Direct Synthesis of Organometallics, IV[◇]

The Mechanism of the Activation of Aromatic Hydrocarbons with Lithium Atoms: Spectroscopic Results and Their Ab Initio Interpretation

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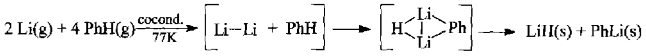
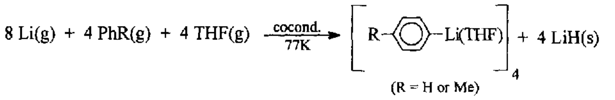
In the presence of THF, lithium atoms are known to be able to activate benzene derivatives under cryogenic reaction conditions. This synthesis affords solid lithium hydride and ring-metalated products selectively. For the determination of the reaction mechanism, the cocondensation reaction was repeated on a reduced scale in a 77-K cryostate, which allowed the measurement of UV/Vis and IR spectra. The spectroscopic results exclude any generation of free electrons; their interpretation suggests that small solvated lithium clusters activate the hydrocarbon bonds. A model reaction was developed by using the spectroscopic results and ab initio calculations. Thus, benzene was added to a Li_2 cluster, which reduces the carbon-hydrogen bond to the phenyl anion and hydride on the surface without the formation of free radicals. In the last step the intermediate mixed organolithium species dismutate to solid lithium hydride and phenyllithium.



The reduction process on the cluster surface is facilitated by coordinating THF to the lithium, which results in a higher redox potential. The complete mechanism is discussed in the terms of geometries of the intermediates and reaction enthalpies in connection with the experimental values. Thus, a distinct new reaction pathway for a substitution on the benzene ring is established.

Lithium atoms are able to activate benzene, when they are cocondensed in the presence of THF at liquid nitrogen temperature[2]. Solid lithium hydride and phenyllithium are obtained as the only products during the experiment. When toluene is used as a reactant, *p*-TolLi without the thermodynamically favored benzyllithium is generated in an unexpected selective hydrocarbon activation reaction [Eq. (1)].

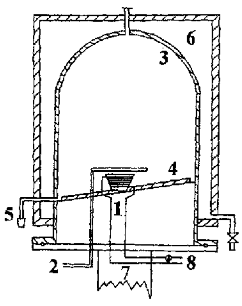


(1)

For the reaction a stainless-steel metal vapor synthesis (MVS) apparatus, which excludes reactions in the gas phase, was used. Because of the low pressure inside the system the gaseous species cannot react before they reach the cold cocondensation vessel. The MVS machine is distinctly different from standard arrangements, because it is equipped with a cooled internal drain in the cocondensation vessel, which allows the isolation of products under Schlenk-type conditions even at low temperature. Details of the construction are shown in Figure 1.

In order to obtain more information about the reaction mechanism by characterizing intermediates, the synthesis was reexamined in an optical cryostate at liquid nitrogen temperature. The amount of cocondensed material was roughly reduced by a factor of 1000 from the preparative gram scale to a milligram scale, which allows spectroscopic transmission measurements in the IR and UV/Vis region. Instead of a cocondensation vessel a KBr (IR) or sapphire (UV/Vis) plate was used. The open crucible was transformed into a Knudsen cell generating a well focused lithium atom beam, which can be cocondensed with a mixture of THF and aromate. The cryostate, which was built up for this issue, is shown in detail in Figure 2. The construction is similar to cryostates for the matrix-isolation technique[3].

Figure 1. Cocondensation apparatus: (1) crucible, (2) inlet system, (3) cocondensation vessel, (4) internal drain, (5) outlet system, (6) liquid nitrogen, (7) high vacuum pump, (8) power supply



IR Measurements

In a first experiment gaseous lithium was cocondensed with an equimolar mixture of benzene and THF at 77 K.

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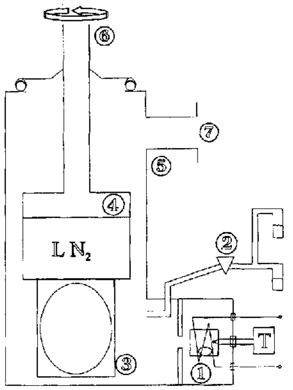
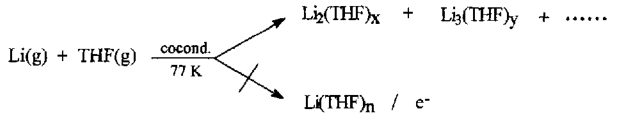
Figure 2. The optical cryostate for IR or UV/Vis measurements; (1) Knudsen cell with temperature control unit, (2) inlet system, (3) KBr or sapphire, (4) cryostate body, (5) vacuum housing, (6) turnable cryostate, (7) high-vacuum system



At once the characteristic solid-state absorption of lithium hydride, which is centered at about 400 wavenumbers, was found in the IR spectrum. During warming-up to the melting point of the matrix no significant change in the IR absorptions was detected. From these observations it was concluded that the hydrocarbon activation takes place at the very beginning of cocondensation at 77 K. Lithium atoms are therefore shown to be able to activate aromatic hydrocarbons in the presence of THF selectively at liquid nitrogen temperature without any photoexitation.

UV/Vis Measurements

Further knowledge of the mechanism is obtained, when the benzene reactant is not cocondensed in the UV/Vis experiments. If lithium atoms are simultaneously frozen down with pure THF, a bright blue matrix with a broad and unstructured absorption at 585 nm is formed. For a successful experiment the concentration of lithium in THF must not exceed 1% to keep the frozen matrix still transparable. The absorption band at 585 nm cannot be explained by free electrons[4] nor by solvated lithium atoms[5,6], which should both absorb at significant longer wavelength. But it is plausible, that small solvated lithium clusters are formed during the cocondensation. Even in a solid argon matrix at 10 K cocondensed atoms are found to diffuse and dimerize, so that cluster formation in vitreous THF at 77 K, which has bigger diffusion canals, is much more likely.



In the non-solvating argon matrix a UV/Vis absorption at 500 nm was reported for the Li_2 cluster[5,6] and an absorption of 513 nm for the solvated cluster $Li_2(H_2O)_6$, was found by a semiempiral calculation on MNDO (CIS).

Furthermore, the absence of free electrons or solvated lithium atoms as potential single-electron reducing agents is in good agreement with the observation, that no biphenyl formed by the dimerization of phenyl radicals was found in the experiment on a preparative scale[2]. Starting from this cluster formation process, which can serve a minimum of two electrons for redox reactions, we may easily explain the reduction of benzene to the phenyl anion and hydride.

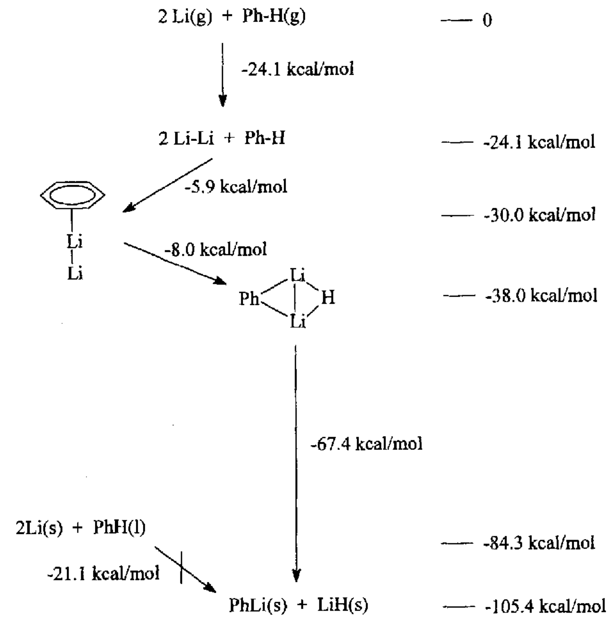
For a deeper understanding of the hydrocarbon activation reaction in this particular cocondensation experiment a model reaction will be presented. The proposed mechanism is in accordance with all experimental observations and is deduced from thermochemical and quantum-chemical data. Even solid lithium should react with benzene to afford lithium hydride and phenyllithium releasing 21 kcal/mol[8]. But this reaction is not detected before gaseous lithium is used, which introduces another 84 kcal/mol[9] into the system [Eq. (2) and (3)].

$$2\,Li(s) + C_6H_6(l) \longrightarrow LiH(s) + PhLi(s) + 21.1\ kcal/mol \qquad (2)$$

$$2\,Li(g) + C_6H_6(g) \longrightarrow LiH(s) + PhLi(s) + 105.4\ kcal/mol \qquad (3)$$

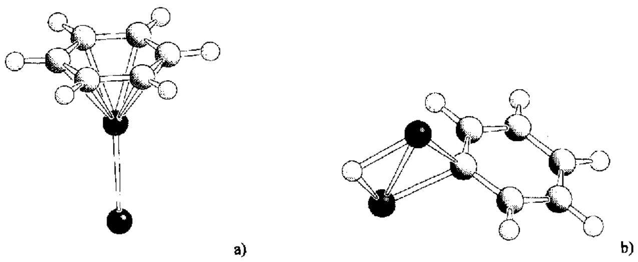
Now enough energy for the homogeneous C–H bond cleavage would be available, but the reaction uses a less energetic pathway. In the simple model reaction it is suggested, that the first step is the formation of a Li_2 cluster (−24 kcal/mol)[10], which is able to form a complex with benzene (−6 kcal/mol). In such a complex a double electron transfer via the aromatic system in the presence of THF breaks the carbon–hydrogen bond and forms in a slightly exothermic step (−8 kcal/mol) an adduct of LiH and LiPh. These species can easily dismutate in a strongly exothermic reaction (−67 kcal/mol) to solid lithium hydride and phenyllithium. In the presence of tetrahydrofuran $(PhLi \cdot THF)_4$ is isolated, which increases the reaction enthalpy by adduct formation even more. The reaction enthalpies as well as the intermediates are presented in Scheme 1.

Scheme 1



In a first step the Li_2 cluster coordinates via a single lithium atom in C_{6v} symmetry to the benzene molecule, which partly overcomes the subcoordination of one lithium atoms in the cluster. While bond lengths and angles in the coordinated benzene molecule do not significantly differ from the free species, the Li−Li bond is lengthened by about 7 pm. After this complexation of the benzene molecule the carbon−hydrogen bond is activated. Thereby an intermediate with C_{2v} symmetry is formed, where a plain phenyl group is bound to the likewise plain HLi_2C ring with a torsion angle of 90°. This may be explained by bridging of a p-orbital of the phenyl C1 with the Li_2 subunit. Such high-energy intermediates like the proposed adduct of LiH and PhLi can only be created, when gaseous lithium is used, which explains the non-observed reaction of benzene with solid lithium. The molecular projections of $PhH \cdot Li_2$ and $PhLi_2H$ are found in Figure 3.

Figure 3. Molecular projection of $PhH \cdot Li_2$(a) and $PhLi_2H$(b) both optimized on the HF/6-31G** level of theory[a]



[a] Selected bond lengths [pm]: (a) Li−Li 277, Li−C 236, C−C 139, C−H 108 (Li−Li in the free Li_2 cluster: 270); (b) Li−Li 231, Li−H 180, Li−C 216, C−C 140 (average).

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Experimental

The cocondensation experiments were performed with a self-constructed 77-K cryostate under high-vacuum conditions ($p > 10^{-5}$ mbar). − Benzene and THF were dried by refluxing with the appropriate drying agent and were distilled before use. The lithium metal (purity 99.9%) was purchased from Chemetall GmbH. − IR: Bruker IFS 28. − UV/Vis Hitachi 100-60 with a self-constructed data digitalization and processing system.

In a typical IR experiment about 5 mg of lithium was vaporized and cocondensed with a mixture of 50 mg of benzene and 50 mg of THF at 77 K. The black matrix was still transparent enough for infrared spectroscopy. Warming-up experiments could be performed up to −100°C; at higher temperature the matrix melted and excess cocondensed lithium crystallized.

In a typical UV/Vis experiment a maximum of 1 mg of lithium was vaporized into an excess of about 100 mg of THF during 15 min. A higher concentration of lithium must be avoided to allow enough transmission for the UV/Vis measurement.

With a view to determining the structures and energies of formation the application of theoretical methods are proved advantageous. For this purpose the program package HyperChem 4.0[7] and Gaussian 92[11] implemented on an IBM compatible Pentium 100 PC with 64 MB RAM memory was used. For the UV/Vis spectrum of $Li_2(H_2O)_6$ a geometry optimization was followed by a CIS calculation both at the MNDO level. Ab initio calculations were performed at the HF/6-31G** level of theory for the species of interest. Harmonic vibrational frequencies, calculated at the same HF/6-31G** level, characterized stationary points and gave the zero-point energy. The sum of the electronic and the zero-point energy was used to calculate differences interpreted as reaction enthalpies and are discussed together with experimental enthalpies by starting at the Li_2(g) and benzene(g) level.

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