The Relation between Ion Pair Structures and Reactivities of Lithium Cuprates

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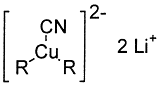
Dedicated to Professor Dr. Harald Günther on the occasion of his 65th birthday

Abstract: From Li^+ well-solvating solvents or complex ligands such as THF, [12]crown-4, amines etc., lithium cuprates $R_2CuLi(\cdot LiX)$ crystallise in a solvent-separated ion pair (SSIP) structural type (e.g. **10**). In contrast, solvents with little donor qualities for Li^+ such as diethyl ether or dimethyl sulfide lead to solid-state structures of the contact ion pair (CIP) type (e.g. **11**). $^1H,^6Li$ HOESY NMR investigations in solutions of $R_2CuLi(\cdot LiX)$ (**15**, **16**) are in agreement with these findings: in THF the SSIP **18** is strongly favoured in the equilibrium with the CIP **17**, and in diethyl ether one observes essentially only the CIP **17**. Salts LiX (X = CN, Cl, Br, I, SPh) have only a minor effect on the ion pair equilibrium. These structural investigations correspond perfectly with Bertz's logarithmic reactivity profiles (LRPs) of reactions of R_2CuLi with enones in diethyl ether and THF: the faster reaction in diethyl ether is due to the predominance of the CIP **17** in this solvent, which is the reacting species; in THF only little CIP **17** is present in a fast equilibrium with the SSIP **18**. A kinetic analysis of the LRPs quantifies these findings. Recent quantum-chemical studies are also in agreement with the CIP **17** being the reacting species. Thus a uniform picture of structure and reactivity of lithium cuprates emerges.

Keywords: cuprates · lithium · structure–reactivity relationships

Introduction

The question of whether the reaction of 2 RLi and 1 CuCN leads to "higher-order" cuprates **1** with "special reactivity",[1] in which the cyano group should be the third substituent at



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$$[\mathrm{R{-}Cu{-}R}]^- \; \mathrm{Li^+ \cdot LiCN}$$

2

Cu^+, or to cyano-Gilman cuprates **2**[2]—a scientific controversy over many years—, found its end in 1999 in favour of **2**: N. Krause titled his Highlight in *Angewandte Chemie*[3] "New Results Regarding the Structure and Reactivity of Cyanocuprates—The End of an Old Controversy". What had led to this conclusion? From NMR investigations by Bertz et al.[2, 4] and by Berger et al.,[5] from EXAFS and XANES investigations,[6] and from quantum-chemical studies[6c, 7] it was strongly indicated that the cyano group is not bonded to Cu^+. Rather, cyano-Gilman cuprates **2** should be formed. The first two solid-state structures of cyano-Gilman cuprates provided at least for these two cases the experimental proof. van Koten et al.[8] determined the structure of the diaryl cyano cuprate $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2CuLi_2(CN)(thf)_4]_\infty$ (**3**), in which the cyano group is bonded to two Li^+ ions, as first proposed by Bertz.[2a] The diaryl cuprate anion is connected with the cation $[Li{-}C{\equiv}N{-}Li]^+$ intramolecularly through its $N(Me)_2CH_2$ group which leads to a polymer chain. The Li^+ ion is four-coordinate through coordination to two additional THF molecules.

The structure of the dialkyl cyanocuprate $[tBu_2CuLi_2(CN)(thf)_2(pmdeta)_2]$ (**4**) (pmdeta = pentamethyldiethylenetriamine) was disclosed by Boche et al.[9] In this case the ate-anion $[tBu{-}Cu{-}tBu]^-$ is completely separated from the cation $[Li{-}C{\equiv}N{-}Li]^+$, in which each Li^+ is pentacoordinate because of the additional solvation by one pmdeta ligand and one THF molecule. The carbon atom of the cyano group (which is indistinguishable from the nitrogen atom) is 845.7 pm away from Cu^+. For reasons which will be of interest in the $^1H,^6Li$ HOESY investigations (see below), the distances Li1–C1 764.6 pm and Li1–C1A 780.6 pm are also mentioned

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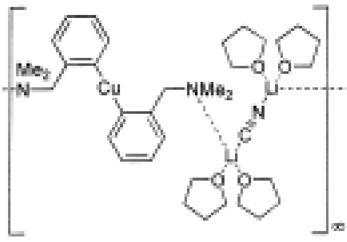

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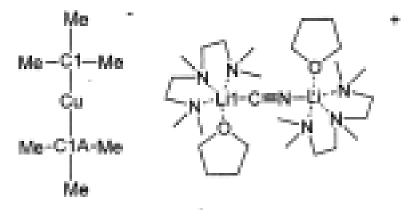

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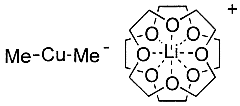
here. The solid-state structures of **3** and **4**, which crystallised from THF with additional help of an amino ligand and the cyanide anion, can thus be regarded as models for the corresponding solvent-separated ion pairs (SSIPs) in solution.[10] Further structures of this type, in which the cyano group is not part of the crystals, were determined by Power et al.,[11] namely [Li([12]crown-4)$_2$CuMe$_2$] (**5**), [Li([12]crown-4)$_2$-CuPh$_2$(THF)] (**6**) and [Li([12]crown-4)$_2$Cu(Br)CH(SiMe$_3$)$_2$] (**7**).



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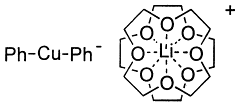

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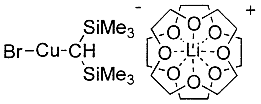

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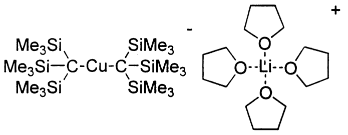

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In **5**–**7** cations and anions are well separated due to the sandwich structures of the cations [Li([12]crown-4)$_2$]$^+$.[11] Another structure (**8**), which also crystallized from THF and is of the SSIP type, was revealed by Eaborn et al.[12]

From these results we raised the following questions which we will answer in this work:

1a) Do lithium cuprates crystallise *generally in a SSIP type* structure from solvents which solvate Li$^+$ well, such as THF, crown ethers, amines or others?

b) How do lithium cuprates crystallise from solvents like diethyl ether (Et$_2$O) or dimethyl sulfide (Me$_2$S) which solvate Li$^+$ only little? Does one observe structures of the *contact ion pair (CIP) type*?

2) What is the ion–pair structure of lithium cuprates *in solutions* of these two types of solvents?

3) What is the influence of these two types of solvents on the *reactivities* of lithium cuprates with enones (and related systems)?

Results and Discussion

Investigations of solid-state structures

The following two solid-state structures confirm the solvent-separated ion pair (SSIP) character if lithium cuprates are crystallized from Li$^+$ well-solvating solvents. The structure of [Li(dme)$_3$]$^+$[Me$_2$Cu]$^-$ **9**[13a] (dme = 1,2-dimethoxyethane) is shown in Figure 1. As in the solid-state structures of **3**–**8**, the cation is completely separated from the anion. The dimethylcuprate anion is essentially linear (C1-Cu1-C2 179.2°), and Li1 is perfectly surrounded by three DME molecules (hexacoordination of Li1!). Of special interest in this structure are the distances Li1–C1 (580.6 pm) and Li1–C2 (591.1 pm; shortest Li–C distances in the unit cell), which are far beyond a bonding distance (< 250 pm) between lithium and carbon.

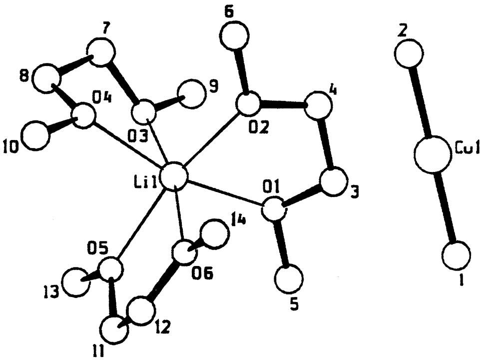

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Figure 1. Solid-state structure of [Li(dme)$_3$]$^+$[Me$_2$Cu]$^-$(**9**). Significant bond lengths [pm] and angles [°]: Li1–C1 580.6, Li1–C2 591.1; C1-Cu1-C2 179.2.

The structure of [Li(dme)$_3$]$^+$[{(Me$_3$Si)CH$_2$}$_2$Cu]$^-$ (**10**)[13b] is similar to that of **9** (Figure 2). The structure of the [Li(dme)$_3$]$^+$ ion in **10** is essentially the same as in **9**. The cuprate anion [{(Me$_3$Si)CH$_2$}$_2$Cu]$^-$ is linear (C1-Cu1-C5 178.9°), and the Li

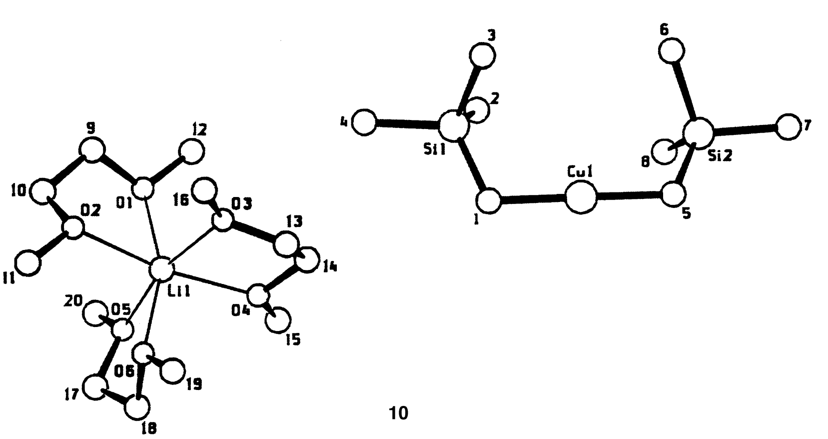

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Figure 2. Solid-state structure of [Li(dme)$_3$]$^+$[{(Me$_3$Si)CH$_2$}$_2$Cu]$^-$ (**10**). Significant bond lengths [pm] and angles [°]: Li1–C1 605.7, Li1–C5 600.1; C1-Cu1-C5 178.9.

cations are far away from the carbon atoms bonded to Cu1: Li1–C1 605.7 pm and Li1–C5 600.1 pm (shortest Li–C distances in the unit cell). These structures are excellent models for *the monomeric solvent-separated ion pair nature of such compounds in Li$^+$ well-solvating solvents*, as results of ^{1}H,^{6}Li HOESY spectroscopy experiments have shown (see below).

A model for the structural situation in Li$^+$ little-solvating solvents was found when two equivalents of $(Me_3Si)CH_2Li$ were allowed to react with one equivalent of CuCN in diethyl ether and the solution was allowed to crystallise at −78 °C to give $[\{[(Me_3Si)CH_2]_2CuLi\}_2]\cdot 3\,Et_2O$ (**11**),[13c] (Figure 3).

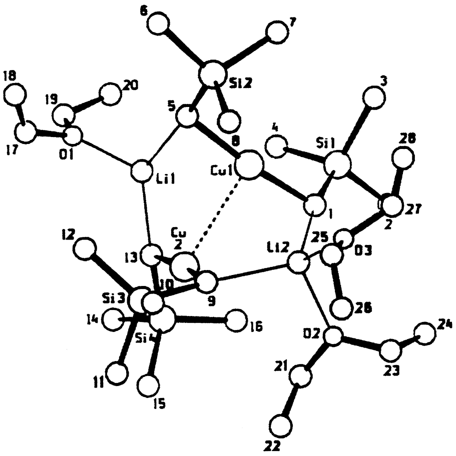

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Figure 3. Solid-state structure of $[\{[(Me_3Si)CH_2]_2CuLi\}_2(Et_2O)_3]$ (**11**). Significant bond lengths [pm], bond angles, and dihedral angles [°]: Li1–C5 219.9, Li1–C13 226.4, Li2–C1 230.5, Li2–C9 231.2, Cu1–Cu2 283.8; C1-Cu1-C5 172.9, C9-Cu2-C13 171.3, C1-Cu1-Cu2-C9 93.7.

As can easily be seen, the structure of **11** is completely different from the structures of **3**–**10**: a lithium cuprate dimer is formed with the cuprate anions being held together by two lithium cations. Thus, short C–Li bonds are found in the *asymmetric unit*: Li1–C5 219.9 pm, Li1–C13 226.4 pm, Li2–C1 230.5 pm and Li2–C9 231.2 pm. As in the solid-state structure of the lower order cyanocuprate $[t\mathrm{BuCu(CN)}\text{-}\mathrm{Li(Et_2O)_2}]_\infty$[9] (also crystallized from Et$_2$O) the two cuprate units C1-Cu1-C5 and C9-Cu2-C13 are essentially orthogonal to each other: the C1-Cu1-Cu2-C9 dihedral angle in **11** is 93.7°, which allows an interaction of the two d^{10} copper cations Cu1 and Cu2 without steric repulsion of the carbon atoms. This interaction is also documented by the angles C1-Cu1-C5 172.9° and C9-Cu2-C13 171.3° with the two Cu atoms being bent towards each other, leading to a Cu1–Cu2 distance of 283.8 pm. Li1 is bonded to one Et$_2$O, and Li2 to two Et$_2$O molecules. Evidently, because of the poor solvating qualities of Et$_2$O, the Li cations prefer bonds with the negatively charged α-carbon atoms of the cuprate anions. Thus **11** is a good model for *a dimeric lithium cuprate contact ion pair in solution*. At the moment we are unable to locate LiCN, which is also formed under the reaction conditions giving **11**. The absence of CN$^-$ (LiCN) in the structure of **11** indicates little affinity of these species to the dimeric cuprate structure, and/or a strong tendency for the formation of $(LiCN)_x$, and of the dimer **11** without LiCN, at least in this particular case.

A strongly related structure of a lithium dialkylcuprate was discovered by Olmstead and Power, when they treated $(Me_3Si)CH_2Li$ in hexane with a solution of CuBr in dimethyl sulfide to give $[Li_2Cu_2(CH_2SiMe_3)_4(SMe_2)_2]_\infty$ (**12**; Figure 4).[14]

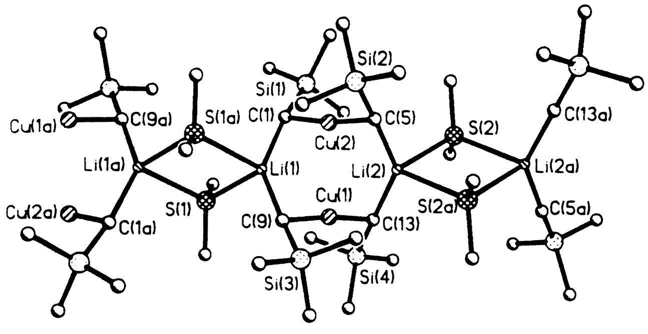

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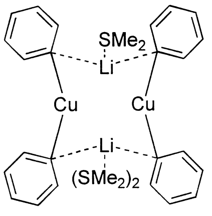
Figure 4. Solid-state structure of $[Li_2Cu_2(CH_2SiMe_3)_4(SMe_2)_2]_\infty$ (**12**).[14] Significant bond lengths [pm], bond angles [°], and dihedral angles [°] in the asymmetric unit: Li1–C1 221.8, Li1–C9 220.5, Li2–C5 220.1, Li2–C13 219.8, Cu1–Cu2 298.4; C9-Cu1-C13 173.8, C1-Cu2-C5 171.5, C5-Cu2-Cu1-C9 94.5.

The data summarized in the caption of Figure 4 reveal that the two cuprate units, held together by two Li cations, are also almost orthogonally oriented towards each other, and the two d^{10} Cu cations are bent towards each other leading to a Cu1–Cu2 distance of 298.4 pm. Interestingly, LiBr is not present in the structure of **12**. Similarly LiCN does not crystallise together with **11**. Instead, each of the two Li cations is bonded besides to the α-carbon atoms of two cuprate anions (Li–C bond lengths between 219.8 and 221.8 pm!) to the sulfur atoms of two Me$_2$S molecules. Since the sulfur atoms are additionally bonded to a second Li$^+$ ion, a polymeric chain is formed through Li-S-Li-S four-membered rings. Excess dimethyl sulfide, as present in solution, could possibly break down the polymer **12** to dimeric units.

The related diaryl cuprate dimer **13** was crystallised from dimethyl sulfide and structurally characterized.[15] Similiarly, the Li diaryl cuprate dimer **14**, also of the CIP type, was obtained from diethyl ether.[16] Thus, one can conclude that lithium cuprates form “dimeric” contact ion pair type structures with short Li–C bonds if they crystallise from Li$^+$ little-solvating solvents such as Me$_2$S, Et$_2$O, hexane, or benzene (**11**–**14**), while one observes structures of the solvent-separated ion pair type with very long Li···C distances if Li$^+$ is well-solvated (THF, DME, crown ether, etc.) (**3**–**10**).



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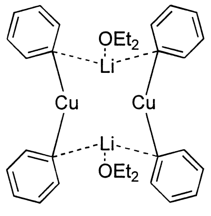

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$^1H,^6Li$ HOESY investigations of lithium cuprates in THF and Et_2O

In 1976 it was concluded that Me_2CuLi (**15**) is a dimer in diethyl ether.[17] This is also the case in dimethyl sulfide solutions.[2a] In contrast, NMR investigations of $Me_2CuLi{\cdot}LiX$ (**15**·LiX; X = I, CN) showed the preference for a monomeric structure in THF.[18, 19] These results are in agreement with EXAFS studies[6] and cryoscopic investigations.[20] We wondered whether the results of $^1H,^6Li$ HOESY investigations[21] of lithium cuprates in THF and diethyl ether, would be in accord with the solid-state structures obtained from the respective solvents (see above).

$H_3C\text{-}Cu\text{-}CH_3^-\ Li^+$

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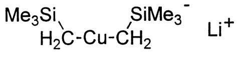

$[(Me_3Si)CH_2\text{-}Cu\text{-}CH_2(SiMe_3)]^-\ Li^+$

16

The intensity of a cross-peak in a $^1H,^6Li$ HOESY spectrum is inversely proportional to the sixth power of the H–Li distance.[22] However, the extremely low sensitivity of the NOE restricts the maximum proton–lithium distance detectable by this method to about 400–500 pm.[22, 23] Therefore, in monomeric solvent-separated ion pairs of lithium cuprates of the type **10**, as well as in the others shown above, the lithium cation should be too far away from the hydrogen atoms at the α-C atoms of the cuprate anions to lead to any detectable dipolar interaction (e.g. in **10**, Figure 2: C1–Li1 605.7 pm). This could be confirmed in a detailed NMR study on the possibilities and limitations of measuring $^1H,^6Li$ HOESY cross-peaks in linear lithium cuprates.[24] In contrast, in dimeric contact ion pair structures (e.g. **11**; Figure 3) the relatively short α-carbon–lithium distances of around 220 pm lead to a clearly detectable dipolar interaction between the methylene groups of $[\{(Me_3Si)CH_2\}_2Cu]^-$ and Li^+. In the following we discuss the $^1H,^6Li$ HOESY spectra of $[\{(Me_3Si)CH_2\}_2CuLi]$ (**16**) in THF and diethyl ether, because we have solid-state models both of a solvent-separated (**10**) as well as of a contact ion pair (**11**) of this cuprate.

A comparison of the $^1H,^6Li$ HOESY spectra of $[\{(Me_3Si)CH_2\}_2CuLi]$ (**16**) in Et_2O (20% Et_2O and 80% $[D_{10}]Et_2O$) and THF (20% THF and 80% $[D_8]$THF) is shown in Figure 5. In both spectra, in the proton dimensions, two signals of the $[\{(Me_3Si)CH_2\}_2Cu]^-$ ion and two originating from 20% of the protonated solvent are observed. The lithium dimensions show only one signal, indicating the presence of either a single species or a fast equilibrium. In Et_2O a very strong cross-peak between the methylene groups of the $[\{(Me_3Si)CH_2\}_2Cu]^-$ ion and the lithium cation can be detected (see Figure 5a). This clearly indicates short distances between the methylene groups and lithium and is in excellent agreement with the dimeric contact ion pair model structure **11** crystallized from Et_2O. Additionally a small cross-peak occurs between the methyl groups of the $[\{(Me_3Si)CH_2\}_2Cu]^-$ ion and the lithium center in both spectra.[25] In contrast to the situation in Et_2O, in THF (see Figure 5b) the strongest cross-peak is between the lithium center and the α-protons of the solvent, and there is only a weak dipolar interaction between lithium and the methylene groups of the $[\{(Me_3Si)CH_2\}_2Cu]^-$ ion (see Figure 5b). Hence one can conclude that the dominating species of $[\{(Me_3Si)CH_2\}_2CuLi]$ (**16**) in THF is the solvent-separated ion pair. Thus, the structure of **16** in THF, which is representative for lithium cuprates in Li^+ well-solvating solvents, can be correlated to the solid-state structure **10** obtained from DME, which shows the existence of a solvent-separated ion pair type structure.

What is the origin of the weak cross-peak between the $CuCH_2$ group and lithium in THF at –60 °C (Figure 5b)? In principle there are two possibilities: first, a *residual contribution* from the solvent-separated ion pair, or second the presence of an *equilibrium* between the monomeric solvent-separated ion pair and the dimeric contact ion pair, in which only the latter contributes to detectable $^1H,^6Li$ cross-peaks of lithium with the protons of the cuprate anion. In the latter case the intensity of the cross-peak between $CuCH_2$ and lithium would give an indication of the position of the

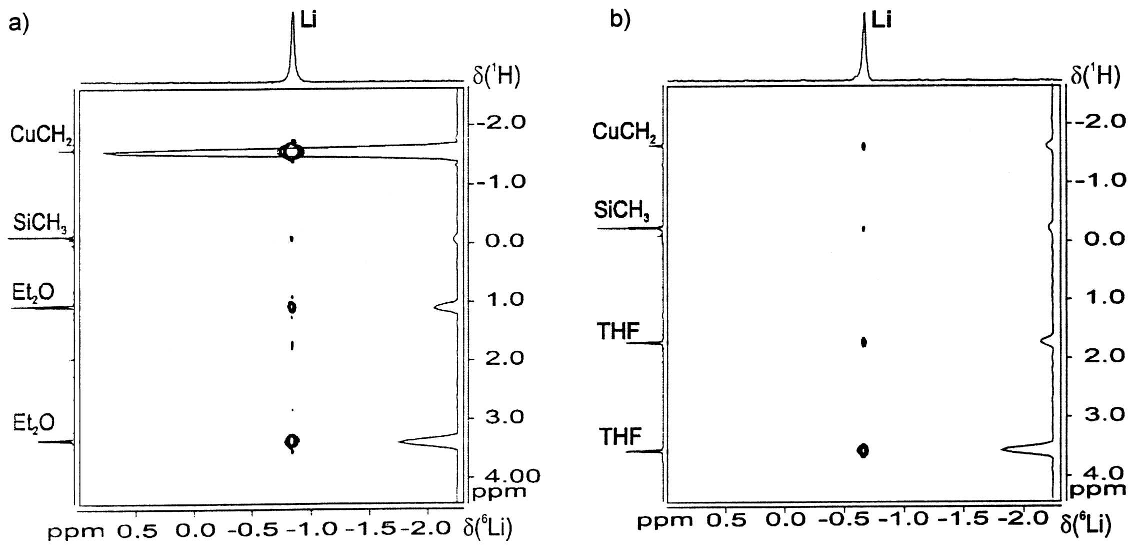

Figure 5. Solvent effects on the $^1H,^6Li$ HOESY spectra of $[\{(Me_3Si)CH_2\}_2CuLi]$ (**16**) at –60 °C in Et_2O (a) and in THF (b).

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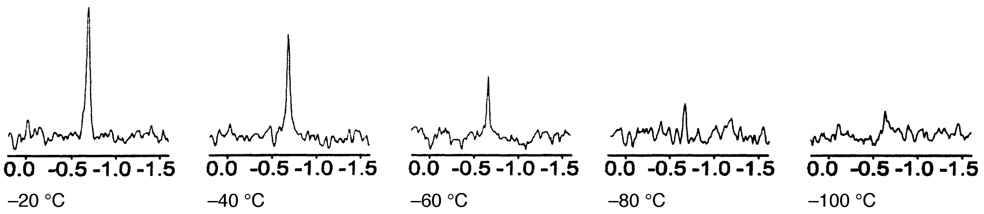
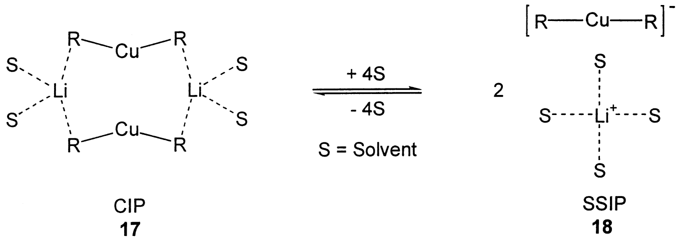


Figure 6. Temperature dependence of the equilibrium between solvent-separated ion pair (SSIP) and contact ion pair (CIP) structures shown by the one-dimensional traces of the methylene/lithium cross-peak of $[\{(Me_3Si)CH_2\}_2CuLi]$ (**16**) in THF ($^1H,^6Li$ HOESY).

equilibrium. The first possibility of a residual contribution of the linear part of the cuprate anion from the solvent-separated ion pair species has been excluded in a detailed NMR study of lithium organocuprates.[24] In the case of an *equilibrium between a CIP and a SSIP*, it is known that the position of the equilibrium is shifted at lower temperatures towards the SSIP due to entropic effects caused by the different number of solvent molecules bonded in the monomeric and the dimeric species.[26] Therefore, at lower temperatures, the existence of such an equilibrium should be shown by a reduced dipolar interaction between the methylene groups of $[\{(Me_3Si)CH_2\}_2Cu]^-$ and lithium. This is nicely demonstrated by temperature-dependent $^1H,^6Li$ HOESY experiments in THF. Figure 6 shows the continuous reduction of the $^1H,^6Li$ HOESY cross-peak intensities between the methylene groups of the cuprate anion and lithium at lower temperatures: at $-100\,^\circ C$ the cross-peak has disappeared almost completely. Furthermore, and also in support of the equilibrium, the phenomenon is reversible.[27]

These latter experiments show that in solution the existence of CIPs or SSIPs is not exclusive. We therefore conclude from the above findings for $[\{(Me_3Si)CH_2\}_2CuLi]$ (**16**) and other lithium diorganocuprates R_2CuLi, especially in Li^+ well-solvating solvents, the existence of a fast equilibrium between a dimeric contact ion pair **17** and a predominant monomeric solvent-separated ion pair **18**, as shown in Scheme 1.



Scheme 1. Equilibrium between contact ion pair (CIP) structures **17** and solvent-separated ion pair (SSIP) structures **18** of lithium diorganocuprates in solution.

Since lithium diorganocuprates are normally synthesized such that salts LiX like LiCN, LiCl, LiBr, LiI and LiSPh are also formed, the influence of the salt (salt effect) on the ion pair equilibria compared to that of the solvent (solvent effect), is furthermore of interest, especially with respect to the reactivity (see below).

Figure 7 shows nicely that the position of the equilibrium in the case of $Me_2CuLi \cdot LiX$ (**15**$\cdot$LiX), as indicated by the magnitude of the $^1H-^6Li$ dipolar interactions of lithium with the methyl groups, is mainly determined by the *solvent*, while the *salt* has only a minor effect. Within one solvent—THF or Et_2O—the intensities of the $^1H,^6Li$ HOESY cross-peaks are smaller (more SSIP is present) if $[Li\text{-}X\text{-}Li]^+$ is comparatively stable (which is the case in the series $X = CN^- > Cl^- > Br^- > {}^-SR$), although the influences of the different LiX groups are marginal. The largest difference is found between salt-containing and salt-free solutions. Thus, salts only slightly favour the SSIP **18** in the equilibrium with the CIP **17**. It is the solvent that dominates the position of ion pair equilibria of lithium cuprates, at least in the case of THF and diethyl ether.

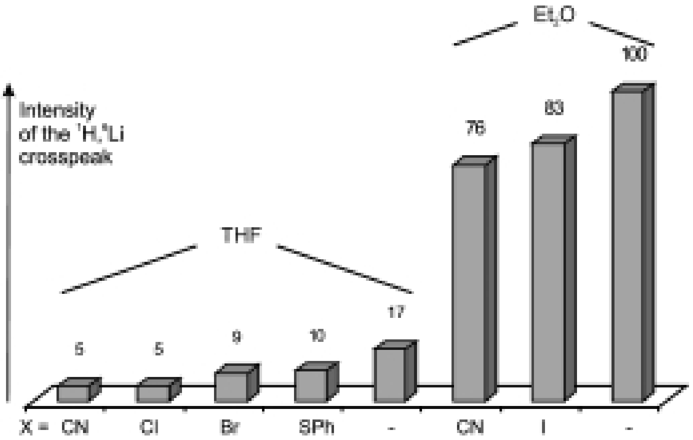
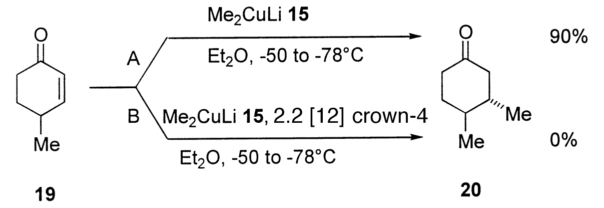


Figure 7. Solvent and salt effects on the magnitude of the $^1H,^6Li$ cross-peak intensities of Me_2CuLi (**15**) and **15**$\cdot$LiX ($^1H,^6Li$ HOESY spectra at $-60\,^\circ C$).

Logarithmic reactivity profiles and the reacting species in lithium cuprate reactions with enones

From the studies of the solid-state and solution structures of lithium cuprates, as well as results from other investigations,[6, 20] it is clear that in diethyl ether solution dimers of the contact ion pair (CIP) type **11**–**14** are at least dominant, while monomers displaying a solvent-separated ion pair (SSIP) nature comparable to **10** are preferred in THF, especially at lower temperatures. Is it possible to decide which of the two species—the CIP or the SSIP—undergoes the reaction with enones, and what determines the different reaction rates in diethyl ether and THF?

In 1977, Ouannes, Dressaire and Langlois[28] investigated the reactions of lithium cuprates with an enone, an acid chloride and the enol ester of a β-keto ester, respectively, both without and in the presence of [12]crown-4. The results of the reactions of **15** with 4-methylcyclohexenone **19** are shown in Scheme 2.



Scheme 2. Reactions of **19** with Me_2CuLi **15** without, and in the presence of 2.2 equivalents of [12]crown-4.[28]

In reaction A, **19** and Me_2CuLi (**15**) react to give the 1,4-adduct **20** in 90% yield. However, in reaction B, in which 2.2 molar equivalents of [12]crown-4 were added to the lithium cuprate **15**, adduct **20** is not formed at all! Similarly, no reaction of the cuprate **15** occurs with the acid chloride and the enol ester of a β-keto ester in the presence of [12]crown-4.[28] Undoubtedly, [12]crown-4 surrounds the lithium cation essentially completely as shown by the solid-state structures **5**–**7**. As outlined above, related structures of the solvent-separated ion pair type are also favoured in THF, DME and other Li^+ well-solvating solvents thereby eliminating Li^+ as a Lewis acid for complexation with the enone carbonyl group, and thus for catalysis, which apparently is a prerequisite for such a cuprate reaction. Monomeric structures of the SSIP type of lithium cuprates in Li^+ well-solvating solvents therefore may be regarded as a "resting state".[8] This fits nicely to the results of Bertz in his systematic studies of logarithmic reactivity profiles (LRPs) of reactions of lithium cuprates with 2-cyclohexenone and iodocyclohexane.[29] Historically, the main purpose of a comparison of logarithmic reactivity profiles of reactions of iodo- versus cyano-Gilman reagents was to show that there is *no special reactivity of the cyano species*.[29] The observations of special interest to us are the *generally faster reactions in diethyl ether than in THF.* This is illustrated by the reactions of the cuprates **21** and **22** with 2-cyclohexenone (**23**) given in Table 1.[29c]

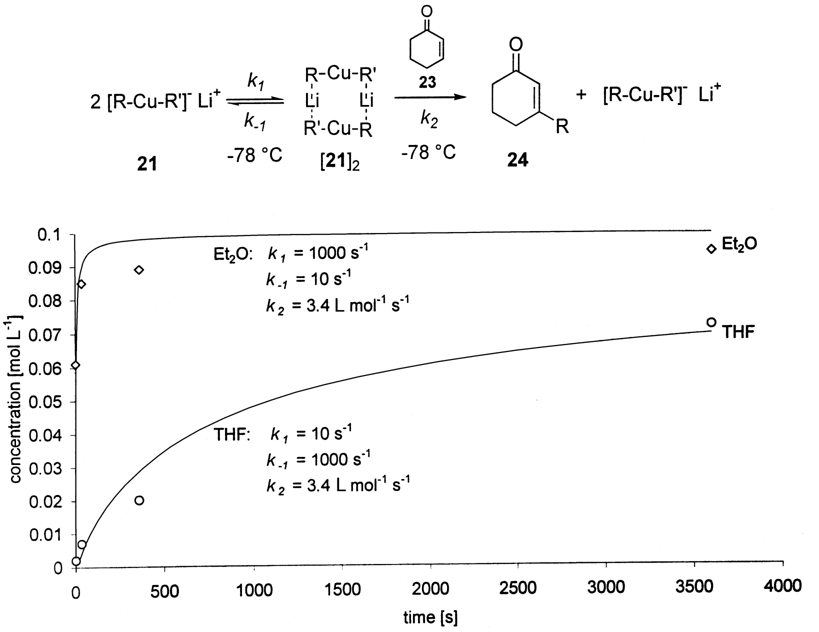
Other examples of homo- and mixed-cuprates confirm the generally faster reactions in diethyl ether than in THF.[29] In order to get further insight into the LRPs as a function of the solvent we analysed the LRPs of the lithium cuprate **21** with 2-cyclohexenone (**23**) in diethyl ether and THF, respectively, to give the corresponding adduct **24** (Scheme 3).

In diethyl ether a fast equilibrium between **21** and [**21**]$_2$ should essentially lie on the side of the dimer [**21**]$_2$ (see the $^1H,^6Li$ HOESY studies). Furthermore, a monomer **21** of the SSIP type should not react with 2-cyclohexenone (**23**) (see Scheme 2). With the concentrations of the lithium cuprate R_2CuLi **21** and 2-cyclohexenone (**23**) being 0.1 molL^{-1}, and the assumptions indicated above, the best fit of the experimental points (see Scheme 3) led to $k_1 = 1000\ s^{-1}$, $k_{-1} = 10\ s^{-1}$, and $k_2 = 3.4\ L mol^{-1} s^{-1}$.[30]

Table 1. Logarithmic reactivity profiles of the reactions of the lithium cuprates **21** (+LiI) and **22** (+LiCN) with 2-cyclohexenone (**23**) in Et_2O and in THF at −78 °C to give the corresponding 1,4 adduct **24** (yields in [%]).[29c]

Time	Et_2O		THF	
	$BuCu(SSiMe_3)Li$ **21** + LiI	BuCu(Th)Li **22** + LiCN	$BuCu(SSiMe_3)Li$ **21** + LiI	BuCu(Th)Li **22** + LiCN
4 s	61	64	2	32
36 s	85	89	7	57
6 min	89	99	20	74
1 h	94	99	72	89

For the reaction in THF (see Scheme 3), we used the same k_2 value as in diethyl ether ($k_2 = 3.4\ L mol^{-1} s^{-1}$). Under these conditions a nice agreement between experimental points and calculated curve (see Scheme 3) was achieved with $k_1 = 10\ s^{-1}$ and $k_{-1} = 1000\ s^{-1}$ which corresponds to the equilibrium between **21** and [**21**]$_2$ lying far on the side of the monomeric SSIP. Although these kinetic data are not more than rough estimates (they agree nicely with recently determined more precise measurements[31]), the much faster reaction of a lithium cuprate with an enone in diethyl ether than in THF[32] clearly results from the ion pair equilibrium of R_2CuLi being far on the CIP side in diethyl ether, while the much slower reaction in THF results from the predominance of the SSIP in this solvent. The kinetics are also in agreement with the SSIP being the much less or even unreactive species ("resting state"[8]). Finally it should be noted that the reaction of the dimeric lithium cuprate contact ion pair with an enone, as shown here, is in perfect agreement with recent quantum-



Scheme 3. Logarithmic reactivity profiles (LPRs) of the reactions of **21** + LiI with 2-cyclohexenone (**23**) in Et_2O and THF at −78 °C to give **24**. Points: experimental values; curves: calculated with the data given in the text. R = Bu, R′ = $SSiMe_3$.

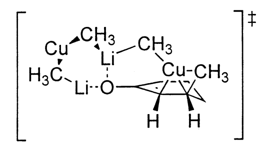


Figure 8. Quantum-chemically determined transition state of the reaction of $[Me_2CuLi]_2$ [**15**]$_2$ with 2-cyclohexenone (**23**).[31]

chemical calculations by Mori and Nakamura.[33] The transition state with the two Li^+ ions of the dimer bonding to the oxygen atom of the enone is shown in Figure 8.[34] Other calculations of Nakamura with a mixed cuprate dimer show a similar transition state.[35]

In conclusion, a systematic study of solid-state structures of lithium cuprates reveals the formation of solvent-separated ion pair (SSIP) types from Li^+ well-solvating solvents, while "dimers" of the contact ion pair (CIP) type are formed in poor solvating solvents. ^1H,^6Li HOESY studies of $[\{(Me_3Si)CH_2\}_2CuLi]$ (**16**) in THF and Et_2O, respectively, provide a similar structural picture; in THF even an equilibrium of the dominating solvent-separated ion pair (SSIP) with the contact ion pair (CIP) is demonstrated. These results, together with the observation that crown ethers (which form solvent-separated ion pairs) suppress the reaction of a lithium cuprate with an enone, acid chloride and the enol ester of a β-keto ester,[28] as well as the logarithmic reaction profile studies of Bertz,[29] allow one to conclude that it is essentially only the dimer of the contact ion pair type of a lithium cuprate which undergoes the reaction, for example, with an enone. A numerical analysis of logarithmic reaction profiles leads also to the dominance of the SSIP in THF and the CIP in diethyl ether as found in the ^1H,^6Li HOESY studies. Furthermore, the transition state involving the contact ion pair type dimer is in agreement with quantum-chemical calculations.[33] Thus, a uniform picture of structure and reactivity of lithium cuprates is presented.

Experimental Section

Crystal structures

$Me_2CuLi \cdot 3DME$ (9): CuI (952.3 mg, 5.0 mmol) was placed into a 50 mL flask and dried under vacuum. The flask was then filled with argon. After adding dry diethyl ether (7.5 mL) the suspension was stirred at −78 °C. Then, methyllithium (10.0 mmol, 1.54 M) in diethyl ether (6.5 mL) was added and the mixture was allowed to warm up to 0 °C. The clear, colorless solution was kept at −78 °C for 24 h. During this time most of the LiI crystallized. At −78 °C the supernatant solution was transferred into a centrifuge tube and 2-cyclohexenone (528.7 mg, 5.5 mmol) in diethyl ether (5.0 mL) was added under stirring. The mixture was stirred at 0 °C for 1 min and then centrifuged at −78 °C. The solution was removed and the yellow precipitate was suspended in dry diethyl ether (5.0 mL) at −78 °C. After adding methyllithium (5.0 mmol, 1.54 M) in diethyl ether (3.25 mL) a clear solution of Me_2CuLi was obtained at −20 °C. This solution (1.2 mL) was diluted with dry diethyl ether (1.5 mL) at −78 °C. Addition of 1,2-dimethoxyethane (1.5 mL) resulted in the precipitation of a white solid which was redissolved at 0 °C and then cooled to −30 °C for 24 h. The solvent was removed from the white precipitate and the solid was diluted in dry THF (0.5 mL) at 0 °C. After 24 h at −50 °C and another 24 h at −78 °C crystals of **9** suitable for X-ray analysis were obtained.

$[\{(Me_3Si)CH_2\}_2CuLi] \cdot 3DME$ (10): CuI (1.9 g, 10.0 mmol) was put into a 50 mL flask and dried under vacuum. The flask was then filled with argon. After adding dry diethyl ether (15.0 mL) the suspension was stirred at −78 °C. Then $(Me_3Si)CH_2Li$ (20.0 mmol, 1.0 M) in pentane (20.0 mL) was added and the mixture was allowed to warm up to −30 °C. The clear, colorless solution was kept at −50 °C for three days. During this time most of the LiI crystallized. At −78 °C the supernatant solution was transferred into a centrifuge tube and 2-cyclohexenone (1.06 g, 11.0 mmol) was added under stirring. The mixture was allowed to warm up to −30 °C and then centrifuged at −78 °C. The solution was removed and to the yellow precipitate dry diethyl ether (5.0 mL) was added at −78 °C. After adding $(Me_3Si)CH_2Li$ (10.0 mmol, 1.0 M) in pentane (10.0 mL) a clear solution of $[\{(Me_3Si)CH_2\}_2CuLi]$ was obtained at −30 °C, which was stored over dry ice. To this solution (0.5 mL) 1,2-dimethoxyethane (0.14 mL) was added at −78 °C. After 24 h at −78 °C crystals of **10** suitable for X-ray analysis were obtained.

$[\{[(Me_3Si)CH_2]_2CuLi\}_2] \cdot 3Et_2O$ (11): CuCN (44.8 mg, 0.5 mmol) was put into a 50 mL flask and dried under vacuum. The flask was then filled with argon. Dry diethyl ether (5.0 mL) was added and the suspension was cooled to −78 °C. After addition of $(Me_3Si)CH_2Li$ (1.0 mmol, 1.0 M) in pentane (1.0 mL) the mixture was warmed to +4 °C. After 20 h at +4 °C the solution was cooled to −78 °C, and after 56 h crystals of **11** suitable for X-ray analysis were obtained.

NMR spectroscopy

All NMR experiments were performed with a Bruker AMX500 spectrometer equipped with pulsed field gradient (PFG) accessory and a triple resonance probe. Unless otherwise noted all experiments were recorded at −60 °C in 80 % $[D_8]$THF or $[D_{10}]Et_2O$. Proton chemical shifts were referenced to external TMS, lithium chemical shifts to a 1 M solution of LiCl in water at 0 °C. The HOESY pulse sequence as described by Rinaldi,[36] and Yu and Levy,[37] was used combined with an additional ^6Li filter, ahead of the sequence and pulsed field gradients, to suppress spectral artefacts.[38] In all two-dimensional spectra the number of complex points/sweep widths were 1024 points/6 ppm for ^6Li and 128 points/9 ppm for ^1H. Quadrature detection in the indirect dimension was achieved with the time-proportional-phase-incrementation (TPPI) method.[39] The data were processed with the software package UXNMR (Bruker). After apodization with a 90° shifted sinebell, zero filling to 256 real points was applied for the indirect dimension. For the direct dimensions Lorentz-to-Gauss transformation was used.

nBu^6Li (1.6 M) in hexane: ^6Li (1.48 g, 246.0 mmol) was cut into small pieces under mineral oil and placed in a 250 mL flask. With an ultraturax the ^6Li was powdered and then filtered over a glass frit. After washing with dry hexane (3 × 20.0 mL) the ^6Li was suspended in dry pentane (20.0 mL). *n*-Butyl chloride (12.2 mL, 117.0 mmol), dissolved in pentane (20.0 mL), was added slowly so that the reaction boiled slightly (3 h). After refluxing for 2 h the mixture was cooled down slowly and the violet solid was allowed to precipitate for 24 h. The supernatant solution was transferred into a Schlenk tube and then dried under vacuum to remove residual *n*-butyl chloride and coupling products. Finally dry hexane (50.0 mL) was added to yield a concentration of 1.54 mol L^{-1}, which was controlled by means of a Gilman double titration.[40]

Me^6Li (1.0 M) in THF or Et_2O: *n*-Butyl ^{6}lithium (8.0 mmol, 1.45 M) in hexane (5.5 mL) were placed in a 10 mL centrifuge tube, which was dried under vacuum and then filled with argon prior to use. Dry diethyl ether (1.0 mL) was added and the solution was cooled to −40 °C. Under stirring, a precooled solution of methyl iodide (0.5 mL, 8.0 mmol) in pentane (5.0 mL) was added slowly. After cooling to −78 °C for 2 h the precipitated methyl ^{6}lithium was centrifuged at −78 °C. The solvent was removed from the white solid and replaced with cooled dry hexane (10.0 mL). The washing procedure was repeated twice. Finally the methyl ^{6}lithium was suspended in cooled dry diethyl ether or dry THF (5.0 mL). Warming to 0 °C yielded a clear colorless solution with a concentration of 0.9 mol L^{-1}, which was controlled by means of a Gilman double titration.[40]

$(Me_3Si)CH_2{}^6Li$ (1.37 M) in pentane: ^6Li (1.50 g, 250 mmol) was powdered with an ultraturax in dry degassed mineral oil. The powder was filtered over a glass frit, washed with dry pentane (3 × 20.0 mL) and transferred into a 100 mL flask. The ^{6}lithium powder was suspended in dry pentane (20.0 mL) and $(Me_3Si)CH_2Cl$ (16.25 mL, 117.0 mmol) in pentane (20.0 mL) was added dropwise under stirring such that the reaction boiled continuously. After completion of the addition the violet solid was allowed to precipitate for 24 h. The supernatant clear solution was transferred into a Schlenk tube and dried under vacuum to remove excess of $(Me_3Si)CH_2Cl$ and coupling products. Finally dry pentane (50.0 mL) was added to yield a concentration of 1.37 mol L^{-1}, which was controlled by means of a Gilman double titration.[40]

Me_2Cu^6Li (salt-free) 0.67 M in THF (80 % $[D_8]$) or Et_2O (80 % $[D_{10}]$) 15: CuI (95.2 mg, 0.5 mmol) was placed in a 10 mL centrifuge tube and dried under vacuum. The flask was then filled with argon (three cycles of drying and filling). Dry diethyl ether (3.0 mL) was added and the suspension was cooled to −40 °C. Under stirring, commercial methyllithium (1.0 mmol, 1.6 M) in diethyl ether (0.62 mL) was added, and after a few minutes a clear solution was obtained. At −78 °C 2-cyclohexenone (48.0 mg, 0.5 mmol) in dry diethyl ether (2.0 mL) was added. Stirring for 5 min gave a yellow precipitate which was centrifuged at −78 °C. The pale yellow supernatant solution was removed and replaced with dry diethyl ether (5.0 mL). The suspension was stirred and then centrifuged again (two cycles of cleaning). Finally the yellow solid was suspended in the corresponding dry solvent (THF or Et_2O) (3.0 mL). Methyl^{6}lithium (0.4 mmol, 0.92 M) in THF or Et_2O (0.43 mL), was added at −78 °C. Warming to −40 °C led to a clear solution which was transferred into a 25 mL flask. If the solution was still yellow it was treated dropwise with methyl^{6}lithium until it became colorless. At 0 °C the solvent was removed under vacuum until a clear oil remained in the flask. The corresponding deuterated solvent [D_8]THF or [D_{10}]Et_2O (0.4 mL), was added and the clear solution was transferred into a NMR tube at −78 °C. The solution was diluted with deuterated solvent until the concentration of 0.67 mol L^{-1} was reached (NMR control). The samples were stable for a few weeks.

$Me_2Cu^6Li\cdot{}^6LiX$ (X = CN, Cl, Br, I, SPh) 0.67 M in THF (80 % [D_8]) or Et_2O (80 % [D_{10}]) 15·LiX: The copper salt (0.4 mmol, CuCN (35.8 mg), CuCl (39.6 mg), CuBr (57.4 mg), CuI (76.2 mg), CuSPh (69.1 mg), respectively) was placed in a 25 mL flask and dried under vacuum. The flask was then filled with argon (three cycles of drying and filling). Dry THF or Et_2O (3.0 mL) was added and the suspension was cooled to −40 °C. Under stirring, methyl^6 lithium (0.8 mmol, 0.92 M) in THF or Et_2O (0.87 mL) was added and after 1 min a clear solution was obtained. At 0 °C the solvent was removed under vacuum until a clear oil remained in the flask. [D_8]THF or [D_{10}]Et_2O (0.5 mL) were added and the clear solution was transferred into a NMR tube at −78 °C. At this temperature the samples were stable for several weeks.

[{$(Me_3Si)CH_2$}$_2Cu^6Li$] (salt-free) 0.67 M in THF (80 % [D_8]) or Et_2O (80 % [D_{10}]) 16: CuBr (107.6 mg, 0.75 mmol) was put into a 10 mL centrifuge tube and dried under vacuum. The tube was then filled with argon (three cycles of drying and filling). Dry dimethyl sulfide (2.25 mL) was added and the slight brown solution was cooled to −20 °C. Under stirring, $(Me_3Si)CH_2{}^6Li$ (1.5 mmol, 1.37 M) in pentane (1.1 mL) was added dropwise. During the addition a white solid precipitated from the solution and the resulting suspension was stirred for 1 h. The solution was centrifuged at −20 °C, and the clear supernatant solution was transferred into a 25 mL Schlenk tube through a syringe filter. The clear solution was then cooled to −78 °C under stirring until a white solid precipitated. The flask was stored over dry ice overnight and then the supernatant solution removed. The remaining white solid was redissolved in the corresponding solvent (THF or Et_2O) (3.0 mL) and the solvent was removed again at −20 °C (Et_2O)/0 °C (THF) under vacuum to remove residual traces of dimethyl sulfide. Addition of deuterated solvent ([D_{10}]Et_2O or [D_8]THF) (0.4 mL) gave a colorless solution, which was transferred into an NMR tube at −78 °C. The samples were diluted with deuterated solvent until the concentration of 0.67 mol L^{-1} was reached. At −78 °C the samples were stable for several weeks.

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[13] a) Crystal structure analysis of **9** ($C_{14}H_{36}CuLiO_6$, $M_r = 370.91$): monoclinic, space group $P2_1/c$, $a = 777.3(1)$, $b = 1770.2(1)$, $c = 1517.0(1)$ pm, $\beta = 93.518(10)^\circ$, $V = 2083.3(3) \times 10^{-30}$ m^3, $Z = 4$, $\rho_{calcd} = 1.183$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 1.068$ mm^{-1}. Data collection on a STOE IPDS area detector system using graphite-monochromated $Mo_{K\alpha}$ radiation at $T = 173(2)$ K. A total of 16208 reflections collected, 4034 unique ($R_{int} = 0.0596$). Solution with direct methods (SHELXS-97)[13e] full-matrix least-squares refinement on F^2 (SHELXL-97),[13f] non-hydrogen atoms anisotropic, hydrogen atoms on calculated positions with fixed isotropic temperature factors. Parameters for the weighting scheme calculated by the program: 0.0696, 0.0000; w$R2$ (R1 for 2874 reflections with $I > 2\sigma(I)$): 0.1114 (0.0405), goodness-of-fit = 0.977; 207 parameters. All calculations were performed on DEC Alpha Stations with VMS;[13g–i] b) Crystal structure analysis of **10** ($C_{20}H_{52}CuLiO_6Si_2$, $M_r = 515.28$): monoclinic, space group $P2_1/n$, $a = 1021.6(1)$, $b = 1926.8(1)$, $c = 1579.2(2)$ pm, $\beta = 90.858(7)$, $V = 3108.2(5) \times 10^{-30}$ m^3, $Z = 4$, $\rho_{calcd} = 1.101$ Mg m^{-3}, $\mu(Cu_{K\alpha}) = 1.940$ mm^{-1}. Data collection on an Enraf Nonius CAD4 diffractometer system using graphite-monochromated $Cu_{K\alpha}$ radiation at $T = 193(2)$ K. A total of 6098 reflections collected, 5880 unique ($R_{int} = 0.1073$). Solution with direct methods (SHELXS-97) [13e] full-matrix least-squares refinement on F^2 (SHELXL-97),[13f] non-hydrogen atoms anisotropic, hydrogen atoms on calculated positions with fixed isotropic temperature factors. Parameters for the weighting scheme calculated by the program: 0.1189, 3.0014; w$R2$ (R1 for 4680 reflections with $I > 2\sigma(I)$): 0.1939 (0.0665), goodness-of-fit = 1.035; 284 parameters. Absorption correction using the DIFABS[13d] procedure in PLATON. All calculations were performed on DEC Alpha Stations with VMS;[13g–i] c) Crystal structure analysis of **11** ($C_{28}H_{74}Cu_2Li_2O_3Si_4$, $M_r = 712.19$): triclinic, space group $P\bar{1}$, $a = 1084.5(1)$, $b = 1091.4(1)$, $c = 1895.6(1)$ pm, $\alpha = 87.682(9)$ $\beta = 81.637(8)$, $\gamma = 82.658(9)$, $V = 2200.9(3) \times 10^{-30}$ m^3, $Z = 2$, $\rho_{calcd} = 1.075$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 1.097$ mm^{-1}. Data collection on an STOE IPDS area detector system using graphite-monochromated $Mo_{K\alpha}$ radiation at $T = 193(2)$ K. A total of 9697 reflections were collected, 5254 unique ($R_{int} = 0.0692$). Solution with direct methods (SHELXS-97),[13e] full-matrix least-squares refinement on F^2 (SHELXL-97),[13f] non-hydrogen atoms anisotropic, hydrogen atoms on calculated positions with fixed isotropic temperature factors. Parameters for the weighting

scheme calculated by the program: 0.0983, 0.0000; w$R2$ (R1 for 2759 reflections with $I > 2\sigma(I)$): 0.1720 (0.0568), goodness-of-fit = 0.886; 371 parameters. The crystal happened to be a twin. The integration[13j] has been performed by using the orientation matrix of the main twin domain. Overlapping reflections have been rejected. All calculations were performed on DEC Alpha Stations with VMS;[13g–i] d) N. Walker, D. Stuart, *Acta Crystallogr. Sect. A* **1983**, *39*, 158; e) G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Göttingen, **1997**; f) G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Göttingen, **1997**; g) A. L. Spek, Platon 94, Program for Geometrical Analysis of Crystal Structures, Utrecht, **1994**; h) E. Keller, SCHAKAL-88B, A FORTRAN Program for the Graphic Representation of Molecular and Crystallographic Models, Freiburg, **1988**; i) Crystallographic data (excluding structure factors) for the structures reported in the paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-139052, CCDC-139053 and CCDC-139054. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk); j) STOE IPDS Software Version 2.84 **1997**

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[31] J. Canisius, A. Gerold, and N. Krause, determined the rate constant of the reaction of $Me_2CuLi \cdot LiI$ with 4,4-dimethyl-2-cyclohexenone in Et_2O at −58 °C to be $k_{\mathrm{Et_2O},\,-58\,^\circ\mathrm{C}} = 8 \times 10^{-3}\,\mathrm{s^{-1}}$ (J. Canisius, A. Gerold, N. Krause, *Angew. Chem.* **1999**, *111*, 1727–1730; *Angew. Chem. Int. Ed.* **1999**, *38*, 1644–1646). From the activation energy of this reaction, the rate at −53 °C was extrapolated to be $k_{\mathrm{Et_2O},\,-53\,^\circ\mathrm{C}} = 2 \times 10^{-2}\,\mathrm{s^{-1}}$. This allows a comparison with the reaction rate determined in THF at −53 °C: $k_{\mathrm{THF},\,-53\,^\circ\mathrm{C}} = 8 \times 10^{-4}\,\mathrm{s^{-1}}$ (J. Canisius, Dissertation, Universität Dortmund, planned **2000**). The ratio $k_{\mathrm{Et_2O},\,-53\,^\circ\mathrm{C}}/k_{\mathrm{THF},\,-53\,^\circ\mathrm{C}}$ is 25:1. If one considers that in THF at −78 °C the equilibrium SSIP $\rightleftharpoons$ CIP is more on the side of the SSIP than at −53 °C (see Figure 6) and thus the reaction with the enone additionally slowed down if compared to that at −53 °C, the rough estimate extrapolated in Scheme 3 is in very good agreement with the precise kinetic measurements. We are very grateful to Professor Krause for the kinetic data.

[32] a) This seems to be a general observation, because B. H. Lipshutz and S. Sengupta (B. H. Lipshutz, S. Sengupta, *Org. React.* **1992**, *41*, 135) noticed on p. 198: "1,4-Additions of .. R_2CuLi to unsaturated systems, *best performed in the absence of good donor solvents*, are usually quite efficient .." (italics by G. Boche et al.). b) Not surprisingly, in dimethyl sulfide (Me_2S) the reactivity of lithium cuprates corresponds to that in diethyl ether, see:S. H. Bertz, G. Dabbagh, *Tetrahedron* **1989**, *45*, 425–434.

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[34] a) It is also assumed that in solutions containing LiCN a heterodimer of the type R-Cu-R-Li-CN-Li instead of [**21**]$_2$ might undergo the reactions with enones, see ref. [29d] and references therein; b) Calculations were carried out by J. P. Snyder on the reaction of a lithium cuprate monomer with an enone, see: J. P. Snyder, *J. Am. Chem. Soc.* **1995**, *117*, 11025–11026.

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