179. Tricarbonyl-chromium Complexes of Benzannelated Cyclopropparenes

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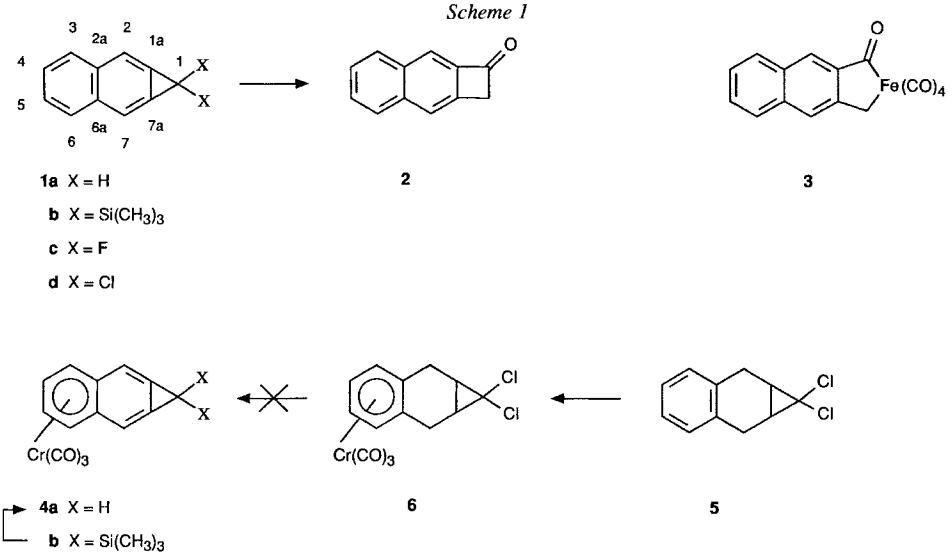
(13.VII.89)

Reaction of 1*H*-cyclopropa[*b*]naphthalene (**1a**) or 1*H*-cyclopropa[*b*]anthracene (**10a**) with tris(acetonitrile)tricarbonylchromium affords cyclobutanaphthalenone and cyclobutaanthracenone **2** and **11**, respectively. In contrast, the bis-silylated cycloproparenes **1b** and **10b** undergo complexation at the terminal benzene ring and lead to the arene-tricarbonylchromium complexes **4b** and **12**, respectively. Desilylation of **4b** to **4a** is effected by *t*-BuOK.

Introduction. – The most important factor determining the chemistry of cycloproparenes is their strain energy of *ca.* 65 kcal/mol [1]. Accordingly, the majority of their reactions involve cleavage of one of the cyclopropene bonds, by which this strain energy can be released [2]. This general tendency of cycloproparenes applies also to their reactions with transition-metal complexes. Typically, cyclopropabenzene reacts with complexes of several 0-valent metals such as Ni, Pd, and Pt to metallacyclobutabenzenes by insertion into one of the lateral cyclopropene bonds [3]. With 1,1-difluoro-cyclopropabenzene attack occurs at the central cyclopropene double bond and leads to metallapropellanes [4]. So far, no η^6-complexes of cycloproparenes have been described. Since the chemistry of tricarbonylchromium complexes of cyclobutabenzenes is well established [5], we started an investigation on preparation and properties of their next lower homologues. As first targets, tricarbonylchromium derivatives of 1*H*-cyclopropa[*b*]naphthalene (**1a**) were selected. Compound **1a** is readily available [1] [6], and it appeared preferable to develop the required reaction conditions with this compound rather than with the parent cyclopropabenzene itself, because it is known for its very penetrating foul odor.

Results and Discussion. – *1H-Cyclopropa[b]naphthalenes.* When treated with 0.68 equiv. of tris(acetonitrile)tricarbonylchromium at 25°, 1*H*-cyclopropa[*b*]naphthalene (**1a**) does not undergo complexation, but is converted to cyclobutanaphthalenone **2** [7] in 57% yield (*Scheme 1*). This result may be interpreted by oxidative addition of the cyclopropene ring to the metal, followed by CO insertion into the C_{Ar}–Cr bond and reductive elimination of the metal. An analogous reaction has already been described: **1a** reacts with $Fe_2(CO)_9$, however, in this case **2** is not formed. The reaction stops at the metallacycle **3**, which has been isolated and identified [8], and no reductive elimination to **2** takes place. The fate of the Cr after the reaction with **1a** is not known, but when a threefold molar excess of **1a** was used, the yield of **2** was only little affected (45%), which indicates that more than one CO of the reagent may participate in the reaction.

Scheme 1



Cyclobutanaphthalenone **2** was also formed (5–10% yield) upon heating of $Cr(CO)_6$ with **1a** to 90°, but under these reaction conditions, considerable decomposition to unidentifiable products occurred. No reaction was observed at 60°.

Although bis-silylation of the CH_2 group of cycloproparenes directs reactivity preferentially to the aromatic ring [9], silylated cycloproparenes may still be converted to metallacyclobutabenzenes with certain transition metals such as Ni and Pd [3][10]. In our hands, 1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene (**1b**) [11] was inert towards $Fe_2(CO)_9$ up to 70° (in toluene). However, with tris(acetonitrile)tricarbonylchromium [12] complexation occurred at the terminal benzene ring and produced **4b** in 51% yield [13]. Upon reaction of **1b** with $Cr(CO)_6$ (in Bu_2O, 120°, 140 h), **4b** is also obtained, but only in a disappointingly low yield of 6% (75% of starting material recovered). The X-ray structure of **4b** has been reported in a preliminary communication [13]. The NMR data are collected in *Table 1*.

Table 1. *^1H-* (200 MHz) *and ^{13}C-NMR* (50 MHz) *Data for Tricarbonylchromium Complexes of 1*H-*Cyclopropa[b]naphthalene* (in C_6D_6)[a])

Compound	X	Nucleus	C(1)	C(1a,7a)	C(2,7)	C(2a,6a)	C(3,6)	C(4,5)	C(CO)
4a	H	^1H	2.68 (*AB*, ^2J = 10.3) δ_A = 2.79, δ_B = 2.57	–	6.67 (*s*)	–	5.31–5.26 (*m*)	4.60–4.64 (*m*)	–
4b	$SiMe_3$	^1H	[b])	–	6.29 (*s*)	–	5.22–5.26 (*m*)	4.61–4.65 (*m*)	–
4a	H	^{13}C	18.8	126.8	112.2	109.1	91.8	92.0	233.3
4c	$SiMe_3$	^{13}C	31.9[c])	134.9	106.4	108.3	91.7	92.1	234.2

[a]) Assignments by analogy with data in [26]. [b]) $\delta(SiCH_3)$: 0.04 (*s*), –0.05 (*s*). [c]) $\delta(SiCH_3)$: –1.2; –1.3.

By treatment with *t*-BuOK in THF at –78° for 100 h, **4b** was desilylated. After rapid chromatography (SiO_2, toluene/hexane 1:3), crude **4a** (69%) was isolated. Recrystallization with toluene/hexane (–30°) was accompanied with much loss, and afforded a 35% yield of crystalline product. A side product was also isolated from the reaction in *ca.* 2% yield to which we ascribe, based on the NMR data, the structure of a tricarbonylchromium complex of a 2-substituted naphthalene. However, its structure could not be unambiguously established.

The ^{1}H-NMR spectrum of **4a** corresponds to that of the silylated derivative **4b** (see *Table 1*), the principal difference consisting in the *AB* system for the cyclopropene H-atoms, centered at 2.68 ppm ($^2J_{AB}$ = 10.3 Hz, δ_A = 2.79, δ_B = 2.57 ppm). By analogy to other tricarbonylchromium complexes [14], the signal at higher field is attributed to the proton *anti*-oriented to the $Cr(CO)_3$ moiety.

The structure of **4a** was established by X-ray structure analysis (*Fig. 1*). Details concerning the structure determination are given in the *Exper. Part.* As in the case of uncomplexed cycloproparenes [15], the structural modifications between the silylated (**4b**) and the desilylated compound (**4a**) are relatively small. The cyclopropene moiety in **4a** is almost identical to that in uncomplexed **1a** (*Table 2*).

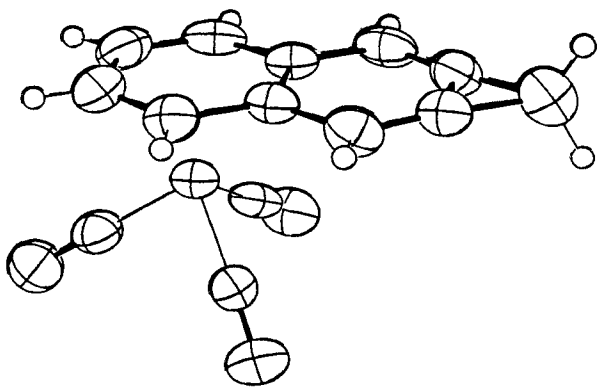


Fig. 1. *X-Ray structure of* **4a**

An alternative access to **4a**, in analogy to the conventional synthesis of 1*H*-cyclopropa[*b*]naphthalene (**1a**) was also attempted. The dichlorocarbene adduct **5** of 1,4-dihydronaphthalene [6] was thermolyzed with $Cr(CO)_6$ to yield the tricarbonyl complex **6** in 25% yield or, alternatively, reacted with tris(acetonitrile)tricarbonylchromium (30% of **6**) or tricarbonyl(naphthalene)chromium [16] (36% of **6**, yield not optimized). However, the very strongly basic reaction conditions required for aromatization of **5** (*t*-BuOK in THF) are too vigorous for **6**, and led to total decomposition of the starting material. Decomposition was also observed when 1,1-dichloro- or 1,1-difluoro-1*H*-cyclopropa-[*b*]naphthalene [17] (**1c** and **1d**, respectively) were exposed to tris(acetonitrile)-tricarbonylchromium. Only in one run, with **1d**, some (38%) of the starting compound could be recovered. Similarly, reaction with 1,1-difluoro-3,4-dimethyl-1*H*-cyclopropabenzene [18] led to decomposition, while complexation of **1d** by $Cr(CO)_6$ failed.

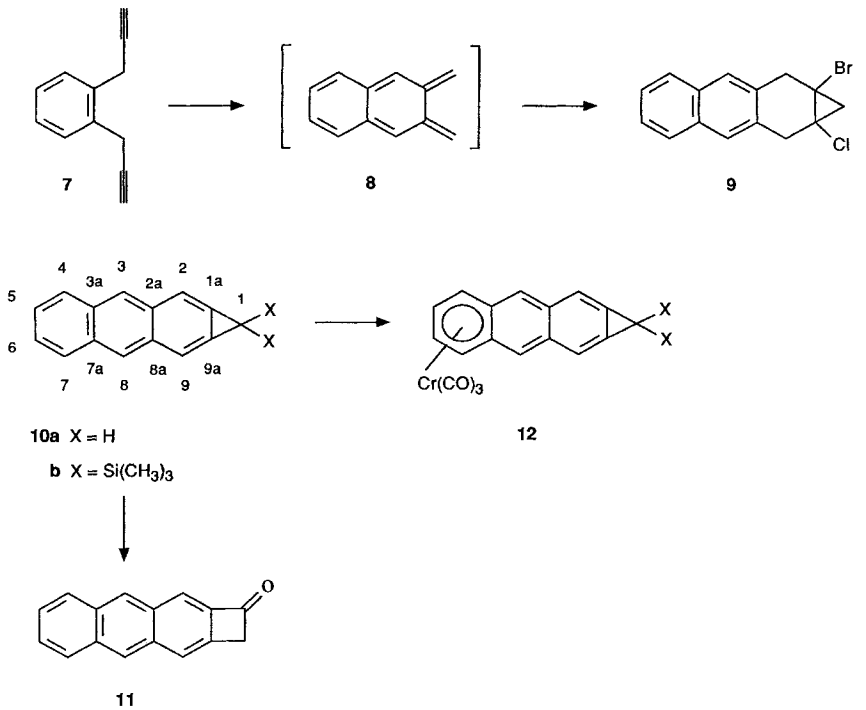
Table 2. *Selected Structural Data for Tricarbonylchromium Complexes of Cycloproparenes*

	4a	**4b**	**1a**	Tricarbonyl-(naphtalene)chromium[a])
C(1)–C(1a)	1.487(8)	1.517(13)	1.504	–
C(1)–C(7a)	1.494(8)	1.502(16)	(1.504)	–
C(1a)–C(7a)	1.368(7)	1.384(14)	1.368	1.392
C(1a)–C(2)	1.321(7)	1.347(13)	1.337	1.415
C(2)–C(2a)	1.439(6)	1.452(16)	1.437	1.406
C(2a)–C(6a)	1.445(6)	1.441(13)	1.439	1.439
C(6a)–C(7)	1.433(6)	1.450(14)	(1.437)	1.438
C(7)–C(7a)	1.333(7)	1.335(17)	(1.337)	1.375
Average C–C distance for C(2a) to C(6a)	1.41(3)	1.42(2)	1.40(3)	1.41(3)
Cr···plane(C(2a)–C(6a))	1.742(2)	1.742(5)	–	1.747
Cr···C(2a)	2.303(4)	2.301(12)	–	2.306
Cr···C(3)	2.215(4)	2.208(9)	–	2.186
Cr···C(4)	2.210(5)	2.209(9)	–	2.191
Cr···C(5)	2.208(5)	2.227(10)	–	2.213
Cr···C(6)	2.210(5)	2.216(9)	–	2.214
Cr···C(6a)	2.310(4)	2.298(11)	–	2.337
C(1a)–C(1)–C(7a)	54.6(3)	54.6(6)	54.1	–
C(1)–C(1a)–C(7a)	63.0(3)	62.2(7)	62.9	–
C(1)–C(7a)–C(1a)	62.4(4)	63.3(7)	(62.9)	–
C(2)–C(1a)–C(7a)	125.5(4)	124.5(11)	124.9	124.9
C(1a)–C(7a)–C(7)	124.3(4)	126.3(9)	(124.9)	119.6

[a]) [1]. [b]) [25].

1H-Cyclopropa[b]anthracenes. 1H-Cyclopropa[*b*]anthracene (**10a**), first described by *Billups et al.* [19], is now more conveniently available *via* base-induced rearrangement of *o*-di(prop-2-ynyl)benzene (**7**), to *o*-naphthoquinodimethane (**8**) [20] and trapping of the latter *in situ* with 1-bromo-2-chlorocyclopropene [21]. The yield for the aromatization of the adduct **9** was significantly improved over that reported by *Billups et al.* by carrying out the reaction under milder conditions [22]. When **10a** was exposed to tris(acetonitrile)tricarbonylchromium at r.t., the ketone **11** was formed in 54% yield as yellow crystals (*Scheme 2*). The structure follows from the analytical and spectroscopic data (see *Exper. Part*). 1*H*-Cyclopropa[*b*]anthracene (**10a**) was silylated quantitatively by two sequential treatments with BuLi and Me_3SiCl. Interestingly, when the silylation was carried out as a competition experiment in the presence of both **1a** and **10a**, only the latter reacted, while the former was recovered unchanged. 1,1-Bis-(trimethylsilyl)-1*H*-cyclopropa[*b*]anthracene (**10b**) was reacted with tris(acetonitrile)tricarbonylchromium at 60° for 5.5 h in analogy to the reaction with **1b**. Complexation was observed at the terminal benzene ring to 40%. The crude product was purified by flash chromatography and recrystallization. Some decomposition occurred during these operations so that the

Scheme 2



final yield of recrystallized **12** was only 32%. This is still remarkable in view of the poor yield reported for the tricarbonylchromium complex of anthracene itself [23]. The cause for this discrepancy has not been investigated; possibly, the presence of the bulky Me_3Si substituents could provide some steric hindrance towards displacement of the organic ligand by the solvent, or the cyclopropane ring could effect distortions of the molecular skeleton, which might favor complexation. Alternatively, the presence of the Me_3Si groups significantly enhances the solubility of the cycloproparene, and this could also be responsible for the improved yield compared with that obtained with unsubstituted anthracene. It is undoubtedly crucial for the separation of **12** from **10b** by column chromatography. The ^{1}H-NMR of **12** (*Fig. 2*) compares in the same way with that of the tricarbonylchromium complex of anthracene [23] as that of **4a** or **4b** with that of tricarbonyl(naphthalene)chromium [16]. The *AA'BB'* system of the protons of the coordinated benzene ring are shifted upfield in the range of 5.6 and 4.8 ppm, respectively, while the other signals are only slightly affected by the complexation. The Me_3Si groups are non-equivalent, as in the case of **4b**. Unfortunately, no suitable crystals could be obtained for an X-ray analysis. Attempted desilylation of **12** under the conditions used for **4b**, afforded, so far, only decomposition products.

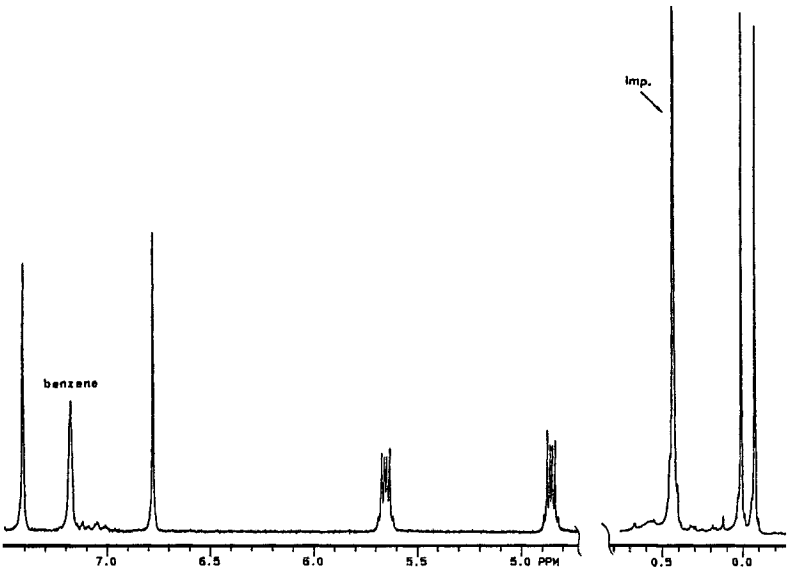


Fig. 2. *^{1}H-NMR of* **12**

This work was supported by the *Swiss National Science Foundation* (project No. 2.602-087). The authors are indebted to Prof. *E. P. Kündig* and Mr. *E. Wenger* for helpful comments on the experimental techniques for carbonyl-chromium complexes.

Experimental Part

1. *General.* Solvents and reagents are of commercial origin (*Fluka, Aldrich*) and were purified and dried, if necessary, according to traditional procedures. The organometallic reactions were carried out on a vacuum line under inert atmosphere; the apparatus was dried by a heat-gun under vacuum, and the solvents freshly distilled from Na. UV spectra were measured in quartz cells of 1-cm width. The positions of the bands are indicated in nm and the intensities in log ε. IR spectra are recorded in soln. (NaCl windows) on *Perkin Elmer 681* or *Mattson Instrument, Polaris* spectrometers. The position of the bands are given in wave numbers (cm^{-1}). ^{1}H- (200 MHz) and ^{13}C-NMR (50 MHz) spectra were recorded on a *Varian XL-200* instrument. The chemical shifts are in ppm relative to TMS. The multiplicity of the ^{13}C signals refers to proton coupling off-resonance. MS were recorded on *Varian SM1* and *EM-600* instruments.

2. *Reactions with 1*H-*Cyclopropa[*b*]naphthalene* (**1a**). *1,2-Dihydrocyclobuta[*b*]naphtalen-1-one* (**2**). To tris(acetonitrile)tricarbonylchromium [12] (145 mg, 0.56 mmol) in a *Schlenk* tube, **1a** (114 mg, 0.81 mmol) and Bu_2O (15 ml) were added under N_2. After degassing (3 ×), the yellow soln. was stirred at r.t. for 23 h under a slow stream of N_2 and with exclusion of light. The soln. was filtered through *Celite*, which was washed with Et_2O until disappearance of the yellow color. After evaporation of the solvent, the residue was purified by FC (SiO_2, toluene). Recrystallization (CCl_4) afforded **2** (78 mg, 57%). M.p. 162°. IR ($CHCl_3$): 3700*w*, 3000*m*, 2950*m*, 2900*w*, 1755*s*, 1600*m*, 1250*w*, 1050*s*, 875*w*. ^{1}H-NMR ($CDCl_3$): 7.97–7.87 (*m*, 4 H); 7.64–7.43 (*m*, 2 H); 4.19 (*s*, 2 H). MS: 168 (88, M^+), 140 (100), 139 (94), 128 (1), 111(3), 98 (5), 85 (5), 69 (18), 63 (16), 56 (10), 52 (5).

*Synthesis of Tricarbonyl(1*H-*Cyclopropa[*b*]naphthalene)chromium* (**4a**). *Tricarbonyl[1,1-Bis(trimethylsilyl)-1*H-*cyclopropa[*b*]naphthalene]chromium* (**4b**). A mixture of **1b** [11] (371 mg, 1.3 mmol), tris(acetonitrile)tricarbonylchromium (228 mg, 0.88 mmol), and Bu_2O (15 ml) was heated to 90° for 2 h under a slow stream of N_2 and with exclusion of light. After cooling to r.t., the resulting soln. was filtered through

Celite, which was extracted with Et_2O until disappearing of the orange color. The solvent was evaporated, and the residue was washed with hexane (2 × 10 ml). Recrystallization (hexane) at 0° and workup of the mother liquor (CC; SiO_2, degassed hexane, followed by degassed CH_2Cl_2) afforded **4b** (187 mg, 51%) as orange crystals. M.p. 179°. IR (hexane): 1968*vs*, 1900*s*, 1475*m*, 1456*m*. ^{1}H- and ^{13}C-NMR: see *Table 1*. MS: 420 (2, M^+), 321(3), 209 (3), 181(5), 155 (5), 111 (5), 80 (4), 73 (76), 59 (4), 52 (100). X-Ray structure: see [13].

Reaction of **1b** *with* $Cr(CO)_6$. A mixture of **1b** (315 mg, 1.1 mmol), $Cr(CO)_6$ (242 mg, 1.1 mmol) in Bu_2O (15 ml), hexane (5.0 ml), and THF (0.5 ml) was degassed (3 ×) and heated to 120° for 137 h. After cooling, the soln. was filtered through *Celite*, which was washed with Et_2O until disappearance of the orange color. Purification as described above afforded **4b** in 6% yield.

Tricarbonyl(1H-cyclopropa[b]naphthalene)chromium (**4a**). To **4b** (106 mg, 0.25 mmol), degassed *t*-BuOH (0.7 ml) and THF (5.0 ml) were added at –78°, followed by dropwise addition of sublimed *t*-BuOK (72 mg, 0.64 mmol) in THF (11 ml) at –78° during 60 min. After stirring at –78° for 104 h, the mixture was quenched with Me_3SiCl (98.5 mg, 0.91 mmol), then filtered through *Celite*, which was washed with Et_2O. After evaporation of the solvent and rapid chromatography (SiO_2, degassed toluene/hexane 1:3), crude **4a** was collected (48 mg, 69%). Recrystallization (toluene/hexane at –30°) gave **4a** in 35% yield. M.p. 126°(dec.). IR (hexane): 1975*vs*, 1912*m*, 1902*m*, 1470*s*, 1460*m*, 1455*s*, 1449*m*, 1376*m*, 725*m*. ^{1}H- and ^{13}C-NMR: see *Table 1*. MS: 276 (3, M^+), 220 (4), 192 (18), 140 (2), 139 (2), 115 (1), 96 (1), 89 (1), 77 (2), 63 (2), 52 (100).

Crystallographic Data of **4a**. Cell parameters and reflection intensities were measured at r.t. on a *Nonius CAD4* diffractometer with graphite monochromated Mo$K\alpha$ radiation. A summary of crystal data, intensity measurements, and structure refinement is given in *Table 3*, and selected geometrical parameters are reported in *Table 2*. The structure was solved by direct methods (MULTAN-87) and refined by least-square analysis with the X-TAL program [27]. Crystallographic data have been deposited with the *Cambridge Crystallographic Data Center*, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, England.

Table 3. *Summary of Crystal Data, Intensity Measurement, and Structure Refinement for* **4a**

Formula	$C_{14}H_8O_3Cr$	μ [mm^{-1}]	0.944
Molecular weight	276.2	$(\sin\theta/\lambda)_{max}$ [Å^{-1}]	0.53
Crystal system	Monoclinic	No. of measured reflections	1513
Space group	$P2_1/n$	No. of observed reflections	1428
Crystal size [mm]	0.08 × 0.25 × 0.41	Criterion for observed	$\|Fo\|>4\sigma(Fo)$
a [Å]	8.7539(12)	No. of parameters	187
b [Å]	15.028(2)	Refinement (on F)	full-matrix
c [Å]	8.9310(13)	Weighting scheme	$\omega = 1/\sigma^2(F)$
β [°]	92.17(1)	H-Atoms	obs. and refined
V [Å^3]	1174.1(2)	Max. and average Δ/σ	0.027, 0.001
Z	4	Max. and min. $\Delta\rho$ [e · Å^{-3}]	0.35, –0.33
D_c [g · cm^{-3}]	1.56	S	2.60
F_{000}	560	R, ωR [%]	3.7, 3.5

Tricarbonyl(1,1-dichloro-1a,2,7,7a-tetrahydrocyclopropa[b]naphthalene)chromium (**6**). A mixture of **5** [1] [6] (429 mg, 2.0 mmol), tris(acetonitrile)tricarbonylchromium (522 mg, 2.0 mmol), and Bu_2O (9.0 ml) was degassed (3 ×) and heated to 90° for 3.5 h under a slow stream of N_2 and with exclusion of light. After cooling, the soln. was filtered through *Celite*, and the *Celite* was washed with Et_2O. After evaporation of the solvent, the crude product was recrystallized (toluene/hexane). The mother liquors were worked up by rapid CC (SiO_2, hexane, followed by toluene) to furnish **6** (210 mg, 30%). M.p. 156–159°. IR (hexane): 1975*s*, 1911*m*, 1904*m*, 1466*m*, 1452*w*, 1380*w*, 725*w*. ^{1}H-NMR (C_6D_6): 4.35–4.20 (*m*, 4 H); 2.26–1.88 (*m*, 4 H); 1.66–1.58 (*m*, 2 H). MS: 352, 350, 348 (2, 8, 10, M^+), 292 (5), 264 (15), 229 (3), 177 (7), 141 (100), 128 (13), 115 (49), 89 (9), 80 (18), 63 (9), 52 (69). Anal calc. for $C_{14}H_{10}CrClO_3$: C 48.16, H 2.88; found: C 48.27, H 2.97.

Upon heating equimolar amounts of **5** and $Cr(CO)_6$ in BuO_2 containing hexane and THF to 160° for 67 h, followed by workup as described above, **6** was also obtained in 25% yield, or by heating **5** (1.5 equiv.) with tricarbonyl(naphthalene)chromium in Et_2O and a small quantity of THF to 70° for 96 h, and then to 80° for 16 h (36% yield, not optimized).

3. *Tricarbonyl[1,1-bis(trimethylsilyl)-1H-cyclopropa[b]anthracene]chromium* (**12**). *1a-Bromo-9a-chloro-1a,2,9,9a-tetrahydro-1H-cyclopropa[b]anthracene* (**9**). To a soln. of *t*-BuOK (2.0 g, 17.8 mmol) and *t*-BuOH (4.0 ml, 41.6 mmol) in degassed THF, **7** [20] [21] (1.0 g, 6.5 mmol) in THF (5 ml) was added dropwise at –78°. After stirring for 30 min, degassed hexane (70 ml) was added, followed by 70 ml of a soln. of MeOH/H_2O 8:3. After extraction, the org. phase was transferred under Ar to a reaction flask cooled to –78°, containing 1.5 g of $NaHCO_3$ and 3.0 g of Na_2SO_4 under Ar. The aq. layer was extracted with 2 additional portions of degassed hexane (70 ml). The combined org. layers containing **8** were transferred under Ar without filtration to a flask cooled to –78°. 1-Bromo-2-chlorocyclopropene, prepared from 1-bromo-2,2-dichloro-1-(trimethylsilyl)-cyclopropane (1.7 g, 6.5 mmol) [24] and stored at –40°, was added under Ar. The mixture was stirred at –78° for 1 h and then allowed to warm up slowly to r.t. After evaporation of the solvent, the residue was purified by CC (SiO_2, hexane) to yield 0.66 g (2.2 mmol, 33%) of **9** [19] [21].

1H-Cyclopropa[b]anthracene (**10a**). To **9** (198 mg, 0.64 mmol) in THF (16 ml), sublimed *t*-BuOK (176 mg, 1.57 mmol) in THF (16 ml) was added dropwise at –78° during 5.5 h. The cooling bath was removed, and the solvent was evaporated *in vacuo* (oil pump). The residue was extracted with pentane (200 ml), and the insoluble salts were removed. Evaporation of the pentane afforded 104.6 mg of crude **10a** which was further purified by chromatography (SiO_2, hexane) to give pure **10a** in 84% yield.

1,1-Bis(trimethylsilyl)-1H-cyclopropa[b]anthracene (**10b**). To **10a** (114 mg, 0.6 mmol) in THF (13 ml) BuLi (1.57M in hexane; 0.6 mmol) was added dropwise at –78°. The soln. was stirred at –40° for 1 h, then cooled to –78°, and Me_3SiCl (115 µl, 0.91 mmol, freshly distilled from CaH_2) was added. Stirring was continued at –40° for 1 h. After cooling to –78°, the sequence of deprotonation-silylation was repeated under identical conditions. After warming up to r.t., the mixture was poured into sat. $NaHCO_3$ (50 ml), which was extracted with CH_2Cl_2. The org. layer was washed with H_2O to neutrality and then dried ($MgSO_4$). Evaporation of the solvent afforded a yellow solid which was purified by CC (SiO_2, petroleum ether) and yielded 184 mg (92%) of **10b**. M.p. 145–146°. UV (cyclohexane): 257.6 (4.98). IR ($CHCl_3$): 3060*m*, 3040*m*, 3010*m*, 2960*s*, 2900*m*, 1692*w*, 1605*w*, 1490*m*, 1438*m*, 1405*m*, 1362*m*, 1280*m*, 1250*s*, 1110*m*, 1020*m*, 1010*m*, 950*s*, 900*s*, 850*l*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.16 (*s*, 2 H); 7.95–7.90 (*m*, 2 H); 7.43–7.39 (*m*, 2 H); 7.14 (*s*, 2 H); 0.056 (*s*, 18 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 134.9 (C); 131.4 (C); 131.2 (C); 127.7 (CH); 124.8 (CH); 124.7 (CH); 106.4 (CH); 29.7 (C); –1.3 (CH_3). MS: 334 (46, M^+), 319 (16), 304 (10), 291 (21), 276 (19), 261 (78), 246 (100), 231 (18), 215 (19), 202 (11), 73 (36). HR-MS ($C_{21}Si_2H_{26}$): calc.: 334.1573; found: 334.1573.

1,2-Dihydrocyclobuta[b]anthracen-1-one (**11**). To **10a** (25.7 mg, 0.14 mmol) and tris(acetonitrile)tricarbonylchromium (50 mg, 0.193 mmol) [12] in Bu_2O (20 ml), THF (10 ml) was added. The soln. was degassed once and stirred at r.t. for 21 h. It was filtered through *Celite*, which was washed with Et_2O. After evaporation of the solvent the crude product was purified by FC to give **11** (15.8 mg, 54%), as yellow solid. M.p. 230–251° (dec.). UV (cyclohexane): 267.3 (4.79), 243.2 (4.52). IR ($CHCl_3$): 3020*m*, 2390*w*, 1765*s*, 1620*m*, 1215*s*, 1085*w*, 925*w*, 900*w*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.60 (*s*, 1 H); 8.45 (*s*, 1 H); 8.09 (*s*, 1 H); 8.05–7.95 (*m*, 3 H); 7.60–7.45 (*m*, 2 H); 4.27 (*s*, 2 H). MS: 218 (62, M^+), 190 (100), 189 (78), 163 (5), 139 (3), 113 (2), 95 (45), 94 (26), 87 (8), 82 (9), 81 (9), 74 (17), 63 (24), 62 (22), 51 (21), 50 (32).

Tricarbonyl[1,1-bis(trimethylsilyl)-1H-cyclopropa[b]anthracene]chromium (**12**). Tris(acetonitrile)-tricarbonylchromium (157 mg, 0.60 mmol) and **10b** (126 mg, 0.38 mmol) were heated in Bu_2O (12 ml) and octane (0.9 ml) to 60° for 5.5 h under a stream of N_2 and with exclusion of light. After cooling to r.t., the soln. was filtered through *Celite*, which was exrtracted exhaustively with Et_2O. The solvent was evaporated, and the crude product was purified by rapid chromatography (SiO_2, toluene/hexane 1:5). Recrystallization from toluene/hexane at –15° afforded **12** (57 mg, 32%) as red crystals. M.p. 154–155° (dec.). UV (heptane): 220.7 (3.66), 272.8 (3.43), 329.2 (4.12), 487.3 (4.43). IR (hexane): 1972*vs*, 1912*s*, 1893*s*, 1375*s*, 725*s*. ^{1}H-NMR (C_6D_6, 200 MHz): 7.40 (*s*, 2 H); 6.78 (*s*, 2 H); 5.67–5.63 (*m*, 2 H); 4.87–4.84 (*m*, 2 H); –0.001 (*s*, 9 H); –0.064 (*s*, 9 H). ^{13}C-NMR (C_6D_6, 50 MHz): 232.96 (CO); 137.8 (C); 133.3 (C); 125.5 (CH); 106.0 (CH); 105.7 (C); 91.9 (CH); 90.3 (CH); –1.29 (CH_3); –1.34 (CH_3). MS: 470 (7, M^+), 414 (4), 386 (5), 370 (46), 334 (13), 261 (21), 245 (38), 231 (9), 215 (14), 149 (9), 110 (9), 73 (100), 59 (23), 52 (39). HR-MS ($C_{24}H_{26}CrSi_2O_3$) calc.: 470.08254; found: 470.0853424.

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