Pergamon

Tetrahedron 56 (2000) 6121–6134

TETRAHEDRON

Directed Lithiation in Arenetricarbonylchromium(0) Complexes: Assessment of Some Directing Group Specificities and of Electrophilic Quench Efficacies

Iyassu K. Sebhat,[a] Yen-Ling Tan,[a] David A. Widdowson,[a,*] René Wilhelm,[a] Andrew J. P. White[b] and David J. Williams[b]

[a]*Department of Chemistry, Imperial College of Science Technology and Medicine, London SW7 2AZ, UK*
[b]*Chemical Crystallography Laboratory, Imperial College of Science Technology and Medicine, London SW7 2AZ, UK*

Received 27 March 2000; revised 26 May 2000; accepted 8 June 2000

Abstract—The synthesis of a series of phenol ethers and 4-triisopropylsilyloxymethylphenol ethers and their η^6-tricarbonylchromium(0) complexes are reported. The directed lithiation of these followed by quenching with a series of electrophiles gave access to a wide range of functionalised complexes for use in synthesis. © 2000 Elsevier Science Ltd. All rights reserved.

The chemistry of η^6-arenetricarbonylchromium complexes has been extensively researched and documented.[1–5] In particular, competitive studies of directed lithiation by functional groups on these complexes have established a unique sequence of directing abilities with fluorine as the most effective of those studied.[6] However, the pronounced basicity of the lithiated complexes produces limitations in the range of electrophilic quenches which are synthetically useful[4] and in addition, with the carbon/oxygen based directing groups, most commonly met with in natural product and related compound synthesis, the distinction in directing ability may not be so clear cut.

We have therefore addressed the first of these limitations by examining a range of electrophiles compatible with the high basicity of the lithiated arenechromium complexes, in the synthesis of 1,2-difunctionalised arenes. In conjunction with this, we have probed the relative efficacy of the directing abilities of a number of ether (and one amine) based directing groups on the aryl rings of the chromium complexed substrates. The objective was to define optimum arene functionality for application, in chiral form, to the asymmetric synthesis of biaryls and related natural products to be reported later.

Accordingly, non-commercially available arene ethers (**1**–**5**, series **a** or **c**) (Table 1), chosen to probe the effect of the precise ether structure on directed lithiation in these chromium complexes, were conventionally synthesised (89–98%) (see Experimental for details) from 4-formylphenol via the alcohols (**1**–**5**, series **b**) which were triisopropylsilylated (series **c**) as shown in Scheme 1. The results are given in Table 1.

Chromium complexes were made in adequate (45%) to high (95%) yield by a general procedure,[7] Scheme 2, and those not previously reported are shown in Table 2.

The aryl ether series were: methoxy (**6a**), previously examined in detail[8] and therefore not listed in the table but used here for comparison, and (**6b**), to assess the regioselectivity in competition with the 4-silyloxymethyl group; methoxymethyl (**7a,b**), to examine the effect of a non-conjugated ether oxygen; ethoxymethyl (**8a,b**), to examine the effect of increased bulk around that second oxygen; 2-methoxyethyl (**9b**), to determine the effect of chain length/ligation ring size; and 2-methoxyethoxymethyl (**10b**), to determine the effect of increased potential ligation. One nitrogen analogue of known high directing ability,[9,10] *N*-Boc-aniline was also produced (**11a**).

Lithiations of these complexes were carried out under the defined conditions by treatment with butyllithium at −78°C in purified THF or ether under a nitrogen atmosphere during 1 h. The resultant lithiated complex was quenched with the electrophile at −78°C and allowed to warm to room temperature before work-up (Scheme 3). The results are given in Table 3. Yields refer to isolated, purified products.

The methoxy group in (**6b**), although a known *ortho*-directing group,[8] gave a low (5%) but isolable yield of the

---

Keywords: phenol ether tricarbonylchromium(0) complex; lithiation; regioselectivity.

* Corresponding author. Tel.: +44-20-7594-5779; fax: +44-20-7594-5804; e-mail: d.widdowson@ic.ac.uk

PII: S0040-4020(00)00562-7

1–5

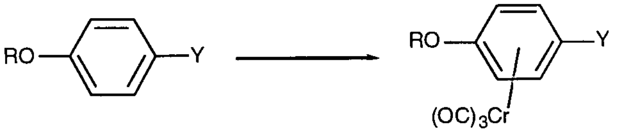
Scheme 1.

Table 1. 4-Triisopropylsiloxymethylphenol ether synthesis

No.	R	Yield (%)		
		a, Y=CHO	**b**, Y=CH_2OH	**c**, Y=CH_2OTIPS
1	Me–			96
2	$MeOCH_2$–	91	98	89
3	$EtOCH_2$–	96	98	93
4	$MeOCH_2CH_2$–	92	93	97
5	$MeOCH_2CH_2OCH_2$–	94	98	96

3-substituted product (**12c**) in addition to the 2-substituted product (**12b**, 87%) on formylation with DMF, despite the presence of the bulky siloxymethyl group at C-4. Directed lithiations, including those in these complexes, involve a combination of the effects of coordination of incoming base and labilisation of the α-hydrogen by the directing group[11,12] and we have already shown that a methoxy group is poorly coordinating because of the electron withdrawal by the chromium unit.[13]

Formylation of the methoxyethoxy analogue to give (**32b**, 74%) was also accompanied by 18% of the 3-isomer (**32c**). Here the poor regiocontrol can reasonably be attributed to the less favourable coordination ring size of the lithiated intermediate [7-membered ring for (**32b**) formation rather than the 6-membered ring in the methoxymethoxy directed equivalent (**14b**), discussed below] resulting in non-selective lithiation.



6–11

Scheme 2.

Table 2. Synthesis of arenetricarbonylchromium(0) complexes

No.	R	Yield (%)	
		a, Y=H	**b**, Y=CH_2OTIPS
6	Me–		87
7	$MeOCH_2$–	78	95
8	$EtOCH_2$–	45	93
9	$MeOCH_2CH_2$–		72
10	$MeOCH_2CH_2OCH_2$–		79
11	[a]	86	

[a] Substituent ^{t}BocNH–.

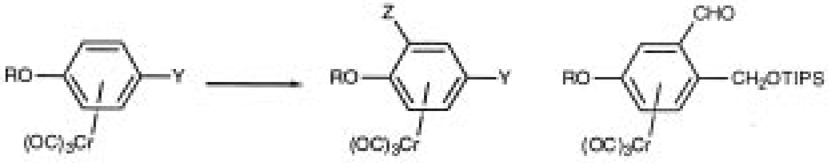
The other ethers examined here all contain a remote, electronically detached oxygen three atoms removed from the aromatic ring, which can act more effectively as a coordinating centre for the lithium base. These all showed apparently complete regiocontrol and none of the 3-functionalised materials could be isolated, presumably reflecting this coordinating ability. Despite this enhanced regiocontrol, isolated yields for 2-formylation of the ethers methoxymethoxybenzenetricarbonylchromium(**7a**), ethoxymethoxybenzenetricarbonylchromium(0) (**8a**) and methoxyethoxymethoxybenzenetricarbonylchromium(0) (**34a**), to generate (**14b**, 61%), (**29b**, 62%) and (**34b**, 73%) respectively, were less than that for the methoxy analogue (**12b**, 87%) a possible consequence of the higher steric crowding in these compounds.

The other factor inherent in these substrates is the increased terminal bulk in the ether side chain [cf. the ethoxymethoxy series (**29a,b**), (**30a,b**) and (**31a**) with the methoxymethoxy analogues (**14a,b**), and (**20a,b**) and (**24a**) respectively], had little significant effect, at least in the cases shown.

The positive effect of the use of the extended coordination ability of methoxyethoxymethoxy function (**34b** vs **14b**) may be some significance (+10%) in the more crowded **b** series and could be of value in difficult cases but we have not made routine use of this more elaborate directing group.

The electrophilic quenches were chosen with a number of objectives in mind. Firstly, the efficacy of internal vs external quench of the lithiated methoxymethoxybenzenetricarbonylchromium complexes (**7a**), (**7b**) and *N*-Boc-anilinetricarbonylchromium (**11a**)[14] was checked using trimethylsilyl chloride to form (**16a,b**) and (**35a**) respectively. In the event, there was no benefit from an internal quench and the figures for external (post lithiation) are quoted. Added lithium chloride[14] had no discernible effect on the 77–84% yield.

The second objective was to introduce functionality which would be especially valuable in the further synthetic exploitation of the products. These functionalities include formyl



12 – 35

12c, R = Me
32c, R = CH_2CH_2OMe

Scheme 3.

Table 3. Directed lithiation of arenetricarbonylchromium(0) complexes

No.	R	Reagent	Z	Yield (%)	
				a, Y=H	**b**, Y=CH_2OTIPS
12	Me–	DMF	OHC–		87[a]
13		Bu_3SnCl	Bu_3Sn–	89	
14	$MeOCH_2$–	DMF	OHC–	83	61
15		PhNCO	PhNHCO–		67
16		Me_3SiCl	Me_3Si–	84	80
17		Me_3SnCl	Me_3Sn–	95	72
18		Bu_3SnCl	Bu_3Sn–	84	
19		$(CH_2O)_n$	$HOCH_2$–	53	72
20		Ph_2CO	$HO(Ph_2)C$–	94	84
21		$(4\text{-}MeOC_6H_4)_2CO$	$HO(4\text{-}MeOC_6H_4)_2C$–	92	
22		PhCHO	HO(Ph)CH–	73	
23		4-MeO C_6H_4CHO	$HO(4\text{-}MeOC_6H_4)CH$–	83	
24		(2,6-MeO)$_2$ C_6H_3CHO	$HO[(2,6\text{-}MeO)_2C_6H_3]CH$–	80	
25		4-O_2N C_6H_4CHO	$HO(4\text{-}O_2NC_6H_4)CH$–	69	
26		$Me_2N^+{=}CH_2I^-$	Me_2NCH_2–		61
27		PhCH=NPh	PhNH(Ph)CH–	95	
28		ICH_2CH_2I	I–	83	95
29	$EtOCH_2$–	DMF	OHC–	82	62
30		Ph_2CO	$HO(Ph_2)C$–	82	92
31		$(4\text{-}MeOC_6H_4)_2CO$	$HO(4\text{-}MeOC_6H_4)_2C$–	80	
32	$MeOCH_2CH_2$–	DMF	OHC–		74[b]
33		Ph_2CO	$HO(Ph_2)C$–		72
34	$MeOCH_2CH_2OCH_2$–	DMF	OHC–		73
35	[c]	Me_3SiCl	Me_3Si–	77	

[a] **12c**, 5% was also formed.
[b] **32c**, 18% was also formed.
[c] Substituent ^{t}BocNH–.

(**12b**; **14a,b**; **29a,b**; **32b** and **34b**), hydroxymethyl (**19a**, **20a,b**, **21a**–**25a**), aminomethyl (**26b**), trimethyl and tributylstannyl (**17a,b** and **13a**,**18a** respectively) and iodide (**28a,b**, for use in palladium coupling reactions).[15]

The third objective was to introduce diastereogenic centres to probe the stereocontrol of the quench. Thus the arylcarbinols of the methoxymethoxy-series (**22a**–**25a**) and the α-aminobenzyl (**27a**) were produced. In agreement with earlier observations of butyllithium deprotonations[14] these products were formed with high stereoselectivity, with only one diastereoisomer being isolated in high yield (69–95%). X-Ray crystallographic analysis of (**22a**) showed this to be *rel*-(1-*pR*, α-*R*)-η^6-[2-(phenylhydroxymethyl)methoxymethoxybenzene]tricarbonylchromium(0) (Fig. 1).

In summary, we have identified the methoxymethoxy function as, on balance, the directing group of choice for butyllithium mediated lithiation of aryl ether complexes and have demonstrated an array of functionalities which can be

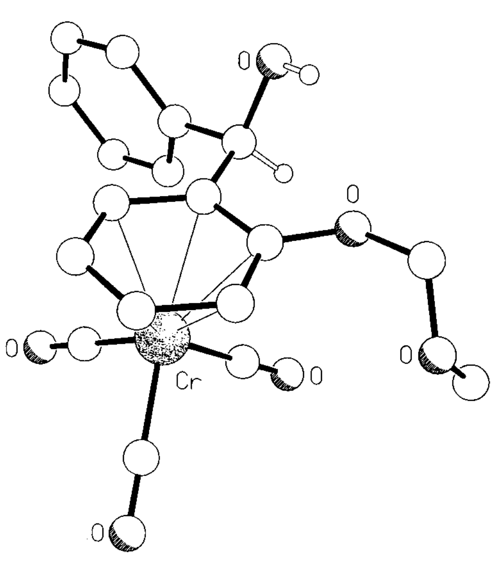


Figure 1.

introduced into these systems with the appropriate quench. The application of these methods to the asymmetric synthesis of chiral complexes will be reported in a subsequent paper.

Experimental

Reactions carried out under nitrogen were performed using standard vacuum line techniques.[16] Methoxymethoxybenzene was prepared according to a literature procedure.[17] 4-Hydroxybenzaldehyde and 4-hydroxymethylanisole were used as received from the Sigma-Aldrich Company. The concentration of butyllithiums were determined by titration against diphenylacetic acid.[18] Flash column chromatography[19] was performed on Sorbisil C-60.

Elemental analyses were carried out at SACS, University of North London and are reported as the average of two runs, or by Imperial College Microanalytical Service as one run. Infrared spectra were recorded on a Perkin–Elmer RX FT-IR System and a Perkin–Elmer 1710 FTIR instrument. NMR spectra were performed in $CDCl_3$ at ambient temperature on a Jeol GSX 270 (270 MHz ^1H and 68 MHz ^{13}C) or a Bruker DRX 300 (300 MHz ^1H and 75 MHz ^{13}C) Spectrometer. Mass spectra were recorded on VG Micromass 7070E or AutoSpec-Q spectrometers. Melting points were taken on a Kofler hot stage apparatus and are uncorrected. Data are given only for new compounds or compounds inadequately characterised in the literature.

For both the free ligands and the chromium complexes, the carbon attached to the directing group has been labelled ArC(1).

Ethoxymethoxybenzene (3, Y=H). This was prepared as for methoxymethoxybenzene[17] in 95% yield. The ^1H NMR spectrum was consistent with the literature data,[20] other data, not earlier reported: ν_{max} (neat)/cm^{-1} 2977s, 2900s, 1598s, 1492s. δ_C (68 MHz) 157.6 (Ar*C*(1)–O), 129.6 (Ar*C*(3,5)H), 121.8 (Ar*C*(4)H), 116.7 (Ar*C*(2,6)H), 92.7 (O–*C*H$_2$–O), 64.2 (O–*C*H$_2$), 15.2 (*Me*). *m*/*z*(EI) 152 (M^+), 122 ($M^+-C_2H_4$), 107 ($M^+-OCH_2CH_3$).

General procedure for the protection of 4-hydroxybenzaldehyde

To a solution of 4-hydroxybenzaldehyde (18.33 g, 150 mmol) and Adogen®(12 g) in DCM (450 mL), under nitrogen, was added a solution of sodium hydroxide (12 g, 300 mmol) in water (150 mL). The appropriate alkyl(chloromethyl)ether (225 mmol) was added and the solution left to stir for 16 h. The organic phase was removed, washed sequentially with water (150 mL), 1 M HCl aq. (150 mL), water (150 mL) and brine (150 mL) and dried ($MgSO_4$). Concentration under reduced pressure followed by flash chromatography afforded the alkoxymethyl ethers. So prepared were:-

4-Methoxymethoxybenzaldehyde (2a). Eluent: 10% ether/hexane; clear colourless oil (91%); spectrally as reported,[21] additionally: δ_C (75 MHz) 190.7 (*C*HO), 162.1 (Ar*C*(1)–O), 131.7 (Ar*C*(3,5)H), 130.6 (Ar*C*(4)–CHO), 116.2 (Ar*C*(2,6)H), 94.0 (O–*C*H$_2$–O), 56.2 (O*Me*). Found: M^+ +H, 167.0711. Calcd for $C_9H_{11}O_3$: 167.0708.

4-(Ethoxymethoxy)benzaldehyde (3a). Eluent: 50% ether/hexane; clear colourless oil (96%). (Found: C, 66.74; H, 6.59. $C_{10}H_{12}O_3$ requires: C, 66.65; H, 6.71%). ν_{max} (neat)/cm^{-1} 3070w, 2978s, 2900s, 2739m, 1697vs, 1601s, 1579s, 1508s, 1427m, 1393m, 1314m, 1234s, 1161s, 1110s, 982vs, 835s. δ_H (270 MHz) 9.85 (1H, s, C*H*O), 7.79 (2H, d, *J*=8.9 Hz, ArC(3,5)*H*), 7.10 (2H, d, *J*=8.9 Hz, ArC(2,6)*H*), 5.26 (2H, s, O–C*H*$_2$–O), 3.69 (2H, q, *J*=7.2 Hz, O–C*H*$_2$), 1.17 (3H, t, *J*=7.2 Hz, *Me*); δ_C (68 MHz) 190.9 (*C*HO), 162.9 (Ar*C*(1)–O), 131.9 (Ar*C*(3,5)H), 130.6 (Ar*C*(4)–CHO), 116.3 (Ar*C*(2,6)H), 92.8 (O–*C*H$_2$–O), 64.8 (O–*C*H$_2$), 15.1 (*Me*). *m*/*z*(EI) 180 (M^+), 149, 135, 121 (M^+-OEt). Found: M^+ 180.0788. Calcd for $C_{10}H_{12}O_3$: 180.0786.

4-(2-Methoxyethoxy)benzaldehyde (4a). But prepared as previously reported;[22] eluent: 50% ether/hexane; clear colourless oil (92%). (Found: C, 66.90; H, 6.61. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71%). ν_{max} (neat)/cm^{-1} 3074w, 3042w, 2930s, 2886s, 2823s, 1747s, 1694vs, 1602s, 1578s, 1509s, 1454s, 1312m, 1260s, 1162s, 1128s, 1057m, 1033m, 834s. δ_H (270 MHz) 9.82 (1H, s, C*H*O), 7.77 (2H, d, *J*=8.9 Hz, ArC(3,5)*H*), 6.98 (2H, d, *J*=8.7 Hz, ArC(2,6)*H*), 4.16–4.13 (2H, m, O–C*H*$_2$), 3.74–3.71 (2H, m, C*H*$_2$–O), 3.40 (3H, s, O*Me*); δ_C (68 MHz) 190.8 (*C*HO), 163.9 (Ar*C*(1)–O), 132.0 (Ar*C*(3,5)H), 130.1 (Ar*C*(4)–CHO), 114.9 (Ar*C*(2,6)H), 70.7 (*C*H$_2$–O), 67.7 (O–*C*H$_2$), 59.3 (O*Me*). *m*/*z*(EI) 180 (M^+), 135, 121 ($M^+-MeOC_2H_4$). Found: M^+ 180.0789. Calcd for $C_{10}H_{12}O_3$: 180.0786.

4-[(2-Methoxyethoxy)methoxy]benzaldehyde (5a).[23] Eluent: 50% ether/hexane; clear colourless oil (94%). (Found: C, 62.53; H, 6.77. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71%). ν_{max} (neat)/cm^{-1} 2927vs, 1701s, 1601s, 1508s, 1161s, 988s, 843s. δ_C (68 MHz) 190.8 (*C*HO), 162.2 (Ar*C*(1)–O), 131.9 (Ar*C*(3,5)H), 130.7 (Ar*C*(4)–CHO), 116.3 (Ar*C*(2,6)H), 93.1 (O–*C*H$_2$–O), 71.5 (*C*H$_2$–O), 68.1 (O–*C*H$_2$), 59.0 (O*Me*). *m*/*z*(CI) 228 (M^++NH_4), 211 (M^++H), 156, 89, 59. Found: M^++NH_4 228.1240. Calcd for $C_{11}H_{18}NO_4$: 228.1236.

General procedure for the reduction of the benzaldehyde function

A solution of the 4-alkoxybenzaldehyde (**1a**–**5a** as appropriate, 142 mmol) in methanol (280 mL) was stirred at 0°C under nitrogen. Sodium borohydride (8 g, 214 mmol) was slowly added over a period of 30 min. The solution was allowed to warm to room temperature and was stirred for a further 16 h. The methanol was removed in vacuo, water (250 mL) was added, and the solution acidified to pH 7–8, saturated with sodium chloride and extracted with ether (5×100 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated under reduced pressure. Column chromatography afforded the title compounds. So prepared were:-

4-Methoxymethoxybenzyl alcohol (2b). Eluent: 50% ethyl acetate/hexane; distillation gave a clear colourless oil (98%), bp 164°C @ 2 mmHg (lit.[24] 122°C @ 2 mmHg) (Found: C, 64.43; H, 7.29. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.29%). Spectral data were consistent with the literature.[25]

4-Ethoxymethoxybenzyl alcohol (3b). Eluent: 50% ether/hexane; clear colourless oil (98%). (Found: C, 65.71; H, 7.83. $C_{10}H_{14}O_3$ requires: C, 65.92; H, 7.74%). ν_{max} (neat)/cm^{-1} 3385brs, 3061w, 3035w, 2977s, 2886s, 1612s, 1512s, 1224s, 1172s, 1107s, 1002s, 845s, 818s. δ_H (270 MHz) 7.24 (2H, d, *J*=8.7 Hz, ArC(3,5)*H*), 7.00 (2H, d, *J*=8.7 Hz, ArC(2,6)*H*), 5.18 (2H, s, O–CH_2–O), 4.56 (2H, s, Ar–CH_2), 3.69 (2H, q, *J*=7.2 Hz, O–CH_2), 2.14 (1H, s, O*H*), 1.19 (3H, t, *J*=7.2 Hz, *Me*); δ_C (68 MHz) 156.9 (Ar*C*(1)–O), 134.3 (Ar*C*(4)–CH_2), 128.6 (Ar*C*(3,5)H), 116.3 (Ar*C*(2,6)H), 93.2 (O–CH_2–O), 64.9 (Ar–CH_2), 64.3 (O–CH_2), 15.2 (*Me*). *m/z*(EI) 182 (M^+),152, 137, 123, 107, 95, 89, 77, 59. Found: M^+ 182.0941. $C_{10}H_{14}O_3$ requires: 182.0943.

4-(2-Methoxyethoxy)benzylalcohol (4b). Eluent: 50% ether/hexane; clear colourless oil (93%). ν_{max} (neat)/cm^{-1} 3405brs, 3063w, 3034w, 2929s, 2878s, 1612s, 1585m, 1512s, 1455m, 1247s, 1127s, 1063m, 925m, 819m. δ_H (270 MHz) 7.25–7.18 (2H, m, ArC(3,5)*H*), 6.87–6.81 (2H, m, ArC(2,6)*H*), 4.50 (2H, d, *J*=9.7 Hz, Ar–CH_2), 4.07–4.01 (2H, m, O–CH_2), 3.72–3.66 (2H, m, CH_2O), 3.39 (3H, s, O*Me*), 2.36 (1H, br s, O*H*); δ_C (68 MHz) 158.3 (Ar*C*(1)–O), 133.6 (Ar*C*(4)–CH_2), 128.6 (Ar*C*(3,5)H), 114.6 (Ar*C*(2,6)H), 71.1 (CH_2–O), 67.3 (O–CH_2), 64.7 (Ar–CH_2), 59.2 (O*Me*). *m/z* (EI) 182 (M^+), 137, 124, 107, 95, 59. Found: M^+ 182.0937. $C_{10}H_{14}O_3$ requires: 182.0943.

4-(2-Methoxyethoxy)methoxybenzyl alcohol (5b). Eluent: 50% ether/hexane; clear colourless oil (98%). (Found: C, 62.37; H, 7.73. $C_{11}H_{16}O_4$ requires: C, 62.25; H, 7.60%). ν_{max} (neat)/cm^{-1} 3428br, 2927m, 2882m, 1613m, 1511s, 1223s, 1104s, 1006s, 847m. δ_H (270 MHz) 7.23 (2H, d, *J*=6.7 Hz, ArC(3,5)*H*), 7.00 (2H, d, *J*=8.7 Hz, ArC(2,6)*H*), 5.22 (2H, s, O–CH_2–O), 4.56 (2H, s, Ar–CH_2), 3.78 (2H, t, *J*=4.4 Hz, O–CH_2), 3.52 (2H, t, *J*=4.7 Hz, CH_2–O), 3.33 (3H, s, O*Me*), 1.24 (1H, s, O*H*); δ_C (68 MHz) 156.8 (Ar*C*(1)–O), 134.5 (Ar*C*(4)–CH_2), 128.6 (Ar*C*(3,5)H), 116.4 (Ar*C*(2,6)H), 93.5 (O–CH_2–O), 71.8 (CH_2–O), 67.6 (O–CH_2), 64.9 (Ar–CH_2), 59.1 (O*Me*). *m/z*(EI) 212 (M^+), 195 (M^+-OH), 137, 107, 89, 59. Found: M^+ 212.1055. $C_{11}H_{16}O_4$ requires: 212.1049.

General procedure for triisopropylsilyl(TIPS) protection[26]

A solution of the 4-alkoxybenzyl alcohol (**1b**–**5b** as appropriate, 137 mmol), imidazole (28 g, 412 mmol) and triisopropylsilyl chloride (35.3 mL, 165 mmol) in DMF (150 mL) was stirred at r.t. for 16 h. Ether (300 mL) was added, extracted with water (5×100 mL) and dried ($MgSO_4$). Concentration under reduced pressure followed by flash chromatography furnished the title compounds. So prepared were:

4-Triisopropylsiloxymethyl(methoxy)benzene (1c). Eluent: 10% ether/hexane; colourless liquid (96%). (Found: C, 69.19; H, 10.17. $C_{17}H_{30}O_2Si$ requires: C, 69.33; H, 10.27%). ν_{max} (neat)/cm^{-1} 2943s, 2866s, 1514s, 1247s, 1095s, 883s, 682s. δ_H (270 MHz) 7.27 (2H, d, *J*=8.9 Hz, ArC(3,5)*H*), 6.87 (2H, d, *J*=8.7 Hz, ArC(2,6)*H*), 4.77 (2H, s, Ar–CH_2), 3.79 (3H, s, O*Me*), 1.16–1.05 (21H, m, *TIPS*); δ_C (68 MHz) 158.6 (Ar*C*(1)–O), 133.9 (Ar*C*(4)–CH_2), 127.2 (Ar*C*(3,5)H), 113.6 (Ar*C*(2,6)H), 64.8 (Ar–CH_2), 55.3 (O*Me*), 18.1 (TIPS–*Me*), 12.1 (Si–*C*H). *m/z*(CI) 312 (M^++NH_4), 294 (M^+), 293 (M^+-H), 268, 251, 138, 121. Found: M^++NH_4 312.2354. $C_{17}H_{34}NO_2Si$ requires: 312.2359.

4-Triisopropylsiloxymethyl(methoxymethoxy)benzene (2c). Eluent: 10% ether/hexane; colourless oil (89%), bp 196°C. (Found: C, 66.48; H, 9.93. $C_{18}H_{32}O_3Si$ requires: C, 66.62; H, 9.94%). ν_{max} (neat)/cm^{-1} 2866vs, 1614w, 1511s, 1464m, 817w. δ_H (270 MHz) 7.29 (2H, d, *J*=8.7 Hz, ArC(3,5)*H*), 7.04 (2H, d, *J*=8.6 Hz, ArC(2,6)*H*), 5.19 (2H, s, O–CH_2–O), 4.79 (2H, s, Ar–CH_2), 3.50 (3H, s, O*Me*), 1.2–1.0 (21H, m, *TIPS*); δ_C (75 MHz) 156.2 (Ar*C*(1)–O), 135.1 (Ar*C*(4)–CH_2), 127.0 (Ar*C*(3,5)H), 116.0 (Ar*C*(2,6)H), 94.5 (O–CH_2–O), 64.7 (Ar–CH_2), 55.8 (O*Me*), 18.1 (TIPS–*Me*), 12.1 (Si–*C*H). *m/z*(CI) 281 ($M^+-C_3H_7$), 168 (M^+-TIPS+H), 151 (M^+-OTIPS), 136 (151−Me). Found: M^++NH_4 342.2460. $C_{18}H_{36}NO_3Si$ requires: 342.2464.

4-Triisopropylsiloxymethyl(ethoxymethoxy)benzene (3c). Eluent: 10% ether/hexane; colourless liquid (93%). (Found: C,67.62: H, 10.09. $C_{19}H_{34}O_3Si$ requires C, 67.41; H, 10.12%). ν_{max} (neat)/cm^{-1} 3063w, 2943vs, 2866s, 1613s, 1587m, 1511s, 1463s, 1375m, 1302m, 1222s, 1171m, 1096vs, 1007s, 919m, 882s. δ_H (270 MHz) 7.28 (2H, d, *J*=8.4 Hz, ArC(3,5)*H*), 7.02 (2H, d, *J*=8.7 Hz, ArC(2,6)*H*), 5.21 (2H, s, O–CH_2–O), 4.78 (2H, s, Ar–CH_2), 3.72 (2H, q, *J*=6.9 Hz, O–CH_2), 1.25 (3H, t, *J*=6.9 Hz, *Me*), 1.34–1.01 (21H, m, *TIPS*); δ_C (68 MHz) 156.4 (Ar*C*(1)–O), 135.04 (Ar*C*(4)–CH_2), 127.1 (Ar*C*(3,5)H), 116.1 (Ar*C*(2,6)H), 93.3 (O–CH_2–O), 64.8 (Ar–CH_2), 64.1 (O–CH_2), 18.0 (TIPS–*Me*), 15.0 (*Me*), 11.9 (Si–*C*H). *m/z*(CI) 338 (M^+), 337 (M^+-H), 312, 295, 265, 176, 165. Found: M^+ 338.2247. $C_{19}H_{34}O_3Si$ requires: 338.2277

4-Triisopropylsiloxymethyl(2-methoxyethoxy)benzene (4c). Eluent: 10% ether/hexane; colourless liquid (97%). (Found: C, 67.64; H, 10.28. $C_{19}H_{34}O_3Si$ requires: C, 67.41; H, 10.12%). ν_{max} (neat)/cm^{-1} 3064w, 3033w, 2942s, 2866s, 2725w, 1613m, 1586w, 1512s, 1463s, 1374m, 1247s, 1129m, 1095m, 1066m, 1012m, 923m, 882s, 807s. δ_H (270 MHz) 7.25 (2H, d, *J*=8.7 Hz, ArC(3,5)*H*), 6.88 (2H, d, *J*=8.7 Hz, ArC(2,6)*H*), 4.75 (2H, s, Ar–CH_2), 4.08 (2H, t, *J*=4.7 Hz, O–CH_2), 3.73 (2H, t, *J*=4.7 Hz, CH_2–O), 3.43 (3H, s, O*Me*), 1.12–0.96 (21H, m, TIPS); δ_C (68 MHz) 157.8 (Ar*C*(1)–O), 134.3 (Ar*C*(4)–CH_2), 127.1 (Ar*C*(3,5)H), 114.3 (Ar*C*(2,6)H), 71.2 (CH_2–O), 67.3 (O–CH_2), 64.8 (Ar–CH_2), 59.3 (O*Me*), 18.1 (TIPS–*Me*), 12.1 (Si–*C*H). *m/z*(CI) 356 (M^++NH_4), 338 (M^+), 337 (M^+-H), 312, 192, 165, 148, 120. Found: M^++NH_4 356.2612. $C_{19}H_{38}NO_3Si$ requires: 356.2621.

4-Triisopropylsiloxymethyl(2-methoxyethoxymethoxy)-benzene (5c). Eluent: 30% ether/hexane; colourless liquid

(96%). (Found: C, 64.96; H, 10.11. $C_{20}H_{36}O_4Si$ requires: C, 65.17; H, 9.84%). ν_{max} (neat)/cm^{-1} 2943s, 2867s, 1511s, 1464m, 1221m, 1097s, 883m, 681m. δ_H (270 MHz) 7.25 (2H, d, *J*=8.7 Hz, ArC(3,5)*H*), 7.00 (2H, d, *J*=8.7 Hz, ArC(2,6)*H*), 5.25 (2H, s, O–C*H*$_2$–O), 4.76 (2H, s, Ar–C*H*$_2$), 3.80 (2H, t, *J*=4.0 Hz, O–C*H*$_2$), 3.54 (2H, t, *J*=4.0 Hz, C*H*$_2$–O), 3.36 (3H, s, O*Me*), 1.19–0.95 (21H, m, *TIPS*); δ_C (68 MHz) 156.2 (Ar*C*(1)–O), 135.2 (Ar*C*(4)–CH$_2$), 127.9 (Ar*C*(3,5)H), 116.1 (Ar*C*(2,6)H), 93.7 (O–*C*H$_2$–O), 71.6 (*C*H$_2$–O), 67.6 (O–*C*H$_2$), 64.7 (Ar–*C*H$_2$), 59.1 (O*Me*), 18.1 (TIPS–*Me*), 12.3 (Si–*C*H). *m/z*(CI) 386 (M$^+$+NH$_4$), 368 (M$^+$), 367 (M$^+$−H), 325, 195, 59. Found: M$^+$+NH$_4$ 386.2714. $C_{20}H_{40}NO_4Si$ requires: 386.2727.

General procedure for the preparation of arenetricarbonylchromium(0) complexes

A mixture of the arene indicated (1.0 equiv.) and chromium hexacarbonyl (0.2–2 equiv.) in a deoxygenated ethereal solvent (dibutyl ether/THF or dioxane) was attached to a wide-bore air condenser or Strohmeier apparatus in line with a water condenser and heated under reflux for 12–48 h under a positive pressure of nitrogen and in subdued light. The resulting yellow/orange solution was cooled, filtered through a short pad of Celite, eluted with ether and concentrated under reduced pressure. Flash column chromatography (FCC) and/or recrystallisation as appropriate furnished the desired complex. So prepared were:-

η^6-[4-Triisopropylsiloxymethyl(methoxy)benzene]tricarbonylchromium(0) (6b). This complex was prepared from 4-triisopropylsiloxymethyl(methoxy)benzene (**1c**, 10.0 g, 34 mmol) and chromium hexacarbonyl (11.22 g, 51.00 mmol), refluxed for 48 h. in dibutyl ether: THF (300 mL: 30 mL). FCC (eluent: 15% ether/hexane) to furnish the *complex* (**6b**) as a bright yellow crystalline solid. (12.73 g, 29.58 mmol, 87%), mp 52–54°C. (Found: C, 55.69; H, 7.00. $C_{20}H_{30}CrO_5Si$ requires: C, 55.80; H, 7.02%). ν_{max} (KBr)/cm^{-1} 2943s, 2864s, 1957vs, 1877vs, 1848vs, 1544m, 1255s, 1105m, 804m, 626s. δ_H (270 MHz) 5.63 (2H, d, *J*=6.9 Hz, ArC(3,5)*H*), 5.11 (2H, d, *J*=6.9 Hz, ArC(2,6)*H*), 4.41 (2H, s, Ar–C*H*$_2$), 3.68 (3H, s, O*Me*), 1.17–1.03 (21H, m, TIPS–*Me*); δ_C (68 MHz) 233.3 (*C*O), 142.7 (Ar*C*(1)–O), 104.7 (Ar*C*(4)–CH$_2$), 93.2 (Ar*C*(3,5)H), 77.6 (Ar*C*(2,6)H), 63.1 (Ar–*C*H$_2$), 55.7 (O*Me*), 18.0 (TIPS–*Me*), 12.0 (Si–*C*H). *m/z*(CI) 448 (M$^+$+NH$_4$), 431 (M$^+$+H), 363 (448−H−3×CO), 346 (M$^+$−3×CO), 312 (448−Cr(CO)$_3$), 294 (M$^+$−Cr(CO)$_3$), 257 (M$^+$−TIPSO), 138, 121, 52. Found: M$^+$ 430.1262. $C_{20}H_{30}CrO_5Si$ requires: 430.1268.

η^6-(Methoxymethoxybenzene)tricarbonylchromium(0) (7a). This complex was prepared from methoxymethoxybenzene (**2, Y=H,** 2.20 g, 20.0 mmol) and chromium hexacarbonyl (5.50 g, 25.0 mmol), refluxed for 8 h in dioxane (120 mL). FCC (eluent: 10% ether/hexane) and recrystallisation (from DCM/hexane), furnished the *complex* (**7a**) as bright yellow crystals (4.28 g, 15.6 mmol, 78%), mp 71–72°C. (Found: C, 47.93; H, 3.64. $C_{11}H_{10}CrO_5$ requires: C, 48.19; H, 3.68%). ν_{max} (Nujol)/cm^{-1} 3019m, 1970s, 1892s, 1215vs, 757s. δ_H (270 MHz) 5.51 (2H, t, *J*=6.4 Hz, ArC(3,5)*H*), 5.29 (2H, d, *J*=6.4 Hz, ArC(2,6)*H*), 5.05 (2H, s, O–C*H*$_2$–O), 4.89 (1H, t, *J*=6.2 Hz, ArC(4)*H*), 3.49 (3H, s, O*Me*); δ_C (75 MHz) 140.6 (Ar*C*(1)–O), 95.3 (O–*C*H$_2$–O), 94.6 (Ar*C*(3,5)H), 86.1 (Ar*C*(4)H), 80.6 (Ar*C*(2,6)H), 56.93 (O*Me*). *m/z*(EI) 274 (M$^+$), 218 (M$^+$−2×CO), 190 (M$^+$−3×CO), 175 (190−Me), 158 (M$^+$−MeOH), 145 (190−CH$_2$OMe). Found: M$^+$ 273.9938. $C_{11}H_{10}CrO_5$ requires 273.9933.

η^6-[4-Triisopropylsiloxymethyl(methoxymethoxy)benzene]tricarbonyl-chromium(0) (7b). This complex was prepared from 4-triisopropyloxymethyl(methoxymethoxy)-benzene (**2c**, 10.0 g, 318 mmol) and chromium hexacarbonyl (13.2 g, 60 mmol), refluxed for 48 h in dibutyl ether: THF (300 mL:20 mL). FCC (eluent: 10% ether/hexane) furnished the *complex* (**7b**) as a bright yellow crystalline solid. (13.50 g, 28.5 mmol, 95%), mp 32–34°C. (Found: C, 54.76; H, 7.19. $C_{21}H_{32}CrO_6Si$ requires: C, 54.77; H, 7.00%). ν_{max} (neat)/cm^{-1} 2944s, 1887brs, 1880brs. δ_H (270 MHz) 5.60 (2H, d, *J*=7.2 Hz, ArC(3,5)*H*), 5.32 (2H, d, *J*=6.9 Hz, ArC(2,6)*H*), 5.03 (2H, s, O–C*H*$_2$–O), 4.42 (2H, s, Ar–C*H*$_2$–O), 3.48 (3H, s, O*Me*), 1.2–1.0 (21H, m, *TIPS*); δ_C (75 MHz) 139.9 (Ar*C*(1)–O), 105.5 (Ar*C*(4)–CH$_2$), 95.4 (O–*C*H$_2$–O), 92.7 (Ar*C*(3,5)H), 80.2 (Ar*C*(2,6)H), 63.0 (Ar–*C*H$_2$), 56.8 (O*Me*), 18.0 (TIPS–*Me*), 11.9 (Si–*C*H). *m/z*(CI) 478 (M$^+$+NH$_4$), 461 (M$^+$+H), 287 (M$^+$−OTIPS), 121 (287−Cr(CO)$_3$). Found: M$^+$+NH$_4$ 478.1723. $C_{21}H_{36}CrNO_6Si$ requires: 478.1717.

η^6-(Ethoxymethoxybenzene)tricarbonylchromium(0) (8a). This complex was prepared from ethoxymethoxy-benzene (**3, Y=H**, 8.0 g, 52.6 mmol) and chromium hexacarbonyl (17.35 g, 78.8 mmol), refluxed for 36 h in dibutyl ether: THF (300 mL: 30 mL). FCC (eluent: 10% ether/hexane) gave the *complex* (**8a**) as bright yellow crystals (6.85 g, 23.8 mmol, 45%), mp 74–76°C. (Found: C, 50.17; H, 4.31 $C_{12}H_{12}CrO_5$ requires: C, 50.01; H, 4.20%). ν_{max} (CHCl$_3$)/cm^{-1} 1969vs, 1890vs. δ_H (270 MHz) 5.50 (2H, t, *J*=6.5 Hz, ArC(3,5)*H*), 5.30 (2H, d, *J*=6.5 Hz, ArC(2,6)*H*), 5.08 (2H, s, O–C*H*$_2$–O), 4.89 (1H, t, *J*=6.5 Hz, ArC(4)*H*), 3.72 (2H, q, *J*=7.1 Hz, O–C*H*$_2$), 1.23 (3H, t, *J*=7.1 Hz, *Me*); δ_C (68 MHz) 233.2 (*C*O), 141.0 (Ar*C*(1)–O), 94.7 (O–*C*H$_2$–O), 93.9 (Ar*C*(3,5)H), 86.1 (Ar*C*(4)H), 80.7 (Ar*C*(2,6)H), 65.2 (O–*C*H$_2$), 15.0 (*Me*). *m/z*(CI) 306 (M$^+$+NH$_4$), 289 (M$^+$+H), 221, 177, 86, 52. Found (CI): M$^+$+H 289.0163. $C_{12}H_{13}CrO_5$ requires 289.0168.

η^6-[4-Triisopropylsiloxymethyl(ethoxymethoxy)benzene]-tricarbonyl-chromium(0) (8b). This complex was prepared from 4-triisopropylsiloxymethyl(ethoxymethoxy)-benzene (**3c**, 10.0 g, 30 mmol) and chromium hexacarbonyl (13 g, 57 mmol), refluxed for 48 h. in dibutyl ether: THF (300 mL:30 mL). FCC (eluent: 10% ether/hexane) furnished the *complex* (**8b**) as a bright yellow crystalline solid. (13.4 g, 28.2 mmol, 93%), mp 52–53°C. (Found: C, 55.88; H, 7.45. $C_{22}H_{34}CrO_6Si$ requires: C, 55.68; H, 7.22%). ν_{max} (KBr)/cm^{-1} 3098w, 2943s, 2865s, 1968vs, 1866vs, 1541m, 1486m, 1228s, 1064s, 970s, 800m, 680m, 630s, 532m. δ_H (270 MHz) 5.69 (2H, d, *J*=7.2 Hz, ArC(3,5)*H*), 5.32 (2H, d, *J*=7.2 Hz, ArC(2,6)*H*), 5.06 (2H, s, O–C*H*$_2$–O), 4.42 (2H, s, Ar–C*H*$_2$–O), 3.70 (2H, q, *J*=7.2 Hz, O–C*H*$_2$), 1.23 (3H, t, *J*=7.2 Hz, *Me*), 1.17–0.98 (21H, m, *TIPS*); δ_C (68 MHz) 233.3 (*C*O), 140.1 (Ar*C*(1)–O), 105.4 (Ar*C*(4)–CH$_2$), 94.1

(O–*C*H$_2$–O), 92.8 (Ar*C*(3,5)H), 80.2 (Ar*C*(2,6)H), 65.2 (Ar–*C*H$_2$), 63.1 (O–*C*H$_2$), 18.0 (TIPS–*Me*), 15.0 (*Me*), 11.9 (Si–*C*H). *m*/*z*(EI) 474 (M$^+$), 390 (M$^+$−3×CO), 348, 318, 295, 289, 159, 52. Found: M$^+$ 474.1552. $C_{22}H_{34}CrO_6Si$ requires: 474.1529.

η^6-[4-Triisopropylsiloxymethyl(2-methoxyethoxy)benzene]tricarbonylchromium(0) (9b). This complex was prepared from 4-triisopropylsiloxymethyl(2-methoxyethoxy)benzene (**4c**, 10.0 g, 30 mmol) and chromium hexacarbonyl (13 g, 57 mmol), refluxed for 48 h in dibutyl ether: THF (300 mL: 30 mL). FCC (eluent: 10% ether/hexane) furnished the *complex* (**9b**) as a bright yellow crystalline solid. (9.9 g, 21.7 mmol, 72%), mp 30–31°C. (Found: C, 55.91; H, 7.18. $C_{22}H_{34}CrO_6Si$ requires: C, 55.68; H, 7.22%). ν_{max} (KBr)/cm^{-1} 3108w, 3078w, 2941s, 2865s, 1966vs, 1884vs, 1548m, 1450s, 1254s, 1129s, 1087s, 882m, 805m, 677s, 685s, 536m. δ_H (270 MHz) 5.60 (2H, d, *J*=6.7 Hz, ArC(3,5)*H*), 5.13 (2H, d, *J*=6.7 Hz, ArC(2,6)*H*), 4.38 (2H, s, Ar–C*H*$_2$), 3.94 (2H, s, O–C*H*$_2$), 3.63 (2H, s, C*H*$_2$–O), 3.36 (3H, s, O*Me*), 1.17–0.98 (21H, m, *TIPS*); δ_C (68 MHz) 233.3 (*C*O), 141.9 (Ar*C*(1)–O), 104.9 (Ar*C*(4)–CH$_2$), 93.2 (Ar*C*(3,5)H), 78.3 (Ar*C*(2,6)H), 70.4 (*C*H$_2$–O), 68.1 (O–*C*H$_2$), 63.1 (Ar–*C*H$_2$), 59.1 (O*Me*), 18.0 (TIPS–*Me*), 11.9 (Si–*C*H). *m*/*z*(CI) 492 (M$^+$+NH$_4$), 475 (M$^+$+H), 391 (M$^+$+H−3×CO), 347, 312, 301, 268, 184, 165. Found: M$^+$ 474.1534. $C_{22}H_{34}CrO_6Si$ requires: 474.1529.

η^6-[4-Triisopropylsiloxymethyl(2-methoxyethoxymethoxy)benzene]tricarbonylchromium(0) (10b). This complex was prepared from 4-triisopropylsiloxymethyl(2-methoxyethoxymethoxy)benzene (**5c**, 6.00 g, 16.30 mmol) and chromium hexacarbonyl (7.17 g, 32 mmol), refluxed for 48 h in dibutyl ether: THF (300 mL: 30 mL). FCC (eluent: 20% ether/hexane) furnished the *complex* (**10b**) as a bright yellow crystalline solid. (6.53 g, 12.87 mmol, 79%), mp 12–14°C. (Found: C, 54.75; H, 7.03. $C_{23}H_{36}CrO_7Si$ requires: C, 54.75; H, 7.19%). ν_{max} (neat)/cm^{-1} 2944s, 2867s, 1988vs, 1883vs, 1485m, 1462m, 1227s, 1109s, 629s. δ_H (270 MHz) 5.59 (2H, d, *J*=6.9 Hz, ArC(3,5)*H*), 5.34 (2H, d, *J*=6.9 Hz, ArC(2,6)*H*), 5.11 (2H, s, O–C*H*$_2$–O), 4.41 (2H, s, Ar–C*H*$_2$), 3.81 (2H, t, *J*=4.2 Hz, O–C*H*$_2$), 3.57 (2H, t, *J*=4.2 Hz, C*H*$_2$–O), 3.37 (3H, s, O*Me*), 1.18–0.93 (21H, m, *TIPS*); δ_C (68 MHz) 233.3 (*C*O), 139.9 (Ar*C*(1)–O), 105.6 (Ar*C*(4)–CH$_2$), 94.3 (O–*C*H$_2$–O), 92.7 (Ar*C*(3,5)H), 80.3 (Ar*C*(2,6)H), 71.4 (*C*H$_2$–O), 68.5 (O–*C*H$_2$), 63.1 (Ar–*C*H$_2$), 59.2 (O*Me*), 18.1 (TIPS–*Me*), 12.3 (Si–*C*H). *m*/*z*(CI) 522 (M$^+$+NH$_4$), 386 (522−Cr(CO)$_3$), 192, 148, 52 (Cr). Found: M$^+$+NH$_4$ 522.1982. $C_{23}H_{40}CrNO_7Si$ requires: 522.1979.

η^6-(*N*-*t*-Butoxycarbonylaniline)tricarbonylchromium(0) (11a). This complex was prepared from *N*-*t*-butoxycarbonylaniline (5.80 g, 30.0 mmol) and chromium hexacarbonyl (7.33 g, 30.0 mmol), refluxed for 48 h in dioxane (150 mL). FCC (eluent: 2–5% ether/hexane) and recrystallisation (from DCM/hexane) furnished the *complex* (**11a**) as bright yellow crystals (8.49 g, 25.8 mmol, 86%), mp 121–122°C. ν_{max} (Nujol)/cm^{-1} 3300m, 2925vs, 1955s, 1892, 1855, 1716, 1463s, 675m, 631m. δ_H (270 MHz) 6.01 (1H, s, N*H*), 5.62–5.51 (4H, m, ArC(2,3,5,6)*H*), 4.92 (1H, t, *J*=6.0 Hz, ArC(4)*H*), 1.49 (9H, s, ^{t}*Bu*); δ_C (75 MHz) 151.9 (*C*OO), 119.2 (Ar*C*(1)–N), 94.6 (Ar*C*(3,5)H), 92.7 (Ar*C*(4)H), 86.4 (Ar*C*(2,6)H), 82.3 (O–*C*Me$_3$), 28.14 (*Me*). *m*/*z*(CI) 347 (M$^+$+NH$_4$), 291 (347−2×CO), 274 (M$^+$−2×CO+H), 230 (347−NH$_2$CO$_2$^{t}Bu), 94 (230−Cr(CO)$_3$). Found: M$^+$+NH$_4$ 347.0708. $C_{14}H_{19}CrN_2O_5$ requires 347.0699.

General procedure for the regiocontrolled deprotonation of arenetricarbonylchromium(0) complexes

Butyllithium (1.1 equiv.) was added to a solution of the complex indicated (1 equiv.) in deoxygenated THF (15 mL) or diethyl ether (20 mL) at −78°C, under nitrogen. The resultant solution was allowed to stir for a further 1 h, then quenched with a suitable electrophile (0.9–5 equiv.) and allowed to warm slowly to room temperature over a period of 3–15 h. The THF was removed in vacuo and replaced with ether (20 mL). Unless otherwise stated, the reaction was worked up with 1 M HCl aq. (5 mL), and the organic phase was washed with water (2×20 mL) and brine (20 mL), dried (MgSO$_4$) and concentrated under reduced pressure. FCC and/or recrystallisation as appropriate furnished the desired functionalised complex. So prepared were:-

(±)-η^6-[2-Formyl-4-triisopropylsiloxymethyl(methoxy)benzene]tricarbonylchromium(0) (12b). This complex was prepared from η^6-[4-triisopropylsiloxymethyl(methoxy)benzene]tricarbonylchromium(0) (**6b**, 280 mg, 0.65 mmol) with a DMF quench (0.10 mL, 1.30 mmol). FCC (eluent: 30% ether/hexane). The first eluted compound was the 3-substituted *complex* (**12c**) as an orange crystalline solid (15 mg, 0.03 mmol, 5%) mp 46–48°C. (Found: C, 55.13; H, 6.78%. $C_{21}H_{30}CrO_6Si$ requires: C, 55.01; H, 6.59%). ν_{max} (KBr)/cm^{-1} 2944m, 2866m, 1973vs, 1902vs, 1886vs, 1681s, 1542m, 1276m, 1116m, 1015m, 655s, δ_H (270 MHz) 9.83 (1H, s, C*HO*), 5.74 (1H, d, *J*=6.9 Hz, ArC(5)*H*), 5.99 (1H, d, *J*=2.2 Hz, ArC(2)*H*), 5.51 (1H, dd, *J*=2.2 Hz 6.9 Hz, ArC(6)*H*), 4.95 (1H, d, *J*=13.9 Hz, Ar–C*H*$_2$), 4.73 (1H, d, *J*=13.9 Hz, Ar–C*H*$_2$), 3.71 (3H, s, O*Me*), 1.22–1.00 (21H, m, *TIPS*); δ_C (68 MHz) 231.4 (*C*O), 189.5 (*C*HO), 139.6 (Ar*C*(1)–O), 108.9 (Ar*C*(4)–CH$_2$), 93.6 (Ar*C*(3)–CHO), 91.0 (Ar*C*(2)H), 81.5 (Ar*C*(5)H), 77.9 (Ar*C*(6)H), 61.3 (C, Ar–*C*H$_2$), 56.4 (C, O*Me*), 18.0 (TIPS–*Me*), 11.9 (Si–*C*H). *m*/*z* (FAB$^+$) 458 (M$^+$), 374 (M$^+$−3×CO), 337, 285, 149, 136. Found: M$^+$, 458.1220. $C_{27}H_{30}CrO_6Si$ requires: 458.1217.

Further elution gave the *complex* (**12b**), as a bright orange crystalline solid (2 equiv., 261 mg, 0.57 mmol, 87%) mp 79–81°C. (Found: C, 55.15; H, 6.37. $C_{21}H_{30}CrO_6Si$ requires: C, 55.01; H, 6.59%). ν_{max} (KBr)/cm^{-1} 2942m, 2865m, 1965vs, 1884vs, 1670s, 1144m, 662s. δ_H (270 MHz) 10.03 (1H, s, C*HO*), 6.29 (1H, d, *J*=1.7 Hz, ArC(3)*H*), 5.99 (1H, dd, *J*=1.7, 7.2 Hz, ArC(5)*H*), 5.04 (1H, d, *J*=7.2 Hz, ArC(6)*H*), 4.48 (1H, d, *J*=12.6 Hz, Ar–C*H*$_2$), 4.42 (1H, d, *J*=12.6 Hz, Ar–C*H*$_2$), 3.83 (3H, s, O*Me*), 1.12–0.81 (21H, m, *TIPS*); δ_C (68 MHz) 230.7 (*C*O), 185.6 (*C*HO), 142.3 (Ar*C*(1)–O), 104.3 (Ar*C*(4)–CH$_2$), 93.1 (Ar*C*(3)H), 90.4 (Ar*C*(5)H), 85.2 (Ar*C*(2)–CHO), 71.5 (Ar*C*(6)H), 62.8 (Ar–*C*H$_2$), 56.2 (O*Me*), 18.0 (TIPS–*Me*), 11.9 (Si–*C*H). *m*/*z*(EI) 458 (M$^+$), 374 (M$^+$−3×CO), 331, 288, 257, 217, 170, 147, 52. Found: M$^+$ 458.1211. $C_{21}H_{30}CrO_6Si$ requires: 458.1217.

(±)-η^6-(2-Tributylstannylanisole)tricarbonylchromium(0) (13a). This complex was prepared from η^6-(anisole)tricarbonylchromium(0) (**6a**, 0.24 g, 1.00 mmol) with a tributyltin chloride (1.4 equiv., 0.40 mL, 1.40 mmol) quench. The reaction was worked up with saturated aqueous KF (10 mL). FCC (eluent: 5% ether/hexane) furnished the *complex* (**13a**) as a yellow oil (0.47 g, 0.89 mmol, 89%). ν_{max} (Nujol)/cm^{-1} 2956s, 1958vs, 1881vs, 1452s. δ_H (270 MHz) 5.61 (1H, ddd, *J*=1.5, 6.2, 6.9 Hz, ArC(5)*H*), 5.50 (1H, dd, *J*=1.5, 5.9 Hz, ArC(3)*H*), 5.01 (1H, d, *J*=6.9 Hz, ArC(6)*H*), 4.84 (1H, dt, *J*=0.5, 6.1 Hz, ArC(4)*H*), 3.68 (3H, s, O*Me*), 1.70–1.48 (6H, m, C*H*$_2$CH$_3$), 1.45–1.20 (6H, m, SnCH$_2$C*H*$_2$), 1.10 (6H, t, *J*=9.4 Hz, SnC*H*$_2$), 0.90 (9H, t, *J*=7.4 Hz, CH$_2$C*H*$_3$); δ_C (75 MHz) 146.6 (Ar*C*(1)–O), 103.1 (Ar*C*(3)H), 95.4 (Ar*C*(4)H), 89.6 (Ar*C*(2)–Sn), 86.8 (Ar*C*(5)H), 74.4 (Ar*C*(6)H), 55.3 (O*Me*), 28.9 (SnCH$_2$*C*H$_2$), 27.8 (*C*H$_2$CH$_3$), 13.6 (Sn*C*H$_2$), 10.7 (CH$_2$*C*H$_3$). *m*/*z*(CI) 534 (M$^+$+H), 477 (M$^+$−2×CO), 291 (Bu$_3$SnH). Found: M$^+$ 533.0964. $C_{22}H_{35}CrO_4Sn$ requires: 533.0957.

(±)-η^6-[2-Formyl(methoxymethoxy)benzene]tricarbonylchromium(0) (14a). This complex was prepared from η^6-(methoxymethoxybenzene)tricarbonylchromium(0) (**7a**, 0.350 g, 1.28 mmol) in ether (25 mL) with a DMF (5 equiv., 0.52 mL, 6.40 mmol) quench. FCC (eluent; 50% ether/hexane) gave the desired *complex* (**14a**) as bright red crystals (0.320 g, 1.059 mmol, 83%), mp 93–94°C. (Found: C, 47.52; H, 3.06. $C_{12}H_{10}CrO_6$ requires: C, 47.68; H, 3.31%). ν_{max} (CHCl$_3$)/cm^{-1} 1972vs, 1891vs (C≡O), 1681s (CHO), 1267s (C–O-ether). δ_H (270 MHz) 10.04 (1H, s, C*H*O), 6.19 (1H, dd, *J*=1.5, 6.4 Hz, ArC(3)*H*), 5.80 (1H, ddd, *J*=1.5, 6.4, 6.9 Hz, ArC(5)*H*), 5.36 (1H, dd, *J*=0.5, 6.9 Hz, ArC(6)*H*), 5.25 (1H, d, *J*=7.2 Hz, O–C*H*H–O), 5.13 (1H, d, *J*=7.2 Hz, O–CH*H*–O), 5.00 (1H, t, *J*=6.4 Hz, ArC(4)*H*), 3.53 (3H, s, O*Me*); δ_C (68 MHz) 230.6 (*C*O), 185.4 (*C*HO), 143.6 (Ar*C*(1)–O), 95.7 (O–*C*H$_2$–O), 95.2 (Ar*C*(3)H), 92.2 (Ar*C*(5)H), 84.7 (Ar*C*(4)H), 86.2 (Ar*C*(2)–C), 76.3 (Ar*C*(6)H), 57.6 (O*Me*). *m*/*z*(CI) 320 (M$^+$+NH$_4$), 303 (M$^+$+H), 167 (303−Cr(CO)$_3$). Found: M$^+$+H 302.9970. $C_{12}H_{11}CrO_6$ requires: 302.9961.

(±)-η^6-[2-Formyl-4-triisopropylsiloxymethyl(methoxymethoxy)benzene]tricarbonylchromium(0) (14b). This complex was prepared from η^6-[4-triisopropylsiloxymethyl (methoxymethoxy)benzene]tricarbonylchromium(0) (**7b**, 300 mg, 0.65 mmol) with a DMF (5 equiv., 0.25 mL, 3.24 mmol) quench. The reaction was worked up with water (10 mL). FCC (eluent: 20% ether/hexane) furnished the *complex* (**14b**) as a bright orange crystalline solid (193 mg, 0.40 mmol, 61%) mp 65°C. (Found: C, 54.14; H, 6.79. $C_{22}H_{32}CrO_7Si$ requires: C, 54.08; H, 6.60%). ν_{max} (KBr)/cm^{-1} 3070w, 2943s, 2866s, 1982vs, 1904vs, 1885vs, 1673vs, 1540m, 1469s, 1084s, 954s, 803m, 607s, 522m. δ_H (270 MHz) 10.05 (1H, s, C*H*O), 6.27 (1H, d, *J*=1.7 Hz, ArC(3)*H*), 5.97 (1H, dd, *J*=1.7, 6.9 Hz, ArC(5)*H*), 5.37 (1H, d, *J*=6.9 Hz, ArC(6)*H*), 5.24 (1H, d, *J*=6.9 Hz, O–CH*H*–O), 5.11 (1H, d, *J*=7.2 Hz, O–C*H*H–O), 4.49 (1H, d, *J*=12.9 Hz, Ar–C*H*$_2$), 4.42 (1H, d, *J*=12.6 Hz, Ar–C*H*$_2$), 3.52 (3H, s, O*Me*), 1.31–0.71 (21H, m, *TIPS*); δ_C (68 MHz) 230.8 (*CO*), 185.6 (*C*HO), 141.1 (Ar*C*(1)–O), 104.1 (Ar*C*(4)–CH$_2$), 95.7 (O–*C*H$_2$–O), 93.4 (Ar*C*(3)H), 89.9 (Ar*C*(5)H), 85.3 (Ar*C*(2)–CHO), 75.5 (Ar*C*(6)H), 62.7 (Ar–*C*H$_2$), 57.5 (O*Me*), 18.0 (TIPS–*Me*), 11.9 (Si–*C*H). *m*/*z*(CI) 506 (M$^+$+NH$_4$), 489 (M$^+$+H), 370 (506−Cr(CO)$_3$). Found: M$^+$+H 489.1399. $C_{22}H_{33}CrO_7Si$ requires: 489.1401.

(±)-η^6-[2-(*N*-Phenylcarboxamido)-4-triisopropylsiloxymethyl(methoxymethoxy)benzene]tricarbonylchromium(0) (15b). This complex was prepared from η^6-[4-triisopropylsiloxy-methyl(methoxy-methoxy)benzene]tricarbonylchromium(0) (**7b**, 300 mg, 0.65 mmol) in ether (20 mL) with a quench of phenyl isocyanate (0.35 mL, 3.24 mmol). The reaction was worked up with water (10 mL). FCC (eluent: 30% ether/hexane) furnished the *complex* (**15b**) as a bright orange crystalline solid (252 mg, 0.44 mmol, 67%) mp 58–60°C. ν_{max} (KBr)/cm^{-1} 3356w, 3090w, 2945m, 2867m, 1962vs, 1896vs, 1877vs, 1671s, 1600m, 1557s, 1443s, 1187m, 1071m, 913m, 659s, 530m. δ_H (270 MHz) 9.12 (1H, N*H*), 7.52–7.23 (5H, m, Ph*H*), 6.6 (1H, d, *J*=1.7 Hz, ArC(3)*H*), 5.87 (1H, dd, *J*=1.7, 6.9 Hz, ArC(5)*H*), 5.42 (1H, d, *J*=6.9 Hz, ArC(6)*H*), 5.34 (1H, d, *J*=6.7 Hz, O–CH*H*–O), 5.23 (1H, d, *J*=6.7 Hz, O–C*H*H–O), 4.53 (1H, d, *J*=12.6 Hz, Ar–C*H*$_2$), 4.43 (1H, d, *J*=12.6 Hz, Ar–C*H*$_2$), 3.59 (3H, s, O*Me*), 1.13–0.98 (21H, m, *TIPS*); δ_C (68 MHz) 231.4 (*CO*), 161.1 (*C*ON), 138.2 (Ar*C*(1)–O), 137.4–127.2 (Ph(*C*)H), 104.8 (Ar*C*(4)–CH$_2$), 96.7 (Ar*C*(3)H), 94.0 (O–*C*H$_2$–O), 93.2 (Ar*C*(5)H), 85.4 (Ar*C*(2)–CON), 76.5 (Ar*C*(6)H), 62.8 (Ar–*C*H$_2$), 57.7 (O*Me*), 18.1 (TIPS–*Me*), 11.9 (Si–*C*H). *m*/*z*(CI) 597 (M$^+$+NH$_4$), 580 (M$^+$+H), 444 (580−Cr(CO)$_3$). Found: M$^+$+H: 580.1812. $C_{28}H_{38}CrO_7SiN$ requires: 580.1823.

(±)-η^6-[2-Trimethylsilyl(methoxymethoxy)benzene]tricarbonylchromium(0) (16a). This complex was prepared from η^6-(methoxymethoxy)benzenetricarbonylchromium(0) (**7a**, 0.27 g, 1.00 mmol) with a chlorotrimethylsilane (5 equiv., 0.63 mL, 5.00 mmol) quench. FCC (eluent 2–5% ether/hexane) and recrystallisation (from DCM/hexane) furnished the *complex* (**16a**) as bright yellow crystals (0.29 g, 0.84 mmol, 84%), mp 63–65°C. (Found: C, 48.27; H, 5.20. $C_{14}H_{18}CrO_5Si$ requires: C, 48.55; H, 5.24%). ν_{max} (Nujol)/cm^{-1} 1962vs (C≡O ligand), 1877vs (C≡O ligand), 764m, 688m. δ_H (270 MHz) 5.65 (1H, ddd, *J*=1.5, 6.0, 7.5 Hz, ArC(5)*H*), 5.60 (1H, dd, *J*=1.5, 7.0 Hz, ArC(3)*H*), 5.28 (1H, d, *J*=7.5 Hz, O–CH*H*–O), 5.17 (1H, d, *J*=7.5 Hz, O–C*H*H–O), 5.00 (1H, d, *J*=7.5 Hz, ArC(6)*H*), 4.80 (1H, dd, *J*=7.0, 6.0 Hz, ArC(4)*H*), 3.49 (3H, s, O*Me*), 0.34 (9H, s, *TMS*); δ_C (75 MHz) 145.1 (Ar*C*(1)–O), 101.4 (Ar*C*(3)H), 96.1 (O–*C*H$_2$–O), 94.6 (Ar*C*(5)H), 88.9 (Ar*C*(2)–Si), 85.4 (Ar*C*(4)H), 77.4 (Ar*C*(6)H), 56.9 (O*Me*), −0.6 (*TMS*). *m*/*z*(EI) 346 (M$^+$), 290 (M$^+$−2×CO), 262 (M$^+$−3×CO), 210 (M$^+$−Cr(CO)$_3$), 201 (262−OCH$_2$OMe), 73 (TMS), 52 (Cr). Found: M$^+$ 346.0332, $C_{14}H_{18}CrO_5Si$ requires: 346.0329.

(±)-η^6-[2-Trimethylsilyl-4-triisopropylsilyloxymethyl-(methoxymethoxy)benzene]tricarbonylchromium(0) (16b). This complex was prepared from η^6-[4-triisopropylsiloxymethyl(methoxymethoxy)benzene]tricarbonylchromium(0) (**7b**, 1.0 g, 2.16 mmol) in ether (20 mL) with a chlorotrimethylsilane (5 equiv., 1.36 mL, 10.86 mmol) quench. The reaction was worked up with water (10 mL). FCC (eluent: 2% ether/hexane) furnished the *complex* (**16b**) as a bright yellow crystalline solid (0.920g, 1.73 mmol, 80%) m.p 34–35°C. (Found: C, 54.03; H, 7.46. $C_{24}H_{40}CrO_6Si_2$ requires: C, 54.11; H, 7.57%). ν_{max} (KBr)/cm^{-1} 3096w, 2941s, 2865s, 1964vs, 1944vs, 1874vs, 1457m, 1245m, 1161s, 1111s, 981s, 841s, 666s, 627s, 535m. δ_H (270 MHz) 5.75 (1H, d, *J*=6.9 Hz, ArC(5)*H*), 5.71 (1H, s, ArC(3)*H*), 5.28 (1H, d, *J*=6.9 Hz, ArC(6)*H*), 5.14 (1H, d, *J*=6.9 Hz, O–CH*H*–O), 4.97 (1H, d, *J*=6.9 Hz, O–C*H*H–O), 4.37 (2H, s, ArCH_2), 3.46 (3H, s, O*Me*), 1.16–0.97 (21H, m, *TIPS*), 0.32 (9H, s, *TMS*); δ_C (68 MHz) 233.7 (*C*O), 144.7 (Ar*C*(1)–O), 104.1 (Ar*C*(4)–CH$_2$), 99.6 (Ar*C*(3)H), 94.6 (O–*C*H$_2$–O), 94.5 (Ar*C*(5)H), 87.8 (Ar*C*(2)–Si), 76.6 (Ar*C*(6)H), 63.2 (Ar–*C*H$_2$), 56.9 (O*Me*), 18.0 (TIPS–*Me*), 11.9 (Si–*C*H), −0.5 (*TMS*). *m/z* (CI) 532 (M$^+$), 448 (M$^+$−3×CO), 396 (448−Cr), 223 (396−OTIPS). Found: M$^+$ 532.1767. $C_{24}H_{40}CrO_6Si_2$ requires: 532.1768.

(±)-η^6-[2-Trimethylstannyl(methoxymethoxy)benzene]-tricarbonylchromium(0) (17a). This complex was prepared from η^6-(methoxymethoxybenzene)tricarbonyl-chromium(0) (**7a**, 0.350 g, 1.28 mmol) in ether (25 mL) with a trimethyltin chloride (2 equiv., 0.514 g, 2.55 mmol) quench. FCC (eluent: 2% ether/hexane) gave the *complex* (**17a**) was obtained as bright yellow crystals (0.539 g, 1.23 mmol, 95%), mp 80–82°C (Found: C, 38.66; H, 4.27. $C_{14}H_{18}O_5CrSn$ requires: C, 38.48; H, 4.15%). ν_{max} (CHCl$_3$)/cm^{-1} 1963vs, 1886vs. δ_H (270 MHz) 5.59 (1H, ddd, *J*=1.5, 6.1, 6.7 Hz, ArC(5)*H*), 5.50 (1H, dd, *J*=1.5, 5.9 Hz, ArC(3)*H*), 5.32 (1H, dd, *J*=0.7, 6.7 Hz, ArC(6)*H*), 5.15 (1H, d, *J*=7.2 Hz, O–CH*H*–O), 4.94 (1H, d, *J*=7.2 Hz, O–C*H*H–O), 4.85 (1H, ddd, *J*=0.7, 5.9, 6.1 Hz, ArC(4)*H*), 3.46 (3H, s, O*Me*), 0.36 (9H, Sn(Me)$_3$); δ_C (68 MHz) 234.1 (*C*O), 144.5 (Ar*C*(1)–O), 102.5 (Ar*C*(3)H), 95.8 (O–*C*H$_2$–O), 94.8 (Ar*C*(5)H), 87.1 (Ar*C*(4)H), 89.0 (Ar*C*(2)Sn), 78.4 (Ar*C*(6)H), 56.9 (O*Me*), −8.2 (Sn(*Me*)$_3$). *m/z* (FAB$^+$) ^{119}Sn 438 (M$^+$), 382 (M$^+$−2×CO), 354 (M$^+$−3×CO); ^{117}Sn 438 (M$^+$), 380 (M$^+$−2×CO), 352 (M$^+$−3×CO). Found: M$^+$ 437.9598. $C_{14}H_{18}CrO_5Sn$ requires: 437.9581.

(±)-η^6-[2-Trimethylstannyl-4-triisopropylsiloxymethyl-(methoxymethoxy)benzene]tricarbonylchromium(0) (17b). This complex was prepared from η^6-[4-triisopropylsiloxymethyl(methoxymethoxy)benzene]tricarbonylchromium(0) (**7b**, 1.0 g, 2.16 mmol) in 20 mL THF was treated as described, quenching over night with a solution of chlorotrimethyltin (2 equiv., 0.86 g, 4.32 mmol) in 5 mL THF. The reaction was worked-up with saturated potassium fluoride solution (10 mL). Chromatography (eluent: 5% ether/hexane) furnished the title *complex* (**17b**) as a bright yellow crystalline solid (0.96 g, 1.54 mmol, 72%) mp 31°C. (Found: C, 46.27; H, 6.67. $C_{24}H_{40}CrO_6SiSn$ requires: C, 46.15; H, 6.46%). ν_{max} (KBr)/cm^{-1} 3104w, 2943s, 2866s, 1957vs, 1877vs, 1457m, 1259m, 1159s, 1082s, 981s, 811s, 668s, 534s. δ_H (270 MHz) 5.70 (1H, d, *J*=6.2 Hz, ArC(5)*H*), 5.63 (1H, s, ArC(3)*H*), 5.33 (1H, d, *J*=6.6 Hz, ArC(6)*H*), 5.13 (1H, d, *J*=7.1 Hz, O–CH*H*–O), 4.93 (1H, d, *J*=6.9 Hz, O–C*H*H–O), 4.39 (2H, s, Ar–CH_2), 3.45 (3H, s, OMe), 1.16–0.97 (21H, m, TIPS), 0.36 (9H, s, *TMS*); δ_C (68 MHz) 234.1 (*C*O), 144.9 (Ar*C*(1)–O), 105.9 (Ar*C*(4)–CH$_2$), 100.6 (Ar*C*(3)H), 94.9 (O–*C*H$_2$–O), 94.1 (Ar*C*(5)H), 88.1 (Ar*C*(2)–Si), 77.6 (Ar*C*(6)H), 63.2 (Ar–*C*H$_2$), 56.8 (O*Me*), 18.1 (TIPS–*Me*) 12.0 (Si–*C*H), −8.2 (Sn(*Me*)$_3$). *m/z*(CI) 620 (M$^+$), 488 (M$^+$−Cr(CO)$_3$), 473 (488−Me), 445 (473-^{i}Pr). Found: M$^+$ 624.1076. $C_{24}H_{40}CrO_6Si^{120}Sn$ requires: 624.1021.

(±)-η^6-[2-Tributylstannyl(methoxymethoxy)benzene]-tricarbonylchromium(0) (18a). This complex was prepared from η^6-(methoxymethoxy)benzenetricarbonyl-chromium(0) (**7a**, 0.27 g, 1.00 mmol), with a tributyltin chloride (1.4 equiv., 0.40 mL, 1.40 mmol) quench. The reaction was worked up with saturated aqueous KF (10 mL). FCC (eluent: 5% ether/hexane) furnished the *complex* (**18a**) as a yellow oil (0.47 g, 0.84 mmol, 84%). ν_{max} (Nujol)/cm^{-1} 2956s, 1958vs, 1880, 664, 628. δ_H (270 MHz) 5.59 (1H, dt, *J*=1.2, 6.1 Hz, ArC(5)*H*), 5.49 (1H, dd, *J*=1.5, 5.9 Hz, ArC(3)*H*), 5.33 (1H, dd, *J*=0.5, 7.1 Hz, ArC(6)*H*), 5.14 (1H, d, *J*=7.2 Hz, O–CH*H*–O), 4.93 (1H, d, *J*=7.4 Hz, O–C*H*H–O), 4.85 (1H, dt, *J*=0.5, 6.0 Hz, ArC(4)*H*), 3.46 (3H, s, O*Me*), 1.71–148 (6H, m, CH_2CH$_3$), 1.45–1.23 (6, H, m, SnCH$_2$CH_2), 1.12 (6H, t, *J*=9.2 Hz, SnCH_2), 0.90 (9H, t, *J*=7.2 Hz, CH$_2$CH_3); δ_C (75 MHz) 144.4 (Ar*C*(1)–O), 102.7 (Ar*C*(3)H), 95.7 (O–*C*H$_2$–O), 94.8 (Ar*C*(4)H), 89.9 (Ar*C*(2)–Sn), 87.2 (Ar*C*(5)H), 78.5 (Ar*C*(6)H), 56.8 (O*Me*), 28.9 (SnCH$_2$*C*H$_2$), 27.3 (*C*H$_2$CH$_3$), 13.6 (Sn*C*H$_2$), 0.8 (CH$_2$*C*H$_3$) *m/z* (CI) 564 (M$^+$+H), 507 (M$^+$−Bu+H), 393 (M$^+$−2×CO−2×Bu). Found: M$^+$+H 564.0998. $C_{23}H_{37}CrO_5Sn$ requires: 564.0990.

(±)-η^6-[2-Hydroxymethyl(methoxymethoxy)benzene)-tricarbonylchromium(0) (19a). This complex was prepared from η^6-(methoxymethoxybenzene)tricarbonyl-chromium(0) (**7a**, 0.27 g, 1.00 mmol), treated as described except that the temperature of the solution was raised to −42°C for a quench with paraformaldehyde (5 equiv., 0.15 g, 5.00 mmol). FCC (eluent: 60–80% ether/hexane) and recrystallisation (from DCM/hexane) furnished the complex (**19a**) as bright yellow crystals (0.16 g, 0.53 mmol, 53%), mp 44–46°C. (Found: C, 47.28; H, 3.68. $C_{12}H_{12}CrO_6$ requires: C, 47.36; H, 3.94%). ν_{max} (Nujol)/cm^{-1} 3400brs (OH), 1964vs, 1865vs, 666s. δ_H (270 MHz) 5.73 (1H, dd, *J*=1.2, 6.2 Hz, ArC(3)*H*), 5.50–5.41 (2H, m, ArC(5,6)*H*), 5.16 (1H, d, *J*=6.9 Hz, O–CH*H*O), 5.06 (1H, d, *J*=6.9 Hz, O–C*H*H–O), 4.96 (1H, dt, *J*=1.2, 6.2 Hz, ArC(4)*H*), 4.64 (1H, dd, *J*=6.7, 13.4 Hz, Ar–CH_2), 4.41 (1H, dd, *J*=5.9, 13.4 Hz, Ar–CH_2), 3.52 (3H, s, O*Me*), 1.97 (1H, t, *J*=6.4 Hz, O*H*); δ_C (75 MHz) 139.1 (Ar*C*(1)–O), 100.3 (Ar*C*(2)–CH$_2$), 95.7 (O–*C*H$_2$–O), 94.4 (Ar*C*(5)H), 93.7 (Ar*C*(3)H), 86.3 (Ar*C*(4)H), 78.6 (Ar*C*(6)H), 59.6 (Ar–*C*H$_2$), 57.1 (O*Me*). *m/z*(EI) 304 (M$^+$), 248 (M$^+$−2×CO), 220 (M$^+$−3×CO, 189 (220− CH$_2$OH), 159 (220−OCH$_2$OMe). Found: M$^+$ 304.0038. $C_{12}H_{12}CrO_6$ requires: 304.0039.

(±)-η^6-[2-Hydroxymethyl-4-triisopropylsiloxymethyl-(methoxymethoxy)benzene]tricarbonylchromium(0) (19b). This complex was prepared from η^6-[4-triisopropylsiloxymethyl(methoxymethoxy)benzene]tricarbonylchromium(0) (**7b**, 300 mg, 0.65 mmol with a paraformaldehyde (5 equiv., 97 mg, 3.24 mmol) quench. The reaction was worked up with water (10 mL). FCC (eluent: 60% ether/hexane) furnished the *complex* (**19b**) as a bright yellow crystalline solid (228 mg, 0.47 mmol, 72%) mp 41–42°C. (Found: C, 54.07; H, 6.55. $C_{22}H_{34}CrO_7Si$ requires: C, 53.86; H, 6.99%). ν_{max} (KBr)/cm^{-1} 3265w. 2944s, 2866s, 1936vs, 1874vs, 1858vs, 1466s, 1240s, 1158s, 989s, 670s, 538m, δ_H (270 MHz) 5.77 (1H, s, ArC(3)*H*), 5.58 (1H, d, *J*=6.7 Hz, ArC(5)*H*), 5.44 (1, H, d, *J*=6.9 Hz, ArC6)*H*), 5.12 (1H, d, *J*=7.0 Hz, O–CH*H*–O), 5.03 (1H, d, *J*=6.6 Hz, O–C*H*H–O), 4.67 (1H, s, Ar–C*H*$_2$), 4.63 (1H, s, Ar–C*H*$_2$), 4.48 (1H, d, *J*=12.9 Hz, Ar–C*H*$_2$–OH), 4.41 (1H, d, *J*=12.9 Hz, Ar–C*H*$_2$–OH), 3.49 (3, H, s, O*Me*), 1.97 (1H, s, O*H*), 1.32–0.83 (21H, m, TIPS; δ_C (68 MHz) 233.0 (*C*O), 138.2 (Ar*C*(1)–O), 105.7 (Ar*C*(4)–CH$_2$), 99.8 (Ar*C*(2)–CH$_2$–OH), 95.9 (O–*C*H$_2$–O), 92.5 (Ar*C*(5)H), 91.4 (Ar*C*(3)H), 78.2 (Ar*C*(6)H), 63.0 (Ar–*C*H$_2$), 59.9 (Ar–*C*H$_2$–OH), 57.1 (O*Me*), 18.0 (TIPS–*Me*), 11.9 (Si–*C*H). *m/z*(CI) 490 (M^+), 473 (M^+−OH), 406 (M^+−3×CO), 337 (473−Cr(CO)$_3$). Found: M^+ 490.1442. $C_{22}H_{34}CrO_7Si$ requires: 490.1478.

(±)-η^6-[2-(Diphenylhydroxymethyl)(methoxymethoxy)-benzene]tricarbonylchromium(0) (20a). This complex was prepared from η^6-(methoxymethoxybenzene)tricarbonylchromium(0) (**7a**, 0.350 g, 1.28 mmol) in ether (25 mL) with a benzophenone (5 equiv., 0.465 g, 6.40 mmol) quench. FCC (eluent: 15% ether/hexane) gave the *complex* (**20a**) as yellow crystals (0.546 g, 1.196 mmol, 94%), mp 164–166°C. (Found: C, 63.27; H, 4.67. $C_{24}H_{20}CrO_6$ requires: C, 63.16; H, 4.42%). ν_{max} (CHCl$_3$)/cm^{-1} 3386m, 1971vs, 1898vs, 1265s. δ_H (270 MHz) 7.23–7.42 (10H, m, Ph*H*), 5.55 (1H, dt, *J*=1.2, 6.3 Hz, ArC(5)*H*), 5.26 (1H, dd, *J*=1.2, 6.8 Hz, ArC(3)*H*), 4.97 (1H, d, *J*=6.9 Hz, O–CH*H*–O) 4.78 (1H, d, *J*=7.2 Hz, O–C*H*H–O), 4.77 (1H, d, *J*=5.9 Hz, ArC(6)*H*), 4.60 (1H, dt, *J*=1.0, 6.3, Hz, ArC(4)*H*), 4.51 (1H, s, O*H*), 3.03 (3H, s, O*Me*); δ_C (68 MHz) 232.5 (*C*O), 146.5 (Ph*C*–C), 142.3 (Ph*C*–C), 138.1 (Ar*C*(1)–O), 128.4, 128.1, 128.0, 127.5, 127.1 (Ph*C*H), 108.95 (Ar*C*(2)–C), 98.2 (Ar*C*(3)H), 94.8 (O–*C*H$_2$–O), 94.7 (Ar*C*(5)H), 82.87 (Ar*C*(4)H), 80.13 (*C*–OH), 76.59 (Ar*C*(6)H), 56.58 (C, O*Me*). *m/z* (FAB$^+$) 456 (M^+), 372 (M^+−3×CO), 355 (M^+−3×CO−OH), 327 (M^+−3×CO−CH$_2$OCH$_3$). Found: M^+ 456.0671. $C_{24}H_{20}CrO_6$ requires 456.0665.

(±)-η^6-[2-(Diphenylhydroxymethyl)-4-triisopropylsiloxymethyl(methoxymethoxy)benzene]tricarbonylchromium(0) (20b). This complex was prepared from η^6-[4-triisopropylsiloxymethyl(methoxymethoxy)benzene]tricarbonylchromium(0) (**7b**, 300 mg, 0.65 mmol) with a quench with a solution of benzophenone (5 equiv., 594 mg, 3.24 mmol) in 3 mL THF. The reaction was worked-up with water (10 mL). FCC (eluent: 10% ether/hexane) furnished the *complex* (**20b**) as a bright yellow crystalline solid (349 mg, 0.55 mmol, 84%) mp 108–109°C. (Found: C, 63.52; H, 6.73. $C_{34}H_{42}CrO_7Si$ requires: C, 63.53; H, 6.59%). ν_{max} (KBr)/cm^{-1} 3557m, 3060w, 2943s, 2865s, 1965vs, 1882vs, 1459s, 1160s, 1086s, 964m, 757s, 701s, 666s, 475m. δ_H (270 MHz) 7.62–7.23 (10H, m, Ph*H*), 5.68 (1H, dd, *J*=1.7, 6.7 Hz, ArC(5)*H*), 5.27 (1H, d, *J*=6.7 Hz, ArC(6)*H*), 4.95 (1H, d, *J*=6.9 Hz, O–CH*H*–O), 4.92 (1H, d, *J*=1.7 Hz, ArC(3)*H*), 4.75 (1H, d, *J*=7.2 Hz, O–C*H*H–O), 4.60 (1H, s, O*H*), 4.23 (2H, s, Ar–C*H*$_2$), 3.02 (3H, s, O*Me*), 1.03–0.95 (21H, m, *TIPS*); δ_C (68 MHz) 232.6 (*C*O), 147.2 (Ar*C*(1)–O), 142.4 (Ph(*C*)–COH), 138.4 (Ph(*C*)–COH), 128.4–127.2 (Ph(*C*)H), 108.9 (Ar*C*(4)–CH$_2$), 102.1 (Ar*C*(2)–COH), 96.7 (Ar*C*(3)H), 94.8 (O–*C*H$_2$–O), 92.8 (Ar*C*(5)H), 80.4 (*C*–OH), 75.9 (Ar*C*(6)H), 63.1 (Ar–*C*H$_2$), 56.5 (O*Me*), 18.0 (TIPS–*Me*), 11.9 (Si–*C*H). *m/z*(FAB$^+$) 642 (M^+), 625 (M^+−OH), 558 (M^+−3×CO), 541 (625−3×CO), 489 (625−Cr(CO)$_3$). Found: M^+ 642.2108. $C_{34}H_{42}CrO_7Si$ requires: 642.2105.

(±)-η^6-[2-(Di-4-methoxyphenylhydroxymethyl)(methoxymethoxy)benzene]tricarbonylchromium(0) (21a). This complex was prepared from η^6-(methoxymethoxybenzene)-tricarbonyl-chromium(0) (**7a**, 0.350 g, 1.28 mmol) in ether (25 mL) with a 4-4′-dimethoxybenzophenone (5 equiv., 1.547 g, 6.40 mmol) quench. FCC (eluent: 50% ether/hexane) gave the *complex* (**21a**) as yellow crystals (0.608 g, 1.177 mmol, 92%), mp 170–172°C. (Found: C, 60.47; H, 4.54. $C_{26}H_{24}CrO_8$ requires: C, 60.47; H, 4.68%). ν_{max} (CHCl$_3$)/cm^{-1} 3423w, 1970vs, 1897vs, 1251s. δ_H (270 MHz) 7.30–7.21 (4H, m, PhC(2,6)*H*), 6.84 (4H, t, *J*=8.5 Hz, PhC(3,5)*H*), 5.55 (1H, t, *J*=6.3 Hz, ArC(5)*H*), 5.27 (1H, d, *J*=6.3 Hz, ArC(3)*H*), 4.97 (1H, d, *J*=7.2 Hz, O–CH*H*–O), 4.79 (1H, d, *J*=7.2 Hz, O–C*H*H–O), 4.78 (1H, d, *J*=6.3 Hz, ArC(6)*H*), 4.61 (1H, t, *J*=6.3 Hz, ArC(4)*H*), 4.50 (1H, s, O*H*), 3.79 (6H, s, PhO*Me*), 3.10 (3H, s, O*Me*); δ_C (68 MHz) 232.7 (*C*O), 159.3, 158.8 (Ph*C*–OMe), 139.0, 138.2 (Ph*C*–C), 135.2 (Ar*C*(1)–O), 129.7, 128.3, 113.2, 113.1 (Ph*C*–H), 109.6 (Ar*C*(2)–C), 98.3 (Ar*C*(3)H), 95.0 (O–*C*H$_2$–O), 94.7 (Ar*C*(5)H), 83.2 (Ar*C*(4)H), 79.7 (*C*–OH), 76.6 (Ar*C*(6)H), 56.8 (O*Me*), 55.3 (PhO*Me*). *m/z* (FAB$^+$) 516 (M^+), 499 (M^+−OH), 432 (M^+−3×CO), 415 (M^+−3×CO−OH). Found: 516.0879. $C_{26}H_{24}CrO_8$ requires: 516.0876.

(±)-η^6-[2-(Phenylhydroxymethyl)methoxymethoxybenzene]tricarbonylchromium(0) (22a). This complex was prepared from η^6-(methoxymethoxy)benzenetricarbonylchromium(0) (**7a**, 0.350 g, 1.28 mmol) in ether (25 mL) with a benzaldehyde (5 equiv., 0.650 mL, 6.40 mmol) quench. FCC (eluent: 80% ether/hexane) gave the *complex* (**22a**) as yellow crystals (0.354 g, 0.931 mmol, 73%), mp 127–129°C. (Found: C, 56.72; H, 4.19. $C_{18}H_{16}CrO_6$ requires: C, 56.85; H, 4.24%). ν_{max} (CHCl$_3$)/cm^{-1} 3597br, 1969vs, 1888vs, 1263s. δ_H (270 MHz) 7.56–7.32 (5H, m, Ph*H*), 5.94 (1H, s, ArC(2)–C–*H*), 5.47 (1H, t, *J*=6.2 Hz, ArC(5)*H*), 5.33 (1H, d, *J*=6.2 Hz, ArC(3)*H*), 5.22 (1H, d, *J*=6.9 Hz, O–CH*H*–O), 5.12 (1H, d, *J*=6.9 Hz, O–C*H*H–O), 5.03 (1H, d, *J*=6.2 Hz, ArC(6)*H*), 4.73 (1H, t, *J*=6.2 Hz, ArC(4)*H*), 3.53 (3H, s, O*Me*); δ_C (68 MHz) 232.5 (*C*O), 140.1 (Ph*C*(1)–C), 139.0 (Ar*C*(1)–O), 128.4, 128.3, 127.0 (Ph*C*H), 103.2 (Ar*C*(2)–C), 96.0 (Ar*C*(3)H), 95.1 (O–*C*H$_2$–O), 94.5 (Ar*C*(5)H), 85.1 (Ar*C*(4)H), 77.2 (Ar*C*(6)H), 70.8 (*C*–OH), 57.3 (*Me*). *m/z* (FAB$^+$) 380 (M^+), 363 (M^+−OH), 296 (M^+−3×CO). Found: M^+ 380.0362. $C_{18}H_{16}CrO_6$ requires: 380.0352.

*Crystal data for (**22a**)*: $C_{18}H_{16}O_6Cr$, M=380.3, monoclinic, space group $P2_1/c$ (no. 14), a=12.488(1), b=13.908(1), c=10.017(1) Å, β=92.05(1)°, V=1738.6(3) Å^3, Z=4, D_c=1.453 g cm^{-3}, μ(Mo-Kα)=6.88 cm^{-1}, F(000)=784, T=293 K; yellow blocks, 0.37×0.35×0.33 mm^3, Siemens P4/PC diffractometer, ω-scans, 3059 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give R_1=0.046, wR_2=0.107 for 2199 independent observed reflections $[|F_o|>4\sigma(|F_o|)$, $2\theta=50^\circ]$ and 218 parameters.

(±)-η^6-[2-(4-Methoxyphenylhydroxymethyl)(methoxymethoxy)benzene]tricarbonylchromium(0) (23a). This complex was prepared from η^6-(methoxymethoxy)benzenetricarbonyl-chromium(0) (**7a**, 0.350 g, 1.28 mmol) in ether (25 mL) with a 4-methoxybenzaldehyde (5 equiv., 0.77 mL, 6.40 mmol) quench. FCC (eluent: 80% ether/hexane) gave the *complex* (**23a**) was obtained as yellow crystals (0.436 g, 1.062 mmol, 83%), mp 118–120°C. (Found: C 55.70, H 4.36. $C_{19}H_{18}CrO_7$ requires: C 55.61, H 4.42%). ν_{max} ($CDCl_3$)/cm^{-1} 3584br, 1969, 1894, 1252. δ_H (270 MHz$_3$) 7.45 (2H, d, *J*=8.7 Hz, Ph*H*), 6.94 (2H, d, *J*=8.7 Hz, Ph*H*), 5.89 (1H, d, *J*=3.5 Hz, ArC(2)–C–*H*), 5.45 (1H, dt, *J*=1.2, 6.4 Hz, ArC(5)*H*), 5.33 (1H, d, *J*=6.4 Hz, ArC(3)*H*), 5.21 (1H, d, *J*=6.9 Hz, O–CH*H*–O), 5.11 (1H, d, *J*=6.9 Hz, O–C*H*H–O), 5.02 (1H, dd, *J*=1.1, 6.4 Hz, ArC(6)*H*), 4.74 (1H, t, *J*=6.4 Hz, ArC(4)*H*), 3.81 (3H, s, PhO*Me*), 3.53 (3H, s, O*Me*), 3.04 (1H, d, *J*=3.5 Hz, –O*H*); δ_C (68 MHz) 232.6 (*C*O), 159.5 (Ph*C*(4)–C), 140.2 (Ph*C*(1)–C), 131.1 (Ar*C*(1)–O), 128.2 (Ph*C*H), 113.8 (Ph*C*H), 103.8 (Ar*C*(2)–C), 96.0 (Ar*C*(3)H), 95.0 (O–*C*H$_2$–O), 94.5 (Ar*C*(5)H), 85.3 (Ar*C*(4)H), 77.3 (Ar*C*(6)H), 70.5 (*C*–OH), 57.3 (O*Me*), 55.4 (PhO*Me*). *m*/*z* (FAB$^+$) 410 (M$^+$), 393 (M$^+$−OH), 326 (M$^+$−3×CO). Found: M$^+$ 410.0458 $C_{19}H_{18}CrO_7$ requires: 410.0473.

(±)-η^6-[2-(2,6-Dimethoxyphenylhydroxymethyl)(methoxymethoxy)benzene]tricarbonylchromium(0) (24a). This complex was prepared from η^6-(methoxymethoxy)benzenetricarbonylchromium(0) (**7a**, 0.350 g, 1.28 mmol) in ether (25 mL) with a 2,6-dimethoxybenzaldehyde (5 equiv., 1.063 g, 6.40 mmol) quench. FCC (eluent: 50% Et$_2$O: 50% hexane) gave the *complex* (**24a**) as yellow crystals (0.452 g, 1.028 mmol, 80%), mp 145–147°C. (Found: C, 54.51; H, 4.48. $C_{20}H_{20}CrO_8$ requires: C, 54.55; H, 4.58%). ν_{max} ($CHCl_3$)/cm^{-1} 3533br, 1965vs, 1884vs, 1233s. δ_H (270 MHz) 7.29 (1H, t, *J*=8.4 Hz, Ph*H*), 6.65 (2H, d, *J*=8.4 Hz, Ph*H*), 6.10 (1H, s, ArC(1)–C–*H*), 5.52 (1H, t, *J*=6.2 Hz, ArC(5)*H*), 5.36 (1H, d, *J*=6.2 Hz, ArC(3)*H*), 5.31 (1H, d, *J*=6.9 Hz, O–CH*H*–O), 5.27 (1H, d, *J*=6.9 Hz, O–C*H*H–O), 5.16 (1H, d, *J*=6.2 Hz, ArC(6)*H*), 4.60 (1H, t, *J*=6.2 Hz, ArC(4)*H*), 3.89 (6H, s, PhO*Me*, 3.56 (3H, s, O*Me*); δ_C (68 MHz) 232.9 (*C*O), 157.9 (Ph*C*–C), 142.0 (Ar*C*(1)–O), 129.7 (Ph*C*H), 114.4 (Ph*C*–O), 104.2, 103.9 (Ph*C*H), 98.8 (Ar*C*(2)–C), 96.3 (Ar*C*(3)H), 95.8 (O–*C*H$_2$–O), 95.5 (Ar*C*(5)H), 83.2 (Ar*C*(4)H), 77.1 (Ar*C*(6)H), 64.3 (*C*–OH), 57.1 (O*Me*), 55.6 (PhO*Me*). *m*/*z* (FAB$^+$): 440 (M$^+$), 423 (M$^+$−OH), 384 (M$^+$−2×CO), 356 (M$^+$−3×CO). Found: M$^+$ 440.0563 $C_{20}H_{20}CrO_8$ requires: 440.0563.

(±)-η^6-{2-[4-Nitrophenyl)hydroxymethyl](methoxymethoxy)benzene}tricarbonylchromium(0) (25a). This complex was prepared from η^6-(methoxymethoxy)benzenetricarbonylchromium(0) (**7a**, 0.350 g, 1.28 mmol) in ether (25 mL) with a 4-nitrobenzaldehyde (5 equiv., 0.963 g, 6.40 mmol) quench. FCC (80% ether/hexane) gave the *complex* (**25a**) as orange crystals (0.375 g, 0.088 mmol, 69%), mp 176–178°C. ν_{max} ($CHCl_3$)/cm^{-1} 3425br, 1973vs, 1902vs, 1384s. δ_C (270 MHz) 8.26–8.32 (2H, m, Ph*H*), 7.78–7.75 (2H, m, Ph*H*), 6.04 (1H, d, *J*=4.1 Hz, ArC(2)–C–*H*), 5.52 (1H, dt, *J*=1.1, 6.4 Hz, ArC(5)*H*), 5.35 (1H, dd, *J*=1.1, 6.4 Hz, ArC(3)*H*), 5.23 (1H, d, *J*=6.9 Hz, O–CH*H*–O), 5.14 (1H, d, *J*=6.9 Hz, O–C*H*H–O), 4.99 (1H, dd, *J*=1.1, 6.4 Hz, ArC(6)*H*), 4.76 (1H, dt, *J*=1.1, 6.4 Hz, ArC(4)*H*), 3.54 (3H, s, O*Me*), 3.09 (1H, d, *J*=4.1 Hz, O*H*); δ_C (68 MHz) 232.6 (*C*O), 146.3 (Ph*C*(4)–N), 139.9 (Ph*C*(1)–C), 132.8 (Ar*C*(1)–O), 127.2 (Ph*C*H), 123.9 (PH*C*H), 105.8 (Ar*C*(2)–C), 95.6 (O–*C*H$_2$–O), 94.2 (Ar*C*(3)H), 91.4 (Ar*C*(5)H), 86.0 (Ar*C*(4)H), 77.4 (Ar*C*(6)H), 67.9 (*C*–OH), 57.2 (O*Me*). *m*/*z* (FAB$^+$) 435 (M$^+$), 341 (M$^+$−3×CO). Found: M$^+$ 425.0203. $C_{18}H_{15}CrNO_8$ requires: 425.0202.

(±)-η^6-[2-(*N*,*N*-Dimethylaminomethyl)-4-triisopropylsiloxymethyl(methoxymethoxy)benzene]tricarbonylchromium(0) (26b). This complex was prepared from η^6-[4-triisopropylsiloxymethyl(methoxymethoxy)benzene]-tricarbonylchromium(0) (**7b**, 300 mg, 0.65 mmol) with a quench with Eschenmoser salt (300 mg, 1.62 mmol). The reaction was worked up with water (10 mL). FCC (eluent: 30% ether/hexane) furnished the *complex* (**26b**), as a yellow oil (209 mg, 0.40 mmol, 61%). ν_{max} (neat)/cm^{-1} 3101w, 2944s, 2866s, 2775m, 1962vs, 1881vs, 1464s, 1197s, 1082s, 977s, 882s, 667s, 532m. δ_H (270 MHz) 5.69 (1H, d, *J*=1.7 Hz, ArC(3)*H*), 5.53 (1H, dd, *J*=1.5, 6.9 Hz, ArC(5)*H*), 5.43 (1H, d, *J*=6.9 Hz, ArC(6)*H*), 5.08 (1H, d, *J*=6.9 Hz, O–CH*H*–O), 5.00 (1H, d, *J*=6.9 Hz, O–C*H*H–O), 4.47 (1H, s, Ar–C*H*$_2$), 4.43 (1H, s, Ar–C*H*$_2$), 3.47 (3H, s, O*Me*), 3.04 (1H, s, C*H*$_2$–N), 2.99 (1H, s, Ar–C*H*$_2$–N), 2.31 (6H, s, N(*Me*)$_2$), 1.17–1.03 (21H, m, *TIPS*); δ_C (68 MHz) 233.3 (*C*O), 138.3 (Ar*C*(1)–O), 106.3 (Ar*C*(4)–CH$_2$), 97.8 (Ar*C*(2)–CH$_2$–N), 95.8 (Ar*C*(3)H), 94.5 (O–*C*H$_2$–O), 91.3 (Ar*C*(5)H), 78.4 (Ar*C*(6)H), 63.1 (Ar–*C*H$_2$), 57.1 (*C*H$_2$–N), 56.9 (O*Me*), 45.7 (N(*Me*)$_2$), 18.0 (TIPS–*Me*), 11.9 (Si–*C*H). *m*/*z* (FAB$^+$) 518 (M$^+$+H), 490 (M$^+$−CO), 433 (M$^+$−3×CO), 403, 389, 162, 58. Found, M$^+$+H: 518.2035. $C_{21}H_{40}CrNO_6Si$ requires: 518.2030.

(±)-η^6-[2-(*N*-Phenyl-α-aminobenzyl)(methoxymethoxy)benzene]tricarbonylchromium(0) (27a). This complex was prepared from η^6-(methoxymethoxy)benzenetricarbonylchromium(0) (**7a**, 0.350 g, 1.28 mmol) in ether (25 mL) with a *N*-benzylideneaniline (5 equiv., 1.159 g, 6.40 mmol) quench. FCC (eluent: 25–30% ether/hexane) gave the *complex* (**27a**) as yellow crystals (0.555 g, 1.22 mmol, 95%), mp 162–164°C. (Found: C, 63.57; H, 4.70; N, 3.06. $C_{24}H_{21}CrNO_5$ requires: C, 63.29; H, 4.65; N, 3.08%). ν_{max} ($CHCl_3$)/cm^{-1} 3423, 1969, 1894, 1248. δ_H (270 MHz) 7.32–7.62 (5H, m, C–PhC*H*), 7.14–6.53 (5H, m, *N*–Ph*H*), 5.61 (1H, s, N–*H*), 5.50 (1H, t, *J*=6.3 Hz, ArC(5)*H*), 5.29 (1H, d, *J*=6.3 Hz, ArC(3)*H*), 5.25 (1H, d, *J*=6.3 Hz, ArC(6)*H*), 5.16 (1H, d, *J*=7.1 Hz, O–CH*H*–O), 5.02 (1H, d, *J*=7.1 Hz, O–C*H*H–O), 4.72 (1H, t, *J*=6.3 Hz, ArC(4)*H*), 4.21 (1H, s, ArC(2)–C*H*), 3.41 (3H, s, O*Me*); δ_C (68 MHz) 232.5 (*C*O), 147.2 (Ph*C*(1)–N), 140.0 (Ph*C*(1)–C), 139.6 (Ar*C*(1)–O), 129.2, 128.7, 127.8 (Ph*C*–C), 128.0, 118.2, 113.7 (Ph*C*–N), 103.7 (Ar*C*(2)–C), 96.1 (Ar*C*(3)H), 95.4 (O–*C*H$_2$–O), 95.0 (Ar*C*(5)H), 84.3 (Ar*C*(4)H), 76.4(Ar*C*(6)H), 57.1 (ArC(2)–*C*–H), 56.5 (O*Me*). *m*/*z* (FAB$^+$) 455 (M$^+$), 371 (M$^+$−3×CO). Found: M$^+$ 455.0831. $C_{24}H_{21}CrNO_5$ requires: 455.0825.

(±)-η^6-[-2-Iodo(methoxymethoxy)benzene]tricarbonylchromium(0) (28a). This complex was prepared from η^6-(methoxymethoxy)benzenetricarbonylchromium(0) (**7a**, 0.27 g, 1.00 mmol) in ether (10 mL) with a quench of a solution of 1,2-diiodoethane (1.2 equiv., 0.34 g, 1.20 mmol) in ether (1 mL). The reaction was worked-up with saturated aqueous sodium thiosulphate (5 mL) followed immediately with FCC (eluent: 5–10% ether/hexane) and recrystallisation (from DCM/hexane) to furnish the *complex* (**28a**) as bright yellow crystals (0.33 g, 0.83 mmol, 83%), mp 107–109°C. ν_{max} (Nujol)/cm^{-1} 2923vs, 1953vs, 1893vs, 1086m, 723w. δ_H (300 MHz) 5.92 (1H, dd, *J*=0.99, 6.18 Hz, ArC(3)*H*), 5.48–5.39 (2H, m, ArC(5,6)*H*), 5.21 (1H, d, *J*=6.93 Hz, O–CH*H*–O), 5.10 (1H, d, *J*=6.93 Hz, O–C*H*H–O), 4.82 (1H, dt, *J*=1.24, 5.56 Hz, ArC(4)*H*), 3.56 (3H, s, O*Me*); δ_C (75 MHz) 138.8 (Ar*C*(1)–O), 102.8 (Ar*C*(3)H), 96.2 (O–*C*H$_2$–O), 92.8 (Ar*C*(5)H), 87.6 (Ar*C*(4)H), 80.6 (Ar*C*(2)–I), 77.9 (Ar*C*(6)H), 57.2 (O*Me*). *m*/*z*(EI) 400 (M^+), 368 (M^+-MeOH), 316 ($M^+-3\times$CO), 264 ($M^+-Cr(CO)_3$), 52 (Cr), 28 (CO). Found: M^+ 399.8906. $C_{11}H_9CrIO_5$ requires: 399.8900.

(±)-η^6-[2-(Iodo(4-triisopropylsiloxymethyl)(methoxymethoxy)benzene]tricarbonylchromium(0) (28b). This complex was prepared from η^6-[(4-triisopropylsiloxymethyl)(methoxymethoxy)benzene]tricarbonylchromium(0) (**7b**, 2 g, 4.32 mmol) with an overnight quench with a solution of 1,2-diiodoethane (1.2 equiv., 1.5 g, 5.32 mmol) in 4 mL THF. The reaction was worked-up with saturated aqueous sodium thiosulphate (20 mL). FCC (eluent: 1% ether/hexane) furnished the *complex* (**28b**) as a bright yellow crystalline solid (2.40 g, 4.07 mmol, 95%). mp 62–63°C. (Found: C, 43.45; H, 5.25. $C_{21}H_{31}CrIO_6Si$ requires: C, 43.01; H, 5.33%). ν_{max} (KBr)/cm^{-1} 3106w, 3074w, 2943s, 2864s, 1969vs, 1893vs, 1865vs, 1466s, 1083s, 970s, 801m, 619s, 531m. δ_H (270 MHz) 5.99 (1H, s, ArC(3)*H*), 5.45–5.43 (2H, m, ArC(5,6)*H*), 5.16 (1H, d, *J*=6.9 Hz, O–CH*H*–O), 5.07 (1H, d, *J*=6.9 Hz, O–C*H*H–O), 4.44 (1H, s, Ar–C*H*$_2$), 4.43 (1H, s, Ar–C*H*$_2$), 3.52 (3H, s, O*Me*), 1.16–0.97 (21H, m, *TIPS*); δ_C (68 MHz) 232.5 (*C*O), 138.1 (Ar*C*(1)–O), 107.2 (Ar*C*(4)–CH$_2$), 100.9 (Ar*C*(3)H), 96.4 (O–*C*H$_2$–O), 90.7 (Ar*C*(5)H), 80.2 (Ar*C*(2)–I), 77.5 (Ar*C*(6)H), 62.6 (Ar–*C*H$_2$), 57.2 (O*Me*), 18.0 (TIPS–*Me*), 11.9 (Si–*C*H). *m*/*z*(CI) 604 (M^++NH_4), 587 (M^++H), 586 (M^+), 460 (M^++H-I). Found: M^+ 586.0343. $C_{21}H_{31}CrIO_6Si$ requires: 586.0339.

(±)-η^6-[2-Formyl(ethoxymethoxy)benzene]tricarbonylchromium(0) (29a). This complex was prepared from η^6-(ethoxymethoxybenzene)tricarbonylchromium(0) (**8a**, 0.369 g, 1.28 mmol) in ether (25 mL) with a DMF (5 equiv., 0.53 mL, 6.40 mmol) quench. FCC (eluent: 50% ether/hexane) gave the *complex* (**29a**) as bright red crystals (0.332 g, 1.049 mmol, 82%), mp 76–78°C. (Found: C, 49.55; H, 3.81. $C_{13}H_{12}CrO_6$ requires: C, 49.38; H, 3.82%). ν_{max} (CHCl$_3$)/cm^{-1} 1984vs, 1917vs, 1682s, 1265s. δ_H (270 MHz) 10.03 (1H, s, C*H*O), 6.21 (1H, dd, *J*=1.5, 6.4 Hz, ArC(3)*H*), 5.80 (1H, ddd, *J*=1.5, 6.4, 6.9 Hz, ArC(5)*H*), 5.40 (1H, d, *J*=6.9 Hz, ArC(6)*H*), 5.28 (1H, d, *J*=7.2 Hz, O–CH*H*–O), 5.19 (1H, d, *J*=7.2 Hz, O–C*H*H–O), 4.98 (1H, t, *J*=6.4 Hz, ArC(4)*H*), 3.76 (2H, q, *J*=7.1 Hz, O–C*H*$_2$), 1.24 (3H, t, *J*=7.1 Hz, *Me*); δ_C (68 MHz) 230.7 (*C*O), 185.5 (*C*HO), 143.8 (Ar*C*(1)–O), 95.2 (O–*C*H$_2$–O), 94.4 (Ar*C*(3)H), 92.2 (Ar*C*(5)H), 84.6 (Ar*C*(4)H), 86.2 (Ar*C*(2)–C), 76.4 (Ar*C*(6)H), 66.0 (O–*C*H$_2$), 15.0 (*Me*). *m*/*z*: (FAB$^+$) 316 (M^+), 232 ($M^+-3\times$CO). Found: M^+ 316.0038. $C_{13}H_{12}CrO_6$ requires 316.0039.

(±)-η^6-[2-Formyl-4-triisopropylsiloxymethyl(ethoxymethoxy)benzene]tricarbonylchromium(0) (29b). This complex was prepared from η^6-[4-(triisopropylsiloxymethyl)(ethoxymethoxy)benzene]tricarbonylchromium(0) (**8b**, 308 mg, 0.65 mmol) in ether (10 mL) with a DMF (2 equiv., 0.13 mL, 1.3. mmol) quench. The reaction was worked-up with water (10 mL). FCC (eluent: 20% ether/hexane) furnished the *complex* (**29b**) as a bright orange crystalline solid (200 mg, 0.40 mmol, 62%) mp 72–74°C. (Found: C, 55.09; H, 7.00. $C_{23}H_{34}CrO_7Si$ requires: C, 54.96; H, 6.82%). ν_{max} (KBr)/cm^{-1} 2943s, 2866s, 1988vs, 1913vs, 1896vs, 1677s, 1468s, 1236s, 1084s, 948s, 665s, 518m. δ_H (270 MHz) 10.04 (1H, s, C*H*O), 6.26 (1H, d, *J*=2.0 Hz, ArC(3)*H*), 5.96 (1H, dd, *J*=2.0, 6.9 Hz, ArC(5)*H*), 5.41 (1H, d, *J*=6.9 Hz, ArC(6)*H*), 5.27 (1H, d, *J*=7.4 Hz, O–CH*H*–O), 5.17 (1H, d, *J*=7.4 Hz, O–C*H*H–O), 4.48 (1H, d, *J*=12.9 Hz, Ar–C*H*$_2$), 4.42 (1H, d, *J*=12.9 Hz, Ar–C*H*$_2$), 3.75 (2H, q, *J*=7.2 Hz, O–C*H*$_2$), 1.24 (3H, t, *J*=7.2 Hz, *Me*), 1.23–1.01 (21H, m, *TIPS*); δ_C (68 MHz) 230.8 (*C*O), 185.7 (*C*HO), 141.1 (Ar*C*(1)–O), 104.0 (Ar*C*(4)–CH$_2$), 94.4 (O–*C*H$_2$–O), 93.4 (Ar*C*(3)H), 90.0 (Ar*C*(5)H), 86.2 (Ar*C*(2)–CHO), 75.7 (Ar*C*(6)H), 65.9 (Ar–*C*H$_2$), 62.8 (O–*C*H$_2$), 18.0 (TIPS–*Me*), 14.9 (*Me*), 11.9 (Si–*C*H). *m*/*z* (CI) 520 (M^++NH_4), 503 (M^++H), 418 ($M^+-3\times$CO), 381, 367 (503$-$Cr(CO)$_3$), 337, 329, 271. Found: M^++H 503.1551. $C_{23}H_{35}CrO_7Si$ requires: 503.1557.

(±)-η^6-[2-(Diphenylhydroxymethyl)(ethoxymethoxy)benzene]tricarbonylchromium(0) (30a). This complex was prepared from η^6-[(ethoxymethoxy)benzene]tricarbonylchromium(0) (**8a**, 0.369 g, 1.28 mmol) in ether (25 mL) with a benzophenone (5 equiv., 1.16 g, 6.40 mmol) quench. FCC (eluent: 15% ether/hexane) gave the *complex* (**30a**) as yellow crystals (0.492 g, 1.048 mmol, 82%), mp 168–170°C (Found: C, 63.97; H, 4.78. $C_{25}H_{22}CrO_6$ requires: C, 63.83; H, 4.71%). ν_{max} (CHCl$_3$)/cm^{-1} 3151 br, 1971vs, 1898vs, 1261s. δ_H (270 MHz) 7.39–7.24 (10H, m, Ph*H*), 5.56 (1H, t, *J*=6.3 Hz, ArC(5)*H*), 5.30 (1H, d, *J*=6.3 Hz, ArC(3)*H*), 4.99 (1H, d, *J*=7.1 Hz, O–CH*H*–O), 4.85 (1H, d, *J*=7.1 Hz, O–C*H*H–O) 4.76 (1H, d, *J*=6.3 Hz, ArC(6)*H*), 4.61 (1H, t, *J*=6.3 Hz, ArC(4)*H*), 4.61 (1H, s, O*H*), 3.31 (1H, m, O–C*H*$_2$), 3.08 (1H, m, O–C*H*$_2$), 1.01 (3H, t, *J*=7.1 Hz, *Me*); δ_C (68 MHz) 232.6 (*C*O), 146.6, 142.42 (Ph*C*–C), 138.3 (Ar*C*(1)–O), 128.5, 128.2, 128.0, 127.9, 127.5, 127.1 (Ph*C*–H), 109.0 (Ar*C*(2)–C), 98.3 (Ar*C*(3)H), 94.8 (O–*C*H$_2$–O), 93.4 (Ar*C*(5)H), 83.0 (Ar*C*(4)H), 80.2 (*C*–OH), 76.6 (Ar*C*(6)H), 65.2 (O–*C*H$_2$), 14.8 (*Me*). *m*/*z* (FAB$^+$) 470 (M^+), 453 (M^+-OH), 386 ($M^+-3\times$CO). Found: M^+ 470.0818. $C_{25}H_{22}CrO_6$ requires: 470.0821.

(±)-η^6-[2-(Diphenylhydroxymethyl)-4-triisopropylsiloxymethyl(ethoxymethoxy)benzene]tricarbonylchromium(0) (30b). This complex was prepared from η^6-[4-triisopropylsiloxymethyl(ethoxymethoxy)benzene]tricarbonylchromium(0) (**8b**, 308 mg, 0.65 mmol) with a quench of benzophenone (5 equiv., 594 mg, 3.24 mmol) in THF

(3 mL). The reaction was worked up with water (10 mL). FCC (eluent: 10% ether/hexane) furnished the *complex* (**30b**) as a bright yellow crystalline solid (390 mg, 0.55 mmol, 92%) mp 82–84°C. (Found: C, 64.18; H, 6.87. $C_{35}H_{44}CrO_7Si$ requires: C, 64.00; H, 6.75%). ν_{max} (KBr)/cm^{-1} 3555w, 3086w, 3063w, 3026w, 2943m, 2865m, 1958vs, 1882vs, 1460m, 1101s, 667s, 481m. δ_H (270 MHz) 7.42–7.25 (10H, m, Ph*H*), 5.67 (1H, dd, *J*=1.7, 6.9 Hz, ArC(5)*H*), 5.30 (1H, d, *J*=6.9 Hz, ArC(6)*H*), 4.96 (1H, d, *J*=7.2 Hz, O–CH*H*–O), 4.91 (1H, d, *J*=1.7 Hz, ArC(3)*H*), 4.83 (1H, d, *J*=7.2 Hz, O–C*H*H–O), 4.64 (1H, s, O*H*), 4.24 (2H, s, Ar–C*H*$_2$), 3.34–3.25 (1H, m, O–C*H*$_2$), 3.12–3.04 (1H, m, O–C*H*$_2$), 1.06–0.93 (24H, m, *TIPS*, *Me*); δ_C (68 MHz) 232.6 (*C*O), 146.8 (Ar*C*(1)–O), 142.4 (Ph(*C*)–COH), 137.7 (Ph(*C*)–COH), 128.4–127.2 (Ph(*C*)H), 108.6 (Ar*C*(4)–CH$_2$), 102.1 (Ar*C*(2)–COH), 96.7 (Ar*C*(3)H), 93.5 (O–*C*H$_2$–O), 92.8 (Ar*C*(5)H), 80.4 (*C*–OH), 76.1 (Ar*C*(6)H), 65.1 (O–*C*H$_2$), 63.1 (Ar–*C*H$_2$), 18.0 (TIPS–*Me*), 14.8 (*Me*), 11.9 (Si–*C*H). *m/z* (CI) 674 (M$^+$+NH$_4$), 656 (M$^+$), 639 (M$^+$+H−OH), 572 (M$^+$−3×CO), 503 (639−Cr(CO)$_3$), 483, 444, 271, 183, 105, 59, 52 (Cr). Found: M$^+$ 656.2272. $C_{35}H_{44}CrO_7Si$ requires 656.2261.

(±)-η^6-[2-(Di-4-methoxyphenylhydroxymethyl)(ethoxymethoxy)benzene]tricarbonylchromium(0) (31a). This complex was prepared from η^6-(ethoxymethoxy)benzenetricarbonylchromium(0) (**8a**, 0.369 g, 1.28 mmol) in ether (25 mL) with a 4,4′-dimethoxybenzophenone (5 equiv., 1.239 g, 6.40 mmol) quench. FCC (eluent: 50% ether/hexane) gave the *complex* (**31a**) as yellow crystals (0.542 g, 1.022 mmol, 80%), mp 132–134°C. (Found: C, 61.03; H, 5.03. $C_{27}H_{26}CrO_8$ requires: C, 61.13; H, 4.94%). ν_{max} (CHCl$_3$)/cm^{-1} 3399 br, 1971vs, 1896vs, 1250s. δ_H (270 MHz) 7.30–7.20 (4H, m, Ph*H*), 6.80–6.87 (4H, t, *J*=8.7 Hz, Ph*H*), 5.55 (1H, t, *J*=6.3 Hz, ArC(5)*H*), 5.30 (1H, d, *J*=6.3 Hz, ArC(3)*H*), 4.99 (1H, d, *J*=7.4 Hz, O–CH*H*–O), 4.86 (1H, d, *J*=7.4 Hz, O–C*H*H–O), 4.77 (1H, d, *J*=6.3 Hz, ArC(6)*H*), 4.61 (1H, t, *J*=6.3 Hz, ArC(4)*H*), 4.53 (1H, s, O*H*), 3.79 (6H, s, PhO*Me*), 3.37 (1H, m, O–C*H*$_2$), 3.17 (1H, m, O–C*H*$_2$), 1.05 (3H, t, *J*=7.2, *Me*); δ_C (68 MHz) 232.7 (*C*O), 159.3, 158.8 (Ph*C*–OMe), 138.7, 135.8 (Ph*C*–C), 132.3 (Ar*C*(1)–O), 129.7, 128.3, 127.8, 113.9, 113.7 (Ph*C*–H), 109.6 (Ar*C*(2)–C), 98.3 (Ar*C*(3)H), 94.8 (O–*C*H$_2$–O), 93.6 (Ar*C*(5)H), 83.2 (Ar*C*(4)H), 79.8 (*C*–OH), 77.0 (Ar*C*(6)H), 65.2 (O–*C*H$_2$), 55.6, 56.4 (Ph–O*Me*), 14.9 (*Me*). *m/z* (FAB$^+$) 530 (M$^+$), 513 (M$^+$−OH), 446 (M$^+$−3×CO). Found: M$^+$ 530.1042. $C_{27}H_{26}CrO_8$ requires: 530.1033.

(±)-η^6-[2-Formyl-4-triisopropylsiloxymethyl(2-methoxyethoxy)benzene]tricarbonylchromium(0) (32b). This complex was prepared from η^6-[4-triisopropylsiloxymethyl (2-methoxyethoxy)benzene]tricarbonylchromium(0) (**9b**, 308 mg, 0.65 mmol) in ether (10 mL) with over night DMF (1.7 equiv., 0.08 mL, 1.11 mmol) quench. The reaction was worked up with water (10 mL). FCC (eluent: 20% ether/hexane) furnished the *meta*-substituted *complex* (**32c**) as a red crystalline solid. (60 mg, 0.12 mmol, 18%), mp 38–40°C. ν_{max} (KBr)/cm^{-1} 2944s, 2866s, 1971vs, 1888vs, 1687s, 1543s, 1276s, 1127s, 653s. δ_H (270 MHz) 9.81 (1H, s, C*H*O), 5.73 (1H, d, *J*=7.2 Hz, ArC(5)*H*), 5.64 (1H, d, *J*=2.2 Hz, ArC(2)*H*), 5.53 (1H, dd, *J*=2.2, 7.2 Hz, ArC(6)*H*), 4.94 (1H, d, *J*=13.9 Hz, Ar–C*H*$_2$), 4.73 (1H, d, *J*=13.9 Hz, Ar–C*H*$_2$), 4.05–3.95 (2H, m, O–C*H*$_2$), 3.67 (2H, t, *J*=4.7 Hz, C*H*$_2$–O), 3.40 (3H, s, O*Me*), 1.20–1.01 (21H, m, *TIPS*); δ_C (68 MHz) 231.4 (*C*O), 189.5 (*C*HO), 138.8 (ArC(1)–O), 108.9 (Ar*C*(4)–CH$_2$), 93.5 (Ar*C*(3)–CHO), 90.9 (Ar*C*(5)H), 82.1 (Ar*C*(2)H), 78.8 (Ar*C*(6)H), 70.4 (*C*H$_2$–O), 68.8 (O–*C*H$_2$), 61.2(Ar–*C*H$_2$), 59.9 (O*Me*), 18.0 (TIPS–*Me*), 11.9 (Si–*C*H). *m/z*(FAB$^+$) 502 (M$^+$), 367, 346, 329, 210, 52. Found: M$^+$ 502.1484. $C_{23}H_{34}CrO_7Si$ requires: 502.1478.

Further elution gave the *complex* (**32b**) as a bright orange crystalline solid (240 mg, 0.48 mmol, 72%) mp 42–44°C. (Found: C, 55.02; H, 6.99. $C_{23}H_{34}CrO_7Si$ requires: C, 54.96; H, 6.82%). ν_{max} (KBr)/cm^{-1} 2943m, 2866m, 1971vs, 1931s, 1891vs, 1666s, 1539m, 1463m, 1354m, 1239m, 1118s, 655s, 520w. δ_H (270 MHz) 10.07 (1H, s, C*H*O), 6.29 (1H, d, *J*=1.7 Hz, ArC(3)*H*), 5.97 (1H, dd, *J*=1.7, 6.9 Hz, ArC(5)*H*), 5.07 (1H, d, *J*=6.9 Hz, ArC(6)*H*), 4.49 (1H, d, *J*=12.6 Hz, Ar–C*H*$_2$), 4.42 (1H, d, *J*=12.6 Hz, Ar–C*H*$_2$), 4.21–4.03 (2H, m, O–C*H*$_2$), 3.72–3.61 (2H, m, C*H*$_2$–O), 3.41 (3H, s, O*Me*), 1.23–1.01 (21H, m, *TIPS*); δ_C (68 MHz) 230.8 (*C*O), 185.6 (*C*HO), 144.9 (Ar*C*(1)–O), 104.0 (Ar*C*(4)–CH$_2$), 93.2 (Ar*C*(3)H), 90.2 (Ar*C*(5)H), 85.4 (Ar*C*(2)–CHO), 72.7 (Ar*C*(6)H), 70.3 (*C*H$_2$–O), 68.9 (O–*C*H$_2$), 62.7 (Ar–*C*H$_2$), 59.9 (O*Me*), 18.0 (TIPS–*Me*), 11.9 (Si–*C*H). *m/z* (FAB$^+$) 503 (M$^+$+H), 446 (M$^+$−2×CO), 418 (M$^+$−3×CO), 390, 375, 359, 347, 277. Found: M$^+$ 502.1476. $C_{23}H_{34}CrO_7Si$ requires: 502.1478.

(+)-η^6-[2-(Diphenylhydroxymethyl)-4-triisopropylsiloxymethyl(2-methoxyethoxy)benzene]tricarbonylchromium(0) (33b). This complex was prepared from η^6-[4-triisopropylsiloxymethyl(2-methoxyethoxy)benzene]tricarbonylchromium(0) (**9b**, 308 mg, 0.65 mmol with a quench of benzophenone (5 equiv., 594 mg, 3.24 mmol) in THF (3 mL). The reaction was worked up with water (10 mL). FCC (eluent: 10% ether/hexane) furnished the *complex* (**33b**) as a bright yellow crystalline solid (301 mg, 0.47 mmol, 72%) mp 36–38°C. (Found: C, 64.20; H, 6.58. $C_{35}H_{44}CrO_7Si$ requires: C, 64.00; H, 6.75%). ν_{max} (KBr)/cm^{-1} 3490m, 3060w, 3026w, 2943s, 2865s, 1964vs, 1889vs, 1447s, 1240m, 1100s, 667s, 537m. δ_H (270 MHz$_3$) 7.37–7.23 (10H, m, Ph*H*), 5.61 (1H, dd, *J*=1.7, 4.0 Hz, ArC(5)*H*), 5.27 (1H, d, *J*=4.0 Hz, ArC(6)*H*), 4.86 (1H, d, *J*=6.7 Hz, O*H*), 4.86 (1H, d, *J*=1.7 Hz, ArC(3)*H*), 4.27 (1H, d, *J*=12.6 Hz, Ar–C*H*$_2$–O), 4.21 (1H, d, *J*=12.6 Hz, Ar–C*H*$_2$), 3.95- 3.79 (2H, m, O–C*H*$_2$), 3.47–3.28 (2H, m, C*H*$_2$–O), 3,3 (3H, s, O*Me*), 1.19–0.84 (21H, m, TIPS); δ_C (68 MHz) 232.5 (*C*O), 152.2 (Ar*C*(1)–O), 147.4 (Ph(*C*)–COH), 137.4 (Ph(*C*)–COH), 128.4–127.1 (Ph(*C*)H), 108.4 (Ar*C*(4)–CH$_2$), 101.9 (Ar*C*(2)–COH), 96.8 (Ar*C*(3)H), 91.9 (Ar*C*(5)H), 76.5 (*C*–OH), 72.8 (Ar*C*(6)H), 69.7 (*C*H$_2$–O), 68.7(O–*C*H$_2$), 63.1 (Ar–*C*H$_2$), 58.9 (OMe), 18.0 (TIPS–*Me*), 11.9 (Si–*C*H). *m/z* (CI) 674 (M$^+$+NH$_4$), 639 (M$^+$+H-OH), 572 (M$^+$−3×CO), 520 (M$^+$−Cr(CO)$_3$), 503 (639−Cr(CO)$_3$), 477, 429, 331, 301, 200. Found: M$^+$+NH$_4$ 674.2601. $C_{35}H_{48}CrNO_7Si$ requires 674.2605.

(+)-η^6-[2-Formyl-4-triisopropylsiloxymethyl(methoxyethoxymethoxy)benzene]tricarbonylchromium(0) (34b). This complex was prepared from η^6-[4-triisopropylsiloxymethyl(methoxy-ethoxymethoxy)benzene]tricarbonylchromium(0) (**10b**, 328 mg, 0.65 mmol) with a quench with DMF (2 equiv., 0.10 mL, 1.30 mmol). FCC (eluent: 50% ether/hexane) furnished the *complex* (**34b**) as a red oil (254 mg, 0.46 mmol, 73%). (Found: C, 53.81, H, 6.78. $C_{24}H_{36}CrO_8Si$ requires: C, 54.12; H, 6.81%). ν_{max} (neat)/cm^{-1} 2945s, 2868s, 1978vs, 1903vs, 1682s, 1466s, 1109s, 660s. δ_H (270 MHz) 10.03 (1H, s, C*H*O), 6.26 (1H, d, *J*=1.7 Hz, ArC(3)*H*), 5.95 (1H, dd, *J*=1.7, 6.9 Hz, ArC(S)*H*), 5.42 (1H, d, *J*=6.9 Hz, ArC(6)*H*), 5.31 (1H, d, *J*=7.2 Hz, O–CH*H*–O), 5,22 (1H, d, *J*=7.2 Hz, O–C*H*H–O), 4.47 (1H, d, *J*=12.6 Hz, Ar–C*H*$_2$), 4.40 (1H, d, *J*=12.6 Hz, Ar–C*H*$_2$), 3.88–3.83 (2H, M, O–C*H*$_2$), 3.58–3.53 (2H, m, *C*H$_2$–O), 3.37 (3H, s, O*Me*), 1. 17–0.97 (21H, m, *TIPS*); δ_C (68 MHz) 230.8 (*C*O), 185.6 (*C*HO), 143.1 (Ar*C*(1)–O), 104.3 (Ar*C*(4)–CH$_2$), 94.7 (O–*C*H$_2$–O), 93.4 (Ar*C*(3)H), 89.9 (Ar*C*(5)H), 85.2 (Ar*C*(2)–CHO), 75.9 (Ar*C*(6)H), 7–1.4 (*C*H$_2$–O), 69.2 (O–*C*H$_2$), 62.8 (Ar–*C*H$_2$), 59.1 (O*Me*), 18.0 (TIPS–*Me*), 11.9 (Si–*C*H). *m/z* (CI) 550 (M^++NH$_4$), 533 (M^++H), 504 ($M^{+\cdot}$CO), 448 ($M^+-3\times$CO), 414, 280, 182. Found: M^+ 532.1584. $C_{24}H_{36}CrO_8Si$ requires: 532.1585.

(+)-η^6-[2-Trimethylsilyl-*N*-Boc-aniline)tricarbonylchromium(0) (35a). This complex was prepared from η^6-(*N*-Boc-aniline)tricarbonylchromium(0) (**11a**, 0.32 g, 1.00 mmol) with a chlorotrimethylsilane (5 equiv., 0.63 mL, 5.00 mmol) quench. FCC (eluent: 2–5% ether/hexane) and recrystallisation (from DCM/hexane) furnished the *complex* (**35a**) as bright yellow crystals (0.24 g, 0.77 mmol, 77%), mp 83–85°C. ν_{max} (Nujol)/cm^{-1} 3456w (NH), 2924vs, 1948vs, 1878vs, 1749s, 1456s, 629s. δ_H (270 MHz) 6.03–6.00 (2H, m, N*H*, ArC(5)*H*), 5.50 (1H, dd, *J*=1.2, 6.5 Hz, ArC(6)*H*), 4.90 (1H, t, *J*=6.2 Hz, ArC(4)*H*), 1.49 (9H, s, C*Me*$_3$), 0.40 (9H, s, *TMS*); δ_C (75 MHz) 152.6 (*C*OO), 121.8 (Ar*C*(1)–N), 100.2 (Ar*C*(3)H), 96.2 (Ar*C*(5)H), 89.4 (Ar*C*(2)–Si), 86.8 (Ar*C*(4)H), 85.8 (Ar*C*(6)H), 8.19 (*C*Me$_3$), 28.1 (*Me*), −0.2 (*TMS*). *m/z*(CI) 419 (M^++86.8 (Ar*C*(4)H), 85.8 (Ar*C*(6)H), 8.19 (*C*Me$_3$), 28.1 (*Me*), −0.2 (*TMS*). *m/z*(CI) 419 (M^++NH$_4$), 402(M^++H), 346 (402−2×CO), 328 (M^+−O^{t}Bu, M^+−TMS), 227 (328−TMS, 328−O^{t}Bu), 193 (328+H−Cr(CO)$_3$). Found: M^+ 402.0832. $C_{17}H_{24}CrNO_5Si$ requires 402.0829.

Acknowledgements

We thank the Engineering and Physical Sciences Research Council and the Government of Singapore for financial support.

References

1. Solladié-Cavallo, A. Chiral arene chromium carbonyl complexes in asymmetric synthesis. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI: London, 1989; Vol. 1, p 99.
2. Davies, S. G.; McCarthy, T. D. In *Comprehensive Organometallic Chemistry II*, Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, 1995; Vol. 12, p 1039.
3. Uemura, M. Tricarbonyl(η^6-arene)chromium complexes in organic synthesis. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI: London, 1991; Vol. 2, p 195.
4. Semmelhack, M. F. Transition Metal Arene Complexes: Ring Lithiation; In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, 1995; Vol. 12, p 1017.
5. Widdowson, D. A. *Phil. Trans. R. Soc. London, A* **1988**, *326*, 595.
6. Dickens, P. J.; Gilday, J. P.; Negri, J. T.; Widdowson, D. A. *Pure Appl. Chem.* **1990**, *62*, 575.
7. Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1990**, *28*, 136.
8. Semmelhack, M. F.; Bisaha, J.; Czarny, M. *J. Am. Chem. Soc.* **1979**, *101*, 768.
9. Gray, M.; Tinkl, M.; Snieckus, V. Main Group Organometallics in Organic Synthesis: Lithium; In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, 1995; Vol. 11, p 1.
10. Gould, S. J.; Eisenberg, R. L. *J. Org. Chem.* **1991**, *56*, 6666.
11. Gschwend, H. W.; Rodriguez, H. R. *Heteroatom-Facilitated Lithiations*; In *Organic Reactions*; Dauben, W. G., Ed.; Wiley: New York, 1979; Vol. 26, p 1.
12. Gilday, J. P.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1235.
13. Gilday, J. P.; Widdowson, D. A. *Tetrahedron Lett.* **1986**, *27*, 5525.
14. Ewin, R. A.; MacLeod, A. M.; Price, D. A.; Simpkins, N. S.; Watt, A. P. *J. Chem. Soc. Perkin Trans. 1* **1997**, 4021.
15. Uemura, M. *Tetrahedron Lett.* **1994**, *35*, 1909.
16. Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*; Wiley: Chichester, 1986.
17. Goff, D. A.; Harris, R. N.; Bottaro, J. C.; Bedford, C. P. *J. Org. Chem.* **1986**, *51*, 4711.
18. Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.
19. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
20. Schaper, U. A. *Synthesis* **1981**, *10*, 794.
21. Gonzalez, A. G.; Rosa, R. D. L.; Trujillo, J. M. *Tetrahedron* **1986**, *42*, 3899.
22. Li, R.; Hansch, C.; Kaufman, B. *J. Med. Chem.* **1982**, *25*, 435.
23. Rigby, J. H.; Qatar, M. *J. Org. Chem.* **1989**, *54*, 5852.
24. Bolnsack, H. *Reichst. Aromen* **1965**, *15*, 1365.
25. Takatori, K.; Nishihara, M.; Nishiyama, Y.; Kajiwara, M. *Tetrahedron* **1998**, *54*, 15861.
26. Bennett, F.; Knight, D. W.; Fenton, G. J. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1543.