



Chemical and physical evidence for metal–metal interchange between lithium alkoxides and di-*n*-butylmagnesium

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Abstract—Mixtures of BuLi with Mg(OCH₂CH₂OEt)₂ and of LiOCH₂CH₂OEt with Bu₂Mg have been studied by ¹H, ¹³C and ⁷Li NMR spectra and by (⁶Li, ¹H) HOESY experiments. It is concluded that the two systems are equivalent and give the same product. The HOESY experiments indicate that partial metal–metal interchange takes place in these two systems leading to the organometallic derivative of the more electropositive metal. © 2002 Elsevier Science Ltd. All rights reserved.

Ever since the reports by Lochmann¹ and Schlosser,² considerable interest has been aroused³ by the combination of an alkyllithium reagent and a heavier alkali metal alkoxide. This combination, which exhibits superbasicity, has found application in organic syntheses⁴ and, to a lesser extent, in polymerization.⁵ Important variants of the so-called LICKOR reagents have been devised by replacing the organolithiums by lithium amides⁶ and a crystal structure of such a system has been reported very recently.⁷ An even more powerful metalating agent reported from this laboratory involves a combination of *n*-butyllithium and the mixed lithium-potassium 2-dimethylaminoethoxide.⁸ This mixed alkoxide exhibits fair solubility in hydrocarbon solvents such as methylcyclohexane, and provides additional activation⁹ to the incipient organopotassium reagent by its tertiary amine moiety. The relatively limited application of the LICKOR systems in polymerization is most probably due to the very low solubility of the organo-alkali reagent generated. For example, in our hands very carefully purified benzylsodium, from BuLi and *t*-BuONa and toluene, failed to react with isoprene. Thus a method for solubilizing alkyl derivatives of the heavier alkali metals in inert solvents such as hydrocarbons appeared to be very desirable. This goal has been achieved by adding magnesium 2-methoxy- or 2-ethoxyethoxide to a preformed, or in situ generated organoalkali reagent.¹⁰ In this way it was found that with phenylsodium, for example, the soluble species has

the ‘unit composition’ Na₂MgPh₂(OCH₂CH₂OEt)₂. It is of interest to note that the same soluble species is formed from sodium 2-ethoxyethoxide and unsolvated diphenylmagnesium.¹¹ These rather novel organometallic reagents exhibit normal organometallic behavior towards conventional electrophiles, but, compared to the corresponding organosodium compounds, exhibit a reduced metalating ability. The same holds true for the alkyllithiums as well. Indeed, the metalating ability of butyllithium in the presence of magnesium 2-ethoxyethoxide is diminished to such an extent that it can survive in tetrahydrofuran without losing its ability to enter into a halogen–metal interchange reaction. Thus it has become possible to generate aryllithiums bearing a labile functional group¹² or a group that can alter the locus of substitution.¹³ Magnesium 2-ethoxyethoxide has also been used as an additive to the ‘higher order’ LICKOR reagent⁸ in a method reported from this laboratory for the polyethylation of methyl aromatics leading to crowded molecules containing either 3-pentyl or *n*-propyl groups, depending on the availability or not of a free *ortho*-position in the polymethyl aromatic compound.¹⁴

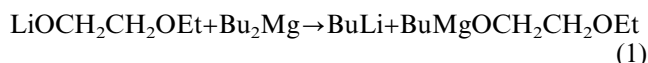
The present letter is addressed to the processes occurring in the systems involving mixed lithium and magnesium alkyls and the corresponding alkoxides. The generation of an organometallic species with organoalkali-like behavior from diphenylmagnesium and sodium or potassium 2-ethoxyethoxide¹¹ implies that a metal–metal interchange reaction takes place. The question then arises as to whether this reaction between the alkali metal alkoxide and the diphenylmagnesium is only characteristic of diarylmagnesiums and the heavier

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alkali metal alkoxides, or if it is true for dialkylmagnesiums and lithium alkoxides as well.

We reasoned that if *n*-butyllithium were formed in the reaction between $\text{LiOCH}_2\text{CH}_2\text{OEt}$ and $n\text{-Bu}_2\text{Mg}$ it should manifest its presence by participating in a halogen–metal interchange reaction. Indeed, by allowing bromobenzene, 10 mmol, to react with 10 mmol of dibutylmagnesium and 20 mmol of lithium 2-ethoxyethoxide, in methylcyclohexane/diethyl ether, followed by carboxylation, we obtained benzoic acid, along with butyric acid, in a yield corresponding to approximately 50% of the available butyl alkyls. The benzoic acid was clearly derived from a phenyl–metal compound. Given that only an alkyllithium could have participated in a halogen–metal interchange reaction, and judging from the yield of benzoic acid, we concluded that butyllithium was produced according to reaction (1).



This conclusion has been confirmed by NMR experiments. We prepared hexadeuterobenzene solutions of $2\text{BuLi} + \text{Mg}(\text{OCH}_2\text{CH}_2\text{OEt})_2$ and of $2\text{LiOCH}_2\text{CH}_2\text{OEt} + \text{Bu}_2\text{Mg}$ and recorded the ^1H , ^{13}C and ^7Li NMR spectra.¹⁵ The ^1H NMR spectra of both systems exhibit two high-field triplets at δ -0.29 and -0.38 ppm. These resonances correspond to methylene groups bonded to a metal, and this was confirmed by a COSY NMR experiment.

In order to determine with absolute certainty whether the lithium is bonded to a butyl group or to an alkoxy group, or even to both, we performed two-dimensional ^6Li , ^1H heteronuclear Overhauser (HOESY) experiments.¹⁶ We prepared the complex from 2 equiv. of $^6\text{LiBu} + \text{Mg}(\text{OCH}_2\text{CH}_2\text{OEt})_2$ and $\text{Bu}_2\text{Mg} + 2$ $^6\text{LiOCH}_2\text{CH}_2\text{OEt}$ and recorded the ^1H , ^{13}C and ^6Li NMR spectra. In both cases there are two peaks for ^6Li at 0.167 and 0.074 ppm for the system $2[{}^6\text{LiBu}] + \text{Mg}(\text{OCH}_2\text{CH}_2\text{OEt})_2$ and at -0.0301 and -0.0498 ppm for the system $2[{}^6\text{LiOCH}_2\text{CH}_2\text{OEt}] + \text{Bu}_2\text{Mg}$ (external reference BuLi^6 in C_6D_6).

The HOESY spectra (Fig. 1) of the system $\text{Bu}_2\text{Mg} + 2\text{LiOCH}_2\text{CH}_2\text{OEt}$ in C_6D_6 at 27°C reveals three cross peaks. One of them is between the ^6Li resonance lines at $\delta = -0.301$ and a $-\text{CH}_2-$ ($\delta = 0.0438$ ppm), and the other two cross peaks are between the ^6Li resonance at $\delta = -0.408$ ppm and the two alkoxyethylene protons $-\text{OCH}_2\text{CH}_2\text{O}-$ at $\delta = 3.90$ and 3.38 ppm, respectively.

On the basis of the above experimental results, we conclude that the two systems are equivalent. Namely, by mixing two equivalents of *n*-butyllithium with 1 equiv. of magnesium alkoxide or 2 equiv. of lithium alkoxide with 1 equiv. of di-*n*-butylmagnesium we obtain the same product (Eq. (2)). In addition, the HOESY experiments demonstrated that partial metal–metal interchange takes place in these two systems. This result correlates with the results from the halogen–

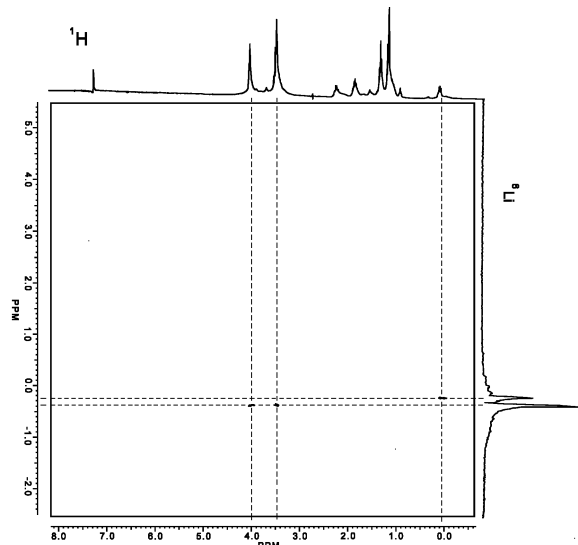
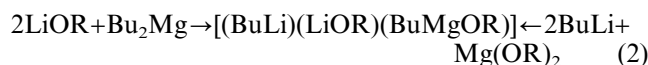


Figure 1. ^6Li , ^1H HOESY spectrum for the system $\text{Bu}_2\text{Mg} + 2\text{LiOCH}_2\text{CH}_2\text{OEt}$ in C_6D_6 at 27°C ; mixing time 2.0 s.¹⁷

metal interconversion experiment (see above). It can be added that the metal–metal interchange reaction leads to the organometallic derivative of the more electropositive metal, just as in the case of $\text{BuLi} + \text{KOBU}^{\prime}$.^{1,2}



($\text{R} = -\text{CH}_2\text{CH}_2\text{OEt}$)

Finally, it should be stressed that the species existing in the two systems mentioned above are most probably in the form of a cocomplex. This is deduced from our observation that a hydrocarbon-soluble lithium alkoxide solubilizes an insoluble dialkylmagnesium and that hydrocarbon-insoluble lithium alkyls and magnesium alkoxides exert mutual solubilization to each other. For example, magnesium *n*-butoxide and cyclohexyllithium form a solution in pentane¹⁸ while lithium ($-$)-menthyl-oxide solubilizes unsolvated di-*n*-butylmagnesium in hydrocarbon media.¹⁹

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