Carbonyl and Benzene Complexes of Lithium: Transition-Metal-Like Behaviour of Lithium in Organolithium Compounds☆

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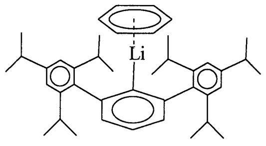
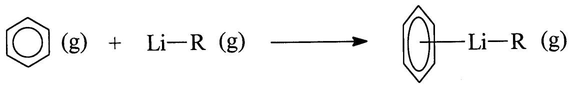
Complexes of CO and aromatic compounds were believed to be an exclusive domain of transition metals caused by their ability of backbonding to these ligands. But recently, (benzene)lithium and (carbonyl)lithium complexes were characterized by X-ray structure analysis and IR spectoscopy. In order to determine geometries of the complexes and the bonding energies of the benzene and CO molecule to the organolithium starting compound suitable models were chosen in combination with high-level ab initio calculations. For the carbonyl derivative a reaction enthalpy of −8 kcal/mol was found while the interaction with benzene reached unexpectedly −21 kcal/mol. This underlines the ability of lithium to act like a transition metal in subcoordinated organyl compounds without having d orbitals available for bonding.

Introduction

Aggregation is a nearly ubiquitous characteristic of organolithium compounds.[1] But if bulky substituents prevent aggregation monomeric organolithium compounds show in benzene solution lithium−benzene π interaction like a transition metal. So (2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$Li crystallizes from benzene/hexane solution as a monomer with a coordination between the lithium center and the benzene molecule.[2]



If the ligands have sterically less demanding *ortho*-substituted phenyl groups a small number of crystal structures show dimers exhibiting lithium−benzene interactions.[2][3] But X-ray crystallography is unable to measure the strength of this π interaction. This paper presents ab initio calculations on MP2 level for geometries and HF level for IR frequencies and zero-point energies which are able to fill the experimental gap. For these calculations there is no need for selecting highly substituted compounds of course. So three simple types of organolithium compounds are chosen (LiH, LiMe, LiPh)[4] which are allowed to interact with a benzene molecule to determine the reaction enthalpy of the process and to compare calculated and experimental structures.



(R = H, Me, Ph)

In a recent spectroscopic study the very early steps of the reaction of organolithium compounds with CO or isonitrile were detected.[5] Liquid xenon (LXe) is used as the reaction medium because it suppresses electron-transfer reactions which are known to complicate the reaction.[6] If this reaction is performed at sufficiently low temperature a coordination of CO is found firstly. This unexpected transition-metal-like behaviour of lithium is followed by insertion of carbon monoxide into the lithium−carbon bond which is again expected for transition metal complexes only.

$$\mathrm{BuLi} + \mathrm{C{\equiv}R} \xrightarrow[\text{-100°C}]{\text{LXe}} [\mathrm{BuLi\text{-}CR}] \xrightarrow[\Delta]{\text{LXe}} [\mathrm{Bu\text{-}C(R)Li}]$$

(R = O,NtBu)

Our investigations show that tetrameric methyllithium in combination with high-level MP2 calculations are a suitable model to determine reaction enthalpies and structures of the intermediates which allow comparison with the experimental data.

Results and Discussion

In a first attempt monomeric lithium hydride, which is the simplest model for an organolithium compound, is allowed to interact with benzene on MP2 level. Upon coordination we find a change in reaction enthalpy of −21 kcal/mol which is unexpectedly high. A weak interaction like a hydrogen bonding would give about −3 kcal/mol only. The Li−H stretching frequency decreases from 1420 cm^{-1} in free LiH to 1338 cm^{-1} in the coordinated LiH which means a total change of 6% indicating a major interaction as well. Correspondingly the Li−H bond length varies from 162.4

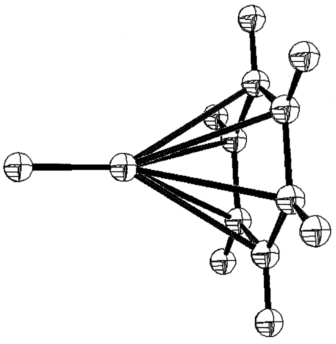
pm to 163.3 pm upon complexation. There is very little change in bond lengths in the benzene molecule. Even the hydrogen atoms stay nearly in the molecular plane. The resulting lithium−carbon bond length of the adduct in C_{6v} symmetry is 252.0 pm.

To verify this first result the reaction of Li^+ with benzene to form an adduct is calculated. Since this reaction enthalpy is measured to be −37 ± 2 kcal/mol applying ion cyclotron resonance technique[7] it is a unique chance to calibrate the ab initio calculations. The expected C_{6v} species exhibits an Li−C bond of 239.1 pm and a C−C bond of 140.6 pm which is slightly longer than in free benzene (139.6 pm). The enthalpy change is slightly overestimated by this calculation (−41 kcal/mol) showing that method (MP2) and basis set (6-31G**) are suitable to describe the system.

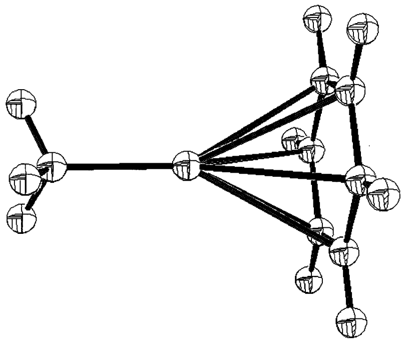
When using monomeric methyllithium as a model the calculation results in −19 kcal/mol for the reaction enthalpy with a new lithium−carbon distance of 251.7 pm. The most precise results are to be expected when monomeric phenyllithium is used since it is nearly the compound found to crystallize with benzene in an η^6-coordination mode. This time the enthalpy change is −21 kcal/mol and a lithium−carbon distance of 247.0 pm is found on average. Figure 1 illustrates the results on the MP2/6-31G** level of theory of the above-mentioned species.

These theoretical results give a consistent picture of the coordination of benzene to organolithium compounds. The calculated geometries of the complexes predict an atom distance of around 250 pm between lithium and carbon in the coordinated benzene. In the X-ray structure a significantly shorter value of 235 pm is determined. The calculations therefore give a reasonable but not excellent prediction of this important parameter. The interaction energy is with about −20 kcal/mol unexpectedly high and shows that the complexes formed are held together with more than weak Li−benzene π interactions as was suggested by the crystal-structure determination.[2] If bis(benzene)chromium is used as a reference compound for the bonding strength of the metal−benzene interaction an interesting comparison becomes available. From thermodynamical values it can be calculated that the reaction of $Cr(C_6H_6)_2$ to a chromium atom and two molecules of benzene needs around 80 kcal/mol.[8] Therefore, the bonding energy of each benzene unit to the chromium center is 40 kcal/mol which is only double the value of the lithium−benzene interaction. The high value is caused by the covalent nature of the lithium−carbon bond in the starting compound making it behave like a transition metal. Because lithium with its only three overall electrons is not able to build up highly ionic organo compounds as its heavier homologues it has to form a polar but covalent bond in a compound like phenyllithium. The subcoordination of lithium is normally moderated by formation of an oligomer with shared bonding electrons. But in the case of $(2,4,6\text{-}i\text{Pr}_3C_6H_2)_2C_6H_3Li$ the bulky substituents force the compound to remain a monomer with only two shared bonding electrons for the lithium center. In benzene solution this bonding type changes dramatically since the six-valence-electron donor benzene can form a stable complex and enables the lithium center to end up with an 8-valence-electron environment.

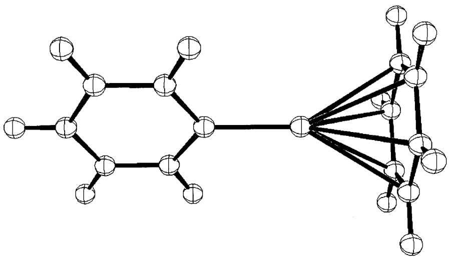
Figure 1. Molecular projections of adducts of benzene with LiH, LiMe, and LiPh; selected bond lengths in pm



LiH: 163.3, LiC: 252.0, CC: 140.1



LiC(benzene): 251.7 (average)



LiC(benzene): 247.0 (average)

Recently, it was shown, that organolithium compounds are also able to interact with CO[5] in a newly developed LXe cell constructed from one piece of single-crystal silicon.[9] In a first step carbon monoxide is complexed with back bonding to *n*BuLi [ν(CO): 2047 cm^{-1}] and inserts in a second step at higher temperatures into the lithium−carbon bond [ν(CO): 1635 cm^{-1}]. Further warming-up to −20°C results in decomposition of the observed pentanoyllithium intermediate. Probably a lithiated oxycarbene is formed favoured by formation of a strong lithium−oxygen bond.

$$\text{nBuLi} + \text{CO} \xrightarrow[-100^\circ C]{\text{LXe}} [\text{nBuLi-CO}] \xrightarrow[-30^\circ C]{\text{LXe}} [\text{nBu-C(O)Li}]$$

$$\xrightarrow[-20^\circ C]{\text{LXe}} \text{further reaction}$$

With tetrameric lithium hydride as a model substance for ab initio calculations of oligomeric organolithium species it was possible to obtain first structural information[5] about the complexation and insertion of the CO molecule. But the insertion turned out to be a sligthly exothermic partial reaction, which is hard to believe in the light of the successful experiment in liquid xenon. With tetrameric methyllithium as a much better substitute we can now show, that the wrong sign of the reaction enthalpy is caused by the inadequate model. The addition of CO to $(LiMe)_4$ releases −7.8 kcal/mol with the formation of a linear LiCO substructure with a relative long lithium−carbon distance of 234.0 pm. For comparison *d*(Li−C) in tetrameric methyllithium is calculated to 221.0 pm. In contrast to the experiment the calculated compound does not show backbonding to CO as indicated by a higher C−O stretching frequency in comparison to free carbon monoxide. The second possible isomer showing a likewise linear LiOC substructure is higher in energy. The insertion reaction of carbon monoxide into the lithium−carbon is now exothermic (−4.2 kcal/mol) and the resulting acetyl group coordinates with its carbon atom

Figure 2. Molecular projections of Li_4Me_4, Li_4Me_4CO, and $Li_4Me_3(COMe)$; selected bond lengths in pm

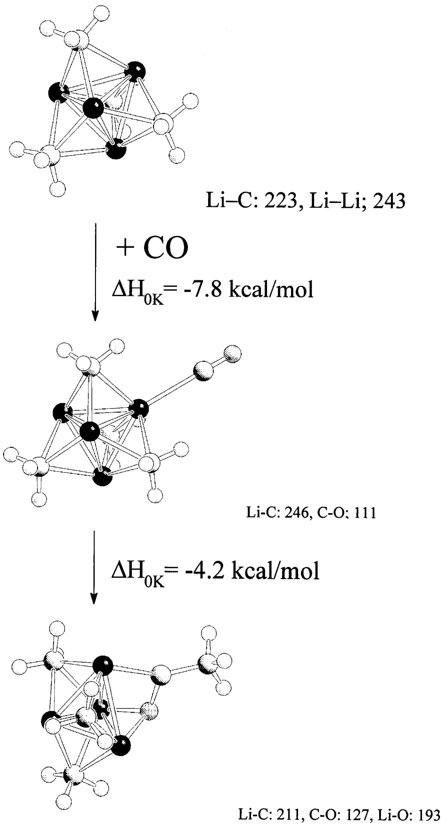


Table 1. Ab initio calculated energies and frequencies for the various intermediates

	electronic energy [Hartrees] (MP2)	zero-point energy [Hartrees] (HF)	ν(CO) [cm^{-1}]
CO	−113.021215	0.004825	2118
Li_4Me_4CO	−302.011968	0.156614	2475
$Li_4Me_3(COMe)$	−302.024139	0.162068	1626
Li^+·PhH	−238.808641	0.110077	
LiH·PhH	−239.538754	0.112874	
LiMe·PhH	−278.724527	0.143982	
LiPh·PhH	−469.881984	0.204110	

Table 2. Ab initio calculated geometries for the various intermediates

Center number	Li^+·PhH Standard orientation Coordinates [A]		
	X	Y	Z
Li1	0.000000	0.000000	1.806913
C2	0.000000	1.405805	−0.126712
C3	1.217463	0.702903	−0.126712
C4	1.217463	−0.702903	−0.126712
C5	0.000000	−1.405805	−0.126712
C6	−1.217463	−0.702903	−0.126712
C7	−1.217463	0.702903	−0.126712
H8	0.000000	2.488179	−0.143186
H9	2.154826	1.244089	−0.143186
H10	2.154826	−1.244089	−0.143186
H11	0.000000	−2.488179	−0.143186
H12	−2.154826	−1.244089	−0.143186
H13	−2.154826	1.244089	−0.143186

Center number	LiH·PhH Standard orientation Coordinates [A]		
	X	Y	Z
H1	0.000000	0.000000	3.508600
Li2	0.000000	0.000000	1.875200
C3	0.000000	1.401195	−0.219208
H4	0.000000	2.483028	−0.207116
C5	0.000000	−1.401195	−0.219208
H6	0.000000	−2.483028	−0.207116
C7	1.213471	0.700598	−0.219208
C8	1.213471	−0.700598	−0.219208
C9	−1.213471	0.700598	−0.219208
C10	−1.213471	−0.700598	−0.219208
H11	2.150365	1.241514	−0.207116
H12	2.150365	−1.241514	−0.207116
H13	−2.150365	1.241514	−0.207116
H14	−2.150365	−1.241514	−0.207116

Center number	LiMe·PhH Standard orientation Coordinates [A]		
	X	Y	Z
Li1	0.000000	0.000000	1.268048
C2	0.000000	0.000000	3.268348
H3	0.000000	−1.010855	3.691113
C4	0.000000	1.400960	−0.822668
H5	−0.875426	0.505428	3.691113
H6	0.875426	0.505428	3.691113
C7	1.213267	−0.700480	−0.822668
C8	−1.213267	−0.700480	−0.822668
H9	0.000000	2.482902	−0.811488
H10	2.150256	−1.241451	−0.811488
H11	−2.150256	−1.241451	−0.811488
C12	0.000000	−1.400979	−0.822775
C13	−1.213283	0.700489	−0.822775
C14	1.213283	0.700489	−0.822775
H15	0.000000	−2.482922	−0.811711
H16	−2.150274	1.241461	−0.811711
H17	2.150274	1.241461	−0.811711

Table 2 *(continued)*

LiPh·PhH Standard orientation

Center number	Coordinates [Å] *X*	*Y*	*Z*
C1	0.000000	0.000000	1.308901
C2	0.000000	0.000000	4.191006
H3	0.000000	0.000000	5.275245
C4	0.000000	1.185759	2.083837
C5	0.000000	−1.185759	2.083837
H6	0.000000	2.152982	1.582074
H7	0.000000	−2.152982	1.582074
C8	0.000000	1.203397	3.484029
C9	0.000000	−1.203397	3.484029
H10	0.000000	2.146635	4.021178
H11	0.000000	−2.146635	4.021178
Li12	0.000000	0.000000	−0.687751
C13	−0.000007	1.401557	−2.721978
C14	0.000007	−1.401557	−2.721978
H15	−0.000011	2.483614	−2.711293
H16	0.000011	−2.483614	−2.711293
C17	1.213925	0.700759	−2.721400
C18	−1.213933	0.700747	−2.721404
C19	−1.213925	−0.700759	−2.721400
C20	1.213933	−0.700747	−2.721404
H21	2.150995	1.241532	−2.708094
H22	−2.151008	1.241512	−2.708094
H23	−2.150995	−1.241532	−2.708094
H24	2.151008	−1.241512	−2.708094

Li_4Me_4CO Standard orientation

Center number	Coordinates [Å] *X*	*Y*	*Z*
O1	0.000000	0.000000	4.016836
C2	0.000000	0.000000	2.869736
Li3	0.000000	0.000000	0.530136
Li4	−1.207885	0.697373	−1.501358
Li5	1.207885	0.697373	−1.501358
Li6	0.000000	−1.394746	−1.501358
C7	0.000000	2.100162	−0.307115
C8	1.818794	−1.050081	−0.307115
C9	−1.818794	−1.050081	−0.307115
C10	0.000000	0.000000	−3.221164
H11	−0.861692	0.497498	−3.695092
H12	0.861692	0.497498	−3.695092
H13	0.000000	−0.994996	−3.695092
H14	0.000000	2.249353	0.782519
H15	0.860769	2.703982	−0.639751
H16	−0.860769	2.703982	−0.639751
H17	1.947997	−1.124677	0.782519
H18	1.911332	−2.097438	−0.639751
H19	2.772101	−0.606543	−0.639751
H20	−1.947997	−1.124677	0.782519
H21	−2.772101	−0.606543	−0.639751
H22	−1.911332	−2.097438	−0.639751

Table 2 *(continued)*

Li_4Me_3COMe Standard orientation

Center number	Coordinates [Å] *X*	*Y*	*Z*
Li1	−1.034062	−1.931743	0.000000
Li2	1.231743	−0.850342	0.000000
C3	1.285637	1.256727	0.000000
O4	0.000000	1.396461	0.000000
C5	2.026287	2.568586	0.000000
Li6	−0.927215	0.156368	1.216750
Li7	−0.927215	0.156368	−1.216750
C8	0.174686	−1.660539	1.814355
C9	0.174686	−1.660539	−1.814355
C10	−2.674889	−0.457851	0.000000
H11	1.357455	3.431790	0.000000
H12	2.682286	2.594098	0.872794
H13	2.682286	2.594098	−0.872794
H14	−3.196468	−1.428345	0.000000
H15	−3.126195	0.062150	−0.860343
H16	−3.126195	0.062150	0.860343
H17	−0.086380	−1.163545	2.763242
H18	1.250917	−1.855296	1.940979
H19	−0.275216	−2.660100	1.936136
H20	−0.086380	−1.163545	−2.763242
H21	1.250917	−1.855296	−1.940979
H22	−0.275216	−2.660100	−1.936136

to one [*d*(LiC) = 210.8 pm] and with the oxygen atom to two lithium atoms of a lithium tetrahedron plane [*d*(LiO) = 196.9 pm]. This coordination in a μ_3 fashion helps to find an exothermic reaction pathway for the insertion. Figure 2 illustrates the results on the MP2/6-31G** level of theory of the above-mentioned reaction steps. A summary of the theoretical results are given in Table 1 (energies and freqencies) while the coordinates of the optimized structures are found in Table 2.

In this second case the high-level calculations correspond with the experimental basis. In the early phase of the LXe experiment at low temperature a coordinated triple-bonded CO group is detected by IR spectroscopy and is assigned to the (carbonyl)lithium. Warming-up leads to the decomposition of this first species while a second one with a double-bonded CO group appears at the same time. It is plausible that the second intermediate is the organolithium-lithium species coordinating the RC=O group in a μ_3 fashion which shifts the carbonyl stretching frequency to 1635 cm^{-1} which, in turn, is only plausible in this extraordinary complexation mode. This second species finally reacts further resulting an IR spectrum with no C−O stretching frequencies above 1500 cm^{-1}.

Again a comparison of the bonding energy of carbon monoxide to lithium or chromium will help to classify the observed transition-metal-like behaviour of lithium. Chromium atoms react with carbon monoxide to $Cr(CO)_6$ and release nearly 180 kcal/mol which is interpreted as an (averaged) bonding energy between Cr and CO of 30 kcal/mol.[8] The result of the calculation for the lithium−CO bonding energy is less than 8 kcal/mol and indicates a relatively weak interaction. This is not unexpected in the second case since the subcoordination and therefore the transition-metal-like behaviour of lithium is markedly less because now a organolithium cluster is involved instead of a monomeric compound.

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Experimental Section

With a view to determining the structures, IR frequencies and energies of formation the application of theoretical methods are proved advantageous. For this purpose the program package GAUSSIAN 92[10] implemented on an IBM-compatible Pentium computer with 64 MB RAM memory was used. Ab initio calculations were performed at the HF (Hartree-Fock) or MP2 (second order Møller-Plesset) level of theory using 6-31G** basis set for the species of interest. Harmonic vibrational frequencies, calculated at the HF/6-31G** level only, characterized stationary points and gave the zero-point energy. Therefore, frequencies are scaled by using a factor of 0.89. Geometries were then optimized on MP2/6-31G** level to deliver the electronic energy and geometries for discussion. The sum of the electronic and the zero-point energy was used to calculate differences interpreted as reaction enthalpies at 0 K. For the visualisation of the calculated structures the program ORTEX 5[11] was used.

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

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