

JOM 23592PC

## Preliminary Communication

### The formation of the metal-stabilized carbocation from an ammonium ion

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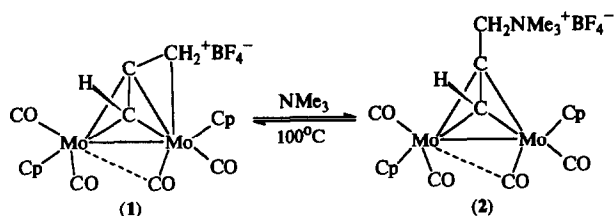
(Received January 20, 1993)

#### Abstract

Thermal decomposition of the ammonium ion  $[(\mu-\eta^2\eta^2\text{-HC}\equiv\text{CCH}_2\text{NMe}_3)\text{Cp}_2\text{Mo}_2(\text{CO})_4]^+\text{BF}_4^-$  leads to the metal-stabilized carbocation  $[(\mu-\eta^2\eta^3\text{-HC}\equiv\text{CCH}_2)\text{Cp}_2\text{Mo}_2(\text{CO})_4]^+\text{BF}_4^-$ .

The first stage of the *E1* elimination reactions is cleavage of the nucleofugic group X to yield a carbenium ion, which in its turn loses a proton to form an alkene [1]. When the carbenium ion being formed is quite stable, the reaction can be stopped after the first stage. Here we report the first example of such a fragmentation leading to the transition metal stabilized carbocation.

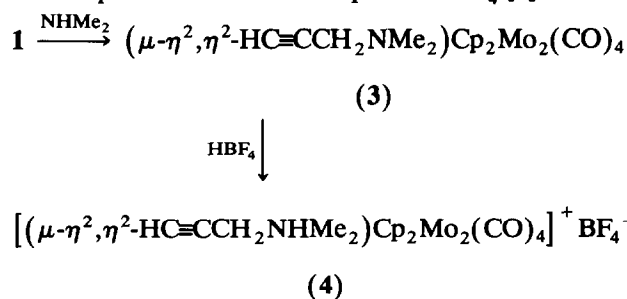
The starting trimethylammonium salt **2** has been prepared by treatment of the salt **1** with an excess of trimethylamine [2].



As the yield of the salt **2** is almost quantitative, the nucleophile attacks the  $\text{CH}_2$  group of the salt **1** selectively, and leaves the triple bond of the coordinated propargylic ligand intact. Thermolysis of **2** in either propionitrile or sulfolane at *ca.*  $100^\circ\text{C}$  yields **1**. Although **1** has not been isolated in analytically pure

form, its formation as the main product of cleavage was unambiguously proven by  $^1\text{H}$  NMR spectroscopy [3].

The dimethylammonium salt **4** was obtained using a slightly different two-step procedure: the dimethylaminopropargylic complex **3**, formed by the treatment of **1** with an excess of dimethylamine, yields the salt **4** upon treatment with aqueous  $\text{HBF}_4$  [4].



No **1** could be detected in the thermolysis of **4** under the conditions described for **2**.

#### References

- 1 C.K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell Univ. Press, Ithaca, 1969, Ch. IX.
- 2 NMR data for the salt **2**:  $^1\text{H}$  (acetone- $d_6$ ):  $\delta$  6.857 (t,  $^4J = 0.5$  Hz,  $\equiv\text{CH}$ ), 5.545 (s, Cp), 4.787 (broadened due to neighbour N atom,  $\text{CH}_2$ ), 3.196 (s,  $\text{NMe}_3$ );  $^{13}\text{C}$  (acetone- $d_6$ ):  $\delta$  53.37 ( $\text{NMe}_3$ ,  $J(\text{C}-\text{H}) = 144$  Hz), 70.99 ( $\text{CH}_2$ ,  $J(\text{C}-\text{H}) = 149.8$  Hz), 84.67 ( $\equiv\text{CH}$ ,  $J(\text{C}-\text{H}) = 213$  Hz), 93.19 (Cp,  $J(\text{C}-\text{H}) = 178$  Hz). Attempts to observe the resonances of quaternary and carbonyl carbons were not made.
- 3 NMR data for the salt **1** (isolated from the thermolysis reaction mixture):  $^1\text{H}$  (acetone- $d_6$ ):  $\delta$  6.868 (d,  $^4J = 1.92$  Hz,  $\equiv\text{CH}$ ), 5.86 (broadened due to stereochemical non-rigidity, Cp), 5.562 (d,  $^4J = 1.92$  Hz,  $\text{CH}_2$ ), 4.907 (s,  $\text{CH}_2$ );  $^1\text{H}$  (acetonitrile- $d_3$ ):  $\delta$  ppm 6.487 (d,  $^4J = 1.94$  Hz,  $\equiv\text{CH}$ ), 5.606 (broad, Cp), 5.354 (d,  $^4J = 1.94$  Hz,  $\text{CH}_2$ ), 4.681 (s,  $\text{CH}_2$ ). Authentic sample of the salt **1**:  $^1\text{H}$  (acetone- $d_6$ ):  $\delta$  6.868 (d,  $^4J = 1.92$  Hz,  $\equiv\text{CH}$ ), 5.852 (broadened due to stereochemical non-rigidity, Cp), 5.554 (d,  $^4J = 1.92$  Hz,  $\text{CH}_2$ ), 4.894 (s,  $\text{CH}_2$ );  $^1\text{H}$  (acetonitrile- $d_3$ ):  $\delta$  ppm 6.489 (d,  $^4J = 1.91$  Hz,  $\equiv\text{CH}$ ), 5.615 (broad, Cp), 5.349 (d,  $^4J = 1.91$  Hz,  $\text{CH}_2$ ), 4.686 (s,  $\text{CH}_2$ ).
- 4 NMR data for complex **3**:  $^1\text{H}$  (acetone- $d_6$ ):  $\delta$  6.379 (t, 0.71 Hz,  $\equiv\text{CH}$ ), 5.37 (s, Cp), 3.528 (broadened due to neighbour N atom,  $\text{CH}_2$ ), 2.197 (s,  $\text{NMe}_3$ ). NMR data for complex **4**:  $^1\text{H}$  (acetone- $d_6$ ):  $\delta$  ppm 6.55 (t,  $^4J = 0.56$  Hz,  $\equiv\text{CH}$ ), 5.521 (s, Cp), 4.534 (d,  $^4J = 0.56$  Hz,  $\text{CH}_2$ ), 3.025 (s, Me). On the interaction of **1** with primary amines see also: M. Gruselle, V. Philomin, F. Chaminant, G. Jaouen and K.M. Nicholas, *J. Organomet. Chem.*, 399 (1990) 317.

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