Elaboration of α-Substituted Benzyl Alkyl Ethers and Sulphides by Suppression of the Wittig and Related Rearrangements *via* Complexation to Tricarbonylchromium

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Co-ordination of benzyl alkyl ethers and sulphides to tricarbonylchromium allows α-substitution *via* the corresponding α-carbanions to be achieved by suppression of the Wittig and related rearrangements. Little stereoselectivity was observed in the α-methylation of tricarbonylchromium complexes of benzyl ethers derived from a variety of chiral alcohols. Excellent stereoselectivities were observed in the mono- and di-methylation reactions of tricarbonyl[*o*-xylene-α,α′-diyl bis(methyl ether)]chromium where single diastereoisomers of the α-methyl and α,α′-dimethyl complexes were formed. Deprotonation and methylation of tricarbonyl-*syn*-1-methoxytetralinchromium occurred stereospecifically with complete retention of configuration under conditions where the corresponding *anti*-complex was inert. On treatment with base tricarbonyl-(3-chloropropyl benzyl ether)chromium cyclises to give tricarbonyl-(2-phenyltetrahydrofuran)chromium. Exposure of arenetricarbonylchromium complexes to air and sunlight quantitatively liberates the free arene.

The complexation of an aromatic ring to the tricarbonylchromium moiety is known to facilitate α-carbanion formation as well as proton abstraction from the aromatic ring. The site of metallation may be influenced by the base used as well as the substituents on the aromatic ring. The use of potassium t-butoxide in dimethyl sulphoxide,[1] sodium hexamethyldisilazide in tetrahydrofuran,[2] sodium hydride in *N,N*-dimethylformamide[3] or butyl-lithium in tetrahydrofuran[4] has been shown to result in predominant benzylic deprotonation. In contrast, treatment with butyl-lithium in tetrahydrofuran or ether is also known to favour aromatic deprotonation particularly of functionalised arenes.[5]

We describe here the use of the tricarbonylchromium moiety to stabilise α-carbanions derived from benzyl alkyl ethers and sulphides. Complete suppression of the Wittig and related rearrangements[6] allows synthetically useful functionalisation at the benzylic position to be achieved. The stereoselectivity of these reactions is also examined. Part of this work has been the subject of a preliminary communication.[7]

Results

Benzyl methyl ether (**1**) and hexacarbonylchromium were heated in a 10:1 mixture of dibutyl ether and tetrahydrofuran at reflux under a nitrogen atmosphere to give after work-up the bright yellow (benzyl methyl ether)tricarbonylchromium complex (**3**) in 84% yield. In an alternative preparation of the complex (**3**), benzyl alcohol and hexacarbonylchromium were heated together in the same solvent mixture to produce after work-up (benzyl alcohol)tricarbonylchromium (**2**) in 74% yield. Treatment of a methanolic dichloromethane solution of (**2**) with tetrafluoroboric acid–dimethyl ether complex at −30 °C or with concentrated sulphuric acid gave, *via* the corresponding chromium-stabilised carbonium ion, complex (**3**) in 84% yield.[8] This latter method was employed in the synthesis of a variety of benzyl alkyl ether complexes [complexes (**3**)—(**6**) in Table 1 and (**19**)—(**21**) in Table 2].

Treatment of benzyl methyl ether (**1**) in tetrahydrofuran at −40 °C with butyl-lithium followed by the addition of methanol gave, after work-up, the expected Wittig rearrangement product, 1-phenylethanol.[6] Treatment of the (benzyl methyl ether)tricarbonylchromium complex (**3**) with butyl-lithium under the same conditions followed by protonation with methanol led to the isolation of only the starting complex (**3**) indicating that complete suppression of the Wittig rearrangement had occurred. Deprotonation of complex (**3**) with butyl-lithium as above followed by addition of methyl iodide gave tricarbonyl(methyl 1-phenylethyl ether)chromium (**7**). A diethyl ether solution of compound (**7**) was allowed to stand in air and sunlight until the characteristic bright yellow colour of the arenetricarbonylchromium complex had disappeared. Work-up gave an essentially quantitative yield of methyl 1-phenylethyl ether (**8**). To confirm unambiguously the structural assignment of the complex (**7**) an independent synthesis was undertaken. 1-Phenylethanol and hexacarbonylchromium were heated in dibutyl ether and tetrahydrofuran (10:1) to give tricarbonyl(1-phenylethanol)chromium (**9**) which on treatment with tetrafluoroboric acid–dimethyl ether complex in methanolic dichloromethane gave the complex (**7**).

The α-deprotonation and subsequent α-methylation of complex (**3**) is a general reaction and the results for a variety of benzyl alkyl ethers complexed to tricarbonylchromium with a variety of electrophiles are given in Tables 1 and 2.

Table 1. Elaboration of α-substituted (benzyl alkyl ether)tricarbonylchromium complexes

$$(PhCH_2OR)Cr(CO)_3 \xrightarrow[ii,\ E^+]{i,\ BuLi} [PhCH(E)OR]Cr(CO)_3$$

Starting material R	Electrophile E^+	Isolated product	Yield (%)
(**3**) Me	MeOH	(**3**)	92
(**3**) Me	MeI	(**7**)	79
(**3**) Me	EtBr	(**10**)	75
(**3**) Me	Pr^iBr	(**11**)	65
(**3**) Me	$PhCO_2Me$	(**12**)	64
(**3**) Me	MeCHO	(**13**)[a]	51
(**4**) Et	MeI	(**14**)	58
(**5**) $PhCH_2$	MeI	(**15**)	68
(**6**) CH_2CHCH_2	MeI	(**16**)	89

[a] Product (**13**) obtained as a 2:1 mixture of diastereoisomers.

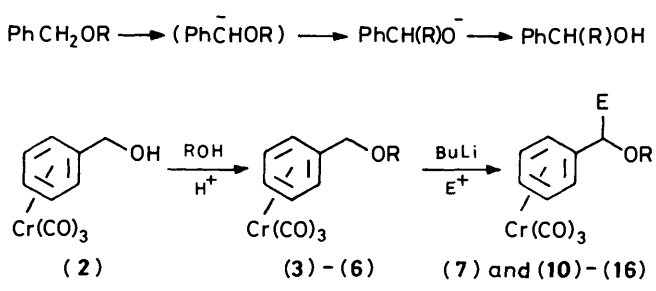
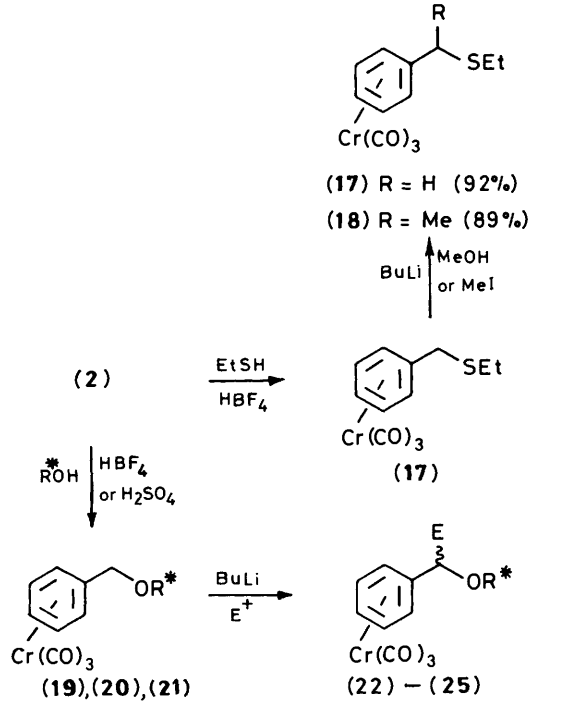


Table 2. Stereoselectivities for the α-methylation of chiral (benzyl alkyl ether)tricarbonylchromium complexes

Starting material R*OH	Electrophile E^+	Product	Yield (%)	Diastereoselectivity[a]
(**19**) (*R*)-butan-2-ol	MeI	(**22**)	71	60:40
(**19**) (*R*)-butan-2-ol	CD_3OD	(**23**)	71	60:40
(**20**) (*S*)-butan-2-ol	MeI	(**24**)	88	40:60
(**21**) Cholesterol	MeI	(**25**)	82	76:24

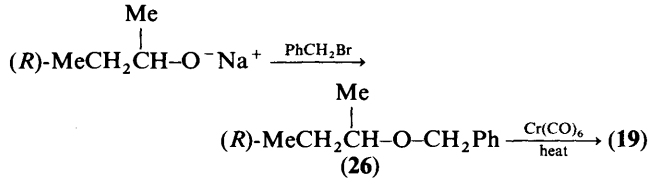
[a] The ratio of diastereoisomers was determined by 300 MHz n.m.r. spectroscopy. The use of (±)-octan-2-ol, (±)-1-phenylethanol, (±)-1-phenylpropanol, 1-menthol, and (±)-but-3-en-2-ol to form the (benzyl alkyl ether)tricarbonylchromium complexes led to no improvement in the diastereoselectivity of subsequent alkylations.



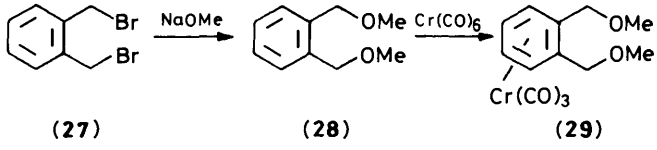
Reaction of the complex (**2**) in dichloromethane at −30 °C with ethanethiol in the presence of an acid, gave the benzyl ethyl sulphide complex (**17**) in 91% yield. Treatment of complex (**17**) in tetrahydrofuran at −40 °C with butyl-lithium followed by methanol or methyl iodide gave the starting complex (**17**) or the α-alkylated complex (**18**) respectively.

The reaction of the anion derived from (benzyl alkyl ether)-tricarbonylchromium complexes $(PhCH_2OR)Cr(CO)_3$ with electrophiles generates a new chiral centre at the benzylic position. We were interested in whether the replacement of R by a chiral alkyl group R* would lead to stereospecific benzylic deprotonation and alkylation (Table 2).

To ensure that no racemisation had occurred in the synthesis of compounds (**19**) and (**20**) an alternative route was employed for the preparation of (**19**). (*R*)-Benzyl butan-2-yl ether (**26**) was prepared by the reaction of benzyl bromide with sodium (*R*)-2-butoxide in 84% yield. Thermolysis of hexacarbonylchromium in the presence of compound (**26**) gave [(*R*)-benzyl butan-2-yl ether]tricarbonylchromium (**19**) in 73% yield. The optical rotations of the compound (**19**) prepared by the two independent routes were identical $[\alpha]_D^{20}$ −13.1° (*c* 0.95, $CHCl_3$).

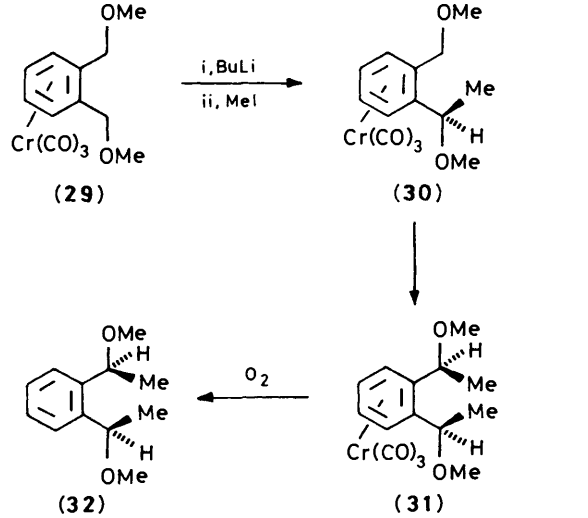


The stabilisation of α-carbanions by the tricarbonylchromium unit is also evident in the xylene-α,α′-diyl ethers. Treatment of α,α′-dibromo-*o*-xylene (**27**) with sodium methoxide in methanol gave *o*-xylene-α,α′-diyl bis(methyl ether) (**28**) in 72% yield. Thermolysis of hexacarbonylchromium in the presence of the ether (**28**) gave tricarbonyl-*o*-xylene-α,α′-diyl bis(methyl ether)chromium (**29**) in 78% yield.

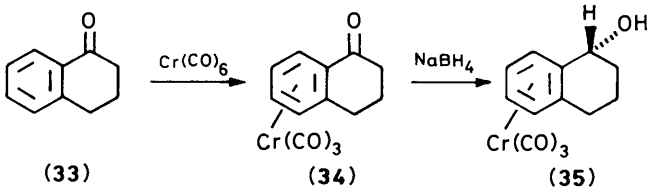


Addition of butyl-lithium to a solution of the complex (**29**) in tetrahydrofuran at −78 °C followed by methyl iodide gave a single diastereoisomer of the mono-α-methylated complex (**30**). Further treatment of compound (**30**) with butyl-lithium followed by methyl iodide gave the α,α′-dimethylated complex (**31**). Only a single diastereoisomer could be detected by ^1H n.m.r. spectroscopy. Decomplexation of (**31**) gave α,α′-dimethyl-*o*-xylene-α,α′-diyl bis(methyl ether) (**32**), and again only one diastereoisomer was observed.

Thermolysis of hexacarbonylchromium in the presence of 1-tetralone (**33**) gave tricarbonyl-1-tetralonechromium (**34**)[9]

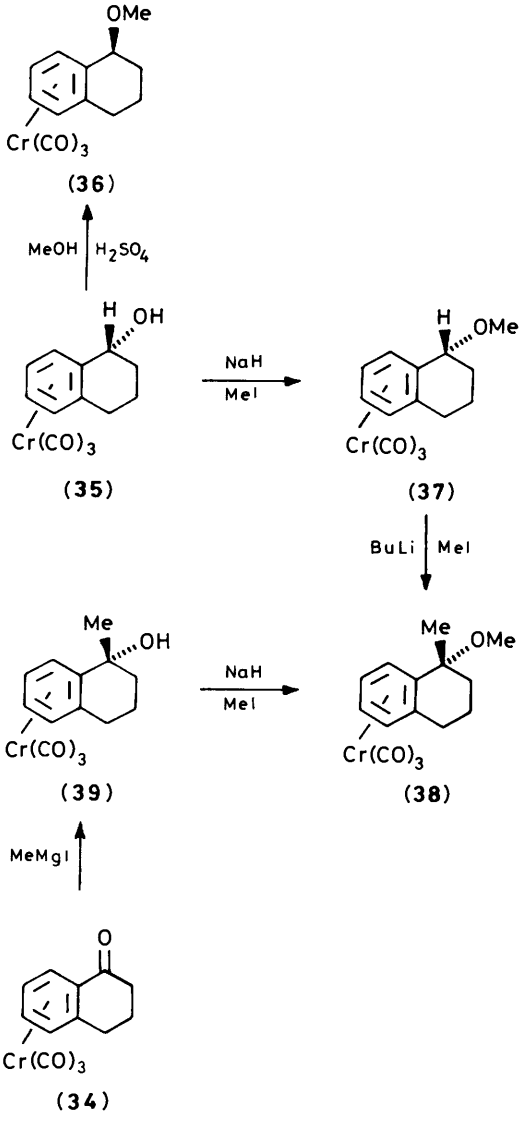


in 52% yield. The reduction of the complex (**34**) with sodium borohydride gave exclusively tricarbonyl-*syn*-1-tetralolchromium (**35**) in 63% yield.[10]



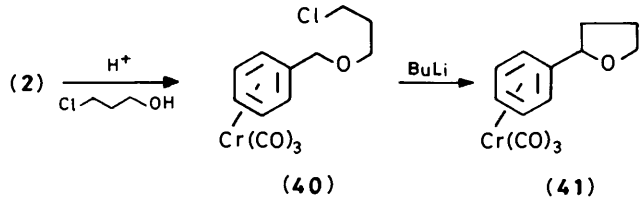
(33) (34) (35)

A methanolic solution of tricarbonyl-*syn*-1-tetralolchromium (**35**) on treatment with H_2SO_4 gave tricarbonyl-*anti*-1-methoxytetralinchromium (**36**).[11] Treatment of compound (**35**) with sodium hydride followed by methyl iodide gave tricarbonyl-*syn*-1-methoxytetralinchromium (**37**) in 62% yield.



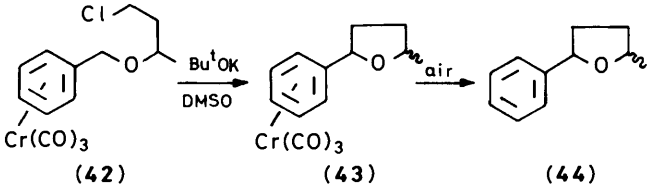
Addition of butyl-lithium at −40 °C to a solution of the *syn*-complex (**37**) followed by addition of methyl iodide gave the stereospecifically methylated product (**38**) in 71% yield. The *anti*-complex (**36**) was completely inert towards methylation under the same conditions. To confirm the identity of complex (**38**) an independent synthesis was undertaken. Treatment of tricarbonyl-1-tetralonechromium (**34**) with methylmagnesium iodide gave *via* exclusive *exo*-addition, the *syn*-hydroxy complex (**39**).[12] Subsequent *O*-methylation with sodium hydride and methyl iodide gave compound (**38**).

Treatment of (benzyl alcohol)tricarbonylchromium (**2**) in dichloromethane with 3-chloropropanol at −30 °C in the presence of an acid gave the benzyl tricarbonyl-(3-chloropropyl ether)chromium complex (**40**). Subsequent treatment of compound (**40**) with butyl-lithium in tetrahydrofuran at −40 °C gave the 2-phenyltetrahydrofuran complex (**41**).



(40) (41)

Similar ring closure on complex (**42**) using potassium t-butoxide in dimethyl sulphoxide gave a 3:2 mixture of diastereoisomers of tricarbonyl-(5-methyl-2-phenyltetrahydrofuran)chromium (**43**). Decomplexation of compound (**43**) by exposure of a diethyl ether solution to air and sunlight liberated, essentially quantitatively, a mixture of *cis*- and *trans*-5-methyl-2-phenyltetrahydrofuran (**44**).

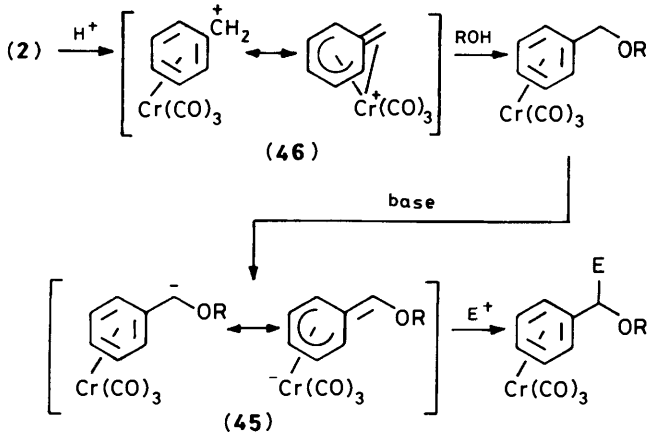


(42) (43) (44)

Discussion

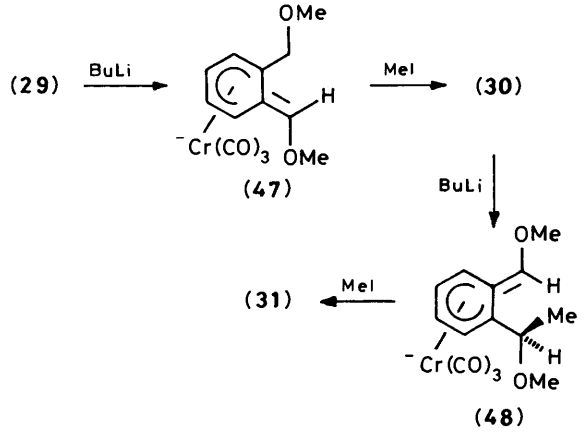
A large number of pharmacologically active aromatic natural products contain chiral heterosubstituted benzylic centres. An attractive synthetic methodology for elaborating such benzylic positions is *via* electrophilic addition to benzylic carbanions. In general however, this has not proved feasible because of difficulties in generating benzylic carbanions and because once formed these anions readily undergo a variety of rearrangement reactions. Thus deprotonation of benzyl methyl ether (**1**) gives, after Wittig rearrangement of the intermediate α-carbanion, 1-phenylethanol. The strong mesomeric electron-withdrawing capability of tricarbonylchromium groups bound to arenes not only increases the acidity of α-protons but also stabilises the resulting α-carbanions against rearrangement. Co-ordination of compound (**1**) to tricarbonylchromium gives compound (**3**), deprotonation of which generates the stabilised α-carbanionic intermediate (**45**) (R = Me). Protonation of compound (**45**) regenerates (**3**) with none of the expected rearranged product, tricarbonyl-1-phenylethanolchromium, being detectable, consistent with complete suppression of the Wittig rearrangement. Benzyl alkyl ethertricarbonylchromium complexes are very readily available from (benzyl alcohol)tricarbonylchromium (**2**) *via* the stabilised carbonium ion (**46**).[8] In none of the deprotonation–alkylation reactions listed in Tables 1 and 2 were any rearrangement products seen. The corresponding benzylic carbanions undergo smooth addition with a variety of electrophiles.

α-Carbanions generated from benzyl alkyl sulphides are even



more prone to rearrangement and decomposition than their corresponding oxygen analogues.[13] However, complexation of such sulphides to tricarbonylchromium again stabilises the derived α-carbanions and allows benzylic alkylation to proceed, *e.g.* (**17**) ⟶ (**18**).

Alkylation of α-carbanions derived from (benzyl alkyl ether)-tricarbonylchromium complexes generates a new chiral centre at the benzylic position. Unfortunately the introduction of a variety of chiral alkyl groups into these complexes, in order to render the benzylic protons diastereotopic, afforded very little stereochemical control in the deprotonation and alkylation reactions (Table 2). Excellent stereochemical control was observed however in the sequential mono- and di-methylation reactions of the dimethyl-*o*-xylenediyl ether complex (**29**). The high stereoselectivities observed in these reactions are consistent with in each case deprotonation giving the sterically less encumbered *anti*-carbanions (**47**) and (**48**) respectively with methylation occurring from the unhindered face away from the tricarbonylchromium moiety.



Stabilisation by the tricarbonylchromium of the transition state for α-deprotonation requires the breaking C–H bond to be close to *anti*- or *syn*-periplanar with the arene–chromium bond. Only deprotonation of the *anti*-arrangement is expected to occur however because the tricarbonylchromium group would hinder approach of the base in the *syn*-arrangement. This is consistent with the *syn*-complex (**37**) (H *anti* to Cr) undergoing smooth deprotonation and methylation with complete retention of configuration to give (**38**), due to both the base and methyl iodide approaching from the unencumbered face, under conditions where the *anti*-complex (**36**) (H *syn* to Cr) is completely inert.

Quantitative decomplexation of arenetricarbonylchromium complexes can be achieved by exposure of diethyl ether solutions to air and sunlight which liberates the free arene.

Experimental

All reactions involving the preparation or utilisation of tricarbonyl-η⁶-(arene)chromium(0) complexes were performed under an atmosphere of nitrogen.

All commercial reagents were purified according to standard techniques.[14] THF and toluene were distilled from sodium diphenylketyl under an atmosphere of nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. Dimethyl sulphoxide was heated (100 °C) over calcium hydride (6 h) and distilled under reduced pressure from fresh calcium hydride. Methanol was distilled before use. Diethyl ether was peroxide free. Hexane refers to that fraction of light petroleum boiling between 67—70 °C. Dibutyl ether was dried over sodium and distilled under an atmosphere of nitrogen prior to use.

Melting points were obtained on a Kofler hot-stage apparatus and are uncorrected. Optical rotations were determined on a Perkin-Elmer 241 instrument operating at the frequency of the sodium D-line.

Benzyl Methyl Ether (**1**).—Sodium hydride (50% w/w dispersion in mineral oil; 5.3 g, 0.11 mol) was washed with petroleum (b.p. 40—60 °C; 2 × 50 ml). A solution of benzyl alcohol (10 g, 93 mmol) in THF (50 ml) was added and stirred (50 °C; 3 h). Methyl iodide (14 g, 0.11 mol) in THF (20 ml) was added to the cooled solution (0 °C) and stirred (20 °C; 16 h). Diethyl ether (200 ml) was added and the mixture filtered through Celite. Evaporation and distillation of the residue gave compound (**1**) as a colourless liquid (10.3 g, 91%), b.p. 29—30 °C, 0.1 mmHg (lit.,[15] 170 °C, 750 mmHg); $\nu_{max.}$(film) 1 090, 740, and 700 cm^{-1}; δ_H (60 MHz; $CDCl_3$), 7.00 (5 H, s), 4.05 (2 H, s), and 3.00 (3 H, s).

η⁶-(*Benzyl methyl ether*)*tricarbonylchromium*(0) (**3**).—A deoxygenated mixture of dibutyl ether (40 ml), THF (4 ml), benzyl methyl ether (**1**) (3.60 g, 29 mmol) and hexacarbonylchromium (7.30 g, 32 mmol) was heated under reflux (30 h). The cooled solution was filtered, concentrated, and chromatographed (Al_2O_3 Grade II–Et_2O). Evaporation of the solvent gave a yellow oil which was crystallised from diethyl ether–hexane to give compound (**3**) (6.39 g, 84%) as a yellow crystalline solid, m.p. 40 °C; $\nu_{max.}$(Nujol) 1 980, 1 905, and 1 095 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.25 (5 H, s), 4.10 (2 H, s), and 3.35 (3 H, s); *m/z* 258 (M^+) (Found: C, 51.3; H, 4.0. $C_{11}H_{10}CrO_4$ requires C, 51.2; H, 3.9%).

η⁶-(*Benzyl alcohol*)*tricarbonylchromium*(0) (**2**).—A deoxygenated mixture of dibutyl ether (40 ml), THF (4 ml), benzyl alcohol (2.50 g, 23 mmol), and hexacarbonylchromium (4.0 g, 18 mmol) was heated under reflux (48 h). Petroleum (b.p. 40—60 °C; 200 ml) was added to the cooled solution. The precipitate was collected by filtration and crystallised from diethyl ether–hexane to give compound (**2**) (3.25 g, 74%) as pale yellow needles, m.p. 92—94 °C (lit.,[16] m.p. 95—96 °C); $\nu_{max.}$(Nujol) 3 280, 3 180br, 1 980, 1 950, and 1 910 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.35 (5 H, s), 4.45 (2 H, s), and 2.35 (br, 1 H); *m/z* 244 (M^+).

General Procedure for the Preparation of η⁶-(*Benzyl alkyl ether*)*tricarbonylchromium*(0) *Systems* (**3**—**6**), (**19**—**20**), (**40**), *and* (**42**).—To a solution of η⁶-(benzyl alcohol)tricarbonyl-

chromium(0) (**2**) (1.05 g, 4.3 mmol) in dichloromethane (25 ml) containing methanol (3 ml, excess) at −30 °C was added dropwise tetrafluoroboric acid–dimethyl ether complex (1.3 ml). After the reaction had been stirred for (10 min), water (2 ml) was added and the mixture was warmed (20 °C) and concentrated. The residue was taken up in diethyl ether and column chromatography of the solution (Al_2O_3 Grade II–Et_2O) followed by removal of the solvent gave a yellow oil which crystallised from diethyl ether–hexane to give η⁶-(benzyl methyl ether)tricarbonylchromium(0) (**3**) (0.94 g, 84%) identical in all respects with the sample obtained above.

η⁶-(*Benzyl ethyl ether*)*tricarbonylchromium*(0) (**4**).—Prepared according to the above procedure using ethanol (3 ml) in place of methanol. The product complex (**4**) was isolated as yellow crystals in 75% yield; $\nu_{max.}$(Nujol) 1 980 and 1 910 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.25 (5 H, s), 4.15 (2 H, s), 3.55 (2 H, q, *J* 7 Hz), and 1.20 (3 H, t, *J* 7 Hz); *m/z* 272 (M^+).

Tricarbonyl-η⁶-(*dibenzyl ether*)*chromium*(0) (**5**).—Prepared according to the above procedure using benzyl alcohol (3 ml) in place of methanol. The product complex (**5**) was isolated as a yellow oil in 62% yield; $\nu_{max.}$(Nujol) 1 980, 1 915, and 1 090 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 7.00 (5 H, s), 5.00 (5 H, s), 4.30 (2 H, s), and 3.90 (2 H, s); *m/z* 334 (M^+).

η⁶-(*Allyl benzyl ether*)*tricarbonylchromium*(0) (**6**).—Prepared according to the above procedure using allyl alcohol in place of methanol. The product complex (**6**) was isolated as a dark yellow oil in 87% yield; $\nu_{max.}$(film) 1 980, 1 910, 1 645, and 1 080 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 6.40—5.80 (1 H, m), 5.50—5.20 (7 H, m), 4.25 (2 H, s), 4.15 (2 H, d, *J* 6 Hz); *m/z* 284 (M^+) (Found: C, 55.1; H, 4.4. $C_{13}H_{12}CrO_4$ requires C, 54.93; H, 4.26%).

η⁶-[(R)-*Benzyl butan-2-yl ether*]*tricarbonylchromium*(0) (**19**).—Prepared according to the above procedure using (*R*)-butan-2-ol in place of methanol. The product complex (**19**) was isolated as yellow plates in 68% yield; m.p. 49—51 °C $[\alpha]_D^{20}$ −13.1° (*c* 0.95, $CHCl_3$); $\nu_{max.}$(Nujol) 1 980, 1 910, and 1 090 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.40 (5 H, s), 4.20 (2 H, s), 3.65—3.40 (1 H, m), 1.75—1.35 (2 H, m), 1.20 (3 H, d, *J* 6 Hz), and 0.95 (3 H, t, *J* 7 Hz); *m/z* 300 (M^+) (Found: C, 56.2; H, 5.15. $C_{14}H_{16}CrO_4$ requires C, 56.00; H, 5.37%).

η⁶-[(S)-*Benzyl butan-2-yl ether*]*tricarbonylchromium*(0) (**20**).—Prepared according to the above procedure using (*S*)-butan-2-ol in place of methanol. The product complex (**20**) was isolated as yellow plates in 68% yield; $[\alpha]_D^{20}$ +9.9° (*c* 0.96, $CHCl_3$). All other experimental data were consistent with the data for compound (**19**) above.

η⁶-(*Benzyl 3-chloropropyl ether*)*tricarbonylchromium*(0) (**40**).—Prepared according to the above procedure using 3-chloropropanol in place of methanol. The product complex (**40**) was isolated as a yellow oil in 77% yield; $\nu_{max.}$(film) 1 980, 1 910, and 1 105 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.35 (5 H, s), 4.25 (2 H, s), 3.70 (4 H, t, *J* 6 Hz), and 2.05 (2 H, quint. *J* 6 Hz); *m/z* 320 and 322 (M^+).

η⁶-(3-*Benzyloxybutyl chloride*)*tricarbonylchromium*(0) (**42**).—Prepared according to the above procedure using 3-chlorobutanol in place of methanol. The product complex (**42**) was isolated as a yellow oil in 65% yield; $\nu_{max.}$(Nujol) 1 980 and 1 910 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.25 (5 H, s), 4.20—4.10 (2 H, m), 3.85—3.45 (3 H, m), 2.05—1.80 (2 H, m), and 1.20 (3 H, d, *J* 7 Hz); *m/z* 334 and 336 (M^+).

η⁶-(*Benzyl cholesteryl ether*)*tricarbonylchromium*(0) (**21**).—Potassium hydride (35% w/w) dispersion in mineral oil; 1.05 g, 26.2 mmol) was washed with light petroleum (40—60 °C; 2 × 30 ml). Cholesterol (10.0 g, 25.9 mmol) and tetrabutylammonium iodide (0.20 g, 26 mmol) were then added and the reaction was stirred (3 h). Benzyl bromide (4.45 g, 26 mmol) was added and stirring was continued (1 h). Diethyl ether (200 ml) was added and the solution was filtered and evaporated to give a colourless solid which on crystallisation from dichloromethane–hexane gave benzyl cholesteryl ether[17] (8.78 g, 71%) as a colourless solid.

A deoxygenated mixture of dibutyl ether (40 ml), THF (4 ml), benzyl cholesteryl ether (1.40 g, 2.94 mmol), and hexacarbonylchromium (0.8 g, 3.6 mmol) was heated under reflux (40 h). The cooled solution was extracted with dichloromethane (50 ml) and chromatographed (Al_2O_3 Grade II–CH_2Cl_2) to give a gelatinous mixture. Washing with hexane (2 × 100 ml) and drying (80 °C, 0.1 mmHg; 4 h) gave (**21**) as a yellow powder (1.24 g, 69%), m.p. 172 °C; $\nu_{max.}$(Nujol) 1 965, 1 895, 1 875, 1 865, 1 115, and 1 090 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 5.20 (6 H, s), 4.10 (2 H, s), 3.40—3.05 (1 H, m), 2.35—0.75 (cholesteryl protons, m), 0.65 (3 H, s, 18-H_3); *m/z* 612 (M^+) (Found: C, 72.65; H, 8.65. $C_{37}H_{52}CrO_4$ requires C, 72.52; H, 8.55%); $[\alpha]_D^{20}$ +25.7° (*c* 1.09, $CHCl_3$).

1-*Phenylethanol* via *Wittig Rearrangement*.—Benzyl methyl ether (**1**) (2.0 g, 16 mmol) was dissolved in THF (25 ml) and cooled (−40 °C). Butyl-lithium (1.6M in hexane; 20 ml, 32 mmol) was added and the reaction was stirred (1 h). Methanol (5 ml) was added, the solution warmed (20 °C), the solvent removed, and the residue extracted with diethyl ether (40 ml). The diethyl ether was removed and the residue distilled to give 1-phenylethanol as a colourless liquid (0.76 g, 38%) identified by comparison with an authentic sample.

General Procedure for the Deprotonation and Alkylation of η⁶-(*Benzyl alkyl ether*)*tricarbonylchromium*(0) *Systems*.—To a solution of η⁶-(Benzyl methyl ether)tricarbonylchromium(0) (**3**) (0.26 g, 1.0 mmol) in THF (20 ml) at −40 °C was added butyl-lithium (1.6M in hexane; 1.60 ml, 2.55 mmol). After the reaction had been stirred (1 h), methanol (2 ml, excess) was added, the solution warmed (20 °C) and the solvent evaporated. The residue was extracted with diethyl ether (10 ml). Column chromatography (Al_2O_3 Grade V–CH_2Cl_2) followed by removal of the dichloromethane gave η⁶-(benzyl methyl ether)-tricarbonylchromium(0) (**3**) (0.24 g, 92%) identical in all respects with the sample prepared above.

Tricarbonyl-η⁶-(*methyl 1-phenylethyl ether*)*chromium*(0) (**7**).—Prepared according to the general procedure, above adding methyl iodide and stirring (1 h) prior to the addition of methanol. The product complex (**7**) was isolated as a yellow oil in 79% yield; $\nu_{max.}$(film) 1 970, 1 885, and 1 100 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.60—5.05 (5 H, m), 4.00 (1 H, q, *J* 6 Hz), 3.20 (3 H, s), and 1.45 (3 H, d, *J* 6 Hz).

Methyl 1-Phenylethyl Ether (**8**).—Tricarbonyl-η⁶-(methyl 1-phenylethyl ether)chromium(0) (**7**) (0.2 g, 0.73 mmol) was dissolved in diethyl ether (100 ml) and allowed to stand in air and sunlight until colourless. The solution was filtered and the solvent removed. The residue was extracted with dichloromethane (5 ml) and the extract filtered (Al_2O_3 Grade II). Removal of the solvent gave methyl 1-phenylethyl ether (**8**) as a colourless liquid (82 mg, 83%); $\nu_{max.}$(film) 1 090, 760, and 700 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 7.25 (5 H, s), 4.25 (1 H, q, *J* 6 Hz), 3.20 (3 H, s), and 1.40 (3 H, d, *J* 7 Hz).

Tricarbonyl-η⁶-(1-*phenylethanol*)*chromium*(0) (**9**).—A deoxy-

genated mixture of dibutyl ether (40 ml), THF (4 ml), 1-phenylethanol (2.0 g, 16 mmol) and hexacarbonylchromium (4.0 g, 18 mmol) was heated under reflux (16 h). The cooled solution was filtered, concentrated, and chromatographed (Al_2O_3 Grade V–CH_2Cl_2). Evaporation of the solvent gave compound (**9**) (2.78 g, 66%) as yellow oil; $\nu_{max.}$(film) 3 390br, 1 965, and 1 885 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.40—5.30 (5 H, m), 4.60 (1 H, q, *J* 6 Hz), 2.70 (1 H, br), and 1.50 (3 H, d, *J* 6 Hz).

Alternative Preparation of Tricarbonyl-η^6*-(methyl 1-phenylethyl ether)chromium*(0) (**7**).—To a solution of tricarbonyl-η^6-(1-phenylethanol)chromium(0) (**9**) (0.63 g, 2.4 mmol) in dichloromethane (20 ml) containing methanol (2 ml) at −30 °C, was added dropwise tetrafluoroboric acid–dimethyl ether complex (0.9 ml). After the reaction had been stirred (10 min), water (2 ml) was added and the mixture warmed (20 °C) and concentrated. The residue was extracted with diethyl ether (10 ml) and subsequent column chromatography (Al_2O_3 Grade II–Et_2O) followed by removal of the solvent gave tricarbonyl-η^6-(methyl 1-*phenylethyl ether*)*chromium*(0) (**7**) (0.38 g, 58%) as a yellow oil identical in all respects with the sample obtained above.

Tricarbonyl-η^6*-(methyl 1-phenylpropyl ether)chromium*(0) (**10**).—This was prepared according to the general procedure for α-deprotonation and alkylation above, adding ethyl bromide and stirring (1 h) prior to the addition of methanol. The product complex (**10**) was isolated as a yellow solid in 75% yield, m.p. 44—46 °C, $\nu_{max.}$(Nujol) 1 970, 1 890, and 1 090 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.55—5.10 (5 H, m), 3.70 (1 H, t, *J* 6 Hz), 2.90 (3 H, s), 1.75—1.45 (2 H, m), and 0.85 (3 H, t, *J* 7 Hz); *m/z* 286 (M^+) (Found: C, 54.65; H, 4.85. $C_{13}H_{14}CrO_4$ requires C, 54.55; H, 4.93%).

Tricarbonyl-η^6*-(methyl 2-methyl-1-phenylpropyl ether)chromium*(0) (**11**).—Prepared according to the general procedure above, adding isopropyl bromide and stirring (1 h) prior to the addition of methanol. The product complex (**11**) was isolated as a yellow solid in 65% yield, m.p. 85—88 °C; $\nu_{max.}$(Nujol) 1 985, 1 915, and 1 095; δ_H (90 MHz; $CDCl_3$) 5.55—5.20 (5 H, m), 3.70 (1 H, m), 3.55 (3 H, s), 2.00—1.86 (m, 1 H), 0.95 (3 H, d, *J* 7 Hz), and 0.85 (3 H, d, *J* 7 Hz); *m/z* 300 (M^+) (Found: C, 56.0; H, 5.5. $C_{14}H_{16}CrO_4$ requires C, 56.02; H, 5.37%).

Tricarbonyl-η^6*-(O-methylbenzoin)chromium*(0) (**12**).—This was prepared according to the general procedure above adding methyl benzoate and stirring (1 h) prior to the addition of methanol. The product complex (**12**) was isolated as a yellow solid in 64% yield, m.p. 130—132 °C; $\nu_{max.}$(Nujol) 1 975, 1 905, and 1 680 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 8.05 (2 H, d, *J* 8 Hz), 7.60—7.40 (3 H, m), 5.80—5.20 (5 H, m), 5.00 (1 H, s), and 3.55 (3 H, s) (Found: C, 59.55; H, 4.05. $C_{18}H_{14}CrO_5$ requires C, 59.67; H, 3.90%).

Tricarbonyl-(η^6*-1-methoxy-1-phenylpropan-2-ol)chromium*(0) (**13**).—Prepared according to the general procedure above, adding acetaldehyde and stirring (0.5 h) prior to the addition of methanol. The product complex (**13**) was isolated as a yellow oil in 51% yield which consisted of 2:1 mixture of diastereoisomers, $\nu_{max.}$(Nujol) 3 370br, 1 965, 1 885, and 1 075; δ_H (300 MHz; $CDCl_3$) 5.61 (1 H, d, *J* 6 (Hz), 5.52—5.20 (4 H, m), 3.65, 3.63 (s, 3 H), 3.54—3.40 (2 H, m), 2.57, 2.37 (1 H, br), 1.20, and 1.10 (3 H, d, *J* 7 Hz); *m/z* 302 (M^+).

Tricarbonyl-(η^6*-ethyl 1-phenylethyl ether)chromium*(0) (**14**).—To a solution of (η^6-(benzyl ethyl ether)tricarbonylchromium(0) (**4**) (0.32 g, 1.22 mmol) in THF (20 ml) at −40 °C was added butyl-lithium (1.6M in hexane; 1.55 ml, 2.50 mmol). After the reaction had been stirred (1 h), methyl iodide (0.16 ml, 2.5 mmol) was added and stirring was continued (1 h). Methanol (2 ml) was added and the solution worked-up as in the general procedure above to give compound (**14**) as low-melting microcrystals (0.20 g, 58%, $\nu_{max.}$(Nujol) 1 970 and 1 900 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.60—5.15 (5 H, m), 5.00 (1 H, g, *J* 6 Hz), 3.55 (2 H, q, *J* 7 Hz), 1.35 (3 H, d, *J* 6 Hz), and 1.15 (3 H, t, *J* 7 Hz); *m/z* 272 (M^+) (Found: C, 54.6; H, 4.8. $C_{13}H_{14}CrO_4$ requires C, 54.90; H, 4.90%).

(η^6*-Benzyl 1-phenylethyl ether)tricarbonylchromium*(0) (**15**).—To a solution of tricarbonyl-(η^6-dibenzyl ether)-chromium(0) (**5**) (0.30 g, 0.90 mmol) in THF (20 ml) at −40 °C was added butyl-lithium (1.6M in hexane; 1.25 ml, 2.0 mmol). After the mixture had been stirred (1 h), methyl iodide (0.15 ml, 2.4 mmol) was added and stirring was continued (1 h). Methanol (2 ml) was added and the solution worked up as in the general procedure above to give compound (**15**) as a yellow oil (0.213 g, 68%), $\nu_{max.}$(film) 1 980 and 1 950 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 7.15 (5 H, s), 5.40—5.05 (5 H, m), 4.45 (2 H, s), 4.10 (1 H, q, *J* 7 Hz), and 1.30 (3 H, d, *J* 7 Hz); *m/z* 348 (M^+) (Found: C, 61.85; H, 4.9. $C_{18}H_{16}CrO_4$ requires: C, 62.07; H, 4.63%).

(η^6*-Allyl 1-phenylethyl ether)tricarbonylchromium*(0) (**16**).—To a solution of (η^6-allyl benzyl ether)tricarbonylchromium(0) (**6**) (0.29 g, 1.02 mmol) in THF (20 ml) at −40 °C was added butyl-lithium (1.65M in hexane; 1.30 ml, 2.14 mmol). After the mixture had been stirred (1 h), methyl iodide was added (0.15 ml, 2.41 mmol) and stirring was continued (1 h). Methanol (2 ml) was added and the solution was worked-up as in the general procedure to give compound (**16**) as a yellow oil (0.27 g, 89%), $\nu_{max.}$(film) 1 980, 1 910, and 1 085 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 6.15—5.70 (1 H, m), 5.65—5.10 (7 H, m), 4.30—4.05 (3 H, m), and 1.40 (3 H, d, *J* 8 Hz); *m/z* 298 (M^+).

(η^6*-Benzyl ethyl sulphide)tricarbonylchromium*(0) (**17**).—To a solution of (η^6-benzyl alcohol)tricarbonylchromium(0) (**2**) (0.61 g, 2.50 mmol) in dichloromethane (15 ml) containing ethanethiol (3 ml) at −30 °C was added dropwise tetrafluoroboric acid–dimethyl ether complex (1.20 ml). After the mixture had been stirred (10 min), water (2 ml) was added, the mixture was warmed (20 °C) and concentrated. The residue was extracted with diethyl ether (15 ml) and subsequent column chromatography (Al_2O_3 Grade II–Et_2O) followed by removal of the solvent gave compound (**17**) as an orange oil (0.65 g, 91%), $\nu_{max.}$(film) 1 980 and 1 910 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.45 (5 H, s), 3.45 (2 H, s), 2.65 (2 H, q, *J* 7 Hz), and 1.30 (3 H, t, *J* 7 Hz); *m/z* 288 (M^+) (Found: C, 49.9; H, 4.4. $C_{12}H_{12}CrO_3S$ requires C, 50.00; H, 4.20%).

General Procedure for the Deprotonation and Alkylation of (η^6*-Benzyl ethyl sulphide)tricarbonylchromium*(0) (**17**).—To a solution of (η^6-benzyl ethyl sulphide)tricarbonylchromium(0) (**17**) (0.57 g, 1.98 mmol) in THF (20 ml) at −40 °C was added butyl-lithium (1.6M in hexane; 2.0 ml, 3.2 mmol). After the mixture had been stirred (1 h), methanol (2 ml) was added, and the solution was warmed (20 °C) and concentrated. The residue was extracted with diethyl ether (15 ml) and subsequent column chromatography (Al_2O_3 Grade II–Et_2O) followed by removal of the solvent gave compound (**17**) (0.525 g, 92%) identical in all respects with the sample obtained above.

Tricarbonyl-(η^6*-ethyl 1-phenylethyl sulphide)chromium*(0) (**18**).—Prepared according to the general procedure above adding methyl iodide and stirring (1 h) prior to the addition of methanol. The product complex (**18**) was isolated as a dark yellow oil in 89% yield, $\nu_{max.}$(film) 1 965 and 1 865; δ_H (60 MHz; $CDCl_3$) 5.75—5.25 (5 H, m), 4.10 (1 H, q, *J* 6 Hz), 3.60

(2 H, q, *J* 7 Hz), 1.40 (3 H, d, *J* 6 Hz), and 1.30 (3 H, t, *J* 7 Hz); *m/z* 302 (M^+) (Found: C, 51.3; H, 4.65. $C_{13}H_{14}CrO_3S$ requires C, 51.64; H, 4.67%).

General Procedure for the Deprotonation and Alkylation of (η^6-*Benzyl alkyl ether*)*tricarbonylchromium*(0) *Systems Bearing Chiral Alkyl Groups* (**19**)—(**21**).—To a solution of [η^6-(*R*)-benzyl 2-butyl ether]tricarbonylchromium(0) (**19**) (0.35 g, 12.16 mmol) in THF (30 ml) at −78 °C was added butyl-lithium (1.6M in hexane; 0.9 ml, 1.44 mmol). After the reaction had been stirred (1 h), methyl iodide was added and stirring was continued (1 h). Methanol (2 ml) was added, the solution was warmed (20 °C), the solvent was removed and the residue extracted with diethyl ether (10 ml). Chromatography (Al_2O_3 Grade II–Et_2O) followed by removal of the solvent gave [η^6-(*R*)-butan-2-yl 1-phenylethyl ether]tricarbonylchromium(0) (**22**) as a yellow oil (0.26 g, 71%). The ratio of diastereoisomers obtained in this case was determined by comparison of the integrals for the doublet, multiplet, and triplet for the 1-, 2-, and 4- protons respectively of the butan-2-yl group. A similar comparison was made for the diastereoisomeric mixture of products (**24**) [R = (*S*)-$MeCH_2CHMe$; E = Me]. For compound (**23**) [R = (*R*)-$MeCH_2CHMe$; E = D] the singlets for the benzylic protons were compared whilst for (**25**) (R = cholesteryl; E = Me) the ratio of diastereoisomers was obtained from a comparison of the integrals for the well resolved signals due to the proton of the alkyl auxiliary α- to the benzylic oxygen on the decomplexed products.

In all cases the reaction was carried out as described in the General Procedure except for the preparation of [η^6-(*R*)-butan-2-yl 1-deuteriobenzyl ether]tricarbonylchromium(0) (**23**) where deuteriomethanol was used as the electrophile in place of methyl iodide.

(R)-*Benzyl Butan*-2-*yl Ether* (**26**).—Sodium hydride (50% w/w dispersion in mineral oil; 0.96 g, 24 mmol) was washed with light petroleum (b.p. 40—60 °C; 2 × 30 ml). (*R*)-Butan-2-ol (1.0 g, 13.1 mmol) in THF (30 ml) was added with stirring and after 4 h, benzyl bromide (2.22 g, 13 mmol) was added and stirring was continued (16 h). Diethyl ether (200 ml) was added, the solution was filtered, and the solvent removed. Distillation of the residue gave compound (**26**) as a colourless liquid (1.82 g, 84%) b.p. 58—61 °C, 0.1 mmHg; δ_H (60 MHz; $CDCl_3$) 7.30 (5 H, s), 4.50 (2 H, s), 3.45 (1 H, q, *J* 6 Hz), 1.80—1.35 (2 H, m), 1.20 (3 H, d, *J* 6 Hz), and 0.95 (3 H, t, *J* 7 Hz).

[η^6-(R)-*Benzyl butan*-2-*yl ether*]*tricarbonylchromium*(0) (**19**): *Alternative Preparation.*—A deoxygenated mixture of dibutyl ether (40 ml), THF (4 ml), (*R*)-benzyl butan-2-yl ether (**26**) (1.02 g, 6.15 mmol) and hexacarbonylchromium (2.0 g, 9.1 mmol) was heated under reflux (40 h). The cooled solution was filtered and concentrated (10 ml) and chromatography of the residue (Al_2O_3 Grade II–Et_2O) followed by removal of the diethyl ether gave compound (**19**) as yellow plates (1.36 g, 73%) identical in all respects with the sample obtained previously.

o-*Xylene*-α,α′-*diyl Bis*(*methyl ether*) (**28**).—Sodium (0.85 g, 37 mmol) was dissolved in methanol (20 ml) and cooled 0 °C. α,α′-Dibromo-*o*-xylene (**27**) (4.0 g, 1.52 mmol) was added and the mixture heated under reflux (1 h). Water (30 ml) was carefully added to the cooled solution which was extracted with diethyl ether (4 × 50 ml). The combined extracts were washed with brine (20 ml) and dried ($MgSO_4$). Removal of the diethyl ether followed by distillation of the residue gave the bisether (**28**) as a colourless liquid (1.82 g, 72%), $\nu_{max.}$(film) 1 090 and 755 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 7.35 (4 H, s), 4.45 (4 H, s), and 3.40 (6 H, s).

Tricarbonyl-[η^6-o-*xylene*-α,α′-*diethyl bis*(*methyl ether*)]-*chromium*(0) (**29**).—A deoxygenated mixture of dibutyl ether (25 ml), THF (3 ml), the dimethyl ether (**28**) (1.0 g, 6.02 mmol) and hexacarbonylchromium (2.0 g, 9.4 mmol) was heated under reflux (40 h). The cooled solution was filtered and concentrated (10 ml). Chromatography (Al_2O_3 Grade II–Et_2O) followed by removal of the diethyl ether gave a yellow oil which crystallised and was recrystallised from diethyl ether–hexane to give compound (**29**) as yellow needles (1.42 g, 78%), m.p. 40—41 °C, $\nu_{max.}$(Nujol) 1 980, 1 905, and 1 090 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.55—5.25 (4 H, m), 4.25, 4.05 (4 H, AB system J_{AB} 6 Hz), and 3.35 (6 H, s); *m/z* 312 (M^+) (Found: C, 51.55; H, 4.4. $C_{13}H_{14}CrO_5$ requires C, 51.66; H, 4.67%).

Tricarbonyl-[η^6-(α-*methyl*-o-*xylene*-α,α′-*diyl bis*(*methyl ether*)]*chromium*(0) (**30**).—To a solution of tricarbonyl-[η^6-xylene-α,α′-bis(methyl ether)]chromium(0) (**29**) (0.20 g, 0.60 mmol) in THF (35 ml) at −78 °C was added butyl-lithium (1.7M in hexane; 0.60 ml, 1.02 mmol). After the reaction had been stirred (1 h), methyl iodide (0.1 ml, 1.6 mmol) was added and stirring continued (1 h). Methanol (2 ml) was added, the solution warmed (20 °C), the solvent removed, and the residue taken up in diethyl ether (10 ml). Chromatography (Al_2O_3 Grade II–Et_2O) of the solution followed by removal of the diethyl ether gave compound (**30**) as a yellow solid (0.17 g, 82%), m.p. 50—52 °C, $\nu_{max.}$(Nujol) 1 985, 1 910, and 1 090 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 5.70—5.25 (4 H, m), 4.20 (1 H, q, *J* 6 Hz), 4.35, 3.95 (2 H, AB system J_{AB} 11 Hz), 3.45 (3 H, s), 3.40 (3 H, s), and 1.40 (3 H, d, *J* 6 Hz); *m/z* 316 (M^+).

Tricarbonyl-[η^6-α,α′-*dimethyl*-o-*xylene*-α,α′-*diyl bis*(*methyl ether*)]*chromium*(0) (**31**).—To a solution of tricarbonyl-[η^6-(α-methyl-*o*-xylene-α,α′-diyl bis(methyl ether)]chromium(0) (**30**) (1.60 g, 5.30 mmol) in THF (50 ml) at −78 °C was added butyl-lithium (1.7M in hexane; 3.80 ml, 6.46 mmol). After the reaction had been stirred (1 h), methyl iodide (0.5 ml, 8.0 mmol) was added and stirring was continued (1 h). Methanol (2 ml) was added, the solution warmed (20 °C), the solvent removed, and the residue taken up in diethyl ether (10 ml). Chromatography (Al_2O_3 Grade II—Et_2O) followed by removal of the diethyl ether gave (**31**) as a yellow solid (1.28 g, 77%), m.p. 87—89 °C, $\nu_{max.}$(Nujol) 1 980 and 1 910 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 5.75—5.25 (4 H, m), 4.15 (2 H, q, *J* 6 Hz), 3.50 (6 H, s), and 1.40 (6 H, d, *J* 6 Hz); *m/z* 330 (M^+) (Found: C, 54.5; H, 5.6. $C_{13}H_{18}CrO_5$ requires C, 54.54; H, 5.49%).

α,α′-*Dimethyl*-o-*xylene*-α,α′-*diyl Bis*(*methyl ether*) (**32**).—Tricarbonyl-[η^6-α,α′-dimethyl-*o*-xylene-α,α′-diyl bis(methyl ethyl ether)]chromium(0) (**31**) (1.10 g, 3.50 mmol) was dissolved in diethyl ether (100 ml) and the solution was allowed to stand in air and sunlight until it became colourless. The solution was filtered and the solvent removed from the filtrate. The residue was distilled to give α,α′-dimethyl-*o*-xylene-α,α′-diyl bis(methyl ether) (**32**) as a low melting solid (0.52 g, 87%), $\nu_{max.}$(Nujol) 1 090 and 760 cm^{-1}; δ_H (300 MHz; $CDCl_3$) 7.49—7.40, 7.35—7.28 (4 H, m), 4.72 (2 H, q, *J* 6 Hz), 3.21 (6 H, s), and 1.43 (6 H, d, *J* 6 Hz).

Tricarbonyl-(η^6-1-*tetralone*)*chromium*(0) (**34**).[9]—A deoxygenated mixture of dibutyl ether (40 ml), THF (4 ml), 1-tetralone (**33**) (1.2 g, 8.22 mmol), and hexacarbonylchromium (2.0 g, 9.1 mmol) was heated under reflux (16 h). The cooled solution was filtered and treated with light petroleum (b.p. 40—60 °C, 150 ml). The solid product was collected by filtration and crystallised from dichloromethane–hexane to give compound (**34**) as red needles (1.21 g, 52%), m.p. 125—127 °C (lit.,[9] 128 °C), $\nu_{max.}$(Nujol) 1 965, 1 870, and 1 670 cm^{-1}; δ_H [300 MHz; $(CD_3)_2CO$], 6.22—5.56 (4 H, m), 3.16—3.06 (1 H, m),

2.79—2.71 (1 H, m), 2.67—2.49 (2 H, m), and 2.22—2.08 (2 H, m); *m/z* 282 (M^+).

Tricarbonyl-syn-(η⁶-1-*tetralol*)*chromium*(0) (**35**).—A solution of tricarbonyl-(η⁶-1-tetralone)chromium(0) (**34**) (0.75 g, 2.66 mmol) in methanol (30 ml) and water (10 ml) was treated with sodium borohydride (1.5 g, 40 mmol) and stirred (1 h). Water (50 ml) was added and the solution was extracted with diethyl ether (3 × 50 ml). The combined extracts were washed with water (3 × 50 ml), dried ($MgSO_4$), and the solvent removed. The residue was crystallised from diethyl ether–hexane to give compound (**35**) as yellow needles (0.48 g, 63%), m.p. 131—132 °C; $\nu_{max.}$(Nujol) 3 400br, 1 950, 1 890, and 1 860 cm^{-1}; δ_H [300 MHz; $(CD_3)_2CO$], 5.93—5.34 (4 H, m), 4.61 (1 H, br s), 4.49 (1 H, d), 2.94 (1 H, br s), 2.76–2.62 (2 H, m), 1.98—1.89 (1 H, m), and 1.79—1.62 (2 H, m) (Found: C, 54.6; H, 4.25. $C_{13}H_{12}CrO_4$ requires C, 54.94; H, 4.25%).

Tricarbonyl-anti-(η⁶-1-*methoxytetralin*)*chromium*(0) (**36**).[11]—To a solution of tricarbonyl-*syn*-(η⁶-1-tetralol)-chromium(0) (**35**) (0.6 g, 2.11 mmol) in methanol (15 ml) at −15 °C was added dropwise sulphuric acid (98%, 5 ml). After the reaction had been stirred (0.5 h), water (20 ml) was added and the solution extracted with diethyl ether (2 × 100 ml). The extracts were washed with water (2 × 50 ml) and concentrated (10 ml). Chromatography (Al_2O_3 Grade II–Et_2O) followed by removal of the solvent gave compound (**36**) as a yellow oil (0.47 g, 74%), $\nu_{max.}$(Nujol) 1 980, 1 950, 1 900, and 1 095 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.80—5.10 (4 H, m), 4.35—4.15 (1 H, m), 3.45 (3 H, s), 2.80—2.50 (2 H, m), and 2.10—1.60 (4 H, m).

Tricarbonyl-syn-(η⁶-1-*methoxytetralin*)*chromium*(0) (**37**).—Sodium hydride (50% w/w dispersion in mineral oil; 0.12 g, 2.50 mmol) was washed with hexane (2 × 50 ml) and THF (30 ml) was added. Tricarbonyl-*syn*-(η⁶-1-tetralol)chromium(0) (**35**) (0.51 g, 1.77 mmol) was added and the reaction was stirred (40 °C; 4 h). Methyl iodide (0.2 ml, 3.2 mmol) was added to the cooled solution and stirring was continued (16 h). Methanol (2 ml) was added, the solvent removed, and the residue taken up in diethyl ether (10 ml). Column chromatography (Al_2O_3 Grade II–Et_2O) of the solution followed by removal of the diethyl ether and crystallisation from diethyl ether–hexane gave compound (**37**) (0.33 g, 62%) as a yellow solid, $\nu_{max.}$(Nujol) 1 960, 1 870, 1 845, and 1 085 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.80—5.00 (4 H, m), 4.20—3.95 (1 H, m), 3.50 (3 H, s), 2.80—2.50 (2 H, m), and 2.10—1.50 (4 H, m) (Found: C, 56.3; H, 4.7. $C_{14}H_{14}CrO_4$ requires C, 56.38; H, 4.73%).

Tricarbonyl-(η⁶-1α-*methoxy*-1β-*methyltetralin*)*chromium*(0) (**38**).—To a solution of tricarbonyl-*syn*-(η⁶-1-methoxytetralin)-chromium(0) (**37**) (0.31 g, 1.04 mmol) in THF (25 ml) at −78 °C was added butyl-lithium (1.6M solution in hexane; 1.0 ml, 1.6 mmol). After the reaction had been stirred (1 h), methyl iodide (0.2 ml, 3.2 mmol) was added and stirring was continued (1 h). Methanol (2 ml) was then added, the solution was warmed (20 °C), the solvent removed, and the residue taken up in diethyl ether (10 ml). Chromatography (Al_2O_3 Grade II–Et_2O) of the solution followed by removal of the diethyl ether and crystallisation from hexane gave compound (**38**) (0.20 g, 71%) as a yellow solid, m.p. 122—124 °C; $\nu_{max.}$(Nujol) 1 980, 1 910, 1 890, and 1 080 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 5.80—5.30 (4 H, m), 3.35 (3 H, s), 2.80—2.45 (2 H, m), 2.20—1.80 (4 H, m), and 1.40 (3 H, s); *m/z* 312 (M^+).

Tricarbonyl-(η⁶-1β-*methyl*-1α-*tetralol*)*chromium*(0) (**39**).[12]—A solution of tricarbonyl-(η⁶-1-tetralone)chromium(0) (**34**) (1.60 g, 5.67 mmol) in diethyl ether (30 ml) was treated with methyl magnesium iodide (1.5M solution in diethyl ether; 10 ml, 15 mmol) and stirred (1 h). Sulphuric acid (1M; 30 ml) was added, the diethyl ether layer separated and concentrated (10 ml). Chromatography (Al_2O_3 Grade V–CH_2Cl_2) followed by removal of the dichloromethane, gave a yellow solid which was recrystallised from dichloromethane–hexane to give (**39**) (1.15 g, 68%) as yellow needles; $\nu_{max.}$(Nujol) 3 590, 1 945, 1 860, and 1 855 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.90 (1 H, d, *J* 6 Hz), 5.50 (1 H, t, *J* 6 Hz), 5.15 (2 H, t, *J* 6 Hz), 2.70—2.50 (2 H, m), 2.00—1.60 (5 H, m), and 1.50 (3 H, s); *m/z* 298 (M^+).

Tricarbonyl-(η⁶-1α-*methoxy*-1β-*methyltetralin*)*chromium*(0) (**38**): *Alternative Preparation*.—Potassium hydride (35% w/w dispersion in mineral oil; 80 mg, 2.0 mmol) was washed with hexane (2 × 30 ml) and THF (30 ml) was added. Tricarbonyl-(η⁶-1β-methyl-1α-tetralol)chromium(0) (**39**), (0.50 g, 1.68 mmol) and tetrabutylammonium iodide (30 mg, 0.08 mmol) were added and the reaction was stirred (3 h). Methyl iodide (0.2 ml, 3.2 mmol) was added and stirring was continued (1 h). Methanol (2 ml) was added, the solvent removed, and the residue was taken up in diethyl ether (10 ml). Chromatography (Al_2O_3 Grade II–Et_2O) followed by removal of the solvent gave compound (**38**) (110 mg, 21%) identical in all respects with the sample obtained previously.

Tricarbonyl-(η⁶-2-*phenyltetrahydrofuran*)*chromium*(0) (**41**).—To a solution of (η⁶-benzyl 3-chloropropyl ether)tricarbonylchromium(0) (**40**) (0.29 g, 0.91 mmol) in THF (25 ml) at −40 °C was added butyl-lithium (1.6M solution in hexane; 0.9 ml, 1.44 mmol). After the reaction had been stirred (1 h), methanol (2 ml) was added, the solution warmed (20 °C), the solvent removed, and the residue taken up in with diethyl ether (10 ml). Chromatography (Al_2O_3 Grade II–CH_2Cl_2) of the solution followed by removal of the dichloromethane gave a yellow solid which crystallised from diethyl ether–hexane to give compound (**41**) (152 mg, 59%), m.p. 103—105 °C; $\nu_{max.}$(Nujol) 1 880 and 1 985 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 5.50—5.20 (5 H, m), 4.65 (1 H, t, *J* 7 Hz), 4.20—3.80 (2 H, m), and 2.50—1.70 (4 H, m); *m/z* 284 (M^+) (Found: C, 54.65; H, 4.45. $C_{13}H_{12}CrO_4$ requires C, 54.93; H, 4.26%).

Tricarbonyl-[η⁶-5-c/t-*methyl*-2-r-*phenyltetrahydrofuran*]-*chromium*(0) (**43**).—η⁶-(3-Benzyloxybutylchloride)tricarbonyl-chromium(0) (**42**) (0.32 g, 0.96 mmol) was dissolved in dimethyl sulphoxide (10 ml) containing potassium *t*-butoxide (1.12 g, 10 mmol) and the mixture was stirred (15 min). Water (100 ml) was then added and the solution was extracted with diethyl ether (3 × 50 ml), washed with water (2 × 50 ml), then brine (50 ml), and the organic extracts were dried ($MgSO_4$). The solution was concentrated (10 ml) and chromatographed (Al_2O_3 Grade II–CH_2Cl_2) to give a 3:2 isomeric mixture of compound (**43**) as a yellow oil (0.13 g, 45%), $\nu_{max.}$ 1 980, 1 910, and 1 090 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 5.30 (5 H, s), 4.70—4.40 (1 H, m), 4.25—4.05 (1 H, m), 2.30—1.50 (4 H, m), and 1.25, 1.20 (3 H, d, *J* 7 Hz); *m/z* 298 (M^+); (Found: C, 56.4; H, 4.75. $C_{14}H_{14}CrO_4$ requires C, 56.38; H, 4.84%).

cis- *and* trans-5-*Methyl*-2-*phenyltetrahydrofuran* (**44**).—A solution of tricarbonyl-(η⁶-5-methyl-2-phenyltetrahydrofuran)-chromium(0) (**43**) (90 mg, 0.30 mmol) in diethyl ether (30 ml) was left to stand in air and sunlight until it became colourless. The solution was filtered and the solvent was removed. The residue was taken up with dichloromethane (5 ml) and filtered (Al_2O_3 Grade II–CH_2Cl_2) to give a 3:2 isomeric mixture of 5-methyl-2-phenyltetrahydrofuran (**44**) as a colourless liquid (43 mg, 88%), δ_H (300 MHz; $CDCl_3$) 7.20—7.10 (5 H, m), 5.01 and 4.84 (1 H, t, *J* 8 Hz), 4.37—4.08 (1 H, m), 2.40—1.70 (4 H, m), and 1.35 and 1.28 (3 H, d, *J* 6 Hz).

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