

1,5-Asymmetric induction during nucleophilic additions to arenetricarbonylchromium complexes: tricarboyl(η^6 -1-methyl-4-{spiro-[(1*R*,2*S*)-1,7,7-trimethylbicyclo[2.2.1]-heptane-3,2'-1,3-dioxolan]-2-yloxy}-benzene)chromium

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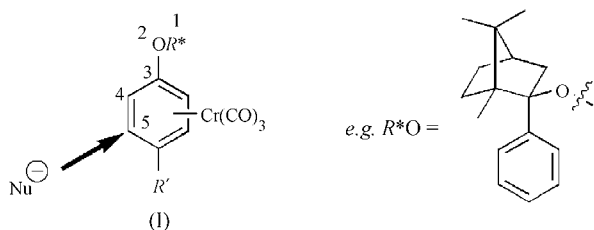
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The tricarboylchromium unit bound to the arene ring of the chiral title complex, $[\text{Cr}(\text{C}_{19}\text{H}_{26}\text{O}_3)(\text{CO})_3]$, is rotated by *ca* 25° in agreement with the proposed mechanism for 1,5-asymmetric induction of nucleophilic attack.

Comment

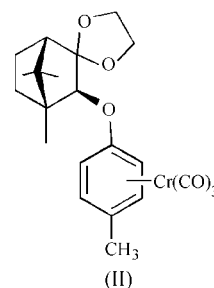
Arenes (Kündig & Pape, 2004, and references therein) can be converted to cyclohexenes and cyclohexenones by the one-pot sequence of nucleophilic addition to the corresponding arenetricarbonylchromium complex, followed by treatment of the resulting dienylchromium complex with a suitable electrophile and then decomplexation, leading to methodology that finds applications in the synthesis of natural products (Schmalz *et al.*, 2004). When alkoxyarenetricarbonylchromium complexes are used in this sequence, carbon nucleophiles add predominantly to the *meta* position, ultimately yielding



5-substituted cyclohexenones. [For examples of application of cyclohexenone synthesis, see Pearson *et al.* (2004).] This reaction can be adapted to give an asymmetric synthesis of 5-substituted cyclohexenones by using chiral alkoxyarenetri-

carbonylchromiums, as reported earlier from our laboratories (Pearson *et al.*, 1996; Pearson & Gontcharov, 1998; Gontcharov, 1997) and by Semmelhack & Schmalz (1996). Nucleophilic addition to chiral complexes of type (I) presents an interesting example of 1,5-asymmetric induction (Hollowood *et al.*, 2003; Evans *et al.*, 2003; O'Malley & Leighton, 2001; Castelot-Deliencourt *et al.*, 2001), rare in the chemical literature, but the mechanism of asymmetric induction in these reactions is not completely understood.

A plausible mechanism for chirality transmission is by a small rotation of the tricarboylchromium tripod on the arene ligand. This would lead to a distortion of the complex lowest unoccupied molecular orbital (LUMO), so that its coefficients at the diastereotopic *meta* positions are unequal, thereby promoting preferential addition at one site (Pearson *et al.*, 1995). In contrast, in simple methoxyarene complexes [(I), with $R^* = \text{CH}_3$], the tricarboylchromium Cr—C bonds eclipse the *ipso* and both *meta* C atoms of the arene (Semmelhack, 1991). As part of an effort to determine the extent to which the chiral alkoxy group causes this rotation, and therefore whether it might be a causative factor in asymmetric induction, the crystal structures of several alkoxyarenetricarbonylchromium complexes are being studied. We have already reported some of these results for complexes having a trimethylsilyl substituent [(I), with $R' = \text{Si}(\text{CH}_3)_3$] *para* to the chiral alkoxy group, all of which structures support our hypothesis (Paramahamsan *et al.*, 2008). In order to show that such rotation of the $\text{Cr}(\text{CO})_3$ group is not specific to the nature of the R' substituents, we have also more recently determined the structure the title complex, (II), a complex bearing a simple alkyl group. The structure of this compound, prepared as described previously (Pearson & Gontcharov, 1998), is reported in the present paper.

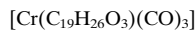


As shown in Fig. 1, there is indeed a significant rotation of the $\text{Cr}(\text{CO})_3$ group (*ca* 25°) [the torsion angles with respect to the centroid (X) of the arene ring are $\text{C}20\text{—Cr}1\text{—}X\text{—C}13 = 25.5$ (2)°, $\text{C}21\text{—Cr}1\text{—}X\text{—C}15 = 25.9$ (2)° and $\text{C}22\text{—Cr}1\text{—}X\text{—C}17 = 24.1$ (2)°], and the direction of rotation is in agreement with the sense of asymmetric induction that we have previously reported during nucleophilic additions to this complex (Pearson & Gontcharov, 1998). The rotation of the $\text{Cr}(\text{CO})_3$ unit also removes the mirror symmetry of the arene; for example, the aromatic bonds to atom C16 differ by 0.018 Å, in agreement with the distortion of the LUMO referred to above. Other geometrical parameters are unremarkable.

Experimental

The title complex, (II), was prepared as described previously (Pearson & Gontcharov, 1998), and crystals were obtained by recrystallization from 1:1 hexane/dichloromethane.

Crystal data



$M_r = 438.43$

Monoclinic, $P2_1$

$a = 7.9484$ (7) Å

$b = 13.6135$ (11) Å

$c = 9.5596$ (8) Å

$\beta = 93.026$ (3)°

$V = 1032.96$ (15) Å³

$Z = 2$

Mo $K\alpha$ radiation

$\mu = 0.59$ mm⁻¹

$T = 120$ (1) K

$0.25 \times 0.15 \times 0.05$ mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 1997)

$T_{\min} = 0.908$, $T_{\max} = 1.000$

(expected range = 0.882–0.971)

8946 measured reflections

4556 independent reflections

4224 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.090$

$S = 1.09$

4556 reflections

263 parameters

1 restraint

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.63$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.42$ e Å⁻³

Absolute structure: Flack (1983),

1898 Friedel pairs

Flack parameter: 0.041 (18)

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR3032). Services for accessing these data are described at the back of the journal.

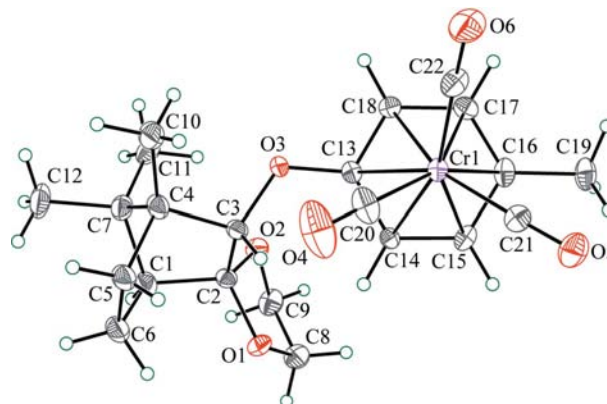


Figure 1

A view of the title complex, (II), projected on to the plane of the arene ring. Displacement ellipsoids are shown at the 50% probability level.

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