Optically Active Naphthalene–Cr(CO)$_3$ Complexes *via* Diastereoselective Carbene Annulation and Haptotropic Metal Migration†

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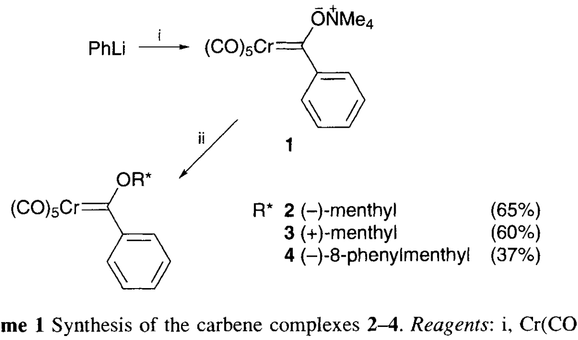
Pentacarbonyl[(+)- and (−)-menthyloxycarbene] complexes of chromium react with 3,3-dimethylbut-1-yne diastereoselectively to give optically active naphthalene–Cr(CO)$_3$ complexes which upon warming undergo an intramolecular haptotropic migration of the metal fragment.

Due to their plane of chirality, metal complexes of unsymmetrically *ortho-* or *meta*-disubstituted arenes have become valuable reagents in stereoselective synthesis.[1] A straightforward access to hydroquinone derivatives of this class of compounds is provided by the chromium-mediated benzannulation of an unsaturated alkoxycarbene ligand by an alkyne and a carbonyl ligand.[2] A diastereoselective modification of this reaction in which the Cr(CO)$_3$ moiety is coordinated selectively to one of both enantiotopic faces of the arene may be based on a chiral carbene complex or a chiral alkyne. Recently, sterically demanding α-chiral prop-2-ynylic ethers have been successfully applied in the benzannulation of vinylcarbene complexes.[3] We have focussed our attention on a more general approach which involves carbene complexes containing readily available chiral alkoxy groups.

Tetramethylammonium pentacarbonylbenzoylchromate **1** is modified into the optically active menthyloxy(phenyl)carbene complexes **2–4** by an acetylation/alcoholysis sequence.[4] In comparison with the methoxy(phenyl)carbene homologue the NMR signals of the menthyloxy group are broadened already at ambient temperature indicating a slower rotation around the $C_{carbene}$–O bond as a consequence of the bulky alkoxy substituent. Below −40 °C complexes **2–4** are detected as an approximate 1 : 2 mixture of *E*/*Z*-isomers (Scheme 1).

To study the stereodifferentiating ability of the menthyl auxiliary in the benzannulation the complexes **2–4** were reacted with the terminal alkyne **5** which is known to undergo a regiospecific incorporation into the naphthohydroquinone skeleton.[5] Protection of the benzannulation products with SiMe$_2$Bu^{t}Cl and chromatographic workup afforded the silyl ethers **6** and **7** in moderate chemical yields and in diastereomeric ratios of **6a** : **6b** = 10 : 1 (81% d.e.) and **7a** : **7b** = 9.2 : 1 (80% d.e.), respectively.‡ Surprisingly, (−)-8-phenylmenthol, generally a more selective auxiliary in cycloaddition reactions,[6] is less efficient in the carbene annulation reaction affording the major diastereomer **8a** in only 50% d.e. (Scheme 2).

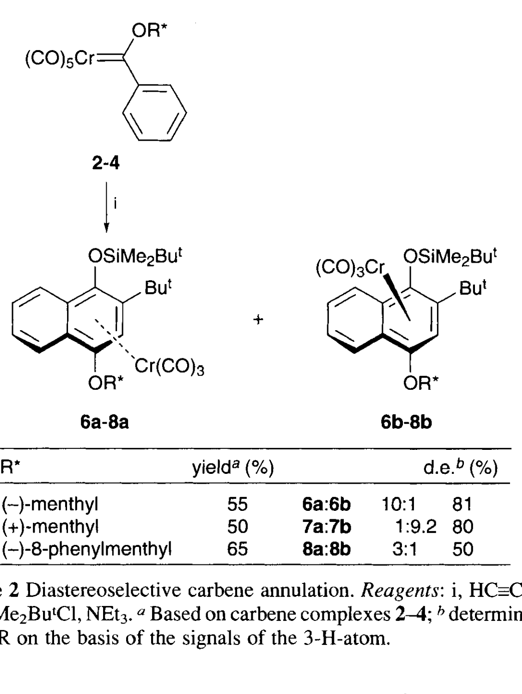
The major diastereomers **6a** and **7b** were isolated as red crystals by low-temperature crystallization from light petroleum and characterized according to the upfield shift of the 3-H atom (δ 5.60 and 5.71, respectively) in the metal-coordinated arene ring formed in the annulation reaction. Their absolute configurations were determined by X-ray analyses.§ Both major diastereomers are enantiomers; in the (−)-menthyloxynaphthalene complex **6a** the arene–metal moiety has the R_p configuration[7] (p = in planar chiral systems) while the (+)-menthyloxy complex **7b** is characterized by the S_p configuration (Fig. 1). The classification of **6a** and **7b** as enantiomers is further evident from their optical rotation data (**6a**: $[\alpha]_D^{25}$ +693; **7b**: $[\alpha]_D^{25}$ −690).



R* **2** (−)-menthyl (65%)
3 (+)-menthyl (60%)
4 (−)-8-phenylmenthyl (37%)

Scheme 1 Synthesis of the carbene complexes **2–4**. *Reagents*: i, Cr(CO)$_6$ then NMe$_4$Br, yield 80%; ii, AcBr then R*OH.

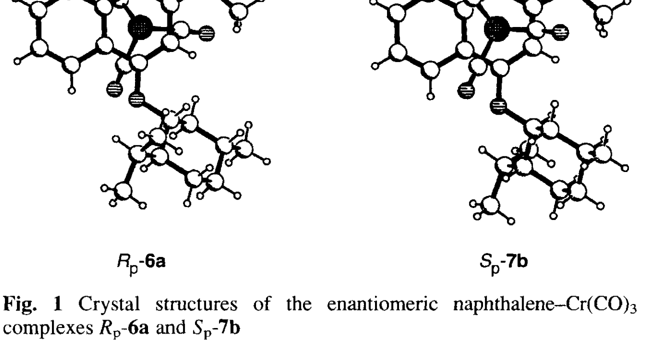
The conformational flexibility of the terpenoxy auxiliaries makes a reliable prediction of the stereochemical outcome difficult. On the basis of the mechanism generally accepted for the benzannulation[8] we suggest that the coupling of the alkyne and the carbene ligand to generate a $\eta^1:\eta^3$-vinylcarbene



6a-8a **6b-8b**

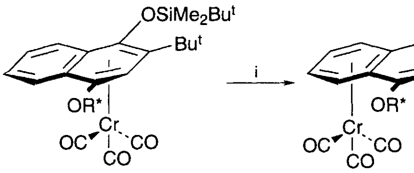
R*	yield[a] (%)		d.e.[b] (%)	
(−)-menthyl	55	**6a**:**6b**	10:1	81
(+)-menthyl	50	**7a**:**7b**	1:9.2	80
(−)-8-phenylmenthyl	65	**8a**:**8b**	3:1	50

Scheme 2 Diastereoselective carbene annulation. *Reagents*: i, HC≡CBu^t **5** then SiMe$_2$Bu^{t}Cl, NEt$_3$. [a] Based on carbene complexes **2–4**; [b] determined by ^{1}H NMR on the basis of the signals of the 3-H-atom.



R_p-**6a** S_p-**7b**

Fig. 1 Crystal structures of the enantiomeric naphthalene–Cr(CO)$_3$ complexes R_p-**6a** and S_p-**7b**



6a [R* = (–)-menthyl] **9**

Scheme 3 *Reagents and conditions*: Bu^n_2O, 90 °C, 20 min; analogously **7b** [R* = (+)-menthyl] → **10**

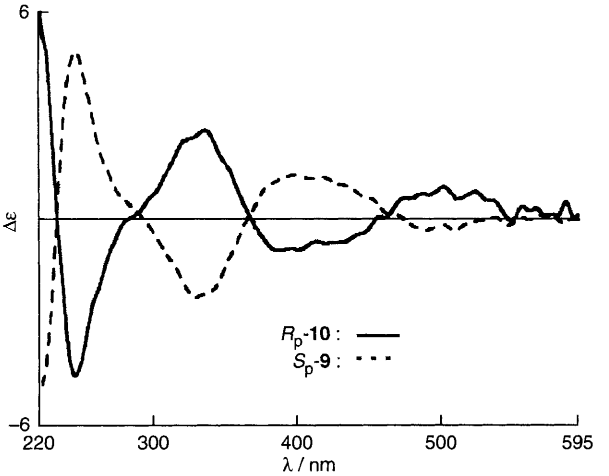


Fig. 2 CD spectra of the enantiomeric naphthalene–$Cr(CO)_3$ complexes S_p-**9** and R_p-**10** (c = 10^{-3} mol dm^{-3}, CH_2Cl_2)

intermediate is the stereodifferentiating step along which the chiral auxiliary controls the migration of the chromium carbonyl fragment to one of both enantiotopic faces of the vinylcarbene ligand.

The chromium-mediated benzannulation of alkoxy(aryl)-carbene complexes allows control over the coordination of the $Cr(CO)_3$ fragment of the fused arene system.[9] Annulation carried out at 55 °C provides kinetic control to produce **6a/b–8a/b**. When enantiomers **6a** and **7b** are warmed in di-*n*-butyl ether to 90 °C a haptotropic migration occurs under thermodynamic control to afford enantiomers **9** and **10** (Scheme 3) as single diastereomers with complementary optical rotation data (**9**: $[\alpha]_D^{25}$ +2.5; **10**: $[\alpha]_D^{25}$ −2.0; c 0.9, $CHCl_3$) and CD spectra (Fig. 2). This result indicates that isomerization occurs intramolecularly along one face of the naphthalene system which is in line with earlier EHMO calculations.[10]

The annulation of optically active carbene complexes derived from readily available auxiliaries provides a direct route to densely functionalized chiral arene–$Cr(CO)_3$ complexes which are promising reagents for elaborate stereoselective synthesis.

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Footnotes

† Reactions of Complex Ligands Part 67. For Part 66 see: O. Kretschik, M. Nieger and K. H. Dötz, *Chem. Ber.*, 1995, **128**, 987.

‡ *General procedure* for the synthesis of **6a/b–8a/b**: All reactions and work up procedures were performed under argon atmosphere. A solution of 2 mmol **2–4** and 8 mmol **5** in 5 ml Bu^tOMe was degassed in three cycles and warmed at 55 °C for 45 min. After cooling to room temperature and filtration over silica gel, 8 mmol $SiMe_2Bu^tCl$ and 8 mmol NEt_3 were added, and the solution stirred at room temp. for 3 h. The solvent was removed under reduced pressure and the residue purified by column chromatography [light petroleum (bp 40–60 °C)–CH_2Cl_2 (5 : 1 *v/v*) at −10 °C] to afford **6a/b**, 0.66 g (55%); **7a/b**, 0.60 g (50%); **8a/b**, 0.90 g (65%). The major diastereomers **6a** and **7b** were isolated by fractional crystallization at −35 °C from light petroleum (bp 40–60 °C).

§ *Crystallographic details* of **6a** [**7b**]: $C_{33}H_{48}CrO_5Si$, red crystals, M = 604.8, space group $P2_12_12_1$ (no. 19), a = 9.349(2) [9.347(3)], b = 11.707(2) [11.721(1)], c = 30.268(4) [30.292(3)] Å, U = 3313(1) [3319(1)] $Å^3$, Z = 4[4], μ(Cu-Kα) = 3.48 mm^{-1}, T = 200 [208] K, $F(000)$ = 1296. 5959[5626] Reflections were measured on an Enraf-Nonius CAD-4 diffractometer with Cu-Kα radiation ($2\theta_{max}$ = 140 [120°]), 5325 [4915] independent reflections were used for all calculations. The structure was solved by direct methods (SHELXTL-PLUS[11a]) and refined anisotropically on F^2 (SHELXL-93[11b]). All hydrogen atoms were refined by using a riding model; $wR2(F^2)$ = 0.077 [0.132] with $R(F)$ = 0.029 [0.049] for 372 [372] parameters. An absorption correction was applied (DIFABS[12] **6a**, ψ-scans **7b**). The absolute configuration was determined {Flack's x-parameter[13] 0.000(4) [0.005(7)]}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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