2556 Organometallics 1993, 12, 2556–2564

A New, Simple Access to Pentacarbonyl(3-aminoallenylidene)chromium Complexes§

Frank Stein,† Michael Duetsch,† Ehmke Pohl,‡ Regine Herbst-Irmer,‡ and
Armin de Meijere*,†

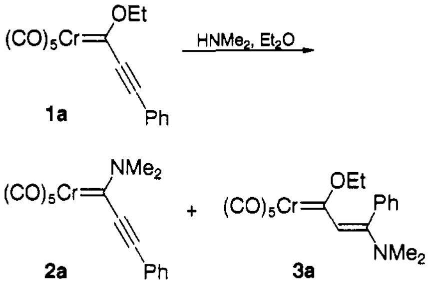
*Institut für Organische Chemie der Georg-August-Universität Göttingen, Tammannstrasse 2,
D-37077 Göttingen, Germany, and Institut für Anorganische Chemie der
Georg-August-Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany*

Received April 28, 1992

Primary and secondary amines react with pentacarbonyl(1-ethoxy-1-alkynylcarbene)chromium complexes **1a–g** to give pentacarbonyl(3-aminoallenylidene)chromium complexes **11–18** and pentacarbonyl[ethoxy(2-aminoethenyl)carbene]chromium complexes **3–10**. Crystal structures of two relevant examples are reported. The product ratio is influenced by the size of the substituent on the acetylene terminus and in the amine, the basicity of the amine, and the reaction temperature. Reaction of **1a–c,f** with lithium amides gave even higher yields of the corresponding allenylidene complexes. Addition of dimethylamine to allenylidene complexes **15f** and **13a** gave quantitative yields of bis(dialkylamino)ethenylcarbene complexes (*E*/*Z*)-**23** and (*E*)-**24**.

α,β-Unsaturated (carbene)chromium complexes have become important reagents in synthetic organic chemistry. The so-called Dötz reaction has made phenyl- and ethenyl-substituted representatives valuable precursors to highly substituted and ring-anellated hydroquinones and cyclohexadienones.[1,2] [[β-(Dialkylamino)ethenyl]carbene]-chromium complexes, which are readily prepared by a Michael type addition of secondary amines to alkynylcarbene complexes **1**,[3–5] react in different ways to give highly substituted cyclopentadienes,[6] cyclopenta[*b*]pyrans,[7] or fulvenes.[8] In a systematic study of the reactions of various primary and secondary amines with complexes of type **1**, we observed that the substitution at C1, reportedly competing with the addition at C3 and favored at low temperature,[4] is the exception rather than the rule.[5] Only complexes **1a** with a phenyl group and **1d** with a trimethylsilyl group[9] gave substitution products along with the addition products **3a** and **3d**. In all other cases, the formation of (3-aminoallenylidene)chromium complexes as byproducts was observed.[5] Since this constitutes a new and simple route to cumulene complexes of types **11–18**,[10,11] which may have interesting applications in organic synthesis, we have looked more closely at these reactions and optimized yields of the cumulene complexes (Scheme II).

Scheme I



We have identified four factors which determine product ratios in the reactions of complexes **1a–g** with primary and secondary amines (Tables I and II). The formation of 3-aminoallenylidene complexes is enhanced by bulky substituents both on the acetylene terminus and in the amine, by increased basicity of the amine, and by higher reaction temperature. When the reactions of **1f** with dimethylamine and dibenzylamine were carried out at 65 °C, the reaction mixture had to be cooled to room

---

* To whom correspondence should be addressed.

† Institut für Organische Chemie der Universität Göttingen.

‡ Institut für Anorganische Chemie der Universität Göttingen.

§ This paper is dedicated to Professor Anton Meller on the occasion of his 60th birthday.

(1) *Cf.*: Dötz, K. H. *Angew. Chem.* **1984**, *96*, 573–594; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. Dötz, K. H. In *Organometallics in Organic Synthesis*; de Meijere, A., tom Dieck, H., Eds., Springer: Heidelberg, 1988. Dötz, K. H. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; NATO ASI Series Vol. 269; Kluwer: Dordrecht, The Netherlands, p 199 ff (see also references cited therein).

(2) *Cf.*: Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, U.K., 1991; Vol. 5, pp 1065–1113 (see also references cited therein).

(3) Fischer, E. O.; Kreissl, F. R. *J. Organomet. Chem.* **1972**, *35*, C47–C51.

(4) Fischer, E. O.; Kalder, H. J. *J. Organomet. Chem.* **1977**, *131*, 57–64.

(5) Duetsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1992**, *125*, 2051–2065.

(6) Duetsch, M.; Stein, F.; Lackmann, R.; de Meijere, A. *Synlett* **1991**, 324–326.

(7) Stein, F.; Duetsch, M.; Lackmann, R.; Noltemeyer, M.; de Meijere, A. *Angew. Chem.* **1991**, *103*, 1669–1671; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1658.

(8) Stein, F.; Duetsch, M.; Lackmann, R.; de Meijere, A. Unpublished results.

(9) (a) This structure assignment rests on the result of a control experiment, in which ethanol was added to the product to give pentacarbonyl[1-(dimethylamino)-3-ethoxypropenylidene]chromium, as was shown by comparison of its spectroscopic data with those reported for pentacarbonyl[3-(dimethylamino)-1-ethoxypropenylidene]chromium: Aumann, R.; Hinterding, P. *Chem. Ber.* **1990**, *123*, 611–620. Addition of ethanol to **11d** would have given pentacarbonyl[3-(dimethylamino)-1-ethoxypropenylidene]chromium. (b) Rahm, A.; Wulff, W. D.; Rheingold, A. L. *Organometallics* **1993**, *12*, 597–599.

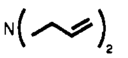
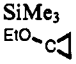
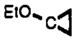
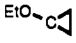
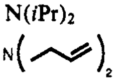
(10) Some allenylidenechromium and -tungsten complexes have been prepared, albeit in moderate yields, by acid-catalyzed elimination of ethanol from [(2-aminoethenyl)ethoxy]carbene complexes: Fischer, E. O.; Kalder, H. J.; Frank, A.; Köhler, F. H.; Huttner, G. *Angew. Chem.* **1976**, *88*, 683–684; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 623.

(11) (a) Berke, H. *Angew. Chem.* **1976**, *88*, 684–685; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 624. (b) Berke, H. *Chem. Ber.* **1980**, *113*, 1370–1376. (c) Berke, H.; Härter, P.; Huttner, G.; von Seyerl, J. *J. Organomet. Chem.* **1981**, *219*, 317–327. (d) Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Z. Naturforsch. B* **1981**, 929–938. (e) Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Chem. Ber.* **1982**, *115*, 695–705. (f) Berke, H.; Grössmann, U.; Huttner, G.; Zsolnai, L. *Chem. Ber.* **1984**, *117*, 3423–3431, 3432–3442.

(12) The analogous 1-methoxy derivative has been reported: Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550–4552.

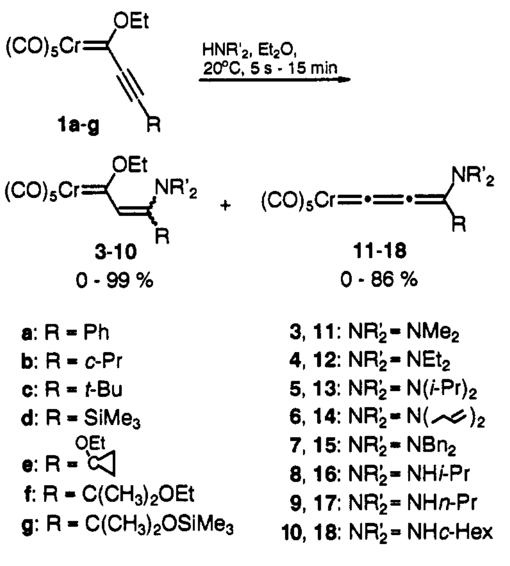
(13) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7565–7567.

Table I. Reactions of (Alkynylcarbene)chromium Complexes 1a–g with Primary and Secondary Amines in Diethyl Ether at 20 °C

entry	starting material	R	NR′$_2$	product	yield (%)	product	yield (%)
1	**1a**^{3}	Ph	NMe$_2$	(E)-**3a**^{4}	94	**11a**	0
2	**1a**^{3}	Ph		(E)-**6a**^{5}	98	**14a**	0
3	**1a**^{3}	Ph	NBn$_2$	(E)-**7a**^{5}	99	**15a**	0
4	**1a**^{3}	Ph	N(iPr)$_2$	(E)-**5a**^{5}	44	**13a**^{5}	53
5	**1b**^{5}	cPr	NMe$_2$	(E)-**3b**^{5}	96	**11b**	0
6	**1b**^{5}	cPr	NHcHex	(Z)-**10b**	86	**18b**	0
7	**1c**^{12}	tBu	NMe$_2$	(Z)-**3c**^{5}	84	**11c**^{5}	8
8	**1c**^{12}	tBu	NBn$_2$	(Z)-**7c**	15	**15c**	71
9	**1d**^{13}	SiMe$_3$	NMe$_2$	(Z)-**3d**^{5}	27	**11d**	0^{a,b}
10	**1d**^{13}	SiMe$_3$	NHcHex	(Z)-**10d**	0	**18d**	0^{c}
11	**1e**^{5}		NMe$_2$	(Z)-**3e**^{5}	85	**11e**^{5}	13
12	**1e**^{5}		NBn$_2$	(Z)-**7e**	53	**15e**	45
13	**1e**^{5}		NHcHex	(Z)-**10e**	80	**18e**	11
14	**1f**^{5}	C(CH$_3$)$_2$OEt	NMe$_2$	(Z)-**3f**^{5}	80	**11f**^{5}	13
15	**1f**^{5}	C(CH$_3$)$_2$OEt	NEt$_2$	(Z)-**4f**^{5}	22	**12f**^{5}	75
16	**1f**^{5}	C(CH$_3$)$_2$OEt	N(iPr)$_2$	(Z)-**5f**	0	**13f**^{5}	68
17	**1f**^{5}	C(CH$_3$)$_2$OEt		(Z)-**6f**^{5}	30	**14f**^{5}	64
18	**1f**^{5}	C(CH$_3$)$_2$OEt	NBn$_2$	(Z)-**7f**^{5}	23	**15f**^{5}	74
19	**1f**^{5}	C(CH$_3$)$_2$OEt	NHnPr	(Z)-**9f**	58	**17f**	41
20	**1f**^{5}	C(CH$_3$)$_2$OEt	NHcHex	(Z)-**10f**	30	**18f**	67
21	**1f**^{5}	C(CH$_3$)$_2$OEt	NHiPr	(Z)-**8f**	11	**16f**	86
22	**1g**	C(CH$_3$)$_2$OSiMe$_3$	NMe$_2$	(Z)-**3g**	87	**11g**	12

[a] This reaction gives pentacarbonyl[1-(dimethylamino)-3-(trimethylsilyl)propynylidene]chromium (30%).[9] [b] Only a small fraction (7%) of the desilylated addition product pentacarbonyl[3-(dimethylamino)-1-ethoxypropenylidene]chromium was isolated from a large amount of unsoluable material. [c] The sole product (79%) was presumably pentacarbonyl[1-(cyclohexylamino)-3-(trimethylsilyl)propynylidene]chromium, based on the comparison of its spectroscopic data with those of the aminolysis product pentacarbonyl[1-(dimethylamino)-3-(trimethylsilyl)propynylidene]chromium obtained in the reaction of **1d** with HNMe$_2$ (entry 9).

Scheme II



temperature a few minutes after addition of the amine to prevent chelation[5,14,15] of the ethenylcarbene complexes **3f** and **7f**, respectively. With the right combination of substituents in the substrate and the amine, yields of the cumulene complexes can be as high as 86% (entry 21 in Table I).

1-Aminocarbene complexes of type **2a** and allenylidene complexes (**11**–**18**) can easily be distinguished by the ^{13}C chemical shifts of their carbene carbons and their IR spectra. The ^{13}C NMR signal of C1 in 1-aminocarbene complexes generally is observed at $\delta_{\mathrm{TMS}} \geq 260$, whereas that of allenylidene complexes is significantly shifted upfield (by about 20–30 ppm) to 230–240 ppm. In the IR spectra, 1-aminocarbene complexes of type **2a** show a characteristic band at ν 2160 cm^{-1} corresponding to the C≡C stretching vibration, whereas allenylidene complexes **11**–**18** show only a weak band or none at all in this region.

Table II. Temperature Dependence of the Formation of 11f and 15f

temp (°C)	solvent	**11f**/**3f** ratio	**15f**/**7f** ratio
−115	Et$_2$O	–/1	0.4/1
−78	Et$_2$O	0.1/1	1.5/1
+20	Et$_2$O	0.2/1	3.0/1
+65	THF	0.4/1	5.1/1

The allenylidene complexes **15f** and **16f** have been confirmed by single crystal X-ray structure analysis (Figures 1 and 2). In the crystal of **16f** the molecule lies on a mirror plane. Only C5 deviates from this symmetry and is refined in two positions with occupancies of 0.5 each. The bond lengths C1–C2 and C3–N1 of both structures are very short for a C═C double and a C—N single bond, respectively. This indicates an overwhelming contribution of the zwitterionic form of **16f** to the resonance hybrid.


16f **16f**

As far as the mechanism is concerned, it has been confirmed that neither ethenylcarbene complexes **3**–**10** react with amines to give **11**–**18** nor allenylidene complexes **11**–**18** react with ethanol to give **3**–**10** under the employed conditions. No such conversion was observed even under

---

(14) Dötz, K. H.; Sturm, W.; Popall, M.; Riede, J. *J. Organomet. Chem.* **1984**, *277*, 267–275.

(15) Dötz, K. H.; Popall, M.; Müller, G.; Ackermann, K. *Angew. Chem.* **1986**, *98*, 909–910; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 911.

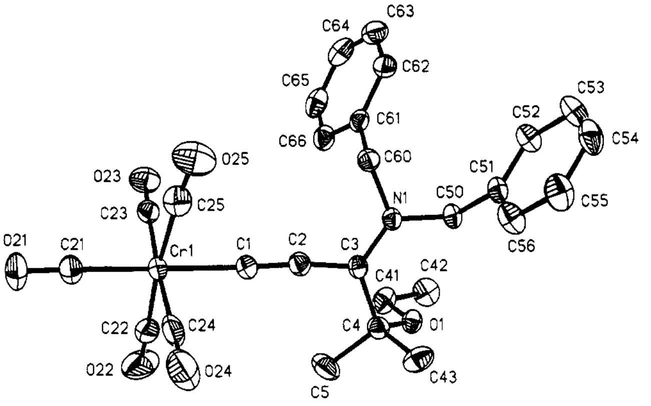


Figure 1. Structure of **15f**, shown with 50% thermal ellipsoids. Selected bond distances (pm) and angles (deg) are as follows: Cr1–C1 199.3(2), C1–C2 122.2(2), C2–C3 138.8(2), C3–C4 154.6(2), C3–N1 132.3(2), Cr1–C1–C2 177.2(1), C1–C2–C3 173.5(2), C2–C3–N1 119.9(1), C2–C3–C4 116.5(1), C4–C3–N1 123.5(1).

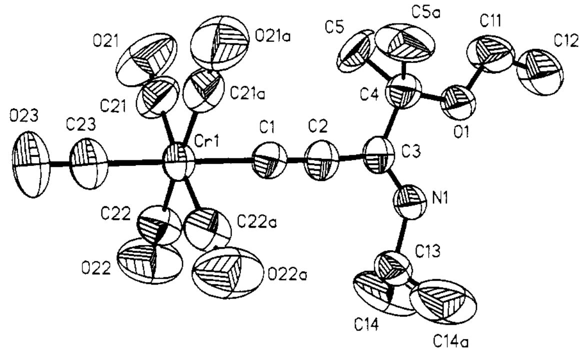
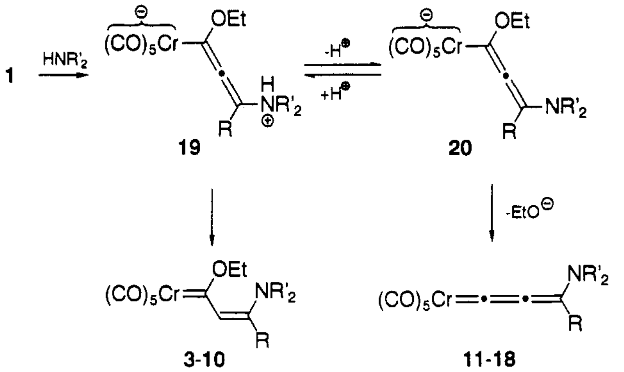


Figure 2. Structure of **16f**, shown with 50% thermal ellipsoids: Selected bond distances (pm) and angles (deg) are as follows: Cr1–C1 200.8(4), C1–C2 120.4(5), C2–C3 139.9(5), C3–C4 151.7(5), C3–N1 128.1(4), Cr1–C1–C2 179.0(3), C1–C2–C3 175.0(4), C2–C3–N1 122.9(3), C2–C3–C4 119.5(3), C4–C3–N1 117.6(3).

more drastic conditions. Treatment of **4f** with various bases such as $LiNEt_2$, LiTMP, and *t*BuLi and subsequent quenching with D_2O yielded quantitative nondeuterated **4f**. Only starting material was isolated after treatment of **12f** with lithium ethoxide. The first step in the formation of both types of products **3–10** and **11–18**, respectively, must be the Michael addition of the amine to the triple bond in **1a–g** to give an intermediate of type **19**. By deprotonation and protonation, **19** can equilibrate with **20**. More basic amines[16] (entry 14 → 16 and 19 → 21 in Table I) deprotonate intermediate **19** more easily to give **20** followed by elimination of ethoxide. In fact, treatment of **1a–c,f** with the lithium amide $LiNR'_2$, which excludes the intermediate formation of **19**, increased the ratio of allenylidene versus ethenylcarbene complexes in every case (Table III).

A small change in the nature of the amine may cause a striking difference in the ratio of addition versus addition/elimination, as demonstrated by the behavior of **2a** and **21** toward dimethylamine and diethylamine, respectively. When reacted with diethylamine, **2a**[4] gives 40% phenyl-3-(diethylamino)allenylidene complex **21** and 28% 1-(dimethylamino)-3-(diethylamino)propenylidene complex **22**, whereas dimethylamine yields only the bis(dimethylamino) analogue of **22**[4] in 44% yield (Scheme IV). Reaction of **21** with dimethylamine yielded quantitatively (*E*)-**22** (Scheme V), but with diethylamine no formation of the 1,3-bis(diethylamino)propenylidene complex was observed. Such differences in reactivity are also known for substitution reactions with dimethylamine and diethylamine with 1-alkoxycarbene complexes.[17] Thus allenylidene complexes **11–18** open a new route to [(dimethylamino)[2-(dialkylamino)ethenyl]carbene]pentacarbonylchromium complexes, as demonstrated by the reactions of **15f** and **13a** with dimethylamine (Scheme V). Both gave quantitative yields of (dialkylamino)[(dialkylamino)ethenyl]carbene complexes (*E*/*Z*)-**23** and (*E*)-**24**. These in turn can be used in cycloaddition reactions with alkynes, as reported by Dötz for (1-aminoethenyl)carbene complexes,[18] and by us for 1-alkoxy[2-(dialkylamino)ethenyl]carbene complexes.[6,7]

Scheme III. Proposed Mechanism for the Formation of 3–18



Experimental Section

All operations were performed under nitrogen. Solvents were dried by distillation from sodium or potassium/benzophenone. ^1H NMR: Bruker AM 250 (250 MHz), WM 270 (270 MHz), Varian XL 200 (200 MHz), VXR 200 (200 MHz), VXR 500 (500 MHz). ^{13}C NMR: Bruker AM 250 (62.89 MHz), WM 270 (67.93 MHz), Varian XL 200 (50.31 MHz), VXR 500 (125.70 MHz). Multiplicities were determined by DEPT (Distortionless Enhancement by Polarization Transfer). Chemical shifts refer to $\delta_{TMS} = 0.00$ according to the chemical shifts of residual solvent signals. IR: Perkin-Elmer 125, 297, 298, 399. MS: Varian MAT CH 7, MAT 731. HRMS: Varian MAT 311 A. Melting points: Büchi 510, uncorrected. Elemental analysis: Mikroanalytisches Laboratorium der Georg-August-Universität Göttingen.

Molecular composition and bulk purity were determined by microanalyses for representative examples of new compounds, for all others molecular masses were confirmed by high resolution mass spectrometry with preselected ion peak matching at $R \approx 10\,000$ to be within ±2 ppm of the exact masses.

X-ray crystal structure determination of **15f** and **16f**: Crystal data of the two structures are presented in Table IV. The data were collected on Stoe-Siemens AED (**15f**) and Stoe-Siemens-Huber AED2 (**16f**), respectively with graphite monochromated Mo Kα (λ = 71.073 pm) radiation. The structures were solved by Patterson and Fourier methods.[19] They were refined with all data on F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$, $P = (F_o^2 + 2F_c^2)/3$ using SHELXL-92.[20] All non hydrogen atoms were refined anisotropically. The hydrogen atoms of **15f** were refined using a riding model. For **16f** a riding model starting from calculated positions for the hydrogen atoms was employed. The hydrogen atom at the nitrogen was refined with a distance

---

(16) Gordon, A. J.; Ford, R. A. *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*; Wiley: New York, 1972, p 58.

(17) Connor, J. A.; Fischer, E. O. *J. Chem. Soc. A* **1969**, 578–584.

(18) Grotjahn, D. B.; Dötz, K. H. *Synlett* **1991**, 381–390.

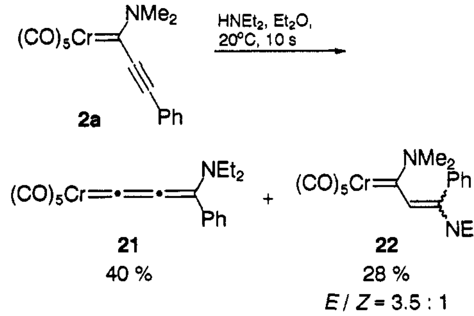
(19) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

Table III. Reactions of (Alkynylcarbene)chromium Complexes 1a–c,f with Primary and Secondary Lithium Amides in Diethyl Ether at 20 °C

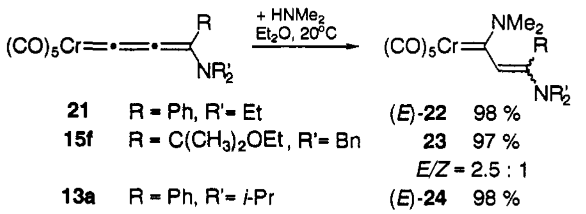
entry	starting material	R	$LiNR'_2$	product	yield (%)	product	yield (%)
1	**1a**[3]	Ph	$LiNMe_2$	(*E*)-**3a**[4]	29	**11a**[10]	43
2	**1a**[3]	Ph	$LiNBn_2$	(*E*)-**7a**[5]	0	**15a**	15
3	**1b**[5]	*c*Pr	$LiNMe_2$	(*E*)-**3b**[5]	20	**11b**	40
4	**1b**[5]	*c*Pr	LiNH*c*Hex	(*Z*)-**10b**	36	**18b**	47
5	**1c**[12]	*t*Bu	$LiNMe_2$	(*Z*)-**3c**[5]	0	**11c**[5]	31[a]
6	**1f**[5]	$C(CH_3)_2OEt$	$LiNMe_2$	(*Z*)-**3f**[5]	0	**11f**[5]	96
7	**1f**[5]	$C(CH_3)_2OEt$	$LiNEt_2$	(*Z*)-**4f**[5]	0	**12f**[5]	95
8	**1f**[5]	$C(CH_3)_2OEt$	LiNH*c*Hex	(*Z*)-**10f**	13	**18f**	84

[a] Pentacarbonyl[1-(dimethylamino)-4,4-dimethylpentenylidene]chromium (**2c**) was obtained as the main product in 44% yield.

Scheme IV



Scheme V



restraint. The atomic coordinates of **15f** and **16f** can be found in Tables V and VI, respectively. Further details of the structure determination (complete bond lengths and angles, structure factors, and displacement parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Germany. Any request for this material should quote the full literature citation and the reference number (CSD 56353).

Pentacarbonyl[1-ethoxy-4-methyl-4-[(trimethylsilyl)oxy]-pentynylidene]chromium (1g). **1g** was prepared according to the previously published method[5] from 2.40 g (15.4 mmol) of 3-methyl-3-[(trimethylsilyl)oxy]butyne and 3.40 g (15.4 mmol) of hexacarbonylchromium. Yield: 4.70 g (75%) of **1g**, R_f = 0.27 (pentane), reddish black oil. IR (film, cm^{-1}) 2980, 2954, 2926, 2910, 2890, 2160 (C≡C), 2048 (C=O), 1996 (C=O), 1945 (C=O), 1463, 1440, 1374, 1361, 1246, 1203, 1162, 1108, 1071, 1038, 999, 911, 840, 753, 681, 650. ^1H NMR (250 MHz, $CDCl_3$; δ, ppm): 0.11 (9H, s, $Si(CH_3)_3$), 0.93 (3H, t, ^3J = 7.0 Hz, OCH_2CH_3), 1.52 (6H, s, $C(CH_3)_2$), 4.05 (2H, q, ^3J = 7.0 Hz, OCH_2CH_3). $^{13}C\{H\}$ NMR (62.89 MHz, $CDCl_3$, add. DEPT; δ, ppm): 1.84 (+, $Si(CH_3)_3$), 14.58 (+, OCH_2CH_3), 32.18 (+, $C(CH_3)_2$), 68.16 (C_{quat}, $C(CH_3)_2$), 76.36 (–, OCH_2CH_3), 86.52 (C_{quat}, C2), 143.43 (C_{quat}, C3), 216.63, 225.51 (C_{quat}, C=O), 317.16 (C_{quat}, C1). MS (EI, 70 eV; *m/e* (relative intensity)): 404 (16) [M^+], 348 (8) [$M^+ - 2CO$], 320 (2) [$M^+ - 3CO$], 292 (23) [$M^+ - 4CO$], 264 (24) [$M^+ - 5CO$], 249 (7), 206 (14), 126 (100), 73 (4), 52 (10) [Cr^+].

General Procedure for the Preparation of (3-Aminoallenylidene)- and [(Aminoethenyl)carbene]chromium Complexes. The amine was added to a solution of 5 mmol of **1** in 50 mL of diethyl ether. The reaction mixture was stirred at 20 °C until no more starting material could be detected by TLC. The solvent was removed under reduced pressure, and the residue was purified by chromatography over 100 g of silica gel to afford the pure compound.

Table IV. Crystal Data for 15f and 16f

	15f	**16f**
chem formula	$C_{27}H_{25}CrNO_6$	$C_{16}H_{19}CrNO_6$
fw	511.48	373.32
data collcn *T*(°C)	−120	20
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/m$
a (pm)	1404.2(1)	1008.7(5)
b (pm)	1360.5(1)	1036.9(5)
c (pm)	1402.3(1)	1011.1(5)
β (deg)	108.35(1)	109.39(2)
cell vol (nm^3)	2.5428(3)	0.9975(8)
formula units per cell	4	2
density calcd (Mg/m^3)	1.336	1.243
μ (mm^{-1})	0.491	0.600
cryst size (mm)	0.4 × 0.5 × 0.7	0.4 × 0.3 × 0.3
cryst color	red	red
2θ-range for data collection (deg)	4–55	8–50
index ranges	$-18 \le h \le 11$, $-17 \le k \le 17$, $-18 \le l \le 18$	$-12 \le h \le 12$, $-12 \le k \le 12$, $-12 \le l \le 12$
no. of reflns collcd	10 912	4073
no. of ind reflns	5882	1859
R_{int}	0.0214	0.0375
abs corr	335 azimuthal ψ-scans	468 azimuthal ψ-scans
max and min transm	0.933 and 0.900	0.986 and 0.889
data/restraints/params	5880/51/342	1858/4/136
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0333$, $wR_2 = 0.0836$	$R_1 = 0.0417$, $wR_2 = 0.1161$
R indices (all data)	$R_1 = 0.0423$, $wR_2 = 0.0899$	$R_1 = 0.0517$, $wR_2 = 0.1267$
largest diff peak [e ($nm^{-3} \times 10^3$)]	0.281	0.202
largest diff hole [e ($nm^{-3} \times 10^3$)]	−0.517	−0.210

Pentacarbonyl[(2*Z*)-3-(dimethylamino)-1-ethoxy-4-methyl-4-[(trimethylsilyl)oxy]pentenylidene]chromium ((*Z*)-3g) and Pentacarbonyl[3-(dimethylamino)-4-[(trimethylsilyl)-oxy]-4-methyl-1,2-pentadienylidene]chromium (11g). To 500 mg (1.24 mmol) of pentacarbonyl[1-ethoxy-4-methyl-4-[(trimethylsilyl)oxy]pentynylidene]chromium (**1g**) was added dimethylamine until a change of color was observed. Purification yielded fraction I: 486 mg (87%) of (*Z*)-**3g**, R_f = 0.26 (pentane/diethyl ether, 5:1), yellow crystals, mp 129 °C; IR (KBr, cm^{-1}) 2994, 2941, 2046 (C=O), 2006 (C=O), 1926 (C=O), 1604, 1542, 1426, 1353, 1238, 1109, 1024, 996, 867, 838, 759, 709, 654; ^1H NMR (250 MHz, $CDCl_3$; δ, ppm) −0.92 (9H, s, $Si(CH_3)_3$), 1.08 (3H, t, ^3J = 7.0 Hz, OCH_2CH_3), 1.21 (6H, s, $C(CH_3)_2$), 2.52 (6H, s, $N(CH_3)_2$), 4.57 (2H, q, ^3J = 7.0 Hz, OCH_2CH_3), 6.39 (1H, s, =CH); $^{13}C\{H\}$ NMR (62.89 MHz, $CDCl_3$, add. DEPT; δ, ppm) 1.65 (+, $Si(CH_3)_3$), 15.78 (+, OCH_2CH_3), 30.12 (+, $C(CH_3)_2$), 45.65 (+, $N(CH_3)_2$), 72.70 (–, OCH_2CH_3), 76.85 (C_{quat}, $C(CH_3)_2$), 113.76 (+, C2), 167.58 (C_{quat}, C3), 220.53, 224.77 (C_{quat}, C=O), 273.85 (C_{quat}, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 449 (3) [M^+], 421 (2) [$M^+ - CO$], 393 (2) [$M^+ - 2CO$], 365 (4) [$M^+ - 3CO$], 337 (1) [$M^+ - 4CO$], 309 (22) [$M^+ - 5CO$], 263 (28), 243 (71), 214 (38),

---

(20) Sheldrick, G. M. SHELXL-92, Program for crystal structure refinement. Universität Göttingen, Germany, 1992.

Table V. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) of 15f

	x	*y*	*z*	*U*(eq)^a
Cr1	2612.1(2)	5887.7(2)	4957.3(2)	26.25(14)
C1	2708.5(11)	5344.9(11)	3670.5(10)	27.3(7)
C2	2741.9(11)	4979.2(11)	2885.9(11)	27.4(7)
C3	2863.6(10)	4642.4(10)	1997.0(10)	23.4(6)
C4	3600.1(11)	5224.5(11)	1591.7(11)	28.9(8)
O1	4160.2(7)	4609.3(8)	1143.6(7)	27.2(5)
C41	4872.8(12)	3965.5(13)	1801.2(12)	35.6(7)
C42	5266.6(13)	3311.1(14)	1151.2(14)	42.8(9)
C43	2990.3(14)	5895.1(12)	747.7(14)	39.4(10)
C5	4299.7(15)	5848.7(14)	2427(2)	47.6(10)
N1	2330.4(9)	3885.5(9)	1522.9(8)	23.3(6)
C50	2358.5(10)	3459.4(11)	559.0(10)	25.4(7)
C51	1325.6(11)	3398.8(11)	−208.3(10)	26.5(7)
C52	940.8(12)	2494.1(12)	−600.7(12)	35.4(8)
C53	2.0(13)	2430.0(14)	−1317.4(13)	43.6(9)
C54	−556.2(12)	3264.1(15)	−1647.7(12)	41.4(8)
C55	−177.4(13)	4163.4(14)	−1270.4(14)	43.2(9)
C56	759.7(13)	4230.7(13)	−550.2(13)	38.2(8)
C60	1658.1(11)	3353.9(11)	1975.6(11)	26.8(7)
C61	2056.5(11)	2354.8(11)	2361.8(10)	25.7(7)
C62	1470.0(12)	1529.3(11)	2033.5(11)	31.1(7)
C63	1807.5(14)	608.4(13)	2410.4(13)	38.8(10)
C64	2740.3(14)	506.7(14)	3116.3(13)	40.8(10)
C65	3331.3(13)	1325.8(14)	3447.7(12)	39.7(8)
C66	2995.4(12)	2249.4(13)	3080.3(11)	33.2(7)
C21	2519.1(12)	6391.3(12)	6168.0(11)	32.5(8)
O21	2477.3(10)	6714.9(10)	6906.7(8)	45.4(8)
C22	3954.0(14)	6324.3(13)	5279.5(12)	40.7(10)
O22	4771.0(12)	6560.6(14)	5496.1(12)	71.5(9)
C23	3092.7(11)	4653.5(12)	5543.6(11)	29.0(7)
O23	3387.3(9)	3905.9(9)	5867.3(10)	42.6(7)
C24	2121(2)	7089.6(13)	4298.2(11)	44.1(12)
O24	1808.9(15)	7807.0(10)	3903.0(10)	72.4(15)
C25	1291.6(13)	5379.8(12)	4531.0(12)	36.0(9)
O25	506.7(10)	5057.2(11)	4221.8(12)	58.0(7)

^{a} *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VI. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) of 16f

	x	*y*	*z*	*U*(eq)^a
Cr1	1113.4(5)	2500	1845.2(5)	62.6(4)
C1	2629(4)	2500	3729(4)	65(2)
C2	3553(4)	2500	4849(4)	71(2)
C3	4535(4)	2500	6204(3)	60(2)
C4	4026(4)	2500	7457(4)	75(2)
O1	5250(2)	2500	8638(2)	70.0(14)
C5	2915(5)	3540(6)	7364(5)	143(5)
C5′	3495(7)	3904(6)	7460(7)	123(5)
C11	5130(5)	2500(7)	9987(4)	131(3)
C12	6431(6)	2500	1063(5)	136(4)
C13	6553(4)	2500	5365(4)	81(2)
C14	7410(7)	3678(5)	5532(6)	167(6)
N1	5866(3)	2500	6447(3)	65(2)
H1	6461(33)	2500	7326(18)	78
C21	163(3)	3756(4)	2526(3)	90.5(15)
O21	−413(3)	4492(4)	2958(4)	151(2)
C22	2118(4)	3803(3)	1289(3)	84(2)
O22	2737(4)	4600(3)	987(4)	140(3)
C23	−279(5)	2500	94(5)	90(3)
O23	−1148(4)	2500	−976(4)	137(3)

^{a} *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

186 (18), 170 (39), 131 (100), 124 (36), 84 (59), 73 (96), 52 (19) [Cr$^+$]. Anal. Calcd for C$_{18}$H$_{27}$CrNO$_7$Si: C, 48.10; H, 6.05; N, 3.12. Found: C, 48.30; H, 6.18; N, 3.14.

II: 58 mg (12%) of **11g**, R_f = 0.04, orange crystals, mp 98 °C; IR (KBr, cm^{-1}) 2992, 2956, 2051 (C=O), 2000 (C=O), 1931 (C=O), 1554, 1404, 1360, 1249, 1164, 1112, 1025, 998, 938, 872, 840, 751, 723, 669; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) −0.12 (9H, s, Si(CH$_3$)$_3$), 1.29 (6H, s, C(CH$_3$)$_2$), 2.40 (3H, s, NCH$_3$), 2.52 (3H, s, NCH$_3$); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 1.57 (+, Si(CH$_3$)$_3$), 30.36 (+, C(*C*H$_3$)$_2$), 41.36 (+, NCH$_3$), 46.31 (+, NCH$_3$), 76.69 (C$_{quat}$, *C*(CH$_3$)$_2$), 121.59 (C$_{quat}$, C2), 160.38 (C$_{quat}$, C3), 218.52, 224.09 (C$_{quat}$, C=O), 230.58 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 403 (18) [M$^+$], 375 (2) [M$^+$ − CO], 347 (4) [M$^+$ − 2CO], 319 (2) [M$^+$ − 3CO], 291 (36) [M$^+$ − 4CO], 263 (57) [M$^+$ − 5CO], 248 (82), 243 (24), 200 (43), 170 (33), 155 (39), 98 (38), 84 (100), 69 (58), 52 (9) [Cr$^+$]. Anal. Calcd for C$_{16}$H$_{21}$CrNO$_6$Si: C, 47.64; H, 5.25. Found: C, 47.56; H, 5.20.

Pentacarbonyl[(2*Z*)-3-(diethylamino)-1,4-diethoxy-4-methylpentenylidene]chromium ((*Z*)-4f) and Pentacarbonyl[3-(diethylamino)-4-ethoxy-4-methyl-1,2-pentadienylidene]chromium (12f). To 500 mg (1.39 mmol) of pentacarbonyl(1-ethoxy-4,4-dimethylpentynylidene)chromium[12] (**1f**) was added 420 mg (1.50 mmol) of diethylamine. After having been stirred for 1 min, the reaction mixture was washed and purified to yield fraction I: 131 mg (22%) of (*Z*)-**4f**, R_f = 0.25 (pentane/diethyl ether, 5:1), orange crystals, mp 96 °C; IR (KBr, cm^{-1}) 2981, 2938, 2907, 2879, 2045 (C=O), 1960 (C=O), 1916 (C=O), 1513, 1479, 1383, 1269, 1230, 1110, 1071, 916, 792, 740, 680; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 1.12–1.21 (9H, m, OCH$_2$C*H*$_3$, N(CH$_2$C*H*$_3$)$_2$), 1.42 (3H, t, ^3J = 7.0 Hz, OCH$_2$C*H*$_3$), 1.55 (6H, s, C(CH$_3$)$_2$OEt), 3.32 (2H, q, ^3J = 7.0 Hz, OC*H*$_2$CH$_3$), 3.72 (4H, q, ^3J = 7.0 Hz, N(C*H*$_2$CH$_3$)$_2$), 4.65 (2H, q, ^3J = 7.0 Hz, OC*H*$_2$CH$_3$), 6.29 (1H, s, =CH); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 13.89 (+, N(CH$_2$*C*H$_3$)$_2$), 15.69 (+, OCH$_2$*C*H$_3$), 15.89 (+, OCH$_2$*C*H$_3$), 27.61 (+, C(*C*H$_3$)$_2$OEt), 47.26 (−, N(*C*H$_2$CH$_3$)$_2$), 59.48 (−, O*C*H$_2$CH$_3$), 72.89 (−, O*C*H$_2$CH$_3$), 79.20 (C$_{quat}$, C(*C*H$_3$)$_2$OEt), 116.16 (+, C2), 164.39 (C$_{quat}$, C3), 219.55, 224.31 (C$_{quat}$, C=O), 274.84 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 433 (11) [M$^+$], 405 (1) [M$^+$ − CO], 377 (4) [M$^+$ − 2CO], 349 (21) [M$^+$ − 3CO], 321 (4) [M$^+$ − 4CO], 293 (63) [M$^+$ − 5CO], 247 (55), 205 (100), 151 (78), 123 (66), 87 (25), 59 (57), 52 (44) [Cr$^+$].

II: 386 mg (72%) of **12f**, R_f = 0.07, red crystals, mp 75 °C; IR (KBr, cm^{-1}) 2980, 2942, 2900, 2875, 2079 (C=C=C), 2009 (C=O), 1930 (C=O), 1902 (C=O), 1551, 1450, 1364, 1301, 1170, 1077, 1000, 849, 683, 666; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 1.18 (3H, t, ^3J = 7.0 Hz, OCH$_2$C*H*$_3$), 1.33 (3H, t, ^3J = 7.5 Hz, NCH$_2$C*H*$_3$), 1.42 (3H, t, ^3J = 7.5 Hz, NCH$_2$C*H*$_3$), 3.40 (2H, q, ^3J = 7.0 Hz, OC*H*$_2$CH$_3$), 3.94 (2H, q, ^3J = 7.5 Hz, NC*H*$_2$CH$_3$), 4.17 (2H, q, ^3J = 7.5 Hz, NC*H*$_2$CH$_3$); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 11.98 (+, NCH$_2$*C*H$_3$), 13.67 (+, NCH$_2$*C*H$_3$), 15.47 (+, OCH$_2$*C*H$_3$), 27.15 (+, C(*C*H$_3$)$_2$OEt), 45.95 (−, N*C*H$_2$CH$_3$), 50.75 (−, N*C*H$_2$CH$_3$), 59.48 (−, O*C*H$_2$CH$_3$), 78.81 (C$_{quat}$, *C*(CH$_3$)$_2$OEt), 122.40 (C$_{quat}$, C2), 158.77 (C$_{quat}$, C3), 217.57, 224.07 (C$_{quat}$, C=O), 229.34 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 387 (20) [M$^+$], 359 (1) [M$^+$ − CO], 331 (2) [M$^+$ − 2CO], 303 (3) [M$^+$ − 3CO], 275 (31) [M$^+$ − 4CO], 247 (100) [M$^+$ − 5CO], 201 (9), 150 (6), 123 (20), 77 (8), 52 (19) [Cr$^+$].

Pentacarbonyl[(2*Z*)-3-(dibenzylamino)-1-ethoxy-4,4-dimethylpentenylidene]chromium ((*Z*)-7c) and Pentacarbonyl[3-(dibenzylamino)-4,4-dimethyl-1,2-pentadienylidene]chromium (15c). To 468 mg (1.42 mmol) of pentacarbonyl(1-ethoxy-4,4-dimethylpentynylidene)chromium[12] (**1c**) was added 420 mg (0.41 mmol) of dibenzylamine. After having been stirred for 1.5 h, the reaction mixture was washed and purified to yield fraction I: 112 mg (15%) of (*Z*)-**7c**, R_f = 0.38 (pentane/diethyl ether, 3:1), yellow crystals, mp 129 °C; IR (KBr, cm^{-1}): 2960, 2040 (C=O), 1960 (C=O), 1903 (C=O), 1420, 1235, 1080, 800, 755, 665; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 0.83 (3H, t, ^3J = 7.0 Hz, OCH$_2$C*H*$_3$), 1.04 (9H, s, C(CH$_3$)$_3$), 4.04 (4H, s, N(CH$_2$)$_2$), 4.71 (2H, q, ^3J = 7.0 Hz, OC*H*$_2$CH$_3$), 6.80–6.92 (4H, m, Ph H), 7.00–7.13 (6H, m, Ph H); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 15.89 (+, CH$_2$*C*H$_3$), 30.60 (+, C(*C*H$_3$)$_3$), 39.01 (C$_{quat}$, C4), 58.04 (−, N(CH$_2$)$_2$), 74.78 (−, O*C*H$_2$CH$_3$), 118.25 (+, C2), 128.53, 128.92, 129.57 (+, Ph C), 136.28 (C$_{quat}$, Ph C), 167.10 (C$_{quat}$, C3), 219.86, 224.61 (C$_{quat}$, C=O), 288.19 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 527 (4) [M$^+$], 499 (2) [M$^+$ − CO], 471 (3) [M$^+$ − 2CO], 443 (11) [M$^+$ − 3CO], 415 (7) [M$^+$ − 4CO], 387 (100) [M$^+$ − 5CO], 52 (43) [Cr$^+$].

II: 484 mg (71%) of **15c**, R_f = 0.10, orange oil; IR (film, cm^{-1}) 2980, 2055 (C=O), 1990 (C=O), 1910 (C=O), 1510, 1270, 1200, 1085, 1035; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 1.00 (9H, s, C(CH$_3$)$_3$), 4.18 (2H, s, NCH$_2$), 4.87 (2H, s, NCH$_2$), 6.97–7.21 (10H, m, Ph H); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 29.93 (+, C(CH$_3$)$_3$), 39.40 (C$_{quat}$, C4), 53.50, 58.31 (–, NCH$_2$), 125.67 (C$_{quat}$, C2), 126.82, 129.26, 133.57 (+, Ph C), 134.45 (C$_{quat}$, Ph C), 169.15 (C$_{quat}$, C3), 218.18, 224.13 (C$_{quat}$, C=O), 237.49 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 481 (3) [M$^+$], 453 (4) [M$^+$ – CO], 425 (6) [M$^+$ – 2CO], 397 (2) [M$^+$ – 3CO], 369 (10) [M$^+$ – 4CO], 341 (100) [M$^+$ – 5CO], 52 (43) [Cr$^+$].

Pentacarbonyl[(2*Z*)-3-(dibenzylamino)-1-ethoxy-3-(1-ethoxycyclopropyl)propenylidene]chromium ((*Z*)-7e) and Pentacarbonyl[3-(dibenzylamino)-3-(1-ethoxycyclopropyl)-1,2-propadienylidene]chromium (15e). To 648 mg (1.80 mmol) of pentacarbonyl[1-ethoxy-3-(1-ethoxycyclopropyl)propynylidene]chromium[5] (1e) was added 530 mg (2.70 mmol) dibenzylamine. After having been stirred for 1.5 h, the reaction mixture was washed and purified to yield fraction I: 529 mg (53%) of (*Z*)-7e, R_f = 0.49 (pentane/diethyl ether, 10:1), yellow crystals, mp 124 °C; IR (KBr, cm^{-1}) 3010, 2970, 2921, 2881, 2041 (C=O), 1930 (C=O), 1908 (C=O), 1887, 1509, 1468, 1362, 1245, 1138, 1065, 919, 807, 750, 669; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 1.02–1.18 (7H, m, cyclopropyl H, OCH$_2$CH$_3$), 1.45 (3H, t, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 3.60 (2H, q, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 4.31 (4H, brs, NCH$_2$), 4.72 (2H, q, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 6.43 (1H, s, =CH), 7.03–7.10 (4H, m, Ph H), 7.28–7.41 (6H, m, Ph H); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 12.13 (–, cyclopropyl CH$_2$), 15.11 (+, OCH$_2$CH$_3$), 15.92 (+, OCH$_2$CH$_3$), 53.34, 57.83 (–, NCH$_2$), 61.04 (C$_{quat}$, cyclopropyl C), 64.30 (–, OCH$_2$CH$_3$), 74.40 (–, OCH$_2$CH$_3$), 118.15 (+, C2), 127.99, 128.21, 128.81 (+, Ph C), 135.75 (C$_{quat}$, Ph C), 157.08 (C$_{quat}$, C3), 218.73, 224.21 (C$_{quat}$, C=O), 295.33 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 555 (1) [M$^+$], 527 (0.5) [M$^+$ – CO], 499 (0.2) [M$^+$ – 2CO], 471 (2) [M$^+$ – 3CO], 433 (2) [M$^+$ – 4CO], 415 (5) [M$^+$ – 5CO], 348 (18), 292 (41), 264 (64), 174 (36), 149 (18), 96 (25), 91 (100) [CH$_2$Ph$^+$], 73 (69), 52 (59) [Cr$^+$].

II: 412 mg (45%) of 15e, R_f = 0.03, orange crystals, mp 99 °C; IR (KBr, cm^{-1}) 3064, 3040, 2998, 2938, 2200 (C=C=C), 2004 (C=O), 1998 (C=O), 1945 (C=O), 1900 (C=O), 1539, 1455, 1434, 1352, 1249, 1177, 1080, 1053, 1030, 975, 933, 905, 760, 699, 688, 659; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 1.03 (3H, t, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 1.23 (2H, mc, cyclopropyl CH$_2$), 1.45 (2H, mc, cyclopropyl CH$_2$), 3.62 (2H, q, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 5.09 (4H, d, ^2J = 15.2 Hz, NCH$_2$), 7.10–7.20 (2H, m, Ph H), 7.31–7.48 (8H, m, Ph H); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 15.09 (+, OCH$_2$CH$_3$), 16.02 (–, cyclopropyl CH$_2$), 53.50, 56.95 (–, NCH$_2$), 62.95 (C$_{quat}$, cyclopropyl C), 65.53 (–, OCH$_2$CH$_3$), 125.02 (C$_{quat}$, C2), 127.63, 128.60, 128.72, 128.89, 129.12, 129.29 (+, Ph C), 133.80, 134.05 (C$_{quat}$, Ph C), 154.77 (C$_{quat}$, C3), 217.22, 223.98 (C$_{quat}$, C=O), 237.86 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 509 (4) [M$^+$], 481 (1) [M$^+$ – CO], 453 (1) [M$^+$ – 2CO], 425 (2) [M$^+$ – 3CO], 397 (11) [M$^+$ – 4CO], 369 (34) [M$^+$ – 5CO], 378 (6), 248 (7), 207 (4), 149 (9), 97 (7), 91 (100) [CH$_2$Ph$^+$], 69 (19), 52 (17) [Cr$^+$]. Anal. Calcd for C$_{27}$H$_{23}$CrNO$_6$: C, 63.65; H, 4.55; N, 2.75. Found: C, 63.53; H, 4.61; N, 2.75.

Pentacarbonyl[(2*Z*)-1,4-diethoxy-)3-(isopropylamino)-4-methylpentenylidene]chromium ((*Z*)-8f) and Pentacarbonyl[4-ethoxy-4-methyl-3-(isopropylamino)-1,2-pentadienyldiene]chromium (16f). To 79 mg (0.22 mmol) of pentacarbonyl(1,4-diethoxy-4-methylpentynylidene)chromium[5] (1f) was added 20 mg (0.33 mmol) of isopropylamine. After having been stirred for 15 min, the reaction mixture was washed and purified to yield fraction I: 10 mg (11%) of (*Z*)-8f, R_f = 0.40 (pentane/diethyl ether, 5:1), yellow crystals, mp 122 °C; IR (KBr, cm^{-1}) 3280 (NH), 2992, 2983, 2936, 2878, 2044 (C=O), 1970 (C=O), 1921 (C=O), 1569, 1507, 1456, 1403, 1340, 1257, 1231, 1132, 1070, 1028, 971, 922, 804, 788, 672; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 1.20 (3H, t, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 1.26 (6H, d, ^3J = 7.1 Hz, CH(CH$_3$)$_2$), 1.53 (6H, s, C(CH$_3$)$_2$OEt), 1.56 (3H, t, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 3.40 (2H, q, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 4.63 (2H, q, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 4.83 (1H, sep, ^3J = 7.1 Hz, CH(CH$_3$)$_2$), 6.21 (1H, s, =CH), 9.42 (brs, 1H, NH); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 15.54 (+, OCH$_2$CH$_3$), 15.62 (+, OCH$_2$CH$_3$), 24.38 (+, CH(CH$_3$)$_2$), 27.10 (+, C(CH$_3$)$_2$OEt), 30.47 (+, CH(CH$_3$)$_2$), 59.12 (–, OCH$_2$CH$_3$), 73.42 (–, OCH$_2$CH$_3$), 76.32 (C$_{quat}$, C(CH$_3$)$_2$OEt), 117.98 (+, C2), 156.86 (C$_{quat}$, C3), 218.97, 223.99 (C$_{quat}$, C=O), 272.60 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 419 (18) [M$^+$], 391 (4) [M$^+$ – CO], 363 (7) [M$^+$ – 2CO], 335 (25) [M$^+$ – 3CO], 307 (17) [M$^+$ – 4CO], 279 (100) [M$^+$ – 5CO], 235 (63), 189 (92), 162 (16), 149 (24), 109 (44), 98 (32), 93 (20), 72 (17), 59 (39), 52 (37) [Cr$^+$].

II: 70 mg (86%) of 16f, R_f = 0.09, orange crystals, mp 99 °C; IR (KBr, cm^{-1}) 3369 (NH), 2975, 2927, 2067 (C=O), 2000 (C=O), 1934 (C=O), 1509, 1469, 1390, 1253, 1201, 1120, 1116, 1092, 1061, 980, 825, 760, 664; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 1.21 (3H, t, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 1.39 (6H, d, ^3J = 7.1 Hz, CH(CH$_3$)$_2$), 1.57 (6H, s, C(CH$_3$)$_2$OEt), 3.52 (2H, q, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 4.50 (1H, sep, ^3J = 7.1 Hz, CH(CH$_3$)$_2$), 8.40 (1H, brs, NH); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 15.77 (+, OCH$_2$CH$_3$), 21.54 (+, CH(CH$_3$)$_2$), 25.28 (+, C(CH$_3$)$_2$OEt), 49.53 (+, CH(CH$_3$)$_2$), 59.09 (–, OCH$_2$CH$_3$), 79.75 (C$_{quat}$, C(CH$_3$)$_2$OEt), 115.20 (C$_{quat}$, C2), 160.75 (C$_{quat}$, C3), 217.53, 223.43 (C$_{quat}$, C=O), 231.16 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 373 (16) [M$^+$], 345 (1) [M$^+$ – CO], 317 (4) [M$^+$ – 2CO], 289 (5) [M$^+$ – 3CO], 261 (24) [M$^+$ – 4CO], 233 (100) [M$^+$ – 5CO], 189 (26), 153 (17), 99 (38), 77 (44), 52 (14) [Cr$^+$], 41 (44). Anal. Calcd for C$_{16}$H$_{19}$CrNO$_6$: C, 51.48; H, 5.13; N, 3.75. Found: C, 51.56; H, 5.19; N, 3.76.

Pentacarbonyl[(2*Z*)-1,4-diethoxy-4-methyl-3-(propylamino)pentenylidene]chromium ((*Z*)-9f) and Pentacarbonyl[4-ethoxy-4-methyl-3-(propylamino)-1,2-pentadienylidene]chromium (17f). To 180 mg (0.50 mmol) of pentacarbonyl(1,4-diethoxy-4-methylpentynylidene)chromium[5] (1f) was added 44 mg (0.75 mmol) of propylamine. After having been stirred for 15 min, the reaction mixture was washed and purified to yield fraction I: 120 mg (58%) of (*Z*)-9f, R_f = 0.44 (pentane/diethyl ether, 5:1), yellow crystals, mp 115 °C; IR (KBr, cm^{-1}) 3279 (NH), 2981, 2960, 2879, 2040 (C=O), 1962 (C=O), 1921 (C=O), 1522, 1500, 1403, 1380, 1331, 1264, 1244, 1218, 1174, 1153, 1139, 1053, 965, 916, 800, 762, 669; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 1.03 (3H, t, ^3J = 7.1 Hz, NCH$_2$CH$_2$CH$_3$), 1.18 (3H, t, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 1.49 (6H, s, C(CH$_3$)$_2$OEt), 1.52 (3H, t, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 1.64 (2H, mc, NCH$_2$CH$_2$CH$_3$), 3.32 (2H, q, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 3.70 (2H, brs, NCH$_2$CH$_2$CH$_3$), 4.74 (2H, q, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 6.28 (1H, s, =CH), 9.32 (H, brs, NH); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 11.34 (+, NCH$_2$CH$_2$CH$_3$), 15.58 (+, OCH$_2$CH$_3$), 15.70 (+, OCH$_2$CH$_3$), 23.67 (–, NCH$_2$CH$_2$CH$_3$), 26.79 (+, C(CH$_3$)$_2$OEt), 47.31 (–, NCH$_2$CH$_2$CH$_3$), 59.06 (–, OCH$_2$CH$_3$), 66.42 (–, OCH$_2$CH$_3$), 73.80 (C$_{quat}$, C(CH$_3$)$_2$OEt), 115.45 (+, C2), 158.21 (C$_{quat}$, C3), 218.93, 224.06 (C$_{quat}$, C=O), 288.27 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 419 (9) [M$^+$], 391 (6) [M$^+$ – CO], 363 (13) [M$^+$ – 2CO], 335 (14) [M$^+$ – 3CO], 307 (7) [M$^+$ – 4CO], 279 (100) [M$^+$ – 5CO], 278 (4), 235 (39), 222 (34), 189 (48), 176 (28), 140 (78), 121 (32), 98 (61), 68 (25), 52 (19) [Cr$^+$]. Anal. Calcd for C$_{18}$H$_{25}$CrNO$_7$: C, 51.55; H, 6.01. Found: C, 51.70; H, 6.10.

II: 76 mg (41%) of 17f, R_f = 0.06, orange crystals, mp 95 °C; IR (KBr, cm^{-1}) 3295 (NH), 2988, 2930, 2899, 2872, 2190 (C=C=C), 2068 (C=O), 2006 (C=O), 1931 (C=O), 1582, 1467, 1420, 1359, 1302, 1277, 1249, 1200, 1161, 1120, 1098, 1064, 971, 818, 799, 763, 740, 661; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 1.02 (3H, t, ^3J = 7.0 Hz, NCH$_2$CH$_2$CH$_3$), 1.20 (3H, t, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 1.56 (6H, s, C(CH$_3$)$_2$OEt), 1.78 (2H, mc, NCH$_2$CH$_2$CH$_3$), 3.48 (2H, t, ^3J = 7.0 Hz, NCH$_2$CH$_2$CH$_3$), 3.72 (2H, q, ^3J = 6.9 Hz, OCH$_2$CH$_3$), 8.70 (1H, brs, NH); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 11.08 (+, NCH$_2$CH$_2$CH$_3$), 15.73 (+, OCH$_2$CH$_3$), 22.02 (–, NCH$_2$CH$_2$CH$_3$), 25.24 (+, C(CH$_3$)$_2$OEt), 59.01 (–, OCH$_2$CH$_3$), 65.80 (–, NCH$_2$CH$_2$CH$_3$), 79.83 (C$_{quat}$, C(CH$_3$)$_2$OEt), 114.97 (C$_{quat}$, C2), 162.35 (C$_{quat}$, C3), 217.54, 223.45 (C$_{quat}$, C=O), 230.09 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 373 (19) [M$^+$], 345 (1) [M$^+$ – CO], 317 (3) [M$^+$ – 2CO], 289 (5) [M$^+$ – 3CO], 261 (12) [M$^+$ – 4CO], 233 (64) [M$^+$ – 5CO], 199 (8), 189 (9), 153 (12), 112 (23), 87 (42), 74 (38), 59 (100), 52 (44) [Cr$^+$]. Anal. Calcd for C$_{16}$H$_{19}$CrNO$_6$: C, 51.48; H, 5.13; N, 3.75. Found: C, 51.26; H, 5.18; N, 3.75.

Pentacarbonyl[(2*Z*)-3-(cyclohexylamino)-3-cyclopropyl-1-ethoxypropenylidene]chromium ((*Z*)-10b). To 208 mg (0.66 mmol) of pentacarbonyl(3-cyclopropyl-1-ethoxypropynylidene)chromium[5] (**1b**) was added 100 mg (1.00 mmol) of cyclohexylamine. After having been stirred for 10 min, the reaction mixture was washed and purified to yield 207 mg (86%) of (*Z*)-**10b**, R_f = 0.29 (pentane/diethyl ether, 10:1), yellow crystals, mp 132 °C; IR (KBr, cm^{-1}) 3321 (NH), 2953, 2931, 2920, 2850, 2041 (C═O), 1969 (C═O), 1925 (C═O), 1560, 1515, 1454, 1400, 1367, 1264, 1100, 1053, 1031, 740, 670; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 0.93–1.10 (4H, m, cyclopropyl CH$_2$), 1.13–1.42 (5H, m, cyclohexyl H), 1.53 (3H, t, ^3J = 6.9 Hz, OCH$_2$C*H*$_3$), 1.55–1.74 (2H, m, cyclohexyl H), 1.75–1.90 (2H, m, cyclohexyl H), 1.98–2.09 (2H, m, cyclohexyl H), 3.71 (1H, brs, C*H*C$_2$H$_4$), 4.62 (2H, q, ^3J = 6.9 Hz, OC*H*$_2$CH$_3$), 5.63 (1H, s, ═CH), 9.41 (1H, d, NH); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 9.57 (–, CHC$_2$H$_4$), 11.79 (+, *C*HC$_2$H$_4$), 15.85 (+, OCH$_2$*C*H$_3$), 24.51, 25.03, 33.72 (–, cyclohexyl C), 52.41 (+, NCH), 72.99 (–, O*C*H$_2$CH$_3$), 111.67 (+, C2), 158.70 (C$_{quat}$, C3), 219.19, 224.07 (C$_{quat}$, C═O), 280.02 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 413 (5) [M$^+$], 385 (3) [M$^+$ – CO], 357 (6) [M$^+$ – 2CO], 329 (7) [M$^+$ – 3CO], 301 (3) [M$^+$ – 4CO], 273 (100) [M$^+$ – 5CO], 52 (42) [Cr$^+$]. Anal. Calcd for $C_{19}H_{23}CrNO_6$: C, 55.20; H, 5.61; N, 3.39. Found: C, 55.29; H, 5.69; N, 3.33.

Pentacarbonyl[(2*Z*)-1-ethoxy-3-(cyclohexylamino)-3-(1-ethoxycyclopropyl)propenylidene]chromium ((*Z*)-10e) and Pentacarbonyl[3-(cyclohexylamino)-3-(1-ethoxycyclopropyl)-1,2-propadienylidene]chromium (18e). To 300 mg (0.84 mmol) of pentacarbonyl[1-ethoxy-3-(1-ethoxycyclopropyl)propynylidene]chromium[5] (**1e**) was added 125 mg (1.25 mmol) of cyclohexylamine. After having been stirred for 15 min, the reaction mixture was washed and purified to yield fraction I: 306 mg (80%) of (*Z*)-**10e**, R_f = 0.20 (pentane/diethyl ether, 5:1), yellow crystals, mp 128 °C; IR (KBr, cm^{-1}) 3314 (NH), 2970, 2960, 2938, 2849, 2044 (C═O), 1985 (C═O), 1908 (C═O), 1560, 1511, 1450, 1394, 1231, 1182, 1131, 1023, 1072, 911, 802, 755, 670, 638; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 0.99 (2H, mc, cyclopropyl CH$_2$), 1.06 (2H, mc, cyclopropyl CH$_2$), 1.11 (3H, t, ^3J = 6.9 Hz, OCH$_2$C*H*$_3$), 1.13–1.53 (6H, m, cyclohexyl CH$_2$), 1.56 (3H, t, ^3J = 6.9 Hz, OCH$_2$C*H*$_3$), 1.68–1.82 (2H, m, cyclohexyl CH$_2$), 1.86–2.01 (2H, m, cyclohexyl CH$_2$), 3.54 (2H, q, ^3J = 6.9 Hz, OC*H*$_2$CH$_3$), 4.10 (1H, mc, NCH), 4.76 (2H, q, ^3J = 6.9 Hz, OC*H*$_2$CH$_3$), 6.20 (1H, s, ═CH), 8.95 (1H, d, ^2J = 13.7 Hz, NH); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 12.98 (–, cyclopropyl CH$_2$), 15.32 (+, OCH$_2$*C*H$_3$), 15.74 (+, OCH$_2$*C*H$_3$), 24.49, 25.08, 34.25 (–, cyclohexyl CH$_2$), 53.00 (+, NCH), 61.42 (C$_{quat}$, cyclopropyl C), 63.83 (–, O*C*H$_2$CH$_3$), 73.60 (–, O*C*H$_2$CH$_3$), 116.92 (+, C2), 150.14 (C$_{quat}$, C3), 218.78, 224.00 (C$_{quat}$, C═O), 290.65 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 457 (11) [M$^+$], 429 (2) [M$^+$ – CO], 401 (4) [M$^+$ – 2CO], 373 (6) [M$^+$ – 3CO], 345 (31) [M$^+$ – 4CO], 317 (98) [M$^+$ – 5CO], 292 (44), 274 (17), 232 (20), 219 (99), 202 (11), 175 (21), 149 (19), 105 (10), 96 (19), 80 (23), 52 (100) [Cr$^+$]. Anal. Calcd for $C_{21}H_{27}CrNO_7$: C, 55.14; H, 5.95; N, 3.06. Found: C, 55.29; H, 5.99; N, 2.99.

II: 25 mg (11%) of **18e**, R_f = 0.04, orange crystals, mp 97 °C; IR (KBr, cm^{-1}) 3320 (NH), 2980, 2922, 2849, 2075 (C═O), 2000 (C═O), 1928 (C═O), 1550, 1441, 1422, 1259, 1114, 1049, 800, 747, 669, 660; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 1.02–1.93 (14H, m, cyclohexyl H, cyclopropyl CH$_2$), 1.19 (3H, t, ^3J = 6.9 Hz, OCH$_2$C*H*$_3$), 3.49 (2H, q, ^3J = 6.9 Hz, OC*H*$_2$CH$_3$), 4.20 (1H, brs, NCH), 8.11 (1H, brs, NH); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 15.26 (–, cyclopropyl CH$_2$), 15.47 (+, OCH$_2$*C*H$_3$), 20.01, 24.20, 31.91 (–, cyclohexyl CH$_2$), 56.52 (+, NCH), 65.65 (–, O*C*H$_2$CH$_3$), 66.60 (C$_{quat}$, cyclopropyl C), 111.58 (C$_{quat}$, C2), 158.84 (C$_{quat}$, C3), 217.54, 223.07 (C$_{quat}$, C═O), 225.74 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 355 (1) [M$^+$ – 2CO], 271 (2) [M$^+$ – 5CO], 205 (13), 190 (73), 180 (11), 148 (4), 124 (9), 108 (100), 98 (18), 83 (45), 67 (20), 52 (18) [Cr$^+$].

Pentacarbonyl[(2*Z*)-3-(cyclohexylamino)-1,4-diethoxy-4-methylpentenylidene]chromium ((*Z*)-10f) and Pentacarbonyl[3-(cyclohexylamino)-4-ethoxy-4-methyl-1,2-pentadienylidene]chromium (18f). To 191 mg (0.53 mmol) of pentacarbonyl(1,4-diethoxy-4-methylpentynylidene)chromium[5] (**1f**) was added 80 mg (0.80 mmol) of cyclohexylamine. After having been stirred for 15 min, the reaction mixture was washed and purified to yield fraction I: 73 mg (30%) of (*Z*)-**10f**, R_f = 0.46 (pentane/diethyl ether, 5:1), yellow crystals, mp 129 °C; IR (KBr, cm^{-1}) 3280 (NH), 2982, 2919, 2840, 2039 (C═O), 1952 (C═O), 1904 (C═O), 1555, 1440, 1396, 1346, 1250, 1212, 1162, 1131, 916, 889, 790, 666; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 1.18 (3H, t, ^3J = 6.9 Hz, OCH$_2$C*H*$_3$), 1.20–1.41 (5H, m, cyclohexyl CH$_2$), 1.50 (6H, s, C(C*H*$_3$)$_2$OEt), 1.53 (3H, t, ^3J = 6.9 Hz, OCH$_2$C*H*$_3$), 1.59–1.85 (3H, m, cyclohexyl CH$_2$), 1.91–2.21 (2H, m, cyclohexyl CH$_2$), 3.39 (2H, q, ^3J = 6.9 Hz, OC*H*$_2$CH$_3$), 4.44 (1H, m, NCH), 4.74 (2H, q, ^3J = 6.9 Hz, OC*H*$_2$CH$_3$), 6.20 (1H, s, ═CH), 9.46 (1H, d, ^3J = 7.4 Hz, NH); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 15.44 (+, OCH$_2$*C*H$_3$), 15.85 (+, OCH$_2$*C*H$_3$), 24.77 (–, cyclohexyl CH$_2$), 25.15 (–, cyclohexyl CH$_2$), 27.42 (+, C(*C*H$_3$)$_2$OEt), 35.29 (–, cyclohexyl CH$_2$), 53.98 (+, NCH), 59.14 (–, O*C*H$_2$CH$_3$), 73.56 (–, O*C*H$_2$CH$_3$), 78.64 (C$_{quat}$, *C*(CH$_3$)$_2$OEt), 115.00 (+, C2), 156.97 (C$_{quat}$, C3), 218.98, 224.03 (C$_{quat}$, C═O), 286.60 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 459 (6) [M$^+$], 431 (1) [M$^+$ – CO], 403 (3) [M$^+$ – 2CO], 375 (11) [M$^+$ – 3CO], 347 (9) [M$^+$ – 4CO], 319 (100) [M$^+$ – 5CO], 275 (41), 246 (13), 229 (53), 180 (17), 149 (40), 98 (41), 83 (8), 59 (16), 52 (24) [Cr$^+$].

II: 147 mg (67%) of **18f**, R_f = 0.05, orange crystals, mp 104 °C; IR (KBr, cm^{-1}) 3264 (NH), 2972, 2920, 2852, 2063 (C═O), 1999 (C═O), 1921 (C═O), 1568, 1439, 1388, 1358, 1198, 1117, 1069, 990, 941, 896, 855, 656; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 1.21 (3H, t, ^3J = 6.9 Hz, OCH$_2$C*H*$_3$), 1.29–1.49 (5H, m, cyclohexyl CH$_2$), 1.53 (6H, s, C(CH$_3$)$_2$OEt), 1.60–1.84 (3H, m, cyclohexyl CH$_2$), 2.04–2.13 (2H, m, cyclohexyl CH$_2$), 3.48 (2H, q, ^3J = 6.9 Hz, OC*H*$_2$CH$_3$), 4.19 (1H, m, NCH), 8.49 (1H, brs, NH); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm) 15.68 (+, OCH$_2$*C*H$_3$), 24.17, 25.20 (–, cyclohexyl CH$_2$), 25.95 (+, C(*C*H$_3$)$_2$OEt), 31.50 (–, cyclohexyl CH$_2$), 56.22 (–, O*C*H$_2$CH$_3$), 59.04 (+, NCH), 79.51 (C$_{quat}$, *C*(CH$_3$)$_2$OEt), 114.63 (C$_{quat}$, C2), 160.74 (C$_{quat}$, C3), 217.58, 223.51 (C$_{quat}$, C═O), 228.07 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 413 (11) [M$^+$], 385 (1) [M$^+$ – CO], 357 (1) [M$^+$ – 2CO], 329 (2) [M$^+$ – 3CO], 301 (21) [M$^+$ – 4CO], 273 (100) [M$^+$ – 5CO], 229 (6), 205 (3), 177 (4), 149 (13), 118 (4), 95 (5), 87 (14), 59 (9), 52 (5) [Cr$^+$]. Anal. Calcd for $C_{19}H_{23}CrNO_6$: C, 55.20; H, 5.61; N, 3.39. Found: C, 54.84; H, 5.62; N, 3.35.

Pentacarbonyl[(2*E*/2*Z*)-3-(diethylamino)-1-(dimethylamino)-3-phenylpropenylidene]chromium ((2*E*/2*Z*)-22) and Pentacarbonyl[3-(diethylamino)-3-phenyl-1,2-propadienylidene]chromium (21). To 716 mg (2.05 mmol) of pentacarbonyl[1-(dimethylamino)-3-phenylpropynylidene]chromium[4] (**2a**) in 20 mL of diethyl ether was added 225 mg (3.08 mmol) of diethylamine at 20 °C. After 5 h the solvent was removed under reduced pressure. Chromatography (70 g of silica gel, pentane/diethyl ether, 2:1) yielded fraction I: 206 mg (29%) of **2a**, R_f = 0.73 (pentane/diethyl ether, 2:1).

II: 241 mg (28%) of **22**, *E*/*Z* 3.5:1, R_f = 0.37, orange crystals, mp 110 °C; IR (KBr, cm^{-1}): 3009, 2061, 2031 (C═O), 2001 (C═O), 1875 (C═O), 1512, 1445, 1373, 1249, 1210, 1182, 1070, 1017, 922, 869, 770, 648; ^{1}H NMR (250 MHz, CDCl$_3$; δ, ppm) 1.08 (6H, t, (*E*)-**22**, ^3J = 7.0 Hz, NCH$_2$C*H*$_3$), 1.08 (6H, t, (*Z*)-**22**, ^3J = 7.0 Hz, NCH$_2$C*H*$_3$), 2.55 (3H, s, (*E*)-**22**, NCH$_3$), 2.58 (3H, s, (*Z*)-**22**, NCH$_3$), 3.07 (4H, mc, (*E*)-**22**, ^3J = 7.0 Hz, NCH$_2$), 3.07 (4H, mc, (*Z*)-**22**, ^3J = 7.0 Hz, NCH$_2$), 3.32 (3H, s, (*E*)-**22**, NCH$_3$), 3.35 (3H, s, (*Z*)-**22**, NCH$_3$), 5.92 (1H, s, (*Z*)-**22**, ═CH), 5.96 (1H, s, (*E*)-**22**, ═CH), 7.21 (5H, m, (*Z*)-**22**, Ph H), 7.30 (5H, m, (*E*)-**22**, Ph H); ^{13}C{H} NMR (62.89 MHz, CDCl$_3$, add. DEPT; δ, ppm, (*E*)-**22**) 11.97 (+, NCH$_2$*C*H$_3$), 44.02 (–, N*C*H$_2$CH$_3$), 45.83 (+, NCH$_3$), 50.06 (+ NCH$_3$), 119.84 (+, C2), 128.39, 128.48, 129.15 (+, Ph C), 137.93 (C$_{quat}$, Ph C), 140.67 (C$_{quat}$, C3), 218.56, 223.42 (C$_{quat}$, C═O), 260.03 (C$_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 422 (11) [M$^+$], 394 (31) [M$^+$ – CO], 366 (47) [M$^+$ – 2CO], 338 (11) [M$^+$ – 3CO], 310 (16) [M$^+$ – 4CO], 282 (63) [M$^+$ – 5CO], 254 (52), 229 (23), 211 (24), 202 (78), 186 (21), 174 (59), 158 (41), 149 (37), 105 (59), 52 (61) [Cr$^+$].

III: 309 mg (40%) of **21**, R_f = 0.07, orange crystals, mp 86 °C; IR (KBr, cm^{-1}) 3014, 2990, 2199 ($\mathrm{C{=}C{=}C}$), 2076 ($\mathrm{C{=}O}$), 2003 ($\mathrm{C{=}O}$), 1915 ($\mathrm{C{=}O}$), 1552, 1492, 1459, 1386, 1349, 1297, 1098, 1077, 1027, 857, 788, 768, 704, 653; ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$; δ, ppm) 1.27 (3H, t, ^3J = 7.1 Hz, $\mathrm{NCH_2C}H_3$), 1.53 (3H, t, ^3J = 7.1 Hz, $\mathrm{NCH_2C}H_3$), 3.59 (2H, q, ^3J = 7.1 Hz, $\mathrm{NC}H_2\mathrm{CH_3}$), 4.11 (2H, q, ^3J = 7.1 Hz, $\mathrm{NC}H_2\mathrm{CH_3}$), 7.48 (5H, m, Ph H); ^{13}C{H} NMR (62.89 MHz, $\mathrm{CDCl_3}$, add. DEPT; δ, ppm) 12.34 (+, $\mathrm{NCH_2}C\mathrm{H_3}$), 13.98 (+, $\mathrm{NCH_2}C\mathrm{H_3}$), 46.92 (−, $\mathrm{N}C\mathrm{H_2CH_3}$), 48.93 (−, $\mathrm{N}C\mathrm{H_2CH_3}$), 125.09 ($\mathrm{C_{quat}}$, C2), 127.74, 128.84, 130.92 (+, Ph C), 134.88 ($\mathrm{C_{quat}}$, Ph C), 152.44 ($\mathrm{C_{quat}}$, C3), 217.47, 224.11 ($\mathrm{C_{quat}}$, $\mathrm{C{=}O}$), 232.59 ($\mathrm{C_{quat}}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 377 (3) [M$^+$], 349 (1) [M$^+$ − CO], 321 (1) [M$^+$ − 2CO], 293 (2) [M$^+$ − 3CO], 265 (7) [M$^+$ − 4CO], 237 (40) [M$^+$ − 5CO], 205 (5), 184 (2), 105 (6), 84 (100), 57 (9), 52 (4) [Cr$^+$]. Anal. Calcd for $\mathrm{C_{18}H_{15}CrNO_5}$: C, 57.29; H, 4.27. Found: C, 57.30; H, 4.01.

Pentacarbonyl[(2*E*/2*Z*)-3-(dibenzylamino)-1-(dimethylamino)-4-ethoxy-4-methylpentenylidene]chromium ((*E*/*Z*)-23). To 300 mg (0.587 mmol) of pentacarbonyl[3-(dibenzylamino)-4-ethoxy-4-methyl-1,2-pentadienylidene]chromium (**15f**) in 15 mL of diethyl ether was added dimethylamine at 20 °C until a change of color was observed, and the solvent was removed under reduced pressure. Chromatography (30 g of silica gel, pentane/diethyl ether, 5:1) yielded 317 mg (97%) of **23**: *E*/*Z* 2.5:1, R_f = 0.31 (pentane/diethyl ether, 5:1), yellow crystals, mp 134 °C; IR (KBr, cm^{-1}): 3099, 3075, 3040, 2995, 2948, 2891, 2158 ($\mathrm{C{=}O}$), 1974 ($\mathrm{C{=}O}$), 1917 ($\mathrm{C{=}O}$), 1614, 1553, 1500, 1449, 1408, 1360, 1213, 1169, 1140, 1078, 1037, 909, 819, 741, 709, 684, 672; ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$; δ, ppm): 0.81 (3H, s, (*E*)-**23**, $\mathrm{CCH_3}$), 0.97 (3H, t, ^3J = 6.9 Hz, (*E*)-**23**, $\mathrm{OCH_2C}H_3$), 1.12 (3H, t, ^3J = 6.9 Hz, (*Z*)-**23**, $\mathrm{OCH_2C}H_3$), 1.39 (3H, s, (*E*)-**23**, $\mathrm{CCH_3}$), 1.60 (3H, s, (*Z*)-**23**, $\mathrm{CCH_3}$), 1.66 (3H, s, (*Z*)-**23**, $\mathrm{CCH_3}$), 2.73 (3H, s, (*Z*)-**23**, $\mathrm{NCH_3}$), 2.87 (3H, s, (*E*)-**23**, $\mathrm{NCH_3}$), 3.20 (2H, mc, (*E*)-**23**, $\mathrm{OC}H_2\mathrm{CH_3}$), 3.52 (2H, d, ^2J = 13.2 Hz, (*Z*)-**23**, $\mathrm{NCH_2}$), 3.54 (2H, mc, (*Z*)-**23**, $\mathrm{OC}H_2\mathrm{CH_3}$), 3.58 (3H, s, (*Z*)-**23**, $\mathrm{NCH_3}$), 3.61 (3H, s, (*E*)-**23**, $\mathrm{NCH_3}$), 3.63 (2H, d, ^2J = 13.2 Hz, (*E*)-**23**, $\mathrm{NCH_2}$), 4.10 (2H, d, ^2J = 13.2 Hz, (*E*)-**23**, $\mathrm{NCH_2}$), 4.61 (2H, d, ^2J = 13.2 Hz, (*Z*)-**23**, $\mathrm{NCH_2}$), 5.79 (1H, s, (*Z*)-**23**, $\mathrm{{=}CH}$), 6.18 (1H, s, (*E*)-**23**, $\mathrm{{=}CH}$), 7.01–7.30 (10H, m, (*E*/*Z*)-**23**, Ph H); ^{13}C{H} NMR (62.89 MHz, $\mathrm{CDCl_3}$, add. DEPT; δ, ppm) 15.95 (+, (*E*)-**23**, $\mathrm{OCH_2}C\mathrm{H_3}$), 16.04 (+, (*Z*)-**23**, $\mathrm{OCH_2}C\mathrm{H_3}$), 21.71, 23.20 (+, (*E*)-**23**, $\mathrm{CCH_3}$), 25.64, 27.96 (+, (*Z*)-**23**, $\mathrm{CCH_3}$), 45.74 (+, (*Z*)-**23**, $\mathrm{NCH_3}$), 45.85 (+, (*E*)-**23**, $\mathrm{NCH_3}$), 50.21 (+, (*Z*)-**23**, $\mathrm{NCH_3}$), 50.53 (+, (*E*)-**23**, $\mathrm{NCH_3}$), 52.91 (−, (*Z*)-**23**, $\mathrm{N(CH_2)_2}$), 56.10 (−, (*E*)-**23**, $\mathrm{N(CH_2)_2}$), 57.80 (−, (*Z*)-**23**, $\mathrm{O}C\mathrm{H_2CH_3}$), 60.15 (−, (*E*)-**23**, $\mathrm{O}C\mathrm{H_2CH_3}$), 78.99 ($\mathrm{C_{quat}}$, (*E*)-**23**, $C\mathrm{(CH_3)_2}$), 79.59 ($\mathrm{C_{quat}}$, (*Z*)-**23**, $C\mathrm{(CH_3)_2}$), 117.81 (+, (*E*)-**23**, C2), 117.84 (+, (*Z*)-**23**, C2), 127.12, 127.38, 128.13, 128.29, 128.72, 129.24 (+, (*E*/*Z*)-**23**, Ph C), 131.59 ($\mathrm{C_{quat}}$, (*E*)-**23**, Ph C), 138.60 ($\mathrm{C_{quat}}$, (*Z*)-**23**, Ph C), 139.62 ($\mathrm{C_{quat}}$, (*E*)-**23**, C3), 140.85 ($\mathrm{C_{quat}}$, (*Z*)-**23**, C3), 217.90 ($\mathrm{C_{quat}}$, (*Z*)-**23**, $\mathrm{C{=}O}$), 218.18 ($\mathrm{C_{quat}}$, (*E*)-**23**, $\mathrm{C{=}O}$), 223.24 ($\mathrm{C_{quat}}$, (*Z*)-**23**, $\mathrm{C{=}O}$), 223.55 ($\mathrm{C_{quat}}$, (*E*)-**23**, $\mathrm{C{=}O}$), 264.51 ($\mathrm{C_{quat}}$, (*E*)-**23**, C1), 268.77 ($\mathrm{C_{quat}}$, (*Z*)-**23**, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 556 (0.5 [M$^+$], 472 (1) [M$^+$ − 3CO], 444 (1) [M$^+$ − 4CO], 416 (4) [M$^+$ − 5CO], 319 (37), 304 (46), 274 (44), 184 (6), 129 (6), 108 (45), 91 (100) [$\mathrm{CH_2Ph^+}$], 80 (65), 52 (66) [Cr$^+$].

Pentacarbonyl[(*E*)-1-(dimethylamino)-3-phenyl-3-(diisopropylamino)propenylidene]chromium ((*E*)-24). To 240 mg (0.592 mmol) of pentacarbonyl[3-phenyl-3-(diisopropylamino)-1,2-propadienylidene]chromium (**13a**) in 15 mL of diethyl ether was added dimethylamine at 20 °C until a change of color was observed, and the solvent was removed under reduced pressure. Chromatography (30 g of silica gel, pentane/diethyl ether, 3:1) yielded 261 mg (98%) of (*E*)-**24**: R_f = 0.40 (pentane/diethyl ether, 3:1), yellow crystals, mp 109 °C; IR (KBr, cm^{-1}) 3026, 2975, 2940, 2881, 2050 ($\mathrm{C{=}O}$), 1971 ($\mathrm{C{=}O}$), 1958 ($\mathrm{C{=}O}$), 1581, 1520, 1498, 1450, 1375, 1280, 1220, 1198, 1158, 1127, 1100, 1030, 933, 869, 798, 780, 738, 707, 680; ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$; δ, ppm) 1.14 (6H, d, ^3J = 7.1 Hz, $\mathrm{NCH(C}H_3\mathrm{)_2}$), 1.18 (6H, d, ^3J = 7.1 Hz, $\mathrm{NCH(C}H_3\mathrm{)_2}$), 2.50 (3H, s, $\mathrm{NCH_3}$), 3.21 (3H, s, $\mathrm{NCH_3}$), 3.45 (1H, sep, ^3J = 7.1 Hz, $\mathrm{NC}H\mathrm{(CH_3)_2}$), 3.49 (1H, sep, ^3J = 7.1 Hz, $\mathrm{NC}H\mathrm{(CH_3)_2}$), 6.22 (1H, s, $\mathrm{{=}CH}$), 7.08–7.24 (5H, m, Ph H); ^{13}C{H} NMR (62.89 MHz, $\mathrm{CDCl_3}$, add. DEPT; δ, ppm) 20.54 (+, $\mathrm{NCH(}C\mathrm{H_3)_2}$), 23.22 (+, $\mathrm{NCH(}C\mathrm{H_3)_2}$), 45.89 (+, $\mathrm{N}C\mathrm{H(CH_3)_2}$), 49.03 (+, $\mathrm{NCH_3}$), 49.75 (+, $\mathrm{NCH_3}$), 120.09 (+, C2), 128.25, 128.39, 129.56 (+, Ph C), 139.66, 139.90 ($\mathrm{C_{quat}}$, Ph C, C3), 218.61, 224.07 ($\mathrm{C_{quat}}$, $\mathrm{C{=}O}$), 258.75 ($\mathrm{C_{quat}}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 450 (29) [M$^+$], 422 (8) [M$^+$ − CO], 394 (1) [M$^+$ − 2CO], 366 (18) [M$^+$ − 3CO], 338 (10) [M$^+$ − 4CO], 310 (100) [M$^+$ − 5CO], 267 (16), 257 (8), 225 (7), 214 (7), 155 (20), 130 (6), 95 (4), 93 (3), 52 (17) [Cr$^+$].

Reaction of 1f with LiTMP. To a solution of 200 mg (0.46 mmol) pentacarbonyl[3-(diethylamino)-1,4-diethoxy-4-methylpentenylidene]chromium in 10 mL of diethyl ether was added 0.2 mL (0.23 mmol) of 1.1 M LiTMP in diethyl ether at −78 °C. The reaction mixture was warmed to 20 °C for 15 min and then quenched with 1 mL of $\mathrm{D_2O}$. The solvent of the organic layer was removed under reduced pressure and gave crude product. Nondeuterated **4f** (180 mg) was obtained after chromatography (pentane/diethyl ether 5:1; 20 g of silica gel).

Addition of LiOEt to 12f. LiOEt (40 mg, 0.77 mmol) was added to a solution of 300 mg (0.77 mmol) pentacarbonyl[3-(diethylamino)-4-ethoxy-1,2-pentadienylidene]chromium (**12f**) in 10 mL of diethyl ether or tetrahydrofuran, respectively. The reaction mixture was stirred at 20 °C for 3 h and heated to reflux for 5 h, followed by quenching with 10 mL of water. The aqueous layer was extracted with 3 × 10 mL of diethyl ether, and the combined organic layers were washed with 3 × 10 mL of water and dried over $\mathrm{MgSO_4}$. Evaporation of the solvent yielded quantitatively **12f**.

General Procedure for the Addition of Lithium Amides to Alkynylcarbene Complexes 1a–c,f. To a solution of 0.5 mmol of pentacarbonyl[alkynylidene]chromium **1a–c,f** in 70 mL diethyl ether was added a mixture of 0.5 mmol of $\mathrm{LiNR'_2}$ and 10 mL of diethyl ether at 20 °C. The reaction mixture was stirred for 15–30 min and then quenched with 1 mL of water. The solvents were removed under reduced pressure, and the crude product was purified by chromatography (pentane/diethyl ether 5:1; 20 g of silica gel).

Pentacarbonyl[(2*E*)-3-(dimethylamino)-1-ethoxy-3-phenylpropenylidene]chromium ((*E*)-3a) and Pentacarbonyl[3-(dimethylamino)-3-phenyl-1,2-propadienylidene]chromium (11a). To 350 mg (0.57 mmol) of pentacarbonyl[1-ethoxy-3-phenylpropynylidene]chromium (**1a**)[3] was added 29 mg (0.57 mmol) of lithium dimethylamide in 11 mL of diethyl ether. After having been stirred for 30 min, the reaction mixture was purified to yield fraction I: 177 mg (29%) of (*E*)-**3a**,[4] R_f = 0.39 (pentane/diethyl ether, 5:1).

II: 85 mg (43%) of **11a**,[10] R_f = 0.04.

Pentacarbonyl[3-(dibenzylamino)-3-phenyl-1,2-propadienylidene]chromium (15a). To 350 mg (0.74 mmol) of pentacarbonyl[1-ethoxy-3-phenylpropynylidene]chromium (**1a**)[3] was added 150 mg (0.74 mmol) of lithium dibenzylamide in 15 mL of diethyl ether. After having been stirred for 15 min, the reaction mixture was purified to afford 55 mg (15%) of **15a**: R_f = 0.03 (pentane/diethyl ether, 5:1), orange crystals, mp 124 °C; IR (KBr, cm^{-1}) 3033, 2955, 2931, 2889, 2854, 2076 ($\mathrm{C{=}C{=}C}$), 1987 ($\mathrm{C{=}O}$), 1916 ($\mathrm{C{=}O}$), 1588, 1537, 1497, 1439, 1356, 1253, 1123, 1003, 953, 886, 811, 780, 701, 659; ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$; δ, ppm) 4.71 (2H, s, $\mathrm{NCH_2}$), 5.23 (2H, s, $\mathrm{NCH_2}$), 7.02–7.58 (15H, m, Ph H of $\mathrm{N(CH_2Ph)_2}$, Ph H); ^{13}C{H} NMR (62.89 MHz, $\mathrm{CDCl_3}$, add. DEPT; δ, ppm) 52.52, 57.43 (−, $\mathrm{NCH_2}$), 123.60 ($\mathrm{C_{quat}}$, C2), 126.99, 128.71, 128.86, 128.97, 129.10, 129.45 (+, Ph C), 133.45, 133.63 ($\mathrm{C_{quat}}$, Ph C), 157.65 ($\mathrm{C_{quat}}$, C3), 217.27, 223.87 ($\mathrm{C_{quat}}$, $\mathrm{C{=}O}$), 235.59 ($\mathrm{C_{quat}}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 501 (2) [M$^+$], 389 (6) [M$^+$ − 4CO], 361 (11) [M$^+$ − 5CO], 279 (11), 167 (21), 108 (72), 80 (100), 52 (91) [Cr$^+$].

Pentacarbonyl[2(*E*)-3-(dimethylamino)-3-cyclopropyl-1-ethoxypropenylidene]chromium ((*E*)-3b) and Pentacarbonyl[3-(dimethylamino)-3-cyclopropyl-1,2-propadienylidene]chromium (11b). To 318 mg (1.16 mmol) of pentacarbonyl[3-cyclopropyl-1-ethoxypropylidene]chromium (**1b**)[5] was added 59 mg (1.16 mmol) of lithium dimethylamide in 23 mL of diethyl ether. After having been stirred for 20 min, the reaction mixture was purified to yield fraction I: 82 mg (20%) of (*E*)-**3b**:[5] R_f = 0.31 (pentane/diethyl ether/dichloromethane, 3:3:1).

II: 147 mg (40%) of **11b**, $R_f = 0.07$, orange crystals, mp 107 °C; IR (KBr, cm^{-1}): 2998, 2941, 2078 (C=C=C), 2017 (C=O), 1973 (C=O), 1921 (C=O), 1575, 1424, 1373, 1262, 1162, 1050, 944, 866, 713, 658; ^1H NMR (250 MHz, $CDCl_3$; δ, ppm) 1.20–1.30 (2H, m, cyclopropyl CH_2), 1.42–1.53 (2H, m, cyclopropyl CH_2), 1.82–1.92 (1H, m, cyclopropyl CH), 3.46 (3H, s, NCH_3), 3.62 (3H, s, NCH_3); $^{13}C\{H\}$ NMR (62.89 MHz, $CDCl_3$, add. DEPT; δ, ppm) 13.97 (–, $\mathrm{CH}\mathit{C}_2\mathrm{H}_4$), 16.79 (+, $\mathit{C}\mathrm{HC}_2\mathrm{H}_4$), 40.25, 45.55 (+, NCH_3), 112.40 (C_{quat}, C2), 162.23 (C_{quat}, C3), 213.41 (C_{quat}, C1), 217.83, 223.19 (C_{quat}, C=O); MS (EI, 70 eV; *m/e* (relative intensity)) 313 (24) [M^+], 285 (5) [$M^+ - CO$], 257 (7) [$M^+ - 2CO$], 229 (7) [$M^+ - 3CO$], 201 (38) [$M^+ - 4CO$], 173 (100) [$M^+ - 5CO$], 130 (7), 120 (9), 86 (10), 52 (49) [Cr^+].

Pentacarbonyl[(2*Z*)-3-(cyclohexylamino)-3-cyclopropyl-1-ethoxypropenylidene]chromium ((*Z*)-10b) and Pentacarbonyl[3-(cyclohexylamino)-3-cyclopropyl-1,2-propadienylidene]chromium (18b). To 285 mg (0.90 mmol) of pentacarbonyl[3-cyclopropyl-1-ethoxypropynylidene]chromium (**1b**)[5] was added 95 mg (0.90 mmol) of lithium cyclohexylamide in 18 mL of diethyl ether. After having been stirred for 15 min, the reaction mixture was purified to afford fraction I: 134 mg (36%) of (*Z*)-**10b**, $R_f = 0.37$ (pentane/diethyl ether, 5:1).

II: 156 mg (47%) of **18b**, $R_f = 0.02$, orange crystals, mp 96 °C; IR (KBr, cm^{-1}) 3339 (NH), 2937, 2860, 2082 (C=C=C), 2011 (C=O), 1929 (C=O), 1870 (C=O), 1567, 1487, 1439, 1377, 1260, 1084, 907, 799, 775, 667; ^1H NMR (250 MHz, $CDCl_3$; δ, ppm) 1.09–2.22 (15H, m, cyclopropyl CH, cyclopropyl CH_2, cyclohexyl CH_2), 4.25 (1H, brs, NCH), 7.29 (1H, brs, NH); $^{13}C\{H\}$ NMR (62.89 MHz, $CDCl_3$, add. DEPT; δ, ppm) 13.19 (–, $\mathrm{CH}\mathit{C}_2\mathrm{H}_4$), 20.74 (+, $\mathit{C}\mathrm{HC}_2\mathrm{H}_4$), 24.38, 24.99, 32.08 (–, cyclohexyl CH_2), 57.34 (+, NCH), 110.97 (C_{quat}, C2), 161.12 (C_{quat}, C3), 217.66 (C_{quat}, C=O), 220.67 (C_{quat}, C1), 223.36 (C_{quat}, C=O); MS (EI, 70 eV; *m/e* (relative intensity)) 367 (17) [M^+], 311 (2) [$M^+ - 2CO$], 283 (5) [$M^+ - 3CO$], 255 (22) [$M^+ - 4CO$], 227 (100) [$M^+ - 5CO$], 174 (18), 108 (79), 80 (92), 52 (64) [Cr^+].

Pentacarbonyl[1-(dimethylamino)-4,4-dimethylpentynylidene]chromium (2c) and Pentacarbonyl[3-(dimethylamino)-4,4-dimethyl-1,2-pentadienylidene]chromium (11c). To 330 mg (1.21 mmol) of pentacarbonyl[1-ethoxy-4,4-dimethylpentynylidene]chromium (**1c**)[12] was added 62 mg (1.21 mmol) of lithium dimethylamide in 24 mL of diethyl ether. After having been stirred for 20 min, the reaction mixture was purified to yield fraction I: 177 mg (44%) of **2c**, $R_f = 0.80$ (pentane/diethyl ether, 5:1), yellow crystals, mp 86 °C; IR (KBr, cm^{-1}) 2973, 2932, 2901, 2868, 2188 (C≡C), 2055 (C=O), 1915 (C=O), 1527, 1455, 1401, 1364, 1267, 1160, 1070, 935, 851, 722, 660; ^1H NMR (250 MHz, $CDCl_3$; δ, ppm) 1.36 (9H, s, $C(CH_3)_3$), 3.55 (3H, s, NCH_3), 3.84 (3H, s, NCH_3); $^{13}C\{H\}$ NMR (62.89 MHz, $CDCl_3$, add. DEPT; δ, ppm) 30.05 (+, $\mathrm{C}(\mathit{C}\mathrm{H}_3)_3$), 47.03, 49.27 (+, NCH_3), 64.23 (C_{quat}, $\mathit{C}(\mathrm{CH}_3)_3$), 83.70 ($C_{quat}$, C2), 140.44 ($C_{quat}$, C3), 217.44, 224.09 ($C_{quat}$, C=O), 250.07 ($C_{quat}$, C1); MS (EI, 70 eV; *m/e* (relative intensity)) 329 (9) [M^+], 273 (5) [$M^+ - 2CO$], 245 (10) [$M^+ - 3CO$], 217 (12) [$M^+ - 4CO$], 189 (100) [$M^+ - 5CO$], 187 (6), 118 (4), 95 (4), 52 (17) [Cr^+].

II: 125 mg (31%) of **11c**,[5] $R_f = 0.06$.

Addition of $HNMe_2$ to 21. Dimethylamine was added to a solution of 80 mg (0.21 mmol) **21** in 20 mL of diethyl ether at 20 °C until no more starting material was detected by TLC. The solvents were removed under reduced pressure, and the residue was purified by chromatography (pentane/diethyl ether, 2:1; 5 g of silica gel) to yield 87 mg (98%) of (*E*)-**22**, $R_f = 0.07$.

Acknowledgment. This work was supported by the "Volkswagen-Stiftung" and the "Fonds der Chemischen Industrie" as well as by the Hoechst AG and Hüls AG through generous gifts of chemicals. M.D. and E.P. are grateful to the "Deutsche Forschungsgemeinschaft" (Graduiertenkolleg "Kinetik und Selektivität chemischer Prozesse in verdichteter, fluider Phase") and the "Stiftung Stipendienfonds des Verbands der chemischen Industrie" for fellowships.

Supplementary Material Available: Tables of crystal data and details of the structure solution, positional and displacement parameters, and bond distances and angles (10 pages). Ordering information is given on any current masthead page.

OM920235M