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# Benzannulation and Cyclopentannulation Reactions of Electron-Poor Amino-Stabilized Alkenyl Fischer Carbene Complexes

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**Abstract**—The alkenyl(amino)carbene complexes of chromium and tungsten bearing an electron-withdrawing group at the $C_\beta$-position **5**–**6** were prepared by condensation of methyl(amino)carbene complexes **1**–**2** and esters of glyoxylic acid. The complexes **5**–**6** were readily α-metallated with *n*-BuLi affording the deuteriated metal carbene complexes **7**–**8**. The chromium complexes **5**, **7** display a remarkable reactivity toward different types of alkynes. These complexes reacted with both unactivated alkynes and terminal electron-poor alkynes to give exclusively the phenol products **11**–**13** via the benzannulation reaction (Dötz reaction). In contrast, the reaction of carbene complexes **5** with internal electron-poor alkynes yielded solely the cyclopentadiene derivatives **15** via the cyclopentannulation reaction. The tetracarbonyl carbene intermediates **16** were isolated and fully characterized. © 2000 Published by Elsevier Science Ltd.

## Introduction

Transition metal carbene complexes are recognized as valuable reagents in organic synthesis. Among them, heteroatom stabilized derivatives (Fischer carbene complexes) of group 6 have received increasing interest, particularly in the last two decades.[1] In spite of that many studies highlight the formation of rings of various sizes, e.g. cyclopropane,[2] cyclobutane,[3] cyclopentane[4] and cycloheptane[5] rings, the most famous reaction of Fischer carbene complexes is by far the coupling of alkenyl (aryl) carbene complexes with alkynes leading to highly susbtituted phenols (naphthols), a process commonly known as the Dötz reaction or benzannulation reaction (Fig. 1).[6] Mostly, the process is thermally conducted, although photoirradiated[7] and dry-state[8] conditions have been eventually used in order to

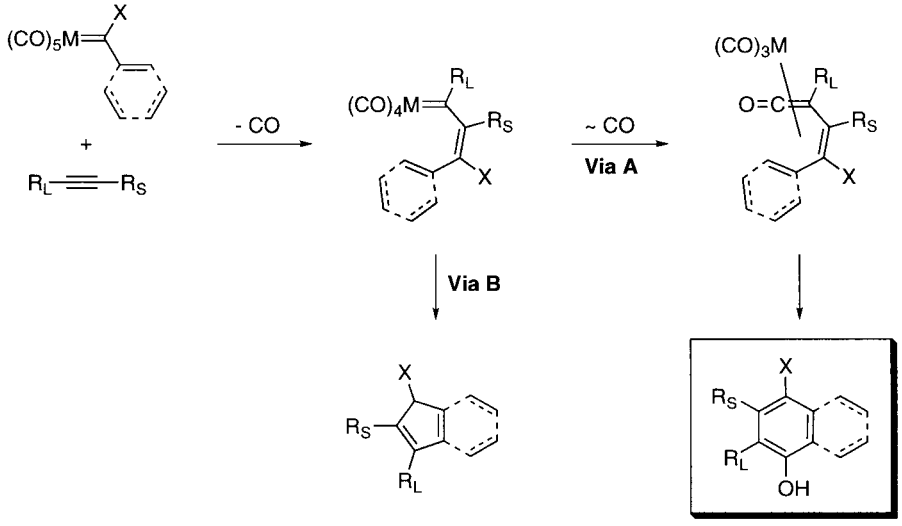


**Figure 1.**

*Keywords*: carbenes and carbenoids; Dötz reactions; phenols; cyclopentadienes.

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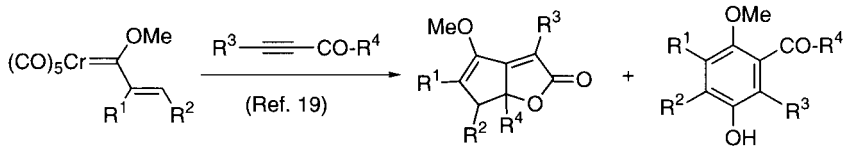



**Figure 2.**

improve the efficiency. Numerous studies directed to reach a good understanding of the mechanism have been reported[9] and some controversy has even generated.[10]

In the benzannulation reaction two ligands, carbene and CO, of the metal complex and the alkyne are assembled in a regioselective way forming the benzene ring (Fig. 1, via A). Thus, the process represents a general access to benzenoids that has been amply used in synthesis of molecules of interest.[11–13] Moreover, the participation of heteroatom-containing alkynes (e.g. tertbutylphosphaacetylene)[14] as well as alkynyl carbene complexes[15] (via the Moore-type cyclization) are recent examples wherein notable variations have been brought about.

The cyclopentannulation appears to be the competing reaction that is most frequently encountered. The cyclopentadiene ring is formed via coupling of the carbene ligand and the alkyne without transfering of CO ligand (Fig. 1, via B).[16] Although several parameters (metal, solvent, concentration, carbene heteroatom, etc.) are known to play a role in the outcome of the reaction, the general trend for chromium complexes can be summarized as follows: (i) alkoxy-stabilized aryl carbene complexes lead to mixtures of benzannulation and cyclopentannulation products; (ii) alkoxy-stabilized alkenyl carbene complexes undergo with great preference the benzannulation reaction; (iii) amino-stabilized aryl carbene complexes yield susbtituted indenes via the cyclopentannulation reaction; (iv) the reaction between amino-stabilized alkenyl Fischer carbene complexes and 1-pentyne can be directed to the formation of phenols, whereas their reaction with internal alkynes fails, as recently reported by Wulff et al.[17,18]

Though a huge number of benzannulation reactions are known for unactivated alkynes, few reports deal with the use of electron-poor alkynes. Wulff et al. have investigated the reaction of alkoxy carbene complexes of chromium with alkynyl ketones and alkynyl esters and found that variable mixtures of lactones (major products for alkynyl ketones) and phenols (major products for alkynyl esters) are formed (Fig. 2).[9e,19]

In recent years, we became fascinated with the potential of Fischer carbene complexes, in particular α,β-unsaturated derivatives, as intermediates in organic synthesis.[20] Concerning the Dötz reaction, we have succeeded in isolating or characterizing real intermediates, like **I** and **II**, in the reaction between amino alkenylcarbene complexes of chromium and electron-deficient alkynes (Fig. 3). The process ultimately yields either phenols or cyclopentadienes, depending on the nature of the alkyne substituent $R^3$.[21]

In a general sense, it is significant to note that the carbene ligand of all alkenyl Fischer carbene complexes hitherto employed contains electron-donating substituents (alkyl, aryl, heteroaryl, alkoxy, amino, etc.).[22] As exceptions, α,β-difluoro-,[23] β-chloro-[24] and β-phenylsulfonyl[25] alkenyl carbene complexes of chromium have been described and their benzannulation studied. In addition, the [[β-(methoxycarbonyl)ethenyl](tert-butyldimethylsiloxy)methylene]pentacarbonylchromium(0) complex has been postulated as a reactive intermediate in the [3+2] cyclization with captodative alkenes.[4b]

Herein, we report on the preparation and characterization of new amino-stabilized β-ethoxycarbonylethenyl Fischer carbene complexes of chromium and tungsten. We also describe the efficient and selective benzannulation and cyclopentannulation reactions of the chromium derivatives to alkynes with diverse electronic demand.[26]

## Results and Discussion

### Preparation of carbene complexes 5, 6

The synthesis of the target complexes **5** (M=Cr) and **6** (M=W) was achieved from the pentacarbonyl(methylpyrrolidinocarbene)chromium(0) **1** and tungsten(0) **2** and

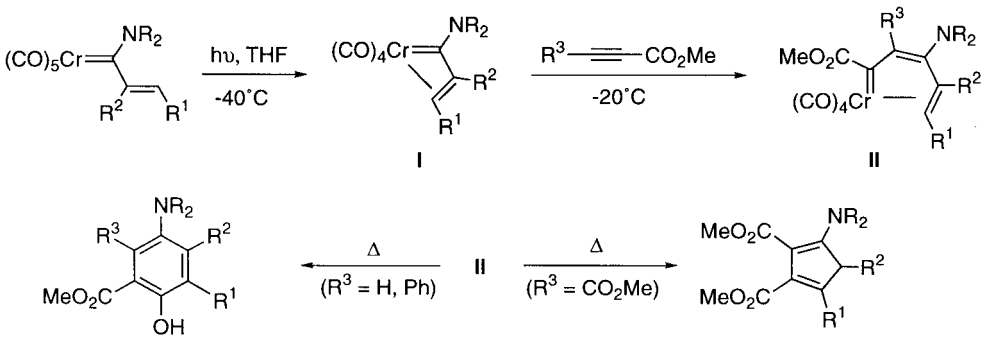
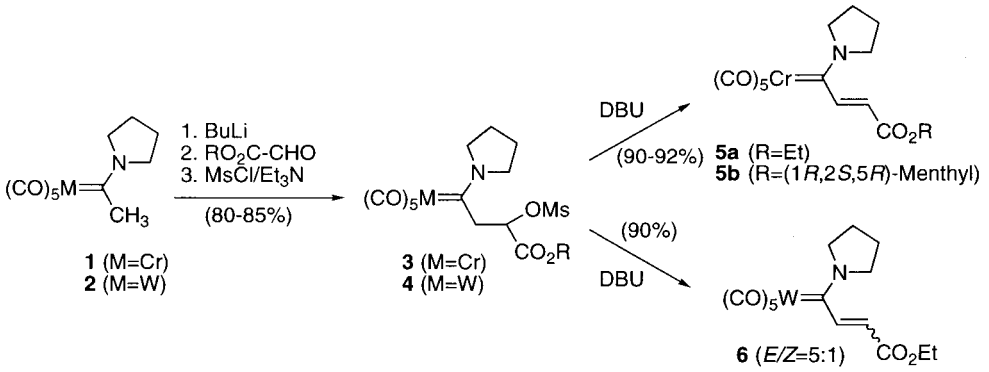



**Figure 3.**




**Scheme 1.**

the corresponding aldehyde in two steps—aldol addition and elimination—according to the standard procedure published by Maiorana et al. (Scheme 1).[27] Thus, the complexes **1**, **2** were deprotonated with BuLi and excess of the corresponding glyoxylic acid ester (5 equiv.) added. The resulting adducts were treated with methanesulfonyl chloride to give the aldol derivatives **3**, **4** which are susceptible to isolation. Then, DBU promoted elimination afforded β-(alkoxycarbonyl)alkenyl carbene complexes **5a**,**b** (72 and 75% overall yield from **1**) as the *E*-isomer exclusively ($^3J_{H-H}$=16.3 Hz) and the β-(ethoxycarbonyl)alkenyl carbene complex **6** (76% overall yield from **2**) as a separable 5:1 *E*/*Z* mixture ($^3J_{H-H}$=16.2 Hz for the *E*-isomer; $^3J_{H-H}$=12 Hz for the *Z*-isomer).

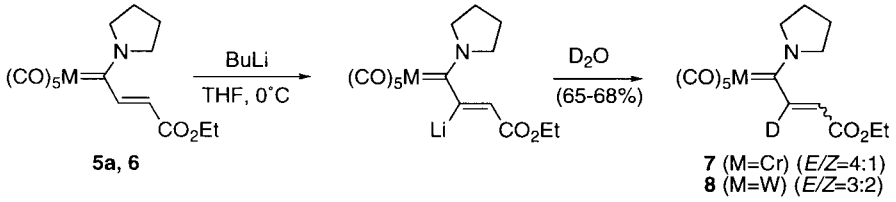
Significantly, the NMR spectra of compounds **5**, **6** indicate a notable deshielding of the $C_\alpha$ and $C_\alpha$-*H* atoms and shielding of the $C_\beta$ and $C_\beta$-*H* atoms in relation with those of β-aryl(alkyl) substituted alkenyl carbene complexes. The resonance of the carbene carbon lies whithin the normal range for aminocarbene complexes. For instance, the spectroscopic features of **5a** are as follows: (i) $^1$H NMR, $\delta$=7.7 (d) (C*H*=CH–$CO_2$Et) and 5.3 (d) (CH=C*H*–$CO_2$Et) ($^3J_{H-H}$=16.3 Hz); (ii) $^{13}$C NMR, $\delta$=262.5 (Cr=*C*), 150.4 (*C*H=CH–$CO_2$Et), and 109.4 (CH=*C*H–$CO_2$Et).[28]

The reactivity of the carbene complexes **5a**, **6** toward butyllithium was first tested (Scheme 2). We found that both Michael-type addition and deprotonation occurred at −50°C, whereas the deprotonation species is formed almost exclusively at 0°C in THF. As far as we are aware, this α-metallation is unknown for conventional alkenyl carbene complexes. Thus, the $C_\alpha$-deuteriated complexes **7** and **8** were readily obtained as 4:1 and 3:2, respectively, mixtures of *E*/*Z* isomers by quenching the reaction with $D_2O$, while carbon electrophiles failed to trap the lithium species. The more characteristic $^1$H and $^{13}$C NMR signals of **8** are as follows: *E*-**8**, $\delta$=5.36 (broad singlet) (CD=C*H*–$CO_2$Et); $\delta$=151.6 (t) (*C*D=CH–$CO_2$Et) ($^1J_{C-D}$=23.1 Hz) and 111.3 (CD=*C*H–$CO_2$Et); *Z*-**8**, $\delta$=5.21 (broad singlet) (CD=C*H*–$CO_2$Et); $\delta$=150.4 (t) (*C*D=CH–$CO_2$Et) ($^1J_{C-D}$=23.2 Hz) and 105.5 (CD=*C*H–$CO_2$Et).

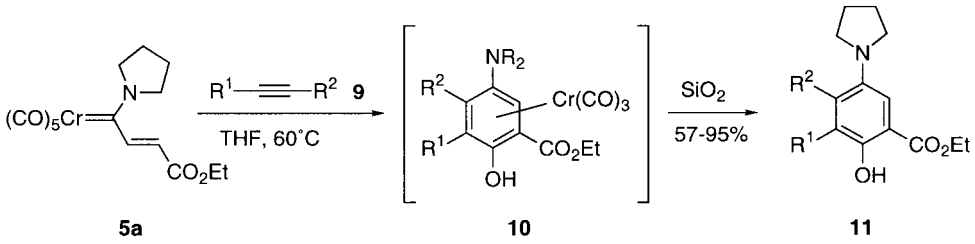
## Benzannulation reaction of carbene complexes 5a and 7

Firstly, the behavior of the new chromium carbene complexes toward terminal alkynes was tested.[29] Thus, the treatment of complex **5a** with an excess of alkyne **9** ($R^2$=H) (1.5–4.0 equiv.) in THF at 60°C for 16 h resulted, after column chromatography, in the formation of the benzannulation products **11a**–**i** in yields ranging from 58 to 95% (Scheme 3; Table 1, entries 1–9). It should be noted that the benzannulation reaction tolerates functional groups on the alkyne, e.g. ferrocenyl (entry 6), alkenyl (entry 7) and trimetylsilyloxy or tosylate (entries 8, 9) functionalities, furnishing **11f**–**i** without appreciable dropping of yield. A further interesting finding was to discover that electron-withdrawing substituted alkynes nicely undergo the benzannulation reaction. The process takes place as above, except that a longer reaction time (48 h) was required (Table 1, entries 10–13).[30] Gratifyingly, the reaction of the carbene complex **5a** with internal alkynes ($R^1$, $R^2$≠H), such as 3-hexyne, diphenylacetylene, and 1-phenyl-1-propyne, produced phenols **11o**–**q** with acceptable yields (entries 15–17). The use of deuteriated reagents, like phenylacetylene-$d_1$ **9** ($R^1$=Ph, $R^2$=D), or carbene complex-$d_1$ **7**, permitted to prepare regiospecifically deuteriated phenols **11n** (entry 14) and **12** (Fig. 4), respectively.

Only one regioisomer was seen in the reaction crude and the regiochemistry found in all cases was that expected on the basis of steric control, regardless of the electronic nature of




**Scheme 2.**




5a 10 11

**Scheme 3.**

**Table 1.** Benzannulation of carbene complex **5a** (all the reactions were carried out in THF at 60°C at 0.03 M in carbene complex)

| Entry | Compd | $R^1$ | $R^2$ | Yield[a] (%) |
|---|---|---|---|---|
| 1 | **11a** | *n*-Pr | H | 72 |
| 2 | **11b** | *n*-Bu | H | 88 |
| 3 | **11c** | *n*-Hex | H | 66 |
| 4 | **11d** | Ph | H | 95 |
| 5 | **11e** | *p*-Tolyl | H | 58 |
| 6 | **11f** | Ferrocenyl | H | 85 |
| 7 | **11g** | 1-Cyclopentenyl | H | 82 |
| 8 | **11h** | $CH_2OTMS$ | H | 73 |
| 9 | **11i**[b] | $(CH_2)_2OTs$ | H | 68 |
| 10 | **11j** | COOEt | H | 94 |
| 11 | **11k** | COOMe | H | 89 |
| 12 | **11l** | COOMent[c] | H | 71 |
| 13 | **11m** | COMe | H | 63 |
| 14 | **11n** | Ph | D | 80 |
| 15 | **11o** | Et | Et | 75 |
| 16 | **11p** | Ph | Ph | 57 |
| 17 | **11q** | Ph | Me | 70 |

[a] Isolated, nonoptimized yields of purified products.
[b] See Fig. 4 for the structure of **11i**.
[c] Alkyne derived from (±)-menthol.

the alkyne. The structure of the regioisomer formed was readily deduced from the coupling constant for the aromatic hydrogens (for compounds **11a–i**; $^4J_{H-H}$=2.5–3.1 Hz) or from 2D NOESY experiments (for compound **11q**) and was unambiguously confirmed in two cases. First, the reaction of **5a** with 3-butynyl tosylate **9** ($R^1$=$CH_2CH_2OTs$, $R^2$=H) afforded the benzannulation/cyclization product **11i** (Fig. 4 and Table 1, entry 9), and second, the benzannulation of **5a** with ethyl propynoate ($R^1$=$CO_2Et$, $R^2$=H) led to the symmetrical adduct **11j** (Fig. 4 and Table 1, entry 10).

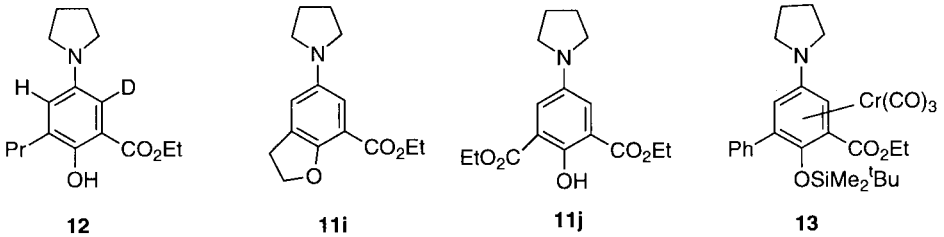
Moreover, the $(CO)_3Cr$-arene intermediate **10** could be easily isolated as the *O*-silylated complex.[31] Thus, complex **13** (Fig. 4) was obtained in 70% yield by heating a solution of **5a** and phenylacetylene in toluene at 60°C for 16 h followed by treatment with $ClSi^tBuMe_2/Et_3N$ and column choromatography.

## Cyclopentannulation reaction of carbene complexes 5a,b

Contrary to the behavior of electron-poor terminal alkynes **9** ($R^2$=H) toward carbene complex **5a**, wherein benzannulation products are selectively formed, substituted propynoic acid esters **14** ($R^2$≠H) did afford exclusively cyclopentannulation derived products. The reaction of **5a**,**b** with alkynes **14** ($R^2$=$CO_2Me$, $CO_2Et$, Ph, Pr) was conducted in THF at 60°C for 14 h to give regioselectively the cyclopentadiene derivatives **15** in high yields after removal of volatiles and column chromatography purification (Scheme 4, Table 2). The tetracarbonyl quelate intermediates **16** could be in some cases isolated by heating the reaction mixture in toluene at 50°C. Complexes **16** were converted quantitatively into the final products **15** by further heating in THF at 60°C.

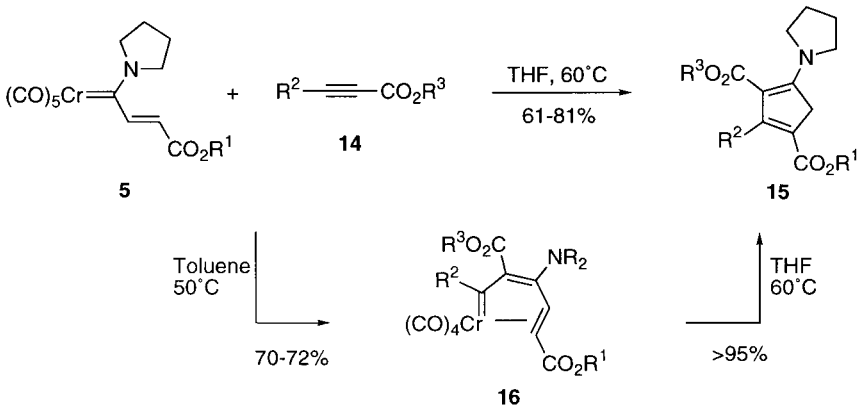
The structure of the tetracarbonyl carbene chromium complexes **16** was determined by comparison of their IR and NMR data with those reported previously (see Fig. 3, compounds **II**).[21] The NMR spectra of complexes **16** are in good accordance with the participation of the terminal carbon–carbon double bond as ligand. For instance, the $^1H$ NMR spectrum of compound **16b** ($R^1$=$R^3$=Et; $R^2$=$CO_2Et$) exhibits the vinylic hydrogen atoms at a field as high as 4.5 and 3.7 ppm ($^3J_{H-H}$=9.1 Hz) and its $^{13}C$ NMR spectrum shows the corresponding $sp^2$-*C*H atoms at 70.0 and 67.9 ppm, while the remaining vinylic carbon atoms appear at 244.1 (Cr=*C*), 157.6 (Cr=C–C=*C*) and 123.8 (Cr=C–*C*=C) ppm.

The regiochemistry of the alkyne insertion became evident from NMR experiments on compound **15c**.[32] The regiochemical outcome of the insertion means that the polarization of metal–carbon and carbon–carbon double bonds likely plays a decisive role in the orientation of the carbene–alkyne approach, a finding that has precedents for conventional carbene complexes.[9e,19] In other words, this implies that the electronic factors override the unfavorable steric interactions when highly polarized alkynes are involved.




12 11i 11j 13

**Figure 4.**




**Scheme 4.**

**Table 2.** Cyclopentannulation of carbene complexes **5a**,**b** (all the reactions were carried out at 50–60°C at 0.03 M in carbene complex in THF or toluene)

| Entry | Compd[a] | $R^1$ | $R^2$ | $R^3$ | Yield[a,b] (%) |
|---|---|---|---|---|---|
| 1 | **15a** (**16a**) | Et | COOMe | Me | 81 (70) |
| 2 | **15b** (**16b**) | Et | COOEt | Et | 77 (72) |
| 3 | **15c** | Et | Ph | Et | 70 |
| 4 | **15d** | Et | Pr | Et | 61 |
| 5 | **15e** | (1*R*,2*S*,5*R*)-Menthyl | COOMe | Me | 67 |

[a] Compounds **16** isolated and their yields are in parenthesis.
[b] Isolated, nonoptimized yields of purified products.

## Conclusions

New alkenyl(amino)carbene chromium and tungsten complexes bearing an electron-withdrawing group at the $C_\beta$-position were prepared for the first time. It is worth noting that the chromium complexes display a remarkable reactivity and selectivity toward both unactivated and electron-poor alkynes. Their reaction with unactivated alkynes or terminal, electron-poor alkynes results exclusively in phenol products formation. In particular, the intermolecular benzannulation of alkenyl(amino)-carbene complexes with internal alkynes is reported for the first time. On the contrary, when internal alkynes having at least one electron-withdrawing substituent are employed the reaction follows a different pathway leading to cyclopentannulation products. Steric reasons are invoked to account for the regioselectivity attained with both unactivated and terminal, electron-poor alkynes, whereas electronic factors seem to prevail in the case of disubstituted, electron-poor alkynes. One feature that should be mentioned is the isolation of chelated tetracarbonyl carbene chromium species, intermediates for the pentannulation, whose synthetic potential is being currently the subject of further investigations in our laboratory.

## Experimental

### General considerations

All common reagents were obtained from commercial suppliers and used without further purificacion unless otherwise indicated. THF and toluene were distilled from sodium benzophenone ketyl under a $N_2$ atmosphere prior to use. Hexane, ethyl acetate, dichloromethane and triethylamine were distilled before use. Flash column chromatography was carried out on silica gel 60 (230–400 mesh). NMR spectra were run on Bruker AC200 and AC300 spectrometers.

### Synthesis of the alkenyl amino carbenes 5a–b and 6

Complex **1** (**2**) (10 mmol) was dissolved in 30 mL of THF and deprotonated with *n*-BuLi (1.6 M solution in hexane, 6.9 mL, 11 mmol) under nitrogen at −78°C for 30 min. To the resulting red solution an excess of the corresponding glyoxylate (50 mmol) was added at −78°C and the resulting mixture was allowed to reach room temperature (14 h) and then treated with water (25 mL), extracted with ether (2×50 mL) and dried over $Na_2SO_4$. The solvents were removed and the resulting crude aldol adduct was used in the next step without further purification.

The crude aldol was dissolved in $CH_2Cl_2$ (30 mL) and MsCl (1.5 mL, 20 mmol) and $Et_3N$ (3.1 mL, 22 mmol) were added at 0°C. The reaction went to completion in 2 h and was quenched with methanol (20 mL). The solvents were removed and the mixture was subjected to column chromatography. Elution with hexane/$CH_2Cl_2$ (1:3) gave first unreacted **1** (**2**) and then pure mesylate **3** (**4**).

The mesylate derivatives **3** and **4** (8 mmol) were dissolved in ether (30 mL) and treated with DBU (1.8 mL, 12 mmol). The resulting mixture was stirred overnight and then treated with water (25 mL) and extracted with ether (3×20 mL). The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed to give essentially pure carbene **5a**,**b** and **6** as yellow oils which solidified upon standing. Complexes **5a**,**b** were further purified by chromatography (silica gel; 3:1 hexane/ethyl acetate as the eluent). Compound **6** was isolated as a 5:1 *E*/*Z* mixture (76% overall yield from **2**). The separation of both isomers was accomplished by chromatography (silica gel; 1:1 hexane/ethyl acetate as the eluent).

**Complex 5a.** Yield (72% from **1**); yellow solid, mp 69–71°C; IR (KBr) 3054, 2980, 2056, 1931, 1742, 1422,

1268 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$=7.7 (d, $J$=16.3 Hz, $^1H$), 5.3 (d, $J$=16.3 Hz, $^1H$), 4.24 (q, $J$=7.1 Hz, 2H), 4.18 (t, $J$=7.0 Hz, 2H), 3.84 (t, $J$=7.0 Hz, 2H), 2.15 (m, 4H), 1.31 (t, $J$=7.1 Hz, 3H); $^{13}C$ NMR ($CDCl_3$): $\delta$=262.5 (C), 222.9 (C), 217.0 (C), 166.2 (C), 150.4 (CH), 109.4 (CH), 60.7 ($CH_2$), 58.8 ($CH_2$), 56.2 ($CH_2$), 25.4 ($CH_2$), 25.0 ($CH_2$), 14.2 ($CH_3$); LRMS(EI) *m/z* 373 (5), 345 (20), 233 (90), 161 (100), 110 (60). Anal. Calcd for $C_{15}H_{15}NO_7Cr$: C, 48.26; H, 4.05; N, 3.75. Found C, 48.27; H, 4.02; N, 3.71.

**Complex 5b.** Yield (75% from **1**); yellow solid, mp 94–96°C; $[\alpha]^D$=−90.2 (in $CH_2Cl_2$, $c$=4.2); $^1H$ NMR ($CDCl_3$): $\delta$=7.67 (d, $J$=16.3 Hz, 1H), 5.26 (d, $J$=16.3 Hz, 1H), 4.78 (m, 1H), 4.18 (m, 2H), 3.66 (m, 2H), 2.1 (m, 4H), 2.0–1.0 (m, 9H), 0.93 (d, $J$=6.7 Hz, 3H), 0.90 (d, $J$=6.7 Hz, 3H), 0.79 (d, $J$=6.7 Hz, 3H); $^{13}C$ NMR ($CDCl_3$): $\delta$=262.8, 223.0, 217.0, 165.8, 150.0, 109.8, 74.7, 58.8, 56.1, 47.1, 40.9, 34.2, 31.3, 26.4, 25.4, 25.1, 23.6, 22.0, 20.6, 16.5. Anal. Calcd for $C_{23}H_{29}NO_7Cr$: C, 57.14; H, 6.05; N, 2.90. Found C, 57.21; H, 6.19; N, 2.80.

**Complex (*E*) 6.** Yellow solid, mp 115–117°C; IR (KBr) 3060, 2990, 2002, 1927, 1858, 1804, 1734, 1630, 140, 1100 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$=7.55 (d, $J$=16.2 Hz, 1H), 5.35 (d, $J$=16.2 Hz, 1H), 4.23 (q, $J$=7.1 Hz, 2H), 4.02 (m, 2H), 3.59 (m, 2H), 2.15 (m, 4H), 1.30 (t, $J$=7.1 Hz, 3H); $^{13}C$ NMR ($CDCl_3$): $\delta$=243.7 (C), 202.9 (C), 197.8 (C), 165.7 (C), 151.6 (CH), 111.3 (CH), 61.1 ($CH_2$), 60.6 ($CH_2$), 54.7 ($CH_2$), 25.5 ($CH_2$), 24.7 ($CH_2$), 14.1 ($CH_3$). Anal. Calcd for $C_{15}H_{15}NO_7W$: C, 35.67; H, 2.99; N, 2.77. Found C, 35.72; H, 3.03; N, 2.77.

**Compound (*Z*) 6.** Yellow solid, mp 123–125°C; 1H ($CDCl_3$): $\delta$=6.80 (d, $J$=12 Hz, 1H), 5.21 (d, $J$=12 Hz, 1H), 4.15 (m, 4H), 3.60 (m, 2H), 2.15 (m, 4H), 1.27 (t, $J$=7.1 Hz, 3H); $^{13}C$ NMR ($CDCl_3$): $\delta$=242.4 (C), 202.6 (C), 197.9 (C), 165.1 (C), 150.4 (CH), 105.5 (CH), 60.3 ($CH_2$), 60.2 ($CH_2$), 53.9 ($CH_2$), 25.2 ($CH_2$), 24.5 ($CH_2$), 13.9 ($CH_3$).

### Synthesis of the deuteriated carbene complexes 7 and 8

To a solution of complex **5a** (0.44 mmol) in THF (20 mL) was added *n*-BuLi (1.6 M solution in hexane, 0.4 mL, 0.66 mmol) and the resulting mixture was stirred for 5 h at 0°C. An excess of $D_2O$ (0.5 mL) was added and the mixture further stirred for 20 min. The solvents were then removed and the mixture was subjected to flash chromatography on silica gel with a 3:1 mixture of hexane/ethyl acetate as the eluent to give the deuteriated complex **7** (65% yield) as a 4:1 mixture of *E*/*Z* isomers. Spectroscopic data for (*E*)-**7**: $^1H$ NMR ($CDCl_3$): $\delta$=5.3 (br s, 1H), 4.24 (q, $J$=7.1 Hz, 2H), 4.18 (t, $J$=7.0 Hz, 2H), 3.84 (t, $J$=7.0 Hz, 2H), 2.15 (m, 4H), 1.31 (t, $J$=7.1 Hz, 3H); $^{13}C$ NMR ($CDCl_3$): $\delta$=262.5 (C), 222.9 (C), 217.0 (C), 166.2 (C), 150.1 (t, $J$=23.2 Hz, CD), 109.3 (CH), 60.7 ($CH_2$), 58.8 ($CH_2$), 56.2 ($CH_2$), 25.4 ($CH_2$), 25.0 ($CH_2$), 14.2 ($CH_3$).

The same experimental procedure starting from (*E*)-**6** gave the complex **8** (68% yield) as a 3:2 mixture of *E*/*Z* isomers. Spectroscopic data for the (*E*)-**8**: $^1H$ NMR ($CDCl_3$): $\delta$=5.36 (br s, 1H), 4.2 (q, $J$=7.1 Hz, 2H), 4.0 (m, 2H), 3.6 (m, 2H), 2.15 (m, 4H), 1.31 (t, $J$=7.1 Hz, 3H); $^{13}C$ NMR ($CDCl_3$): $\delta$=243.7 (C), 202.9 (C), 197.8 (C), 165.7 (C), 151.6 (t, $J$=23.1 Hz, CD), 111.3 (CH), 61.1 ($CH_2$), 60.5 ($CH_2$), 54.7 ($CH_2$), 25.6 ($CH_2$), 24.7 ($CH_2$), 14.0 ($CH_3$). Spectroscopic data for (*Z*)-**8**: $^1H$ NMR ($CDCl_3$): $\delta$=5.21 (br s, 1H), 4.1 (m, 4H), 3.6 (m, 2H), 2.1 (m, 4H), 1.27 (t, $J$=7.1 Hz, 3H); $^{13}C$ NMR ($CDCl_3$): $\delta$=242.4 (C), 202.6 (C), 197.9 (C), 165.0 (C), 150.4 (t, $J$=23.2 Hz, CD), 105.5 (CH), 60.3 ($CH_2$), 60.2 ($CH_2$), 53.9 ($CH_2$), 25.2 ($CH_2$), 24.5 ($CH_2$), 13.9 ($CH_3$).

### General procedure for the benzannulation reaction. Synthesis of compounds 11 and 12

To a solution of the carbene complex **5a** (74 mg, 0.2 mmol) in THF (7 mL) was added an excess of the corresponding alkyne. The mixture was stirred at 60°C (16 h for **11a–i** and **11n**, 48 h for **11j–m** and **11o–q**), cooled to rt and stirred with silica gel (1 g) for 30 min. After filtration the solvent was removed and the resulting residue was subjected to flash chromatography to yield pure phenol derivatives **11**. The yields of compounds **11** are given in Table 1.

**Phenol 11a.** Yellow oil; $^1H$ ($CDCl_3$): $\delta$=10.5 (s, 1H), 6.85 (d, $J$=3.0 Hz, 1H), 6.70 (d, $J$=3.0 Hz, 1H), 4.4 (q, $J$=7 Hz, 2H), 3.24 (m, 4H), 2.6 (t, $J$=7.6 Hz, 2H), 2.0 (m, 4H), 1.66 (m, 2H), 1.41 (t, $J$=7.0, 3H), 1.0 (t, $J$=7 Hz, 3H); $^{13}C$ NMR ($CDCl_3$): $\delta$=170.8 (C), 151.2 (C), 140.9 (C), 131.3 (C), 121.3 (CH), 111.8 (C), 108.3 (CH), 61.0 ($CH_2$), 48.2 ($CH_2$), 32.3 ($CH_2$), 25.2 ($CH_2$), 22.8 ($CH_2$), 14.2 ($CH_3$), 14.0 ($CH_3$). Anal. Calcd for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05. Found C, 69.41; H, 8.38; N, 5.16.

**Phenol 11b.** Yellowish oil; $^1H$ NMR ($CDCl_3$): d 10.5 (s, 1H), 6.84 (d, $J$=3.0 Hz, 1H), 6.70 (d, $J$=3.0 Hz, 1H), 4.4 (q, $J$=7.1 Hz, 2H), 3.24 (m, 4H), 2.64 (t, $J$=6.5 Hz, 2H), 2.0 (m, 4H), 1.60 (m, 2H), 1.41 (m, 5H), 0.94 (t, $J$=7.3 Hz, 3H); $^{13}C$ NMR ($CDCl_3$): d 170.8 (C), 151.2 (C), 140.9 (C), 131.5 (C), 121.2 (CH), 111.8 (C), 108.2 (CH), 61.0 ($CH_2$), 48.3 ($CH_2$), 31.9 ($CH_2$), 29.9 ($CH_2$), 25.2 ($CH_2$), 22.6 ($CH_2$), 14.2 ($CH_3$), 14.0 ($CH_3$). Anal. Calcd for $C_{17}H_{25}NO_3$: C, 70.07; H, 8.65; N, 4.81. Found C, 70.21; H, 8.57; N, 4.89.

**Phenol 11c.** Yellowish oil; $^1H$ NMR ($CDCl_3$): $\delta$=10.5 (s, 1H), 6.84 (d, $J$=3.1 Hz, 1H), 6.70 (d, $J$=3.1 Hz, 1H), 4.39 (q, $J$=7.0 Hz, 2H), 3.24 (m, 4H), 2.62 (t, $J$=6.4 Hz, 2H), 1.9 (m, 4H), 1.6 (m, 2H), 1.42 (t, $J$=7.0 Hz, 3H), 1.29 (m, 6H), 0.91 (m, 3H); $^{13}C$ NMR ($CDCl_3$): $\delta$=170.7, 151.2, 140.8, 131.3, 121.2, 111.9, 108.1, 61.1, 48.3, 32.0, 30.0, 29.3, 27.7, 25.4, 22.5, 14.2, 14.0. Anal. Calcd for $C_{19}H_{29}NO_3$: C, 71.44; H, 9.15; N, 4.38. Found C, 71.49; H, 9.22; N, 4.31.

**Phenol 11d.** Yellow solid, mp 116–118°C; $^1H$ NMR ($CDCl_3$): $\delta$=10.68 (s, 1H), 7.64–7.36 (m, 5H), 7.04 (d, $J$=3 Hz, 1H), 6.87 (d, $J$=3 Hz, 1H), 4.4 (q, $J$=7.1 Hz, 2H), 3.30 (m, 4H), 2.02 (m, 4H), 1.45 (t, $J$=7.1 Hz, 3H); $^{13}C$ NMR ($CDCl_3$): d 170.7 (C), 150.1 (C), 141.1 (C), 138.0 (C), 130.7 (C), 129.3 (CH), 128.0 (CH), 127.1 (CH), 121.5 (CH), 112.6 (C), 110.3 (CH), 61.3 ($CH_2$), 48.3 ($CH_2$), 25.3 ($CH_2$), 14.2 ($CH_3$). Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found C, 73.39; H, 6.71; N, 4.62.

**Phenol 11e.** Orange oil; $^1H$ ($CDCl_3$): $\delta$=10.67 (s, 1H), 7.52 (d, $J$=8.0 Hz, 2H), 7.28 (d, $J$=8.0 Hz, 2H), 7.04 (d,

$J$=3.1 Hz, 1H), 6.88 (d, $J$=3.1 Hz, 1H), 4.45 (q, $J$=7.1 Hz, 2H), 3.31 (m, 4H), 2.43 (s, 3H), 2.04 (m, 4H), 1.46 (t, $J$=7.1 Hz, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$=170.5, 149.9, 140.8, 136.6, 134.8, 130.4, 129.2, 128.5, 121.2, 112.3, 109.8, 61.0, 48.0, 25.0, 20.9, 14.0. Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30. Found C, 73.85; H, 7.21; N, 4.16.

**Phenol 11f.** Orange oil; $^1$H NMR ($CDCl_3$): $\delta$=10.8 (s, 1H), 7.09 (d, $J$=3.1 Hz, 1H), 6.95 (d, $J$=3.1 Hz, 1H), 4.86 (t, $J$=1.9 Hz, 2H), 4.36 (q, $J$=7.1 Hz, 2H), 4.32 (t, $J$=1.9 Hz, 2H), 4.11 (s, 5H), 3.32 (m, 4H), 2.05 (m, 4H), 1.45 (t, $J$=7.1, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$=171.0 (C), 151.0 (C), 140.7 (C), 127.5 (C), 119.8 (CH), 112.4 (C), 109.2 (CH), 82.5 (C), 69.4 (CH), 68.8 (CH), 68.4 (CH), 61.2 ($CH_2$), 48.3 ($CH_2$), 25.3 ($CH_2$), 14.3 ($CH_3$). Anal. Calcd for $C_{23}H_{25}NO_3Fe$: C, 65.88; H, 6.01; N, 3.34. Found C, 65.71; H, 6.24; N, 3.42.

**Phenol 11g.** Yellow oil; $^1$H NMR ($CDCl_3$): d 10.98 (s, 1H), 6.91 (d, $J$=3H, 1H), 6.80 (d, $J$=3Hz, 1H), 6.58 (m, 1H), 4.41 (q, $J$=7.0 Hz, 2H), 3.27 (m, 4H), 2.83 (m, 2H), 2.57 (m, 2H), 2.01 (m, 6H), 1.43 (t, $J$=7.0 Hz, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$=171.0, 151.6, 140.8, 138.8, 131.4, 126.4, 119.5, 112.1, 109.3, 61.2, 48.3, 35.2, 33.9, 25.2, 22.7, 14.2. Anal. Calcd for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65. Found C, 71.78; H, 7.52; N, 4.71.

**Phenol 11h.** Yellow oil; $^1$H ($CDCl_3$): $\delta$=10.5 (s, 1H), 7.03 (d, $J$=3.0 Hz, 1H), 6.88 (d, $J$=3.0 Hz, 1H), 4.79 (s, 2H), 4.4 (q, $J$=7.1 Hz, 2H), 3.28 (m, 4H), 2.01 (m, 4H), 1.42 (t, $J$=7.1 Hz, 3H), 0.19 (s, 9H); $^{13}$C NMR ($CDCl_3$): $\delta$=170.7 (C), 149.7 (C), 141.2 (C), 129.7 (C), 118.5 (CH), 111.6 (C), 108.9 (CH), 61.1 ($CH_2$), 59.5 ($CH_2$), 48.2 ($CH_2$), 25.3 ($CH_2$), 14.2 ($CH_3$), −0.4 ($CH_3$). Anal. Calcd for $C_{17}H_{27}NO_4Si$: C, 60.50; H, 8.06; N, 4.15. Found C, 60.42; H, 8.19; N, 4.13.

**Benzofuran derivative 11i.** Brownish oil; $^1$H NMR ($CDCl_3$): $\delta$=6.86 (d, $J$=2.5 Hz, 1H), 6.69 (d, $J$=2.5 Hz, 1H), 4.62 (t, $J$=8.6 Hz, 2H), 4.36 (q, $J$=7.1 Hz, 2H), 3.24 (m, 4H), 3.17 (t, $J$=8.6 Hz, 2H), 1.99 (m, 4H), 1.38 (t, $J$=7.1 Hz, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$=165.9 (C), 151.7 (C), 142.7 (C), 130.0 (C), 114.0 (CH), 112.8 (C), 110.8 (CH), 71.6 ($CH_2$), 60.6 ($CH_2$), 48.3 ($CH_2$), 29.7 ($CH_2$), 25.3 ($CH_2$), 14.3 ($CH_3$). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found C, 70.17; H, 7.19; N, 5.48.

**Phenol 11j.** Yellow solid, mp 121–123°C; $^1$H NMR ($CDCl_3$): $\delta$=10.9 (s, 1H), 7.26 (s, 2H), 4.4 (q, $J$=7.1 Hz, 4H), 3.29 (m, 4H), 2.0 (m, 4H), 1.42 (t, $J$=7.1, 6H); $^{13}$C NMR ($CDCl_3$): $\delta$=168.1 (C), 152.4 (C), 140.4 (C), 118.5 (CH), 116.7 (C), 61.3 ($CH_2$), 48.1 ($CH_2$), 25.3 ($CH_2$), 14.2 ($CH_3$). Anal. Calcd for $C_{16}H_{21}NO_5$: C, 62.53; H, 6.89; N, 4.56. Found C, 62.69; H, 6.72; N, 4.53.

**Phenol 11k.** Yellow oil; 1H ($CDCl_3$): $\delta$=11.0 (s, 1H), 7.26 (s, 2H), 4.4 (q, $J$=7.0 Hz, 2H), 3.9 (s, 3H), 3.3 (m, 4H), 2.1 (m, 4H), 1.41 (t, $J$=7.0, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$=168.4 (C), 168.3 (C), 152.4 (C), 140.5 (C), 119.0 (CH), 118.4 (CH), 116.9 (C), 116.5 (C), 61.3 ($CH_2$), 52.2 ($CH_3$), 48.2 ($CH_2$), 25.3 ($CH_2$), 14.2 ($CH_3$). Anal. Calcd for $C_{15}H_{19}NO_5$: C, 61.42; H, 6.53; N, 4.77. Found C, 61.29; H, 6.60; N, 4.81.

**Phenol 11l.** Yellow oil; 1H ($CDCl_3$): $\delta$=10.9 (s, 1H), 7.27 (br s, 2H), 5.0 (m, 1H), 4.4 (q, $J$=7.1 Hz, 2H), 3.28 (m, 4H), 2.0 (m, 4H), 1.9–0.8 (m, 21H); $^{13}$C NMR ($CDCl_3$): $\delta$=168.0, 167.8, 152.4, 140.5, 118.9, 118.0, 117.4, 116.7, 75.4, 61.2, 48.1, 47.1, 40.8, 34.2, 31.4, 26.5, 25.3, 23.7, 22.0, 20.6, 16.6, 14.3. Anal. Calcd for $C_{24}H_{35}NO_5$: C, 69.04; H, 8.45; N, 3.35. Found C, 69.17; H, 8.50; N, 3.40.

**Phenol 11m.** Yellowish oil; $^1$H NMR ($CDCl_3$): $\delta$=10.93 (s, 1H), 7.23 (d, $J$=3.2 Hz, 1H), 7.20 (d, $J$=3.2 Hz, 1H), 4.4 (q, $J$=7.1 Hz, 2H), 3.3 (m, 4H), 2.7 (s, 3H), 2.0 (m, 4H), 1.42 (t, $J$=7.1, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$=200.4 (C), 169.4 (C), 153.0 (C), 140.6 (C), 125.8 (C), 119.0 (CH), 117.7 (CH), 115.1 (C), 61.5 ($CH_2$), 48.1 ($CH_2$), 31.0 ($CH_3$), 25.3 ($CH_2$), 14.2 ($CH_3$). Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.97; H, 6.90; N, 5.05. Found C, 65.12; H, 6.79; N, 4.83.

**Phenol 11n.** Yellow oil; $^1$H NMR ($CDCl_3$): d 10.7 (s, 1H), 7.7–7.3 (m, 5H), 7.0 (s, 1H), 4.4 (q, $J$=7.1 Hz, 2H), 3.30 (m, 4H), 2.02 (m, 4H), 1.45 (t, $J$=7.1 Hz, 3H); $^{13}$C NMR ($CDCl_3$): d 170.7 (C), 150.2 (C), 141.0 (C), 138.0 (C), 130.6 (C), 129.3 (CH), 128.0 (CH), 127.1 (CH), 121.3 (d, $J$=22 Hz, CD), 112.6 (C), 110.4 (CH), 61.3 ($CH_2$), 48.3 ($CH_2$), 25.2 ($CH_2$), 14.2 ($CH_3$).

**Phenol 11o.** Yellow oil; $^1$H NMR ($CDCl_3$): $\delta$=10.94 (s, 1H), 7.52 (s, 1H), 4.40 (q, $J$=7.1 Hz, 2H), 3.00 (m, 4H), 2.77 (m, 4H), 1.93 (m, 4H), 1.42 (t, $J$=7.1 Hz, 3H), 1.22 (m, 6H); $^{13}$C NMR ($CDCl_3$): $\delta$=170.5, 156.5, 147.7, 141.1, 131.2, 118.3, 109.4, 61.0, 53.9, 24.5, 21.3, 19.5, 15.3, 14.3, 14.1. Anal. Calcd for $C_{17}H_{25}NO_3$: C, 70.07; H, 8.65; N, 4.81. Found C, 70.14; H, 8.79; N, 4.73.

**Phenol 11p.** Yellowish oil; $^1$H NMR ($CDCl_3$): $\delta$=10.73 (s, 1H), 7.46 (s, 1H), 7.2–7.0 (m, 10H), 4.45 (q, $J$=7.4 Hz, 2H), 2.72 (m, 4H), 1.68 (m, 4H), 1.45 (t, $J$=7.4 Hz, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$=170.3, 153.3, 141.3, 140.3, 139.0, 136.5, 131.4, 130.7, 130.6, 127.3, 127.2, 126.3, 126.2, 114.7, 110.9, 61.3, 51.0, 24.7, 14.3. Anal. Calcd for $C_{25}H_{25}NO_3$: C, 77.49; H, 6.50; N, 3.61. Found C, 77.60; H, 6.37; N, 3.60.

**Phenol 11q.** Yellow oil; $^1$H NMR ($CDCl_3$): $\delta$=10.79 (s, 1H), 7.52 (s, 1H), 7.47–7.25 (m, 5H), 4.42 (q, $J$=7.0 Hz, 2H), 3.06 (m, 4H), 2.08 (s, 3H), 1.95 (m, 4H), 1.43 (t, $J$=7.0 Hz, 3H): $^{13}$C NMR ($CDCl_3$): $\delta$=170.4 (C), 154.5 (C), 141.6 (C), 139.7 (C), 137.2 (C), 131.7 (C), 129.8 (CH), 128.2 (CH), 127.1 (CH), 116.3 (CH), 109.4 (C), 61.2 ($CH_2$), 51.9 ($CH_2$), 24.3 ($CH_2$), 17.5 ($CH_3$), 14.2 ($CH_3$). Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30. Found C, 73.59; H, 7.25; N, 4.33.

**Phenol 12.** The deuteriated phenol **12** was prepared by heating complex **7** (0.2 mmol) with 1-pentyne (0.3 mmol) in THF (7 mL) at 60°C for 16 h. The solvent was removed at reduced pressure and the crude phenol **12** was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1 as the eluent). $^1$H NMR ($CDCl_3$): $\delta$=10.5 (s, 1H), 6.71 (s, 1H), 4.4 (q, $J$=7 Hz, 2H), 3.26 (m, 4H), 2.6 (t, $J$=7.6 Hz, 2H), 2.0 (m, 4H), 1.66 (m, 2H), 1.42 (t, $J$=7.0, 3H), 0.99 (t, $J$=7.0 Hz, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$=170.8 (C), 151.3 (C), 140.9 (C), 131.3 (C), 121.3 (CH), 111.7 (C), 108.3 (t, $J$=22 Hz, CD), 61.1 ($CH_2$), 48.3 ($CH_2$), 32.3 ($CH_2$), 25.2 ($CH_2$), 22.8 ($CH_2$), 14.2 ($CH_3$), 14.0 ($CH_3$).

### Experimental procedure for the synthesis of the $(CO)_3Cr$-arene derivative 13

A solution of the carbene complex **5a** (74 mg, 0.2 mmol) and phenyl acetylene (88 mL, 0.8 mmol) in toluene (7 mL) was degassed by the freeze-pump-thaw method (three cycles) and heated under a nitrogen atmosphere at 60°C until the carbene complex is consumed (16 h). After cooling TBSCl (120 mg, 0.8 mmol) and triethylamine (120 μL, 0.8 mmol) were added and the resulting mixture stirred for 16 h at rt. The solvent was removed at reduced pressure and the arene complex **13** was isolated as a brown oil after chromatographic purification (silica gel, hexane/ethyl acetate 4:1 as the eluent). $^1$H NMR ($CDCl_3$): $\delta$=7.6 (m, 2H), 7.4 (m, 3H), 5.32 (d, $J$=2 Hz, 1H), 5.14 (d, $J$=2 Hz, 1H), 4.5 (m, 1H), 4.2 (m, 1H), 3.2 (m, 4H), 1.4 (t, $J$=7 Hz, 3H), 0.8 (s, 9H), −0.17 (s, 3H), −0.56 (s, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$=234.7, 166.7, 135.5, 131.1, 130.2, 128.6, 127.8, 125.2, 105.6, 88.2, 79.0, 75.5, 61.8, 48.2, 25.8, 25.0, 18.1, 14.2, −4.8, −4.9. Anal. Calcd for $C_{28}H_{35}NO_6CrSi$: C, 59.88; H, 6.28; N, 2.49. Found C, 60.01; H, 6.12; N, 2.60.

### General procedure for the cyclopentannulation reaction. Synthesis of compounds 15

To a solution of the carbene complex **5a,b** (0.2 mmol) in THF (7 mL) was added the substituted propynoic ester **14** (0.24 mmol). The mixture was stirred at 60°C for 16 h. Removal of the solvent and chromatographic purification on silica gel (hexane/$CH_2Cl_2$ 1:5 as the eluent) furnished the cyclopentadiene derivatives **15** as yellow oils. The yields of compounds **15** are given in Table 2.

**Cyclopentadiene 15a.** $^1$H NMR ($CDCl_3$): $\delta$=4.2 (q, $J$=7.0 Hz, 2H), 3.9 (s, 3H), 3.7 (s, 3H), 3.6 (m, 4H), 3.5 (s, 2H), 2.0 (m, 4H), 1.3 (t, $J$=7.0 Hz, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$=166.2, 165.4, 163.2, 162.7, 151.1, 111.8, 103.2, 59.9, 52.1, 51.3, 50.9, 41.1, 25.5, 14.2. Anal. Calcd for $C_{16}H_{21}NO_6$: C, 53.43; H, 6.55; N, 4.33. Found C, 53.44; H, 6.69; N, 4.17.

**Cyclopentadiene 15b.** $^1$H NMR ($CDCl_3$): $\delta$=4.4 (q, $J$=7.0 Hz, 2H), 4.2 (m, 4H), 3.6 (m, 2H), 3.4 (s, 2H), 3.3 (m, 2H), 2.0 (m, 4H), 1.4 (t, $J$=7.0 Hz, 3H), 1.3 (t, $J$=7.0 Hz, 6H); $^{13}$C NMR ($CDCl_3$): $\delta$=166.8 (C), 165.3 (C), 163.0 (C), 162.7 (C), 151.0 (C), 111.7 (C), 100.4 (C), 61.1 ($CH_2$), 59.8 ($CH_2$), 59.7 ($CH_2$), 51.9 ($CH_2$), 41.2 ($CH_2$), 26.4 ($CH_2$), 14.3 ($CH_3$), 14.1 ($CH_3$), 14.0 ($CH_3$). Anal. Calcd for $C_{18}H_{25}NO_6$: C, 61.52; H, 7.17; N, 3.99. Found C, 61.60; H, 7.29; N, 3.82.

**Cyclopentadiene 15c.** $^1$H NMR ($CDCl_3$): $\delta$=7.3–7.1 (m, 5H), 4.00 (q, $J$=7.0 Hz, 2H), 3.76 (q, $J$=7.0 Hz, 2H), 2.52 (s, 2H), 3.4 (m, 4H), 2.0 (m, 4H), 0.97 (t, $J$=7.0 Hz, 3H), 0.68 (t, $J$=7.0 Hz, 3H); $^{13}$C NMR (CDCl3): $\delta$=165.5 (C), 164.4 (C), 162.2 (C), 160.0 (C), 137.9 (C), 127.5 (CH), 127.0 (CH), 126.7 (CH), 111.9 (C), 106.4 (C), 59.6 ($CH_2$), 58.9 ($CH_2$), 51.4 ($CH_2$), 41.7 ($CH_2$), 25.8 ($CH_2$), 13.9 ($CH_3$), 13.3 ($CH_3$). Anal. Calcd for $C_{21}H_{25}NO_4$: C, 70.96; H, 7.09; N, 3.94. Found C, 70.88; H, 7.17; N, 4.01.

**Cyclopentadiene 15d.** $^1$H NMR ($CDCl_3$): $\delta$=4.2 (m, 4H), 3.4 (m, 6H), 2.9 (t, $J$=7.6 Hz, 2H), 2.0 (m, 4H), 1.54 (m, 2H), 1.3 (m, 6H), 0.9 (t, $J$=7 Hz, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$=165.6 (C), 165.0 (C), 163.7 (C), 163.6 (C), 110.2 (C), 104.6 (C), 59.7 ($CH_2$), 58.8 ($CH_2$), 51.5 ($CH_2$), 41.4 ($CH_2$), 30.3 ($CH_2$), 25.5 ($CH_2$), 23.0 ($CH_2$), 14.5($CH_3$), 14.4 ($CH_3$), 14.3 ($CH_3$). Anal. Calcd for $C_{18}H_{27}NO_4$: C, 67.26; H, 8.47; N, 4.36. Found C, 67.40; H, 8.58; N, 4.27.

**Cyclopentadiene 15e.** $[\alpha]^D$=−80.6 (in $CH_2Cl_2$, $c$=5.1); $^1$H NMR ($CDCl_3$): $\delta$=5.0 (m, 1H), 3.9 (s, 3H), 3.7 (s, 3H), 3.3 (m, 6H), 2.0 (m, 4H), 1.9–0.8 (m, 18H); $^{13}$C NMR ($CDCl_3$): $\delta$=165.1, 163.7, 163.2, 161.5, 161.2, 112.8, 107.1, 74.7, 51.8, 50.7, 49.7, 41.2, 41.0, 34.0, 31.2, 26.5, 25.5, 23.7, 22.1, 20.6, 16.5. Anal. Calcd for $C_{24}H_{35}NO_6$: C, 66.49; H, 8.14; N, 3.23. Found C, 66.55; H, 8.27; N, 3.19.

### Isolation of the tetracarbonyl complexes 16a,b

To a solution of the carbene complex **5a** (0.2 mmol) in dry toluene (7 mL) was added dimethyl (diethyl) acetylenedicarboxylate (0.24 mmol). The mixture was stirred for 2 h at 60°C. The solvent was removed and the mixture was subjected to column chromatography. Elution with hexane/ethyl acetate (1:1) gave first unreacted **5a** and then pure tetracarbonyl derivatives **16a** (**16b**) as dark green oils.

**Complex 16a.** IR (KBr) 3169, 2016, 1919, 1905, 1680, 1304, 1217 cm$^{-1}$; $^1$H ($CDCl_3$): $\delta$=4.5 (d, $J$=9.1 Hz, 1H), 4.3–4.0 (m, 4H), 3.7 (s, 3H), 3.65 (d, $J$=9.1 Hz, 1H), 3.6 (m, 1H), 3.55 (s, 3H), 3.5 (m, 1H), 2.4–1.9 (m, 4H), 1.2 (t, $J$=6.9 Hz, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$=244.2 (C), 235.0 (C), 229.0 (C), 226.6 (C), 221.1 (C), 176.8 (C), 176.0 (C), 171.1 (C), 157.7 (C), 123.7 (C), 69.9 (CH), 67.8 (CH), 60.8 ($CH_2$), 54.0 ($CH_2$), 52.7 ($CH_2$), 51.7 ($CH_3$), 50.7 ($CH_3$), 25.6 ($CH_2$), 24.6 ($CH_2$), 14.0 ($CH_3$). Anal. Calcd for $C_{20}H_{21}CrNO_{10}$: C, 49.29; H, 4.34; N, 2.87. Found C, 49.32; H, 4.40; N, 2.91.

**Complex 16b.** $^1$H ($CDCl_3$): $\delta$=4.5 (d, $J$=9.1 Hz, 1H), 4.3–4.0 (m, 6H), 3.7 (d, $J$=9.1 Hz, 1H), 3.5 (m, 2H), 2.4–1.9 (m, 4H), 1.3 (m, 6H); $^{13}$C NMR ($CDCl_3$): $\delta$=244.1, 235.1, 229.3, 226.8, 221.3, 176.2, 171.3, 157.6, 123.8, 70.0, 67.9, 60.92, 60.87, 59.8, 54.1, 52.7, 25.7, 24.8, 14.4, 14.1, 13.8. Anal. Calcd for $C_{22}H_{25}CrNO_{10}$: C, 51.27; H, 4.89; N, 2.72. Found C, 51.40; H, 4.93; N, 2.80.

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