The Reaction of RLi Species with CO and Isonitriles: IR Spectroscopic Investigations in Liquid Xenon and Ab-Initio Calculations of the Intermediates

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Solutions of alkyl- or aryllithium compounds were treated with CO or *t*Bu−NC in liquid xenon (LXe) at low temperature. Carbonyllithium compounds, acyllithium and the corresponding isolobal isonitrile products were characterized by IR spectroscopy for the first time. The structures, energies and characteristic IR frequencies of the intermediates were calculated by using ab-initio methods and discussed with the experimental values.

Organolithium compounds are known to be versatile reagents in organometallic synthesis. The most important application is the nucleophilic addition of these reagents to carbonyl compounds. The reaction of the simplest case – the CO molecule itself – was extensively studied with regard to the products, which are stable at ambient temperature[1]. At low temperature the synthesis of *n*-butyl trimethylsilyl ketone starting from *n*BuLi and CO/Me_3SiCl is successful[2]. The intermediate acyllithium compound was deduced from those experiments [Eq. (1)]:

$$n\text{BuLi} + \text{CO} \xrightarrow[-135\,^{\circ}\text{C}]{\text{Me}_2\text{O/THF}} [n\text{Bu-C(O)Li}] \xrightarrow[-\text{LiCl}]{\text{Me}_3\text{SiCl}} n\text{BuC(O)SiMe}_3 \qquad (1)$$

These results suggest that an investigation of the early stages of the reaction between CO or *t*BuNC and a variety of RLi species in liquid xenon (LXe) at low temperatures would be most worthwhile. Organolithium compounds are sufficiently soluble in LXe and the temperature range (−112°C to −20°C) seems to be ideal for the existence of the expected intermediates. The IR spectroscopic results will be discussed with the structures and energies of the intermediates calculated by ab-initio methods applied to nonsubstituted and noncoordinated lithium compounds[3]. In spite of these simplifications a good agreement between theory and experiment was found for the intermediates.

In a first experiment a pressure of 2 bar of CO at −100°C was applied to a saturated solution of *n*BuLi in liquid xenon. Surprisingly, no free CO was observed but a carbonyl adduct of the lithium alkyl[4] was detected at 2047 cm^{-1} ($\nu_{(^{13}CO)}$: 2008 cm^{-1}). Warming up to −30°C led to a new absorption at 1635 cm^{-1}, while the IR band of the carbonyl adduct vanished. The new absorption was therefore attributed to the acyllithium compound, which also decomposed at slightly higher temperature (−20°C) [Eq. (2)]:

$$n\text{BuLi} + \text{CO} \xrightarrow[-100\,^{\circ}\text{C}]{\text{LXe}} [n\text{BuLi-CO}] \xrightarrow[-30\,^{\circ}\text{C}]{\text{LXe}} [n\text{Bu-C(O)Li}] \qquad (2)$$

For the following experiments the lithium compounds were changed. With PhLi the corresponding carbonyllithium compound with an absorption at 2047 cm^{-1} could be reproduced, but with the sterically hindered *t*BuLi no complexation of CO was detected. The adduct of PhLi decomposed during warming up, but detectable amounts of acyllithium species could not be found under these reaction conditions.

For further investigations *t*BuNC, which is isolobal to CO, was dissolved in liquid xenon. An appropriate IR absorption of 0.5−1 was achieved by condensing degassed isonitrile from an ampoule into the xenon solution. With PhLi and *t*BuLi the band of the lithium isonitrile adduct at 2135 cm^{-1} was found beneath that of free isonitrile at 2179 cm^{-1}, while *n*BuLi did not undergo complexation. Only the adduct of *t*BuLi reacted further to afford the lithiated Schiff base ($\nu_{(C=N)}$: 1510 cm^{-1}) up to −20°C [Eq. (3)], which is the maximum temperature of the cell used during the experiments:

$$t\text{BuLi} + \text{R-NC} \xrightarrow[-100\,^{\circ}\text{C}]{\text{LXe}} [t\text{BuLi-CN-R}] \xrightarrow[-20\,^{\circ}\text{C}]{\text{LXe}} [t\text{Bu(Li)C=NR}] \qquad (3)$$

Only the most reactive *t*BuLi is able to attack the carbon-nitrogen triple bond at temperatures below −20°C. For the less reactive organolithium compounds (PhLi, *n*BuLi) higher temperatures in ordinary solvents like pentane are appropriate to synthesize their lithiated Schiff bases. However, for their detection IR spectroscopy seems to be unsuitable, because the $\nu_{(C=N)}$ will be hidden by strong CH deformation modes of the solvents.

For the determination of the structures, energies of formation and characteristic IR frequencies theoretical methods are advantageous. For this purpose, the program package Gaussian 92[5] implemented on an IBM-compatible 80486/66-MHz PC with 36 MB RAM memory was used, which allows ab-initio calculations at the HF/6-31G** level of theory for the species of interest. In order to reduce the number of internal coordinates of the olegomeric organolithium compounds the tetrameric lithium hydride served as a model. The addition and insertion of one molecule of CO into the lithium−hydrogen bond of $(LiH)_4$ (**1**) was investigated first. The resulting structures are presented in Figure 1, while energies and frequencies are given in Table 1.

The addition causes release of 23 kJ of reaction enthalpy with the formation of only a linear LiCO substructure **2**. The long lithium−carbon distance of 236 pm corresponds to the small addition enthalpy. Especially this lowered enthalpy is the cause for

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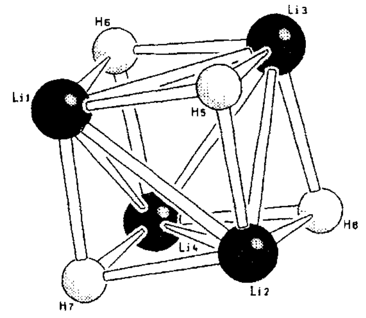
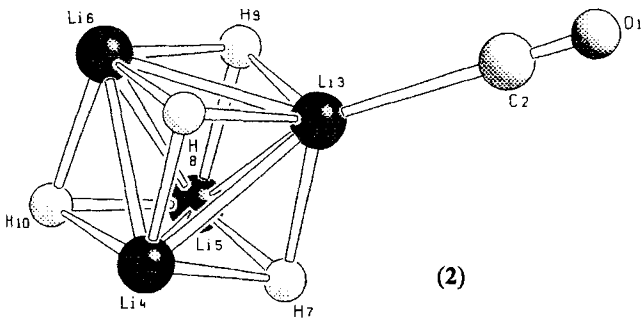
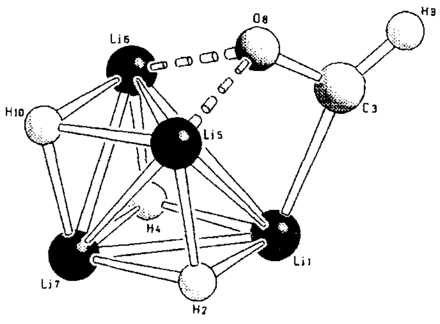
Figure 1. Molecular projection of Li_4H_4 (**1**), Li_4H_4CO (**2**) and $Li_4H_3(COH)$ (**3**). Selected bond lengths in pm: (**1**) Li–Li 255; Li–H 190; (**2**) Li–Li 254–257; Li3–C2 236; C2–O1 111; (**3**) Li–Li 247–279; Li1–C3 213; C3–O8 126; Li5–O8/Li6–O8 195



(**1**)



(**2**)



(**3**)

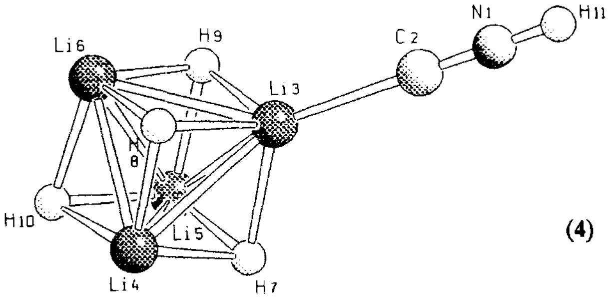
Table 1. Ab-initio-calculated energies and frequencies for the various intermediates[a]

	electronic energy (Hartrees)	zero-point energy (Hartrees)	ν(CO)/(CN) (cm^{-1})
CO	-112.7378770	0.0055566	2171
Li_4H_4(**1**)	-32.1442042	0.0294716	
Li_4H_4CO (**2**)	-144.8923204	0.0365446	2207
$Li_4H_3(COH)$ (**3**)	-144.8877286	0.0421075	1441
CNH	-92.8596125	0.0170010	2054
Li_4H_4CNH (**4**)	-125.0232154	0.0481952	2108
$Li_4H_3(CHNH)$ (**5**)	-125.0517834	0.0563780	1426

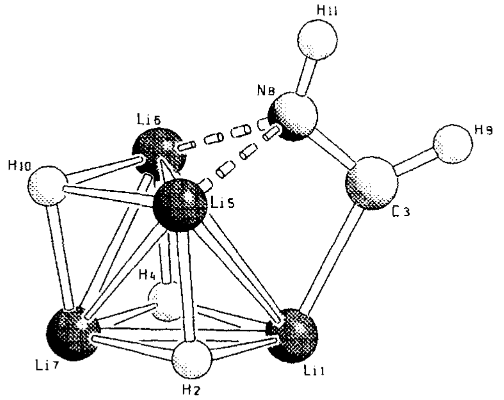
[a] Reaction enthalpies were calculated for 0 K and corrected by the zero-point vibrational energy, frequencies are scaled by using a factor of 0.89.

the small number of known main group carbonyl compounds, even when a subcoordinated species is synthesized. The CO stretching frequency was calculated to be 2207 cm^{-1}, which differs significantly from the experimental value (2047 cm^{-1}). The fact that the carbonyl lithium unit is backbonded like an ordinary d-metal carbonyl compound cannot be deduced from the ab-initio calculation. The formation of the formyl compound 3 is a slightly endothermic but irreversible process (+27 kJ). The lithium–carbon bond of 213 pm is relatively short compared to 231 pm in solid Li_4Me_4[6], and the formyl group coordinates with its carbon atom to one and with the oxygen to two lithium atoms of a lithium-tetrahedron plane. This gives evidence of the next reaction step, because by further clevage of the carbon atom from the lithium a carbene is formed, which is believed to be the essential step forming the room-temperature stable products of the RLi/CO reaction[1]. The calculated IR absorption of the formyl group appears at 1441 cm^{-1}, while in the experiment a value of 1635 cm^{-1} was measured. It seems that the lithium-oxygen interaction is overestimated by the ab-initio calculation, which results in a too low-lying carbon-oxygen stretching frequency. It may be caused by using Li_4H_4 as a simple model for organolithium compounds. An alkyl group donates more electron density to the Li_4 core and thus reduces the subcoordination of the compound. So the lithium-oxygen interaction becomes weaker, and a higher CO stretching frequency was observed in the experiment.

Figure 2. Molecular projection of Li_4H_4CNH (**4**) and $Li_4H_3(CHNH)$ (**5**). Selected bond lengths in pm: (**4**) Li–Li 252–260; Li3–C2 225; C2–N1 115; (**5**) Li–Li 246–277; Li1–C3 213; C3–N8 131; Li5–N8/Li6–N8 208



(**4**)



(**5**)

Further investigations were carried out to determine the structures of the compounds formed in the isonitrile reaction (Figure 2). Addition of HNC to the lithium hydride tetramer was accompanied by the release of an energy of 46 kJ/mol, and a long lithium-carbon bond was formed (225 pm). The resulting adduct (**4**) includes a linear LiCNH unit and displays C_{3v} symmetry. The

CN stretching frequency was calculated to be 2108 cm^{-1}, which differs by only 27 wave numbers from the experimental value. The second step of the reaction involved again insertion into the lithium–hydrogen bond. In contrast to the CO insertion this partial reaction is exothermic (−54 kJ/mol), but a similiar product (**5**) with C_s symmetry was found. The HCNH group coordinates to all three lithium atoms on a lithium tetrahedron plane. The lithium–carbon distance was with 213 pm found to be identical with that in **2**. The calculated CN stretching frequency (1426 cm^{-1}) was again calculated a tittle too low compared to the experimental value of 1510 cm^{-1}.

To sum up it may be said that the theoretical model explains in general the bonding in the adducts (**2, 4**), where triple bonds are still intact and small reaction enthalpies were obtained. For the insertion products **3** and **5** low-lying CN and CO stretching frequencies were calculated and measured, due to intramolecular coordination weakening the CO(N) double bond.

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Experimental

The organolithium species were obtained from Aldrich (R = Ph, *t*Bu) or Chemetall (R = *n*Bu) and were injected in 0.5 ml portions as solutions in pentane (R = *n*Bu) or ether/pentane (R = Ph, *t*Bu) by means of a syringe. High purity gases (Xe 5.0, Linde AG, CO 4.7, Messer Griesheim) and reagents (*t*Bu–NC, 99%, Aldrich) were used as purchased. Liquid xenon was used for these experiments for two reasons: It is totally transparent in the IR region and allows measurements at temperatures between −112°C and −20°C. This is the range in which the wanted intermediates exist. IR spectra were recorded with a Bruker IFS 28 FT-IR spectrometer (4000–1000 cm^{-1}, 128 scans, resolution 2 cm^{-1}). For the low-temperature experiments a pressure-resistant IR cell built from single-crystal silicon was used. For details of the construction and spectral properties see ref.[8].

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