

A New Reaction of Aminocarbene Complexes of Chromium upon Alkyne Insertions: Deoxygenation Rearrangement of Ketene Intermediates. Formation and X-Ray Structure of a Tetrahydroindolizine Complex

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Aminocarbene complexes (1) of chromium bearing suitable substituents on nitrogen react with alkynes to give, besides the expected heterocyclic compounds (5) and (6) originating from cascade alkyne-CO insertion-rearrangement reactions, deoxygenation-rearrangement products (8) of ketene intermediates, whereas when nitrogen bears substituents of low migratory aptitude, ketene complexes (4) and their derivatives (7) could be isolated and fully characterized either by spectroscopy or by X-ray crystallography.

There is much current interest in the chemistry of aminocarbene complexes of chromium both for the photochemical synthesis of lactams^{1,2} and for the thermal synthesis of 1-azabicyclo compounds.^{3,4} We recently reported on the synthesis of a series of aminocarbene complexes (1) which undergo a new rearrangement upon alkyne-CO insertion reactions to give heterocycles (5) and (6). The purpose of this communication is to show that in some cases the intermediate enamino-ketene complexes could be isolated and that they might also undergo an unprecedented deoxygenation to vinylidene carbene complexes prior to rearrangement.

Thus, when refluxed in anhydrous benzene, in the presence of PhC≡CPh, complex (1; *n* = 5, R = H) bearing the stable piperidine group, gives a very polar complex (60%) which precipitates from the solution, upon cooling, as yellow needles (m.p. 155 °C). Spectroscopic data indicate that this

complex contains an aryl chromium tricarbonyl moiety and the mass spectrum as well as elemental analyses are in agreement with the insertion of both the alkyne group and of one molecule of CO into (1); structure (4),[†] an enamino-ketene complex, was therefore attributed to this complex.

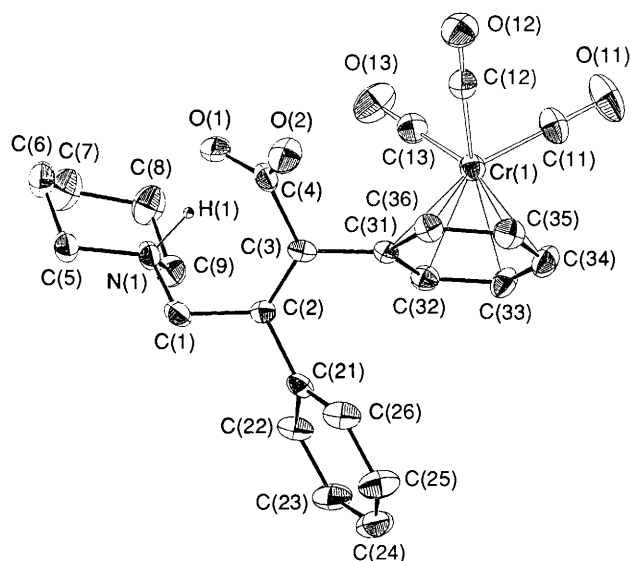
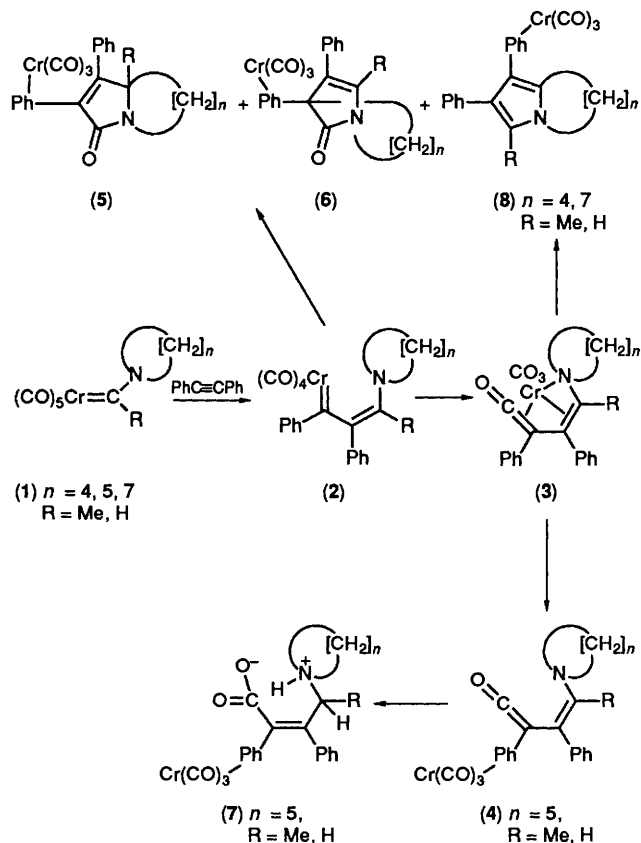


Figure 1. ORTEP view of complex (7). Relevant bond lengths (Å): N(1)–C(1) 1.500(9), C(1)–C(2) 1.513(9), C(2)–C(3) 1.333(9), C(3)–C(4) 1.545(9), C(4)–O(1) 1.265, C(4)–O(2) 1.218(7), N(1)–H(1) 1.075(5).

[†] All compounds were isolated as analytically pure samples. NMR data: (4; R = H) δ_{H} (200 MHz, C₆D₆) 7.39 and 7.19 (5H, m), 5.74 (1H, d), 5.25 (1H, s), 4.74 (1H, t), 4.12 (1H, t), 3.05 (2H, m), 2.30 (2H, m), 0.91 (6H, m); δ_{C} (50.1 MHz, CD₂Cl₂) 235.5 [Cr(CO)₃], 170.0 (C=O), 147.7, 140.2, 134.3, 129.1, 128.8, 115.0, 111.5 (Ph, C-1, C-2), 96.4, 89.2, 87.6 (Ph-Cr), 54.8 (C-5, C-9), 22.3, 21.8 (C-6, C-7, C-8).

(7; R = Me) δ_{H} (200 MHz, CDCl₃) 7.25, 7.18 (5 H, m), 6.57 (1H, d), 5.30 (1H, m), 5.19 (2H, m), 4.80 (1H, m), 3.85 (1H, br.), 3.62 (1H, q), 3.59 (1H, br.), 2.75 (1H, br.), 2.4 (1H, br.), 1.92 (6H, m), 1.42 (3H, d); δ_{C} (50.1 MHz, CDCl₃) 232.7 [Cr(CO)₃], 169.7 (C=O), 139.6, 129.0, 128.3, 139.4, 129.0, 128.3, 104.4 (Ph, C-2, C-3), 98.1, 97.3, 93.6, 89.7, 88.5 (Ph-Cr), 66.5 (C-1), 50 (C-5, C-9), 24.0 (C-6, C-8), 22.7 (C-7), 14.4 (CH₃).

(8) δ_{H} (200 MHz, CDCl₃) 7.14 (5 H, m), 5.29, 5.14 (5H, m), 3.66 (2H, m), 2.98 (2H, m), 2.17 (3H, s), 2.05 (2H, m), 1.98 (2H, m); δ_{C} (50.1 MHz, CDCl₃) 235.9 [Cr(CO)₃], 136.0, 130.8, 128.2, 127.6, 125.9 (Ph, C-1, C-2, C-3, C-9), 95.0, 93.2, 90.1 (Ph-Cr), 43.3 (C-4), 23.9 (C-7), 23.3 (C-5), 21.0 (C-6), 10.0 (C-4).

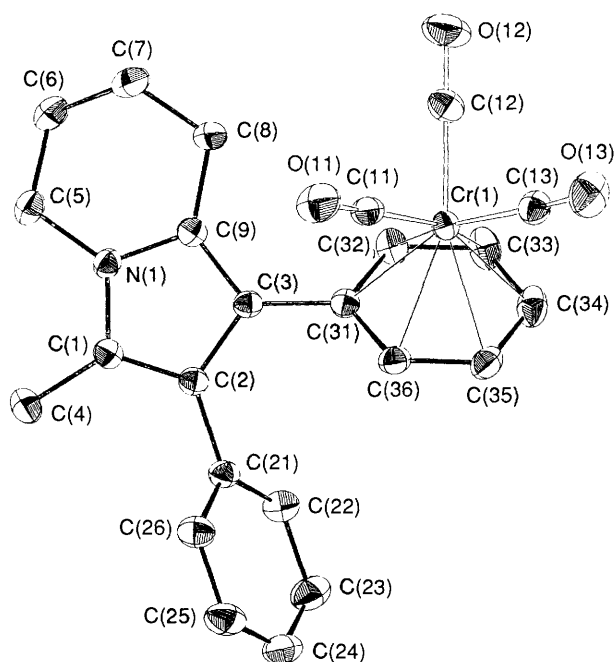


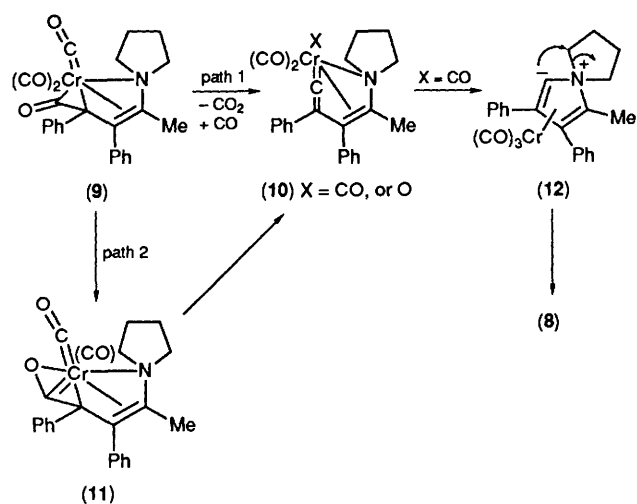
Figure 2. ORTEP view of complex (8). Relevant bond lengths (Å): C(1)–C(2) 1.370(3), C(2)–C(3) 1.431(3), C(3)–C(9) 1.379(3), C(8)–C(9) 1.483(3), C(9)–N(1) 1.376(3), N(1)–C(1) 1.379(3), C(1)–C(4) 1.486(3).

Indeed, when the same reaction was conducted in moist benzene, the corresponding amino acid complex (7) was isolated as yellow crystals (21%, m.p. 180 °C). Structure (7) was confirmed by an X-ray analysis (Figure 1);[‡] the amino acid which is formed upon hydrolysis of (4) is present as the ammonium carboxylate, with the chromium bound to a phenyl group. Similar results were observed for (1; $n = 5$, R = Me).

[‡] Crystal data for (7): $C_{24}H_{23}CrNO_5$, $M = 457.4$, monoclinic, space group $P2_1/a$, $a = 12.139(9)$, $b = 11.425(2)$, $c = 16.336(3)$ Å, $\beta = 107.49(4)^\circ$, $D_c = 1.41$ g cm⁻³ for $Z = 4$. 2001 data were collected at room temperature on a Nonius CAD4 diffractometer. No absorption correction was made (flat ψ scan). Anomalous dispersion terms 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. H atoms were placed in calculated positions, except the nitrogen H which was located on a difference Fourier maps, and not refined with an overall isotropic thermal parameter. 1155 reflections with $I > 3\sigma(I)$ were used to solve and refine the structures to $R = 0.0358$ and $R_w = 0.0393$, 281 least-squares parameters. The programs used were CRYSTALS and ORTEP-2.

For (8): $C_{24}H_{21}CrNO_3$, $M = 423.4$, triclinic, space group $P\bar{1}$, $a = 6.918(1)$, $b = 10.057(1)$, $c = 15.193(2)$ Å, $\alpha = 72.410(9)$, $\beta = 84.99(1)$, $\gamma = 84.66(3)^\circ$, $D_c = 1.40$ g cm⁻³ for $Z = 2$. 5820 data were collected at room temperature on a Nonius CAD4 diffractometer. No absorption correction was made (flat ψ scan). Anomalous dispersion terms 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. All H atoms were located on difference Fourier maps and refined with an overall isotropic thermal parameter. 3647 reflections with $I > 3\sigma(I)$ were used to solve and refine the structure; $R = 0.0372$, $R_w = 0.0369$, 328 least-squares 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.



Scheme 1

The reactivity of complexes (1; $n = 4$, R = Me or H) bearing the pyrrolidine group was quite different. For example, under the same conditions as above, complex (1; $n = 4$, R = Me) gave the expected complex (6) (32%, m.p. 146 °C) upon alkyne–CO insertion and rearrangement. However, a new, less polar complex, the structure of which was determined both by elemental analysis and by spectroscopic means, was isolated as yellow crystals (25%, m.p. 145 °C). The ¹H and ¹³C NMR spectra both showed the presence of an aryl chromium tricarbonyl moiety. Elemental analyses as well as the mass spectrum confirmed the insertion of the alkyne group, but of only the carbon atom of one CO molecule; thus a deoxygenation must have taken place. Moreover, the NMR spectra showed the presence of a methyl group associated with a double bond and of a single N–CH₂ group, although decoupling experiments were in agreement with the presence of the –N–[CH₂]₄–subunit. This reveals again a rearrangement with N–CH₂ bond rupture. All these data are consistent with structure (8), which was determined by a single crystal X-ray diffraction study (Figure 2).[‡] The structure indeed shows the presence of a substituted tetrahydroindoline, co-ordinated by one of its phenyl groups to Cr(CO)₃. Similar results were also observed starting from (1; $n = 7$, R = H or Me). The unexpected formation of this complex could only be explained by a chromium-promoted deoxygenation of a co-ordinated ketene (3) giving the vinylidene complex (10). At least two mechanisms could account for this transformation (Scheme 1); (i) reduction of (9) promoted by the chromium carbonyl with elimination of CO₂; (ii) deoxygenation by chromium of (11), with formation of an oxo-chromium species, as a result of the carbenoid character⁵ of the central atom of the ketene. Interaction of the carbene function in (10) with the amino group would then lead to the zwitterionic species (12) and finally to (8), the product of nitrogen-to-carbon migration with N–C bond rupture. Whereas ketene decarbonylations have often been observed,⁶ ketene deoxygenation reactions are rare,^{7–9} the closest example being the deoxygenation of diphenylketene by Fe(CO)₅ to diphenyl vinylideneoctacarbonyl-di-iron.⁷ Therefore mechanism (i) is the most likely to apply in the present case.

To conclude, it appears that, like alkoxyarylcabene complexes of chromium,^{10,11} aminocarbene complexes of this metal undergo CO insertion reactions easily. However it

seems now clear that the prerequisite for the observed rearrangement of zwitterionic species is the formation of carbene complexes such as (2) and (10) which can directly interact with the amino groups.

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