Tricarbonyl(naphthoquinone)chromium: Synthesis and Application in [4+2] Cycloaddition Reactions[‡]

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Tricarbonyl(naphthoquinone)chromium (**9**) has been prepared in an 82 % overall yield by direct complexation of TBS-protected naphthohydroquinone (**6**) and subsequent deprotection/oxidation. Complex **9** underwent [4+2] cycloaddition reactions with a series of dienes to give products in good to excellent yields. The cycloaddition reaction revealed that the tricarbonylchromium fragment exhibits perfect *endo* selectivity and has an *anti*-directing role, as established by X-ray analyses of the Diels–Alder products **10**–**13**.

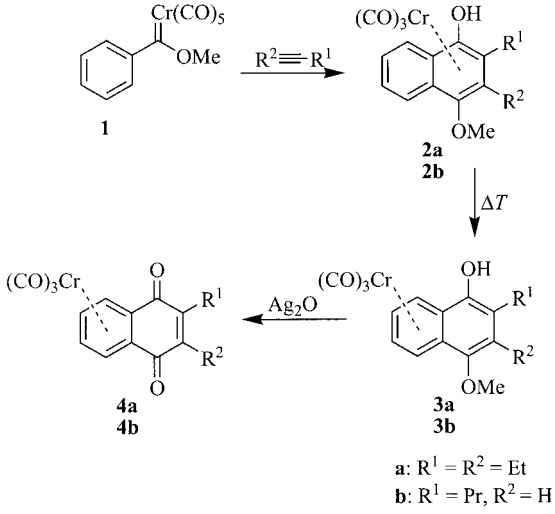
Over the past three decades (η^6-arene)tricarbonylchromium complexes have been developed as powerful reagents in stereoselective organic synthesis.[1] The pronounced electron-withdrawing properties of the metal fragment result in an Umpolung of the customary arene reactivity; they allow the addition of nucleophiles to the arene ligand and facilitate nucleophilic substitution at benzylic and homobenzylic positions. Moreover, the steric bulk of the metal-carbonyl moiety effectively shields one face of the arene and this has been widely exploited in diastereoselective synthesis. Finally, arene complexes with an appropriate 1,2- or 1,3-disubstitution pattern have a chiral plane and their enantiomers have been used in efficient enantioselective reactions.[2] The ability of the tricarbonylchromium moiety to block one π face of the arene has been reported for [4+2] cycloaddition reactions of (hetero)dienophiles[3] and dienes.[4]

Quinones are very efficient dienophiles in Diels–Alder reactions; however, the complexation of arenes fused to a quinone ring is not straightforward and requires protecting-group strategies. So far, only a very limited number of tricarbonyl(naphthoquinone)chromium complexes have been reported and their syntheses have mainly been based on a chromium-templated benzannulation/haptotropic metal migration/oxidation sequence.[5] We herein present an efficient protocol for the synthesis of tricarbonyl(1,4-naphthoquinone)chromium complexes and describe the results of their application in [4+2] cycloaddition reactions.

Results and Discussion

Naphthoquinone $Cr(CO)_3$ Complexes through Benzannulation

Our initial efforts directed towards the synthesis of tricarbonyl(naphthoquinone)chromium complexes focused on a sequence based on the benzannulation of phenyl(methoxy)carbene complex **1** by alkynes,[6] the haptotropic metal migration of the kinetic benzannulated products **2** to give their thermodynamic regioisomers[7] **3** and a final oxidation to naphthoquinone complexes **4** (Scheme 1).[5b]



Scheme 1. Synthetic strategy to naphthoquinone $Cr(CO)_3$ complexes through chromium-templated benzannulation.

Whereas both the benzannulation and the metal migration proceeded with synthetically useful yields, the final oxidation to the quinone turned out to be the crucial step. We investigated a variety of oxidants and experimental con-

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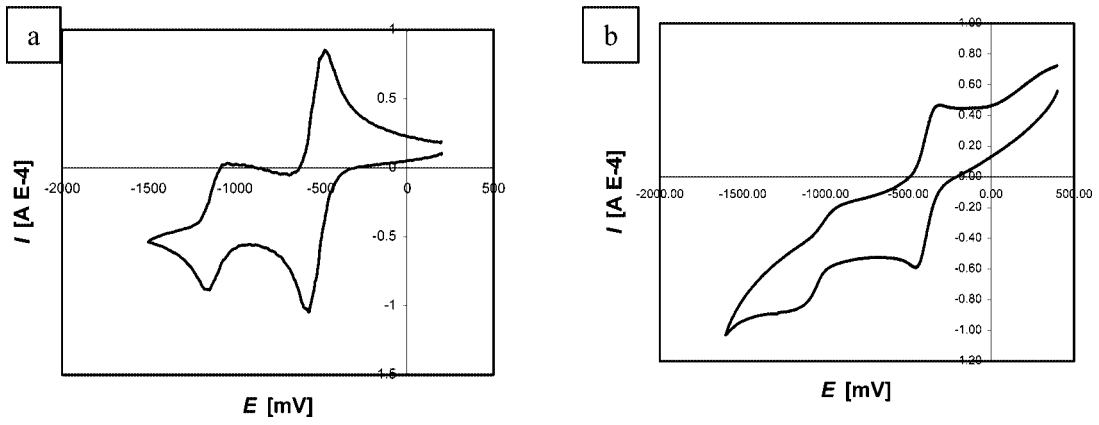


Figure 1. a) Cyclovoltammogram of **4b** in CH_2Cl_2 versus SCE; c = 6 mmol L^{-1}, Bu_4NPF_6 = 0.2 mol L^{-1}, 200 mV s^{-1}, glassy carbon electrode, Ø = 3 mm. b) Cyclovoltammogram of **9** in CH_2Cl_2 versus decamethylferrocene; c = 3 mmol L^{-1}, Bu_4NPF_6 = 0.2 mol L^{-1}, 100 mV s^{-1}, glassy carbon electrode, Ø = 3 mm.

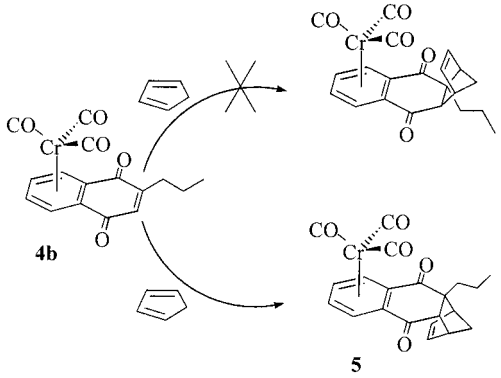
ditions which, however, resulted in unsatisfactory yields. In order to adjust the oxidation conditions, the redox properties of **4** were studied by cyclovoltammetry. A CV investigation of **4b** (see a in Figure 1) indicated two reversible electron-transition steps [$E_{1/2}$ = –520 mV (ΔE = 72 mV) and –1100 mV (ΔE = 73 mV) versus SCE] as is expected for quinone reduction.[8] On the other hand, no oxidation of the chromium moiety was observed up to +950 mV (versus SCE). As the oxidation potential is strongly dependent on the electron density at the metal, the electron-withdrawing effect of the fused quinone ring in complex **4b** should lead to a relatively high oxidation potential.[9] A closer analysis of the reduction steps by means of the convolution method revealed two transition steps for each peak with a difference of only 40 mV which may result from the two different quinoidic carbonyl groups in **4b**. This splitting is not observed in the cyclovoltammogram of the unsubstituted quinone **9** (b in Figure 1) [$E_{1/2}$ = –380 mV (ΔE = 60 mV) and $E_{1/2}$ = –980 mV (ΔE = 75 mV) versus decamethylferrocene].[10]

These results suggest Ag^+ ($E_{1/2}$ = 800 mV) to be a suitable oxidant that would be expected to form the quinone without cleaving the $Cr(CO)_3$ fragment. The oxidation was carried out by using 1.5 equivalents of Ag_2O in the presence of $MgSO_4$ in *tert*-butyl methyl ether (TBME) to yield 20% of **4a** and 16% of **4b** as violet solids after purification. Their IR spectra reveal the electron-withdrawing nature of the quinone ring: whereas for the benzannulated and rearrangement products,[6b] **2a/b** and **3a/b,** the $\tilde{\nu}$(CO) absorptions (A_1) of the carbonyl ligands are observed between 1950 and 1970 cm^{-1}, a significant hypsochromic shift to 1993 cm^{-1} is observed for the quinone complexes **4a** and **4b**.

Diels–Alder Reactions of (Alkyl)naphthoquinone Complexes 4

[4+2] Cycloaddition reactions are known to be sensitive to the substitution pattern of the dienophile.[11] Generally, increasing the steric bulk at the C=C bond significantly reduces the tendency for cycloaddition. This trend is also exhibited by naphthoquinone complexes **4**: while the monoalkyl complex **4b** reveals a modest reactivity towards cyclopentadiene at room temperature, giving a 29% yield of **5** after chromatographic work up, no cycloaddition reaction was observed for its diethyl analogue **4a** under these conditions.

The Diels–Alder adduct **5** was isolated as a single diastereomer and its stereochemistry was established by X-ray analysis, which confirmed the *anti* addition of the diene with respect to the chromium fragment resulting in an *endo* configuration of the cycloaddition product (Scheme 2, Figure 2). The $Cr(CO)_3$ group adopts a staggered conformation with respect to the fused ring system. The carbonyl groups of the fused ring are slightly bent out of the plane towards the $Cr(CO)_3$ moiety by 1.9 and 4.1°, respectively.



Scheme 2. *anti*-Selective [4+2] cycloaddition of cyclopentadiene to the 2-propylnaphthoquinone complex **4b**.

Complexation of Naphthalene Derivatives

In order to reduce the steric implications associated with the quinone alkyl-substitution pattern, we focused on the parent naphthoquinone complex **9**, which could allow enantiomer-enriched derivatives to be obtained by enantioselective reduction of the quinone moiety subsequent to the cycloaddition step. Since both the benzannulation approach is ineffective with ethyne and the direct complexation of

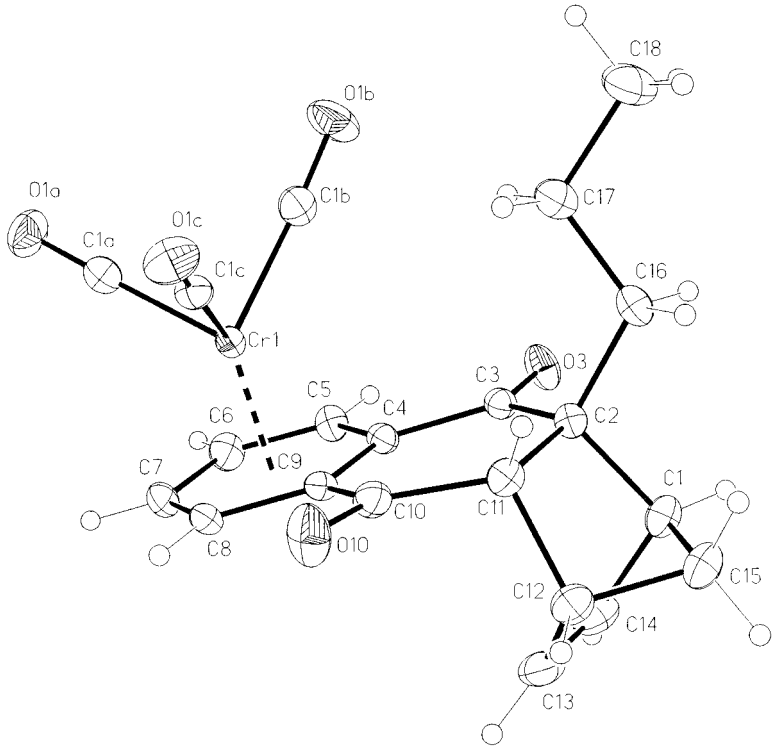
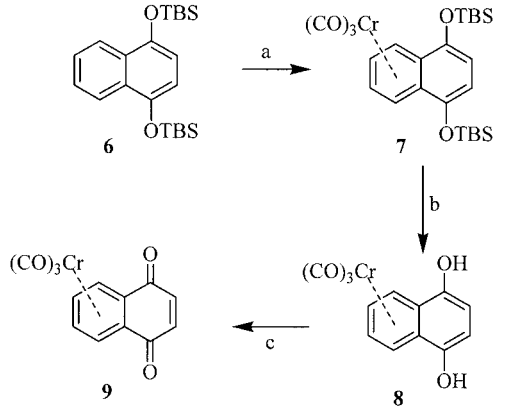


Figure 2. Molecular structure of cycloaddition product **5**. The numbering of atoms differs from that used in the NMR characterization. Selected distances [Å] and angles [°]: Cr1–C4: 2.200(2), Cr1–C5: 2.212(2), Cr1–C6: 2.215(2), Cr1–C7: 2.215(2), Cr1–C8: 2.198(2), Cr1–C9: 2.179(2), Cr1–Z(Ar): 1.691(1), C(1)–C(2)–C(3): 106.9(1), C(10)–C(11)–C(12): 108.4(1), O3–C3–C4–C5: –1.7(2), C8–C9–C10–O10: –4.1(2).

naphthoquinone by $Cr(CO)_3$ transfer reagents fails,[12] we envisaged a protection/complexation/oxidative deprotection protocol for the synthesis of this complex.

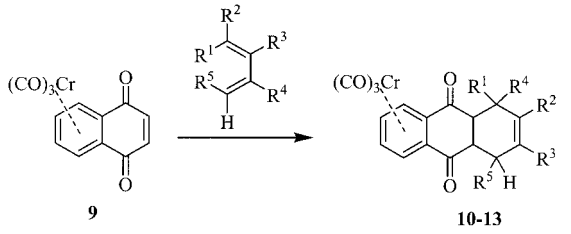
Whereas naphthohydroquinone and 1,4-bis(acetoxy)-naphthalene gave unsatisfactory yields of complexation products upon reaction with $Cr(CO)_6$ in refluxing nBu_2O/THF (10:1), the bis-TBDMS-protected naphthohydroquinone **6**[13] could be coordinated under comparable conditions (nBu_2O/THF, 5:1) to give the 4a-8a-η^6-arene–$Cr(CO)_3$ complex **7** in 96% yield.[14] The air-stable orange solid was efficiently desilylated with TBAF to form naphthohydroquinone complex **8** after protic work up. Subsequent oxidation with silver(I) oxide afforded naphthoquinone complex **9** in 86% yield (from **7**) as a violet solid (Scheme 3).



Scheme 3. Synthesis of the naphthoquinone–$Cr(CO)_3$ complex **9** by a complexation/deprotection/oxidation protocol. (a) 0.75 equiv. $Cr(CO)_6$, nBu_2O/THF, 5:1, 120 °C, 74 h, 96%; (b) 1.5 equiv. TBAF, TBME, room temp., 30 min; (c) 1.5 equiv. Ag_2O, $MgSO_4$, TBME, room temp., 30–60 min, 86% yield of **9** from **7**.

Diels–Alder Reactions of Naphthoquinone Complex 9

The parent tricarbonyl(naphthoquinone)chromium complex **9** is significantly more prone to [4+2] cycloaddition than its alkyl homologues **4a** and **4b**. Upon reaction with cyclopentadiene at ambient temperature for 4 hours, a 66% yield of cycloaddition product **10** was isolated as an orange



R		Conditions	Yield
R^1-R^5 = (CH_2), R^2, R^3, R^4 = H	**10**	neat, 20 °C, 4h	66 %
R^3, R^4 = CH_3, R^1, R^2, R^5 = H	**11**	neat, 65 °C, 4.5h	88 %
R^1-R^5 = $(CH_2)_2$, R^2, R^3, R^4 = H	**12**	neat, 65 °C, 4.5h	93 %
R^1-R^5 = $(CH_2)_2$, R^4 = OCH_3, R^2, R^3, = H	**13**	neat, 50 °C, 25 min	88 %

Scheme 4. [4+2] Cycloaddition reactions of cyclic and acyclic dienes to the naphthoquinone complex **9**.

solid after chromatographic work up. The Diels–Alder reaction was extended to 2,3-dimethylbutadiene, 1,3-cyclohexadiene and 1-methoxy-1,3-cyclohexadiene, which, on moderate warming to 50–65 °C, afforded the corresponding cycloaddition products **11**–**13** in excellent yields (Scheme 4).

Similar to the alkyl complex **5**, the non-alkylated analogues **10**–**13** were also isolated as single diastereomers. Their molecular structures demonstrate the efficient stereocontrol exerted by the chromium fragment which forces the diene to add exclusively from the *anti* face to give the *endo* products (Figures 3, 4, 5, 6). The $Cr(CO)_3$ moiety in the Diels–Alder products **10**–**13** again adopts a staggered conformation relative to the fused ring system as previously observed for complex **5**. The tetracyclic Diels–Alder addition products **10** and **13** differ considerably in their molecular structures. Although the carbonyl groups in the C_s symmetrical complex **10** are nearly coplanar with the adjacent arene ring (Figure 3: C2–C3–C4–O4 = 0.77°), they are significantly bent out of the plane towards the $Cr(CO)_3$ fragment by 11.6 and 15.4° in **13**. A similar distortion is observed for the analogues **11** and **12** as indicated by dihedral angles of 4.1 and 17.2° for **11** and 9.1 and 13.7° for **12**, respectively; this may be a result of the stereocontrolled formation of the new ring *anti* to the chromium moiety

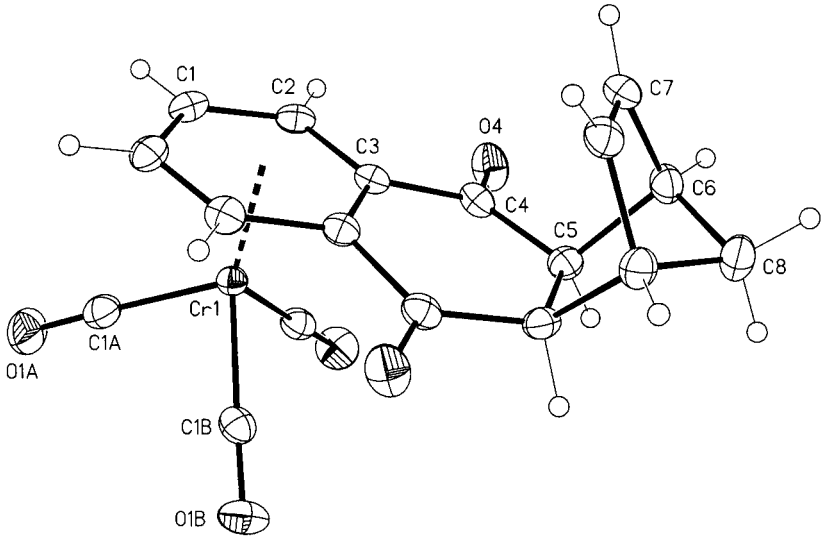


Figure 3. Molecular structure of cycloaddition product **10**. The numbering of atoms differs from that used in the NMR characterization. Selected distances [Å] and angles [°]: Cr1–C1: 2.227(1), Cr1–C2: 2.213(1), Cr1–C3: 2.175(1), Cr1–Z(Ar): 1.692(2), C(4)–C(5)–C(6): 109.7(1), C2–C3–C4–O4: –0.77(2).

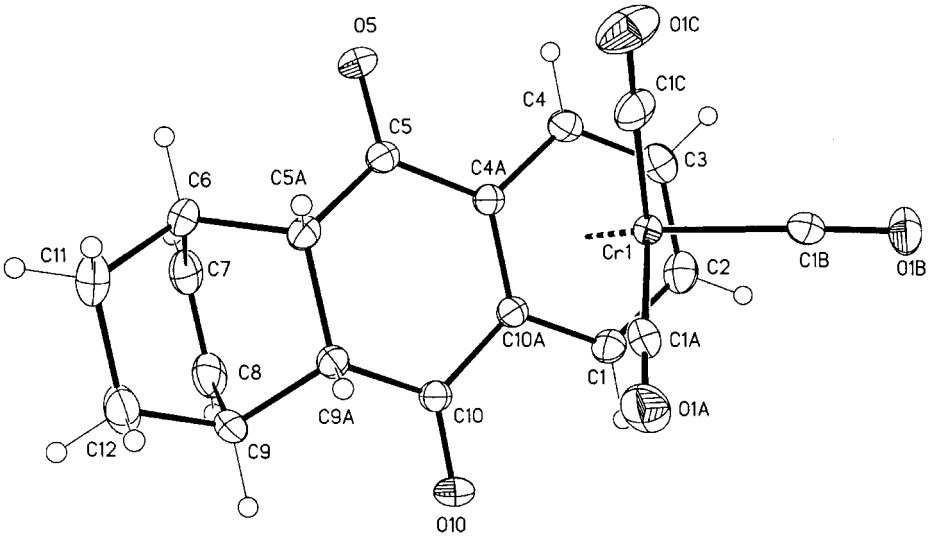


Figure 4. Molecular structure of cycloaddition product **12**; the numbering of atoms differs from that used in the NMR characterization. Selected distances [Å] and angles [°]: Cr1–C1: 2.222(1), Cr1–C2: 2.223(2), Cr1–C3: 2.229(2), Cr1–C4: 2.223(1), Cr1–C4A: 2.200(1), Cr1–C10A: 2.179(1), Cr1–Z(Ar): 1.702(1), C(5)–C(5A)–C(6): 109.1(1), C(9)–C(9A)–C(10): 108.5(1), C4–C4A–C5–O5: 13.7(2), O10–C10–C10A–C1: –9.1(2).

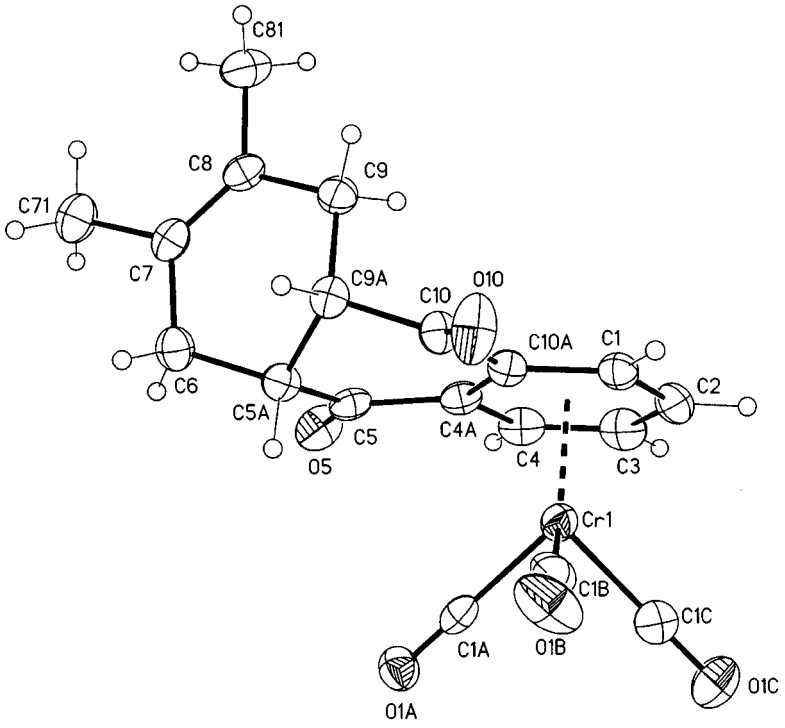


Figure 5. Molecular structure of cycloaddition product **11**; the numbering of atoms differs from that used in the NMR characterization. Selected distances [Å] and angles [°]: Cr1–C1: 2.200(2), Cr1–C2: 2.207(2), Cr1–C3: 2.213(2), Cr1–C4: 2.207(2), Cr1–C4A: 2.178(2), Cr1–C10A: 2.183(2), Cr1–Z(Ar): 1.687(1), C(5)–C(5A)–C(6): 112.6(2), C(9)–C(9A)–C(10): 110.6(2), O10–C10–C10A–C1: –17.2(3), C4–C4A–C5–O5: –4.1(3), C10A–C4A–C5–C5A: –2.4(3), C9A–C10–C10A–C4A: –21.3(3).

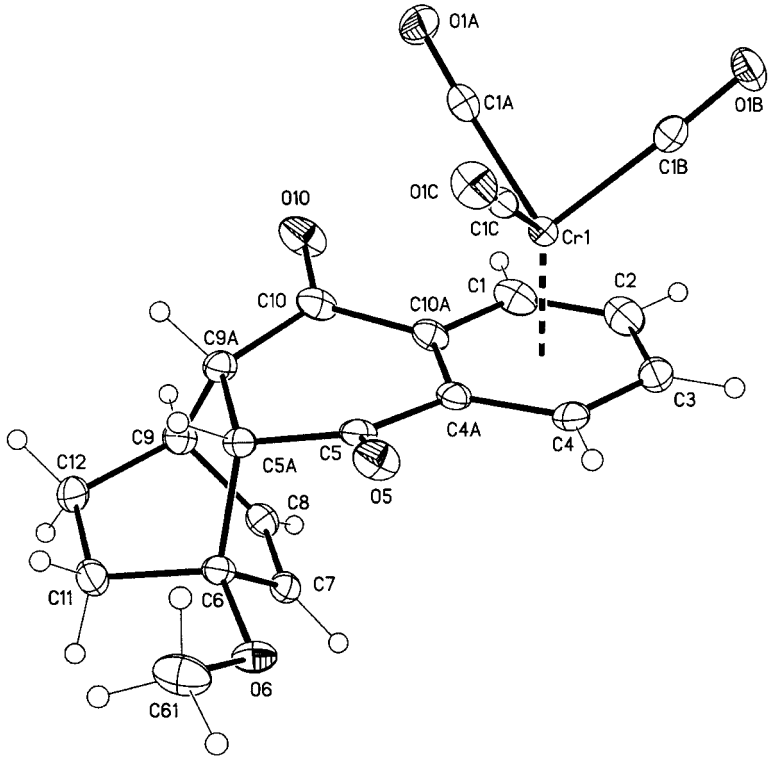


Figure 6. Molecular structure of cycloaddition product **13**; the numbering of atoms differs from that used in the NMR characterization. Selected distances [Å] and angles [°]: Cr1–C1: 2.196(2), Cr1–C2: 2.211(2), Cr1–C3: 2.211(2), Cr1–C4: 2.202(2), Cr1–C4A: 2.192(1), Cr1–C10A: 2.186(1), Cr1–Z(Ar): 1.685(1), C(5)–C(5A)–C(6): 109.3(1), C(9)–C(9A)–C(10): 106.8(1), C4–C4A–C5–O5: 15.4(2), O10–C10–C10A–C1: –11.6(2).

which leads to a boat conformation. As is often observed for complexes of fused arenes the arene rings in **5** and **10**–**13** are coordinated unsymmetrically to the metal. Whereas, in general, the metal is shifted towards the periphery of the aromatic skeleton, the distances of the chromium atom to the inner carbon atoms next to the carbonyl groups in complexes **5** and **10**–**13** are slightly shorter (2.18–2.19 Å) than the distances to the outer C-2 and C-3 atoms of **11**–**13** and the C-1 atom of **10** (2.21–2.22 Å). This displacement is typical for electron-withdrawing groups in complexed aromatic rings.[15] The molecular structures of complexes **11**–**13** are depicted in Figures 4, 5, 6 and the crystal data and refinement parameters of **5** and **10**–**13** are summarized in Table 1.

Conclusions

An efficient synthesis of the parent tricarbonyl(naphthoquinone)chromium complex **9** has been established through complexation of TBDMS-protected naphthohydroquinone **7** followed by desilylation and oxidation. Complex **9** stereoselectively adds cyclic and acyclic dienes to its sterically less-hindered face to give *endo* [4+2] cycloaddition products in good-to-excellent yields. The stereocontrol of the bulky chromium fragment has been demonstrated by X-ray analyses of the cycloaddition products **5** and **10**–**13**.

Experimental Section

General Remarks: All reactions were performed in flame-dried glassware and under dry argon. Dichloromethane and *tert*-butyl methyl ether were dried by distillation from calcium hydride. Petroleum ether (40/60) was distilled from lithium aluminium hydride; dibutyl ether and THF were distilled from sodium. All solvents are saturated with argon. Cyclopentadiene was freshly prepared from its dimer. Liquid reactants were carefully degassed using the freeze-pump–thaw method (three cycles). Silica gel (E. Merck, grade 60, 0.062–0.200 mm or Macherey–Nagel silica gel 60, 0.015–0.025 mm) was used for column chromatography. TLC was carried out on precoated silica gel sheets (E. Merck 60F254).

^{1}H and ^{13}C NMR spectra were recorded with Bruker AVANCE 300 and DRX 500 instruments. All chemical shifts are given in ppm relative to $CDCl_3$ as the internal standard; *J* values are given in Hz. MS (EI) and HR-MS (EI) were recorded with Kratos MS-50 and Thermoquest MAT 95 XL instruments. IR spectra were recorded with a Nicolet Magna 550 FT-IR spectrometer. Cyclovoltammetry experiments were performed with a Potentiostat/Galvanostat Model Autolab PGSTAT 100, Eco Chemie B.V, apparatus.

The following reagents were prepared according to literature procedures: pentacarbonyl[methoxy(phenyl)carbene]chromium (**1**) and naphthol complexes **2a/b** and **3a/b**.[6b]

1,4-Bis[(*tert*-butyl)dimethylsiloxy]naphthalene (6): 1,4-Naphthohydroquinone (2.47 g, 15.4 mmol) was dissolved in TBME (80 mL) and NEt_3 (8 mL, 1.85 equiv.), *tert*-butyl(chloro)dimethylsilane (7 g, 46.7 mmol, 1.5 equiv.) and a catalytic amount of DMAP (100 mg) were added to this solution at room temperature. The mixture was heated at 50 °C for 18 h, cooled to room temperature and washed twice with water. The organic solvent was removed and the crude product was purified by column chromatography to afford 4.78 g (12.3 mmol) of the silylated product as a colourless oil which solidified after several days. Yield: 80%; R_f = 0.8 (PE/TBME, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.29 (s, 12 H, $Si(CH_3)_2$), 1.13 (s, 18 H, $SiC(CH_3)_3$), 6.75 (s, 2 H, H-2, H-3), 7.49 (dd, ^3J(H,H) = 6.5, $^4J_{H,H}$ = 3.3 Hz, 2 H, H-Ar), 8.16 (dd, $^3J_{H,H}$ = 6.5, $^4J_{H,H}$ = 3.3 Hz, 2 H, H-Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = –4.2 ($Si(CH_3)_2$), 18.5 ($SiC(CH_3)_3$), 26.0 ($SiC(CH_3)_3$), 112.2 (C-Ar), 122.6 (C-Ar), 125.4 (C-Ar), 128.8 (C-Ar), 145.7 (C-Ar) ppm. MS (EI, 70 eV): *m*/*z* (%) = 388 (100) $[M]^+$, 331 (44) $[M - C_4H_9]^+$, 273 (3) $[M - C_4H_9, C_4H_{10}]^+$. HR-MS: calcd. for $C_{22}H_{36}O_2Si_2$: 388.225387; found 388.2256.

Tricarbonyl[(η^6-1,2,3,4,4a,8a)-5,8-bis[(*tert*-butyl)dimethylsiloxy]-naphthalene]chromium (7): 1,4-Bis[(*tert*-butyl)dimethylsiloxy]naphthalene (**6**) (1.46 g, 3.75 mmol) and $Cr(CO)_6$ (550 mg, 2.5 mmol), nBu_2O (15 mL) and THF (3 mL) were placed in a round-bottomed flask equipped with a condenser. The mixture was protected from light and stirred at 120 °C (oil bath temperature) for 74 hours. The solvent was removed under reduced pressure at 50 °C. The crude product was purified by column chromatography to afford 1.26 g of complex **7** as an orange solid. Yield: 96%; R_f = 0.63 (PE/TBME, 3:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.33 (s, 6 H, $SiCH_3$), 0.36 (s, 6 H, $SiCH_3$), 1.11 (s, 18 H, $SiC(CH_3)_3$), 5.48 (dd, $^3J_{H,H}$ = 5.2, $^4J_{H,H}$ = 2.85 Hz, 2 H, H-Ar), 6.41 (dd, $^3J_{H,H}$ = 5.2, $^4J_{H,H}$ = 2.85 Hz, 2 H, H-Ar), 6.52 (s, 2 H, H-Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = –4.5 ($SiCH_3$), –4.4 ($SiCH_3$), 18.3 ($SiC(CH_3)_3$), 25.8 ($SiC(CH_3)_3$), 86.0, 91.6 (5-C, 6-C, 7-C, 8-C), 101.2 (4a-C, 8a-C), 111.1 (2-C, 3-C), 144.7 (1-C, 4-C), 232.1 ($Cr(CO)_3$) ppm. IR (PE): $\tilde{\nu}$(C=O) = 1972, 1909, 1900 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 524 (8) $[M]^+$, 468 (6) $[M - 2CO]^+$, 460 (100) $[M - 3CO]^+$, 388 (40) $[M - Cr(CO)_3]^+$. HR-MS: calcd. for $C_{25}H_{36}CrO_5Si_2$: 524.150641; found 524.1509.

Tricarbonyl[(η^6-1,2,3,4,4a,8a)-1,4-naphthohydroquinone]chromium (8): Complex **7** (525 mg, 1 mmol) was dissolved in *tert*-butyl methyl ether (20 mL) and a 1 M solution of tetrabutylammonium fluoride in THF (3 mL) was added to this solution. The reaction mixture was stirred for 30 min at room temperature and the solvent was then decanted from the brown oil. The residue was hydrolyzed with an aqueous solution of $NaHCO_3$ and extracted with *tert*-butyl methyl ether. The solvent was evaporated at reduced pressure to give a red oil which was used directly in further reactions. IR (PE): $\tilde{\nu}$(C=O) = 1969, 1905, 1892 cm^{-1}.

General Procedure for the Preparation of Quinone Complexes 4a, 4b and 9: The corresponding hydroquinone (monomethyl ether) complexes were dissolved in *tert*-butyl methyl ether (0.05–0.1 mol L^{-1}). $MgSO_4$ (ca. 2 g mmol^{-1}) and Ag_2O (1.5–2 equiv.) were added to the solution and the mixture was stirred for 30–60 min at room temperature. The reaction was monitored by TLC and IR spectroscopy. The mixture was then filtered, and the solvent of the filtrate was evaporated. The residue was purified by chromatography using petroleum ether/*tert*-butyl methyl ether (3:1) as eluent to give the quinone complexes as violet solids.

Tricarbonyl[(η^6-1,2,3,4,4a,8a)-6,7-diethyl-5,8-naphthoquinone]chromium (4a): Yield: 20%; R_f = 0.34 (PE/TBME, 3:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.13 (t, $^3J_{H,H}$ = 7.55 Hz, 6 H, CH_3), 2.53 (dq, $^2J_{H,H}$ = 12.5, $^3J_{H,H}$ 7.55 Hz, 2 H, CH_2), 2.62 (dq, $^2J_{H,H}$ = 12.5, $^3J_{H,H}$ 7.55 Hz, 2 H, CH_2), 5.67 (dd, $^3J_{H,H}$ = 4.8, $^3J_{H,H}$ = 2.8 Hz, 2 H, H-Ar), 6.21 (dd, $^3J_{H,H}$ = 4.8, $^3J_{H,H}$ = 2.8 Hz, 2 H, H-Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 13.6 (CH_3), 20.2 (CH_2CH_3), 89.7, 92.2 (C-5- to C-8-Ar), 92.7 (C-4a-Ar, C-8a-Ar), 148.2 (C-2, C-3), 184.4 (C=O), 229.9 ($Cr(CO)_3$) ppm. IR (PE): $\tilde{\nu}$(C=O) = 1993, 1946, 1940 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 350

(15) $[M]^+$, 294 (12) $[M - 2CO]^+$, 266 (100) $[M - 3CO]^+$, 214 (13) $[M - Cr(CO)_3]^+$, 52 (61) $[Cr]^+$.

(R_p/S_p)-Tricarbonyl[(η⁶-1,2,3,4,4a,8a)-6-propyl-5,8-naphthoquinone]chromium (4b): Yield: 16%; R_f = 0.27 (PE/TBME, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.99 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 1.59 (m, 2 H, CH_2), 2.41 (dddd, $^2J_{H,H}$ = 14.9, $^3J_{H,H}$ = 8.29, $^3J_{H,H}$ = 6.8, $^4J_{H,H}$ = 1.3 Hz, 1 H, CH_2), 2.55 (dddd, $^2J_{H,H}$ = 14.9, $^3J_{H,H}$ = 8.47, $^3J_{H,H}$ = 6.5, $^4J_{H,H}$ = 1.3 Hz, 1 H, CH_2), 5.70 (m, 2 H, H-Ar), 6.17 (m, 2 H, H-Ar), 6.67 (t, $^4J_{H,H}$ = 1.3 Hz, 1 H, H-3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 13.7 (CH_3), 21.2 (CH_2CH_3), 31.8 (Ar–CH_2), 89.7, 89.9, 92.1, 92.3 (C-5- to C-8-Ar), 92.5, 92.7 (C-4a-Ar, C-8a-Ar), 134.0 (C-2), 152.0 (C-3), 184.5, 184.8 (C=O), 229.7 ($Cr(CO)_3$) ppm. IR (PE): $\tilde{\nu}$(C=O) = 1993, 1945, 1940 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 336 (17) $[M]^+$, 280 (9) $[M - 2CO]^+$, 252 (100) $[M - 3CO]^+$, 200 (14) $[M - Cr(CO)_3]^+$, 185 (4) $[M_{200} - CH_3]^+$, 157 (4) $[M_{200} - CH_3CO]^+$, 105 (5) $[C_6H_5CO]^+$, 76 (3) $[C_6H_4]^+$, 52 (42) $[Cr]^+$. HR-MS: calcd. for $C_{16}H_{12}CrO_5$: 336.00898; found 336.0086.

Tricarbonyl[(η⁶-1,2,3,4,4a,8a)-5,8-naphthoquinone]chromium (9): Yield: 86% from (**7**); R_f = 0.48 (PE/TBME, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.72 (dd, $^3J_{H,H}$ = 4.9, $^4J_{H,H}$ = 2.83 Hz, 2 H, H-Ar), 6.15 (dd, $^3J_{H,H}$ = 4.9, $^4J_{H,H}$ = 2.83 Hz, 2 H, H-Ar), 6.87 (s, 2 H, H-2, H-3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 89.8, 92.2 (C-5- to C-8-Ar), 92.1 (C-4a-Ar, C-8a-Ar), 138.5 (C-2, C-3), 184.5, (C=O), 229.5 ($Cr(CO)_3$) ppm. IR (PE): $\tilde{\nu}$(C=O) = 2002, 1950 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 294 (24) $[M]^+$, 238 (11) $[M - 2CO]^+$, 210 (62) $[M - 3CO]^+$, 158 (100) $[M - Cr(CO)_3]^+$, 138 (38) $[M_{158} - CO]^+$, 102 (38) $[M_{158} - 2\ CO]$. HR-MS: calcd. for $C_{13}H_6CrO_5$: 293.962033; found 293.9614.

General Procedure for the Cycloaddition Reaction: The quinone complex (≈0.1 mmol) was dissolved in the diene (≈0.5 mL). The reaction details are given in Scheme 4. The reaction was monitored by TLC while product formation was accompanied by a colour change from violet to orange. The solvent was evaporated at reduced pressure and the residue was purified by chromatography using a petroleum ether/*tert*-butyl methyl ether mixture (2:1) as eluent to give the cycloaddition products as orange solids.

Tricarbonyl[(*S*$_p$,5*R*,8*S*,8a*R*,10a*S*)/(*R*$_p$,5*S*,8*R*,8a*S*,10a*R*)-(η⁶-1,2,3,4,4a,9a)-(5,8,8a,10a-tetrahydro-5,8-methano-8a-propylanthracene-9,10-dione)]chromium (5): Yield: 29%; R_f = 0.47 (PE/TBME, 2:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.93 (t, $^3J_{H,H}$ = 6.97 Hz, 3 H, CH_3), 1.44 (m, 4 H), 1.53 (d, $^2J_{H,H}$ = 8.9 Hz, 1 H, bridge-CH_2), 1.76 (d, $^2J_{H,H}$ = 9.2 Hz, 1 H, bridge-CH_2), 2.25 (m, 1 H, $CH_2CH_2CH_3$), 3.07 (d, $^3J_{H,H}$ = 3.8 Hz, 1 H, H-11), 3.17, 3.45 (m, 1 H, H-1, H-12), 5.42 (qpent, 1 H, H-Ar), 5.72 (d, $^3J_{H,H}$ = 3.4 Hz, 2 H, H-Ar), 5.96 (dd, $^3J_{H,H}$ = 2.8, $^3J_{H,H}$ = 5.7 Hz, 1 H, H-13 or H-14), 6.08 (dpent, 2 H, H-Ar and H-13 or H-14) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 14.6 (CH_3), 19.4 (CH_2CH_3),

Table 1. Crystal data and structure refinement parameters of **5** and **10**–**13**.

Compound	**5**	**10**	**11**	**12**	**13**
Empirical formula	$C_{21}H_{18}CrO_5$	$C_{18}H_{12}CrO_5$	$C_{19}H_{16}CrO_5 \cdot ½Et_2O$	$C_{19}H_{14}CrO_5$	$C_{20}H_{16}CrO_6$
Formula weight	402.35	360.28	413.38	374.30	404.33
Temperature [K]	123(2)	123(2)	123(2)	123(2)	123(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic
Space group	*P*21/*n* (No.14)	*Pbcm* (No.57)	P2/*n* (No.13)	$P\bar{1}$ (No.2)	*P*21/*c* (No.14)
Unit cell dimensions					
a [Å]	10.7269(2)	10.5607(2)	7.4673(2)	6.9355(2)	13.6285(3)
b [Å]	13.3225(2)	12.7293(3)	11.1415(4)	9.5951(2)	11.3366(2)
c [Å]	12.7476(2)	11.0576(2)	22.7458(9)	12.5084(4)	11.6997(2)
α [°]	90	90	90	93.664(1)	90
β [°]	99.620(1)	90	90.480(1)	95.636(1)	109.779(1)
γ [°]	90	90	90	108.044(1)	90
V [Å^3]	1796.13(5)	1486.48(5)	1892.31(11)	783.71(4)	1700.97(6)
Z	4	4	4	2	4
$D_{calcd.}$ [g cm^{-3}]	1.488	1.610	1.451	1.586	1.579
μ [mm^{-1}]	0.667	0.796	0.637	0.758	0.709
F(000)	832	736	860	384	832
Crystal size [mm]	0.45×0.30×0.15	0.50×0.40×0.15	0.30×0.15×0.15	0.60×0.50×0.40	0.50×0.40×0.30
Diffractometer	Nonius-KappaCCD	Nonius-KappaCCD	Nonius-KappaCCD	Nonius-KappaCCD	Nonius-KappaCCD
$2\theta_{max}$ [°]	50	55	50	55	55
Limiting indices	$-12 \le h \le 12$	$-13 \le h \le 13$	$-8 \le h \le 8$	$-8 \le h \le 9$	$-17 \le h \le 17$
	$-15 \le k \le 15$	$-16 \le k \le 16$	$-12 \le k \le 13$	$-12 \le k \le 12$	$-14 \le k \le 14$
	$-15 \le l \le 15$	$-14 \le l \le 13$	$-27 \le l \le 27$	$-16 \le l \le 15$	$-15 \le l \le 15$
Reflections collected/	33853/3144	13203/1769	14574/3295	11563/3478	19612/3810
unique	[*R*(int) = 0.0394]	[*R*(int) = 0.0431]	[*R*(int) = 0.0429]	[*R*(int) = 0.0365]	[*R*(int) = 0.0344]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Paramters/restrains	244/0	115/0	267/78	226/0	244/0
Goodness-of-fit on F^2	1.084	1.055	0.986	1.060	1.069
Final *R* indices	R_1 = 0.0250,	R_1 = 0.0272,	R_1 = 0.0347,	R_1 = 0.0277,	R_1 = 0.0275,
[$I > 2\sigma(I)$]	wR_2 = 0.0687	wR_2 = 0.0773	wR_2 = 0.0813	wR_2 = 0.0736	wR_2 = 0.0774
R indices (all data)	R_1 = 0.0305,	R_1 = 0.0328,	R_1 = 0.0565,	R_1 = 0.0311,	R_1 = 0.0331,
	wR_2 = 0.0708	wR_2 = 0.0800	wR_2 = 0.0887	wR_2 = 0.0752	wR_2 = 0.0794
Largest diff. peak/ hole [e Å^{-3}]	0.259/–0.302	0.275/–0.478	0.254/–0.263	0.374/–0.434	0.329/–0.393

42.8 (*C*H$_2$–Ar), 47.5 (bridge-CH$_2$), 51.6, 55.6 55.7 (C-1, C-11, C-12), 57.8 (C-2), 86.6, 90.2, 90.7, 94.2 (C-5, C-6, C-7, C-8), 95.2, 96.8 (C-4, C-9), 135.5, 137.7 (C-13, C-14), 198.4, 198.6 (C-3, C-10), 229.3 (Cr(CO)$_3$) ppm. IR (PE): $\tilde{\nu}$(C=O) = 1998, 1944, 1934 cm^{-1}. MS (FAB): *m*/*z* (%) = 402 (3) [M]$^+$, 346 (3) [M – 2CO]$^+$, 336 (2) [M – C$_5$H$_6$]$^+$, 318 (3.5) [M – 3CO]$^+$, 280 (2) [M – 2CO – C$_5$H$_6$]$^+$, 252 (100) [M – 3CO – C$_5$H$_6$]$^+$, 200 (18) [M – Cr(CO)$_3$, C$_5$H$_6$]$^+$, 66 (90) [C$_5$H$_6$]$^+$, 52 (65) [Cr]$^+$, 43 (53) [C$_3$H$_7$]$^+$. HR-MS: calcd. for C$_{21}$H$_{18}$CrO$_5$: 402.0559; found 402.0564.

Tricarbonyl[(5*R*,8*S*,8a*R*,10a*S*)-(η^6-1,2,3,4,4a,9a)-(5,8,8a,10a-tetrahydro-5,8-methanoanthracene-9,10-dione)]chromium (10): Yield: 66%; R_f = 0.64 (PE/TBME, 1:1). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 1.50 (m, 1 H, bridge-CH$_2$), 1.57 (dt, $^2J_{H,H}$ = 8.84, $^3J_{H,H}$ = 1.83 Hz, 1 H, bridge-CH$_2$), 3.41 (dd, $^3J_{H,H}$ = 2.1, $^3J_{H,H}$ = 1.67 Hz, 2 H, H-2, H-11), 3.66 (m, 2 H, H-1, H-12) 5.60 (dd, $^3J_{H,H}$ = 5.06, $^4J_{H,H}$ = 2.80 Hz, 2 H, H-Ar), 5.93 (dd, $^3J_{H,H}$ = 5.01, $^4J_{H,H}$ = 2.85 Hz, 2 H, H-Ar), 6.12 (t, $^3J_{H,H}$ = 1.56 Hz, 2 H, H-13, 14 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ = 48.3 (bridge-CH$_2$), 48.7, 49.1 (C-2, C-11 and C-1, C-12), 88.9, 92.6 (C-5, C-6, C-7, C-8), 96.0 (C-4, C-9), 135.9 (C-13, C-14), 196.3 (C-3, C-10), 228.9 (Cr(CO)$_3$) ppm. IR (PE) $\tilde{\nu}$(C=O): 2000, 1946 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 360 (24) [M]$^+$, 304 (20) [M – 2CO]$^+$, 276 (38) [M – 3CO]$^+$, 224 (12) [M – Cr(CO)$_3$]$^+$, 210 (100) [M – 3CO – C$_5$H$_6$]. HR-MS: calcd. for C$_{18}$H$_{12}$CrO$_5$: 360.008983; found 360.0092.

Tricarbonyl[(8a*R*,10a*S*)-(η^6-1,2,3,4,4a,9a)-(5,8,8a,10a-tetrahydro-5,7-dimethylanthracene-9,10-dione)]chromium (11): Yield: 93%; R_f = 0.32 (PE/TBME, 2:1). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 1.64 (s, 6 H, CH$_3$), 2.14 (m, 2 H, CH$_2$), 2.50 (m, 2 H, CH$_2$), 3.35 (ddd, $^3J_{H,H}$ = 6.5, $^3J_{H,H}$ = 4.74, $^3J_{H,H}$ = 1.77 Hz, 2 H, CH), 5.61 (dd, $^3J_{H,H}$ = 5.01, $^4J_{H,H}$ = 2.78 Hz, 2 H, H-Ar), 5.97 (dd, $^3J_{H,H}$ = 4.99, $^4J_{H,H}$ = 2.84 Hz, 2 H, H-Ar) ppm. ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ = 18.8 (CH$_3$), 30.6 (CH$_2$), 45.9 (CH), 89.1, 92.5 (C-5, C-6, C-7, C-8), 94.3 (C-4, C-9), 123.4 (C-13, C-14), 197.4 (C=O), 229.2 (Cr(CO)$_3$) ppm. IR (PE): $\tilde{\nu}$(C=O) = 2000, 1948, 1939 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 376 (38) [M]$^+$, 320 (16) [M – 2CO]$^+$, 292 (88) [M – 3CO]$^+$, 240 (16) [M – Cr(CO)$_3$]. HR-MS: calcd. for C$_{19}$H$_{16}$CrO$_5$: 376.040283; found 376.0409.

Tricarbonyl[(5*R*,8*S*,8a*R*,10a*S*)-(η^6-1,2,3,4,4a,9a)-(5,8,8a,10a-tetrahydro-5,8-ethanoanthracene-9,10-dione)]chromium (12): Yield: 88%; R_f = 0.35 (PE/TBME, 2:1). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 1.33 (m, 2 H, CH$_2$), 1.69 (m, 2 H, CH$_2$), 3.10 (m, 2 H, CH), 3.34 (m, 2 H, CH), 5.60 (dd, $^3J_{H,H}$ = 5.14, $^4J_{H,H}$ = 2.80 Hz, 2 H, H-Ar), 5.95 (dd, $^3J_{H,H}$ = 5.14, $^4J_{H,H}$ = 2.80 Hz, 2 H, H-Ar), 6.25 (dd, $^3J_{H,H}$ = 4.52, $^3J_{H,H}$ = 3.11 Hz, 2 H, H-13, H-14) ppm. ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ = 24.5 (CH$_2$), 35.3 (CH), 49.0 (CH), 88.9, 92.6 (C-5, C-6, C-7, C-8), 95.8 (C-4, C-9), 134.0 (C-13, C-14), 196.3 (C=O), 228.9 (Cr(CO)$_3$) ppm. IR (PE): $\tilde{\nu}$(C=O) = 1998, 1949, 1937 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 374 (21) [M]$^+$, 318 (18) [M – 2CO]$^+$, 290 (100) [M – 3CO]$^+$, 238 (8) [M – Cr(CO)$_3$]$^+$, 210 (72) [M – 3CO – C$_6$H$_{10}$]. HR-MS: calcd. for C$_{19}$H$_{14}$CrO$_5$: 374.024633; found 374.0248.

Tricarbonyl[(*S*$_p$,5*R*,8*R*,8a*S*,10a*S*)/(*R*$_p$,5*S*,8*S*,8a*R*,10a*R*)-(η^6-1,2,3,4,4a,9a)-(5,8,8a,10a-tetrahydro-5-methoxy-5,8-ethanoanthracene-9,10-dione)]chromium (13): Yield: 88%; R_f = 0.42 (PE/TBME, 1:2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 1.40 (m, 1 H, CH$_2$), 1.56 (dd, $^2J_{H,H}$ = 12.21, $^3J_{H,H}$ = 3.17 Hz, 1 H, CH$_2$), 1.85 (m, 1 H, CH$_2$), 2.06 (dd, $^2J_{H,H}$ = 10.64, $^3J_{H,H}$ = 3.01 Hz, 1 H, CH$_2$), 3.16 (dd, $^3J_{H,H}$ = 8.76, $^3J_{H,H}$ = 2.73 Hz, 1 H, CH), 3.19 (m, 1 H, CH), 3.45 (d, $^3J_{H,H}$ = 8.85, 1 H, CH), 3.50 (s, 3 H, OCH$_3$), 5.53 (dd, $^3J_{H,H}$ = 6.26, $^4J_{H,H}$ = 1.38 Hz, 1 H, H-Ar), 5.58 (dd, $^3J_{H,H}$ = 6.22, $^4J_{H,H}$ = 1.26 Hz, 1 H, H-Ar), 5.90 (dd, $^3J_{H,H}$ = 6.40, $^4J_{H,H}$ = 1.32 Hz, 1 H, H-Ar), 5.99 (dd, $^3J_{H,H}$ = 6.40, $^4J_{H,H}$ = 1.32 Hz, 1 H, H-Ar), 6.12 (dd, $^3J_{H,H}$ = 10.27, $^3J_{H,H}$ = 8.76 Hz, 1 H, H-13 or H-14), 6.14 (d, $^3J_{H,H}$ = 8.66 Hz, 1 H, H-13 or H-14) ppm. ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ = 24.1 (CH$_2$), 29.0 (CH$_2$), 36.5 (CH), 50.2 (OCH$_3$), 50.4 (CH), 51.2 (CH), 79.8 (*C*OCH$_3$), 88.8, 90.1, 92.2, 92.3 (C-5, C-6, C-7, C-8), 94.7, 96.7 (C-4, C-9), 131.5, 136.3 (C-13, C-14), 192.4, 195.8 (C=O), 229.0 (Cr(CO)$_3$) ppm. IR (PE): $\tilde{\nu}$(C=O) = 2000, 1945 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 404 (4) [M]$^+$, 348 (3) [M – 2CO]$^+$, 320 (17) [M – 3CO]$^+$, 294 (12) [M – C$_7$H$_{12}$O]$^+$, 210 (53) [M – 3CO – C$_7$H$_{12}$O]. HR-MS: calcd. for C$_{20}$H$_{16}$CrO$_6$: 404.035198; found 404.0348.

Crystal Structure Determination of Cycloaddition Products 5 and 10–13: Dark-red crystals of complexes were grown from diethyl ether at room temperature. Data were collected with a Nonius-Kappa CCD diffractometer at 123 K. The molecular structures of **5**, **10**, **11** and **13** were solved by direct methods (SHELXS-97).[16] The molecular structure of **12** was solved by Patterson methods. An empirical absorption correction was applied to the data of **10**. The non-hydrogen atoms were refined anisotropically on F^2 (SHELXS-97);[17] hydrogen atoms were refined isotropically using a riding model.

CCDC-243070 (for **5**), -243071 (for **10**), -243072 (for **11**), -243073 (for **12**) and -243074 (for **13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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