

Biphenyl Tricarbonylchromium Complexes. Part 8.¹ Optical Resolutions, Chiroptical Properties, Kinetics and Absolute Chiralities of Mono-tricarbonylchromium Complexes of *o,o'*-Bridged Biphenyls

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Chiral biphenyls and their tricarbonylchromium complexes can be conveniently resolved by medium pressure chromatography on triacetylcellulose in ethanol or ether. Thereby the mono-Cr(CO)₃ *exo*-complexes of 9,10-dihydrophenanthrene (1) and of the corresponding *o,o'*-bridged ketone (3) [(1m) and (3m), respectively] were separated into enantiomers whereas the mixtures of the dimethylated biphenyls (2) and (4) [(2m) and (4m), respectively] could be separated in one run into all four stereoisomers, *i.e.* the enantiomers of *exo*- and *endo*-forms. The chiroptical properties of these complexes are reported. From kinetic studies based on the relative intensities of diagnostic bands in the circular dichroism spectra a barrier of $\Delta G^\ddagger \approx 90 \text{ kJ mol}^{-1}$ was found for the interconversion *exo* \rightleftharpoons *endo*-(2m) [*i.e.* an epimerization (*R*)_a \rightleftharpoons (*S*)_a around the biphenyl axis without affecting the metallocene chirality (*R*)_m or (*S*)_m]. From the results of the photochemical decomplexation of the optically active complexes (2m) and (4m) (to give the active ligands of known configurations) and by optical comparison with the corresponding complexes (1m) and (3m) the axial chiralities and (on the basis of general stereochemical considerations) also the metallocene chiralities were deduced.

Biphenyls if appropriately substituted are (axial) chiral. With two equal pairs of substituents they have C₂ symmetry; optical resolutions are however possible only if the torsional barrier is sufficiently high ($\Delta G^\ddagger > 80 \text{ kJ mol}^{-1}$; $\tau_{0.5}^{20} \sim 10 \text{ min.}$), even with chromatographic methods which now can be performed at -10°C (*vide infra*). Therefore optically labile biphenyls are accessible only at low temperatures; the first example for such a preparation was the deamination of 2,2'-diamino-6,6'-dimethylbiphenyl at -35°C .²

Complexation of biphenyls [*e.g.* with Cr(CO)₆] to give mono- and bis-(tricarbonylchromium) complexes ('benchrotrenes') seems to be a much more general and promising approach, since after optical resolution these 'benchrotrene' derivatives can be photochemically cleaved at low temperatures. This was recently realised for the lactone of 2'-hydroxymethylbiphenyl-2-carboxylic acid with a half-life of racemization of *ca.* 10 min at -20°C .³

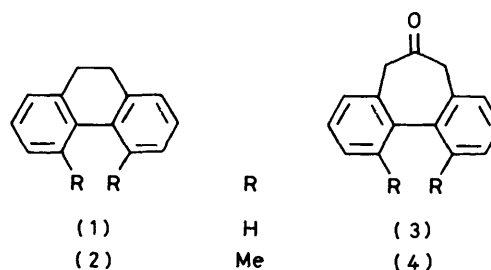
In order to gain detailed information on the conformations and configurations as well as on the chiroptical properties of such 'benchrotrenes' the Cr(CO)₃ complexes of the four bridged biphenyls (1)–(4) were chosen, since the molecular geometries of all the compounds and the absolute chiralities of the methyl derivatives (2) and (4) are known.

Some general considerations as to the stereochemistry, the preparations as well as the relative configurations and conformations of the complexes (1m)–(4m) [and (1b)–(3b)][†] are presented in the preceding paper.¹

In this paper we report the optical resolution of the dimethylated biphenyls (2) and (4) and of the mono-complexes (1m)–(4m) by chromatography on triacetylcellulose (TAC), their chiroptical properties, kinetic racemization studies, and the absolute configurations of (1m)–(4m).

Results and Discussion

Because of the two elements of chirality present (axial and metallocene chirality) four stereoisomers are possible for every mono-complex as schematically shown in Figure 1 [for (1) and (2)]. In the case of (1) and (3) one diastereoisomer



(namely *exo*) predominates, from the dimethylated biphenyls (2) and (4) two (*exo* and *endo*) were isolated in practically equal amounts.¹ Each of them represents a pair of enantiomers with regard to their metallocene chirality: (*R*)_m/*(S)*_m. All mono-complexes have C₁ symmetry.

If it were possible to separate all four stereoisomers (*e.g.* by chromatography) torsion around the biphenyl axis would produce an equilibrium between *exo*- and *endo*-stereoisomers [(*R*)_a \rightleftharpoons (*S*)_a] dependent on the energy difference ΔG° . Other conversions, such as (*R*)_m \rightleftharpoons (*S*)_m would require a ligand exchange which however was never observed under the reactions conditions.

Optical Resolutions and Kinetics.—Ligands. The chromatographic resolution on triacetylcellulose (TAC) of various axial chiral arenes and metallocenes including some representatives of biphenyls and their Cr(CO)₃ complexes was recently described and gave good to excellent results.⁴ Therefore this method was chosen for the resolutions of the bridged biphenyls under investigation. Although the chromatographic resolution can now be performed in ether even at -10°C , the barrier of racemization has to be at least *ca.* 80 kJ mol⁻¹ to allow the handling of enantiomers.

With both dimethylated biphenyls (2) and (4) a complete separation of the enantiomers could be achieved (Table 1, Figure 2a), thereby making these and other optically active biphenyls easily accessible in amounts sufficient for further operations. Previous preparations of optically active (2) and (4) were rather tedious, multistep procedures.^{5,6}

In all cases circular dichroism (c.d.) spectra of the separated

[†] The letters m and b stand for mono- and bis-Cr(CO)₃ complexes, respectively.

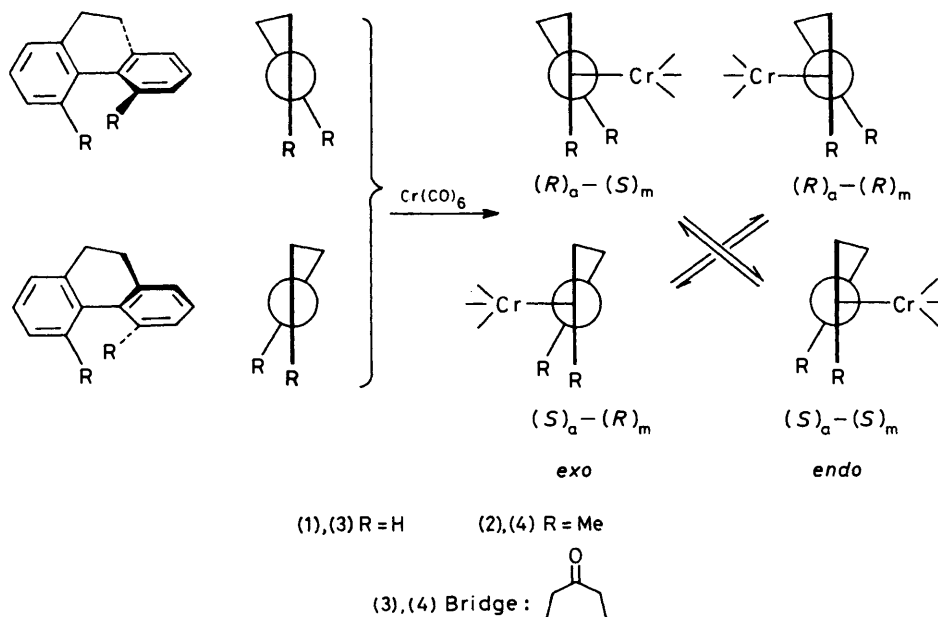


Figure 1. Stereoisomeric mono-tricarbonylchromium complexes of bridged biphenyls

Table 1. Chromatographic resolutions of bridged biphenyls and their mono-Cr(CO)₃ complexes on triacetylcellulose

Compd.	Solvent	T (°C)	V (ml)	R	E.e. (%)	$[\alpha]_D^{20}$ (°)	Solvent (c 0.01—0.1)	Ref.	Config'n.	Chirality
(2)	Et ₂ O	15	123	5.9	100	+235 ± 10	Iso-octane	9	—	(S) _A
			492		100	-234 ± 10				(R) _A
(4)	EtOH	34	164	5.9	100	-580 ± 30	Iso-octane	8	—	(S) _A
			354		100	+610 ± 30				(R) _A
(1m)	Et ₂ O	0	350	<0.5	?	-127 ± 25	EtOH		<i>exo</i>	(R) _A -(S) _m
			388		?	+196 ± 30				(S) _A -(R) _m
(2m) ^a	Et ₂ O	0	200 ^a	—	?	<i>b</i>	—		<i>endo</i>	(S) _A -(S) _m
			230 ^a		?	<i>b</i>				(R) _A -(R) _m
(3m)	EtOH	30	491	1.3	>80	-1 080 ± 25	EtOH		<i>exo</i>	(S) _A -(R) _m
			593		>80	+970 ± 25				(R) _A -(S) _m
(4m)	EtOH	20	303 ^c	—	?	(-) ^b	Iso-octane		<i>endo</i>	(R) _A -(R) _m
			426		1.5	>80				(+) ^b
(4m)	EtOH	20	341	1.5	>80	~-900	Iso-octane		<i>exo</i>	(S) _A -(R) _m
			426		>80	~+900				(R) _A -(S) _m

^a See Figure 4a. ^b Because of low enantiomeric purities no reliable rotations could be measured. ^c See Figure 2c.

enantiomers were run in order to ensure enantiomeric relationships (Figure 3).⁷

For (2) a strong retention and the high enantioselectivity are remarkable (Table 1).

From kinetic measurements (Table 2) the rotational barrier $\Delta G^{\ddagger}_{293}$ was determined as 97.3 ± 0.4 (in CHCl₃) and 98.4 ± 0.4 kJ mol⁻¹ (in ether) in excellent agreement with the value (98.4 kJ) obtained previously.⁵

Because of its high activation energy (*ca.* 150 kJ) for (4)⁸ no kinetics could be measured. On the other hand the barriers of (1) and (3) are too low (17 and 71 kJ, respectively),^{1,5,9}

therefore for these biphenyls no optical resolution on triacetylcellulose was attempted.

Mono-tricarbonylchromium Complexes.—Complexation of (1) gives the pure *exo*-isomer, *exo*-(1m), as was established by n.m.r.¹ Chromatography on TAC in ether at 0 °C gave two peaks (Figure 2b) which according to their n.m.r. spectra (determined from four fractions of each peak) were homogeneous, but enantiomers according to their c.d. spectra (Figure 3b). Consequently, a separation of the *exo*-isomers (R)_A-(S)_m and (S)_A-(R)_m has been achieved (Figure 1).

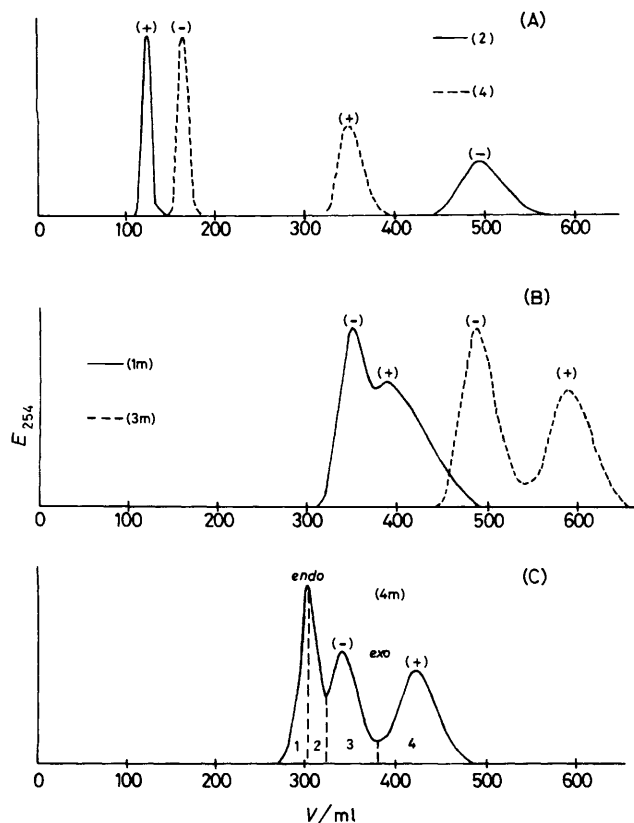


Figure 2. Chromatographic resolutions of bridged biphenyls and their mono-Cr(CO)₃ complexes on triacetylcellulose (for conditions see Table 1 and Experimental section)

The racemic monocomplex (2m) of the dimethyl derivative (2) is an almost equimolar mixture of all four possible stereoisomers as shown in Figure 1, since according to n.m.r. spectroscopy *exo*- and *endo*-forms are present in a ratio of *ca.* 50 : 50,¹ each of them being necessarily a racemic mixture. A partial separation with simultaneous optical resolution was achieved by chromatography on TAC in ether at 0 °C (Table 1, Figure 4a). This was established by the c.d. spectra of the four fractions taken (Figure 4b). Accordingly, fractions (1) and (2) are enriched enantiomers of *endo*-(2m), fractions (3) and (4) of *exo*-(2m). The relative configurations (*endo* and *exo*, respectively) of these fractions were established by n.m.r. spectroscopy¹ and t.l.c. Recording of the temperature dependence of c.d. band intensities confirms an *endo*-*exo* equilibrium between fractions (1) and (4) on the one hand and (2) and (3) on the other, which finally reaches equimolarity (according to the n.m.r. spectra). This rather surprising fact that *exo*- and *endo*-(2m) are of comparable energy was discussed previously.¹

Fraction (1) of (2m) shows in its c.d. spectrum (Figures 3c, 4b) a charge-transfer band at 434 nm which decreases in the equilibrium to 50% intensity with a simultaneous appearance of a second band at 355 nm [with twice the intensity of the 434 nm band at equilibrium (Figure 4b)]. Consequently, these bands are diagnostic for *endo*-(434 nm) and *exo*-(355 nm) (2m). Kinetic studies using the intensities of these bands (Table 2) allowed the determination of the barrier ΔG^\ddagger for the interconversion process *exo* \rightleftharpoons *endo* (Figure 1) as being 90.4 ± 0.4 kJ mol⁻¹ (in ether) in excellent agreement with the value obtained from n.m.r. spectroscopy.¹ Since for the ligand (2) a value for ΔG^\ddagger of 98.4 kJ had been found,¹ this result

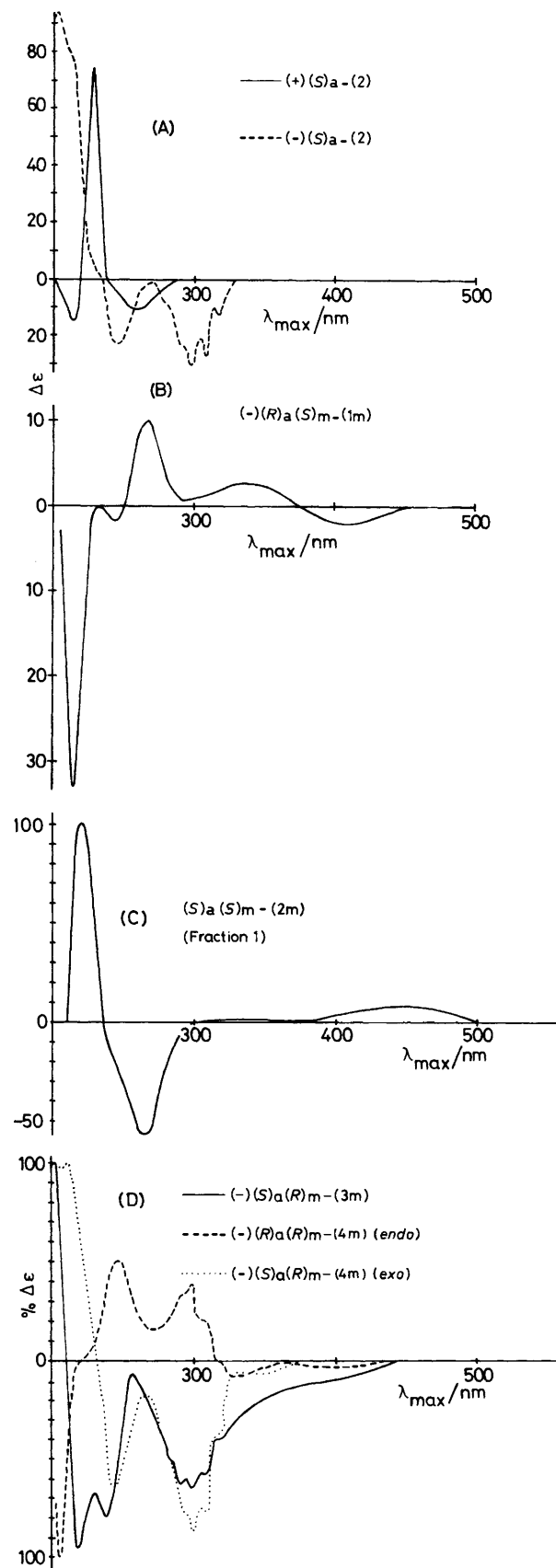
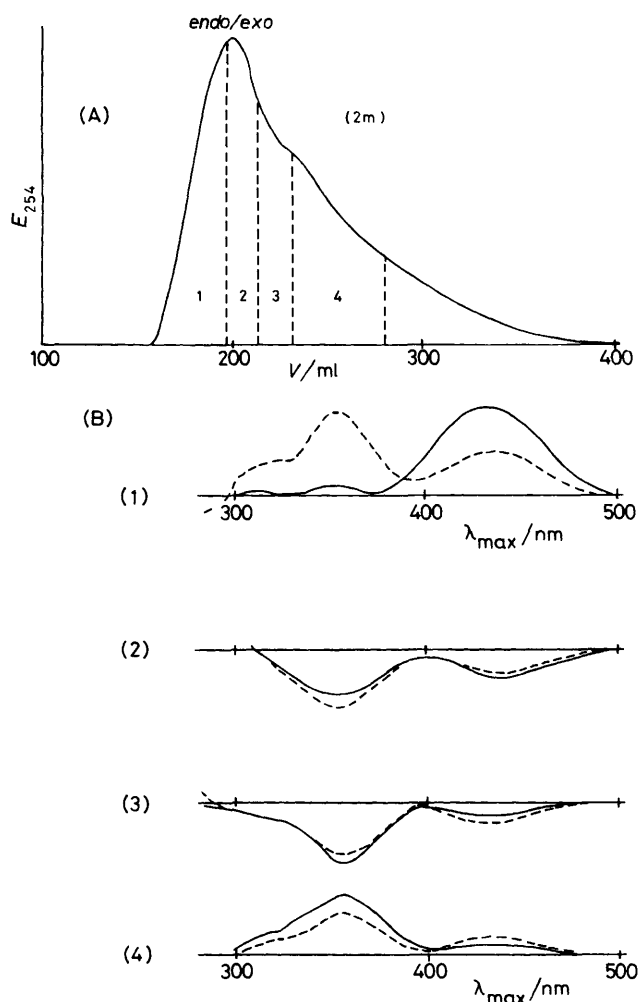


Figure 3. C.d. spectra of bridged biphenyls and their mono-Cr(CO)₃ complexes in iso-octane (A), (B), (D), and ether (C). (C), (D) (see also Figure 4B): since no reliable concentrations could be determined, $\Delta\epsilon$ values are given in % relative to the most intensive bands

Table 2. Kinetic data for the racemization (2) and epimerization (2m), respectively, based on c.d. bands at 260 and 434 nm, respectively

Compd.	T^a		$\tau_{0.5}$ min	$k \cdot 10^5$ s^{-1}	ΔG^\ddagger^b kJ mol^{-1}	ΔS^\ddagger^c $\text{J mol}^{-1} \text{K}^{-1}$	Solvent
	$^\circ\text{C}$	K					
(2)	19.3	292.5	233	2.48	97.3	-46	CHCl_3
	25.7	298.9	110	5.25	97.7	-46	CHCl_3
	27.0	300.2	98	5.89	97.8	-46	CHCl_3
	33.3	306.5	46	12.6	98.0	-46	CHCl_3
	19.0	292.2	366	1.58	98.3	-56	Et_2O
	21.0	294.2	296	1.95	98.5	-56	Et_2O
	27.0	300.2	146	3.96	98.8	-56	Et_2O
	(2m)	0.0	273.2	196	2.95	90.4	0
	5.0	278.2	87	6.64	90.2	0	Et_2O
	10.0	283.2	46.5	12.4	90.4	0	Et_2O
	15.0	288.2	23.5	24.6	90.4	0	Et_2O

^a ± 0.1 . ^b ± 0.4 . ^c ± 20 .**Figure 4.** Chromatography of (2m) on triacetylcellulose in ether at 0 °C (A) and c.d. spectra of the four fractions taken in ether (B): initial spectra, - - - - at equilibrium

means than complexation—at least in this case—decreases the rotational barrier.

Both mono-complexes (3m) and (4m) were obtained in high enantiomeric purities by chromatography on TAC (Table 1). While complexation of (3) yields only the *exo*-complex (3m),

from (4) both diastereoisomers *exo*- and *endo*-(4m) are obtained in about equal amounts.¹ Consequently, (3m) was separated on TAC into (-)- and (+)-*exo*-(3m) [in analogy with (1m)], whereas from the racemic mixture of (4m) on TAC in a much better separation [than for (2m)] four stereoisomers were obtained (Figure 2b and 2c).

Again the *endo*-isomers are less strongly adsorbed than the *exo* forms; the latter are cleanly separated into their enantiomers while the *endo* peak had to be cut into two fractions which proved to be (-)- and (+)-enantiomers on the basis of their optical rotations (Table 1) and c.d. spectra (Figure 3d).

Absolute Configurations.—The configurations of the ligands (2) and (4) were known as (+)(*S*)-(2) and (-)(*S*)-(4), respectively.^{6,10} Photochemical decomplexation of their optically active complexes (2m) and (4m) in ether and ethanol, respectively gave the optically active ligands; from their c.d. spectra the axial chiralities [(*R*)_a and (*S*)_a] could easily be deduced. From fraction (1) of (2m) (Figure 3c) a ligand (2) was obtained the c.d. spectrum of which was identical with that of (+)(*S*)-(2). Decomplexation of (+)-*exo*- and (-)-*endo*-(4m) gave the dextrorotatory ligand (4) with (*R*)_a configuration.

On the basis of optical comparisons with the dimethylated biphenyls (2m) and (4m) the following biphenyl configurations were assigned to the *exo*-complexes (1m) and (3m): (*S*)_a to (+)-(1m) and (-)-(3m), and (*R*)_a to (-)-(1m) and (+)-(3m).

The general considerations presented in the introduction and summarized in Figure 1 permit also the assignments of the absolute metallocene chiralities to all complexes, since both the relative stereochemical relations (*exo/endo*) and the absolute axial chiralities are now known. These assignments are summarized in Table 1 for (1m), (3m), and (4m). For the fractions of (2m) (see Figure 4b) no reliable optical rotations could be measured because of low enantiomeric purities. Their configurational assignments (Table 1) have to be correlated to their c.d. spectra as shown in Figures 3c and 4b.

Enantiomeric purities were tentatively assumed from the peak forms in the TAC chromatograms (Table 1). Photochemical decomplexation of (4m) (*vide supra*) and correlation with the known enantiomeric purity of the ligand (4) gave no conclusive results because partly photochemical decarbonylation⁸ and thereby partly racemization of the ligand had occurred.

Experimental

T.l.c. was run on silica gel plates (60F-254 Merck) in hexane-ethyl acetate or ether-hexane mixtures. Spectra were recorded

on Cary 15 (UV), Bruker WM 250 (in CDCl_3 with SiMe_4 as internal standard) and on a dichrograph Mark III (Jobin Yvon). Optical rotation values were determined with a Perkin-Elmer 141 in 1-dm cells at $20 \pm 0.1^\circ\text{C}$.

The preparations and properties of the tricarbonylchromium complexes used in this work are described in the preceding paper.¹

Chromatographic Resolutions.—These were performed on thermostatted columns (30 by 2.5 cm) of triacetylcellulose (10–30 μm) prepared as described in ref. 4 with ether (at 2–4 bar, 300–400 ml/h) or ethanol (at 5–7 bar, 55–75 ml/h). Ether may reduce the number of theoretical plates from 800 to *ca.* 100 if the temperature is decreased from 20 to 0 $^\circ\text{C}$. Samples of 5 mg/ml (ligands) and 0.5–2 mg/ml (complexes) were applied by a four-way tap fitted with a sample loop. Separations were followed with an u.v.-detector (at 254 nm) *via* a flatbed chart recorder. Optically labile fractions were collected in tubes cooled with solid CO_2 ; their chiroptical properties were recorded immediately afterwards. The results are summarized in Table 1 and shown in Figures 2 and 4a.

Chiroptical Properties.—The fractions obtained by chromatography were carefully evaporated at reduced pressure either at room temperature or, if necessary at 0 $^\circ\text{C}$, the residues dissolved in 2 ml of the solvent for measuring the optical rotations (Table 1), and after further dilution used for recording the c.d. spectra (Figures 3a–d). The concentrations as determined by u.v. spectrometry were 10^{-4} to 10^{-5} mol l^{-1} .

Kinetics.—Only for (2) and (2m) the kinetics could be measured from the c.d. data. Previous to the measurements the cuvettes filled with the solutions obtained directly from the chromatographic separation on TAC (*vide supra*) were thermostatted for 15 min in the cuvette compartment of the dichrograph. The temperature was recorded with a thermocouple at the cuvette block which itself was thermostatted to $\pm 0.1^\circ\text{C}$.

Photochemical Decomplexation.—The bright yellow solutions of the complexes (2m) (fraction 1 in ether) and (4m)

[(+)-*exo* and (–)-*endo* in ethanol] were irradiated with a photolamp (2 000 W) at room temperature. After 20 min the colourless solutions were filtered and used for recording the c.d. spectra of the ligands which were identified by t.l.c. and n.m.r. spectroscopy. In the solutions obtained from (4m) some decarbonylation product was present (*cf.* ref. 8) which had to be racemic and therefore did not interfere with the c.d. results. It prohibited however the determination of the enantiomeric purity of (4m) by correlation with (4). The results are summarized in Table 1.

Acknowledgements

Generous support of the 'Hochschuljubiläums-Stiftung der Stadt Wien' is gratefully acknowledged.

References

- 1 Part 7, H. Kalchauer, K. Schlögl, W. Weissensteiner, and A. Werner, *J. Chem. Soc., Perkin Trans. 1*, preceding paper; the present paper is also Part 51 of the series 'Stereochemistry of Metallocenes'; Part 50, preceding paper.
- 2 W. Theilacker and H. Böhm, *Angew. Chem.*, 1967, **79**, 232; *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 25.
- 3 M. Eyer, K. Schlögl, and R. Schölm, *Tetrahedron*, 1981, **37**, 4239.
- 4 K. Schlögl and M. Widhalm, *Chem. Ber.*, 1982, **115**, 3042.
- 5 K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, jun., *J. Am. Chem. Soc.*, 1964, **86**, 1733.
- 6 K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, and C. Djerassi, *J. Am. Chem. Soc.*, 1960, **82**, 4740.
- 7 For previous extensive c.d. studies in the biphenyl series see E. Bunnenberg, C. Djerassi, K. Mislow, and A. Moscovitz, *J. Am. Chem. Soc.*, 1962, **84**, 2823.
- 8 K. Mislow and A. J. Gordon, *J. Am. Chem. Soc.*, 1963, **85**, 3521.
- 9 K. Mislow and H. B. Hopps, *J. Am. Chem. Soc.*, 1962, **84**, 3018.
- 10 K. Mislow and C. Djerassi, *J. Am. Chem. Soc.*, 1960, **82**, 5247.

Received 6th December 1982; Paper 2/2030