Reactions of Complex Ligands, LXX[◇]

An Intramolecular Alkyne Insertion/Carbonylation/Cyclization Sequence of Chromium Aminocarbene Complexes: A Novel Access to Indole and Indenoindole Skeletons

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2-Alkynylanilinocarbene chromium complexes **1**–**7** bearing a rigid arene C_2 spacer between the aminocarbene and alkyne units were prepared from pentacarbonyl(aroyl)chromates(−I), acetyl bromide, and 2-alkynylanilines. They undergo intramolecular cyclization the course of which depends on the substitution pattern at the alkyne terminus. A tandem alkyne insertion into the metal–carbene bond/carbonylation sequence affords $Cr(CO)_3$-coordinated 3-indolylketenes **8**, **9**, **12**–**14** by using a bulky substituent; the rate of the reaction increases with *N*-alkylation. Less bulky *n*-alkynylanilinocarbene complexes **4**, **5** exhibit two competing carbene annulation sequences: Benzannulation leads to benzo[*a*]carbazoles **15**, **16**, whereas cyclopentannulation without prior carbonylation furnishes indeno[1,2-*b*]indoles **17**, **18**.

Since the 1970s Fischer-type metal carbene complexes $(CO)_5M{=}C(XR^2)R^1$[2] have been gradually developed to useful reagents in selective carbon–carbon bond formation. Their synthetic potential is based both on the strongly electrophilic carbene carbon atom and on the template properties of a low-valent metal center. Especially chromium complexes have been widely exploited in carbene ligand-centered C–C coupling as well as in metal-centered cycloaddition reactions[3]. The bifunctionality of carbonyl carbene complexes is most evident from the benzannulation[4] (Scheme 1), a formal [3 + 2 + 1] cycloaddition of α,β-unsaturated *alkoxy*carbene complexes of chromium, an alkyne and a carbonyl ligand which was also applied in the synthesis of various natural products[5].

Under photochemical conditions carbene carbonyl complexes represent metal-coordinated ketene equivalents which undergo both cycloaddition and addition reactions with nucleophiles; this strategy was applied to aminocarbene complexes in the synthesis of β-lactams and amino acids[3f]. Annulation of *amino*(aryl)carbene ligands by alkynes was studied in less detail and predominantly resulted in the formation of five-membered rings without incorporation of a CO ligand[6] (Scheme 1). If, however, the electron-releasing ability of the amino substituent is decreased by *N*-acceptor substitution or by incorporation of the nitrogen lone pair into an aromatic 6π-system, benzannulation again overrides cyclopentannulation[7]. Recent reports on inter- and intramolecular alkenyl(amino)carbene[8,9] or intramolecular aryl(*aryl*ethynylanilino)carbene benzannulation reactions[1] of chromium complexes may suggest that the driving force for CO incorporation is multifaceted in origin. We now report on the synthesis of (*alkyl*ethynylanilino)carbene complexes and their propensity for carbene annulation reactions.

Synthesis of Anilinocarbene Precursors

The alkyne insertion/carbonylation/cyclization sequence requires pentacarbonyl(alkynylanilino)carbene complexes which are accessible from tetramethylammonium pentacarbonyl(acyl)chromates[10]. Low-temperature *O*-acylation by acetyl bromide produces the extremely electrophilic acyloxycarbene complex intermediates which represent the organometallic analogs of carboxylic acid anhydrides[11]. Subsequent aminolysis with 2-alkynylanilines[12] in the presence of a base such as triethylamine affords the alkynylanilinocarbene complexes **1**–**5** in good to excellent yields (Scheme 2). The resulting aminocarbene complexes can be further alkylated as shown for compound **3**: Low-temperature deprotonation with lithium diisopropylamide followed by alkylation with methyl iodide or benzyl bromide leads to complexes **6** and **7**.

The monosubstituted aminocarbene complexes **1**–**5** were obtained as mixtures of (*E*/*Z*) isomers whereas single isomers were isolated for compounds **6** and **7**, the *N*-alkylated analogs of **3**. The isomeric mixtures were analyzed on the basis of their N–*H* and N–C*H*$_2$R ^{1}H-NMR chemical shifts in isotropic and anisotropic solvents[13]. For (*E*)- and (*Z*)-(*N*-alkylaminocarbene) complexes the differences of the

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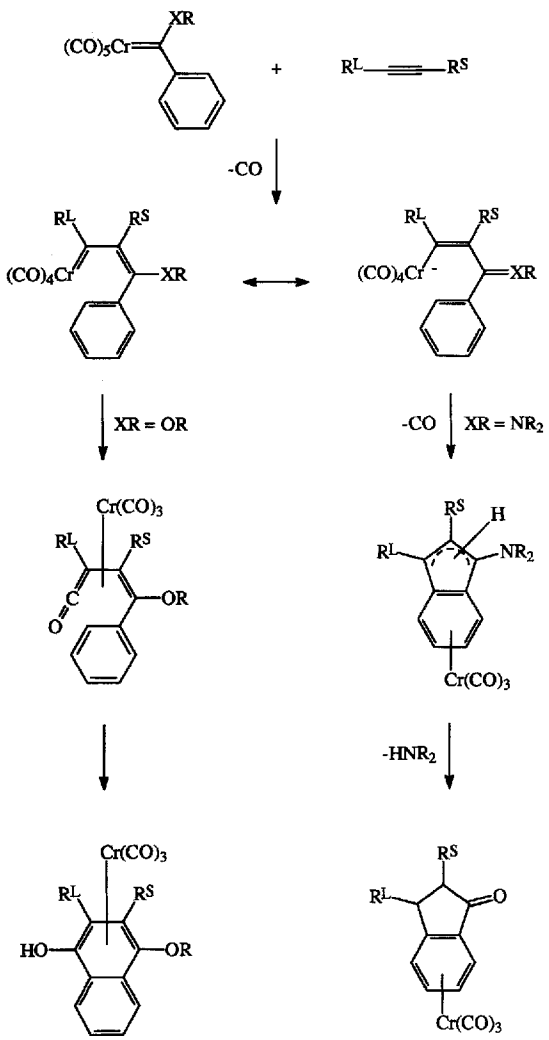
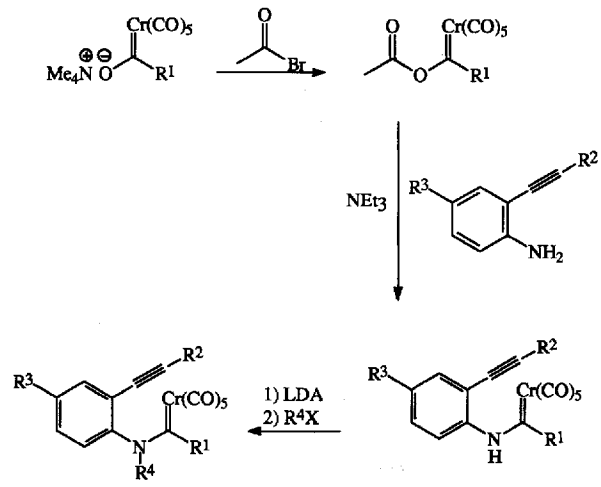
Scheme 1



Scheme 2



	R^1	R^2	R^3	R^4	E/Z	Yield (%)
1	C_6H_5	$C(CH_3)_3$	H	H	1/1	89
2	4-CH_3-C_6H_4	$C(CH_3)_3$	H	H	7/4	83
3	4-CH_3-C_6H_4	$C(CH_3)_3$	CH_3	H	1/1	76
4	C_6H_5	$CH_2CH_2CH_3$	H	H	9/4	90
5	4-CH_3-C_6H_4	$CH_2CH_2CH_3$	H	H	5/2	83
6	4-CH_3-C_6H_4	$C(CH_3)_3$	CH_3	CH_3	[a]	65[b]
7	4-CH_3-C_6H_4	$C(CH_3)_3$	CH_3	$CH_2C_6H_5$	[c]	80[b]

[a] Single isomer of undefined stereochemistry. - [b] Refers to 3. - [c] Only Z isomer.

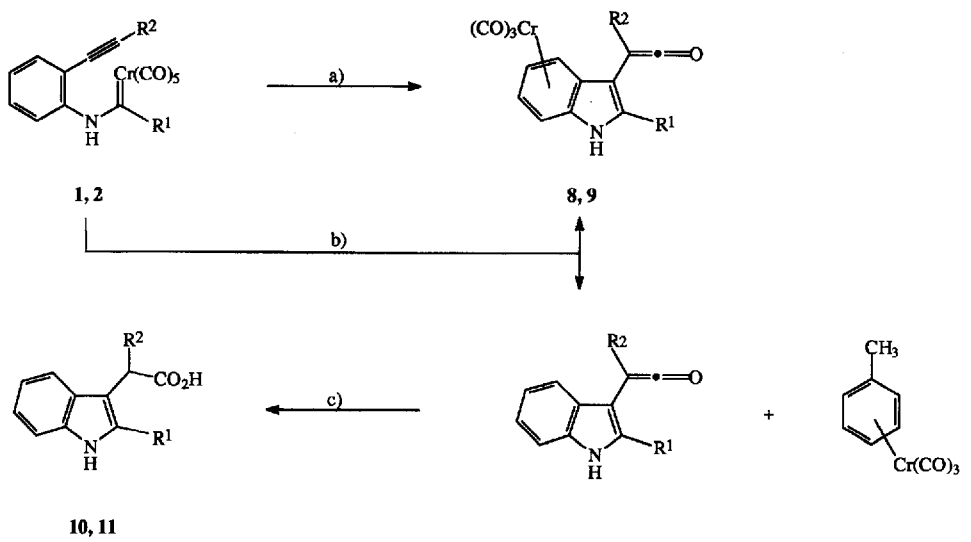
NCH_2 chemical shifts for the (*E*) isomers generally exceed those for the (*Z*) isomers when $CDCl_3$ is replaced as solvent by C_6D_6[14a]. An inverse correlation was observed for N–*H* hydrogen atoms in allyl- and propylaminocarbene complexes of chromium the (*Z*) isomers of which exhibit larger $\Delta[\delta\ (CDCl_3) - \delta\ (C_6D_6)]$ values than their (*E*) analogs[14b]. For example, a distinct upfield shift of $\delta = 1.09$ is observed for the N–*H* signal of (*E*)-**3** in C_6D_6 (relative to $CDCl_3$) while the corresponding signal in (*Z*)-**3** is shifted upfield by only $\delta = 0.23$. The NCH_2 hydrogen atoms in the *N*-benzylanilinocarbene complex **7** give rise to a pair of doublets ($^2J_{H,H} = 13.8$ Hz); this indicates that the carbene ligand deviates from planarity making these hydrogen atoms diastereotopic. Their chemical shifts are independent of the solvent used which suggests the presence of the (*Z*) isomer.

Alkyne Insertion/Carbonylation/Cyclization Sequence

On warming in toluene to 85°C the alkynylanilinocarbene complexes **1** and **2** undergo a tandem alkyne insertion/carbonylation to give the 3-indolylketene complexes **8** and **9** which were isolated in moderate yields after chromatographic work-up (Scheme 3). NMR spectra of the crude products indicate the formation of (toluene)$Cr(CO)_3$ as well as the presence of uncoordinated indolylketenes which can be modified to 3-indolylacetic acids **10** and **11** on work-up in aqueous acetone. In a non-aromatic solvent such as di-*n*-butyl ether the reaction proceeds more selectively, and chromatographic work-up afforded the indolylketene complexes **8** and **9** in good yields. The ketene moiety exhibits characteristic absorptions in the IR spectra ($\tilde{\nu}_{C=C=O} \approx 2100\ cm^{-1}$)[15] and ^{13}C-NMR spectra ($\delta \approx 194$ and 14)[15,16].

The indolylketene formation can be rationalized in terms of an insertion of the alkyne into the chromium–carbene bond to generate a 3-indolylcarbene complex intermediate. A carbonyl transfer from the metal to the newly formed carbene carbon atom affords the ketene which finally remains coordinated to the $Cr(CO)_3$ fragment via the former aniline arene skeleton. Similar indolylketene intermediates have been shown to undergo an electrocyclic ring-closure

Scheme 3



	1	2	8	9	10	11
R^1	C_6H_5	4-CH_3-C_6H_4	C_6H_5	4-CH_3-C_6H_4	C_6H_5	4-CH_3-C_6H_4
R^2	$C(CH_3)_3$	$C(CH_3)_3$	$C(CH_3)_3$	$C(CH_3)_3$	$C(CH_3)_3$	$C(CH_3)_3$
Yield (%)			70[a]	82[a]	27	15
			20[b]	57[b]		

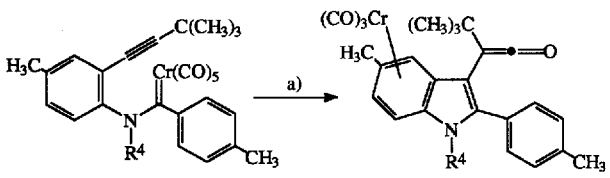
[a] Di-n-butyl ether, 85°C, 1h. - [b] Toluene, 85°C, 1h. - [c] Acetone/H_2O, 25°C, 24h.

involving the π system in position 2 which results in the formation of oxygenated 9*H*-carbazoles and 11*H*-benzo[*a*]carbazoles[1]. The final cyclization requires a transition state in which the ketene and the indole units are essentially coplanar, a conformation which is obviously hampered by the presence of the sterically demanding *tert*-butyl-group. A similar restriction on the ring-closure was observed earlier for an analogous indolyl(trimethylsilyl)ketene[6c].

Intramolecular Diels-Alder reactions with aminocarbene complexes have demonstrated that the conformation within the aminocarbene ligand depends on the nature of *N* substitution[17]. Thus, we compared the *N*-methylated and -benzylated compounds **6** and **7** with complex **3**. Under our standard conditions (di-*n*-butyl ether, 85°C), the rate of ketene formation gradually increases with increasing steric demands of the *N* substituent (Scheme 4). We speculate that *N* substitution favours a conformation within the alkynylanilino substituent required for the coordination of the alkyne to the metal center.

To test the hypothesis that the bulky *tert*-butyl group at the alkyne terminus of the aminocarbene complexes **1**–**3** is responsible for the reluctance of the indolyl ketene intermediates to undergo cyclization, we extended our studies to less crowded alkyl analogs. At slightly higher temperature the *n*-pentynyl complexes **4** and **5** afford two different annulation products arising from the presumed alkyne insertion intermediates in low to moderate yields (Scheme 5). Along with the expected benzannulation products **15** and **16** the cyclopentannulation products **17** and **18** could be isolated.

Scheme 4



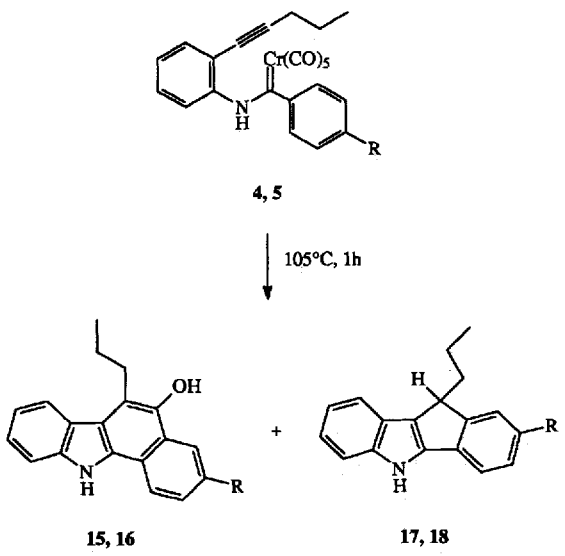
	12	13	14
R^4	H	CH_3	$CH_2C_6H_5$
Time (min)	60	30	15
Yield (%)	82	85	63

a) Di-n-butyl ether, 85°C.

The chemoselectivity of the cyclization reaction depends on the solvent used: Whereas in toluene both annulation products are formed in approximately equal amounts the better coordinating solvent di-*n*-butyl ether favours the formation of the benzocarbazoles **15** and **16** which were isolated as the main products in a 2.5:1 and 4:1 ratio, respectively.

Recently, oxygenated 11*H*-benzo[*a*]carbazoles were prepared via organoiron or other routes[18] while the synthesis

Scheme 5



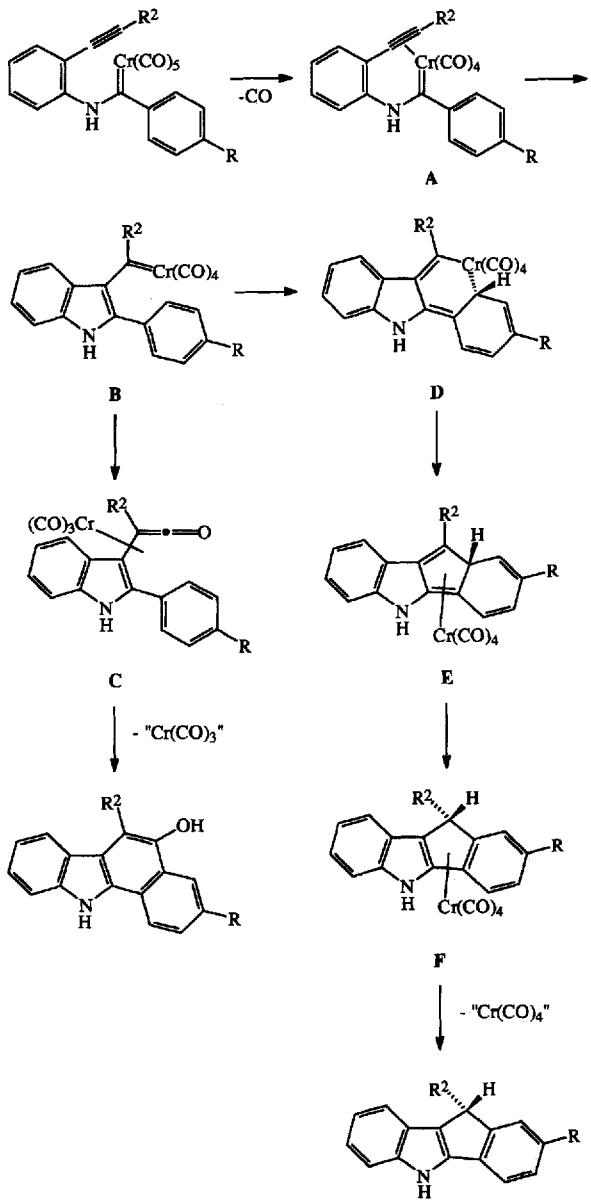
R	Solvent	Yield (%)			
		15	**16**	**17**	**18**
H	toluene	21		18	
CH_3	toluene		23		16
H	di-n-butyl ether[a]	34		14	
CH_3	di-n-butyl ether[a]		39		10

[a] The crude reaction mixture was stirred for 24h in the air in acetone/H_2O to remove traces of $Cr(CO)_3$ complexes.

of the 5,10-dihydroindeno[1,2-*b*]indole skeleton is generally based on flash vacuum pyrolysis of 2-phenylquinoline-3,4-dicarboxylic anhydride[19]. The competitive formation of both types of products can be traced back to a common indolylcarbene complex intermediate **B** as outlined in Scheme 6. We suggest a reaction sequence which starts with a thermally induced decarbonylation followed by coordination of the alkyne to give the alkyne carbene complex **A**. Similar alkyne carbene chelates were isolated from low-temperature photodecarbonylation of pentacarbonyl[alkoxy(2-alkynylphenyl)carbene] complexes and were structurally characterized[20]. Subsequent insertion of the alkyne into the metal–carbene bond is accompanied by the formation of the indole nucleus and leads to the 3-indolylcarbene complex intermediate **B**. The formation of the benzo[*a*]carbazole skeleton can be rationalized in terms of an insertion of a carbonyl ligand into the newly formed chromium–carbene bond to give the $Cr(CO)_3$-coordinated ketene intermediate **C** which may undergo an electrocyclic ring-closure and, finally, after cleavage of the chromium fragment affords the oxygenated benzo[*a*]carbazole.

We suggest that in the indolylcarbene complex intermediate **B** the carbonyl insertion has to compete with an electrophilic addition of the coordinatively unsaturated 16-electron chromium center to the *ortho* position of the 2-aryl substituent to give the chromacyclohexadiene intermediate **D**. Reductive elimination is supposed to generate a central cyclopentadiene ring coordinated to the $Cr(CO)_4$ fragment (**E**). A suprafacial sigmatropic 1,5-*H* shift which was demonstrated to be involved in a related cyclopentannulation sequence[21] allows the regeneration of the aromatic systems in the adjacent indole and the benzene rings. Cleavage of the $Cr(CO)_4$ fragment from the tetracyclic complex intermediate **F** may occur either directly or stepwise by decarbonylation and haptotropic $Cr(CO)_3$ migration to an aromatic ring and finally affords the indeno[1,2-*b*]indole products.

Scheme 6



The competition between benzannulation and cyclopentannulation is governed by the substitution pattern at

the alkyne terminus in the starting anilinocarbene complex. If the alkyl substituent is replaced by *aryl* groups the cyclization via the ketene intermediate **C** is favoured and only benzo[*a*]carbazoles could be isolated after chromatographic work-up[1]. The reason for the preference of *aryl*ethynylanilinocarbene complexes to undergo an alkyne insertion/carbonylation/cyclization sequence is still a matter of speculation. One might argue that in the indolylcarbene complex intermediate **B** the electrophilicity of the unsaturated chromium center is reduced as a consequence of π-bonding contribution from the arene substituent bound to the carbene carbon atom which is supposed to hamper its propensity to undergo electrophilic addition to the other arene ring generating the chromacyclohexadiene intermediate **D**.

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Experimental

All operations were carried out under inert gas. Solvents were dried by using standard methods, distilled, saturated, and stored under argon. Merck silica gel 60 (0.063−0.200 mm) was used for column chromatography. ^{1}H and ^{13}C NMR: Bruker AM-400 and WM-250. For aminocarbene complexes obtained as (*E*/*Z*) mixtures [a] denotes signals of the (*E*) isomers whereas [b] refers to signals of the (*Z*) isomers. − MS: Kratos MS 50 and Varian MAT CH 7A. − FT-IR: Nicolet Magna 550. − Elemental analyses: Heraeus CH-O-Rapid. − Melting Points: Büchi SMP 20, uncorrected.

(E/Z)-{[2-(tert-Butylethynyl)phenylamino]phenylcarbene}pentacarbonylchromium(0) (**1**): A solution of 924 mg (2.49 mmol) of tetramethylammonium [pentacarbonyl(benzoyl)chromate(−I)] in 30 ml of CH_2Cl_2 was cooled to −40 °C and, after addition of acetyl bromide (306 mg, 0.186 ml, 2.49 mmol), stirred for 1 h. Then a solution of 2-(*tert*-butylethynyl)aniline (500 mg, 2.89 mmol) and triethylamine (292 mg, 0.40 ml, 2.89 mmol) in 5 ml of CH_2Cl_2 (degassed by a triple "freeze-pump-thraw" sequence) was added slowly at −78 °C. After stirring for 4 h at this temperature, the reaction mixture was allowed to warm to room temp. The solvent was removed at reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, 3:1) to give 1.01 g (89%) of **1** as a yellow solid [(*E*/*Z*) ratio 1:1]. R_f = 0.30 (petroleum ether/dichloromethane, 3:1). − M.p. 145 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.87[a] (br, 1H, NH), 9.96[b] (br, 1H, NH), 7.57 (dd, 1H, *J* = 1.87, 7.39 Hz), 7.54 (dd, 1H, *J* = 1.57, 7.43 Hz), 7.49 (dt, 1H, *J* = 1.86, 7.43 Hz), 7.46−7.43 (m, 2H), 7.40 (dd, 1H, *J* = 1.47, 7.82 Hz), 7.35 (t, 1H, *J* = 7.44 Hz), 7.28−7.23 (m, 5H), 7.13 (t, 1H, *J* = 7.44 Hz), 7.05 (dt, 1H, *J* = 0.98, 7.53 Hz), 6.90−6.84 (m, 3H), 6.38 (d, 1H, *J* = 7.82 Hz), 1.42 (s, 9H), 1.31 (s, 9H). − ^{1}H-NMR (400 MHz, C_6D_6): δ = 10.53[a] (br, 1H, NH), 8.67[b] (br, 1H, NH), 7.38 (dd, 1H, *J* = 1.37, 7.39 Hz), 7.18−7.03 (m, 7H), 7.00 (dt, 1H, *J* = 1.37, 7.63 Hz), 6.94 (dt, 1H, *J* = 1.37, 7.63 Hz), 6.89−6.84 (m, 2H), 6.77−6.71 (m, 3H), 6.49 (dt, 1H, *J* = 1.25, 7.65 Hz), 6.31 (dt, 1H, *J* = 1.37, 7.73 Hz), 6.02 (d, 1H, *J* = 8.02 Hz), 1.37 (s, 9H), 1.23 (s, 9H). − ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 289.0[a] (Cr=C), 287.3[b] (Cr=C), 224.4[b] (CO_{trans}), 223.6[a] (CO_{trans}), 217.0[a] (CO_{cis}), 216.6[b] (CO_{cis}), 155.5, 150.5, 142.4, 139.5, 133.4, 132.8, 129.5, 128.7, 128.4, 128.3, 128.2, 127.6, 124.6, 122.5, 121.2, 120.7, 118.7, 108.0 (C≡C), 106.1 (C≡C), 74.6 (C≡C), 73.7 (C≡C), 30.8, 30.7, 30.2, 28.5, 28.4. − IR (toluene): $\tilde{\nu}$ = 2054 m, 1976 w, 1936 vs cm^{-1}. − MS (EI); *m/z* (%): 453 (4) [M$^+$], 425 (8) [M$^+$ − CO], 397 (2) [M$^+$ − 2 CO], 369 (2) [M$^+$ − 3 CO], 341 (5) [M$^+$ − 4 CO], 313 (24) [M$^+$ − 5 CO], 261 (18) [M$^+$ − $Cr(CO)_5$], 220 (28), 204 (100). − $C_{24}H_{19}NO_5Cr$ (453.1): calcd. C 63.58, H 4.22, N 3.09; found C 63.29, H 4.23, N 3.05.

(E/Z)-{[2-(tert-Butylethynyl)phenylamino]-p-tolylcarbene}pentacarbonylchromium(0) (**2**): Preparation and work-up as described for **1**. Tetramethylammonium [pentacarbonyl(*p*-toluoyl)chromate(−I)] (967 mg, 2.51 mmol), acetyl bromide (309 mg, 0.187 ml, 2.51 mmol), 2-(*tert*-butylethynyl)aniline (500 mg, 2.89 mmol), triethylamine (292 mg, 0.40 ml, 2.89 mmol). Yield: 972 mg (83%), yellow oil [(*E*/*Z* ratio 7:4)]. R_f = 0.33 (petroleum ether/dichloromethane, 3:1). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.82[a] (br, 1H, NH), 9.93[b] (br, 1H, NH), 7.59−7.50 (m, 2H), 7.47 (dt, 1H, *J* = 1.76, 7.87 Hz), 7.44 (dd, 1H, *J* = 1.56, 7.23 Hz), 7.39 (dd, 1H, *J* = 1.27, 7.73 Hz), 7.24−7.15 (m, 3H), 7.07−7.02 (m, 5H), 6.88 (dt, 1H, *J* = 1.27, 7.88 Hz), 6.77 (d, 1H, *J* = 8.22 Hz), 6.36 (d, 1H, *J* = 8.41 Hz), 2.39[b] (s, 3H), 2.28[a] (s, 3H), 1.42 (s, 9H), 1.31 (s, 9H). − ^{1}H NMR (400 MHz, C_6D_6): δ = 10.55[a] (br, 1H, NH), 8.79[b] (br, 1H, NH), 7.38 (dd, 1H, *J* = 1.37, 7.63 Hz), 7.18 (d, 1H, *J* = 7.54 Hz), 7.14 (dd, 1H, *J* = 1.17, 7.65 Hz), 7.08 (d, 1H, *J* = 7.54 Hz), 7.01 (dt, 1H, *J* = 1.57, 7.58 Hz), 6.97 (dd, 1H, *J* = 1.37, 7.92 Hz), 6.94 (dt, 1H, *J* = 1.37, 7.67 Hz), 6.78−6.64 (m, 6H), 6.50 (dt, 1H, *J* = 1.37, 7.69 Hz), 6.34 (dt, 1H, *J* = 1.56, 7.94 Hz), 6.09 (d, 1H, *J* = 8.22 Hz), 2.11[b] (s, 3H), 1.86[a] (s, 3H), 1.41[a] (s, 9H), 1.30[b] (s, 9H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 289.3[a] (Cr=C), 287.0[b] (Cr=C), 224.4[b] (CO_{trans}), 223.6[a] (CO_{trans}), 217.0[a] (CO_{cis}), 216.7[b] (CO_{cis}), 153.1[b], 147.9[a], 142.6[b], 139.7[a], 138.4[b], 137.4[a], 133.4[b], 132.8[a], 129.4[b], 129.0[b], 128.9[a], 128.6[b], 127.7[b], 127.6[a], 127.0[a], 124.6[a], 122.5[a], 121.7[b], 121.0[a], 118.6[a], 107.8[a] (C≡C), 106.0[b] (C≡C), 74.7[b] (C≡C), 73.7[a] (C≡C), 30.8, 28.5[b], 26.9[a], 21.1. − IR (toluene): $\tilde{\nu}$ = 2054 m, 1980 w, 1931 vs cm^{-1}. − MS (FAB); *m/z* (%): 467 (31) [M$^+$], 383 (22) [M$^+$ − 3 CO], 355 (13) [M$^+$ − 4 CO], 327 (100) [M$^+$ − 5 CO].

(E/Z)-{[2-(tert-Butylethynyl)-4-methylphenylamino]-p-tolylcarbene}pentacarbonylchromium(0) (**3**): Preparation as described for **1**. Tetramethylammonium [pentacarbonyl(*p*-toluoyl)chromate(−I)] (770 mg, 2.0 mmol), acetyl bromide (246 mg, 0.149 ml, 2.0 mmol), 2-(*tert*-butylethynyl)-4-methylaniline (412 mg, 2.20 mmol), triethylamine (223 mg, 0.305 ml, 2.20 mmol). The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, 1.5:1) to give 730 mg (76%) of **3** as a yellow oil [(*E*/*Z*) ratio 1:1)]. R_f = 0.49 (petroleum ether/dichloromethane, 1.5:1). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.78[a] (br, 1H, NH), 9.88[b] (br, 1H, NH), 7.39 (d, 2H, *J* = 7.82 Hz), 7.29−7.21 (m, 4H), 7.17 (d, 2H, *J* = 7.83 Hz), 7.06 (d, 2H, *J* = 7.82 Hz), 6.78 (d, 1H, *J* = 8.22 Hz), 6.68 (d, 1H, *J* = 8.22 Hz), 6.26 (d, 1H, *J* = 8.22 Hz), 2.40 (s, 6H), 2.29 (s, 3H), 2.21 (s, 3H), 1.41 (s, 9H), 1.31 (s, 9H). − ^{1}H NMR (400 MHz, C_6D_6): δ = 10.55[a] (br, 1H, NH), 8.81[b] (br, 1H, NH), 7.25 (s, 1H), 7.12 (d, 1H, *J* = 7.82 Hz), 7.09 (d, 1H, *J* = 8.21 Hz), 6.98 (d, 2H, *J* = 8.22 Hz), 6.87 (d, 1H, *J* = 7.83 Hz), 6.78 (d, 2H, *J* = 8.21 Hz), 6.74 (d, 2H, *J* = 8.22 Hz), 6.18 (d, 1H, *J* = 8.37 Hz), 6.02 (d, 1H, *J* = 8.30 Hz), 2.12 (s, 3H), 2.00 (s, 3H), 1.88 (s, 3H), 1.72 (s, 3H), 1.43 (s, 9H), 1.33 (s, 9H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 287.6[a] (Cr=C), 286.6[b] (Cr=C), 224.5[b] (CO_{trans}), 223.7[a] (CO_{trans}), 217.2[a] (CO_{cis}), 216.8[b] (CO_{cis}), 153.1, 148.0, 140.3, 139.7, 138.3, 137.5, 137.2, 137.1, 133.7, 133.0, 129.4, 129.0, 128.9, 128.5, 127.5, 124.3, 122.2, 121.7, 121.0, 118.3, 107.3 (C≡C), 105.4 (C≡C), 74.8 (C≡C), 73.9 (C≡C), 30.8, 28.4, 28.2, 21.14, 21.11, 20.9, 20.6. − IR (di-*n*-butyl ether): $\tilde{\nu}$ = 2054 m, 1985 w, 1933 vs cm^{-1}. − MS (EI); *m/z* (%): 481 (2) [M$^+$], 453 (4) [M$^+$ − CO], 425 (23) [M$^+$ − 2 CO],

397 (8) [$M^+ - 3$ CO], 369 (30) [$M^+ - 4$ CO], 341 (85) [$M^+ - 5$ CO], 289 (32) [$M^+ - Cr(CO)_5$].

(E/Z)-Pentacarbonyl{[2-(1-pentynyl)phenylamino]phenylcarbene}chromium(0) (**4**): Preparation and work-up as described for **1**. Tetramethylammonium [pentacarbonyl(benzoyl)chromate(−I)] (743 mg, 2.0 mmol), acetyl bromide (246 mg, 0.149 ml, 2.0 mmol), 2-(1-pentynyl)aniline (350 mg, 2.2 mmol), triethylamine (223 mg, 0.305 ml, 2.20 mmol). Yield: 789 mg (90%), yellow oil [(*E*/*Z*) ratio 9:4]. R_f = 0.43 (petroleum ether/dichloromethane, 3:1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.92[a] (br, 1H, NH), 9.95[b] (br, 1H, NH), 7.63–7.32 (m, 8H), 7.30–7.23 (m, 3H), 7.22 (d, 1H, *J* = 7.83 Hz), 7.14 (t, 1H, *J* = 7.23 Hz), 7.06 (t, 1H, *J* = 7.44 Hz), 6.92–6.82 (m, 3H), 6.38 (d, 1H, *J* = 8.02 Hz), 2.54[a] (t, 2H, *J* = 6.85 Hz), 2.44[b] (t, 2H, *J* = 6.84 Hz), 1.74[a] (sext, 2H, *J* = 7.44 Hz), 1.63[b] (sext, 2H, *J* = 7.24 Hz), 1.10[a] (t, 3H, *J* = 7.40 Hz), 1.03[b] (t, 3H, *J* = 7.44 Hz). – ^{1}H NMR (400 MHz, C_6D_6): δ = 10.70[a] (br, 1H, NH), 8.74[b] (br, 1H, NH), 7.50 (dd, 1H, *J* = 1.57, 8.32 Hz), 7.40 (dd, 1H, *J* = 1.56, 7.33 Hz), 7.16–7.12 (m, 4H), 7.07–7.02 (m, 3H), 7.00 (dd, 1H, *J* = 1.76, 7.53 Hz), 6.97 (dt, 1H, *J* = 1.37, 7.53 Hz), 6.91–6.86 (m, 2H), 6.78–6.73 (m, 2H), 6.51 (dt, 1H, *J* = 1.17, 7.64 Hz), 6.30 (dt, 1H, *J* = 1.37, 7.88 Hz), 6.03 (d, 1H, *J* = 7.33 Hz), 2.37[a] (t, 2H, *J* = 7.04 Hz), 2.24[b] (t, 2H, *J* = 6.84 Hz), 1.59[a] (sext, 2H, *J* = 7.44 Hz), 1.49[b] (sext, 2H, *J* = 7.24 Hz), 1.00[a] (t, 3H, *J* = 7.40 Hz), 0.92[b] (t, 3H, *J* = 7.44 Hz). – ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 284.8[a] (Cr=C), 284.5[b] (Cr=C), 225.4[b] (CO_{trans}), 224.8[a] (CO_{trans}), 218.1[a] (CO_{cis}), 217.8[b] (CO_{cis}), 155.9, 151.1, 142.8, 142.7, 133.8[a], 133.0[b], 130.2[b], 129.7[a], 128.9[a], 128.8[b], 128.7[a], 128.5[b], 128.4[a], 128.3[b], 128.1[b], 127.2[a], 123.6[a], 122.2[a], 121.8[b], 121.3[b], 98.2[a] (C≡C), 97.6[b] (C≡C), 77.4[a] (C≡C), 77.3[b] (C≡C), 22.6[a], 22.5[b], 21.8, 13.8[a], 13.7[b]. – IR (toluene): ṽ = 2056 m, 1981 w, 1936 vs cm^{-1}. – MS (FAB); *m/z* (%): 438 (26) [M^+], 299 (100) [$M^+ - 5$ CO].

(E/Z)-Pentacarbonyl{[2-(1-pentynyl)phenylamino]-p-tolylcarbene}chromium(0) (**5**): Preparation and work-up as described for **1**. Tetramethylammonium [pentacarbonyl(*p*-toluoyl)chromate(−I)] (867 mg, 2.25 mmol), acetyl bromide (227 mg, 0.168 ml, 2.25 mmol), 2-(1-pentynyl)aniline (412 mg, 2.59 mmol), triethylamine (262 mg, 0.359 ml, 2.59 mmol). Yield: 847 mg (83%), yellow oil [(*E*/*Z*) ratio 5:2]. R_f = 0.42 (petroleum ether/dichloromethane, 3:1). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 10.87[a] (br, 1H, NH), 9.91[b] (br, 1H, NH), 7.60–7.35 (m, 9H), 7.21–7.16 (m, 2H), 7.10 (d, 1H, *J* = 7.80 Hz), 7.03 (d, 2H, *J* = 7.35 Hz), 6.90 (dt, 1H, *J* = 0.93, 7.80 Hz), 6.77 (d, 2H, *J* = 7.80 Hz), 6.38 (d, 1H, *J* = 8.26 Hz), 2.53[a] (t, 2H, *J* = 7.34 Hz), 2.43[b] (t, 2H, *J* = 7.35 Hz), 2.40[b] (s, 3H), 2.30[a] (s, 3H), 1.71[a] (sext, 2H, *J* = 7.34 Hz), 1.63[b] (sext, 2H, *J* = 7.34 Hz), 1.04[a] (t, 3H, *J* = 7.35 Hz), 1.01[b] (t, 3H, *J* = 7.34 Hz, 3H). – ^{1}H-NMR (400 MHz, C_6D_6): δ = 10.70[a] (br, 1H, NH), 8.89[b] (br, 1H, NH), 7.41 (dd, 1H, *J* = 1.66, 8.32 Hz), 7.18–7.24 (m, 2H), 7.08–6.98 (m, 6H), 6.74–6.68 (m, 4H), 6.55 (dt, 1H, *J* = 0.98, 7.63 Hz), 6.39 (dt, 1H, *J* = 1.27, 7.87 Hz), 6.11 (d, 1H, *J* = 8.02 Hz), 2.38[a] (t, 2H, *J* = 7.04 Hz), 2.26[b] (t, 2H, *J* = 7.04 Hz), 2.14[b] (s, 3H), 1.89[a] (s, 3H), 1.60[a] (sext, 2H, *J* = 7.24 Hz), 1.51[b] (sext, 2H, *J* = 7.43 Hz), 1.01[a] (t, 3H, *J* = 7.43 Hz), 0.94[b] (t, 3H, *J* = 7.43 Hz). – ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 285.3[a] (Cr=C), 283.9[b] (Cr=C), 225.5[b] (CO_{trans}), 224.8[a] (CO_{trans}), 218.2[a] (CO_{cis}), 217.9[b] (CO_{cis}), 153.5, 149.0, 144.9, 142.9, 138.5, 137.0, 133.8[a], 133.0[b], 130.1, 129.7, 129.4[a], 128.9[b], 128.7, 128.6, 128.5, 128.0, 123.7, 122.6[a], 121.8, 121.6[b], 98.4[a] (C≡C), 97.7[b] (C≡C), 77.47[a] (C≡C), 77.44[b] (C≡C), 22.7[a], 22.6[b], 21.9, 21.1[a], 21.0[b], 13.8. – IR (toluene): ṽ = 2055 m, 1980 w, 1935 vs cm^{-1}. – MS (EI); *m/z*: 453 (4) [M^+], 425 (1) [$M^+ - CO$], 397 (2) [$M^+ - 2$ CO], 369 (2) [$M^+ - 3$ CO], 341 (5) [$M^+ - 4$ CO], 313 (24) [$M^+ - 5$ CO], 261 (18) [$M^+ - Cr(CO)_5$], 204 (100), 52 (63) [Cr^+].

Pentacarbonyl{[N-methyl-2-(tert-butylethynyl)-4-methylphenylamino]-p-tolylcarbene}chromium(0) (**6**): A solution of 730 mg (1.52 mmol) of **3** in 4 ml of tetrahydrofuran was added dropwise at −78 °C to a solution of lithium diisopropylamide prepared from 0.26 ml (1.82 mmol) of diisopropylamine and 1.19 ml (1.82 mmol) of a 1.53 M *n*-butyllithium solution in 20 ml of tetrahydrofuran. After 1 h 0.11 ml (1.82 mmol) of methyl iodide was added and the reaction mixture was allowed to warm to room temp. overnight. After removal of the solvent and purification of the residue by chromatography on silica gel (eluent: petroleum ether/dichloromethane, 2:1) 490 mg (65%) of **6** was obtained as a yellow oil. R_f = 0.51 (petroleum ether/dichloromethane, 2:1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (s, 1H), 7.30–7.21 (m, 4H), 6.92 (dd, 1H, *J* = 1.76, 8.02 Hz), 6.74 (dd, 1H, *J* = 2.06, 7.93 Hz), 3.29 (s, 3H, N-CH_3), 2.48 (s, 3H), 2.47 (s, 3H), 1.38 (s, 9H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 283.1 (Cr=C), 224.9 (CO_{trans}), 216.6 (CO_{cis}), 151.2, 148.8, 139.0, 135.5, 134.5, 129.9, 129.3, 129.2, 126.0, 120.6, 118.6, 118.2, 104.2 (C≡C), 74.5 (C≡C), 47.4 (N-CH_3), 30.8, 28.2, 21.0, 20.8. – IR (di-*n*-butyl ether): ṽ = 2054 m, 1985 w, 1933 vs cm^{-1}. – MS (FAB); *m/z* (%): 495 (12) [M^+], 411 (20) [$M^+ - 3$ CO], 383 (9) [$M^+ - 4$ CO], 355 (100) [$M^+ - 5$ CO].

{[N-Benzyl-2-(tert-butylethynyl)-4-methylphenylamino]-p-tolylcarbene}pentacarbonylchromium(0) (**7**): As described for the preparation of **6** the reaction of 1.30 g (2.78 mmol) of **3** with 2.18 ml (3.34 mmol) of 1.53 M *n*-butyllithium, 0.47 ml (3.34 mmol) of diisopropylamine and 0.40 ml (3.34 mmol) of benzyl bromide gave 1.24 g (80%) of **7** as a yellow solid. R_f = 0.43 (petroleum ether/dichloromethane, 2:1). – M.p. 89–91 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 (s, 1H), 7.36 (d, 1H, *J* = 7.55 Hz), 7.33 (d, 1H, *J* = 7.65 Hz), 7.20–7.10 (m, 3H), 7.05 (d, 1H, *J* = 7.85 Hz), 7.01 (d, 1H, *J* = 7.84 Hz), 6.98 (d, 1H, *J* = 8.54 Hz), 6.87 (d, 2H, *J* = 7.15 Hz), 6.65 (d, 1H, *J* = 8.05 Hz), 5.37 (d, 1H, *J* = 13.81 Hz), 4.58 (d, 1H, *J* = 13.81 Hz), 2.43 (s, 3H), 2.36 (s, 3H), 1.47 (s, 9H). – ^{1}H NMR (500 MHz, C_6D_6): δ = 7.42 (s, 1H), 7.31 (d, 1H, *J* = 6.87 Hz), 7.19–7.12 (m, 3H), 7.07–6.99 (m, 2H), 6.88 (d, 2H, *J* = 8.14 Hz), 6.86 (d, 1H, *J* = 6.85 Hz), 6.65 (d, 1H, *J* = 6.86 Hz), 5.40 (d, 1H, *J* = 13.83 Hz), 4.61 (d, 1H, *J* = 13.85 Hz), 2.22 (s, 3H), 1.98 (s, 3H), 1.48 (s, 9H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 283.9 (Cr=C), 225.0 (CO_{trans}), 216.5 (CO_{cis}), 150.7, 145.4, 138.8, 135.4, 134.4, 133.7, 129.4, 129.2, 129.1, 129.0, 128.7, 128.4, 128.2, 120.9, 119.9, 118.6, 104.3 (C≡C), 75.0 (C≡C), 61.6, 30.9, 30.5, 21.0, 20.8. – IR (di-*n*-butyl ether): ṽ = 2052 m, 1984 w, 1933 vs cm^{-1}. – IR (KBr): ṽ = 3007 vw, 2977 w, 2928 w, 2869 vw, 2052 m, 1981 m, 1947 s, 1938 s, 1914 s, 1896 s, 1494 m, 1469 m, 1455 m, 702 m, 692 m, 671 m, 655 m, 642 m cm^{-1}. – MS (FAB); *m/z* (%): 487 (13) [$M^+ - 3$ CO], 459 (4) [$M^+ - 4$ CO], 431 (100) [$M^+ - 5$ CO). – $C_{33}H_{29}NO_5Cr$ (571.6): calcd. C 69.34, H 5.11, N 2.45; found C 69.13, H 5.42, N 2.65.

[3a–7a-η^6-3-(tert-Butylketenyl)-2-phenylindole]tricarbonylchromium(0) (**8**): A solution of 450 mg (0.99 mmol) of **1** in 20 ml of di-*n*-butyl ether was warmed at 85 °C for 1.5 h (while the reaction was monitored by IR spectroscopy and TLC). The solvent was removed at reduced pressure, and chromatography of the residue on silica gel (eluent: petroleum ether/dichloromethane, 1:1.5) as eluent gave 295 mg (70%) of **8** as a yellow solid. R_f = 0.49 (petroleum ether/dichloromethane, 1:1.5). – ^{1}H NMR (250 MHz,C_6D_6): δ = 7.25–7.21 (m, 2H), 7.11–7.06 (m, 3H), 6.49 (br, 1H, NH), 5.59 (d, 1H, *J* = 6.88 Hz), 5.23 (d, 1H, *J* = 6.88 Hz), 4.58 (t, 1H, *J* = 6.43 Hz), 4.50 (d, 1H, *J* = 6.42 Hz), 0.90 (s, 9H). – ^{13}C NMR (62.5 MHz, C_6D_6): δ = 235.2 [$Cr(CO)_3$], 194.1 (C=*C*=O), 145.3, 131.2, 129.2, 128.7, 115.9, 105.2, 102.3, 90.9, 88.2, 87.6, 77.8, 31.2, 30.2, 14.0 (*C*=C=O). – IR (di-*n*-butyl ether): ṽ = 2100 s, 1958 s, 1880 s cm^{-1}. – IR (KBr): ṽ = 3427 s, 2965 w, 2935 w, 2905 w,

2869 w, 2394 vw, 2380 vw, 2100 s, 1948 vs, 1873 vs, 1842 vs, 1462 m, 1097 w, 1075 w, 812 m, 771 w, 695 m, 677 m, 628 m cm^{-1}. – MS (EI); *m/z* (%): 425 (19) [M^+], 341 (42) [$M^+ - 3$ CO], 311 (52), 297 (87), 204 (100). – $C_{23}H_{19}NO_4Cr$ (425.4): calcd. C 64.94, H 4.50, N 3.39; found C 65.15, H 4.90, N 3.01.

[3a–7a-η⁶-3-(tert-Butylketenyl)-2-p-tolylindole]tricarbonylchromium(0) (**9**): A solution of 490 mg (1.05 mmol) of **2** in 20 ml of di-*n*-butyl ether was warmed at 85°C for 1.5 h. The solvent was removed at reduced pressure, and chromatography of the residue on silica gel (eluent: petroleum ether/dichloromethane, 1:1.5) as eluent gave 378 mg (82%) of **9** as a yellow solid. R_f = 0.45 (petroleum ether/dichloromethane, 1:1.5). – ^{1}H NMR (250 MHz, C_6D_6): δ = 7.22 (d, 2H, *J* = 7.80 Hz), 6.94 (d, 2H, *J* = 7.80 Hz), 6.61 (br, 1H, NH), 5.91 (d, 1H, *J* = 6.43 Hz), 5.30 (d, 1H, *J* = 6.89 Hz), 4.79 (t, 1H, *J* = 6.20 Hz), 4.50 (d, 1H, *J* = 6.43 Hz), 2.11 (s, 3H), 0.90 (s, 9H). – ^{13}C NMR (62.5 MHz, C_6D_6): δ = 235.3 [Cr(CO)$_3$], 194.2 (C=*C*=O), 145.5, 139.4, 129.5, 128.4, 116.0, 105.5, 101.8, 90.9, 88.3, 87.6, 78.0, 32.1, 30.3, 14.0 (*C*=C=O). – IR (di-*n*-butyl ether): $\tilde{\nu}$ = 2103 s, 1957 s, 1881 s cm^{-1}. – IR (KBr): $\tilde{\nu}$ = 3404 s, 2968 w, 2932 w, 2868 w, 2400 vw, 2380 vw, 2110 s, 1951 vs, 1871 vs, 1841 vs, 1460 w, 1444 w, 822 w, 678 w, 640 w, 534 w cm^{-1}. – MS (EI); *m/z* (%): 439 (41) [M^+], 355 (48) [$M^+ - 3$ CO], 325 (61), 311 (100).

2-tert-Butyl-2-(2-phenyl-3-indolyl)acetic Acid (**10**): A solution of 470 mg (1.04 mmol) of **1** in 20 ml of toluene was warmed at 85°C for 75 min. The solvent was removed at reduced pressure, and chromatography of the residue on silica gel (eluent: petroleum ether/dichloromethane, 1:1 → 1:3) furnished first a mixture of tricarbonyl(toluene)chromium and *tert*-butyl(2-phenyl-3-indolyl)-ketene; the following band afforded 88 mg (20%) of **8** as a yellow solid. The products arising from the first band were dissolved in 20 ml of acetone/H_2O and the solution was stirred for 24 h under ambient conditions. After removal of the solvent and chromatography of the residue on silica gel (eluent: petroleum ether/diethyl ether, 1:1) 87 mg (27%) of **10** was isolated as a white solid. R_f = 0.37 (petroleum ether/dichloromethane, 1:1). – M.p. 186–190°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.09 (br, 1H, COOH), 8.14 (br, 1H, NH), 8.01 (d, 1H, *J* = 8.22 Hz), 7.59–7.55 (m, 2H), 7.49 (t, 2H, *J* = 7.83 Hz), 7.43 (d, 1H, *J* = 7.43 Hz), 7.35 (d, 1H, *J* = 8.22 Hz), 7.17 (t, 2H, *J* = 7.44 Hz), 7.10 (t, 1H, *J* = 7.43 Hz), 3.99 (s, 1H), 0.92 (s, 9H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.8 (C=O), 138.6, 135.2, 133.3, 129.6, 128.9, 128.3, 127.7, 123.2, 121.8, 119.7, 110.4, 107.8, 52.4, 36.0, 28.6. – IR (KBr): $\tilde{\nu}$ = 3452 m, 3427 m, 3060 s, 2959 m, 2908 vw, 2873 w, 1710 vs, 1456 m, 1245 m, 748 s, 706 m cm^{-1}. – MS (EI); *m/z* (%): 307 (23) [M^+], 250 (100), 204 (70). HR-MS; *m/z*: $C_{20}H_{21}NO_2$ [M^+]: calcd. 307.1572; found 307.1572.

2-tert-Butyl-2-(2-p-tolyl-3-indolyl)acetic Acid (**11**): A solution of 630 mg (1.35 mmol) of **2** in 20 ml toluene was warmed at 85°C for 75 min. The solvent was removed at reduced pressure, and chromatography of the residue on silica gel (eluent: petroleum ether/dichloromethane 1:1 → 1:3) yielded first a mixture of tricarbonyl(toluene)chromium and *tert*-butyl(2-*p*-tolyl-3-indolyl)-ketene; the second band afforded 340 mg (57%) of **9** as a yellow solid. The products of the first band were dissolved in 20 ml of acetone/H_2O and the solution was stirred for 24 h under ambient conditions. Removal of the solvent and chromatography of the residue on silica gel (eluent petroleum ether/diethyl ether, 1:1) afforded 65 mg (15%) of **11** as a white solid. R_f = 0.36 (petroleum ether/dichlormethane, 1:1). – M.p. 185–189°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.08 (br, 1H, COOH), 8.10 (br, 1H, NH), 8.00 (d, 1H, *J* = 7.83 Hz), 7.45 (d, 2H, *J* = 7.81 Hz), 7.34 (d, 1H, *J* = 7.82 Hz), 7.29 (d, 1H, *J* = 7.82 Hz), 7.17 (ddd, 1H, *J* = 1.17, 7.04, 8.24 Hz), 7.10 (ddd, 1H, *J* = 1.17, 7.04, 8.25 Hz), 7.10 (t, 1H, *J* = 7.43 Hz), 3.98 (s, 1H), 2.42 (s, 3H), 0.92 (s, 9H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.4 (C=O), 138.6, 138.1, 135.6, 130.2, 129.5, 129.3, 127.6, 123.0, 121.7, 119.6, 110.4, 107.5, 52.2, 36.0, 28.4, 21.3. – IR (KBr): $\tilde{\nu}$ = 3425 m, 3026 vw, 2968 m, 2872 vw, 1707 vs, 1457 m, 1249 m, 907 m, 824 m, 757 m, 730 m cm^{-1}. – MS (EI); *m/z* (%): 321 (13) [M^+], 264 (53), 218 (24), 84 (100). – HR-MS; *m/z*: $C_{21}H_{23}NO_2$ [M^+]: calcd. 321.1729; found 321.1730. – $C_{21}H_{23}NO_2$ (321.4): calcd. C 78.47, H 7.21, N 4.36; found C 78.50, H 6.92, N 4.56.

[tert-Butyl(3a–7a-η⁶-5-methyl-2-p-tolyl-3-indolyl)ketene]tricarbonylchromium(0) (**12**): A solution of 530 mg (1.0 mmol) of **3** in 20 ml of di-*n*-butyl ether was warmed at 85°C for 1 h. The solvent was removed at reduced pressure, and chromatography of the residue on silica gel (eluent: petroleum ether/dichloromethane, 1:2) furnished 389 mg (82%) of **12** as a yellow solid. R_f = 0.35 (petroleum ether/dichloromethane, 1:2). – ^{1}H NMR (250 MHz, C_6D_6): δ = 7.25 (d, 2H, *J* = 8.22 Hz), 6.96 (d, 2H, *J* = 7.82 Hz), 6.58 (br, 1H, NH), 6.17 (s, 1H), 5.46 (d, 1H, *J* = 6.65 Hz), 4.73 (dd, 1H, *J* = 1.17, 6.65 Hz), 2.14 (s, 3H), 1.91 (s, 3H), 0.92 (s, 9H). – ^{13}C NMR (125 MHz, C_6D_6): δ = 235.7 [Cr(CO)$_3$], 194.3 (C=*C*=O), 146.5, 138.9, 130.5, 130.0, 129.0, 111.0, 106.2, 104.0, 102.1, 91.7, 88.3, 78.7, 30.6, 30.0, 20.8, 20.3, 13.8 (*C*=C=O). – IR (di-*n*-butyl ether): $\tilde{\nu}$ = 2101 s, 1953 s, 1873 s cm^{-1}. – IR (KBr): $\tilde{\nu}$ = 2970 w, 2933 w, 2869 vw, 2101 s, 1937 vs, 1851 vs, 1473 m, 1427 w, 1383 w, 821 m, 678 m, 634 m, 625 w, 540 m cm^{-1}. – MS (FAB); *m/z* (%): 453 (55) [M^+], 369 (73) [$M^+ - 3$ CO], 232 (100). – $C_{25}H_{23}NO_4Cr$ (453.5): calcd. C 66.22, H 5.11, N 3.09; found C 65.92, H 5.43, N 3.34.

[tert-Butyl(3a–7a-η⁶-5,N-dimethyl-2-p-tolyl-3-indolyl)ketene]tricarbonylchromium(0) (**13**): A solution of 490 mg (1.05 mmol) of **6** in 20 ml of di-*n*-butyl ether was warmed at 85°C for 30 min. The solvent was removed at reduced pressure, and chromatography of the residue on silica gel (eluent: petroleum ether/dichloromethane, 1:2) furnished 393 mg (85%) of **13** as a yellow solid. R_f = 0.31 (petroleum ether/dichloromethane, 1:2). – ^{1}H NMR (250 MHz, C_6D_6): δ = 7.05 (d, 2H, *J* = 8.22 Hz), 6.96 (d, 2H, *J* = 7.82 Hz), 6.13 (s, 1H), 5.31 (d, 1H, *J* = 6.65 Hz), 4.72 (dd, 1H, *J* = 1.17, 6.65 Hz), 2.81 (s, 3H), 2.08 (s, 3H), 1.89 (s, 3H), 0.92 (s, 9H). – ^{13}C-NMR (125 MHz, C_6D_6): δ = 235.4 [Cr(CO)$_3$], 194.3 (C=*C*=C), 149.4, 138.9, 130.0, 129.0, 115.1, 105.5, 103.3, 102.1, 91.1, 88.5, 77.0, 30.7, 30.6, 30.0, 20.8, 20.3, 13.8 (*C*=C=O). – IR (di-*n*-butyl ether): $\tilde{\nu}$ = 2102 s, 1954 s, 1870 s cm^{-1}. – IR (KBr): $\tilde{\nu}$ = 2970 w, 2933 w, 2869 vw, 2101 s, 1937 vs, 1851 vs, 1473 m, 1427 w, 1383 w, 821 m, 678 m, 634 m, 625 w, 540 m cm^{-1}. – MS (EI); *m/z* (%): 467 (41) [M^+], 411 (5) [$M^+ - 2$ CO], 383 (32) [$M^+ - 3$ CO], 329 (100). – $C_{26}H_{25}NO_4Cr$ (467.5): calcd. C 66.80, H 5.39, N 3.00; found C 66.55, H 5.72, N 3.19.

[(3a–7a-η⁶-1-Benzyl-5-methyl-2-p-tolyl-3-indolyl)-tert-butylketene]tricarbonylchromium(0) (**14**): A solution of 1.10 g (1.92 mmol) of **7** in 20 ml of di-*n*-butyl ether was warmed at 85°C for 15 min. The solvent was removed at reduced pressure, and chromatography of the residue on silica gel (eluent: petroleum ether/dichloromethane, 2:1) delivered 650 mg (63%) of **14** as a yellow solid. R_f = 0.40 (petroleum ether/dichloromethane, 2:1). – ^{1}H NMR (500 MHz, C_6H_6): δ = 7.25 (d, 2H, *J* = 7.55 Hz), 7.18–7.11 (m, 3H), 6.94–6.90 (m, 4H), 6.19 (s, 1H), 5.38 (dd, 1H, *J* = 0.94, 6.80 Hz), 4.76 (d, 2H, *J* = 10.43 Hz), 4.55 (d, 1H, *J* = 6.76 Hz), 2.07 (s, 3H), 1.90 (s, 3H), 1.06 (s, 9H). – ^{13}C NMR (125 MHz, C_6D_6): δ = 235.6 [Cr(CO)$_3$], 194.6 (C=*C*=O), 150.3, 139.4, 136.7, 130.2, 129.3, 129.1, 128.1, 127.9, 127.7, 127.4, 126.1, 115.0, 106.4, 104.3,

102.8, 91.1, 88.2, 79.0, 48.5, 30.5, 30.3, 21.0, 20.4, 14.0 (*C*=C=O). – IR (di-*n*-butyl ether): $\tilde{\nu}$ = 2103 s, 1955 s, 1880 s, 1873 s cm^{-1}. – IR (KBr): $\tilde{\nu}$ = 3092 vw, 3066 vw, 3036 vw, 2964 w, 2932 w, 2906 vw, 2868 vw, 2102 s, 1945 vs, 1856 vs, 1495 w, 1465 m, 1452 m, 1351 w, 1179 m, 825 m, 674 m, 633 m, 534 m cm^{-1}. – MS (FAB); *m/z* (%): 543 (22) [M^+], 459 (100) [M^+ – 3 CO]. – $C_{32}H_{29}NO_4Cr$ (543.5): calcd. C 70.71, H 5.38, N 2.58; found C 70.38, H 5.61, N 2.79.

5-Hydroxy-6-propyl-11H-benzo[a]carbazole (**15**) *and 5,10-Dihydro-10-propylindeno[1,2-b]indole* (**17**): A solution of 810 mg (1.82 mmol) of **4** in 20 ml of toluene was warmed at 105°C for 1 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel (eluent: petroleum ether/dichloromethane, 1:1 → 1:3) gave first 65 mg (14%) of **17** as a red-brown solid; the following band afforded 168 mg (34%) of **15** as a light brown solid.

17: R_f = 0.48 (petroleum ether/dichloromethane, 1:1). – M.p. 84–85°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (br, 1H, NH), 7.64 (d, 1H, *J* = 7.63 Hz), 7.49 (d, 1H, *J* = 7.44 Hz), 7.44–7.40 (m, 2H), 7.30 (t, 1H, *J* = 7.44 Hz), 7.21 (t, 1H, *J* = 7.63 Hz), 7.16 (m, 2H), 3.94 (dd, 1H, *J* = 5.67, 7.04 Hz), 2.13 (m, 1H), 1.77 (m, 1H), 1.48 (sext, 2H, *J* = 7.63), 0.94 (t, 3H, *J* = 7.44 Hz). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.6, 142.5, 140.7, 134.4, 128.5, 126.1 (6 × C_q); 126.6, 124.9, 124.5, 121.6, 120.2, 119.4, 117.2, 112.1 (8 × CH); 43.1 (C-10), 35.2, 20.3, 14.4. – IR (KBr): $\tilde{\nu}$ = 3424 s, 2961 m, 2933 m, 2872 m, 1715 m, 1616 m, 1457 m, 1264 m, 1102 m, 1018 m, 804 m, 745 s, 699 m cm^{-1}. – MS (EI); *m/z* (%): 247 (32) [M^+], 217 (20), 203 (100). – HR-MS, *m/z*: $C_{18}H_{17}N$ [M^+]: calcd. 247.1361; found 247.1363.

15: R_f = 0.31 (petroleum ether/dichloromethane, 1:1). – M.p. 121–123°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.71 (br, 1H, NH), 8.02–7.99 (m, 1H), 8.13 (d, 2H, *J* = 8.26 Hz), 7.62–7.54 (m, 3H), 7.42 (t, 1H, *J* = 7.57 Hz), 7.27 (t, 1H, *J* = 8.15 Hz), 4.91 (s, 1H, OH), 3.33 (t, 2H, *J* = 7.34 Hz), 1.97 (sext, 2H, *J* = 7.34 Hz), 1.18 (t, 3H, *J* = 7.35 Hz). – IR (KBr): $\tilde{\nu}$ = 3447 vs, 3421 vs, 3074 vw, 3051 vw, 2955 w, 2928 w, 2868 w, 2360 w, 2342 w, 1472 m, 1453 m, 1249 m, 1220 s, 1147 m, 969 m, 752 m, 741 s, 737 s cm^{-1}. – MS (EI); *m/z* (%): 275 (100) [M^+], 246 (67), 217 (23). – HR-MS; *m/z*: $C_{19}H_{17}NO$ [M^+]: calcd. 275.1310; found 275.1308.

5-Hydroxy-3-methyl-6-propyl-11H-benzo[a]carbazole (**16**) *and 5,10-Dihydro-8-methyl-10-propylindeno[1,2-b]indole* (**18**): A solution of 800 mg (1.76 mmol) of **5** in 20 ml of toluene was warmed at 105°C for 1 h. The solvent was removed at reduced pressure, and chromatography of the residue on silica gel (eluent: petroleum ether/dichloromethane, 1:1 → 1:3) as eluent yielded first 46 mg (10%) of **18** as a red brown solid; the following band afforded 196 mg (39%) of **16** as a light brown solid.

18: R_f = 0.45 (petroleum ether/dichloromethane, 1:1). – M.p. 87–89°C. – ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 8.28 (br, 1H, NH), 7.67 (d, 1H, *J* = 7.62 Hz), 7.41 (d, 1H, *J* = 7.73 Hz), 7.36–7.28 (m, 2H), 7.18–7.13 (m, 2H), 7.11 (d, 1H, *J* = 7.88 Hz), 3.90 (dd, 1H, *J* = 5.05, 7.29 Hz), 2.43 (s, 3H), 2.12 (m, 1H), 1.76 (m, 1H), 1.50 (sext, 2H, *J* = 7.34 Hz), 0.95 (t, 3H, *J* = 7.44 Hz). – ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 152.9, 142.6, 140.5, 134.7, 131.7, 125.3, 124.9 (7 × C_q); 127.1, 125.5, 121.2, 120.1, 119.1, 116.9, 111.9 (7 × CH); 42.9 (C-10), 35.4, 21.6, 20.4, 14.4. – IR (KBr): $\tilde{\nu}$ = 3415 s, 2957 m, 2930 m, 2874 m, 2852 m, 2360 w, 2342 w, 1944 w, 1608 m, 1458 m, 1098 m, 814 m, 741 m cm^{-1}. – MS (EI); *m/z* (%): 261 (39) [M^+], 218 (100). – HR-MS; *m/z*: $C_{19}H_{19}N$ [M^+]: calcd. 261.1517; found 261.1520. – $C_{19}H_{19}N$ (261.4): calcd. C 87.31, H 7.33, N 5.36; found C 87.50, H 6.98, N 5.35.

16: R_f = 0.26 (petroleum ether/dichloromethane, 1:1). – M.p. 117–119°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.63 (br, 1H, NH), 8.10 (d, 1H, *J* = 7.80 Hz), 8.07 (s, 1H), 8.02–7.96 (m, 1H), 7.55 (t, 1H, *J* = 7.34 Hz), 7.39 (t, 2H, *J* = 7.34 Hz), 7.31–7.28 (m, 1H), 4.83 (s, 1H, OH), 3.32 (t, 2H, *J* = 7.34 Hz), 2.59 (s, 3H), 1.90 (sext, 2H, *J* = 7.34 Hz), 1.18 (t, 3H, *J* = 7.35 Hz). – IR (KBr): $\tilde{\nu}$ = 3443 s, 3422 s, 2967 w, 2960 w, 2875 vw, 2367 w, 2345 w, 1636 m, 1469 m, 1456 m, 1262 m, 1175 m, 1107 m, 766 m, 748 m, 742 m cm^{-1}. – MS (EI); *m/z* (%): 289 (100) [M^+], 260 (68), 244 (18), 218 (25). – HR-MS; *m/z*: $C_{20}H_{19}NO$ [M^+]: calcd. 289.1467; found 289.1460.

[1] T. Leese, K. H. Dötz, submitted for publication.
[2] K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreißl, U. Schubert, K. Weiss, *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, **1983**.
[3] [3a] K. H. Dötz, *Angew. Chem.* **1984**, *96*, 573; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 587. – [3b] K. H. Dötz in *Organometallics in Organic Synthesis: Aspects of a Modern Interdisciplinary Field* (Eds.: H. tom Dieck, A. de Meijere), Springer-Verlag, Berlin, **1988**. – [3c] H. U. Reißig in *Organometallics in Organic Synthesis 2* (Eds.: H. Werner, G. Erker), Springer-Verlag, Berlin, **1989**. – [3d] R. Aumann, *Angew. Chem.* **1988**, *100*, 1512; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1456. – [3e] W. D. Wulff in *Comprehensive Organometallic Chemistry II*, (Eds.: A. W. Abel, F. G. A. Stone, G. Wilkinson) Pergamon Press, Oxford, **1995**, vol. 12, p. 469ff. – [3f] L. S. Hegedus in *Comprehensive Organometallic Chemistry II*, (Eds.: A. W. Abel, F. G. A. Stone, G. Wilkinson) Pergamon Press, Oxford, **1995**, vol. 12, p. 549ff. – [3g] H. G. Schmalz, *Angew. Chem.* **1994**, *106*, 311; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 303.
[4] K. H. Dötz, *Angew. Chem.* **1975**, *87*, 672; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 644.
[5] [5a] K. H. Dötz, I. Pruskil, J. Mühlemeier, *Chem. Ber.* **1982**, *115*, 1278. – [5b] M. F. Semmelhack, J. J. Bozell, T. Keller, T. Sato, E. Spiess, W. D. Wulff, A. Zask, *Tetrahedron* **1985**, *41*, 5803. – [5c] W. D. Wulff, Y.-C. Xu, *J. Am. Chem. Soc.* **1988**, *110*, 2312. – [5d] K. H. Dötz, M. Popall, *Angew. Chem.* **1987**, *99*, 1220; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1158. – [5e] A. Yamashita, A. Toy, T. A. Scahill, *J. Org. Chem.* **1988**, *54*, 3425. – [5f] K. A. Parker, C. A. Coburn, *J. Org. Chem.* **1991**, *56*, 1666. – [5g] D. L. Boger, I. C. Jacobson, *J. Org. Chem.* **1991**, *56*, 2115. – [5h] J. King, P. Quayle, J. F. Malone, *Tetrahedron Lett.* **1990**, *31*, 5221.
[6] [6a] A. Yamashita, *Tetrahedron Lett.* **1986**, *28*, 5915. – [6b] K. H. Dötz, H.-G. Erben, K. J. Harms, *Chem. Soc., Chem. Commun.* **1989**, 692. – [6c] D. B. Grotjahn, K. H. Dötz, *Synlett* **1991**, 381. – [6d] E. Chelain, M. Parlier, M. Audouin, H. Rudler, J.-C. Daran, J. Vaissermann, *J. Am. Chem. Soc.* **1993**, *115*, 10568. – [6e] A. Parlier, M. Rudler, H. Rudler, R. Goumont, J.-C. Daran, J. Vaissermann, *Organometallics* **1995**, *14*, 2760.
[7] [7a] K. H. Dötz, D. B. Grotjahn, K. Harms, *Angew. Chem.* **1989**, *101*, 1425; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1384. – [7b] D. B. Grotjahn, F. E. K. Kroll, T. Schäfer, K. Harms, K. H. Dötz, *Organometallics* **1992**, *11*, 298. – [7c] I. Merino, L. S. Hegedus, *Organometallics* **1995**, *14*, 2522.
[8] W. D. Wulff, A. M. Gilbert, R. P. Hsung, A. Rahm, *J. Org. Chem.* **1995**, *60*, 4566.
[9] A. Rahm, W. D. Wulff, *Tetrahedron Lett.* **1995**, *36*, 8753.
[10] E. O. Fischer, A. Maasböl, *Chem. Ber.* **1967**, *100*, 2245.
[11] [11a] E. O. Fischer, T. Selmayr, F. R. Kreißl, *Chem. Ber.* **1977**, *110*, 2947. – [11b] L. S. Hegedus, L. M. Schultze, J. Montgomery, *Organometallics* **1989**, *8*, 2189.
[12] T. Leese, Ph. D. Thesis, University of Bonn, **1995**.
[13] [13a] J. S. Waugh, R. W. Fessenden, *J. Am. Chem. Soc.* **1957**, *79*, 846. – [13b] C. E. Johnson, F. A. Bovery, *J. Chem. Phys.* **1958**, *29*, 1012. – [13c] P. Laszlo, *Progr. N.M.R. Spectroscopy* **1967**, *3*, 231.
[14] [14a] C. G. Kreiter, Habilitationsschrift, Technical University of Munich, **1971**. – [14b] H.-G. Erben, Ph. D. Thesis, Technical University of Munich, **1988**.
[15] [15a] K. H. Dötz, *Angew. Chem.* **1979**, *91*, 1021. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 954. – [15b] K. H. Dötz, B. Fügen-Köster, *Chem. Ber.* **1980**, *113*, 1449. – [15c] L. Hill, C. R. Richards, S. E. Thomas, *Pure Appl. Chem.* **1990**, *62*, 2057.
[16] J. Firl, W. Runge, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *29B*, 393.
[17] K. H. Dötz, D. Böttcher, M. Jendro, *Inorg. Chim. Acta* **1994**, *222*, 291.

[18] [18a] H.-J. Knölker, *Advances in Nitrogen Heterocycles*, vol. 1, JAI Press, Greenwich, **1995**. – [18b] H.-J. Knölker, M. Bauermeister, J.-B. Pannek, M. Wolpert, *Synthesis* **1995**, 397. – [18c] C. J. Moody, *Synlett* **1994**, 681. – [18d] E. M. Beccalli, A. Marchesini, T. Pilati, *J. Chem. Soc., Perkin Trans. 1* **1994**, 579. – [18e] H.-J. Knölker, *Synlett* **1992**, 371. – [18f] J. Bergman, B. Pelcam, *Pure Appl. Chem.* **1990**, *62*, 1967.

[19] [19a] R. F. C. Braun, K. J. Coulsten, F. W. Eastwood, M. R. Moffat, *Tetrahedron* **1992**, *48*, 7763. – [19b] J. J. Eisch, T. Abraham, *Tetrahedron Lett.* **1976**, 1647.

[20] [20a] K. H. Dötz, T. Schäfer, F. Kroll, K. Harms, *Angew. Chem.* **1992**, *104*, 1257; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1236. – [20a] K. H. Dötz, F. Hohmann, S. Siemoneit, M. Nieger, S. Kotila, manuscript in preparation.

[21] [21a] K. H. Dötz, T. Schäfer, K. Harms, *Angew. Chem.* **1990**, *102*, 188; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 176. – [21b] K. H. Dötz, T. O. Schäfer, K. Harms, *Synthesis* **1992**, 146.

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