was refined as a rigid group with a variable occupancy constrained so that the total occupancy for each Cp ring was one. The refined occupancies for the major location of three rings are 0.54, 0.83, and 0.67, respectively. An ORTEP drawing of the molecule is shown in Figure 1. Selected bond lengths and angles are listed in Table I.

Clearly MeCN has inserted into the uranium–carbon bond of I forming an $NC(Me)CHP(Ph)_2Me$ ligand that coordinates through nitrogen. The uranium–nitrogen bond distance, 2.06 (1) Å, is the shortest reported and can be compared to 2.29 (1) Å found in $Cp_3UN(Ph)_2$,[13] which is a typical U–N bond distance for a uranium amide. Such a short U–N bond suggests multiple-bond character; in principle, nitrogen could donate as many as three electron pairs to uranium.

The U–N–C(1) angle of 163 (1)°, while consistent with considerable multiple-bond character, deviates significantly from 180° which would be expected for a sp hybridized nitrogen. Additionally the N–C(1) and C(1)–C(2) distances of 1.34 (2) and 1.39 (2) Å are shorter than normal single bonds. The C(2)–P distance of 1.74 (2) Å is shorter than the P–CH_3 distance, 1.83 (2) Å, but is somewhat longer than observed in simple unsubstituted ylides: 1.661 (8) Å in $H_2C{=}P(Ph)_3$[15] and 1.640 (6) Å in $H_2{=}P(Me)_3$.[16] Bond angles around C(1) and C(2) are consistent with predominant sp^2 hybridization for these atoms. In view of the bond angles and distances several resonance structures are probably important in describing the bonding in II. These include:

$$\underset{\text{i}}{Cp_3U{\equiv}NC(Me){=}CHP(Ph)_2Me} \leftrightarrow$$

$$\underset{\text{ii}}{Cp_3U{=}\ddot{N}C(Me){=}CHP(Ph)_2Me} \leftrightarrow$$

$$\underset{\text{iii}}{Cp_3U{=}N{=}C(Me)CH{=}P(Ph)_2Me}$$

Their combination implies a highly delocalized π system and a uranium–nitrogen bond order between 2 and 3.

We have already discussed the relationship between I and other metal–carbon multiply bonded species[7,8] and pointed out similarities in carbon monoxide insertion chemistry.[9] This comparison can now be extended since products similar to (II), $R_3MNC(Me)CHCMe_3$, have been reported for the insertion of MeCN into metal–carbon double bonds of the alkylidene complexes $R_3MCHCMe_3$ (M = Ta and Nb; R = $(CH_3)_3CCH_2$).[14] Schrock draws these compounds with metal–nitrogen double bonds[14] but reports no structural data. In contrast to the reaction of I with MeCN, which requires 24 h at elevated temperature, the reaction of $R_3TaCHCMe_3$ with MeCN is described[14] as "quite vigorous".

Uranium (IV) is a very electron-deficient ion. "In the actinide series ... the energies of the 5f, 6d, 7s, and 7p orbitals are about comparable over a range of atomic numbers (especially U–Am), and since the orbitals also overlap spatially, bonding can involve any or all of them".[17] Thus, a closed-shell configuration would consist of 32 electrons. In Cp_3UCH_3 there are 22 electrons in the uranium valence shell while for $Cp_3U{=}CHP(Ph)_2Me$ the electron count rises to 24, still far short of 32. Steric crowding among the ligands is considerable for $Cp_3U{=}CHP(Ph)_2Me$[7] so that addition of another ligand to increase the electron count is not feasible. However, in II the electron count is as high as 26 for the resonance form i, identical with that of Cp_4U. Organouranium compounds are sterically saturated but electronically unsaturated.[18] *As such uranium has a high affinity for small ligands with several available electron pairs.* Oxygen ligands fall into this category, and the affinity of uranium for oxygen is well-known. The U–X multiple bonds, as in $Cp_3U{=}CHP(Ph)_2Me$ and $Cp_3U{\equiv}NC(Me)CHP(Ph)_2Me$, also fulfill this role. Their discovery confirms the ability of U(IV) and, presumably, other actinide ions to form multiple bonds with multiple electron pair donor ligands.

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Registry No. I, 77357-86-9; II, 88780-83-0.

Supplementary Material Available: Summary of crystal data (Table II), a listing of observed and calculated structure factors (Table III), and positional and thermal parameters for group and nongroup atoms (Tables IV–VI) for $Cp_3UNC(Me)CHP(Ph)_2Me{\cdot}C_6H_5CH_3$ (26 pages). Ordering information is given on any current masthead page.

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Dimerization Energy Decomposition of Lithium First-Row Hydrides

M. Hodošček and T. Šolmajer*

Boris Kidrič Institute of Chemistry
61000 Ljubljana, Yugoslavia
LEK—Pharmaceutical and Chemical Works
61000 Ljubljana, Yugoslavia

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Currently there is wide interest in molecules containing lithium and organic fragments. The reason stems largely from their use as synthetic reagents and their novel bonding properties.[1,2] These molecules can form multicenter electron-deficient, coordinate, ionic, and covalent bonds.[3] Streitwieser et al.[4] have anticipated that the driving force for oligomerization is largely that of ionic aggregation. On the basis of projection functions and Mulliken population[5] analyses, they proposed that the C–Li bond in the $(CH_3Li)_2$ dimer has essentially no shared covalent character. On the other hand,[6] charge distributions of dimers of first-row metal hydrides invoking more than one bridging hydrogen were found difficult to generalize. In order to investigate the degree of nonionic character in lithium dimers of the first-row atoms, we have performed energy decomposition analyses, which proved especially fruitful in the calculation of the properties of hydrogen-bonded[7] and electron donor–acceptor[8] complexes. Our purpose is to provide some insight into the origin of the dimerization of monomeric $LiXH_n$[9] molecules, where XH_n is a first-row atom hydride, and total dimerization energy

$$\Delta E = E(LiXH_n)_2 - 2E(LiXH_n) \quad (n = 0, 1, 2, 3)$$

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Table I. Energy Decomposition (kcal/mol) for (LiH_2) and $(LiF)_2$. 4-31G Optimized Geometry

	basis set	ΔE	ES	EX	PL	CT	MIX
$(LiH)_2$	STO-3G	−52.8	−64.7	59.4	−6.3	−17.1	−23.1
	4-31G	−49.1	−77.7	49.3	−13.5	−55.3	48.2
	321 G	−50.1	−75.4	47.0	−11.8	−47.3	37.3
	6-31G**	−50.5	−78.5	50.2	−17.7	−59.8	55.4
$(LiF)_2$	4-31G	−84.1	−98.7	42.4	−8.7	−14.5	−4.5
	6-31G**	−80.5	−97.2	43.8	−16.7	−14.9	4.5

Table II. Energy Decomposition (kcal/mol) for First-Row Atoms, X, Lithium-Bonded Dimers, $(LiXH_n)_2$

monomer unit	E	ES	EX	PL	CT	MIX	DEF[a]
LiBeH	−28.8	−49.2	49.7	−39.7	−102.6	113.1	9.9
$LiBH_2$ plan	−47.4	−82.5	61.1	−34.4	−68.2	76.6	12.9
$LiBH_2$ perp	−35.1	−65.0	59.9	−35.2	−63.8	69.0	11.7
LiH	−49.1	−77.7	49.3	−13.5	−55.3	48.2	4.0
$LiCH_3$	−59.3	−102.4	64.9	−24.3	−34.8	37.1	16.7
$LiNH_2$ plan	−62.9	−94.4	51.6	−20.0	−11.4	11.3	19.7
$LiNH_2$ perp	−84.4	−115.0	51.1	−15.7	−15.1	10.3	11.0
LiOH	−88.3	−113.5	47.3	−12.9	−10.9	−0.2	14.2
LiF	−84.1	−98.9	42.4	−8.7	−14.5	−4.5	8.0

[a] DEF is defined as the deformation energy required to stretch the monomer geometry to its geometry in the dimer.

with possible characterization of the remarkable linear relationship between Pauling electronegativities and electrostatic charges observed recently by Schleyer et al.[10] The series was investigated by means of standard MO calculations.[11] Full geometry optimization was performed on dimers by using the split valence basis set 4-31G.[12] Previous calculations on $(LiH)_2$[3,13] and $(LiCH_3)_2$[9a,14] have shown that correlation effects are not important in adequate determination of binding energies[15-20] of these clusters. Pilot dimerization energy decompositions were performed on $(LiH)_2$[7e] and $(LiF)_2$[7h] in order to assure that the results of the decomposition do not depend on the choice of the basis set. Results are summarized in Table I. Energy decomposions using a different basis set gave essentially identical results for ΔE close to the experimental value, while for individual terms[3,21-23] one can judge that use of the minimal basis set would not have been justified. Polarization functions were used to correct for the effect of the overestimated polarity of isolated molecules with 4-31G basis. They do not influence significantly the resulting energy decomposition terms and support the semiquantitative significance of the results. We observe that the three-center two-electron bond in case of $(LiH)_2$ and the three-center four-electron bond of $(LiF)_2$ differ mainly in the increase of the charge transfer contribution of the former while in the latter both polarization and charge transfer terms are of minor importance when compared with electrostatic term. Also the large mixed term (vide supra) in $(LiH)_2$ indicates the difference of these two dimers.

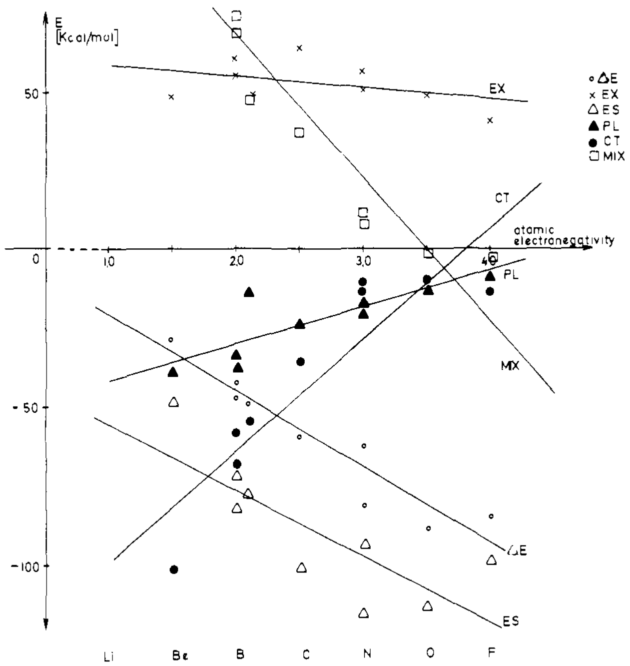

Figure 1. Energy decomposition of dimerization energy of lithium-bonded first-row atoms hydrides. Graphs were drawn with least-squares method.

In Table II the energies of the dimeric lithium bridged structures are given relative to the appropriate sums of monomer energies decomposed into electrostatic (ES), exchange (EX), polarization (PL), and charge transfer (CT) components and the mixed term (MIX), which contains the coupling interactions between these components. If the deformation energy, required to stretch the monomer from its equilibrium structure, is added, good correlation with results of previous calculations is obtained.[7e,10b,13,14b,c]

The electrostatic energy term parallels the total energy variation while the exchange term is approximately constant in the series (Figure 1). The opposite trend is observed with charge transfer and polarization energy contributions. Both terms decrease, charge transfer more strongly if the hydride-forming atom is varied from Be to F. It is interesting to observe that CT is the dominant attractive contribution at equilibrium distance for the BeH dimer while for all other hydride dimers the electrostatic term prevails. The large positive value of the mixed term when the electronegativity of the hydride-forming atoms X is lowered indicates that the interaction between other components EX–CT, EX–PL, and CT–PL is increasing. In other words the multicenter covalent bonding[3,10] where orbitals from three centers of the double-bridged dimer simultaneously share a pair of bonding electrons is gaining importance. The linear relationship between electronegativities of first-row atoms and the electrostatic energy contribution to the dimerization energy may now be discussed. From the results of the energy decomposition, we obtain that the increased stability of the dimers with most electronegative atoms of the series O and F is principally the effect on increased ES with importance of PL and CT decreasing. This increased role of ES can be attributed to the greater polarity of the OH and F compared to BeH and BH_2. Electronegativity is a traditionally used average parameter[2,4] describing how the individual AO energy levels are corrected when they form a molecular form and is to some extent a function of the detailed nature of chemical bonds formed. On the other hand, the diagonal elements of the dimer molecule Fock matrix[7d] can be visualized as the classical electrostatic interaction between occupied MOs without any mixing between MOs of the isolated molecules. The nondiagonal elements of the Fock matrix (EX,

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PL, and CT) describe the deviation from this diagonal representation. This is reflected in the greater relative contribution of other terms, especially CT and MIX, denoting the increased amount of multicenter electron delocalization and CT at atoms with low electronegativity Be, B, and C.

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Registry No. Li, 7439-93-2; $LiBH_2$, 64360-74-3; $LiCH_3$, 917-54-4; $LiNH_2$, 7782-89-0; LiOH, 1310-65-2; LiF, 7789-24-4; $(Li_2)_2$, 12596-49-5; $(LiBH_2)_2$, 88656-95-5; $(LiCH_3)_2$, 33825-29-5; $(LiNH_2)_2$, 88656-96-6; $(LiOH)_2$, 54251-08-0; $(LiF)_2$, 12265-82-6.

Supplementary Material Available: 4-31G/4-31G geometries (coordinates and *Z* matrices) for dimers $(LiXH_n)_2$ (9 pages). Ordering information is given on any current masthead page.

Dimerization Energies of Lithium Compounds with First-Row Substituents

Elmar Kaufmann, Timothy Clark, and
Paul von Ragué Schleyer*

Institut für Organische Chemie
der Friedrich-Alexander-Universität
Erlangen-Nürnberg, D-8520 Erlangen
Federal Republic of Germany

Received September 26, 1983

Lithium compounds have a marked tendency to oligomerize;[1] methyllithium is tetrameric in the crystal,[2] in solution,[3] and even in the gas phase.[4] Only a few aggregation energies are known experimentally: the dimerization energies of LiH,[5] LiOH,[6] and the lithium halides[6] and the trimerization energies of LiF and LiCl.[6] The energy of Li_4, the formal dimer of Li_2, has also been reported recently.[7] A number of calculations, some at very high levels of theory, are available for $(Li_2)_2$,[8] $(LiCH_3)_2$,[9] $(LiNH_2)_2$,[10] $(LiOH)_2$,[11] and $(LiF)_2$.[12] To complete the first-row set, we carried out calculations at uniform levels for all the $LiXH_n$ monomers and dimers where XH_{n+1} is the corresponding first-row hydride.[13] This set of data clarifies the essential nature of the interaction and permits detailed interpretations of the dimerization energies.

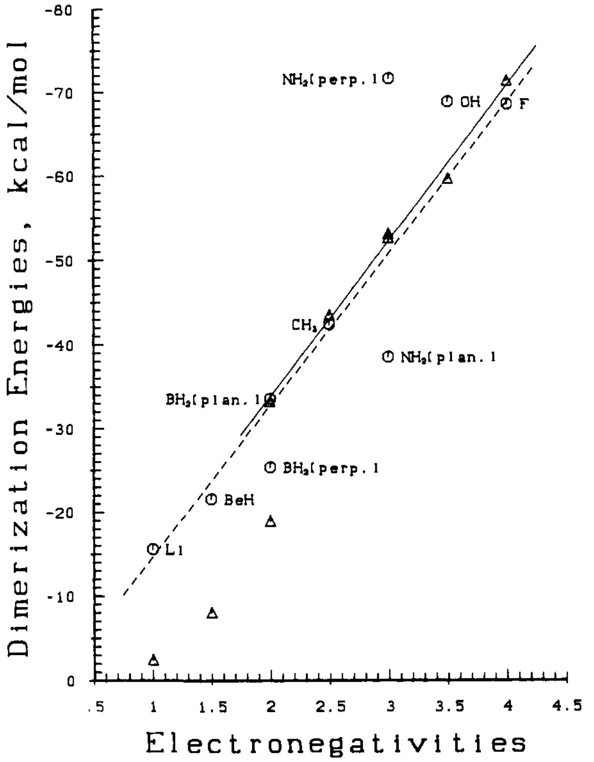

Figure 1. LiX dimerization energies (MP2/6-31G*//3-21G(est)) plotted against the Pauling electronegativities of X (circles and dashed line). Triangular points (and the solid correlation line) are the results of calculations assuming a simple Coulomb model (+ at Li and − at X) using the 3-21G geometries for both LiX monomers and $(LiX)_2$ dimers (see text). At lower theoretical levels similar correlation lines are found but with different slopes.

Earlier calculations[8-12] showed that all the dimers $(LiXH_n)_2$ favor the same rhomboid structures with alternating Li and first-row atoms, X, and all Li–X distances equal. Consequently D_{2h} symmetry was imposed on all dimers except $(LiCH_3)_2$, which has C_{2h} symmetry.[9] For both $LiBH_2$ and $LiNH_2$ two alternative structures were considered, corresponding to perpendicular and planar arrangements of the XH_2 groups.

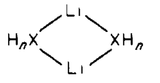

Table I shows that the final theoretical estimates[14] are not far

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