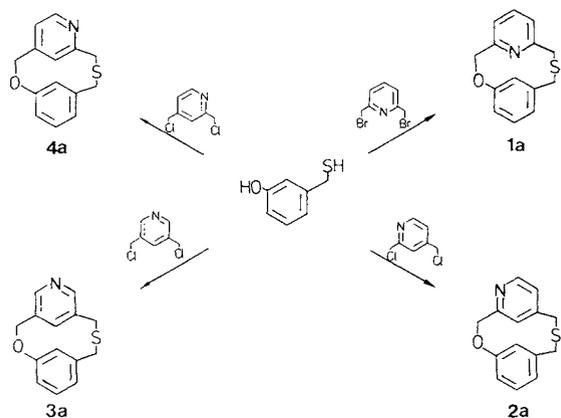


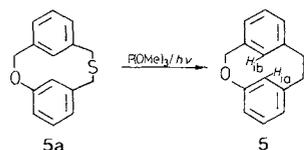
the fact that the shortest intramolecular distance known so far [C(8)–C(6) 257.9 pm] is observed in **3** (for comparison: 268.9 pm in [2.2]metacyclophane).

The synthesis of **5** has already been reported, but the method used involved several steps and the yields were low (only milligram amounts were isolated).^[5] To obtain the pyridinophanes **1–4** in the required gram amounts we have developed a new, generally applicable two-step synthesis for heteroarenes: a bis(halogenomethyl)-substituted arene or heteroarene is cyclized with 3-(mercaptomethyl)phenol under dilution conditions^[9] and in the presence of cesium carbonate^[11] in ethanol to a [3.2]phane as precursor in good yields (up to 45%) (Scheme 1). Subse-



Scheme 1.

quent desulfurization^[10] in a thiophilic solvent [P(OMe)₃ or P(OEt)₃] (Scheme 2) leads to the narrow-bracketed product in remarkably good yields (up to 40%), considering the hitherto narrowest [2.2]phane ring.



Scheme 2.

For the determination of the ring-inversion barriers of the [3.2]phanes **1a–5a** we have used the coalescence of the ¹H-NMR signals of the CH₂–O group: the free enthalpy of activation for **3a** is 95 kJ mol⁻¹. **1a** shows no coalescence up to –55°C (90 MHz) because of the small steric demands of the lone pair of the nitrogen atom;^[11] the corresponding barriers for **2a**, **4a** and **5a** all lie at 88 kJ mol⁻¹.

To gain a better insight into the influence of chromophore orientation on the circular dichroism we are currently studying further helical molecules with formal clockwise rotation of the chromophore in the molecule.

Experimental

Cyclization: The solutions of bis(halogenomethyl)arene [e.g. 1,3-bis(bromomethyl)benzene] (10.0 mmol) in ethanol (250 mL) and of 3-(mercaptomethyl)phenol (10.0 mmol) and potassium *tert*-butoxide (11.0 mmol) in 85% ethanol (250 mL) were added dropwise within 10 h to 1 L of boiling ethanol (dilution principle apparatus [12]). The cyclization was noticeably favored by addition of a spatula-tip of Cs₂CO₃. After a further 3 hours' boiling the reaction mixture was worked up column chromatographically [silica gel, dichloromethane/acetone mixture (20/1 to 10/1)].

Desulfurization: the [3.2]phane (3.00 mmol) was dissolved in P(OMe)₃ (freshly distilled over sodium) and irradiated in a quartz flask with a high-pressure mercury lamp (HQ 600; 15 h, argon, 30°C). P(OMe)₃ was removed under vacuum and the residue chromatographed on silica gel [dichloromethane/acetone mixture (20/1 to 10/1)] [14].

Crystal structure analysis of 3 [14]: colorless crystals; crystal dimensions: 0.15 × 0.25 × 0.5 mm³; *M*_r = 211.2, space group *P*2₁2₁2₁, *a* = 589.1(4), *b* = 784.0(3), *c* = 2336.8(13) pm. *V* = 1.079 nm³, *Z* = 4, ρ_{calcd} = 1.30 g cm⁻³, μ(MoKα) = 0.08 mm⁻¹; 1886 symmetry independent reflections (2θ_{max} = 50°); 1617 reflections with |*F*| > 3σ(*F*) were used for the structure solution (direct methods) and refinement (145 parameters); non-hydrogen atoms anisotropically, H atoms (located by difference electron density determination) refined with a riding model: *R* = 0.055 [*R*_w = 0.053, w⁻¹ = σ²(*F*) + 0.005 *F*²]. The absolute configuration could not be determined.

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Blocking of the Retro-Diels–Alder Reaction by Complex Formation: [(η⁵-Cyclopentadienyl)(η⁵-dicyclopentadienyl)iron]**

By Janet Blümel, Frank H. Köhler,* Gerhard Müller, and Dallas L. Wilkinson

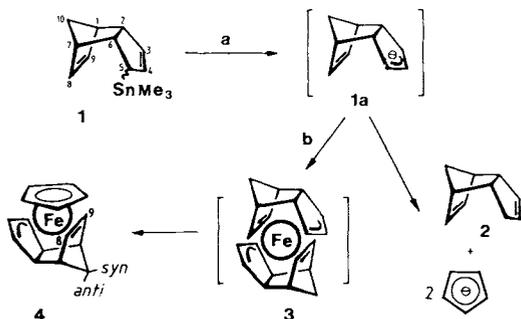
The retro-Diels–Alder reaction is part of the standard repertoire^[1,2] of the preparative chemist; nonetheless, a great deal of work is being invested towards the improvement of this reaction—for example, to circumvent the usually dras-

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tic conditions required by pyrolysis. Recent chemical approaches have included the acceleration of the reaction by the incorporation of silyl groups,^[2a] by acid catalysis in the aza variant,^[2b] and by reducing the molecular strain^[2c] or the basicity^[2d-k] on going from the educt to the products. With regard to the latter variant, we recently found that the retro-Diels-Alder reaction can even proceed so rapidly that the actual starting compound cannot be observed.^[3] For instance, the reaction of the stannylated dicyclopentadiene **1** with methyllithium leads to dicyclopentadiene **2** and cyclopentadienyllithium even at -78°C . We have not yet been able to detect the proposed intermediate **1a**.



Scheme 1. a) $\text{MeLi}/\text{Et}_2\text{O}$, THF, -78°C ; b) $\text{Fe}_2\text{Cl}_4(\text{THF})_3$, $-78 \rightarrow 25^{\circ}\text{C}$; the counterions are Li^{\oplus} .

We have now found that **1a** may be trapped with solvated iron(II) chloride; the title compound η^5 -cyclopentadienyl-(η^5 -dicyclopentadienyl)iron,^[4] **4**, the only isolable iron compound, is thereby formed in a yield of 20% (not optimized, based on **1**; Scheme 1). The identity of **4** ("DicpFeCp") follows from the correct elemental analysis and the spectroscopic data.^[5] Important features include the following: The number of NMR signals corresponds to C_s symmetry in solution. The $\delta(^1\text{H})$ and $\delta(^{13}\text{C})$ data indicate the formation of an allylic system; the bonding of C8/9 to the iron is not supported by $\delta(\text{H}8/9)$, since a signal shift of only ca. -0.4 ppm is observed on going from **2** or **1**^[3] to **4**. For the same transformations, however, the signal for C8/9 is shifted by ca. -60 ppm, which does reflect coordination of C8/9 to iron. $^1J(\text{C}8-\text{H}8)$ [$^1J(\text{C}9-\text{H}9)$]^[5,6] thereby decreases by only ca. 3 Hz; the rehybridization and a conceivable charge transfer from the allylic moiety to C8/9 thus have little effect. Noteworthy are the coupling constants $^1J(\text{CH})$ ^[5,6] of **4**, which are 5–8 Hz smaller for C1/7 and C2/6 than those of **2**; this indicates a reduction in the angles at the corresponding carbon atoms owing to the binding to iron (compare below). Comparison of **4** with ferrocene reveals that the position of the ^{13}C -NMR signal of C_5H_5 at $\delta \approx 80$ is unusual; we ascribe this to a transannular effect of the Dicp ligand on Cp, which is much larger than that observed for ferrocenes.^[7,8]

The X-ray structure analysis^[9] of **4** (cf. Fig. 1) confirms the findings outlined above. A ferrocene analogue is present in which a Cp ligand is replaced by Dicp, with the Dicp forming a basketlike ligand. Both the olefinic and allylic moieties of the Dicp coordinate to the Fe atom. As a result, the double bond C8-C9 (1.420(4) Å) is characteristically lengthened^[10] and the allyl plane (C3, C4, C5) is bent away from iron by 27.0° with respect to the plane A (C2, C3, C5, C6). The interplanar angle A/D (cf. caption to Figure 1) is 117.0° , and B/D is only 108.8° , so that the distances of the olefinic C atoms (C8/9) from the termini of

the allylic moiety (C5/3) are only 2.69 and 2.67 Å, respectively. The Fe-C distances for Dicp and Cp are thus similar (except for Fe-C4, 2.017(2) Å). The Fe-C bond lengths lead to a distance of only 1.21 Å between the best plane E through C3, C4, C5, C8, and C9 and the iron, whereas the Fe-Cp(center) distance is 1.73 Å. The two planes form an angle of 3.6° and are thus ca. 0.4 Å closer in **4** than the corresponding planes in ferrocene;^[11] this is revealed as a transannular effect in the ^{13}C -NMR data. These results and the absence of ferrocene (cf. Scheme 1) make the following route for the formation of **4** plausible: **3** is initially formed; the mutual steric hindrance of Dicp ligands in **3** is so large, however, that one of the two ligands cleaves off cyclopentadiene. The retro-Diels-Alder reaction is therefore only partially blocked. Thus, a general route^[12] is now possible to complexes of the (Cp-metal) type, which are strongly perturbed owing to formal separation of the olefinic and allylic moieties.

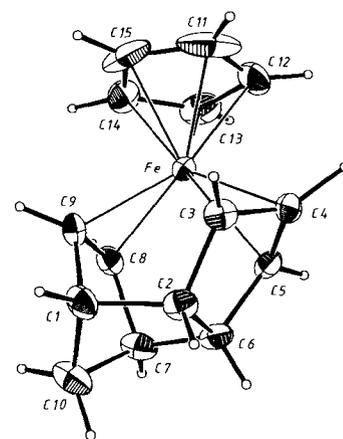


Fig. 1. Molecular structure of DicpFeCp **4** (ORTEP, displacement ellipsoids 50%, H atoms with arbitrary radii). Selected distances [Å]: Fe-C3 2.091(2), Fe-C4 2.017(2), Fe-C5 2.092(2), Fe-C8 2.077(2), Fe-C9 2.081(2), Fe-C11 2.109(3), Fe-C12 2.106(3), Fe-C13 2.101(3), Fe-C14 2.084(2), Fe-C15 2.111(3), C3-C4 1.413(4), C4-C5 1.421(4), C8-C9 1.420(4), C2-C6 1.573(3); interplanar angles [$^{\circ}$]: A/D 117.0, B/D 108.8, B/C 127.2, C/D 124.1 with A=C2, C3, C5, C6, B=C1, C7, C8, C9, C=C1, C7, C10, D=C1, C2, C6, C7.

The redox behavior of **4** is similar to that of ferrocene. Cyclovoltammetry^[13] shows a reversible ($I_{pa}/I_{pc} = 0.94$) oxidation, the half-wave potential of which is cathodically shifted by 260 mV relative to internal ferrocene. This finding is apparently typical^[14] of the perturbation of ferrocenes, either by alkylation or by interruption of the cyclic conjugation in the ligands.

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Modified Cyclodextrins— Novel, Highly Enantioselective Stationary Phases for Gas Chromatography**

By Wilfried A. König,* Sabine Lutz, and Gerhard Wenz

Capillary gas chromatography on chiral stationary phases^[1] is being employed increasingly for the determination of the configuration of natural products, for investigating the enantiomeric purity of chiral pharmaceuticals, and for determining enantiomeric excesses of asymmetric

syntheses or enzymatic transformations, ever since suitable columns with thermostable phases have become commercially available^[2] and new methods of derivatization^[3] have enabled the separation of a large number of substances.

In most cases "chiral recognition" can be attributed to diastereomeric associates formed by hydrogen bonding between chiral substrate and stationary phase.^[4] Hence, with few exceptions, only derivatives capable of such interactions (amides, carbamates, oximes, some alcohols) are separable in this way.

In the case of cyclodextrins, which are employed in liquid chromatography as chiral supports,^[5] it is known that inclusion effects play an important role in the separation of enantiomers. A separation is achieved when the enantiomers differ in their ability to be accommodated in the cavity of the macrocyclic cyclodextrin molecule. Sybilska et al.^[6] recently showed that this type of intermolecular interaction is also suitable for gas chromatographic enantiomeric separations. Due to their high melting points, however, the free cyclodextrins are suitable only as stationary phases for gas-solid chromatography. It was therefore thought worthwhile attempting to lower the melting point and increase the thermal stability by introducing hydrophobic moieties. This was achieved both by complete alkylation as well as by partial alkylation and acylation of the hydroxy functions of the cyclodextrins.^[7]

It emerged that, e.g., per-*n*-pentylated α -cyclodextrin (Phase I) as well as the β -cyclodextrin pentylated at the hydroxy groups in position 2 and 6 and acetylated in position 3 (Phase II) exhibit a marked selectivity toward enantiomers. Especially high separation factors are obtained in the case of the enantiomers of trifluoroacetylated carbohydrates, methylglycosides, and the 1,5-anhydroalditols^[9] as obtained on reductive degradation of polysaccharides.^[8] Moreover, derivatives of many other chiral molecules are separated, including building blocks for natural product syntheses, e.g. hydroxy acids (Fig. 1), polyols, triols, vicinal diols, alcohols (Fig. 2), amino alcohols, amines and amino acids. The separation factors for trifluoroacetylated α -chi-

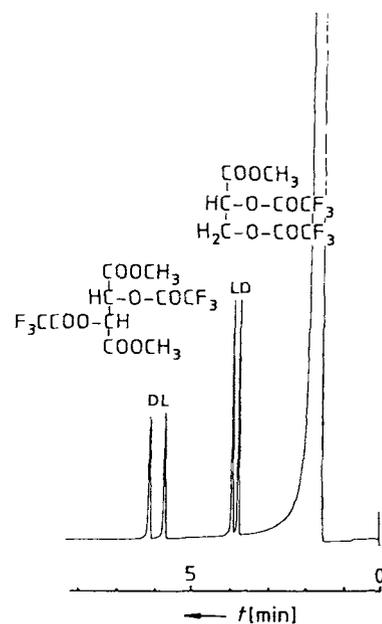


Fig. 1. Enantiomer separation of glyceric acid and of tartaric acid after esterification with methanol and trifluoroacetylation. 40-m glass capillary with perpentylated α -cyclodextrin. Column temperature 90°C; Carrier gas: 1 bar H₂.

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