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Biphenyl Tricarbonylchromium Complexes, Part 10 [1]

The Influence of the Tricarbonylchromium Moiety Modified by CO-Exchange on the Rotational Barriers and Population of Stereoisomeric Dimethyldihydrophenanthrene Complexes

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One CO group of the dimethyldihydrophenanthrene mono-$Cr(CO)_3$ complex (**1**) was photochemically substituted for CS (**2**) or $P(C_6H_5)_3$ (**3**). Separation of all four possible stereoisomers $[(R)_m(R)_b/(S)_m(S)_b$ and $(R)_m(S)_b/(S)_m(R)_b]$ of the complexes **1**-**3** was accomplished by two successive chromatographic steps: Separation of the enantiomers on triacetylcellulose was followed by MPLC at low temperatures to yield both epimers (*exo* and *endo*). Their configurational assignment is based on optical comparison of the CD-spectra and on ^1H-NMR-spectroscopy. The kinetics of the biphenyl flip were followed by CD and NMR. The results revealed that the rotational barriers around the biphenyl bond are hardly altered by the substitution of CO for CS or even $P(C_6H_5)_3$. Whereas *exo* and *endo*-isomers of **1** and **2** are obtained in appr. equal amounts, in the more crowded complex **3** the *exo*-isomer predominates over the *endo*-form by 80:20%.

(Keywords: Triacetylcellulose; Optical resolution; Chiroptical properties; Absolute chiralities; Photochemical ligand exchange)

Biphenyl-Tricarbonylchrom-Komplexe, 10. Mitt.: Der Einfluß des durch CO-Austausch modifizierten Tricarbonylchrom-Restes auf die Rotationsbarriere und die Population stereoisomerer Dimethyldihydrophenanthren-Komplexe

Im 4,5-Dimethyl-9,10-dihydrophenanthren-tricarbonylchrom-Komplex (**1**) wurde eine CO-Gruppe photochemisch gegen CS (**2**) oder $P(C_6H_5)_3$ (**3**) ausgetauscht. Die Trennung aller vier möglichen Stereoisomeren $[(R)_m(R)_b/(S)_m(S)_b$ und $(R)_m(S)_b/(S)_m(R)_b]$ der Komplexe **1**–**3** erfolgte in zwei chromatographischen Schritten: Zuerst wurden die Enantiomeren an Triacetylcellulose und anschließend die beiden (*exo*/*endo*) Epimeren durch Mitteldruckchromatographie

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** Dedicated to Prof. *K. Komarek* with cordial wishes on the occasion of the 60th anniversary of his birthday.

bei tiefen Temperaturen getrennt. Die Konfigurationen konnten auf Grund der CD-Spektren und der ^{1}H-NMR-Spektren zugeordnet werden; diese Methoden dienten auch zum Studium der Kinetik der Inversion um die Biphenylbindung (*exo*/*endo*-Isomerisierung): Die entsprechenden Rotationsbarrieren werden durch den Austausch von CO gegen CS oder selbst gegen $P(C_6H_5)_3$ kaum geändert. Die *exo*- und *endo*-Isomeren von **1** und **2** fallen in gleichen Mengen an, während im sterisch gehinderten Komplex **3** die *exo*-Form zu 80% überwiegt.

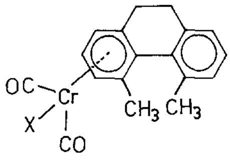
Introduction

Biphenyls become (axial)chiral by appropriate substitution. Sufficient restriction of the rotation (e.g. by bridging or ortho-substitution) enables a separation into (stable) enantiomers. Complexation of arenes—for instance with $Cr(CO)_3$ to yield tricarbonylchromium complexes—not only alters (sometimes dramatically) the reactivity (via mesomeric and inductive effects [2]) but also the symmetry of the ligand (by the resulting change of the molecular geometry [3]). In biphenyls such a complexation may also change the rotational barrier: Thus, e.g., for the tricarbonylchromium complex **1** this barrier is appr. 8 kJ mol^{-1} lower than for the ligand [4].

This and other results [5] led us to the assumption that the complexation could possibly influence the planar transition state (with a coplanar biphenyl system) in such a way that the inductive and mesomeric effects of all groups taking part in the complex might either increase or decrease the rotational barrier.

It therefore seemed of interest to study in some detail the influence of the variation of the tricarbonylchromium moiety by exchange of one CO group for CS or $P(C_6H_5)_3$ (via electronic or steric effects) on the conformational mobility of the biphenyl system and on the isomeric (*exo*/*endo*) ratios.

As a model for these investigations we chose the bridged biphenyl 4,5-dimethyl-9,10-dihydrophenanthrene. In this case rotation around the biphenyl bond gives rise to two preferred conformers which represent

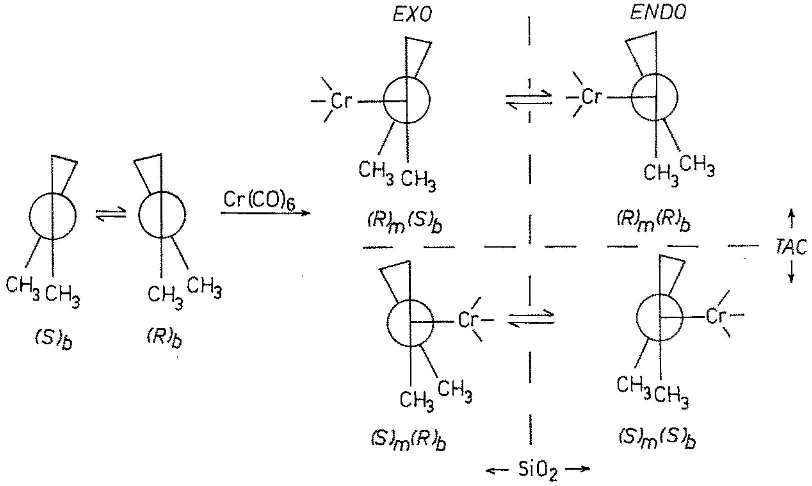


	X
1	CO
2	CS
3	$P(C_6H_5)_3$

enantiomers because of their C_2-symmetry (see Scheme 1). The torsional barrier of $98 \pm 0.5\,\mathrm{kJ\,mol^{-1}}$ lies in a range easily accessible to measurements [4 b].

The variation of $Cr(CO)_3$ in complex **1** was accomplished by photochemical substitution of one CO group for CS or $P(C_6H_5)_3$ to give the complexes **2** and **3** in good yields. According to the different steric requirements and electronic densities of the groups involved [CO, CS and $P(C_6H_5)_3$] (see also Ref. [5]) significant results could be expected.

Scheme 1. Schematic representation of the steric possibilities in complexes of bridged biphenyls and separation of the stereoisomers on TAC and silicagel



Results and Discussion

Synthesis of the Complexes and Isomeric Ratios

For the photochemical exchange of one CO group we used the diastereoisomeric mixture of the tricarbonylchromium complex **1** which is according to previous results [4] an equimolar mixture of the *exo/endo* epimers. After purification by medium pressure liquid chromatography (MPLC) at room temperature the complexes **2** and **3** were obtained as mixtures of isomers in form of yellow microcristalline compounds. In contrast to **1** and **2** the triphenylphosphine derivate **3** is (especially in solution and even at low temperature in the dark) very unstable, which makes its handling rather difficult. From the ^{1}H-NMR spectra of the isomeric mixtures of **2** and **3** the isomeric ratios were deduced by repeated

Table 1 a. *Chromatographic resolution of racemic complexes* **1**–**3** *according to their metallocene chirality (separation of enantiomers)*[a]

Compd.	Solvent	T[°C]	v[ml/h]	w[mg]	V_1/V_2	k_1/k_2	α	$(X)_m$
1	*Et*OH	40	106	70[b]	377 525	2.70 4.15	1.5	$(S)_m$ $(R)_m$
2	*Et*OH	40	96	90	306 451	1.94 3.34	1.7	$(R)_m$ $(S)_m$
3	*Et*OH	20			Decomplexation			

Table 1 b. *Separation of the mixture of exo-endo-epimers (separation of diastereoisomers)*

Compd.	Solvent	T[°C]	v[ml/h]	w[mg]	V_1/V_2	k_1/k_2	α	
1[c]	*PE*/*EA* 12% *EA*	0	2000	10	738 1000	3.34 4.94	1.5	*endo* *exo*
2[c]	*PE*/*EA* 30% *EA*	−10	2400	40	402 486	1.44 1.95	1.4	*endo* *exo*
3[a, d]	*Me*OH	−22	135	10	181 271	0.34 1.01	3	*endo* *exo*

[a] Column: 300 × 25 mm, thermostattet, packed with microcristalline triacetylcellulose (20–30 μm), detection: UV (254 nm).

[b] Repetitive run ("recycling chromatography"), see Ref. [7].

[c] *PE* = Petrolether, *EA* = Ethylacetate; Column: 200 × 38 mm, thermostatted, Merck Lichroprep Si 60 (25–40 μm), detection: UV (280 mm).

[d] Added in proof: In the meantime, this separation was also achieved on silica at −25 °C. (cf.[c]).

integration of the methylsignals. **2** (like **1**) is an equimolar mixture of both (*exo* and *endo*) epimers. In contrast, in **3** the apparently energetically favoured *exo*-form predominates by 80% *.

Separation of Isomers

In attempts to separate the four possible stereoisomeric biphenyl complexes (cf. Scheme 1) one has to take into account their chemical and particularly their conformational lability. Although in some favourable cases an (at least partial) separation of all four isomers on triacetylcel-

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* In Ref. [3] the ratio for **3** was reported as 98 : 2; this preliminary result is due to the instability of **3**.

lulose (TAC) is possible (cf. [4 b] and [1 a]), a twostep chromatographical separation of such biphenylcomplexes has now proved to be very efficient.

For this purpose in the first step the complexes are separated at room temperature and at 40 °C, resp., according to their metallocene chirality on microcristalline TAC in ethanol (see Table 1). Under these conditions the enantiomers are optically stable; in the case of **1** and **2**, however, because of the low rotational barrier a permanent *exo/endo* equilibration occurs. During the separation of **3** on the TAC column (even at 15 °C) complete decomplexation takes place within a few minutes. Consequently, the optically active complex **1** was transformed by photochemical CO-exchange into optically active **3** (with defined metallocene chirality, see Exp.). Thereby it was also demonstrated that under the reaction conditions employed an intramolecular migration of the $Cr(CO)_3$ moiety can be excluded since this effect would cause racemization.

In the second step two of the optically active complexes are separated at -20 °C to -30 °C by MPLC on silica gel: In the cases of **1** and **2** the labile torsional isomers could be isolated. They are stored without noticeable isomerization at -20 °C after removal of the solvent at the same temperature. **3**, however, could be separated into *exo/endo* isomers on TAC in methanol at -22 °C. The chromatographic results are compiled in Table 1.

^{1}H-*NMR Spectra*

The proton NMR spectra of the pure *exo* and *endo* isomers of **1** and **2** were recorded at -30 °C in $CDCl_3$. The AA′BB′-systems of the $-CH_2-CH_2$-bridge protons could be assigned by computer simulation and their coupling constants J calculated. From Figs. 1 and 2 and the data of Table 2 it follows that the spectra of **1** and **2** differ only insignificantly with regard to their chemical shifts and coupling constants. Their CD spectra, however, are remarkably different (cf. Fig. 4).

In the spectra of **1** and **2** for the "benchrotrene" protons (H-1 to H-3) a change in the position of the signal H-1/H-3 + H-3 (with regard to their chemical shifts) can be observed if going from the *exo* to the *endo* isomers. This indicates a restriction of the rotation around the (formal) *Ar*-Cr-bond and that, therefore, the $Cr(CO)_3$ moiety in the ground state adopts a preferred position with regard to the "benchrotrene"-protons (cf. also Ref. [6]): In one case H-2 is staggered, in the other epimer this proton is eclipsed to the CO or CS group in **1** or **2**, resp. Further investigations on this aspect of a hindered "chromium carousel" are in progress.

For the unstable **3** the NMR spectrum could be recorded only from the mixture of epimers (at equilibrium). Because of the excess of the *exo* isomer only for this stereoisomer reliable data were obtained. This

Table 2. ^{1}H-*NMR chemical shifts in* CDCl$_3$ (*δ in ppm, TMS*) *and assignments*

Compound	Methyl-		Methylene-				*J* (Hz)		Aromatic Protons							
	4	5	9 e	9 a	10 e	10 a			1	2	3	4	5	6	7	8
Ligand[a]	2.33	2.33	2.71	2.57	2.71	2.57	9 e/9 a 9 e/10 e 9 e/10 a 9 a/10 e 9 a/10 a 10 a/10 e	−14.1 2.2 3.8 3.8 15.0 −14.1	7.12–7.28			—	—	7.12–7.28		
exo **1**	2.12	2.53	2.52	2.47	2.78	2.72	9 a/9 e 9 a/10 a 10 a/10 e	−14.3 14.6 −15.0	5.30[b]	5.51	5.30[b]	—	—	7.0–7.16		
exo **2**	2.17	2.60	2.49	2.43	2.73	2.70	9 e/9 a 9 e/10 e 9 e/10 a 9 a/10 e 9 a/10 a 10 e/10 a	−13.4 3.0 3.5 4.2 15.5 −15.5	5.42[b]	5.72	5.38[b]	—	—	7.28	7.2	7.07
exo **3**	2.15	2.64	2.60–2.70						5.13[b]	4.49	3.58[b]	—	—	7.2	7.15	7.0
endo **1**	2.23	2.29	2.41	2.28	2.86	3.08	9 e/9 a 9 e/10 e 9 e/10 a 9 a/10 e 9 a/10 a 10 e/10 a	−14.5 2.5 4.0 4.0 14.7 −15.3	5.49	5.33	5.57	—	—	7.0–7.21		
endo **2**	2.25	2.30	2.45	2.29	2.84	3.14	9 e/9 a 9 e/10 e 9 e/10 a 9 a/10 e 9 a/10 a 10 e/10 a	−12.8 2.1 4.0 4.0 13.9 −14.9	5.78[b]	5.46	5.70[b]	—	—	7.15	7.22	7.10
endo **3**	2.03	2.24	2.6–2.7						3.48[b]	5.25	4.62[b]	—	—	[c]	[c]	[c]

[a] 4,5-Dimethyl-9,10-dihydrophenanthrene.

[b] Interchangeable.

[c] Not found because of signal overlap

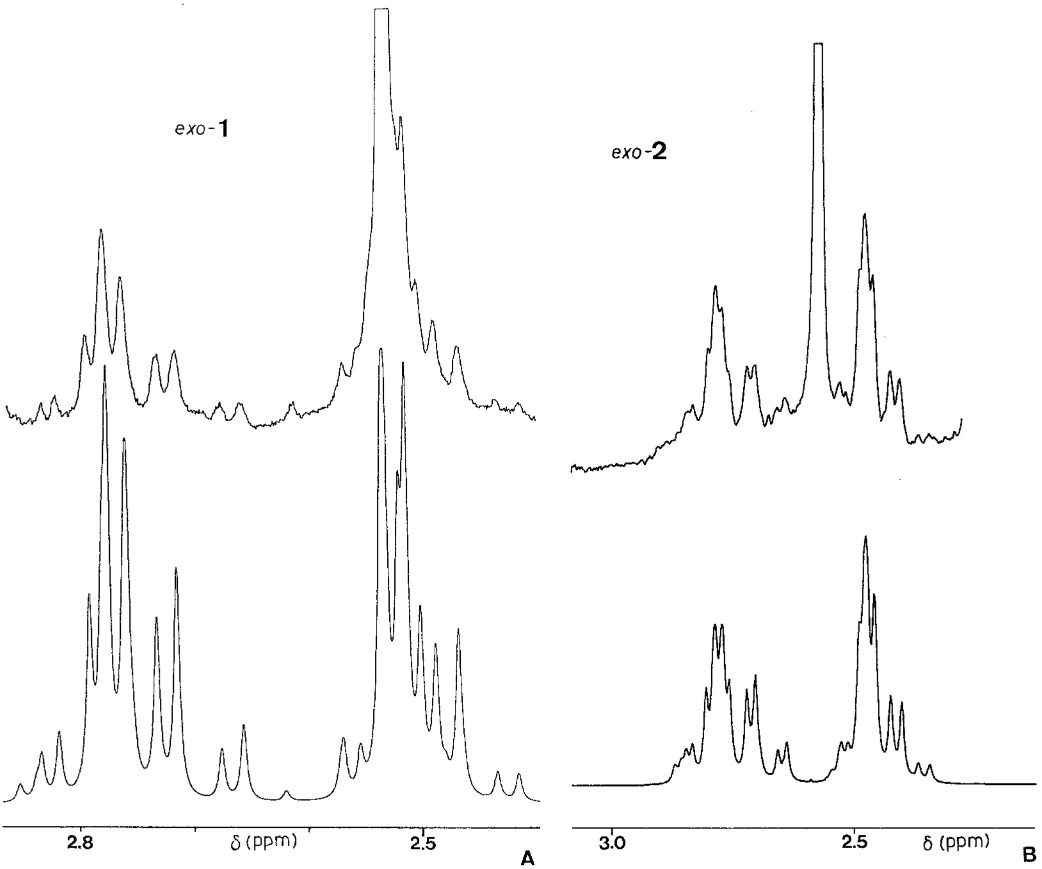

Fig. 1. 250 MHz ^{1}H-NMR spectra of *exo*-**1** (**A**) and *exo*-**2** (**B**) recorded (top) and computed (bottom)

spectrum differs from those of the complexes **1** and **2** with regard to the shift both of H-1 to H-3 and of the bridge protons (CH_2). The AA′BB′-system of the latter reveals very little shift differences and could not be evaluated by calculation because of its poor resolution. In addition, in *exo*-**3** H-1(H-3) exhibits a very strong upfield shift, an effect which might be attributed to the close proximity of the $P(C_6H_5)_3$ moiety. This result also indicates a preferred position of the conformation of the "Cr-tripod" with respect to the biphenyl ligand. Furthermore, a splitting of the signal of this proton (H-1) can be observed which is caused by a $^{31}P-^{1}H$-coupling.

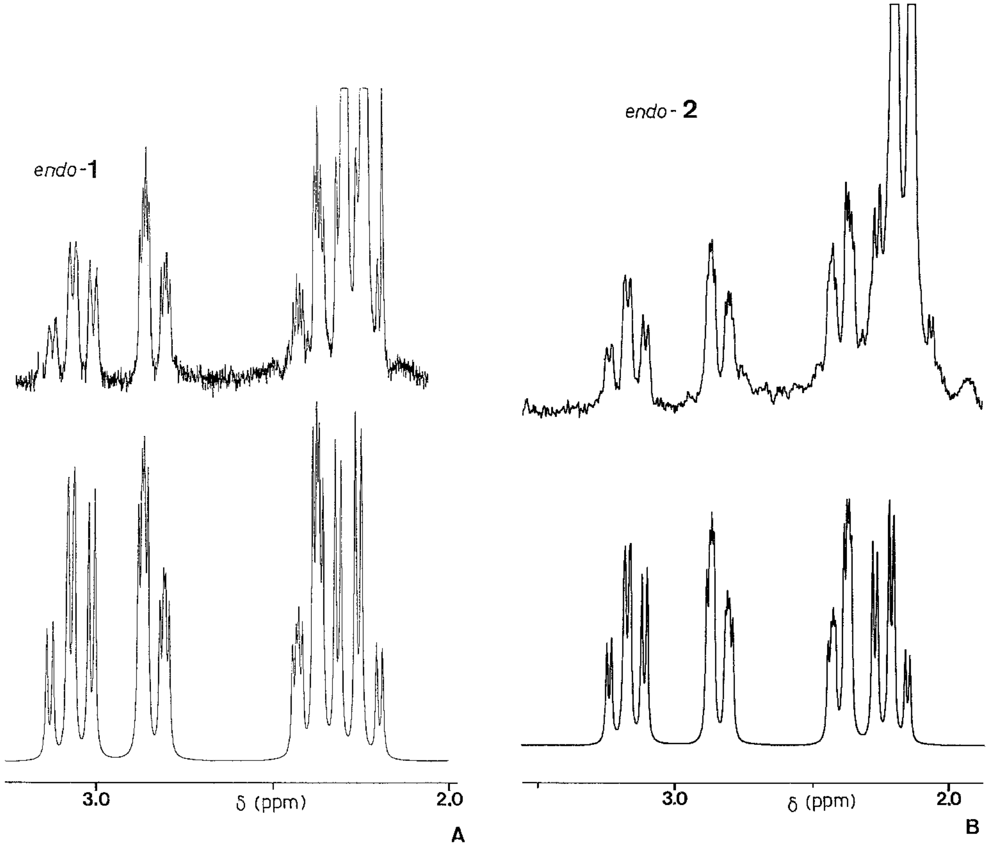

Fig. 2. 250 MHz ^{1}H-NMR spectra of *endo*-**1** (**A**) and *endo*-**2** (**B**) recorded (top) and computed (bottom)

CD Spectra and Absolute Chiralities of the Complexes

The CD spectra of the fractions collected from TAC-chromatograms were recorded at − 15 °C immediately after elution. Concentrations were determined by UV spectrometry (at room temperature from the equilibrium mixture). All solutions were degassed with Ar in order to prevent decomplexation as far as possible.

Figs. 3 and 4 show the CD spectra of the isomers with metallocene chirality $(S)_m$ together with those of the mixtures obtained by equilibration (after 2 h at 25 °C in the dark).

The complex **1** served as a standard for determining the absolute chiralities, since both its metallocene and biphenyl chirality had been established previously from NMR data, CD comparison and by low

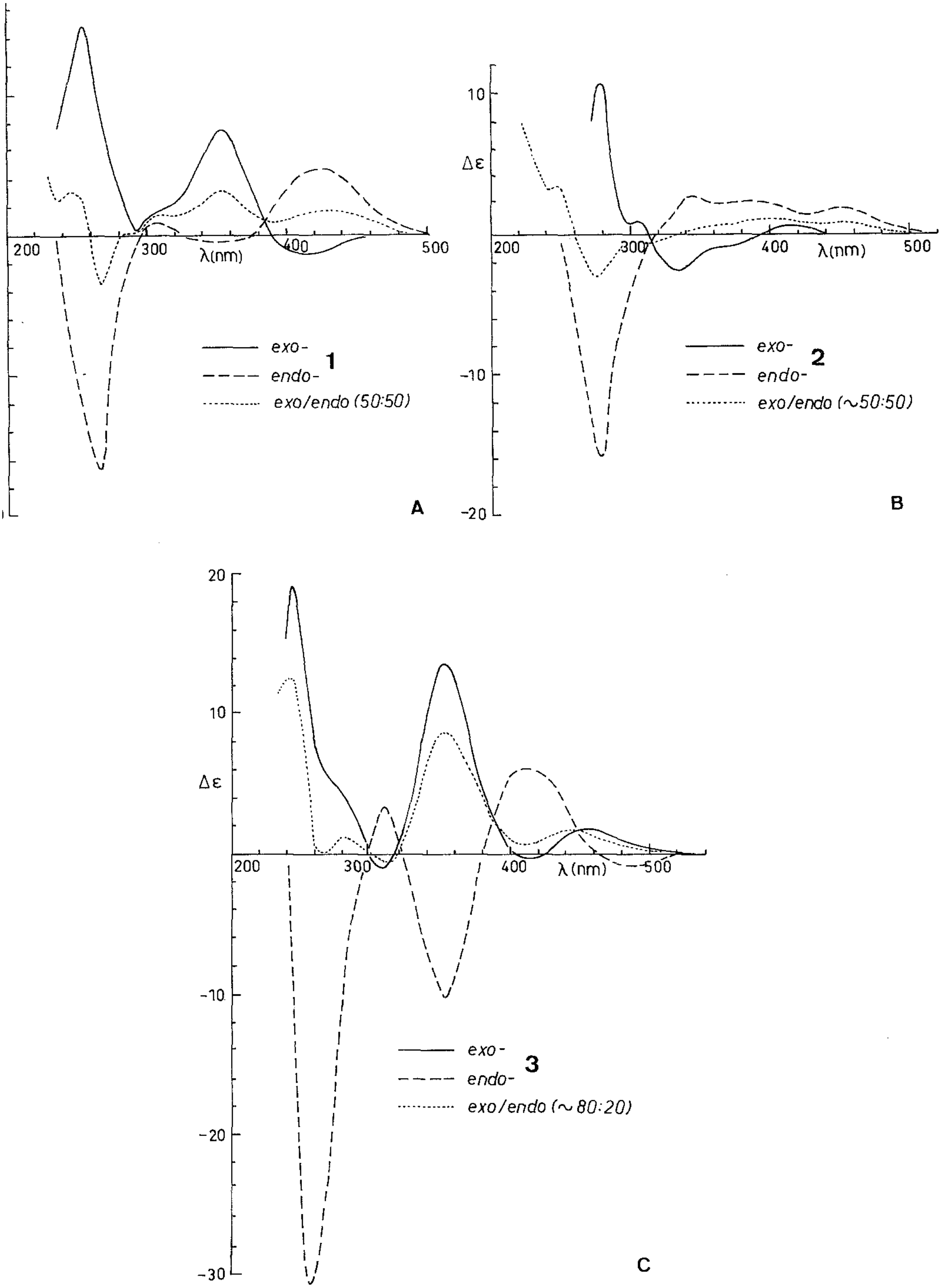

Fig. 3. CD spectra of the complexes **1**–**3** (*exo*, *endo*, and equilibrium mixtures)

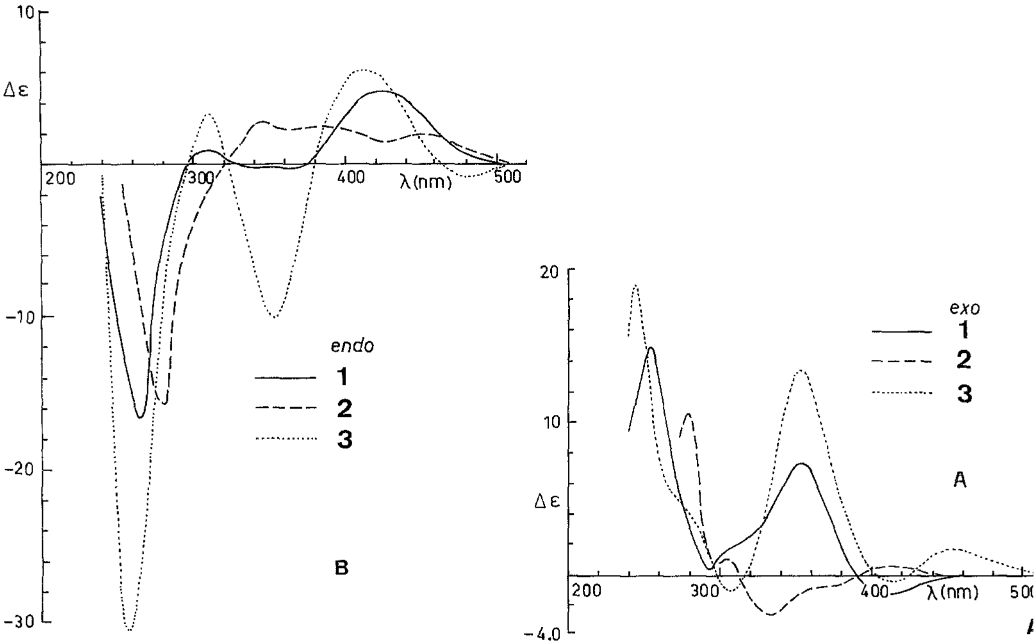

Fig. 4. CD spectra of (**A**) *exo*- and (**B**) *endo*-complexes **1**–**3**

temperature decomplexation [4]. According to this and other results [1 a] the metallocene chirality determines the sign of the charge transfer band with *Cotton* effects between 350 and 450 nm: A positive effect indicates $(S)_m$ configuration. The axial chirality can be deduced from the biphenyl band in the region 240–280 nm: A negative band is significant for an $(S)_b$ configuration. Therefrom also the biphenyl chirality of **2** can be established; in the long wavelength region, however, the general appearance of the spectum is so different from that of **1** that a comparison of both spectra (**1** and **2**, Fig. 4) does not allow a statement as to the metallocene chirality of **2**. As mentioned above, from $(+)(S)_m$-**1** $(+)(S)_m$-**3** was obtained by ligand exchange. In the case of the latter it seems remarkable (Fig. 3 c) that the band at 353 nm (*exo* and *endo*!) has the same sign as the biphenyl band (at 250 ± 5 nm); apparently this band (353 nm) is not due to a charge transfer transition, but conceals it (*exo*!).

Kinetics, Torsional Barriers

The transformation in question can be formulated as follows:

$$EXO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ENDO;\ k_{\mathrm{inv}} = k_1 + k_{-1}$$

The torsional barrier of **1** had been determinated by NMR and CD spectroscopy (cf. Ref. [4]).

The more reliable data (from CD kinetics) are:

$\Delta G^{\neq}_{273} = 90.4 \pm 0.4\,\mathrm{kJ\,mol^{-1}}$; $k_1 = 2.95 \cdot 10^{-5}\,\mathrm{s^{-1}}$ (273 K); $\Delta S^{\neq} = 0 \pm 10\,\mathrm{J\,mol^{-1}\,deg^{-1}}$.

Epimerization of the complex **2** was followed by ^{1}H-NMR spectroscopy in $CDCl_3$ and gave the following values:

$\Delta G^{\neq}_{293} = 91.84 \pm 0.2\,\mathrm{kJ\,mol^{-1}}$; $k_1 = 2.51 \cdot 10^{-4}\,\mathrm{s^{-1}}$ (293 K); $\Delta S^{\neq} = -100 \pm 50\,\mathrm{J\,mol^{-1}\,deg^{-1}}$.

The methyl signals of the diastereoisomers were used as indicator protons. Repeated integration afforded the concentrations; the kinetic data for this first order reactions were calculated from least-squares fits. More reliable data were gained from following the epimerization by CD spectroscopy; this technique was applicable since only the *endo*-epimer reveals a CD band at 450 nm. In order to obtain comparable results the spectra were recorded in $CHCl_3$. From the measurements at 288, 293, and 298 K the following data were obtained:

$\Delta G^{\neq}_{293} = 91.65 \pm 0.05\,\mathrm{kJ\,mol^{-1}}$; $k_1 = 2.87 \cdot 10^{-4}\,\mathrm{s^{-1}}$ (293 K); $\Delta S^{\neq} = -50 \pm 25\,\mathrm{J\,mol^{-1}\,deg^{-1}}$.

The torsional barrier of **3** for *exo* → *endo* was determined as follows:

$\Delta G^{\neq}_{exo > endo} = 89.8 \pm 1\,\mathrm{kJ\,mol^{-1}}$ at 273 K; $k_1 = 3.7 \cdot 10^{-5}\,\mathrm{s^{-1}}$.

whereas the back reaction (*endo* → *exo*) has the following parameters (on the basis of an isomeric ratio of 8 : 2*):

$$\Delta G^{\neq}{}_{endo > exo} = 86.7 \pm 1\,\mathrm{kJ\,mol^{-1}} \text{ at } 273\,\mathrm{K};\ k_{-1} = 1.5 \cdot 10^{-4}\,\mathrm{s^{-1}}.$$

A more exact determination of the data as well as an estimation of $\Delta S^{\neq}$ was impossible due to the low stability of the complexes **3**.

Conclusions

The results outlined above show that in the case of the bridged biphenyl investigated the rotational barriers around the biphenyl bond are hardly altered by the substitution of CO for CS or even $P(C_6H_5)_3$. Whereas *exo*- and *endo*-isomers of **1** and **2** are obtained in appr. equal amounts, in the more crowded complex **3** the *exo*-isomer predominates over the *endo*-form by 80 : 20**.

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[*] An "equilibrium-CD spectrum" was calculated using $0.8 \times \Delta\varepsilon_{exo} + 0.2 \times \Delta\varepsilon_{endo}$: It was superimposable on the experimental CD spectrum of the mixture obtained by thermal (*exo*/*endo*) equilibration.

[**] For a comparison we also studied 2,2′-dimethylbiphenyl, which with a rotational barrier of appr. 71 kJ mol^{-1} is able to rotate "freely" and to adopt every angle preferable with respect to the steric requirements of the chromium moiety in its chromiumtricarbonyl complex. On substitution of one CO for $P(C_6H_5)_3$ in this complex the isomeric ratio remains at 94 : 6.

Acknowledgements

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Experimental

All reactions were conducted under argon. Melting points were determined on a *Kofler* microscope and are uncorrected. MPLC chromatography was run on silica gel (Merck Lichroprep Si 60 25–40 μm) in home-made columns (38 × 400 mm; $N = 5\,000$–$7\,000$) with a FMI pump and a ISCO UA-5 UV-detector. UV spectra were measured on a Perkin-Elmer Lambda-7 spectrometer. IR spectra were recorded on a Perkin-Elmer 237 spectrometer and mass spectra on a Varian MAT CH-7. Optical rotations were measured on a Perkin-Elmer 241 polarimeter and the CD spectra recorded on a dichrograph Mark III (Jobin-Yvon). All NMR spectra were measured on a Bruker WM-250 spectrometer in FT mode using an ASPECT 2000 computer. In all cases the spectra were measured in $CDCl_3$ as a solvent and the deuterium resonance was used for field-frequency lock. Typical acquisition parameters were: memory size 32 K; acquisition time 6.55 s; pulse width 1 μs (15°); number of scans 80–400.

Spectra calculations were performed on the ASPECT 2000 using standard software of Bruker (PANIC 84).

4,5-Dimethyl-9,10-dihydrophenanthrene was prepared according to Ref. [8] in 7 steps.

4,5-Dimethyl-9,10-dihydrophenanthrene tricarbonylchromium (**1**)

The ligand was refluxed with a threefold molar amount of $Cr(CO)_6$ in di-*n*-butylether with 10% *THF* for 24 h. After the solvent and the excess of $Cr(CO)_6$ had been removed *in vacuo,* the resulting oily residue was purified by MPLC.

Yield 58%; m.p. 151–153 °C (decomp.); UV [*Et*OH; λ [nm] (ε)]: 246 (16 500), 328 (8 350), 415 sh (1 560). IR (CH_2Cl_2, ν[cm^{-1}]): 1 880 s, 1 965 s; MS (*m*/*z*): 344 (*M*, 7%; $C_{19}H_{16}CrO_3$ requires 344.4), 288 (*M*-2 CO, 10%), 260 (*M*, 7%; $C_{19}H_{16}CrO_3$ requires 344.4), 288 (*M*-2 CO, 10%), 260 (*M*-3 CO, 10%), 208 (*M*-Cr, −3 CO, 5%). Optical rotation of $(S)_m$ epimers: $[\alpha]_D^{20} = +368 \pm 10°$ (*c* 0.019, *Et*OH).

4,5-Dimethyl-9,10-dihydrophenanthrene dicarbonylthiocarbonylchromium (**2**)

A solution of 400 mg of **1** in Ar-saturated benzene and 2 ml of *cis*-cyclooctene was irradiated with a Hanau mercury high-pressure UV-lamp without filter for 30 min. Then 300 mg of triphenylphosphine and 9 ml of CS_2 were added. After stirring for 20 min the dark brown-red solution was filtered over silica under argon. After removing the solvent *in vacuo* the product was purified by MPLC.

Yield 45%; m.p. 118–119° (decomp.); UV [$CHCl_3$; λ [nm], (ε)]: 263 (18 500), 343 (7 340), 440 sh (1 100). IR (CH_2Cl_2 ν[cm^{-1}]): 1 955 s, 1 905 s, 1 210 s; MS (*m*/*z*): 360 (*M*, 5%; $C_{19}H_{16}CrO_2S$ requires 360.4), 304 (*M*-CO, 14%), 260 (*M*-2 CO, − CS, 14%), 208 (*M*-Cr, − 2 CO, − CS, 100%). Optical rotation of $(R)_m$-epimers: $[\alpha]_D^{20} = +181 \pm 10°$ (*c* 0.02, *Et*OH).

4,5-Dimethyl-9,10-dihydrophenanthrene dicarbonyltriphenylphosphinechromium (**3**)

A solution of 400 mg of **1** in Ar-saturated benzene and a twofold molar excess of triphenylphosphine was irradiated for 40 min (*vide supra*). The solution of the reaction products was filtered over silica under argon. After removing the solvent *in vacuo* the product was purified by MPLC.

Yield 62%; m.p. 173–175 °C (decomp.); UV [*Me*OH, λ[nm], (ε)]: 240 sh (27 000), 260 sh (18 100), 342 (9 190). IR (CH_2Cl_2; $\nu[cm^{-1}]$): 1965 s, 1 885 s; MS (*m*/*z*): 578 (*M*; 3.5%; $C_{36}H_{31}O_2CrP$ requires 578.15), 522 (*M*-2 CO, 20%), 314 (*M*-CrP*Ph*$_3$; 56%), 262 (P*Ph*$_3$, 57%), 208 (*L*; 20%).

A reaction with 30 mg of $(S)_m$-**1** was conducted in the same way giving $(S)_m$-**3** in 60% yield. Optical rotation of $(S)_m$ epimers: $[\alpha]^{20} = +336 \pm 2°$ (*c* 0.09, *Et*OH).

References

[1] a) Part 9: *Eyer M, Schlögl K, Widhalm M* (1984) Monatsh Chem 115: 1429; b) This paper is also part 54 of the series "Stereochemistry of metallocenes"; for part 53 see [1 a]

[2] See for instance: *Solladie-Cavallo A* (1985) Polyhedron 4: 901

[3] *Schlögl K* (1986) J Organometal Chem 300: 219 and literature cited therein

[4] a) *Kalchhauser H, Schlögl K, Weissensteiner W, Werner A* (1983) J Chem Soc Perkin Trans I: 1723; b) *Schlögl K, Werner A, Widhalm M* (1983) J Chem Soc Perkin Trans I: 1731

[5] *Tsoy AA, Baranetkaya NK, Setkina VN, Kursanov DN* (1981) J Organometal Chem 212: 377

[6] a) *Schöllkopf K, Stezowski J, Effenberger F,* (1985) Organometallics 4: 922; b) *McGlinchey M, Bougeard P, Sayer B, Hofer R, Lock C* (1984) J Chem Soc, Chem Comm 1984: 789 and literature cited therein

[7] *Schlögl K, Widhalm M* (1984) Monatsh Chem 115: 1113

[8] *Wittig G, Zimmermann H* (1953) Chem Ber 86: 629