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Journal of Organometallic Chemistry 567 (1998) 83–100

Journal of Organometallic Chemistry

Reaction of aminocarbene complexes of chromium with alkynes 10. From large to small cyclic amines: single versus double alkyne insertions

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

Abstract

For the purpose of comparing the reaction of various aminocarbene complexes of chromium with alkynes and to ascertain several points of the mechanism of their interaction, a series of complexes derived from large cyclic amines, $HN(CH_2)_n$ ($n \geq 6$) and from a small cyclic amine ($n = 2$) was synthesized. In the case of the larger amines, all the complexes examined herein, led to the expected bridgehead lactams **12** as the major product, providing strong evidence for a concerted rearrangement of an intermediate nitrogen-ylid complex such as **4**. The X-ray structure of the lactam complex **12d** ($n = 12$) has been established in order to confirm the ring opening and the migration of the twelve carbon-atom alkyl chain from nitrogen to the γ-carbon. Interestingly, the last possibility, the migration from nitrogen to oxygen in **4**, which had so far not been observed but which according to calculations should also be possible, took place in the case of complex **10b** ($n = 7$), giving rise, yet in low yield, to an alkoxypyrrole **14**. Minor products resulting from annulation reactions without CO insertions, were also observed. For aminocarbene complexes derived from methylaziridine ($n = 2$), important results, which substantiate previous observations, have been obtained especially as far as the mechanism of the insertion reaction is concerned: the regioselectivity of the ring-opening reaction could be established by X-ray crystallography on two isomeric complexes **25** and **26**, the timing of the various steps could be determined by the examination of the reactivity of vinyl–aziridinyl carbene complexes **31** and **35** which led surprisingly to aziridinyl phenols **33** and **36**. Finally, an unexpected product, the structure of which could also be established by X-ray crystallography as **27**, and resulting from the oxidation at the α position of the carbonyl in complexes **25** or **26** was isolated during the interaction of complex **23** with diphenylacetylene.

Keywords: Alkyne insertions; Aminocarbenes; Chromium; Nitrogen-containing heterocycles

1. Introduction

Although the chemistry of aminocarbene complexes and especially their use as synthons in organic chemistry had been neglected for a long time, in contrast to alkoxycarbene complexes, a fairly rapid progress in their use as starting material together with alkynes for the synthesis of elaborate heterocyclic compounds, has been observed [1–5].

At the same time, a thorough examination of the mechanism of the depicted transformations has been successfully undertaken. Most of the details of the mechanism depicted in Scheme 1 could be deduced from the insertion of diphenylacetylene into piperidine-substituted aminocarbene complexes **1**. The key step is

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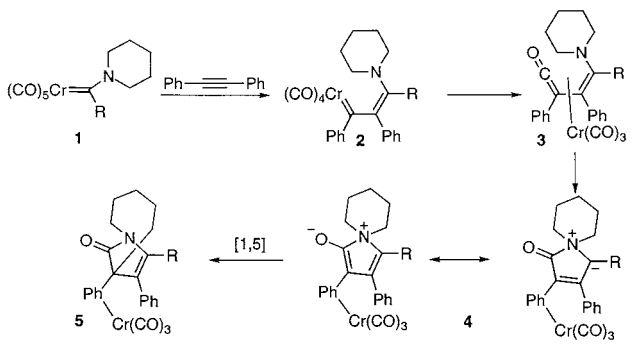
0022-328X/98/$19.00
PII S0022-328X(98)00671-8

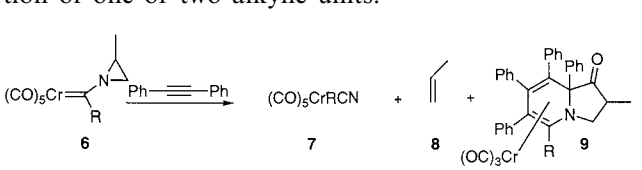


Scheme 1.

the formation of a stable nitrogen ylid intermediate **4** resulting from the successive insertion of the alkyne and CO, leading via a new carbene complex **2**, to a ketene complex **3** bearing in γ with respect to the electrophilic central carbon atom of the ketene, a tertiary amine. This favorable geometry induces the formation of a zwitterionic intermediate **4**, the rearrangement of which leads mostly to a bridgehead lactam **5**. Almost all the steps of this insertion reaction could firmly be established.

The most probable mechanism for the rearrangement, in agreement with theoretical work, is likely to be a series of concerted (1,5) migrations of alkyl groups from nitrogen to carbon. In the case of the smaller cyclic amine methylaziridine, it has been found that the course of the reaction was different since two series of products were observed [6]. In the first one, the products are independent of the presence of the alkyne. In the second one, a double insertion of alkyne, and a single insertion of CO were observed: no ketene was however formed (Scheme 2). Several mechanisms which will be discussed, could account for the structure of the end products.

The purpose of this paper is thus to further the possibilities of these reactions, to provide more evidence for the concertedness of the rearrangement reaction, by the examination of the insertion of diphenylacetylene into aminocarbene complexes derived from large cyclic amines: if concerted, the reaction should lead to bridgehead lactams in fairly good yields, whatever the size of the cyclic amines may be. In the case of aziridine-substituted complexes, experiments are provided to establish that the ring-opening reaction is regiospecific and that it probably takes place at the very end of the transformation, and at least after the insertion of one or two alkyne units.



Scheme 2.

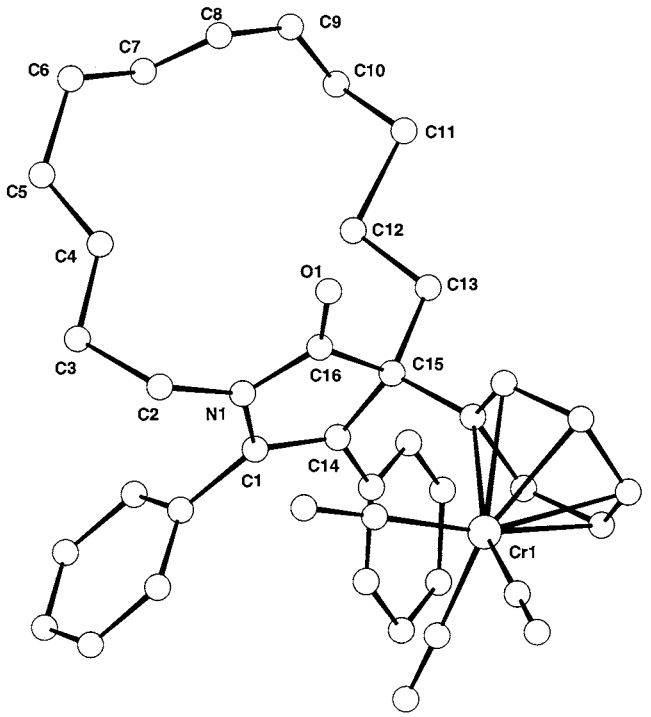


Fig. 1. Cameron projection of compound **12d** with the atom numbering scheme.

2. Results and discussion

2.1. Aminocarbene complexes derived from large cyclic amines: intermolecular insertion of diphenylacetylene

The aminocarbene complexes **10a–d** were synthesized either by direct aminolysis of the alkoxycarbene complexes according to Fischer, [7] or from the corresponding amides by the use of the method of Hegedus, [8] and isolated in respectively 59% ($n = 6$), 90% ($n = 7$), 80% ($n = 8$), and 63% ($n = 12$) yields as yellow solids. The physical data of these new complexes agree with those of previously described aminocarbene complexes (see the experimental section).

2.2. Reaction with diphenylacetylene

When complex **10a** was heated in refluxing benzene in the presence of an excess of diphenylacetylene, complete disappearance of the starting material was observed after 24 h together with the formation of several new complexes. Silica gel chromatography allowed the separation of the main product of the reaction (47.3%) as a yellow solid, m.p. 176°C. The physical data of this complex agreed with those of the expected bridgehead lactam complex **11a** with an IR absorption at 1690cm^{-1}, two typical multiplets for the protons of the NCH_2 group, at δ 4.04 and 3.33 ppm in the ^{1}H-NMR spectrum, and in the ^{13}C-NMR spectrum, a signal for the carbonyl group at δ 180.0 ppm. Treatment of further fractions of the chromatography with pyridine, in order to remove the metal, and for the sake of simplicity, allowed the separation of three products, the pyrrole

Table 1

Crystal data for **26**	$C_{44}H31O_4NCr$
F_w	689.7
a (Å)	16.809(7)
b (Å)	12.183(3)
c (Å)	18.702(5)
α(°)	90.
β(°)	109.40(3)
γ(°)	90.
V (Å^3)	3612(36)
Z	4
Crystal system	Monoclinic
Space group	$P2_1/a$
Linear absorption coefficient μ (cm^{-1})	3.49
Density ρ (g cm^{-3})	1.27
Diffractometer	CAD4 Enraf–Nonius
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71069$ Å)
Scan type	$\omega/2\theta$
Scan range (°)	$0.8+0.345$ tg θ
θ Limits (°)	1–25
Temperature of measurement	Room temperature
Octants collected	−19,18; 0,14; 0,22
Nb of data collected	6992
Nb of unique data collected	6338
Nb of unique data used for refinement	1295 $(F_o)^2 > 3\sigma(F_o)^2$
R_{int}	0.064
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.090
$R_w = [\Sigma\, w(\|\|F_o\|-\|-\|F_c\|)^2/\Sigma\, wF_o^2]^{1/2}$	0.096
Extinction parameter	No
Nb of variables	201
$\Delta\rho_{min}$ (e Å^{-3})	−0.40
$\Delta\rho_{max}$ (e Å^{-3})	0.40
Crystal data for **25**	C44H3104NCr
F_w	689.7
a (Å)	13.216(12)
b (Å)	28.684(13)
c (Å)	11.098(6)
α(°)	90
β(°)	100.66(8)
γ(°)	90
V (Å^3)	4134
Z	4
Crystal system	Monoclinic
Space group	$P2_1/n$
Linear absorption coefficient μ (cm^{-1})	3.05
Density ρ (g cm^{-3})	1.11
Diffractometer	Philips PW 1100
Radiation	Mo–K$_\alpha$($\lambda = 0.71069$ Å)
Scan type	$\omega/2\theta$
Scan range (°)	$0.8+0.345$ tg θ
θ Limits (°)	2–25
Temperature of measurement	Room temperature
Octants collected	−13,13; 0,30; 0,11
Nb of data collected	5520
Nb of unique data collected	5069
Nb of unique data used for refinement	1632 $(F_o)^2 > 3\sigma(F_o)^2$
R_{int}	0.059
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.124
$R_w = [\Sigma\, w(\|\|F_o\|-\|-\|F_c\|)^2/\Sigma\, wF_o^2]^{1/2}$	0.127
Extinction parameter	No
Nb of variables	241
$\Delta\rho_{min}$ (e Å^{-3})	−1.06
$\Delta\rho_{max}$ (e Å^{-3})	1.38

Table 1 (Continued)

Crystal data for **20b**	$C_{22}H_{21}NO_5Cr$
F_w	431.4
a (Å)	16.856(4)
b (Å)	12.167(5)
c (Å)	21.154(7)
α(°)	90.
β(°)	94.62(2)
γ(°)	90.
V (Å^3)	4324(3)
Z	8
Crystal system	Monoclinic
Space group	$P2_1/a$
Linear absorption coefficient μ (cm^{-1})	5.45
Density ρ (g cm^{-3})	1.33
Diffractometer	CAD4 Enraf–Nonius
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71069$ Å)
Scan type	$\omega/2\theta$
Scan range (°)	$0.8+0.345$ tg θ
θ Limits (°)	1–25
Temperature of measurement	Room temperature
Octants collected	0,20; 0,14; −25,25
Number of data collected	8275
Number of unique data collected	7586
Number of unique data used for refinement	4515$(F_o)^2 > 3\sigma(F_o)^2$
R_{int}	0.0424
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.0617
$R_w = [\Sigma\, w(\|\|F_o\|-\|-\|F_c\|)^2/\Sigma\, wF_o^2]^{1/2}$	0.0735
Extinction parameter	843
Nb of variables	525
$\Delta\rho_{min}$ (e Å^{-3})	−0.29
$\Delta\rho_{max}$ (e Å^{-3})	0.65
Crystal data for **17d**	$C_{33}H_{39}N$
F_w	449.7
a (Å)	8.595(7)
b (Å)	23.163(11)
c (Å)	13.515(10)
α(°)	90
β(°)	103.65(7)
γ(°)	90
V (Å^3)	2615(3)
Z	4
Crystal system	Monoclinic
Space group	$P2_1/a$
Linear absorption coefficient μ (cm^{-1})	0.60
Density ρ (g cm^{-3})	1.14
Diffractometer	CAD4 Enraf–Nonius
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71069$ Å)
Scan type	$\omega/2\theta$
Scan range (°)	$0.8+0.345$ tg θ
θ Limits (°)	1.5–22
Temperature of measurement	Room temperature
Octants collected	0,9; 0,24; −14,13
Number of data collected	3562
Number of unique data collected	3196
Number of unique data used for refinement	1238 $(F_o)^2 > 3\sigma(F_o)^2$
R_{int}	0.0118
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.135
$R_w = [\Sigma\, w(\|\|F_o\|-\|-\|F_c\|)^2/\Sigma\, wF_o^2]^{1/2}$	0.136
Extinction parameter	No
Nb of variables	138
$\Delta\rho_{min}$ (e Å^{-3})	−0.45
$\Delta\rho_{max}$ (e Å^{-3})	0.82

Table 1 (Continued)

Crystal data for complex **27**	$[C_{44}H_{35}N_1O_5Cr]_2$
Crystal parameters	
$F_w(g)$	1419.5
Shape (color)	Box(red)
Size, mm	0.27, 0.17, 0.13
Crystal system	Orthorhombic
Space group	Pbca
a, Å	12.155(1)
b, Å	33.375(4)
c, Å	35.694(5)
V Å^3	14480
Z	8
$F(000)$	5909
ρ (calc.), g cm^{-3}	1.302
μ (Mo–K$_\alpha$) cm^{-1}	3.523
Data collection	
Diffractometer	IPDS Stoe
Monochromator	Graphite
Radiation	Mo–K$_\alpha$ ($\lambda = 0{,}71073$)
Detector distance, mm	100
Scan mode	ϕ
ϕ Range, deg	$0 < \phi < 200$
ϕ Incr., deg	1.4
Exposure time, mn	8
2θ range, deg	$2.3 < 2\theta < 42$
No. of reflections collected	56911
No. of independent reflections (R_m)	7623(0.081)
Reflections used, ($I > 2\sigma(I)$)	3712
Refinement	
R	0.0437
R_w	0.0397
Weighting scheme	Chebyshev
Coefficient Ar	3.01, −0.457, 2.70
GOF	1.20
No. of variable parameters	461

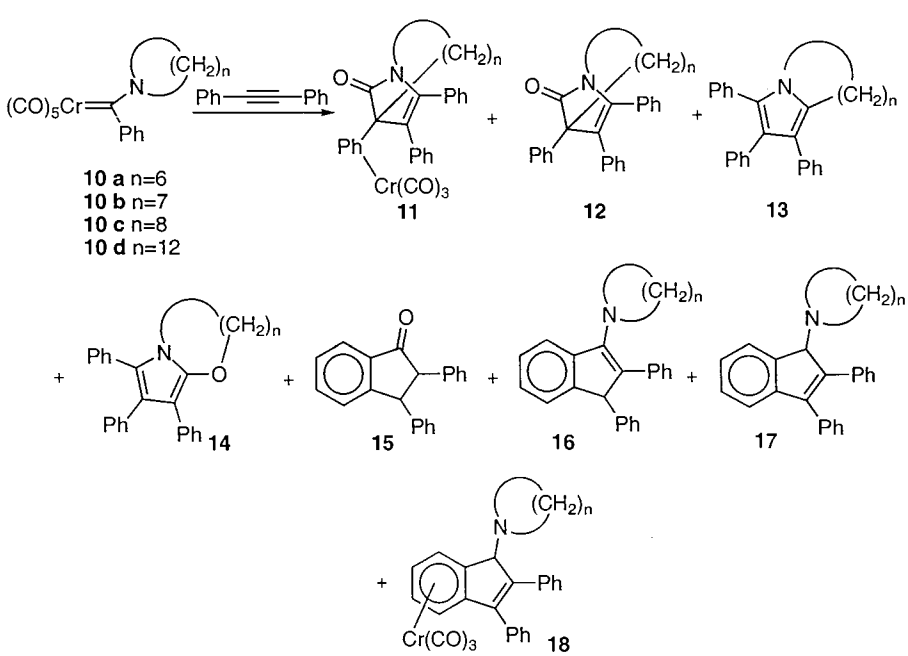
13a (0.7%), the bridgehead lactam **12a**, and the known diphenylindanone **15**.

Structure **13** could be assigned to the less polar product on the grounds of its physical data. The high resolution mass spectrum, the IR, and the ^{13}C-NMR spectra confirmed the absence of oxygen but confirmed also the presence of a single NCH_2 group (δ 4.03 and 41.6 ppm), and agreed with that of a pyrrole resulting from the migration from nitrogen to the carbonyl-carbon in the intermediate ylid complex of the type **4**, followed by the elimination of oxygen. Similar products had already been obtained during previous investigations [4].

Complex **10b** had a slightly different behaviour: indeed, besides the expected complex **11b** (yellow solid, 32.6%), its metal-free analog **12b** (white solid, 10%), the pyrrole **13b** (0.6%), the indanone **15** (23%), and the amine **16b** (3.9%), a new compound was isolated yet in low yield (1.5%) as a white solid. Although the mass spectrum indicated the presence of all the elements of the bridgehead lactam, and especially oxygen, no carbonyl was present either in the IR, or in the ^{13}C-NMR spectra.

Both the ^{1}H- and ^{13}C-NMR spectra agreed however with the presence of a single NCH_2 group with signals respectively at δ 3.85 and 39.96 ppm, very close to those observed in the pyrrole **13b** (δ 4.13 and 44.36 ppm). Surprisingly, a deshielded signal appeared also in the ^{1}H- and ^{13}C-NMR spectra, at respectively δ 3.96 ppm (for 2 protons) and at δ 74.71 ppm (for a methylene group): these observations are in agreement with the presence of an OCH_2 group. Taken together, all these data fit with a structure such as **14**, a result which confirms that migration from nitrogen to oxygen can take place during the rearrangement of the intermediate nitrogen ylid complexes.

Complexes **10c** and **10d** gave, in almost similar yields



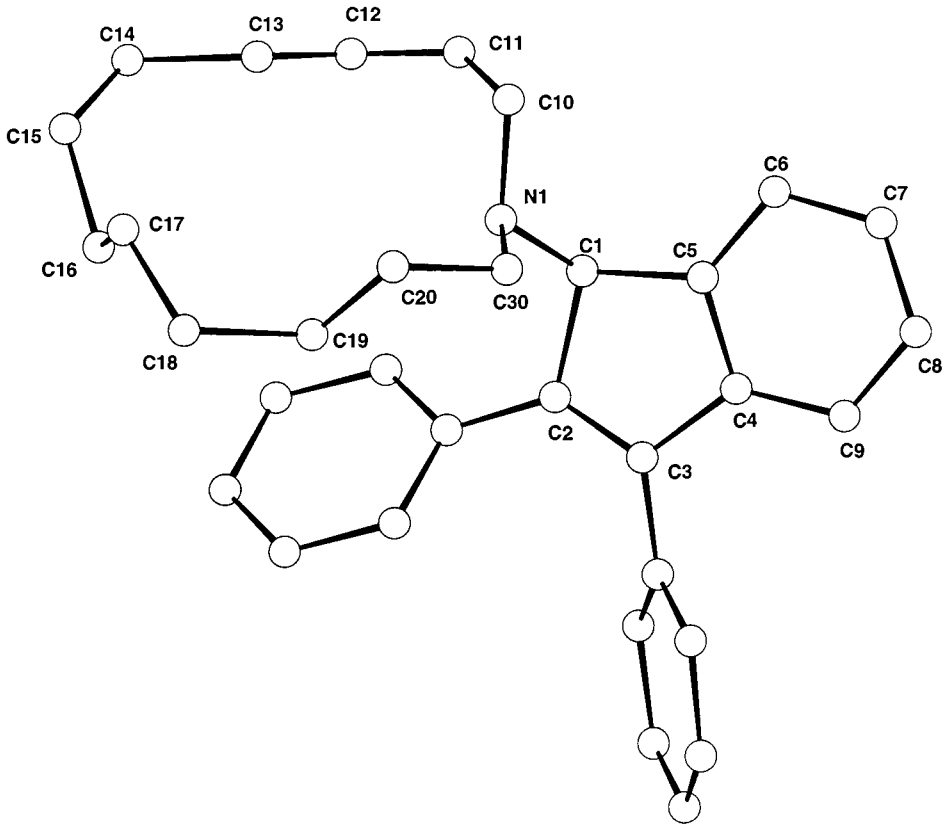


Fig. 2. Cameron projection of compound **17d** with the atom numbering scheme.

compounds **11c,d**. However, as for $n = 6$, no products derived from a nitrogen to oxygen migration could be detected. The structure of the bridgehead lactam **12d** containing a 15-membered lactam could be ascertained by an X-ray diffraction study. Its CAMERON projection appears in Fig. 1, with the most important bond distances and bond angles gathered in Table 2.

In the case of **10d**, the structure of the annulation product **17d** has been established by X-ray in order to locate the carbon–carbon double bond: Fig. 2 confirms the allylic nature of the amine. The most important bond distances and bond angles can be found in Table 3.

The formation of compounds **15, 16** and **17** can be pictured as in Scheme 3: these compounds are the result of annulation reactions without CO insertions, followed by hydrogen migrations, respectively (1,3) for **17**, and (1,5) for **15** and **16** [3,9–11].

Table 2
Selected interatomic distances (Å) and bond angles for 12d

O(1)–C(16)	1.23(1)	N(1)–C(1)	1.42(1)
N(1)–C(2)	1.44(1)	N(1)–C(16)	1.35(1)
C(1)–C(14)	1.33(1)	C(14)–C(15)	1.53(1)
C(15)–C(16)	1.52(1)		
C(1)–N(1)–C(2)	126.6(8)	C(1)–N(1)–C(16)	108.9(8)
C(2)–N(1)–C(16)	124.5(8)	N(1)–C(1)–C(14)	111.8(8)
C(1)–C(14)–C(15)	108.8(8)	C(14)–C(15)–C(16)	100.7(7)
O(1)–C(16)–N(1)	123.9(9)	O(1)–C(16)–C(15)	126.4(9)
N(1)–C(16)–C(15)	109.6(9)		

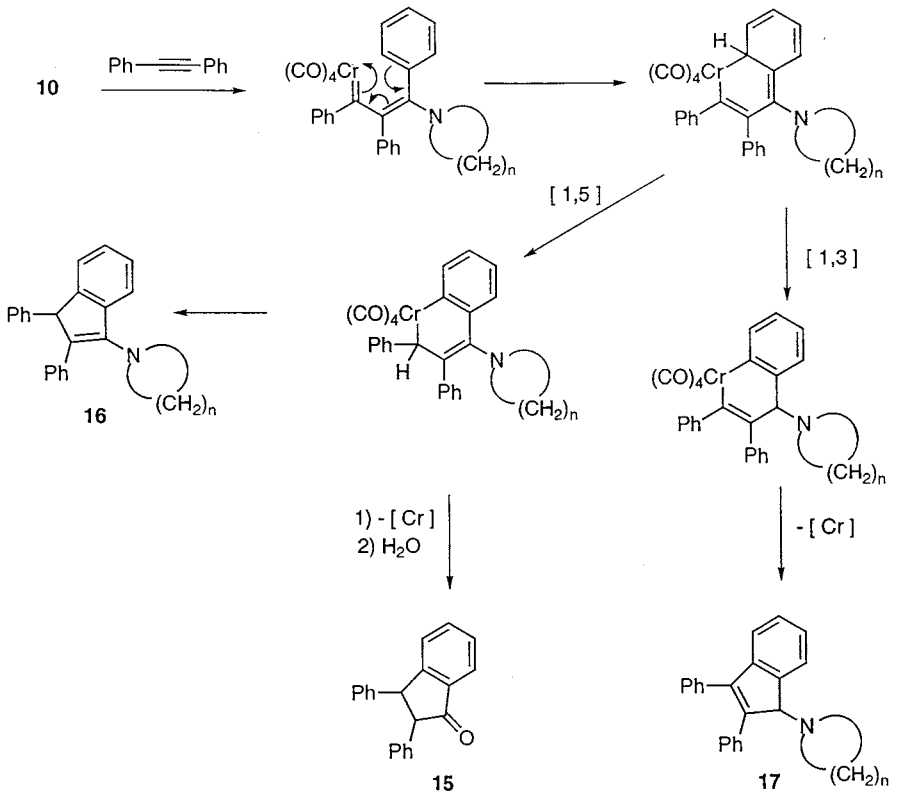
All the results observed herein confirm that even with large cyclic amines the course of the reaction is what one would expect for a concerted migration from nitrogen to carbon: whatever the size of the ring in the starting aminocarbene complexes, the main product of the reaction is due to a migration, from nitrogen to the γ–carbon.

2.3. Aminocarbene complexes derived from large cyclic amines: attempts to carry out intramolecular reactions

The successful insertion of diphenylacetylene into aminocarbene complexes derived from large amines prompted us to attempt the intramolecular version of this reaction by incorporating the triple bond into the cyclic amines. Previous results of this laboratory have indeed demonstrated that alkynes, tethered to aminocarbene complexes, can lead, upon insertion, to interesting polycyclic systems [3,5]. Similar results might be expected, at least on paper, starting for example from aminocarbene complexes of structure **21**.

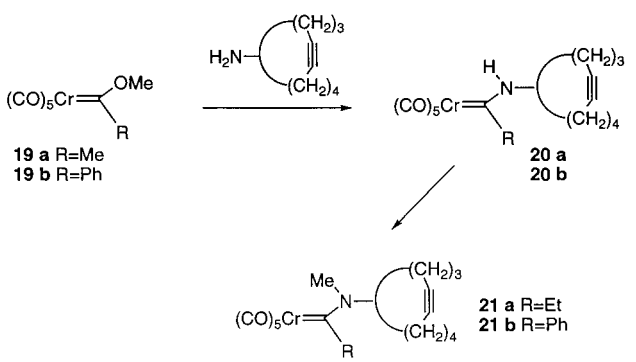
For that purpose, cyclodecynylamine which is readily available from decalone, was synthesized, [12] and used to prepare two new complexes **21a** and **21b** (R = Et, Ph).

In order to have an idea about the geometry, and



Scheme 3.

especially the orientation of the triple bond with respect to the metal, which is fundamental for the insertion reaction, an X-ray analysis was undertaken on complex **20b** (R = Ph). The most important bond distances and bond angles are found in Table 4. As it appears on the ORTEP projection of Fig. 3, the phenyl group and the ten-membered ring system are Z, a geometry which is unfavorable for the insertion reaction since it moves the triple bond away from the metal.



Alkylation was nevertheless attempted on complexes **20a,b**: it led to the yellow complexes **21a,b** in 53% yield.

2.3.1. Thermolysis of complexes *21a,b*

Heating of **21a** or **21b** in boiling benzene induced a fast disappearance of the starting complexes. However, only an intractable black mixture of products was obtained. It is likely that, due to the distance of the triple bond from the metal center, intermolecular reactions prevail, leading exclusively to polymers.

2.4. Aminocarbene complexes derived from small cyclic amines: case of methyl aziridine

In a previous publication, [6] the insertion of alkynes into aziridinylcarbene complexes was described. Several conclusions had already been reached as far as their reactivity and the mechanism of the insertion were concerned.

Table 3
Selected interatomic diatances (Å) and bond angles (°) for 17d

N(1)–C(1)	1.47(2)	C(1)–C(2)	1.57(2)
C(1)–C(5)	1.54(2)	C(2)–C(3)	1.32(2)
C(3)–C(4)	1.48(2)	C(4)–C(5)	1.40(2)
C(4)–C(9)	1.39(2)	C(5)–C(6)	1.38(2)
C(6)–C(7)	1.40(2)	C(7)–C(8)	1.37(2)
C(8)–C(9)	1.41(2)		
N(1)–C(1)–C(2)	111.4(13)	N(1)–C(1)–C(5)	116.9(13)
C(2)–C(1)–C(5)	101.3(13)	C(1)–C(2)–C(3)	110.1(13)
C(2)–C(3)–C(4)	111.2(14)	C(3)–C(4)–C(5)	108.6(14)
C(3)–C(4)–C(9)	130.8(16)	C(5)–C(4)–C(9)	120.5(16)
C(1)–C(5)–C(4)	108.8(15)	C(1)–C(5)–C(6)	128.8(16)
C(4)–C(5)–C(6)	122.1(17)	C(5)–C(6)–C(7)	115.8(18)
C(6)–C(7)–C(8)	123.8(19)	C(7)–C(8)–C(9)	119.3(19)
C(4)–C(9)–C(8)	117.9(17)		

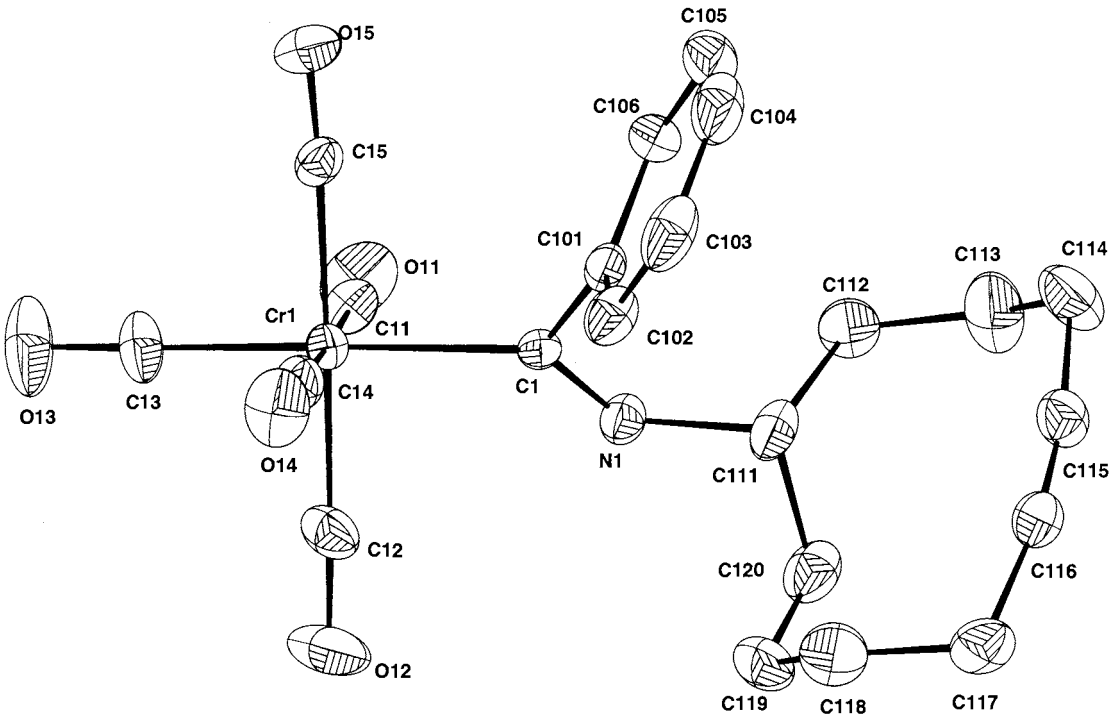


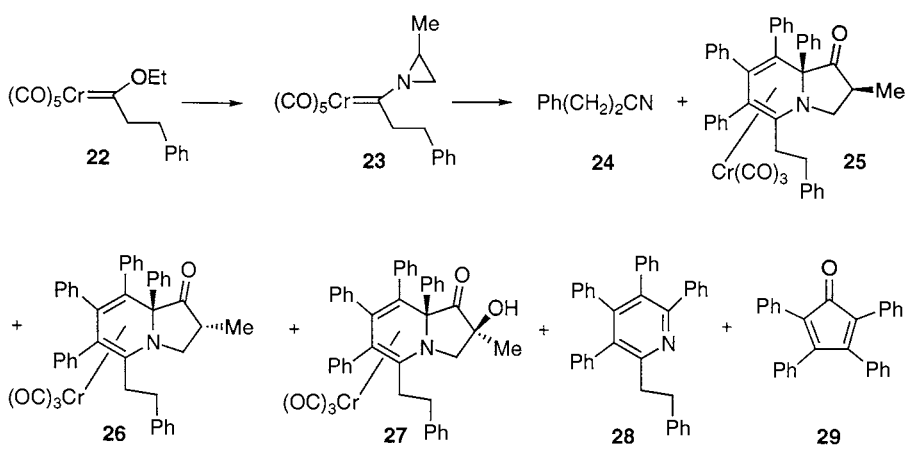
Fig. 3. Cameron projection of complex **20b** with the atom numbering scheme.

- aziridinyl carbene complexes **6** do not behave like other aminocarbene complexes since two main reactions are observed: a reaction without insertion of the alkyne leading, after destruction of the aziridine ring-system, to nitriles and propene. (Scheme 2)
- a double insertion of the alkyne together with the cleavage of the three membered ring and CO insertion. No products containing the intact aziridine were however observed. On a mechanistic point of view, it appears clearly that no ketene was formed during the insertion.

*2.4.1. Regioselectivity of the ring-opening: X-ray structure of two isomeric complexes **25** and **26***

For all the reactions examined so far two isomeric complexes were obtained but no decisive information was available from their physical data allowing the determination of their exact structure, since crystals suitable for an X-ray analysis could only be obtained from one isomer. Thus, new attempts were made to solve this problem by the introduction of a phenethyl group on the carbene–carbon. Complex **22**, prepared in 50% yield from $Cr(CO)_6$ and the corresponding lithium derivative $PhCH_2CH_2Li$ followed by alkylation at oxygen, reacted with methylaziridine to give the yellow complex **23** as a mixture of *E*, *Z* isomers, in 90% yield.

Heating of complex **23** in refluxing benzene in the presence of a two-fold excess of diphenylacetylene gave six products which were separated by silica gel chromatography: the nitrile **24** (50% yield) resulting from the thermal decomposition of the carbene complex, without insertion of the alkyne (Scheme 5, path A), two



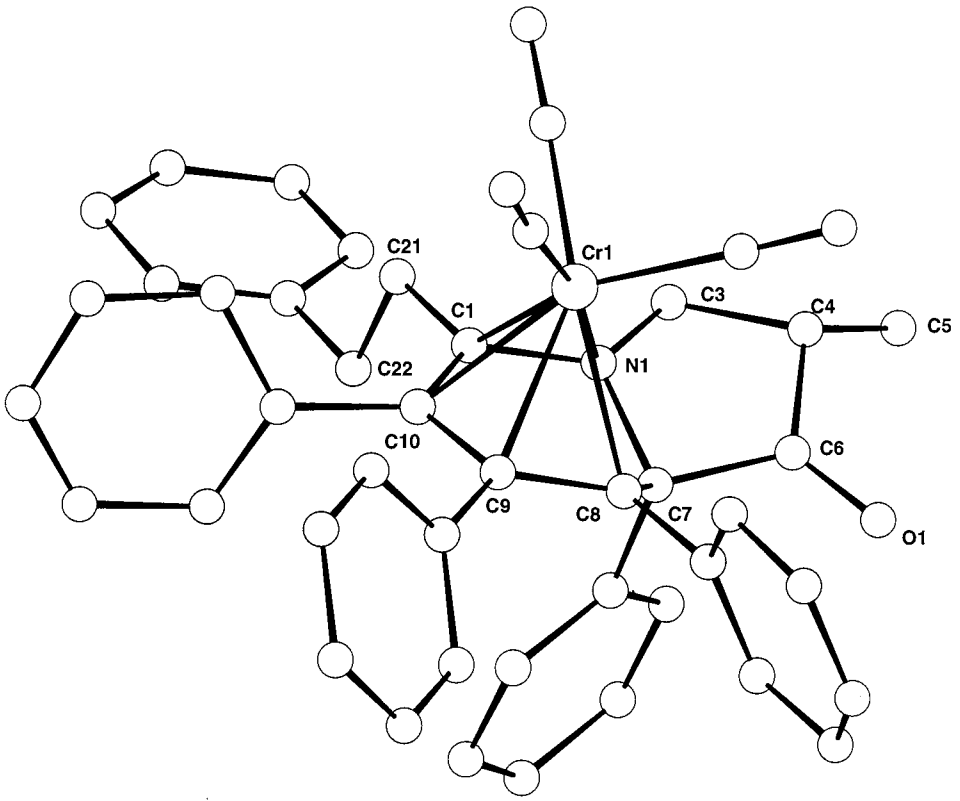


Fig. 4. Cameron Projection of complex **25** with the atom numbering scheme.

complexes, in respectively 30.7 and 6.6% yields, as red solids; a slightly more polar third complex as a red solid, in 1.8% yield, and finally two organic products. To the two first complexes were assigned structures **25** and **26**, the $Cr(CO)_3$ complexes of substituted tetrahydroindolizidones. The physical data of these two products, which are very close to those observed for similar complexes prepared previously in this laboratory differ only slightly: in their ^{1}H- and ^{13}C-NMR spectra: indeed the methyl groups give doublets at respectively 1.46 and 1.85 ppm in the ^{1}H-NMR spectrum, and signals at δ 12.82 and 17.41 ppm in the ^{13}C-NMR spectrum.

The structure of the two isomers could finally be established by X-ray crystallography. The ORTEP projections appear in Figs. 4 and 5, with the most important bond distances and bond angles in Table 5. It follows clearly that in both complexes the methyl group is in α to the carbonyl group in the five-membered ring, and that the difference originates from the orientation of the methyl group with respect to the $Cr(CO)_3$ group, being *trans* in the main product of the reaction. All other structural features are similar to those of the previously described complexes of this type [6].

Finally, to the last complex, obtained in very low yield as tiny red crystals was given structure **27**: in contrast to the other complexes, its ^{1}H-NMR spectrum disclosed a singlet for the methyl group at δ 2.25 ppm. Moveover, the protons of the NCH_2 group gave a set of two doublets, at δ 3.56 and 3.35 ppm. It results that the methyl group must now be on a tertiary carbon. The structure of this product was finally assessed by an X-ray analysis which showed surprisingly the presence of a hydroxyl group geminated to the methyl group. Its Cameron projection is given in Fig. 6 and the bond distances and bond angles in Tables 6 and 7. The mass spectrum confirmed also the presence of a tertiary alcohol, since an ion due to the loss of water is observed. The origin of this complex is subject to speculation: although the α position with respect to such a ketone is easily oxidized, the result is unexpected, since the insertion reactions were run by careful exclusion of oxygen. Moreover, when the reaction was carried out under an atmosphere of oxygen or in the presence of water, the insertion reaction took place nevertheless, giving complexes **25**, **26**, and **27**: however no increase in the yield of the last complex was observed.

To the last isolated products were assigned respectively, structure **29**, tetraphenylcyclopentadienone, a common product to most insertion reactions, and **28**, a substituted pyridine. It originates from the tetrahydroindolizidones **25** or **26**, which are in fact substituted dihydropyridines, as the result of the thermal cleavage of a carbon–carbon and a carbon–nitrogen bond and the formation of a carbon–nitrogen bond.

The important result of these investigations is the fact that the three-membered ring is opened in a regioselective manner, by cleavage at the more substituted carbon atom. This result is akin to the ring-opening of substituted *N*-acylaziridines by nucleophiles which also takes place at the more substituted carbon [13]. It is thus likely

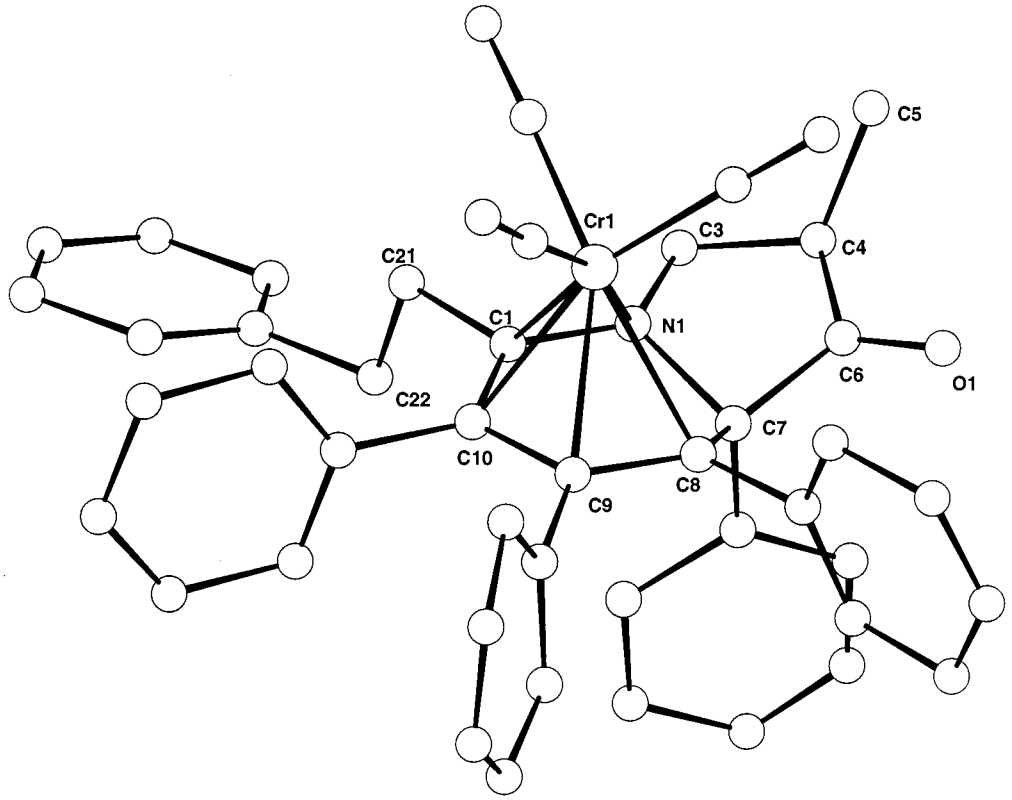


Fig. 5. Cameron projection of complex **26** with the atom numbering scheme.

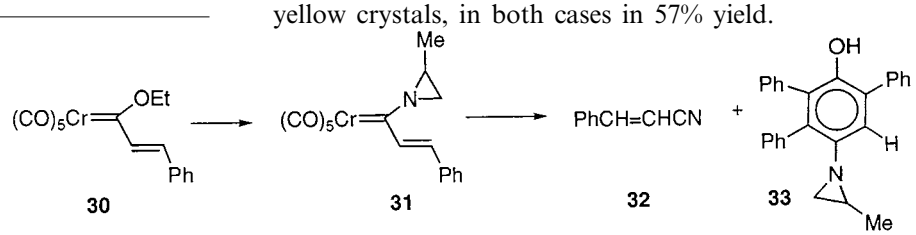
that a nucleophilic ring-opening also takes place during the insertion of the alkynes into **23** to give **25** and **26**. Its nature will be established by the following experiences.

*2.5. Insertion of diphenylacetylene in vinyl (aziridinyl) carbene complexes **31** and **35**: formation of aziridinyl-substituted phenols*

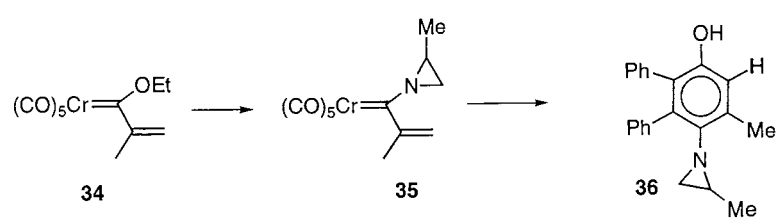
The question that might be asked is whether the aziridine-ring system will survive during an alkyne insertion reaction, as in path B. A known reaction in which the heteroatom-containing moiety of carbene complexes is not directly involved in the alkyne insertion is the benzannulation reaction, and also its analog, the vinylannulation reaction (Scheme 4) [14,15].

In previous work, we demonstrated however, that for phenyl-substituted aziridinylcarbene complexes (**6**, R = Ph), no benzannulation reaction was observed: only the phenyl-substituted tetrahydroindolizidone complexes (**9**, R = Ph) were formed. This result is probably linked to the prefered *cis* relationship between the aziridine ring-system and the metal, in the intermediate carbene complex (Scheme 5) [6]. Such a preference might be avoided by using less demanding substituents, such as the vinyl group.

For that reason, the synthesis of complexes **31** and **35** was undertaken via complexes **30** and **34** and isolated as yellow crystals, in both cases in 57% yield.



30 **31** **32** **33**



34 **35** **36**

Thermolysis of **31** in boiling benzene, in the presence of an excess of diphenylacetylene, did not lead to the expected tetrahydroindolizidone complexes (**9**, R=CH=CHPh) but gave, as in the previous cases, the nitrile **32**, in 53% yield, but also the aziridinyl-substituted phenol **33** in 19.4% yield, the product expected from an annulation reaction with insertion of CO. Its structure was established on the grounds of its combustion analysis and its spectroscopic data: the ^{1}H-NMR spectrum confirmed the presence of 16 aromatic protons, a proton for the OH group at δ 4.98 ppm, and all the protons of the aziridinyl ring system. Complex **35** behaved almost similarly, the nitrile, methylacrylonitrile, being lost during work-up. A single product, the phenol **36** was isolated in 15.4% yield and characterized by its physical data.

The important observation of this set of reactions is the survival of the aziridine ring during the alkyne insertion reaction, although a second reaction, during which destruction of the ring takes place, is again observed.(**31** → **32**)

Two mechanisms could account for the first set of experimental observations:

- a mechanism in which the first step of the reaction, the ring-opening of the aziridine common to the two observed products **7** and **9**, is followed either by a double alkyne insertion reaction (Scheme 5, path A) or by the elimination of propene giving a nitrile complex.
- a mechanism in which the aziridine ring remains as such until at least the first insertion of the alkyne or almost until the end of the insertion reaction (path B).

The latter set of results involving the vinyl aziridinyl carbene complexes is rather in support of path B: two independent reactions can thus take place, the first one

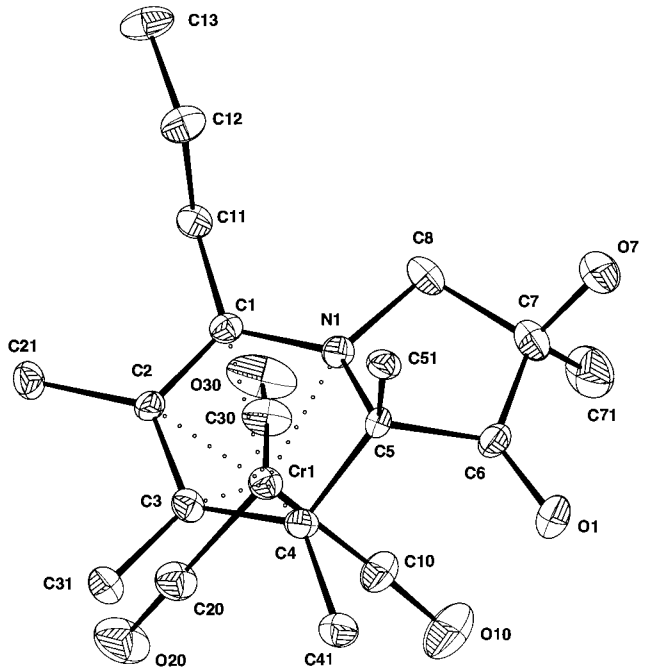


Fig. 6. Cameron projection of complex **27** with the atom numbering scheme (the phenyl groups have been omitted for sake of simplicity).

Table 4
Selected interatomic distances (Å) and bond angles (°) for **20b**

Cr(l)–C(1)	2.100(4)	N(1)–C(1)	1.307(5)
N(1)–C(111)	1.492(6)	C(111)–C(112)	1.620(8)
C(111)–C(120)	1.475(8)	C(112)–C(113)	1.442(9)
C(113)–C(114)	1.47(1)	C(114)–C(115)	1.478(9)
C(115)–C(116)	1.158(7)	C(116)–C(117)	1.462(8)
C(117)–C(118)	1.47(1)	C(118)–C(119)	1.49(1)
C(119)–C(120)	1.52(1)		
Cr(2)–C(2)	2.086(4)	N(2)–C(2)	1.304(5)
N(2)–C(211)	1.487(5)	C(211)–C(212)	1.555(7)
C(211)–C(220)	1.509(7)	C(212)–C(213)	1.493(8)
C(213)–C(214)	1.500(8)	C(214)–C(215)	1.488(7)
C(215)–C(216)	1.173(7)	C(216)–C(217)	1.456(8)
C(217)–C(218)	1.513(8)	C(218)–C(219)	1.532(9)
C(219)–C(220)	1.526(8)		
C(1)–N(1)–C(111)	128.5(4)	Cr(l)–C(1)–N(1)	123.5(3)
N(1)–C(111)–C(112)	110.9(4)	N(1)–C(111)–C(120)	108.2(5)
C(112)–C(111)–C(120)	110.6(5)	C(111)–C(112)–C(113)	118.3(5)
C(112)–C(113)–C(114)	125.2(8)	C(113)–C(114)–C(115)	112.8(6)
C(114)–C(115)–C(116)	168.0(6)	C(115)–C(116)–C(117)	169.5(6)
C(116)–C(117)–C(118)	113.2(5)	C(117)–C(118)–C(119)	120.8(7)
C(118)–C(119)–C(120)	118.5(5)	C(111)–C(120)–C(119)	109.9(5)
C(2)–N(2)–C(211)	129.4(3)	Cr(2)–C(2)–N(2)	124.4(3)
N(2)–C(211)–C(212)	108.5(4)	N(2)–C(211)–C(220)	108.0(4)
C(212)–C(211)–C(220)	114.8(4)	C(211)–C(212)–C(213)	118.7(4)
C(212)–C(213)–C(214)	119.2(5)	C(213)–C(214)–C(215)	111.9(5)
C(214)–C(215)–C(216)	169.1(5)	C(215)–C(216)–C(217)	168.2(5)
C(216)–C(217)–C(218)	111.2(4)	C(217)–C(218)–C(219)	115.1(5)
C(218)–C(219)–C(220)	117.1(4)	C(211)–C(220)–C(219)	113.9(4)

Table 5
Selected interatomic distances (Å) and bond angles (°) for **25**

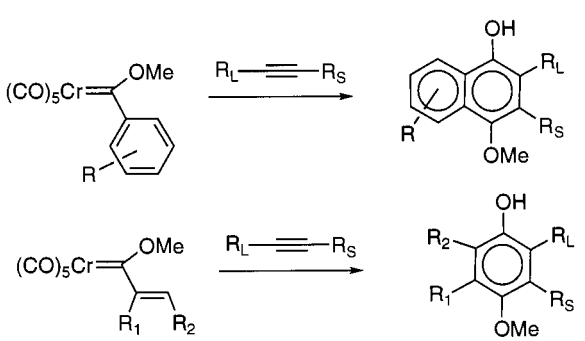
Cr(1)–N(1)	2.11(1)	Cr(l)–C(1)	2.15(2)
Cr(1)–C(8)	2.28(2)	Cr(l)–C(9)	2.18(2)
Cr(l)–C(10)	2.21(2)	O(1)–C(6)	1.21(2)
N(1)–C(1)	1.41(2)	N(1)–C(3)	1.50(2)
N(1)–C(7)	1.51(2)	C(1)–C(10)	1.39(2)
C(1)–C(21)	1.50(2)	C(3)–C(4)	1.57(2)
C(4)–C(5)	1.54(3)	C(4)–C(6)	1.51(2)
C(6)–C(7)	1.55(2)	C(7)–C(8)	1.52(2)
C(8)–C(9)	1.41(2)	C(9)–C(10)	1.44(2)
C(21)–C(22)	1.57(2)	C(22)–C(23)	1.51(2)
C(1)–N(1)–C(3)	122.8(13)	C(1)–N(1)–C(7)	118.6(13)
C(3)–N(1)–C(7)	111.9(12)	N(1)–C(1)–C(10)	116.0(13)
N(1)–C(1)–C(21)	118.1(14)	C(10)–C(1)–C(21)	125.4(14)
N(1)–C(3)–C(4)	99.4(13)	C(3)–C(4)–C(5)	112.5(15)
C(3)–C(4)–C(6)	102.8(15)	C(5)–C(4)–C(6)	114.1(15)
O(1)–C(6)–C(4)	124.7(17)	O(1)–C(6)–C(7)	122.7(17)
C(4)–C(6)–C(7)	112.6(14)	N(1)–C(7)–C(6)	97.5(13)
N(1)–C(7)–C(8)	101.7(12)	C(6)–C(7)–C(8)	115.9(13)
C(7)–C(8)–C(9)	115.7(14)	C(8)–C(9)–C(10)	120.0(15)
C(1)–C(10)–C(9)	119.5(14)	C(1)–C(21)–C(22)	109.8(14)
C(21)–C(22)–C(23)	109.5(14)		

Table 6
Selected interatomic distances (Å) and bond angles (°) for **26**

Cr(1)–N(1)	2.14(2)	Cr(1)–C(1)	2.11(2)
Cr(1)–C(8)	2.32(2)	Cr(1)–C(9)	2.25(2)
Cr(1)–C(10)	2.21(2)	O(1)–C(6)	1.23(2)
N(1)–C(1)	1.39(2)	N(1)–C(3)	1.50(2)
N(1)–C(7)	1.56(2)	C(1)–C(10)	1.39(2)
C(1)–C(21)	1.59(2)	C(3)–C(4)	1.50(3)
C(4)–C(5)	1.59(3)	C(4)–C(6)	1.57(2)
C(6)–C(7)	1.50(3)	C(7)–C(8)	1.55(2)
C(8)–C(9)	1.40(2)	C(9)–C(10)	1.45(2)
C(21)–C(22)	1.59(3)	C(22)–C(23)	1.55(3)
C(1)–N(1)–C(3)	124.8(16)	C(1)–N(1)–C(7)	120.6(15)
C(3)–N(1)–C(7)	108.5(15)	N(1)–C(1)–C(10)	121.2(18)
N(1)–C(1)–C(21)	118.0(16)	C(10)–C(1)–C(21)	120.7(18)
N(1)–C(3)–C(4)	103.8(16)	C(3)–C(4)–C(5)	116.0(18)
C(3)–C(4)–C(6)	104.1(17)	C(5)–C(4)–C(6)	109.6(17)
O(1)–C(6)–C(4)	123.3(19)	O(1)–C(6)–C(7)	126.0(18)
C(4)–C(6)–C(7)	110.3(17)	N(1)–C(7)–C(6)	95.4(16)
N(1)–C(7)–C(8)	100.6(14)	C(6)–C(7)–C(8)	113.9(17)
C(7)–C(8)–C(9)	118.8(18)	C(8)–C(9)–C(10)	121.8(18)
C(1)–C(10)–C(9)	116.4(18)	C(1)–C(21)–C(22)	107.8(16)
C(21)–C(22)–C(23)	105.7(16)		

the driving force of which is the relief of ring strain, via path A, gives nitriles, the second one, via path B, gives an intermediate alkylidene complex **38**, after a single or a double alkyne insertion: nucleophilic attack of the nitrogen atom at the alkylidene carbon would then lead to the *N*-ylid **39**, a well established reaction from this laboratory [16]. Finally, an intramolecular nucleophilic, and regioselective ring-opening would lead to the metallacycle **40** which upon cyclocarbonylation can give the observed complexes **9**. Conversely, sigmatropic and electrocyclic rearrangements of **37** or **38** could lead to the same intermediate **40**.

All the steps outlined in the above mechanism are known from the literature. The exact reason for the double alkyne insertion is not clear: it might be due to a steric interaction between the substituted aziridine and the metal, which inhibits the coordination of the nitrogen to the metal, and thus the insertion of a CO group.



Scheme 4.

3. Conclusion

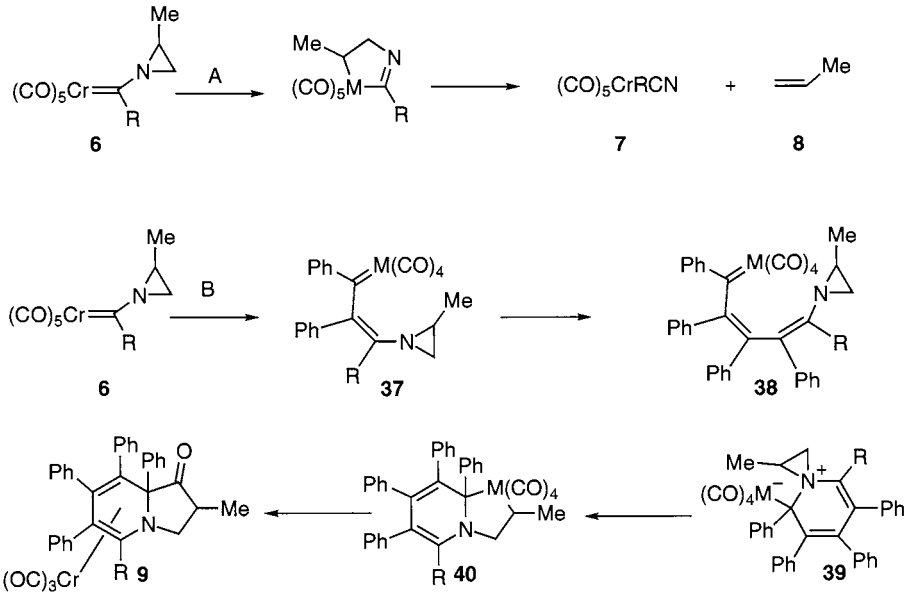
A striking difference in the reactivity of aminocarbene complexes derived from large and from small cyclic amines resulted from these investigations: whereas the former complexes lead in most cases essentially, via the classical insertion-rearrangement reactions to bridgehead lactams, the latter complexes undergo a double alkyne insertion reaction without formation of intermediate ketenes and a regioselective ring-opening followed by the insertion of CO. Side products due to benzannulation reactions without insertion of CO also took place in the case of the large cyclic amines, whereas vinyl-substituted aziridinyl carbene complexes led to annulation products with insertion of CO.

4. Experimental

General methods: ^{1}H- and ^{13}C-NMR spectra were recorded respectively at 200 or 400 and 50 or 100 MHz. IR spectra were recorded as solutions. Mass spectra are *m*/*z*. Column chromatography was performed with Merck silica gel (70–230 mesh) using various ratios of ethyl acetate (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 performed under an argon atmosphere in carefully dried glassware. Solvents were dried by distillation from a drying agent: THF and Et_2O from Na/benzophenone; CH_2Cl_2 from CaH_2 and P_2O_5.

4.1. Pentacarbonyl (N-hexamethylene) benzylidene chromium (0) ***10a***

This complex was obtained from $(CO)_5$ Cr=C(OEt)Ph and hexamethylene imine (1.45 ml, 12.9 mmol) in diethyl ether (150 ml) at 0°C. Evaporation of the solvent under vacuum gave complex **10a** as a yellow solid (2.38 g, 58.7%); m.p. 71–72°C. IR($CHCl_3$) 2040, 1960, 1915 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.39 (2H, t, $J = 6$Hz, Ar), 7.16 (1H, t, $J = 7.6$ Hz, Ar), 6.74 (2H, dd, $J = 8.5$ and 1.3 Hz, Ar), 4.45 (2H, t, $J = 6$ Hz, NCH_2), 3.58 (2H, t, $J = 6.3$ Hz, NCH_2), 2.13–2.09 (2H, m, NCH_2CH_2), 1.82–1.78 (2H, m, NCH_2CH_2), 1.68–1.64 (2H, m, $NCH_2CH_2CH_2$), 1.58–1.54 (2H, m, $NCH_2CH_2CH_2$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 274.17 (Cr=C), 224.35, 217.56 (CO), 153.20, 128.53, 125.57, 118.73 (Ar), 62.94, 56.96 (NCH_2), 29.18, 28.03 (NCH_2CH_2), 26.48, 26.34 ($NCH_2CH_2CH_2$). Anal. found (%): C, 56.87; H, 4.53, N, 3.66. Calc. for $C_{18}H_{17}NO_5Cr$: C, 56.99; H, 4.49; N, 3.69.



Scheme 5.

4.2. Pentacarbonyl (N-heptamethyleneimine) benzylidene chromium (0) **10b**

This was obtained from the corresponding amide $PhCON(CH_2)_7$ according to the method of Hegedus from $Na_2Cr(CO)_5$, TMSCl and Al_2O_3 as a yellow solid (89.6%); m.p. 80°C; IR ($CHCl_3$) 2040, 1970, 1920cm^{-1}; ^{1}H-NMR ($CDCl_3$, 100 MHz) δ 7.38 (2H, t, $J = 7.6$ Hz, Ar), 7.14 (1H, t, $J = 7.4$ Hz, Ar), 6.74 (2H, d, $J = 7$ Hz, Ar), 4.40 (2H, t, $J = 5.8$ Hz, NCH_2), 3.64 (2H, t, $J = 6.1$ Hz, NCH_2), 2.18–2.12 (2H, m, CH_2), 1.84–1.80 (2H, m, CH_2) 1.65–1.40 (6H, m, CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 275.23 (Cr=C), 224.47, 217.50 (CO), 153.43, 128.36, 125.55, 118.94 (Ar), 63.96 (NCH_2), 56.36 (NCH_2), 27.17, 26.57, 25.28, 23.79 (CH_2). Anal. found (%): C, 58.00; H, 4.84; N, 3.47. Calc. for $C_{19}H_{19}NO_5Cr$: C, 58.01; H, 4.83; N, 3.56.

4.3. Pentacarbonyl (N-octamethyleneimine) benzylidene chromium (0) **10c**

This was obtained as above from the corresponding amide as a yellow solid (80.6%); m.p. 77°C; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.38 (2H, t, $J = 7.7$ Hz, Ar), 7.14 (1H, t, $J = 7.4$ Hz, Ar), 6.77 (2H, d, $J = 7.7$ Hz, Ar), 4.44 (2H, t, $J = 5.4$ Hz, NCH_2), 3.68 (2H, t, $J = 5$ Hz, NCH_2), 2.28–2.26 (2H, m, NCH_2CH_2), 1.97–1.95 (2H, m, NCH_2CH_2) 1.66–1.59 (8H, m, CH_2);

^{13}C-NMR ($CDCl_3$, 100 MHz) δ 276.67 (Cr=C), 224.48, 217.48 (CO), 153.95, 133.28, 128.49, 125.42, 118.84 (Ar), 64.10, 57.53 (NCH_2), 27.61, 27.34, 27.20, 26.99, 26.39, 26.09 (CH_2). Anal. found (%): C, 58.89; H, 5.10; N, 3.57. Calc. for $C_{20}H_{21}NO_5Cr$: C, 58.97; H, 5.16; N, 6.06.

4.4. Pentacarbonyl (N-dodecamethyleneimine) benzylidene chromium (0) **10d**

This complex was obtained from the corresponding amide according to the method of Hegedus as a yellow oil in 63% yield. IR ($CHCl_3$) 2040, 1965, 1910 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz,) δ 7.37–6.73 (5H, m, Ar), 4.28 (2H, t, NCH_2), 3.38 (2H, t, NCH_2), 2.06 (2H, m), 1.63–1.19 (18H, m); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 273.72 (Cr=C), 224.26, 217.60 (CO), 153.24, 128.41, 125.51, 118.90 (Ar), 60.02, 54.48 (NCH_2), 26.99, 26.07, 25.97, 25.56, 25.20, 24.89, 24.39, 23.26 (CH_2). HRMS found (M^+–5CO): 323.1705. Calc. for $C_{19}H_{29}NCr$: 323.1706.

4.5. Reaction of complex **10a** with diphenylacetylene

A solution of complex **10a** (2.38 g, 6.28 mmol) in benzene (85 ml) was refluxed in the presence of diphenylacetylene (1.34 g, 7.53 mmol) for 22 h. After evaporation of the solvent under vacuum, the residue was chromatographed on silica gel. Elution with PE/CH_2Cl_2 (80/20) then with PE/AcOEt (95/5) gave a series of fractions containing mixtures of non-polar complexes and organic products. Elution with PE/AcOEt (90/10) first gave fractions containing **12a** (0.19g, 7.6%) as a white solid; m.p. 134–135 °C; IR ($CHCl_3$) 1692 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.4–6.86 15H, m, Ar), 4.08–4.02 (1H, m, NCHH), 3.39–3.35 (1H, m, CHH), 2.76 (1H, dd, $J = 13$ and 7.4 Hz, ArCHH), 2.38 (1H, t, $J = 12$ Hz, Ar CCHH), 1.97–1.83 (2H, m, CH_2), 1.80–1.58 (4H, m, CH_2), 1.49–1.29 (2H, m, CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 183.22 (CO), 141.73, 138.71, 133.96, 128.76, 128.66,

127.67, 127.53, 123.60 (C = C, Ar), 61.54 (CPh), 41.75 (NCH_2), 35.68 (NCH_2), 25.77, 25.57, 25.21, 20.05 (CH_2). HRMS calc. for $C_{28}H_{27}NO$ (M^+): 393.2091. Found: 393.2092. Then fractions containing complex **11a** (1.57 g, 47.3%) as yellow crystals; m.p. 176°C, IR ($CHCl_3$) 2010, 1930, 1690 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.34–6.99 (10H, m, Ar), 5.65–5.04 (5H, m, Ar), 4.06–4.00 (1H, m, CHH), 3.36–3.29 (1H, m, NCH), 2.68(1H, dd, $J = 13.5$ and 7 Hz, Ar C–CH), 2.24 (1H, t, $J = 12$ Hz, ArC–CH), 1.98–1.88 (2H, m, CH_2), 1.69–1.52 (4H, m, CH_2), 1.38–1.18 (2H, m, CH_2). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 232.86 (CO), 180.00 (CO), 143.08, 134.28, 130.10, 129.69, 128.86, 128.66, 128.54, 127.15, 120.88, 109.94 (C=C, Ar), 93.74, 93.05, 90.43 (Ar–Cr), 58.37 (PhC(CH_2)), 42.22 (NCH_2), 40.42 (PhC(CH_2)) 26.22, 25.74, 25.44, 21.53 (CH_2). HRMS found (M^+–3CO): 445.1496. Calc. for $C_{28}H_{27}NOCr$ (M^+3CO): 445.1498. The less polar fraction of the first chromatography were treated with pyridine. Evaporation of pyridine under vacuum, followed by chromatography of the residue gave first with PE/CH_2Cl_2 (80/20) the pyrrole **13a** (16 mg, 0.7%) as an oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.56–6.87 (15H, m, Ar), 4.04–4.03 (2H, m, NCH_2), 2.78–2.76 (2H, m, C=C–CH_2), 1.83–1.28 (8H, m, 4 CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 136.91–119.99 (C=C, Ar), 41.59, (NCH_2), 33.22, 31.52, 26.18, 24.14, 23.92 (CH_2). HRMS calc. for $C_{28}H_{27}N$. Found: 377.2143. Elution with PE/AcOEt (95/5) gave fractions containing diphenylindanone **15** (0.17 g, 9.7%) as an oil; IR($CHCl_3$) 1705 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.94–7.14 (m, 14H, Ar), 4.62 (1H, d, COCHPh), 3.85 (1H, d, CHPh); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 205.4 (CO), 156.3–123.9 (Ar), 64.7 (COCHPh), 53.82 (CHPh).

4.6. Reaction of complex *10b* with diphenylacetylene

The reaction was carried out as above with complex **10b** (2 g, 5.09 mmol) and diphenylacetylene (1.1 g, 6.11 mmol). A first chromatography of the residue gave with PE/CH_2Cl_2 fractions containing both organic products and complexes. Elution with PE/AcOEt (95/5) gave diphenylindanone **15** (0.42 g, 23%); elution with PE/AcOEt (90/10) gave **12b** (0.3 g, 14.7%) as a white solid; m.p. 60°C; IR ($CHCl_3$) 1698 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400MHz) δ 7.36–6.77 (15H, m, Ar), 3.95–3.80 (1H, m, NCHH), 3.23–3.10 (1H, m, NCHH), 2.64–2.54 (1H, m, PhCCHH), 2.44–2.34 (1H, m, PhCCHH), 1.68–1.25 (10H, m, 5 CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 181.70 (CO), 142.82–123.41 (C=C, Ar), 61.33 (CPh), 41.41 (NCH_2), 33.91, 27.17, 23.43, 22.44, 20.68, 20.30 (CH_2). HRMS found (M^+): 407.2249. Calc. for $C_{29}H_{29}NO$: 407.2249. Elution with PE/AcOEt (70/30) gave complex **11b** (0.9 g, 32.6%) as a yellow solid, m.p. 67°C; IR($CHCl_3$) 2008, 1930, 1690cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.38–7.00 (10H, m, Ar), 5.96–4.99 (5H, m, ArCr), 4.01–3.97 (1H, m, NCH), 3.25–3.16 (1H, m, NCH), 2.66 (1H, dd, $J = 13.8$ and 7.8 Hz, PhC–CH), 2.30 (1H, t, $J = 12.5$ Hz, PhC–CH), 2.06–1.85 (2H, m, CH_2), 1.71–1.28 (8H, m, CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 232.78 (CO), 178.53 (CO), 144.44, 134.65, 130.22, 129.86, 129.25, 128.87, 128.68, 128.48, 127.77, 127.19, 126.95, 126.26, 119.50, 111.03 (C=C, Ar), 93.44, 93.34, 92.77, 91.07, 90.93 (PhCR), 58.05 (PhC(CH_2)), 41.59 (NCH_2), 40.19, (PhC(CH_2)), 27.09, 23.33, 22.10, 21.03, 20.36 (CH_2). HRMS found (M^+–3CO): 459.1654. Calc. for $C_{32}H_{29}NO_4$ Cr 459.1654.

The first fractions of the chromatography were gathered and treated with pyridine. A second chromatography of the residue first gave with PE/CH_2Cl_2 (85/15) the pyrrole **13b** (12 mg, 0.6%) as a white solid; m.p. 142°C; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.26–6.81 (15H, m, Ar), 4.13 (2H, t, $J = 5.9$ Hz, NCH_2), 2.73 (2H, t, $J = 5.4$ Hz, C=C–CH_2), 1.85–1.22 (10H, m, CH_2). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 136.88–124.66 (C=C, Ar), 44.36 (NCH_2), 30.63, 30.12, 29.74, 27.06, 26.92, 20.30 (CH_2). HRMS found (M^+): 391.2299. Calc. for $C_{29}H_{29}N$: 391.2299. Elution with PE/CH_2Cl_2 (80/20) gave pyrrole **14** (31 mg, 1.5%) as a solid; m.p. 51°C; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.34–6.92 (15H, m, Ar), 3.96 (2H, t, $J = 5.3$ Hz, OCH_2), 3.85 (2H, m, NCH_2), 1.64–1.49 (10H, m, CH_2). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 143.71–119.94, 104.42 (C=C, Ar), 74.71 (OCH_2), 39.96 (NCH_2), 29.73, 27.83, 26.84, 24.92, 23.29 (CH_2). HRMS found (M^+) 407.2249. Calc. for $C_{29}H_{29}NO$: 407.2249. Then the amine **17b** (75 mg, 3.9%) as a white solid; m.p. 38°C; ^{1}H-NMR ($CDCl_3$, 400 MHz), δ 7.69–7.02 (14H, m, Ar), 5.01 (1H, s, CH), 2.73 (4H, m, 2 NCH_2), 1.75–1.21 (10H, m, 5 CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 144.94–120.44(C=C, Ar), 74.73 (CH), 52.02 (2CH_2), 28.53, 27.89, 25.03 (CH_2). HRMS found (M^+) 379.2299. Calc. for $C_{28}H_{29}N$: 379.2299.

4.7. Reaction of complex *10c* with diphenylacetylene

The reaction was carried out as above with complex **10c** (2.0 g, 4.91 mmol) and diphenylacetylene (1.0 g, 5.89 mmol). Silica gel chromatography as above first gave complex **18c** (0.15 g, 5.8%) as a yellow solid; m.p. 140°C; IR ($CHCl_3$) 1960, 1885 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.4–7.1 (9H, m, Ar), 6.15–5.05 (6H, m, ArCr), 2.75 (4H, m, 2 NCH_2), 1.8–1.05 (12H, m, 6CH_2); ^{13}C-NMR ($CDCl_3$,100 MHz) δ 233.56 (CO), 146,5–114.17, (C=C, Ar), 92.8–86.76 (ArCr) 73 27 (CH), 49.8 (2 NCH_2), 26.4, 24.9, 22.2 (6CH_2). HRMS found (M^+): 529.1709. Calc. for $C_{32}H_{31}NO_3Cr$: 529.1706. Then the amine **17c** (88 mg, 4.6%) as a solid; m.p. 102°C. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.73–6.97 (14H, m, Ar), 5.07 (1H, s, CH), 2.75–2.60 (4H, m, 2NCH_2), 1.50–0.92 (12H, m, 6CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 146.01–120.49 (Ar, C=C), 72.95 (NCH), 50.04 (2 NCH_2), 26.63, 25.05, 22.26 (6CH_2). HRMS found (M^+): 393.2456. Calc. for $C_{29}H_{31}N$:

Table 7
Selected bond angles (°) and interatomic distances for complex **27**

Molecule 1	
Bond angles	
C(10)–Cr(1)–C(20)	86.3(2)
C(10)–Cr(1)–C(30)	89.8(2)
C(20)–Cr(l)–C(30)	83.3(2)
C(10)–Cr(1)–N(1)	106.3(2)
C(20)–Cr(1)–N(1)	167.3(2)
C(30)–Cr(1)–N(1)	97.7(2)
C(10)–Cr(1)–C(1)	143.8(2)
C(20)–Cr(1)–C(1)	129.5(2)
C(30)–Cr(l)–C(1)	90.0(2)
Cr(1)–C(10)–O(10)	176.9(5)
Cr(1)–C(20)–O(20)	174.0(5)
Cr(l)–C(30)–O(30)	176.1(5)
Cr(1)–N(1)–C(5)	96.0(2)
C(1)–N(1)–C(5)	122.4(3)
Cr(1)–N(1)–C(8)	127.5(3)
C(1)–N(1)–C(8)	122.0(4)
C(5)–N(1)–C(8)	110.1(3)
N(1)–C(1)–C(2)	117.4(4)
Cr(1)–C(1)–C(11)	128.3(3)
N(1)–C(1)–C(11)	119.1(4)
C(2)–C(1)–C(11)	123.6(4)
C(1)–C(2)–C(3)	119.5(4)
Cr(1)–C(2)–C(21)	133.0(3)
C(1)–C(2)–C(21)	119.0(4)
C(3)–C(2)–C(21)	121.4(4)
C(2)–C(3)–C(4)	120.6(4)
Cr(1)–C(3)–C(31)	132.6(3)
C(2)–C(3)–C(31)	118.7(4)
C(4)–C(3)–C(31)	120.5(4)
Cr(1)–C(4)–C(5)	89.1(3)
C(3)–C(4)–C(5)	118.1(4)
Cr(l)–C(4)–C(41)	129.1(3)
C(3)–C(4)–C(41)	119.0(4)
C(5)–C(4)–C(41)	119.2(4)
N(1)–C(5)–C(4)	103.0(3)
N(1)–C(5)–C(6)	97.0(3)
C(4)–C(5)–C(6)	115.3(4)
N(1)–C(5)–C(51)	115.0(4)
C(4)–C(5)–C(51)	115.4(4)
C(6)–C(5)–C(51)	109.6(4)
C(5)–C(6)–C(7)	110.3(4)
C(5)–C(6)–O(1)	126.5(5)
C(7)–C(6)–O(1)	123.1(5)
C(6)–C(7)–C(8)	103.1(4)
C(6)–C(7)–O(7)	107.8(4)
C(8)–C(7)–O(7)	105.3(4)
C(6)–C(7)–C(71)	113.3(5)
C(8)–C(7)–C(71)	114.8(5)
O(7)–C(7)–C(71)	111.8(5)
N(1)–C(8)–C(7)	104.4(4)
C(1)–C(11)–C(12)	114.2(4)
C(11)–C(12)–C(13)	110 2(4)
Interatomic distances (Å)	
Cr(1)–C(10)	1.828(6)
Cr(1)–C(20)	1.806(6)
Cr(1)–C(30)	1.807(6)
Cr(1)–N(1)	2.135(4)
Cr(1)–C(1)	2.154(4)
Cr(l)–C(2)	2.183(5)
Cr(1)–C(3)	2.229(4)
Cr(1)–C(4)	2.291(4)
C(10)–O(10)	1.163(5)
C(20)–O(20)	1.170(6)
C(30)–O(30)	1.170(6)
N(1)–C(1)	1.400(6)
N(1)–C(5)	1.509(5)
N(1)–C(8)	1.474(6)
C(1)–C(2)	1 393(6)
C(1)–C(11)	1.512(6)
C(2)–C(3)	1.440(6)
C(2)–C(21)	1.502(6)
C(3)–C(4)	1.405(6)
C(3)–C(31)	1.483(7)
C(4)–C(5)	1 539(6)
C(4)–C(41)	1.498(7)
C(5)–C(6)	1.522(7)
C(5)–C(51)	1.531(7)
C(6)–C(7)	1.549(7)
C(6)–O(1)	1.198(5)
C(7)–C(8)	1.529(7)
C(7)–O(7)	1.426(6)
C(7)–C(71)	1 499(8)
C(11)–C(12)	1.526(7)
C(12)–C(13)	1.511(7)

393.2456. Then the enamine **16c** (0.10 g, 5.2%) as a solid; m.p. 114°C. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.6–7.0 (14H, m, Ar) 4.76 (1H, s, CH), 3.21 (4H, m, 2 NCH_2), 1.8–1.45 (12H, m, 6 CH_2); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 148.25–120.5 (Ar), 57.3 (CH), 51.5 ($2NCH_2$), 27.5, 25.6, 23.0 ($6CH_2$). HRMS found (M^+): 393.2456. Calc. for $C_{29}H_{31}N$: 393.2456. Then diphenylindanone **15** (0.10 g, 8%) and then complex **11c** (1.02 g, 37,4%) as a yellow solid; m.p. 148°C; IR ($CHCl_3$) 1965, 1885, 1685 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.5–7.0 (10H, m, Ar), 6.2–4.8 (5H, m, ArCr), 4.2 (1H, dt, $J = 14$ and 4 Hz, NCH), 3.3 (1H, dt, $J = 14$ and 4 Hz, NCH), 2.6–2.3 (2H, m, Ph–C–CH_2), 1.9–1.1 (12H, m, $6CH_2$). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 232.8 (CO), 178.48 (CO), 143.57–111.58, (C=C, Ar), 94.11–90.6 (ArCr), 57.92 (Ph–C), 41.56 (NCH_2), 40.28 (Ph–C–CH_2), 26.92, 26.59, 26.37, 24.43, 23.38, 23.12 ($6CH_2$). HRMS found (M^+–3CO): 473.1811. Calc. for $C_{30}H_{31}NO$: 473.1811. And finally **12c** (0.21 g, 11%) as a white solid; m.p. 173–174°C; IR ($CHCl_3$) 1696 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.4–6.59 (15H, m, Ar), 4.07 (1H, dt, $J = 14$ and 4 Hz, NCH), 3.06 (1H, dt, $J = 14$ and 4 Hz, NCH), 2.6–2.3 (2H, m, Ph–C–CH_2), 1.7–1.0 (12H, m, $6CH_2$). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 181.55 (CO), 141.87–123.48, (C=C, Ar), 41.28 (NCH_2), 32.70 ($PhCCH_2$), 26.83, 26.65, 26.56, 24.71, 23.06, 21.56 ($6CH_2$). HRMS found (M^+) 421.2404. Calc. for $C_{30}H_{31}NO$: 421.2405.

*4.8. Reaction of complex **10d** (n = 12) with diphenylacetylene*

The reaction was carried out as above starting from complex **10d** (2 g, 4.32 mmol) and diphenylacetylene (0.9 g, 20% excess). Silica gel chromatography of the residue gave with PE as eluent the amine **17d** (37 mg, 1.9%) as a solid; m.p. 166°C; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.59–7.08 (14H, m, Ar), 5.01 (1H, s, NCH), 2.55–2.51 (2H, m, NCH_2), 2.36–2.32 (2H, m, NCH_2), 1.38–1.08 (20H, m, CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz), δ 145.85–120.51 (C=C, Ar), 69.40 (NCH), 50.97 (NCH_2), 27.33, 26.59, 25.94, 25.45, 25.21 (CH_2). HRMS found (M^+): 449.3082. Calc. for $C_{33}H_{39}NO$: 449.3082. Elution with PE/CH_2Cl_2 (95/5) gave complex **18d** (0.31 g, 12.3%) as an orange solid; m.p. 136°C; IR ($CHCl_3$) 1960, 1880 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.40–7.22 (10H, m, Ar), 6.09–5.26 (5H,m, ArCr and NCH), 2.67–2.35 (4H,m, NCH_2), 1.47–1.19 (20H, m, 10 CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 233.57 (CO), 146.28–127.88, 116.74, 114.14 (C=C, Ar), 92.83, 91.53, 90.62, 89.97, 86.81 (ArCr), 70.05 (NCH), 50.82 (NCH_2), 27.21, 26.47, 25.82, 25.39, 25.22 (CH_2). HRMS found (M^+): 585.2333. Found for $C_{36}H_{39}NO_3Cr$: 585.2335. Elution with PE/CH_2Cl_2 (90/20) first gave diphenyl indanone (0.14 g, 11.3%) then diphenyl indenone (0.047 g, 3.9%). Elution with PE/CH_2Cl_2 (95/5) gave complex **11d** (0.82 g, 31%) as orange crystals; m.p. 178°C; IR ($CHCl_3$) 1975, 1900, 1697 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.45–6.99 (10H, m, Ar), 6.18–4.92 (5H, m, ArCr), 4.08–4.05 (1H, m, NCH), 3.27–3.22 (1H, m, NCH), 2.40–2.34 (2H, m, $PhCCH_2$), 1.57–1.09 (20H, m, CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 232.79 (CO), 177.72 (CO), 143.45–110.82 (C=C, Ar), 93.91, 93.69, 90.80, 90.24 (ArCr), 57.79 ($PhC(CH_2)$), 41.72 (NCH_2), 41.11 ($PhC(CH_2)$), 28.76, 28.38, 27.51, 27.17, 26.88, 26.71, 26.26, 25.84, 25.69 (CH_2). HRMS found (M^+): 613.2284. Calc. for $C_{37}H_{39}NO_4$ Cr: 613.2284. Data for **12d** white solid; m.p. 161°C; IR ($CHCl_3$) 1688 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.38–6.69 (15H,m, Ar), 3.77–3.71 (1H, m, NCH), 3.01–2.94 (1H, m, NCH), 2.49–2.42 (1H,m, PhCCH), 2.11–2.06 (1H, m, PhCCH), 1.64–1.14 (20H, m, CH_2); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 180.89 (CO), 141.73–122.44 (C=C, Ar), 60.44 ($PhCCH_2$), 41.63 (NCH_2), 34.43, 28.93, 28.51, 27.66, 27.23, 27.11, 26.65, 26.57, 26.38, 26.04, 24.50 (CH_2). HRMS found (M^+): 477.3032. Calc. for $C_{34}H_{39}NO$: 477.3032.

*4.9. Pentacarbonyl (N-cyclodecynylamine) ethylidene chromium (0) **20a***

This complex was obtained upon aminolysis of complex **19a** with cyclodecynylamine as yellow crystals in 56% yield; m.p. 102°C; IR ($CHCl_3$) 2045, 1965, 1915 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz,) δ 8.48 (1H, s, NH), 4.87–4.75 (1H, m, NCH), 2.26 (3H, s, Me), 2.65–2.53 (1H, m, CH–C<u>H</u>H), 2.36–2.23 (2H, m, C=C–CH<u>H</u>), 2.18–2.10 (2H, m, C=C–C<u>H</u>H), 1.96–1.60 (8H, m, 4 CH_2), 1.57–1.47 (1H, m); ^{13}C-NMR ($CDCl_3$, 100MHz) δ 277.78 (C=Cr), 223.0, 218.17 (CO), 85.57, 84.05 (C≡C), 56.39 (NCH), 35.31 (Me), 34.60, 31.21, 24.92, 24.37, 23.99, 18.61, 18.49 (CH_2). Anal. calc. for $C_{17}H_{19}NO_5Cr$ (%): C, 55.28; H, 5.15; N, 3.79. Found: C, 55.13; H, 5.20; N, 3.67.

*4.10. Pentacarbonyl (N-methyl-cyclodecynylamine) propylidene chromium (0) **21a***

This complex was obtained upon alkylation of complex **20a** as above with methyl iodide in the presence of LDA. Work up as usual gave complex **21a** as a yellow solid in 53.5% yield; m.p. 60°C; IR ($CHCl_3$) 2040, 1960, 1915 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 5.26–5.21 (1H, m, NCH), 3.51 (3H, s, Me), 3.43–3.34 (1H, m), 3.25–3.16 (1H, m), 2.33–2.19 (2H, m), 2.19–2.04 (2H, m), 1.97–1.89 (1H, m), 1.81–1.58 (8H, m), 1.08 (3H t, $J = 7.6$ Hz, Me); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 280.09 (Cr=C), 223.75, 218.55 (CO), 85.64, 83.78 (C≡C), 61.44 (NCH), 44.99 (NMe), 44.57, 32.74, 29.22, 26.41, 24.17, 23.78, 18.89, 18.16, 11.11 (CH_2). Anal. calc. for $C_{19}H_{23}NO_5Cr$ (%): C, 57.43; H, 5.79; N, 3.53. Found: C, 57.26; H, 5.84; N, 3.49.

*4.11. Pentacarbonyl (N-cyclodecynylamine) benzylidene chromium (0) **20b***

This complex was obtained as above by aminolysis of complex **19b** with the corresponding amine as a yellow solid in 41% yield; m.p. 110°C; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.72 (1H, s, NH), 8.08–6.86 (5H, m, Ar), 4.34–4.24 (1H, m, NCH), 2.42–2.34 (1H, m), 2.13–2.07 (1H, m), 1.95–1.50 (10H, m), 1.49–1.40 (1H, m), 1.23–1.12 (1H, m); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 279.34 (C=Cr), 223.53, 217.52 (CO), 149.76, 129.64, 128.51, 126.93 (Ar), 85.13, 83.54 (C≡C), 59.78 (NCH), 35.47, 31.65, 24.94, 24.21, 23.93, 18.34, 18.06 (CH_2). Anal. calc. for $C_{22}H_{21}NO_5Cr$ (%): C, 61.25; H, 4.87; N, 3.25. Found: C, 61.14; H, 4.94; N, 3.26.

*4.12. Pentacarbonyl (N-methyl-cyclodecynylamine) benzylidene chromium (0) **21b***

This complex was obtained upon methylation of **20b** as above with methyl iodide in the presence of LDA as a yellow solid; m.p. 125°C; IR ($CHCl_3$) 2040, 1970, 1920 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.41–6.74 (5H, m, Ar), 4.88–4.81 (1H, m, NCH), 3.78 (3H, s, Me), 2.27–2.19 (1H, m), 2.08–2.01 (1H, m), 1.91–1.52 (10H, m), 1.52–1.45 (1H, m), 1.38–1.29 (1H, m); ^{13}C-

NMR ($CDCl_3$, 50 MHz) δ 275.18 (Cr=C), 220.44, 217.66 (CO), 128.44, 128.14, 125.91, 120.20, 118.75 (Ar), 84.87, 83.16 (C≡C), 66.14 (NCH), 43.56 (NMe), 32.62, 29.30, 25.91, 23.95, 23.36, 18.59, 17.68 (CH_2). Anal. calc. for $C_{23}H_{23}NO_5Cr$ (%): C, 62.02; H, 5.17; N, 3.15. Found: C, 61.82; H, 5.39; N, 3.12.

4.13. Pentacarbonyl (ethoxy) phenyl-3-propenylidene chromium (0) **22**

This was obtained from $Cr(CO)_6$ (4.4 g, 20 mmol) in a diethyl ether (125 ml) at −78°C, and $PhCH_2CH_2Li$ prepared from $PhCH_2CH_2I$ (4.64 g, 20 mmol) in a mixture of diethyl ether (80 ml) and pentane (125 ml) and by reaction with *t*-BuLi (40 mmol, 1.7 M in hexanes). After heating to room temperature, the solvent was evaporated under vacuum. Water (100 ml) was then added to the residue, then Et_3OBF_4 until the solution was acid. After extraction with diethyl ether, the solution was dried on $MgSO_4$. Evaporation of the solvent followed by filtration of the residue on silica gel, gave complex **22** as an orange oil (3.5 g, 49.5%). IR ($CHCl_3$) 2027, 1998, 1945 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.41–7.23 (5H, m, Ar), 5.16 (2H, q, $J = 7.6$ Hz, OCH_2), 3.67 (2H, t, $J = 7.8$ Hz, CH_2CH_2Ph), 2.86 (2H, t, $J = 7.8$ Hz, CH_2CH_2Ph), 1.32 (3H, t, $J = 7.6$ Hz, Me); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 358.56 (Cr=C), 223.09, 223.27, 216.51 (CO), 140.32, 128.71, 128.47, 126.45 (Ar), 78.12 (OCH_2), 64.46 (CH_2CH_2Ph), 32.42 (CH_2CH_2Ph), 15.03 (Me). Anal. calc. for $C_{16}H_{14}O_6Cr$ (%): C, 54.23; H, 3.95. Found: C, 54.32; H, 4.04.

4.14. Pentacarbonyl(2-methylaziridinyl)phenyl-3-propylidene chromium (0) **23**

To a solution of $(CO)_5Cr{=}C(OEt)(CH_2)_2Ph$ (3.4 g, 9.6 mmol) in Et_2O (125 ml), at −40°C, was added 2-methylaziridine (0.8 ml). The solution was kept at this temperature overnight, then the solvent was evaporated under vacuum to give complex **23** as yellow crystals (3.12 g, 88%); m.p. 78°C; IR ($CHCl_3$) 2020, 1963, 1915 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (two *E*, *Z* isomers), 7.37–7.23 (10H, m, Ar), 3.40–3.30 (2H, m, $PhCH_2CHH$), 3.28–3.22 (2H, m, NCH de Z), 3.13–2.94 (7H, m, NCHH, CH_2Ph, $PhCH_2CHH$), 2.70 (1H, m, NCHH), 2.51–2.45 (1H, m, NCH), 2.36 (1H, m, NCHH), 1.55 (3H, d, $J = 5.7$ Hz, Me), 1.48 (1H, m, NCHH), 1.4 (3H, d, $J = 5.7$ Hz, Me); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 271.09, 267.93 (Cr=C), 223.09, 223.02, 218.33, 218.23 (CO), 140.67, 140.56, 129.06, 128.85, 128.8, 126.63 (Ar), 55.67, 55.25 (C–CH_2CH_2Ph), 37.53 (NCH), 39.11 (NCH), 33.66, 33.11 ($PhCH_2$), 32.74, 32.38 (NCH_2), 17.29 (Me), 16.89 (Me). Anal. calc. for $C_{17}H_{13}NO_3Cr$ (%): C, 55.89; H, 4.10; N, 3.83. Found: C, 55.93; H, 4.11; N, 3.90.

4.15. Pentacarbonyl (2-methylaziridinyl) phenyl-3-propenylidene chromium (0) **31**

This complex was obtained as above from the corresponding ethoxycarbene complex (2.7 g, 1.6 mmol) and methyl-2-aziridine (0.52 g, 9.10 mmol) as red crystals (1.56 g, 57%); m.p. 82°C; IR ($CHCl_3$) 2045, 1968, 1923 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.49–7.08 (14H, m, Ar, CH=CH, two *E*, *Z* isomers), 3.41 (1H, m, NCH), 3.21 (2H, m, NCH), 2.83 (2H, m, NCH_2), 2.49 (1H, m, NCH), 1.74 (3H, d, $J = 5.7$ Hz, Me), 1.51 (3H, d, $J = 5.6$ Hz, Me); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 258.82 (Cr=C), 223.43, 218.46 (CO), 143.69, 142.69 (CH=**C**HPh), 136.31, 135.35 (CH=**C**HPh), 130.19, 130.08, 129.10, 128.14 (Ar), 37.71 (NCH), 35.0 (NCH), 33.38 (NCH_2), 32.53 (NCH_2), 17.75(Me), 17.43 (Me). Anal calc. for $C_{17}H_{13}NO_3Cr$ (%): C, 56.19; H, 3.58; N, 3.85. Found: C, 56.30; H, 3.69; N, 3.84.

4.16. Pentacarbonyl (2-methylaziridinyl) methyl-2-propenylidene chromium (0) **35**

This complex was obtained as above by treatment of complex **34** (2.5 g, 8.6 mmol) with methyl-2-aziridine (0.59 g, 10 mmol) in Et_2O, and isolated, after silica gel chromatography as a yellow oil (1.49 g, 57.3%). IR ($CHCl_3$) 2045, 1970, 1915 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 4.74 (2H, m, =CHH), 4.47–4.43 (2H, m, CHH), 3.44 (1H, m, NCH), 3.13 (2H, m, NCH and NCHH), 2.74 (2H, m, NCH_2), 2.31 (1H, m, NCHH), 1.95 (6H, 2Me), 1.71 (3H, d, N–CH–Me), 1.46 (3H, d, N–CH–Me); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 271.14, 270.03 (Cr=C), 223.65, 223.61, 217.91, 217.83 (CO), 155.97, 155.38, (Me**C**=**C**), 105.43, 105.12 (=CH_2), 37.31 (NCH), 35.29 (NCH), 32.39 (NCH_2), 32.30 (NCH_2), 20.53 (Me), 17.53 (N–CH–Me), 17.03 (N–CH–Me). Anal. calc. for $C_{12}H_{11}NO_3Cr$ (%): C, 47.84; H, 3.65; N, 4.65. Found: C, 47.80; H, 3.73; N, 4.55.

4.17. Reaction of complex **23** with diphenylacetylene

Heating of complex **23** (2.5 g, 6.8 mmol), in the presence of diphenylacetylene (2.4 g, 13.7 mmol), in benzene (50 ml) for 12 h gave after evaporation of the solvent a residue which was chromatographed on silica gel. Elution with PE/AcOEt (95/5) first gave tetraphenylacyclopentadienone **29** (47 mg), then phenylpropionitrile **24** (0.45 g, 50%) as an oil; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.29 (4H, m, Ar), 2.94 (2H, t, $J = 7.3$ Hz, CH_2CN), 2.62 (2H, t, $J = 7.3$ Hz, CH_2Ph). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 138.02, 128.79, 128.22, 127.13 (Ar), 119.15 (CN), 31.45 (CH_2CN), 19.25 (CH_2Ph). MS found (M^+): 131. Calc. for C_9H_9N: 131. Elution with PE/AcOEt (90/10) gave compound **28** (0.15 g) as a white solid; m.p. 138°C; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.4–6.72 (25H, m, Ph), 3.05 (4H, s,

CH_2–CH_2); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.67–125.76 (Ar), 38.42 (CH_2–CH_2Ph). HRMS found (M^+): 487.2299. Calc. for $C_{37}H_{29}N$: 487.2299. Elution with PE/AcOEt (80/20) gave complex **25** (1.45 g, 30.7%) as red crystals; m.p. 130°C; IR ($CHCl_3$) 1947, 1880, 1845, 1760 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.55–6.50 (25H, m, Ar), 3.65 (1H, m, C$\underline{H}$$CH_3$), 3.58 (1H, t, $J = 8$ Hz, NC$\underline{H}$H), 3.23 (1H, t, $J = 8$ Hz, NCH$\underline{H}$), 2.99 (1H, m, Ph–C$\underline{H}$H), 2.46 (1H, m, PhCH$\underline{H}$), 2.17 (1H, m, Ph-CH_2C$\underline{H}$H), 1.84 (1H, m, Ph–CH_2CH$\underline{H}$), 1.46 (3H, d, $J = 6.84$ Hz, Me). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 235–230 (CO), 208.43 (CO), 139.44–104.74 (C=C, Ar), 79.96 (N–C–CO), 53.63 (NCH_2), 43.41 (CHCO), 34.21, 32.76 (CH_2CH_2Ph), 12.82 (Me). HRMS found (M^+ –3CO): 609.2125. Found for $C_{41}H_{35}NOCr$: 609.2124. Then complex **26** (0.31 g, 6.6%) as red crystals; m.p. 125°C; IR ($CHCl_3$) 1955, 1890, 1845, 1770 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.60–6.57 (25H, m, Ar), 3.73 (1H, t, $J = 8$ Hz, NC$\underline{H}$H), 3.18–3.01 (2H, m, Ph–C$\underline{H}$H; NCH$\underline{H}$), 2.82 (1H, m, COCH), 2.53 (2H, m, Ph CH$\underline{H}$, Ph CH_2C$\underline{H}$H), 2.24–2.17 (1H, m, Ph–CH_2CH$\underline{H}$), 1.85 (3H, d, $J = 8$ Hz, Me); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 203 (CO), 139.72–123.58 (Ar, **C**–CH_2 CH_2Ph), 117.22, 92.91 (C=**C**–Ph), 83.26 (N–C–CO), 53.08 (NCH_2), 40.88 (CHCO), 35.17, 33.39 (CH_2CH_2Ph), 17.41 (Me). Anal. calc. for $C_{44}H_{35}NO_4Cr$ (%): C, 76.19; H, 5.05; N, 2.02. Found: C, 76.06; H, 5.04; N, 1.99. And finally with the same mixture of eluents complex **27** (85 mg, 1.8%) as red crystals; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.89–6.52 (H, m, Ar), 3.56 (1H, t, $J = 10.9$ Hz, NC$\underline{H}$H), 3.35 (1H, t, $J = 10.9$ Hz, NCH$\underline{H}$), 3.05–2.98 (1H, m, Ph–C$\underline{H}$H; NCH$\underline{H}$), 2.45–2.32 (2H, m, PhC$\underline{H}$H, Ph CH_2C$\underline{H}$H), 2.25 (3H, s, Me), 2.08–1.98 (1H, m, Ph CH_2CH$\underline{H}$).

4.18. Reaction of complex *27* with pyridine

Refluxing of complex **27** in pyridine for 12 h gave, after evaporation of the solvent and filtration through silica gel, compound **27a** as a solid; m.p. 80°C; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.67–6.57 (30H, m, Ar), 4.14 (1H, d, $J = 9,9$ Hz, NC$\underline{H}$H), 4.08 (1H, d, $J = 9,9$ Hz, NCH$\underline{H}$), 2.71–2.65 (1H, m, Ph–C$\underline{H}$H), 2.52–2.45 (1H, m, PhCH$\underline{H}$), 2.42–2.35 (1H, m, Ph CH_2 C$\underline{H}$H), 2.01–1.94 (1H, m, Ph CH_2CH$\underline{H}$), 1.49 (3H, s, Me). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 215.97 (CO), 143.68–118.68 (Ar, C=C), 76.54 (HO–C–Me), 72.63 (N–C–CO), 58.44 (NCH_2), 34.25, 32.04 (CH_2CH_2Ph), 25.10 (Me). HRMS found (M^+): 555.2562. Calc. for $C_{41}H_{35}NO_2$: 555.2561.

4.19. Reaction of complex *31 a* with diphenylacetylene

Complex **31** (1.8 g) was refluxed in benzene (50 ml) for 10 h in the presence of diphenylacetylene (1.76 g). Evaporation of the solvent followed by silica gel chromatography of the residue gave first with PE/AcOEt (95/5) phenylacrylonitrile **32** (0.34 g, 53.3%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.44 (5H, m, Ph), 7.4 (1H, t, $J = 16.7$ Hz, CHCN), 5.89 (1H, d, $J = 16.7$ Hz, CHPh); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 150.69 (CH–Ph), 133.63, 131.36, 129.26, 127.52 (Ar), 118.35 (CN), 96.24 (CH–CN). IR ($CHCl_3$) 2210 (CN), 1673 cm^{-1}. Then with PE/AcOEt (90/10) the phenol **33** (0.96 g, 19.4%) as a white solid; m.p. 94°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.7–7 (16H, m, Ar) 4.98 (1H, s, OH), 2.0–1.83 (2H, m, NCH_2), 1.78 (1H, m NCH), 0.64, 3H, d, $J = 5.3$ Hz, Me). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.02, 144.93, 138.32–121.9 (Ar), 37.37 (NCH), 35.93 (NCH_2), 17.61 (Me). IR ($CHCl_3$): 3575, 3530 cm^{-1}. Anal. calc. for $C_{28}H_{25}NOCl_2$($C_{27}H_{23}NO + CH_2Cl_2$) (%): C, 72.72; H, 5.41; N, 3.03. Found: C, 72.85; H, 5.52; N, 2.85.

4.20. Reaction of complex *35* with diphenylacetylene

Refluxing complex **35** (1.57 g, 5.2 mmol) in benzene (50 ml) in the presence of diphenylacetylene (1.85 g, 10.43 mmol) for 15 h, gave after evaporation of the solvent and silica gel chromatography, compound **36** (0.25 g, 15.4%) as a solid; m.p. 67°C; IR ($CHCl_3$) 3585, 3520 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.28–6.83 (11H, m, Ar), 5.31 (1H, s, OH), 2.44 (3H, s, Ar–Me), 1.83 (1H, m, NCH), 1.77, 1.73 (2H, m, NCH_2), 0.8 (3H, d, $J = 5.4$ Hz, NCHC$\underline{H}_3$). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 146.48, 142.96 (C=C–OH, C=C–NH), 137.91–115.84 (Ar), 37.63 (NCH), 37.31 (NCH_2), 18.24 (Ph–Me), 16.40 (NCHC$\underline{H}_3$). HRMS found (M^+): 315.1623. Calc. for $C_{22}H_{21}NO$: 315.1624.

4.20.1. Structure solution and refinement

For complexes **12d**, **17d**, **20b, 25** and **26:** 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 data and collection parameters are listed in Table 1. The data corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[17] Scattering factors and corrections for anomalous absorption were taken from [18]. The structures were solved by Fo–Patterson technique or direct method (SHELXS [19] for **17d**. Refinements were carried out by full-matrix least-squares. For **12d** and **20b** all non-hydrogen atoms were anisotropically refined, hydrogen atoms were introduced in calculated positions except on nitrogen atoms for **20b** and except on the carbon atoms with high value of $u(iso)$ for **12d**. For **17d**, **25**, and **26**, the measured diffraction intensities were very weak, due to the small size of the crystals. Therefore, only the $Cr(CO)_3$ fragment in **25** was anisotropically refined and for **17d** and **26** all atoms were left isotropic and hydrogen atoms were

not [H1]included. This led to higher values of the reliability factor for these three compounds.

For complex **27**, data were collected at room temperature on a Stoe diffractometer imaging plate diffraction system (IPDS) equipped with a graphite oriented monochromator utilizing Mo–K_α radiation ($\lambda =$ 0.71073). The asymetric unit is built up of two independent molecules. Only one of these molecules (1) is represented in Fig. 5. The final unit cell parameters were derived from the least-squares refinement of 2000 selected reflections. The structure was solved by direct methods (SIR92) [21] and refined by least-squares procedures on Fobs. H atoms were introduced in calculation in idealized positions (d(CH) = 0.96 Å) and their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon to which they are attached. The calculations were carried out with the CRYTALS package programs [17], running on a Compaq Prolinea 5100e. The drawing of the molecule was realized with the program CAMERON [20].

5. Supplementary material

Fractional atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, atomic coordinates for H atoms, complete lists onf 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.

Acknowledgements

This research was supported by the Commission of the European Communities (DGSRD, International Scientific Cooperation), Centre National de la Recherche Scientifique and MENRT (grant to S. Lafollée-Bezzenine).

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