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Degenerate Lithium−Hydrogen Exchange Reactions: An Alternative Mechanism for Metalation of CH_4 in Gas Phase and Tetrahydrofuran Solution

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We report here the results of an ab initio study of the lithium−hydrogen exchange reaction of $CH_4 + (CH_3Li)_2$ both in gas phase and in tetrahydrofuran (THF) solution. All the species involved in the reaction have been characterized at the Hartree−Fock, second-order Möller−Plesset (MP2)(full), and density functional theory (B3LYP) levels using the 6-31G(d,p) basis set. The effect of the solvent (THF) has been modeled using the Polarizable Continuum Model developed by the group in Pisa that includes both electrostatic and nonelectrostatic (cavitation and dispersion repulsion terms) contributions to the solvation energy. A main result of this study is the finding of a nonplanar transition state structure that leads to a barrier ~2 kcal/mol lower at the MP2 level than the one calculated based on a C_s six-membered ring transition state previously reported by Schleyer et al. for the same reaction *(J. Comput. Chem.* **10**, 437 (1989)). We include here a detailed discussion of the differences between these two mechanistic alternatives and the effect of the solvent on both of them. The performance of the B3LYP hybrid functional is examined against our MP2 results to assess whether this methodology is reliable for the study of more complex metalation reactions in which the size of the reactant system prevents the use of MP2 methods as a way for including electron correlation.

1. Introduction

Metalation of acidic carbon atoms by reaction of organic compounds with organolithium reagents is usually introduced in elementary organic chemistry courses as a very effective and selective way to incorporate new functional groups into organic molecules.[1] Despite its widespread use in synthesis, some mechanistic aspects of this group of reactions are still the subject of experimental and theoretical research, because a complete understanding of how the reaction proceeds has not yet been reached. In particular, for the so-called *directed ortho-lithiation*[2] of aromatic compounds, different terms and concepts (like *"complex-induced proximity effects"*,[3] *"agostic activations"*,[4,5] *and "kinetically enhanced metalation"*[6] have been invoked to rationalize the observed regiospecific outcome of the reaction and the reactivity of the species involved as a function of the nature of the directing group present in the reactant.

In recent times, several communications have reported semiempirical[5,7,8] (MNDO and PM3) and ab initio[6,8a] (Hartree-Fock [HF] and second-order Möller−Plesset MP2 levels calculations on the lithiation reaction of aromatic compounds. Two main conclusions can be extracted from these reports: (a) directing and activated effects of electronegative substituents in aromatic compounds would mainly be transition state phenomena;[6] (b) semiempirical methods are often not valid tools for studying lithiation reactions, even qualitatively. On the one hand, it is a well-documented drawback of the MNDO and derived methods that repulsion between Li core and C lone pair electrons is underestimated,[9] leading to the overestimation of the Li−C bond strength. On the other hand, steric repulsions are considerably overestimated by these methods.[10] All these elements together can be responsible for the problems reported by different authors, such as giving incorrect geometries for molecules containing Li−C bonds or predicting erroneous regioselectivity for lithiation of systems where two differently hybridized C centers of the substrate may be involved.[8a]

Although the experimental evidence shows that the solvent has a very strong influence both in the outcome and rate of lithiation reactions,[1] only a few theoretical studies have considered the influence of the solvent on the process. Moreover, even when this has been done, the effect of the solvent has been mimicked through the inclusion of 2−3 discrete water molecules in the supermolecule which do not actively take part in the reaction.[7,8] Water is a solvent not generally used in experimental conditions, and moreover 2−3 molecules are a poor representation of the bulk solvent. In the present work we have addressed the study of the effect of a more realistic solvent (tetrahydrofuran, [THF]) using a continuum dielectric model developed by us at the University of Pisa.[11]

We started our study analyzing the mechanism and energetics for one of the simplest lithiation reactions, the degenerate Li−H exchange between methane and dimeric methyllithium

$$\mathrm{THFH_3C{-}H + (LiCH_3)_2(H_3CLi + CH_4{\cdot}LiCH_3} \qquad (1)$$

both in gas phase and in bulk THF. The choice of dimeric methyllithium as lithiating reagent is based on the experimental

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[†] Professor Ciuffarin died while the present work was in progress. He was the one who called our attention to the mechanistic aspects of lithiation reactions. We would like to dedicate this article to his memory.

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evidence discarding monomeric forms as reagents. In fact, the aggregation state of the organolithium compound strongly depends on the specific solvent (for example, it has been determined that *n*-BuLi exists in a tetramer-dimer equilibrium in pure THF solution[12]).

In a gas-phase theoretical study which appeared several years ago, Kaufmann and Schleyer[13] reported an ab initio C_s symmetry six-membered ring structure for the transition state of this reaction which yields a barrier height of 46.1 kcal/mol at the HF/3-21G (zero point energies [ZPE] corrected) level. In the present work we conducted a more extended search on the potential energy surface (PES), characterizing an intermediate complex (not explicitly studied by the Erlangen group[13,14]) of CH_4 with $(LiCH_3)_2$, and looking for alternative transition state structures to gain better insight into the mechanism of this kind of process.

A final issue addressed in the present article is related to the study of the more complex reactions involving aromatic compounds and larger lithiating agents, such as *n*-butyllithium. Opitz et al.[8] showed that both semiempirical and Hartree−Fock methodologies are qualitatively incorrect for the study of the Li−H exchange reaction between phenol and LiH. In that case these methods predict an artificial agostic interaction in the initial complex for the reaction. Moreover, even where the aforementioned methods are capable of giving an adequate picture of the lithiation process under study, Schleyer et al.[6,14] showed that including correlation effects in the calculations can lead to a reduction of more than 10 kcal/mol in the estimated barriers. However, the larger size of the molecules involved in most of the lithiation reactions of synthetic interest makes it difficult to perform expensive ab initio correlated calculations for correctly determining energetics and structural features of the species taking part in these processes.

In the past few years density functional theory (DFT) methods[15] have been considered as a possible alternative for including electron correlation in studies of organolithium compounds at a lower computational cost. Pratt and Khan[16] have reported a study of a set of organolythium reagents (including both monomeric and dimeric methyllithium) using local density functionals. Their results seem to be in good agreement both with the ab initio calculations and the experimental information available on these species. More recently, Kremer et al.[6c] have successfully applied Becke3LYP hybrid functional calculations to obtain energetics of species related to metalation of ortho-substituted toluenes. These facts have encouraged us to apply the B3LYP functional to the study of reaction 1 to assess its reliability not only in predicting energetics of metalation processes, but also in providing structural data (both nuclear and electronic) for the species involved in the mechanisms of these reactions. Our final aim is to assess whether B3LYP provides a reliable alternative to approach the study in gas phase and solution of the lithiation of molecules considerably more complex than CH_4.

2. Methodological and Computational Aspects

Exploratory calculations on the gas-phase PES for H−Li exchange between CH_4 and $(CH_3Li)_2$ have been performed at the HF/3-21G[17] level, the same used by Kaufmann and Schleyer[13] to locate a C_s transition state for this reaction. Then a series of more accurate calculations has been done for each of the stationary points found at the HF, MP2(full) perturbational theory levels,[17] and Becke's hybrid density functional B3LYP[18] using the 6-31G(d,p) basis set.[17] The structures of three stable species (CH_4, $(CH_3Li)_2$, and the $CH_4{\cdot}(CH_3Li)_2$ intermediate complex) and two first-order saddle points (the C_s six-membered ring transition state originally proposed by Kaufmann and Schleyer[13] (**TS6MR**) and a new four-membered ring-like structure (**TS4MR**) proposed here for the first time) have been fully optimized in vacuo at each level of theory without imposing any symmetry constraint. The nature of every stationary point has been determined at each of the levels considered, based on the number of negative eigenvalues of the Hessian matrix, as usual. Harmonic frequencies were calculated at each level of theory. ZPEs, contributions due to thermal motions, and entropy at 298 K were also calculated in order to determine in vacuo Gibbs free energy values for all these species. ZPEs have been scaled using factors determined to better reproduce experimental values: 0.9182,[19a] 0.9826,[19a] and 0.9643[19a,b] at the HF, B3LYP, and MP2(full) levels, respectively. The Gaussian92[20a] and Gaussian94[20b] electronic structure packages have been used to perform all the gas-phase calculations. Atomic charges and bond orders for each of the species involved in the two mechanisms considered were also calculated using Natural Population (NPA) and Natural Bond Orbital (NBO)[21] Analysis.

The effect of the bulk solvent (THF, dielectric constant = 7.580) has been modeled using the Polarizable Continuum Model (PCM)[11] developed at the University of Pisa, coded into a locally modified version of the Gaussian94 package.[22] All the PCM calculations of the electrostatic component (G_{el}) of the solvation free energy (G_{solv}) have been performed at the HF/6-31G(d,p) and B3LYP/6-31G(d,p) levels on the MP2(full)/6-31G(d,p) geometries optimized in vacuo, within the recently proposed Integral Equation Formalism (PCM/IEF).[23] In calculating the nonelectrostatic contributions to the solvation energy, we used the Pierotti SPT approach[24a] for the cavitation energy (G_{cav}).[24b] Dispersion (G_{dis}) and repulsion (G_{rep}) terms were calculated using empirical two-bodies potentials and a continuum distribution in a general-shaped cavity.[25]

A critical issue in calculating G_{el} using PCM is the choice of the radii required for constructing the general-shaped cavity that contains the solute. Actually, together with the dielectric constant of the continuum isotropic medium, these are the only empirical parameters required as an input for performing PCM calculations of G_{el}. More than 15 years of experience applying PCM to a wide range of solute/solvent systems was shown us that molecular cavities obtained intersecting spheres of van der Waals radii conveniently scaled by a constant factor of 1.2 perform a good job for neutral solutes,[11b] so we have resorted to that approach in a case where the changes of the molecular surface along the reaction coordinate can be a driving force of the process in THF solution. For another definition of cavity radii developed for reproducing experimental solvation energies for stable species using PCM, see the work recently done by Barone et al.[26]

The size of the C and H atoms has been well determined. Values taken from the literature are in the range of 1.6−1.7 Å for C and of 1.2 Å for H.[27] The information available for Li is less accurate than for the other two atoms. In an unpublished study on the best radii for light metal ions in solvents of various types, Bonaccorsi et al.[28a] suggested for Li a radius of about 1.40 Å for solvents such as THF. Badenhoop and Weinhold proposed[28b] for Li in LiH and LiF (on the basis of their natural steric analysis calculated at the HF/6-31G* level) van der Waals radii equal to 2.128 and 1.394 Å, respectively. Arteca et al.[29] proposed transferable isodensity spheres (TIDS) for Li with a radius in the range 0.99−1.38 Å. The values limiting this range correspond, respectively, to the radii of spheres that contain the

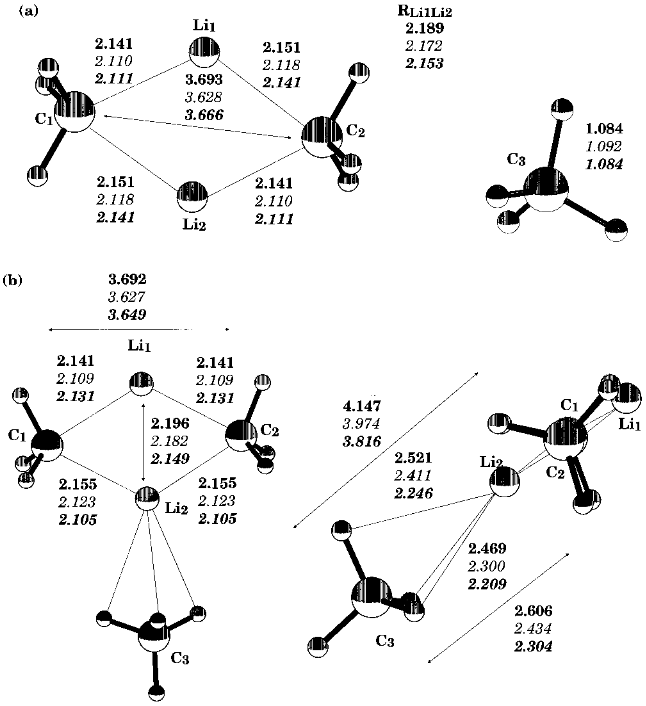


Figure 1. In vacuo optimized structures for the stable species involved in the reaction: (a) reagents; (b) frontal and side view of the intermediate complex. Selected structural information is given in the following order: first entry HF, second entry (italic) B3LYP, and third entry (bold) MP2(full) results obtained with the 6-31G(d,p) basis set.

same amount of the electron density (calculated at the HF/6-31G(d,p) level) that is contained in a sphere of 1.6 Å for C or of 1.2 Å for H. Because for light elements such as Li core electrons are farther from the nucleus than heavier atoms such as C, we consider the value of 1.38 Å a lower limit. We have performed exploratory PCM/IEF calculations at the HF and DFT levels with Li radii in the range 1.38−1.80 Å. An increase in the Li radii essentially produces some changes in the electrostatic component of the solvation energy, but the differential effects in comparing the transition state of the alternative mechanism relative with that already known are rather modest and do not affect our conclusions. Thus the data reported in this article refer to calculations performed with an effective Li radius equal to 1.66 Å (obtained by scaling 1.38 Å by 1.2 as explained in the previous paragraph).

3. Results and Discussion

3.1. Gas-Phase Results: The Alternative Mechanism. Both saddle points we have found are directly connected via an intrinsic reaction coordinate (IRC)[30] path to an unique initial complex, topologically defined as a local minimum, which has not been characterized in related work previously done by other authors.

TABLE 1: NPA Atomic Charges for Heavy Atoms in the Species Involved in Mechanisms 4MR and 6MR Calculated in Vacuo at Each of the Levels of Theory Considered in This Work Using the 6-31G(d,p) Basis Set (in Atomic Units)

level of theory	atom[a]	reagents	intermediate complex	TS4MR	TS6MR
HF	Li$_1$	+0.870	+0.870	+0.915	+0.905
	Li$_2$	+0.870	+0.864	+0.915	+0.897
	C$_1$	−1.475	−1.469	−1.484	−1.480
	C$_2$	−1.475	−1.469	−1.228	−1.244
	C$_3$	−0.878	−0.928	−1.228	−1.246
MP2	Li$_1$	+0.840	+0.834	+0.888	+0.884
	Li$_2$	+0.840	+0.817	+0.885	+0.860
	C$_1$	−1.468	−1.453	−1. 476	−1.472
	C$_2$	−1.468	−1.453	−1.221	−1.229
	C$_3$	−0.895	−0.966	−1.221	−1.231
DFT (B3LYP)	Li$_1$	+0.843	+0.841	+0.893	+0.880
	Li$_2$	+0.843	+0.828	+0.893	+0.868
	C$_1$	−1.499	−1.489	−1.508	−1.502
	C$_2$	−1.499	−1.489	−1.244	−1.255
	C$_3$	−0.932	−0.999	−1.242	−1.258

[a] See Figure 1 for the numeration assigned to each atom.

The structure of this stationary point on the PES is reported in Figure 1 together with the geometry of the reagents. It has the appearance of the substrate (the CH$_4$ molecule at the left corner in the picture) weakly interacting with one of the Li atoms in the methyllithium dimer. To give a clearer picture of the spatial arrangement of the atoms in the complex we also included a side view of this structure in the same figure. Notice that both Li atoms lie almost on the same plane defined by the three C atoms, and three of the four H atoms in methane moiety are interacting with the closest Li atom, in a way similar to that reported for the complex between methane and LiCH$_3$.[13,14] We display in this figure numerical values of the most significant distances obtained at the HF, MP2, and B3LYP levels using the 6-31G(d,p) basis set. There are no large differences in the geometries obtained with the three methods: we only remark that the inclusion of correlation in the calculation results in a shortening of about 0.2−0.3 Å for the distance between the Li atom and the carbon of the CH$_4$ reactant, this effect being slightly stronger at the MP2 level. A similar trend is observed for the C−C and C−Li in the methyllithium moiety.

Thus, there is a remarkable asymmetry in the interaction of CH$_4$ with both Li atoms. This fact is confirmed after examination of the molecular charge distribution in the methyllithium dimer and the intermediate complex of the reaction. (See NPA atomic charges reported in Table 1 for the heavy atoms in each of the species involved in the mechanisms considered.) A charge polarization process takes place when CH$_4$ approaches (CH$_3$Li)$_2$ to form the complex by mutual polarization of the fragments: the Li atoms placed near and far to methane bear now positive charges which are smaller than in the isolated methyllithium dimer, particularly for the former atom. The ionic nature of the complex evident from the analysis of the set of charges and the subunits assigned by the NBO bond order analysis performed: two CH$_3$ anions (charge ~-0.8 au each) and two Li cations (charge $\sim+0.8$ au) plus a neutral methane subunit are detected.

In Table 2 we report gas phase relative energies, ZPE corrected energies, enthalpies, and Gibbs free energies (the last two quantities evaluated at 298 K) calculated at each of the theoretical levels considered for the species studied. (Absolute energetics at each of the levels used, including the exploratory calculations performed at the HF/3-21G level, are given as supplementary information.) Relative values are given as differences with respect to those of the CH$_4$ and (CH$_3$Li)$_2$ moieties separated at the infinite. Kaufmann and Schleyer[13] estimated (using data calculated at the MP2(FC)/6-31+G//HF/6-31G* level + ZPE) a value of −4.1 kcal/mol for the relative energy of this intermediate complex, assuming that the association energy for methane and methyllithium dimer is about the same as that obtained for the interaction between methane and the monomer. Comparing this estimation with the value calculated at the MP2(full)/6-31G(d,p) level (−5.1 kcal/mol) it is clear that the assumption was justified at a qualitative level considering the height of the barrier predicted. However, it deserves to be mentioned that at the HF/3-21G level (the one used in Kaufmann and Schleyer's work for characterizing the

TABLE 2: In Vacuo Relative Energetics[a] for the Species Involved in Mechanisms 4MR and 6MR at Each of the Levels of Theory Considered in This Work Using the 6-31G(d,p) Basis Set (in kcal/mol)

level of theory		intermediate complex	TS4MR	TS6MR	barrier height[b] 4MR	6MR
HF	ΔE_0	−1.7	43.9	45.1		
	ΔH_0	−1.1	42.9	43.3	44.0	44.4
	ΔH_{298}	−0.5	41.8	42.4	42.3	43.9
	ΔG_{298}	5.9	36.0	35.3	30.1	29.4
MP2(full)	ΔE_0	−5.1	29.4	31.3		
	ΔH_0	−4.1	28.4	29.9	32.5	34.0
	ΔH_{298}	−3.9	27.3	28.7	31.2	32.6
	ΔG_{298}	4.5	39.0	41.0	34.5	36.5
DFT (B3LYP)	ΔE_0	−3.2	28.7	30.2		
	ΔH_0	−2.5	27.7	28.2	30.2	30.7
	ΔH_{298}	−2.1	26.7	27.5	28.8	29.6
	ΔG_{298}	4.6	38.5	37.8	33.9	33.2

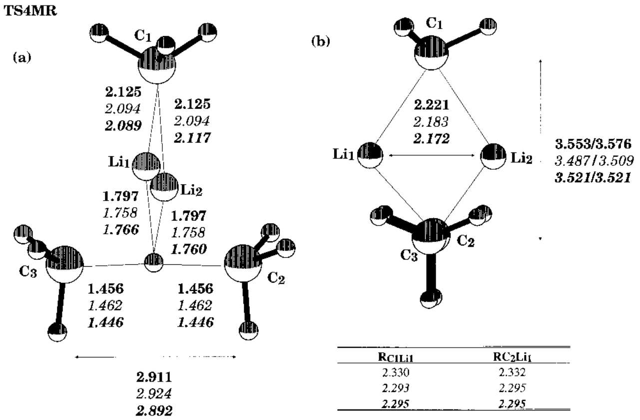
[a] Calculated with respect to the reagents CH_4 and methyllithium dimer $(CH_3Li)_2$ at an infinite distance. [b] Taken from the bottom of the well of the intermediate complex $[CH_4 \cdot (CH_3Li)_2]$.

transition state for the reaction involving the methyllithium dimer[13]) this quantity is only about 2 kcal/mol, a value close to the one obtained at the B3LYP/6-31G(d,p) level (2.5 kcal/mol). Hence, using this estimation leads to predicting a barrier for the process which is artificially raised by more than 3 kcal/mol at that level. Remember that compared with the association energies of the order of just a few kilocalories per mole, the uncompleteness of the basis set used here can give an appreciable basis set superposition error (as a matter of fact, MP2 has been shown recently to give too negative binding energies for the complexes between LiH and benzene and toluene,[6c] a fact that seemed to be corrected at the B3LYP level). Thus, although these values should just be considered rough estimations of the absolute complexation energy, because both alternative reaction pathways here considered start at the same intermediate complex, this fact does not affect the validity of the analysis performed in this work.

Notice that when the thermal contributions at 298 K are considered, both MP2 and B3LYP methods converge to approximately the same value (+4.5 kcal/cal) for the Gibbs free relative energy of the complex, the HF estimation of this value being a little higher (+5.9 kcal/mol). As expected, the value becomes positive because of the unfavorable entropic contributions required to form the more organized structure of the intermediate complex in gas phase. Because this species has an ionic character and a net dipolar moment of about 0.8 D, it is expected it will be stabilized to some extent by THF when the reaction happens in condensed phase. (See the next section for a detailed discussion on this topic.)

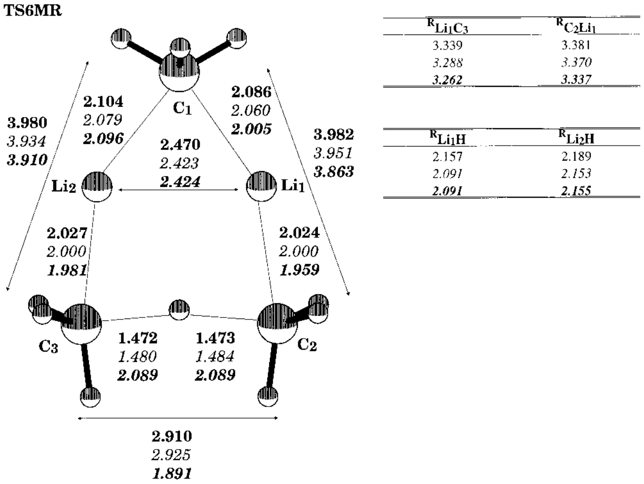
In Figures 2 and 3, respectively, we report the structural parameters obtained at the different levels of theory for the four-membered ring (TS4MR) and the six-membered ring (TS6MR) transition states characterized in this work. Here again, the gas-phase energetics for both transition states is reported in Table 2.

A first glance at the structural data shows that although the asymmetry in the interaction between the two Li atoms with the exchanging H atom we remarked in the intermediate complex has practically disappeared in TS4MR, it is still present in TS6MR (even if at a modest extent, which persists in changing the techniques of optimization and the symmetry of the starting point for the search on the surface). Moreover, the examination of the atomic charges reported in Table 1 further supports these observations: both transition states are ionic, with a symmetrical distribution of charge in TS4MR (the positive or negative net charges at each of the Li atoms and in the couple of C atoms involved in the C−H−C bridge, respectively, are the same) and an asymmetric distribution in TS6MR. According to the principle of microscopic reversibility, a symmetric transition state should be expected to connect reactants and products for a degenerate exchange reaction. This fact seems to give some support to the mechanism involving the more symmetric TS, that is, 4MR in our study. More arguments in support of the 4MR mechanism will be presented in the following pages.



R_{C1Li1}	R_{C2Li1}
2.330	2.332
2.293	*2.295*
2.295	***2.295***

Figure 2. Structure of the new transition state proposed for the reaction: TS4MR. Selected structural information is given in the following order: first entry HF, second entry (italic) B3LYP, and third entry (bold) MP2(full) results obtained with the 6-31G(d,p) basis set.



$R_{Li_1C_3}$	$R_{C_2Li_1}$
3.339	3.381
3.288	*3.370*
3.262	***3.337***

R_{Li_1H}	R_{Li_2H}
2.157	2.189
2.091	*2.153*
2.091	***2.155***

Figure 3. Structure of the six-centered ring transition state proposed by Kaufmann and Schleyer:[13] TS6MR. Selected structural information is given in the following order: first entry HF, second entry (italic) B3LYP, and third entry (bold) MP2(full) results obtained with the 6-31G(d,p) basis set.

The first transition state, TS6MR, was proposed originally by Kaufmann and Schleyer,[13] as we have already stated. Our results, obtained at better levels of theory than the HF/3-21G used by those authors, essentially confirm their findings. The six-membered ring (composed of the three carbon atoms, alternating the two Li atoms and the exchanged H) is planar, almost at C_s symmetry. The migrating H atom is located at almost the midpoint between the two C atoms, but as mentioned previously, the interaction of this bridging atom with the Li atoms is not symmetrical (for example, at the MP2/6-31G(d,p) level the calculated values for these two bond lengths are 2.091 and 2.155 Å, respectively). A closer look at the charges collected in Table 1 reveals the ionic nature of this structure, with the Li and C atoms that are closer to the exchanging H exhibiting higher net atomic charges than their respective partners placed a little farther from the bridge hydrogen. It is worth mentioning that although NBO analysis is in agreement at the HF and DFT levels (predicting the existence of 2 CH_3 anions, 2 Li cations, and a slightly negatively charged CH_4 unit), the MP2 level gives a different picture: one CH_3Li_2+ unit, with a net charge of +0.92 au involving a three-centered Li−C−Li bond, plus a CH_3 anion, and also a slightly negatively charged CH_4 unit. No attractive interactions between the migrating H and the Li atoms are found.

The second transition state, TS4MR, is proposed here for the first time. The three C atoms and the exchanging H almost lie on the same plane. A four-membered ring placed orthogonal to that plane is formed by the H atom, the two Li atoms, and the C atom at the upper CH_3 spectator group. This structure is closer than TS6MR to the geometry predicted for the TS of the reaction involving methyllithium monomer;[13] actually, TS4MR is more in line than TS6MR with the experimental evidence that suggests an ionic, four-membered ring TS for this kind of reaction.[31] It exhibits attractive interactions between the migrating H and both Li atoms (Li−H distances ranging from 1.76 to 182 Å, according to the level of calculation), a fact that would make it possible to anticipate a lower barrier for this mechanism than that of the 6MR one. In passing from the SCF level to the MP2 and DFT correlated levels of calculation, the distances between the elements of the ring progressively decrease without appreciable changes in the ratios of the various interatomic distances. It also might be remarked that at the MP2 level there is a lowering in the symmetry of the system (one of the Li atoms is slightly closer to the methyl group in the upper position), at the limit of modelistic interest.

Notice that while in TS6MR the C−H−C subsystem exhibits a nonlinearity of the order of 18 degrees, in TS4MR the hydrogen bridge is practically linear (with deviations of 1−2 degrees according to the level of calculation). This finding agrees with the already quoted reports[13,14] modeling metalation processes involving organolithium compounds in which no evidence supporting a bent nature of the C−H−C bridge in the transition states is found. The hypothesis of nonlinearity in the transition state was proposed by Liotta et al.[32] on the basis of the experimental study of isotopic effects in the intramolecular nondegenerate metalation of 2-(3-furyl)ethyllithium, actually a chemical system significantly different from ours. The transition states characterized in this or other theoretical research performed on the matter exhibit a linear or near linear bridge. In both cases, the exchanging hydrogens bear positive charges, of about +0.2 au. Hence, no matter what reaction pathway is preferred, the process is always described as a H atom transfer.

The energy values reported in Table 2 for the two TSs indicate that there generally is similarity between the barrier heights for the two mechanisms considered, with some indications of lower barriers for mechanism 4MR, the exception being the free-energy barriers at 298K at the HF and DFT levels. Notice, however, that the latter are less accurate because no optimal scaling factors are available for thermal corrections as for ZPEs, and unfortunately the scale factors used for correcting the systematic error introduced by ab initio and DFT vibrational frequencies are different depending on their specific uses.[19] There are on the contrary large changes in the energy and enthalpy values in passing from the HF level to methods including some electron correlation; a lowering of 10−15 kcal/mol is observed in the classical barrier heights after including correlation in the calculations (a fact already pointed out by other authors in the study of more complex metalation reactions[6,14]). Despite the presence of attractive interactions between the Li ions and the exchanging H in TS4MR that are absent in TS6MR, the former TS is not considerably more stable than the latter. This is probably because the rearrangement of atoms required to reach the saddle point in the 4MR channel also involves a shortening of the distance between the two Li atoms. This repulsive interaction partially cancels the stabilizing effects of the Li−H interactions.

Concerning the absolute estimation of the barrier for lithiation of CH_4 itself, our best in vacuo results predict a value of 30.2 kcal/mol calculated at 0 K with respect to the intermediate complex, and of 28.8 kcal/mol in terms of ΔH_{298}. The closest Li−H degenerate exchange process for which experimental data are available is activation of methane by reaction with methyllated organolanthanides $Cp_2{}^*MCH_3$ (with M = Y, Lu, Sc) in cyclohexane-d_{12} at 343 K.[33] In these studies the apparent bimolecular rate constants for exchange are reported, but no estimation of the barrier heights is given, hence any direct comparison between theory and experiment becomes difficult. Assuming a simple Arrhenius equation to be valid in this case, Kaufmann and Schleyer[13] estimated that the barrier for lutetium−hydrogen exchange ranges from 18 to 23 kcal/mol. Solvation and the use of a different metal instead of lithium might be the clues to explain this apparent quantitative disagreement between theory and experimental findings. The first of these two factors will be addressed in the next section.

3.2. Solvent Effects on the Reaction Paths. The calculations in solution reported here mainly refer to in vacuo structures characterized at the MP2(full)/6-31G(d,p) level. The use of this approach is supported by the fact that no significant changes in the solvation energies are introduced when using other geometries. To check of the validity of this assumption, full geometry optimization of the stable species involved in the process, CH_4, $(CH_3Li)_2$, and the intermediate complex $[CH_4\cdots(CH_3Li)_2]$, have been performed in THF solution at the B3LYP/6-31G(d) level, considering all the contributions to the solvation energy. To this end, we have exploited the efficient new implementation PCM/IEF[22a] for which analytic first derivatives of the energy with respect to the nuclear coordinates are already available at the HF and DFT levels[22b] in our locally modified version of the Gaussian94 package.[21] A summary of the changes introduced by the solvent on the structural parameters and energetics of these species at the B3LYP/6-31G(d,p) level is given in Table 3. By comparison of these data and the information reported in Table 4 (obtained by solvation of the MP2 in vacuo structures) it is clear that the regions near the minima in the solvated PES are quite flat, a relaxation of the structures in the field of the solvent resulting in small changes of solvation free energy.

Some common structural modifications induced by solvation are observed within the ionic moieties of the stable species: the C−Li distances are lengthened by ∼0.02 Å both in the methyllithium dimer and in the intermediate complex as a way of increasing the separation of charge; at the same time, both C_1-C_2 and Li_1-Li_2 distances are increased (specially for the latter distance, which becomes ∼0.05 Å longer in solution) to reduce any repulsive interaction between centers which bear net charge of the same sign. The slight asymmetry observed at the in vacuo structure of the intermediate complex is still more pronounced in THF solution. Each of the Li atoms is no longer positioned equidistant from the C_1 and C_2 atoms in the methyllithium moiety, and the strength of the weakly attractive interaction between CH_4 and $(LiCH_3)_2$ in the intermediate complex is enhanced in solution; the distance between Li_2 and

TABLE 3: Effects of Nuclear Relaxation in THF Solution for the Stable Species Involved in Mechanisms 4MR and 6MR[a]

	absolute energies (au)		relative energetics in THF (kcal/mol)				structural data[b]	
species	G_{el}	G_{sol}	ΔG_{el}	ΔG_{cav}	$\Delta G_{disp-rep}$	ΔG_{solv}		
CH_4	−40.524014	−40.522132	−0.14	4.8	−1.8	2.9	R_{CH}	1.091
							α_{HCH}	109.5
$(CH_3Li)_2$	−94.880371	−94.891263	−13.2	9.1	−2.8	−6.9	R_{C1C2}	3.637
							R_{C1Li1}	2.130
							R_{C1Li2}	2.141
							R_{Li1Li2}	2.238
							$\alpha_{C1Li1C2}$	116.8
							$\alpha_{Li1C1Li2}$	63.2
$[CH_4\cdots(CH_3Li)_2]$	−135.425438	−135.411716	−10.0	12.0	−4.28	−2.3	R_{C1C2}	3.630
							R_{C1Li1}	2.120
							R_{C1Li2}	2.142
							R_{Li1Li2}	2.236
							R_{C1C3}	3.948
							R_{C3Li2}	2.383
							$R_{Hmet1Li2}$	2.258
							$R_{Hmet2Li2}$	2.278
							$R_{Hmet3Li2}$	2.338
							$\alpha_{C1Li1C2}$	116.0
							$\alpha_{Li1C1Li2}$	63.3

[a] Calculated at the B3LYP/6-31G(d,p) level WITHPCM/IEF. [b] See Figure 1 for the numeration assigned to each atom.

TABLE 4: Solvation Energy and Components of the Solvation Energy for Each of the Species Involved in the Mechanisms 4MR and 6MR in Bulk THF Solution (in kcal/mol)

components of the solvation energy	species				
	CH_4	$(CH_3Li)_2$	$CH_4.(CH_3Li)_2$	TS4MR	TS6MR
ΔG_{el}[a]	−0.14	−13.3	−9.7	−11.6	−10.2
	−0.13	*−13.2*	*−8.5*	*−10.2*	*−9.0*
ΔG_{cav}	4.9	9.1	11.9	11.2	11.4
$\Delta G_{disp-rep}$	−1.8	−2.8	−4.3	−4.2	−4.3
ΔG_{solv}[a]	3.0	−7.0	−2.1	−4.6	−3.1
	3.0	*−6.9*	*−0.9*	*−3.2*	*−1.9*

[a] Values in normal and italic fonts, correspond to HF and DFT electrostatic free energies, respectively, at 298 K.

TABLE 5: Differential Effects of Solvation (THF) on the Barrier Height for Mechanisms 4MR and 6MR Calculated Using PCM at the HF and DFT Levels (in kcal/mol)

	differential effects of solvation				
mechanism	ΔG_{el}[a]	ΔG_{cav}	$\Delta G_{disp-rep}$	ΔG_{tot}[a]	barrier height[b]
4MR	−1.9	−0.7	0.09	−2.5	41.5/39.8
	−1.7			*−2.3*	*27.9/26.5*
					30.2/28.9
6MR	−0.54	−0.5	0.02	−1.0	43.4/42.9
	−0.53			*−1.0*	*29.7/28.6*
					33.0/31.6
differences[c]	1.4	0.2	−0.07	1.5	1.9/3.1
	1.2			*1.3*	*1.8/2.1*
					2.8/3.0

[a] Values in normal and italic fonts correspond to HF and DFT free energies, respectively, in THF solution at 298 K. [b] Calculated by addition of the differential solvent effects to the corresponding gas phase $\Delta H_0/\Delta H_{298}$ barriers reported in Table 2. Third entry in bold type corresponds to MP2 in vacuo barriers + differential solvation effects calculated at the B3LYP level. [c] Differences taken as 6MR-4MR.

C_3 is shortened by 0.05 Å, and the shortest interfragment H−Li_2 distance is reduced from 2.300 to 2.258 Å.

In Table 5 we collect the differential effects due to solvation in the estimate of the reaction barriers for mechanisms 4MR and 6MR, with their decomposition into electrostatic, dispersion-repulsion, and cavitation terms. At the right end of the Table we report final estimations of the free-energy barrier heights in THF solution, calculated by adding differential solvent effects to the in vacuo barriers. This information is complemented by the data already collected in Table 4 reporting the components of the solvation energy obtained for all the structures involved in each reaction mechanism.

Notice that solvation energies reported in Tables 4 and 5 are not largely affected by the quality of the quantum-mechanical description of the solute used (both HF and B3LYP calculations give similar results in THF). We recall that the quantities reported in Table 5 are differences between solvation energies and that the differential solvent effects due to electron correlation are to a fair extent dampened in making these differences.

Analyzing the data collected in Tables 4 and 5, the most relevant feature is that for both mechanisms the global effect of the solvent is to stabilize their transition states with respect to the intermediate complex, reducing the values of the corresponding barriers by ~2.5 kcal/mol for TS4MR and 1 kcal/mol for TS6MR, hence further favoring the alternative mechanism proposed in this work. A more detailed inspection of the data reveals that for most of the species considered the principal contribution to the solvation energy is given by the cavitation component (a destabilizing term), an expected result considering the low dielectric constant of the medium. Notice that in passing from the isolated reagents to the intermediate complex, and from this one to the transition states TS4MR and TS6MR, the cavitation term becomes smaller, reflecting the fact that the molecular surface of the solute is reduced as a consequence of the progressive approaching of the two methyl groups involved in the H-transfer process. This differential effect (which makes it easier for the reaction to proceed when compared with the gas phase) is slightly more pronounced for TS4MR.

On the other hand, the electrostatic component evolves along the reaction path following the changes in the ionic character of the species involved in the process, as well as the variations in the extent Li atoms are exposed to interact with the oxygen atoms present in solvent molecules (see Figures 1 and 2). Starting from methyllithium dimer, which exhibits the strongest electrostatic stabilization of 13.2 kcal/mol, this component is reduced to 8.5 kcal/mol at the intermediate complex, to be increased to 10 and 9 kcal/mol at TS4MR and TS6MR, respectively. At the intermediate complex, because of its internal position in the solute structure, one of the Li atoms practically does not feel the effect of the field of the solvent

TABLE 6: NPA Atomic Charges for Heavy Atoms in the Species Involved in Mechanisms 4MR and 6MR Calculated in THF Solution at the HF and B3LYP Levels Using the 6-31G(d,p) Basis Set (in atomic units)

level of theory	atom[a]	reagents	intermediate complex	TS4MR	TS6MR
HF	Li_1	+0.890	+0.887	+0.925	+0.921
	Li_2	+0.890	+0.861	+0.923	+0.904
	C_1	−1.460	−1.452	−1.231	−1.473
	C_2	−1.460	−1.452	−1.231	−1.248
	C_3	−0.886	−0.951	−1.467	−1.246
DFT (B3LYP)	Li_1	+0.861	+0.859	+0.906	+0.900
	Li_2	+0.861	+0.828	+0.904	+0.879
	C_1	−1.483	−1.474	−1.492	−1.495
	C_2	−1.483	−1.474	−1.243	−1.256
	C_3	−0.932	−1.001	−1.243	−1.254

[a] See Figure 1 for the numeration assigned to each atom.

(compare the NPA charges calculated in vacuo reported in Table 1 with their respective values in THF solution collected in Table 6). The solvent in turn seems to favor the process of charge reorganization between fragments already pointed out in gas phase, a fact that is further confirmed by the results resported in Table 3 obtained after geometry optimization of this species in solution. At the transition states, the ionic character increases and the internal Li atom becomes more exposed, specially in TS4MR, leading to a differential stabilization of this saddle point over TS6MR.

One can conclude from the facts discussed for each reaction that the presence of the solvent makes mechanism 4MR even more favorable than 6MR in vacuo, increasing the difference between the two barriers by 1.5 kcal/mol. Our better estimation for the barrier height of the process in THF solution based on this mechanism (calculated by adding the differential effects of solvation to the corresponding gas phase ΔH_{298} barrier) has now been lowered to 26.5 kcal/mol at the B3LYP level. Although this value is closer to the barrier height estimated for the degenerate exchange involving methyllutetium, it is likely this is still an upper bound of the effective barrier of the reaction. We recall that the degenerate H−Li exchange studied herein involves migration of a light H atom between two heavier CH_3 groups, a typical case in which the minimum energy reaction path lies on a large curvature PES. Hence, tunneling through the barrier will surely play a nonnegligible role in the kinetics of the process, especially at low temperatures, lowering the effective barrier for the reaction. This and other dynamic aspects related to the reaction are under consideration in our group and will be the subject of another article.

3.3. Performance of the B3LYP Density Functional. In conclusion, the B3LYP method has been shown to be reliable in predicting structural information and energetics in vacuo and solution for metalation reactions. It is clear from our results that B3LYP can be considered a good alternative to introduce correlation effects in the study of this group of reactions. Structures obtained in gas phase are quite close to the ones obtained with the MP2(full) method (which may be considered possibly the standard in the study of complex organic reactions at the current state-of-art in the field), and energetics are also similar, correcting the extremely high barriers predicted by noncorrelated approaches. The only significant difference in gas phase is noted in the charge distribution, which depicts a slightly more ionic character for the species considered (see Table 1). In calculating solvation energies using in vacuo structures, the B3LYP method produces results that are not far from the HF ones, but it is still recommended for optimizing structures in solution, because correlation plays a nontrivial role in finding the correct structure for the species involved in the reaction. These results encourage the application of the method not only for improving the description of the HF energetics of the metalation reactions in gas phase, as recently done by Kremer et al.;[6c] used in combination with the PCM/IEF method, B3LYP can also give a computationally efficient approach to represent the effect of solvation both on the structure and energetics of lithiation reactions. This fact is particularly important in shedding light on several aspects of the mechanism of lithiation of more complex aromatic compounds which still remain as a matter of discussion,[6c,7d] and for which more accurate and affordable calculations are required, in particular for obtaining kinetic data.

4. Concluding Remarks

In this work we have performed a detailed study of the mechanism of the simplest degenerate H−Li exchange reaction that involves an aliphatic hydrocarbon, both in gas phase and THF solution. A weak intermediate complex and a transition state alternative to the saddle point introduced in a previous study of this process have been fully characterized. This TS, proposed here for the first time, seems to be more in line with the assumptions made on the basis of experimental kinetic results about the structure of the TS for reactions of this kind. The effect of the solvent on each mechanistic alternative has been quantified using a continuum model, our results showing that the main changes in the solvation energy are due both to the cavitation and electrostatic terms. A favorable reduction of the molecular surface of the solute and a more effective stabilization of the species by electrostatic interactions between the Li ions and solvent molecules follow the evolution from reagents to TS in both cases, these effects being more important for the new TS, which is further stabilized relative to the saddle point previously proposed. Finally, this study demonstrates how the B3LYP level used in conjunction with the PCM model is able to give an accurate description of the H migration process in solution at a reasonable computational cost, preparing the way for a more realistic modeling of complex lithiation reactions.

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Supporting Information Available: Table of absolute energies (1 page). Ordering information is given on any current masthead page.

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