Alkeneamino-carbene Complexes of Chromium: Unexpected Ring-expansion and Ring-contraction Reactions upon Alkyne Insertions

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The cycloaminocarbene complex (**1**) $(OC)_5Cr{=}C(Me)(\overline{NCH_2CH{=}CHCH_2CH_2})$ reacts in boiling benzene with diphenylacetylene to give, upon alkyne insertion, C–N bond cleavage, rearrangement, and CO insertion, two new arene chromium complexes of unsaturated lactams (**3**) and (**4**) which result from, respectively, a ring contraction and a ring expansion reaction, and which have been fully characterized by *X*-ray analysis.

Carbene complexes of chromium and tungsten are now recognized as useful synthons in organic chemistry.[1—4] Following our discovery that alkene-carbene complexes promote alkyne insertion–cyclopropanation reactions, we attempted to carry out the same reaction on aminocarbene complexes of the same type for chromium. We showed that these complexes lead, depending on their structure, either to azabicyclo [4.1.0]heptane systems,[5] or to the oxidation products of these latter compounds.[6] This communication describes the behaviour of the carbene complex (**1**), bearing a tetrahydropyridine substituent, towards alkynes.

Owing to its dipolar structure,[7] and unlike its carbon

analogue of tungsten, complex (**1E,Z**) does not undergo intramolecular double bond co-ordination to give (**2**). We thought therefore that upon insertion of an alkyne into the metal–carbon bond of (**1**), the new carbon chain might be long and flexible enough to allow co-ordination and thus to allow cyclopropanation reactions to occur. However, complex (**1**) reacts in an unexpected manner. Thus, when refluxed in benzene in the presence of PhC≡CPh, complex (**1E,Z**) gives, after 4 h, two new complexes (**3**) and (**4**) (60:40), in 50% yield. They were separated on silica gel and fully characterized by ^{1}H and ^{13}C n.m.r. spectroscopy as well as by *X*-ray analysis.

Spectroscopic data† indicate that both complexes contain an aryl chromium tricarbonyl moiety, and their elemental analyses show that they are the result of the insertion of the alkyne group and of one molecule of CO. Complex (**3**) (m.p. 166 °C) shows the presence of a monosubstituted and a tetrasubstituted double bond, as well as a methyl group on a tertiary carbon atom. The *X*-ray crystal structure appears in Figure 1. Complex (**3**) contains an α,β unsaturated lactam fused to a five-membered ring system; it is obvious that this complex is the result of a ring contraction.

The second complex (**4**) (m.p. 168 °C) shows similar spectroscopic features, *i.e.*, a disubstituted and a tetrasubstituted double bond and also a methyl group on a tertiary carbon atom. The crystal structure‡ of (**4**) is in Figure 2; this complex contains an α,β unsaturated lactam fused to a seven-membered unsaturated ring system and is thus the result of a ring expansion. As far as the mechanism of this unexpected reaction is concerned, it is possible to ascribe the formation of both compounds to an electrocyclic rearrangement promoted by the metal centre, in the first case with participation of the double bond of the tetrahydropyridine system (Scheme 1), and in the second case probably without direct participation of the double bond (Scheme 2). Both reactions are therefore characterized by an unexpected C–N bond cleavage, followed by reductive C–C bond formation, and CO insertion.

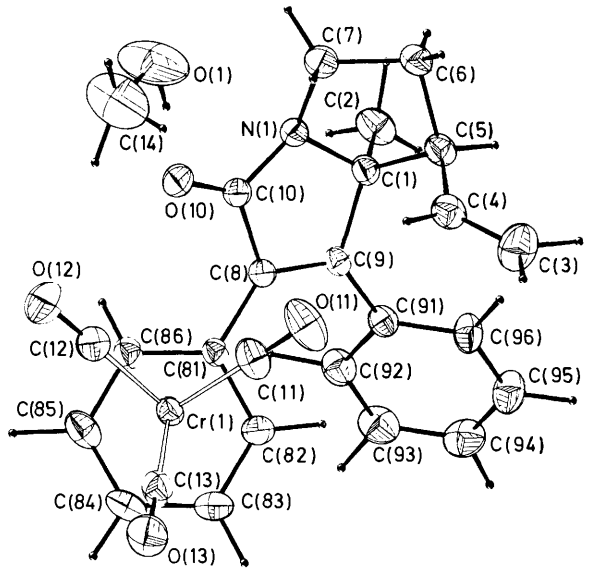


Figure 1. ORTEP view of complex (**3**). Relevant bond lengths (Å): C(1)–C(5) 1.564(3), C(1)–C(9) 1.518(3), C(3)–C(4) 1.295(4), C(8)–C(9) 1.350(3), C(10)–O(10) 1.218(3), C(10)–N(1) 1.365(3).

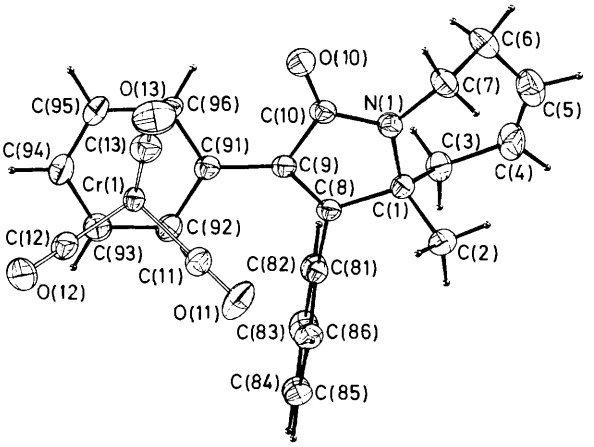
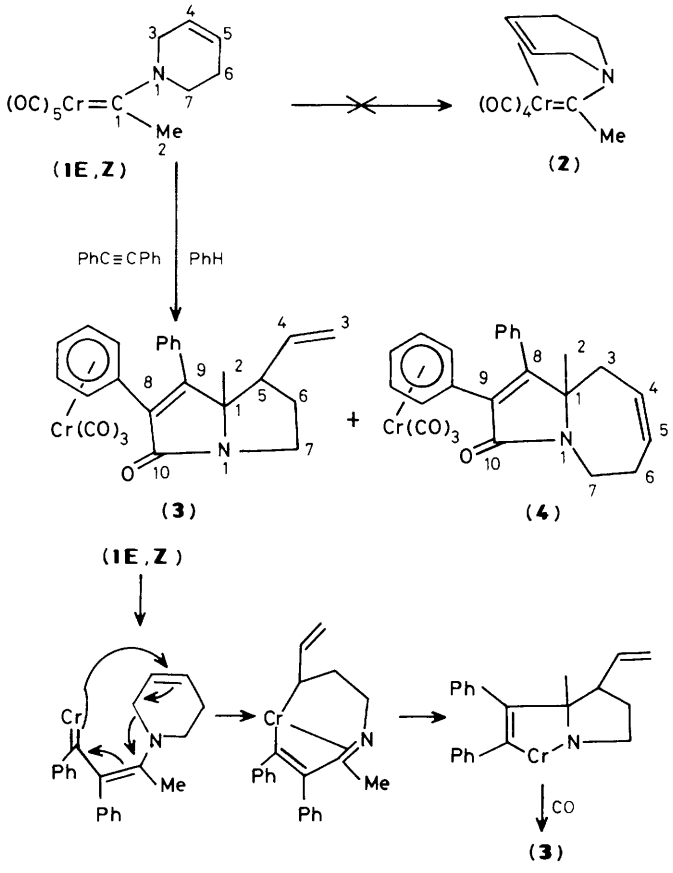


Figure 2. ORTEP view of complex (**4**). Relevant bond lengths (Å): C(1)–C(3) 1.549(6), C(1)–C(8) 1.530(6), C(1)–N(1) 1.457(5), C(3)–C(4) 1.520(8), C(4)–C(5) 1.302(9), C(5)–C(6) 1.495(9), C(6)–C(7) 1.514(8), C(7)–N(1) 1.463(6), C(8)–C(9) 1.353(5), C(10)–O(10) 1.229(5).

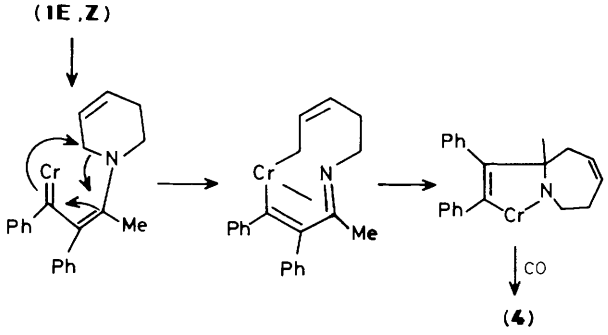
† All compounds were isolated as analytically pure samples. ^{1}H and ^{13}C N.m.r. data: (**3**), orange crystals, m.p. 166 °C, δ (200 MHz, C_6D_6): 7.15 (5H, m), 6.14 (1H, d), 5.74 (1H, dq), 5.10 (1H, d), 5.05 (1H, m), 4.98 (1H, d), 4.52 (2H, m), 4.10 (1H, t), 3.78 (1H, m), 3.25 (3H, s, MeOH solvate), 3.02 (1H, m), 2.42 (1H, m), 2.08 (1H, m), 1.70 (1H, m), 0.88 (3H, s); δ (50.1 MHz, C_6D_6): 232.5 [$Cr(CO)_3$], 170.9 (C=O), 136.8, 132.9, 129.4, 129.1, 128.8, 128.2 (Ph), 116.2, 117.7 (C-8, C-9), 96.3, 93.5, 92.7, 90.3, 89.6 (Ph–Cr), 75.1 (C-1), 49.2 (C-7), 40.0 (C-5), 34.8 (C-6), 23.0 (C-2). (**4**), Yellow crystals, m.p. 168 °C, δ (200 MHz, C_6D_6): 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); δ (50.1 MHz, C_6D_6): 232.7 [$Cr(CO)_3$], 161.1 (C=O), 133.2, 131.1, 129.2, 128.9, 128.4, 127.6 (Ph), 126.1, 125.4 (C-8, C-9), 98.9, 93.9, 93.5, 92.0, 91.3 (Ph–Cr), 65.8 (C-1), 36.9 (C-7), 36.0 (C-3), 28.1 (C-6), 19.7 (C-2).

‡ *Crystal data* for (**3**): $C_{25}H_{21}CrO_4 \cdot CH_3OH$, M = 483.5, triclinic, space group $P\bar{1}$, a = 9.057(2), b = 10.955(2), c = 13.983(4) Å, α = 73.96(2), β = 77.36(2), γ = 64.09(2)°, D_c = 1.35 g cm^{-3} for Z = 2, μ(Mo-K_α) = 5.0 cm^{-1}. 4035 data were collected at room temperature on a Philips PW 1100 diffractometer. No absorption correction was made. Anomalous dispersion terms and a correction for secondary extinction were applied. The structure was solved by standard Patterson–Fourier techniques and refined by least squares using anisotropic thermal parameters for all non-hydrogen atoms and a single isotropic value for hydrogen atoms whose positions were refined. Although all hydrogen atoms were located on difference electron density maps, calculated positions were included for the methyl H and H of the phenyl ring not bonded to Cr. 3338 reflections with $I > 3\sigma(I)$ were used to solve and refine the structure; R = 0.024, R_w = 0.0564, 343 least squares parameters.

Crystal data for (**4**): $C_{25}H_{21}CrNO_4$, M = 451.4, monoclinic, space group $P2_1/c$, a = 10.994(4), b = 19.117(4), c = 11.240(6), β = 118.60°, D_c = 1.45 g cm^{-3} for Z = 4, μ(Mo-K_α) = 5.7 cm^{-1}. 3646 data were collected at room temperature on a Nonius CAD 4 diffractometer. No absorption correction was made. Anomalous dispersion terms and a correction for secondary extinction were applied. The structure was solved by standard Patterson–Fourier techniques and refined by least squares using anisotropic thermal parameters for all non-hydrogen atoms. Although all H atoms were located on difference electron maps, they were placed in calculated positions. 2049 reflections with $I > 3\sigma(I)$, were used to solve and refine the structure; R = 5.11, R_w = 5.85, 281 variables. Computer programs used were CRYSTALS, ORTEP-2, and locally written routines. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1



Scheme 2

This reaction therefore provides an unprecedented transformation of a six-membered amino-carbene complex, promoted by the alkyne insertion reaction.

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