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Heterobimetallic Dibenzoindenyl ($Cr(CO)_3$—$Re(CO)_3$) Complexes via Chromium-Templated [3 + 2 + 1]Benzannulation: Synthesis and Molecular Structures

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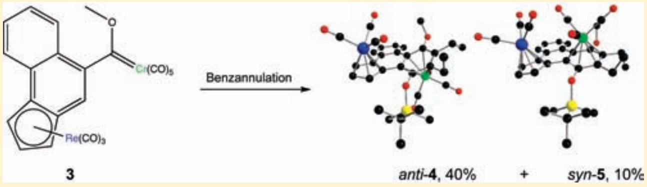
Supporting Information

ABSTRACT: Heterobimetallic (di)benzoindenyl Re—Cr complexes have been prepared by a sequence starting from (8-bromobenzo[*e*]-indenyl)potassium. Reaction with pentacarbonylrhenium bromide affords tricarbonylrhenium complex **2**, which has been modified to rhenium—chromium carbene complex **3**. Its chromium-templated [3 + 2 + 1]benzannulation afforded the anti($Cr(CO)_3$—$Re(CO)_3$) dibenzoindenyl complex **4** as the major product along with the syn diastereoisomer **5**. The molecular structures of all heterobimetallic complexes were established by X-ray analyses.



■ INTRODUCTION

Over the past decades organometallic complexes bearing two different metal centers have received increased interest due to potential cooperativity effects controlled by the nature of the two metal units.[1] However, in this context arene (Cr, Re) complexes have rarely been reported,[2] and to our knowledge, no study on an extended aromatic π system connecting these two metals is available. Thus, we decided to connect a tricarbonylrhenium moiety with a tricarbonylchromium unit via a dibenzoindenyl π bridge in order to study whether the extended aromatic platform allows communication between the different two metal fragments.[3] We based our synthetic strategy on the chromium-templated [3 + 2 + 1]benzannulation[4] of a Fischer arylcarbene bearing an additional tricarbonyl rhenium label—a methodology known for its regiodefined construction of arene $Cr(CO)_3$ complexes and its tolerance of additional organometallic functionalities.

■ RESULTS AND DISCUSSION

Synthesis of the aromatic platform started from 8-bromobenzo[*e*]-1*H*-indene **1e**, which was obtained in 57% overall yield using a five-step sequence (Scheme 1).[5,6] To incorporate the tricarbonylrhenium unit, we followed a procedure that we already successfully applied to the coordination of this fused arene to a tricarbonylmanganese moiety.[6] Deprotonation by potassium hydride in tetrahydrofuran and metalation by addition of pentacarbonylrhenium bromide at room temperature afforded the half-sandwich tricarbonyl{η^5-1,2,3,3a,9a-(8-bromobenzo[*e*]indenyl)}rhenium complex **2** as a yellow powder in low yield (Scheme 2).

The ^1H NMR spectra of **1e** and **2** reveal an upfield shift of 0.5—1.3 ppm for hydrogen atoms H2—H3 and a downfield shift of about 3.2 ppm for H1, indicating complexation of the cyclopentadienyl ring by the rhenium entity. Similarly, in the ^{13}C NMR spectra the resonance absorption of Cp carbon atom C1 is shifted downfield by 40 ppm, whereas the signals of carbon atoms C2/C3 and C3a/C9b are shifted upfield by 45—62 and 42—48 ppm, respectively. The coordination mode of the cyclopentadienyl part is further corroborated by a resonance absorption at 193.3 ppm corresponding to the three carbonyl ligands and by three typical IR bands at 2027 (s), 1936 (vs), and 1886 (vs) cm^{-1}. In comparison to the homologous tricarbonylmanganese complex,[6] the electron-withdrawing character of the rhenium moiety is increased as is apparent from the NMR signals of protons H1, H2, and H3 which are shifted downfield by about 1 ppm with respect to the manganese complex.

The transformation of the rhenium complex **2** into the chromium carbene **3** has to take into account that the bromobenzoindenyl—Re-$(CO)_3$ substitution pattern offers two competing electrophilic sites for reaction with an organolithium reagent. This problem has been overcome by the fact that at low temperature the halogen—metal exchange is significantly faster than the nucleophilic attack at the carbonyl ligand. Thus, sequential addition of *n*-butyl lithium and hexacarbonyl chromium to bromobenzoindenyl complex **2** at −78 °C resulted in formation of the desired acylchromate intermediate which upon *O*-alkylation with methyl triflate afforded the heterobimetallic pentacarbonyl {[1,2,3,3a,

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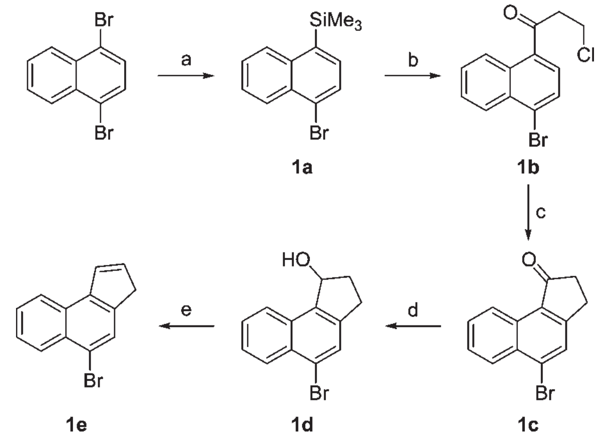
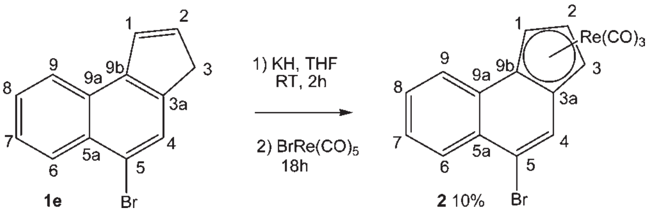
Scheme 1. Synthesis of 8-Bromobenzo[*e*]-1*H*-indene (1e)[a]

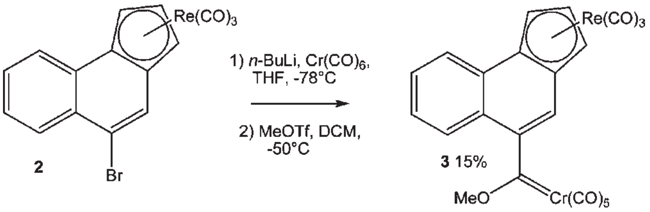


[a] Conditions: (a) (1) *n*-BuLi, Et_2O, −20°C, 2 h. (2) TMSCl, room temperauture, 15 min, 99%. (b) $AlCl_3$, $ClCH_2CH_2C(O)Cl$, DCM, −78 °C to room temperauture, 100 min, 96%. (c) $AlCl_3/H_2SO_4$, 70−98°C, 3 h, 83%. (d) $NaBH_4$, toluene/ethanol 5:3, overnight, 99%. (e) *p*-TsOH, toluene, 15 min, 73%.

Scheme 2. Synthesis of Tricarbonyl{8-bromobenzo-[*e*]indenyl}rhenium (2)



Scheme 3. Synthesis of {(Benzo[*e*]indenyl)rhenium}-chromium Carbene Complex 3



9-η^5-8-benzo[*e*]indenyl]tricarbonylrhenium(methoxy)carbene]}-chromium complex **3** as a dark red solid in 15% isolated yield (Scheme 3).

Dark red crystals of **3** suitable for X-ray analysis were grown from dichloromethane at 4 °C by slow evaporation of the solvent. The benzo[*e*]indenyl ligand is nearly planar with a torsion angle φ (C1−C9B−C9A−C9) = 2.84(4)°. The respective Re−C_{Cp} bond lengths indicate that the rhenium moiety is slightly shifted toward carbon atom C2 pointing away from the $Cr(CO)_5$ unit. The average distance between the metal atom and the five carbon atoms of the cyclopentadienyl ring is 2.32 Å, which is 0.17 Å longer than that found for the homologous tricarbonylmanganese complex.[6]

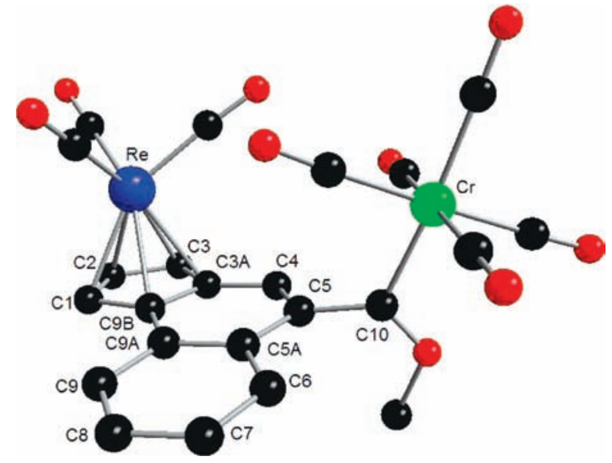


Figure 1. Molecular structure of benzoindenylrhenium-functionalized chromium carbene **3**. Selected bond lengths (Å): Re−C1 2.30(1), Re−C2 2.29(1), Re−C3 2.30(1), Re−C3A 2.35(1), Re−C13 2.36(1). Dihedral angle φ (C1−C9B−C9A−C9) = 2.84(4)°.

The carbene plane C5−C10−O is almost perpendicular to the arene platform, and the $Cr(CO)_5$ fragment adopts a syn position relative to the $Re(CO)_3$ moiety, most probably resulting from packing effects in the crystal (Figure 1 and Table 1).

Extension of the arene platform and its π coordination to the $Cr(CO)_3$ fragment was achieved by chromium-templated benzannulation of carbene complex **3** with 3-hexyne in TBME at 60 °C. Two diastereomers, first the anti isomer **4** and then the syn isomer **5**, were isolated from chromatographic workup in 40% and 10% yield, respectively, after *O*-protection with TBDMS triflate (Scheme 4).

Both diastereomers **4** and **5** show indistinguishable ν(CO) absorption bands and very similar ^{1}H and ^{13}C NMR spectra which only differ in details and do not allow a reliable assignment of the relative position of both metal fragments. As expected, mass spectra are characterized by a sequential loss of the carbonyl ligands. To establish unequivocally the molecular structure of the heterobimetallic complexes **4** and **5**, X-ray-suitable dark red crystals were grown from dichloromethane at 4 °C (**4**) and from diethyl ether at 4 °C (**5**). The average distance between the Re atom and the five C_{Cp} carbon atoms is about 2.31 (**4**) and 2.33 Å (**5**). In the syn diastereomer **5** the Re−C3A bond is elongated to 2.40 Å, suggesting a considerable steric interaction with the $Cr(CO)_3$ moiety; the $Cr(CO)_3$ tripod is eclipsed,[7a] as indicated by the different dihedral angles α1, α2, and α3, whereas an almost staggered conformation is observed for the anti diastereomer **4**[7b] (Figures 2 and 3 and Table 1).

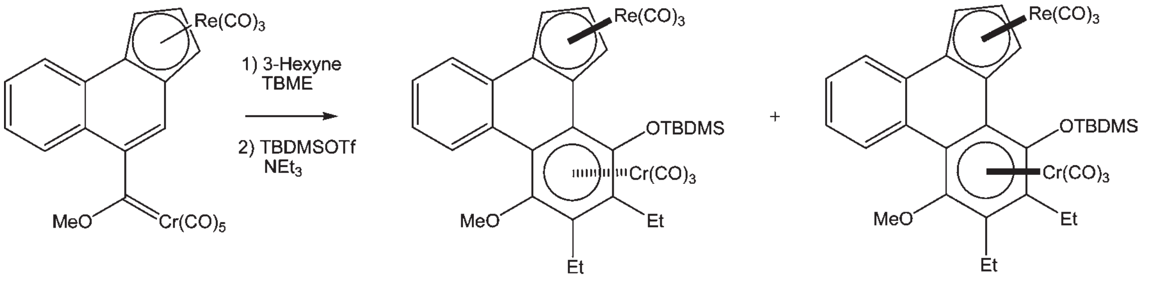
■ CONCLUSION

In summary, we demonstrated that a sequential heterobismetalation ($Re(CO)_3/Cr(CO)_3$) of a benzoindenyl platform can be based on a rhenation with $BrRe(CO)_5$ followed by transformation into a chromium arylcarbene complex and its subsequent benzannulation to afford syn and anti heterobimetallic complexes of a hydroquinoid dibenzo[*c*,*e*]indenyl skeleton. NMR and X-ray studies suggest that both metal fragments do not communicate with each other in the trans diastereomer, while a significant steric interaction results from the cis relationship in the syn diastereomer.

Table 1. Crystal Data and Structure Refinement Parameters for Complexes 3−5

	3	4	5
empirical formula	$C_{23}H_{11}CrO_9Re$	$C_{34}H_{35}CrO_8ReSi \cdot CH_2Cl_2$	$C_{34}H_{35}CrO_8ReSi \cdot 0.5Et_2O$
fw	669.52	837.92−84.93	837.92−1/2(74.12)
temp. [K]	123(2)	123(2)	123(2)
wavelength [Å]	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No.2)	$P2_1/c$ (No.14)	$P2_1/n$ (No.14)
unit cell dimensions			
a [Å]	6.6632(2)	14.6363(4)	11.6018(2)
b [Å]	7.6117(2)	14.0920(4)	15.0366(5)
c [Å]	21.2929(6)	19.1872(5)	21.1396(6)
α [deg]	86.9302(13)	90	90
β [deg]	83.6408(16)	112.4210(10)	98.7583(15)
γ [deg]	89.4973(16)	90	90
V [$Å^3$]	1071.75(5)	3658.29(17)	3644.84(17)
Z	2	4	2
D_{calcd} [mg/m^3]	2.075	1.676	1.594
μ [mm^{-1}]	6.204	3.830	3.669
$F(000)$	640	1832	1748
cryst size [mm]	0.64 × 0.20 × 0.16	0.50 × 0.48 × 0.20	0.64 × 0.14 × 0.14
diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
θ range [deg]	2.68−29.99	1.85−25.00	2.71−29.00
	$-9 \leq h \leq 9$	$-14 \leq h \leq 17$	$-15 \leq h \leq 15$
limiting indices	$-10 \leq k \leq 10$	$-16 \leq k \leq 16$	$-20 \leq k \leq 18$
	$-29 \leq l \leq 29$	$-22 \leq l \leq 14$	$-28 \leq l \leq 28$
reflns collected/unique	9732/4039	16 451/6147	25 464/9660
	[R(int) = 0.0781]	[R(int) = 0.0440]	[R(int) = 0.0461]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	5912/0/329	6147/0/433	9660/31/459
goodness-of-fit on F^2	1.015	1.193	0.918
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0242$	$R1 = 0.0259$	$R1 = 0.0270$
	$wR2 = 0.0520$	$wR2 = 0.0765$	$wR2 = 0.0470$
R indices (all data)	$R1 = 0.0274$	$R1 = 0.0328$	$R1 = 0.0453$
	$wR2 = 0.0527$	$wR2 = 0.0943$	$wR2 = 0.0501$
largest diff. peak and hole [eÅ^{-3}]	1.739 and −1.719	0.970 and −1.882	0.774 and −0.774
CCDC deposition number	705494	705495	705496

Scheme 4. Chromium-Templated Benzannulation of Benzoindenylrhenium-Functionalized Chromium Carbene 3



3 **4** 40% **5** 10%

■ EXPERIMENTAL SECTION

General. All experiments involving organometallic compounds were carried out under an argon inert gas atmosphere using standard Schlenk techniques. Solvents were distilled, dried using standard methods, saturated, and stored under argon. Degassed silica gel MN 60 (Macherey Nagel, 0.015−0.025 mm) was used for column chromatography. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 instrument at room temperature. IR spectra were obtained from a Nicolet Magna 550 FT spectrometer in petroleum ether. Mass spectra (FAB+ and EI) were

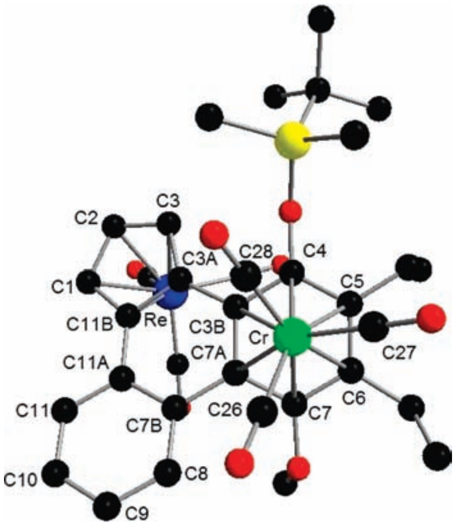


Figure 2. Molecular structure of *anti*-dibenzoindenyl (Cr−Re) complex **4**. Selected bond lengths (Å): Re−C1 2.31(1), Re−C2 2.30(1), Re−C3 2.29(0), Re−C3A 2.31(0), Re−C11B 2.33(0), Cr−C4 2.28(0), Cr−C5 2.24(0), Cr−C6 2.25(1), Cr−C7 2.25(1), Cr−C7A 2.23(0), Cr−C3B 2.33(1). Dihedral angles: α1 (C3B−Cr$_{proj.}$−Cr−C28) = −23.70(2)°, α2 (C5−Cr$_{proj.}$−Cr−C27) = −24.67(2)°, and α3 (C7−Cr$_{proj.}$−Cr−C26) = −22.63(2)°. Torsion angles: φ (C1−C11B−C11A−C11) = −12.10(3)°, φ1 (C7−C7A−C7B−C8) = 23.14(3)°, and φ2 (C3−C3A−C3B−C4) = 6.17(3)°.

recorded on a Kratos MS 50 spectrometer. Melting points were determined with a Reichert Austria apparatus. A Nonius KappaCCD diffractometer equipped with a low-temperature device (Oxford Cryosystems) using graphite-monochromated Mo Kα radiaton (λ = 0.71073 Å) was used for the X-ray crystallographic analyses of complexes **3**−**5**. The structures were solved using direct methods and refined by full-matrix least-squares techniques on F^2 using the ShelX program.[8] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions using a riding model. Crystallographic data as well as CCDC deposition numbers are listed in Table 1.

Tricarbonyl[1,2,3,3a,9-η^5-(8-bromobenzo[*e*]indenyl)]rhenium (2). KH (0.40 g, 10.0 mmol) was added to a solution of 8-bromobenzo[*e*]-1*H*-indene[6] (2.45 g, 10.0 mmol) in 50 mL of freshly distilled absolute THF, and the suspension was stirred under argon for 1 h at room temperature. Then BrRe(CO)$_5$ (4.06 g, 10.0 mmol) was added, and the reaction mixture was stirred under reflux for 4 h. After the solvent was stripped off, the residue was purified by column chromatography (petroleum ether/dichloromethane 3/1) at 5 °C to give 0.51 g of complex **2** (10%) as an air-sensitive yellow powder. Mp: 136 °C. IR (petroleum ether): ν(CO) 2027 (s), 1936 (vs), 1886 (vs) cm^{-1}. ^{1}H NMR (500 MHz, acetone-d_6): δ (ppm) 6.03 (1H, dd, ^3J = 2.8 Hz, ^3J = 2.8 Hz, H2), 6.15 (1H, dd, ^3J = 2.8 Hz, ^4J = 1.6 Hz, H3), 6.68 (1H, ddd, ^3J = 2.8 Hz, ^4J = 1.6 Hz, ^4J = 0.8 Hz, H1), 7.70−7.76 (2H, m, H5 and H6), 8.01 (1H, d, ^4J = 0.8 Hz, H9), 8.21 (1H, ddd, ^3J = 7.4 Hz, ^4J = 1.9 Hz, ^5J = 0.4 Hz, H4 or H7), 8.29 (1H, ddd, ^3J = 7.6 Hz, ^4J = 1.5 Hz, ^5J = 0.4 Hz, H4 or H7). ^{13}C NMR (125 MHz, acetone-d_6): δ (ppm) 72.7, 74.4, 90.0 (C1−C3), 102.8, 104.8 (C3a, C9a), 121.9 (ArC), 123.7, 124.1, 128.2 (3 ArCH), 128.4 (ArC), 128.7 (ArCH), 128.8 (ArC), 129.2 (ArCH), 193.3 (Re(CO)$_3$). MS (EI): *m*/*z* 513.9 [M$^+$, 73], 485.9 [M$^+$ − 1CO, 40], 457.9 [M$^+$ − 2CO, 9], 429.9 [M$^+$ − 3CO, 100].

Pentacarbonyl{[tricarbonyl-(1,2,3,3a,9b-η^5-(8-benzo[*e*]indenyl)rhenium](methoxy)carbene}chromium (3). Tricarbonyl[1,2,3,3a,9-η^5-(8-bromobenzo[*e*]indenyl)]rhenium (**2**) (0.40 g, 0.78 mmol) was dissolved in 30 mL of freshly distilled THF to give a yellow solution.

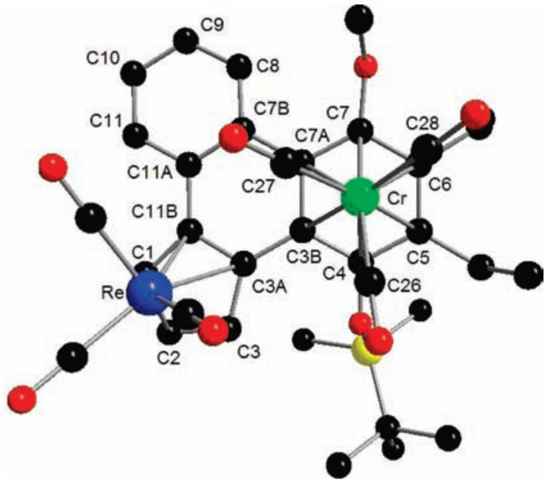


Figure 3. Molecular structure of *syn*-dibenzoindenyl (Cr−Re) complex **5**. Selected bond lengths (Å): Re−C1 2.30(1), Re−C2 2.28(0), Re−C3 2.31, Re−C3A 2.41, Re−C11B 2.34(0), Cr−C4 2.27(0), Cr−C5 2.24, Cr−C6 2.21(0), Cr−C7 2.24(1), Cr−C7A 2.30(1), Cr−C3B 2.22(0). Dihedral angles: α1 (C7A−Cr$_{proj.}$−Cr−C27) = 5.87(2)°, α2 (C6−Cr$_{proj.}$−Cr−C28) = 5.54(2)°, and α3 (C4−Cr$_{proj.}$−Cr−C26) = 6.48(2)°. Torsion angles: φ (C1−C11B−C11A−C11) = 5.93(4)°, φ1 (C7−C7A−C7B−C8) = 2.71(3)°, and φ2 (C3−C3A−C3B−C4) = 7.66(4)°.

At −78 °C a 2.5 M solution of *n*-BuLi in hexane (0.31 mL, 0.78 mmol) was added drop by drop, while the solution turned immediately brown. After 5 min Cr(CO)$_6$ (0.172 g, 0.78 mmol) was added, and the solution was allowed to reach 20 °C within 1 h. Then the solvent was stripped off in vacuo; the resulting brown oil was dissolved in 30 mL of dichloromethane and cooled down to −50 °C. Methyltriflate (0.246 g, 1.5 mmol) was added dropwise to the solution, which was then warmed to room temperature within 0.5 h and stirred for an extra hour. The solution became deep dark red. Chromatography on fine silica gel at 5 °C with petroleum ether/dichloromethane (3/1) afforded 0.078 g (0.116 mmol) of complex **3** as an air-sensitive dark red powder which undergoes decomposition upon heating to 140 °C. IR (petroleum ether): ν(CO) 2067 (vw), 2011 (s), 1971 (vw), 1936 (m), 1894 (vs) cm^{-1}. ^{1}H NMR (500 MHz, acetone-d_6): δ (ppm) 4.17 (3H, s, OCH$_3$), 5.30 (1H, pt, CpH), 5.78 (1H, pt, ^3J = 2.8 Hz, CpH), 5.90 (1H, m, CpH), 6.93 (1H, s, H9), 7.36 (1H, d, ^3J = 8.2 Hz, ArH), 7.56 (1H, m, ArH), 7.65 (1H, m, ArH), 8.07 (1H, d, ^3J = 8.1 Hz, ArH). ^{13}C NMR (125 MHz, acetone-d_6): δ (ppm) 66.6 (OCH$_3$), 75.4 (C1 and C3), 90.4 (C2), 112.9, 124.3, 126.3 (3 ArCH), 126.5, 128.1, 128.3 127.9 (4 ArC), 128.5, 129.3 (2 ArCH), 193.4 (Re(CO)$_3$), 216.1 (4 *trans*-Cr(CO)), 224.8 (1 *cis*-Cr(CO)), 356.2 (C10). MS (EI): *m*/*z* 670.0 [M$^+$, 39], 614.0 [M$^+$ − 2CO, 10], 586.0 [M$^+$ − 3CO, 3], 558.0 [M$^+$ − 4CO, 20], 530.0 [M$^+$ − 5CO, 100].

***anti*-Tricarbonyl{{tricarbonyl{7b,8,9,10,11,11a-η^6-[9,10-diethyl-8-methoxy-11-(*tert*-butyl)dimethylsilyloxy-[1,2,3,3a,11b-η^5-(dibenzo[*c*,*e*]indenyl)]rhenium}}chromium (4) and *syn*-{{Tricarbonyl{7b,8,9,10,11,11a-η^6-[9,10-diethyl-8-methoxy-11-(*tert*-butyl)dimethylsilyloxy-[1,2,3,3a,11b-η^5-(dibenzo[*c*,*e*]indenyl)]rhenium}}chromium (5).** A solution of carbene complex **3** (0.10 g, 0.15 mmol) and 3-hexyne (0.05 g, 0.60 mmol) in 5 mL of *tert*-butylmethylether was warmed to 65 °C (oil bath temperature) for 2 h. Then the phenolic group was protected at room temperature by addition of triethylamine (0.06 mL, 0.60 mmol) and *tert*-butyl-dimethylsilyl triflate (0.14 mL, 0.60 mmol). After stirring for 2 h, chromatography on fine silica gel at 5 °C with petroleum ether/dichloromethane (3/2) afforded first anti diastereomer **4** (0.050 g, 40%) followed by syn diastereomer **5** (0.012 g, 10%) as air-sensitive orange powders. Crystallization from dichloromethane at 4 °C gave crystals suitable for X-ray analysis. Major diastereomer **4**: mp 156 °C. IR (petroleum ether): ν(CO) 2011 (s), 1961 (w), 1892 (vs) 1866 (sh) cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) 0.44 (3H, s, $SiCH_3$), 0.63 (3H, s, $SiCH_3$), 1.15 (9H, s, $SiC(CH_3)_3$), 1.29 (3H, t, ^3J = 7.4 Hz, CH_2CH_3), 1.33 (3H, ^3J = 7.5 Hz, CH_2CH_3), 2.49−2.53 (2H, m, CH_2CH_3), 2.62 (1H, m, CH_2CH_3), 2.98 (1H, m, CH_2CH_3), 3.53 (3H, s, OCH_3), 5.64 (1H, pt, ^3J = 3.0 Hz, H2), 6.24 (1H, dd, ^3J = 3.0 Hz, ^4J = 1.7 Hz, H1 or H3), 6.74 (1H, dd, ^3J = 3.0 Hz, ^4J = 1.7 Hz, H1 or H3), 7.52 (1H, m, ArH), 7.58 (1H, m, ArH), 7.85 (1H, dd, ^3J = 7.6 Hz, ^4J = 1.3 Hz, ArH), 9.01 (1H, dd, ^3J = 8.5 Hz, ^4J = 0.9 Hz, ArH). ^{13}C NMR (125 MHz, CD_2Cl_2): δ (ppm) −2.0 ($SiCH_3$), 0.0 ($SiCH_3$), 15.3 (CH_2CH_3), 18.0 (CH_2CH_3), 19.4 ($SiC(CH_3)_3$), 20.2 (CH_2CH_3), 21.1 (CH_2CH_3), 26.3 ($SiC(CH_3)_3$), 61.8 (OCH_3), 75.1 (C2), 84.9 (C1 or C3), 85.7 (ArC), 86.2 (C1 or C3), 92.5, 103.8, 106.2, 107.5, 111.6, 120.0 (6 ArC), 123.7 (ArCH), 125.0 (ArC), 128.2, 128.4, 129.7 (3 ArCH), 130.1, 140.6 (2 ArC), 193.7 ($Re(CO_3)$), 234.0 ($Cr(CO_3)$). MS (EI): *m*/*z* 838.1 [M$^+$, 13], 754.1 [M$^+$ − 3CO, 100], 702.1 [M$^+$ − 3CO − Cr, 28]. Minor diastereomer **5**: mp 141 °C. IR (petroleum ether): ν(CO) 2009 (s), 1961 (w), 1892 (vs) 1866 (sh) cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) 0.25 (3H, s, $SiCH_3$), 0.29 (3H, s, $SiCH_3$), 1.05 (9H, s, $SiC(CH_3)_3$), 1.27 (3H, t, ^3J = 7.4 Hz, CH_2CH_3), 1.40 (3H, t, ^3J = 7.5 Hz, CH_2CH_3), 2.39 (1H, m, CH_2CH_3), 2.60 (1H, m, CH_2CH_3), 2.72 (1H, m, CH_2CH_3), 3.01 (1H, m, CH_2CH_3), 3.64 (3H, s, OCH_3), 5.56 (1H, s$_{br}$, CpH), 6.01 (1H, s$_{br}$, CpH), 6.72 (1H, s$_{br}$, CpH), 7.58 (1H, pt, ^3J = 8.1 Hz, ArH), 7.63 (1H, pt, ^3J = 7.2 Hz, ArH), 7.81 (1H, d, ^3J = 7.2 Hz, ArH), 9.00 (1H, d, ^3J = 8.1 Hz, ArH). ^{13}C NMR (125 MHz, CD_2Cl_2): δ (ppm) −1.4 ($SiCH_3$), −0.3 ($SiCH_3$), 15.2 (CH_2CH_3), 19.2 (CH_2CH_3), 19.3 ($SiC(CH_3)_3$), 20.4 (CH_2CH_3), 21.7 (CH_2CH_3), 26.2 ($SiC(CH_3)_3$), 64.5 (OCH_3), 72.2 (C2), 83.7, 85.1 (C1, C3), 90.4, 102.3, 104.7, 112.9 (4 ArC), 123.5(ArCH), 127.7, 128.2 (2ArC), 128.9 (ArCH), 129.6 (ArC), 129.9, 130.5 (2 ArCH), 140.1 (ArC), 193.5 ($Re(CO_3)$), 233.7 ($Cr(CO_3)$). MS (EI): *m*/*z* 838.1 [M$^+$, 57], 754.1 [M$^+$ − 3CO, 100], 702.1 [M$^+$ − 3CO − Cr, 86].

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ^{1}H and ^{13}C NMR spectra of compounds **2**−**5** and CIF files with listings of the crystallographic and structural data for complexes **3**-**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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