Reactions of Complex Ligands. 80. Chromium-Mediated Benzannulation and Cyclopentannulation of [2.2]Metacyclophane Carbene Complexes with Alkynes†

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Pentacarbonyl(4-[2.2]metacyclophanyl(methoxy)carbene)chromium (**1**) reacts with alkynes to give the naphthalenophane complexes **2**, **3a**, and **3b**. The benzannulation of **1** with 3,3-dimethyl-1-butyne diastereoselectively gave the *anti*-isomer **2**, as indicated by X-ray structure analysis, whereas the reaction with 3-hexyne resulted in a diastereomeric mixture of the *syn*- and *anti*-isomers **3a,b**. Thermal rearrangement of the major isomer **3a** led to a haptotropic metal migration. Cyclopentannulation of the amino carbene analogue **7** with alkynes afforded the indanonophane derivatives **8** and **9**. The molecular structure for the iminoindanonophane **9** has been established by X-ray structure analysis showing a cis orientation of the ethyl groups which are both bonded to the same face as the $Cr(CO)_3$ fragment. The reaction of **7** with 3,3-dimethyl-1-butyne resulted in the formation of the indanonophane complex **8**. X-ray structure analyses for **2**, **3a**, **6**, and **9** verify a dependence of the ring deformation on the position of the metal fragment.

Introduction

Over the years, cyclophanes have received considerable attention due to their peculiar molecular structures.[1] For instance, in [2.2]metacyclophanes in which two ethylene spacers bridge two aromatic decks, the arene rings are significantly distorted from planarity and adopt unsymmetrical boatlike conformations.[2] The boat conformations are maintained upon coordination of the metal fragments to the arene rings; no significant flattening of the arene decks has been observed in a series of X-ray studies on $Cr(CO)_3$, FeCp, and RuC_6Me_6 complexes.[3] A similar distortion is observed in sandwich-type paracyclophane complexes which contain chromium inside the cavity of the cyclophane; in this type of compound the intramolecular arene−arene distance may be considerably reduced depending on the length of the bridging chains.[4] Half-sandwich $Cr(CO)_3$ complexes of cyclophanes[5] have been used to stabilize the *syn*-conformation of [2.2]metacyclophane[6] and—exploiting the acceptor properties of the $Cr(CO)_3$ fragment—to achieve electrophilic substitution reactions at the arene ring, thus avoiding the undesired dehydrogenation to give dihydropyrenes.[7]

Whereas the customary synthesis of cyclophane $Cr(CO)_3$ complexes containing benzene and fused arene decks is based on the complexation of the preformed cyclophane skeleton,[8] we focused our attention on the growth of the arene deck via chromium-mediated carbene annulation reactions[9] and report here on the synthesis and structure of densely functionalized naphthaleno- and indanonophanes.

Results and Discussion

Benzannulation of Methoxycarbene Complex 1 with Alkynes. Racemic pentacarbonyl(4-[2.2]metacyclophanyl(methoxy)carbene)chromium (**1**) reacts with 3,3-dimethyl-1-butyne to give—after in situ protection of the phenol intermediate by tert-butyldimethylsilyl

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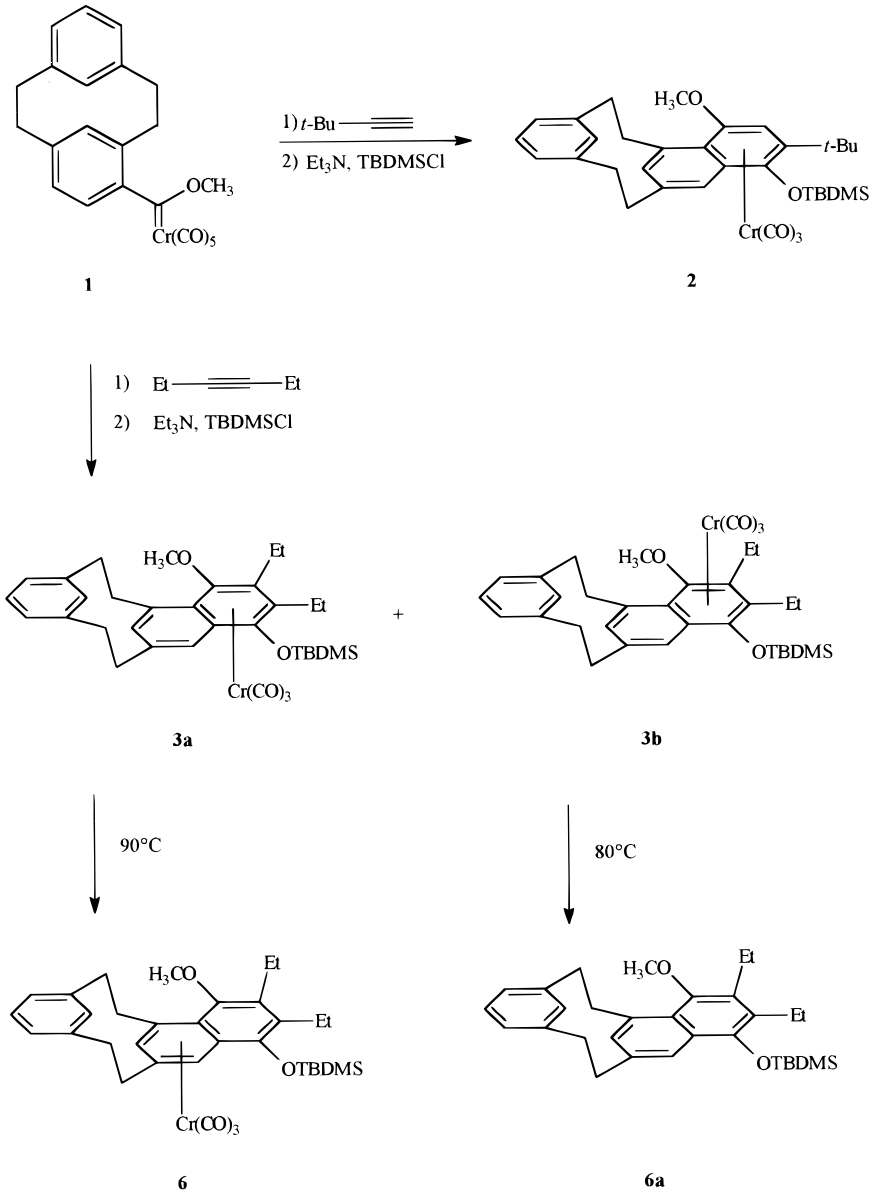
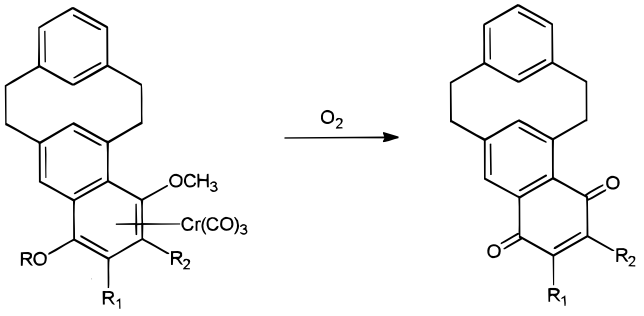
Scheme 1. Benzannulation of Methoxy Carbene Complex 1 with Alkynes



chloride—a single diastereomer of naphthalenophane complex **2** in 50% yield (Scheme 1). Isolation of pure samples of the unprotected annulation product is tedious due to partial oxidation to quinone **4** (Scheme 2). As well-precedented for terminal alkynes, the benzannulation is regioselective, exclusively affording the isomer which arises from the coupling of the carbene carbon atom with the unsubstituted alkyne carbon atom.[10] An X-ray study on complex **2** (vide infra) indicated that the $Cr(CO)_3$ fragment is coordinated to the naphthalenophane from the less hindered face. We speculated whether this preference is influenced by the bulky alkyne substituent. Indeed, the reaction of

Scheme 2. Oxidation of the Chromium Tricarbonyl Compounds



R = H, TBDMS

R_1 = *t*-Bu, R_2 = H **4**

$R_1 = R_2$ = Et **5**

chromium carbene **1** with the sterically less demanding 3-hexyne affords a 2:1 mixture of two diastereomers **3a,b** which could be separated by column chromatog-

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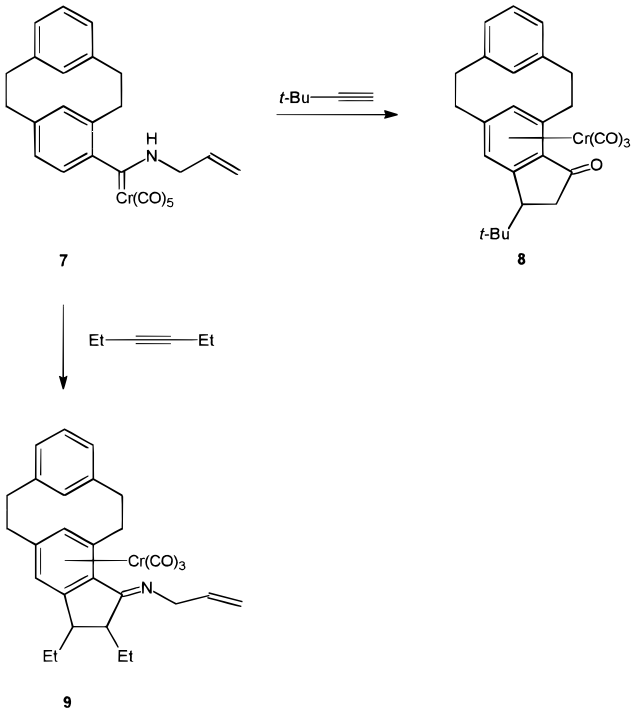
raphy. An X-ray structure analysis (vide infra) performed for the minor diastereomer **3b** confirmed that in this complex the metal fragment is coordinated to the more hindered *syn* face.

Haptotropic Metal Migration. Naphthalene $Cr(CO)_3$ complexes are known to undergo haptotropic metal migrations.[11] Whereas a reversible migration of the $Cr(CO)_3$ fragment has been observed for 1,4-dimethylnaphthalene,[12] the formation of 5−10-η^6-1,4-naphthohydroquinones from their 1−4,9:10-η^6 isomers is irreversible in the temperature range of 60−90 °C applied in benzannulation reactions.[13] Recent studies on enantiopure benzannulation products have indicated that the metal transfer is an intramolecular process along the same face of the naphthalene skeleton which occurs with retention of configuration.[14] Extended Hückel MO calculations have suggested that the metal fragment migrates along the periphery of the aromatic system rather than following the shortest pathway.[15] We were interested in whether the chromium fragment is prone to migrate even to a severely distorted arene ring. Warming of the major *anti*-diastereomer **3a**, arising from the benzannulation of **1** with 3-hexyne in di-*n*-butyl ether to 80 °C, results in a haptotropic metal migration from the hydroquinone ring to the adjacent cyclophane-bridged arene ring to give the *anti*-isomer **6**. Warming of the *syn*-isomer to 80 °C results in a loss of the metal fragment as expected. The migration of $Cr(CO)_3$ to the central ring should lead to strong interactions between $Cr(CO)_3$ and the inner protons as well as the benzylic hydrogens.

Cyclopentannulation of Allylaminocarbene Complex 7 with Alkynes. Annulation of aminocarbene complexes results in the formation of five-membered annulation products without incorporation of a CO ligand.[16] In contrast to methoxycarbene complexes, the aminocarbene analogues require more drastic conditions for the primary decarbonylation step as a consequence of the better donor properties of the amino substituent. The annulation of pentacarbonyl(4-[2.2]metacyclophanyl[*E*-(2′-propenyl-1′-amino)carbene])chromium (**7**) with 3,3-dimethyl-1-butyne in di-*n*-butyl ether at 90 °C afforded the benzenoindanophane complex **8** in 40% yield (Scheme 3). The reaction of **7** with 3-hexyne carried out under similar conditions gave the iminoindane derivative **9**, which represents an intermediate on the way to the indanone skeleton usually observed as the ultimate cyclopentannulation product.[16,17] Obviously, the presence of the cyclophane skeleton hampers hydrolysis, generally occurring upon chromatographic workup on silica gel.[18] Suprisingly, in the iminoindanophane complex **9**, the ethyl groups adopt a *cis*-orientation and are both bound to the same face of the indane deck as the $Cr(CO)_3$ fragment (vide infra). This result contrasts previous structural studies on the configuration in the five-membered ring of the indanones obtained from cyclopentannulation of aminocarbene complexes by internal alkynes which revealed a *trans*-configuration of the alkyl groups arising from the alkyne.[19] A mechanism suggested for the cyclopentannulation involves coordination and subsequent insertion of the alkyne into the metal−carbene bond followed by cyclization to give a chromacyclohexadiene intermediate. Reductive elimination, a sigmatropic 1,5-H shift of the former aryl hydrogen atom, and a haptotropic metal migration generate a 1-aminoindene complex which rearranges to the iminoindane tautomer (Scheme 4).[20] The suprafacial hydrogen migration has been made responsible for the relative *syn*-stereochemistry of the 1-alkyl group and the $Cr(CO)_3$ fragment. In an unhindered indane, the tautomerization is assumed to occur under thermodynamic control, which results in the formation of the 2,3-*trans*-isomer. Along the formation of **9**, a similar pathway is hampered by the bulky arene deck of the cyclophane skeleton, which only tolerates a *syn*-addition of the amino hydrogen to the β-position of the enamine and, thus, forces the 2-ethyl group to the same face as the metal fragment.

Scheme 3. Benzannulation of Amino Carbene Complex 7 with Alkynes



Comparative NMR and X-ray Studies. In [2.2]-metacyclophanes, the benzene rings adopt an unsymmetrical boat conformation to avoid steric interactions between the inner aryl hydrogen atoms. As a result of the ring current imposed by the opposite arene deck, these protons give rise to a significant upfield shift ($\Delta\delta$

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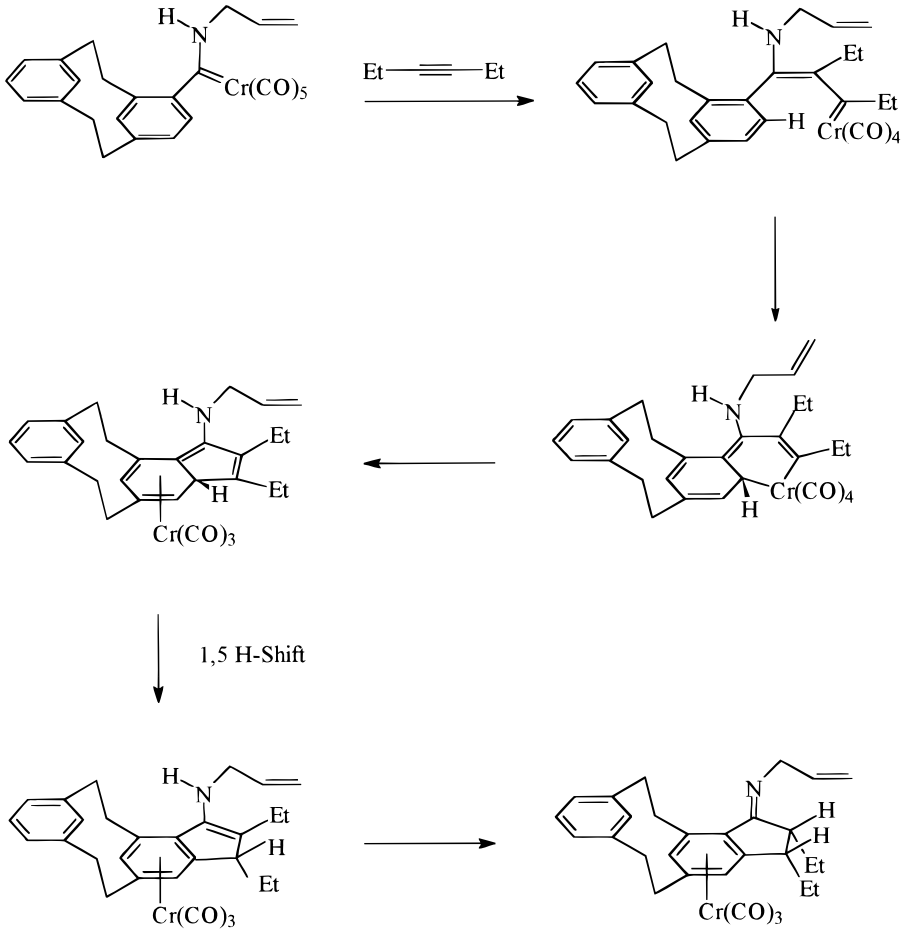
Scheme 4. Suggested Mechanism for the Cyclopentannulation



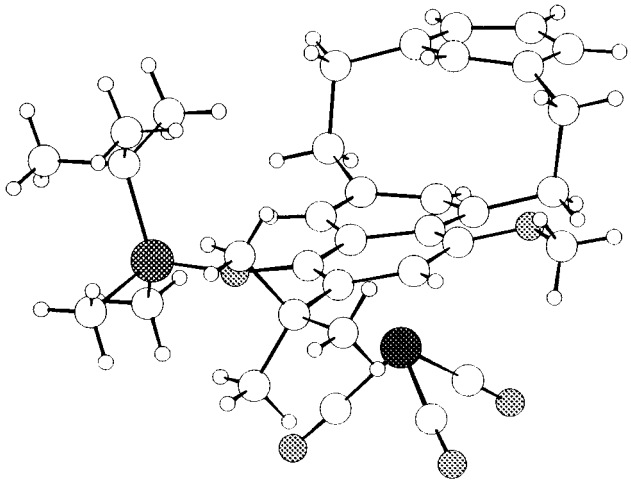


Figure 1. Molecular structure of **2**.

≈ 3 ppm) in the ^{1}H NMR.[21] An additional upfield shift results from the coordination of a $Cr(CO)_3$ fragment as demonstrated for the inner protons of the coordinated arene rings in **6**, **8**, and **9** that resonate at $\delta \approx 2.5$ ppm.

The boatlike deformation of the arene decks is obvious from X-ray studies performed for the naphthalenophane complexes **2**, **3b**, and **6** as well as for the indenophane complex **9** (Figures 1−4). The deformation further reflects the coordination of a $Cr(CO)_3$ fragment. When the metal is attached to ring B (complexes **6** and **9**), the adjacent rings tend to be flattened and the boat deformation of the complexed ring B is less significant. Obviously, the metal forces the inner carbon atoms C-10 toward the ethylene bridges even though the C-10−C-18 distances do not differ significantly from those observed for the parent [2.2]metacyclophane skeleton (Figure 5, Table 1).[22] A comparison of the torsion angles across the C-3a−C-7a bond reveals that rings B and C are twisted upon coordination to the metal fragment. This deformation is most significant in the 3a,7a-η^6-naphthalenophane complexes **2** and **3b**, possibly due to steric interactions between the CO ligands and the substituents of the coordinated arene ring.

The chromium to arene distance as defined to the best plane of the arene ring is slightly increased compared with that observed in (benzene)$Cr(CO)_3$ (172.4 pm).[23] This distance does not deviate significantly from the distance between the metal and the center of the coordinated rings, which indicates that—in contrast to a series of $Cr(CO)_3$ complexes of fused arenes[24]—the chromium is bound close to the center of the benzene rings. The conformation of the $Cr(CO)_3$ fragment relative to the coordinated arene depends on its coordination to either ring B or C. In complexes **2** and **3b** in which the metal is coordinated to the angular arene ring, the

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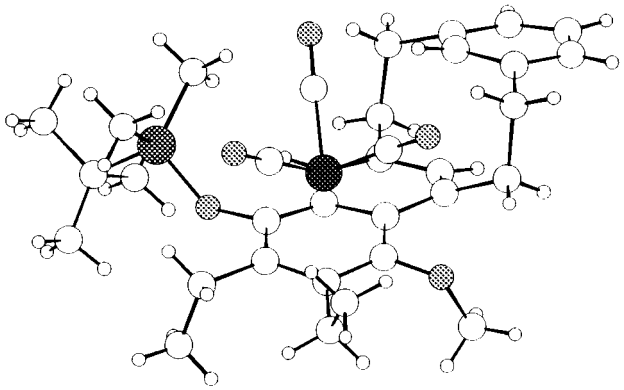

Figure 2. Molecular structure of **3b**.

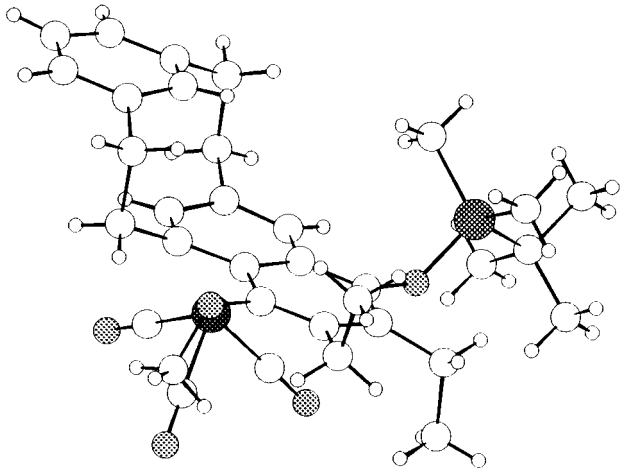

Figure 3. Molecular structure of **6**.

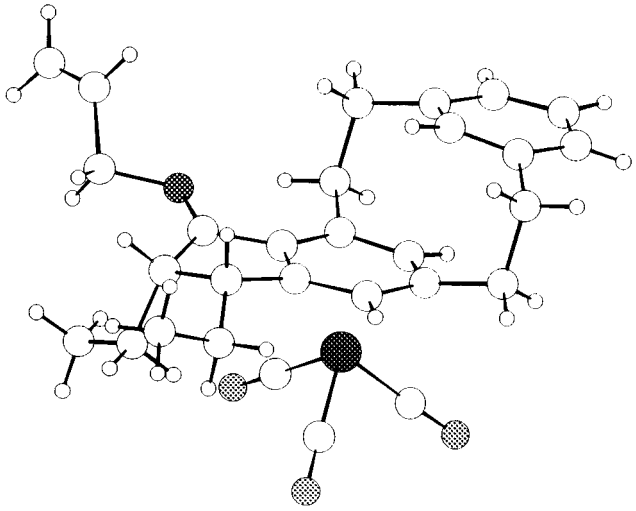

Figure 4. Molecular structure of **9**.

$Cr(CO)_3$ moiety adopts an eclipsed conformation, whereas a staggered orientation is observed for complexes **6** and **9** bearing the metal attached to the central arene ring.

Conclusion

This study demonstrates that the carbene annulation methodology is compatible with strained and sterically demanding arenes and provides access to [2.2]metacyclophanes bearing metal-coordinated and densely substituted fused arene decks. The inherent plane of chirality in the metal carbene modified cyclophane results in moderate diastereoselectivities.

Table 1. Structure Parameters

	3b	2	6	9[a]
Cr distance to ring plane, pm	177.1	179.0	177.3	174.6
Cr distance to ring center, pm	177.5	177.1	177.5	174.6
C-10···C-18, pm[b]	263.5	266.5	262.1	259.0
Torsion Angles, deg[b]				
C-4−3a−7a−8	172.0	169.2	179.5	173.9
C-3−3a−7a−8	3.5	12.1	1.1	1.3
C-4−3a−7a−7	10.0	5.3	0.9	4.2
C-3−3a−7a−7	174.5	173.4	177.4	176.8
Deformation of Cyclophane, pm				
a	−5.9	−5.3	−5.4	−6.0
b	−11.3	−12.9	−12.3	−10.7
c	13.0	11.9	7.6	9.9
d	0.8	10.9	−0.5	1.4
Angle Between Plane, deg				
BC	10.1	7.7	2.4	
AB	8.1	5.4	0.4	2.8

[a] For complex **9**, the corresponding carbon atoms. [b] Numbering refers to Figure 5 and differs from that in the molecular structures.

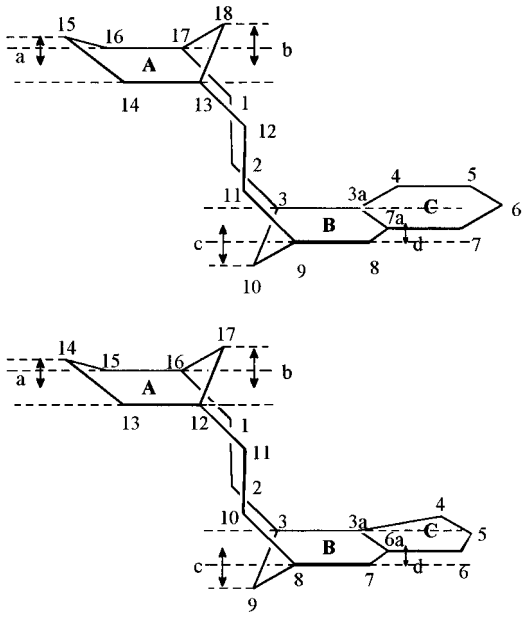

Figure 5. Deformation of the cyclophane skeleton.

Experimental Section

All operations involving the organometallic complexes were carried out under argon. Solvents were dried by using standard methods, distilled, saturated, and stored under argon. Merck silica gel 60 (0.063−0.200 mm) was used for column chromatography. ^1H and ^{13}C NMR: Bruker AM-400, AM-250, and DRX-500. FT-IR: Nicolet Magna 550. MS (EI, 70 eV): Kratos MS 50. Pentacarbonyl{4-[2.2]metacyclophanyl-(methoxy)carbene}chromium(0) and pentacarbonyl{4-[2.2]-metacyclophanyl[*E*-(2′-propenyl-1′-amino)carbene]}chromium-(0) were prepared according to methods reported in a previous paper.[22]

3a,4,5,6,7a,7-η^6-Tricarbonyl{7-*tert*-butyldimethylsilyl-oxy-6-*tert*-butyl-4-methoxy-[2](1,3)-benzeno[2](1,3)naph-thalenophane}-*anti*-chromium(0) (2). Pentacarbonyl{4-[2.2]metacyclophanyl(methoxy)carbene}chromium(0) (**1**; 0.5 mmol) and 0.18 mL of 3,3-dimethyl-1-butyne were dissolved in 10 mL of THF, degassed by freeze−pump−thaw, and stirred for 2 h at 50 °C. A solution of 302 mg of *tert*-butyldimethylsilyl chloride (2 mmol) and 0.28 mL of triethylamine (2 mmol) in 10 mL of THF was added. After 2 h at room temperature, the solvent was removed and the product purified by column

chromatography (silica gel, −15 °C, petroleum ether 40−60/diethyl ether, 1:1) to give 150 mg (50%) of a red solid. R_f = 0.53 (petroleum ether 40−60/diethyl ether, 1:1). IR (hexane): $\tilde{\nu}$ = 1956 cm^{-1} (vs, A_1, CO), 1888 (s, E, CO), 1875 (s, E, CO). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.48 (s, 3 H, Si−CH_3), 0.52 (s, 3 H, Si−CH_3), 1.16 (s, 9 H, Si-*t*-Bu), 1.54 (s, 9 H, *t*-Bu), 1.83 (tm, J = 11.4 Hz, 1 H, $H_{benzyl,ax}$), 2.15−2.30 (m, 3 H, $H_{benzyl,ax}$), 3.12−3.22 (m, 3 H, $H_{benzyl,eq}$), 3.92 (s, 3 H, OCH_3), 4.31 (s, 1 H, H-18), 4.41 (s, 1 H, H-10), 4.57 (dt, J = 12.1 Hz, 1 H, $H_{benzyl,eq}$), 5.26 (s, 1 H, H-5), 7.11 (d, J = 7.4 Hz, 1 H, H-16), 7.15 (d, J = 7.4 Hz, 1 H, H-14), 7.36 (t, J = 7.4 Hz, 1 H, H-15), 7.57 (s, 1 H, H-8). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −1.1 (Si−CH_3), 1.9 (Si−CH_3), 20.2 (Si−*C*$(CH_3)_3$), 27.1 (Si−C(*C*$H_3)_3$), 31.4 (C(*C*$H_3)_3$), 35.8 (*C*$(CH_3)_3$), 40.1, 40.8, 41.0, 41.7 (C_{benzyl}), 57.7 (OCH_3), 74.3 (C-18), 97.4, 109.2, 112.7 (C_{aryl}), 121.4 (C-8), 125.8, 126.6 (C-14, C-16), 130.3 (C-15), 135.2 (C-3), 136.5 (2 C_{aryl}), 136.7 (C-9), 137.8 (C-10), 138.0 (C-18), 139.6 (C-13), 140.9 (C-17), 234.9 (CO). MS (EI): *m*/*z* 610 (5) [M^+], 554 (1) [M^+ − 2CO], 526 (100) [M^+ − 3CO], 474 (83) [M^+ − $Cr(CO)_3$]. HR-MS calcd for $C_{34}H_{42}CrO_5Si$ 610.2206, found 610.2216.

3a,4,5,6,7,7a-η^6-Tricarbonyl{7-*tert*-butyldimethylsilyloxy-4-methoxy-5,6-diethyl-[2](1,3)benzeno[2](1,3)naphthalenophane}-*anti*-chromium(0) (3a) and 3a,4,5,6,7,7a-η^6-Tricarbonyl{7-*tert*-butyldimethylsilyloxy-4-methoxy-5,6-diethyl-[2](1,3)benzeno[2](1,3)-naphthalenophane}-*syn*-chromium(0) (3b). Pentacarbonyl{4-[2.2]metacyclophanyl-(methoxy)carbene}chromium(0) (**1**; 221 mg, 0.5 mmol) and 0.23 mL of 3-hexyne were dissolved in 10 mL of THF, degassed by freeze−pump−thaw, and stirred for 3 h at 55 °C. A solution of 302 mg of *tert*-butyldimethylsilyl chloride (2 mmol) and 0.28 mL of triethylamine (2 mmol) in 10 mL of THF was added. After stirring the mixture for 2.5 h at room temperature, the solvent was removed and the product purified by column chromatography (silica gel, −10 °C, petroleum ether 40−60/diethyl ether, 5:1) to give 160 mg (52%) of a red solid which consists of the two diastereomeric chromium tricarbonyl complexes in a 2:1 ratio.

anti-Isomer **3a**: R_f = 0.59 (petroleum ether 40−60/diethyl ether, 5:1). IR (hexane): $\tilde{\nu}$ 1946 cm^{-1} (vs, A_1, CO), 1863 (s, E, CO). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.43 (s, 3 H, Si−CH_3), 0.48 (s, 3 H, Si−CH_3), 1.14 (s, 9 H, Si-*t*-Bu), 1.34 (t, J = 7.4 Hz, 6 H, CH_2CH_3), 2.03 (m, 2 H, CH_2CH_3), 2.18 (td, J = 11.6, 4 Hz, 1 H, $H_{benzyl,ax}$), 2.37 (td, J = 12.7, 4 Hz, 1 H, $H_{benzyl,ax}$), 2.54−2.64 (m, 2 H, $H_{benzyl,ax}$), 2.64−2.74 (m, 1 H, CH_2CH_3), 2.80−2.94 (m, 1 H, CH_2CH_3), 3.11−3.25 (m, 3 H, $H_{benzyl,eq}$), 3.97 (s, 3 H, OCH_3), 4.21−4.29 (m, 1 H, $H_{benzyl,eq}$), 4.36 (s, 1 H, H-18), 4.56 (s, 1 H, H-10), 7.08−7.17 (m, 2 H, H-14, H-16), 7.36 (dd, J = 7.6, 7.3 Hz, 1 H, H-15), 7.73 (s, 1 H, H-8). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ −1.8 (Si−CH_3), −0.9 (Si−CH_3), 15.7 (CH_2CH_3), 17.5 (CH_2CH_3), 20.9 (CH_2CH_3), 22.2 (CH_2CH_3), 26.8 (C(*C*$H_3)_3$), 27.6 (*C*$(CH_3)_3$), 40.5, 40.9, 41.2, 41.7 (C_{benzyl}), 67.9 (OCH_3), 98.6, 102.4, 103.3, 111.7 (C_{aryl}), 123.5 (C-8), 125.9, 126.6 (C-14, C-16), 130.6 (C-15), 132.2 (C_{aryl}), 136.8 (C-18), 138.5 (C-13), 138.8 (C-17), 139.9 (C-10), 140.3 (C_{aryl}), 234.2 (CO) (2 C_{aryl} not observed). MS (EI): *m*/*z* 610 (7) [M^+], 554 (3) [M^+ − 2CO], 526 (100) [M^+ − 3CO], 474 (65) [M^+ − $Cr(CO)_3$]. HR-MS calcd for $C_{34}H_{42}CrO_5Si$ 610.2206, found 610.2211.

syn-Isomer **3b**: R_f = 0.5 (petroleum ether 40−60/diethyl ether, 5:1). IR (hexane): $\tilde{\nu}$ 1944 cm^{-1} (vs, A_1, CO), 1863 (s, E, CO). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.52 (s, 3 H, Si−CH_3), 0.55 (s, 3 H, Si−CH_3), 1.12 (s, 9 H, Si-*t*-Bu), 1.25 (t, J = 7.6 Hz, 3 H, CH_2CH_3), 1.35 (t, J = 7.6 Hz, 3 H, CH_2CH_3), 2.00−2.40 (m, 3 H, $H_{benzyl,ax}$), 2.47−2.57 (m, 2 H, CH_2CH_3), 2.59−2.73 (m, 1 H, CH_2CH_3), 2.95−3.25 (m, 5 H, 1 H CH_2CH_3, 4 H_{benzyl}), 3.76 (s, 3 H, OCH_3), 4.19 (s, 1 H, H-18), 4.88 (dt, J = 12.4, 3.7 Hz, 1 H, $H_{benzyl,eq}$), 5.03 (s, 1 H, H-10), 7.07−7.17 (m, 2 H, H-14, H-16), 7.35 (t, J = 7.3 Hz, 1 H, H-15), 7.54 (s, 1 H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$): δ −3.4 ($SiCH_3$), −1.6 ($SiCH_3$), 14.8 (CH_2CH_3), 17.1 (CH_2CH_3), 20.0 (CH_2CH_3), 21.0 (CH_2CH_3), 25.9 (C(*C*$H_3)_3$), 29.0 (*C*$(CH_3)_3$), 38.5, 39.1, 40.4, 41.1 (C_{benzyl}), 62.3 (OCH_3), 93.4, 105.3, 107.3, 107.6 (C_{aryl}), 119.5 (C-8), 124.9, 125.6 (C-14, C-16), 129.6 (C-15), 134.8 (C_{aryl}), 135.6 (C-18), 137.8 (C-10), 138.8, 141.0, 141.7 (C_{aryl}), 235.2 (CO) (2 C_{aryl} not observed). MS (EI): *m*/*z* 610 (7) [M^+], 554 (3) [M^+ − 2CO], 526 (100) [M^+ − 3CO], 474 (65) [M^+ − $Cr(CO)_3$]. HR-MS calcd for $C_{34}H_{42}CrO_5Si$ 610.2207, found 610.2211.

General Procedure for the Oxidation of the Chromium Tricarbonyl Complexes. A solution of 0.2 mmol of **2** or **3** in 10 mL of dichloromethane was stirred at room temperature in an open flask. After 16 h, no arene complex could be detected and the naphthoquinone was isolated after column chromatography (petroleum ether 40−60/chloroform 1:1) as a yellow solid.

6-*tert*-Butyl[2](1,3)benzeno[2](1,3)naphtho-4,7-quinonophane (4): 70 mg (70%). R_f = 0.5 (petroleum ether 40−60/chloroform 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.37 (s, 9 H, *t*-Bu), 1.86 (td, J = 11.6 Hz, 3.2 Hz, 1 H, $H_{benzyl,ax}$), 2.18−2.25 (m, 3 H, 1 $H_{benzyl,ax}$), 3.20−3.32 (m, 3 H, $H_{benzyl,eq}$), 4.39 (s, 1 H, H-18), 4.50 (d, J = 1.7 Hz, 1 H, H-10), 4.74 (ddd, J = 11.6, 3.2, and 3.1 Hz, 1 H, $H_{benzyl,eq}$), 6.79 (s, 1 H, H-5), 7.12 (d, J = 7.5 Hz, 1 H, H-16), 7.17 (d, J = 7.6 Hz, 1 H, H-14), 7.38 (dd, J = 7.6, 7.5 Hz, 1 H, H-15), 7.90 (d, J = 1.7 Hz, 1 H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.8 (C(*C*$H_3)_3$), 35.7 (*C*$(CH_3)_3$), 39.1, 40.3, 40.8, 41.6 (C_{benzyl}), 125.6 (C-8), 125.9, 126.5 (C-14, C-16), 126.9 (C-3a), 130.2 (C-15), 135.9 (C-7a), 136.2, 136.4 (C-5, C-18), 138.2 (C-3), 139.8, 141.1 (C-13, C-17), 143.9 (C-10), 144.8 (C-9), 156.8 (C-6), 188.5 (CO), 188.5 (CO). MS (EI): *m*/*z* 344 (100) [M^+], 329 (44) [M^+ − CH_3], 316 (10) [M^+ − CO], 287 (10) [M^+ − *t*-Bu]. HR-MS calcd for $C_{24}H_{24}O_2$ 344.1776, found 344.1768.

5,6-Diethyl-[2](1,3)benzeno[2](1,3)naphtho-4,7-quinonophane (5): 70 mg (70%). R_f = 0.45 (petroleum ether 40−60/chloroform 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 1.17 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 1.83 (td, J = 11.7 Hz, 2.9 Hz, 1 H, $H_{benzyl,ax}$), 2.1−2.15 (m, 1 H, $H_{benzyl,ax}$), 2.16 (d, J = 11.9 Hz, 1 H, $H_{benzyl,ax}$), 2.17 (td, J = 11.9 Hz, 1 H, $H_{benzyl,ax}$), 2.22 (td, J = 12.1, 2.9 Hz, 1 H, $H_{benzyl,eq}$), 2.55−2.76 (dq, J = 12.5, 7.4 Hz, 4 H, CH_2CH_3), 3.17−3.28 (m, 2 H, $H_{benzyl,eq}$), 4.38 (s, 1 H, H-18), 4.47 (d, J = 1.6 Hz, 1 H, H-10), 4.66 (ddd, J = 11.5, 4.4, and 3.1 Hz, 1 H, $H_{benzyl,eq}$), 7.03 (d, J = 7.4 Hz, 1 H, H-16), 7.13 (d, J = 7.4 Hz, 1 H, H-14), 7.34 (t, J = 7.4 Hz, 1 H, H-15), 7.87 (d, J = 1.6 Hz, 1 H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9, 14.0 (CH_2CH_3), 20.0, 20.4 (CH_2CH_3), 39.1, 39.8, 40.4, 41.1 (C_{benzyl}), 124.5 (C-8), 125.4, 126.1 (C-14, C-16), 127.4 (C-3a), 129.8 (C-15), 134.1 (C-8a), 136.0 (C-18), 137.8 (C-3), 139.5 (C-13), 140.7 (C-17), 143.6 (C-10), 143.9 (C-9), 146.3, 149.4 (C-5, C-6), 185.7 (CO), 187.4 (CO). MS (EI): *m*/*z* 344 (30) [M^+], 329 (10) [M^+ − CH_3], 207 (100) [$C_{16}H_{15}^+$]. HR-MS calcd for $C_{24}H_{24}O_2$ 344.1776, found 344.1781.

3,3a,7a,8,9,10-η^6-Tricarbonyl{7-*tert*-butyldimethylsilyloxy-4-methoxy-5,6-diethyl-[2](1,3)benzeno[2](1,3)naphthalenophane}-*anti*-chromium(0) (6). 3a (120 mg, 0.2 mmol) was dissolved in 10 mL of di-*n*-butyl ether and degassed by freeze−pump−thaw. The solution was stirred at 80 °C for 3 h. The solvent was removed under reduced pressure, and the product was purified by column chromatography (silica gel, −10 °C, petroleum ether 40−60/diethyl ether, 5:1) to give 84 mg (70%) of a red solid which was recrystallized from hexane. R_f = 0.4 (petroleum ether 40−60/diethyl ether, 5:1). IR (KBr): $\tilde{\nu}$ 1950 cm^{-1} (vs, A_1, CO), 1879 (s, E, CO), 1855 (s, E, CO). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.34 (s, 3 H, Si−CH_3), 0.42 (s, 3 H, Si−CH_3), 1.15 (s, 9 H, Si-*t*-Bu), 1.21 (t, J = 7.4 Hz, 6 H, CH_2CH_3), 1.87 (td, J = 12.3, 2.9 Hz, 1 H, $H_{benzyl,ax}$), 2.03 (td, J = 12.5, 3.9 Hz, 1 H, $H_{benzyl,ax}$), 2.30 (td, J = 12.4, 2.6 Hz, 1 H, $H_{benzyl,ax}$), 2.37 (td, J = 12.5, 3.6 Hz, 1 H, $H_{benzyl,ax}$), 2.43 (d, J = 1.4 Hz, 1 H, H-10), 2.61 (dq, J = 13.7, 7.4 Hz, 1 H, CH_2CH_3), 2.68 (dq, J = 13.7, 7.4 Hz, 1 H, CH_2CH_3), 2.80−2.88 (m, 3 H, 2 H CH_2CH_3, 1 $H_{benzyl,eq}$), 3.28 (dt, J = 12.9, 3.5 Hz, 1 H, $H_{benzyl,eq}$), 3.32 (dt, J = 12.9 Hz, 3.8 Hz, 1 H, $H_{benzyl,eq}$), 3.97 (s, 3 H, OCH_3), 4.43 (ddd, J = 12.5 Hz, 4.3 Hz, 2.8 Hz, 1 H, $H_{benzyl,eq}$), 5.17 (s, 1 H, H-18), 6.25 (d, J = 1.5 Hz, 1 H, H-8), 7.12 (d, J = 7.45 Hz, 1 H, H-14), 7.15 (d, J = 7.45 Hz, 1 H,

Table 2. Crystallographic Data and Summary of Data Collection and Refinement

	3b	2	9	6
formula	$C_{34}H_{42}CrO_5Si$	$C_{34}H_{42}CrO_5Si$	$C_{29}H_{31}CrNO_3$	$C_{34}H_{42}CrO_5Si$
dimensions, mm	0.04 × 0.13 × 0.18	0.08 × 0.10 × 0.20	0.13 × 0.20 × 0.25	0.08 × 0.20 × 0.30
cryst syst	triclinic	monoclinic	orthorhombic	triclinic
space group	$P\bar{1}$ (No.2)	$P2_1/n$ (No.14)	$Pna2_1$ (No.33)	$P\bar{1}$ (No.2)
a, Å	10.200(5)	10.815(1)	19.621(2)	11.182(1)
b, Å	12.522(5)	29.378(2)	12.457(1)	12.247(2)
c, Å	14.638(5)	11.263(1)	10.128(1)	13.578(1)
α, deg	112.68(3)			84.31(1)
β, deg	94.98(3)	117.63(1)		76.65(1)
γ, deg	108.48(3)			68.42(1)
V, Å^3	1589.6(13)	3170.4(5)	2475.5(4)	1682.2(3)
Z	2	4	4	2
ρ_{cacl}, g cm^{-3}	1.28	1.28	1.32	1.21
μ	3.63	3.64	4.04	3.43
F(000)	648	1296	1040	648
diffractometer	Enraf-Nonius CAD4			
radiation	Cu Kα			
λ, Å	1.54184			
T, K	293	293	200	293
max 2*θ*, deg	120	120	120	136
no. of data	4905	5033	3905	6980
no. of unique data	4690	4709	1953	6118
no. of unique data [$I > 2\theta(I)$]	2389	2616	1702	4161
no. of variables	366	371	306	436
no. of restraints	45		8	229
R(*F*)[a]	0.059	0.070	0.035	0.065
wR2(F^2) for all data	0.174	0.224	0.092	0.203

[a] For $I > 2\theta(I)$.

H-16), 7.39 (t, *J* = 7.45 Hz, 1 H, H-15). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* −2.3 (Si−CH_3), −2.1 (Si−CH_3), 14.9 (CH_2CH_3), 16.1 (CH_2CH_3), 20.6 (CH_2CH_3), 21.0 (CH_2CH_3), 26.4 (C(CH_3)$_3$), 29.3 ($C(CH_3)_3$), 39.1, 39.5, 40.4, 40.7 (C_{benzyl}), 62.1 (OCH_3), 87.8 (C-8), 97.3 (C_{aryl}), 98.1 (C-10), 101.5, 108.2, 111.7 (C_{aryl}), 126.3, 126.9 (C-14, C-16), 129.2 (C_{aryl}), 131.1 (C-15), 131.3, 138.0 (C_{aryl}), 138.1 (C-18), 139.6, 145.3, 148.2 (C_{aryl}), 234.5 (CO). MS (EI): *m*/*z* 610 (7) [M$^+$], 554 (1) [M$^+$ − 2CO], 526 (100) [M$^+$ − 3CO], 474 (37) [M$^+$ − Cr(CO)$_3$]. HR-MS calcd for $C_{34}H_{42}CrO_5Si$ 610.2206, found 610.2204.

7-*tert*-Butyldimethylsilyloxy-4-methoxy-5,6-diethyl[2]-(1,3)benzeno[2](1,3)naphthalenophane (6a). 3b (70 mg, 0.1 mmol) was dissolved in 20 mL of di-*n*-butyl ether and degassed by freeze−pump−thaw. The solution was stirred at 80 °C for 2 h until the red color disappeared. The solvent was removed under reduced pressure and the product was purified by column chromatography (silica gel, 0 °C, petroleum ether 40−60/diethyl ether, 7:1) to give 30 mg (70%) of a white solid. R_f = 0.7 (petroleum ether 40−60/diethyl ether, 7:1). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 0.21 (s, 3 H, $SiCH_3$), 0.23 (s, 3 H, $SiCH_3$), 1.16 (s, 9 H, Si-*t*-Bu), 1.21 (t, *J* = 7.6 Hz, 3 H, CH_2CH_3), 1.35 (t, *J* = 7.6 Hz, 3 H, CH_2CH_3), 2.05−2.09 (m, 2 H, $H_{benzyl,ax}$), 2.22 (td, *J* = 12.1, 3.7 Hz, 1 H, $H_{benzyl,ax}$), 2.35 (td, *J* = 12.1, 3.8 Hz, 1 H, $H_{benzyl,ax}$), 2.74−3.01 (m, 4 H, CH_2CH_3), 3.09−3.16 (m, 2 H, $H_{benzyl,eq}$), 3.34 (dt, *J* = 12.1, 3.4 Hz, 1 H, $H_{benzyl,eq}$), 3.77 (s, 3 H, OCH_3), 4.23 (s, 1 H, H-18), 4.49 (d, *J* = 1.7 Hz, 1 H, H-10), 4.52−4.55 (m, 1 H, $H_{benzyl,eq}$), 7.10 (dm, *J* = 7.4 Hz, 1 H, H_{aryl}), 7.13 (dm, *J* = 7.5 Hz, 1 H, H_{aryl}), 7.33 ("t", *J* = 7.45 Hz, 1 H, H-15), 7.85 (d, *J* = 1.7 Hz, 1 H, H-8). ^{13}C NMR (125.8 MHz, $CDCl_3$): *δ* −3.0 (Si−CH_3), −2.1 (Si−CH_3), 15.2 (CH_2CH_3), 16.6 (CH_2CH_3), 20.5 (CH_2CH_3), 21.0 (CH_2CH_3), 26.6 (C(CH_3)$_3$), 30.1 ($C(CH_3)_3$), 40.4, 41.0, 41.3, 41.4 (C_{benzyl}), 61.8 (OCH_3), 121.6 (C-8), 125.2 (C-14), 125.9 (C-16), 129.2 (C-15), 129.3 (C_{aryl}), 132.9 (C_{aryl}), 133.4 (C_{aryl}), 135.9 (C_{aryl}), 136.5 (C-18), 137.8 (C-10), 138.7, 140.8 (C-13, C-17) (4 C_{aryl} not observed). MS (EI): *m*/*z* 474 (100) [M$^+$], 459 (27) [M$^+$ − CH_3], 417 (4) [M$^+$ − *t*-Bu], 388 (8) [M$^+$ − *t*-Bu − CH_3 − CH_2]. HR-MS calcd for $C_{27}H_{42}SiO_2$ 474.2754, found 474.2951.

3,3a,6a,7,8,9-*η*^{6}-Tricarbonyl{6-*tert*-butyl-[2](1,3)benzeno-[2](1,3)-4-indanonophane}-*anti*-chromium(0) (8). Pentacarbonyl{4-[2.2]metacyclophanyl[*E*-(2′-propenyl-1′-amino)-carbene]}chromium(0) (**7**; 80 mg, 0.8 mmol) and 0.39 mL of 3,3-dimethyl-1-butyne (3.2 mmol) were dissolved in 10 mL of di-*n*-butyl ether and degassed by freeze−pump−thaw. The solution was stirred for 3 h at 90 °C, and then the solvent was removed. Column chromatography (silica gel, −10 °C, petroleum ether 40−60/diethyl ether, 1:1) yielded 140 mg (40%) of a red solid which was recrystallized from hexane. R_f = 0.61 (petroleum ether 40−60/diethyl ether, 1:1). IR (KBr): $\tilde{\nu}$ 1954 cm^{-1} (vs, A_1, CO), 1874 (s, E, CO), 1724 (m, CO). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 1.20 (s, 9 H, *t*-Bu), 1.67 (td, *J* = 12.3, 3.8 Hz, 1 H, $H_{benzyl,ax}$), 1.86 (td, *J* = 12.4, 4.0 Hz, 1 H, $H_{benzyl,ax}$), 2.21 (td, *J* = 12.6, 3.5 Hz, 1 H, $H_{benzyl,ax}$), 2.32 (td, *J* = 12.5, 3.6 Hz, 1 H, $H_{benzyl,ax}$), 2.39 (s, 1 H, H-9), 2.67 (d, *J* = 8 Hz, 1 H, CH_2), 2.68 (d, *J* = 8.3 Hz, 1 H, CH_2), 2.84 (dt, *J* = 12.6, 3.4 Hz, 2 H, $H_{benzyl,eq}$), 3.24−3.32 (m, 2 H, $H_{benzyl,eq}$), 3.43 (dd, *J* = 8.3, 8 Hz, 1 H, H-6), 4.02 (dt, *J* = 12.2, 3.5 Hz, 1 H, $H_{benzyl,eq}$), 5.27 (s, 1 H, H-17), 5.70 (s, 1 H, H-7), 7.09 (d, *J* = 7.5 Hz, 1 H, H-15), 7.14 (d, *J* = 7.5 Hz, 1 H, H-13), 7.38 (t, *J* = 7.5 Hz, 1 H, H-14). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 29.2 (C(CH_3)$_3$), 33.6 (C_{benzyl}), 34.3 ($C(CH_3)_3$), 39.4, 40.6, 40.9 (C_{benzyl}), 41.2 (C-5), 47.6 (C-6), 93.5 (C-7), 96.2 (C-9), 96.5 (C-3a), 110.1 (C-6a), 110.9 (C-3), 119.3 (C-8), 126.7, 127.1 (C-13, C-15), 131.4 (C-14), 138.0 (C-12), 138.8 (C-16), 138.8 (C-17), 206.4 (CO), 233.8 (CO). MS (EI): *m*/*z* 454 (8) [M$^+$], 409 (8) [M$^+$ − 2CO], 370 (100) [M$^+$ − 3CO]. Hr-MS calcd for $C_{26}H_{26}CrO_4$ 454.1235, found 454.1236.

3,3a,6a,7,8,9-*η*^{6}-Tricarbonyl{5,6-diethyl-[2](1,3)benzeno-[2](1,3)-4-imino-*N*-allylindanonophane}-*anti*-chromium-(0) (9). Pentacarbonyl{4-[2.2]metacyclophanyl[*E*-(2′-propenyl-1′-amino)carbene]}chromium (0) (**7**; 234 mg, 0.5 mmol) and 0.3 mL of 3-hexyne (2.6 mmol) were dissolved in 10 mL of di-*n*-butyl ether and degassed by freeze−pump−thaw. The solution was stirred for 3 h at 90 °C, and then the solvent was removed. Column chromatography (silica gel, −10 °C, petroleum ether 40−60/dichloromethane, 1:1) yielded 100 mg (40%) of an orange solid, which was recrystallized from hexane. R_f = 0.5 (petroleum ether 40−60/dichloromethane, 1:1). IR (KBr): $\tilde{\nu}$ 1947 cm^{-1} (vs, A_1, CO), 1862 (s, E, CO). ^{1}H NMR (500 MHz, benzene-d_6): *δ* 0.90 (t, *J* = 7.6 Hz, 3 H, CH_3), 1.30 (t, *J* = 7.6 Hz, 3 H, CH_3), 1.48 (td, *J* = 12.6, 3.6 Hz, 1 H, $H_{benzyl,ax}$), 1.62−1.74 (m, 2 H, 1 $H_{benzyl,ax}$, 1 H CH_2), 1.92−2.14 (m, 4 H, 1 $H_{benzyl,ax}$, 3 H CH_2), 2.31 (td, *J* = 12.5, 3.1 Hz, 1 H, $H_{benzyl,ax}$), 2.40 (dt, *J* = 12.7, 3.3 Hz, 1 H, $H_{benzyl,eq}$), 2.58 (s, 1 H, H-9), 2.71 (m, 1 H, C−H), 2.80 (dt, *J* = 12.4, 3.3 Hz, 1 H, $H_{benzyl,eq}$),

3.00 (dt, J = 12.5, 3.6 Hz, 1 H, $H_{benzyl,eq}$), 3.14−3.19 (m, 1 H, C−H), 3.60−3.68 (m, 1 H, NCH_2), 3.74−3.84 (m, 2 H, 1 $H_{benzyl,eq}$, 1 H NCH_2), 5.19 (dd, J = 10.4 Hz, 1.5 Hz, 1 H, $=CH_{2cis}$), 5.26 (s, 1 H, H-17), 5.38 (dd, J = 17.1 Hz, 1.5 Hz, 1 H, $=CH_{2trans}$), 5.45 (s, 1 H, H-7), 5.99−6.08 (m, 1 H, =CH), 6.87 (d, J = 7.5 Hz, 1 H, H-15), 6.93 (d, J = 7.5 Hz, 1 H, H-13), 7.23 (t, J = 7.5 Hz, 1 H, H-14). ^{13}C NMR (62.9 MHz, benzene-d_6): δ 13.5, 14.2 (CH_3), 18.9, 28.1 (CH_2), 34.7, 38.7, 40.5, 40.6 (C_{benzyl}), 48.6 (2 CH), 51.4 (NCH_2), 94.7 (C-3a), 94.8 (C-7), 97.8 (C-9), 105.0 (C-6a), 106.7 (C-8), 115.8 (C=C), 115.9 (C-8), 126.4, 126.6 (C-13, C-15), 130.9 (C-14), 136.6 (C=C), 138.3 (C-12), 138.5 (C-17), 138.6 (C-16), 140.0 (CN), 206.4 (CO), 236.0 (CO). MS (EI): m/z 493 (12) [M^+], 409 (100) [M^+ − 3CO], 367 (95) [M^+ − 3CO − C_3H_6], 357 (38) [M^+ − $Cr(CO)_3$]. HR-MS calcd for $C_{26}H_{31}CrNO_3$ 493.1709, found 493.1717.

X-ray Crystallographic Studies of 3b, 2, 9, and 6. The structures were solved by direct methods (SHELXTL-Plus).[25] The non-hydrogen atoms were refined anisotropically on F^2 (SHELXL-93).[26] H atoms were refined using a riding model. In **3b** the silyl group, in **9** an ethyl-group, and in **6** the siloxyl group are disordered. An absorption correction on the basis of ψ-scans was applied to all structures. In **6**, an extinction correction was applied. In DOE39, the absolute structure was determined by refinement of Flack's parameter x = −0.01(1).[27] Further details are given in Table 2.

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Supporting Information Available: Crystal structure data for **2**, **3b**, **6**, and **9**, including tables of crystal data and refinement details, atomic parameters, anisotropic displacement parameters, bond distances and bond angles (25 pages). Ordering information is given on any current masthead page.

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