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Preliminary communication

Reactivity of aminocarbene complexes of chromium containing a coordinated C=C double bond towards alkynes: Formation of azabicyclo[4.1.0]heptene systems

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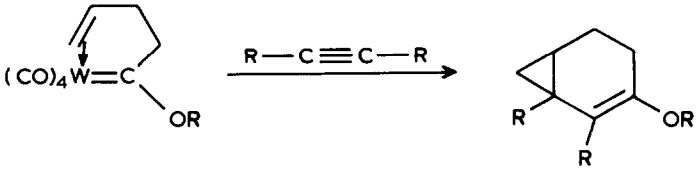
Abstract

Chromium complexes containing the bidentate aminocarbene-alkene ligand react with alkynes to give, after insertion followed by an intramolecular cyclopropanation reaction, azabicyclo[4.1.0]heptene systems, which react rapidly with oxygen, during work up, to lead to the corresponding cyclopropanic amidoketones.

We have shown very recently [1] that carbene complexes containing a coordinated C=C double bond are highly reactive towards alkynes and undergo an interesting insertion-cyclopropanation reaction (Scheme 1). Recent papers by Yamashita [2] and Semmelhack [3] on the reactivity of aminocarbene complexes towards alkynes prompt us to disclose our results in the field of aminocarbene complexes bearing a coordinated C=C double bond. Aminocarbene complexes of W and Cr **1** undergo an intramolecular coordination reaction to give complexes **2** [4].



Scheme 1.

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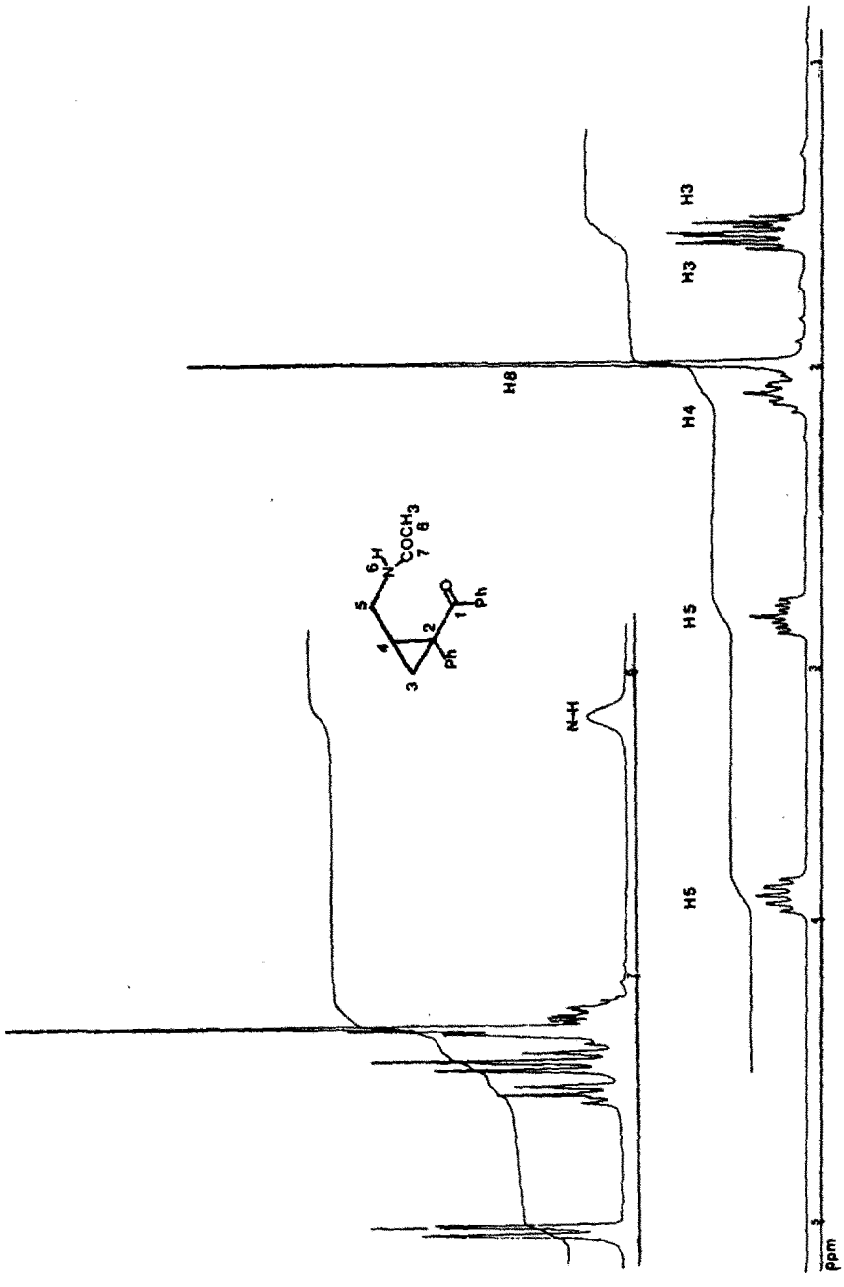


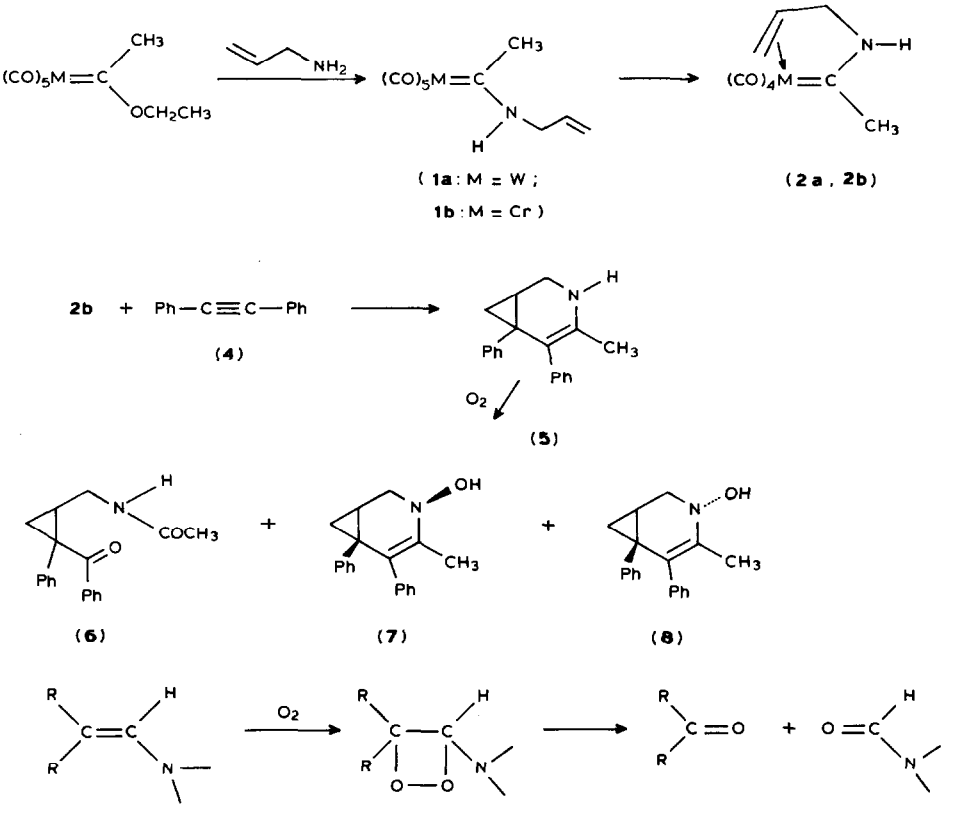
Fig. 1. ^1H NMR spectrum (250 Mz, $CDCl_3$), of compound **6** with TMS as internal reference.

Whereas the W complex **2a** was unreactive, the Cr complex **2b** underwent the insertion reaction. Thus, when **2b** was heated in refluxing benzene for 3 h, in the presence of diphenyacetylene, complete disappearance of the starting material, with formation of a single organic compound (TLC) is observed. During work-up and silica gel chromatography, this product disappeared to give three new products.

According to the mass spectrum and to the spectroscopic properties, the less polar product (55% yield) **6** is the oxidation product of the expected enamine **5**, a cyclopropanic keto-amide.

The IR and ^{13}C spectra confirmed the presence of a ketone and an amide (ν(CO) 1690 and 1650 cm^{-1}, δ(CO) 160 and 210 ppm). The ^{1}H NMR spectrum (Fig. 1) shows the presence, besides the aromatic protons, of three different cyclopropanic protons at 1.49, 1.52 and 2.07 ppm, of a NH group, at 6.2 ppm, a $COCH_3$ group at 1.97 ppm and two non-equivalent protons of a NCH_2 group, at 2.83 and 3.78 ppm. 2D ^{1}H NMR experiments unambiguously confirmed structure **6**.

The structure of the minor compounds (10% yield), was more difficult to assess. According to their mass spectra, these compounds contain one more oxygen atom than the expected enamine **5**, but no carbonyl is present in the IR spectum. The ^{13}C NMR spectra show the presence of a C=C double bond, the chemical shifts of the carbon atoms being related to those of the C=C double bond of an enamine: δ73 and 166 ppm for **7** and δ77 and 171 ppm for **8**. The ^{1}H NMR spectra are almost



Scheme 2.

similar: besides the aromatic protons, one again observes three different cyclopropanic protons (δ1.05, 1.27 and 1.59 ppm for **7** and 0.94, 1.21 and 1.79 ppm for **8**), one methyl group at 1.79 for **7** and 2.0 ppm for **8**, an OH group at 2.7 for **7** and for **8**, and two non equivalent protons of a NCH_2 group at 4.25 and 4.17 ppm for respectively **7** and **8**.

Taken together, the spectroscopic properties only agree with the structures of hydroxy-enamines **7** and **8**. It thus appears that the initial product of the insertion reaction is indeed the enamine **5** which is readily oxidized giving compounds **6**, **7** and **8**. The high reactivity of the expected enamine **5** towards oxygen is due to the presence of the enamine function: it is indeed known that enamines readily undergo oxygen-mediated double bond rupture [5,6,7] (Scheme 2).

This insertion-cyclopropanation-oxidation reaction is a general reaction which has been carried out with a series of other alkynes, and gives cyclopropanic aminomethyl derivatives, which are known [8] to show interesting pharmacological properties.

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