Carbene-complex-promoted Ring Expansion of Aziridine: Formation of the 1-Azabicyclo[4.3.0] Ring System by a Double Alkyne and a Single Carbon Monoxide Insertion Reaction

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A chromium carbene complex (**2**) bearing a 2-methylaziridine ring system on the carbene carbon atom easily undergoes a double diphenylacetylene and a single CO insertion reaction to give a 1-oxotetrahydroindolizine derivative (**4**), which has been fully characterized by *X*-ray analysis of its Cr(CO)$_3$ adduct (**3**).

Pursuing our efforts towards the discovery of new reactions promoted by transition metal carbene complexes,[1—3] we found that heterocyclic aminocarbene complexes bearing a double bond β with respect to the nitrogen atom readily undergo ring expansion or contraction during the alkyne insertion reaction. For example, the complex derived from tetrahydropyridine gives both 5,7- and the 5,5-fused heterocyclic ring systems,[4] whereas the complex derived from 2,5-dihydropyrrole[5] gives as sole product the 5,6-fused system (Scheme 1).

Here we outline the behaviour of the carbene complex (**2**) derived from the three-membered aziridine system towards alkynes. The complex (**2**) is prepared by aminolysis of the methyl (ethoxy) carbene complex (**1**) and is obtained as a pale yellow oil. According to the ^{13}C n.m.r. spectrum, it exists as a 50 : 50 mixture of the *E*- and *Z*-isomers. These isomers were not further separated but were treated with diphenylacetylene in refluxing benzene. A fast reaction was observed, leading to a new complex, which could be purified by silica gel chromatography and obtained (in 25% yield) as bright red crystals.†

According to the ^{1}H and ^{13}C n.m.r. spectra, this complex is the result of the insertion of two molecules of diphenylacetyl-

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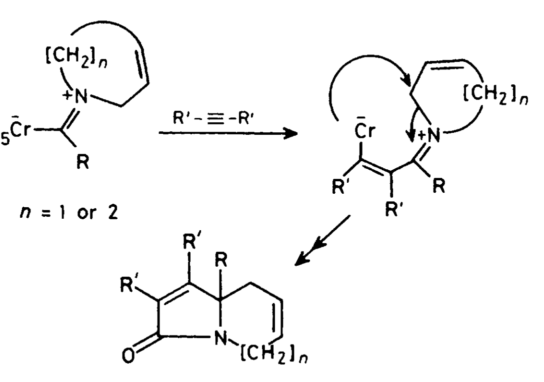
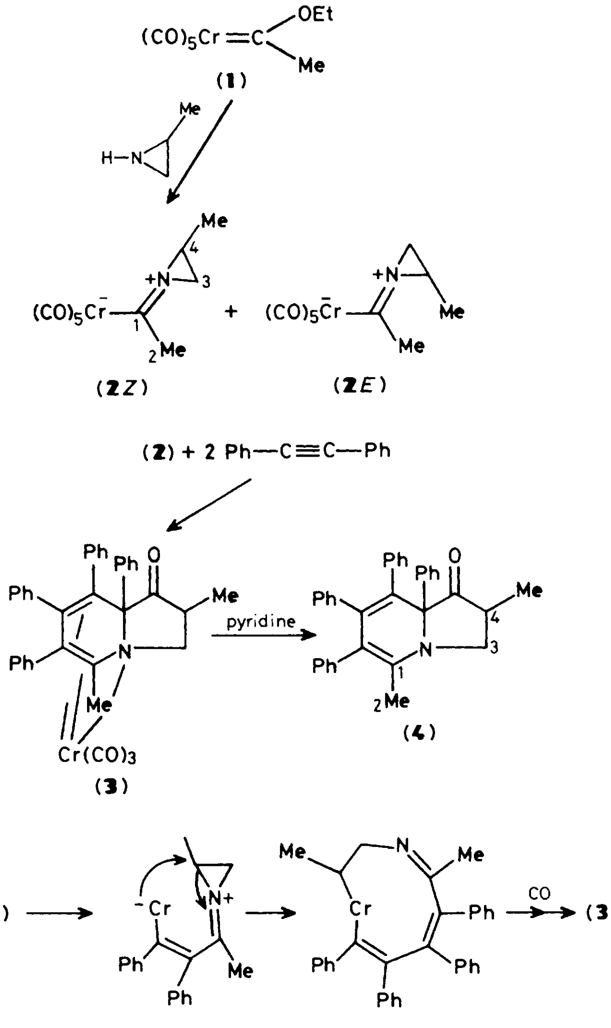
† All compounds were isolated as analytically pure samples: (**2***E*), δ_C (50.1 MHz; C_6D_6) 16.1 (C-5), 30.9 (C-2), 35.0 (C-4), 39.6 (C-3), 218.6 and 223.6 (CO), and 265 (C-1); (**2***Z*), δ_C (50.1 MHz; C_6D_6) 16.3 (C-5), 32.4 (C-2), 36.0 (C-4), 40.5 (C-3), 218.6 and 223.6 (CO) and 268 (C-1); (**3**), m.p. 260 °C; δ_H (200 MHz, $CDCl_3$) 7.3 (20H, m), 3.51 (1H, t), 3.46 (1H, m), 3.12 (1H, t), 2.31 (3H, s), and 1.19 (3H, d); δ_C (50 MHz; $CDCl_3$), 230 [$Cr(CO)_3$], 206.4 (=CO), 137.4—126.4 (aromatic), 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), and 13.7 (C-5); i.r. (KBr) 1760 (=CO), 1850, 1880, and 1900 cm^{-1} (terminal CO); (**4**) δ_H (200 MHz; $CDCl_3$) 7.25 (20H, aromatic), 4.33 (1H, t), 3.62 (1H, t), 2.75 (1H, m), 2.03 (3H, s), and 1.19 (3H, d); δ_C (50.1 MHz; $CDCl_3$), 210 (=CO), 132.0—125.4 (aromatic), 51.7 (C-7), 42.7 (C-3), 29.7 (C-4), 16.7 (C-2) and 12.6 (C-5): i.r. ($CHCl_3$) 1760 cm^{-1} (CO).

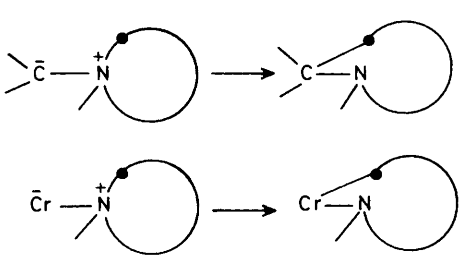


Scheme 1



Scheme 2

ene and one molecule of CO. Indeed, the ^{1}H n.m.r. spectrum shows, besides signals due to 20 aromatic protons, a doublet at δ 1.19 due to the methyl group of the aziridine, a multiplet at δ 3.43 due to the hydrogen geminal to the methyl group, two triplets at δ 3.12 and 3.51 due to the N-CH_2 group, and a singlet at δ 2.31 due to the methyl group of the starting carbene complex. The ^{13}C n.m.r. spectrum, with a signal at δ 206, and the i.r. spectrum (ν_{CO} 1760 cm^{-1}), confirm the presence of a five-membered ring ketone. Furthermore, the ^{13}C n.m.r. spectrum shows the absence of an arenechromium tricarbonyl moiety, but instead shows the presence of terminal metal–CO groups with weak signals at δ 230.



Scheme 3

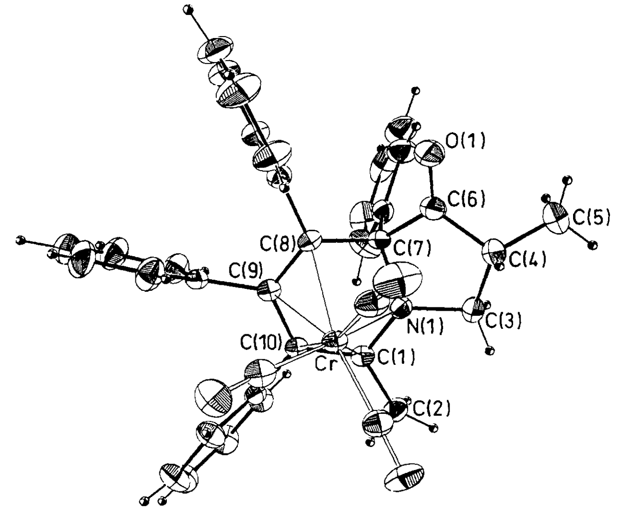


Figure 1. ORTEP view of the structure (3). Important bond lengths (Å): Cr(1)-C(1) 2.160(3), Cr(1)-N(1) 2.133(3), Cr(1)-C(8) 2.312(3), Cr(1)-C(9) 2.231(3), Cr(1)-C(10) 2.206(3), C(1)-N(1) 1.401(4), N(1)—C(3) 1.487(5), C(3)-C(4) 1.524(5), C(4)-C(6) 1.520(5), C(6)-C(7) 1.544(5), C(7)-C(8) 1.528(5), C(8)-C(9) 1.406(5), C(9)-C(10) 1.441(5), C(1)-C(10) 1.403(5) and N(1)-C(7) 1.492(4). Important bond angles(°): 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(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).

Taken together, these characteristics are in agreement with a structure in which the organic ligand (**4**) is co-ordinated either, like a diene, to $Cr(CO)_4$, or, like a dihydropyridine, to $Cr(CO)_3$. The mass spectrum and an *X*-ray structure determination‡ confirmed the second hypothesis, in agreement with structure (**3**). An ORTEP view appears in Figure 1, showing the 5,6-fused ring system with its four phenyl groups almost perpendicular to the plane of the diene system.

Similar results were observed with other carbene complexes [*e.g.* the ethoxy (phenyl) carbene complex] and other alkynes (*e.g.* 1-phenylpropyne).

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‡ *Crystal data*: $C_{37}H_{29}CrO_4N$, M = 603.6, monoclinic, space group $P2_1/a$, a = 18.189(4), b = 11.235(6), c = 15.018(1) Å, =94.68(2)°, D_c = 1.31 g cm^{-3} for Z = 4; 4885 reflections were collected with a Philips PW1100 diffractometer. The structure was solved by standard Patterson–Fourier techniques. Least-squares refinement of all non-hydrogen atoms with anisotropic temperature factors and all hydrogen atoms with an overall isotropic thermal parameter converged to an agreement factor of 0.042 (3267 independent reflections with $I > 3\sigma(I)$; 477 variable parameters. 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.

Treatment of the complex (**3**) in refluxing pyridine gave compound (**4**) as a yellowish oily solid, the i.r. spectrum of which confirms the presence of a five-membered ring ketone.

In relation to reactions previously described, three points must be emphasized.

(i) The insertion reaction is much faster than in the previous cases.

(ii) It appears that the driving force for these reactions is the formation of a 5,6-fused ring system: thus, in the case of the aziridine ring system two molecules of alkyne must be inserted consecutively in order to attain the requisite ring size (Scheme 2).

(iii) The presence of a double bond in the heterocyclic amine substituent is not a necessary requirement for the ring-opening reaction.

The reaction described here thus provides a new route to heterocyclic compounds and constitutes a new example of a transition-metal-mediated reaction related to a known reaction in the organic chemistry, here the Stevens rearrangement of C^{-}–N^{+} ylides (Scheme 3).

Received, 5th April 1988; Com. 8/01319E

References

1 A. Parlier, H. Rudler, N. Platzer, M. Fontanille, and A. Soum, *J. Chem. Soc., Dalton Trans.*, 1987, 1041.
2 A. Parlier, H. Rudler, J. C. Daran, and C. Alvarez, *J. Organomet. Chem.*, 1987, **333**, 245.
3 A. Parlier, H. Rudler, R. Yefsah, and C. Alvarez, *J. Organomet. Chem.*, 1987, **328**, C-21.
4 A. Parlier, H. Rudler, R. Yefsah, J. C. Daran, and C. Knobler, *J. Chem. Soc., Chem. Commun.*, 1988, 635.
5 Unpublished results of this laboratory.