Tetrakis Fischer-Type Carbene Complexes:[1] Synthesis, Molecular Structure, and [3 + 2 + 1]-Benzannulation

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Tetrakis{pentacarbonyl[(methyleneoxy)phenylcarbene]chromium}methane (**3**) and tetrakis-{pentacarbonyl[(methyleneoxy)(2-methoxyphenyl)carbene]chromium}methane (**4**) have been synthesized from tetramethylammonium acylchromate precursors **1** and **2** and pentaerythritol by an acylation/alcoholysis sequence. The X-ray structure analysis of **3** established a distorted-tetrahedral structure, whereas an averaged regular tetrahedral arrangement is indicated for **3** and **4** by NMR spectroscopy in solution. Upon reaction with 3-hexyne the phenyl complex **3** underwent complete benzannulation at all four carbene centers. The reaction was only moderately diastereoselective, and resulted—after in situ silylation—in at least seven inseparable stereoisomers of tetrakis-$(CO)_3$Cr-coordinated tetrakis[1-((*tert*-butyldimethylsilyl)oxy)-2,3-diethyl-4-(methyleneoxy)naphthyl]methane. Oxidative demetalation gave an 80% yield of tetrakis[1-((*tert*-butyldimethylsilyl)oxy)-2,3-diethyl-4-(methyleneoxy)-naphthyl]methane (**5**). Benzannulation is blocked by increasing steric bulk of the arylcarbene ligand such as in the (2-methoxyphenyl)carbene complex analogue **4**.

Introduction

A major aim in the development and application of Fischer-type carbene complexes[2] in stereoselective synthesis and catalysis during the past three decades concentrated on the chiral modification of the carbene side chain.[3] Relevant work has focused almost exclusively on complexes which bear a single metal carbene moiety, and studies on more complex structures containing more than one carbene complex functionality are rare.[4] The growing importance of organometallic chemistry in macromolecular, supramolecular, and dendrimer chemistry[5] provides an obvious motif to multiply the scope and applications of metal carbenes. We recently focused on oligo(alkoxy)carbene chromium complexes derived from the tetrafunctional pentaerythritol skeleton which serves as a popular core in dendrimer synthesis. We now report both on the synthesis and molecular structure of these types of oligofunctional metal carbenes and on their application in chromium-mediated carbene benzannulation.[2,6]

Results and Discussion

Tetrakis{pentacarbonyl[(methyleneoxy)phenylcarbene]chromium}methane (3) and Tetrakis-{pentacarbonyl[(methyleneoxy)(2-methoxyphenyl)-carbene]chromium}methane (4). The most general synthetic routes to carbonyl carbene complexes are based on combinations of an organometallic electrophile and an organonucleophile[7] or vice versa,[8] leading to stable acylmetalate intermediates. Subsequent alkyla-

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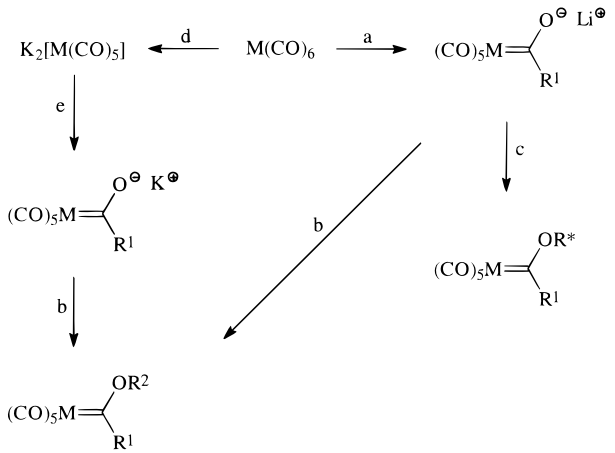
Scheme 1. Common Approaches to Fischer-Type Alkoxycarbene Complexes[a]

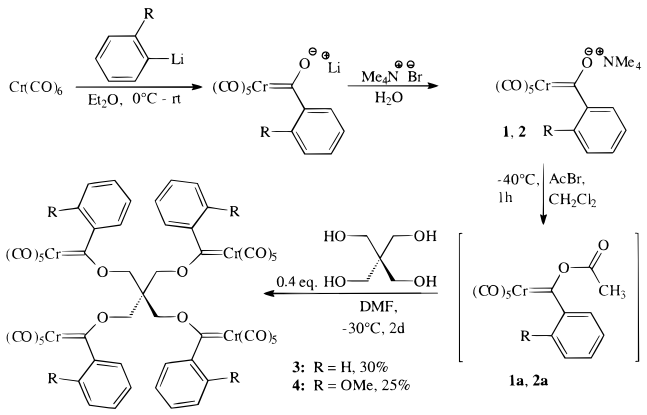


[a] Legend: (a) LiR^1; (b) $R^2{}_3O^+BF_4^-$ or $R^2SO_3CF_3$; (c) $NR^3{}_4{}^+Br^-$, RC(O)Cl, R*OH; (d) C_8K; (e) $R^1C(O)Cl$.

tion with hard C-electrophiles such as Meerwein salts or trifluoromethanesulfonic acid esters affords alkoxycarbene complexes (Scheme 1; paths a, b and d, e, b). Alternatively, acylation of tetramethylammonium acylmetalates, accessible from the lithium salts by in situ metathesis, generates even more electrophilic acyloxycarbene complexes, which undergo alcoholysis upon addition of primary and secondary alcohols[9] (Scheme 1; path a, c).

The latter sequence is the standard protocol for the synthesis of optically active carbene complexes based on chiral alcohol auxiliaries and has been exploited in diastereoselective Michael addition,[3a,10] Diels−Alder,[11] and benzannulation reactions.[3] We have applied this tandem acylation/alcoholysis methodology to the synthesis of tetrakis(alkoxy)carbene complexes **3** and **4** bearing the pentaerythritol core. Generally, dichloromethane is used as solvent for both the acylation of the tetramethylammonium chromate and the subsequent alcoholysis step. However, the strong inter- and intramolecular hydrogen bonds of pentaerythritol hamper its solubility in dichloromethane and prevented the desired alcoholysis of acyloxycarbene complexes **1a** and **2a**. Thus, an aprotic solvent was required which combines high polarity with inertness to the reaction conditions. Dimethylformamide, which complies with these requirements and which is able to dissolve pentaerythritol readily under ultrasonic conditions, turned out to be the solvent of choice. It allowed for the alcoholysis of acyloxycarbene complexes **1a** and **2a** to give moderate yields of tetrakis{pentacarbonyl[(methyleneoxy)arylcarbene]chromium}methane (**3**, 30%; **4**, 25%) (Scheme 2.).

Scheme 2. Synthesis of the Tetrakis(alkoxy)Carbene Complexes 3 and 4



Various attempts to further optimize the reaction conditions by variation of concentration and reaction time as well as by use of an excess of acylmetalate did not result in increased yields. It became obvious that the synthesis of oligo(alkoxy)carbene complexes differs from that of monofunctional alkoxycarbene complexes[9] and from synthetic strategies toward dendritic molecules.[5] Whereas the yields of monofunctional alkoxycarbene complexes generally increase by applying a properly moderate excess of the alcohol, the synthesis of the tetrakis(carbene) complexes **3** and **4** required a carefully adjusted, well-defined excess of acyloxycarbene complex intermediates. A more concentrated solution or a higher excess of the acyloxycarbene complexes lowered the yields of the oligo(alkoxy)carbene complexes and resulted in additional problems arising from the isolation and separation of these products from less stable byproducts. A smaller excess of acylmetalates could not be compensated by extended reaction times, and the oligo(alkoxy)carbene complexes were again obtained in decreased yields. Since the tetrakis(alkoxy) metal carbenes may be considered as first-generation dendritic molecules, a large excess of the acyloxycarbene intermediates is not advisable. However, such excesses are recommended for divergent dendritic syntheses to complete the reaction at all surface groups of a multifunctional core and to increase both the yields and the molecular monodispersity.

A single set of methylene signals observed in the ^1H NMR spectra of **3** and **4** at room temperature suggested an averaged regular tetrahedral structure (T_d) for the tetrakis(metal carbene) skeleton in solution at the NMR time scale (see Experimental Section). In contrast, X-ray analysis established a spheric distorted tetrahedron for the molecular structure of **3** in the solid state (Figure 1, Tables 1−3). The distortion may reflect, in part, crystal-packing effects and the steric bulk of the carbene moieties but may be also rationalized in terms of intermolecular hydrogen bonding[12] between aromatic hydrogen atoms and carbonyl ligands as well as of sporadic intermolecular attractive van der Waals interactions between carbonyl oxygen atoms that accomplish an intermolecular distance of approximately 2.85 Å, which is obviously lower than the summarized van der Waals radius of oxygen (3.0 Å). Both intermolecular

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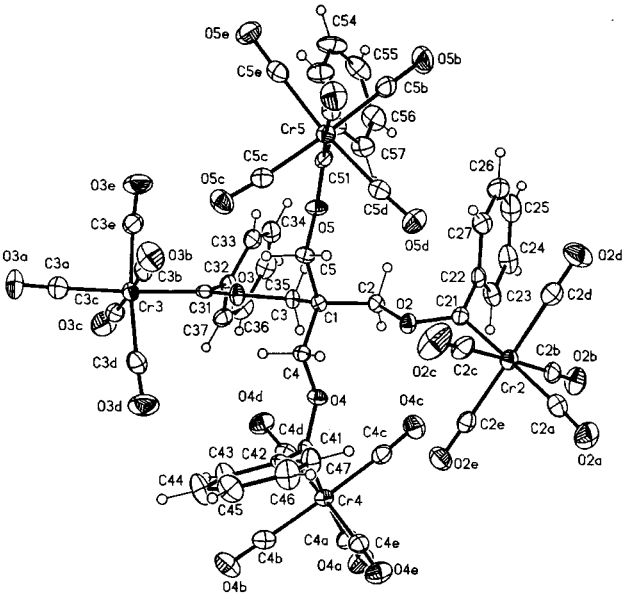


Figure 1. Molecular structure of tetrakis{pentacarbonyl-[(methyleneoxy)phenylcarbene]chromium}methane (**3**).

Table 1. Crystallographic Data for 3 and Summary of Data Collection and Refinement

formula	$C_{53}H_{28}Cr_4O_{24}$
fw	1256.75
cryst dimens, mm	0.25 × 0.15 × 0.05
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	12.9252(3)
b, Å	13.7727(5)
c, Å	17.7046(6)
α, deg	105.005(2)
β, deg	91.960(2)
γ, deg	116.727(2)
V, Å^3	2677.78(15)
Z	2
ρ_{calcd}, g cm^{-3}	1.559
μ, mm^{-1}	0.876
F(000)	1286
diffractometer	Nonius-Kappa-CCD
radiation; λ, Å	Mo Kα; 0.710 73
T, K	123(2)
max 2θ, deg	56.52
no. of data	46102
no. of unique data	12861
no. of variables	730
R1(*F*)	0.037
all data	0.0810
data with $I > 2\sigma(I)$	0.0373
wR2(F^2)	
all data	0.0732
data with $I > 2\sigma(I)$	0.0664

interactions suggest significant variations of the carbonyl C−O bond lengths.

The spheric distortion of the tetrakis(metal carbene) tetrahedron is already evident from the inequivalence of bond angles within the pentaerythritol core. The angles between the central carbon atom C1 and two opposite carbon neighbors C(2)−C(1)−C(3) = 103.99(16)° and C(4)−C(1)−C(5) = 105.62(16)° are distinctly smaller than their counterparts C(2)−C(1)−C(4) = 112.43(15)° and C(3)−C(1)−C(5) = 111.68(15)°. Closer to the periphery of the molecule the distortion becomes even more obvious; the angles between the central carbon atom and pairs of opposite chromium atoms Cr(2)−C(1)−Cr(3) = 166.4° and Cr(4)−C(1)−Cr(5) = 158.9° are in contrast to those formed by Cr(2)−C(1)−Cr(4) = 79.6° and Cr(3)−C(1)−Cr(5) = 98.9°. This distortion also reflects the inequivalency of two pairs of intramolecular atomic distances between the central carbon and the four carbene carbon atoms C(1)−C(21)/C(1)−C(31) ≈ 3.70/3.69 Å versus C(1)−C(41)/C(1)−C(51) ≈ 3.66/3.66 Å. The intramolecular atomic distances between the central carbon atom and the four chromium atoms vary within 0.5 Å (C(1)−Cr(2) ≈ 5.34 Å, C(1)−Cr(3) ≈ 5.21 Å, C(1)−Cr(4) ≈ 5.14 Å, C(1)−Cr(5) ≈ 4.88 Å), reflecting "soft" torsion angles which vary along the four-molecule axis (C(2)−O(2)−C(21)−Cr(2) ≈ −164.3°, C(3)−O(3)−C(31)−Cr(3) ≈ 174.8°, C(4)−O(4)−C(41)−Cr(4) ≈ 174.1°, and C(5)−O(5)−C(51)−Cr(5) ≈ 4.0°). Additional release of steric strain in the tetrakis(metal carbene) skeleton is provided by the persistent orthogonal orientation of the arene and carbene (Cr−$C_{carbene}$−O) planes within the carbene ligands. This rigid conformation of the arene rings collapses in solution at room temperature, as indicated by two pairs of a single set of signals for the *ortho* and *meta* aryl carbon atoms in the ^{13}C NMR spectra.

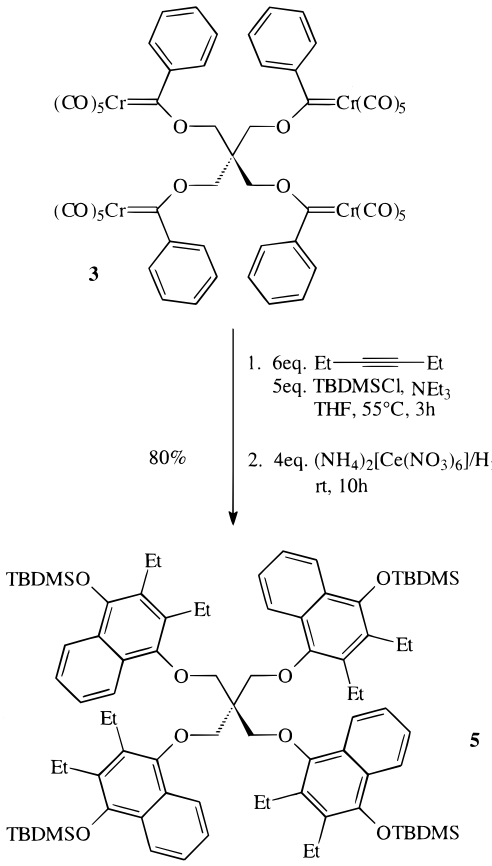
Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for 3

C(1)−C(2)	1.528(3)	C(1)−C(4)	1.530(3)
C(1)−C(3)	1.528(3)	C(1)−C(5)	1.534(3)
C(2)−C(1)−C(3)	103.99(16)	C(2)−C(1)−C(4)	112.43(15)
C(4)−C(1)−C(5)	105.62(16)	C(3)−C(1)−C(5)	111.68(15)
C(1)−C(21)	3.700(3)	C(1)−Cr(2)	5.338(2)
C(1)−C(31)	3.692(3)	C(1)−Cr(3)	5.209(2)
C(1)−C(41)	3.664(3)	C(1)−Cr(4)	5.136(2)
C(1)−C(51)	3.662(3)	C(1)−Cr(5)	4.880(2)
C(21)−C(1)−C(31)	159.4(2)	Cr(2)−C(1)−Cr(3)	166.4(2)
C(21)−C(1)−C(41)	89.4(2)	Cr(2)−C(1)−Cr(4)	79.6(2)
C(41)−C(1)−C(51)	164.7(2)	Cr(4)−C(1)−Cr(5)	158.9(2)
C(31)−C(1)−C(51)	93.6(2)	Cr(3)−C(1)−Cr(5)	98.9(2)
C(2)−O(2)−C(21)−Cr(2)		−164.32(13)	
C(3)−O(3)−C(31)−Cr(3)		174.80(13)	
C(4)−O(4)−C(41)−Cr(4)		174.12(13)	
C(5)−O(5)−C(51)−Cr(5)		4.0(3)	
O(2)−C(21)−C(22)−C(23)		−91.7(2)	
Cr(2)−C(21)−C(22)−C(27)		−94.1(2)	
O(3)−C(31)−C(32)−C(33)		−65.8(2)	
Cr(3)−C(31)−C(32)−C(37)		−68.3(2)	
O(4)−C(41)−C(42)−C(43)		108.7(2)	
Cr(4)−C(41)−C(42)−C(47)		106.0(2)	
O(5)−C(51)−C(52)−C(53)		−34.4(3)	
Cr(5)−C(51)−C(52)−C(57)		−40.3(3)	
C(21)−Cr(2)	1.9905(19)	C(3C)−O(3C)	1.139(3)
C(31)−Cr(3)	1.985(2)	C(3D)−O(3D)	1.139(2)
C(41)−Cr(4)	1.997(2)	C(3E)−O(3E)	1.141(2)
C(51)−Cr(5)	2.039(2)	C(4A)−O(4A)	1.139(2)
d(C═O)	1.130(3)−1.152(2)	C(4B)−O(4B)	1.142(3)
C(2A)−O(2A)	1.152(2)	C(4D)−O(4D)	1.144(2)
C(2E)−O(2E)	1.142(2)	C(5A)−O(5A)	1.147(2)
C(3A)−O(3A)	1.137(3)	C(5B)−O(5B)	1.130(3)
C(3B)−O(3B)	1.143(3)	C(5E)−O(5E)	1.146(2)

Table 3. Intermolecular Distances of Potential Hydrogen Bonds and van der Waals Interactions (Å) for 3

O(2E)−H(35)	2.734	O(5B)−H(45)	2.544
O(3B)−H(54)	2.701	O(5E)−H(33)	2.607
O(3C)−H(27)	2.623	O(5B)−O(3E)	2.836
O(3D)−H(55)	2.721	O(3E)−O(5B)	2.836
O(4A)−H(57)	2.597	O(5A)−O(3A)	2.916
O(4B)−H(25)	2.618	O(3A)−O(5A)	2.916
O(4D)−H(23)	2.690		

Scheme 3. Multiple Benzannulation of Tetrakis(alkoxy)carbene Complex 3



Multiple Benzannulation to Tetrakis[(1-((*tert*-butyldimethylsilyl)oxy)-2,3-diethyl-4-(methyleneoxy)naphthyl]methane (5). Upon gentle warming in THF to 55 °C in the presence of an excess of 3-hexyne, tetrakis{pentacarbonyl[(methyleneoxy)phenylcarbene]-chromium}methane (**3**) underwent complete benzannulation at all four carbene moieties. In situ protection of the naphthol intermediate by *tert*-butyldimethylsilyl chloride followed by oxidative demetalation with an aqueous solution of cerium(IV) ammonium nitrate gave an 80% yield of tetrakis[(1-((*tert*-butyldimethylsilyl)oxy)-2,3-diethyl-4-(methyleneoxy)naphthyl]methane (**5**) (Scheme 3).

Attempts to protect the oxidation-sensitive naphthol intermediate in a separate step after its formation resulted in decomposition to give 2,3-diethyl-1,4-naphthoquinone. As already stated for the synthesis of the tetrakis(alkoxy)carbene precursors **3** and **4**, the benzannulation of **3** is similarly sensitive to variations of the reaction parameters, especially to changes of the alkyne excess and the reaction temperature. Both a larger excess of alkyne and an increased temperature (refluxing in THF at 65 °C) distinctly diminished the yields to about 20%. Obviously, the increased rate of formation of the naphthol intermediates is overcompensated by their accelerated oxidative decomposition as a result of their slower protection reaction. Generally, the [3 + 2 + 1]-benzannulation of alkoxycarbene complexes generates $(CO)_3$Cr-complexed naphthohydroquinones bearing a chiral plane. Diastereoselective benzannulation protocols have been developed that are based on chiral alkoxy auxiliaries,[3b] on unsaturated carbene carbon side chains[13] or on α-chiral propargylic ethers.[14] Whereas these strategies allow, in part, synthetically useful diastereoselectivities for mono(carbene) systems, an extension to bis(carbene) complexes turned out to be crucial. The bis-benzannulation of BINOL-based bis-(carbene) chromium complexes only gave disappointingly low diastereomeric excess (de) values.[4a] A similarly modest diastereoselection has been observed for the benzannulation of the tetrakis(alkoxy)carbene complex **3** by 3-hexyne. ^{13}C NMR spectra of the crude product revealed the formation of at least seven diastereomers, which hampered their separation by chromatographic techniques and, instead, encouraged us to destroy the chiral plane by oxidative demetalation.

Upon gentle warming in solution or under solid-state high-vacuum conditions pentacarbonyl[alkoxy(2-methoxybenzylidene)]chromium complexes are known to undergo decarbonylation and subsequent chelation of the methoxy substituent to give tetracarbonylmetal carbene chelates[15] which represent chelation-stabilized model complexes for the first intermediate in the [3 + 2 + 1]-benzannulation.[16] We speculated whether the dense packing of the carbene moieties on the molecular surface and the rigid conformation of the tetrakis(metal carbene) complexes as demonstrated by the spheric molecular structure of **3** would still allow a stable coplanar conformation of a (2-methoxyphenyl)carbene ligand, resulting in an *o*-anisylcarbene chromium chelate. However, our attempts to induce decarbonylation and chelation both under standard solution-state (55−65 °C, THF) and dry-state conditions (70 °C, 10^{-3} bar) were unsuccessful and, rather, resulted in slow decomposition of the pentacarbonyl precursor complex **4**. This result suggests that the steric bulk of the anisylcarbene ligand is not compatible with the coplanar conformation required for chelation.

Conclusion

We have demonstrated that spheric oligofunctional alcohols such as pentaerythritol may serve as dendritic cores for tetrakis(alkoxy)carbene complexes. These compounds are accessible by a modified Fischer route based on an acylation/alcoholysis sequence which requires strictly defined reaction conditions. The reaction of tetrakis(alkoxy)phenylcarbene complex **3** with 3-hexyne results in complete benzannulation but proceeds with only poor diastereoselectivity. The diastereomeric $(CO)_3$Cr-coordinated benzannulation products undergo oxidative demetalation to give spheric tetrakis(naphthohydroquinone) assemblies which represent promising

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building blocks for functional supramolecular structures such as cages and siderophores.[17]

Experimental Section

All operations involving organometallic compounds were carried out under argon using Schlenk techniques. Solvents were dried by using standard methods, distilled, saturated, and stored under argon. Merck silica gel 60 (0.063−0.200 mm) used for column chromatography was degassed at high vacuum and stored under argon. ^{1}H and ^{13}C NMR: Bruker DRX-500. FT-IR: Nicolet Magna 550. MS (FAB): Kratos Concept 1H. Tetramethylammonium [benzoyl(pentacarbonyl)]chromate (**1**) and tetramethylammonium [2-methoxybenzoyl(pentacarbonyl)]chromate (**2**) were prepared according to methods reported previously. NMR spectra were recorded in acetone-d_6 if not stated otherwise.

General Procedure for the Synthesis of the Tetrakis(alkoxy)carbene Complexes 3 and 4. A yellow suspension of 10 mmol (2.5 equiv) of tetramethylammonium [benzoyl(pentacarbonyl)]chromate (**1**) or tetramethylammonium [2-methoxybenzoyl(pentacarbonyl)]chromate (**2**) in 20 mL of CH_2Cl_2 was cooled to −40 °C. After addition of an equimolar amount of acetyl bromide the color changed to dark red. The suspension was stirred about 0.5 h to complete the reaction. A solution of 1 mmol (1 equiv) of pentaerythritol in 50 mL of dimethylformamide (prepared under ultrasonic conditions) was added within 3 h at −35 °C. The reaction mixture was stirred for 2 days at −30 °C while the color changed again to dark orange. At the same temperature 50 mL of diethyl ether was added, and the solution was washed three times with argon-saturated water (cooled to 0 °C) to extract dimethylformamide, unstable byproducts, and tetramethylammonium bromide. Then the organic solvents were stripped off, and the dark red residue was purified by column chromatography at 5 °C using a petroleum ether/dichloromethane (5:3) mixture as eluent.

Tetrakis{pentacarbonyl[(methyleneoxy)phenylcarbene]chromium}methane (3). Chromatography yielded 309 mg (30 mmol, 30%) of **3** as a red amorphous solid. Crystallization from petroleum ether at −30 °C gave red crystals. R_f = 0.70 (5:3 petroleum ether/CH_2Cl_2). ^{1}H NMR (500 MHz): δ 5.37 (s, 8H, CH_2), 7.03, 7.43 (2m, 20H, Ar H). ^{13}C NMR (125 MHz): δ 47.3 ($C(CH_2)_4$), 78.1 (CH_2), 122.3 (*p*-Ar C), 129.4, 131.0 (*m*-Ar C, *o*-Ar C), 154.0 (*ipso*-Ar C), 216.5 (*cis*-CO), 225.2 (*trans*-CO), 354.5 (carbene C). FT-IR (cm^{-1}, PE): ν_{CO} 2065 (m, $A_1$1), 1957 (vs, E + $A_1$2). MS (FD): calcd for $C_{53}H_{28}O_{24}Cr_4$ (M^+) *m*/*z* (%) 1259.9 (10), 1258.9 (30), 1257.9 (64), 1256.9 (100), 1255.9 (100), 1254.9 (17), 1253.9 (19); found for M^+ *m*/*z* (%) 1260.2 (10), 1259.2 (33), 1258.2 (75), 1257.1 (100), 1256.1 (100), 1255.3 (16), 1254.1 (13).

Tetrakis{pentacarbonyl[(methyleneoxy)(2-methoxyphenyl)carbene]chromium}methane (4). Chromatography yielded 305 mg (25 mmol, 25%) of **4** as a red viscous oil. R_f = 0.68 (5:3 petroleum ether/CH_2Cl_2). ^{1}H NMR (500 MHz): δ 3.70, 3.76, 3.83, 3.89 (4s, 12H, OCH_3), 4.76 (s, 8H, CH_2), 7.10, 7.43 (2m, 16H, Ar H). ^{13}C NMR (125 MHz): δ 45.9 ($C(CH_2)_4$), 56.1 (OCH_3), 76.0 (CH_2), 112.5 (*m*-Ar C), 121.8 (*m*-Ar C, *o*-Ar C), 131.4 (*ipso*-Ar C, *o*-Ar C, *p*-Ar C), 216.5 (*cis*-CO), 225.9 (*trans*-CO), 356.8 (carbene C). FT-IR (cm^{-1}, PE): ν_{CO} 2064 (m, $A_1$1), 1987 (w, B), 1965.9 (s, E), 1957 (vs, $A_1$2). MS (FAB): *m*/*z* (%) 1065 ($M^+ - (CO)_5CrCC_6H_4OCH_3$, 32), 956 ($M_{1065}{}^+ - 15CO$, 14), 844 ($M_{1065}{}^+ - 19CO$, 37), 816 ($M_{1065}{}^+ - 20CO$, 40), 765 ($M_{1065}{}^+ - (CO)_5CrC_6H_4OCH_3 - H$, 65), 646 ($M_{816}{}^+ - CrCC_6H_4OCH_3$, 20), 460 ($M_{646}{}^+ - CrCOC_6H_4OCH_3$, 100).

Tetrakis[1-((*tert*-butyldimethylsilyl)oxy)-2,3-diethyl-4-(methyleneoxy)naphthyl]methane (5). A 165 mg (0.13 mmol) amount of tetrakis{pentacarbonyl[(methyleneoxy)-phenylcarbene]chromium}methane (**3**), 0.36 mL (3.14 mmol, 6 equiv) of 3-hexyne, and a solution of 393 mg (2.6 mmol, 5 equiv) of *tert*-butyldimethylsilyl chloride in 0.73 mL (5.2 mmol, 10 equiv) of triethylamine were dissolved in 6 mL of THF. The solution was degassed by freeze−pump−thaw cycles and stirred at 55 °C for 3 h. Then a solution of 288 mg (2.1 mmol, 4 equiv) of cerium(IV) ammonium nitrate in 5 mL of H_2O was added. The mixture was stirred at room temperature for 10 h, the solvents were removed, and the product was purified by column chromatography (silica gel, 5:3 dichloromethane/petroleum ether) to give 144 mg (80%) of a white solid. R_f = 0.62 (5:3 dichloromethane/petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.15 (s, 24H, $Si(CH_3)_2$), 1.05 (m, 24H, CH_3), 1.58 (s, 36H, $SiC(CH_3)_3$), 2.77 (m, 16H, CH_2), 4.87 (s, 8H, $C(CH_2)_4$), 7.97, 8.37 (dm, 16H, Ar H). ^{13}C NMR (125 MHz, $CDCl_3$): δ −3.1 (2 $(H_3C)_2Si$), 14.1, 14.9 (CH_3), 18.7 (SiC), 20.3, 20.4 (CH_2), 26.1 ($SiC(CH_3)_3$), 47.1 ($C(CH_2)_4$), 74.8 (H_2CO), 122.2, 123.1, 123.9, 124.9, 127.3, 127.4, 129.4, 132.6, (8C, Ar C), 144.9, 146.8 (2C, Ar C−O). MS (FAB): *m*/*z* (%) 1386 (M^+, 8), 1072 ($M_{1386}{}^+ - C_{14}H_{14}OSiMe_2tBu$, 97), 760 ($M_{1386}{}^+ - 2\ C_{14}H_{14}OSiMe_2tBu$, 15), 431 ($M_{760}{}^+ - C_{14}H_{14}O_2SiMe_2tBu$, 18), 329 ($C_{14}H_{14}O_2SiMe_2tBu^+$, 100), 314 ($C_{14}H_{14}OSiMe_2tBu^+$, 27).

X-ray Analysis of 3. Crystallization of **3** from petroleum ether at −30 °C afforded red crystals which were subjected to single-crystal X-ray analysis. The structure was solved by direct methods (SHELXS-97).[18a] The non-hydrogen atoms were refined anisotropically on F^2 (SHELXL-97).[18b] Hydrogen atoms were refined using a riding model. Further details are given in Tables 1−3 and Figure 1.

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Supporting Information Available: Structural drawings of **3**−**5** and tables of X-ray crystallographic data, atomic coordinates, hydrogen atom coordinates, anisotropic thermal parameters, and interatomic distances and angles for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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