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Preliminary communication

Successive formation of enaminoketene and arenetricarbonyl nitrogen ylid chromium complexes during intramolecular alkyne insertions into aminocarbene complexes

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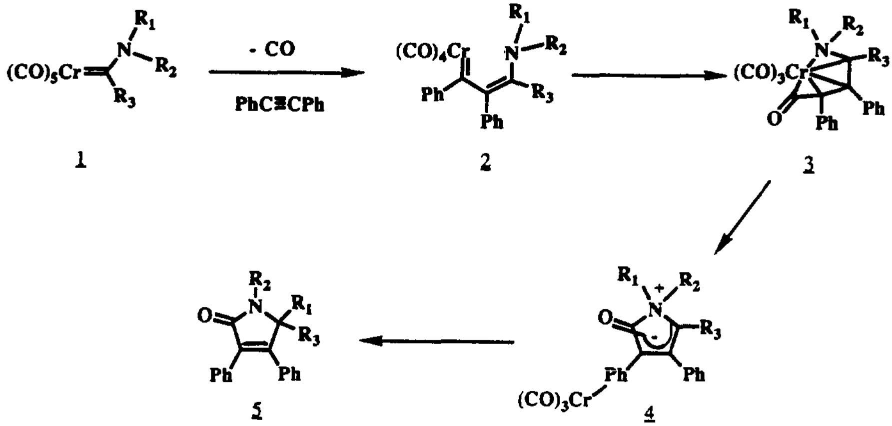
Abstract

Upon heating, alkyne(aminocarbene) complexes $[(CO)_5CrC(NR_1R_2)(CH_2)_3C{\equiv}CPh]$ undergo an intramolecular insertion reaction to give, first, complexes containing enaminoketene coordinated to $Cr(CO)_3$, and then arene tricarbonyl chromium nitrogen ylides, which finally lead to rearranged organic products. Both types of complex were fully characterized by X-ray analysis.

Among carbene complexes of chromium, aminocarbene complexes display a peculiar behaviour giving, after alkyne and CO insertions followed by a rearrangement, heterocyclic compounds [1–3]. Thus, in the case of intermolecular reactions, and provided that no ligand, such as an alkene is present, and that no coordinating solvent is used, the alkyne and CO insertions take place, as for other carbene complexes [4] (Scheme 1). However, two important differences from other carbene complexes must be emphasized: first, the intermediate enaminoketenes, **3**, lead to nitrogen-ylides, **4**, upon intramolecular interaction of nitrogen with the ketene function. Then migration of an alkyl group from nitrogen to carbon gives rearranged products, **5**. Second, and also unexpected, is the lack of benzannulation products in almost all examples of phenyl-substituted aminocarbene complexes [3] so far examined.

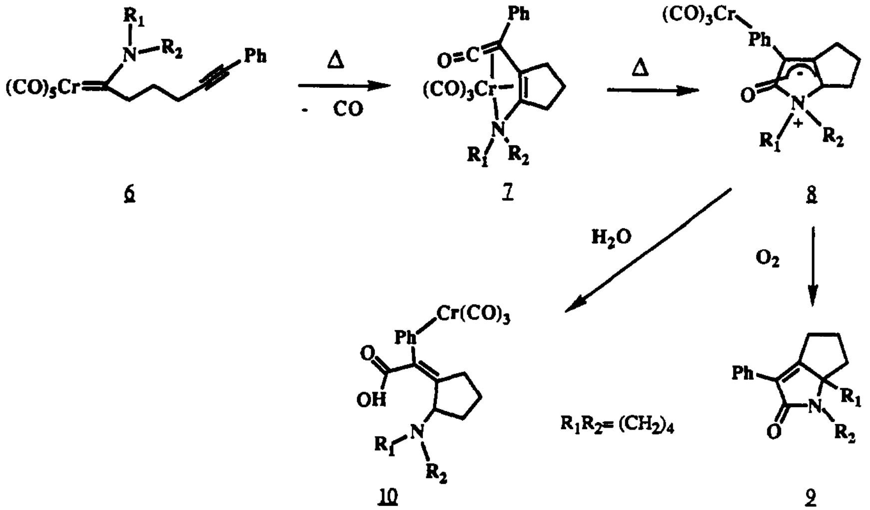
A recent report [5] on the isolation of an enaminoketene complex during an intramolecular alkyne insertion reaction prompts us to describe the successive formation of enaminoketene complexes **7**, nitrogen-ylid complexes **8**, and finally their rearrangement products **9** (Scheme 2).



Scheme 1

Because the presence of phenyl groups is crucial in intermolecular reactions for the isolation and the characterization of various reaction intermediates [6], we synthesized complexes of structure **6** ($R_1 = R_2 = CH_3$, $R_1R_2 = (CH_2)_4$, $R_1R_2 = (CH_2)_5$) starting either from complex **1** ($R_3 = CH_3$) or from the amides O=C–N(R_1R_2)(CH_2)$_3$C≡C–Ph [7].

The high reactivity of complexes **6** towards intramolecular insertion was already evident during their preparation: upon workup and evaporation of the solvent at slightly over the room temperature ketene complexes **7** * were detected by TLC. This was confirmed by heating complex **6** ($R_1R_2 = (CH_2)_5$) in cyclohexane, at 70 ° C: the solution rapidly turned deep-red and, upon cooling, red crystals (m.p. 140 ° C, 81%) separated out. The spectroscopic data of this complex ($\delta(^{13}C)$: 251 (CO), 109.5 and 107.8 ppm (carbon atoms of the coordinated ketene) were in agreement with those observed previously [5] and thus with structure **7**, an



Scheme 2

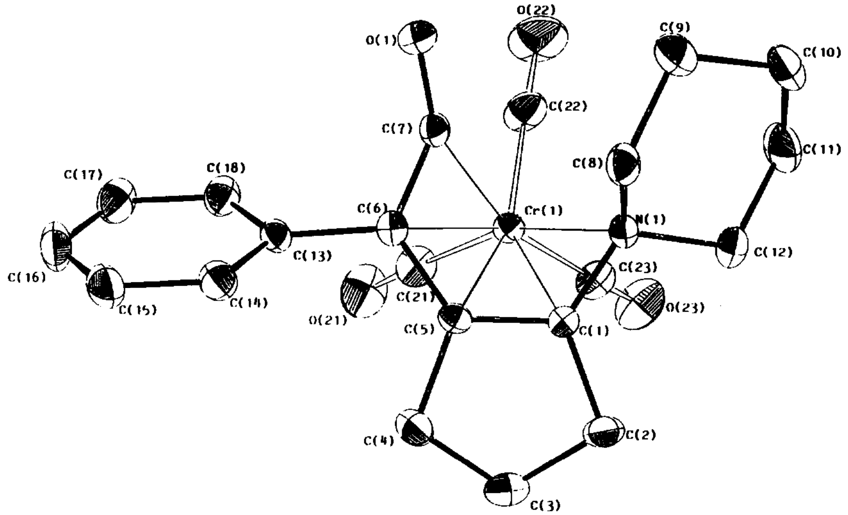


Fig. 1. ORTEP view of complex **7** with the atom labelling scheme. Selected bond distances (Å) and angles (°): N(1)–C(1) 1.408(5); C(1)–C(5) 1.400(6); C(5)–C(6) 1.417(6); C(6)–C(7) 1.438(6); C(7)–O(1) 1.201(5); C(6)–C(7)–O(1) 136.8(4).

enaminoketene coordinated to $Cr(CO)_3$. This complex was fully characterized by X-ray analysis (Fig. 1).

When the same complex was heated in boiling benzene for 12 h, the solution again turned red very rapidly. However, upon cooling a new yellow complex, **8** *, precipitated. This complex, which was much more polar than **7**, appeared to be very moisture-sensitive giving, even on TLC, the complex **10**. However, no crystals suitable for an X-ray analysis could be obtained.

Complex **6** ($R_1 = R_2 = CH_3$) behaved similarly: in boiling cyclohexane, the same type of yellow precipitate was obtained, in 44% yield, after 4 h. The spectroscopic

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* *Crystal data.* Compound **8**: $C_{18}H_{17}O_4NCr$, $M = 363.3$, monoclinic, space group $P2_1$, $a = 6.375(2)$, $b = 12.228(5)$, $c = 10.825(5)$ Å, $\beta = 102.72(3)$°, $V = 823(6)$ Å^3, $D_0 = 1.47$ g cm^{-3}, $Z = 2$, $\mu(\text{Mo-}K_\alpha) = 6.97$ cm^{-1}. Due to the poorly diffracting crystal, only 809 data were collected at room temperature on an Enraf Nonius CAD4 diffractometer. Absorption corrections, (DIFABS), 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. Owing to the poor data-to-variables ratio, all atoms were left isotropic. Hydrogen atoms were placed in calculated positions. 621 Reflections with $I > 3\sigma(I)$ were used to solve and refine the structure to $R = 0.069$ and $R_w = 0.076$ (103 least-squares parameters).

Compound **7**: $C_{21}H_{21}O_4NCr$, $M = 403.4$, orthorhombic, space group $P2_12_12_1$, $a = 8.819(2)$, $b = 11.371(2)$, $c = 19.038(2)$ Å, $V = 1909.2(5)$ Å^3, $D_c = 1.40$ g cm^{-3}, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 6.08$ cm^{-1}. 1933 Data collected at room temperature on an Enraf Nonius CAD4 diffractometer. Absorption corrections applied (DIFABS), 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. H atoms were located on a difference Fourier map and refined with an overall refinable isotropic thermal parameter. 1461 Reflections with $I > 3\sigma(I)$ were used to solve and refine the structure to $R = 0.031$ and $R_w = 0.033$ (310 least-squares parameters).

For both compounds, the programs used were CRYSTALS and ORTEP-II.

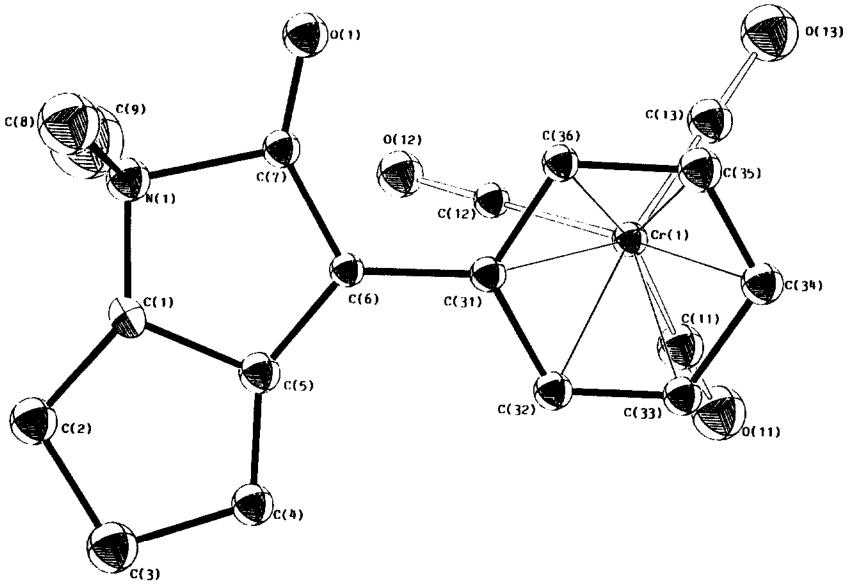

Fig. 2. ORTEP view of complex **8** with the atom labelling scheme. Selected bond distances (Å) and angles (°): N(1)–C(1) 1.38(4); C(1)–C(5) 1.50(3); C(5)–C(6) 1.40(3); C(6)–C(7) 1.40(3); C(7)–O(1) 1.21(2); C(7)–N(1) 1.62(3); C(6)–C(7)–O(1) 140.3(19).

data of this complex (m.p. 150 °C) were in all respects comparable to those of **8** ($R_1R_2 = (CH_2)_5$, ν(CO), 1710, 1875 and 1955 cm^{-1}; $\delta(^{13}C)$: 234.9 ($ArCr(CO)_3$, 168.2 (CO) ppm). Fortunately, crystals suitable for an X-ray analysis could be grown from hexane/methylene chloride. This structure (Fig. 2) reveals that the $Cr(CO)_3$ group has moved onto the phenyl group, and that the nitrogen atom of the enamine now interacts with the central carbon atom of the ketene function, the carbon–nitrogen distance being equal to 1.62(3) Å. Thus, the same type of intermediate as for the intermolecular reactions is obtained upon the alkyne/CO insertion, leading to a complex which is best described as a nitrogen-ylid, the negative charge being delocalized over both the carbonyl group and the allylic system of the enaminoketene.

The same series of intermediates was obtained from complex **6** ($R_1R_2 = (CH_2)_4$) upon heating either in benzene or in cyclohexane. Moreover, when the corresponding ylid complex, **8**, was exposed to dioxygen in dichloromethane at room temperature, for 12 h, the organic product, **9** ($R_1R_2 = (CH_2)_4$), was isolated in 13% yield: thus migration of the alkyl chain from nitrogen to the adjacent carbon atom takes place.

These results again show that the key steps in the insertion of alkynes into aminocarbene complexes of chromium are the initial formation of ketene complexes which then rearrange to nitrogen-ylid complexes.

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