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Journal of Organometallic Chemistry 658 (2002) 21–33

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Chlorotrimethylsilane-mediated Michael addition reactions of chiral benzylic anions derived from η^6-chromiumtricarbonyl complexes

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Received 26 April 2002; accepted 9 May 2002

Abstract

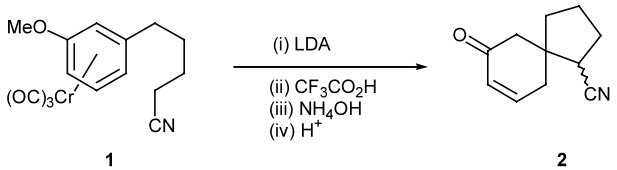
The Michael addition of chiral organolithiums, resulting from benzylic metallation of certain η^6-chromiumtricarbonyl complexes, to α,β-unsaturated ketones and esters, is strongly influenced by the presence of chlorotrimethylsilane. In most cases yields of Michael adducts are greatly improved in the presence of Me_3SiCl. Some further transformations of the Michael adducts were carried out, including a ring expansion process of a cyclohexanone derivative and a SmI_2 mediated cyclisation of a complex bearing an acyclic ketone appendage.

Keywords: Asymmetric synthesis; η^6-Chromiumtricarbonyl; Michael addition; Chlorotrimethylsilane; Chiral lithium amide

1. Introduction

Over 20 years ago, seminal work by the research group of Semmelhack established the scope of nucleophilic substitution reactions of η^6-chromiumtricarbonyl complexes [1]. Particularly interesting in the context of natural product synthesis were the classic examples of intramolecular addition reactions leading to various kinds of annulated products, e.g. Scheme 1, [2].

There is sustained interest in such reactions and also in cyclisations of chromium arenes that lead to polycyclic product complexes, for example using palladium chemistry and reductive radical processes [3,4]. A notable example is the SmI_2 mediated cyclisation of complex **4** described by Schmalz and co-workers (Scheme 2) [5].



1 2

Scheme 1.

In this case the ketone intermediate **4** was prepared by Michael addition of the benzylic anion derived from **3** to α-silyl-MVK, followed by de-blocking of protected positions on the aromatic nucleus.

It might be expected that the use of Michael additions of such benzylic anions would be a popular way to assemble the types of side-chain functionalised complexes required for further cyclisation and elaboration [6]. In fact, this type of reaction is extremely rare, with only a few examples related to the transformation of **3** into **4** having emerged from the research group of Schmalz.

The use of benzylic anions derived from chromium arenes for Michael reactions appears even more attractive bearing in mind the availability of highly enantioenriched complexes through chiral lithium amide base methodology, e.g. Scheme 3, [7].

Here the asymmetric metallation of **6** to give a number of products of structure **7** can be effected with very high selectivity by use of the bis-lithium amide **8** however, no Michael additions were described.

The key objective of our research was to establish a general procedure for the asymmetric Michael addition of benzylic anions derived from chromium arene complexes. Our results indicate that this is not generally

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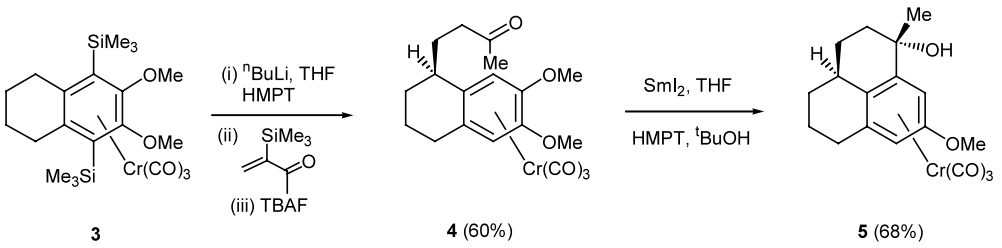
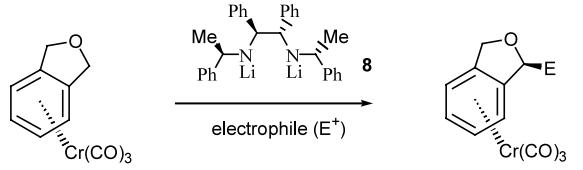


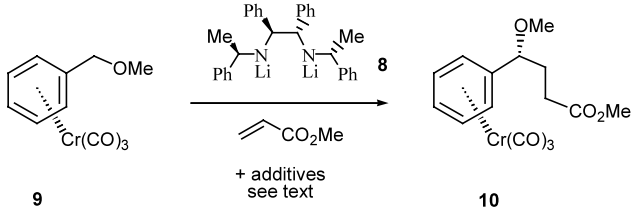
3 4 (60%) 5 (68%)

Scheme 2.



6 7 (up to 99% ee)

Scheme 3.



9 10

Scheme 4.

possible under standard conditions and we have developed a novel procedure, which employs chlorotrimethylsilane as additive, that enables good yields of chiral Michael adducts to be obtained in many cases.

2. Results and discussion

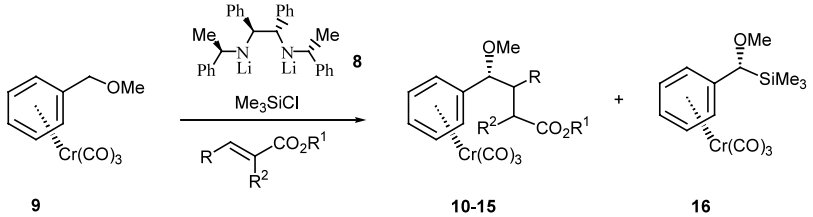
We chose to start our investigation with reactions of benzylic ether complex **9** since Gibson and co-workers had previously demonstrated the highly enantioselective substitution of this system using our bis-lithium amide base **8** [8]. Initial test reactions were carried out by metallating the methoxymethyl substituted complex **9** and then adding methyl acrylate, as shown in Scheme 4.

Under standard conditions, using THF as solvent at −78 °C, we obtained none of the desired Michael product **10**. Instead the starting material was consumed in what we assume is a polymerisation process due to uncontrolled Michael additions. Even in the presence of solvent additives such as DMPU we were unable to achieve yields of more than about 20% of the Michael adduct.

At this point we decided to investigate the use of Me_3SiCl as an additive. We reasoned that C-silylation of the initial metallated complex might be relatively slow at low temperature, allowing Michael addition to take place to give an intermediate enolate that would be rapidly O-silylated. In this way we hoped to control the polymerisation problems that dogged the initial test reactions. This idea proved to work reasonably well in a number of cases, as shown in Table 1.

Michael adducts from simple acrylates, entries 1–3, were formed in good yield, except in the case of *tert*-

Table 1
Michael additions of complex **9**



9 10-15 16

Entry	R	R^1	R^2	Compound (%)	16 (%)
1	H	Me	H	**10** (77)	< 5
2	H	Et	H	**11** (69)	< 5
3	H	^{n}Bu	H	**12** (55)	10
4	H	^{t}Bu	H	**13** (7)	21
5	Me	Me	H	**14** (45)	14
6	H	Me	Me	**15** (7)	20
7	H	^{t}Bu	Me	–	17

butyl acrylate (entry 4), which gave mainly the unwanted C-silylated complex **16**. This product was also formed if the relative proportion of Me_3SiCl in the mixture was increased above the optimal level of 1.5 equivalents with respect to the starting complex, or if the amount of Michael acceptor was decreased from about three equivalents with respect to the starting complex. This undesired mode of reaction also appeared significant in cases where the Michael addition might be expected to be slowed due to additional substituents on the Michael acceptor. In this respect the reaction proved more sensitive to additional α-substitution than β-substitution in the Michael acceptor, methyl crotonate giving acceptable results but methylmethacrylate giving a very low yield (entries 5 and 6, respectively). In the case of *tert*-butyl methacrylate the desired mode of reaction was shut down completely. The yields given in the table do not take into account variable quantities of unreacted starting complex that were also recovered from the reactions.

We believe that the role of Me_3SiCl is to minimise polymerisation by trapping of the intermediate enolate as a silyl ketene acetal, although we were unable to isolate these sensitive compounds in the above cases. In the unsuccessful reactions it appears that additional substitution around the α-position of the acceptor hinders enolate silylation, thus allowing uncontrolled polymerisation to occur.

All of the products **10**–**15** were obtained in optically active form and in the case of methyl acrylate we were able to demonstrate that the adduct **10** was formed with an ee of 96%, in accord with expectations from previous work. The absolute stereochemistry shown was assigned by analogy with the results of Gibson and co-workers [8].

A range of other substrates was employed in this work, with varying levels of success. Cyclohexenone was found to give good results, the ketone adduct **18** being isolated as a 1:1 mixture of diastereoisomers in 71% yield following a mildly acidic work-up procedure (Scheme 5).

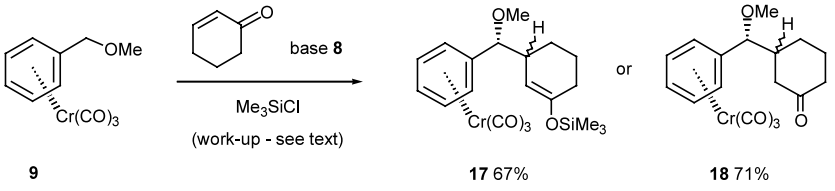
By changing to a mildly basic work-up procedure we were also able to isolate the enol silane **17** in good yield, accompanied by only traces of ketone **18**.

Methyl vinyl ketone proved an especially problematic substrate, and under the standard conditions used for acrylate derivatives we obtained only the 1,2-addition product **19** (Scheme 6).

However, by including HMPA as co-solvent, in addition to Me_3SiCl, we were able to minimise this problem and obtain a respectable yield of the desired adduct **20**. Some reactions were also run using the enantiomer of base **8**, and gave similar results.

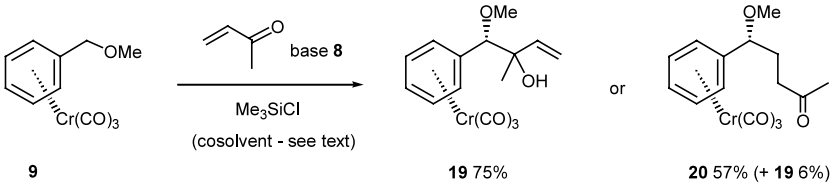
Acrylonitrile was another acceptor that gave none of the desired adduct when Michael addition of **9** was attempted in THF alone. By inclusion of Me_3SiCl the reaction worked well, to give a mixture of adducts **21** and **22** (Scheme 7).

Some other well-known Michael acceptors, including phenyl vinyl sulfone and *N*,*N*-dimethylacrylamide, did not furnish the desired adducts.



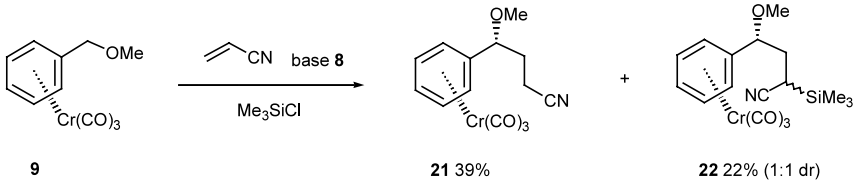
9 **17** 67% **18** 71%

Scheme 5.



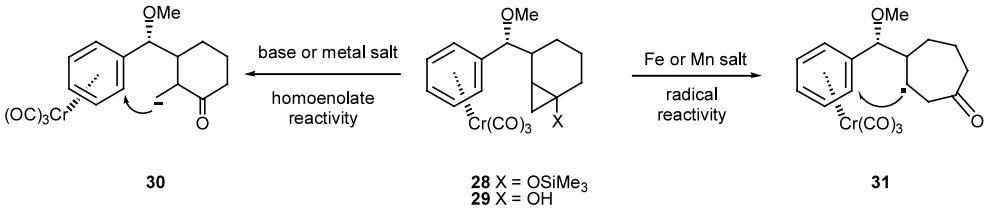
9 **19** 75% **20** 57% (+ **19** 6%)

Scheme 6.



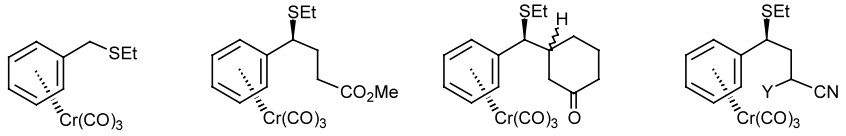
9 **21** 39% **22** 22% (1:1 dr)

Scheme 7.



Scheme 8.

A more limited survey was also carried out of Michael reactions using a closely related sulfur containing complex as starting material, i.e. conversion of **23** into each of the adducts **24**–**27**.



product. Reaction of hydroxycyclopropane **29** under several types of conditions known to generate reactive homoenolate species of the type **30** required (e.g. ^{t}BuOK in Et_2O–HMPA, or AgF in EtOH–MeCN), [11] gave no annulated products, but instead only low yields of methylcyclohexanone derivatives. Related efforts aimed at cyclopropane ring opening with electrophilic metal salts such as $Hg(OAc)_2$, followed by transmetallation to cuprate species were also unrewarding [12].

In these cases the stereochemical sense of the induction originating from the chiral base reaction is assumed to be reversed, compared to the methoxy-substituted complexes, as was previously demonstrated for alkylations [8]. The level of enantioselectivity seen in the synthesis of **24** was also somewhat reduced compared with that for **10**, which is also in line with previous work. Otherwise, the reactions are broadly similar to those described in more detail above.

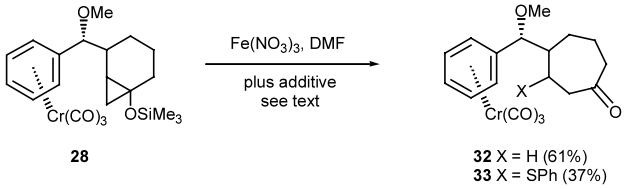
Having established a novel protocol for the asymmetric Michael addition of metallated complexes to a number of acceptors, we were interested to see if cyclised products could be obtained using the types of procedure outlined in Schemes 1 and 2.

Unfortunately, compared to their higher homologues, nitriles such as **21** and **26** are known not to undergo cyclisation onto the aromatic nucleus [9]. Similarly, the acrylate and enone adducts are not suitable for enolate mediated cyclisations, based on previous findings. However, the availability of enol silane **17** suggested the possibility of forming the derived silyloxy or hydroxy cyclopropane derivatives, which would provide hitherto unexplored possibilities for ring closure via homoenolate or radical intermediates (Scheme 8).

Cyclopropanation of **17** under standard conditions provided straightforward access to both cyclopropanes **28** and **29** [10]. This process appeared to be diastereoselective, each of the enol silanes in the diastereomeric mixture of **17** giving rise to one major cyclopropane

The idea to try radical type additions to chromium arene complexes is far less well precedented than the use of conventional nucleophiles, although a few examples, e.g. Scheme 2, are known [13]. We had in mind the reaction of **28** or **29** with iron or manganese salts, which is known to effect regioselective cyclopropane cleavage to give an intermediate that reacts as the β-keto radical **31** [14]. The intermediate radical is capable of cyclising onto an unsaturated appendage, as demonstrated by the groups of Booker-Milburn and Narasaka.

We attempted this type of reaction and observed no annulation onto the aromatic nucleus although, by means of consolation, we were able to demonstrate the conversion of **28** into the cycloheptanone derivatives **32** and **33** (Scheme 9).



Scheme 9.

Using $Fe(NO_3)_3$ in combination with 1,4-cyclohexadiene gave a good yield of **32**, whereas a more modest yield of the sulfide **33** was obtained by including PhSSPh in the reaction mixture [15]. The survival of the chromium complexes under these fairly oxidising conditions is especially notable. This type of overall ring-expansion, first described using $FeCl_3$ by the group of Saegusa, [16] has not been previously demonstrated on this type of complex as far as we are aware, and may prove useful in other synthetic work.

The most apparent use for the complexes having ketonic side chains, e.g. **18**, **20**, **25** and **32**, prepared by our new method is in the type of SmI_2 mediated reductive process outlined in Scheme 2. Since our ketones are rather different to structure **4** and its relatives we decided to conduct a test reaction starting with ketone **20** (the opposite enantiomer to that shown in Scheme 6 was used) (Scheme 10).

Reaction of **20** with SmI_2, under similar conditions to those employed by Schmalz resulted in the formation of the two bicyclic dienes **34** and **35** as the major products. These compounds presumably arise by a similar sequence of events to that seen in the previous work, and in fact Schmalz observed the formation of one diene product in his work [5a]. Stereoselective intramolecular addition of an initially formed ketyl radical generates a 17-electron η^5-cyclohexadienyl radical complex, which is then reduced by further electron transfer from SmI_2 to give the more familiar anionic complex. Protonation and decomplexation then leads to the products. The absence of a ring oxygen in our system, compared to that shown in Scheme 2, means that elimination from the anionic intermediate in order to regenerate a η^6-complex cannot occur, and the dienyl addition products result instead. The structures of the two products are fully supported by nOe studies, which demonstrated that the compounds are regioisomeric rather than stereoisomeric. The formation of more than one isomeric diene is understandable as the result of well established equilibration processes involving very rapid hydride migrations in the intermediate diene complex [17].

In conclusion, we have demonstrated a new protocol for the Michael addition of metallated η^6-chromium-tricarbonyl complexes to a range of acceptors, including unsaturated esters, ketones and a nitrile. In addition, we have shown that an iron-mediated ring expansion protocol is compatible with a typical chromium arene.

The novel asymmetric Michael reactions described above constitute another useful addition to the synthetic repertoire of chromium arenes and the products available via this route should find many applications in metal templated synthesis using these types of complex.

3. Experimental

3.1. General details

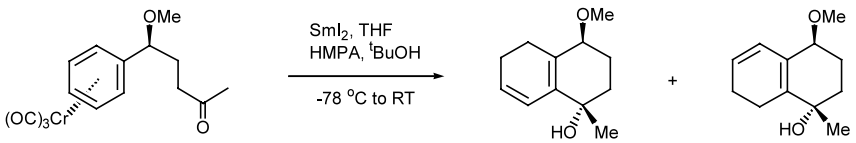
M.p.s were recorded on a Stuart Scientific SMP3 apparatus and are uncorrected. Microanalytical data were obtained on a Perkin–Elmer 240B elemental analyser. IR spectra were recorded on a Perkin–Elmer 1600 or a Nicolet Protégé 460 FTIR machine and are reported in cm^{-1}.

NMR spectra were recorded on Bruker WP250, AM400, AV400, DRX500, JEOL FX 270, or Varian Unity Inova 300 machines, using $CDCl_3$ as solvent at 298 K. Chemical shifts are given in ppm downfield from Me_4Si, using either the Me_4Si or residual protic solvent as an internal standard. *J* values are recorded in Hz and rounded to the nearest half integer value. The following abbreviations apply: app., apparent; b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, double doublet etc. Where necessary, proton and carbon assignments were assisted with ^1H COSY, HMQC, DEPT or nOe sequences. The chemical shifts of multiplets corresponding to a single proton are quoted as a point, representing the centre of the multiplet. Where the signals for two or more protons overlap, a range is quoted.

Mass spectra were obtained using a VG Micron Autospec or VG Micromass 70E spectrometer, using electron impact (EI), chemical ionisation (CI), electrospray (ES), or fast atom bombardment (FAB), using *meta*-nitrobenzyl alcohol as the matrix.

Optical rotations were recorded using a JASCO DIP370 digital polarimeter. Enantiomeric excesses were determined by high performance liquid chromatography (HPLC) using either Chiralcel OD or OJ columns at temperatures ranging from 20 to 40 °C as stated. Detection was by UV at the stated frequency and data was processed using an HP-3D Dos chemstation.

All reaction mixture temperatures refer to values recorded for an external cooling bath. Room tempera-



20 **34** 20% **35** 16%

Scheme 10.

ture (r.t.) implies temperatures in the range 20–25 °C. Reaction progress was monitored by thin layer chromatography (TLC) performed on Merck Kieselgel 60 F_{254} aluminium backed plates, which were visualised by a combination of ultraviolet light and $KMnO_4$. Flash column chromatography was performed using Merck Kieselgel 60 (230–440 mesh), in the indicated solvent. Degassing of solvent was undertaken by bubbling Ar through the solvent.

Organic solvents and reagents were dried by distillation from the following as required: THF, Et_2O (Na/benzophenone ketyl); MeOH (Mg); DMF ($MgSO_4$); Me_3SiCl (CaH_2). Petrol refers to petroleum ether (b.p. 40–60 °C), which was distilled before use. Michael acceptors were distilled from $CaCl_2$ prior to use. All other solvents and reagents were used as received from commercial suppliers unless otherwise stated. Compounds prepared and used subsequently without further purification were judged to be of suitable purity by NMR analysis.

3.2. Typical procedure for Me_3SiCl-mediated Michael additions

3.2.1. (+)-Tricarbonyl[η^6-1-{methyl(1*R*)-1-methoxybutanoate}-benzene]chromium(0) (**10**)

A solution of chiral bis-lithium amide **8** was prepared by addition of ^{n}BuLi (1.6 M in C_6H_{14}, 0.97 ml, 1.55 mmol) to a stirred solution of the corresponding chiral diamine (326 mg, 0.78 mmol) in THF (10 ml) at −78 °C under an atmosphere of nitrogen. The resultant purple solution was allowed to warm to r.t. and then recooled to −78 °C prior to cannula addition of a solution of LiCl (33 mg, 0.78 mmol) in THF (5 ml). After 5 min a precooled (−78 °C) solution of complex **9** (200 mg, 0.78 mmol) in THF (5 ml) was added dropwise via a cannula (2 min) giving an orange solution. This was stirred at −78 °C for 1 h, after which time a solution of methyl acrylate (0.21 ml, 2.33 mmol) and Me_3SiCl (0.15 ml, 1.16 mmol) in THF (1 ml) was added resulting in an immediate lightening of colour to pale yellow. After 10 min at −78 °C, saturated aq. $NaHCO_3$ solution (1 ml) was added and the reaction mixture was allowed to warm to r.t. prior to extraction with Et_2O (3 × 5 ml). The combined organics were washed with water (10 ml), brine (10 ml), dried ($MgSO_4$) and concentrated in vacuo to give a yellow oil. Flash chromatography (SiO_2; Et_2O–petrol, 1:4), afforded the *title complex* **10** (206 mg, 77%) as a yellow oil, $[\alpha]_D^{25}$ +63 (*c* 0.87 in $CHCl_3$); ν_{max} ($CHCl_3$, cm^{-1}) 2954, 2259, 1972 and 1897 (C≡O), 1732 (C=O), 1108; δ_H (300 MHz; $CDCl_3$) 1.92 (1H, td, *J* 14.0, 7.5, 2-H*H*), 2.11 (1H, m, 2-*H*H), 2.38 (2H, dd, *J* 16.5, 7.5, 3-H*H*), 2.49 (1H, dd, *J* 16.5, 7.5, 3-*H*H), 3.49 (3H, s, OCH_3), 3.67 (3H, s, CO_2CH_3), 3.95 (1H, dd, *J* 7.5, 3.5, 1-H), 5.23–5.37 (4H, m, 2 × H *ortho*, 2 × H *meta*), 5.55 (1H, bd, *J* 6.0, H *para*); δ_C (125 MHz; $CDCl_3$) 29.5 (C-3), 32.9 (C-2), 51.5 (CO_2CH_3), 58.3 ($CHOCH_3$), 79.7 (C-1), 91.1 (ArCH), 91.2 (ArCH), 91.3 (ArCH), 91.4 (ArCH), 93.1 (ArCH), 111.3 (ArC), 173.3 (C=O), 232.7 (C≡O); *m*/*z* (FAB) 344 ([M^+], 2%), 288 ([M−2CO], 3), 260 ([M−3CO], 11), 154 (100), 136 (66) (Found [M^+]: 344.0360. $C_{15}H_{16}CrO_6$ requires: 344.0352). Complex **10** was separated on a Chiracel OD column using a C_6H_{14}–IPA (95:5) eluent at 30 °C with a flow rate of 1.0 ml min^{-1}, detecting at 215 nm. The enantiomeric excess was determined as 96% with retention times of 28.0 (major enantiomer) and 31.3 min (minor enantiomer). Also isolated was α-silyl complex **16** (13 mg, 5%) whose spectroscopic data were in accordance with the previously reported literature [18].

3.2.2. (+)-Tricarbonyl[η^6-1-{ethyl(1*R*)-1-methoxybutanoate}-benzene]chromium(0) (**11**)

The general procedure was employed, starting with complex **9** (200 mg, 0.78 mmol). Purification of the crude product by flash chromatography (SiO_2; Et_2O–petrol, 1:4), afforded the *title complex* **11** (191 mg, 69%) as a yellow oil, $[\alpha]_D^{25}$ +58 (*c* 1.00 in $CHCl_3$); ν_{max} ($CHCl_3$, cm^{-1}) 2983, 2935, 2829, 1977 and 1909 and 1873 (C≡O), 1726 (C=O), 1107; δ_H (500 MHz; $CDCl_3$) 1.27 (3H, t, *J* 7.0, OCH_2CH_3), 1.92 (1H, td, *J* 14.0, 7.5, 2-H*H*), 2.10 (1H, m, 2-*H*H), 2.32–2.51 (2H, m, 3-H), 3.51 (3H, s, OCH_3), 3.96 (1H, dd, *J* 7.5, 3.0, 1-H), 4.14 (2H, q, *J* 7.0, OCH_2CH_3), 5.20–5.43 (4H, m, 2 × H *ortho*, 2 × H *meta*), 5.57 (1H, d, *J* 5.5, H *para*); δ_C (125 MHz; $CDCl_3$) 14.2 (CH_3), 29.9 (C-3), 33.1 (C-2), 58.5 (OCH_3), 60.5 (OCH_2CH_3), 79.8 (C-1), 91.1 (ArCH), 91.3 (ArCH), 91.4 (ArCH), 91.5 (ArCH), 93.2 (ArCH), 111.5 (ArC), 173.0 (C=O), 232.8 (C≡O); *m*/*z* (FAB) 358 ([M^+], 15%), 302 ([M−2CO], 24%), 274 ([M−3CO], 25), 191 (72), 117 (100) (Found [M^+]: 358.0514. $C_{16}H_{18}CrO_6$ requires: 358.0508). Also isolated were the α-silyl complex **16** (5 mg, 3%) and starting complex **9** (55 mg, 28%).

3.2.3. (+)-Tricarbonyl[η^6-1-{^{n}butyl(1*R*)-1-methoxybutanoate}-benzene]chromium(0) (**12**)

The general procedure was employed, starting with complex **9** (200 mg, 0.78 mmol). Purification of the crude product by flash chromatography (SiO_2; Et_2O–petrol, 1:4), afforded the *title complex* **12** (164 mg, 55%) as a yellow oil, $[\alpha]_D^{25}$ +45 (*c* 1.20 in $CHCl_3$); ν_{max} ($CHCl_3$, cm^{-1}) 2962, 2935, 2875, 2837, 1973 and 1891 (C≡O), 1726 (C=O), 1109; δ_H (500 MHz; $CDCl_3$) 0.94 (3H, t, *J* 7.5, CH_3), 1.38 (2H, app. sextet, *J* 7.5, 7-H), 1.16 (2H, app. quintet, *J* 7.5, 6.5, 6-H), 1.92 (1H, td, *J* 14.0, 8.0, 2-H*H*), 2.10 (1H, m, 2-*H*H), 2.13–2.51 (2H, m, 3-H), 3.50 (3H, s, OCH_3), 3.95 (1H, dd, *J* 8.0, 4.0, 1-H), 4.08 (2H, t, *J* 6.5, 5-H), 5.26–5.35 (4H, m, 2 × H *ortho*, 2 × H *meta*), 5.56 (1H, bd, *J* 6.0, H *para*); δ_C (125 MHz; $CDCl_3$) 13.6 (CH_3), 19.1 (C-7), 29.9 (C-3), 30.6

(C-6), 33.2 (C-2), 58.5 (OCH_3), 64.4 (C-5), 79.9 (C-1), 91.0 (ArCH), 91.1 (ArCH), 91.2 (ArCH), 91.3 (ArCH), 93.0 (ArCH), 111.3 (ArC), 173.1 (C=O), 232.7 (C≡O); *m/z* (EI) 386 ([M^+], 4%), 330 ([M−2CO], 27), 302 ([M−3CO], 100) (Found [M^+]: 386.0831. $C_{18}H_{22}CrO_6$ requires: 386.0821). Also isolated were α-silyl complex **16** (26 mg, 10%) and starting complex **9** (35 mg, 18%).

3.2.4. (+)-Tricarbonyl[η^6-1-{^{t}butyl(1*R*)-1-methoxybutanoate}-benzene]chromium(0) (**13**)

The general procedure was employed, starting with complex **9** (200 mg, 0.78 mmol). Purification of the crude product by flash chromatography (SiO_2; Et_2O–petrol, 3:7), afforded the *title complex* **13** (21 mg, 7%) as an orange oil, $[\alpha]_D^{28}$ +43 (*c* 1.00 in $CHCl_3$); ν_{max} ($CHCl_3$, cm^{-1}) 2980, 1971 and 1898 (C≡O), 1719 (C=O), 1105; δ_H (400 MHz; $CDCl_3$) 1.46 (9H, s, $OC(CH_3)_3$), 1.80–1.97 (1H, m, 2-H*H*), 2.00–2.12 (1H, m, 2-*H*H), 2.21–2.43 (2H, m, 3-H), 3.51 (3H, s, OCH_3), 3.96 (1H, dd, *J* 8.0, 4.0, 1-H), 5.20–5.38 (4H, m, 2 × H *ortho*, 2 × H *meta*), 5.57 (1H, bd, *J* 5.5, H *para*); δ_C (125 MHz; $CDCl_3$) 28.2 (CH_3), 32.0 (C-3), 33.5 (C-2), 56.8 (OCH_3), 58.7 ($OC(CH_3)_3$), 80.0 (C-1), 90.7 (ArCH), 91.3 (ArCH), 91.5 (ArCH), 93.1 (ArCH), 111.7 (ArC), 174.3 (C=O), 232.9 (C≡O); *m/z* (EI) 358 ([M^+ −CO], 5%), 302 ([M^+ −3CO], 61%), 274 (100). Also isolated were α-silyl complex **16** (55 mg, 21%) and starting complex **9** (48 mg, 24%).

3.2.5. (+)-Tricarbonyl[η^6-1-{methyl(1*R*)-1-methoxy-2-methylbutanoate}-benzene]chromium(0) (**14**)

The general procedure was employed, starting with complex **9** (200 mg, 0.78 mmol). Purification of the crude product by flash chromatography (SiO_2; Et_2O–petrol, 3:7), afforded the *title complex* **14** as an inseparable 1:1 mixture of two diastereoisomers (124 mg, 45%) as a yellow oil, $[\alpha]_D^{24}$ +48 (*c* 0.90 in $CHCl_3$); ν_{max} ($CHCl_3$, cm^{-1}) 2953, 2832, 1975 and 1907 (C≡O), 1731 (C=O), 1099; δ_H (500 MHz; $CDCl_3$) 1.03 (3H, d, *J* 6.0, CH_3), 2.18 (1H, dd, *J* 15.0, 8.0, 3-H*H*), 2.27 (1H, m, 2-H), 2.36 (1H, dd, *J* 15.0, 5.0, 3-*H*H), 3.57 (3H, s, OCH_3), 3.63 (3H, s, CO_2CH_3), 3.76 (1H, d, *J* 4.3, 1-H), 5.20–5.42 (4H, m, 2 × H *ortho*, 2 × H *meta*), 5.61 (1H, d, *J* 5.0, H *para*); δ_C (125 MHz; $CDCl_3$) 17.1 (CH_3), 35.9 (C-3), 38.0 (C-2), 51.7 (CO_2CH_3), 59.9 (OCH_3), 84.5 (C-1), 90.7 (ArCH), 90.8 (ArCH), 91.4 (ArCH), 92.4 (ArCH), 93.8 (ArCH), 109.6 (ArC), 173.2 (C=O), 232.9 (C≡O); *m/z* (EI) 358 ([M^+], 14%), 330 ([M−2CO], 16), 302 ([M−2CO], 89), 114 (100) (Found [M^+]: 358.0499. $C_{16}H_{18}CrO_6$ requires: 358.0508). Also isolated were α-silyl complex **16** (35 mg, 14%) and starting complex **9** (30 mg, 15%).

3.2.6. (+)-Tricarbonyl[η^6-1-{methyl(1*R*)-1-methoxy-3-methylbutanoate}-benzene]chromium(0) (**15**)

The general procedure was employed, starting with complex **9** (200 mg, 0.78 mmol). Purification of the crude product by flash chromatography (SiO_2; Et_2O–petrol, 3:7), afforded the *title complex* **15** as an inseparable 1:1 mixture of two diastereoisomers (21 mg, 7%) as a yellow oil, $[\alpha]_D^{21}$ +67 (*c* 1.02 in $CHCl_3$); ν_{max} ($CHCl_3$, cm^{-1}) 2935, 1966 and 1906 and 1874 (C≡O), 1730 (C=O), 1106; δ_H (400 MHz; $CDCl_3$) both diastereoisomers: 1.19 (1.5H, d, *J* 7.0, CH_3), 1.22 (1.5H, d, *J* 7.0, CH_3), 1.71 (1H, m, 2-H*H*), 2.13 (1H, m, 2-*H*H), 2.66 (0.5H, dd, *J* 7.0, 6.5, 3-H), 2.77 (0.5H, ddd, *J* 10.5, 7.0, 3.5, 3-H), 3.48 (3H, s, CO_2CH_3), 3.66 (1.5H, s, OCH_3), 3.73 (1.5H, s, OCH_3), 3.92 (1H, m, 1-H), 5.20–5.43 (4H, m, 2 × H *ortho*, 2 × H *meta*), 5.58 (1H, bs, H *para*); δ_C (125 MHz; $CDCl_3$) both diastereoisomers: 17.5, 18.2 (CH_3), 36.1, 36.7 (C-3), 42.3, 43.1 (C-2), 51.9 (CO_2CH_3), 58.5, 58.9 (OCH_3), 79.5, 79.6 (C-1), 91.1 (ArCH), 91.2 (ArCH), 91.4 (ArCH), 91.6 (ArCH), 93.4 (ArCH), 110.8, 111.5 (ArC), 176.7 (CO_2CH_3), 232.9 (C≡O); *m/z* (FAB) 358 ([M^+], 7%), 302 ([M−2CO], 26), 274 ([M−3CO], 75), 121 (100) (Found [M^+]: 358.0505. $C_{16}H_{18}CrO_6$ requires: 358.0508). Also isolated was α-silyl complex **16** (52 mg, 20%).

3.2.7. (+)-Tricarbonyl[η^6-1-{(1*R*)-1-methoxy-1-(4-cyclohexen-2-yl-4-trimethylsilyloxy)methyl}benzene]chromium(0) (**17**) and (+)-tricarbonyl[η^6-1-{(1*R*)-1-methoxy-1-(4-cyclohexanone-2-yl)methyl}benzene]chromium(0) (**18**)

The general procedure was employed, starting with complex **9** (200 mg, 0.78 mmol), except that Et_3N (6 ml) was added to the mixture immediately before quenching with saturated aq. $NaHCO_3$ solution. Purification of the crude product by flash chromatography (SiO_2; Et_2O–petrol, 1:20), afforded *title complex* **17** as an inseparable 2.5:1 mixture of two diastereoisomers (221 mg, 67%) as a yellow oil, $[\alpha]_D^{25}$ +53 (*c* 0.54 in $CHCl_3$); (Found: C, 56.61; H, 6.17. $C_{20}H_{26}CrO_5Si$ requires: C, 56.32; H, 6.14%); ν_{max} ($CHCl_3$, cm^{-1}) 2934, 2864, 1971 and 1891 (C≡O), 1663 (C=C), 1254, 847; δ_H (500 MHz; $CDCl_3$) major diastereoisomer: 0.18 (9H, s, $Si(CH_3)_3$), 1.40–1.80 (4H, m, 2 × CH_2), 1.86–2.00 (2H, m, CH_2), 2.49 (1H, m, 2-H), 3.57 (3H, s, OCH_3), 3.63 (1H, d, *J* 5.5, 1-H), 4.79 (1H, bs, 3-H), 5.21 (2H, s, 2 × ArH), 5.29 (1H, m, ArH), 5.38 (1H, m, ArH), 5.62 (1H, app. t, *J* 6.5, ArH), minor diastereoisomer: 0.17 (9H, s, $Si(CH_3)_3$), 1.40–1.68 (4H, m, 2 × CH_2), 1.95 (2H, bs, CH_2), 1.84–2.02 (1H, m, 2-H), 3.57 (3H, s, OCH_3), 3.67 (1H, d, *J* 5.5, 1-H), 4.66 (1H, bs, 3-H), 5.21 (2H, s, 2 × ArH), 5.29 (1H, m, ArH), 5.38 (1H, m, ArH), 5.62 (1H, app. t, *J* 6.5, ArH); δ_C (125 MHz; $CDCl_3$) major diastereoisomer: 0.4 ($Si(CH_3)_3$), 21.7 (CH_2), 25.0 (CH_2), 29.8 (CH_2), 42.5 (C-2), 59.5 (OCH_3), 84.9 (C-1), 90.4 (ArCH), 90.7 (ArCH), 91.6 (ArCH), 92.7 (ArCH), 93.8 (ArCH),

103.8 (C-3), 110.3 (ArC), 152.8 (C-4), 233.0 (C≡O), minor diastereoisomer: 0.4 ($Si(CH_3)_3$), 21.4 (CH_2), 23.8 (CH_2), 29.7 (CH_2), 42.8 (C-2), 59.4 (OCH_3), 84.5 (C-1), 90.3 (ArCH), 90.7 (ArCH), 91.7 (ArCH), 92.9 (ArCH), 93.7 (ArCH), 104.4 (C-3), 110.6 (ArC), 152.8 (C-4), 233.0 (C≡O); *m/z* (EI) 426 ([M^+], 8), 370 ([M−2CO], 47%), 354 (38), 342 (80), 298 (100), 281 (30) (Found [M^+]: 426.0946. $C_{20}H_{26}CrO_5Si$ requires: 426.0955). Further elution (SiO_2; Et_2O–petrol, 2:3), afforded ketone complex **18** as an inseparable 2.5:1 mixture of two diastereoisomers (11 mg, 4%) as a yellow solid, m.p. 130–132 °C (from Et_2O–petrol); $[\alpha]_D^{25}$ +53 (*c* 0.97 in $CHCl_3$); (Found: C, 57.37; H, 5.08. $C_{17}H_{18}CrO_5$ requires: C, 57.63; H, 5.12%); ν_{max} ($CHCl_3$, cm^{-1}) 2940, 2871, 1971 and 1897 (C≡O), 1708 (C=O), 1115; δ_H (500 MHz; $CDCl_3$) major diastereoisomer: 1.42–1.83 (3H, m), 1.87–2.18 (3H, m, incorporating 2-H), 2.20–2.42 (3H, m, incorporating 3-H), 3.61 (3H, s, OCH_3), 3.93 (1H, s, 1-H), 5.15 (1H, app. t, *J* 6.0, ArH), 5.26 (1H, app. t, *J* 5.5, ArH), 5.31–5.43 (2H, m, ArH), 5.55 (1H, d, *J* 5.5, ArH), minor diastereoisomer: 1.42–1.83 (3H, m), 1.87–2.18 (3H, m, incorporating 2-H), 2.20–2.42 (3H, m, incorporating 3-H), 3.58 (3H, s, OCH_3), 3.77 (1H, s, 1-H), 5.15 (1H, app. t, *J* 6.0, ArH), 5.26 (1H, app. t, *J* 5.5, ArH), 5.31–5.43 (2H, m, 2 × ArH), 5.60 (1H, d, *J* 5.5, ArH), δ_C (125 MHz; $CDCl_3$) major diastereoisomer: 24.7 (CH_2), 28.3 (CH_2), 41.0 (CH_2), 41.1 (CH_2), 46.4 (C-2), 60.0 (OCH_3), 83.5 (C-1), 90.9 (ArCH), 91.0 (ArCH), 91.1 (ArCH), 91.2 (ArCH), 93.5 (ArCH), 109.0 (ArC), 211.1 (C=O), 232.7 (C≡O), minor diastereoisomer: 24.6 (CH_2), 28.3 (CH_2), 41.1 (CH_2), 44.6 (CH_2), 46.0 (C-2), 59.9 (OCH_3), 83.8 (C-1), 90.7 (ArCH), 90.8 (ArCH), 91.0 (ArCH), 91.6 (ArCH), 93.6 (ArCH), 109.1 (ArC), 210.6 (C=O), 232.7 (C≡O); *m/z* (EI) 354 ([M^+], 10), 298 ([M−2CO], 7), 270 ([M−3CO], 9%), 121 (100) (Found [M^+]: 354.0565. $C_{17}H_{18}CrO_5$ requires: 354.0559).

Another reaction was carried out in the same way, except that the reaction mixture was worked up with saturated aq. NH_4Cl solution (1 ml) in place of saturated aq. $NaHCO_3$. Washing of the crude organic extract with 2 M HCl solution was carried out until all of the enol silane in the mixture was converted into the ketone complex. Flash column chromatography then gave the ketone complex **18**, with spectroscopic data as described above.

3.2.8. (+)-Tricarbonyl[η^6-1-{(1*S*)-1-methoxy-2-methyl-3-buten-2-ol}-benzene]chromium (0) (**19**)

The general procedure was employed, starting with complex **9** (200 mg, 0.78 mmol). Purification of the crude product by flash chromatography (SiO_2; Et_2O–petrol, 1:4), afforded the *title complex* **19** as an inseparable 2:1 mixture of two diastereoisomers (170 mg, 75%) as a yellow oil, $[\alpha]_D^{25}$ +45 (*c* 0.80 in $CHCl_3$); ν_{max} ($CHCl_3$, cm^{-1}) 3562 (O–H), 2934, 2834, 1964 and 1906 and 1874 (C≡O), 1650 (C=C), 1099; δ_H (500 MHz; $CDCl_3$) major diastereoisomer: 1.23 (3H, s, CH_3), 2.27 (1H, s, exch. OH), 3.65 (4H, s, OCH_3 and 1-H), 5.07–5.28 (4H, m, 2 × ArH and 4-H), 5.34–5.48 (2H, m, 2 × ArH), 5.67 (1H, m, ArH), 5.89 (1H, dd, *J* 17.5, 10.5, 3-H), minor diastereoisomer: 1.28 (3H, s, CH_3), 2.22 (1H, s, exch. OH), 3.65 (4H, s, OCH_3 and 1-H), 5.07–5.28 (4H, m, 2 × ArH and 4-H), 5.34–5.48 (2H, m, 2 × ArH), 5.65 (1H, m, ArH), 5.89 (1H, dd, *J* 17.5, 10.5, 3-H); δ_C (125 MHz; $CDCl_3$) major diastereoisomer: 23.8 (CH_3), 60.5 (OCH_3), 75.8 (C-2), 87.2 (C-1), 89.0 (ArCH), 89.6 (ArCH), 93.1 (ArCH), 95.2 (ArCH), 105.7 (ArC), 114.9 (C-4), 141.0 (C-3), 232.9 (C≡O), minor diastereoisomer: 23.8 (CH_3), 60.5 (OCH_3), 75.9 (C-2), 87.2 (C-1), 89.0 (ArCH), 89.5 (ArCH), 93.3 (ArCH), 95.1 (ArCH), 105.8 (ArC), 114.5 (C-4), 140.8 (C-3), 232.9 (C≡O); *m/z* (FAB) 329 ([MH^+, 12%), 307 (25), 289 (12), 244 (12), 176 (39), 154 (100), 136 (73) (Found [MH^+]: 329.0453. $C_{15}H_{17}CrO_5$ requires: 329.0481). Also isolated was α-silyl complex **16** (13 mg, 5%).

3.2.9. (+)-Tricarbonyl[η^6-1-{(1*R*)-1-methoxy-4-pentanone}-benzene]chromium(0) (**20**)

A solution of the chiral base **8** (2.33 mmol in THF (28 ml), generated as described previously), was added dropwise via a cannula (7 min) to a precooled (−78 °C) solution of complex **9** (600 mg, 2.33 mmol) in THF (10 ml). The resultant orange solution was stirred at −78 °C for 1 h after which time HMPA (3 ml) was added to the reaction mixture. After 5 min a solution of MVK (0.58 ml, 6.98 mmol) and Me_3SiCl (0.44 ml, 3.49 mmol) in HMPA (1 ml) was added. The reaction mixture immediately lightened in colour to a yellow solution. After 5 h at −78 °C, saturated aq. $NaHCO_3$ solution (2 ml) was added and the reaction mixture was allowed to warm to r.t. prior to extraction with Et_2O (3 × 10 ml). The combined organics were washed with water (5 × 20 ml), brine (20 ml), dried ($MgSO_4$) and concentrated in vacuo to give an orange oil. Flash chromatography (SiO_2; Et_2O–petrol, 3:7), eluted the 1,2-addition adduct **19** as an inseparable 2:1 mixture of two diastereoisomers (42 mg, 6%) as a yellow oil. Spectroscopic details were in accordance with those described above. Further elution (SiO_2; Et_2O–petrol, 2:3), afforded the *title complex* **20** (372 mg, 57%) as a yellow solid, m.p. 35 °C (from Et_2O–petrol); $[\alpha]_D^{26}$ +72 (*c* 1.35 in $CHCl_3$); (Found: C, 54.73; H, 4.85. $C_{15}H_{16}CrO_5$ requires: C, 54.88; H, 4.91%); ν_{max} ($CHCl_3$, cm^{-1}) 2933, 2830, 1965 and 1907 and 1873 (C≡O), 1714 (C=O), 1358, 1108; δ_H (400 MHz; $CDCl_3$) 1.84 (1H, td, *J* 14.0, 8.0, 2-H*H*), 2.08 (1H, m, 2-*H*H), 2.16 (3H, s, CH_3), 2.47–2.66 (2H, m, 3-H), 3.48 (3H, s, OCH_3), 3.93 (1H, dd, *J* 8.0, 3.5, 1-H), 5.56–5.99 (4H, m, 2 × H *ortho*, 2 × H *meta*), 5.55 (1H, bd, *J* 5.8, H *para*); δ_C (100 MHz; $CDCl_3$) 30.1 (C-3), 32.0 (C-2), 39.0 (CH_3), 58.5 (OCH_3), 79.9 (C-1), 91.0 (ArCH), 91.3 (ArCH),

91.4 (ArCH), 91.5 (ArCH), 93.2 (ArCH), 111.5 (ArC), 208.0 (C=O), 233.0 (C≡O); *m/z* (FAB) 328 ([M^+], 10), 272 ([M−2CO], 26%), 244 ([M−3CO], 100) (Found [M^+]: 328.0397. $C_{15}H_{16}CrO_5$ requires: 328.0403).

Similar reactions were run using the enantiomer of base **8**, which gave similar yields of product, which was identical in all respects except the sign of the specific rotation.

3.2.10. (+)-Tricarbonyl[η^6-1-{(1*R*)-1-methoxybutanenitrile}-benzene]chromium(0) (**21**) and silyl derivative (**22**)

The general procedure was employed, starting with complex **9** (261 mg, 1.01 mmol). Purification of the crude product by flash chromatography (SiO_2; Et_2O–petrol, 2:3), afforded silyl complex **22** as an inseparable 1:1 mixture of two diastereoisomers (87 mg, 22%) as a yellow solid, m.p. 108–111 °C (from Et_2O–petrol); $[\alpha]_D^{25}$ +81 (*c* 1.10 in $CHCl_3$); (Found: C, 53.11; H, 5.44; N, 3.61. $C_{17}H_{21}CrNO_4Si$ requires: C, 53.25; H, 5.52; N, 3.65%); ν_{max} ($CHCl_3$, cm^{-1}) 2957, 2831, 2223 (C≡N), 1968 and 1907 (C≡O), 1110, 862; δ_H (400 MHz; $CDCl_3$) both diastereoisomers: 0.22 (9H, s, $Si(CH_3)_3$), 1.69 (0.5H, ddd, *J* 14.0, 10.5, 3.5, 2-H*H*), 1.82–1.92 (1.5H, m, 2-H*H* and 3-H), 2.03 (0.5H, ddd, *J* 14.0, 11.5, 5.5, 2-*H*H), 2.24 (0.5H, dd, *J* 12.5, 3.5, 2-*H*H), 3.53 (1.5H, s, OCH_3), 3.56 (1.5H, s, OCH_3), 4.02 (0.5H, app. t, *J* 5.5, 1-H), 4.09 (0.5H, dd, *J* 10.5, 2.5, 1-H), 5.22–5.37 (2H, m, 2 × ArH), 5.43 (1H, m, ArH), 5.59 (1H, m, H *para*); δ_C (100 MHz; $CDCl_3$) both diastereoisomers: −3.3 (9H, s, $Si(CH_3)_3$), 14.2, 15.6 (C-3), 34.0, 36.5 (C-2), 57.7, 58.8 (OCH_3), 79.3, 80.4 (C-1), 89.9, 90.2 (ArCH), 91.1 (ArCH), 91.8 (ArCH), 92.5 (ArCH), 93.7, 94.5 (ArCH), 110.1 (ArC), 121.6, 121.7 (C≡N), 232.6, 232.7 (C≡O). Further elution (SiO_2; Et_2O–petrol, 1:1), afforded the *title complex* **21** (122 mg, 39%) as a yellow oil, $[\alpha]_D^{26}$ +89 (*c* 1.02 in $CHCl_3$); (Found: C, 54.11; H, 4.22; N, 4.33. $C_{14}H_{13}CrNO_4$ requires: C, 54.02; H, 4.21; N, 4.50%); ν_{max} ($CHCl_3$, cm^{-1}) 3310, 2937, 2832, 2249 (C≡N), 1978 and 1913 (C≡O), 1110; δ_H (400 MHz; $CDCl_3$) 1.94 (1H, m, 2-H*H*), 2.12 (1H, m, 2-*H*H), 2.46 (1H, ddd, *J* 17.0, 7.0, 5.5, 3-H*H*), 2.57 (1H, app. dt, *J* 17.0, 8.0, 3-*H*H), 3.53 (3H, s, OCH_3), 4.03 (1H, dd, *J* 9.0, 3.5, 1-H), 5.26–5.34 (3H, m, 3 × ArH), 5.35 (1H, app. t, *J* 6.0, ArH), 5.55 (1H, d, *J* 6.5, ArH); δ_C (100 MHz, $CDCl_3$) 13.5 (C-3), 33.7 (C-2), 58.6 (OCH_3), 79.0 (C-1), 90.7 (ArCH), 91.1 (ArCH), 91.4 (ArCH), 91.7 (ArCH), 93.8 (ArCH), 109.4 (ArC), 119.1 (C≡N), 232.5 (C≡O); *m/z* (FAB) 311 ([M^+], 36%), 283 ([M−CO], 26), 255 ([M−2CO], 66), 227 ([M−3CO], 82), 149 (63) (Found [MNH_4^+]: 329.0595. $C_{14}H_{17}CrN_2O_4$ requires: 329.0593). Also isolated were α-silyl complex **16** (60 mg, 18%) and starting complex **9** (19 mg, 7%).

3.2.11. (−)-Tricarbonyl[η^6-1-{methyl(1*S*)-1-thioethylbutanoate}-benzene]chromium(0) (**24**)

The general procedure was employed, starting with complex **23** (200 mg, 0.69 mmol). Purification of the crude product by flash chromatography (SiO_2; Et_2O–petrol, 1:4), afforded the *title complex* **24** (187 mg, 72%) as a yellow oil, $[\alpha]_D^{24}$ −32 (*c* 1.20 in $CHCl_3$); ν_{max} ($CHCl_3$, cm^{-1}) 2955, 2930, 2872, 1965 and 1909 (C≡O), 1731 (C=O); δ_H (500 MHz; $CDCl_3$) 1.23 (3H, t, *J* 7.5, SCH_2CH_3), 2.02 (1H, m, 2-H*H*), 2.23 (1H, m, 2-*H*H), 2.46–2.71 (4H, m, SCH_2CH_3 and 3-H), 3.45 (1H, dd, *J* 10.5, 4.0, 1-H), 3.71 (3H, s, CO_2CH_3), 5.24–5.41 (4H, m, 2 × H *ortho*, 2 × H *meta*), 5.50 (1H, d, *J* 6.5, H *para*); δ_C (125 MHz; $CDCl_3$) 14.4 (SCH_2CH_3), 24.6 (SCH_2CH_3), 30.0 (C-3), 31.8 (C-2), 47.2 (C-1), 51.4 (CO_2CH_3), 91.3 (ArCH), 91.9 (ArCH), 92.8 (ArCH), 94.2 (ArCH), 113.7 (ArC), 173.3 (C=O), 232.7 (C≡O); *m/z* (EI) 318 ([M−2CO], 35%), 290 ([M−3CO], 100), 238 (38) (Found [M−2CO]: 318.0381. $C_{14}H_{18}CrO_3S$ requires: 318.0382). Complex **24** was separated on a Chiracel OD column using a C_6H_{14}–IPA (95:5) eluent at 30 °C with a flow rate of 1.0 ml min^{-1}, detecting at 215 nm. The enantiomeric excess was determined as 74% with retention times of 27.2 (minor enantiomer) and 32.3 min (major enantiomer). Also isolated was starting complex **23** (52 mg, 26%).

3.2.12. (−)-Tricarbonyl[η^6-1-{(1*S*)-1-thioethyl-1-(4-cyclohexanon-2-yl) methyl}-benzene]chromium(0) (**25**)

The general procedure was employed, starting with complex **23** (415 mg, 1.44 mmol). Purification of the crude product by flash chromatography (SiO_2; Et_2O–petrol, 1:20), gave firstly a small amount of the enol silane corresponding to **25** (i.e. the analogue of **17**) as an inseparable 1.6:1 mixture of two diastereoisomers (66 mg, 10%) as a yellow oil, $[\alpha]_D^{28}$ −55 (*c* 0.64 in $CHCl_3$); ν_{max} ($CHCl_3$, cm^{-1}) 2932, 1970 and 1899 (C≡O), 1663 (C=C), 862 (Si–CH_3); δ_H (400 MHz; $CDCl_3$) major diastereoisomer: 0.19 (9H, s, $Si(CH_3)_3$), 1.30 (3H, t, *J* 7.5, SCH_2CH_3), 1.41–1.64 (2H, m, CH_2), 1.71–1.85 (2H, m, CH_2), 1.87–2.08 (2H, m, CH_2), 2.60–2.86 (3H, m, SCH_2CH_3 and 2-H), 3.42 (1H, s, 1-H), 4.70 (1H, bs, 3-H), 5.19 (1H, app. t, *J* 6.0, ArH), 5.30 (1H, app. t, *J* 6.5, ArH), 5.37 (1H, app. t, *J* 7.0, ArH), 5.43 (1H, d, *J* 6.0, ArH), 5.94 (1H, d, *J* 6.5, ArH), minor diastereoisomer: 0.20 (9H, s, $Si(CH_3)_3$), 1.30 (3H, t, *J* 7.5, SCH_2CH_3), 1.41–1.64 (2H, m, CH_2), 1.71–1.85 (2H, m, CH_2), 1.87–2.08 (2H, m, CH_2), 2.60–2.86 (3H, m, SCH_2CH_3 and 2-H), 3.43 (1H, s, 1-H), 4.77 (1H, bs, 3-H), 5.15 (1H, app. t, *J* 6.0, ArH), 5.26 (1H, app. t, *J* 6.5, ArH), 5.37 (1H, app. t, *J* 7.0, ArH), 5.43 (1H, app. t, *J* 6.0, ArH), 5.90 (1H, d, *J* 6.5, ArH); δ_C (125 MHz; $CDCl_3$) major diastereoisomer: 0.5 ($Si(CH_3)_3$), 14.7 (SCH_2CH_3), 22.0 (CH_2), 25.5 (CH_2), 27.2 (SCH_2CH_3), 30.0 (CH_2), 43.4 (C-2), 54.8 (C-1), 89.4 (ArCH), 89.9 (ArCH), 94.4 (ArCH), 95.0 (ArCH), 95.7 (ArCH), 106.6

(C-3), 111.9 (ArC), 152.6 (C-4), 233.0 (C≡O), minor diastereoisomer: 0.4 ($Si(CH_3)_3$), 14.7 (SCH_2CH_3), 22.1 (CH_2), 25.5 (CH_2), 27.0 (SCH_2CH_3), 30.0 (CH_2), 43.4 (C-2), 54.9 (C-1), 90.2 (ArCH), 90.3 (ArCH), 94.2 (ArCH), 94.6 (ArCH), 94.8 (ArCH), 104.0 (C-3), 112.5 (ArC), 153.5 (C-4), 233.0 (C≡O); *m/z* (FAB) 400 ([M−2CO], 3%), 372 ([M−3CO], 17), 154 (100) (Found [M−3CO]: 372.1035. $C_{18}H_{28}CrOSSi$ requires: 372.1006%). Further elution (SiO_2; Et_2O–petrol, 1:9), afforded the *title complex* **25** as an inseparable 1.6:1 mixture of two diastereoisomers (279 mg, 50%) as a yellow solid, m.p. 93 °C (decomposition) (from Et_2O–petrol); $[\alpha]_D^{28}$ −45 (*c* 1.00 in $CHCl_3$); (Found: C, 56.23; H, 5.36. $C_{18}H_{20}O_4SCr$ requires: C, 56.24; H, 5.24%); ν_{max} ($CHCl_3$, cm^{-1}) 2932, 2871, 1966 and 1907 (C≡O), 1710 (C=O); δ_H (400 MHz; $CDCl_3$) major diastereoisomer: 1.32 (3H, t, *J* 7.0, SCH_2CH_3), 1.36–2.48 (9H, m, 4 × CH_2 and 2-H), 2.61–2.89 (2H, m, SCH_2CH_3), 3.50 (1H, s, 1-H), 5.19 (1H, app. t, *J* 6.0, ArH), 5.25–5.38 (2H, m, 2 × ArH), 5.43 (1H, m, ArH), 5.80 (1H, d, *J* 6.5, ArH), minor diastereoisomer: 1.32 (3H, t, *J* 7.0, SCH_2CH_3), 1.36–2.48 (9H, m, 4 × CH_2 and 2-H), 2.80 (2H, m, SCH_2CH_3), 3.35 (1H, s, 1-H), 5.19 (1H, app. t, *J* 6.0, ArH), 5.25–5.38 (1H, m, 2 × ArH), 5.43 (1H, m, ArH), 5.90 (1H, d, *J* 6.0, ArH); δ_C (125 MHz; $CDCl_3$) major diastereoisomer: 14.6 (SCH_2CH_3), 24.7 (CH_2), 27.7 (CH_2), 29.8 (SCH_2CH_3), 41.0 (CH_2), 43.3 (CH_2), 46.6 (C-2), 54.5 (C-1), 90.1 (ArCH), 90.4 (ArCH), 94.1 (ArCH), 94.5 (ArCH), 94.6 (ArCH), 111.2 (ArC), 210.4 (C=O), 232.7 (C≡O), minor diastereoisomer: 14.6 (SCH_2CH_3), 25.2 (CH_2), 26.1 (CH_2), 29.1 (SCH_2CH_3), 41.0 (CH_2), 44.2 (CH_2), 46.6 (C-2), 54.8 (C-1), 89.8 (ArCH), 90.0 (ArCH), 94.6 (ArCH), 94.7 (ArCH), 95.0 (ArCH), 111.2 (ArC), 210.7 (C=O), 232.7 (C≡O); *m/z* (FAB) 300 ([M−3CO], 6%), 284 (100), 151 (76) (Found [M−3CO]: 300.0651. $C_{15}H_{20}CrOS$ requires: 300.0640).

*3.2.13. (−)-Tricarbonyl[η⁶-1-{(1S)-1-thioethylbutanenitrile}-benzene]chromium(0) (**26**) and silyl derivative (**27**)*

The general procedure was employed, starting with complex **23** (261 mg, 1.01 mmol). Purification of the crude product by flash chromatography (SiO_2; Et_2O–petrol, 1:4), gave α-silyl complex **27** as an inseparable 1:1 mixture of two diastereoisomers (54 mg, 15%) as a yellow solid, $[\alpha]_D^{21}$ −66 (*c* 0.60 in $CHCl_3$); (Found: C, 52.68; H, 5.70; N, 3.58. $C_{18}H_{23}CrNO_3SSi$ requires: C, 52.28; H, 5.61; N, 3.39%); ν_{max} ($CHCl_3$, cm^{-1}) 2961, 2930, 2873, 2223 (C≡N), 1978 and 1914 and 1874 (C≡O), 869; δ_H (400 MHz; $CDCl_3$) both diastereoisomers: 0.24 (4.5H, s, $Si(CH_3)_3$), 0.25 (4.5H, s, $Si(CH_3)_3$), 1.27 (1.5H, t, *J* 7.5, SCH_2CH_3), 1.29 (1.5H, t, *J* 7.5, SCH_2CH_3), 1.70 (0.5H, ddd, *J* 14.0, 12.5, 3.5, 2-H*H*), 1.98 (0.5H, ddd, *J* 14.0, 8.0, 3.0, 2-H*H*), 2.08 (0.5H, dd, *J* 11.0, 3.0, 3-H), 2.16 (1.0H, m, 2-*H*H and 3-H), 2.45 (0.5H, dd, *J* 12.5, 3.5, 3-H), 2.55–2.75 (2H, m, SCH_2CH_3), 3.55 (0.5H, dd, *J* 8.0, 2.0, 1-H), 3.59 (0.5H, dd, *J* 12.0, 3.0, 1-H), 5.21–5.34 (2H, m, 2 × H *ortho*), 5.41–5.52 (2H, m, 2 × H *meta*), 5.58 (1H, d, *J* 5.0, H *para*); δ_C (100 MHz; $CDCl_3$) both diastereoisomers: −3.3 (9H, s, $Si(CH_3)_3$), 14.4, 14.5 (SCH_2CH_3), 17.2, 17.6 (C-3), 25.6 (C-2), 33.2, 33.7 (SCH_2CH_3), 47.9, 48.2 (C-1), 89.9, 90.2 (ArCH), 90.3 (ArCH), 93.4, 93.8 (ArCH), 94.3 (ArCH), 94.7, 94.9 (ArCH), 111.4, 113.8 (ArC), 121.2, 121.6 (C≡N), 232.5 (C≡O); *m/z* (FAB) 414 ([MH^+], 30%), 358 ([M−2CO], 35), 341 (31), 313 (31), 285 (71), 257 (79), 114 (100) (Found [M−2CO]: 357.0684. $C_{16}H_{23}CrNOSiS$ requires: 357.0675%). Further elution (SiO_2; Et_2O–petrol, 1:4), afforded *title complex* **26** (133 mg, 45%) as a yellow oil, $[\alpha]_D^{21}$ −40 (*c* 0.60 in $CHCl_3$); ν_{max} ($CHCl_3$, cm^{-1}) 2931, 2250 (C≡N), 1973 and 1906 (C≡O); δ_H (400 MHz; $CDCl_3$) 1.27 (3H, t, *J* 7.5, SCH_2CH_3) 2.27 (1H, m, 2-H*H*), 2.31 (1H, m, 2-*H*H), 2.50–2.65 (2H, m, 3-H), 2.71 (2H, q, *J* 7.5, SCH_2CH_3), 3.47 (1H, dd, *J* 11.0, 3.5, 1-H), 5.27–5.34 (3H, m, 3 × ArH), 5.41 (1H, app. t, *J* 6.0, ArH), 5.48 (1H, d, *J* 6.5, ArH); δ_C (100 MHz, $CDCl_3$) 14.4 (SCH_2CH_3), 15.8 (C-3), 25.0 (SCH_2CH_3), 30.9 (C-2), 46.9 (C-1), 91.0 (ArCH), 91.6 (ArCH), 93.1 (ArCH), 94.1 (ArCH), 112.3 (ArC), 118.6 (C≡N), 232.4 (C≡O); *m/z* (FAB) 341 ([M^+], 31%), 313 ([M−CO], 28), 285 ([M−2CO], 27), 257 ([M−3CO], 33) (Found [MNH_4^+]: 359.0520. $C_{15}H_{19}CrN_2O_3S$ requires: 359.0521). Also isolated was starting complex **23** (42 mg, 16%).

*3.2.14. Tricarbonyl[η⁶-1-{1-methoxy-1-(bicyclo[4.1.0]hept-2-yl-5-trimethylsilyloxy) methyl}-benzene]chromium(0) (**28**) and corresponding desilylated derivative (**29**)*

Diethyl zinc (1.0 M in C_6H_{14}, 1.94 ml, 1.94 mmol) was added dropwise to a stirred solution of complex **17** (514 mg, 1.29 mmol) in Et_2O (0.20 ml, 1.94 mmol) at 0 °C under an atmosphere of nitrogen. Diiodomethane (0.16 ml, 1.94 mmol) was rapidly added and the turgid white solution was warmed to r.t. and stirred for 15 min. The resultant red solution was diluted with Et_2O (10 ml) and cooled to 0 °C before dropwise addition of MeOH (2 ml). The reaction mixture was diluted with Et_2O (50 ml), washed with ice cold saturated aq. NH_4Cl (2 × 50 ml), ice cold brine (2 × 100 ml), dried (Na_2SO_4) and concentrated in vacuo to give a yellow oil. Flash chromatography (SiO_2; CH_2Cl_2–petrol, 1:1), afforded the *title complex* **28** as a ca. 1.5:1 mixture of two main inseparable diastereoisomers (380 mg, 71%) as a yellow oil, ν_{max} ($CHCl_3$, cm^{-1}) 2939, 2869, 1977 and 1912 and 1866 (C≡O), 1707, 1454, 862; δ_H (400 MHz; $CDCl_3$) major diastereoisomer: 0.15 (9H, s, $Si(CH_3)_3$), 0.23 (1H, app. t, *J* 6.0, *endo* 4-H), 0.83 (1H, dd, *J* 10.5, 6.0, *exo* 4-H), 0.92 (1H, dm, *J* 10.5, 3-H), 1.03–1.20 (2H, m, CH_2), 1.37 (1H, m, CH*H*), 1.53–1.85 (3H, m, C*H*H and CH_2), 2.13 (1H, m, 2-H), 3.63 (3H, s, OCH_3), 3.77 (1H, d, *J* 5.0, 1-H), 5.21–5.46 (4H, m, 2 × H *ortho* and 2 × H

meta), 5.68 (1H, d, *J* 6.5, H *para*), minor diastereoisomer: 0.15 (9H, s, $Si(CH_3)_3$), 0.31 (1H, app. t, *J* 6.0, *endo* 4-H), 0.83 (1H, dd, *J* 10.5, 6.0, *exo* 4-H), 0.92 (1H, m, 3-H), 1.03–1.20 (2H, m, CH_2), 1.37 (1H, m, CH*H*), 1.53–1.85 (3H, m, C*H*H and CH_2), 2.13 (1H, m, 2-H), 3.62 (3H, s, OCH_3), 4.02 (1H, d, *J* 4.0, 1-H), 5.21–5.46 (4H, m, 2 × H *ortho* and 2 × H *meta*), 5.68 (1H, d, *J* 6.5, H *para*); δ_C (125 MHz; $CDCl_3$) major diastereoisomer: 1.3 ($Si(CH_3)_3$), 14.9 (C-4), 18.5 (CH_2), 21.0 (CH_2), 24.6 (C-3), 31.3 (CH_2), 46.7 (C-2), 56.8 (C-5), 59.6 (OCH_3), 84.9 (C-1), 90.6 (ArCH), 91.2 (ArCH), 91.7 (ArCH), 92.7 (ArCH), 94.2 (ArCH), 110.2 (ArC), 232.9 (C≡O), minor diastereoisomer: 1.3 ($Si(CH_3)_3$), 12.3 (C-4), 18.5 (CH_2), 19.8 (CH_2), 27.1 (C-3), 30.9 (CH_2), 46.5 (C-2), 56.9 (C-5), 59.6 (OCH_3), 84.5 (C-1), 90.6 (ArCH), 90.9 (ArCH), 91.4 (ArCH), 92.7 (ArCH), 93.5 (ArCH), 110.0 (ArC), 232.9 (C≡O); *m*/*z* (FAB) 440 ([M^+], 11%), 356 ([M−3CO], 100), 73 (65) (Found [M^+]: 440.1111. $C_{21}H_{28}CrO_5Si$ requires: 440.1124).

Alternatively, the crude reaction mixture, obtained as described above, was dissolved in degassed MeOH (20 ml) and rapidly stirred with K_2CO_3 (8 mg, 0.06 mmol) for 18 h. The resultant red solution was diluted with Et_2O (100 ml), washed with saturated aq. NH_4Cl (2 × 50 ml), dried ($MgSO_4$) and concentrated in vacuo to give a yellow oil. Flash chromatography (SiO_2; CH_2Cl_2–petrol, 1:1), then gave *title complex* **29** as a mixture of diastereomers. δ_H (400 MHz; $CDCl_3$) major diastereoisomer: 0.28 (1H, app. t, *J* 5.5, *endo* 4-H), 0.78–1.00 (2H, m, 3-H and *exo* 4-H), 1.02–1.50 (3H, m, CH_2), 1.59–1.85 (3H, m, CH_2), 2.15–2.32 (2H, m, 2-H and OH), 3.62 (3H, s, OCH_3), 3.82 (1H, d, *J* 5.0, 1-H), 5.21–5.46 (4H, m, 2 × H *ortho* and 2 × H *meta*), 5.68 (1H, d, *J* 6.5, H *para*); δ_C (125 MHz; $CDCl_3$) 13.8 (C-4), 18.7 (CH_2), 20.9 (CH_2), 23.2 (C-3), 31.2 (CH_2), 46.2 (C-2), 55.2 (C-5), 59.9 (OCH_3), 84.8 (C-1), 90.9 (ArCH), 91.4 (ArCH), 91.7 (ArCH), 93.6 (ArCH), 94.1 (ArCH), 110.0 (ArC), 233.0 (C≡O); *m*/*z* (FAB) 284 ([M−3CO], 5%), 176 (31), 136 (50), 57 (100) (Found [M−3CO]: 284.0879. $C_{15}H_{20}CrO_2$ requires: 284.0868).

3.2.15. Tricarbonyl[η^6-1-{1-methoxy-1-(5-cycloheptanone)methyl}-benzene]chromium(0) (*32*)

A solution of $Fe(NO_3)_3 \cdot 9H_2O$ (576 mg, 1.43 mmol) in DMF (5 ml) was stirred over molecular sieves for 15 h under an Ar atmosphere. The resulting red solution was degassed and added over 30 min via syringe pump to a solution of complex **28** (267 mg, 0.65 mmol) and 1,4-cyclohexadiene (0.19 ml, 1.94 mmol) in degassed DMF (5 ml) at 0 °C. The solution was stirred for a further 30 min at 0 °C before pouring into water (100 ml) and Et_2O (50 ml). The aq. layer was separated and extracted further with Et_2O (2 × 50 ml) and the combined organic extracts were washed with water (5 × 50 ml), brine (50 ml), dried (Na_2SO_4) and concentrated in vacuo to give a yellow oil. Flash chromatography (SiO_2; Et_2O–petrol, 1:1), afforded the *title complex* **32** as an inseparable 1:1 mixture of two diastereoisomers (145 mg, 61%) as a yellow solid, m.p. 85–86 °C (from Et_2O–petrol); (Found: C, 58.61; H, 5.43. $C_{18}H_{20}CrO_5$ requires: C, 58.69; H, 5.47%); ν_{max} ($CHCl_3$, cm^{-1}) 2936, 1975 and 1904 (C≡O), 1697 (C=O), 1101; δ_H (400 MHz; $CDCl_3$) both diastereoisomers: 1.35–1.67 (3H, m, CH*H* and CH_2), 1.68–1.88 (2H, m, C*H*H and 2-H), 1.89–2.10 (2H, m, CH_2), 2.39–2.60 (4H, m, 4-H and 6-H), 3.58 (3H, s, OCH_3), 3.84 (0.5H, d, *J* 3.5, 1-H), 3.87 (0.5H, d, *J* 3.5, 1-H), 5.19 (1H, dd, *J* 6.5, 1.0, ArH), 5.29 (1H, m, ArH), 5.33–5.42 (2H, m, 2 × ArH), 5.61 (1H, m, ArH); δ_C (100 MHz, $CDCl_3$) major diastereoisomer: 23.2 (CH_2), 26.8 (CH_2), 30.3 (CH_2), 33.1 (CH_2), 43.4 (CH_2), 48.7 (C-2), 59.7 (OCH_3), 85.4 (C-1), 91.3 (ArCH), 91.7 (ArCH), 93.5 (ArCH), 110.1 (ArC), 214.3 (C=O), 232.9 (C≡O), minor diastereoisomer: 24.3 (CH_2), 26.8 (CH_2), 30.3 (CH_2), 33.1 (CH_2), 42.2 (CH_2), 48.3 (C-2), 59.7 (OCH_3), 85.4 (C-1), 91.3 (ArCH), 91.7 (ArCH), 93.5 (ArCH), 110.1 (ArC), 214.3 (C=O), 232.9 (C≡O); *m*/*z* (EI) 368 ([M^+], 9%), 284 ([M−3CO], 66), 252 (22), 121 (100) (Found [M^+]: 368.0716. $C_{18}H_{20}CrO_5$ requires: 368.0716).

3.2.16. Tricarbonyl[η^6-1-{1-methoxy-1-(3-(phenylsulfanyl)-5-cycloheptanone)methyl}-benzene]chromium(0) (*33*)

A solution of $Fe(NO_3)_3 \cdot 9H_2O$ (442 mg, 1.10 mmol) in DMF (4 ml) was stirred over molecular sieves for 15 h under an Ar atmosphere. The resulting red solution was degassed under Ar and added over 30 min via syringe pump to a solution of complex **28** (205 mg, 0.50 mmol) and diphenyldisulfide (326 mg, 1.49 mmol) in dry, degassed DMF (5 ml) at 0 °C. The solution was stirred for a further 30 min at 0 °C before pouring into water–Et_2O (100:50 ml). The aq. layer was separated and extracted further with Et_2O (2 × 50 ml) and the combined organic extracts were washed with water (5 × 50 ml), brine (50 ml), dried (Na_2SO_4) and concentrated in vacuo to give a yellow oil. Flash chromatography (SiO_2; CH_2Cl_2–petrol, 7:3), afforded the *title complex* **33** as a complex mixture (2:2:1:1) of four inseparable diastereomers (88 mg, 37%) as a yellow oil, δ_H (400 MHz; $CDCl_3$) 1.26 (1H, m), 1.50–2.06 (3H, m), 2.22 (1H, m, 2-H), 2.31–2.67 (2H, m), 2.70–3.14 (3H, m), 3.16 (0.5H, s, OCH_3), 3.23 (0.5H, s, OCH_3), 3.49 (1H, s, OCH_3), 3.58 (1H, s, OCH_3), 4.35 (0.17H, d, *J* 8.5, 1-H), 4.38 (0.33H, d, *J* 4.0, 1-H), 4.77 (0.17H, d, *J* 4.5, 1-H), 4.88 (0.33H, bs, 1-H), 5.11 (0.5H, d, *J* 6.0, CrArH), 5.18 (0.5H, app. t, *J* 6.0, CrArH), 5.26–5.42 (3H, m, CrArH), 5.53 (0.5H, d, *J* 6.5, CrArH), 5.59 (0.5H, bs, CrArH), 7.21–7.55 (5H, m, 5 × ArH); δ_C (100 MHz, $CDCl_3$) both major diastereoisomers: 20.7, 21.3 (CH_2), 24.8, 27.3 (CH_2), 43.3, 43.8 (CH_2), 45.0 (C-2), 47.1, 47.9 (CH_2), 48.5 (C-2), 49.7, 53.3 (C-3), 58.9, 60.0 (OCH_3), 81.6, 81.8 (C-1), 90.6, 90.8 (CrArCH), 90.8, 90.9 (CrArCH), 91.0, 91.2

(CrArCH), 91.8, 91.9 (CrArCH), 93.1, 93.6 (CrArCH), 109.2, 110.3 (CrArC), 129.1 (ArCH), 129.4 (ArCH), 132.1, 132.7 (ArCH), 139.6, 140.3 (ArC), 210.8, 210.9 (C=O), 232.7, 232.8 (C≡O); *m/z* (EI) 340 ([M−Cr(CO)$_3$)], 5%), 198 (43), 121 (100), 14 (77) (Found [M−Cr(CO)$_3$]: 340.1488. $C_{21}H_{24}O_2S$ requires: 340.1497). Further elution (SiO_2; CH_2Cl_2–petrol, 9:1), gave the cycloheptanone complex **32** (26 mg, 14%) as a yellow oil; spectroscopic details were in accordance with those described above.

3.2.17. 4-Methoxy-1-methyl-1,2,3,4,5,6-hexahydro-1-naphthalenol (*34*) and 4-methoxy-1-methyl-1,2,3,4,7,8-hexahydro-1-naphthalenol (*35*)

A solution of complex (−)-**20** (224 mg, 0.72 mmol) and ^{t}BuOH (0.20 ml, 2.15 mmol) in THF (30 ml) was degassed and added over 1 h via syringe pump to a degassed solution of samarium(II) iodide (18 ml, 1.80 mmol) and HMPA (2.50 ml, 14.40 mmol) at −78 °C under an atmosphere of Ar. The solution remained a deep purple colour and was stirred for a further 1 h at −78 °C before allowing to warm to r.t. over 30 min. Addition of saturated aq. $NaHCO_3$ (10 ml) gave a bright orange solution which was stirred for 5 min. The aq. layer was separated and extracted further with EtOAc (3 × 10 ml) and the combined organic extracts were washed with water (2 × 20 ml), brine (2 × 10 ml), dried ($MgSO_4$) and concentrated in vacuo to give a green oil. Flash chromatography (SiO_2; CH_2Cl_2–petrol, 7:3), afforded the *title compound* **34** as a single diastereoisomer (27 mg, 20%) as a colourless oil, $[\alpha]_D^{16}$ +23 (*c* 1.00 in $CHCl_3$); ν_{max} ($CHCl_3$, cm^{-1}) 3596 (O–H), 2934, 2824, 1659 and 1626 (C=C), 1076; δ_H (400 MHz; $CDCl_3$) 1.34 (3H, s, CH_3), 1.42 (1H, s, exch. OH), 1.62–1.85 (2H, m, 3-H), 1.90–2.10 (3H, m, 2-H and 5-H), 2.12–2.20 (2H, m, 6-H), 2.37 (1H, m, 5-H), 3.38 (3H, s, OCH_3), 3.66 (1H, bs, 4-H), 5.91 (1H, dt, *J* 10.0, 4.5, 7-H), 6.18 (1H, d, *J* 10.0, 8-H); δ_C (100 MHz, $CDCl_3$) 22.6 (CH_2), 24.1 (CH_2), 24.5 (CH_2), 27.3 (CH_3), 35.6 (CH_2), 56.6 (OCH_3), 69.4 (C-1), 77.3 (C-4), 123.1 (olefinic CH), 127.6 (olefinic CH), 131.1 (olefinic C), 135.0 (olefinic C); *m/z* (EI) 194 ([M$^+$], 45%), 177 (6), 163 (9), 146 (13), 129 (54), 121 (100) (Found [M$^+$]: 194.1300. $C_{12}H_{18}O_2$ 194.1307). Further elution (SiO_2; CH_2Cl_2–petrol, 7:3), afforded the *title compound* **35** as a single diastereoisomer (22 mg, 16%) as a colourless oil, $[\alpha]_D^{18}$ +21 (*c* 0.90 in $CHCl_3$); ν_{max} ($CHCl_3$, cm^{-1}) 3445 (O–H), 2937, 2824, 1637 (C=C), 1077; δ_H (400 MHz; $CDCl_3$) 1.35 (3H, s, CH_3), 1.45 (1H, s, exch. OH), 1.66 (1H, m, 3-H), 1.82 (1H, m, 3-H), 1.90–2.05 (2H, m, 2-H), 2.10–2.22 (3H, m, 7-H and 8-H), 2.27 (1H, m, 8-H), 3.37 (3H, s, OCH_3), 3.68 (1H, bs, 4-H), 5.78–5.92 (1H, m, 6-H), 6.10 (1H, d, *J* 10.0, 5-H); δ_C (100 MHz, $CDCl_3$) 21.4 (CH_2), 23.1 (CH_2), 23.8 (CH_2), 26.7 (CH_3), 35.4 (CH_2), 56.4 (OCH_3), 70.4 (C-1), 77.3 (C-4), 126.0 (olefinic CH), 126.6 (olefinic CH), 129.2 (olefinic C), 137.0 (olefinic C); *m/z* (EI) 194 ([M$^+$], 43%), 177 (7), 162 (58), 145 (87), 118 (100) (Found [M$^+$]: 194.1304. $C_{12}H_{18}O_2$ requires: 194.1307%). Also isolated was metal-free starting arene (57 mg, 41%) as a colourless oil, ν_{max} ($CHCl_3$, cm^{-1}) 2931, 2826, 1713 (C=O), 1454, 1359, 1105; δ_H (400 MHz; $CDCl_3$) 1.98 (1H, m, 2-H), 2.12 (3H, s, CH_3), 2.51 (2H, app. t, *J* 7.5, 3-H), 3.21 (3H, s, OCH_3), 4.15 (1H, dd, *J* 8.0, 5.5, 1-H), 7.25–7.40 (5H, m, 5 × ArH); δ_C (125 MHz, $CDCl_3$) 29.9 (C-3), 32.0 (C-2), 39.7 (CH_3), 56.7 (OCH_3), 82.8 (C-1), 126.5 (ArCH), 127.7 (ArCH), 128.4 (ArCH), 141.7 (ArC), 208.5 (C=O); *m/z* (EI) 192 ([M$^+$], 3%), 177 (6), 134 (44), 121 (100), 77 (11) (Found [M$^+$]: 192.1141. $C_{12}H_{16}O_2$ requires: 192.1150).

Acknowledgements

We would like to thank the Engineering and Physical Sciences Research Council (EPSRC) and AstraZeneca for support of R.E.J.B.

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