Journal of Organometallic Chemistry, 354 (1988) C23–C25
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Transformation of aziridinocarbene complexes of chromium and tungsten into nitrile complexes and olefins

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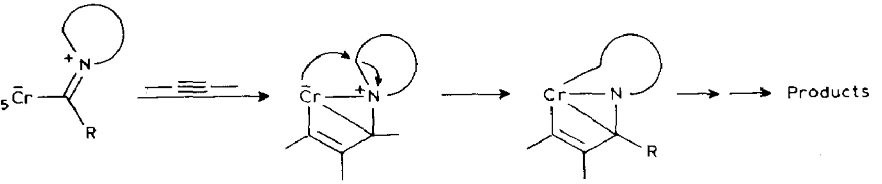
(Received June 24th, 1988)

Abstract

Carbene complexes of chromium and of tungsten bearing the methylaziridine group on the carbene carbon atom undergo a thermal rearrangement with elimination of propene to give nitrile complexes of the metals.

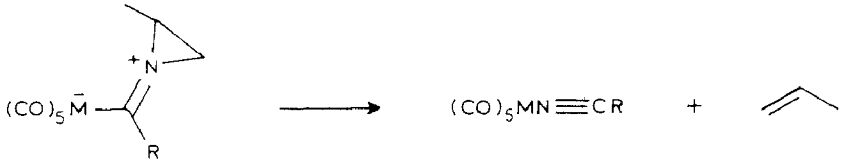
Very recently [1,2,3] we described the unexpected ring-opening with C–N bond rupture of cycloaminocarbene complexes of chromium during their reaction with alkynes. This unusual mode of reaction has been ascribed to the formation of a metal–carbon-centered 1,2 ylid which undergoes a Stevens-like rearrangement (eq. 1). We now report that whereas the five- and six-membered saturated and unsaturated cycloaminocarbene complexes are stable in refluxing benzene in the absence of alkynes the methylaziridine-substituted carbene complexes of chromium and of tungsten undergo thermal rearrangement, as described below.



(1)

When a solution of the E,Z isomeric mixture of complex **1** in benzene was heated under reflux evolution of propene, detected by GC (Porapak Q, room temperature) was observed, and a new complex was isolated as yellow crystals (m.p. 118 °C, yield 25%). Its spectroscopic properties agree with those in the literature [4,5,6,7] for $(CO)_5WN{\equiv}CPh$ (ν(CN) 2238 cm^{-1}, ν(CO) 2075, 1950, 1930 cm^{-1}, ^{1}H

NMR (CD_2Cl_2): 7.74, 7.71, 7.59 and 7.55 ppm, ^{13}C NMR (CD_2Cl_2): 200.4, 196.7, 134.4, 133.3, 129.7, 124.8, 110.6 ppm).

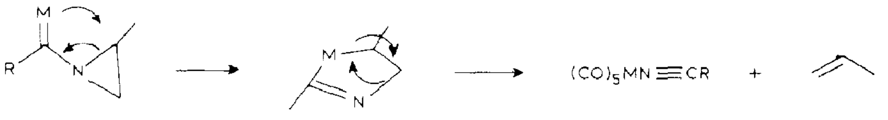


(2)

(1 : M = W, R = Ph;
2 : M = Cr, R = Ph;
5 : M = W, R = CH_3;
6 : M = Cr, R = CH_3)

(3 : M = W, R = Ph;
4 : M = Cr, R = Ph;
7 : M = W, R = CH_3;
8 : M = Cr, R = CH_3)

Complex **2** shows similar behaviour in refluxing cyclohexane, propene being evolved and complex **4** $(CO)_5CrN{\equiv}CPh$ [4] (pale yellow crystals, m.p. 118 °C, 17% yield, ν(CN) 2240 cm^{-1}, m/z 295 (M^+)) being isolated. When the same reaction was carried out in benzene, the main product, in addition to propene and free benzonitrile, was the benzenechromium tricarbonyl complex $(CO)_3CrPhH$.

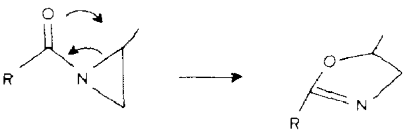


(3)

(1) (9) (3)

In the case of complexes **5** and **6**, $(CO)_5WN{\equiv}CCH_3$ (**7**) (yellow crystal, m.p. 82 °C, m/z 365 (M^+)) and $(CO)_5CrN{\equiv}CCH_3$ (yellow crystals, 30% yield, dec. 80 °C) were isolated, and found to be identical to samples prepared by a published method [4] from $W(CO)_6$, $Cr(CO)_6$ and CH_3CN.

We suggest that the mechanism of this new reaction involves an electrocyclic ring-opening with formation of a five-membered metallacycle **9** (eq. 3). Rearrangement of this intermediate, with elimination of propene, could then lead to the nitrile complexes **3**.



(4)

(10) (11)

The transformation of the aziridino carbene complexes into a mixture of propene and nitrile complexes is a new example of a transition metal mediated rearrangement which has analogies in organic chemistry; the reactions of carbene complexes can be compared with those of ketones or esters, and this analogy holds again in the new rearrangement reported above. It is known [8] that α-aziridino ketones such as **10** undergo a thermal rearrangement to a five-membered heterocycle **11**, the analogue of **9**. Owing to the presence of the metal centre, the intermediate **9** can react further, and give a mixture of olefin and a nitrile complex.

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