

# Cyclopropanation of tricarbonyl(styrene)chromium(0) and (–)-Ar(1*R*,2*S*)-tricarbonyl[2-(trimethylsilyl)styrene]chromium(0)

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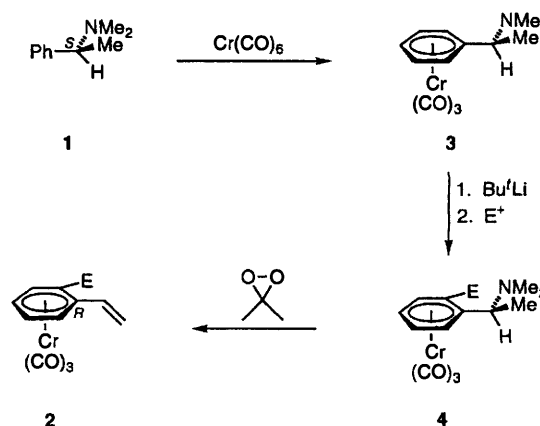
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Addition of the lithium anion of isobutyronitrile and iodomethane to (–)-Ar(1*R*,2*S*)-tricarbonyl[2-(trimethylsilyl)styrene]chromium(0) (–)-2' gave (–)-Ar(1*R*,2*S*)-tricarbonyl{(4*S*)-2,2-dimethyl-4-[2-(trimethylsilyl)phenyl]pentanenitrile}chromium(0) (–)-6, the stereochemistry of which was determined by an X-ray crystallographic analysis. Tricarbonyl(styrene)chromium(0) 5 and (–)-Ar(1*R*,2*S*)-tricarbonyl[2-(trimethylsilyl)styrene]chromium(0) (–)-2' reacted with sulfur and phosphorus ylides, and  $\alpha$ -chloro organometallics to give tricarbonylchromium(0) complexes of mono-, di- and tri-substituted cyclopropanes. The stereochemistry of one of the products, (–)-Ar(1*R*,2*S*)-tricarbonyl{(1*S*,2*S*)-*trans*-1-methoxy-2-[2-(trimethylsilyl)phenyl]cyclopropane}chromium(0) (–)-18 was determined by an X-ray crystallographic analysis. Desilylation of (–)-18 proceeded smoothly to give (–)-tricarbonyl[(1*S*,2*S*)-*trans*-1-methoxy-2-phenylcyclopropane]chromium(0) (–)-11.

We recently demonstrated that (*S*)- $\alpha$ -methylbenzylidimethylamine 1, derived from readily available (*S*)- $\alpha$ -methylbenzylamine, could be converted into enantiomerically pure tricarbonylchromium(0) complexes of *ortho*-substituted styrenes 2 by firstly heating the amine with hexacarbonylchromium(0) to give complex 3, secondly conducting a diastereoselective *ortho*-lithiation/electrophilic quench step to give 4, and finally oxidising 4 chemoselectively with dimethyldioxirane (Scheme 1).<sup>1,2</sup> A range of electrophiles were used in this sequence but of particular note from a synthetic viewpoint is the introduction of a trimethylsilyl substituent leading to the generation of complex 2 in which E = SiMe<sub>3</sub>. In principle, reactions of the carbon–carbon double bond of this enantiomerically pure complex [(–)-2'] should not only result in the creation of new chiral centres under good stereochemical control, but should also generate enantiomerically pure products from which the stereodirecting *ortho*-substituent is readily removed. In order to test this hypothesis, it was considered prudent to begin by examining a reaction already developed on the achiral parent compound, and so a literature survey of the reactivity of tricarbonyl(styrene)chromium(0) 5 was undertaken. This revealed that the carbon–carbon double bond of the styrene complex undergoes Pauson–Khand chemistry,<sup>3</sup> rhodium-catalysed hydroformylation,<sup>4</sup> cycloadditions with cyclopentadiene<sup>5</sup> and nitrile oxides,<sup>6</sup> and attack by nucleophiles.<sup>5,7</sup> After some deliberation, we elected to begin our study of the reactivity of complex (–)-2' by examining its reactivity with nucleophiles. The results of this study, which evolved into an examination of a novel cyclopropanation reaction, are described herein. Part of this work has been the subject of a preliminary communication.<sup>8</sup>

## Results and discussion

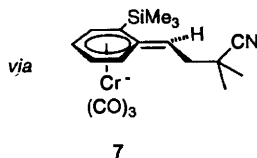
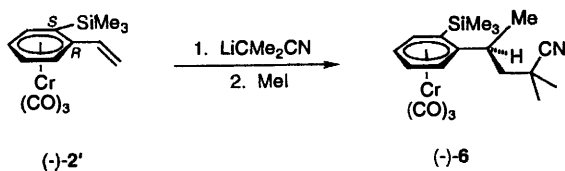
The first report<sup>5</sup> of nucleophilic attack on tricarbonyl(styrene)chromium(0) 5 demonstrated that attack occurred at the  $\beta$ -carbon of the alkene. This report was followed, some time later, by a more detailed survey of the scope and limitations of the reaction,<sup>7</sup> which revealed *inter alia* that the  $\alpha$ -carbanions generated on nucleophilic attack may be quenched with



Scheme 1

electrophiles. Much more recently, enantiomerically pure tricarbonyl(2-methoxystyrene)chromium(0) was shown to undergo a completely stereoselective tandem  $\beta$ -nucleophilic,  $\alpha$ -electrophilic addition sequence with *tert*-butyl lithium and iodomethane.<sup>9</sup> Thus, the likelihood of a  $\beta$ -nucleophilic,  $\alpha$ -electrophilic addition sequence on complex (–)-2' proceeding with high stereochemical control seemed good. Indeed it was found that addition of the lithium anion of isobutyronitrile to complex (–)-2' followed by quenching with iodomethane gave the predicted product (–)-6 as a single diastereoisomer in 61% yield (Scheme 2). The relative stereochemistry of (–)-6, which was determined by an X-ray crystal structure analysis (Fig. 1), may be explained by invoking intermediate 7, in which interactions between the trimethylsilyl substituent and the alkene substituents are minimised and attack of the electrophile occurs on the face away from the tricarbonylchromium(0) rotor (the *exo* face of the complex).

Although we were initially encouraged by the formation of complex (–)-6 as one diastereoisomer in acceptable yield, we were subsequently disappointed to find that the range of nucleophiles and electrophiles that gave similar results was very limited. Low yields had also been obtained with anything other



Scheme 2

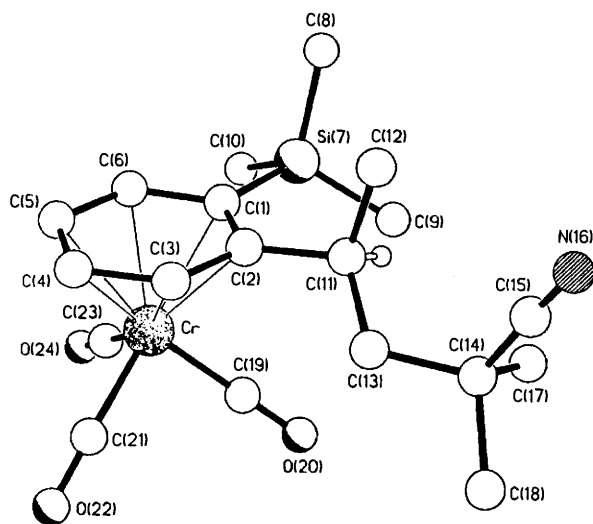
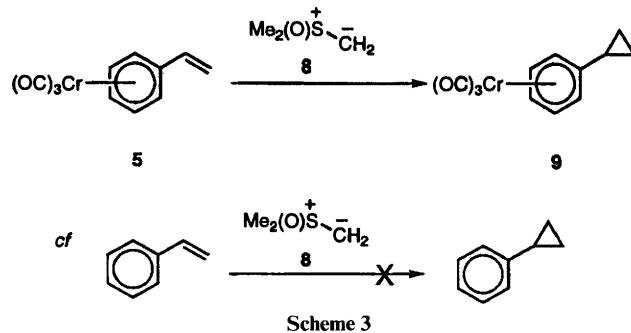


Fig. 1 Molecular structure of complex (-)-6 (C<sub>19</sub>H<sub>25</sub>CrNO<sub>3</sub>Si). Selected bond lengths (Å) and bond angles (°): C(1)–C(2) 1.438(9), C(2)–C(3) 1.424(10), C(3)–C(4) 1.403(12), C(4)–C(5) 1.34(2), C(5)–C(6) 1.42(2), C(1)–C(6) 1.420(12), C(1)–Si(7) 1.899(8) and C(2)–C(11) 1.507(9); C(6)–C(1)–Si(7) 114.9(6), C(2)–C(1)–Si(7) 127.7(5), C(1)–C(2)–C(11) 121.0(6) and C(3)–C(2)–C(11) 119.7(6)

than a narrow range of reagents in the studies of the parent complex **5**; these were attributed to an apparent ready reversibility of the nucleophilic addition step<sup>7</sup> and/or the formation of dimeric products arising from attack of the  $\alpha$ -carbanions on a second molecule of the styrene complex.<sup>5,7</sup> We reasoned that incorporation of an intramolecular electrophilic quench may limit the severity of these problems. It was decided to test this hypothesis on a relatively simple substrate before examining the stereochemical implications of using complex (-)-2'. Accordingly, tricyclopentadienylchromium(0) **5** was synthesised using a literature procedure<sup>3</sup> and then treated with sulfur ylide **8** [derived from (Me<sub>3</sub>SO)<sup>+</sup>CH<sub>2</sub><sup>-</sup>/NaH<sup>10</sup>]. After the reaction between **5** and **8** had proceeded for 3 days at room temperature, we were pleased to find that tricyclopentadienyl-(phenylcyclopropane)chromium(0) **9** could be isolated from the product mixture in 61% yield (Scheme 3). In contrast, reaction of styrene itself with ylide **8** at room temperature for 1 day did not generate any phenylcyclopropane.

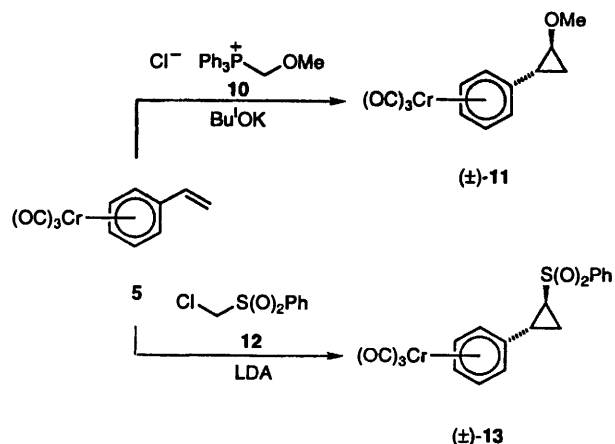
Tricyclopentadienylchromium(0) complexes of cyclopropyl substituted arenes have received surprisingly little attention to date. Although tricyclopentadienyl(phenylcyclopropane)chromium(0) **9** has been prepared in 20% yield from phenylcyclopropane and [Cr(CO)<sub>3</sub>(NH<sub>3</sub>)<sub>3</sub>]<sup>11</sup> and it has been used in arene exchange studies,<sup>12</sup> and, more recently, a tricyclopentadienylchromium(0) complex of *cis*-1-(2-methoxyphenyl)-2-phenylcyclopropane has been formed by the asymmetric cyclopropanation of styrene with an iron carbene derived from [C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>]<sup>-</sup> and (-)-tricyclopentadienyl(2-methoxybenzaldehyde)chromium(0),<sup>13</sup> to the



Scheme 3

best of our knowledge, these are the only reports of tricyclopentadienylchromium(0) complexes of cyclopropyl-substituted arenes to date. Thus, in order to probe our newly discovered mode of reactivity of tricyclopentadienyl(styrene)chromium(0) **5** further, and to test not only whether or not more highly substituted cyclopropanes may be synthesised by this method but also how effective different types of nucleophiles and electrophiles would be, the sulfur ylide **8** was replaced with several other reagents which, it was proposed, would react in a similar manner.

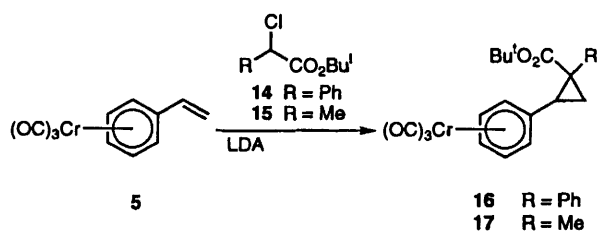
As certain phosphorus ylides are known to add to activated alkenes to give cyclopropanes,<sup>14</sup> the ylide generated from [MeOCH<sub>2</sub>PPh<sub>3</sub>]<sup>+</sup>Cl<sup>-</sup> **10** and Bu<sup>t</sup>OK was treated with complex **5** with a view to generating a disubstituted cyclopropane (Scheme 4). Examination of the <sup>1</sup>H NMR spectrum of the crude



Scheme 4

product mixture revealed that indeed the disubstituted cyclopropane complex (±)-**11** had been formed with a diastereoisomeric excess of 63%. Purification of the product mixture by column chromatography and crystallisation gave diastereoisomerically enriched material (92% de) in 56% yield. On the basis of the coupling constant observed between CHOMe and CHAr (<sup>3</sup>J = 2.5 Hz), the geometry of the major diastereoisomer of (±)-**11** was assigned as *trans*. The reaction between the lithium anion of ClCH<sub>2</sub>S(O)<sub>2</sub>Ph<sup>15</sup> **12** and complex **5** proved to be more selective. Only one diastereoisomer could be detected in the crude product mixture generated from this reaction and work-up led to the isolation of a 74% yield of (±)-**13** of high diastereoisomeric purity (>98% de). The geometry of complex (±)-**13** was also assigned on the basis of *J* values as *trans*. Thus the major product obtained from the reaction of complex **5** with reagents **10** and **12** proved to be the *trans* cyclopropane.

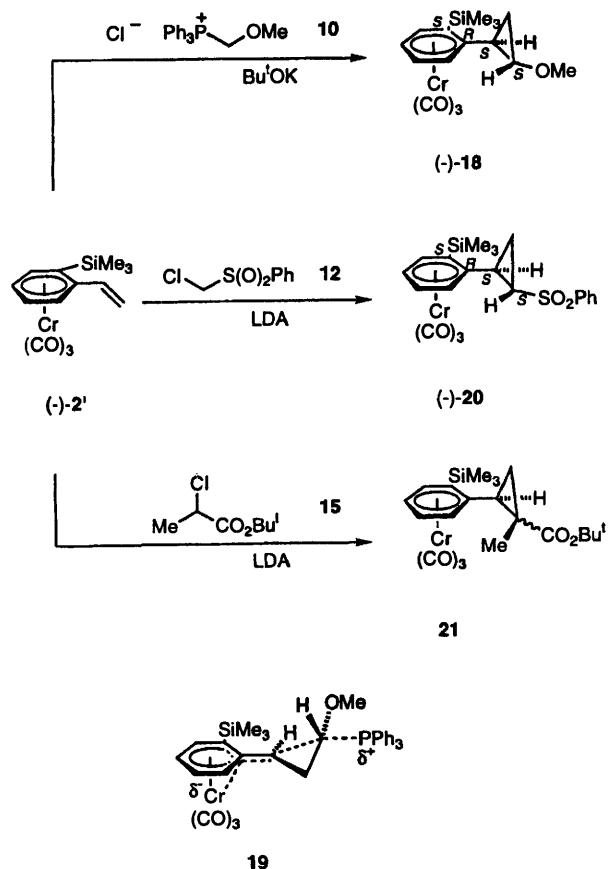
To determine whether or not trisubstituted cyclopropanes could be synthesised from tricyclopentadienyl(styrene)chromium(0) **5**, the lithium anion of PhCH(Cl)CO<sub>2</sub>Bu<sup>16</sup> was synthesised and treated with complex **5** (Scheme 5). Although the trisubstituted cyclopropane **16** was formed in this reaction, its



Scheme 5

diastereoisomeric purity in the crude product mixture was very low (10% de). Subsequent purification proved very difficult and it only proved possible to generate material of moderate diastereoisomeric enrichment (40% de) in 66% yield. In contrast, the reaction between the lithium anion of  $\text{MeCH}(\text{Cl})\text{CO}_2\text{Bu}^t$  **15**<sup>16</sup> and complex **5** proved more selective. The diastereoisomeric excess of product **17** in the crude product mixture was determined to be 62% and chromatography and crystallisation afforded a sample of the trisubstituted cyclopropane **17** of high diastereoisomeric purity (>98% de) in 58% yield. Unfortunately the stereochemistry of the major diastereoisomer of complex **17** could not be determined with any degree of certainty from the data available.

Having established that the deprotonated derivatives of reagents **10**, **12** and **15** react with tricarbyl(styrene)chromium(0) **5** to form cyclopropanes, and that the products of each of these reactions [(±)-**11**, (±)-**13** and **17** respectively] may be isolated in acceptable yield (56–74%) and good diastereoisomeric purity (92–>98% de) after chromatography and crystallisation, we then refocused our attention on the enantiomerically pure 2-(trimethylsilyl)styrene complex (–)-**2'**. We began our examination of the reactivity of this complex towards the deprotonated derivatives of reagents **10**, **12** and **15** (Scheme 6) by adding (–)-tricarbyl[2-(trimethylsilyl)styrene]chromium(0), (–)-**2'**, to a solution of the ylide derived



Scheme 6

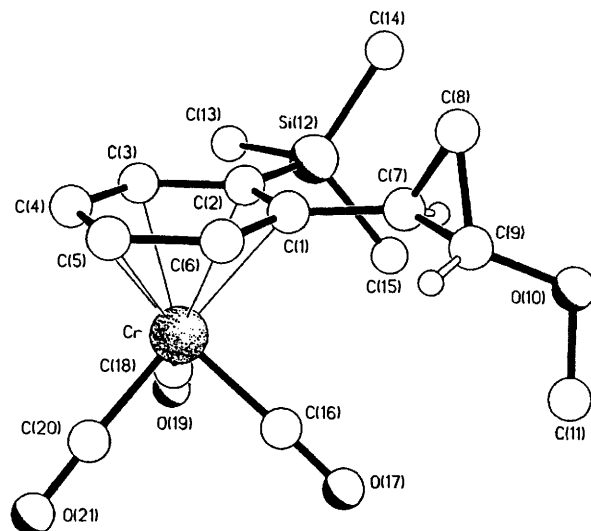


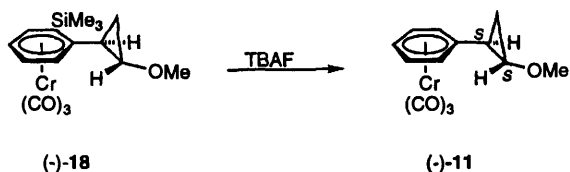
Fig. 2 Molecular structure of complex (–)-**18** ( $\text{C}_{16}\text{H}_{20}\text{CrO}_4\text{Si}$ ). Selected bond lengths (Å) and bond angles ( $^\circ$ ): C(1)–C(7) 1.483(9), C(7)–C(8) 1.517(10), C(8)–C(9) 1.447(11), C(7)–C(9) 1.487(9) and C(9)–O(10) 1.390(8); C(1)–C(7)–C(8) 118.7(7), C(1)–C(7)–C(9) 125.5(6), C(9)–C(7)–C(8) 57.6(5), C(9)–C(8)–C(7) 60.2(5), C(8)–C(9)–C(7) 62.2(5), O(10)–C(9)–C(8) 116.2(7) and O(10)–C(9)–C(7) 119.5(6)

from phosphonium salt **10** and  $\text{Bu}^t\text{OK}$ . This gave a crude product mixture which contained only two diastereoisomers in a ratio of 89:11 [assuming the (arene)tricarbylchromium(0) unit is stereochemically stable, four possible diastereoisomers could have been generated in this reaction]. Subsequent chromatography and crystallisation gave (–)-**18** of good diastereoisomeric purity (>98%) in 66% yield. Examination of the coupling constants in the  $^1\text{H}$  NMR spectrum of the major diastereoisomer of (–)-**18** led to the conclusion that it was one of the two possible *trans* diastereoisomers. Assuming that interactions between the trimethylsilyl substituent and the alkene substituents are minimised in the transition state and that nucleophilic attack occurs from the *exo* face of the complex, as was observed in the formation of (–)-**6**, we predicted that the reaction of complex (–)-**2'** with the ylide derived from **10** would occur through transition state **19** and generate Ar-(1*R*,2*S*)-tricarbyl{(1*R*,2*R*)-*trans*-1-methoxy-2-[2-(trimethylsilyl)phenyl]cyclopropane}chromium(0). A subsequent X-ray crystal analysis of (–)-**18** revealed, however, that in fact it was the stereoisomer Ar-(1*R*,2*S*)-tricarbyl{(1*S*,2*S*)-*trans*-1-methoxy-2-[2-(trimethylsilyl)phenyl]cyclopropane}chromium(0) which had been formed (Fig. 2). It is thus postulated that this is the thermodynamically more stable diastereoisomer and that equilibration occurs *via* cleavage of the cyclopropane ring, a process facilitated by the ring's electron donor and acceptor substituents.

Reaction of complex (–)-**2'** with the lithium anion of  $\text{ClCH}_2\text{S}(\text{O})_2\text{Ph}$  gave a crude product containing three diastereoisomers of the product cyclopropane in a 58:21:21 ratio. Purification produced a 40% yield of the major diastereoisomer of good diastereoisomeric purity (>98% de). Assuming that once again the thermodynamically more stable stereoisomer has been isolated, complex (–)-**20** is predicted to be Ar(1*R*,2*S*)-tricarbyl{(1*S*,2*S*)-*trans*-1-(phenylsulfonyl)-2-[2-(trimethylsilyl)phenyl]cyclopropane}chromium(0). Addition of complex (–)-**2'** to the lithium anion of  $\text{MeCHClCO}_2\text{Bu}^t$  **15** gave a crude product mixture containing three diastereoisomers of the trisubstituted cyclopropane **21** in a 2:2:1 ratio; despite careful and repeated attempts to isolate pure diastereoisomers, only a mixture of two of the diastereoisomers (47% yield, 10% de) could be obtained from this reaction.

Finally, in order to determine whether or not the trimethylsilyl group could be removed from the cyclopropane products under mild conditions and without loss of

stereochemistry, a sample of (–)-**18** was treated with tetrabutylammonium fluoride at 0–5 °C for 1.5 h. Solvent removal and column chromatography gave the desilylated product (–)-**11** (Scheme 7) which was determined to be of 98%



Scheme 7

ee by HPLC using a chiral column and the sample of (±)-**11** generated earlier as a reference; subsequent crystallisation gave (–)-tricarbonyl[(1*S*,2*S*)-*trans*-1-methoxy-2-phenylcyclopropane] chromium(0) (–)-**11** of 99.4% ee in 91% yield.

## Experimental

All reactions were performed under nitrogen using standard vacuum line and Schlenk tube techniques.<sup>17</sup> Reactions and operations involving (arene)tricarbonylchromium(0) complexes were protected from light. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Diethyl ether was stored over sodium wire for several days before use. Light petroleum (40–60 °C) was redistilled for all column chromatography. The tricarbonyl(styrene)chromium(0) complexes (–)-**2**<sup>2</sup> and **5**,<sup>3</sup> phenyl chloromethyl sulfone **12**,<sup>15</sup> the  $\alpha$ -chloro esters **14** and **15**<sup>16</sup> and the ylide Me<sub>2</sub>S(O)CH<sub>2</sub> **8**<sup>10</sup> were synthesised according to published procedures. All other reagents were used as obtained from commercial sources. Column chromatography was performed on silica gel (40–63  $\mu$ m, BDH Laboratory Supplies).

Melting points were obtained on an Electrothermal IA9100 Digital melting point apparatus and are uncorrected. Elemental analyses were performed by the Imperial College Microanalytical Service. Optical rotations were recorded on a Perkin-Elmer 241 Polarimeter using a 10 cm pathlength and are given in units of 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup>. Concentrations are given in g 100 cm<sup>-3</sup>. IR spectra were obtained on a Mattson 5000 FTIR instrument. NMR spectra were recorded in CDCl<sub>3</sub> at room temperature on JEOL GSX 270, Bruker DRX 400 and Bruker AM 500 spectrometers. *J* Values are given in Hz. Mass spectra were recorded on a VG Micromass 7070E and an AutoSpec-Q instrument using EI and CI techniques. Chiral HPLC analyses were carried out on an ATI Unicam Crystal 200 HPLC with an ATI Unicam Spectra 100 UV–VIS detector using a Chiralcel OD-H column (0.46 cm  $\Phi$   $\times$  25 cm, Daicel Chemical Industries Ltd).

LDA refers to lithium diisopropylamide. The notation 'dia.<sub>major</sub>' and 'dia.<sub>minor</sub>' refers to major and minor diastereoisomers, respectively.

### (–)-Ar(1*R*,2*S*)-Tricarbonyl[(4*S*)-2,2-dimethyl-4-[2-(trimethylsilyl)phenyl]pentanenitrile]chromium(0) (–)-**6**

To a cooled (–78 °C) solution of butyllithium (1.75 cm<sup>3</sup> of a 1.5 mol dm<sup>-3</sup> solution in hexane, 2.63 mmol) in THF (8 cm<sup>3</sup>) was added dropwise isobutyronitrile (182 mg, 2.63 mmol) with stirring. The reaction mixture was allowed to reach –20 °C over 30 min. To this solution was added (–)-Ar(1*R*,2*S*)-tricarbonyl[2-(trimethylsilyl)styrene]chromium(0) (674 mg, 1.88 mmol) (–)-**2**<sup>2</sup> in THF (5 cm<sup>3</sup>) at –78 °C. The reaction mixture was allowed to reach –20 °C quickly and subsequently stirred for 2 h as it warmed from –20 to 0 °C. After cooling again to –78 °C, iodomethane (441 mg, 3.10 mmol) was administered dropwise. After warming from –20 to 0 °C with stirring over 2 h, the reaction mixture was allowed to reach room temperature. The solvent was removed under reduced pressure and the resulting residue was taken up in Et<sub>2</sub>O (30

cm<sup>3</sup>), washed with sat. aqueous NH<sub>4</sub>Cl (10 cm<sup>3</sup>) and brine (10 cm<sup>3</sup>), dried over MgSO<sub>4</sub> and concentrated. Purification by column chromatography (SiO<sub>2</sub>; light petroleum–CH<sub>2</sub>Cl<sub>2</sub>, 2:1 to 1:1) followed by crystallisation (hexane–CH<sub>2</sub>Cl<sub>2</sub>) yielded yellow crystals of the *title compound* (–)-**6** (453 mg, 61%), mp 112–114 °C, [ $\alpha$ ]<sub>D</sub><sup>23</sup> –25.6 (*c* 1.36, CHCl<sub>3</sub>); (Found: C, 57.7; H, 6.4; N, 3.5. C<sub>19</sub>H<sub>25</sub>CrNO<sub>3</sub>Si requires C, 57.70; H, 6.37; N, 3.54%);  $\nu_{\max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 1963vs and 1885vs (C=O);  $\delta_{\text{H}}$ (270 MHz) 0.41 (9 H, s, SiMe<sub>3</sub>), 1.45 (3 H, d, *J* 6, CH<sub>3</sub>), 1.46 (3 H, s, CH<sub>3</sub>), 1.49 (3 H, s, CH<sub>3</sub>), 1.88 (1 H, dd, *J* 14 and 10, CH<sub>2</sub>), 1.95 (1 H, dd, *J* 14 and 3, CH<sub>2</sub>), 2.89 (1 H, dqd, *J* 10, 6 and 3, CH), 4.98 (1 H, dd, *J* 6 and 1, ArH), 5.19 (1 H, dt, *J* 6 and 1, ArH), 5.44 (1 H, dd, *J* 6 and 1, ArH) and 5.57 (1 H, dt, *J* 6 and 1, ArH);  $\delta_{\text{C}}\{^1\text{H}\}$ (67.5 MHz) 1.1 (SiMe<sub>3</sub>), 25.5 and 25.8 (2  $\times$  CH<sub>3</sub>), 30.0 (CH<sub>3</sub>CH), 30.6 (C–CN), 34.0 (CH<sub>2</sub>), 45.7 (CHMe), 88.4, 90.4, 95.4 and 100.4 (4  $\times$  ArC), 99.0 and 125.4 (2  $\times$  ArC<sub>ipso</sub>), 127.4 (C $\equiv$ N) and 233.2 (C=O); *m/z* (EI, 70 eV, 240 °C) 395 (M<sup>+</sup>, 1.3%), 367 (M – CO, 0.5), 354 (M – CN – CH<sub>3</sub>, 3), 339 (M – CN – 2  $\times$  CH<sub>3</sub>, 3), 311 [M – CH<sub>3</sub> – NCCH(CH<sub>3</sub>)<sub>2</sub>, 100] and 52 (Cr, 100).

### Tricarbonyl(phenylcyclopropane)chromium(0) **9**

To a solution of tricarbonyl(styrene)chromium(0) **5** (519 mg, 2.16 mmol) in THF (3 cm<sup>3</sup>) was added at room temp. a solution of Me<sub>2</sub>S(O)CH<sub>2</sub> **8** (35.8 cm<sup>3</sup> of 0.067 mol dm<sup>-3</sup> solution in THF, 2.40 mmol). After stirring for 2 d at this temperature, another batch (6.45 cm<sup>3</sup>, 0.43 mmol) of the ylide was administered and the reaction was continued for a further day. The solvent was removed under reduced pressure and the residue taken up in Et<sub>2</sub>O (30 cm<sup>3</sup>), washed with sat. aqueous NH<sub>4</sub>Cl solution (20 cm<sup>3</sup>) and brine (20 cm<sup>3</sup>), dried over MgSO<sub>4</sub> and concentrated. Purification by column chromatography (SiO<sub>2</sub>; light petroleum–Et<sub>2</sub>O, 1:2) yielded after recrystallisation (Et<sub>2</sub>O–hexane) the *title compound* **9** as a yellow powder (335 mg, 61%), mp 86–87 °C (Found: C, 56.6; H, 4.1. C<sub>12</sub>H<sub>10</sub>CrO<sub>3</sub> requires C, 56.70; H, 3.97%);  $\nu_{\max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 1966vs and 1885vs (C=O);  $\delta_{\text{H}}$ (270 MHz) 0.71 (2 H, m, CH<sub>2</sub>), 1.02 (2 H, m, CH<sub>2</sub>), 1.62 (1 H, tt, *J* 8 and 5, Ar–CH), 5.08–5.15 (3 H, m, ArH) and 5.38 (2 H, t, *J* 6, ArH);  $\delta_{\text{C}}\{^1\text{H}\}$ (100 MHz) 9.8 (2  $\times$  CH<sub>2</sub>), 14.6 (Ar–CH), 89.9, 90.1 and 93.7 (3  $\times$  ArC), 117.3 (ArC<sub>ipso</sub>) and 233.4 (C=O); *m/z* (CI, NH<sub>3</sub>) 272 (MNH<sub>4</sub><sup>+</sup>, 17%), 255 (MH, 100), 118 [M – Cr(CO)<sub>3</sub>, 4] and 52 (Cr, 13).

**Control experiment.** To a solution of ylide **8** (10 cm<sup>3</sup> of a 0.045 mol dm<sup>-3</sup> solution in THF, 0.45 mmol) was added styrene (42 mg, 0.40 mmol) *via* a syringe. After stirring for 24 h at room temp., the reaction mixture was concentrated under reduced pressure (0 °C; 1 Torr) and taken up in Et<sub>2</sub>O (10 cm<sup>3</sup>). The organic layer was washed with sat. aqueous NH<sub>4</sub>Cl (5 cm<sup>3</sup>) and brine (5 cm<sup>3</sup>), dried over MgSO<sub>4</sub> and concentrated under reduced pressure (20 °C; 25 Torr). No signals corresponding to phenylcyclopropane could be detected in the crude <sup>1</sup>H NMR spectrum.

### Tricarbonyl(*trans*-1-methoxy-2-phenylcyclopropane)-chromium(0) (±)-**11**

To a solution of potassium *tert*-butoxide (370 mg, 3.30 mmol) in THF (10 cm<sup>3</sup>) was added (methoxymethyl)triphenylphosphonium chloride **10** (1.03 g, 3.00 mmol), as a solid. After stirring at room temp. for 30 min, tricarbonyl(styrene)chromium(0) **5** (480 mg, 2.00 mmol) was added at 0 °C as a solid. After stirring for 30 min, the reaction temperature was allowed to reach room temp. over 30 min. The solvent was removed under reduced pressure and the residue was taken up in Et<sub>2</sub>O (30 cm<sup>3</sup>). The organic layer was washed with sat. aqueous NH<sub>4</sub>Cl solution (20 cm<sup>3</sup>) and brine (20 cm<sup>3</sup>), dried over MgSO<sub>4</sub> and concentrated. The diastereoisomeric excess of the crude reaction mixture was determined to be 63% by integration of the OCH<sub>3</sub> signals ( $\delta_{\text{major}}$  3.41,  $\delta_{\text{minor}}$  3.25) of the crude <sup>1</sup>H NMR spectrum. Purification by column chromatography (SiO<sub>2</sub>; light petroleum–CH<sub>2</sub>Cl<sub>2</sub>, 1:1 to 1:2) and

recrystallisation (hexane-CH<sub>2</sub>Cl<sub>2</sub>) gave the *title compound* ( $\pm$ )-**11** as yellow crystals (317 mg, 56%, de 92%), mp 51–55 °C. A second crystallisation yielded further ( $\pm$ )-**11** as a yellow solid (96 mg, 17%, de 80%) (Found: C, 54.8; H, 4.4. C<sub>13</sub>H<sub>12</sub>CrO<sub>4</sub> requires C, 54.94; H, 4.26%);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  1966vs and 1886vs (C=O);  $\delta_{\text{H}}(270 \text{ MHz})$  0.96 (1 H, q, *J* 6, CH<sub>2</sub>), 1.32 (1 H, ddd, *J* 10, 6 and 4, CH<sub>2</sub>), 1.79 (1 H, ddd, *J* 10, 6 and 2.5, Ar-CH), 3.32 (1 H, ddd, *J* 6, 4 and 2.5, CHOMe), 3.41 (3 H, s, OMe), 5.03 (1 H, d, *J* 6, ArH), 5.18 (2 H, m, ArH) and 5.35 (2 H, m, ArH);  $\delta_{\text{C}}\{^1\text{H}\}(125.8 \text{ MHz})$  16.6 (CH<sub>2</sub>), 22.3 (Ar-CH), 58.2 (CHOMe), 63.1 (OMe), 90.2, 90.6, 91.3, 92.8 and 92.9 (5 × ArC), 113.7 (ArC<sub>ipso</sub>) and 233.0 (C=O); *m/z* (CI, NH<sub>3</sub>) 302 (MNH<sub>4</sub><sup>+</sup>, 12%), 285 (MH, 100), 200 [M - (CO)<sub>3</sub>, 18], 148 [M - Cr(CO)<sub>3</sub>, 4] and 52 (Cr, 34).

#### Tricarbonyl[*trans*-1-phenyl-2-(phenylsulfonyl)cyclopropane]-chromium(0) ( $\pm$ )-**13**

To a cooled (−78 °C) solution of LDA (1.31 cm<sup>3</sup> of a 1.5 mol dm<sup>−3</sup> solution in hexane, 1.96 mmol) in THF (5 cm<sup>3</sup>) was added solid phenyl chloromethyl sulfone **12** (357 mg, 1.87 mmol). After 30 min, a solution of tricarbonyl(styrene)chromium(0) **5** (375 mg, 1.56 mmol) in THF (5 cm<sup>3</sup>) was added *via* a cannula. The temperature was allowed to reach room temp. over 5 h and was stirred for 10 h at this temperature. The solvent was removed under reduced pressure and the residue taken up in Et<sub>2</sub>O (100 cm<sup>3</sup>), washed with sat. aqueous NH<sub>4</sub>Cl solution (20 cm<sup>3</sup>) and brine (20 cm<sup>3</sup>), dried over MgSO<sub>4</sub> and concentrated. In the crude <sup>1</sup>H NMR spectrum, only one diastereoisomer could be detected. Purification by column chromatography (SiO<sub>2</sub>; light petroleum-CH<sub>2</sub>Cl<sub>2</sub>, 1:2 to 1:8) yielded after recrystallisation (CH<sub>2</sub>Cl<sub>2</sub>-hexane) the *title compound* ( $\pm$ )-**13** as a yellow powder (455 mg, 74%, de >98%), mp 92 °C (Found: C, 54.6; H, 3.4. C<sub>18</sub>H<sub>14</sub>CrO<sub>5</sub>S requires C, 54.82; H, 3.58%);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  1971vs and 1896vs (C=O);  $\delta_{\text{H}}(270 \text{ MHz})$  1.43 (1 H, dt, *J* 8.5 and 6, CH<sub>2</sub>), 1.87 (1 H, dt, *J* 10 and 6, CH<sub>2</sub>), 2.63 (1 H, ddd, *J* 10, 6 and 5, Ar-CH or CHSO<sub>2</sub>Ph), 2.71 (1 H, ddd, *J* 8.5, 6 and 5, Ar-CH or CHSO<sub>2</sub>Ph), 5.02 (1 H, m, ArH), 5.18–5.30 (4 H, m, ArH), 7.57–7.72 (3 H, m, PhH) and 7.93 (2 H, m, PhH);  $\delta_{\text{C}}\{^1\text{H}\}(125.8 \text{ MHz})$  13.8 (CH<sub>2</sub>), 22.5 (Ar-CH), 42.0 (CHSO<sub>2</sub>Ph), 91.3, 91.3, 91.4, 92.2, and 92.9 (5 × ArC), 107.9 (ArC<sub>ipso</sub>), 127.6, 129.5 and 133.9 (3 × PhC), 139.7 (PhC<sub>ipso</sub>) and 232.1 (C=O); *m/z* (CI, NH<sub>3</sub>) 412 (MNH<sub>4</sub><sup>+</sup>, 57%), 395 (MH, 7), 276 [MNH<sub>4</sub> - Cr(CO)<sub>3</sub>, 100], 259 [MH - Cr(CO)<sub>3</sub>, 8], 117 [M - Cr(CO)<sub>3</sub> - SO<sub>2</sub>Ph, 62] and 52 (Cr, 18).

#### Tricarbonyl[1-(*tert*-butoxycarbonyl)-1,2-diphenylcyclopropane]-chromium(0) **16**

To a cooled (−78 °C) solution of LDA (1.33 cm<sup>3</sup> of a 1.5 mol dm<sup>−3</sup> solution in hexane, 2.00 mmol) in THF (10 cm<sup>3</sup>) was added dropwise with stirring a solution of *tert*-butyl 2-chloro-2-phenylacetate **14** (454 mg, 2.00 mmol) in THF (91.5 cm<sup>3</sup>). After 20 min, tricarbonyl(styrene)chromium(0) **5** (240 mg, 1.00 mmol) was administered as a solid and the reaction mixture was allowed to reach 0–5 °C within 1 h and stirred for a further 12 h at this temperature. The solvent was removed under reduced pressure, the residue taken up in Et<sub>2</sub>O and filtered through silica gel (Et<sub>2</sub>O as eluent), yielding a yellow oil. The diastereoisomeric excess was determined to be 10% by integration of the CO<sub>2</sub>Bu<sup>t</sup> signals ( $\delta_{\text{major}}$  1.38;  $\delta_{\text{minor}}$  1.19) in the crude <sup>1</sup>H NMR spectrum. Purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>-hexane) gave the *title compound* **16** as a yellow powder (66%, de 40%), mp 117–123 °C (Found: C, 63.9; H, 5.0. C<sub>23</sub>H<sub>22</sub>CrO<sub>5</sub> requires C, 64.18; H, 5.15%);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  1968vs and 1891vs (C=O) and 1712s (C=O); *m/z* (CI, NH<sub>3</sub>) 448 (MNH<sub>4</sub><sup>+</sup>, 71%), 431 (MH, 7), 392 (MNH<sub>4</sub> - 2CO, 100), 375 (MH - 2CO, 27), 312 [MNH<sub>4</sub> - Cr(CO)<sub>3</sub>, 24], 256 [MH - Cr(CO)<sub>3</sub>C<sub>4</sub>H<sub>8</sub>, 57] and 52 (Cr, 9); Major diastereoisomer:  $\delta_{\text{H}}(270 \text{ MHz})$  1.38 [9 H, s, C(CH<sub>3</sub>)<sub>3</sub>], 1.65 (1 H, dd, *J* 7 and 5,

CH<sub>2</sub>), 2.08 (1 H, dd, *J* 9 and 5, CH<sub>2</sub>), 2.66 (1 H, dd, *J* 9 and 7, ArCH), 4.17 (1 H, d, *J* 6, ArH), 4.94 (1 H, dt, *J* 6 and 1, ArH), 5.04 (1 H, tt, *J* 6 and 1, ArH), 5.28–5.50 (2 H, m, ArH) and 7.05–7.45 (5 H, m, PhH);  $\delta_{\text{C}}\{^1\text{H}\}(100 \text{ MHz})$  19.0 (CH<sub>2</sub>), 27.9 [C(CH<sub>3</sub>)<sub>3</sub>], 30.1 (ArCH), 39.7 (MeCCO<sub>2</sub>Bu<sup>t</sup>), 81.6 [C(CH<sub>3</sub>)<sub>3</sub>], 89.4, 90.4, 92.4, 93.0 and 93.5 (5 × ArC), 108.7 (ArC<sub>ipso</sub>), 127.3, 128.0 and 131.7 (3 × PhC), 134.3 (PhC<sub>ipso</sub>), 171.4 (CO<sub>2</sub>Bu<sup>t</sup>) and 232.9 (C=O); Minor diastereoisomer:  $\delta_{\text{H}}(270 \text{ MHz})$  1.19 [9 H, s, C(CH<sub>3</sub>)<sub>3</sub>], 1.63 (1 H, *J* 9 and 6, CH<sub>2</sub>), 2.11 (1 H, dd, *J* 7 and 6, CH<sub>2</sub>), 2.51 (1 H, dd, *J* 9 and 7, ArCH), 5.21 (1 H, t, *J* 6, ArH), 5.28–5.50 (4 H, m, ArH) and 7.05–7.45 (5 H, m, PhH);  $\delta_{\text{C}}\{^1\text{H}\}(100 \text{ MHz})$  17.4 (CH<sub>2</sub>), 27.8 [C(CH<sub>3</sub>)<sub>3</sub>], 31.6 (ArCH), 40.1 (MeCCO<sub>2</sub>Bu<sup>t</sup>), 81.5 [C(CH<sub>3</sub>)<sub>3</sub>], 90.7, 92.7, 92.8, 93.2 and 93.5 (5 × ArC), 107.9 (ArC<sub>ipso</sub>), 127.4, 128.3, 129.6 (3 × PhC), 139.4 (PhC<sub>ipso</sub>), 169.0 (CO<sub>2</sub>Bu<sup>t</sup>) and 232 (C=O).

#### Tricarbonyl[1-(*tert*-butoxycarbonyl)-1-methyl-2-phenylcyclopropane]chromium(0) **17**

To a cooled (−78 °C) LDA solution (0.60 cm<sup>3</sup> of a 1.5 mol dm<sup>−3</sup> solution in hexane, 0.90 mmol) in THF (6 cm<sup>3</sup>) was added dropwise with stirring a solution of *tert*-butyl 2-chloropropanoate **15** (123 mg, 0.75 mmol) in THF (1 cm<sup>3</sup>). After 20 min, tricarbonyl(styrene)chromium(0) **5** (80 mg, 0.33 mmol) in THF (1 cm<sup>3</sup>) was administered and the reaction mixture was allowed to reach room temp. over 5 h and stirred for a further 12 h. The solvent was concentrated under reduced pressure, the residue taken up in Et<sub>2</sub>O and filtered through silica gel (Et<sub>2</sub>O as eluent), yielding a yellow oil. The diastereoisomeric excess was determined to be 62% by integration of the CO<sub>2</sub>Bu<sup>t</sup> ( $\delta_{\text{major}}$  1.45;  $\delta_{\text{minor}}$  1.24) and CH<sub>3</sub> signals ( $\delta_{\text{major}}$  1.09;  $\delta_{\text{minor}}$  1.40) in the crude <sup>1</sup>H NMR spectrum. Purification by column chromatography (SiO<sub>2</sub>; light petroleum-Et<sub>2</sub>O, 5:1) gave after crystallisation (Et<sub>2</sub>O-pentane) the major diastereoisomer of the *title compound* **17** as yellow crystals (70.0 mg, 58%, de >98%) mp 101–102 °C. Crystallisation of the second column fraction gave the minor diastereoisomer of **17** (15 mg, 12%, de >98%) as a yellow solid; major diastereoisomer (Found: C, 58.7; H, 5.1. C<sub>18</sub>H<sub>20</sub>CrO<sub>5</sub> requires C, 58.68; H, 5.48%);  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  1969vs and 1891vs (C=O) and 1710s (C=O);  $\delta_{\text{H}}(270 \text{ MHz})$  0.96 (1 H, dd, *J* 7 and 5, CH<sub>2</sub>), 1.09 (3 H, s, CH<sub>3</sub>), 1.45 [9 H, s, C(CH<sub>3</sub>)<sub>3</sub>], 1.63 (1 H, dd, *J* 9 and 5, CH<sub>2</sub>), 2.24 (1 H, dd, *J* 9 and 7, 1 H, ArCH), 5.03 (1 H, d, *J* 6, ArH), 5.19 (1 H, m, ArH) and 5.29–5.42 (3 H, m, ArH);  $\delta_{\text{C}}\{^1\text{H}\}(125.8 \text{ MHz})$  14.4 (CH<sub>3</sub>), 19.3 (CH<sub>2</sub>), 27.3 (MeCCO<sub>2</sub>Bu<sup>t</sup>), 28.0 [C(CH<sub>3</sub>)<sub>3</sub>], 29.6 (Ar-CH), 80.9 [C(CH<sub>3</sub>)<sub>3</sub>], 90.5, 91.2, 92.8, 93.3 and 93.7 (5 × ArC), 108.8 (ArC<sub>ipso</sub>), 173.1 (CO<sub>2</sub>Bu<sup>t</sup>) and 232.8 (C=O); *m/z* (CI, NH<sub>3</sub>) 386 (MNH<sub>4</sub><sup>+</sup>, 100%), 369 (MH, 21), 330 (MNH<sub>4</sub> - 2CO, 83), 313 (MH - 2CO, 49), 250 [MNH<sub>4</sub> - Cr(CO)<sub>3</sub>, 12], 233 [MH - Cr(CO)<sub>3</sub>, 4] and 52 (Cr, 22); minor diastereoisomer:  $\delta_{\text{H}}(270 \text{ MHz})$  1.12 (1 H, dd, *J* 8 and 5, CH<sub>2</sub>), 1.24 [9 H, s, C(CH<sub>3</sub>)<sub>3</sub>], 1.40 (3 H, s, CH<sub>3</sub>), 1.75 (1 H, dd, *J* 7 and 5, CH<sub>2</sub>), 2.24 (1 H, dd, *J* 8 and 7, Ar-CH), 5.17 (1 H, m, ArH), and 5.25–5.45 (4 H, m, ArH); *m/z* (CI, NH<sub>3</sub>) 386 (MNH<sub>4</sub><sup>+</sup>, 55%), 369 (MH, 12), 330 (MNH<sub>4</sub> - 2CO, 100), 313 (MH - 2CO, 71), 250 [MNH<sub>4</sub> - Cr(CO)<sub>3</sub>, 4] and 52 (Cr, 11).

#### (−)-Ar(1*R*,2*S*)-Tricarbonyl{(1*S*,2*S*)-*trans*-1-methoxy-2-[2-(trimethylsilyl)phenyl]cyclopropane}chromium(0) (−)-**18**

To a solution of potassium *tert*-butoxide (110 mg, 0.98 mmol) in THF (10 cm<sup>3</sup>) was added (methoxymethyl)triphenylphosphonium chloride **10** (343 mg, 1.00 mmol) as a solid. After stirring at room temp. for 30 min, a solution of (−)-Ar(1*R*,2*S*)-tricarbonyl[2-(trimethylsilyl)styrene]chromium(0) (−)-**2** (156 mg, 0.50 mmol) in THF (3 cm<sup>3</sup>) was added at −40 °C *via* a cannula. The reaction temperature was allowed to reach −20 °C over 1.5 h, cooled again to −78 °C and quenched by the addition of sat. aqueous NH<sub>4</sub>Cl solution (10 cm<sup>3</sup>). Most of the THF was removed under reduced pressure and the residue was taken up in Et<sub>2</sub>O (20 cm<sup>3</sup>) and a sufficient amount of H<sub>2</sub>O to dissolve all salts. The aqueous layer was

removed, the organic layer washed with brine (10 cm<sup>3</sup>), dried over MgSO<sub>4</sub> and concentrated. The diastereoisomeric excess of the crude reaction mixture was determined to be 78% by integration of the OMe signals ( $\delta_{\text{major}}$  3.47;  $\delta_{\text{minor}}$  3.38) in the crude <sup>1</sup>H NMR spectrum. Purification by column chromatography (SiO<sub>2</sub>; light petroleum–CH<sub>2</sub>Cl<sub>2</sub>, 1:1 to 1:2) yielded the *title compound* (–)-**18** as a yellow solid (137 mg, 77%, de 94%). Recrystallisation (hexane–CH<sub>2</sub>Cl<sub>2</sub>) gave yellow crystals (117 mg, 66%, de >98%), mp 84–85 °C (Found: C, 53.8; H, 5.5. C<sub>16</sub>H<sub>20</sub>CrO<sub>4</sub>Si requires C, 53.92; H, 5.66%); [ $\alpha$ ]<sub>D</sub><sup>29.5</sup> –164.8 (c 0.52, CHCl<sub>3</sub>);  $\nu_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>–1</sup> 1964vs and 1886vs (C≡O);  $\delta_{\text{H}}$ (270 MHz) 0.43 (9 H, s, SiMe<sub>3</sub>), 0.82 (1 H, q, J 6, CH<sub>2</sub>), 1.34 (1 H, ddd, J 10, 6 and 3.5, CH); 1.95 (1 H, ddd, J 10, 6 and 2.5, Ar–CH), 3.47 (3 H, s, OMe), 3.61 (1 H, ddd, J 6, 3.5 and 2.5, CHOMe), 4.63 (1 H, dd, J 6 and 1, ArH), 5.02 (1 H, dt, J 6 and 1, ArH), 5.49 (1 H, dd, J 6 and 1, ArH) and 5.53 (1 H, dt, J 6 and 1, ArH);  $\delta_{\text{C}}\{^1\text{H}\}$ (125.8 MHz) 0.4 (SiMe<sub>3</sub>), 20.4 (CH<sub>2</sub>), 22.8 (Ar–CH), 58.5 (CHOMe), 61.3 (OMe), 87.1, 88.5, 95.6 and 100.5 (4 × ArC), 98.6 and 120.2 (2 × ArC<sub>ipso</sub>) and 233.4 (C≡O); *m/z* (CI, NH<sub>3</sub>) 374 (MNH<sub>4</sub><sup>+</sup>, 34%), 357 (MH, 100), 325 [MH – MeOH, 26], 238 [MNH<sub>4</sub> – Cr(CO)<sub>3</sub>, 11], 221 [MH – Cr(CO)<sub>3</sub>, 6], 90 (SiMe<sub>3</sub>NH<sub>4</sub>, 88) and 52 (Cr, 29).

(–)-Ar(1*R*,2*S*)-Tricarbonyl{(1*S*,2*S*)-*trans*-1-(phenylsulfonyl)-2-[2-(trimethylsilyl)phenyl]cyclopropane}chromium(0) (–)-**20**

To a cooled (–78 °C) solution of LDA (0.4 cm<sup>3</sup> of a 1.5 mol dm<sup>–3</sup> solution in hexane, 0.60 mmol) in THF (2 cm<sup>3</sup>) was added phenyl chloromethyl sulfone **12** (105 mg, 0.55 mmol) as a solid. After 30 min, a solution of (–)-Ar(1*R*,2*S*)-tricarbonyl[2-(trimethylsilyl)styrene]chromium(0) (–)-**2'** (156 mg, 0.50 mmol) in THF (3 cm<sup>3</sup>) was added *via* a cannula and the temperature was allowed to reach –60 °C quickly. After stirring for 2 h at this temperature the reaction mixture was allowed to reach –40 °C over 2 h. The solvent was removed under reduced pressure and the residue taken up in Et<sub>2</sub>O (100 cm<sup>3</sup>), washed with sat. aqueous NH<sub>4</sub>Cl solution (10 cm<sup>3</sup>) and brine (10 cm<sup>3</sup>), dried over MgSO<sub>4</sub> and concentrated. The diastereoisomeric ratio of the crude reaction mixture was determined to be 58:21:21 by integration of the SiMe<sub>3</sub> signals ( $\delta_{\text{major}}$  0.50;  $\delta_{\text{minor}}$  0.32 and 0.27) in the crude <sup>1</sup>H NMR spectrum. Purification by column chromatography (SiO<sub>2</sub>; light petroleum–CH<sub>2</sub>Cl<sub>2</sub>, 1:2) yielded the *title compound* (–)-**20** as a yellow solid from the first fraction (108 mg, 46%, de 90%) and a yellow oil (75 mg, 32%) containing a mixture of diastereoisomers from the second fraction. Crystallisation of the first fraction (hexane–CH<sub>2</sub>Cl<sub>2</sub>) yielded a yellow powder (93 mg, 40%, de 98%), mp 195 °C (decomp.) (Found: C, 54.3; H, 4.6. C<sub>21</sub>H<sub>22</sub>CrO<sub>5</sub>SSi requires C, 54.06; H, 4.75%); [ $\alpha$ ]<sub>D</sub><sup>28.5</sup> –370.7 (c 0.74, CHCl<sub>3</sub>);  $\nu_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>–1</sup> 1967vs and 1893vs (C≡O);  $\delta_{\text{H}}$ (270 MHz) 0.50 (9 H, s, SiMe<sub>3</sub>), 1.48 (1 H, dt, J 8 and 6, CH<sub>2</sub>), 1.79 (1 H, dt, J 10 and 6, CH<sub>2</sub>), 2.72 (1 H, ddd, J 8, 6 and 4, Ar–CH), 2.96 (1 H, ddd, J 10, 6 and 4, CHSO<sub>2</sub>Ph), 4.50 (1 H, d, J 6, ArH), 5.05 (1 H, t, J 6, ArH), 5.50 (2 H, m, ArH), 7.55–7.68 (3 H, m, PhH) and 7.90 (2 H, d, J 6, PhH);  $\delta_{\text{C}}\{^1\text{H}\}$ (67.5 MHz) 0.5 (SiMe<sub>3</sub>), 15.5 (CH<sub>2</sub>), 22.0 (Ar–CH), 43.6 (CHSO<sub>2</sub>Ph), 85.5, 88.9, 95.2 and 100.0 (4 × ArC), 99.9 and 115.1 (2 × ArC<sub>ipso</sub>), 127.7, 129.5, 133.5 (3 × PhC), 139.9 (PhC<sub>ipso</sub>) and 232.8 (C≡O); *m/z* (CI, NH<sub>3</sub>) 484 (MNH<sub>4</sub><sup>+</sup>, 47%), 467 (MH, 7), 348 [MNH<sub>4</sub> – Cr(CO)<sub>3</sub>, 92], 327 (MH<sub>2</sub> – SO<sub>2</sub>Ph, 90), 90 (SiMe<sub>3</sub>NH<sub>4</sub>, 100) and 52 (Cr, 19).

Tricarbonyl{1-(*tert*-butoxycarbonyl)-1-methyl-2-[2-(trimethylsilyl)phenyl]cyclopropane}chromium(0) **21**

To a cooled (–78 °C) solution of LDA (0.7 cm<sup>3</sup> of a 1.5 mol dm<sup>–3</sup> solution in hexane, 1.05 mmol) in THF (2 cm<sup>3</sup>) was added dropwise *tert*-butyl 2-chloropropionate **15** (105 mg, 0.55 mmol). After 30 min, a solution of (–)-Ar(1*R*,2*S*)-tricarbonyl[2-(trimethylsilyl)styrene]chromium(0) (–)-**2'** (156 mg, 0.50 mmol) in THF (3 cm<sup>3</sup>) was added *via* a cannula. The reaction temperature was allowed to reach –40 °C over 30 min,

kept at this temperature for 2 h and finally warmed to –10 °C over 1 h. The reaction was quenched by addition of sat. aqueous NH<sub>4</sub>Cl solution (2 cm<sup>3</sup>) and the THF was removed under reduced pressure and replaced by Et<sub>2</sub>O (20 cm<sup>3</sup>). The organic layer was washed with sat. aqueous NH<sub>4</sub>Cl solution (10 cm<sup>3</sup>) and brine (10 cm<sup>3</sup>), dried over MgSO<sub>4</sub> and concentrated. The diastereoisomeric ratio of the crude reaction mixture was determined to be 2:2:1 by integration of the CO<sub>2</sub>Bu' ( $\delta_{\text{major}}$  1.45 and 1.46;  $\delta_{\text{minor}}$  1.49) and SiMe<sub>3</sub> signals ( $\delta_{\text{major}}$  0.36 and 0.41;  $\delta_{\text{minor}}$  0.40) in the crude <sup>1</sup>H NMR spectrum. Purification by column chromatography (SiO<sub>2</sub>; light petroleum–CH<sub>2</sub>Cl<sub>2</sub>, 1:1) yielded a yellow oil (201 mg, 86%). Crystallisation (CH<sub>2</sub>Cl<sub>2</sub>–hexane) gave yellow crystals (109 mg, 47%), which were shown to be a mixture of two diastereoisomers of the *title compound* **21** (de 10%), mp 67–70 °C (Found: C, 57.2; H, 6.2. C<sub>21</sub>H<sub>28</sub>CrO<sub>5</sub>Si requires C, 57.26; H, 6.41%);  $\nu_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>–1</sup> 1965vs and 1888vs (C≡O) and 1711s (C≡O);  $\delta_{\text{H}}$ (270 MHz) 0.36 (9 H, s, SiMe<sub>3</sub> of dia.<sub>min</sub>), 0.41 (9 H, s, SiMe<sub>3</sub> of dia.<sub>maj</sub>), 0.82 (1 H, dd, J 7 and 4, CH<sub>2</sub> of dia.<sub>maj</sub> or dia.<sub>min</sub>), 1.06 (1 H, dd, J 7 and 5, CH<sub>2</sub> of dia.<sub>maj</sub> or dia.<sub>min</sub>), 1.07 (3 H, s, CH<sub>3</sub> of dia.<sub>min</sub>), 1.34 (3 H, s, CH<sub>3</sub> of dia.<sub>maj</sub>), 1.45 (9 H, s, C<sub>4</sub>H<sub>9</sub> of dia.<sub>maj</sub>), 1.46 (9 H, s, C<sub>4</sub>H<sub>9</sub> of dia.<sub>min</sub>), 1.61 (1 H, dd, J 9 and 5, CH<sub>2</sub> dia.<sub>maj</sub> or dia.<sub>min</sub>), 1.67 (1 H, dd, J 10 and 4, CH<sub>2</sub> of dia.<sub>maj</sub> or dia.<sub>min</sub>), 2.67 (1 H, dd, J 10 and 7, Ar–CH of dia.<sub>maj</sub> or dia.<sub>min</sub>) and 2.73 (1 H, dd, J 9 and 7, ArCH of dia.<sub>maj</sub> or dia.<sub>min</sub>); aryl protons of dia.<sub>maj</sub> and dia.<sub>min</sub>: 4.85 (1 H, d, J 6.7), 5.06 (1 H, m), 5.06 (1 H, dd, J 6.2 and 1.0), 5.11 (1 H, d, J 6.7) and 5.54 (4 H, m);  $\delta_{\text{C}}\{^1\text{H}\}$ (67.5 MHz) of dia.<sub>maj</sub> and dia.<sub>min</sub>: 0.2 and 0.6 (SiMe<sub>3</sub>), 13.8 and 16.7 (CH<sub>3</sub>), 19.4 and 24.9 (CH<sub>2</sub>), 26.9 and 29.8 [C(Me)CO<sub>2</sub>Bu'], 27.9 and 28.0 [C(CH<sub>3</sub>)<sub>2</sub>], 29.8 and 30.0 (Ar–CH), 81.0 and 81.1 [C(CH<sub>3</sub>)<sub>2</sub>], 88.8, 89.1, 89.5, 92.9, 94.9, 95.3, 100.7 and 100.9 (8 × ArC), 99.2, 100.5, 114.7 and 116.9 (4 × ArC<sub>ipso</sub>), 173.0 and 173.2 (CO<sub>2</sub>Bu'), 233.1 and 233.3 (C≡O); *m/z* (CI, NH<sub>3</sub>) 458 (MNH<sub>4</sub><sup>+</sup>, 72%), 441 (MH, 84), 402 [MNH<sub>4</sub> – (CO)<sub>2</sub>, 59], 385 [MH – (CO)<sub>2</sub>, 100], 322 [MNH<sub>4</sub> – Cr(CO)<sub>3</sub>, 23], 266 [MNH<sub>4</sub> – Cr(CO)<sub>3</sub> – C<sub>4</sub>H<sub>9</sub>, 59], 249 [MNH<sub>4</sub> – Cr(CO)<sub>3</sub> – C<sub>4</sub>H<sub>9</sub>, 34], 90 (SiMe<sub>3</sub>NH<sub>4</sub>, 57) and 52 (Cr, 10).

(–)-Tricarbonyl[(1*S*,2*S*)-*trans*-1-methoxy-2-phenylcyclopropane]chromium(0) (–)-**11**

To a solution of Ar(1*R*,2*S*)-(–)-tricarbonyl{(1*S*,2*S*)-*trans*-1-methoxy-2-[2-(trimethylsilyl)phenyl]cyclopropane}chromium(0) (–)-**18** (80 mg, 224 μmol) in THF (5 cm<sup>3</sup>) was added at 0–5 °C tetrabutylammonium fluoride (0.25 cm<sup>3</sup> of a 1 mol dm<sup>–3</sup> solution in THF, 250 μmol). After stirring for 1.5 h at this temperature the solvent was removed under reduced pressure and the residue purified by column chromatography (SiO<sub>2</sub>; light petroleum–CH<sub>2</sub>Cl<sub>2</sub>, 1:1) to yield after recrystallisation (CH<sub>2</sub>Cl<sub>2</sub>–hexane) yellow crystals of the *title compound* (–)-**11** (58 mg, 91%), mp 41–42 °C. The enantiomeric excess of the product was determined by HPLC using a chiral column (Chiralcel OD-H; hexane–propan-2-ol, 7:3; detector λ = 380 nm; retention times: major enantiomer, 9.17 min; minor enantiomer, 7.47 min) and found to be 98% after column chromatography and 99.4% after recrystallisation; [ $\alpha$ ]<sub>D</sub><sup>22</sup> –79.7 (c 0.78, CHCl<sub>3</sub>); the other spectroscopic data were in good agreement with the data reported for the racemic compound (see above).

X-Ray crystallographic analysis of (–)-**6**

**Crystal data.** C<sub>19</sub>H<sub>25</sub>CrNO<sub>3</sub>Si, *M* = 395.5, orthorhombic, *a* = 8.046(3), *b* = 15.893(6), *c* = 16.417(5) Å, *V* = 2099(1) Å<sup>3</sup>, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *Z* = 4, *D*<sub>c</sub> = 1.25 g cm<sup>–3</sup>, Cu-Kα radiation, λ = 1.541 78 Å, μ(Cu-Kα) = 5.16 mm<sup>–1</sup>, *F*(000) = 832. Yellow plates, crystal dimensions 0.66 × 0.37 × 0.10 mm.

**Data collection and processing.** Data were measured on a Siemens P4/PC diffractometer with Cu-Kα radiation (graphite monochromator) using ω-scans. 1829 Independent reflections were measured (2θ ≤ 126°) of which 1606 had |*F*<sub>o</sub>| > 4σ(*F*<sub>o</sub>)

and were considered to be observed. The data were corrected for Lorentz and polarisation factors and a semi-empirical absorption correction was applied; the maximum and minimum transmission factors were 0.710 and 0.336 respectively.

**Structure analysis and refinement.** The structure was solved by direct methods and all the full occupancy non-hydrogen atoms and the major occupancy non-hydrogen atoms of the 60:40 disordered trimethylsilane were refined anisotropically. The positions of the hydrogen atoms were idealised (C–H, 0.96 Å), assigned isotropic thermal parameters,  $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  [ $U(\text{H}) = 1.5U_{\text{eq}}(\text{C-Me})$ ], and allowed to ride on their parent atoms. Refinement was by full-matrix least-squares based on  $F^2$  to give  $R_1 = 0.053$ ,  $wR_2 = 0.145$  for 240 parameters. The maximum and minimum residual electron densities in the final  $\Delta F$  map were 0.28 and  $-0.78 \text{ e \AA}^{-3}$  respectively. The mean and maximum shift/error ratios in the final refinement cycle were  $-0.070$  and  $0.008$  respectively. The absolute structure of the molecule was determined *via* both Flack [ $x^+ = 0.00(2)$ ,  $x^- = 0.99(2)$ ] and  $R$ -factor tests [ $R^+ = 0.053$ ,  $R^- = 0.088$ ]. Computations were carried out on a 50 MHz 486 PC computer using the SHELXTL PC program system.<sup>18</sup>

#### X-Ray crystallographic analysis of (–)-18

**Crystal data.**  $\text{C}_{16}\text{H}_{20}\text{CrO}_4\text{Si}$ ,  $M = 356.4$ , orthorhombic,  $a = 7.088(2)$ ,  $b = 15.171(4)$ ,  $c = 16.452(5) \text{ \AA}$ ,  $V = 1769(1) \text{ \AA}^3$ , space group  $P2_12_12_1$ ,  $Z = 4$ ,  $D_c = 1.34 \text{ g cm}^{-3}$ , Cu-K $\alpha$  radiation,  $\lambda = 1.54178 \text{ \AA}$ ,  $\mu(\text{Cu-K}\alpha) = 6.09 \text{ mm}^{-1}$ ,  $F(000) = 744$ . Thin yellow plates, crystal dimensions  $0.54 \times 0.13 \times 0.01 \text{ mm}$ .

**Data collection and processing.** Data were measured on a Siemens P4/PC diffractometer with Cu-K $\alpha$  radiation (graphite monochromator) using  $\omega$ -scans. 1661 Independent reflections were measured ( $2\theta \leq 126^\circ$ ) of which 1222 had  $|F_o| > 4\sigma(|F_o|)$  and were considered to be observed. The data were corrected for Lorentz and polarisation factors and a numerical absorption correction was applied; the maximum and minimum transmission factors were 0.944 and 0.414 respectively.

**Structure analysis and refinement.** The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealised (C–H, 0.96 Å), assigned isotropic thermal parameters,  $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  [ $U(\text{H}) = 1.5U_{\text{eq}}(\text{C-Me})$ ], and allowed to ride on their parent atoms. Refinement was by full-matrix least-squares based on  $F^2$  to give  $R_1 = 0.047$ ,  $wR_2 = 0.078$  for 200 parameters. The maximum and minimum residual electron densities in the final  $\Delta F$  map were 0.24 and  $-0.26 \text{ e \AA}^{-3}$  respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.001 and 0.000 respectively. The absolute structure of the molecule was determined *via* both Flack [ $x^+ = -0.05(2)$ ,  $x^- = +1.00(2)$ ] and  $R$ -factor tests

[ $R^+ = 0.047$ ,  $R^- = 0.087$ ]. Computations were carried out on a 50 MHz 486 PC computer using the SHELXTL PC program system.<sup>18</sup>

Atomic coordinates, bond lengths and angles and thermal parameters for compounds (–)-6 and (–)-18 have been deposited at the Cambridge Crystallographic Data Centre. For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1.

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