Organometallics **1998,** *17,* 4353−4361 4353

Diarylcarbene Complexes of Chromium from Diazo Precursors: Synthesis and Reaction with Electron-Rich Alkynes[1]

Jürgen Pfeiffer[†] and Karl Heinz Dötz*

Kekulé-Institut für Organische Chemie und Biochemie, Universität Bonn,
Gerhard-Domagk-Strasse 1, D-53121 Bonn, Germany

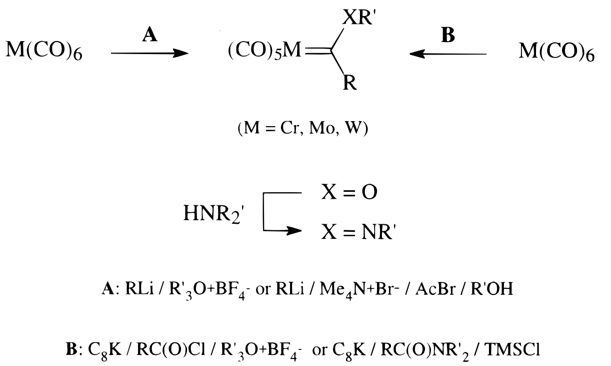
Received December 10, 1997

By reaction with pentacarbonyl(η^2-*cis*-cyclooctene)chromium(0) (**1**) various diaryl diazo compounds have been converted into the corresponding chromium carbene complexes **9**−**15**, **18**, and **19** which, in certain cases, show extraordinary low-field ^{13}C NMR shifts (>400 ppm) for the carbene carbon atoms. The carbene complexes obtained by this "diazo route" undergo insertion of nucleophilic alkynes such as 1-(diethylamino)-1-propyne or ethoxyethyne into the metal−carbene bond to yield the α,β-unsaturated carbene complexes **20**−**28** by C_2 homologization.

Introduction

Fischer-type carbene complexes have become valuable tools for stereoselective carbon−carbon bond formation over the last two decades.[2] Since their invention, several strategies have been developed for the synthesis of this class of compounds. The two most important synthetic pathways are the classical *Fischer* route[3] (Scheme 1, **A**) and the dianion route, developed by *Semmelhack* and *Hegedus* (Scheme 1, **B**),[4] both based upon complementary strategies of electrophile/nucleophile combinations starting from the $M(CO)_6$ complexes (M = Cr, Mo, W).

Scheme 1. Synthesis of Fischer-Type Carbene Complexes



Following an earlier approach to $C_5H_5(CO)(L)M{=}CPh_2$ (M = Mn, L = CO; M = Cr, L = NO)[5] or to ruthenium complexes,[6] we focused our interest on the preparation of pentacarbonyl carbene complexes from diazo precursors and group 6 metal complexes $(CO)_5M{-}L$, bearing the weakly bonded ligand L (M = Cr, W; L = e.g. THF, *cis*-cyclooctene). Recently, we reported the synthesis of the first tricyclic carbene complexes from diazo precursors and pentacarbonyl(η^2-*cis*-cyclooctene)chromium(0) (**1**) and their benzannulation reaction with 1-hexyne.[7] We extended this route to a variety of aryl diazo compounds in order to elucidate the scope of this complementary approach to metal carbenes which we subsequently exploited in carbon−carbon bond formation using electron-rich alkynes.

Results and Discussion

Reaction of Aryl Diazo Compounds with Chromium and Tungsten Complexes $(CO)_5M{-}L$ (M = Cr, W; L = *cis*-Cyclooctene, THF). Addition of a solution of the diaryl diazo compounds **2**−**5** in PE/CH_2Cl_2 (9/1 v/v; PE = petroleum ether) to a suspension of

---

[†] Present address: Institut für Anorganische Chemie der Technischen Universität Wien, Getreidemarkt 9/153, A-1060 Wien, Austria.

(1) Reactions of Complex Ligands. 79. Part 78: Pfeiffer, J.; Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2828.

(2) For reviews see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; VCH: Weinheim, Germany, 1983. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone F. G. A., Wilkinson G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 12, p 549. (d) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 5, p 1065. (e) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 12, p 469. (f) Harvey, D. F., Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271. (g) de Meijere, A. *Pure Appl. Chem.* **1996**, *68*, 61. (h) Barluenga, J. *Pure Appl. Chem.* **1996**, *68*, 543. (i) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163.

(3) (a) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580. (b) Fischer, E. O.; Selmayr, T.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 2947. (c) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 4364.

(4) (a) Öfele, K. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 950. (b) Rees, C. W.; von Angerer, E. *J. Chem. Soc., Chem. Commun.* **1972**, 420. (c) Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702. (d) Schwindt, M. A.; Miller, J. R.; Hegedus, L. S. *J. Organomet. Chem.* **1991**, *413*, 143. (e) Schwindt, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814. (f) Semmelhack, M. F.; Lee, G. R. *Organometallics* **1987**, *6*, 1839.

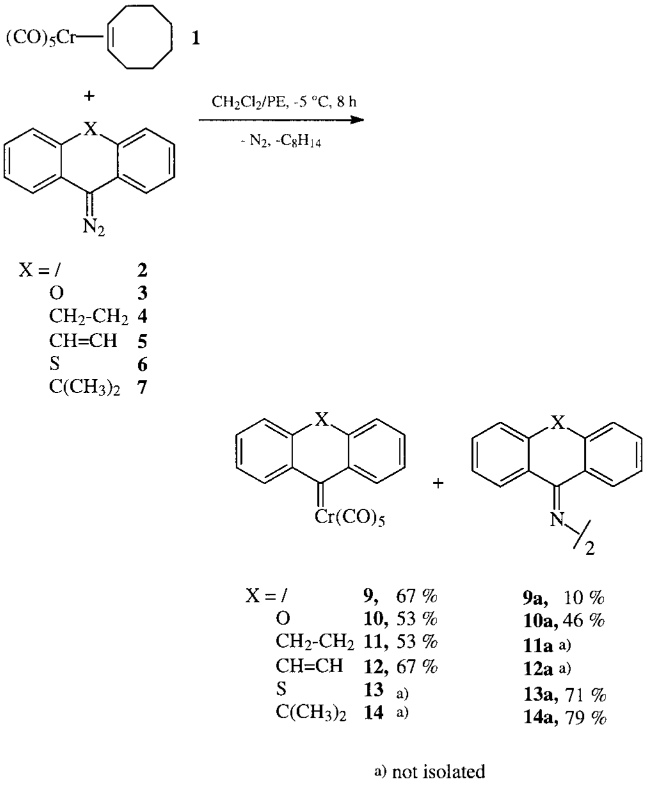
(5) (a) Herrmann, W. A., *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 599. (b) Herrmann, W. A. *Chem. Ber.* **1975**, *108*, 486. (c) Herrmann, W. A.; Hubbard, J. L.; Bernal, I.; Korp, J. D.; Haymore, B. L.; Hillhouse, G. L. *Inorg. Chem.* **1984**, *23*, 2978.

(6) (a) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039. (b) Schwab, P.; Ziller, J. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 100.

(7) Dötz, K. H.; Pfeiffer, J. *J. Chem. Soc., Chem. Commun.* **1996**, 895.

S0276-7333(97)01086-8 CCC: $15.00
Publication on Web 09/04/1998

Scheme 2. Synthesis of Tricyclic Diarylcarbene Complexes 9−14

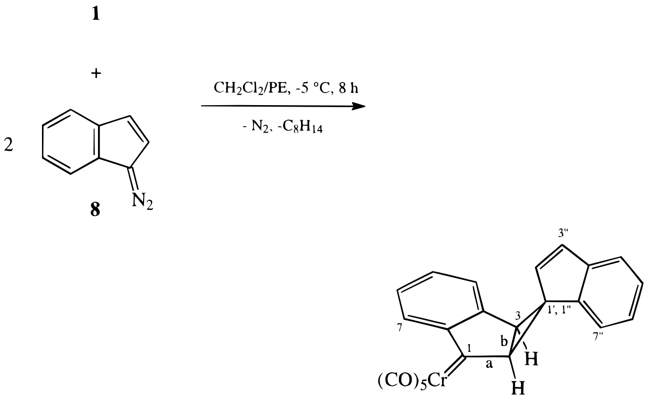


pentacarbonyl(η^2-*cis*-cyclooctene)chromium(0) (**1**) in CH$_2$Cl$_2$ at −5 °C over 8 h was accompanied by evolution of nitrogen and afforded intensely colored reaction mixtures. Crystallization at −78 °C followed by chromatographic workup on silica gel led to the tricyclic diarylcarbene complexes **9**−**12** in good yields along with the corresponding azines **9a**−**12a** as the major byproducts (Scheme 2). Reaction of 9-diazo-(9*H*)-thioxanthene (**6**) also resulted in formation of an intensely blue reaction mixture, but the corresponding thioxanthenylidene complex could not be isolated; decomposition occurred during chromatographic workup, giving only the azine **13a**. In the case of 9-diazo-9,10-dihydro-10,10-dimethylanthracene (**7**), the reaction required temperatures above +5 °C, the dark red color of the reaction mixture diminished within a few minutes after the addition of **7** was completed, and again, only the corresponding azine **14a** could be obtained.

To support the formation of **13** and **14** by NMR spectroscopy, equimolar amounts of **1** and **6** or **7**, respectively, were dissolved in CDCl$_3$ at −30 °C and warmed to room temperature for 5 min. After the temperature was lowered to −30 °C again, ^{1}H and ^{13}C NMR spectra of the samples were recorded. Subtraction of the known resonances of **1**, **13a**, and **14a**, respectively, allowed the unambiguous identification of the carbene complexes **13**[8] and **14**.[9]

Surprisingly, reaction of 1-diazo-(1*H*)-indene (**8**) with cyclooctene complex **1** did not yield the expected 1(1*H*)-indenylidene complex; instead, the pentacarbonylchromium carbene complex **15** was formed, arising from the incorporation of two indene moieties. Spectroscopic data indicated the formation of a novel pentacyclic carbon skeleton (Scheme 3).

Scheme 3. Synthesis of the Pentacyclic Carbene Complex 15



15, 47 %

The ^{1}H NMR spectrum of **15** is characterized by two AX systems corresponding to the cyclopropyl protons (δ 4.29, 5.52; $^3J_{HH}$ = 3.33 Hz) and the alkene protons of the spiro-linked indene unit (δ 5.27, 6.76; $^3J_{HH}$ = 5.66 Hz). Most indicative for the formation of the cyclopropane skeleton are the ^{13}C NMR signals at 77.08 (s), 67.45 (d, 178.3 Hz), and 47.79 (d, 178.6 Hz) ppm. We assume an *exo* stereochemistry of the spirocyclic structure, since no characteristic upfield shift of the indenylidene arene protons H-6″ and H-7″ is observed as expected for an *endo* cycloadduct due to anisotropy arising from the ring current of the indylidene complex moiety.

Reaction of the unbridged diaryl diazo compounds **16** and **17** with cyclooctene complex **1** gave similar good yields of diarylcarbene complexes **18** and **19**, respectively (Scheme 4).

The choice of the *cis*-cyclooctene complex as a source for the metal fragment is crucial. When 9-diazo-(9*H*)-

---

(8) Assignment of the ^{13}C NMR signals was achieved by subtraction of the resonances known for **1**.[23] Spectroscopic data obtained after column chromatographic workup (eluent dichloromethane) for **bis[9-(9*H*)-thioxanthenylidene]azine (13a):** orange solid; R_f 0.7 (CH$_2$Cl$_2$); mp 282 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.32−7.42 (m, 6H, Ar H), 7.43−7.48 (m, 4H, Ar H), 7.56 (d, 2H, $^3J_{HH}$ = 7.77 Hz, Ar H), 8.10 (d, 2H, $^3J_{HH}$ = 7.93 Hz, Ar H), 8.18 (d, 2H, $^3J_{HH}$ = 7.34 Hz, Ar H); ^{13}C NMR (125.6 MHz, CDCl$_3$) δ 125.20 (2C, Ar C$_t$), 125.43 (2C, Ar C$_t$), 126.11 (2C, Ar C$_t$), 126.70 (2C, Ar C$_t$), 127.49 (2C, Ar C$_t$), 127.62 (2C, Ar C$_q$), 128.88 (2C, Ar C$_t$), 129.77 (2C, Ar C$_t$), 131.86 (2C, Ar C$_t$), 132.63 (2C, Ar C$_q$), 132.69 (2C, Ar C$_q$), 135.09 (2C, Ar C$_q$), 150.12 (2C, C═N); FT-IR (KBr) 3057 (*m*, CH), 1577 (*s*, C═N), 1544 (*s*, C═N), 1462 (*s*), 1435 (*s*), 1070 (*m*), 768 (*s*), 732 (*vs*) cm^{-1}; MS (EI) *m*/*z* (%) 420 (M$^+$, 100), 387 (12), 343 (35), 236 (52), 210 (19), 196 (24), 152 (51); HR-MS calcd for $C_{26}H_{16}N_2S_2$ 420.0755, found 420.0760 (M$^+$).

(9) Assignment of the ^{13}C NMR signals was achieved by subtraction of the resonances known for **1**[23] and **14a**. Spectroscopic data obtained after decomposition of **14** and column chromatographic workup (eluent dichloromethane) for **bis(9,10-dihydro-10,10-dimethyl-9-anthracenylidene)azine (14a):** orange solid; R_f 0.45 (CH$_2$Cl$_2$); mp 212 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.71 (s, 12H, CH$_3$), 7.27 (t, 2H, $^3J_{HH}$ = 7.55 Hz, Ar H), 7.32 (t, 2H, $^3J_{HH}$ = 7.43 Hz, Ar H), 7.38 (t, 2H, $^3J_{HH}$ = 7.75 Hz, Ar H), 7.39 (t, 2H, $^3J_{HH}$ = 7.80 Hz, Ar H), 7.58 (d, 2H, $^3J_{HH}$ = 7.35 Hz, Ar H), 7.64 (d, 2H, $^3J_{HH}$ = 7.84 Hz, Ar H), 8.06 (d, 2H, $^3J_{HH}$ = 7.85 Hz, Ar H), 8.19 (d, 2H, $^3J_{HH}$ = 7.60 Hz, Ar H); ^{13}C NMR (125.6 MHz, CDCl$_3$) δ 31.59 (4C, CH$_3$), 39.54 (2C, C-10, C-10′), 123.89 (2C, Ar C$_t$), 124.28 (2C, Ar C$_t$), 125.55 (2C, Ar C$_t$), 126.14 (2C, Ar C$_t$), 126.60 (2C, Ar C$_t$), 129.08 (2C, Ar C$_t$), 129.57 (2C, Ar C$_q$), 129.85 (2C, Ar C$_t$), 130.44 (2C, Ar C$_t$), 134.41 (2C, Ar C$_q$), 145.99 (2C, Ar C$_q$), 148.05 (2C, Ar C$_q$), 149.24 (2C, C═N); FT-IR (KBr) 3057 (*m*), 2969 (*m*), 1591 (*s*, C═N), 1560 (*s*, C═N), 1476 (*s*), 1448 (*s*), 1261 (*s*), 792 (*s*), 756 (*vs*), 669 (*s*) cm^{-1}; MS (EI) *m*/*z* (%) 440 (M$^+$, 66), 425 (M$^+$ − CH$_3$, 100), 410 (M$^+$ − 2CH$_3$, 40), 395 (M$^+$ − 3CH$_3$, 18), 246 (22), 207 (37), 191 (28), 149 (25); HR-MS calcd for $C_{32}H_{28}N_2$ 440.2252, found 440.2254 (M$^+$). Anal. Calcd for $C_{32}H_{28}N_2$: C, 87.24; H, 6.41; N, 6.36. Found: C, 87.06; H, 6.35; N, 6.24.

Scheme 4. Synthesis of Diarylcarbene Complexes 18 and 19

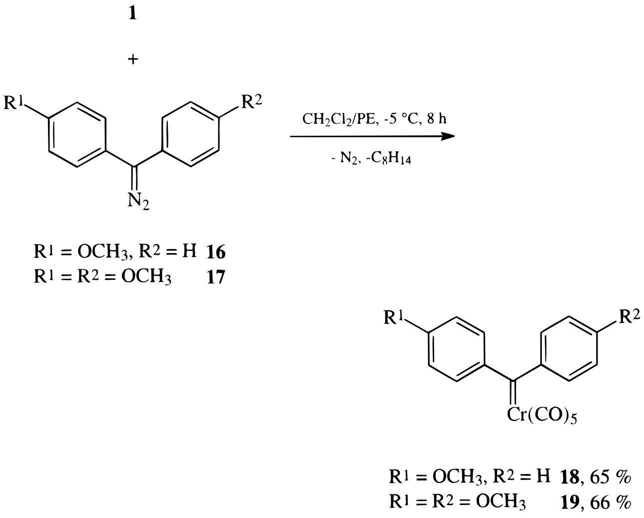


Table 1. ^{13}C NMR Chemical Shifts for the Carbene and Carbonyl Carbon Atoms in 9−15, 18 and 19

compd	$\delta_{CO_{cis}}$	$\delta_{CO_{trans}}$	$\delta_{C_{carbene}}$
9	217.45	238.78	361.29
10	218.55	230.03	314.94
11	215.22	234.74	419.14
12	214.53	237.37	404.24
13	215.49	235.39	357.80
14	216.73	233.65	378.64
15	216.56	232.85	370.89
18	216.49	234.24	385.77
19	216.71	233.47	380.18

fluorene (**2**) and 9-diazo-(9*H*)-xanthene (**3**) were reacted with $(CO)_5Cr{-}THF$, the fluorenylidene complex **9** could be obtained only in poor yield (8%), whereas reaction of **3** only gave azine **10a**. The reactions of **2** and **3** with the analogous tungsten complexes $(CO)_5W{-}L$ (L = *cis*-cyclooctene, THF) did not afford the expected tungsten carbene complexes at all; instead, the azines **9a** and **10a** were obtained in 81−88% yield.

The formation of the carbene complexes **9**−**15**, **18**, and **19** can be rationalized either in terms of an electrophilic attack of the Lewis acid $Cr(CO)_5$ at the diazo carbon atom followed by loss of molecular nitrogen or by *side-on*[10] or *end-on*[11] coordination of the diazo compound at the $Cr(CO)_5$ fragment followed by metal migration.[7]

The spectroscopic properties and thermal stabilities of the carbene complexes **9-15** depend on the ability of the carbene substituents to stabilize the electron deficiency at the carbene carbon atom. This capability is controlled by the arene-bridging, electron-releasing heteroatom as well as by the geometry of the central ring system bearing the pentacarbonylmetal fragment and is reflected by the ^{13}C NMR shifts (Table 1).

Accordingly, the xanthenylidene complex **10** can be regarded as a vinylogous aryloxycarbene complex. As a consequence, **10** can be handled at room temperature and benzannulation requires gentle warming above ambient temperature (40 °C).[7] The fluorenylidene complex **9** and the spiro compound **15** show upfield chemical shifts for the carbene carbon atom compared to those found for the unbridged pentacarbonyl(diphenylcarbene)chromium(0) (399.4 ppm).[12] This result reflects the rigid, almost planar fluorenylidene and indenylidene moiety, respectively, resulting in an optimal overlap of the arene π orbital and the p orbital at the carbene carbon atom. In contrast, this interaction is hampered in carbene complexes **11** and **12** bearing a nonplanar seven-membered central carbocycle.[13] Thus, to the best of our knowledge, these two complexes exhibit the largest downfield shifts observed for metal-coordinated carbene carbon atoms so far (419.1 and 404.2 ppm, respectively).

Insertion Reaction of 1-(Diethylamino)-1-propyne with 9−12, 15, 18, and 19. Insertion of nucleophilic alkynes such as ynamines and ynol ethers into a metal−carbene bond is a straightforward approach to α,β-unsaturated carbene complexes.[14] To explore the reactivity of the carbene complexes obtained from diazo precursors, **9**−**12**, **15**, **18**, and **19** were treated with equimolar amounts of the ynamine $Et_2NC{\equiv}CMe$. Reaction of **9**, **10**, and **15** occurred smoothly at −60 °C in CH_2Cl_2 within 2 min, whereas the unbridged diarylcarbene complexes **18** and **19** required temperatures above −20 °C. This reduced reactivity is presumably a consequence of the free rotation of the aryl substituents, hampering the approach of the ynamine. Surprisingly, reaction of **11** and **12** with 1-(dimethylamino)-1-propyne did not occur below room temperature, and even under these conditions, the dibenzocycloheptenylidene complex **12** gave only a low yield, whereas no insertion product from **11** could be obtained at all. Chromatographic workup on silica gel afforded the α,β-unsaturated aminocarbene complexes **20**−**25** in moderate to good yields (Scheme 5).

The ynamine insertion into the chromium−carbene carbon bond of complexes bearing unsymmetric carbene ligands such as **15** and **18** results in the formation of diastereomers differing in the configuration of the newly formed C═C bond. The diastereomers of **23** (ratio 3.4:1) could be separated by fractional crystallization from hexane at −78 °C, whereas in the case of **24** (ratio 5.6:1), only the major isomer could be obtained as a diastereomerically pure sample. According to previous work on the stereoselectivity of the ynamine insertion,[14d,15] the major isomers are presumed to adopt the *E* configuration.

The ^{1}H NMR spectra of carbene complexes **20**−**25** are characterized by a fine structure (doublets of quartets) of the NCH_2 proton resonances, which adopt the shape of a pseudosextet due to the fact that the coupling

---

[10] Nakamura, A.; Yoshida, T.; Cowie, M.; Otsuka, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2108.

[11] (a) Herrmann, W. A. *J. Organomet. Chem.* **1975**, *84*, C25. (b) Dahl-Schramm, K.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 2932.

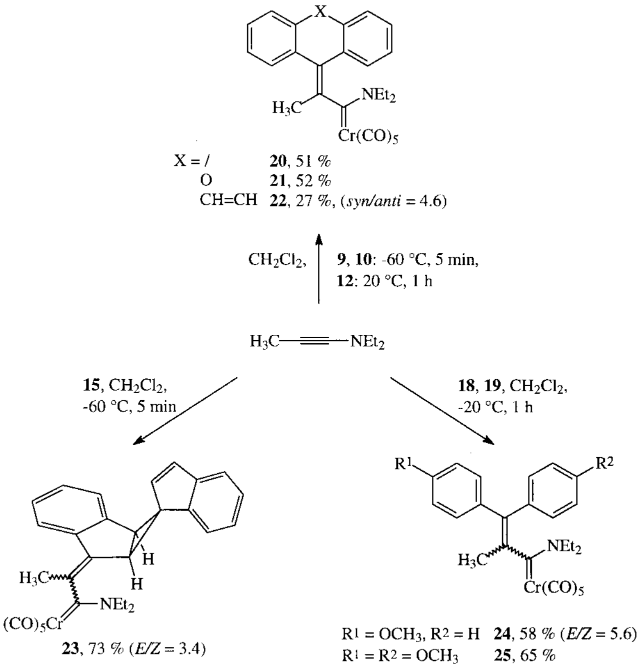
[12] Fischer, E. O.; Held, W.; Kreissl, F. R.; Frank, A.; Huttner, G. *Chem. Ber.* **1977**, *110*, 656.

[13] Crystal structures are known for the analogous ketones: (a) Oddon, Y.; Darbon, N.; Reboul, J. P.; Cristeau, B.; Soyfer, J. C.; Pèpe G. *Acta Crystallogr.* **1984**, *C40*, 524. (b) Reboul, J. P.; Soyfer, J. C.; Cristeau, B.; Darbon, N.; Oddon, Y.; Pèpe, G. *Acta Crystallogr.* **1983**, *C39*, 600.

[14] (a) Dötz, K. H.; Kreiter, C. G. *J. Organomet. Chem.* **1975**, *99*, 309. (b) Dötz, K. H.; Kreiter, C. G. *Chem. Ber.* **1976**, *109*, 2026. (c) Dötz, K. H. *Chem. Ber.* **1977**, *110*, 78. (d) Dötz, K. H.; Pruskil, I. *J. Organomet. Chem.* **1977**, *132*, 115. (e) Aumann, R.; Heinen, H.; Hinterding, P.; Sträter, N.; Krebs, B. *Chem. Ber.* **1991**, *124*, 1229. (f) Aumann, R.; Heinen, H.; Goddard, R.; Krüger, C. *Chem. Ber.* **1991**, *124*, 2587. (g) Dötz, K. H.; Ehlenz, R.; Paetsch, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2376.

[15] Pruskil, I. Ph.D. Thesis, TU Munich, 1980.

Scheme 5. Ynamine Insertion Reactions of Carbene Complexes 9, 10, 12, 15, 18, and 19



constants $^2J_{HH}$ are almost twice as large as the coupling constants $^3J_{HH}$. This fine structure indicates the diastereotopy of the NCH_2 protons due to the presence of atropisomers as a consequence of a restricted rotation along the α-C_{alkene}−$C_{carbene}$ bond[14d,16] which may be separable in certain cases.[17] Due to the nonplanarity of the central seven-membered ring,[18] the NMR spectra of **22** show the presence of two diastereomers (ratio 4.6:1) which, however, could not be separated.

As a result of the planarity of the fluorenylidene system and the conformational flexibility of the xanthene moiety, respectively,[19] the atropisomers of carbene complexes **20** and **21** represent pairs of atropisomeric enantiomers. When solutions of **20** and **21** were subjected to chiral HPLC (Chiracel OD), equal amounts of both enantiomers were observed in both cases.[20]

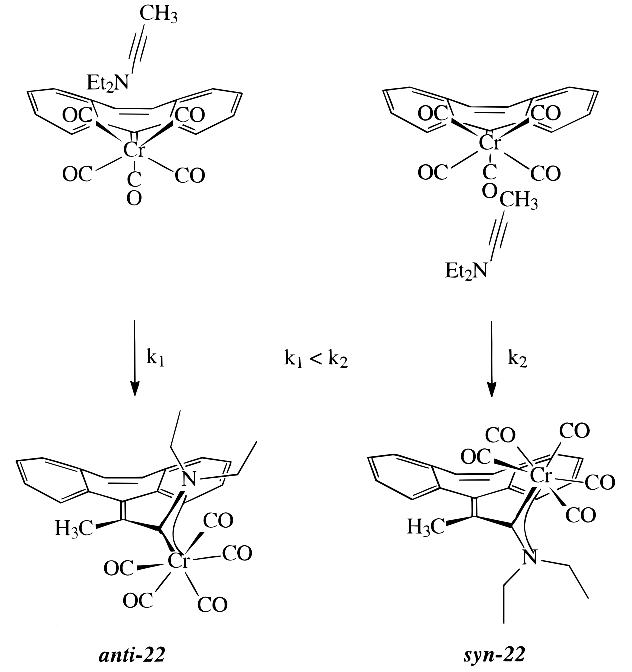


Figure 1. Stereochemical preference in the ynamine insertion reaction with **22**.

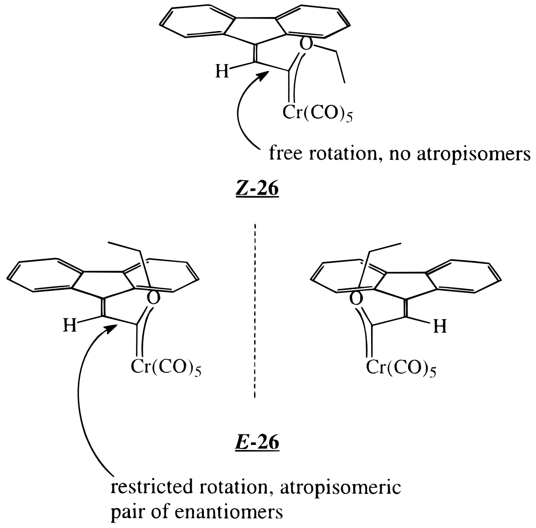


Figure 2. Stereoisomers of **26** at −40 °C.

The preference of one diastereomer of **22** over the other may be explained in terms of the tilted tricyclic ligand in **12** favoring the approach of the ynamine from the lower (convex) face. As a result, the thermodynamically less stable isomer bearing the arene rings and the $(CO)_5Cr$ fragment *syn* to each other is formed as the major diastereomer, as established by NMR-spectroscopy (Figure 1). A mixture of the *syn* and *anti* isomers was warmed in a NMR tube to 50 °C, and ^{1}H NMR spectra were recorded every 10 min to monitor the isomer ratio. Within 110 min the isomer ratio changed from 4.6:1 to 0.94:1. After this period, integration of the signals became inaccurate due to decomposition.

Insertion Reaction of Ethoxyethyne with 9, 10, and 15. To explore the insertion of the less nucleophilic ynol ethers into the metal−carbene carbon bond of polycyclic arylcarbene complexes, compounds **9**, **10**, and **15**, respectively, were treated with equimolar amounts of ethoxyethyne. The reactions were run in CH_2Cl_2 at −20 °C—reflecting the lower reactivity of the ynol ether compared to that of 1-(diethylamino)-1-propyne—and led to reddish brown solutions within 2 h. Chromatographic workup on silica gel afforded the α,*β*-unsaturated alkoxycarbene complexes **26**−**28** as brown oils in moderate yields (Scheme 6). Again, reaction with spiroindene complex **15** afforded two diastereomers (ratio 1.6:1) the major of which could be obtained in pure form by fractional crystallization.

---

[16] (a) Fischer, E. O.; Aumann, R. *Chem. Ber.* **1968**, *101*, 954. (b) Fischer, E. O.; Brunner, H.; Doppelberger, J.; Lappus, M. *J. Organomet. Chem.* **1976**, *112*, 66.

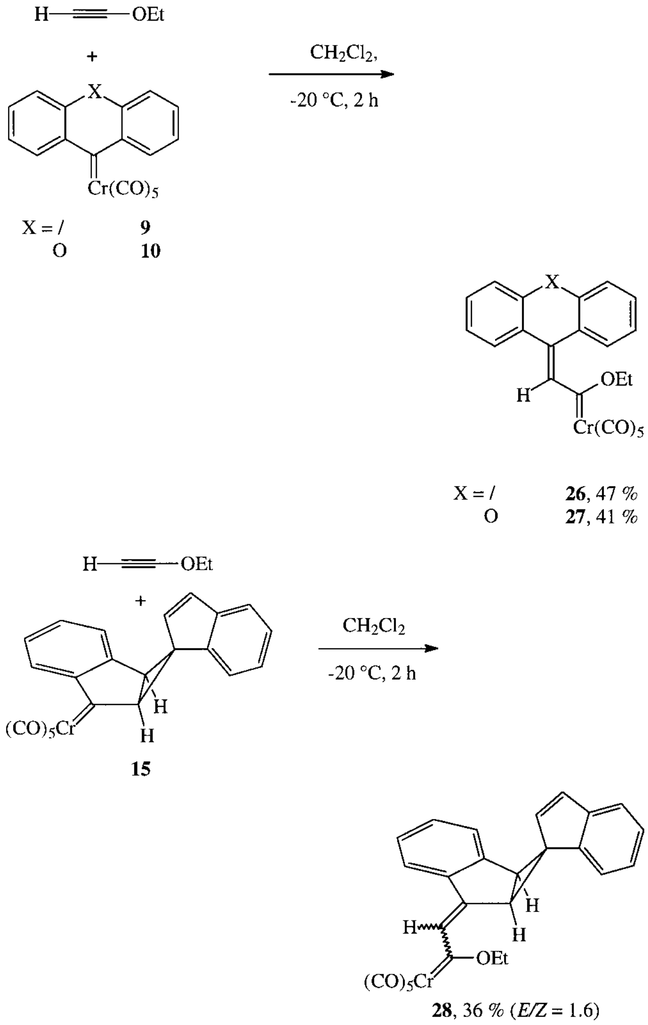
[17] Kretschik, O. Ph.D. Thesis, Universität Bonn, 1996.

[18] The nonplanarity of the dibenzo[*a*,*d*]cycloheptenylidene system in the solid state has been established by several X-ray crystal structure analyses, e.g. the ketone.[13] The temperature for the inversion of this tricyclic carbon skeleton has been found to be as high as 250 °C; see: Schönberg, A.; Sodke, U.; Praefcke, K. *Chem. Ber.* **1969**, *102*, 1453. The separation of enantiomers—which are conformationally stable at room temperature—resulting from the nonplanarity of the dibenzo[*a*,*d*]cycloheptenylidene system has been reported; see: Ebnother, A.; Jucker, E.; Stoll, A. *Helv. Chim. Acta* **1965**, *48*, 1237.

[19] (a) Aroney, M. J.; Hoskins, G. M.; LeFevre, R. *J. Chem. Soc. B* **1969**, 980. (b) McKinley, S. V.; Grieco, P. A.; Young, A. E.; Freedman, H. H. *J. Am. Chem. Soc.* **1970**, *92*, 5900.

[20] Retention times: **20**, 7.95, 9.83 min; **21**, 6.75, 7.98 min.

Scheme 6. Ynol Ether Insertion Reactions of Carbene Complexes 9, 10, and 15



NMR spectra of **26** and **27** recorded at −40 °C allowed us to detect *E*/*Z* isomers due to restricted rotation along the carbene carbon−oxygen bond under these conditions (*E*/*Z* ratio: for **26**, 2.4:1; for **27**, 1.2:1). According to previous work,[21] the major isomers are presumed to adopt the *E* configuration. In both cases, the CH_2 protons of the major isomers are magnetically inequivalent, indicating the presence of atropisomeric enantiomers (Figure 2) due to the restricted rotation around the α-C_{alkene}−$C_{carbene}$ bond.

Conclusions

The diazo route based on a *cis*-η^2-cyclooctene-stabilized pentacarbonylchromium fragment provides a straightforward approach to carbonyl complexes bearing oligocyclic carbene ligands. This methodology allows the synthesis of either bridged or nonbridged (di)arylcarbene complexes, the electrophilicity of which can be controlled by the bridge connecting the aryl substituents. Nonplanar tricyclic systems such as the dibenzocycloheptylidene complex **11** exhibit unprecedented downfield shifts for the carbene carbon atoms in the ^{13}C NMR spectra. The electrophilic nature of this type of metal carbene allows insertion reactions of nucleophilic alkynes and has been exploited in the synthesis of tricyclic *exo*-alkenyl carbene complexes, some of which are promising precursors for tetracyclic arenes with a defined substitution pattern.[22]

Experimental Section

All operations were performed using flame-dried glassware and an atmosphere of argon. Solvents (petroleum ether, bp 40−60 °C) were dried by distillation from sodium hydride or calcium hydride and saturated with argon. Silica gel (Merck, 0.063−0.200 mm) was degassed under high vacuum and stored under argon. The separation of the atropisomers of **20** and **21** was performed with a Knauer HPLC system using a Chiracel OD column (4.6 × 250 mm) from Daicel Chemical Industries Ltd. ($\lambda_{detector}$ 400 nm, *n*-hexane/2-propanol (9/1 v/v)). Pentacarbonyl(η^2-*cis*-cyclooctene)chromium(0) (**1**)[23] and -tungsten(0) (**1a**),[24] 9-diazo-(9*H*)-fluorene (**2**),[25] 9-diazo-(9*H*)-xanthene (**3**),[26] 5-diazo-(5*H*)-dibenzo[*a*,*d*]cycloheptane (**4**),[27] 5-diazo-(5*H*)-dibenzo[*a*,*d*]cycloheptene (**5**),[28] 9-diazo-(9*H*)-thioxanthene (**6**),[26] 9-diazo-9,10-dihydro-10,10-dimethylanthracene (**7**),[29] 1-diazo-(1*H*)-indene (**8**),[30] (4-methoxyphenyl)phenyldiazomethane (**16**),[31] and bis(4-methoxyphenyl)diazomethane (**17**)[31] were prepared according to the literature.

General Procedure for the Synthesis of the Carbene Complexes 9−15, 18, and 19. A solution of 5 mmol of the diazo compounds **2**−**8**, **16**, and **17** (for the preparation of **15**: 10 mmol ≡ 1.42 g of **8**) in 100 mL of petroleum ether/dichloromethane (9/1 v/v) was added over 8 h to a stirred suspension of 5 mmol (1.51 g) of pentacarbonyl(η^2-*cis*-cyclooctene)chromium(0) (**1**) in 10 mL of dichloromethane cooled to −10 °C. The workup was performed according to one of the following procedures.

Procedure A. The reaction mixture was cooled to −78 °C for 4 days. Then the precipitate was filtered off at the same temperature and washed with 40 mL of petroleum ether/dichloromethane (2/1 v/v) at −20 °C, leaving most of the azines undissolved. The washing liquid was adsorbed on 50 mL of silica gel at −40 °C. Purification by column chromatography (−40 °C, SiO_2, eluents petroleum ether/dichloromethane (2/1) for **9** and **11**−**15**, petroleum ether/chloroform (2/1) for **10**) afforded the carbene complexes. The mother liquors resulting from the crystallization were also adsorbed on 50 mL of silica gel at −40 °C and separated by column chromatography (−40 °C, SiO_2; eluent petroleum ether/dichloromethane (6/1)).

Procedure B. The reaction mixture was adsorbed on 50 mL of silica gel at −25 °C and purified by column chromatography (−25 °C, SiO_2; eluent petroleum ether/dichloromethane (2/1)).

Pentacarbonyl[9(9*H*)-fluorenylidene]chromium(0) (9). The workup was carried out according to procedure **A**. Washing of the precipitate yielded 0.09 g (0.25 mmol, 10% based on **2**) of the bis[9-(9*H*)-fluorenylidene]azine compound **9a** as an

---

[21] Kreiter, C. G.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 761.

[22] (a) Dötz, K. H.; Pruskil, I. *Chem. Ber.* **1978**, *111*, 2059. (b) Dötz, K. H.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 851.

[23] Grevels, F. W.; Skibbe, V. *J. Chem. Soc., Chem. Commun.* **1984**, 681.

[24] Dalla Riva Toma, J. M.; Toma, P. H.; Fanwick, P. E.; Bergstrom, D. E.; Byrn, S. R. *J. Crystallogr. Spectrosc. Res.* **1993**, *23*, 41.

[25] Schönberg, A.; Awad, W.; Latif, N. *J. Chem. Soc.* **1951**, 1368.

[26] (a) Lapin, S. C.; Schuster, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 4243. (b) Holton, T. C. Ph.D. Thesis, The Ohio State University, 1970.

[27] Moritani, I.; Murahashi, S.-I.; Yoshinaga, K.; Ashitaka, H. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1506.

[28] Murahashi, S.-I;, Moritani, I.; Nishino, M. *Tetrahedron* **1971**, *27*, 5131.

[29] (a) Davies, M. A.; Winthrop, S. O;, Thomas, R. A.; Herr, F.; Charest, M.-P.; Gaudry, R. *J. Med. Chem.* **1964**, *7*, 8. (b) Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 4175.

[30] Rewicki, D.; Tuchscherer, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 44.

[31] Back, C.; Praefke, K. *Chem. Ber.* **1979**, *112*, 2744.

orange solid. The workup of the washing liquids yielded 0.89 g (2.5 mmol, 50%) of **9** as a dark green solid followed by 0.03 g (0.09 mmol, 4% based on **2**) of 9,9′-bis(fluorenylidene) species **9b** as a dark red solid. The workup of the mother liquor yielded 0.24 g (0.8 mmol, 16%) of **1** followed by 0.3 g (0.85 mmol, 17%) of **9**.

9: dark green solid, 1.19 g (67%); R_f 0.45 (petroleum ether/CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, 253 K) δ 7.26 (d, $^3J_{HH}$ = 7.49 Hz, 2H, H-4, H-5), 7.29 (t, $^3J_{HH}$ = 7.89 Hz, 2H, Ar H), 7.35 (t, $^3J_{HH}$ = 7.32 Hz, 2H, Ar H), 8.05 (d, $^3J_{HH}$ = 7.55 Hz, 2H, H-1, H-8); ^{13}C NMR (100.6 MHz, $CDCl_3$, 253 K) δ 118.06 (2C, Ar C), 128.95 (2C, Ar C), 132.51 (2C, Ar C), 133.66 (2C, Ar C), 136.52 (2C, C-4a, C-4b), 148.21 (2C, C-8a, C-9a), 217.45 (4C, CO_{cis}), 238.78 (1C, CO_{trans}), 361.29 (1C, $C_{carbene}$); FT-IR (hexane) ($\nu_{C=O}$) 2060 (m, A_1), 1972 (vs, E), 1946 (sh, A_1) cm^{-1}; MS (EI) *m/z* (%) 356 (M^+, 27), 328 (M^+− CO, 100), 300 (M^+− 2CO, 17), 272 (M^+− 3CO, 1), 216 (M^+− 5CO, 54), 164 (M^+− 5CO − Cr, 5), 52 (Cr^+, 5); HR-MS calcd for $C_{18}H_8CrO_5$ 355.9777, found 355.9758 (M^+).

Pentacarbonyl[9(9*H*)-xanthenylidene]chromium(0) (10). The workup was carried out according to procedure **A**. Washing of the precipitate yielded 0.45 g (1.16 mmol, 46% based on **3**) of the bis[9-(9*H*)-xanthenylidene]azine species **10a** as an orange solid. The workup of the washing solutions afforded 0.84 g (2.25 mmol, 45%) of **10** as a black solid. The workup of the mother liquor gave 0.67 g (2.2 mmol, 44%) of **1** followed by 0.15 g (0.4 mmol, 8%) of **10**.

10: black solid, 0.99 g (54%); R_f 0.55 (petroleum ether/$CHCl_3$ 1/1); mp 83 °C dec; ^1H NMR (500 MHz, $CDCl_3$, 253 K) δ 7.68 (d, $^3J_{HH}$ = 8.60 Hz, 2H, H-4, H-5), 7.69 (t, $^3J_{HH}$ = 8.65 Hz, 2H, Ar H), 7.90 (t, $^3J_{HH}$ = 7.54 Hz, 2H, Ar H), 9.19 (d, $^3J_{HH}$ = 8.44 Hz, 2H, H-1, H-8); ^{13}C NMR (100.6 MHz, $CDCl_3$, 253 K) δ 118.94 (2C, Ar C), 125.14 (2C, Ar C), 136.85 (2C, Ar C), 140.42 (2C, Ar C), 140.65 (2C, C_q), 141.01 (2C, C_q), 218.55 (4C, CO_{cis}), 230.03 (1C, CO_{trans}), 314.94 (1C, $C_{carbene}$); FT-IR (hexane) ($\nu_{C=O}$) 2045 (m, A_1), 1945 (vs, E), 1903 (sh, A_1) cm^{-1}; MS (EI): *m/z* (%) 372 (M^+, 8), 344 (M^+ − CO, 4), 316 (M^+ − 2CO, 3), 260 (M^+ − 4CO, 5), 232 (M^+ − 5CO, 38), 180 (M^+ − 5CO − Cr, 100), 52 (Cr^+, 5); HR-MS calcd for $C_{18}H_8CrO_6$ 371.9726, found 371.9702 (M^+). Anal. Calcd for $C_{18}H_8CrO_6$: C, 58.08; H, 2.17. Found: C, 57.84; H, 2.41.

Pentacarbonyl{5(5*H*)-dibenzo[*a,d*]cycloheptylidene}-chromium(0) (11). The workup was carried out according to procedure **A**. The workup of the precipitate yielded 0.6 g (1.56 mmol, 31%) of **11** as a black solid. The workup of the mother liquor gave 0.54 g (1.8 mmol, 36%) of **1** followed by 0.43 g (1.12 mmol, 22%) of **11**.

11: black solid, 1.14 g (53%); R_f 0.65 (petroleum ether/CH_2Cl_2 1/1); ^1H NMR (500 MHz, $CDCl_3$, 253 K)[32] δ 3.10 (s, 4H, H-10, H-11), 7.00−7.40 (m, 8H, Ar H); ^{13}C NMR (125.6 MHz, $CDCl_3$, 253 K) δ 32.39 (2C, C-10, C-11), 123.92 (2C, Ar C), 125.04 (2C, C_q), 125.43 (2C, Ar C), 128.53 (2C, Ar C), 128.92 (2C, Ar C), 165.05 (2C, C_q), 215.22 (4C, CO_{cis}), 234.74 (1C, CO_{trans}), 419.14 (1C, $C_{carbene}$); FT-IR (hexane) ($\nu_{C=O}$) 2066 (m, A^1), 1981 (vs, E), 1960 (m, A^1) cm^{-1}; MS (EI) *m/z* (%) 356 (M^+ − CO, 1), 300 (M^+ − 3CO, 1), 272 (M^+ − 4CO, 3), 244 (M^+ − 5CO, 2), 192 (M^+ − 5CO − Cr, 60), 191 (M^+ − 5CO − Cr − H, 100), 165 ($C_{13}H_9^+$, 40), 52 (Cr^+, 9); HR-MS calcd for $C_{19}H_{12}CrO_4$ 356.0141, found 356.0142 (M^+ − CO).

Pentacarbonyl{5(5*H*)-dibenzo[*a,d*]cycloheptenylidene}-chromium(0) (12). The workup was carried out according to procedure **A**. The workup of the precipitate yielded 1.11 g (2.9 mmol, 58%) of **12** as a black solid and 0.04 g of an unidentified *cis*-tetracarbonyl chromium complex. The workup of the mother liquor afforded 0.34 g (1.13 mmol, 23%) of **1** followed by 0.17 g (0.45 mmol, 9%) of **12**.

12: black solid, 1.28 g (67%); R_f 0.6 (petroleum ether/CH_2Cl_2 2/1); ^1H NMR (500 MHz, $CDCl_3$, 253 K)[32] δ 6.88 (s, 2H, H-10, H-11), 7.10−7.55 (m, 8H, Ar H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 253 K) δ 119.58 (2C, C_q), 123.28 (2C), 126.98 (2C), 128.01 (2C), 128.29 (2C), 131.86 (2C) (10C, Ar C_t, C-10 and C-11), 162.68 (2C, C_q), 214.53 (4C, CO_{cis}), 237.37 (1C, CO_{trans}), 404.24 (1C, $C_{carbene}$); FT-IR (hexane) ($\nu_{C=O}$) 2068 (m, A^1), 1987 (vs, E), 1958 (m, A^1) cm^{-1}; MS (EI) *m/z* (%) 354 (M^+ − CO, 5), 298 (M^+ − 3CO, 8), 270 (M^+ − 4CO, 12), 242 (M^+ − 5CO, 21), 190 (M^+ − 5CO − Cr, 100), 52 (Cr^+, 41); HR-MS calcd for $C_{19}H_{10}CrO_4$ 353.9984, found 353.9944 (M^+ − CO).

***exo*-Pentacarbonyl{spiro-(1″*H*)-indeno-(1″,1′)cycloprop-[2′,3′-b]-1(1*H*)-indylidene}chromium(0) (15).** The workup was carried out according to procedure **A**. The workup of the precipitate yielded 0.86 g (2.04 mmol, 41%) of **15** as a black solid. The workup of the mother liquor afforded 0.23 g (0.76 mmol, 15%) of **1** followed by 0.12 g (0.28 mmol, 6%) of **15**.

15: black solid, 0.98 g (47%); R_f 0.7 (petroleum ether/CH_2Cl_2 2/1); ^1H NMR (250 MHz, $CDCl_3$, 253 K) δ 4.29 (d, $^3J_{HH}$ = 3.33 Hz, 1H, H-3), 5.27 (d, $^3J_{HH}$ = 5.66 Hz, 1H, H-2″), 5.51 (d, $^3J_{HH}$ = 3.33 Hz, 1H, H-2), 6.76 (d, $^3J_{HH}$ = 5.66 Hz, 1H, H-3″), 7.28−7.33 (m, 3H, Ar H), 7.40−7.45 (m, 2H, Ar H), 7.54−7.60 (m, 2H, Ar H), 8.46 (d, $^3J_{HH}$ = 8.29 Hz, 1H, Ar H); ^{13}C NMR (125.6 MHz, $CDCl_3$, 263 K) δ 47.54 (d, $^1J_{CH}$ = 178.3 Hz, 1C, C-3), 67.19 (d, $^1J_{CH}$ = 178.6 Hz, 1C, C-2), 77.08 (s, 1 C, C-1′), 118.24 (d), 121.16 (d), 124.13 (d), 124.95 (d), 127.37 (d), 128.00 (d), 130.72 (d), 132.54 (d), 133.09 (d), 135.01 (d) (10C, Ar C_t, C-2″ and C-3″), 142.02 (1C, C_q), 144.05 (1C, C_q), 144.73 (1C, C_q), 153.77 (1C, C_q), 216.56 (4C, CO_{cis}), 232.85 (1C, CO_{trans}), 370.89 (1C, $C_{carbene}$); FT-IR (hexane) ($\nu_{C=O}$) 2056 (m, A_1), 1976 (m, A_1), 1964 (s, E) cm^{-1}; MS (EI) *m/z* (%) 420 (M^+, 1), 392 (M^+ − CO, 1), 364 (M^+ − 2CO, 1), 336 (M^+ − 3CO, 2), 308 (M^+ − 4CO, 3), 280 (M^+ − 5CO, 18), 228 (M^+ − 5CO − Cr, 100), 115 ($C_9H_7^+$, 14), 52 (Cr^+, 46); HR-MS calcd for $C_{23}H_{12}CrO_5$ 420.0090, found 420.0090 (M^+).

Pentacarbonyl[(4-methoxyphenyl)phenylcarbene]-chromium(0) (18). The workup according to procedure **B** yielded 0.38 g (1.27 mmol, 25%) of **1** followed by 1.26 g (3.25 mmol, 65%) of **18**.

18: black solid, 1.26 g (65%); R_f 0.4 (petroleum ether/CH_2Cl_2 2/1); ^1H NMR (500 MHz, $CDCl_3$, 253 K) δ 3.91 (s, 3H, OCH_3), 6.81 (d, $^3J_{HH}$ = 7.45 Hz, 2H, H-2′, H-6′), 6.91 (d, $^3J_{HH}$ = 8.79 Hz, 2H, H-3, H-5), 7.27 (t, $^3J_{HH}$ = 7.45 Hz, 1H, H-4′), 7.35 (t, $^3J_{HH}$ = 7.45 Hz, 2H, H-3′, H-5′), 7.43 (d, $^3J_{HH}$ = 8.79 Hz, 2H, H-2, H-6); ^{13}C NMR (125.6 MHz, $CDCl_3$, 253 K) δ 55.76 (1C, OCH_3), 113.15 (2C, C-3, C-5), 121.23 (2C, Ar C), 127.13 (2C, Ar C), 127.77 (1C, C-4′), 132.06 (2C, Ar C), 153.93 (1C, C-4), 165.02, 165.22 (2C, C-1, C-1′), 216.49 (4C, CO_{cis}), 234.24 (1C, CO_{trans}), 385.77 (1C, $C_{carbene}$); FT-IR (hexane) ($\nu_{C=O}$) 2055 (m, A_1), 1966 (vs, E), 1956 (sh, A_1) cm^{-1}; MS (EI) *m/z* (%) 360 (M^+ − CO, 24), 304 (M^+ − 3CO, 22), 276 (M^+ − 4CO, 74), 248 (M^+ − 5CO, 79), 196 (M^+ − 5CO − Cr, 100), 181 (M^+ − 5CO − Cr − CH_3, 72), 165 (M^+ − 5CO − Cr − OCH_3, 25); HR-MS calcd for $C_{18}H_{12}CrO_5$ 360.0090, found 360.0085 (M^+ − CO).

Pentacarbonyl[bis(4-methoxyphenyl)carbene]chromium(0) (19). Workup according to procedure **B** yielded 0.36 g (1.2 mmol, 24%) of **1** followed by 1.37 g (3.3 mmol, 66%) of **19**.

19: black solid, 1.37 g (66%); R_f 0.3 (petroleum ether/CH_2Cl_2 2/1); ^1H NMR (250 MHz, $CDCl_3$, 253 K) δ 3.95 (s, 6H, OCH_3), 6.85 (d, $^3J_{HH}$ = 7.28 Hz, 4H, H-3, H-5, H-3′, H-5′), 7.15 (d, $^3J_{HH}$ = 7.28 Hz, 4H, H-2, H-6, H-2′, H-6′); ^{13}C NMR (62.5 MHz, $CDCl_3$, 253 K) δ 55.62 (2C, OCH_3), 112.47 (4C, C-3, C-5, C-3′, C-5′), 129.48 (4C, C-2, C-6, C-2′, C-6′), 157.34 (2C, C-4, C-4′), 162.78 (2C, C-1, C-1′), 216.71 (4C, CO_{cis}), 233.47 (1C, CO_{trans}), 380.18 (1C, $C_{carbene}$); FT-IR (hexane) ($\nu_{C=O}$) 2051 (m, A_1), 1961 (vs, E), 1949 (sh, A_1) cm^{-1}; MS (EI) *m/z* (%) 390 (M^+ − CO, 15), 334 (M^+ − 3CO, 14), 306 (M^+ − 4CO, 9), 278 (M^+ − 5CO, 12), 226 (M^+ − 5CO − Cr, 39), 211 (M^+ − 5CO − Cr − CH_3, 41), 80 ($CrCO^+$, 100), 52 (Cr^+, 5); HR-MS calcd for $C_{19}H_{14}CrO_6$ 390.0195, found 390.0203 (M^+ − CO).

---

(32) No NMR spectra free of impurities could be obtained for compounds **11**, **12**, and **22**. The thermolability of **11** and **12** requires temperatures below −40 °C during workup, preventing sufficient removal of the solvent; in the case of **22**, traces of the solvent remained in the samples due to the oily to waxy consistence.

NMR Spectroscopic Evidence for the Carbene Complexes 13 and 14. A 0.1 mmol amount of diazo compound **6** or **7**, respectively, and 0.1 mmol (0.03 g) of pentacarbonyl(η^2-*cis*-cyclooctene)chromium(0) (**1**) were dissolved in 4 mL of $CDCl_3$ at −30 °C. The mixture was warmed to room temperature, stirred for 5 min, and cooled to −30 °C again. A sample was transferred into an NMR tube, and ^{1}H NMR and ^{13}C NMR spectra were recorded at −30 °C.

Pentacarbonyl[9(9*H*)-thioxanthenylidene]chromium(0) (13): ^{1}H NMR (500 MHz, $CDCl_3$, 243 K) δ 7.45 (t, 2H, $^{3}J_{HH}$ = 7.46 Hz, Ar H), 7.51 (t, 2H, $^{3}J_{HH}$ = 7.41 Hz, Ar H), 7.60 (d, 2H, $^{3}J_{HH}$ = 7.85 Hz, Ar H), 8.37 (d, 2H, $^{3}J_{HH}$ = 7.94 Hz, H-1, H-8); ^{13}C NMR (125.6 MHz, $CDCl_3$, 243 K) δ 118.92 (2C, C-4a, C-4b), 124.31 (2C, Ar C_t), 126.34 (2C, Ar C_t), 130.65 (2C, Ar C_t), 132.20 (2C, Ar C_t), 154.96 (2C, C-8a, C-9a), 215.49 (4C, CO_{cis}), 235.39 (1C, CO_{trans}), 357.80 (1C, $C_{carbene}$).[8]

Pentacarbonyl(9,10-dihydro-10,10-dimethyl-9-anthracenylidene)chromium(0) (14): ^{13}C NMR (125.6 MHz, $CDCl_3$, 243 K) δ 31.31 (2C, CH_3), 39.67 (1C, C-10), 122.60 (2C, ArC_t), 126.34 (2C, ArC_t), 130.51 (2C, ArC_t), 131.60 (2C, C-4a, C-10a), 131.69 (2C, ArC_t), 158.64 (2C, C-8a, C-9a), 216.73 (4C, CO_{cis}), 233.65 (1C, CO_{trans}), 378.64 (1C, $C_{carbene}$).[9]

General Procedure for the Reaction of the Carbene Complexes 9−12, 15, 18, and 19 with $Et_2NC{\equiv}CMe$. To a stirred solution of 1 mmol of the carbene complex in 20 mL of dichloromethane (**9**, **10**, and **15**, −60 °C; **18** and **19**, −20 °C; **11** and **12**, room temperature) was added 1 mmol (0.11 g) of 1-(diethylamino)-1-propyne in 2 mL of dichloromethane over 2 min. After consumption of the starting material (TLC control) and removal of the solvent under reduced pressure, the residue was purified by column chromatography (−10 °C; eluents petroleum ether/dichloromethane (2/1) for **20**, **21**, and **23**, petroleum ether/dichloromethane (1/1) for **24**, petroleum ether/dichloromethane (1/3) for **25**, and dichloromethane for **22**). Complexes **20**, **21**, and **23**−**25** were obtained as yellow solids, whereas **22** had an oily to waxy consistence.

(±)-Pentacarbonyl{(diethylamino){1-[9′(9′*H*)-fluorenylidene]ethyl}carbene}chromium(0) (20): yellow solid, 0.24 g (51%); R_f 0.45 (petroleum ether/CH_2Cl_2 2:1); mp 65−68 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (t, $^{3}J_{HH}$ = 7.37 Hz, 3H, $NCH_2C\mathit{H}_3$), 1.57 (t, $^{3}J_{HH}$ = 7.08 Hz, 3H, $NCH_2C\mathit{H}_3$), 2.52 (s, 3H, CH_3), 3.56 (dq, $^{2}J_{HH}$ = 13.99 Hz, $^{3}J_{HH}$ = 7.08 Hz, 1H, $NC\mathit{H}H$), 3.76 (dq, $^{2}J_{HH}$ = 13.99 Hz, $^{3}J_{HH}$ = 7.08 Hz, 1H, $NC\mathit{H}H$), 4.43 (q, $^{3}J_{HH}$ = 7.37 Hz, 2H, NCH_2), 7.25 (m, 1H, Ar H), 7.32 (m, 2H, Ar H), 7.38 (m, 2H, Ar H), 7.76 (d, $^{3}J_{HH}$ = 7.04 Hz, 1H, Ar H), 7.86 (m, 1H, Ar H), 7.88 (m, 1H, Ar H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.96 (1C, $NCH_2\mathit{C}H_3$), 13.12 (1C, $NCH_2\mathit{C}H_3$), 21.59 (1C, CH_3), 48.60 (1C, $N\mathit{C}H_2CH_3$), 52.99 (1C, $N\mathit{C}H_2CH_3$), 119.58 (1C, Ar C), 119.85 (1C, Ar C), 120.81 (1C, C-9′), 124.45 (1C, Ar C), 125.46 (1C, Ar C), 126.08 (1C, Ar C), 126.85 (1C, Ar C), 126.99 (1C, Ar C), 127.09 (1C, Ar C), 136.97, 138.21, 138.93, 140.31, 145.61 (5C, C-1, C-4a′, C-4b′, C-8a′, C-9a′), 216.54 (4C, CO_{cis}), 222.38 (1C, CO_{trans}), 272.00 (1C, $C_{carbene}$); FT-IR (hexane) ($\nu_{C=O}$) 2055 (m, A_1), 1977 (m, B), 1939, 1930 (vs, E) cm^{-1}; FT-IR (KBr) 2981 (m, ν_{C-H}), 1612 (*w*), 1591 (*w*), 1516, 1446 (m, $\nu_{C=C}$), 781 (*m*), 732 (*m*), 653 (*s*) cm^{-1}; MS (EI) *m*/*z* (%) 411 (M^+ − 2CO, 12), 383 (M^+ − 3CO, 9), 355 (M^+ − 4CO, 21), 327 (M^+ − 5CO, 100), 275 (M^+ − 5CO − Cr, 22), 256 (M^+ − 5CO − NEt_2, 30), 203 (M^+ − 5CO − Cr − NEt_2 − H, 15), 52 (Cr^+, 67); HR-MS calcd for $C_{23}H_{21}CrNO_3$ 411.0927, found 411.0924 (M^+ − 2CO). Anal. Calcd for $C_{25}H_{21}CrNO_5$: C, 64.24; H, 4.53; N, 3.00. Found: C, 64.08; H, 4.83; N, 2.87.

(±)-Pentacarbonyl{(diethylamino){1-[9′(9′*H*)-xanthenylidene]ethyl}carbene}chromium(0) (21): yellow solid, 0.25 g (52%); R_f 0.5 (petroleum ether/CH_2Cl_2 2/1); mp 72 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, $^{3}J_{HH}$ = 7.15 Hz, 3H, $NCH_2C\mathit{H}_3$), 1.48 (t, $^{3}J_{HH}$ = 7.08 Hz, 3H, $NCH_2C\mathit{H}_3$), 2.19 (s, 3H, CH_3), 3.51 (dq, $^{2}J_{HH}$ = 14.10 Hz, $^{3}J_{HH}$ = 7.15 Hz, 1H, $NC\mathit{H}H$), 3.98 (dq, $^{2}J_{HH}$ = 14.10 Hz, $^{3}J_{HH}$ = 7.15 Hz, 1H, $NCH\mathit{H}$), 4.15 (dq, $^{2}J_{HH}$ = 13.89 Hz, $^{3}J_{HH}$ = 7.08 Hz, 1H, $NC\mathit{H}H$), 4.43 (dq, $^{2}J_{HH}$ = 13.89 Hz, $^{3}J_{HH}$ = 7.08 Hz, 1H, $NCH\mathit{H}$), 7.02 (d, $^{3}J_{HH}$ = 6.43 Hz, 2H, Ar H), 7.13 (t, $^{3}J_{HH}$ = 7.43 Hz, 2H, Ar H), 7.16−7.30 (m, 3H, Ar H), 7.54 (d, $^{3}J_{HH}$ = 7.83 Hz, 1H, Ar H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.94 (1C, $NCH_2\mathit{C}H_3$), 13.17 (1C, $NCH_2\mathit{C}H_3$), 20.60 (1C, CH_3), 48.11 (1C, NCH_2), 52.84 (1C, NCH_2), 112.99 (1C, C-9′), 116.47 (1C, Ar C), 116.50 (1C, Ar C), 122.52 (1C, Ar C), 122.63 (1C, Ar C), 127.17 (1C, Ar C), 128.11 (1C, Ar C), 128.16 (1C, Ar C), 128.47 (1C, Ar C), 124.18, 125.03 (2C, C-8a′, C-9a′), 140.39 (1C, C-1), 152.72, 154.11 (2C, C-4a′, C-4b′), 216.67 (4C, CO_{cis}), 222.38 (1C, CO_{trans}), 273.67 (1C, $C_{carbene}$); FT-IR (hexane) ($\nu_{C=O}$) 2051 (m, A_1), 1973 (w, B), 1937 (vs, E), 1911 (s, A_1) cm^{-1}; FT-IR (KBr) 2965 (m, ν_{C-H}), 1523, 1450 (m, $\nu_{C=C}$), 1261 (s, ν_{C-O-C}), 1103, 1023 (*s*), 798 (*s*), 754 (*m*), 671 (*m*) cm^{-1}; MS (EI) *m*/*z* (%) 427 (M^+ − 2CO, 12), 399 (M^+ − 3CO, 4), 371 (M^+ − 4CO, 17), 343 (M^+ − 5CO, 33), 291 (M^+ − 5CO − Cr, 48), 276 (M^+ − 5CO − Cr − CH_3, 30), 219 (M^+ − 5CO − Cr − CH_3 − C_2H_5 − C_2H_4, 100), 52 (Cr^+, 39); HR-MS calcd for $C_{23}H_{21}CrNO_4$ 427.0876, found 427.0878 (M^+ − 2CO). Anal. Calcd for $C_{25}H_{21}CrNO_6$: C, 62.11; H, 4.38; N, 2.90. Found: C, 61.88; H, 4.13; N, 2.97.

(*syn*/*anti*)-Pentacarbonyl{(diethylamino){1-[5′(5′*H*)-dibenzo[*a*,*d*]cycloheptenylidene]ethyl}carbene}chromium(0) (22): yellow oily wax, 0.27 g (27%, *syn*/*anti* = 4.9); R_f 0.65 (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) *syn* isomer[32] δ 1.40 (t, $^{3}J_{HH}$ = 7.23 Hz, 3H, $NCH_2C\mathit{H}_3$), 1.54 (t, $^{3}J_{HH}$ = 7.15 Hz, 3H, $NCH_2C\mathit{H}_3$), 1.81 (s, 3H, CH_3), 3.71 (dq, $^{2}J_{HH}$ = 13.82 Hz, $^{3}J_{HH}$ = 6.84 Hz, 1H, $NC\mathit{H}H$), 3.91 (dq, $^{2}J_{HH}$ = 13.87 Hz, $^{3}J_{HH}$ = 6.90 Hz, 1H, $NC\mathit{H}H$), 4.37 (dq, $^{2}J_{HH}$ = 13.88 Hz, $^{3}J_{HH}$ = 6.94 Hz, 1H, $NCH\mathit{H}$), 4.84 (dq, $^{2}J_{HH}$ = 13.69 Hz, $^{3}J_{HH}$ = 6.84 Hz, 1H, $NCH\mathit{H}$), 6.80 (d, $^{3}J_{HH}$ = 7.42 Hz, 1H, Ar H), 6.97 (d, $^{3}J_{HH}$ = 11.83 Hz, 1H, =CH), 7.01 (d, $^{3}J_{HH}$ = 11.83 Hz, 1H, =CH), 7.19 (t, $^{3}J_{HH}$ = 8.36 Hz, 1H, Ar H), 7.21 (d, $^{3}J_{HH}$ = 6.67 Hz, 1H, Ar H), 7.25 (t, $^{3}J_{HH}$ = 7.66 Hz, 1H, Ar H), 7.30 (d, $^{3}J_{HH}$ = 6.59 Hz, 1H, Ar H), 7.31 (t, $^{3}J_{HH}$ = 6.65 Hz, 1H, Ar H), 7.35 (d, $^{3}J_{HH}$ = 7.45 Hz, 1H, Ar H), 7.37 (t, $^{3}J_{HH}$ = 7.87 Hz, 1H, Ar H), *anti* isomer δ 0.74 (t, $^{3}J_{HH}$ = 7.21 Hz, 3H, $NCH_2C\mathit{H}_3$), 0.96 (t, $^{3}J_{HH}$ = 7.18, 3H, $NCH_2C\mathit{H}_3$), 1.88 (s, 3H, CH_3), 2.81 (dq, $^{2}J_{HH}$ = 13.83 Hz, $^{3}J_{HH}$ = 6.98 Hz, 1H, $NC\mathit{H}H$), 3.77 (dq, $^{2}J_{HH}$ = 14.02 Hz, $^{3}J_{HH}$ = 6.92 Hz, 1H, $NC\mathit{H}H$), 4.07 (dq, $^{2}J_{HH}$ = 13.83 Hz, $^{3}J_{HH}$ = 6.98 Hz, 1H, $NCH\mathit{H}$), 4.35 (dq, $^{2}J_{HH}$ = 14.02 Hz, $^{3}J_{HH}$ = 6.92 Hz, 1H, $NCH\mathit{H}$), 6.65 (d, $^{3}J_{HH}$ = 7.56 Hz, 1H, Ar H), 6.83 (d, $^{3}J_{HH}$ = 10.81 Hz, 1H, =CH), 6.85 (d, $^{3}J_{HH}$ = 10.81 Hz, 1H, =CH);[33] ^{13}C NMR (100.6 MHz, $CDCl_3$) *syn* isomer δ 14.49 (1C, $NCH_2\mathit{C}H_3$), 15.14 (1C, $NCH_2\mathit{C}H_3$), 18.50 (1C, CH_3), 50.21 (1C, $N\mathit{C}H_2$), 53.09 (1C, $N\mathit{C}H_2$), 125.48 (1C, C-5′), 127.13 (1C), 127.25 (1C), 127.68 (1C), 127.80 (1C), 128.07 (1C), 128.88 (1C), 129.65 (1C), 130.10 (1C), 131.73 (1C), 131.79 (1C) (10C, Ar C, C-10′ and C-11′), 135.16, 135.73, 137.89, 138.94, 145.57 (5C, C-1, C-4a′, C-5a′, C-9a′, C-11a′), 217.34 (4C, CO_{cis}), 223.71 (1C, CO_{trans}), 276.22 (1C, $C_{carbene}$), *anti* isomer: δ 13.05 (1C, $NCH_2\mathit{C}H_3$), 14.57 (1C, $NCH_2\mathit{C}H_3$), 20.96 (1C, CH_3), 48.01 (1C, $N\mathit{C}H_2$), 54.42 (1C, $N\mathit{C}H_2$), 120.92 (1C, C-5′), 126.33 (1C), 127.07 (1C), 128.26 (1C), 128.34 (1C), 128.68 (1C), 129.76 (1C), 130.57 (1C), 130.88 (1C), 131.45 (1C), 131.95 (1C) (10C, Ar C, C-10′ and C-11′), 134.06, 134.42, 138.02, 139.64, 145.00 (5C, C-1, C-4a′, C-5a′, C-9a′, C-11a′), 218.35 (4C, CO_{cis}), 223.27 (1C, CO_{trans}), 272.63 (1C, $C_{carbene}$); FT-IR (hexane) ($\nu_{C=O}$) 2053 (m, A_1), 1971 (m, B), 1939, 1930 (vs, E) cm^{-1}; MS (EI) *m*/*z* (%) 437 (M^+ − 2CO, 6), 409 (M^+ − 3CO, 2), 381 (M^+ − 4CO, 10), 353 (M^+ − 5CO, 100), 301 (M^+ − 5CO − Cr, 12), 229 (M^+ − 5CO − NEt_2, 55), 191 ($C_{15}H_{11}^+$, 44); HR-MS calcd for $C_{25}H_{23}CrNO_3$ 437.1083, found 437.1083 (M^+ − 2CO).

***(E/Z)*-Pentacarbonyl{(diethylamino)[1‴-(*exo*-spiro-(1″*H*)-indeno-(1″,1′)-cycloprop[2′,3′-*b*]-1(1*H*)-indenylidene)ethyl]carbene}chromium(0) (23) (Figure 3):** yellow solid, 0.38 g (73%, *E*/*Z* = 3.4); R_f 0.4 (petroleum ether/CH_2Cl_2 2/1); mp 73−75 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$)[34] *E* isomer δ

---

[33] The signals of the aromatic protons of the *anti* isomer are covered by the signals of the *syn* isomer.

[34] Assignment according to H,H- and C,H-COSY experiments.

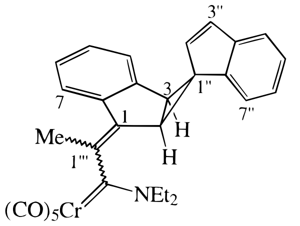


Figure 3. Atom labeling of (*E*/*Z*)-**23**.

1.33 (t, $^3J_{\mathrm{HH}} = 6.95$ Hz, 3H, $\mathrm{NCH_2C}H_3$), 1.48 (t, $^3J_{\mathrm{HH}} = 7.01$ Hz, 3H, $\mathrm{NCH_2C}H_3$), 2.37 (s, 3H, $\mathrm{CH_3}$), 2.91 (d, $^3J_{\mathrm{HH}} = 5.80$ Hz, 1H, H-3), 3.12 (dq, $^2J_{\mathrm{HH}} = 13.84$ Hz, $^3J_{\mathrm{HH}} = 6.95$ Hz, 1H, $\mathrm{NCH}H$), 3.77 (d, $^3J_{\mathrm{HH}} = 5.80$ Hz, 1H, H-2), 3.95 (dq, $^2J_{\mathrm{HH}} = 13.84$ Hz, $^3J_{\mathrm{HH}} = 6.95$ Hz, 1H, $\mathrm{NC}H\mathrm{H}$), 4.10 (dq, $^2J_{\mathrm{HH}} = 13.77$ Hz, $^3J_{\mathrm{HH}} = 7.01$ Hz, 1H, $\mathrm{NC}H\mathrm{H}$), 4.18 (dq, $^2J_{\mathrm{HH}} = 13.77$ Hz, $^3J_{\mathrm{HH}} = 7.01$ Hz, 1H, $\mathrm{NCH}H$), 5.67 (d, $^3J_{\mathrm{HH}} = 5.65$ Hz, 1H, H-2″), 6.87 (d, $^3J_{\mathrm{HH}} = 5.65$ Hz, 1H, H-3″), 7.00 (d, $^3J_{\mathrm{HH}} = 7.39$ Hz, 1H, H-4″), 7.18 (d, $^3J_{\mathrm{HH}} = 7.41$ Hz, 1H, H-5″), 7.25 (d, $^3J_{\mathrm{HH}} = 7.43$ Hz, 1H, H-6″), 7.26 (d, $^3J_{\mathrm{HH}} = 7.44$ Hz, 1H, H-5), 7.32 (d, $^3J_{\mathrm{HH}} = 7.55$ Hz, 1H, H-7″), 7.35 (t, $^3J_{\mathrm{HH}} = 7.44$ Hz, 1H, H-6), 7.36 (d, $^3J_{\mathrm{HH}} = 7.49$ Hz, 1H, H-4), 7.72 (d, $^3J_{\mathrm{HH}} = 7.79$ Hz, 1H, H-7). *Z* isomer δ 1.12 (t, $^3J_{\mathrm{HH}} = 7.09$ Hz, 3H, $\mathrm{NCH_2C}H_3$), 1.59 (t, $^3J_{\mathrm{HH}} = 7.05$ Hz, 3H, $\mathrm{NCH_2C}H_3$), 2.05 (s, 3H, $\mathrm{CH_3}$), 3.43 (dq, $^2J_{\mathrm{HH}} = 13.90$ Hz, $^3J_{\mathrm{HH}} = 7.09$ Hz, 1H, $\mathrm{NCH}H$), 3.58 (d, $^3J_{\mathrm{HH}} = 6.04$ Hz, 1H, H-3), 3.70 (d, $^3J_{\mathrm{HH}} = 6.04$ Hz, 1H, H-2), 3.90 (dq, $^2J_{\mathrm{HH}} = 13.90$ Hz, $^3J_{\mathrm{HH}} = 7.09$ Hz, 1H, $\mathrm{NCH}H$), 4.25 (dq, $^2J_{\mathrm{HH}} = 13.72$ Hz, $^3J_{\mathrm{HH}} = 7.05$ Hz, 1H, $\mathrm{NC}H\mathrm{H}$), 4.51 (dq, $^2J_{\mathrm{HH}} = 13.72$ Hz, $^3J_{\mathrm{HH}} = 7.05$ Hz, 1H, $\mathrm{NC}H\mathrm{H}$), 5.98 (d, $^3J_{\mathrm{HH}} = 5.66$ Hz, 1H, H-2″), 6.89 (d, $^3J_{\mathrm{HH}} = 5.66$ Hz, 1H, H-3″), 7.10−7.35 (m, 7H, Ar H), 7.42 (d, $^3J_{\mathrm{HH}} = 7.25$ Hz, 1H, Ar H). ^{13}C NMR (125.6 MHz, $\mathrm{CDCl_3}$)[34] *E* isomer δ 13.73 (q, 1C, $\mathrm{NCH_2}C\mathrm{H_3}$), 13.91 (q, 1C, $\mathrm{NCH_2}C\mathrm{H_3}$), 19.19 (q, 1C, $\mathrm{CH_3}$), 35.53 (d, $^1J_{\mathrm{CH}} = 170.9$ Hz, 1C, C-3), 38.36 (d, $^1J_{\mathrm{CH}} = 175.3$ Hz, 1C, C-2), 49.22 (1C, C-1″), 49.32 (t, 1C, $\mathrm{N}C\mathrm{H_2}$), 52.96 (t, 1C, $\mathrm{N}C\mathrm{H_2}$), 116.93 (d, 1C, C-4″), 121.23 (d, 1C, C-4), 123.09 (1C, C-1‴), 124.07 (d, 1C, C-5″), 124.14 (d, 1C, C-7), 124.73 (d, 1C, C-7″), 125.82 (d, 1C, C-6″), 126.99 (d, 1C, C-6), 127.46 (d, 1C, C-5), 131.10 (d, 1C, C-3″), 134.31 (d, 1C, C-2″), 139.07, 143.31, 143.34, 144.83, 146.43 (5C, C-3a, C-7a, C-3a″, C-7a″, C-1), 217.16 (4C, $\mathrm{CO_{cis}}$), 223.53 (1C, $\mathrm{CO_{trans}}$), 275.01 (1C, $\mathrm{C_{carbene}}$); *Z* isomer δ 13.17 (q, 1C, $\mathrm{NCH_2}C\mathrm{H_3}$), 13.69 (q, 1C, $\mathrm{NCH_2}C\mathrm{H_3}$), 20.47 (q, 1C, $\mathrm{CH_3}$), 37.42 (d, $^1J_{\mathrm{CH}} = 173.4$ Hz, 1C, C-3), 38.42 (d, $^1J_{\mathrm{CH}} = 175.3$ Hz, 1C, C-2), 47.35 (t, 1C, $\mathrm{N}C\mathrm{H_2}$), 49.30 (s, 1C, C-1″), 53.20 (t, 1C, $\mathrm{N}C\mathrm{H_2}$), 117.45 (d, 1C, Ar C), 121.45 (d, 1C, Ar C), 124.24 (d, 1C, Ar C), 124.79 (d, 1C, Ar C), 125.72 (d, 1C, Ar C), 126.08 (d, 1C, Ar C), 126.32 (d, 1C, Ar C), 127.01 (d, 1C, Ar C), 127.48 (s, 1C, C-1‴), 130.95 (d, 1C, C-3″), 134.91 (d, 1C, C-2″), 139.21, 141.01, 143.20, 144.38, 146.50 (5C, C-3a, C-7a, C-3a″, C-7a″, C-1), 216.92 (4C, $\mathrm{CO_{cis}}$), 222.54 (1C, $\mathrm{CO_{trans}}$), 273.51 (1C, $\mathrm{C_{carbene}}$); FT-IR (hexane) ($\nu_{\mathrm{C=O}}$) 2054 (m, $\mathrm{A_1}$), 1974 (m, $\mathrm{B_1}$), 1941, 1932 (vs, E), 1913 (s, $\mathrm{A_1}$) cm^{-1}; MS (EI) *m*/*z* (%) 503 ($\mathrm{M^+} - \mathrm{CO}$, 5), 475 ($\mathrm{M^+} - 2\mathrm{CO}$, 6), 447 ($\mathrm{M^+} - 3\mathrm{CO}$, 8), 419 ($\mathrm{M^+} - 4\mathrm{CO}$, 10), 391 ($\mathrm{M^+} - 5\mathrm{CO}$, 100), 339 ($\mathrm{M^+} - 5\mathrm{CO{-}Cr}$, 52), 324 ($\mathrm{M^+} - 5\mathrm{CO{-}Cr{-}CH_3}$, 55), 310 ($\mathrm{M^+} - 5\mathrm{CO} - \mathrm{Cr} - \mathrm{C_2H_5}$, 19), 267 ($\mathrm{M^+} - \mathrm{Cr\text{-}5CO} - \mathrm{NEt_2}$, 30); HR-MS calcd for $\mathrm{C_{27}H_{25}CrNO_2}$ 447.1290, found 447.1287 ($\mathrm{M^+} - 3\mathrm{CO}$). Anal. Calcd for $\mathrm{C_{30}H_{25}CrNO_5}$: C, 67.79; H, 4.74; N, 2.64. Found: C, 67.73; H, 5.07; N, 2.29.

(*E*/*Z*)-Pentacarbonyl{(diethylamino)[1-(4′-methoxyphenyl)-1-phenyl-2-propenyl]carbene}chromium(0) (24): yellow solid, 0.29 g (58%, *E*/*Z* = 5.6); R_f 0.45 (petroleum ether/$\mathrm{CH_2Cl_2}$ 1/1). ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$) *E* isomer δ 1.39 (t, $^3J_{\mathrm{HH}} = 7.03$ Hz, 3H, $\mathrm{NCH_2C}H_3$), 1.49 (t, $^3J_{\mathrm{HH}} = 6.86$ Hz, 3H, $\mathrm{NCH_2C}H_3$), 1.92 (s, 3H, $\mathrm{CH_3}$), 3.68 (dq, $^2J_{\mathrm{HH}} = 13.95$ Hz, $^3J_{\mathrm{HH}} = 7.03$ Hz, 1H, $\mathrm{NCH}H$), 3.86 (s, 3H, $\mathrm{OCH_3}$), 4.09 (dq, $^2J_{\mathrm{HH}} = 13.95$ Hz, $^3J_{\mathrm{HH}} = 7.03$ Hz, 1H, $\mathrm{NCH}H$), 4.21 (dq, $^2J_{\mathrm{HH}} = 13.81$ Hz, $^3J_{\mathrm{HH}} = 6.86$ Hz, 1H, $\mathrm{NC}H\mathrm{H}$), 4.43 (dq, $^2J_{\mathrm{HH}} = 13.81$ Hz, $^3J_{\mathrm{HH}} = 6.86$ Hz, 1H, $\mathrm{NC}H\mathrm{H}$), 6.90−6.96 (m, 4H, Ar H), 7.16−7.27 (m, 5H, Ar H); *Z* isomer δ 1.86 (s, 3H, $\mathrm{CH_3}$), 3.78 (s, 3H, $\mathrm{OCH_3}$), 6.72 (d, $^3J_{\mathrm{HH}} = 8.35$ Hz, 2H, Ar H), 6.79 (d, $^3J_{\mathrm{HH}} = 8.25$ Hz, 2H, Ar H);[35] ^{13}C NMR (125.6 MHz, $\mathrm{CDCl_3}$) *E* isomer δ 13.17 (1C, $\mathrm{NCH_2}C\mathrm{H_3}$), 13.59 (1C, $\mathrm{NCH_2}C\mathrm{H_3}$), 20.63 (1C, $\mathrm{CH_3}$), 48.97 (1C, $\mathrm{N}C\mathrm{H_2}$), 52.60 (1C, $\mathrm{N}C\mathrm{H_2}$), 55.21 (1C, $\mathrm{OCH_3}$), 113.71 (2C, C-3′, C-5′), 126.06 (s, 1C, C-1), 127.18 (d, 1C, C-4″), 127.73 (d, 2C, C-2″, C-6″), 129.09 (d, 2C, C-3″, C-5″), 131.10 (2C, C-2′, C-6′), 133.84 (1C, $\mathrm{C_q}$), 140.78 (1C, $\mathrm{C_q}$), 143.66 (1C, C-2), 158.31 (1C, C-4′), 217.09 (4C, $\mathrm{CO_{cis}}$), 222.86 (1C, $\mathrm{CO_{trans}}$), 276.37 (1C, $\mathrm{C_{carbene}}$), *Z* isomer δ 13.22 (1C, $\mathrm{NCH_2}C\mathrm{H_3}$), 13.53 (1C, $\mathrm{NCH_2}C\mathrm{H_3}$), 20.52 (1C, $\mathrm{CH_3}$), 48.75 (1C, $\mathrm{N}C\mathrm{H_2}$), 53.20 (1C, $\mathrm{N}C\mathrm{H_2}$), 55.23 (1C, $\mathrm{OCH_3}$), 113.17 (2C, C-3′, C-5′), 125.54 (1C, C-1), 126.70 (1C, C-4″), 128.35 (2C, C-2″, C-6″), 129.94 (2C, C-3″, C-5″), 130.32 (2C, C-2′, C-6′), 133.03 (1C, $\mathrm{C_q}$), 141.81 (1C, $\mathrm{C_q}$), 142.35 (1C, C-2), 158.86 (1C, C-4′), 217.20 (4C, $\mathrm{CO_{cis}}$), 222.81 (1C, $\mathrm{CO_{trans}}$), 276.32 (1C, $\mathrm{C_{carbene}}$); FT-IR (hexane) ($\nu_{\mathrm{C=O}}$) 2053 (m, $\mathrm{A^1}$), 1971 (w, $\mathrm{B^1}$), 1940, 1928 (vs, E), 1912 (s, $\mathrm{A_1}$) cm^{-1}; MS (EI) *m*/*z* (%) 443 ($\mathrm{M^+} - 2\mathrm{CO}$, 9), 387 ($\mathrm{M^+} - 4\mathrm{CO}$, 2), 359 ($\mathrm{M^+} - 5\mathrm{CO}$, 33), 307 ($\mathrm{M^+} - 5\mathrm{CO} - \mathrm{Cr}$, 54), 292 ($\mathrm{M^+} - 5\mathrm{CO} - \mathrm{Cr} - \mathrm{CH_3}$, 100), 235 ($\mathrm{M^+} - 5\mathrm{CO} - \mathrm{Cr} - \mathrm{NEt_2}$, 45), 52 ($\mathrm{Cr^+}$, 24); HR-MS calcd for $\mathrm{C_{24}H_{25}CrNO_4}$ 443.1189, found 443.1197 ($\mathrm{M^+} - 2\mathrm{CO}$). Anal. Calcd for $\mathrm{C_{26}H_{25}CrNO_6}$: C, 62.52; H, 5.09; N, 2.80. Found: C, 62.11; H, 4.82; N, 3.02.

Pentacarbonyl{(diethylamino)[1,1-bis(4′-methoxyphenyl)-2-propenyl]carbene}chromium(0) (25): yellow solid, 0.34 g (65%); R_f 0.5 (petroleum ether/$\mathrm{CH_2Cl_2}$ 1/3). ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$) δ 1.39 (t, $^3J_{\mathrm{HH}} = 7.06$ Hz, 3H, $\mathrm{NCH_2C}H_3$), 1.51 (t, $^3J_{\mathrm{HH}} = 7.25$ Hz, 3H, $\mathrm{NCH_2C}H_3$), 1.89 (s, 3H, $\mathrm{CH_3}$), 3.68 (dq, $^2J_{\mathrm{HH}} = 13.94$ Hz, $^3J_{\mathrm{HH}} = 7.06$ Hz, 1H, $\mathrm{NCH}H$), 3.79 (s, 3H, $\mathrm{OCH_3}$), 3.86 (s, 3H, $\mathrm{OCH_3}$), 4.12 (dq, $^2J_{\mathrm{HH}} = 14.57$ Hz, $^3J_{\mathrm{HH}} = 7.25$ Hz, 1H, $\mathrm{NCH}H$), 4.15 (dq, $^2J_{\mathrm{HH}} = 14.57$ Hz, $^3J_{\mathrm{HH}} = 7.25$ Hz, 1H, $\mathrm{NC}H\mathrm{H}$), 4.43 (dq, $^2J_{\mathrm{HH}} = 13.94$ Hz, $^3J_{\mathrm{HH}} = 7.06$ Hz, 1H, $\mathrm{NC}H\mathrm{H}$), 6.77 (d, $^3J_{\mathrm{HH}} = 8.74$ Hz, 2H, Ar H), 6.83 (d, $^3J_{\mathrm{HH}} = 8.74$ Hz, 2H, Ar H), 6.93 (d, $^3J_{\mathrm{HH}} = 8.55$ Hz, 2H, Ar H), 7.20 (d, $^3J_{\mathrm{HH}} = 8.54$ Hz, 2H, Ar H); ^{13}C NMR (125.6 MHz, $\mathrm{CDCl_3}$) δ 13.21 (1C, $\mathrm{NCH_2}C\mathrm{H_3}$), 13.52 (1C, $\mathrm{NCH_2}C\mathrm{H_3}$), 20.54 (1C, $\mathrm{CH_3}$), 48.79 (1C, $\mathrm{N}C\mathrm{H_2}$), 52.54 (1C, $\mathrm{N}C\mathrm{H_2}$), 55.20 (1C, $\mathrm{OCH_3}$), 55.22 (1C, $\mathrm{OCH_3}$), 113.13 (2C, Ar C), 113.65 (2C, Ar C), 125.73 (1C, C-1), 130.32 (2C, Ar C), 131.10 (2C, Ar C), 133.46 (1C, C-1′), 134.05 (1C, C-1′), 142.53 (1C, C-2), 158.25 (1C, C-4′), 158.84 (1C, C-4′), 217.11 (4C, $\mathrm{CO_{cis}}$), 222.86 (1C, $\mathrm{CO_{trans}}$), 276.48 (1C, $\mathrm{C_{carbene}}$); FT-IR (hexane) ($\nu_{\mathrm{C=O}}$) 2052 (m, $\mathrm{A^1}$), 1971 (w, $\mathrm{B^1}$), 1938, 1928 (vs, E), 1911 (s, $\mathrm{A_1}$) cm^{-1}; MS (EI) *m*/*z* (%) 473 ($\mathrm{M^+} - 2\mathrm{CO}$, 9), 417 ($\mathrm{M^+} - 4\mathrm{CO}$, 2), 389 ($\mathrm{M^+} - 5\mathrm{CO}$, 35), 337 ($\mathrm{M^+} - 5\mathrm{CO} - \mathrm{Cr}$, 64), 322 ($\mathrm{M^+} - 5\mathrm{CO} - \mathrm{Cr} - \mathrm{CH_3}$, 100), 265 ($\mathrm{M^+} - 5\mathrm{CO} - \mathrm{Cr} - \mathrm{NEt_2}$, 60), 52 ($\mathrm{Cr^+}$, 13); HR-MS calcd for $\mathrm{C_{25}H_{27}CrNO_5}$ 473.1294, found 473.1288 ($\mathrm{M^+} - 2\mathrm{CO}$). Anal. Calcd for $\mathrm{C_{27}H_{27}CrNO_7}$: C, 61.24; H, 5.14; N, 2.65. Found: C, 61.09; H, 5.19; N, 2.47.

General Procedure for the Reactions of the Carbene Complexes 9, 10, and 15 with Ethoxyethyne. To a stirred solution of 1 mmol of the carbene complexes **9**, **10**, and **15**, respectively, in 20 mL of $\mathrm{CH_2Cl_2}$, cooled to −20 °C, was added a solution of 0.07 g (1 mmol) of ethoxyethyne in 2 mL of $\mathrm{CH_2Cl_2}$ over 5 min. After 2 h the reaction was complete, yielding a reddish brown solution. Removal of the solvent under reduced pressure and column chromatographic workup (−20 °C, eluent petroleum ether/dichloromethane 2/1) gave **26**−**28** as brown or red oils.

Pentacarbonyl{ethoxy[9(9*H*)-fluorenylidenemethyl]carbene}chromium(0) (26): red oil, 0.20 g (47%); R_f 0.45 (petroleum ether/$\mathrm{CH_2Cl_2}$ 2/1); ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, 298 K) δ 1.56 (t, 3H, $^3J_{\mathrm{HH}} = 7.15$ Hz, $\mathrm{CH_3}$), 4.85 (b, 2H, $\mathrm{OCH_2}$), 7.24 (t, 1H, $^3J_{\mathrm{HH}} = 7.55$ Hz, Ar H), 7.29 (d, 1H, $^3J_{\mathrm{HH}} = 7.35$ Hz, Ar H), 7.31 (d, 1H, $^3J_{\mathrm{HH}} = 7.55$ Hz, Ar H), 7.36 (t, 2H, $^3J_{\mathrm{HH}} = 6.95$ Hz, Ar H), 7.58 (s, 1H, $\mathrm{C{=}C(R)H}$), 7.66 (d, 2H, $^3J_{\mathrm{HH}} = 7.85$ Hz, Ar H), 7.67 (t, 1H, $^3J_{\mathrm{HH}} = 7.70$ Hz, Ar H). ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, 233 K, *E*/*Z* = 2.4:1) δ 1.55 (b, 3H, $\mathrm{CH_{3(\mathit{E})}}$), 1.73 (b, 3H, $\mathrm{CH_{3(\mathit{Z})}}$), 4.57 (b, 1H, $\mathrm{OCH}H_{(E)}$), 4.69 (b, 1H, $\mathrm{OC}H\mathrm{H}_{(E)}$), 5.35 (b, 2H, $\mathrm{OCH_{2(\mathit{Z})}}$), 7.20−7.80 (m, 18H, Ar

---

[35] The signals of the aromatic protons of the *Z* isomer are partially covered by the signals of the *E* isomer.

$H_{(E+Z)}$ and C═C(R)$H_{(E+Z)}$); ^{13}C NMR (125.6 MHz, $CDCl_3$, 298 K) δ 15.04 (1C, CH_3), 76.20 (1C, OCH_2), 120.11 (2C, Ar C), 120.29 (1C, Ar C), 120.84 (1C, Ar C), 124.36 (1C, Ar C), 127.34 (1C, Ar C), 127.37 (1C, Ar C), 129.21 (1C, Ar C), 129.54 (1C, Ar C), 131.67, 135.09, 137.99, 140.54, 141.42 (5C, C-4a, C-4b, C-8a, C-9, C-9a), 215.83 (4C, CO_{cis}), 224.17 (1C, CO_{trans}), 346.51 (1C, $C_{carbene}$); ^{13}C NMR (125.6 MHz, $CDCl_3$, 233 K) *E* isomer δ 15.89 (1C, CH_3), 76.56 (1C, OCH_2), 120.91, 121.09, 121.46, 124.30, 127.99, 128.31, 129.68, 130.11, 131.09 (9C, Ar C and C═*C*(R)H), 130.03, 135.31, 137.90, 140.65, 141.36 (5C, C-4a, C-4b, C-8a, C-9, C-9a), 216.42 (4C, CO_{cis}), 225.31 (1C, CO_{trans}), 347.39 (1C, $C_{carbene}$); *Z* isomer δ 15.57 (1C, CH_3), 78.29 (1C, OCH_2), 120.75, 120.98, 121.72, 123.74 (2C), 125.24, 126.77, 127.67, 127.91 (9C, Ar C and C═*C*(R)H), 135.46, 135.56, 138.81, 141.14, 142.21 (5C, C-4a, C-4b, C-8a, C-9, C-9a), 216.20 (4C, CO_{cis}), 224.40 (1C, CO_{trans}), 344.41 (1C, $C_{carbene}$); FT-IR (hexane) ($\nu_{C=O}$) 2064 (m, A_1), 1989 (w, B), 1965 (vs, E), 1951 (vs, A_1) cm^{-1}; MS (EI) *m/z* (%) 426 (M^+, 5), 370 ($M^+ - 2CO$, 20), 342 ($M^+ - 3CO$, 17), 314 ($M^+ - 4CO$, 26), 286 ($M^+ - 5CO$, 85), 242 ($M^+ - 5CO - OC_2H_5 - H$, 75), 52 (Cr^+, 100); HR-MS calcd for $C_{22}H_{14}CrO_6$ 426.0195, found 426.0184 (M^+).

Pentacarbonyl{ethoxy[9(9*H*)-xanthenylidenemethyl]carbene}chromium(0) (27): brown oil, 0.18 g (41%); R_f 0.75 (petroleum ether/dichloromethane 2/1). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 1.45 (t, 3H, $^3J_{HH}$ = 7.05 Hz, CH_3), 4.69 (q, 2H, $^3J_{HH}$ = 7.05 Hz, OCH_2), 7.15 (t, 1H, $^3J_{HH}$ = 7.15 Hz, Ar H), 7.16 (d, 1H, $^3J_{HH}$ = 7.17 Hz, Ar H), 7.24−7.28 (m, 4H, Ar H), 7.39−7.44 (m, 2H, Ar H and C═C(R)H), 7.77 (d, 1H, $^3J_{HH}$ = 8.64 Hz, Ar H); ^{1}H NMR (500 MHz, $CDCl_3$, 233 K, *E*/*Z* = 1.2:1) δ 1.2−1.6 (m, 6H, $CH_{3(E+Z)}$), 4.10 (b, 1H, OCH$H_{(E)}$), 4.65 (b, 1H, OCHH$_{(E)}$), 5.00 (b, 2H, $OCH_{2(Z)}$), 7.00−7.80 (m, 18H, Ar $H_{(E+Z)}$ and C═C(R)$H_{(E+Z)}$); ^{13}C NMR (125.6 MHz, $CDCl_3$, 298 K) δ 14.73 (1C, CH_3), 75.66 (1C, OCH_2), 117.26, 117.40, 123.35, 123.59, 124.32 (2C), 128.53, 130.21, 130.58 (9C, Ar C and C═*C*(R)H), 119.88 (1C, C_q), 121.41 (1C, C_q), 130.88 (1C, C_q), 152.27, 152.44 (2C, C-4a, C-4b), 216.47 (4C, CO_{cis}), 224.15 (1C, CO_{trans}), 343.52 (1C, $C_{carbene}$); ^{13}C NMR (125.6 MHz, $CDCl_3$ 233 K) δ 14.53, 14.77 (2C, $CH_{3(E+Z)}$), 75.09, 76.34 (2C, $OCH_{2(E+Z)}$), 216.94 (8C, $CO_{cis(E+Z)}$), 224.69, 225.24 (2C, $CO_{trans(E+Z)}$), 337.89, 346.39 (2C, $C_{carbene(E+Z)}$);[36] FT-IR (hexane) [ν(C═O)] 2059 (m, A_1), 1983 (w, B), 1956 (vs, E), 1946 (vs, A_1) cm^{-1}; MS (EI) *m/z* (%) 442 (M^+, 2), 414 ($M^+ - CO$, 4), 386 ($M^+ - 2CO$, 14), 358 ($M^+ - 3CO$, 10), 330 ($M^+ - 4CO$, 30), 302 ($M^+ - 5CO$, 55), 250 ($M^+ - 5CO - Cr$, 17), 245 (30), 205 ($M^+ - 5CO - Cr - OEt$, 100), 52 (Cr^+, 85); HR-MS calcd for $C_{22}H_{14}CrO_7$ 442.0145, found 442.0120 (M^+). Anal. Calcd for $C_{22}H_{14}CrO_7$: C, 59.74; H, 3.19. Found: C, 59.74; H, 3.91.

(*E*/*Z*)-Pentacarbonyl{ethoxy[1-(*exo*-spiro-(1″*H*)-indeno-(1″,1′)-cycloprop[2′,3′-*b*]-1(1*H*)-indylidene)methyl]carbene}chromium(0) (*E*/*Z*-28): red solid, 0.18 g (36%, *E*/*Z* = 1.6:1); R_f 0.7 (petroleum ether/dichloromethane 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) *E* isomer δ 0.89 (t, 3H, $^3J_{HH}$ = 7.07 Hz, CH_3), 3.86 (d, 1H, $^3J_{HH}$ = 4.97 Hz, H-3), 3.95 (dd, 1H, $^3J_{HH}$ = 4.97 Hz, $^4J_{HH}$ = 1.05 Hz, H-2), 4.78 (dq, 1H, $^2J_{HH}$ = 10.38 Hz, $^3J_{HH}$ = 7.07 Hz, OCH*H*), 4.85 (dq, 1H, $^2J_{HH}$ = 10.38 Hz, $^3J_{HH}$ = 7.07 Hz, OC*H*H), 5.53 (d, 1H, $^3J_{HH}$ = 5.66 Hz, H-2″), 6.82 (dd, 1H, $^3J_{HH}$ = 5.66 Hz, $^4J_{HH}$ = 0.59 Hz, H-3″), 7.16 (d, 1H, $^3J_{HH}$ = 7.45 Hz, Ar H), 7.24 (t, 1H, $^3J_{HH}$ = 7.25 Hz, Ar H), 7.29 (t, 1H, $^3J_{HH}$ = 7.40 Hz, Ar H), 7.34−7.40 (m, 4H, Ar H), 7.74 (d, 1H, $^3J_{HH}$ = 6.95 Hz, Ar H), 8.05 (d, 1H, $^4J_{HH}$ = 1.05 Hz, C═C(R)H); *Z* isomer δ 1.60 (t, 3H, $^3J_{HH}$ = 7.09 Hz, CH_3), 3.87 (d, 1H, $^3J_{HH}$ = 5.02 Hz, H-3), 4.05 (dd, 1H, $^3J_{HH}$ = 5.02 Hz, $^4J_{HH}$ = 1.14 Hz, H-2), 4.80 (m, 1H, OC*H*H), 4.96 (dq, 1H, $^2J_{HH}$ = 10.31 Hz, $^3J_{HH}$ = 7.09 Hz, OCH*H*), 6.16 (d, 1H, $^3J_{HH}$ = 5.46 Hz, H-2″), 6.72 (t, 1H, $^3J_{HH}$ = 7.68, Ar H), 6.89 (d, 1H, $^3J_{HH}$ = 5.46 Hz, H-3″), 7.98 (d, 1H, $^3J_{HH}$ = 7.65 Hz, Ar H), 8.16 (d, 1H, $^4J_{HH}$ = 1.14 Hz, C═C(R)H);[35] ^{13}C NMR (125.6 MHz, $CDCl_3$) *E* isomer δ 14.34 (q, 1C, CH_3), 39.65 (d, 1C, $^1J_{HH}$ = 176.3 Hz, C-2 or C-3), 40.87 (d, 1C, $^1J_{CH}$ = 180.4 Hz, C-2 or C-3), 57.48 (s, 1C, C-1″), 76.40 (t, 1C, OCH_2), 117.78, 121.53, 122.38, 124.87, 125.11, 126.89, 127.43, 131.46, 132.35, 133.08, 133.29 (11C, Ar C and C═*C*(R)H), 139.72, 141.52, 142.90, 145.42, 148.14 (s, 5C, C-1, C-3a, C-7a, C-3a″, C-7a″), 216.88 (s, 4C, CO_{cis}), 224.31 (s, 1C, CO_{trans}), 328.23 (s, 1C, $C_{carbene}$); *Z* isomer δ 14.82 (1C, CH_3), 37.36, 38.17 (2C, C-2, C-3), 52.04 (1C, C-1″), 75.86 (1C, OCH_2), 216.46 (4C, CO_{cis}), 223.92 (1C, CO_{trans}), 328.09 (1C, $C_{carbene}$);[37] FT-IR (hexane) ($\nu_{C=O}$) 2055 (m, A_1), 1979 (w, B), 1954 (vs, E), 1946 (vs, A_1) cm^{-1}; MS (EI) *m/z* (%) 490 (M^+, 0.2), 462 ($M^+ - CO$, 0.2), 434 ($M^+ - 2CO$, 0.2), 406 ($M^+ - 3CO$, 2), 378 ($M^+ - 4CO$, 0.4), 350 ($M^+ - 5CO$, 40), 298 ($M^+ - 5CO - Cr$, 9), 253 ($M^+ - 5CO - Cr - OCH_2CH_3$, 11), 115 ($C_7H_9^+$, 100), 80 ($CrCO^+$, 35); HR-MS calcd for $C_{22}H_{18}CrO$ 350.0762, found 350.0772 ($M^+ - 5CO$).

Acknowledgment. Support by the Fonds der Chemischen Industrie and the Graduiertenkolleg "Spektroskopie isolierter und kondensierter Moleküle" is gratefully acknowledged.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all compounds described (45 pages). Ordering information is given on any current masthead page.

OM971086G

---

(36) The signals in the aromatic region are not resolved.

(37) The signals of the aromatic carbon atoms of the *Z* isomer are covered by the signals of the *E* isomer.