Benzannulation with Metal Carbene Functionalized Alkynes: Synthesis and Structure of Bimetallic Naphthohydroquinone Complexes Bearing Tricarbonylchromium and Pentacarbonylcarbenetungsten Moieties[1]

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Pentacarbonyl(1-methoxybenzylidene)chromium(0) (**1**) undergoes benzannulation upon reaction with ethyl *trans*-2-(phenylethynyl)cyclopropanecarboxylate (**2**) and pentacarbonyl-[methoxy(*trans*-2-(phenylethynyl)cyclopropyl)methylidene]tungsten(0) (**6**) with surprisingly high regioselectivity (>97/3) but lower diastereoselectivity (60−62% de) to give pairs of naphthohydroquinone complexes **3**/**4** and **7**/**8** as 4:1 mixtures of diastereomers arising from $Cr(CO)_3$ coordination to one or the other diastereotopic face of the naphthalene skeleton. The minor diastereomer (R_p,S_p,1*RS*,2*RS*)-1,2,3,4,9,10-η^6-tricarbonyl[ethyl *trans*-2-(1-((*tert*-butyldimethylsilyl)oxy)-4-methoxy-2-phenylnaphthalen-3-yl)cyclopropanecarboxylate]chromium-(0) (**4**) and the major diastereomer (R_pS_p,1*SR*,2*SR*)-pentacarbonyl{{*trans*-2-[1,2,3,4,9,10-η^6-(tricarbonylchromium(0))-1-((*tert*-butyldimethylsilyl)oxy)-4-methoxy-2-phenylnaphthalen-3-yl)]cyclopropyl}methoxymethylidene}tungsten(0) (**7**) have been characterized by X-ray analysis.

Introduction

Fischer-type carbene complexes have become valuable reagents for stereoselective carbon−carbon bond formation. The most widely utilized application of Fischer carbene complexes in organic synthesis[2] is the benzannulation reaction of α,β-unsaturated chromium carbenes with alkynes.[3] It occurs at moderate temperatures under neutral conditions, is compatible with a variety of functional groups within the alkyne, and, thus, has been intensively used in the synthesis of densely substituted oxygenated arenes or quinone derivatives[2] which are accessible after oxidative workup. Since metal-mediated cyclization reactions are generally sensitive to steric congestion, we extended our studies to sterically demanding alkynes. Recently we reported the synthesis of diastereomerically pure (2-ethynylcyclopropyl)methoxycarbene complexes of chromium and tungsten in which the alkyne triple bond is attached to a bulky organometallic group via the cyclopropane ring.[4] Since the cyclopropyl group is a strong donor ligand,[5] these complexes are fairly thermostable which makes them attractive candidates for annulation reactions. We now report on the chromium-mediated benzannulation reaction using as alkynes pentacarbonyl[methoxy(*trans*-2-(phenylethynyl)cyclopropyl)methylidene]tungsten(0) (**6**) and the analogous ethyl cyclopropanecarboxylate **2** which—on the basis of isolobal analogy—exhibits similar electronic characteristics.

Results and Discussion

Benzannulation with Ethyl *trans*-2-(Phenylethynyl)cyclopropanecarboxylate (2). In order to explore the regio- and diastereoselectivity of the benzannulation reaction using cyclopropyl-substituted alkynes,[6] pentacarbonyl(1-methoxybenzylidene)chromium(0) (**1**) was reacted with 2 equiv of ethyl *trans*-2-(phenylethynyl)cyclopropanecarboxylate (**2**). After warming in *tert*-butyl methyl ether at 55 °C for 1.5 h followed by *in situ* protection of the phenolic group with TBDMSCl,[7] a mixture of two diastereomeric naphthohydroquinone−$Cr(CO)_3$ complexes was obtained. Chromatographic workup on silica gel afforded a 44% overall yield of pure diastereomers **3** and **4** in a ratio of **3**:**4** = 4.1:1 (Scheme 1).

To ascertain whether the formation of diastereomers is due to a regio*un*selective incorporation of the unsymmetrical alkyne **2** into the naphthalene skeleton or to the coordination of the $Cr(CO)_3$ fragment to one or the other diastereotopic face of the naphthohydroquinone, the mixture of diastereomers **3**/**4** was oxidized in air to

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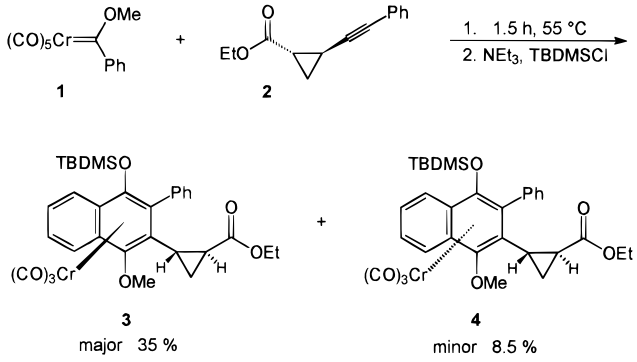
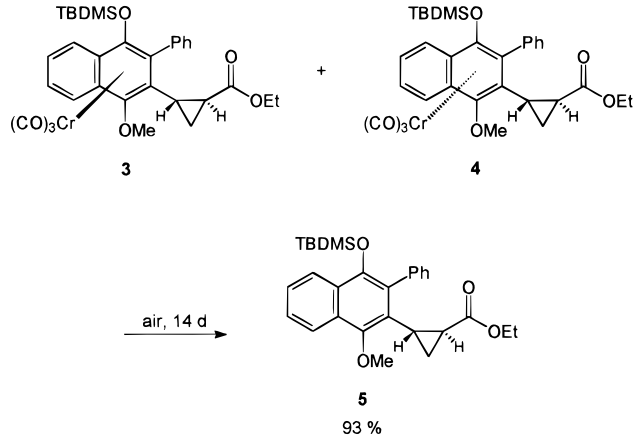
Scheme 1. Benzannulation of 1 by Cyclopropanecarboxylate 2



Scheme 2. Oxidative Demetalation of 3 and 4



cleave the $Cr(CO)_3$ moiety and, thus, to remove the element of planar chirality (Scheme 2).

The uncoordinated naphthohydroquinone was identified spectroscopically and finally isolated as a single regioisomer **5**. The crude product was contamined by a trace (<3%) of a byproduct which reveals an identical mass spectrum and thus may be regarded as the complementary regioisomer. Obviously, the benzannulation occurred highly regioselective within the limits of detection which is quite surprising. Generally, unsymmetrically substituted alkynes form both possible regioisomers, and their ratio approaches unity with a decreasing difference in steric demand of the two alkyne substituents.[8] As a rule, the larger substituent is incorporated adjacent to the phenolic group originating from the former carbonyl ligand. Our result is comparable with regioselectivities so far restricted to terminal alkynes which typically afford a single regioisomer.[8] Since the structures of benzannulation products **3** and **4** could not be assigned unambiguously by spectroscopic means as far as the regioselective incorporation of alkyne **2** and the relative configuration in the three-membered ring with respect to the plane of chirality are concerned, the structure of the minor diastereomer **4** was established by X-ray analysis (Figure 1).

The molecular structure of **4** demonstrates the regioselective incorporation of alkyne **2** placing the phenyl substituent as the "larger" substituent (R_L) adjacent to the silyloxy group; on the other hand, the cyclopropyl group is incorporated as the "smaller" alkyne substitu-

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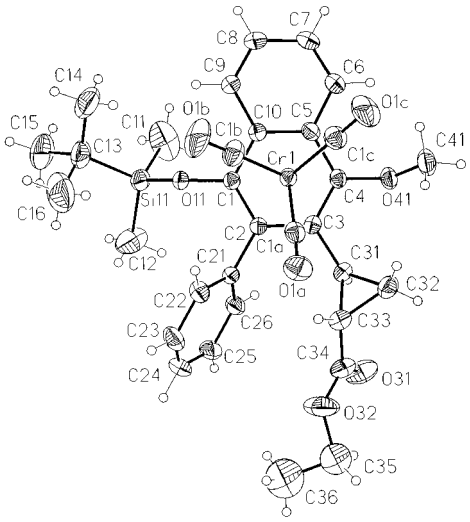
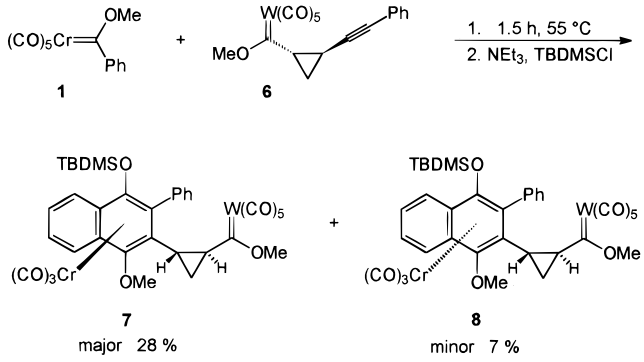


Figure 1. Molecular structure of **4**. Thermal ellipsoids are drawn at the 35% level.

Scheme 3. Benzannulation of 1 by Tungsten Carbene Alkyne 6



ent (R_S) into the aromatic system next to the carbene derived methoxy group. Obviously, as a consequence of the *trans*-configuration in the three-membered ring, the ester group does not effectively enhance the steric demand of the cyclopropyl system during the cyclization. The *cis*-diastereomer of **2** does not undergo benzannulation upon reaction with carbene complex **1** under similar conditions.

Benzannulation with Pentacarbonyl[methoxy-(*trans*-2-(phenylethynyl)cyclopropyl)methylidene]-tungsten(0) (6). We were interested in the modification of the cyclopropane substitution pattern, and thus, we extended our study to the tungsten carbene complex **6** as an alkyne component for the benzannulation of chromium carbene **1**. Using 1 equivalent of **6** and following the experimental protocol for the preparation of esters **3/4**, a mixture of diastereomeric annulation products **7/8** was obtained in moderate yield (Scheme 3).

Separation of both diastereomers by column chromatography on silica gel gave a ratio of **7**/**8** = 4.2/1, which is similar to that observed for the annulation of **1** with cyclopropylanecarboxylate **2**. Complexes **7** and **8** were isolated as crystalline orange solids which can be briefly handled in air at ambient temperature. The molecular structure of the major diastereomer **7** was determined by X-ray analysis (Figure 2) and confirmed the regiochemistry expected for the incorporation of the organometallic alkyne **6** as the isolobal analogue of ester **2**. The tungsten carbene acceptor moiety and the tricar-

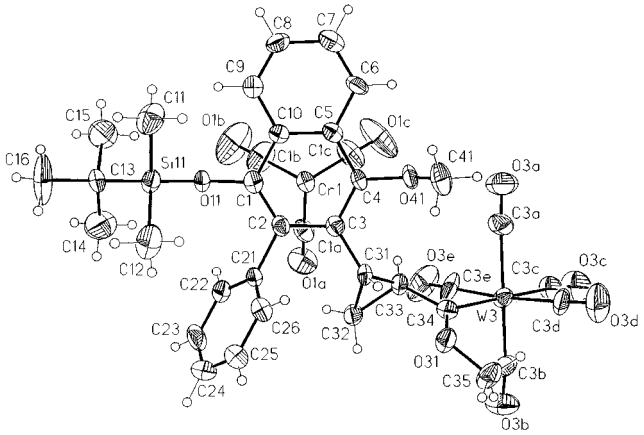


Figure 2. Molecular structure of **7**. Thermal ellipsoids are drawn at the 35% level.

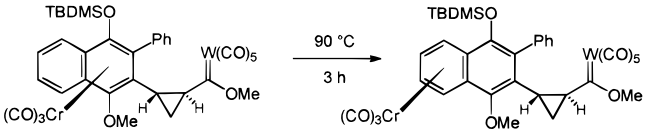
bonyl(η^6-arene)chromium π-system are bridged by the *trans*-substituted cyclopropane skeleton.

Haptotropic $Cr(CO)_3$ Migration in Naphthohydroquinone−$Cr(CO)_3$ Complex 7. In contrast to most synthetic methods used for the preparation of arene−$Cr(CO)_3$ complexes,[9] the chromium-mediated benzannulation of aryl-substituted alkoxycarbene complexes can be carried out *either* under thermodynamic *or* under kinetic control to govern the site of η^6-coordination of the arene to the metal.[8] Under the mild conditions (55 °C, 1 h) used in the annulation reactions affording complexes **7** and **8** the $Cr(CO)_3$ moiety ends up coordinated to the newly formed hydroquinoid ring exclusively (Scheme 3). Previous studies have indicated that naphthalene−$Cr(CO)_3$ complexes obtained via carbene annulation may undergo a haptotropic metal migration[10] which—on the basis of an EHMO calculation[11] —has been suggested to occur along the periphery of the aromatic π-system. Recently, studies on chiral optically active annulation products have provided first experimental evidence that this haptotropic rearrangement is an intramolecular process.[12] This conclusion is further corroborated by the thermally induced isomerization of the diastereomerically pure complex **7**: Warming a solution of **7** in di-*n*-butyl ether at 90 °C for 3 h affords a single diastereomer **9**. Although no proof is provided by X-ray analysis for which face of the arene is complexed by the $Cr(CO)_3$ unit, this result strongly supports an intramolecular stereocontrolled haptotropic rearrangement along the same face of the aromatic system. As expected, the coordination of the $Cr(CO)_3$ fragment to the less substituted arene ring is demonstrated by significant upfield shifts both for the carbon (up to 30 ppm) and the hydrogen atoms (1.7 and 2.1 ppm) of the chromium-coordinated arene ring (Scheme 4).

Conclusions

The methoxy(phenyl)carbene complex of chromium **1** undergoes a surprisingly regioselective carbene annulation upon reaction with cyclopropyl-and phenyl-substituted acetylenes **2** and **6**. Under kinetic control, a pair of naphthohydroquinone−$Cr(CO)_3$ diastereomers (**3/4** and **7/8**, respectively) are formed as a consequence of the combination of two chiral centers of the cyclopropane ring and the plane of chirality. A metal carbene functionalized alkyne allows the elaboration of densely substituted bimetallic annulation products which undergo a stereocontrolled intramolecular haptotropic metal migration under thermodynamic conditions.

Scheme 4. Haptotropic $Cr(CO)_3$ Migration in Naphthohydroquinone Complex 7



7 **9**

65 %

Experimental Section

All operations (except the oxidation of **3** and **4)** were performed using flame-dried glassware and an atmosphere of argon. Solvents (petroleum ether, bp 40−60 °C) were dried by distillation from sodium/potassium alloy or sodium hydride and saturated with argon. Silica gel (Merck, 0.063−0.200 mm) was degassed at high vacuum and stored under argon. TBDMSCl (Fluka) was used without further purification.

General Procedure for the Synthesis of Naphthohydroquinone−$Cr(CO)_3$ Complexes 3/4 and 7/8. A solution of 1.56 g (5 mmol) of pentacarbonyl(1-methoxybenzylidene)-chromium(0) **(1)** and 2 equiv of alkyne **2** (for the preparation of **7** and **8**: 1 equiv alkyne **6**) in 15 mL of *tert*-butyl methyl ether is deoxygenated by the freeze−pump−thaw method (−196 °C/25 °C, 3 cycles) and then warmed to 55 °C for 1.5 h, recooled to room temperature, and filtered through silica gel. The filtered solution is added to a solution of 1.5 g (10 mmol) of TBDMSCl and 1.4 mL (10 mmol) of triethylamine in 100 mL of dichloromethane and stirred for 3 h. After removal of the solvents under reduced pressure the residue is purified by column chromatography (−10 °C, SiO_2, eluents dichloromethane for **3/4** and 2/1 petroleum ether/dichloromethane for **7/8**) and the complexes **3**, **4,** and **7**, **8,** respectively, are isolated as orange or red crystals.

(R_pS_p,1*SR*,2*SR*)-1,2,3,4,9,10-η^6-Tricarbonyl[ethyl *trans*-2-(1-((*tert*-butyldimethylsilyl)oxy)-4-methoxy-2-phenylnaphthalen-3-yl)cyclopropanecarboxylate]chromium-(0) (3): Orange needles, 1.06 g (35% based on **1**), R_f = 0.61 (CH_2Cl_2), mp 152 °C (petroleum ether/CH_2Cl_2). Anal. Calcd for $C_{32}H_{36}CrO_7Si$: C, 62.73; H, 5.92. Found: C, 62.97; H, 6.15. ^{1}H NMR (500 MHz, $CDCl_3$): δ = −0.65 (s, 3H; Si−CH_3), −0.08 (s, 3H; Si−CH_3), 0.94 (s, 9H; $C(CH_3)_3$), 0.97 (ddd, $^3J_{cis}$ = 9.36 Hz, $^3J_{trans}$ = 5.48 Hz, $^3J_{trans}$ = 5.16 Hz, 1H; 1-H or 2-H), 1.09 (ddd, $^3J_{cis}$ = 8.45 Hz, $^3J_{trans}$ = 7.05 Hz, $^3J_{trans}$ = 5.16 Hz, 1H; 1-H or 2-H), 1.29 (t, $^3J_{HH}$ = 7.15 Hz, 3H; CH_2CH_3), 2.11 (ddd, $^3J_{cis}$ = 8.45 Hz, $^3J_{trans}$ = 5.48 Hz, $^2J_{HH}$ = 4.67 Hz, 1H; 3-H), 2.35 (ddd, $^3J_{cis}$ = 9.36 Hz, $^3J_{trans}$ = 7.05 Hz, $^2J_{HH}$ = 4.67 Hz, 1H; 3-H), 3.94 (s, 3H; O−CH_3), 4.16 (dq, $^2J_{HH}$ = 12.38 Hz, $^3J_{HH}$ = 7.15 Hz, 1H; O−C*H*H), 4.17 (dq, $^2J_{HH}$ = 12.38 Hz, $^3J_{HH}$ = 7.15 Hz, 1H; O−CH*H*), 7.35−7.41 (m, 3H; Ph), 7.42−7.49 (m, 2H; Ph), 7.54 (m_c, 1H; Ar-H), 7.75 (d, $^3J_{HH}$ = 7.35 Hz; Ar-H), 7.92 (d, $^3J_{HH}$ = 8.74 Hz; Ar-H), 8.01 (d, $^3J_{HH}$ = 8.84 Hz; Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = −4.5 (Si−CH_3), −3.4 (Si−CH_3), 14.3 (CH_2CH_3), 16.1 (C-3), 18.7 ($C(CH_3)_3$), 21.3 (C-1), 25.5 (C-2), 25.8 ($C(CH_3)_3$), 60.7 (O−CH_2), 62.8 (O−CH_3), 98.1 (C_q, η-C), 101.8 (C_q, η-C), 105.4 (C_q, η-C), 105.5 (C_q, η-C), 123.4 (Ar-C), 126.2 (Ar-C), 127.1 (Ar-C), 127.5 (Ar-C), 128.2 (Ar-C), 128.3 (Ar-C), 129.1 (Ar-C), 129.5 (C_q, η-C), 131.8 (Ar-C), 132.1 (C_q,

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η-C), 132.8 (*ipso*-C), 134.3 (Ar-C), 173.7 (C═O), 232.3 (Cr(CO)$_3$). FT-IR (hexane): ν(C═O) = 1969 (vs), 1963 (s),1911 (s), 1900 (s), 1890 (s) cm^{-1}. MS (EI): m/z (%) = 612 (14), 528 (83), 476 (100), 452 (22), 373 (22), 313 (69), 73 (88), 51 (10).

(R_p,S_p,1*RS*,2*RS*)-1,2,3,4,9,10-η^6-Tricarbonyl[ethyl *trans*-2-(1-((*tert*-butyldimethylsilyl)oxy)-4-methoxy-2-phenylnaphthalen-3-yl)cyclopropanecarboxylate]chromium-(0) (4): Red crystals, 0.26 g (8.5% based on **1**), R_f = 0.56 (CH_2Cl_2), mp 158 °C (petroleum ether/CH_2Cl_2). Anal. Calcd for $C_{32}H_{36}CrO_7Si$: C, 62.73; H, 5.92. Found: C, 62.93; H, 5.89. ^{1}H NMR (500 MHz, $CDCl_3$): δ = −0.73 (s, 3H; Si−CH_3), −0.07 (s, 3H; Si−CH_3), 0.94 (s, 9H; C(CH_3)$_3$), 1.15 (t, $^3J_{HH}$ = 7.15 Hz, 3H; CH_2CH_3), 1.43 (ddd, $^3J_{cis}$ = 9.34 Hz, $^3J_{trans}$ = 6.76 Hz, $^2J_{HH}$ = 4.67 Hz, 1H; 3-H), 1.58 (m, 1H; 3-H), 1.78 (m, 1H; 1-H or 2-H), 2.38 (ddd, $^3J_{cis}$ = 8.84 Hz, $^3J_{trans}$ = 6.76 Hz, $^3J_{trans}$ = 4.87 Hz, 1H; 1-H or 2-H), 3.82 (dq, $^2J_{HH}$ = 12.38 Hz, $^3J_{HH}$ = 7.15 Hz, 1H; O−C*H*H), 3.95 (dq, $^2J_{HH}$ = 12.38 Hz, $^3J_{HH}$ = 7.15 Hz, 1H; O−CH*H*), 3.99 (s, 3H; O−CH_3), 7.23−7.29 (m, 2H; Ph), 7.34 (m$_c$, 1H; Ar-H), 7.43−7.56 (m, 3H; Ph), 7.76 (d, $^3J_{HH}$ = 7.65 Hz; Ar-H), 7.94 (d, $^3J_{HH}$ = 8.75 Hz; Ar-H), 8.01 (d, $^3J_{HH}$ = 8.84 Hz; Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = −4.5 (Si−CH_3), −3.3 (Si−CH_3), 14.1 (CH_2CH_3), 18.7 (*C*(CH_3)$_3$), 19.2 (C-3), 20.9 (C-1), 21.8 (C-2), 25.8 (C(*C*H$_3$)$_3$), 60.4 (O−CH_2), 62.5 (O−CH_3), 98.6 (C$_q$, η-C), 101.2 (C$_q$, η-C), 105.7 (C$_q$, η-C), 106.0 (C$_q$, η-C), 123.7 (Ar-C), 126.0 (Ar-C), 127.3 (Ar-C), 127.5 (Ar-C), 128.2 (Ar-C), 128.6 (Ar-C), 128.9 (Ar-C), 129.0 (C$_q$, η-C), 131.0 (Ar-C), 132.6 (C$_q$, η-C), 133.1 (*ipso*-C), 134.3 (Ar-C), 173.9 (C═O), 232.3 (Cr(CO)$_3$). FT-IR (hexane): ν(C═O) = 1967 (vs),-1909 (m), 1904 (m), 1886 (m) cm^{-1}. MS (EI): m/z (%) = 612 (8), 528 (53), 476 (88), 373 (20), 313 (59), 73 (100), 51 (11).

(R_p,S_p,1*SR*,2*SR*)-Pentacarbonyl{{*trans*-2-[1,2,3,4,9,10-η^6-(tricarbonylchromium(0))-1-((*tert*-butyldimethylsilyl)oxy)-4-methoxy-2-phenylnaphthalen-3-yl)]cyclopropyl}-methoxymethylidene}tungsten(0) (7): Red crystals, 1.27 g (28% base on **1**), R_f = 0.34 (petroleum ether/CH_2Cl_2, 2/1), mp 152 °C (petroleum ether/CH_2Cl_2). Anal. Calcd for $C_{36}H_{34}CrO_{11}SiW$: C, 47.69; H, 3.78. Found: C, 47.67; H, 4.05. ^{1}H NMR (500 MHz, $CDCl_3$): δ = −0.61 (s, 3H; Si−CH_3), −0.09 (s, 3H; Si−CH_3), 0.85 (m$_c$, 1H; *c*-C_3H_4), 0.92 (s, 9H; C(CH_3)$_3$), 1.44 (m$_c$, 1H; *c*-C_3H_4), 1.97 (m$_c$, 1H; *c*-C_3H_4), 2.73 (m$_c$, 1H; *c*-C_3H_4), 3.92 (s, 3H; Ar−OCH_3), 4.42 (s, 3H; O−CH_3), 7.22−7.29 (m, 1H; Ph), 7.32−7.51 (m, 4H; Ph), 7.57 (m$_c$, 1H; Ar-H), 7.77 (d, $^3J_{HH}$ = 7.55 Hz, 1H; Ar-H), 7.90 (d, $^3J_{HH}$ = 8.84 Hz, 1H; Ar-H), 8.01 (d, $^3J_{HH}$ = 8.74 Hz, 1H; Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = −4.2 (Si−CH_3), −3.4 (Si−CH_3), 18.7 (*C*(CH_3)$_3$), 25.5 (C-3), 25.8 (C(*C*H$_3$)$_3$), 30.5 (C-2), 56.4 (C-1), 64.1 (Ar−OCH_3), 69.3 (O−CH_3), 97.1 (C$_q$, η-C), 102.9 (C$_q$, η-C), 104.2 (C$_q$, η-C), 104.5 (C$_q$, η-C), 123.2 (Ar-C), 126.5 (Ar-C), 126.7 (Ar-C), 127.4 (Ar-C), 128.4 (Ar-C), 128.6 (Ar-C), 129.3 (Ar-C), 130.7 (C$_q$, η-C), 130.8 (C$_q$, η-C), 131.8 (Ar-C), 132.9 (*ipso*-C), 134.8 (Ar-C), 197.4 (s, d, $^1J_{CW}$ = 129.0 Hz, W−*cis*-C═O), 203.4 (s, d, $^1J_{CW}$ = 117.2 Hz, W−*trans*-C═O), 232.4 (Cr(CO)$_3$), 325.9 (s, d, $^1J_{CW}$ = 102.8 Hz, W═C). FT-IR (hexane): ν(C═O) = 2070 (m), 1989 (w), 1958 (sh), 1956 (m), 1940 (s), 1913 (w), 1901 (w), 1892 (w) cm^{-1}. MS (FAB): m/z (rel ^{184}W, %) = 906 (22), 822 (4), 682 (47), 599 (23), 514 (14), 467 (16), 442 (52), 390 (100), 307 (59), 215 (39), 165 (33).

(R_p,S_p,1*RS*,2*RS*)-Pentacarbonyl{{*trans*-2-[1,2,3,4,9,10-η^6-(tricarbonylchromium(0))-1-((*tert*-butyldimethylsilyl)oxy)-4-methoxy-2-phenylnaphthalen-3-yl)]cyclopropyl}-methoxymethylidene}tungsten(0) (8): Orange needles, 0.30 g (7% based on **1**), R_f = 0.18 (petroleum ether/CH_2Cl_2, 2/1), mp 154 °C (petroleum ether/CH_2Cl_2). Anal. Calcd for $C_{36}H_{34}CrO_{11}SiW$: C, 47.69; H, 3.78. Found: C, 47.86; H, 3.96. ^{1}H NMR (500 MHz, $CDCl_3$): δ = −0.65 (s, br, 3H; Si−CH_3), −0.11 (s, 3H; Si−CH_3), 0.86 (br, 1H; *c*-C_3H_4), 0.92 (s, 9H; C(CH_3)$_3$), 1.25 (br, 1H; *c*-C_3H_4), 1.77 (br, 1H; *c*-C_3H_4), 3.09 (br, 1H; *c*-C_3H_4), 3.94 (s, 3H; Ar−OCH_3), 4.45 (br, 3H; O−CH_3), 7.18−7.28 (m, 2H; Ph), 7.34−7.51 (m, 3H; Ph), 7.54 (dd, $^3J_{HH}$ = 8.84 Hz, $^3J_{HH}$ = 6.95 Hz, 1H; Ar-H) 7.78 (d, $^3J_{HH}$ = 6.95 Hz, 1H; Ar-H), 7.91 (d, $^3J_{HH}$ = 8.84 Hz, 1H; Ar-H), 8.00 (d, $^3J_{HH}$ = 8.84 Hz, 1H; Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = −4.4 (br, Si−CH_3), −3.4 (Si−CH_3), 18.7 (*C*(CH_3)$_3$), 25.8 (C(*C*H$_3$)$_3$), 26.9 (C-3), 30.0 (C-2), 52.1 (C-1), 62.9 (Ar-O-CH_3), 69.4 (br, O−CH_3), 97.6 (C$_q$, η-C), 101.7 (C$_q$, η-C), 104.5 (C$_q$, η-C), 104.9 (C$_q$, η-C), 123.6 (Ar-C), 126.2 (Ar-C), 127.1 (Ar-C), 128.4 (Ar-C), 128.5 (Ar-C), 129.1 (Ar-C), 129.9 (C$_q$, η-C), 130.7 (C$_q$, η-C), 131.0 (*ipso*-C), 131.4 (Ar-C), 132.7 (Ar-C), 134.5 (Ar-C), 197.2 (s, d, $^1J_{CW}$ = 127.2 Hz, W−*cis*-C═O), 203.4 (W−*trans*-C═O), 232.3 (Cr(CO)$_3$), 326.7 (s, d, $^1J_{CW}$ = 104.1 Hz, W═C). FT-IR (hexane): ν(C═O) = 2070 (m), 1989 (w), 1958 (s), 1942 (vs), 1913 (s), 1888 (s) cm^{-1}. MS (FAB): m/z (rel ^{184}W, %) = 906 (24), 822 (3), 682 (40), 599 (17), 442 (38), 390 (71), 215 (21), 154 (100).

Oxidation of 3 and 4. A solution containing 1.06 g (1.7 mmol) of **3** and 0.26 g (0.4 mmol) of **4** in 25 mL of diethyl ether was mixed with 25 mL of nitric acid (1 M) and stirred for 14 d at room temperature. Then the reaction mixture was extracted with ether and the organic layers were washed with brine, dried over $MgSO_4$, and evaporated. The resulting yellow solid was purified by column chromatography (silica gel, 2/1 petroleum ether/ether) to give **5** as colorless crystals.

Ethyl *trans*-2-(1-((*tert*-Butyldimethylsilyl)oxy)-4-methoxy-2-phenylnaphthalen-3-yl)cyclopropanecarboxylate (5): Colorless crystals, 0.95 g (93% based on **3/4**), R_f = 0.46 (petroleum ether/ether, 2/1), mp 150 °C (hexane). Anal. Calcd for $C_{29}H_{36}O_4Si$: C, 73.07; H, 7.61. Found: C, 73.20; H, 7.73. ^{1}H NMR (500 MHz, $CDCl_3$): δ = −0.48 (s, 3H; Si−CH_3), −0.38 (s, 3H; Si−CH_3), 0.89 (s, 9H; C(CH_3)$_3$), 1.15 (m$_c$, 1H; *c*-C_3H_4), 1.16 (t, $^3J_{HH}$ = 7.15 Hz, 3H; CH_2CH_3), 1.35 (m$_c$, 2H; *c*-C_3H_4), 2.45 (m$_c$, 1H; *c*-C_3H_4), 3.86 (dq, $^2J_{HH}$ = 10.73 Hz, $^3J_{HH}$ = 7.15 Hz, 1H; O−C*H*H), 3.97 (dq, $^2J_{HH}$ = 10.73 Hz, $^3J_{HH}$ = 7.15 Hz, 1H; O−CH*H*), 4.00 (s, 3H; O−CH_3), 7.25−7.40 (m, 5H; Ph), 7.43 (ddd, $^3J_{HH}$ = 8.19 Hz, $^3J_{HH}$ = 6.68 Hz, $^4J_{HH}$ = 1.56 Hz, 1H; Ar-H), 7.48 (ddd, $^3J_{HH}$ = 8.14 Hz, $^3J_{HH}$ = 6.68 Hz, $^4J_{HH}$ = 1.57 Hz, 1H; Ar-H), 8.08 (dd, $^3J_{HH}$ = 8.14 Hz, $^4J_{HH}$ = 1.56 Hz, 1H; Ar-H), 8.11 (dd, $^3J_{HH}$ = 8.19 Hz, $^4J_{HH}$ = 1.57 Hz, 1H; Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = −4.2 (Si−CH_3), −3.8 (Si−CH_3), 14.2 (CH_2CH_3), 18.4 (C-3), 18.6 (*C*(CH_3)$_3$), 22.5 (C-1), 24.0 (C-2), 26.1 (C(*C*H$_3$)$_3$), 60.2 (O−CH_2), 61.7 (q, $^1J_{CH}$ = 143.8 Hz; O−CH_3), 121.9 (Ar-C), 123.6 (Ar-C), 125.3 (Ar-C), 126.1 (Ar-C), 126.5 (Ar-C$_q$), 126.7 (*p*-C), 127.7 (*o*-C), 127.9 (*o*-C), 128.2 (Ar-C$_q$), 128.3 (Ar-C$_q$), 130.2 (Ar-C$_q$), 131.4 (*m*-C), 131.9 (*m*-C), 137.8 (*ipso*-C), 144.3 (Ar-C$_q$), 150.6 (Ar-C$_q$), 174.2 (s, C═O). IR (KBr): ν = 2928, 2858, 1724 (C═O), 1582, 1358, 1182, 1078, 868, 766, 702 cm^{-1}. MS (EI): m/z (%) = 476 (88), 373 (22), 313 (63) 73 (100).

Haptotropic Rearrangement of Naphthohydroquinone−Cr(CO)$_3$ Complex 7. A solution of diastereomerically pure complex **7** (0.45 g, 0.5 mmol) in 10 mL of di-*n*-butyl ether was warmed to 90 °C for 3 h while the reaction was monitored by IR spectroscopy. Finally, the solvent was removed under reduced pressure, and the residue was purified by column chromatography (−10 °C, SiO_2, 2/1 petroleum ether/dichloromethane).

Pentacarbonyl{{*trans*-2-[5,6,7,8,9,10-η^6-tricarbonylchromium(0))-1-((*tert*-butyldimethylsilyl)oxy)-4-methoxy-2-phenylnaphthalen-3-yl)]cyclopropyl}methoxymethylidene}tungsten(0) (9): Red crystals, 0.29 g (65% based on **7**), R_f = 0.34 (petroleum ether/CH_2Cl_2, 2/1), mp 146 °C (petroleum ether/CH_2Cl_2). Anal. Calcd for $C_{36}H_{34}CrO_{11}SiW$: C, 47.69; H, 3.78. Found: C, 47.46; H, 3.91. ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.45 (s, 3H; Si−CH_3), −0.14 (s, 3H; Si−CH_3), 0.89 (s, 9H; C(CH_3)$_3$), 1.25−1.58 (m, 3H; *c*-C_3H_4), 2.74 (ddd, $^3J_{cis}$ = 9.15 Hz, $^3J_{trans}$ = 7.68 Hz, $^3J_{trans}$ = 4.50 Hz, 1H; 1-H), 3.91 (s, 3H; Ar−OCH_3), 4.39 (s, 3H; O−CH_3), 5.48−5.54 (m, 2H; Ar-H), 6.33 (dd, $^3J_{HH}$ = 6.26 Hz, $^4J_{HH}$ = 1.56 Hz, 1H; Ar-H), 6.44 (dd, $^3J_{HH}$ = 6.31 Hz, $^4J_{HH}$ = 1.66 Hz, 1H; Ar-H), 7.25−7.39 (m, 5H; Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = −4.0 (Si−CH_3), −3.6 (Si−CH_3), 18.6 (*C*(CH_3)$_3$), 25.9 (C(*C*H$_3$)$_3$), 27.3 (C-3), 31.9 (C-2), 38.7 (C-1), 61.8 (Ar−OCH_3), 70.6 (O−CH_3), 85.8 (η-C), 86.1 (η-C), 91.6 (η-C), 92.0 (η-C), 101.0 (C$_q$, η-C), 101.3 (C$_q$, η-C), 123.7 (*o*-C), 125.4 (*o*-C), 127.0 (*p*-C), 127.5 (Ar-C$_q$), 128.8 (Ar-C$_q$), 129.8 (*m*-C), 130.8 (*m*-C), 136.2 (*ipso*-C),

Table 1. Crystallographic Data for the Structure Determination of Complexes 4 and 7

	4	**7**
formula	$C_{32}H_{36}CrO_7Si$	$C_{36}H_{34}CrO_{11}SiW$
cryst system	monoclinic	orthorhombic
space goup	$P2_1/n$ (No. 14)	$Pna2_1$ (No. 33)
a, Å	9.774(3)	18.789(6)
b, Å	28.900(10)	7.370(2)
c, Å	11.642(4)	27.472(7)
β, deg	107.87(2)	
V, Å^3	3130(2)	3804(2)
Z	4	4
ρ_{calc}, g cm^{-3}	1.30	1.58
μ	0.45	3.39
diffractometer	Nicolet R3m	Nicolet R3m
radiation	Mo Kα	Mo Kα
λ, Å	0.710 73	0.710 73
T, K	293	293
max 2θ, deg	50	50
no. of data	8048	8350
no. of unique data	5545	6735
R_{int}	0.037	0.029
no. of variables	367	451
no. of restraints	3	1
w$R2$	0.139	0.099
R (for $\|I\| > 2\sigma(I)$)	0.050	0.042

144.1 (Ar-C_q), 149.4 (Ar-C_q), 197.4 (s, d, $^1J_{CW}$ = 127.6 Hz, W−*cis*-C═O), 203.5 (W−*trans*-C═O), 232.1 ($Cr(CO)_3$), 326.7 (W═C). FT-IR (hexane): ν(C═O) = 2070 (m), 1990 (w), 1971 (m), 1956 (s), 1940 (vs), 1911 (m), 1904 (m). MS (FAB): m/z (rel ^{184}W, %) = 906 (11), 822 (4), 682 (36), 599 (16), 514 (13), 467 (20), 442 (55), 390 (73), 301 (31), 126 (100).

X-ray Structure Determination of 4 and 7. The crystal structures of **4** and **7** were solved by direct methods. The non-hydrogen atoms were refined anisotropically on F^2. H atoms were refined isotropically using a riding model. A semi-empirical absorption correction on the basis of ψ-scans (**7**, $T_{min/max}$ = 0.651/0.807) was applied. In **4** the ethoxy group is disordered ($sof_{C35,C36}$ = 0.63(1)). For **7,** the absolute structure was determined (Flack's x-parameter −0.04(1)). Further details are given in Table 1. Programs used: SHELXTL-Plus, G. M. Sheldrick, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1989; SHELXL-93, G. M. Sheldrick, University of Göttingen, Germany, 1993.

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Supporting Information Available: Crystal structure data for **4** and **7**, including tables of crystal data and refinement details, atomic parameters, anisotropic displacement parameters, bond distances, and bond angles (14 pages). Ordering information is given on any current masthead page.

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