [3 H, d, *J* 6.3 Hz, ArCH(OH)CH_3], and 0.41 [9 H, s, ArSi(CH_3)$_3$]; *m/z* 330 (M^+). Fraction two, the major isomer, was evaporated to give a yellow solid. Recrystallisation from CH_2Cl_2-light petroleum gave (SR-*tricarbonyl*(η^6-o-*trimethylsilyl*-1-*phenethanol*)*chromium*(0) (+)-(**14**) as yellow blocks (137 mg, 83%), m.p. 39–40 °C (Found: C, 51.2; H, 5.5. $C_{14}H_{18}CrO_4Si$ requires C, 50.9; H, 5.4%); $[\alpha]_D^{21}$ +20° (*c* 1.01 in $CHCl_3$); ν_{max} 3 595 (OH), 1 970 and 1 889br (CO), and 1 610 cm^{-1} (arene ring); δ($CDCl_3$) 5.63—5.56, 5.23–5.17 (2 H, 2 t, ArH), 5.51–5.48, 5.29—5.26 (2 H, 2 d, ArH), 4.84–4.72 [1 H, m, ArC*H*(OH)CH_3], 1.78 [1 H, d, *J* 5.3 Hz, ArCH(O*H*)CH_3], 1.56 [3 H, d, *J* 6.5 Hz, ArCH(OH)CH_3], and 0.41 [9 H, s, ArSi(CH_3)$_3$]; δ(C_6D_6) 4.97. (1 H, d, ArH), 4.72–4.65 (t, 1 H, ArH), 4.41–4.38 (2 H, m, ArH), 4.31 [1 H, q, *J* 6.3 Hz, ArC*H*(OH)CH_3], 0.99 [3 H, d, *J* 6.5 Hz, ArCH(OH)CH_3], and 0.22 [9 H, s, ArSi(CH_3)$_3$]; *m/z* 330 (M^+).

General Procedure for Decomplexation of Tricarbonyl(η^6-*arene*)*chromium*(0) Complexes.—An Et_2O solution of the complex was exposed to air and sunlight until a colourless solution with a green or brown precipitate resulted. Filtration through Celite followed by removal of the solvent by distillation or evaporation, gave the crude arene.

Desilylation and Decomplexation of (SR)-*Tricarbonyl*(η^6-o-*trimethylsilyl*-1-*phenethanol*)*chromium*(0) (+)-(**14**).—Tetrabutylammonium fluoride trihydrate (301 mg, 0.96 mmol) was added to a CH_2Cl_2 (5 ml) solution of (*SR*)-tricarbonyl(η^6-*o*-trimethylsilyl-1-phenethanol)chromium(0) (+)-(**14**) (210 mg, 0.64 mmol) and the solution stirred (2 h). After filtration (Al_2O_3, Et_2O) and evaporation of the solvent, Et_2O (10 ml) was added and the mixture allowed to decomplex under standard conditions (72 h). Work-up and distillation gave (*R*)-1-phenethanol (+)-(**16**) as a clear, colourless oil (65 mg, 83%), identified by comparison with a commercially available sample,[10] $[\alpha]_D^{20}$ +51° {*c* 1.35 in $CHCl_3$); lit.,[10] $[\alpha]_D$ +39.5° (neat)}; δ($CDCl_3$) 7.43–7.29 (5 H, m, ArH), 4.93 [1 H, q, *J* 6.5 Hz, ArC*H*(OH)CH_3], 1.90 [1 H, s, br, ArCH(O*H*)CH_3], 1.53 (3 H, d, *J* 6.4 Hz, ArCH(OH)CH_3].

Addition of MeMgI *to Tricarbonyl*(η^6-o-*trimethylsilylbenzaldehyde*)*chromium*(0) (**1**).—Tricarbonyl(η^6-*o*-trimethylsilylbenzaldehyde)chromium(0) (**1**) (600 mg, 1.91 mmol) in THF (8 ml) was treated with MeMgI (2.00M; 2.00 ml, 4.00 mmol) under standard conditions. Column chromatography (Al_2O_3, Et_2O–light petroleum, 1:1) gave two fractions both as yellow solids in a ratio of 83:17. Fraction one, the major isomer, was identified as (*RR,SS*)-tricarbonyl(η^6-*o*-trimethylsilyl-1-phenethanol)-chromium(0) (**15**) (523 mg, 83%), and fraction two, the minor isomer, was identified as (*RS,SR*)-tricarbonyl(η^6-*o*-trimethylsilyl-1-phenethanol)chromium(0) (**14**) (105 mg, 17%), both by comparison with authentic samples.

Magnesium Bromide–Diethyl Ether.[13].—Magnesium (192 mg, 8.00 mmol) was stirred vigorously under nitrogen until the metal surface darkened. Dry Et_2O (10 ml) was added followed by 1,2-dibromoethane (1.36 g, 7.23 mmol). The solution was gently warmed to initiate reaction and then stirred (10 min) until no further reaction was observed. The resultant crude solution of $MgBr_2$·OEt_2 (*ca.* 0.08M) was used without further purification.

General Procedure for the Addition of Nucleophiles to Tricarbonyl(η^6-o-*trialkylsilylbenzaldehyde*)*chromium*(0) *Complexes in the Presence of* $MgBr_2$·OEt_2.—$MgBr_2$·OEt_2 in Et_2O was added to a solution of the complex in Et_2O and the darkened mixture was stirred (10 min). An Et_2O or THF solution of the nucleophile was added slowly to the mixture and the resultant yellow solution stirred (30 min). Sufficient MeOH was added to quench the reaction and the solvent evaporated to give a residue containing the crude product.

Addition of MeLi *to Tricarbonyl*(η^6-o-*trimethylsilylbenzaldehyde*)*chromium*(0) (**1**) *Pre-treated with* $MgBr_2$·OEt_2—Tricarbonyl(η^6-*o*-trimethylsilylbenzaldehyde)chromium(0) (**1**) (518 mg, 1.65 mmol) in Et_2O (10 ml) was treated with $MgBr_2$·OEt_2 (0.80M; 10.0 ml, 8.00 mmol) followed by MeLi (1.50M; 1.60 ml, 2.40 mmol) under standard conditions. Work-up and column chromatography (Al_2O_3, Et_2O–light petroleum, 1:1) gave two fractions, both as yellow solids in a ratio of 87:13. Fraction one, the major isomer, was identified as (*RR,SS*)-tricarbonyl(η^6-*o*-trimethylsilyl-1-phenethanol)chromium(0) (**15**) (474 mg, 87%) and fraction two, the minor isomer, was identified as (*RS,SR*)-tricarbonyl(η^6-*o*-trimethylsilyl-1-phenethanol)chromium(0) (**14**) (71 mg, 13%), both by comparison with authentic samples.

Addition of MeMgI *to* (−)-*Tricarbonyl*(η^6-o-*trimethylsilylbenzaldehyde*)*chromium*(0) (−)-(**1**) *Pre-treated with* $MgBr_2$·OEt_2.—(−)-Tricarbonyl(η^6-*o*-trimethylsilylbenzaldehyde)-chromium(0) (−)-(**1**) (100 mg, 0.32 mmol) in Et_2O (8 ml) was treated with $MgBr_2$·OEt_2 (0.80M; 3.33 ml, 2.66 mmol) followed by MeMgI (1.00M; 0.51 ml, 0.51 mmol) under standard conditions. Work-up and column chromatography (Al_2O_3, Et_2O–light petroleum, 1:1) gave two fractions both as yellow solids in a ratio of 89:11. Fraction one, the major isomer, was identified as (*RR*)-tricarbonyl(η^6-*o*-trimethylsilyl-1-phenethanol)chromium(0) (−)-(**15**) (84 mg, 80%) by comparison with an authentic sample, $[\alpha]_D^{21}$ −36° (*c* 0.765 in $CHCl_3$). Fraction two, the minor isomer, was identified as (*RS*)-tricarbonyl(η^6-*o*-trimethylsilyl-1-phenethanol)chromium(0) (−)-(**14**) (10 mg, 10%), also by comparison with an authentic sample.

Desilylation and Decomplexation of (RR)-*Tricarbonyl*(η^6-o-*trimethylsilyl*-1-*phenethanol*)*chromium*(0) (−)-(**15**).—Tetrabutylammonium fluoride trihydrate (115 mg, 0.37 mmol) was added to a CH_2Cl_2 (5 ml) solution of (*RR*)-tricarbonyl(η^6-*o*-trimethylsilyl-1-phenethanol)chromium(0) (−)-(**15**) (80 mg, 0.24 mmol) and the solution stirred (3 h). After filtration (Al_2O_3, Et_2O) and evaporation of the solvent, Et_2O (100 ml) was added and the mixture allowed to decomplex under standard conditions (72 h). Work-up and distillation gave (*R*)-1-phenethanol (+)-(**16**) as a clear, colourless oil (12 mg, 41%) identified by comparison with an authentic sample, $[\alpha]_D^{20}$ +56° {*c* 0.46 in $CHCl_3$, lit.,[10] $[\alpha]_D$ +39.5° (neat)}.

Tricarbonyl[η^6-2-o-*trimethylsilylphenyl*)-2-*methyl*-1,3-*dioxolane*]*chromium*(0) (**24**).—Tricarbonyl(η^6-2-phenyl-2-methyl-1,3-dioxolane)chromium(0) (**23**) (200 mg, 0.67 mmol) in THF (8 ml) was treated with butyl-lithium (1.65M; 0.43 ml, 0.71 mmol) and chlorotrimethylsilane (228 mg, 2.10 mmol) under

standard conditions. Work-up and column chromatography (Al_2O_3, Et_2O–light petroleum, 3:1) gave a single compound as a yellow solid. Recrystallisation from Et_2O–hexane gave the title compound (**24**) as a yellow needles (213 mg, 85%), m.p. 98–100 °C (Found: C, 51.4; H, 5.3. $C_{16}H_{20}CrO_5Si$ requires C, 51.6; H, 5.4%); ν_{max} 1 963 and 1 882br, 1 882br (CO) and 1 601 cm^{-1} (arene ring); $\delta(CDCl_3)$ 5.56–5.45 (3 H, m, ArH), 5.28–5.20 (1 H, m, ArH), 4.16–4.00 (4 H, m, OCH_2CH_2O), 1.62 [3 H, s, $ArC(OR)_2CH_3$], 0.40 [9 H, s, $ArSi(CH_3)_3$]; *m/z* 373 ($M^+ + 1$).

Tricarbonyl(η⁶-o-*trimethylsilylacetophenone*)*chromium*(0) (**22**).—Tricarbonyl[η⁶-2-(*o*-trimethylsilylphenyl)-2-methyl-1,3-dioxolane]chromium(0) (**24**) (120 mg, 0.32 mmol) was dissolved in THF (5 ml) and aqueous HCl (3M, 3 ml) added. The solution was stirred for 24 h after which removal of the solvent gave an orange oil. Column chromatography (SiO_2, Et_2O–light petroleum, 1:1) gave, on evaporation of the solvent, the title compound (**22**) as an orange solid (106 mg, (100%); ν_{max} 1 979 and 1 908br (CO) and 1 696 cm^{-1} (C=O); $\delta(CDCl_3)$ 5.71–5.68 (1 H, d, ArH), 5.60–5.55 (2 H, m, ArH), 5.45–5.39 (1 H, t, ArH), 2.49 (3 H, s, RCH_3), and 0.32 [9 H, s, $ArSi(CH_3)_3$]; *m/z* 328 (M^+).

Addition of $LiEt_3BH$ *to Tricarbonyl*(η⁶-o-*trimethylsilylacetophenone*)*chromium*(0) (**22**).—Tricarbonyl(η⁶-*o*-trimethylsilylacetophenone)chromium(0) (**22**) (100 mg, 0.30 mmol) in THF (8 ml) was treated with $LiEt_3BH$ (1.00M in THF; 0.90 ml, 0.90 mmol) under standard conditions (−78 °C, 30 min). Work-up and column chromatography (Al_2O_3, Et_2O) gave, on evaporation of the solvent, (*RR,SS*)-tricarbonyl(η⁶-*o*-trimethylsilyl-1-phenethanol)chromium(0) (**15**) as a yellow solid (84 mg, 85%), identified by comparison with an authentic sample.

Addition of $LiEt_2BD$ *to Tricarbonyl*(η⁶-o-*trimethylsilylbenzaldehyde*)*chromium*(0) (**1**).—*Method* 1. Tricarbonyl(η⁶-*o*-trimethylsilylbenzaldehyde)chromium(0) (**1**) (320 mg, 1.02 mmol) in THF (8 ml) was treated with $LiEt_3BD$ (1.00M in THF; 1.60 ml, 1.60 mmol) under standard conditions (−78 °C, 20 min). Column chromatography (Al_2O_3, Et_2O) gave, on evaporation of the solvent, a yellow solid, identified as a 92:8 mixture of (*RS,SR*)-tricarbonyl(η⁶-*o*-trimethylsilyl-α-deuteriobenzyl alcohol)chromium(0) (**25**) and (*RR,SS*)-tricarbonyl-(η⁶-*o*-trimethylsilyl-α-deuteriobenzyl alcohol)chromium(0) (**26**) respectively (323 mg, 100%); $\delta(CDCl_3)$ (**25**): 4.61 [1 H, m, $ArCH(OH)D$], (**26**): 4.50 [1 H, m, $ArCH(OH)D$], (**25**) and (**26**): 5.70–5.64 and 5.19–5.13 (2 H, 2 t, ArH), 5.55–5.52 and 5.42–5.39 (2 H, 2 d, ArH), 1.87 [1 H, s, br, $ArCH(OH)D$], and 0.39 [9 H, s, $ArSi(CH_3)_3$]; $\delta(C_6D_6)$ (**25**): 4.06 [1 H, m, $ArCH(OH)D$], (**26**): δ 3.88 [1 H, m, $ArCH(OH)D$], (**25**) and (**26**): 4.93–4.90, 4.76–4.71 (2 H, 2 d, ArH), 4.79–4.67, 4.25–4.18 (2 H, 2 t, ArH), 0.97 [d, 1 H, *J* 6.3 Hz, $ArCH(OH)D$], and 0.10 [9 H, s, $ArSi(CH_3)_3$]; $\delta_D(CHCl_3)$ (**25**): 4.60 [1 D, s, $ArCH(OH)D$], (**26**): 4.50 [1 D, s, $ArCH(OH)D$]; *m/z* 317 (M^+).

Method 2. Tricarbonyl(η⁶-*o*-trimethylsilylbenzaldehyde)-chromium(0) (**1**) (292 mg, 0.93 mmol) in THF (8 ml) (cooled to −100 °C) was treated with $LiEt_3BD$ (1.00M in THF; 2.00 ml, 2.00 mmol) under standard conditions (−100 °C, 20 min). Column chromatography (Al_2O_3, Et_2O) gave, on evaporation of the solvent, a yellow solid, identified as a 92:8 mixture of complexes (**25**) and (**26**) (289 mg, 98%), by comparison with an authentic mixture.

Method 3. Tricarbonyl(η⁶-*o*-trimethylsilylbenzaldehyde)-chromium(0) (**1**) (309 mg, 0.98 mmol) in CH_2Cl_2 (15 ml) (cooled to −100 °C) was treated with $LiEt_3BD$ (1.00M in THF; 2.00 ml, 2.00 mmol) under standard conditions (−100 °C, 5 min). Column chromatography (Al_2O_3, Et_2O) gave, on evaporation of the solvent, a yellow solid, identified as a 75:25 mixture of complexes (**25**) and (**26**) (309 mg, 99%), by comparison with an authentic mixture.

Method 4. Tricarbonyl(η⁶-*o*-trimethylsilylbenzaldehyde)-chromium(0) (**1**) (600 mg, 1.91 mmol) in toluene (15 ml) (cooled to −91 °C) was treated with $LiEt_3BD$ (1.00M in THF; 3.30 ml, 3.30 mmol) under standard conditions (−91 °C, 20 min). Column chromatography (Al_2O_3, Et_2O) gave, on evaporation of the solvent, a yellow solid, identified as an 80:20 mixture of complexes (**25**) and (**26**) (540 mg, 89%), by comparison with an authentic mixture.

Addition of $LiEt_3BD$ *to Tricarbonyl*(η⁶-o-*trimethylsilylbenzaldehyde*)*chromium*(0) (**1**) *Pre-treated with* $MgBr_2{\cdot}OEt_2$.—Tricarbonyl(η⁶-*o*-trimethylsilylbenzaldehyde)chromium(0) (**1**) (240 mg, 0.76 mmol) in Et_2O (5 ml) was treated with $MgBr_2{\cdot}OEt_2$ (0.80M; 6.80 ml, 5.44 mmol) followed by $LiEt_3BD$ (1.0M in THF; 4.00 ml, 4.00 mmol) under standard conditions. Work-up and column chromatography (Al_2O_3, Et_2O) gave, on evaporation of the solvent, a yellow solid, identified as a 12:88 mixture of complexes (**25**) and (**26**) (229 mg, 95%), by comparison with an authentic mixture.

Addition of $LiAlD_4$ *to Tricarbonyl*(η⁶-o-*trimethylsilylbenzaldehyde*)*chromium*(0) (**1**).—Tricarbonyl(η⁶-*o*-trimethylsilylbenzaldehyde)chromium(0) (**1**) (335 mg, 1.07 mmol) in THF (8 ml) was treated with powdered $LiAlD_4$ (100 mg, 2.38 mmol) under standard conditions (−78 °C, 10 min). Column chromatography (Al_2O_3, Et_2O) gave, on evaporation of the solvent, a yellow solid, identified as a 38:62 mixture of complexes (**25**) and (**26**) (339 mg, 100%) by comparison with an authentic mixture.

Addition of $LiAlD_4$ *to Tricarbonyl*(η⁶-o-*trimethylsilylbenzaldehyde*)*chromium*(0) (**1**) *Pre-treated with* $MgBr_2{\cdot}OEt_2$.—Tricarbonyl(η⁶-*o*-trimethylsilylbenzaldehyde)chromium(0) (**1**) (369 mg, 1.18 mmol) in Et_2O (5 ml) was treated with $MgBr_2{\cdot}OEt_2$ (0.80M; 6.80 ml, 5.44 mmol) followed by powdered $LiAlD_4$ (110 mg, 2.62 mmol) under standard conditions. Work-up and column chromatography (Al_2O_3, Et_2O) gave, on evaporation of the solvent, a yellow solid, identified as a 4:96 mixture of complexes (**25**) and (**26**) (270 mg, 72%), by comparison with an authentic sample.

Addition of $LiEt_3BD$ *to* (−)-*Tricarbonyl*(η⁶-o-*trimethylsilylbenzaldehyde*)*chromium*(0) (−)-(**1**).—(−)-Tricarbonyl(η⁶-*o*-trimethylsilylbenzaldehyde)chromium(0) (−)-(**1**) (310 mg, 0.99 mmol) in THF (8 ml) was treated with $LiEt_3BD$ (1.00M in THF; 1.60 ml, 1.60 mmol) under standard conditions (−78 °C, 20 min). Column chromatography (Al_2O_3, Et_2O) gave, on evaporation of the solvent, a yellow solid, identified as a 92:8 mixture of (*RS*)-tricarbonyl(η⁶-*o*-trimethylsilyl-α-deuteriobenzyl alcohol)chromium(0) (**25**) and (*RR*)-tricarbonyl(η⁶-*o*-trimethylsilyl-α-deuteriobenzyl alcohol)chromium(0) (**26**) (313 mg, 100%), by comparison with an authentic racemic mixture, $[\alpha]_D^{20}$ ~0° (*c* 0.865 in $CHCl_3$).

Addition of $LiAlD_4$ to (−)-*Tricarbonyl*(η⁶-o-*trimethylsilylbenzaldehyde*)*chromium*(0) (−)-(**1**) *Pre-treated with* $MgBr_2{\cdot}OEt_2$.—(−)-Tricarbonyl(η⁶-*o*-trimethylsilylbenzaldehyde)-chromium(0) (−)-(**1**) (100 mg, 0.32 mmol) in Et_2O (5 ml) was treated with $MgBr_2{\cdot}OEt_2$ (0.80M; 3.33 ml, 2.66 mmol) followed by powdered $LiAlD_4$ (25 mg, 0.60 mmol) under standard conditions. Work-up and column chromatography (Al_2O_3, Et_2O) gave, on evaporation of the solvent, a yellow solid, identified as a 4:96 mixture of (*RS*)-tricarbonyl(η⁶-*o*-trimethylsilyl-α-deuteriobenzyl alcohol)chromium(0) (**25**) and (*RR*)-tricarbonyl(η⁶-*o*-trimethylsilyldeuteriobenzyl alcohol)-chromium(0) (**26**) (80 mg, 79%), by comparison with an authentic racemic mixture, $[\alpha]_D^{20}$ ~0° (*c* 0.60 in $CHCl_3$).

Desilylation and Decomplexation of a 92:8 *Mixture of* (RS)- *and* (RR)-*Tricarbonyl*(η^6-o-*trimethylsilyl*-α-*deuteriobenzyl alcohol*)*chromium*(0) *Complexes* (**25**) *and* (**26**).—Tetrabutylammonium fluoride trihydrate (299 mg, 0.95 mmol) was added to a CH_2Cl_2 (8 ml) solution of a 92:8 mixture of (*RS*)- and (*RR*)-tricarbonyl(η^6-*o*-trimethylsilyl-α-deuteriobenzyl alcohol)-chromium(0) complexes (**25**) and (**26**) (200 mg, 0.63 mmol) and the solution stirred (1 h). After filtration (Al_2O_3, Et_2O) and evaporation of the solvent, Et_2O (75 ml) was added and the mixture allowed to decomplex under standard conditions (60 h). Work-up and distillation gave (*S*)-α-deuteriobenzyl alcohol (*S*)-(**27**) as a clear, colourless oil (46 mg, 44%), identified by comparison with an authentic racemic sample,[18] b.p. 80 °C (21 mmHg); δ($CDCl_3$) 7.40–7.25 (5 H, m, ArH), 4.99 [1 H, s, ArC*H*(OH)D], and 1.71 [1 H, s, ArCH(O*H*)D]; *m*/*z* 109 (M^+).

Desilylation and Decomplexation of a 4:96 *Mixture of* (RS)- *and* (RR)-*Tricarbonyl*(η^6-o-*trimethylsilyl*-α-*deuteriobenzyl alcohol*)*chromium*(0) *Complexes* (**25**) *and* (**26**).—Tetrabutylammonium fluoride trihydrate (100 mg, 0.32 mmol) was added to a CH_2Cl_2 (5 ml) solution of a 4:96 mixture of (*RS*)- and (*RR*)-tricarbonyl(η^6-*o*-trimethylsilyl-α-deuteriobenzyl alcohol)-chromium(0) complexes (**25**) and (**26**) (80 mg, 0.25 mmol) and the solution stirred (12 h). After filtration (Al_2O_3, Et_2O) and evaporation of the solvent, Et_2O (25 ml) was added and the mixture allowed to decomplex under standard conditions (48 h). Work-up and distillation gave (*R*)-α-deuteriobenzyl alcohol (*R*)-(**27**) as a clear, colourless oil (18 mg, 66%), identified by comparison with an authentic racemic sample.[18]

Addition of MeLi *to Tricarbonyl*(η^6-o-*tri-isopropylsilylbenzaldehyde*)*chromium*(0) (**2**).—*Method* 1. Tricarbonyl(η^6-*o*-tri-isopropylsilylbenzaldehyde)chromium(0) (**2**) (84 mg, 0.21 mmol) in THF (8 ml) was treated with MeLi (1.50M; 0.28 ml, 0.42 mmol) under standard conditions with Pr^{i}OH (0.50 ml) quench. Column chromatography (Al_2O_3) gave two fractions in 85:15 ratio. Fraction one (Et_2O–hexane, 1:1) was evaporated to give a yellow oil. Crystallisation from hexane gave *tricarbonyl*(η^6-O-*tri-isopropylsilyl*-1-*phenethanol*)*chromium*(0) (**28**) as yellow plates (63 mg, 72%), m.p. 45–46 °C (Found: C, 58.2; H, 7.4. $C_{20}H_{30}CrO_4Si$ requires C, 58.0; H, 7.29%); ν_{max} 1 970 and 1 890br cm^{-1} (CO); δ(C_6D_6) 5.07–5.03 and 4.73–4.71 (2 H, 2 d, ArH), 4.45–4.35 [4 H, m, ArH, ArC*H*(OH)CH_3], 1.17 [3 H, d, *J* 6.3 Hz, ArCH(OH)C*H*$_3$], and 1.11–0.94 {21 H, m, ArSi[C*H*(CH_3)$_2$]$_3$}; *m*/*z* 414 (M^+). Fraction two (Et_2O) was evaporated to give a yellow oil. Crystallisation of this from hexane gave (*RS,SR*)-tricarbonyl(η^6-*o*-tri-isopropylsilyl-1-phenethanol)chromium(0) (**30**) as tiny yellow crystals (11 mg, 13%); δ($CDCl_3$) 5.71–5.65 and 5.25–5.19 (2 H, 2 t, ArH), 5.53–5.50, 5.46–5.43 (2 H, 2 d, ArH), 4.72 [1 H, m, ArC*H*(OH)CH_3], 1.72 [1 H, d, *J* 4.8 Hz, ArCH(O*H*)CH_3], 1.59 [3 H, d, *J* 6.3 Hz, ArCH(OH)C*H*$_3$], 1.54–1.34 {3 H, m, ArSi[C*H*(CH_3)$_2$]$_3$}, and 1.26–1.18 {18 H, m, ArSi[CH(C*H*$_3$)$_2$]$_3$}; *m*/*z* 415 (M^+ + 1).

Method 2. (+)-Tricarbonyl(η^6-*o*-tri-isopropylsilylbenzaldehyde)chromium(0) (+)-(**2**) (60 mg, 0.15 mmol) in THF (5 ml) was treated with MeLi (1.50M; 0.20 ml, 0.30 mmol) under standard conditions with water (1 drop) quench. Column chromatography (Al_2O_3) gave two fractions in 36:64 ratio. Fraction one (Et_2O–hexane, 1:1) was evaporated to give (*R*)-tricarbonyl(η^6-*O*-tri-isopropylsilyl-1-phenethanol)chromium(0) (**28**) as a yellow oil (22 mg, 36%), identified by comparison with an authentic racemic sample. Fraction two (Et_2O) was evaporated to a yellow solid (40 mg, 64%). Recrystallisation from hexane gave (*SR*)-tricarbonyl(η^6-*o*-tri-isopropylsilyl-1-phenethanol)chromium(0) (+)-(**30**) as tiny yellow crystals, identified by comparison with an authentic racemic sample, $[\alpha]_D^{20}$ +129° (*c* 0.14 in $CHCl_3$).

Desilylation and Decomplexation of (R)-*Tricarbonyl*(η^6-*o*-*tri-isopropylsilyl*-1-*phenethanol*)*chromium*(0) (**28**).—Tetrabutylammonium fluoride trihydrate (114 mg, 0.36 mmol) was added to a CH_2Cl_2 (2 ml) solution of (*R*)-tricarbonyl(η^6-*o*-tri-isopropylsilyl-1-phenethanol) chromium(0) (**28**) (22 mg, 53 μmol) and the solution stirred (2 h). After filtration (Al_2O_3, Et_2O) and evaporation of the solvent, Et_2O (10 ml) was added and the mixture allowed to decomplex under standard conditions (24 h). Work-up gave (*R*)-1-phenethanol (+)-(**16**) as a clear, colourless oil (6 mg, 93%), identified by comparison with an authentic sample.

Desilylation and Decomplexation of (SR)-*Tricarbonyl*(η^6-o-*tri-isopropylsilyl*-1-*phenethanol*)*chromium*(0) (+)-(**30**).—Tetrabutylammonium fluoride trihydrate (38 mg, 0.12 mmol) was added to a CH_2Cl_2 (2 ml) solution of (*SR*)-tricarbonyl(η^6-*o*-tri-isopropylsilyl-1-phenethanol)chromium(0) (+)-(**30**) (5 mg, 12 μmol) and the solution stirred (30 min). After filtration (Al_2O_3, Et_2O) and evaporation of the solvent, Et_2O (10 ml) was added and the mixture allowed to decomplex under standard conditions (24 h). Work-up gave (*R*)-1-phenethanol (+)-(**16**) as a clear, colourless oil (1.4 mg, 96%), identified by comparison with an authentic sample.

Addition of MeMgI *to Tricarbonyl*(η^6-o-*tri-isopropylsilylbenzaldehyde*)*chromium*(0) (**2**).—Tricarbonyl(η^6-*o*-tri-isopropylsilylbenzaldehyde)chromium(0) (**2**) (98 mg, 0.25 mmol) in THF (8 ml) was treated with MeMgI (1.00M; 1.00 ml, 1.00 mmol) under standard conditions with Pr^{i}OH (0.5 ml) quench. Column chromatography (Al_2O_3) gave two fractions in 50:50 ratio. Fraction one (Et_2O–hexane, 1:2) was evaporated to a yellow solid (47 mg, 45%). Recrystallisation of this from hexane gave (*RR,SS*)-*tricarbonyl*(η^6-o-*tri-isopropylsilyl*-1-*phenethanol*)-*chromium*(0) (**31**) as yellow needles, m.p. 67—68 °C (Found: C, 58.3; H, 7.3. $C_{20}H_{30}CrO_4Si$ requires C, 58.0; H, 7.29%); ν_{max} 1 965 and 1 890br cm^{-1} (CO); δ($CDCl_3$) 5.79–5.73, 5.22–5.15 (2 H, 2 t, ArH), 5.55–5.51 and 5.48–5.45 (2 H, 2 d, ArH), 4.68 [1 H, d of q, J_d 2.1 Hz, J_q 6.1 Hz, ArC*H*(OH)CH_3], 2.03 [1 H, d, *J* 2.1 Hz, ArCH(O*H*)CH_3], 1.47 [3 H, d, *J* 6.3 Hz, ArCH(OH)C*H*$_3$], 1.41–1.31 {3 H, m, ArSi[C*H*(CH_3)$_2$]$_3$}, and 1.27 and 1.19 {18 H, 2 d, J_1 6.0 Hz, J_2 6.6 Hz, ArSi[CH(C*H*$_3$)$_2$]$_3$}; *m*/*z* 415 (M^+ +1). Fraction two (Et_2O) was evaporated to give (*RS,SR*)-tricarbonyl(η^6-*o*-tri-isopropylsilyl-1-phenethanol)chromium(0) (**30**) as a yellow oil (47 mg, 45%), identified by comparison with an authentic sample.

Addition of MeMgI *to* (+)-*Tricarbonyl*(η^6-o-*tri-isopropylsilylbenzaldehyde*)*chromium*(0) (+)-(**2**) *pre-treated with* $MgBr_2$·OEt_2.—(+)-Tricarbonyl(η^6-*o*-tri-isopropylsilylbenzaldehyde)chromium(0) (+)-(**2**) (65 mg, 0.16 mmol) in Et_2O (5 ml) was treated with $MgBr_2$·OEt_2 (0.80M; 3.33 ml, 2.66 mmol) followed by MeMgI (1.00M; 0.30 ml, 0.30 mmol) under standard conditions. Work-up and column chromatography (Al_2O_3, Et_2O) gave, on evaporation of the solvent, a single fraction as a yellow solid. Recrystallisation from hexane gave (*SS*)-tricarbonyl(η^6-*o*-tri-isopropylsilyl-1-phenethanol)chromium(0) (+)-(**31**) as a yellow powder (66 mg, 99%), identified by comparison with an authentic sample, $[\alpha]_D^{20}$ +79° (*c* 0.835 in $CHCl_3$).

Desilylation and De-complexation of (SS)-*Tricarbonyl*(η^6-o-*tri-isopropylsilyl*-1-*phenethanol*)*chromium*(0) (+)-(**31**).—Tetrabutylammonium fluoride trihydrate (107 mg, 0.34 mmol) was added to a CH_2Cl_2 (2 ml) solution of (*SS*)-tricarbonyl(η^6-*o*-tri-isopropylsilyl-1-phenethanol)chromium(0) (+)-(**31**) (64 mg, 0.15 mmol) and the solution stirred (30 min). After filtration (Al_2O_3, Et_2O) and evaporation of the solvent, Et_2O (10 ml) was added and the mixture allowed to decomplex under

Table 3. ^{1}H n.m.r. chemical shifts used to check diastereoisomeric excesses of the (*R*)-Mosher's esters of prepared samples of chiral 1-phenethanol (**16**).

(*R*)-α-Methoxy-α(trifluoromethyl)phenylacetate ester	^{1}H NMR chemical shift					
	$ROCH_3$			RCH_3		
	(*RS*)	Ratio	(*RR*)	(*RS*)	Ratio	(*RR*)
(*R,S*)-1-Phenethanol (**16**)	δ 3.59, s	50:50	δ 3.50, s	δ 1.66, d	50:50	δ 1.60, d
(*R*)-1-Phenethanol (+)-(**16**) from (+)-(**14**)		0:100	δ 3.49, s		0:100	δ 1.60, d
(*R*)-1-Phenethanol (+)-(**16**) from (−)-(**15**)		0:100	δ 3.49, s		0:100	δ 1.60, d
(*R*)-1-Phenethanol (+)-(**16**) from (**28**)		0:100	δ 3.49, s		0:100	δ 1.59, d
(*R*)-1-Phenethanol (+)-(**16**) from (+)-(**30**)		0:100	δ 3.49, s		0:100	δ 1.59, d
(*S*)-1-Phenethanol (+)-(**16**) from (+)-(**31**)	δ 3.59, s	100:0		δ 1.66, d	100:0	

standard conditions (24 h). Work-up gave (*S*)-1-phenethanol (−)-(**16**) as a clear, colourless oil (18 mg, 100%), identified by comparison with an authentic sample.

General Procedure for Preparation of (R)-α-*Methoxy-α-(trifluoromethyl)phenylacetate Esters (Mosher's Esters).*[14]—A sample of chiral or racemic alcohol (0.15 mmol) was dissolved in CH_2Cl_2 (0.25 ml) containing 4-dimethylaminopyridine (1 crystal) and pyridine (6 drops), and (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (1.55M in CH_2Cl_2; 0.17 ml, 0.26 mmol) added. The solution was stirred (24 h) and aqueous H_2SO_4 (0.5M; 2 ml) added. The mixture was extracted with Et_2O (3 × 2 ml) and the organic extracts were combined, dried ($MgSO_4$), and evaporated to give an oil. A $CDCl_3$ (0.5 ml) solution of the ester was filtered through a short plug of silica prior to ^{1}H n.m.r. spectroscopy.

(R)-α-*Methoxy-α-(trifluoromethyl)phenylacetate Ester of* 1-*Phenethanol* (**16**).—The (*R*)-α-methoxy-α-(trifluoromethyl)-phenylacetate esters of racemic and chiral samples of 1-phenethanol (**16**) were prepared under standard conditions. The ^{1}H n.m.r. chemical shifts used to check diastereoisomeric excesses of the esters, and hence enantiomeric excesses of the free alcohols, are presented in Table 3.

Tricarbonyl(η^6-o-*tri-isopropylsilylbenzyl alcohol)-chromium*(0).—Tricarbonyl(η^6-*o*-tri-isopropylsilylbenzaldehyde)chromium(0) (**2**) (100 mg, 0.25 mmol) in THF (5 ml) was treated with $LiEt_3BH$ (1.00M in THF; 0.50 ml, 0.50 mmol) under standard conditions (−78 °C, 5 min) with water (3 drops) quench. Column chromatography (Al_2O_3, Et_2O–hexane 1:1) gave, on evaporation of the solvent, the title compound as a yellow oil (95 mg, 95%); δ(CD_3COCD_3) 6.03–5.96 and 5.41–5.34 (2 H, 2 t, ArH), 5.79–5.76, 5.67–5.64 (2 H, 2 d, ArH), 4.73–4.68 (1 H, m, $ArCH_2OH$), 4.54, 4.45 (2 H, ABX system, J_{AX} 5.4 Hz, J_{BX} 5.1 Hz, J_{AB} 13.2 Hz, $ArCH_2OH$), 1.53–1.32 {3 H, m, $ArSi[CH(CH_3)_2]_3$}, and 1.26–1.12 {18 H, m, $ArSi[CH(CH_3)_2]_3$}.

Addition of $LiEt_3BD$ to *Tricarbonyl*(η^6-o-*tri-isopropylsilyl-benzaldehyde)chromium*(0)(**2**).—Tricarbonyl(η^6-*o*-tri-isopropylsilylbenzaldehyde)chromium(0) (**2**) (100 mg, 0.25 mmol) in THF (8 ml) was treated with $LiEt_3BD$ (1.00M in THF; 0.45 ml, 0.45 ml, 0.45 mmol) under standard conditions (−78 °C, 5 min) with water (3 drops) quench. Column chromatography (SiO_2, Et_2O) gave, on evaporation of the solvent, an 86:14 mixture of (*RS,SR*)-tricarbonyl(η^6-*o*-tri-isopropylsilyl-α-deuteriobenzyl alcohol)chromium(0) and (*RR,SS*)-tricarbonyl(η^6-*o*-tri-isopropylsilyl-α-deuteriobenzyl alcohol)chromium(0) complexes (**32**) and (**33**) respectively as a yellow oil (99 mg, 99%); δ($CDCl_3$) (**32**): 4.53 [1 H, s, $ArCH(OH)D$], (**33**): 4.43 [1 H, s, $ArCH(OH)D$], (**32**) and (**33**): 6.03–5.96, 5.41–5.35 (2 H, 2 t, ArH), 5.79–5.76 and 5.68–5.63 (2 H, 2 d, ArH), 4.70–4.67 [1 H, m, $ArCH(OH)D$], 1.53–1.32 {3 H, m, $ArSi[CH(CH_3)_2]_3$}, 1.26–1.09 {18 H, m, $ArSi[CH(CH_3)_2]_3$}; *m/z* 402 ($M^+ + 1$).

Addition of $LiEt_3BD$ *to Tricarbonyl*(η^6-o-*tri-isopropylsilyl-benzaldehyde)chromium*(0) (**2**). *Pre-treated with* $MgBr_2{\cdot}OEt_2$.—Tricarbonyl(η^6-*o*-tri-isopropylsilylbenzaldehyde)chromium(0) (**2**) (100 mg, 0.25 mmol) in Et_2O (5 ml) was treated with $MgBr_2{\cdot}OEt_2$ (0.80M; 3.33 ml, 2.66 mmol) followed by $LiEt_3BD$ (1.00M; 0.50 ml, 0.50 mmol) under standard conditions. Work-up and column chromatography (Al_2O_3, Et_2O-hexane, 2:1) gave on evaporation of the solvent, a 12:88 mixture of complexes (**32**) and (**33**) as a yellow oil (92 mg, 92%), identified by comparison with an authentic mixture.

Addition of $LiAlD_4$ *to Tricarbonyl*(η^6-o-*tri-isopropylsilyl-benzaldehyde)chromium*(0) (**2**).—Tricarbonyl(η^6-*o*-tri-isopropylsilylbenzaldehyde)chromium(0) (**2**) (120 mg, 0.30 mmol) in THF (8 ml) was treated with powdered $LiAlD_4$ (60 mg, 1.43 mmol) under standard conditions (−78 °C, 10 min). Column chromatography (Al_2O_3, Et_2O–hexane, 1:1) gave, on evaporation of the solvent, a 30:70 mixture of complexes (**32**) and (**33**) as a yellow oil (120 mg, 100%), identified by comparison with an authentic mixture.

Addition of $LiAlD_4$ *to Tricarbonyl*(η^6-o-*tri-isopropylsilyl-benzaldehyde)chromium*(0) (**2**) *Pre-treated with* $MgBr_2{\cdot}OEt_2$.—Tricarbonyl(η^6-*o*-tri-isopropylsilylbenzaldehyde)chromium(0) (100 mg, 0.25 mmol) in Et_2O (5 ml) was treated with $MgBr_2{\cdot}OEt_2$ (0.80M; 3.33 ml, 2.66 mmol) followed by powdered $LiAlD_4$ (50 mg, 1.19 mmol) under standard conditions. Work-up and column chromatography (Al_2O_3, Et_2O–hexane, 1:1) gave, on evaporation of the solvent, a 6:94 mixture of complexes (**32**) and (**33**) (65 mg, 65%), identified by comparison with an authentic mixture.

Addition of $LiAlD_4$ *to* (−)-*Tricarbonyl*(η^6-o-*tri-isopropylsilyl-benzaldehyde)chromium*(0) (−)-(**2**) *Pre-treated with* $MgBr_2{\cdot}OEt_2$.—(−)-Tricarbonyl(η^6-*o*-tri-isopropylsilylbenzaldehyde)-chromium(0) (−)-(**2**) (60 mg, 0.15 mmol) in Et_2O (5 ml) was treated with $MgBr_2{\cdot}OEt_2$ (0.80M; 3.33 ml, 2.66 mmol) followed by powdered $LiAlD_4$ (50 mg, 1.19 mmol) under standard conditions. Work-up and column chromatography (Al_2O_3, Et_2O–hexane, 1:1) gave, on evaporation of the solvent, a 6:94 mixture of (*RS*)-tricarbonyl(η^6-*o*-tri-isopropylsilyl-α-deuteriobenzyl alcohol)chromium(0) (**32**) and (*RR*)-tricarbonyl(η^6-*o*-tri-isopropylsilyl-α-deuteriobenzyl alcohol)chromium(0) (**33**) as a yellow solid (60 mg, 100%), identified by comparison with an authentic racemic mixture, $[\alpha]_D^{18}$ −50 °C (*c* 0.715 in $CHCl_3$).

Desilylation and Decomplexation of a 6:94 *Mixture of* (RS)-*and* (RR)-*Tricarbonyl*(η^6-o-*tri-isopropylsilyl-α-deuteriobenzyl*

Table 4. ^{1}H NMR chemical shifts used to check diastereoisomeric excesses of the (*R*)-Mosher's esters of prepared samples of (*R*)- and (*S*)-α-deuteriobenzyl alcohol (*R*)- and (*S*)-(**27**).

(*R*)-α-Methoxy-α-(trifluoromethyl)phenylacetate ester	^{1}H NMR chemical shift (C_6D_6)		
	ArC*H*(OH)R		
	δ 4.96, 4.86 AB system		
Benzyl alcohol	(*RS*)	Ratio	(*RR*)
(*S*)-α-Deuteriobenzyl alcohol (*S*)-(**27**) from a 92:8 mixture of (*RS*)- and (*RR*)-(*o*-trimethylsilyl-α-deuteriobenzyl alcohol) $Cr(CO)_3$ complexes (**25**) and (**26**)	δ 4.83, s	92:8	δ 4.93, s
(*R*)-α-Deuteriobenzyl alcohol (*R*)-(**27**) from a 4:96 mixture of (*RS*)- and (*RR*)-(*o*-trimethylsilyl-α-deuteriobenzyl alcohol) $Cr(CO)_3$ complexes (**25**) and (**26**)	δ 4.82, s	4:96	δ 4.92, s
(*R*)-α-Deuteriobenzyl alcohol (*R*)-(**27**) from a 6:94 mixture of (*RS*)- and (*RR*)-(*o*-tri-isopropylsilyl-α-deuteriobenzyl alcohol) $Cr(CO)_3$ complexes (**32**) and (**33**)	δ 4.83, s	6:94	δ 4.93, s

alcohol)chromium(0) *Complexes* (**32**) *and* (**33**).—Tetrabutylammonium fluoride trihydrate (98 mg, 0.31 mmol) was added to a CH_2Cl_2 (2 ml) solution of a 6:94 mixture of (*RS*)- and (*RR*)-tricarbonyl(η^6-*o*-tri-isopropylsilyl-α-deuteriobenzyl alcohol)chromium(0) complexes (**32**) and (**33**) (25 mg, 63 μmol) and the solution stirred (30 min). After filtration (Al_2O_3, Et_2O) and evaporation of the solvent, Et_2O (10 ml) was added and the mixture allowed to decomplex under standard conditions (24 h). Work-up gave (*R*)-α-deuteriobenzyl alcohol (*R*)-(**27**) as a clear, colourless oil (7 mg, 100%), identified by comparison with an authentic racemic sample.[18]

(R)-α-*Methoxy*-α-(*trifluoromethyl*)*phenylacetate Esters of Benzyl Alcohol and* α-*Deuteriobenzyl Alcohol* (**27**).—The (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetate esters of benzyl alcohol and chiral samples of (*R*- and (*S*)-α-deuteriobenzyl alcohol (*R*)- and (*S*)-(**27**) were prepared under standard conditions. The ^{1}H n.m.r. chemical shifts used to check diastereoisomeric excesses of the esters, and hence enantiomeric excesses of the free alcohols, are presented below in Table 4.

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