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Letters to the Editor

Electrophilic substitution at the unsaturated carbon atom in $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^2\text{-}HC{\equiv}C{-}CR{=}CH_2)$ complexes (R = H or Me)

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An interesting way of using metal-stabilized carbocations is their application in organic synthesis (see Ref. 1 and references cited therein). A well developed version of this approach is that the double bond of a coordinated alkenyne is functionalized by successive treatment of the latter with electrophilic and nucleophilic reagents. It has been illustrated with hexacarbonyldicobalt complexes containing coordinated vinylacetylene or its derivatives (see Refs. 2, 3 and references cited therein) that an intermediate cation is rather stable and allows stepwise addition of electrophilic and nucleophilic reagents.

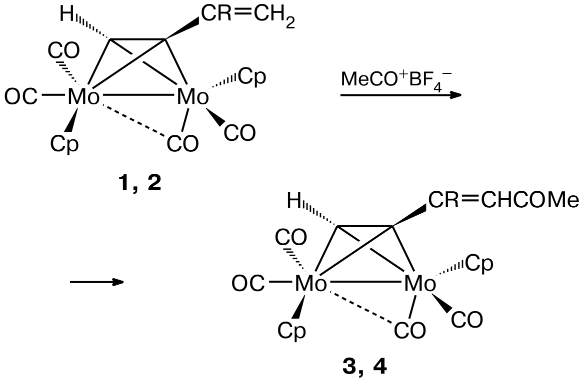
$$\mu\text{-}\eta^2,\eta^2\text{-}(HC{\equiv}CCH{=}CH_2)Co_2(CO)_6 \xrightarrow{E^+}$$

$$\longrightarrow [(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCHCH_2E)Co_2(CO)_6]^+ \xrightarrow{Nu}$$

$$\longrightarrow [\mu\text{-}\eta^2,\eta^2\text{-}HC{\equiv}CCH(Nu)CH_2E]Co_2(CO)_6$$

Molybdenum analogs of cobalt complexes, which contain two cyclopentadienyl ligands instead of two carbonyl ones, namely, $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^2\text{-}HC{\equiv}C{-}CR{=}CH_2)]$ (R = H (**1**) and Me (**2**)), are also precursors of metal-stabilized $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}C{-}CRMe)]^+$ carbocations. The latter are more stable than the above cobalt analogs.[4,5] It was interesting to find out how replacement of the metal and one of the ligands would affect the reactivities of coordinated alkenynes **1** and **2**.

The reactions of compounds **1** and **2** with acetylium tetrafluoroborate at −70 °C followed by treatment of the reaction mixture with MeOH (under the conditions similar to those for cobalt analogs) did not yield products of successive addition of the MeCO and OMe groups to the double bond of these compounds. Instead, the sole reaction products were alkenynes **3** and **4** resulted from the addition of the acetylium cation followed by proton elimination.



1, 2

3, 4

R = H (**1**, **3**), Me (**2**, **4**)

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Formally, this process can be regarded as electrophilic substitution at the unsaturated carbon atom of the coordinated alkenyne ligand and is the first example of such reactions. The structures of substitution products **3** and **4** were confirmed by ^{1}H NMR data. The protons of the substituted vinyl group in compound **3** give an AB spectral pattern. ^{1}H NMR (benzene-d$_6$), δ: 2.03 (s, 3 H, Me); 4.79 (s, 10 H, Cp); 5.36 (d, 1 H, $\underline{\text{H}}$C≡CCH=CH, ^4J = 0.7 Hz); 6.25 (d, 1 H, CH=C$\underline{\text{H}}$COMe, ^3J = 15.2 Hz); 7.89 (dd, 1 H, C$\underline{\text{H}}$=CHCOMe, ^3J = 15.2 Hz, ^4J = 0.7 Hz). IR (Vaseline oil), ν/cm^{-1}: 1675 (C=O).

The ^{1}H NMR spectrum of compound **4** shows five sets of signals, which correlates with the structure proposed. ^{1}H NMR (acetone-d$_6$), δ: 2.08 (d, 3 H, C$\underline{\text{Me}}$=CHCOMe, ^4J = 0.4 Hz); 2.18 (d, 3 H, CMe=CHCO$\underline{\text{Me}}$, ^4J = 1.1 Hz); 5.47 (s, 10 H, Cp); 6.14 (qq, 1 H, CMe=C$\underline{\text{H}}$COMe, ^3J = 1.1 Hz, ^4J = 0.4 Hz); 6.20 (s, 1 H, $\underline{\text{H}}$C≡CC(Me)=CH). IR (Vaseline oil), ν/cm^{-1}: 1665 (C=O).

Variation of the reaction conditions (ratio of the starting reagents, temperature, and the nature of the electrophile and the nucleophile) did not result in successive addition of an electrophile and an nucleophile; in all cases, substitution products were isolated only.

The use of molybdenum complexes opens a potentially novel route to alkenynes functionalized at the double bond, which differs from functionalization promoted by cobalt complexes.

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