A Study on Electronic Interaction between Two [2.2]Metacyclophane Systems Connected with a C=C Bond: Preparation, Structure and Complexation of (*E*)- and (*Z*)-8,8′-(Ethene-1,2-diyl)bis(5-*tert*-butyl[2.2]metacyclophane)

Tsutomu Ishi-i[a], Tsuyoshi Sawada[b], Shuntaro Mataka[b], Masashi Tashiro*[b], and Thies Thiemann[c]

Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University[a],
Institute of Advanced Material Study, Kyushu University[b],
6-1 Kasuga-kohen, Kasuga-shi, Fukuoka 816, Japan

Laboratory of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Coimbra[c],
3000 Coimbra, Portugal

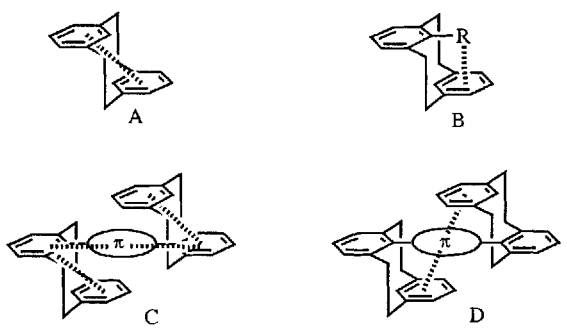
Received August 18, 1995

Key Words: Bis[2.2]metacyclophanes / Stilbenes / π-π Interaction / Tricarbonylchromium complexes / Charge-transfer

(*E*)-8,8′-(Ethene-1,2-diyl)bis(5-*tert*-butyl[2.2]metacyclophane) (**2**) was obtained from a McMurry reaction of 5-*tert*-butyl-8-formyl[2.2]metacyclophane (**1**). Irradiation of **2** with a high-pressure mercury lamp gave the corresponding (*Z*) isomer **3**. X-ray crystallographic analyses of **2** and **3** show a certain degree of twisting of the bond connecting the metacyclophane unit and the central π system due to steric crowding. UV spectra of **2** and **3** and of the charge-transfer complexes [**2**/TCNE] and [**3**/TCNE] allow for a discussion of π-π interaction between the central stilbene subunit and the outer benzene rings of the metacyclophane units. Bis[2.2]metacyclophanes **2** and **3** reacted regioselectively with hexacarbonylchromium on the outer benzene rings giving 1:1 and 1:2 complexes **9**–**14** with tricarbonylchromium. No 1:3 and 1:4 complexes formed due to steric restrictions. Analysis of UV spectral data of the complexed [2.2]metacyclophanes was performed for an indication of π-π interactions in the complexes.

In [2.2]metacyclophanes (MCPs)[1], the two benzene rings are positioned very close to each other, and the internal substituent (R) is situated above the opposing benzene ring at a short distance; thus electronic interactions[2,3] of type **A** and **B** (Figure 1) can be expected.

Figure 1. Electronic interactions in [2.2]MCP systems



When two [2.2]MCPs units are connected by a π system to furnish compounds of type **C**/**D**, two new types of electronic interactions can be envisaged (Figure 1). Type **C** shows a π-π interaction between the two outer benzene rings of each [2.2]MCP system through the central π linkage and the two inner benzene rings. In type **D**, the π-π interaction between the outer benzene rings includes only the central π system. By these potential interactions, the electronic nature of the "top" benzene ring should influence the electronic properties on the "bottom" benzene ring.

In this paper we report on the preparation, the X-ray crystallographic analyses and their complexation behavior of novel bis[2.2]MCPs connected by an ethene bridge at the internal positions. Indications for a π-π interaction in these systems are sought for.

Preparation

(*E*)-Bis[2.2]MCP **2** was prepared in 78% yield by treatment of 8-formyl[2.2]MCP **1**[3d] with $TiCl_3(DME)_{1.5}$ and Zn-Cu according to McMurry's procedure[4] (Scheme 1). Irradiation of **2** with a high-pressure mercury lamp gave a mixture of **2** and the corresponding (*Z*) isomer **3** in the ratio 13:87. From the mixture, **3** was isolated in 69% yield. Reference compounds **5** and **6** were prepared similarly (Scheme 1). Bis[2.2]MCP **8** with an ethan bridge linkage was prepared by the reductive coupling reaction of 8-(bromomethyl)[2.2]MCP **7**[3d] by using PhLi in 93% yield (Scheme 1).

UV-Spectra

The long-wavelength absorption bands in the UV spectra (λ_{max}) of [2.2]MCPs **2** and **3** and of the reference compounds **5** and **6** are listed in Table 1 as well as the bathochromic shifts ($\Delta\lambda_{max}$) of **2** and **3** in reference to **5** and **6**.

The long-wavelength absorption bands in **2**, **3**, **5**, and **6** are described to an electronic transition of the stilbene chromophore[5]. It is well-known[5] that increasing hindrance to planarity in stilbenes results in hypso- and hypochromic effects in these absorption bands. This phenomenon is evi-

  0009–2940/96/0303–0289 $ 10.00+.25/0

Scheme 1

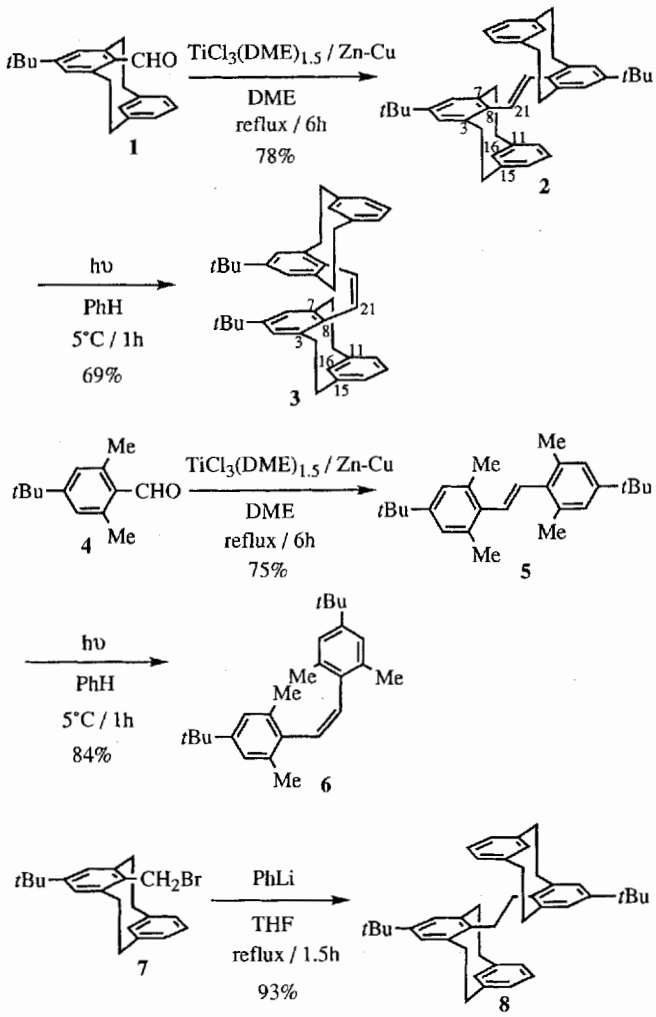


Table 1. UV spectral data of **2**, **3**, **5**, and **6** in cyclohexane ($5 \cdot 10^{-5}$ M)

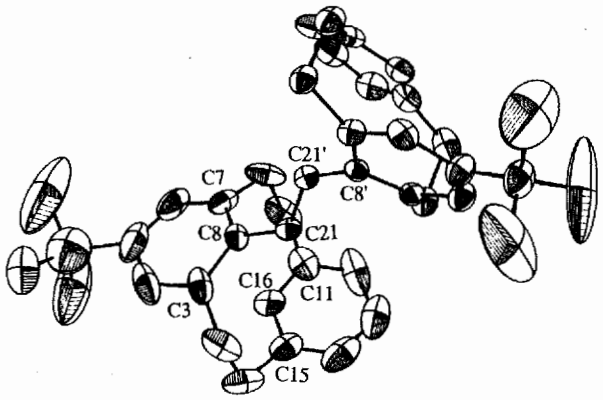
	λ_{max} (nm)	log ε		λ_{max} (nm)	log ε	$\Delta\lambda_{max}$ (nm)
2	280	4.05	**5**	264	4.22	16
3	280	3.77	**6**	261	4.21	19

dent in **2**, **3**, **5**, and **6** (in comparison $\lambda_{max\ [parent\ (E)\text{-stilbene}]}$ = 294 nm: lg ε = $4.46_{[hexane]}$)[6]. A Comparison of the λ_{max} value of **2** (280 nm) with that of **3** (280 nm) shows that the steric crowding in **2** and **3** is very similar. The bathochromic shifts of **2** and **3** in comparison to **5** and **6** ($\Delta\lambda_{max}$ = 16–19 nm) are due to a π-π interaction between the outer benzene rings and the central stilbene subunit and/or the strain of the benzene rings in **2** and **3**.

X-ray Crystallographic Analyses

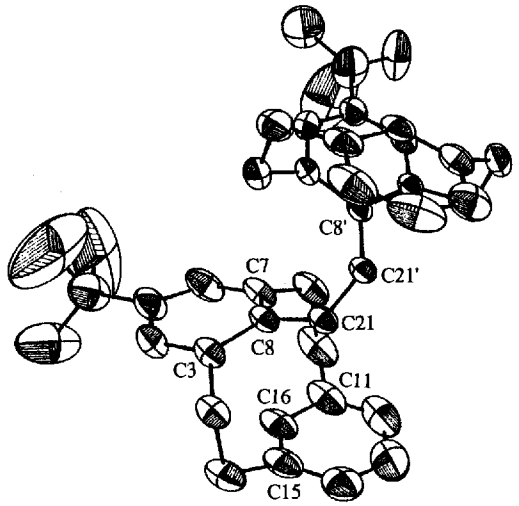
The ORTEP drawings of bis[2.2]MCPs **2** and **3** are shown in Figures 2 and 3. The olefinic bridge between the two MCP subunits with 1.34 (**2**) and 1.36 Å (**3**) shows the typical bond length of an ethylene bond conjugated to two benzene rings, which is estimated to be 1.35 Å by molecular mechanics calculation[5d]. The torsional angle C(8)–C(21)–C(21′)–C(8′) of **2** is 168.0° (180–12°), the corresponding angle of **3** is 9.0°. The interplanar angles (Θ) between the ethene bridge and the inner benzene rings of **2** (46.8–53.7°) and **3** (43.1–50.6°) are similar, where **3** as a (*Z*) olefin typically shows slightly smaller twisting than the (*E*) olefin **2**. This twisting is affected by steric crowding due to the two voluminous MCP subunits on the central olefinic linkage. The values of Θ suggest the existence of a weak conjugation in the stilbene subunits. These results are also in agreement with the UV spectra of **2** and **3**. It may be pointed out that the strain due to steric overcrowding in the vicinity of the π linkage in **2** and **3** is alleviated for the most part by the twisting around of the single bonds C(8)–C(21)/C(8′)–C(21′) rather than by stretching or bending of the double bond C(21)–C(21′).

Figure 2. ORTEP drawing of **2**. Selected atomic distances [Å] and bond angles [°]: C(3)–C(4) 1.40(1), C(3′)–C(4′) 1.38(1), C(3)–C(8) 1.44(1), C(3′)–C(8′) 1.42(1), C(4)–C(5) 1.39(1), C(4′)–C(5′) 1.37(2), C(5)–C(6) 1.39(1), C(5′)–C(6′) 1.37(2), C(6)–C(7) 1.41(1), C(6′)–C(7′) 1.43(2), C(7)–C(8) 1.39(1), C(7′)–C(8′) 1.41(2), C(8)–C(21) 1.45(1), C(8′)–C(21′) 1.46(1), C(21)–C(21′) 1.34(1); C(3)–C(4)–C(5) 124.3(9), C(3′)–C(4′)–C(5′) 124(1), C(3)–C(8)–C(7) 117.3(8), C(3′)–C(8′)–C(7′) 118.0(9), C(3)–C(8)–C(21) 119.4(8), C(3′)–C(8′)–C(21′) 122.7(9), C(4)–C(3)–C(8) 117.9(8), C(4′)–C(3′)–C(8′) 119(1), C(4)–C(5)–C(6) 115.6(9), C(4′)–C(5′)–C(6′) 117(1), C(5)–C(6)–C(7) 122.2(8), C(5′)–C(6′)–C(7′) 124(1), C(6)–C(7)–C(8) 120.7(8), C(6′)–C(7′)–C(8′) 117(1), C(7)–C(8)–C(21) 123.3(8), C(7′)–C(8′)–C(21′) 119.3(9), C(8)–C(21)–C(21′) 123.5(8), C(8′)–C(21′)–C(21) 124.5(8)



The geometry of the two [2.2]MCP units in bis[2.2]MCPs **2** and **3** is similar to that of the parent [2.2]MCP[7]. The atomic distances C(8)···C(16) and C(8′)···C(16′) in **2** (2.68 and 2.71 Å) and **3** (2.72 and 2.70 Å) are close to that (2.63 Å) of the parent [2.2]MCP[6]. The carbon atoms C(21) and C(21′) of the ethene bridge in **2** are situated above (below) the outer benzene rings of the MCP units and closely approach the carbon atoms C(11), C(15), C(16) and C(11′), C(15′), (16′) at the distances of 3.29–3.36 and 3.33–3.36 Å, respectively. The corresponding distances in **3** are 3.27–3.34 Å. These short contacts should enable the π-π interaction between the central ethene bridge and the two outer benzene rings in **2** and **3**.

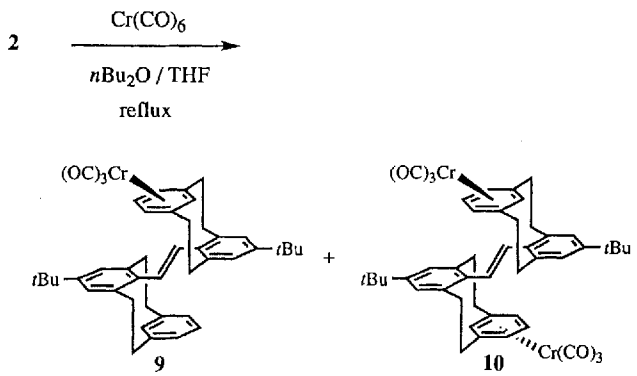
Figure 3. ORTEP drawing of **3**. Selected atomic distances [Å] and bond angles [°]: C(3)–C(4) 1.384(6), C(3')–C(4') 1.388(6), C(3)–C(8) 1.410(6), C(3')–C(8') 1.410(6), C(4)–C(5) 1.392(7), C(4')–C(5') 1.387(6), C(5)–C(6) 1.371(8), C(5')–C(6') 1.409(8), C(6)–C(7) 1.379(6), C(6')–C(7') 1.374(7), C(7)–C(8) 1.407(6), C(7')–C(8') 1.405(6), C(8)–C(21) 1.478(5), C(8')–C(21') 1.470(6), C(21)–C(21') 1.358(6); C(3)–C(4)–C(5) 122.0(5), C(3')–C84')–C(5') 123.8(4), C(3)–C(8)–C(7) 117.8(4), C(3')–C(8')–C(7') 117.5(4), C(3)–C(8)–C(21) 118.6(4), C(3')–C(8')–C(21') 119.3(4), C(4)–C(3)–C(8) 119.1(4), C(4')–C(3')–C(8') 118.9(4), C(4)–C(5)–C(6) 116.6(5), C(4')–C(5')–C(6') 114.6(4), C(5)–C(6)–C(7) 123.5(5), C(5')–C(6')–C(7') 123.4(4), C(6)–C(7)–C(8) 118.4(4), C(6')–C(7')–C(8') 119.6(4), C(7)–C(8)–C(21) 123.3(4), C(7')–C(8')–C(21') 123.1(4), C(8)–C(21)–C(21') 126.3(4), C(8')–C(21')–C(21) 129.0(3)



Tricarbonylchromium Complexes

The π-π interaction in the tricarbonylchromium complexes of small cyclophanes have been studied extensively[8]. The reactions of **2**, **3**, **5**, **6**, and **8** with hexacarbonylchromium [$Cr(CO)_6$] were carried out in dry di-*n*-butyl ether/THF (10:1) under refluxing conditions. The results are shown in Schemes 2–5.

Scheme 2

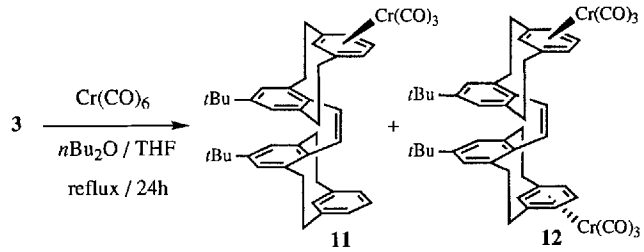


		yield (%)		
2 / $Cr(CO)_6$	time(h)	**2**	**9**	**10**
1 / 1	24	50	35	0
1 / 2	24	19	59	16
1 / 5	24	3	50	43
1 / 20	93	0	0	79

In the reaction of **2** with one equivalent of $Cr(CO)_6$, only 1:1 complex **9** with one tricarbonylchromium was obtained in 35% yield (Scheme 2). When two equivalents of $Cr(CO)_6$ were used, the 1:2 complex **10** was obtained in 16% yield, although the major product still was **9** (59%). In the reaction with a large excess of $Cr(CO)_6$ (5 equivalents), **9** was obtained in 50% yield together with **10** in 43% yield. The formation of **10** is slow compared to that of **9**. Presumably, the uncomplexed bottom (outer) benzene ring of **9** is deactivated by the electron-withdrawing $Cr(CO)_3$ moiety of the top (outer) benzene ring through a π-π interaction between the central stilbene subunit and the outer benzene rings, although the formation of **10** could not quite be inhibited. Complex **10** was selectively formed in a reaction by using twenty equivalents of $Cr(CO)_6$ with a long reaction time (93 h). In no cases could a 1:3 or a 1:4 complex be obtained.

(*Z*)-Bis[2.2]MCP **3** gave similar results to those of **2** (Scheme 3), showing that the electronic interactions of **2** and **3** may be comparable.

Scheme 3

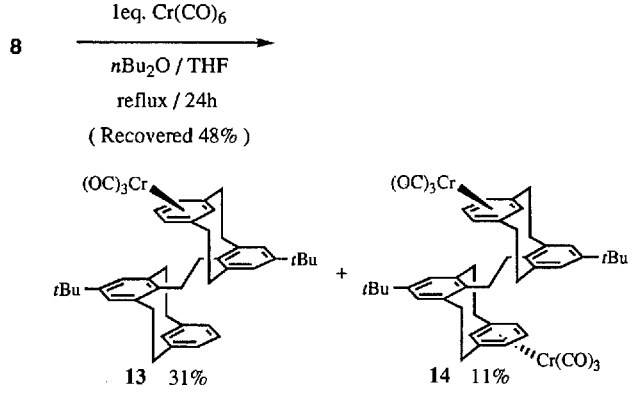


	yield (%)		
3 / $Cr(CO)_6$	**3**	**11**	**12**
1 / 1	67	25	0
1 / 2	17	57	21
1 / 5	3	52	42

The reaction of **8** with one equivalent of $Cr(CO)_6$ afforded not only the 1:1 complex **13** in 31% yield but also the 1:2 complex **14** in 11% yield (Scheme 4). Thus the reactivity of **8** is different from **2** or **3**, as the two latter MCPs only formed 1:1 complexes **9** and **11** under the same conditions. The $Cr(CO)_3$ moiety of **13** was expected not to influence the electron density of the remaining uncomplexed outer benzene ring, as the two [2.2]MCP subunits of **13** are electronically independent.

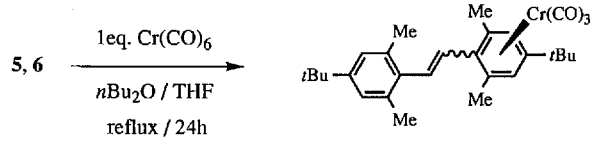
In the ^{1}H-NMR spectra of the complexes **9**–**14**, the signals of the protons (H-12,13,14,16) of the complexed benzene rings are shifted to higher magnetic field by 1.66–1.92 ppm, as compared to the corresponding protons of the uncomplexed [2.2]MCPs **2**, **3**, and **8** (Table 2)[8c,8e,9]. From the these results, it is clear that the $Cr(CO)_3$ groups in **9**–**14** are located on the outer benzene rings as expected[10]. That no complexation of the inner benzene rings in **9**–**14** takes place is attributed to the steric hindrance caused by the proximity of the outer benzene rings and the bulky *tert*-butyl groups. These inner benzene rings are sterically much more hindered than the corresponding benzene rings of **5** and **6** carring only the *tert*-butyl group. The reaction of **5**

Scheme 4



and **6** with $Cr(CO)_6$ give the corresponding 1:1 complexes **15** and **16** (Scheme 5).

Scheme 5



15 (*E*) (17%, recovered **5**: 52%)

16 (*Z*) (17%, recovered **6**: 54%)

(Arene)tricarbonylchromium complexes show an intramolecular charge-transfer band in their UV spectra at about 320 nm, characteristic of an electronic transition in the complexed aromatic ring[8c,8e,11]. The charge-transfer bands (λ_{CT}) of complexes **9**–**14** are listed in Table 3.

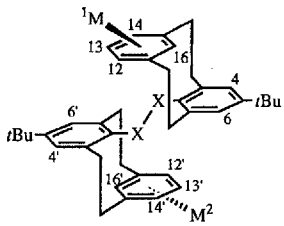
Bathochromic shifts ($\Delta\lambda_{CT}$ = 4–5 nm) in the 1:2 complexes **10** and **12** were observed as compared to the 1:1 complexes **9** and **11**. The values of these shifts are small. Nevertheless these bathochromic shifts are thought to be due to a weak electronic interaction between the central stilbene subunit and the outer benzene rings of **10** and **12**. This is in line with the fact that the 1:2 complex **14**, which lacks the central π system, did not exhibit a bathochromic shift as compared to the 1:1 complex **13**. The molar extinction coefficient (ε) of **14** was about twice of that of **13**. Interestingly, unconjugated bis[2.2]MCP **13** shows a bathochromic shift as compared to the conjugated bis[2.2]MCPs **9** and **11**. The reason for this is currently unknown.

Charge-Transfer Complex with TCNE

Charge-transfer complexes of small cyclophanes with TCNE have been studied to evaluate the π basicity of the cyclophane rings and to demonstrate π-π interaction in such systems[8b,12]. This has led to success especially in the field of paracyclophanes (PCPs), e.g. [2.2]PCPs and [3.3]PCPs, where π-π interactions are natually more pronounced[12a–c,e,f]. Previously, Sato and Hayashi[12d] reported that [2.2]MCP afforded only a 1:1 complex with TCNE which is stabilized due to the π-π interaction. Likewise, the work of Langer and Lehner[8b] showed the formation of only 1:1 complexes with substituted and unsubstituted [2.2]MCPs.

Also the bis[2.2]MCPs **2** and **3** form exclusively 1:1 charge-transfer complexes with TCNE (λ_{max}, 490 nm; K = 2.97 mol^{-1} for **2**, 480 nm for **3**) in dichloromethane, as can be deduced from a Job[13] (Figure 4) and a Benesi-Hildebrand plot[14] (Figure 5). Interestingly, the charge-transfer band (λ_{max}, 510 nm) of unconjugated bis[2.2]MCP **8** with TCNE is due to the formation of a 1:1 complex as well and not a 1:2 complex (Figure 4). Similar results were observed in certain aromatic systems. 2,2-Spirobiindanes, which can show no π-π interaction because of geometrical constraints, are known to form only 1:1 complexes with TCNE[8b]. It may well be that a contribution towards the stability of TCNE complexes resulting from effects other than π-π in-

Table 2. ^{1}H-NMR chemical shifts (δ) and complexation shifts ($\Delta\delta = \delta_{complex} - \delta_{uncomplexed}$ values in parentheses) for [2.2]MCPs **2**, **3**, **8** and their tricarbonylchromium complexes **9**–**14** in $CDCl_3$ at 25 °C



	M^1	M^2	X–X
2	–	–	(*E*) –CH=CH–
9	$Cr(CO)_3$	–	(*E*) –CH=CH–
10	$Cr(CO)_3$	$Cr(CO)_3$	(*E*) –CH=CH–
3	–	–	(*Z*) –CH=CH–
11	$Cr(CO)_3$	–	(*Z*) –CH=CH–
12	$Cr(CO)_3$	$Cr(CO)_3$	(*Z*) –CH=CH–
8	–	–	$–CH_2CH_2–$
13	$Cr(CO)_3$	–	$–CH_2CH_2–$
14	$Cr(CO)_3$	$Cr(CO)_3$	$–CH_2CH_2–$

	H-12,14	H-13	H-16	H-4,6	H-4',6'	H-12',13',14'	H-16'
2	6.97		3.68	7.01			
9	5.06 (–1.91)	5.24 (–1.73)	1.97 (–1.71)	7.07 (+0.06)	7.03 (+0.02)	7.01 (+0.04)	3.74 (+0.06)
10	5.06 (–1.91)	5.23 (–1.74)	2.01 (–1.67)	7.09 (+0.08)			
3	6.97		3.64	6.66			
11	5.05 (–1.92)	5.25 (–1.72)	1.93 (–1.71)	6.72 (+0.06)	6.69 (+0.03)	7.01 (+0.04)	3.71 (+0.07)
12	5.08 (–1.89)	5.28 (–1.69)	1.98 (–1.66)	6.75 (+0.09)			
8	6.90		3.54	6.82			
13	5.00 (–1.90)	5.16 (–1.74)	1.83 (–1.71)	6.86 (+0.04)	6.83 (+0.01)	6.93 (+0.03)	3.59 (+0.05)
14	5.02 (–1.88)	5.18 (–1.72)	1.86 (–1.68)	6.86 (+0.04)			

Table 3. Charge-transfer bands (λ_{CT}) of **9**–**14** in dichloromethane ($5 \cdot 10^{-5}$ M)

	λ_{CT} (nm)	ε		λ_{CT} (nm)	ε	$\Delta\lambda_{CT}$ (nm)
9	319	16527	**10**	324	28047	5
11	320	12423	**12**	324	27320	4
13	324	11044	**14**	324	23596	0

teraction (multipoles, induced multipole and dispersion forces) cannot be taken into account sufficiently.

Figure 4. Job plot of charge-transfer complexes of bis[2.2]MCPs **2**, **3**, and **8** with TCNE in dichloromethane ($1 \cdot 10^{-2}$ M)

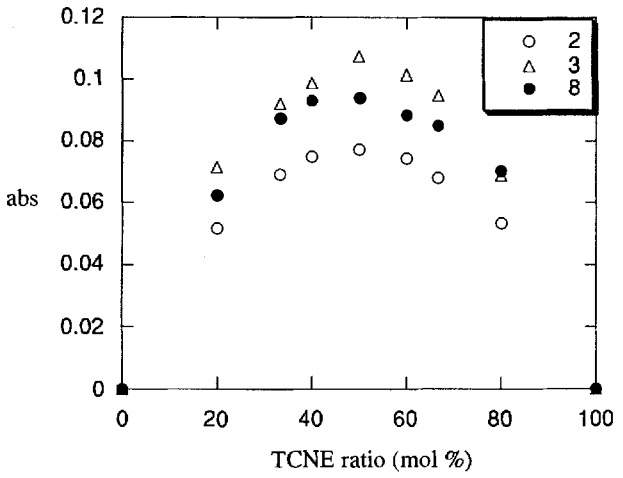
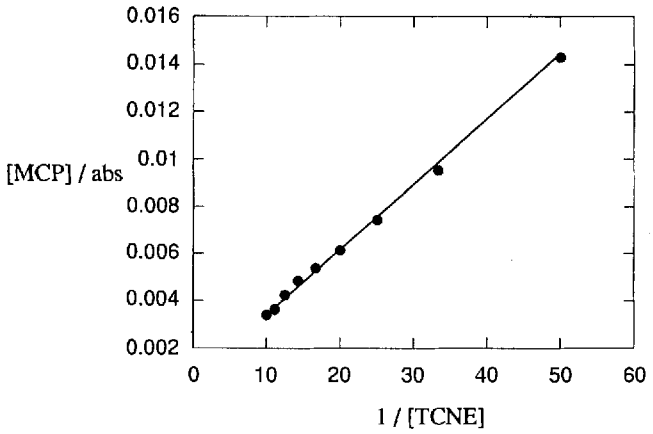


Figure 5. Benesi-Hildebrand plot of charge-transfer complex of **2** with TCNE in dichloromethane (**2**: $2 \cdot 10^{-4}$ M, TCNE: $2 \cdot 10^{-2} \sim 1 \cdot 10^{-1}$ M); the correlation coefficient (R) is 0.999, the equilibrium constant (K) is 2.97 mol^{-1}, the molar extinction coefficient (ε) is 1259 mol^{-1} cm^{-1}



Conclusion

In summary, the novel compounds (*E*)- and (*Z*)-bis[2.2]MCPs **2** and **3** constitute structures with layered π systems. The X-ray crystallographic analyses of **2** and **3** show the ethene linkage of the molecules to be situated above the top (outer) and bottom (outer) benzene rings at the short distance of ca. 3.3 Å. This geometry should favor a π-π interaction between the outer ring systems by the central stilbene subunit. Bis[2.2]MCPs **2** and **3** form charge-transfer complexes with TCNE. Complexation with tricarbonylchromium leads to the 1:1 complexes **9** and **11** and the 1:2 complexes **10** and **12**. The effects of π-π interaction in [2.2]MCPs in general are small, especially when compared with [2.2]PCPs due to the effectively different geometrical arrangement of the rings in the two systems. Thus, while electronic interactions can be followed with great success even in multi-layered [2.2]PCPs[12f] and their complexes[8c], this cannot be done with the same case in systems constructed with [2.2]MCP units. Nevertheless, analysis of the charge-transfer bands of the complexes **9**–**12** suggests a weak π-π interaction involving the outer ring systems and the central π linkage of the two [2.2]MCP subunits. The electronic interaction would be essentially distinguished into the two types of π-π interaction (type **C** and type **D**) proposed in the introductory part. However, it is not clear which type of interaction is dominant in bis[2.2]MCP systems. Further studies on the bis[2.2]MCPs connected by a π system are in progress.

Experimental

Melting points: Uncorrected values. – IR (KBr): Jasco IR-700, Nippon Denshi JIR-AQ2OM. – ^1H and ^{13}C NMR: Joel EX-270, in $CDCl_3$, tetramethylsilane as reference. – MS: Jeol JMS-01-SG-2, EI (75 eV). – Elemental analyses: Yanako MT-5. – UV: Hitachi 220A spectrophotometer, in cyclohexane and dichloromethane.

(E)-8,8'-(Ethene-1,2-diyl)bis(5-tert-butyl[2.2]metacyclophane) (**2**): To a suspension of $TiCl_3(DME)_{1.5}$ (2314 mg, 8.0 mmol) in dry DME (40 ml), Zn-Cu (2190 mg, 30.8 mmol) was added under argon, and the mixture was heated at reflux for 2 h. After cooling to room temp. a solution of **1**[3d] (585 mg, 2.0 mmol) in dry-DME (4 ml) was added dropwise within 1 min, and the mixture was heated at reflux for 6 h. After cooling to room temp., the reaction mixture was diluted with ether, filtered through a pad of Florisil, and evaporated in vacuo. The residue was purified by silica gel column chromatography by eluting with hexane/ether (50:1) to give **2** in 78% yield (433 mg, 0.784 mmol), colorless needles (ethanol), m.p. 289–290°C. – IR (KBr): $\tilde{\nu}$ = 2990 cm^{-1}, 2960, 1590, 1480, 1460, 1430, 1360, 1265, 1180, 970, 950, 870, 785, 730, 715. – ^1H NMR ($CDCl_3$): δ = 1.36 (s, 18H, *t*Bu), 2.11 (dt, *J* = 4.6, 12.2 Hz, 4H, C_2H_4), 2.42 (dt, *J* = 4.0, 12.2 Hz, 4H, C_2H_4), 2.74 (ddd, *J* = 2.6, 4.6, 12.2 Hz, 4H, C_2H_4), 2.89 (ddd, *J* = 2.6, 4.0, 12.2 Hz, 4H, C_2H_4), 3.68 (br. s, 2H, ArH), 3.83 (s, 2H, olefin), 6.97 (s, 6H, ArH), 7.01 (s, 4H, ArH). – ^{13}C NMR ($CDCl_3$): δ = 31.57 [q, $C(CH_3)_3$], 34.23 [s, $C(CH_3)_3$], 37.13, 41.49 (t, CH_2CH_2), 123.07 (d, ArCH-4,6), 125.82 (d, ArCH-12,14), 126.77 (d, ArCH-13), 131.93 (d, olefin), 134.16 (d, ArCH-16), 136.95, 138.63 (s, ArC), 143.27 (s, ArC-8), 150.58 (s, ArC-5). – MS, *m/z* (%): 552 (100) [M^+]. – UV (cyclohexane): λ_{max} (lg ε) = 216 nm (4.72), 280 (4.05). – $C_{42}H_{48}$ (552.8): calcd. C 91.25, H 8.75; found C 90.95, H 8.85.

(E)-1,1'-(Ethene-1,2-diyl)bis(4-tert-butyl-2,6-dimethylbenzene) (**5**) (118 mg, 75%, 0.339 mmol) was obtained from **4**[3b] (190 mg, 1.0 mmol), $TiCl_3(DME)_{1.5}$ (1157 mg, 4.0 mmol), and Zn-Cu (1095 mg, 15.4 mmol) in dry DME (20 ml). Colorless needles (hexane), m.p. 198–200°C. – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 2930, 2880, 1605, 1480, 1460, 1355, 1300, 1230, 1200, 975, 860, 740. – ^1H NMR ($CDCl_3$): δ = 1.33 (s, 18H, *t*Bu), 2.42 (s, 12H, Me), 6.58 (s, 2H, olefin), 7.12 (s, 4H, ArH). – ^{13}C NMR ($CDCl_3$): δ = 22.70 (q, CH_3), 32.29 [q, $C(CH_3)_3$], 35.22 [s, $C(CH_3)_3$], 125.91 (d, ArCH), 132.97 (d, olefin), 135.80 (s, ArC-1), 136.64 (s, ArC-2,6), 150.42 (s, ArC-4). – MS, *m/z* (%): 348 (100) [M^+], 333 (92) [M^+ – Me]. – UV (cyclohexane): λ_{max} (lg ε) = 214 nm (4.55), 264 (4.22). – $C_{26}H_{36}$ (348.6): calcd. C 89.59, H 10.41; found C 89.26, H 10.40.

(Z)-8,8'-(Ethene-1,2-diyl)bis(5-tert-butyl[2.2]metacyclophane) (**3**): A solution of **2** (166 mg, 0.3 mmol) in degassed benzene (5 ml) was irradiated with a high-pressure mercurry lamp at 5°C for 1 h under argon. The reaction mixture was evaporated in vacuo. The residue was purified by silica gel column chromatography by eluting with hexane/ether (50:1) to give **3** in 69% yield (115 mg, 0.208

mmol) and unchanged **2** in 10% yield (17 mg, 0.031 mmol). **3**: Colorless prisms (hexane), m.p. 260–261 °C. – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 1590, 1475, 1355, 1175, 865, 780, 715. – ^1H NMR ($CDCl_3$): δ = 1.22 (s, 18H, *t*Bu), 1.97 (dt, *J* = 3.6, 12.2 Hz, 4H, C_2H_4), 2.09 (dt, *J* = 3.6, 12.2 Hz, 4H, C_2H_4), 2.45 (dt, *J* = 12.2, 3.6 Hz, 4H, C_2H_4), 2.81 (dt, *J* = 12.2, 3.6 Hz, 4H, C_2H_4), 3.56 (s, 2H, olefin), 3.64 (br. s, 2H, ArH), 6.66 (s, 4H, ArH), 6.97 (s, 6H, ArH). – ^{13}C NMR ($CDCl_3$): δ = 31.45 [q, $C(CH_3)_3$], 34.09 [s, $C(CH_3)_3$], 36.69, 41.17 (t, CH_2CH_2), 121.38 (d, ArCH-4,6), 125.68 (d, ArCH-12,14), 126.68 (d, ArCH-13), 128.98 (d, olefin), 135.24 (d, ArCH-16), 137.09, 137.66 (s, ArC), 140.91 (s, ArC-8), 150.26 (s, ArC-5). – MS, *m/z* (%): 552 (81) [M^+], 57 (100). – UV (cyclohexane): λ_{max} (lg ε) = 218 nm (4.69), 280 (3.77). – $C_{42}H_{48}$ (552.8): calcd. C 91.25, H 8.75; found C 91.43, H 8.77.

(Z)-1,1'-(Ethene-1,2-diyl)bis(4-tert-butyl-2,6-dimethylbenzene) (**6**) (293 mg, 84%, 0.841 mmol) was obtained from **5** (349 mg, 1.0 mmol) in benzene (15 ml). Unchanged **5** was recovered in 4% yield (13 mg, 0.0373 mmol). Colorless prisms (hexane), m.p. 88–89 °C. – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 1600, 1480, 1440, 1355, 860, 760. – ^1H NMR ($CDCl_3$): δ = 1.27 (s, 18H, *t*Bu), 1.97 (s, 12H, Me), 6.63 (s, 2H, olefin), 6.93 (s, 4H, ArH). – ^{13}C NMR ($CDCl_3$): δ = 20.61 (q, CH_3), 31.32 [q, $C(CH_3)_3$], 34.16 [s, $C(CH_3)_3$], 124.73 (d, ArCH), 129.99 (d, olefin), 134.36 (s, ArC-1), 135.29 (ArC-2,6), 149.38 (s, ArC-4). – MS, *m/z* (%): 348 (100) [M^+], 335 (35) [M^+ – Me], 57 (89). – UV (cyclohexane): λ_{max} (lg ε) = 214 nm (4.50), 261 (4.21). – $C_{26}H_{36}$ (348.6): calcd. C 89.59, H 10.41; found C 89.26, H 10.48.

8,8'-(Ethane-1,2-diyl)bis(5-tert-butyl[2.2]metacyclophane) (**8**): To a solution of **7**[3d] (1072 mg, 3.0 mmol) in dry THF (15 ml) a 1.01 M cyclohexane/ether solution of PhLi (15 ml, 15.3 mmol) was added dropwise under argon, and the mixture was heated at reflux for 1.5 h. After cooling to room temp., the reaction mixture was poured into ice/water and extracted with ether. The extracts were washed with water, and the solvent was evaporated in vacuo. The residue was recrystallized from hexane to give **8** in 93% yield (775 mg, 1.40 mmol). Colorless prisms (hexane), m.p. 235–237 °C. – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 2870, 1590, 1470, 1450, 1430, 1355, 1180, 945, 865, 780, 710. – ^1H NMR ($CDCl_3$): δ = 0.46 (s, 4H, C_2H_4), 1.32 (s, 18H, *t*Bu), 1.99 (dt, *J* = 5.0, 12.2 Hz, 4H, C_2H_4), 2.22 (dt, *J* = 4.3, 12.2 Hz, 4H, C_2H_4), 2.60 (ddd, *J* = 2.3, 5.0, 12.2 Hz, 4H, C_2H_4), 2.84 (ddd, *J* = 2.3, 4.3, 12.2 Hz, 4H, C_2H_4), 3.54 (br. s, 2H, ArH), 6.82 (s, 4H, ArH), 6.90 (s, 6H, ArH). – MS, *m/z* (%): 554 (70) [M^+], 277 (95) [M^+/2], 57 (100). – $C_{42}H_{50}$ (554.9): calcd. C 90.92, H 9.08; found C 90.55, H 9.24.

Complexation Reaction of **2** *with Hexacarbonylchromium Affording* **9** *and* **10**: To a solution of **2** (221 mg, 0.4 mmol) in dry di-*n*-butyl ether (4 ml) and dry THF (0.4 ml) hexacarbonylchromium (177 mg, 0.8 mmol) was added under argon, and the mixture was heated at reflux for 24 h. After cooling to room temp., the reaction mixture was filtered through a pad of celite, washed with dichloromethane, and evaporated in vacuo. Separation and purification of the residue by silica gel column chromatography by eluting with hexane/ether (10:1) gave unchanged **2** in 19% yield (42 mg, 0.076 mmol), **9** in 59% yield (162 mg, 0.236 mmol), and **10** in 16% yield (52 mg, 0.064 mmol).

Tricarbonyl[11–16-η⁶-(E)-8,8'-(ethene-1,2-diyl)bis(5-tert-butyl[2.2]metacyclophane)]chromium(0) (**9**): Yellow powder (hexane/dichloromethane), m.p. 224–226 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1}, 2940, 1970 (CO), 1870 (CO), 1850 (CO), 1590, 1470, 1440, 1360, 1260, 1180, 1095, 1030, 870, 800, 720, 670. – ^1H NMR ($CDCl_3$): δ = 1.35, 1.38 (s, each 9H, *t*Bu), 1.85 (dt, *J* = 4.9, 12.1 Hz, 2H, C_2H_4), 1.97, 3.74 (br. s, each 1H, ArH), 2.17, 2.47 (dt, *J* = 4.4, 12.1 Hz, each 2H, C_2H_4), 2.55–2.99 (m, 10H, C_2H_4), 3.97, 4.71 (d, *J* = 16.5 Hz, each 1H, olefin), 5.06 (d, *J* = 6.9 Hz, 2H, ArH), 5.24 (t, *J* = 6.9 Hz, 1H, ArH), 7.01 (s, 3H, ArH), 7.03, 7.07 (s, each 2H, ArH). – MS, *m/z* (%): 552 (9) [M^+ – $Cr(CO)_3$], 57 (100). – UV (dichloromethane): λ_{max} (lg ε) = 230 nm (4.65), 319 (4.22). – $C_{45}H_{48}CrO_3$ (688.9): calcd. C 78.46, H 7.02; found C 78.44, H 7.13.

[11–16-η⁶,11'–16'-η⁶-(E)-8,8'-(Ethene-1,2-diyl)bis(5-tert-butyl[2.2]metacyclophane)]bis[tricarbonylchromium(0)] (**10**): Yellow powder (hexane/dichloromethane), m.p. >218 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 2870, 1950 (CO), 1870 (CO), 1590, 1475, 1430, 1390, 1360, 1180, 1145, 970, 870, 660. – ^1H NMR ($CDCl_3$): δ = 1.37 (s, 18H, *t*Bu), 1.80–2.06 (m, 4H, C_2H_4), 2.01 (br. s, 2H, ArH), 2.55–2.82 (m, 8H, C_2H_4), 2.86–3.07 (m, 4H, C_2H_4), 4.88 (s, 2H, olefin), 5.06 (d, *J* = 6.3 Hz, 4H, ArH), 5.23 (t, *J* = 6.3 Hz, 2H, ArH), 7.09 (s, 4H, ArH). – UV (dichloromethane): λ_{max} (lg ε) = 230 nm (4.72), 324 (4.45). – $C_{48}H_{48}Cr_2O_6$ (824.9): calcd. C 69.89, H 5.86; found C 69.50, H 5.81.

Complexation Reaction of **3** *with Hexacarbonylchromium Affording* **11** *and* **12**: The reaction of **3** (221 mg, 0.4 mmol) with hexacarbonylchromium (177 mg, 0.8 mmol) in di-*n*-butyl ether (4 ml) and THF (0.4 ml) gave unchanged **3** in 17% yield (38 mg, 0.069 mmol), **11** in 57% yield (157 mg, 0.228 mmol), and **12** in 21% yield (69 mg, 0.084 mmol).

Tricarbonyl[11–16-η⁶-(Z)-8,8'-(ethene-1,2-diyl)bis(5-tert-butyl[2.2]metacyclophane)]chromium(0) (**11**): Yellow powder (hexane/dichloromethane), m.p. 258–260 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3038 cm^{-1}, 2950, 2856, 1957 (CO), 1873 (CO), 1593, 1478, 1444, 1361, 1181, 866, 792, 759, 718, 665, 628. – ^1H NMR ($CDCl_3$): δ = 1.22, 1.24 (s, each 9H, *t*Bu), 1.60–2.90 (m, 16H, C_2H_4), 1.93, 3.71 (br. s, each 1H, ArH), 3.81, 4.49 (d, *J* = 11.5 Hz, each 1H, olefin), 5.05 (d, *J* = 6.3 Hz, 2H, ArH), 5.25 (t, *J* = 6.3 Hz, 1H, ArH), 6.69, 6.72 (s, each 2H, ArH), 7.01 (s, 3H, ArH). – MS, *m/z* (%): 552 (62) [M^+ – $Cr(CO)_3$], 57 (100). – UV (dichloromethane): λ_{max} (lg ε) = 231 nm (4.61), 320 (4.09). – $C_{45}H_{48}CrO_3$ (688.9): calcd. C 78.46, H 7.02; found C 78.39, H 7.10.

[11–16-η⁶,11'–16'-η⁶-(Z)-8,8'-(Ethene-1,2-diyl)bis(5-tert-butyl[2.2]metacyclophane)]bis[tricarbonylchromium(0)] (**12**): Yellow prisms (hexane/dichloromethane), m.p. 261–265 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 2880, 1950 (CO), 1860 (CO), 1590, 1435, 1395, 1355, 1180, 1000, 870, 830, 765, 660. – ^1H NMR ($CDCl_3$): δ = 1.25 (s, 18H, *t*Bu), 1.65–1.86 (m, 4H, C_2H_4), 1.98 (br. s, 2H, ArH), 2.23–2.42 (m, 4H, C_2H_4), 2.45–2.68 (m, 8H, C_2H_4), 4.78 (s, 2H, olefin), 5.08 (d, *J* = 6.3 Hz, 4H, ArH), 5.28 (t, *J* = 6.3 Hz, 2H, ArH), 6.75 (s, 4H, ArH). – UV (dichloromethane): λ_{max} (lg ε) = 230 nm (4.74), 324 (4.44). – $C_{48}H_{48}Cr_2O_6$ (824.9): calcd. C 69.89, H 5.86; found C 69.83, H 5.87.

Complexation Reaction of **8** *with Hexacarbonylchromium Affording* **13** *and* **14**: The reaction of **8** (222 mg, 0.4 mmol) with hexacarbonylchromium (88 mg, 0.4 mmol) in di-*n*-butyl ether (4 ml) and THF (0.4 ml) gave unchanged **8** in 48% yield (106 mg, 0.191 mmol), **13** in 31% yield (85 mg, 0.123 mmol), and **14** in 11% yield (37 mg, 0.045 mmol).

Tricarbonyl[11–16-η⁶-8,8'-(ethane-1,2-diyl)bis(5-tert-butyl-[2.2]metacyclophane)]chromium(0) (**13**): Yellow needles (hexane/dichloromethane), m.p. 221–223 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3042 cm^{-1}, 2948, 2862, 1957 (CO), 1870 (CO), 1595, 1478, 1453, 1361, 1181, 870, 716, 665, 629. – ^1H NMR ($CDCl_3$): δ = 0.65, 1.04 (t, *J* = 6.9 Hz, each 2H, CH_2), 1.31, 1.33 (s, each 9H, *t*Bu), 1.72 (dt, *J* = 5.3, 12.0 Hz, 2H, C_2H_4), 1.83, 3.59 (br. s, each 1H, ArH), 2.02 (dt, *J* = 5.0, 12.0 Hz, 2H, C_2H_4), 2.23, 2.37 (dt, *J* = 4.0, 12.0 Hz, each 2H, C_2H_4), 2.48–2.91 (m, 8H, C_2H_4), 5.00 (d, *J* = 6.3 Hz,

2H, ArH), 5.16 (t, J = 6.3 Hz, 1H, ArH), 6.83, 6.86 (s, each 2H, ArH), 6.93 (s, 3H, ArH). – MS, *m/z* (%): 554 (100) [M^+ – $Cr(CO)_3$], 57 (51). – UV (dichloromethane): λ_{max} (lg ε) = 231 nm (4.59), 324 (4.04). – $C_{45}H_{50}CrO_3$ (690.9): calcd. C 78.23, H 7.29; found C 78.11, H 7.33.

[11–16-η⁶,11′–16′-η⁶-8,8′-(Ethane-1,2-diyl)bis(5-tert-butyl-[2.2]metacyclophane)]bis[tricarbonylchromium(0)] (**14**): Yellow plates (hexane/dichloromethane), m.p. 243–245°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1}, 1956 (CO), 1877 (CO), 1477, 1450, 1402, 1363, 1183, 666, 628. – ^1H NMR ($CDCl_3$): δ = 1.25 (s, 4H, C_2H_4), 1.32 (s, 18H, *t*Bu), 1.60–1.83 (m, 4H, C_2H_4), 1.86 (br. s, 2H, ArH), 2.25–2.80 (m, 12H, C_2H_4), 5.02 (d, J = 5.6 Hz, 4H, ArH), 5.18 (t, J = 5.6 Hz, 2H, ArH), 6.86 (s, 4H, ArH). – UV (cyclohexane): λ_{max} (lg ε) = 231 nm (4.72), 324 (4.37). – $C_{48}H_{50}Cr_2O_6$ (826.9): calcd. C 69.72, H 6.09; found C 69.49, H 6.11.

Tricarbonyl[η⁶-(E)-4,4′-(ethene-1,2-diyl)bis(3,5-dimethyl-tert-butylbenzene)]chromium(0) (**15**): The reaction of **5** (139 mg, 0.4 mmol) with hexacarbonylchromium (88 mg, 0.4 mmol) in di-*n*-butyl ether (4 ml) and THF (0.4 ml) gave unchanged **5** in 52% yield (73 mg, 0.209 mmol) and **15** in 17% yield (32 mg, 0.066 mmol). Yellow needles (hexane), m.p. 180–181°C. – IR (KBr): $\tilde{\nu}$ = 2975 cm^{-1}, 1930 (CO), 1870 (CO), 1850 (CO), 1480, 1455, 1370, 1030, 975, 870, 670. – ^1H NMR ($CDCl_3$): δ = 1.33 (s, 18H, *t*Bu), 2.32, 2.41 (s, each 6H, Me), 5.23, 7.12 (s, each 2H, ArH), 6.32, 6.76 (d, J = 17.1 Hz, each 1H, olefin). – MS, *m/z* (%): 484 (15) [M^+], 400 (100) [M^+ – 3 CO]. – $C_{29}H_{36}CrO_3$ (484.6): calcd. C 71.88, H 7.49; found C 71.54, H 7.52.

Tricarbonyl[η⁶-(Z)-1,1′-(ethene-1,2-diyl)bis(4-tert-butyl-2,6-dimethylbenzene)]chromium(0) (**16**): The reaction of **6** (105 mg, 0.3 mmol) with hexacarbonylchromium (66 mg, 0.3 mmol) in di-*n*-butyl ether (3 ml) and THF (0.3 ml) gave unchanged **6** in 54% yield (56 mg, 0.161 mmol) and **16** in 17% yield (25 mg, 0.052 mmol). Yellow prisms (hexane), m.p. 158–159°C. – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 1945 (CO), 1880 (CO), 1860 (CO), 1480, 1460, 1435, 1375, 1360, 1260, 1220, 1100, 1030, 870, 800, 765, 670. – ^1H NMR ($CDCl_3$): δ = 1.27, 1.28 (s, each 9H, *t*Bu), 1.89, 2.03 (s, each 6H, Me), 5.14, 6.97 (s, each 2H, ArH), 6.46, 6.76 (d, J = 12.5 Hz, each 1H, olefin). – MS, *m/z* (%): 484 (17) [M^+], 400 (100) [M^+ – 3 CO], 348 (8) [M^+ – $Cr(CO)_3$]. – $C_{29}H_{36}CrO_3$ (484.6): calcd. C 71.88, H 7.49; found C 71.99, H 7.59.

Charge-Transfer Complexation of **2**, **3**, *and* **8** *with Tetracyanoethylene:* Tetracyanoethylene was recrystallized from chlorobenzene and sublimed at 125°C/1–2 Torr. The complexes were prepared in dichloromethane. In the case of Figure 4, the total concentration of [2.2]MCPs **2**, **3**, **8** and TCNE was 0.02 M, and their ratio was varied from 0.0 to 1.0. In the case of Figure 5, the concentration of TCNE was varied from 0.02 to 0.1 M, while the concentration of **2** was kept constant at $2 \cdot 10^{-4}$ M. The equilibrium constant (K) and molar extinction (ε) were obtained according to ref.[14]: [MCP]/abs = $1/(K \cdot \varepsilon \cdot [TCNE]) + 1/\varepsilon$. [MCP]: concentration of **2**; abs: absorbance; [TCNE]: concentration of TCNE.

X-Ray Crystallographic Analysis of **2**: Intensity data were collected on an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods (SIR 88)[15]. All non-hydrogen atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located by calculation. All non-hydrogen atoms treated anisotropically were refined by full-matrix least-squares calculation. Hydrogen atoms treated isotropically were refined by full-matrix least-squares calculation; their isotropic thermal parameters were held fixed at 5.0 Å^2. The *tert*-butyl groups are disordered [site occupation factors (C18, C19, C20) = 0.90, (C17′, C19′) = 0.50]. All calculations were performed with a micro VAX 3100 computer using MolEN[16]. The final cell parameters and specific data collection parameters are summarised in Table 4.

Table 4. Crystallographic data for [2.2]MCPs **2** and **3**

	2	**3**
Formula	$C_{42}H_{48}$	$C_{42}H_{48}$
Mw	552.85	552.85
Crystal system	orthorhombic	monoclinic
Space group	Pbca	$P2_1/a$
a [Å]	10.900 (35)	20.502 (2)
b [Å]	41.247 (4)	14.913 (2)
c [Å]	15.213 (2)	11.354 (3)
V [Å^3]	6839.8	3386.5
D_{calc} [g cm^{-3}]	1.07	1.08
Z	8	4
μ(Cu-Kα) [Å]	1.54184	1.54184
Crystal size [mm]	0.15 x 0.11 x 0.50	0.40 x 0.40 x 0.20
T [°C]	23±1	23±1
Abs. correct	empirical	empirical
Scan mode	ω-2θ	ω-2θ
Scan range (θ) [°]	20 - 42	21 - 42
Measured data	6500	12167
Unique data	5813	6064
Observed	2157	3640
No. of parameters	593	479
Obs. criterion	$Fo \geq 3\sigma(Fo)$	$Fo \geq 3\sigma(Fo)$
R[a]	0.104	0.097
R_w[b]	0.117	0.144
Weighting scheme	$w = 4Fo^2 / \sigma^2(Fo^2)^2$	$w = 4Fo^2 / \sigma^2(Fo^2)^2$
Residual density [e Å^{-3}]	0.43 to -0.42	0.93 to -0.44

[a] $R = [\Sigma||Fo|-|Fc||]/\Sigma|Fo|]$. – [b] $Rw = /[\Sigma w(|Fo|-|Fc|)^2]/[\Sigma wFo^2]^{1/2}$.

X-Ray Crystallographic Analysis of **3**: Intensity data were collected on an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods (SIR 88)[15]. All non-hydrogen atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bound. All non-hydrogen atoms treated anisotropically were refined by full-matrix least-squares calculation. The *tert*-butyl group is disordered [site occupation factor (C20′) = 0.60]. All calculations were performed with a micro VAX 3100 computer using MolEN[16]. The final cell parameters and specific data collection parameters are summarised in Table 4[17].

[1] For reviews see: F. Vögtle, P. Neumann, *Angew. Chem.* **1972**, *84*, 75–85; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 73–83; M. P. Keehn, S. M. Rosenfeld, *Cyclphanes*, Academic Press, New York, **1983**; F. Vögtle, *Cyclophane Chemistry*, John Wiley and Sons, Chichester, **1993**.

[2] M. Tashiro, K. Koya, T. Yamato, *J. Am. Chem. Soc.* **1982**, *104*, 3707–3710; A. Tsuge, T. Ishii, S. Mataka, M. Tashiro, *J. Chem. Res. (S)* **1992**, 312–313; A. Tsuge, T. Moriguchi, S. Mataka, M. Tashiro, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 2211–2215; *Bull. Chem. Soc. Jpn.* **1994**, *67*, 277–279.

[3] [3a] M. Tashiro, T. Yamato, *J. Org. Chem.* **1981**, *46*, 4556–4562. – [3b] M. Tashiro, T. Yamato, *J. Org. Chem.* **1983**, *48*, 1461–1468. – [3c] M. Tashiro, T. Arimura, T. Yamato, *Chem. Pharm. Bull.* **1983**, *31*, 370–371. – [3d] A. Tsuge, T. Ishii, T. Sawada, S. Mataka, M. Tashiro, *Chem. Lett.* **1994**, 1529–1532.

[4] J. E. McMurry, T. Lectka, J. G. Rico, *J. Org. Chem.* **1989**, *54*, 3748–3749.

[5] [5a] H. H. Jaffe, M. Orchin, *J. Chem. Soc.* **1960**, 1078–1087. – [5b] D. Gegiou, K. A. Muszkat, E. Fischer, *J. Am. Chem. Soc.* **1968**, *90*, 3907–3918. – [5c] K. Ogawa, H. Suzuki, M. Futakami, *J. Chem. Soc., Perkin Trans. 2*, **1988**, 39–43. – [5c] K. Ogawa, T. Sano, S. Yoshimura, Y. Takeuchi, K. Toriumi, *J. Am. Chem. Soc.* **1992**, *114*, 1041–1051.
[6] R. N. Beale, E. M. F. Roe, *J. Chem. Soc.* **1953**, 2755–2763.
[7] C. J. Brown, *J. Chem. Soc.* **1953**, 3278–3285; Y. Kai, N. Yasuoka, N. Kasai, *Acta Crystallogr., Sect. B*, **1977**, *33*, 754–762.
[8] [8a] D. J. Cram, D. I. Wilkinson, *J. Am. Chem. Soc.* **1960**, *82*, 5721–5723. – [8b] E. Langer, H. Lehner, *Tetrahedron* **1973**, *29*, 375–383. – [8c] H. Ohno, H. Horita, T. Otsubo, Y. Sakata, S. Misumi, *Tetrahedron Lett.* **1977**, 265–268. – [8d] A. F. Mourad, H. Hopf, *Tetrahedron Lett.* **1979**, 1209–1212. – [8e] R. H. Mitchell, T. K. Vinod, G. J. Bodwell, G. W. Bushnell, *J. Org. Chem.* **1989**, *54*, 5871–5879.
[9] W. McFarlane, S. O. Grim, *J. Organomet. Chem.* **1966**, *5*, 147–154; J. T. Price, T. S. Sorensen, *Can. J. Chem.* **1968**, *46*, 515–522; E. Langer, H. Lehner, *J. Organomet. Chem.* **1979**, *173*, 47–52.
[10] F. Vögtle, J. Schulz, M. Nieger, *Chem. Ber.* **1991**, *124*, 1415–1423; J. Schulz, M. Nieger, F. Vögtle, *ibid.* **1991**, *124*, 2797–2810; J. Schulz, S. Bartram, M. Nieger, F. Vögtle, *ibid.* **1992**, *125*, 2553–2569.
[11] G. A. Razuvaev, V. A. Kuznetsov, A. N. Egorochkin, A. A. Klimov, *J. Organomet. Chem.* **1977**, *128*, 213–218.
[12] [12a] D. J. Cram, R. H. Bauer, *J. Am. Chem. Soc.* **1959**, *81*, 5971–5977. – [12b] L. A. Singer, D. J. Cram, *J. Am. Chem. Soc.* **1963**, *85*, 1080–1084. – [12c] M. Sheehan, D. J. Cram, *J. Am. Chem. Soc.* **1969**, *91*, 3553–3558. – [12d] S. Hayashi, T. Sato, *Nippon Kagaku Zasshi* **1970**, *91*, 950–957. – [12e] D. T. Longone, H. S. Chow, *J. Am. Chem. Soc.* **1970**, *92*, 994–998. – [12f] T. Otsubo, S. Mizogami, I. Otsubo, Z. Tozuka, A. Sakagami, Y. Sakata, S. Misumi, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3519–3530. – [12g] T. Yamato, J. Matsumoto, N. Shinoda, S. Ide, M. Shigekuni, M. Tashiro, *J. Chem. Res. (S)* **1994**, 178–179.
[13] P. Job, *Ann. Chem.* **1928**, *9*, 113–134.
[14] H. A. Benesi, J. H. Hildebrand, *J. Am. Chem. Soc.* **1958**, *80*, 2778–2782.
[15] M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, D. Vitebo, *J. Appl. Crystallogr.* **1989**, *22*, 389.
[16] MolEN, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, The Netherlands, **1990**.
[17] Further details of the crystal-structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-404611 (**2**) and -404612 (**3**).

[95229]