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Unexpected ring opening of cycloaminocarbene complexes of chromium upon alkyne insertion reactions

H. Rudler *, **A. Parlier, R. Yefsah, B. Denise**

Laboratoire de Chimie Organique, Université P. et M. Curie, UA 408, 4 Place Jussieu, 75252 Paris Cedex 05 (France)

J.C. Daran, J. Vaissermann and C. Knobler,

Laboratoire de Chimie des Métaux de Transition, Université P. et M. Curie, UA 604, 4 Place Jussieu 75252 Paris Cedex 05 (France)

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Abstract

Aminocarbenechromium complexes of the general structure $(CO)_5Cr{=}C(R)N(CH_2)_nXCH_2$ ($n = 0$, $X = CH_2$; $n = 1$, $X = CH_2$; $n = 1$, $X = CH{=}CH$; $n = 2$, $X = CH{=}CH$; $R = CH_3$, Ph) react with alkynes to give, by insertion of one or two molecules of alkyne and one molecule of CO, and C–N bond cleavage, new polycyclic heterocycles. The reactions of the pyrroline-, the tetrahydropyridine-, the pyrrolidine- and the methylaziridine-substituted complexes are mainly considered, and the results of X-ray structural studies of the new products are presented. The mechanism of the rearrangement of a 1,5 dipole is discussed.

Introduction

Since their discovery by Fischer in 1964 [1], carbene complexes of transition metals have been the subject of much research activity. Much work has been directed towards the applications of these new species in organic synthesis. Because of the analogy that can be drawn between organic carbenes and these complexes, one of the first applications was the cyclopropanation of olefins, and it was shown that activated olefins such as enol esters and unsaturated esters reacted with the complexes to give cyclopropanes. It was later found that unactivated olefins could be cyclopropanated intramolecularly [3,4].

The discovery that such species are involved in the olefin metathesis reaction and in the alkyne polymerization and oligomerization reactions [6] broadened even further the scope of their application.

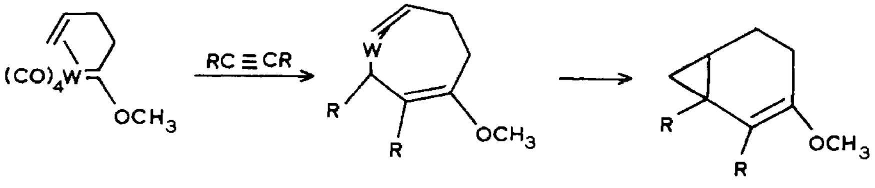
Examples include the benzannulation reaction, discovered by Doetz in 1975 [7,8] and mainly developed by other groups [9], the coupled alkyne insertion/olefin cyclopropanation reactions [10] studied in our group, and the intramolecular double alkyne insertion reaction [11].

We describe here a previously unobserved reaction which is coupled with the alkyne insertion reaction, namely the ring-opening with C–N bond cleavage of a series of cycloaminocarbene complexes of chromium [12].

Results

As a continuation of our work on the coupled alkyne insertion/olefin cyclopropanation reactions [10,13], we synthesized a series of aminocarbene complexes of chromium and studied their behaviour in the alkyne insertion reaction. Thus complex **4**, like its analog of tungsten **1**, reacts with alkynes to give compounds of the general structure **6**. In the reaction with RC≡CPh, the insertion-cyclopropanation product was isolated as the arenechromium complex **7** [14].

Bearing in mind the behaviour of the tungsten complexes bearing more elaborate alkene-carbene ligands such as **8**, which undergo the double bond coordination reaction to give **10**, we synthesized a series of carbene complexes of structure **11** containing the unsaturated cycloamino substituent. Unlike complexes **8**, complexes **11** do not undergo the double bond coordination reaction to give complexes of the structure **12** even in boiling toluene. This behaviour can be attributed to the special structure of aminocarbene complexes, which are best described as 1,3 dipoles, involving a C=N double bond and a chromium carbon bond with a multiplicity closer to one than to two [15–17].



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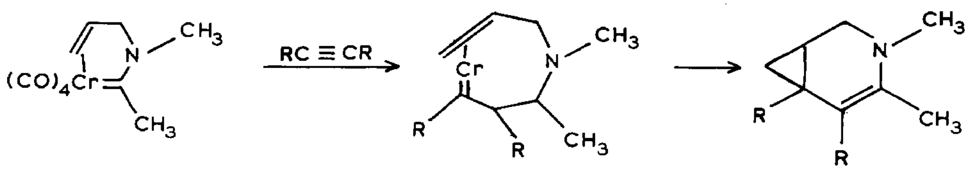

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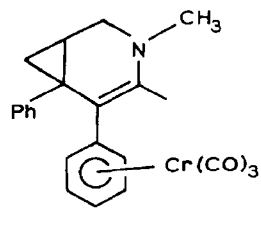

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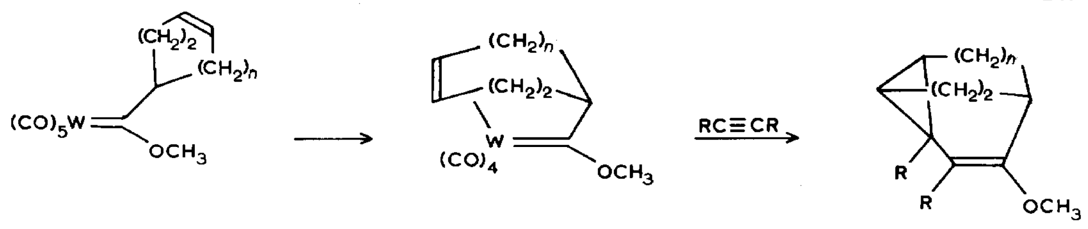
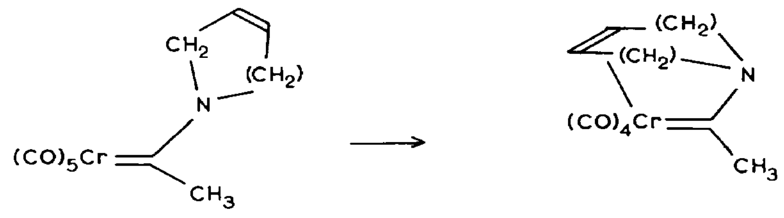


(8) (9) (10)

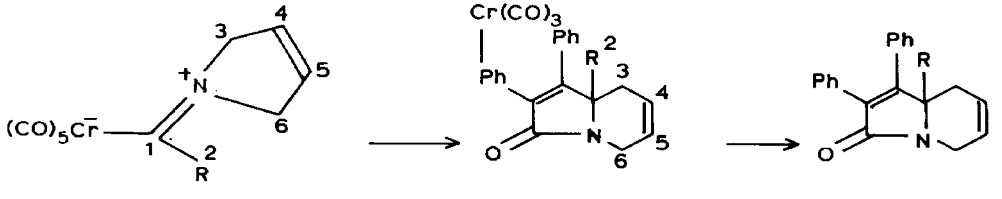
This general feature is illustrated by the structure of complex **13** ($n = 1$) which is obtained as pale yellow needles (m.p. 107 °C): the ORTEP view, shown in Fig. 1 reveals that the organic ligand, containing the carbene-carbon atom and the pyrroline substituent, is almost planar, with its carbon–carbon double bond lying well removed from the metal centre. The Cr–C(1) bond (2.123 Å) is much longer than expected for a metal–carbon double bond, whereas the C(1)–N(1) bond (1.300 Å) is best described as a carbon–nitrogen double bond.



(11) (12)

Reaction of complexes 13 and 16 with diphenylacetylene

It has been shown by Yamashita [18] that aminocarbene complexes of Cr react in refluxing DMF with alkynes to give insertion products. When a solution at complex **13** in benzene was refluxed for 6 h, a new complex was isolated (after silica gel chromatography) as orange crystals (m.p. 188 °C 58% yield). Its ^1H and ^{13}C NMR spectra are consistent with there having been insertion of one molecule of alkyne into the starting complex with formation of an arene-chromium complex, and show the presence of a methyl group on a tertiary carbon, a disubstituted double bond, an NCH_2 group, and an additional CH_2 group. The IR spectrum confirms the presence of a ketone (ν(CO) 1680 cm^{-1}) and a $Cr(CO)_3$ group. The presence of the double bond confirms that no cyclopropanation has taken place. The presence of only one $N-CH_2$ group is an indication that a major rearrangement has taken place. Only structure **14** was in agreement with the spectroscopic data, and this structure was confirmed by an X-ray diffraction study.



(**13** : R = CH_3; **16** : R = Ph) (**14** : R = CH_3; **17** : R = Ph) (**15** : R = CH_3; **18** : R = Ph)

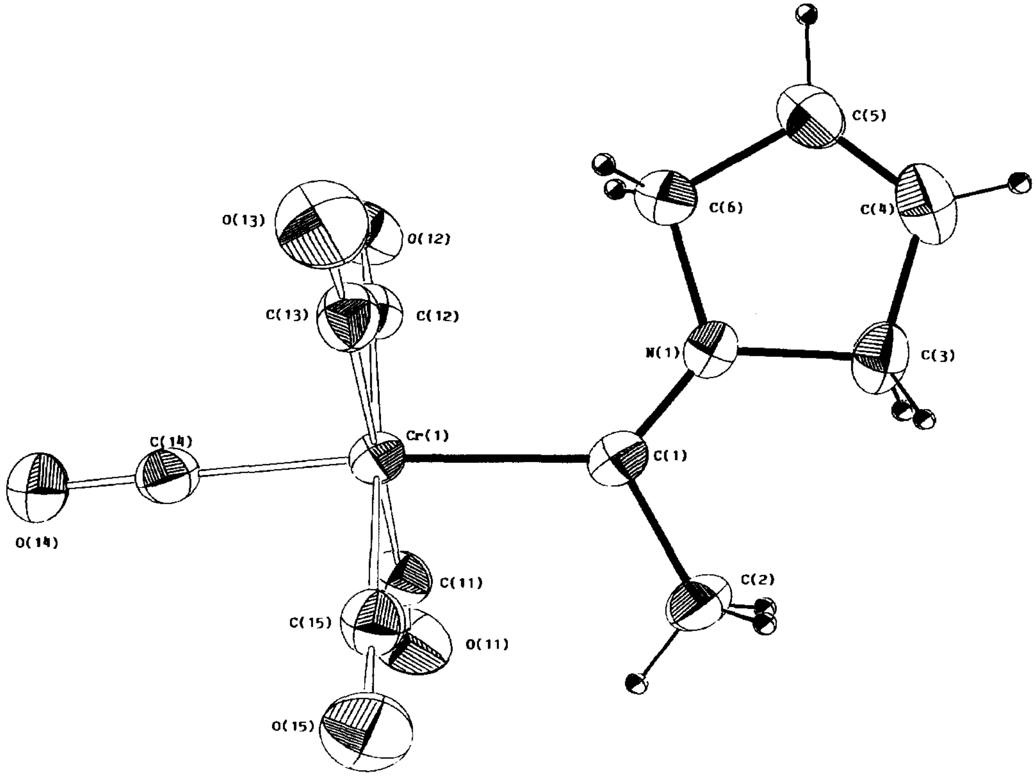


Fig. 1. ORTEP projection for complex **13**.

Suitable crystals of **14** were grown from CH_2Cl_2/EtOH. An ORTEP view of **13** is shown in Figure 1, and of **14** in Fig. 2. It confirms that the carbene moiety has been inserted into one of the N–CH_2 bonds of **13**, and complex **14** is thus the result of an insertion of alkyne and CO combined with an unexpected rearrangement.

Treatment of complex **14** in boiling pyridine for 4 h gives **15**, as white crystals (m.p. 122° C). The ^{1}H NMR spectrum of the product shows the presence of 10 aromatic protons (multiplet at 7.30 ppm), a disubstituted double bond at 5.89 ppm, two magnetically different NCH protons at 4.70 and 3.69 ppm, a CH_2 group at 2.43 ppm, and finally a methyl group on a tertiary carbon atom, at 1.30 ppm.

Similar behaviour is observed for complex **16** which upon reaction with diphenylacetylene gives a mixture of **17** (32.6%, m.p. 95° C) and **18** (49.5%, m.p. 88° C). The ^{1}H NMR spectrum of **17** confirms the structural analogy between the methyl- and the phenyl-substituted compounds, but **17** is much less stable than compound **14** and undergoes rapid air oxidation in solution to give **18** directly.

Reaction of complexes 19 and 24

Tetrahydropyridine reacts at room temperature with methylethoxy and phenylethoxychromium(0) carbene complexes to give complexes **19** and **24**, respectively, in about 85–90% yield. Owing to the 1,3-dipolar structure of these carbene complexes and to the dissymetry of the cycloamine, they exist as pairs of *E*,*Z*-isomers around the carbon–nitrogen double bond. This shows up clearly in the ^{13}C NMR spectra where all signals but that from C(1) can be distinguished. For example, in the case

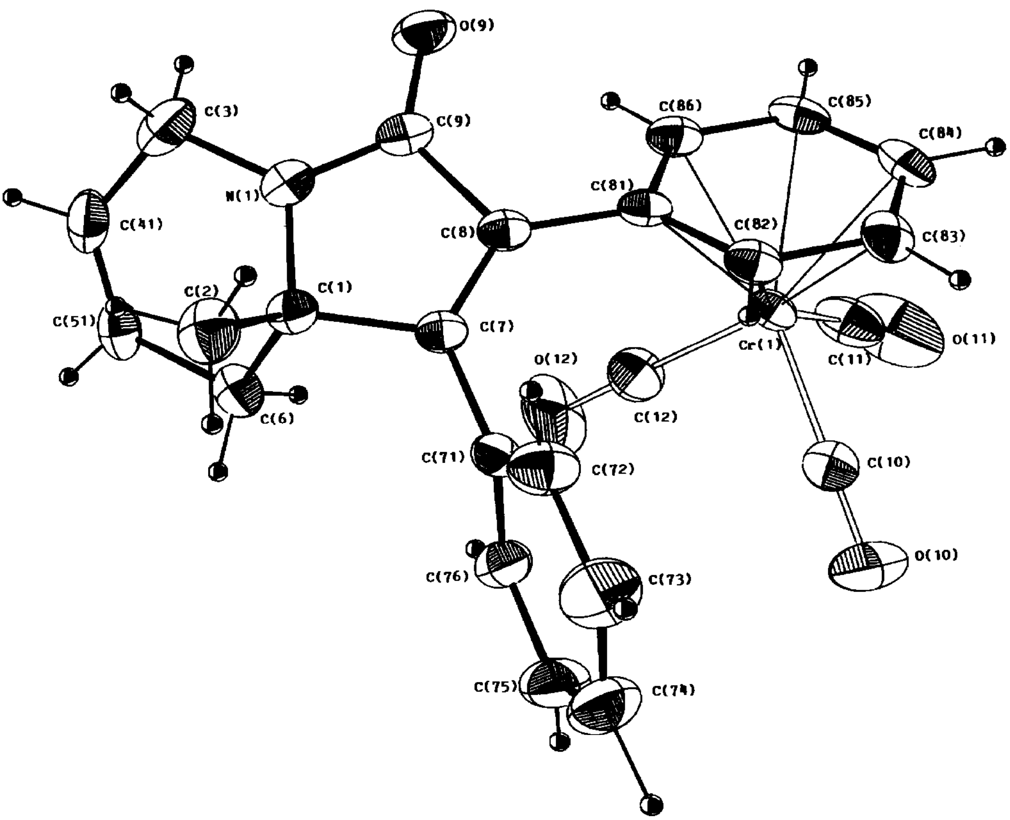


Fig. 2. ORTEP projection for complex **14**.

of **19**-*E*,*Z*, there are signals from the double bond carbons at 126.9, 122.3, 125.7 and 124.8 from C(6) at 27.04 and 27.06, from C(4) at 39.6 and 38.2, from C(3) at 50.1 and 49.6, and from C(7) at 58.3 and 61.4 ppm.

Complex **19** reacts with PhC≡CPh in boiling benzene during 12 h to give two new complexes. These were separated on silica gel and fully characterized by their spectroscopic data and by X-ray diffraction studies. The faster moving complex was assigned structure **20** on the following grounds. Firstly the mass and the IR spectra indicate that this complex is the result of the insertion of the alkyne and of CO into **19**. The presence of an arenechromium moiety is also present in the ^{1}H and ^{13}C NMR spectra with ^{1}H signals at 6.14, 5.83 and 4.35 ppm, and ^{13}C signals at 232.7, 93.9, 93.5, 92.0, and 91.3 ppm. The signals from two non-equivalent hydrogens on the carbon–carbon double bond appear at 5.66 and 5.24 ppm. Again the methyl group of the starting complex gives rise to a singlet at high field, and this rules out a rearrangement of the framework. The structure of this complex was confirmed by an X-ray diffraction study which showed that the type of rearrangement noted in the previous example had taken place, giving in this case a 5,7 fused ring system. An ORTEP view is shown in Fig. 3.

The second complex was assigned structure **21**. The presence of the CO group of the arenechromium and that of a methyl group on a quaternary carbon atom were established as for complexes **14**, **17** and **20**. There is a striking difference however, in the ^{1}H NMR spectrum, where signals due to a vinyl group are clearly evident, and

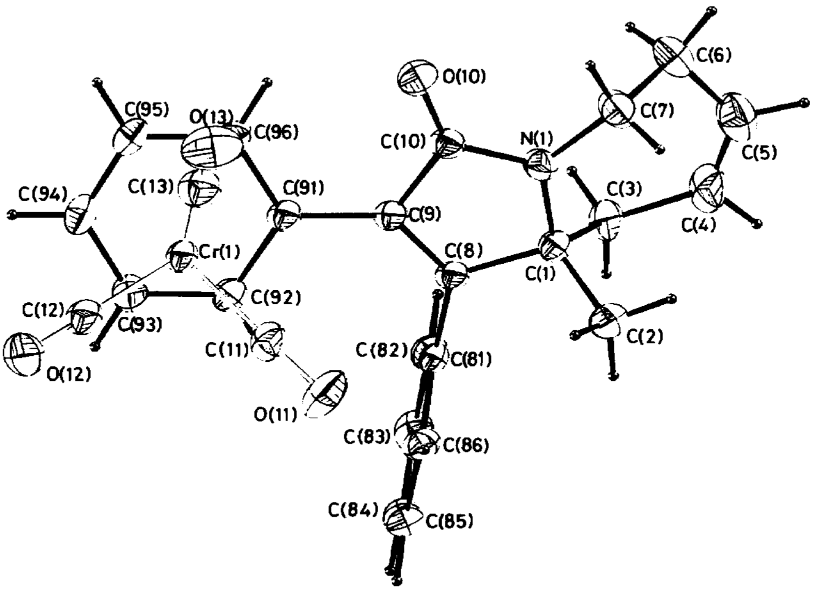
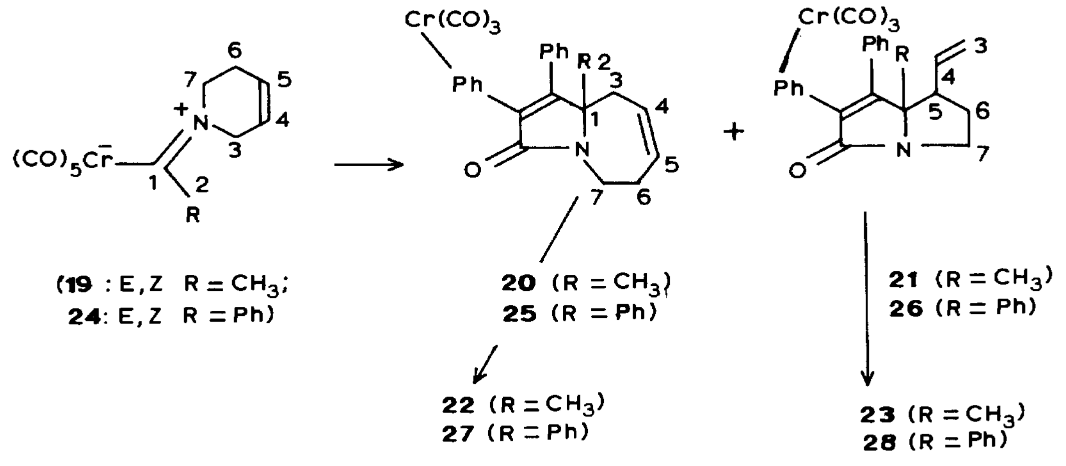


Fig. 3. ORTEP projection for complex **20**.

thus the disubstituted double bond of the starting complex **19** has been transformed into a mono-substituted double bond. Structure **21** was also confirmed by an X-ray diffraction. The ORTEP view shown in Fig. 4: in the crystal **21** was associated with one molecule of the solvent MeOH (which can be observed in the ^1H NMR spectrum), the solvent being associated through a hydrogen bond with the carbonyl group of the ketone.

The $Cr(CO)_3$ groups in **20** and **21** can be removed by treatment with boiling pyridine. Thus complex **20** gives **22** (m.p. 168° C), which was fully characterized from its NMR spectrum, which shows signals due to 10 hydrogens at 7.3 ppm, the olefinic hydrogens at 6.08 and 5.77 ppm two non-equivalent NCH hydrogens at 4.49 and 3.09 ppm, and the remaining CH_2 group as a multiplet at 2.46 ppm. In the case



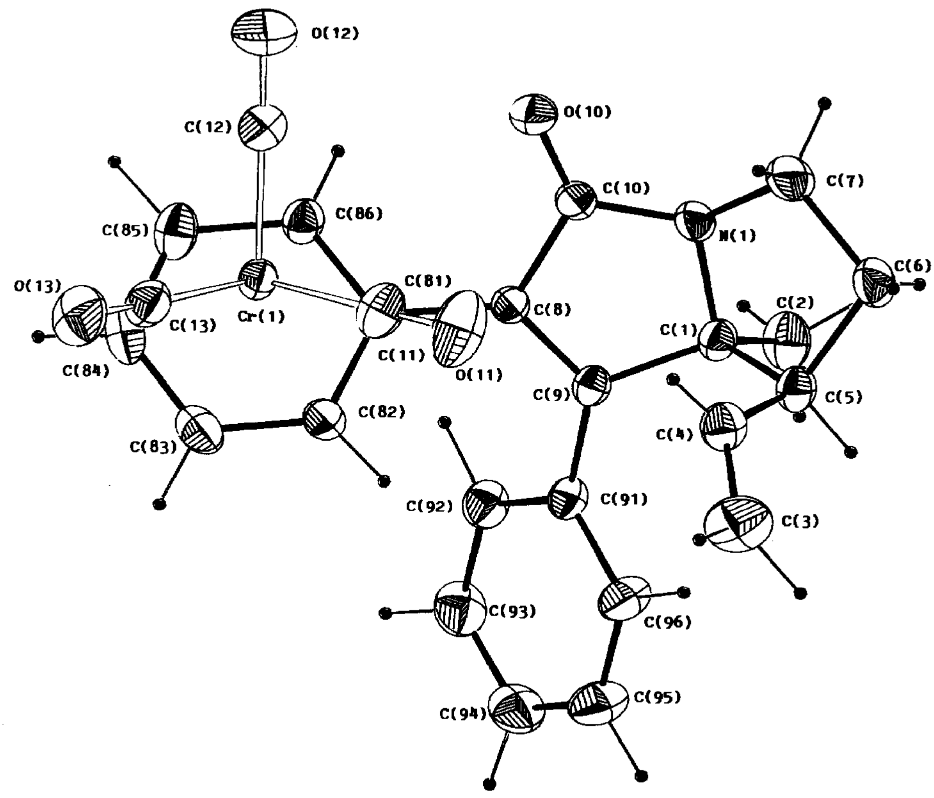


Fig. 4. ORTEP projection for complex **21**.

of compound **23**, all the hydrogen atoms are non-equivalent, as shown by the ^1H NMR spectrum (Fig. 5) recorded at 200 MHz. Complex **24** reacts in the same way with PhC≡CPh, but gives, along with the expected complexes **25** and **26**, the $Cr(CO)_3$-free compounds **27** and **28**. The mixture was thus treated directly with pyridine and the major product of the reaction, the 5,5 fused ring system **28**, characterized by analysis and spectroscopic data.

Reaction of saturated cycloaminocarbene complexes 29 and 31 with PhC≡CPh

In order to ascertain whether or not the insertion reaction is limited to aminocarbene complexes containing a carbon–carbon double bond in the cycle, we investigated the reactions of complexes **29** and **31**, the first one a typical saturated complex and the second falling between a saturated and an unsaturated aminocarbene complex.

Reaction of complex 29. Complex **29** is obtained as pale-yellow crystals (m.p. 72 ° C, 90%) by aminolysis of the corresponding ethoxycarbene complex. In the ^1H NMR spectrum of **29**, the protons of the two $N{-}CH_2$, *E* and *Z* with respect to the metal, appear as two multiplets at 3.58 and 4.13 ppm, with the two CH_2 groups β to the nitrogen being almost equivalent.

The complex reacts with PhC≡CPh in boiling benzene to give, after 16 h, among other products, a crystalline complex (m.p. 120 ° C, 12%) the ^1H NMR spectroscopic data for which correspond to those of **14**, **20** and **21** showing signals from one phenyl group at 7.02 ppm (multiplet), one arenechromium group at 5.18 4.76 and

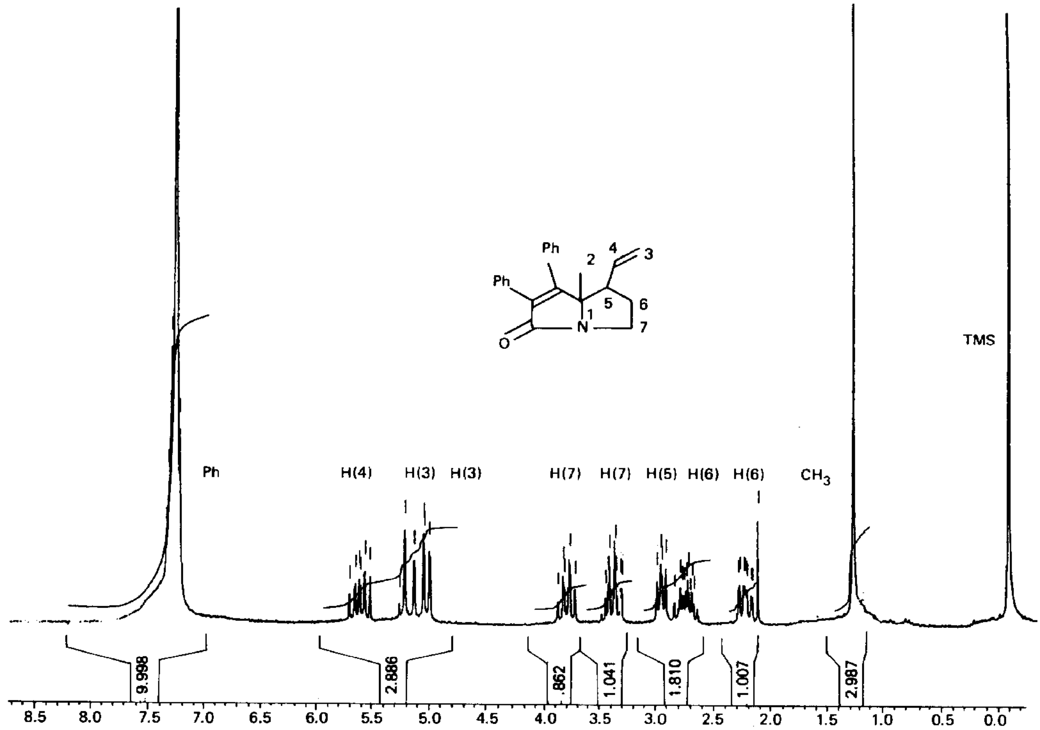
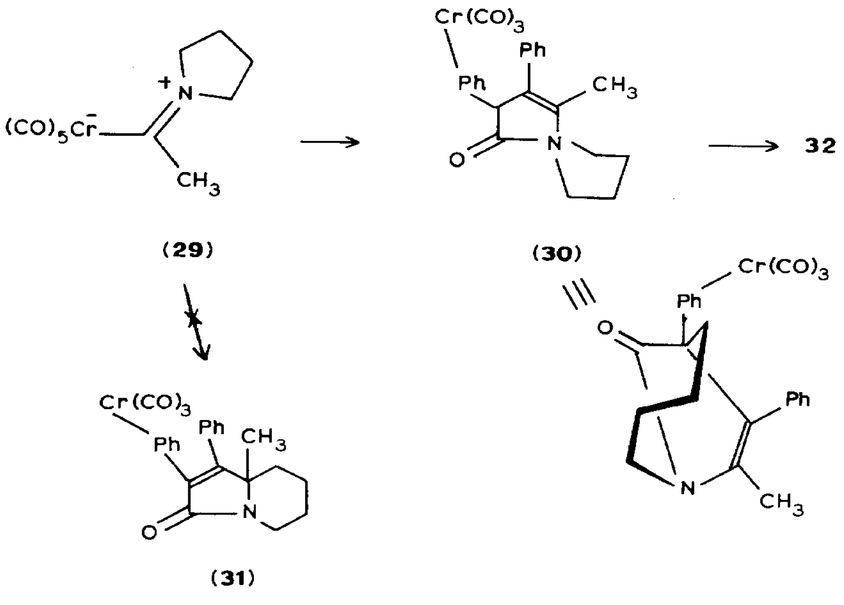


Fig. 5. ^1H NMR (200 MHz) of compound **23**.

4.25 ppm, two magnetically different N–CH protons, at 3.39 and 2.43 ppm, three CH_2 groups at 2.04, 1.88 and 1.29 ppm, and one CH_3 group as a singlet at 1.50 ppm. However the fact that the CH_3 group (δ 1.5 ppm) is on a carbon–carbon double bond rather than at a ring junction (δ 0.80 ppm in **14**), together with the appearance of an IR bond at 1760 cm^{-1}, indicated that this complex cannot have



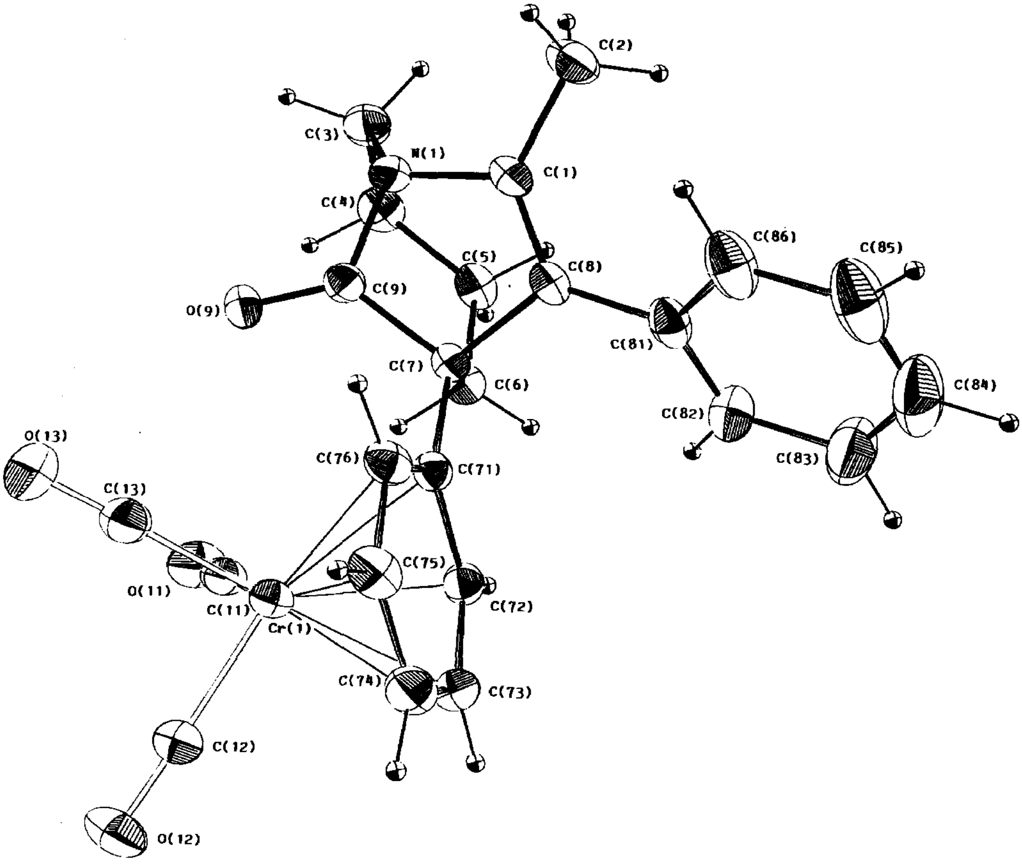


Fig. 6. ORTEP projection of complex **30**.

the expected structure **31**. This conclusion was confirmed by the X-ray study, which showed that the rearrangement had taken place, but that a new carbon–carbon coupling had occurred to give complex **30**.

An ORTEP view of this complex is shown in Fig. 6, and confirms that, as in the previous cases, insertion of PhC≡CPh had taken place along with C–N cleavage.

Reaction of complex 33. Complex **33** is readily prepared from commercially available methylaziridine. It exists as a 50/50 mixture of *E*/*Z* isomers: all the carbon atoms except for those of the CO ligand give rise to doublets in the ^{13}C NMR spectrum.

Complex **33** is much more reactive towards alkynes than the complexes considered above. The insertion reaction is complete within about 2 h in boiling benzene, and leads to two new complexes. The major product was isolated as bright-red crystals (m.p. 260 °C) by recrystallization of the mixture from hexane/methylene chloride. Its ^{1}H NMR spectrum shows that two molecules of alkyne have been inserted into the starting complex **33** and that the signals due to the $N-CH_2$ and the $CH-CH_3$ groups of the aziridine are still present. However, the chemical shift of the signal from the methyl group of the carbene, 2.48 ppm, indicates that it is located on a conjugated system. The IR spectrum is in agreement with the presence of a $Cr(CO)_3$ group and of a five-membered ring ketone (ν(CO) 1760 cm^{-1}).

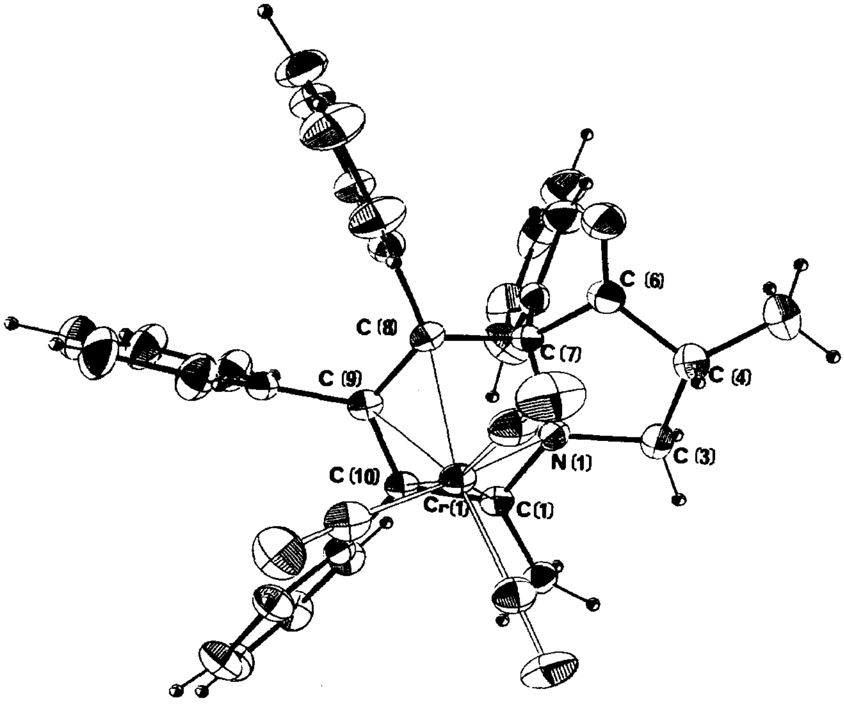
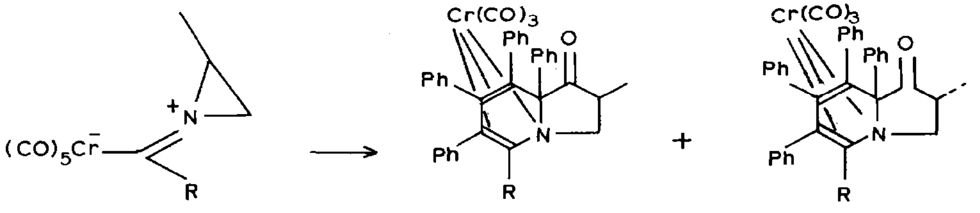


Fig. 7. ORTEP projection of complex 34.



(33: R = CH_3; 36: R = Ph)

(34: R = CH_3; 37: R = Ph)

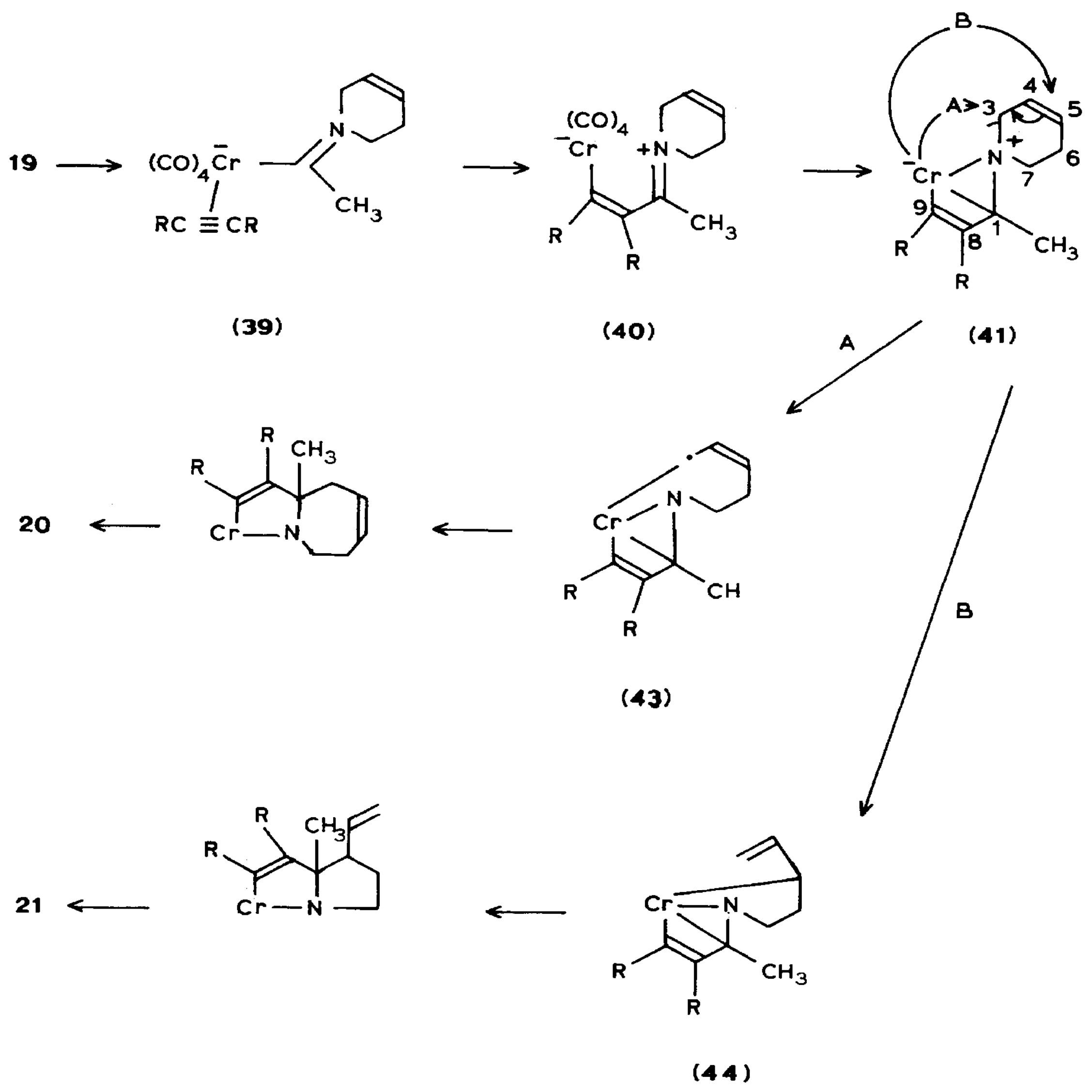
(35: R = CH_3; 38: R = Ph)

Taken together, these spectroscopic data are consistent only with structure 34 and this was verified by the X-ray diffraction study. The ORTEP view, in Fig. 7, confirms that two molecules of alkyne have been inserted, that the aziridine ring, like the other ring-systems, has been opened, and that a five-membered ring ketone is also present. Surprisingly, the $Cr(CO)_3$ group is bound both to the diene and to the nitrogen atom at the ring junction. According to the ^1H NMR spectrum, the minor product of the reaction (~ 5%), is the isomer 35 of 34.

Complex 36 shows the same behaviour towards PhC≡CPh and gives a mixture of complexes 37 and 38 in about 18% yield.

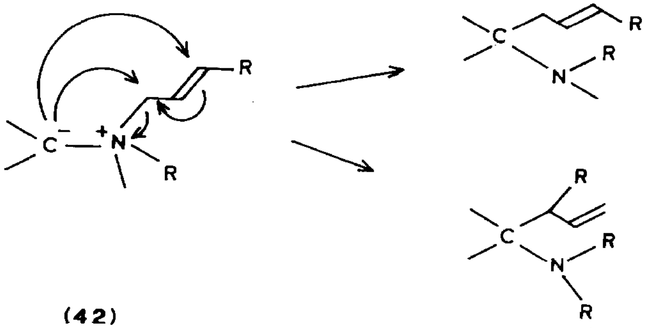
Discussion

All the results described above confirm that the ring-opening reaction, induced by the alkyne insertion is general. The structure of the products is highly dependent on the nature of the cycloamine and on the presence or absence of a double bond β to nitrogen. However a distinction has to be made the first three examples and the aziridine case. In the first three cases an unsaturated lactam is formed, but insertion of CO between the alkyne and the nitrogen is observed. A mechanism which could account for the reactions of complex **19**, for example, is as follows: The first step of all the insertion reactions is probably decoordination of one CO group by the alkyne to give the intermediate **39**. Insertion of the alkyne could then lead to the new 1,5-dipole **40**. Recoordination of the electron-deficient carbon–nitrogen double bond to the electron-rich, coordinatively unsaturated metal centre could then give complex **41**. This complex can be regarded as a chromium–nitrogen-centered 1,2 ylid. Such a structure is reminiscent of the well known organic carbon–nitrogen 1,2 ylids which promote the Stevens rearrangement [19,20], and so the intermediate **41** might undergo a rearrangement, as **42** does, to give on the other hand the seven-membered ring system via **43**, and on the other hand the five-membered ring system via **44** (allylic rearrangement). The presence of the metal centre then allows the



(39) (40) (41) (43) (44)

C(1)–C(3) or the C(1)–C(5) coupling and the CO insertion reaction to occur with ultimate formation of the α,β-unsaturated lactams. It is clear that the coupling reaction could also occur between C(3) and C(9) and this is observed in the transformation of complex **29** into complex **30**, via the intermediate **45**.



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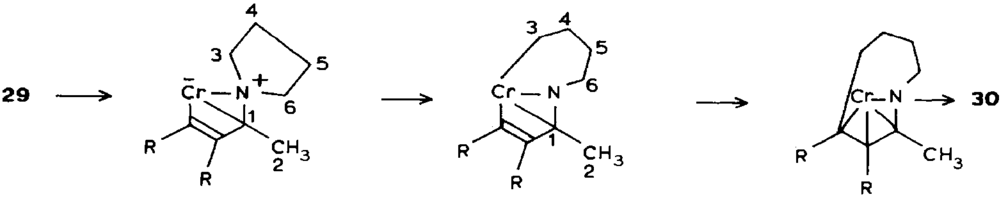
In the case of complex **33**, it is probable that the insertion of one molecule of alkyne would lead to very strained intermediates, and so there is insertion of two molecules of alkyne leading to the triene **46**, the electrocyclization of which could give **47**, and then, by CO insertion, complex **34**. It is noteworthy that in the case of



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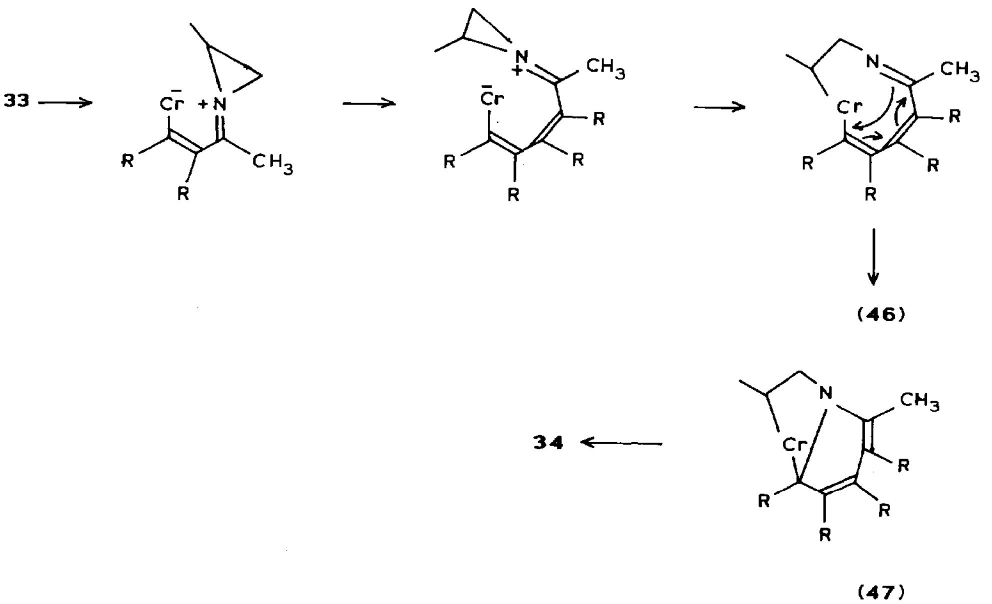

(46)

(47)

phenyl-substituted carbene complexes such as **16** and **24**, no benzannulation, the organometallic analog of the Sommelet–Hauser reaction, takes place [21].

In conclusion we note that we have discovered a new reaction promoted by transition metal carbene complexes which can be related to the organic Stevens rearrangement. Since this reaction can be used with a wide variety of complexes and substrates, it may find application in the field of alkaloid synthesis.

Work is in progress to explore the scope and limitations of this new reaction and to establish its mechanism.

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 or WM 500 spectrometer. IR spectra were recorded with a Beckman 4240 spectrophotometer and mass spectra with a Kratos MS 3P. Melting points were determined on a Reichert Köfler block and are uncorrected.

Complex 13. To a solution of $(CO)_5Cr{=}C(CH_3)(OCH_2CH_3)$ (5.7 g, 2.16×10^{-2} mol) in Et_2O (250 ml) at room temperature was added 3-pyrroline (4.5 ml) (a commercial sample containing 20% of piperidine). The reaction was monitored by TLC. After 15 min, all the starting complex had disappeared. Evaporation of the solvent gave complex **13** (6.2 g, 10%), which was recrystallized from $EtOH/CH_2Cl_2$ to give yellow crystals (m.p. 107 °C).

^1H NMR (200 MHz, C_6D_6): δ 4.98 (2H, dm, J 1.6 Hz), 4.36 (2H, s, C(3)), 2.90 (2H, s, C(6)), 2.00 (3H, s, C(2)). ^{13}C NMR (25 MHz, C_6D_6): δ 270.6 (C(1), 223.5, 218.7 (CO), 125.8 and 124.0 (C(5)–C(4)), 65.3 (C(3)), 57.7 (C(6)), 40.7 (C(2)); m/z: 287 (M^+) (Found: C, 46.1; H, 2.98; N, 4.81. $C_{11}H_9NO_5Cr$ calcd.: C, 45.99; H, 3.13; N, 4.88%).

Complex 14. A solution of complex **13** (2.9 g, 10^{-2} mol), and $PhC{\equiv}CPh$ (1.8 g, 10^{-2} mol) in benzene (150 ml) was refluxed for 12 h. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with PE/acetone (92/8) first gave product **15** (0.7 g). Elution with PE/acetone (80/20) then gave complex **14** (1.2 g, total yield 58%).

Complex **14**: orange crystals, m.p. 188 °C; IR 1970, 1900 and 1680 cm^{-1} (ν(CO)); ^1H NMR (C_6D_6, 200 MHz) δ 7.00 (5H, m), 5.98 (2H, m, CH=CH), 5.25 and 4.34 (5H, m, Ar–Cr), 4.64 (1H, dd, J 19.2 Hz, NCH), 3.23 (1H, dd, J 19.2 Hz, NCH), 1.92 (1H, dd, J 16.8 Hz, C(3)–H), 1.56 (1H, dd, J 16.8 Hz, C(3)–H), 0.85 (3H, s, CH_3). ^{13}C NMR (50.1 MHz, $CDCl_3$): δ 232.7 (CO), 161.7 (CO, lactam), 133.0, 129.3, 129.0, 128.1 and 126.1 (C aromatic), 123.4 and 121.7 (C(4)–C(5)), 98.7 ($NCCH_2$), 94.1, 93.7, 92.3, 91.2, 91.1 (Ar–Cr), 61.0 (N–C(CH_3)), 38.0 (N–CH_2), 20.4 (CH_3); m/z: 437 (M^+) (Found: C, 66.06; H, 4.17; N, 3.08. $C_{24}H_{19}NO_4Cr$ calcd.: C, 65.90; H, 4.35; N, 3.20%.)

Compound 15. Complex **14** (1.2 g) was refluxed in pyridine (30 ml) for 6 h. Evaporation of the solvent and chromatography of the residue on silica gel with 80/20 PE/CH_2Cl_2 as eluent gave a white solid (0.94 g, 95%). Recrystallization from $EtOH/CH_2Cl_2$ gave white crystals m.p. 122°C; IR 1680 cm^{-1} (ν(CO)); ^1H NMR (200 MHz, $CDCl_3$) σ 7.31 (10H), 5.8 (2H, m), 4.70 (1H, d, N–CH), 3.70 (1H, d, N–CH), 2.43 (2H, m, CH_2), 1.30 (3H, s, CH_3) m/z: 301 (M^+). (Found: C, 82.80; H, 6.36; N, 4.56. $C_{21}H_{19}NO$ calcd.: C, 83.7; H, 6.97; N, 4.65%.)

Complex 16. Pyrroline (2 equiv.) was added to a solution of $(CO)_5Cr{=}C(Ph)(OCH_2CH_3)$ (3 g, 92 mmol), in Et_2O (150 ml) at room temperature. After 30 min the solvent was evaporated and the residue chromatographed on silica gel with 80/20 PE/CH_2Cl_2 as eluent to give complex **16** (3.25 g, 100%). Recrystallization from PE/CH_2Cl_2 gave yellow crystals m.p. 108–110°C. ^1H NMR (200 MHz, $CDCl_3$): δ 7.45 (2H, m), 7.720 (1H, m), 6.35 (2H, m), 6.10 (1H, m), 5.80 (1H, m), 5.05 (2H, s, N–CH_2), 4.00 (2H, s, N–CH_2). m/z: 349 (M^+).

Complex 17. A solution of complex **16** (3 g, 8.6 mmol), and $PhC{\equiv}CPh$ (1.8 g) was refluxed in benzene for 12 h. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with PE/acetone (90/10) first gave complex **17** (1.4 g); elution with PE/acetone (80/20) and then the organic product **18** (1.55 g) as a white solid.

Complex **17**, m.p. 105–110°C (dec.). ^1H NMR (200 MHz, $CDCl_3$): δ 7.42, 6.73 (10H, m), 6.23, 5.37, 5.27, 4.46 and 4.20 (5H, m, Ar–Cr), 5.81 (2H, m), 4.62 (1H, d, J 16 Hz), 3.31 (1H, d, J 16 Hz), 2.92 (1H, d, J 16 Hz), 2.38 (1H, d, J 16 Hz). m/z: 499 (M^+).

Compound 18. A solution of complex **17** (1.4 g) was refluxed in pyridine for 8 h. Evaporation of the solvent followed by chromatography on silica gel with 80/20 PE/CH_2Cl_2 as eluent gave a white solid (1.04 g), which was recrystallized in $MeOH/CH_2Cl_2$ to give white crystals m.p. 88–90°C; IR 1680 cm^{-1} (ν(CO)). ^1H NMR (200 MHz, $CDCl_3$) δ 7.24, 6.71 (15H, m), 5.87 (1H, m), 5.71 (1H, m), 4.65 (1H, d, J 18 Hz), 3.31 (1H, d, J 18 Hz), 3.07 (1H, d, J 18 Hz), 2.46 (1H, d, J 18 Hz), m/z 363 (M^+). (Found: C, 82,52; H, 5.92; N, 3.61. $C_{28}H_{25}NO_2$ calcd.: C, 82.02, H, 6.3; N, 3.54 %.)

Complex 19 E,Z. Tetrahydropyridine (1.8 g, 21.7 mmol) was added at room temperature to a solution of $(CO)_5Cr(CH_3)(OCH_2CH_3)$ (3.8 g, 14.3 mmoles) in Et_2O (150 ml). After 6 h the solvent was evaporated to leave an oil (3.3 g, 74%). Recrystallization from PE/CH_2Cl_2 gave crystals of one of the isomers; m.p. 70–71°C. ^1H NMR (200 MHz, C_6D_6) δ 5.38 (1H, m), 4.80 (1H, m), 3.94 (2H, m), 2.96 (2H, s), 2.10 (3H, s), 1.89 (2H, m). ^{13}C NMR (50.1 MHz, $CDCl_3$): δ 267.0 (C(1)), 223.6, 217.8 (CO), 126.9 (124.8 (C=C), 58.3 (C(3)), 50.1 (C(7)), 39.7 (C(2)), 27.4 (C(6)). m/z 301 (M^+)

Complexes 20 and 21. A solution of complex **19** (0.8 g, 2.7 mmol) and $PhC{\equiv}CPh$ (0.8 g, 3 mmol) in benzene was refluxed for 12 h. After evaporation of the solvent the residue was chromatographed on silica gel. Elution with PE/acetone (90/10) gave a mixture of complexes **20** and **21**. Careful chromatography of this mixture gave pure samples of both complexes (total yield 0.66 g, 58%).

Complex 20. Yellow crystals, m.p. 168°C. ^1H NMR (200 MHz, C_6D_6): δ 7.10 (5H, m), 6.14 (1H, d), 5.83 (1H, m), 5.66 (1H, m), 5.26 (1H, m), 4.35 (4H, m), 2.53 (1H, m), 2.15 (1H, m), 1.95 (2H, d), 1.80 (1H, m), 0.93 (3H, s). ^{13}C NMR (50.1 MHz, C_6D_6): δ 232.7 ($Cr(CO)_3$), 161.1 (C + O), 133.2, 131.1, 129.2, 128.9, 128.4, 127.6 (Ar), 126.1, 125.4 (C(8), C(9)) 98.9, 93.9, 93.5, 92.0, 91.3 (Ar–Cr), 65.8 (C(1)), 36.9 (C(7)), 36.0 (C(3)), 28.1 (C(6)), 19.7 (C(2)). m/z 395 ($M^+ - 2CO$).

Complex 21. Orange-yellow crystals, m.p. 166°C. IR 1980, 1900 and 1680 cm^{-1} (ν(CO)). ^1H NMR (200 MHz, C_6D_6): δ 7.15 (5H, m), 6.14 (1H, d), 5.74 (1H, dq), 5.10 (1H, d), 5.05 (1H, m), 4.98 (1H, d), 4.52 (2H, m), 4.10 (1H, t), 3.78 (1H, m), 3.25 (3H, s, CH_3OH), 3.02 (1H, m), 2.42 (1H, m), 2.08 (1H, m), 1.70 (1H, m), 0.88 (3H, s). ^{13}C NMR (50.1 MHz, C_6D_6): δ 232.5 ($Cr(CO)_3$), 170.9 (C=O), 136.8, 132.9, 129.4, 129.1, 128.8, 128.2 (Ar), 116.2, 117.7 (C(8), C(9)), 96.3, 93.5, 92.7, 90.3, 89.6, (Ar–Cr), 75.1 (C(1)), 49.2 (C(7)), 40.0 (C(5)), 34.8 (C(6)), 23.0 (C(2)). m/z 395 $(M^+ - 2CO)$. (Found: C, 82.73; H. 6.88; N, 4.12. $C_{25}H_{21}O_4NCr$ calcd.: C, 82.24; H, 6.5; N, 4.3%.)

Compound ***22.*** Complex **20** (0.2 g) was refluxed in pyridine for 12 h. After evaporation of the solvent the residue was chromatographed on silica gel with 80/20 PE/CH_2Cl_2 as eluent to give white crystals of **22** (0.12 g); m.p. 168–170 °C. IR 1680 cm^{-1} (ν(CO)). ^{1}H NMR (200 MHz, C_6D_6): δ 7.40 (10H, m), 6.10 (1H, m), 5.71 (1H, m), 4.49 (1H, d), 3.09 (1H, m), 2.42 (4H, m), 1.47 (3H, s). m/z 321 (M^+). (Found: C, 80.08; H, 6.73; N, 4.09. $C_{22}H_{21}ON$ calcd.: C, 82.2; H, 6.5; N, 4.3%.)

Compound ***23.*** Complex **21** (0.45 g) was refluxed in pyridine for 12 h, and work up as for compound **22** gave **23** (0.3 g) as white crystals, m.p. 180 °C; IR 1680 cm^{-1} (ν(CO)). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.28 (10H, m), 5.59 (1H, dt), 5.15 (2H, dd), 3.80 (1H, q), 3.40 (1H, t), 3.00 (1H, t), 2.77 (1H, m), 2.28 (1H, m), 1.32 (3H, s). m/z 321 (M^+) (Found: C, 82.73; H, 6.88; N, 4.17. $C_{22}H_{21}ON$ calcd.: C, 82.24; H, 6.5; N, 4.3%.)

Complex ***24*** *E,Z.* Tetrahydropyridine (2 g) was added to a solution of $(CO)_5Cr{=}C(Ph)(OCH_2CH_3)$ (4 g, 12 mmol) in Et_2O (100 ml). After 2 h the solvent was evaporated and the residue purified as described for compound **22** over silica gel to give (E,Z) **24** as a yellow solid (3.9 g, 87%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.32, 6.71 (5H, m), 5.95 (3H, m), 5.42 (1H, m), 5.0 (2H, s), 4.60 (2H, t), 3.89 (2H, m), 3.58 (2H, t), 2.65 (2H, m), 2.15 (2H, m). ^{13}C NMR (50.1 MHz, $CDCl_3$): δ 272.0 (C(1)), 224.0, O, 217.0 (CO), 128.6, 126.6, 125.9, 124.1, 123.0, 119.1, 118.9 (2C=C, C(aromatic)). 59.7, 57.2, 54.1, 51.9 (2N–C), 28.0, 27.5 (2 C–*C*–C=). m/z 363 (M^+).

Complexes ***25*** *and* ***26.*** A solution of complex **24** (3.2 g, 8.7 mmol) and PhC≡CPh (1.8 g) in benzene (50 ml) was refluxed for 8 h. After evaporation of the solvent the residue was chromatographed on silica gel. Elution with PE/acetone (90/10) gave a mixture of complexes **25** and **26** and the organic products **27** and **28** (2.2 g). A sample of **26**, the most important product, was purified by TLC.

Compound **26**, orange crystals, m.p. 65 °C; IR 1680 cm^{-1} (ν(CO)). ^{1}H NMR (200 MHz, C_6D_6): δ 7.65, 7.01 (15H, m), 5.75 (1H, dt, $CH{=}CH_2$), 5.05 (2H, dd, $CH{=}CH_2$), 3.90 (1H, q, N–CH), 3.25 (1H, q, N–CH), 3.08 (1H, m, $CH{-}CH{=}CH_2$), 1.7 (2H, m, CH_2). m/z 377 (M^+).

Complex ***29.*** Pyrrolidine (1.5 g) was added to a solution of $(CO)_5Cr{=}C(CH_3)(OCH_2CH_3)$ (2.64 g, 26.4 mmol) in Et_2O (50 ml) at room temperature. After 5 h the solvent was evaporated chromatography of the residue on silica gel with 80/20 PE/CH_2Cl_2 as eluent gave complex **29** (2.4 g, 86%) as a yellow solid, m.p. 72 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.13 (2H, m, $N{-}CH_2$), 3.58 (2H, m, $N{-}CH_2$), 2.66 (3H, s, CH_3), 2.11 (4H, m, $CH_2{-}CH_2$). ^{13}C NMR (50.1 MHz, $CDCl_3$): δ 268.9 (C(1)), 224.1, 218.9 (CO), 61.24 (N–C), 53.24 (C–N), 41.41 (CH_3), 26.11 (CH_2), 25.73 (CH_2). m/z 289 (M^+).

Complex ***30.*** A solution of complex **29** (1.45 g, 10 mmol) and PhC≡CPh (1 g) in benzene (50 ml) was refluxed for 12 h. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with PE/acetone (95/5) gave complex **30** (0.25 g, 12%) as a yellow solid. Recrystallization from PE/CH_2Cl_2 gave yellow crystals, m.p. 120 °C. IR 1980, 1890, 1740 cm^{-1} (ν(CO)). ^{1}H NMR (200 MHz,

Table 1

Crystallographic data

	$Cr(CO)_5(C_6H_9N)$ **(13)**	$Cr(CO)_3(C_{21}H_{19}ON)$ **(14)**	$Cr(CO)_3(C_{21}H_{21}ON)$ **(30)**
fw	287.2	437.4	439.4
crystal dimensions (mm)	0.4×0.35×0.2	0.5×0.5×0.18	0.5×0.5×0.1
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/a$
a (Å)	12.975(3)	13.011(4)	14.059(4)
b (Å)	11.811(2)	11.196(6)	12.746(1)
c (Å)	8.318(3)	14.772(2)	12.498(5)
β (°)	96.80(1)	108.24(4)	110.76(1)
V (Å^3)	1266	2044	2094
Z	4	4	4
D_c (g cm^{-3})	1.51	1.42	1.39
μ (Mo-K_α) (cm^{-1})	8.91	5.74	5.6
diffractometer	PW1100	PW1100	PW1100
reflexions measured	2326	3575	3497
reflexions merged	2144 (0.0243)	3359 (0.0159)	3240 (0.0182)
reflexions kept ($F > 3\sigma(F)$	1923	2639	2442
R	0.026	0.051	0.036
R_w	0.027	0.052	0.037
data/parameters	10	8.2	7.3

	$C_{25}H_{21}O_4NCr$ **20**	$C_{25}H_{21}O_4Cr$, CH_3OH **21**	$C_{37}H_{29}O_4NCr$ **34**
fw	451.4	483.5	603.6
crystal dimensions	0.25×0.20×0.1	0.32×0.32×0.45	0.7×0.3×0.06
crystal system	monoclinic	triclinic	monoclinic
space group	$P21/c$	$P\bar{1}$	$P21/a$
a (Å)	10.994(4)	9.057(2)	18.189(4)
b (Å)	19.117(4)	10.955(2)	11.255(6)
c (Å)	11.240(6)	13.983(4)	15.018(1)
α (°)	90.0	73.96(2)	90.0
β (°)	118.60(3)	77.36(2)	94.68(2)
γ (°)	90.0	64.09(2)	90.0
V (Å^3)	2074	1192	3058
Z	4	2	4
D_c (g cm^{-3})	1.45	1.347	1.31
μ(Mo-K_α) (cm^{-1})	5.68	5.02	4.03
diffractometer	CAD4	CAD4	CAD4
reflexions measured	3846	4212	5223
reflexions merged (R)	3646(0.032)	4035(0.010)	4885(0.024)
reflexions kept ($I > 3\sigma(I)$)	2049	3338	3267
R	0.0511	0.042	0.042
R_w	0.0591	0.043	0.043
data/parameters	7.3	9.7	6.8

C_6D_6): δ 7.10, 6.61 (5H, m), 5.18, 4.77, 4.39, 4.28, 4.10 (5H, Ar–Cr), 3.39 (1H, dd), 2.43 (1H, m), 2.02 (2H, m), 1.90 (2H, m), 1.50 (3H, s), 1.23 (2H, m). m/z 439 (M^+). Complex **30** slowly decomposes into complex **32**, the structure of which has not yet been established.

Complex 33. To a solution of $(CO)_5Cr{=}C(CH_3)(OCH_2CH_3)$ (5 g, 19 mmol) in Et_2O (100 ml) was added freshly distilled methylaziridine (two-fold excess, 2 ml). After 1 h work-up, as described for complex **29**, a yellow oil was formed (4.5 g, 86%).

33*E*. δ ^{13}C NMR (50.1 MHz, C_6D_6): δ 16.1 (C(5)), 30.9 (C(2)), 35.0 (C(4)), 39.6 (C(3)), 218.6, 223.6 (CO), 265 (C(1)).

33*Z*. ^{13}C NMR: δ 16.3 (C(5)), 32.4 (C(2)), 36.0 (C(4)), 40.5 (C(3)), 218.6, 223.6 (CO), 268 (C(1)). *m/z* 275 (M^+) (Found: C, 43.97; H, 3.13; N, 5.23. $C_{10}H_9O_5NCr$ calcd.: C, 43.64; H, 3.27; N, 5.09%.)

Complex 34. A solution of complex **33** (2 g, 7.2 mmol) and $PhC{\equiv}CPh$ (1.5 g) in benzene (50 ml) was refluxed for 2 h. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with PE/CH_2Cl_2 (80/20) gave a red solid (1.25 g, 26%). Recrystallization from PE/CH_2Cl_2 gave bright red crystals of complex **34**, m.p. 260 °C; IR 1950, 1880, 1850 and 1760 cm^{-1} (ν(CO)). ^1H NMR (200 MHz, CD_2Cl_2): δ 7.3 (20H, m), 3.51 (1H, t), 3.46 (1H, m), 3.12 (1H, t), 2.31 (3H, s), 1.19 (3H, d). ^{13}C NMR (50.1 MHz, CD_2Cl_2): δ 230.0 ($Cr(CO)_3$), 206.5 (=CO), 137.4–126.4 (Ar), 117.6, 108.6, 104.6, 83.0 (C(8), C(9), C(10), C(1)), 76.6 (C(7)), 54.1 (C(3)), 42.6 (C(4)), 17.5 (C(2)), 13.7 (C(5)). IR 1900, 1880, 1850, 1760 cm^{-1} (KBr, ν(CO)). *m/z* 603 (M^+). Also 0.05 g on complex **35** was obtained as a red powder. ^1H NMR (200 MHz, $CDCl_3$): δ 7.25 (20H), 3.69 (1H, t, N–CH), 2.95 (1H, d, N–CH), 2.5 (1H, m, $CH{-}CH_3$), 2.40 (3H, s, CH_3), 1.71 (3H, d, $CH{-}CH_3$).

Complex 36. To a solution of $(CO)_5Cr{=}C(Ph)(OCH_2CH_3)$ (4.4 g, 13 mmol) in Et_2O (50 ml) was added freshly distilled methylaziridine (1.4 ml). After 2 h work-up, as described for complex **29**, gave complex **36** (2.65 g, 58%) as an oil. ^1H NMR (200 MHz, C_6D_6): δ 7.03 (5H, m), 2.55 (1H, m), 2.36 (1H, m), 1.99 (1H, m), 1.11 (3H, s), 0.29 (3H, d).

Table 2

Main interatomic distances (Å) and bond angles (°) for $Cr(CO)_5(C_6H_9N)$ (**13**)

Cr(1)–C(11)	1.896(3)	C(11)–O(11)	1.135(3)
Cr(1)–C(12)	1.893(3)	C(12)–O(12)	1.138(3)
Cr(1)–C(13)	1.892(3)	C(13)–O(13)	1.134(3)
Cr(1)–C(14)	1.863(3)	C(14)–O(14)	1.149(3)
Cr(1)–C(15)	1.894(3)	C(15)–O(15)	1.140(3)
Cr(1)–C(1)	2.123(2)	C(1)–C(2)	1.510(3)
C(1)–N(1)	1.300(3)	N(1)–C(3)	1.498(3)
N(1)–C(6)	1.474(3)	C(3)–C(4)	1.473(4)
C(4)–C(5)	1.296(4)	C(5)–C(6)	1.483(4)
C(12)–Cr(1)–C(11)	88.0(1)	C(13)–Cr(1)–C(12)	90.4(1)
C(14)–Cr(1)–C(11)	89.5(1)	C(14)–Cr(1)–C(12)	89.1(1)
C(14)–Cr(1)–C(13)	89.9(1)	C(15)–Cr(1)–C(11)	91.7(1)
C(15)–Cr(1)–C(13)	89.8(1)	C(15)–Cr(1)–C(14)	88.1(1)
O(11)–C(11)–Cr(1)	178.3(3)	O(12)–C(12)–Cr(1)	176.4(2)
O(13)–C(13)–Cr(1)	177.2(2)	O(14)–C(14)–Cr(1)	179.4(2)
O(15)–C(15)–Cr(1)	178.4(2)		
C(6)–N(1)–C(3)	108.8(2)	C(4)–C(3)–N(1)	102.6(2)
C(5)–C(4)–C(3)	113.4(3)	C(6)–C(5)–C(4)	111.2(3)
C(5)–C(6)–N(1)	103.9(2)		

Table 3

Fractional atomic parameters for $Cr(CO)_5(C_6H_9N)$ (13)

Atom	x/a	y/b	z/c	U_{eq}
Cr(1)	0.08253(3)	0.15674(3)	0.23976(4)	0.0389
C(11)	0.0137(2)	0.0200(2)	0.2807(3)	0.0512
O(11)	−0.0253(2)	−0.0634(2)	0.3048(2)	0.0731
C(12)	0.1879(2)	0.1157(2)	0.4067(3)	0.0511
O(12)	0.2533(2)	0.0875(2)	0.5014(3)	0.0736
C(13)	0.1550(2)	0.2912(2)	0.2017(3)	0.0533
O(13)	0.2003(2)	0.3696(2)	0.1741(3)	0.0795
C(14)	0.1547(2)	0.0805(2)	0.0919(3)	0.0510
O(14)	0.1984(1)	0.0337(2)	−0.0003(2)	0.0700
C(15)	−0.0197(2)	0.1934(2)	0.0658(3)	0.0516
O(15)	−0.0803(2)	0.2135(2)	−0.0410(2)	0.0778
C(1)	−0.0127(2)	0.2384(2)	0.3953(3)	0.0404
C(2)	−0.1286(2)	0.2212(3)	0.3635(4)	0.0625
N(1)	0.0144(1)	0.3042(2)	0.5182(2)	0.0412
C(3)	−0.0574(2)	0.3619(3)	0.6203(3)	0.0568
C(4)	0.0143(3)	0.4289(3)	0.7334(4)	0.0683
C(5)	0.1111(3)	0.4136(3)	0.7147(3)	0.0674
C(6)	0.1223(2)	0.3322(3)	0.5823(4)	0.0577

Complex 37. A solution of complex **36** (2 g, 6 mmol) and PhC≡CPh (2.2 g) in benzene (50 ml) was refluxed for 2 h. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with PE/CH_2Cl_2 (60/40) gave complex

Table 4

Main interatomic distances (Å) for $Cr(CO)_3(C_{21}H_{19}ON)$ (14)

Cr(1)–C(11)	1.828(6)	C(11)–O(11)	1.157(6)
Cr(1)–C(12)	1.829(5)	C(12)–O(12)	1.147(6)
Cr(1)–C(13)	1.837(5)	C(13)–O(13)	1.155(6)
Cr(1)–C(81)	2.248(4)	Cr(1)–C(84)	2.218(4)
Cr(1)–C(82)	2.211(4)	Cr(1)–C(85)	2.217(5)
Cr(1)–C(83)	2.209(4)	Cr(1)–C(86)	2.223(5)
C(1)–C(2)	1.524(7)	N(1)–C(1)	1.456(6)
N(1)–C(3)	1.453(6)	C(1)–C(6)	1.545(6)
C(3)–C(41)	1.52(1)	C(3)–C(42)*	1.500(9)
C(51)–C(41)	1.28(1)	C(52)*–C(42)*	1.290(9)
C(51)–C(6)	1.537(9)	C(2)–C(52)*	1.50(2)
C(7)–C(1)	1.519(6)	C(8)–C(7)	1.335(6)
C(9)–C(8)	1.509(6)	C(9)–N(1)	1.352(6)
C(9)–O(9)	1.223(5)		
C(7)–C(71)	1.476(6)	C(8)–C(81)	1.485(6)
C(71)–C(72)	1.391(6)	C(81)–C(82)	1.411(6)
C(71)–C(76)	1.390(6)	C(81)–C(86)	1.415(6)
C(72)–C(73)	1.358(7)	C(82)–C(83)	1.412(6)
C(73)–C(74)	1.377(9)	C(83)–C(84)	1.385(7)
C(74)–C(75)	1.355(9)	C(84)–C(85)	1.405(7)
C(75)–C(76)	1.383(7)	C(85)–C(86)	1.401(7)

Table 5

Main bond angles (°) for $Cr(CO)_3(C_{21}H_{19}ON)$ (**14**)

C(11)–Cr(1)–C(13)	87.6(2)		
C(12)–Cr(1)–C(13)	87.7(2)		
C(12)–Cr(1)–C(11)	90.0(3)		
O(9)–C(9)–C(8)	128.1(4)	N(1)–C(9)–C(8)	105.5(4)
N(1)–C(9)–O(9)	126.3(4)	C(7)–C(8)–C(9)	108.8(4)
C(1)–C(7)–C(8)	110.4(4)	C(1)–N(1)–C(9)	113.8(4)
C(3)–N(1)–C(1)	121.0(4)	N(1)–C(1)–C(7)	101.2(3)
C(6)–C(1)–N(1)	108.0(4)	C(41)–C(3)–N(1)	108.5(5)
C(42)* –C(3)–N(1)	108.6(7)	C(52)* –C(2)–C(1)	103.0(7)
C(6)–C(51)–C(41)	125.0(7)	C(51)–C(41)–C(3)	124.0(7)
C(51)–C(6)–C(1)	108.7(5)	C(42)* –C(52)* –C(2)	135.2(14)
C(52)* –C(42)* –C(3)	117.5(12)		
C(86)–C(81)–C(82)	118.0(4)	C(76)–C(71)–C(72)	117.0(4)
C(83)–C(82)–C(81)	120.5(4)	C(73)–C(72)–C(71)	122.2(5)
C(84)–C(83)–C(82)	120.8(5)	C(74)–C(73)–C(72)	120.4(6)
C(85)–C(84)–C(83)	119.4(5)	C(75)–C(74)–C(73)	118.3(6)
C(86)–C(85)–C(84)	120.2(5)	C(76)–C(75)–C(74)	122.3(6)
C(86)–C(86)–C(81)	121.0(5)	C(75)–C(76)–C(71)	119.7(5)

Table 6

Fractional atomic parameters for $Cr(CO)_3(C_{21}H_{19}ON)$ (**14**)

Atom	x/a	y/b	z/c	U_{eq}
Cr(1)	0.25294(5)	0.17902(6)	0.11381(5)	0.0368
C(11)	0.1772(4)	0.0601(5)	0.1491(5)	0.0656
O(11)	0.1282(4)	−0.0141(5)	0.1716(5)	0.1041
C(12)	0.1463(4)	0.1916(6)	−0.0009(4)	0.0633
O(12)	0.0802(3)	0.2032(6)	−0.0729(3)	0.0935
C(13)	0.1762(4)	0.2859(4)	0.1617(3)	0.0509
O(13)	0.1269(3)	0.3523(4)	0.1915(3)	0.0793
C(1)	0.3027(3)	0.4333(4)	−0.1803(3)	0.0433
C(2)	0.3527(4)	0.5509(5)	−0.1972(4)	0.0616
N(1)	0.3655(3)	0.3326(4)	−0.1965(3)	0.0545
C(3)	0.3791(5)	0.3126(6)	−0.2893(4)	0.0673
C(41)	0.2741(8)	0.3452(8)	−0.3657(5)	0.0585
C(51)	0.1908(7)	0.3875(7)	−0.3482(5)	0.0512
C(42)*	0.397(2)	0.431(1)	−0.330(1)	0.0881
C(52)*	0.384(2)	0.526(2)	−0.285(1)	0.0822
C(6)	0.1860(4)	0.4206(4)	−0.2487(3)	0.0517
C(7)	0.3082(3)	0.4126(4)	−0.0772(3)	0.0356
C(71)	0.2665(3)	0.5052(4)	−0.267(3)	0.0399
C(72)	0.3366(4)	0.5872(5)	0.0324(4)	0.0574
C(73)	0.3011(6)	0.6742(6)	0.0793(5)	0.0720
C(74)	0.1924(6)	0.6860(6)	0.0678(5)	0.0714
C(75)	0.1227(5)	0.6074(6)	0.0103(5)	0.0672
C(76)	0.1571(4)	0.5172(5)	−0.0373(4)	0.0515
C(8)	0.3574(3)	0.3092(4)	−0.0457(3)	0.0379
C(81)	0.3746(3)	0.2454(4)	0.0460(3)	0.0374
C(82)	0.3883(3)	0.3059(4)	0.1328(3)	0.0405
C(83)	0.4052(3)	0.2413(5)	0.2183(3)	0.0443
C(84)	0.4064(4)	0.1176(5)	0.2185(4)	0.0496
C(85)	0.3915(4)	0.0559(4)	0.1325(4)	0.0468
C(86)	0.3756(4)	0.1191(4)	0.0474(4)	0.0460
C(9)	0.3958(3)	0.2548(4)	−0.1229(3)	0.0459
O(9)	0.4474(3)	0.1628(3)	−0.1196(3)	0.0595

Table 7

Main interatomic distances (Å) for $Cr(CO)_3(C_{21}H_{21}ON)$ (**30**)

Cr(1)–C(11)	1.840(4)	C(11)–O(11)	1.158(4)
Cr(1)–C(12)	1.836(3)	C(12)–O(12)	1.153(4)
Cr(1)–C(13)	1.841(4)	C(13)–O(13)	1.154(4)
Cr(1)–C(71)	2.258(3)	Cr(1)–C(72)	2.213(3)
Cr(1)–C(73)	2.218(4)	Cr(1)–C(74)	2.216(4)
Cr(1)–C(75)	2.217(3)	Cr(1)–C(76)	2.229(3)
C(1)–C(2)	1.501(5)	C(1)–N(1)	1.433(4)
C(1)–C(8)	1.338(5)	N(1)–C(3)	1.495(5)
N(1)–C(9)	1.401(4)	C(3)–C(4)	1.532(6)
C(4)–C(5)	1.533(5)	C(5)–C(6)	1.548(5)
C(6)–C(7)	1.576(4)	C(7)–C(8)	1.524(4)
C(7)–C(9)	1.522(4)	C(9)–O(9)	1.202(4)
C(7)–C(71)	1.513(4)	C(8)–C(81)	1.474(5)
C(71)–C(72)	1.422(4)	C(81)–C(82)	1.379(6)
C(71)–C(76)	1.405(4)	C(81)–C(86)	1.411(5)
C(72)–C(73)	1.396(5)	C(82)–C(83)	1.388(6)
C(73)–C(74)	1.418(5)	C(83)–C(84)	1.375(7)
C(74)–C(75)	1.391(5)	C(84)–C(85)	1.368(8)
C(75)–C(76)	1.413(5)	C(85)–C(86)	1.390(6)

37 (0.60 g, 18%) as dark-red crystals, m.p. 275–280 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.2 (20h, m), 3.45 (1H, t), 2.6 (1H, m), 2.25 (1H, m), 1.75 (3H, t). m/z 665 (M^+).

X-ray studies

In each case preliminary unit cell dimensions and symmetry information were derived from precession and Laue photographs. The crystal was then set up on a

Table 8

Main bond angles (°) for $Cr(CO)_3(C_{21}H_{21}ON)$ (**30**)

C(12)–Cr(1)–C(11)	88.3(2)	O(11)–C(11)–Cr(1)	179.1(3)
C(13)–Cr(1)–C(11)	88.4(2)	O(12)–C(12)–Cr(1)	178.2(3)
C(13)–Cr(1)–C(12)	87.4(2)	O(13)–C(13)–Cr(1)	178.7(3)
N(1)–C(1)–C(2)	116.9(3)	C(8)–C(1)–C(2)	130.9(3)
C(8)–C(1)–N(1)	112.1(3)	C(3)–N(1)–C(1)	119.0(3)
C(9)–N(1)–C(1)	107.4(3)	C(9)–N(1)–C(3)	112.4(3)
C(4)–C(3)–N(1)	109.9(3)	C(5)–C(4)–C(3)	116.2(3)
C(6)–C(5)–C(4)	118.7(3)	C(7)–C(6)–C(5)	116.6(3)
C(8)–C(7)–C(6)	111.4(3)	C(9)–C(7)–C(6)	99.3(3)
C(9)–C(7)–C(8)	101.8(3)	C(7)–C(8)–C(1)	107.6(3)
C(7)–C(9)–N(1)	106.6(3)	O(9)–C(9)–N(1)	124.3(3)
O(9)–C(9)–C(7)	128.3(3)		
C(76)–C(71)–C(72)	117.6(3)	C(86)–C(81)–C(82)	117.4(4)
C(73)–C(72)–C(71)	121.2(3)	C(83)–C(82)–C(81)	122.2(5)
C(74)–C(73)–C(72)	120.0(3)	C(84)–C(83)–C(82)	119.5(5)
C(75)–C(74)–C(73)	119.7(3)	C(85)–C(84)–C(83)	119.9(5)
C(76)–C(75)–C(74)	119.9(3)	C(86)–C(85)–C(84)	121.0(5)
C(75)–C(76)–C(71)	121.6(3)	C(85)–C(86)–C(81)	119.9(5)

Table 9

Fractional atomic parameters for $Cr(CO)_3(C_{21}H_{21}ON)$ (**30**)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Cr(1)	0.13946(4)	0.13215(4)	0.49215(5)	0.0354
C(11)	0.0258(3)	0.1776(3)	0.5193(3)	0.0427
O(11)	−0.0460(2)	0.2049(2)	0.5365(2)	0.0568
C(12)	0.1539(2)	0.0288(3)	0.5991(3)	0.0407
O(12)	0.1646(2)	−0.0344(2)	0.6684(2)	0.0555
C(13)	0.2168(3)	0.2167(3)	0.6103(3)	0.0496
O(13)	0.2657(2)	0.2682(2)	0.6858(3)	0.0718
C(1)	0.0913(2)	0.4628(3)	0.1896(3)	0.0383
C(2)	0.1164(3)	0.5445(3)	0.1173(3)	0.0545
N(1)	0.0810(2)	0.4978(2)	0.2939(2)	0.0404
C(3)	−0.0002(3)	0.5756(3)	0.2881(3)	0.0525
C(4)	−0.0997(3)	0.5183(3)	0.2743(3)	0.0516
C(5)	−0.1245(3)	0.4226(3)	0.1948(3)	0.0460
C(6)	−0.0696(2)	0.3176(3)	0.2401(3)	0.0408
C(7)	0.0495(2)	0.3168(3)	0.2736(3)	0.0337
C(71)	0.1008(2)	0.2142(3)	0.3219(3)	0.0335
C(72)	0.0481(2)	0.1170(3)	0.3078(3)	0.0391
C(73)	0.1002(3)	0.0229(3)	0.3447(3)	0.0457
C(74)	0.2073(3)	0.0234(3)	0.4006(3)	0.0477
C(75)	0.2601(3)	0.1178(3)	0.4172(3)	0.0447
C(76)	0.2069(3)	0.2125(3)	0.3774(3)	0.0389
C(8)	0.0808(2)	0.3587(3)	0.1767(3)	0.0367
C(81)	0.0958(3)	0.2933(3)	0.0867(3)	0.0444
C(82)	0.0310(4)	0.2122(4)	0.0349(4)	0.0633
C(83)	0.0427(5)	0.1531(4)	−0.0529(4)	0.0831
C(84)	0.1219(5)	0.1750(5)	0.898(4)	0.0826
C(85)	0.1889(4)	0.2536(5)	−0.0387(4)	0.0744
C(86)	0.1783(3)	0.3124(4)	0.0501(3)	0.0605
C(9)	0.0767(2)	0.4084(3)	0.3573(3)	0.0376
O(9)	0.0794(2)	0.4103(2)	0.4545(2)	0.0459

Table 10

Interatomic distances for compound **20** with esd's in parentheses

Cr(1)–C(11)	1.834(5)	C(8)–C(81)	1.475(6)
Cr(1)–C(12)	1.841(5)	C(9)–C(10)	1.490(6)
Cr(1)–C(13)	1.838(5)	C(9)–C(91)	1.477(6)
Cr(1)–C(91)	2.226(4)	C(10)–N(1)	1.353(6)
Cr(1)–C(92)	2.196(4)	C(10)–O(10)	1.229(5)
Cr(1)–C(93)	2.211(5)	C(11)–O(11)	1.153(6)
Cr(1)–C(94)	2.215(5)	C(12)–O(12)	1.148(6)
Cr(1)–C(95)	2.219(5)	C(13)–O(13)	1.154(6)
Cr(1)–C(96)	2.210(5)	C(81)–C(82)	1.377(6)
C(1)–C(2)	1.529(7)	C(81)–C(86)	1.397(6)
C(1)–C(3)	1.549(6)	C(82)–C(83)	1.387(7)
C(1)–C(8)	1.530(6)	C(83)–C(84)	1.385(8)
C(1)–N(1)	1.457(5)	C(84)–C(85)	1.355(8)
C(3)–C(4)	1.520(8)	C(85)–C(86)	1.383(7)
C(4)–C(5)	1.302(9)	C(91)–C(92)	1.428(6)
C(5)–C(6)	1.495(9)	C(91)–C(96)	1.413(6)
C(6)–C(7)	1.514(8)	C(92)–C(93)	1.389(6)
C(7)–N(1)	1.463(6)	C(93)–C(94)	1.398(6)
C(8)–C(9)	1.353(5)	C(94)–C(95)	1.373(7)
C(95)–C(96)	1.418(6)		

Table 11

Interatomic angles for compound 20 with esd's in parentheses

C(12)–Cr(1)–C(11)	90.5(2)	N(1)–C(7)–C(6)	112.2(5)
C(13)–Cr(1)–C(11)	89.2(2)	C(9)–C(8)–C(1)	110.0(4)
C(13)–Cr(1)–C(12)	87.4(2)	C(81)–C(8)–C(1)	119.7(3)
C(91)–Cr(1)–C(11)	90.2(2)	C(81)–C(8)–C(9)	130.4(4)
C(91)–Cr(1)–C(12)	160.2(2)	C(10)–C(9)–C(8)	108.2(4)
C(91)–Cr(1)–C(13)	112.4(2)	C(91)–C(9)–C(8)	128.6(4)
C(92)–Cr(1)–C(11)	86.9(2)	C(91)–C(9)–C(10)	123.2(3)
C(92)–Cr(1)–C(12)	122.7(2)	N(1)–C(10)–C(9)	107.3(3)
C(92)–Cr(1)–C(13)	149.7(2)	O(10)–C(10)–C(9)	128.4(4)
C(92)–Cr(1)–C(91)	37.7(2)	O(10)–C(10)–N(1)	124.3(4)
C(93)–Cr(1)–C(11)	111.5(2)	O(11)–C(11)–Cr(1)	178.7(4)
C(93)–Cr(1)–C(12)	94.2(2)	O(12)–C(12)–Cr(1)	179.3(5)
C(93)–Cr(1)–C(13)	159.1(2)	O(13)–C(13)–Cr(1)	178.0(5)
C(93)–Cr(1)–C(91)	67.2(2)	C(82)–C(81)–C(8)	121.0(4)
C(93)–Cr(1)–C(92)	36.7(2)	C(86)–C(81)–C(8)	120.1(4)
C(94)–Cr(1)–C(11)	148.2(2)	C(86)–C(81)–C(82)	118.8(4)
C(94)–Cr(1)–C(12)	89.6(2)	C(83)–C(82)–C(81)	120.9(4)
C(94)–Cr(1)–C(13)	122.5(2)	C(84)–C(83)–C(82)	119.3(5)
C(94)–Cr(1)–C(91)	79.5(2)	C(85)–C(84)–C(83)	120.4(4)
C(94)–Cr(1)–C(92)	66.6(2)	C(86)–C(85)–C(84)	120.8(5)
C(94)–Cr(1)–C(93)	36.8(2)	C(85)–C(86)–C(81)	119.8(5)
C(95)–Cr(1)–C(11)	156.8(2)	C(9)–C(91)–Cr(1)	127.5(3)
C(95)–Cr(1)–C(12)	112.4(2)	C(92)–C(91)–Cr(1)	70.0(2)
C(95)–Cr(1)–C(13)	94.6(2)	C(92)–C(91)–C(9)	122.7(4)
C(95)–Cr(1)–C(91)	67.2(2)	C(96)–C(91)–Cr(1)	70.8(2)
C(95)–Cr(1)–C(92)	78.2(2)	C(96)–C(91)–C(9)	120.1(4)
C(95)–Cr(1)–C(93)	65.5(2)	C(96)–C(91)–C(92)	117.2(4)
C(96)–Cr(1)–C(11)	120.1(2)	C(91)–C(92)–Cr(1)	72.3(2)
C(96)–Cr(1)–C(12)	149.2(2)	C(93)–C(92)–Cr(1)	72.2(3)
C(96)–Cr(1)–C(13)	89.6(2)	C(93)–C(92)–C(91)	121.2(4)
C(96)–Cr(1)–C(91)	37.2(1)	C(92)–C(93)–Cr(1)	71.0(3)
C(96)–Cr(1)–C(92)	66.8(2)	C(94)–C(93)–Cr(1)	71.8(3)
C(96)–Cr(1)–C(93)	78.4(2)	C(94)–C(93)–C(92)	120.6(4)
C(95)–Cr(1)–C(94)	36.1(2)	C(93)–C(94)–Cr(1)	71.4(3)
C(96)–Cr(1)–C(94)	66.5(2)	C(95)–C(94)–Cr(1)	72.1(3)
C(96)–Cr(1)–C(95)	37.3(2)	C(95)–C(94)–C(93)	119.7(4)
C(3)–C(1)–C(2)	111.7(4)	C(94)–C(95)–Cr(1)	71.8(3)
C(8)–C(1)–C(2)	111.9(4)	C(96)–C(95)–Cr(1)	71.0(3)
C(8)–C(1)–C(3)	109.5(4)	C(96)–C(95)–C(94)	120.8(4)
N(1)–C(1)–C(2)	110.6(4)	C(91)–C(96)–Cr(1)	72.0(2)
N(1)–C(1)–C(3)	111.2(4)	C(95)–C(96)–Cr(1)	71.7(3)
N(1)–C(1)–C(8)	101.6(3)	C(95)–C(96)–C(91)	120.5(4)
C(4)–C(3)–C(1)	114.2(4)	C(7)–N(1)–C(1)	124.6(4)
C(5)–C(4)–C(3)	125.9(5)	C(10)–N(1)–C(1)	112.8(4)
C(6)–C(5)–C(4)	125.0(5)	C(10)–N(1)–C(7)	122.6(4)
C(7)–C(6)–C(5)	113.2(5)		

four circle 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 1. Intensities of standard reflections showed no change during data collection. Corrections were made for Lorentz and polarization effects. Computations were performed

Table 12

Fractional atomic coordinates for compound **20** esd's in parentheses. $U_{eq} = [U_{11}^{\star}U_{22}^{\star}U_{33}]^{**}1/3$

Atom	x/a	y/b	z/c	U_{eq}
Cr(1)	0.12141(6)	0.15440(4)	0.08046(7)	0.0367
C(1)	0.6343(4)	0.0277(2)	0.3179(4)	0.0386
C(2)	0.7245(5)	0.0699(3)	0.2744(6)	0.0531
C(3)	0.7232(5)	−0.0153(3)	0.4479(5)	0.0483
C(4)	0.8258(5)	−0.0646(3)	0.4370(6)	0.0609
C(5)	0.7948(6)	−0.1156(3)	0.3506(7)	0.0682
C(6)	0.6519(6)	−0.1328(3)	0.2414(7)	0.0639
C(7)	0.5817(5)	−0.0725(3)	0.1454(6)	0.0545
C(8)	0.5339(4)	0.0743(2)	0.3401(4)	0.0349
C(9)	0.4017(4)	0.0554(2)	0.2545(4)	0.0343
C(10)	0.4046(4)	−0.0040(2)	0.1701(4)	0.0399
C(11)	0.2625(5)	0.1934(3)	0.0596(5)	0.0490
C(12)	0.0106(5)	0.2306(3)	−0.0023(5)	0.0472
C(13)	0.0527(5)	0.1152(3)	−0.0889(5)	0.0551
C(81)	0.5888(4)	0.1300(2)	0.4436(4)	0.0351
C(82)	0.6230(5)	0.1165(2)	0.5763(5)	0.0455
C(83)	0.6768(5)	0.1686(3)	0.6738(5)	0.0535
C(84)	0.6953(5)	0.2352(3)	0.6365(5)	0.0485
C(85)	0.6617(5)	0.2491(2)	0.5061(6)	0.0472
C(86)	0.6089(4)	0.1974(2)	0.4083(5)	0.0441
C(91)	0.2722(4)	0.0848(2)	0.2428(4)	0.0363
C(92)	0.2668(4)	0.1511(2)	0.2987(4)	0.0410
C(93)	0.1424(5)	0.1782(3)	0.2819(5)	0.0470
C(94)	0.0183(4)	0.1417(3)	0.2070(5)	0.0477
C(95)	0.0200(4)	0.0776(3)	0.1528(5)	0.0470
C(96)	0.1456(4)	0.0487(2)	0.1686(5)	0.0413
N(1)	0.5391(4)	−0.0173(2)	0.2078(4)	0.0418
O(10)	0.3063(3)	−0.0356(2)	0.0800(4)	0.0526
O(11)	0.3528(4)	0.2169(2)	0.0480(4)	0.0687
O(12)	−0.0581(4)	0.2781(2)	−0.0549(4)	0.0650
O(13)	0.0119(5)	0.0921(3)	−0.1961(4)	0.0801

Table 13

Interatomic distances for compound **21** with esd's in parentheses

Cr(1)–C(11)	1.844(3)	C(9)–C(91)	1.478(3)
Cr(1)–C(12)	1.842(3)	C(10)–O(10)	1.218(3)
Cr(1)–C(13)	1.847(3)	C(10)–N(1)	1.365(3)
Cr(1)–C(81)	2.236(2)	C(11)–O(11)	1.149(4)
Cr(1)–C(82)	2.205(3)	C(12)–O(12)	1.149(4)
Cr(1)–C(83)	2.224(3)	C(13)–O(13)	1.152(3)
Cr(1)–C(84)	2.207(3)	C(14)–O(14)	1.261(7)
Cr(1)–C(85)	2.209(3)	C(81)–C(82)	1.427(3)
Cr(1)–C(86)	2.210(2)	C(81)–C(86)	1.401(3)
C(1)–C(2)	1.527(4)	C(82)–C(83)	1.393(4)
C(1)–C(5)	1.564(3)	C(83)–C(84)	1.410(5)
C(1)–C(9)	1.518(3)	C(84)–C(85)	1.392(5)
C(1)–N(1)	1.470(3)	C(85)–C(86)	1.424(4)
C(3)–C(4)	1.295(4)	C(91)–C(92)	1.393(4)
C(4)–C(5)	1.497(4)	C(91)–C(96)	1.385(4)
C(5)–C(6)	1.552(4)	C(92)–C(93)	1.381(4)
C(6)–C(7)	1.529(4)	C(93)–C(94)	1.387(5)
C(7)–N(1)	1.471(3)	C(94)–C(95)	1.372(5)
C(8)–C(9)	1.350(3)	C(95)–C(96)	1.393(4)
C(8)–C(10)	1.495(3)	O(14)–H(14)	0.77(4)
C(8)–C(81)	1.477(3)		

Table 14

Interatomic bond angles for compound **21** with esd's in parentheses

C(12)–Cr(1)–C(11)	88.7(1)	N(1)–C(7)–C(6)	103.5(2)
C(13)–Cr(1)–C(11)	89.2(1)	C(10)–C(8)–C(9)	109.0(2)
C(13)–Cr(1)–C(12)	87.4(1)	C(81)–C(8)–C(9)	128.4(2)
C(81)–Cr(1)–C(11)	91.2(1)	C(81)–C(8)–C(10)	122.4(2)
C(81)–Cr(1)–C(12)	112.6(1)	C(8)–C(9)–C(1)	109.8(2)
C(81)–Cr(1)–C(13)	160.0(1)	C(91)–C(9)–C(1)	122.3(2)
C(82)–Cr(1)–C(11)	89.2(1)	C(91)–C(9)–C(8)	127.5(2)
C(82)–Cr(1)–C(12)	149.9(1)	O(10)–C(10)–C(8)	128.0(2)
C(82)–Cr(1)–C(13)	122.6(1)	N(1)–C(10)–C(8)	106.6(2)
C(82)–Cr(1)–C(81)	37.49(8)	N(1)–C(10)–O(10)	125.4(2)
C(83)–Cr(1)–C(11)	114.2(1)	O(11)–C(11)–Cr(1)	178.4(3)
C(83)–Cr(1)–C(12)	156.9(1)	O(12)–C(12)–Cr(1)	179.3(3)
C(83)–Cr(1)–C(13)	94.9(1)	O(13)–C(13)–Cr(1)	178.5(3)
C(83)–Cr(1)–C(81)	66.84(9)	C(8)–C(81)–Cr(1)	128.0(1)
C(83)–Cr(1)–C(82)	36.7(1)	C(82)–C(81)–Cr(1)	70.1(1)
C(84)–Cr(1)–C(11)	151.2(1)	C(82)–C(81)–C(8)	120.1(2)
C(84)–Cr(1)–C(12)	120.0(1)	C(86)–C(81)–Cr(1)	70.6(1)
C(84)–Cr(1)–C(13)	90.9(1)	C(86)–C(81)–C(8)	121.5(2)
C(84)–Cr(1)–C(81)	79.30(9)	C(86)–C(81)–C(82)	118.3(2)
C(84)–Cr(1)–C(82)	66.7(1)	C(81)–C(82)–Cr(1)	72.4(1)
C(84)–Cr(1)–C(83)	37.1(1)	C(83)–C(82)–Cr(1)	72.4(2)
C(85)–Cr(1)–C(11)	156.5(1)	C(83)–C(82)–C(81)	121.1(2)
C(85)–Cr(1)–C(12)	91.8(1)	C(82)–C(83)–Cr(1)	70.9(1)
C(85)–Cr(1)–C(13)	114.4(1)	C(84)–C(83)–Cr(1)	70.8(2)
C(85)–Cr(1)–C(81)	66.95(9)	C(84)–C(83)–C(82)	119.9(2)
C(85)–Cr(1)–C(82)	78.7(1)	C(83)–C(84)–Cr(1)	72.1(2)
C(85)–Cr(1)–C(83)	66.3(1)	C(85)–C(84)–Cr(1)	71.7(2)
C(86)–Cr(1)–C(11)	119.0(1)	C(85)–C(84)–C(83)	119.9(2)
C(86)–Cr(1)–C(12)	88.3(1)	C(84)–C(85)–Cr(1)	71.5(1)
C(86)–Cr(1)–C(13)	151.4(1)	C(86)–C(85)–Cr(1)	71.2(1)
C(86)–Cr(1)–C(81)	36.72(9)	C(86)–C(85)–C(84)	120.2(3)
C(86)–Cr(1)–C(82)	66.71(9)	C(81)–C(86)–Cr(1)	72.7(1)
C(86)–Cr(1)–C(82)	78.7(1)	C(85)–C(86)–Cr(1)	71.2(1)
C(85)–Cr(1)–C(84)	36.7(1)	C(85)–C(86)–C(81)	120.5(2)
C(86)–Cr(1)–C(84)	67.1(1)	C(92)–C(91)–C(9)	119.7(2)
C(86)–Cr(1)–C(85)	37.6(1)	C(96)–C(91)–C(9)	121.7(2)
C(5)–C(1)–C(2)	111.5(2)	C(96)–C(91)–C(92)	118.7(2)
C(9)–C(1)–C(2)	110.8(2)	C(93)–C(92)–C(91)	120.5(3)
C(9)–C(1)–C(5)	118.3(2)	C(94)–C(93)–C(92)	120.3(3)
N(1)–C(1)–C(2)	111.7(2)	C(95)–C(94)–C(93)	119.7(3)
N(1)–C(1)–C(5)	101.4(2)	C(96)–C(95)–C(94)	120.2(3)
N(1)–C(1)–C(9)	102.3(2)	C(95)–C(96)–C(91)	120.6(3)
C(5)–C(4)–C(3)	124.6(3)	C(7)–N(1)–C(1)	112.9(2)
C(4)–C(5)–C(1)	113.4(2)	C(10)–N(1)–C(1)	112.0(2)
C(6)–C(5)–C(1)	101.0(2)	C(10)–N(1)–C(7)	123.1(2)
C(6)–C(5)–C(4)	110.4(2)	C(7)–C(6)–C(5)	105.4(2)

by use of the CRYSTALS system [22] adapted for a MICROVAX-II computer. Atomic scattering factors for neutral Cr, O, C, N and H were taken from ref. 23. Anomalous dispersion was taken into account.

The positions of Cr atom were derived by Harker vector analysis of three dimensional Patterson maps. All remaining non-hydrogen atoms were found from

Table 15

Fractional atomic coordinates for compound **21**. $U_{eq} = 1/3[U_{11} + U_{22} + U_{33}]$

Atom	x/a	y/b	z/c	U_{eq}
Cr(1)	0.10599(5)	0.27019(4)	0.21799(3)	0.0370
C(1)	−0.0107(3)	−0.2080(3)	0.3199(2)	0.0371
C(2)	0.0578(4)	−0.3566(3)	0.3801(2)	0.0539
C(3)	−0.1664(6)	−0.0628(4)	0.0745(3)	0.0728
C(4)	−0.1653(3)	−0.0629(3)	0.1670(2)	0.0471
C(5)	−0.1378(3)	−0.1873(3)	0.2508(2)	0.0401
C(6)	−0.2962(3)	−0.1658(3)	0.3264(2)	0.0486
C(7)	−0.2901(3)	−0.0822(4)	0.3956(2)	0.0511
C(8)	0.0998(3)	−0.0452(2)	0.3065(2)	0.0322
C(9)	0.1272(3)	−0.1591(2)	0.2738(2)	0.0334
C(10)	−0.0592(3)	−0.0073(3)	0.3739(2)	0.0373
C(11)	−0.0666(4)	0.2709(3)	0.1679(2)	0.0502
C(12)	−0.0455(4)	0.3704(3)	0.3088(2)	0.0532
C(13)	0.0813(4)	0.4376(3)	0.1314(2)	0.0497
C(14)	−0.4970(7)	0.3654(6)	0.4402(7)	0.1195
C(81)	0.1965(3)	0.0413(2)	0.2771(2)	0.0336
C(82)	0.2654(3)	0.0690(3)	0.1755(2)	0.0422
C(83)	0.3546(4)	0.1521(3)	0.1457(2)	0.0523
C(84)	0.3719(4)	0.2152(3)	0.2155(3)	0.0533
C(85)	0.3050(4)	0.1902(3)	0.3148(2)	0.0490
C(86)	0.2153(3)	0.1041(3)	0.3456(2)	0.0410
C(91)	0.2757(3)	−0.2397(2)	0.2132(2)	0.0377
C(92)	0.4321(3)	−0.2719(3)	0.2368(2)	0.0483
C(93)	0.5723(4)	−0.3443(3)	0.1796(3)	0.0593
C(94)	0.5591(4)	−0.3868(3)	0.0983(3)	0.0599
C(95)	0.4058(4)	−0.3567(4)	0.0749(3)	0.0624
C(96)	0.2641(3)	−0.2841(3)	0.1326(2)	0.0511
O(10)	−0.1313(2)	0.0952(2)	0.4108(1)	0.0484
O(11)	−0.1748(3)	0.2693(3)	0.1387(3)	0.0687
O(12)	−0.1397(3)	0.4341(3)	0.3649(2)	0.0758
O(13)	0.0637(4)	0.5435(2)	0.0791(2)	0.0665
O(14)	−0.4624(4)	0.2378(4)	0.4735(4)	0.1096
N(1)	−0.1139(2)	−0.1089(2)	0.3847(1)	0.0382

successive electron density maps. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located on a difference Fourier map and their coordinates refined. They were assigned an overall refinable isotropic thermal parameter. Refinement was by least squares with a large-block approximation to the normal matrix. In complex **14**, the C(1), N(1), C(3), C(41), C(51) ring is disordered, with a statistical distribution of the two C(41) and C(51) carbon atoms around a pseudo-mirror plane containing the C(5) and C(6) carbon atoms. The criteria for a satisfactory completed analysis were the ratios of the parameter shifts to standard deviations, and no significant features in the final difference map.

In Tables 2–18 are listed main interatomic distances, bond angles and fractional atomic parameters for compounds **13**, **14**, **20**, **21**, **30**, and **34**.

Full Tables of C–H bond lengths and thermal parameters, and lists of calculated and observed structure factors are available from the authors.

Table 16

Interatomic distances for compound **34** with esd's in parentheses

Cr(1)–C(11)	1.836(4)	C(11)–O(11)	1.155(5)
Cr(1)–C(12)	1.842(4)	C(12)–O(12)	1.149(5)
Cr(1)–C(13)	1.838(4)	C(13)–O(13)	1.151(4)
Cr(1)–C(1)	2.160(3)	Cr(1)–N(1)	2.133(3)
Cr(1)–C(8)	2.312(3)	Cr(1)–C(9)	2.231(3)
Cr(1)–C(10)	2.206(3)		
C(1)–N(1)	1.401(4)	N(1)–C(3)	1.487(5)
C(3)–C(4)	1.524(5)	C(4)–C(6)	1.520(5)
C(6)–C(7)	1.544(5)	C(7)–C(8)	1.528(5)
C(8)–C(9)	1.406(5)	C(9)–C(10)	1.441(5)
C(1)–C(10)	1.403(5)	N(1)–C(7)	1.492(4)
C(6)–O(1)	1.199(4)		
C(1)–C(2)	1.498(5)	C(4)–C(5)	1.512(6)
C(7)–C(71)	1.542(5)	C(8)–C(81)	1.501(5)
C(71)–C(72)	1.363(6)	C(81)–C(82)	1.384(5)
C(71)–C(76)	1.383(5)	C(81)–C(86)	1.362(5)
C(72)–C(73)	1.385(6)	C(82)–C(83)	1.381(6)
C(73)–C(74)	1.345(8)	C(83)–C(84)	1.347(7)
C(74)–C(75)	1.336(8)	C(84)–C(85)	1.356(7)
C(75)–C(76)	1.379(7)	C(85)–C(86)	1.392(6)
C(9)–C(91)	1.502(5)	C(10)–C(101)	1.506(5)
C(91)–C(92)	1.374(5)	C(101)–C(102)	1.392(5)
C(91)–C(96)	1.371(5)	C(101)–C(106)	1.379(5)
C(92)–C(93)	1.367(6)	C(102)–C(103)	1.379(5)
C(93)–C(94)	1.349(7)	C(103)–C(104)	1.365(6)
C(94)–C(95)	1.354(7)	C(104)–C(105)	1.371(6)
C(95)–C(96)	1.414(6)	C(105)–C(106)	1.381(6)

Table 17

Bond angles for compound **34** with esd's in parentheses

C(7)–N(1)–C(1)	122.1(3)	C(7)–N(1)–C(3)	108.8(3)
C(4)–C(3)–N(1)	103.5(3)	C(6)–C(4)–C(3)	104.4(3)
C(7)–C(6)–C(4)	109.8(3)	C(6)–C(7)–N(1)	99.2(3)
C(8)–C(7)–N(1)	104.0(3)	C(9)–C(8)–C(7)	117.0(3)
C(10)–C(9)–C(8)	121.2(3)	C(9)–C(10)–C(1)	119.1(3)
C(12)–Cr(1)–C(11)	86.5(2)	C(1)–Cr(1)–C(11)	132.9(2)
C(13)–Cr(1)–C(11)	87.7(2)	C(1)–Cr(1)–C(12)	87.4(2)
C(13)–Cr(1)–C(12)	88.9(2)	C(1)–Cr(1)–C(13)	138.7(2)
N(1)–Cr(1)–C(11)	168.9(1)	N(1)–Cr(1)–C(12)	98.2(2)
N(1)–Cr(1)–C(13)	102.3(2)	N(1)–Cr(1)–C(1)	38.1(1)
C(8)–Cr(1)–C(11)	110.6(1)	C(8)–Cr(1)–C(12)	162.8(2)
C(8)–Cr(1)–C(13)	94.0(2)	C(8)–Cr(1)–C(1)	79.2(1)
C(9)–Cr(1)–C(13)	125.7(2)	C(9)–Cr(1)–C(11)	92.9(2)
C(9)–Cr(1)–C(1)	67.9(1)	C(8)–Cr(1)–N(1)	64.6(1)
C(9)–Cr(1)–N(1)	77.5(1)	C(9)–Cr(1)–C(12)	145.4(2)
C(9)–Cr(1)–C(8)	36.0(1)	C(10)–Cr(1)–C(11)	102.3(2)
C(10)–Cr(1)–C(12)	108.5(2)	C(10)–Cr(1)–C(13)	160.1(2)
C(10)–Cr(1)–C(1)	37.5(1)	C(10)–Cr(1)–N(1)	66.7(1)
C(10)–Cr(1)–C(8)	66.5(1)	C(10)–Cr(1)–C(9)	37.9(1)
O(11)–C(11)–Cr(1)	175.7(4)	O(12)–C(12)–Cr(1)	178.9(4)
O(13)–C(13)–Cr(1)	177.2(4)		
C(2)–C(1)–Cr(1)	130.3(3)	N(1)–C(1)–Cr(1)	69.9(2)
N(1)–C(1)–C(2)	118.1(3)	C(10)–C(1)–Cr(1)	73.0(2)

Table 17 (continued)

C(10)–C(1)–C(2)	125.1(3)	C(10)–C(1)–N(1)	116.7(3)
C(1)–N(1)–Cr(1)	72.0(2)	C(3)–N(1)–Cr(1)	127.0(2)
C(3)–N(1)–C(1)	123.5(3)	C(7)–N(1)–Cr(1)	96.7(2)
C(5)–C(4)–C(3)	115.7(4)	C(6)–C(4)–C(5)	112.9(4)
O(1)–C(6)–C(4)	125.0(4)	C(7)–C(6)–O(1)	125.2(4)
C(71)–C(7)–N(1)	114.0(3)	C(71)–C(7)–C(6)	109.8(3)
C(8)–C(7)–C(6)	115.1(3)	C(8)–C(7)–C(71)	113.8(3)
C(72)–C(71)–C(7)	121.6(4)	C(76)–C(71)–C(7)	121.4(4)
C(76)–C(71)–C(72)	117.0(4)	C(73)–C(72)–C(71)	121.4(5)
C(74)–C(73)–C(72)	120.6(5)	C(75)–C(74)–C(73)	119.0(5)
C(76)–C(75)–C(74)	121.7(5)	C(75)–C(76)–C(71)	120.3(5)
C(7)–C(8)–Cr(1)	88.7(2)	C(81)–C(8)–Cr(1)	132.7(2)
C(81)–C(8)–C(7)	118.3(3)	C(9)–C(8)–Cr(1)	68.9(2)
C(9)–C(8)–C(81)	119.8(3)	C(82)–C(81)–C(8)	119.1(3)
C(86)–C(81)–C(8)	123.3(4)	C(86)–C(81)–C(82)	117.6(4)
C(83)–C(82)–C(81)	121.1(4)	C(84)–C(83)–C(82)	120.4(4)
C(85)–C(84)–C(83)	119.6(4)	C(86)–C(85)–C(84)	120.6(5)
C(85)–C(86)–C(81)	120.7(4)	C(8)–C(9)–Cr(1)	75.1(2)
C(91)–C(9)–Cr(1)	133.5(2)	C(91)–C(9)–C(8)	119.5(3)
C(10)–C(9)–Cr(1)	70.1(2)	C(10)–C(9)–C(91)	118.9(3)
C(92)–C(91)–C(9)	117.1(3)	C(96)–C(91)–C(9)	125.0(4)
C(96)–C(91)–C(92)	117.7(4)	C(93)–C(92)–C(91)	122.4(4)
C(94)–C(93)–C(92)	120.5(5)	C(95)–C(94)–C(93)	118.9(4)
C(96)–C(95)–C(94)	121.4(5)	C(95)–C(96)–C(91)	119.1(4)
C(1)–C(10)–Cr(1)	69.5(2)	C(9)–C(10)–Cr(1)	72.0(2)
C(101)–C(10)–Cr(1)	131.0(2)	C(101)–C(10)–C(1)	119.3(3)
C(101)–C(10)–C(9)	121.6(3)	C(102)–C(101)–C(10)	118.9(3)
C(106)–C(101)–C(10)	122.6(3)	C(106)–C(101)–C(102)	118.5(3)
C(103)–C(102)–C(101)	120.5(4)	C(104)–C(103)–C(102)	120.0(4)
C(105)–C(104)–C(103)	120.5(4)	C(105)–C(106)–C(101)	120.8(4)
C(106)–C(105)–C(104)	119.7(4)		

Table 18

Fractional atomic parameters for compound **34** with esd's in parentheses

Atom	x/a	y/b	z/c	U_{eq}
Cr(1)	0.86758(3)	0.01222(5)	0.32025(4)	0.0365
C(11)	0.8797(2)	0.1363(4)	0.2432(3)	0.0486
O(11)	0.8889(2)	0.2185(3)	0.1992(2)	0.0686
C(12)	0.8614(2)	0.1261(4)	0.4076(3)	0.0507
O(12)	0.8568(2)	0.1982(3)	0.4611(2)	0.0715
C(13)	0.9683(2)	0.0112(4)	0.3444(3)	0.0532
O(13)	1.0312(2)	0.0152(4)	0.3607(3)	0.0756
C(1)	0.7714(2)	−0.0698(3)	0.3694(2)	0.0363
C(2)	0.7244(2)	−0.0306(4)	0.4413(2)	0.0482
N(1)	0.8343(2)	−0.1379(3)	0.3941(2)	0.0363
C(3)	0.8587(2)	−0.1685(4)	0.4882(2)	0.0482
C(4)	0.9362(2)	−0.2177(4)	0.4821(3)	0.0497
C(5)	0.9592(3)	−0.3160(5)	0.5473(3)	0.0680
C(6)	0.9375(2)	−0.2560(4)	0.3852(3)	0.0478
O(1)	0.9890(2)	−0.3017(3)	0.3536(2)	0.0647
C(7)	0.8619(2)	−0.2308(3)	0.3343(2)	0.0368
C(71)	0.8152(2)	−0.3455(3)	0.3286(2)	0.0438
C(72)	0.7401(3)	−0.3419(4)	0.3239(4)	0.0652

continued

Table 18 (continued)

Atom	x/a	y/b	z/c	U_{eq}
C(73)	0.6983(3)	−0.4449(5)	0.3146(4)	0.0792
C(74)	0.7310(4)	0.5519(5)	0.3115(3)	0.0677
C(75)	0.8046(4)	−0.5576(4)	0.3169(4)	0.0722
C(76)	0.8477(3)	−0.4566(4)	0.3257(3)	0.0626
C(8)	0.8652(2)	−0.1672(3)	0.2448(2)	0.0351
C(81)	0.9132(2)	−0.2190(4)	0.1779(2)	0.0414
C(82)	0.8874(2)	−0.3146(4)	0.1262(3)	0.0513
C(83)	0.9284(3)	−0.3620(4)	0.0613(3)	0.0638
C(84)	0.9953(3)	−0.3172(5)	0.0482(3)	0.0687
C(85)	1.0219(3)	−0.2241(6)	0.0983(4)	0.0740
C(86)	0.9811(2)	−0.1752(5)	0.1637(3)	0.0632
C(9)	0.8044(2)	−0.0961(3)	0.2156(2)	0.0336
C(91)	0.8952(2)	−0.0790(3)	0.1172(2)	0.0372
C(92)	0.7253(2)	−0.1403(4)	0.0793(3)	0.0572
C(93)	0.7061(3)	−0.1393(5)	−0.0106(3)	0.0693
C(94)	0.7452(3)	−0.0746(5)	−0.0659(3)	0.0732
C(95)	0.8043(4)	−0.0121(5)	−0.0310(3)	0.0784
C(96)	0.8262(3)	−0.0147(4)	0.0615(3)	0.0638
C(10)	0.7551(2)	−0.0500(3)	0.2776(2)	0.0325
C(101)	0.6864(2)	0.0180(3)	0.2464(2)	0.0362
C(102)	0.6180(2)	−0.0337(4)	0.2559(3)	0.0479
C(103)	0.5539(2)	0.0254(4)	0.2272(3)	0.0562
C(104)	0.5574(2)	0.1358(5)	0.1898(3)	0.0574
C(105)	0.6242(3)	0.1875(4)	0.1784(3)	0.0638
C(106)	0.6885(2)	0.1285(4)	0.2068(3)	0.0516

References

1 E.O. Fischer, A. Maasböl, Angew. Chemie. Int. Ed. Engl., 3 (1964) 580.
2 E.O. Fischer, K.H. Dör, Chem. Ber., 103 (1970) 1273.
3 C.P. Casey, A.J. Shusterman, N. Vollendorf, K.J. Haller, J. Am. Chem. Soc., 104 (1982) 2417.
4 C. Alvarez, H. Rudler, J.C. Daran, Y. Jeannin, J. Chem. Soc., Chem. Commun., 106 (1984) 375.
5 R.L. Banks, G.C. Bailey, Ind. and Eng. Chem., 3 (1964) 170.
6 T.J. Katz, S.I. Lee, J. Am. Chem. Soc., 102 (1980) 422.
7 K.H. Dötz, Angew. Chem. Int. Ed. Engl., 14 (1975) 2033.
8 K.H. Dötz, M. Popau, G. Möller, J. Organomet. Chem., 334 (1987) 57.
9 K.S. Chan, G.A. Peterson, T.A. Brandvold, K.L. Faron, C.A. Challener, C. Hyldahl, W.D. Wulff, J. Organomet. Chem., 334 (1987) 9.
10 A. Parlier, H. Rudler, N. Platzer, M. Fontanille, A. Soum, J. Chem. Soc., Dalton, (1987) 1041.
11 Y.C. Xu, W. Wulff, J. Organomet. Chem., 52 (1987) 3263.
12 J. Chem. Soc., Chem. Commun., in press.
13 A. Parlier, H. Rudler, R. Yefsah, C. Alvarez, J. Organomet. Chem., 328 (1987) C21.
14 Unpublished results.
15 J.A. Connor, E.O. Fischer, J. Chem. Soc., A, (1969) 578.
16 A. Parlier, H. Rudler, J.C. Daran, C. Alvarez, F. Delgado Reyes, J. Organomet. Chem., 337 (1987) 339.
17 J.T. Guy, D.W. Bennett, Transition Met. Chem., 9 (1984) 43.
18 A. Yamashida, Tetrahedron Lett., 26 (1986) 5915.
19 W.R. Bamford, T.S. Stevens, J. Chem. Soc., (1952) 467.
20 G. Wittig, H. Tenhaeff, W. Schoch, G. Koenig, Ann., 1 (1951) 572.
21 M. Sommelet, C.R. Acad. Sci. Paris, 56 (1937) 205.
22 J.R. Carruthers and D.J. Watkin, Crystals, an advanced crystallographic program system, Chemical Crystallography Laboratory University of Oxford, England, 1985.
23 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, England, 1974, Vol. 4.