Journal of Organometallic Chemistry, 386 (1990) 51–62
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20533

Synthesis and reactivity of aziridinocarbene complexes of chromium and tungsten: formation of nitrile and acetiminoester complexes

B. Denise, A. Massoud, A. Parlier, H. Rudler *

Laboratoire de Chimie Organique, Université Pierre et Marie Curie, UA 408 T 45, 4 Place Jussieu 75252 Paris Cedex 05 (France)

J.C. Daran and J. Vaissermann,

Laboratoire de Chimie des Métaux de Transition, Université Pierre et Marie Curie, UA 608, 4 Place Jussieu 75252 Paris Cedex 05 (France)

C. Alvarez, R. Patino, and R.A. Toscano,

Instituto de Quimica, Universidad Nacional Autonoma de Mexico, Ciudad Universitaria, Delegacion Coyoacan, 045510 Mexico D.F. (Mexico)

(Received October 9th, 1989)

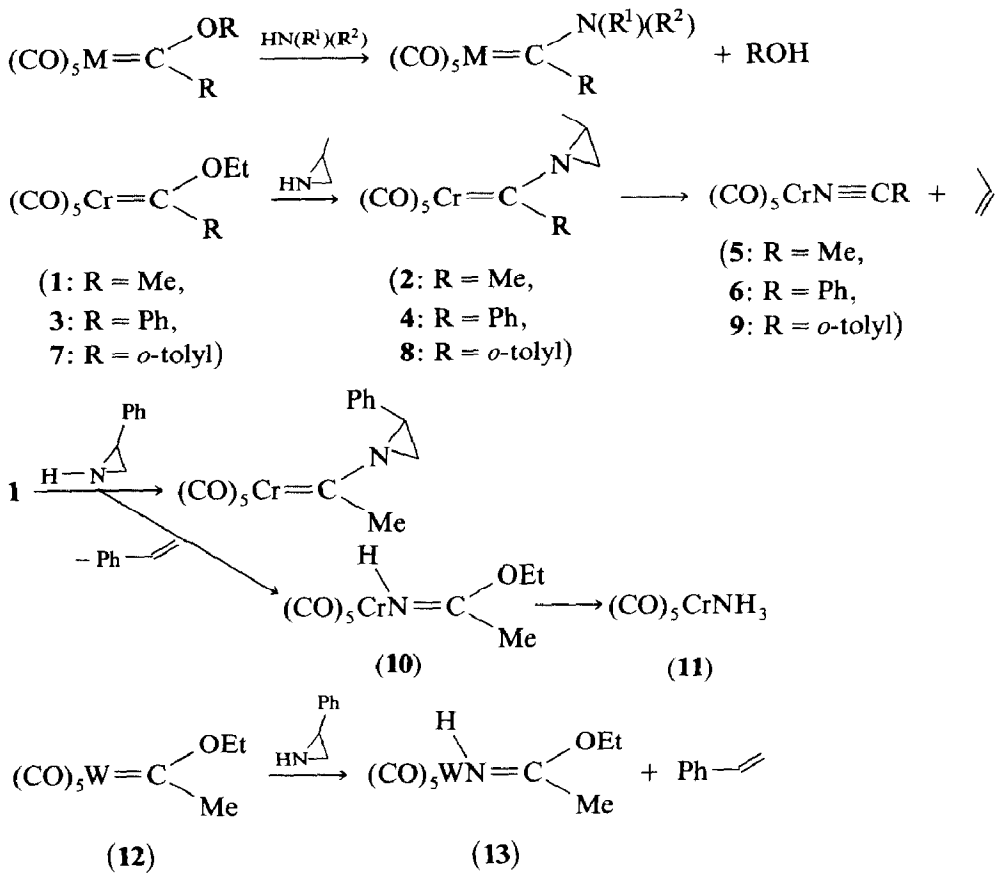
Abstract

2-Methylaziridine $HN\overline{CH_2CH}CH_3$ reacts with alkyl- and aryl-(alkoxy)carbene complexes of chromium and tungsten to give alkyl- and aryl-aziridinocarbene complexes. The latter undergo a thermal transformation to give olefins and alkyl- or aryl-nitrilechromium pentacarbonyl complexes, e.g. $(CO)_5CrN{\equiv}C$-*o*-tolyl (which has been characterized by X-ray crystallography). 2-Phenylaziridine $HN\overline{CH_2CH}Ph$ in turn reacts with the carbene complexes to give directly styrene and the acetiminoester complexes $(CO)_5WHN{=}C(CH_3)OCH_2CH_3$ and $(CO)_5CrHN{=}C(CH_3)OCH_2CH_3$. The latter gives, upon hydrolysis $(CO)_5CrNH_3$. The structures of $(CO)_5WHN{=}C(CH_3)OCH_2CH_3$ and $(CO)_5CrNH_3$ have been determined by X-ray diffraction. The mechanisms of the two reactions are discussed.

Introduction

During investigations directed toward the use of aziridine substituted carbene complexes as starting materials in organic synthesis [1,2] we prepared a series of such complexes by use of the general method established by Fischer [3], and outlined in Scheme 1, for the preparation of aminocarbene complexes.

0022-328X/90/$03.50



Scheme 1.

We describe below a study aimed at extending the scope of this reaction and report the unusual behaviour of 2-phenylaziridine in this type of substitution reaction.

Results and discussion

We have previously described the synthesis of the aziridinocarbene complexes of chromium **2** and **4** and, in a preliminary communication [4], their thermal transformation into nitrile complexes **5** and **6** and propene. The more crowded *o*-tolyl(ethoxy)carbene complex **7**, showed similar behaviour; thus the reaction of **7** with a slight excess of 2-methylaziridine gave the new complex **8** as a 35/65 mixture of the *E* and *Z* isomers. This is evident from the ^{13}C NMR spectrum, which shows two signals from the carbene carbon at 271.9 and 273.2 ppm, and also from the ^{1}H NMR spectrum, in which the signals from the methyl of the aziridine appear at 1.75 and 1.07 ppm, respectively, as two doublets, and those from the methyl groups on the aromatic ring at 2.10 and 2.07 ppm.

When a solution of complex **8** in cyclohexane was refluxed for 3 h, a new complex was obtained as pale yellow needles, m.p. 120 °C, in 18% yield. The mass spectrum (M^+, $m/z = 309$) and the elemental analysis were consistent with species

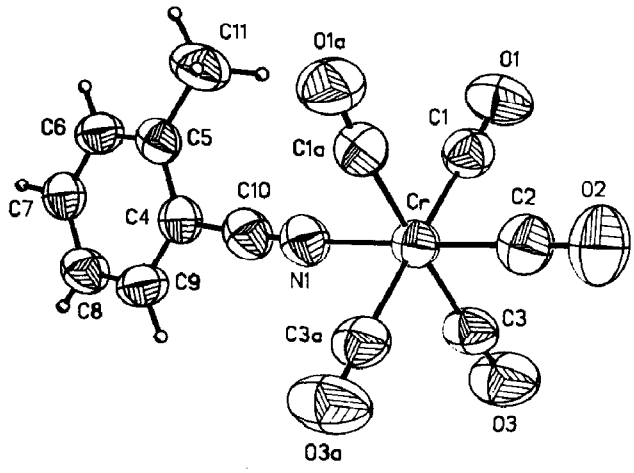


Fig. 1. ORTEP view and labelling scheme of complex **9**.

9, a chromium pentacarbonyl complex of *o*-tolunitrile. The ^{1}H NMR spectrum confirmed the absence of the methyl group α to nitrogen and the presence of the *ortho*-methyl group, signals appearing at 6.73 and 6.45 ppm (4H) and at 1.76 ppm (3H). The structure of **9** was confirmed by comparison with a sample obtained

Table 1

Interatomic distances (Å) and bond angles (°) for complex **9**

Bond lengths (Å)			
Cr–C(1)	1.902(5)	Cr–C(2)	1.842(7)
Cr–C(3)	1.913(5)	Cr–N(1)	2.053(6)
Cr–C(1a)	1.902(5)	Cr–C(3a)	1.912(5)
C(1)–O(1)	1.136(6)	C(2)–O(2)	1.150(9)
C(3)–O(3)	1.133(6)	C(4)–C(5)	1.399(9)
C(4)–C(9)	1.397(9)	C(4)–C(10)	1.443(10)
C(5)–C(6)	1.370(10)	C(5)–C(11)	1.508(10)
C(6)–C(7)	1.372(10)	C(7)–C(8)	1.375(10)
C(8)–C(9)	1.368(10)	C(10)–N(1)	1.139(9)
Bond angles (°)			
C(1)–Cr–C(2)	88.9(2)	C(1)–Cr–C(3)	90.3(2)
C(2)–Cr–C(3)	89.2(2)	C(1)–Cr–N(1)	90.4(2)
C(2)–Cr–N(1)	179.0(3)	C(3)–Cr–N(1)	91.5(2)
C(1)–Cr–C(1a)	88.7(3)	C(2)–Cr–C(1a)	88.9(2)
C(3)–Cr–C(1a)	177.9(2)	N(1)–Cr–C(1a)	90.4(2)
C(1)–Cr–C(3a)	177.9(2)	C(2)–Cr–C(3a)	89.2(2)
C(3)–Cr–C(3a)	90.6(3)	N(1)–Cr–C(3a)	91.5(2)
C(1a)–Cr–C(3a)	90.3(2)	Cr–C(1)–O(1)	176.0(4)
Cr–C(2)–O(2)	180.0(7)	Cr–C(3)–O(3)	177.2(4)
C(5)–C(4)–C(9)	121.3(6)	C(5)–C(4)–C(10)	119.0(6)
C(9)–C(4)–C(10)	119.7(6)	C(4)–C(5)–C(6)	117.4(6)
C(4)–C(5)–C(11)	121.0(6)	C(6)–C(5)–C(11)	121.6(6)
C(5)–C(6)–C(7)	121.9(7)	C(6)–C(7)–C(8)	120.0(6)
C(7)–C(8)–C(9)	120.4(7)	C(4)–C(9)–C(8)	118.9(6)
C(4)–C(10)–N(1)	176.0(7)	Cr–N(1)–C(10)	176.1(6)

Table 2

Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for complex **9**

Atom	x	y	z	U_{eq} [a]
Cr	2500	8815(1)	5853(1)	52(1)
C(1)	729(7)	8281(2)	5788(3)	61(2)
O(1)	−278(5)	7946(1)	5788(3)	86(1)
C(2)	2500	8745(3)	7109(5)	68(2)
O(2)	2500	8703(3)	7893(4)	99(3)
C(3)	688(6)	9342(2)	5960(3)	63(2)
O(3)	−385(5)	9651(1)	6061(3)	100(2)
C(4)	2500	8851(3)	2685(4)	56(2)
C(5)	2500	8354(2)	2270(4)	57(2)
C(6)	2500	8338(3)	1332(5)	63(3)
C(7)	2500	8788(3)	811(4)	63(2)
C(8)	2500	9274(3)	1228(5)	69(3)
C(9)	2500	9312(3)	2162(5)	68(3)
C(10)	2500	8884(3)	3672(5)	66(3)
H(1)	2500	8879(2)	4452(4)	63(2)
C(11)	2500	7858(3)	2837(5)	86(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 3

Crystallographic data for complexes **9**, **11** and **13**

Complex	**13**	**11**	**9**
Empirical formula	$C_9H_9NO_6W$	$C_5H_3NO_5Cr$	$C_{13}H_7NO_5Cr$
Molecular weight	411.0	209.1	309.2
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/n$	$Pc2_1n$	$Cmca$
a, Å	7.966(1)	6.348(1)	7.505(7)
b, Å	16.861(2)	10.861(2)	25.375(9)
c, Å	9.552(2)	11.572(1)	14.599(7)
β, °	96.56(1)		
V, Å^3	1275	798	2780
Z	4	4	6
μ(Mo-K_α), cm^{-1}	92.71	13.8	8.2
ρ(calcd), g·cm^{-3}	2.14	1.74	1.48
Diffractometer	CAD4	CAD4	R3m
Temperature, °C	20	20	20
Radiation	Mo-K_α	Mo-K_α	Mo-K_α
Absorption	ψ scan	no	no
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
2θ range, deg	3–46	3–50	3–50
Reflection collected	2240	1019	1230
Reflections used ($I \geq 2\sigma(I)$)	1571	668	878
R [a]	0.0210	0.0296	0.049
R_w	0.0240	0.0301	0.054
Ratio of obs. to param.	8.6	5.6	4.2

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

photochemically from *o*-tolunitrile and $Cr(CO)_6$, and also by X-ray crystallography. The ORTEP view, given in Fig. 1, shows that the nitrile group is bound to the metal in the usual end-on manner. The most important bond lengths and bond angles, along with the crystallographic data, are listed in Tables 1–3.

Since bulky substituents on the carbene carbon had no influence on the course of the substitution reaction, we examined the influence of the substituents on the aziridine moiety, and especially that of a phenyl group. Thus, when 2-phenylaziridine [5] was treated with complex **1** in diethyl ether at room temperature there was a rapid disappearance of the starting complex accompanied by formation of a new yellow complex (m.p. 64°C). The mass spectrum of this complex was consistent with a species resulting from addition of an NH group to **1** with loss of styrene. The ^1H NMR spectrum of the crude reaction mixture showed signals due to the protons of the styrene as multiplets at 7.32 ppm, at 6.71 ppm (1H, doublet, *J* 17.4 and 10.8 Hz), 5.74 ppm (1H, doublet, *J* 17.4 Hz), and 5.23 ppm (1H, doublet, *J* 10.8 Hz). The new complex was purified by silica gel chromatography and fully characterized spectroscopically. The most salient features of its ^1H NMR spectrum are the absence of signals from the phenyl group and the presence of the signals due to the

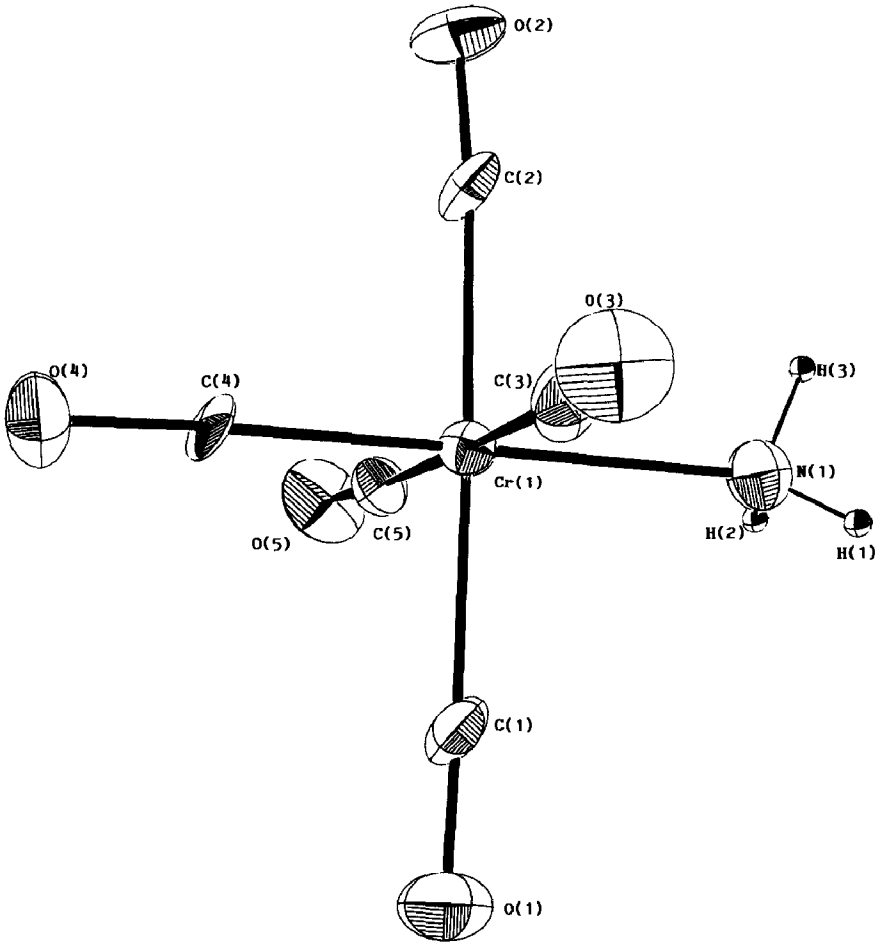


Fig. 2. ORTEP view and labelling scheme of complex **11**.

protons of the starting complex, at 4.16 ppm from the methylene protons of the ethoxy group, a singlet at 2.21 ppm from the methyl group on the former carbene carbon, and a triplet at 1.46 from the methyl protons of the ethoxy group. There was also a signal due to a N–H proton at 6.35 ppm. These data are consistent with structure **10**. However, attempts to obtain crystals from $MeOH/CH_2Cl_2$ in order to determine the structure by X-ray failed: both the elemental analysis and the X-ray structure of the isolated product were inconsistent with structure **10**. The ORTEP view (Fig. 2) of the isolated complex shows that during the recrystallization hydrolysis of the imine took place, to give finally the known ammonia complex $(CO)_5CrNH_3$ (**11**) [6]; the most important bond lengths and bond angles, and the crystallographic data are listed in Tables 3–5.

When the same reaction was carried out on the tungsten complex **12**, the ^1H NMR spectrum of the crude product mixture revealed again formation, along with styrene, of the acetiminoester complex as a 85/15 mixture of two isomers differing in orientation about the carbon–nitrogen double bond. The new complex, which was isolated as yellow crystals, m.p. 73°C, is much more stable than **10**, and could be recrystallized from $EtOH/CH_2Cl_2$. The mass spectrum and the elemental analysis were consistent with structure **13**.

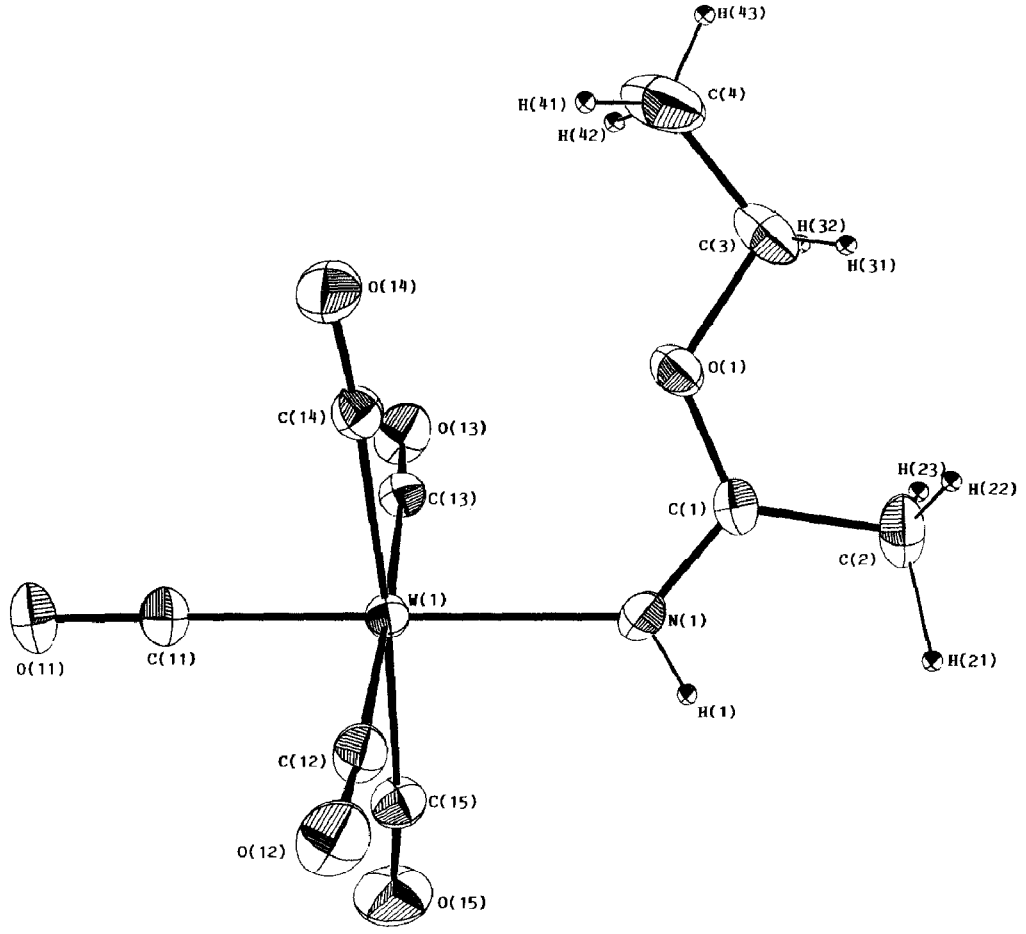


Fig. 3. ORTEP view and labelling scheme of complex **13**.

The ^1H NMR spectrum confirmed the acetiminoethyl ester structure, showing signals at 6.99 ppm from the proton on nitrogen, at 4.20 ppm from the methylene proton of the ethoxy group, at 2.23 ppm from the methyl group on the imine carbon, and at 1.47 ppm from the methyl of the ethoxy group. In the ^{13}C NMR spectrum, signals due to the tungsten pentacarbonyl group appeared at 203.2 and 198.3 ppm, and those due to the carbon doubly linked to nitrogen at 175 ppm. Structure **13** was unambiguously confirmed by an X-ray diffraction study. The ORTEP view, shown in Fig. 3 shows the presence of an acetiminoester function bound end-on to tungsten, the W–N bond being *Z* with respect to the ethoxy group. The important bond lengths and bond angles, and the crystallographic data are listed in Tables 3, 6 and 7.

Discussion

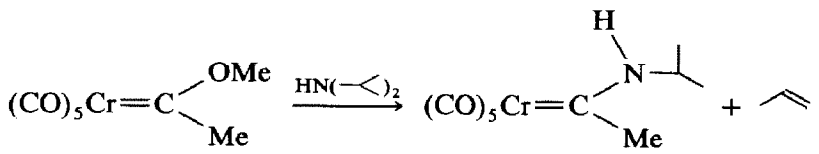
A common feature to the two reactions described above is the concomittant rupture of two carbon–nitrogen single bonds to give an olefin and a nitrene species N–R, where R is either H (in the reaction of phenylaziridine with alkoxycarbene complexes) or $(CO)_5Cr{=}CCH_3$ (in the decomposition of aziridino carbene complexes).

Relevant to such direct cleavage of C–N bonds is the reaction observed by Fischer and coworkers [7] between secondary amines, such as diisopropylamine and *N*-methylbenzylamine, and alkoxycarbene complexes of chromium and tungsten; instead of the expected aminocarbene complexes bearing a secondary amine on the carbene carbon, they obtained aminocarbene complexes bearing a primary amine, as a result of the elimination of an isopropyl or a methyl group. In the first case the fate of the leaving group was clearly demonstrated by detection of propene during the reaction, but this was not the case for the second example, in which a methyl group was lost (Scheme 2).

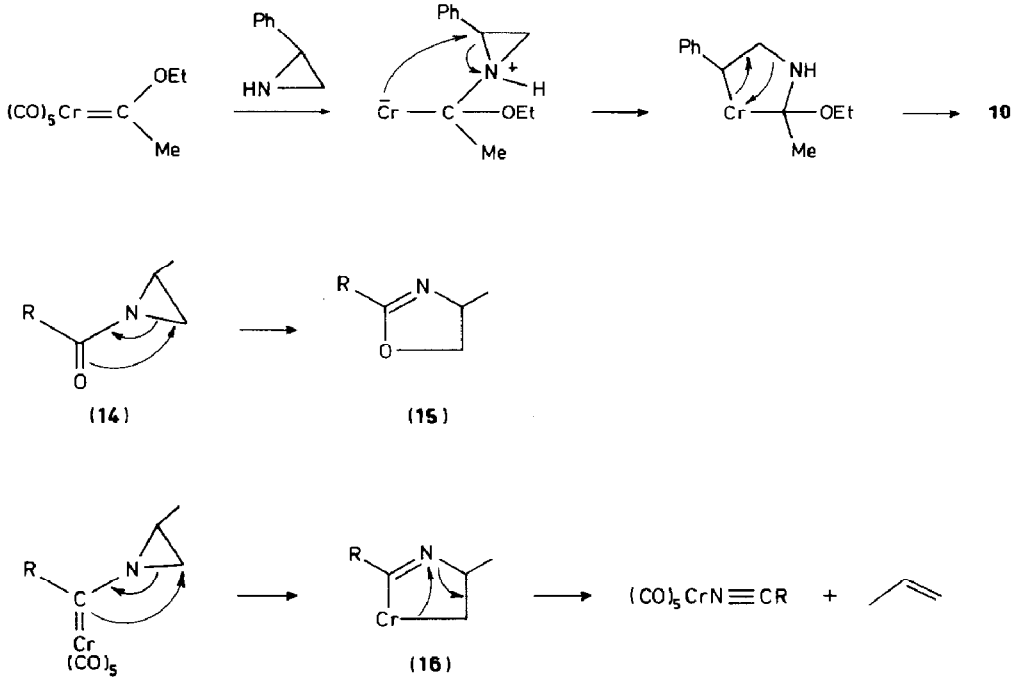
N-Methylbenzylamine and phenylaziridine are structurally related, and so it seems likely that the first step of both reactions is nucleophilic attack of the amine on the carbene-carbon. Furthermore, since ring-opening of aziridines by nucleophiles is well established [8], it is probable that the second step is an intramolecular ring-opening promoted by the nucleophilic metal centre (Scheme 3). This latter reaction would lead to a chromacyclopentane which, in turn, could rearrange to styrene and the acetiminoester complex.

Acetiminoester complexes such as **10** and **13** had been obtained previously from alkoxycarbene complexes and hydroxylamine [9], and so could be identified spectroscopically.

Since the presence of free styrene was established unambiguously by NMR spectroscopy, it is unlikely that free radicals, which would induce its polymerization, are involved in this rearrangement reaction.



Scheme 2.



Scheme 3.

The direct rearrangement of aziridinocarbene complexes can be compared with the electrocyclic rearrangement of amides of the type **14**, that is known in organic chemistry [10], and which under thermal excitation gives 2-oxazolines **15**. However, in the case of the aziridino complex the intermediate five-membered ring **16** still contains chromium, and can thus undergo a further, metal mediated, electrocyclic rearrangement to give an olefin and a nitrile complex.

Conclusion

We had previously established that during alkyne insertion reactions chromium aminocarbene complexes underwent an easy carbon–nitrogen bond cleavage reaction. We have now found that such bond rupture can also be promoted thermally when the aminocarbene complexes contain strained cycloamines. We have confirmed the occurrence of this type of C–N bond rupture, which had been observed previously by Fischer and his coworkers, during attempts to prepare phenylaziridinocarbene complexes.

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 on 70–230 mesh Merck silica gel, and preparative (PLC) and thin layer chromatography (TLC) on Merck G60 silica gel. Light petroleum (PE) was used as eluent.

NMR spectra were recorded on a JEOL FX-90 spectrometer or on a Bruker WM 200 spectrometer. IR spectra were recorded with a Beckman 4240 spectrophotome-

ter and mass spectra with a Kratos MS 3P. Melting points were determined with a Reichert Köfler block and are uncorrected.

Pentacarbonyl((ethoxy)(o-tolyl)carbene)chromium(0) (7)

A solution of *o*-tolyllithium (140 ml, 2.8×10^{-2} mol) in Et_2O was added at room temperature to a suspension of $Cr(CO)_6$ (6.27 g, 2.8×10^{-2} mol) in Et_2O (150 ml). After 10 min stirring, the solvent was evaporated under vacuum. After addition of water (100 ml) to the residue, and removal of unchanged $Cr(CO)_6$ by filtration triethyloxonium tetrafluoroborate (5.3 g, 2.8×10^{-2} mol) was added. Extraction with PE followed by evaporation of the solvent under vacuum gave complex **7** (6.9 g, 71%) as red crystals, m.p. 47–48°C.

^1H NMR (200 MHz, $CDCl_3$) 7.20, 6.87 (4H, m, ArH), 4.45 (2H, m), 2.14 (3H, s, CH_3), 1.55 (3H, t, CH_3). ^{13}C NMR (50.1 MHz, $CDCl_3$) 357.0 (Cr=C), 224.1, 215.7 (CO), 151.7, 130.1, 127.5, 125.6 (Ar), 18.2 (CH_3), 14.6 (CH_3). Anal. Found: C, 52.63; H, 3.47. $C_{15}H_{12}O_6Cr$ calcd.: C, 52.94; H, 3.52%. Mass spectrum $m/z = 340$ (M^+).

Pentacarbonyl((2-methylaziridino)(o-tolyl)carbene)chromium(0) (8)

To a solution of complex **7** at room temperature (5.3 g, 1.55×10^{-2} mol) in Et_2O (50 ml) was added 2-methylaziridine (1.7 g, 3×10^{-2} mol). After 12 h the solvent was evaporated under vacuum and the residue taken up in benzene and chromatographed on silica gel. Elution with PE gave complex **8** (3.85 g) as a yellow solid, m.p. 80°C. ^1H NMR (200 MHz, $CDCl_3$) 7.20 (4H, m, ArH), 3.55, 3.26, 2.88, 2.56 (N–CH), 2.10, 2.07 (s, CH_3), 1.75, 1.07 (d, CH_3). Anal. Found: C, 54.83; H, 3.60; N, 4.01. $C_{16}H_{13}O_5NCr$ calcd.: C, 54.7; H, 3.70; N, 3.99%. Mass spectrum $m/z = 351$ (M^+).

Thermal decomposition: Pentacarbonyl(o-tolunitrile)chromium(0) (9)

A solution of complex **8** (1.1 g) in cyclohexane (50 ml) was refluxed for 3 h. After evaporation of most of the solvent under vacuum the residue was chromatographed on silica gel. Elution with PE/CH_2Cl_2 (95/5) gave complex **9** (0.18 g, 18%) as yellow crystals, m.p. 120°C. ^1H NMR (200 MHz, C_6D_6) 6.73, 6.45 (4H, m, Ar), 1.76 (3H, s, CH_3). ^{13}C NMR (50.1 MHz, $CDCl_3$) 219.3, 214.3 (CO), 142.7, 133.6, 132.3, 130.5, 126.5 (Ar), 111.6 ($C{\equiv}N$), 20.3 (CH_3). Anal. Found: C, 50.54; H, 2.21; N, 4.49. $C_{13}H_7O_5NCr$ calcd.: C, 50.48; H, 2.26; N, 4.53%. Mass spectrum $m/z = 309$ (M^+).

Pentacarbonyl(acetiminoethyl ester)chromium(0) (10)

A solution of 2-phenylaziridine (1.35 g, 1.13×10^{-2} mol) in Et_2O (10 ml) was added at room temperature to one of complex **1** (2 g, 0.75×10^{-2} mol) in Et_2O (100 ml). Reaction was immediate. After evaporation of the solvent under vacuum the residue was taken up in a small amount of benzene and chromatographed on silica gel. Elution with PE/CH_2Cl_2 (95/5) gave complex **10** as yellow crystals (0.90 g, 42%), which were recrystallized from hexane/methylene chloride, m.p. 64°C. IR ($CHCl_3$): 1935, 1980 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) 6.34 (1H, s, N*H*), 4.17 (2H, q, *J* 6.34 Hz, OCH_2CH_3), 2.21 (3H, s, CH_3), 1.45 (3H, t, *J* 6.34 Hz, OCH_2CH_3). ^{13}C NMR (50.1 MHz, $CDCl_3$) 222.08, 215.5 (CO), 175.8 (HN=C), 66.3 (OCH_2), 21.24 (CH_3), 14.56 (OCH_2CH_3). Anal. Found: C, 38.6; H, 3.25; N, 5.06.

Table 4

Interatomic distances (Å) and bond angles (°) for complex **11**

Cr(1)–C(1)	1.916(5)	C(1)–O(1)	1.125(6)
Cr(1)–C(2)	1.888(6)	C(2)–O(2)	1.137(7)
Cr(1)–C(3)	1.94(1)	C(3)–O(3)	1.13(1)
Cr(1)–C(4)	1.81(1)	C(4)–O(4)	1.14(1)
Cr(1)–C(5)	1.90(1)	C(5)–O(5)	1.14(1)
Cr(1)–N(1)	2.20(1)		
C(2)–Cr(1)–C(1)	177.6(4)	C(3)–Cr(1)–C(1)	89.5(5)
C(3)–Cr(1)–C(2)	89.6(5)	C(4)–Cr(1)–C(1)	89.1(5)
C(4)–Cr(1)–C(2)	88.7(5)	C(4)–Cr(1)–C(3)	87.9(3)
C(5)–Cr(1)–C(1)	89.9(6)	C(5)–Cr(1)–C(2)	90.9(5)
C(5)–Cr(1)–C(3)	177.6(6)	C(5)–Cr(1)–C(4)	89.8(6)
N(1)–Cr(1)–C(1)	89.8(5)	N(1)–Cr(1)–C(2)	92.4(5)
N(1)–Cr(1)–C(3)	90.2(5)	N(1)–Cr(1)–C(4)	177.8(5)
N(1)–Cr(1)–C(5)	92.1(3)		
O(1)–C(1)–Cr(1)	177.8(5)	O(2)–C(2)–Cr(1)	175.4(11)
O(3)–C(3)–Cr(1)	173.9(11)	O(4)–C(4)–Cr(1)	176.7(12)
O(5)–C(5)–Cr(1)	173.7(12)		

$C_9H_9NO_6Cr$ calcd.: C, 38.7; H, 3.22; N, 5.01%. Mass spectrum $m/z = 279$ (M^+).

Complex **11**, m.p. 64°C, IR ($CDCl_3$): 1980, 1895 cm^{-1}. Anal. Found: C, 28.21; H, 1.53; N, 6.24. $C_5H_3O_5NCr$ calcd.: C, 28.2; H, 1.41; N, 6.58%. Mass spectrum $m/z = 209$ (M^+).

*(Pentacarbonyl)(acetiminoethylester)tungsten(0) (**13**)*

The procedure used for **10**, but starting from complex **12** (0.5 g, 0.12×10^{-2} mol) gave 0.16 g of **13** (32%) as yellow crystals, which were recrystallized from EtOH/CH_2Cl_2, m.p. 73°C. IR ($CHCl_3$): 1925, 1975 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 6.99 (1H, s, N*H*), 4.21 (2H, q, *J* 7.04 Hz, OCH_2), 2.28 (3H, s, CH_3), 1.47 (3H, t, *J* 7.04 Hz, OCH_2CH_3). ^{13}C NMR (50.1 MHz, $CDCl_3$): 203, 198.3 (CO), 175.0 (N=*C*), 66.8 (OCH_2), 20.70 (CH_3), 14.56 (OCH_2CH_3). Anal. Found: C, 26.45; H, 2.23; N, 3.29. $C_9H_9NO_6W$ calcd.: C, 26.27; H, 2.18; N, 3.40%. Mass spectrum $m/z = 411$ (M^+).

Table 5

Fractional parameters for complex **11**

Atom	*x*	*y*	*z*	U_{eq}
Cr(1)	0.0665(1)	0.010(2)	0.12991(7)	0.0260
C(1)	−0.1832(9)	0.009(2)	0.0369(4)	0.0327
C(2)	0.3187(9)	0.008(2)	0.2164(5)	0.0327
C(3)	0.189(2)	0.132(2)	0.027(1)	0.0373
C(4)	0.177(2)	−0.107(2)	0.037(1)	0.0211
C(5)	−0.051(2)	−0.114(2)	0.225(1)	0.0335
O(1)	−0.3260(7)	0.008(2)	−0.0207(4)	0.0554
O(2)	0.4749(7)	0.001(2)	0.2639(4)	0.0513
O(3)	0.269(2)	0.195(2)	−0.0376(8)	0.0528
O(4)	0.238(2)	−0.185(2)	−0.0201(8)	0.0561
O(5)	−0.111(1)	−0.196(1)	0.2769(6)	0.0581
N(1)	−0.069(2)	0.158(2)	0.237(1)	0.0418

Table 6

Interatomic distances (Å) and bond angles (°) for complex **13**

W(1)–C(11)	1.964(9)	C(11)–O(11)	1.16(1)
W(1)–C(12)	2.022(8)	C(12)–O(12)	1.148(9)
W(1)–C(13)	2.027(7)	C(13)–O(13)	1.146(9)
W(1)–C(14)	2.032(9)	C(14)–O(14)	1.14(1)
W(1)–C(15)	2.06(1)	C(15)–O(15)	1.12(1)
W(1)–N(1)	2.250(7)		
N(1)–C(1)	1.28(1)	C(1)–C(2)	1.50(1)
C(1)–O(1)	1.31(1)	O(1)–C(3)	1.45(1)
C(3)–C(4)	1.46(2)		
C(12)–W(1)–C(11)	89.2(4)	C(14)–W(1)–C(13)	87.7(4)
C(13)–W(1)–C(11)	88.5(4)	C(15)–W(1)–C(11)	88.6(4)
C(13)–W(1)–C(12)	177.6(3)	C(15)–W(1)–C(12)	89.5(4)
C(14)–W(1)–C(11)	87.0(3)	C(15)–W(1)–C(13)	90.9(4)
C(14)–W(1)–C(12)	91.8(4)	C(15)–W(1)–C(14)	175.4(3)
N(1)–W(1)–C(11)	178.1(3)	N(1)–W(1)–C(14)	94.4(3)
N(1)–W(1)–C(12)	92.2(3)	N(1)–W(1)–C(15)	90.0(3)
N(1)–W(1)–C(13)	90.2(3)		
O(11)–C(11)–W(1)	179.4(9)	O(14)–C(14)–W(1)	175.6(7)
O(12)–C(12)–W(1)	176.6(8)	O(15)–C(15)–W(1)	174.9(9)
O(13)–C(13)–W(1)	176.1(8)	C(1)–N(1)–W(1)	130.5(6)
C(2)–C(1)–N(1)	122.0(9)	O(1)–C(1)–N(1)	115.4(7)
O(1)–C(1)–C(2)	122.5(9)	C(3)–O(1)–C(1)	121.9(8)
C(4)–C(3)–O(1)	107.1(10)		

Crystal data

Selected crystals for each complex were mounted on an automatic four-circle diffractometer. Accurate unit cell dimensions and crystal orientation matrices were

Table 7

Fractional parameters for complex **13**

Atom	x	y	z	U_{eq}
W(1)	0.12637(4)	0.24588(2)	0.97446(3)	0.0377
C(11)	0.304(1)	0.3263(5)	1.013(1)	0.0511
O(11)	0.4078(9)	0.3738(4)	1.0369(8)	0.0693
C(12)	0.094(1)	0.2359(6)	1.1813(9)	0.0543
O(12)	0.0828(8)	0.2484(6)	1.2999(6)	0.0744
C(13)	0.1675(9)	0.2486(6)	0.7690(8)	0.0471
O(13)	0.1965(7)	0.2539(5)	0.6545(6)	0.0708
C(14)	0.313(1)	0.1633(5)	1.005(1)	0.0519
O(14)	0.4247(8)	0.1208(4)	1.0255(9)	0.0736
C(15)	−0.048(1)	0.3362(6)	0.941(1)	0.0579
O(15)	−0.132(1)	0.3890(4)	0.923(1)	0.0901
N(1)	−0.0808(9)	0.1562(4)	0.9240(9)	0.0478
C(1)	−0.079(1)	0.0886(5)	0.8641(9)	0.0476
C(2)	−0.236(2)	0.0408(8)	0.828(1)	0.0703
O(1)	0.0697(7)	0.0641(3)	0.8372(6)	0.0538
C(3)	0.090(2)	−0.0077(6)	0.758(1)	0.0666
C(4)	0.270(2)	−0.0147(9)	0.742(2)	0.0937

obtained from least-squares refinements of the setting angles of 25 reflections. Two standard reflections were monitored, periodically, and showed no change during data collection. Crystallographic data and other pertinent information are listed in Table 1. Correction were made for Lorentz and polarization effects.

Computations were performed by use of CRYSTALS [11] adapted for a MICRO-VAX II in the case of complexes **11** and **13**, but the SHELXTL package [12] was used for compound **9**. Atomic form factors for neutral W, Cr, C, N, O and H atoms were taken from ref. 13. The structures were solved by the heavy-atom technique and refined by full-matrix least squares for compounds **11** and **13** and by block-cascade least squares for **9**. Hydrogen atoms were located from difference electron density maps, and their coordinates refined with an overall isotropic thermal parameter. Anisotropic temperature factors were used for all non-hydrogen atoms. The criteria for a satisfactory refinement was that the ratio of the rms shift to standard deviation was less than 0.1 and there were no significant features in the final difference map.

Atomic coordinates are given in Tables 2, 5, 7 and bond lengths and bond angles in Tables 1, **4** and 6. Tables of thermal parameters and lists of observed and calculated structure factor for complexes **9**, **11** and **13** are available from the authors.

References

1 B. Denise, A. Parlier, H. Rudler, J. Vaissermann and J.C. Daran, J. Chem. Soc., Chem. Commun., (1988) 1303.
2 H. Rudler, A. Parlier, R. Yefsah, B. Denise, J.C. Daran, J. Vaissermann and C. Knobler, J. Organomet. Chem., 358 (1988) 245.
3 U. Klabunde and E.O. Fischer, J. Am. Chem. Soc., (1967) 7141.
4 B. Denise, A. Parlier and H. Rudler, J. Organomet. Chem., 354 (1988) C23.
5 S.J. Brois, J. Org. Chem., 27 (1962) 3532.
6 L. Knoll and H. Wolff, Chem. Ber., 112 (1979) 2709.
7 J.A. Connor and E.O. Fischer, J. Chem. Soc., Chem. Commun., (1967) 1024.
8 W. Klotzer, Monatsh. Chem., 101 (1970) 1841.
9 E.O. Fischer and R. Aumann, Angew. Chem., 7 (1967) 191.
10 J. March, Advanced Organic Chemistry, Wiley, New York, 1985, p. 1020.
11 D.J. Watkin, J.R. Carruthers and P.W. Betteridge, Crystals User Guide, 1985, Chemical Crystallography Laboratory, University of Oxford, Oxford, England.
12 G.M. Sheldrick, SHELXTL, revision 4.1, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction data, Univ. of Göttingen, FRG.
13 International Tables for X-ray crystallography, Kynoch Press, Birmingham, England, 1974, Vol. IV.