# Aminocarbene Complexes of Chromium in Heterocyclic Chemistry, XI[+]

# Synthesis of Functionalized Quinolizines and Homoquinolizines from *N*-Alkynylaminocarbene Complexes of Chromium Intramolecular C–H Activation

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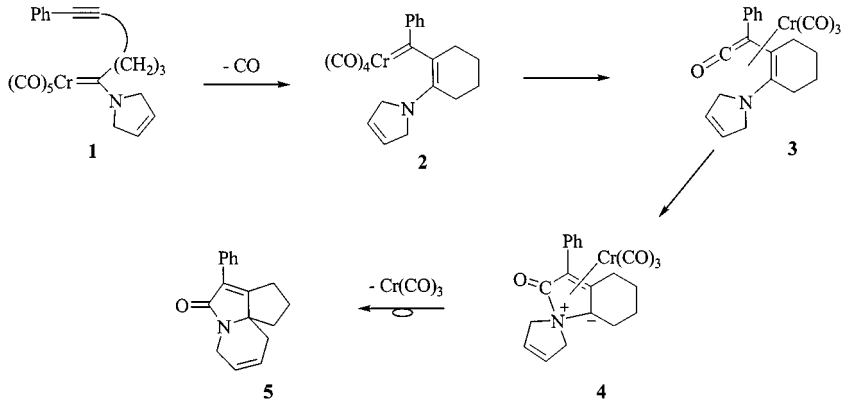
*N*-alkynyl aminocarbene complexes **15d** and **e** derived from piperidin-2-one, **15f** and **g** and from azepan-2-one yield, upon thermolysis, functionalized quinolizines **16**–**18d**,**e** and homoquinolizines **16**–**18f**,**g** as the result of a triple-bond insertion, a carbon–hydrogen bond activation, followed by a CO insertion. No reaction was observed in the case of complexes derived from pyrrolidin-2-one.

## Introduction

The key step in the transformation of aminocarbene complexes of chromium and alkynes into pyrrolinones is the through-space interaction of the nitrogen atom with the central carbon atom of the ketene function in an intermediate aminoketene complex.[2][3] This leads to *N*-ylide complexes which give pyrrolinones upon rearrangement. Both the inter- and the intramolecular versions of this reaction have been described. The intramolecular reaction is exemplified by the transformation of complex **1** into pyrrolinone **5** via a new carbene complex **2**, a ketene complex **3**, and a *N*-ylide complex **4**.[3]

However, even slight modifications of the structure of the starting carbene complexes can change the course of the reaction: thus, when the phenyl group of the triple bond in **1** was substituted by a methyl as in **6** no pyrrolinonesuch as **5** was formed. Instead, the ketone **7** was isolated.[4]

This product is the result of the insertion of both the triple bond and CO, and of the activation of a C−H bond β to the nitrogen. Although it seems possible for the carbene complex (or the ketene complex) formed upon insertion of the triple bond (and of CO) to interact with the nitrogen atom, it surprisingly did not take place.




Scheme 1

Yet carbene complexes could be designed for which the interaction between nitrogen and the carbene complex (or the ketene complex) is not possible at all. Indeed, the spatial arrangement of the nitrogen atom with respect to the ketene function in intermediate **3** is highly dependent on the structure of the starting carbene complex. An interaction between the two functions can only take place either during intermolecular insertions of alkynes, or when the alkynyl

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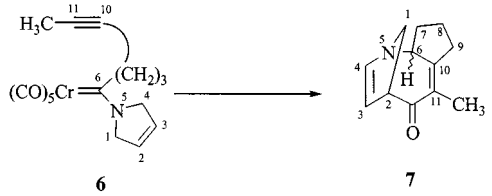
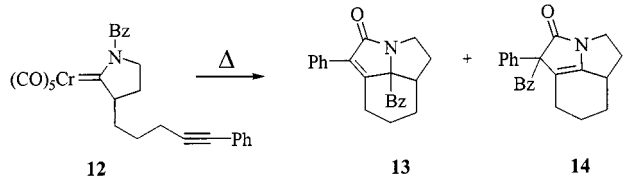


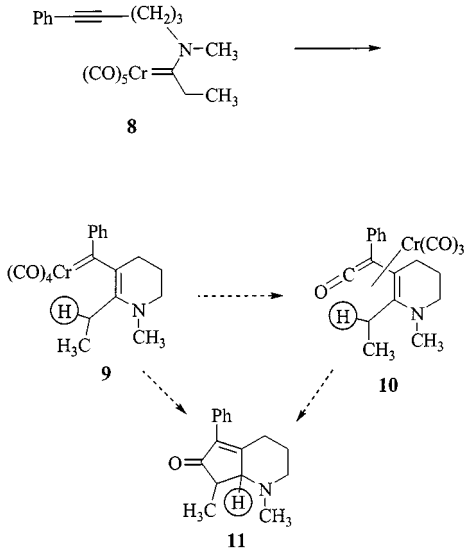
Scheme 2



Scheme 4

chain is directly bound to the α-carbon atom of the carbene function.[3]

This is clearly evident in, for example, complex **8**: even if the insertion of the alkyne takes place, no through-space interaction between a hypothetical carbene **9** (or ketene **10**) and nitrogen can take place. Nevertheless, a clean reaction took place upon thermolysis, which led to product **11**: an intramolecular insertion of the triple bond, an insertion of a CO group, and a carbon-hydrogen bond activation were indeed observed.



Scheme 3

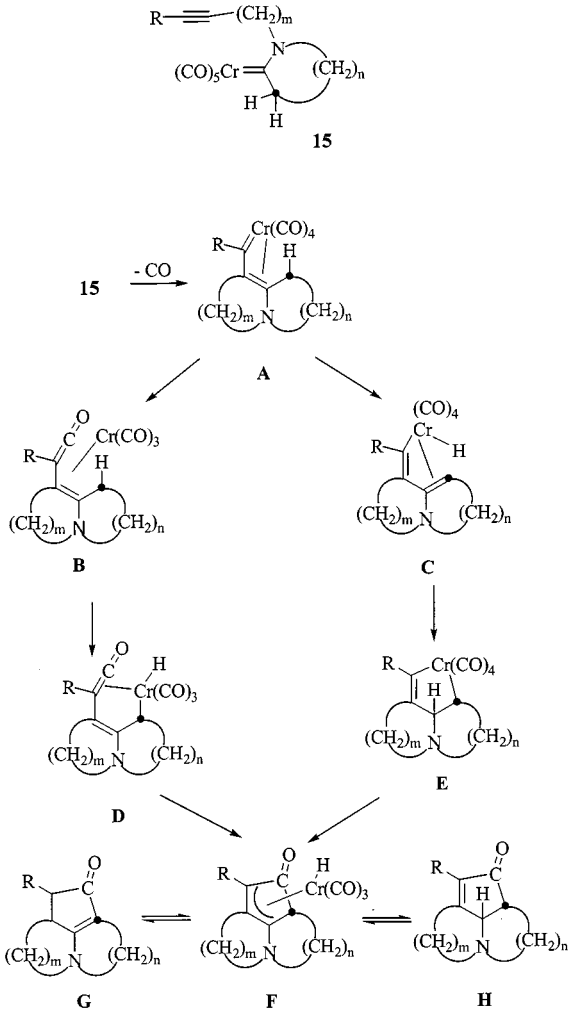
However, several points had not been settled and remained a matter of speculation:

– the first point concerned the scope of the reaction: since carbene complexes of the type **12**, in which the nitrogen atom is already part of a cycle, gave tricyclic pyrrolinones **13** and **14**, will complexes such as **15**, bearing the alkynyl chain on nitrogen, also lead to tricyclic compounds by a transformation akin to that of **8** into **11**?

– the second point deals with the timing of the various steps leading to the final products.

– and the final point is related to the nature of the intermediates: are ketene complexes really involved in the transformation of **8** into **11**?

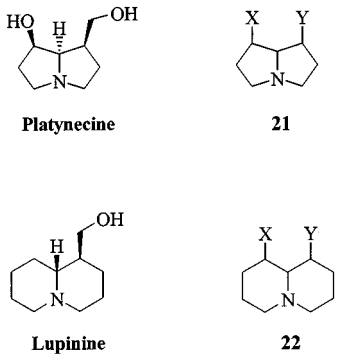
The choice of the structure of the complexes **15** was guided by the structures of the possible end-products, as shown by the retrosynthetic scheme (Scheme 5) which is based on the transformation of **8** into **11**. Indeed, according to such a scheme, complexes such as **15** might possibly lead to structures **G** or **H**. This could be accomplished first by



Scheme 5

the insertion of the triple bond (15→**A**), followed either by insertion of CO to give a ketene complex **B**, and then insertion of the metal in the C–H bond, to give **F**, or by insertion of the carbene complex into the allylic C–H bond to give the metallacycle **E** (via **C**) and then **F**.

It then appears that for $n = m = 2$, hexahydrocyclopentapyrrolizinones, precursors of functionalized pyrrolizines **21**, might be formed. Similarly, for $n = m = 3$, octahydroazaacenaphtylenones, precursors of functionalized quinolizines **22**, might be formed. This approach would constitute a direct access to platynecine and lupinine-type alkaloids. Moreover, homologues of these bicyclic N-containing compounds would also be attainable by the same approach (m, n >3).

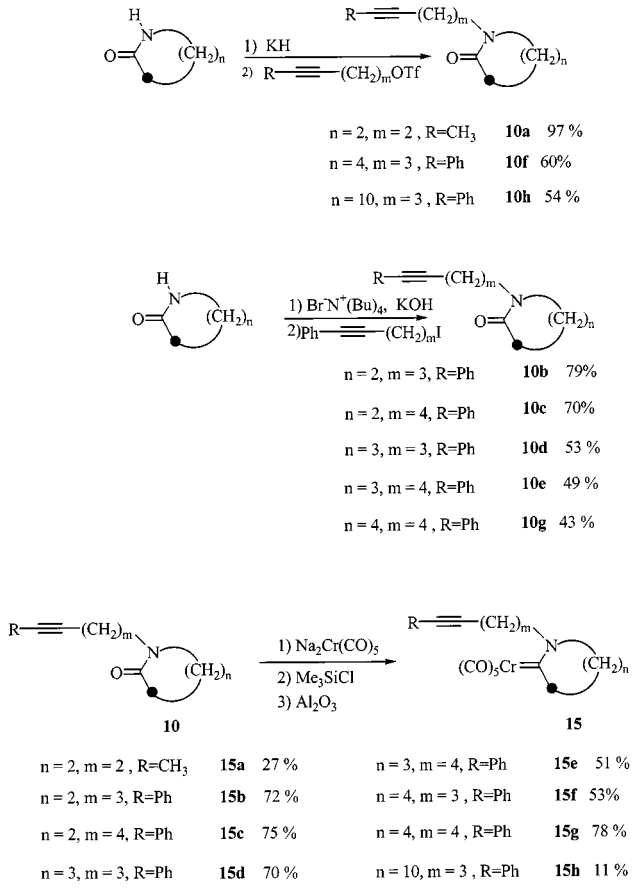



Scheme 6

## Results

The synthesis of the carbene complexes **15** from commercially available lactams was straightforward, except for **15a**, **15f** and **15h** where the classical alkylation at nitrogen with the corresponding alkynyl iodides under phase-transfer conditions (KOH, tetrabutylammonium bromide) failed. Thus, the corresponding triflates in conjunction with KH had to be used.[5][6] The lactams were characterized by their physical data (see Experimental Section). The alkylated lactams were transformed into the carbene complexes according to the method of Hegedus[7][8] in satisfactory yields [except for **15a** (27%) and **15h** (11%)]. The reactivity of complex **15h** was not further investigated.

The analytical and physical data for these new carbene complexes can be found in the Experimental Section.




Scheme 7

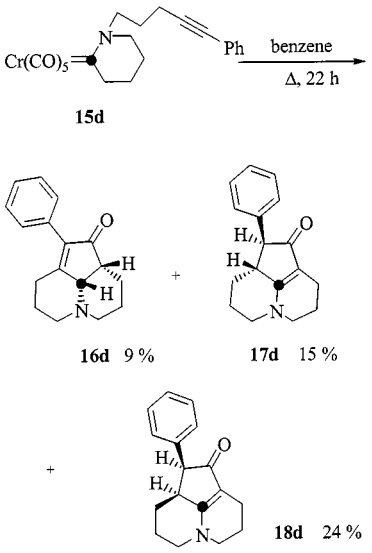
### Thermolysis of Complex 15a−c

The first attempts to thermally rearrange complexes **15a−c** were disappointing. When benzene solutions of these complexes were heated at reflux, a fast disappearance of the starting material was observed, but a major new product or complex was neither formed according to TLC, nor could products be isolated upon silica-gel chromatography.

### Thermolysis of Complexes 15d−g

Fortunately, the behaviour of complexes **15d−g** was completely different. Under the same conditions as for **15a−c**, complete consumption of the starting complex **15d** was observed, together with the formation of three polar organic compounds. These were separated by silica-gel chromatography. Structure **16d** (9%) was assigned to the less polar compound by consideration of its two dimensional NMR data (C−H and H−H correlations). The high-resolution mass spectrum agreed with this structure. The $^1$H NMR spectrum confirmed, among others, the presence of two $NCH_2$ groups (multiplets between δ 2.84 and 2.22) and of a NCH group (doublet at δ 2.92). The $^{13}$C NMR and the IR spectra agreed with the presence of a cyclopentenone [$\tilde{\nu}$(CO) = 1703 cm$^{-1}$, δ(CO) = 207.64]. All the $CH_2$ groups gave clearly separated signals.

Finally, crystals suitable for an X-ray structure determination could be grown: the CAMERON projection of the




Scheme 8

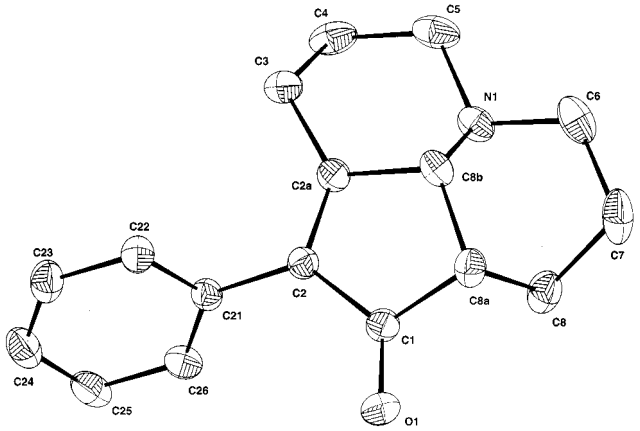



Figure 1. CAMERON projection of compound **16d** with relevant bond lengths (Å) and bond angles (°): O(1)−C(2), 1.217(3), C(2)−C(2a), 1.341(4), N(1)−C(6), 1.459(4),; N(1)−C(5), 1.465(4), N(1)−C(8b), 1.472(3); C(5)−N(1)−C(6), 111.8(3), C(6)−N(1)−C(8b), 108.9(2), C(5)−N(1)−C(8b), 109.9(2)

tetracyclic compound **16d** appears in Figure 1. These data confirm the insertion of the alkyne and of CO, formation of a C(1)−C(8a) bond via activation of a C−H bond β to nitrogen, and of a conjugated cyclopentenone. Moreover, H-8a and H-8b are *cis*.

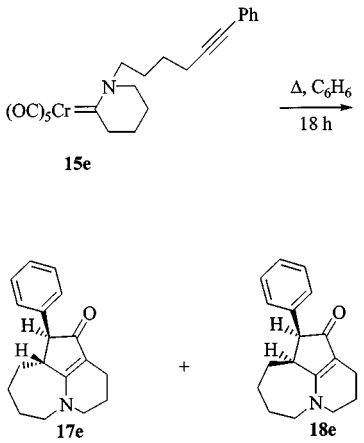
The second product, **17d**, was isolated as an oil (15% yield). According to its mass spectrum, it is an isomer of **16d**. The most significant structural informations are given by the IR and $^{13}C$ NMR spectra: they are typical for an enaminone with $\tilde{\nu}$(CO) = 1575 $cm^{-1}$, $\tilde{\nu}$(C=C) = 1660 $cm^{-1}$, δ(CO) = 198.04 and δ(C=C) = 171.98 and 108.04.[9][10] The $^{13}C$ NMR spectra also confirmed the presence of two methine groups at δ = 58.15 and 46.14, as well as two methylene groups at δ = 49.54.

Structure **18d** was assigned to the third product, isolated in 24% yield as a yellow solid. It is a stereoisomer of **17d**: its spectroscopic data are very similar to those of **16d**. The IR and $^{13}C$ NMR spectra confirm again the presence of an enaminone [$\tilde{\nu}$(CO) = 1570 $cm^{-1}$, $\tilde{\nu}$(C=C) = 1660 $cm^{-1}$; δ(CO) = 198.55; δ(C=C) = 173.33 and 109.21]. The difference appears in the coupling constant between H-2 and H-2a, which is 6.8 Hz in **18d**, vs 5.6 Hz in **17d.** This is in agreement with a *trans* geometry (vide infra).

Increasing the length of the alkynyl chain considerably decreased the yield of the reaction: two enaminones **17e** and **18e** were formed in 6% and 5% respectively, from **15e**. Their spectroscopic data were in all respects similar to those of the enaminones described above (see Experimental Section). No conjugated ketones could be detected in this case.

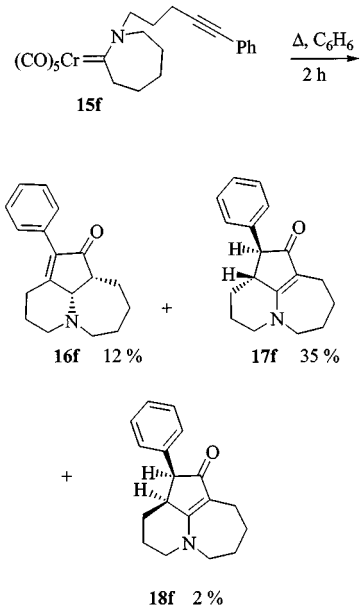
As far as complex **15f** is concerned, in which the size of the nitrogen-containing heterocycle increased from 6 to 7, its thermolysis led to the same distribution of products as for complex **15d**. Three compounds were isolated: a ketone **16f** (12%) and two enaminones **17f** and **18f** in a 37% combined yield.

Crystals of **17f** suitable for an X-ray analysis could be grown: the CAMERON projection, shown in Figure 2, clearly confirmed the presence of a tricyclic system with an enaminone function and a *trans* stereochemistry of H-2




Scheme 9

with respect to H-2a. This result is also in agreement with the observed lower value of the coupling constant ($J$ = 5.1 Hz) for the *trans* isomer as compared to $J$ = 7.6 Hz for the *cis* isomer **18f**, the phenyl ring being in both cases is in an equatorial position.




Scheme 10

Finally, increasing both the size of the N-containing heterocycle (7-membered ring) and the length of the alkynyl chain (m = 4) led to the expected 5, 7, 7 fused tricyclic system in a 52% yield. Again, no conjugated ketone was formed.

## Thermolysis of Complexes 15d and 15g in the Presence of Ethanol

As already indicated in the introduction for complex **8**, its transformation into **11** could involve among others, either a carbene complex **9**, which might insert into an activated carbon−hydrogen bond, or a ketene complex **10**, the

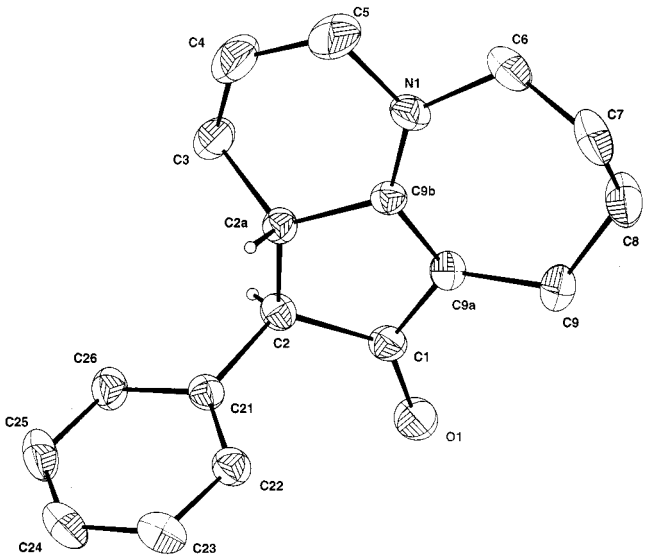
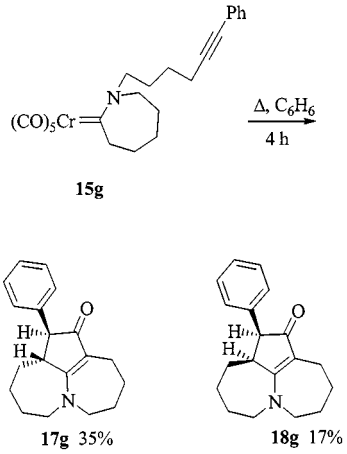



Figure 2. CAMERON projection of compound **17f** with relevant bond lengths (Å) and bond angles (°): O(1)−C(1), 1.223 (2), C(9b)−C(9a), 1.371(4), N(1)−C(6), 1.464 (4), N(1)−C(5), 1.454(5), N(1)−C(9b), 1.348(4); C(5)−N(1)−C(6), 111.1(3), C(6)−N(1)−C(9b), 123.1(3), C(5)−N(1)−C(9b), 119.3(3)

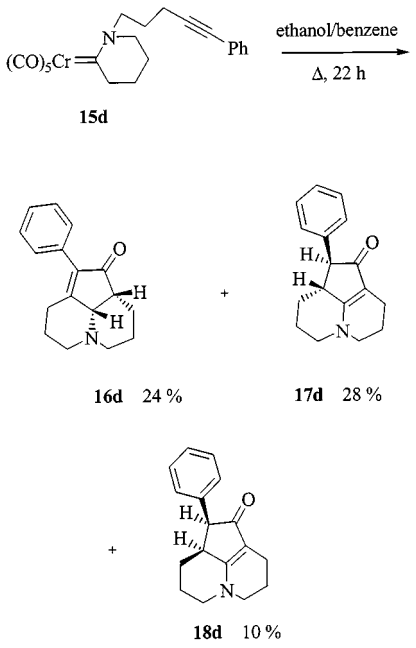



Scheme 11

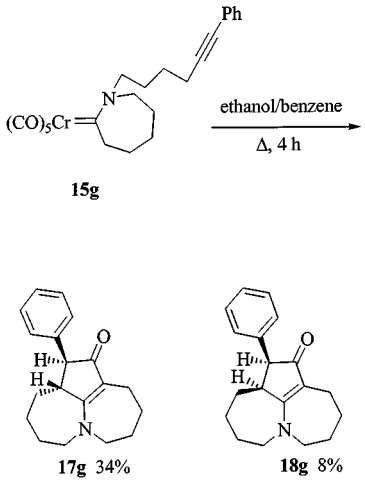
transformation of which might also lead to the bicyclic compound **11**.[4][11]

A way to distinguish between the two suggested mechanisms would be to trap an intermediate, in the present case, the ketene complex **10**.[12][13] This might be possible by carrying out the insertion reaction in the presence of ethanol, which would convert the ketene into the corresponding ester. However, when complex **15d** was heated in refluxing benzene for 22 h, in the presence of ethanol, a mixture of the same three compounds **16d**, **17d** and **18d** was obtained in 24%, 28% and 10% yield, respectively.

Similarly, under the same conditions, **15g** led to **17g** (8%) and **18g** (34%).




Scheme 12




Scheme 13

Table 1. Yields of the products of thermolysis in the different solvents

| Compound | $C_6H_6$/EtOH | $C_6H_6$ |
|---|---|---|
| **16d** | 24% | 9% |
| **17d** | 28% | 15% |
| **18d** | 10% | 24% |
| **17g** | 8% | 35% |
| **18g** | 34% | 17% |

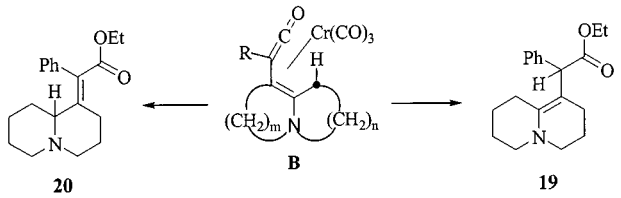
## Discussion

Three points warrant a comment:

− first, ethanol neither inhibits the insertion, nor leads to different products: indeed, according to Scheme 5, the possible intermediate **B**, a ketene complex, might have resulted in the formation of ester **19** or **20**, upon solvolysis by ethanol.

– second, in the first example, the total yield of cyclized products is even higher in the presence than in the absence of ethanol (68% vs 48%).

– as far as the distribution of the various products is concerned, differences are nevertheless noticed in going from benzene to a mixture of benzene and ethanol. The reasons behind this are not clear. It is however likely that, whereas in benzene the different isomers are formed in a reversible way (**F** ⇌ **G**, **H**, Scheme 5) via intramolecular hydride transfers, in the presence of ethanol, the reactions are probably irreversible. Once formed, the hydride complex **F** either reacts rapidly or is destroyed by the solvent ethanol, the resulting carbon–chromium bond then being cleaved by ethanol. It is thus likely that in the presence of ethanol the kinetic products are observed whereas in its abscence, the thermodynamic products are isolated.




Scheme 14

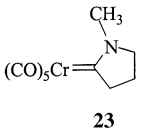
### Behavior of Carbene Complexes Derived from Pyrrolidone

As indicated above, complexes **15a–c**, in which nitrogen is part of a five-membered ring, behaved peculiarly since they did not lead to the expected insertion products. Again, the reasons behind this were not clear:

– it is not due to the size of the ring, since complex **12** gave the insertion products **13** and **14** in a 40% overall yield.

– it could be linked to the nature of the substituent on nitrogen. Indeed, replacement of the benzyl group of **12** by a methyl group completely inhibited the insertion reaction.

Similarly, no intermolecular reaction between diphenylacetylene and complex **23** was observed: all the starting carbene complex was recovered after prolongated heating in refluxing benzene.




Scheme 15

The role of the benzyl group would thus be to activate the metal, by removing a carbonyl group (1,4-bidentate effect) for the coordination of the triple bond: no such an activation can take place either for **15a–c** or for **23**.

## Conclusion

Although no through-space interaction between the nitrogen atom and the carbene complex formed upon insertion of the triple bond in the starting complexes can occur, a through-bond interaction is likely to take place between the nitrogen atom and the carbene-carbon atom. The electron-rich metal can thus undergo an oxidative addition of a close C–H bond in **A** (Scheme 5). This leads finally, upon carbon–carbon bond formation and CO insertion, to a cyclopentenone. The success of the reaction depends both on the size of the nitrogen-containing heterocycle and the length of the chain on nitrogen bearing the triple bond. Thus, starting from simple aminocarbene complexes, tricyclic, N-containing compounds can easily and smoothly be obtained. Of special interest in this regard is the formation of functionalized quinolizines precursors of lupinine alkaloids.

## Experimental Section

**General:** All reactions were performed under a dry argon atmosphere using Schlenk techniques. – Solvents were distilled from sodium/benzophenone ketyl (diethyl ether, tetrahydrofuran), phosphorous pentoxide (dichloromethane) and saturated with argon. – Silica gel (Merck, type 60, 0.063–0.200 mm was used for column chromatography. – $^1$H NMR: Bruker AC-200 (200 MHz), Bruker ARX-400 (400 MHz); $^{13}$C NMR: Bruker AC-200 (50 MHz) and Bruker ARX-400 (100 MHz). All NMR spectra were recorded in $CDCl_3$ unless stated otherwise with $CHCl_3$ as internal standard. – MS and HRMS: Kratos MS 50. – M.p.: Reichert, the reported melting points are uncorrected. – TLC: 0.25 mm Merck silica gel plates 60 $F_{254}$.

**General Procedure for the Alkylation of Lactams with Alkynyl Triflates (Method A):** To a solution of the lactam in THF (0.4 mmol in 1 mL) a suspension of potassium hydride (1.2 equiv.) in THF (0.48 mmol in 1 mL) was added. After stirring for 10 min, the triflate (1.2 equiv.) in THF (2.4 mmol in 1 mL) was added. The mixture was then stirred at room temperature for a few hours until completion of the reaction (2–15 h). Ethanol was then slowly added to destroy the excess of hydride. Extraction with dichloromethane followed by evaporation of the solvents gave an oil which was purified by silica-gel chromatography.

**General Procedure for the Alkylation of Lactams with Alkynyl Iodides (Method B):** In a two-necked flask fitted with a refrigerant and a dropping funnel $N^+(Bu)_4Br^-$ (0.2 equiv.) was added to a suspension of powdered KOH (1.2 equiv.) in THF (1 mL/ mmol). A mixture of lactam and iodide (1 equiv.) in THF (1 mL/ 1 mmol) was then added and stirred at room temperature, then refluxed for 13–15 h until completion of the reaction. The suspension was then filtered, the solvent evaporated, and the residue purified by chromatography on silica gel.

**1-(4-Methylbut-3-ynyl)pyrrolidin-2-one (10a):** Preparation from pyrrolidinone (3.4 g, 39.90 mmol) according to method A gave an oil (4.4 g, 38.70 mmol, 97%). – $^1$H NMR (200 MHz): δ = 3.50 (t, 2 H, $NCH_2$), 3.36 (t, 2 H, $NCH_2$), 2.38–2.27 (m, 4 H), 2.06–1.94 (m, 2 H), 1.72 (t, 3 H, $CH_3$). – $^{13}$C NMR (50 MHz) δ = 174.86 (CO), 47.67, 41.97, 38.91, 19.37, 18.04, 3.40 ($CH_3$). – MS( EI, 70 eV); *m*/*z*: 151 ($M^+$)

**1-(5-Phenylpent-4-ynyl)pyrrolidin-2-one (10b):** Preparation from pyrrolidinone (1.52 g, 17.86 mmol) according to method B gave a yellowish oil (3.2 g, 14. 1 mmol, 79%). Eluent petroleum ether/ethyl acetate 50:50. − $^1$H NMR (200 MHz) δ = 7.35 (m, 5 H, ArH), 3.45 (m, 4 H, H-6, H-5), 2.46 (t, 2 H, H-8), 2.40 (t, 2 H, H-3), 2.03 (m, 2 H, H-4), 1.86 (m, 2 H, H-7); − $^{13}$C NMR (100 MHz) δ = 175.24 (CO), 131.63, 128.33, 127.79 (Ar), 89.06 (C-10), 81.24 (C-9), 47.56 (C-6), 42.04 (C-5), 31.13 (C-3), 26.60 (C-7), 18.07 (C-4), 17.25 (C-8). − HRMS: calcd. for $C_{15}H_{17}NO$ ($M^+$) 227.1310; found 227.1310.

**1-(6-Phenylhex-6-ynyl)pyrrolidin-2-one (10c):** Preparation from pyrrolidinone (2.13 g, 25 mmol) according to method B gave an oil (4.22 g, 17.44 mmol, 70%). Eluent petroleum ether/ethyl acetate 60:40. − $^1$H NMR (200 MHz) δ = 7.38−7.23 (m, 5 H, ArH), 3.39−3.27 (m, 4 H, H-5, H-6), 2.46−2.32 (m, 4 H, H-3, H-9), 2.05−1.94 (m, 2 H, H-4), 1.72−1.55 (m, 4 H, H-7, H-8). − $^{13}$C NMR (50 MHz), δ = 175.00 (CO), 131.57, 128.27, 127.65, 123.89 (Ar), 89.66 (C-11) 81.07 (C-10), 47.06 (C-6), 42.00 (C-5), 31.15 (C-3), 26.45 (C-7), 25.91 (C-8), 19.12 (C-4), 17.96 (C-9). − HRMS: calcd for $C_{16}H_{19}NO$ ($M^+$) 241.1467; found 241.1471.

**1-(5-Phenylpent-4-ynyl)piperidin-2-one (10d):** Preparation from piperidone (2.48 g, 25 mmol) according to method B gave an oil (3.17 g, 13.15 mmol, 53%). − IR ($CHCl_3$): $\tilde{\nu}$ = 1620 cm$^{-1}$. − $^1$H NMR (400 MHz) δ = 7.38−7.24 (m, 5 H, ArH), 3.47 (m, 2 H, H-7), 3.30 (m, 2 H, H-6), 2.42 (t, 2 H, H-9), 2.35 (m, 2 H, H-3), 1.85 (dt, 2 H, H-8), 1.76 (m, 4 H, H-5, H-4). − $^{13}$C NMR (100 MHz) δ = 169.89 (CO), 131.60, 128.30, 127.72, 123.87 (Ar), 89.39 (C-11), 81.14 (C-10), 48.37 (C-6), 46.67 (C-7), 32.44 (C-3), 26.36 (C-8), 23.38 (C-5) 21.44 (C-4), 17.21 (C-9). − HRMS: calcd for $C_{16}H_{19}NO$ ($M^+$) 241.1466; found 241.1466.

**1-(6-Phenyl-hex-6-ynyl)piperidin-2-one (10e):** Preparation from piperidone (2.48 g, 25 mmol) according to method B gave an oil (3.18 g, 12.46 mmol, 49%). − IR ($CHCl_3$): $\tilde{\nu}$ = 1620 cm$^{-1}$. − $^1$H NMR (400 MHz) δ = 7.34−6.91 (m, 5 H, ArH), 3.34 (t, 2 H, H-7),3.23−3.17 (m, 2 H, H-6), 2.41−2.30 (m, 4 H, H-3, H-10), 1.74−1.44 (m, 8 H). − $^{13}$C NMR (100 MHz) δ = 169.68 (CO), 131.56, 128.24, 127.60, 123.94 (Ar), 89.86 (C-12), 80.96 (C-11), 47.79 (C-6), 46.51 (C-7), 32.38 (C-3), 26.28, 26.00 (C-8,C-9), 23.31 (C-5), 21.43 (C-4), 19.24 (C-10). − HRMS: calcd for $C_{17}H_{21}NO$ ($M^+$) 255.1623; found 255.1617.

**1-(5-Phenylpenty-4-ynyl)azepan-2-one (10f):** Preparation from azepan-2-one (3.39 g, 30 mmol) according to method A gave an oil (4.6 g, 18.04 mmol, 60%). Eluent petroleum ether/ethyl acetate 65:35. − IR ($CHCl_3$): $\tilde{\nu}$ = 1625 cm$^{-1}$. − $^1$H NMR (400 MHz) δ = 7.33−7.20 (m, 5 H, ArH), 3.44 (t, 2 H, H-8), 3.33−3.30 (m, 2 H, H-7), 2.47−2.44 (m, 2 H, H-3), 2.37 (t, 2 H, H-10), 1.80−1.73 (m, 2 H, H-9), 1.74−1.58 (m, 6 H). − $^{13}$C NMR (100 MHz) δ = 175.93 (CO), 131.63, 128.30, 127.72, 123.89 (Ar), 89.40 (C-12) 81.12 (C-11), 50.09 (C-7), 47.85 (C-8), 37.42 (C-3), 30.08 (C-6), 28.85 (C-4), 27.39 (C-9), 23.54 (C-5), 17.21 (C-10). − HRMS: calcd for $C_{17}H_{21}NO$ ($M^+$) 255.1623, found 255.1623.

**1-(6-Phenylhex-6-ynyl)azepan-2-one (10g):** Preparation from azepan-2-one (2.94 g, 26 mmol) according to method B gave an oil (2.99 g, 11.12 mmol, 43%). − IR ($CHCl_3$): $\tilde{\nu}$ = 2190, 1620 cm$^{-1}$. − $^1$H NMR (400 MHz) δ = 7.38−7.22 (m, 5 H, ArH), 3.42−3.29 (m, 4 H, H-7, H-8), 2.51−2.39 (m, 4 H, H-3, H-11), 1.67−1.55 (m, 10 H). − $^{13}$C NMR (100 MHz) δ = 175.64 (CO), 131.39, 128.08, 127.43, 123.81 (Ar), 89.74 (C-13), 81.84 (C-12), 49.36 (C-7), 47.42 (C-8), 37.18 (C-3), 29.88 (C-6), 28.57 (C-4), 27.17 (C-9), 25.80 (C-10), 23.35 (C-5), 19.07 (C-11). − HRMS: calcd for $C_{18}H_{23}NO$ ($M^+$) 269.1780; found 269.1778.

**1-(5-Phenylpent-4-ynyl)azacyclotridecan-2-one (10h):** Preparation from azacyclotridecan-2-one (2 g, 10 mmol) according to method A gave an oil (1.82 g, 5.37 mmol, 54%). − IR ($CHCl_3$): $\tilde{\nu}$ = 1600 cm$^{-1}$. − $^1$H NMR (400 MHz) (mixture of two isomers). − ***Isomer 1:*** δ = 7.39−7.19 (m, 5 H, ArH), 4.32−4.24 (m, 1 H), 3.75−3.67 (m, 1 H), 3.24−3.13 (m, 1 H), 2.61−2.55 (m, 1 H), 2.71−2.64 (m, 1 H), 2.39−2.35 (m, 2 H), 2.13−2.06 (m, H), 1.81−1.18 (m, 20 H). − ***Isomer 2:*** δ = 7.39−7.19 (m, 5 H, ArH), 3.40−3.36 (t, 2 H), 3.24−3.13 (t, 2 H), 2.37−2.33 (t, 2 H), 2.28−2.23 (m, 2 H), 1.81−1.18 (m, 20 H). − $^{13}$C NMR (100 MHz) δ = 174.38 and 173.82 (CO), 131.53−123.47 (Ar), 89.43, 88.42, 81.81, 81.10, 46.91, 45.53, 44.34, 33.18, 32.21, 27.92−23.51 (18 signals), 17.18, 16.78. − HRMS: calcd for $C_{23}H_{33}NO$ ($M^+$) 339.2562, found 339.2561.

**Carbene Complexes. − General Procedure:** To a solution of $Na_2Cr(CO)_5$ in THF (2 equiv.) at −78 °C was added via a cannula, the lactam (1 equiv.) in THF (25 mL) over a period of 10 min. The solution is then stirred at −78 °C for 30 min, then at 0 °C for the same period. TMSCl (3.3 equiv.) was added and the solution stirred for 30 min at −78 °C. After that, neutral alumina (30 g) was added and the solution warmed to room temperature. The solvent was then evaporated under vacuum and the residue poured on a column of silica gel. Elution with petroleum ether first gave naphthalene.

**Carbene Complex 15a:** Preparation from **10a** (3.4 g, 22.5 mmol) gave yellow crystals (2 g, 27%), m.p. 68 °C. − $^1$H NMR (200 MHz) δ = 4.15 (t, 2 H), 3.81 (t, 2 H), 3.33 (t, 2 H), 2.62 (m, 2 H), 1.90 (t, 2 H), 1.77 (s, 3 H). − $^{13}$C NMR (50 MHz) δ = 267.8 (Cr=C), 223.23, 218.02 (CO), 78.9, 74.1, 59.89, 56.40, 53.83, 21.13, 18.77, 3.38. − $C_{14}H_{13}NO_5Cr$ (327): calcd. C 51.37, H 3.97, N 4.28; found C 50.62, H 3.93, N 4.10.

**Carbene Complex 15b:** Preparation from **10b** (2.7 g, 12.5 mmol) eluted with petroleum ether/$CH_2Cl_2$ 85:15 gave a yellow oil (3.63 g, 9.00 mmol, 72%). − IR ($CHCl_3$):$\tilde{\nu}$ = 2040, 1965, 1915 cm$^{-1}$. − $^1$H NMR (400 MHz) δ = 7.35−7.18 (m, 5 H, ArH), 4.11 (t, 2 H, H-6), 3.72 (t, 2 H, H-5), 3.26 (t, 2 H, H-3), 2.54 (t, 2 H, H-8), 2.02 (m, 2 H, H-7), 1.82 (m, 2 H, H-4). − $^{13}$C NMR (100 MHz) δ = 266.69 (C-2), 223.16, 218.16 (CO), 131.62, 128.36, 128.02, 123.41 (Ar), 87.70 (C-10), 82.09 (C-9), 59.22 (C-5), 56.51 (C-3), 54.72 (C-6), 27.15 (C-7), 21.11 (C-4), 17.08 (C-8). − $C_{20}H_{17}O_5N$ (351): calcd. C 59.55, H 4.22, N 3.47; found C 59.59, H 4.22, N 3.31.

**Complex 15c:** Preparation from **10c** (3.01 g, 12.5 mmol) gave an orange oil (3.93 g, 9.42 mmol, 75%). Eluent petroleum ether/$CH_2Cl_2$ 85:15. − IR ($CHCl_3$): $\tilde{\nu}$ = 2040, 1965, 1915 cm$^{-1}$. − $^1$H NMR (400 MHz) δ = 7.78−6.93 (m, 5 H, ArH), 4.06 (t, 2 H, H-6), 3.76 (t, 2 H, H-5), 3.32 (t, 2 H, H-3), 2.52 (t, 2 H, H-9), 2.01−1.89 (m, 4 H, H-7, H-8), 1.85−1.69 (m, 2 H, H-4). − $^{13}$C NMR (100 MHz) δ = 265.48 (C-2), 223.29, 218.22,(CO), 131.60, 128.36, 127.84, 123.71 (Ar), 89.02 (C-11), 81.51 (C-10), 58.93 (C-5), 56.41 (C-3), 55.10 (C-6), 27.57 (C-7), 25.68 (C-8), 21.07 (C-4), 19.28 (C-9). − $C_{21}H_{19}NO_5Cr$ (417): calcd C 60.43, H 4.56, N 3.36; found C 60.40, H 4.55, N 3.42.

**Complex 15d:** Preparation from **10d** (3.01 g, 12.5 mmol) gave a yellow solid (3.63 g, 8.69 mmol, 70%); m.p. 38 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2040, 1963, 1915 cm$^{-1}$. − $^1$H NMR (400 MHz) δ = 7.45−7.28 (m, 5 H, ArH), 4.28 (t, 2 H, H-7), 3.52 (t, 2 H, H-6), 3.21 (t, 2 H, H-3), 2.63 (t, 2 H, H-9), 2.11 (m, 2 H, H-8), 1.81 (m, 2 H, H-5), 1.58 (m, 2 H, H-4). − $^{13}$C NMR (100 MHz) δ = 271.79 (Cr=C),223.46, 218.15 (CO), 131.68, 128.40, 128.05 (Ar), 87.83 (C-11), 82.11 (C-10), 63.84 (C-7), 51.18(C-6), 49.81 (C-3), 27.60 (C-8), 21.76 (C-5), 17.26 (C-4), 16.83 (C-9). − $C_{21}H_{19}NO_5Cr$ (417): calcd C 60.43, H 4.56, N 3.36; found C 60.34, H 4.59 N 3.24.

**Complex 15e:** Preparation from **10e** (2.9 g, 11.37 mmol) gave a red oil (2.52 g, 5.82 mmol, 51%). − IR ($CHCl_3$): $\tilde{\nu}$ = 2040, 1960, 1915

$cm^{-1}$. − $^1H$ NMR (400 MHz) δ = 7.39−7.25 (m, 5 H, ArH), 4.16−4.08 (m, 2 H, H-7), 3.46 (t, 2 H, H-6), 3.16 (t, 2 H, H-3), 2.51 (t, 2 H, H-10), 2.03- 1.90 (m, 2 H, H-8), 1.80−1.50 (m, 6 H). − $^{13}C$ NMR (100 MHz) δ = 270.13 (Cr=C), 223.50, 218.12 (CO), 131.57, 128.33, 127.83 (Ar), 89.02 (C-12), 81.78 (C-11), 64.24 (C-7), 50.96 (C-6), 49.68 (C-3), 27.93 (C-8), 25.39 (C-9), 21.69 (C-5), 19.27 (C-4), 17.27 (C-10). − $C_{22}H_{21}NO_5Cr$ (431): calcd C 61.25, H 4.87, N 3.25; found C 61.14, H 4.93, N 3.38.

**Complex 15f:** Preparation from **10f** (2.89 g, 12.5 mmol) gave a red oil (2.83 g, 6.57 mmol, 53%). − $^1H$ NMR (200 MHz) δ = 7.43−7.25 (m, 5 H, ArH), 4.34−4.25 (m, 2 H, H-8), 3.82−3.78 (m, 2 H, H-7), 3.29−3.24 (m, 2 H, H-3), 2.59 (t, 2 H, H-10), 2.13−2.05 (m, 2 H, H-9), 1.74−1.58 (m, 6 H). − $^{13}C$ NMR (50 MHz) δ = 278.02 (Cr=C), 228.65, 217.82 (CO), 131.65, 128.37, 128.01 123.47 (Ar), 87.81 (C-12), 82.06 (C-11), 65.07 (C8), 54.26 (C-7), 52.29 (C-3), 28.92 (C-9), 27.45 (C-6), 26.30 (C-4), 21.13 (C-5), 16.78 (C-10). − HRMS: calcd for $C_{21}H_{22}NO_4Cr$ ($MH^+$−CO): 404.0954, found 404.0983.

**Complex 15g:** Preparation from **10g** (2.6 g, 9.66 mmol) gave an orange oil (3.01 g, 7.52 mmol, 78%). − IR ($CHCl_3$): $\tilde{\nu}$ = 2040, 1960, 1915 $cm^{-1}$. − $^1H$ NMR (400 MHz) δ = 7.41−7.25 (m, 5 H, Ar), 4.20−4.12 (m, 2 H, H-8), 3.80−3.75 (m, 2 H, H-7), 3.28−3.23 (m, 2 H, H-3), 2.51 (t, 2 H, H-11), 2.03−1.95 (m, 2 H, H-9), 1.76−1.56 (m, 8 H). − $^{13}C$ NMR (100 MHz) δ = 277.10 (Cr=C), 223.56, 217.84 (CO), 131.56, 128.33, 127.82 (Ar), 89.02 (C-13), 81.78 (C-12), 65.45 (C-8), 54.12 (C-7), 52.20 (C-3), 28.98 (C-9), 27.88 (C-6), 26.27 (C-4), 25.36 (C-10), 21.14 (C-5), 19.26 (C-11). − $C_{23}H_{23}NO_5Cr$(445): calcd C 62.02, H5.17, N 3.15; found C 61.99, H 5.22, N 3.10.

**Complex 15h:** Preparation from **10h** (1.76 g, 5.19 mmol) gave a red oil (0.30 g, 0.59 mmol, 11%). Eluent petroleum ether/ethyl acetate 85:15. − $^1H$ NMR (400 MHz) δ = 7.43−7.28 (m, 5 H, ArH), 4.25−4.06 (m, 2 H, H-14), 3.57−3.47 (m, 2 H, H-13), 3.08−2.98 (m, 2 H, H-3), 2.61−2.37 (m, 2 H, H-16), 1.86−1.33 (m, 20 H). − $^{13}C$ NMR (100 MHz) δ = 278.10 (Cr=C), 223.43, 218.46 (CO), 137.28−123.48 (Ar), 87.94 (C-18), 82.12 (C-17), 62.65 (C-14), 52.74 and 50.45 (C-13, C-3), 29.36, 28.09, 26.65, 26.41, 25.46, 24.78, 24.56, 23.66, 22.38, 21.76, 16.83. − MS (*m*/*z*) for $C_{28}H_{33}NO_5Cr$ [403 (M − 4CO)].

**Thermolysis of Complex 15d:** Thermolysis of **15d** (1.74 g, 4.17 mmol) was carried out in boiling anhydrous benzene (150 mL) for 22 h. After evaporation of the solvent under vacuum, the residue was purified by chromatography on silica gel. Elution with petroleum ether/ethyl acetate 70:30 gave **16d** (92 mg, 0.36 mmol, 9%) as a solid; m.p. 42°C. − IR ($CHCl_3$): $\tilde{\nu}$ = 1703, 1648 $cm^{-1}$. − $^1H$ NMR (400 MHz) δ = 7.43−7.31 (m, 5 H, ArH), 2.96 (dd, *J* = 13.7 and 4.5, 1 H, H-3), 2.92 (d, *J* = 6.5, 1 H, H-8b), 2.84−2.81 (m, 1 H, H-5), 2.81−2.75 (m, 1 H, H-6), 2.29 (dt, *J* = 10.3, 1 H, H-8a), 2.32−2.22 (m, 3 H, H-3, H-5, H-6), 2.21−1.78 (m, 3 H, H-4, H-7, H-8), 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) δ = 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), 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. − Elution with petroleum ether/ethyl acetate 90:10 gave **17d** as an oil. − IR ($CHCl_3$): $\tilde{\nu}$ = 1660, 1575 $cm^{-1}$. − $^1H$ NMR (400 MHz) δ = 7.35−7.19 (m, 5 H, ArH), 3.33−3.24 (m, 2 H, H-5, H-6), 3.30 (d, *J* = 5.6, 1 H, H-2), 3.09−3.02 (m, 2 H, H-5, H-6), 2.64−2.61 (m, 1 H, H-2a), 2.45−2.37 (m, 1 H, H-8), 2.27−2.19 (m, 1 H, H-8), 2.14−2.10 (m, 1 H, H-3), 2.01−1.76 (m, 4 H, H-4, H-7), 1.45−1.35 (m, 1 H, H-3). − $^{13}C$ NMR (100 MHz) δ = 198.04 (CO), 171.98 (C-8b), 140.43, 128.64, 128.56, 126.66 (Ar), 108.04 (8a), 58.15 (C-2), 49.54 (C-5, C-6), 46.14 (C-2a), 25.82 (C-3), 23.33, 21.47 (C-4, C-7), 18.15 (C-8). − HRMS: calcd for $C_{17}H_{19}NO$ ($M^+$) 253.1467; found 253.1470.

Further elution with petroleum ether/ethyl acetate 90:10 gave **18d** as a solid (258 mg, 1.02 mmol, 24%); m.p. 183°C. − IR ($CHCl_3$): $\tilde{\nu}$ = 1660, 1570 $cm^{-1}$. − $^1H$ NMR (400 MHz) δ = 7.23−6.97 (m, 5 H, ArH), 3.73 (d, *J* = 6.8, 1 H, H-2), 3.17−3.13 (m, 2 H, H-5, H-6), 3.00−2.83 (m, 3 H, H-2a, H-5, H-6), 2.38−2.35 (m, 2 H, H-8), 2.21−2.17 (m, 1 H, H-8), 1.91−1.75 (m, 4 H, H-4, H-7), 1.36−1.31 (m, 1 H, H-3), 0.68−0.59 (m, 1 H, H-3). − $^{13}C$ NMR (100 MHz) δ = 198.55 (CO), 173.33 (C-8b), 139.34, 128.93, 128.42, 128.08, 126.42 (Ar), 109.21 (C-8a), 55.16 (C-2), 49.24 (C-5, C-6), 40.68 (C-2a), 23.01, 21.31 (C-3, C-4, C-7), 17.77 (C-8). − HRMS: calcd for $C_{17}H_{19}$ NO ($M^+$) 253.1467; found 253.1470.

**Thermolysis of Complex 15e:** Using the same procedure, 1.5 g (3.49 mmol) of **15e** gave, after silica-gel chromatography with petroleum ether/ethyl acetate 20:80, **17e** as an oil (58 mg, 0.27 mmol, 6%); − IR ($CHCl_3$): $\tilde{\nu}$ = 1650, 1560 $cm^{-1}$. − $^1H$ NMR (400 MHz) δ = 7.25−7.08 (m, 5 H, ArH), 3.50−3.43 (m, 1 H, H-6), 3.38−3.26 (m, 2 H, H-7), 3.10−3.06 (m, 2 H, H-2, H-6), 2.65−2.53 (m, 1 H, H-2a), 2.31−2.10 (m, 3 H, H-3, H-9), 1.92−1.74 (m, 4 H, H-4, H-5, H-8), 1.47−1.34 (m, 3 H, H-3, H-4, H-5). − $^{13}C$ NMR (100 MHz) δ = 197.86 (CO), 175.84 (C-9b), 141.57, 128.66, 127.87, 126.62 (Ar), 107.57 (C-9a), 59.73 (C-2), 54.43 (C-6), 51.74 (C-7), 49.86 (C-2a), 34.19 (C-3), 29.90 (C-4, C-5), 21.77 (C-8), 17.71 (C-9). − HRMS: calcd for $C_{18}H_{21}NO$ ($M^+$) 267.1623; found 267.1618.

Elution with petroleum ether/ethyl acetate 98:2 gave **18e** as a solid (42 mg, 0.16 mmol, 5%); m.p. 49°C. − IR ($CHCl_3$): $\tilde{\nu}$ = 1645, 1560 $cm^{-1}$. − $^1H$ NMR (400 MHz) δ = 7.29−6.99 (m, 5 H, ArH), 3.84 (d, *J* = 7.1, 1 H, H-2), 3.52−3.49 (m, 1 H, H-6), 3.37−3.26 (m, 2 H, H-7), 3.10−3.05 (m, 1 H, H-6), 3.03−2.98 (m, 1 H, H-2a), 2.30−2.21 5m, 2 H, H-9), 1.81−1.73 (m, 4 H, H-4, H-5, H-8), 1.37−1.13 (m, 3 H, H-3, H-4, H-5), 0.87−0.71 (m, 1 H, H-3). − $^{13}C$ NMR (100 MHz) δ = 198.57 (CO), 176.34 (C-9b), 139.10, 130.42, 128.14, 126.56 (Ar), 108.52 (C-9a), 55.67 (C-2), 54.49 (C-6), 51.86 (C-7), 43.92 (C-2a), 31.10 (C-3), 29.94, 29.37 (C-4, C-5), 21.75 (C-8), 17.73 (C-9). − HRMS: calcd for $C_{18}H_{21}NO$ ( $M^+$) 267.1623; found 267.164.

**Thermolysis of Complex 15f:** 1.5 g (3.48 mmol) of **15f** gave, after purification using petroleum ether/ethyl acetate 70:30 as the eluent, **16f** (110 mg, 0.41 mmol, 12%) as a solid; m.p. 103°C. − IR ($CHCl_3$) $\tilde{\nu}$ = 1705, 1648 $cm^{-1}$. − $^1H$ NMR (400 MHz) δ = 7.34−7.19 (m, 5 H, Ar), 3.16−3.12 (m, 1 H, H-5), 2.99−2.88 (m, 3 H, H-3, H-6, H-9b), 2.73−2.67 (m, 1 H, H-9a), 2.29−2.11 (m, 4 H, H-3, H-5, H-6, H-9), 2.02−1.96 (m, 1 H, H-8), 1.85−1.79 (m, 1 H, H-7), 1.76−1.61 (m, 3 H, H-4, H-7), 1.58−1.49 (m, 2 H, H-8, H-9). − $^{13}C$ NMR (100 MHz) δ = 205.85 (CO), 167.65 (C-2a), 137.37 (C-2), 131.01, 129.30, 128.29, 127.85 (Ar), 68.12 (C-9b), 62.95 (C-5), 54.80 (C-6), 53.64 (C-9a), 26.69 (C-3), 26.39 (C-4), 25.60 (C-8), 25.11 (C-7), 23.92 (C-9). − HRMS: calcd for $C_{18}H_{21}NO$ ($M^+$) 267.1623, found 267.1620.

Elution with petroleum ether/ethyl acetate 60:40 gave **17f** as a solid (323 mg, 1.21 mmol, 35%); m.p. 150°C. − IR ($CHCl_3$): $\tilde{\nu}$ = 1650, 1568 $cm^{-1}$. − $^1H$ NMR (400 MHz) δ = 7.27−7.08 (m, 5 H, ArH), 3.35−3.26 (m, 3 H, H-5, H-6), 3.14 (d, *J* = 5.1, 1 H, H-2), 3.08−3.02 (m, 1 H, H-5), 2.58−2.45 (m, 2 H, H-2a, H-9), 2.35−2.27 (m, 1 H, H-9), 2.10−2.02 (m, 1 H, H-3), 1.93−1.65 (m, 5 H, H-4, H-7, H-8), 1.55−1.49 (m, 1 H, H-8), 1.39−1.28 (m, 1 H, H-3). − $^{13}C$ NMR (100 MHz) δ = 200.95 (CO), 172.16 (C-9b), 140.70, 128.64, 128.50, 126.66 (Ar), 111.80 (C-9a), 57.14 (C-2),

56.82 (C-6), 51.52 (C-5), 47.19 (C-2a), 28.67 (C-7), 26.51 (C-8), 25.21 (C-3), 24.08 (C-9), 22.93 (C-4). − $C_{18}H_{21}NO$ (267): calcd C 80.90, H 7.87, N 5.24; found C 80.75, H 7.86, N 5.13.

Elution with petroleum ether/ethyl acetate 50:50 gave **18f** (19 mg, 0.07 mmol, 2%) as a white solid; m.p.158°C. − IR ($CHCl_3$): $\tilde{\nu}$ = 1650, 1565 $cm^{-1}$. − $^1H$ NMR (400 MHz) δ = 7.20−6.98 (m, 5 H, ArH), 3.69 (d, *J* = 7.6, 1 H, H-2), 3.31−3.24 (m, 3 H, H-5, H-6), 3.02−2.89 (m, 2 H, H-2a, H-5), 2.62−2.55 (m, 1 H, H-9), 2.36−2.29 (m, 1 H, H-9),1.93−1.70 (m, 5 H, H-4, H-7, H-8), 1.65−1.56 (m, 1 H, H-8), 1.36−1.29 (m, 1 H, H-3), 0.74−0.61 (m, 1 H, H-3). − $^{13}C$ NMR (100 MHz) δ = 201.74 (CO), 174.08 (C-9b), 139.77, 129.44, 128.44, 126.81 (Ar), 113.94 (C-9a), 56.58 (C-6), 54.31 (C-2), 51.99 (C-5), 42.28 (C-2a), 28.67 (C-7), 26.67 (C-8), 23.65 (C-9), 23.41 (C-4), 23.06 (C-3). − HRMS: calcd for $C_{18}H_{21}NO$ ($M^+$) 267.1623; found 267.1622.

**Thermolysis of Complex 15g:** 1.8 g (4.7 mmol) of **15g** gave, after chromatography on silica gel with petroleum ether/ethyl acetate 70:30, compound **17g** (432 mg, 1.58 mmol, 35%) as a solid, m.p. 91°C. − IR ($CHCl_3$): $\tilde{\nu}$ = 1650, 1560 $cm^{-1}$. − $^1H$ NMR (400 MHz) δ = 7.22−7.06 (m, 5 H, ArH), 3.60−3.53 (m, 1 H, H-6), 3.47−3.38 (m, 2 H, H-6, H-7), 3.12−3.06 (m, 2 H, H-2, H-7), 2.65−2.61 (m, 1 H, H-2a), 2.48−2.32 (m, 2 H, H-10), 2.12−2.08 (m, 1 H, H-3), 1.92−1.71 (m, 6 H, H-4, H-5, H-8, H-9), 1.49−1.35 (m, 3 H, H-3, H-4, H-8). − $^{13}C$ NMR (100 MHz) δ = 200.65 (C=O), 179.40 (C-10b), 141.63, 128.68, 127.81, 126.62 (Ar), 113.74 (C-10a), 60.38 (C-2), 55.46 (C-7), 55.38 (C-6), 50.59 (C-2a), 34.70 (C-3), 29.60 (C-4), 29.26 (C-8), 28.57 (C-5), 25.56 (C-9), 21.23 (C-10). − HRMS: calcd for $C_{19}H_{23}NO$ 281.1780; found 281.1769.

Elution with petroleum ether/ethyl acetate 60:40 gave **18g** (225 mg, 0.8 mmol, 17%) as a solid, m.p. 144°C. − IR ($CHCl_3$): $\tilde{\nu}$ = 1645, 1560 $cm^{-1}$. − $^1H$ NMR (400 MHz) δ = 7.22−6.99 (m, 5 H, ArH), 3.86 (d, *J* = 7.1, 1 H, H-2), 3.57−3.51 (m, 2 H, H-6, H-7), 3.48−3.40 (m, 1 H, H-6), 3.10−3.06 (m, 1 H, H-7), 2.99−2.94 (m, 1 H, H-2a), 2.47−2.43 (m, 2 H, H-10), 1.88−1.64 (m, 5 H, H-4, H-5, H-8, H-9), 1.46−1.14 (m, 3 H, H-3, H-4, H-8), 0.83−0.73 (m, 1 H, H-3). − $^{13}C$ NMR (100 MHz): δ = 201.73 (CO), 180.86 (C-10b), 139.50, 130.70, 128.52, 126.92 (Ar), 111.03 (C-10a), 56.55 (C-2), 55.75 (C-6, C-7), 45.09 (C-2a), 31.60, 29.99, 29.21, 28.84, 25.81, 21.33 (C-3, C-4, C-5, C-8, C-9, C-10). − HRMS: calcd for $C_{19}H_{23}NO$ ($M^+$) 281.1780; found 281.1768.

**Thermolysis of Complexes 15d and 15g in the Presence of Ethanol:** Complex **15d** (1.7 g, 4.08 mmol) was heated at reflux in a mixture of benzene (150 mL) and ethanol (35 mL) for 22 h. After evaporation of the solvents, the residue was purified by chromatography on silica gel and the different products separated and characterized as above. − The same reaction was repeated on complex **15g** (1.59 g, 3.35 mmol).

**X-ray Crystal Structure Determination of Compounds 16d and 17f:** Accurate cell dimensions and orientation matrices were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collections. Complete crystallographic data and collection parameters are listed in Table x. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[14] Scattering factors and corrections for anomalous absorption were taken from ref.[15] The structures were solved by direct methods. (SHELXS).[16] Refinements were carried out by full-matrix least-squares. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were introduced in calculated positions and only one overall isotropic thermal parameter was refined. Selected bond lengths and bond angles are listed in Tables y and z.

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-116001 and -116002. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].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