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Preliminary communication

Preparation, isolation and chemical reactivity of the α-CF_3-propargylium ion stabilized by a heterobimetallic [Co–Mo] cluster

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Abstract

The synthesis of a diastereomeric α-CF_3 derivative of a propargylic alcohol complexed in a hetero-bimetallic [Co–Mo] cluster is described. By the action of HBF_4 on the alcohol, one variety of complexed propargylium ion is formed.

Keywords: Cobalt; Molybdenum; Trifluoropropargylic alcohol derivative; Nucleophilic attack; Binuclear complex

Despite the potent electron-withdrawing character of the trifluoromethyl group, numerous studies have now firmly established that α-CF_3-substituted carbenium ions are stable [1]. A variety of these cations have been generated or postulated as intermediates in synthetic and mechanistic studies, in particular when an adjacent electron-donating group is present. In some cases they are sufficiently stabilized by charge delocalization to be observable by NMR spectroscopy [2] or in the gas phase [3].

Alkyne bimetallic clusters are efficient stabilizers of carbenium ions and prevent isomerization of triple bonds [4]. In this context we report the isolation and preliminary reactivity results of a CF_3-substituted propargylium ion stabilized by a metallic cluster.

Initially, the dicobalt hexacarbonyl complex **1** of propargylic alcohol **2** was prepared in 55% yield [5], as shown in Scheme 1.

When the complexed alcohol **1** in CD_2Cl_2 solution was treated with HBF_4/Et_2O a carbenium ion was formed, as indicated by the resonance shift of the CF_3 group in the ^{19}F-NMR spectrum (from -83.9 to -93.4 ppm). This cation could not be isolated.

Replacing one $Co(CO)_3$ moiety by the isolobal $MoCp(CO)_2$ group is known to provide a better stabilization of the propargylium ion [6]. We therefore prepared the [Co–Mo] cluster of the alcohol **2** by modifying a procedure described by D'Agostino et al. [7]. The exchange of the $Co(CO)_3$ vertex by $MoCp(CO)_2$ in complex **1** was performed using $Na[MoCp(CO)_3]$ as a nucleophilic reagent [8], as shown in Scheme 2.

The diastereomeric alcohols **3a** and **3b** were obtained in a 1:1 ratio in 94% yield and separated by chromatography on silica plates (Et_2O:pentane, 1:6) [9]. The protonation of **3a** and **3b** in an ethereal solution by HBF_4/Et_2O resulted in the formation of a solid product identified as the carbenium ion salt **4** [10].

Some preliminary experiments on the reactivity of the cation **4** towards nucleophiles and/or bases have been performed and are summarized in Scheme 3.

The action of dimethylamine and/or sodium methanethiolate afforded the ethylenic compound **5** in 40% yield. With hydride reagents ($NaBH_4$ or $NaBH_3CN$) a mixture of elimination and reduction products **5** and **6** was obtained, in 1:1 ratio in 50% yield [11]. In the presence of water, the carbenium ion salt **4** leads exclusively and quantitatively to the alcohols **3a** and **3b** in 1:1 ratio. This nucleophilic addition, rather than elimination, of water is not observed with bimetallic complexes of non-fluorinated tertiary carbenium ions [4d].

In conclusion, through the interaction of a heterobimetallic cluster with a compound containing an acetylenic bond, an α-CF_3-substituted carbenium ion

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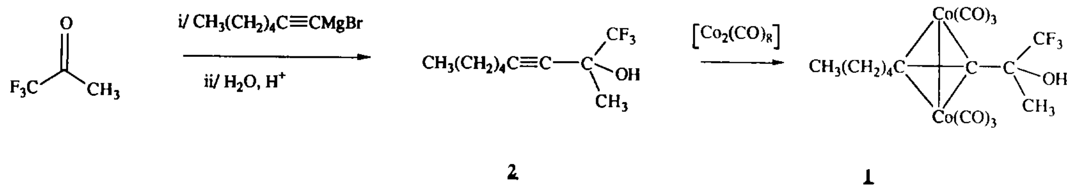
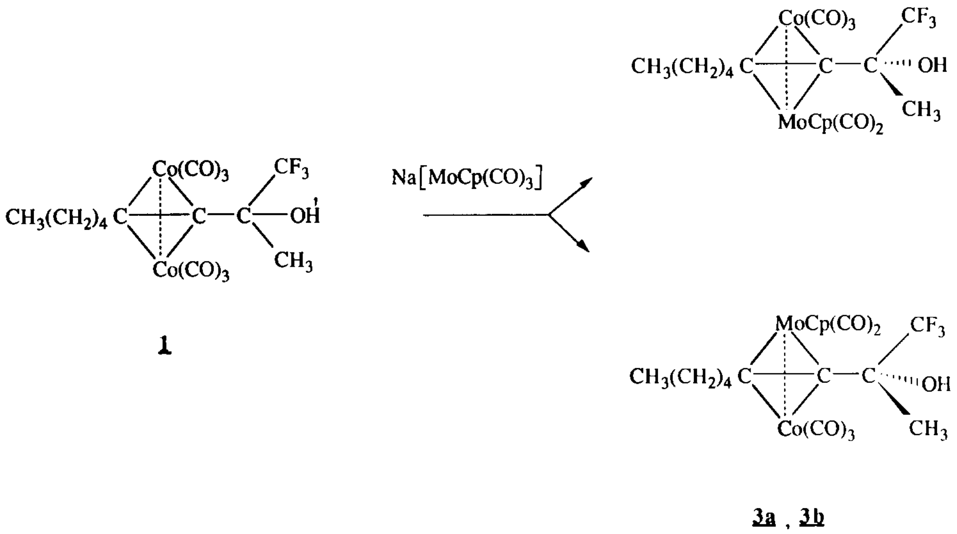
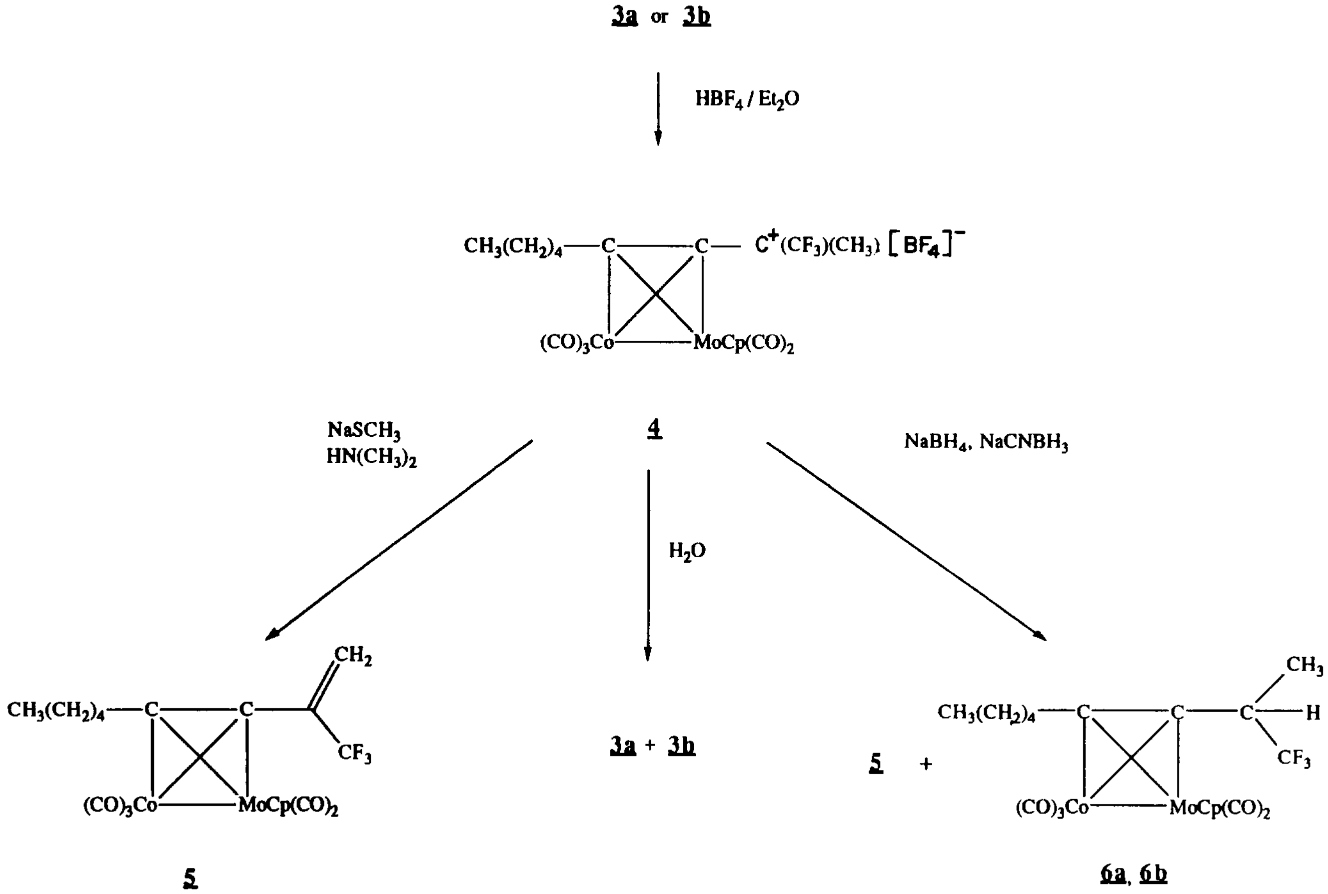


Scheme 1.



Scheme 2.



Scheme 3.

complex has been isolated for the first time. This allows the previously difficult nucleophilic substitution of α-CF_3 alcohols to be easily undertaken.

A study is in progress of other fluorinated α-CF_3-carbenium ions, especially secondary ions.

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[5] The ethyl magnesium bromide was obtained starting from 0.24 g of Mg (10^{-2} mol) and 0.75 ml of bromoethane (10^{-2} mol). 0.96 g (10^{-2} mol) of 1-heptyne in 20 ml of ether was added dropwise at room temperature and then heated under reflux for 1 h. After cooling to 0°C, 1.12 g (10^{-2} mol) of trifluoromethylketone in 10 ml of ether was added dropwise and the mixture was stirred 1 h. The reaction mixture was poured onto ice and neutralized. After classical workup 1.12 g of the crude product **2** was recovered.

0.416 g (2×10^{-3} mol) of **2** in 10 ml of ether was added under argon to an ethereal solution of 0.684 g (2×10^{-3} mol) of $[Co_2(CO)_8]$. After 1 h the reaction was complete and the crude product was flash chromatographed on silica gel (eluent: pentane/ether 1:1). 0.55 g of a red-brown oil **1** was recovered in 55% yield.

1, ^{1}H-NMR ($CDCl_3$): 2.76 (2H, m); 2.30 (1H, s); 1.70 (3H, s). 1.65–1.35 (6H, m); 0.93 (3H, t $J = 7.5$ Hz). ^{13}C-NMR($CDCl_3$): 198.7, 125.5, (q, $^1J_{C-F} = 280.7$ Hz), 100.8, 92.8, 75.0, (q, $J_{C-F} = 33.02$ Hz), 32.63, 31.29, 31.23, 24.61, 20.06, 13.48. ^{19}F-NMR (CD_2Cl_2): −83.9. IR (CH_2Cl_2) cm^{-1}: 2027.8, 2056.2, 2094.5. Anal. for $C_{16}H_{15}Co_2F_3O_7$: Calcd. C 38.87; H 3.04. Found: C 38.82; H 2.99%.

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[8] The methodology used by D'Agostino et al. was modified using Na/Hg as a reducing agent (H. El Haffa, Thesis, University Pierre et Marie Curie, Paris, 1992).

[9] For **3a** (the less polar isomer), ^{1}H-NMR ($CDCl_3$): 5.47 (5H, s); 2.95 (2H, m); 2.13 (1H, s); 1.82 (2H, m); 1.59 (3H, q, $^4J_{H-F} = 1$ Hz); 1.40 (4H, m); 0.91 (3H, t, $J = 7.5$ Hz). ^{13}C-NMR (CD_2Cl_2): 203.48; 126.0 (q, $^1J_{C-F} = 280.3$ Hz); 105.92; 91.88; 90.24; 77.6 (q, $^2J_{C-F} = 31.4$ Hz); 34.87; 31.87; 31.10; 24.87; 22.24; 13.80. ^{19}F-NMR (CD_2Cl_2): −85.0. IR (CD_2Cl_2) cm^{-1}: 1904.3; 1939.8; 1981.8; 2000.0; 2049.2; 2071.1. Anal. for $C_{20}H_{20}CoF_3MoO$; Calcd. C 42.25; H 3.52. Found: C 42.39; H 3.65%.

For **3b** (the most polar isomer), ^{1}H-NMR ($CDCl_3$): 5.47 (5H, s); 2.97 (2H, m); 2.19 (1H, s); 1.70 (2H, m); 1.53 (3H, q, $^4J_{H-F} = 1$ Hz); 1.40 (4H, m); 0.90 (3H, t, $J = 7.5$ Hz). ^{13}C-NMR (CD_2Cl_2): 203.6; 125.5 (q, $^1J_{C-F} = 276.8$ Hz); 106.38; 92.26; 90.26; 77.10 (obscured by $CDCl_3$ peaks) 34.75; 31.90; 31.06; 24.83; 22.25; 13.80. ^{19}F-NMR (CD_2Cl_2): −85.3. IR (CH_2Cl_2) cm^{-1}: 1938.6; 1984.9; 2000.9; 2051.2. Anal. for $C_{20}H_{20}CoF_3MoO_6$: Calcd. C 42.25; H 3.52. Found: C 43.29; H 3.77.

[10] To an ethereal solution of 0.06g (0.1 mmol) of **3a** or **3b**, at room temperature, was added 0.2 ml of $HBF_4 \cdot Et_2O$, leading to the formation of a non-soluble red–brown oil, turning rapidly to a fine yellow-brown powder. After several washes with ether, the powder was dried under vacuum. Yield 78% (0.05 g).

For **4**, ^{1}H-NMR (CD_2Cl_2): 5.86 (5H, s); 2.97 (2H, m); 2.01 (3H, s); 1.92 (1H, m); 1.59 (1H, m); 1.39 (4H, m); 0.91 (3H, s). ^{13}C-NMR (CD_2Cl_2): 216.51; 210.01; 199.21; 126.5 (q, $^1J_{C-F} = 276.7$ Hz); 108.89; 92.36; 36.75; 32.93; 31.59; 22.51; 21.70; 13.90. ^{19}F-NMR (CD_2Cl_2): −101.74 (s). IR (CD_2Cl_2): 1943.6; 1988.9; 2005.0; 2053.7; 2063.2; 2102.3. Anal. For $C_{20}H_{19}BCoF_7MoO_5$: Calcd. C 37.62; H 2.98. Found: C 36.56; H 3.01%.

[11] For **5**, ^{1}H-NMR ($CDCl_3$): 5.81 (1H, s); 5.42 (1H, s); 5.30 (5H, s); 2.92 (2H, m); 1.70–1.20 (6H, m); 0.91 (3H, t).

For **6a**, **6b**, ^{1}H-NMR ($CDCl_3$): 5.40 (5H, s); 3.50 (1H, m); 2.92 (2H, m); 1.70–1.20 (6H, m); 1.34 (3H, d) and 5.38 (5H, s), 3.50 (1H, m); 2.92 (2H, m); 1.70–1.20 (6H, m) 1.27 (3H, d) 0.92 (3H, t).