Biphenyl Tricarbonylchromium Complexes. Part 7.[1] Preparation, Static and Dynamic Stereochemistry of Mono- and Bis-tricarbonylchromium Complexes of *o,o'*-Bridged Biphenyls

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Mono- and bis-$Cr(CO)_3$ complexes of 9,10-dihydrophenanthrene (1) and the corresponding ketone (3) (with a CH_2COCH_2 bridge) and their *o,o'*-dimethyl derivatives (2) and (4) have been prepared. Compounds (1) and (3) give *exo*-complexes whereas (2a) and (4) afford a 50:50 mixture of *exo*- and *endo*-isomers separable by medium pressure chromatography. According to lanthanide induced shift n.m.r. spectroscopy (LIS) complexation does not change the torsional angles of the biphenyl system to a significant degree. Isomeric ratios and relative (*exo, endo*) configurations were determined from ^1H n.m.r. spectra. The *exo* ⇌ *endo* equilibria are determined by steric interactions between bridge, ring (methyl) protons and the $Cr(CO)_3$ groups. Kinetic studies on the interconversion rate of the isomeric mono-complexes of dimethyldihydrophenanthrene (2) revealed that complexation decreases the inversion barrier from *ca.* 97 [in (2)] to *ca.* 91 kJ mol^{-1} (in the complex).

Complexation of benzene derivatives with hexacarbonylchromium not only changes the reactivity [2] of the ligand but also decreases the symmetry of the resulting tricarbonylchromium complexes (' benchrotrenes ') as compared with the starting arenes. From appropriately substituted benzenes thereby chiral complexes (with symmetry C_1 or C_2) are obtained which are resolvable into enantiomers, *e.g.* most conveniently by chromatography on triacetylcellulose.[3] Since, moreover, these complexes can be cleaved under rather mild conditions (*e.g.* photochemically at low temperatures) tricarbonylchromium can serve as a very useful stereochemical protecting group.

After conformational [4] and configurational [5] studies in this field we have by this approach recently prepared an optically labile biphenyl derivative.[1]

In the case of biphenyls mono- or bis-complexation introduces in addition to the axial chirality of the ligand a second element of chirality, namely metallocene chirality † thereby giving rise to four stereoisomers (two pairs of enantiomers)—see Figure 1 and ref. 7. The diastereoisomers are designated as *exo* and *endo*, respectively with regard to the positions of the bridge relative to $Cr(CO)_3$; *cis* and *trans* designate the relations of $Cr(CO)_3$ groups in the bis-complexes (see Figure 1).

In all cases of the bis-complexes of *o,o'*-disubstituted biphenyls studied so far (mainly derivatives of diphenic acid) [5] the *exo-trans*-forms [with the two substituents and two $Cr(CO)_3$ units pointing into four different quadrants of the Newman projection, with a torsional angle φ of 90—100° between the benzene planes] were the only stereoisomers isolated. This was first shown by the lanthanide induced shift (LIS) n.m.r. technique [4b] and afterwards confirmed by *X*-ray analyses.[5b]

We have now investigated in some detail the static and dynamic stereochemistry of tricarbonylchromium complexes of *o,o'*-bridged (axial chiral) biphenyls and report in this and in the subsequent paper [7] the results on the complexes of dihydrophenanthrene (1) and 6,7-dihydro-5*H*-dibenzo[*a,c*]-cyclohepten-6-one (3) and their *o,o'*-dimethyl derivatives (2) and (4).

† There is some ambiguity as to the stereochemical classification of metallocenes. Whereas in the CIP system the stereochemical nomenclature formally follows that for centrochirality,[6] chiral metallocenes may also be regarded as planar chiral. We therefore prefer the expression ' metallocene chirality ' and designate enantiomers as $(R)_m$ and $(S)_m$, respectively with the assignment of these symbols following the formal requirements of the determination of centrochiral compounds.[6]

Results and Discussion

Syntheses.—As stated above, complexation of bridged biphenyls with C_2-symmetry may give rise to two stereoisomeric mono- (*exo* and *endo*) and three bis-complexes (*cis*, *trans-exo* and *trans-endo*). For the ligands (1)—(4) under investigation neither the reaction time (up to 60 h) nor the reagent [$Cr(CO)_6$ or $(NH_3)_3Cr(CO)_3$] had any significant influence on the ratios of mono- and bis-complexes. Obviously in every case a thermodynamic equilibrium between ligand and complexes had been established. With regard to its two mono-complexes (Table 1) the ketone (4) seems to be a special case since its high torsional barrier ($\Delta G^{\ddagger} \approx 150$ kJ mol^{-1}, *vide infra*) under the reaction conditions (60 h, 120 °C) allowed no equilibrium to be attained. Thus the formation of equal amounts of both mono-complexes could be determined by kinetic control.

Table 1 summarizes the yields and ratios of the stereoisomeric complexes obtained from the ligands (1)—(4).

The *exo*/*endo* ratios as well as the configurations given were established from ^1H n.m.r. spectra (*vide infra*) and from i.r. spectra (see Experimental section).

The mono-complexes of (4) could be separated by preparative layer chromatography. Owing to the low inversion barrier ($\Delta G^{\ddagger}$ *ca.* 90 kJ mol^{-1}, *vide infra*) and to the resulting short half-life (*ca.* 15 min at room temperature) a fast chromatographic separation at low temperature had to be employed for the separation of the stereoisomeric mono-complexes (2m) of dimethyldihydrophenanthrene (2). They were separated by medium pressure liquid chromatography on a 20 cm silica gel column at 15 °C in hexane–ethyl acetate and immediate freezing of the eluate. Fractions 1 and 4 furnished the isomers in 87 and 80% purity (Figure 2; see also the n.m.r. spectra).

Conformations and Configurations; ^1H *N.M.R. Spectra.*—The conformations of the ligands have been extensively studied.[8,9] The torsional angles φ have been reported as 15° and 29° for (1) and (2), respectively [8,9] and as 52° for (3) and (4).[10]

The rotational barriers $\Delta G^{\ddagger}$ have been determined from

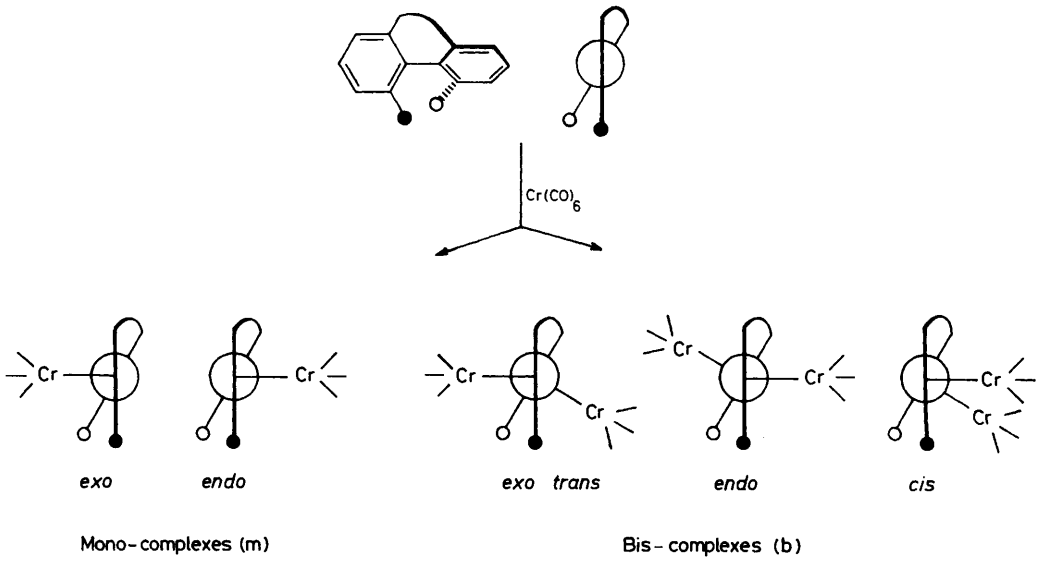
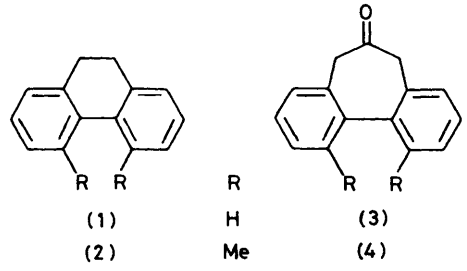


Figure 1. Stereoisomeric mono- and bis-$Cr(CO)_3$ complexes of bridged biphenyls (only one enantiomer is shown)



racemization experiments as 98.4 kJ for (2) [10] and 150.7 kJ for (4); [11] for the unsubstituted biphenyls (1) and (3) the barriers (17 and 71 kJ mol^{-1}) were proposed on the basis of additivity rules.[10] According to ref. 10 *o,o'*-dimethylation increases the torsional barrier by *ca.* 80 kJ. The value for (3) (71 kJ) could now be confirmed from the coalescence temperature of the AB system of the ethylene protons in a 250 MHz ^1H n.m.r. spectrum. For (1) down to −120 °C no splitting of this signal occurred; consequently the barrier is lower than *ca.* 30 kJ mol^{-1} (if no accidental isochrony is present).

According to an *X*-ray structure of the mono-complex *exo*-(1m) with a torsional angle of 15° [12] [the same as for the ligand (1), *vide supra*] and to our LIS studies of the mono-complexes of (3) and (4) [*exo*-(3m), *exo*- and *endo*-(4m)] complexation does not change the torsional angles φ (and thus the geometries of the ligands) to a significant degree. For (3) and (4) the LIS values for the protons both of the ligands and the mono-complexes of (4) were recorded and then compared. Since the values for corresponding resonances are very close (Table 2) a conformational change can be excluded: $\Delta\varphi \leqslant \pm 5°$.

Mono-complexation decreases the symmetry of the ligands (1)—(4) from C_2 to C_1 whereas it remains unchanged in the *trans*-bis-complexes (see also Figure 1). These symmetries are also reflected in the ^1H n.m.r. spectra.

Ligands.—The ^1H n.m.r. spectra show in the benzene region one ABCD system for (1) and (3) and an ABC system for the dimethylated biphenyls (2) and (4). The four ethylene protons of the bridge appear as an AA'BB' system for (2) (Figure 3) and as an AB system for (3) and (4). Because of the low inversion barrier in dihydrophenanthrene (*vide supra*) only a singlet appears in (1).

For the ketones (3) and (4) the signals could be assigned on the basis of the LIS data. The higher LIS values were ascribed to the equatorial protons 9e-H and 10e-H, the lower to the axial protons (Figure 4). Also 1-H and 8-H in (3) and (4) are more strongly shifted than the protons 4 and 5 [in (3)] and 3-H and 6-H [in (4)], respectively. Selective decoupling experiments were used to distinguish between 2-H and 3-H on the one hand and 6-H and 7-H on the other.

The benzene proton signals of (1) and (3) could also be assigned by double resonance; thereby 4-H [in (1)] is shifted downfield as compared with 1-H.

The AA'BB' system of (2) shows a broadening of the AA' part at higher field caused by coupling with 1-H and 8-H. In contrast to the ketones (3) and (4) the axial protons of (1) and (2) appear at higher field. The decoupled AA'BB' system could be analyzed by computation.

Mono-complexes.—Because of the lower symmetry (C_1) of the complexes the spectra of (1m)—(4m) are more complex than those of the ligands (C_2).

As mentioned above (see also Figure 1) torsion around the biphenyl axis gives rise to an *exo-endo* epimerization of the mono-complexes, whereas the same process in the ligands causes racemization. If the torsional barrier is high enough, the spectra of both isomers can be recorded separately. Thus the *exo* and *endo* stereoisomers of (2m) and (4m) exhibit separate signals at room temperature, those of (3m) only at −20 °C, whereas in (1m) down to −90 °C no separate signals could be observed.

Since both stereoisomers of (2m) and (4m) could be isolated, their n.m.r. spectra could be analyzed separately. The assignment for the ketones was based on the LIS technique, for the bridge protons of (1m) and (2m) by means of computation (Table 3).

The spectra of the mono-complexes (1m)—(4m) show characteristic features as compared with those of the ligands (1)—(4): (a) $Cr(CO)_3$ causes an upfield shift of the aromatic protons of the benchrotrene ring.

(b) This shift is also valid for the methyl protons 4-H as could be established from the nuclear Overhauser effect: irradiation of the upfield methyl signals caused an increase

Table 1. Complexation of *o,o'*-bridged biphenyls. Yields and ratios of isomeric $Cr(CO)_3$ complexes

	Mono-[$Cr(CO)_3$] complexes			Bis-[$Cr(CO)_3$] complexes			
Biphenyl	No.	Yield (%)	*exo/endo* (±2)	No.	Yield (%)	*cis* (%)	*trans exo/endo* (±2)
(1)	(1m)	76	100/0	(1b)	12	2	100/0
(2)	(2m)	28	50/50	(2b)	2	—	50/50
(3)	(3m)	30 [a]	90/10	(3b)	2—3	—	>90/10
(4)	(4m)	30	50/50	(4b)[b]			

[a] $Cr(CO)_6$ in di-n-butyl ether at 120 °C gives several by-products, such as products from a decarbonylation of the ligand (*cf.* ref. 11). With $(NH_3)_3Cr(CO)_3$ in dioxan the reaction proceeds considerably faster and much purer products are obtained, although with the same yields and with the same isomer ratios as with $Cr(CO)_6$. [b] Several by-products prevent the isolation of bis-complexes.

Table 2. LIS values, standardized to $\delta\Delta = 1$ [a] for the protons 9e and 10e (see Figure 4) and average value (9e + 10e)/2, respectively

	Methylene protons				Aromatic protons							
Compd.	9a	9e	10a	10e	1	2	3	4 [b]	5 [b]	6	7	8
(3)	0.889	1	0.889	1	0.500	0.170	0.200	0.360	0.360	0.200	0.170	0.500
(4)	0.882	1	0.882	1	0.214	0.075	0.091	0.116	0.116	0.091	0.075	0.214
exo-(4m)	0.861	0.905	0.920	1.095	0.131	0.044	0.088	0.124	0.098	0.088	0.088	0.307
endo-(4m)	0.813	0.976	0.927	1.024	0.163	0.081	0.098	0.114	0.098	0.033	0.033	0.179

[a] $\delta\Delta$ (p.p.m.) = $\delta\Delta_{stand} \cdot f$ for the values $L_0 : S_0 = 1 : 1$ [f: (3) 2.53; (4) 4.4; *exo*-(4m) 0.69; *endo*-(4m) 0.62)]. [b] For (3) H; for (4) CH_3.

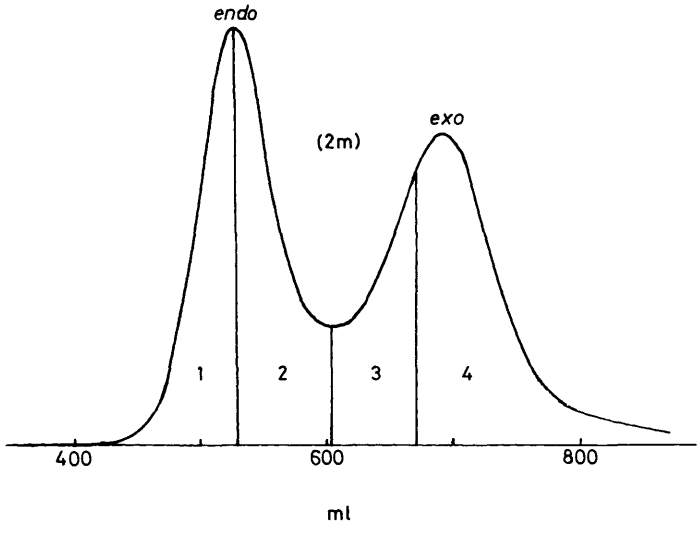


Figure 2. Chromatographic separation of (2m) on silica gel in hexane–ethyl acetate at 15 °C

in the intensity of the signals at the adjacent proton in the benchrotrene ring (3-H).

(c) In analogy the methylene protons 9a-H are shifted upfield as compared with 10a-H (like 9e-H as compared with 10e-H). The influence of the complexation on the chemical shifts is shown schematically in Figure 5 (A and B) for the methylene region.

The spectra of the isomeric (*exo* and *endo*) complexes exhibit distinct shift differences either for the methylene or the methyl proton signals.

In one isomer the axial proton 10a-H (Figures 4 and 5) is shifted strongly to lower field, whereas the methyl group (5-H) is almost unchanged. In the other isomer the methyl group 5-H is shifted strongly downfield.

Studies with molecular models reveal that in the *exo*-complexes the methyl group at the benzene ring (Figure 4) is in the deshielding region of $Cr(CO)_3$, whereas in the *endo*-isomers the methylene proton 10a-H is in the deshielding region.

Consequently the *endo*-configuration is assigned to those complexes in which the axial methylene protons (10a, adjacent to the benzene ring, see Figures 4 and 5) absorb at *lower* field.

Based on these results, from the n.m.r. spectrum of the complex (1m) a pronounced preference for the *exo*-isomer can be deduced. The preponderance of one isomer follows also from the vicinal coupling constants: $^3J_{9a,10a} \sim 13.7$ Hz—rather similar to that of the pure isomer (2m) (14.6 Hz).

Ratios of Isomers.—As mentioned above these ratios for (2m), (3m), and (4m) (see Table 1) were deduced from the integration of suitable signal groups in the n.m.r. spectra. While the pure isomers of (4m) are stable at room temperature (with no isomerization detectable in the spectra) in the mono-complex (2m) at room temperature a fast equilibration

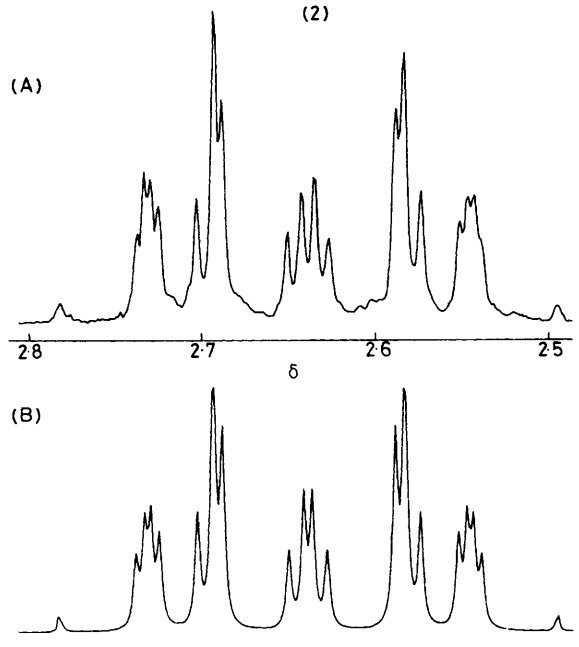


Figure 3. Decoupled 250 MHz ^{1}H n.m.r. spectrum of 4,5-dimethyldihydrophenanthrene (2) in the methylene region (in $CDCl_3$): (A) observed, (B) calculated

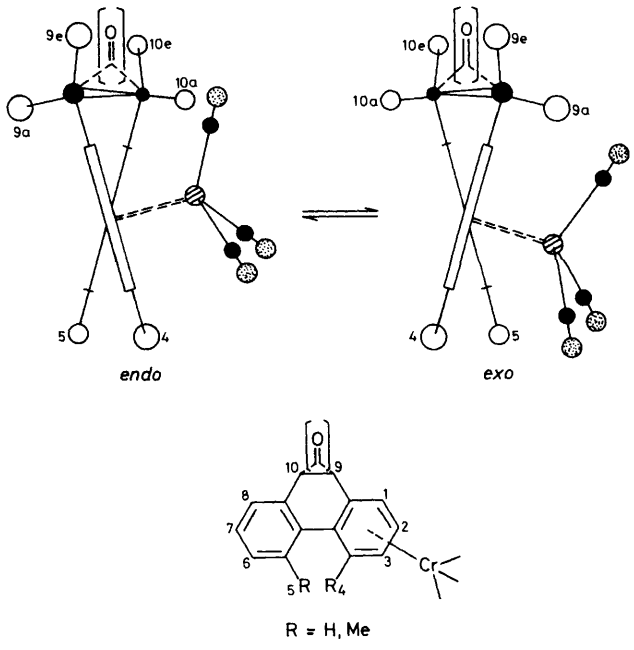


Figure 4. *endo* and *exo* Stereoisomeric mono-$Cr(CO)_3$ complexes

occurs resulting in a 50 : 50 mixture. Within experimental error the equilibrium constant is temperature independent between −20 and +30 °C. In the case of (3m) the *exo*-form is preferred. At −20 °C the *exo*/*endo* ratio is 90 : 10. Also for (1m) a similar preference (for *exo*) is observed.

As a plausible reason for these stereoisomeric relations, interactions between the methyl and methylene protons (of the uncomplexed benzene ring) with $Cr(CO)_3$ can be assumed. In the unmethylated mono-complexes (1m) and (3m) this interaction can occur only with the CH_2 protons, being much weaker in the *exo*- than in the *endo*-isomers.

Bis-complexes.—These complexes (1b), (2b), and (3b) could be isolated in small amounts (Table 1). For the assignments of their configurations it is assumed that the influence of the two $Cr(CO)_3$ groups on the chemical shifts is approximately additive. The experimental and calculated shift values are summarized in Figure 5. The calculation was carried out as follows: by the mono-complexation of the ligand [*e.g.* of (2), Figure 5] an axial proton (10a-H) is shifted downfield (full line in Figure 5). Additional complexation to the bis-complex causes a shift of the proton 9a-H towards lower field by approximately the same amount (dotted line in Figure 5).

Kinetics.—From kinetic studies on the racemization of the ligands (2) and (4) their activation energies $\Delta G^{\ddagger}$ have been determined as 98.4 [7,10] and 150.7 kJ mol^{-1}, respectively.[10] For the unmethylated biphenyls (1) and (3) only calculated values (17 and 71 kJ, respectively) have been reported.[8]

We have now determined the $\Delta G^{\ddagger}$ value for (3) as 71.0 kJ and the lower limit for (1) (<30 kJ mol^{-1}) from n.m.r. experiments on the basis of the coalescence of the AB system of the bridge protons.

The influence of the complexation on the rotational barrier was demonstrated for (2) and its mono-complex (2m); only these compounds have half lives ($\tau_{0.5} \approx$ 10—60 min) suitable for a direct observation of the racemization and isomerization, respectively.

For this purpose the isomerization rates of the complexes (2m) were determined by n.m.r. (see Experimental section) and compared with the racemization rate of the ligand (2). Both for *exo*- and *endo*-(2m) a torsional barrier of $\Delta G^{\ddagger}_{293} = 90.6 \pm 0.8$ kJ mol^{-1} (in $CHCl_3$) was found whereas the ligand (2) has a barrier of 97.3 ± 0.4 kJ (also in $CHCl_3$) as determined from its circular dichroism spectrum.[7] (For $\Delta S^{\ddagger}$-values see ref. 7.)

Consequently, complexation in this case *decreases* the inversion barrier to a significant degree (*ca.* 6.5 kJ). The same effect is observed for the complexation of (3). The mono-complex (3m) shows at room temperature a combined signal for the CH_2 protons while the ligand (3) exhibits separate signals (as an AB system).

Studies on the optical resolution of the ligands and their $Cr(CO)_3$ complexes as well as racemization experiments and the assignments of absolute configurations to the optically active complexes are described in the following paper.

Experimental

All reactions were carried out under argon in the dark. M.p.s were determined on a Kofler microscope and are uncorrected. All compounds were pure on t.l.c. (silica gel plates, 60F-254 Merck in hexane–ethyl acetate). Column chromatography was run on silica gel (Merck-60; 0.04—0.063) at a pressure of 3 bar. I.r. spectra were recorded on a Perkin-Elmer 237 instrument and mass spectra on a Varian MAT-CH-7. All n.m.r. spectra were measured on a Bruker WM-250 spectrometer in the FT mode using an ASPECT 2000 computer (80 K memory). Low temperature spectra were recorded with the aid of a low-temperature unit in CS_2–CD_2Cl_2 (1 : 1), all other spectra in $CDCl_3$ unless stated otherwise. In all cases the deuterium resonance of the solvent was used for field-frequency lock. Typical acquisition parameters were: memory size 32 K; acquisition time 6.55 s; pulse width 1 μs (*ca.* 15°); number of scans 80—400. Spectra calculations were performed on the ASPECT 2000 using standard software of Bruker (PANIC 81).

The required starting biphenyls were prepared according to

Table 3. ^{1}H N.m.r. chemical shifts in $CDCl_3$ (p.p.m., $SiMe_4$) and assignments

Compd.	Methyl 4	Methyl 5	Methylene 9e	9a	10e	10a	J/Hz	Aromatic protons [a] 1	2	3	4	5	6	7	8
(1)	—	—		2.88			—		7.23—7.36			7.77		7.23—7.36	
exo-(1m)	—	—	2.62	2.78	2.89	3.03	9a/9e −15.3; 9e/10e 3.6; 9e/10a 5.6; 9a/10e 5.3; 9a/10a 13.7; 10e/10a −15.4	5.41	5.32	5.47	5.87	7.58 [b]		7.17—7.32	
trans-(1b)	—	—	2.60	2.95	2.60	2.95	9a/9e −15.6; 9e/10e 2.0; 9e/10a 5.0; 9a/10e 5.0; 9a/10a 13.6; 10e/10a −15.6	5.35	5.39	5.47	5.64	5.64	5.47	5.39	5.35
(2)	2.33	2.33	2.71	2.57	2.71	2.57	9a/9e −14.1; 9e/10e 2.2; 9e/10a 3.8; 9a/10e 3.8; 9a/10a 15.0; 10a/10e −14.1				7.12—7.28				
exo-(2m)	2.12	2.53	2.52	2.47	2.78	2.72	9a/9e −14.3; 9a/10a 14.6; 10a/10e −15.0 [c]	5.30	5.51	5.30	—	—		7.0—7.16	
endo-(2m)	2.23	2.29	2.41	2.28	2.86	3.08	9a/9e −14.5; 9e/10e 2.5; 9e/10a 4.0; 9a/10e 4.0; 9a/10a 14.7; 10e/10a −15.3 [c]	5.49 [d]	5.33	5.57 [d]	—	—		7.0—7.21	
exo-(2b)	2.41	2.41		2.60 [b]			—	5.23 [d]	5.49	5.28 [d]	—	—	5.28 [d]	5.49	5.23 [d]
endo-(2b)	2.36	2.36	2.56	2.80	2.56	2.80	—	5.23 [d]	5.38	5.28 [d]	—	—	5.28 [d]	5.38	5.23 [d]
(3)	—	—	3.51	3.57	3.51	3.57	a/e −14.5	7.25	7.41	7.33	7.55	7.55	7.33	7.41	7.25
exo-(3m)	—	—	3.16	3.60	3.57	3.73	9a/9e −14.7; 10a/10e −16.2	5.33 [d]	5.36	5.52 [d]	5.81	7.58	7.41	7.50	7.25
endo-(3m)	—	—	3.32	3.39	3.86	4.55	9a/9e −15.1; 10a/10e −17.1	5.33 [d]	5.36	5.52 [d]	5.81	7.58	7.41	7.50	7.25
exo-(3b)	—	—	3.27	3.73	3.27	3.73	a/e −15.2	5.24	5.37 [d]	5.47 [d]	5.87	5.87	5.47 [d]	5.37 [d]	5.24
(4)	2.20	2.20	3.30	3.50	3.30	3.50	a/e −15.3		7.03—7.09		—	—		7.21—7.27	
exo-(4m)	2.07	2.69	2.88	3.49	3.39	3.69	9a/9e −14.6; 10a/10e −15.4	4.98	5.60	5.24	—	—	7.2—7.36		7.06
endo-(4m)	2.12	2.23	3.14	3.25	3.75	5.14	9a/9e −16; 10a/10e −16	5.28	5.54	5.36	—	—	7.2—7.36		7.12

[a] 1-H to 8-H are ' benchrotrene ' and/or benzene protons, respectively. See Figure 4 for numbering of ring positions. [b] Centre of multiplet. [c] J ±1.5 Hz owing to signal overlapping with methyl signals. [d] Interchangeable.

the literature, purified mainly by medium pressure liquid chromatography (m.p.l.c.) and their purity checked by n.m.r. and mass spectrometry. 9,10-Dihydrophenanthrene (1), 4 steps from diphenic acid,[13] its 4,5-dimethyl derivative (2) in 7 steps from *m*-nitrotoluic acid.[14] 6,7-*Dihydro*-5H-*dibenzo*[a,c]*cyclohepten*-6-*one* (3) was obtained from 2,2′-bisbromomethylbiphenyl [13,15] and its dimethyl derivative 1,11-*dimethyl*-6,7-*dihydro*-5H-*dibenzo*[a,c]*cycloheptene*-6-*one* (4) from the corresponding 6,6′-dimethyl precursor.[14,15]

Complexation of the Ligands (1)—(4) *to Tricarbonyl*(η^6-*biphenyl*)*chromium Derivatives*: *General Procedure*.—The ligand was refluxed with a four-fold molar amount of $Cr(CO)_6$ in dry di-n-butyl ether–heptane (2 : 1) (20 ml for 1 mmol of ligand) for at least 24 h. The course of reaction was followed by t.l.c. After completion (*i.e.* if no further change of the mixture could be observed within 2—3 h) the mixture was filtered, solvent and excess of $Cr(CO)_6$ removed under reduced pressure, and the resulting oily residue purified and separated into products by m.p.l.c. on silica gel. Reactions with $(NH_3)_3Cr(CO)_3$ [16] were performed in dioxan and gave purer products within shorter reaction times (see Table 1). Yields and isomer ratios of the complexes are presented in Table 1, n.m.r. spectra in Table 3.

Complexation of (1). Reaction time one week: (1m), m.p. 106—107 °C, $\nu_{max.}$ (CH_2Cl_2) 1 892s and 1 970s cm^{-1} (Cr–CO); *m*/*z* (relative abundance) 316 (*M*, 45. $C_{17}H_{12}CrO_3$ requires 316.3), 260 (*M* − 2CO, 53), 232 (*M* − 3CO, 100), 180 (*M* − Cr, −3CO, 38). *trans*-(1b), m.p. 182 °C (decomp.), $\nu_{max.}$ (CH_2Cl_2) 1 900s and 1 970s cm^{-1} (Cr–CO); *m*/*z* 452 (*M*, 6. $C_{20}H_{12}Cr_2O_6$ requires 452.3), 396 (*M* − 2CO, 2), 368 (*M* − 3CO, 4), 340 (*M* − 4CO, 8), 312 (*M* − 5CO, 13), 284 (*M* − 6CO, 8), 232 (*M* − Cr, −6CO, 30). *cis*-(1b), m.p. 200 °C (decomp.); $\nu_{max.}$ (CH_2Cl_2) 1 895s, 1 912s, and 1 990s cm^{-1} (Cr–CO bands split; mass spectrum identical with that of *trans*-(1b). Because of very low solubility no n.m.r. spectrum was recorded.

Complexation of (2). Reaction time 28 h: (2m) (*exo*/*endo*-mixture), m.p. 151—153 °C (decomp.); $\nu_{max.}$ (CH_2Cl_2) 1 880s, 1 965s cm^{-1}; *m*/*z* 344 (*M*, 7. $C_{19}H_{16}CrO_3$ requires 344.4), 288 (*M* − 2CO, 10), 260 (*M* − 3CO, 58), 208 (*M* − Cr, −3CO, 5). (2b), m.p. 170—171 °C (decomp.); $\nu_{max.}$ (CH_2Cl_2) 1 890s,

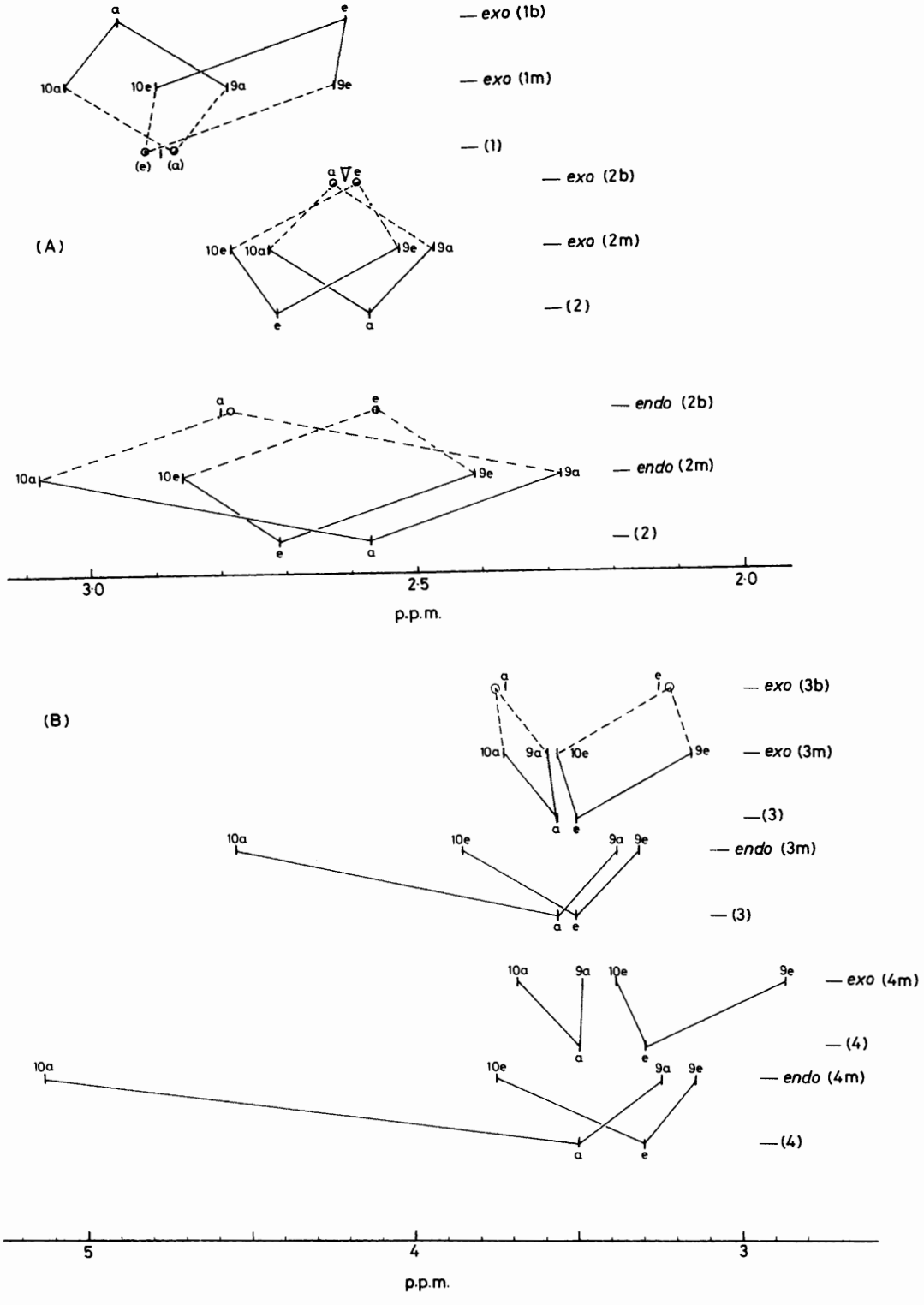


Figure 5. Influence of complexation on the chemical shifts of bridge methylene protons. (A): for (1) and (2) and their complexes. (B): for (3) and (4) and their complexes. I Observed shifts, O calculated shifts. [The AA'BB' system of *exo*-(2b) could not be calculated; ▽ centre of unresolved multiplet.]

1 965s cm^{-1} (Cr–CO); *m/z* 480 (*M*, 1.5. $C_{22}H_{16}Cr_2O_6$ requires 480.4), 396 (*M* − 3CO, 2), 344 (*M* − Cr, −3CO, 3), 312 (*M* − 6CO, 3), 288 (*M* − 2Cr, −5CO, 5), 260 (*M* − Cr, −6CO, 32).

Chromatographic separation of exo- *and* endo-(2m). Because of the low half-life of epimerization (15 min at room temperature) attempts to separate the stereoisomers of (2m) by preparative layer chromatography failed. Application of m.p.l.c. however on a thermostatted (15 °C) column (200 × 3.5 cm) of silica gel (Si-60, 40—63 μm; dead volume 170 ml,

1 100 theoretical plates) in hexane, containing 12 vol% ethyl acetate (pre-cooled to 15 °C) allowed a separation of 20 mg of (2m) within 15 min (40 ml solvent/min); k'_1 2.16 and k'_2 3.08 for the *endo*- and *exo*-isomers, respectively ($\alpha = 1.4$). The fractions were collected in vessels cooled to −40 to −50 °C and the solutions evaporated at low pressure at *ca.* −10 °C. Purity (from n.m.r.): *endo* 87%, *exo* 80%.

Complexation of (3). Reaction time 30 h: [with $(NH_3)_3Cr(CO)_3$ 6 h]: (3m), m.p. 147—152 °C (decomp.); $\nu_{max.}$ (CH_2Cl_2) 1 725d (CO), 1 900, and 1 978s cm^{-1} (Cr–CO); *m/z* 345 (*M* + 1, 2), 344 (*M*, 6. $C_{18}H_{12}CrO_4$ requires 344.3), 288 (*M* − 2CO, 5), 260 (*M* − 3CO 40), 208 (*M* − Cr, −3CO, 6), (3b), m.p. 210—212 °C (decomp.); $\nu_{max.}$ (CH_2Cl_2) 1 730 (m, CO), 1 910, and 1 975s cm^{-1} (Cr–CO); *m/z* 481 (*M* + 1, 1) 480 (*M*, 2. $C_{21}H_{12}Cr_2O_7$ requires 480.3), 396 (*M* − 3CO, 1), 368 (*M* − 4CO, 1), 344 (*M* − Cr, −3CO, 1), 340 (*M* − 5CO, 0.5), 312 (*M* − 6CO, 15), 260 (*M* − Cr, −6CO, 3), 208 (*M* − 2Cr, −6CO 7).

Complexation of (4). Reaction time 24 h: (4m), m.p. 165—170 °C; $\nu_{max.}$ (CH_2Cl_2) 1 720 (*endo*, CO), 1 730 (*exo*, CO), 1 895, and 1 970 cm^{-1} (*exo* and *endo*, Cr–CO); *m/z* (*exo* and *endo*) 373 (*M* + 1, 3), 372 (*M*, 10. $C_{20}H_{16}CrO_4$ requires 372.3), 366 (*M* − 2CO, 9), 288 (*M* − 3CO, 70), 260 (*M* − 4CO, 18), 236 (*M* − Cr, −3CO 6).

Isomerization of (2m): *N.M.R. Kinetics.*—The complexes *exo*- and *endo*-(2m) obtained by chromatography (*vide supra*) were dissolved in $CDCl_3$ at −60 °C and the solutions quickly filtered through a small column of silica gel to remove paramagnetic contaminants. Immediately before the commencement of measurements the samples were thermostatted for 3 min at the required temperature. The temperature within the probe head was kept constant with the control unit of the 250 MHz spectrometer; O_2 was removed by flushing with Ar. The intervals between the measurements were determined by a micro-program and the time of measurements relative to the intervals was kept as short as possible. Typical parameters were: intervals 180, 360, 540, 840, 1 140, 1 440, 1 740, 2 040, 2 340, and 2 840 s; memory size 16 K; acquisition time 3.2 s; number of scans 8. Therefore time of measurement 26 s.

For determining the isomerization ratios the real intensities of the methyl proton signals were used for graphical evaluation of the data. Two series of measurements furnished the following reaction rates:

(1) 283 K: *endo* $1.74.10^{-4}$ and *exo* $1.77.10^{-4}$; 303 K: *endo* $1.07.10^{-3}$ and *exo* $1.18.10^{-3}$.

(2) Only from *endo*-(2m): 283 K $1.74.10^{-4}$; 293 K $3.43.10^{-4}$; 298 K $6.34.10^{-4}$; and 303 K $1.135.10^{-3}$.

From series (1) by interpolation a value for $\Delta G^{\ddagger}_{293}$ of 90.4 kJ mol^{-1} was obtained and from series (2) by least-squares fit a value of 90.6 ± 0.8 kJ.

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