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Organic Syntheses *via* Transition Metal Complexes. 84.[1] Stereoselective Route to (Aminoalkynylcarbene)chromium Complexes *via* Addition of (1-Alkynyl)lithium Compounds to Isocyanide Ligands

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N-Lithio iminoacylates $(CO)_5Cr{=}C(NRLi)C{\equiv}CR^1$ [(E)-**3a**−**e**] are obtained by addition of 1-lithioalkynes $LiC{\equiv}CR^1$ (**2a,b**) (R^1 = Ph, $SiMe_3$) to isocyano complexes $(CO)_5Cr(CNR)$ (**1a**−**d**) (R = c-C_6H_{11}, Ph, p-MeC_6H_4, o-MeC_6H_4). Protonation and alkylation, respectively, of the N-cyclohexyl compound **3a** with EX {H_2O, MeI, $[Et_3O]BF_4$, $BrCH_2CH(O)CH_2$} (**5a**−**d**) produces aminocarbene complexes $(CO)_5Cr{=}C(NRE)C{\equiv}CR^1$ (**6a**−**d**) in 75−90% overall yield. The latter compounds are generated stereoselectively in (E) configuration (E/Z = 14:1 to 29:1) by kinetic reaction control and are isomerized at 80 °C to give the corresponding (Z) stereoisomers as main products. The stereochemical course of alkylation of **3** is strongly influenced by substituents at the nitrogen atom of **3** as well as by the type of electrophile EX involved. Alkylation of N-aryl compounds $(CO)_5Cr{=}C(NArLi)C{\equiv}CR^1$ (**3c**−**e**) (Ar = Ph, p-MeC_6H_4, o-MeC_6H_4) yields aminocarbene complexes **6** predominately of (Z) configuration by kinetic reaction control. Parent (CH)-alkynylcarbene complexes $(CO)_5Cr{=}C(N$-c-$C_6H_{11}R)C{\equiv}CH$ (**6h,i**) (R = H, Me) were obtained by fluorine-induced desilylation of the Me_3Si derivatives **6e,f**. (Z)-**6i** was characterized by X-ray diffraction.

Aminolysis of Alkynylcarbene Complexes

We recently reported on a novel [3 + 2] cyclopentadiene annulation[2d] reaction of ethoxyalkynylcarbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CR$ (M = Cr, W) to enamines.[2] In context with the extension of our investigation also to amino derivatives $(CO)_5Cr{=}C(NRR^1)C{\equiv}CR$, we found that the access to such compounds was rather limited. Even though it is well established that aminolysis of $(CO)_5Cr{=}C(OEt)C{\equiv}CPh$ with dimethylamine produces the aminoalkynylcarbene complex $(CO)_5Cr{=}C(NMe_2)C{\equiv}CPh$ together with the Michael adduct $(CO)_5Cr{=}C(OEt)CH{=}C(NMe_2)Ph$,[3] it was shown only recently that high-yield formation of aminoalkynylcarbene complexes by aminolysis of the corresponding ethoxyalkynylcarbene complexes is achieved in rare cases only,[4−6] while for most cases (2-aminoalkenyl)carbene and/or 3-aminoallenylidene complexes[4,7] are obtained as major products. Severe restrictions with respect to the formation of 1-aminoalkynylcarbene complexes are encountered especially with arylamines and also with sterically congested aliphatic amines. We thus were probing a different approach to the generation of 1-aminoalkynylcarbene complexes *via* addition of 1-lithioalkynes to isocyanide complexes $(CO)_5Cr$(isocyanide).

Isocyanides and Isocyanide Ligands

Isocyanides possessing α-hydrogen atoms undergo deprotonation by organolithium compounds rather than addition.[8] In the absence of a α-hydrogen atom, isocyanides react by insertion into an alkyllithium bond to give (iminoacyl)lithium compounds, for which both a η^1-bonding mode **A** and a η^2-bonding mode **B** (implying aminocarbene character of this species) have been suggested (Scheme 1).

(Iminoacyl)lithium derivatives (=1-lithio aldimines[9]) are sufficiently stable to be used in further reactions.[10] Multiple insertion of isocyanides is possible and leads to production of oligomers[11] or polymers.[12] An umpolung of the reactivity pattern of isocyanides is achieved

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Scheme 1. Addition of Organolithium Compounds to Isocyanides and Isocyanide Ligands

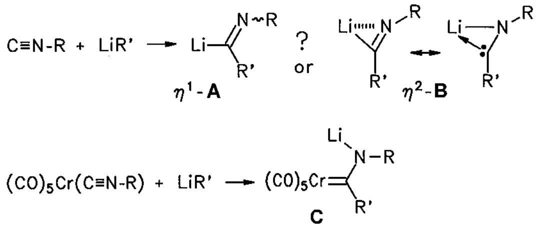
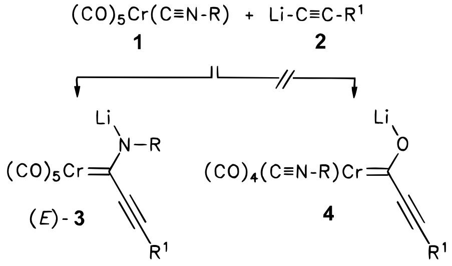


Table 1. Substitution Pattern of Compounds 1−3

1	R	2	R^1	3	R	R^1
a	*c*-C_6H_{11}	**a**	Ph	**a**	*c*-C_6H_{11}	Ph
b	Ph	**b**	$SiMe_3$	**b**	*c*-C_6H_{11}	$SiMe_3$
c	*p*-MeC_6H_4			**c**	Ph	Ph
d	*o*-$MeOC_6H_4$			**d**	*p*-MeC_6H_4	Ph
				e	*o*-$MeOC_6H_4$	Ph

Scheme 2. Regioselective Formation of Aminoalkynylcarbene Complexes 3 *via* Addition of 1-Lithioalkynes 2 to Isocyanide Complexes 1



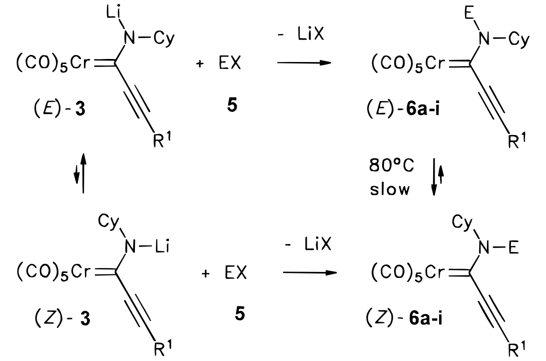
through coordination to a transition metal moiety.[13] The addition of an organolithium compound LiR′ to the isocyano complexes $(CO)_5Cr(CNR)$ was found to be highly regioselective and also stereoselective with respect to the formation of an aminocarbene adduct **C** of (*E*) configuration (Scheme 1).

Aminoalkynylcarbene Complexes

Isocyano pentacarbonylchromium complexes **1a**−**d** (Table 1) give *N*-lithio iminoacylates (*E*)-**3a**−**e** by 1,2-addition of 1-lithioalkynes **2a,b**. This reaction is slow (20−40 h in THF at 20 °C) but highly regioselective with respect to an addition of **2** to the carbon atom of the isocyanide ligand. Formation of an *O*-lithio acylate **4** by addition of **2** to a carbon monoxide ligand of **1a**−**d** has not been observed so far (Scheme 2).[14]

The reaction progress between **1** and **2** has been monitored by ^1H NMR spectra of samples being quenched with water to give the corresponding (*NH*-amino)-carbene complexes **6**. Furthermore, the reaction could be most conveniently followed by TLC, since (red) compounds **6** are spontaneously generated by hydrolysis of (*E*)-**3** on silica gel (Scheme 3) and are easily distinguished from (almost colorless) starting material **1**. The lithium complexes (*E*)-**3a**−**e** have not been isolated but instead were transformed into aminocarbene complexes **6** by addition of electrophilic reagents (Schemes 3 and 4, Tables 2 and 3).

Scheme 3. Generation and Stereochemistry of (Cyclohexylamino)alkynylcarbene Complexes 6a−i



Scheme 4. Mechanistic Considerations

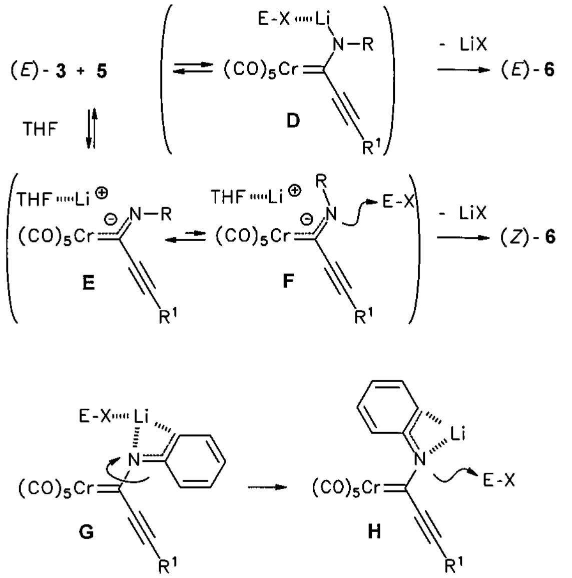


Table 2. Electrophilic Agents for Quenching of *N*-Lithio Compounds 3a,b

5	EX	5	EX
a	H_2O or H_3PO_4	**d**	$BrCH_2$-CH(-O-)CH_2
b	MeI	**e**	$ClCH_2$-CH(-O-)CH_2
c	$[Et_3O]BF_4$	**f**	$BrCH_2$-CH=CH_2

Stereochemistry of Aminoalkynylcarbene Complexes 6

The high stereoselectivity encountered in the formation of aminoalkynylcarbene complexes **6** *via* the isocyanide route is governed by two factors: (a) kinetic reaction control by (supposedly) *anti* addition of the 1-lithioalkyne to the isocyano group with formation of (*E*)-**3**; (b) (possibly) stabilization of the (*E*) configuration by an interaction of the lithium atom with the nitrogen atom as well as an oxygen atom (or two neighboring oxygen atoms) of the (negatively polarized) $(CO)_5Cr$ moiety (Scheme 3). Conclusion as to the configuration of (*E*)-**3a** is based on the configuration of the (*NH*-

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Table 3. Substitution Pattern and (*E*/*Z*) Ratio of 6 under Different Reaction Conditions

6	R	R^1	E	EX	(*E*)/(*Z*)-**6** (%)		
					[a]	[b]	[c]
a	c-C_6H_{11}	Ph	H	**5a**	85/5	[d]	[d]
b	c-C_6H_{11}	Ph	Me	**5b**	82/5	1/1	1/2
c	c-C_6H_{11}	Ph	Et	**5c**	87/3	1/9	1/9
d	c-C_6H_{11}	Ph	$CH_2CH(O)CH_2$	**5d**	70/5	1/15	1/15
	c-C_6H_{11}	Ph	$CH_2CH(O)CH_2$	**5e**	5/76	1/15	1/15
e	c-C_6H_{11}	$SiMe_3$	H	**5a**	82/0	[d]	[d]
f	c-C_6H_{11}	$SiMe_3$	Me	**5b**	69/5	3/1	3/2
g	c-C_6H_{11}	$SiMe_3$	Et	**5c**	87/5	4/1	1/1
h	c-C_6H_{11}	H[e]	H		92/0	[d]	[d]
i	c-C_6H_{11}	H[f]	Me		90/0	2/3[g]	1/3[h]
j	Ph	Ph	H	**5a**	85/0	[d]	[d]
k	Ph	Ph	Et	**5b**	5/74	1/1	1/1
l	Ph	Ph	$CH_2CH{=}CH_2$	**5f**	0/75	[d]	[d]
m	*p*-MeC_6H_4	Ph	Et	**5b**	5/83	1/1	1/1
n	*o*-$MeOC_6H_4$	Ph	H	**5a**	80/0	[d]	[d]
o	*o*-$MeOC_6H_4$	Ph	$CH_2CH(O)CH_2$	**5e**	35/45	35/45	35/45

[a] Product ratio (*E*)/(*Z*)-**6** of the initial reaction mixture (according to ^1H NMR analysis). [b] Product ratio (*E*)/(*Z*)-**6** obtained from the (*E*) isomer after 1.5 h, 80 °C. [c] Product ratio after 7.5 h, 80 °C. [d] Product ratio not determined. [e] Generated by desilylation of **5a**. [f] Generated by desilylation of **5b**. [g] Isomer ratio produced from isomerically pure (*E*) isomer after 1.5 h, 50 °C. [h] Product ratio after 7.5 h, 50 °C.

amino)carbene complex (*E*)-**6a**, obtained by hydrolysis of the lithio compound. It is asumed that protonation of (*E*)-**3a** would proceed with retention of configuration.

Protonation and alkylation, respectively, of the *N*-lithio *N*-cyclohexyl compound **3a** with (polar) electrophilic reagents **5a**−**c** affords aminocarbene complexes **6a**−**c** of (*E*) configuration (Table 3). Retention of configuration on alkylation of **3a** may be due to initial formation of an adduct **D** (Scheme 4). Alkylation of **3a** with 1-*bromo*-2,3-epoxypropane (**5d**) follows the same route and accordingly yields compound (*E*)-**6d**. It is obvious that compound (*E*)-**6d** must result from kinetic reaction control, since isomerically pure samples of both stereoisomers, (*E*)-**6d** and (*Z*)-**6d**, at 80 °C produce a identical (E/Z) = 1/15 equilibrium mixtures. Quite unexpected, alkylation of **3a** with 1-*chloro*-2,3-epoxypropane (**5e**) involves an inversion of configuration to give (*Z*)-**6d** as the main product. It appears to us that the striking change of stereochemistry observed on alkylation of **3a** with **5d** and **5e**, respectively, could be associated with a change of reaction mechanism. An overall inversion of configuration *via* intermediates **H** and **F** may become more effective if weaker electrophiles other than **5a**−**d** are employed (Scheme 4).

The stereoisomers (*E*)-**6a**−**d** of the *N*-cyclohexyl complexes are destabilized by a sterically unfavorable *syn*-periplanar arrangement of the alkynyl toward the cyclohexyl unit. Steric constraint is reduced in the corresponding (*Z*) isomers, since the plane defined by the carbene ligand bisects the angle between two *cis* carbonyl ligands of the $(CO)_5Cr$ moiety (see Figure 1). Accordingly, thermal (E/Z) isomerization of these compounds at 80 °C affords mixtures, in which the (*Z*) isomers predominate (Table 3). Other than with aminoalkynylcarbene complexes **6a**−**e**, the (*E*) isomers of *N*-lithio compounds **3a**−**e** are assumed to be stabilized by chelate interaction with the oxygen atoms of the $(CO)_5Cr$ unit (*v.s.*). Furthermore, the lithio compounds (*E*)-**3a**−**e** are expected to be less reactive toward electrophilic attack for steric reasons than the corresponding (*Z*)-**3a**−**e** isomers.

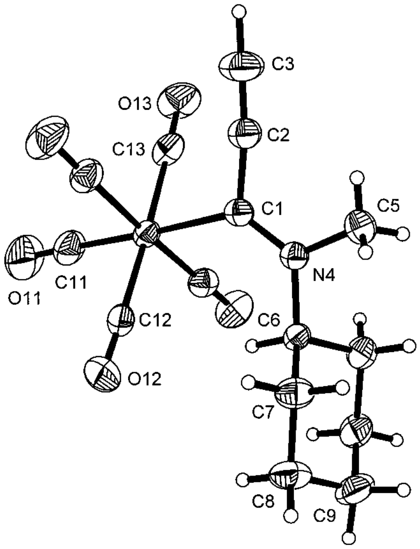

Figure 1. Molecular structure of (*CH*)-alkynylcarbene complex (*Z*)-**6i**.

Alkylation of *N*-aryl derivatives of **3** leads to production of aminocarbene complexes **6** with (*E*/*Z*) ratios different from those found for *N*-alkyl derivatives of **3**. While protonation of the *N*-lithio *N*-aryl compounds **3c,e** affords (*NH*)-aminocarbene complexes **6j,n** of (*E*) configuration, alkylation of **3c,d** with $[Et_3O]BF_4$ (**5c**) or $BrCH_2CH{=}CH_2$ (**5f**) yields aminocarbene complexes **6k**−**m** of (*Z*) configuration mainly. Since thermal isomerization of (*Z*)-**6k,m** produces (*E*/*Z*) mixtures in approximately 1:1 ratio, the latter compounds appear to result from kinetic reaction control (Table 3). The principles outlined above for alkylation of the *N*-alkyl compound **3a** may apply also for *N*-aryl compounds, except for two points: (a) An (*E*/*Z*) isomerization of *N*-aryl *N*-lithium derivatives **3c,d** by rotation of the $C_{carbene}{-}N$ bond is expected to become easier due to charge delocalization into the aryl group (eventually involving an interaction of the lithium atom with an *ortho* position of the aryl group) (Scheme 4). (b) The overall nucleophilicity of the *N*-aryl compounds **3c**−**e** is expected to be lower than that of *N*-alkyl compounds **3a,b**. In line with these expectation, hydrolysis seems to follow the route *via* intermediate **G**, while other electrophiles seem to prefer the reaction path *via* a (*Z*)-**3** intermediate **H**.

(*CH*)-Alkynylcarbene Complexes

Much attention has been focused recently on the preparation of parent alkynylcarbene complexes $(CO)_5M{=}C(NR_2)C{\equiv}CH$ (M = Cr, W) having a terminal alkynyl group. Concern over the assignment of structures was raised by controversal reports, in which an allenylidene $(CO)_5Cr{=}C{=}C{=}CH(NR_2)$[4b] as well as an alkynyl structure[6] has been suggested, based on spectroscopic evidence. Since a crystal structure analysis has not been carried out so far, we wish to report on successful generation of three (*CH*)-alkynylcarbene complexes (*E*)-**6h**, (*E*)-**6i**, and (*Z*)-**6i** by fluorine-induced desilylation of compounds (*E*)-**6e,f** and the unambiguous structure assignment on the basis of an X-ray structure determination of (*Z*)-**6i** (Figure 1).

Figure 1 shows the molecular structure of complex (*Z*)-**6i** and Tables 4 and 5 give the experimental details

Scheme 5. Generation of (*CH*)-Alkynylcarbene Complexes 6h,i

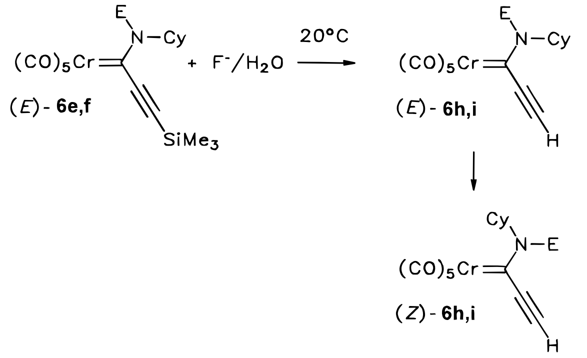

Table 4. Crystal Data and Structure Analysis for (*Z*)-6i and (*Z*)-6k

	(*Z*)-**6i**	(*Z*)-**6k**
empirical formula	$C_{15}H_{15}NO_5Cr$	$C_{22}H_{15}NO_5Cr$
fw	341.28	425.35
temp(K)	223(2)	223(2)
wavelength (Å)	0.71073	0.71073
cryst system	orthorhombic	monoclinic
space group	*Pnma* (No. 62)	$P2_1/c$ (No. 14)
a (Å)	14.707(1)	11.403(1)
b (Å)	10.248(2)	9.868(1)
c (Å)	10.663(1)	18.514(2)
β (deg)		98.51(1)
V (Å^3)	1607.1(4)	2060.3(4)
Z	4	4
calcd density (mg m^3)	1.411	1.371
F(000)	704	872
μ (mm^{-1})	0.73	0.59
abs corr	Ψ-scan	Ψ-scan
Θ-range (deg)	2.3–26.3	2.3–26.3
data collcd	1724	4311
data obsd ($I \geq 2\sigma(I)$)	1433	4174
refined params	120	263
R (all data/obsd)	0.048/0.033	0.045/0.033
wR^2 (all data/obsd)	0.103/0.087	0.102/0.093
diff Fourier (e Å^{-3})	0.38/−0.33	0.54/−0.37
diffractometer	Enraf-Nonius MACHIII	
programs used	SHELX86, SHELX93, XP	

Table 5. Selected Bond Lengths (Å) and Angles (deg) for (*Z*)-6i

Cr–C(11)	1.869(3)	N(4)–C(6)	1.482(3)
Cr–C(12)	1.900(2)	C(6)–C(7)	1.528(2)
Cr–C(13)	1.900(2)	C(7)–C(8)	1.529(3)
Cr–C(1)	2.117(3)	C(8)–C(9)	1.517(3)
C(1)–N(4)	1.313(4)	C(11)–O(11)	1.147(4)
C(1)–C(2)	1.444(4)	C(12)–O(12)	1.141(3)
C(2)–C(3)	1.181(5)	C(13)–O(13)	1.139(3)
N(4)–C(5)	1.469(4)		
C(13)–Cr–C(1)	88.3(1)	C(5)–N(4)–C(6)	115.7(2)
N(4)–C(1)–C(2)	114.4(3)	N(4)–C(6)–C(7)	112.0(1)
N(4)–C(1)–Cr	132.6(2)	C(7)[a]–C(6)–C(7)	111.5(2)
C(2)–C(1)–Cr	112.9(2)	C(6)–C(7)–C(8)	109.1(2)
C(3)–C(2)–C(1)	172.1(4)	C(9)–C(8)–C(7)	111.2(2)
C(1)–N(4)–C(5)	122.6(2)	C(8)[a]–C(9)–C(8)	111.3(3)
C(1)–N(4)–C(6)	121.7(2)		

[a] Symmetry transformations used to generate equivalent atoms: (a) *x*, $-y + 1/2$, *z*.

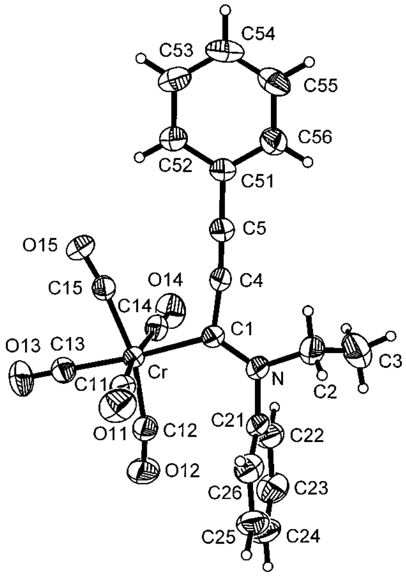

Figure 2. Molecular structure of *N*-phenylaminocarbene complex (*Z*)-**6k**.

Table 6. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Paremters (Å^3 × 10^3) for (*Z*)-6i

	x	*y*	*z*	*U*(eq)[a]
Cr	3528(1)	2500	9821(1)	28(1)
C(1)	4819(2)	2500	8943(3)	26(1)
C(2)	5562(2)	2500	9827	35(1)
C(3)	6092(3)	2500	10660(4)	54(1)
N(4)	5070(2)	2500	7761(2)	26(1)
C(5)	6029(2)	2500	7375(3)	34(1)
C(6)	4397(2)	2500	6728(2)	26(1)
C(7)	4460(2)	1268(2)	5926(2)	37(1)
C(8)	3694(2)	1277(3)	4957(2)	44(1)
C(9)	3727(3)	2500	4156(3)	51(1)
C(11)	1716(2)	2500	11144(3)	73(1)
C(12)	3111(1)	1139(2)	8757(2)	33(1)
O(12)	2854(1)	303(2)	8146(2)	49(1)
C(13)	3972(2)	1207(2)	10943(2)	38(1)
O(13)	4230(2)	449(2)	11637(2)	61(1)

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

of the X-ray structure analysis. The plane defined by N–C1–C2 approximately bisects the angle between two neighboring carbonyl groups at the chromium atom with C2–C1–Cr–C13 = 44.2°. The C_3 unit C1–C2–C3 = 172.1(4)° is almost linear, as has been found with alkynylcarbene complexes of related structures.[6,15,16] The distance C2–C3 of 1.181(5) Å lies within the normal range of a C≡C bond, and the distances Cr=C of 2.117(3) Å and C1–N of 1.313(4) Åcorrespond to those found in other (aminocarbene)chromium complexes [e.g. $(CO)_5Cr{=}C(NEt_2)Cl$:[17] Cr=C, 2.110(5) Å, C1–N, 1.299(8) Å].

(1-Arylamino)alkynylcarbene Complexes

An X-ray structure determination of an (*N*-arylamino)alkynylcarbene complex has not yet been reported. Figure 2 shows the molecular structure of complex (*Z*)-**6k**, and Tables 4 and 6 give experimental details of the X-ray structure analysis. The plane defined by N-C1–C2 is almost coplanar with two *cis* carbonyl groups at the chromium atom with C4–C1–Cr–C15 = 8.8°. The *N*-Ph group adopts a conformation C1–N–C21–C22 = 88.5°, which excludes π conjugation. Therefore, the bond distance N–C21 of 1.447(2) Å from the nitrogen atom to the aryl unit is only slightly shorter than N–C2 of 1.493(3) Å to the alkyl group. The carbon skeleton

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[15] Huttner, G.; Lorenz, H. *Chem. Ber.* **1975**, *108*, 1864–1870.

[16] Aumann, R.; Jasper, B.; Fröhlich, R. *Organometallics* **1995**, *14*, 2447–2455.

[17] Huttner, G.; Frank, A.; Fischer, E. O.; Kleine, W. *J. Organomet. Chem.* **1977**, *141*, C17–C20.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for (*Z*)-6k

Cr−C(13)	1.866(2)	C(14)−O(14)	1.135(3)
Cr−C(11)	1.883(2)	C(15)−O(15)	1.143(2)
Cr−C(12)	1.892(2)	C(1)−N	1.322(2)
Cr−C(14)	1.895(2)	C(1)−C(4)	1.427(3)
Cr−C(15)	1.898(2)	N−C(21)	1.447(2)
Cr−C(1)	2.100(2)	N−C(2)	1.493(3)
C(11)−O(11)	1.141(3)	C(2)−C(3)	1.440(5)
C(12)−O(12)	1.146(2)	C(4)−C(5)	1.199(3)
C(13)−O(13)	1.145(2)	C(5)−C(51)	1.432(3)
C(13)−Cr−C(1)	176.05(8)	C(4)−C(1)−Cr	115.2(1)
C(11)−Cr−C(1)	84.91(8)	C(1)−N−C(21)	122.0(2)
C(12)−Cr−C(1)	101.20(8)	C(1)−N−C(2)	124.7(2)
C(14)−Cr−C(1)	84.98(8)	C(21)−N−C(2)	113.2(2)
C(15)−Cr−C(1)	92.54(8)	C(3)−C(2)−N	114.1(3)
N−C(1)−C(4)	114.6(2)	C(5)−C(4)−C(1)	173.8(2)
N−C(1)−Cr	130.2(1)	C(4)−C(5)−C(51)	178.9(2)

Table 8. Atomic Coordinates ($\times 10^4$ and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for (*Z*)-6k

	x	*y*	*z*	*U*(eq)[a]
Cr	8968(1)	1368(1)	2890(1)	29(1)
C(11)	8429(2)	3121(2)	2608(1)	39(1)
O(11)	8095(2)	4191(2)	2464(1)	62(1)
C(12)	7432(2)	687(2)	2556(1)	43(1)
O(12)	6559(2)	271(2)	2250(1)	67(1)
C(13)	9247(2)	826(2)	1965(1)	40(1)
O(13)	9404(2)	480(2)	1396(1)	60(1)
C(14)	9446(2)	−308(2)	3339(1)	40(1)
O(14)	9733(2)	−1296(2)	3627(1)	64(1)
C(15)	10562(2)	1981(2)	2988(1)	35(1)
O(15)	11516(1)	2322(2)	2976(1)	50(1)
C(1)	8781(2)	2002(2)	3950(1)	34(1)
N	7819(1)	2108(2)	4268(1)	47(1)
C(21)	6670(2)	1651(2)	3915(1)	40(1)
C(22)	6326(2)	332(3)	4000(1)	53(1)
C(23)	5186(2)	−59(2)	3696(2)	62(1)
C(24)	4428(2)	855(3)	3321(1)	58(1)
C(25)	4782(2)	2151(3)	3235(1)	56(1)
C(26)	5912(2)	2564(2)	3535(1)	48(1)
C(2)	7779(2)	2772(4)	4988(1)	79(1)
C(3)	7426(3)	1883(6)	5534(2)	125(2)
C(4)	9848(2)	2436(2)	4390(1)	40(1)
C(5)	10802(2)	2751(2)	4709(1)	41(1)
C(51)	11951(2)	3108(2)	5081(1)	40(1)
C(52)	12927(2)	3088(3)	4713(1)	60(1)
C(53)	14040(2)	3409(3)	5081(2)	69(1)
C(54)	14188(2)	3739(3)	5806(2)	61(1)
C(55)	13234(2)	3760(3)	6171(1)	55(1)
C(56)	12113(2)	3458(2)	5816(1)	47(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized **U***ij* tensor.

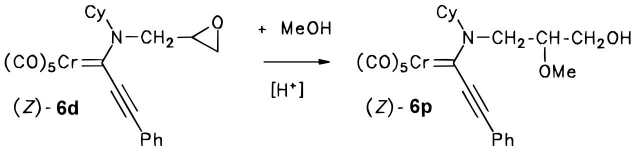
C1−C4−C5 of 173.8(2)° is slightly bent, as has been found with alkynylcarbene complexes of related structures.[15,16] A deviation from linearity is also found for Cr−C12−O12 = 169.4(2)°. The distance C4−C5 of 1.199(3) Å lies within the normal range of a C≡C bond, and the distances Cr=C of 2.100(2) Å and C1−N of 1.322(2) Å resemble those found for compound (*Z*)-**6i**.

Spectroscopy

Spectroscopic features characteristic of aminoalkynylcarbene complexes **6** comprise the ν(C≡C) band at 2155−2168 cm^{-1} in the IR spectrum and ^{13}C NMR signals of C1 (δ 245−260), C2 (R^1 = Ph, δ 91−94; $SiMe_3$, 104−106; H, 82−83), and C3 (R^1 = Ph, δ 118−124; $SiMe_3$, 139−140; H, 117−118).

The configurational assignment of (*NH*)-aminocarbene complexes **6a,h** is based on the ^3J(C,H) coupling constants of the *H*NC*C*^{2}≡C^3 unit, which strongly depend on the dihedral angle ^3J(C,H)-*trans* ≫ ^3J(C,H)-*cis* {e.g. (*E*)-**6a**, δ 122.3 [Cq, ^4J(C,H) < 1 Hz, C3], 89.5 [Cq, ^3J(C,H)-*trans* = 17 Hz, C2]; (*Z*)-**6a**, δ 118.4 [Cq, ^4J(C,H)- < 1 Hz, C3], 93.4 [Cq, ^3J(C,N*H*)-*cis* ≤ 1 Hz, C2]}. The [ν(N−H)] frequencies in the IR spectrum of (*E*) isomers are shifted to higher frequencies than in the corresponding (*Z*) isomer[18] {e.g. (*E*)-**6a**, [ν(N−H)] 3363.4 cm^{-1}; (*Z*)-**6a**, 3300.0}.

Scheme 6. Transformation of Epoxy Derivatives 6d



The presence of a C^2≡C^{3}H moiety in the N−Me derivative (*E*)-**6i** is indicated by the coupling constants *J*(C,H) {δ 118.2 [CH, ^1J(C,H) = 255 Hz, C3), 83.5 [Cq, ^2J(C,H) = 48 Hz, C2]}, which are almost identical to those found in the corresponding N−H compound (*E*)-**6h** {δ 118.1 [CH, ^1J(C,H) = 255 Hz, C3], 82.5 [Cq, ^2J(C,H) = 48 Hz, ^3J(C,N*H*) = 17, C2]}.

Configurational assignment of the *N*-cyclohexyl derivatives **6a−i** is easily achieved, if NMR spectra of *both* stereoisomers are available, since the proton as well as the carbon signal of the N−CH unit is shifted downfield, if arranged toward the metal unit (e.g. δ (N−C*H*): (*E*)-**6c**, 4.50; (*Z*)-**6c**, 5.00. δ(N−CH_2): (*E*)-**6c**, 3.90; (*Z*)-**6c**, 3.32. δ(N−*C*H): (*E*)-**6c**, 69.9; (*Z*)-**6c**, 71.4. δ(N−*C*H_2): (*E*)-**6c**, 51.4; (*Z*)-**6c**, 47.8).

Methanolysis of Epoxide 6d

The epoxy derivatives **6d,o** were subjected to further transformations. It has been shown that, e.g., methanolysis of (*Z*)-**6d** in presence of an acid catalyst affords the ether (*Z*)-**6p** with retention of configuration. This reaction may exemplify that the isocyanide route to aminocarbene complexes opens a means for the stereoselective generation of highly substituted compounds.

Experimental Section

All operations were performed under argon. Solvents were dried by distillation from sodium/benzophenone. Melting points are uncorrected. Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were obtained with Bruker WM 300 and WP 360 spectrometers. (Multiplicities were determined by DEPT. Chemical shifts refer to δ_{TMS} = 0.00 ppm.) Other analyses: IR Digilab FTS 45; MS Finnigan MAT 312; elemental analysis, Perkin-Elmer 240 elemental analyzer; column chromatography, Merck-Kieselgel 100; TLC, Merck DC-Alufolien Kieselgel 60 F 254. R_f values refer to TLC tests.

Pentacarbonyl[1-(cyclohexylamino)-3-phenylpropynylidene]chromium [(*E*)-6a and (*Z*)-6a]. Pentacarbonyl(cyclohexylisocyano)chromium (**1a**) (301 mg, 1.00 mmol) in 1 mL of dry THF is added to (phenylethynyl)lithium (**2a**) in 3 mL of dry THF [freshly prepared by reaction of *n*-butyllithium (1.50 mL of a 1.6 M solution in hexane) with phenylacetylene (2.55 mg, 2.50 mmol) in 3 mL of THF at 20 °C] in a 5-mL screw-top vessel. The reaction is followed by TLC, by monitoring the relative intensities of compounds **1a** and **6a**. While the mixture gradually turns brownish, compound **1a** is con-

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[18] Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1969**, *16*, 275−282; **1968**, *13*, 387−398.

sumed almost completely after approximately 35−45 h at 20 °C, after which time the solution is poured onto 10 mL of ice water. Extraction with diethyl ether affords orange crystals of (*E*)-**6a**/(*Z*)-**6a** = 17:1 (^{1}H NMR analysis). Crystallization from diethyl ether/pentane at −15 °C yields (*E*)-**6a** (342 mg, 85%, $R_f = 0.5$ in 10:1 pentane/diethyl ether, orange crystals, mp 78 °C), while (*Z*)-**6a** is accumulated in the mother liquor and can be isolated by chromatography (20 mg, 2%, $R_f = 0.2$ in 10:1 pentane/diethyl ether, yellow-orange crystals, mp 88 °C). Hydrolysis of a reaction mixture of **1a** with **2a** after 45−60 h at 20 °C leads to an increase in the relative amount of (*Z*)-**6a**.

(*E*)-6a. ^{1}H NMR (C_6H_6): δ 8.53 (1 H, s broad, NH), 7.50 and 7.03 (2:3 H, m each, Ph), 3.80 (1 H, m, N−CH, cyclohexyl), 1.60 (4 H, m, cyclohexyl), 1.10−0.90 (7 H, m, cyclohexyl). ^{13}C NMR (C_6D_6; δ) δ 252.4 [Cr=C, ^2J(C,H) = 5 Hz], 223.8 and 218.0 [1:4 C, *trans*- and *cis*-CO $Cr(CO)_5$], 131.4 (Cq, *i*-C Ph); 132.3, 130.7, and 128.9 (2:1:2, CH each, Ph); 122.3 [Cq, ^4J(C,H) < 1 Hz, C3], 89.5 [Cq, ^3J(C,H)-*trans* = 17 Hz, C2], 62.7 (N−CH); 31.9, 25.2, and 24.9 (2:2:1, CH_2 each, cyclohexyl). IR (diffuse reflection) (cm^{-1} (%)): 3363.4 (25) [ν(N−H)], 2168.5 (30) [ν(C≡C)]; 2053.3 (60), 1977.0 (40), and 1914.1 (100) [ν(C≡O)]; 1507.1 (50) [δ(N−H)]. IR (hexane): 2168.7 (10) [ν(C≡C)], 2054.4 (40), 1976.4 (10), 1935.4 (100) [ν(C≡O)]. MS (70 eV) (*m*/*e* (%)): 403 (20) [M$^+$], 375 (5), 361 (10), 347 (20), 319 (30), 291 (30), 263 (80) [M$^+$ − 5CO], 153 (30), 102 (40), 97 (30), 52 (100). Anal. Calcd for $C_{20}H_{17}CrNO_5$ (403.4): C, 59.56; H, 4.25; N, 3.47. Found: C, 59.43; H, 4.35; N, 3.53.

(*Z*)-6a. ^{1}H NMR (C_6H_6): δ 8.23 (1 H, s broad, NH), 7.70 and 7.12 (2:3 H, m each, Ph), 4.30 (1 H, m, N−CH, cyclohexyl), 1.80 (2 H, m, cyclohexyl), 1.50−0.90 (9 H, m, cyclohexyl). ^{13}C NMR (C_6D_6; δ): 249.8 [Cr=C, ^2J(C,H) < 1 Hz], 224.3 and 217.5 [1:4 C, *trans*- and *cis*-CO $Cr(CO)_5$]; 131.9, 129.5, and 128.3 (2:1:2, CH each, Ph); 122.2 (Cq, *i*-C Ph), 118.4 [Cq, ^4J(C,H) < 1 Hz, C3], 93.4 [Cq, ^3J(C,H)-*cis* ≤ 1 Hz, C2], 62.3 (N−CH); 32.6, 24.9, and 24.7 (2:1:2, CH_2 each, cyclohexyl). IR (diffuse reflection) (cm^{-1} (%)): 3300.0 (15) [ν(N−H)], 2177.3 (30) [ν(C≡C)]; 2053.7 (60), 1978.5 (40), and 1919.8 (100) [ν(C≡O)]; 1521.5 (50) [δ(N−H)].

Pentacarbonyl[1-(cyclohexylmethylamino)-3-phenylpropynylidene]chromium [(*E*)-6b and (*Z*)-6b]. Pentacarbonyl(cyclohexylisocyano)chromium (**1a**) (301 mg, 1.00 mmol) in 5 mL of dry THF is reacted as described above with (phenylethynyl)lithium (**2a**). Methyl iodide (142 mg, 1.00 mmol) is added after the starting material has been consumed. The solution is stirred for an additional 15 min at 20 °C. Chromatography on silica gel (column 20 × 2 cm) with pentane/dichloromethane (4:1) yields an orange band of (*E*)-**6b**:(*Z*)-**6b** = 16:1 (^{1}H NMR analysis). Crystallization from diethyl ether/pentane at −15 °C affords (*E*)-**6b** (341 mg, 82%, $R_f = 0.5$ in 4:1 pentane/dichloromethane, orange crystals). A ^{1}H NMR spectrum of (*E*)-**6b** in C_6D_6 at 80 °C after 1.5 h shows (*E*)/(*Z*)-**6b** = 1:1, and after 7.5 h (*E*)/(*Z*)-**6b** = 2:1.

(*E*)-6b. ^{1}H NMR (C_6H_6): δ 7.60 and 7.05 (2:3 H, m each, Ph), 4.60 (1 H, m, N−CH, cyclohexyl), 3.20 (3 H, q, N−CH_3), 1.55 (4 H, m, cyclohexyl), 1.10−0.90 (7 H, m, cyclohexyl). ^{13}C NMR (C_6D_6; δ): 247.7 (Cr=C), 225.7 and 219.0 [1:4 C, *trans*- and *cis*-CO $Cr(CO)_5$], 132.9 (Cq, *i*-C Ph); 133.0, 130.4, and 130.1 (2:1:2, CH each, Ph); 123.9 (Cq, C3), 91.7 (Cq, C2), 70.7 (N−CH), 43.1 (N−CH_3); 31.9, 26.7, and 26.1 (2:2:1, CH_2 each, cyclohexyl). IR (hexane) (cm^{-1} (%)): 2168.7 (10) [ν(C≡C)], 2054.4 (40), 1976.4 (10), 1935.4 (100) [ν(C≡O)]. MS (70 eV): *m*/*e* (%), 417 (20) [M$^+$], 389 (5), 361 (10), 333 (20), 305 (30), 277 (80) [M$^+$ − 5 CO], 225 (40), 153 (30), 129 (40), 93 (60), 52 (100). Anal. Calcd for $C_{21}H_{19}CrNO_5$ (417.4): C, 60.43; H, 4.59; N, 3.36. Found: C, 60.17; H, 4.58; N, 3.63.

(*Z*)-6b. ^{1}H NMR (C_6H_6): δ 7.54 and 7.15 (2:3 H, m each, Ph), 4.90 (1 H, m, N−CH, cyclohexyl), 2.65 (3 H, q, N−CH_3), 1.50−0.60 (10 H, m, cyclohexyl). ^{13}C NMR (C_6D_6; δ): 246.0 (Cr=C), 224.9 and 218.0 [1:4 C, *trans*- and *cis*-CO $Cr(CO)_5$]; 132.7, 130.5, and 129.6 (2:1:2, CH each, Ph); 125.0 (Cq, *i*-C Ph), 122.8 (Cq, C3), 91.8 (Cq, C2), 71.8 (N−CH), 40.3 (N−CH_3); 31.5, 25.2, and 25.0 (2:1:2, CH_2 each, cyclohexyl).

Pentacarbonyl[1-(cyclohexylethylamino)-3-phenylpropynylidene]chromium [(*E*)-6c and (*Z*)-6c]. Pentacarbonyl(cyclohexylisocyano)chromium (**1a**) (301 mg, 1.00 mmol) in 5 mL of dry THF is reacted as described above with (phenylethynyl)lithium (**2a**). The solution is quenched by addition of $[Et_3O]BF_4$ (190 mg, 1.00 mmol) in 5 mL of dichloromethane and stirred for 15 min at 20 °C. Chromatography on silica gel (column 20 × 2 cm) with pentane/dichloromethane (4:1) affords an orange band of (*E*)-**6c**:(*Z*)-**6c** = 30:1. Compound (*E*)-**6c** is obtained pure in orange crystals from diethyl ether/pentane at −15 °C (366 mg, 85%, $R_f = 0.5$ in 4:1 pentane/dichloromethane, mp 87 °C). A ^{1}H NMR spectrum of 43 mg (0.01 mmol) (*E*)-**6c** in C_6D_6 at 80 °C after 1.5 h shows (*E*)/(*Z*)-**6c** = 9:1, and after 7.5 h (*E*)/(*Z*)-**6c** = 9:1. (*Z*)-**6c** crystallizes from diethyl ether/pentane at −15 °C (38 mg, 87%, R_f = 0.5 in pentane/dichloromethane (4:1), mp 110 °C, dec).

(*E*)-6c. ^{1}H NMR (C_6D_6): δ 7.70 and 7.00 (2:3 H, m each, Ph), 4.50 (1 H, m, N−CH, cyclohexyl), 3.90 (2 H, q, N−CH_2), 1.55 (4 H, m, cyclohexyl), 1.15 (3 H, t, CH_3), 1.10−0.90 (7 H, m, cyclohexyl). ^{13}C NMR (C_6D_6; δ): 246.5 (Cr=C), 224.9 and 218.3 [1:4 C, *trans*- and *cis*-CO $Cr(CO)_5$], 132.0 (Cq, *i*-C Ph); 131.8, 130.5, and 129.1 (2:1:2, CH each, Ph); 123.0 (Cq, C3), 91.5 (Cq, C2), 69.9 (N−CH), 51.4 (N−CH_2); 32.2, 26.2, and 25.5 (2:1:2, CH_2 each, cyclohexyl), 17.1 (CH_3). IR (hexane) (cm^{-1} (%)): 2165.0 (10) [ν(C≡C)], 2053.7 (40), 1975.3 (10), 1936.1 (100) [ν(C≡O)]. MS (70 eV) (*m*/*e* (%)): 431 (20) [M$^+$], 403 (5), 375 (10), 357 (20), 319 (30), 291 (80) [M$^+$ − 5 CO], 270 (40), 239 (30), 156 (40), 153 (60), 52 (100). Anal. Calcd for $C_{22}H_{21}CrNO_5$ (431.4): C, 61.25; H, 4.91; N, 3.25. Found: C, 61.32; H, 5.01; N, 3.43.

(*Z*)-6c. ^{1}H NMR (C_6D_6): δ 7.70 and 7.05 (2:3 H, m each, Ph), 5.00 (1 H, m, N-CH, cyclohexyl), 3.32 (2 H, q, N-CH_2), 1.55 (4 H, m, cyclohexyl); 1.80, 1.55, 1.15 and 0.85 (3:3:2:2 H, m each, cyclohexyl), 0.82 (3 H, t, CH_3). ^{13}C NMR (C_6D_6; δ): 245.0 (C=C), 224.7 and 217.9 [1:4 C, *trans*- and *cis*-CO $Cr(CO)_5$]; 131.7, 130.5, and 129.0 (2:1:2, CH each, Ph); 130.5 (Cq, *i*-C Ph), 122.8 (Cq, C3), 91.4 (Cq, C2), 71.4 (N−CH), 51.4 (N−CH_2); 31.5, 25.2, and 25.0 (2:1:2, CH_2 each, cyclohexyl), 15.7 (CH_3). IR (hexane) (cm^{-1} (%)): 2165.0 (10) [ν(C≡C)], 2053.7 (40), 1975.3 (10), 1936.1 (100) [ν(C≡O)]. MS (70 eV) (*m*/*e* (%)): 431 (20) [M$^+$], 403 (5), 375 (10), 357 (20), 319 (30), 291 (80) [M$^+$ − 5 CO], 270 (40), 239 (30), 156 (40), 153 (60), 52 (100). Anal. Calcd for $C_{22}H_{21}CrNO_5$ (431.4): C, 61.25; H, 4.91; N, 3.25. Found: C, 61.44; H, 5.18; N, 3.45.

Pentacarbonyl{1-[(2,3-epoxypropanyl)cyclohexylamino]-3-phenylpropynylidene}chromium [(*E*)-6d and (*Z*)-6d]. Pentacarbonyl(cyclohexylisocyano)chromium (**1a**) (301 mg, 1.00 mmol) in 5 mL of dry THF is reacted as described above with (phenylethynyl)lithium (**2a**). The solution is quenched by addition 2,3-epoxypropyl *bromide* (137 mg, 1.00 mmol), and after 15 min at 20 °C the solvent is removed in vacuo. The residue is separated by chromatography on silica gel (column 20 × 2 cm) with pentane/dichloromethane (4:1) to give an orange band of a 14:1 mixture of (*E*)/(*Z*)-**6d**. (*E*)-**6d** forms orange crystals from diethyl ether/pentane at −15 °C (321 mg, 70%, $R_f = 0.5$ in pentane/dichloromethane (5:1)). Reaction of the lithium salt in THF with 2,3-epoxypropyl *chloride* (93 mg, 1.00 mmol) affords a 1:17 mixture of (*E*)/(*Z*)-**6d**. (*Z*)-**6d** forms orange crystals from diethyl ether/pentane (349 mg, 76%, $R_f = 0.4$ in pentane/dichloromethane (5:1), mp 96 °C). A solution of (*E*)-**6d** in C_6D_6 after 1.5 h at 80 °C shows a ^{1}H NMR spectrum of (*E*)/(*Z*)-**6d** = 1:15, which remains unchanges after 7.5 h at 80 °C.

(*E*)-6d. ^{1}H NMR (C_6D_6): δ 7.64 and 7.05 (2:3 H, m each, Ph), 4.50 (1 H, m, N−CH, cyclohexyl), 4.83 and 3.23 (1 H each, dd each, ^2J = −14.5 Hz, ^3J = 0.5 and 7.0, diastereotopic N−CH_2), 2.80 (1 H, dddd, CH epoxide), 2.40 and 2.00 (1 H each, dd each, ^2J = 4.5 Hz, ^3J = 4.5 and 2.5, respectively; diastereotopic CH_2, epoxide), 1.70−0.85 (10 H, m, cyclohexyl). ^{13}C NMR (C_6D_6; δ): 250.5 (Cr=C), 224.5 and 217.7 [1:4 C, *trans*-

and *cis*-CO $Cr(CO)_5$], 133.6 (Cq, *i*-C Ph); 131.8, 130.5, and 129.0 (2:1:2, CH each, Ph); 122.5 (Cq, C3), 92.0 (Cq, C2), 70.0 (N−CH), 58.7 (N−CH_2), 52.0 (CH, epoxide), 45.3 (CH_2, epoxide); 31.7, 30.9, and 26.0 (2:1:2, CH_2 each, cyclohexyl). IR (hexane) (cm^{-1} (%)): 2166.4 (10) [$\nu(C\equiv C)$], 2052.8 (40), 1975.9 (10), 1932.1 (100) [$\nu(C\equiv O)$]. MS (70 eV) (*m/e* (%)): 459 (20) [M^+], 431 (5), 403 (10), 375 (20), 347 (30), 319 (80) [$M^+ - 5$ CO], 301 (40), 249 (30), 167 (40), 52 (100).

(*Z*)-6d. ^1H NMR (C_6D_6; δ): 7.60 and 7.00 (2:3 H, m each, Ph), 5.00 (1 H, m, N−CH, cyclohexyl), 3.58 and 3.20 (1 H each, dd each, $^2J = -14.5$ Hz, $^3J = 5.0$ and 3.5, diastereotopic N−CH_2), 2.65 (1 H, dddd, $^3J = 5.0$, 3.5, 4.0, and 2.1 Hz, CH epoxide), 2.19 and 2.03 (1 H each, dd each, $^2J = 5.0$ Hz, $^3J =$ 4.0 and 2.1, respectively; diastereotopic CH_2, epoxide); 1.62, 1.10−1.00 (4:6 H, m each, CH_2 cyclohexyl). ^{13}C NMR (C_6D_6; δ): 250.0 ($Cr{=}C$), 225.9 and 219.1 [1:4 C, *trans*- and *cis*-CO $Cr(CO)_5$], 133.6 (Cq, *i*-C Ph); 131.8, 130.2, and 129.2 (2:1:2, CH each, Ph); 123.7 (Cq, C3), 92.0 (Cq, C2), 72.0 (N−CH), 55.7 (N−CH_2), 51.8 (CH, epoxide), 47.5 (CH_2, epoxide); 32.2, 26.3, and 25.5 (2:1:2, CH_2 each, cyclohexyl). IR (hexane) (cm^{-1} (%)): 2166.4 (10) [$\nu(C\equiv C)$], 2052.8 (40), 1975.9 (10), 1932.1 (100) [$\nu(C\equiv O)$]. MS (70 eV) (*m/e* (%)): 459 (20) [M^+], 431 (5), 403 (10), 375 (20), 347 (30), 319 (80) [$M^+ - 5$ CO], 301 (40), 249 (30), 167 (40), 52 (100). Anal. Calcd for $C_{23}H_{21}CrNO_6$ (459.4): C, 60.13; H, 4.61; N, 3.05. Found: C, 60.34; H, 4.73; N, 3.14.

Pentacarbonyl[1-(cyclohexylamino)-3-(trimethylsilyl)propynylidene]chromium [(*E*)-6e]. Pentacarbonyl(cyclohexylisocyano)chromium (**1a**) (301 mg, 1.00 mmol) in 1 mL of dry THF is reacted subsequently with ((trimethylsilyl)ethynyl)lithium (**2b**) [freshly prepared by addition of *n*-butyllithium (1.50 mL of a 1.6 M solution in hexane) to (trimethylsilyl)acetylene (245 mg, 2.50 mmol) in 3 mL of THF at 20 °C] and phosphoric acid (100 mg of H_3PO_4 in 2 mL of water). The latter is added dropwise with stirring at 0 °C. Chromatography on silica gel (column 20 × 2 cm) with pentane/dichloromethane (4:1) yields an orange band of compound (*E*)-**6e** (327 mg, 82%, $R_f = 0.5$ in pentane/dichloromethane (6:1), orange crystals from diethyl ether/ pentane, mp 106 °C). ^1H NMR (C_6D_6; δ): 8.52 (1 H, s broad, NH), 3.90 (1 H, m, N-CH, cyclohexyl); 1.53, 0.85, 0.75 (5:3:2 H, m each, cyclohexyl), 0.10 [9 H, s, $Si(CH_3)_3$]. ^{13}C NMR (C_6D_6; δ): 255.7 ($Cr{=}C$), 224.7 and 218.7 [1:4 C, *trans*- and *cis*-CO $Cr(CO)_5$], 140.2 (Cq, C3), 103.9 (Cq, C2), 63.4 (N−CH); 32.6, 25.5, and 25.2 (2:1:2, CH_2 each, cyclohexyl), 0.01 [$Si(CH_3)_3$]. IR (diffuse reflection) (cm^{-1} (%)): 3355.2 (30) [ν(N−H)], 2160.6 (5) [$\nu(C\equiv C)$]. IR (hexane) 2056.6 (30), 1980.2 (10), 1946.5 (100) [$\nu(C\equiv O)$]. MS (70 eV) (*m/e* (%)): 399 (20) [M^+], 371 (5), 343 (20), 315 (20), 287 (30), 259 (80) [$M^+ - 5$ CO], 207 (30), 83 (100), 52 (100). Anal. Calcd for $C_{17}H_{21}CrNO_5Si$ (399.4): C, 51.12; H, 5.30; N, 3.51. Found: C, 50.98; H, 5.25; N, 3.54.

Pentacarbonyl[1-(cyclohexylmethylamino)-3-(trimethylsilyl)propynylidene]chromium [(*E*)-6f and (*Z*)-6f]. Pentacarbonyl(cyclohexylisocyano)chromium (**1a**) (301 mg, 1.00 mmol) in 5 mL of dry THF is reacted as described above with ((trimethylsilyl)ethynyl)lithium (**2b**). Methyl iodide (142 mg, 1.00 mmol) is added, and the solution is stirred for 15 min at 20 °C. Chromatography on silica gel (column 20 × 2 cm) with pentane/dichloromethane (6:1) yields an orange band which according to a ^1H NMR spectrum consists of (*E*)/(*Z*)-**6f** = 14:1. Compound (*E*)-**6f** is obtained in orange crystals from diethyl ether/pentane at −15 °C (285 mg, 69%, $R_f = 0.5$ in pentane/dichloromethane (6:1), mp 84 °C). The ^1H NMR spectrum of (*E*)-**6f** in C_6D_6 at 80 °C after 1.5 h shows (*E*)/(*Z*)-**6f** = 3:1, and after 7.5 h (*E*)/(*Z*)-**6f** = 3:2.

(*E*)-6f. ^1H NMR (C_6D_6; δ): 4.54 (1 H, m, N−CH, cyclohexyl), 3.10 (3 H, s, N−CH_3); 1.35, 1.05, 0.95, 0.60 (4:2:2:2 H, m each, cyclohexyl), 0.15 [9 H, s, $Si(CH_3)_3$]. ^{13}C NMR (C_6D_6; δ): 249.8 ($Cr{=}C$), 225.2 and 218.8 [1:4 C, *trans*- and *cis*-CO $Cr(CO)_5$], 138.8 (Cq, C3), 104.9 (Cq, C2), 70.2 (N−CH), 42.5 (N−CH_3); 31.3, 26.2, and 25.5 (2:1:2, CH_2 each, cyclohexyl), 0.01 [$Si(CH_3)_3$]. IR (diffuse reflection) (cm^{-1} (%)): 2167.5 (10) [$\nu(C\equiv C)$]. IR (hexane): 2056.7 (40), 1981.3 (10), 1938.4 (100) [$\nu(C\equiv O)$]. MS (70 eV) (*m/e* (%)): 413 (20) [M^+], 485 (5), 357 (10), 329 (20), 301 (30), 273 (80) [$M^+ - 5$ CO], 150 (40), 149 (30), 83 (90), 52 (100). Anal. Calcd for $C_{18}H_{23}CrNO_5Si$ (413.5): C, 52.29; H, 5.61; N, 3.39. Found: C, 52.43; H, 5.80; N, 3.52.

(*Z*)-6f. ^1H NMR (C_6D_6; δ): 4.73 (1 H, m, N−CH, cyclohexyl), 2.65 (3 H, s, N−CH_3); 1.32, 1.05, 0.90, and 0.58 (4:2:2:2 H, m each, cyclohexyl), 0.11 [9 H, s, $Si(CH_3)_3$].

Pentacarbonyl[1-(cyclohexylethylamino)-3-(trimethylsilyl)propynylidene]chromium [(*E*)-6g and (*Z*)-6g]. Pentacarbonyl(cyclohexylisocyano)chromium (**1a**) (301 mg, 1.00 mmol) in 5 mL of dry THF is reacted as described above with ((trimethylsilyl)ethynyl)lithium (**2b**) and quenched with $[Et_3O]BF_4$. Chromatography on silica gel (column 20 × 2 cm) with pentane/dichloromethane (6:1) yields an orange band, which according to a ^1H NMR spectrum consists of (*E*)/(*Z*)-**6g** = 25:1. (*E*)-**6g** is obtained pure in orange crystals from diethyl ether/pentane at −15 °C (372 mg, 87%, $R_f = 0.5$ in pentane/dichloromethane (4:1), mp 76 °C). A ^1H NMR spectrum of 43 mg (0.01 mmol) of (*E*)-**6g** in C_6D_6 at 80 °C after 1.5 h shows (*E*)/(*Z*)-**6g** = 9:1, and after 7.5 h (*E*)/(*Z*)-**6g** = 1:1. (*Z*)-**6g** crystallizes from diethyl ether/pentane at −15 °C (38 mg, 87%, $R_f = 0.5$ in pentane/dichloromethane (4:1)).

(*E*)-6g. ^1H NMR (C_6D_6; δ): 4.35 (1 H, m, N−CH, cyclohexyl), 3.75 (2 H, q, N−CH_2); 1.35, 1.05, 0.95, 0.60 (4:2:2:2 H, m each, cyclohexyl), 1.05 (3 H, t, CH_3, Et), 0.20 [9 H, s, $Si(CH_3)_3$]. ^{13}C NMR (C_6D_6; δ): 249.8 ($Cr{=}C$), 225.4 and 218.8 [1:4 C, *trans*- and *cis*-CO $Cr(CO)_5$], 140.2 (Cq, C3), 105.5 (Cq, C2), 70.4 (N−CH), 51.9 (N−CH_2); 32.6, 26.6, and 25.9 (2:2:1, CH_2 each, cyclohexyl), 17.5 (3 H, CH_3, Et), 0.01 [$Si(CH_3)_3$]. IR (diffuse reflection) (cm^{-1} (%)): 2155.5 (10) [$\nu(C\equiv C)$]. IR (hexane): 2054.8 (40), 1977.9 (10), 1938.6 (100) [$\nu(C\equiv O)$]. MS (70 eV) (*m/e* (%)): 427 (20) [M^+], 399 (5), 371 (10), 343 (20), 315 (30), 287 (80) [$M^+ - 5$ CO], 235 (40), 73 (100). Anal. Calcd for $C_{19}H_{25}CrNO_5Si$ (427.5): C, 53.38; H, 5.89; N, 3.28. Found: C, 53.54; H, 5.98; N, 3.45.

(*Z*)-6g. ^1H NMR (C_6D_6; δ): 4.85 (1 H, m, N−CH, cyclohexyl), 3.20 (2 H, q, N−CH_2); 1.65, 1.35, and 1.12 (4:4:2 H, m each, cyclohexyl), 0.75 (3 H, t, CH_3, Et), 0.10 [9 H, s, $Si(CH_3)_3$].

Pentacarbonyl[1-(cyclohexylamino)propynylidene]chromium [(*E*)-6h]. To a suspension of pentacarbonyl(1-(cyclohexylamino)-3-(trimethylsilyl)propynylidene)chromium [(*E*)-**6e**] (200 mg, 0.50 mmol) in 0.80 mL of ethanol is added with stirring tetramethylammonium fluoride pentahydrate (100 mg, 0.55 mmol). A dark yellow solution is obtained within 2−3 min, which according to a TLC does not contain any starting material. After addition of 1 mL of water a yellow crystalline material is precipitated, which is dissolved in 1 mL of diethyl ether and diluted with 1 mL of hexane. Yellow crystals of (*E*)-**6h** are obtained at pentane/dichloromethane (4:1) (150 mg, 92%, $R_f = 0.5$ in pentane/dichloromethane (4:1), orange crystals from diethyl ether/pentane).

(*E*)-6h. ^1H NMR (C_6D_6; δ): 8.30 (1 H, s broad, NH), 4.98 (1 H, s, ≡CH), 3.55 (1 H, m, N−CH, cyclohexyl); 1.25, 0.85, 0.54 (5:2:3 H, m each, cyclohexyl). ^{13}C NMR (C_6D_6; δ): 255.7 ($Cr{=}C$), 223.6 and 217.7 [1:4 C, *trans*- and *cis*-CO $Cr(CO)_5$], 118.1 [CH, $^1J(C,H) = 255$ Hz, C3), 82.5 [Cq, $^2J(C,H) = 48$ Hz, $^3J(C,H) = 17$, C2], 62.5 (N−CH); 31.3, 25.0, and 24.7 (2:2:1, CH_2 each, cyclohexyl). IR (diffuse reflection) (cm^{-1} (%)): 3350.8 (30) [ν(N−H)], 3299.5 (30) [$\nu(\equiv CH)$], 2163.4 (2) [$\nu(C\equiv C)$]. IR (hexane): 2058.6 (30), 1983.6 (10), 1942.5 (100) [$\nu(C\equiv O)$]. Anal. Calcd for $C_{14}H_{13}CrNO_5$ (327.3): C, 51.38; H, 4.00; N, 4.28. Found: C, 51.63; H, 4.18; N, 4.43.

Pentacarbonyl[1-(cyclohexylmethylamino)propynylidene]chromium [(*E*)-6i and (*Z*)-6i]. To a suspension of pentacarbonyl(1-(cyclohexylmethylamino)-3-(trimethylsilyl)propynylidene)chromium ((*E*)-**6f**) (207 mg, 0.50 mmol) in 0.80 mL of ethanol is added with stirring tetramethylammonium fluoride pentahydrate (100 mg, 0.55 mmol) and 0.30 mL of THF. A dark yellow solution is obtained within 2−3 min, which according to a TLC does not contain any starting material. Addition of 1 mL of water leads to precipitation of yellow crystalline material, which is dissolved in 1 mL of diethyl ether. After addition of 1 mL of pentane yellow crystals of (*E*)-**6i** are obtained (154 mg, 90%, $R_f = 0.6$ in pentane/dichloromethane (10:1), bright yellow crystals from diethyl ether/pentane, mp 75−90 °C dec). The ^{1}H NMR spectrum of (*E*)-**6i** in C_6D_6 at 50 °C after 1.5 h shows (*E*)/(*Z*)-**6i** = 2:3, and after 7.5 h (*E*)/(*Z*)-**6i** = 2:1. Compound (*E*)-**6i** has been isolated by fractional crystallization from diethyl ether/pentane at −15 °C ($R_f = 0.4$ in pentane/dichloromethane (10:1), amber-colored crystals, mp 90−95 °C, dec).

(*E*)-6i. ^{1}H NMR (C_6D_6; δ): 5.35 (1 H, s, ≡CH), 4.50 (1 H, m, N−CH, cyclohexyl), 3.25 (N−CH_3); 1.45, 1.05, 0.85, 0.75 (3:2:3:2 H, m each, cyclohexyl). ^{13}C NMR (C_6D_6; δ): 249.6 (Cr=C), 224.0 and 217.7 [1:4 C, *trans*- and *cis*-CO Cr(CO)$_5$], 118.2 (CH, ^1J = 255 Hz, C3), 83.5 (Cq, ^2J = 48 Hz, C2), 69.2 (N−CH), 39.0 (N−CH_3); 30.3, 25.0, and 24.7 (2:2:1, CH_2 each, cyclohexyl). IR (diffuse reflection) (cm^{-1} (%)): 3305.5 (30) [ν(≡CH)], 2158.3 (10) [ν(C≡C)]. IR (hexane): 2055.6 (30), 1971.0 (10), 1936.5 (100) [ν(C≡O)]. MS (70 eV) (*m*/*e* (%)): 341 (40) [M$^+$], 313 (5), 285 (40), 257 (60), 229 (60), 201 (80) [M$^+$ − 5 CO], 118 (80), 94 (100), 79 (100). Anal. Calcd for $C_{15}H_{15}CrNO_5$ (341.3): C, 52.79; H, 4.43; N, 4.10. Found: C, 52.84; H, 4.49; N, 4.28.

(*Z*)-6i. ^{1}H NMR (C_6D_6; δ): 5.20 (1 H, s, ≡CH), 4.75 (1 H, m, N−CH, cyclohexyl), 2.52 (N−CH_3); 1.50, 1.36, 1.25, 0.86, and 0.70 (2:3:2:2:1 H, m each, cyclohexyl). ^{13}C NMR (C_6D_6; δ): 248.2 (Cr=C), 222.3 and 216.4 [1:4 C, *trans*- and *cis*-CO Cr(CO)$_5$], 116.9 (CH, ^1J = 255 Hz, C3), 84.2 (Cq, ^2J = 46 Hz, C2), 70.3 (N−CH), 38.7 (N−CH_3); 30.1, 24.8, and 24.5 (2:2:1, CH_2 each, cyclohexyl). IR (diffuse reflection) (cm^{-1} (%)): 3305.5 (30) [ν(≡CH)], 2158.3 (10) [ν(C≡C)]. IR (hexane): 2054.8 (30), 1970.5 (10), 1935.6 (100) [ν(C≡O)]. MS (70 eV) (*m*/*e* (%)): 341 (40) [M$^+$], 313 (8), 285 (30), 257 (60), 229 (40), 201 (75) [M$^+$ − 5 CO], 118 (80), 94 (100), 79 (100). Anal. Calcd for $C_{15}H_{15}CrNO_5$ (341.3): C, 52.79; H, 4.43; N, 4.10. Found: C, 52.86; H, 4.54; N, 4.15.

Pentacarbonyl[3-phenyl-1-(phenylamino)propynylidene]chromium [(*E*)-6j]. Pentacarbonyl(phenylisocyano)chromium (**1b**) (295 mg, 1.00 mmol) in 1 mL of dry THF is reacted as described above with (phenylethynyl)lithium (**2a**) in 3 mL of dry THF [freshly prepared by reaction of *n*-butyllithium (1.50 mL of a 1.6 M solution in hexane) with phenylacetylene (2.55 mg, 2.50 mmol) in 3 mL of THF at 20 °C] in a 5-mL screw-top vessel, and the solution is quenched after 4 h at 20 °C by ice water. Chromatography on silica gel (column 20 × 2 cm) with pentane/dichloromethane (4:1) yields a red band of compound (*E*)-**6j** (337 mg, 85%, $R_f = 0.5$ in pentane/dichloromethane (4:1), red crystals from diethyl ether/pentane). ^{1}H NMR (C_6D_6; δ): 9.50 (1 H, s broad, NH); 7.20, 6.90, and 6.55 (2:6:2 H, m each, 2 Ph). ^{13}C NMR (C_6D_6; δ): 260.4 (Cr=C), 224.3 and 218.0 [1:4 C, *trans*- and *cis*-CO Cr(CO)$_5$], 141.3 (Cq, *i*-C NPh), 135.5 (Cq, *i*-C 3-Ph); 132.8, 131.3, 129.9, 129.1, 128.6, 124.0 (2:1:2:2:1:2, CH each, 2 Ph); 124.0 (Cq, C3), 92.0 (Cq, C2). IR (hexane) (cm^{-1} (%)): 2166.8 (15) [ν(C≡C)], 2055.9 (40), 1982.7 (10), 1947.5 (100) [ν(C≡O)]. IR (diffuse reflection): 3363.6 [ν(N−H)]. MS (70 eV) (*m*/*e* (%)): 397 (20) [M$^+$], 369 (5), 341 (10), 313 (20), 285 (30), 257 (80) [M$^+$ − 5 CO], 205 (40), 204 (60), 178 (20), 149 (20), 103 (60), 102 (80), 52 (100). Anal. Calcd for $C_{20}H_{11}CrNO_5$ (397.3): C, 60.46; H, 2.79; N, 3.53. Found: C, 60.26; H, 2.97; N, 3.57.

Pentacarbonyl[1-(ethylphenylamino)-3-phenylpropynylidene]chromium [(*E*)-6k and (*Z*)-6k]. Pentacarbonyl(phenylisocyano)chromium (**1b**) (295 mg, 1.00 mmol) in 5 mL of dry THF is reacted as described above by subsequent addition of (phenylethynyl)lithium (**2a**) [following the procedure for the preparation of the *N*-aryl derivative (*E*)-**6j**] and [Et_3O]BF_4. Chromatography on silica gel (column 20 × 2 cm) with pentane/dichloromethane (4:1) yields an orange band of **6k**, which according to the ^{1}H NMR spectrum is a mixture (*E*)/(*Z*)-**6k** = 1:15. The isomer (*Z*)-**6k** is obtained pure by fractional crystallization from diethyl ether/pentane at −15 °C (315 mg, 74%, $R_f = 0.5$ in pentane/dichloromethane (4:1), orange crystals, mp 110 °C, dec). A solution of (*Z*)-**6k** in C_6D_6 after 1.5 h at 80 °C shows a ^{1}H NMR spectrum of a mixture of (*E*)/(*Z*)-**6k** = 1:1. This product ratio remains unchanged after 7.5 h at 80 °C.

(*Z*)-6k. ^{1}H NMR (C_6D_6; δ): 7.70, 7.20, and 7.00 (2:6:2 H, m each, 2 Ph), 3.85 (2 H, q, N−CH_2), 0.95 (3 H, t, CH_3). ^{13}C NMR (C_6D_6): δ 254.6 (Cr=C), 225.4 and 218.2 [1:4 C, *trans*- and *cis*-CO Cr(CO)$_5$], 148.1 (Cq, *i*-C NPh), 131.6 (Cq, *i*-C Ph); 132.6, 130.9, 130.3, 129.6, 129.3, 127.6 (2:1:2:2:1:2, CH each, 2 Ph); 123.1 (Cq, C3), 92.0 (Cq, C2), 58.8 (N−CH_2), 14.0 (CH_3). IR (hexane) (cm^{-1} (%)): 2165.7 (10) [ν(C≡C)], 2053.3 (40), 1974.9 (10), 1936.7 (100) [ν(C≡O)]. MS (70 eV) (*m*/*e* (%)): 425 (20) [M$^+$], 397 (5), 369 (10), 341 (20), 313 (30), 285 (80) [M$^+$ − 5 CO], 233 (30), 232 (40), 204 (40), 153 (50), 52 (100). Anal. Calcd for $C_{22}H_{15}CrNO_5$ (425.4): C, 62.12; H, 3.55; N, 3.29. Found: C, 62.10; H, 3.40; N, 3.36.

(*E*)-6k. ^{1}H NMR (C_6D_6; δ): 7.30, 7.20, 7.10, and 6.70 (2:2:4:2 H, m each, 2 Ph), 4.25 (2 H, q, N−CH_2), 1.15 (3 H, t, CH_3).

Pentacarbonyl[1-(allylphenylamino)-3-phenylpropynylidene]chromium [(*Z*)-6l]. Pentacarbonyl(phenylisocyano)chromium (**1b**) (295 mg, 1.00 mmol) in 5 mL of dry THF is reacted as described with (phenylethynyl)lithium (**2a**) [following the procedure for the preparation of the *N*-aryl derivative (*Z*)-**6j**]. Allyl bromide (121 mg, 1.00 mmol) is added. After 15 min at 20 °C solvent is removed. Chromatography on silica gel (column 20 × 2 cm) with pentane/dichloromethane (4:1) yields an orange band of compound (*Z*)-**6l** (326 mg, 75%, $R_f = 0.4$ in pentane/dichloromethane (10:1), orange crystals from diethyl ether/pentane, mp 84 °C). ^{1}H NMR (C_6D_6; δ): 7.80, 7.20, and 7.00 (2:6:2 H, m each, 2 Ph), 5.80 (1 H, ddt, ^3J = 17.0, 10.5 and 6.5 Hz, =CHC), 5.20 and 5.05 (1 H each, d each, ^3J = 17.0 and 10.5 Hz, =CH_2), 4.50 (2 H, d, ^3J = 6.5 Hz, N−CH_2). ^{13}C NMR (C_6D_6; δ): 257.5 (Cr=C), 226.6 and 219.6 [1:4 C, *trans*- and *cis*-CO Cr(CO)$_5$], 149.7 (Cq, *i*-C NPh), 131.6 (Cq, *i*-C Ph); 132.4, 131.0, 130.4, 129.7, 129.4, 127.9 (2:1:2:2: 1:2, CH each, 2 Ph); 124.2 (Cq, C3), 122.1 (=CH_2), 93.7 (Cq, C2), 67.4 (N−CH_2). IR (hexane) (cm^{-1} (%)): 2166.6 (10) [ν(C≡C)], 2053.6 (40), 1973.0 (10), 1935.5 (100) [ν(C≡O)]. MS (70 eV) (*m*/*e* (%)): 437 (20) [M$^+$], 409 (5), 381 (40), 353 (60), 325 (30), 297 (80) [M$^+$ − 5 CO], 245 (70), 244 (40), 204 (40), 156 (50), 52 (100). Anal. Calcd for $C_{23}H_{15}CrNO_5$ (437.4): C, 63.16; H, 3.46; N, 3.20. Found: C, 63.11; H, 3.60; N, 3.23.

Pentacarbonyl[1-(ethyl-*p*-tolylamino)-3-phenylpropynylidene]chromium [(*E*)-6m and (*Z*)-6m]. Pentacarbonyl(*p*-tolylisocyano)chromium (**1c**) (309 mg, 1.00 mmol) in 5 mL of dry THF is reacted as described above by subsequent addition of (phenylethynyl)lithium (**2a**) [following the procedure for the preparation of the *N*-aryl derivative (*E*)-**6j**] and [Et_3O]BF_4. Chromatography on silica gel (column 20 × 2 cm) with pentane/dichloromethane (4:1) yields an orange band of **6m**, which according to the ^{1}H NMR spectrum consist of (*E*)-/(*Z*)-**6m** = 1:17. The isomer (*Z*)-**6m** is obtained pure by fractional crystallization from diethyl ether/pentane at −15 °C (364 mg, 83%, $R_f = 0.5$ in pentane/dichloromethane (6:1), orange crystals from diethyl ether/pentane, mp 113 °C, dec). A solution of (*Z*)-**6m** in C_6D_6 after 1.5 h at 80 °C shows a ^{1}H NMR spectrum of a mixture of (*E*)/(*Z*)-**6m** = 1:1. This product ratio remains unchanged after 7.5 h at 80 °C.

(*Z*)-6m. ^{1}H NMR (C_6D_6; δ): 7.70, 7.10, 7.00, and 6.90 (2:3:2:2 H, m each, Ph and *p*-tolyl), 3.90 (2 H, q, N−CH_2), 2.20 (3 H, CH_3, tolyl), 0.95 (3 H, t, CH_3, ethyl). ^{13}C NMR (C_6D_6; δ): 252.6 (Cr=C), 223.5 and 216.4 [1:4 C, *trans*- and *cis*-CO Cr(CO)$_5$], 143.9 (Cq, C4′, *p*-tolyl), 138.0 (Cq, *i*-C, *p*-tolyl), 131.0 (Cq, *i*-C, Ph); 132.5, 130.9, 130.1, 128.7, 127.4 (2:1:2:2:2, CH each, Ph and *p*-tolyl); 121.3 (Cq, C3), 90.2 (Cq, C2), 56.9 (N−CH_2), 19.6 (CH_3, *p*-tolyl), 12.1 (CH_3, ethyl). IR (hexane) (cm^{-1} (%)): 2165.3 (10) [ν(C≡C)], 2053.0 (40), 1974.2 (10), 1935.8 (100) [ν(C≡O)]. MS (70 eV) (*m*/*e* (%)): 439 (20) [M$^+$], 397 (5), 369 (10), 341 (20), 313 (30), 285 (80) [M$^+$ − 5 CO], 233 (30), 232 (40), 204 (40), 153 (50), 52 (100). Anal. Calcd for $C_{22}H_{15}$-

$CrNO_5$ (439.4): C, 62.87; H, 3.90; N, 3.19. Found: C, 62.86; H, 3.81; N, 3.27.

(*E*)-6m. ^{1}H NMR (C_6D_6; δ): 7.30, 7.10, 6.95, and 6.60 (2:3:2:2 H, m each, Ph and *p*-tolyl), 4.20 (2 H, q, N−CH_2), 1.80 (3 H, CH_3, tolyl), 1.15 (3 H, t, CH_3, ethyl).

Pentacarbonyl[1-(o-anisylamino)-3-phenylpropynylidene]chromium [(*E*)-6n]. Pentacarbonyl(*o*-anisylisocyano)chromium (**1c**) (335 mg, 1.00 mmol) in 5 mL of dry THF is reacted as described above by subsequent addition of (phenylethynyl)lithium (**2a**) [following the procedure for the preparation of the *N*-aryl derivative (*E*)-**6j**] and ice water. Chromatography on silica gel (column 20 × 2 cm) with pentane/dichloromethane (4:1) yields an orange band of compound (*E*)-**6n** (342 mg, 80%, $R_f = 0.5$ in pentane/dichloromethane (3:1), orange crystals from diethyl ether/pentane, mp 94 °C, dec). ^{1}H NMR (C_6D_6; δ): 10.50 (1 H, s broad, NH); 7.85, 7.05, 6.85, and 6.40 (1:1:1:1 H; d, t, t, d; *o*-anisyl); 7.60 and 7.10 (2:3 H, m each, Ph), 3.20 (3 H, OCH_3). ^{13}C NMR (C_6D_6; δ): 257.4 (Cr=C), 224.2 and 217.7 [1:4 C, *trans*- and *cis*-CO $Cr(CO)_5$], 150.8 (Cq, C2′, *o*-anisyl), 135.8 (Cq, *i*-C, *o*-anisyl), 130.5 (Cq, *i*-C, Ph); 132.3, 129.2, and 129.0 (2:1:2, CH each, Ph); 130.8, 123.1, 120.0, and 111.3 (1:1:1:1, CH each, *o*-anisyl); 122.4 [Cq, C3], 91.8 [Cq, ^3J(C,H) = 16.1 Hz, C2], 55.4 (OCH_3). IR (hexane) (cm^{-1} (%)): 2164.5 (10) [ν(C≡C)], 2055.1 (40), 1980.0 (10), 1940.5 (100) [ν(C≡O)]. IR (diffuse reflection): 3360.3 [ν(N−H)]. MS (70 eV) (*m*/*e* (%)): 427 (20) [M^+], 399 (2), 371 (20), 343 (20), 315 (30), 287 (80) [$M^+ - 5$ CO], 272 (30), 235 (40), 206 (40), 159 (30), 52 (100). Anal. Calcd for $C_{21}H_{13}CrNO_6$ (427.3): C, 59.02; H, 3.07; N, 3.28. Found: C, 58.99; H, 3.04; N, 3.38.

Pentacarbonyl{1-[(2,3-epoxypropanyl)-*o*-anisylamino]-3-phenylpropynylidene}chromium [(*E*)-6o and (*Z*)-6o]. Pentacarbonyl(*o*-anisylisocyano)chromium (**1d**) (335 mg, 1.00 mmol) in 5 mL of dry THF is reacted as described above with (phenylethynyl)lithium (**2a**) [following the procedure for the preparation of the *N*-aryl derivative (*E*)-**6j**]. The solution is quenched by addition epichlorhydrine (93 mg, 1.00 mmol). After 15 min at 20 °C solvent is removed in vacuo and the residue is separated by chromatography on silica gel (column 20 × 2 cm) with pentane/dichloromethane (4:1) to give an orange band, which according to a ^{1}H NMR spectrum contains a 7:9 mixture of (*E*)/(*Z*)-**6o** (386 mg, 80%, $R_f = 0.5$ in pentane/dichloromethane (2:1), orange crystals from diethyl ether/pentane, mp 98 °C).

(*E*)-6o. ^{1}H NMR (C_6D_6; δ): 7.45 and 6.96 (2:3 H, m each, Ph); 7.15, 7.05, 6.83, and 6.51 (1 H each, *o*-MeOC_6*H*$_4$), 4.53 and 3.59 (1 H each, dd each, $^2J = -14.0$ Hz, $^3J = 5.0$ and 5.0, diastereotopic N−CH_2), 3.26 (3 H, OCH_3), 2.85 (1 H, dddd, CH epoxide), 2.11 and 1.86 (1 H each, dd each, $^2J = 4.5$ Hz, $^3J =$ 4.5 and 2.5, respectively; diastereotopic CH_2, epoxide). ^{13}C NMR (C_6D_6; δ): 260.3 (Cr=C), 225.3 and 217.9 [1:4 C, *trans*- and *cis*-CO $Cr(CO)_5$], 154.3 (Cq, 4′-C *o*-MeOC_6H_4), 136.3 (Cq, *i*-C Ph), 132.6 (Cq, *i*-C *o*-MeOC_6H_4); 132.0, 130.9, 128.9 (2:1:2, CH each, Ph); 130.6, 129.1, 121.2, and 112.4 (CH each, *o*-MeOC_6H_4), 122.3 (Cq, C3), 92.2 (Cq, C2), 64.6 (OCH_3), 55.4 (N−CH_2), 48.9 (CH, epoxide), 46.3 (CH_2, epoxide). IR (hexane) (cm^{-1} (%)): 2166.9 (10) [ν(C≡C)], 2053.5 (40), 1974.8 (10), 1936.4 (100) [ν(C≡O)]. MS (70 eV) (*m*/*e* (%)): 483 (20) [M^+], 455 (5), 427 (20), 399 (20), 371 (30), 343 (80) [$M^+ - 5$ CO], 273 (40), 170 (30), 127 (40), 52 (100). Anal. Calcd for $C_{24}H_{17}CrNO_7$ (483.4): C, 59.63; H, 3.54; N, 2.90. Found: C, 59.46; H, 3.59; N, 3.00.

(*Z*)-6o. ^{1}H NMR (C_6D_6; δ): 7.45 and 6.96 (2:3 H, m each, Ph); 7.25, 7.12, 6.79, and 6.44 (1 H each, *o*-MeOC_6*H*$_4$), 4.35 and 3.68 (1 H each, dd each, $^2J = -14.0$ Hz, $^3J = 5.0$ and 5.0, diastereotopic N−CH_2), 3.30 (3 H, OCH_3), 2.70 (1 H, dddd, CH epoxide), 2.07 and 1.81 (1 H each, dd each, $^2J = 4.5$ Hz, $^3J =$ 4.5 and 2.5, respectively; diastereotopic CH_2, epoxide). ^{13}C NMR (C_6D_6; δ): 259.8 (Cr=C), 225.3 and 217.9 [1:4 C, *trans*- and *cis*-CO $Cr(CO)_5$], 154.3 (Cq, 4′-C *o*-MeOC_6H_4), 136.8 (Cq, *i*-C Ph), 132.2 (Cq, *i*-C *o*-MeOC_6H_4); 132.0, 130.9, 128.9 (2:1:2, CH each, Ph); 130.5, 129.1, 121.0, and 112.6 (CH each, *o*-MeOC_6H_4), 122.3 (Cq, C3), 92.2 (Cq, C2), 63.2 (OCH_3), 54.9 (N−CH_2), 49.3 (CH, epoxide), 44.9 (CH_2, epoxide).

Pentacarbonyl{1-[cyclohexyl(3-hydroxy-2-methoxypropyl)amino]-3-phenylpropynylidene}chromium [(*Z*)-6p]. To pentacarbonyl[1-((2,3-epoxypropanyl)cyclohexylamino)-3-phenylpropynylidene]chromium ((*Z*)-5c) (230 mg, 0.50 mmol) in 2 mL of methanol is added 1 drop of a 40% solution of HBF_4 in diethyl ether. The hydrolysis is followed by a TLC test. After 12 h, 20 °C the starting material is consumed completely and polar red (*Z*)-**6p** is obtained and isolated by chromatography on silica gel (column 20 × 2 cm) with dichloromethane (210 mg, 86%, $R_f = 0.5$ in dichloromethane, red crystals from dichloromethane/pentane at −15 °C, mp 82 °C, dec).

^{1}H NMR (C_6D_6; δ): 7.52 and 7.00 (2:3 H, m each, Ph), 5.06 (1 H, m, NCH, cyclohexyl), 4.30 (1 H, s, OH), 4.00 (1 H, m, O−CH), 3.60 and 3.49 (1 H each, dd each, $^2J = -14.5$ Hz, ^3J = 4.0 and 8.0, diastereotopic NCH_2), 3.05 and 2.95 (1 H each, dd each, $^2J = 9.5$ Hz, $^3J = 4.0$ and 5.0, diastereotopic OCH_2), 2.90 (3 H, s, OCH_3); 1.90, 1.75, 1.65, 1.53, 1.40, 1.20, and 0.85 (1:1:2:2:2:1:1 H, m each, CH_2 cyclohexyl). ^{13}C NMR (C_6D_6; δ): 249.0 (Cr=C), 224.8 and 217.8 [1:4 C, *trans*- and *cis*-CO $Cr(CO)_5$], 132.4 (Cq, *i*-C Ph); 131.6, 130.4, 127.7 (2:1:2, CH each, Ph); 122.7 (Cq, C3), 92.0 (Cq, C2), 74.8 (N−CH_2), 71.9 and 69.9 (CH each, NCH and OCH), 58.8 (OCH_3), 56.1 (OCH_2); 31.9, 25.3 and 25.2 (2:1:2, CH_2 each, cyclohexyl). IR (hexane) (cm^{-1} (%)): 2165.0 (10) [ν(C≡C)], 2054.0 (40), 1976.5 (10), 1933.1 (100) [ν(C≡O)]. MS (70 eV) (*m*/*e* (%)): 491 (20) [M^+], 435 (5), 379 (20), 351 (40) [$M^+ - 5$ CO], 321 (40), 252 (30), 167 (40), 52 (100). Anal. Calcd for $C_{24}H_{25}CrNO_7$ (491.5): C, 58.65; H, 5.13; N, 2.85. Found: C, 58.84; H, 5.17; N, 3.18.

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Supporting Information Available: Tables of data collection parameters and bond distances and angles and structure diagrams (12 pages). Ordering information is given on any current masthead page.

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