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Preliminary communication

INITIAL FORMATION OF AN OLEFIN-COPPER(I) π-COMPLEX IN CONJUGATE ADDITION OF LITHIUM DIMETHYLCUPRATE TO t-BUTYL CINNAMATE

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Summary

The ^{13}C NMR spectrum observed upon mixing lithium dimethylcuprate and t-butyl cinnamate in toluene-d_8/THF at −70°C shows the signals of the olefinic carbons shifted to lower δ values. These are attributed as due to a π-complex formed by coordination of copper to the carbon–carbon double bond of the cinnamate.

The conjugate addition of lithium diorganocuprates to α,β-unsaturated carbonyl compounds is a well established and valuable procedure for the formation of carbon–carbon bonds, the reaction being highly regio- and stereoselective [1]. However, despite considerable efforts to clarify the reaction mechanism, some open questions still remain, e.g. how does the cuprate first approach the enone?

We are at present studying the reaction between lithium dimethylcuprate, $LiMe_2Cu$, and some cinnamic acid esters in various solvents. Cinnamates were chosen as substrates since they undergo conjugate addition relatively slowly, which makes it possible to monitor the reactions at low temperatures using NMR techniques.

In a typical experiment $LiMe_2Cu$ is prepared in diethyl ether by addition of methyllithium to copper(I) iodide. After evaporation of most of the ether, toluene-d_8 and some THF is added and the residual ether is evaporated off. The solution is transferred to an NMR tube sealed with a septum. After cooling to −78°C a solution of t-butyl cinnamate is added. ^{13}C NMR spectra have been recorded for the temperature range −70 to 0°C. Conjugate addition is slow at temperatures below −30°C, and the initial interactions between $LiMe_2Cu$ and the cinnamate can be studied. The ^{13}C NMR data for t-butyl cinnamate and for a

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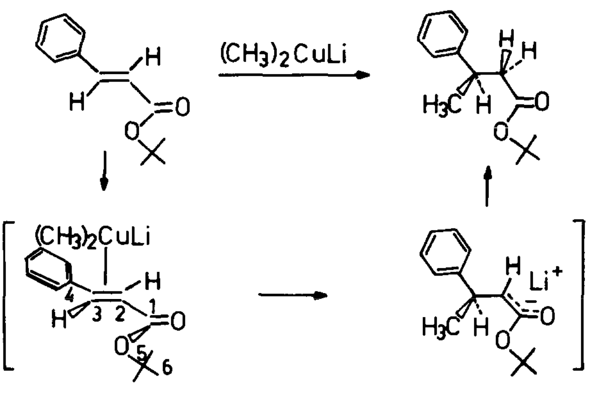

SCHEME 1

mixture of t-butyl cinnamate and $LiMe_2Cu$ in toluene-d_8/THF are summarized in Table 1. The olefinic carbons C-2 and C-3 are shifted from 120.0 and 144.0 ppm to 52.8 and 61.4 ppm, respectively, on addition of $LiMe_2Cu$. On increasing the temperature from −20°C these signals broaden and disappear before the appearance of the spectrum of the lithium enolate, the primary product of the conjugate addition. At −70°C several signals between −6 and −10 ppm are also observed, in contrast to the spectrum of $LiMe_2Cu$ in toluene-d_8/THF which shows only a single absorption at −10.30 ppm.

TABLE 1

^{13}C NMR CHEMICAL SHIFTS FOR t-BUTYL CINNAMATE IN TOLUENE-d_8/THF AND FOR A MIXTURE OF t-BUTYL CINNAMATE AND $LiMe_2Cu$ IN TOLUENE-d_8/THF. SPECTRA WERE RECORDED AT −70°C WITH TMS AS INTERNAL STANDARD AT 67.9 MHz. "CH_3Cu" DESIGNATES THE METHYL GROUP BONDED TO COPPER IN THE CUPRATE AND IN THE π-COMPLEX

Substrate	Chemical shifts for carbon atoms, ppm						"CH_3Cu"
	1	2	3	4	5	6	
t-Butylcinnamate	166.0	120.0	144.0	134.9	79.9	27.9	—
t-Butylcinnamate + $LiMe_2Cu$	174.3	52.8 J 155 Hz	61.4 J 153 Hz	144.0	77.9	28.7	−9.3, −8.4, −6.8

The large shifts, $\Delta\delta$, of the ^{13}C signals for the olefinic carbons (67.2 and 82.6 ppm for C-2 and C-3, respectively) are consistent with the formation of a olefin-copper π-complex, such shifts being generally observed on coordination of a transition metal to a carbon—carbon double bond [2]. In the present case an electron rich "Me_2Cu^-" species is interacting with an electron deficient alkene bond. The σ-bonding interaction obtained by donation of olefin π-electrons to empty copper *s* or *p* orbitals can be assumed to give a weak contribution while the π-bonding interaction due to back donation from filled copper *d* orbitals to empty olefin π★-orbitals could be relatively important.

Coordination of copper(I) to C=C bonds has been reported e.g., for simple alkene complexes of copper(I) chloride and copper(I) triflate [3,4]. However, olefin-copper π-complexes have not been observed in conjugate addition of cuprates to enones or enoates. Work is now in progress to characterize the olefin-copper π-complex further and to study its reactions.

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