# 181. Bicyclo[4.2.0]octa-1,3,5-triene: 2-Mono- and 2,5-Disubstituted Derivatives *via* Highly Regioselective Lithiation of Its $Cr(CO)_3$ Complex and *via* Reductive Silylation/Oxidation

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Treatment of [$\eta^6$-(bicyclo[4.2.0]octa-1,3,5-triene)]tricarbonylchromium(0) (**2**) with BuLi or lithium 2,2,6,6-tetramethylpiperidinide (TMPLi) gives rise to a highly regioselective deprotonation at C(2). Subsequent reaction with electrophiles (6 examples) gives [$\eta^6$-(2-R-bicyclo[4.2.0]octa-1,3,5-triene)]tricarbonylchromium complexes **3** and **5–9** in moderate (R=I, 50%; R=CHO, 67%) to good (R=Me, D, $SiMe_3$, $CO_2Me$, > 80%) yield (*Scheme 1*). Analogous reactions with tricarbonyl ($\eta^6$-indane)chromium (**10**) give mixtures of complexes substituted at C(4) and C(5) (*Scheme 2*). In **10**, deprotonation $\beta$ to the ring junction is strongly favoured with the bulky base TMPLi. Double lithiation/electrophile additions to **2** give access to [$\eta^6$-(2-R′-5-R″-bicyclo[4.2.0]octa-1,3,5-triene)]tricarbonylchromium complexes (*e.g.* **13** (R′=R″=$Me_3Si$) and **14** (R′=$Me_3Si$, R″=CHO)) as single products. The $Cr(CO)_3$ group can be easily removed by oxidation ($I_2$, Ce(IV), $O_2$/light; 2 examples each) to give the free arenes. Base-catalyzed (CsF, DMF/$D_2O$) deuterodesilylation of **13** yields the [(2,5-$^2H_2$)bicyclo[4.2.0]octa-1,3,5-triene]chromium complex **15**, and treatment of 2,5-bis(trimethylsilyl) compound **16** with $CF_3COOD$ gives the 2,4-dideuterated **17**. Compound **16** is also accessible more directly *via* reductive silylation/oxidation of bicyclo[4.2.0]octa-1,3,5-triene (**1**). Stereoselective base-catalyzed (*t*-BuOK) H/D exchange of the benzylic H-atoms opposite to the $Cr(CO)_3$ moiety in **2** takes place rapidly in ($D_6$)DMSO, but benzylic functionalization *via* this route remains elusive.

**Introduction.** – The properties and chemistry of bicyclo[4.2.0]octa-1,3,5-triene (=1,2-dihydrocyclobutabenzene; **1**) have stimulated much interest from both synthetic and physical organic chemists [1–5], and the development of synthetic routes to selectively functionalized derivatives of **1** is, therefore, of considerable importance. Transformations of arenes *via* $\pi$-complexation to the electrophilic $Cr(CO)_3$ group have found widespread application [6], and this, when applied to **1**, has the potential to lead to new and useful chemistry and would constitute a particularly attractive method for the elaboration of regio- and stereoselective routes to functionalized bicyclo[4.2.0]octa-1,3,5-trienes. In this context, we also note our recent finding that a $\pi$-bound bicyclo[4.2.0]octa-1,3,5-triene can undergo ring opening to an *ortho*-quinodimethane intermediate without loss of metal coordination [7c]. To this date, only a few studies have focused on the synthesis and reactivity of **1** coordinated to Cr [7–9]. In this article, we report on lithiation/electrophile-addition reactions of [$\eta^6$-(bicyclo[4.2.0]octa-1,3,5-triene)]tricarbonylchromium (**2**). They provide access to 2-mono- and 2,5-disubstituted bicyclooctatriene complexes, and, after removal of the metal, to the substituted bicyclooctatrienes [10–13]. We also describe an alternative efficient synthesis of the new 2,5-bis(trimethylsilyl)bicyclo[4.2.0]octa-1,3,5-triene (**16**) *via* reductive silylation/oxidation.

The acidity of aromatic and benzylic C–H bonds is enhanced by $\pi$-complexation of the arene to the electrophilic $Cr(CO)_3$ group, and this allows ring lithiation under very

mild conditions. Parallel with directing effects observed in the metallation of uncomplexed arenes [14], many functional groups, by a combination of electron-withdrawing effects and ligation of the incoming base, direct lithiation to an *ortho*-site[1]) [15–17]. In those [Cr(arene)$(CO)_3$] complexes that lack a directing group, mixtures of products are the rule; in [Cr(alkylarene)$(CO_3)$]complexes, competitive benzylic deprotonation occurs [16][17]. The latter (thermodynamically favoured) is a side reaction under kinetic-control conditions (BuLi, THF, −78°), but when weaker bases (*e.g. t*-BuOK in DMSO, 20°) are used, it is the exclusive mode of reaction, and benzylic functionalization *via* this route has found wide application in synthesis [18–22].

**Results and Discussion.** – Complex **2** reacted readily with BuLi at −100° in THF and yielded, after addition of $SiMe_3Cl$ and crystallization from hexane, the 2-(trimethylsilyl)bicyclooctatriene complex **3** in 90% yield (*Scheme 1*). NMR Analysis of the crude reaction mixture revealed the presence of a small amount ( < 3%) of another isomer to which we tentatively assigned the structure of the 3-substituted regioisomer **4** ($^1$H-NMR: 0.12 ($Me_3Si$) and 5.20 ppm (br. *s*, H–C(2))[2]). Other electrophiles could be introduced likewise, and in all cases 2-substituted products were obtained highly selectively in moderate to excellent yields (see **5–9**, *Scheme 1*).

By contrast, **2** was recently reported to be metallated by BuLi in *N,N,N′,N′*-tetramethylethylene diamine (TMEDA)/THF at C(2) and C(3) to give, after silylation, a 3:2 mixture **3**/**4** [9]. As deprotonation of [Cr(arene)$(CO)_3$] complexes with BuLi is irreversible [23a], a possible explanation for the competitive lithiation at C(2) and C(3) by BuLi/TMEDA is the bulk of the base. There is precedent to this in the lithiation of [Cr(naphthalene)$(CO)_3$] where BuLi gave a 7:3 mixture of 2- and 1-lithiation, whereas lithium 2,2,6,6-tetramethylpiperidinide (TMPLi) selectively removed the more accessible H-atom at C(2) [23b]. Different product distributions were also reported from the reactions of **1** with pentylsodium [24] and with BuLi/TMEDA [10][25], but the low yields and/or mixtures obtained make interpretation difficult and the approach limited. The hypothesis that the bulk of the base is a strongly contributing factor to regioselectivity of lithiation in complex **2** could not be confirmed. The sequential reaction of complex **2** with TMPLi and $SiMe_3Cl$ gave a 75% yield of **3**, and no **4** was observed in this reaction. The higher kinetic acidity of H–C(2) in **2** thus established, it remained to check the possibility of equilibration of the aryllithium complex. We have previously shown that such an equilibration can be induced by addition of $(i\text{-}Pr)_2NH$ given the proximity of $pK_a$ of the protons of the aromatic ring in [Cr(arene)$(CO)_3$] complexes and this amine [23a][26]. Following lithiation of **2** with BuLi as described above, 1 mol-equiv. of $(i\text{-}Pr)_2NH$ was added, but after 2 h at −78° followed by addition of $SiMe_3Cl$, again only **3** (88%) was obtained.

As pointed out above, lithiations of [Cr(alkylarene)$(CO)_3$] complexes are generally not selective, and the formation of a single product in the deprotonation of **2** is, thus, unusual but tallies with the order of acidities observed in **1**. In the next higher homologue, [Cr(indane)$(CO)_3$] (**10**), in which the increased CH acidity at aryl positions adjacent to fused strained rings is largely attenuated, regioselectivity is different. Treatment of **10**

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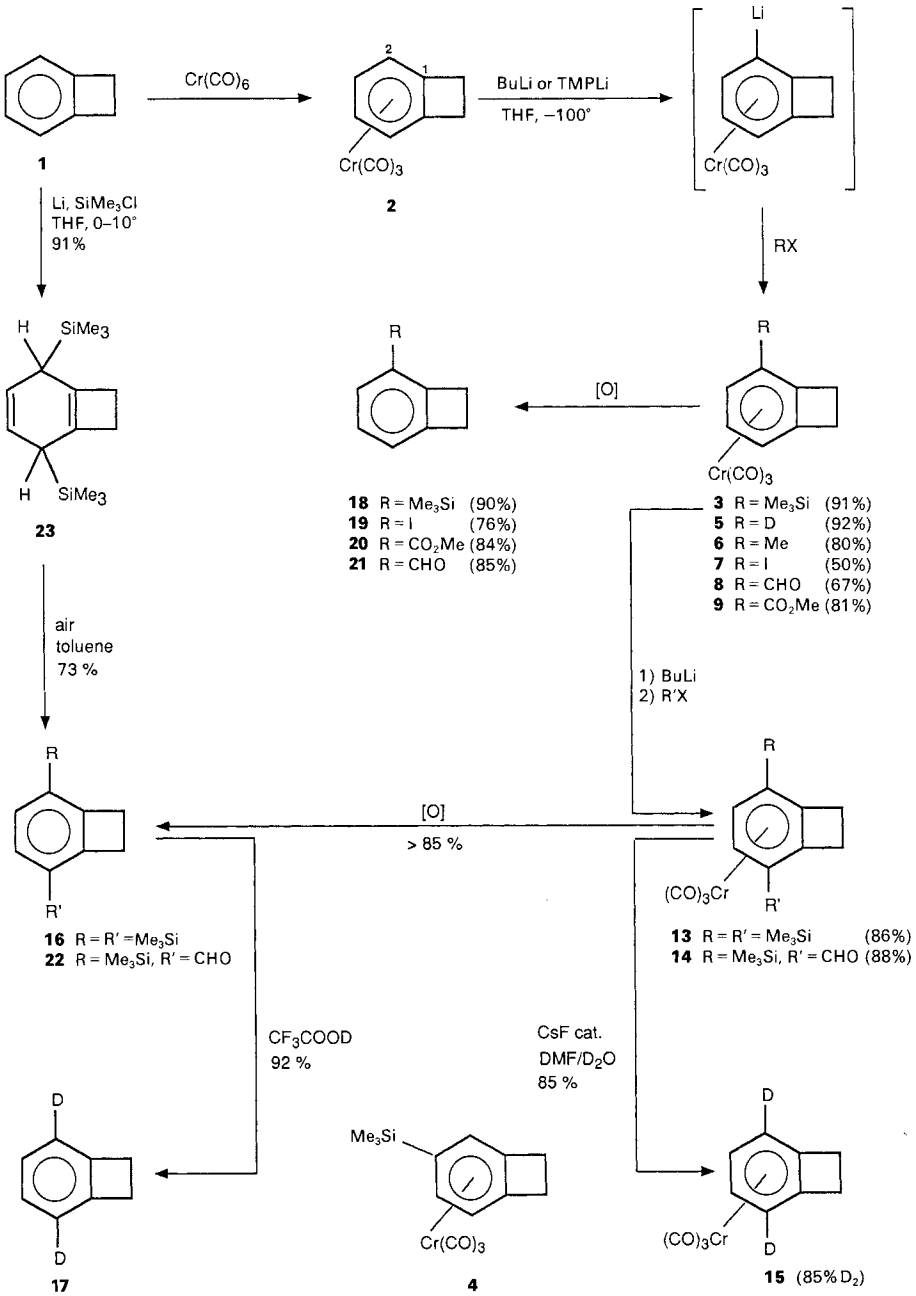
[1]) The order of directing ability is modified on complexation, the most remarkable change being the high efficiency of the F-group.

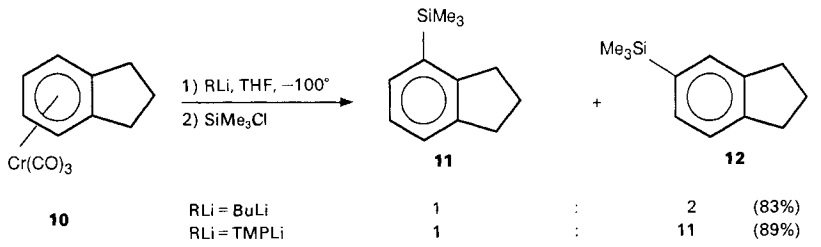
[2]) The *AB* system of H–C(4) and H–C(5) of **4** overlaps with a signal associated with **3** (4.61 ppm). When the lithiation was carried out at −40°, 7% of **4** and 82% of **3** were formed.

*Scheme 1*


Cr(CO)6
BuLi or TMPLi
THF, –100°
Li, SiMe3Cl
THF, 0–10°
91%
RX
[O]
air
toluene
73 %
1) BuLi
2) R'X
[O]
> 85 %
CF3COOD
92 %
CsF cat.
DMF/D2O
85 %
18 R = Me3Si (90%)
19 R = I (76%)
20 R = CO2Me (84%)
21 R = CHO (85%)
3 R = Me3Si (91%)
5 R = D (92%)
6 R = Me (80%)
7 R = I (50%)
8 R = CHO (67%)
9 R = CO2Me (81%)
16 R = R' = Me3Si
22 R = Me3Si, R' = CHO
13 R = R' = Me3Si (86%)
14 R = Me3Si, R' = CHO (88%)
15 (85% D2)
17
4

with BuLi and $SiMe_3Cl$ gave a 1:2 mixture of 4- and 5-substituted products **11** and **12** (*Scheme 2*). With TMPLi, the selectivity shifted in favour of the 5-substituted product (**11**/**12** 1:11). This reflects the stronger interaction between the incoming base and the benzylic $CH_2$ group in **10** as compared to **2**. By fractional crystallization, **12** was obtained pure in 64% yield. Benzylic deprotonation was insignificant in these reactions.

*Scheme 2*




The 2-substituted bicyclo[4.2.0]octa-1,3,5-trienes are also accessible *via* nucleophilic addition of stabilized carbanions to complex **2** [7a], *via* zirconocene metallacycles [13], and *via* directed lithiation of chlorobenzene [27]. Organometallic approaches are thus often the methods of choice for the synthesis of these compounds, and the reactions of complex **2** complement the electrophilic substitution of **1** which, although complicated by ring-opening reactions, characteristically occurs at the 3-position [1][3]).

As the $Cr(CO)_3$ group is retained in the products **3** and **5**–**9**, the lithiation/electrophile-addition sequence can be repeated. Thus, complexes **13** and **14** (*Scheme 1*) were obtained as single products from **3**. Base-catalyzed deuterodesilylation (CsF, DMF, $D_2O$), based on a procedure developed by *Effenberger et al.* for the reaction of arylsilanes with benzaldehydes [28], was applied to **13** to give the dideuterated complex **15** (85% $D_2$, 15% protodesilylation). Electrophilic deuterodesilylation ($CF_3CO_2D$) of **16** gave **17** (92%). Together with the benzylic H/D exchange described below, **15** and **17** were used in the unambiguous NMR spectral assignment of the resonances of the parent complex **2** and of **1**, respectively.

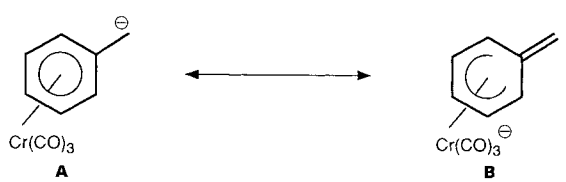
The $^1$H-NMR spectrum of **17** confirms previous data for **1** [30] which show H–C(3) and H–C(4) to be associated with the lower and H–C(2) and H–C(5) with the higher-field resonance of the *AA'BB'* system, a reversal of the usual pattern of aromatic $^1$H-NMR resonances. In agreement with data reported by *Elschenbroich et al.* [8], the order of aromatic resonances is reversed in the $Cr(CO)_3$ complex **2**. Our assignment of the $^1$H-NMR signals to the benzylic H-atoms pointing to the opposite (*'exo'*) or the same side (*'endo'*) as the $Cr(CO)_3$ moiety is, however, at variance with the previous report [8].

The $Cr(CO)_3$ group is readily removed from the functionalized arene by oxidative decomplexation as demonstrated by the reactions of **3** and **13** with Ce(IV) yielding the substituted bicyclooctatrienes **18** and **16**, respectively, of complexes **7** and **9** with $I_2$ yielding **19** and **20**, respectively, and of complexes **8** and **14** with $O_2$ (air) and light yielding **21** and **22**, respectively (*Scheme 1*).

[3]) The 2-isomer is occasionally obtained as minor product; *e.g.* in the sulfonation of **1** where the ratio of the 3- to the 2-isomer is 9:1 [29].

The introduction of silyl groups into arenes *via* reductive silylation/oxidative aromatization has been described by several groups [31–34]. When applied to **1**, this sequence provided an alternative and more direct route to 2,5-bis(trimethylsilyl)bicyclo[4.2.0]octa-1,3,5-triene (**16**). Thus, **1** was added to a mixture of Li sand and $SiMe_3Cl$ in THF at 5° under Ar within 30 min. Samples were analyzed at intervals by GLC showing the formation of *ca.* 1:1 mixture of two compounds which were assigned to *cis*- and *trans*-2,5-bis(trimethylsilyl)bicyclo[4.2.0]octa-1(6),3-diene (*cis*- and *trans*-**23**, *Scheme 1*). No tetrasilylated products were observed. These side products are reported to be formed in roughly equal amounts together with the disilylated products in analogous reactions with *o*-xylene [34b] and tetralin [34a]. They most likely arise from initial 1,2 silyl addition, followed by rapid reductive disilylation of the generated conjugated diene to give the tetrasilylated product. In **1**, the enhanced reactivity of aryl positions adjacent to the strained 4-membered ring may account for the observed high selectivity. When dry air was passed through a toluene solution of the mixture **23**, the aromatic compound **16** was formed efficiently[4]). After 2 h, the isomer with the longer GLC retention time had practically disappeared, and based on literature precedent [33], this was assigned to *cis*-**23**; *trans*-**23** reacted 5–10 times slower. After 24 h, **16** was isolated in 82% yield based on **1**.

[Cr(cycloalkabenzene)$(CO)_3$] complexes readily undergo stereoselective base-catalyzed benzylic H/D exchange [35]. In $(D_6)$DMSO, the benzylic protons of complex **2** give rise to an *AA'BB'* system centered at 2.97 and 3.20 ppm. On addition of a small amount of *t*-BuOK, the signal at 3.20 ppm (low-field part of *AA'BB'*) completely disappeared within min. Concomitantly, a *s* grew in at 2.94 ppm. This latter was, therefore, assigned to the kinetically less acidic benzylic H-atoms lying on the same side as the $Cr(CO)_3$ moiety. Encouraged by this result and in analogy with extensive literature precedent [18–22], we attempted alkylations *via* benzylic deprotonation (with *t*-BuOK in DMSO or NaH in DMF or THF). These efforts failed to yield 7-substituted bicyclo[4.2.0]octa-1,3,5-triene complexes, however, and instead gave complex mixtures of compounds. Translithiation from the aromatic-ring to the benzylic position as reported for [Cr(toluene)$(CO)_3$] [36] was also unsuccessfully tried. On quenching the reaction between BuLi and **2**, after warming to 20° for 2 h, with $SiMe_3Cl$, complex **3** was again obtained as the sole product in 53% yield. The stabilization of benzylic anions in [Cr(arene)$(CO)_3$] complexes can be ascribed to charge delocalization as represented by the limiting structures **A** and **B**. The unsuccessful benzylic alkylation of **2** may be due to the instability of the benzylic carbanion as charge delocalization into the $Cr(CO)_3$ fragment would result in an increase of ring strain.




**A** **B**

[4]) The addition of silica gel accelerated aromatization but also caused some desilylation. Simple air oxidation was found superior.

While the stereoselective benzylic alkylation of **2** has not been attained, the work described here shows efficient and highly selective routes to 2-substituted and 2,5-disubstituted bicyclo[4.2.0]octa-1,3,5-trienes, a substitution pattern which complements that obtained *via* electrophilic substitution.

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## Experimental Part

1. *General.* All manipulations involving organometallics were carried out under purified $N_2$ or Ar and using an inert gas/vacuum double manifold and standard *Schlenk* techniques. Toluene was refluxed for 4 h over Na before distillation. THF was distilled from sodium-benzophenone ketyl immediately prior to use. ($D_6$)Benzene and ($D_6$)DMSO *(Ciba-Geigy)* were vacuum-transferred after stirring with $CaH_2$. $CF_3COOD$ and $D_2O$ *(Ciba-Geigy)*, Li (2% Na; 15% in hexane; *Fluka*) were used as received. CsF *(Fluka)* was heated under vacuum to remove traces of $H_2O$. BuLi *(Fluka)* was titrated before use according to [37]. Alkyl halides, tetramethylpiperidine, and DMF *(Fluka)* were dried and distilled before use. Column chromatography: flash method according to [38]. GLC: *Hewlett-Packard-5890* spectrometer, flame ionization detector, 15-m *OV-31* capillary column. M.p.: *Büchi-510* apparatus; not corrected. IR spectra: *Perkin-Elmer-681* grating spectrometer or *Mattson-Instruments-Polaris-FT* spectrometer; NaCl soln. cells. $^1$H- and $^{13}$C-NMR spectra: *Bruker-WM-360* ($^1$H at 360 MHz, $^{13}$C at 90.6 MHz) and *Varian-XL-200* spectrometer ($^1$H at 200 MHz, $^{13}$C at 50.3 MHz); $\delta$ in ppm rel. to $SiMe_4$. EI-MS (70 eV): *Varian-CH-4* or *-SM-1* spectrometer; rel. intensities in parenthesis. HR-MS: *VG* analytical *7070 E* instrument (data system *11 250*, resolution 7000). Elemental analyses were performed by *H. Eder*, Service de Microchimie, Institut de Chimie Pharmaceutique, Université de Genève.

2. *Complexes.* Complex **2** [39] and [Cr(indane)$(CO)_3$] (**10**) [39][40] were prepared as described previously [41][42].

*[$\eta^6$-(Bicyclo[4.2.0]octa-1,3,5-triene)]tricarbonylchromium(0)* (**2**). IR (hexane): 1978*s*, 1913*s*, 1904*s*. $^1$H-NMR (360 MHz, $C_6D_6$): 2.26–2.36 (*AA'BB'*(*m*), $H_{endo}$–C(7), $H_{endo}$–C(8)); 2.57–2.67 (*AA'BB'*(*m*), $H_{exo}$–C(7), $H_{exo}$–C(8)); 4.22–4.28 (*AA'BB'*(*m*), H–C(3), H–C(4)); 4.64–4.70 (*AA'BB'*(*m*), H–C(2), H–C(5)). MS: 52 (100), 77 (7), 103 (5), 156 (45), 184 (7), 212 (2), 240 (11).

3. *Reactions of* **2** *with BuLi and Electrophiles.* 3.1. A THF soln. of **2** (20 ml/mmol) was cooled to −100°, treated with BuLi (1.0 equiv.) and stirred at −78° for 0.5 h. Then, 1 mol-equiv. of the neat electrophile was added dropwise and the temp. of the mixture raised to 0° within 0.5–1 h. Volatiles were removed *in vacuo* and the complexes isolated as described below.

3.2. *$SiMe_3Cl$.* The solid residue obtained from 260 mg (1.08 mmol) of **2** was taken up in warm hexane, filtered over *Celite*, concentrated, and placed first at −40°, then overnight at −78°. 308 mg (91%) of bright yellow needles of *tricarbonyl{$\eta^6$-[2-(trimethylsilyl)bicyclo[4.2.0]octa-1,3,5-triene]}chromium(0)* (**3**). M.p. 82–83° (hexane). IR (hexane): 1973*s*, 1909*s*, 1902*s*. $^1$H-NMR (360 MHz, $C_6D_6$): 0.20 (*s*, 9 H); 2.30–2.43 (*m*, 1 H); 2.50–2.68 (*m*, 2 H); 2.85–2.95 (*m*, 1 H); 4.22 (*t*, *J* = 6, H–C(4)); 4.61 (*d*, *J* = 6, 1 H); 4.95 (*d*, *J* = 6, 1 H). MS: 52 (100), 91 (6), 129 (4), 161 (4), 228 (27), 256 (2), 312 (3). HR-MS: 312.0236 ($C_{14}H_{16}CrO_3Si$, $M^+$, calc. 312.0273).

3.3. *$D_2O$.* The solid residue, obtained from 260 mg (1.08 mmol) of **2** was taken up in warm hexane, filtered over *Celite*, concentrated, and placed first at −0°, then at −40°: 235 mg (92%) of yellow needles of *[$\eta^6$-((2-$^2$H)bicyclo[4.2.0]octa-1,3,5-triene)]tricarbonylchromium(0)* (**5**). $^1$H-NMR (360 MHz, $C_6D_6$): 2.26–2.36 (*AA'BB'*(*m*), $H_{endo}$–C(7), $H_{endo}$–C(8)); 2.57–2.67 (*AA'BB'*(*m*), $H_{exo}$–C(7), $H_{exo}$–C(8)); 4.18–4.28 (*m*, 2 H); 4.62–4.68 (*m*, 1 H). MS: 90:10 rel int. of 157 and 156, indicating *ca.* 90% monodeuteration.

3.4. *MeI.* The solid residue obtained from 261 mg (1.09 mmol) of **2** was taken up in toluene, filtered over *Celite*, and concentrated. Hexane was added and the soln. passed again through *Celite*. Crystallization, first at 0°, then at −40° (overnight) yielded 220 mg (80%) of yellow needles of *tricarbonyl[$\eta^6$-(2-methylbicyclo[4.2.0]octa-1,3,5-triene)]chromium(0)* (**6**). M.p. 84–86° (hexane). IR (hexane): 1972*s*, 1905*s*, 1898*s*. $^1$H-NMR (360 MHz, $C_6D_6$): 1.66 (*s*, 3 H); 2.23–2.41 (*m*, 2 H); 2.57–2.64 (*m*, 1 H); 2.70–2.80 (*m*, 1 H); 4.15 (*d*, *J* = 6.5, 1 H); 4.43 (*t*, *J* = 6.5, H–C(4)); 4.52 (*d*, *J* = 6.5, 1 H). MS: 52 (100), 77 (4), 80 (3), 170 (19), 198 (1), 254 (3). HR-MS: 254.0005 ($C_{12}H_{10}CrO_3$, $M^+$, calc. 254.0035).

3.5. *$I_2$.* $I_2$ was added as soln. in THF (10 ml; 1-mmol scale). After warming to 0°, volatiles were removed *in vacuo* and the residue extracted with $Et_2O$ and 1N aq. HCl. The org. phase was washed with $H_2O$, dried ($MgSO_4$), and filtered through *Celite* to give, after crystallization from hexane, yellow *tricarbonyl[$\eta^6$-(2-iodobicyclo[4.2.0]octa-1,3,5-triene)]chromium(0)* (**7**; 184 mg, 50%). M.p. 72–73° (hexane). IR (hexane): 1980*s*, 1921*s*, 1912*s*. $^1$H-NMR (360 MHz, $C_6D_6$): 2.14–2.32 (*m*, 2 H); 2.47–2.64 (*m*, 2 H); 4.04 (*t*, *J* = 6, H–C(4)); 4.41 (*d*, *J* = 6, 1 H); 4.65 (*d*, *J* = 6, 1 H). MS: 52 (100), 77 (25), 103 (33), 154 (8), 282 (14), 310 (5), 338 (2), 366 (5). HR-MS: 365.8884 ($C_{11}H_7CrO_3I$, $M^+$, calc. 365.8844).

3.6. *Ph(Me)NCHO.* The solid (1.0-mmol scale) was extracted with $Et_2O$, and washed with 1N aq. HCl and $H_2O$. The org. phase was dried ($MgSO_4$), filtered, and evaporated. Recrystallization from $Et_2O$/hexane at −78° yielded red orange crystals of *[$\eta^6$-(bicyclo[4.2.0]octa-1,3,5-triene-2-carbaldehyde)]tricarbonylchromium(0)* (**8**; 181 mg, 67%). M.p. 59–60°. IR (hexane): 1990*s*, 1926*s* (br.), 1698*w*. $^1$H-NMR (360 MHz, $C_6D_6$): 2.26–2.48 (*m*, 2 H); 2.60–2.70 (*m*, 1 H); 2.90–3.00 (*m*, 1 H); 4.08 (*t*, *J* = 6, H–C(4)); 4.85 (*d*, *J* = 6, 1 H); 4.98 (*d*, *J* = 6, 1 H); 9.12 (*s*, 1 H). MS: 52 (100), 77 (7), 80 (5), 103 (3), 184 (7), 268 (1). HR-MS: 267.9791 ($C_{12}H_8CrO_4$, $M^+$, calc. 267.9827).

3.7. *$CO_2$.* The soln. obtained from 0.95 mmol of **2** was transferred *via* cannula onto dry ice. The temp. was slowly raised to 0° and the mixture treated with 1N aq. HCl and extracted with $Et_2O$. The org. phase was dried ($MgSO_4$) and filtered. A freshly prepared $Et_2O$ soln. of $CH_2N_2$ was added dropwise, the mixture evaporated and the crude product crystallized from hexane: bright red crystals of *tricarbonyl[$\eta^6$-(methyl bicyclo[4.2.0]octa-1,3,5-triene-2-carboxylate)]chromium(0)* (**9**; 231 mg, 81%). M.p. 74–76°. IR (hexane): 1985*s*, 1923*s*, 1915 (sh), 1735*m*. $^1$H-NMR (200 MHz, $C_6D_6$): 2.28–2.37 (*m*, 1 H); 2.46–2.56 (*m*, 1 H); 2.78–2.88 (*m*, 1 H); 3.12–3.23 (*m*, 1 H); 3.41 (*s*, 3 H); 4.12 (*t*, *J* = 6.5, H–C(4)); 4.75 (*d*, *J* = 6.5, 1 H); 5.45 (*d*, *J* = 6.5, 1 H). MS: 52 (100), 77 (10), 80 (5), 103 (5), 156 (5), 214 (8), 298 (1). Anal. calc. for $C_{13}H_{10}CrO_5$: C 52.36, H 3.38; found: C 52.58, H 3.54.

4. *Lithiation/Silylation of Complex* **2** *with TMPLi.* A soln. of TMPLi was prepared by addition of BuLi (1.1 mmol; 0.73 ml of 1.5M soln. in hexane) to a cold (−78°) soln. of 2,2,6,6-tetramethylpiperidine (0.185 ml, 1.1 mmol) in THF (8 ml). After stirring at 0° for 0.5 h and recooling to −78°, **2** (254 mg, 1 mmol) was added *via* a solid-addition tube. Stirring was continued for 1 h at −78° and then $SiMe_3Cl$ (0.3 ml) added dropwise. The mixture was stripped of volatiles while warming up and the resulting residue extracted with hexane. The soln. was filtered through *Celite* and evaporated. $^1$H-NMR of the crude product: only **2** (18%) and **3** (75%).

5. *Lithiation/Silylations with [Cr(indane)(CO)$_3$]* (**10**). 5.1. *Deprotonation with BuLi.* Conditions identical to those described in *Exper. 3.2.* $^1$H-NMR of the crude product (83% yield): **11**/**12** in a ratio of 1:2 and traces of a 3rd product whose structure was tentatively assigned to be [Cr{1-(trimethylsilyl)indane}(CO)$_3$].

5.2. *Deprotonation with TMPLi.* Conditions identical to those described in *Exper. 4.* $^1$H-NMR of the crude product (89% yield): **11**/**12** in a ratio of 1:11 and only traces of a 3rd product. Crystallization from hexane at −78° yielded pure *tricarbonyl{$\eta^6$-[5-(trimethylsilyl)indane]}chromium(0)* (**12**; 64%). M.p. 72–73° (hexane). IR (hexane): 1970*s*, 1901*s*. $^1$H-NMR (360 MHz, $C_6D_6$): 0.15 (*s*, 9 H); 1.42–1.54 (*m*, 1 H); 1.78–1.92 (*m*, 1 H); 2.04–2.30 (*m*, 3 H); 2.38–2.45 (*m*, 1 H); 4.63 (*d*, *J* = 6.5, H–C(7)); 4.86 (*dd*, *J* = 6.5, 1, H–C(6)); 5.23 (br. *s*, H–C(4)). MS: 52 (100), 176 (5), 242 (20), 270 (1), 326 (2). HR-MS: 326.0428 ($C_{15}H_{18}CrO_3Si$, $M^+$, calc 326.0431).

*Tricarbonyl{$\eta^6$-[4-(trimethylsilyl)indane]}chromium(0)* (**11**). $^1$H-NMR (360 MHz, $C_6D_6$): 0.17 (*s*, 9 H); 4.40 (*t*, *J* = 6.5, 1 arom. H); 4.94 (*d*, *J* = 6.5, 1 arom. H); 5.04 (*d*, *J* = 6.5, 1 arom. H).

6. *2,5-Disubstituted [Cr(Bicyclo[4.2.0]octa-1,3,5-triene)(CO)$_3$] Complexes* via *Lithiation.* 6.1. *{$\eta^6$-[2,5-Bis(trimethylsilyl)bicyclo[4.2.0]octa-1,3,5-triene]}tricarbonylchromium(0)* (**13**). Complex **3** (920 mg, 2.89 mmol) was reacted with BuLi and $SiMe_3Cl$ under identical conditions as described in *Exper. 3.2* to yield, after crystallization from pentane, yellow crystalline **13** (950 mg, 86%). M.p. 99–100° (pentane). IR (hexane): 1967*s*, 1900*s*, 1895*s*. $^1$H-NMR (200 MHz, $C_6D_6$): 0.23 (*s*, 18 H); 2.45–2.95 (*AA'BB'*(*m*), 4 H); 4.47 (*s*, 2 H). $^{13}$C-NMR (90.6 MHz, $C_6D_6$): −1.2 ($Me_3Si$); 30.8 (C(7), C(8)); 95.5 (C(3), C(4)); 99.1 (C(2), C(5)); 121.7 (C(1), C(6)); 234.5 (CO). MS: 52 (100), 67 (9), 73 (19), 80 (5), 145 (3), 159 (2), 300 (34), 328 (2), 384 (2). Anal. calc. for $C_{17}H_{24}O_3CrSi$: C 53.10, H 6.29; found: C 52.99, H 6.25.

6.2. *Tricarbonyl{$\eta^6$-[5-(trimethylsilyl)bicyclo[4.2.0]octa-1,3,5-triene-2-carbaldehyde]}chromium(0)* (**14**). Proceeding as above (1-mmol scale), **3** was lithiated, and DMF (5-fold excess) was added and the reaction worked up as described in *Exper. 3.6*: crude **14** (300 mg, 88%). A sample was crystallized from pentane at −40° to give orange crystals which became oily at 20°. IR (hexane): 1983*s*, 1932*s*, 1913*s*, 1700*m*. $^1$H-NMR (200 MHz, $C_6D_6$): 0.12 (*s*, 9 H); 2.35–2.98 (*m*, 4 H); 4.38 (*d*, *J* = 6.5, 1 H); 4.98 (*d*, *J* = 6.5, 1 H); 9.22 (*s*, 1 H). MS: 52 (56), 73 (21), 161 (48), 189 (100), 256 (53), 340 (10). HR-MS: 340.0216 ($C_{15}H_{16}CrO_4Si$, $M^+$, calc 340.0223).

7. *Oxidative Cleavage of the Cr(CO)$_3$ Group.* 7.1. *With Ce(IV): 2-(Trimethylsilyl)bicyclo[4.2.0]octa-1,3,5-triene* (**18**). A soln. of $Ce(NH_4)_2(NO_3)_6$ (1.48 g, 2.7 mmol) in THF (20 ml) was added dropwise to a cold (−78°) soln.

of **3** (278 mg, 0.89 mmol) in THF (5 ml). The mixture, whose colour had changed rapidly from yellow to green-brown, was warmed to 0°. $Et_2O$ and $H_2O$ were added, and the org. phase was washed with aq. $NaHCO_3$ soln. and dried ($MgSO_4$). Bulb-to-bulb distillation yielded **18** (142 mg, 90%) as a colourless oil. IR ($CHCl_3$): 3070*m*, 3010*s*, 2960*s*, 2940*s*, 1420*m*, 1395*s*, 1250*s*, 1142*m*, 840v*s*. $^1$H-NMR (360 MHz, $C_6D_6$): 0.29 (*s*, 9 H); 3.18–3.30 (*AA'BB'*(*m*), 4 H); 7.06 (*d*, *J* = 7.5, 1 H); 7.21 (*t*, *J* = 7.5, H–C(4)); 7.35 (*d*, *J* = 7.5, 1 H). MS: 45 (24), 51 (14), 53 (17), 73 (24), 77 (13), 103 (6), 133 (7), 135 (10), 161 (100), 176 (21). HR-MS: 176.1036 ($C_{11}H_{16}Si$, $M^+$, calc. 176.1021).

7.2. *2,5-Bis(trimethylsilyl)bicyclo[4.2.0]octa-1,3,5-triene* (**16**). By the same procedure as described in *Exper. 7.1*, **13** (900 mg, 2.34 mmol) gave, after chromatography on alumina (act.1, hexane), crystalline **16** (560 mg, 96%). M.p. 51–52°. IR ($CHCl_3$): 3010*m*, 2960*s*, 2940*m*, 1450*w*, 1420*w*, 1340*m*, 1250*s*, 1195*m*, 900*m*, 790v*s*. $^1$H-NMR (360 MHz, $C_6D_6$): 0.33 (*s*, 18 H); 3.12 (*s*, 4 H); 7.44 (*s*, 2 H). $^{13}$C-NMR (90.5 MHz, $CDCl_3$): –1.01, 31.25, 131.39, 135.28, 150.57. MS: 45 (62), 59 (36), 73 (100), 109 (11), 145 (7), 159 (7), 233 (31), 248 (6). Anal. calc. for $C_{14}H_{24}Si_2$: C 67.66, H 9.73; found: C 67.65, H 9.77.

7.3. *With $I_2$: 2-Iodobicyclo[4.2.0]octa-1,3,5-triene* (**19**). A soln. of $I_2$ (380 mg, 1.5 mmol) in THF (5 ml) was added dropwise to **7** (178 mg, 0.49 mmol) in THF (5 ml) at –20°. After stirring for 3 h at 20°, $Et_2O$ and $H_2O$ were added, and the org. phase was washed sequentially with 10% aq. $NaHSO_3$ soln., $H_2O$, and sat. aq. NaCl soln. Evaporation after drying ($MgSO_4$) yielded **19** as oil which was purified by prep. TLC (silica gel, hexane): 86 mg (76%). IR ($CHCl_3$): 3010*m*, 2960*s*, 2940*s*, 2850*s*, 1575*m*, 1450*m*, 1420*m*, 1380*w*, 1330*w*, 1200*w*, 1100*m*, 905*m*, 900*w*, 865*m*. $^1$H-NMR (360 MHz, $CDCl_3$): 3.04–3.13 (*AA'BB'*(*m*), 4 H); 6.94 (*t*, *J* = 7.5, H–C(4)); 7.05 (*d*, *J* = 7.5, 1 H); 7.52 (*d*, *J* = 7.5, 1 H). MS: 51 (67), 62 (15), 77 (91), 103 (100), 127 (14), 230 (56). HR-MS: 229.9586 ($C_8H_7I$, $M^+$, calc. 229.9592).

7.4. *Methyl Bicyclo[4.2.0]octa-1,3,5-triene-2-carboxylate* (**20**). By the same procedure as described in *Exper. 7.3*, **20** was obtained in 84% yield. IR ($CHCl_3$): 2960*m*, 2940*m*, 1718v*s*, 1610*w*, 1475*w*, 1440*m*, 1340*w*, 1295v*s*, 1195*m*, 1180*w*, 1145*m*, 1120*s*. $^1$H-NMR (200 MHz, $CDCl_3$): 3.16–3.25 (*AA'BB'*(*m*), 2 H); 3.33–3.41 (*AA'BB'*(*m*), 2H); 3.88 (*s*, 3 H); 7.15–7.30 (*m*, 2 H); 7.78 (*d*, *J* = 7.5, 1 H). MS: 51 (81), 77 (72), 73 (100), 91 (51), 103 (62), 119 (34), 131 (42), 147 (46), 162 (100). HR-MS: 162.0671 ($C_{10}H_{10}O_2$ $M^+$, calc. 162.0678).

7.5. *With Air/hν: Bicyclo[4.2.0]octa-1,3,5-triene-2-carbaldehyde* (**21**). Complex **8** (160 mg, 0.6 mmol) was dissolved in $CH_2Cl_2$ and exposed to air and sunlight until the soln. was colourless (4 h). The soln. was filtered through a short column of silica gel and evaporated: **21** (67 mg, 85%) as colourless oil. IR ($CHCl_3$): 1690v*s*. $^1$H-NMR (200 MHz, $CDCl_3$): 3.22–3.26 (*AA'BB'*(*m*), 2 H); 3.37–3.41 (*AA'BB'*(*m*), 2 H); 7.18 (*dd*, *J* = 7.5, 1, 1 H); 7.28 (*t*, *J* = 7.5, H–C(4)); 7.56 (*dd*, *J* = 7.5, 1, 1 H); 9.90 (*s*, CHO). MS: 51 (32), 63 (12), 78 (45), 103 (71), 132 (100). HR-MS: 132.0581 ($C_9H_8O$, $M^+$, calc. 132.0575).

7.6. *5-(Trimethylsilyl)bicyclo[4.2.0]octa-1,3,5-triene-2-carbaldehyde* (**22**). By the same procedure as described in *Exper. 7.5*, **22** was obtained in 90% yield. IR ($CHCl_3$): 2960*m*, 2940*m*, 1695*s*, 1605*m*, 1560*w*, 1355*m*, 1255*m*, 910*s*, 840*s*. $^1$H-NMR (200 MHz, $CDCl_3$): 0.28 (*s*, 9 H); 3.28–3.35 (*AA'BB'*(*m*), 2 H); 3.38–3.46 (*AA'BB'*(*m*), 2 H); 7.45 (*AB*(*d*), *J* = 7.5, 1 H); 7.58 (*AB*(*d*), *J* = 7.5, 1 H); 10.02 (*s*, CHO). MS: 45 (98), 75 (62), 115 (17), 131 (13), 161 (21), 189 (26), 204 (100). HR-MS: 204.0973 ($C_{13}H_{16}OSi$, $M^+$, calc. 204.0970).

8. *Deuterodesilylation of* **13** *and* **16**. 8.1. *[η⁶-(2,5-²H₂)Bicyclo[4.2.0]octa-1,3,5-triene]tricarbonylchromium(0)* (**15**). A soln. of $D_2O$ (80 µl, 4 mmol) in dry DMF (4 ml) at 0° was added under $N_2$ to dry CsF (74 mg, 0.49 mmol) and **13** (373 mg, 0.97 mmol). The mixture was stirred overnight at 0° and then treated with $H_2O$ (5 ml). HCl (0.1N) was added dropwise until neutral pH followed by extraction with $Et_2O$. After drying ($MgSO_4$), filtration over *Celite*, and evaporation, hexane was added and the soln. placed at –78°. The precipitated product (200 mg, 85%) ws shown by $^1$H-NMR to consist of **15** (85%), **2**, and **5** (15%).

When the reaction was carried out at 25° (0.3 h), the crude product showed, in addition to **15**, **2**, and **5**, the presence of *ca.* 4% of **8**.

**15**: $^1$H-NMR (200 MHz, $C_6D_6$): 2.20–2.40 (*AA'BB'*(*m*), 2 H); 2.50–2.70 (*AA'BB'*(*m*), 2 H); 4.23 (*s*, 2 H).

8.2. *(2,5-²H₂)Bicyclo[4.2.0]octa-1,3,5-triene* (**17**). $CF_3CO_2D$ (1 ml) was added dropwise to a stirred soln. of **16** (248 mg, 1 mmol) in $CCl_4$ (3 ml). After stirring overnight at r.t., the mixture was diluted with $CH_2Cl_2$ and poured into cold (0°) aq. $NaHCO_3$ soln. The org. phase was washed with $H_2O$ and aq. NaCl soln. and dried ($MgSO_4$). Bulb-to-bulb distillation at 100 mbar yielded **17** (97 mg, 92%). $^1$H-NMR (360 MHz, $CDCl_3$): 3.22 (*s*, 4 H); 7.20 (*s*, 2 H).

9. *Reductive Silylation/Oxidation of Bicyclo[4.2.0]octa-1,3,5-triene* (**1**). *Via* syringe, **1** (1.32 g, 12.7 mmol) was added to a stirred suspension of Li sand (2% Na; 263 mg, *ca.* 37 mmol) in THF (20 ml) and $SiMe_3Cl$ (5.1 g, 6 ml, 47 mmol) under Ar. The rate of addition of **1** was chosen such that the temp. was maintained at 0–10°. After completion of the addition (0.5 h), a sample was analyzed by capillary GLC ($T_{init.}$ = 100° (1 min), then 15°/min to

220°; carrier He 40 ml/min): 2 major peaks of similar intensity at 4.5 and 5.3 min, assigned to *trans*- and *cis*-**23**, resp.; only traces of **1**. The mixture was concentrated, hexane (30 ml) added, and the suspension filtered under $N_2$ over *Celite* to give, after evaporation, crude **23** as a yellow oil (2.9 g, 91%).

cis-*2,5-Bis(trimethylsilyl)bicyclo[4.2.0]octa-1(6),3-diene* (*cis*-**23**). $^1$H-NMR (200 MHz, $C_6D_6$): 0.08 (*s*, 18 H); 2.34–2.38 (*m*, 2 H); 2.52–2.68 (*m*, 4 H); 5.61–5.66 (*m*, 2 H).

trans-*2,5-Bis(trimethylsilyl)bicyclo[4.2.0]octa-1(6),3-diene* (*trans*-**23**). $^1$H-NMR (200 MHz, $C_6D_6$): 0.10 (*s*, 18 H); 2.23–2.27 (*m*, 2 H); 2.52–2.68 (*m*, 4 H); 5.58–5.62 (*m*, 2 H).

Purified (conc. $H_2SO_4$, NaOH) air was passed through a soln. of crude **23** (1.84 g, 7.35 mmol) in dry toluene (40 ml). GLC of samples removed indicated the rapid disappearance of the isomer with longer retention time (5.3 min, *cis*-**23**), the slower disappearance of *trans*-**23**, and the growth of the band associated with **16** (5.9 min). After 24 h, volatiles were removed, the residue was taken up in hexane, filtered through a short plug of silica gel, evaporated and placed at –78° to give colourless crystals of **16** (1.225 g). A second crop of **16** (137 mg) was obtained after concentration of the mother liquor. Total: 1.362 g (73%) of **16**.

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