Reaction of Aminocarbene Complexes of Chromium with Alkynes. 2. Intramolecular Insertions Leading to Polycyclic Lactams

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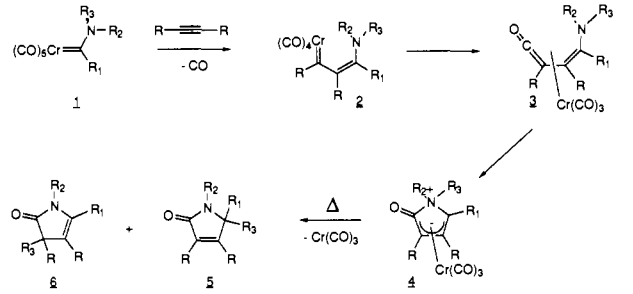
Abstract: Thermolysis of chromium-containing carbene complexes of the general structure $(CO)_5Cr{=}C(NR_2R_3)$-$(CH_2)_nC{\equiv}C{-}R_1$ has been examined. When nitrogen is part of a strained cycle ($R_2R_3 = (CH_2)_m$, $m = 2, 3$) or in an allylic position, or if $m > 4$, then the insertions of the triple bond and of CO, followed by a rearrangement to tricyclic lactams, are observed. This was the case for **14** ($R_2R_3 = (CH_2)_3$, $n = 4$, R_1 = Ph), for **18** ($R_2R_3 = (CH_2)_3$, $n = 3$, R_1 = Ph), and for **27** ($R_2R_3 = CH_2CH{=}CHCH_2$, $n = 4$, R_1 = Ph), which led respectively to **15**, **19**, and **28**, the structures of which could be established by X-ray crystallography. However C-H bond activations, followed by CO insertion, were observed for **31** ($R_2R_3 = CH_2CH{=}CHCH_2$, $n = 3$, R_1 = Me), which gave **32**, and for $(CO)_5Cr{=}C(Et)N$-$(Me)(CH_2)_3C{\equiv}C{-}Ph$ (**69**) and $(CO)_5Cr{=}C(Me)N(Me)(CH_2)_3C{\equiv}C{-}Ph$ (**72**), in which the triple bond is tethered to nitrogen and which led to the cyclopentenones **70** and **73**. Finally, double CO insertions, confirmed by an X-ray structure determination on **60** were observed for complexes **14**, **18**, **22**, and **58**, derived from azetidine and from methylaziridine, whereas double alkyne insertions, with or without CO insertion and propene elimination, leading to substituted pyridines and dihydropyridines, were observed for **58** and **65**, the aminocarbene complexes derived from methylaziridine.

Introduction

The interaction of aminocarbene complexes of chromium with alkynes resulted in an unexpected and rewarding chemistry.[1,4c] Though these complexes[4a,b] reacted with alkynes like alkoxycarbene complexes to give vinylketene intermediates **3** (Scheme I), a new reaction was observed at this stage: provided that the amino group was *cis* with respect to the ketene function in **3**, then an intramolecular interaction between the tertiary amine and the central carbon atom of the ketene, leading to a nitrogen ylide **4** occurred. Rearrangement of these intermediates according to routes close to those observed for the Stevens rearrangement of organic ylides led to lactams **5** and **6**.[2]

In a previous publication,[3] we described the general aspects, especially focused on mechanistic points related to the formation, structure, and rearrangement, of nitrogen ylide complexes obtained upon *inter-* and *intramolecular* insertions of alkynes. In the case of *intermolecular* reactions (Scheme I), the factors which govern the formation and stability of the nitrogen ylide complexes have been established and are as follows: (1) When nitrogen bore substituents of high propensity for the migration (benzyl, allyl) or was part of a strained cycle, no ylide intermediates could be isolated and direct formation of lactams was observed. (2) In the case of aminocarbene complexes in which the nitrogen atom bore groups of known low propensity for the migration, then the nitrogen ylide complexes could be isolated. Nevertheless, they could be rearranged thermally to the same type of lactams. Methyl and phenyl groups, which are the worst groups for the Stevens rearrangement in terms of migratory aptitude, could nevertheless be forced to migrate to some extend.[5] (3) Furthermore, aminocarbene complexes bearing on the carbene carbon a phenyl group did only partially undergo the known and expected benzannulation reaction. The main reaction path was again the same as that for alkyl-substituted aminocarbene complexes, the formation of phenyl-substituted lactams, via nitrogen ylides. (4) As far as the *intramolecular* reactions were concerned, a few examples of such alkyne insertions into aminocarbene complexes had already been disclosed. It has been shown, by Wulff and co-workers, that the insertions of both the alkyne and CO take place, leading to stable η^4-vinylketene complexes.[6] No further reaction of this intermediate could be observed. Conversely, we

Scheme I



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(1) Parlier, A.; Rudler, H.; Yefsah, R.; Daran, J. C.; Knobler, C. *J. Chem. Soc., Chem. Commun.* **1988**, 635.

(2) Rudler, H.; Parlier, A.; Goumont, R.; Daran, J. C.; Vaissermann, J. *J. Chem. Soc., Chem. Commun.* **1991**, 1075.

(3) Chelain, E.; Goumont, R.; Hamon, L.; Parlier, A.; Rudler, M.; Rudler, H.; Daran, J. C.; Vaissermann, J. *J. Am. Chem. Soc.* **1992**, *114*, 8088.

(4) For reviews and recent articles on the synthesis and uses of aminocarbene complexes see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (b) Schubert, U. *Advances in metal carbene chemistry*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989. (c) Rudler, H.; Audouin, M.; Chelain, E.; Denise, B.; Massoud, A.; Goumont, R.; Parlier, A.; Pacreau, A.; Rudler, M.; Yefsah, R.; Alvarez, C.; Delgado-Reyes, F. *Chem. Soc. Rev.* **1991**, *20*, 503. (d) Schwindt, M. A.; Miller, J. R.; Hegedus, L. S. *J. Organomet. Chem.* **1991**, *413*, 143. (e) Grotjahn, D. G.; Dötz, K. H. *Synlett* **1991**, 381. (f) Dötz, K. H.; Schäfer, T. O.; Harms, K. *Synthesis* **1992**, 146. (g) Grotjahn, D. B.; Kroll, F. E. K.; Schäfer, T. O.; Harms, K. *Organometallics* **1992**, *11*, 298. (h) Dötz, K. H.; Grotjahn, D.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1384. (i) Hegedus, L. S.; Lastra, E.; Narukawa, Y.; Snustad, D. C. *J. Am. Chem. Soc.* **1992**, *114*, 2991. (j) Anderson, B. J.; Wulff, W. D.; Powers, T. S.; Tribbitt, S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 10784. (k) Merlic, C. A.; Xu, D.; Gladstone, B. G. *J. Org. Chem.* **1993**, *58*, 538.

(5) Unpublished results, in preparation.

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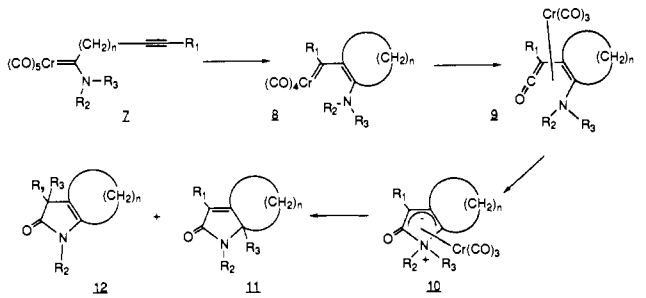
Scheme II



described in a previous publication several examples where the reaction stopped either at the ketene or at the ylide stage.[3] Again, no further reaction (for example, rearrangement) could be established. However, we found that the benzyl-substituted aminocarbene complex (**7**, n = 3, R_1 = Ph, R_2 = CH_3, R_3 = CH_2Ph, Scheme II) tethered by an alkyne chain was indeed a precursor of the lactams **11** and **12**, the formation of which could again be rationalized in terms of the rearrangement of the same type of nitrogen ylides **10** as depicted in Scheme II.

The present publication will deal with the generalization of the reaction outlined in Scheme II and try to establish the possibilities and limits of these *intramolecular* reactions. We will focus attention on the use of aminocarbene complexes originating from cycloamines which have been found to easily undergo, in the *intermolecular reactions*, ring opening/rearrangement. As will be established, such transformations lead to interesting nitrogen-containing polycyclic intermediates.

Results

Azetidine-Substituted Carbene Complexes. Previous investigations came to the conclusion that azetidine-substituted carbene complexes were among the most reactive carbene complexes in the insertion/rearrangement reaction, leading upon 1,2 migrations (**5**, R_2R_3 = $(CH_2)_3$, in Scheme I) to pyrrolizidine derivatives in good to excellent yields. No profound influence of the nature of the substituent R_1 on the course of the reaction could be established. Especially remarkable was the absence of benzannulation products in the case where R_1 = Ph.[4c]

We have therefore synthesized a series of complexes of the type **7** in which several important structural modifications could be introduced, for example the length of the tethered chain and the nature of the substituents on the triple bond. Since we had established, in the case of the intermolecular reactions, that the best results were observed with phenyl-substituted alkynes, most of the intramolecular reactions were carried out on complexes bearing a phenyl group on the triple bond. However, and in order to be able to later introduce structural modifications, we examined also the behavior of the complex in which R_1 = $SiMe_3$.

The carbene complexes **14**, **18**, and **22** were obtained as pale-yellow oils from the related ethoxycarbene complexes by aminolysis with azetidine, in respectively 95, 90, and 68% yield. Complexes **13**, **17**, and **21** were in turn prepared using standard synthetic procedures. Details are provided in the Experimental Section.

When complex **14** was refluxed in benzene for 12 h, complete disappearance of the starting material was established by TLC. Silica gel chromatography afforded two new compounds **15** and **16**, in respectively 23 and 13% yield. To the less polar and most abundant compound (white crystals, mp 109 °C) was attributed structure **15** on the following grounds. The high-resolution mass spectrum (m/e = 253) was in agreement with the molecular formula $C_{17}H_{19}NO$. Both the IR and ^{13}C NMR spectra confirmed the presence of an unsaturated lactam (ν CO, 1670 cm^{-1}; δ CO, 175.06; δ C=C, 160.61 and 131.54). The ^{13}C NMR spectrum accounted for and distinguished all seven methylene groups with signals at δ 41.87 (NCH_2), 37.25, 31.24, 27.57, 27.13, 26.52, and 22.88, the quaternary carbon appearing at δ 71.97. The ^1H NMR spectrum clearly distinguished only the NCH_2 protons, at δ 3.64 and 3.31, and one allylic proton, at δ 3.06. Although these data agreed with a structure such as **15**, the occurrence of which fell into Scheme II, a final assessment was obtained by an X-ray analysis.

(6) Anderson, B. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 8615.

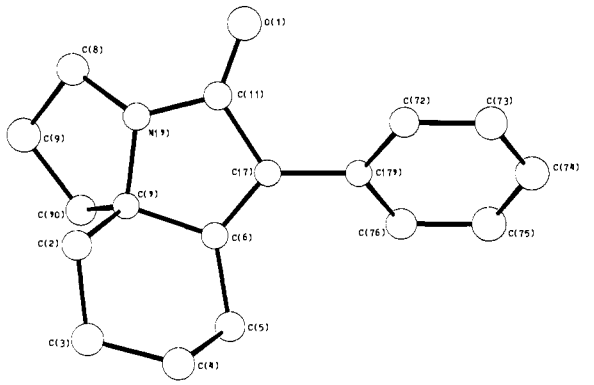


Figure 1. Perspective drawing of **15** with hydrogen atoms omitted for clarity.

Table I. Selected Bond Distances (Å) for Compounds **15**, **19**, **29**, and **60**

	$C_{16}H_{17}ON$ (**19**)		
O(1)–C(10)	1.215(5)	N(1)–C(1)	1.466(5)
N(1)–C(7)	1.476(5)	N(1)–C(10)	1.366(5)
C(1)–C(2)	1.531(6)	C(1)–C(5)	1.510(5)
C(1)–C(9)	1.524(5)	C(2)–C(3)	1.551(7)
C(3)–C(4)	1.542(6)	C(4)–C(5)	1.494(5)
C(5)–C(6)	1.326(5)	C(6)–C(10)	1.502(5)
C(7)–C(8)	1.525(6)	C(8)–C(9)	1.540(6)
	$C_{21}H_{19}O_4NCr$ (**29**)		
C(1)–C(11)	1.542(6)	C(2)–C(3)	1.520(6)
C(3)–C(4)	1.511(7)	C(4)–C(5)	1.529(7)
C(5)–C(6)	1.494(6)	C(6)–C(7)	1.324(5)
C(7)–C(12)	1.492(5)	C(8)–C(9)	1.487(7)
C(9)–C(10)	1.305(7)	C(10)–C(11)	1.505(7)
N(1)–C(1)	1.456(5)	N(1)–C(8)	1.443(5)
N(1)–C(12)	1.342(5)	C(1)–C(2)	1.538(6)
C(1)–C(6)	1.506(6)		
	$C_{17}H_{19}ON$ (**15**)		
O(1)–C(11)	1.240(6)	N(1)–C(1)	1.472(6)
N(1)–C(8)	1.486(7)	N(1)–C(11)	1.350(6)
C(1)–C(2)	1.529(7)	C(1)–C(6)	1.501(7)
C(1)–C(10)	1.537(7)	C(2)–C(3)	1.536(8)
C(3)–C(4)	1.521(8)	C(4)–C(5)	1.537(8)
C(5)–C(6)	1.494(7)	C(6)–C(7)	1.336(7)
C(7)–C(11)	1.486(7)	C(8)–C(9)	1.528(8)
C(9)–C(10)	1.531(8)		
	$C_{17}H_{17}O_2N$ (**60**)		
O(1)–C(10)	1.205(4)	O(2)–C(11)	1.219(5)
N(1)–C(1)	1.446(5)	N(1)–C(7)	1.472(5)
N(1)–C(11)	1.395(5)	C(1)–C(2)	1.526(5)
C(1)–C(5)	1.498(5)	C(1)–C(10)	1.539(5)
C(2)–C(3)	1.536(5)	C(3)–C(4)	1.541(6)
C(4)–C(5)	1.480(5)	C(5)–C(6)	1.341(5)
C(6)–C(11)	1.483(5)	C(7)–C(8)	1.543(5)
C(8)–C(9)	1.517(5)	C(8)–C(10)	1.506(5)

Solid-State Structure of Compound 15. The crystal structure clearly established that both the alkyne/CO insertions, followed by a rearrangement with C–N bond rupture and C–C bond formation, leading finally to the tricyclic structure **15**, took place. Its precise geometry, which showed several interesting features, appears in Figure 1. The most important bond distances are given in Table I.

The value for the amide C–N bond length was 1.350(6) Å, which is, as expected, intermediate between the single-bond C–N length of 1.47 Å and the double-bond C=N length of 1.24 Å.

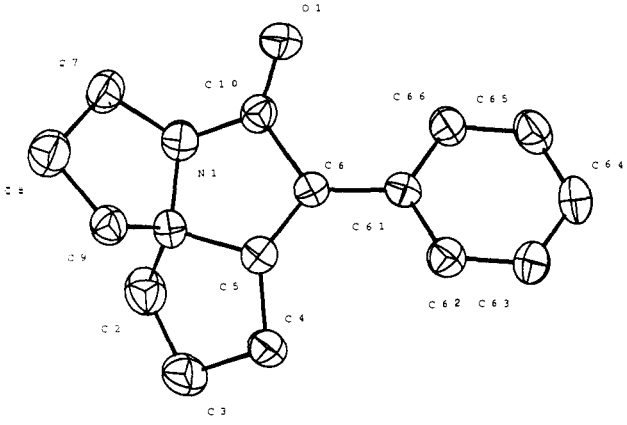


Figure 2. Perspective drawing of **19** with hydrogen atoms omitted for clarity.

However, in contrast to what is generally observed in amides, the summation of the three valence angles around the nitrogen, 343°, is different from the expected value of 360°, an observation which indicates that the nitrogen atom is not entirely planar.

As far as the more polar compound **16** was concerned, it differed from **15** according to the mass spectrum by the presence of an additional CO group. This was also confirmed by a new signal in the ^{13}C NMR spectrum at δ 205.06 besides the signal for the amide at δ 169.0.

Taken together with the IR spectrum (ν CO, 1670 and 1710 cm^{-1}), these indications agreed with the presence of an unsaturated amide, as for **15**, and of a six-membered ketone. DEPT experiments confirmed again the presence of seven methylene groups at δ 37.51, 37.16, 36.13, 27.56, 26.20, 25.04, and 20.87. Moreover, COSY LR experiments established a coupling, besides the geminal and vicinal couplings, between a NCH proton and a proton C(10)-H, α to the carbonyl group, at δ 2.42, establishing the presence of the $N(CH_2)_3CO$ fragment and thus structure **16**.

Complexes **18** and **22** behaved similarly: under the same conditions, they gave two sets of compounds, the expected tricyclic compounds **19** (31%) and **23** (14%), besides the unexpected dicarbonyl products **20** (12%) and **24** (11%). Their structures were established essentially by the use of extensive ^1H and ^{13}C NMR spectroscopy and, for **19**, by an X-ray diffraction study. An ORTEP projection appears in Figure 2, the most important bond distances and bond angles being listed in Table I. The conformation of the azatriquinane derivative **19** is similar to that of **15**: due to the ring strains, no planarity of the lactam function is observed, the nitrogen atom lying again beneath the best plane determined by C(1), C(5), C(6), C(10), and O(1).

Pyrroline-Substituted Carbene Complexes. In the same way as azetidine-substituted carbene complexes led to pyrrolizidines, pyrroline-substituted carbene complexes gave selectively indolizidine derivatives upon *intermolecular* alkyne insertion reactions, as a result of a 1,2 migration of an alkyl group from nitrogen to the adjacent carbon atom (**5**, R_2R_3 = $CH_2CH{=}CHCH_2$, in Scheme I).

The alkyne-tethered carbene complexes **25**, **27**, and **31** were prepared either by the classical aminolysis reaction, for complexes **25** and **27**, or by alkylation of [methylpyrrolinomethylene]-pentacarbonylchromium(0) (**30**) with the appropriate triflate in the presence of BuLi, for complex **31**.[7] These complexes were characterized by their spectroscopic data and their elemental analysis.

Under the same conditions as for the previous complexes, complex **25** gave, after silica gel chromatography, a single organic product in only 15% yield, as an oil. The IR and ^{13}C NMR spectra were in agreement with the presence of a conjugated lactam as for the previous products (ν CO, 1670 cm^{-1}; δ CO, 170.4). The ^1H NMR spectrum confirmed the presence of the disubstituted double bond, with a multiplet at δ 5.80–5.87 for two hydrogens, whereas the ^{13}C NMR spectrum showed signals for five CH_2 groups at δ 39.14, 32.81, 32.28, 25.97, and 23.32, for a quaternary carbon at δ 66.59, and for two sp^2 carbons at δ 124.32 and 121.53. Thus structure **26**, a tricyclic lactam, was assigned to this compound, by analogy with our previous findings.

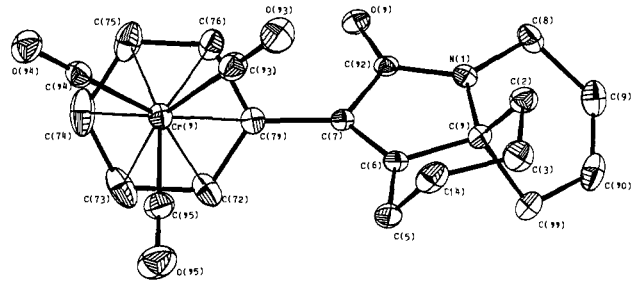


Figure 3. Perspective drawing of **29** with hydrogen atoms omitted for clarity.

In the case of **27**, two new products were isolated, an organic product **28** and its $Cr(CO)_3$ complex **29**, in a 71% overall yield. They were separated by silica gel chromatography. The more polar compound, isolated in 40% yield as yellow crystals (mp 164 °C) was assigned structure **29**, in agreement with the elemental analysis and the mass spectrum. The IR confirmed the presence of the $Cr(CO)_3$ moiety (ν CO, 1965 and 1890 cm^{-1}) and of a conjugated amide (ν CO, 1670 cm^{-1}). The ^{13}C NMR spectrum established the presence of the amide function (δ CO, 166.8 ppm), of a nonconjugated double bond (δ 123.94 and 121.75 ppm), of a quaternary carbon atom at δ 60.17, and of six CH_2 groups at δ 21.77, 25.37, 27.98, 31.17, 35.23, and 37.93. A final confirmation of the structure was obtained by a single-crystal X-ray analysis.

Solid-State Structure of Complex 29. The ORTEP view (Figure 3) established that three reactions had indeed occurred as in the previous cases, the alkyne insertion with formation of a six-membered ring system in a chair conformation, the insertion of CO, leading to a planar five-membered unsaturated lactam, and finally a C–N bond rupture with migration of the alkyl chain from nitrogen to C(1), creating a six-membered unsaturated ring system. Whereas the value for the amide C(12)–N(1) bond length (1.342(5) Å) was very close to that observed in compounds **15** and **19**, the geometry around the nitrogen atom appeared to be quite different and reflected the influence of the size of cycle A on the general conformation of these tricyclic systems. As for classical amides, planarity around the nitrogen atom was observed, the summations of the three valence angles being exactly equal to 360°.

Treatment of complex **29** in boiling pyridine gave quantitatively one organic compound, as an oil, the spectroscopic data of which were in all respects identical with those of **28** isolated directly from the reaction mixture (see the Experimental Section).

Unexpected Behavior of Complex 31. In contrast to the previous complexes which gave heterocylic compounds the formation of which could be explained (vide infra) in the light of previous results, the thermal transformation of **31** followed a quite different pathway. Its reaction in boiling benzene was very fast and led, after a few hours, to a single polar organic compound isolated as white crystals, in 41% yield. The mass spectrum (m/e = 189) and elemental analysis were in agreement with the molecular formula $C_{12}H_{15}NO$ and thus with a structure resulting from the loss of $Cr(CO)_3$ and the insertion of CO. This was also apparent in the IR and ^{13}C NMR spectra (ν CO, 1640 cm^{-1}; δ CO, 203.7). Moreover, the ^{13}C NMR spectrum revealed the presence of all the carbons, of which five were sp^2 (δ 203.7, 154.3, 141.9, 125.8, and 117.9); thus it had to contain three cycles besides a carbon–carbon double bond and conjugated ketone. Its structure could finally be established by extensive ^1H and ^{13}C NMR spectroscopy

(7) Wulff, W. D.; Anderson, B. J.; Isaacs, L. D. *Tetrahedron Lett.* **1989**, *30*, 4061.

together with deuterium labeling: DEPT experiments confirmed the presence of four methylene groups, for C(5) at δ 50.71 C(7) at δ 33.36, C(9) at δ 31.67, and C(8) at δ 19.25, of two methines, for C(6) at δ 72.91 and C(2) at δ 56.91, and of one methyl group, for C(12) at δ 15.73. A HETCOR spectrum furnished the attribution for all the protonated carbons, whereas the others were connected via their long-range couplings: C(1) with H(2) and H(5), C(10) with H(7,7′) and H(9,9′).

The insertion reaction carried out on the labeled complex **31b** led to the dideuterated product **32b**, the NMR spectrum of which confirmed the signal assignments (vide infra).

All together, these data ascertained structure **32** for this unexpected rearrangement product.

Tetrahydropyridine-Substituted Carbene Complex 34. We had established previously that, during the *intermolecular* insertions of alkynes into tetrahydropyridine-substituted carbene complexes, both ring-contraction and ring-expansion reactions took place.[1] This contrasted with the sole ring-contraction products observed in the Stevens rearrangement of organic nitrogen ylides derived from the same amine.[8] The *intramolecular version* of this insertion reaction was performed on complex **34** prepared in several steps from *N*-acetyltetrahydropyridine via the amide **33**. The Hegedus method[9] gave complex **34** in 36% yield. Heating this complex in benzene under reflux gave, after silica gel chromatography, a first fraction of two inseparable organic compounds in 30% yields and then a yellow complex **36** as a single isomer which, according to its spectroscopic data, contained an arene $Cr(CO)_3$ fragment. Heating of this complex in pyridine gave quantitatively one of the products contained in the first fraction. Both the mass spectrum and the elemental analysis agreed with a structure such as **35**: the most significant feature in the ^1H NMR spectrum was the presence of a vinyl group, with signals for three hydrogens at δ 5.30, 5.04, and 4.91. The ^{13}C NMR spectrum revealed again the presence of a conjugated five-membered lactam (δ CO, 174.36; δ C=C, 158.00 and 140.59), of a quaternary N—C carbon, at δ 74.37, of six methylene groups, at δ 46.08 (NCH_2), 40.43, 38.48, 27.02, 26.71, and 22.92, and of a methine, at δ 34.01.

To the second product of the first fraction was given structure **37** on the basis of a difference ^1H NMR spectrum: especially revealing was the presence of signals due to the disubstituted double bond as characteristic multiplets at δ 6.02 and 5.72, which were also observed in the analogous compound obtained in the *intermolecular* reaction (**5**, $R_2R_3 = (CH_2)_2CH{=}CHCH_2$, Scheme I).

Pyrrolidino-Substituted Carbene Complexes 39 and 42. Among the most stable and less prone to rearrangement were the pyrrolidinocarbene complexes such as **38**. Thus, complex **38** gave only, among others, moderate yields of insertion/rearrangement product **6** (Scheme I, $R_2R_3 = (CH_2)_4$).[10] The behavior of two alkynylpyrrolidinocarbene complexes **39** and **42** was nevertheless examined. They were synthesized respectively from the known complex **38**, which was alkylated with the appropriate alkynyl triflate in the presence of BuLi (51%), and from the amide **41** and $Cr(CO)_5Na_2$ (72%).

When complex **39** was refluxed in benzene for 12 h, complete disappearance of the starting product was observed. Silica gel chromatography of the residue gave a single organic product in 37% yield, the structure of which was established to be ethylidenecyclopentanone (**40**) by comparison with an authentic sample prepared from cyclopentanone.[28] The mass spectrum (m/e = 110) and the elemental analysis were in agreement with such a structure. Both the IR (ν CO, 1730 cm^{-1}; ν C=C, 1690 cm^{-1}) and the ^{13}C NMR spectra (δ CO, 206.7; δ C=C, 138.3 and 130.8) confirmed the presence of a conjugated ketone. In the ^1H NMR spectrum, signals for a vinylic hydrogen at δ 6.54 (m) and a methyl group coupled to it at δ 1.75 (d, J = 7.2 Hz), besides three multiplets at δ 2.52 (2H), 2.26 (2H), and 1.91 (2H), confirmed this proposal.

The case of complex **42**, bearing instead a phenyl group on the triple bond, had already been examined: it gave upon heating either in benzene or cyclohexane a 45% yield of the ylide **43**.[3] However, upon heating in toluene, no rearranged products could be detected: only decomposition took place. Rearrangement of **43** could nevertheless be induced, to some extend, upon oxygenation under UV irradiation. Under such conditions, a 13% yield of the tricyclic lactam **44** could be obtained. All the spectroscopic data agreed with such a structure: the IR (ν CO, 1660 cm^{-1}) and the ^{13}C NMR spectrum (δ CO, 169.9; δ C=C, 167.4 and 132.2) with signals at δ 69.1 (N—C) and at δ 38.7, 33.3, 29.8, 25.6, 25.4, 23.1, and 21.2 for the seven CH_2 groups.

It must be noticed here that complexes **45**, bearing like **34** an allyl group on nitrogen, and **46**, bearing like **41** two alkyl groups on nitrogen, did not undergo the expected insertion/rearrangement reactions upon heating: only decomposition of the starting material was observed.

Case of Piperidine and Hexamethylenimine Carbene Complexes 48a,b. Complexes **48a** and **48b** were synthesized from the corresponding amides **47a,b** in 45 and 51% yield. Their thermolysis in cyclohexane gave the expected ylides **49a,b** in respectively 84 and 52% yield, which were fully characterized by their elemental analysis as well as by their spectroscopic data. Only small amounts of organic products could be detected in these reactions. However, when the same reactions were carried out directly in refluxing toluene, then three sets of organic products could be separated and fully characterized: the classical bridgehead lactams **50a,b**, the bridgehead lactams **52a,b** (in trace amounts) with the double bond in cycle A, and finally the conjugated lactams **51a,b**.[11]

The structures of **50** and **51** were easily established by comparison of their spectroscopic data with those of the related compounds obtained during the *intermolecular* reactions carried out on various piperidine- and hexamethylenimine-substituted carbene complexes (Scheme I, $R_2R_3 = (CH_2)_5$ and $(CH_2)_6$).

Thus for example, in the case of **48a**, three compounds could be separated by silica gel chromatography. The more polar compound (17%) was assigned structure **51a**, a conjugated lactam, essentially on the basis of its IR (ν CO, 1660 cm^{-1}) and NMR data. The ^{13}C NMR spectrum disclosed, besides the signal for a carbonyl carbon at δ 170.2, a signal for the quaternary N–C carbon, at δ 65.7, and distinguished all nine CH_2 groups.

The second product (24%) was assigned structure **50a**; its ^{13}C NMR spectrum displayed signals for the nonconjugated carbonyl carbon, at δ 189.08, for the double bond, at δ 138.5 and 119.8, and for the quaternary carbon, at δ 59.4, and again nine signals for the different methylene groups. Finally, the spectroscopic data for the less polar compound (3%) agreed with structure **52a**; indeed, the ^1H NMR spectrum confirmed the presence of a trisubstituted double bond, one substituent being nitrogen with a multiplet at δ 4.83 (1H). The ^{13}C NMR spectrum gave signals at δ 183.0 for the CO, at δ 142.8 and 96.1 for the C=C double bond, and at δ 54.3 for the quaternary carbon to the carbonyl group and finally nine signals for the eight methylene groups and the methine group. Similar results were observed upon thermolysis of the ylide **49a**: compounds **50a**, **51a**, and **52a** were isolated in respectively 27, 15, and 6% yield.

The spectroscopic data for the set of compounds **50b** (31%), **51b** (2%), and **52b** (6%), obtained from **48b**, will be found in the Experimental Section.

Pyrrolidinone-Derived Carbene Complex 56. A further way to build nitrogen-containing polycyclic compounds would be to start from carbene complexes of the type **53** in which R_2 could be an

(8) Mageswaran, S.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1053.
(9) Imwinkelreid, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702.
(10) Rudler, H.; Parlier, A.; Yefsah, R.; Denise, B.; Daran, J. C.; Vaissermann, J.; Knobler, C. *J. Organomet. Chem.* **1988**, *358*, 245.
(11) For a recent review on bridgehead lactams see: *Molecular Structure and Energetics. Structure and Reactivity*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1988; Vol. 7, p 139.

alkyl group, R_3 a hydrogen or an alkyl group, R_2R_3 a cycle, and so on. As a probe for such a reaction, we synthesized complex **56** from the corresponding amide **54**, by alkylation with the appropriate iodide and finally by submitting the amide **55** to $Cr(CO)_5Na_2/TMSCl/Al_2O_3$. **56** could be isolated as a yellow oil in 70% yield.

When **56** was heated in refluxing benzene for one night, two organic compounds were obtained, after silica chromatography, in respectively 6 and 34% yield as single isomers. The most abundant product (white crystals, mp 95 °C) was assigned structure **57a** on the following grounds. The mass spectrum (m/e = 329) confirmed the loss of $Cr(CO)_4$ and thus the incorporation of one CO group in the organic ligand of complex **56** in accordance with the IR spectrum (ν CO, 1680 cm^{-1}). The position of the signals associated with the two benzylic hydrogens, which appeared as two doublets at δ 3.50 and 3.21 (J = 12 Hz), confirmed that the benzylic group migrated from nitrogen to a carbon atom. The ^{13}C NMR spectrum accounted for and distinguished all carbon atoms, except those for the phenyl group. DEPT experiments allowed assignment of the nature of the various carbons, whereas the relationship between carbons and protons could be laid down by a heteronuclear shift-correlated ^2D NMR spectrum. As a result, the shifts of the various carbons were as follows: δ C(2), 113.8; δ C(3), 147.1; δ C(4), 67.5; δ C(5), 32.5; δ C(7), 43.1; the methylene carbons, δ 40.3, 35.9, 32.5, 29.1, 23.9, and 21.6. Especially informative was the presence of signals assignable to those of a carbon–carbon double bond at δ 147.1 and 113.4. All this data were in agreement with those of a compound of Scheme II (n = 3, R_1 = Ph, R_2 = Me, R_3 = CH_2Ph) disclosing the same structural features, and thus with structure **57a**. For similar reasons, structure **57b** was assigned to the less polar product of the reaction.

Aziridine-Substituted Carbene Complexes. The behavior of aziridine-substituted carbene complexes toward external alkynes has been found to be peculiar. Two types of products were observed: those arising from their decomposition without incorporation of the alkyne, such as nitriles, and those arising from a double alkyne and a single CO insertion.[12,13] No products due to monoinsertion of the alkyne and CO had been detected. Complexes **58** and **65** containing respectively one and two triple bonds were therefore synthesized, and two series of reactions were carried out, the first one by simply heating **58** and **65** and the second one by heating **58** in the presence of a second alkyne.

When complex **58** was heated as usual, three products could be separated. The less polar one, obtained as an oil (17%), was assigned structure **59**, in agreement with its mass spectrum (m/e = 160). The IR spectrum indicated indeed the presence of a nitrile (ν CN, 2240 cm^{-1}). The ^{13}C NMR spectrum confirmed structure **59**: signals for the aromatic carbons, and for the carbons of the triple bond (δ 87.5 and 82.9), besides those for three methylene groups, were observed. The second product (11%, white solid, mp 144 °C) contained according to the IR (ν CO, 1690 and 1740 cm^{-1}) and the ^{13}C NMR spectra (δ CO, 213.0 and 180.1) two carbonyl groups assigned to a conjugated lactam and to a cyclopentanone. The ^1H NMR spectrum revealed signals for a NCH_2 group, as two multiplets at δ 4.55 and 3.10, and for a $CHCH_3$ fragment, with a doublet for the methyl group at δ 1.15 and a multiplet for the CH, at δ 2.85. The ^{13}C NMR spectrum confirmed the presence of four CH_2 groups, at δ 48.0 (NCH_2), 33.0, 26.3, and 24.6, of a CH at δ 46.2, and of a quaternary carbon at δ 79.7. Structure **60** was finally ascribed to this product by an X-ray diffraction study.

Solid-State Structure of 60. Crystals of **60** could be grown from hexane/methylene chloride. The ORTEP projection appears in Figure 4. The most important bond distances (Å) are listed

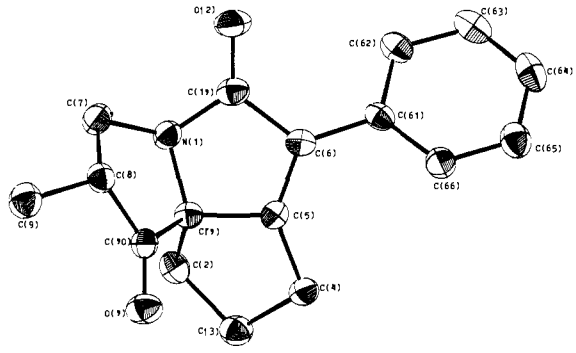


Figure 4. Perspective drawing of **60** with hydrogen atoms omitted for clarity.

in Table I. It confirms the presence of an azatriquinane system, with an unsaturated amide and a second CO group between carbons C(1) and C(8), respectively the carbene carbon and a carbon which was linked to nitrogen in *N*-methylaziridine. As far as the conformation of this system is concerned, it is again interesting to notice the nonplanarity of the amide group, the summation of the angles around the nitrogen atom being equal to 340°.

The last fraction was in fact a 2.5/1 mixture of two compounds, the substituted pyridine **62** and the functionalized tetrahydroquinolizine as its $Cr(CO)_3$ complex **63**: both compounds are the result of the interaction of **58** with **59**. The ^{13}C NMR spectrum of the mixture indicated indeed two series of signals: those attributable to **63** and those attributable to **62**. Attributions of the signals were rendered possible by comparison of the spectroscopic data with those of **61** (vide infra) and of **64**, the complex resulting from the *intermolecular* insertion of diphenylacetylene into the methyl(methylaziridino)methylene$Cr(CO)_5$ complex. The mass spectrum of a mixture of **62** and **63** (m/e = 338) was in agreement with a structure such as **62** but, according to previous results, also with structure **63**: it corresponds to a loss of C_4H_6-$OCr(CO)_3$. Such a fragmentation had been observed in the case of complex **64**, both in its mass spectrum and upon heating in pyridine. The ^{13}C NMR spectrum of **62** and **63** showed signals for the $Cr(CO)_3$ group at δ 232.0, for the cyclopentanone carbonyl group at δ 207.7, for the pyridine at δ 164.3, 158.41, 147.2, and 141.6, for the coordinated dihydropyridine at δ 119.1, 112.6, 102.5, and 79.3, for the NCH_2 at δ 53.6, and for the *C*HCO at δ 43.5. When the same reaction was carried out in the presence of a 10-fold excess of diphenylacetylene, only the nitrile **59** (48%) and the substituted pyridine **61** (31%) were isolated. The last compound could be characterized by its mass spectrum and elemental analysis, as well as by its ^1H NMR and ^{13}C NMR spectra, in which signals for the pyridine carbons appeared at δ 164.3, 156.6, 146.1, and 141.2 and for the three CH_2 groups at δ 34.8, 30.7, and 23.1.

Finally, and to reinforce the generality of this double alkyne insertion reaction, the dialkynylaziridino carbene complex **65** was synthesized from the related alkoxycarbene complex. Its heating in benzene gave indeed again two products, the nitrile **66** and the $Cr(CO)_3$ complex of the tetrahydroindolizidine **67**. Their structures were established as for the previous compounds of the same type, by their mass spectra and spectroscopic data.

N-Alkyne-Substituted Aminocarbene Complexes. Two series of aminocarbene complexes of this type were synthesized: those like **69** and **72** and those like **75** and **76**, bearing either an alkyl or a phenyl group on the carbene carbon.

Complexes **69**, **72**, and **76** were obtained from **68**, **71**, and **74** by reaction with the appropriate alkynylamine,[14] followed by alkylation at nitrogen.[15] Thermolysis of **69** gave a single organic compound **70** (42%), the mass spectrum of which indicated loss

(12) Denise, B.; Parlier, A.; Rudler, H.; Vaissermann, J.; Daran, J. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1303.

(13) Denise, B.; Massoud, A.; Parlier, A.; Rudler, H.; Vaissermann, J.; Daran, J. C.; Alvarez, C.; Patino, R.; Toscano, R. A. *J. Organomet. Chem.* **1990**, *386*, 51.

(14) Marszak-Fleury, A. *Bull. Soc. Chim. Fr.* **1958**, 490.

(15) Casey, C. P.; Boggs, R. A.; Anderson, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 8947.

of $Cr(CO)_4$ along with the insertion of CO into the organic ligand and agreed with the molecular formula $C_{16}H_{19}NO$; thus **70** had to contain, besides the aromatic ring, two additional rings. The IR (ν CO, 1700 cm^{-1}) and the ^{13}C NMR spectra (δ CO, 206.2; δ C=C, 168.80 and 131.24) confirmed the presence of a cyclopentenone. Signals for two methyl groups at δ 2.43 (NCH_3) and δ 1.30 (d, $CHCH_3$) were observed in the ^1H NMR spectrum. The ^{13}C NMR spectrum distinguished all the carbon atoms, and their nature could be assigned by DEPT experiments: δ C(1), 206.2; δ C(2), 46.7; δ C(3), 73.36; δ C(5), 56.12; δ C(6), 25.81; δ C(7), 27.09; δ C(8), 168.80; δ C(9), 131.24. Taken together with mechanistic considerations, these data agreed with structure **70**. Complex **71** led, under the same conditions, to a single product **73** (21%, mp 92 °C). The mass spectrum agreed with a structure resulting from the insertion of CO into the organic carbene together with loss of two hydrogen atoms. Both the IR (ν CO, 1680 cm^{-1}; ν C=C, 1660 cm^{-1}) and the ^{13}C NMR spectra (δ CO, 199.5; δ C=C, 167.2, 137.1, 121.8, 99.4) indicated the presence of a dienone. Structure **73** could finally be confirmed by ^{13}C and ^1H NMR spectroscopies. Partial structures [$N(Me)CH_2CH_2C(H)$=C] and [=C(H)COC(H)(Ph)C], established by means of chemical shifts and proton–proton couplings, were connected on the basis of $^2J_{C-H}$ and $^3J_{C-H}$ correlations. The downfield-shifted vinylic carbon, at δ 167.1 C(3), was correlated with the N-methyl protons at δ 3.00, H(16), the vinylic protons at δ 5.17, H(2), and δ 5.76 H(7), and the downfield-shifted methylene protons at δ 3.32–3.52, H(5), on the grounds of its spectroscopic data and of its chemical behavior. When the same reaction was carried out on the labeled complex **72b**, formation of **73** was again observed, with complete loss of deuterium: this result is easily undertandable, since both C(2)-H and C(9)-H can be exchanged upon silica gel chromatography.

In the case of complex **75**, two organic products were isolated. To the less polar product (54%) obtained as orange crystals was given structure **77**. Both the IR (ν CO, 1650 cm^{-1}) and the ^{13}C NMR spectra (δ CO, 184.1), together with the ^1H NMR spectrum, which showed signals for nine aromatic protons and three contiguous CH_2 groups, at δ 4.14 (t), 2.56 (t), and 1.79 (q), agreed with structure **77**, which indeed, upon air oxidation, led to the fully aromatic compound **78**, the second product of the reaction (23%). Only aromatic protons appeared in the ^1H NMR spectrum of **78**, besides a broad signal, for one proton, at δ 5.84, establishing the presence of a phenol.

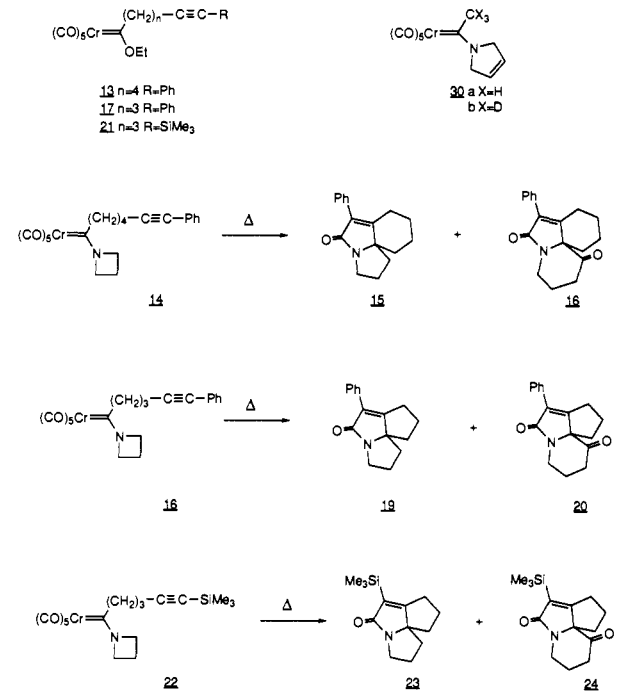
Thermolysis of **76** gave two products, an organic compound **79** (30%) and a complex **80a** (17%). Both the mass and the ^1H NMR spectra agreed with structure **79**: nine aromatic protons, a phenolic proton, at δ 5.1, three CH_2 groups, at δ 3.21, 2.44, and 1.84, and an NCH_3 group, at δ 2.92 characterized this compound. As far as the second product was concerned, both the ^1H and ^{13}C NMR confirmed the presence of an arene $Cr(CO)_3$ function. High-field signals for the five protonated carbons were observed at δ 54.22 (NCH_2), 52.75 (CHPh), 40.74 (NCH_3), 23.10, and 19.9 ($2CH_2$). The ^1H NMR spectrum also confirmed this structure, with the presence of signals for an isolated benzylic proton at δ 4.39, an NCH_2 group at δ 3.07–3.01, an NCH_3 group at δ 2.84, and multiplets for two CH_2 groups at δ 2.25–1.65. Air oxidation of **80a** gave the metal-free organic compound **80b** characterized by its mass spectrum and its NMR data.

Discussion

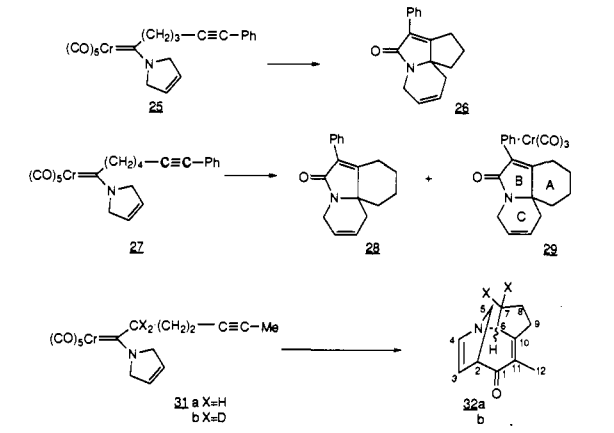
1. Expected Insertion Rearrangement Reactions via Nitrogen Ylides. The first and most striking feature which emerges from these experiments is the following: provided, on the one hand, that nitrogen bears substituents of high propensity for the migration (benzylic or allylic groups) or is part of a cycle (with the exception of the five-membered ring) and, on the other hand, that the triple bond bears a substituent which is able to stabilize both the carbene and the ketene functions (Ph, $SiMe_3$),[16] then

(16) Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* **1980**, *113*, 1449.

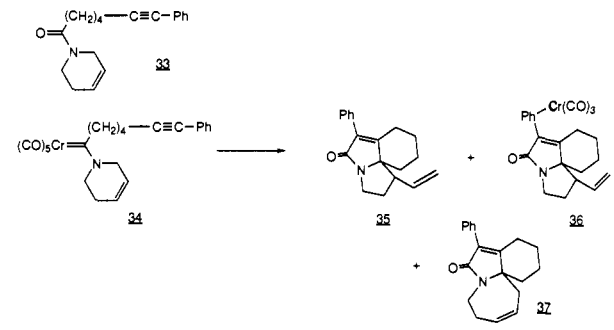
Scheme III



Scheme IV

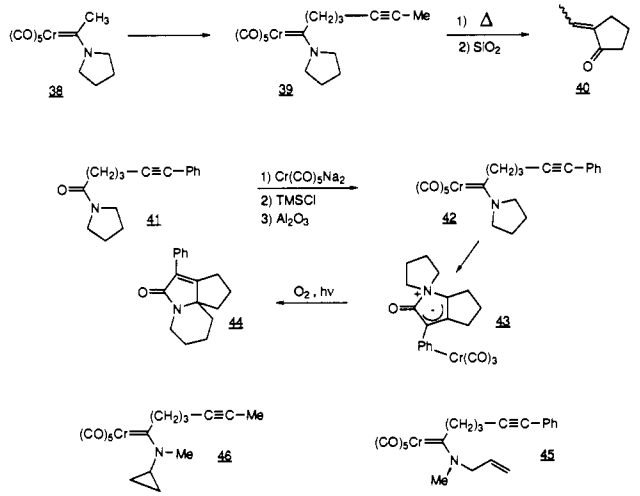


Scheme V

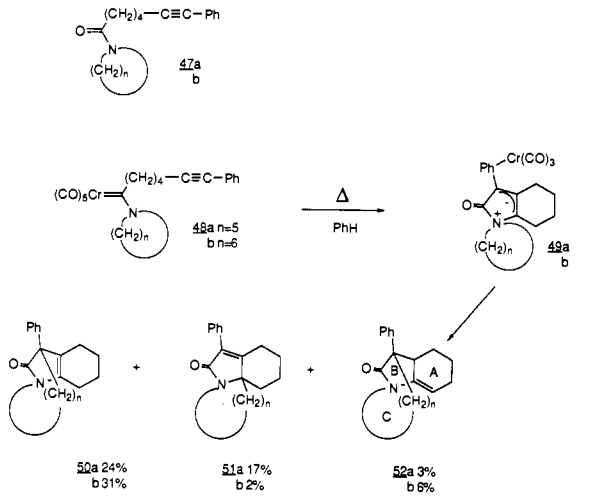


the insertion/rearrangement takes place to the same extent as for the *intermolecular* reactions. This was the case for the examples of Scheme III, for the two first examples of Scheme IV, and for the examples of Schemes V, VII, and VIII. Minor differences were nevertheless found in the case of **48a** and **48b**: whereas in the *intermolecular* reactions only bridgehead lactams of the type **6** (Scheme I) were observed, products due to both 1,2 (**51**) and 1,4 migrations (**50**) were found during the *intramolecular* reactions. This is probably a result of the strain introduced by the presence of a fused [5,6] ring system. A second point is related to the position of the double bond in these bridgehead

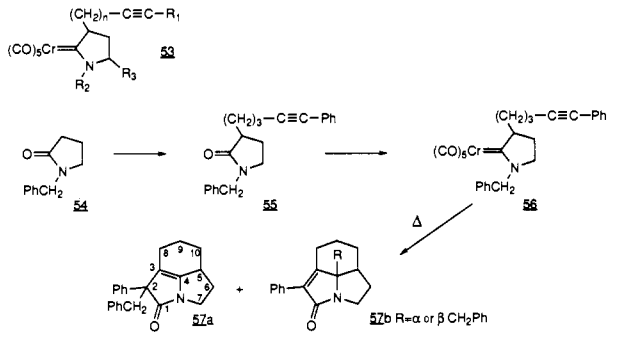
Scheme VI



Scheme VII



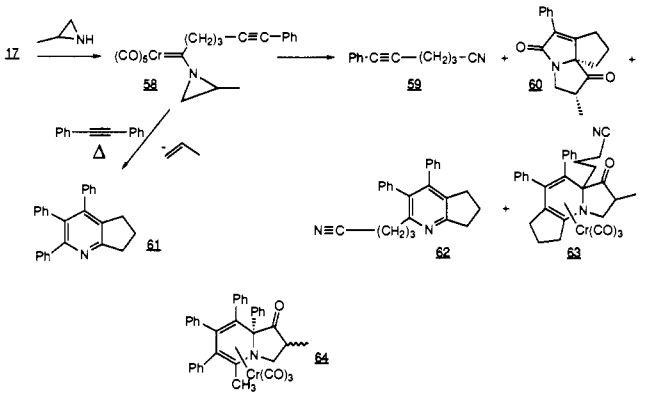
Scheme VIII



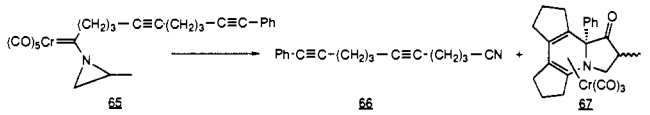
lactams: small amounts of lactams **52** in which the double bond is located in cycle A have been isolated. Their origin is not clear, although isomerization of the double bond of **50**, induced by Cr(O) species, might lead to **52**. However, exceptions to the rule were nevertheless observed. In spite of the fact that complex **45** fulfilled both conditions, an allyl group on nitrogen and a phenyl group on the triple bond, only trace amounts of organic products were formed upon its thermolysis. It is likely that in this case the coordination of the triple bond was hampered by the presence of the double bond. A similar negative result was observed for complex **46**, although the cyclopropyl group has been found to migrate, to a certain extend, during the *intermolecular* insertion reaction.[3]

2. C–H Bond Activation Reactions. The observations made so far nicely fit with the mechanistic proposal depicted in Scheme

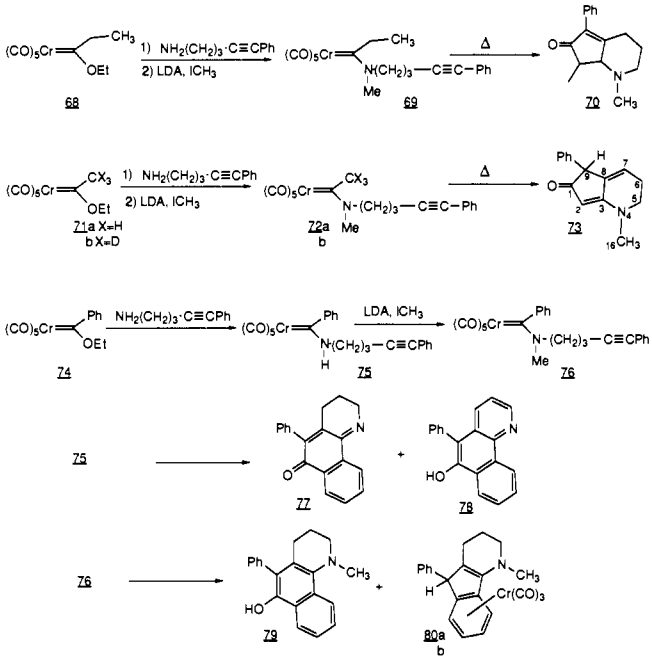
Scheme IX



Scheme X



Scheme XI

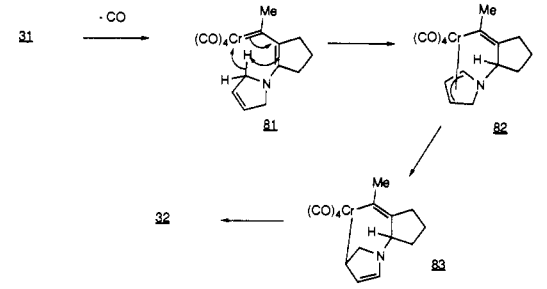


II: since the first step of the insertion reaction probably is the coordination of the triple bond to chromium with loss of CO followed by a fast rearrangement to a new carbene complex **8**, the evolution of **8** will be highly dependent on the nature of both R_1 and the amine. If R_1 = Ph, $SiMe_3$, and if the amine is not too crowded, then CO insertion promoted by the presence of the tertiary amine might take place, followed by the *intramolecular* through-space interaction of the amine with the ketene to give the ylide **10**. If R_1 = alkyl and if the hydrogens α to nitrogen are activated (for example by a double bond), then an *intramolecular* insertion of the C–H bond into the carbene function can take place. Such reactions are well documented both in the chemistry of organic carbenes and in the chemistry of carbene complexes generated for example from α-diazoesters and various catalysts such as rhodium and copper.[17] Moreover, the formation of cyclopentenones from alkyl-substituted alkoxy chromium carbene complexes, resulting from activation of an α-hydrogen, has been disclosed recently by Wulff and co-workers.[18]

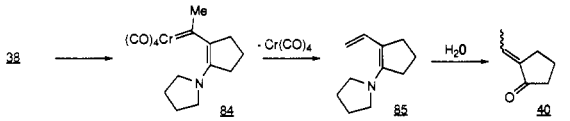
A striking example for such a reaction is found in the transformation of **31** into **32**: insertion of the triple bond will

(17) Maas, G. *Top. Curr. Chem.* **1987**, *137*, 75 and references cited therein.

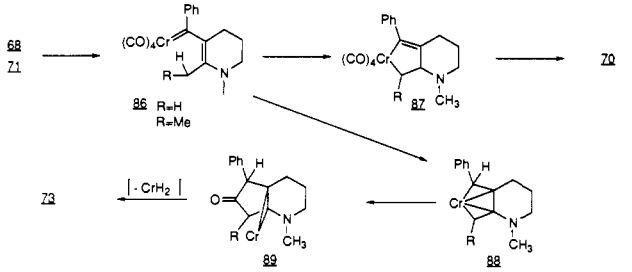
Scheme XII



Scheme XIII



Scheme XIV



lead to the new carbene complex **81**, in which the C(9)-H is doubly activated, by the presence of the heteroatom and the double bond. The insertion reaction might lead to **82**, an η^3-allyl complex, and then to **83**, the corresponding η^1-allyl complex. Insertion of CO would then give **32**. In this case, a small substituent on the carbene carbon in **81** probably promotes the direct insertion of the carbene complex into the NC–H bond (Scheme XII).

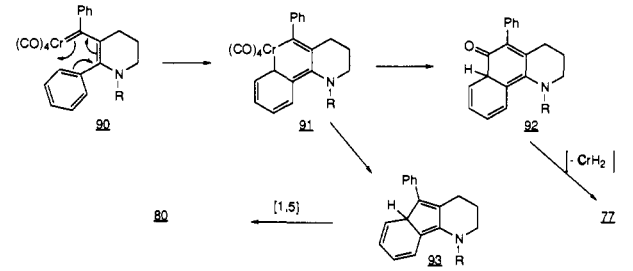
Conversely, if the hydrogen atoms α to nitrogen are not reactive enough and if CO insertion does not take place (or is reversible), then the reaction might end after the first step, the formation of the new carbene complex. This is exemplified in the transformation of **38** into the ketone **40**: collapse of the newly formed carbene **84** (Scheme XIII), due to β-hydrogen migration, will lead to the dienamine **85** and finally by hydrolysis to ethylidenecyclopentanone (**40**).

The complexes given in Scheme VIII behaved similarly but for different reasons: according to the general scheme, applied to **68** and **70** in Scheme XIV, no through-space interaction between nitrogen and the carbene function can take place in **86**. Thus both the ketene and the ylide formations are prevented. However, a through-bond interaction between nitrogen and the metal as in classical aminocarbene complexes can take place, the consequence of which might be a buildup of negative charge on chromium. As a result, CO insertion with formation of a ketene complex might be inhibited, but oxidative addition of the allylic C–H bond would be made easier: such a reaction leads either to **87** or to **88**, depending on the site of migration of the hydrogen atom. Insertion of CO into **87** would then give **70**, whereas the same reaction on **88**, followed by dehydrogenation, might lead to **73**.

Although such a mechanism can account for most of the experimental results, it is not possible to completely discard a pathway involving first the formation of a ketene complex which might then undergo C–H insertion and reductive elimination reactions.[19]

(18) Challener, C. A.; Wulff, W. D.; Anderson, B. A.; Chamberlin, S.; Faron, K. L.; Kim, O. K.; Murray, C. K.; Xu, Y.; Yang, D. C.; Darling, S. D. *J. Am. Chem. Soc.* **1993**, *115*, 1359.

Scheme XV



3. Phenyl-Substituted Alkynylaminocarbene Complexes. A similar situation could be envisaged in the case of complexes **75** and **76**. Once the first step leading to **90** had occurred, no interaction between the carbene function and the tertiary amine can take place. However, in that case, an electrocyclization of the chromahexadiene **90** might lead to **91**, a chromacyclohexadiene. CO insertion could then give **77**, via **92** (R = H), and finally the fully aromatic polycyclic compound **78** (Scheme XV).

For complex **76** (R = Me), the course of the reaction was slightly different. Although the expected phenol **79** could be isolated, no further reaction took place. Moreover, complex **80**, resulting from the electrocyclization without CO insertion, was also obtained. Again, formation of a ketene complex from **75** and **76**, before the cyclization step, might also lead to **78** and **79**.

Similar *intramolecular* reactions on phenyl-substituted alkynylaminocarbene complexes had also been carried out by Dötz and co-workers.[20] However, no CO insertion was observed: this result was probably linked to the presence of a chelating methoxy group β to the carbene carbon, able to dissociate a CO ligand prior to the insertion of the alkyne.

4. Dicarbonylation/Rearrangement Reactions. A surprising result which was observed both in the case of azetidine- and aziridine-substituted carbene complexes is the formation of complexes **16**, **20**, **24**, and **60**, in which two CO groups had been inserted in the organic ligand of the corresponding carbene complexes.

These products could originate either from diradical species, such as **94**, or from organometallics, such as **98**. Indeed, since radicals have been detected during the Stevens rearrangement of nitrogen ylides[21] and since formation of ketones as the result of the interaction of CO with radicals is now well documented,[22] carbonylation of **94**, resulting from the ylides **10**,[23] might give **95**, an acyl radical, and, upon ring closure, compound **16**. However, such a mechanism should be discarded on grounds presented earlier.[3] As far as organometallics such as **98** are concerned, several pathways could lead to them. The first one is depicted in Scheme XVI and starts from complex **8**: both the metal-mediated ring opening with CO insertion of aziridines and azetidines and the rearrangement of vinyl-substituted strained heterocycles are known.[24,25] Ring opening might thus lead to **97** via **96** and, upon a double CO insertion, to **16** via **98**. However, such a mechanism would exclude the intermediary of N-ylide species.

(19) Audouin, M.; Blandinieres, S.; Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1990**, 23.

(20) Dötz, K. H.; Schäfer, T.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 176.

(21) Ollis, W. D.; Rey, M.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1009.

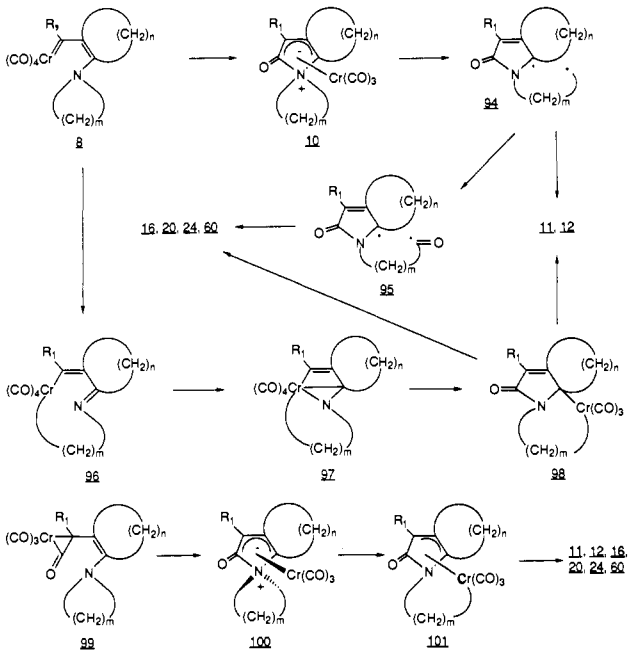
(22) Ryu, I.; Yamazaki, H.; Ogawa, A.; Kanube, N.; Sonoda, N. *J. Am. Chem. Soc.* **1993**, *115*, 1187 and references therein.

(23) Since in **4** and **10** the negative charge is delocalized over the carbon and oxygen atoms, they should in fact be termed *N,N*-dialkylpyrrolinium oxides. *Stricto sensu*, only the canonical form in which the negative charge is α to the nitrogen atom is a nitrogen ylide.

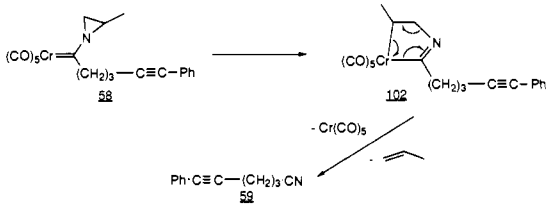
(24) (a) Calet, S.; Urso, F.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 931. (b) Roberto, D.; Alper, H.; *J. Am. Chem. Soc.* **1989**, *111*, 7539. (c) De Wang, M.; Alper, H. *J. Am. Chem. Soc.* **1992**, *114*, 7018.

(25) (a) Suzuki, M.; Oda, Y.; Noyori, R. *J. Am. Chem. Soc.* **1979**, *101*, 1623. (b) Wiger, G. R.; Rettig, M. F. *J. Am. Chem. Soc.* **1976**, *98*, 4168. (c) Horton, A. M.; Hollinshead, D. M.; Ley, S. V. *Tetrahedron* **1984**, *40*, 1737. (d) Bates, R. W.; Diez-Martin, D.; Kerr, W. J.; Knight, J. G.; Ley, S. V. *Tetrahedron* **1990**, *46*, 4063.

Scheme XVI



Scheme XVII

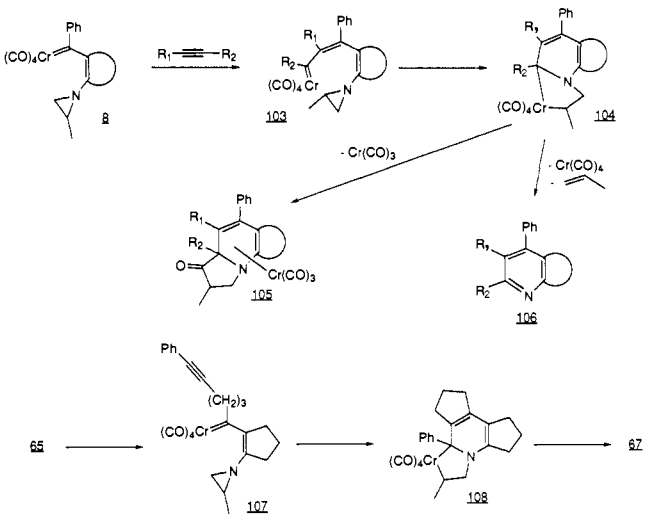


Yet another mechanism, of a broader implication, suggested by a reviewer and supported by recent observations of our laboratory,[26] could account for the direct transformation of aminocarbene complexes **8** into both single- and double-carbonylated products. Indeed, insertion of CO in carbene complex **8** might lead to an activated η^2-ketene complex **99**. Nucleophilic addition of the tertiary amine would then give an η^3-ylide complex **100**. Insertion of the negatively charged metal into one of the nitrogen–carbon bonds, followed either by reductive elimination or by CO insertion, might lead respectively to **11** and **12** and to **16**. Such a mechanism would have stereochemical implications which need to be verified. It is interesting to notice that such a dicarbonylation reaction has recently been described by Herndon during an alkyne insertion reaction into a cyclopropyl-substituted carbene complex of chromium.[27]

5. Special Case of Aziridino-substituted Carbene Complexes. Aside from **60**, the product originating from a double CO insertion/rearrangement reaction, several other products were observed. Among them are the nitriles **59** and **66**, which are the result of the rearrangement of the starting carbene complex, before the insertion of the alkyne. This type of a reaction had already been observed during the *intermolecular* insertion reactions: aziridine-substituted carbene complexes probably rearrange, like *N*-acylaziridine derivatives, via a five-membered metallacycle **102**, to give a nitrile and an olefin,[13] in the present case propene (Scheme XVII). Along with the nitrile, only products resulting from the di-insertion of the alkyne, with or without elimination of propene, were obtained, e.g. **64** from methylaziridinocarbene complex **62**, and **63** from **58**.[12]

The formation of these different compounds could be rationalized as shown in Scheme XVIII: insertion of a second alkyne into **8** might lead to **103**. A sigmatropic rearrangement could then afford **104**, which upon elimination of propene or insertion of CO would lead respectively to **105** and **106**. Three examples illustrate this scheme: the transformations of **58** into **61** in the presence of diphenylacetylene, and of **65** into **67**, and the interaction of **8** with the alkyne **58** formed in situ, leading to **63**.

Scheme XVIII



Conclusion

The results discussed in this paper provide evidence for the generality of the reaction of aminocarbene complexes with alkynes, leading to lactams as a result of triple bond and CO insertions followed by the rearrangement of nitrogen ylides. According to all the examples gathered in this and previous papers, it now seems possible to devise structures of the starting carbene complexes which might lead to elaborate polycyclic systems. Several features which are able to modify the course of the reaction could be determined, the most important being the nature of the substituents on nitrogen and on the triple bond. Others, such as the experimental conditions for carrying out the insertion reactions (nature of the solvent, presence of external ligands such as CO, temperature), are soon to examined. We are now confident that further investigations in this area will bring to light applications of aminocarbene complexes to the synthesis of natural heterocyclic compounds.

Experimental Section

General Methods. Tetrahydrofuran (THF), diethyl ether, and benzene were distilled from blue solutions of sodium benzophenone ketyl under argon prior to use. Methylene chloride (CH_2Cl_2) was distilled from calcium hydride. NMR spectra were obtained on a Bruker AC 200, a Bruker AM 500, or a JEOL GSX400 NMR spectrometer; chemical shifts are reported in δ units (ppm) relative to tetramethylsilane as internal standard. Infrared spectra were recorded on a Beckman 4240 spectrophotometer, and mass spectra were recorded with a Kratos MS 3P. Melting points were determined on a Reichert Kōfler block and are uncorrected.

Preparation of Aminocarbene Complexes. Two general methods were used: either aminolysis of an alkoxycarbene complex[10,28] or reaction of $Na_2Cr(CO)_5$ with an amide followed by dehydration with Me_3SiCl/Al_2O_3.[9]

$(CO)_5Cr{=}C[N(CH_2)_3](CH_2)_4C{\equiv}CPh$ (14). This complex was obtained from $(CO)_5Cr{=}C(OEt)(CH_2)_4C{\equiv}CPh$ and azetidine: yield, 95%, yellow crystals; mp 78 °C; IR ($CHCl_3$) 2040, 1960, 1915 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.39–7.24 (m, 5H, Ar), 4.65 (t, J = 8.2 Hz, 2H, NCH_2), 4.33 (t, J = 8.2 Hz, 2H, NCH_2), 2.74–2.66 (m, CH_2), 2.50–2.32 (m, $2CH_2$), 1.72–1.57 (m, 4H, $2CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 268.35 (Cr=C), 222.87, 218.38 (CO), 131.58, 128.34, 127.78 (Ar), 89.35, 81.37 (C≡C), 60.27, 55.84 (NCH_2), 48.35, 28.72, 24.79, 19.13, 13.52 (CH_2). Anal. Calcd for $C_{21}H_{19}NO_5Cr$: C, 62.84; H, 4.74; N, 3.49. Found: C, 62.84; H, 4.78; N, 3.49.

(26) Bouancheau, C.; Rudler, M. Unpublished results.
(27) Tumer, S. U.; Herndon, J. W.; Mc Mullen, L. A. *J. Am. Chem. Soc.* **1992**, *114*, 8394.
(28) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1968**, *15*, 147.
(29) English, J., Jr.; Lamberti, V. *J. Am. Chem. Soc.* **1952**, *74*, 1909.

$(CO)_5Cr{=}C[N(CH_2)_3](CH_2)_3C{\equiv}CPh$ (18) was obtained from $(CO)_5Cr{=}C(OEt)(CH_2)_3C{\equiv}CPh$ and azetidine: yield, 90%, yellow oil; IR ($CHCl_3$) 2040, 1960, 1915 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.39–7.25 (m, 5H, Ar), 4.6 (t, J = 8 Hz, 2H, NCH_2), 4.3 (t, J = 8 Hz, 2H, NCH_2), 2.8 (t, J = 8 Hz, 2H), 2.5 (t, J = 6.6 Hz, 2H), 2.4 (t, J = 8 Hz, 2H), 1.85–1.77 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 267.79 (Cr=C), 222.73, 218.22 (CO), 131.44, 123.48 (Ar), 88.64, 81.79 (C≡C), 60.19, 55.96 (NCH_2), 47.79 (C_1), 25.06, 19.53, 13.44 ($4CH_2$). Anal. Calcd for $C_{20}H_{17}NO_5Cr$: C, 59.55; H, 4.22; N, 3.47. Found: C, 59.54; H, 4.03; N, 3.41.

$(CO)_5Cr{=}C[N(CH_2)_3](CH_2)_3C{\equiv}C{-}SiMe_3$ (22) was obtained from $(CO)_5Cr{=}C(OEt)(CH_2)_3C{\equiv}C{-}SiMe_3$ and azetidine: yield, 68%, yellow crystals; mp 30 °C; IR ($CHCl_3$) 2030, 1960, 1915 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.66 (t, J = 8 Hz, 2H, NCH_2), 4.36 (t, J = 8 Hz, 2H, NCH_2), 2.82–2.74 (m, 2H), 2.49–2.29 (m, 4H), 1.74–1.66 (m, 2H), 0.13 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 267.76 (Cr=C), 222.7, 218.1 (CO), 105.82, 85.92 (C≡C), 60.04, 55.96 ($2NCH_2$), 47.65, 27.79, 19.87, 13.38 ($4CH_2$), 0.99 ($Si(CH_3)_3$). Anal. Calcd for $C_{17}H_{21}NO_5SiCr$: C, 51.12; H, 5.30; N, 3.51. Found: C, 50.90; H, 5.68; N, 2.88 MS $C_{17}H_{21}O_5NSiCr^+$ 399, found 399.

Lactams 15 and 16. Thermolysis of complex **4** (1.1 g, 0.0026 mol) was carried out in boiling benzene (50 mL) for 12 h. After evaporation of the volatiles under vacuum, the residue was chromatographed on silica gel with petroleum ether/ethyl acetate as eluent (75/25 then 60/40). Appropriate fractions were collected to give first compound **15** as white crystals (0.155 g 23%): mp 109 °C; IR ($CHCl_3$) 1670 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.44–7.26 (m, 5H, Ar), 3.68–3.58 (m, 1H, NCH), 3.35–3.23 (m, 1H, NCH), 3.09–3.04 (m, 1H), 2.31–2.15 (m, 4H), 2.06–1.79 (m, 3H), 1.47–1.23 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 175.06 (CO), 160.61 and 131.54 (C=C), 129.21, 128.56, 128.16, 127.54 (Ar), 71.97 (C quat), 41.87 (NCH_2), 37.25, 31.24, 27.57, 27.13, 26.52, 22.88 ($6CH_2$); HRMS calcd for $C_{17}H_{19}NO$ (M^+) 253.1466, found m/e 253.1467. Then **16** as an oil (0.094 g, 13%): IR ($CHCl_3$) 1710, 1670 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.44–7.26 (m, 5 H, Ar), 4.40 (dt, J = 13.2, 5.2 Hz, 1H, NCH), 3.26 (ddd, J = 14, 10, 4.5 Hz, 1H, NCH), 3.01 (dm, J = 13.8 Hz, 1H), 2.86 (dt, J = 13.2, 5.8 Hz, 1H), 2.68 (ddd, J = 16, 11, 5 Hz, 1H), 2.58 (dm, J = 13 Hz, 1H), 2.44 (dt, J = 16, 5 Hz, 1H), 2.12–1.95 (m, 3H), 1.70–1.34 (m, 4H), 0.72 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 205.06, 169.00 (CO), 154.51, 130.97 (C=C), 129.89, 129.46, 128.27, 127.96 (Ar), 72.29 (C quat), 37.51 ($C(O)CH_2$), 36.13 (NCH_2), 37.16, 27.50, 26.20, 25.04, 20.87 ($6CH_2$); HRMS calcd for $C_{18}H_{19}NO_2$ (M^+) 281.1415, found m/e 281.1411.

Lactams 19 and 20. Thermolysis of **18** (0.9 g, 0.0022 mol) as above gave upon chromatography first **19** as white crystals (0.165 g, 31%): mp 92 °C; IR ($CHCl_3$) 1673 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.69–7.24 (m, 5H, Ar), 3.69–3.55 (m, 1H, NCH), 3.35–3.23 (m, 1H, NCH), 2.86–2.74 (m, 1H), 2.64–2.47 (m, 1H), 2.34–2.08 (m, 4H), 1.95–1.85 (m, 2H), 1.47–1.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.85 (CO), 166.70, 131.79 (C=C), 128.4–127.7 (Ar), 78.28 (C quat), 42.92 (NCH_2), 33.80, 33.10, 28.86, 26.12, 24.18 (5 CH_2); HRMS calcd for $C_{16}H_{17}NO$ (M^+) 239.1310, found m/e 239.1310. Anal. Calcd for $C_{16}H_{17}NO$: C, 80.33; H, 7.11; N, 5.86. Found: C, 79.39; H, 7.18; N, 5.90. Then compound **20** as white crystals (0.072 g, 12%): mp 81 °C; IR ($CHCl_3$) 1718, 1677 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.70–7.25 (m, 5H, Ar), 4.35–4.23 (m, 1H, NCH), 3.34–3.21 (m, 1H, NCH), 3.02–2.94 (m, 1H), 2.68–2.54 (m, 2H), 2.47–2.33 (m, 2H), 2.25–2.20 (m, 4H), 1.52–1.42 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 205.58, 171.96 (CO), 161.33, 131.39 (C=C), 128.62–128.37 (Ar), 78.97 (C quat), 38.11 (NCH_2), 37.40, 33.19, 26.11, 24.89, 24.06 ($5CH_2$); HRMS calcd for $C_{17}H_{17}NO_2$ (M^+) 267.1259, found m/e 267.1259.

Lactams 23 and 24. Thermolysis of complex **22** (1.95 g, 0.0049 mol) as above gave upon silica gel chromatography first **23** as white crystals (0.16 g, 14%): mp 64 °C; IR ($CHCl_3$) 1650, 1610 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.60–3.46 (m, 1H, NCH), 3.19–3.08 (m, 1H, NCH), 2.56–2.47 (m, 2H), 2.26–2.03 (m, 4H), 1.84–1.68 (m, 2H), 1.38–1.23 (m, 2H), 0.19 (s, 9H, $SiMe_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 183.23 and 128.21 (C=C), 182.34 (CO), 81.15 (C quat), 42.87 (NCH_2), 33.94, 33.55, 29.30, 25.57, 23.98 ($5CH_2$), –1.16 ($SiMe_3$). Anal. Calcd for $C_{13}H_{21}NOSi$: C, 66.33; H, 8.99; N, 5.95. Found: C, 66.55; H, 9.08; N, 5.79. Then compound **24** as white crystals (0.13 g, 10%): mp 98 °C; IR ($CHCl_3$) 1705, 1660, 1615 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.21–4.09 (m, 1H, NCH), 3.24–3.11 (m, 1H, NCH), 2.90–2.78 (m, 1H), 2.59–1.98 (m, 8H), 1.58–1.41 (m, 1H), 0.22 (s, 9H, $SiMe_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9 (CO), 177.6 (CO), 177.2, 130.3 (C=C), 82.5 (C quat), 38.8, 38.7, 34.3, 26.6, 25.9, 25.2 ($6CH_2$), 0.0 ($SiMe_3$); HRMS calcd for $C_{14}H_{21}O_2NSi$ (M^+) 263.1341, found m/e 263.1339.

$(CO)_5Cr{=}C[N(CH_2CH{=}CHCH_2)](CH_2)_3C{\equiv}CPh$ (25) was obtained from $(CO)_5Cr{=}C(OEt)(CH_2)_3C{\equiv}CPh$ (**17**) and pyrroline: yield, 93%, yellow crystals; mp 62 °C; IR ($CHCl_3$) 2040, 1960, 1915 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.39–7.25 (m, 5H, Ar), 6.05–6.01 (m, 1H, C*H*=CH), 5.92–5.88 (m, 1H, CH–C*H*), 4.85 (s, 2H, NCH_2), 4.49 (s, 2H, NCH_2), 3.22–3.13 (m, 2H), 2.58 (t, J = 6.6 Hz, 2H), 1.86–1.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 276.04 (Cr=C), 222.90, 218.22 (CO), 131.42–123.43 (Ar, C=C), 88.50, 81.88 (C≡C), 66.39, 57.39 (NCH_2), 52.84, 24.20, 19.61 ($3CH_2$); MS $C_{21}H_{17}NO_5Cr^+$ (M^+) 415, found m/e 415. Anal. Calcd for $C_{21}H_{17}NO_5Cr$: C, 60.72; H, 4.12; N, 3.37. Found: C, 60.38; H, 4.30; N, 3.36.

Lactam 26 was obtained by thermolysis of complex **25** as above: yield, 15%, as an oil; IR ($CHCl_3$) 1670 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.76–7.26 (m, 5H, Ar), 5.87–5.80 (m, 2H, CH=CH), 4.60 (dm, J = 18 Hz, 1H, NCH), 3.70 (dm, J = 18 Hz, 1H, NCH), 2.95–2.76 (m, 1H), 2.70–1.87 (m, 6H), 1.31–1.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.39 (CO), 166.88, 131.99 (C=C), 128.62–121.53 (Ar, C=C), 66.59 (C quat), 39.14 (NCH_2), 32.81, 32.28, 25.97, 23.32 (4 CH_2); HRMS calcd for $C_{17}H_{17}NO$ (M^+) 251.1310, found m/e 251.1310.

$(CO)_5Cr{=}C[N(CH_2CH{=}CHCH_2)](CH_2)_4C{\equiv}CPh$ (27) was obtained from complex **13** and pyrroline: yield, 95%, yellow oil; IR ($CHCl_3$) 2040, 1960, 1910 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.37 (m, 5H, Ar), 6.06–5.98 (m, 1H), 5.86–5.78 (m, 1H, CH=C*H*), 4.84 (s, 2H, NCH_2), 4.45 (s, 2H, NCH_2), 3.06–2.99 (m, 2H, CH_2), 2.53–2.46 (m, 2H), 1.90–1.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 275.64 (Cr=C), 223.01, 218.22 (CO), 131.40–123.63 (Ar, C=C), 89.19, 81.31 (C≡C), 66.33, 57.10 (NCH_2), 52.93, 28.33, 23.48, 18.82 ($4CH_2$). Anal. Calcd for $C_{22}H_{19}NO_5Cr$: C, 61.54; H, 4.43; N, 3.26. Found: C, 61.50; H, 4.38; N, 3.40.

Lactam 28 and Complex 29. Thermolysis of complex **27** (1 g, 0.0023 mol) as above gave upon chromatography first **28** as an oil (0.190 g, 31%): IR ($CHCl_3$) 1670 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.48–7.25 (m, 5H, Ar), 5.88–5.69 (m, 2H, CH=CH), 4.63–4.53 (dm, J = 17 Hz, 1H, NCH), 3.71–3.59 (dm, J = 17 Hz, 1H, NCH), 3.06–2.97 (dm, J = 13.6 Hz, 1H), 2.55 (ddd, J = 16.6, 6.6, 1.5 Hz, 1H), 2.34–1.08 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.36 (CO), 160.08, 131.79 (C=C), 129.48–122.09 (Ar, C=C), 59.97 (C quat), 38.13, 35.48, 31.20, 28.17, 22.28 ($5CH_2$); HRMS calcd for $C_{18}H_{19}NO$ (M^+) 265.1466, found m/e 265.1467. Then complex **29** as yellow crystals (0.35 g, 40%): mp 164 °C; IR ($CHCl_3$) 1965, 1890, 1670 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.78–5.28 (m, 7H, ArCr, CH=CH), 4.50 (d, J = 19 Hz, 1H, NCH), 3.66 (d, J = 19 Hz, 1H, NCH), 3.30 (d, J = 14 Hz, 1H), 2.57 (dd, J = 16.7, 4.8 Hz, 1H), 2.34–2.08 (m, 3H), 1.94–1.14 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 232.88 (CO), 166.84, 163.55 (C=C), 123.94, 121.75 (C=C), 100.28, 95.06, 94.48, 92.45, 92.38 (ArCr), 60.17 (C quat), 37.93 (NCH_2), 35.23, 31.17, 27.98, 25.37, 21.77 ($5CH_2$). Anal. Calcd for $C_{21}H_{19}NO_4Cr$: C, 62.84; H, 4.74; N, 3.49. Found: C, 62.84; H, 4.78; N, 3.49.

$(CO)_5Cr{=}C[N(CH_2CH{=}CHCH_2)](CH_2)_3C{\equiv}C{-}Me$ (31a) was obtained from $(CO)_5Cr{=}C[N(CH_2CH{=}CHCH_2)]CH_3$ (**30a**) and $Me{-}C{\equiv}C{-}(CH_2)_2{-}OTf$ and LDA: yield, 62%, yellow solid; mp 50 °C; IR ($CHCl_3$) 2050, 1925 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.05 (dt, J = 6.2 Hz, 1H, C*H*=CH), 5.94 (dt, J = 6.2 Hz, 1H, CH=C*H*), 4.83 (s, 2H, NCH_2), 4.45 (s, 2H, NCH_2), 3.11–3.03 (m, 2H), 2.35–2.20 (m, 2H), 1.77 (t, J = 2Hz, 3H, CH_3), 1.70–1.67 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 275.0 (Cr=C), 223.0, 216.9 (CO), 125.6, 124.0 (C=C), 78.0, 76.9 (C≡C), 66.3 (NCH_2), 56.8 (NCH_2), 53.0, 24.3, 19.1 ($3CH_2$), 3.1 (CH_3). Anal. Calcd for $C_{11}H_9NO_5Cr$: C, 54.08; H, 4.25; N, 3.94. Found: C, 54.46; H, 4.32; N, 3.81.

$(CO)_5Cr{=}C[N(CH_2CH{=}CH{-}CH_2)]CD_2(CH_2)_2C{\equiv}C{-}Me$ (31b) was obtained from $(CO)_5Cr{=}C[N(CH_2CH{=}CHCH_2)]CD_3$ as above: yield, 95%, yellow crystals; mp 48 °C; IR ($CHCl_3$) 2040, 1965, 1920 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.05 (dt, J = 6, 2 Hz, 1H, C*H*=CH), 5.94 (dt, J = 6, 2 Hz, 1H, CH=C*H*), 4.83 (s, 2H, NCH_2), 4.45 (s, 2H, NCH_2), 2.28–2.25 (m, 2H), 1.77 (t, J = 2 Hz, 3H, CH_3), 1.69–1.64 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 276.08 (Cr=C), 223.01, 218.27 (CO), 126.44, 124.31 (C=C), 66.39, 65.45, 58.35, 57.31 ($4CH_2$), 52.91 (CD_2), 24.29, 18.95 ($2CH_2$), 3.38 (CH_3); HRMS calcd for $C_{16}D_2H_{13}NO_5Cr$ (M^+) 355.0480, found m/e 355.0480.

Compound 32a was obtained as above by thermolysis of **31a** (1.8 g, 0.0046 mol) after silica gel chromatography: yield, 41%, white crystals; mp 31 °C; IR ($CHCl_3$) 1640, 1610 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.18 (d, J = 5 Hz, 1H, C(4)H), 5.50 (t, J = 8 Hz, 1H, C(3)H), 3.72–3.58 (m, 1H, C(6)H), 3.26 (m, 1H, C(2)H), 3.20 (m, 1H, C(5)H), 3.10–3.01 (m, 1H, C(5)H′), 2.45–2.35 (m, 2H, C(9)H_2), 2.0 (m, 1H, C(7)H), 1.75–1.53 (m, 6H, C(8)H_2, C(7′)H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 203.67 (CO), 154.33 (C(10)), 141.67 (C(4)), 125.82 (C(11)), 117.9

(C(3)), 72.9 (C(6)), 56.9 (C(2)), 50.71 (C(5)), 33.36 (C(7)), 31.67 (C(9)), 19.25 (C(8)), 15.73 (C(12)). Anal. Calcd for $C_{12}H_{15}NO$: C, 76.19; H, 7.93; N, 7.40. Found: C, 76.04; H, 7.94; N, 7.12.

Compound 32b was obtained as above from **31b**: yield, 32%, white crystals; mp 29 °C; IR ($CHCl_3$) 1640, 1610 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.18 (d, 1H, C(4)H), 5.50 (t, 1H, C(3)H), 3.72–3.58 (m, 1H, C(6)H), 3.26 (m, 1H, C(2)H), 3.20 (m, 1H, C(5)H), 3.10–3.01 (m, 1H, C(5)H'), 2.45–2.35 (m, 2H), 1.75–1.53 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 203.93 (CO), 154.61, 141.92, 125.92, 118.07, 72.93, 56.99, 50.83, 33.48, 31.78, 19.23, 15.86. HRMS calcd for $C_{12}D_2H_{13}NO$ (M^+) 191.1279, found *m/e* 191.1278.

$(CO)_5Cr{=}C[N(CH_2CH{=}CHCH_2CH_2)](CH_2)_4C{\equiv}CPh$ (34) was prepared according to the second method from the corresponding amide **33**: yield, 36% (3/1 E/Z mixture), red oil; ^1H NMR (200 MHz, $CDCl_3$) δ 7.29 (m, 10H), 5.91 and 5.48 (m, 4H, 2CH=CH), 4.81 (m, NCH), 4.41 (m, NCH), 4.28 (m, NCH), 3.83 (m, 8H, NCH) 3.18 (m, 4H, Cr=C—CH_2), 2.49 (m, 8H), 1.66 (m, 4H). Anal. Calcd for $C_{23}H_{21}NO_5Cr$: C, 63.30; H, 4.74; N, 3.16. Found: C, 62.49; H, 4.60; N, 3.12.

Thermolysis of Complex 34: Formation of Lactams 35, 36, and 37. Silica gel chromatography first gave a mixture of **35** and **37**: yield, 30%. Then complex **36**: yield, 47%, yellow crystals; mp 186 °C; IR ($CHCl_3$) 1965, 1890, 1670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.62 (d, J = 6 Hz, 1H, ArCr), 5.47–5.17 (d, J = 6 Hz, 1H, ArCr), 4.99 (d, J = 15 Hz, 1H, =C*H*H), 4.88 (d, J = 10 Hz, 1H, =CH*H*), 3.65–3.60 (m, 1H, NCH), 3.27–3.21 (m, 1H, NCH), 3.17–3.14 (m, 1H), 2.75–2.71 (m, 1H), 2.56–2.51 (m, 1H), 2.18–2.15 (m, 5H), 2.05–1.98 (m, 3H), 1.80–1.77 (m, 1H), 1.46–1.35 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 232.74 (CO), 172.82 (CO), 161.71, 135.21 (C=C), 125.53, 115.55 (C=C), 99.75, 95.16, 94.40, 92.17, 91.94, 91.88 (ArCr), 74.62 (C quat), 45.91 (CH), 40.36, 38.28, 33.67, 27.16, 27.07, 22.57 (6CH_2). Anal. Calcd for $C_{22}H_{21}NO_4Cr$: C, 63.61; H, 5.06; N, 3.37. Found: C, 63.74; H, 5.10, N, 3.23.

Heating of complex **36** in pyridine gave quantitatively lactam **35** as white crystals: mp 134 °C; IR ($CHCl_3$) 1665 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.39–7.20 (m, 5H, Ar), 5.42–5.25 (m, 1H, C*H*=CH_2), 5.04 (dd, J = 16, 2 Hz, 1H, C*H*=C), 4.92 (dd, J = 16, 2 Hz, 1H, C*H*=C), 3.78–3.64 (m, 1H, NCH), 3.38–3.26 (m, 1H, NCH), 3.01–2.93 (m, 1H), 2.83–2.75 (m, 1H), 2.68–2.53 (m, 1H), 2.25–1.80 (m, 5H), 1.56–1.29 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.36 (CO), 158.00, 140.59 (C=C), 136.00–114.93 (Ar, C=C), 74.37 (C quat), 46.08 (NCH_2), 40.43, 38.48, 34.01, 27.02, 26.71, 22.92 (5CH_2, CH). Anal. Calcd for $C_{19}H_{21}NO$: C, 81.72; H, 7.53; N, 5.02. Found: C, 81.57; H, 7.59; N, 4.89.

$(CO)_5Cr{=}C[N(CH_2)_4](CH_2)_3C{\equiv}CCH_3$ (39) was prepared from $(CO)_5Cr{=}C[N(CH_2)_4]CH_3$ by alkylation with CH_3—C≡C—$(CH_2)_3$-OTf in the presence of LDA: yield, 51%, yellow solid; mp 50 °C; IR ($CHCl_3$) 2040, 1995, 1920 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.15–4.05 (m, 2H, NCH_2), 3.72–3.62 (m, 2H, NCH_2), 3.10–3.02 (m, 2H), 2.32–2.18 (m, 2H), 2.18–2.05 (m, 4H), 1.76 (t, J = 2.4 Hz, 3H, CH_3), 1.72–1.56 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 271.61 (Cr=C), 223.49, 219.06 (CO), 78.10, 76.09 (C≡C), 61.11 (NCH_2), 52.84, 51.24, 24.95, 24.54, 24.28, 19.12, 3.16 (6CH_2, CH_3). Anal. Calcd for $C_{16}H_{17}NO_5Cr$: C, 54.08; H, 4.79; N, 3.94. Found: C, 54.22; H, 4.81; N, 3.78.

Ethylidenecyclopentanone (40) was obtained by thermolysis of complex **39** (2.8 g, 0.008 mol): yield, 37%, oil; IR ($CHCl_3$) 1730, 1690 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.71–6.50 (m, 1H), 2.56–2.49 (m, 2H), 2.30–2.22 (m, 2H), 1.94–1.83 (m, 3H, CH_3), 1.74 (dm, J = 7 Hz, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 206.72 (CO), 138.30, 130.83 (C=C), 38.54, 26.44, 19.65, 15.09 (4CH_2). Anal. Calcd for $C_7H_{10}O$: C, 76.36; H, 9.09. Found: C, 76.42; H, 9.14.

Lactam (44) was obtained from complex **43** (0.6 g, 0.0015 mol) as an oil (0.05 g, 13%) upon irradiation in methylene chloride (50 mL) under a flow of oxygen with a Philipps 400-W lamp for 6 h. The solution turned green-brown with formation of a precipitate. After filtration through Celite and evaporation of the solvent in vacuo, the residue was purified by silica gel chromatography and eluted with petroleum ether/ethyl acetate (85/15): IR ($CHCl_3$) 1660 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.74–7.28 (m, 5H, Ar), 4.41–4.31 (m, 1H, NCH), 2.89–2.73 (m, 2H), 2.66–2.54 (m, 1H), 2.23–2.00 (m, 4H), 1.91–1.52 (m, 4H), 1.39–1.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.92 (CO), 167.39, 132.23 (C=C), 129.10–127.10 (Ar), 69.10 (C quat), 38.76, 33.38, 29.87, 25.62, 25.42, 23.16, 21.24 (7CH_2); HRMS calcd for $C_{17}H_{17}NO$ (M^+) 253.1466, found *m/e* 253.1465.

$(CO)_5Cr{=}C[N(CH_2CH{=}CH_2)CH_3](CH_2)_3C{\equiv}C$—Ph (45) was obtained in two steps by aminolysis of $(CO)_5Cr{=}C(OEt)(CH_2)_3C{\equiv}CPh$ (**17**) with allylamine, which gave $(CO)_5Cr{=}C[NH(CH_2CH{=}CH_2)]$-$(CH_2)_3C{\equiv}CPh$: yield, 97%, yellow oil (3/1 *E*/*Z* mixture); ^1H NMR (200 MHz, $CDCl_3$) δ 8.76 (br s, 1H, NH), 7.40–7.25 (m, 5H, Ar), 6.04–5.83 (m, 1H, C*H*=CH_2), 5.80–5.41 (m, 2H, CH=C*H*$_2$), 4.60–4.54 (m, 2H, (Z)NCH_2), 4.19–4.14 (m, 2H, (E)NCH_2), 3.21–3.09 (m, 2H), 2.59–2.45 (m, 2H), 1.96–1.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 279.02 (Cr=C), 223.15, 217.92 (CO), 131.6–118.6 (8 peaks, Ar), 57.30, 51.34, 51.17, 25.37, 19.11 (CH_2). Anal. Calcd for $C_{29}H_{17}NO_5Cr$: C, 59.55; H, 4.22; N, 3.47. Found: C, 59.63; H, 4.36; N, 3.42. Followed by LDA/ICH_3 alkylation at nitrogen, which gave **45**: yield, 97%, yellow oil (3/1 E/Z mixture); ^1H NMR (200 MHz, $CDCl_3$) δ 7.38–7.25 (m, 5H, Ar), 6.0–5.67 (m, 1H, C*H*=CH_2), 5.45–5.09 (m, 2H, CH=C*H*$_2$), 4.77–4.6 and 4.33–4.31 (m, 2H, NCH_2), 3.78 and 3.29 (s, 3H, NCH_3), 3.26–3.14 (m), 2.57–2.51 (m), 1.84–1.71 (m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 280.58 (Cr=C), 222.37, 217.69 (CO), 131.5–119.2 (8 peaks, Ar), 88.33, 82.06, 55.80, 55.47, 50.22, 46.78, 25.77, 25.42, 19.48, 18.73. Anal. Calcd for $C_{21}H_{19}NO_5Cr$: C, 60.43; H, 4.56; N, 3.36. Found: C, 58.94; H, 4.73; N, 3.23.

$(CO)_5Cr{=}C[N(CHCH_2CH_2)](CH_2)_3C{\equiv}C$—$CH_3$ (46) was obtained in two steps from $(CO)_5Cr{=}C[(NCHCH_2CH_2)(CH_3)]CH_3$ by alkylation with CH_3—C≡C$(CH_2)_2$OTf in the presence of LDA: yield, 64%, yellow oil (3/1 *E*/*Z* mixture); ^1H NMR (200 MHz, $CDCl_3$) δ 3.82 (s, NCH_3), 3.53–3.45 (m, Cr=C—CH_2), 3.25–3.17 (m, Cr=C—CH_2), 3.13 (s, NCH_3), 2.30–2.15 (m, CH_2—C≡C), 1.75 (br, C≡C—CH_3), 1.68–1.57 (m), 1.13–0.86 (C*H*$_2$CHC*H*$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 286.75, 283.0 (Cr=C), 223.69, 218.29 (CO), 78.26, 76.82, 52.99, 52.26, 51.72, 46.86, 38.78, 37.29, 25.26, 24.77, 19.23, 18.97, 9.71, 9.46, 3.65; MS $C_{16}H_{17}NO_5Cr^+$ 355, found 355.

$(CO)_5Cr{=}C[N(CH_2)_5](CH_2)_4C{\equiv}C$—Ph (48a) was obtained from the corresponding amide according to the second method: yield, 57%, reddish oil; ^1H NMR (200 MHz, $CDCl_3$) δ 7.36–7.25 (m, 5H, Ar), 4.29–4.24 (m, 2H, NCH_2), 3.75–3.69 (m, 2H, NCH_2), 3.15–3.07 (m, 2H), 2.50–2.44 (m, 2H), 1.87–1.56 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 270.98 (Cr=C), 223.41, 217.81 (CO), 131.40, 128.24, 127.69, 123.65 (Ar), 89.19, 81.29 (C≡C), 63.32, 51.94 (NCH_2), 51.01, 28.93, 28.20, 28.00, 27.75, 24.16, 18.88 (7CH_2). Anal. Calcd for $C_{23}H_{23}NO_5Cr$: C, 62.02; H, 5.17; N, 3.15. Found: C, 62.38; H, 5.43; N, 3.20.

Complex 49a was obtained by refluxing a solution of **48a** (0.83 g, 0.0019 mol) in benzene (50 mL) for 8 h, after filtration: yield, 84%, yellow solid; mp 182 °C; IR ($CHCl_3$) 1950, 1870, 1700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.81–5.77 (m, 1H, ArCr), 5.62–5.45 (m, 3H, ArCr), 5.04–4.94 (m, 1H, ArCr), 3.94–3.75 (m, 1H, NCH), 3.48–3.35 (m, 2H), 2.96–2.88 (m, 1H), 2.62–2.50 (m, 2H), 2.01–1.69 (m, 12H). Anal. Calcd for $C_{22}H_{23}NO_4Cr$: C, 63.30; H, 5.51; N, 3.36. Found: C, 62.58; H, 5.48; N, 3.33.

Lactams 50a, 51a, and 52a were obtained upon thermolysis of complex **48a** (1 g, 0.0022 mol) in toluene, followed by silica gel chromatography with petroleum ether/ethyl acetate as eluent. Appropriate fractions were collected and evaporated to give first **52a** as an oil (0.012 g, 3%): IR ($CHCl_3$) 1705, 1670 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.85–4.82 (m, 1H, CH=C), 4.40–4.20 (m, 1H, NCH), 3.42–3.32 (m, 1H, NCH), 2.84–2.75 (m, 1H), 2.55–2.45 (m, 1H), 2.26–1.57 (m, 13H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 183.05 (CO), 142.08 and 96.18 (C=C), 140.53–126.63 (Ar), 54.37 (C quat), 44.92, 40.97, 40.42, 24.87, 23.72, 23.43, 22.30, 21.14 (8CH_2); HRMS calcd for $C_{19}H_{23}NO$ (M^+) 281.1779, found *m/e* 281.1782. Then **50a** as an oil (0.15 g, 24%): IR ($CHCl_3$) 1700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.35–7.16 (m, 5H, Ar), 4.19–4.04 (m, 1H, NCH), 3.25–3.16 (m, 1H, NCH), 2.33–2.25 (m, 4H), 1.93–1.24 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.08 (CO), 137.95, 128.26, 127.29, 126.61, 119.68 (Ar, C=C), 59.46 (C quat), 44.19 (NCH_2), 40.33, 35.88, 25.62, 23.41, 22.55, 22.52, 21.38, 20.60 (8CH_2); HRMS calcd for $C_{19}H_{23}NO$ (M^+) 281.1779, found *m/e* 281.1782. Then **51a** as an oil (0.1 g, 17%): IR ($CHCl_3$) 1660 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.49–7.26 (m, 5H, Ar), 4.06–3.99 (m, 1H, NCH), 3.04–2.84 (m, 2H), 2.44–2.15 (m, 3H), 1.91–1.20 (m, 11H), 0.86–0.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.25 (CO), 157.63, 131.69 (C=C), 129.46, 129.26, 128.06, 127.42 (Ar), 65.69 (C quat), 40.16 (NCH_2), 40.00, 35.77, 29.92, 28.08, 26.63, 24.62, 22.04, 21.62 (8CH_2); HRMS calcd for $C_{19}H_{23}$-NO (M^+) 281.1779, found *m/e* 281.1726.

$(CO)_5Cr{=}C[N(CH_2)_6](CH_2)_4C{\equiv}C$—Ph (48b) was prepared from the corresponding amide; yield 45%, orange oil; IR ($CHCl_3$) 2040, 1960, 1915 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.36–7.25 (m, 5H, Ar), 4.28–4.24 (m, 2H, NCH_2), 3.80–3.74 (m, 2H, NCH_2), 3.12–3.04 (m, 2H), 2.50–2.44 (t, 2H), 1.99–1.59 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 275.2 (Cr=C), 223.5, 218.3 (CO), 131.4, 128.2, 127.6, 123.6 (Ar), 89.1, 81.2 (C≡C), 64.5, 52.7 (NCH_2), 50.8, 28.9, 28.2, 27.8, 26.9, 25.5, 24.5, 18.8 (8CH_2); MS $C_{24}H_{25}NO_5Cr^+$ 459, found 459.

Complex 49b was obtained as above from **49a** (2 g, 0.0045 mol): yield 52%, yellow solid; mp 159 °C; IR ($CHCl_3$) 1950, 1870, 1690 cm^{-1}; ^1H NMR (200 MHz, CD_2Cl_2) δ 5.83 (d, J = 6.4 Hz, 1H), 5.59–5.53 (m, 5H, ArCr), 3.52–3.41 (m, 2H, NCH_2), 3.17–3.06(m, 2H, NCH_2), 2.56–2.50 (m, 2H), 2.34–2.26 (m, 2H), 1.82–1.69 (m, 12H); MS $C_{24}H_{25}NO_5Cr^+$ 459, found 459.

Lactams 50b, 51b, and 52b were obtained upon thermolysis of complex **48b** as above, followed by chromatography, which gave first **50b** as an oil (0.3 g, 31%): IR ($CHCl_3$) 1690, 1670 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.32–7.15 (m, 5H, Ar), 3.92–3.85 (m, 1H, NCH), 3.23–3.16 (m, 1H, NCH), 2.32–2.26 (m, 2H), 2.06–2.0 (m, 2H), 1.93–1.09 (m, 14H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.38 (CO), 138.90, 138.04, 128.64, 127.59, 126.94, 119.58 (C=C, Ar), 59.50 (C quat), 40.44, 34.85, 26.36, 26.10, 22.92, 22.14, 21.86, 20.72; HRMS calcd for $C_{20}H_{25}NO$ (M^+) 295.1936, found m/e 295.1935. Then **52b** as an oil (0.057 g, 6%): IR ($CHCl_3$) 1710, 1660 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.43–7.21 (m, 5H, Ar), 4.81–4.78 (m, 1H, C=CH), 4.14–4.04 (m, 1H, NCH), 3.38–3.28 (m, 1H, NCH), 2.88–2.78 (m, 1H, C=CCH), 2.31–2.21 (m, 2H), 2.03–1.40 (m, 14H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 178.68 (CO), 143.21, 140.99, 128.14, 127.06, 126.48, (*C*=CH, Ar), 94.56 (C=*C*H), 53.81 (C quat), 45.91, 40.24, 35.81, 26.90, 25.37, 23.61, 22.51, 21.59, 21.34 (CH, $8CH_2$); HRMS calcd for $C_{20}H_{25}NO$ (M^+) 295.1936, found m/e 295.1935. Then **51b** as white crystals (0.020 g, 2%): mp 95 °C; IR ($CHCl_3$) 1660 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.49–7.26 (m, 5H, Ar), 4.04–3.91 (m, 1H, NCH), 3.06–2.92 (m, 2H), 2.25–1.00 (m, 17H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.19 (CO), 157.78, 132.00 (C=C), 129.78–127.60 (Ar), 65.55 (C quat), 39.73, 39.11, 29.99, 28.53, 27.56, 27.08, 24.81, 24.55, 22.09, 21.83 ($10CH_2$); HRMS calcd for $C_{20}H_{25}NO$ (M^+) 295.1936, found m/e 295.1871.

$(CO)_5Cr$=C—N(CH_2Ph)(CH_2)$_2$CH(CH_2)$_3$C≡C—Ph (56) was obtained from the corresponding amide according to the second method of preparation of the aminocarbene complexes: yield, 75%, yellow oil; IR ($CHCl_3$) 2040, 1960, 1915 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.40–7.23 (m, 10H, Ar), 5.44 (d, J = 14 Hz, 1H, CHPh), 5.05 (d, J = 14 Hz, 1H, CHPh), 3.51–3.45 (m, 3H, NCH_2, C*H*—CH_2), 2.53–2.46 (m, 2H), 2.35–1.90 (m, 2H), 1.86–1.67 (m, 3H), 1.40–1.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 272.00 (Cr=C), 222.0, 218.0 (CO), 133.9–123.7 (8 peaks) (Ar), 89.2, 81.2 (C≡C), 65.8 (CH_2Ph), 59.5 (NCH_2), 57.4 (CH), 30.1, 27.4, 26.1, 19.4 ($4CH_2$). Anal. Calcd for $C_{27}H_{23}NO_5Cr$: C, 65.72; H, 4.66; N. 2.84. Found: C, 65.13; H, 4.74; N, 2.65.

Thermolysis of complex 56 (2g, 0.004 mol) followed by silica gel chromatography with petroleum ether/CH_2Cl_2 as eluents gave compound **57a** as an oil (0.08 g, 6%): IR ($CHCl_3$) 1680 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.45–7.20 (m, 10H, Ar), 3.98–3.88 (m, 1H, NCH), 3.05 (d, J = 13 Hz, 1H, CHPh), 2.95 (d, J = 13 Hz, 1H, CHPh), 2.95–2.85 (m, 1H, NCH), 2.75–2.64 (m, 2H), 2.25–2.15 (m, 1H), 2.06–1.75 (m, 3H), 1.65–1.25 (m, 2H), 1.02–0.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.35 (CO), 164.3, 136.0 (C=C), 132.5–126.7 (Ar), 61.7 (C quat), 45.4, 44.9 ($2CH_2$), 43.0 (CH), 35.1, 28.3, 24.3, 23.6 ($4CH_2$); HRMS calcd for $C_{23}H_{23}NO$ (M^+) 329.1779, found m/e 329.1779. Then compound **57b** as a white solid (0.45 g, 34%): mp 95 °C; IR ($CHCl_3$) 1680 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48–7.17 (m, 10H, Ar), 3.60–3.55 (m, 1H, NCH), 3.50 (d, J = 12 Hz, 1H, CHPh), 3.20 (d, J = 12 Hz, 1H, CHPh), 2.98–2.91 (m, 1H, NCH), 2.19–2.14 (m, 2H), 1.97–1.90 (m, 2H), 1.86–1.77 (m, 1H), 1.75–1.68 (m, 1H), 1.58–1.48 (m, 2H), 0.95–0.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9 (CO), 147.1, 113.4 (C=C), 139.4–126.6 (9 peaks, Ar), 67.1 (C quat), 42.7 (NCH_2), 39.9 (CH_2Ph), 35.6 (C(6)), 32.1 (C(5)), 28.8 (C(10)), 23.6 (C(9)), 20.8 (C(8)); HRMS calcd for $C_{23}H_{23}NO$ (M^+) 329.1779, found m/e 329.1785.

$(CO)_5Cr$=C[N(CH_2CHCH_3)](CH_2)$_3$C≡C—Ph (58) was obtained from complex **17** and methylaziridine: yield, 81%, yellow oil (47/53 E/Z mixture); IR ($CHCl_3$) 2040, 1965, 1915 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.40–7.25 (m, 5H, Ar), 3.45–3.35 (m, 1H, NCH), 3.14–3.03 (m, 6H), 2.82–2.78 (m, 2H), 2.52–2.35 (m, 5H), 2.05–1.80 (m, 4H), 1.65 (d, J = 5.5 Hz, 3H, CH_3), 1.48 (d, J = 5.5 Hz, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 279.5, 272.9 (Cr=C), 222.9, 218.0, 217.9 (CO), 131.4, 128.2, 127.8, 123.4 (Ar), 88.7, 81.7 (C≡C), 52.7, 52.1 (NCH_2), 37.3, 32.7, 32.2, 26.5, 26.0, 19.3, 19.1, 17.4, 17.1 (CH_2, CH_3). Anal. Calcd for $C_{20}H_{17}NO_5Cr$: C, 59.55; H, 4.22; N, 3.47. Found: C, 59.63; H, 4.36; N, 3.43.

Thermolysis of complex 58 as above, followed by silica gel chromatography, gave first **59** as an oil (0.057 g, 17%): IR ($CHCl_3$) 2240 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.40–7.25 (m, 5H, Ar), 2.62–2.52 (m, 4H), 2.05–1.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1, 128.8, 123.7, 119.7 (Ar, CN), 87.5, 82.9 (C≡C), 25.2, 19.1, 16.7 ($3CH_2$); HRMS calcd for $C_{12}H_{11}N$ (M^+) 169.0891, found m/e 169.0891. Then **60** as white crystals (0.05 g, 11%): mp 144 °C; IR ($CHCl_3$) 1740, 1690 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.64–7.36 (m, 5H, Ar), 4.61–4.51 (m, 1H, NCH), 3.16–3.04 (m, 1H, NCH), 3.00–2.75 (m, 1H), 2.70–2.55 (m, 3H), 2.24–2.05 (m, 2H), 1.65–1.38 (m, 1H, C*H*CH_3), 1.15 (d, J = 7 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.0 (CO), 180.1 (CO), 162.5, 131.0 (C=C), 129.7, 129.1, 128.9, 128.7, 128.6 (Ar), 79.7 (C quat), 48.0, 46.2, 33.0, 26.3, 24.6 (CH, $4CH_2$), 12.7 (CH_3): HRMS calcd for $C_{17}H_{17}NO_2$ (M^+) 267.1259, found m/e 267.1277. Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.40; H, 6.36; N, 5.24. Found: C, 75.32; H, 6.37; N, 5.02. Then a 2.5/1 mixture of **62** and **63** (0.074 g): IR ($CHCl_3$) 2240, 1725 cm^{-1}; **62** ^{13}C NMR (50 MHz, $CDCl_3$) δ 163.29, 158.46, 147.25, 141.64 (pyridine), 138.21–128.18 (Ar), 34.9, 30.6, 28.6, 26.1, 23.2, 17.4 ($6CH_2$); **63** ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.21–128.18 (Ar, CN), 119.13, 112.4, 102.5, 79.35 (dihydropyridine $Cr(CO)_6$), 53.06, 43.56, 31.07, 30.85, 27.45, 26.65, 22.6, 17.07, 13.94; MS $C_{28}H_{28}N_2O$ (M^+) 408, found 338 (M – 70).

Compound 61 was obtained upon pyrolysis of complex **58** (1 g, 0.0025 mol) in boiling benzene in the presence of diphenylacetylene (4.4 g, 0.025 mol). Evaporation of the volatiles in vacuo followed by silica gel chromatography gave with petroleum ether/CH_2Cl_2 (70/30) first **59** (0.2 g, 48%) and then with petroleum ether/CH_2Cl_2 (40/60) **61** as white crystals (0.27 g, 31%): mp 163 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.26–6.81 (m, 15H, Ar), 3.23–3.16 (m, 2H), 2.88–2.80 (m, 2H), 2.26–2.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.34, 156.68, 146.11, 141.28, 138.39, 138.13, 134.40–126.06 (Ar), 34.88, 30.76, 23.17 ($3CH_2$). Anal. Calcd for $C_{26}H_{21}N$: C, 89.91; H, 6.05; N, 4.03. Found: C, 89.68; H, 6.17; N, 3.81.

$(CO)_5Cr$=C[N$CH_2CH(CH_3)$](CH_2)$_3$C≡C—(CH_2)$_3$C≡CPh (65) was synthesized from $(CO)_5Cr$=C(OEt)(CH_2)$_3$C≡C—(CH_2)$_3$C≡CPh (which was obtained from $Cr(CO)_6$ and PhC≡C—(CH_2)$_3$C≡C—(CH_2)$_3$-Li/Et_3OBF_4 as an unstable orange oil (yield 74%)) and methylaziridine as a yellow oil: yield, 20% (1/1 E/Z mixture); ^1H NMR (200 MHz, $CDCl_3$) δ 7.35–7.25 (m, 5H, Ar), 3.4–2.2 (m, 10H), 1.86–1.71 (m, 4H), 1.61 and 1.48 (d, J = 5.4 Hz, 3H, $CHCH_3$).

Compounds 66 and 67. Thermolysis of complex **65** (0.45 g, 0.001 mol) as above gave compound **66** as an oil (0.016 g, 7%): IR ($CHCl_3$) 2240 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.39–7.25 (m, 5H, Ar), 2.53–2.44 (m, 4H), 2.36–2.30 (M, 4H), 1.90–1.83 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 131.70, 128.35, 127.79, 123.95, 119.43 (Ar, CN), 89.23, 81.50, 81.36, 78.07 (2C≡C), 28.83, 28.21, 25.05, 18.74, 18.09, 16.25; HRMS calcd for $C_{17}H_{17}N$ (M^+) 235.1360, found m/e 235.1325. Then complex **67** (0.065 g, 16%), a mixture of two isomers which could be separated by thick-layer chromatography into **67a**: orange solid, mp 98 °C; IR ($CHCl_3$) 1940, 1860, 1840, 1750 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.25–6.91 (m, 5H), 3.45–2.82 (m, 8H), 2.55–2.36 (m, 5H), 1.92–1.85 (m, 1H), 1.54–1.48 (M, 1H), 0.99 (d, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.0 (CO), 206.1 (CO), 135.2, 129.0, 128.4, 126.6, 112.3, 110.5, 99.2, 82.8, 79.1, 53.7, 42.7, 31.9, 30.1, 29.06, 28.9, 22.6, 21.3, 14.3; HRMS calcd for $C_{24}H_{23}NO_4Cr$ (M^+) 441.1032, found m/e 441.1032. And **67b**: orange oil; ^1H NMR (200 MHz, $CDCl_3$) δ 7.28–6.86 (m, 5H), 3.76–3.67 (m, 1H), 3.35–2.74 (m, 6H), 2.52–2.30 (m, 6H), 1.85–1.80 (m, 1H), 1.64 (d, J = 7.4 Hz, 3H), 1.55–1.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.0 (CO), 203.9 (CO), 135.0, 129.1, 128.5, 124.4, 110.7, 110.1, 99.4, 83.9, 79.6, 53.1, 38.5, 31.7, 30.1, 28.6, 22.7, 21.4, 16.4.

$(CO)_5Cr$=C(Et)N(Me)(CH_2)$_3$C≡C—Ph (69) was obtained in two steps from $(CO)_5Cr$=C(Et)OEt and the corresponding amine PhC≡C(CH_2)$_3NH_2$: yield, 91%, yellow oil; IR ($CHCl_3$) 2050, 1930 cm^{-1}; Z isomer ^1H NMR (200 MHz, $CDCl_3$) 9.0 (br, 1H, NH), 7.37–7.31 (m, 5H, Ar), 4.14–4.05 (m, 2H, NCH_2), 3.06–2.94 (m, 2H, C*H*$_2$-CH_3), 2.67–2.54 (m, 2H, CH_2C≡C), 2.10–1.92 (m, 2H, $CH_2CH_2CH_2$), 1.1 (t, 3H, CH_3); E isomer ^1H NMR (200 MHz, $CDCl_3$) δ 8.7 (br, 1H, NH), 7.37–7.31 (m, 5H, Ar), 3.68–3.58 (m, 2H, NCH_2), 3.06–2.94 (m, 2H, C*H*$_2CH_3$), 2.67–2.54 (m, 2H, CH_2C≡C), 2.10–1.92 (m, 2H, CH_2CH_2), 1.1 (t, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 280.4 (Cr=C), 223.4, 218.1 (CO), 131.6–123.2 (Ar), 94.0, 87.0 (C≡C), 53.1 (NCH_2), 49.5 (CH_2CH_3), 28.2 (CH_2C=), 16.6 ($CH_2CH_2CH_2$), 10.4 (CH_3). Anal. Calcd for $C_{19}H_{17}NO_5Cr$: C, 58.31; H, 4.35; N, 3.58. Found: C, 58.54; H, 4.38; N, 3.64. Alkylation of ICH_3 in the presence of LDA gave complex **69**: yield, 96%, yellow oil (1/3 E/Z mixture); IR ($CHCl_3$) 2050, 1930 cm^{-1}; Z isomer ^1H NMR (200 MHz, $CDCl_3$) δ 7.42–7.31 (m, 5H, Ar), 4.35–4.25 (m, 2H, NCH_2), 3.31 (s, 3H, NCH_3), 3.21–3.10 (m, 2H, C*H*$_2CH_3$), 2.64–2.50 (m, 2H, C*H*$_2$C≡C), 2.10–1.90 (m, 2H, $CH_2CH_2CH_2$), 1.1 (t, 3H, CH_2CH_3); E isomer ^1H NMR (200 MHz, $CDCl_3$) δ 7.42–7.31 (m, 5H, Ar), 3.8 (s, 3H, NCH_3), 3.75–3.70 (m, 2H, NCH_2), 3.21–3.10 (m, 2H, C*H*$_2CH_3$), 2.50–2.45 (t, 2H, C*H*$_2$C≡C), 2.10–1.90 (m, 2H, $CH_2CH_2CH_2$), 1.1 (t, 3H, CH_2CH_3);

^{13}C NMR (50 MHz, $CDCl_3$) δ 287.0 (Cr=C), 222.7, 218.0 (CO), 131.6–123.2 (Ar), 87.3, 82.5 (C≡C), 50.9 (NCH_2), 49.4 (NCH_3), 45.18, 27.7, 16.6 ($3CH_2$), 10.6 (CH_3). Anal. Calcd for $C_{20}H_{20}NO_5Cr$: C, 59.26; H, 4.69; N, 3.46. Found: C, 59.10; H, 4.96; N, 3.32.

Aminoketone 70 was obtained by thermolysis of complex **69** as an oil: yield, 42%; IR ($CHCl_3$) 1700 cm^{-1}; ^1H NMR (200 MHZ, $CDCl_3$) δ 7.38–7.10 (m, 5H, Ar), 3.05–2.93 (m, 2H, NCH_2), 2.64 (br s, 1H, NCH), 2.43 (s, 3H, NCH_3), 2.38–2.10 (m, 3H, C(2)H and $C(7)H_2$), 1.90–1.65 (m, 2H, $C(6)H_2$), 1.30 (d, J = 7.6 Hz, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 206.21 (C(1)), 168.8 (C(8)), 137.3 (C(10)), 131.2 (C(9)), 131.24, 129.3, 127.9 (Ar), 73.36 (C(3)), 56.12 (C(5)), 46.7 (C(2)), 44.27 (C(16)), 27.8 (C(7)), 25.8 (C(17)); HRMS calcd for $C_{16}H_{19}NO$ (M^+) 241.1466, found m/e 241.1466.

$(CO)_5Cr$=C(Me)N(Me)$(CH_2)_3$C≡C—Ph (72) was obtained in two steps from $(CO)_5Cr$=C(Me)OEt by aminolysis with the appropriate amine PhC≡C—$(CH_2)_3NH_2$, which gave $(CO)_5Cr$=C(Me)-$NH(CH_2)_3C$≡CPh: yield, 95%, yellow solid; mp 50 °C; IR ($CHCl_3$) 2040, 1970, 1920 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.8 (1H, NH), 7.38–7.31 (m, 5H, Ar), 3.75–3.60 (m, 2H, NCH_2), 2.70 (s, 3H, CH_3), 2.58–2.54 (m, 2H, CH_2), 2.05–1.96 (m, 2H, $CH_2CH_2CH_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 282.0 (Cr=C), 222.9, 217.8 (CO), 131.6, 128.3, 128.1, 123.1 (Ar), 87.1, 82.5 (C≡C), 47.0 (NCH_2), 35.4 (CH_2C≡C), 16.6 ($CH_2CH_2CH_2$). Anal. Calcd for $C_{18}H_{15}NO_5Cr$: C, 57.29; H, 3.98; N, 3.71. Found: C, 57.28; H, 4.07; N, 3.62. Treatment of this complex with LDA/ICH_3 gave complex **72**: yield, 75%, orange oil; IR ($CHCl_3$) 2050, 1965, 1920 cm^{-1}; E isomer ^1H NMR (200 MHz, $CDCl_3$) δ 7.4 (m, 5H, Ar), 3.9 (s, 3H, NCH_3), 3.8 (m, 2H, NCH_2), 2.85 (s, 3H, Cr=C-(CH_3)), 2.5 (t, 2H, CH_2C≡C), 2.0 (m, 2H, $CH_2CH_2CH_3$); Z isomer ^1H NMR (200 MHz, $CDCl_3$) δ 7.4 (m, 5H, Ar), 4.35 (m, 2H, NCH_2), 3.26 (s, 3H, NCH_3), 2.68 (s, 3H, CH_3), 2.58 (m, 2H, CH_2C≡C), 2.06 (m, 2H, $CH_2CH_2CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 285 (Cr=C), 223, 218 (CO), 131.58, 128.46, 128.23, (Ar), 87.26, 82.58 (C≡C), 54.17 (NCH_2), 51.08 (NCH_3), 39.57 (CH_3) 26.92 (CH_2C≡C), 16.94 (CH_2CH_2-CH_2). Anal. Calcd for $C_{19}H_{17}NO_5Cr$: C, 58.31; H, 4.35; N, 3.58. Found: C, 59.15; H, 4.52; N, 3.34.

Aminoketone 73 was obtained upon thermolysis of complex **72**: yield, 21%, white crystals; mp 92 °C; IR ($CHCl_3$) 1680, 1660 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.26–7.13 (m, 5H, Ar), 5.76 (m, 1H, H(7)), 5.72–5.66 (tt, J = 4.2, 1.4 Hz, 1H), 5.17 (d, J = 1.2 Hz, 1H, H(2)), 4.01 (d, J = 1.2 Hz, 1H, H(9)), 3.52–3.32 (m, 2H, NCH_2), 3.00 (s, 3H, NCH_3), 2.47–2.41 (tdd, J = 7, 4.2, 1.7 Hz, 2H, $C(6)H_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.54 (CO), 137.16 (C(8)), 128.51 (C(11), C(15)), 128.26 (C(12), C(14)), 126.71 (C(13)), 121.84 (C(7)), 99.41 (C(2)), 54.28 (C(9)), 47.73 (C(5)), 39.38 (C(16)), 24.04 (C(6)); HRMS calcd for $C_{15}H_{15}NO$ (M^+) 225.1153, found m/e 225.1150.

$(CO)_5Cr$=C(CD_3)N(Me)$(CH_2)_3$C≡C—Ph (72b) was obtained from $(CO)_5Cr$=C(CD_3)OEt by the same method as that for complex **72a** via $(CO)_5Cr$=C$(CD_3)NH(CH_2)_3C$≡CPh: yield, 95%, yellow crystals; mp 51 °C; IR ($CHCl_3$) 2040, 1970, 1920 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.86 (1H, NH), 7.3 (m, 5H, Ar), 3.6 (m, 2H, NCH_2), 2.5 (m, 2H, CH_2C≡C), 1.9 (m, 2H, $CH_2CH_2CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 283.1 (Cr=C), 228.8, 217.9 (CO), 132.6–123.1 (Ar), 87.0, 82.6 (C≡C), 47.1 (NCH_2), 27.8 (CH_2C≡C), 16.7 ($CH_2CH_2CH_2$); HRMS calcd for $C_{18}D_3H_{12}NOCr$ (M^+) 380.0543, found m/e 380.0545. **72b**: yield, 99% orange oil; IR ($CHCl_3$) 2040, 1965, 1920 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.3 (m, 5H, Ar), 3.86 (s, 3H, NCH_3), 3.8 (m, 2H, NCH_2), 2.5 (t, 2H, CH_2C≡C), 2.00 (m, 2H, $CH_2CH_2CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 283.15 (Cr=C), 223.41, 217.92 (CO), 131.55–123.01 (Ar), 87.64, 82.41 (C≡C), 54.06 (NCH_2), 50.97 (NCH_3), 26.7, 16.83, (CH_2—CH_2—CH_2); MS $C_{19}D_3H_{14}NOCr$ (M^+) 394, found m/e 254 (M −5CO). Thermolysis of complex **72b** gave aminoketone **73** (24%) identical in all respects to the product obtained from **72a**.

$(CO)_5Cr$=C(Ph)NH$(CH_2)_3$C≡C—Ph (75) was obtained from $(CO)_5$-Cr=C(Ph)OEt and PhC≡C$(CH_2)_3NH_2$: yield, 88%, yellow oil; IR ($CHCl_3$) 2025, 1980, 1930 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.2 (s, 1H, NH), 7.4–6.79 (m, 10H, Ar), 4.28 (q, 2H, NCH_2), 2.67 (t, 2H, CH_2C≡C), 2.15 (m, 2H, $CH_2CH_2CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 283.0 (Cr=C), 224.0 217.2 (CO), 155.0–119.0 (7 peaks, Ar), 87.76, 82.68 (C≡C), 53.3 (NCH_2), 28.12 (CH_2C≡C), 17.47 ($CH_2CH_2CH_2$). Anal. Calcd for $C_{23}H_{17}NO_5Cr$: C, 62.87; H, 3.87; N, 3.19. Found: C, 62.90; H, 4.02; N, 3.01.

$(CO)_5Cr$=C(Ph)N$(CH_3)(CH_2)_3$C≡C—Ph (76) was obtained as above from **75** and LDA/ICH_3: yield, 56%, yellow crystals; mp 66 °C; IR ($CHCl_3$) 2050, 1930 cm^{-1}; E isomer ^1H NMR (200 MHz, $CDCl_3$) δ 7.4–6.6 (m, 10H, Ar), 3.99 (s, 3H, NCH_3), 3.56–3.48 (m, 2H, NCH_2), 2.29–2.16 (t, 2H, CH_2C≡C), 1.98–1.86 (m, 2H, $CH_2CH_2CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 275.66 (Cr=C), 224.0, 217.3 (CO), 153.4–118.56 (Ar), 87.0, 82.1 (C≡C), 62.9 (NCH_2), 49.0 (NCH_3), 27.67 (CH_2C≡C), 16.84 ($CH_2CH_2CH_2$). Anal. Calcd for $C_{24}H_{19}NO_5Cr$: C, 63.57; H, 4.19; N, 3.09. Found: C, 62.61; H, 4.36; N, 2.91.

Thermolysis of complex 75 (1.5 g, 0.0034 mol) in benzene gave, after silica gel chromatography with petroleum ether/ethyl acetate as eluent, first compound **77** as an orange oil (0.5 g, 54%): IR ($CHCl_3$) 1650, 1600 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.35–7.17 (m, 5H, Ar), 4.14 (t, 2H, NCH_2), 2.56 (t, 2H, CH_2C≡C), 1.79 (m, 2H, $CH_2CH_2CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 184.1 (CO), 156.0 (N=C), 146.1–121.6 (Ar), 51.6 (NCH_2), 29.7 (CH_2C=C), 22.4 ($CH_2CH_2CH_2$). The HRMS spectrum of **76** corresponds to the spectrum of **78**, which is also obtained by oxidation in the air or upon heating of **77**. Then complex **78** as white crystals (0.21 g, 23%): mp 158 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 9.31–8.3 (m, 3H, N = CH—CH=CH), 7.8–7.3 (m, 9H, Ar), 5.84 (br s, 1H, OH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.7 (COH), 133.5–115.8 (Ar); HRMS calcd for $C_{19}H_{13}NO$ (M^+) 271.0997, found m/e 271.1001. Thermolysis of complex **76** in benzene gave, after silica gel chromatography with petroleum ether/ethyl acetate as eluent, first compound **79**: yield, 30%, white crystals; mp 162–164 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 8.22–7.25 (m, 9H, Ar), 5.1 (s, 1H, OH), 3.25–3.15 (m, 2H, NCH_2), 2.92 (s, 3H, NCH_3), 2.44–2.36 (m, 2H, CH_2C=C), 1.95–1.75 (m, 2H, $CH_2CH_2CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.7 (COH), 138.1–122.02 (Ar), 51.12 (NCH_2), 44.58 (NCH_3), 27.04 (CH_2C=C), 16.11 ($CH_2CH_2CH_2$); HRMS calcd for $C_{20}H_{19}NO$ (M^+) 289.1466, found m/e 289.1469. Then complex **80a**: yield, 17.6% orange oil; ^1H NMR (200 MHz, $CDCl_3$) δ 7.48–7.01 (m, 5H, Ar), 5.69 (d, 1H), 5.52 (d, 1H), 5.25 (t, 1H), 5.15 (t, 1H, ArCr), 4.39 (s, 1H, PhC*H*), 3.07–3.01 (m, 2H, NCH_2), 2.85 (s, 3H, NCH_3), 2.25–1.65 (m, 4H, CH_2CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 233.7 (CO), 143.9–117.4 (C=C, Ar), 95.7, 94.2, 83.9, 81.6 (ArCr), 54.2 (NCH_2), 53.0 (NCH_3), 40.7 (CPh), 23.1, 19.3 ($2CH_2$). Air oxidation of **80a** gave **80b** as an oil: ^1H NMR (200 MHz, $CDCl_3$) δ 7.2 (m, 9H, Ar), 4.30 (s, 1H, CHPh), 3.11 (m, 2H, NCH_2), 2.97 (s, 3H, NCH_3), 2.09 (m, 2H), 1.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.99–118.78 (13 peaks, Ar), 55.47, 52.84, 40.77, 22.46, 19.39; HRMS calcd for $C_{19}H_{19}N$ (M^+) 261.313, found m/e 261.313.

Crystal Data. Intensity data were collected at room temperature on a Nonius CAD4 diffractometer using graphite monochromated Mo Kα radiation. In each case, accurate unit cell dimensions and orientation matrix were obtained from least-squares refinements of the setting angles of 25 well-defined reflections. Crystal data and data collection parameters are listed in Tables S1–S22. Intensities of standard reflections showed no change during data collections. Computations were performed by use of the CRYSTALS[30] system adapted for a MICROVAX-II computer. Atomic scattering factors for neutral Cr, O, C, and N were taken from ref 31. Anomalous dispersion term were applied. All structures were solved by direct methods (SHELXS[32]) and standard Fourier techniques and refined by least squares. For compounds **19**, **26**, and **60**, refinements were performed using anisotropic thermal parameters for all non-hydrogen atoms. H atoms were located on difference Fourier maps. For compound **26**, their coordinates were refined with an overall isotropic thermal parameter. For compounds **19** and **60** they were left in fixed positions and only an overall isotropic thermal parameter was refined. For compound **15**, due to the poor diffracting ability of these crystals, only 773 data points were available; thus it was necessary to reduce the number of variable parameters. Consequently all atoms were left isotropic; H atoms located on a difference Fourier map were left in fixed positions.

Supplementary Material Available: Crystal structure data (Tables S1–S22) for **15**, **19**, **29** and **60** including complete lists of interatomic distances (Tables S5–S11) and bond angles (Tables S13–S22), fractional parameters (Tables S12–S15), and anisotropic thermal parameters (Tables S16–S18) (18 pages); tables of observed and calculated structure factors (Tables S19–S22) (10 pages). Ordering information is given on any current masthead page.

(30) Watkins, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS User Guide*; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1986.

(31) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(32) Sheldrick, G. M. SHELXS86, Program for Crystal Structure Solution, University of Göttingen, 1986.