155. Organometallic Derivatives of Cycloproparenes

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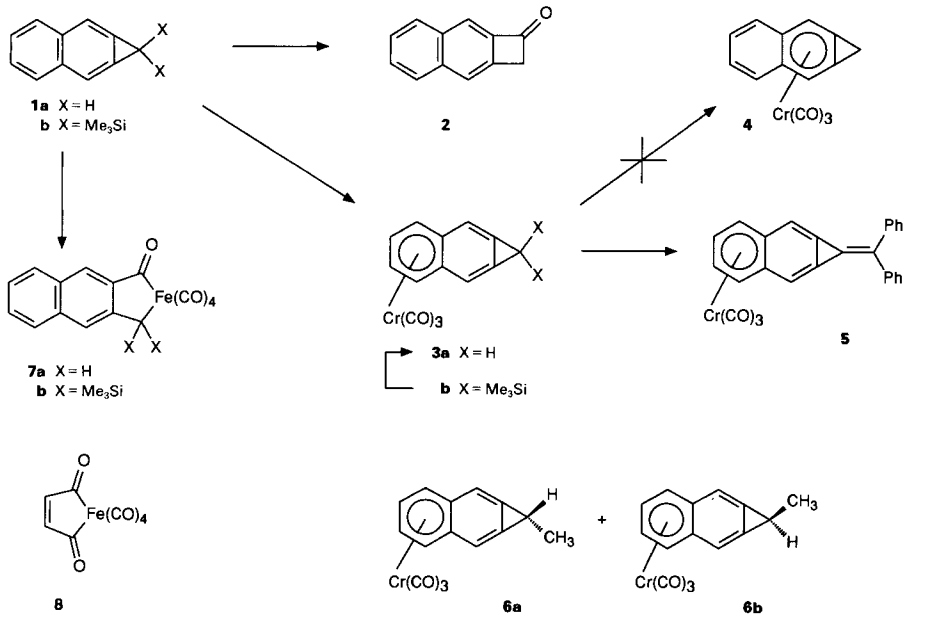
The tricarbonylchromium complex of cyclopropa[*b*]naphthalene (**3a**) is deprotonated at C(1) with BuLi. Quenching of the resulting anion with MeI results in a 1:1 mixture of stereoisomeric methyl derivatives **6a** and **6b**. *Peterson* olefination of the bis-silylated complex **3b** affords the complexed alkylidenecycloproparene **5** in low yield. The tricarbonylchromium complex of cyclopropa[*b*]anthracene (**10**) is accessible *via* bis-hydro-desilylation of **9**. Its X-ray structure is also reported. All attempts to synthesize a tricarbonylchromium complex of benzocyclopropene (**11a**) failed.

Introduction. – Transition metals react with cycloproparenes preferentially at one of the cyclopropene C–C bonds or at the C=C bond of the cyclopropene moiety. Attack at the C–C bonds results in formation of metallacyclobutenes, while reaction at the C=C bond leads to metallapropellanes. The preferential mode of the reaction is determined by the substituents at the methylene position of the cyclopropene, the metal, and its ligands.

Scheme 1



Recently we reported that 1*H*-cyclopropa[*b*]naphthalene (**1a**) reacts with $[Cr(CO)_6]$ or $[Cr(CH_3CN)_3(CO)_3]$ at the cyclopropene ring to afford cyclobuta-naphthalenone **2** (*Scheme 1*). However, when the methylene position of **1a** was protected with Me_3Si groups, the reaction took a different course and led to formation of an η^6-complex **3b** by attack at the terminal benzene ring [1]. This complex has been desilylated, and the isolation of tricarbonyl(1*H*-cyclopropa[*b*]naphthalene)chromium (**3a**) demonstrated the compatibility of the cycloproparene structure with the presence of the $Cr(CO)_3$ tripod [2].

Here, we report on the reactions of $Cr(CO)_3$-complexed cycloproparenes and attempts to achieve complexation of benzocyclopropene itself.

Results and Discussion. – 1. *1*H-*Cyclopropa[*b*]naphthalene.* The complexation of 1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene (**1b**) with $[Cr(CH_3CN)_3(CO)_3]$ proceeds at 90° and gives **3b** in 51% yield [1] [2]. Reaction occurs also with $[Cr(CO)_6]$ at 120°, but **3b** forms only to a minor extent (6%), while most of the starting cycloproparene **1b** (75%) is recovered. Since 120° is about the limit of thermal stability of the silylated cycloproparene **1b**, no experiments at higher temperatures were attempted. Alternatively, **3b** was synthesized in 78% yield by arene exchange between **1b** and tricarbonyl(naphthalene)chromium at 70°.

The preference of **1b** to undergo complexation at the terminal benzene ring has been ascribed to steric factors. Indeed, the X-ray structure of **3b** [1] shows considerable crowding at the benzene ring adjacent to the cyclopropene by the Me_3Si groups, which direct the complexing reagent to the terminal position. Since no steric hindrance occurs in the parent complex **3a** [2], the sythesis of the isomeric complex **4**, which has the $Cr(CO)_3$ tripod bonded to the central benzene ring, was attempted by haptotropic rearrangement [3] of **3a**. It was hoped that the undesired attack at the cyclopropane C–C bonds would not occur under these conditions, because in haptotropic rearrangements the metal remains bonded to the arene. The desilylated complex **3a** was, therefore, heated in an NMR tube in (D_{12}) cyclohexane, both in the presence or absence of (D_8)THF. Decomposition products appeared starting from 80°, and decomposition was total at 100° after 2 h. No signals corresponding to the rearranged complex **4** were observed, however. Apparently, the limited thermal stability of **3a** precludes the temperature which is usually required to effect the haptotropic rearrangement.

Bis-silylated cycloproparenes are precursors for alkylidenecycloproparenes, a recently discovered class of aromatics [4]. Alkylidenecycloproparenes react with Rh^I or Pt^0 complexes by attack at the cyclopropene ring to metallacyclobutarenes or, when CO ligands are present, to metallacyclopentenones [5]. No organometallic derivatives of alkylidenecycloproparenes having a metal bonded to the cycloproparene moiety are known. The successful hydro-desilylation of the complexed cycloproparene **3b** opens a potential route to such compounds *via Peterson* olefination, which is the standard synthesis of alkylidenecycloproparenes [4]. Indeed, when the desilylation of **3b** was carried out under the usual conditions (*t*-BuOK), but in the presence of benzophenone, tricarbonyl[1-(diphenylmethylidene)-1*H*-cyclopropa[*b*]naphthalene]chromium (**5**) was formed. Unfortunately, the compound could not be crystallized, and chromatography was accompanied by much decomposition. The ^{1}H-NMR (*Fig. 1*) of the isolated material (80%) is, however, consistent with the structure of the expected complex. The *AA'BB'* system of the protons of the terminal benzene ring is found at 4.63 and 5.28 ppm, and the

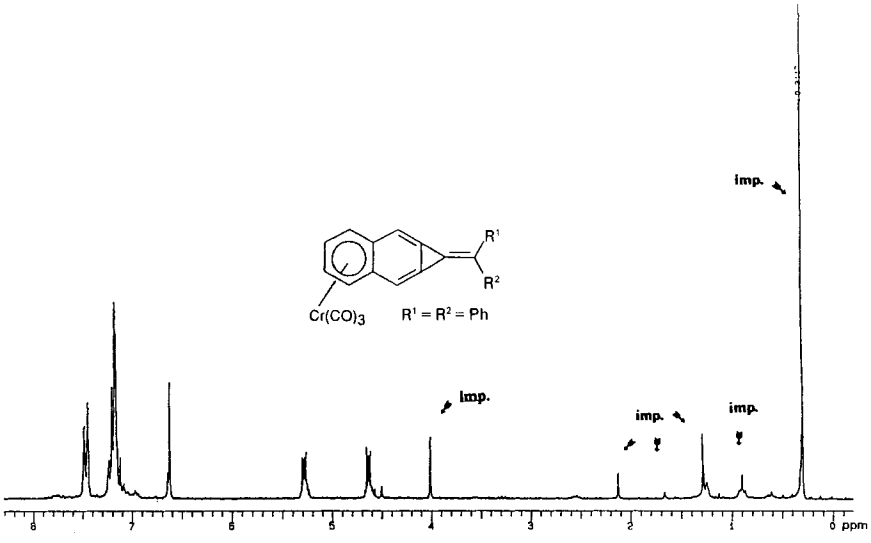


Fig. 1. *^{1}H-NMR of tricarbonyl[1-(diphenylmethylidene)-1*H*-cyclopropa[b]naphthalene]chromium* (**5**)

protons of the central benzene ring resonate at 6.63 ppm. This compares favorably with the pattern of the complexed cycloproparene **3a** which exhibits the corresponding signals at 4.62, 5.28, and 6.67 ppm. The signals of the Ph groups are in the normal range of 7.1–7.5 ppm. Direct complexation of alkylidene cycloproparenes, so far, led only to decomposition products.

The desilylation of the complexed cycloproparene **3b** must necessarily proceed *via* a carbanion, formally derived from deprotonation at C(1), and capable of existence at least as a reaction intermediate. The pK_a of cyclopropabenzene has been estimated to 36 [6], and both, cyclopropabenzene and cyclopropa[*b*]naphthalene (**1a**) are deprotonated with BuLi. Since (benzene)(tricarbonyl)chromium has about the same acidity (pK_a 34.8) [7] as cyclopropabenzene, it would be difficult to predict at what position **3a** would be deprotonated. Treatment of **3a** with BuLi at −78° afforded only decomposition products. However, reaction at −100°, followed by quenching of the resulting anion at the same temperature with MeI gave rise to a *ca.* 1:1 mixture (66% with respect to starting material) of the two C(1) stereoisomeric methyl derivatives **6a** and **6b**, which were separable by HPLC, together with unreacted starting material. To **6a**, having the signal of the Me group more deshielded [8] (1.19 ppm) and that of the methine H-atom more shielded (3.18 ppm), was attributed the *syn*-configuration. The corresponding signals of the *anti*-isomer **6b** are found at 1.12 and 3.44 ppm, respectively.

The structure of the intermediate anion is at present unknown. Theoretical calculations predict that anions derived from uncomplexed cyclopropabenzenes should be aromatic [9], but experiments to observe such anions by NMR so far failed. The low reaction temperature used for the deprotonation of **3a** suggests that the reaction proceeded under kinetic control, and the question on the relative thermodynamic acidity of the different sites of the complexed cycloproparene remains open.

The first reaction ever reported between a cycloproparene and a transition-metal reagents is that of cyclopropa[*b*]naphthalene (**1a**) with $Fe_2(CO)_9$, which proceeds by

oxidative addition of the cyclopropane to the metal, followed by CO insertion. The product **7a** has been characterized by ^{1}H-NMR and its structure established by X-ray-crystallography [10]. While the Me_3Si groups offer sufficient protection to direct complexation of **1b** with $Cr(CO)_3$ reagents to the aromatic moiety, it is inefficient in the case of Fe_2CO_9. The reaction of unprotected **1a** with this reagent leads to **7a** at 25°. The silylated derivative **1b**, when exposed to $Fe_2(CO)_9$, does not react at room temperature, but reaction occurs at 60° (5 h) to furnish the analogous complex **7b** in 40% yield. The structure of the complex follows from the analytical data and from the comparison of its ^{13}C-NMR spectrum with that of tetracarbonyl(1,4-dioxobut-2-ene-1,4-diyl)iron (**8**), the structure of which is known from X-ray crystallography [11]. For **7b**, the signal at 199 ppm corresponds to the CO groups perpendicular to the symmetry plane of the molecule, while the CO groups in the plane resonate at 201 and 204, and that in α-position of the aromatic at 251 ppm. The corresponding resonance lines of **8** occur at 199, 201, and 245 ppm, respectively.

The preference of $Fe_2(CO)_9$ to react by oxidative addition of the cyclopropane bond rather than by complexation of the aromatic rings may be attributed to the fact that the (expected) products would be η^4-$Fe(CO)_3$ complexes. In these complexes, the coordination of two rather than three C=C bonds with the metal disturbs the aromaticity of the system [12]. Other metals such as Ni and Pd react with silylated cycloproparenes also at the cyclopropane bonds to afford metallacyclobutenes [13].

2. *Synthesis and Structure of Tricarbonyl(1H-cyclopropa[b]anthracene)chromium.* The complexation of 1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]anthracene with $[Cr(CH_3CN)_3(CO)_3]$ has been reported in [2]. Meanwhile, conditions were found which allowed the desilylation of the complex **9** (*Scheme 2*) by a procedure analogous to that used for desilylation of **3b**, but with a modified workup. During isolation of **3a**, some

Scheme 2

9 **10**

decomposition occurred after filtration of the reaction mixture through *Celite*, when the temperature was allowed to reach 25°, and this decomposition was attributed to the presence of excess *t*-BuOK. The decomposition was suppressed, when the *t*-BuOK was quenched with Me_3SiCl. Application of the same treatment to **10** led to its destruction. The complex could, however, be purified, if a small quantity of silica gel was placed on the *Celite*, and if filtration was performed at −78°.

The ^{1}H-NMR spectrum of **10** is almost identical to that of **9** except for the *AB* system of the methylenic protons, which is centered at 2.99 (3.03 (*syn*), 296 (*anti*)). The X-ray structure of **10** is shown in *Fig. 2*, and some structural data are collected in *Table 1*.

The structure of **10** is essentially a superposition of that of the tricarbonylchromium complexes of anthracene [14] and of 1*H*-cyclopropa[*b*]naphthalene (**3b**) [15]. The cycloproparene is almost planar, with a maximum deviation from the mean plane of the

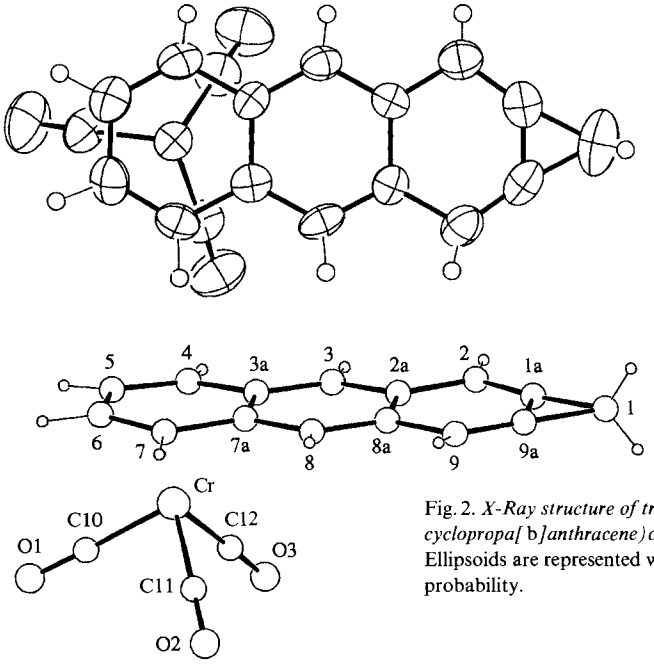


Fig. 2. *X-Ray structure of tricarbonyl(1H-cyclopropa[b]anthracene)chromium* (**10**). Ellipsoids are represented with 50% probability.

Table 1. *Structural Data of Tricarbonylchromium Complexes of Cycloproparenes*

	10	(Anthracene)-tricarbonylchromium[a])	**3a**	
C(1)–C(1a)	1.48(1)	–	1.487	C(1)–C(1a)
C(1)–C(9a)	1.49(1)	–	1.494	C(1)–C(7a)
C(1a)–C(9a)	1.36(1)	1.413	1.368	C(1a)–C(7a)
C(1a)–C(2)	1.34(1)	1.380	1.321	C(1a)–C(2)
C(2)–C(2a)	1.43(1)	1.441	1.439	C(2)–C(2a)
C(2a)–C(8a)	1.464(9)	1.435	1.455	C(2a)–C(6a)
C(2a)–C(3)	1.386(9)	1.380	1.433	C(2a)–C(3)
C(3)–C(3a)	1.388(9)	1.413	1.378	C(3)–C(4)
C(3a)–C(4)	1.435(9)	1.442	–	
C(3a)–C(7a)	1.433(9)	1.449	1.404	C(4)–C(5)
C(4)–C(5)	1.39(1)	1.420	–	
C(5)–C(6)	1.41(1)	1.416	–	
Cr···plane (C(3a)–C(7a))	1.758(1)	1.76	1.742	(C(2a)–C(6a))
Cr···C(3a)	2.345(6)	2.340	2.303	Cr···C(2a)
Cr···C(4)	2.220(7)	2.215	2.215	Cr···C(3)
Cr···C(5)	2.205(6)	2.221	2.210	Cr···C(4)
Cr···C(6)	2.212(7)	2.217	2.208	Cr···C(5)
Cr···C(7)	2.220(6)	2.219	2.210	Cr···C(6)
Cr···C(7a)	2.348(6)	2.324	2.310	Cr···C(6a)
C(1a)–C(1)–C(9a)	54.5(5)	–	54.6	C(1a)–C(1)–C(7a)
C(1)–C(1a)–C(9a)	63.0(6)	–	63.0	C(1)–C(1a)–C(7a)
C(1)–C(9a)–C(1a)	62.5(6)	–	62.4	C(1)–C(7a)–C(1a)
C(2)–C(1a)–C(9a)	126.1(7)	–	125.5	C(2)–C(1a)–C(7a)
C(1a)–C(9a)–C(9)	124.4(7)	–	124.3	C(1a)–C(7a)–C(7)
C(1a)–C(2)–C(2a)	114.0(6)	–	114.9	C(1a)–C(2)–C(2a)

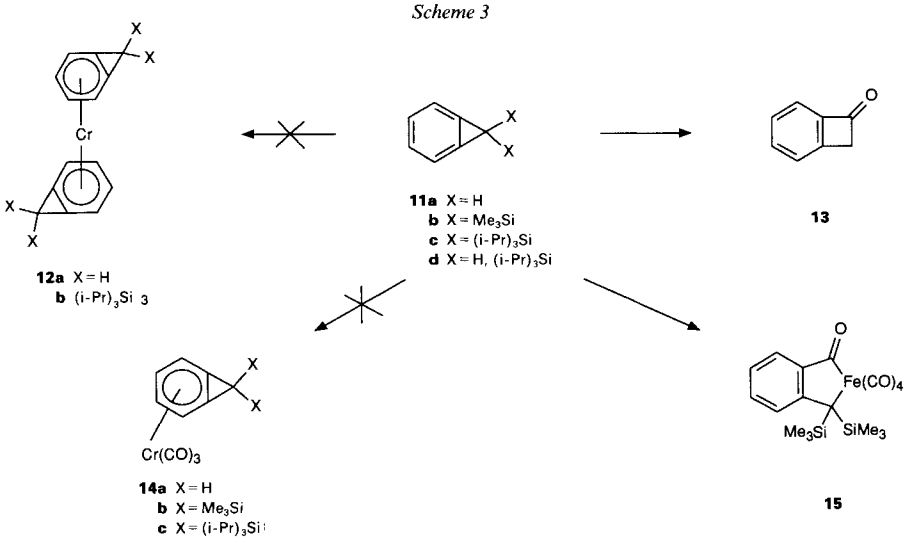
[a]) The numbering corresponds to that of **10**.

molecule (passing through C(1) to C(9a)) of 0.040 Å for C(6). The Cr-atom is situated at 1.758(1) Å from the plane defined by C(3a) to C(7a), which compares well with the value on the tricarbonylchromium complex of anthracene. The C–Cr distances vary slightly from 2.22 (C(4), C(7)) to 2.21 (C(5), C(6)) and 2.35 (C(3a), C(7a)), which corresponds to a decentered position of the $Cr(CO)_3$ tripod away from the center of the molecule. This phenomenon appears also in other complexes of cyclopropabenzenes [1] [2], and also in the one of anthracene [14].

The structure of the complex is of some interest, as it is the first cyclopropa[*b*]-anthracene structure ever determined. The parent cyclopropa[*b*]anthracene and its 1,1-difluoro- or 1,1-bis(trimethylsilyl) derivatives provide no crystals suitable for X-ray analysis. It has been suggested [16], that annelated cyclopropabenzenes should show evidence for the *Mills-Nixon* effect (bond fixation) [17], which does not appear in the lower homologues [18]. The structure of **10** reveals, however, no unusual geometries, particularly around the cyclopropene moiety. It could be argued, that bond fixation might not be observable in **10** because of the perturbation due to the presence of the $Cr(CO)_3$ group. However, it is known from the structures of cyclopropa[*b*]naphthalene (**1a**) and its complex **3a** [2] that complexation provokes practically no changes on the molecular geometry around the cyclopropene, and, for this reason, it is very unlikely, that evidence for bond fixation will be found in the uncomplexed 1*H*-cyclopropa[*b*]anthracene.

3. *Towards Complexed Cyclopropabenzenes.* 3.1. *Reactions with Cyclopropabenzenes.* The co-condensation of 1*H*-cyclopropabenzene (**11a**) and Cr-atoms has been attempted by *Gladysz* and coworkers some years ago [19]. The desired complex **12a** was not formed, however, and the reaction produced, in addition to unreacted **11a**, some toluene, and polymers (*Scheme 3*). In our hands, when 1,1-bis(triisopropylsilyl)-1*H*-cyclopropabenzene [20] (**11c**) was used in the co-condensation, the cyclopropabenzene was almost quantitatively recovered.

Scheme 3

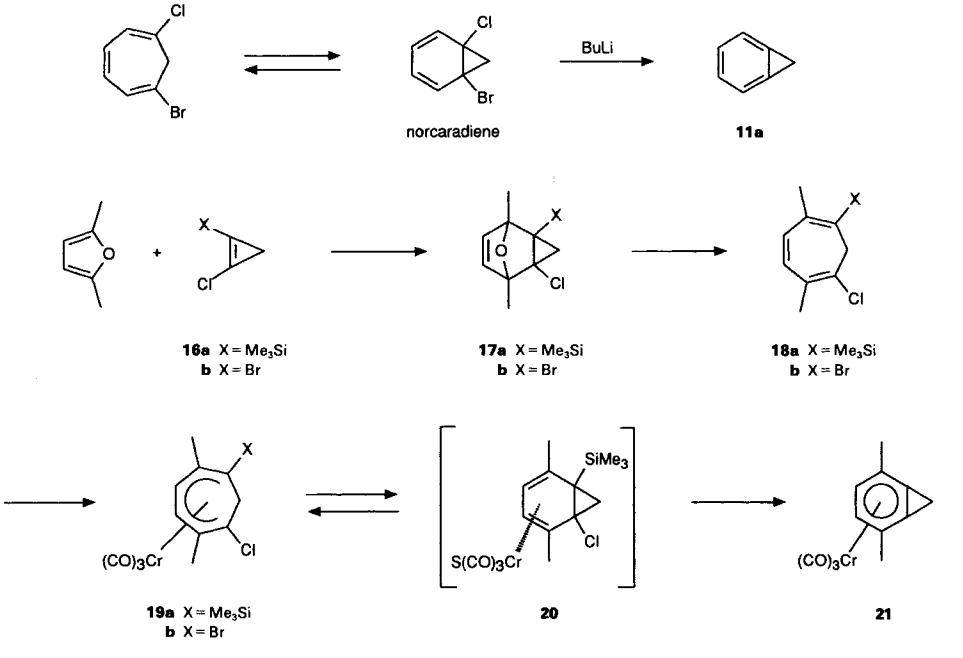


The parent 1*H*-cyclopropabenzene (**11a**) reacts like the higher homologues with $[Cr(CH_3CN_3)(CO)_3]$ to cyclobutabenzenone (**13**). Protection of the CH_2 group of **11a** with Me_3Si or $(i\text{-}Pr)_3Si$ groups [20] blocks this reaction, but at the same time also inhibits arene complexation, so that the desired products **14b, c** may not be obtained from **11b** and **11c**. Both are recovered unchanged from the reaction mixture. The known monosilylated cyclopropabenzene **11d** [20], which we could only obtain as a mixture, contaminated with **11c**, decomposed under the condition of the complexation. Similarly, the attempted arene exchange of tricarbonyl(naphthalene)chromium with **11b** (70–80°) and the mixture **11c**/**11d** (40–80°) afforded no complexed cycloproparenes.

The Me_3Si-protected cyclopropabenzene **11b** reacted with $Fe_2(CO)_9$ in the expected fashion and delivered **15**, identified by comparison of the spectral data with that of the higher homologue. In contrast, no reaction was observed between the more crowded **11c** and $Fe_2(CO)_9$.

3.2. *Attempted Cyclization of a $Cr(CO)_3$-Complexed Cycloheptatriene.* A recent approach to cyclopropabenzenes consists in reaction of 1a,5a-dihalogenocyclopropabenzene with BuLi [21]. The reaction is believed to proceed *via* a metallated norcaradiene which undergoes β-elimination (*Scheme 4*).

Scheme 4



The application of this sequence to a $Cr(CO)_3$-complexed precursor requires replacement of the Br-substituent by a Me_3Si group, since the former is incompatible with the $Cr(CO)_3$ reagents [22]. This precursor was synthesized from 2,5-dimethylfuran and 1-chloro-2-(trimethylsilyl)cyclopropene (**16a**) [23]. The choice of this particular precursor follows from previous experiments. It is known that the *exo*-adduct **17b** of 1-bromo-2-

chlorocyclopropene (**16b**) to 2,5-dimethylfuran may be converted to the cycloheptatriene **18b** with low-valent Ti [21]. By analogy, the silylated derivative **17a** afforded the triene **18a** in 78% yield, and complexation [24] with $[Cr(CH_3CN)_3(CO)_3]$ produced **19a** (44%). Cyclization of **19a** with F^- ions was attempted under a variety of conditions, but in no case the expected cyclopropparene **21** was formed. With Bu_4NF hydro-desilylation occurred resulting in complex **19b**. The same result was obtained even when the fluoride salt was dried over molecular sieves. With KF in large excess (−10°) and a catalytic amount of $(Bu)_4NF$ in MeCN [25] or in THF in the presence of 18-crown-6 (85°) the starting material was recovered. Negative results were also obtained with CsF in THF and *t*-BuOK in THF (−78 to 85°).

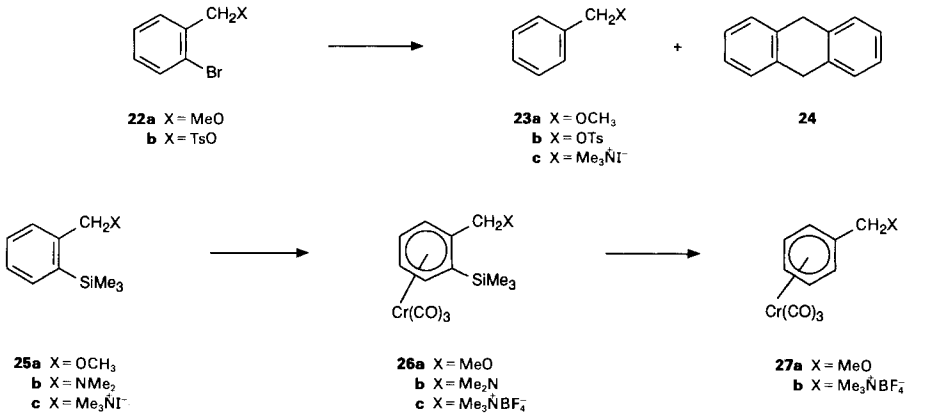
The failure of the attempted cyclization of **19a** is not too surprising. The formation of a norcaradiene, which is the prerequisite for formation of a complexed cyclopropparene, requires partial decomplexation of **19a** to an η^4-complex (**20**) in which a solvent molecule replaces one of the coordinated C=C bonds of the original cycloheptatriene. Apparently, this state cannot be reached under the conditions compatible with the de-chloro-de-trimethylsilyl-elimination. The anion derived from attack of F^- on the silane is sufficiently stabilized by $Cr(CO)_3$ group that it may survive the reaction and pick up a proton from the solvent rather than to eliminate. More surprising is the observation, that the desilyation of **19a** is so difficult, and does not occur under conditions which are usually appropriate for such reactions.

3.3. *Attempted Cyclization of* o-*Substituted Benzyl Derivatives.* The synthesis of 1*H*-cyclopropabenzene (**11a**) *via* intramolecular cyclization of 1-bromo-1-(methoxymethyl)benzene (**22a**) in the presence of BuLi has been reported by *Radlick* and *Crawford* some time ago [26]. At a first glance, this should be an attractive route for complexed cyclopropabenzenes. Unfortunately, only a single application of the *Radlick* procedure has been reported [27], and other authors have encountered difficulties, when they applied the methodology to other cyclopropparenes [28]. On the other hand, cyclopropenes or cyclobutabenzenes, which are both significantly less strained than cyclopropparenes, are readily available by this approach.

We ascribed the failure of the *Radlick* procedure in part to the choice of the low nucleofugality of the MeO substituent. Accordingly, 2-bromobenzyl *p*-toluenesulfonate (**22b**) [29] was prepared and subjected to BuLi (*Scheme 5*). Only a faint odor of cyclopropabenzene was obtained. Benzyl *p*-toluenesulfonate (**23b**) [30] and 9,10-dihydroanthracene (**24**) were isolated, but no cyclopropabenzene. The cyclization of 1-(methoxymethyl)-2-(trimethylsilyl)benzene (**25a**), synthesized from the 2-bromo derivative **22a** [31], was attempted without success under a variety of conditions. The starting material was recovered with *t*-BuOK/THF (20 to 80°) and CsF in MeCN (−20 to 100°). Hydrodesilylation to **23a** occurred, however, with Bu_4NF, or with *t*-BuOK/DMF (−10°, 19 h). (Trimethyl)[2-(trimethylsilyl)benzyl]ammonium iodide (**25c**), available *via* quaternisation [32] of **25b** [33] afforded with fluoride or *t*-butoxide under a variety of conditions only the desilylated ammonium salt **23c** [34]. In no case was any cyclopropabenzene detected.

An important side-product in the attempted cyclization of the uncomplexed compounds such as 2-halogenobenzyl bromide or chloride is 9,10-dihydroanthracene (**24**), which derives from an intermolecular reaction [35]. Presumably, such processes could be disfavored with $Cr(CO)_3$ complexes owing to steric hindrance. We have, therefore, syn-

Scheme 5



thesized complex **26a** from 1-(methoxymethyl)-2-(trimethylsilyl)benzene (**25a**) by arene exchange with naphthalene tricarbonylchromium. (Dimethyl)[2-(trimethylsilyl)benzyl]-amine (**25b**) [33] was complexed by reaction with $[Cr(CH_3CN)_3(CO)_3]$ and the complex **26b** transformed to the ammonium salt **26c** with trimethyloxonium tetrafluoroborate [36]. Reaction of **26a** with *t*-BuOK resulted in hydro-desilylation and produced **27a** [37]. The salt **26c**, in turn, reacted with CsF in MeCN or KF in the presence of a small quantity of Bu_4NF in MeCN to **27b**.

Since the cyclization reaction fails not only with the $Cr(CO)_3$-complexed compounds, but also with the uncomplexed analogues, we ascribe the failure to obtain cyclopropabenzenes by this route to the strain in cycloproparenes (65–68 kcal/mol), which exceeds that in analogous systems, where the reaction works, by some 15 (cyclopropenes) [38] [39] and *ca.* 32 kcal/mol (cyclobutabenzenes) [30] [32] [40]. The stabilization of negative charge in the intermediate anions by the $Cr(CO)_3$ tripod could further disfavor the required elimination in the case of **26a** and **26c**.

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Experimental Part

General. See [2].

Reactions with 1H-Cyclopropa[b]naphthalene. Tricarbonyl[1-(diphenylmethylidene)-1H-cyclopropa[b]-naphthalene]chromium (**5**). To *[1,1-bis(trimethylsilyl)-1H-cyclopropa[b]naphthalene](tricarbonyl)chromium* (**3b**) [2] (61 mg, 0.14 mmol) in THF (10 ml) at −90° was added rapidly benzophenone (54 mg, 0.29 mmol) in THF (2 ml). The soln. was stirred during 15 min, and *t*-BuOK (34 mg, 0.3 mmol) in THF (10 ml) was added dropwise in 30 min. The red mixture was stirred during 144 h at −90° and then filtered at this temp. through silica gel (230–240 mesh) and *Celite*, which was washed with Et_2O at −78°. After evaporation, the residue was dissolved in toluene and filtered through silica gel and *Celite*, and the column was washed with toluene. A red fraction was collected, followed by a yellow one. After evaporation of the solvent, **5** was purified by prep. TLC (alox basic, CH_2Cl_2) of the yellow fraction. Yield 5 mg (8%). IR (hexane): 1974*s*, 1912*m*, 1902*m*. ^{1}H-NMR (C_6D_6, 200 MHz): 7.49–7.44 (*m*, 4 H); 7.25–7.10 (*m*, 6 H); 6.63 (*s*, 2 H); 5.30–5.27 (*m*, 2 H); 4.65–4.61 (*m*, 2 H). MS: 440 (0.2, M^+), 304 (2), 227 (1), 178 (1), 166 (2), 156 (1), 150 (2), 138 (2), 128 (2), 126 (2), 114 (1), 102 (1), 88 (1), 77 (34), 76 (3), 74 (2), 52 (100).

Tricarbonyl ('endo'- and 'exo'-1-methyl-1H-cyclopropa[b]naphthalene)chromium (**6a** and **6b**, resp.). To **3a** (30 mg, 0.109 mmol) in THF (3.0 ml) was added 1.6M BuLi in hexane (68 µl, 0.109 mmol) at −110° in 30 s. The orange soln. turned red. It was stirred between −100 and −110° during 60 min. MeI (19 µl) in THF (2.0 ml), cooled to −78°, was added in one portion. After 5 min of stirring at −100°, the green mixture was filtered through silica gel (230–400 mesh) and *Celite*, which were washed with Et_2O until disappearance of the orange color. After evaporation, the product was purified by column chromatography (silica gel, toluene/hexane 1:3), and then precipitated by cooling with dry-ice. The precipitate (27 mg) was composed of a mixture of **3a** (30%), **6a** (28%), and **6b** (28%) (by NMR). The compounds were separated by HPLC (*Supercosil LC-Si*, 5 µm, 250 × 10 mm, flow 5 ml/min, hexane/i-Pr_2O 15:1). **6a**: IR (hexane): 1974*vs*, 1911*s*, 1901*s*. ^{1}H-NMR (C_6D_6, 200 MHz): 6.75 (*s*, 2 H); 5.33–5.30 (*m*, 2 H); 4.67–4.63 (*m*, 2 H); 3.18 (*q*, ^3J = 6.2, 1 H); 1.19 (*d*, ^3J = 6.2, 3 H). ^{13}C-NMR (C_6D_6, 100 MHz): 233.2 (CO); 133.4 (C); 111.7 (CH); 108.8 (C); 91.9 (CH); 91.7 (CH); 28.4 (CH); 19.7 (CH_3). MS: 290 (1, M^+), 234 (1), 206 (6), 178 (0.4), 154 (2), 139 (0.4), 126 (1), 77 (3), 52 (100).

6b: IR (hexane): 1973*vs*, 1910*s*, 1900*s*. ^{1}H-NMR (C_6D_6, 200 MHz): 6.76 (*s*, 2 H); 5.33–5.30 (*m*, 2 H); 4.67–4.63 (*m*, 2 H); 3.44 (*q*, ^3J = 6.2, 1 H); 1.12 (*d*, ^3J = 6.2, 3 H).

Tetracarbonyl[naphthalene-2-bis(trimethylsilyl)methylene-3-carbonyl]iron (**7b**). To a soln. of **3b** (104 mg, 0.37 mmol) in benzene (8.0 ml) was added $Fe_2(CO)_9$ (134 mg, 0.37 mmol). The mixture was degassed three times, stirred during 60 min at 25°, and then heated to 60° during 5 h. After filtration through *Celite*, which was washed with Et_2O, and evaporation of the solvent, **7b** was purified by column chromatography (silica gel 60, 70–230 mesh, hexane/CH_2Cl_2 9:1). Yield: 71 mg (0.148 mmol, 40%). M.p. 121–123° (dec.). IR ($CHCl_3$): 3012*m*, 2100*s*, 2050*s*, 2025*vs*, 1662*m*, 1644*m*, 1638*m*, 1250*m*, 969*s*, 850*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.10 (*s*, 1 H); 7.74–7.65 (*m*, 2 H); 7.47 (*s*, 1 H); 7.41–7.36 (*m*, 2 H); 0.2 (*s*, 18 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 251 (CO); 204.6 (CO); 201.9 (CO); 199.7 (CO); 153.3 (C); 149.2 (C); 141.1 (CH); 132.8 (C); 132.6 (C); 127.3 (CH); 125.8 (CH); 125.2 (CH); 124.7 (CH); 121.9 (CH); 78.2 (C); 1.30 (CH_3). MS: 452 (1), 424 (1), 396 (3), 368 (4), 340 (9), 286 (16), 226 (27), 211 (21), 198 (29), 195 (18), 185 (18), 169 (16), 152 (12), 73 (100), 59 (29). Anal. calc. for $C_{22}H_{24}FeO_5Si_2$: C 55.00, H 5.04; found: C 55.21, H 5.00.

Tricarbonyl(1H-cyclopropa[b]anthracene)chromium (**10**). To **9** (66 mg, 0.14 mmol) in THF (10 ml) at −85° was added *t*-BuOH (0.45 ml) in THF (2.0 ml) cooled to −78°. *t*-BuOK (44 mg, 0.39 mmol) in THF (5.0 ml) was added dropwise in 30 min. The mixture was stirred during 118 h at −85° and filtered at low temperature through silica gel (230–400 mesh) and *Celite*, which were washed with Et_2O at −78° until disappearance of the red color. After evaporation **10** (26 mg, 0.08 mmol, 57%) was isolated by recrystallization with toluene/hexane 1:1 at −30°. M.p. 180–181° (dec.). IR (hexane): 1974*vs*, 1917*s*, 1898*s*. ^{1}H-NMR (C_6D_6, 400 MHz): 7.48 (*s*, 2 H); 7.09 (*s*, 2 H); 5.68–5.66 (*m*, 2 H); 4.90–4.88 (*m*, 2 H); 2.99 (*AB*, δ_A = 2.96, δ_B = 3.03, ^2J = 10.8, 2 H). ^{13}C-NMR (C_6D_6, 50 MHz): 232.5 (CO); 137.5 (C); 128.4 (CH); 125.1 (C); 111.3 (CH); 105.7 (C); 92.4 (CH); 90.0 (CH); 18.3 (CH_2). MS: 326 (1, M^+), 270 (3), 242 (15), 220 (3), 190 (7), 189 (11), 165 (4), 91 (12), 80 (5), 63 (3), 52 (100). HR-MS ($C_{18}H_{10}CrO_3$): M_{obs} 326.004715; M_{calc} 326.00348.

X-Ray Data for **10**. Cell parameters and reflection intensities were measured at r.t. on a *Philips PW 1100* diffractometer with MoK_α radiation. Intensities were corrected for *Lorentz* polarization and for absorption [41]. A summary of crystal data, intensity measurements, and structure refinement is given in *Table 2*, and selected

Table 2. *Crystal Data, Intensity Measurement, and Structure Refinement for* **10**

Formula	$C_{18}H_{10}O_3Cr$	$((\sin\theta)/\lambda)_{max}$ [Å^{-1}]	0.53
Mol. wt.	274.9	Temperature [K]	298
Crystal size [mm]	0.08 × 0.18 × 0.35	No. measured reflc.	1824
Crystal color	violet	No. observed reflc.	1301
Crystal system	Monoclinic	Criterion for observed	$\lvert F_o\rvert > 4\sigma(F_o)$
Space group	$P2_1/n$	R_{int} for equivalent reflc.	0.045
a [Å]	8.396(2)	A^* min., max.	1.069, 1.160
b [Å]	15.841(5)	Refinement (on F)	full-matrix
c [Å]	10.721(2)	No. parameters	229
β [°]	95.42(1)	Weighting scheme	$1/\sigma^2(F_o)$
V [Å^3]	1419.5(6)	Max. and average Δ/σ	$5\cdot10^{-4}$, 10^{-4}
Z	4	Max. and min. $\Delta\rho$[e·Å^{-3}]	0.51, −0.52
F(000)	948	S	1.92
D_c [g·cm^{-3}]	1.29	R, wR (%)	5.3, 2.6
μ(MoK_α) [mm^{-1}]	0.085		

geometrical parameters are reported in *Table 1*. The structure was solved with direct methods (MULTAN-87) and refined by least-square analysis with the X-TAL program [42]. All coordinated of H-atoms have been observed and refined.

Reactions with Cyclopropabenzene. 1,2-Dihydrocyclobutabenzen-1-one (**13**). To $[Cr(CH_3CN)_3(CO)_3]$ (796 mg, 3.07 mmol) was added *1H-cyclopropabenzene* (**11a**; 225 mg, 2.5 mmol) in Et_2O (15 ml). After three cycles of degassing, the yellow soln. was stirred at 25° during 16 h, protected from light by aluminium foil. The brownish mixture was filtered through *Celite*, which was washed with Et_2O until disappearance of the yellow color. After evaporation, **13** [43] was purified by column chromatography (silica gel 60, 70–230 mesh, pentane/Et_2O 1:1). Yield: 52 mg (0.44 mmol, 18%). IR ($CDCl_3$): 3000*w*, 1980*m*, 1912*w*, 1785*s*, 1759*vs*, 1585*m*, 1464*m*, 1410*w*, 1344*w*, 1283*w*, 1150*w*, 1100*w*, 962*m*, 912*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.54–7.30 (*m*, 4 H); 3.99 (*s*, 2 H). MS (C_8H_6O): 118 (74, M^+), 91 (15), 90 (100), 89 (93), 86 (6), 74 (6), 64 (17), 63 (43), 62 (21), 61 (9), 51 (15), 50 (14).

[Benzene-1-bis(trimethylsilyl)methylene-2-carbonyl]tetracarbonyliron (**15**). To **11b** [4] (133 mg, 0.57 mmol) in benzene was added $Fe_2(CO)_9$ (411 mg, 1.13 mmol). The mixture was degassed three times, then stirred at r.t. during 15 min and finally heated to 60° during 4 h. After filtration through *Celite*, which was extracted exhaustively with Et_2O until the deep-green color disappeared, the solvent was evaporated, and **15** was purified by column chromatography (silica gel 60, 230–400 mesh, hexane/CH_2Cl_2 9:1) to give 129 mg (55%) as an amorphous material. M.p. 81–82°. IR ($CHCl_3$): 3025*m*, 2105*s*, 2053*s*, 2026*vs*, 1651*m*, 1646*m*, 1263*m*, 1012*m*, 969*m*, 900*m*, 838*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.62–7.57 (*m*, 1 H); 7.18–6.98 (*m*, 3 H); 0.15 (*s*, 18 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 251.5 (CO); 204.8 (CO); 202.0 (CO); 199.9 (CO); 155.9 (C); 147.9 (C); 142.1 (CH); 126.0 (CH); 125.7 (CH); 124.8 (CH); 78.4 (C); 1.2 (CH_3). MS: 402 (0.3), 374 (0.2), 346 (1), 318 (3), 303 (1), 290 (5), 234 (2), 216 (12), 214 (5), 189 (2), 162 (3), 161 (15), 158 (3), 145 (19), 135 (25), 114 (10), 104 (19), 104 (1), 88 (1), 77 (4), 73 (100), 56 (13). Anal. calc. for $C_{18}H_{22}FeO_5Si_2$: C 50.23, H 5.15; found: C 50.13, H 5.10.

Tricarbonyl[2,5-dimethyl-6-(trimethylsilyl)cyclohepta-1,3,5-triene]chromium (**19b**). *1a*-endo-*Chloro-2,5-epoxy-1a,2,5,5a-tetrahydro-2,5-dimethyl-5a*-endo-*(trimethylsilyl)-1H-benzocyclopropene* (**17a**). To 1-bromo-2,2-dichloro-1-(trimethylsilyl)cyclopropane [23] (2.11 g, 8.0 mmol) in hexane (15 ml) was added, at −78°, BuLi (5.0 ml, 1.6M in hexane, 8.0 mmol) dropwise in 15 ml. The mixture was stirred during 10 min at −78°, and for additional 10 min at r.t. Et_2O (28 ml) and 2,5-dimethylfuran (3.98 g, 41.4 mmol), both freshly filtered through basic aluminium oxide, were added rapidly, and the resulting mixture was stirred at r.t. during 65 h. After addition of H_2O (50 ml) and extraction with CH_2Cl_2 (60 ml and twice 25 ml), the org. layer was washed to neutrality and dried ($MgSO_4$). The solvent was evaporated and **17a** purified by column chromatography (silica gel 60, 70–230 mesh, pentane/CH_2Cl_2 1:1). Yield: 1.09 g (56%). IR ($CHCl_3$): 3012*m*, 2975*m*, 2950*m*, 2925*w*, 1450*w*, 1382*m*, 1305*w*, 1265*m*, 1250*s*, 1170*w*, 1140*w*, 1062*w*, 987*w*, 900*w*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 6.43 (*AB*, $\delta_A = 6.44$, $\delta_B = 6.41$, $^3J_{AB} = 5.4$, 2 H); 2.10 (*d*, $^2J = 5.0$, 1 H); 1.59 (*s*, 3 H); 1.43 (*s*, 3 H); 1.20 (*d*, $^2J = 5.0$, 1 H); 0.1 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 143.4 (CH); 141.4 (CH); 88.9 (C); 87.0 (C); 66.3 (C); 30.7 (C); 27.9 (CH_2); 17.9 (CH_3); 14.2 (CH_3); −0.3 ($(CH_3)_3Si$). MS ($C_{12}H_{19}ClOSi$): 243/241 (1/2, M^+), 226 (2), 208 (2), 207 (13), 203 (2), 191 (2), 183 (2), 169 (3), 163 (4), 149 (2), 134 (3), 133 (4), 119 (5), 118 (2), 96 (22), 93 (8), 75 (8), 73 (100).

1-Chloro-2,5-dimethyl-6-(trimethylsilyl)cyclohepta-1,3,5-triene (**18a**). To $TiCl_3$ (657 mg, 4.26 mmol) in THF (10 ml) was added at r.t. $LiAlH_4$ (82 mg, 2.16 mmol) in small portions. The mixture was stirred during 30 min, and **17a** (206 mg, 0.85 mmol) in THF (10 ml) was added to the black soln. After 16 h of stirring at r.t. CH_2Cl_2 (40 ml) and sat. Na_2CO_3 (40 ml) were added. After filtration through *Celite*, which was extracted with CH_2Cl_2, the org. layer was washed with sat. NaCl to neutrality and dried with K_2CO_3. Compound **18a** was purified by column chromatography (silica gel 60, 70–230 mesh, pentane/CH_2Cl 1:1). Yield: 150 mg, 78%. IR ($CHCl_3$): 3012*w*, 2950*m*, 2925*m*, 2850*w*, 1654*w*, 1623*w*, 1432*w*, 1376*w*, 1247*s*, 1000*w*, 957*w*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 6.37 (*AB*, $\delta_A = 6.43$, $\delta_B = 6.30$, $^3J_{AB} = 11.4$, 2 H); 2.66 (*s*, 2 H); 1.95 (*s*, 3 H); 1.91 (*s*, 3 H); 0.23 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 142.7 (C); 135.3 (CH); 132.9 (CH); 132.1 (C); 128.3 (C); 120.9 (C); 40.3 (CH_2); 21.2 (CH_3); 18.7 (CH_3); 0.16 ($(CH_3)_3Si$). MS: ($C_{12}H_{19}ClSi$): 228/226 (1/2, M^+), 213 (2), 211 (4), 183 (3), 175 (8), 173 (5), 159 (2), 15e (3), 149 (2), 118 (16), 117 (14), 115 (4), 104 (4), 93 (7), 91 (6), 74 (9), 73 (100).

Tricarbonyl[1-chloro-2,5-dimethyl-6-(trimethylsilyl)cyclohepta-1,3,5-triene]chromium (**19a**). To $[Cr(CH_3CN)_3CO)_3]$ (244 mg, 0.94 mmol) was added **18a** (179 mg, 0.79 mmol) in freshly distilled Bu_2O (15 ml). The mixture was degassed three times and then heated to 90° under a slow current of N_2 and protected from light during 2.5 h. The deep-brown mixture was filtered through *Celite*, which was washed with Et_2O until disappearance of the red color. After evaporation of the solvent, the residue was purified by column chromatography (silica gel 60, 230–400 mesh, hexane/CH_2Cl_2 10:1) and yielded 91 mg of **19a** (32%). M.p. 136°. IR (hexane): 1987*vs*, 1930*s*, 1905*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 5.77 (*AB*, $\delta_A = 5.93$, $\delta_B = 5.62$, $^3J_{AB} = 9.0$, 2 H); 2.34 (*AB*, $\delta_A = 3.10$, $\delta_B = 1.57$, $^2J_{AB} = 14.3$, 2 H); 2.18 (*s*, 3 H); 2.16 (*s*, 3 H); 0.36 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 230.9 (CO); 121.1 (C); 108.6 (C); 101.9 (CH); 98.4 (CH); 73.5 (C); 55.3 (C); 38.2 (CH_2); 24.9 (CH_3); 23.4 (CH_3); 0.01

($(CH_3)_3Si$). MS: 364/362 (0.4/1, M^+), 334 (1), 306 (1), 280 (2), 278 (5), 265 (1), 263 (3), 227 (2), 191 (4), 184 (5), 175 (8), 170 (23), 163 (6), 145 (3), 119 (3), 117 (3), 115 (5), 105 (3), 91 (4), 80 (4), 77 (5), 73 (55), 67 (5), 59 (17), 53 (16), 52 (100), 50 (6), 45 (26). HR-MS ($C_{15}H_{19}ClCrSiO_3$): M_{obs} 362.018631; M_{calc} 362.01969. Anal. calc. for $C_{15}H_{19}ClCrSiO_3$: C 49.65, H 5.28; found: C 49.07, H 5.18.

Tricarbonyl(1-chloro-2,5-dimethylcyclohepta-1,3,5-triene)chromium (**19b**). To **19a** (31 mg, 0.09 mmol) in THF (10 ml) was added, dropwise in 10 min, Bu_4NF (0.1 ml, 1.1M in THF; 0.11 mmol) in THF (2.0 ml) from −78 to −60°. H_2O (10 µl) was added, and the orange soln. was stirred at r.t. during 20 min. After filtration of the mixture through silica gel and *Celite*, which were subsequently washed with Et_2O until disappearance of the orange color, the solvent was evaporated, and the residue purified by column chromatography (silica gel 60, 230–400 mesh, hexane/CH_2Cl_2 10:1). Yield: 11 mg (44%) of **19b**. IR (hexane): 1992*vs*, 1936*s*, 1904*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 5.90 (*d*, ^3J = 8.8, 1 H); 5.79 (*dd*, ^3J = 8.8, ^4J = 1.8, 1 H); 3.39 (*dm*, ^3J = 9.8, 1 H); 3.23 (*dm*, ^3J = 9.8, ^2J = 14.4, 1 H); 2.25–2.22 (*m*, 1 H); 2.17 (*s*, 3 H); 1.99 (*s*, 3 H). MS: 292/290 (2/5, M^+), 262 (5), 234 (7), 206 (8), 166 (10), 119 (100), 120 (10), 103 (6), 91 (15), 77 (12), 65 (6), 52 (35). HR-MS ($C_{12}H_{11}ClCrSiO_3$): M_{obs} 289.9750061; M_{calc} 289.98017.

Attempted Cyclization of o-*Substituted Benzyl Derivatives. 1-(Methoxymethyl)-2-(trimethylsilyl)benzene* (**25a**). To a soln. of THF (6.0 ml) at −90° was added BuLi 1.6M in hexane (1.0 ml, 1.6 mmol). *1-Bromo-2-(methoxymethyl)benzene* [31] (**22a**) (186 mg, 0.93 mmol) in THF (6.0 ml) was added dropwise at −100° in 45 min. After stirring during 20 min, Me_3SiCl (0.25 ml, 1.98 mmol) was added, and the soln. was stirred at −100° for 2 h, and 30 min at 25°. After addition of sat. $NaHCO_3$ (15 ml), the aq. layer was extracted with Et_2O (3 × 20 ml). After washing (sat. NaCl) and drying ($MgSO_4$), the solvent was evaporated, and the residue was purified by column chromatography (SiO_2 60, 230–400 mesh, hexane/CH_2Cl_2 1:1) to afford 155 mg (86%) of **25a**. IR ($CHCl_3$): 3025*s*, 2950*m*, 2900*m*, 2825*w*, 1462*w*, 1387*w*, 1250*s*, 1226*m*, 1200*w*, 1125*m*, 1100*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.57–7.51 (*m*, 1 H); 7.43–7.23 (*m*, 3 H); 4.52 (*s*, 2 H); 3.39 (*s*, 3 H); 0.32 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 143.6 (C); 138.6 (C); 134.8 (CH); 129.2 (CH); 128.5 (CH); 127.1 (CH); 75.0 (CH_2); 58.0 (CH_3); 0.40 (CH_3Si). MS: 194 (1, M^+), 179 (43), 163 (3), 149 (100), 134 (5), 121 (14), 105 (12), 73 (9).

Tricarbonyl[1-(methoxymethyl)-2-(trimethylsilyl)benzene]chromium (**26a**). To tricarbonyl(naphthalene)-chromium (185 mg, 0.7 mmol) was added **25a** (150 mg, 0.77 mmol) in THF (7.0 ml). The mixture was degassed three times and then heated to 70° in a pressure resistant *Schlenk* tube during 195 min. The solvent was evaporated and the residue purified by column chromatography (SiO_2 60, 230–400 mesh, hexane/CH_2Cl_2 3:1) and recrystallization at −30° (Et_2O/hexane) to yield 118 mg (51%) of **26a**. M.p. 36°. IR (hexane): 1978*vs*, 1911*s*. ^{1}H-NMR: ($CDCl_3$, 200 MHz): 5.59 (*tm*, ^3J = 6.5, 1 H); 5.48 (*dm*, ^3J = 6.5, 1 H); 5.25 (*dm*, ^3J = 6.5, 1 H); 5.11 (*tm*, ^3J = 6.5, 1 H); 4.20 (*AB*, ^2J = 11.6, δ_A = 4.39; δ_B = 4.02, 2 H); 3.43 (*s*, 3 H); 0.35 (*s*, 9 H). ^{13}C-NMR (C_6D_6, 50 MHz): 233.7 (CO); 113.8 (C); 100.8 (CH); 98.5 (C); 95.4 (CH); 91.9 (CH); 89.7 (CH); 73.7 (CH_2); 58.1 (CH_3); 0.3 (CH_3Si).

Complex **26a** was also synthesized in 27% yield upon heating of **25a** with hexacarbonylchromium in Bu_2O at 160° for 49 h.

Tricarbonyl[(methoxymethyl)benzene]chromium (**27a**). To *t*-BuOK (41 mg, 0.37 mmol) in degassed THF (5.0 ml), was added at −20° **26a** (63 mg, 0.19 mmol) in THF (2.0 ml) during 15 min. After stirring of the mixture for 4 h, it was filtered through SiO_2 and *Celite*, both of which being subsequently washed with Et_2O until disappearance of the yellow color. After evaporation, the product was purified by column chromatography to give 27 mg (55%) of **27a**. ^{1}H-NMR (C_6D_6, 200 MHz): 4.65 (*d*, ^3J = 6.3, 2 H); 4.45 (*t*, ^3J = 6.3, 2 H); 4.30 (*t*, ^3J = 6.3, 1 H); 3.60 (*s*, 2 H); 2.99 (*s*, 3 H). For additional data, see [37].

Dimethyl[2-(trimethylsilyl)benzyl]amine (**25b**). To a soln. of BuLi 1.6M in hexane (30 ml, 48.1 mmol) was added at 20° Et_2O (7.0 ml) and *N,N*-dimethylbenzylamine (5.0 g, 37 mmol) at once. The mixture was heated to reflux until evolution of butane ceased. A white suspension formed gradually. THF (20 ml) was added, and the mixture was cooled to −70°. Me_3SiCl (7.0 ml, 55.5 mmol) was added dropwise in 15 min, and the mixture was allowed to warm up to 25°. After addition of sat. $NaHCO_3$ (75 ml) and extraction with Et_2O (3 × 50 ml), the org. layer was washed with sat. NaCl (3 × 50 ml) and dried (K_2CO_3). Crude **25b** was obtained (7.36 g, 96%) after evaporation, and was used without further purification. IR ($CHCl_3$): 3062*w*, 2950*s*, 2925*s*, 2862*s*, 2825*s*, 2775*s*, 1600*w*, 1462*s*, 1443*s*, 1437*m*, 1368*m*, 1250*vs*, 1175*m*, 1125*s*, 1075*s*, 1025*m*. ^{1}H-NMR (CD_2Cl_2, 200 MHz): 7.49 (*dd*, ^3J = 6, ^4J = 2, 1 H); 7.38–7.13 (*m*, 3 H); 3.45 (*s*, 2 H); 2.14 (*s*, 6 H); 0.28 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 145.3 (C); 138.8 (C); 134.8 (CH); 129.0 (CH); 128.9 (CH); 126.3 (CH); 64.7 (CH_2); 45.4 (CH_3); 0.63 (CH_3Si). MS: 207 (2, M^+), 192 (8), 177 (1), 176 (4), 149 (7), 134 (5), 121 (4), 119 (2), 105 (3), 87 (13), 73 (23), 58 (100).

Tricarbonyl{dimethyl[2-(trimethylsilyl)benzyl]amine}chromium (**26b**). To $[Cr(CH_3CN)_3(CO)_3]$ (1.53 g, 5.93 mmol) was added **25b** (1.06 g, 5.1 mmol) in Bu_2O (20 ml). The mixture was three times degassed, and then heated to 90° during 2 h under a stream of N_2. After cooling, the mixture was filtered through *Celite*, which was washed until

disappearance of the yellow color. The soln. was concentrated to *ca.* 8 ml, and hexane (10 ml) was added. The product recrystallized upon cooling with dry-ice. Yield: 1.03 g (59%). M.p. 43–44°. IR (hexane): 1976*vs*, 1908*vs*. ^{1}H-NMR (C_6D_6, 200 MHz): 5.04 (*dd*, $^3J = 6$, $^4J = 2$, 1 H); 4.79 (*dt*, $^3J = 6$, $^4J = 2$, 1 H); 4.57 (*dd*, $^3J = 6$, $^4J = 2$, 1 H); 4.30 (*dt*, $^3J = 6$, $^4J = 2$, 1 H); 2.94 (*AB*, $^2J = 13$, $\delta_A = 3.47$, $\delta_B = 2.42$, 2 H); 1.83 (*s*, 6 H); 0.28 (*s*, 9 H). ^{13}C-NMR (C_6D_6, 50 MHz): 233.9 (CO); 115.8 (C); 101.2 (CH); 99.7 (C); 95.2 (CH); 93.4 (CH); 89.9 (CH); 63.4 (CH_2); 44.7 (CH_3); 0.46 (CH_3Si). MS: 343 (1, M^+), 287 (1), 259 (6), 244 (1), 216 (16), 214 (1), 192 (1), 149 (2), 134 (1), 119 (2), 95 (49), 90 (1), 73 (6), 58 (23), 52 (100). Anal. calc. for $C_{15}H_{21}CrNO_3Si$: C 52.46, H 6.16, N 4.08; found: C 52.37, H 6.10, N 4.18.

Tricarbonyl{trimethyl-[2-(trimethylsilyl)benzyl]ammonium}chromium Tetrafluoroborate. To trimethyloxonium tetrafluoroborate [36] (315 mg, 2.13 mmol) in CH_2Cl_2 (10 ml) was added rapidly **26b** (735 mg, 2.14 mmol) in CH_2Cl_2 (25 ml). The mixture was stirred at 22° during 3 h. The complex **26c** was separated by filtration, washed with Et_2O, and dried *in vacuo*. Yield: 927 mg (97%). M.p. 209 (dec.). IR (MeCN): 3012*w*, 2950*w*, 1974*vs*, 1900*vs*, 1450*s*, 1381*m*, 1262*w*, 1100*m*, 1062*s*, 925*w*, 850*m*. ^{1}H-NMR (CD_3CN, 200 MHz): 5.85 (*dt*, $^3J = 6$, $^4J = 1.6$, 1 H); 5.69–5.2 (*m*, 3 H); 4.14 (*AB*, $^2J = 14$, $\delta_A = 4.16$, $\delta_B = 4.12$, 2 H); 3.08 (*s*, 3 H); 0.44 (*s*, 9 H). ^{13}C-NMR (CD_3CN, 50 MHz): 233.2 (CO); 103.4 (C); 103.0 (C); 101.7 (CH); 97.8 (CH); 96.3 (CH); 95.9 (CH); 69.0 (CH_2); 54.3 (CH_3); 1.8 (CH_3Si). MS: 357 (10, $[M - 1]^+$), 298 (100). Anal. calc. for $C_{16}H_{24}BCrF_4NO_3Si$: C 43.16, H 5.43, N 3.15; found: C 42.92, H 5.35, N 3.23.

Tricarbonyl[(trimethyl)(benzyl)ammonium]chromium Tetrafluoroborate (**27b**). To CsF (186 mg, 1.22 mmol) in MeCN (2.0 ml) was added dropwise, at −40°, **26c** (278 mg, 0.62 mmol) in MeCN (13 ml). The mixture was stirred at −40° during 4 h. *t*-BuOH (1.0 ml) in MeCN (5.0 ml) was added. The mixture was filtered through SiO_2 and *Celite*, which were washed with MeCN until disappearance of the yellow color. **27b** (184 mg, 80%) was obtained upon evaporation of the solvent. M.p. 211° (dec.). IR (MeCN): 3000*m*, 1971*vs*, 1894*vs*, 1433*m*, 1423*m*, 1413*m*, 1375*m*, 1365*m*, 1057*s*, 1038*s*, 913*m*. ^{1}H-NMR (CD_3CN, 200 MHz): 6.69–5.75 (*m*, 3 H); 5.59–5.52 (*m*, 2 H); 4.09 (*s*, 2 H); 3.04 (*s*, 9 H). ^{13}C-NMR (CD_3CN, 50 MHz): 232.8 (CO); 99.3 (CH); 96.6 (CH); 95.8 (C); 93.6 (CH); 68.6 (CH_2); 53.5 (CH_3). MS: 285 (49, $[M - 1]^+$), 226 (100).

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