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Reaction of aminocarbene complexes of chromium and tungsten 6. Rearrangements of and insertions of alkynes into aziridinylcarbene complexes

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Abstract

Pentacarbonyl[(2-methylaziridinyl)(methyl)carbene]chromium(0) (**2a**) reacts with LiBu followed by H_2O to regenerate the starting carbene complex. Treatment of the same reaction mixture with D_2O leads to the perdeuteromethyl carbene complex **2D$_3$**. However, addition of CH_3I instead of D_2O gives pentacarbonyl(*N*-methyl-2-aza-3-methylcyclopentylidene)chromium(0) (**28**) by ring opening followed by alkylation at nitrogen. The aziridinylcarbene complexes $[(CO)_5M = C(\overline{NCH(CH_3)CH_2})R_1$ (M = Cr, R_1 = Me, **2a**, R_1 = Ph, **2b**, R_1 = cyclopropyl, **2c** react with diphenylacetylene or phenylpropyne) to give **30a–c**, **33** and **34** via double alkyne and single CO insertions. However, complex **2d** (M = W, R_1 = Me) gave only trace amounts of the expected complex **30d**. Treatment of **30a** with pyridine led to the metal-free derivative **31**. Complex **30b** (R_1 = Ph) was fully characterized by X-ray diffraction.

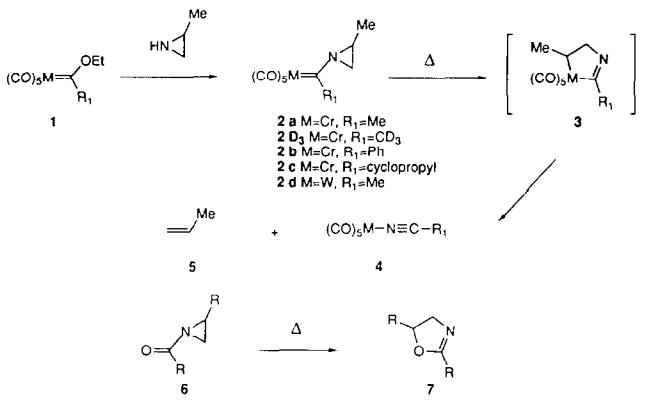
Keywords: Copper; Tungsten; Carbene complexes; Alkyne insertion; X-ray structure; Chromium

1. Introduction

In a series of previous papers [1,2], we have described some aspects of the peculiar behavior of aziridinylcarbene complexes of chromium and tungsten. In contrast to other aminocarbene complexes of these metals, they undergo easy thermal rearrangement leading to nitrile complexes on extrusion of an olefin (Scheme 1). This transformation of complexes **2** can be viewed as the result of two successive sigmatropic rearrangements giving via a chromazolidine **3**, a nitrile **4** and an olefin **5**. The first step of this transformation (**2** → **3**) is reminiscent of the known thermal rearrangement of *N*-acylaziridines (**6**) to 2-oxazolidines (**7**).

A second unexpected result had already been observed during attempts to synthesize phenyl-substituted aziridinylcarbene complexes because the interaction of 2-phenylaziridine (**8**) with complex **1** did not lead to the expected complex **2**. Instead, elimination of styrene (**9**) along with the formation of an iminoester complex (**10**) was observed (Scheme 2) involving the formal coupling of the nitrene NH with the carbene $CH_3(OEt)C$:. This result could be related to the reaction of a phenyl-substituted aziridine (**11**) with an organic carbene such as dichlorocarbene (**12**) which leads to an olefin (**14**) and a dichloroimine (**15**) (Scheme 3) presumably by formation of an unstable *N*-ylide (**13**) [3].

A third, unexpected result came from the interaction of aziridinylcarbene complex **2a** with diphenylacety-



Scheme 1.

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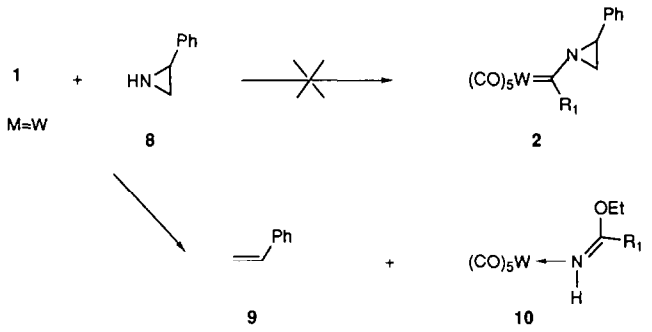


Scheme 2.

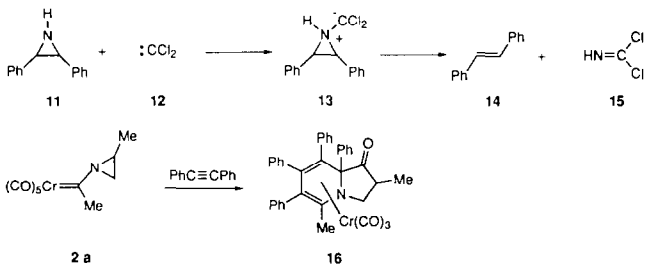
lene. Only a di-insertion product of the alkyne was isolated, the structure of which was shown to be $Cr(CO)_3$-coordinated kind of substituted dihydropyridine (**16**) by X-ray crystallography [1]. The mechanism of this insertion appeared to be different from the general mechanism established for the insertion of alkynes into aminocarbene complexes since it could not originate from the intramolecular interaction of an amine with a ketene complex [4].

The purpose of this paper is to substantiate further the analogy between aziridinylcarbene complexes and *N*-acylaziridines and also to confirm that, whatever the structure of the starting complexes **2** might be, only alkyne di-insertion products of the type **16** could be isolated. These organic ligands can, in turn, be released upon heating in pyridine.

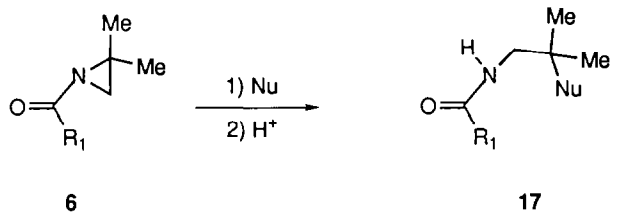
2. Results and discussion

2.1. Rearrangement of aziridinylcarbene complexes

N-acyl and *N*-aroylaziridines **6** react with nucleophiles to give linear amides **17** (Scheme 4) upon nitrogen–carbon bond cleavage [5,6]. The intramolecular version of this reaction has been studied by Laurent and co-workers [7,8]. Thus, aziridine **6** gave pyrrolidone **20** upon lithium diethylamide-promoted hydrogen abstraction. This transformation was considered to occur via the electrocyclic rearrangement of the enolate **18** (Scheme 5). It is also known that aminocarbene complexes of the general type **21** undergo easy hydrogen



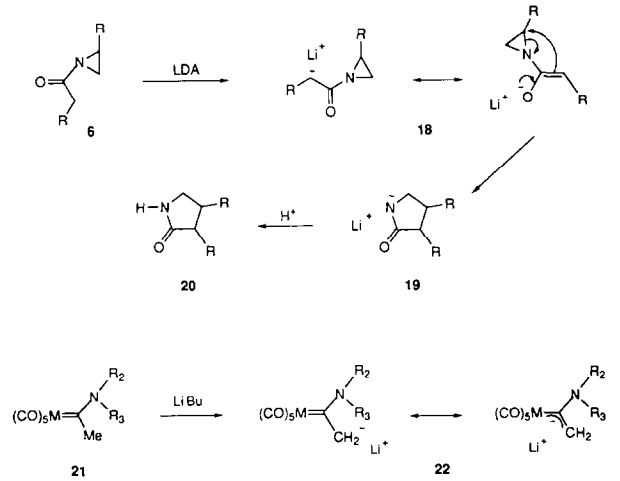
Scheme 3.



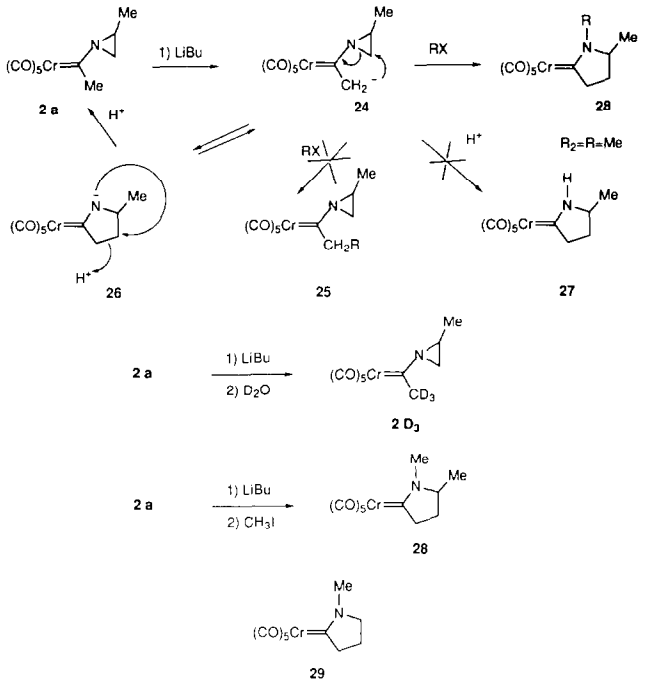
Scheme 4.

abstractions from the carbon α to the carbene function and lead to anionic $M(CO)_5$-stabilized species **22** [9]. Applied to complex **2**, this reaction might lead to the starting material upon reprotonation of **24** or to **25** upon alkylation at carbon, or to a wide variety of new aminocarbene complexes **27** or **28** suitable for the synthesis of polycyclic heterocycles [10], in the event of an intramolecular rearrangement reaction such as that observed for the corresponding *N*-acylaziridines (Scheme 6).

After complex **2a** was treated with LiBu at low temperature, almost all the starting material was recovered after protonation. No trace of the expected complex **27** could be detected. That deprotonation of **2a** nevertheless had occurred was established by treatment of the reaction mixture with D_2O instead of H_2O. Both the ^1H and ^{13}C NMR spectra and the mass spectrum ($m/z = 278$ instead of 275 for **2a**) confirmed extensive deuterium incorporation into the methyl group. The ^1H and ^{13}C NMR spectra showed weak signals for both the protons and the carbon of the methyl group on the carbene carbon at δ 2.70 and 40.5 ppm, respectively, thus confirming structure $\mathbf{2D_3}$. It appears thus that complex **2a** behaves like complex **1a** with facile incorporation of deuterium on the methyl group [11,12]. However, treatment of the reaction mixture obtained upon deprotonation of **2a** with CH_3I did not lead to **25** upon alkylation of **24**, but to the expected rearranged and alkylated complex **28**.



Scheme 5.



Scheme 6.

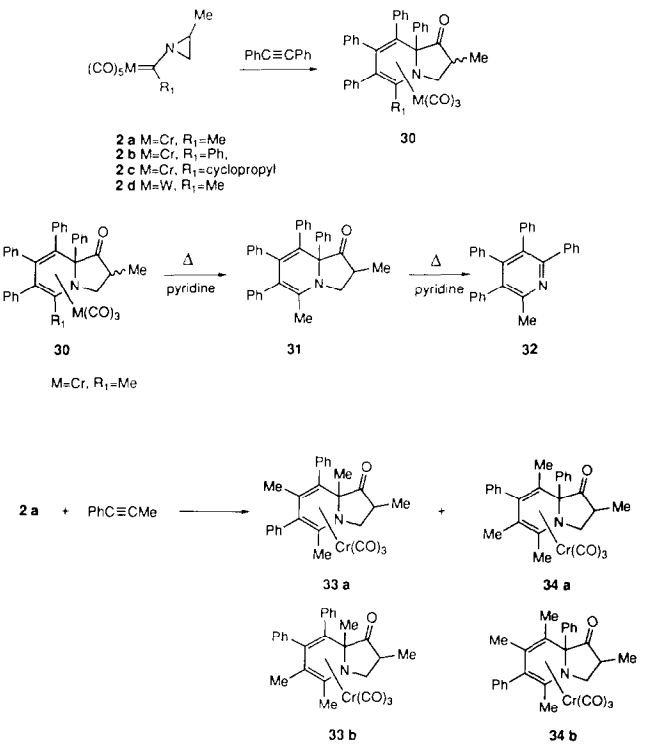
The ^{1}H and ^{13}C NMR data of this complex were very similar to those of the related complex **29** obtained from the corresponding amide and $Na_2[Cr(CO)_5]$ [13]. The ^{1}H NMR spectrum showed signals at δ 3.98 ppm ($NCHCH_3$), 3.60 (NCH_3), 3.28 ($=CCH_2$), 2.10 and 1.53 for the two diastereotopic $NCH(CH_3)CH_2$ protons and at 1.32 ppm ($CHCH_3$). The ^{13}C NMR spectra of **28** and **29** were also very similar. For example, **28** also exhibits signals at δ 266.01 (Cr=C), 223.28 and 218.3 (CO), 69.58, 40.05 and 19.33, with an extra signal at 29.33 ppm for the $CHCH_3$ carbon.

It therefore appears that, as for the corresponding amide, deprotonation followed by rearrangement takes place irreversibly giving, in the presence of CH_3I, the five-membered carbene complex **28** upon alkylation at nitrogen by CH_3I. In the absence of alkylating agent, ring opening probably occurred also but the intermediate **26** reversibly led back to the starting carbene complex upon protonation of **24** at carbon.

2.2. Reaction with alkynes: formation of tetrahydroindolizidinones complexed by $Cr(CO)_3$

We have already described [1] the insertion of diphenylacetylene into complex **2a**, a reaction which led to the formation of tetrahydroindolizidinone complex **30** (M = Cr, $R_1 = CH_3$). The metal could be removed from this complex by heating it in refluxing pyridine for 2 h. Under such conditions, the organic product **31** could be isolated in up to 90% yield. However, heating for 24 h led to methyltetraphenylpyridine (**32**) by elimination of $-CH_2CHMeCO-$ (Scheme 7).

The reaction of complex **2a** with phenylpropyne led to a mixture of regioisomers **33a** or **33b** (12%) and **34a** or **34b** (8%), which could be separated by silica gel chromatography, one of them having, according to the ^{1}H NMR spectrum, a methyl group at the ring junction. In order to check the influence of the substituents on the carbene carbon, complexes **2b** (R_1 = Ph) and **2c** (R_1 = cyclopropyl) were also prepared. As with **2a**, **2b** and **2c** led to the expected complexes **30b** and **30c** in 23% and 14% yield, respectively. That **30b** had a structure similar to the established structure for **30a** was shown by an X-ray structure determination. Suitable dark-red crystals of **30b** were grown from hexane–methylene chloride. The ORTEP view of this complex is shown in the Fig. 1 and selected bond distances (Å) and bond angles (°) are given in Table 1. As in **30a**, the highly crowded tetrahydroindolizidinone is coordinated to $Cr(CO)_3$ via both its double bonds and nitrogen. The phenyl groups at C(7), C(8) and C(9) are almost perpendicular to the best plane formed by the tetrahyroindolizidinone ring system, whereas the axis of the phenyl rings at C(1) and C(11) form angles of 54° and 66°, respectively, with this plane. As far as the reaction of complex **2c** is concerned, no participation of the cyclopropyl group during the insertion reaction was observed, although such a participation was noted for alkyne insertions into cyclopropyl-substituted alkoxycarbene complexes of chromium, leading to ring-opened insertion products [14].



Scheme 7.

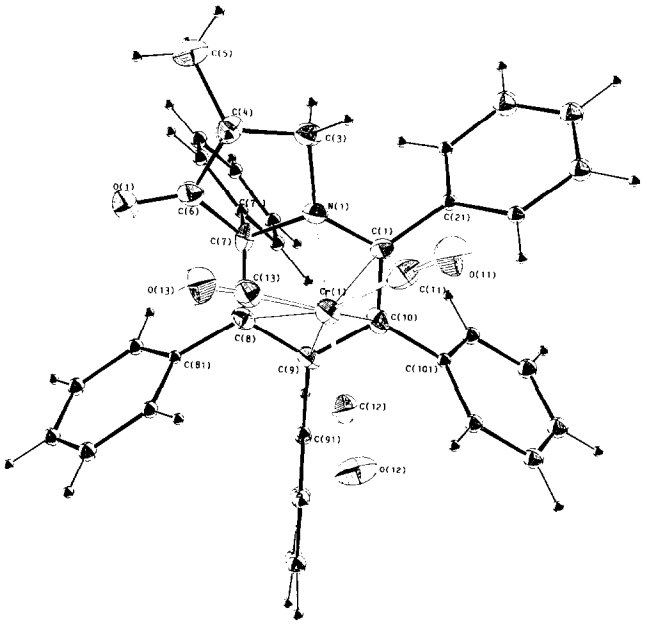


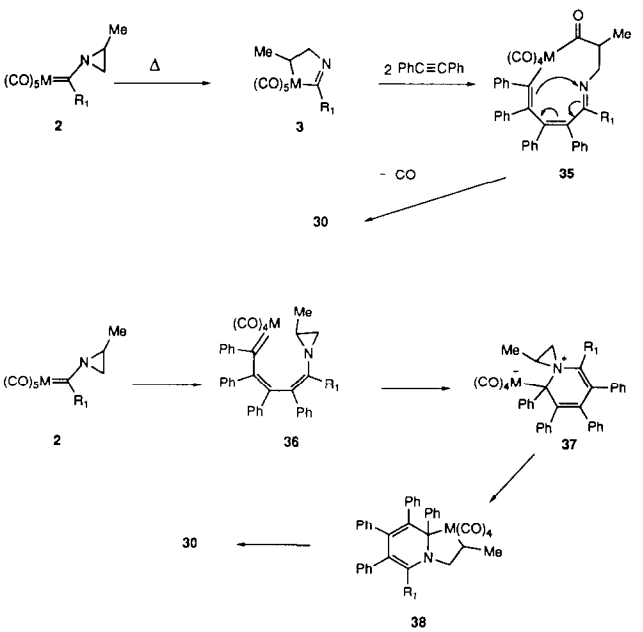
Fig. 1. ORTEP projection of complex **30b**.

In order to gain insight into the role of the metal in these reactions, the insertion was also carried out on complex **2d** (M = W). Carbene complexes of tungsten are generally reluctant to undergo CO insertions and aminocarbene complexes of this metal do not easily undergo either alkyne or CO insertions [15]. In addition, aziridinylcarbene complexes of the type **2d** had been found to rearrange easily thermally to olefins and nitrile complexes according to the Scheme 1 [2] but the best conditions for such a reaction were not met with these complexes. Thus, when complex **2d** was submitted to reaction with diphenylacetylene, most of the starting complex decomposed. A very low yield (1%) of the expected tetrahydroindolizidinone complex **30d** was characterized after silica gel chromatography. The NMR data for this complex are in all respects comparable to those of the corresponding complex **30a** (see Experimental).

Table 1
Selected interatomic distances (Å) and bond angles (°) for complex **30b**

Cr(1)–C(11)	1.86(1)	C(11)–O(11)	1.13(1)
Cr(1)–C(12)	1.80(1)	C(12)–O(12)	1.16(1)
Cr(1)–C(13)	1.83(1)	C(13)–O(13)	1.15(1)
Cr(1)–N(1)	2.15(1)	Cr(1)–C(1)	2.19(1)
Cr(1)–C(8)	2.30(1)	Cr(1)–C(9)	2.23(1)
Cr(1)–C(10)	2.21(1)		
N(1)–C(1)	1.40(1)	N(1)–C(3)	1.47(2)
N(1)–C(7)	1.52(1)	C(1)–C(10)	1.38(2)
C(1)–C(21)	1.49(2)	C(3)–C(4)	1.52(2)
C(4)–C(5)	1.51(2)	C(4)–C(6)	1.53(2)
C(6)–O(1)	1.21(1)	C(6)–C(7)	1.54(2)
C(7)–C(8)	1.50(2)	C(7)–C(71)	1.50(1)
C(8)–C(9)	1.43(2)	C(9)–C(10)	1.45(2)
C(12)–Cr(1)–C(11)	84.7(5)	O(11)–C(11)–Cr(1)	174.3(13)
C(13)–Cr(1)–C(11)	89.7(6)	O(12)–C(12)–Cr(1)	173.5(12)
C(13)–Cr(1)–C(12)	88.1(6)	O(13)–C(13)–Cr(1)	173.9(11)
C(3)–N(1)–C(1)	124.9(10)	C(10)–C(1)–N(1)	116.8(11)
C(7)–N(1)–C(1)	121.5(9)	C(21)–C(1)–N(1)	118.0(11)
C(7)–N(1)–C(3)	109.1(9)	C(21)–C(1)–C(10)	124.8(12)
C(4)–C(3)–N(1)	103.8(10)	C(5)–C(4)–C(3)	116.1(12)
C(6)–C(4)–C(3)	102.6(10)	C(6)–C(4)–C(5)	114.5(11)
O(1)–C(6)–C(4)	123.7(12)	C(7)–C(6)–C(4)	111.6(11)
C(7)–C(6)–O(1)	124.6(12)	C(6)–C(7)–N(1)	97.6(9)
C(8)–C(7)–N(1)	103.7(8)	C(8)–C(7)–C(6)	112.9(10)
C(9)–C(8)–C(7)	116.6(10)		
C(10)–C(9)–C(8)	120.2(10)		
C(9)–C(10)–C(1)	119.9(11)		

Since metal-induced ring opening via **3** could probably take place during the alkyne insertion reaction, CO insertion followed by double alkyne insertion might lead to the intermediate **35**. An electrocyclization followed by reductive elimination of the metal fragment would then lead to **30**. However, a mechanism which has some precedents in the chemistry of carbene complexes [20,21] could involve the formation of a nitrogen ylid **37** through interaction of the nitrogen atom in **36** with the electrophilic carbene complex formed upon insertion of two molecules of alkyne into **2**. Rearrange-



Scheme 8.

As far as the mechanism of these reactions is concerned, the reasons for the double alkyne insertion are not clear. Although double alkyne insertions have already been observed by Wulff and co-workers [16,17] in alkoxycarbene complexes of chromium, we have so far observed only one example for alkoxycarbene complexes of tungsten and aminocarbene complexes of chromium [18,19]. At least two mechanisms, different from the general mechanism established for the alkyne/CO insertions into other aminocarbene complexes, may account for the formation of complexes **30**.

ment of this ylid into **38** followed by insertion of CO might also give **30** (Scheme 8).

The formation of the pyridine **32** upon reaction of the complex **30** with pyridine is linked to the formation of the free tetrahydroindolizidinone **31**. It has been shown that dihydropyridines, which in general are readily oxidized to pyridines, are very stable as $Cr(CO)_3$ complexes [22,23]. Thus decoordination of the metal followed by a dealkylation reaction led to the pyridine **32**.

3. Conclusion

Like acylaziridines, aziridinylcarbene complexes of chromium and tungsten very easily undergo rearrangements with ring opening which can lead in some instances to new carbene complexes useful for the synthesis of heterocyclic compounds. In the presence of alkynes, a general reaction leading to substituted tetrahydroindolizidinone upon insertion of two alkynes and CO, and again with opening of the aziridine ring system, has been established.

4. Experimental

4.1. General methods

^1H and ^{13}C NMR spectra were recorded on a JEOL GX 400 or on a Bruker WM 200 spectrometer. IR spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. Mass spectra were recorded on a ZAB HSQ instrument (Fisons). Column chromatography was performed with Merck silica gel (70–230 mesh) using ethyl acetate–hexanes or dichloromethane–hexanes as eluent. All reagents were obtained from commercial suppliers and used as received. Reactions were performed under argon in carefully dried glassware. Benzene, tetrahydrofuran (THF) and diethyl ether were distilled from sodium–benzophenone ketyl under dinitrogen Dichloromethane was distilled from calcium hydride under dinitrogen.

4.2. Pentacarbonyl(N-methyl-2-aza-3-methylcyclopentylidene)chromium(0) (28)

LiBu (4.6 ml, 75 mmol, 1.6 M in hexanes) was added dropwise to a solution of complex **2a** (1.5 g, 54.5 mmol) in THF (100 ml) at −78 °C. After heating to room temperature and stirring for 1 h, the solution was again cooled to −78 °C and methyl iodide (0.47 ml) was added. After heating to room temperature and stirring for 1 h, extraction as usual gave a residue after evaporation of the solvent under vacuum. Silica gel chromatography of this residue with ethyl acetate–light petroleum (5:95) gave complex **28** (0.85 g, 54%) as yellow crystals: m.p. 57–58 °C; IR ($CHCl_3$) 1940, 2040 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.97 (m, 1H, $NCHCH_3$), 3.60 (s, 3H, NCH_3), 3.28 (m, 2H, $=CCH_2$), 2.10 (m, 1H, CHH), 1.53 (m, 1H, CHH), 1.32 (d, $J = 6.6$ Hz, 3H, $CHCH_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 266.01 (Cr=C, 223.28, 218.30 (CO), 69.58 (NCH), 54.25 ($C=CH_2$), 40.05 (NCH_3), 29.33 (CH_2), 19.39 ($CHCH_3$). Anal. Found: C, 45.19; H, 3.75; N, 4.64. calc. for $C_{11}H_{11}CrNO_5$: C, 45.67; H, 3.80; N, 4.84%.

4.3. Pentacarbonyl(N-methyl-2-azacyclopentylidene) chromium(0) (29)

This was obtained from *N*-methylpyrrolidinone and $Na_2[Cr(CO)_5]$ according to Ref. [13]. ^1H NMR (200 MHz, $CDCl_3$) δ 3.78 (m, 2H, NCH_2), 3.65 (s, 3H, NCH_3), 3.42 (m, 2H, $=CH_2$), 1.91 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 265.81 (Cr=C), 223.36, 218.26 (CO), 62.67 (NCH_2), 56.52 ($=CCH_2$), 42.19 (NMe), 21.08 (CH_2).

4.4. Pentacarbonyl[(methylaziridino)(deuteromethyl) carbene]chromium(0) ($2D_3$)

This was obtained as above from **2a** after addition of LiBu and D_2O instead of CH_3I, yield 68%: yellow oil; IR ($CHCl_3$) 2060, 1930 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.36 (m, 1H, NCH), 2.70 (m, 5H, $=C(CH_3)$, NCH_2), 2.30 (m, 1H, NCH), 1.65 (d, $J = 5.6$ Hz, 3H, $CHCH_3$); ^{13}C NMR (50 MHz, $CDCl_3$) *E–Z* mixture: δ 268.78 and 267.09 (Cr=C), 223.38, 218.12 (CO), 36.51 and 35.31 (NCH_2), 32.63 and 31.76 (NCH), 17.08 and 16.99 (CCH_3). MS calc. for $C_{10}H_6D_3CrNO_5$ 278 (M^+); found 278.

4.5. Complex 30a

A solution of complex **2a** (2 g, 7.2 mmol) and diphenylacetylene (2.8 g, 16 mmol) in benzene (80 ml) was heated under reflux for 2 h. After evaporation of the solvent under vacuum, the residue was chromatographed on silica gel to give with light petroleum–CH_2Cl_2 (80:20) complex **30a** (1.25 g, 26%) as red crystals: m.p. 260 °C; IR ($CHCl_3$) 1950, 1880, 1850, 1760 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.54–6.77 (m, 20H, Ar), 4.33 (t, 1H, NCH), 3.61 (t, 1H, NCH), 2.85 (m, 1H, $CHCH_3$), 2.03 (s, 3H, CH_3), 1.19 (d, 3H, $CHCH_3$); ^{13}C NMR (50 MHz, CD_2Cl_2) δ 231.0, ($Cr(CO)_3$), 206.42 (CO), 137.45–117.65 (Ar), 117.65, 106.61, 104.64, 83.89, 76.64 ((C=C)Cr, NCPh), 54.17 (NCH_2), 42.87 ($CHCH_3$), 17.57, 13.77 (CH_3). Anal. found: C, 73.03; H, 4.72; N, 2.49. Calc. for $C_{37}H_{29}CrNO_4$: C, 73.63; H, 4.80; N, 2.32%.

4.6. Compound 31

A solution of complex **30a** (1 g, 1.6 mmol) in pyridine (50 ml) was heated under reflux for 2 h. After filtration through Celite and evaporation of the solvent under vacuum, the residue was chromatographed on a short column of silica gel to give **31** (0.7 g, 90%) as a white–brownish solid: m.p. 175 °C; IR ($CHCl_3$) 1760 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.54–6.77 (m, 20H, Ar), 4.33 (t, 1H, NCH), 3.62 (t, $J = 9.6$ Hz, NCH), 2.79 (m, 1H, $CHCH_3$), 2.04 (s, 3H, CH_3), 1.20 (d, $J = 5$ Hz, $CHCH_3$). Anal. found: C, 87.68; H, 6.20; N, 2.45. Calc. for $C_{34}H_{29}NO$: C, 87.31; H, 6.20; N, 2.99%.

4.7. Methyltetraphenylpyridine (32)

This was obtained when the same reaction as above was carried out for 24 h; evaporation of the solvent followed by silica gel chromatography gave **32** as a white solid: m.p. 156 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.25–6.65 (m, 20H, Ar), 2.47 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 156.22, 149.35, 140.97; 135.85–126.13 (Ar), 24.28 (CH_3). MS for $C_{30}H_{23}N$: 397(M^+); found 397.

4.8. Complexes 33 and 34

These were obtained upon heating a solution of complex **2a** (2 g, 7.2 mmol) and 1-phenyl-1-propyne (1.9 g, 14 mmol) in benzene (80 ml) under reflux for 12 h. After evaporation of the volatiles under vacuum, the residue was chromatographed on silica gel. Elution with light petroleum–acetone (90:10) gave a mixture of **33** and **34**. The complexes were then separated by thin-layer chromatography. The less polar product (0.427 g, 12%) was isolated as a red solid; m.p. 145 °C; IR ($CHCl_3$) 1950, 1875, 1840, 1760 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.42–6.98 (m, 10H, ArH), 3.51 (t, 1H, NCH), 3.25 (m, 1H, $CHCH_3$), 3.16 (t, 1H, NCH), 2.68 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 1.08 (d, $J = 6.8$ Hz, $CHCH_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 232.39 (CrCO), 207.30 (CO), 137.77, 131.11–127.55 (Ar), 115.15, 104.54, 96.96, 78.05, 75.17 C=C), 54.52 (NC), 42.59 ($CHCH_3$), 17.28, 16.24, 15.79, 13.78 (4 Me). Anal. found: C, 66.45; H, 5.15; N, 2.81. Calc. for $C_{27}H_{25}CrNO_4$: C, 67.64; H, 5.21; N, 2.92%. MS: 479 (M^+).

The more polar product (0.285 g, 8.1%) was obtained as red crystals: m.p. 245 °C; IR ($CHCl_3$) 1950, 1875, 1845, 1760 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.25–7.00 (m, 10H, ArH), 3.39 (t, 1H, NCH), 3.31 (m, 1H, C*H*CH_3), 3.03 (t, 1H, NCH), 2.58 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 1.17 (d, $J = 6.8$ Hz, 3H, CHC*H*$_3$), 0.89 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 231.84 (CrCO), 207.87 (CO), 136.62–126.56 (Ar), 118.23, 104.41, 94.14, 84.97, 74.57 (C=C), 53.55 (NCH_2), 41.73 (*C*HCH_3), 22.16, 17.62, 15.71, 12.90 (4 CH_2). Anal. found: C, 66.70; H, 5.18; N, 2.84. Calc. for $C_{27}H_{25}CrNO_4$: C, 67.64; H, 5.21; N, 2.92%. MS: 479 (M^+); found 479.

4.9. Complex 30b

Complex **30b** was obtained upon heating a solution of complex **2b** (2 g, 6 mmol) and diphenylacetylene (2.2 g, 12 mmol) in benzene (80 ml) under reflux for 12 h. After evaporation of the solvent under vacuum, followed by silica gel chromatography of the residue with light petroleum–acetone (80:20), complex **30b** was obtained as dark red crystals which were recrystallized from CH_2Cl_2–hexane: m.p. 262 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.60–6.41 (m, 25H, ArH), 3.55 (m, 1H, C*H*CH_3), 2.98 (t, $J = 10.8$ Hz, 1H, NCH), 2.84 (t, $J = 10.8$ Hz, 1H, NCH), 1.31 (d, $J = 7.2$ Hz, 3H, CHC*H*$_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 231.20 (CrCO), 207.26 (CO), 135.41–126.64 (Ar), 115.83, 112.17, 106.39, 84.27, 78.30 (C=C), 55.63 (NCH_2), 43.73 (*C*HCH_3), 12.98 (CHC*H*$_3$). Anal. found: C, 75.14; H, 4.64; N, 2.01. Calc. for $C_{42}H_{31}CrNO_4$: C, 75.78; H, 4.66; N, 2.10%. MS: 665 (M^+); found 665.

4.10. Complex 1c

Complex **1c** was obtained from cyclopropyllithium prepared from t-butyllithium (33.7 ml, 1.7 M in hexanes) and bromocyclopropane (2.3 ml, 28 mmol) in Et_2O (70 ml) at −78 °C which was added to a suspension of [$Cr(CO)_6$] (6.27 g, 28 mmol), in Et_2O (100 ml) at 0 °C. After stirring for 1 h, evaporation of the solvent under vacuum and addition of triethyloxonium fluoroborate gave complex **1c** (7.7 g, 93%) as a yellow solid: m.p. 38 °C; IR ($CHCl_3$) 2050, 1930 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.97 (q, 2H, OCH_2), 3.44 (m, 1H, CH), 1.52 (t, 3H, CH_2CH_3), 1.35 (m, 2H, CH_2), 1.16 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 351.1 (Cr=C), 223.6, 216.9 (CO), 76.6 (OCH_2), 41.2 (CH), 17.63 (CH_3), 14.8 (CH_2). Anal. Found: C, 45.42; H, 3.59. Calc. for $C_{11}H_{10}CrO_6$: C, 54.51; H, 3.44%.

4.11. Complex 2c

Complex **2c** was obtained upon addition of methylaziridine (3 ml, 41.3 mmol) to a solution of complex **1c** (4 g, 13.8 mmol) in Et_2O (100 ml) at 0 °C. After 24 h, the solvent was evaporated under vacuum and the residue chromatographed on silica gel. Elution with light petroleum–CH_2Cl_2 (80:20) gave, after evaporation of the volatiles under vacuum, complex **2c** (3.7 g, 89%) as a yellow oil (2:3 mixture of *E* and *Z* isomers, which were not separated). ^1H NMR (200 MHz, $CDCl_3$) δ 3.15 (m, NCH), 3.00 (m, CH), 2.85 (m, CH), 2.38

(m, CH), 1.62 (d, $J = 5.4$ Hz, 3H, CH_3), 1.50 (d, $J = 5.4$ Hz, 3H, CH_3), 1.21 (m, CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 273.44 (Cr=C), 270.95 (Cr=C), 223.05, 218.47, 218.36 (CO), 38.64, 34.04, 33.37, 33.13, 32.76, 32.00, 17.92, 17.19, 11.94, 11.50, 11.16, 10.87. Anal. found: C, 48.39; H, 3.83. N, 4.81. Calc. for $C_{21}H_{11}CrNO_5$: C, 47.84; H, 3.65; N, 4.65%.

4.12. Complex 30c

Complex **30c** was obtained upon heating a solution of complex **2c** and diphenylacetylene in benzene under reflux as above, as red crystals (14%): m.p. 225 °C; IR ($CHCl_3$) 1950, 1880, 1760 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.52–6.74 (m, 20H, ArH), 3.55 (m, 2H, NC*H* and C*H*CH_3), 3.21 (m, 1H, NC*H*), 1.94 (m, 1H, CH), 1.37 (d, $J = 6.2$ Hz, 3H, CHCH_3), 0.56 (m, 1H), 0.48 (m, 1H), 0.055 (m, 1H), −0.39 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 231.89 (CrCO), 207.60 (CO), 137.56–126.38 (Ar), 116.50, 110.12, 106.47, 82.05, 77.10 (C=C, NCPh), 54.23 (NCH_2), 43.63 (*C*HCH_3), 13.07, 12.35, 9.34, 8.26. Anal. Found: C, 74.59; H, 4.84; N, 2.03. Calc. for $C_{39}H_{31}CrNO_4$: C, 74.40; H, 4.92; N, 2.22%.

4.13. Complex 2d

Complex **2d** was obtained upon addition of methylaziridine (1.4 ml, 18.9 mmol) to a solution of **1d** (M = W, R_1 = Me) in Et_2O (100 ml) at 0 °C. After stirring at room temperature for 1 h, the solvent was evaporated under vacuum and the residue chromatographed on silica gel. Elution with light petroleum – CH_2Cl_2 (95:5) gave complex **2d** (3.8 g, 74%) as a yellow solid (*E–Z* mixture): m.p. 47 °C; IR ($CHCl_3$) 2060, 1920 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.16, 2.88, 2.52, 2.32 (m, NCH), 2.75, 2.73 (s, 3H, CH_3), 1.61, 1.50 (d, 3H, C*H*CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 247.98 and 244.95 (Cr = C), 203.76, 198.86

Table 2
Crystallographic data for complex **30b**

Chemical formula	$C_{42}H_{31}O_4NCr$
Formula mass	665.7
Crystal system	Orthorhombic
Space group	*Fdd*2
a (Å)	20.325(4)
b (Å)	61.06(1)
c (Å)	10.779(2)
V (Å^3)	13378
Z	8
ρ (calc.) (g cm^{-3})	1.32
μ (Mo Kα) (cm^{-1})	3.75
Diffractometer	CAD4
Monochromator	Graphite
Radiation	Mo Kα (0.71070)
Temperature (°C)	20
Scan type	$\omega/2\theta$
Scan range, θ (°)	1.2 + 0.34 tan θ
2θ range, (°)	4–40
Reflections collected	1671
Reflections used ($I > 3\sigma(I)$)	1379
R	0.056
R_w [a]	0.062
Abs. corr. DIFABS	Min. 0.77; max. 1.33
Weighting scheme	Unit weights
Shift/esd (last ref.)	0.10
I.s. parameters	283

[a] $R_w = [\Sigma_i W_i (F_o - F_o)^2 / \Sigma_i W_i F_o^2]^{1/2}$.

Table 3
Fractional parameters for complex **30b**

Atom	*x*	*y*	*z*	*U*(eq)	*U*(iso)
Cr(1)	−0.1694	0.20399(3)	0.764(2)	0.0321	
C(11)	−0.2453(6)	0.2203(2)	0.793(3)	0.0429	
O(11)	−0.2934(4)	0.2296(2)	0.801(2)	0.0568	
C(12)	−0.2178(6)	0.1904(2)	0.648(3)	0.0374	
O(12)	−0.2511(5)	0.1837(1)	0.569(2)	0.0562	
C(13)	−0.1442(6)	0.2237(2)	0.646(3)	0.0351	
O(13)	−0.1335(5)	0.2357(2)	0.566(2)	0.0606	
N(1)	−0.1098(5)	0.2147(1)	0.918(2)	0.0325	
C(1)	−0.1560(6)	0.1997(2)	0.964(3)	0.0330	
C(3)	−0.1037(6)	0.2377(2)	0.958(3)	0.0377	
C(4)	−0.0642(6)	0.2483(2)	0.855(3)	0.0400	
C(5)	−0.0234(8)	0.2679(2)	0.892(3)	0.0593	
C(6)	−0.0244(6)	0.2291(2)	0.803(3)	0.0373	
O(1)	0.0191(4)	0.2311(1)	0.727(2)	0.0494	
C(7)	−0.0446(5)	0.2072(2)	0.864(3)	0.0264	
C(8)	−0.0641(5)	0.1901(2)	0.771(3)	0.0300	
C(9)	−0.1115(6)	0.1741(2)	0.811(3)	0.0315	
C(10)	−0.1564(6)	0.1792(2)	0.912(3)	0.0319	
C(21)	−0.1950(5)	0.2063(2)	1.075(2)		0.043(3)
C(22)	−0.2619(6)	0.2068(2)	1.076(2)		0.046(4)
C(23)	−0.2950(7)	0.2122(3)	1.183(3)		0.081(5)
C(24)	−0.2615(8)	0.2178(3)	1.288(3)		0.091(6)
C(25)	−0.1943(8)	0.2174(3)	1.291(3)		0.109(7)
C(26)	−0.1601(7)	0.2107(3)	1.184(3)		0.069(5)
C(71)	0.0030(5)	0.2010(2)	0.964(2)		0.036(3)
C(72)	0.0551(6)	0.2146(2)	0.996(3)		0.051(4)
C(73)	0.0993(7)	0.2083(2)	1.086(3)		0.062(4)
C(74)	0.0929(6)	0.1889(2)	1.149(3)		0.055(4)
C(75)	0.0424(6)	0.1752(2)	1.119(3)		0.057(4)
C(76)	−0.0015(6)	0.1813(2)	1.027(3)		0.047(3)
C(81)	−0.0191(5)	0.1843(2)	0.669(2)		0.028(3)
C(82)	−0.0409(6)	0.1838(2)	0.547(2)		0.046(4)
C(83)	−0.0006(6)	0.1767(2)	0.452(2)		0.058(4)
C(84)	0.0635(6)	0.1704(2)	0.478(2)		0.054(4)
C(85)	0.0868(6)	0.1711(2)	0.597(3)		0.056(4)
C(86)	0.0451(6)	0.1783(2)	0.692(2)		0.049(4)
C(91)	−0.1098(5)	0.1517(2)	0.755(2)		0.035(3)
C(92)	−0.0748(7)	0.1361(2)	0.821(3)		0.059(4)
C(93)	−0.0705(8)	0.1147(2)	0.780(3)		0.086(5)
C(94)	−0.0991(7)	0.1089(2)	0.671(3)		0.064(4)
C(95)	−0.1358(7)	0.1234(2)	0.606(3)		0.064(4)
C(96)	−0.1399(7)	0.1449(2)	0.648(3)		0.057(4)
C(101)	−0.2007(5)	0.1614(2)	0.963(2)		0.035(3)
C(102)	−0.1901(7)	0.1536(2)	1.081(3)		0.061(4)
C(103)	−0.2296(7)	0.1374(2)	1.129(3)		0.070(5)
C(104)	−0.2776(8)	0.1287(2)	1.058(3)		0.076(5)
C(105)	−0.2877(7)	0.1354(2)	0.940(3)		0.069(5)
C(106)	−0.2490(6)	0.1522(2)	0.891(3)		0.054(4)

Table 4
Anisotropic thermal parameters for complex **30b**

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Cr(1)	0.031(1)	0.035(1)	0.031(1)	−0.002(1)	−0.002(1)	0.003(1)
C(11)	0.040(8)	0.050(9)	0.05(1)	0.001(8)	−0.019(8)	−0.009(7)
O(11)	0.036(6)	0.068(7)	0.094(9)	−0.011(6)	−0.007(6)	0.021(5)
C(12)	0.022(7)	0.045(9)	0.06(1)	−0.009(8)	0.004(7)	0.005(7)
O(12)	0.059(6)	0.051(6)	0.073(8)	−0.011(6)	−0.025(6)	−0.005(5)
C(13)	0.027(8)	0.06(1)	0.031(9)	−0.010(7)	−0.006(7)	−0.002(7)
O(13)	0.084(8)	0.056(7)	0.052(7)	0.013(6)	−0.010(6)	−0.010(6)
N(1)	0.035(7)	0.029(6)	0.036(6)	−0.008(5)	0.001(5)	0.001(5)
C(1)	0.029(8)	0.046(9)	0.035(8)	−0.017(7)	−0.001(7)	−0.009(7)
C(3)	0.026(7)	0.047(9)	0.06(1)	−0.023(8)	−0.006(7)	0.002(6)
C(4)	0.035(8)	0.034(8)	0.054(9)	0.005(8)	−0.001(8)	−0.002(7)
C(5)	0.07(1)	0.05(1)	0.07(1)	−0.015(9)	−0.004(9)	−0.018(9)
C(6)	0.036(8)	0.06(1)	0.029(9)	−0.009(7)	−0.006(7)	−0.004(7)
O(1)	0.056(6)	0.055(6)	0.041(6)	−0.003(5)	0.009(5)	−0.000(5)
C(7)	0.017(7)	0.040(8)	0.034(7)	0.015(7)	−0.005(6)	−0.000(6)
C(8)	0.031(7)	0.033(7)	0.028(7)	−0.003(7)	−0.003(7)	0.004(6)
C(9)	0.034(7)	0.035(8)	0.029(8)	−0.008(6)	0.002(6)	0.006(7)
C(10)	0.047(8)	0.036(8)	0.023(7)	0.008(7)	0.008(7)	0.001(7)

(CO), 42.65 and 41.68 (NCH), 37.42 and 35.43 (NCH_2), 33.51 and 31.91 (CH_3) 17.07 and 16.60 ($CHCH_3$). Anal. Found: C, 29.67; H, 2.30; N, 3.40. Calc. for $C_{10}H_{19}WNO_5$: C, 29.48; H, 2.21; N, 3.43%.

4.14. Complex **30d**

Complex **30d** was obtained upon heating a solution of complex **2d** (4 g, 9.8 mmol) and diphenylacetylene (3.7 g, 20 mmol) in benzene (100 ml) under reflux for 12 h. Work-up as above gave, after silica gel chromatography with light petroleum – acetone (90.10), complex **30d** (0.080 g, 1%) as dark red crystals: m.p. 193 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.15–6.35 (m, 20H, ArH), 4.11 (m, 1H, NCH), 3.12 (m, 1H, NCH), 2.41 (m, 1H, $CHCH_3$), 2.16 (s, 3H, CH_3), 0.97 (d, J = 6.8 Hz, 3H, $CHCH_3$). MS: 735 (M^+); found 735.

4.15. Structure solution and refinement

Crystal data and data collection parameters are listed in Table 2. Computations were performed using CRYSTALS adapted on a Microvax-II computer [24]. Solution of the structure was accomplished by using direct methods (SHELXS) and standard Fourier techniques [25]. Phenyl groups were refined isotropically with restraints on bond lengths and bond angles in order to keep a realistic value of the data to parameters ratios. All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions as fixed contributors and recalculated after each refinement. Atomic parameters for non-hydrogen atoms are given in Table 3. Selected interatomic distances and bond angles are listed in Table 1. Anisotropic thermal parameters are given in Table 4. Supplementary material for complex 306 (Tables S1–S3: interatomic distances, bond angles, observed and calculated structure factor amplitudes) have been deposited with the Cambridge Crystalographic Data Centre.

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