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Reactivity of *N*-disubstituted aminocarbene complexes of chromium: nitrogen to carbon migration of the benzyl and allyl groups following alkyne insertions

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Abstract

Chromium aminocarbene complexes $(CO)_5Cr{=}C(CH_3)N(CH_2Ph)(CH_3)$ (**3**), $(CO)_5Cr{=}C(H)N(CH_2Ph)(CH_3)$ (**5**) and $(CO)_5Cr{=}C(H)N(CH_2CH{=}CH_2)(CH_3)$ (**7**) react with diphenylacetylene in boiling benzene to give, after insertions of the alkyne and CO and migration of the benzyl or the allyl group from nitrogen to carbon, substituted 2- and 3-pyrrolinones (**10**–**15**). The structures of $(CO)_5Cr{=}C(CH_3)N(CH_2Ph)CH_3$ (**3***Z*) (R 0.031 R_w 0.030) and of the chromium tricarbonyl complex of the pyrrolinone **10**, $(CO)_3Cr$ $(C_{24}H_{23}ON)$ (**9**) (R 0.034 R_w 0.035) were determined by the X-ray diffraction.

Although aminocarbene complexes are easy to obtain [1], their use as synthons in organic chemistry has received little attention [2,3]. This is probably due to the lower reactivity of these complexes, the presence of nitrogen on the carbene carbon decreasing the lability of the carbon monoxide ligands [4]. For example, aminocarbene complexes of chromium bearing a phenyl group on the carbene carbon have been used recently for the synthesis of indanones by an alkyne-insertion benzannulation reaction carried out at high temperature [3]. We have now found that disubstituted aminocarbene complexes undergo a novel reaction with alkynes which leads to heterocyclic compounds after an unprecedented rearrangement, the characteristics of which are close to the Stevens rearrangement [5] of a nitrogen-carbon centered zwitterionic species. We previously described [6,7] the behaviour of aminocarbene complexes derived from cycloamines. We now report on the reaction of *N*-(methyl)benzyl- and *N*-(methyl)allyl-aminocarbene complexes with alkynes.

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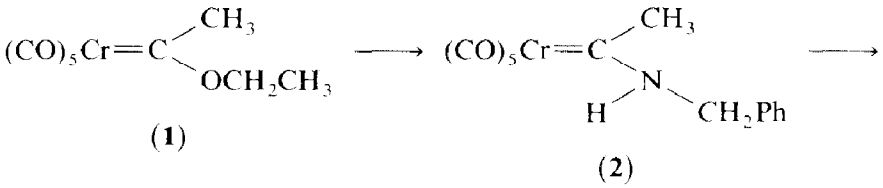
Such structures are interesting from a mechanistic point of view, since it has been shown that in the Stevens rearrangement of benzyl- and ethyl-substituted ammonium compounds, these groups preferentially migrate from nitrogen to carbon.

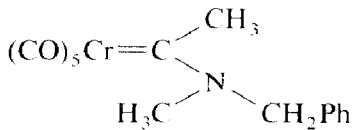
Results and discussion

(A) Preparation of carbene complexes 3, 5 and 7

Since Fischer [8] showed that aminolysis of complex **1** with *N*-(methyl)benzylamine did not give the expected complex **3** but instead complex **2**, with elimination of a methyl group, we prepared complex **3** indirectly by aminolysis of **1** with benzylamine, a reaction leading to (**2***E*), followed by an alkylation at a nitrogen [9], at −60 °C. Thus treatment of (**2***E*) with a slight excess of lithium-diisopropylamide (LDA), then with methyl iodide gave complex **3** in 77% yield as a yellow oil. According to its ^{1}H NMR spectrum, the product is a 20/80 mixture of the *E* and *Z* isomers. Recrystallization from ethanol/methylene chloride gave crystals of (**3***Z*) suitable for a single crystal X-ray study, which revealed the structure shown in Fig. 1. The structural features associated with the carbene portion of (**3***E*) are similar, and typical of those noted for other Fischer type pentacarbonylchromium amino-carbene complexes [9,10–13].



(**1**) (**2**)



(**3***E*,*Z*)

Atomic positions and selected bond lengths (Å) and bond angles (°) are listed in Tables 4 and 1. Of interest is the *Z* geometry of the benzyl group with respect to the metal: since in the starting complex **2** the benzyl group was *E*, an inversion at nitrogen took place during the alkylation reaction. This was be easily demonstrated since treatment of **2***E* with lithium diisopropylamine (LDA), followed by protonation, gave, according to the ^{1}H NMR spectrum a 35/65 mixture of **2***E*,*Z*.

Complexes **5** and **7** were obtained by a method developped recently by Hegedus [14]. Thus, when *N*-(methyl)benzylamide (**4**) was treated first with $(CO)_5CrNa_2$, in THF at −60 °, and then with Me_3SiCl, complex **5** was obtained as pale yellow crystals (m.p. 130 °C, 75% yield). The ^{1}H NMR spectrum was consistent with complex **5** as a 70/30 mixture of the *E* and *Z* isomers: a typical signal appears in each case at low field (11.13 ppm for **5***E* and 11.02 ppm for **5***Z*, attributable to the hydrogen atoms on the carbene carbon.

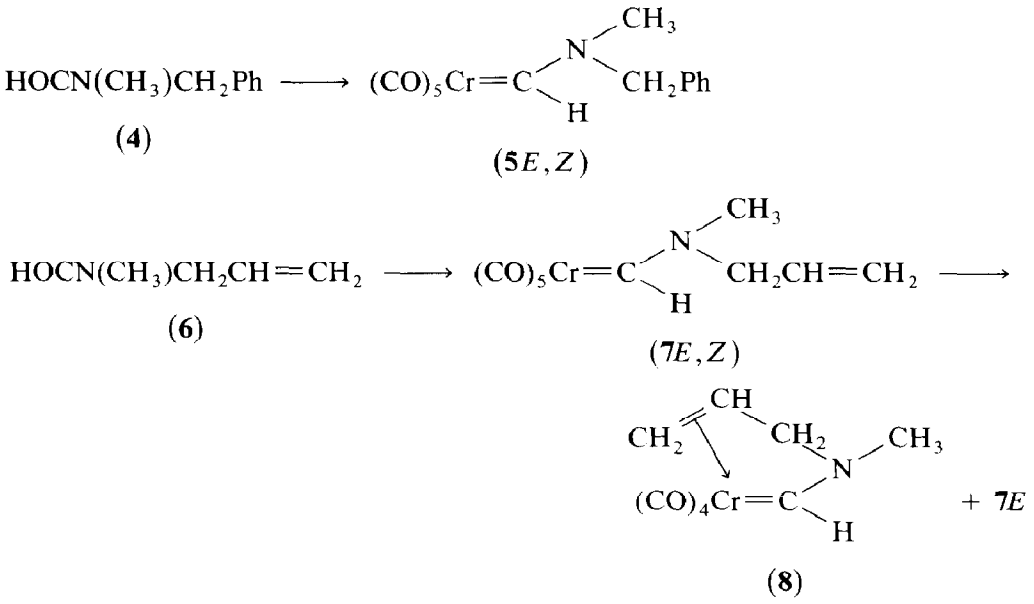


Fig. 1. ORTEP view of the chromium aminocarbene complex **3Z** showing the crystallographic numbering scheme. Selected bond lengths (Å) and angles (deg): Cr1–C1 2.134(3), N1–C3 1.482(3), N1–C4 1.473(3), C1–C2 1.511(4), C1–N1 1.310(4), C4–C5 1.502(4), C2–C1–Cr1 123.6(2), N1–C1–C2 112.9(2), C4–N1–C1 123.6(2), C5–C4–N1 113.5(2), C10–C5–C4 120.6(2), N1–C1–Cr1 130.2(2), C3–N1–C1 124.4(2), C4–N1–C3 11.9(2), C6–C5–C4 120.7(3).

Table 1

Interatomic distances (Å) and bond angles (°) for $Cr(CO)_5(C_{10}H_{13}N)$ for complex **3Z**

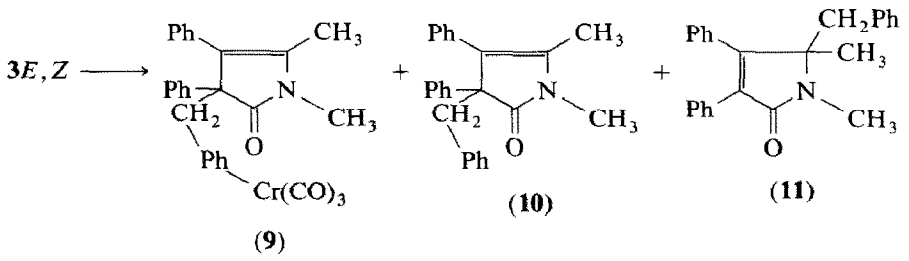
Cr(1)–C(11)	1.898(3)	C(11)–O(11)	1.139(3)
Cr(1)–C(12)	1.888(3)	C(12)–O(12)	1.143(3)
Cr(1)–C(13)	1.898(3)	C(13)–O(13)	1.138(3)
Cr(1)–C(14)	1.859(3)	C(14)–O(14)	1.151(3)
Cr(1)–C(15)	1.883(3)	C(15)–O(15)	1.144(3)
Cr(1)–C(1)	2.134(3)		
C(1)–C(2)	1.511(4)	N(1)–C(3)	1.482(3)
C(1)–N(1)	1.310(3)	N(1)–C(4)	1.473(3)
C(4)–C(5)	1.502(4)		
C(5)–C(6)	1.381(4)	C(5)–C(10)	1.386(4)
C(6)–C(7)	1.389(4)	C(7)–C(8)	1.359(5)
C(8)–C(9)	1.365(5)	C(9)–C(10)	1.383(4)
C(12)–Cr(1)–C(11)	174.6(1)	C(13)–Cr(1)–C(11)	88.4(1)
C(13)–Cr(1)–C(12)	91.3(1)	C(14)–Cr(1)–C(11)	86.9(1)
C(14)–Cr(1)–C(12)	87.7(1)	C(14)–Cr(1)–C(13)	91.3(1)
C(15)–Cr(1)–C(11)	92.2(1)	C(15)–Cr(1)–C(12)	88.1(1)
C(15)–Cr(1)–C(14)	179.1(1)	C(15)–Cr(1)–C(14)	89.5(1)
C(1)–Cr(1)–C(11)	89.4(1)	C(1)–Cr(1)–C(12)	96.0(1)
C(1)–Cr(1)–C(13)	93.6(1)	C(1)–Cr(1)–C(14)	173.9(1)
C(1)–Cr(1)–C(15)	85.7(1)		
O(11)–C(11)–Cr(1)	176.7(3)	O(12)–C(12)–Cr(1)	175.9(3)
O(13)–C(13)–Cr(1)	178.6(3)	O(14)–C(14)–Cr(1)	179.2(3)
O(15)–C(15)–Cr(1)	178.2(3)		
C(2)–C(1)–Cr(1)	116.8(2)	N(1)–C(1)–Cr(1)	130.2(2)
N(1)–C(1)–C(2)	112.9(2)	C(3)–N(1)–C(1)	124.4(2)
C(4)–N(1)–C(1)	123.6(2)	C(4)–N(1)–C(3)	111.9(2)
C(5)–C(4)–N(1)	113.5(2)	C(6)–C(5)–C(4)	120.7(3)
C(10)–C(5)–C(4)	120.6(2)	C(10)–C(5)–C(6)	118.7(3)
C(7)–C(6)–C(5)	120.2(3)	C(8)–C(7)–C(6)	120.4(3)
C(9)–C(8)–C(7)	120.2(3)	C(10)–C(9)–C(8)	120.3(3)
C(9)–C(10)–C(5)	120.3(3)		

carbene carbon at 265.3 ppm for 7*Z*, and at 264.4 ppm for 7*E*, and those from the carbons associated with the terminal double bond at 130.60 and 120.6 ppm for 7*Z* and at 130.8 and 120.9 ppm for 7*E*.

Complex 7*E* was readily obtained pure by heating the 7*E*, *Z* mixture in refluxing benzene: only the 7*Z* isomer underwent intramolecular coordination of the terminal double bond to give **8**. 7*E* (yellow oil) was readily separated from **8** by silica gel chromatography, and obtained as yellow crystals.

(B) Reaction of complexes 3E,Z, 5E,Z and 7E,Z with diphenylacetylene

When complex **3***E*, *Z* was refluxed in benzene for 15 h in the presence of diphenylacetylene a mixture of three new compounds was obtained, as revealed by TLC. Chromatography on silica gel gave successively **10** (15%, white crystals, m.p. 105 °C), **9** (15%, yellow crystals, m.p. 200 °C), and **11** (20%, white crystals, m.p. 120 °C).



Compounds **9**, **10** and **11** were fully characterized from their spectroscopic data. Salient NMR features for complex **9** include a multiplet at 6.63–7.35 ppm due to 10 aromatic protons, multiplets near 5 ppm assigned to an arenechromium tricarbonyl moiety, two pairs of doublets at 3.53 and 2.83 ppm due to the benzylic hydrogens finally, a singlet at 3.03 ppm due to the $N-CH_3$ group and a singlet at 2.19 ppm due to a methyl group associated with a double bond. The presence of an arene-$Cr(CO)_3$ and that of an amide group were confirmed by the ^{13}C NMR spectrum, which showed signals at 107–90.8 ppm, and at 180 ppm (CO).

A single crystal X-ray structure of **9** (see Fig. 2) clearly revealed the insertion of one molecule of diphenylacetylene and of one CO group into **3**, with migration of the benzyl group from nitrogen to a carbon of the alkyne. The solid-state structure of **9** contains a $Cr(CO)_3$ group bound to the phenyl of the benzyl group, the pyrrolinone ring being almost planar.

Atomic positions and selected bond lengths (Å) and bond angles (°) are listed in Tables 2 and 5.

Table 2

Selected interatomic distances (Å) and bond angles (°) for $Cr(CO)_3(C_{25}H_{23}ON)$ (**9**)

Cr(1)–C(41)	2.209(3)	Cr(1)–C(42)	2.210(3)
Cr(1)–C(43)	2.200(3)	Cr(1)–C(44)	2.221(3)
Cr(1)–C(45)	2.214(3)	Cr(1)–C(46)	2.219(3)
N(1)–C(1)	1.423(4)	N(1)–C(3)	1.456(4)
N(1)–C(7)	1.348(4)	C(1)–C(2)	1.495(4)
C(1)–C(6)	1.336(4)	C(4)–C(5)	1.535(4)
C(4)–C(41)	1.503(4)	C(5)–C(6)	1.519(4)
C(5)–C(7)	1.542(4)	C(5)–C(51)	1.535(4)
C(6)–C(61)	1.478(4)	C(7)–O(1)	1.218(3)
C(7)–N(1)–C(1)	111.2(2)	C(3)–N(1)–C(1)	126.8(3)
C(7)–N(1)–C(3)	121.9(3)	C(6)–C(1)–N(1)	110.5(2)
C(2)–C(1)–C(6)	132.4(3)	C(2)–C(1)–N(1)	117.1(3)
C(5)–C(4)–C(41)	114.7(2)	C(7)–C(5)–C(6)	102.0(2)
C(7)–C(5)–C(4)	109.2(2)	C(4)–C(5)–C(6)	114.3(2)
C(7)–C(5)–C(51)	105.2(2)	C(51)–C(5)–C(4)	112.4(2)
C(51)–C(5)–C(6)	112.7(2)	C(1)–C(6)–C(5)	108.8(2)
C(1)–C(6)–C(61)	128.6(3)	C(5)–C(6)–C(61)	122.5(2)
C(5)–C(7)–N(1)	107.1(2)	N(1)–C(7)–O(1)	126.6(3)
C(5)–C(7)–O(1)	126.2(3)	C(4)–C(41)–C(42)	121.2(2)
C(4)–C(41)–C(46)	120.5(3)	C(5)–C(51)–C(52)	122.6(3)
C(5)–C(51)–C(56)	119.8(3)	C(6)–C(61)–C(62)	121.5(3)
C(6)–C(61)–C(66)	121.3(3)		

Table 3

Crystallographic data for complexes **3***Z* and **9**

	Compound **3**	Compound **9**
Formula	$C_{15}H_{13}O_5NCr$	$C_{28}H_{23}O_4NCr$
fw	339.3	489.5
Size (mm)	0.20×0.22×0.8	0.03×0.05×0.6
Cryst. system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a, Å	11.770(8)	9.361(1)
b, Å	12.528(2)	12.234(1)
c, Å	11.662(2)	20.834(3)
β, deg	110.16(2)	78.50(1)
V, Å^3	1614	2338
Z	4	4
σ calcd, g cm^{-3}	1.34	1.39
μ (Mo-K_α), cm^{-1}	7.08	5.10
Diffractometer	PW 1100	CAD4
Temp., °C	20	20
Radiation	Mo-K_α	Mo-K_α
Absorption	1.53–1.13	none
Scan range θ, deg	1.4+0.34tan θ	1.0+0.34tan θ
2 θ range, deg	4–50	3–50
Refl. collected	2728	4319
Refl. merged, (Rm)	2594 (0.046)	4112 (0.027)
Refl. used	2119	2931
Criteria	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Computer program	Crystals	Crystals
Structure solution	Patterson	Patterson
Weight unit	1	1
R	0.031	0.034
R_w	0.030	0.035
rms (shift/esd)	0.26	0.11
l.s. parameters	240	378
degrees of freedom	1879	2559

Air oxidation of **9** gave the corresponding organic compound **10**, which could also be isolated from the reaction mixture. The ^{1}H and ^{13}C NMR spectra of **10** show signals at 7.20 ppm due to the protons of three phenyl groups. As for **9**, there are two doublets due to the benzylic protons, at 3.77 and 3.16 ppm, and two singlets at 2.92 and 2.01 ppm, assigned respectively to the N–CH_3 group and to the CH_3 group associated with the double bond. Both the ^{13}C and IR spectra (δ(CO), 180.2 ppm and ν(CO), 1695 cm^{-1}) confirmed the presence of an unsaturated five-membered lactam. The second organic compound was assigned structure **11** on the following grounds. The IR and the ^{13}C NMR spectra indicated the presence of a conjugated five-membered lactam (δ(CO), 169.5 ppm, ν(CO), 1690 cm^{-1}). There are differences in the ^{1}H NMR spectra of **10** and **11**: in **11** the benzylic protons are equivalent and appear as a singlet, at 2.62 ppm; moreover, the methyl groups give signals at 2.75 ppm (N–CH_3) and at 1.00 ppm respectively, indicating that the latter signal corresponds to a methyl linked to a quaternary carbon. These data are consistent with structure **11**.

When complex **5***E*,*Z* was treated with diphenylacetylene under the same conditions only one insertion-rearrangement product (**12**) was isolated as white crystals (m.p. 180 °C, 49%). The ^{1}H NMR spectrum of **12** is very close to that of **10**: there are signals due to the protons of the three phenyl rings at 7.20 ppm, the doublet of doublets due to the benzylic protons at 3.90 and 3.40 ppm, and the singlet due to

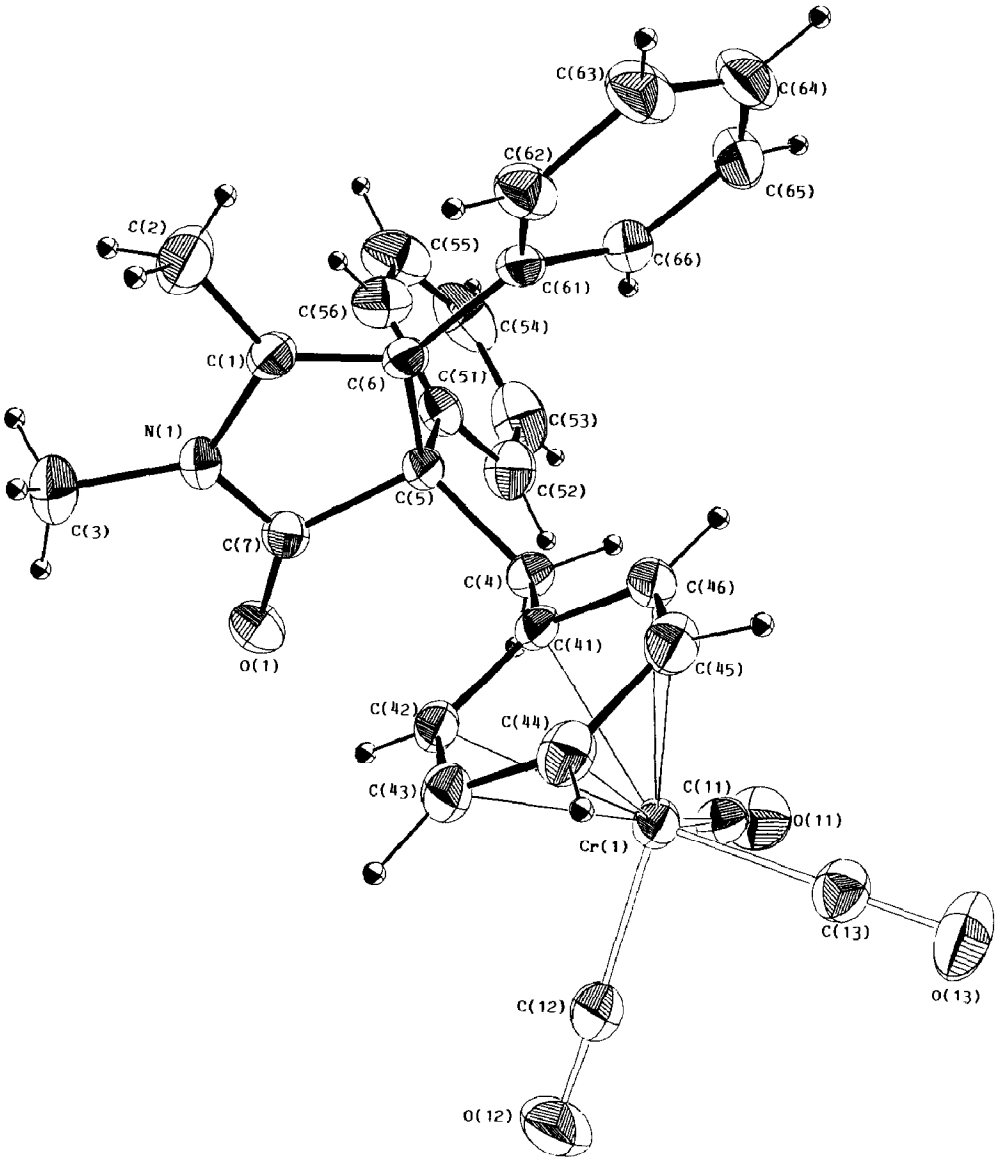
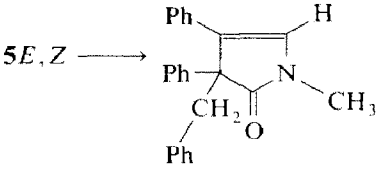


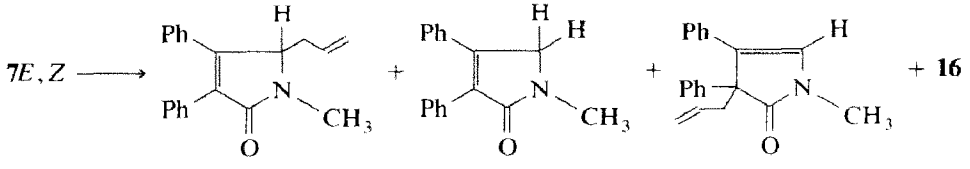
Fig. 2. ORTEP view of the chromium tricarbonyl complex (**9**) showing the crystallographic numbering scheme. Selected bond lengths (Å) and angles (deg): N1–C1 1.423(4), N1–C7 1.348(4), C1–C 1.336(4), C4–C(41) 1.503(4), C5–C7 1.542(4), N1–C3 1.456(4), C1–C2 1.495(4), C4–C5 1.535(4), C7–O1 1.218(3), C3–N1–C1 126.8(3), C7–C5–C4 109.2(2), C7–N1–C1 111.2(2), C7–N1–C3 121.9(3), C5–C7–N1 107.1(2), O1–C7–C5 126.2(3), C2–C1–N1 117.1(2), C6–C1–N1 110.5(2), C6–C1–C2 132.4(3), C6–C5–C4 114.3(2), C7–C5–C6 102.0(2), O1–C7–N1 126.6(3).

the N–Me group at 2.88 ppm, with the signal of the methyl group associated with the double bond in **10** replaced by a singlet at 6.64 ppm due to a hydrogen associated with the double bond of 12.

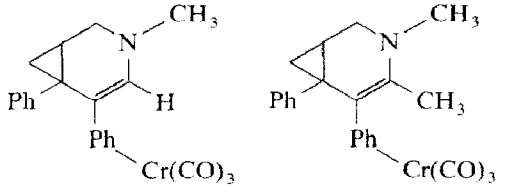


(12)

The behaviour of complex **7** in the insertion reaction parallels that of complex **3***E*, *Z*. The most abundant product, obtained as an oil (40% yield), was assigned structure **13**. The ^{1}H NMR spectrum exhibits, besides signals between 7.40 and 7.15 ppm (10H), a multiplet at 5.3 ppm (1H) and two doublets at 4.95 and 4.86 ppm (*J* 17 and 9.6 Hz) (2H) characteristic of an allyl group, a triplet at 4.55 ppm (1H) due to the N–C*H* proton, adjacent to the allyl group, a singlet at 3.09 ppm ($N-CH_3$), and two multiplets at 2.60 and 2.28 ppm each due to one proton and assignable to the allylic CH_2 group. Both the IR and ^{13}C NMR spectra confirm the presence of an α,β-unsaturated lactam (δ(CO), 169.7 ppm, ν(CO), 1680 cm^{-1}).



(13) **(14)** **(15)**



(16) **(17)**

The second product was assigned structure **15**. In addition to the signals from the protons of the two phenyl groups, the ^{1}H NMR spectrum shows a singlet at 7.00 ppm due to the vinylic hydrogen, the characteristic signals of the allyl group, at 5.45 (1H, m), 4.94 (2H, dd), 3.3 (1H, dd) and 2.95 ppm (1H, dd), and the signal due to the $N-CH_3$ group, at 3.12 ppm.

A third product, which contains neither an allylic group nor a cyclopropane, was assigned structure **14**. The ^{1}H NMR spectrum shows the signals of the aromatic protons (10H) and two singlets due respectively to a $N-CH_2$ group (at 4.23 ppm) and to a $N-CH_3$ group (at 3.11 ppm). The IR spectrum (ν(CO), 1680 cm^{-1}) is consistent with this structure.

The remaining product was assigned structure **16** (orange crystals, m.p. 147–148°C, 5%). This is the result of an intramolecular cyclopropanation reaction of the terminal double bond of (7Z). The IR and ^{13}C NMR spectra confirm the presence of an arenechromium tricarbonyl moiety. The presence of the cyclopropane is confirmed by multiplets, in the ^{1}H NMR spectra, at high field, at 0.88 (1H),

Table 4

Fractional parameters for $Cr(CO)_5(C_{10}H_{13}N)$ (**3Z**)

Atom	x/a	y/b	z/c	U_{eq}
Cr(1)	0.27695(4)	0.44238(3)	0.09631(4)	0.0458
C(11)	0.4183(3)	0.3903(3)	0.0718(3)	0.0667
O(11)	0.5047(2)	0.3570(2)	0.0624(3)	0.0984
C(12)	0.1405(2)	0.4862(2)	0.1342(2)	0.0510
O(12)	0.0596(2)	0.5082(2)	0.1625(2)	0.0721
C(13)	0.3725(3)	0.5533(2)	0.1936(3)	0.0577
O(13)	0.4305(2)	0.6184(2)	0.2540(2)	0.0854
C(14)	0.3152(3)	0.3518(2)	0.2305(3)	0.0622
O(14)	0.3380(3)	0.2948(2)	0.3127(2)	0.0873
C(15)	0.1804(3)	0.3341(2)	−0.0017(3)	0.0581
O(15)	0.1202(2)	0.2679(2)	−0.0591(3)	0.0811
C(1)	0.2342(2)	0.5318(2)	−0.0690(2)	0.0477
C(2)	0.2528(3)	0.4766(3)	−0.1763(3)	0.0709
N(1)	0.1879(2)	0.6275(2)	−0.0958(2)	0.0483
C(3)	0.1516(3)	0.6762(3)	−0.2190(3)	0.0732
C(4)	0.1576(2)	0.6966(2)	−0.0082(3)	0.0514
C(5)	0.2055(2)	0.8084(2)	−0.0030(2)	0.0461
C(6)	0.1274(3)	0.8943(2)	−0.0352(3)	0.0627
C(7)	0.1727(4)	0.9975(3)	−0.0264(3)	0.0708
C(8)	0.2941(4)	1.0148(3)	0.0138(3)	0.0725
C(9)	0.3725(3)	0.9308(3)	0.0456(3)	0.0725
C(10)	0.3290(3)	0.8275(2)	0.0377(3)	0.0577

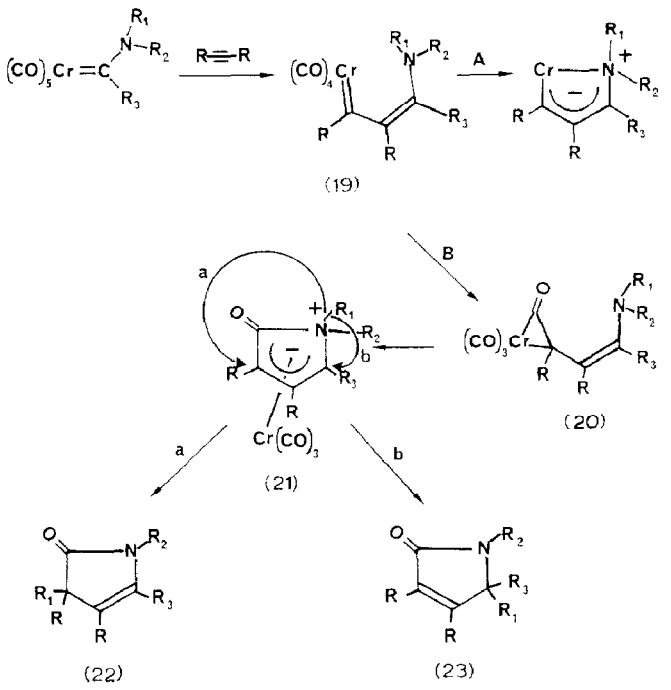
0.96 (1H) and 1.67 (1H) ppm. The $N-CH_3$ group gives a singlet at 2.19 ppm, whereas the $N-CH_2$ protons appear as two multiplets at 2.50 (1H) and 2.72 (1H) ppm, the vinylic proton giving a signal at 6.31 ppm. The spectroscopic data for **16** are very close to those for **17**, the structure of which has been established by X-ray crystallography [15].

Discussion

The net result of the reactions described is the insertion of the alkyne and CO into the starting complexes, with a concomitant rearrangement involving the migration of a benzyl or an allyl group from nitrogen to carbon. A second feature which must be taken into account is the loss in one case of the migrating group during the reaction.

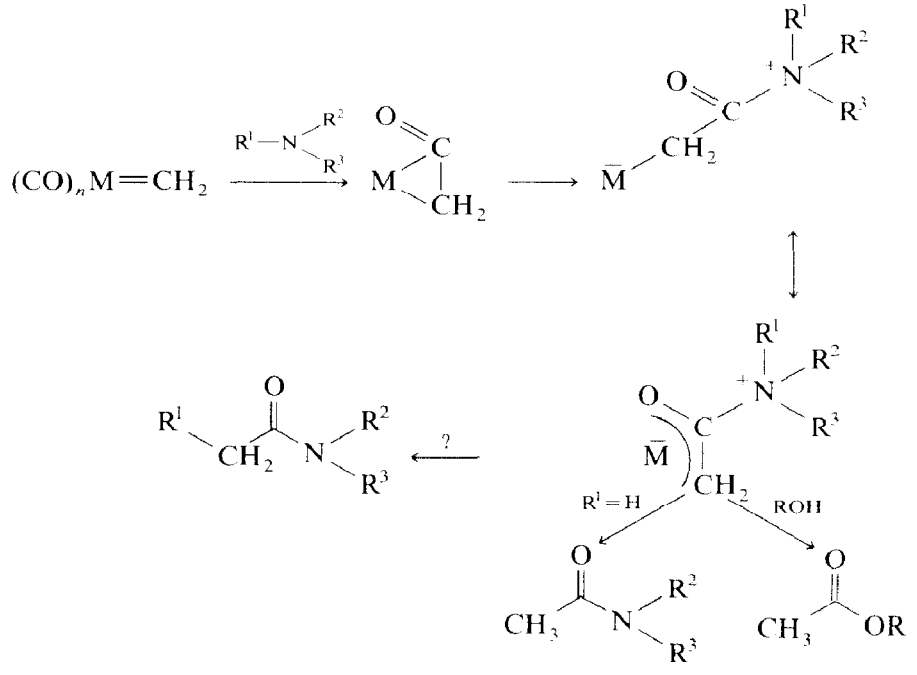
Among the discrete steps which can be used to represent the overall reaction, two are already known: the insertion of alkynes into a carbene complex [4], which leads to a new carbene complex and the insertion of CO into carbene complexes, a reaction leading to coordinated ketene complexes [16,17,18].

The important new step is therefore the nitrogen to carbon migration. At this point, the question of the timing of the different steps must be adressed. It is likely that the first step indicated in the general Scheme 1, is the insertion of the alkyne, since the starting complexes are stable under such conditions in the absence of alkynes. This reaction probably leads to a new carbene complex **19**, which can either undergo a rearrangement, with participation of the metal (route A), or insert CO to give the ketene complex **20** (route B). It has been shown [19,20,21], that when the



Scheme 1

insertion reactions are carried out in the presence of alcohols, esters are formed, which means that an alcohol is able to trap the ketene before any other reaction can take place. Moreover, in the chemistry of iron and palladium carbene complexes, it is known [22] that amines both induce the CO insertion and participate in the



Scheme 2

Table 5

Fractional parameters for $Cr(CO)_3(C_{25}H_{23}ON)$ (**9**)

Atom	x/a	y/b	z/c	U_{eq}
Cr(1)	0.04533(5)	0.44504(4)	0.20708(2)	0.0360
C(11)	0.1689(3)	0.5571(3)	0.1747(1)	0.0444
O(11)	0.2484(3)	0.6267(2)	0.1548(1)	0.0640
C(12)	0.0280(4)	0.5042(3)	0.2893(2)	0.0511
O(12)	0.0186(4)	0.5389(2)	0.3412(1)	0.0743
C(13)	−0.1076(4)	0.5283(3)	0.1922(2)	0.0496
O(13)	−0.2018(3)	0.5818(2)	0.1826(1)	0.0710
N(1)	0.4909(3)	0.1173(2)	0.1753(1)	0.0429
C(1)	0.4256(3)	0.0828(2)	0.1226(1)	0.0406
C(2)	0.3872(4)	−0.0356(3)	0.1202(2)	0.0653
C(3)	0.5323(4)	0.0483(3)	0.2255(2)	0.0630
C(4)	0.3709(3)	0.3647(2)	0.1249(1)	0.0396
C(5)	0.4768(3)	0.2682(2)	0.1088(1)	0.0351
C(6)	0.4108(3)	0.1672(2)	0.0838(1)	0.0354
C(7)	0.5172(3)	0.2257(3)	0.1725(1)	0.0411
O(1)	0.5667(2)	0.2798(2)	0.2120(1)	0.0533
C(41)	0.2185(3)	0.3335(2)	0.1578(1)	0.0348
C(42)	0.1846(3)	0.3067(2)	0.2244(1)	0.0381
C(43)	0.0402(3)	0.2846(2)	0.2552(1)	0.0438
C(44)	−0.0727(3)	0.2866(2)	0.2201(2)	0.0462
C(45)	−0.0382(3)	0.3113(2)	0.1531(2)	0.0447
C(46)	0.1040(3)	0.3332(2)	0.1221(1)	0.0407
C(51)	0.6221(3)	0.3018(2)	0.0650(1)	0.0417
C(52)	0.6679(4)	0.4092(3)	0.0577(2)	0.0589
C(53)	0.7989(5)	0.4349(4)	0.0176(2)	0.0710
C(54)	0.8868(4)	0.3570(5)	−0.0149(2)	0.0709
C(55)	0.8437(4)	0.2505(4)	−0.0072(2()	0.0715
C(56)	0.7137(4)	0.2231(3)	0.0323(2)	0.0583
C(61)	0.3477(3)	0.1686(2)	0.0242(1)	0.0375
C(62)	0.2417(3)	0.0932(3)	0.0149(2)	0.0507
C(63)	0.1875(4)	0.0923(3)	−0.0421(2)	0.0587
C(64)	0.2316(4)	0.1693(4)	−0.0891(2)	0.0601
C(65)	0.3314(4)	0.2471(3)	−0.0804(2)	0.0590
C(66)	0.3893(4)	0.2359(3)	−0.0242(2)	0.0503

solvolysis of the ketenes, primary and secondary amines leading to amides (Scheme 2). In the case of tertiary amines and in the presence of an alcohol, the formation of an ester is observed, probably via the zwitterionic intermediate of Scheme 2. Such a process in the present case would involve complex **20** carrying out an intramolecular nucleophilic attack on the ketene carbonyl carbon, to form a zwitterion **21**. Such nitrogen carbon centered zwitterionic species are well known in organic chemistry and undergo the Stevens rearrangement [23,24] with migration of alkyl groups from nitrogen to carbon, the benzyl and allyl groups migrating preferentially to any other alkyl groups. This rearrangement will lead to either **22** or **23**.

Since the involvement of radicals has been established in the Stevens rearrangement [25,26] it is clear that benzyl or allyl radicals can escape from the solvent cage, a fact which accounts for the formation of **14**, and for the presence of trace amounts of bibenzyl in the product mixture from **4***E*, *Z*.

Nevertheless, reaction by route A in which the Stevens-like rearrangement takes

place before the CO insertion reaction, via **24**, cannot be excluded since it is well established that owing to the dipolar structure of the nitrogen-substituted carbene complexes, the nitrogen has lost most of its nucleophilicity. Work is in progress on ketene model complexes to try to establish the mechanism of this new reaction.

Conclusion

We have demonstrated that the reaction observed in the case of cycloaminocarbene complexes can be extended to other complexes bearing various alkyl groups on the nitrogen atom. The behaviour of these complexes reflects features of the Stevens rearrangement of C–N centered zwitterions, in that there is preferential migration of benzyl and allyl groups, probably via radical intermediates.

Experimental

All reactions were carried out in oven-dried glassware under nitrogen. Benzene, diethyl ether (Et_2O), and tetrahydrofuran (THF) were distilled from $LiAlH_4$. Preparative column chromatography was performed with 70–230 mesh Merck silica gel, and preparative (PLC) and thin layer chromatography (TLC) with Merck G60 silica gel. Low boiling petroleum ether (PE) was used as eluent.

NMR spectra were recorded on a JEOL FX-90 spectrometer or on a Bruker WM 200 or WM 500 spectrometer. IR spectra were recorded with a Beckman 4240 spectrophotometer, and mass spectra with a Kratos MS 3P. Melting points were determined on a Reichert Köfler block and are uncorrected.

Pentacarbonyl(benzylamino)(methyl)carbene)chromium(0) 2E and 2Z

Benzylamine (3.7 ml) was added to a solution of complex **1** (7.8 g, 28 mmol) in Et_2O (180 ml) at room temperature. The mixture was kept at room temperature overnight. Crystals of **3**E (m.p. 150 °C, 8.5 g, 95%) which separated were filtered off. ^1H NMR (200 MHz, CD_2Cl_2) δ 9.02 (1H, bs, N–*H*), 7.40–7.30 (5H, m, Ph), 4.63 (2H, s, N–C*H*$_2$), 2.72 (3H, s, C*H*$_3$). ^{13}C NMR (50.1 MHz, CD_2Cl_2) δ 277.5 (Cr–*C*), 223.4, 217.8 (CO), 134.9, 129.5, 129.1, 128.6 (Ph), 53.6 (Ph–*C*H$_2$), 3.60 (C–*C*H$_3$).

A solution of complex **3***E* (5 g, 15 mmol) in THF at −60 °C was treated with one equivalent of LDA, in THF (50 ml). The mixture was warmed to room temperature, and after addition of distilled water (2 ml) and evaporation of the solvent, the product was extracted with diethyl ether. After evaporation of the solvent, the residue was taken up in a small amount of benzene and chromatographed on silica gel. Elution with petroleum ether (PE) gave **3***E* (2.2 g). Elution with PE/Et_2O (98/2) gave **3***Z* (2.3 g). **3***Z*, m.p. 75 °C. ^1H NMR (200 MHz, CD_2Cl_2) δ 8.80 (1H, bs, N–*H*), 7.40 (5H, m, Ph), 5.10 (2H, d, NC*H*$_2$), 2.75 (3H, s, C*H*$_3$). ^{13}C {^1H} (50.1 MHz, CD_2Cl_2) δ 276.5 (Cr=*C*), 223.5, 218.0 (CO), 134.9, 129.4, 128.9, 128.6 (Ph), 57.9 (N–*C*H$_2$), 45.3 (*C*H$_3$).

Pentacarbonyl(N-methyl-N-benzylamino)(methyl)carbene)chromium(0) (3E,Z)

To a solution of complex **2***E* (2.5 g) in THF (100 ml), at −70 °C, was added one equivalent of LDA. The mixture was warmed to room temperature then cooled again to −70 °C, and ICH_3 (4 ml) added. Then the mixture was warmed to room temperature, the solvent was evaporated under vacuum, and the residue extracted

with Et_2O. Evaporation of the solvent followed by silica gel chromatography of the residue in a small amount of benzene gave with PE/CH_2Cl_2 (80/20) complex **3***E*, *z* (2.0 g, 77%). Recrystallization from CH_3OH/CH_2Cl_2 gave crystals of **3***E*, m.p. 45°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.30 (5H, m), 5.44 (2H, s, N–CH_2), 3.08 (3H, s, N–CH_3), 2.80 (3H, s, C–CH_3). ^{13}C {^{1}H} NMR (50.1 MHz, $CDCl_3$) δ 276.1 (Cr=*C*), 223.4, 217.6 (CO), 134.3, 129.5, 128.6, 127.5 (Ph), 69.3 (N–*C*H_2), 40.6 (N–*C*H_3), 40.3 (C–*C*H_3). Anal. Found: C, 52.87; H, 3.85; N, 4.17. $C_{15}H_{13}NO_5Cr$ calcd.: C, 53.09; H, 3.83; N, 4.13%.

Carbene complexes 5E, Z and 7E, Z; general method

To a solution of $Na_2Cr(CO)_5$ (20 mmol), prepared from $Cr(CO)_6$ in THF (250 ml) and sodium naphtalenide (42 mmol) in THF (100 ml), was added, at −78°C, *N*-methyl-*N* benzylamide (10 mmol). The mixture was stirred for 30 min at −78°C, then 30 min at 0°C. Chlorotrimethylsilane (30 mmol) was then added to the solution at −78°C, and the mixture stirred for 30 min at this temperature. Neutral alumina was added and the mixture warmed to room temperature. The solvent was evaporated and the impregnated alumina transferred to a column of silica gel Elution with PE gave napthalene, and elution with PE/CH_2Cl_2 (80/20) then gave the expected carbene complex.

Pentacarbonyl((N-methyl-N-benzylamine)carbene)chromium(0) (5E and 5Z)

By the above method, **5***E*, *Z* was obtained as a yellow oil (95%). Recrystallization from PE/MeOH gave crystals of **5***E*, m.p. 130–131°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 11.13 (1H, s, Cr=C-*H*), 7.34 (5H, m, Ph), 4.76 (2H, s, Ph–CH_2), 3.57 (3H, s, CH_3). ^{13}C {^{1}H} NMR (50.1 MHz, $CDCl_3$) δ 266.5 (Cr=*C*), 223.7, 217.5 (CO), 133.6, 129.4, 128.6, 127.7 (Ph), 77.0 (N–*C*H_2), 44.3 (N–*C*H_3). IR ($CHCl_3$): 2045, 2010, 1980 cm^{-1}. Anal. Found: C, 51.68; H, 3.37; N, 4.25. $C_{14}H_{11}O_5NCr$ calcd.: C, 51.69; H, 3.83; N, 4.30%.

Pentacarbonyl((N-methyl-N-allylamino)carbene)chromium(0) (7E and 7Z)

The mixture of the two complexes, obtained in quantitative yield from *N*-methyl -*N*-benzylformamide , by the above general method as yellow crystals, m.p. 130–131°C. Complex **7***E* was obtained in pure form, by the following method.

A solution of the mixture **7***E*, **7***Z* (3 g, 12 mmol) in benzene was boiled for 4 h. After evaporation of most of the solvent, the residue was chromatographed on silica gel. Elution with PE gave complex **7***E* (1.5 g) as a yellow oil. Then pentacarbonyl-η^2-*N*-allyl-*N*-methylamino)carbene) chromium(0) (**8**), as orange crystals (0.6 g, m.p. 77–78°C). ^{1}H NMR (200 MHz, $CDCl_3$) 9.94 (1H, s, Cr=C–*H*), 4.60–4.53 (1H, m, H_2C=C*H*), 4.20 (1H, dd, NC*H*H), 3.77 (1H, dd, NCH*H*), 3.27 (3H, s, N–CH_3), 3.16 (2H, dd, CH_2=CH). IR ($CHCl_3$) 2010, 1970, 1910, 1880 cm^{-1}. *m/z* 247 (*M*$^+$).

7*E* liquid: ^{1}H NMR (200 MHz, $CDCl_3$) δ 10,9 (1H, s, Cr=C–*H*), 5.8 (1H, m, C*H*=CH_2), 5.43 (1H, m, HC=CH_2), 4.20 (2H, d, N–CH_2), 3.63 (3H, s, N–CH_3). *m/z* 275 (*M*$^+$).

Reaction of (3E,Z) with diphenylacetylene

A solution of complex **3***E*, *Z* (2.2 g, 6.6 mmol) in benzene (50 ml) containing diphenylacetylene (2 g, 11 mmol) was refluxed for 15 h. After evaporation of most of the solvent under vacuum, the residue was chromatographed on silica gel. Elution

with PE gave first unchanged diphenylacetylene and then complex **3***E*, *Z* (0.2 g). Elution with PE/CH_2Cl_2 (90/10) gave **10** (0.28 g, 15%) m.p. 105 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.20 (5H, m, Ph), 3.77 (1H, d, *J* 12 Hz, Ph–C*H*–H), 3.16 (1H, d, *J* 12 Hz, PhCH–*H*), 2.92 (3H, s, N–CH_3), 2.01 (3H, s, CH_3). ^{13}C {^{1}H} NMR δ (50.1 MHz, $CDCl_3$) 180.2 (CO), 140.3–120.44 (Ar, C=C), 61.41 (Ph–*C*–C=O), 39.82 (N–*C*H_3), 26.5 (Ph–*C*H_2), 12.8 (C–*C*H_3). IR ($CHCl_3$) 1695 cm^{-1}. Anal. Found: C, 84.45; H, 6.60; N, 3.84. $C_{25}H_{23}NO$ calcd.: C, 84.98; H, 6.51; N, 3.97%. Elution with PE/CH_2Cl_2 (85/15) gave complex **9** (0.74 g, 15%) m.p. 200 °C

9: ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.63–7.35 (10H, m, Ar), 5.28, 5.09, 4.35 (5H, m, ArCr), 3.53 (1H, d, *J* 12 Hz, C*H*H), 3.03 (3H, s, N–CH_3), 2.83 (1H, d, *J* 12 Hz, CH*H*), 2.19 (3H, s, CH_3). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 232.8 (CO), 180 (CO), 139.1, 137.9, 133.6, 129.2, 128.6, 127.8, 126.6, 126.4 (Ph), 107.5, 94.5, 93.3, 92.9, 90.8 (Ar–Cr). IR ($CHCl_3$) 1695, 1880, 1960 cm^{-1}. Anal. Found: C, 68.55; H, 4.80; N, 2.80. $C_{28}H_{23}O_4NCr$ calcd.: C, 68.71; H, 4.70; N, 2.80%. *m/z* 461 (*M* – CO).

Elution with PE/CH_2Cl_2 (85/15) gave **11** (0.38 g) m.p. 120 °C.

11: ^{1}H NMR (200 MHz, C_6D_6) δ 7.16 (15H, m), 2.75 (3H, s, N–CH_3), 2.62 (2H, s, N–CH_2), 1.00 (3H, s, CH_3). ^{13}C {^{1}H} NMR δ 169.5 (CO), 156.4 (*C*=*C*), 135.6 –127.1 (Ph), 67.3 (N–*C*), 41.4 (N–*C*), 25.4 (*C*H_2Ph), 23.0 (*C*H_3). IR ($CHCl_3$) 1680 cm^{-1}. Anal. Found: C, 84.34; H, 6.47; N, 3.82. $C_{25}H_{23}NO$ calcd.: C, 84.98; H, 6.51; N, 3.97%. *m/z* 353 (*M*$^+$).

Reaction of complex (5E,Z) with diphenylacetylene; formation of ***12***

A solution of complex **5***E*, *Z* (1.62 g, 5 mmol) in benzene (70 ml) containing diphenylacetylene was refluxed for 12 h. After evaporation of most of the benzene, the residue was transferred to a column of silica gel. Elution with PE/CH_2Cl_2 (80/20) gave **12** (0.8 g, 50%) as white crystals, m.p. 180–181 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.20 (15H, m), 6.64 (1H, s, C=C*H*), 3.90 (1H, d, *J* 12 Hz, PhC–*H*H), 3.40 (1H, d, *J* 12 Hz, Ph–C–H*H*), 2.88 (3H, s, N–CH_3). ^{13}C {^{1}H} NMR (C_6D_6) δ 179.3 (CO), 140.1–123.4 (*C*=*C*, Ph), 60.9 (*C*–CO), 40.42 (N–*C*H_3), 28.4 (*C*H_2–Ph). IR ($CHCl_3$) 1690 cm^{-1}. Anal. Found: C, 84.68; H, 6.25; N, 4.15. $C_{24}H_{21}ON$ calcd.: C, 84.95; H, 6.19; N, 4.13%. *m/z* 339 (*M*$^+$).

Reaction of complex (7E,Z) with diphenylacetylene

A solution of complex 7*E*, *Z* (1.5 g, 6.5 mmol) in benzene (50 ml) was refluxed for 7 h in the presence of diphenylacetylene (1 g, 8 mmol). After evaporation of the solvent, the residue was taken up with CH_2Cl_2 and absorbed on a small amount of silica gel. After evaporation of the solvent, the impregnated silica was transferred to a column of silica gel. Elution with PE/CH_2Cl_2 (90/10) gave **13** as an oil (0.6 g, 40%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.40–7.15 (10H, m, Ph), 5.3 (1H, m, C*H*=CH_2), 4.98 (2H, m, CH_2=CH), 4.54 (1H, t, *J* 4 Hz, N–C–*H*), 3.09 (3H, s, N–CH_3), 2.64–2.54 (1H, m, C(H)*H*), 2.33–2.22 (1H, m, C(*H*)–H). ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 169.7 (CO), 154.1, 132.6 (*C*=*C*), 131.2–127.4 (Ph), 62.06 (N–*C*H), 32.6 (*C*H_2), 27.2 (N-*C*H_3). IR ($CHCl_3$) 1680 cm^{-1}. Anal. Found: C, 82.91; H, 6.56; N, 4.72; $C_{20}H_{19}ON$ calcd.: 83.04; H, 6.57; N, 4.87%. *m/z* 289 (*M*$^+$).

Elution with PE/CH_2Cl_2 (80/20) gave **15** (0.4 g, 27%) as an oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.36–7.09 (10H, m, Ph), 7.00 (1H, s, *H*C=C), 5.58–5.37 (1H, m, CH_2=C*H*), 5.03–4.91 (2H, m, CH_2=C), 3.35–3.21 (1H, m, C(H)*H*), 3.12 (3H, s, N-CH_3), 2.97–2.85 (1H, m, C(*H*)H). IR ($CHCl_3$) 1690 cm^{-1}. *m/z* 289 (*M*$^+$). Then

14 as an oil (0.15 g, 10%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.4–7.28 (10H, m, Ph), 4.23 (2H, s, N–CH_2), 3.11 (3H, s, N–CH_3). IR ($CHCl_3$) 1680 cm^{-1}, *m/z* 249 (M^+).

Elution with PE/CH_2Cl_2 (50/50) gave complex **16** as orange crystals (0.1 g) m.p. 147–148°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25–7.12 (5H, m, Ph), 6.67 (1H, s, C*H*=C), 5.42–4.85 (5H, m, Ph–Cr(CO)$_3$), 3.41–3.32 (1H, m, N–C*H*(H)), 3.11–3.01 (1H, m, N–C(H)*H*), 2.87 (3H, s, N–CH_3), 2.02–1.96 (1H, m, C*H*), 1.26–1.24 (1H, m, C(H)*H*), 1.06–1.01 (1H, m, C(H)*H*). ^{13}C NMR (50.1 MHz, C_6D_6) δ 235.0 (CO), 144.2, 102.9 (Ph, *C*=*C*), 94.5–87.0 (Ph–Cr), 47.2 (N–*C*H$_2$), 42.03 (N–*C*H$_2$), 30.1 (*C*–PhOH), 20.5 (*C*H$_2$). IR ($CHCl_3$) 1955, 1880 cm^{-1}. *m/z* 397 (M^+).

Crystal data

Crystal data and crystal data collection parameters are listed in Table 3. Accurate cell dimensions were obtained from least-squares refinements of the setting angles of 25 well defined reflections. Intensities of two standard reflections showed no change during the data collection. Corrections were made for Lorentz and polarization effects. Anomalous dispersion was taken into account. The positions of the Cr atom were derived by Harker vector analysis of three dimensional Patterson maps. All remaining non-hydrogen atoms were found from successive/electron density maps. Final refinement was by least squares with a large block approximation to the normal matrix with all non-hydrogen atoms anisotropic [27]. Hydrogen atoms were located on difference Fourier maps and their coordinates refined with an overall refinable isotropic thermal parameter. The criteria for a satisfactory completed analysis were the average shifts to standard deviations. In tables 1, 2, 4 and 5 are listed the main interatomic distances, bond angles, and fractional atomic parameters for compounds **3***Z* and **9**.

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