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PREPARATION OF OPTICALLY ACTIVE BRIDGED BIPHENYLS VIA A STEREOSELECTIVE SYNTHESIS OF THEIR MONO (TRICARBONYLCHROMIUM) COMPLEXES. CHIROPTICAL PROPERTIES AND ABSOLUTE CHIRALITIES OF THE COMPLEXES AND LIGANDS[1,2]

M. EYER, K. SCHLÖGL* and R. SCHÖLM
Institut für Organische Chemie der Universität Wien, A-1090 Wien, Austria

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Abstract—Reaction of the mono(tricarbonylchromium) complex **3** of diphenic acid anhydride with chiral amines gave the optically active imides **9–11**. **10** and **11**, from (*S*)-(−) and (*R*)(+)-phenylalaninol, respectively were separated by chromatography into *exo*- and *endo*-diastereomers (**a** and **b**) with opposite metallocene chiralities but with the same axial chirality. The (*S*)-(−)- amino-alcohol induces $(S)_a$-chirality and *vice versa*. The absolute configurations of the metallocene and axial-chiral parts of the biphenyl system were deduced from the circular dichroism spectra, the former [$(R)_m$ or $(S)_m$] by comparison with the CD of benchrotrenes of known absolute configuration, the latter [$(R)_a$ or $(S)_a$] by applying the exciton model of coupled oscillators to the optically stable biphenyl ligands [i.e. the imides (−)- and (+)-**8** easily accessible from **10** and **11** by photochemical decomplexation]. $(R)_m$-$(S)_a$ for the complex (+)-**10a** (*exo*) and $(S)_m$-$(S)_a$ for the *endo*-isomer (−)-**10b**, and *vice versa* for the complex **11**. The parent ligands have the configurations $(S)_a$(−)-**8** and $(R)_a$(+)-**8**, respectively.

Photochemical cleavage of the optically active bis(tricarbonylchromium) complex (−)-**13** of the biphenyl lactone **12** at −60°C afforded optically labile **12** with a half-life time of racemization of *ca* 10 min at −20°. On the basis of its CD the configuration $(R)_a$ is tentatively proposed for **12**.

The work described represents the first example of the preparation of optically-active biphenyls *via* benchrotrene precursors.

Benzene derivatives react easily with hexacarbonylchromium to the corresponding tricarbonylchromium complexes (benchrotrenes). Thereby both the reactivity and especially the symmetry of the parent benzene ligand are changed, e.g. from C_s to C_1 (i.e. from achiral to chiral structures).[3] Cleavage of the benchrotrenes can then be achieved under mild conditions (e.g. photochemically).[3] Therefore, $Cr(CO)_3$ may serve as a useful protecting group for stereochemical transformations in the benzene series.

This principle (see Refs. 3, 4 for recent applications) should allow access to otherwise not, or only difficulty, accessible torsional isomeric biphenyls.

First studies in this field included the preparation,[5] conformational analysis,[5a, 6] kinetic resolution and tentative configurational assignment of biphenyl mono and bis(tricarbonylchromium) complexes, especially of biphenyl-2,2′-dicarboxylic acid (diphenic acid) and its derivatives, including X-ray structures of two key compounds.[2]

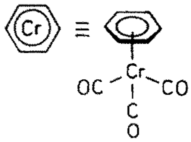
The optical resolution both *via* diastereomeric salts and by kinetic resolution gave low enantiomeric purities (up to 33% only) and was successful only for bis(tricarbonylchromium) complexes.[2]

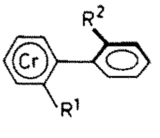
In this paper a stereoselective synthesis of stereoisomeric imides of diphenic acid mono(tricarbonylchromium) is reported, as well as the preparation of the optically labile lactone **12** of 2′-hydroxymethylbiphenyl-2-carboxylic acid by low temperature decomplexation of the corresponding chiral bis-complex (−)-**13**.

Absolute configurations are proposed for both the biphenyl ligands and for their tricarbonylchromium complexes on the basis of their chiroptical properties.

Stereochemistry of bridged biphenyl mono(tricarbonylchromium complexes

General considerations. (Mono)complexation of enantiomeric biphenyls gives rise to diastereomers in which the torsional barrier of the biphenyl system is considerably increased.[5] Conformational analyses reveal that for 2,2′-disubstituted mono(tricarbonylchromium) complexes from the two stereoisomers the *exo*- configuration **1** is preferred.[2, 6] This should also be true for bridged biphenyl complexes such as **2** (Scheme 1). As two elements of chirality are present, four stereoisomers are possible as shown in Scheme 1 and designated as (+)- and (−)-, *exo* and *endo*, respectively. [The subscripts m and a in the symbols (*R*) and (*S*) stand for metallocene and axial chirality. $(R)_m$ or $(S)_m$ refers to carbon 1. For the application of stereochemical nomenclature to metallocenes see Ref. 7. (+) and (−) in Scheme 1 symbolize enantiomeric relationships].

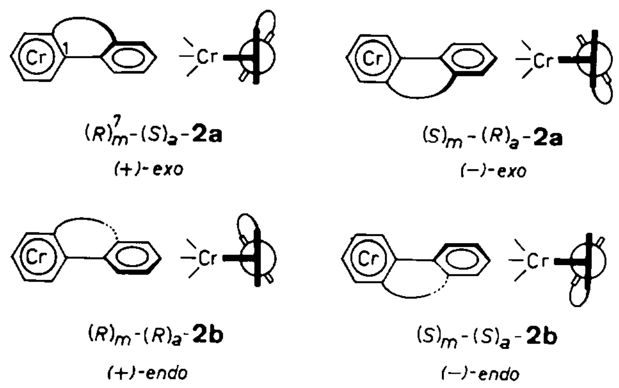




exo-**1**

Stereoisomeric imides of diphenic acid and their mono(tricarbonylchromium) complexes

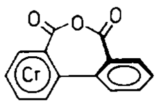
Reaction of arylamides (and imides) with hexacarbonylchromium is not straightforward as several byproducts are formed.[8]



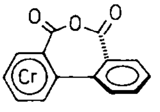
Scheme 1.

Therefore diphenic acid anhydride mono(tricarbonylchromium) (**3**) was chosen as a starting material for the desired amides and imides (such as **9**, **10** and **11**) which should be especially suitable for chromatographic separation of stereoisomeric biphenyl complexes.[9]

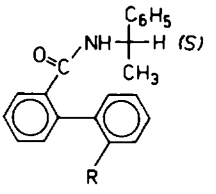
Attempts to prepare **3** from diphenic acid anhydride and $Cr(CO)_6$ failed. **3** could be obtained, however, from diphenic acid mono(tricarbonylchromium)[5b] and cyclohexylcarbodi-imide as a 99:1 mixture of stereoisomers separable by crystallization and preparative layer chromatography. From the chromatographic behaviour and IR spectral data the (expected) *exo*-configuration **3a** was deduced for the main product. No equilibration of the isomers **3a** and **3b** took place after 2 h in boiling chloroform.



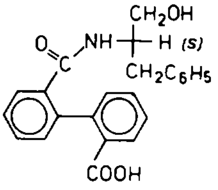
3a



3b



4 H
5 COOH
6 COOCH$_3$



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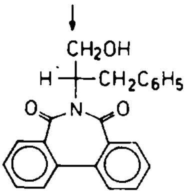

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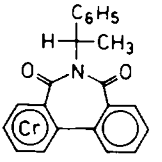
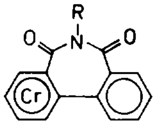
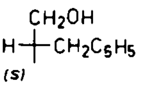


9



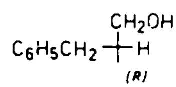
R



$H-\overset{CH_2OH}{C}-CH_2C_6H_5$ (S)

10

R



$C_6H_5CH_2-\overset{CH_2OH}{C}-H$ (R)

11

The reaction of methylbenzoic acid anhydrides (methylbenchrotrenecarboxylic acid anhydrides) with (−)-α-phenethylamine (PEA) had been employed both for the first kinetic resolution of benchrotrenes and for establishing their absolute configurations.[10] Consequently, from the asymmetric amidation of **3** with chiral amines and especially amino-alcohols stereoisomeric amides ought to be expected suitable for chromatographic resolution.

Treatment of diphenic acid anhydride with (−)-PEA and (*S*)-(−)-phenylalaninol (PHE-ol) gave the expected amides **5** and **7**, respectively with good yields. The ^1H-NMR spectrum of the methyl ester **6** of **5** exhibits two doublets for the C-methyl group which coalesce at 85°; from this the activation energy for this dynamic process was calculated[11] to be approximately 75 kJ/mole (18 kcal/mole).[12] An analogous barrier was found for **4**, easily accessible from the chloride of biphenyl-2-carboxylic acid and (−)-PEA. Consequently, the hindered rotation is due only to restriction around the CO–NH-bond and not to a torsional barrier around the biphenyl single bond. These results prevented attempts to resolve biphenyls such as **4**, **5** or **6** by chromatographic methods.

On the other hand the rotational barrier of 2-substituted biphenyl tricarbonylchromium complexes[5a] is high enough to allow a resolution into enantiomers.

Reaction of **3a** (or of the mixture of **3a** and **3b**) with (*S*)-(−)PEA or (*S*)-(−)PHE-ol did not give the amides (corresponding to **4** and **7**) but the laevorotatory imides **9** and **10**, respectively ($[\alpha]_D^{20} = -30°$) with good yields even under mild conditions (e.g. at 0° or 20°C). With (*R*)-(+) PHE-ol the imide **11** ($[\alpha]_D^{20} = +29°$) was obtained. In contrast to these results, the uncomplexed amide **7** could be cyclized to the imide **8** only under rather drastic conditions (see Experimental section) whereas **5** gave no imide. This provides another striking example for the different reactivities of benzenes and the corresponding benchrotrenes.

Incomplete reaction of **3** with (−)-PEA to **9** left racemic starting material; therefore obviously no kinetic resolution had occurred.

Medium pressure chromatography of **9**, **10** and **11** in benzene–ethanol (100:1) on silica gel caused only partial separation of the mixture of stereoisomers of **9** (see Scheme 1). Four fractions with rotations from $[\alpha]_D^{20} = -21°$ to −54° were obtained. **10** and **11** on the other hand were easily separated into two stereoisomers (**a** and **b**) of approximately equal amounts and $[\alpha]_D^{20}$-values of +135° and −142° (for **10a** and **b**) and −145° and +152°, respectively (for **11a** and **b**); in both cases **a** was the more strongly-adsorbed isomer.

Chiroptical properties and chiralities of the imides

The CD-spectrum of **9** is obviously influenced by the Cotton effect induced by the (−)-PEA-residue. The $\Delta\epsilon$-values of (−)-PEA are low (−0.6 at 215 nm) whereas the long wavelength (charge transfer) Cotton effect of **9** at 330 nm exhibits $\Delta\epsilon$ −0.3. The signs of the CD-bands of the four fractions of **9** are negative but of different magnitude (from −0.5 to −1.0), thus furnishing an additional proof that in contrast to **10** and **11** no satisfactory chromatographic separation had occurred.

The CD-spectra of **10a** and **b** as well as of **11a** and **b** exhibit mirror image effects at 320 and 380 nm whereas the CD bands of the aromatic transitions at 280 nm have identical signs, namely (+) for **10** and (−) for **11** (Fig. 1).

The chiroptical properties of **10** should be mainly determined by the metallocene and axial chiralities (Scheme 1) while the influence of the centrochiral part [$(S)_c$ in **10**, and $(R)_c$ in **11**] may be neglected; (−)-PHE-ol has a $\Delta\epsilon$ −1.3 at 220 nm.[13]

Previous studies on an optically active bridged biphenyl bis(tricarbonylchromium) complex, the lactone **13**, had led to the conclusion that the long wavelength (charge transfer) Cotton effect caused by the metallocene chromophore seems to be specific for the configuration of the benchrotrene part.[2] Thus for (−)-**13** the configuration $(S)_m$ was deduced from the negative Cotton effects at 365 and 470 nm.

Because of the related topologies of **10** and **11** on the one hand and **13** on the other the configuration $(S)_m$ may tentatively be assigned to (−)-**10b** and (−)-**11a** and $(R)_m$ to the enantiomers (+)-**10a** and (+)-**11b**. (An unambiguous proof for the configuration is intended to be gained from X-ray structure analyses. So far no suitable crystals have been obtained).

The Cotton effects around 280 nm on the other hand seem to be specific for the biphenyl configuration, i.e. the axial chirality $(R)_a$ or $(S)_a$.[2, 14] From the signs of these bands (Fig. 1) it follows that (+)-**10a** and (−)-**10b** as well as (+)-**11b** and (−)**11a** have identical axial chiralities. In contrast to expectations (*vide supra* and Scheme 1) the dextro and laevorotatory stereoisomeric imides **11** and **10**, respectively represent *exo*- *endo*-stereoisomers, corresponding to (+)-**2a** and (−)-**2b** or (−)-**2a** and (+)-**2b** in Scheme 1. Consequently, the chromatographic resolution had occurred only with regard to the metallocene chiral part, i.e. had separated $(R)_m$-$(S)_a$-$(S)_c$ from $(S)_m$-$(S)_a$-$(S)_c$ (**10a** and **b**) and *vice versa* for **11**.

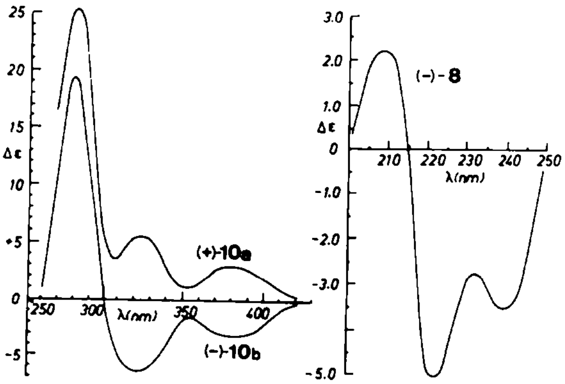
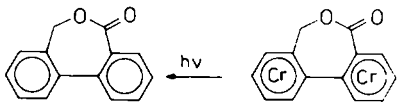


Fig. 1. CD-spectra of diphenic acid imides derived from (*S*)(−)-phenylalaninol (in ethanol). Stereoisomeric mono(tricarbonylchromium)complexes (+)-**10a** (*exo*) and (−)-**10b** (*endo*) and the ligand (obtained therefrom by irradiation) (−)-**8**. The derivatives of (*R*)(+)-phenylalaninol **11a** and **11b** and (+)-**8**, respectively exhibit mirror image spectra.

This assumption is also supported by the chromatographic behaviour (*vide supra*), as it can be expected that the *endo*-isomers **10b** and **11b** are less strongly adsorbed than the *exo*-stereoisomers **a**.

Information as to the axial chiral biphenyl system [$(R)_a$ or $(S)_a$] could be gained from the chiroptical properties of the free (uncomplexed) biphenyl ligand **8**.



12 **13**

Decomplexation of the optically active tricarbonylchromium complexes **10** *and* **13**: *absolute chiralities of the biphenyls* **8** *and* **12**

Optically active biphenyls with low rotational barriers may be obtained from optically stable precursors by appropriate reactions at low temperature. (See the desamination of 6,6′-diamino-2,2′-biphenyl at −35° to optically active dimethylbiphenyl.)[15]

For this purpose a mild photochemical decomplexation of optically active biphenyl tricarbonylchromium complexes seemed to be a very promising approach.

Both the diastereomeric mixture of **10** and its stereoisomers **10a** and **10b** (obtained by chromatographic separation) gave on illumination with a photo lamp in ethanol at 20° and −60° the same biphenyl derivative (−)-**8** ($[\alpha]_D^{20} = -18°$) with a temperature independent CD-spectrum (Fig. 1). (−)-**8** was optically stable in refluxing benzene for 1 hr. From **11** the enantiomer (+)-**8** ($[\alpha]_D^{20} = +18°$) was obtained. Its CD-spectrum is the mirror image of that shown for (−)-**8** in Fig. 1.

These results furnish an additional proof that **10a** and **b** as well as **11a** and **b** are *exo*- and *endo*-stereoisomers with the same axial but opposite metallocene chiralities (Scheme 1).

The amide **8** has C_2-symmetry as far as the biphenyl system is concerned; its configuration could therefore be deduced from its CD-spectrum (Fig. 1) on the basis of the exciton model of coupled oscillators.[14, 16]

The UV spectrum of **8** is only weakly structurated; therefore the assignment of the transitions ^1B_b, ^1L_a and ^1L_b was only possible in the CD-spectrum (Fig. 1). The shortwavelength ^1B_b transition at 215 nm (polarized in the aromatic plane) exhibits a high ϵ-value of *ca.* 90000 which is a necessary condition for the application of the exciton model to the corresponding Cotton effects.[16]

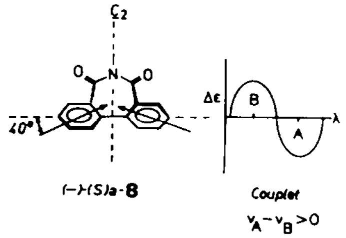


Fig. 2. Absolute axial chirality of the imide (−)-**8** obtained from its mono(tricarbonylchromium)complex **10**.

The positions of the transition vectors of both "partial chromophores" with respect to the C_2-axis of the molecule (see Fig. 2) are described by four stereochemical parameters, namely d, α, β and γ. An assumed configuration (and conformation) is described by a certain set of parameters whereby the geometry of the transition vectors with regard to the "partial chromophores" must be known. From these parameters the band splitting of the CD-couplet ($\Delta\nu$) can be calculated according to eqn (1).

$$\Delta\nu = \nu_A - \nu_B = \frac{2\mu_1^2}{h\cdot c\cdot d^3}(\cos^2\gamma - \cos^2\beta + 2\cos^2\alpha) \qquad (1)$$

The rotational strengths of the bands with A- and B-symmetry, respectively follow from eqn (2), where μ is the electrical transition moment and ν^0 corresponds to the position of the transition in cm^{-1}.

$$R_A = -R_B = \pi \cdot \nu^0 \cdot d\mu^2 \cdot \cos\beta \cdot \cos\gamma. \qquad (2)$$

Direction and amount of the transition moments with regard to the "partial chromophore" were determined by a PPP-SCF-MO-CI calculation.[17] The PPP calculation was performed for a N-methylimide with the usual parameters.[17] The most intensive band occurs around 220 nm (^1B_b). A control of the matrix of the charge density revealed that shifts of the charge are localized mainly within one ring (including the attached CO-group).

The vector of polarisation lies between the biphenyl and the aryl-CO-axis, deviates from the latter for appr. 40° and is rotated out from the aromatic plane towards the nitrogen in an angle of 15° (see Fig. 2).

The value of μ for the ^1B_b transition is 1.6 (μ_B). An evaluation of the experimental UV-spectrum by band integration was not possible (*vide supra*). The CD-parameters $\Delta\nu$ and R were deduced from the experimental CD-curve (Fig. 1) by curve fitting using a computer program. The values obtained thereby ($\Delta\nu = +900\,cm^{-1}$, $R = 4\text{–}5 \times 10^{-39}$) were then compared with those computed for several simulated conformations with the stereochemical parameters obtained by a COORD program. (QCPE-Program No. 136).

The best agreement was found for the following parameters: $d = 4$ Å, $\alpha = 120°$, $\beta = 170°$ and $\gamma = 36°$ ($\Delta\nu = 672\,cm^{-1}$ and $R = -5.5 \times 10^{-39}$). These values correspond to the absolute configuration $(S)_a$ for (−)-**8** obtained from **10** [and consequently to $(R)_a$ for the imide from **11**] (see Fig. 2).

Therefore the following configurations may be assigned to the stereoisomeric tricarbonylchromium complexes **10** and **11**: $(R)_m$-$(S)_a$-$(S)_c$ for (+)-**10a** and $(S)_m$-$(S)_a$-$(S)_c$ for (−)-**10b**. (−)-**11a** and (+)-**11b**, respectively are the corresponding enantiomers and have therefore the configurations $(S)_m$-$(R)_a$-$(R)_c$ and $(R)_m$-$(R)_a$-$(R)_c$, respectively.

Finally, the optically active tricarbonylchromium complex (−)-**13** of the lactone **12** (with an enantiomeric purity of 33%)[2] was photochemically cleaved at −60° in ethanol and the CD of the free ligand **12** immediately recorded at −45° (Fig. 3). At room temperature fast racemization took place while at −45° **11** was optically stable for at least 1 hr. From the CD-values at −20° a half life time for the racemization of approximately 10 min was deduced.

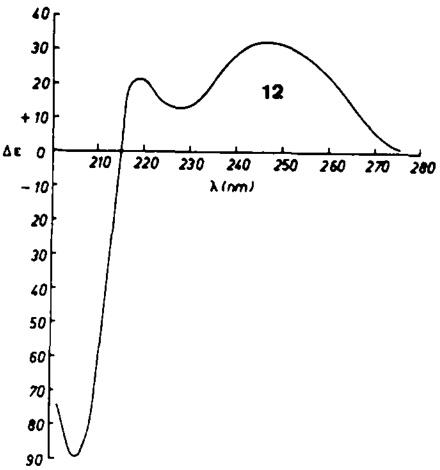


Fig. 3. CD-spectrum of the lactone **12** (at −45° in ethanol) obtained by photochemical decomplexation of its bis(tricarbonylchromium) complex (−)-**13**. Corrected for enantiomeric purity.

The CD-curve of **12** is similar in its shape to that of **8** (Fig. 1). For **12** however application of the exciton model is not possible since it has no C_2 symmetry. From a comparison of the CD-spectra of **12** and **8** the $(R)_a$ configuration may however tentatively be proposed for **12** [from (−)-13] as already had been suggested previously[2] on the basis of the signs of the charge transfer Cotton effects of (−)-**13**. (As no low-temperature attachment for the polarimeter was available, the optical rotation could not be measured).

CONCLUSIONS

Reaction of the mono(tricarbonylchromium) complex **3** of diphenic acid anhydride proceeds with a high degree of stereoselectivity (degree not known; as however careful thin layer chromatography did not reveal any trace of a stereoisomer either in **10a** or **10b** a high degree of stereoselectivity may be assumed). (*S*)(−)-PHE-ol induces the $(S)_a$ chirality and the (+)-enantiomer the $(R)_a$ chirality of the biphenyl system. In each case almost equal amounts of the *exo*- and *endo*-stereoisomers of the imide **10** and **11**, respectively [corresponding to **2a** and **2b**, respectively in Scheme 1 and being enantiomers with respect to the metallocene chirality, i.e. $(R)_m$ and $(S)_m$] are formed. Since they are diastereomers [$(R)_m$-$(S)_a$ and $(S)_m$ − $(S)_a$] they can be separated by chromatography.

The mechanism of diastereoselective formation of the imides **10** and **11** is not yet understood. Further work on this and related problems is in progress.

EXPERIMENTAL

All reactions were carried out under argon in the dark. Melting points were determined on a Koflermicroscope and are uncorrected. All compounds were pure on thin layer chromatography which was run on silica gel plates (60F-254 Merck) in benzene-ethanol or ether-hexane mixtures. Preparative layer chromatography was performed on 0.3 mm layers of silica gel in benzene-ethanol (100:1). Column chromatography was run on silica gel (Merck-60; 0.04–0.063) at a pressure of 6 bar. Spectra were recorded on Perkin-Elmer 237, Cary 15, Varian EM 360 and XL-100 (in $CDCl_3$ with TMS as internal standard; chemical shifts, δ in ppm; multiplicities and the number of protons are given). Mass spectra were determined on a Varian MAT-CH-7. CD spectra were determined on a dichrograph Mark III (Jobin-Yvon). Optical rotation values were determined with a Perkin-

Elmer 141 in 1 dm cells at 20 ± 0.1°C (solvents ethanol or acetone). 100 MHz-NMR-spectra were recorded by Drs. E. Haslinger and W. Silhan, mass spectra by Dr. A. Nikiforov. Elemental analyses were performed in the microanalytical laboratory of Dr. J. Zak (Vienna).

Biphenyl-2,2'-dicarboxylic acid anhydride mono(tricarbonylchromium) **3**. A solution of 500 mg (1.32 mmole) of diphenic acid mono-tricarbonylchromium)[5b] in 50 ml of dry benzene was treated with three portions of (each) 272 mg (1.32 mmole) of dicyclohexylcarbodiimide (DCC) in 50 ml of dry benzene as follows. The first portion was added dropwise with stirring at 40°. After 1 hr the mixture was cooled (to approx. 5°), filtered from dicyclohexylurea and the filtrate treated at 40° with the second portion of DCC. After stirring for 1 hr, cooling and filtration the third portion was added and stirring continued at 40° for 5 hr. Filtration, cooling for 1 hr, renewed filtration and evaporation *in vacuo* gave a residue which was treated with 100 ml of ether and 100 ml of sat Na_2CO_3. After shaking, the mixture was filtered, the precipitate was washed with 5 ml of ether and the ether layer was separated. After drying (here and subsequently over sodium sulphate) and evaporation *in vacuo* the residue was stirred with ether (30 ml). The red powder **3a** was filtered off and washed with ether (2 × 5 ml). The filtrate was evaporated to dryness and the residue treated again with 5 ml of ether. This procedure was repeated until tlc (ether–hexane, 2:1) showed that **3b** (orange powder) was present. R_f (**3a**) 0.57; (**3b**) 0.86. Smaller amounts of the mixture (*ca.* 50 mg) were separated by preparative layer chromatography in ether–hexane (2:1). Attempts to simplify the procedure of preparation resulted in a considerable decrease of the yield of **3**.

3a, 350 mg (74%). m.p. 143–144°. NMR 7.5 (m, 4H), 5.4 (m, 4H). IR (CCl_4) 1990 and 1925 (s, Cr–CO), 1740 and 1670 cm^{-1} (CO). Mass spectrum: *m/e* 360. Anal. ($C_{17}H_8CrO_6$) C, H.

3b, 2–5 mg (0.4–1%). m.p. 86°. IR (CCl_4) 1990 and 1930, 1910 (d, Cr–CO), 1740 and 1670 cm^{-1} (CO). Mass spectrum: *m/e* 360.

Biphenyl-2-carboxylic acid (−)-α-phenethylamide **4**. A solution of 2.0 g (9.2 mmoles) of biphenyl-2-carboxylic acid chloride (from the methyl ester[5b] via the carboxylic acid) in 15 ml of dry ether was added dropwise under stirring at room temperature to a solution of 2.42 g (20 mmoles) of (−)-α-phenethylamine (Fluka) in 20 ml of dry ether. After 2 hr at room temperature the filtered solution was washed with sat Na_2CO_3, then with 2 N hydrochloric acid and with water, dried and evaporated *in vacuo*, which gave 2.30 g (76%) of colourless crystals, m.p. 170–172°C. NMR 7.8–6.8 (m, 14H), 5.5 (d, J = 8 Hz, 1H), 5.1 (m, 1H), 1.60 and 1.16 (2d, J = 7 Hz, 3H). Mass spectrum: *m/e* 287. Anal. ($C_{20}H_{17}NO$) C, H, N. The coalescence temperature (80°) was determined for the methylsignal in perchlorobutadiene (NMR, 100 MHz, TMS).

Biphenyl-2,2'-dicarboxylic acid (−)-α-phenethylamide **5**. A solution of diphenic acid anhydride[18] (1.03 g, 4.6 mmoles) and of (−)-α-phenethylamine (0.606 g, 5 mmoles) in 50 ml of dry pyridine was stirred for 3 hr at room temperature, then for 1 hr at 40° and then diluted with benzene (100 ml). This mixture was washed with 2 N hydrochloric acid to remove pyridine, then with water, the organic layer separated together with some product and evaporated *in vacuo*. The residue was dissolved in methylene chloride, the solution was dried and evaporated to give 1.30 g (80%) of a pale yellow powder, m.p. 208–210°. NMR 7.9–7.0 (m, 14H), 5.0 (m, 1H), 1.3 and 0.8 (d, J = 2 Hz, 3H). Anal. ($C_{23}H_{21}NO_3$) N.

The methylester **6** was prepared from **5** with diazomethane in the usual way. Yield 90% of colourless crystals. m.p. 121–123°. NMR 8.0–6.5 (m. 14H), 5.2–4.7 (m, 1H), 3.7 (s, 3H), 1.3–0.8 (2d, J = 6 Hz, 3H). Mass spectrum: *m/e* 359. Anal. ($C_{23}H_{21}NO_3$) C, H, N. The coalescence temperature (85°) of the methyl doublets was determined in perchlorobutadiene (NMR, 100 MHz, TMS).

Biphenyl-2,2'-dicarboxylic acid (−)(S)-phenylalaninol amide (**7**) *and imide* (**8**). A solution of diphenic acid anhydride(1.03 g, 4.6 mmole) and of (*S*)(−)-phenylalaninol[19] (0.755 g, 5 mmole) in 50 ml of dry pyridine was stirred for 3 hr at room temperature and then for 1 hr at 40°. Workup as described for **5** gave 1.60 g (80%) of a slowly crystallizing product m.p. 94°. NMR 8.0–7.1 (m, 13H), 4.0 (m, 1H), 3.2–2.1 (m, 4H).

Cyclization of **7** to the amide **8** was achieved by heating 500 mg of **7** for 1 hr at 200° (bath temp) and 0.13 mbar in a "Kugelrohr" (three bulb tube) and subsequent distillation from this tube at 200–210° (air bath temp). Yield 450 mg (95%) of a highly viscous oil. NMR 7.9–7.0 (m, 14H), 5.5 (m, 2H), 2.8 (m, 2H). Mass spectrum: *m/e* 357. UV (ethanol) shoulder around 215 nm (ε 90000), broad maximum around 280 nm (ε 3000). $[\alpha]_D^{20} = 0°$ (c 1.0, ethanol and acetone). Anal. ($C_{23}H_{19}NO_3$) C, H, N.

(−)-N-(α-phenethyl)-biphenyl-2,2'-dicarboxylic acid imide mono-tricarbonylchromium) **9**. A solution of 850 mg (6.65 mmole) of (−)-PEA in 20 ml of dry benzene was added dropwise under stirring to a solution of 1.0 g (2.8 mmole) of **3a** in 100 ml of dry pyridine at room temp. After 4 hr, 100 ml of benzene was added, the mixture washed with 2 N hydrochloric acid, sat Na_2CO_3 and water, the benzene layer was dried and evaporated. The crude product was purified by chromatography on silica gel in ether at 6 bar. Yield 380 mg (30%). m.p. 152–153° (dec) $[\alpha]_D^{20} = -34°$ (c 0.5, acetone). NMR 7.2 (m, 9H), 5.5 (m, 4H), 4.1 (m, 1H), 1.5 (m, 3H). Anal. ($C_{25}H_{17}NCrO_3$) C, H, N. Chromatography of 640 mg on a silica gel column (100 × 1.5 cm) in ether/hexane (3:1) gave 4 approximately equal fractions, $[\alpha]_D^{20}$ (c 0.5, acetone). (1) −21°, (2) −36.5°, (3) −28°, (4) −54°. CD(ethanol), Δε (nm): (1) −4.4(215), +0.3(245), −1.0(325); (4) −5.9(220), +0.3(250), −0.5(330). Also in benzene/ethanol (100:1) on tlc no better separation could be achieved.

(−)-N-(1-Hydroxy-3-phenyl-2-propyl)-biphenyl-2,2'-dicarboxylic acid imide mono(tricarbonylchromium) **10**. 1.0 g (2.8 mmole) of **3a** in dry pyridine (100 ml) was reacted with 0.9 g (6 mmole) of (*S*)(−)-phenylalaninol in pyridine/benzene (1:1, 100 ml) and the product isolated as described for **9**. Yield 700 mg (51%) of a yellow powder, m.p. 150–160° (dec.). NMR 7.4 (m, 9H), 5.5 (m, 4H), 3.2 (m, 2H), 2.8 (d, J = 7 Hz, 2H). $[\alpha]_D^{20} = -30°$ (c 0.5, acetone). Anal. ($C_{27}H_{19}NCrO_5$) C, H, N. With (+)(*R*)-phenylalaninol the stereoisomer (+)-**11** was obtained in 55% yield. $[\alpha]_D^{20} = +29°$ (c 0.7, acetone).

Chromatographic separation of **10**. 700 mg on a silica gel column (100 × 3 cm) in benzene/ethanol (100:1) at 6 bar, 12.8 ml/min. Two separate fractions **a** (140 mg) and **b** (152 mg) were obtained. Standard widths and retention times: 21 cm and 101.5 min for **a**, 15 cm and 71.5 min for **b**. **a**, m.p. 162–165° (dec), $[\alpha]_D^{20} = +135°$ (c 0.6, acetone). CD (ethanol) +26(282), +5.5(320), +1.0(355), +2.8(380) (Fig. 1), **b** m.p. 168–170° (dec), $[\alpha]_D^{20} = -142°$ (c 0.5, acetone). CD (ethanol) +19(282), −6.5(320), −1.5(355), −3.0(380) (Fig. 1).

Separation of 420 mg of (+)-**11** gave 180 mg of **11a** and 190 mg of **11b**. $[\alpha]_D^{20}$ (c 0.5, acetone) −145° (**a**) and +152° (**b**). **10a** and **11a** on the one hand and **10b** and **11b** on the other are identical on tlc (benzene/ethanol, 100:1).

Photochemical decomplexation. General procedure. A 10^{-3} molar solution of the tricarbonylchromium complex in ethanol was illuminated in a suitable vessel under Ar with cooling (either with ice or acetone/dry ice) with a 1000 W photolamp for 30 min. The colourless solution was then rapidly filtered by suction with a pipette through cotton wool under Ar. For the low temperature CD this solution was transferred immediately into the precooled (−45°) compartment of the dichrograph. In every case the purity of the free ligands was checked by NMR and/or tlc.

Decomplexation of **10a** or **10b** gave the imide (−)-**8**, m.p. 206–208° (decomp). NMR identical with racemic **8** (*vide supra*). $[\alpha]_D^{20} = -18°$ (c 1.0, ethanol). CD (ethanol), Δε (nm): +2.2(208), −5.1(224), −2.7(230), −3.5(238) (Fig. 1).

Both **11a** and **11b** gave (+)-**8**. $[\alpha]_D^{20} = +18°$ (c 0.9, ethanol). CD (ethanol) −2.0(206), +5.2(225), +2.5(230), +3.4(240). Decomplexation of (−)-**13** ($[\alpha]_D^{20} = -364°$, enantiomeric purity 33%)[2] gave the lactone **12**, CD (ethanol at −45°) −30(205), +7(218), +4.5(228), +11(246). In Fig. 3 the CD spectrum is shown for the optically pure product.

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