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Reactions of complex ligands 85: chiral quinoid and hydroquinoid [2.2]metacyclophanes via chromium-mediated intramolecular benzannulation☆

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Abstract

A *meta*-alkynyl (chromium alkenylcarbene) functionalized benzene **5** is synthesized in a six-step sequence starting from 3-bromomethyliodobenzene. Upon gentle warming in tetrahydrofuran methoxy[alkynylaryl(alkenyl)carbene complex **5** undergoes an intramolecular benzannulation to give [2.2]metacyclophane **6** bearing two chiral planes due both to the cyclophane skeleton and the $Cr(CO)_3$-coordinated methyl-substituted benzohydroquinone deck. In situ oxidation of the benzannulation product by cerium(IV) ammonium nitrate directly affords chiral [2.2]metabenzoquinonophane **7**.

Keywords: Benzannulation; Carbene complexes; Chromium complexes; Cyclophanes; Quinones

1. Introduction

The construction of strained carbocycles is an ongoing challenge in organic synthesis [2]. Among these compounds cyclophanes have received considerable interest in organometallic chemistry [3]. The unsymmetrical boatlike conformation imposed on the benzene decks in [2.2]*para*- and *meta*-cyclophanes has stimulated efforts to explore the ability of distorted arenes for coordination to organometallic fragments [4] culminating in the metal vapor cocondensation synthesis of the [2.2]paracyclophane chromium sandwich [5]. The synthesis of cyclophanes is generally based on the dilution principle [6], the cesium template effect [7] and the junction of the arene decks via a temporary assistance by heteroatoms which are finally removed by oxidation and reductive elimination [8,9]. We pursued a complementary strategy based on a transition metal template-mediated assembly of a densely substituted distorted arene deck, and we now report on our efforts to apply the intramolecular version of the benzannulation of alkenyl(alkoxy)carbene chromium complexes with alkynes [10] to the synthesis of chiral [2.2]metahydroquinono- and quinonophanes.

2. Synthesis of the alkynyl(alkenylcarbene) complex precursor

Early studies directed towards pyranoquinone antibiotics demonstrated that the intramolecular chromium-mediated benzannulation is favored by a flexible spacer separating the alkyne and the aryl-(or vinyl-)carbene moieties [11]. If, however, both π-systems are connected by a rigid arene bridge, the alkyne insertion into the chromium–carbene bond, which represents the first carbon–carbon bond forming step in the benzannulation, is blocked; instead, an intermolecular reaction results in an unusual formal dimerization of the

☆ For part 84 see Ref. [1].

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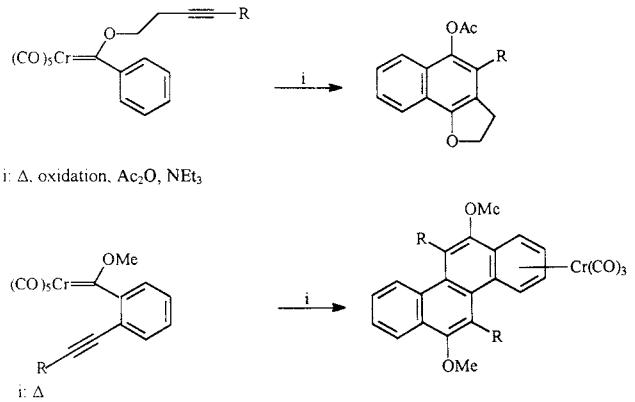
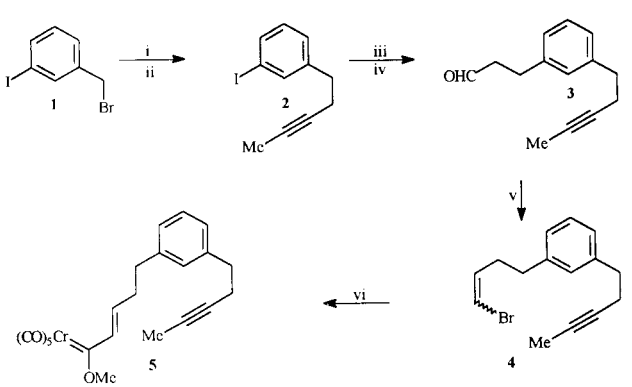


Scheme 1. Intramolecular benzannulation and carbene dimerization to chrysenes.

(alkynylaryl)carbene ligand to give a chrysene skeleton [12] (Scheme 1).

The construction of the cyclophane hydroquinone deck via intramolecular benzannulation requires a tailored alkoxycarbene chromium complex **5** bearing a vinyl–carbene substituent separated from the alkyne moiety by a *meta*-diethylene benzene spacer. A suitable starting material was 3-bromomethyl-1-iodobenzene **1** which allowed for the sequential elaboration of the alkynyl and the chromiumalkenylcarbene side chain (Scheme 2). Coupling of the benzyl bromide with allenylmagnesium bromide followed by methylation with methyl iodide gave 3-(3′-pentynyl)-1-iodobenzene **2** in excellent yield [13,14].

Attempts to replace the iodo substituent for the required formylethyl side chain via the Heck reaction using allyl alcohol [15] were successful with the iodobenzene model compound [16]. However, this approach failed with the alkynyliodoarene substrate **2** probably due to deactivation of the palladium catalyst



i: CH_2=C=CHMgBr, ii: LDA, MeI, iii: 2-(bromomethyl)-1,3-dioxane
iv: a) MeOH/HCl/AcOH, b) HCl/AcOH,
v: $[Ph_3P{=}CH_2Br]^+Br^-$, vi: *tert*.-BuLi, $Cr(CO)_6$, $[Me_3O]^+BF_4^-$

Scheme 2. Synthesis of alkynyl(alkenylcarbene) complex **5**.

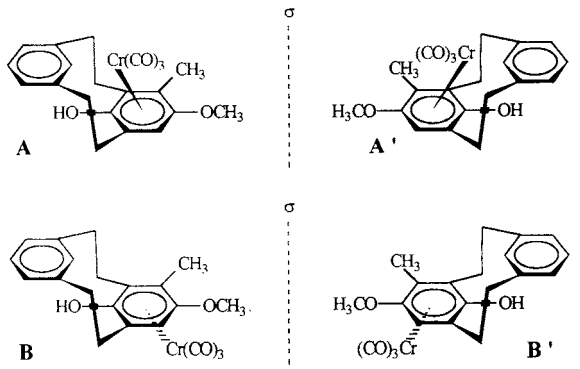
by coordination to the C≡C bond. Thus, we focused on a propanal equivalent provided by (2-bromomethyl)-1,3-dioxane which was attached to the arene after iodine/lithium exchange. Deprotection of the acetal occurred via acidic transacetalization by methanol. Olefination of aldehyde **3** was first achieved by a two-step sequence via the geminal dibromide applying the tetrabromomethane/triphenylphosphine protocol [17] followed by debromination with lithium tri-*n*-butylzincate [18] which resulted in the formation of bromoalkene **4** in a low overall yield of 27% as a 1.1/1 mixture of *E*/*Z*-isomers. The yield could be improved by a one-step 'salt free' Wittig protocol using triphenyl(bromomethyl)phosphonium bromide/potassium *tert*-butoxide [19] which afforded a 1/9 *E*/*Z*-mixture of isomers.

The synthesis of the alkene–alkyne carbene complex **5** was based on the Fischer route [20]. Low temperature lithiation of bromoalkene **4** by *tert*-butyllithium and addition of hexacarbonylchromium was followed by alkylation of the resulting acylchromate with trimethyloxonium tetrafluoroborate to give a 47% yield of **5**. NMR studies confirmed the exclusive formation of the *E*-isomer ($^3J_{HH} = 15.1$ Hz) irrespective of the ratio of *E*/*Z*-isomers in the bromoalkene precursor **4** suggesting a configurational lability of the lithioalkene intermediate under the reaction conditions.

3. Diastereoselective intramolecular benzannulation

Previous studies on metal carbene modified [2.2]metacyclophanes [21] have demonstrated that the boatlike deformation of the benzene ring does not hamper further elaboration of the arene deck. Pentacarbonyl[4-[2.2]metacyclophanyl(methoxy- or amino)-carbene]chromium underwent clean intermolecular diastereoselective benzannulation and cyclopentannulation upon reaction with alkynes [22]. In order to investigate whether this type of reaction can be extended to the synthesis of strained and distorted oxygenated arenes we aimed at an intramolecular benzannulation of (alkynylaryl)alkenylcarbene complex **5**.

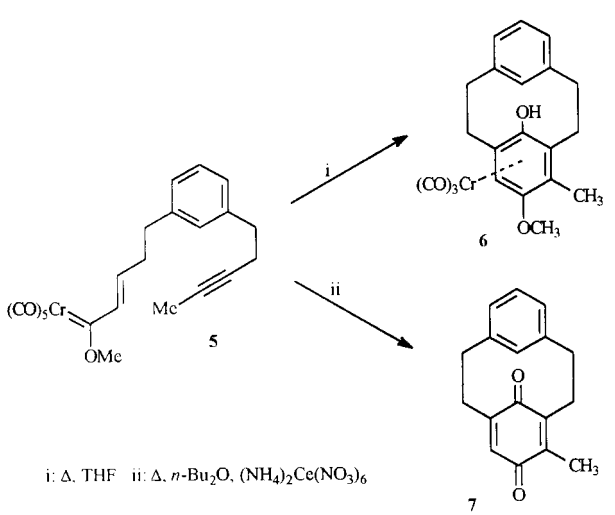
Warming a carefully deoxygenated 0.27 N solution of carbene complex **5** in tetrahydrofuran to 65°C resulted in the intramolecular [3 + 2 + 1]cycloaddition to give the [2.2]metahydroquinonophane complex **6** which was isolated as a yellow solid in 38% yield after chromatographic workup. IR- and ^{13}C-NMR spectra—which reveal significantly shielded arene carbon atoms for the substituted hydroquinone deck—indicate that the $Cr(CO)_3$ fragment is coordinated to the hydroquinoid ring formed upon the benzannulation. At low temperature in solution [2.2]metacyclophane may adopt a *syn*-conformation containing superimposed benzene rings; above 0°C, however, it is known to rearrange to the



Scheme 3. Possible *anti*-pairs of enantiomers **A**/**A**′ and **B**/**B**′.

thermodynamically favored *anti*-conformation in which both arene decks are arranged in a stepwise manner [8,23]. The *anti*-conformation is generally observed for metal-coordinated [2.2]metacyclophanes [4]. As a consequence of two planes of chirality arising from the non-symmetric substitution pattern of the hydroquinone ring and the coordination of the metal from either the top or the bottom face of the hydroquinone two *anti*-pairs of enantiomers **A**/**A**′ and **B**/**B**′ might be expected for the benzannulation product **6** (Schemes 3 and 4).

The intramolecular benzannulation occurred with considerable diastereoselectivity; only a single diastereomer of **6** could be detected and isolated from the reaction mixture. Intermolecular benzannulation of the *anti*-[2.2]metacyclophane skeleton generating a naphthohydroquinoid deck has been shown to favor the formation of the *anti*-diastereomer bearing the $Cr(CO)_3$ fragment on the remote arene ring opposite to the other arene deck; at elevated temperature the metal underwent a haptotropic migration along the '*exo*' face to the less substituted naphthalene ring. The other



Scheme 4. Synthesis of [2.2]metahydroquinonophane complex **6** and quinonophane **7** via intramolecular benzannulation.

diastereomer bearing the metal on the more congested '*endo*' face of the hydroquinone may be formed as a minor product; however, attempts to induce a similar haptotropic migration of the $Cr(CO)_3$ moiety in this isomer resulted in decomplexation [22]. Obviously, the inner hydrogen atom of the other benzene deck does not tolerate the coordination of the central arene ring from the '*endo*' face. On the basis of these results, supported by the fact that a sharp singlet is observed for the $Cr(CO)_3$ group in the ^{13}C-NMR spectrum indicating an unhindered rotation along the arene–chromium axis on the NMR time scale, we favor the assignment of enantiomers **B**/**B**′ for the intramolecular benzannulation product **6**.

Achiral [2.2]metabenzoquinonophanes and -hydroquinonophanes have been previously synthesized from two adequately substituted xylene-type precursors via the classical disulfone route, and their electron donor acceptor properties have been extensively studied by Staab [24]. They form intramolecular quinhydrones which reveal transannular charge transfer phenomena for both the *syn* and the *anti* conformations. The intramolecular benzannulation strategy also provides a straightforward access to chiral [2.2]metaquinonophanes. In situ oxidation of the benzannulation product obtained from carbene complex **5** by cerium(IV) ammonium nitrate afforded a 40% yield of benzoquinonophane **7** bearing a single plane of chirality (Scheme 4).

4. Conclusion

Intramolecular benzannulation of (alkynylaryl)alkenylcarbene complexes of chromium provides a novel straightforward synthetic access to chiral $Cr(CO)_3$-coordinated [2.2]metahydroquinonophanes bearing two planes of chirality. It is based on the assembly of a densely substituted distorted arene deck mediated by a chromium template, and thus complements the customary syntheses of cyclophanes which rely on the heteroatom-assisted combination of two differently functionalized *meta*-xylene precursors. The benzannulation is *anti*-diastereoselective generating a single pair of enantiomers. In situ oxidation affords a chiral [2.2]metaquinonophane.

5. Experimental

All operations involving organometallics were carried out in flame-dried glassware under an atmosphere of argon. Di-*n*-butyl ether, dichloromethane and petroleum ether were dried over calcium hydride, diethyl ether and THF over Na/K. All solvents were saturated with argon and stored over molecular sieves.

Silica gel (Merck, 0.063–0.200 mm) was degassed under vacuum and stored under argon. FT-IR spectra were recorded on a Nicolet Magna 550 spectrometer, NMR spectra on a Bruker DRX 500, AM 400 or AM 250 spectrometer. All chemical shifts are given in ppm relative to TMS as external standard. HR-MS were determined on a Kratos MS-50 spectrometer.

5.1. 3-(3′-Pentynyl)-1-iodobenzene **2**

A 2 N solution of allenylmagnesium bromide (98 mmol, 49 ml) in diethyl ether was added at 0°C to 3-iodobenzyl bromide (89.8 mmol, 23.0 g) dissolved in 60 ml of tetrahydrofuran. The mixture was allowed to warm to room temperature (r.t.), stirred for another 3 h, hydrolyzed at 0°C, extracted with diethyl ether and dried over magnesium sulfate. Distillation gave 20.9 g (81.7 mmol, 91%) of 3-(3′-butynyl)-1-iodobenzene.

HR-MS: Found: 255.9756. $C_{10}H_9I$ Calc.: 255.9749. MS (EI): m/z 256 (31%), 217 (58%), 129 (100%), 90 (58%). ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 7.58$ (t, 1H, $^4J_{HH} = 1.6$ Hz, aryl-H), 7.55 (d, 1H, $^3J_{HH} = 7.8$ Hz, aryl-H), 7.18 (d, 1H, $^3J_{HH} = 7.7$ Hz, aryl-H), 7.02 (pseudo-t, 1H, aryl-H), 2.75 (t, 2H, $^3J_{HH} = 7.4$ Hz, aryl-CH_2), 2.45 (td, 2H, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 2.6$ Hz, CH_2–C≡C), 1.98 ppm (t, 1H, $^4J_{HH} = 2.6$ Hz, C≡CH). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 142.7$, 137.4, 135.4, 129.9, 127.7, 94.4 (6C, aryl-C), 83.1 (C≡CH), 69.3 (C≡CH), 34.1 (aryl-CH_2), 20.3 ppm (CH_2–C≡C).

A solution of 86.4 mmol (8.74 g) diisopropyl amine and 86.4 mmol of *n*-butyllithium in 40 ml of tetrahydrofuran was added to a solution of 73.7 mmol (19.9 g) of 3-(3′-butynyl)-1-iodobenzene in 60 ml of tetrahydrofuran at 0°C. After 30 min 110.57 mmol (15.69 g) methyl iodide were added; then the mixture was allowed to warm slowly to r.t., stirred for 3 h, the reaction quenched with water at 0°C and the mixture extracted with diethyl ether. The organic phase was washed with water and dried over magnesium sulfate. Distillation gave 16.33 g (60.44 mmol, 82%) of **2**.

HR-MS: Found: 269.9908. $C_{11}H_{11}I$ Calc.: 269.9906. MS (EI): m/z 270 (50%), 217 (82%), 143 (100%), 128 (29%), 90 (46%). ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 7.58$ (t, 1H, $^4J_{HH} = 1.6$ Hz, aryl-H), 7.55 (d, 1H, $^3J_{HH} = 7.8$ Hz, aryl-H), 7.18 (d, 1H, $^3J_{HH} = 7.7$ Hz, aryl-H), 7.02 (pseudo-t, 1H, $^3J_{HH} = 7.7$ Hz, aryl-H), 2.72 (t, 2H, $^3J_{HH} = 7.5$ Hz, aryl-CH_2), 2.38 (tq, 2H, $^3J_{HH} = 7.5$ Hz, $^5J_{HH} = 2.5$ Hz, CH_2–C≡C), 1.75 ppm (t, 3H, $^5J_{HH} = 2.5$ Hz, CH_3). ^{13}C-NMR (62.9 MHz, $CDCl_3$): $\delta = 143.46$, 137.70, 135.30, 130.18, 127.88, 94.50 (6C, aryl-C), 78.18 (C≡CCH_3), 76.70 (C≡CCH_3), 35.08 (aryl-CH_2), 20.90 (CH_2–C≡C), 3.64 ppm (CH_3).

5.2. 3-(3′-Pentynyl)-phenylpropanal **3**

A solution of alkyne **2** (11.46 g, 42 mmol) in 20 ml of diethyl ether was added slowly at −10°C to 45 mmol of *n*-BuLi dissolved in 40 ml diethyl ether. The mixture was stirred for 30 min and then cooled to −50°C before 50 mmol (9.75 g) of 2-(2′-bromoethyl)-1,3-dioxane were slowly added. The mixture was allowed to warm to r.t. overnight, the reaction quenched with water and the mixture extracted with diethyl ether. The combined organic layers were dried over magnesium sulfate and concentrated to dryness. The resulting oil was purified by column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) to give 6.13 g (23.73 mmol, 56%) of {2-[1-(3′-pentynyl)-3-(2″-phenylethyl)]}-1,3-dioxane.

HR-MS: Found: 258.1628. $C_{17}H_{22}O_2$ Calc. 258.1620. MS (EI): m/z 258 (3%), 182 (22%), 129 (24%), 87 (100%). ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 7.07$–7.26 (m, 4H, aryl-CH), 4.54 (t, 1H, CH), 4.15 (ddd, 2H, CH), 3.78 (ddd, 2H, CH), 2.80 (t, 2H, CH_2), 2.73 (t, 2H, CH_2), 2.43 (tq, 2H, CH_2), 2.13 (dtt, 1H, CH), 1.94 (m, 2H, CH_2), 1.81 (t, 3H, CH_3), 1.37 ppm (dtt, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 142.16$, 141.46 (2C, aryl-C), 129.08, 128.76, 126.72, 126.31 (4C, aryl-CH), 79.09 (C≡CCH_3), 76.53 (C≡CCH_3), 67.31 (C-3,5), 37.11 (CH_2CH), 35.95 (CH_2CH_2C≡C), 30.49 (CH_2CH_2CH), 26.27 (C-4), 21.40 (CH_2C≡C), 3.92 ppm (CH_3).

The dioxane acetal (7.04 mmol, 1.82 g) was cleaved by stirring in a mixture of 75 ml of methanol, 20 ml of glacial acetic acid and 0.5 ml of conc. hydrochloric acid for 3 days. This mixture was cautiously poured into a saturated aqueous solution of sodium hydrogen carbonate, and the dimethyl acetal was extracted with diethyl ether. The combined extracts were dried over magnesium sulfate and evaporated. Then the residue was dissolved in a mixture consisting of 50 ml of glacial acetic acid, 5 ml of water and 0.5 ml of conc. hydrochloric acid and stirred for another 3 days. The solution was slowly poured into saturated aqueous sodium hydrogen carbonate. Additional sodium hydrogen carbonate was added until the solution became basic. Extraction with diethyl ether, drying over magnesium sulfate, evaporation of the solvent and column chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as eluent afforded 5.84 mmol (1.17 g, 83%) of aldehyde **3**.

HR-MS: Found: 200.1199. $C_{14}H_{16}O$ Calc.: 200.1201. MS (EI): m/z 200 (1%), 147 (22%), 105 (100%). ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 9.81$ (t, 1H, $^3J_{HH} = 1.5$ Hz, CHO), 7.03–7.28 (m, 4H, aryl-CH), 2.91 (t, 2H, CH_2), 2.78 (t, 4H, CH_2), 2.40 (tq, 2H, CH_2),1.75 ppm (t, 3H, CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 202.06$ (CHO), 141.78, 140.75 (2C, aryl-C), 128.76, 126.81, 126.73, 126.62 (4C, aryl-CH), 78.97 (C≡CCH_3), 76.66 (C≡CCH_3), 45.68 (CH_2CHO), 35.95 (ArCH_2), 28.51 (ArCH_2CH_2CHO), 21.38 (CH_2C≡CCH_3), 3.92 ppm (CH_3).

5.3. 1-Bromo-4-(3′-pentyn-3″-yl-phenyl)-1-butene **4**

A total of 5 mmol (0.56 g) of potassium *tert*-butoxide was added at −78°C to a suspension of 5 mmol (2.18 g) of $[Ph_3PCH_2Br]Br$ in 15 ml of tetrahydrofuran, and the mixture was stirred for 30 min. Then a solution of 5 mmol (1.00 g) of aldehyde **3** in 5 ml of tetrahydrofuran was added slowly at −78°C. After 30 min the mixture was allowed to warm to r.t. and stirred for another 2 h. The mixture was hydrolyzed with water and extracted with petroleum ether. Chromatography on silica gel using petroleum ether as eluent gave 1.84 mmol (0.51 g, 37%) of bromoalkene **4** as a 1/9 *E*/*Z* mixture of isomers.

HR-MS: Found: 276.0505. $C_{15}H_{17}Br$ Calc.: 276.0514. MS (EI): *m*/*z* 276 (0.3%), 197 (52%), 143 (100%). ^{1}H-NMR (500 MHz, $CDCl_3$): *Z*-isomer: $\delta = 7.18–7.23$ (m, 1H, aryl-H), 6.97–7.08 (m, 3H, aryl), 6.18* (m, 1H, C<u>H</u>=CHBr), 6.16 (dm, 1H, $^3J_{HH} = 7.0$ Hz, CHBr), 6.10 (pseudo-q, 1H, $^3J_{HH} = 6.9$ Hz, C<u>H</u>=CHBr), 6.02* (dm, 1H, $^3J_{HH} = 13.5$ Hz, CHBr), 2.64–2.84 (m, 4H, 2 CH_2), 2.31–2.53 (m, 4H, 2 CH_2), 1.77 ppm (t, 3H, CH_3). ^{13}C-NMR (500 MHz, $CDCl_3$): $\delta = 141.28$ (2C, aryl-C), 134.09 (<u>C</u>H=CHBr), 128.77, 128.55, 126.43, 126.31 (4C, aryl-CH), 108.53 (CH=<u>C</u>HBr), 78.82 (<u>C</u>≡CCH$_3$), 76.33 (C≡<u>C</u>CH$_3$), 35.68 (aryl-<u>C</u>H$_2$CH$_2$C≡C), 34.34 (<u>C</u>H$_2$CH=CHBr), 31.53 (aryl-<u>C</u>H$_2$CH$_2$CH=CHBr), 21.18 (<u>C</u>H$_2$C≡CCH$_3$), 3.68 ppm (CH_3).

The asterisk (*) denotes signals of the minor *E*-isomer.

5.4. Pentacarbonyl{(E)-1-methoxy-5-[(3′-(pentyn-3″-yl)-phenyl]-2-pentenylidene}chromium **5**

A solution of 2.02 mmol (0.56 g) of bromoalkene **4** in 5 ml of diethyl ether was added at −78°C to a solution of 4.16 mmol *tert*-BuLi in 10 ml diethyl ether. The mixture was stirred for 2 h and then 2.04 mmol (0.45 g) of hexacarbonyl chromium were added at −78°C. After 30 min the mixture was allowed to slowly reach r.t., and was stirred for another 3 h. Then the solvent was evaporated and the brown residue was dissolved in dichloromethane. The solution was cooled to −20°C, 3.04 mmol (0.45 g) of trimethyloxonium tetrafluoroborate was added and the mixture was allowed to warm to r.t. overnight. After removal of the solvent the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (3:1) as eluent to give 0.95 mmol (0.41 g, 47%) of carbene complex **5**.

HR-MS: Found: 432.0652. $C_{22}H_{20}O_6Cr$ Calc.: 432.0650. MS (EI): *m*/*z* 432 (0.2%, M^+), 404 (0.1%, $M^+ - CO$), 376 (1.2% $M^+ - 2CO$), 348 (2.3%, $M^+ - 3CO$), 320 (2%, $M^+ - 4CO$), 292 (11%, $M^+ - 5CO$), 240 (7%, $M^+ - Cr(CO)_5$), 201 (26%), 159 (100%), 105 (61%), 52 (54%). FT-IR (petroleum ether): $\tilde{\nu}$(CO) 2061 (m), 1987 (w), 1962 (s), 1948 (vs.) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 7.30$ (dm, 1H, $^3J_{HH} = 15.1$ Hz, C<u>H</u>=CHCH$_2$), 7.21 (m, 1H, aryl-CH), 7.01–7.07 (m, 3H, aryl-CH), 6.31 (dt, 1H, $^3J_{HH} = 15.1$, 7.1 Hz, CH$_2$C<u>H</u>=CH), 4.71 (s, 3H, OCH_3), 2.76 (m, 4H, aryl-CH_2), 2.49 (td, 2H, $^3J_{HH} = 7.4$, 7.1 Hz, C<u>H</u>$_2$CH=CH), 2.39 (tq, 2H, $^3J_{HH} = 7.4$ Hz, $^5J_{HH} = 2.4$ Hz, C<u>H</u>$_2$C≡C), 1.77 ppm (t, 3H, $^5J_{HH} = 2.4$ Hz, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 336.14$ (Cr=C), 223.98 (*trans*-CO), 216.70 (*cis*-CO), 144.47 (<u>C</u>H=CHCH$_2$), 141.29, 140.61 (2C, aryl-C), 135.62 (CH=<u>C</u>HCH$_2$), 128.60, 128.51, 126.34, 126.14 (4C, aryl-CH), 78.59 (<u>C</u>≡CCH$_3$), 76.18(C≡<u>C</u>CH$_3$), 66.40 (OCH_3), 35.48 (aryl-<u>C</u>H$_2$CH$_2$C≡C), 34.55 (<u>C</u>H$_2$CH=CH), 34.00 (aryl-<u>C</u>H$_2$CH$_2$CH=CH), 21.00 (<u>C</u>H$_2$C≡C), 3.50 ppm (CH_3).

5.5. Tricarbonyl[3,4,5,6,7,8-η^6-(8-hydroxy-5-methoxy-4-methyl[2.2]metacyclophane)]chromium **6**

A solution of 0.81 mmol (0.35 g) of carbene complex **5** in 30 ml of tetrahydrofuran was warmed to 65°C for 3 h while the reaction was monitored by FT-IR spectroscopy focusing on the decrease of the A_1^1 $\tilde{\nu}$(CO) absorption band of **5** and the increase of the E $\tilde{\nu}$(CO) absorption band of the arene complex formed. Then the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (3:1) as eluent to give 0.31 mmol (0.124 g, 38%) of cyclophane complex **6** as a yellow solid.

HR-MS: Found: 404.0715. $C_{21}H_{20}O_5Cr$ Calc.: 404.0716. MS (EI): *m*/*z* 404 (14%, M^+), 376 (4%, $M^+ - CO$), 348 (11%, $M^+ - 2CO$), 320 (79%, $M^+ - 3CO$), 268 (100%, $M^+ - 3CO - Cr$), 236 (78%, $M^+ - Cr(CO)_3 - CH_3OH$). FT-IR (petroleum ether): $\tilde{\nu}$(CO) 1956 (vs.), 1878 (s) cm^{-1}. ^{13}C-NMR (125 MHz, C_6D_6): $\delta = 235.03$ ($Cr(CO)_3$), 136.29, 134.95 (2C, aryl-C), 129.25, 126.51, 126.48, 126.29 (4C, aryl-CH), 124.37, 119.57 ($Cr(CO)_3$–arene–<u>C</u>), 112.80 ($Cr(CO)_3$–arene–<u>C</u>H), 92.23, 92.07, 91.12 ($Cr(CO)_3$–arene–<u>C</u>), 68.27 (OCH_3), 29.17, 29.13, 28.84, 25.26 (4C, benzyl-<u>C</u>H), 14.45 ppm (CH_3).

5.6. 4-Methyl-[2.2]metacyclophane-5,8-dione **7**

A solution of 0.35 mmol (0.15 g) of carbene complex **5** in 10 ml of di-*n*-butyl ether was warmed to 90°C for 2 h while the reaction was monitored by FT-IR spectroscopy. Then the solvent was removed, and the residue was dissolved in 10 ml of diethyl ether. This mixture was treated with 20 ml of a 0.5 N solution of cerium(IV)ammonium nitrate overnight. Then water was added to the mixture, and the product was ex-

tracted with diethyl ether. Chromatographic workup on silica gel using petroleum ether/diethyl ether (2:1) gave 0.14 mmol (0.036 g, 40%) of quinone **7**.

HR-MS: Found: 252.1147. $C_{17}H_{16}O_2$ Calc.: 252.1150. MS (EI): m/z 252 (100%, M^+), 234 (77%), 206 (56%), 191 (22%), 104 (88%). FT-IR (petroleum ether): $\tilde{\nu}$(CO) 1671 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 7.35$ (t, 1H, $^3J_{HH} = 7.6$ Hz, H-13), 7.01 (m, 2H, H-12,14), 6.79 (t, 1H, $^4J_{HH} = 1.8$ Hz, H-16), 6.40 (s, 1H, H-6), 2.92–3.00 (m, 2H, benzyl-H), 2.60–2.78 (m, 5H, benzyl-H), 2.50 (m, 1H, benzyl-H), 2.03 ppm (s, 3H, CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 188.08$ (C-5), 187.06 (C-8), 156.64 (C-3), 150.44 (C-7), 142.18, 141.49 (C-4,11,15), 132.39 (C-16), 130.37 (C-6), 129.98 (C-13), 126.91, 126.68 (C-12,14), 38.79, 37.07, 35.59, 32.34 (4C, benzyl-CH), 11.81 ppm (CH_3).

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References

[1] See: K.H. Dötz, D. Böttcher, M. Jendro, J. Organomet. Chem., in press.
[2] B. Halton (Ed.), Advances in Strain in Organic Chemistry, vol. 1–5, JAI Press, Greenwich, 1996.
[3] F. Vögtle, Cyclophane Chemistry, Wiley, Chichester, 1993.
[4] (a) J. Schulz, F. Vögtle, Top. Curr. Chem. 172 (1994) 41. (b) A. de Meijere, O. Reiser, M. Stöbbe, J. Kopf, G. Adiwidjaja, V. Sinnwell, S.I. Khan, Acta Chim. Scand. A 42 (1988) 611.
[5] C. Elschenbroich, R. Möckel, U. Zenneck, Angew. Chem. 90 (1978) 560; Angew. Chem. Int. Ed. Engl. 17 (1978) 531.
[6] P. Knops, N. Sendhoff, H.-B. Mekelburger, F. Vögtle, Top. Curr. Chem. 161 (1991) 1.
[7] A. Ostrowicki, E. Koepp, F. Vögtle, Top. Curr. Chem. 161 (1991) 37.
[8] (a) F. Vögtle, Angew. Chem. 81 (1969) 258; Angew. Chem. Int. Ed. Engl. 8 (1969) 274. (b) L. Rossa, F. Vögtle, Top. Curr. Chem. 113 (1983) 1. (c) J. Dohm, F. Vögtle, Top. Curr. Chem. 161 (1991) 69.
[9] H. Takemura, T. Shinmyozu, T. Inazu, Tetrahedron Lett. 29 (1988) 1031.
[10] (a) K.H. Dötz, Angew. Chem. 87 (1975) 672; Angew. Chem. Int. Ed. Engl. 14 (1975) 644. (b) K.H. Dötz, Pure Appl. Chem. 55 (1983) 1689. (c) Reviews: K.H. Dötz, Angew. Chem. 96 (1984) 573; Angew. Chem. Int. Ed. Engl. 23 (1984) 587. (d) W.D. Wulff, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 5, Pergamon, New York, 1991, p. 1065. (e) K.H. Dötz, P. Tomuschat, Chem. Soc. Rev., accepted for publication.
[11] (a) M.F. Semmelhack, J.J. Bozell, T. Sato, W. Wulff, E. Spiess, A. Zask, J. Am. Chem. Soc. 104 (1982) 5850. (b) M.F. Semmelhack, J.J. Bozell, L. Keller, T. Sato, E.J. Spiess, W. Wulff, A. Zask, Tetrahedron 41 (1985) 5803.
[12] F. Hohmann, S. Siemoneit, M. Nieger, S. Kotila, K.H. Dötz, Chem. Eur. J. 3 (1997) 853.
[13] R.T. Wang, F.-L. Chou, F.-T. Luo, J. Org. Chem. 55 (1990) 4848.
[14] L. Brandsma, H. Verkruijsse, Preparative Polar Organometallic Chemistry 1, Springer-Verlag, Berlin, 1987, p. 63.
[15] R.F. Heck, J. Am. Chem. Soc. 90 (1968) 5526.
[16] A. Gerhardt, Dissertation, Universität Bonn, 1997.
[17] (a) F. Ramirez, N.B. Desai, N. Mekelvic, J. Am. Chem. Soc. 84 (1962) 1745. (b) E.J. Corey, P.L. Fuchs, Tetrahedron Lett. 36 (1972) 3769. (c) H.J. Bestmann, H. Frey, Liebigs Ann. Chem. (1980) 2061.
[18] T. Harada, T. Katsuhira, D. Hara, Y. Kotani, K. Maejima, R. Kaji, A. Oku, J. Org. Chem. 58 (1993) 4897.
[19] M. Matsumoto, K. Kuroda, Tetrahedron Lett. 21 (1980) 4021.
[20] E.O. Fischer, Adv. Organomet. Chem. 14 (1976) 1.
[21] A. Longen, M. Nieger, F. Vögtle, K.H. Dötz, Chem. Ber./Receuil 130 (1997) 1105.
[22] (a) A. Longen, M. Nieger, K. Airola, K.H. Dötz, Organometallics 17 (1998) 1538. (b) Benzannulation at the alkene bridge in [2.2]paracyclophane has also been reported: A. de Meijere, in: H. Werner, G. Erker (Eds.), Organometallics in Organic Synthesis 2, Springer-Verlag, Berlin, 1989. (c) J. Höfer, Dissertation, Universität Hamburg, 1989.
[23] (a) R.H. Mitchell, V. Boekelheide, J. Am. Chem. Soc. 96 (1974) 1547. (b) R.H. Mitchell, T.K. Vinod, G.J. Bodwell, K.S. Weerawarna, W. Anker, R.V. Williams, G.W. Bushnell, Pure Appl. Chem. 58 (1986) 15.
[24] (a) H.A. Staab, M. Jörns, C. Krieger, M. Rentzea, Chem. Ber. 118 (1985) 796. (b) H.A. Staab, L. Schanne, C. Krieger, V. Taglieber, Chem. Ber. 118 (1985) 1204. (c) H.A. Staab, W.R.K. Reibel, C. Krieger, Chem. Ber. 118 (1985) 1230. (d) H. Vogler, L. Schanne, H.A. Staab, Chem. Ber. 118 (1985) 1254. (e) M. Tashiro, K. Koya, T. Yamato, J. Am. Chem. Soc. 104 (1982) 3707.