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Planar chiral (η^6-arene)tricarbonylchromium complexes derived from mandelic acid

Paul D. Woodgate *, Amir Ashoorzadeh, Ali Hosseini, Clifton E.F. Rickard, Lee-Kei Yang

Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand

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Abstract

The enantiomers of mandelic acid have each been converted into 1,3-dioxolan-4-one derivatives. Formation of the planar chiral (η^6-arene)tricarbonylchromium complexes has enabled an investigation of their potential to promote discrimination between the diastereotopic *ortho* and/or *meta* arene hydrogens during lithiation–silylation.

Keywords: Tricarbonylchromium; Mandelic acid; Planar chiral

1. Introduction

(η^6-Arene)tricarbonylchromium complexes of aromatic ligands which are substituted unsymmetrically at either the *ortho* or *meta* positions are not superimposable on their mirror image. This stereochemical feature, known as planar chirality [1], has been exploited in recent years as a key element in enantioselective syntheses [2–8] of bioactive compounds. There are two general approaches to the synthesis of planar chiral (η^6-arene)$Cr(CO)_3$ complexes. In one approach a non-racemic base is used as an external chiral reagent to deprotonate selectively one of the enantiotopic *ortho* (or *meta*) hydrogens of the prochiral complex; subsequent addition of an electrophile can lead to significant enantiomeric excess in the functionalised aromatic complex [9–12]. An alternative method relies on the attachment of a chiral auxiliary to the arene ring prior to complexation. An additional stereochemical element, planar chirality, is then created by intramolecular chelation of an achiral base, which ideally leads to abstraction of only one of the diastereotopic *ortho* (or *meta*) hydrogens [13–21]. These studies commonly refer to complexes of either benzaldehyde or acetophenone derivatives. 2-Hydroxy aldehydes are a related class of compounds, which possess significant potential as chiral building blocks in synthesis [22]. In continuation of our studies of the stereoselective functionalisation of (η^6-arene)$Cr(CO)_3$ complexes [23–26], we report here the results of work aimed at utilising the readily available enantiomers of mandelic acid (2-hydroxy-2-phenylacetic acid) as an internal chiral auxiliary, potentially leading to chiral 2-hydroxyarylacetaldehydes.

2. Results and discussion

Most of the chiral auxiliaries reported to be effective in promoting directed metallation contain oxygen and/or nitrogen functionalities such as tertiary amines, ethers, oxazolidines, aminals, or acetals (1,3-dioxolanes). We decided to investigate the extension of this set to 1,3-dioxolan-4-ones, since the carbonyl group in this lactone-acetal could, after reduction and protection, act as an additional locus to influence the diastereoselectivity of the arene deprotonation step. The fact that both enantiomers of mandelic acid are commercially available made it an attractive precursor to the dioxolanone, which was reduced to a lactol and the alcohol protected as its TBDMS ether. The phenyl ring was then converted into its $Cr(CO)_3$ η^6 complex, and the lithiation–silylation sequence was studied.

* Corresponding author. Fax: +64-9-3737422.
E-mail address: p.woodgate@auckland.ac.nz (P.D. Woodgate).

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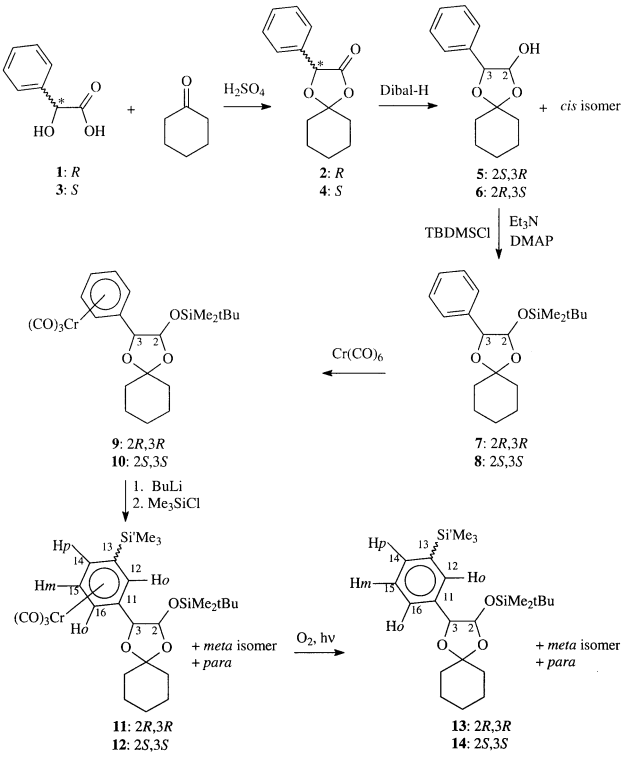
Reaction of (*R*)-mandelic acid (**1**) with cyclohexanone in 1,4-dioxane with a catalytic amount of concentrated H_2SO_4 at room temperature for 30 min afforded (*R*)-3-phenyl-1,4-dioxaspiro[4.5]decan-2-one (**2**) (Scheme 1). The crude product was recrystallised from hexanes to give white crystals of the 1,4-dioxolan-2-one **2** in 90% yield. The pseudomolecular ion at *m*/*z* 233 $[M+H]^+$ in the mass spectrum, together with carbonyl signals at 1808 cm^{-1} in the IR spectrum and 171.5 ppm in the ^{13}C-NMR spectrum, confirmed formation of the lactone, $[\alpha]_D^{20}$ −86.4° (*c* 1.02, dichloromethane). Similarly, *S*-mandelic acid (**3**) gave the *S*-lactone **4** (88%), $[\alpha]_D^{20}$ + 81.6° (*c* 1.01, dichloromethane).

The next step involved reduction of the lactone to a lactol (formally equivalent to an α-hydroxy aldehyde). A solution of (*R*)-3-phenyl-1,4-dioxaspiro[4.5]decan-2-one (**2**) in toluene, was treated with Dibal-H −78 °C, and after 30 min aqueous HCl was added slowly. Workup and filtration of the crude material through a short pad of silica gel gave (2*S*,3*R*)-3-phenyl-1,4-dioxaspiro[4.5]decan-2-ol (**5**) (81%). The presence of a broad OH band at 3392 cm^{-1} in the IR spectrum, together with a signal for the molecular ion at *m*/*z* 234 in the mass spectrum, confirmed that reduction had been achieved. In the ^1H-NMR spectrum, the signals in the region 4.97–5.52 ppm due to H2 and H3 were used to estimate the ratio of diastereoisomers as 84:16 in favour of 2*S*,3*R* (*trans*). Similar reduction of the *S*-lactone **4** with Dibal-H gave (2*R*,3*S*)-3-phenyl-1,4-dioxaspiro[4.5]decan-2-ol (**6**) (100%; contains 8% of the *cis* isomer).

Prior to η^6-$Cr(CO)_3$ complexation of the phenyl ring the alcohol group was protected as a TBDMS ether. Triethylamine (4.4 M equivalents) and a catalytic amount of DMAP were added to a solution of the (2*S*,3*R*)-lactol **5** in dichloromethane, and then TBDMSCl (4.4 M equivalents) was added slowly at 0 °C. After 46 h at room temperature, workup and flash chromatography followed by recrystallisation gave (2*R*,3*R*)-2-*t*-butyl(dimethyl)[(3-phenyl-1,4-dioxaspiro-[4.5]decan-2-yl)oxy]silane (**7**) (66%), $[\alpha]_D^{20}$ +46° (*c* 1.02, dichloromethane). The presence of signals at 1089 and 839 cm^{-1} due to Si–O–C and Si–C stretching vibrations in the IR spectrum, and in the mass spectrum at *m*/*z* 348, 291, and 188 corresponding to $[M^{+\bullet}]$, $[M-t\,Bu]^+$, and $[M-HCO_2SiMe_2t\,Bu]^+$, confirm protection of the lactol. The *trans*–*cis* mixture (24:1) of TBDMS ethers recovered from chromatography was highly soluble in both polar and non-polar solvents. Hexanes, pentane, petroleum spirits or benzene were used for recrystallisation, but in all cases the resulting crystals were of only moderate quality for determination of the structure by X-ray analysis (Fig. 1). Although the values of the *R* indices for all data ($R_1 = 0.1321$, $wR_2 = 0.1795$) and the final *R* indices ($R_1 = 0.0724$, $wR_2 = 0.1593$) were relatively large, there is no doubt of the relative stereochemistry (*trans*) and therefore of the absolute stereochemistry of the major chiral non-racemic diastereoisomer **7**.

The enantiomer (2*S*,3*S*)-2-*t*-butyl(dimethyl)[(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane (**8**) was prepared similarly from lactols **6**. Chromatography afforded only the *trans* diastereoisomer **8** (65%), $[\alpha]_D^{20}$ −46.1° (*c* 1.02, dichloromethane).

Preparation of {[(2*R*,3*R*)-(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}tricarbonylchromium (**9**) was achieved by thermolysis of (2*R*,3*R*)-2-*t*-butyl(dimethyl)[(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane (**7**) with



Scheme 1.

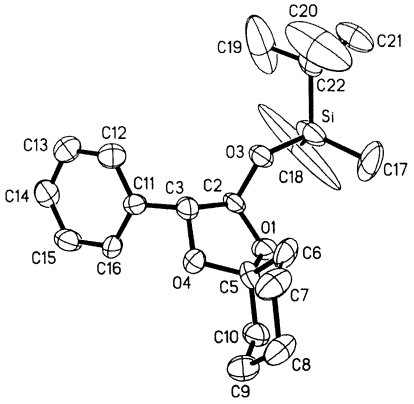


Fig. 1. The atomic arrangement in (2*R*,3*R*)-**7**.

$Cr(CO)_6$ in 1,4-dioxane for 48 h. Flash chromatography gave the η^6 complex **9** as a single isomer (*trans*; 58%), $[\alpha]_D^{20}$ +39.8° (*c* 1.06, dichloromethane). Attempted recrystallisation of the yellow viscous oil using a range of non-polar solvents and applying different methods was not successful. The presence of absorptions due to carbonyl ligands in the IR spectrum at 1971 and 1893 cm^{-1} and in the ^{13}C-NMR spectrum at 232.35 ppm, and of peaks in the mass spectrum at *m*/*z* 484, 428, 400, and 52 corresponding to $[M^{+\bullet}]$, $[M-2CO]^+$, $[M-3CO]^+$ and Cr^+, confirmed that η^6 complexation had occurred. Furthermore, in both the ^1H- and ^{13}C-NMR spectra the signals (Table 1) due to the arene ring in complex **9** were shifted upfield relative to those of the free ligand (*trans* **7**). Moreover, the NMR spectra both indicated that only one isomer was present.

Thermolysis of (2*S*,3*S*)-2-*t*-butyl(dimethyl)[(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)-oxy]silane (**8**) with $Cr(CO)_6$ followed by purification using flash chromatography also afforded a single (*trans*) isomer (69%). The ^1H-, ^{13}C-NMR, mass, and IR spectra of {[(2*S*,3*S*)-(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}tricarbonylchromium (**10**) were identical with those of enantiomer **9**. As expected, the value of the optical rotation of **10** {$[\alpha]_D^{20}$ −37.7° (*c* 1.04, dichloromethane)} was comparable with that of **9** but of opposite sign. Again, however, recrystallisation of complex **10** could not be achieved from a range of non-polar solvents.

With each pure enantiomeric η^6-$Cr(CO)_3$ complex **9** and **10** available, the influence of the mandelic acid-derived auxiliary in potentially promoting distinction chemically between the diastereotopic *ortho* and/or *meta* arene hydrogens was investigated. Thus, {[(2*R*,3*R*)-(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}tricarbonylchromium (**9**) was stirred in THF and cooled to −78 °C. BuLi (2.3 M equivalents in hexanes) was injected and the solution was stirred at −78 °C for 2.5 h. Chlorotrimethylsilane (2.3 M equivalents) was added, the mixture was stirred for 2.5 h, and then allowed to warm to room temperature overnight. Workup and flash chromatography gave a mixture of three regioisomers of {[(2*R*,3*R*)-(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-(3ζ-trimethylsilyl)phenyl)-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}tricarbonylchromium (**11**) in 50% yield as a yellow oil. The presence in the mass spectrum of signals at *m*/*z* 556, 472, 73, and 52 corresponding to $[M^{+\bullet}]$ ($C_{26}H_{40}{}^{52}CrO_6Si_2$), $[M-3CO]^+$, $(Si'Me_3)^+$, and Cr^+ confirmed that lithiation–silylation of the chiral non-racemic complex **9** had taken place. The structures of the trimethylsilylarene regioisomers were established by NMR experiments (COSY, long range COSY, HSQC, and HSQC-TOCSY) to be one *meta* diastereoisomer (39%), the other *meta* diastereoisomer (42%), and the *para* diastereoisomer (19%). That is, the *meta*–*para* ratio is ca. 4:1; there was no evidence for either *ortho*-silylated isomer.

Decomplexation of the mixture of three silylated products by exposure of a solution in $CDCl_3$ to oxygen and daylight gave [(2*R*,3*R*)-(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-(3ζ-(trimethylsilyl)phenyl)-1,4-dioxaspiro-[4.5]decan-2-yl)oxy]silane (**13**) as a mixture of two regioisomers. The absence of both C≡O absorptions due to carbonyl ligands in the IR spectrum, the presence of signals in the mass spectrum at *m*/*z* 420 [$M^{+\bullet}$, $C_{23}H_{40}O_3Si_2$] and 73 $(Si'Me_3)^+$, and the loss of the yellow colour all indicated detachment of the η^6-$Cr(CO)_3$ moiety. This decomplexation was carried out to allow better resolution of the ^1H- and ^{13}C-NMR data to enable definitive assignment of structure to the regioisomers. A series of COSY, long-range COSY, HSQC, and HSQC-TOCSY NMR experiments were carried out in $CDCl_3$, and then in C_6D_6, and the data were interpreted in detail for the hydrogen and carbon atoms of **13**. The signals due to the arene ring hydrogen and carbon atoms of the *meta* and *para* trimethylsilylated isomers are included in Table 2. As expected, decomplexation produced only one *meta*-$SiMe_3$ compound [as opposed to two *meta* diastereoisomers in the η^6-(arene)$Cr(CO)_3$ complex], as well as the *para*-$SiMe_3$ isomer. The *meta*–*para* ratio was 84:16.

Deprotonation-electrophile/quenching of (2*S*,3*S*)-2-*t*-butyl(dimethyl)[(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane (**10**) was carried out in THF under the same experimental conditions as for the (2*R*,3*R*) enantiomer **9**. Flash chromatography gave the silylated product **12** (78%) as a mixture of diastereoisomers. Again, the structures of these isomers were assigned by detailed interpretation of COSY, long range HSQC and HSQC-TOCSY NMR experiments. They were one *meta* diastereoisomer (42%), the other *meta* diastereoisomer (40%) and the *para* diastereoisomer (18%). Table 3 includes ^1H- and ^{13}C-NMR data for the arene ring of

Table 1
^1H- and ^{13}C-NMR data for *trans* ligand **7** and *trans* complex **9**

Arene H	δ_H Ligand **7** (ppm)	δ_H Complex **9** (ppm)	Arene C	δ_C Ligand **7** (ppm)	δ_C Complex **9** (ppm)
H12, H16	7.27–7.37 (m)	5.30–5.44 (m)	C12, C16	125.95	90.31, 90.63
H13, H15 and H14			C14, C15	127.83	91.63
			C13	128.46	92.10
			C11	139.18	108.92

Table 2
Selected ^{1}H- and ^{13}C-NMR data (C_6D_6) for decomplexed $ArSiMe_3$ regioisomers **13**

Hydrogen	δ_H *meta* (84%) (ppm) (*J*, Hz)	δ_H *para* (16%) (ppm) (*J*, Hz)	Carbons	δ_C *meta* (84%) (ppm)	δ_C *para* (16%) (ppm)
Si′Me_3	0.231 (s)	0.189 (s)	Si′Me_3	−1.12	Weak
H_m	7.26 (t, 7.4)	7.48 (d, 7.6)	C16	126.53	125.73
$H_{m'}$	Absent	7.48 (d, 7.6)	C15	128.22	133.89
$H_{o'}$	7.40 (d, 7.3)	7.55 (d, 7.6)	C12	131.15	125.73
H_p	7.59 (d, 7.6)	Absent	C14	133.21	141.41
H_o	7.76 (s)	7.55 (d)	C11	139.09	Not detected
			C13	140.63	133.89

each *meta* isomer (the *para* isomer was identified by the singlet due to Si′Me_3 at 0.294 ppm).

Decomplexation of the silylated product **12** gave [(2*S*,3*S*)-(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-(3ζ-trimethylsilyl)phenyl)-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane (**14**) as a mixture of a single *meta* isomer (86%) and the *para* isomer (14%). The structures of the silylated free ligands were again confirmed by COSY, long range HSQC and HSQC-TOCSY NMR experiments, and also by mass and IR spectroscopy. The results were similar to those from decomplexation of the mixture **13**.

The preparation of racemic *trans* 2-*t*-butyl(dimethyl)[(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane was carried out in parallel during the present work. The derived racemic complex **9/10** was able to be crystallised, and single crystal X-ray analysis showed the conformation of its η^6-$Cr(CO)_3$ tripod to be nearly *syn*-eclipsed (Fig. 2). Although the η^6-$Cr(CO)_3$ complexes of the analogous chiral non-racemic ligands **7** and **8** could not be crystallised, and therefore X-ray analyses of either stereoisomer **9** or **10** could not be carried out, it is assumed that for both enantiomers the *syn*-eclipsed conformer is also preferred in the solid state.

In the above work the lactone carbonyl group had been reduced and then the lactol protected as the TBDMS ether deliberately, in order to avoid competing deprotonation of the benzylic proton H5 during reaction of the η^6-(arene)$Cr(CO)_3$ complexes with BuLi. As expected, lithiation of the complexed arene ring in the lactol derivatives **9** and **10** occurred in good overall yield. Unfortunately, however, quenching of the resulting carbanions did not lead to any discrimination between the diastereotopic *meta* arene hydrogen atoms. Since it was likely that the $Cr(CO)_3$ tripod would prefer

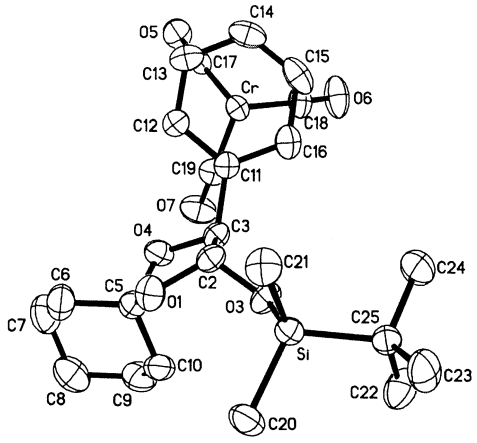
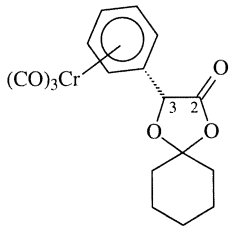


Fig. 2. The atomic arrangement in *rac-trans*-{[(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}tricarbonylchromium (**9/10**).

a different conformation in the tricarbonylchromium complex of the parent lactone, (*R*)-3-phenyl-1,4-dioxaspiro[4.5]decane-2-one (**2**) was converted into its η^6-(arene) complex **15**. Indeed, X-ray analysis of a single



15: *R*

crystal of (*R*)-**15** (Fig. 3) indicated a preferred near-*anti* staggered conformation for the η^6-(arene)$Cr(CO)_3$ moi-

Table 3
Selected ^{1}H- and ^{13}C-NMR data for η^6-$Cr(CO)_3$ *meta*-Si′Me_3 regioisomers **12**

Hydrogen	δ_H *meta* (42%) (ppm) (*J*, Hz)	δ_H *meta* (40%) (ppm) (*J*, Hz)	Carbons	δ_C *meta* (42%) (ppm)	δ_C *meta* (40%) (ppm)
Si′Me_3	0.256 (s)	0.297 (s)	Si′Me_3	−1.21	Weak
H_m	5.13 (t, 6.4)	5.17 (t, 6.4)	C16	89.12	89.63
H_o	5.50 (s)	Not detected	C15	92.67	93.95
H_p	5.43 (d, 6.4)	5.39 (d, 6.3)	C12	96.94	98.10
$H_{o'}$	5.65 (bd, 6.8)	5.63 (d, 7.6)	C14	98.67	99.29

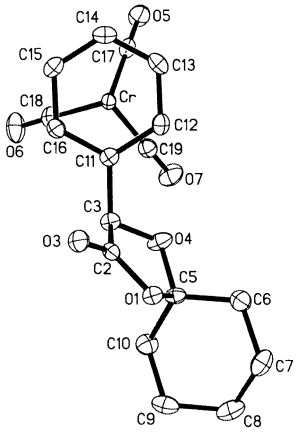


Fig. 3. The atomic arrangement in (*R*)-**15**.

ety. In this structure one of the carbon monoxide ligands points towards O4, indicating the possibility of an electrostatic interaction between these two units. Furthermore, the X-ray analysis confirmed that the absolute configuration at C3 had not been changed via enolisation during exposure to the acid necessary for formation of the 1,4-dioxolan-2-one. Complex **15** was not investigated further, however, since treatment with BuLi would result in loss of the stereogenic centre incorporated from the enantiopure mandelic acids.

2.1. Summary

The regioselectivity of deprotonation of a complexed arene ring can often be related to the orientation of the tricarbonylchromium tripod [27]. An *anti* eclipsed conformation (as for electron withdrawing or bulky substituents) commonly directs attack of the base to the *ortho* (and *para*) position(s) while a *syn* eclipsed conformation, like that shown in Fig. 2, directs deprotonation to the *meta* position(s). This regioselection reflects a further decrease in the electron density around the aromatic C–H bond by the very electropositive carbon of a CO ligand, which eclipses it. Bulky substituents also prevent *ortho* deprotonation due to a steric effect. Therefore, the experimental result that *meta*-silylation of **9** and **10** dominated (to the exclusion of *ortho* silylation) is in agreement with the regiochemical outcome expected from both electronic and steric considerations. Unfortunately, the fact that both *meta*-silylated diastereoisomers were formed, and in equal amounts, in THF means that the planar chirality present in complexes **9** and **10** has not been translated into chemical discrimination between the diastereotopic *meta* hydrogens. Presumably, this is because the stereogenic centre C3 present in the chiral auxiliary is too remote from the *meta* sites to exert any influence via selective intramolecular chelation of the BuLi during deprotonation.

2.2. X-ray crystal structures of (2R,3R)-7, rac-trans-(9/10) and (R)-15

Data were collected on a Siemens SMART area detector diffractometer using 0.3° frames and profile fitting. Lorentz, polarisation and absorption corrections [28] were applied and equivalent reflections averaged. Unit cell parameters were obtained by least-squares fit to all data with $I > 10\sigma(I)$. The structures were solved by direct methods [29] and refined by full matrix least-squares on F^2 [30]. Hydrogen atoms were placed geometrically and refined with a riding model, including free rotation for methyl groups, with thermal parameter 20% (50% for methyl groups) greater than U_{iso} of the carrier atom. All non-hydrogen atoms were refined with anisotropic thermal parameters. The *t*-butyldimethylsilyl group for **7** has large thermal vibration elipsoids. This is presumably indicative of some disorder in these atoms. The anisotropic thermal parameters have been allowed to take up this disorder. Crystal data and refinement parameters are given in Table 4 and the structures are shown in Figs. 1–3.

3. Experimental

Structures were assigned using HRMS ($\Delta \leq 5$ ppm) for the molecular formula, in combination with complete assignment of the ^{1}H- and ^{13}C-NMR spectra and selected infrared data.

3.1. (R)-3-Phenyl-1,4-dioxaspiro[4.5]decan-2-one (2) and (S)-3-phenyl-1,4-dioxaspiro[4.5]decan-2-one (4)

(*R*)-Mandelic acid (**1**) (5 g, 32.89 mmol) was stirred in dry 1,4-dioxane (14.4 ml), cyclohexanone (6.9 ml, 66.67 mmol) was added, and the reaction mixture was stirred for 10 min. Sulphuric acid (1.7 ml, 18 mol l^{-1}) was added dropwise and the reaction mixture was left to stir for 30 min. A solution of NaOH (90 ml, 0.6 mol l^{-1}) in water was added. A white precipitate formed which was extracted into CH_2Cl_2 (3×40 ml). The extract was washed with aq. $NaHCO_3$ (3×40 ml) and brine (3×40 ml), and dried ($MgSO_4$). The solvents were removed in vacuo and the crude product was recrystallised from hexanes to afford (*R*)-3-phenyl-1,4-dioxaspiro[4.5]decan-2-one (**2**) (6.88 g, 90%) as white needles, m.p. 107–109 °C. $[\alpha]_D^{20}$ −86.4° (*c* 1.02, CH_2Cl_2). (Found: $[M+H]^+$ 233.1181. $C_{14}H_{17}O_3$ requires 233.1178 (−1.3 ppm)). ν_{max} (KBr) 3060 (C–H, aromatic), 2941 (C–H), 1808 (C=O), 1456 (C=C), 946 (C–O–C) cm^{-1}. δ_H 1.45–1.96 (m, 10H, C_6H_{10}), 5.38 (s, 1H, H3), 7.35–7.49 (m, 5H, H12, H16, H13, H15, H14) ppm. δ_C 22.99 (CH_2, C8), 23.07 (CH_2, C7), 24.46 (CH_2, C9), 35.75 (CH_2, C6), 36.74 (CH_2, C10), 75.46 (CH, C3), 111.79 (C, C5), 126.36 (CH, C12, C16), 128.68 (CH, C13, C15),

Table 4
X-ray data collection and processing parameters

	(2*R*,3*R*)-**7**	*rac*-*trans*-(**9**/**10**)	(*R*)-**15**
Formula	$C_{20}H_{32}O_3Si$	$C_{23}H_{32}O_5Si$	$C_{17}H_{16}CrO_6$
Molecular weight	348.55	484.58	368.30
Temperature (K)	150	150	150
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Tetragonal	Orthorhombic	Orthorhombic
Space group	$P4_3$	*Pbcn*	$P2_12_12_1$
Unit cell dimensions			
a (Å)	11.1754(4)	31.4744(11)	5.9191(1)
b (Å)	11.1754(4)	13.4151(5)	14.0193(2)
c (Å)	16.4808(8)	11.7832(4)	19.0677(1)
V (Å^3)	2058.28(14)	4975.2(3)	1582.27(4)
Z	4	8	4
D_{calc} (g cm^{-3})	1.125	1.294	1.546
μ (mm^{-1})	0.13	0.54	0.75
F(000)	760	2048	760
Crystal size (mm)	0.48 × 0.12 × 0.08	0.42 × 0.26 × 0.15	0.55 × 0.16 × 0.10
2θ Range (°)	1.8–25.0	1.6–26.7	1.8–26.3
Reflections collected	10 920	27 642	9619
Independent reflections	3609 [$R_{int} = 0.0927$]	5276 [$R_{int} = 0.0223$]	3200 [$R_{int} = 0.0173$]
A (min/max)	0.941, 0.989	0.804, 0.923	0.682, 0.928
R_1 (observed data)	0.0724, $wR_2 = 0.1593$	0.0317, $wR_2 = 0.0826$	0.01989, $wR_2 = 0.0507$
R_1 (all data)	0.1321, w$R_2 = 0.1795$	0.0402, $wR_2 = 0.0887$	0.0213, $wR_2 = 0.0515$
Goodness-of-fit on F^2	0.730	1.057	1.052
Difference map (min/max) (e Å^{-3})	+0.37, −0.35	+0.29, −0.44	+0.16, −0.30

$R = \Sigma \, ||F_o| - |F_c|| / \Sigma \, |F_o|$, $wR_2 = \{\Sigma \, [w(F_o^2 - F_c^2)2] / \Sigma \, [w(F_o^2)^2]\}^{1/2}$.

128.86 (CH, C14), 134.73 (C, C11), 171.50 (C=O, C2) ppm.

Similarly, (*S*)-mandelic acid (**3**) gave (*S*)-3-phenyl-1,4-dioxaspiro[4.5]decan-2-one (**4**) (88%) as white needles, m.p. 105–107 °C (hexanes). $[\alpha]_D^{20}$ +81.6° (*c* 1.01, CH_2Cl_2). (Found: $[M+H]^+$ 233.11769. $C_{14}H_{17}O_3$ requires 233.11777 (0.3 ppm)). ν_{max} (KBr) 3054 (C–H, aromatic), 2945 (C–H), 1785 (C=O), 1451 (C=C), 945 (C–O–C) cm^{-1}. δ_H 1.45–1.96 (m, 10H, C_6H_{10}), 5.38 (s, 1H, H3), 7.35–7.49 (m, 5H, H12, H16, H13, H15, H14) ppm. δ_C 22.98 (CH_2, C8), 23.08 (CH_2, C7), 24.44 (CH_2, C9), 35.73 (CH_2, C6), 36.73 (CH_2, C10), 75.44 (CH, C3), 111.77 (C, C5), 126.34 (CH, C12, C16), 128.66 (CH, C13, C15), 128.84 (CH, C14), 134.73 (C, C11), 171.48 (C=O, C2) ppm.

3.2. (2*S*,3*R*)-3-Phenyl-1,4-dioxaspiro[4.5]decan-2-ol (**5**) and (2*R*,3*S*)-3-phenyl-1,4-dioxaspiro[4.5]decan-2-ol (**6**)

A solution of (*R*)-3-phenyl-1,4-dioxaspiro[4.5]decan-2-one (**2**) (1 g, 4.31 mmol) in dry $C_6H_5CH_3$ (10.8 ml) was stirred and cooled in a dry-ice bath (−78 °C) under an atmosphere of nitrogen. DIBAL-H (7.2 ml, 1 mol l^{-1} solution in $C_6H_5CH_3$, 7.2 mmol) was added. The mixture was stirred at the same temperature for 30 min, and then HCl (7.2 ml, 1 mol l^{-1}) was added very slowly. The solution was left to stir at room temperature (r.t.) for another 30 min, and then was extracted into EtOAc (3 × 8 ml). The extract was passed through a short pad of silica gel and the solvent was removed under reduced pressure to provide (2*S*,3*R*)-3-phenyl-1,4-dioxaspiro[4.5]decan-2-ol (**5**) (0.82 g, 81%) as colourless crystals, m.p. 73–76 °C. (Found: $[M^{+\bullet}]$ 234.1257. $C_{14}H_{18}O_3$ requires 234.1256 (−0.6 ppm)). ν_{max} (KBr) 3392 (O–H), 3064 (C–H, aromatic), 2935 (C–H), 1450 (C=C), 942 (C–O–C) cm^{-1}. δ_H for major isomer (*trans*, 84% by ^{1}H-NMR) 1.41–1.95 (m, 10H, C_6H_{10}), 3.53 (d, b, $J = 4.0$ Hz, 1H, OH), 4.97 (d, $J = 3.7$ Hz, 1H, H3), 5.28 (t, $J = 3.8$ Hz, 1H, H2), 7.15–7.39 (m, 5H, H12, H16, H13, H15, H14) ppm. δ_C for major *trans* isomer 23.72 (CH_2, C8), 23.82 (CH_2, C7), 25.07 (CH_2, C9), 36.24 (CH_2, C6), 37.08 (CH_2, C10), 84.18 (CH, C3), 101.71 (CH, C2), 111.94 (C, C5), 126.13 (CH, C12, C16), 128.08 (CH, C13, C15), 128.50 (CH, C14), 138.44 (C, C11) ppm. δ_H for minor isomer (*cis*, 16% by ^{1}H-NMR) 5.16 (d, $J = 3.7$ Hz, 1H, H3), 5.52 (dd, $J = 3.8$ Hz, $J' = 6.6$ Hz, 1H, H2) ppm. δ_C for minor *cis* isomer 23.06 (CH_2, C7), 24.44 (CH_2, C9), 35.30 (CH_2, C6), 38.46 (CH_2, C10), 81.08 (CH, C3), 95.39 (CH, C2), 126.83 (CH, C12, C16), 128.19 (CH, C13, C15), 129.01 (CH, C14) ppm.

Similarly, (*S*)-3-phenyl-1,4-dioxaspiro[4.5]decan-2-one (**4**) afforded (2*R*,3*S*)-3-phenyl-1,4-dioxaspiro[4.5]decan-2-ol (**6**) (100%) as colourless crystals, m.p. 78–80 °C. (Found: $[M^{+\bullet}]$ 234.1254. $C_{14}H_{18}O_3$ requires 234.1256 (0.7 ppm)). ν_{max} (KBr) 3364 (O–H), 3067 (C–H, aromatic), 2934 (C–H), 1450 (C=C), 947 (C–O–C)

cm^{-1}. δ_H for major isomer (*trans*, 92% by ^{1}H-NMR) 1.40–1.95 (m, 10H, C_6H_{10}), 3.58 (d, b, $J = 4.0$ Hz, 1H, OH), 4.97 (d, $J = 3.8$ Hz, 1H, H3), 5.29 (t, $J = 3.9$ Hz, 1H, H2), 7.25–7.42 (m, 5H, H12, H16, H13, H15, H14) ppm. δ_C for major isomer 23.71 (CH_2, C8), 23.81 (CH_2, C7), 25.06 (CH_2, C9), 36.24 (CH_2, C6), 37.08 (CH_2, C10), 84.17 (CH, C3), 101.70 (CH, C2), 111.94 (C, C5), 126.12 (CH, C12, C16), 128.08 (CH, C13, C15), 128.49 (CH, C14), 138.41 (C, C11) ppm. δ_H for minor isomer (*cis*, 8% by ^{1}H-NMR) 5.16 (d, $J = 3.8$ Hz, 1H, H3), 5.51 (dd, $J = 3.8$ Hz, $J' = 6.6$ Hz, 1H, H2) ppm. δ_C for minor isomer 35.29 (CH_2, C6), 38.45 (CH_2, C10), 81.08 (CH, C3), 95.38 (CH, C2), 126.83 (CH, C12, C16) ppm.

3.3. (2*R*,3*R*)-2-*t*-Butyl(dimethyl)[(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane (**7**) and (2*S*,3*S*)-2-*t*-Butyl(dimethyl)[(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane (**8**)

To a stirred solution of (2*S*,3*R*)-3-phenyl-1,4-dioxaspiro[4.5]decan-2-ol (**5**) (0.8 g, 3.42 mmol), Et_3N (1 ml, 6.84 mmol) and DMAP (75.2 mg, 0.62 mmol) in dry CH_2Cl_2 (30 ml) was added slowly a solution of *t*-butylchlorodimethylsilane (2.27 g, 15 mmol) in dry CH_2Cl_2 (7.5 ml) at 0 °C and under an atmosphere of nitrogen. The mixture was stirred for 2 h at the same temperature, and then stirred at r.t. for 48 h. A deep red solution resulted. The solution was washed with HCl (18.8 ml, 1 mol l^{-1}), saturated aq. $NaHCO_3$ (3×20 ml) and brine (3×20 ml), and dried ($MgSO_4$). It was then filtered through a short pad of silica gel and concentrated to provide a yellow oil. Hexanes–EtOAc (2 ml, 90:1) was added to dilute the syrupy residue and the solution was then adsorbed onto silica gel (1 g). Flash chromatography on silica gel with hexanes–EtOAc (99:1, 95:1, 90:1) gave (2*R*,3*R*)-2-*t*-butyl(dimethyl)[(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane (**7**) (0.783 g, 66%) as milky crystals, m.p. 63–65 °C. $[\alpha]_D^{20}$ +46° (*c* 1.02, CH_2Cl_2). (Found: $[M^{+\bullet}]$ 348.2120. $C_{20}H_{32}O_3Si$ requires 348.2121 (0.2 ppm)). ν_{max} (KBr) 3065 (C–H, aromatic), 2934 (C–H), 1449 (C=C), 1089 (Si–O–C), 943 (C–O–C), 839 (Si–C) cm^{-1}. δ_H for major isomer (*trans*, 96% by ^{1}H-NMR) 0.057 (s, 3H, Si–CH_3), 0.098 (s, 3H, Si–CH_3), 0.899 (s, 9H, Si–C–$(CH_3)_3$), 1.40–1.94 (m, 10H, C_6H_{10}), 4.95 (d, $J = 3.2$ Hz, 1H, H3), 5.20 (d, $J = 3.2$ Hz, 1H, H2), 7.30–7.37 (m, 5H, H12, H16, H13, H15, H14) ppm. δ_C for major isomer −5.19 (Si–CH_3), −4.31 (Si–CH_3), 17.81 (C, Si–C–$(CH_3)_3$), 23.78 (CH_2, C8), 23.93 (CH_2, C7), 25.25 (CH_2, C9), 25.60 (CH_3, Si–C–$(CH_3)_3$), 36.18 (CH_2, C6), 37.14 (CH_2, C10), 85.81 (CH, C3), 102.39 (CH, C2), 111.75 (C, C5), 125.93 (CH, C12, C16), 127.82 (CH, C14), 128.44 (CH, C13, C15), 139.17 (C, C11) ppm. δ_H for minor isomer (*cis*, 4% by ^{1}H-NMR) 5.03 (d, $J = 3.4$ Hz, 1H, H3), 5.41 (d, $J = 3.7$ Hz, 1H, H2) ppm.

Similarly, (2*R*,3*S*)-3-phenyl-1,4-dioxaspiro[4.5]decan-2-ol (**6**) gave (2*S*,3*S*)-2-*t*-butyl(dimethyl)[(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane (**8**) (65%), as milky crystals m.p. 64–66 °C. $[\alpha]_D^{20}$ −46.1° (*c* 1.02, CH_2Cl_2). (Found: $[M^{+\bullet}]$ 348.2122. $C_{20}H_{32}O_3Si$ requires 348.2121 (−0.4 ppm)). ν_{max} (KBr) 3052 (C–H, aromatic), 2936 (C–H), 1450 (C=C), 1089 (Si–O–C), 942 (C–O–C), 840 (Si–C) cm^{-1}. δ_H 0.056 (s, 3H, Si–CH_3), 0.097 (s, 3H, Si–CH_3), 0.899 (s, 9H, Si–C–$(CH_3)_3$), 1.40–1.94 (m, 10H, C_6H_{10}), 4.95 (d, $J = 3.3$ Hz, 1H, H3), 5.20 (d, $J = 3.3$ Hz, 1H, H2), 7.27–7.37 (m, 5H, H12, H16, H13, H15, H14) ppm. δ_C −5.17 (CH_3, Si–CH_3), −4.29 (CH_3, Si–CH_3), 17.83 (C, Si–C–$(CH_3)_3$), 23.80 (CH_2, C8), 23.95 (CH_2, C7), 25.27 (CH_2, C9), 25.61 (CH_3, Si–C–$(CH_3)_3$), 36.20 (CH_2, C6), 37.16 (CH_2, C10), 85.83 (CH, C3), 102.41 (CH, C2), 111.77 (C, C5), 125.95 (CH, C12, C16), 127.83 (CH, C14), 128.45 (CH, C13, C15), 139.19 (C, C11) ppm.

3.4. {[(2*R*,3*R*)-(1,2,3,4,5,6-η)-2-*t*-Butyl(dimethyl)-(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}tricarbonylchromium (**9**)

$Cr(CO)_6$ (0.19 g, 0.863 mmol) was added to a solution of (2*R*,3*R*)-2-*t*-butyl(dimethyl)[(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane (**7**) (0.244 g, 0.701 mmol) in dry 1,4-dioxane (10 ml) and the mixture was degassed by freeze–pump–thaw cycling (three times). It was then heated under reflux (sand bath, 130–140 °C) with stirring for 48 h, during which time nitrogen was bled slowly through a bubbler. The crude product was passed through a Celite pad and the solvent was removed from the filtrate in vacuo. Flash chromatography using hexanes–EtOAc (95:5, 90:10) gave {[(2*R*,3*R*)-(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}tricarbonylchromium (**9**) (0.197 g, 58%), $[\alpha]_D^{20}$ +39.8° (*c* 1.06, CH_2Cl_2). (Found: $[M^{+\bullet}]$ 484.1372. $C_{23}H_{32}{}^{52}CrO_6Si$ requires 484.1373 (0.2 ppm)). ν_{max} 3053 (C–H, aromatic), 2936 (C–H), 1971 (C≡O), 1893 (C≡O), 1450 (C=C), 1089 (Si–O–C), 941 (C–O–C), 840 (Si–C) cm^{-1}. δ_H 0.121 (s, 3H, Si–CH_3), 0.135 (s, 3H, Si–CH_3), 0.904 (s, 9H, Si–C–$(CH_3)_3$), 1.42–1.85 (m, 10H, C_6H_{10}), 4.58 (d, $J = 3.0$ Hz, 1H, H3), 5.23 (d, $J = 3.0$ Hz, 1H, H2), 5.30–5.44 (m, 5H, H12, H16, H13, H15, H14) ppm. δ_C −5.21 (CH_3, Si–CH_3), −4.21 (CH_3, Si–CH_3), 17.78 (C, Si–C–$(CH_3)_3$), 23.70 (CH_2, C8), 23.82 (CH_2, C7), 25.11 (CH_2, C9), 25.59 (CH_3, Si–C–$(CH_3)_3$), 36.15 (CH_2, C6), 37.02 (CH_2, C10), 83.67 (CH, C3), 90.31 and 90.63 (CH, C12, C16), 91.63 (CH, C14 and C13 or C15), 92.10 (CH, C15 or C13), 102.05 (CH, C2), 108.92 (C, C11), 112.63 (C, C5), 232.35 (C, C≡O) ppm. *m/z* 484 (14, $[M^{+\bullet}]$), 428 (5, [M−2CO]), 400 (72, [M−3CO]), 302 (5, 400−$C_6H_{10}O$), 287 (50, (302−CH_3)), 245 (100, 302−*t*Bu), 52 (30, Cr^+).

3.5. {[(2S,3S)-(1,2,3,4,5,6-η)-2-t-Butyl(dimethyl)-(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}tricarbonylchromium (**10**)

Reaction of $Cr(CO)_6$ (0.34 g, 1.55 mmol) with (2*S*,3*S*)-2-*t*-butyl(dimethyl)[(3-phenyl-1,4-dioxaspiro-[4.5]decan-2-yl)oxy]silane (**8**) (0.42 g, 1.21 mmol) in dry 1,4-dioxane (17 ml) as above gave {[(2*S*,3*S*)-(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}tricarbonylchromium (**10**) (0.403 g, 69%), $[\alpha]_D^{20}$ −37.7° (*c* 1.04, CH_2Cl_2). (Found: $[M^{+\bullet}]$ 484.1371. $C_{23}H_{32}{}^{52}CrO_6Si$ requires 484.1373 (0.5 ppm)). ν_{max} 3054 (C–H, aromatic), 2936 (C–H), 1971 (C≡O), 1891 (C≡O), 1450 (C=C), 1092 (Si–O–C), 942 (C–O–C), 840 (Si–C) cm^{-1}. δ_H 0.126 (s, 3H, Si–CH_3), 0.132 (s, 3H, Si–CH_3), 0.905 (s, 9H, Si–C–$(CH_3)_3$), 1.42–1.83 (m, 10H, C_6H_{10}), 4.58 (d, $J = 3.0$ Hz, 1H, H3), 5.23 (d, $J = 3.0$ Hz, 1H, H2), 5.32–5.42 (m, 5H, H12, H16, H13, H15, H14) ppm. δ_C −5.21 (CH_3, Si–CH_3), −4.21 (CH_3, Si–CH_3), 17.77 (C, Si–C–$(CH_3)_3$), 23.70 (CH_2, C8), 23.82 (CH_2, C7), 25.11 (CH_2, C9), 25.59 (CH_3, Si–C–$(CH_3)_3$), 36.15 (CH_2, C6), 37.02 (CH_2, C10), 83.67 (CH, C3), 90.31 (CH, C12, C16), 91.62 (CH, C13, C15), 92.10 (CH, C14), 102.06 (CH, C2), 108.94 (C, C11), 112.62 (C, C5), 232.36 (C, C≡O) ppm.

3.6. Deprotonation–silylation of {[(2R,3R)-(1,2,3,4,5,6-η)-2-t-butyl(dimethyl)-(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}tricarbonylchromium (**9**)

{[(2*R*,3*R*)-(1,2,3,4,5,6-η)-2-*t*-Butyl(dimethyl)-(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)-oxy]silane}tricarbonylchromium (**9**) (0.15 g, 0.31 mmol) was stirred in dry THF (10 ml) and cooled to −78 °C under an atmosphere of nitrogen for 30 min. Butyllithium (0.31 ml, 2.2 mol l^{-1} in hexanes, 0.682 mmol) was injected and the solution was stirred at −78 °C for 2.5 h. Chlorotrimethylsilane (0.09 ml, 0.704 mmol, freshly distilled from CaH_2) was injected into the mixture, which was stirred at the same temperature for 2.5 h and then allowed to warm to r.t. over 30 min. The solvent was evaporated under reduced pressure and the residue was taken up in EtOAc (20 ml) and filtered through Celite. Evaporation of the solvent under vacuum gave an orange syrup. Flash chromatography using hexanes–EtOAc (20:1) gave {[(2*R*,3*R*)-(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-(3ζ-trimethylsilyl)phenyl)-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}tricarbonylchromium (**11**) as a yellow oil, (87 mg, 50%). (Found: $[M^{+\bullet}]$ 556.1767. $C_{26}H_{40}{}^{52}CrO_6Si_2$ requires 556.1769 (0.3 ppm)). ν_{max} 3054 (C–H, aromatic), 2936 (C–H), 1968 (C≡O), 1892 (C≡O), 1450 (C=C), 1090 (Si–O–C), 943 (C–O–C), 840 (Si–C) cm^{-1}. δ_H for one major isomer (*meta*, 39% by ^{1}H-NMR) 0.055 (s, 3H, Si–CH_3), 0.247 (s, 9H, Si′–$(CH_3)_3$), 4.53 (d, $J = 3.3$ Hz, 1H, H3) ppm. δ_C for one major isomer 89.12 (CH, C16), 92.66 (CH, C15), 96.94 (CH, C12), 98.67 (CH, C14) ppm. δ_H for other major isomer (*meta*, 42% by ^{1}H-NMR) 0.137 (s, 3H, Si–CH_3), 0.160 (s, 3H, Si–CH_3), 0.287 (s, 9H, Si′–$(CH_3)_3$), 0.909 (s, 9H, Si–C–$(CH_3)_3$), 1.42–1.87 (m, 10H, C_6H_{10}), 4.58 (d, $J = 2.6$ Hz, 1H, H3), 5.49 (s, 1H, H_o), 5.65 (d, b, $J = 5.5$ Hz, 2H, $H_{o'}$, H_p) ppm. δ_C for other major isomer −5.21 (CH_3, Si–CH_3), −4.24 (CH_3, Si–CH_3), −1.22 (CH_3, Si′–$(CH_3)_3$), 17.74 (C, Si–C–$(CH_3)_3$), 23.81 (CH_2, C8), 23.95 (CH_2, C7), 25.12 (CH_2, C9), 25.60 (CH_3, Si–C–$(CH_3)_3$), 36.06 (CH_2, C6), 37.02 (CH_2, C10), 83.67 (CH, C3), 98.09 (CH, C12), 99.29 (CH, C14), 102.38 (CH, C2), 112.41 (C, C5), 232.74 (C, C≡O) ppm. δ_H for minor isomer (*para*, 19% by ^{1}H-NMR) 0.094 (s, 3H, Si–CH_3), 0.127 (s, 3H, Si–CH_3), 0.362 (s, 9H, Si′–$(CH_3)_3$), 4.64 (d, $J = 3.1$ Hz, 1H, H3) ppm.

3.7. Deprotonation–silylation of {[(2S,3S)-(1,2,3,4,5,6-η)-2-t-butyl(dimethyl)-(3-phenyl-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}tricarbonylchromium (**10**)

Reaction of {[(2*S*,3*S*)-(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-phenyl-1,4-dioxaspiro-[4.5]decan-2-yl)-oxy]silane}tricarbonylchromium (**10**) (0.1 g, 0.207 mmol) in dry THF with BuLi (0.21 ml, 2.2 mol l^{-1} in hexanes, 0.462 mmol) and then chlorotrimethylsilane (0.06 ml, 0.469 mmol) gave {[(2*S*,3*S*)-(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-(3ζ-trimethyl-silyl)phenyl)-1,4-dioxaspiro[4.5]-decan-2-yl)oxy]silane}tricarbonylchromium (**12**) as a yellow oil (90 mg, 78%). (Found: $[M^{+\bullet}]$ 556.1771. $C_{26}H_{40}{}^{52}CrO_6Si_2$ requires 556.1769 (−0.5 ppm)). ν_{max} 3054 (C–H, aromatic), 2936 (C–H), 1968 (C≡O), 1893 (C≡O), 1450 (C=C), 1090 (Si–O–C), 943 (C–O–C), 839 (Si–C) cm^{-1}. δ_H for one major isomer (*meta*, 42% by ^{1}H-NMR) 0.065 (s, 3H, Si–CH_3), 0.104 (s, 3H, Si–CH_3), 0.256 (s, 9H, Si′–$(CH_3)_3$), 0.903 (s, 9H, Si–C–$(CH_3)_3$), 1.42–1.91 (m, 10H, C_6H_{10}), 4.53 (d, $J = 3.2$ Hz, 1H, H3), 5.13 (t, $J = 6.4$ Hz, 1H, H_m), 5.21 (d, b, 1H, H2), 5.43 (d, $J = 6.4$ Hz, 1H, H_p), 5.50 (s, 1H, H_o), 5.65 (d, b, $J = 6.8$ Hz, 1H, $H_{o'}$) ppm. δ_C for one major isomer −5.21 (CH_3, Si–CH_3), −4.17 (CH_3, Si–CH_3), −1.21 (CH_3, Si′–$(CH_3)_3$), 17.74 (C, Si–C–$(CH_3)_3$), 23.83 (CH_2, C8), 23.97 (CH_2, C7), 25.12 (CH_2, C9), 25.61 (CH_3, Si–C–$(CH_3)_3$), 36.07 (CH_2, C6), 37.02 (CH_2, C10), 83.67 (CH, C3), 89.12 (CH, C16), 92.67 (CH, C15), 96.94 (CH, C12), 98.67 (CH, C14), 102.38 (CH, C2), 112.41 (C, C5), 232.74 (C, C≡O) ppm. δ_H for other major isomer (*meta*, 40% by ^{1}H-NMR) 0.146 (s, 3H, Si–CH_3), 0.169 (s, 3H, Si–CH_3), 0.297 (s, 9H, Si′–$(CH_3)_3$), 0.917 (s, 9H, Si–C–$(CH_3)_3$), 4.59 (d, $J = 2.8$ Hz, 1H, H3), 5.17 (t, $J = 6.4$ Hz, 1H, H_m), 5.31 (d, b, 1H, H2), 5.39 (d, $J = 6.3$ Hz, 1H, H_p), 5.63 (d, $J = 7.6$ Hz, 1H, H_o) ppm. δ_C for other major isomer 89.63 (CH, C16), 93.95 (CH, C15), 98.10 (CH, C12), 99.29 (CH,

C14) ppm. δ_H for minor isomer (*para*, 18% by ^{1}H-NMR) 0.127 (s, 3H, Si–CH_3), 0.136 (s, 3H, Si–CH_3), 0.294 (s, 9H, Si′–$(CH_3)_3$), 0.925 (s, 9H, Si–C–$(CH_3)_3$), 4.63 (d, $J = 2.4$ Hz, 1H, H3), 5.25 (d, $J = 3.1$ Hz, 1H, H2) ppm.

3.8. Decomplexation of {[(2R,3R)-(1,2,3,4,5,6-η)-2-t-butyl(dimethyl)-(3-(3ζ-(trimethyl silyl)phenyl)-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}-tricarbonylchromium (11)

$CDCl_3$ (2 ml) was added to {[(2*R*,3*R*)-(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-(3ζ-(trimethylsilyl)phenyl)-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}tricarbonylchromium (**11**) (87 mg, 0.156 mmol) and the solution was exposed to air for 10 min. It was then capped and exposed to laboratory light for 48 h. The solution turned cloudy green and was filtered through cotton wool; a colourless solution resulted. Removal of the solvent gave [(2*R*,3*R*)-(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-(3ζ-(trimethylsilyl)phenyl)-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane (**13**). (Found: [$M^{+\bullet}$] 420.2513. $C_{23}H_{40}O_3Si_2$ requires 420.2516 (0.6 ppm)). ν_{max} ($CDCl_3$) 2934 (C–H), 1093 (Si–O–C), 839 (Si–C) cm^{-1}. δ_H (C_6D_6) for major isomer (*meta*, 84% by ^{1}H-NMR) 0.029 (s, 3H, Si–CH_3), 0.122 (s, 3H, Si–CH_3), 0.231 (s, 9H, Si′–$(CH_3)_3$), 0.960 (s, 9H, Si–C–$(CH_3)_3$), 1.30–2.04 (m, 10H, C_6H_{10}), 5.20 (d, $J = 3.4$ Hz, 1H, H3), 5.39 (d, $J = 3.4$ Hz, 1H, H2), 7.26 (t, $J = 7.4$ Hz, 1H, H_m), 7.40 (d, $J = 7.3$ Hz, 1H, $H_{o'}$), 7.59 (d, $J = 7.6$ Hz, 1H, H_p), 7.76 (s, 1H, H_o) ppm. δ_C (C_6D_6) for major isomer −5.09 (CH_3, Si–CH_3), −4.12 (CH_3, Si–CH_3), −1.12 (CH_3, Si′–$(CH_3)_3$), 18.09 (C, Si–*C*–$(CH_3)_3$), 24.25 (CH_2, C8), 24.30 (CH_2, C7), 25.61 (CH_2, C9), 25.84 (CH_3, Si–C–$(CH_3)_3$), 36.67 (CH_2, C6), 37.76 (CH_2, C10), 86.26 (CH, C3), 103.09 (CH, C2), 111.89 (C, C5), 126.53 (CH, C16), 128.22 (CH, C15), 131.15 (CH, C12), 133.21 (CH, C14), 139.09 (C, C11), 140.63 (C, C13) ppm. δ_H (C_6D_6) for minor isomer (*para*, 16% by ^{1}H-NMR) 0.009 (s, 3H, Si–CH_3), 0.114 (s, 3H, Si–CH_3), 0.189 (s, 9H, Si′–$(CH_3)_3$), 0.947 (s, 9H, Si–C–$(CH)_3)_3$), 4.94 (d, $J = 3.2$ Hz, 1H, H3), 5.41 (d, $J = 3.4$ Hz, 1H, H2), 7.48 (d, $J = 7.6$ Hz, 1H, H_o), 7.55 (d, $J = 7.6$ Hz, 1H, H_p) ppm. δ_C (C_6D_6) for minor isomer 125.73 (CH, C12, C16), 133.89 (CH, C13, C15), 141.41 (C, C14) ppm.

3.9. Decomplexation of {[(2S,3S)-(1,2,3,4,5,6-η)-2-t-butyl(dimethyl)-(3-(3ζ-trimethyl silyl)phenyl)-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}tricarbonylchromium (12)

$CDCl_3$ (2 ml) was added to {[(2*S*,3*S*)-(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-(3ζ-(trimethylsilyl)phenyl)-1,4-dioxaspiro[4.5]decan-2-yl)oxy]silane}tricarbonylchromium (**12**) (90 mg, 0.162 mmol). The solution was exposed to air for 10 min and then to laboratory light for 48 h to give [(2*S*,3*S*)-(1,2,3,4,5,6-η)-2-*t*-butyl(dimethyl)-(3-(3ζ-trimethylsilyl)phenyl)-1,4-dioxaspiro-[4.5]decan-2-yl)oxy]silane (**14**). (Found: [$M^{+\bullet}$] 420.2513. $C_{23}H_{40}O_3Si_2$ requires 420.2516 (0.7 ppm)). ν_{max} ($CDCl_3$) 2929 (C–H), 1095 (Si–O–C), 839 (Si–C) cm^{-1}. δ_H for major isomer (*meta*, 86% by ^{1}H-NMR) 0.065 (s, 3H, Si–CH_3), 0.105 (s, 3H, Si–CH_3), 0.257 (s, 9H, Si′–$(CH_3)_3$), 0.904 (s, 9H, Si–C–$(CH_3)_3$), 1.42–1.92 (m, 10H, C_6H_{10}), 4.97 (d, $J = 3.2$ Hz, 1H, H3), 5.20 (d, $J = 3.2$ Hz, 1H, H2), 7.26–7.37 (m, 2H, $H_{o'}$, H_m), 7.44 (d, $J = 6.8$ Hz, 1H, H_p), 7.49 (s, 1H, H_o) ppm. δ_C for major isomer −5.16 (CH_3, Si–CH_3), −4.28 (CH_3, Si–CH_3), −1.17 (CH_3, Si′–$(CH_3)_3$), 17.75 (C, Si–*C*–$(CH_3)_3$), 23.80 (CH_2, C8), 23.94 (CH_2, C7), 25.27 (CH_2, C9), 25.61 (CH_3, Si–C–$(CH_3)_3$), 36.22 (CH_2, C6), 37.16 (CH_2, C10), 85.91 (CH, C3), 102.42 (CH, C2), 112.25 (C, C5), 126.16 (CH, C16), 127.85 (CH, C15), 130.87 (CH, C12), 132.80 (CH, C14) ppm. δ_H for minor isomer (*para*, 14% by ^{1}H-NMR) 4.95 (d, $J = 3.0$ Hz, 1H, H3), 5.23 (d, $J = 3.1$ Hz, 1H, H2) ppm.

3.10. Tricarbonyl{(R)-[(1,2,3,4,5,6-η)-3-phenyl-1,4-dioxaspiro-[4.5]-decan-2-one]}chromium (15)

A mixture of (*R*)-3-phenyl-1,4-dioxaspiro[4.5]decan-2-one (**2**) (0.50 g, 2.16 mmol) and $Cr(CO)_6$ (0.576 g, 2.62 mmol) in 1,4-dioxane (30 ml) was refluxed for 48 h. Workup and flash column chromatography (C_6H_{14}–EtOAc, 90:10) gave: (i) tricarbonyl{(*R*)-[(1,2,3,4,5,6-η)-3-phenyl-1,4-dioxaspiro-[4.5]-decan-2-one]}chromium (**15**) as a yellow solid (0.556 g, 70%), m.p. 158–160 °C. (Found: [$M^{+\bullet}$] 368.0348. Calc. for $C_{17}H_{16}{}^{52}CrO_6$, 368.0352 (1.0 ppm)). ν_{max} (KBr); 3072 (C–H aromatic), 1977 (C≡O), 1873 (C≡O), 1782 (C=O), 1495 (C–C aromatic), 938 (C–O–C) cm^{-1}. δ_H (400 MHz) 1.457–1.532 (m, 2H, H8), 1.653–1.826 (m, 4H, H7 and H9), 1.851–1.964 (m, 4H, H6 and H10), 5.036 (s, 1H, H3), 5.30–5.40 (m, 3H, 2 × *meta* and 1 *para* H), 5.528 (d, $J = 6.4$ Hz, 1H, *ortho*), 5.567 (d, $J = 6.4$ Hz, 1H, *ortho*) ppm. δ_C 22.9 (C7), 23.0 (C9), 24.3 (C8), 35.6 (C10), 36.4 (C6), 73.2 (C3), 88.8 (*ortho*), 90.7 (*ortho*), 91.3(*meta*), 91.6 (*meta*), 92.2 (*para*), 103.8 (*ipso*), 112.6 (C5), 169.5 (C2), 231.8 (C≡O) ppm. *m*/z 368 (11, [$M^{+\bullet}$]), 340 (0.5, [M−CO]), 312 (16, [M−2CO]), 284 (80, [M−3CO]), 256 (5, [M−4CO]), 240 (12, 284−CO_2), 186 (25, 284−$C_6H_{10}O$), 142 (46, $PhCH^{52}Cr^+$), 105 (2.0, $PhCO^+$), 91 (7, $C_7H_7^+$), 77 (3, Ph^+), 52 (100, $^{52}Cr^+$); and (ii) the free ligand **2** (0.150 g, 30%).

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 177802–177804 for compounds (2*R*,3*R*)-**7**, *rac-trans*-(**9**/**10**) and

(*R*)-**15**. Copies are available free of charge from the Director, CCDC, 12 Union road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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