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Bidentate alkene aminocarbene complexes of chromium: alkyne insertion with ring expansion versus alkyne insertion with cyclopropanation: formation and crystal structure of a dihydroazepinechromium tricarbonyl complex

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Abstract

Whereas $(CO)_4Cr{=}C(H)N(CH_3)$ (η^2-$CH_2CH{=}CH_2$) (**3**) reacts with diphenylacetylene to give the expected azabicyclo[4.1.0]heptene complex (**6**), $(CO)_4Cr{=}C(CH_3)N(CH_2CH{=}CH_2)(\eta^2$-$NCH_2CH{=}CH_2)$ (**12**) and $(CO)_4Cr{=}C(CH_3)N(CH_2Ph)$ (η^2-$CH_2CH{=}CH_2$) (**9**) give, along with the azabicyclo[4.1.0]heptene complexes, the new dihydroazepine η^3-$Cr(CO)_3$ complexes, the complex with a CH_2Ph group has been fully characterized by X-ray diffraction. A mechanism for the formation of the η^3 complexes is suggested.

Introduction

1,4-Bidentate alkene-carbene complexes undergo a general alkyne insertion with intramolecular double bond cyclopropanation to give bicycloheptene derivatives [1,2]. This reaction has been extended to alkyne insertion with intermolecular cyclopropanation [3], and also to reactions of aminocarbene complexes of the type **1** in which one carbon atom of the unsaturated side-chain has been replaced by nitrogen [4,5]. The purpose of this publication is to show that in this latter case the structure of the products is dependent on the nature of the substituents on nitrogen.

Results and discussion

We previously described the reaction of **1** (R = H, R′ = CH_3) and of **2** (R = CH_3, R′ = CH_3) with alkynes, which gave either the expected complexes **4** and **5** or their

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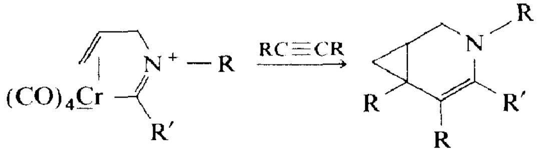
oxidation products [4,5]. In order to broaden the scope of application of this reaction, we prepared complexes **3**, **7** and **10** and submitted them to the alkyne insertion reaction.

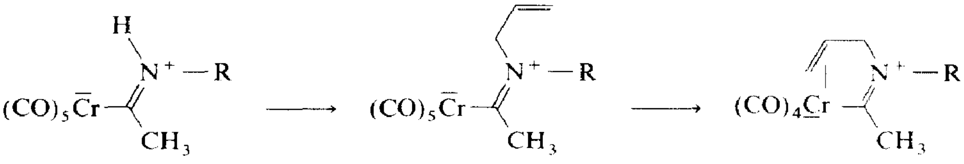


(**1**, R = H, R′ = CH_3;
2, R = R′ = CH_3;
3 R = CH_3, R′ = H)

(**4**,
5,
6)

Complex **3** (R = CH_3, R′ = H) was prepared as described by Hegedus [6,7] from *N*,*N*-(methyl)(allyl) formamide: treatment with $Cr(CO)_5Na_2$, at low temperature, followed by Me_3SiCl [6,7], gave **3** as a yellow oil in 75% yield. Heating of this oil in refluxing benzene gave, after silica gel chromatography, complex **3** as yellow crystals m.p. 77 °C. The spectroscopic data for complex **3** are very similar to those for complex **1** [14].

Complexes **9** and **12** were prepared from the corresponding *N*-(benzyl)methyl and *N*-(allyl)methyl carbene complexes by the use of the classical *N*-alkylation reaction [8] (lithium diisopropylamide, allyl bromide) followed by thermal intramolecular coordination of a double bond [9,10].



(**7**, R = CH_2Ph;
10, R = $CH_2CH{=}CH_2$)

(**8**, R = CH_2Ph;
11, R = $CH_2CH{=}CH_2$)

(**9**, R = CH_2Ph
12, R = $CH_2CH{=}CH_2$)

For complex **9**, the ^1H NMR spectrum shows, in addition to multiplets at 7.36 and 7.03 ppm (5H), a doublet of doublets at 4.62 ppm for the two benzylic protons, and multiplets at high field for the coordinated double bond, at 4.35 ppm as a multiplet (1H), at 3.07 (1H) as a doublet (*J* 8.6 Hz), and at 3.03 ppm (1H) as a doublet (*J* 13.0 Hz). The ^{13}C NMR spectrum confirms the presence of a coordinated double bond, with signals at 65.6 and 62.3 ppm for the carbons associated with the double bond.

In the case of complex **12**, the ^1H NMR spectrum shows signals due to a free double bond, as a multiplet at 5.66 ppm (1H), a doublet at 5.27 ppm (1H, *J* 10 Hz), and a doublet at 5.8 ppm (1H, 17.2 Hz), as well as those due to a coordinated double bond, at 4.47 ppm (1H), 3.12 ppm (doublet, *J* 8.6 Hz), and at 3.04 ppm (doublet, *J* 12.8 Hz). The presence of these two double bonds is also confirmed by the ^{13}C NMR spectrum, in which signals associated with the free and the coordinated double bonds appear respectively at 129.5 and 118.3 ppm and at 73.2 and 63.7 ppm.

When a solution of complex **3** in boiling benzene containing diphenylacetylene was heated, the new complex **6** (yellow crystals, m.p. 147–146 °C) was obtained in 70% yield. The ^1H, ^{13}C NMR, and infrared spectra indicate the insertion of the

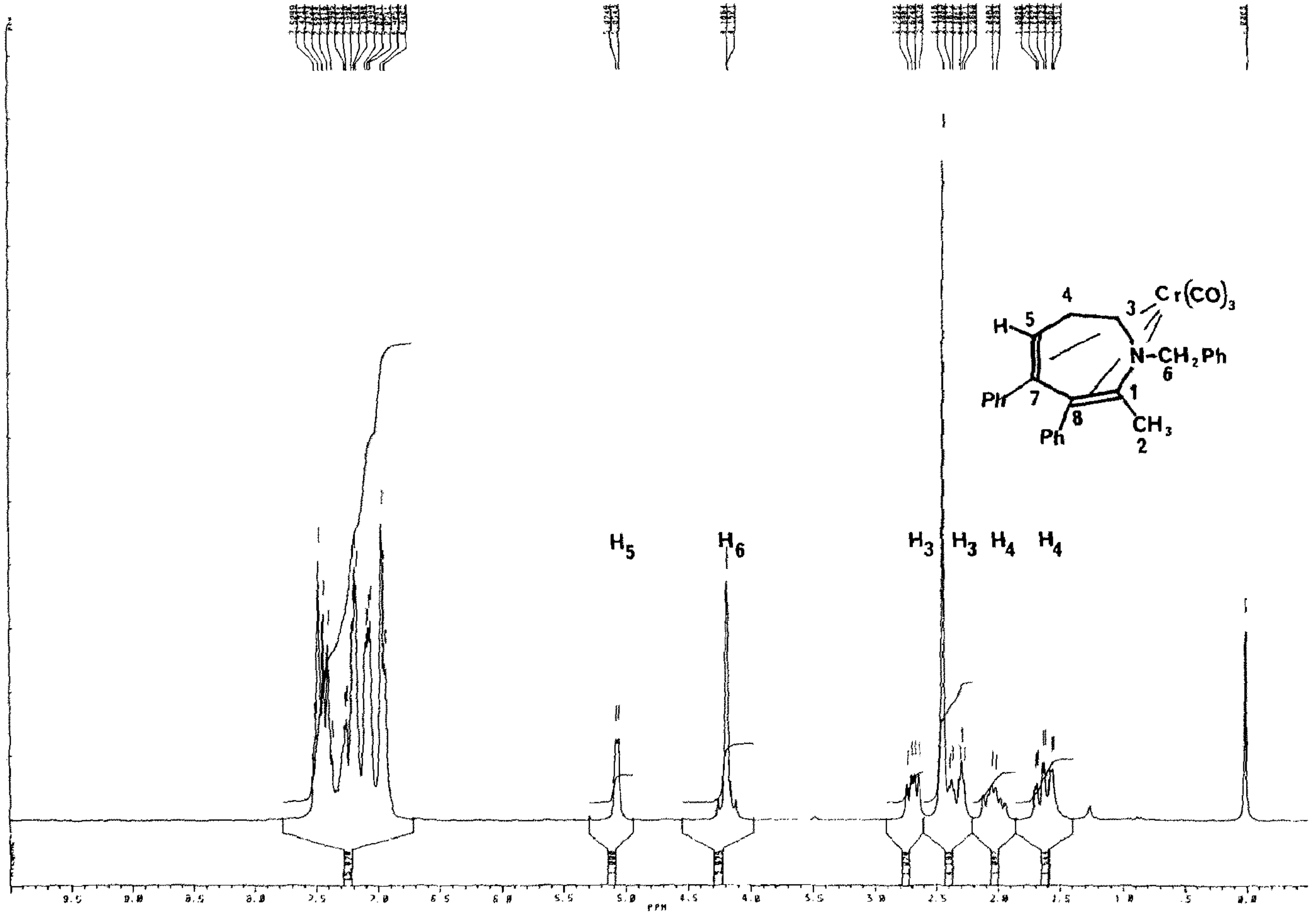


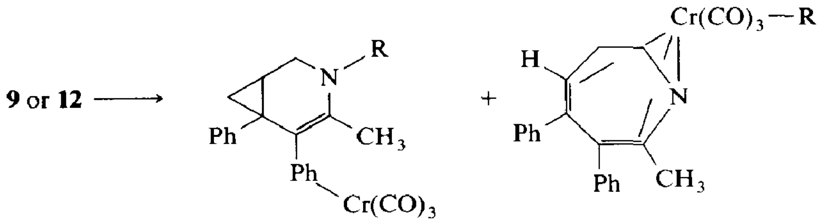
Fig. 1. ^{1}H NMR spectrum (200 MHz, C_6D_6) for the chromium tricarbonyl complex **14** with TMS as internal reference.

alkyne and the presence of an arenechromium tricarbonyl moiety. Moreover, signals at high field (1H at 1.06 ppm 1H at 1.24 ppm and 1H at 2.02 ppm) are consistent with the presence of a cyclopropane ring: these data thus confirm that intramolecular cyclopropanation has followed the alkyne insertion reaction, to give complex **6**.

Table 1

Main bond lengths in $Cr(CO)_3(C_{26}H_{25}N)$

Cr(1)-N(1)	2.18(1)	Cr(1)-C(1)	2.15(1)
Cr(1)-C(5)	2.26(1)	Cr(1)-C(7)	2.18(1)
Cr(1)-C(8)	2.21(1)		
Cr(1)-C(11)	1.78(2)	C(11)-O(11)	1.19(2)
Cr(1)-C(12)	1.82(1)	C(12)-O(12)	1.17(1)
Cr(1)-C(13)	1.82(1)	C(13)-O(13)	1.15(1)
N(1)-C(1)	1.42(2)	N(1)-C(3)	1.51(2)
N(1)-C(6)	1.49(2)	C(1)-C(2)	1.52(2)
C(1)-C(8)	1.39(2)	C(3)-C(4)	1.48(2)
C(4)-C(5)	1.49(2)	C(5)-C(7)	1.38(2)
C(6)-C(61)	1.50(2)	C(7)-C(8)	1.46(2)
C(7)-C(71)	1.52(2)	C(8)-C(81)	1.47(2)
C(61)-C(62)	1.39(1)	C(61)-C(66)	1.38(2)
C(62)-C(63)	1.40(1)	C(63)-C(64)	1.37(1)
C(64)-C(65)	1.35(1)	C(65)-C(66)	1.40(1)
C(71)-C(72)	1.39(1)	C(71)-C(76)	1.38(2)
C(72)-C(73)	1.40(1)	C(73)-C(74)	1.37(1)
C(74)-C(75)	1.38(1)	C(75)-C(76)	1.39(1)
C(81)-C(82)	1.39(1)	C(81)-C(86)	1.38(2)
C(82)-C(83)	1.40(1)	C(83)-C(84)	1.36(1)
C(84)-C(85)	1.38(1)	C(85)-C(86)	1.39(1)
Cr(201)-N(201)	2.19(1)	Cr(201)-C(201)	2.16(1)
Cr(201)-C(205)	2.25(1)	Cr(201)-C(207)	2.21(1)
Cr(201)-C(208)	2.19(1)		
Cr(201)-C(221)	1.80(2)	C(221)-O(221)	1.17(2)
Cr(201)-C(222)	1.79(1)	C(222)-O(222)	1.20(1)
Cr(201)-C(223)	1.84(2)	C(223)-O(223)	1.14(1)
N(201)-C(201)	1.41(1)	N(201)-C(203)	1.52(2)
N(201)-C(206)	1.50(2)	C(201)-C(202)	1.50(2)
C(201)-C(208)	1.42(2)	C(203)-C(204)	1.49(2)
C(204)-C(205)	1.49(2)	C(205)-C(207)	1.41(2)
C(206)-C(261)	1.50(2)	C(207)-C(208)	1.45(2)
C(207)-C(271)	1.51(2)	C(208)-C(281)	1.49(2)
C(261)-C(262)	1.38(1)	C(261)-C(266)	1.36(2)
C(262)-C(263)	1.40(1)	C(263)-C(264)	1.37(1)
C(264)-C(265)	1.36(1)	C(265)-C(266)	1.39(1)
C(271)-C(272)	1.41(1)	C(271)-C(276)	1.37(2)
C(272)-C(273)	1.40(1)	C(273)-C(274)	1.37(1)
C(274)-C(275)	1.38(1)	C(275)-C(276)	1.40(1)
C(281)-C(282)	1.39(1)	C(281)-C(286)	1.39(2)
C(282)-C(283)	1.40(1)	C(283)-C(284)	1.37(1)
C(284)-C(285)	1.37(1)	C(285)-C(286)	1.40(1)



(13: R = CH$_2$Ph;
15: R = CH$_2$CH=CH$_2$)

(14: R = CH$_2$Ph;
16: R = CH$_2$CH=CH$_2$)

In contrast, under the same conditions, complex 9 gave two new complexes, which were separated by silica gel chromatography. The faster moving complex was

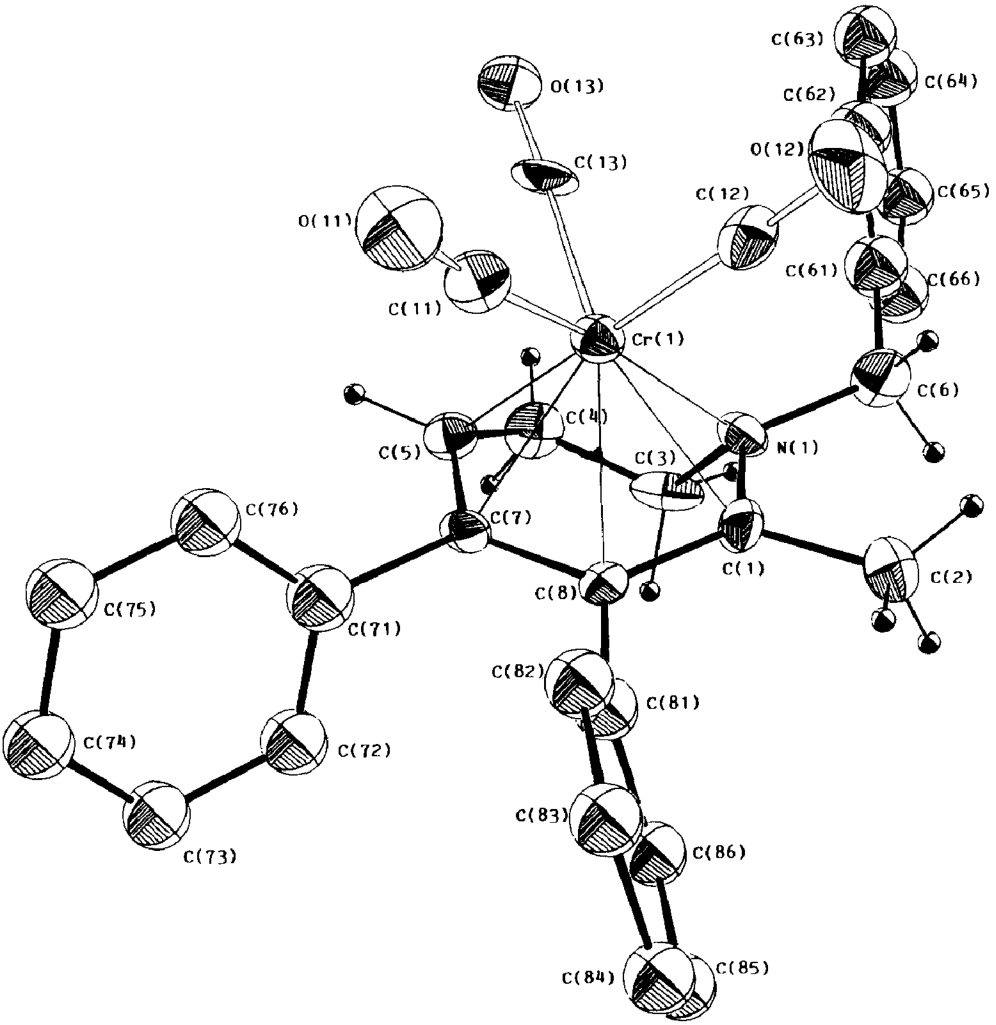


Fig. 2. ORTEP view of one of the two independent molecules of the chromium tricarbonyl complex showing the crystallographic numbering scheme. Selected bond lengths (Å) and bond angles (°): N(1)-C(1) 1.42(2), N(1)-C(3) 1.51(2), C(3)-C(4) 1.48(2), C(4)-C(5) 1.49(2), C(5)-C(7) 1.38(2), C(7)-C(8) 1.46(20, C(8)-C(1) 1.39(2), Cr(1)-N(1) 2.18(1), Cr(1)-C(1) 2.15(1), Cr(1)-C(7) 2.18(1), C(8)-C(1)-N(1) 119.9(12), C(7)-C(8)-C(1) 122.8(12), C(8)-C(7)-C(5) 128.4(12).

Table 2

Main bond angles in $Cr(CO)_3(C_{26}H_{25}N)$

C(1)–Cr(1)–N(1)	38.2(4)	C(5)–Cr(1)–N(1)	77.8(4)
C(5)–Cr(1)–C(1)	88.4(5)	C(7)–Cr(1)–N(1)	83.3(4)
C(7)–Cr(1)–C(1)	70.6(5)	C(7)–Cr(1)–C(5)	36.1(5)
C(8)–Cr(1)–N(1)	67.2(4)	C(8)–Cr(1)–C(1)	37.1(4)
C(8)–Cr(1)–C(5)	69.8(5)	C(8)–Cr(1)–C(7)	38.8(5)
C(11)–Cr(1)–N(1)	168.3(5)	C(11)–Cr(1)–C(1)	130.1(6)
C(11)–Cr(1)–C(5)	105.9(6)	C(11)–Cr(1)–C(7)	93.2(6)
C(11)–Cr(1)–C(8)	103.3(5)	C(12)–Cr(1)–N(1)	95.7(5)
C(12)–Cr(1)–C(1)	90.7(6)	C(12)–Cr(1)–C(5)	170.5(6)
C(12)–Cr(1)–C(7)	151.0(6)	C(12)–Cr(1)–C(8)	114.4(6)
C(12)–Cr(1)–C(11)	81.9(6)	C(13)–Cr(1)–N(1)	101.4(5)
C(13)–Cr(1)–C(1)	139.6(6)	C(13)–Cr(1)–C(5)	81.3(6)
C(13)–Cr(1)–C(7)	115.4(6)	C(13)–Cr(1)–C(8)	150.4(6)
C(13)–Cr(1)–C(11)	90.2(6)	C(13)–Cr(1)–C(12)	93.3(7)
C(1)–N(1)–Cr(1)	69.8(7)	C(3)–N(1)–Cr(1)	114.1(8)
C(3)–N(1)–C(1)	114.4(10)	C(6)–N(1)–Cr(1)	125.1(8)
C(6)–N(1)–C(1)	116.5(11)	C(6)–N(1)–C(3)	111.1(11)
N(1)–C(1)–Cr(1)	72.0(7)	C(2)–C(1)–Cr(1)	128.6(10)
C(2)–C(1)–N(1)	119.5(12)	C(8)–C(1)–Cr(1)	73.9(8)
C(8)–C(1)–N(1)	119.9(12)	C(8)–C(1)–C(2)	120.6(12)
C(4)–C(3)–N(1)	108.9(11)	C(5)–C(4)–C(3)	112.1(12)
C(4)–C(5)–Cr(1)	103.8(9)	C(7)–C(5)–Cr(1)	68.7(8)
C(7)–C(5)–C(4)	126.9(12)	C(61)–C(6)–N(1)	117.1(11)
C(5)–C(7)–Cr(1)	75.1(8)	C(8)–C(7)–Cr(1)	71.6(7)
C(8)–C(7)–C(5)	128.4(12)	C(71)–C(7)–Cr(1)	131.9(10)
C(71)–C(7)–C(5)	115.9(12)	C(71)–C(7)–C(8)	115.7(11)
C(1)–C(8)–Cr(1)	69.0(7)	C(7)–C(8)–Cr(1)	69.5(7)
C(7)–C(8)–C(1)	122.8(12)	C(81)–C(8)–Cr(1)	134.5(9)
C(81)–C(8)–C(1)	116.8(11)	C(81)–C(8)–C(7)	120.3(11)
C(62)–C(61)–C(6)	120.2(13)	C(66)–C(61)–C(6)	120.5(13)
C(66)–C(61)–C(62)	119.1(11)	C(63)–C(62)–C(61)	120.2(10)
C(64)–C(63)–C(62)	119.5(10)	C(65)–C(64)–C(63)	121.0(11)
C(66)–C(65)–C(64)	120.4(11)	C(65)–C(66)–C(61)	119.8(11)
C(72)–C(71)–C(7)	116.2(12)	C(76)–C(71)–C(7)	125.1(12)
C(76)–C(71)–C(72)	118.7(10)	C(73)–C(72)–C(71)	120.3(10)
C(74)–C(73)–C(72)	120.3(10)	C(75)–C(74)–C(73)	119.9(10)
C(76)–C(75)–C(74)	119.5(10)	C(75)–C(76)–C(71)	121.2(10)
C(82)–C(81)–C(8)	122.7(12)	C(86)–C(81)–C(8)	118.7(11)
C(86)–C(81)–C(82)	117.9(10)	C(83)–C(82)–C(81)	120.9(10)
C(84)–C(83)–C(82)	120.3(10)	C(85)–C(84)–C(83)	119.6(10)
C(86)–C(85)–C(84)	120.1(10)	C(85)–C(86)–C(81)	121.2(10)
O(11)–C(11)–Cr(1)	173.6(14)	O(12)–C(12)–Cr(1)	176.2(13)
O(13)–C(13)–Cr(1)	178.3(14)		
C(201)–Cr(201)–N(201)	37.9(4)	C(205)–Cr(201)–N(201)	76.3(4)
C(205)–Cr(201)–C(201)	88.5(5)	C(207)–Cr(201)–N(201)	82.3(4)
C(207)–Cr(201)–C(201)	70.8(5)	C(207)–Cr(201)–C(205)	36.9(4)
C(208)–Cr(201)–N(201)	67.1(4)	C(208)–Cr(201)–C(201)	38.0(4)
C(208)–Cr(201)–C(205)	70.1(5)	C(208)–Cr(201)–C(207)	38.4(4)
C(221)–Cr(201)–N(201)	95.0(5)	C(221)–Cr(201)–C(201)	88.4(6)
C(221)–Cr(201)–C(205)	169.1(6)	C(221)–Cr(201)–C(207)	149.6(6)
C(221)–Cr(201)–C(208)	112.9(6)	C(222)–Cr(201)–N(201)	165.6(5)
C(222)–Cr(201)–C(201)	127.8(6)	C(222)–Cr(201)–C(205)	106.5(5)
C(222)–Cr(201)–C(207)	91.7(6)	C(222)–Cr(201)–C(208)	100.2(5)
C(222)–Cr(201)–C(221)	83.6(6)	C(223)–Cr(201)–N(201)	104.3(5)
C(223)–Cr(201)–C(201)	141.7(6)	C(223)–Cr(201)–C(205)	85.8(6)

Table 2 (continued)

C(223)-Cr(201)-C(207)	120.0(5)	C(223)-Cr(201)-C(208)	155.5(5)
C(223)-Cr(201)-C(221)	90.1(7)	C(223)-Cr(201)-C(222)	90.0(6)
C(201)-N(201)-Cr(201)	69.9(7)	C(203)-N(201)-Cr(201)	114.3(8)
C(203)-N(201)-C(201)	113.8(10)	C(206)-N(201)-Cr(201)	122.2(8)
C(206)-N(201)-C(201)	116.5(10)	C(206)-N(201)-C(203)	113.2(10)
N(201)-C(201)-Cr(201)	72.2(7)	C(202)-C(201)-Cr(201)	132.8(10)
C(202)-C(201)-N(201)	120.6(12)	C(208)-C(201)-Cr(201)	72.1(8)
C(208)-C(201)-N(201)	117.6(11)	C(208)-C(201)-C(202)	121.3(12)
C(204)-C(203)-N(201)	107.0(10)	C(205)-C(204)-C(203)	109.0(11)
C(204)-C(205)-Cr(201)	105.6(8)	C(207)-C(205)-Cr(201)	70.2(7)
C(207)-C(205)-C(204)	127.9(12)	C(261)-C(206)-N(201)	113.8(10)
C(205)-C(207)-Cr(201)	72.9(7)	C(208)-C(207)-Cr(201)	70.2(7)
C(208)-C(207)-C(205)	126.1(11)	C(271)-C(207)-Cr(201)	132.0(9)
C(271)-C(207)-C(205)	114.7(11)	C(271)-C(207)-C(208)	119.1(10)
C(201)-C(208)-Cr(201)	69.9(7)	C(207)-C(208)-Cr(201)	71.4(7)
C(207)-C(208)-C(201)	124.2(11)	C(281)-C(208)-Cr(201)	131.9(9)
C(281)-C(208)-C(201)	118.0(11)	C(281)-C(208)-C(207)	117.7(10)
C(262)-C(261)-C(206)	119.7(12)	C(266)-C(261)-C(206)	122.2(12)
C(266)-C(261)-C(262)	118.2(10)	C(263)-C(262)-C(261)	120.1(10)
C(264)-C(263)-C(262)	121.1(10)	C(265)-C(264)-C(263)	118.6(10)
C(266)-C(265)-C(264)	120.5(10)	C(265)-C(266)-C(261)	121.6(10)
C(272)-C(271)-C(207)	113.5(11)	C(276)-C(271)-C(207)	126.9(11)
C(276)-C(271)-C(272)	119.5(10)	C(273)-C(272)-C(271)	120.0(10)
C(274)-C(273)-C(272)	120.1(10)	C(275)-C(274)-C(273)	119.5(10)
C(276)-C(275)-C(274)	121.2(10)	C(275)-C(276)-C(271)	119.7(10)
C(282)-C(281)-C(208)	120.7(12)	C(286)-C(281)-C(208)	119.8(12)
C(286)-C(281)-C(282)	119.5(10)	C(283)-C(282)-C(281)	119.3(10)
C(284)-C(283)-C(282)	119.7(10)	C(285)-C(284)-C(283)	122.1(10)
C(286)-C(285)-C(284)	118.6(10)	C(285)-C(286)-C(281)	120.7(10)
O(221)-C(221)-Cr(201)	177.6(14)	O(222)-C(222)-Cr(201)	176.5(12)
O(223)-C(223)-Cr(201)	178.2(14)		

identified as **13**; its spectroscopic characteristics are again comparable to those of **5** and confirm that it is an arenechromium tricarbonyl complex (ν(CO) 1950 and 1870 cm^{-1}). The ^1H NMR spectrum indicates the presence of a coordinated phenyl group with multiplets at 5.18, 4.71, 4.46 and 4.29 ppm, two benzylic hydrogens at 3.89 ppm as a doublet of doublets (J 17 Hz), a $N-CH_2$ group, which gives two doublets at 3.09 ppm (J 12.6 and 6.4 Hz) and at 2.76 ppm (J 12.6 and 3.4 Hz), and there is a signal due to the methyl group associated with the double bond, at 1.97 ppm. The protons of the cyclopropane give signals at 1.74 ppm (1H) and at 0.99 ppm (2H).

The second product, obtained as orange crystals, m.p. 173° C, was identified as **14** on the following grounds. The mass spectrum ($m/z = 487$) as well as the elemental analysis show that this complex to be an isomer of **13**. Although the ^{13}C NMR spectrum indicates the presence of terminal CO's (δ(CO) at 232 ppm) these do not belong to an arenechromium tricarbonyl group, since no signals around 95 ppm are observed. The presence of a $Cr(CO)_3$ group is however confirmed by the IR spectrum, which contains bands at 1830, 1870 and 1950 cm^{-1}. The observation in the ^1H NMR spectrum of a multiplet at 5.06 ppm (Fig. 1) indicates the presence of a trisubstituted double bond. This is confirmed by the ^{13}C NMR spectrum, which

Table 3

Crystallographic data for $Cr(CO)_3(C_{26}H_{25}N)$

Size (mm)	$0.06 \times 0.14 \times 0.5$
System	Triclinic
Space group	$P\bar{1}$
a (Å)	8.681(14)
b (Å)	12.936(5)
c (Å)	22.011(8)
α (deg)	86.90(40)
β (deg)	83.42(9)
γ (deg)	89.07(6)
V (Å^3)	2452
Z	4
M (g)	487.5
D_c (g/cm^3)	1.32
μ(Mo-K_α) (cm^{-1})	4.83
Reflexions measured	3883
Reflexions kept ($I > 3\ \sigma(I)$)	2065
Weighting scheme	unit weights
R	0.064
R_w	0.071
Par/var	5.3
Absorption	no

also indicates the presence of a tetrasubstituted double bond, the two double bonds giving rise to signals at 91.0, 112.7, 113.9 and 115.9 ppm. Complex **14**, in which a dihydroazepine is coordinated to $Cr(CO)_3$, agreed best with these data, and this structure was confirmed by X-ray study.

An ORTEP view of **14** showing the crystallographic numbering appears in Fig. 2. The most important bond distances and bond angles are given in Tables 1 and 2, and the crystallographic data and the atomic coordinates appear in Tables 3 and 4, respectively. As expected, C(1), C(8), C(7), C(5) and N(1) are almost coplanar (Table 5).

Complex **12** bearing two allyl groups on nitrogen, behaved similarly, reaction with diphenylacetylene again giving two complexes **15** and **16**. The spectroscopic data for **15** (see Experimental section) (m.p. 70 ° C), which are very similar to those for **5**, **6** and **13**, confirm that it is the product of an intramolecular cyclopropanation, whereas **16** (m.p. 175 ° C) is the product of ring expansion: the ^1H NMR spectrum shows, in addition to multiplets in the region of 7 ppm, the signals due to the free allylic group linked to nitrogen, at 5.74 ppm (1H), 4.87 (1H), 3.11 (1H) and 2.78 (1H), and a signal at 5.0 ppm due to the proton associated with the coordinated double bond.

Discussion

In all the cases studied herein the main product is the result of intramolecular alkyne insertion followed by double bond cyclopropanation. The dihydroazepine complexes, which are isomers of the cyclopropane complexes, could conceivably

Table 4

Fractional atomic coordinates for $Cr(CO)_3(C_{26}H_{25}N)$

Atom	x	y	z	U_{eq}	U_{iso}
Cr(1)	0.1811(3)	0.6587(2)	−0.2090(1)	0.0374	
N(1)	0.136(1)	0.4999(8)	−0.1744(5)	0.0368	
C(1)	0.033(2)	0.530(1)	−0.2177(6)	0.0409	
C(2)	−0.142(2)	0.522(1)	−0.1996(7)	0.0572	
C(3)	0.259(2)	0.423(1)	−0.1970(7)	0.0466	
C(4)	0.404(2)	0.480(1)	−0.2180(7)	0.0505	
C(5)	0.377(2)	0.570(1)	−0.2604(6)	0.0402	
C(6)	0.064(2)	0.468(1)	−0.1114(6)	0.0507	
C(7)	0.255(2)	0.586(1)	−0.2947(6)	0.0337	
C(8)	0.091(1)	0.5628(8)	−0.2769(6)	0.0257	
C(61)	0.167(1)	0.464(1)	−0.0615(5)		0.070(2)
C(62)	0.201(1)	0.554(1)	−0.0339(6)		0.070(2)
C(63)	0.287(1)	0.549(1)	0.0160(6)		0.070(2)
C(64)	0.338(1)	0.455(1)	0.0376(5)		0.070(2)
C(65)	0.306(1)	0.367(1)	0.0114(6)		0.070(2)
C(66)	0.220(1)	0.370(1)	−0.0389(6)		0.070(2)
C(71)	0.295(1)	0.630(1)	−0.3598(6)		0.063(2)
C(72)	0.289(1)	0.562(1)	−0.4061(6)		0.063(2)
C(73)	0.331(1)	0.595(1)	−0.4671(6)		0.063(2)
C(74)	0.378(1)	0.695(1)	−0.4819(6)		0.063(2)
C(75)	0.385(1)	0.763(1)	−0.4363(6)		0.063(2)
C(76)	0.344(1)	0.730(1)	−0.3754(6)		0.063(2)
C(81)	−0.023(1)	0.580(1)	−0.3215(4)		0.052(2)
C(82)	−0.086(1)	0.677(1)	−0.3346(4)		0.052(2)
C(83)	−0.209(1)	0.6874(9)	−0.3704(4)		0.052(2)
C(84)	−0.268(1)	0.603(1)	−0.3934(4)		0.052(2)
C(85)	−0.207(1)	0.506(1)	−0.3807(4)		0.052(2)
C(86)	−0.084(1)	0.495(1)	−0.3451(5)		0.052(2)
C(11)	0.184(2)	0.786(1)	−0.2449(7)	0.0453	
O(11)	0.178(1)	0.8733(8)	−0.2637(5)	0.0701	
C(12)	0.032(2)	0.717(1)	−0.1565(7)	0.0423	
O(12)	−0.064(1)	0.7597(9)	−0.1251(6)	0.0736	
C(13)	0.337(2)	0.693(1)	−0.1653(6)	0.0409	
O(13)	0.438(1)	0.7156(8)	−0.1391(4)	0.0597	
Cr(201)	0.3206(3)	0.8475(2)	0.2279(1)	0.0351	
N(201)	0.236(1)	0.9805(8)	0.1747(4)	0.0302	
C(201)	0.260(2)	1.010(1)	0.2338(6)	0.0385	
C(202)	0.352(2)	1.104(1)	0.2416(7)	0.0492	
C(203)	0.066(2)	0.974(1)	0.1647(6)	0.0437	
C(204)	0.026(1)	0.863(1)	0.1677(6)	0.0404	
C(205)	0.068(1)	0.814(1)	0.2265(6)	0.0358	
C(206)	0.333(2)	1.033(1)	0.1218(6)	0.0481	
C(207)	0.090(1)	0.862(1)	0.2807(5)	0.0241	
C(208)	0.178(1)	0.9550(9)	0.2848(6)	0.0290	
C(261)	0.309(1)	0.994(1)	0.0606(5)		0.059(2)
C(262)	0.228(1)	1.0535(9)	0.0211(6)		0.059(2)
C(263)	0.205(1)	1.018(1)	−0.0360(6)		0.059(2)
C(264)	0.263(1)	0.924(1)	−0.0540(5)		0.059(2)
C(265)	0.343(1)	0.8647(9)	−0.0148(6)		0.059(2)
C(266)	0.366(1)	0.900(1)	0.0421(6)		0.059(2)
C(271)	0.017(1)	0.8070(7)	0.3388(6)		0.051(2)
C(272)	−0.144(1)	0.7913(7)	0.3397(5)		0.051(2)

Table 4 (continued)

Atom	x	y	z	U_{eq}	U_{iso}
C(273)	−0.228(1)	0.7442(7)	0.3916(6)		0.051(2)
C(274)	−0.155(1)	0.7131(7)	0.4414(5)		0.051(2)
C(275)	0.002(1)	0.7288(7)	0.4402(5)		0.051(2)
C(276)	0.089(1)	0.7756(7)	0.3888(6)		0.051(2)
C(281)	0.191(2)	0.9916(8)	0.3471(6)		0.061(2)
C(282)	0.327(1)	0.9755(7)	0.3743(6)		0.061(2)
C(283)	0.335(1)	1.0084(8)	0.4336(6)		0.061(2)
C(284)	0.209(2)	1.0566(7)	0.4637(5)		0.061(2)
C(285)	0.075(1)	1.0738(7)	0.4379(6)		0.061(2)
C(286)	0.066(2)	1.0407(8)	0.3789(6)		0.061(2)
C(221)	0.521(2)	0.884(1)	0.2143(7)	0.0536	
C(221)	0.653(1)	0.906(1)	0.2071(6)	0.0949	
C(222)	0.387(2)	0.762(1)	0.2860(6)	0.0396	
C(222)	0.440(1)	0.7064(8)	0.3243(5)	0.0643	
C(223)	0.357(2)	0.746(1)	0.1722(7)	0.0485	
O(223)	0.375(1)	0.6831(8)	0.1379(5)	0.0684	

have been formed by a chromium-promoted isomerization of the three-membered ring, but since **2** and **3** give no dihydroazepine complexes this probably is not the explanation. Moreover, when complex **13** was heated in benzene, in the absence or in the presence of $Cr(CO)_6$, there was no transformation into **14**.

Thus complexes **14** and **16** must be formed directly, probably via intermediates which can also lead to **13** and **15**: these intermediates could be metallacycles of type **18**, a precursor of the cyclopropane complexes. The cyclopropane is the result of the coupling of carbons C(4) and C(7). A second way in which the intermediate **18** might collapse, is by a β-elimination of a hydrogen at C(5), followed by its migration to C(4). The result would be a ring expansion to give **14**.

Since this second transformation is only observed in the cases in which nitrogen bears bulky groups, it could be attributable to steric effects, which could operate to flatten the intermediate **18**, thus moving C(4) away from C(7). The formation of the seven-membered ring could also be attributable to an increase in the basicity of the

Table 5

Plane atom C(1) C(8) C(7) N(1)

Equation of the plane:

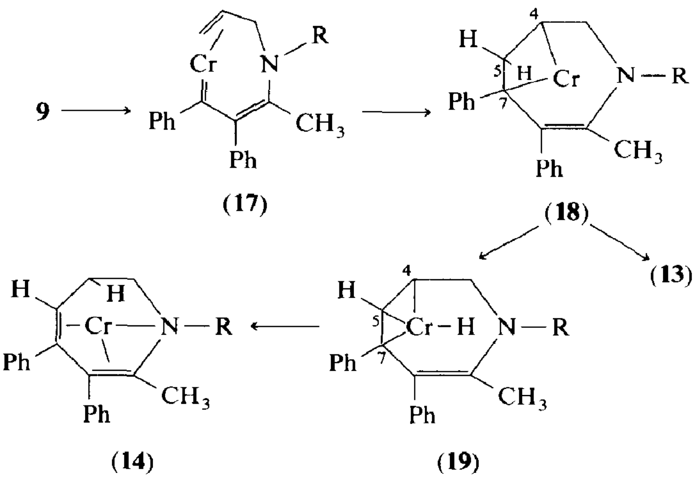
$-0.60367\,X + 12.22668\,Y + 7.79869\,Z = 4.706$

Deviations from the plane, in angstrom, are given by Zp

Coordinates of the defining atoms projected onto the best plane

Type	Serial	Weight	Xp	Yp	Zp
C	1	1.000	1.311	−0.352	0.059
C	8	1.000	0.139	−1.086	−0.041
C	7	1.000	−1.190	−0.486	0.001
C	5	1.000	−1.518	0.860	0.017
N	1	1.000	1.258	1.065	−0.036

X, Y and Z are in crystal fractions amine and thus of the metal to which it is coordinated, which might favour the insertion of the chromium in the C(5)–H bond.



Conclusion

These results show again that slight changes in the structure of the starting carbene complexes can modify the course of the insertion reaction in an unexpected way. It thus seems that a wide range of aminocarbene complexes is likely to be versatile synthons for the preparation of a large variety of organic compounds.

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. Light petroleum ether (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 spectrophotometer and mass spectra with a Kratos MS 3P. Melting points were determined on a Reichert Köfler block and are uncorrected.

$(CO)_5Cr{=}C(CH_3)N(CH_2Ph)(\eta^2\text{-}CH_2CH{=}CH_2)$ (9)

A solution of lithium diisopropylamide (LDA) prepared from BuLi (6.87 ml, 1.6*N*, 10^{-2} mol) and diisopropylamine (1.44 ml, 10^{-2} mol) in THF (50 ml), at −60 °C, was added to a solution of $(CO)_5Cr{=}C(CH_3)N(H)(CH_2Ph)$ (3.25 g, 10^{-2} mol) in THF (50 ml), at −60 °C. The solution was then warmed to room temperature, and a solution of allyl bromide (1.21 g, 10^{-2} mol) cooled to −60 °C was added. The mixture was stirred at room temperature for 1 h then water (1 ml) was added, the solvent evaporated under vacuum, and the residue extracted with Et_2O. After evaporation of the extract, the residue was dissolved in CH_2Cl_2 and the solution was absorbed on silica gel, the solvent was evaporated off, and the powder placed on a column of silica gel. Elution with petroleum ether/methylene chloride

(90/10) gave complex **8** containing a small amount of complex **9** as a yellow oil (2.1 g, 57%). Elution with petroleum ether/methylene chloride (80/20) gave the starting complex **7** (1.1 g).

Coordination reaction

A solution of complex **8** (2.6 g, 7 × 10^{-3} mol) in benzene (60 ml) was refluxed for 24 h. After evaporation of most of the solvent, the residue was chromatographed on silica gel. Elution with PE gave small amounts of starting material. Elution with Et$_2$O gave complex **9** (2.2 g, 92%) as a yellow crystals (m.p. 60 °C).

^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.36–7.03 (5H, m), 4.62 (2H, d, J 14 Hz, PhCH_2), 4.35 (1H, m, CH=CH$_2$), 4.40 (1H, d, J 12.8 Hz, N–CHH), 4.02 (1H, d, J 12.8 Hz, NCHH), 3.07 (1H, d, J 8.6 Hz, CHH=CH), 3.03 (1H, d, J 13.0 Hz, CHH=CH), 2.51 (3H, s). ^{13}C NMR (50.1 MHz, CDCl$_3$) δ 283.4 (Cr=C), 232.6, 225.7, 225.4, 224.9 (CO), 133.5, 129.2, 128.2, 126.5 (Ph), 73.4, 63.9 (C=C), 62.2 (N–CH), 54.4 (N–C), 33.4 (CH$_3$); m/z = 337 (M^+). Anal. Found: C, 56.43; H, 4.30; N, 3.82. C$_{17}$H$_{15}$O$_5$NCr calcd.: C, 56.97; H, 4.45; N, 4.15%.

*(CO)$_4$Cr=Cr(Me)N(CH$_2$-CH=CH$_2$)(η^2-CH$_2$CH=CH$_2$) (**12**)*

This complex was prepared by the procedure described above. The residue from the reaction was taken up in a small amount of benzene and chromatographed on silica gel. Elution with PE/CH$_2$Cl$_2$ (95/5) gave complex **11** as an oil (47% yield). Elution with PE/CH$_2$Cl$_2$ (90/10) gave unchanged starting material.

A solution of complex **11** (5.9 g, 1.9 × 10^{-2} mol) in benzene was refluxed for 2 h. After evaporation of most of the solvent, the residue was chromatographed on silica gel. Elution with PE/CH$_2$Cl$_2$ (90/10) gave complex **12** (5.3g, 96%) as a yellow oil.

^{1}H NMR (200 MHz, CDCl$_3$) δ 5.66 (1H, m, CH=CH$_2$), 5.27 (1H, d, J 10 Hz, CHH=CH), 5.8 (1H, d, J 10 Hz, CHH=CH), 4.47 (1H, m, CH=CH$_2$), 4.37, 4.03 (4H, m, CH$_2$–N–CH$_2$), 3.12 (1H, d, J 8.6 Hz, CHH=CH), 3.04 (1H, d, J 12.8 Hz, CHH=CH), 2.37 (3H, s, CH_3). ^{13}C NMR (50.1 MHz, CDCl$_3$) δ 283 (Cr=C), 232.6, 225.5, 255.0 (CO), 129.5, 118.3 (CH$_2$=CH), 73.2, 65.5 (CH$_2$=SCNH), 63.6, 62.3 (CH$_2$–N–CH$_2$), 32.7 (CH$_3$); m/z = 287 (M^+). Anal. Found: C, 50.70; H, 4.42; N, 4.99. C$_{12}$H$_{13}$O$_4$NCr calcd.: C, 50.17; H, 4.52; N, 4.83%.

Reaction of complex 3 with PhC≡CPh complex 6

A solution of complex **3** (0.6 g, 0.24 × 10^{-2} mol) in benzene (30 ml) containing diphenylacetylene (0.55 g, 0.3 × 10^{-3} mol) was refluxed for 5 h. Then most of the solvent was evaporated and the residue chromatographed on silica gel. Elution with PE/CH$_2$Cl$_2$ (95/5) gave complex **6** (0.41 g, 70%) as yellow crystals. m.p. 147 °C. IR (CHCl$_3$) 1955, 1880 cm^{-1}.

^{1}H NMR (200 MHz, CDCl$_3$) δ 7.25 × 7.12 (5H, m, Ph), 6.67 (1H, s, CH=C), 5.42–4.85 (5H, m, Ph–Cr), 3.41 (1H, m, N–CHH), 3.11 (1H, m, N–CHH), 2.87 (3H, s, N–CH_3), 2.00 (1H, m, C–H), 1.25 (1H, m, CHH), 1.06 (1H, m, CHH). ^{13}C NMR (50.1 MHz, C$_6$D$_6$) δ 235.0 (CO), 144.2, 102.9 (Ph, C=C), 94.5–87.0 (Ph–Cr), 47.2 (N–CH_2), 42.03 (N–CH$_3$), 30.1 (C–Ph), 25.2 (CH), 20.5 (CH$_2$); m/z = 397 (M^+).

Reaction of complex 9 with PhC≡CPh; complexes 13 and 14

A solution of complex **9** (1.8 g, 0.5 × 10^{-2} mol) in benzene (60 ml) containing diphenylacetylene (1.5 g) was refluxed for 12 h. Most of the solvent was then evaporated under vacuum and the residue chromatographed on silica gel. Elution with PE/acetone (99/1) first gave complex **13** (0.62 g, 24%) as yellow crystals, m.p. 130 °C. IR ($CHCl_3$) 1870 and 1950 cm^{-1}.

^1H NMR (200MHz, C_6D_6) δ 7.05 (5H, m, Ph), 5.19, 4.70, 4.51, 4.31 (5H, Ph–Cr), 3.89 (2H, dd, J 16.6 Hz, CH_2–Ph), 3.09 (1H, dd, N–C*H*H), 2.76 (1H, dd, NCH*H*), 1.98 (3H, s, CH_3), 1.74 (1H, m, C*H*), 0.99 (2H, m, CH_2). ^{13}C NMR (50.1MHz, $CDCl_3$) δ 234.5 (CO), 145.5C5–105.2 (Ph, *C* = *C*), 96.9, 95.2, 92.1, 92.0, 91.0 (Ph–Cr), 54.6, 50.4 (CH_2NCH_2), 26.5, 25.16, 20.2 (–*C*–, *C*H, CH_2), 17.8 (CH_3); $m/z = 487$ (M^+). Anal. Found: C, 71.45; H, 5.13; N, 2.87. $C_{29}H_{25}O_3NCr$ calcd.: C, 70.88; H, 5.18; N, 2.84%.

Then complex **14** (0.31 g, 12%) as orange crystals. m.p. 174 °C. IR ($CHCl_3$) 1830, 1870, 1950 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$) δ 7.51–6.93 (15H, m, Ph), 5.08 (1H, m, C*H*=C), 4.19 (2H, dd, J 13.4 Hz, CH_2–Ph), 2.67 (1H, m, NC*H*H), 2.29 (3H, s, CH_3), 2.27 (1H, m, N–CH*H*), 2.08 (1H, m, C*H*H), 1.63 (1H, m, CH*H*). ^{13}C NMR (50.1MHz, $CDCl_3$) δ 232.3 (CO), 143.6–126.3 (Ph), 115.9, 113.9, 112.7, 91.0 (2*C*=*C*), 62.1 (N–CH_2), 48.9 (N–CH_2), 39.2 (N–CH_2–CH_2), 19.4 (CH_3). $m/z = 487$ (M^+) Anal. Found: C, 69.78; H, 5.44; N, 2.47. $C_{29}H_{25}O_3NCr$ calcd.: C, 71.45; H, 5.13; N, 2.87%.

Reaction of complex 12 with PhC≡CPh; complexes 15 and 16

A solution of complex **12** (3.15 g, 10^{-2} mol) in benzene (50 ml) containing diphenylacetylene (0.55 g, 0.3×10^{-2} mol) was refluxed for 12 h. Most of the solvent was then evaporated under vacuum and the residue chromatographed on silica gel. Elution with PE/Et_2O (95/5) gave complex **15** (0.8 g, 18%) as yellow crystals, m.p. 75 °C. IR ($CHCl_3$) 1860, 1880 and 1940 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$) δ 7.16 (10H, Ph), 5.61 (1H, m, C*H*=CH_2), 5.33–5.01 (5H, Ph–Cr), 3.82 (2H, ddd, J 17 and 4.8 Hz, N–CH_2–C), 3.53 (1H, dd, N–C*H*H), 3.03 (1H, dd, NCH*H*), 2.28 (3H, s, CH_3), 1.89 (1H, m, C*H*H), 1.29 (1H, m, C*H*), 0.96 (1H, m, CH*H*). ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 234.2 (CO), 145.2, 144.7, 134.5, 128.1, 127.0, 125.3, 116.6, 116.0 (*C*=*C*, Ph), 96.6, 94.9, 91.6, 90.8 (Ph–Cr), 53.2, 49.6 (CH_2–N–CH_2), 26.1, 25.0, 19.6 (–*C*–, *C*H CH_2), 17.2 (CH_3). $m/z = 437$ (M^+). Anal. found: C, 68.56; H, 5.46; N, 3.07. $C_{25}H_{23}O_3NCr$ calcd.: C, 68.64; H, 5.26; N, 3.20%.

Elution with PE/Et_2O (85/15) gave complex **16** (0.4 g, 9%) as orange crystals, m.p. 175 °C. IR ($CHCl_3$) 1830, 1870, 1940 and 1950 cm^{-1}. ^1H NMR (200 MHz, C_6D_6) δ 7.41–6.84 (10H, Ph), 5.74 (1H, m, C*H*=CH_2), 5.00 (1H, m, C*H*=C), 4.87 (1H, d, J 10.2 Hz, C*H*H=CH), 4.70 (1H, d, J 16.6 Hz, CH*H*=CH), 3.11 (1H, m, NC*H*H), 2.76 (1H, m, N–CHH), 2.22 (1H, m, C*H*H), 1.92 (3h, s, CH_3), 1.73 (1H, m, CH*H*). ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 138.7, 133.7, 132.9, 131.4, 130.9, 128.0, 127.5, 126.6, 126.4, 121.4, 115.6, 113.16, 111.0, 90.52 (Ph, 3C=C), 62.6, 49.1 (CH_2–N–CH_2), 39.2 (CH_2–CH_2–N), 18.4 (CH_3). $m/z = 437$ (M^+). Anal. Found: C, 68.42; H, 5.21; N, 3.24. $C_{25}H_{23}O_3NCr$ calcd.: C, 68.64; H, 5.26; N, 3.20%.

X-ray studies

The crystal was mounted on a PW 1100 Philips diffractometer and the accurate cell dimensions and orientation matrix were obtained from least squares refinements of the setting angles of 25 well defined reflections.

Crystal data and crystal data collection parameters are listed in Table 3. Intensities of standard reflections showed no change during data collection. Corrections were made for Lorentz and polarization effects. Computations were performed by use of the CRYSTALS system [11] adapted for a MICROVAX II computer. Atomic scattering factors for neutral Cr, O, C, N and H were taken from ref. 12. Anomalous dispersion was taken into account. Structure resolution was by SHELXS [13]. The number of available data was small relative to the large number of independant atoms present. (The asymetric unit is made of 2 molecular units with the same geometry). Thus all phenyl groups were refined isotropically (with an overall refinable thermal parameter for each of them) with restraint on bonds and angles. All H atoms were included in the refinement in calculated positions, though non-phenyl H atoms were clearly evident in a difference Fourier map.

Final refinement was by least squares with a large block approximation to the normal matrix. In Tables 1, 2, 3 and 4 are listed main interatomic distances, bond angles, crystallographic data and fractional atomic parameters. Tables of thermal parameters and lists of observed and calculated structure factors are available from the authors.

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