Synthesis and Properties of Novel (Tricarbonyl)(heptalene)chromium Complexes

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A number of novel (tricarbonyl)chromium complexes of heptalenes **10**–**13**, **16**–**20** and **23**–**25** have been prepared by reaction of the heptalenes with $[Cr(CO)_3L_3]$ (L=NH_3, Py; *cf. Schemes 3–6*). Surprisingly, the off-state complexes **17** and **19**, in which the $Cr(CO)_3$ group complexes on the diester ring, have been obtained with excellent regioselectivity. The directing effect of ester C=O groups on the regioselectivity of the $Cr(CO)_3$ coordination to heptalene rings has been discussed. These complexes undergo thermal rearrangements *via* 1,2-intra-ring shift and inter-ring migration of the $Cr(CO)_3$ fragment to give the thermodynamically more stable on-state complexes **16** and **27**, respectively (*cf. Schemes 8* and *9*). The analogous thermal behavior of other prepared complexes has also been investigated. A new procedure for the selective preparation of complexes **10** and **13**, in which the $Cr(CO)_3$ group is coordinated to the phenyl ring of the styryl substituent has also been developed (*Scheme 7*). The attachment of the $Cr(CO)_3$ fragment to the phenyl group has a visible influence on the UV/VIS behavior of the on-state complexes **10** and **13a**, as well as on the photochemical behavior of the DBS isomers **13a**/**13b** (*cf. Scheme 10*).

1. Introduction. – So far, quite little is known about metallocarbonyl complexes of heptalenes [1], mainly because of the difficulties associated with the synthesis of various substituted heptalenes and their relative instability (*cf.* [2][3]). Nevertheless, a number of tricarbonylchromium complexes of heptalenes have been synthesized, and their dynamic behavior has been investigated (*Scheme 1*) [4].

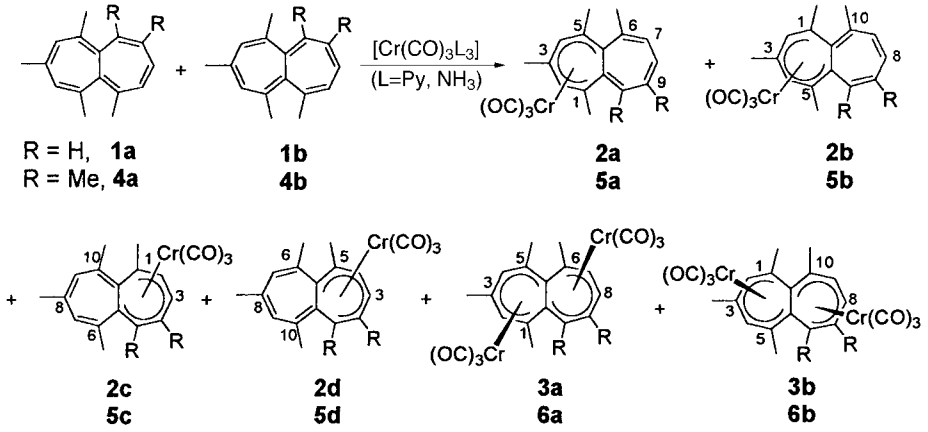
The following events have been established: *1*) Two thermally inducible rearrangements proceed in mononuclear complexes **2a**–**2d** and **5a**–**5d** (*Scheme 2*): *a*) intra-ring 1,2-shift (IRS) of the $Cr(CO)_3$ group and *b*) inter-ring migration (IRM) of the $Cr(CO)_3$ group. Both migrations are accompanied by a cyclic C=C-bond shift (DBS) at the heptalene skeleton. Direct transformations **2b** to **2d**, as well as **2a** to **2c**, without DBS has been excluded [4b]. The thermal inter-ring migration of the $Cr(CO)_3$ group within complex **5c** to yield **5b** has been the first example of an inter-ring haptotropic rearrangement in nonplanar complexes of bicyclic π-systems [4a].

2) 1,2-Haptotropic shifts and the inter-ring haptotropic migrations of the $Cr(CO)_3$ group are intramolecular processes. Activation barriers for both processes are quite similar [4].

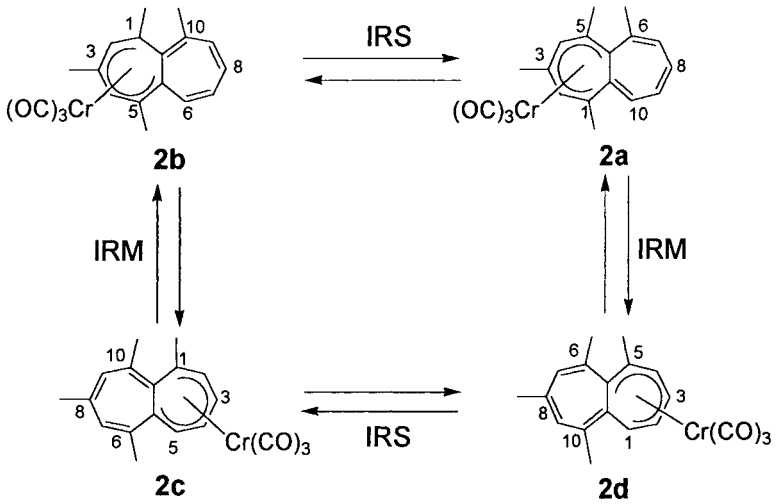
3) The occupancy of all four peri-positions in complexes **5a**–**5d** by Me groups leads to activation barriers close to those for purely thermal decomplexation reactions [4a].

4) The thermodynamically most stable complex **2a** carries the coordinating $Cr(CO)_3$ group at the seven-membered ring, which is substituted with three electron-donating Me groups [4b].

Scheme 1



Scheme 2



5) Two $Cr(CO)_3$ groups in binuclear complexes **3a**/**3b** and **6a**/**6b** are attached to the same face of the ligand (*cis*-coordination mode) [4].

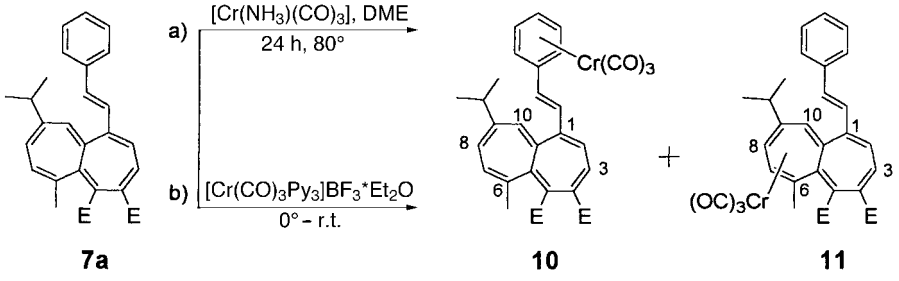
When substituents with an aromatic group, such as (*E*)-styryl (2-phenylethenyl), is attached to the heptalene core, the complexation of $Cr(CO)_3$ group is possible with either one of the heptalene rings or with the aromatic ring of the side chain, thus modifying the reactivity [5] of the 12π-electron heptalene framework itself, as well as its attached substituent.

To obtain more information about $Cr(CO)_3$-complex formation of heptalenes, especially with respect to the regio- and site-selectivity, as well as changes in heptalene reactivity due to complexation, we have synthesized a number of new $Cr(CO)_3$ complexes of differently substituted heptalenes. In addition, we have studied the photochemical and thermal behavior of the new complexes.

2. Results and Discussion. – 2.1. *Synthesis of the Cr(CO)$_3$ Complexes of Heptalenes.* The Cr(CO)$_3$ complexes **10**–**13** of 1-(*E*)-styryl- and 1-[(*E*,*E*)-4-phenylbuta-1,3-dienyl]heptalene-4,5-dicarboxylates **7a**–**9a** were prepared by complexation of heptalenes with [Cr(CO)$_3$L$_3$] species. To find the best reaction conditions for the complexation of the heptalene ligands, two known methods (*Scheme 3*) have been screened with dimethyl 9-isopropyl-6-methyl-1-[(*E*)-styryl]heptalene-4,5-dicarboxylate (**7a**) as ligand. Heating [Cr(NH$_3$)$_3$(CO)$_3$] with **7a** in 1,2-dimethoxyethane (DME) (*Rausch* method) [6] gave two isomeric complexes **10** (10%) and **11** (32%) (*Scheme 3*,*a*). Significant amounts of starting heptalene **7a** were recovered from the reaction mixture. Therefore, all yields of Cr(CO)$_3$ complexes are calculated based on the recovered ligand for correct comparisons. Assignment of the C=C bond position in all new complexes has been performed, based on the ^{1}H-NMR vicinal coupling constants, as described in [3d][4b]. The location of the Cr(CO)$_3$ group on the heptalene core has been ascertained by the ^{1}H-NMR upfield shift observed for the signals of the H-atoms that are directly attached to the complexed ring [4].

The *Öfele* procedure [7], which takes advantage of the facile reaction with [Cr(CO)$_3$Py$_3$] at ambient temperature, also yields both complexes **10** and **11** (*Scheme 3*,*b*). The **10**/**11** ratio depends on the reaction time: after 3 h, only the kinetically controlled complex **10** was isolated (44%), while, after 24 h, complex **11** (16%) was the only organometallic compound to be separated from the reaction mixture. Most likely, complex **10** formed initially undergoes isomerization to the thermodynamically more stable complex **11**, accompanied by concomitant decomplexation over time.

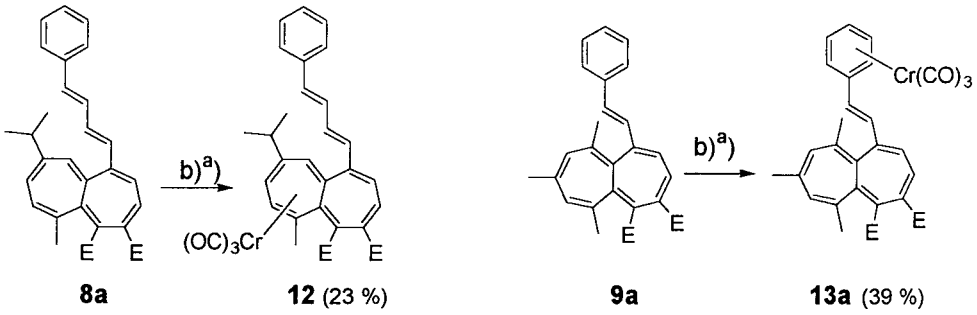
Scheme 3



7a **10** **11**

The common weakness of both methods tested is the nonselective complexation by the Cr(CO)$_3$ group. The yields of the complexes obtained are not high, and a substantial amount of starting material remains uncomplexed, which is due to side reactions of organometallic reagent [8] and the decomposition of product metal complexes during prolonged reaction times. Analogously, the synthesis of Cr(CO)$_3$ complexes of heptalene-4,5-dicarboxylates **8a** according to the standard *Öfele* protocol (*Scheme 4*) led to the regioselective formation of complex **12** (23%), in which the Cr(CO)$_3$ group is (6,7,8,9,10,10a-η)-coordinated to the heptalene skeleton. Surprisingly, when heptalene **9a** is treated under the same reaction conditions, site-selective formation of only complex **13** (39%) was observed, in which the (*E*)-styryl ring is complexed.

Scheme 4



[a]) See *Scheme 3* for b).

It has been established [9] that electron-donating substituents in polycyclic aromatic systems favor and electron-withdrawing substituents disfavor the complexation of the $Cr(CO)_3$ fragment on the substituted ring. For example, $Cr(CO)_3$ complexes can be regioselectively prepared from the substituted naphthalenes bearing electron-donor ($R=SnMe_3$, $SiMe_3$) or electron-acceptor ($R=Br$) substituents [10].

Comparatively electron-poor arenes, which contain more than two electron-withdrawing substituents, are usually unreactive toward direct complexation with the $Cr(CO)_3$ group [11]. However, quite stable $Cr(CO)_3$ arene complexes substituted with several electron-acceptor groups have been prepared by ligand-modification reactions at already coordinated arenes [12].

It should be emphasized that $Cr(CO)_3$ complexes of heptalene-4,5-dicarboxylates **7a**–**9a**, in which the $Cr(CO)_3$ group is coordinated to the heptalene ring, carrying two ester groups, have not been obtained. We assume that the reason is the reduced electron density in this ring because of the strong electron-withdrawing character of two MeOCO groups and probably styryl substituent. Complexation of the $Cr(CO)_3$ fragment to the disubstituted heptalene ring becomes unfavorable in comparison with the Ph ring or the alkyl-substituted seven-membered ring of heptalene.

We, therefore, studied also the complexation behavior of alkyl-substituted heptalene-dicarboxylates. The novel $Cr(CO)_3$ complexes of 9-isopropyl-1,6-dimethylheptalene-4,5-dicarboxylate (**14a**) and 1,6,8,10-tetramethylheptalene-4,5-dicarboxylate (**15a**) have thus been synthesized according to the *Öfele* procedure. Three new mononuclear complexes **16**, **17**, and **19**, as well as two binuclear complexes **18** and **20**, have been obtained (*Scheme 5*).

In complex **16**, the position of the C=C bonds is the same as in the starting heptalene-dicarboxylate **14a**[1]). In contrast to this, the main mononuclear complex **17**, which carries the $Cr(CO)_3$ group at the diester-substituted heptalene ring, as well as the binuclear complex **18** are derived from the DBS isomer of **14a**[2]). At ambient

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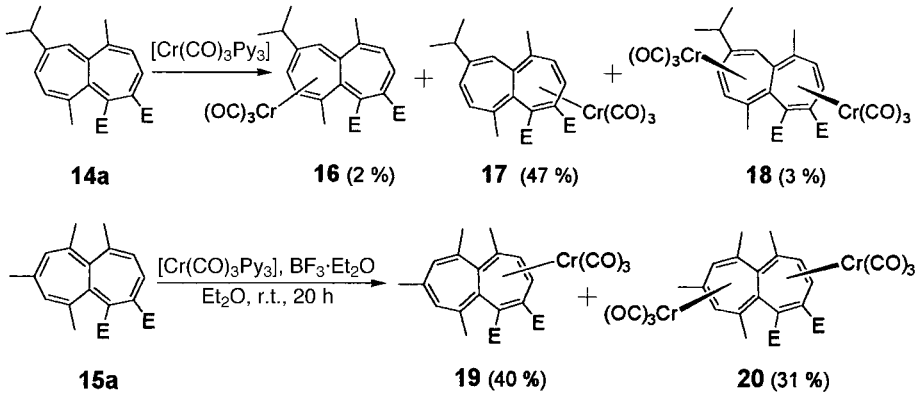
1) The so-called 'on-state' location of the C=C bonds in heptalenes, bringing the substituent at C(1) in conjugation with the ester group or any other substituent at C(4), *via* the enclosed buta-1,3-diene subunit.

2) The so-called 'off-state' isomer with the reverse location of the C=C bonds compared with the 'on-state' form.

Scheme 5



temperature, $< 0.5\%$ of this DBS isomer is found in thermal equilibrium with **14a** [3]. It is also of interest to note that the mononuclear complex **19** and the binuclear complex **20**, derived from **15a**, represent complexes of the DBS isomer of **15a**. In this case, the establishment of the thermal equilibrium between **15a** and its DBS isomer needs a temperature $> 60°$, and, at 100°, no more than 11% of the DBS isomer is in equilibrium with **15a** [13].

The formation of the mononuclear complexes **17** and **19**, in which the diester substituted ring is complexed, is quite surprising, since, as discussed above, the $Cr(CO)_3$ group should preferably coordinate to the electron-rich ring. Their formation with excellent regioselectivity is probably due to the operation of a kinetic directing effect, where the chromium fragment is initially coordinated to the ester carbonyl group and then transferred to the closest heptalene ring. The nonplanar geometry of the heptalene framework does not allow such transfer to occur to the neighboring ring.

As far as we know, the observed effect would be the first example of carbonyl-directed complexation of the $Cr(CO)_3$ group to the strongly electron-poor ring of polycyclic system. Moreover, the $Cr(CO)_3$ complexes of the thermodynamically less stable heptalene-diesters are formed.

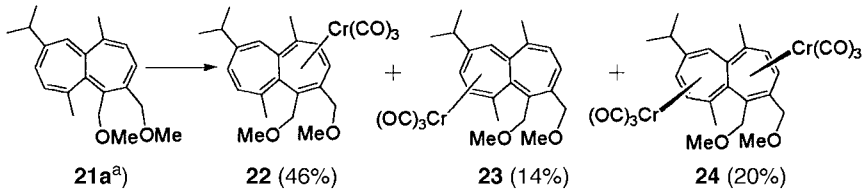
Directing effects in the complexation of the $Cr(CO)_3$ group with various cyclic systems have already been reported by several research groups [8][9c][14]. *Uemura et al.* [14a,b] have described the stereoselective formation of $Cr(CO)_3$ arene complexes directed by benzylic O-functions. The effect of heteroatom functions on the stereochemistry of the $Cr(CO)_3$ complexation with biaryls has also been investigated [15][16].

To study the reactivity of the $Cr(CO)_3$ complexes of heptalenes towards nucleophiles, several modified heptalene structures have been prepared. These modified heptalenes have no CO or other functional groups to react with organometallic reagents. *O*-Methylation of the known 9-isopropyl-1,6-dimethylheptalene-4,5- and -1,2-diols [17] by MeI has been chosen for the preparation of the model heptalene methyl ethers **21** according to a procedure originally described for the methylation of 1,2-bis(hydroxymethyl)cyclooctatetraene [18].

The *Öfele* method is not suitable for the synthesis of $Cr(CO)_3$ complexes of the heptalenes **21a** and **21b** because of their polymerization in the presence of *Lewis* acids, such as BF_3.

After refluxing of the mixture of DBS isomers **21a**/**21b** (95:5) and $[Cr(NH_3)_3(CO)_3]$ in DME according to the *Rausch* procedure [5], two of four possible mononuclear $Cr(CO)_3$ complexes **22** and **23**, and one of two possible binuclear complexes **24** were isolated (*Scheme 6*).

Scheme 6



21a[a]) **22** (46%) **23** (14%) **24** (20%)

[a]) 95% of the mixture with **22b**.

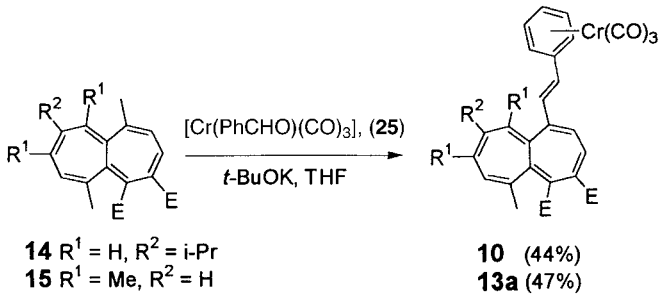
As expected from the previous observations of the complexation of other heptalenes, only the on-state complex **23** with (6,7,8,9,10,10a-η)-coordination of the $Cr(CO)_3$ group and the off-state complexes **22** and **24** with (1,2,3,4,5,5a-η)- and (1,2,3,4,5,5a-η:6,7,8,9,10,10a-η)-coordination of the $Cr(CO)_3$ group, respectively, have been obtained. Again, the preferred formation of complex **22** can be explained by primary coordination of Cr with the lone electron pair of the O-atoms of the MeO groups. The change in regioselectivity of complexation observed for complexes **19**/**26** (see *Scheme 9*) (**19** only), **17**/**16** (21:1), and **22**/**23** (3.3:1) is in agreement with the increase in the steric bulk around the coordinating O-atoms [14c][19].

As mentioned above, direct complexation reaction of (*E*)-styryl-substituted heptalenes is not site-selective, and, in some cases, the complex with coordination of the $Cr(CO)_3$ group to the Ph ring is not formed at all. For the selective preparation of complexes **10** and **13a**, in which Cr is coordinated to the Ph ring, a new procedure has, therefore, been developed, which includes the condensation reaction of (benzaldehyde)tricarbonylchromium (**25**) with the corresponding heptalenes (*Scheme 7*). *Drefahl et al.* [20] have shown that *Wittig* reagents readily react with the aldehyde function of **25** to give the corresponding stilbene complexes in good yields. On the other hand, we have reported that the condensation reaction of 1-methylheptalene-4,5-dicarboxylates with various benzaldehydes in THF in the presence of *t*-BuOK gives 1-[(*E*)-styryl]heptalene-4,5-dicarboxylates [21] in one step and moderate yields. Both methods have now been combined to synthesize specifically complexes **10** and **13a**, in which the $Cr(CO)_3$ group is attached exclusively to the Ph rings.

Deprotonation of Me–C(1) in **14** and **15** has been achieved by treatment with 2.6 mol-equiv. of *t*-BuOK in THF. After addition of **25** and stirring at ambient temperature for 6 h, the expected $Cr(CO)_3$ complexes **10** and **13** have been isolated by column chromatography in 44–47% yields (*Scheme 7*).

2.2. *Thermal Rearrangements of the $Cr(CO)_3$ Complexes.* Surprisingly, only the off-state complexes **19** and **20** have been obtained from heptalene **15a**, while the same reaction with **14a** gave also some amount of the on-state complex **16**, together with the

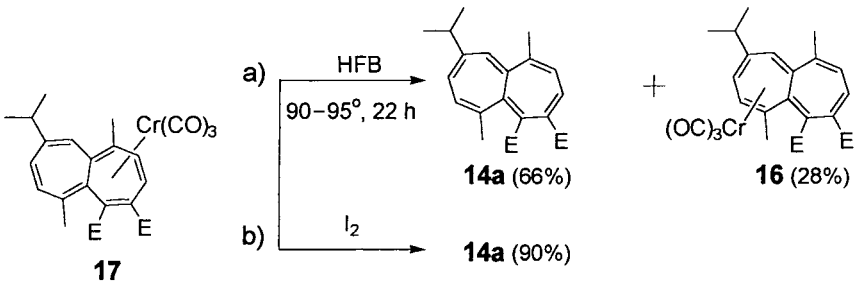
Scheme 7



off-state complexes **17** and **18** (*Scheme 5*). These observations are in agreement with the fact that two thermally inducible rearrangements, namely the intra-ring 1,2-shift and inter-ring migration of the $Cr(CO)_3$ group, could take place during the *Öfele* reaction after primary formation of the off-state complexes *via* directing assistance of the ester groups. Furthermore, we assume that complexes **17** and **19** with (1,2,3,4,5,10a-η)-coordination are kinetically controlled products and will undergo thermal rearrangements to the thermodynamically more stable isomers with (6,7,8,9,10,10a-η)-coordination. To verify this assumption, the thermal isomerizations of complexes **16**–**20** have been investigated (*Schemes 8* and *9*).

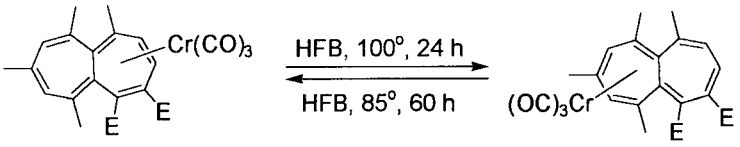
Complex **17** represents the first example of the stable off-state position of the C=C bonds in **14a** fixed by complexation with $Cr(CO)_3$. It immediately returns to the on-state ligand **14a** after oxidative decomplexation at room temperature (*Scheme 8,b*) or undergoes the thermal rearrangement at 90–95° to give the on-state complex **16** in a yield of 28% (*Scheme 8,a*). Concomitant decomplexation reaction of **17** also takes place under these conditions to give uncomplexed heptalene **14a** in 66% yield. Some amount of the starting complex **17** (6%) remained unchanged. We have also found that complexes **11** and **16** do not undergo any thermal inter-ring or intra-ring migrations of the $Cr(CO)_3$ group. Only the decomplexation reaction is observed.

Scheme 8



Thermal isomerization of the off-state complex **19** led to the DBS isomeric complex **26** with a yield of 39%. Again, the corresponding ligand **15a** (22%) and some amount of unchanged complex **19** (4%) have also been separated (*Scheme 9*).

Scheme 9



19 **26**

Therefore, the formation of the on-state complex **26** is the result of two expected rearrangement processes, namely inter-ring haptotropic migration and intra-ring 1,2-shift of the $Cr(CO)_3$ group (see *Introduction*).

Thermal isomerization of the on-state complex **26** gave the off-state isomer **19** (10%) and the corresponding ligand **15a** (21%). However, a lot of starting complex **26** (68%) remained unchanged, much more than in the case of the isomerization of complex **19**. This speaks for the thermal equilibrium between **19** and **26** with a preponderance of **26** in the equilibrium mixture at 100°, as expected[3]). Thermolysis of binuclear complex **20** gave the equilibrium mixture of DBS isomers **19** (10%) and **26** (30%), and the corresponding ligand **15a** (25%).

In summary, we can draw the following conclusions: *1*) In heptalene-4,5-dicarboxylates, the $Cr(CO)_3$ group stabilizes the off-state position of the C=C bonds (no 'through-conjugation' with the ester group), when it is coordinated to the diester-substituted heptalene ring. The on-state position is favored, when the complexation takes place at the other heptalene ring. Neither on-state complexes, in which the $Cr(CO)_3$ fragment is coordinated to diester-substituted heptalene ring, nor off-state complexes with the opposite coordination of the $Cr(CO)_3$ group could be observed.

2) The two processes, namely intra-ring 1,2-shift and inter-ring migration of the $Cr(CO)_3$ group, can be induced thermally in complexes **17**, **19**, and **26**. There are only a few published examples of such inter-ring haptotropic rearrangements in nonplanar complexes of bicyclic π-systems (see *Introduction*). However, in the present case, it cannot be excluded that the inter-ring rearrangement is the result of an intermolecular transfer of the $Cr(CO)_3$ unit.

3) It has been found that these thermal rearrangements are reversible and accompanied by the concomitant decomplexation reaction in every case.

4) The off-state complexes **17** and **19** carry the coordinating $Cr(CO)_3$ group at the seven-membered ring, which is substituted with an electron-donating Me group and two electron-withdrawing ester groups. These complexes undergo thermal rearrangements to give the thermodynamically more stable on-state complexes **16** and **26**, respectively. However, thermolysis of **26** gives the isomeric complex **19** with a much smaller conversion. The analogous on-state complexes **11** and **16** do not undergo rearrangement at all. These observations establish a greater thermodynamic stability of the on-state complexes **16**, **26**, and **11**, in which the $Cr(CO)_3$ group is coordinated with

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[3]) According to calculations performed with Spartan PM3, complex **26** ($\Delta H_f^0 = -155.7$ kcal/mol) is more stable than complex **19** ($\Delta H_f^0 = -148.5$ kcal/mol). Similar results are obtained for complexes **16** and **17** ($\Delta\Delta H_f^0 = -6.3$ kcal/mol).

the heptalene ring containing two or three electron-donating alkyl groups. This is in good agreement with the substituent effects observed for other polycyclic π-ligands in $Cr(CO)_3$ complexes (see *Introduction*).

2.3. *Photochemical Properties of the $Cr(CO)_3$ Complexes.* The influence of the $Cr(CO)_3$ coordination of the UV/VIS behavior of all new complexes **10**–**13** have been investigated. *Fig. 1*,*b* and *c*, demonstrates that UV/VIS spectra of complexes **11** and **12** are very similar to those of the corresponding ligands **7a** and **8a** (see [2d] and *Table 1*). However, complex **12** exhibits a stronger shoulder for heptalene band I at *ca.* 420 nm, and the heptalene band III of **12** is bathochromically shifted by 10 nm relative to the heptalene band III of **8a**. Thus, the coordination of the $Cr(CO)_3$ group in **11** and **12** at room temperature with the heptalene ring, which does not contain the ester groups, causes no visible changes in the habitus of the UV/VIS spectra because no additional 'through-conjugation' is possible. No changes in UV/VIS behavior after irradiation of complexes **11** and **12** have been observed, nor of their corresponding ligands.

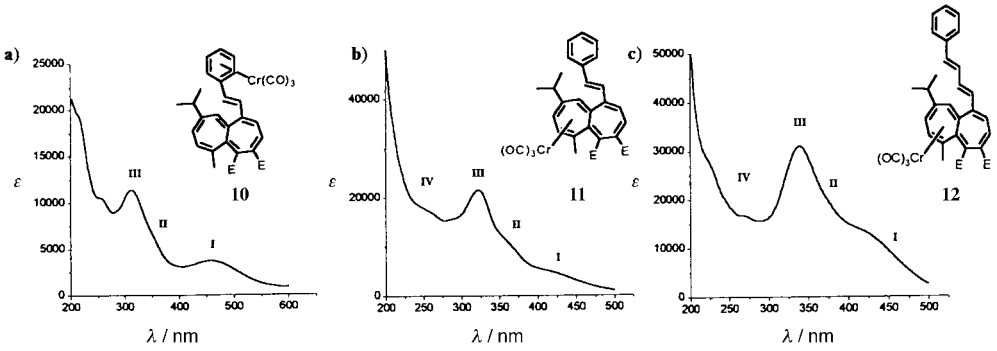


Fig. 1. *UV/VIS Spectra of $Cr(CO)_3$ complexes* **10**–**12**

The effect of the introduction of the strong π-acceptor group the $Cr(CO)_3$ into the styryl moiety of the complexes **10** and **13a** is recognizable by a strong enhancement of heptalene band I at *ca.* 460 nm and its bathochromic shift by 60 nm compared to the corresponding heptalenes **7a** and **9a** (*Table 1*), respectively. Coordination of the $Cr(CO)_3$ group to the styryl substituents at C(1) still enhances the hypochromism of all heptalene bands I–III. Also, it should be noted that the heptalene band II in **10** and **13a** is hardly recognizable.

Thus, the attachment of a π-acceptor substituent to the Ph ring of the styryl group has a visible influence on the UV/VIS behavior of the on-state complexes **10** and **13a**. This effect is more pronounced in the region of band I and is opposite in character to that observed for heptalenes, where the π-donor group MeO is attached in *p*-position to the Ph group [2d][22]. Such an opposite influence of the introduction of π-acceptor or π-donor substituent into styryl moiety is in good agreement with theoretical expectations.

The coordination of the $Cr(CO)_3$ group with the styryl moiety in heptalene-4,5- and heptalene-1,2-dicarboxylates has a distinct influence on the photochemical behavior of the DBS isomers. Complex **13** exists at room temperature as on-state isomer **13a** and

Table 1. *UV/VIS Spectra of Complexes* **10**–**13** *and Their Corresponding Heptalene Ligands*[a])

Compound	λ_{max} [nm]			
	I	II	III	IV
7a[b])	*ca.* 400 (sh, 3.72)	353 (sh, 4.12)	320 (4.41)	260 (4.21), 200 (4.54)
10[b])	457 (3.57)	354 (sh, 3.79)	312 (4.06)	258 (sh, 4.02), 191 (3.99)
11[c])	*ca.* 400 (sh, 3.72)	360 (sh, 4.04)	322 (4.33)	2.57 (4.22), 200 (4.72)
8a[b])	*ca.* 400 (sh, 4.06)	360 (sh, 4.26)	336 (4.39)	269 (4.18)
12[b])	*ca.* 400 (sh, 4.13)	–	345 (4.44)	258 (4.31)
9a[c])	*ca.* 400 (sh, 3.61)	356 (sh, 3.97)	322 (4.21)	266 (4.19)
13a[c])	*ca.* 400 (sh, 3.26)	–	310 (4.13)	255 (sh, 4.28), 210 (4.58)

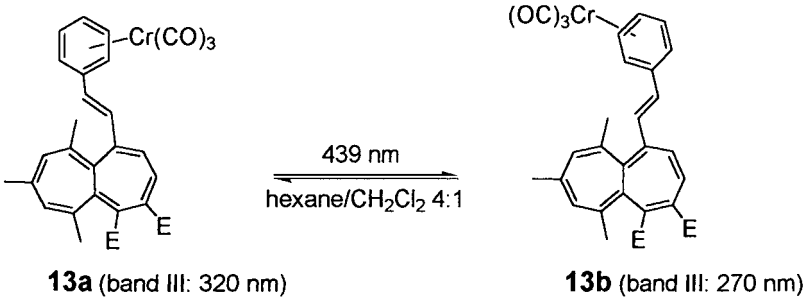
[a]) Data from [2d][22]. [b]) In cyclohexane. [c]) In MeCN.

can at least qualitatively be switched to off-state isomer **13b** by irradiation with light of 439 nm (*Scheme 10*).

Unfortunately, all our attempts to separate the pure off-state isomer **13b** after photochemical reaction have failed because of its decomplexation on silica gel. Thus, we could record only the UV/VIS spectrum of **13b** with the photodiode-array detector of a *Waters* instrument and determine the ratio of both DBS isomers after irradiation according to the HPLC chromatogram (*Fig. 2*). Indeed, the on-state isomer **13a** exhibits band I (450 nm) still more intense and better separated from band II (350 nm) because of the conjugative interaction of the styryl substituent at C(1) with MeOCO–C(4), while, in the off-state isomer **13b**, this band intensity is markedly decreased because of the absence of such conjugation with the styryl moiety bearing the strong π-accepting $Cr(CO)_3$ group. The effect of the coordination is more pronounced in the region of band III, where the on-state isomer **13a** shows a broad and flat absorption compared to the intense absorption of the off-state isomer **13b**. Also, band III in **13a** (320 nm) seems to be bathochromically shifted by 50 nm relative to the maximum of the band III in **13b** (270 nm). Thus, the difference in UV/VIS behavior of the DBS isomers of the complexed heptalene **13** is very similar to that of the DBS isomers of the corresponding free ligand **9**.

In summary, we can conclude that the (6,7,8,9,10,10a-η)-coordination of the $Cr(CO)_3$ group at the heptalene skeleton has no noticeable influence on the UV/VIS behavior of the complexes **11** and **12**. On the other hand, the $Cr(CO)_3$ complexation on the Ph ring of 1-[(*E*)-styryl]- and 1-[(*E*,*E*)-4-phenylbuta-1,3-dienyl]heptalene-4,5-

Scheme 10



13a (band III: 320 nm) **13b** (band III: 270 nm)

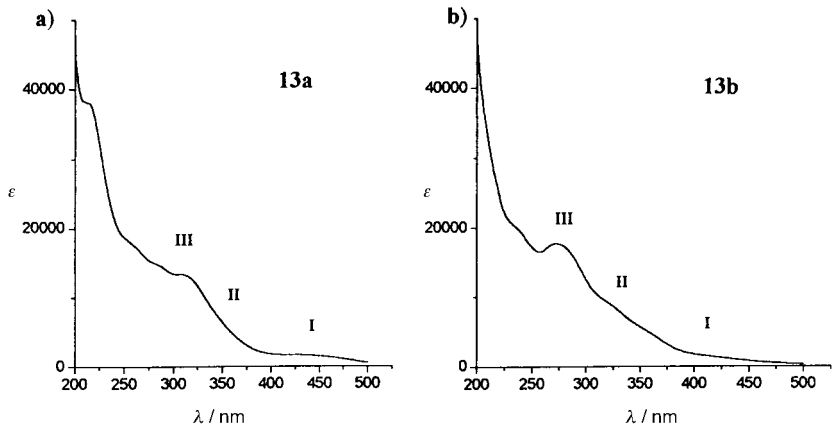


Fig. 2. *UV/VIS Spectra of complex* **13a** (a) *and* **13b** (b) *in hexane/CH_2Cl_2 5 : 1*

dicarboxylate obviously changes the habitus of the UV/VIS spectra of the corresponding complexes **10** and **13**, respectively. The photochemical behavior of the complexes **19**, **20**, and **26** has also been investigated and compared with those of the complexes **2** and **3**, and the corresponding ligands **15a** and **15b** (*Fig. 3* and *Table 2*). Thus, the UV/VIS spectra of the mononuclear complexes **19** and **26** (*Fig. 3,a*) show a much less pronounced and hypsochromically shifted absorption band II at *ca.* 320 nm as compared with the mononuclear complexes **2** [4a]. Also, the difference in UV/VIS behavior of complexes **2**, and **19** or **26** appears in the region of band III, where the complexes **2** exhibit a barely discernable shoulder at *ca.* 270 nm, while complexes **19** and **26** display maximum absorption intensities corresponding to band III. Since the UV/VIS spectra of the mononuclear complexes **19** and **26** are very similar, we could not determine a remarkable difference in the UV/VIS properties of these DBS isomers in comparison with the obvious difference in UV/VIS behavior of the DBS isomers of the corresponding ligand **15** [3d]. However, the habitus of the UV/VIS spectra of the binuclear complex **20** before and after irradiation are distinctly different from each other (*Fig. 3,b*).

The UV/VIS spectrum of the binuclear complex **20** is almost identical to that of complexes **3** [4a], in which band III appears as a barely discernable shoulder at 268 nm

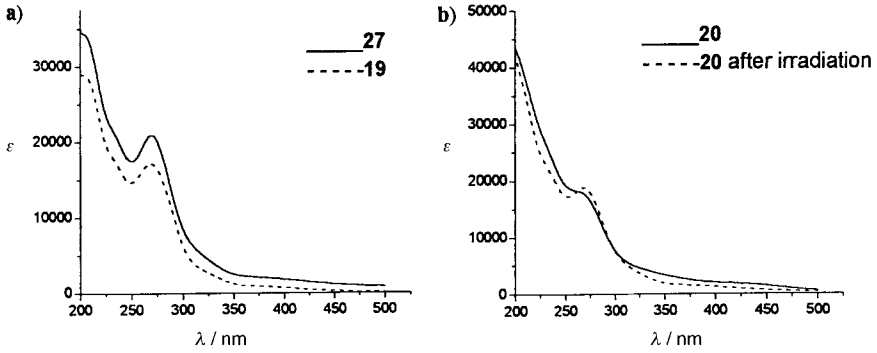


Fig. 3. *UV/VIS Spectra of $Cr(CO)_3$ complexes* **19** *and* **27** (a), *and* **20** (b)

Table 2. *UV/VIS Spectra of the Cr(CO)$_3$ Complexes* **2**–**3**[a]) *and* **19**, **20**, **27**, *and Their Corresponding Ligands* **15a**/**15b**[b])

Compound	λ_{max} [nm]			
	I	II	III	IV
2a	420(sh)	360	265(sh)	222
2c	431	342	270(sh)	221
3a	430	342(sh), 311(sh)	277(sh)	218
15a	*ca.* 370	320 (sh)	*ca.* 280	261, 236 (sh)
15b	390	318 (sh)	268	233 (sh)
19	*ca.* 410 (sh, 3.17)	–	268 (4.27)	206 (4.52)
20	*ca.* 410 (sh, 3.45)	332 (sh, 3.72)	266 (sh, 4.22)	206 (4.63)
27	407 (3.24)	–	265 (4.26)	206 (4.51)

[a]) Data from [4a]; UV spectra of **2a**/**2c** (in hexane) and **3a** (in hexane with 7% i-PrOH) were recorded with the photodiode-array detector of a *Waters* HPLC system. [b]) Data from [2d].

(*Table 2*). But the UV/VIS spectrum of binuclear complex **20** after irradiation at 310 or 439 nm becomes the same as for the corresponding mononuclear complexes **19** and **27** with maximum absorption in the region of band III. This observation indicates the loss of one of the Cr(CO)$_3$ groups, in good agreement with the results obtained by thermolysis of **20** (*Sect. 2.2*).

Thus, we can conclude that the complexation of any heptalene ring in heptalene-4,5- and heptalene-1,2-dicarboxylates with the Cr(CO)$_3$ group has no distinct influence on the UV/VIS behavior of the mononuclear off-state complex **19** and its DBS isomer **26** in comparison with the significantly different UV/VIS behavior of the corresponding ligands **15a** and **15b**, respectively. The habitus of the UV/VIS spectrum of the binuclear complex **20** is quite different from that of the mononuclear complexes **19** and **26**, and shows a hyperchromic effect of band III in comparison with the corresponding noncomplexed heptalene **15b**.

2.4. *Reactivity Study of Several Cr(CO)$_3$ Complexes of Heptalenes.* First of all, the most expressed effect of the Cr(CO)$_3$ complexation, namely reduction of the electron density in the coordinated heptalene ring, has been investigated. It should cause an enhanced electrophilicity of the coordinated ring C=C bonds, as well as an increase in the acidity of the H-atoms attached to the coordinated ring. Therefore, the addition/oxidation reaction [23] was expected with reactive C-nucleophiles [24]. Thus, nucleophiles, including PhLi, MeLi, *t*-BuLi and 2-Li-1,3-dithianyl, have been tested in substitution reactions with the complexes **23**–**25**, followed by I_2 as oxidizing reagent.

We have established that RLi (R=Ph, Me, Bu,1,3-dithianyl) nucleophiles are not effective in the addition reaction to complexes **23**–**25**, and no products of nucleophilic substitution have been observed. Only decomplexation of the starting complexes has been verified in each case.

For the Cr(CO)$_3$ complex **19**, we can expect the enhancement of acidity of the H-atoms of the side chain at C(5) due to the complexation to the the Cr(CO)$_3$ group. Therefore, the deprotonation should be more favorable in complex **19** than in the corresponding heptalene **15b**. However, all attempts to deprotonate **19** with different bases, including *t*-BuOK, NaH, and LDA, and to trap the product with PhCHO have not been successful. Thus, direct functionalization of the heptalene core, coordinated

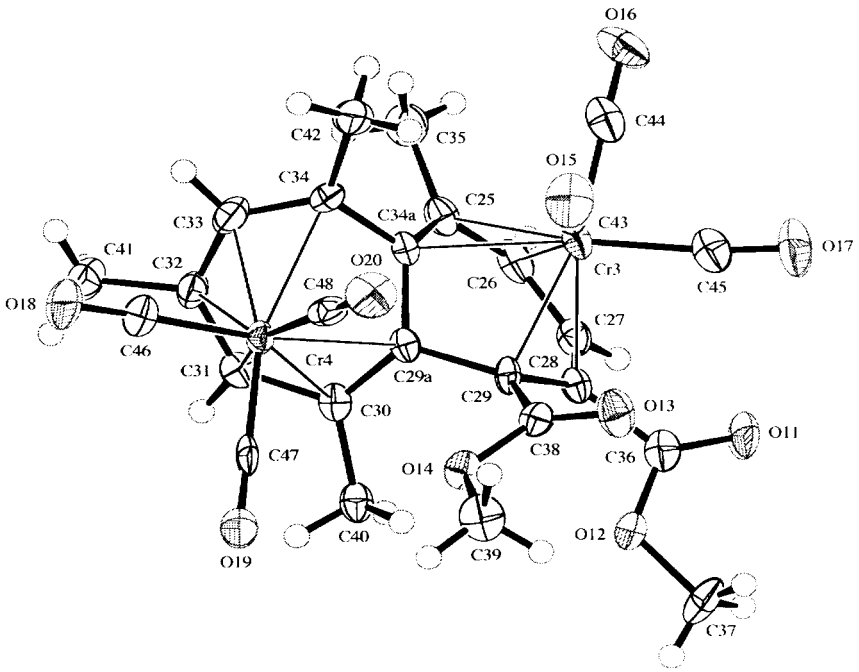


Fig. 4. *ORTEP Representation of the X-ray crystal structure of* **20** *with atomic numbering* (top-view of complexed rings)

with the $Cr(CO)_3$, has failed so far. The heptalene reactivity towards nucleophiles and bases is not altered significantly after coordination with the $Cr(CO)_3$.

2.5. *X-Ray Crystal-Structure Analysis of the Binuclear $Cr(CO)_3$ Complex* **20**. The *cis*-relationship of both $Cr(CO)_3$ groups in complex **20** has been established by an X-ray crystal-structure analysis. *Fig. 4* shows the molecular geometry of the complex **20**, in which both Cr-atoms are on the same side of the bicyclic ligand, as has also been found in the binuclear $Cr(CO)_3$ complex **3** and **6** (see *Introduction*). Even though the compound is racemic, the space group has been found to be noncentrosymmetric (*cf. Table 3* in *Exper. Part*). Refinement of the absolute structure parameter indicated that the crystals of complex **20** are merohedral twins, and, therefore, there is no preferential direction of the polar axis (see *Exper. Part*). The asymmetric unit contains two symmetry-independent molecules of the same configuration. There are no significant conformational differences between the two molecules. However, in total, the unit cell contains four pairs of **20** of opposite configuration, so that the crystals are non-enantiomorphic[4]).

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[4]) The *cis*-structure of **20**, calculated with Spartan PM3, is in good agreement with the X-ray crystal structure of **20**. On the other hand, the *trans*-structure of **20** with two $Cr(CO)_3$ groups on the opposite sides of the two rings has a ΔH_f^0 value that is by more than 20 kcal/mol larger than for the formed *cis*-configuration. Therefore, one can conclude that the bis(tricarbonylchromium) complexes **18** and **25** possess also the *cis*-relationship of the two $Cr(CO)_3$ groups.

We thank Dr. *A. Linden* and his co-workers, especially *J. Toedtli*, for X-ray crystal-structure analyses, Prof. *M. Hesse* and his co-workers for mass spectra, our NMR department for NMR measurements, and our analytical laboratory for elemental analyses. The financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. All solvents (Et_2O, THF, DME) were purified by refluxing over sodium diphenylketyl and are distilled therefrom just before use. All reactions with Cr ligands were performed under Ar. M.p.: *Büchi FP5* melting-point apparatus; values are not corrected. Column chromatography (CC): silica gel *60* (40–63 μm; *Chemie Uetikon AG*). Prep. MPLC: a MPLC instrument with a *Lichroprep Si 60* (*B*) column; a UV/VIS detector (*Dynamax*) was used. Anal. HPLC: *Waters 911* instrument with a photodiode-array detector (optical resolution: ±1.5 nm) with a *Spherisorb CN* column (ODS 5 μm: length 250, diam. 4.6 mm). UV/VIS Spectra: *Perkin-Elmer Lambda 9* instrument or taken as '*ad hoc*' spectra with the photodiode array detector of a *Waters* HPLC instrument. Irradiation experiments were performed in *t*-BuOMe or MeCN at 10–14° with the high-pressure Hg lamp (*Hanau Quarzlampengesellschaft*, type *TQ150*) through a *Pyrex* filter (thickness 1.5 mm). IR Spectra: *Perkin-Elmer* spectrophotometer, models *FT-IR 1600* and IR '*Spectrum One*'. NMR Spectra: *Bruker ARX-300* or *Bruker AMX-600* spectrometers; assignments of the signals based on additional COSY, NOESY, and ^1H,^{13}C-correlation spectra (HSQC and HMBC techniques). MS: *Varian MAT-112S* (chemical ionization (CI)) and *Finnigan MAT-SSQ-700* instruments (electron impact ionization (EI); 70 eV), *m/z* (rel. %).

1. Formation of $Cr(CO)_3$ Complexes. – 1.1. *Synthesis of 1-[(*E*)-Styryl]- and 1-[(*E,E*)-4-Phenylbuta-1,3-dienyl]heptalene-4,5-dicarboxylate $Cr(CO)_3$ Complexes* **10**–**13** (*Schemes 3* and *4*). Rausch *Method. General Procedure.* A mixture of heptalene-4,5-dicarboxylate **7a** (0.81 g, 1.9 mmol) and $[Cr(NH_3)_3(CO)_3]$ (0.35 g, 2 mmol) in 50 ml of 1,2-dimethoxyethane (DME) was refluxed for 24 h under Ar. Then, the mixture was filtered, and the solvent was removed from the filtrate *in vacuo*. The residue was purified by FC (silica gel; 30–40% Et_2O in hexane) to give, in the first fraction, unreacted heptalene (0.43 g, 53%), in the second fraction complex **11** (0.16 g, 15 (32)%)[5]) and complex **10** (0.05 g, 4.7 (10)%) in the third fraction.

Öfele *Method. General Procedure.* To a stirred mixture of heptalene-4,5-dicarboxylate **7a** (0.11 g, 0.26 mmol) and $[Cr(CO)_3(C_5H_5N)_3]$ (0.1 g, 0.27 mmol) in 7 ml of Et_2O (freshly distilled) $Et_2O \cdot BF_3$ (0.3 ml, 2.1 mmol) was added dropwise at 0° under dry Ar. The mixture was stirred during 30 min at this temp. and then 2 h at r.t. The color of the soln. changed from orange-red to dark-brown. H_2O was added, and the mixture was extracted with Et_2O (3×). The combined Et_2O layers were dried ($MgSO_4$), and the solvent was then evaporated. The residue was purified by FC (silica gel; 30–40% Et_2O in hexane) to give, in the first fraction, unreacted heptalene **7a** (0.05 g, 45.5%) and, in the second fraction, complex **10** (0.04 g, 24 (44)%).

The *Öfele* method gave heptalene **7a** (27%) and complex **11** (12(16)%) after 20 h.

*Data of Tricarbonyl(η⁶-[(*E*)-2-[4,5-bis(methoxycarbonyl)-6-methyl-9-(1-methylethyl)heptalen-1-yl]ethenyl]benzene)chromium* (**10**): Red-brown crystals (hexane/Et_2O). M.p. 230–232°. UV/VIS (cyclohexane): λ_{max} 457 (3.57), 354 (3.79), 312 (4.06), 258 (4.02), 191 (3.99); λ_{min} 405 (3.49), 279 (3.95). IR (KBr): 3417*w*, 2950*s*, 1874*s* (CO), 1718*w* (CO), 1706*w* (CO), 1613*s*, 1555*s*, 1434*s*, 1373*s*, 1266*s*, 1159*s*, 1091*s*, 767*s*, 173*s*, 157*s*, 127*w*. ^1H-NMR (300 MHz, C_6D_6, δ (C_6D_5H) 7.19): 7.55 (*d*, $^3J(2,3) = 6.5$, H–C(3)); 6.73 (*d*, $^3J(1',2') = 15.7$, H–C(1')); 6.35 (*d*, $^3J(2,3) = 6.8$, H–C(2)); 6.31 (*d*, $^3J(7,8) = 6.8$, H–C(8)); 6.22 (*d*, $^3J(7,8) = 6.5$, H–C(7)); 5.99 (*d*, $^3J(1',2') = 15.6$, H–C(2')); 5.81 (*s*, H–C(10)); 5.34–5.29 (*m*, 4 arom. H); 5.20–5.16 (*t*-like, $^3J = 5.5$, H_p of Ph); 3.65, 3.64 (2*s*, 2 COO*Me*); 2.44 (*sept.*, $^3J = 6.8$, Me_2CH); 1.90 (*s*, Me–C(6)); 1.01, 0.98 (2*d*, $^3J = 7.7$, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.65 (Me); 22.26 (Me); 22.94 (Me); 35.42 (CH); 52.02 (COO*Me*); 52.13 (COO*Me*); 90.52 (CH); 90.89 (CH); 92.62 (CH); 104.26 (CH); 125.83 (CH); 127.74 (CH); 127.98 (CH); 128.36 (CH); 128.71 (C); 129.56 (CH); 131.06 (CH); 134.03 (C); 138.63 (CH); 148.43 (C); 167.35 (*C*OOMe); 167.72 (*C*OOMe); CO of $Cr(CO)_3$ were not observed. CI-MS (NH_3): 565 (18, $[M+1]^+$), 534 (44, $[M-CH_3O]^+$), 533 (100, $[M-MeOH]^+$), 480 (8, $[M-3\,CO]^+$), 397 (12).

*Data of Tricarbonyl((6,7,8,9,10,10a-η)-[4,5-bis(methoxycarbonyl)-6-methyl-9-(1-methylethyl)-1-[(*E*)-2-phenylethenyl]]heptalene)chromium* (**11**): Red crystals (Et_2O/hexane). M.p. 80–82°. UV/VIS (MeCN): λ_{max} 400 (sh, 3.72), 360 (sh, 4.04), 322 (4.33); λ_{min} 278 (4.18). ^1H-NMR (300 MHz, $CDCl_3$, δ ($CHCl_3$) 7.26): 7.5 (*d*, $^3J(2,3) = 7.2$, H–C(3)); 7.38–7.28 (*m*, 5 arom. H); 6.91 (*d*, $^3J(1',2') = 15.8$, H–C(1')); 6.65 (*d*, $^3J(1',2') = 15.8$,

[5]) All yields in parentheses are based on the recovered starting material.

H–C(2′)); 6.59 (*d*, ^3J(2,3) = 7.2, H–C(2)); 5.73 (*d*, ^3J(7,8) = 7.1, H–C(8)); 4.90 (*d*, ^3J(7,8) = 7.4, H–C(7)); 4.77 (*s*, H–C(10)); 3.71, 3.69 (2*s*, 2 COO*Me*); 2.80 (*sept.*, ^3J = 6.9, Me_2CH); 1.99 (*s*, Me–C(6)); 1.44, 1.33 (2*d*, ^3J = 6.9, 6.8, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 22.94 (Me); 24.04 (Me); 25.67 (Me); 36.80 (CH); 52.18 (COO*Me*); 52.32 (COO*Me*); 70.90 (C); 80.70 (C); 94.07 (CH); 99.38 (CH); 102.66 (CH); 120.37 (C); 123.14 (CH); 127.06 (CH); 128.62 (CH); 128.81 (CH); 130.24 (CH); 130.76 (C); 132.03 (CH); 136.05 (C); 138.69 (CH); 142.46 (C); 146.02 (C); 166.04 (*C*OOMe); 168.06 (*C*OOMe); CO of $Cr(CO)_3$ were not observed.

The *Öfele* reaction of **8a** was carried out during 1.5 h, followed by usual workup. After CC (silica gel; 15% Et_2O in hexane), starting heptalene **8a** (13%; first fraction) and complex **12** (20 (23)%; second fraction) were obtained.

*Data of Tricarbonyl[(6,7,8,9,10,10a-η)-4,5-bis(methoxycarbonyl)-6-methyl-9-(1-methylethyl)-1-[(*E,E*)-4-phenylbuta-1,3-dienyl]heptalene}chromium* (**12**): Brown-red crystals (hexane/Et_2O). M.p. 115–117°. UV/VIS (cyclohexane): λ_{max} 400 (sh, 4.13), 345 (4.44), 258 (4.31); λ_{min} 302 (4.26); (MeCN): λ_{max} 400 (sh, 4.12), 340 (4.49), 265 (4.22), 224 (4.44); λ_{min} 288 (4.19). IR (KBr): 3431*w*, 2953*w*, 2868*w*, 1968*s* (CO), 1907*s* (CO), 1886*s* (CO), 1720*m*, 1538*w*, 1435*w*, 1260*m*, 1197*w*, 1098*w*, 1044*w*, 987*w*, 854*w*, 749*w*, 692*w*, 651*w*, 622*w*, 611*w*, 524*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.46 (*d*, ^3J(2,3) = 7.6, H–C(3)); 7.36–7.28 (*m*, 5 arom. H); 6.91 (*dd*, ^3J(3′,4′) = 15.5, ^3J(2′,3′) = 10.5, H–C(3′)); 6.78 (*dd*, ^3J(1′,2′) = 14.6, ^3J(2′,3′) = 10.4, H–C(2′)); 6.74 (*d*, ^3J(3′,4′) = 15.4, H–C(4′)); 6.53 (*d*, ^3J(2,3) = 7.7, H–C(2)); 6.17 (*d*, ^3J(1′,2′) = 14.7, H–C(1′)); 5.71 (*d*, ^3J(7,8) = 7.5, H–C(8)); 4.90 (*d*, ^3J(7,8) = 7.5, H–C(7)); 4.72 (*s*, H–C(10)); 3.71, 3.69 (2*s*, 2 COO*Me*); 2.79 (*sept.*, ^3J = 6.8, Me_2CH); 1.44, 1.32 (2*d*, ^3J = 6.9, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 23.05 (Me); 24.14 (Me); 25.80 (Me); 36.92 (CH); 52.29 (COO*Me*); 52.44 (COO*Me*); 70.77 (C); 81.06 (C); 94.15 (CH); 99.53 (CH); 102.74 (CH); 120.30 (C); 123.05 (CH); 126.85 (CH); 128.24 (CH); 128.74 (CH); 133.09 (CH); 134.21 (CH); 135.91 (CH); 136.81 (C); 138.71 (CH); 142.47 (C); 167.77 (*C*OOMe); 167.78 (*C*OOMe); CO of $Cr(CO)_3$ were not observed. CI-MS (NH_3): 591 (10, M^+), 472 (88, $[(M + NH_3) - Cr(CO)_3]^+$), 455 (29, $[M - Cr(CO)_3]^+$), 423 (100, $[M - (Cr(CO)_3 + MeOH)]^+$), 421 (18). EA: Calc. For $C_{33}H_{30}O_7Cr$: C 67.12, H 5.09; found: C 67.58, H 5.60.

The *Öfele* reaction of heptalene-4,5-dicarboxylate **9a** and $[Cr(CO)_3Py_3]$ during 3 h at r.t. gave, after purification (CC; 15% Et_2O in hexane), unreacted heptalene **2a** (23%) and complex **13** (30(39)%).

*Data of Tricarbonyl(η⁶-{(*E*)-2-[4,5-bis(methoxycarbonyl)-6,8,10-trimethylheptalen-1-yl]ethenyl}benzene)-chromium* (**13a**). Red-brown crystals (hexane/Et_2O). M.p. 221–223°. UV/VIS (cyclohexane): λ_{max} 209 (4.59), 321 (4.41), 420 (3.74); λ_{min} 275 (4.18), 387 (3.8); (MeCN): λ_{max} 400 (sh, 3.26), 310 (4.13), 210 (4.58). IR (KBr): 3444*m*, 2951*w*, 1964*s* (CO), 1888*vs* (2CO), 1720*m*, 1637*w*, 1436*w*, 1260*m*, 1087*w*, 1052*w*, 774*w*, 659*w*, 631*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.65 (*d*, ^3J(2,3) = 6.1, H–C(3)); 6.77 (*d*, ^3J(1′,2′) = 15.3, H–C(2′)); 6.55 (*d*, ^3J(2,3) = 6.2, H–C(2)); 6.21 (*s*, H–C(9)); 6.12 (*s*, H–C(7)); 5.85 (*d*, ^3J(1′,2′) = 15.7, H–C(1′)); 5.44 (*t*, ^3J = 7.9, H_m of Ph); 5.33 (*t*, ^3J = 5.6, H_p of Ph); 5.28 (*d*, ^3J = 4.8, H_o of Ph); 3.49, 3.46 (2*s*, 2 COO*Me*); 2.10 (*s*, Me–C(6)); 1.90 (*s*, Me–C(8)); 1.64 (*s*, Me–C(10)). ^{13}C-NMR (75 MHz, $CDCl_3$): 18.61 (Me); 21.56 (Me); 25.19 (Me); 30.35 (CH); 52.00 (COO*Me*); 52.23 (COO*Me*); 91.27 (CH); 91.55 (CH); 92.18 (CH); 104.31 (C); 119.11 (C); 127.89 (CH); 129.38 (CH); 129.56 (CH); 130.05 (CH); 131.12 (C); 132.64 (C); 132.77 (C); 138.17 (CH); 140.18 (C); 140.36 (C); 167.3 (*C*OOMe); 167.4 (*C*OOMe); CO of $Cr(CO)_3$ were not observed. EI-MS: 551 (6, $M^{+\bullet}$), 467 (41, $[M - 3\,CO]^{+\bullet}$), 435 (27, $[M - (3\,CO + MeOH)]^{+\bullet}$), 415 (16, $[M - (Cr(CO)_3]^{+\bullet}$), 383 (100, $[M - (Cr(CO)_3 + MeOH)]^{+\bullet}$), 295 (26).

1.2. *Synthesis of $Cr(CO)_3$ Complexes* **16**–**20** *of Dimethyl 1,6-Dimethyl-9-(1-methylethyl)heptalene-4,5-dicarboxylate* (**14a**) *and Dimethyl 1,6,8,10-Tetramethylheptalene-4,5-dicarboxylate* (**15a**) (*Scheme 5*). The reaction was carried out according to the general *Öfele* method during 24 h. After purification on silica gel (10% Et_2O in hexane, followed 15%), complex **17** (43 (47)%) was collected in the first fraction, unreacted heptalene **14a** (8%) in the second fraction, complex **16** (2%) in the third fraction, and the binuclear complex **18** (30% Et_2O in hexane; 3%) in the last fraction.

Data of Tricarbonyl[(6,7,8,9,10,10a-η)-4,5-bis(methoxycarbonyl)-1,6-dimethyl-9-(1-methylethyl)heptalene]-chromium (**16**): Dark-red crystals (hexane/Et_2O). M.p. 152–154°. UV/VIS (MeCN): λ_{max} 400 (2.97), 321 (3.65), 282 (4.13), 251 (4.22), 204 (4.50); λ_{min} 272 (4.12), 244 (4.22). IR (KBr): 3434*m*, 2959*w*, 2924*w*, 1965*s* (CO), 1919*s* (CO), 1896*s* (CO), 1714*m*, 1583*w*, 1431*w*, 1266*m*, 1152*w*, 1046*w*, 960*w*, 852*w*, 745*w*, 651*w*, 613*w*, 532*w*. ^{1}H-NMR (300 MHz, $CDCl_3$, δ ($CHCl_3$) 7.26): 7.15 (*d*, ^3J(2,3) = 7.2, H–C(3)); 6.11 (*d*, ^3J(2,3) = 7.2, H–C(2)); 5.75 (*d*, ^3J(7,8) = 7.3, H–C(8)); 4.83 (*d*, ^3J(7,8) = 7.4, H–C(7)); 4.69 (*s*, H–C(10)); 3.69, 3.67 (2*s*, 2 COO*Me*); 2.75 (*sept.*, ^3J = 6.8, Me_2CH); 2.12 (*s*, Me); 1.98 (*s*, Me); 1.42, 1.31 (2*d*, ^3J = 6.9, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 22.98 (Me); 23.88 (Me); 25.60 (Me); 28.67 (Me); 36.74 (CH); 52.07 (COO*Me*); 52.23 (COO*Me*); 69.94 (C); 81.31 (C); 94.60 (CH); 98.73 (CH); 102.04 (CH); 119.94 (C); 126.89 (CH); 128.38 (C); 130.48 (C); 139.20 (CH); 142.12 (C); 147.12 (C); 166.43 (*C*OOMe); 167.63 (*C*OOMe); 240 (CO). CI-MS: 477 (100, M^+), 358 (45, $[M - (MeOH + 3\,CO)]^{+\bullet}$), 341 (12, $[M - Cr(CO)_3]^{+\bullet}$), 309 (24, $[M - (Cr(CO)_3 + MeOH)]^{+\bullet}$).

Data of Tricarbonyl[(1,2,3,4,5,5a-η)-1,2-bis(methoxycarbonyl)-5,10-dimethyl-7-(1-methylethyl)heptalene]-chromium (**17**): Dark-green crystals (hexane/Et_2O). M.p. 151–153°. ^{1}H-NMR (300 MHz, $CDCl_3$, $\delta(CHCl_3)$ 7.26): 6.20 (*d*, $^3J(8,9) = 11.9$, H–C(8)); 6.10 (*d*, $^3J(8,9) = 11.9$, H–C(9)); 6.03 (*d*, $^3J(3,4) = 8.9$, H–C(3)); 5.97 (*d*, $^3J(3,4) = 8.8$, H–C(4)); 5.62 (*s*, H–C(6)); 3.89, 3.73 (2*s*, 2 COO*Me*); 2.55 (*sept.*, $^3J = 6.8$, Me_2CH); 1.95 (*s*, Me); 1.59 (*s*, Me); 1.17, 1.13 (2*d*, $^3J = 6.4$, 6.6, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 16.57 (Me); 20.49 (Me); 22.45 (Me); 22.70 (Me); 34.91 (CH); 43.67 (C); 51.92 (COO*Me*); 53.31 (COO*Me*); 98.03 (CH); 98.64 (C); 99.02 (CH); 107.00 (C); 114.92 (C); 121.76 (CH); 123.90 (C); 130.28 (CH); 134.13 (CH); 136.75 (C); 149.47 (C); 168.47 (*C*OOMe); 169.10 (*C*OOMe); 230.28 (CO). CI-MS: 477 (100, M^+), 361 (6, $[M - (MeOH + 3\ CO)]^{+\cdot}$), 341 (8, $[M - Cr(CO)_3]^{+\cdot}$), 309 (50, $[M - (Cr(CO)_3 + MeOH)]^{+\cdot}$).

Data of cis-*{(1,2,3,4,5,5a-η:6,7,8,9,10,10a-η)-[1,2-bis(methoxycarbonyl)-5,10-dimethyl-7-(1-methylethyl)-heptalene]bis[(tricarbonyl)chromium]}* (**18**): Dark-red crystals (Et_2O/hexane). M.p. 170–172°. ^{1}H-NMR (300 MHz, $CDCl_3$, $\delta(CHCl_3)$ 7.26): 6.01 (*d*, $^3J(3,4) = 8.8$, H–C(3)); 5.67 (*d*, $^3J(3,4) = 8.6$, H–C(4)); 5.60 (*d*, $^3J(8,9) = 8.6$, H–C(8)); 5.16 (*d*, $^3J(8,9) = 8.7$, H–C(9)); 3.21 (*s*, H–C(6)); 3.84, 3.83 (2*s*, 2 COO*Me*); 2.66 (*sept.*, $^3J = 6.8$, Me_2CH); 1.78 (*s*, Me); 1.65 (*s*, Me); 1.38, 1.09 (2*d*, $^3J = 6.6$, 6.1, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 23.01 (Me); 23.94 (Me); 25.56 (Me); 28.76 (Me); 36.52 (CH); 52.34 (COO*Me*); 53.53 (COO*Me*); 69.94 (C); 81.3 (C); 94.63 (CH); 98.68 (CH); 102.07 (CH); 119.93 (C); 126.89 (CH); 128.37 (C); 130.52 (C); 139.16 (CH); 142.10 (C); 147.08 (C); 166.43 (*C*OOMe); 167.26 (*C*OOMe); 240.00 (CO).

The *Öfele* reaction of **15a** (*Scheme 5*) gave, after the purification by FC (silica gel; 30–40% Et_2O in hexane), complex **19** (21 (40)%) in the first fraction, unchanged starting heptalene (48%) in the second fraction, and binuclear complex **20** (16 (31)%) in the third fraction.

Data of Tricarbonyl[(1,2,3,4,5,5a-η)-1,2-bis(methoxycarbonyl)-5,6,8,10-tetramethylheptalene]chromium (**19**): Dark-green crystals (Et_2O/hexane). M.p. 157–159°. UV/VIS (MeCN): λ_{max} 410 (sh, 3.17), 268 (4.27), 206 (4.52); λ_{min} 250 (4.22). IR (KBr): 3443*m*, 2959*w*, 2921*w*, 1988*s* (CO), 1939*s* (CO), 1902*s* (CO), 1705*m*, 1436*w*, 1263*m*, 1196*w*, 1165*w*, 1126*w*, 1098*w*, 976*w*, 848*w*, 780*w*, 651*w*, 619*w*, 587*w*, 529*w*. ^{1}H-NMR (300 MHz, $CDCl_3$, δ ($CHCl_3$) 7.26): 6.14 (*d*, $^3J(3,4) = 8.9$, H–C(3)); 6.04 (*s*, H–C(7)); 5.84 (*s*, H–C(9)); 5.72 (*d*, $^3J(3,4) = 9.0$, H–C(4)); 3.88, 3.75 (2*s*, 2 COOMe); 2.20 (*s*, Me–C(10)); 1.95 (*s*, Me–C(5)); 1.90 (*s*, Me–C(8)); 1.61 (*s*, Me–C(6)). ^{13}C-NMR (75 MHz, $CDCl_3$): 16.82 (Me); 20.43 (Me); 25.32 (Me); 27.81 (Me); 46.64 (C); 52.31 (COO*Me*); 53.49 (COO*Me*); 96.43 (CH); 99.60 (CH); 103.95 (C); 110.22 (C); 113.40 (C); 120.00 (C); 129.91 (CH); 130.80 (CH); 132.94 (C); 137.34 (C); 137.56 (C); 168.94 (*C*OOMe); 169.21 (*C*OOMe); 230.10 (CO). EI-MS: 462 ($M^{+\cdot}$), 406 (4, $[M - 2\ CO]^{+\cdot}$), 378 (18, $[M - 3\ CO]^{+\cdot}$), 326 ($[M - Cr(CO)_3]^{+\cdot}$), 318 (16), 262 (27), 207 (17), 73 (24). EA: Calc. for $C_{23}H_{22}O_7Cr$: C 59.74, H 4.76; found: C 59.53, H 4.90.

Data of cis-*{(1,2,3,4,5,5a-η:6,7,8,9,10,10a-η)-[1,2-bis(methoxycarbonyl)-5,6,8,10-tetramethylheptalene]bis-[(tricarbonyl)chromium]}* (**20**): Brown crystals (Et_2O/hexane). M.p. 186–188°. UV/VIS (MeCN): λ_{max} 410 (sh, 3.45), 332 (3.72), 266 (4.22), 206 (4.63); λ_{min} 385 (3.50), 303 (3.79). IR (KBr): 3432*m*, 2925*w*, 2002*s* (CO), 1966*s* (CO), 1956*s* (CO), 1920*s* (CO), 1897*s* (CO), 1875*s* (CO), 1732*m*, 1705*w*, 1436*w*, 1266*m*, 1255*w*, 1097*w*, 1032*w*, 741*w*, 664*w*, 647*w*, 607*w*, 582*w*, 530*w*, 516*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.23 (*d*, $^3J(3,4) = 8.7$, H–C(3)); 5.41 (*d*, $^3J(3,4) = 8.9$, H–C(4)); 5.08 (*s*, H–C(7)); 4.82 (*s*, H–C(9)); 3.83, 3.84 (2*s*, 2 COO*Me*); 2.41 (*s*, Me–C(10)); 2.18 (*s*, Me–C(5)); 1.80 (*s*, Me–C(8)); 1.72 (*s*, Me–C(6)). ^{13}C-NMR (75 MHz, $CDCl_3$): 18.90 (Me); 17.86 (Me); 26.02 (Me); 26.90 (Me); 52.54 (COO*Me*); 53.64 (COO*Me*); 65.75 (C); 87.67 (C); 94.36 (CH); 95.50 (CH); 97.44 (CH); 102.75 (CH); 107.81 (C); 113.11 (C); 116.03 (C); 127.23 (C); 129.51 (C); 132.73 (C); 137.42 (C); 168.62 (*C*OOMe); 168.64 (*C*OOMe); 238.04 (CO). CI-MS: 621 $[M + Na]^+$, 542 $[M - 2\ CO]^{+\cdot}$, 515 $[M - 3\ CO]^{+\cdot}$. Anal. calc. for $C_{26}H_{22}O_{10}Cr_2$ (558): C 52.17, H 3.68; found: C 52.20, H 3.79.

The structure of **20** was confirmed by an X-ray crystal-structure analysis (*Fig. 4*).

1.3. *Synthesis of the Cr(CO)$_3$ Complexes* **22**–**24** *of 4,5-Bis(methoxymethyl)-1,6-dimethyl-9-(1-methylethyl)heptalene* (**21a**) *and 1,2-Bis(methoxymethyl)-5,10-dimethyl-7-(1-methylethyl)heptalene* (**21b**; *Scheme 6*). 1.3.1. *Synthesis of Starting Ligands* **21**. A soln. of 1,6-dimethyl-9-(1-methylethyl)heptalene-4,5-/-1,2-diol (0.78 g, 2.7 mmol) in THF (10 ml) was added to the stirred suspension of NaH (1.08 g, 27 mmol) in THF (30 ml) under Ar. The resulting mixture was warmed 2 h at 50°, then, after cooling to r.t., MeI (3.1 ml, 48.7 mmol) was added, and the mixture was stirred an additional 2 h at 50°. The mixture was dropped into H_2O (50 ml) and extracted (2×) with Et_2O. Then, the org. layers were combined and washed with sat. NaCl soln. and dried (Na_2SO_4). After evaporation of the solvent and purification of the residue (silica gel; 5% AcOEt in hexane), the methylated product (0.67 g, 80%) was obtained as a mixture of its two DBS isomers **21a** and **21b**.

Data of **21a**: Yellow-orange oil in a mixture with 5% of its DBS isomer **21b**. ^{1}H-NMR (300 MHz, $CDCl_3$, δ ($CHCl_3$) 7.256): 6.31 (*d*, $^3J(2,3) = 6.9$, H–C(3)); 6.13 (*d*, $^3J(7,8) = 6.2$, H–C(2)); 6.08 (*d*, $^3J(7,8) = 6.1$, H–C(8)); 6.00 (*d*, $^3J(2,3) = 6.1$, H–C(7)); 5.72 (*s*, H–C(10)); 4.70, 3.70 (2*d*, $^2J = 12.4$, CH_2–C(4)); 4.10 and 3.99 (2*d*, $^2J = 10.7$, CH_2–C(5)); 3.31, 3.08 (2*s*, 2 COO*Me*); 2.43 (*sept.*, $^3J = 6.8$, Me_2CH); 2.10 (*s*, Me–C(6)); 2.04

(*s*, Me–C(1)); 1.04, 1.00 (2*d*, $^3J = 6.9$, *Me*$_2$CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 22.35 (Me); 23.07 (Me); 23.89 (Me); 24.04 (Me); 35.96 (CH); 55.90 (COO*Me*); 58.36 (COO*Me*); 68.57 (CH_2); 76.04 (CH_2); 122.85 (CH); 123.96 (CH); 125.69 (CH); 126.97 (CH); 129.19 (C); 129.82 (C); 131.67 (CH); 136.58 (C); 137.55 (C); 137.94 (C); 138.93 (C); 148.48 (C). EI-MS: 312 (77, $M^{+\bullet}$), 281 (16, $[M - MeO]^{+\bullet}$), 267 (20), 198 (100). Anal. calc. for $C_{21}H_{28}O_2$ (312): C 80.77, H 8.97; found: C 80.76, H 9.02.

Data of **21b**: In a mixture with 95% of its DBS isomer **21a**. ^{1}H-NMR (300 MHz, $CDCl_3$, δ ($CHCl_3$) 7.256): 6.45 (*d*, $^3J(3,4) = 11.8$, H–C(3)); 5.74 (*d*, $^3J(3,4) = 9.1$, H–C(4)); 5.63 (*s*, H–C(6)); 4.44, 3.76 (2*d*, $^3J = 12.3$, CH_2–C(2)); 4.24, 4.12 (*AB*, $^3J = 11.8$, CH_2–C(1)); 3.33, 3.23 (2*s*, 2 COO*Me*); 2.49 (*sept.*, $^3J = 6.9$, Me_2CH); 1.72 (*s*, Me–C(10)); 1.65 (*s*, Me–C(5)); 1.12, 1.11 (2*d*, $^3J = 6.9$, *Me*$_2$CH). The signals for H–C(8) and H–C(9) were not found. ^{13}C-NMR (75 MHz, $CDCl_3$): 16.74 (Me); 17.94 (Me); 22.60 (Me); 22.86 (Me); 34.47 (CH); 57.55 (COO*Me*); 57.72 (COO*Me*); 71.28 (CH_2); 72.92 (CH_2); 121.26 (CH); 128.44 (C); 129.19 (C); 130.71 (C); 130.97 (CH); 131.12 (CH); 132.92 (C); 135.23 (CH); 135.56 (C); 137.36 (C); 147.87 (C).

1.3.2. *Formation of the Cr(CO)$_3$ Complexes.* The mixture **21a**/**21b** (0.52 g, 1.67 mmol) and $[Cr(NH_3)_3(CO)_3]$ (0.31 g, 1.77 mmol) was refluxed in DME (50 ml) for 6.5 h under Ar. Then, the solvent was evaporated under reduced pressure, and the residue was purified (silica gel; 10% Et_2O in hexane, followed by 15% Et_2O in hexane) to give complex **22** (0.23 g, 31 (46) %) as the first fraction. The second fraction contained the starting mixture **21a**/**21b** (0.17 g, 33%). The third fraction contained the binuclear complex **24** (0.13 g, 13 (20)%), and the last fraction complex **23** (0.07 g, 9 (14)%).

Data of Tricarbonyl[(1,2,3,4,5,5a-η)-1,2-bis(methoxymethyl)-5,10-dimethylheptalene]chromium (**22**): Red oil. ^{1}H-NMR (300 MHz, $CDCl_3$, δ ($CHCl_3$) 7.256): 6.15 (*dd*, $^3J(8,9) = 11.8$, $^3J = 1$, H–C(8)); 5.99 (*d*, $^3J(8,9) = 11.8$, H–C(9)); 5.63 (*s*, H–C(6)); 5.62 (*AB*, $^3J \approx 9.0$, H–C(4,3)); 4.53, 3.80 (2*d*, $^2J = 11.8$, CH_2–C(2)); 4.26, 3.97 (*AB*, $^2J = 12.0$, CH_2–C(1)); 3.48, 3.40 (2*s*, 2 COO*Me*); 2.53 (*sept.*, $^3J = 6.9$, Me_2CH); 1.96 (*s*, Me–C(10)); 1.65 (*s*, Me–C(5)); 1.15, 1.12 (2*d*, $^3J = 6.9$, *Me*$_2$CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.56 (Me); 20.63 (Me); 22.52 (Me); 22.69 (Me); 34.61 (CH); 58.56 (COO*Me*); 58.61 (COO*Me*); 69.32 (C); 74.13 (CH_2); 74.46 (CH_2); 83.29 (C); 96.70 (CH); 98.15 (CH); 108.04 (C); 113.12 (C); 122.80 (CH); 129.92 (CH); 131.52 (C); 133.24 (C); 133.77 (CH); 148.91 (C); 231.36 (CO). EI-MS: 448 ($M^{+\bullet}$), 416 ($[M - MeOH]^{+\bullet}$), 364 (34, $[M - 3\ CO]^{+\bullet}$), 332 (41), 302 (28), 250 (100). Anal. calc. for $C_{24}H_{28}O_5Cr$ (448.48): C 64.29, H 6.25; found: C 64.45, H 6.51.

Data of Tricarbonyl[(6,7,8,9,10,10a-η)-4,5-bis(methoxymethyl)-1,6-dimethyl-9-(1-methylethyl)heptalene]-chromium (**23**): Red oil. ^{1}H-NMR (300 MHz, $CDCl_3$, δ ($CHCl_3$) 7.256): 6.12 (*d*, $^3J(2,3) = 6.8$, H–C(3)); 6.00 (*d*, $^3J(2,3) = 6.8$, H–C(2)); 5.55 (*d*, $^3J(7,8) = 6.8$, H–C(8)); 4.87 (*d*, $^3J(7,8) = 6.8$, H–C(7)); 4.62 (*s*, H–C(10)); 4.46, 3.57 (2*d*, $^2J = 12.4$, CH_2–C(4)); 3.82 (*AB*, CH_2–C(5)); 3.30, 3.07 (2*s*, 2 COO*Me*); 2.66 (*sept.*, $^3J = 6.8$, Me_2CH); 2.17 (*s*, Me–C(6)); 2.14 (*s*, Me–C(1)); 1.31, 1.25 (2*d*, $^3J = 6.8$, *Me*$_2$CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 22.91 (Me); 25.45 (Me); 26.14 (Me); 27.70 (Me); 36.71 (CH); 56.14 (COO*Me*); 58.51 (COO*Me*); 66.73 (CH_2); 72.62 (C); 76.04 (CH_2); 87.20 (C); 93.86 (CH); 98.50 (CH); 100.06 (CH); 119.94 (C); 127.50 (CH); 132.10 (CH); 134.67 (C); 135.10 (C); 137.63 (C); 140.37 (C); CO of $Cr(CO)_3$ were not observed. EI-MS: 448.48 (11, $M^{+\bullet}$), 420 (15, $[M - CO]^{+\bullet}$), 392 (8, $[M - 2\ CO]^{+\bullet}$), 364 (56, $[M - 3\ CO]^{+\bullet}$), 332 (64, $[M - (3\ CO + MeOH)]^{+\bullet}$), 302 (38), 250 (95), 235 (100), 198 (37). Anal. calc. for $C_{24}H_{28}O_5Cr$ (448): C 64.29, H 6.25; found: C 64.77, H 6.39.

Data of cis-*{[(1,2,3,4,5,5a-η:6,7,8,9,10,10a-η)-1,2-Bis(methoxymethyl)-5,10-dimethyl-7-(1-methylethyl)heptalene]bis[tricarbonylchromium]}* (**24**): Red crystals (Et_2O/hexane). M.p. 160–162°. IR (KBr): 3443*m*, 2925*m*, 1989*s*, 1954*s*, 1932*s*, 1905*s*, 1874*s*, 1858*s*, 1450*w*, 1373*w*, 1187*w*, 1113*w*, 1087*w*, 665*w*, 622*w*, 605*w*, 526*w*. ^{1}H-NMR (300 MHz, $CDCl_3$, δ ($CHCl_3$) 7.256): 5.71 (*d*, $^3J(8,9) = 9.2$, H–C(8)); 5.40 (*d*, $^3J(3,4) = 9.2$, H–C(4)); 4.99 (*d*, $^3J(8,9) = 9.2$, H–C(9)); 4.50 (*d*, $^3J(3,4) = 10.9$, H–C(3)); 4.45 (*d*, $^2J = 12.5$, CH_2–C(2)); 4.02 (*dd*, $^2J = 12.2$, $^3J = 3$, CH_2–C(1)); 3.88 (*s*, H–C(6)); 3.49, 3.48 (2*s*, 2 COO*Me*); 2.68 (*sept.*, $^3J = 6.7$, Me_2CH); 1.74 (*s*, Me–C(10)); 1.64 (*s*, Me–C(5)); 1.38, 1.11 (2*d*, $^3J = 6.8$, *Me*$_2$CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 18.91 (Me), 19.19 (Me), 19.35 (Me), 26.56 (Me), 36.43 (CH), 56.74 (COO*Me*), 58.35 (COO*Me*), 66.86 (C), 73.98 (CH_2), 78.37 (CH_2), 79.50 (C), 93.60 (CH), 95.18 (CH), 96.74 (CH), 100.29 (CH), 110.00 (C), 117.58 (C), 118.29 (C), 124.28 (C), 229.73 (CO). EI-MS: 584 ($M^{+\bullet}$), 553 ($[M - MeO]^+$), 472 ($[M - 4\ CO]^{+\bullet}$), 416 (100, $[M - 6\ CO]^{+\bullet}$), 384 (38), 364 (17, $[M - (Cr(CO)_6]^{+\bullet}$), 332 (27), 302 (72), 250 (41), 235 (48).

1.4. *Synthesis of Complexes* **10** *and* **13a** *by Condensation of [Cr(PhCHO)(CO)$_3$]* (**25**) *with the 1-Methylheptalene-4,5-dicarboxylates* **7a** *and* **15a** (*Scheme 7*). *General Procedure.* To the stirred mixture of **7a** (1.40 g, 4.2 mmol) and **25** (1.00 g, 4.2 mmol) in 12 ml THF, a soln. of *t*-BuOK (1.6 ml, 14 mmol) was added dropwise at 0° during 10 min. Then, the mixture was stirred 6 h at r.t. H_2O was added, and the mixture was extracted (3 ×) with Et_2O. The combined Et_2O phases were washed with brine, dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The brown residue was purified by FC (silica gel; 25% Et_2O in hexane) to give yellow starting heptalene **7a** (0.61 g, 43%) in the first fraction and complex **10** (0.60 g, 25 (44)%) in the second fraction.

The same procedure starting from **15a** gave, after workup and purification by FC (silica gel; 30–40% Et_2O in hexane), yellow unreacted heptalene **15a** (47%) in a first fraction and complex **13a** (25 (47)%) in a second fraction.

2. Thermal Isomerizations of Complexes 11, 16, 17, 19, and 20. – A small amount (0.2–0.6 mmol) of each complex was dissolved in 5–10 ml of HFB and heated at 85–95° in a *Schlenk* flask under Ar during 24–60 h. After cooling to r.t., the solvent was evaporated, and the residue was purified by FC (silica gel; 30–40% Et_2O in hexane). The thermal isomerization of complex **17** (*Scheme 8,a*) gave, after flash chromatography, the green starting complex **17** (5.6%) as the first fraction, then uncomplexed heptalene **14a** (66%) as the second fraction, and finally, the red complex **16** (28%) is in the third fraction.

The thermal isomerization of complex **19** (*Scheme 9*) led, after purification by CC (silica gel; 30% Et_2O in hexane), to the starting complex **19** (4%) as a first, green fraction, the noncomplexed heptalene (**15a** (22%) as a second, yellow fraction, and the on-state complex **26** (39%) as a third, red fraction.

Data of Tricarbonyl[(6,7,8,9,10,10a-η)-4,5-bis(methoxycarbonyl)-1,6,8,10-tetramethylheptalene]chromium (**26**): Red crystals (Et_2O). M.p. 156–158°. UV/VIS (MeCN): λ_{max} 407 (sh, 3.24), 265 (4.26), 206 (4.51); λ_{min} 253 (4.25). IR (KBr): 3435*m*, 2950*w*, 1954*s* (CO), 1893*s* (CO), 1880*s*, 1866*s*, 1731*m*, 1714*m*, 1580*w*, 1439*m*, 1383*w*, 1274*m*, 1217*w*, 1151*w*, 1090*w*, 1053*w*, 771*w*, 661*m*, 613*w*, 529*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.25 (*d*, $^3J(2,3) = 6.2$, H–C(3)); 6.21 (*d*, $^3J(2,3) = 6.5$, H–C(2)); 5.32 (*s*, H–C(9)); 4.72 (*s*, H–C(7)); 3.56, 5.58 (2*s*, 2 COO*Me*); 2.41 (*s*, Me–C(6)); 2.18 (*s*, Me–C(1)); 1.93 (*s*, Me–C(8)); 1.88 (*s*, Me–C(10)). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.34 (Me); 23.06 (Me); 25.74 (Me); 29.78 (Me); 52.06 (COO*Me*); 52.09 (COO*Me*); 74.06 (C); 77.36 (C); 97.22 (CH); 101.01 (CH); 110.56 (C); 111.94 (C); 127.07 (CH); 127.35 (C); 129.30 (C); 138.16 (CH); 144.09 (C); 145.54 (C); 166.59 (*C*OOMe); 166.98 (*C*OOMe); 226–227 (CO). CI-MS: 462 (100, $M^{+\bullet}$), 396 (27), 329 (5), 294 (9, $[M - (Cr(CO)_3 + MeOH)]^{+\bullet}$).

Ther thermal isomerization of complex **26** (*Scheme 9*) gave, after purification by FC (silica gel; 20–30% Et_2O in hexane), the green off-state complex **19** (10%) in a first fraction, noncomplexed heptalene **15a** (21%) in a second fraction, and starting complex **26** (68%) in a third fraction.

The thermal isomerization of the binuclear complex **20** gave, after work-up according to the *General Procedure* and FC (silica gel), complex **19** (10%), complex **27** (30%), noncomplexed **15a** (25%), and starting binuclear complex **20** (20%).

The thermal isomerization of complexes **11** and **16** during 60 h gave starting complexes **11** (40%) and **16** (30%), and their corresponding heptalene ligands **7a** (23%) and **14a** (21%), respectively.

3. X-Ray Crystal-Structure Determination of 20[6]. – All measurements were conducted on a *Rigaku AFC5R* diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å) and a 12-kW rotating anode generator. The intensities of three standard reflections were measured after every 150 reflections and remained stable throughout the data collection. The intensities were corrected for *Lorentz* and polarization effects. An empirical absorption correction based on azimuthal scans of several reflections [25] was applied. Data collection and refinement parameters are given in *Table 3*. A view of the molecule is shown in the *Fig. 4*. The structure was solved by direct methods with SIR92 [26], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were fixed in geometrically calculated positions (d(C–H) = 0.95 Å), and each was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom. Refinement of the structure was carried out on F using full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o| - |F_c|)$ [25]. Refinement of the absolute structure parameter [27] yielded a value of 0.49(4), which indicates that the compound is a merohedral twin. Neutral-atom-scattering factors for non-H-atoms were taken from [28a], and the scattering factors for H-atoms from [29]. Anomalous dispersion effects were included in F_c [30]; the values for f' and f'' were those of [28b]. All calculations were performed with the TEXSAN crystallographic software package [31].

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[6]) Crystallographic data for the structure of **20** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-174752. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 3. *Crystallographic Data for Compound* **20**

Crystallized from	Et_2O/pentane
Empirical formula	$C_{26}H_{22}Cr_2O_{10}$
Formula weight [g mol^{-1}]	598.44
Crystal color, habit	dark red, prism
Crystal dimensions [mm]	$0.45 \times 0.50 \times 0.60$
Temp. [K]	173(1)
Crystal system	orthorhombic
Space group	$Pca2_1$ (#29)
Z	8 (2 formula units per asymmetric unit)
Reflections for cell determination	25
2θ range for cell determination [°]	38 – 40
Unit-cell parameters a [Å]	34.232(3)
b [Å]	9.675(3)
c [Å]	15.415(3)
V [Å^3]	5106(2)
$F(000)$	2448
D_x [g cm^{-3}]	1.557
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]	0.909
$2\theta_{(\max)}$ [°]	55
Transmission factors (min; max)	0.783; 1.000
Total reflections measured	7482
Symmetry independent reflections	6072
Reflections used [$I > 2\sigma(I)$]	5249
Parameters refined	684
Final R	0.0461
wR	0.0474
Goodness-of-fit	2.320
Final $\Delta_{\max}/\sigma$	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.81; – 0.55
$\sigma(d(\mathrm{C-C}))$ [Å]	0.008 – 0.01

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