Study of the Origin of the Hindered Rotation of an Aryl Ring in Chromium Aminocarbene Complexes Bearing an Aromatic Ring Attached to the Carbene Carbon Atom

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Received June 30, 2006

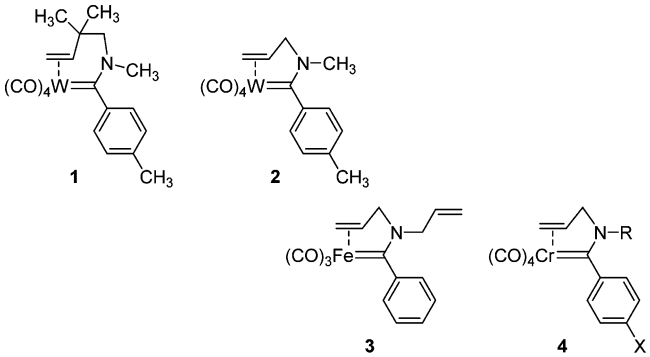
The substituted chromium aminocarbene complexes *cis*-tetracarbonyl[(η^2-*N*-allyl-*N*-allylamino)(4-X-phenyl)carbene]chromium(0) (X = MeO, Me, H, Cl, CO_2Me, CF_3) were prepared by the reaction of the corresponding *N*,*N*-diallylamides with $Na_2Cr(CO)_5$ and Me_3SiCl. Using dynamic NMR, the rotational barrier of the aryl ring in these complexes was established. The obtained values are higher for the complexes bearing electron acceptors compared to those bearing donor substituents and correspond with the Hammett equation. This indicates that the restricted rotation of aryl ring in the chromium aminocarbene complexes is a balance between steric and conjugation effects; while the former increases the barrier, the latter decreases it by stabilizing the transition state of the rotation. This finding is compatible with the fact that in the related *cis*-tetracarbonyl[(*N*-alkyl-η^2-*N*-allylamino)(phenyl)carbene]chromium(0) complexes (alkyl = Me, Et, *i*-Pr) the rotational barrier grows steadily with the growing steric demand of the substituent. The introduction of the methyl group to the ortho position of the aryl ring resulted in an increase of the rotational barrier above 76 kJ mol^{-1} even for the *N*-Me derivative.

Introduction

It has been known for a long time that the rotation of an aromatic ring directly attached to the carbene carbon atom of transition-metal carbene complexes is hindered. In the case of the highly electrophilic carbene complex $Cp(CO)_2Fe{=}CHC_6H_5^+$ it has been shown that the barrier is a result of extensive π interaction between the aryl substituent and the carbene atom. The complex is stabilized by positively charged delocalization into the aromatic ring, and as a result, the aryl ring is coplanar with the $Fe-C_{carb}-C_{ipso}$ plane. Using dynamic NMR, barriers of 9.1 and 10.4 kcal mol^{-1} have been determined for $Cp(CO)_2Fe{=}CHC_6H_5^+$ and $Cp(CO)_2Fe{=}CH(4\text{-}CH_3C_6H_4)^+$, respectively.[1]

The situation with heteroatom-stabilized alkoxy- and aminocarbene complexes is more complicated. These complexes are stabilized mainly by strong π-donation from the heteroatom. An aryl ring, thus, competes with π-donation from the heteroatom and its contribution to the stabilization of the system is suppressed. Diminished interaction between the aryl ring and the carbene carbon atom is apparent from solid-state structures of alkoxy- and aminocarbene complexes of group 6 metals. These structures reveal considerable distortion of an aryl ring from the metal−carbene π plane.[2] In the case of chromium and tungsten aminocarbene complexes this distortion of the aryl ring was proved also in solution.[3] This kind of noncoplanar orientation should suppress the π interaction of the aryl ring with the rest of the molecule. However, spectroscopic investigation of aryl(methoxy)- and aryl(amino)carbene complexes of this type has revealed that in solution the electronic properties of the carbene ligand are influenced by substituents on an aryl group.[4] This shows that in solution partial conjugation of an aryl ring with carbene ligand exists.

Chelated alkene−carbene complexes appeared to be especially suitable for measurement of a barrier to the rotation of the aryl substituent, since chelation generates helicity, aromatic protons in ortho and meta positions of an aromatic ring became diastereotopic, and their dynamic behavior in solution can be studied by ^1H NMR. By this way Casey found the energy barrier to the tolyl group rotation $\Delta G^{\ddagger}_{298}$ = 17.0 kcal mol^{-1} (71.1 kJ mol^{-1}) in tungsten carbene complex **1** and $\Delta G^{\ddagger}_{298}$ = 11.5 kcal mol^{-1} (48.1 kJ mol^{-1}) for complex **2**.[5] We have recently



obtained the barrier to rotation of the phenyl group $\Delta G^{\ddagger}_{298}$ = 60.7 kJ mol^{-1} in the related complex *cis*-tricarbonyl[(η^2-*N*-allyl-

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10.1021/om0605837 CCC: $33.50
Publication on Web 10/14/2006

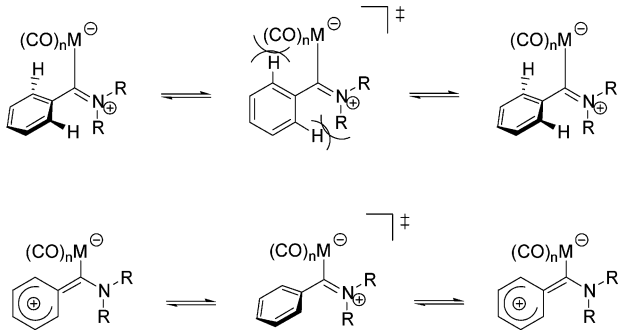


Figure 1. Possible reasons for the hindered rotation of the aryl ring in transition-metal aminocarbene complexes (steric versus π interaction).

N-allylamino)(phenyl)carbene]iron(0) (**3**).[6] Casey explained the existence of the rotational barrier by steric reasons.[5] According to Moretó,[7] the rotational barrier is cased by the π interaction of the aryl ring with the carbene carbon atom. This leads to the partial double-bond character of the aryl ring−carbene bond, which results in hindered rotation. The aryl ring, thus, competes with nitrogen in the stabilization of the carbene ligand (Figure 1).

Such a π interaction of the aryl ring with the carbene ligand should be influenced by the electronic nature of the aromatic ring—the presence of electron-donor substituents on the aryl ring will stabilize this conjugation, and rotation of the aryl ring then becomes more hindered, the influence of electron acceptors being in the opposite direction. Herein we report our results in the study od the origin of restricted rotation of an aryl ring in transition-metal aminocarbene complexes. The influence of electronic effects of the substituents on benzene ring was studied on the chelated tetracarbonyl[(η^2-*N*-allyl-*N*-alkylamino)(aryl)-carbene]chromium(0) complexes **4**. The effect of the steric factors was followed on the corresponding N-substituted complexes **13**, while the influence of the aromatic ortho substituent was studied on the 2-methylphenyl derivatives **14**.

Preparation of Model Complexes

The complexes **4a**−**f** (X = CH_3O, CH_3, H, Cl, CF_3, CO_2CH_3) were prepared by reaction of the corresponding *N*,*N*-diallylbenzamides with $Na_2[Cr(CO)_5]$ in the presence of chlorotrimethylsilane[8] (Scheme 1). Because of identity of the N substituents, the reaction was not complicated by the formation of *E*/*Z* isomers on the partial double $C_{carbene}$−N bond. An inseparable mixture of chelated complex **4** and nonchelated complex **5** was formed in all cases. Heating of this mixture led to the chelation of **5**, and pure **4** was obtained (Scheme 1). The original ratio of **4** to **5** strongly depends on the electronic nature of the substituent on the aromatic ring (Table 1). Thus, the chelated 4-CH_3O derivative **4a** was accompanied by only traces of nonchelated complex **5a** (Table 1, entry 1), while **4e**, bearing the strongly electron withdrawing CF_3 group, was obtained in a nearly 1:1 ratio with nonchelated **5e** (Table 1, entry 5). The overall yield of carbene complexes is decreased by the presence of electron-withdrawing groups (Table 1, entries 4−6). The ratio of **4** to **5** in Table 1 reflects the ratio in which the complexes were formed. This ratio does not change during workup and isolation (checked by ^{1}H NMR).

Scheme 1. Preparation of Chromium Aminocarbene Complexes 4a−f

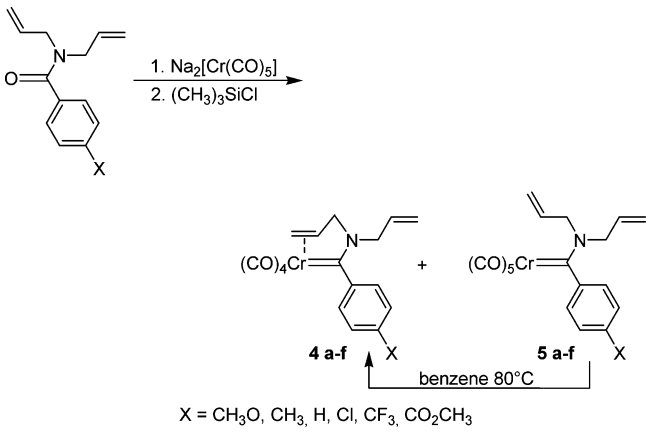
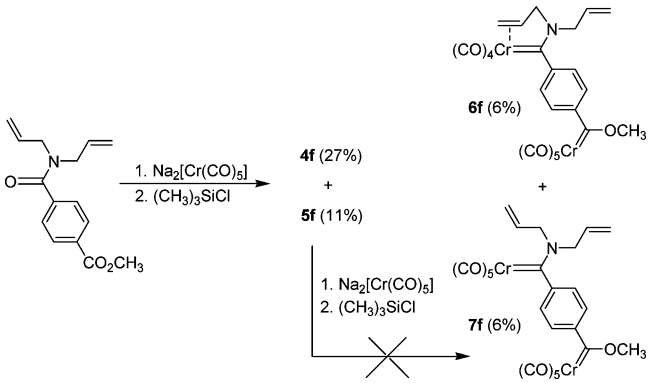


Table 1. Reaction of *N*,*N*-Diallylbenzamides with $Na_2[Cr(CO)_5]$ and Me_3SiCl (Scheme 1)

entry	R	compd (yield, %)[a]	ratio[b] **4**:**5**
1	4-(CH_3O)C_6H_4	**4a** + **5a** (70)	97:3
2	4-(CH_3)C_6H_4	**4b** + **5b** (91)	95:5
3	C_6H_5	**4c** + **5c** (75)	93:7[c]
4	4-(Cl)C_6H_5	**4d** + **5d** (83)	74:26
5	4-(CF_3)C_6H_5	**4e** + **5e** (37)	54:46
6	4-(CH_3O_2C)C_6H_5	**4f** + **5f** (38)	71:29

[a] Overall isolated yield of the carbene fraction before thermal chelation. Individual complexes were not separated. [b] Obtained by ^{1}H NMR. [c] Reference 6.

Scheme 2. Formation of Alkoxycarbene Complexes 6f and 7f during the Preparation of 4f



Interestingly, in the reaction of *N*,*N*-diallyl-4-(methoxycarbonyl)benzamide, besides the expected aminocarbenes **4f** and **5f**, also a mixture of chelated and nonchelated mixed methoxy−amino bis(carbene) complexes **6f** and **7f** were isolated (Scheme 2). This mixture afforded the chelated complex **6f** upon heating to 50 °C in benzene solution. The structure of **6f** is apparent from the characteristic NMR signals of the methoxy group (4.78 ppm in ^{1}H NMR and 67.2 ppm in ^{13}C NMR) and the signal of the carbene carbon at 347.9 ppm in ^{13}C NMR (ref 9 reports 352.0 ppm for $(CO)_5Cr{=}C(Ph)OCH_3$, and the value for **4b** is

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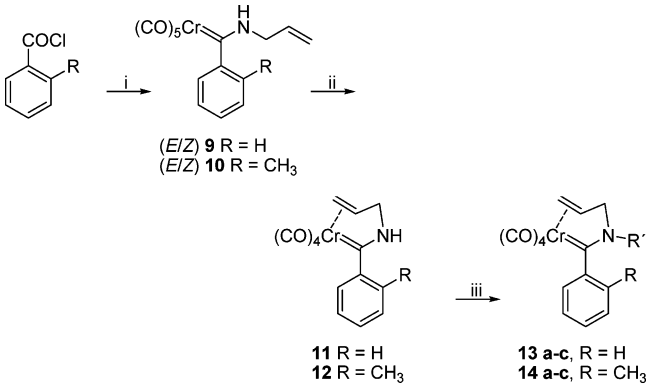
Scheme 3. Preparation of the Aminocarbene Complexes 13 and 14[a]



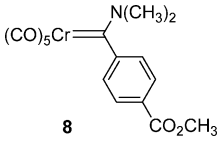
[a] Legend: (i) (1) $Na_2[Cr(CO)_5]$, (2) CH_3COBr, (3) $CH_2{=}CHCH_2NH_2$; (ii)100 °C, 1500 Pa; (iii) (1) NaH, DMF, (2) R′I.

Table 2. Preparation of Carbene Complexes 13 and 14 (Scheme 3)

carbene complex	yield,[a] %	carbene complex	yield,[a] %
9	75 ($E + Z$, 5:1)	**13b**	87
10	54 ($E + Z$, 4:1)	**13c**	79
11	40	**14a**	88[b]
12	14	**14b**	83[b]
13a	85	**14c**	77[b]

[a] Isolated yield. [b] Mixture of diastereoisomers.

283.9 ppm). The above finding is surprising, since formation of alkoxycarbene complexes from the reaction of carboxylic acid esters with $[Cr(CO)_5]^{2-}$ and Me_3SiCl has never been observed.[10] To find out if the presence of the chromium *N*,*N*-dialkylaminocarbene moiety is responsible for the formation of the alkoxycarbene complex, the reaction of *N*,*N*-dimethyl-4-(methoxycarbonyl)benzamide with $[Cr(CO)_5]^{2-}$ and Me_3SiCl was attempted. However, only the corresponding aminocarbene complex **8** was obtained in 34% yield and formation of the



chromium alkoxycarbene complex was not observed. Also, the reaction of the above mixture of aminocarbene esters **4f** and **5f** with $[Cr(CO)_5]^{2-}$ and Me_3SiCl did not produce any **6f** and/or **7f**. Thus, the reason for the formation of alkoxycarbene complexes in the reaction of *N*,*N*-dimethyl-4-(methoxycarbonyl)dimethylbenzamide with $[Cr(CO)_5]^{2-}$ and Me_3SiCl remains unknown.

For the study of the influence of the *N* or ortho aromatic substituent on the rotation barrier, the (*N*-(η^2-allyl)-*N*-alkylamino)(fenyl)carbene complexes **13a**−**c** (R′ = CH_3, CH_2CH_3, $CH(CH_3)_2$) and 2-methyl derivatives **14a**−**c** were prepared. Starting compounds for the preparation of complexes **13** and **14** were the *N*-allylaminocarbene complexes **9** and **10**, prepared according to the Semmelhack protocol.[11] These complexes were thermally chelated to **11** or **12**, respectively, and finally alkylated with the appropriate alkyl iodide (Scheme 3 and Table 2). Due to the hindered rotation of the aryl ring and the helicity of the chelated allyl group, the complexes **14a**−**c** were obtained as mixtures of two pairs of enantiomers.

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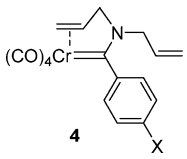
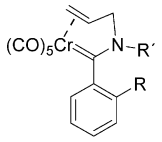
Table 3. Activation Parameters of the Aminocarbene Complexes 4a−f Obtained Using CLSA in $CDCl_3$



complex	X	T_c, K	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{298}$, kJ mol^{-1}
4a	CH_3O	273	39.6 ± 2.5	−50.7 ± 4.8	54.3
4b	CH_3	293	49.1 ± 1.6	−34.2 ± 3.0	59.3
4c	H	303	59.8 ± 4.5	9.0 ± 8.2	62.5
4d	Cl	310	55.8 ± 1.2	−18.6 ± 2.2	61.4
4e	CF_3	325	81.8 ± 9.5	53.0 ± 17	66.5
4f	CO_2CH_3	330	73.4 ± 2.5	20.1 ± 4.4	67.7

Table 4. Coalescence Temperature T_c and the Corresponding Activation Free Energy $\Delta G^{\ddagger}_{T_c}$ of the Complexes 13a−c and 14a−c in d_8-Toluene[a]



complex	R	R′	T_c, K	$\Delta G^{\ddagger}_{T_c}$, kJ mol^{-1}
13a	H	CH_3	278	55
13b	H	CH_2CH_3	303	62
13c	H	$CH(CH_3)_2$	353	73
14a	CH_3	CH_3	−373	76[b]
14b	CH_3	CH_2CH_3	−373	77[b]
14c	CH_3	$CH(CH_3)_2$	−373	>72[b]

[a] T_c was determined to ±5 K, which causes $\Delta G^{\ddagger}_{T_c}$ to be accurate to within 1.3 kJ mol^{-1}. [b] These approximate values correspond to decomplexation−complexation of the η^2-allyl group rather than to the rotation of the aryl ring (see text).

Results and Discussion

The diastereotopic ortho hydrogens of the aromatic ring in the complexes **4a**−**f**, **13a**−**c**, and **14a**−**c** were used to obtain the values of rotational barriers using dynamic NMR (Tables 3 and 4) in $CDCl_3$ (**4a**−**f**) and in d_8-toluene (**13a**−**c** and **14a**−**c**). In the case of complexes **4a**−**f** complete line shape analysis (CLSA) was performed to obtain the activation parameters $\Delta G^{\ddagger}_{298}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ (see the Experimental Section). An example of temperature dependence for the case of the *p*-methyl-substituted derivative **4b** is outlined in Figure 2. At ambient temperature an average ortho aromatic proton due to fast chemical exchange was observed. Lowering the temperature led to gradual broadening of the signal with coalescence at 293 K. Subsequent lowering of the temperature induced the appearance of new signals at 233 K, indicating the presence of two ortho aromatic protons with different chemical environments and, thus, proving the existence of restricted rotation of the aromatic ring in the chromium aminocarbene complexes. In other cases (**13a**−**c** and **14a**−**c**), the corresponding ortho aromatic resonances in the temperature-dependent spectra were not separated well enough so that the CLSA could be performed thoroughly. Therefore, the activation free energies $\Delta G^{\ddagger}$ were obtained using coalescence temperatures (see the Experimental Section).

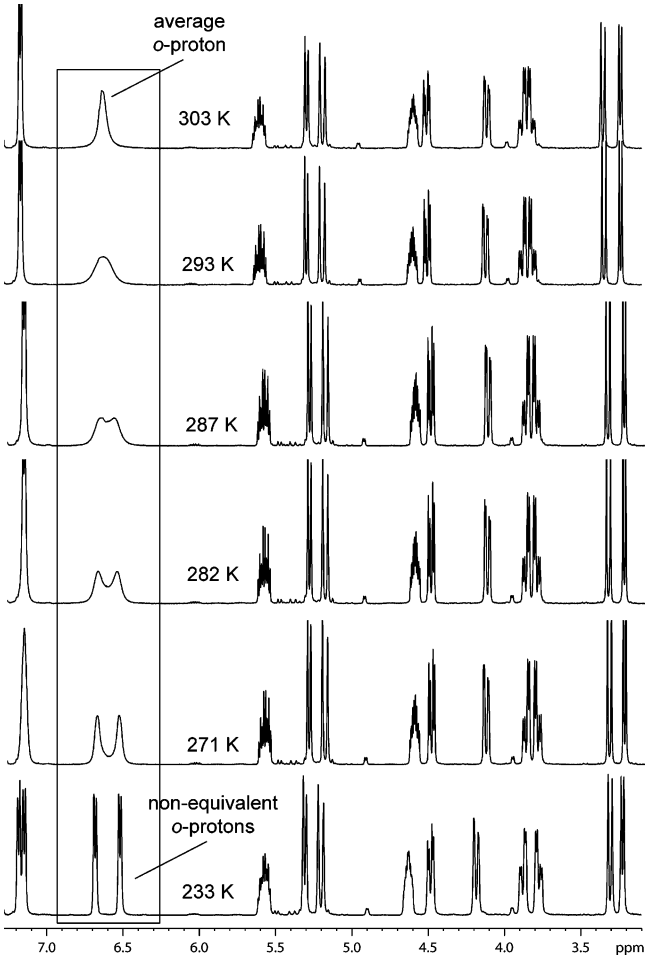


Figure 2. Temperature-dependent ^{1}H NMR spectra of **4b** in $CDCl_3$.

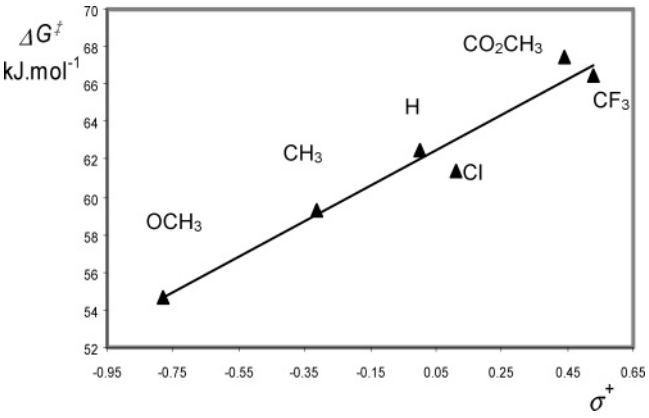


Figure 3. Hammett correlation of $\Delta G^{\ddagger}$ of **4a**−**f** with σ^+ constants of the substituents.

In the case of complexes **4a**−**f** a significant influence of the electronic nature of the aromatic substituent on the value of activation parameters was observed (Table 3). The stronger the electron-acceptor properties of the substituent, the higher the values of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$. Consequently, the values of the activation parameters correlate with the Hammett constants σ^+. The correlation of $\Delta G^{\ddagger}$ is the best (Figure 3), while the correlations of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ suffer from a high degree of inaccuracy; however, the trend remains the same.

The observed dependence of rotational barrier on the electronic nature of the substituents is exactly opposite to that expected for the case where the rotation is evoked by the conjugation of an aryl ring with the carbene π system. The electron-rich aryl ring should donate electrons to a greater extent, and a higher rotational barrier would be expected. The obtained results show that direct conjugation of the aryl ring with the carbene carbon atom plays only a diminished role in the stabilization of aryl(amino)carbene complexes. This is consistent with the reported nonplanar arrangement of the aromatic ring in the solid state and in solution. The observed trend—lowering of the rotational barrier by donor substituents—can easily be explained by lowering the energy of the transition state of the rotation process. In the transition structure, the aryl ring becomes coplanar with the carbene π system and is therefore in direct conjugation with the carbene moiety.

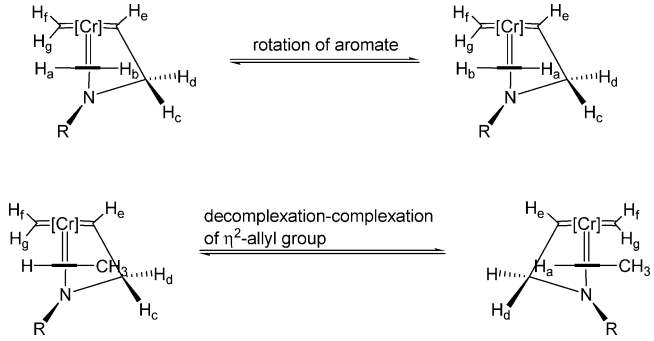


Figure 4. Dynamic processes observed with N-substituted *N*-(η^2-allyl)(2-methylphenyl)aminocarbene chromium(0) complexes **14** (a view from the ipso aromatic carbon to the carbene carbon atom).

More evidence that the π interaction of the aryl ring with the carbene π system does not substantially contribute to the stabilization of aryl(amino)carbene complexes comes from ^{15}N NMR shifts of the complexes **4a**,**c**−**e** bearing differently substituted aryl rings. Higher electron donation from the aryl ring should suppress donation of electrons from the nitrogen, resulting in lower s character of the nitrogen atom and vice versa. This should be reflected by the ^{15}N NMR shifts of these compounds. However, the ^{15}N NMR shifts of these complexes are almost identical (**4a**, 207.3 ppm; **4c**, 208.4 ppm; **4d**, 208.2 ppm; **4e**, 208.1 ppm). This shows that there is no detectable change in the hybridization of the aminocarbene nitrogen atom and that the contribution of an aryl ring to the stabilization of aminocarbene complexes is very low.

The rotational barriers of the N-substituted complexes **13a**−**c** in d_8-toluene (Table 4) strongly depend on the bulkiness of the N substituent. The value increases from the *N*-methyl derivative **13a** ($\Delta G^{\ddagger}_{T_c} = 54.5$ kJ mol^{-1}) to the *N*-isopropyl derivative **13c** ($\Delta G^{\ddagger}_{T_c} = 73.2$ kJ mol^{-1}) (Table 4). Since the electronic effects of the different alkyl groups are very similar, the observed differences in the rotational barrier should be the result of steric interactions of the N substituent with ortho hydrogens of the benzene ring.

The situation in the series of 2-methylphenyl derivatives **14a**−**c** is different. As a result of the high rotational barrier of the aryl ring, the ^{1}H NMR spectrum of these complexes in $CDCl_3$ at room temperature reveals the presence of two diastereoisomers in 4:3, 2:1, and 2:1 ratios. Surprisingly, the coalescence temperatures of ortho hydrogens as well as *o*-methyl groups of all the 2-methylphenyl complexes **14a**−**c** in d_8-toluene were very similar: around 100 °C (Table 4). Closer investigation of the NMR spectra revealed that at a temperature above approximately 80 °C reversible decomplexation of the η^2-allyl group starts. Complexation of the double bond from the opposite face has the same result as the rotation of the aryl ring (Figure 4). Therefore, in ^{1}H NMR coalescence of nonequivalent ortho H atoms and also *o*-CH_3 is observed. This is accompanied also

by the coalescence of the pairs of diastereotopic protons of the η^2-allyl group. Such a decomplexation−complexation process was previously observed with the homoallyl carbene **1**, but not with allyl carbene complexes **2** and **3**.[5,6] This reversible decomplexation excluded determination of rotational barrier of the aryl ring in the complexes **14a**−**c** using dynamic NMR. In accordance with the literature,[12] exchange of the allyl groups was not observed.

The obtained results indicate that the restricted rotation of the aryl ring in the chromium aminocarbene complexes is a balance between steric and conjugation effects. Conjugation stabilizes the planar transition state during the rotation, and the importance of this is demonstrated by the influence of the para substituents on the phenyl ring. Steric repulsion is then forcing the phenyl ring out of the plane. This is apparent from the influence of the size of the N substituent on the rotation barrier and especially by the substantial increase of the barrier by the introduction of an *o*-methyl group in the phenyl ring. This suggests that the introduction of suitable substituents at the ortho positions of the aryl ring may increase the rotation barrier to such an extent that the isolation of enantiomers resulting from the axial chirality of such a complex would be possible.

Experimental Section

Melting points were determined on a Kofler block and are uncorrected. All experiments were carried out under argon. Tetrahydrofuran was distilled from benzophenone ketyl under Ar prior to use. Chromium hexacarbonyl and Me_3SiCl were purchased from Aldrich and were used without purification. Silica was obtained from Merck. *N*,*N*-Diallylbenzamide,[13] *N*,*N*-diallyl-4-methylbenzamide,[14] and *N*,*N*-dimethyl-4-(methoxycarbonyl)benzamide[15] were prepared according to the reported procedures.

NMR Spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini 300 and Bruker DRX 500 Avance spectrometers (^{1}H at 300 or 500 MHz, ^{13}C at 75.4 or 125.8 MHz) using tetramethylsilane as an internal standard. Standard ^{1}H−^{15}N HMBC spectra were recorded on a Bruker DRX 500 Avance spectrometer operating at a frequency of 50.7 MHz for nitrogen.^{15}N chemical shifts were referenced to the signal of nitromethane (381.7 ppm). Unambiguous assignment of NMR signals was based on ^{13}C APT, 2D COSY, ^{1}H−^{13}C HMQC, and ^{1}H−^{13}C HMBC experiments. Spatial connectivities were determined using 1D ^{1}H DPFGSE-NOE experiments.

The values of rotational barriers were obtained using dynamic NMR spectroscopy. The temperature-dependent ^{1}H NMR experiments were carried out on a Bruker DRX 500 Avance spectrometer. In case of complexes **4a**−**f** full line shape analysis was performed to obtain activation parameters (Table 3). Fifteen ^{1}H NMR spectra were acquired in the temperature range of 213−327 K in $CDCl_3$. Five of the spectra in the intermediate chemical exchange regime were employed to determine the exchange rate constant. The spectra were subjected to line shape analysis using the gNMR 4.1 program (Cherwell Scientific, Oxford, U.K.). The determined exchange rate constants k were used in the subsequent calculation of thermodynamic parameters using the Eyring equation (eq 1, where $\Delta G^{\ddagger}$ is the activation free energy, $\Delta H^{\ddagger}$ is the activation enthalpy, $\Delta S^{\ddagger}$ is activation entropy, k_B, h, and R are the Boltzmann, Planck, and gas constants, respectively, and T is the absolute temperature).

$$k = (k_B T/h) \exp(-\Delta G_T^{\ddagger}/RT) \quad (1)$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \quad (2)$$

In case of the complexes **13a**−**c** and **14a**−**c** (Table 4) ^{1}H NMR temperature-dependent spectra in a large temperature range were acquired in order to determine the coalescence temperature T_c. The coalescence temperature was used for calculation of the activation free energy $\Delta G^{\ddagger}_{T_c}$ (eq 3, where $\Delta\nu$ is the chemical shift difference of the exchanging types in the absence of chemical exchange).

$$\Delta G_{T_c}^{\ddagger} = RT_c[22.96 + \ln(T_c/\Delta\nu)] \quad (3)$$

Preparation of the Starting *N*,*N*-Diallylcarboxamides. New *N*,*N*-diallylcarboxamides were prepared by the reaction of the corresponding acyl chloride with *N*,*N*-diallylamine and triethylamine in diethyl ether.

***N*,*N*-Diallyl-4-methoxybenzamide.** Yield: 51%. Mp: 38.5−40 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.82 (s, 3H, OC*H*$_3$), 4.00 (br s, 4H, NC*H*$_2$), 5.16−5.25 (m, 4H, =C*H*$_2$), 5.81 (br s, 2H, −CH=), 6.88 (dd, J = 1.6, 6.6 Hz, 2H, Ar *H*), 7.42 (dd, J = 2.2, 6.6 Hz, 2H, Ar *H*). ^{13}C NMR ($CDCl_3$, APT, 75 MHz): δ 170.6 (CO), 160.0 (Ar *C*), 132.5 (Ar *C*H), 127.5 (Ar *C*), 127.8 (Ar *C*H), 116.6 (=CH_2), 112.8 (−CH=), 54.4 (OCH_3), 50.4 br (NCH_2), 47.2 br (NCH_2). IR ($CHCl_3$): ν 3009 (w), 1614 (s), 1457 (m), 1414 (w), 1302 (w), 1251 (s), 1176 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.56; H, 7.57; N, 6.09.

***N*,*N*-Diallyl-4-chlorobenzamide.** Yield: 89%; Mp: 58.5−59 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.82 (br s, 2H, NC*H*$_2$), 4.11 (br s, 2H, NC*H*$_2$), 5.16−5.26 (m, 4H, =C*H*$_2$), 5.70−5.79 (br m, 2H, −C*H*=), 7.37(m, 4H, Ar *H*). ^{13}C NMR ($CDCl_3$, APT, 75 MHz): δ 170.5 (CO), 135.6 (Ar *C*), 134.5 (Ar *C*), 132.7 br (CH), 128.5 (CH), 128.1 (CH), 117.7 (=CH_2), 50.6 br (NCH_2), 47.1 br (NCH_2). IR ($CHCl_3$): ν 3014 (w), 1627 (s), 1598 (w), 1459 (m), 1415 (m), 1261 (w), 1092 (w), 930 (w) cm^{-1}. Anal. Calcd for $C_{13}H_{14}NOCl$: C, 66.24; H, 5.99; N, 5.94. Found: C, 65.86; H, 6.10; N, 5.91.

***N*,*N*-Diallyl-4-(trifluoromethyl)benzamide.** Yield: 61%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.80 (br s, 2H, NC*H*$_2$), 4.14 (br s, 2H, NC*H*$_2$), 5.15−5.30 (m, 4H, =C*H*$_2$), 5.71 (br m, 1H, −C*H*=), 5.83 (br m, 1H, −C*H*=), 7.55 (d, J = 8.3 Hz, 2H, Ar *H*), 7.66 (d, J = 7.7 Hz, 2H, Ar *H*). ^{13}C NMR ($CDCl_3$, APT, 75 MHz): δ 170.2 (CO), 139.8 (Ar *C*), 132.6 br (CH), 132.3 br (CH), 131.4 (q, J = 32 Hz, *C*−CF_3), 126.9 (CH), 125.3 (CH), 121.9 (q, J = 272 Hz, CF_3), 117.8 (=CH−), 117.7 (=CH_2), 50.5 (NCH_2), 47.0 (NCH_2). IR ($CHCl_3$): 1641 (s), 1416 (m), 1328 (s), 1168 (m), 1128 (m), 1066 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{14}NOF_3$: C, 62.45; H, 5.24; N, 5.20. Found: C, 62.06; H, 4.95; N, 4.92.

***N*,*N*-Diallyl-4-(methoxycarbonyl)benzamide.** Yield: 98%; Mp: 49−50 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.69 (br s, 2H, NC*H*$_2$), 3.82 (s, 3H, OC*H*$_3$), 4.04 (br s, 2H, NC*H*$_2$), 5.04−5.16 (m, 4H, =C*H*$_2$), 5.62 (br m, 1H, −C*H*=), 5.77 (br m, 1H, −C*H*=), 7.40 (d, J = 8.2 Hz, 2H, Ar *H*), 7.97 (d, J = 8.2 Hz, 2H, Ar *H*). ^{13}C NMR ($CDCl_3$, APT, 75 MHz): δ 170.6 (CO), 166.1 (CO), 140.5 (Ar *C*), 132.7 (CH), 132.4 (CH), 131.0 (Ar *C*), 129.6 (Ar *C*H), 126.5 (Ar *C*H), 117.7 (=CH_2), 52.1 (CH_3), 50.5 (NCH_2), 46.9 (NCH_2). IR ($CHCl_3$): ν 1726 (s), 1646 (s), 1414 (m), 1280 (s), 1116 (m) cm^{-1}. Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.31; H, 6.40; N, 5.29.

General Procedure for the Preparation of Diallylaminocarbene Complexes. A solution of sodium naphthalenide, prepared from sodium (0.6 g, 26 mmol) and naphthalene (3.4 g, 26.5 mmol) in THF (60 mL), was slowly added under an argon atmosphere to a stirred suspension of $Cr(CO)_6$ (2.20 g, 10 mmol) in THF (40 mL) at −78 °C. The mixture was warmed to 0 °C and kept at this temperature until all solid carbonyl dissolved (0.5 h). After this mixture was cooled to −78 °C, a solution of the corresponding

(12) The barrier to rotation about the carbene carbon−nitrogen bond in $(CO)_5Cr{=}C(CH_3)N(CH_3)_2$ was found to be greater than 25 kcal mol^{-1} (105 kJ mol^{-1}): Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1968**, *13*, 387.
(13) Brace, N. O. *J. Org. Chem.* **1971**, *36*, 3187.
(14) Agwada, V. C. *J. Chem. Eng. Data* **1984**, *29*, 231.
(15) Kikugawa, Y. *Chem. Pharm. Bull.* **1976**, *24*, 1059.

amide (7 mmol) in THF (15 mL) was added through a double-ended needle. The mixture was stirred at −78 °C for 30 min and then for 30 min at 0 °C. After this mixture was cooled to −78 °C, Me_3SiCl (1.8 mL, 14 mmol) was added via a syringe. The solution was stirred at −78 °C for 30 min, then the cooling bath was removed, the mixture was warmed to 0 °C, and neutral alumina (8 g) was added. The solvent was removed under reduced pressure on a rotary evaporator (<30 °C), and the residue was dried for several hours under high vacuum to remove all of the THF. Light petroleum (50 mL) was then added, and the mixture was stirred vigorously for several minutes under an argon atmosphere. The formed suspension was then transferred on top of a column filled with 70 g of silica. Naphthalene was eluted with pure light petroleum, and further elution with a light petroleum−CH_2Cl_2 mixture (5:1 to 1:1) gave the product.

Tetracarbonyl[(*N*-(η^2-allyl)-*N*-allylamino)(4-methoxyphenyl)-carbene]chromium(0) (4a) and Pentacarbonyl[(*N*,*N*-diallylamino)-(4-methoxyphenyl)carbene]chromium(0) (5a). The general procedure with *N*,*N*-diallyl-4-methoxybenzamide (1.62 g, 7 mmol) as the starting material furnished after chromatography (3:1 light petroleum−dichloromethane) the chelated aminocarbene complex **4a** (1.86 g, 70%) containing approximately 3% of nonchelated complex **5a**. The analytically pure sample of chelated complex **4a** was obtained by reflux of the solution of the above mixture (0.10 g) in degassed benzene (20 mL) for 2 h. The solution was then filtered through Celite, the solvent was evaporated under vacuum, and the residue was chromatographed on silica (20 g, 4:1 light petroleum−dichloromethane). Chelated complex **4a** (0.095 g, 95%) was obtained as an orange oil.

Tetracarbonyl[(*N*-(η^2-allyl)-*N*-allylamino)(4-methoxyphenyl)-carbene]chromium(0) (4a). Orange oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.21 (d, J = 8.8 Hz, 1H, chelated =C*H*H), 3.32 (d, J = 13.2 Hz, 1H, chelated =CH*H*), 3.78−3.95 (m, 2H, NCH_2), 3.81 (s, 3H, OCH_3), 4.09 (dd, J = 3.5, 14.0 Hz, 1H, chelated NCH_2), 4.42−4.64 (m, 2H, chelated NCH_2 and chelated =C*H*−), 5.17 (dd, J = 1.1, 17.0 Hz, 1H, =C*H*H), 5.27 (d, J = 9.9 Hz, 1H, =CH*H*), 5.59 (m, 1H, =C*H*−), 6.67 (d, J = 8.2 Hz, 2H, Ar *H*), 6.88 (d, J = 9.3 Hz, 2H, Ar *H*). ^{13}C NMR ($CDCl_3$, APT, 75 MHz): δ 282.6 (Cr=C), 231.8 (CO), 227.9 (CO), 224.8 (C=O), 225.0 (CO), 158.2 (Ar *C*), 141.1 (Ar *C*), 131.3 (CH), 121.5 (CH), 119.7 (CH_2), 113.8 (CH), 76.0 (chelated −CH=), 66.2 (CH_2), 60.8 (CH_2), 56.0 (CH_2), 55.1 (OCH_3); IR ($CHCl_3$): ν 2012 (s), 1914 (vs), 1519 (w), 1501 (w) cm^{-1}. Anal. Calcd for $C_{18}H_{17}CrNO_5$: C, 56.99; H, 4.52; N, 3.69. Found: C, 57.23; H, 4.54; N, 3.51.

Pentacarbonyl[(*N*,*N*-diallylamino)(4-methoxyphenyl)carbene]-chromium(0) (5a). ^{1}H NMR ($CDCl_3$, 300 MHz, signals were recorded from the above mixture of **4a** and **5a**): δ 5.38 (d, J = 17.0 Hz, 1H, =C*H*H), 5.47 (d, J = 10.0 Hz, 1H, =CH*H*), 6.03 (m, 1H, =C*H*−).

Tetracarbonyl[(*N*-(η^2-allyl)-*N*-allylamino)(4-methylphenyl)-carbene]chromium(0) (4b) and Pentacarbonyl[(*N*,*N*-diallylamino)-(4-methylphenyl)carbene]chromium(0) (5b). The general procedure with *N*,*N*-diallyl-4-methylbenzamide (1.08 g, 5 mmol) as the starting material afforded after chromatography (3:1 light petroleum−dichloromethane) a mixture of **4b** and **5b** (1.65 g, 91%) in a 95:5 ratio (NMR). An analytically pure sample of chelated complex **4b** was obtained by thermolysis of the above mixture as described for the preparation of **4a**.

Tetracarbonyl[(*N*-(η^2-allyl)-*N*-allylamino)(4-methylphenyl)-carbene]chromium(0) (4b). Red oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.34 (s, 3H, CH_3), 3.23 (d, J = 9.3 Hz, 1H, chelated =C*H*H), 3.36 (d, J = 13.2 Hz, 1H, chelated =CH*H*), 3.83 (m, 2H, NCH_2), 4.11 (dd, J = 3.9, 14.3 Hz, 1H, chelated NCH_2), 4.49 (dd, J = 5.2, 14.0 Hz, 1H, chelated NCH_2), 4.62 (m, 1H, coord =C*H*−), 5.17 (dd, J = 1.1, 17.0 Hz, 1H, =C*H*H), 5.28 (dd, J = 1.1, 9.9 Hz, 1H, =CH*H*), 5.59 (m, 1H, =C*H*−), 6.63 (br s, 2H, Ar *H*), 7.16 (d, J = 8.3 Hz, 1H, Ar *H*). ^{13}C NMR ($CDCl_3$, APT, 75 MHz): δ 283.9 (Cr=C), 231.1 (CO), 227.4 (CO), 224.6 (CO), 224.4 (CO), 145.5 (Ar *C*), 136.2 (Ar *C*), 131.4 (CH), 129.1 (CH), 119.9 (=CH_2), 75.3 (chelated −CH=), 65.8 (CH_2), 61.2 (CH_2), 56.3 (CH_2), 21.1 (CH_3). IR ($CHCl_3$): ν 2013 (vs), 1913 (vs), 1521 (w), 1500 (w) cm^{-1}. Anal. Calcd for $C_{18}H_{17}CrNO_4$: C, 59.50; H, 4.72; N, 3.86. Found: C, 59.20; H, 4.63; N, 3.87.

Pentacarbonyl[(*N*,*N*-diallylamino)(4-methylphenyl)carbene]-chromium(0) (5b). ^{1}H NMR ($CDCl_3$, 300 MHz, signals were recorded from the mixture of **4b** and **5b**): δ 2.34 (s, 3H, CH_3), 3.96 (d, J = 5.0 Hz, 2H, NCH_2), 4.93 (d, J = 5.5 Hz, 2H, NCH_2), 5.14 (d, J = 17.0 Hz, 1H, =C*H*H), 5.39 (d, J = 17.0 Hz, 1H, =CH*H*), 5.47 (d, J = 9.9, 1H, =C*H*H), 6.02 (m, 1H, =C*H*−).

Tetracarbonyl[(*N*-(η^2-allyl)-*N*-allylamino)(4-chlorophenyl)-carbene]chromium(0) (4d) and Pentacarbonyl[(*N*,*N*-diallylamino)-(4-chlorophenyl)carbene]chromium(0) (5d). The general procedure with *N*,*N*-diallyl-4-chlorobenzamide (0.589 g, 2.5 mmol) as the starting material furnished after chromatography (3:1 light petroleum−dichloromethane) an inseparable mixture of chelated aminocarbene complex **4d** and nonchelated aminocarbene complex **5d** (0.80 g, 83%) in a 74:26 ratio (NMR). An analytically pure sample of chelated complex **4d** was obtained by thermolysis of the above mixture as described for the preparation of **4a**.

Tetracarbonyl[(*N*-(η^2-allyl)-*N*-allylamino)(4-chlorophenyl)-carbene]chromium(0) (4d). Yellow solid. Mp: 50−52 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.22 (d, J = 8.8 Hz, 1H, chelated =C*H*H), 3.33 (d, J = 13.2 Hz, 1H, chelated =CH*H*), 3.82 (m, 2H, NCH_2), 4.11 (dd, J = 3.9, 14.3 Hz, 1H, chelated NCH_2), 4.50 (dd, J = 5.2, 14.0 Hz, 1H, chelated NCH_2), 4.59 (m, 1H, chelated =C*H*−), 5.17 (d, J = 17.0 Hz, 1H, =C*H*H), 5.29 (d, J = 9.9, 1H, =CH*H*), 5.57 (m, 1H, =C*H*−), 6.69 (br s, 2H, Ar *H*), 7.33 (d, J = 7.7 Hz, 2H, Ar *H*). ^{13}C NMR ($CDCl_3$, APT, 75 MHz): δ 283.0 (Cr=C), 230.8 (CO), 227.1 (CO), 224.4 (CO), 224.1 (CO), 146.54 (Ar *C*), 132.6 (Ar *C*), 131.2 (CH), 129.0 (CH), 121.2 (CH), 120.3 (=CH_2), 75.3 (coord −CH=), 66.0 (CH_2), 61.5 (CH_2), 57.0 (CH_2). IR ($CHCl_3$): ν 2014 (vs), 1915 (vs), 1519 (w), 1484 (w) cm^{-1}. Anal. Calcd for $C_{17}H_{14}CrNO_4$: C, 53.21; H, 3.68; N, 3.65. Found: C, 53.47; H, 3.70; N, 3.61.

Pentacarbonyl[(*N*,*N*-diallylamino)(4-chlorophenyl)carbene]-chromium(0) (5d). ^{1}H NMR ($CDCl_3$, 300 MHz, signals were recorded from the above mixture of **4d** and **5d**): δ 3.96 (d, J = 5.0 Hz, 2H, NCH_2), 4.93 (d, J = 5.5 Hz, 2H, NCH_2), 5.13 (dd, J = 1.1, 17.0 Hz, 1H, =C*H*H), 5.30−5.37 (m, 2H, =CH_2), 5.45 (d, J = 14.8 Hz, 1H, =CH*H*), 6.05 (m, 1H, =C*H*−), 6.68 (d, J = 8.2 Hz, 2H, Ar *H*), 7.34 (d, J = 8.2, 2H, Ar *H*).

Tetracarbonyl[(*N*-(η^2-allyl)-*N*-allylamino)(4-(trifluoromethyl)-phenyl)carbene]chromium(0) (4e) and Pentacarbonyl[(*N*,*N*-diallylamino)(4-(trifluoromethyl)phenyl)carbene]chromium(0) (5e). The general procedure with *N*,*N*-diallyl-4-(trifluoromethyl)-benzamide (0.674 g, 2.5 mmol) as the starting material furnished after chromatography (4:1 light petroleum−dichloromethane) an inseparable mixture of chelated aminocarbene complex **4e** and nonchelated aminocarbene complex **5e** (0.39 g, 37%) in a 54:46 ratio (NMR). An analytically pure sample of chelated complex **4e** was obtained by thermolysis of the above mixture, as described for the preparation of **4a**.

Tetracarbonyl[(*N*-(η^2-allyl)-*N*-allylamino)(4-(trifluoromethyl)-phenyl)carbene]chromium(0) (4e). Red oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.24 (d, J = 8.8 Hz, 1H, chelated =C*H*H), 3.34 (d, J = 13.2 Hz, 1H, chelated =CH*H*), 3.82 (m, 2H, NCH_2), 4.14 (dd, J = 3.3, 14.3 Hz, 1H, chelated NCH_2), 4.52 (dd, J = 5.2, 14.0 Hz, 1H, chelated NCH_2), 4.61 (m, 1H, chelated =C*H*−), 5.18 (d, J = 17.0 Hz, 1H, =C*H*H), 5.31 (d, J = 9.9, 1H, =CH*H*), 5.58 (m, 1H, =C*H*−), 6.74 (d, J = 7.7 Hz, 1H, Ar *H*), 6.89 (d, J = 7.7 Hz, 1H, Ar *H*), 7.61 (s, 2H, Ar *H*). ^{13}C NMR ($CDCl_3$, APT, 75 MHz): δ 282.2 (Cr=C), 230.6 (CO), 226.9 (CO), 224.3 (CO), 223.9 (CO), 151.2 (Ar *C*), 131.0 (CH), 128.8 (q, J = 32 Hz, *C*−CF_3), 125.9 (CH), 122.5 (q, J = 119 Hz, −CF_3), 120.6 (CH), 120.5 (=CH_2),

119.5 (CH), 75.3 (chelated −CH═), 66.1 (CH_2), 61.5 (CH_2), 57.0 (NCH_2). IR ($CHCl_3$): ν 2014 (vs), 1917 (vs), 1526 (w) cm^{-1}. Anal. Calcd for $C_{18}H_{14}CrF_3NO_4$: C, 51.81; H, 3.38; N, 3.36. Found: C, 51.88; H, 3.54; N, 3.36.

Pentacarbonyl[(*N*,*N*-diallylamino)(4-(trifluoromethyl)phenyl)carbene]chromium(0) (5e). ^{1}H NMR ($CDCl_3$, 300 MHz, signals were recorded from the mixture of **4e** and **5e**): δ 3.95 (d, J = 5.5 Hz, 2H, NCH_2), 4.96 (d, J = 5.5 Hz, 2H, NCH_2), 6.05 (m, 1H, ═C*H*−), 6.85 (d, J = 7.7 Hz, 2H, Ar *H*), 7.63 (d, J = 7.7 Hz, 1H, Ar *H*).

Reaction of *N*,*N*-Diallyl-4-(methoxycarbonyl)benzamide with $Na_2[Cr(CO)_5]$. Formation of Tetracarbonyl[(*N*-(η^2-allyl)-*N*-allylamino)(4-carboxymethylphenyl)carbene]chromium(0) (4f), Pentacarbonyl[(*N*,*N*-diallylamino)(4-(carboxymethyl)phenyl)carbene]chromium(0) (5f), [(η^2-CH_2CH═CH_2)(−CH_2CH═CH_2)N(C═$Cr(CO)_4$)][1,4-C_6H_4](C═$Cr(CO)_5$)(OMe) (6f), and [(−CH_2CH═CH_2)(−CH_2CH═CH_2)N(C═$Cr(CO)_5$)][1,4-C_6H_4](C═$Cr(CO)_5$)(OMe) (7f). The general procedure with *N*,*N*-diallyl-4-(methoxycarbonyl)benzamide (0.648 g, 2.5 mmol) as the starting material was used. Chromatography (3:1 light petroleum−dichloromethane) first afforded a deep red fraction containing a mixture of chelated and nonchelated alkoxy- and aminocarbene complexes **6f** and **7f** (0.18 g, 12%) in an approximately 1:1 ratio (NMR). Further elution gave a mixture of chelated and nonchelated aminocarbene complexes **4f** and **5f** (0.40 g, 38%) in a 71:29 ratio (NMR). An analytically pure sample of chelated complex **4f** was obtained by thermolysis of the above mixture of aminocarbenes **4f** and **5f** as described for the preparation of **4a**.

The mixture of alkoxy- and aminocarbene complexes **6f** and **7f** was dissolved in degassed benzene (20 mL), and the solution was stirred under argon for 2 h at 50 °C. The solution was then filtered through Celite, and the solvent was evaporated under vacuum. Chromatography on silica (20 g, 3:1 light petroleum−dichloromethane) gave 0.02 g of pure **6f**.

Tetracarbonyl[(*N*-(η^2-allyl)-*N*-allylamino)(4-(carboxymethyl)phenyl)carbene]chromium(0) (4f). Red oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.23 (d, J = 8.2 Hz, 1H, chelated ═C*H*H), 3.34 (d, J = 13.2 Hz, 1H, chelated ═CH*H*), 3.81 (br s, 2H, NCH_2) 3.91 (s, 3H, OCH_3), 4.13 (m, 1H, chelated NCH_2), 4.51 (dd, J = 5.2, 14.0 Hz, 1H, chelated NCH_2), 4.62 (m, 1H, chelated ═C*H*−), 5.17 (d, J = 17.0 Hz, 1H, ═C*H*H), 5.29 (d, J = 9.9 Hz, 1H, ═CH*H*), 5.56 (m, 1H, ═C*H*−), 6.68 (d, J = 7.1, 1H, Ar *H*), 6.83 (d, J = 7.7 Hz, 1H, Ar *H*), 8.03 (br s, 2H, Ar *H*). ^{13}C NMR ($CDCl_3$, APT, 75 MHz): δ 282.5 (Cr═C), 230.6 (CO), 227.0 (CO), 224.3 (CO), 224.0 (CO), 166.8 (*C*O−OMe), 152.1 (Ar *C*), 131.0 (CH), 130.3 (CH), 128.5 (Ar *C*), 120.5 (═CH_2), 120.2 (*o*-Ar *C*H), 119.4 (*o*-Ar *C*H), 75.3 (chelated −CH═), 66.0 (CH_2), 61.4 (CH_2), 57.0 (CH_2), 52.6 (OCH_3). IR ($CHCl_3$): ν 2015 (vs), 1917 (vs), 1719 (w), 1525 (w) cm^{-1}. Anal. Calcd for $C_{19}H_{17}CrNO_6$: C, 56.02; H, 4.21; N, 3.44. Found: C, 55.96; H, 4.53; N, 3.12.

Pentacarbonyl[(*N*,*N*-diallylamino)(4-(carboxymethyl)phenyl)carbene]chromium(0) (5f). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.92 (s, 3H, OCH_3), 3.94 (m, 2H, NCH_2), 4.95 (d, J = 5.5 Hz, 2H, NCH_2), 5.13 (d, J = 17.0 Hz,1H, ═C*H*H), 5.31 (d, J = 9.3 Hz, 1H, ═CH*H*), 5.41 (d, J = 17.0 Hz, 1H, ═C*H*H), 5.50 (d, J = 9.9, 1H, ═CH*H*), 5.56 (m, 1H, ═C*H*−), 6.05 (m, 1H, ═C*H*−), 6.80 (m, 2H, Ar *H*), 8.05 (m, 2H, Ar *H*).

[(η^2-CH_2CH═CH_2)(−CH_2CH═CH_2)N(C═$Cr(CO)_4$)[1,4-C_6H_4]-(C═$Cr(CO)_5$)(OMe) (6f). Red oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.24 (d, J = 8.8 Hz, 1H, chelated ═C*H*H), 3.35 (d, J = 13.2 Hz, 1H, chelated ═CH*H*), 3.82 (m, 2H, NCH_2), 4.12 (dd, J = 3.8, 13.7 Hz, 1H, chelated NCH_2), 4.52 (dd, J = 5.2, 10.0 Hz, 1H, chelated NCH_2), 4.61 (m, 1H, chelated ═C*H*−), 4.78 (s, 3H, OCH_3), 5.16 (d, J = 17.0 Hz, 1H, ═C*H*H), 5.29 (d, J = 9.9, 1H, ═CH*H*), 5.60 (m, 1H, ═C*H*−), 6.68 (br s, 1H, Ar *H*), 6.79 (br s, 1H, Ar *H*), 7.39 (d, J = 7.1 Hz, 2H, Ar *H*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 347.9 (Cr═C−O), 282.3 (Cr═C−N), 230.3 (CO), 226.9 (CO), 224.0 (CO), 223.8 (CO), 216.2 (CO), 151.5 (Ar *C*), 149.7 (Ar *C*), 130.7 (CH), 124.3 (CH), 120.1 (═CH_2), 119.6 br (Ar *C*H), 118.9 br (Ar *C*H), 75.0 (chelated −C*H*═), 67.2 (OCH_3), 65.7 (CH_2), 61.1 (CH_2), 56.5 (CH_2).

[(−CH_2CH═CH_2)$_2$N(C═$Cr(CO)_5$)[1,4-C_6H_4](C═$Cr(CO)_5$)-(OMe) (7f). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.97 (d, J = 5.5 Hz, 2H, NCH_2), 4.78 (s, 3H, OCH_3), 4.94 (d, J = 6.1 Hz, 2H, NCH_2), 5.13 (d, J = 17.0 Hz, 1H, ═C*H*H), 5.31 (d, J = 10.4 Hz, 1H, ═CH*H*), 5.41 (d, J = 17.0 Hz, 1H, ═C*H*H), 5.50 (d, J = 9.9, 1H, ═CH*H*), 5.58 (m, 1H, ═C*H*−), 6.04 (m, 1H, ═C*H*−), 6.78 (d, J = 8.8 Hz, 2H, Ar *H*), 7.41 (d, J = 8.2 Hz, 2H, Ar *H*).

Pentacarbonyl[(*N*,*N*-dimethylamino)(4-(methoxycarbonyl)phenyl)carbene]chromium(0) (8). The general procedure with *N*,*N*-dimethyl-4-(methoxycarbonyl)benzamide (1.45 g, 7 mmol) as the starting material furnished after chromatography (2:1 light petroleum−dichloromethane) and crystallization (heptane−dichloromethane) pentacarbonyl[(*N*,*N*-dimethylamino)(4-(methoxycarbonyl)phenyl)carbene]chromium(0) (1.02 g, 38%) as the only carbene product. Yellow solid. Mp: 109−112 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.07 (s, 3H, NCH_3), 3.92 (s, 3H, OCH_3), 4.02 (s, 3H, NCH_3), 6.78 (d, J = 8.2 Hz, 2H, Ar *H*), 8.07 (d, J = 8.0 Hz, 2H, Ar *H*). IR ($CHCl_3$): ν 2056 (w), 1975 (w), 1932 (s), 1719 (w) cm^{-1}. Anal. Calcd for $C_{16}H_{13}NO_7Cr$: C, 50.14; H, 3.42; N, 3.65. Found: C, 50.17; H, 3.50; N, 3.61.

(*E*)- and (*Z*)-Pentacarbonyl[(*N*-allylamino)(phenyl)carbene]-chromium(0) (9). To a solution of chromium hexacarbonyl (1.32 g, 6 mmol) in THF (30 mL) was added at −78 °C via syringe a solution of sodium naphthalenide prepared from sodium (0.36 g, 16 mmol) and naphthalene (2.04 g, 16 mmol) in THF (30 mL). The reaction mixture was then warmed to 0 °C, stirred at this temperature for 30 min, and cooled to −78 °C, and benzoyl chloride (0.78 g, 5.5 mmol) in THF (5 mL) was added via syringe. The solution was warmed to 0 °C for 15 min and then evaporated in vacuo at 0 °C. The residue was redissolved in CH_2Cl_2 (50 mL) at −40 °C and stirred for 30 min. Then acetyl bromide (0.45 mL, 6 mmol) was added dropwise at −30 °C. In the next 30 min the mixture was warmed to −10 °C. After the reaction mixture was recooled to −40 °C, allylamine (1.35 mL, 18 mmol) was added. The mixture was stirred for 1 h without cooling, and neutral alumina (5 g) was added. Solvents were removed under reduced pressure, and the residue was dried under high vacuum. Light petroleum (8 mL) was then added and the suspension that formed was transferred onto the top of a column filled with silica gel (50 g). Naphthalene was eluted with light petroleum, and further elution with a light petroleum−dichloromethane mixture (3:1) gave the desired mixture of (*E*)- and (*Z*)-**9** as yellow crystals (1.39 g, 75%), which was directly used in the next step for the preparation of **11**.

^{1}H NMR ($CDCl_3$, 300 MHz, *E* and *Z* isomers in 5:1 ratio): δ 3.84 (tt, J = 5.8, 1.6 Hz, 2H, −CH_2−, *E*), 4.74 (t, J = 5.8 Hz, 2H, −CH_2−, *Z*), 5.27−5.37 (m, 2H, ═CH_2, *E*), 5.40−5.48 (m, 2H, ═CH_2, *Z*), 5.71−5.85 (m, 1H, −C*H*═, *E*), 6.00−6.14 (m, 1H, −C*H*═, *Z*), 6.80 (m, 2H, Ph *H*, *E*), 6.99 (m, 2H, Ph *H*, *Z*), 7.18−7.31 (m, 1H, Ph *H*), 7.35−7.43 (m, 2H, Ph *H*), 8.55 (bs, 1H, −N*H*−, *Z*), 9.05 (bs, 1H, −N*H*−, *E*).

***cis*-Tetracarbonyl[(*N*-(η^2-allyl)amino)(phenyl)carbene]chromium(0) (11).** The mixture of **9** (1.01 g, 3 mmol) was stirred without solvent at 100 °C under diminished pressure (1.5 kPa) for 6 h. After it was cooled to room temperature, the resulting mixture was subjected to column chromatography on silica gel (30 g). Elution with a hexane−dichloromethane mixture (3:1) gave a mixture of nonchelated (*E*)- and (*Z*)-**9**[16] (0.48 g); further elution with a hexane−dichloromethane mixture (1:1) provided **11** as orange crystals (0.37 g, 40%; 76% based on consumed mixture **9**). Mp: 84−85 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.17−3.30 (m, 2H, ═CH_2), 4.22 (d, J = 14.0 Hz, 1H, −CH_2−), 4.34 (dd, J = 14.0, 5.0 Hz, 1H, −CH_2−), 4.74 (m, 1H, −C*H*═), 7.17−7.26 (m, 2H, Ph *H*), 7.33−7.43 (m, 3H, Ph *H*), 8.45 (bs, 1H, −N*H*−).^{13}C

NMR ($CDCl_3$, 75 MHz): δ 283.5 (C═Cr), 232.3 (CO), 226.5 (CO), 225.8 (CO), 224.2 (CO), 147.5 (Ph *C*), 130.0 (Ph *C*H), 128.6 (Ph *C*H), 123.6 (Ph *C*H), 77.1 (−CH═), 65.2 (−CH_2−), 53.8 (═CH_2). IR ($CHCl_3$): ν 2014, 1917, 1889, 1534, 1350, 1327 cm^{-1}. Anal. Calcd for $C_{14}H_{11}NO_4Cr$: C, 54.38; H, 3.59; N, 4.53. Found: C, 54.08; H, 3.63; N, 4.47.

***cis*-Tetracarbonyl[(*N*-(η^2-allyl)-*N*-methylamino)(phenyl)carbene]chromium(0) (13a).** To a mixture of **11** (93 mg, 0.3 mmol) and a 60% suspension of NaH in mineral oil (20 mg, 0.5 mmol) was slowly added DMF (0.5 mL) at 0 °C with stirring. The yellow suspension was stirred for 1 h at room temperature. After the suspension was cooled to 0 °C, iodomethane (0.25 mL, 4 mmol) was added dropwise. The resulting mixture was stirred for 3 h at room temperature. Water was added (10 mL), and the product was extracted with ether (3 × 10 mL). The combined extracts were dried over Na_2SO_4 and evaporated to give the crude product, which was purified by column chromatography on silica gel (5 g). Elution with a hexane−dichloromethane mixture (3:1) afforded **13a** as yellow crystals (82 mg, 85%). Mp: 122−123 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.93 (s, 3H, N−CH_3), 3.23 (d, J = 8.5 Hz, 1H, ═CH_2), 3.33 (d, J = 12.9 Hz, 1H, ═CH_2), 4.08−4.17 (m, 1H, −CH_2−), 4.46-4.56 (m, 1H, −CH_2−), 4.58 (m, 1H, −C*H*═), 6.69 (d, J = 6.6 Hz, 2H, *o*-Ph *H*), 7.18 (t, J = 7.4 Hz, 1H, *p*-Ph *H*), 7.36 (t, J = 7.6 Hz, 2H, *m*-Ph *H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 281.4 (C═Cr), 231.0 (CO), 226.9 (CO), 224.7 (CO), 224.5 (CO), 148.2 (Ph *C*), 128.4 (*m*-Ph *C*H), 126.4 (*p*-Ph *C*H), 119.6 b (*o*-Ph *C*H), 74.0 (−CH═), 65.2 (═CH_2), 63.7 (−CH_2−), 41.1 (CH_3−N). IR ($CHCl_3$): ν 2926, 2014, 1914, 1537, 1486, 1440, 1405 cm^{-1}. MS: *m*/*z* (%) 323 ($M^{\bullet+}$, 14), 295 (10), 267 (9), 239 (29), 171 (77), 158 (50), 118 (39), 93 (100). HRMS: *m*/*z* calcd 323.0250, found 323.0239.

***cis*-Tetracarbonyl[(*N*-(η^2-allyl)-*N*-ethylamino)(phenyl)carbene]chromium(0) (13b).** The same method as was used for the preparation of **13a** with iodoethane (0.32 mL, 4 mmol) provided yellow crystals of **13b** (88 mg, 87%). Mp: 74−76 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.08 (t, J = 7.3 Hz, 3H, −CH_3), 3.19−3.34 (m, 4H, ═CH_2 + −CH_2−), 4.09−4.17 (m, 1H, NCH_2−), 4.48−4.56 (m, 1H, NCH_2−), 4.58 (m, 1H, −C*H*═), 6.69 (bs, 2H, *o*-Ph *H*), 7.17 (t, J = 7.4 Hz, 1H, *p*-Ph *H*), 7.36 (t, J = 7.7 Hz, 2H, *m*-Ph *H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 281.5 (C═Cr), 230.9 (CO), 227.2 (CO), 224.5 (CO), 224.3 (CO), 148.1 (Ph *C*), 128.3 (*m*-Ph *C*H), 126.1 (*p*-Ph *C*H), 119.6 b (*o*-Ph *C*H), 119.1 b (*o*-Ph *C*H), 74.6 (−CH═), 65.2 (═CH_2), 60.6 (−CH_2-N), 48.5 (−CH_2−), 14.3 (CH_3). IR ($CHCl_3$): ν 2985, 2012, 1913, 1520, 1484, 1383, 1289, 1185 cm^{-1}. Anal. Calcd for $C_{16}H_{15}NO_4Cr$: C, 56.98; H, 4.48; N, 4.15. Found: C, 56.50; H, 4.41; N, 4.13.

***cis*-Tetracarbonyl[(*N*-(η^2-allyl)-*N*-isopropylamino)(phenyl)carbene]chromium(0) (13c).** The same method as was used for the preparation of **13a** with 2-iodopropane (0.40 mL, 4 mmol) gave yellow crystals of **13c** (83 mg, 79%). Mp: >120 °C dec. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.11 (d, J = 6.6 Hz, 3H, −CH_3), 1.19 (d, J = 6.6 Hz, 3H, −CH_3), 3.22 (d, J = 8.7 Hz, 1H, ═CH_2), 3.27 (d, J = 13.1 Hz, 1H, ═CH_2), 3.93 (sep, J = 6.6 Hz, 1H, −C*H*−), 4.06 (dd, J = 13.9, 3.0 Hz, 1H, −CH_2−), 4.46 (dd, J = 13.9, 4.9 Hz, 1H, −CH_2−), 4.58 (m, 1H, −C*H*═), 6.64 (d, J = 7.3 Hz, 1H, *o*-Ph *H*), 6.73 (d, J = 7.3 Hz, 1H, *o*-Ph *H*), 7.18 (t, J = 7.3 Hz, 1H, *p*-Ph *H*), 7.37 (m, 2H, *m*-Ph *H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 281.3 (C═Cr), 230.7 (CO), 227.4 (CO), 224.1 (CO), 224.0 (CO), 148.3 (C−Ph), 128.5 (*m*-Ph *C*H), 128.4 (*m*-Ph *C*H), 126.0 (*p*-Ph *C*H), 119.2 (*o*-Ph *C*H), 118.7 (*o*-Ph *C*H), 74.9 (−CH═), 64.9 (═CH_2), 54.7 (−CH_2−), 54.6 (−CH<), 21.1 (CH_3), 20.8 (CH_3). IR ($CHCl_3$): ν 2012, 1912, 1598, 1513, 1438, 1371, 1265, 1176 cm^{-1}. Anal. Calcd for $C_{17}H_{17}NO_4Cr$: C, 58.12; H, 4.88; N, 3.99. Found: C, 57.92; H, 4.91; N, 3.71.

(*E*)- and (*Z*)-Pentacarbonyl[(*N*-allylamino)(2-methylphenyl)carbene]chromium(0) (10). The same method as was used for the preparation of **1**, with 2-methylbenzoyl chloride (0.86 g, 5.5 mmol) as the starting material, gave yellow crystals of the mixture of (*E*)- and (*Z*)-**10** (1.05 g, 54%), which was directly used in the next step for the preparation of **12**. ^{1}H NMR ($CDCl_3$, 300 MHz, *E* and *Z* isomers in 4:1 ratio): δ 2.16 (s, 3H, Ar CH_3), 3.77 (m, 2H, −CH_2−, *E*), 4.76 (t, J = 5.9 Hz, 2H, −CH_2−, *Z*), 5.26−5.38 (m, 2H, ═CH_2, *E*), 5.41−5.50 (m, 2H, ═CH_2, *Z*), 5.71−5.86 (m, 1H, −C*H*═, *E*), 5.99−6.14 (m, 1H, −C*H*═, *Z*), 6.74 (d, J = 7.7 Hz, 1H, Ar *H*, *E*), 6.88 (d, J = 7.4 Hz, 1H, Ar *H*, *Z*), 7.10−7.27 (m, 3H, Ar *H*), 8.56 (bs, 1H, −N*H*−, *Z*), 9.08 (bs, 1H, −N*H*−, *E*).

***cis*-Tetracarbonyl[(*N*-(η^2-allyl)amino)(2-methylphenyl)carbene]chromium(0) (12).** The mixture of **10** (1.05 g, 3 mmol) was stirred without solvent at 100 °C under diminished pressure (1.5 kPa) for 6 h. After it was cooled to room temperature, the resulting mixture was subjected to column chromatography on silica gel (30 g). Elution with a hexane−dichloromethane mixture (3:1) gave a mixture of nonchelated (*E*)- and (*Z*)-**10**[16] (0.74 g); further elution with a hexane−dichloromethane mixture (1:1) provided **12** as orange crystals (0.14 g, 14%; 47% based on consumed mixture of **10**). Mp: 75−76 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.13 (s, 3H, Ar CH_3), 3.27 (d, J = 11.0 Hz, 2H, ═CH_2), 4.15 (d, J = 14.0 Hz, 1H, −CH_2−), 4.36 (dd, J = 14.0, 5.2 Hz, 1H, −CH_2−), 4.79 (m, 1H, −C*H*═), 6.76 (d, J = 6.9 Hz, 1H, *o*-Ar *H*), 7.04−7.23 (m, 3H, Ar *H*), 8.41 (bs, 1H, −N*H*−). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 290.8 (C═Cr), 231.4 (CO), 226.6 (CO), 224.9 (CO), 224.2 (CO), 148.8 (Ar *C*), 130.4 (Ar *C*H), 127.7 (Ar *C*), 127.4 (Ar *C*H), 125.4 (Ar *C*H), 121.7 (Ar *C*H), 77.9 (−CH═), 65.1 (−CH_2−), 53.9 (═CH_2), 19.0 (Ar *C*H_3). IR ($CHCl_3$): ν 3308, 2016, 1918, 1891, 1536, 1348, 1330 cm^{-1}. Anal. Calcd for $C_{15}H_{13}NO_4Cr$: C, 55.73; H, 4.05; N, 4.33. Found: C, 55.48; H, 4.24; N, 4.31.

***cis*-Tetracarbonyl[(*N*-(η^2-allyl)-*N*-methylamino)(2-methylphenyl)carbene]chromium(0) (14a).** The same method as was used for the preparation of **13a** with **12** (97 mg, 0.3 mmol) gave yellow crystals of **14a** (89 mg, 88%). Mp: 108−109 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, two diastereoisomers in 4:3 ratio): δ 1.98 (s, 3H, Ar CH_3, minor), 2.11 (s, 3H, Ar CH_3, major), 2.87 (s, 3H, NCH_3, major), 2.90 (s, 3H, NCH_3, minor), 3.18−3.33 (m, 2H, ═CH_2), 4.12−4.26 (m, 1H, −CH_2−), 4.50−4.57 (m, 1H, −CH_2−), 4.61 (m, 1H, −C*H*═), 6.53 (d, J = 7.5 Hz, 1H, *o*-Ar *H*, major), 6.73 (d, J = 7.5 Hz, 1H, *o*-Ar *H*, minor), 7.08−7.26 (m, 3H, Ar *H*).^{13}C NMR ($CDCl_3$, 75 MHz): δ 283.2 (C═Cr), 283.1 (C═Cr), 231.2 (CO, major), 230.8 (CO, minor), 226.7 (CO, minor), 226.2 (CO, major), 225.5 (CO, major), 225.4 (CO, major), 224.9 (CO, minor), 224.4 (CO, minor), 147.4 (Ar *C*, minor), 147.3 (Ar *C*, major), 130.3 (Ar *C*H, major), 130.2 (Ar *C*H, minor), 126.8 (Ar *C*, major), 126.5 (Ar *C*H, minor), 126.4 (Ar *C*H, major), 126.1 (Ar *C*, minor), 125.9 (Ar *C*H, major), 125.8 (Ar *C*H, minor), 120.9 (*o*-Ar *C*H, minor), 119.5 (*o*-Ar *C*H, major), 74.5 (−CH═, minor), 73.1 (−CH═, major), 65.6 (═CH_2, minor), 63.6 (═CH_2, major + −CH_2−, minor), 63.0 (−CH_2−, major), 40.6 (CH_3N, minor), 40.5 (CH_3N, major), 18.8 (Ar CH_3). IR ($CHCl_3$): ν 2925, 2014, 1914, 1537, 1481, 1404 cm^{-1}. Anal. Calcd for $C_{16}H_{15}NO_4Cr$: C, 56.98; H, 4.48; N, 4.15. Found: C, 56.78; H, 4.47; N, 3.92.

***cis*-Tetracarbonyl[(*N*-(η^2-allyl)-*N*-ethylamino)(2-methylphenyl)carbene]chromium(0) (14b).** The same method as was used for the preparation of **13a** with **12** (97 mg, 0.3 mmol) and iodoethane (0.32 mL, 4 mmol) gave a yellow oil of **14b** (87 mg, 83%). ^{1}H NMR ($CDCl_3$, 500 MHz, two diastereoisomers in 2:1 ratio): δ 1.04 (t, J = 7.3 Hz, 3H, −CH_3, major), 1.11 (s, J = 7.3

(16) The mixture was used as a starting material for the preparation of the next crop of **11** or **12** with somewhat lower yield (30% of **11** and 10% of **12** in this and further runs). In the case of the preparation of the 2-methylphenyl complex **12**, after several runs, practically pure (*E*)-**10** remained in the reaction mixture whereas all (*Z*)-**10** vanished. This was also accompanied by lowering of yield of **12** (from 10 to 2%) in these repeated preparations. In contrast, the yield of **11** was in all runs around 30% and no changes in (*E*)-**9**:(*Z*)-**9** ratios were observed. This behavior indicates that the *E*/*Z* isomerization step is much slower for **10** in comparison with **9**. It probably reflects the much higher rotation barrier of aryl ring in **10** compared with that in **9**.

Hz, 3H, −CH_3, minor), 2.02 (s, 3H, Ar CH_3, minor), 2.13 (s, 3H, Ar CH_3, major), 3.09−3.43 (m, 4H, =CH_2 + −CH_2−), 4.02−4.68 (m, 2H, NCH_2−), 4.45-4.68 (m, 1H, −C*H*=), 6.55 (d, J = 6.6 Hz, 1H, *o*-Ar *H*, major), 6.74 (d, J = 6.7 Hz, 1H, *o*-Ar *H*, minor), 7.07−7.27 (m, 3H, Ar *H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 282.8 (C=Cr, minor), 282.6 (C=Cr, major), 231.3 (CO, major), 230.6 (CO, minor), 227.1 (CO, minor), 226.3 (CO, major), 225.4 (CO, major), 225.2 (CO, major), 224.5 (CO, minor), 223.9 (CO, minor), 147.3 (Ar *C*, minor), 147.0 (Ar *C*, major), 130.3 (Ar *C*H, major), 130.2 (Ar *C*H, minor), 126.7 (Ar *C*, major), 126.3 (Ar *C*H, minor), 126.2 (Ar *C*H, major), 126.0 (Ar *C*, minor), 125.6 (Ar *C*H, major), 120.7 (*o*-Ar *C*H, minor), 119.5 (*o*-Ar *C*H, major), 75.5 (−CH=, minor), 73.4 (−CH=, major), 66.4 (=CH_2, minor), 63.4 (=CH_2, major), 60.6 (−CH_2N, minor), 59.7 (−CH_2N, major), 48.5 (−CH_2−, minor), 48.2 (−CH_2−, major), 19.1 (Ar CH_3, minor), 19.0 (Ar CH_3, major). IR ($CHCl_3$): ν 2928, 2013, 1914, 1525, 1383, 1185 cm^{-1}. MS: *m*/*z* (%) 351 ($M^{\bullet+}$, 10), 323 (18), 295 (9), 267 (41), 239 (100), 210 (31), 186 (79), 172 (81), 128 (29), 118 (53), 107 (77). HRMS: *m*/*z* calcd 351.0563, found 351.0560.

***cis*-Tetracarbonyl[(*N*-(η^2-allyl)-*N*-isopropylamino)(2-methylphenyl)carbene]chromium(0) (14c).** The same method as was used for the preparation of **13a** with **12** (97 mg, 0.3 mmol) and 2-iodopropane (0.40 mL, 4 mmol) gave yellow crystals of **14c** (84 mg, 77%). Mp: 92−94 °C (methanol). ^{1}H NMR ($CDCl_3$, 500 MHz, two diastereoisomers in 2:1 ratio): δ 1.03 (d, J = 6.4 Hz, 3H, −CH_3, major), 1.17 (d, J = 6.6 Hz, 3H, −CH_3, minor), 1.20 (d, J = 6.3 Hz, 3H, −CH_3, major + minor), 2.04 (s, 3H, Ar CH_3, minor), 2.10 (s, 3H, Ar CH_3, major), 3.07 (d, J = 12.9 Hz, 1H, =CH_2, major), 3.13 (d, J = 8.7 Hz, 1H, =CH_2, major), 3.35 (d, J = 8.5 Hz, 1H, =CH_2, minor), 3.48 (d, J = 13.2 Hz, 1H, =CH_2, minor), 3.75 (sep, J = 6.6 Hz, 1H, −C*H*<), 3.84 (m, 1H, −CH_2−, minor), 4.26 (d, J = 14.1 Hz, 1H, −CH_2−, major), 4.39 (dd, J = 14.1, 4.7 Hz, 1H, −CH_2−, major), 4.50−4.59 (m, 1H, −CH_2−, minor), 4.50−4.67 (m, 1H, −C*H*=), 6.49 (d, J = 7.4 Hz, 1H, *o*-Ar *H*, major), 6.73 (d, J = 7.4 Hz, 1H, *o*-Ar *H*, minor), 7.06−7.27 (m, 3H, Ar *H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 282.6 (C=Cr, minor), 282.1 (C=Cr, major), 231.3 (CO, major), 229.9 (CO, minor), 227.9 (CO, minor), 226.3 (CO, major), 225.6 (CO, major), 225.3 (CO, major), 223.0 (CO, minor), 222.6 (CO, minor), 147.6 (Ar *C*, minor), 147.1 (Ar *C*, major), 130.3 (Ar *C*H, major), 130.2 (Ar *C*H, minor), 126.5 (Ar *C*, major), 126.4 (Ar *C*, minor), 126.2 (Ar *C*H, minor), 126.1 (Ar *C*H, major), 125.8 (Ar *C*H, minor), 125.6 (Ar *C*H, major), 120.1 (*o*-Ar *C*H, minor), 118.9 (*o*-Ar *C*H, major), 78.1 (−CH=, minor), 72.9 (−CH=, major), 67.8 (=CH_2, minor), 62.5 (=CH_2, major), 55.3 (−CH_2-, minor), 55.2 (−CH<, minor), 54.7 (-CH<, major), 53.9 (−CH_2−, major), 21.1 (CH_3, major), 20.9 (CH_3, minor), 20.5 (CH_3, minor), 20.1 (CH_3, major), 19.3 (Ar CH_3, minor), 19.0 (Ar CH_3, major). IR ($CHCl_3$): ν 2013, 1912, 1889, 1513, 1478, 1177 cm^{-1}. Anal. Calcd for $C_{18}H_{19}NO_4Cr$: C, 59.18; H, 5.24; N, 3.83. Found: C, 58.88; H, 5.36; N, 3.58.

Acknowledgment. This work was supported by Grant Nos. 203/00/1240 and 203/04/0487 from the Czech Grant Agency and by the Research Project MSM6046137301 of the Ministry of Education, Youth and Sport of the Czech Republic.

OM0605837