# Aminocarbene Complexes of Chromium. 8. Access to the Pyrroloindole and Pyrrolochinoline Frameworks and Synthesis of Substituted Lycoranes

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The use of alkynylaminocarbene complexes of chromium as starting material for the synthesis of pyrroloindole, pyrrolochinoline, and azaacenaphtylenone skeletons via cascade insertions of alkynes and CO followed by the rearrangement of zwitterionic intermediates was examined. Both the precursor complexes, synthesized from the appropriate functionalized lactams, as well as their thermolysis products were obtained in satisfactory yields and could be fully characterized. This reaction was finally applied to the synthesis of substituted lycoranes, a result which confirmed its general scope.

## Introduction

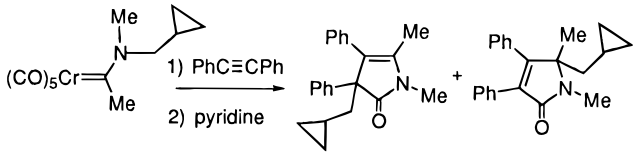
The recent discovery of a new reaction[1−3] of aminocarbene complexes of chromium with alkynes leading via the same intermediates, in the intermolecular version, to monocyclic lactams (Scheme 1) and, in the intramolecular version (Scheme 2), to polycyclic, nitrogen-containing heterocycles led us to attempt to use this approach for the synthesis of more complex heterocyclic skeletons, and especially those of alkaloids and their precursors.

Among the very important structures which have attracted our attention appear the tricyclic pyrroloindoles I which are found interalia in ibophyllidine alkaloids and the pyrrolochinolines II, common to aspidosperma and lycorane alkaloids.[4−8]

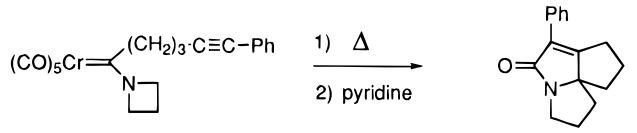
Both systems I and II might be viewed, at least on paper, as arising via the same sequence from aminocarbene complexes of the general structure **1**.

Indeed, previous work of this laboratory confirmed the general behavior of aminocarbene complexes toward alkynes, especially in the intramolecular version,[3] so that speculation about the formation of derivatives of I and II from complexes **1** ($n$ = 2, 3) were well-founded. A

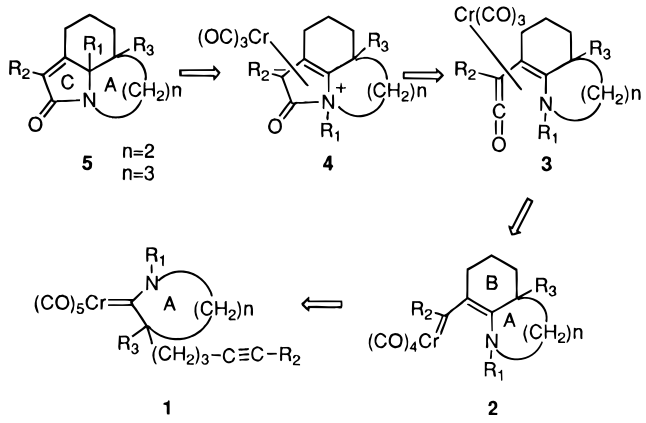
**Scheme 1**




**Scheme 2**




**Scheme 3**




retrosynthetic analysis of these tricyclic structure targets is given in Scheme 3 and involves the following thoroughly established steps from the preformed, cycle C-containing carbene complex **1**: insertion of the alkyne into the carbene function leading to **2** with formation of cycle B; insertion of CO into the new carbene function of **2** giving the ketene complex **3**; interaction of the nitrogen atom with the central carbon atom of the ketene **3** leading to a nitrogen ylide complex **4** and thus to cycle A; rearrangement of **4** into the target products **5** upon alkyl migration from nitrogen to the α- (or δ-, not shown in the scheme) carbon of the allylic system.

Depending on the size of the nitrogen-containing ring in the starting complex **1**, access to both systems should be possible.

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

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

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

(3) Chelain, E.; Parlier, A.; Audouin, M.; Rudler, H.; Daran, J. C.;Vaissermann, J. *J. Am. Chem. Soc.* **1993**, *115*, 10568.

(4) (a)Saxton, J. E. In *The Chemistry of Heterocyclic Compounds*; Taylor, E. C., Ed.; John Wiley: Chichester, 1994; Vol. 25, pp 487−521. (b) Gallagher, T.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 4739. (c) Wenkert, E.; Hudlicky, T. *J. Org. Chem*. **1988**, *53*, 1953. (d) LeMenez, P.; Kunesh, N. *J. Org. Chem*. **1991**, *56*, 2915. (e)Desmaële, D.; d'Angelo, J. *J. Org. Chem*. **1994**, *59*, 2292. (f) Wenkert, E.; Liu, S. *J. Org. Chem*. **1994**, *59*, 7677.

(5) Kuehne, M. E.; Xu Feng. *J. Org. Chem*. **1993**, *58*, 7490.

(6) (a) Ghosal, S. *Phytochem*. **1985**, *24*, 2141. (b) Gabrielsen, B.; Monath, T. P.; Huggins, J. W.; Kefauver, D. F. *J. Nat. Prod*. **1992**, *55*, 1569.

(7) (a) Banwell, M. G.; Cowden, C. J.; Mackay, M. F. *J. Chem. Soc., Chem. Commun*. **1994**, 61. (b) Gonzalez, C.; Pérez, D.; Guitian, E.; Castedo, L. *J. Org. Chem*. **1995**, *60*, 6318. (c) Holoboski, M. A.; Smyth, M. S. *J. Am. Chem. Soc*. **1996**, *118*, 6210.

(8) (a)Bäckvall, J. E.; Anderson, P. G.; Stone, G. B.; Gogoll, A. *J. Org. Chem*. **1991**, *56*, 2988. (b) Pearson, W. H.; Schkeryantz, J. M. *J. Org. Chem*. **1992**, *57*, 6783. (c) Grotjahn, D. B.; Vollhardt, K. P. C. *Synthesis* **1993**, 579. (d) Banwell, M. G.; Wu, A. W. *J. Chem. Soc., Chem. Commun*. **1994**, 2671.

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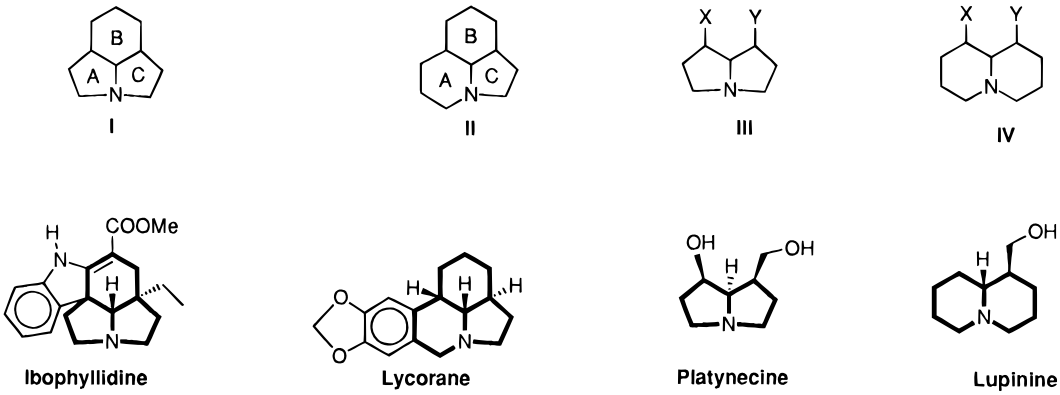
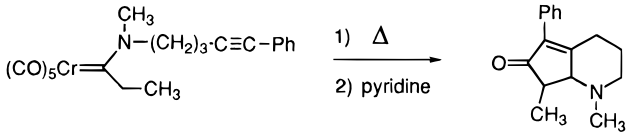



An exception to this rule was nevertheless observed for aminocarbene complexes in which the alkynyl chain was directly linked to the nitrogen atom (Scheme 4): in that case, for geometrical reasons, no ylide can be formed after the insertion reactions.

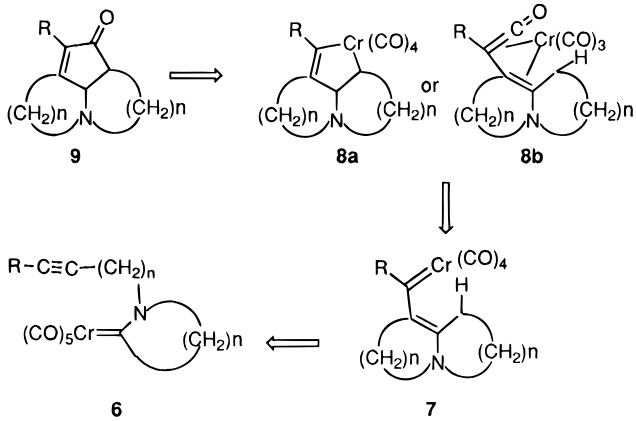
One might thus speculate upon the behavior of more elaborate complexes of this type, derived either from pyrrolidinones or piperidones. A retrosynthetic analysis (Scheme 5) shows that for $n = 3$ or 4 in **6**, formation of functionalized pyrrolizines III, *via* hexahydrocyclopentapyrrolizinone **9** ($n = 2$), or quinolizines IV, *via* octahydroazaacenaphtylenones **9** ($n = 3$), would be conceivable. Indeed, either a formal insertion of the new carbene into a CH bond in b to the nitrogen atom (**7** → **8a**) and finally a reductive cyclocarbonylation might give a cyclopentenone (**8a** → **9**) or a metal-mediated hydrogen activation on the ketene complex **8b** might lead to the same tricyclic system **9**.[9,10]

The purpose of this paper is thus to describe, on the first hand, the synthesis of the starting carbene complexes with their modifications (introduction of the alkyne-bearing chains, of extra substituents) and, on the second hand, the thermolysis of these elaborate complexes giving finally, in the case of **1** substituted lycoranes and in the case of **6**, a potential precursor of quinolizidine alcaloids. The possibilities (highs) and the limits (lows) of this approach both as far as the synthesis of the starting complexes and of the result of their thermolysis reactions are concerned will be outlined and analyzed.

**Scheme 4**



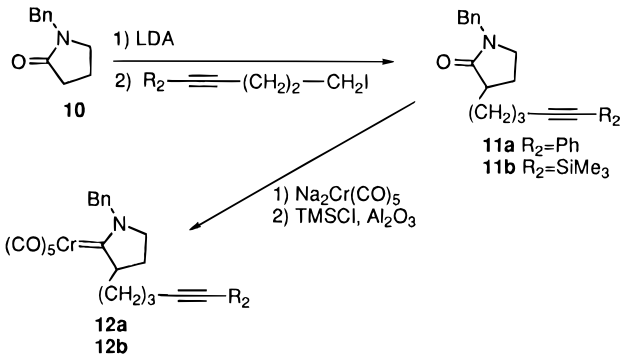

**Scheme 5**




## Results and Discussion

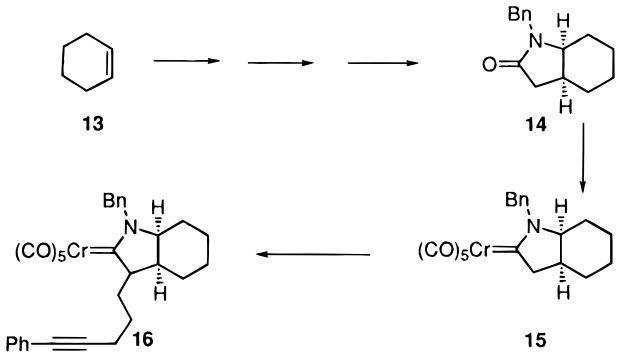
**Synthesis of the Starting Carbene Complexes 1 ($n$ = 2, 3).** Two strategies have been applied for the synthesis of the desired carbene complexes: the first one involved the transformation of N-substituted pyrrolidinones or piperidones into α-alkylated, alkyne-containing lactams.[10,11] These lactams were then subjected to the Hegedus reaction possibly giving rise to functionalized aminocarbene complexes.[12,13] The second one involved the direct transformation of the commercially available lactams, via the same method, into carbene complexes which might be further alkylated for the introduction of the alkyne function.

Thus, 1-benzylpyrrolidin-2-one (**10**) led to lactams **11a**,**b** upon alkylation with the corresponding iodide, in the presence of LDA, in respectively 69 and 68% yield. Reaction of **11a**,**b** with $Na_2Cr(CO)_5$ followed by treatment with trimethylchlorosilane and chromatography over alumina led to the aminocarbene complexes **12a**,**b** in 87 and 75% yield.

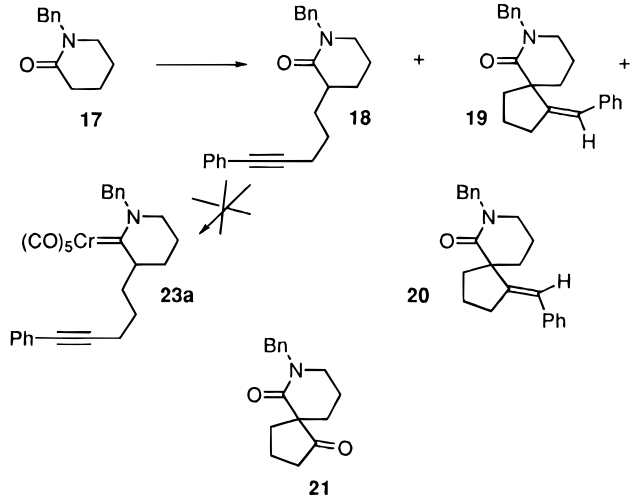



Similarly, the more elaborate carbene complex **16**, derived from 1-benzyldecahydroindolin-2-one (**14**) (prepared in several steps from cyclohexene **13**)[14−17] could be obtained in 51% yield from this lactam.

(9) (a) Audouin, M; Blandinières, S; Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1990**, 23. (b) Challener, C. A.; Wulff, W. D.; Anderson, B. A.; Chamberlin, S.; Faron, K.L.; Kim, O. K.; Murray, C. K.; Xu Yao-Chang; Yang, D. C.; Darling, S. D. *J. Am. Chem. Soc.* **1993**, *115*, 1359.
(10) Fisher, M. J.; Overman, L. E. *J. Org. Chem.* **1990**, *55*, 1447.
(11) Xia, Y.; Kozikowski, A. P. *J. Am. Chem. Soc.* **1989**, *111*, 4116.
(12) Imwinkelried, R; Hegedus, L. S. *Organometallics* **1988**, *7*, 702.
(13) Borel, C.; Hegedus, L. S.; Krebs, J.; Satoh, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1101.
(14) Ziegler, K. *Annalen* **1942**, *551*, 80.

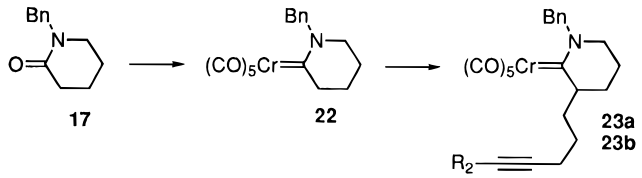



When the same approach was used for the six-membered lactam **17** only a low yield (15%) of the expected alkylated lactam **18** was observed. The major products of the reaction were assigned structures **19** and **20**. They result from an intramolecular addition of the α-lithio form of **18** to the triple bond (1,5-alkynyllithium cyclization).[18] The absence of signals for the carbons of the triple bond in **19** and **20**, together with the presence of signals at respectively δ 6.46 and 6.22 ppm (151.6 and 121.24 and 151.6 and 123.8 ppm) confirmed the formation of these two unsaturated spirolactams. Also, cleavage of the double bond of **19** by ozone led to the keto lactam **21** (together with the corresponding enol ether **21′**; see Experimental Section), the spectroscopic data of which agreed with such a structure (δ CO, 210.0 and 170.5 ppm).



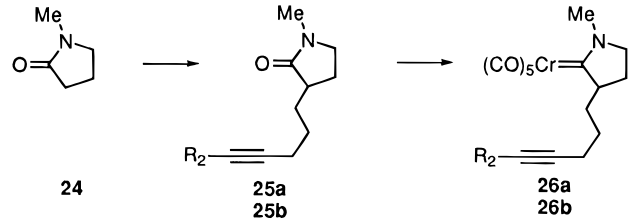

Attempts to transform the lactam **18** into complex **23a** failed also: this result as well as the transformation of **17** into **19** and **20** reflect the ease by which protons can be abstracted from **18**, either by LDA, giving rise by an intramolecular reaction, to **19** and **20**, or by $Na_2Cr(CO)_5$, leading finally to the pentacarbonyl chromium complex of the lactam **18**.

Access to complexes **23a**,**b** was nevertheless achieved in good yields by following the second strategy. Transformation of **17** into the carbene complex **22** was straightforward. Alkylation of **22** with the corresponding iodide

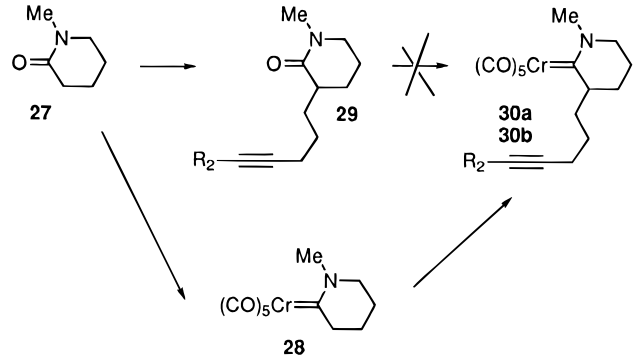



gave the expected monoalkylated carbene complexes **23a**,**b** in 57 and 16% yield. Moreover, use of the corresponding triflates increased the yields up to respectively 72 and 57%.

The transformation of *N*-methylpyrrolidinone (**24**) into the corresponding carbene complexes **26a**,**b** via the alkylated pyrrolidinone **25a**,**b** was again successful (88% and 52% yield) when the triflates were used instead of the iodides for the second step.




Surprisingly, the corresponding 1-methylpiperidone (**27**) only gave a poor yield of the corresponding carbene complexes **30a**,**b**. Whereas the classical method, via the alkylated lactam **29a** (76%), did not yield at all the complex **30a**, the alkylation of the carbene complex **28** only gave low yields of **30a** (16%) and **30b** (19%).

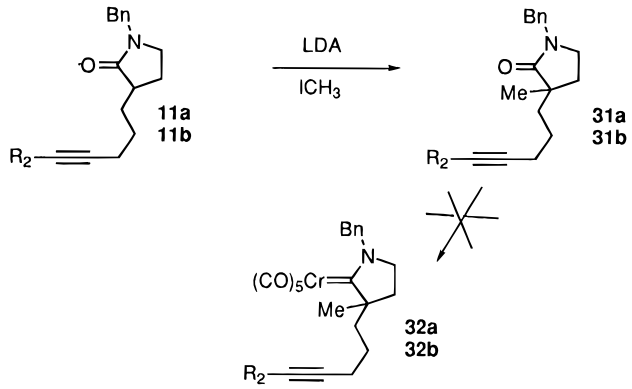


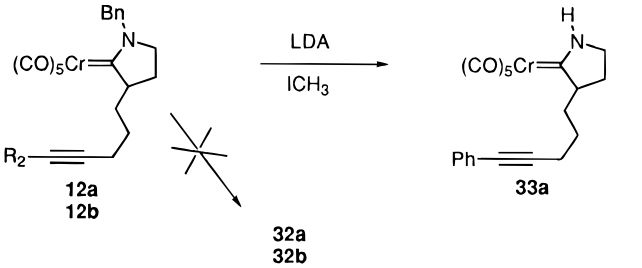

**Attempts at α-Dialkylation.** The presence of an ethyl group at the ring junction in ibophyllidine prompted us to make a few attempts for the introduction of an alkyl group ($R_3$) in our model tricyclic compounds of the type **5**. For that purpose, either the pyrrolidinones **11a**,**b** or the corresponding carbene complexes **12a**,**b** had to be alkylated in the α-position with respect to the carbene function. Whereas in the case of **11a**,**b** the expected lactams **31a**,**b** were obtained in satisfactory yields by successive alkylation with the required alkynyl triflate and methyl iodide, in the presence of LDA, their conversion into the carbene complexes **32a**,**b** failed.

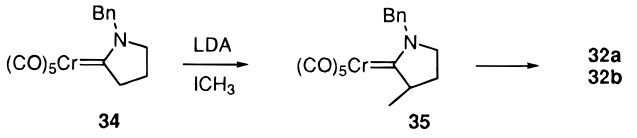
Conversely, attempts at dialkylating **12a**,**b** with LDA/$ICH_3$, were unsuccessful. Instead, an unexpected LDA induced debenzylation occurred to give **33a**. It is interesting to notice at this point that similar dealkylations at nitrogen were observed in other instances, even for substituents at nitrogen different from benzyl (unpublished results). It appears thus that the replacement of

(15) Knouzi, N.; Vaultier, M.; Carrié, R. *Bull. Soc. Chim. Fr.* **1985**, 815.
(16) Stork, G.; Mah, R. *Heterocycles* **1989**, *28*, 723.
(17) Wulff, W. D.; Yao-Chang, X. *Tetrahedron Lett.* **1989**, *31*, 4061.
(18) (a) Bailey, W. F.; Ovaska, T. V. *J. Am. Chem. Soc.* **1993**, *115*, 3080. (b) Bailey, W. F.; Wachter-Jurcak, N. M.; Pineau, M. R.; Ovaska, T. M.; Warren, R. R.; Lewis, C. E. *J. Org. Chem.* **1996**, *61*, 8216.

the oxygen atom in the lactams by the $Cr(CO)_5$ fragment can considerably modify their reactivity.



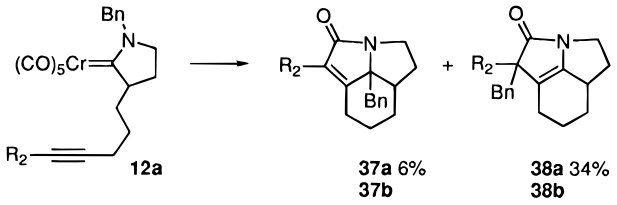




However, the expected dialkylated carbene complex could be prepared, yet in low yield, by the following means. Complex **34** obtained in high yield from the corresponding pyrrolidinone could be alkylated with $ICH_3$/LDA, again in high yield, to give complex **35**. Alkylation of **35** with the appropriate alkynyl triflate, led to the expected dialkylated complex **32a** in 5% yield. No further efforts were, however, made to improve this result.

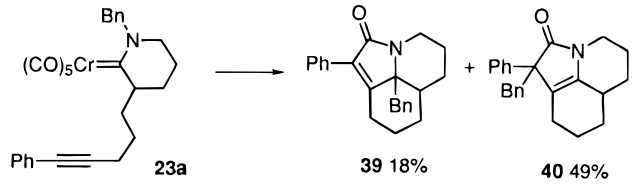
Although this latter result was disapointing, all of the desired carbene complexes likely to lead to the desired tricyclic compounds of the type **5** (Scheme 3) had thus been obtained by either of the two designed methods.

**Thermolysis of Complexes 12a, 23a, 25b, and 30a.** Having in hand a series of elaborate carbene complexes of the type **1**, we submitted them to a thermolysis reaction under conditions already outlined in previous reports.[3] Thus, when complex **12a** was heated in refluxing benzene for 12 h, two organic compounds **37a** and **38a** were obtained and isolated in respectively 6 and 34% yield and fully characterized. The IR and $^{13}C$ NMR spectra of **37a** confirmed the presence of a conjugated lactam ($\nu$ CO, 1670 $cm^{-1}$, $\delta$ CO, 178.35 ppm). Extended $^1H$ and $^{13}C$ NMR experiments allowed the assignment of all the signals of this compound (see the Experimental Section). Similarly, structure **38a** was given to the second compound on the grounds of its physical data ($\nu$ CO, 1685 $cm^{-1}$; $\delta$ CO 180.25 ppm).

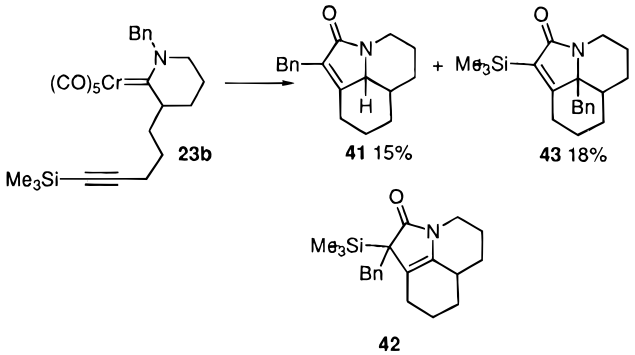
Under the same conditions, complex **23a** led to a mixture of **39** ($\nu$ CO, 1665 $cm^{-1}$; $\delta$ CO, 172.57 ppm) and




**40** ($\nu$ CO, 1700 $cm^{-1}$; $\delta$ CO, 181.40 ppm) in respectively 18 and 49% yield.




The case of **23b** was interesting from both a synthetic and mechanistic point of view: the introduction of a trimethylsilyl group in the starting carbene complex was a prerequisite for further structural modifications in the thermolysis products.

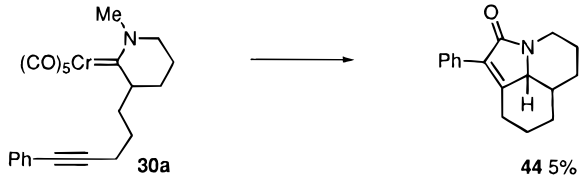



As already observed by Dötz,[19] the presence of a trimethylsilyl-substituted alkyne can stabilize an intermediate silylketene complex. This might hinder, in our case (Scheme 3, $n = 3$, $R_1 = CH_2Ph$, $R_2 = SiMe_3$, $R_3 = H$), the formation and rearrangement of the *N*-ylide complex **4**. Surprisingly, however, the thermolysis took place as in the previous cases to give two insertion−rearrangement products **41** and **43** in a satisfactory 33% overall yield. Whereas **43** had the expected structure, a conjugated lactam resulting from the migration of the benzyl group from nitrogen to the α-carbon, **41**, was the result of the insertion−rearrangement of **23b** to the expected product **42**, an α-trimethylsilyl lactam, followed by loss of the silyl group in α to the carbonyl during workup or chromatography over silica gel.[20]

The behavior of **30a** was, however, quite different: its thermolysis led mostly to decomposition giving an intractable mixture of polar products from which **44** ($\nu$ CO, 1660 $cm^{-1}$; $\delta$ CO, 167 ppm) could be isolated in a low 5% yield: the most striking feature of the $^1H$ NMR spectrum of this compound was indeed the absence of a signal due to a methyl group.

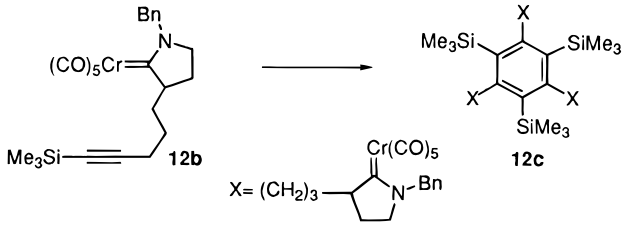
The rearrangement of the intermediate *N*-ylide **4** ($n = 3$, $R_1 = CH_3$, $R_2 = Ph$, $R_3 = H$) thus took place with loss of the methyl group, a feature which had already been

(19) Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* **1980**, *113*, 1149.
(20) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.




observed during intramolecular insertions of alkynes into *N*-methylaminocarbene complexes of chromium.[21,22]

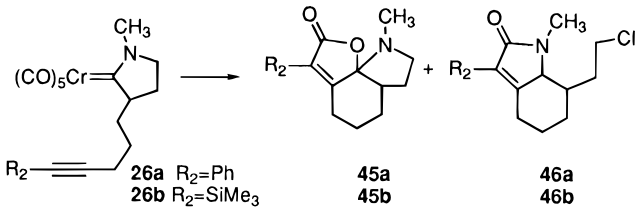
**Unexpected Behavior of Complexes 12b, 16, and 26a,b. Remarks on the Structure of Their Thermolysis Products.** In contrast to **12a**, complex **12b** did not yield the expected insertion products **37b** and **38b**. Instead only a new aminocarbene complex the spectroscopic data of which were very close to those of the starting complex **12b** ($\delta$ Cr=C, 273.36 ppm; $\delta$ CO, 222.78 ppm; $\nu$ CO, 2020, 1960, and 1920 $cm^{-1}$) could be isolated in 13.5% yield. Important modifications were, however, observed both in the $^{13}C$ NMR spectrum, with the disappearance of the signals of the triple bond at $\delta$ 107.1 and 84.7 ppm and the appearance of additional signals for quaternary aromatic carbons at $\delta$ 153.9, 141.3 and 140.1 ppm, and in the IR spectrum, with the disappearance of the triple bond vibration at 2170 $cm^{-1}$.



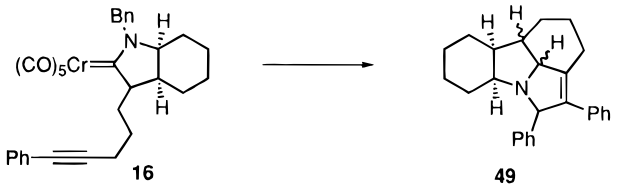

Although this complex could not be further characterized due to its instability, it was tentatively assigned structure **12c** and results thus from the trimerization of the starting complex **12b**.

The behavior of the pyrrolidinone derived complexes **26a**,**b** was also peculiar: although disappearence of the starting complexes took place upon heating, no products due to the classical insertion−rearrangement reactions were isolated. That, however, the intermediate ylides **4** ($n = 2$, $R_1$ = Me, $R_2$ = Ph, $SiMe_3$, $R_3$ = H) were formed to some extend was confirmed by the isolation of two type of products, yet in minute quantities: the aminolactones **45a**,**b** resulting from the oxidation of the ylide complexes (by trace amounts of oxygen), a reaction which had previously been observed and fully described in the case of isolable ylide complexes,[1,23] and the chlorolactams **46a**,**b**, the products probably due to a homolytic cleavage of the intermediate *N*-ylide complexes **4**, followed by trapping of the radicals by a source of $Cl^0$ (probably residual dichloromethane). This result is probably linked to the low propensity of the methyl group for the migration.

**45a**,**b** were characterized by their IR ($\nu$ CO, 1730 $cm^{-1}$) and $^{13}C$ NMR spectra ($\delta$ CO, 173.33 and 172.14 ppm, and $\delta$ 106.4 and 106.6 ppm for the carbon linked to both oxygen and nitrogen). The spectroscopic data of **46a**,**b** agreed with those of a conjugated lactam ($\delta$ CO, 171 ppm) containing a $CH_2CH_2Cl$ group ($\delta$ $CH_2Cl$ respectively at

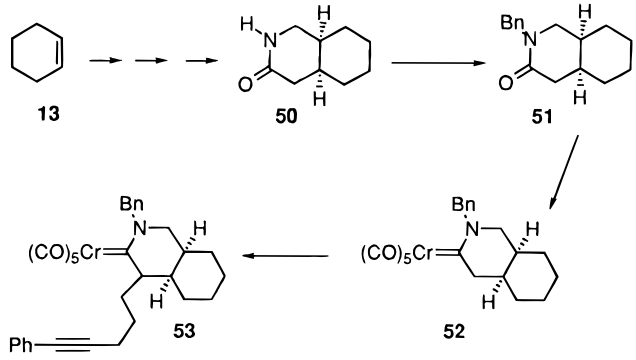



$\delta$ 42.94 and 42.89 ppm), the presence of which was clearly established by a typical fragmentation in the mass spectrum.




Thermolysis of complex **16** led also to a surprising result: whereas **12a** gave the expected tricyclic lactams, the fusion of a six-membered ring to the pyrrolidone-derived carbene complex modified considerably the course of the reaction and led to **49**, as a mixture of two isomers, in 44% yield. Although insertion of the alkyne took place, no CO insertion was observed in that case. Instead, activation of a C−H bond of the benzyl group occurred with formation of a new five-membered ring system (Scheme 6).

**Toward Substituted Lycoranes.** According to Scheme 3, a direct approach to substituted lycoranes might be possible starting from aminocarbene complexes **66a**,**b**. However, since in going from **12a** to **16a** the course of the insertion reaction was considerably modified, we first synthesized carbene complexes **53** and **58** in order to establish the influence, if any, of substituents on the nitrogen-containing ring system, and especially of the presence of a fused six-membered ring.




Thus, *N*-benzyldecahydro-3-isoquinolinone (**51**) was synthesized, according to the literature,[24−26] from cyclohexene. The corresponding carbene complex **52** was obtained in 32% yield by applying the Hegedus reaction. Alkylation with the alkynyltriflate led to the expected complex **53** in 57% yield. Similarly, the carbene complex **57** was obtained from phenacetyl chloride **54** via the 1,4-dihydro-2-benzyl-3-isoquinolinone (**56**).[27] Alkylation at

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(22) Unpublished results from this laboratory.
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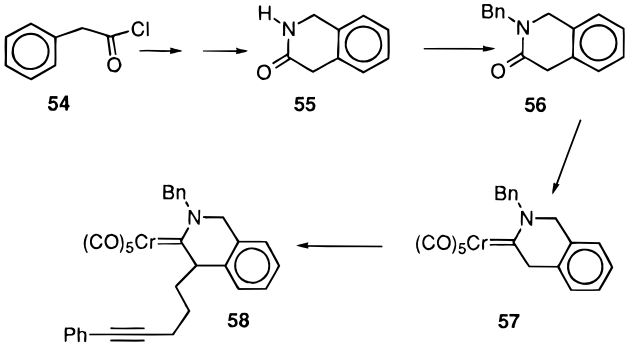
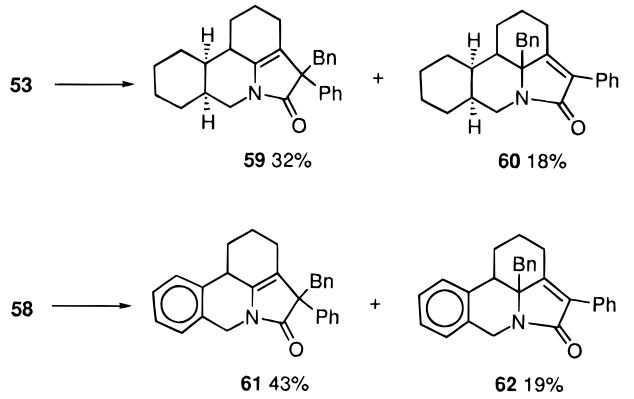
the α-position gave the desired complex **58** in 48% yield.

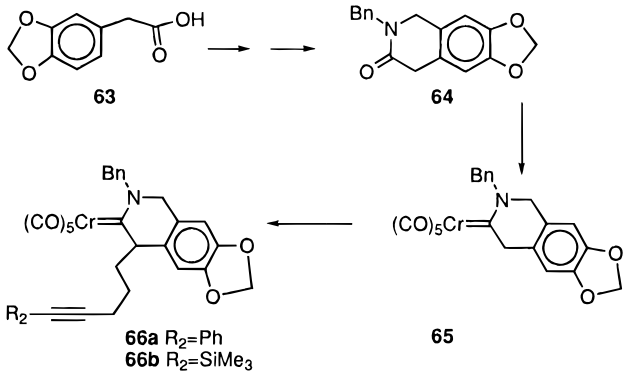



**Thermolysis of Complexes 53 and 58.** Heating of complex **53** in refluxing benzene led to the two expected tetracyclic lactams **59** ($\nu$ CO, 1695 cm$^{-1}$; $\delta$ CO, 181.25ppm) and **60** ($\nu$ CO, 1660 cm$^{-1}$; $\delta$ CO, 171.50 ppm).

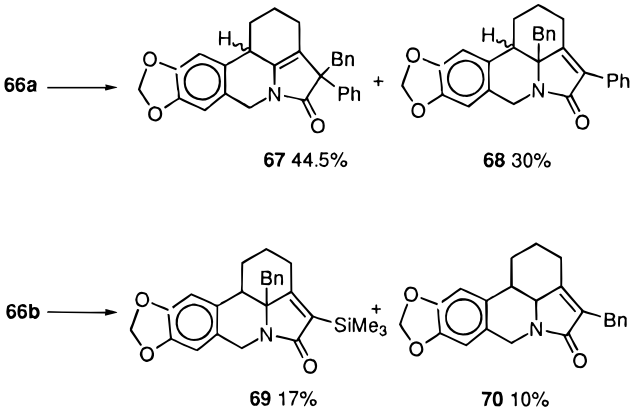



Complex **58** behaved similarly: its thermolysis led to a mixture of **61** ($\nu$ CO, 1700 cm$^{-1}$; $\delta$ CO, 178.6 ppm) and **62** ($\nu$ CO, 1670 cm$^{-1}$; $\delta$ CO, 172.10 ppm). Thus, the expected polycyclic lactams were obtained as expected, a result which urged us to synthesize precursors of lycorane.

**Synthesis of the Precusors of Substituted Lycoranes and Their Thermolysis.** Having demonstrated that complexes **53** and **58** behaved like the simpler complexes **23**, in spite of the presence of an extra fused ring, we synthesized finally the carbene complexes **66a**,**b** ($R_2$ = Ph, $SiMe_3$) from 3,4-(methylenedioxy)phenylacetic acid (**63**) *via N*-benzyl-1,4-dihydro-7,8-(methylenedioxy)-3-isoquinolinone (**64**).[28] Alkylation with the phenyl substituted alkynyltriflate gave the expected complex **66a** in 63% yield and, with the (trimethylsilyl)-substituted triflate, complex **66b** in 55% yield.




Thermolysis of the first complex **66a** led to a mixture of **67** ($\nu$ CO, 1700 cm$^{-1}$; $\delta$ CO, 178.47 ppm) and **68** ($\nu$ CO, 1665 cm$^{-1}$; $\delta$ CO, 171.76 ppm) in a 74% overall yield.



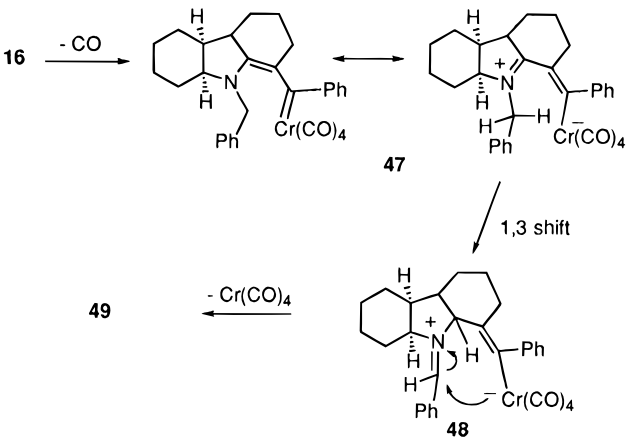

As for the previous examples, the structures were confirmed by extended $^1$H and $^{13}$C NMR spectroscopies. Similarly, complex **66b** gave a mixture of the conjugated lactam **69** (17%; $\nu$ CO, 1650 cm$^{-1}$; $\delta$ CO, 175.71 ppm) and **70** (10%; $\nu$ CO, 1665 cm$^{-1}$; $\delta$ CO, 171.76 ppm), which has lost, as already observed (*vide supra*), the trimethylsilyl group in α to the carbonyl group.

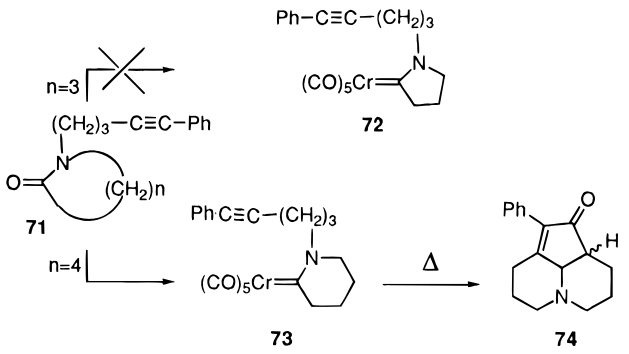
**Attempts To Synthesize Heterocyclic Compounds of the Type III and IV Related to the Pyrrolizidine and Quinolizidine Alkaloids.** As outlined in Scheme 4, such products might be obtained from carbene complexes of the type **6** provided that they rearrange in a way similar to the simpler structures.

These complexes should in turn be attainable from pyrrolidinones and piperidones after alkylation at nitrogen. Although the lactams **71** ($n$ = 3, 4) could be easily prepared (in respectively 76 and 57% yields) from the corresponding alkynyltriflates, for reasons that are not clear (since **14** gave **15**) the transformation of **71** ($n$ = 2) into **72** did not take place, in contrast to **71** ($n$ = 4), which gave **73** in 50.5% yield.

Thermolysis of **73** in refluxing benzene led, yet in low yield (18%), to **74** ($\nu$ CO, 1703 cm$^{-1}$; $\delta$ CO, 207.44 ppm), the structure of which could be completely and unambiguously established by $^1$H and $^{13}$C NMR spectroscopies. Functionalization of both of the six-membered rings would thus be possible. Like the transformation depicted in Scheme 4, the transformation of **73** into **74** involves the activation of a CH bond in α with respect to the carbene function, followed by CO insertion.

**Scheme 6**






## Conclusion

Carbene complexes of the Fischer type have experienced a tremendous expansion of their scope of application in organic chemistry and especially in the field of natural product synthesis. Among of them, one can mention antibiotics, vitamins, lactams, sterols and sterol-like molecules, nucleosides, etc...[29−37] The present utilization describing the synthesis of polycyclic, nitrogen-containing heterocycles, and especially precursors of alkaloids, even broadens the scope of their applications.

Although a few complexes described herein failed to lead to the expected polycyclic compounds, the method, based on the intramolecular insertion of a carbon−carbon triple bond and of a carbonyl group, followed by the rearrangement of intermediate zwitterions, provides access to new pyrroloindole and pyrrolochinoline structures, among which are substituted lycoranes.

## Experimental Section

**General Methods.** $^1$H and $^{13}$C NMR spectra were recorded respectively at 200 or 400 and 50 or 100 MHz. IR spectra were recorded as solutions. Mass spectra are *m*/*z*. Column chromatography was performed with Merck silica gel (70−230 mesh) using various ratios of ethyl acetate/light petroleum ether or dichloromethane/light petroleum ether as eluent. All reagents were obtained from commercial suppliers and used as received. Reactions were performed under an argon atmosphere in carefully dried glassware. Solvents were dried by distillation from a drying agent: THF and $Et_2O$ from Na/benzophenone, $CH_2Cl_2$ from $CaH_2$. The alkynyl iodides and triflates were obtained according to literature procedures.[1,3,38]

The following general procedures were used for the preparation of substituted lactams in the presence of LDA with either an alkynyl iodide or triflate.

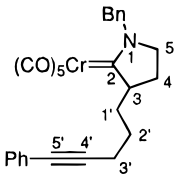
LDA was prepared from diisopropylamine in THF, at −78 °C; 1.1 equiv of BuLi was then added.

In the case of an iodide: To a solution of the lactam in THF (1 mmol/mL) at −78 °C, 1.2 equiv of LDA was transfered by means of a cannula. Then 1 equiv of iodide in THF (1 mmol/mL) was added. The medium was then warmed to room temperature. Water was added and the solution extracted with diethyl ether. The organic phase was then washed with water and brine and dried over $Na_2SO_4$. Evaporation of the solvents under reduced pressure followed by filtration of the residue on silica gel gave the alkylated lactam.

In the case of a triflate: LDA (1 mmol/1.2 mL of THF) was added to a THF solution of the lactam (1 mmol/mL) at −78 °C. Ten minutes later, the triflate (1 equiv, in THF 1 mmol/mL) was added. After stirring for 15 min at −78 °C, the solution was warmed to −20 °C and stirred at this temperature for 30−60 min and then at 0 °C for 10 min. The progress of the reaction was followed by TLC. After hydrolysis (6 mL of $H_2O$/mmol of triflate), workup as above was carried out.

The carbene complexes were prepared from the corresponding lactams, according to the following procedure described by Hegedus. To a solution of naphtalene (6.7 g, 52 mmol) in THF (100 mL) was added a slight excess of sodium (1.3 g, 56 mmol). The green solution was then stirred at room temperature for 5 h, then transfered *via* a cannula, over 1 h, to a suspension of $Cr(CO)_6$ (5.5 g, 25 mmol) in THF (250 mL) maintained at −78 °C. The solution was then allowed to warm to room temperature and stirred at this temperature for a further 12 h. The solution was then again cooled to −78 °C and the amide (22 mmol) added via a cannula over a period of 2 min. The mixture was then stirred at this temperature for 30 min and then at 0 °C for the same time. TMSCl (10 mL, 75 mmol) was then added, at −78 °C and the solution again stirred at this temperature for 30 min, and finally neutral alumina (70 g) was added. The suspension was then allowed to warm to room temperature and the solvent evaporated under reduced pressure. The residue adsorbed on alumina was then poured on a column of silica gel. Petroleum ether eluted the naphtalene whereas various mixtures of petroleum ether/dichloromethane gave the expected carbene complexes.

**Pentacarbonylchromium carbene complex 12a** was




prepared from $Cr(CO)_6$ (5.5 g, 25 mmol), naphtalene (6.7 g, 52 mmol), sodium (1.3 g, 56 mmol), the lactam **11a** (4 g, 12.6 mmol), TMSCl (5.33 mL, 41.6 mmol) and alumina (50 g): yellow solid (5.4 g, 87%); mp 43−44 °C; IR ($CHCl_3$, $cm^{-1}$) 2020, 1960, 1920; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.43−7.23 (m, 10 H, Ar), 5.44 (d, 1 H, $J$ = 14.6 Hz, CHPh), 5.04 (d, 1 H, $J$ = 14.6 Hz, CHPh), 3.53−3.41 (m, 3 H, 2 H-5 and H-3), 2.50 (t, 2 H, $J$ = 7 Hz, 2 H-3′), 2.19 (m, 1 H, H-1′), 2.02 (m, 1 H, H-4), 1.78−1.59 (m, 3 H, H-4, 2 H-2′), 1.33 (m, 1 H, H-1′); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 274.40 (Cr=C), 224.0, 218.04 (CO), 133.95, 131.49, 129.21, 128.55, 128.21, 127.64, 127.57 (Ar), 89.27, 81.24 (C-4′ and C-5′), 65.84 ($CH_2$Ph), 59.52 (C-5), 57.47 (C-3), 30.18 (C-1′), 27.40 (C-2′), 26.10 (C-4), 19.47 (C-3′). 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.

**Pentacarbonylchromium carbene complex 12b** was prepared as above form $Cr(CO)_6$ (5.6 g, 25.6 mmol) and the lactam **11b** (4.7 g, 75%): yellow crystals; mp 61−62 °C; IR ($CHCl_3$, $cm^{-1}$) 2185, 2025, 1970, 1920; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.43−7.22 (m, 5 H, Ar), 5.35 (d, 1 H, $J$ = 14 Hz, CHPh), 5.12 (d, 1 H, $J$ = 14 Hz, CHPh), 3.52−3.44 (m, 3 H, 2 H-5, H-3), 2.30 (t, 2 H, $J$ = 6.9 Hz, 2 H-3′), 3.13 (m, 1 H, H-1′), 1.96 (m, 1 H, H-4), 1.74−1.54 (m, 3 H, H-4, 2 H-2′), 1.24 (m, 1 H, H-1′), 0.12 (s, 9 H, $SiMe_3$); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 273.11 (Cr=C), 222.80, 218.11 (CO), 134.02, 129.29, 128.64, 127.63 (Ar), 106.50, 85.29 (C-4′, C-5′), 65.91 (C-3), 59.56 ($CH_2$Ph), 57.51 (C-5), 30.09 (C-1′), 27.33 (C-2′), 26.18 (C-4), 19.96 (C-3′), 0.15 ($SiMe_3$). HRMS calcd for $C_{24}H_{27}NO_5SiCr$: 489.1063. Found: 489.1062.

**Pentacarbonylchromium complex 15** was obtained as above from $Cr(CO)_6$ (1.06 g, 4.8 mmol) and the lactam **14** as a pale yellow solid (0.495 g, 51%): mp 94 °C; IR ($CHCl_3$, $cm^{-1}$)

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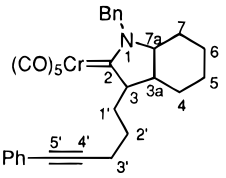
2020, 1965, 1920; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.45−7.26 (m, 5 H, Ar), 5.83 (d, 1 H, $J$ = 15 Hz, CHPh), 4.74 (d, 1 H, $J$ = 15 Hz, CHPh), 3.58 (m, 1 H, H-9), 3.41 (m, 1 H, H-3), 3.15 (m, 1 H, H-3), 2.23 (m, 1 H), 1.96 (m, 1 H), 1.59−1.30 (m, 6 H), 1.18 (m, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 269.92 (Cr=C), 223.39, 218.16 (CO), 134.28, 129.23, 128.53, 127.53 (Ar), 66.67 (C-7a), 59.30, 56.73 (C-3, CHPh), 35.14 (C-3a), 26.79, 25.55, 22.11, 21.35 (C-4, C-5, C-6, C-7). HRMS calcd for $C_{15}H_{19}NCr$ ($M^+$ − 5CO): 265.0922. Found: 265.0922.

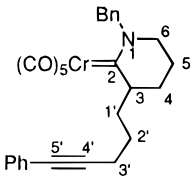
**Pentacarbonyl chromium complex 16** was obtained




from complex **15** (0.48 g, 1.185 mmol), LDA (1.42 mmol), and 5-(trifluoromethanesulfonato)-1-phenylpent-1-yne (0.35 g, 1.185 mmol) as a yellow oil (0.47 g, 87%) after silica gel chromatography (eluent, petroleum ether:dichloromethane 98:2); IR ($CHCl_3$ cm$^{-1}$) 2020, 1965, 1920; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41−7.23 (m, 10, Ar), 5.95 (d, 1 H, $J$ = 14.8 Hz, CHPh), 4.71 (d, 1 H, $J$ = 14.8 Hz, CHPh), 3.83 (m, 1 H, H-3), 2.53 (m, 2 H, 2 H-3′), 2.03 (m, 2 H, H-8, H-1′), 1.80 (m, 2 H, 2 H-2′), 1.70 (m, 1 H, H-4), 1.62 (m, 2 H, H-6, H-5), 1.45 (m, 1 H, H-7), 1.27 (m, 1 H, H-1′), 1.20 (m, 2 H, H-6, H-5), 1.02 (m, 1 H, H-4); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 277.41 (Cr=C), 22.94, 218.02 (CO), 133.84−123.82 (Ar), 89.40, 81.37 (C-4′, C-5′), 71.26 (C-3), 64.78 (C-7a), 56.45 (CHPh), 38.25 (C-3a), 28.18 (C-2′), 27.98 (C-4), 26.33 (C-1′), 25.22 (C-7), 23.47 , 21.07 (C-5, C-6), 19.60 (C-3′). HRMS calcd for $C_{26}H_{29}NCr$ ($M^+$ − 5CO) 407.1705. Found: 407.1705.

**Pentacarbonylchromium carbene complex 22** was obtained as above from $Cr(CO)_6$ (7 g, 31.8 mmol) and 1-benzylpiperidin-2-one (3 g, 15.87 mmol) as yellow crystals (3.9 g, 67%): mp 84−86 °C; IR ($CHCl_3$, cm$^{-1}$) 2020, 1960, 1910; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.44−7.28 (m, 5 H, Ar), 5.40 (s, 2 H, $CH_2$Ph), 3.37−3.30 (m, 4 H, 2 H-3, 2 H-6), 1.72−1.68 (m, 2 H, 2 H-5), 1.63−1.59 (m, 2 H, 2 H-4); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 273.34 (Cr=C), 223.40, 217.91 (CO), 134.62, 129.20, 128.59, 127.56, 123.30 (Ar), 68.24 (CHPh), 51.22 (C-6), 50.04 (C-3), 21.81 (C-5), 17.74 (C-4). Anal. Calcd for $C_{17}H_{15}NO_5Cr$: C, 55.89; H, 4.11; N, 3.83. Found: C, 55.82; H, 4.03; N, 3.73.

**Pentacarbonylchromium carbene complex 23a** was




obtained upon alkylation of complex **22** (1.6 g, 4.38 mmol) in the presence of LDA (5.26 mmol) and 5-(trifluoromethansulfonato)-1-phenylpent-1-yne (1.3 g, 4.38 mmol) as an orange oil (1.6 g, 72%): IR ($CHCl_3$, cm$^{-1}$) 2020, 1960, 1920; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.44−7.21 (m, 10 H, Ar), 5.44 (d, 1 H, $J$ = 14.5 Hz, CHPh), 5.21 (d, 1 H, $J$ = 14.5 Hz, CHPh), 3.77 (m, 1 H, H-3), 3.36−3.17 (m, 2 H, 2 H-6), 2.55−2.46 (m, 2 H, 2 H-3′), 1.98-1.88 (m, 2 H, H-1′, H-5), 1.82−1.69 (m, 5 H, 2 H-4, 2 H-2′, H-5′), 1.41−1.21 (m, 1 H, H-1′); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 273.92 (Cr=C), 223.24, 217.89 (CO), 134.72, 131.58, 129.25, 128.35, 127.41, 123.88 (Ar), 89.49, 81.44 (C-4′, C-5′), 68.89 (CHPh), 57.65 (C-3), 50.15 (C-6), 27.49 (C-7), 19.79 (C-9), 26.79, 19.05 (C-2′, C-4′, C-5). HRMS calcd for $C_{24}H_{25}NOCr$ ($M^+$ − 4CO): 395.1341. Found: 395.1342.

**Pentacarbonylchromium carbene complex 23b** was obtained upon alkylation of complex **22** (2.75 g, 7.53 mmol) with 1-(trifluromethanesulfonato)-1-(trimethylsilanyl)pent-4-yne (2.17 g, 7.53 mmol) in the presence of LDA (9.04 mmol) and obtained after silica gel chromatography (eluent, petroleum ether:dichloromethane 90:10) as an orange solid (1.96 g, 52%): mp 87−89 °C; IR ($CHCl_3$, cm$^{-1}$) 2180, 2020, 1960, 1920; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.46−7.25 (m, 5 H, Ar), 5.45 (d, 1 H, $J$ = 14 Hz, CHPh), 5.24 (d, 1 H, $J$ = 14 Hz, CHPh), 3.78 (m, 1 H, H-3), 3.38 (m, 1 H, H-6), 3.25 (m, 1 H, H-6), 2.34 (m, 2 H, 2 H-3′), 1.90 (m, 2 H, H-1′, H-2′), 1.76−1.68 (m, 5 H, 2 H-4, H-2′, 2 H-5), 1.30 (m, 1 H, H-1′), 0.15 (s, 9 H, $SiMe_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 277.92 (Cr=C), 223.25, 217.84 (CO), 134.71, 129.26, 128.56, 127.39, 122.98 (Ar), 106.67, 85.36 (C-4′, C-5′), 68.86 (CHPh), 57.56 (C-3), 50.06 (C-6), 27.18 (C-1′), 20.18 (C-3′), 26.54, 18.96, 18.90 (C-2′, C-4, C-5), 0.20 ($SiMe_3$). Anal. Calcd for $C_{25}H_{29}NO_5SiCr$: C, 59.64; H, 5.76; N, 2.78. Found: C, 59.49; H, 5.92; N, 2.76.

**Pentacarbonylchromium carbene complex 26a** was obtained from $Cr(CO)_6$ (1.88 g, 8.5 mmol) and the lactam **25a** (1.03 g, 4.3 mmol) as an orange oil (1.57 g, 88%) after silica gel chromatography (eluent, petroleum ether:dichlomethane 80:20); IR ($CHCl_3$, cm$^{-1}$) 2020, 1960, 1920; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.43−7.28 (m, 5 H, Ar), 3.86−3.81 (m, 2 H, 2 H-5), 3.68 (s, 3 H, $CH_3$), 3.36 (m, 1 H, H-3), 2.54−2.51 (m, 2 H, 2 H-3′), 2.25 (m, 1 H, H-1′), 2.09 (m, 1 H, H-4), 1.81−1.70 (m, 3 H, H-4, 2 H-2′), 1.43 (m, 1 H, H-1′); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 271.01 (Cr=C), 222.96, 218.31 (Co), 131.65, 128.34, 127.76, 123.93 (Ar), 89.52, 81.29 (C-4′, C-5′), 66.06 (C-3), 61.59 (C-5), 42.79 ($NCH_3$), 31.32 (C-1′), 27.39 (C-2′), 26.64 (C-4), 19.59 (C-3′). Anal. Calcd for $C_{21}H_{19}NO_5Cr$: C, 60.43; H, 4.56; N, 3.36. Found: C, 60.37; H, 4.56; N, 3.27.

**Pentacarbonylchromium carbene complex 26b** was obtained from lactam **25b** (1.35 g, 5.69 mmol) and $Cr(CO)_6$ (2.5 g, 11.4 mmol) after silica gel chromatography (eluent, petroleum ether:dichloromethane 80:20) as an orange oil (1.21 g, 52%); IR ($CHCl_3$, cm$^{-1}$) 2160, 2020, 1960, 1920; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.82 (m, 1 H, H-5), 3.72 (m, 1 H, H-5), 3.68 (s, 3 H, $NCH_3$), 3.31 (m, 1 H, H-3), 2.32 (t, 2 H, $J$ = 7 Hz, 2 H-3′), 2.18 (m, 1 H, H-1′), 2.07 (m, 1 H, H-4), 1.75 (m, 1 H, H-4), 1.66−1.58 (m, 2 H, 2 H-2′), 1.28 (m, 1 H, H-1′), 0.17 (s, 9 H, $SiMe_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 270.94 (Cr=C), 22.99, 218.25 (CO), 106.60, 85.23 (C-4′, C-5′), 66.01 (C-3), 61.50 (C-5), 42.75 ($NCH_3$), 31.11 (C-1′), 27.24 (C-2′), 26.63 (C-4), 19.97 (C-3′), 0.19 ($SiMe_3$). HRMS calcd for $C_{13}H_{23}NSiCr$ ($M^+$ − 5CO): 273.1004. Found: 273.1005.

**Pentacarbonylchromium carbene complex 28** was obtained as above from *N*-methylpiperidone (1.42 mL, 56 mmol) and $Cr(CO)_6$ (5.5 g, 25 mmol) as a yellow solid (3.25 g, 90%) after silica gel chromatography (eluent, petroleum ether: dichloromethane 80:20): mp 44−45 °C; IR ($CHCl_3$, cm$^{-1}$) 2020, 1960, 1910; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 3.77 (s, 3 H, $NCH_3$), 3.47 (t, 2 H, $J$ = 6.3 Hz, 2 H-6), 3.24 (m, 2 H, 2 H-3), 1.83 (quintet, 2 H, 2 H-5), 1.51 (quintet, 2 H, 2 H-4); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 270.31 (Cr=C), 223.49, 217.33 (CO), 54.69 (C-6), 52.47 ($NCH_3$), 49.83 (C-3), 22.16 (C-5), 18.04 (C-4). Anal. Calcd for $C_{11}H_{11}NO_5Cr$: C, 45.67; H, 3.81; N, 4.84. Found: C, 45.50; H, 3.79; N, 4.78.

**Pentacarbonylchromium complex 30a** was obtained as above from complex **28** (1.5 g, 5.19 mmol) and 5-(trifluoromethanesulfonato)-1-phenylpent-1-yne (1.51 g, 5.19 mmol) and LDA (6.23 mmol) after silica gel chromatography (eluent, petroleum ether:dichloromethane 85:15) as and orange oil (0.36 g, 16%): IR ($CHCl_3$, cm$^{-1}$) 2020, 1980, 1915; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41−7.29 (m, 5 H, Ar), 3.75 (s, 3 H, $NCH_3$), 3.62 (m, 1 H, H-3), 3.51 (m, 2 H, 2 H-6), 2.55−2.48 (m, 2 H, 2 H-3′), 2.02 (m, 1 H, H-1′), 1.90−1.67 (m, 6 H, 2 H-4, 2 H-2′, 2 H-5), 1.33 (m, 1 H, H-1′); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 274.89 (Cr=C), 223.41, 218.26 (CO), 131.60, 128.35, 127.75, 123.90 (Ar), 89.59, 81.28 (C-4′, C-5′), 56.59 (C-3), 53.27 (C-6), 53.14 ($NCH_3$), 27.49 (C-1′), 19.77 (C-3′), 26.69, 18.49, 18.06 (C-2′, C-4, C-5). Anal. Calcd for $C_{22}H_{21}NO_5Cr$: C, 61.25; H, 4.87; N, 3.25. Found: C, 59.55; H, 4.93; N, 3.08.

**Pentacarbonylchromium carbene complex 30b** was obtained from complex **28** (1.17 g, 4.05 mmol) and the corresponding triflate (1.17 g, 4.05 mmol) in the presence of LDA (4.86 mmol) as an orange oil (0.33 g, 19%) after silica gel chromatography (eluent, petroleum ether:dichloromethane 85: 15); IR ($CHCl_3$, cm$^{-1}$) 2160, 2020, 1960, 1915; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 3.71 (s, 3 H, $NCH_3$), 3.51−3.44 (m, 3 H, H-3, 2 H-6), 2.30−2.25 (m, 2 H, 2 H-3′), 1.98−1.58 (m, 7 H, H-1′, 2 H-4, 2 H-2′, 2 H-5), 1.24 (m, 1 H, H-1′), 0.13 (s, 9 H, $SiMe_3$);

$^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 274.91 (Cr=C), 223.42, 218.22 (CO), 106.75, 85.19 (C-4′, C-5′), 56.50 (C-3), 53.17 ($NCH_3$, C-6), 27.21 (C-1′), 20.15 (C-3′), 26.43, 18.39, 18.01 (C-2′, C-4, C-5), 0.20 ($SiMe_3$). MS calcd for $C_{19}H_{25}NO_5SiCr$ ($M^+ - Cr(CO)_5$): 287. Found: 287.

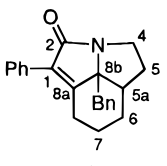
**Pentacarbonylchromium complex 33a** was obtained upon alkylation of complex **12a** (1.4 g, 2.84 mmol) with methyl iodide (0.18 mL, 2.84 mmol) in the presence of butyllithium (3.41 mmol) at −78 °C. After workup as usual and silica gel chromatography (eluent, petroleum ether:dichloromethane 70:30), complex **33a** (0.30 g, 26%) was isolated as a yellow oil: IR ($CHCl_3$,cm$^{-1}$) 2020, 1965, 1920; $^{13}$C NMR (400 MHz, $CDCl_3$) $\delta$ 8.76 (bs, 1 H, NH), 7.42−7.28 (m, 5 H, Ph), 3.76 (t, 2 H, $J$ = 8 Hz, 2 H-5), 3.30 (m, 1 H, H-3), 2.53 (t, 2 H, $J$ = 7 Hz, 2 H-3′), 2.35 (M, 1 H, H-1′), 2.13 (m, 1 H, H-4), 1.82−1.61 (m, 3 H, H-4, 2 H-2′), 1.48 (m, 1 H, H-1′); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 277.82 (Cr=C), 22.69, 217.88 (CO), 133.25, 131.54, 128.62, 127.67, 123.61 (Ar), 89.37, 81.18 (C-4′, C-5′), 62.82 (C-3), 54.14 (C-5), 31.42 (C-6), 27.05 (C-2′), 25.99 (C-4), 19.34 (C-3′). HRMS calcd for $C_{15}H_{17}NCr$ ($M^+$ − 5CO): 263.0766. Found: 263.0766.

**Pentacarbonylchromium Complex 34.** This complex was obtained as above from *N*-benzylpyrrolidinone (2.02 mL, 12.6 mmol) and $Cr(CO)_6$ (6.3 g, 25.2 mmol) as a yellow solid (4.42 g, 99%) after silica gel chromatography (eluent, petroleum ether:dichloromethane 80:20): mp 99 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.43−7.30 (m, 5 H, Ar), 5.28 (s, 2 H, $CH_2Ph$), 3.54 (m, 2 H, $NCH_2$), 3.43 (m, 2 H, $CCH_2$), 1.87 (m, 2 H, $CH_2$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 267.79 (Cr=C), 223.22, 218.09 (CO), 134.11, 129.3, 128.71, 127.90 (Ar), 59.37 (C-5), 58.90 (C-3), 56.56 ($CH_2Ph$), 21.06 (C-4). Anal. Calcd for $C_{16}H_{13}NO_5Cr$: C, 54.70; H, 3.70; N, 3.98. Found: C, 54.83; H, 3.65; N, 4.10.

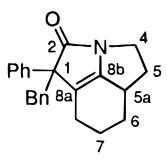
**Pentacarbonylchromium Carbene Complex 35.** Alkylation of complex **34** (1.5 g, 4.27 mmol) with methyl iodide (0.27 mL, 4.27 mmol) in the presence of LDA (5.13 mmol, in THF) gave after workup as usual complex **35** as a yellow solid (1.32 g, 85%) after silica gel chromatography (eluent, petroleum ether:dichloromethane 85:15): mp; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.45−7.24 (m, 5 H, Ar), 5.47 (d, 1 H, $J$ = 16 Hz, CHPh), 5.08 (d, 1 H, $J$ = 16 Hz, CHPh), 3.59−3.48 (m, 3 H, 2 H-5, 1 H-3), 2.06 (m, 1 H, H-4), 1.60 (m, 1 H, H-4), 1.31 (d, 3 H, $J$ = 10.5 Hz, Me); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 273.76 (Cr=C), 223.20, 218.23 (CO), 134.15, 129.33, 128.67, 127.66, 122.0 (Ar), 60.63 (C-3), 59.55 (C-5), 57.55 ($CH_2Ph$), 29.21 (C-4), 17.94 (Me). Anal. Calcd for $C_{17}H_{15}NO_5Cr$: C, 55.89; H, 4.10; N, 3.83. Found: C, 56.05; H, 4.12; N, 3.85.

**Pentacarbonylchromium Carbene Complex 32a.** Alkylation of complex **35** (0.7 g, 1.92 mmol) with the appropriate alkynyl iodide (0.52 g, 1.92 mmol) in the presence of LDA (2.3 mmol) as above gave complex **32a** as an amorphous yellow oil (0.05 g, 5%) after silica gel chromatography (eluent, petroleum ether:dichloromethane); $^1$H NMR (400 Mhz, $CDCl_3$) $\delta$ 7.45−7.25 (m, 10 H, Ar), 5.35 (s, 2 H, $CH_2Ph$), 3.55 (m, 2 H, 2 H-5), 2.52 (m, 2 H, 2 H-3′), 1.90−1.45 (m, 6 H, 2 H-1′, 2 H-2′, 2 H-4), 1.37 (s, 3 H, Me); $^{13}$C NMR (100 Mhz, $CDCl_3$) $\delta$ 278.40 (Cr=C), 222.43, 218.30 (CO), 134.05, 131.63, 128.28, 127.71, 127.65 (Ar), 89.4, 81.30 (C-4′, C-5′), 65.33 (CHPh), 60.30 (C-5), 58.27 (C-3), 38.55 (C-1′), 33.42 (C-2′), 24.15 (C-4), 23.62 (Me), 20.02 (C-3′). HRMS calcd for $C_{23}H_{25}NCr$ ($M^+$ − 5CO): 367.1392. Found: 367.1390.

**8b-Benzyl-1-phenyl-5,5a,6,7,8b-hexahydro-4*H*-pyrrolo(3,2,1-*hi*)indol-2-one (37a) and 1-Benzyl-1-phenyl-4,5,5a,6,7,8-hexahydro-1*H*-pyrrolo(3,2,1-*hi*)indol-2-one (38a).** Complex **12a** (3 g, 6.08 mmol) was heated in refluxing



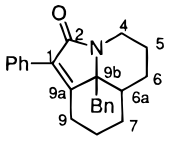

**37a**



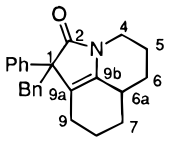

**38a**

benzene (100 mL) for 20 h. After evaporation of the solvent under vaccuum, the residue was chromatographed on silica gel. Elution with petroleum ether:ethyl acetate (80:20) gave compound **37a** as an oil (0.10 g, 6%). Elution with petroleum ether:diethyl acetate (70/30) gave **38a** (0.285 g, 34%) as a solid. Physical data for **37a**: IR ($CHCl_3$, cm$^{-1}$) 1670, 1600; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.51−7.21 (m, 10 H, Ar), 4.07−3.86 (m, 1 H, H-4), 3.07−2.84 (m, 3 H, $CH_2Ph$, H-4), 2.74−2.67 (m, 2 H), 2.34−2.11 (m, 1 H), 2.04−1.69 (m, 3 H), 1.03−0.84 (m, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 178.35 (CO), 164.34 (C-8a), 136.07 (C-1), 131.75−126.76 (Ar), 72.79 (C-8b), 45.42 (C-4), 44.96 ($CH_2Ph$), 43.02 (C-5a), 35.14 (C-5), 28.34 (C-6), 24.38 (C-7), 23.62 (C-8). HRMS for $C_{23}H_{23}NO$ calcd: 329.1779. Found: 329.1779. For **38a**: mp 95 °C; IR ($CHCl_3$, cm$^{-1}$) 1685, 1600; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.39−7.18 (m, 10 H, Ar), 3.70−3.64 (m, 1 H, H-4), 3.57 (d, 1 H, $J$ = 12.5 Hz, CHPh), 3.27 (d, 1 H, $J$ = 12.5 Hz, CHPh), 3.07−2.95 (m, 1 H, H-4), 2.31−2.18 (m, 2 H, H-5, H-5a), 2.12−1.98 (m, 2 H, H-6, H-7), 1.95−1.86 (m, 1 H, H-7), 1.83−1.77 (m, 1 H, H-8), 1.75−1.56 (m, 2 H, H-5, H-7), 1.06−0.89 (m, 1 H, H-6); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 180.05 (CO), 147.28 (C-8b), 139.56−126.39 (Ar), 113.60 (C-8a), 67.31 (C-1), 42.93 (C-4), 40.16 (CHPh), 35.74 (C-5), 32.30 (C-5a), 28.94 (C-6), 23.75 (C-7), 20.97 (C-8). HRMS calcd for $C_{23}H_{23}NO$: 329.1779. Found: 329.1785.

**9b-Benzyl-1-phenyl-4,5,6,6a,7,8,9,9b-octahydropyrrolo(3,2,1-*ij*)quinolin-2-one (39) and 1-Benzyl-1-phenyl-1,4,5,6,6a,7,8,9-octahydropyrrolo(3,2,1-*ij*)quinolin-2-one (40).** Thermolysis of complex **23a** (1.8 g, 3.52 mmol) as




**39**




**40**

above gave a mixture of two compounds which were separated by silica gel chromatography. Elution with petroleum ether:ethyl acetate (85:15) gave **40** (0.60 g, 49%) and elution with petroleum ether:ethyl acetate (75:25) gave **39** (0.215 g, 18%). Physical data for **39**: yellowish oil; IR ($CHCl_3$, cm$^{-1}$) 1665, 1600; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.31−6.96 (m, 10 H, Ar), 4.07 (m, 1 H, H-4), 3.03 (bs, 2 H, $CH_2Ph$), 2.95 (m, 1 H, H-4), 2.71 (m, 1 H, H-9), 2.33 (m, 1 H, H-9), 2.07 (m, 1 H, H-6a), 1.95 (m, 1 H, H-5), 1.88 (m, 1 H, H-7), 1.74 (m, 1 H, H-8), 1.55 (m, 1 H, H-11), 1.37 (m, 2 H, H-8, H-7), 1.25 (m, 1 H, H-6), 0.99 (m, 1 H, H-6); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 172.57 (CO), 158.05 (C-9a), 135.33 (C-1), 129.52−126.80 (Ar), 66.64 (C-9b), 42.58 (C-6a), 42.29 ($CH_2Ph$), 34.54 (C-4), 27.80 (C-7), 24.95 (C-9), 23.89 (C-5), 23.70 (C-8), 23.38 (C-6). HRMS calcd for $C_{24}H_{25}NO$: 343.1936. Found: 343.1936. For **40**: mp: 109−111 °C; IR ($CHCl_3$, cm$^{-1}$) 1700, 1600; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.37−7.14 (m, 10 H, Ar), 3.57 (d, 1 H, $J$ = 12.5 Hz, CHPh), 3.50 (m, 1 H, H-4), 3.21 (m, 1 H, $J$ = 12.5 Hz, CHPh), 2.99 (m, 1 H, H-4), 2.15 (m, 1 H, H-9), 2.02 (m, 1 H, H-9), 1.95 (m, 1 H, H-8), 1.85−1.67 (m, 4 H, H-5, H-7, H-6a, H-6), 1.55 (m, 1 H, H-8), 1.28 (m, 2 H, H-5, H-7), 0.99 (m, 1 H, H-6); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 181.40 (CO), 139.62 (C-4), 136.58, 129.68, 127.45, 126.97, 126.43 (Ar), 114.66 (C-9a), 61.13 (C-1), 40.06 ($CH_2Ph$), 39.52 (C-4), 33.41 (C-6a), 29.15 (C-7), 27.39 (C-6), 22.62 (C-5), 22.48 (C-8), 21.18 (C-9). HRMS calcd for $C_{24}H_{25}NO$: 343.1936. Found: 343.1936.

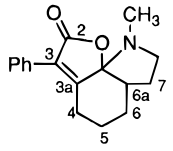
**1-Benzyl-4,5,6,6a,7,8,9,9b-octahydropyrrolo(3,2,1-*ij*)quinolin-2-one (41) and 9b-Benzyl-1-trimethylsilanyl-4,5,6,6a,7,8,9,9b-octahydropyrrolo(3,2,1-*ij*)quinolin-2-one (43).** Thermolysis of complex **23b** as above gave a mixture of **41** and **43**, which were separated by silica gel chromatography. Elution with petroleum ether: ethyl acetate (85:15) gave **43** as an oil (0.164 g, 18%) and elution with petroleum ether:ethyl acetate (75:25) gave **41** as an oil (0.11 g, 15%). Physical data for **41**: IR ($CHCl_3$, cm$^{-1}$) 1660; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.28−7.15 (m, 10 H, Ar), 4.17 (m, 1 H, H-4), 3.64 (d, 1 H, $J$ = 14.9 Hz, CHPh), 3.57 (d, 1 H, $J$ = 14.9 Hz, CHPh), 3.06 (d, 1 H, $J$ = 11 Hz, H-9b), 2.55 (m, 1 H, H-4), 2.49 (m, 1 H, H-9), 2.16 (m, 1 H, H-9), 1.98 (m, 1 H, H-8), 1.78 (m, 2 H, H-7, H-5), 1.69 ( m, 1 H, H-6), 1.45 (m, 1 H, H-5), 1.39−1.25 (m, 3 H, H-8, H-7, H-6), 0.97 (m, 1 H, H-6a); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 169.60 (CO), 152.79 (C-9a), 140.04

(C-1), 128.65, 128.47, 128−7.85, 126.02 (Ar) , 65.24 (C-9b), 47.35 (C-6a), 39.17 (C-4) , 30.03 (C-7), 29.75 (CHPh), 29.41 (C-6), 27.77 (C-8), 26.70 (C-5), 25.36 (C-9). HRMS for $C_{18}H_{21}NO$ calcd: 267.1623. Found: 267.1622. For **43**: IR ($CHCl_3$, $cm^{-1}$) 1645; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.28−6.96 (m, 5 H, Ar), 4.03 (m, 1 H, H-4), 3.00 (bs, 2 H, $CH_2Ph$), 2.90 (m, 1 H, H-4), 2.72 (m, 1 H, H-9), 2.37 (m, 1 H, H-9), 2.10 (m, 1 H, H-6a), 1.94−1.89 (m, 3 H, H-5, H-7, H-8), 1.59 (m, 1 H, H-5), 1.46−1.42 (m, 2 H, H-7, H-8), 1.29 (m, 1 H, H-6), 0.99 (m, 1 H, H-6), 0.03 (s, 9 H, $SiMe_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 177.54 (CO), 173.73 (C-9a), 136.17 (C-1), 131.66, 130.17, 129.29, 129.13, 128.40, 127.27 (Ar), 70.07 (C-9b), 43.17 (C-6a), 42.61 (CHPh), 34.69 (C-4), 28.26 (C-7), 27.62 (C-9), 25.14 (C-5), 24.59 (C-8), 24.06 (C-6), 0.00 ($SiMe_3$). HRMS calcd for $C_{21}H_{29}NOSi$: 339.2035. Found: 339.2034.

**1-Phenyl-4,5,6,6a,7,8,9,9b-octahydropyrrolo (3,2,1-*ij*)-quinolin-2-one (44).** Thermolysis of complex **30a** (0.75 g, 1.74 mmol) gave upon silica gel chromatography (eluent, petroleum ether:ethyl acetate 70:30) compound **44** as a viscous oil (0.020 g, 5%): IR ($CHCl_3$, $cm^{-1}$) 1660; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 7.53−7.25 (m, 5 H, Ar), 4.30−4.21 (d, 1 H, $J$ = 10.5 Hz, H-9b), 3.05−2.91 (m, 2 H, H-4, H-9), 2.42−2.29 (m, 1 H, H-8), 1.86−1.71 (m, 3 H, H-7, H-5, H-6), 1.62−1.29 (m, 4 H, H-5, H-8, H-7, H-6), 1.2−1.12 (m, 1 H, H-6a); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 167.14 (CO), 152.26 (C-9a), 131.01 (C-1), 127.98, 127.19, 126.46 (Ar), 63.99 (C-9b), 46.10 (C-6a), 38.13 (C-4), 29.09 (C-7), 28.39 (C-6), 26.78 (C-8), 25.55 (C-5), 24.85 (C-9). HRMS calcd for $C_{17}H_{19}NO$: 253.1466. Found: 253.1465.

**Chromium Carbene Complex 12c.** Thermolysis of complex **12b** (4 g, 8.18 mmol) in refluxing benzene (200 mL) for 12 h led to a dark-brown solution from which, according to TLC, all starting complex had disappeared. Evaporation of the solvent under vacuum gave a residue which was chromatographed on silica gel. Elution with petroleum ether:ethyl acetate (80:20) led to fractions containing **12c** (0.510 g, 13.5%) as a pale yellow oil: IR ($CHCl_3$, $cm^{-1}$) 2020, 1960, 1920; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.41−7.16 (m, 5 H, Ar), 5.39 (m, 1 H, CHPh), 5.04 (m, 1 H, CHPh), 3.39 (m, 2 H), 2.53 (m, 2 H), 2.24−1.08 (m, 9 H), 0.25 (s, 9 H, $SiMe_3$); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 273.36 (Cr═C), 222.78, 218.14 (CO), 153.98, 134.08, 141.31, 140.11, 130.25−121.51 (Ar), 65.59 (CH), 59.58 ($CH_2Ph$), 57.66 ($NCH_2$), 32.04, 29.81, 26.19, 22.81 ($CH_2$), −0.18 ($SiMe_3$).

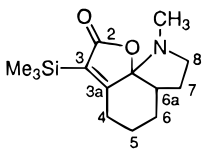
**7-(2-Chloroethyl)-1-methyl-3-phenyl-1,4,5,6,7,7a-hexahydroindol-2-one (46a) and 9-Methyl-3-phenyl-5,6,6a,7,8,9-hexahydro-4*H*-1-oxa-9-azacyclopenta(*d*)inden-2-one (45a).**



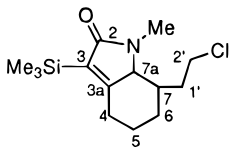

**45a**

Thermolysis of complex **26a** (1.5 g, 3.60 mmol) as above led to a mixture of two compounds which were separated by chromatography. Elution with petroleum ether:ethyl acetate (85:15) gave **45a** (0.024 g, 2.5%). Elution with the same solvents (60:40) gave **46a** (0.050 g, 5%). Physical data of **45a**: IR ($CHCl_3$, $cm^{-1}$) 1730; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 7.52−7.29 (m, 5 H, Ar), 3.35 (m, 1 H, H-8), 2.90 (m, 2 H, H-4, H-8), 2.31 (m, 3 H, H-6a, H-7, H-4), 2.22 (s, 3 H, $NCH_3$), 1.97 (m, 1 H, H-5), 1.74−1.35 (m, 4 H, H-7, H-5, 2 H-6); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 173.33 (CO), 160.71 (C-3a), 130.35 (C-3), 129.34, 128.74, 127.32 (Ar), 106.66 (C-1), 52.09 (C-8), 49.75 (C-6a), 32.0 ($NCH_3$), 31.23, 29.98, 28.16 (C-7, C-5, C-6), 27.94 (C-4). MS for $C_{17}H_{19}NO_2$ calcd 269 ($M^+$). Found: 269. For **46a**: IR ($CHCl_3$, $cm^{-1}$) 1670; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.49−7.28 (m, 5 H, Ar), 3.97 (d, 1 H, H-7a), 3.61 (m, 1 H), 3.51 (m, 1 H), 3.04 (s, 3 H, $NCH_3$), 2.75 (m, 1 H, H-7), 2.33 (m, 1 H), 1.97−1.49 (m, 7 H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 171.0 (CO), 151.55, 131.46 (C-3, C-3a), 130.47−127.79 (Ar), 64.69 (C-7a), 42.89 (C-2′), 34.63 (C-7), 27.27 ($NCH_3$), 26.33, 26.09, 25.42 (C-1′, C-5, C-6), 20.93 (C-4). MS calcd for $C_{17}H_{18}NOCl$: 289 ($M^+$). Found: 289 ($M^+$), 254 ($M^+$ − Cl), 226 ($M^+$ − $CH_2CH_2Cl$).

**9-Methyl-3-(trimethylsilanyl)-5,6,6a,7,8,9-hexahydro-1-oxa-9-azacyclopenta(*d*)inden-2-one (45b) and 7-(2-Chloroethyl)-1-methyl-3-(trimethylsilanyl)-1,4,5,6,7,7a-hexahydroindol-2-one (46b).** Thermolysis of complex **26b**



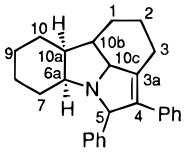

**45b**




**46b**

as above gave a mixture of **45b** (0.040 g, 5%) and **46b** (0.012 g, 2%) as oils. Physical data for **45b**: IR ($CHCl_3$, $cm^{-1}$) 1720; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 3.32 (m, 1 H, H-8), 2.86 (m, 1 H, H-8), 2.77 (m, 1 H, H-4), 2.29 (m, 1 H, H-7), 2.24 (m, 1 H, H-4), 2.21 (m, 1 H, H-6a), 2.13 (s, 3 H, $NCH_3$), 2.02 (m, 1 H, H-5), 1.71 (m, 1 H, H-6), 1.58 (m, 1 H, H-7), 1. 48 (m, 1 H, H-6), 1.36 (m, 1 H, H-5), 0.31 (s, 9 H, $SiMe_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 175.39 (CO), 172.50 (C-3a), 125.87 (C-3), 106.39 (C-1), 50.77 (C-8), 48.76 (C-6a), 30.59 ($NCH_3$), 29.78 (C-6), 27.59 (C-6), 26.80 (C-5), 26.44 (C-4), 0.00 ($SiMe_3$). MS for $C_{14}H_{23}O_2NSi$ ($M^+$) calcd: 265. Found: 265. For **46b**: IR ($CHCl_3$, $cm^{-1}$) 1650; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 3.77 (d, 1 H, $J$ = 5.8 Hz, H-7a), 3.50 (m, 2 H), 2.88 (s and m, 4 H, H-7, $NCH_3$), 2.59 (m, 2 H), 2.17 (m, 3 H), 1.81−1.24 (m, 3 H), 0.33 (s, 9 H, $SiMe_3$); $^{13}$ C NMR (100 MHz, $CDCl_3$) $\delta$ 67.32 (C-7a), 42.94 (C-2′), 34.89 (C-7), 28.34 ($CH_2$), 26.59 ($NCH_3$), 26.19, 25.33 ($CH_2$), 21.61 (C-4), −0.28 ($SiMe_3$). MS calcd for $C_{14}H_{24}ONSiCl$ ($M^+$): 285. Found: 285 ($M^+$), 250 ($M^+$ − Cl), 222 ($M^+$ − $CH_2CH_2Cl$).

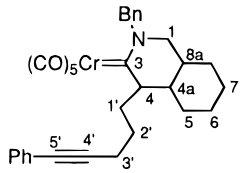
**4,5-Diphenyl-1,2,3,5,6a,7,8,9,10,10a,10b-dodecahydropyrrolo(3,2,1-*jk*)carbazole (49).** Thermolysis of complex **16**




(0.44 g, 0.804 mmol) in refluxing benzene led to **49** (0.127 g, 44.5%) after silica gel chromatography of the residue of the reaction (elution, petroleum ether:ethyl acetate 80:20) as an oil: IR ($CHCl_3$, $cm^{-1}$) 1600; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.43−7.13 (m, 5 H, Ar), 4.31 (s, 1 H, H-5, one isomer), 4.28 (s, 1 H, H-5, second isomer), 4.10 (m), 3.38 (m, H-10c, H-6a for the two isomers), 2.95−1.07 (m); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ (major isomer) 144.31, 137.80 (C-4, C-3a), 128.92−127.24 (Ar), 70.40 , 63.81, 59.97 (C-5, C-10c,C-6a), 51.78, 49.11 (C-10a, C-10b), 30.53, 29.74, 28.12, 25.50, 25.30, 22.32, 20.17 $CH_2$); (minor isomer) 156.37, 142.45, 128.92−12724, 84.02, 65.27, 64.59, 46.58, 37.82, 30.35, 28.86, 28.33, 25.25, 23.38, 22.17, 21.58. MS calcd for $C_{26}H_{29}N$: 355 ($M^+$). Found: 355.

**Pentacarbonylchromium Carbene Complex 52.** This complex was obtained as above from **51** (0.70 g, 2.88 mmol) and $Cr(CO)_6$ (1.27 g, 5.76 mmol) as a yellow oil (0.39 g, 32%) after silica gel chromatography (eluent, petroleum ether: dichloromethane 90:10): IR ($CHCl_3$, $cm^{-1}$) 2020, 1960, 1910; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.45−7.27 (m, 5 H, Ar), 5.45 (d, 1 H, $J$ = 14.6 Hz, CHPh), 5.35 (d, 1 H, $J$ = 14.6 Hz, CHPh), 3.48 (m, 2 H, 2 H-1), 3.25 (m, 2 H, 2 H-4), 1.96 (m, 1 H), 1.79 (m, 1 H) (H-4a, H-8a), 1.55−1.28 (m, 8 H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 271.54 (Cr═C), 223.09, 218.02 (CO), 134.64, 129.13, 128.38, 127.36, 127.09 (Ar), 68.78, 55.46, 55.13 ($CH_2Ph$, C-1, C-4), 32.35, 30.28 (C-4a, C-8a), 28.33, 26.43, 22.79, 22.40 (C-5, C-6, C-7, C-8). HRMS calcd for $C_{16}H_{21}NCr$ ($M^+$ − 5CO): 279.1079. Found: 279.1079.

**Pentacarbonylchromium Carbene Complex 53.** Alkylation of complex **52** (0.35 g, 0.835 mmol) as above with the related triflate (0.244 g, 0.835 mmol) in the presence of LDA (1.09 mmol) gave complex **53** as an orange oil (0.19 g, 57%) after silica gel chromatography (eluent, petroleum ether: dichloromethane 90:10) besides starting complex (29%): IR ($CHCl_3$, $cm^{-1}$) 2020, 1960, 1920; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.43−7.27 (m, 10 H, Ar), 5.70 (d, 1 H, $J$ = 14.4 Hz,CHPh),

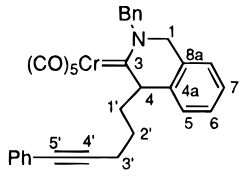


5.04 (d, 1 H, $J$ = 14.4 Hz, CHPh), 3.58 (m, 1 H, H-4), 3.19 (m, 2 H, 2 H-1), 2.52 (m, 2 H, 2 H-3′), 2.26 (m, 1 H, H-8a), 2.12 (m, 1 H, H-1′), 1.77 (m, 2 H, 2 H-2′), 1.73−167 (m, 3 H, H-4a, H-6, H-7), 1.42 (m, 2 H, H-5, H-8), 1.32−1.17 (m, 5 H, H-5, H-6, H-7, H-8, H-1′); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 275.96 (Cr=C), 223.04, 217.94 (CO), 135.09−123.88 (Ar), 89.57, 81.37 (C-4′, C-5′), 69.37 (CHPh), 54.03 (C-1), 33.50 (C-4a), 29.80 (C-1′), 29.08 (C-6 or C-7), 27.73 (C-5 or C-8), 27.33 (C-8a), 26.81 (C-2′), 25.10 (C-6 or C-7), 21.18 (C-5 or C-8), 19.85 (C-3′). HRMS calcd for $C_{27}H_{31}NCr$ ($M^+$ − 5C0): 421.1861. Found: 421.1862.

**2-Benzyl-2,4-dihydro-1*H*-isoquinolin-3-one (56).** This lactam was obtained as above from 2,4-dihydro-1*H*-isoquinolin-3-one (0.88 g, 5.98 mmol), benzyl bromide (1.07mL), and sodium hydride (0.14 g, 5.98 mmol) as an oil after silica gel chromatography (eluent, petroleum ether:ethyl acetate, 75:25); IR ($CHCl_3$, $cm^{-1}$) 1655; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.35−7.09 (m, 5 H, Ar), 4.79 (s, 2 H, $CH_2Ph$), 4.41 (s, 2 H, 2 H-1), 3.74 (s, 2 H, 2 H-4); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 169.06 (CO), 136.73−125.26 (Ar), 50.28, 49.99 (C-1, CHPh), 37.47 (C-4). HRMS calcd for $C_{16}H_{15}NO$: 237.1153. Found: 237.1152.

**Pentacarbonylchromium Carbene Complex 57.** This complex was prepared as above from the lactam **56** (0.95 g, 4 mmol) and $Cr(CO)_6$ (1.76 g, 8 mmol) and isolated as an orange solid (0.27 g, 16%) after silica gel chromatography (eluent, petroleum ether:dichloromethane 80:20); mp 75−76 °C; IR ($CHCl_3$, $cm^{-1}$) 2025, 1965, 1930; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41−6.98 (m, 9 H, Ar), 5.60 (s, 2 H, $CH_2Ph$), 4.43 (s, 2 H, 2 H-1), 4.35 (s, 2 H, 2 H-4); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 268.51 (Cr=C), 223.20, 217.39 (CO), 133.97−124.45 (Ar), 67.17, 57.70 , 55.88 (C-1, CHPh, C-4). HRMS calcd for $C_{16}H_{15}NCr$ ($M^+$ − 5CO): 273.0609. Found: 273.0610.

**Pentacarbonylchromium Carbene Complex 58.** This



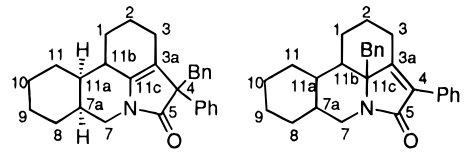
complex was obtained as above from complex **57** (0140 g, 0.34 mmol) and the corresponding triflate (0.10 g, 0.34 mmol) in the presence of LDA (0.373 mmol) as a yellow oil (0.09 g, 48.5%) after silica gel chromatography (eluent, petroleum ether:dichloromethane 85:15): IR ($CHCl_3$, $cm^{-1}$) 2020, 1970, 1920; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.43−7.02 (m, 14 H, Ar), 5.80 (d, 1 H, $J$ = 14.6 Hz, CHPh), 5.36 (d, 1 H, $J$ = 14.6 Hz, CHPh), 4.90 (m, 1 H, H-4), 4.49 (d, 1 H, $J$ = 16.8 Hz, H-1), 4.26 (d, 1 H, $J$ = 16.7 Hz, H-1), 2.41 (t, 2 H, $J$ = 6.9 Hz, 2 H-3′), 2.11 (m, 1 H, H-1′), 1.81 (m, 1 H, H-2′), 1.53 (m, 1 H, H-2′), 1.28 (m, 1 H, H-1′); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 272.82 (Cr=C), 22.95, 217.44 (CO), 134.12−125.27 (Ar), 89.18, 81.44 (C-4′, C-5′), 68.15 (CHPh), 66.55 (C-4), 55.28 (C-1), 27.01 (C-1′), 26.80 (C-2′), 19.53 (C-3′). HRMS calcd for $C_{28}H_{25}NOCr$ ($M^+$ − 4CO): 443.1341. Found: 443.1341.

**Pentacarbonylchromium Carbene Complex 65.** This complex was obtained as above from the lactam **64** (1.77 g, 6.3 mmol) and $Cr(CO)_6$ (2.77 g, 12.6 mmol) as a pale yellow solid (0.410 g, 14%): mp 168 °C; IR ($CHCl_3$, $cm^{-1}$) 2025, 1970, 1925; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.36−7.17 (m, 5 H, Ar), 6.79 (s, 1 H, H-4), 6.40 (s, 1 H, H-9), 5.94 (s, 2 H, $OCH_2$), 5.54 (s, 2 H, $CH_2Ph$), 4,28 (s, 2 H) and 4.20 (s, 2 H) (2 H-5, 2 H-8); $^{13}$ C NMR (50 MHz, $CDCl_3$) $\delta$ 268.14 (Cr=C), 223.10, 217.39 (CO), 148.26, 146.91 (C-1, C-3), 133.95, 128.69, 127.56, 124.98, 124.35 (C-8a, C-4a, Ar), 106.79, 105.13 (C-4, C-9), 101.33 (OCO), 66.95 (CHPh), 57.56, 55.72 (C-1, C-4). Anal. Calcd for $C_{22}H_{15}NO_7Cr$: C, 57.77; H, 3.28; N, 3.06. Found: C, 57.69; H, 3.40; N, 2.99.

**Pentacarbonylchromium Carbene Complex 66a.** This complex was prepared as above from the complex **65** (0.39 g, 0.853 mmol) and the corresponding triflate (0.25 g, 0.853 mmol) in the presence of LDA (0.938 mmol) and isolated as a yellow oil (0.246 g, 63%) after silica gel chromatography: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.43−7.18 (m, 10 H, Ar), 6.75 (s, 1 H), 6.48 (s, 1 H) (H-4, H-9), 5.98 (s, 2 H, $OCH_2$), 5.72 (d, 1 H, $J$ = 14.6 Hz, CHPh), 5.37 (d, 1 H, $J$ = 14.6 Hz, CHPh), 4.79 (m, 1 H, H-8), 4.33 (d, 1 H, $J$ = 15.3 Hz, H-5), 4.21 (d, 1 H, $J$ = 15.3 Hz, H-5), 2.43 (t, 2 H, $J$ = 7 Hz, 2 H-3′), 2.08 (m, 1 H, H-1′), 1.80 (m, 1 H, H-2′), 1.55 (m, 1 H, H-2′), 1.25 (m, 1 H, H-1′); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 272.28 (Cr=C), 222.72, 217.42 (CO), 147.72, 146.36 (C-1, C-3), 131.57−122.91 (C-8a, C-4a, Ar), 106.90, 104.60 (C-4, C-9), 100.28 (OCO), 89.09, 81.36 (C-4′, C-5′), 66.77 (CHPh, 65.30 (C-8), 54.01 (C-1), 51.58 (C-1′), 25.79 (C-2′), 18.43 (C-3′). MS calcd for $C_{33}H_{25}NO_7Cr$.

**Pentacarbonylchromium Carbene Complex 66b.** This complex was obtained as above from complex **65** (0.63 g, 1.38 mmol) and the corresponding triflate (0.397 g, 1.38 mmol) in the presence od LDA (2.07 mmol) as a yellow oil (0.368 g, 55%): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.37−7.25 (m, 5 H, Ar), 6.69 (s, 1 H), 6.44 (s, 1 H) (H-4, H-9), 5.95 (s, 2 H, $OCH_2O$), 5.68 (d, 1 H, $J$ = 14.6 Hz, CHPh), 5.33 (d, 1 H, $J$ = 14.6 Hz, CHPh), 4.70 (m, 1 H, H-8), 4.34 (d, 1 H, $J$ = 16.4 Hz, H-5), 4.10 (d, 1 H, $J$ = 16.4 Hz, H-5), 2.19 (m, 2 H, 2 H-3′), 1.97−1.10 (m, 4 H, 2 H-1′, 2 H-2′), 0.09 (s, 9 H, $SiMe_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 272.06 (Cr=C), 223.21, 217.42 (CO), 148.05, 146.69 (C-1, C-3), 134.07−122.89 (C-8a, C-4a, Ar), 108.03, 105.73 (C-4, C-9), 105.29 (C-5′), 101.42 (OCO), 85.54 (C-4′), 67.74 (CHPh), 66.21 (C-8), 54.93 (C-5), 26.63, 26.46 (C-1′, C-2′), 19.81 (C-3′), 0.18 ($SiMe_3$). HRMS calcd for $C_{25}H_{29}NO_2SiCr$ ($M^+$ − 5CO): 455.1372. Found: 455.1370.

**4-Benzyl-4-phenyl-1,2,3,4,7,7a,8,9,10,11,11a,11b-dodecahydropyrrolo(3,2,1-*de*)phenanthridin-5-one (59) and 11c-Benzyl-4-phenyldodecahydropyrrolo(3,2,1-*de*)phenanthridin-5-one (60).** Thermolysis of complex **53a** (0.20 g, 0.356



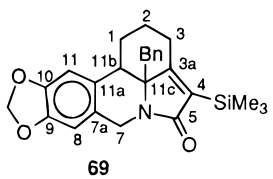
59 60

mmol) in refluxing benzene (25 mL) for 4 h led to two compounds, which were separated by silica gel chromatography. Elution with petroleum ether/ethyl acetate gave compound **59** (0.045 g, 32%); elution with the same solvents (85:15) gave **60** (0.025 g, 18%). Physical data for **59**: mp 156 °C; IR ($CHCl_3$, $cm^{-1}$) 1695; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.40−7.14 (m, 10 H, Ar), 3.57 (d, 1 H, $J$ = 12.5 Hz, CHPh), 3.20 (m, 3 H, CHPh, 2 H-7), 2.20−0.92 (m, 17 H); $^{13}$C NMR (100 MHz,$CDCl_3$) $\delta$ 181.96 (CO), 139.59 (C-4), 137.90−127.04 (Ar), 114.93 (C-3a), 61.46 (C-4), 45.17 (C-7), 40.11 (CHPh), 36.04 (C-11a), 35.13 (C-7a), 28.80 (C-11b), 26.96, 26.61, 26.16, 26.02, 22.67, 20.96 (C-11, C-10, C-9, C-8, C-2, C-1), 19.55 (C-3). HRMS calcd for $C_{28}H_{31}NO$ ($M^+$): 397.2405. Found: 397.2406. For **60**: oil; IR ($CHCl_3$, $cm^{-1}$) 1660; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.32−7.06 (m, 10 H, Ar), 4.40 (m, 1 H, H-7), 3.20 (d, 1 H, $J$ = 13.6 Hz, CHPh), 3.15 (d, 1 H, $J$ = 13.6 Hz, CHPh), 2.81 (m, 1 H, H-3), 2.52 (m, 1 H, H-7), 2.41 (m, 1 H, H-3), 2.32 (m, 1 H, H-11b), 2.26 (m, 1 H, H-7a), 1.89 (m, 2 H, H-1, H-2), 1.77−1.69 (m, 3 H, H-10, H-9, H-1), 1.61 (m, 1 H, H-8), 1.49 (m, 1 H, H-11), 1.35−1.18 (m, 6 H, H-2, H-8, H-11a, H-11, H-10, H-9); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 172.45 (CO), 158.09 (C-3a), 135.49 (C-4), 131.66−126.85 (Ar), 67.59 (C-11c), 41.86 (C-7), 41.73 (CHPh), 39.31 (C11b), 37.00 (C-7a), 30.34 (C-11a), 28.84 (C-8), 25.96, 25.57, 25.41 (C-10, C-9, C-3), 23.46 (C-2), 23.33 (C-1), 20.92 (C-11). HRMS calcd for $C_{28}H_{31}NO$: 397.2405. Found: 397.2406.

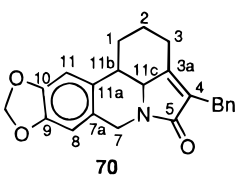
**4-Benzyl-4-phenyl-1,2,3,4,7,11b-hexahydropyrrolo(3,2,1-*de*)phenanthridin-2-one (61) and 11c-Benzyl-4-phenyl-1,2,3,7,11b,11c-hexahydropyrrolo(3,2,1-*de*)phenanthridin-5-one (62).** Thermolysis of complex **58** (0.150 g, 0.270 mmol) in refluxing benzene (10 mL) for 2.5 h led to two compounds, which were separated by silica gel chromatography. Elution with petroleum ether:ethyl acetate (90:10) gave **61** as a solid (0.045 g, 43%): mp 64 °C; IR ($CHCl_3$, $cm^{-1}$) 1700; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.43−7.04 (m, 14 H, Ar), 4.79 (d, 1 H, $J$ = 16 Hz, CHPh), 3.90 (d, 1 H, $J$ = 16 Hz, CHPh), 3.66 (d, 1 H, $J$ = 12.5 Hz, H-7), 3.30 (d, 1 H, $J$ = 12.5, H-7), 3.11 (m, 1 H, H-11b), 2.57 (m, 1 H, H-1), 2.36−2.03 (m, 3 H, 2 H-3, H-2), 1.75−1.63 (m, 2 H, H-1, H-2); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 178.66 (CO), 136.48 (C-11c), 132.15−124.75 (Ar), 114.41 (C-3a), 62.38 (C-4), 41.45 (CHPh), 40.48 (C-7), 32.67 (C-11b), 26.78 (C-1), 22.26 (C-2), 21.02 (C-3). HRMS calcd for $C_{28}H_{25}NO$ ($M^+$): 391.1936. Found: 391.1934. Elution with the same solvents (80:20) gave **62** (0.020 g, 19%) as a solid: mp 170 °C; IR ($CHCl_3$, $cm^{-1}$) 1670; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.41−7.15 (m, 14 H, Ar), 5.14 (d, 1 H, $J$ = 16.1 Hz, CHPh), 4.14 (d, 1 H, $J$ = 16.1 Hz, CHPh), 3.34 (d, 1 H, $J$ = 13.7 Hz, H-7), 3.31 (m, 1 H, H-11b), 3.19 (d, 1 H, $J$ = 13.6 Hz, H-7), 2.95−2.91 (m, 1 H, H-3), 2.63−2.59 (m, 1 H, H-3), 2.14 −2.08 (m, 2 H, H-1, H-2 ), 1.96 (m, 1 H, H-1), 1.79 (m, 1 H, H-2); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 172.10 (CO), 159.87 (C-3a), 135.25 (C-4), 132.48−126.45 (Ar), 66.02 (C-11c), 44.57 (C-11b), 43.42 (C-7), 41.49 (CHPh), 25.80 (C-1), 24.31 (C-2), 23.49 (C-3). HRMS calcd for $C_{21}H_{18}NO$ ($M^+$): 300.1388. Found: 300.1388.

**4-Benzyl-9,10-methylenedioxo-4-phenyl-1,2,3,4,7,11b-hexahydropyrrolo(3,2,1-*de*)phenanthridin-5-one (67) and 11c-Benzyl-9,10-(methylenedioxo)-4-phenyl-1,2,3,7,11b-hexahydropyrrolo(3,2,1-*de*)phenanthridin-5-one (68).** Thermolysis of complex **66a** (0.23 g, 0.387 mmol) in refluxing benzene (20 mL) for 5.5 h led to two compounds, which were separated by silica gel chromatography. Elution with petroleum ether:ethyl acetate 85:15 gave **67** (0.075 g, 44.5%) as a solid: mp 102 °C; IR ($CHCl_3$, $cm^{-1}$) 1700; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.41−7.01 (m, 10 H, Ar), 6.74 (s, 1 H), 6.59 (s, 1 H, H-8, H-11), 5.96 (s, 2 H, $OCH_2O$), 4.66 (d, 1 H, $J$ = 15.8 Hz, CHPh), 3.79 (d, 1 H, $J$ = 15.7, CHPh), 3.65 (d, 1 H, $J$ = 12.6, H-7), 3.28 (d, 1 H, $J$ = 12.5 Hz, C-7), 3.03 (m, 1 H, H-11a), 2.46 (m, 1 H, H-1), 2.24 (m, 1 H, H-3), 2.09−2.05 (m, 2 H, H-2, H-3), 1.68 (m, 1 H, H-2), 1.58 (m, 1 H, H-1); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 178.47 (CO), 147.23, 146.04 (C-9, C-10), 138.90 (C-11c), 137.25−125.40 (C-7a, C-11a, Ar), 114.24 (C-3a), 107.23, 105.39 (C-8, C-11), 101.18 (OCO), 62.38 (C-4), 41.37 (CHPh), 40.37 (C-7); 32.49 (C-11b), 27.22 (C-1), 22.20 (C-2), 20.99 (C-3). HRMS calcd for $C_{29}H_{25}NO_3$ ($M^+$): 435.1834; Found: 435.1834. Elution with the same solvents (80:20) gave **68** as a solid (0.050 g, 30%): mp 225 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.77−7.15 (m, 10 H, Ar), 6.73 (s, 1 H), 6.70 (s, 1 H) (H-8, H-11), 5.94 (s, 2 H, $OCH_2O$), 5.01 (d, 1 H, $J$ = 16 Hz, CHPh), 4.04 (d, 1 H, $J$ = 16 Hz, CHPh), 3.31 (d, 1 H, $J$ = 13.6 Hz, H-7), 3.20 (m, 1 H, H-11b), 3.17 (d, 1 H, $J$ = 13.6 Hz, H-3), 2.93 (m, 1 H, H-3), 2.58 (m, 1 H, H-3), 2.05 (m, 2 H, H-1, H-2), 1.87 (m, 1 H, H-1), 1.75 (m, 1 H, H-2); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 172.19 (CO), 159.84 (C-3a), 146.92, 146.09 (C-9, C-10), 135.25 (C-4), 132.56−128.11 (C-9, C-10, Ar), 101.06 (OCO), 65.85 (C-11c), 44.56 (C-11b), 43.28 (C-7), 41.46 (CHPh), 26.00 (C-2), 23.44 (C-3). Anal. Calcd for $C_{29}H_{25}NO_3$: C, 80.0, H, 5.75; N, 3.22. Found: C, 78.20, H, 5.82; N, 3.19.

**11c-Benzyl-9,10-(methylenedioxo)-4-(trimethylsilyl)-1,2,3,7,11b,11c-hexahydropyrrolo(3,2,1-*de*)phenanthridin-5-one (69) and 4-Benzyl-9,10-(methylenedioxo)-1,2,3,7,11b,11c-hexahydropyrrolo(3,2,1-*de*)phenanthridin-5-one (70).** Thermolysis of complex **66b** (0.33 g, 0.555 mmol)



**69**



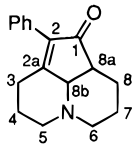
**70**

in refluxing benzene led to two compound, which were separated by silica gel chromatography. Elution with petroleum ether:ethyl acetate 85:25 gave **69** ( 0.040 g, 17%) as a solid: mp 40−42 °C; IR ($CHCl_3$, $cm^{-1}$) 1650; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.39−7.06 (m, 5 H, Ar), 6.68 (s, 1 H), 6.66 (s, 1 H) (H-8, H-11), 5.93 (s, 2 H, $OCH_2O$), 4.89 (d, 1 H, $J$ = 15.8 Hz, CHPh), 3.97 (d, 1 H, $J$ = 15.8 Hz, CHPh), 3.17 (d, 1 H, $J$ = 13.7 Hz, H-7), 3.09 (m, 1 H, H-11b), 3.01 (d, 1 H, $J$ = 13.7 Hz, H-7), 2.80 (m, 1 H, H-3), 2.55 (m, 1 H, H-3), 2.10 (m, 1 H, H-2), 1.93 (m, 1 H, H-1), 1.73 (m, 2 H, H-2, H-1), 0.09 (s, 9 H, $SiMe_3$); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 175.71 (CO), 174.46 (C-3a), 146.63, 145.95 (C-9, C-10), 135.27 (C-4), 132.34−126.79 (C-11a, C-7a, Ar), 107.26, 106.57 (C-8, C-11), 100.91 (OCO), 68.26 (C-11c), 44.76 (C-11b), 42.69 (C-7), 40.69 (CHPh), 26.22 (C-1), 24.98 (C-3), 0.98 ($SiMe_3$). HRMS cald for $C_{20}H_{29}NO_3Si$ ($M^+$): 431.1923. Found: 431.1922. Elution with the same sovents (70:30) gave **70** (0.029 g, 10%) as a solid: mp 54−56 °C; IR ($CHCl_3$, $cm^{-1}$) 1665; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.29−7.19 (m, 5 H, Ar), 6.75 (s, 1 H), 6.71 (s, 1 H (H-8, H-11), 5.96 (s, 2 H, $OCH_2O$), 4.85 (d, 1 H, $J$ = 10.8 Hz, CHPh), 4.46 (d, 1 H, $J$ = 16.8 Hz, CHPh), 3.68 (dd, 2 H, $J$ = 12.2 and 14.8 Hz, 2 H-7), 3.32 (d, 1 H, $J$ = 10.7 Hz, H-11c), 2.79 (m, 1 H, H-3), 2.38 (m, 1 H, H-1), 2.20−2.17 (m, 3 H, H-3, H-2, H-11b), 1.47 (m, 2 H, H-1, H-2); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 171.76 (CO), 153.80 (C-3a), 147.20, 146.61 (C-9, C-10), 139.69 (C-4), 128.69−126.20 (C-11a, C-7a, Ar), 107.60, 104.63 (C-8, C-11), 101.25 (OCO), 62.28 (C-11c), 45.42 (C-11b), 43.39 (CHPh), 29.69 (C-7), 27.08 (C-2), 25.83 (C-1), 25.36 (C-13). HRMS calcd for $C_{23}H_{21}NO_3$ ($M^+$): 359.1521. Found: 359.1520.

**1-(5′-Phenylpent-4′-ynyl)piperidin-2-one (71, *n* = 4).** Alkylation of piperidin-2-one (3.96 g, 40 mmol) as above with the related triflate (13.1 g, 45 mmol) in the presence of NaH (2 g, 50 mmol) led after silica gel chroamtography (eluent, petroleum ether:dichloromethane 80:20) to **73** (5.5 g, 57%) as an oil: $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.38−7.24 (m, 5 H, Ar), 3.47 (m, 2 H, H-1′), 3.30 (m, 2 H, H-6), 2.42 (t, 2 H, $J$ = 7.3 Hz, H-3′), 2.35 (m, 2 H, H-3), 3.85 (dt, 2 H, $J$ = 7.1 and 7.3, H-2′), 1.76 (m, 4 H, H-4, H-5); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 169.89 (CO), 131.60, 128.30, 127.72, 123.87 (Ar), 89.39 (C-4′), 81.14 (C-5′), 48.37 (C-6), 46.67 (C-1′), 32.44 (C-3), 26.36 (C-2′), 23.38 (C-5), 21.44 (C-4), 17.21 (C-3′). HRMS calcd for $C_{16}H_{19}NO$ ($M^+$): 241.1466. Found: 241.1466.

**Pentacarbonylchromium Carbene Complex 73.** This complex was obtained as above from lactam **71** (3 g, 12.5 mmol), and $Cr(CO)_6$ as a yellow solid (2.63 g, 50.5%) after silica gel chromatography (eluent, petroleum ether:dichloromethane 80:20); mp 38 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.44−7.28 (m, 5 H, Ar), 4.28 (m, 2 H, H-1′), 3.52 (t, 2 H, $J$ = 6.1 Hz, H-6), 3.20 (t, 2 H, $J$ = 6.5 Hz, H-3), 2.62 (t, 2 H, $J$ = 6.7 Hz, H-3′), 2.11 (m, 2 H, H-2′), 1.81 (m, 2 H, H-5), 1.58 (m, 2 H, H-4); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 271.79 (Cr═C), 223.46, 218.15 (CO), 131.68, 128.40, 128.05 (Ar), 87.83 (C-4′), 82.11 (C-5′), 63.84 (C-1′), 51.18 (C-6), 49.81 (C-3), 27.60 (C-2′), 21.76 (C-5), 17.26 (C-4), 16.83 (C-3′). Anal. Calcd for $C_{21}H_{19}NO_5Cr$: C, 60.43; H, 4.55; N, 3.35. Found: C, 60.34; H, 4.59; N, 3.24.

**2-Phenyl-3,4,5,6,7,8,8a,8b-octahydro-5a-azaacenaphthylen-1-one (74).** Thermolysis of complex **(73)** (2.0 g, 4.80




mmol) in refluxing benzene (60 mL) for 12 h led to compound **74** (0.22 g, 18%) after silica gel chromatography (elution, petroleum ether:ethyl acetate 60:40): white solid; mp 42 °C; IR ($CHCl_3$, $cm^{-1}$) 1703; $^1H$ NMR (400 Mhz, $CDCl_3$) $\delta$ 7.43−7.31 (m, 5 H, Ar), 2.96 (dd, 1 H, $J$ = 13.7 and 4.5 Hz, H-3), 2.92 (d, 1 H, $J$ = 6.5 Hz, H-8b), 2.84 (d, 1 H, $J$ = 10.3 Hz, H-11), 2.81−2.75 (m, 1 H, H-11), 2.29 (dt, 1 H, $J$ = 10.3 Hz, H-8a), 2.32−2.22 (m, 3 H, H-5, H-3, H-6), 2.21−1.78 (m, 3 H, H-4, H-8, H-7), 1.77−1.64 (m, 2 H, H-4, H-8), 1.60−1.50 (m, 1 H, H-7); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 207.64 (CO), 170.97

(C-2a), 136.64 (C-2), 131.39, 129.18, 128.37, 127.86 (Ar), 64.19 (C-8b), 54.23 (C-5), 51.31 (C-6), 45.04 (C-8a), 27.65 (C-3), 26.62 (C-8), 21.66 (C-7), 20.47 (C-4). HRMS calcd for $C_{17}H_{19}NO$ ($M^+$): 253.1466. Found: 253.1465.

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**Supporting Information Available:** $^1H$ and $^{13}C$ NMR spectra of compounds **12b**, **16**, **20**, **30b**, **39**, **40**, **44**, **45b**, **53**, **58**, **60**, **62**, **69**, **70**, and **74** and synthesis of compounds **11a**,**11b**, **14**, **18a**, **19**, **20**, **21**, **21′**, **25a**, **25b**, **25c**, **29**, **31a**, **31b**, and **51** (20 pages). This material is contained in librairies on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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