Synthesis, Characterization, and Some Reactions of Tricarbonyl(cyclobutabenzene)chromium(0) Derivatives

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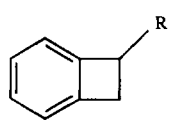
The tricarbonyl(cyclobutabenzene)chromium(0) complexes **12**–**20**, have been prepared from the free ligand and triammintricarbonylchromium(0) or hexacarbonylchromium(0). The complexes have been characterized by spectroscopic methods (IR, ^{1}H NMR, ^{13}C NMR) and mass spectrometry, and ^{1}H-NMR signal assignments have been verified by an NOE experiment. Diastereomeric ratios have been determined by ^{1}H NMR and the diastereomers of the 1-methyl derivative **16** separated by HPLC. A crystal-structure analysis is presented for *exo*-**16**. A photochemical ligand exchange takes place in 70% yield for the 1-trimethylsilyl derivative **19**. Metalation with *n*-butyllithium/tmeda at −78°C has been observed only for the aromatic and not for the benzylic protons.

Since their discovery more than thirty years ago, transition-metal complexes of cyclic conjugated π systems have attracted the interest of the chemist. Although cyclopentadienyl complexes of numerous transition metals have found use in organic synthesis, this is the case for only a few arene complexes, and the field is dominated by tricarbonylchromium(0) complexes. Investigations of indane and tetrahydronaphthalene complexes by Jackson[1c,2], Jaouen[3], des Abbayes[4], and others[5] have provided some insight into the stereochemical features of annulated species of this class of compounds. However, systems with annulated five- or six-membered rings are conformationally flexible, thus allowing the systems to avoid steric or electronic interactions by conformational changes. In contrast, compounds with smaller annulated rings are conformationally rigid. Surprisingly, only few small-ring-annulated cyclopentadienyl or arene complexes[1] have been reported. Suitable ligands in this context are cyclopropabenzene, cyclobutabenzene, and their derivatives. Tricarbonyl(cyclopropabenzene)chromium(0) is unknown[6], althouth a cyclopropanaphthalene and a cyclopropaanthracene complex have been prepared by Müller[7]. However, in these complexes the coordinated arene is not directly annulated to the small ring. Only a few cyclobutabenzene tricarbonylchromium complexes have been mentioned in the literature[1c–f]. Here, we report on the synthesis and characterization of a number of substituted tricarbonyl(cyclobutabenzene)chromium(0) derivatives and on some of their reactions.

Our interest in these compounds originates from investigations on the influence of transition-metal complexation on the reactivity of the coordinated ligands, e.g. ring opening and other reactions[8]. The material presented in this paper has in part been the subject of preliminary communications[9].

Results and Discussion

Cyclobutabenzene (**1**) and its derivatives are prepared by literature methods. 1-Chlorocyclobutabenzene (**5**) serves as a convenient source for the corresponding Grignard reagent (this should be stored at −78°C in THF solution, see Experimental). From this reagent, the substituted derivatives [1-D]**1** and **6**–**10** are easily obtained by reaction with CH_3OD or the appropriate halides in the presence of a cat-



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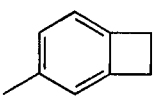

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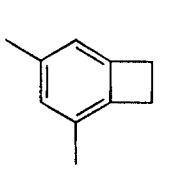

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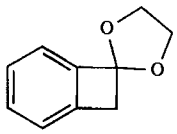

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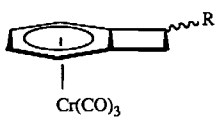

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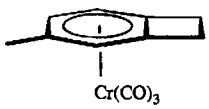

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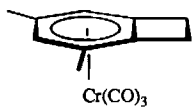

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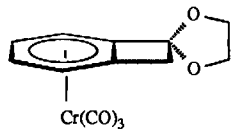

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	1, 12	[1-D]1, [1-D]12	5	6, 16	7, 17	8, 18	9, 19	10, 20	11
R	H	D	Cl	CH_3	$[CH_2]_3CH_3$	$[CH_2]_2CH{=}CH_2$	$Si(CH_3)_3$	$Sn(CH_3)_3$	OH

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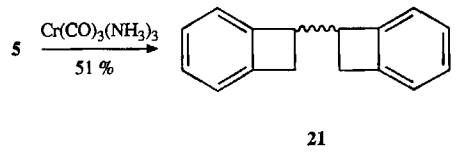
alytic amount of Li_2CuCl_4. The cyclobutabenzene derivatives are treated with $Cr(CO)_3(NH_3)_3$[10] in dioxane at 101 °C to afford the cyclobutabenzene complexes **12**–**20** in satisfactory yields (Table 1).

Table 1. Tricarbonyl(cyclobutabenzene)chromium(0) derivatives

Complex	Yield (%)	*endo/exo*[a]
12[1c]	51	–
[1-D]**12**	53	50:50
13	65	–
14	60	–
15	83	–
16	62	40:60
17	27	50:50
18	49	50:50 (40:60[b])
19	64	12:88
20	89	24:76

[a] Ratios determined by ^1H NMR. – [b] Ratio determined by HPLC.

Complexation experiments involving 1-chlorocyclobutabenzene (**5**) have been unsuccessful: coupled 1,1′-bicyclobutabenzene (**21**) is obtained in 51% yield[11]. 1-Hydroxycyclobutabenzene (**11**) reacts with $Cr(CO)_6$/di-*n*-butyl ether/THF at 120 °C[12] to give **22** (4%) and **23** (28%). The reaction of **11** with $Cr(CO)_3(NH_3)_3$ at 101 °C gives a product mixture whose mass spectrum indicates the formation of tricarbonylchromium complexes of **22** and **23**. Apparently, a ring opening of **11** followed by a disproportionation and coupling occurs.



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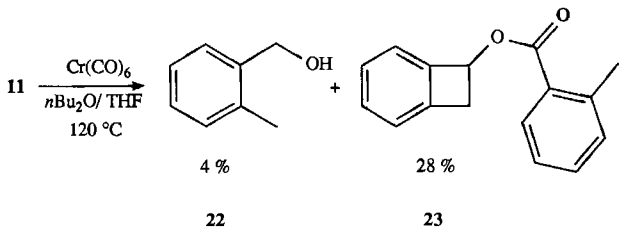


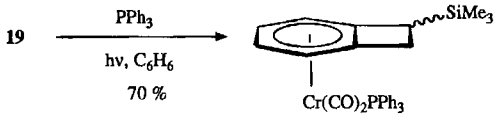
22 **23**

Complexation to the cyclobutabenzene derivatives can take place on either side of the arene π system. Depending on the substitution pattern, this has stereochemical consequences. Cyclobutabenzene (**1**) has two planes of symmetry, and complexes of this ligand are hence achiral. Substituted ligands **2**, **3**, and **4** have σ_v as the only symmetry element whose elimination by complexation causes the formation of chiral complexes. Ligands **5**–**11** are chiral, and complexation on either side of the arene π system generates another element of asymmetry, resulting in the formation of *endo* and *exo* diastereomers. Yields and *endo/exo* diastereomeric ratios of the complexes prepared are listed in Table 1.

The rather low yield of the butyl complex **17** (27%) limits the significance of the observed *endo/exo* ratio (50:50). The equimolar yield of *endo*- and *exo*-[1-D]**12** shows that H and D are not sufficiently different to allow diastereoselectivity. In most other cases the *exo* diastereomers predominate presumably for steric reasons. Highest diastereomeric excesses are observed for the 1-trimethylsilyl compound **19** (88:12) and for the 1-trimethylstannyl compound **20** (76:24). The constitution of all new compounds has been verified by spectroscopic methods (IR, ^1H NMR, ^{13}C NMR), MS, HRMS, and elemental analyses.

Two approaches are used to assign the diastereomers: 1-trimethylsilyl derivative **19** has been the subject of an NOE-NMR investigation, and the diastereomers of the 1-methyl compound **16** are separated by HPLC and separately characterized, among others by a crystal structure determination of the *exo* diastereomer.

As a representative compound, *endo/exo*-tricarbonyl[(1-trimethylsilyl)cyclobutabenzene]chromium(0) (*endo/exo*-**19**) is treated with triphenylphosphine under photochemical conditions to afford the corresponding dicarbonyltriphenylphosphine complex *exo*-**24** in 70% yield. Due to the diastereomeric ratio of *endo/exo*-**19** (12:88), the small amount of *endo*-**24** is not observed by ^1H NMR. The proton-bearing substituents at the phosphine ligand make an NOE measurement[13] possible, which confirms the assigned structure: Irradiation with the frequency assigned to *endo*-1-H causes an NOE for the signal assigned to the *ortho* protons of the PPh_3 ligand, whereas irradiation with the frequency assigned to the *ortho* protons of the PPh_3 ligand causes a corresponding NOE at the signal assigned to *endo*-1-H. This result is in accord with data collected for related compounds by Ustynyuk[14].



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For the purpose of NMR signal assignment and to elucidate the separation possibilities of diastereomers, the 1-methylcyclobutabenzene complexes *endo/exo*-**16** are separated by HPLC[15] under inert conditions. *exo*-**16** is eluted first, followed by the *endo* diastereomer. A comparison of the ^1H-NMR chemicals shifts of *endo*- and *exo*-**16** shows the expected differences for the protons bound to the cyclobutane rings. More surprisingly, differences of up to 0.3 ppm are observed for the protons bound to the aromatic systems. Since inductive effects can be excluded to account for this observation, we suggest that an interaction between $Cr(CO)_3$ and the *endo* methyl group occurs.

X-ray crystal-structure determination of *exo*-**16** provides final proof of the assigned stereochemistry. The crystal structure of *exo*-**16** (Figure 1; final atomic coordinates are given in Table 3) does not show any abnormal features. All bond lengths are within the typical range. The bonds C2a–C3, C4–C5, and C6–C6a are slighly shorter than the other

ones within the arene system[16]. This is presumably a result of the preferential adoption by the tricarbonylchromium(0) fragment of a conformation in which one of the carbonyl ligands is located below the annulated small ring of the bicyclic ligand. The orientation of a $Cr(CO)_3$ group with respect to an arene ligand annulated to another ring has been the subject of theoretical work[17].

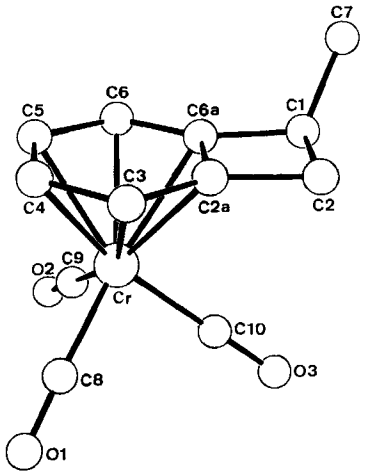
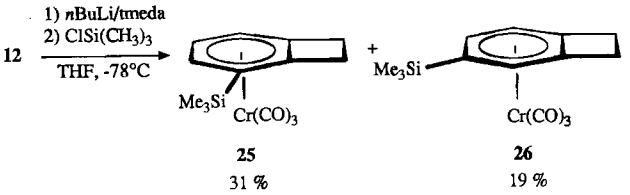


Figure 1. Crystal structure of *exo*-**16**[16]

The protons bound to the aromatic system in arenetricarbonylchromium(0) complexes show enhanced acidity compared to that of the free ligand[18]. However, reports on the sites of deprotonation of alkyl-substituted or annulated arenetricarbonylchromium(0) complexes differ remarkably, presumably as a result of the different reaction conditions applied. There are reports which suggest that deprotonation by the action of potassium *tert*-butoxide/[D_6]DMSO at room temperature occurs preferentially at the benzylic protons[19].

Cyclobutabenzene (**1**) and some of its derivatives have also been the subject of similar investigations. An early report by Finnigan[20] indicates position 3 to be the most acidic in reactions with *n*-butylpotassium. Reaction of ligand **1** with *n*-butyllithium/tmeda in diethyl ether at reflux temperature results after quenching with chlorotrimethylsilane in the formation of all three (trimethylsilyl)cyclobutabenzenes besides a 1,2-bis(trimethylsilyl) derivative[21]. The enhanced acidity of position 3 in arene systems fused to a strained ring has been rationalized by Streitwieser[22].

It is therefore of interest to investigate the behavior of tricarbonyl(cyclobutabenzene)chromium(0) (**12**). If deprotonation occurs in a selective manner, quenching reactions could provide an access to derivatives of **12**. **12** has been treated with *n*-butyllithium/tmeda followed by quenching of the anion with chlorotrimethylsilane in THF at −78°C (in contrast to the conditions used by Eaborn for the reaction of ligand **1**[21]), and the 3-trimethylsilyl derivative **25** and the 4-trimethylsilyl derivative **26** are formed as a 62:38 mixture in satisfactory overall yield[23]. The product **20** of a benzylic deprotonation has not been observed. The electron withdrawal from C-3 by the fusion of the strained ring[22] and the electron withdrawal by the $Cr(CO)_3$ complexation apparently complement each other. Possibly, a benzylic anion is less favored, since the rigidity of the small annulated ring does not allow the doubly occupied sp^3 orbital to orient itself favorably parallel to the arene π orbitals. Due to the electronic requirements of the $Cr(CO)_3$ group this might be more important for **12** than for **1**.



The thermochemical behavior of tricarbonyl(cyclobutabenzene)chromium(0) derivatives is of special interest with respect to ring opening reactions[8]. To gain insight into this, differential scanning calorimetry (DSC) is applied to a number of tricarbonyl(cyclobutabenzene)chromium(0) derivatives. Figure 2 shows a typical DSC plot for the acetal complex **15**.

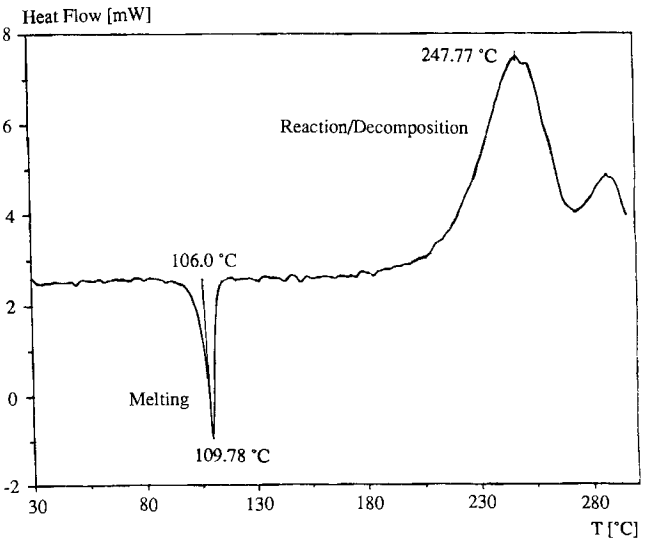


Figure 2. DSC plot of **15** (heating rate 10 K/min)

To determine the influence of the complexation on the $Cr(CO)_3$ group, the result is compared with that obtained for the less volatile free ligand **4**. Of additional interest is whether the annulated small ring influences the thermochemistry of the compounds.

The DSC plot of **15** shows endothermic melting with a maximum of the heat flow at 110°C. At temperatures above 180°C an exothermic process is observable, and a similar process can be observed in the DSC plot of ligand **4**. All the DSC results are compiled in Table 2.

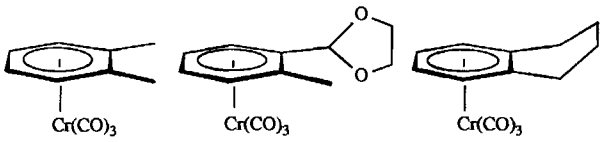
In order to determine the effect of complexation of the ligands on the $Cr(CO)_3$ group, the data obtained for some cyclobutabenzene complexes have been compared with those obtained for the free ligands along with data obtained for the ring-opened analogs **27**[24] and **28**[25] and for tricarbo-

Table 2. DSC results (heating rate 10 K/min)

Compound	m.p. [°C]	Start temp.[a] [°C]	Max. temp.[b] [°C]	Dec. temp.[c] [°C]
12	88.5	220	268	279
16	(38.2)[e]	217	273	289
15	106.0	180	248	273
27	90.4	–	–	237
28	120.4	–	–	225–255
29	118	–	–	252
1[d]	–	–	–	–
7[d]	–	–	–	–
4	–	162	234	–

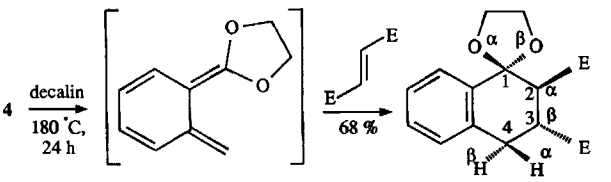
[a] Temperature, at which the plot leaves the base line. – [b] Temperature of maximum heat flow. – [c] Decomposition temperature of the DSC sample. – [d] DSC failed due to low boiling point, material (neat or dissolved in pentadecane) evaporated. – [e] M.p. determined by DSC is insignificant, because the diastereomeric mixture of **16** has been used.

nyl(tetrahydronaphthalene)chromium(0)[26] (**29**) as a representative compound containing a medium-sized annulated ring. The data clearly indicate that the exothermic process observed at temperatures above 180°C for cyclobutabenzene complexes and above 160°C for the free ligands is a typical feature of the small-ring-annulated cyclobutabenzene derivatives. Neither the ring-opened complexes **27** and **28** nor the tetrahydronaphthalene complex **29** show a comparable behavior.



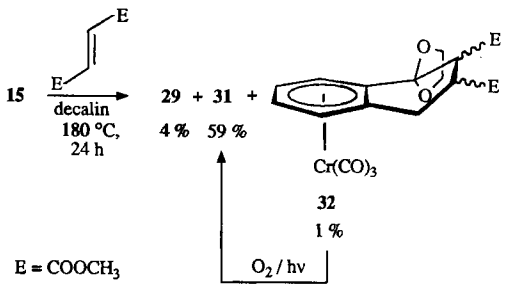
27 **28** **29**

Two questions arise: Is the same exothermic process operative for the complexes and the free ligands, and if so, what is its nature? To answer these questions we have decided to investigate the reaction of the acetal complex **15** on a preparative scale. **15** has been chosen because of its low reaction temperature (Table 2). **4** is reported *not* to undergo a thermal ring opening to the corresponding *ortho*-quinodimethane derivative **30**, but to decompose at elevated temperatures with the formation of 1-oxocyclobutabenzene[27]. In contrast to these literature reports, we have succeeded in opening the ring in **4** thermally by refluxing in decalin for 24 h and trapping the *ortho*-quinodimethane derivative **30** with dimethyl fumarate. Cycloadduct **31** is obtained in 68% yield and characterized spectroscopically (IR, ^{1}H, ^{13}C NMR), by MS, and by elemental analysis.



E = COOCH3 **30** **31**

The corresponding reaction with complex **15** is less successful. It is carried out in decalin (tetralin contents 0.17%, GC) as the solvent and yields decomplexed cycloadduct **31** and tetrahydronaphthalene complex **29** besides a small amount of a tricarbonylchromium(0) complex. The mass spectrum of this compound as well as the ^{1}H-NMR spectrum of the reaction mixture are in accord with the structure of the cycloadduct complex **32**. Since the amount isolated is too small to allow for complete spectroscopic characterization, the product mixture is treated with air in order to decompose the complex, and the material obtained is analyzed by GC. Since no additional compound is detected, in connection with the mass spectrum the formation of cycloadduct complex **32**, albeit in small yield, is suggested. The formation of the tetrahydronaphthalene complex **29** indicates that arene exchange reactions take place under the reaction conditions used. In order to avoid these reactions, we are currently investigating the synthesis of cyclobutabenzene complexes which undergo such ring opening reactions more easily.



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Experimental

All operations are performed in an argon atmosphere in flame-dried reaction vessels. Hydrocarbon solvents, THF, and dioxane are dried with $LiAlH_4$ and distilled from Na/K alloy/benzophenone under argon. $CHCl_3$ is dried with P_4O_{10} and distilled under argon. – M.p. (uncorrected): Büchi SMP-20, determined in sealed glass capillaries in an argon atmosphere for organometallic compounds. – IR: Nicolet 7199 FT-IR. – UV: Varian CARY 2300. – ^{1}H NMR: Bruker WH 400 (400.1 MHz), AM 200 (200.1 MHz), WP 80 (80 MHz). – ^{13}C NMR: Bruker WM 300 (75.5 MHz), AM 200 (50.3 MHz); signal multiplicities are determined either by inspection of gated spectra or by application of the DEPT technique; for diastereomeric mixtures signal assignments are based on the signal intensities according to the diastereomeric ratio, unless otherwise mentioned; chemical shifts refer to $\delta_{TMS} = 0.00$ according to the chemical shift of residual solvent signals. – ^{31}P NMR: Bruker WP 80 (32.4 MHz) with H_3PO_4 as external standard. – MS: Varian 311 A. – GC-MS: Perkin-Elmer GDF 22 and Finnigan CH 7 A. – HRMS: Finnigan MAT 820. – GC (anal.): Becker-Packard 417,

FID, 30 m glass capillary PS 240, carrier gas H_2. – GC (prep.): Gerstel AMPG-60. – HPLC (anal.): Varian 5560 or Gynkotek M300C and Shimadzu CT06A + SPD6A, UV detection 254 nm. – HPLC (prep.): Shimadzu LC-8A + SPD-6A + FCV-100B; NP = normal phase, RP = reversed phase; retention times are given as k' values [k' = (gross retention time – dead time)/dead time]. – DSC: DuPont TA 9900. – Elemental analyses: Mikroanalytisches Laboratorium Dornis und Kolbe, Mülheim a.d. Ruhr.

1-(Chloromagnesio)cyclobutabenzene[28]: A flame-dried 500-ml three-necked round bottom flask is equipped with a reflux condenser, a 250-ml dropping funnel and a magnetic stirring bar, and 12.15 g (0.50 mol) of magnesium filings and a crystal of iodine are added. The flask is evacuated and heated until the purple color of the iodine has disappeared. The flask is filled with argon, and 40 ml of THF is added. With stirring, 67.25 g (0.49 mol) of **5**[28] is slowly added dropwise until the exothermic reaction starts, the mixture becoming yellow. The remaining **5** in the dropping funnel is diluted with 100 ml of THF and added to the reaction flask at a rate such that the temperature of the mixture remains at ca. 40°C. After the addition, the mixture is stirred at 40°C for 2 h. The yellow-brown reaction mixture is diluted with THF to ca. 400 ml and filtered through a P4 frit into a calibrated flask. The solution is diluted with THF to a volume of 486 ml (ca. 1 M) and may be stored at –78°C for several months without loss of activity. – ^{1}H NMR (80 MHz, [D$_8$]THF): δ = 1.8 (m, THF), 2.24 (dd, 1H, 1β-H), 2.93 (dd, 1H, 2α-H, ABX line system), 3.02 (dd, 1H, 2β-H, $^3J_{2,1}$ = 4.8 Hz), 6.47 (m, 2H, 3-H; 5-H), 6.58 (d, 1H, 6-H), 6.74 (dd, 1H, 4-H).

General Procedure for the Preparation of Cr(CO)$_3$ Complexes of Cyclobutabenzene Derivatives: The cyclobutabenzene derivative is placed into a flame-dried two-necked round-bottom flask equipped with a magnetic stirring bar and a reflux condenser. Dioxane and $Cr(CO)_3(NH_3)_3$[10] are added, and the mixture is refluxed for 3.5 h. After cooling to 25°C, the dioxane is evaporated in vacuo. The black-green residue is extracted with 40-ml portions of boiling pentane until the extract is no longer yellow. After filtration through a P4 frit into a Schlenk flask, the solution is stored at –30°C for ca. 24 h and then at –78°C for another 24 h. The crystals formed are separated from the mother liquor and are dried under reduced pressure at room temperature. The product is recrystallized from pentane and then stored at –30°C under argon.

Tricarbonyl(η^6-cyclobutabenzene)chromium[1c,d] (**12**): 10.0 g (96.0 mmol) of **1**[29], 250 ml of dioxane, 19.8 g (106 mmol) of $Cr(CO)_3(NH_3)_3$[10]. Yield 11.8 g (51%) of yellow needles, m.p. 88–89°C (ref.[1c] 88–89°C), subliming at 80°C/0.001 mbar. – IR (cyclohexane): $\tilde{\nu}$ = 1975 cm^{-1} (s, C=O), 1907 (s, C=O), 655, 620. – UV (cyclohexane): λ_{max} (lg ε) = 216 nm (4.424), 318 (4.028). – ^{1}H NMR (400 MHz, [D$_6$]benzene): δ = 2.25 and 2.55 [AA'BB' line system, 4H, *endo*-1(2)-H, *exo*-1(2)-H], 4.19 [m, 2H, 4(5)-H], 4.60 (m, 2H, 3(6)-H]. – ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 30.4 [t, C-1(2), $^1J_{C,H}$ = 168 Hz], 92.0 [d, C-3(6), $^1J_{C,H}$ = 179 Hz], 92.9 [d, C-4(5), $^1J_{C,H}$ = 172 Hz], 118.3 [s, C-2a(6a)], 235.0 (s, CO). – MS (70 eV): *m/z* (%) = 240 (25) [M$^+$], 212 (5) [M$^+$ – CO], 284 (8) [M$^+$ – 2 CO], 156 (63) [M$^+$ – 3 CO], 52 (100) [Cr$^+$].

$C_{11}H_8CrO_3$ (240.02) Calcd. C 55.01 H 3.36 Cr 21.65
Found C 54.88 H 3.31 Cr 21.49

Tricarbonyl[η^6-(1-deuteriocyclobutabenzene)]chromium(0) ([1-D]**12**): 1.01 g (9.6 mmol) of [1-D]**1**[30], 20 ml of dioxane, 1.00 g (5.3 mmol) of $Cr(CO)_3(NH_3)_3$[10]. Yield 0.68 g (53%) [*endo*/*exo* (50:50)] of fine, yellow needles, m.p. 88.2°C. – IR (cyclohexane): $\tilde{\nu}$ = 1975 cm^{-1} (s, C=O), 1907 (s, C=O); (KBr): $\tilde{\nu}$ = 2208 cm^{-1} (w, C–D), 1950 (s, br., C=O), 1860 (s, br., C=O), 1418, 670, 635. – ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 2.35 (m, 2H, *exo*-1-H, *exo*-2-H), 2.60 (m, 2H, *endo*-1-H, *endo*-2-H), 4.29 (m, 2H, 4-H, 5-H), 4.69 (m, 2H, 3-H, 6-H). – ^{13}C NMR (50 MHz, [D$_6$]benzene): δ = 29.6 (t, $^1J_{C,D}$ = 21.8 Hz, C-1), 29.8 (t, C-2), 90.1 (d, C-3, C-6), 91.0 (d, C-4, C-5), 116.5 (s, C-6a or C-2a), 116.6 (s, C-2a or C-6a), 234.3 (s, CO). – MS (70 eV): *m/z* (%) = 241 (8) [M$^+$], 213 (3) [M$^+$ – CO], 185 (6) [M$^+$ – 2 CO], 157 (31) [M$^+$ – 3 CO], 52 (100) [Cr$^+$], degree of deuteriation >96%.

$C_{11}H_7CrDO_3$ (241.19) Calcd. C 54.78 H/D 3.76 Cr 21.56
Found C 54.68 H/D 3.61 Cr 21.33

Tricarbonyl[η^6-(4-methylcyclobutabenzene)]chromium(0) (**13**): 2.23 g (18.9 mmol) of **2**[29], 40 ml of dioxane, 2.00 g (10.7 mmol) of $Cr(CO)_3(NH_3)_3$[10]. Yield 1.75 g (65%) of orange-yellow needles, m.p. 71.5°C, 73°C (DSC) subliming at 80°C/0.001 mbar. – IR (cyclohexane): $\tilde{\nu}$ = 1971 cm^{-1} (s, C=O), 1902 (s, C=O), 660, 620. – ^{1}H NMR (400 MHz, [D$_6$]benzene): δ = 1.52 (s, 3H, CH$_3$), 2.27 (m, 1H, *exo*-2-H, $^2J_{2,2}$ = –13.4 Hz, $^3J_{2,exo\text{-}1}$ = 6.3 Hz, $^3J_{exo\text{-}2,endo\text{-}1}$ = 2.7 Hz), 2.37 (m, 1H, *exo*-1-H, $^2J_{1,1}$ = –13.8 Hz, $^3J_{exo\text{-}1,endo\text{-}2}$, $^3J_{exo\text{-}2,endo\text{-}1}$ = 2.7 Hz), 2.51 (m, 1H, *endo*-2-H, $^3J_{endo\text{-}2,endo\text{-}1}$ = 5.5 Hz), 2.7 (m, 1H, *endo*-1-H), 4.08 (d, 1H, 6-H, $^3J_{6,5}$ = 6.3 Hz), 4.49 (s, 1H, 3-H), 4.76 (d, 1H, 5-H). – ^{13}C NMR (50 MHz, [D$_6$]benzene): δ = 20.9 (q, CH$_3$, $^1J_{C,H}$ = 129 Hz), 29.2 (t, C-1 or C-2, $^1J_{C,H}$ = 142 Hz), 29.5 (t, C-2 or C-1, $^1J_{C,H}$ = 141 Hz), 90.2 (d, C-6 or C-3 or C-5, $^1J_{C,H}$ = 174 Hz), 90.6 (d, C-5 or C-3 or C-6, $^1J_{C,H}$ = 172 Hz); 91.0 (d, C-3 or C-5 or C-6, $^1J_{C,H}$ = 175 Hz), 107.3 (s, C-4), 113.0 (s, C-6a), 117.7 (s, C-2a), 234.5 (s, CO). – MS (70 eV): *m/z* (%) = 254 (64) [M$^+$], 226 (6) [M$^+$ – CO], 198 (29) [M$^+$ – 2 CO], 170 (98)[M$^+$ – 3 CO], 52 (100) [Cr$^+$].

$C_{12}H_{10}CrO_3$ (254.21) Calcd. C 56.70 H 3.97 Cr 20.45
Found C 56.75 H 4.02 Cr 20.32
Calcd. 254.0035 Found 254.0033 (HRMS)

Tricarbonyl[η^6-(3,5-dimethylcyclobutabenzene)]chromium(0) (**14**): 1.27 g (9.6 mmol) of **3**[29], 20 ml of dioxane, 1.00 g (5.3 mmol) of $Cr(CO)_3(NH_3)_3$[10]. Yield 0.86 g (60%) of fine, bright yellow powder, m.p. 97–98°C subliming at 80°C/0.001 mbar. – IR (cyclohexane): $\tilde{\nu}$ = 1966 cm^{-1} (s, C=O), 1896 (s, C=O), 670, 630. – ^{1}H NMR (400 MHz, [D$_6$]benzene): δ = 1.69 (s, 3H, 3-CH$_3$ or 5-CH$_3$), 1.78 (s, 3H, 5-CH$_3$ or 3-CH$_3$), 2.37 (m, 1H, *exo*-1-H or *exo*-2-H), 2.56 (m, 2H, *exo*-2-H or *exo*-1-H and *endo*-1-H or *endo*-2-H), 2.83 (m, 1H, *endo*-1-H or *endo*-2-H) 4.17 (s, 1H, 6-H or 4-H), 4.53 (s, 1H, 4-H or 6-H). – ^{13}C NMR (50 MHz, [D$_6$]benzene): δ = 15.9 (q, 3-CH$_3$, $^1J_{C,H}$ = 129 Hz), 21.0 (q, 5-CH$_3$, $^1J_{C,H}$ = 128 Hz), 28.1 (t, C-2 or C-1, $^1J_{C,H}$ = 142 Hz), 28.9 (t, C-1 or C-2, $^1J_{C,H}$ = 142 Hz), 88.1 (d, C-6, $^1J_{C,H}$ = 174 Hz), 92.2 (d, C-4, $^1J_{C,H}$ = 170 Hz), 107.9 (s, C-5), 109.2 (s, C-3), 112.3 (s, C-6a), 118.4 (s, C-2a), 235.0 (s, CO). – MS (70 eV): *m/z* (%) = 268 (12) [M$^+$], 212 (8) [M$^+$ – 2 CO], 184 (73) [M$^+$ – 3 CO], 52 (100) [M$^+$ – $C_{10}H_{12}O_3$].

$C_{13}H_{12}CrO_3$ (268.23) Calcd. C 58.21 H 4.51 Cr 19.38
Found C 58.98 H 4.56 Cr 18.78

Tricarbonyl{η^6-[1-(ethylendioxy)cyclobutabenzene]}chromium(0) (**15**): 9.08 g (56.0 mmol) of **4**[27a,31], 11.5 g (61.7 mmol) of $Cr(CO)_3(NH_3)_3$[10], and 250 ml of dioxane are refluxed at 101°C for 7 h. After evaporation of the solvent, the residue is extracted with pentane in a Soxhlet apparatus for 6 d causing **15** to precipitate. Additional **15** is crystallized by cooling the mother liquor to –30°C. The collected solid reaction product is washed three times with pentane to yield 12.4 g (83%) of light, lemon-yellow powder, m.p. 106°C. Solvent evaporation from the mother liquor yields 0.90 g (5.60 mmol) of unreacted **4**. – IR (cyclohexane): $\tilde{\nu}$ = 1983 cm^{-1} (s, C=O), 1913 (s, C=O). – ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 3.08 (d, 1H, 2-*exo*-H, $^2J_{2,2}$ = –13.7 Hz), 3.27 (d, 1H, 2-*endo*-H), 3.38–3.63 (m, 4H, CH_2CH_2), 4.1 (dd, 1H, 4-H, $^3J_{4,3}$ =

Table 3. Atomic fractional coordinates of *exo*-**16**; $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$

Atom	x	y	z	U_{eq}
Cr	0.1948(1)	0.2142(1)	0.4877(1)	0.038
O(1)	0.4530(3)	0.0559(1)	0.4025(1)	0.076
O(2)	−0.1397(3)	0.2070(2)	0.3045(1)	0.083
O(3)	0.4407(3)	0.3684(1)	0.3922(1)	0.072
C(1)	0.1953(4)	0.4370(2)	0.6080(2)	0.050
C(2)	0.4246(4)	0.3894(2)	0.6499(2)	0.058
C(2a)	0.3172(3)	0.2850(2)	0.6335(1)	0.047
C(3)	0.3510(4)	0.1801(2)	0.6429(2)	0.056
C(4)	0.1662(5)	0.1183(2)	0.6160(2)	0.064
C(5)	−0.0383(4)	0.1598(2)	0.5790(2)	0.065
C(6)	−0.0685(4)	0.2663(2)	0.5661(2)	0.056
C(6a)	0.1124(3)	0.3273(2)	0.5959(1)	0.044
C(7)	0.0987(5)	0.5031(2)	0.6790(2)	0.061
C(8)	0.3529(4)	0.1156(2)	0.4365(1)	0.049
C(9)	−0.0106(3)	0.2089(2)	0.3750(2)	0.053
C(10)	0.3443(3)	0.3088(2)	0.4283(2)	0.046

6.3 Hz, $^3J_{4,5}$ = 6.3 Hz), 4.47 (dd, 5-H, $^3J_{5,6}$ = 6.3 Hz), 4.59 (d, 1 H, 6-H), 4.97 (d, 1 H, 3-H). — ^{13}C NMR (75 MHz, [D$_6$]benzene): δ = 47.0 (t, C-2, $^1J_{C,H}$ = 142 Hz), 65.4 (t, *exo*-CH_2 or *endo*-CH_2, $^1J_{C,H}$ = 150 Hz), 65.5 (t, *endo*-CH_2 or *exo*-CH_2, $^1J_{C,H}$ = 151 Hz), 86.5 (d, C-6 or C-3 or C-4 or C-5, $^1J_{C,H}$ = 178 Hz), 87.6 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 174 Hz), 88.9 (d, C-4 or C-3 or C-5 or C-6, $^1J_{C,H}$ = 176 Hz), 93.6 (d, C-5 or C-3 or C-4 or C-6, $^1J_{C,H}$ = 173 Hz), 109.8 (s, C-1 or C-2a or C-6a), 112.9 (s, C-1 or C-2a or C-6a), 114.7 (s, C-1 or C-2a or C-6a), 233.0 (s, CO). — MS (70 eV): *m/z* (%) = 298 (25) [M$^+$], 270 (4) [M$^+$ − CO], 242 (18) [M$^+$ − 2 CO], 214 (47) [M$^+$ − 3 CO], 186 (20), 184 (30), 142 (77) [$CrC_7H_6^+$], 52 (100) [Cr$^+$].

$C_{13}H_{10}CrO_5$ (298.22) Calcd. C 52.36 H 3.38 Cr 17.44
Found C 52.38 H 3.37 Cr 17.52

Tricarbonyl[η^6-(1-methylcyclobutabenzene)]chromium(0) (**16**): 1.13 g (9.6 mmol) of **6**[28], 20 ml of dioxane, 1.00 g (5.3 mmol) of $Cr(CO)_3(NH_3)_3$[10]. Yield 0.84 g (62%) [*endo/exo* (40:60)] of lemon-yellow fine needles, partially decomposing above 80°C. An analytical sample (52 mg) of the diastercomeric mixture is separated by NP-HPLC [Nucleosil 3−100, column 150 × 4.5 mm, *n*-heptane/2-propanol (99.5:0.5, v/v)] to yield 9 mg of *exo*-**16** (*k'* = 1.12, m.p. 52.3°C) and 5 mg of *endo*-**16** (*k'* = 1.53, m.p. 66.3°C). 600 mg of the diastereomeric mixture is separated by prep. NP-HPLC [Polygosil 7−100, column 250 × 25 mm, *n*-heptane/2-propanol (99.5:0.5, v/v)]: Fraction 1: 170 mg of *exo*-**16**; fraction 2: 200 mg of *endo*-**16**. — IR (cyclohexane): $\tilde{\nu}$ = 1975 cm^{-1} (m, C=O), 1906 (m, C=O), 660, 620. — ^{1}H NMR (400 MHz, [D$_6$]benzene): *exo*-**16** (60%): δ = 0.83 (d, 3H, CH_3, $^3J_{7,1}$ = 7.1 Hz), 1.98 (dd, 1 H, *exo*-2-H, $^2J_{2,2}$ = −14 Hz, $^3J_{exo\text{-}2,1}$ = 2.5 Hz), 2.81 (dd, 1 H, *endo*-2-H, $^3J_{endo\text{-}2,1}$ = 5.1 Hz), 3.09 (m, 1 H, 1-H), 4.3 (m, 2 H, 4-H, 5-H), 4.75 (m, 2 H, 3-H, 6-H); *endo*-**16** (40%): δ = 1.16 (d, 3H, CH_3, $^3J_{7,1}$ = 6.8 Hz), 2.31 (dd, 1 H, *endo*-2-H, $^2J_{2,2}$ = −13.9 Hz, $^3J_{endo\text{-}2,1}$ = 2.8 Hz), 2.54 (dd, 1 H, *exo*-2-H, $^3J_{exo\text{-}2,1}$ = 5.9 Hz), 2.75 (m, 1 H, 1-H), 4.12 (dd, 1 H, 5-H, $^3J_{5,4}$ = 6.3 Hz, $^3J_{5,6}$ = 6.3 Hz), 4.45 (d, 1 H, 3-H, $^3J_{3,4}$ = 6.3 Hz), 4.57 (dd, 1 H, 4-H), 4.87 (d, 1 H, 6-H). — ^{13}C NMR (50 MHz, [D$_6$]benzene)[32]: *exo*-**16**: δ = 19.3 (q, CH_3, $^1J_{C,H}$ = 128 Hz), 37.8 (t, C-2, $^1J_{C,H}$ = 141 Hz), 38.8 (d, C-1, $^1J_{C,H}$ = 143 Hz), 89.1 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 173 Hz), 89.9 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 176 Hz), 90.7 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 177 Hz), 91.1 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 172 Hz), 114.7 (s, C-2a), 121.0 (s, C-6a), 234.2 (s, CO); *endo*-**16**: δ = 21.6 (q, CH_3, $^1J_{C,H}$ = 128 Hz), 37.1 (t, C-2, $^1J_{C,H}$ = 140 Hz), 37.5 (d, C-1, $^1J_{C,H}$ = 138 Hz), 86.2 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 176 Hz), 87.1 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 177 Hz), 91.7 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 174 Hz), 94.5 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 171 Hz), 116.0 (s, C-2a), 120.8 (s, C-6a), 234.4 (s, CO). — MS (70 eV): *m/z* (%) = 254 (10) [M$^+$], 226 (1) [M$^+$ − CO], 198 (5) [M$^+$ − 2 CO], 170 (33) [M$^+$ − 3 CO], 52 (100) [Cr$^+$].

$C_{12}H_{10}CrO_3$ (254.21) Calcd. C 56.70 H 3.97 Cr 20.45
Found C 56.58 H 3.91 Cr 20.36

[η^6-(1-Butylcyclobutabenzene)]tricarbonylchromium(0) (**17**): 1.53 g (9.6 mmol) of **7**[28], 20 ml of dioxane, 1.00 g (5.3 mmol) of $Cr(CO)_3(NH_3)_3$[10]. Yield 0.42 g (27%) [*endo/exo* (50:50)] of bright yellow, microcrystalline powder liquifying at 25°C and partially decomposing above 80°C. — IR (cyclohexane): $\tilde{\nu}$ = 1971 cm^{-1} (s, C=O), 1902 (s, C=O), 655, 620. — ^{1}H NMR (200 MHz, [D$_8$]toluene)[32]: *exo*-**17** (50%): δ = 0.82 (t, 3H, CH_3), 1.00−1.68 (m, 6H, $[CH_2]_3$), 2.15 (dd, 1 H, *exo*-2-H), 2.88 (dd, 1 H, *endo*-2-H), 3.08 (m, 1 H, 1-H), 4.4 [dd, 2H, 4-H, 5-H], 4.84 (d, 1 H, 6-H), 4.91 (d, 1 H, 3-H); *endo*-**17** (50%): δ = 0.89 (t, 3H, CH_3), 1.00−1.68 (m, 6H, $[CH_2]_3$), 2.4 (dd, 1 H, *endo*-2-H), 2.65 (dd, 1 H, *exo*-2-H), 2.76 (m, 1 H, 1-H), 4.20 (dd, 1 H, 4-H), 4.54 (d, 1 H, 6-H), 4.66 (dd, 1 H, 5-H), 4.97 (d, 1 H, 3-H). — ^{13}C NMR (50 MHz, [D$_6$]benzene)[32]: *exo*-**17**: δ = 14.2 (q, CH_3, $^1J_{C,H}$ = 122 Hz), 22.8 (t, CH_2CH_3, $^1J_{C,H}$ = 128 Hz), 30.0 (t, $CH_2CH_2CH_2$, $^1J_{C,H}$ = 125 Hz), 34.3 (t, $CH_2[CH_2]_2$, $^1J_{C,H}$ = 125 Hz), 36.2 (t, C-2, $^1J_{C,H}$ = 139 Hz), 44.2 (d, C-1, $^1J_{C,H}$ = 145 Hz), 86.2 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 179 Hz), 89.4 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 179 Hz), 90.7 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 173 Hz), 94.5 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 169 Hz), 115.0 (s, C-2a), 120.2 (s, C-6a), 234.2 (s, CO); *endo*-**17**: δ = 14.1 (q, CH_3, $^1J_{C,H}$ = 122 Hz), 22.7 (t, CH_2CH_3, $^1J_{C,H}$ = 128 Hz), 30.5 (t, $CH_2CH_2CH_2$, $^1J_{C,H}$ = 125 Hz), 35.8 (t, C-2, $^1J_{C,H}$ = 142 Hz), 37.5 (t, $CH_2[CH_2]_2$, $^1J_{C,H}$ = 125 Hz), 42.8 (d, C-1, $^1J_{C,H}$ = 138 Hz), 87.0 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 178 Hz), 89.7 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 176 Hz), 91.1 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 177 Hz), 92.7 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 170 Hz), 116.3 (s, C-2a), 120.1 (s, C-6a), 234.0 (s, CO). — MS (70 eV): *m/z* (%) = 296 (12) [M$^+$], 240 (6) [M$^+$ − 2 CO], 212 (65) [M$^+$ − 3 CO], 170 (45) [M$^+$ − $Cr(CO)_3$], 52 (100) [Cr$^+$].

$C_{15}H_{16}CrO_3$ (296.29) Calcd. C 60.81 H 5.44 Cr 17.55
Found C 60.84 H 5.48 Cr 17.45
Calcd. 296.0507 Found 296.0509 (HRMS)

1-(3-Butenyl)cyclobutabenzene (**8**): In a 500-ml three-necked round-bottom flask equipped with a rubber septum, a magnetic stirring bar, and an inert-gas inlet, 80 ml (80 mmol) of a 1 M solution of 1-(chloromagnesio)cyclobutabenzene in THF is cooled to −78°C. With a gastight syringe 3.2 ml (0.32 mmol) of a 0.1 M solution of Li_2CuCl_4 in THF[28] is added through the septum. The mixture is stirred at −78°C for 1 h, then 11.9 g (88 mmol) of 4-bromo-1-butene is slowly added by a syringe. The stirred mixture is allowed to warm to 25°C during ca. 12 h and then hydrolyzed with 200 ml of water. After separation of the organic layer, the aqueous layer is extracted three times with 100 ml of pentane. The organic layers are combined and washed once with diluted HCl and twice with water and then dried with $MgSO_4$. The solvent is evaporated under reduced pressure, and the residue is twice distilled through a spinning-band column at 0.1 mbar. Yield 6.57 g (52%) of a colorless oil with an intense odor, b.p. 49−51°C/0.1 mbar. — IR (film): $\tilde{\nu}$ = 3070 cm^{-1} (m, olef. CH_2), 2920 (s, aliph. CH_2), 2840 (m, aliph. CH_2), 1640 (m, olef. C=C), 1600 (w, arom. C=C), 1455 (s, CH_2), 1195 (m), 1185 (m), 995 (m, olef. CH), 910 (s, olef. CH), 740 (s, *o*-disubst. arom. CH), 710 (m). — ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 1.55−1.75 (m, 2H, CH_2CH_2CH=), 2.03−2.24 (m, 2H,

$CH_2CH=$), 2.57 (dd, 1H, *trans*-2-H, $^2J_{2,2}$ = −13.9 Hz, $^3J_{trans\text{-}2,1}$ = 2.4 Hz), 3.15 (dd, 1H, *cis*-2-H, $^3J_{cis\text{-}2,1}$ = 6.1 Hz), 3.27−3.36 (m, 1H, 1-H), 4.93−5.09 (m, 2H, $=CH_2$), 5.66−5.87 (m, 1H, CH=), 6.90−7.03 (m, 2H, arom. H), 7.06−7.21 (m, 2H, arom. H). − ^{13}C NMR (75 MHz, [D$_6$]benzene): δ = 32.9 (t, $CH_2CH_2CH=$), 34.2 (t, $CH_2CH=$), 36.3 (t, C-2), 43.4 (d, C-1), 115.0 (t, $=CH_2$), 122.3 (d, arom. C), 123.4 (d, arom. C), 127.2 (d, arom. C), 127.7 (d, arom. C), 138.9 (d, CH=), 144.0 (s, C-2a), 150.0 (s, C-6a). − MS (70 eV): *m/z* (%) = 158 (10) [M$^+$], 143 (71), 130 (40), 129 (55), 128 (32), 117 (100), 116 (41), 115 (98), 104 (24), 77 (17), 65 (11), 63 (10), 51 (12), 41 (8), 39 (20).

$C_{12}H_{14}$ (158.24) Calcd. C 91.08 H 8.92
Found C 91.11 H 9.06

{η^6-[1-(3-Butenyl)cyclobutabenzene]}tricarbonylchromium(0) (**18**): 1.53 g (9.7 mmol) of **8**, 20 ml of dioxane, 1.00 g (5.3 mmol) of $Cr(CO)_3(NH_3)_3$[10]. Yield 0.77 g (49%) [*endo/exo* (50:50) determined by ^{1}H NMR, (40:60) determined by HPLC] of a yellow oil solidifying at −30°C. − Anal. NP-HPLC (Partisil 7−100, 243 × 4.5 mm, *n*-heptane): Fraction 1 (*k'* = 5.15): *exo*-**18**; fraction 2 (*k'* = 5.75): *endo*-**18**. − IR (cyclohexane): ṽ = 1973 cm^{-1} (s, C=O), 1905 (s, C=O). − ^{1}H NMR (200 MHz, [D$_8$]THF)[32]: *exo*-**18**: δ = 1.76−1.93 (m, 2H, $CH_2CH_2CH=$), 2.06−2.31 (m, 2H, $CH_2CH=$), 2.68 (dd, 1H, *exo*-2-H, $^2J_{endo\text{-}2,exo\text{-}2}$ = −13.8 Hz, $^3J_{exo\text{-}2,1}$ = 2.7 Hz), 3.23 (dd, 1H, *endo*-2-H, $^3J_{endo\text{-}2,1}$ = 6.1 Hz), 3.42 (m, 1H, 1-H), 4.93−5.08 (m, 2H, $=CH_2$), 4.9−6.0 (m, 4H, 3-H, 4-H, 5-H, 6-H), 5.7−5.98 (m, 1H, CH=); *endo*-**18**: δ = 1.76−1.93 (m, 2H, $CH_2CH_2CH=$), 2.06−2.31 (m, 2H, $CH_2CH=$), 2.73 (dd, 1H, *endo*-2-H, $^2J_{endo\text{-}2,exo\text{-}2}$ = −14.0 Hz, $^3J_{endo\text{-}2,1}$ = 2.5 Hz), 3.22 (dd, 1H, *exo*-2-H, $^3J_{exo\text{-}2,1}$ = 4.7 Hz), 3.42 (m, 1H, 1-H), 4.93−5.08 (m, 2H, $=CH_2$), 5.1−5.9 (m, 4H, 3-H, 4-H, 5-H, 6-H), 5.7−6.0 (m, 1H, CH=). − ^{13}C NMR (50 MHz, [D$_6$]benzene)[32]: *exo*-**18**: δ = 29.9 (t, $CH_2CH_2CH=$), 32.7 (t, $CH_2CH=$), 36.3 (t, C-2), 43.9 (d, C-1), 89.8 (d, C-3 or C-4 or C-5 or C-6), 90.0 (d, C-3 or C-4 or C-5 or C-6), 90.8 (d, C-3 or C-4 or C-5 or C-6), 91.4 (d, C-3 or C-4 or C-5 or C-6), 115.1 (s, C-2a), 115.5 (t, $=CH_2$), 120.0 (s, C-6a), 137.9 (d, CH=), 234.3 (s, CO); *endo*-**18**: δ = 32.2 (t, $CH_2CH_2CH=$), 35.9 (t, $CH_2CH=$), 37.1 (t, C-2), 42.3 (d, C-1), 86.5 (d, C-3 or C-4 or C-5 or C-6), 87.4 (d, C-3 or C-4 or C-5 or C-6), 92.9 (d, C-3 or C-4 or C-5 or C-6), 94.7 (d, C-3 or C-4 or C-5 or C-6), 115.7 (t, $=CH_2$), 116.4 (s, C-2a), 119.9 (s, C-6a), 138.1 (d, CH=), 234.5 (s, CO). − MS (70 eV): *m/z* (%) = 294 (15) [M$^+$], 210 (65) [M$^+$ − 3 CO], 170 (12), 167 (16), 166 (13), 52 (100) [Cr$^+$].

$C_{15}H_{14}CrO_3$ (294.27) Calcd. C 61.22 H 4.80 Cr 17.67
Found C 61.18 H 4.70 Cr 17.54

Tricarbonyl{η^6-[1-(trimethylsilyl)cyclobutabenzene]}chromium(0) (**19**): 1.69 g (9.6 mmol) of **9**[28], 20 ml of dioxane, 1.00 g (5.3 mmol) of $Cr(CO)_3(NH_3)_3$[10]. Yield 1.07 g (64%) [*endo/exo* (12:88)] of bright yellow plates subliming at 90°C/0.001 mbar. − IR (cyclohexane): ṽ = 1972 cm^{-1} (s, C=O), 1904 (s, C=O), 1898 (s, C=O), 1100, 805. − ^{1}H NMR (200 MHz, [D$_6$]benzene)[32]: *exo*-**19** (88%): δ = −0.24 (s, 9H, 3 CH_3), 2.42 (dd, 1H, *exo*-2-H), 2.64 (m, 1H, 1-H), 2.91 (dd, 1H, *endo*-2-H), 4.31 (dd, 1H, 5-H or 4-H), 4.42 (dd, 1H, 4-H or 5-H), 4.76 (d, 1H, 6-H or 3-H); *endo*-**19** (12%): δ = 0.11 (s, 9H, 3 CH_3), 4.19 (dd, 1H, 4-H), 4.51 (d, 1H, 6-H), 4.65 (dd, 1H, 5-H), 4.90 (d, 1H, 3-H) (the integral shows the signals of 1-H, *exo*-2-H, and *endo*-2-H to be superposed by those of *exo*-**19**). − ^{13}C NMR (50 MHz, [D$_6$]benzene)[32]: *exo*-**19**: δ = −3.6 (q, 3 CH_3, $^1J_{C,H}$ = 120 Hz), 31.4 (t, C-2, $^1J_{C,H}$ = 141 Hz), 33.2 (d, C-1, $^1J_{C,H}$ = 135 Hz), 87.8 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 176 Hz), 89.7 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 174 Hz), 90.8 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 175 Hz), 91.4 (d, C-3 or C-4 or C-5 or C-6, $^1J_{C,H}$ = 174 Hz), 114.9 (s, C-2a), 121.6 (s, C-6a), 234.5 (s, CO); *endo*-**19**: δ = −2.4 (q, 3 CH_3), 31.2 (t, C-2), 33.5 (d, C-1), 86.5 (d, C-3 or C-4 or C-5 or C-6), 87.3 (d, C-3 or C-4 or C-5 or C-6), 92.9 (d, C-3 or C-4 or C-5 or C-6), 94.3 (d, C-3 or C-4 or C-5 or C-6), 117.3 (s, C-2a), 118.1 (s, C-6a), 234.9 (s, CO). − MS (70 eV): *m/z* (%) = 312 (11) [M$^+$], 256 (10) [M$^+$ − 2 CO], 228 (57) [M$^+$ − 3 CO], 212 (42), 52 (100) [Cr$^+$].

$C_{14}H_{16}CrO_3Si$ (312.36) Calcd. C 53.83 H 5.16 Cr 16.65 Si 9.00
Found C 54.00 H 5.20 Cr 16.77 Si 8.89

Tricarbonyl{η^6-[1-(trimethylstannyl)cyclobutabenzene]}chromium(0) (**20**): 2.58 g (9.6 mmol) of **10**[20], 20 ml of dioxane, 1.00 g (5.3 mmol) of $Cr(CO)_3(NH_3)_3$[10]. Yield 1.92 g (89%) [*endo/exo* (24:76)] of bright yellow plates subliming at 80°C/0.001 mbar. − IR (cyclohexane): ṽ = 1970 cm^{-1} (m, C=O), 1904 (m, C=O), 1896 (m, C=O). − ^{1}H NMR (400 MHz, [D$_8$]toluene)[32]: *exo*-**20** (76%): δ = −0.11 (m, 9H, 3 CH_3, $^2J_{CH_3,^{119}Sn}$ = 54.1 Hz, $^2J_{CH_3,^{117}Sn}$ = 51.6 Hz), 2.55 (m, 1H, *exo*-2-H, $^2J_{2,2}$ = −14.3 Hz, $^3J_{2,1}$ = 2.7 Hz, $^3J_{2,Sn}$ = 39.0 Hz), 2.84 (m, 1H, 1-H, $^1J_{1,Sn}$ = 32.9 Hz, $^3J_{1,endo\text{-}2}$ = 5.6 Hz), 3.11 (m, 1H, *endo*-2-H, $^3J_{2,Sn}$ = 25.6 Hz), 4.22 (dd, 1H, 5-H or 4-H), 4.36 (dd, 1H, 4-H or 5-H), 4.65 (d, 1H, 6-H or 3-H), 4.85 (d, 1H, 3-H or 6-H); *endo*-**20** (24%): δ = 0.26 (m, 9H, 3 CH_3, $^2J_{CH_3,^{119}Sn}$ = 54.4 Hz, $^2J_{CH_3,^{117}Sn}$ = 51.9 Hz), 2.64 (m, 1H, 1-H, $^3J_{1,endo\text{-}2}$ = 3.1 Hz, $^3J_{1,exo\text{-}2}$ = 6.3 Hz), 2.72 (dd, 1H, *exo*-2-H, $^2J_{2,2}$ = −14 Hz), 2.9 (m, 1H, *endo*-2-H, $^3J_{2,Sn}$ = 28.6 Hz), 4.17 (m, 1H, 3-H or 4-H or 5-H or 6-H). − ^{13}C NMR (75 MHz, [D$_6$]toluene)[32]: *exo*-**20**: δ = −10.9 (q + 2 d, 3 CH_3, $^1J_{C,H}$ = 129 Hz, $^1J_{CH_3,^{119}Sn}$ = 334.7 Hz, $^1J_{CH_3,^{117}Sn}$ = 320.4 Hz), 28.6 (d + 2 d, C-1, $^1J_{C,H}$ = 144 Hz, $^1J_{1,^{119}Sn}$ = 295.0 Hz, $^1J_{1,^{117}Sn}$ = 281.8 Hz), 34.1 (t + d, C-2, $^1J_{C,H}$ = 141 Hz, $^2J_{2,Sn}$ = 15.3 Hz), 86.5 (d, C-6, $^1J_{C,H}$ = 171.4 Hz), 88.8 (d, C-4, $^1J_{C,H}$ = 173 Hz), 90.4 (d, C-5, $^1J_{C,H}$ = 176 Hz), 91.2 (d, C-3, $^1J_{C,H}$ = 173 Hz), 113.8 (s + d, C-2a, $^3J_{2a,Sn}$ = 27.5 Hz), 124.3 (s + d, C-6a, $^2J_{6a,Sn}$ = 18.3 Hz), 234.3 (s, CO); *endo*-**20**: δ = −9.1 (q, 3 CH_3, $^1J_{C,H}$ = 130 Hz, $J_{CH_3,^{119}Sn}$ observed, but not exactly determined), 30.0 (d + 2 d, C-1, $^1J_{C,H}$ = 134 Hz, $^1J_{1,^{119}Sn}$ = 318.4 Hz, $^1J_{1,^{117}Sn}$ = 303.2 Hz), 33.7 (t + d, C-2, $^1J_{C,H}$ = 141 Hz, $^2J_{2,Sn}$ = 12.3 Hz), 86.3 (d, C-6, $^1J_{C,H}$ = 176 Hz), 87.7 (d, C-4, $^1J_{C,H}$ = 174 Hz), 91.6 (d, C-5, $^1J_{C,H}$ = 173 Hz), 92.9 (d, C-3, $^1J_{C,H}$ = 174 Hz), 117.1 (s, C-2a), 123.4 (s, C-6a), 234.3 (s, CO). − MS (70 eV): *m/z* (%) = 404 (7) [M$^+$], 348 (8) [M$^+$ − 2 CO], 320 (16) [M$^+$ − 3 CO], 129 (15), 52 (100) [Cr$^+$].

$C_{14}H_{16}CrO_3Sn$ (402.97) Calcd. C 41.73 H 4.00 Cr 12.90 Sn 29.45
Found C 41.88 H 4.23 Cr 12.74 Sn 29.49

Reaction of **11** *with* $Cr(CO)_6$: A mixture of 1.5 g (12.5 mmol) of **11**[34], 0.5 g (2.3 mmol) of $Cr(CO)_6$, 15 ml of di-*n*-butyl ether, and 1.25 ml of THF is refluxed for 4 h, during which time the mixture becomes yellow. The solvents are evaporated into a cold trap. The crude reaction mixture is analyzed (^{1}H and ^{13}C NMR, MS) to be a mixture of **22** and **23**. The crude product is dissolved in ether, and small amounts of metal complexes are decomposed by daylight irradiation in the air. After filtration through a P4 glass frit, the ether is removed in a rotary evaporator. Yield 0.44 g or a green-white product mixture consisting of 10.2% of **22** (yield 4%) and 76.4% of **23** (yield 28%) (GC). 440 mg of the mixture is separated by prep. GC (20% SE-30 on Volaspher A4, 100−120 mesh):

Fraction 1 (column temp. 180°C; rel. ret. time: 1): 10 mg (0.7%) of **22** (purity 88.3%, besides 3.1% of **23**), identified by a comparison with an authentic sample.

Fraction 2 (column temp. 250°C, rel. ret. time 3.09): 120 mg (8%) of **23** (purity 97%). − IR ($CDCl_3$): ṽ = 1721 cm^{-1} (s, C=O), 1275 (s, C−O−C). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.37 (s, 3H, CH_3), 3.05 (dd, 1H, *trans*-2-H, $^2J_{2,2}$ = −16.5 Hz, $^3J_{trans\text{-}2,1}$ = 3.1 Hz), 3.33 (dd, 1H, *cis*-2-H, $^3J_{cis\text{-}2,1}$ = 12.1 Hz), 5.75 (dd, 1H, 1-H), 7.14−7.34 (m, 4H, arom. H), 7.42 (dd, 1H, arom. H), 7.52 to 7.66 (m, 2H, arom. H), 8.16 (d, 1H, arom. H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1 (q, CH_3, $^1J_{C,H}$ = 127 Hz), 34.5 (t, C-2,

$^1J_{C,H}$ = 130 Hz), 77.3 (d, C-1, $^1J_{C,H}$ = 146 Hz), 125.3 (s, O_2CC), 126.1 (d, C-3, $^1J_{C,H}$ = 158 Hz), 126.5 (d, $O_2CCCHCH$, $^1J_{C,H}$ = 160 Hz), 127.3 (d, C-6, $^1J_{C,H}$ = 160 Hz), 127.9 (d, C-4 or C-5, $^1J_{C,H}$ = 168 Hz), 128.5 (d, C-4 or C-5, $^1J_{C,H}$ = 161 Hz), 130.5 (d, CH_3CCH or O_2CCCH, $^1J_{C,H}$ = 163 Hz), 130.7 (d, CH_3CCH or O_2CCCH, $^1J_{C,H}$ = 163 Hz), 133.8 (d, CH_3CCHCH, $^1J_{C,H}$ = 160 Hz), 134.9 (s, C-6a), 136.5 (s, C-2a), 139.3 (s, CH_3C), 165.4 (s, CO). – MS (70 eV, evaporation temp. 70°C): *m/z* (%) = 238 (20) [M^+], 179 (7), 178 (9), 119 (20) [$M^+ - C_8H_7O$], 118 (100) [$M^+ - C_8H_8O$], 91 (23), 90 (43), 89 (19), 77 (5), 65 (11), 63 (9), 51 (5), 39 (10).

$C_{16}H_{14}O_2$ (238.29) Calcd. C 80.65 H 5.92
Found C 81.18 H 6.28

Reaction of **11** *with* $Cr(CO)_3(NH_3)_3$: A mixture of 0.82 g (6.8 mmol) of **11**[34], 1.52 g (8.1 mmol) of $Cr(CO)_3(NH_3)_3$[10], and 20 ml of dioxane is refluxed for 4 h, during which time the mixture becomes green-black. The solvent is evaporated at 0.001 mbar into a cold trap, and the residue is extracted with diethyl ether in a Soxhlet apparatus. After solvent removal, 0.69 g of a crystalline gold yellow residue is obtained. – IR (THF): $\tilde{\nu}$ = 1963 cm^{-1} (s, C=O), 1928 (m, C=O), 1887 (s, C=O). – MS (70 eV, evaporation temp. 75°C): *m/z* (%) = 258 (17) [M^+], 230 (3) [$M^+ - CO$], 202 (7) [$M^+ - 2\,CO$], 174 (38) [$M^+ - 3\,CO$], 156 (52) [$174 - H_2O$], 105 (20), 91 (27), 69 (26), 52 (100) [Cr^+]; (70 eV, evaporation temp. 135°C): 374 (4) [M^+], 346 (2) [$M^+ - CO$], 318 (5) [$M^+ - 2\,CO$], 290 (18) [$M^+ - 3\,CO$], 246 (22), 91 (12), 69 (4), 52 (100) [Cr^+], 28 (14).

Reaction of **19** *with Triphenylphosphine under Photochemical Conditions:* A solution of 0.31 g (1 mmol) of **19** in 150 ml of benzene is filled into a photolysis cell (Duran glass) equipped with a magnetic stirring bar. To the solution is added a solution of 0.52 g (2 mmol) of triphenylphosphine in 10 ml of benzene. The reaction mixture is irradiated by means of a 125-W high-pressure mercury lamp (Phillips HPK 125) until no more carbon monoxide is evolved (ca. 40 min). The brown solution is filtered through a P4 frit into a 250-ml Schlenk flask, and the benzene is evaporated in vacuo. The residue is liberated from residual solvent by the application of a high vacuum for 2 h. 0.78 g of a brown, viscous solid is obtained. Signal intensities in the ^{1}H-NMR spectrum indicate ca. 70% conversion. Mixture components:

1) *exo*-**24**: ^{1}H NMR (400 MHz, [D_6]benzene): δ = –0.15 (s, 9H, 3 CH_3), 2.64 (dd, 1H, *exo*-2-H, $^2J_{2,2}$ = –13.6 Hz, $^3J_{exo\text{-}2,endo\text{-}1}$ = 3.0 Hz), 2.95 (m, 1H, *endo*-1-H, $^3J_{1,endo\text{-}2}$ = 5.8 Hz), 3.28 (dd, 1H, *endo*-2-H), 3.97 (m, 1H, 5-H, $^3J_{5,4}$ = 6.5 Hz, $^3J_{5,6}$ = 5.7 Hz, $J_{5,P}$ = 3.5 Hz), 4.09 (m, 1H, 4-H, $^3J_{4,3}$ = 5.8 Hz, $J_{4,P}$ = 2.3 Hz), 4.43 (m, 1H, 6-H, $J_{6,P}$ = 3.0 Hz), 4.66 (m, 1H, 3-H, $J_{3,P}$ = 2.2 Hz), 7.31–7.41 (m, 9H, *meta*-, *para*-H), 7.69 (m, 6H, *ortho*-H); NOE: Irradiation with the frequency assigned to *ortho*-H gives an NOE for *endo*-1-H and vice versa; irradiation with the frequency assigned to *exo*-2-H gives an NOE for 3-H and *endo*-2-H, but not for *ortho*-H; irradiation with the frequency assigned to CH_3 does not show an NOE for *ortho*-H. – ^{31}P NMR (32.3 MHz, [D_6]benzene): δ = 93.49.

2) *exo*-**19**.

3) Triphenylphosphine.

Reaction of **12** *with n-Butyllithium/tmeda/Chlorotrimethylsilane:* A solution of 0.24 g (1 mmol) of **12** in 11.2 ml of THF in a two-necked 50-ml round-bottom flask equipped with a magnetic stirring bar, rubber septum, and a reflux condenser is cooled to –78°C. Then, 0.75 ml (1.1 mmol) of a 1.46 M *n*-butyllithium solution in hexane and 0.13 g (1.1 mmol) of tmeda are subsequently added through the rubber septum. The mixture is stirred at –78°C for 1 h, and a color change from yellow to reddish is observed. Then, 0.13 g (1.2 mmol) of chlorotrimethylsilane is added through the rubber septum, and the mixture is allowed to warm to 25°C during ca. 12 h. The mixture is hydrolyzed by addition of 10 ml of oxygen-free water. It is extracted rapidly three times with diethyl ether. The collected organic layers are washed with oxygen-free water and then dried with $MgSO_4$. After filtration through a P4 glass frit the solvent is evaporated under reduced pressure. The product is crystallized from pentane. Yield 0.15 g (50%) of a green-yellow solid, which is identified as a mixture (62:38) of **25** and **26** by ^{1}H NMR. An analytical sample (128 mg) is separated by RP-HPLC [Polygosil 100-7-C16/E and Polygosil 100-7-C18/A, column 250 × 25 mm, methanol/water (9:1, v/v), degassed under Ar]:

Fraction 1 (*k'* = 0.81): 25 mg (9%) of **25**: IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1} (w), 2920 (m), 2850 (m), 1940 (s, C=O), 1985 (s, C=O), 1460 (w), 1355 (w), 1248 (m, $SiMe_3$), 1190 (w), 1130 (w), 925 (m), 881 (m), 833 (s, $SiMe_3$), 760 (w), 695 (m), 665 (s), 630 (s), 580 (w), 530 (m). – ^{1}H NMR (200 MHz, [D_6]benzene): δ = 0.14 (s, 9H, 3 CH_3), 2.23–2.36 (m, 1H, 1-H or 2-H), 2.41–2.60 (m, 2H, 1-H or 2-H), 2.76–2.90 (m, 1H, 1-H or 2-H), 4.16 (dd, 1H, 5-H, $^3J_{4,5}$ = 6.1 Hz, $^3J_{5,6}$ = 6.1 Hz), 4.55 (dd, 1H, 6-H, *J* = 0.7 Hz), 4.89 (d, 1H, 4-H). – ^{13}C NMR (50 MHz, [D_6]benzene): δ = –1.0 (q, 3 CH_3, $^1J_{C,H}$ = 119 Hz), 30.1 (t, C-1 or C-2, $^1J_{C,H}$ = 140 Hz), 31.8 (t, C-2 or C-1, $^1J_{C,H}$ unresolved), 90.2 (d, C-5 or C-6, $^1J_{C,H}$ = 174 Hz), 93.2 (d, C-5 or C-6, $^1J_{C,H}$ = 175 Hz), 98.4 (s, C-3), 98.4 (d, C-4, $^1J_{C,H}$ = 172 Hz), 116.0 (s, C-2a or C-6a), 124.1 (s, C-2a or C-6a), 234.8 (s, CO). – MS (70 eV): *m/z* (%) = 313 (8) [M^+ (^{53}Cr)], 312 (24) [M^+ (^{52}Cr)], 256 (10) [$M^+ - 2\,CO$], 230 (10) [$M^+ - 3\,CO$ (^{54}Cr)], 229 (29) [$M^+ - 3\,CO$ (^{53}Cr)], 228 (100) [$M^+ - 3\,CO$], 111 (8), 52 (22) [Cr^+].

Fraktion 2 (*k'* = 2.22): 4 mg (1%) of **26**: δ = 0.23 (s, 9H, 3 CH_3), 2.29–3.05 (m, 4H, 1-H, 2-H), 4.23 (d, 1H, 5-H), 4.59 (s, 1H, 3-H), 4.64 (d, 1H, 6-H).

$C_{14}H_{16}CrO_3Si$ (312.36) Calcd. C 53.83 H 5.16 Cr 16.65 Si 8.99
Isomeric mixture Found C 53.72 H 5.23 Cr 16.74 Si 9.11

Reaction of **4** *with Dimethyl Fumarate:* Into a 250-ml two-necked round-bottom flask equipped with a reflux condenser, a magnetic stirring bar, and an argon inlet are placed 324 mg (2.0 mmol) of **4**[30], 288 mg (2.0 mmol) of dimethyl fumarate, and 150 ml of decalin[35]. The mixture is refluxed for 24 h. Then the solvent is evaporated into a cold trap at 0.001 mbar. The residue is liberated from residual solvent at 0.001 mbar during ca. 12 h. 416 mg (68%) of **31** is obtained as a colorless, viscous oil, which solidifies within 3 d. Threefold recrystallization of an analytical sample (217 mg) from hexane affords 114 mg (19%) of **31** as a white powder, m.p. 90–91°C. – IR (film): $\tilde{\nu}$ = 3440 cm^{-1} (w), 3020 (w), 2960 (s), 2910 (s), 2850 (w), 1730 (s, C=O), 1605 (w), 1580 (w), 1488 (m), 1445 (s), 1377 (m), 1350 (m), 1328 (m), 1295 (m), 1260 (m), 1220 (s, C–O, acetal), 1198 (s, C–O, ester), 1175 (s, C–O, ester), 1165 (s, C–O, ester), 1100 (s, acetal), 1065 (m), 1035 (m), 1015 (m), 980 (m), 960 (m, acetal), 920 (m), 900 (w), 835 (m), 760 (s, *o*-disubst. arene), 730 (w), 705 (w), 598 (m). – ^{1}H NMR (200 MHz, [D_8]THF): δ = 2.89 (dd, 1H, 4β-H, $^2J_{4\alpha,4\beta}$ = –16.2 Hz, $^3J_{3,4\beta}$ = 10.7 Hz), 3.15 (dd, 1H, 4α-H, $^3J_{4\alpha,3}$ = 5.6 Hz), 3.30 (d, 1H, 2-H, $^3J_{2,3}$ = 10.6 Hz), 3.42 (ddd, 1H, 3-H), 3.64 (s, 6H, 2 CH_3), 4.00 (m, 3H, OCH_2, OC*H*H), 4.18 (m, 1H, OCH*H*), 7.10 (m, 3H, 5-H, 6-H, 7-H), 7.40 (m, 1H, 8-H). – ^{13}C NMR (50 MHz, [D_8]THF): δ = 31.7 (t, C-4), 42.1 (d, C-3), 51.8 (q, 1 CH_3), 51.9 (q, 1 CH_3), 52.4 (d, C-2), 65.9 (t, 1 OCH_2), 67.0 (t, 1 OCH_2), 108.2 (s, C-1), 125.9 (d, C-5 or C-6 or C-7 or C-8), 126.9 (d, C-5 or C-6 or C-7 or C-8), 128.7 (d, C-5 or C-6 or C-7 or C-8), 129.2 (d, C-5 or C-6 or C-7 or C-8), 136.1 (s, C-4a), 138.8 (s, C-8a), 171.8 (s, 3-CO_2), 174.5 (s, 2-CO_2). – MS (70 eV): *m/z* (%) = 306 (12) [M^+], 274 (6), 247 (16), 246 (10), 215 (27), 171 (16), 163 (11), 162 (100), 115 (18), 105 (41), 59 (8).

$C_{16}H_{18}O_6$ (306.32) Calcd. C 62.74 H 5.92
Found C 62.71 H 5.99

Reaction of **15** *with Dimethyl Fumarate:* a) In a two-necked round-bottom flask a solution of 256 mg (0.86 mmol) of **15** and 243 mg (1.68 mmol) of dimethyl fumarate in 150 ml of decalin (tetrahydronaphthalene contents 0.17%, GC) is refluxed for 24 h. The mixture is filtered through a P4 glass frit, and the solvent is evaporated into a cold trap at 0.001 mbar. 260 mg of a yellow viscous oil is obtained, which is subjected to flash chromatography [silica gel, column 60 × 2 cm, pentane/diethyl ether (1:2), later diethyl ether].

Fraction 1: 10 mg (4.3%) of **29**, identified by a comparison with an authentic sample[29] (^{1}H NMR, IR, MS).

Fraction 2: 50 mg (20%) of **15**, identified by a comparison with an authentic sample (^{1}H NMR, IR, MS).

Fraction 3: 154 mg (59%) of **31**.

Fraction 4: 3 mg (1%) of **32**, bright yellow solid. – ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 2.82 (dd, 1H, 4β-H, $^2J_{4\alpha,4\beta}$ = −16.5 Hz, $^3J_{4\beta,3}$ = 11.4 Hz), 2.98 (dd, 1H, 4α-H, $^3J_{4\alpha,3}$ = 5.2 Hz), 3.19 (d, 1H, 2-H, $^3J_{2,3}$ = 11.7 Hz), 3.42 (ddd, 1H, 3-H), 3.65 (s, 6H, 2 CH$_3$), 3.98 (m, 2H, α-OCH$_2$ or β-OCH$_2$), 4.08 (m, 1H, α-OC*H*H or β-OCH*H*), 4.20 (m, 1H, α-OCH*H* or β-OCH*H*), 5.18 (d, 1H, 5-H or 8-H, $^3J_{5,6}$ = 6.3 Hz), 5.25 (dd, 1H, 6-H or 7-H, $^3J_{6,7}$ = 6.0 Hz), 5.57 (dd, 1H, 7-H or 6-H), 5.82 (d, 1H, 8-H or 5-H). – MS (70 eV): *m/z* (%) = 387 (1) [M$^+$ − 2 CO (^{53}Cr)], 386 (5) [M$^+$ − 2 CO (^{52}Cr)], 359 (3) [M$^+$ − 3 CO (^{53}Cr)], 358 (16) [M$^+$ − 3 CO (^{52}Cr)], 274 (22), 270 (14), 254 (12), 242 (16), 240 (13), 216 (16), 215 (100), 171 (78), 162 (37), 128 (14), 127 (24), 115 (40), 105 (38), 52 (92) [Cr$^+$], 28 (54) [CO$^+$]. – GC: After decomposition of the complex with O$_2$/hv: 86% of **31**, identified by a comparison with an authentic sample; rel. retention time: 7.08 (*cis*-decalin: rel. ret. time 1).

Fraction 5: 1 mg (0.3%) of **32**; after decomposition of the complex with O$_2$/hv: 96% of **31**.

b) Comparable results are obtained when the reaction is carricd out in *n*-dodecane.

*Crystal-Structure Determination of exo-***16**[36]: $C_{12}H_{10}CrO_3$; crystal size 0.32 × 0.32 × 0.47 mm; color: yellow; a = 6.231(1), b = 13.079(1), c = 13.873(2) Å; β = 99.92(1)°; V = 1113.7 Å^3; $d_{calcd.}$ = 1.52 g · cm^{-3}; μ = 9.88 cm^{-1}; Mo-K_α radiation, λ = 0.71069 Å; F(000) = 520 e; crystal system: monoclinic; space group: $P2_1/c$; Z = 4; Nonius CAD4 diffractometer; scan mode: ω − 2Θ; (sin Θ/λ)$_{max.}$ = 0.70; 3341 measured (±h, +k, +l), 3201 independent, 2315 observed reflections [$I > 2\sigma(I)$] for 175 refined parameters; structure solved by heavy-atom method; H-atom positions located and refined with fixed isotropic parameters (0.05 Å^2); R = 0.034; R_w = 0.036 [$w = 1/\sigma^2(F_o)$]; EOF = 1.91; residual electron density 0.32 e Å^{-3}.

CAS Registry Numbers

1: 649-87-1 / [1-D]**1**: 31458-01-2 / **2**: 22250-74-4 / **3**: 28749-81-7 / **4**: 14458-33-4 / **5**: 61599-88-0 / **6**: 55337-80-9 / **7**: 78920-29-3 / **8**: 122057-61-8 / **9**: 38341-54-7 / **10**: 38194-40-0 / **11**: 35447-99-5 / **12**: 99537-78-7 / *exo*-[1-D]**12**: 122120-88-1 / *endo*-[1-D]**12**: 122210-17-7 / **13**: 122113-96-6 / **14**: 122113-97-7 / **15**: 130495-59-9 / *exo*-**16**: 122120-89-2 / *endo*-**16**: 122211-05-6 / *exo*-**17**: 122210-18-8 / *endo*-**17**: 122113-98-8 / *exo*-**18**: 122210-19-9 / *endo*-**18**: 122113-99-9 / *exo*-**19**: 122210-20-2 / *endo*-**19**: 122114-00-5 / *exo*-**20**: 122210-21-3 / *endo*-**20**: 122114-01-6 / **22**: 89-95-2 / **22** · Cr(CO)$_3$: 12181-99-6 / **23**: 130469-01-1 / *exo*-**24**: 122114-04-9 / **25**: 122120-87-0 / **26**: 122148-44-1 / **29**: 12154-63-1 / **31**: 130469-02-2 / **32**: 130495-60-2 / Cr(CO)$_3$(NH$_3$)$_3$: 14974-11-9 / Cr(CO)$_6$: 13007-92-6 / Li_2CuCl_4: 15489-27-7 / dimethyl fumarate: 624-49-7 / 1-(chloromagnesio)cyclobutabenzene: 130469-03-3 / 4-bromo-1-butene: 5162-44-7

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