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AN NMR INVESTIGATION OF THE REACTION BETWEEN CINNAMIC ACID ESTERS AND LITHIUM DIMETHYLCUPRATE. INITIAL FORMATION OF AN OLEFIN-COPPER π-COMPLEX

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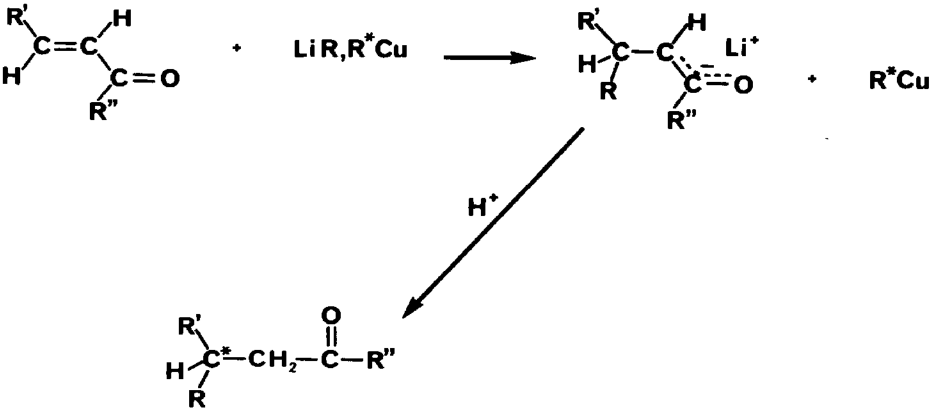
Summary

The reaction between lithium dimethylcuprate and methyl or t-butyl *trans*-cinnamate has been studied by ^1H and ^{13}C NMR spectroscopy in the temperature range −110 to +60°C. Below −35°C conjugate addition is slow, and a large shift in the olefinic hydrogen and carbon signals is observed. The temperature dependence of the spectra is interpreted in terms of two new species in slow equilibrium, one being an olefin-copper π-complex and the other involving complexation of lithium to the ester carbonyl oxygen. Above −35°C the lithium enolate from conjugate addition of the cuprate is formed, probably via the π-complex.

The addition of lithium diorganocuprates to α,β-unsaturated ketones and esters is known to be highly regio- and stereo-selective [1], and we have investigated the potential of chiral lithium diorganocuprates for asymmetric synthesis. The addition

SCHEME 1

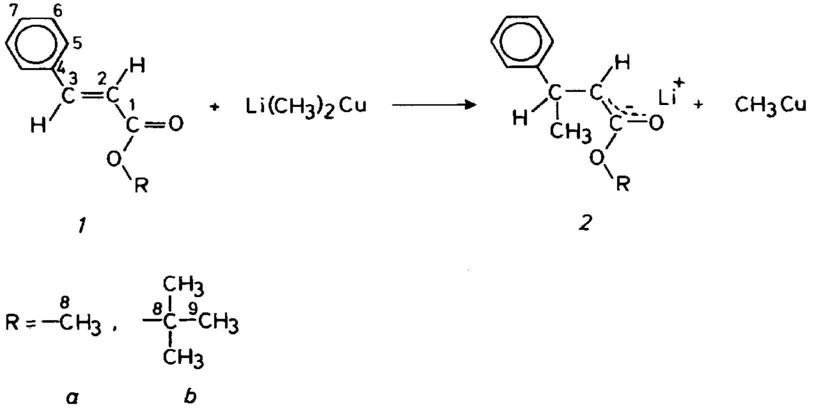


of chiral cuprates to prochiral enones and enoates gives high chemical yields and moderate enantiomeric excesses of the product (Scheme 1) [2].

Although several different mechanisms for the conjugate addition of lithium diorganocuprates, LiR_2Cu, to α-ethylenic carbonyl compounds have been proposed [3–8], it is generally agreed that in the first step a complex is formed between the reactants. This complex is most often thought of as being a lithium-carbonyl complex, as suggested by House and coworkers [3], and the kinetics of the formation of conjugate addition product from this complex have been investigated [4]. However, the rate expression obtained is also compatible with the olefin-copper π-complex suggested by Rivière [5] and by Berlan [6], or with a charge transfer complex [7]. In no case has it been possible to study the structure of the intermediate complex.

The aim of the present study [9] was to gain further insight into the reaction mechanism, and to look for the proposed complexes or any intermediates along the reaction path. We used as a model reaction the reaction between lithium dimethylcuprate, $LiMe_2Cu$, and esters of *trans*-3-phenylpropenoic acid, and studied this in various solvents and at various temperatures by ^1H and ^{13}C NMR spectroscopy; cinnamates were chosen because of their moderate reactivity towards cuprates (Scheme 2).

SCHEME 2



$LiMe_2Cu$ is a fairly stable cuprate and its NMR spectrum is easily distinguishable from those of the substrate, **1**, any intermediate, or the product enolate, **2**.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker WH 270 MHz (67.89 MHz, ^{13}C) spectrometer. Samples for NMR investigation were prepared as follows.

Lithium dimethylcuprate was prepared by addition of methyllithium (2 equiv.) to a slurry of copper(I) iodide (1 equiv.) in a small volume of diethyl ether, Et_2O, at 0°C. (Usually the lithium iodide formed was not removed, but in two experiments it was removed by washing the solid MeCu several times with ether.) The diethyl ether was evaporated under argon, but some equivalents of ether were retained by the cuprate as observed previously [10]. Dichloromethane-d_2 was then added and the CD_2Cl_2/Et_2O solution used as such. For the second set of samples addition of toluene-d_8 was followed by addition of some tetrahydrofuran, THF, and the remaining diethyl ether was evaporated off to leave a $C_6D_5CD_3$/THF solution. The cuprate solutions were transferred to NMR tubes sealed with rubber septa and cooled to −78°C before addition of methyl cinnamate, **1a**, or t-butyl cinnamate, **1b**, via syringe.

The concentration of $LiMe_2Cu$ was approximately 0.5 *M* in the ^{13}C samples and ca. 1 *M* in the ^1H NMR samples: accurate estimation of the concentration was difficult because of the method of preparation. $LiMe_2Cu$ was present in excess in the samples for ^{13}C NMR. The ^1H and ^{13}C NMR spectra were recorded in the temperature range −110 to +60°C and the reproducibility of the spectra was checked by alternately increasing and decreasing the temperature in the −110 to −35°C range. Above −35°C irreversible conjugate addition is observed.

The presence of copper greatly affects the magnetic susceptibility of these samples, thus necessitating extensive adjustment of the shim currents of the spectrometer magnet, and all the signals observed are somewhat broadened.

All handling of organometallic reagents and NMR samples was carried out under argon. THF and diethyl ether were distilled from sodium benzophenone ketyl. Commercial deuterated solvents (toluene-d_8 and dichloromethane-d_2) were used without purification. Commercial methyllithium in diethyl ether was used after titration, and copper(I) iodide was recrystallized [11] before use. Methyl cinnamate and t-butyl cinnamate [12] were prepared by standard procedures.

Assignments

The NMR spectra were recorded on solutions containing LiI from the preparation of $LiMe_2Cu$ except in two control experiments, 12 and 13, Table 2.

Some selected ^{13}C NMR data for the solutions of $LiMe_2Cu$ and methyl cinnamate, **1a**, or t-butyl cinnamate, **1b**, are summarized in Table 1, together with data for the pure esters. The temperature dependence of the ^{13}C NMR spectrum of a solution of $LiMe_2Cu$ and **1a** is shown schematically in Fig. 1.

Signals observed as doublets (J(C–H) ca. 160 Hz) at 52 ppm and 61.8 ppm from a solution of $LiMe_2Cu$ and **1a** in toluene-d_8/THF at −70°C, exp. 4, are assigned to

TABLE 1

^{13}C NMR CHEMICAL SHIFT DATA (relative to TMS) FOR METHYL CINNAMATE **1a** OR t-BUTYL CINNAMATE **1b** IN THE PRESENCE OF LITHIUM DIMETHYLCUPRATE

Exp no.	Substrate	δ(ppm)				$(CH_3)_2CuLi$ δ(ppm)	Temperature (°C)	Solvent
		C(1)	C(2) [a]	C(3) [a]	C(4)			
1	**1a**	167.6	118.4	145.0	135.0	–	25	CD_2Cl_2
2	**1a** + LiI	170.3	117.3	147.7	134.7	–	25	CD_2Cl_2/Et_2O
3	**1a**	166.9	117.7	144.9	134.5	–	−60	$C_6D_5CD_3$/THF
4	**1a** + $LiMe_2Cu$	173.9	(52.0) [b]	61.8	143.4	−9.1	−70	$C_6D_5CD_3$/THF
5	**1a** + $LiMe_2Cu$	173.3	(62.3) [c]	74.6	139.4	−7.8; −13.6	−70	CD_2Cl_2/Et_2O
	enolate **2a**	161.8	73.8	36.5	150.1	−9.7	0	CD_2Cl_2/Et_2O
6	**1b**	166.0	120.0	144.0	134.9	–	−70	$C_6D_5CD_3$/THF
7	**1b** + $LiMe_2Cu$	174.3	52.8	61.4	144.0	−6.8; −8.4; −9.3	−70	$C_6D_5CD_3$/THF

[a] Signals assigned to C(2) and C(3) were observed as doublets, J(C–H) ~ 160 Hz. [b] Coincides with the signal from C(8). [c] Coincides with one ether signal.

carbon C(2) and C(3), respectively, in the ester **1a**. However, the signal at 52 ppm coincides with that due to the methyl ester carbon C(8). The signals observed at 173.9 ppm, assigned to the carbonyl carbon C(1), and at 143.4 ppm, the quarternary carbon C(4) in the aromatic ring, indicate that C(1) and C(4) have become deshielded relative to the pure ester, exp. 3. One signal at −9.1 ppm is assigned to the methyl groups in $LiMe_2Cu$. The ^{13}C NMR chemical shift for pure $LiMe_2Cu$ has been found to vary from −8.7 (CD_2Cl_2/diethyl ether [13]) to −10.30 ppm (toluene-d_8/THF).

The spectrum of $LiMe_2Cu$ and **1a** in CD_2Cl_2/diethyl ether, exp. 5, shows similar effects, although the shift differences relative to pure **1a** exp. 1, are smaller. Two signals observed at −7.8 ppm and −13.6 ppm are assigned to $LiMe_2Cu$.

For t-butyl cinnamate, **1b**, and $LiMe_2Cu$ in toluene-d_8/THF the signals from C(2) and C(3) are well separated from solvent and other ester signals, and are observed at 52.8 and 61.4 ppm, respectively, in good agreement with the data for **1a**. Three signals, at −6.8, −8.4 and −9.3 ppm, respectively, are assigned to the cuprate.

Selected ^1H NMR data for methyl cinnamate **1a** and for its solutions with $LiMe_2Cu$ are listed in Table 2, which also shows the changes in shifts with variations in temperature over the range −110 to −13°C. The corresponding data for t-butyl cinnamate, **1b**, are summarized in Table 3.

In the ^1H NMR spectrum of the solution of **1a** and an excess of $LiMe_2Cu$ in CD_2Cl_2/diethyl ether at −110°C, exp. 10, the signals assigned to H(2) and H(3) were found to be shifted to δ 4.3 and 4.6 ppm, respectively, appearing as two broad doublets, $J_{2,3}$ 12.5 Hz. The aromatic protons were shifted from δ 7.47 and 7.65 ppm for the pure ester to 7.28 and 7.35 ppm, respectively. The methyl groups of $LiMe_2Cu$ gave rise to five signals instead of the normal singlet at ca. −1 ppm [13,14]. In addition to these signals, very weak broad signals at δ 6.6 and 8.0 ppm, attributed H(2) and H(3) in a different species were observed.

When the ester **1a** and **1b** are taken in excess relative to $LiMe_2Cu$ two sets of signals are observed more clearly, cf. exp. 11 in Table 2 and exp. 15 in Table 3. For the ester **1b** and $LiMe_2Cu$ in toluene-d_8/THF at −90°C the major component has its H(2) and H(3) signals shifted slightly downfield to δ 6.7 and 8.4 ppm, exp. 15. The minor component has its H(2) and H(3) signals shifted upfield to between 3.9 and 4.3 ppm. Two sets of aromatic protons of unequal intensity are also observed for both esters. When approximately equal concentrations of **1b** and $LiMe_2Cu$ are used, exp. 16 in Table 3, the two sets of signals assigned to H(2) and H(3) in the different species are of equal intensity.

The cuprate methyl groups gave several signals in the presence of **1a** while one broad signal was observed for the cuprate in the presence of the t-butyl ester. The ^1H NMR spectrum of pure $LiMe_2Cu$ in toluene-d_8/THF shows a singlet at −0.85 ppm in the presence of LiI.

When ^1H NMR spectra were obtained from solutions from which most of the LiI (from preparation of $LiMe_2Cu$) had been removed some difference in the down-field region of the spectra were observed, exps. 12 and 13 in Table 2. In the spectrum of **1a** in the presence of excess $LiMe_2Cu$ two sets of signals are again observed at −80°C attributable to two components, of different concentrations, (exp. 12). The major component has its H(2) and H(3) signals shifted to 4.2 and 4.56 ppm, and these appear as sharp doublets. The corresponding methoxy signal, H(8), appears at

3.72 ppm and the aromatic protons appear at 7.19 and 7.28 ppm. The minor component has its H(2) and H(3) signals shifted to 6.6 and 7.9 ppm, and the methoxy signal, H(8), to 3.84 ppm. The aromatic protons are observed at 7.43 and 7.58 ppm.

With the ester **1a** in a large excess, one major component is observed, exp. 13. The H(2) and H(3) signals are observed at 6.59 and 7.84 ppm as doublets, and the methoxy protons, H(8), at 3.84 ppm. The minor component is observed only as weak signals in the aromatic region, 7.0–7.1 ppm.

The ^1H and ^{13}C NMR spectra for a solution of **1a** and LiI were also obtained, exp. 2 in Table 1 and exp. 9 in Table 2. The small downfield shifts relative to pure **1a**

TABLE 2

^1H NMR CHEMICAL SHIFT DATA (relative to TMS) FOR METHYL CINNAMATE, **1a**, AND FOR ITS SOLUTIONS WITH LiMe$_2$Cu IN DICHLOROMETHANE-d_2/DIETHYL ETHER (d = doublet, b = broad, vb = very broad, bd = broad doublet, Numbers in parentheses refer to species in low concentration.)

Exp no.	Olefinic hydrogens, δ(ppm)		LiMe$_2$Cu, δ(ppm)	Temperature (°C)	Comments
	H(2)	H(3)			
8	6.55 d	7.73 d	–	−60	pure ester **1a**
	16.1 Hz	16.1 Hz			aromatic H: δ 7.47, 7.65 ppm
9	6.60 d	8.02 d	–	25	ester **1a** + LiI
	16 Hz	16 Hz			
10	4.3 bd; (6.6 b);	4.6 bd; (8.0 b)	−0.89, −0.98, −1.05,	−110	**1a** + excess LiMe$_2$Cu
	12.5 Hz	12.5 Hz	−1.14, −1.22		aromatic H: δ 7.28, 7.35 ppm
	4.3 b (6.6 b)	4.6 b (8.0 b)	−0.93, −0.99, −1.05	−90	very broad signals
	– –	– –	−0.9	−70	coalescence, aromatic H: broad
	6.2 vb	hidden	−0.96	−53	
	6.4 b	7.8 b	−0.96	−43	product enolate **2a** appearing
	6.6 bd	8.0 bd	−0.96	−33	product enolate **2a** appearing
	16 Hz	16 Hz			
11	(4.3 b) 6.8 b	(4.6 b) 8.2 b	−0.5, −0.6, −0.93,	−110	LiMe$_2$Cu + excess **1a**
			−1.08		aromatic H: δ 7.5, 7.7 ppm
	(4.3 b) 6.8 d	(4.6 b) 8.1 d	−0.95, −1.0	−90	aromatic H: δ (7.1, 7.25)
	15 Hz	15 Hz			7.25, 7.45 ppm
	(4.3 vb) 6.7 bd	(4.6 vb) 8.1 bd	−0.97 b	−73	aromatic H: δ 7.44, 7.66 ppm
	– –	– –	−0.93 b	−50	coalescence, arom. H:
					δ 7.4, 7.6 ppm
	6.4 vb	hidden	−0.90	−33	
	6.5 b	7.8 b	−0.86	−25	product enolate **2a** appearing
	6.60 d	8.00 d	−0.83	−15	product enolate **2a** appearing
	16 Hz	16 Hz			aromatic H: δ 7.4, 7.6 ppm sharp
12	4.22 d (6.65 b)	4.56 d (7.93 b)	−1.02, −1.10	−80	**1a** + excess LiMe$_2$Cu[a]
					aromatic H: δ 7.19, 7.28;
					(7.45, 7.58) ppm
13	6.59 d	7.84 d	−0.9 b	−85	LiMe$_2$Cu + excess **1a**[a]
					aromatic H: δ 7.4,
					7.5 (7.0, 7.1) ppm
	6.56 b	7.82 b	−0.9 b	−60	
	–	–		−50	coalescence
	6.45 b	7.67 b	−0.9	−40	
	6.51 d	7.77 d	−0.8	−20	

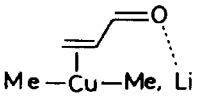
[a] After removal of LiI.

are interpreted in terms of lithium coordination to the carbonyl oxygen. Similar shift changes have been observed previously for solutions of carbonyl compounds and $LiClO_4$ [15].

Discussion

In the ^{13}C NMR spectra of the esters **1a** and **1b** in the presence of $LiMe_2Cu$ the high field doublets in the region 50 to 70 ppm can be assigned to the olefinic carbons C(2) and C(3) of the esters. The strong shielding of these carbons is assumed to be caused by coordination between the esters and $LiMe_2Cu$ rather than by any reaction which would change the structure of the esters.

Since the largest perturbations are observed for the olefinic carbons C(2) and C(3) rather than for the carbonyl carbon or the aromatic carbons it is reasonable to suggest that the cuprate interacts with the ester by coordination of copper to the olefinic π-bond, **3**. Lithium coordination to the carbonyl oxygen would cause a small downfield shift of the signals for C(1) and C(3), cf. exp. 2 Table 1. On the basis of our results we can not rule out the possibility that complexation of the carbonyl oxygen by lithium takes place within the olefin-copper π-complex, **3**.



3

The large upfield shifts, $\Delta\delta = -67.2$ for C(2) and -82.6 for C(3), in toluene-d_8/THF, are what might be expected from a consideration of the Dewar–Chatt–Duncanson model [16] for olefin-transition metal π-complexes. Thus, while donation of electrons from the carbon–carbon π-orbital to empty orbitals on copper, to form a σ-bond, should cause deshielding of the olefinic carbons, this effect is offset by back-donation of electrons from filled copper *d*-orbitals to an olefin π^*-orbital which results in a total shielding of the olefinic carbons. Kochi et al. have studied the formation of π-complexes between simple alkenes and copper(I) triflate [17]. The maximum shielding for a Cu^+-alkene complex was observed as a shift upfield by 29 ppm in the ^{13}C NMR. It is reasonable to assume that copper in $LiMe_2Cu$ is more electron rich, resembling a Me_2Cu^- anion, and thus on π-complex formation back-donation would be the stronger perturbation and also much stronger than that in the copper triflate-alkene complex. The chemical shifts observed are of the same order as those observed for other enone-transition metal π- complexes [18].

The set of shielded olefinic hydrogens H(2) and H(3) in the ^1H NMR spectra of esters **1a** and **1b** in the presence of $LiMe_2Cu$ are in good agreement with the suggested copper-olefin coordination in **3**. It is well established that on coordination of transition metals to olefins the atoms attached to the C=C bond are bent slightly away from the metal [19]. This effect of coordination is related to a change, from sp^2 to sp^3, in the character of the C=C carbons and is consistent with the reduced coupling constants $J_{2,3}$ 12.5 Hz, cf. exps. 10 and 16, and the observed upfield shifts of the aromatic protons, exps. 10, 11, 12 and 15 as well as the deshielding of the carbonyl carbon, exps. 4, 5 and 7. These shifts indicate reduced conjugation between the carbonyl group and the aromatic ring via the C=C bond on coordination. (Compare the C=O ^{13}C shifts for methyl propanoate at 173.3 ppm and methyl acrylate at 164.5 ppm.)

The second set of protons H(2) and H(3) observed at low temperatures in the ^1H NMR spectra is assigned to a species **4** with deshielded olefinic hydrogens, the shift of which cannot be explained by copper-olefin coordination. The H(2) and H(3) signals at δ 6.71 and 8.41 ppm, respectively, observed in exp. 15 point to lower electron density on C(2) and C(3) in this species, **4**, compared to the pure ester **1b**. This effect is probably caused by lithium coordination to the carbon oxygen and comparison of chemical shifts for H(2) and H(3) in exps. 10 and 11 with the shifts for H(2) and H(3) in the complex formed between **1a** and LiI in exp. 9 supports this hypothesis. A lithium-ester carbonyl complex can be formed either by coordination of LiI formed in the preparation of $LiMe_2Cu$ or by coordination of lithium in the cuprate.

$C{=}C{-}C{=}O + LiI \rightleftharpoons C{=}C{-}C{=}O \cdots LiI$

$C{=}C{-}C{=}O + LiMe_2Cu \rightleftharpoons C{=}C{-}C{=}O \cdots LiMe_2Cu$

The ^1H NMR spectra obtained for solutions of **1a** and $LiMe_2Cu$ from which LiI had been removed indicate the presence of the π-complex **3** when $LiMe_2Cu$ is present in excess, exp. 12, as would be expected from exp. 10. However, in the presence of a large excess of **1a** the signals obtained for the major component must be assigned to the uncomplexed ester **1a**. The minor component is the π-complex **3**, exp. 13. Thus in the absence of LiI a lithium-carbonyl complex is not formed and we conclude that complex **4** observed in exps. 10, 11, 15 and 16 is formed by coordination of LiI to the carbonyl oxygen.

So far we have not discussed the possible structures of $LiMe_2Cu$ or the olefin-copper π-complex **3**. It is generally assumed that lithium diorganocuprates are dimeric in solution. X-ray data [20] molecular weight measurements [14,20] and NMR investigations [14,20] of $LiMe_2Cu$ have been interpreted in terms of a cyclic, symmetrical dimeric structure. It is, however, not known if this is the reacting species in conjugate addition to enones or enoates. NMR data for $LiMe_2Cu$ indicate a substantial influence of the solvent on the character of the cuprate, and this is also reflected in the change in reactivity with solvent previously reported [13].

The geometry at copper in $LiMe_2Cu$ is assumed to be roughly linear in solution [20,21]. On going from disubstituted copper in $LiMe_2Cu$ to at least threefold coordination of copper in the π-complex; the geometry at copper is likely to change to either trigonal planar or tetrahedral. Our data do not allow a choice between these geometries. However, the observation of several cuprate methyl signals at low temperature indicates that the methyl groups in $LiMe_2Cu$ become non-equivalent upon coordination to the esters, exps. 5, 7, 10 and 11.

A substantial effect on the chemical shifts of the olefinic protons and carbons in π-complex **3** was caused by a change of solvent, cf. exps. 4, 5 and 7 in Table 1 and exps. 15, 16 and Table 3. Some effect is also observed on the shift for $LiMe_2Cu$, while the effect on the signals in the aromatic region is negligible. The toluene-d_8/THF induced chemical shifts in the ^{13}C NMR are -10 ppm for C(2) and -13 ppm for C(3) at -70°C relative to CD_2Cl_2/Et_2O. Coordination of THF to lithium in the cuprate bonded as in **3** leads to an increase in electron density on copper, and thus the back-bonding becomes stronger in toluene-d_8/THF than in CD_2Cl_2/Et_2O [22].

Dynamic NMR spectra

The ^1H and ^{13}C NMR spectra for solutions of **1a** or **1b** and $LiMe_2Cu$ were found to vary with the temperature. The temperature dependence of the ^{13}C NMR spectrum was studied in exp. 5, and is summarized in Fig. 1. On warming the solution containing the π-complex **3a** (exp. 5), the signals assigned to C(2) and C(3) broadened and disappeared into the base line. At temperatures above −40°C signals assigned to the product enolate **2a** appeared.

The variation of the ^1H NMR spectra with an increase in temperature was studied in exps. 10, 11, 13 and 15. Fig. 2 summarizes the change in chemical shift observed for signals assigned to H(2) and H(3) (exps. 10 and 11). Spectra for the solution of **1a** and $LiMe_2Cu$ were recorded at ca. 10°C intervals over the temperature range −110 to −13°C. When $LiMe_2Cu$ was used in excess, exp. 10, the π-complex **3a** was the major component in solution, while complex **4a** was present in very low concentration. On raising the temperature the cuprate methyl signals collapsed to one signal while the two sets of H(2) and H(3) signals were broadened. At about −70°C coalescence of the two H(2) signals and the two H(3) signals occurred, cf.

TABLE 3

^1H NMR CHEMICAL SHIFT DATA (relative to TMS) FOR t-BUTYL CINNAMATE, **1b**, AND ITS SOLUTIONS WITH $LiMe_2Cu$ IN DIFFERENT SOLVENTS AND AT VARIOUS TEMPERATURES (b = broad, vb = very broad, d = doublet, bd = broad doublet. Numbers in parenthesis refer to signals of low intensity.)

Exp no.	Olefinic hydrogens, δ(ppm)		$LiMe_2Cu$ δ(ppm)	Temperature (°C)	Solvent	Comments
	H(2)	(H3)				
14	6.43 d	7.77 d	–	−55	$C_6D_5CD_3$/	pure ester **1b**
	16 Hz	16 Hz			THF	
15	(hidden) 6.71 b	(4.23 b) 8.41 b	−0.1 b	−90	$C_6D_5CD_3$/	$LiMe_2Cu$ + excess **1b**
					THF	aromatic H: δ 7.07, 7.58 ppm
	– –	– –	−0.17	−40		coalescence
	6.1 vb	hidden	−0.22	−35		
	6.1 b	7.4 b	−0.32	−10		aromatic H: δ 7.1, 7.4 ppm
	6.30 bd	7.59 bd	−0.38	10		
	6.51 d	7.81 d	−0.37	60		products present
	16 Hz	16 Hz				
16	4.08 bd 6.65 b	4.53 bd 7.92 b	−1.0	−100	CD_2Cl_2/	$LiMe_2Cu$ + **1b**
	12.5 Hz	12.5 Hz			Et_2O	

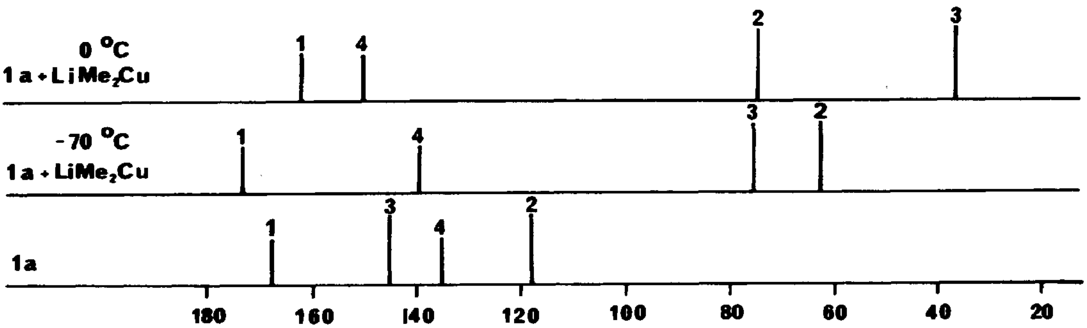


Fig. 1. ^{13}C NMR for **1a** and for the solution of $LiMe_2Cu$ and **1a** at −70 and at 0°C (after reaction has taken place). The spectrum obtained at 0°C is assigned to the enolate ion **2a** formed on warming the sample.

Fig. 2a. After further warming to −53°C a new H(2) signal was observed as a very broad singlet at δ 6.2 ppm, while the H(3) signal was seen as a shoulder on the aromatic signals. The new set of H(2) and H(3) signals moved further downfield as the temperature was increased and finally appeared as doublets, $J_{2,3}$ 16 Hz, at δ 6.6 and 8.0 ppm at −33°C. Simultaneously signals assigned to the product enolate **2a** appeared, and at −13°C only signals from **2a** and excess $LiMe_2Cu$ were seen.

When the esters **1a** and **1b** were used in excess relative to the cuprate, exps. 11 and 15, respectively, the lithium complex **4** was the major component, cf. Fig. 2b, and the π-complex the minor one. On warming the solution the same type of changes as in exp. 10 took place. After coalescence, at −50°C (**1a**) and −40°C (**1b**), respectively two new signals appeared, and these moved downfield on further warming. Again conjugate addition was observed to take place above −30°C with **1a** and above 10°C with the t-butyl ester. The two doublets, observed at δ 6.60 and 8.00 ppm, were again assigned to H(2) and H(3) respectively, $J_{2,3}$ 16 Hz.

The temperature dependence of the NMR spectra implies that several dynamic processes are taking place in solution, including at least one reversible reaction and the irreversible conjugate addition. Below −75°C equilibration of complexes **3** and **4** is slow and distinct signals for both complexes are observed, as well as several

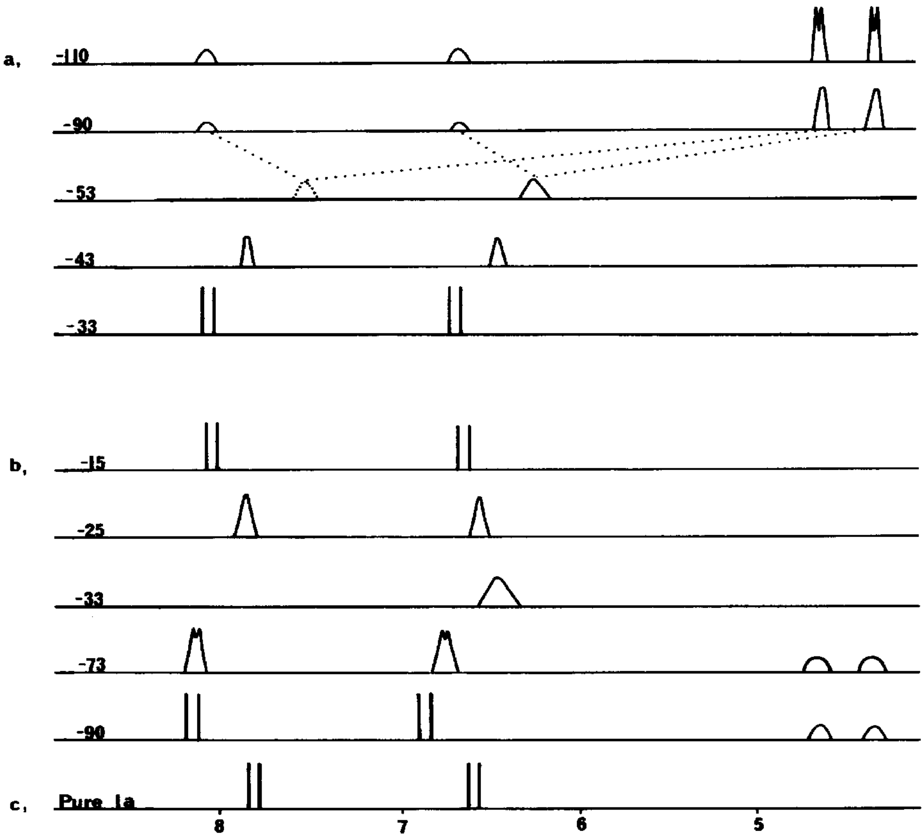


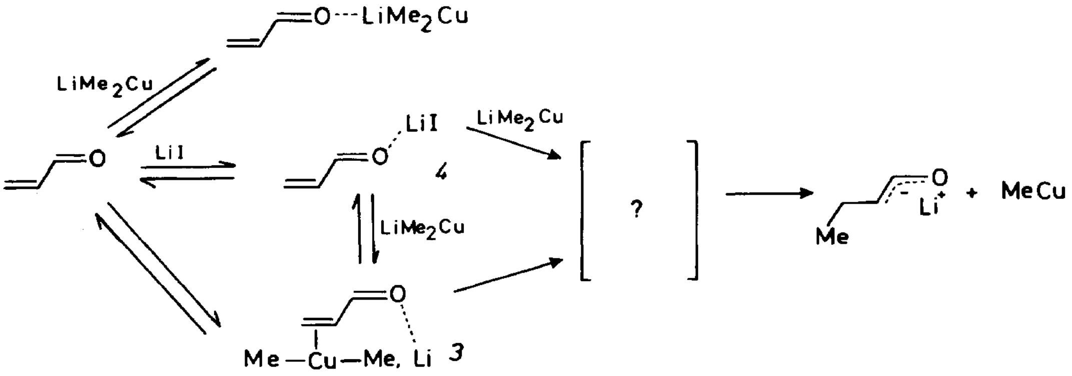
Fig. 2. Temperature dependence of the ^1H NMR data for H(2) and H(3) in species **3** and **4**. (a) Spectra obtained for a solution of **1a** in the presence of excess $LiMe_2Cu$, exp. 10, (b) $LiMe_2Cu$ and an excess **1a**, exp. 11, (c) pure **1a**, exp. 8.

signals for the cuprate methyl groups. On coordination of $LiMe_2Cu$ to an ester the methyl groups are obviously no longer equivalent. When the temperature is increased an exchange reaction becomes faster, and after broadening of both sets of H(2) and H(3) signals, coalescence of the sets occurs, leading to one set of very broad signals, at intermediate positions for H(2) and H(3) determined by the equilibrium. When the exchange is fast on the NMR time scale only one signal for the cuprate methyl groups is observed. On further increase of the temperature the time-averaged signals from H(2) and H(3) are shifted downfield, finally reaching the shift values typical of lithium-coordinated ester, cf. exp. 9 with the simultaneous formation of enolate **2**.

If equilibration of complexes **3** and **4** were the only process taking place in solution the time-averaged chemical shift positions for H(2) and H(3) would be expected to be constant unless the position of the equilibrium is strongly temperature dependent. However, alongside the increase in the rate of the interconversion of **3** and **4**, conjugate addition begins to take place at a measurable rate. We postulate that the π-complex **3** takes part in the conjugate addition to form the enolate ion **2**, and thus the concentration of **3** is decreased, causing the downfield shift in position for H(2) and H(3) with increasing temperature (Scheme 3).

In conclusion, our NMR data suggest that upon mixing of $LiMe_2Cu$ (LiI) and an unsaturated ester, two complexes, **3** and **4**, are formed and co-exist in equilibrium at low temperatures. The relative ratio of **3** and **4** in solution seems to depend on the temperature and the relative ratios of $LiMe_2Cu$, LiI and the ester. The olefin-copper π-complex is the major component at low temperature in the presence of an excess $LiMe_2Cu$. The lithium-carbonyl complex, **4**, is the major component when the ester is present in excess and also at higher temperatures when the concentration of $LiMe_2Cu$/π-complex has been reduced by formation of the enolate **2** in conjugate addition. We thus suggest that a copper-olefin π-complex lies on the reaction path which ends at the formation of the enolate. However, we do not wish to speculate on the nature of any intermediate between the π-complex and the enolate **2**, which is the final, thermodynamic product. The initial formation of a π-complex between the reactants can be equally well accomodated by the mechanisms suggested for conjugate addition of cuprates to enones or enoates [3–8], and does not rule out the participation of lithium coordination within the π-complex.

SCHEME 3



Further work is in progress to elucidate the structure of the olefin-copper π-complex and its role in the conjugate addition.

Spectral data

Methyl *trans*-cinnamate, **1a**. ^{1}H NMR (270 MHz, CD_2Cl_2/diethyl ether, $-60°C$) δ 7.73 (1H, d, $J_{2,3}$ 16.1 Hz, H(3)), 7.64 (2H, m), 7.47 (3H, m), 6.55 (1H, d, $J_{2,3}$ 16.1, H(2)), 3.81 (3H, s) ppm.

^{13}C NMR (67.9 MHz, $C_6D_5CD_3$/THF, $-60°C$) δ 166.9 (C(1)), 144.9 (C(3)), 134.5 (C(4)), 117.7 (C(2)), 51.4 (C(8)) ppm. C(5), C(6) and C(7) coincide with toluene signals.

π-complex **3a** between methyl cinnamate and $LiMe_2Cu$. ^{1}H NMR (270 MHz, CD_2Cl_2/diethyl ether, $-80°C$) δ 7.28, 7.19 (5H, H(5,6,7)), 4.56 (1H, d, $J_{2,3}$ 12.5 Hz, H(3)), 4.22 (1H, d, $J_{2,3}$ 12.5 Hz, H(2)), 3.72 (3H, s, H(8)), -1.02, -1.10 (CH_3–Cu) ppm.

^{13}C NMR (67.9 MHz, $C_6D_5CD_3$/THF, $-80°C$) δ: 173.9 (C(1)), 143.4 (C(4)), 61.8 (d, J(C–H) 155 Hz, C(3)), 52 (d, J(C–H) 148 Hz, C(2)), 51.0 (C(8)), -9.1 (CH_3–Cu) ppm. Signals due to C(5), C(6) and C(7) hidden under toluene signals.

t-Butyl *trans*-cinnamate **1b**. ^{1}H NMR (270 MHz, $C_6D_5CD_3$/THF, $-55°C$) δ 7.77 (1H, d, $J_{2,3}$ 16 Hz, H(3)), 7.0 (5H, m), 6.43 (1H, d, $J_{2,3}$ 16 Hz, H(2)), 1.47 (9H, s, H(9)) ppm.

^{13}C NMR (67.9 MHz, $CDCl_3$) δ 166.2 (C(1)), 143.5 (dJ(C–H) 157 Hz, C(3)), 134.6 (C(4)), 129.9 (C(7)), 128.7, 127.9 (C(5), C(6)), 120.1 (d, J(C–H) 163 Hz, C(2)), 80.4 (C(8)), 28.1 (C(9)) ppm.

The same ^{13}C chemical shifts were observed for **1b** in $C_6D_5CD_3$/THF solution at $-70°C$.

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