Synthesis and Characterization of Amphiphilic Azobenzene Sugar Chromium Carbenes

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The azobenzene-functionalized Fischer carbene complexes **5a**−**c** have been synthesized using organozinc compounds generated in situ by lithium/zinc exchange. Aminolysis of the 4′-substituted methoxycarbene complexes **5a** and **5b** with an amino sugar derivative yields aminocarbene complexes, which can be deprotected under mild conditions to give the amphiphilic azobenzene Fischer carbene complexes **1a** and **1b**. The spectroscopic properties and the aggregation behavior of the target compounds in the gas phase have been studied using ESI-MS.

Introduction

Azobenzene compounds have been intensively studied for almost 150 years. They are widely and commercially used as dyes and, more recently, have been applied to photoresponsive molecular switches and materials. They have found broad application in nonlinear optics, optical storage media, polymer chemistry, chemosensors, and optical switches.[1] They also allow for the control of self-aggregation phenomena.[2] Azo transition-metal complexes represent an interesting field of azobenzene chemistry,[3] as they combine the optical, redox, and magnetic properties of the metal complex with the photoisomerization properties of the azo function. To the best of our knowledge, there is only a single report of an azobenzene-containing chromium complex, so far.[4] Our research interest is focused on the chemistry of group VI carbene complexes, which are widely applied as reagents for organic synthesis.[5] The [3+2+1]-benzannulation reaction of aryl- or vinylcarbene chromium complexes with alkynes provides direct access to functionalized benzenoids and fused arenes selectively labeled with a $Cr(CO)_3$ fragment.[6] These $Cr(CO)_3$ complexes are valuable reagents in asymmetric synthesis due to their planar chirality.[7] Moreover, they undergo thermally or coligand-controlled haptotropic metal migrations which may be applied to organometallic switches.[8] Fischer-type carbene complexes are also suited for the organometallic functionalization of carbohydrates.[9] Recently, we described a class of amphiphilic carbohydrate-functionalized Fischer carbene complexes which are able to form gels in aromatic and chlorinated solvents by three-dimensional self-aggregation.[10] Extending this approach, we concentrated on the incorporation of an azobenzene moiety as the hydrophobic part of the molecule and aimed at the synthesis of carbene complexes **1a** and **1b** (Scheme 1).

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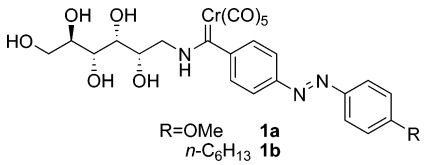
Scheme 1. Amphiphilic Azobenzene Metal Carbenes



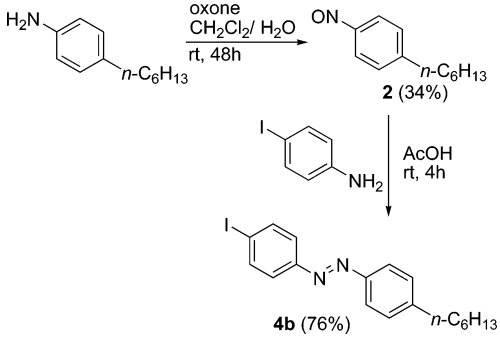
Results and Discussion

The synthesis of azobenzene-functionalized Fischer carbene complexes represents a synthetic challenge resulting from the high reactivity of the azo functionality toward the nucleophilic and reducing reagents applied in the protocols of metal carbene synthesis. Among several options for the synthesis of these complexes, the classical Fischer route,[11] based on the subsequent addition of an organolithium nucleophile and an electrophile across a carbonyl ligand, appeared to be the most attractive approach. An alternative strategy via the Semmelhack−Hegedus route[12] turned out to be unsuccessful.

Undesired side reactions between the nucleophile and the azo group have to be considered. Organolithium reagents are known to add to the azo function even at low temperatures (−78 °C),[13] a reaction which has been used for the selective synthesis of tri- and tetrasubstituted hydrazines.[14] Less reactive organometallic compounds (M = Zn, Mn) do not react under these conditions, but lead to reduction products when applied at higher temperatures.[15] Upon reaction with organolithium compounds electron-rich azobenzene derivatives (4-(dimethylamino)azobenzene) undergo alkylation at the 2-position instead of addition to the N=N double bond, while 4-methoxyazobenzene affords mixtures of *N*- and ortho-lithiation products under these conditions.[16] Despite these possible side reactions, the synthesis of lithiated azobenzene derivatives, required as starting materials for the Fischer chromium carbene synthesis, by halogen lithium exchange could be achieved at very low temperatures (−100 °C).[17] Subsequent low-temperature transmetalation upon zinc[18] is expected to form highly functionalized organozincs,[19] which—compared to organolithium reagents—are less reactive but offer the chance for the selective formation of the acyl metalate.

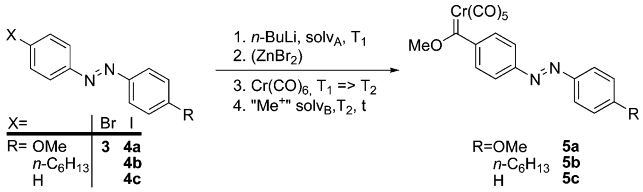
Synthesis of Haloazobenzene Precursors. For the carbene synthesis following the Fischer route a set of 4′-substituted 4-bromoazobenzenes (**3**, R′ = OMe) and 4-iodoazobenzenes (**4a**−**c**, R = OMe, *n*-C_6H_{13}, H) have been synthesized. The methoxyazobenzenes were prepared by azo coupling of the appropriate haloaniline with phenol and subsequent *O*-alkylation under standard conditions. For the preparation of the *n*-C_6H_{13}-substituted iodoazobenzene (**4b**), 4-hexylnitrosobenzene (**2**) was synthesized by oxidation of 4-hexylaniline.[20] Acid-catalyzed coupling of **2**, respectively nitrosobenzene, with 4-iodoaniline yielded the azobenzene precursors **4b** and **4c** (Scheme 2).

Scheme 2. Synthesis of Iodoazobenzene Derivative 4b



Synthesis of Azobenzene Chromium Carbenes. The synthesis of carbene complexes **5a**−**c** requires conditions for the Fischer protocol carefully adjusted to the substitution pattern of the azobenzene precursor. The methoxy-substituted chromium carbene **5a** is accessible from 4-bromoazobenzene **3** using standard conditions such as bromine/lithium exchange with *n*-BuLi at −78 °C in THF, addition of hexacarbonylchromium at this temperature, warming to −10 °C, solvent exchange to CH_2Cl_2, and methylation with Meerwein's salt (Scheme 3, entry 1). Alternative alkylation protocols did not improve the yield: Methylation with methyl triflate afforded even slightly lower yields, whereas methylation in water failed completely due to the low water solubility of the acyl metalate. In all cases, the formation of a complex mixture of intensively colored side products was observed. GC/MS analysis indicated the formation of different isomers of substituted hydrazines along with the dehalogenated azo compound.

Scheme 3. Synthesis of the Azobenzene-Functionalized Fischer Methoxycarbene Complexes



	R	X	$solv_A$	T_1 [°C]	$ZnBr_2$	"Me^+"	$solv_B$	T_2 [°C]	t [h]	cy [%]
1	OMe	Br	THF	-78	-	Me_3OBF_4	CH_2Cl_2	-10	16	24
2	OMe	Br	THF	-78	-	Me_3OBF_4	H_2O	rt	0.5	--
3	OMe	Br	THF	-78	-	MeOTf	CH_2Cl_2	-20	16	19
4	OMe	I	THF	-100	+	Me_3OBF_4	CH_2Cl_2	-10	16	22
5	*n*-C_6H_{13}	I	Et_2O	-100	+	Me_3OBF_4	CH_2Cl_2	rt	3	36
6	*n*-C_6H_{13}	I	THF	-78	+	Me_3OBF_4	CH_2Cl_2	-10	16	--
7	H	I	Et_2O	-100	+	Me_3OBF_4	CH_2Cl_2	rt	3	28
8	H	I	Et_2O	-100	-	Me_3OBF_4	CH_2Cl_2	rt	3	--
9	H	I	THF	-100	+	Me_3OBF_4	CH_2Cl_2	rt	3	--

When these standard conditions were applied to the synthesis of complexes **5b** and **5c**, no carbene complex could be isolated; only the formation of the mentioned side products was observed. Obviously, the addition of the organolithium compound to the azo group becomes predominant for the less electron-rich azobenzenes **4b** and **4c**.

These chromium carbene complexes, however, are accessible using a modified protocol. The iodine/lithium exchange in diethyl ether at −100 °C was found to avoid undesired side reactions, and upon addition of butyl lithium, nearly no color change of the slightly orange solution, characteristic of the addition to the azo group, is observed. In contrast, THF activates the organolithium nucleophile, and a color change to deep red indicates reduction of the azo group (Scheme 3, entries 6 and 9). The reactivity of the organometallic nucleophile can be adjusted by transmetalation to zinc. Low-temperature addition

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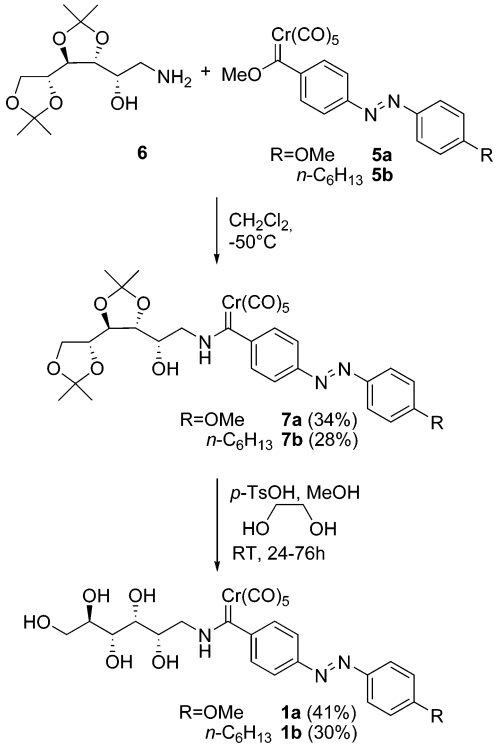
of the organozinc intermediate to hexacarbonylchromium followed by *O*-alkylation afforded the desired carbene complexes. The reaction conditions, e.g., the choice of solvent and the transmetalation, are crucial to obtain the products in moderate yields.

Synthesis of Amphiphilic Azobenzene Chromium Carbenes. The hydrophilic functionalization of the azo carbene chromium complexes was addressed by *O*-protected aminosugar derivatives. Low-temperature aminolysis of methoxycarbene complexes **5a**,**b** with glucamine derivative **6** afforded moderate yields of chromium glucose aminocarbenes **7a**,**b** (Scheme 4).

Scheme 4. Aminolysis and Deprotection of the Methoxycarbene Complexes 5a,b



While TLC analysis immediately after aminolysis revealed two colored spots and IR spectra suggested a clean formation of the desired pentacarbonyl aminocarbene complexes, a complex mixture of products was observed after evaporation of the solvent under reduced pressure, indicating partial decomposition. Chromatographic workup afforded single diastereomers of sugar aminocarbene complexes **7a**,**b**. This result may be rationalized in terms of initial formation of *E*/*Z*-isomers with respect to the $C_{carbene}-N$ bond[21] followed by preferred decomposition of one stereoisomer to give tetracarbonyl complex intermediates as suggested by IR monitoring. Only the *Z*-isomer can adopt a geometry required for chelation,[22] which may assist the decomposition. This idea is in line with NMR spectroscopic observations resulting from solvent-dependent shifts for the NCH_2 protons. The shift differences found in an anisotropic solvent (C_6D_6) and an isotropic solvent ($CDCl_3$) for the *E*-isomers have been reported to exceed those observed for the *Z*-isomers.[23] On the basis of this argument and the relatively large shift differences of $\Delta\delta = 0.80$ and 0.55 ppm for the two diastereotopic NCH_2 protons, we propose a preferred decomposition of the *Z*-isomer assisted by *O*-chelation after decarbonylation while the *E*-isomer could be isolated.

The deprotection of the sugar hydroxy groups requires a mild protocol, which is compatible with the metal carbene functionality. The standard methodology based on an acid-catalyzed cleavage of the isopropylidene groups[24] is hampered by the tendency of aminocarbene complexes to form iminium halo pentacarbonyl metalates upon reaction with mineral acids.[25] In our hands, *p*-toluenesulfonic acid, generating a virtually nonnucleophilic conjugate base, when applied in methanolic solution and in the presence of excess ethylene glycol[26] turned out as the reagent of choice and afforded moderate yields of the chromium carbene amphiphiles **1a**,**b** (Scheme 4). The absence of ethylene glycol results in an only partial deprotection to give the 4′-substituted pentacarbonyl[(4-[(*E*)-(phenyl)diazenyl]phenyl)(3:4-*O*-isopropylidene-D-glucamino)-1-ylidene]chromium.

Photoisomerization and Aggregation Behavior of Azobenzene Chromium Aminocarbenes. The azobenzene chromophore reveals two characteristic UV absorptions at approximately 355 and 245 nm indicative of the $\pi-\pi^*$ transition of the azo group and of electronic transitions in the arene ring.[27] The higher intensity band nearly coincides with the predominant UV transition—reflecting a ligand to metal charge transfer—in aminocarbene complexes,[10,28] which show an additional low-intensity absorption at approximately 355 nm (metal to ligand transfer) as illustrated for the amino(glycosyl)carbene complex **9** (Figure 1a). The incorporation of the azo functionality into the chromium carbene **1a** imposes a strong UV response in these two regions, the bathochromic one being of particular interest for a switch of the *E*/*Z* isomerization in azobenzenes.[1−3] The *E* to *Z* photoisomerization of the azobenzene moiety in solution could be achieved by UV irradiation ($320 \text{ nm} < \lambda < 370 \text{ nm}$), revealing a progressive change in the UV/vis spectra (Figure 1b). A decrease in the band at 355 nm ($\pi-\pi^*$ transition) is accompanied by a slight increase of the very weak $n-\pi^*$ band at 450 nm. A photostationary state was observed after 3 min of irradiation. IR spectra of the irradiated solutions remained unchanged, indicating the stability of the pentacarbonylchromium carbene moiety under these conditions.

A prominent feature of amphiphilic molecules is their tendency to undergo aggregation, and ESI mass spectrometry is a powerful tool to study these properties in the gas phase.[29] Recently, we have applied this technique to carbohydrate-functionalized chromium aminocarbene organogelators,[30] which were found to form aggregates up to triply charged dodecamers.

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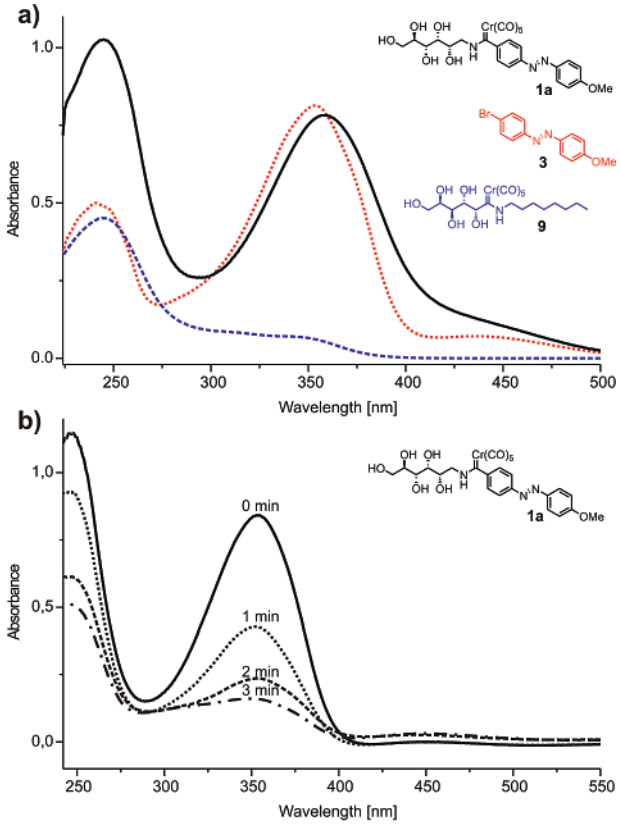

Figure 1. (a) UV/vis spectra of azobenzene **3** and aminocarbene complexes **1a** and **9** (3×10^{-5} mol/L, **3** and **1a** in $CHCl_3$, **9** in MeCN). (b) Time-dependent UV/vis spectra of **1a** (3×10^{-5} mol/L in CH_2Cl_2) after irradiation with UV light ($320 < \lambda < 370$ nm).

The mass spectrum of **1a** recorded in methanol also revealed an—even though less pronounced—aggregation (Figure 2). The most intense signal arises from the deprotonated carbene complex, $[M - H]^-$, but in addition, signals for aggregates up to pentamers, $[5M - H]^-$, have been detected. Each signal of the deprotonated aggregate is accompanied by the signal of the corresponding chloride-bridged cluster ion.

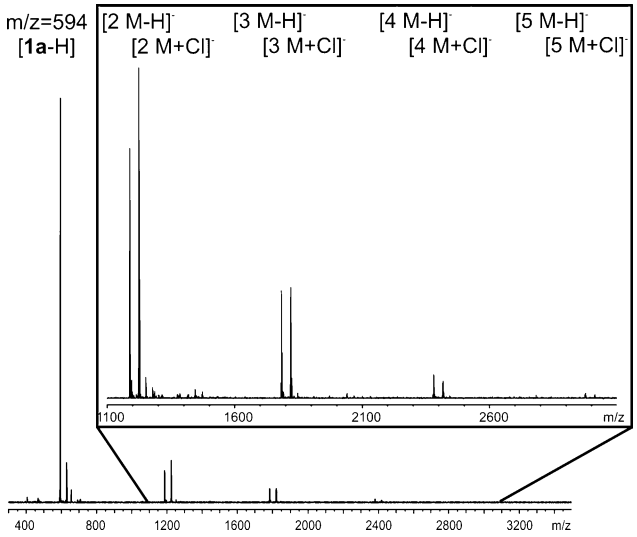

Figure 2. Negative ion FT-ICR-ESI mass spectrum of chromium carbene amphiphile **1a** in methanol.

Conclusion

In this paper, we presented the first synthesis of azobenzene-functionalized carbene complexes. Introduction of an amino-sugar generates amphiphilic carbene complexes which are shown to undergo aggregation in the gas phase. UV irradiation induces *E*/*Z* photoisomerization, leaving the pentacarbonylchromium moiety intact, which makes this type of complex feasible for organometallic switches.

Experimental Section

All operations involving organometallic compounds were carried out under argon using standard Schlenk techniques. Solvents were dried according to standard procedures and saturated with and stored under argon. (*E*)-1-(4-Bromophenyl)-2-(4-methoxyphenyl)diazene (**3**),[31] (*E*)-1-(4-iodophenyl)-2-(4-methoxyphenyl)diazene (**4a**),[32] (*E*)-1-(4-iodophenyl)-2-phenyldiazene (**4c**),[33] 1-amino-1-deoxy-3,4:5,6-bis-*O*-(1-methylethylidene)-D-glucitol (**6**),[34] and pentacarbonyl[D-*galacto*-hex-(*N*-*n*-octylamino)-1-ylidene]chromium (**9**)[10] were synthesized according to literature procedures. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX-300, DPX-400, and DRX-500 spectrometers. Mass spectrometric measurements were performed using a Kratos Magna 550 (EI), a Kratos Concept 1H (FAB), a Bruker MicroTOF Q (ESI), or a Bruker APEX IV Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with an Apollo electrospray ion source equipped with an off-axis 70° spray needle (ESI-FT-ICR). IR spectra were recorded on a Nicolet Magna 550. For UV/vis measurements, a Perkin-Elmer Lambda 18 was used. UV irradiation of **1a** was performed in a quartz cuvette using a Heraeus TQ 150 lamp and a filter solution[35] (band-pass filter 320−370 nm).

Synthesis of 1-Hexyl-4-nitrosobenzene (2). A 2.48 g (14 mmol) sample of 4-hexylaniline was dissolved in 75 mL of dichloromethane, and a solution of 17.21 g (28 mmol) of oxone was added. The reaction mixture was stirred for 39 h at room temperature under argon. The aqueous phase was extracted with dichloromethane. The combined organic layers were washed with 1 N HCl, saturated bicarbonate solution, and brine and dried over magnesium sulfate. After removal of the solvent under reduced pressure chromatography on silica gel (−15 °C, petroleum ether/dichloromethane, 1:1) yielded 0.90 g (4.7 mmol, 34%) of **2** as a green liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ [ppm]): 7.80 (d, J = 8.4 Hz, 2 H, H-2), 7.37 (d, J = 8.4 Hz, 2 H, H-3), 2.67 (t, J = 7.6 Hz, 2 H, $ArCH_2$−), 1.64 (tt, J = 7.6 Hz, J = 7.3 Hz, 2 H, $ArCH_2CH_2$−), 1.40−1.18 (m, 6 H, CH_2), 0.87 (t, J = 6.9 Hz, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, δ [ppm]): 165.54, 151.89 (Ar C_{quart}), 128.94, 121.10 (Ar CH), 36.07, 31.47, 30.68, 28.78, 22.41 (CH_2), 13.89 (CH_3). EI-MS (*m*/*z* (rel intens)): 191 (100) $[M]^+$, 161 (16) $[M - NO]^+$. EI-HRMS (*m*/*z*): calcd for $C_{12}H_{17}NO$ 191.1310, found 191.1310.

Synthesis of (*E*)-1-(4-Hexylphenyl)-2-(4-iodophenyl)diazene (4b). A 0.90 g (4.7 mmol) sample of 1-hexyl-4-nitrosobenzene (**2**) and 1.02 g (4.7 mmol) of 4-iodoaniline were dissolved in 20 mL of acetic acid, and the resulting solution was stirred for 4 h at room temperature under argon. A 50 mL sample of water was added, and the aqueous phase was extracted with diethyl ether. The combined organic layers were washed with brine and dried, and the solvent was removed under reduced pressure. Chromatography on silica gel (petroleum ether/dichloromethane, 2:1) yielded 1.40 g (3.6 mmol, 76%) of **4b** as an orange solid. Mp: 65 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ [ppm]): 7.88−7.81 (m, 4 H, H-2′, H-3), 7.63 (d, J = 8.7 Hz, 2 H, H-2), 7.32 (d, J = 8.6 Hz, 2 H, H-3′), 2.69 (t, J = 7.6 Hz, 2 H, $ArCH_2$−), 1.66 (tt, J = 7.6 Hz, J = 7.3 Hz, 2 H,

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$ArCH_2CH_2-$), 1.40−1.25 (m, 6 H, CH_2), 0.90 (t, $J = 7.0$ Hz, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, δ [ppm]): 152.05, 150.74, 147.03 (Ar C_{quart}), 138.27, 129.14, 124.35, 122.97 (Ar CH), 97.16 (C-1), 35.92, 31.68, 31.21, 28.93, 22.58 (CH_2), 14.07 (CH_3). IR (KBr pellet, ν [cm^{-1}]): 2954 (m), 2924 (s), 2852 (s), 1603 (w), 1568 (m), 1437 (m), 1389 (m), 1294 (w), 1155 (m), 1001 (s), 835 (m). EI-MS (*m*/*z* (rel intens)): 392 (100) $[M]^+$, 231(9) $[M - C_6H_4C_6H_{13}]^+$, 203 (28) $[M - C_6H_4C_6H_{13}N_2]^+$, 161 (76) $[M - C_6H_4IN_2]^+$. EI-HRMS (*m*/*z*): calcd for $C_{18}H_{21}IN_2$ 392.0749, found 392.0749.

Synthesis of Pentacarbonyl[(4-[(*E*)-(4′-methoxyphenyl)diazenyl]phenyl)(methoxy)-1-ylidene]chromium (5a). A 680 mg (2.34 mmol) sample of **3** was dissolved in 35 mL of freshly distilled THF and the resulting solution cooled to −78 °C. 1.61 mL (2.57 mmol) of *n*-butyllithium (1.6 M in hexane) were added slowly, and the solution was stirred for 30 min at this temperature. 617 mg (2.80 mmol) of hexacarbonylchromium were added, and the solution was allowed to warm to −15 °C over 3 h. 613 mg (4.14 mmol) of trimethyloxonium tetrafluoroborate were added, and the mixture was stirred for 16 h at −10 °C. The solvent was removed under reduced pressure, and after purification by column chromatography (petroleum ether/dichloromethane, 1:1, −10 °C) 250 mg (0.56 mmol, 24%) of **5a** were obtained as a red solid. Mp: 98−102 °C dec. ^1H NMR (400 MHz, $CDCl_3$, δ [ppm]): 7.95 (d, $J =$ 9.0 Hz, 2 H, H-2′), 7.92 (d, $J = 8.5$ Hz, 2 H, H-2), 7.44 (d, $J = 8.5$ Hz, 2 H, H-3), 7.03 (d, $J = 9.0$ Hz, 2 H, H-3′), 4.76 (s, 3 H, carbene−OMe), 3.89 (s, 3 H, Ar−OMe). ^{13}C NMR (100 MHz, $CDCl_3$, δ [ppm]): 349.32 (Cr═C), 224.03 (CO_{trans}), 216.05 (CO_{cis}), 162.60, 154.17, 153.15, 147.10 (Ar C_{quart}), 125.11 124.27. 122.43, 114.32 (Ar CH), 67.19 (carbene−OMe), 55.58 (Ar−OMe). IR (PE, ν_{CO} [cm^{-1}]): 2064 (m, A_1^1), 1984 (w, B^1), 1952 (vs, E). EI-MS (*m*/*z* (rel intens)): 446 (5) $[M]^+$, 418 (8) $[M - CO]^+$, 390 (8) $[M - 2CO]^+$, 375 (3) $[M - 2CO - CH_3]^+$, 362 (4) $[M - 3CO]^+$, 334 (30) $[M - 4CO]^+$, 306 (100) $[M - 5CO]^+$. EI-HRMS: calcd for $C_{20}H_{14}CrN_2O_7$ 446.0206, found 446.0202.

General Procedure for the Preparation of Carbene Complexes 5b and 5c. A solution of **4b** or **4c** in 200 mL of diethyl ether was cooled to −100 °C, and 1 equiv of *n*-butyllithium (2.5 M in hexane) was added slowly. After 15 min, 0.5 equiv of freshly annealed zinc bromide was added, and after an additional 5 min, 1.4 equiv of hexarbonylchromium were added. The reaction mixture was warmed to −70 °C and then over 30 min to −40 °C and was stirred for an additional 1 h at this temperature. The solvent was removed under reduced pressure, and the residue was suspended in 100 mL of dichloromethane. After addition of 2.5 equiv of trimethyloxonium tetrafluoroborate, the reaction mixture was stirred for 3 h at room temperature. The solvent was removed under reduced pressure, and after purification by column chromatography over silica gel (petroleum ether/diethyl ether, 10:1, −5 °C) the methoxycarbene complexes were obtained as red solids.

Pentacarbonyl[(4-[(*E*)-(4′-hexylphenyl)diazenyl]phenyl)-(methoxy)-1-ylidene]chromium (5b). A 1.51 g (3.8 mmol) sample of **4b** was reacted with 1.5 mL (3.8 mmol) of *n*-butyllithium, 0.43 g (1.9 mmol) of zinc bromide, and 1.19 g (5.4 mmol) of hexacarbonylchromium. After alkylation with 1.42 g (9.6 mmol) of trimethyloxonium tetrafluoroborate and column chromatography, 0.69 g (1.4 mmol, 36%) of **5b** were obtained. Mp: 55 °C. ^1H NMR (500 MHz, $CDCl_3$, δ [ppm]): 7.97 (d, $J = 8.5$ Hz, 2 H, H-2), 7.91 (d, $J = 8.3$ Hz, 2 H, H-2′), 7.48 (d, $J = 8.5$ Hz, 2 H, H-3), 7.37 (d, $J = 8.3$ Hz, 2 H, H-3′), 4.79 (s, 3 H, OMe), 2.73 (t, $J = 7.6$ Hz, 2 H, $ArCH_2-$), 1.71 (tt, $J = 7.6$ Hz, $J = 7.3$ Hz, 2 H, $ArCH_2CH_2-$), 1.40−1.21 (m, 6 H, CH_2), 0.94 (t, $J = 7.1$ Hz, 3 H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, δ [ppm]): 349.45 (Cr═C), 224.00 (CO_{trans}), 216.00 (CO_{cis}), 154.45, 153.00, 150.93, 147.33 (Ar C_{quart}), 129.17, 123.75, 123.10, 122.62 (Ar CH), 67.20 (OMe), 35.93, 31.67, 31.19, 28.93, 22.57 (CH_2), 14.06 (CH_3). IR (Et_2O, ν_{CO} [cm^{-1}]): 2063 (m, A_1^1), 1965 (sh, E^1), 1956 (vs, E^2). EI-MS (*m*/*z* (rel intens)): 500 (22) $[M]^+$, 472 (25) $[M - CO]^+$, 388 (4) $[M - 4CO]^+$, 360 (10) $[M - 5CO]^+$. EI-HRMS (*m*/*z*): calcd for $C_{20}H_{24}CrN_2O$ ($[M - 5CO]^+$) 360.1294, found 360.1293.

Pentacarbonyl[(4-[(*E*)-(phenyl)diazenyl]phenyl)(methoxy)-1-ylidene]chromium (5c). A 1.23 g (4 mmol) sample of **3c** was reacted with 1.6 mL (4 mmol) of *n*-butyllithium, 0.45 g (2 mmol) of zinc bromide, and 1.23 g (5.6 mmol) of hexacarbonylchromium. After alkylation with 1.48 g (10 mmol) of trimethyloxonium tetrafluoroborate and column chromatography, 0.47 g (1.1 mmol, 28%) of **5c** were obtained. Mp: 103 °C dec. ^1H NMR (500 MHz, $CDCl_3$, δ [ppm]): 8.03−7.89 (m, 4 H, HAr), 7.59−7.47 (m, 3 H, HAr), 7.46−7.39 (m, 2 H, HAr), 4.76 (s, 3 H, OMe). ^{13}C NMR (125 MHz, $CDCl_3$, δ [ppm]): 349.62 (Cr═C), 223.97 (CO_{trans}), 215.95 (CO_{cis}), 154.73, 152.78, 152.60 (Ar C_{quart}), 131.55, 129.16, 123.99, 123.07, 122.78 (Ar CH), 67.24 (OMe). IR (Et_2O, ν_{CO} [cm^{-1}]): 2063 (m, A_1^1), 1978 (w, B^1), 1967 (s, E^1), 1956 (vs, E^2), 1944 (sh, B_1). EI-MS (*m*/*z* (rel intens)): 416 (4) $[M]^+$, 388 (6) $[M - CO]^+$, 360 (8) $[M - 2CO]^+$, 332 (5) $[M - 3CO]^+$, 304 (20) $[M - 4CO]^+$, 276 (100) $[M - 5CO]^+$. EI-HRMS (*m*/*z*): calcd for $C_{19}H_{12}CrN_2O_6$ 416.0100, found 416.0093.

Pentacarbonyl[(4-[(*E*)-(4′-methoxyphenyl)diazenyl]phenyl)-(3:4,5:6-di-*O*-isopropylidene-D-glucamino)-1-ylidene]chromium (7a). A solution of 250 mg (0.56 mmol) of **5a** in 20 mL of dichloromethane was cooled to −50 °C and slowly treated with a solution of 145 mg (0.56 mmol) of **6** in 5 mL of dichloromethane. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (petroleum ether/dichloromethane/diethyl ether, 1:1:1, 0 °C) to yield 130 mg (0.20 mmol, 34%) of **7a** as an orange oil. ^1H NMR (HH-COSY, CH-COSY, 500 MHz, $CDCl_3$, δ [ppm]): 9.87−9.76 (m, 1 H, NH), 7.98−7.88 (m, 4 H, Ar H-2′, Ar H-3), 7.02 (d, $J = 8.9$ Hz, 2 H, Ar H-3′), 6.96 (d br, $J = 7.7$ Hz, 2 H, Ar H-2), 4.15 (dd, $J = 8.6$ Hz, $J = 6.0$ Hz, 1 H, H-6), 4.08−3.83 (m, 8 H, OCH_3, H-2, H-3, H-4, H-5, H-6′), 3.62 (ddd, $J = 13.8$ Hz, $J = 8.0$ Hz, $J = 4.2$ Hz, 1H, H-1), 3.35 (ddd, $J = 13.8$ Hz, $J = 4.6$ Hz, $J = 3.2$ Hz, 1H, H-1′), 2.47 (d, $J = 9.2$ Hz, 1 H, OH), 1.48, 1.43, 1.36, 1.31 (4 s, each 3 H, $-C(CH_3)_2$). ^{13}C NMR (CH-COSY, 125 MHz, $CDCl_3$): 282.88 (Cr═C), 223.28 (CO_{trans}), 217.09 (CO_{cis}), 162.22, 151.03, 150.94, 146.95 (Ar C_{quart}), 124.81, 123.10, 120.10, 114.24 (Ar CH), 110.76, 110.02 ($-C(CH_3)_2$), 82.02 (C-3), 77.27, 77.01 (C-4, C-5), 67.92 (C-6) 67.32 (C-2), 55.55 (C-1), 54.81 (OMe), 26.92, 26.65, 26.59, 25.01 ($-C(CH_3)_2$). IR (Et_2O, ν_{CO} [cm^{-1}]): 2056 (m, A_1^1), 1978 (w, B^1), 1942 (vs, E^1), 1919 (s, E^2). FAB-MS (mNBA, *m*/*z* (rel intens)): 676 (4) $[M + H]^+$, 647 (1) $[M - CO]^+$, 591 (2) $[M - 3CO]^+$, 563 (2) $[M - 4CO]^+$, 535 (60) $[M - 5CO]^+$. EI-HRMS (*m*/*z*): calcd for $C_{26}H_{33}CrN_3O_6$ ($[M - 5CO]^+$) 535.1774, found 535.1749.

Pentacarbonyl[(4-[(*E*)-(4′-hexylphenyl)diazenyl]phenyl)(3:4,5:6-di-*O*-isopropylidene-D-glucamino)-1-ylidene]chromium (7b). A solution of 790 mg (1.58 mmol) of **5b** in 40 mL of dichloromethane was cooled to −50 °C and slowly treated with a solution of 412 mg (1.58 mmol) of **6** in 8 mL of dichloromethane. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (petroleum ether/dichloromethane/diethyl ether, 1:1:1, 0 °C) to yield 323 mg (0.44 mmol, 28%) of **7b** as an orange oil. ^1H NMR (HH-COSY, CH-COSY, 500 MHz, C_6D_6, δ [ppm]): 9.85−9.75 (m, 1 H, NH), 8.03 (d, $J =$ 8.2 Hz, 2 H, Ar H-2′), 7.98 (d, $J \approx 8$ Hz, 2 H, Ar H-3), 7.11 (d, $J = 8.2$ Hz, 2 H, Ar H-3′), 6.78 (d, $J \approx 8$ Hz, 2 H, Ar H-2), 3.88 (dd, $J = 8.7$ Hz, $J = 5.6$ Hz, 1 H, H-6), 3.82 (dd, $J = 8.7$ Hz, $J =$ 3.7 Hz, 1 H, H-6′), 3.78−3.71 (m, 2 H, H-4, H-5), 3.62 (dd, $J =$ 7.3 Hz, $J \approx 2.6$ Hz, 1 H, H-3), 3.52 (ddd br, $J \approx 9$ Hz, $J = 3.4$ Hz, $J \approx 2.6$ Hz, 1 H, H-2), 3.04 (ddd, $J = 14.0$ Hz, $J \approx 9$ Hz, $J = 3.4$ Hz, 1 H, H-1), 2.56 (ddd, $J = 14.0$ Hz, $J = 3.6$ Hz, $J = 3.4$ Hz, 1H, H-1′), 2.44 (t, $J = 7.6$ Hz, 2 H, $ArCH_2-$), 2.09 (d, $J = 7.9$ Hz, 1 H, OH), 1.46 (tt, $J = 7.6$ Hz, $J = 7.4$ Hz, 2 H, $ArCH_2CH_2-$), 1.39−1.10 (m, 18 H, CH_2, $-C(CH_3)_2$), 0.87 (t, $J = 7.0$ Hz, 3 H,

CH_3). ^{13}C NMR (CH-COSY, 125 MHz, C_6D_6, δ [ppm]): 281.32 (Cr═C), 223.69 (CO_{trans}), 217.80 (CO_{cis}), 151.65, 151.52, 151.47, 147.02 (Ar C_{quart}), 129.46 (Ar C-3′), 123.83 (Ar C-3), 123.48 (Ar C-2′), 120.48 (Ar C-2), 110.78, 110.04 ($-C(CH_3)_2$), 82.67 (C-3), 77.57, 77.41 (C-4, C-5), 68.08 (C-6) 67.22 (C-2), 54.76 (C-1), 36.10 ($ArCH_2-$), 31.98, 31.43, 29.23 (CH_2), 27.03, 26.69, 26.60, 25.13 ($-C(CH_3)_2$), 22.91 (CH_2), 14.27 (CH_2CH_3). IR (PE, ν_{CO} [cm^{-1}]): 2056 (m, A_1^1), 1979 (w, B^1), 1942 (vs, E^1), 1919 (sh, E^2). FAB-MS (mNBA, *m*/*z* (rel intens)): 730 (2) $[M + H]^+$, 701 (1) $[M - CO]^+$, 645 (2) $[M - 3CO]^+$, 617 (2) $[M - 4CO]^+$, 589 (100) $[M - 5CO]^+$. ESI-HRMS (MeOH, negative mode, *m*/*z*): calcd for $C_{36}H_{42}CrN_3O_{10}$ ($[M - H]^-$) 728.2281, found 728.2289.

Pentacarbonyl[(4-[(*E*)-(4′-methoxyphenyl)diazenyl]phenyl)-(D-glucamino)-1-ylidene]chromium (1a). An 80 mg (0.10 mmol) sample of **7a** was dissolved in 10 mL of methanol and the resulting solution cooled in an ice bath. 50 mg (0.8 mmol) of ethylene glycol and 66 mg (0.39 mmol) of *p*-toluenesulfonic acid were added, and the reaction mixture was stirred for 24 h at room temperature. After the solution was cooled in an ice bath, 0.1 mL of triethylamine was added, and the solvent was removed under reduced pressure. After column chromatography on silica gel (dichloromethane/methanol, 8:1, 8 °C), 29 mg (0.05 mmol, 41%) of **1a** were obtained as a yellow solid. Mp: 104 °C dec. ^1H NMR (HH-COSY, CH-COSY, 500 MHz, CD_3OD, δ [ppm]): 7.97−7.92 (m, 4 H, Ar H-2′, Ar H-3), 7.95 (d, $J = 9.0$ Hz, 2 H, Ar H-3′), 7.06 (d, $J = 8.2$ Hz, 2 H, Ar H-2), 4.01 (ddd br, $J = 7.3$ Hz, $J = 4.4$ Hz, $J = 4.3$ Hz, 1 H, H-2), 3.93 (s, 3 H, OMe), 3.77 (dd, $J = 11.0$ Hz, $J = 3.4$ Hz, 1 H, H-6), 3.75 (dd, $J = 4.3$ Hz, $J = 2.0$ Hz, 1 H, H-3), 3.68 (ddd, $J = 7.8$ Hz, $J = 5.6$ Hz, $J = 3.4$ Hz, 1 H, H-5), 3.62 (dd, $J = 11.0$ Hz, $J = 5.6$ Hz, 1 H, H-6′), 3.58 (dd, $J = 7.8$ Hz, $J = 2.0$ Hz, 1 H, H-4), 3.53 (dd, $J = 13.6$ Hz, $J = 4.4$ Hz, 1 H, H-1), 3.53 (dd, $J = 13.6$ Hz, $J = 7.3$ Hz, 1 H, H-1′). ^{13}C NMR (CH-COSY, 125 MHz, CD_3OD, δ [ppm]): 276.63 (Cr═C), 225.27 (CO_{trans}), 218.91 (CO_{cis}), 164.21, 153.44, 152.41, 148.60 (Ar C_{quart}), 126.06, 124.15, 122.10, 115.68 (Ar CH), 73.28 (2 C), 72.48, 72.31 (C-2, C-3, C-4, C-5), 65.03 (C-6), 56.43 (C-1), 55.08 (OMe). IR (Et_2O, ν_{CO} [cm^{-1}]): 2054 (m, A_1^1), 1934 (vs, E). ESI-MS ($MeOH/CH_2Cl_2$, positive mode, *m*/*z* (rel intens)): 618 (5) $[M + Na]^+$, 596 (10) $[M + H]^+$, 402 (100) $[M - HCr(CO)_5]^+$. ESI-HRMS ($MeOH/CH_2Cl_2$, positive mode, *m*/*z*): calcd for $C_{25}H_{26}CrN_3O_{11}$ ($[M + H]^+$) 596.0967, found 596.0960.

Pentacarbonyl[(4-[(*E*)-(4′-hexylphenyl)diazenyl]phenyl)(D-glucamino)-1-ylidene]chromium (1b). A 210 mg (0.29 mmol) sample of **7b** was dissolved in 20 mL of methanol and the resulting solution cooled in an ice bath. 100 mg (1.6 mmol) of ethylene glycol and 150 mg (0.78 mmol) of *p*-toluenesulfonic acid were added, and the reaction mixture was stirred for 76 h at room temperature. After the solution was cooled in an ice bath, 0.1 mL of triethylamine was added, and the solvent was removed under reduced pressure. After column chromatography on silica gel (dichloromethane/methanol, 8:1, 0 °C), 57 mg (0.09 mmol, 30%) of **1b** were obtained as a yellow solid. Mp: 102−103 °C dec. ^1H NMR (HH-COSY, CH-COSY, 500 MHz, CD_3OD, δ [ppm]): 7.93 (d, $J \approx 8.4$ Hz, 2 H, Ar H-3), 7.82 (d, $J = 8.3$ Hz, 2 H, Ar H-2′), 7.34 (d, $J = 8.3$ Hz, 2 H, Ar H-3′), 7.03 (d, $J \approx 8.4$ Hz, 2 H, Ar H-2), 3.96 (ddd br, $J \approx 7.6$ Hz, $J \approx 6$ Hz, $J \approx 5$ Hz, 1 H, H-2), 3.72 (dd, $J = 11.1$ Hz, $J \approx 3.0$ Hz, 1 H, H-6), 3.71 (dd, $J \approx 5$ Hz, $J = 1.8$ Hz, 1 H, H-3), 3.64 (ddd, $J = 8.0$ Hz, $J \approx 7$ Hz, $J \approx 3$ Hz, 1 H, H-5), 3.57 (dd, $J = 11.1$ Hz, $J \approx 7$ Hz, 1 H, H-6′), 3.53 (dd, $J = 8.0$ Hz, $J = 1.8$ Hz, 1 H, H-4), 3.48 (dd, $J \approx 14$ Hz, $J \approx 6$ Hz, 1 H, H-1), 3.48 (dd, $J \approx 14$ Hz, $J \approx 7.6$ Hz, 1 H, H-1′), 2.69 (t, $J = 7.6$ Hz, 2 H, $ArCH_2-$), 1.66 (tt, $J = 7.6$ Hz, $J = 7.3$ Hz, 2 H, $ArCH_2CH_2-$), 1.46−1.32 (m, 6 H, CH_2), 0.90 (t, $J = 6.9$ Hz, 3 H, CH_3). ^{13}C NMR (CH-COSY, 125 MHz, $CDCl_3$, δ [ppm]): 276.51 (Cr═C), 225.27 (CO_{trans}), 218.90 (CO_{cis}), 153.79, 152.61, 152.34, 148.42 (Ar C_{quart}), 130.56 (Ar C-3′), 124.38 (Ar C-3), 124.19 (Ar C-2′), 122.13 (Ar C-2), 73.28 (2 C, C-4, C-5), 72.47 (C-2), 72.31 (C-3), 65.02 (C-6), 55.11 (C-1), 37.11 ($ArCH_2-$), 33.14, 32.79, 30.33, 23.96 (CH_2), 14.70 (CH_2CH_3). IR (Et_2O, ν_{CO} [cm^{-1}]): 2054 (m, A_1^1), 1972 (w, B^1), 1932 (vs, E). FAB-MS (mNBA, *m*/*z* (rel intens)): 650 (2) $[M + H]^+$, 509 (20) $[M - 5CO]^+$. ESI-HRMS (MeOH, negative mode, *m*/*z*): calcd for $C_{30}H_{34}CrN_3O_{10}$ $[M - H]^-$ 648.1655, found 648.1656.

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