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Journal of Organometallic Chemistry 567 (1998) 101–117

Journal of Organometallic Chemistry

Reaction of aminocarbene complexes of chromium with alkynes 9. From nitrogen ylid complexes toward alkaloid frameworks

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Received 16 October 1997; received in revised form 5 January 1998

Abstract

Aminocarbene complexes of chromium having the general structure $(CO)_5Cr{=}C(R)NR_1R_2$ react with diphenylacetylene to give pyrrolinones as the result of the insertions of the alkyne, of CO and the migration of an alkyl group from nitrogen to a carbon atom in α or γ with respect to the nitrogen atom. The mechanism of this new reaction has been thoroughly investigated: a nitrogen ylid originating from the interaction of the nitrogen atom of the starting aminocarbene complex with the central carbon of the ketene formed by insertion of the alkyne and of CO into the aminocarbene complex, is a crucial intermediate in these reactions. This ylid complex, the structure of which could be established as **25**, leads to the observed pyrrolinones upon thermolysis. Mechanisms involving radicals have been discarded on the grounds of the reaction of cyclopropylcarbinyl-substituted aminocarbene complexes **45a,b**: no rearrangement of the cyclopropylcarbinyl group is observed upon its migration, as shown by the X-ray structure of the pyrrolinone **46b**. Mechanisms involving ion pairs or the participation of the metal have also been eliminated. For that purpose, the X-ray structures of two complexes, **51** and **52**, in which the metal is not bound to the phenyl ring of the migrating groups, have been established. Finally, concerted (l,5) sigmatropic migrations of the alkyl groups from nitrogen to the carbons of the five-membered heterocycle in **25** account best for the observed results. The role of the metal could also be determined by the examination of the reactivity of the metal-free *N*-ylides. No rearrangement similar to that observed for complexes **25** is observed; only products arising from the cleavage of the bond between nitrogen and the central carbon of the ketene were obtained. As an application of this original reaction of carbene complexes, the synthesis of **102**, **103**, **105** and **106** which are derivatives of the lycorane alkaloid will be described: the keypoint is the use of intramolecular insertions of alkynes into suitably substituted aminocarbene complexes of chromium **101** and **104**.

Keywords: Aminocarbenes; Chromium; Alkyne insertions; *N*-ylide complexes

1. Introduction

An early achievement of organometallic chemistry was to make visible to the eye the structure of unstable organic species, by their coordination to a suitably substituted transition metal and by carrying out the X-ray structure of the adduct. Quite often, however, these unstable species had to be synthesized in the coordination sphere of the metal. This could be done by the choice of a stable precursor complex.[1].

Let us examine the case of organic carbenes **1**. Although these unstable species can be detected by physical methods, stratagems had to be found in order to increase their stability, by modification of their structure as soon as formed. A way to detect these species easily by UV spectroscopy is to allow them to react with pyridine at low temperatures, an interaction which

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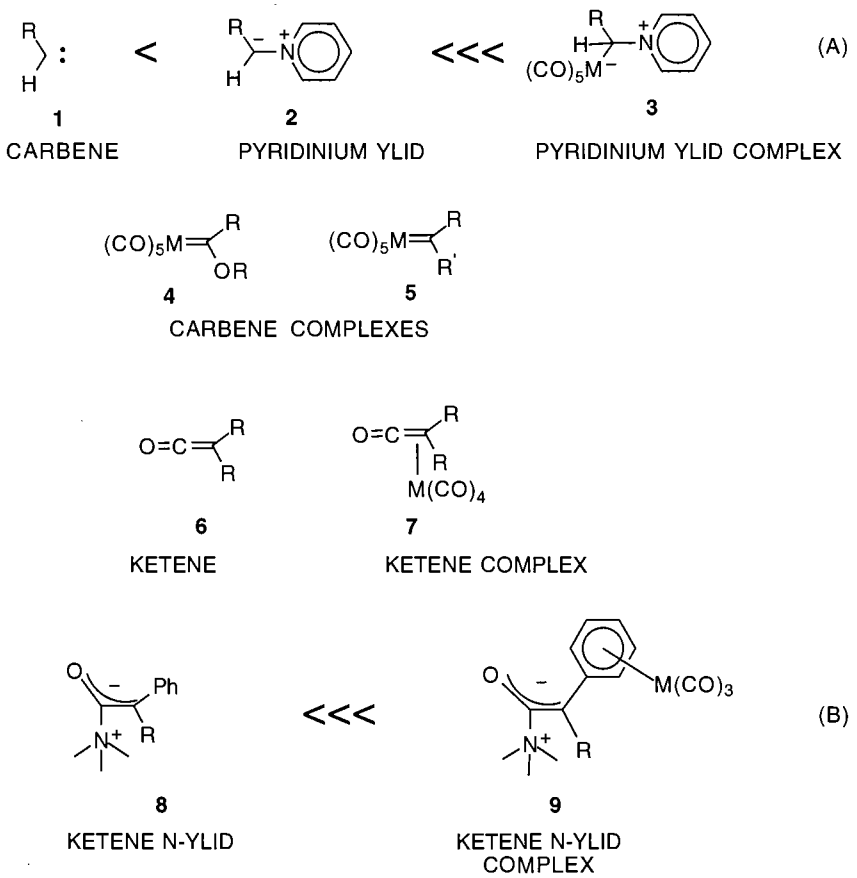
0022-328X/98/$19.00
PII S0022-328X(98)00672-X



Scheme 1.

leads to new adducts, pyridinium ylids **2**, yet not isolable, the lifetime of which is nevertheless considerably lengthened [2] (Scheme 1(A)).

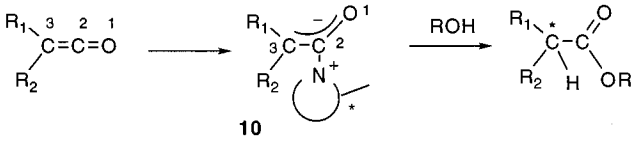
However, a prominent example of the remarkably stabilizing properties of transition metals came from the work of E.O. Fischer who prepared, from a transition metal coordinated CO group, stable carbene complexes of the type **4** [3]. Later on, a few less stable complexes of the type **5** could also be isolated [4–6].

Very recently, we discovered that pyridinium ylids of the type **2** could also be stabilized by their coordination to a transition metal and isolated as room temperature stable complexes **3** [7]. Their synthesis relies on the analogy which exists between alkoxycarbene complexes of the type **4** and carbonyl compounds and was also carried out in the coordination sphere of the metal: reduction of alkoxycarbene complexes of chromium and tungsten with dihydropyridines led indeed to stable pyridinium ylid complexes **3**. Therefore, a tremendous increase of the stability is also observed in going from **1** to **3** (Scheme 1(A)).

In contrast to carbenes, ketenes **6** are much more stable and can, for some of them, be prepared, isolated, and handled at room temperature. Others have to be prepared at low temperature or stabilized in the form of complexes of the structure **7** [8–10]. Like carbenes, they react even at low temperature, with pyridine or tertiary amines to give very labile adducts, pyridinium or tetraalkylammonium ylids **8**, detectable by infra-red spectroscopy [11,12].

In the present review, we demonstrate that such nitrogen ylids derived from ketenes can be synthesized in the coordination sphere of chromium by the insertion of alkynes into aminocarbene complexes of this metal, and can be isolated in several cases as stable complexes **9** via ketene complexes **7**. As for **2**, an important increase in the stability is observed upon coordination to a metal center (Scheme 1(B)). Moreover, it will be shown that the thermolysis of the ylid complexes **9** leads to lactams by migration of an alkyl group from the positively charged nitrogen to the negatively charged carbon, a transformation which is reminiscent of the Stevens rearrangement of organic nitrogen ylids.

The intramolecular version of this reaction will be examined in detail and applied successfully to the synthesis of elaborate heterocyclic compounds such as derivatives of the lycorane alkaloids.



Scheme 2.

2. Results and discussion

2.1. Interaction of tertiary amines with ketenes: experimental and theoretical approaches

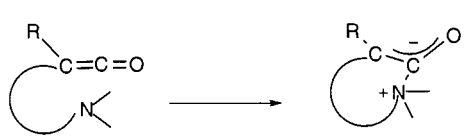
The interaction of tertiary amines with ketenes, in a reversible way, leading to nitrogen ylid intermediates, has been suspected in several reactions. Examples which are well documented are the addition of chloral to ketenes in the presence of a tertiary amine, of imines to ketenes, the addition of alcohols to ketenes, leading to optically active esters, in the presence of a chiral tertiary amine (Scheme 2) [13–15]. However, the suspected intermediates **10** could not even be detected by physical methods. Molecular orbital calculations from this laboratory confirmed however the existence, as labile intermediates of such ylids. Important modifications of the charges on the interacting species are observed with an increase of the negative charge on oxygen and a decrease of the negative charge on nitrogen. Delocalization of the negative charge is also observed on C-3, the terminus of the ketene function [16].

Stabilization of such intermediates might be achieved by two approaches:

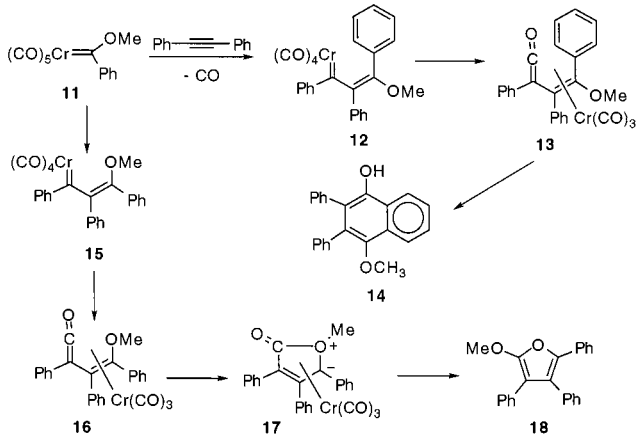
- By an intramolecular reaction, starting from an amine tethered to a ketene, the distance between the two functions being judiciously adjusted (Scheme 3).
- By withdrawal of the negative charge on the terminal carbon of the ketene, such as in **9**, to render the central carbon of the ketene more electrophilic.

2.2. Origin of the ketenes and the ketene complexes: the benzannulation reaction

That ketenes and ketene complexes can be formed by CO insertions into carbene complexes of transition metals is well established. Of special interest for our approach to nitrogen ylids are the mechanistic aspects of the well known benzannulation reaction of alkoxycarbene complexes discovered by Dötz [17]. The present status of this reaction as far as the mechanism is concerned is the following: Aryl (and vinyl)-substituted



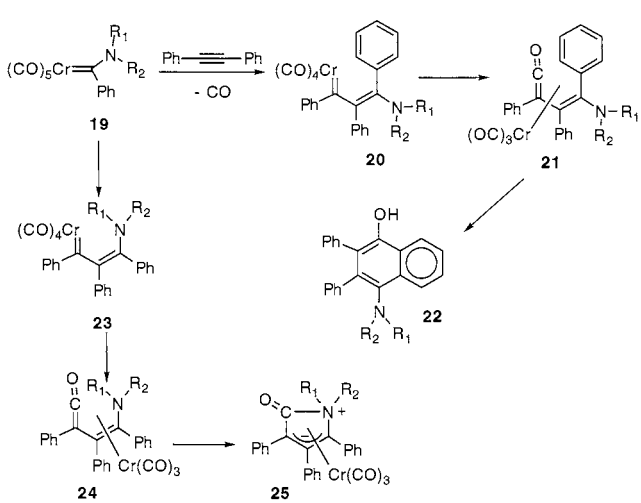
Scheme 3.



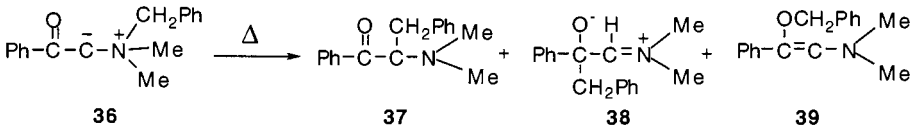
Scheme 4.

alkoxycarbene complexes of chromium **11** react with alkynes, to lead successively via a carbene complex **12** and a ketene complex **13**, to a phenol **14**. The spatial proximity of the phenyl ring to the ketene function allows an electrocyclization reaction to occur on the intermediate **13**. It is clear that the opposite geometry, as in **16**, would not lead to annulation products but rather, via an oxonium ylid **17**, to the alkoxyfurane **18**, a minor product which is indeed observed in this reaction (Scheme 4).

In the case of aminocarbene complexes **19** bearing a vinyl and more scarcely a phenyl group on the carbene carbon, we [16,18] and others [19] demonstrated that similar annulation reactions could also take place and lead to aminophenols **22** via **20** and **21**. However in that case, the configuration **24** in which the tertiary amine is *cis* to the metal, is of the highest interest since the nitrogen atom is now in close proximity to the central carbon atom of the ketene **24**. The formation of a five-membered *N*-ylid complex **25** should thus be possible (Scheme 5).



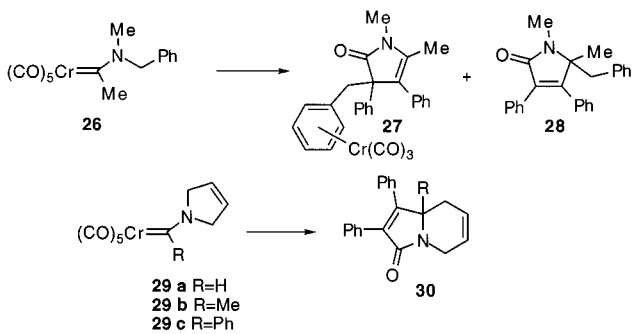
Scheme 5.



Scheme 6.

2.3. The unexpected reactions of alkyl and phenyl substituted aminocarbene complexes with alkynes

A way to avoid the annulation reaction is to start from alkyl-substituted aminocarbene complexes. Although less reactive than alkoxycarbene complexes towards alkynes, aminocarbene complexes of chromium undergo insertion reactions with alkynes at the reflux temperature of benzene. Thus complex **26** led to two pyrrolinones **27** and **28** upon its reaction with diphenylacetylene [20]. The structure of these products, established by X-ray crystallography for **27**, confirmed the insertion of the alkyne and of CO as in the benzannulation reaction, but also the migration of the benzyl group from nitrogen to the γ-carbon for the main product **27**, or to the α-carbon for the minor product **28**. A similar behavior was observed for pyrroline-substituted carbene complexes **29a,b,c**. The same insertions, accompanied by the cleavage of a carbon–nitrogen bond of the five-membered ring and migration of the alkyl chain from nitrogen to the α-position led to bicyclic pyrrolinones **30a,b,c** even in the case of complex **29c** (R = Ph) [21].



These unexpected products are most probably, as we will see, the result of the formation and the rearrangement of *N*-ylid complexes **33** and **35** originating from the aminoketene complexes **32** and **34**.

2.4. Analogy with the Stevens rearrangement of organic N-ylids

Migrations of alkyl groups from nitrogen to carbon are well known in organic chemistry. They occur in the Stevens rearrangement of nitrogen ylids of the type **36** [22].

Such ylids are easily prepared from tertiary α-aminoketones via their ammonium salts, and undergo a thermal rearrangement with migration of a substituent from nitrogen to the α-carbon (**36**→**37**), akin to that observed in the above reactions of aminocarbene complexes (Scheme 6).

As minor pathways, migrations on the carbon and on the oxygen of the carbonyl group were also observed in some special cases (**36**→**38** + **39**) [23]. Applied to the reaction of complex **26**, a plausible mechanism might indeed involve the formation and rearrangement of an ylid complex **33**, and lead by migration of the benzyl group, to the observed pyrrolinones **27** and **28**. Similarly, complex **29** might give, after the insertion reaction the *N*-ylid complex **35** (Scheme 7).

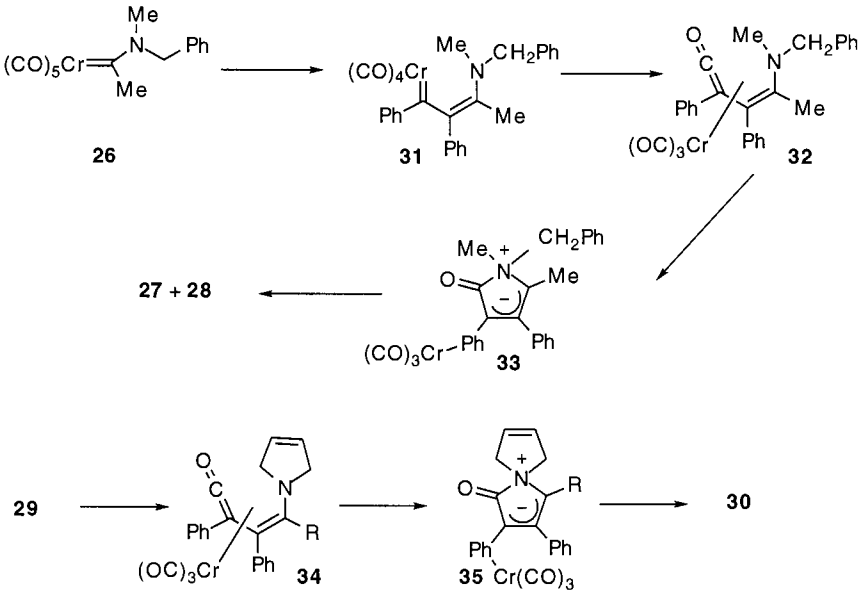
Opening of the five-membered unsaturated ring followed by a carbon–carbon bond formation, would then give the bicyclic compound **30**.

This series of results is thus in strong agreement with the intermediate formation of *N*-ylid complexes upon insertions of alkynes and CO, into aminocarbene complexes of chromium. Attempts were thus made to detect, possibly to characterize, and to try to rearrange such intermediates into lactams.

2.5. Isolation and rearrangement of N-ylid complexes obtained from aminocarbene complexes of chromium. Confirmation of the postulated mechanism.

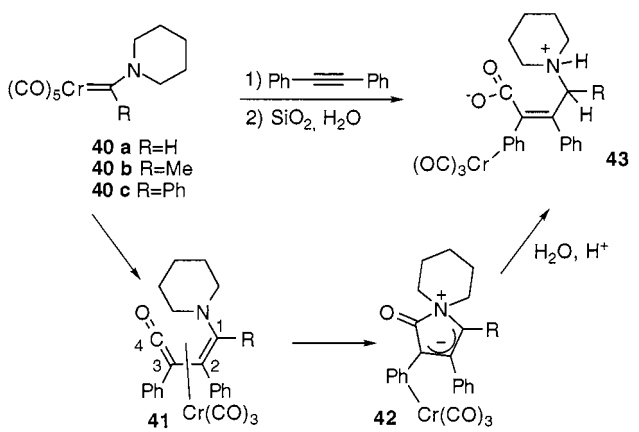
The aminocarbene complexes examined so far bore on nitrogen either a benzyl group as in **26**, or an allyl group as in **29**. It is known from investigations on the Stevens rearrangement of organic *N*-ylids that the propensity for the migration is very high for the allyl and the benzyl groups, the ylid **36** being indeed very unstable, even at room temperature. However, this propensity is much lower for alkyl groups, falling almost to zero in the case of piperidine-substituted ylids: in the latter case, cleavage of the ylid with liberation of the tertiary amine is observed (Scheme 8) [24].

We reasoned therefore that the chance to isolate an *N*-ylid complex from the reaction of an aminocarbene complex with an alkyne would be the highest for aminocarbene complexes derived from piperidine or from dialkyl-substituted amines. And this was indeed the case. Thus a series of aminocarbene complexes **40a,b,c** derived from piperidine was prepared. The reaction of **40a** with diphenylacetylene in cyclohexane or benzene led, after 12 h at reflux temperature, to the formation of a yellow precipitate which appeared to be unstable on silica gel (TLC) and to give a very polar complex. Attempts to purify this precipitate by silica gel



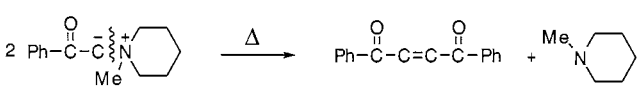
Scheme 7.

chromatography led indeed to a complex which according to its physical data and to the X-ray crystallography, was the chromium tricarbonyl complex of the aminoacid **43**, the hydrolysis product of the intermediate aminoketene complex **41**.



Thus purification of the precursor of the aminoacid by silica gel had to be avoided. Crystallization in anhydrous solvents appeared to be the method of choice for its purification. After much effort, crystals suitable for an X-ray structure determination could finally be grown. Clearly, as shown in Fig. 1, the precursor of the aminoacid is the *N*-ylid complex **42** and not the aminoketene complex **41**. A bond exists between the nitrogen atom and the central carbon of the former ketene function as shown by the C(4)–N(1) bond distance, 1.590 Å, the non-linearity of the former ketene function with an angle C(3)–C(4)–O(1) of 138°, and the tetrahedral geometry at the nitrogen atom: the interaction of this complex with water induces, in the presence of acidic silica gel, the rupture of the C(4)–N(1) bond with formation of the aminoacid complex **43**.

The same type of *N*-ylid complexes could be isolated from the piperidine-substituted carbene complexes **40b,c** (R=CH_3, Ph), the most stable ylid complex being **42c**. Aminocarbene complexes derived from dialkyl-



Scheme 8.

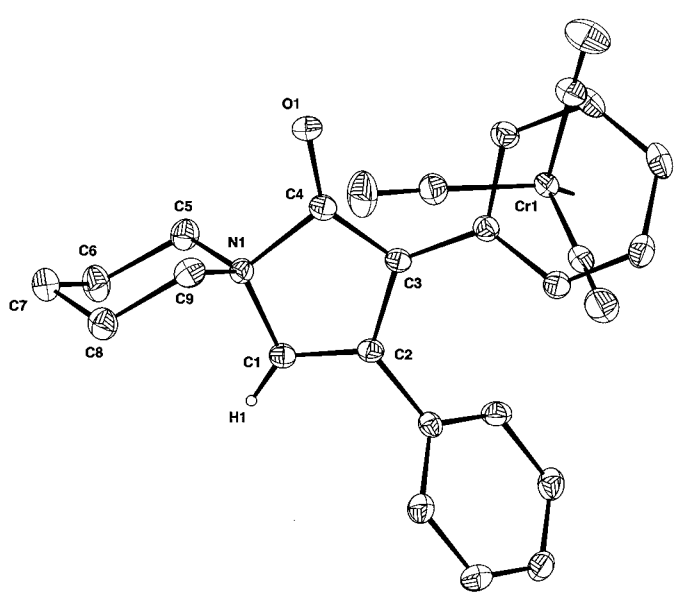
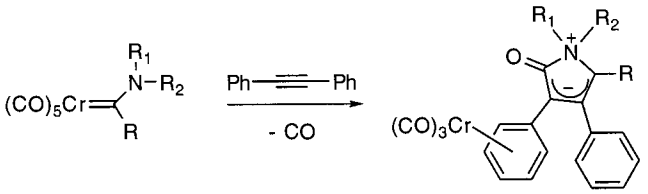


Fig. 1. ORTEP projection of complex **42c** with the atom numbering scheme.

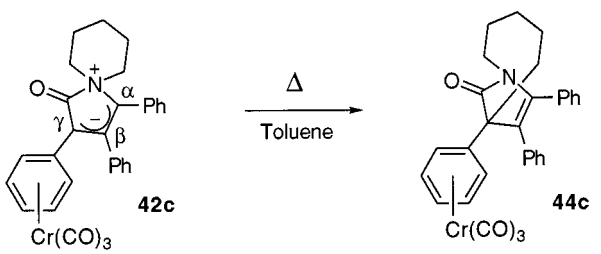
amines (dimethylamine, methylcyclopropylamine) behaved similarly, and led to fairly stable ylid complexes.



R=H $R_1R_2=(CH_2)_5$	60%
R=Me $R_1R_2=(CH_2)_5$	70%
R=Me $R_1=R_2=Me$	80%
R=Ph $R_1=R_2=Me$	55%
R=Me $R_1=Me$ $R_2=Cyclopropyl$	57%
R=Ph $R_1=Me$ $R_2=Cyclopropyl$	47%

The point was therefore to know if these *N*-ylides would undergo a rearrangement, akin to that observed in the direct transformation of aminocarbene complexes such as **26** and **29** into **27**, **28** and **30**.

Since the *N*-ylid proved to be stable up to the reflux temperature of benzene, attempts were made to rearrange them in boiling toluene: and indeed clean reactions were observed leading in high yield to the expected lactams, the structure of which was also confirmed by X-ray crystallography (**42c** → **44c**).



The rearrangement of these *N*-ylid complexes into bridgehead lactams or pyrrolinones was of a general scope. It is thus likely that the direct formation of pyrrolinones upon insertion of alkynes into aminocarbene complexes, occurs also via the intermediary of N-ylid complexes.

2.6. Rearrangement of the N-ylid complexes: mechanistic aspects

The Stevens rearrangement of purely organic *N*-ylids has been thoroughly studied. Depending on the nature of the substituents, it was found to be concerted (for allyl groups) or radicalar (for benzyl groups). In this latter case, tight radical pairs are involved, since a chiral carbon radical (C(H)MePh) was transferred without racemization. A rearrangement via ion pairs has also been discarded. Side reactions, in which migrations to the carbon or to the oxygen atom of the carbonyl group took place, were also observed.

As far as the rearrangement of the *N*-ylid complexes is concerned, a general trend appeared. In most cases,

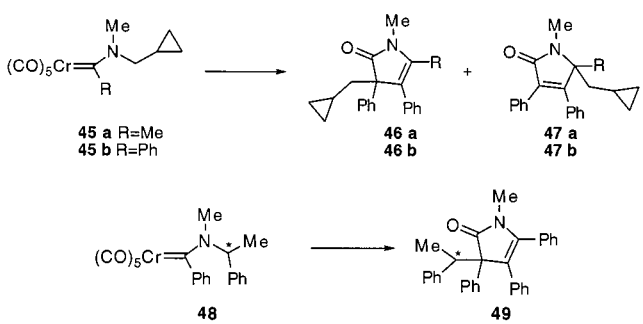
Scheme 9.

the main product of the reaction arose from the migration from nitrogen to the γ-carbon, even for *N*-ylides derived from large cyclic amines. The question that could be raised was thus about the mechanism of these migrations: will it be radicalar, metal-assisted or concerted? or by ion pairs?

2.7. Reaction of the cyclopropylcarbinyl carbene complexes 45a and 45b with diphenylacetylene: migration without rearrangement of the cyclopropylcarbinyl group

A powerful tool for the detection of radicalar pathways in rearrangement reactions, is to use the cyclopropylcarbinyl substituent as the migrating group: the cyclopropylcarbinyl radical ring-opening is indeed a very fast reaction leading to the homoallyl radical (Scheme 9) [25]. Thus, if such a radical were formed during the rearrangement of the intermediate ylid complexes, products bearing instead the butenyl group should be detected, at least in part.

We synthesized thus carbene complexes **45a** and **45b** by aminolysis of the corresponding alkoxycarbene complexes with cyclopropylcarbinylamine. They were obtained in, respectively, 70 and 65% yield. Reaction with diphenylacetylene led in both cases to a mixture of pyrrolinones **46a,b** and **47a,b** in, respectively, 29 and 5% yields, and 62 and 7% yields. However, no compound bearing the butenyl group could be detected.



45 a R=Me
45 b R=Ph

46 a
46 b

47 a
47 b

48

49

Confirmation of the structure of these products and especially of the presence of the cyclopropylcarbinyl group was obtained by NMR spectroscopy, and the location of the group that migrated by X-ray crystallography carried out on **46b**. The ORTEP projection is shown in Fig. 2 with the most important bond distances and bond angles in Table 4. As in the previous cases, the cyclopropylcarbinyl group migrated from nitrogen to the γ-carbon. It is thus likely that a radicalar mechanism can be excluded at least for the main pathway. In

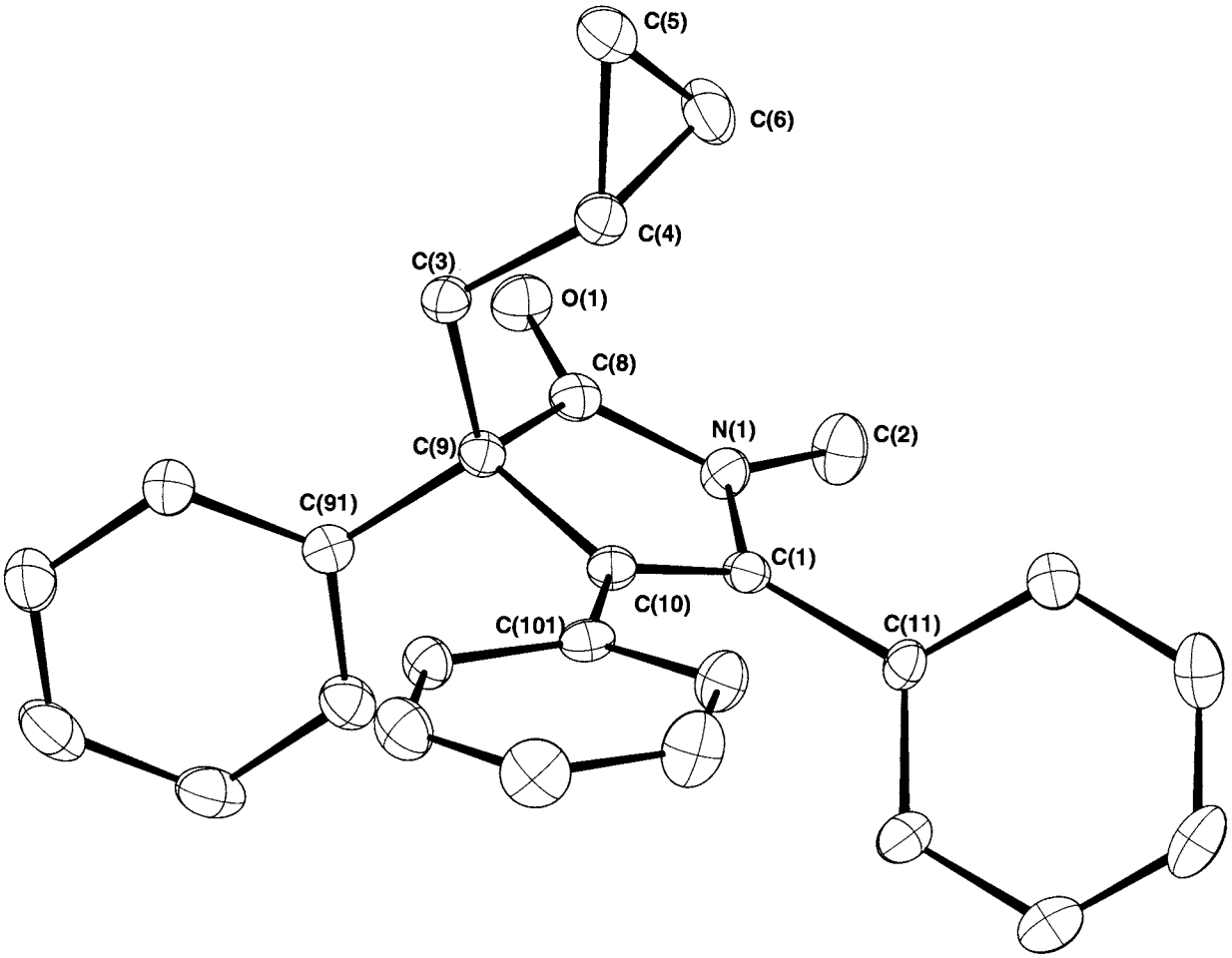


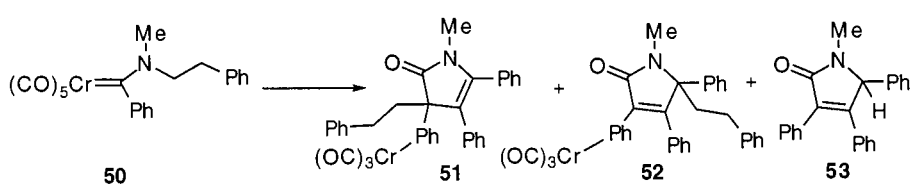
Fig. 2. CAMERON projection of complex **46b** with the atom numbering scheme.

agreement with the preceding finding, albeit less convincing, is the behavior of complex **48**, bearing on nitrogen a chiral methylbenzyl group CHPhMe. Almost complete retention (or complete inversion) at the chiral center was observed in the insertion products **49**, as demonstrated by NMR spectroscopy [27].

2.8. Metal-assisted rearrangement

Since the metal is present from the beginning of the reaction until the formation of the final products in most of the examined reactions, a metal-assisted migration cannot be excluded and might even be a sound hypothesis.

In most of the pyrrolinones isolated as $Cr(CO)_3$ complexes, the metal is coordinated to the phenyl group in α to the carbonyl, thus very close to the site of the former carbene carbon and of the inserted CO group. There was however an exception: insertion of diphenylacetylene into complex **26** derived from *N*-methylbenzylamine led to a $Cr(CO)_3$ complex of pyrrolinones **27** in which the metal is coordinated to the phenyl of the transferred benzyl group: this might be an indication for the involvement of the metal in the migration reaction. If so, a similar behavior could be expected for complex **50**, the $Cr(CO)_3$ group ending up on the phenyl of the homobenzyl group. However, this was not the case: the X-ray structures of both pyrrolinones **51** and **52** confirmed indeed that the $Cr(CO)_3$ group is on the phenyl in α to the carbonyl. Their ORTEP projections are shown on Figs. 3 and 4, the most important bond distances and angles being gathered in Tables 5 and 6.



50 51 52 53

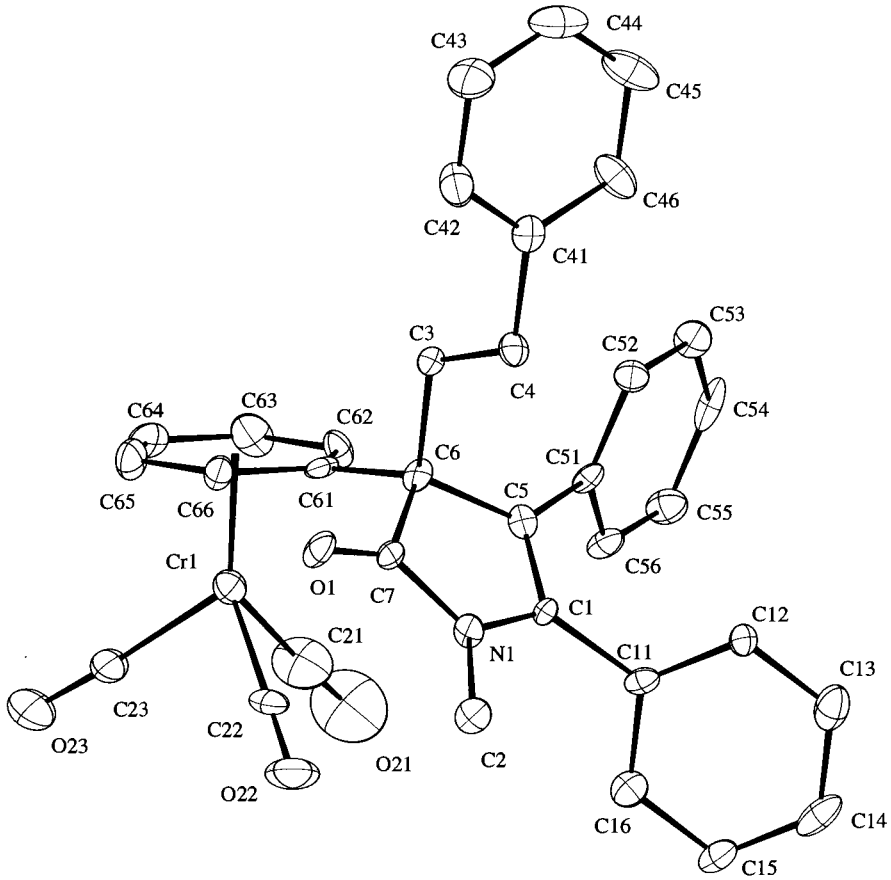
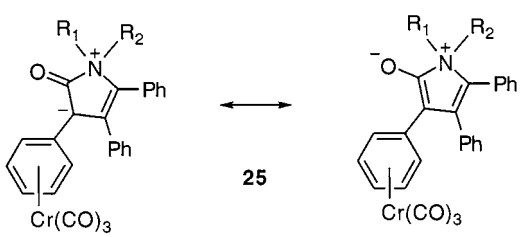


Fig. 3. CAMERON projection of complex **51** with the atom numbering scheme.

It is also interesting to notice at this point the surprising formation of the pyrrolinone **53** in which the CH_2CH_2Ph group is missing. This might be an indication for a radicalar process, with escape of the migrating radical. Such loss of migrating groups has precedents both in this chemistry [26], in the case of a migrating methyl group, and in the Stevens rearrangement of benzyl-substituted *N*-ylides [24].

2.9. The concerted (1,5)-sigmatropic rearrangement

One of the resonance forms of the *N*-ylid complex is **25**: it can be compared to a substituted cyclopentadiene.



Hexaalkylated cyclopentadienes like substituted pyrrazoles are known to undergo thermal rearrangements by (1,5)-sigmatropic migrations of a substituent from the tetrahedral carbon center [28–30]. The migratory group remains here continuously and covalently bonded to the rest of the molecule as transfer from one ring atom to another proceeds.

Such a process, occurring in a concerted manner, could also take place in the case of the *N*-ylid complexes described herein. Two clockwise (1,5)-sigmatropic migrations would bring the alkyl group from nitrogen to the carbon in α to the carbonyl group via the carbonyl carbon, whereas a counterclockwise (1,5) migration would lead to a product bearing the alkyl group on the α-carbon with respect to nitrogen (Scheme 10). Both experimental and theoretical results are in agreement with such a proposal.

Molecular orbital calculations on complex **25** confirmed indeed that the rearrangement was not under charge control but rather under orbitalar control, the charges being localized on oxygen and on nitrogen, whereas the largest coefficients of the HOMO are on the γ-carbon, the experimentally most often observed site of migration.

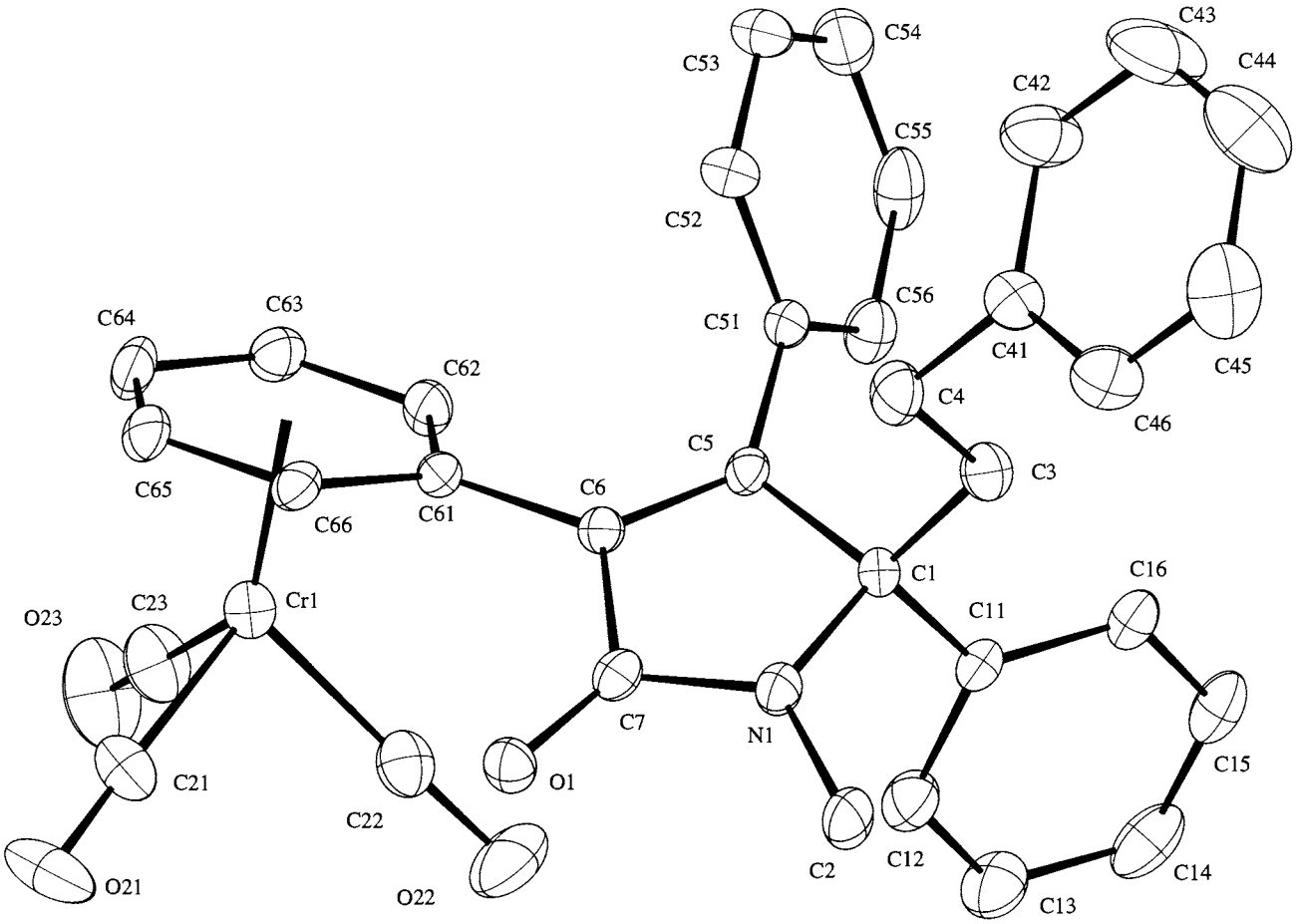
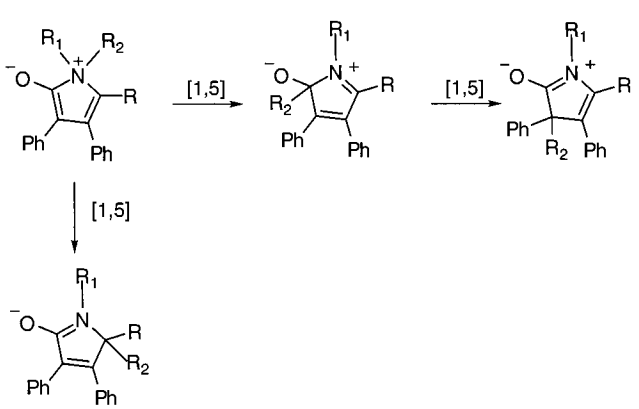


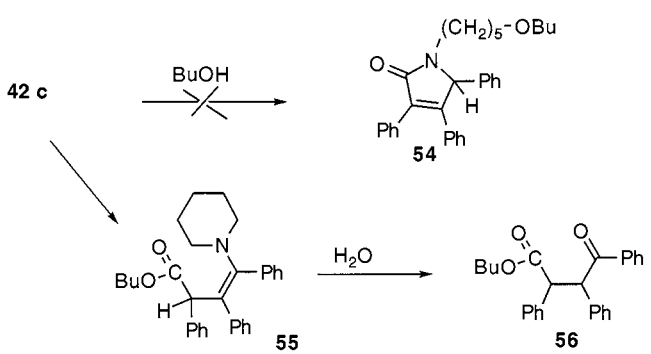
Fig. 4. CAMERON projection of complex **52** with the atom numbering scheme.

2.10. Mechanism by ion pairs

A mechanism by ion pair does not operate here, even partially, since the rearrangement carried out in the presence of methanol or in pure butanol did not lead to ethers such as **54**. Instead, cleavage of the C(4)–N(1) bond took place with formation of esters **56**, thus the same reaction as observed with water which led to the aminoacid **43**.



Scheme 10.



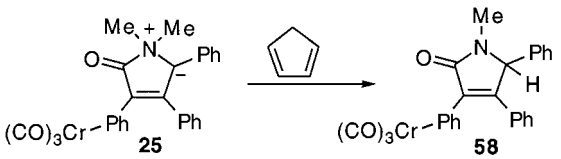
2.11. Role of the metal

Besides inducing the insertion of the alkyne and of CO, the metal probably plays an important role in the formation and the stabilization of the intermediate *N*-ylid complexes. It is striking to notice that in all of the stable *N*-ylid complexes isolated so far, the metal is coordinated to a phenyl group located in α with

respect to the carbonyl group. This benzylic α-carbon bears an important amount of the negative charge due to the interaction of the nitrogen atom with the central carbon of the ketene, according to semi-empiricl AM1 calculations [16]. Now it is also known that benzylic carbanions are stabilized by the coordination of the $Cr(CO)_3$ group to the phenyl ring. It results that, due to the presence of the metal, the reverse reaction, the formation of the enaminoketene from the *N*-ylid complex is unlikely.

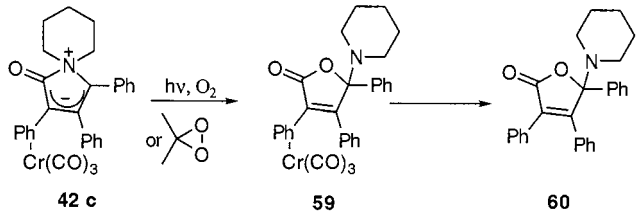
A way to confirm this assumption would be either to carry out a typical reaction of ketenes on the ylid complexes **25**, or to remove the metal from the *N*-ylid complexes and to see whether the rearrangement reaction would be suppressed.

As far as the first option is concerned, ketenes are known to give cycloaddition products with olefins; however, when complex **25** was refluxed in benzene in the presence of cyclopentadiene, no cycloaddition reaction was observed. Instead a protonation-demethylation of the *N*-ylid leading to **58** took place. Cyclopentadiene is thus an acid strong enough to protonate the ylid, its conjugated base being then able to remove a methyl group from the positively charged nitrogen atom [31].



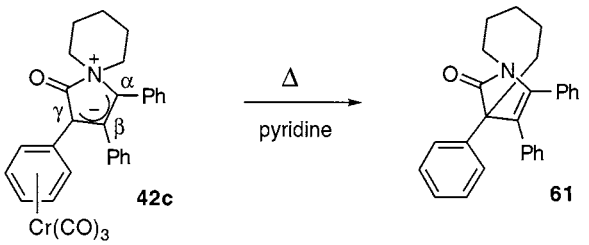
25 **58**

In the case of the second option, a classical method to remove a $Cr(CO)_3$ group from an aromatic ring is to oxidize the metal with oxygen under irradiation or to heat the complex in the presence of pyridine. However, in the case of complex **42c**, both methods led to unexpected results [32]. Although the metal could be removed by oxidation, a first reaction leading to a complexed aminolactone complex **59** resulting from the insertion of an oxygen atom between C(1) and C(4) and cleavage of the C(1)–N(1) bond took place, followed by a second oxidation in which the metal was finally removed to give the aminolactone **60**. Use of the milder oxidation reagent dimethyldioxirane led to the same clean results.



42 c **59** **60**

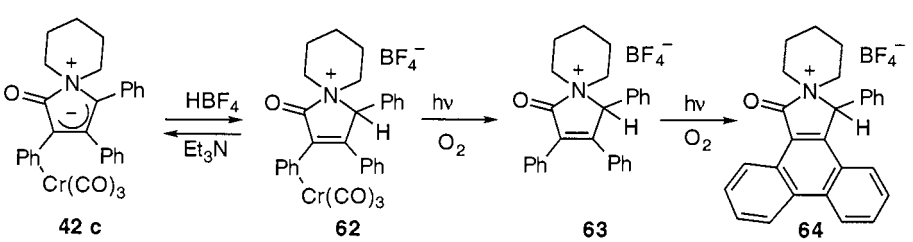
Use of the second approach was also negative. The main product of the reaction of the ylide complex **42c** with pyridine was the rearranged bridgehead lactam **61**.



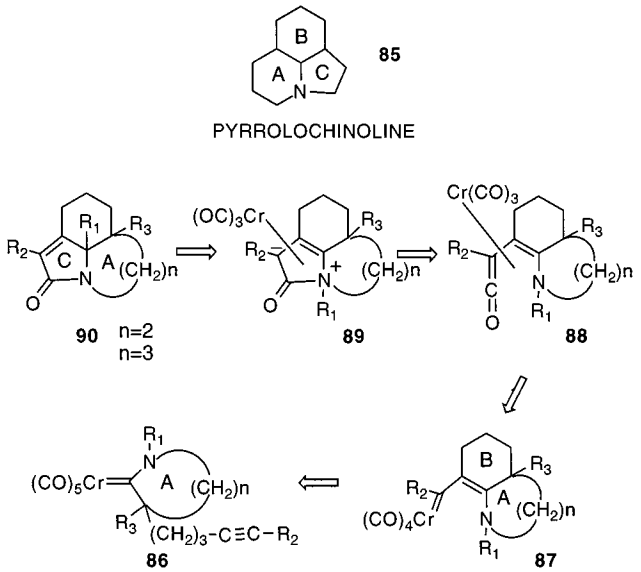
42c **61**

An indirect method had thus to be found in order to remove the metal without destroying the complex. Protonation of the ylid complex takes place very easily as exemplified by the behavior of the weak acid cyclopentadiene (vide supra). Such a protonation occurs also on silica gel, and can also be carried out with trifluoroacetic acid, or with fluoroboric acid. In this latter case, a stable complex could be isolated as dark-red crystals and fully characterized by X-ray crystallography. Protonation at the carbon α to nitrogen took place giving a very stable piperidinium tetrafluoroborate **62**. This reaction is reversible since deprotonation of complex **62** with triethylamine took place quantitatively, at room temperature.

Decoordination of the metal could be accomplished as above under oxygen with UV or sunlight irradiation. The stepwise formation of two metal-free piperidinium fluoroborates **63** and **64** was observed [32], the first one being the expected metal-free product, and the second one arising from **63** by a known photochemical oxidative cyclization reaction [33].

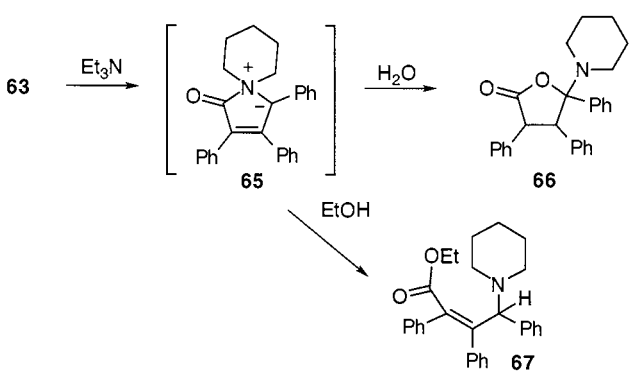


42 c **62** **63** **64**



Scheme 11.

Since deprotonation of complex **62** with triethylamine could be carried out at room temperature with quantitative regeneration of the starting *N*-ylid complex **42c**, attempts to convert the metal-free piperidinium fluoroborate **63** into the metal-free *N*-ylid **65** were undertaken. Although the deprotonation reaction took place as expected, the *N*-ylid was not obtained. Instead, trace amounts of water converted the assumed intermediate **65** into one of its hydrolysis products, the aminolactone **66**, whereas in the presence of ethanol, even at low temperature, the aminoester **67** was obtained.



According to this latter result the role of the metal is double:

- During the process of formation of these ylids complexes, it activates the ketene for the nucleophilic addition of the tertiary amine.
- It then stabilizes the benzylic anion in the ylid complex by release of negative charge. Removal of the metal weakens the bond between the nitrogen atom and the central carbon of the former ketene: as observed, easy solvolysis to the acid or the lactone can take place.

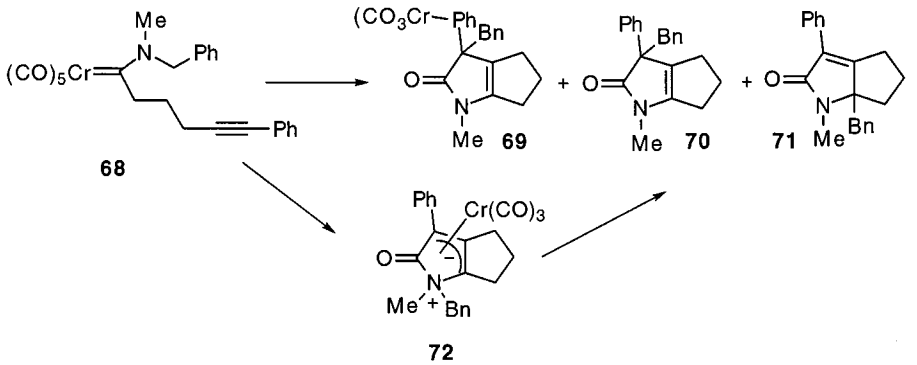
2.12. Intramolecular insertion reactions

So far we have demonstrated that aminocarbene complexes could be used for the synthesis of original pyrrolinones and bridgehead lactams. More interesting as far as the structure of the products is concerned, will be the application of this chemistry to intramolecular insertion reactions.

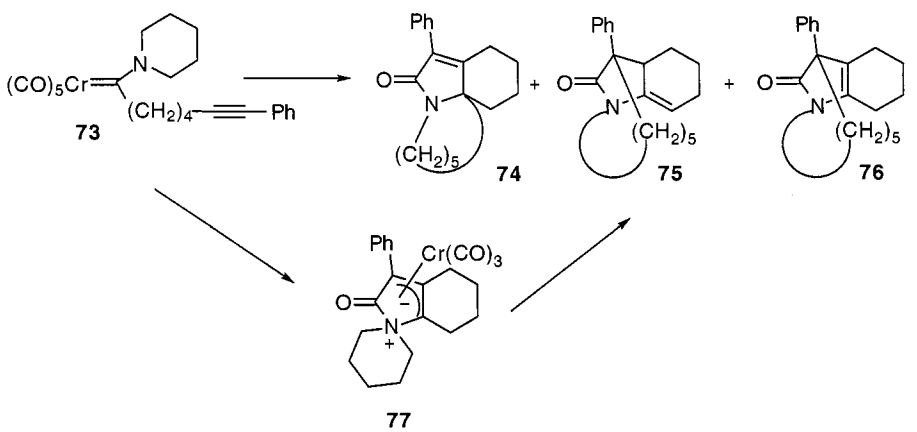
One of the simplest complexes which was submitted to an intramolecular insertion reaction had structure **68** bearing thus a benzyl group, the propensity for the migration of which is known to be high. Its thermolysis in boiling benzene led to a mixture of complexed and metal-free bicyclic compounds **69**, **70** and **71**, the structure of which could be established by NMR spectroscopy and for complex **69**, by X-ray crystallography [34].

Table 1
Crystal data for **46b** $C_{27}H_{25}NO$

Formula weight	379.5
a (Å)	12.655(3)
b (Å)	18.802(5)
c (Å)	8.983(11)
α (°)	90
β (°)	91.86(8)
γ (°)	90
V (Å^3)	2136
Z	4
Crystal system	Monoclinic
Space group	P $2_1/n$
Linear absorption coefficient μ (cm^{-1})	0.66
Density ρ (g cm^{-3})	1.18
Diffractometer	Philips PW1100
Radiation	Mo—Kα ($\lambda = 0.71069$ Å)
Scan type	$\omega/2\theta$
Scan range (°)	$0.8+0.345$ tgθ
θ Limits (°)	2–25
Temperature or measurement	Room temperature
Octants collected	−15,15; 0,22; 0,10
Nb of data collected	4153
Nb of unique data collected	3632
Nb of unique data used for refinement	1541 $(Fo)^2 > 3\sigma(Fo)^2$
R_{int}	0.019
$R = \Sigma\|\|Fo\|-\|Fc\|\|/\Sigma wFo\|$	0.0482
$R_w = [\Sigma w(\|Fo\|-\|Fc\|)^2/\Sigma wFo^2]^{1/2}$	0.0483
Extinction parameter	No
Nb of variables	263
$\Delta\rho$min (e Å^{-3})	−0.20
$\Delta\rho$max (e Å^{-3})	0.47

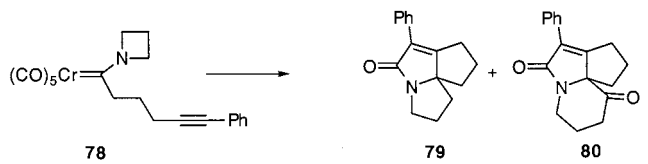


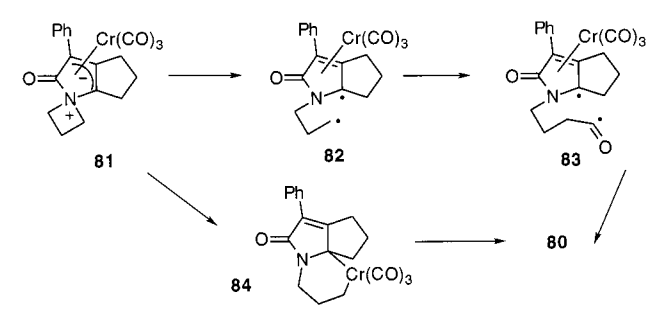
The three compounds originate probably from a common, non-isolated intermediate **72**, a nitrogen ylid complex, the rearrangement of which, according to the same mechanism as above, can give either **69** or **70**, the main products of the reaction, by migration of the benzyl group from nitrogen to the γ-carbon, or in the case of **70**, by migration to the α-carbon with respect to the nitrogen atom.



As a second example, we choose complex **73** derived from piperidine: its thermolysis should lead to a stable piperidinium ylid complex if the insertion reaction follows the same pathway as for the intermolecular insertion reactions. Therefore, two type of reactions were carried out: the first one in toluene which led to a mixture of three tricyclic compounds **74**, **75**, and **76** in 40% yield; the second one in cyclohexane, which gave a new complex the spectroscopic data of which agreed with structure **77**, a tricyclic *N*-ylid complex. Its thermolysis in toluene gave the same series of tricyclic lactams **74**, **75**, and **76** in 38% yield, as in the direct insertion reaction [34].

As far as the mechanistic points of the rearrangement are concerned, the behavior of complex **78** derived from azetidine, was of special interest. Its thermolysis did not lead to the expected bridgehead lactam but to the azatriquinane **79**, probably for steric reasons. Interestingly, a second tricyclic product **80** was also isolated in 12% yield. Its structure, close to that of **79**, contains an extra carbonyl group.





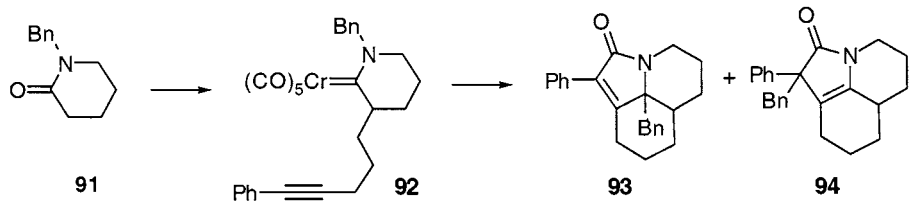
This result is of importance and constitutes a strong indication for a partial non-concerted rearrangement of the intermediate *N*-ylid complex **81**. Its formation might be the result of a radicalar pathway (**81**→**82**) with formation of an acyl radical **83**, upon insertion of CO, followed by a ring closure to **80**. Such a sequence has indeed recently been described in the chemistry of alkyl radicals [35].

It might also be the result of a metal-mediated rearrangement, a nucleophilic ring-opening giving **84** followed by a cyclocarbonylation reaction (**81** → **84** → **80**). This is thus the second example showing clearly that depending on the nature of the substituents, the rearrangement can follow several distinct pathways.

2.13. Approach to the synthesis of alkaloid skeletons

Having demonstrated that the intramolecular version of the alkyne insertion reaction into aminocarbene complexes could lead in good yields to elaborate polycyclic compounds, we attempted to use this new reaction for the synthesis of alkaloid skeletons related to lycorane [36]. Derivatives of this alkaloid have inter alia interesting anti-tumor properties. The tricyclic skeleton which is found in the lycorane alkaloids, a pyrrolochinoline **85**, might be obtained at least on paper, from aminocarbene complexes of the general structure **86** via successive insertion of the triple bond, of CO, formation of a nitrogen-ylid complex, followed by its rearrangement according to the retrosynthetic Scheme 11 (**87** → **90**) [37].

In order to test the possibilities of such an approach to the pyrrochinoline skeleton, we synthesized the carbene complex **92** from the corresponding lactam **91** according to the method of Hegedus [38]. Thermolysis of complex **92** led to a mixture of two tricyclic products **93** and **94** in, respectively, 18 and 49% yields. Their structures were assigned by the use of two dimensional NMR spectroscopy.



91 92 93 94

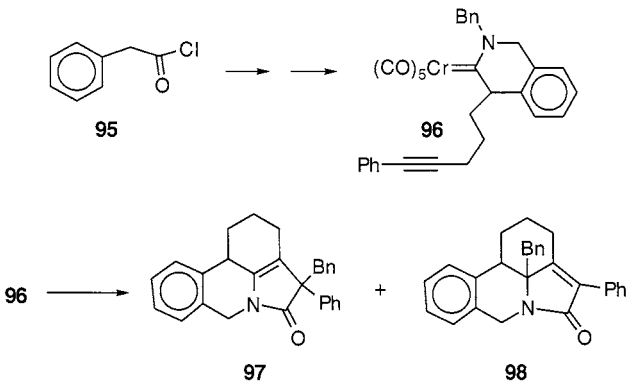
Table 2
Crystal data for **51** $C_{34}H_{27}NO_4Cr$

Formula weight	565.6
a (Å)	18.924(4)
b (Å)	9.100(1)
c (Å)	17.011(9)
α (°)	90
β (°)	94.43(4)
γ (°)	90
V (Å^3)	2921
Z	4
Crystal system	Monoclinic
Space group	C c
Linear absorption coefficient μ (cm^{-1})	4.17
Density ρ (g cm^{-3})	1.29
Diffractometer	Philips PW1100
Radiation	Mo—Kα ($\lambda = 0.71069$ Å)
Scan type	$\omega/2\theta$
Scan range (°)	$1.1+0.345$ tgθ
θ Limits (°)	2–25
Temperature of measurement	Room temperature
Octants collected	−22,22; 0,10; 0,20
Nb of data collected	2852
Nb of unique data collected	2562
Nb of unique data used for refinement	1524 (Fo)$^2 > 2\sigma$(Fo)^2
R_{int}	0.025
$R = \Sigma\|\|Fo\|-\|Fc\|\|/\Sigma wFo\|$	0.0598
$R_w = [\Sigma w(\|Fo\|-\|Fc\|)^2/\Sigma wFo^2]^{1/2}$	0.0627
Extinction parameter	No
Nb of variables	313
$\Delta\rho$min (e Å^{-3})	−1.01
$\Delta\rho$max (e Å^{-3})	0.88

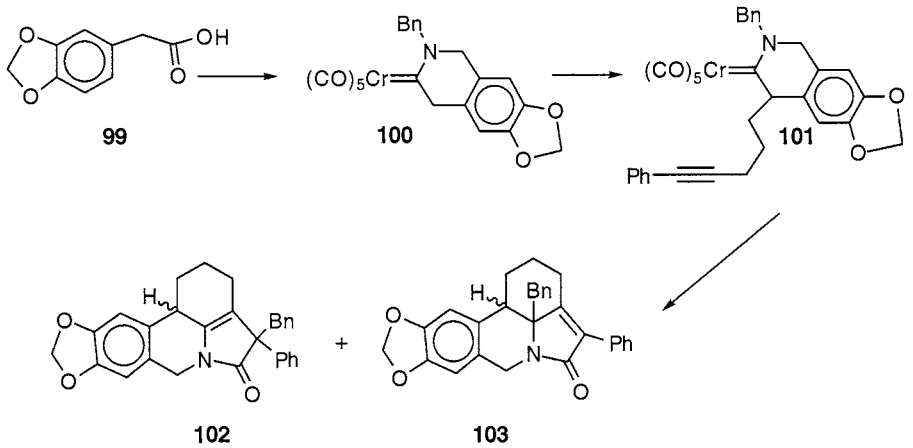
Table 3
Crystal data for **52** $C_{34}H_{27}NO_4Cr,CH_2Cl_2$

Formula weight	650.5
a (Å)	10.982(5)
b (Å)	11.330(1)
c (Å)	14.803(5)
α (°)	100.55(7)
β (°)	95.26(2)
γ (°)	115.13(2)
V (Å^3)	1596
Z	2
Crystal system	Triclinic
Space group	P-1
Linear absorption coefficient μ (cm^{-1})	5.55
Density ρ (g cm^{-3})	1.35
Diffractometer	Philips PW1100
Radiation	Mo—Kα ($\lambda = 0.71069$ Å)
Scan type	$\omega/2\theta$
Scan range (°)	$0.9+0.345$ tgθ
θ Limits (°)	2–22.5
Temperature of measurement	Room temperature
Octants collected	−11,11; −12,11; 0,15
Nb of data collected	4055
Nb of unique data collected	3832
Nb of unique data used for refinement	1968 (Fo)$^2 > 2\sigma$(Fo)^2
R_{int}	0.0213
$R = \Sigma\|\|Fo\|-\|Fc\|\|/\Sigma wFo\|$	0.0569
$R_w = [\Sigma w(\|Fo\|-\|Fc\|)^2/\Sigma wFo^2]^{1/2}$	0.0585
Extinction parameter	28
Nb of variables	390
$\Delta\rho$min (e Å^{-3})	−0.45
$\Delta\rho$max (e Å^{-3})	0.45

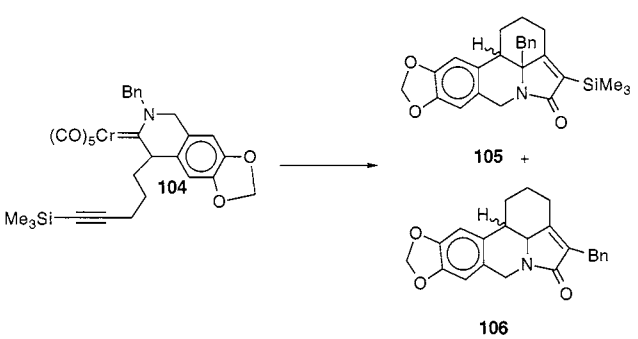
A further step towards the synthesis of the lycorane skeleton was achieved by the synthesis and successful thermolysis of complex **96**. This complex was obtained in several steps from the acid chloride **95**. Heating of this carbene complex in benzene led to the expected products **97** and **98** in 43 and 19% yields, their structures being again ascertained by extended NMR spectroscopies.



Finally, the precursor **101** which was supposed to lead to the substituted lycoranes was synthesized from the acid **99**. Its thermolysis led to the sought-after lycorane derivatives **102** and **103** in 44.5 and 30% yields.



In order to keep the possibility to further modify the structure of the insertion products, the carbene complex **104** bearing a trimethylsilyl group instead of a phenyl group on the triple bond, was also synthesized.



Its thermolysis led to two compounds **105** and **106**, albeit in lower yield, one of the products having lost its trimethylsilyl group during the silica gel purification step [39].

Thus, important structural modifications of the starting carbene complexes do not hinder the normal course of the alkyne insertion reactions, the same sequence being always observed: insertion of the alkyne, insertion of CO, formation of an ylid complex, and rearrangements with nitrogen to carbon migrations.

Table 4
Selected bond lengths (Å) and bond angles(°) for **46b**

Bond lengths (Å)			
O(1)–C(8)	1.215(5)	N(1)–C(1)	1.412(6)
N(1)–C(2)	1.452(6)	N(1)–C(8)	1.358(6)
C(1)–C(10)	1.349(6)	C(1)–C(11)	1.481(6)
C(3)–C(4)	1.506(6)	C(3)–C(9)	1.537(6)
C(4)–C(5)	1.504(7)	C(4)–C(6)	1.506(7)
C(5)–C(6)	1.508(7)	C(8)–C(9)	1.542(6)
C(9)–C(10)	1.541(6)	C(9)–C(91)	1.527(6)
C(10)–C(101)	1.471(6)		
Bond angles (°)			
C(1)–N(1)–C(2)	128.1(4)	C(1)–N(1)–C(8)	111.1(3)
C(2)–N(1)–C(8)	120.9(4)	N(1)–C(1)–C(10)	111.3(4)
N(1)–C(1)–C(11)	118.7(4)	C(10)–C(1)–C(11)	130.0(4)
C(4)–C(3)–C(9)	113.4(4)	C(3)–C(4)–C(5)	120.4(4)
C(3)–C(4)–C(6)	120.4(4)	C(5)–C(4)–C(6)	60.1(3)
C(4)–C(5)–C(6)	60.0(3)	C(4)–C(6)–C(5)	59.9(3)
O(1)–C(8)–N(1)	126.5(4)	O(1)–C(8)–C(9)	125.7(4)
N(1)–C(8)–C(9)	107.8(4)	C(3)–C(9)–C(8)	108.1(4)
C(3)–C(9)–C(10)	111.8(4)	C(8)–C(9)–C(10)	101.6(4)
C(3)–C(9)–C(91)	114.8(4)	C(8)–C(9)–C(91)	107.0(3)
C(10)–C(9)–C(91)	112.5(4)	C(1)–C(10)–C(9)	108.2(4)
C(1)–C(10)–C(101)	129.1(4)	C(9)–C(10)–C(101)	122.4(4)

3. Conclusion

The examination of the reaction of aminocarbene

Table 5
Selected interatomic distances (Å) and bond angles (°) for **51**

Interatomic distances (Å)			
N(1)–C(1)	1.41(1)	N(1)–C(2)	1.45(1)
N(1)–C(7)	1.36(1)	O(1)–C(7)	1.20(1)
C(1)–C(5)	1.36(2)	C(1)–C(11)	1.49(1)
C(3)–C(4)	1.52(2)	C(3)–C(6)	1.56(1)
C(4)–C(41)	1.51(1)	C(5)–C(6)	1.55(1)
C(5)–C(51)	1.48(1)	C(6)–C(7)	1.57(2)
C(6)–C(61)	1.56(1)		
Bond angles (°)			
C(1)–N(1)–C(2)	125.8(9)	C(1)–N(1)–C(7)	112.9(g)
C(2)–N(1)–C(7)	121.1(10)	N(1)–C(1)–C(5)	111.4(g)
N(1)–C(1)–C(11)	121.3(9)	C(5)–C(1)–C(11)	127.1(10)
C(4)–C(3)–C(6)	116.0(9)	C(3)–C(4)–C(41)	111.5(9)
C(1)–C(5)–C(6)	107.4(10)	C(1)–C(5)–C(51)	125.2(9)
C(6)–C(5)–C(51)	127.4(10)	C(3)–C(6)–C(5)	113.7(9)
C(3)–C(6)–C(7)	108.2(9)	C(5)–C(6)–C(7)	102.7(9)
C(3)–C(6)–C(61)	105.5(8)	C(5)–C(6)–C(61)	116.4(8)
C(7)–C(6)–C(61)	110.2(9)	N(1)–C(7)–0(1)	125.8(10)
N(1)–C(7)–C(6)	105.7(10)	O(1)–C(7)–C(6)	128.4(10)

complexes of chromium with alkynes, has been at the origin of interesting results both on a mechanistic and synthetic point of view. New polar arene tricarbonyl chromium nitrogen ylids could be isolated and fully characterized. They lead by an unexpected rearrangement highly dependent on the presence of the metal, to original heterocyclic compounds, the most elaborate being derivatives of alkaloids of the lycorane type. Work is in progress in using the same approach for the synthesis of pyrrolizidine, lupinine and stemona alkaloid skeletons.

4. Experimental

4.1. 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 carried out with Merck silica gel (70-230 mesh) using various ratios of ethyl acetate (EtOAc)/light petroleum ether (PE) or dichloromethane/light petroleum ether as eluent. All reagents were obtained from commercial suppliers and used as received. Reactions were carried out 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.

4.2. Pentacarbonyl (N-methyl-cyclopropylcarbinyl) benzylidene chromium (0) **45b**

That compound was obtained from $(CO)_5Cr{=}C(Ph)OEt$ (4 g, 12.3 mmol) and (cyclopropylmethyl)amine (1 ml, 11.9 ml) in diethyl ether (80 ml) at room temperature. The reaction is instantaneous. Evaporation of the solvent followed by filtration of the residue through short column of silica gel with petroleum ether/methylene chloride (95/5) as eluent gave $(CO)_5Cr{=}C(Ph)NH(C_4H_7)$ (3.12 g, 74%) as a yellow oil. Spectral data: ^{1}H-NMR ($CDCl_3$) δ (two isomers) 9.15 (s, 1H, NH, E), 8.71 (s, 1H, NH, Z), 7.46–6.80 (m, 5H, Ar), 3.96 (q, 2H, NCH_2, Z), 3.05 (q, 2H, NCH_2, E), 1.26 (m, 1H, CH, Z), 1.06 (m, 1H, CH, E), 0.75–0.26 (m, 4H, CH_2); ^{13}C-NMR ($CDCl_3$) δ 281.41 (Cr=C), 223.38, 217.32 (CO), 128.70, 128.59, 127.79, 126.77, 121.09, 119.04 (Ar), 58.51, 55.70 (NCH_2), 10.45, 10.26, 4.08, 3.78 (CH, CH_2). MS calcd for $C_{16}H_{13}O_5NCr$, 351 (M^+), found 351.

A solution of $(CO)_5Cr{=}C(Ph)NH(C_4H_7)$ in THF (60 ml) was treated at -60°C with LDA (10.24 mmol) in THF (20 ml). Then methyl iodide (1 ml, 15.9 mmol) was introduced. After heating to room temperature, the solvent was evaporated, the residue hydrolyzed and extracted as usual. The residue was then chromatographed on silica gel. Elution with petroleum ether/dichloromethane (95/5) gave complex **45b** (2.4 g, 77%) as a yellow oil. Spectral data of **45b** (mixture of E, Z isomers):^{1}H-NMR ($CDCl_3$) δ 7.42–6.68 (m, 5H, Ar), 4.20 (d, $J = 6.8$ Hz, 2H, CH_2, Z), 4.03 (s, 3H, CH_3, E), 3.21 (d, $J = 6.8$ Hz, 2H, CH_2, E), 3.08 (s, 3H, CH_3, E), 1.25 (m, CH, Z), 0.91 (m, CH, E), 0.85–0.11 (m, 4H, CH_2); ^{13}C-NMR ($CDCl_3$) δ 274.51 and 273.34 (Cr=C), 224.10 and 217.40 (CO), 153.15, 152.36, 129.35, 128.70, 128.40, 126.89, 125.75, 119.23, 118.81 (Ar), 67.87 and 62.34 (NCH_2), 49.04 and 43.09 (NCH_3), 10.26, 10.07,

Table 6
Selected interatomic distances (Å) and bond angles (°) for **52**

Interatomic distances			
O(1)–C(7)	1.222(9)	N(1)–C(1)	1.47(1)
N(1)–C(2)	1.46(1)	N(1)–C(7)	1.351(9)
C(1)–C(3)	1.53(1)	C(1)–C(5)	1.53(1)
C(1)–C(11)	1.54(1)	C(3)–C(4)	1.55(1)
C(4)–C(41)	1.50(1)	C(5)–C(6)	1.32(1)
C(5)–C(51)	1.48(1)	C(6)–C(7)	1.52(1)
C(6)–C(61)	1.49(1)		
Bond angles (°)			
C(1)–N(1)–C(2)	123.2(6)	C(1)–N(1)–C(7)	113.8(7)
C(2)–N(1)–C(7)	122.8(7)	N(1)–C(1)–C(3)	110.7(7)
N(1)–C(1)–C(5)	100.9(6)	C(3)–C(1)–C(5)	112.8(7)
N(1)–C(1)–C(11)	109.3(7)	C(3)–C(1)–C(11)	112.6(7)
C(5)–C(1)–C(11)	109.9(6)	C(1)–C(3)–C(4)	115.5(7)
C(3)–C(4)–C(41)	110.7(7)	C(1)–C(5)–C(6)	110.4(7)
C(1)–C(5)–C(51)	121.9(7)	C(6)–C(5)–C(51)	127.5(7)
C(5)–C(6)–C(7)	109.5(7)	C(5)–C(6)–C(61)	129.1(8)
C(7)–C(6)–C(61)	121.4(7)	O(1)–C(7)–N(1)	126.9(8)
O(1)–C(7)–C(6)	127.9(7)	N(1)–C(7)–C(6)	105.1(7)

4.58, 4.31, 3.63 (CH, CH_2). MS calcd for $C_{17}H_{15}O_5NCr$: 365 (M^+), found 365.

4.3. Reaction of complex **45b** with diphenylacetylene

A solution of complex **45b** (2.2 g, 6.0 mmol) and diphenylacetylene (1.6 g, 9 mmol) in benzene (50 ml) was refluxed for 48 h. Evaporation of the solvent under vacuum led to a residue which was refluxed in pyridine (30 ml) for 24 h. Evaporation of the solvent followed by silica gel chromatography of the residue gave first with petroleum ether/ethyl acetate (90/10) as eluent **46b** (1.41 g, 62%) as a white solid which was recrystallized from methanol-dichloromethane, mp 169°C; then with petroleum ether/ethyl acetate (80/20) **47b** (0.16 g, 7%) as an oil. Spectral data for **46b**: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.49–6.72 (m, 15H, Ar), 2.94 (s, 3H, NCH_3), 2.40 (dd, 1H, CHPh), 2.12 (dd, 1H, CHPh), 0.65 (m, 1H, CH), 0.30–0.03 (m, 4H, $2CH_2$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 180.97 (CO), 141.38–122.15 (13 peaks, Ar), 60.51 (C_q), 38.14 (CH_2), 28.24 (NCH_3), 6.48, 3.89, 3.65 (cyclopropane). Anal. Calc. for $C_{27}H_{25}NO$ (%): C, 85.45; H, 6.64; N, 3.69. Found: C, 85.47; H, 6.64; N, 3.61. Spectral data for **47b**: ^{1}H-NMR ($CDCl_3$, 200MHz) δ 7.42–6.64 (m, l5H, Ar), 2.73 (s, 3H, NCH_3), 2.10 (m, 2H, CH_2), 0.53 (m, 2H), 0.40 (m, 1H), 0.06 (m, 1H), −0.10 (m, 1H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 170.50 (CO), 138.35–126.88 (12 peaks, Ar), 72.22 (C_q), 35.97 (CH_2), 25.56 (NCH_3), 4.73, 4.23, 4.12 (cyclopropane). HRMS calcd for $C_{27}H_{25}NO$ (M^+) 379.1936; measd 379.1934.

4.4. Pentacarbonyl (N-methyl-phenethyl) benzylidene chromium (0) **50**

This complex was obtained in two steps from pentacarbonyl (ethoxy) benzylidene chromium (0) (3.3 g, 8.2 mmol) and phenethylamine (2.5 ml, 19.8 mmol) in diethyl ether. Yellow solid (3.3 g, 67%); mp 35°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ (E, Z mixture) 9.0 and 8.45 (bs, 1H, NH), 7.36–6.54 (m, 10H, Ar), 4.40, 3.45, 3.20, 2.84 (m, 4H, CH_2CH_2); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 282.64 and 279.17 (Cr=C), 223.38, 217.08 (CO), 149.45–119.0 (Ar), 54.16, 51.82, 35.93, 35.51 (CH_2CH_2). MS (DCPI, NH_3) calcd for $C_{20}H_{15}NO_5Cr + NH_4$: 419. Found: 419. To the previous complex (3.2 g, 7.9 mmol) in THF (50 ml) at −80°C was added LDA obtained from iPr_2NH (0.9 ml) and BuLi (8.8 ml). The solution was then brought to room temperature for 1 h, then cooled to −40°C and excess methyl iodide added. Workup as usual and purification on silica gel gave complex **50** (2.7 g, 82%) as an oil. ^{1}H-NMR (200 MHz, $CDCl_3$) δ (mixture of two E, Z isomers) 7.33–6.44 (m, 10 H, Ar), 4.45 (m, CH_2), 3.98 (s, CH3), 3.56 (m, CH_2), 3.24 (m, CH_2), 2.96 (s, CH_3), 2.83 (m, CH_2). MS (DPCI, NH_3) calcd for $C_{21}H_{17}NO_5Cr + NH_4$: 433. Found: 433.

4.5. Reaction of complex **50** with diphenylacetylene

Complex **50** (2.5 g, 6.0 mmol) was refluxed in benzene (50 ml) in the presence of diphenyacetylene (2.35 g, 13.8 mmol) for 12 h. After evaporation of the solvent, the residue was chromatographed on silica gel in order to separate the two complexes **51** and **52** from the organic products. Elution with PE/EtOAc (90/10) gave fractions containing complex **51**. Yellow solid. Mp 130°C; IR ($CHCl_3$) 1970, 1890, 1690 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.43–6.78 (m, 15H, Ar), 6.18, (d, 1H, ArCr), 5.25 (m, 2H, ArCr), 4.93 (t, 1H, ArCr), 2.97 (s, 3H, Me), 2.58 (m, 4H, CH_2CH_2). Anal. Calc. for $C_{34}H_{27}NO_4Cr$ (%): C, 72.21; H, 4.78; N, 2.48. Found: C, 72.33; H, 4.82; N, 2.48. Then fractions containing complex **52**, isolated as an orange solid. Mp 90°C; IR ($CHCl_3$) 1970, 1895, 1675 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.34–6.70 (m, 15H, Ar), 6.21 (d, 1H, ArCr), 5.29 (m, 2H, ArCr), 5.03 (t, 1H, ArCr), 2.78 (s, 3H, Me), 2.48–2.34 (m, 4H, CH_2CH_2). HRMS calc. for $C_{34}H_{27}NO_4Cr$ (M^+): 565.1345. Found: 565.1345.

4.6. Removal of $Cr(CO)_3$ from complexes **51** and **52**: formation of the pyrrolinones **51a** and **52a**

All the fractions were then gathered, the solvent evaporated under vacuum and the residue heated in boiling pyridine for 12 h. Evaporation of the solvent followed by chromatography gave with PE/CH_2Cl_2 (80/20) diphenylindenone (0.05 g, 3%), then with PE/EtOAc (97/3) diphenylindanone (0.06 g, 3.6%), with PE/EtOAc (95/5) tetraphenylcyclopentadienone (0.020 g), with PE/EtOAc (90/10) compound **51a** (1.10 g, 42.6%) as a white solid. Mp 162°C; NMR IR (200 Mhz, $CHCl_3$) δ 7.51–6.83 (m, 20H, Ar), 3.03 (s, 3H, Me), 2.90 (m, 1H, CH), 2.59 (m, 2H, CH_2), 2.30 (m, 1H, CH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 180.42 (CO), 141.67, 140.21, 133.24, 130.0–122.15 (Ar, C=C), 60.30 (C_q), 35.41 (Me), 30.94 (CH_2), 28.42 (CH_2). HRMS calc. for $C_{31}H_{27}NO$ (M^+): 429.2091. Found: 429.2088. Then with PE/EtOAc (85/15) compound **52a** (0.15 g, 5.8%) as an oil; IR ($CHCl_3$) 1690 cm^{-1}; ^{1}H-NMR (200 Mhz, $CDCl_3$) δ 7.48–6.67 (m, 20H, Ar), 2.78 (s, 3H, Me), 2.44 (m, 4H, CH_2CH_2); ^{13}C-NMR (50 Mhz, $CDCl_3$) δ 170.47 (CO), 155.96, 141.15, 137.84, 129.78–126.24 (Ar, C=C), 71.50 (C_q), 33.38 (Me), 29.14 (CH_2), 25.17 (CH_2). HRMS calc. for $C_{31}H_{27}NO$ (M^+): 429.209. Found: 429.209. Elution with PE/EtOAc (80/20) gave compound 53 (0.08 g, 4.1%) as a white solid. Mp 198°C; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.47–6.98 (m, 20H, Ar), 5.28 (s, 1H, CHPh), 2.90 (s, 3H, Me).

4.7. Structure: solution and refinement

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 collection. Complete crystallographic data and collection parameters listed in Tables 1–3. The data were corrected for Lorentz and polarization effects. Computations were carried out by using the PC version of CRYSTALS [40]. Scattering factors and corrections for anomalous absorption were taken from [41]. The structures were solved by Fo–Patterson technique for **51** and **52** or direct method (SHELXS [42]) for **46b**. Refinements were carried out by full-matrix least-squares. All non-hydrogen atoms were anisotropically refined, hydrogen atoms were introduced in calculated positions. Selected bond distances and bond angles are listed in Tables 4–6. The drawing of the molecules was carried out with the program CAMERON [43].

Fractional atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, atomic coordinates for H atoms, and complete lists of bond distances and bond angles have been deposited at the Cambridge Crystallographic Data Center. Copies of the data free of charge can be obtained on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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