Ethynylthioamide Complexes: Synthesis, Reactivity and an Unusual Coupling Reaction with Diethylaminopropyne

Normen Szesni, Matthias Drexler, Bernhard Weibert, and Helmut Fischer

Fachbereich Chemie, Universität Konstanz, Fach M727, D-78457 Konstanz, Germany

Reprint requests to Prof. Dr. H. Fischer. E-mail: helmut.fischer@uni-konstanz.de

Z. Naturforsch. **2007**, *62b,* 346 – 356; received July 20, 2006

Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65 th birthday

The reaction of $[(CO)_5Cr(THF)]$ with propynethioic acid amides, R–C≡C–C(=S)NMe_2 (R = H, $SiMe_3$), yields the thioamide complexes $[(CO)_5Cr–S=C(NMe_2)C≡C–H]$ (**1a**) and $[(CO)_5Cr–S=C(NMe_2)C≡C–SiMe_3]$ (**1b**). Treatment of solutions of **1a** or **1b** with methyllithium generates, *via* deprotonation or desilylation, the lithium salt $Li[(CO)_5Cr–S=C(NMe_2)C≡C]$ (**2**). On filtration over silica, **2** is readily reprotonated. Complex **1a** is inert towards methanol, however, adds diethylamine across the C≡C bond to give the thioacrylamide complex $[(CO)_5Cr–S=C(NMe_2)C(H)=C(H)NMe_2]$ (**3**). Thiourea displaces the thioamide ligand to give $[(CO)_5Cr–S=C(NH_2)_2]$ (**4**). Complex **1a** reacts with half an equivalent of diethylaminopropyne in a three-component coupling to form the homobinuclear complex $[(CO)_5Cr–S=C(NEt_2)–C(CH_3)=C(H)–C(H)=C(NMe_2)–C≡C–C(NMe_2)=S–Cr(CO)_5]$ (**5**) in high yield. The solid state structures of complexes **1a** and **5** were established by X-ray structural analyses.

Key words: Thioamide Complexes, Chromium Complexes, Nucleophilic Addition, Coupling Reaction