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Preparation, structure and reactivity of aminocarbene complexes of chromium and molybdenum derived from primary amines

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Abstract

The synthesis and reactivity towards diphenylacetylene of a series of aminocarbene complexes of general structure $(CO)_5M{=}C(NHR')R$ (M = Cr, R = CH_3, Ph, R′ = cyclohexyl, cyclopropyl, benzyl) are described: they lead by alkyne insertion followed by a 1,4 hydrogen shift, to imine complexes, which, upon hydrolysis, give the corresponding ketones. When R′=CH_2Ph, along with the expected imine, a tetraphenylcyclopentadiene resulting from the coupling of two PhC≡CPh and of a carbene moiety, is formed; its structure has been determined by an X-ray study. In the case of aminopyridine, bidentate carbene complexes (the structure of which was confirmed by an X-ray study of $(CO)_4Cr{=}C(CH_3)NHNC_5H_5$) are formed, and these also react with PhC≡CPh to give, for M = Mo, new pyrrolinones through alkyne/CO insertion followed by a 1,2 hydrogen shift.

Introduction

Aminocarbene complexes of transition metals are being increasingly seen as versatile starting materials for the synthesis of nitrogen-containing heterocycles [1–14]. Their behaviour has been found to be fundamentally different from that of related alkoxycarbene complexes, since nitrogen ylides, derived from ketene intermediates, have been isolated and shown to rearrange upon thermolysis to give pyrrolinones by 1,2 and 1,4 nitrogen to carbon migrations of alkyl groups. Up to now attention had been mainly focused on the reactions of tungsten and chromium aminocarbenes derived from secondary amines, the former being reluctant to undergo insertion of alkynes even under drastic conditions.

We describe herein the synthesis, structure, and reactions of carbene complexes obtained from primary amines. A key point of this study lies in the difference of reactivity between the chromium and molybdenum complexes.

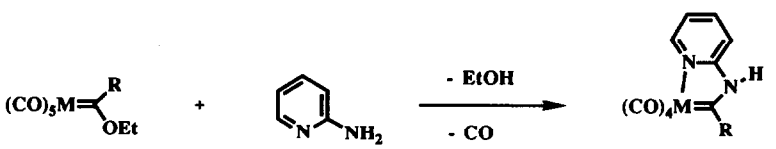
I. Synthesis of the aminocarbene complexes

The synthesis of the various carbene complexes, some of which had been prepared previously, was by the general procedure described by Fischer and coworkers [15,16]. Aminolysis of complexes **1** and **2** was in general straightforward, and gave the expected complexes in good yields as *E,Z* mixtures, the most abundant being the *E* isomer.

1 R=CH_3
2 R=Ph

5 R=CH_3, R'=cyclohexyl
6 R=CH_3, R'=cyclopropyl
7 R=CH_3, R'=benzyl

However, in the case of aminopyridine, following the aminolysis reaction spontaneous coordination of the pyridine-nitrogen atom was observed, giving rise to the bidentate complexes **8–11**. Both the elemental analyses and the mass spectra of



1 M=Cr, R=CH_3
2 M=Cr, R=Ph
3 M=Mo, R=CH_3
4 M=Mo, R=Ph

8
9
10
11

these complexes were in agreement with the presence of only four CO groups. The ^{1}H NMR spectrum of complex **8** shows a broad signal at δ 10.16 attributable to the N–H proton, a series of multiplets at 8.8 (d), 8.0 (t), 7.6 (d) and 7.3 (t) from the different protons of the pyridine nucleus, and a signal at δ 3.2 from the methyl group associated with the carbene carbon. The bidentate nature of the aminopyridine group was confirmed by an X-ray diffraction study on complex **8** (M = Cr, R = Me). An ORTEP view of this complex appears in Fig. 1. The crystal data and experimental details for complex **8** are listed in Table 1, and interatomic distances and the bond angles are in Tables 2 and 3.

II. Reactivity of carbene complexes 5–7

In contrast to alkoxycarbene complexes, aminocarbene complexes derived from primary amines have been shown to be thermally stable and to be decomposed only in the presence of pyridine, usually when their solutions in this solvent are refluxed; imine complexes are obtained as a result of a nitrogen to carbene–carbon atom migration of a hydrogen atom (Scheme 1) [17,18]. It was therefore of interest to see whether this type of carbene complex would react in boiling benzene or cyclohexane to give the corresponding imines, even in the presence of an alkyne, or to insert the alkyne and CO, a type of reaction that has been observed for aminocarbene complexes derived from secondary amines.

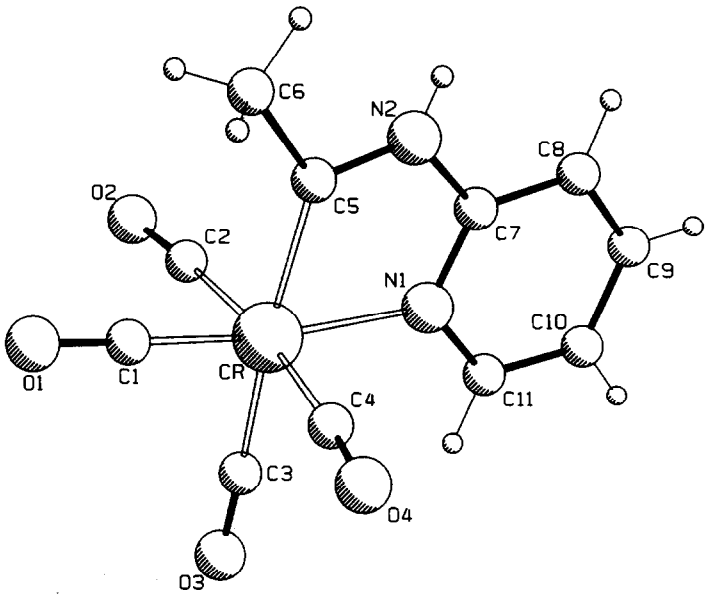
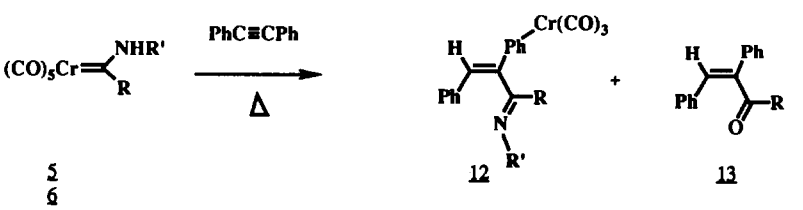


Fig. 1. ORTEP view of compound **8**.

Refluxing of a solution of complex **5** and diphenylacetylene in benzene for 12 h gave a mixture of two products, which were separated by silica chromatography. To the most abundant product, isolated as a yellow oil (78% yield) was given structure **12** on the following grounds. Both the mass spectrum and the ^{1}H and ^{13}C NMR spectra were in agreement with the presence of the imine of 3,4-diphenyl-3-buten-2-one as a $Cr(CO)_3$ complex. Besides the signals due to the aromatic protons, between δ 7 and 7.63, and those due to the arenechromium tricarbonyl group, between δ 5.75 and 5, there is a signal from the olefinic proton at δ 6.97. Treatment of complex **12** in boiling pyridine, followed by hydrolysis, gave the conjugated ketone **13** in 62% yield. Thus, the alkyne insertion took place without CO insertion.



5
6

12 13

Along with complex **12**, the $Cr(CO)_3$ complex of ketone **13** was isolated in 5% yield. The reaction of complex **6** followed the same course: the imine complex was obtained in 41% yield, after 17 h heating. Along with the imine complex, a 2.5% yield of tetraphenylcyclopentadienone, the result of a cyclocarbonylation reaction probably induced by unsaturated chromium species, was isolated.

The behaviour of complex **7** was somewhat different: besides the expected ketone **13**, the hydrolysis product of imine **12** ($R' = CH_2Ph$), a second organic product is formed that, according to the mass spectrum and the elemental analysis, has resulted from coupling of two diphenylacetylene molecules and the organic carbene

Table 1

Crystal data for compounds **8** and **14**

	8	**14**
Empirical formula	$C_{25}H_{21}CrN_6O_6$	$C_{37}H_{31}N$
Molecular weight	489.7	553.47
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a, Å	25.072(7)	10.354(6)
b, Å	7.639(1)	11.152(5)
c, Å	31.492(8)	14.722(6)
α, °	90	66.06(3)
β, °	114.15(2)	68.11(4)
γ, °	90	68.06(4)
V, Å^3	5504(5)	1391(3)
Z	8	2
μ, cm^{-1}	38.74(Cu-K_α)	0.62(Mo-K_α)
ρ(calcd), g cm^{-3}	1.34	1.17
Diffractometer	Nicolet	Philips PW1100
Temperature, °C	23	20
Radiation	Cu-K_α	Mo-K_α (graphite monochromator)
Scan type	$\theta/2\theta$	$\theta/2\theta$
Scan range θ, deg	1.0+0.345 tan θ	1.2+0.345 tan θ
Max 2θ, deg	110.1	50
reflections used	1986	2405 ($I > 3\sigma(I)$)
R [a]	0.043	0.0375
R_w	0.059	0.0355
rms (shift/esd)	0.03	0.24
Ratio of observed to parameters	5.8	5.5
Largest peak in final differential map	0.19	0.12

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$.

Table 2

Bond lengths (Å) in compound **8** with esd's in parentheses

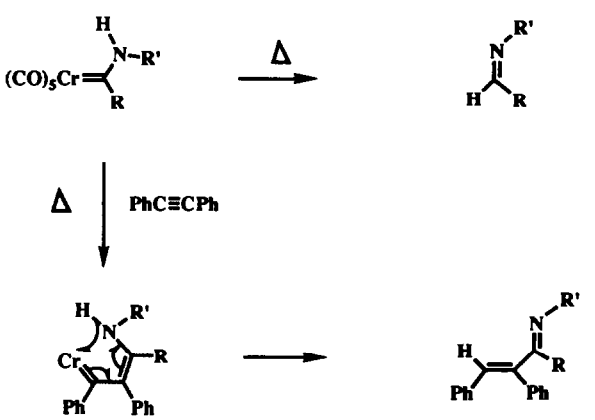
Cr–C1	1.796(6)	N5–C23	1.337(7)
Cr–C3	1.858(7)	N5–C19	1.340(6)
Cr–C4	1.867(7)	N6–C24	1.350(7)
Cr–C2	1.876(8)	N6–C19	1.400(6)
Cr–C5	2.000(5)	C5–C6	1.497(7)
Cr–N1	2.110(4)	C7–C8	1.395(6)
O1–C1	1.182(6)	C8–C9	1.378(7)
O2–C2	1.150(7)	C9–C10	1.374(7)
O3–C3	1.153(7)	C10–C11	1.365(7)
O4–C4	1.145(7)	C12–C13	1.391(8)
O5–C17	1.217(6)	C13–C14	1.36(1)
O6–C24	1.219(6)	C14–C15	1.34(1)
N1–C7	1.328(6)	C15–C16	1.37(1)
N1–C11	1.349(6)	C17–C18	1.479(8)
N2–C5	1.333(6)	C19–C20	1.387(7)
N2–C7	1.391(6)	C20–C21	1.365(8)
N3–C12	1.324(6)	C21–C22	1.34(1)
N3–C16	1.348(8)	C22–C23	1.377(9)
N4–C17	1.374(7)	C24–C25	1.488(7)
N4–C12	1.390(7)		

Table 3

Bond angles (°) in compound **8** with esd's in parentheses

C1–Cr–C3	93.2(2)	O4–C4–Cr	174.7(6)
C1–Cr–C4	85.6(3)	N2–C5–C6	113.2(4)
C1–Cr–C2	85.1(3)	N2–C5–Cr	115.9(3)
C1–Cr–C5	94.0(2)	C6–C5–Cr	130.9(4)
C1–Cr–N1	170.9(2)	N1–C7–N2	113.7(4)
C3–Cr–C4	89.1(3)	N1–C7–C8	124.5(4)
C3–Cr–C2	89.7(3)	N2–C7–C8	121.8(5)
C3–Cr–C5	172.4(2)	C9–C8–C7	117.5(5)
C3–Cr–N1	95.8(2)	C10–C9–C8	118.9(4)
C4–Cr–C2	170.5(2)	C11–C10–C9	119.5(4)
C4–Cr–C5	93.9(2)	N1–C11–C10	123.4(5)
C4–Cr–N1	94.4(2)	N3–C12–N4	112.6(5)
C2–Cr–C5	88.5(2)	N3–C12–C13	122.9(6)
C2–Cr–N1	95.1(2)	N4–C12–C13	124.4(6)
C5–Cr–N1	77.0(2)	C14–C13–C12	118.3(6)
C7–N1–C11	116.2(4)	C15–C14–C13	120.0(6)
C7–N1–Cr	114.8(3)	C14–C15–C16	119.0(7)
C11–N1–Cr	129.0(3)	N3–C16–C15	123.4(6)
C5–N2–C7	118.4(4)	O5–C17–N4	122.7(6)
C12–N3–C16	116.4(5)	O5–C17–C18	123.5(6)
C17–N4–C12	127.7(5)	N4–C17–C18	113.8(5)
C23–N5–C19	116.5(5)	N5–C19–C20	123.2(5)
C24–N6–C19	128.8(5)	N5–C19–N6	113.3(4)
O1–C1–Cr	178.9(5)	C20–C19–N6	123.5(5)
O2–C2–Cr	174.1(5)	C21–C20–C19	118.1(6)
O3–C3–Cr	117.0(5)	C22–C21–C20	120.0(5)
C21–C22–C23	119.1(6)		
N5–C23–C22	123.2(6)		
O6–C24–N6	122.5(6)		
O6–C24–C25	121.7(5)		
N6–C24–C25	115.7(5)		

ligand of **7**. Neither CO insertion, nor coordination of a chromium carbonyl species is observed. The ^{1}H NMR spectrum clearly shows the presence of 25 aromatic protons with signals between δ 6.63–7.41, of a N–CH_2–Ph group, with a singlet at



Scheme 1

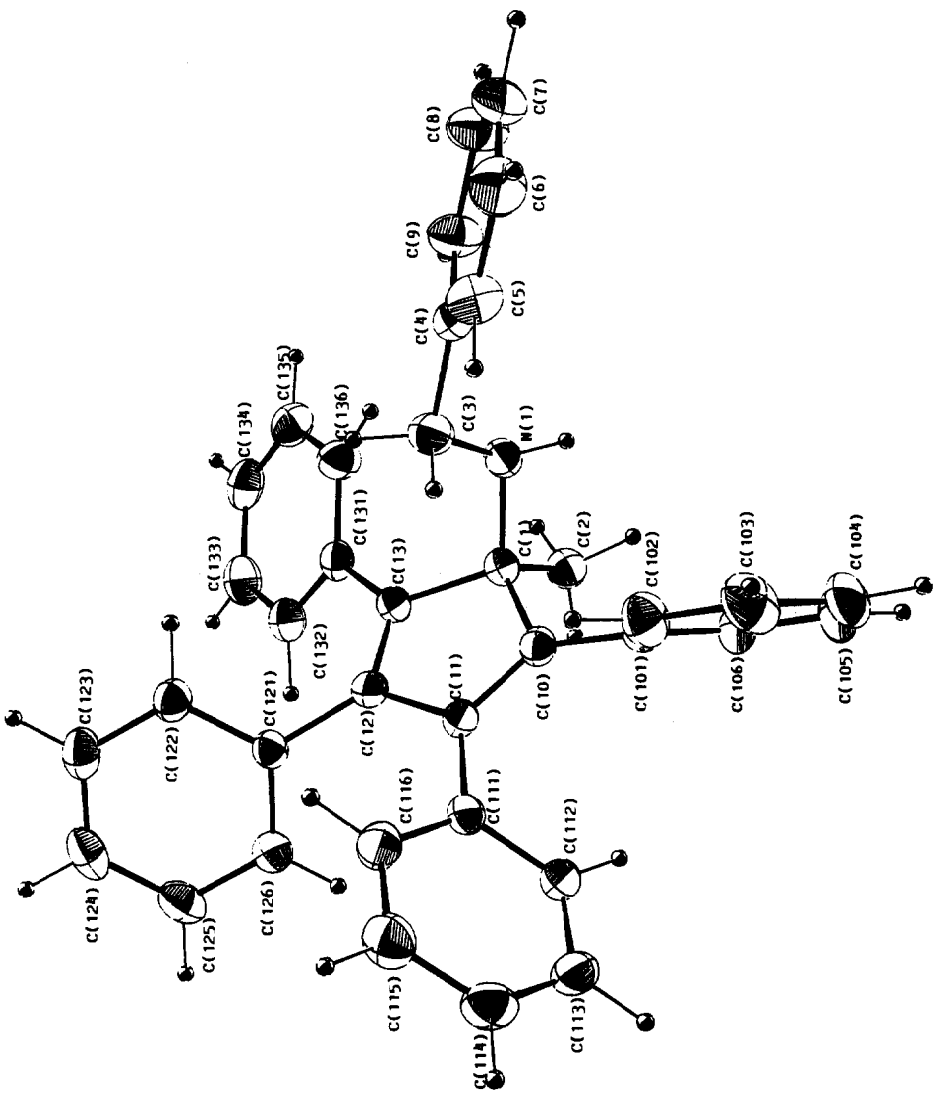


Fig. 2. ORTEP view of compound **14**.

Table 4

Bond lengths (Å) in compound **14** with esd's in parentheses

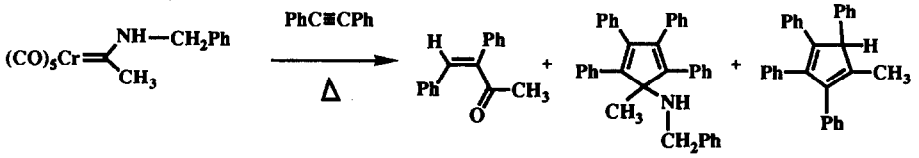
N(1)–C(1)	1.478(3)	N(1)–C(3)	1.463(3)
C(1)–C(2)	1.524(4)	C(1)–C(10)	1.527(4)
C(1)–C(13)	1.531(3)	C(3)–C(4)	1.502(4)
C(4)–C(5)	1.368(4)	C(4)–C(9)	1.376(4)
C(5)–C(6)	1.383(4)	C(6)–C(7)	1.352(5)
C(7)–C(8)	1.377(5)	C(8)–C(9)	1.380(4)
C(10)–C(11)	1.345(3)	C(10)–C(101)	1.487(3)
C(11)–C(12)	1.494(3)	C(11)–C(111)	1.475(4)
C(12)–C(13)	1.348(4)	C(12)–C(121)	1.483(3)
C(13)–C(131)	1.488(4)	C(101)–C(102)	1.386(4)
C(101)–C(106)	1.385(4)	C(102)–C(103)	1.395(4)
C(103)–C(104)	1.368(5)	C(104)–C(105)	1.358(5)
C(105)–C(106)	1.390(4)	C(111)–C(112)	1.396(4)
C(111)–C(116)	1.391(4)	C(112)–C(113)	1.380(4)
C(113)–C(114)	1.369(4)	C(114)–C(115)	1.374(4)
C(115)–C(116)	1.378(4)	C(121)–C(122)	1.393(4)
C(121)–C(126)	1.390(4)	C(122)–C(123)	1.381(4)
C(123)–C(124)	1.375(4)	C(124)–C(125)	1.368(4)
C(125)–C(126)	1.386(4)	C(131)–C(132)	1.401(4)
C(131)–C(136)	1.385(4)	C(132)–C(133)	1.388(4)
C(133)–C(134)	1.380(4)	C(134)–C(135)	1.358(4)
C(135)–C(136)	1.390(4)		

Table 5

Bond angles (°) in compound **14** with esd's in parentheses

C(3)–N(1)–C(1)	115.0(2)	C(2)–C(1)–N(1)	106.7(2)
C(10)–C(1)–N(1)	112.1(2)	C(10)–C(1)–C(2)	113.0(2)
C(13)–C(1)–N(1)	112.4(2)	C(13)–C(1)–C(2)	110.9(2)
C(13)–C(1)–C(10)	101.9(2)	C(4)–C(3)–N(1)	110.5(2)
C(5)–C(4)–C(3)	120.7(3)	C(9)–C(4)–C(3)	120.7(3)
C(9)–C(4)–C(5)	118.6(3)	C(6)–C(5)–C(4)	120.9(3)
C(7)–C(6)–C(5)	120.3(3)	C(8)–C(7)–C(6)	119.7(3)
C(9)–C(8)–C(7)	119.9(3)	C(8)–C(9)–C(4)	120.6(3)
C(11)–C(10)–C(1)	110.5(2)	C(101)–C(10)–C(1)	121.3(2)
C(101)–C(10)–C(11)	127.6(3)	C(12)–C(11)–C(10)	108.4(2)
C(111)–C(11)–C(10)	125.8(2)	C(111)–C(11)–C(12)	125.7(2)
C(13)–C(12)–C(11)	109.7(2)	C(121)–C(12)–C(11)	124.6(2)
C(121)–C(12)–C(13)	125.6(2)	C(12)–C(13)–C(1)	109.4(2)
C(131)–C(13)–C(1)	121.9(2)	C(131)–C(13)–C(12)	128.2(2)
C(102)–C(101)–C(10)	119.8(3)	C(106)–C(101)–C(10)	122.2(3)
C(106)–C(101)–C(102)	118.0(3)	C(103)–C(102)–C(101)	120.7(3)
C(104)–C(103)–C(102)	119.7(4)	C(105)–C(104)–C(103)	120.6(3)
C(106)–C(105)–C(104)	119.9(3)	C(106)–C(106)–C(101)	121.1(3)
C(112)–C(111)–C(11)	119.5(3)	C(116)–C(111)–C(11)	122.9(3)
C(116)–C(111)–C(112)	117.5(3)	C(113)–C(112)–C(111)	121.3(3)
C(114)–C(113)–C(112)	119.8(3)	C(115)–C(114)–C(113)	120.1(3)
C(116)–C(115)–C(114)	120.4(3)	C(115)–C(116)–C(111)	120.8(3)
C(122)–C(121)–C(12)	120.2(2)	C(126)–C(121)–C(12)	120.9(2)
C(126)–C(121)–C(122)	118.7(3)	C(123)–C(122)–C(121)	120.5(3)
C(124)–C(123)–C(122)	119.9(3)	C(125)–C(124)–C(123)	120.5(3)
C(126)–C(125)–C(124)	120.1(3)	C(125)–C(126)–C(121)	120.2(3)
C(132)–C(131)–C(13)	121.1(3)	C(136)–C(131)–C(13)	121.1(3)
C(136)–C(131)–C(132)	117.8(3)	C(133)–C(132)–C(131)	120.5(3)
C(134)–C(133)–C(132)	120.3(3)	C(135)–C(134)–C(133)	119.8(3)
C(136)–C(135)–C(134)	120.6(3)	C(135)–C(136)–C(131)	121.0(3)

δ 3.60, of a CH_3 group at δ 1.53, and a singlet at δ 1.57 attributable to a NH proton. The ^{13}C NMR spectrum confirms the presence, besides aromatic and olefinic carbons, of three aliphatic carbon atoms, at 23.4 (CH_3), 47.9 (CH_2) and 74.4 (C) ppm, respectively. Finally, the structure of compound **14** was determined by an X-ray study. An ORTEP view of **14** is shown in Fig. 2. The crystallographic data, the interatomic distances, and the bond angles are listed in Tables 1, 4 and 5, respectively.



7 13 14 15

In addition to the two afore-mentioned compounds, a third product was isolated in 4% yield and characterized as methyltetraphenylcyclopentadiene ($m/z = 384$). The ^1H NMR spectrum is in agreement with such a structure: besides signals due to twenty aromatic protons, there is a signal at δ 5.12 (benzylic protons) and one at δ 2.01 attributable to a methyl group associated with a double bond. It is likely that **15** is the result of the hydrogenolysis of **14**.

Although double alkyne insertion reactions are known in the chemistry of Fischer carbene complexes, they have always been accompanied by a CO insertion reaction [19,20]. To the best of our knowledge, this constitutes the first example of such a coupling in this chemistry. A reaction leading to the same type of cyclopentadienes originating from a carbene and two alkynes has recently been described in cobalt chemistry [21]. However, in this case, the coupling starts from a cobaltacyclopentadiene which undergoes the insertion of a carbene generated from a diazoester.

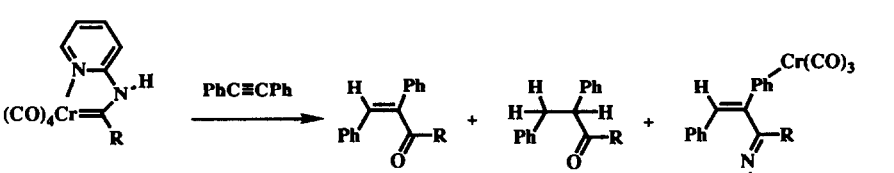
These results show that the vinylogous aminocarbene complexes obtained upon insertion of the alkyne have the same behaviour as the starting complexes **5–7**; a facile hydrogen migration from nitrogen to the γ-carbon atom is observed, leading in almost all cases to the vinylogous imines **12** (Scheme 1).

III. Reactivity of carbene complexes 8–11

(a) Case of the chromium complexes 8 and 9

As has been shown in previous papers, and confirmed later by other groups, a general feature in the case of bidentate aminocarbene complexes of chromium is on the one hand the insertion of the alkyne, and on the other the absence of CO insertion reactions. In the special case of bidentate alkyne-aminocarbene complexes, the alkyne insertion was in general followed by an intramolecular cyclopropanation.

However, the reactions of complexes **8** and **9** towards diphenylacetylene turned out to be disappointing; complex **9** did not insert the alkyne at all and complex **8** gave only small amounts of insertion product.



8 R=CH_3
9 R=Ph

13 16 12 R'=pyridyl

Thus reaction of complex **8** with PhC≡CPh, in boiling benzene, led, after silica chromatography, to the isolation of two compounds; diphenylbutanone **16**, contaminated with small amounts of diphenylbutenone **13** and imine **12**, in less than 5% yield. The mode of reaction of **8** is therefore the same as that of complexes **5–7** but the yield is much lower. It is likely that the hydrogenation of **13** to give **16** is due to the presence of unsaturated chromium species, which, in the presence of trace amounts of water, are transformed into hydrides. Such hydrogenation reactions have been observed previously for reactions involving chromium carbene complexes [22].

(b) Case of molybdenum carbene complexes 10 and 11

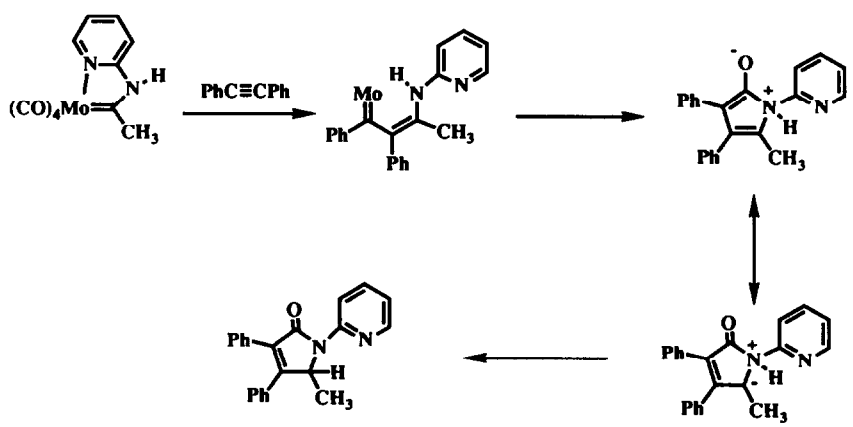
Little was previously known about the chemistry of molybdenum carbene complexes, probably because of their instability. Nevertheless, the aminocarbene complexes **10** and **11** were obtained from their alkoxycarbene precursors in satisfactory yields (52 and 54% yield), as red-brown crystals. The products are, however, less stable than their chromium counterparts.

The molybdenum aminocarbene complexes show a high reactivity. Thus both **10** and **11** underwent a fast reaction with PhC≡CPh in boiling benzene. After 3 h, all the starting complex had already disappeared. For example, complex **10**, gave (after chromatography) an organic compound in 40% yield, to which structure **17**, a substituted pyrrolinone, was assigned.

10 R=CH_3
11 R=Ph

17 R=CH_3
18 R=Ph

The mass spectrum and the elemental analysis confirmed the insertion of both the alkyne and of CO. The presence of a lactam was evident from in the IR



Scheme 2

spectrum (ν(CO) 1690 cm^{-1}) and in the ^{13}C NMR spectrum (δ(C=O) 170 ppm). Finally, the presence of a signal at low field for one hydrogen at δ 5.7 as a quartet, and of a signal at δ 1.39 as a doublet for a methyl group, were consistent with such a structure.

The same type of product was obtained by treating complex **11** with PhC=CPh. In the case of **18**, a highly deshielded signal attributable to the N–C*H*Ph proton appears at δ 6.6.

The transformations **10** → **17** and **11** → **18** can be understood in terms of an alkyne insertion followed by the formation of a ketene complex. Interaction of nitrogen with the ketene could lead to a *N*-ylid, which would rearrange, by a 1–2 nitrogen-to-carbon hydrogen shift, to **17** and **18** (Scheme 2), respectively [23].

Conclusion

Although alkyne insertions into chromium aminocarbene complexes derived from secondary amines is now a well documented reaction, leading to interesting heterocyclic compounds, it appears that in general carbene complexes derived from primary amines give less interesting insertion products. The only exception to this rule comes from the behaviour of the bidentate molybdenum aminocarbene complexes; they undergo insertion of both the alkyne and CO, and lead, after a rearrangement which parallels that for secondary aminocarbene complexes of chromium, the same type of pyrrolinone.

Experimental

All reactions were carried out in oven-dried glassware under nitrogen. Benzene, diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone. Preparative column chromatography was performed with 70–230 mesh Merck silica gel, and preparative thin layer chromatography with Merck G60 silica gel. Light petroleum ether was used as eluent.

NMR spectra were recorded on a Bruker W-M 200. 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((cyclohexylamino)methylcarbene)chromium(0), 5

Cyclohexylamine (2 ml, 17.5 mmol) was added to a solution of complex **1** (3 g, 11.3 mmol) in diethyl ether (50 ml). After 12 h at room temperature, the pale yellow solution was evaporated under vacuum and the residue was chromatographed on silica with a mixture of petroleum ether and methylene chloride as eluent to give, after evaporation of the appropriate fractions, a yellow solid (3.2 g, 88%); m.p. 115 °C; *m/z*: 317 (M^+).

Analysis: Found: C, 49.41; H, 4.86; N, 4.35. $C_{13}H_{15}CrNO_5$ calc.: C, 49.21; H, 4.73; N, 4.41%. ^1H NMR (200 MHz, $CDCl_3$): δ 8.6 (1H, NH); 3.7 (1H, m, NHC*H*); 2.7 (3H, s, CH_3); 1.9 (4H, m, $CH(CH_2)_2$); 1.4 (6H, m, $(CH_2)_3$). ^{13}C NMR (50 MHz, $CDCl_3$): 278 δ (C-carbene); 223.0, 218.0 (CO); 56.8 (NHCH); 35.1, 32.6, 24.5 (CH_2); 24.9 (CH_3).

Pentacarbonyl((cyclopropylamino)methylcarbene)chromium(0), 6

Cyclopropylamine (1.6 ml, 23.1 mmol) was added at room temperature to a solution of complex **1** (4.4 g, 16.6 mmol) in anhydrous diethyl ether (50 ml). After 10 min the solution was evaporated under vacuum at room temperature, and the residue chromatographed on a short column of silica with petroleum ether and 5% methylene chloride. Appropriate fractions were collected and evaporated under vacuum to give the title compound **6** as yellow crystals (4.3 g, 94%) as a 4:1 mixture of *E,Z* isomers. m.p. 35°C; *m/z*: 275 (M^+).

Analysis: Found: C, 43.83; H, 3.24; N, 5.10. $C_{10}H_9NO_5Cr$ calc.: C, 43.64; H, 3.27, N, 5.09%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.81 (1H, s, NH); 3.55 (1H, m, N–CH); 2.83 (3H, s, CH_3); 0.99 (2H, m, CH_2); 0.83 (2H, m, CH_20. ^{13}C NMR (50 MHz, $CDCl_3$): δ 287.15 (C-carbene); 223.3, 217.84 (CO); 37.12 (N–CH); 30.23 (CH_3); 7.92 (CH_2CH_2).

Pentacarbonyl((benzylamino)methylcarbene)chromium(0), 7

This complex was prepared as described by Fischer [16] from complex **1**, and obtained as yellow crystals in 87% yield.

Reaction of complex 5 with diphenylacetylene

A solution of complex **5** (2.5 g, 7.8 mmol) in benzene (50 ml) was refluxed in the presence of diphenylacetylene (2 g, 11.2 mmol) for 12 h. After evaporation of most of the solvent, the residue was chromatographed on silica, first with petroleum ether/methylene chloride as eluent and then with petroleum ether/acetone. Appropriate fractions were collected and evaporated under vacuum to give first the complex of ketone **13** as a yellow oil (0.15 g, 5%) [*m/z*: 357 (M^+). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.63–7.0 (6H, aromatic and =–H); 5.75–5.0 (5H, m, $ArCr(CO)_3$); 2.57 (3H, s, CH_3)] and then complex **12** (2.7 g, 78%) as an orange oil [*m/z*: 439 (M^+). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.3 (5H, m); 6.97 (1H, s); 5.9–5.2 (5H, m, $Cr(CO)_3$); 3.2 (1H, m, CH); 2.28 (3H, s, CH_3); 1.9–0.8 (10H, m, $5CH_2$)].

Heating of complex **12** in refluxing pyridine (20 ml) for 4 h, followed by evaporation of the solvent, treatment of the residue with 10 *N* HCl in methanol for 12 h at 40°C, and extraction of the organic product, gave ketone **13** (0.85 g, 62%) as white crystals, m.p. 53°C (litt. 53–54°C); IR: 1660, 1610 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.64 (s, 1H); 7.1 (10H, m); 2.27 (3H, s, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 198.7, 140.7, 138.5, 136.7, 134.4, 130.6, 129.3, 128.7, 128.2, 117.6.

Reaction of complex 6 with diphenylacetylene

A solution of complex **6** (1.4 g, 5.09 mmol) in benzene (50 ml) was refluxed in the presence of diphenylacetylene (1.2 g, 6.74 mmol) for 17 h. After evaporation of most of the solvent, the residue was chromatographed on silica, first with petroleum ether/methylene chloride as eluent and then with petroleum ether/acetone. Appropriate fractions were collected and evaporated under vacuum to give first complex **6** (0.25 g, 18%) then tetraphenylcyclopentadienone (0.05 g, 2.5%), m.p. 218°C (litt. [27] m.p. 218°C) [*m/z*: 383 (M^+). IR ($CHCl_3$): 1708 cm^{-1} (ν(CO))] and finally complex **12** (0.82 g, 41%) m.p. 123°C [*m/z*: 397 (M^+). IR ($CHCl_3$): 1970, 1885 cm^{-1} (ν(CO)). Analysis. Found: C, 66.61; H, 4.98; N, 3.41. $C_{22}H_{19}CrNO_3$ calc.: C, 66.61; H, 4.78; N, 3.53%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.70 (2H, m); 0.85 (2H, m); 2.16 (3H, s); 2.93 (2H, m); 5.41, 5.57, 5.64 (5H, m); 7.02 (1H, s); 7.3–7.4 (10H, m)].

Reaction of complex 7 with diphenylacetylene

A solution of complex **7** (2 g, 6.15 mmol) in benzene (50 ml) was refluxed for 12 h in the presence of diphenylacetylene (2.6 g, 13.1 mmol). After evaporation of most of the solvent the residue was chromatographed on silica with petroleum ether and 20% methylene chloride as eluents. Appropriate fractions were collected and evaporated under vacuum to give first ketone **13** (0.4 g, 30%) as white crystals, m.p. 53°C, then compound **15** (0.1 g, 4%), m.p. 152°C [*m/z*: 384 (M^+). Analysis. Found: C, 93.59; H, 6.18. $C_{30}H_{24}$ calc.: C, 93.71; H, 6.29%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.7–7.5 (20H, m); 5.05 (1H, s); 2.12 (3H, s)] and finally compound **14** (0.9 g, 30%), m.p. 189°C. Analysis. Found: C, 91.16; H, 6.31; N, 2.72. $C_{37}H_{31}N$ calc.: C, 90.79; H, 6.34; N, 2.86.IR ($CHCl_3$): 3675 cm^{-1} (NH). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.8–7.4 (25H, m); 3.80 (2H, s, CH_2Ph); 1.58 (1H, s, N–H); 1.53 (3H, s, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 126–146 (21H, aromatics); 74.38 (N–CH); 47.92 (N–C); 23.39 (CH_3).

Bidentate tetracarbonyl(aminopyridino methylcarbene)chromium (0), 8

A solution of complex **1** (3.4 g, 12.5 mmol) and aminopyridine (1.5 g, 15.8 mmol) in methylene chloride (50 ml) was kept at room temperature for 18 h. After evaporation of the solvent under vacuum, the residue was chromatographed on silica with petroleum ether and methylene chloride as eluent. Appropriate fractions were collected and evaporated under vacuum, and the residue was recrystallized from methanol to give the title compound **8**. (2.5 g 28%) as red crystals, m.p. 158°C, *m/z*: 284 (M^+). Crystals suitable for an X-ray study were grown from hexane/methylene chloride, but, it appeared that during recrystallization, oxidation of the carbene complex took place, to give the corresponding amide which co-crystallized with complex **8**.

IR ($CHCl_3$): 2007, 1910, 1846 cm^{-1} (ν(CO)). ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.16 (s, 1H); 8.77 (d, 1H); 7.77 (t, 1H); 7.25 (d, 1H); 7.09 (t, 1H); 3.25 (s, 3H). ^{13}C NMR (75 MHz, $(CD_3)_2CO$): δ 309.6 (C-carbene); 234.0, 232.0, 216.5 and 205.9 (CO); 157.5, 153.1, 139.1, 121.6, 114.4 (C aromatic); 36.5 (CH_3).

Bidentate tetracarbonyl((aminopyridino)phenylcarbene)chromium(0), 9

A solution of complex **2** (3.2 g, 9.7 mmol) and aminopyridine (1.3 g, 13.6 mmol) in methylene chloride (50 ml) was kept at room temperature for 18 h. After evaporation of the solvent at room temperature the residue was chromatographed on silica with mixture of petroleum ether and 5–30% acetone as eluents. Appropriate fractions were collected and evaporated under vacuum to give the title complex **9** as red crystals. Yield 2.24 g (67%); m.p. 174–176°C; *m/z*: 346 (M^+).

Analysis. Found: C, 55.28; H, 3.13; N, 7.79. $C_{16}H_{10}CrN_2O_4$ calc.: C, 55.4; H, 3.46; N, 8.09%. IR (KBr): 2000, 1910 and 1846 cm^{-1} (ν(CO)). ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 12.4 (NH); 8.9, 8.05, 7.8, 7.5 and 7.3 (aromatics). ^{13}C NMR (60 MHz, $(CD_3)_2CO$): δ 300.96 (C carbene); 235.7, 231.2, 216.7 and 206.4 (CO); 158.6, 153.3, 148.5, 139.5, 131.5, 129.3, 126.4, 122.1 and 115.8 (C aromatic).

Bidentate tetracarbonyl((aminopyridino)methylcarbenemolybdenum(0), 10

A solution of aminopyridine (1.9 g, 20 mmol) in methylene chloride (50 ml) was added to a solution of complex **3** (2.9 g, 10 mmol) in diethyl ether (40 ml). The residue was kept at room temperature for 18 h. After evaporation of the solvent,

under vacuum, at room temperature the residue was chromatographed on silica with a mixture of petroleum ether and ethyl acetate as eluents. Appropriate fractions were collected and evaporated under vacuum to give the title compound **10** as red crystals. Yield 1.56 g (52%); m.p.: 130 °C (dec); *m/z*: 328 (M^+).

Analysis. Found: C, 39.6; H, 2.61; N, 8.68. calc.: $C_{11}H_8MoN_2O_4$. C, 40.24; H, 2.44; N, 8.53%. IR: 2000, 1920 and 1850 cm^{-1} (ν(CO)). ^1H NMR (200 MHz, acetone): δ 12.4 (NH); 8.75, 8.05, 7.65 and 17.35 (m, aromatic); 3.08 (s, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 297.9 (C carbene); 225.5, 255.0, 206,3, 205.3 (CO); 156.6, 152.1, 139.2, 121.6 and 114.7 (C pyridine).

Bidentate tetracarbonyl((aminopyridino)phenylcarbene)molybdenum(0), 11

A solution of complex **4** (4.75 g, 12.5 mmol) and of aminopyridine (1.2 g, 12.5 mmol) in methylene chloride (100 ml) was kept at room temperature for 24 h. After evaporation of the solvent at room temperature under vacuum, the residue was chromatographed on silica with a 60/40 mixture of petroleum ether and ethyl acetate as eluent. Appropriate fractions were collected and evaporated under vacuum to give the title compound **11** as dark-red crystals. Yield 2.55 g (50.9%); m.p.: 138 °C; *m/z*: 390 (M^+).

Analysis. Found: C, 49.17; H, 3.10; N, 6.93. $C_{16}H_{10}MoN_2O_4$ calc.: C, 49.23; H, 2.5; N, 7.17%. ^1H NMR (200 MHz, $CDCl_3$): δ 10.32 (NH); 8.83, 7.76, 7.58, 7.25 (10H, m). ^{13}C NMR (50MHz, $CDCl_3$): δ 288.2 (C-carbene); 226.1, 224.5, 219.8, 206.0 (CO); 156.3, 152.1, 147.1, 138.2, 134.6, 132.8, 129.0, 126.6, 120.9, 114.4 (C-aromatic).

Reaction of complex 8 with diphenylacetylene

A solution of complex **8** (1 g, 3.52 mmol) in benzene (50 ml) was refluxed in the presence of diphenylacetylene (0.8 g, 4.5 mmol) for 2 days. After evaporation of the solvent under vacuum, the residue was chromatographed on silica with mixtures of petroleum ether and 5–15% acetone as eluents. Appropriate fractions were collected and evaporated under vacuum to give first the ketone **16** (0.04 g), then the imine **12** as a yellow $Cr(CO)_3$ complex (0.035 g).

Ketone **16**: *m/z*: 224 (M^+. IR: 1713 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.36 (10H, m); 3.92 (t, 1H0; 3.41 (dd, 1H); 2.91 (dd, 1H); 2.02 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.4 (CO); 139.5, 138.2, 128.8, 128.7, 128.2, 127.3, 125.9 (C-aromatic); 61.4, 38.3, 29.5 (2CH, CH_3).

Imine **12**: *m/z*: 434 (M^+). ^1H NMR (200 MHz, $CDCl_3$): δ 7.38 (m, 11H); 5.69, 5.30, 5.08 and 4.67 (Ar–$Cr(CO)_3$); 2.27 (3H, CH_3).

Reaction of complex 10 with diphenylacetylene: formation of pyrrolinone 17

A solution of complex **10** (0.5 g, 1.5 mmol) in benzene (50 ml) was refluxed for 3 h in the presence of diphenylacetylene (0.4 g, 2.25 mmol). After evaporation of the solvent under vacuum the residue was chromatographed on silica with a mixture of petroleum ether and methylene chloride as eluent. Appropriate fractions were combined and evaporated to give the title compound **17** as white crystals (0.2 g, 40%), which were recrystallized from hexane. m.p. 138 °C; *m/z*: 326 (M^+).

Analysis. Found: C, 80.54; H, 5.62; N, 8.42. $C_{22}H_{18}N_2O$ calc.: C, 80.98; H, 5.52, N, 8.58%. IR ($CDCl_3$): 1690 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 8.42 (m, 2H); 7.73 (m, 1H); 7.34 (m, 10H); 7.07 (m, 1H); 5.70 (q, 1H); 1.39 (d, 3H). ^{13}C NMR (50

MHz, $CDCl_3$): δ 169.0 (CO); 156.0, 151.0, 147.6, 137.8, 132.4, 131.2, 129.7, 129.2, 128.7, 128.2, 128.0, 119.1, 115.4, 57.3, 18.5.

*Reaction of complex **11** with diphenylacetylene: formation of pyrrolinone **18***

A solution of complex **11** (2 g, 4.78 mmol) in benzene (50 ml) was refluxed for 3 h in the presence of an excess of diphenylacetylene (1 g, 5.61 mmol). After evaporation of the solvent under vacuum the residue was chromatographed on silica with a mixture of petroleum ether and methylene chloride as eluent. Appropriate fractions were combined and evaporated and the residue was crystallized from

Table 6

Atom coordinates and temperature factors for compound **8**

Atom	x	y	z	B_{eq}
Cr	0.15908(3)	0.2511(1)	0.56335(3)	4.59(4)
O1	0.2874(2)	0.2015(7)	0.5952(1)	9.0(3)
O2	0.1826(2)	0.5719(7)	0.5175(2)	10.4(3)
O3	0.1747(2)	0.4681(8)	0.6474(2)	11.3(3)
O4	0.1672(2)	−0.0730(8)	0.6199(2)	9.3(3)
O5	0.9549(2)	0.0590(6)	0.6138(1)	8.0(2)
O6	0.9882(2)	0.4363(7)	0.3733(1)	8.1(2)
N1	0.0670(2)	0.2622(5)	0.5313(1)	3.8(2)
N2	0.0834(2)	0.1130(6)	0.4752(1)	4.5(2)
N3	0.9193(2)	0.2602(6)	0.7225(2)	5.7(2)
N4	0.9752(2)	0.1787(7)	0.6849(1)	5.3(2)
N5	0.9220(2)	0.2445(6)	0.2370(1)	5.2(2)
N6	0.9916(2)	0.3253(6)	0.3081(1)	4.9(2)
C1	0.2365(2)	0.2205(8)	0.5830(2)	6.0(3)
C2	0.1705(2)	0.452(1)	0.5338(2)	6.2(3)
C3	0.1671(2)	0.386(1)	0.6147(2)	7.2(3)
C4	0.1613(2)	0.050(1)	0.5977(2)	5.9(3)
C5	0.1399(2)	0.1198(7)	0.5040(2)	4.4(2)
C6	0.1785(2)	0.0275(9)	0.4854(2)	6.2(3)
C7	0.0430(2)	0.1896(6)	0.4894(2)	3.7(2)
C8	−0.0169(2)	0.1828(7)	0.4619(2)	4.5(2)
C9	−0.0535(2)	0.2575(8)	0.4796(2)	4.8(2)
C10	−0.0297(2)	0.3285(7)	0.5235(2)	4.7(2)
C11	0.0295(2)	0.3314(7)	0.5476(2)	4.5(2)
C12	0.9192(3)	0.2060(7)	0.6825(2)	5.1(3)
C13	0.8683(3)	0.189(1)	0.6421(2)	7.6(4)
C14	0.8165(3)	0.230(1)	0.6440(3)	8.8(4)
C15	0.8154(3)	0.286(1)	0.6838(3)	8.6(4)
C16	0.8669(3)	0.3016(9)	0.7223(2)	7.5(4)
C17	0.9906(3)	0.1141(8)	0.6508(2)	5.8(3)
C18	1.0542(3)	0.119(1)	0.6631(2)	7.2(3)
C19	0.9324(2)	0.2943(6)	0.2805(2)	4.5(2)
C20	0.8887(3)	0.3104(9)	0.2966(2)	6.2(3)
C21	0.8329(3)	0.269(1)	0.2669(2)	7.7(4)
C22	0.8214(3)	0.216(1)	0.2234(3)	8.1(4)
C23	0.8666(3)	0.2053(9)	0.2093(2)	6.7(3)
C24	1.0167(3)	0.3863(8)	0.3521(2)	5.3(3)
C25	1.0817(3)	0.3881(9)	0.3736(2)	6.5(3)

hexane to give the title compound **18** as white crystals (0.8 g, 40%), m.p. 211°C; *m/z*: 388 (M^+).

Analysis. Found: C, 78.3; H, 5.07; N, 6.80. $C_{27}H_{20}N_2O$ calc.: C, 83.50; H, 5.15; N, 7.21. IR ($CHCl_3$): 1690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.2 (1H); 8.1 (1H); 7.6–6.8 (m, 17H); 6.6 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6 (CO); 154.6, 150.3, 147.6, 137.5, 136.6, 132.4, 131.4, 129.7, 128.7, 128.3, 128.2, 127.7, 126.5, 119.3, 115.5, 65.4.

*Determination of the structures of compounds **8** and **14***

Selected crystals were set up on automatic four-circle diffractometer. Accurate unit cell dimensions and crystal orientation matrices were obtained from least-

Table 7

Atom coordinates and temperature factors for compound **14**

Atom	*x*	*y*	*z*	U_{eq}
N(1)	−0.0942(2)	0.3900(2)	0.3614(2)	0.0454
C(1)	−0.1019(3)	0.2705(3)	0.3456(2)	0.0420
C(2)	−0.1309(3)	0.1658(3)	0.4517(2)	0.0513
C(3)	−0.0537(3)	0.497893)	0.2669(2)	0.0544
C(4)	−0.0762(3)	0.6239(3)	0.2909(2)	0.0461
C(5)	−0.1587(4)	0.7461(3)	0.2438(3)	0.0625
C(6)	−0.1815(4)	0.8621(3)	0.2669(3)	0.0707
C(7)	−0.1232(4)	0.8562(4)	0.3374(3)	0.0713
C(8)	−0.0402(4)	0.7342(4)	0.3859(3)	0.0754
C(9)	−0.0170(3)	0.6186(3)	0.3625(3)	0.0619
C(10)	−0.2146(3)	0.3075(3)	0.2885(2)	0.0420
C(11)	−0.1528(3)	0.2753(3)	0.2004(2)	0.0404
C(12)	0.0053(3)	0.2150(3)	0.1912(2)	0.0415
C(13)	0.0364(3)	0.2113(3)	0.2735(2)	0.0407
C(101)	−0.3652(3)	0.3862(3)	0.3233(2)	0.0457
C(102)	−0.4188(3)	0.5137(3)	0.2599(3)	0.0639
C(103)	−0.5590(4)	0.5902(4)	0.2920(3)	0.0780
C(104)	−0.6439(3)	0.5397(5)	0.3875(3)	0.0722
C(105)	−0.5937(4)	0.4150(4)	0.4509(3)	0.0745
C(106)	−0.4544(3)	0.3381(3)	0.4192(2)	0.0614
C(111)	−0.2280(3)	0.2954(3)	0.1257(2)	0.0419
C(112)	−0.3579(3)	0.2595(3)	0.1610(2)	0.0488
C(113)	−0.4357(3)	0.2836(3)	0.0941(3)	0.0573
C(114)	−0.3852(4)	0.3435(3)	−0.0091(3)	0.0629
C(115)	−0.2567(4)	0.3780(4)	−0.0461(2)	0.0676
C(116)	−0.1784(3)	0.3540(3)	0.0202(2)	0.0573
C(121)	0.1101(3)	0.1641(3)	0.1053(2)	0.0412
C(122)	0.2329(3)	0.2116(3)	0.0501(2)	0.0486
C(123)	0.3386(3)	0.1541(3)	−0.0223(2)	0.0567
C(124)	0.3226(3)	0.0496(4)	−0.0407(2)	0.0595
C(125)	0.2006(4)	0.0045(3)	0.0104(2)	0.0602
C(126)	0.0934(3)	0.0620(3)	0.0828(2)	0.0537
C(131)	0.1753(3)	0.1450(3)	0.3030(2)	0.0447
C(132)	0.2653(30	0.0234(3)	0.2835(2)	0.0535
C(133)	0.3924(3)	−0.0395(3)	0.3142(2)	0.0593
C(134)	0.4309(3)	0.0164(4)	0.3653(3)	0.0618
C(135)	0.3438(3)	0.1334(4)	0.385893)	0.0643
C(136)	0.2163(3)	0.1978(3)	0.3554(3)	0.0581

squares refinements of the setting angles of 25 reflections. Three standard reflections were monitored periodically; they showed no change during data collection. Crystallographic data and other pertinent details are summarized in Table 1. Correction was made for Lorentz and polarization effects.

Computations were performed by using either CRYSTALS [24] for compound **14** or by using SHELXTL for complex **8** adapted for a Microvax II. Atomic form factors for neutral Cr, C, N and H atoms were taken from reference 26. The structure were solved using SHELXS [26]. Hydrogen atoms were located on difference electron density maps. Their coordinates were refined with an overall isotropic thermal parameter for compound **14**. For compound **8**, only the H atoms attached to N were refined, their isotropic thermal parameters were not refined. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Least-squares refinements with approximation to the normal matrix were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The criteria for a satisfactory complete analysis were a ratio of the rms shift to standard deviation of < 0.3, and the absence of significant features in the final difference maps. Atomic coordinates are given in Table 6 for **8**, and Table 7 for **14**. Bond lengths and angles are given in Tables 2 and 3 for **8** and Tables 4 and 5 for **14**.

A complete list of bond angles for **14**, lists of thermal parameters, hydrogenation atom coordinates, and structure factors are available from the authors.

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References

1 A. Yamashita, Tetrahedron Lett., 27 (1986) 5915.
2 C. Alvarez, A. Parlier, H. Rudler, R. Yefsah, J.C. Daran and C. Knobler, Organometallics, 8 (1989) 2253.
3 A. Parlier, H. Rudler and R. Yefsah, J. Organomet. Chem., 328 (1987) C21.
4 A. Parlier, H. Rudler, R. Yefsah, J.C. Daran and C. Knobler, J. Chem. Soc., Chem. Commun., (1988) 635.
5 H. Rudler, A. Parlier, R. Yefsah, B. Denise, J.C. Daran, J. Vaissermann and C. Knobler, J. Organomet. Chem., 358 (1988) 245.
6 M. Audouin, S. Blandiniere, A. Parlier and H. Rudler, J. Chem. Soc., Chem. Commun., (1990) 23.
7 B. Denise, A. Parlier, R. Goumont, J. Vaissermann, J.C. Daran and H. Rudler, J. Chem. Soc., Chem. Commun., (1990) 1238.
8 C. Borel, L.S. Hegedus, S. Krebs and Y. Satoh, J. Am. Chem. Soc., 109 (1987) 1101.
9 L.S. Hegedus and D.B. Miller, Jr, J. Org. Chem., 54 (1989) 1249.
10 K.H. Dotz, H. Erben and K. Hams, J. Chem. Soc. Chem. Commun., (1989), 692.
11 K.H. Dötz, T. Schäffer and K. Harms, Angew. Chem., Int. Ed. Engl., 29 (1990) 176.
12 R. Aumann and P. Hinterding, Chem. Ber., 123 (1989) 611.
13 W.D. Wulff, B.A. Anderson, L.D. Isaac, Tetrahedron Lett., 30 (1985) 4061.
14 B.A. Anderson and W.D. Wulff, J. Am. Chem. Soc., 112 (1990) 8615.
15 E.O. Fischer and R. Aumann, Angew. Chem., 79 (1967) 191.
16 E.O. Fischer and J.A. Connor, J. Am. Chem. Soc., 89 (1967) 714.
17 E.O. Fischer and M. Leupold, Chem. Ber., 105 (1972) 599.

18 J.A. Connor and P.D. Rose, J. Organomet. Chem., 46 (1972) 329.
19 W.D. Wulff, R.W. Kaesler, G.A. Peterson and P.C. Tang, J. Am. Chem. Soc., 107 (1985) 1060.
20 A. Parlier, H. Rudler, N. Platzer, M. Fontanille and A. Soum, J. Chem. Soc., Dalton Trans., (1987) 1041.
21 J.M. O'Connor, L. Pu, R. Uhrhammer and J.A. Johnson, J. Am. Chem. Soc., 111 (1989) 1889.
22 J.W. Herndon and S.W. Tumer, Tetrahedron Lett., 30 (1989) 295.
23 H. Rudler, A. Parlier, R. Goumont, J.C. Daran and J. Vaissermann, J. Chem. Soc., Chem. Commun., (1991) 1075.
24 D.J. Watkin, J.R. Carruthers and P.W. Betteridge, CRYSTALS User Guide, Chemical Crystallography Laboratory, University of Oxford, Oxford, England, 1985.
25 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.
26 G.M. Sheldrick, SHELXS86, Program for Crystal Structure Solution, University of Göttingen, 1986.