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## Ab Initio Mechanisms for the Addition of $\text{CH}_3\text{Li}$ , $\text{HLi}$ , and Their Dimers to Formaldehyde

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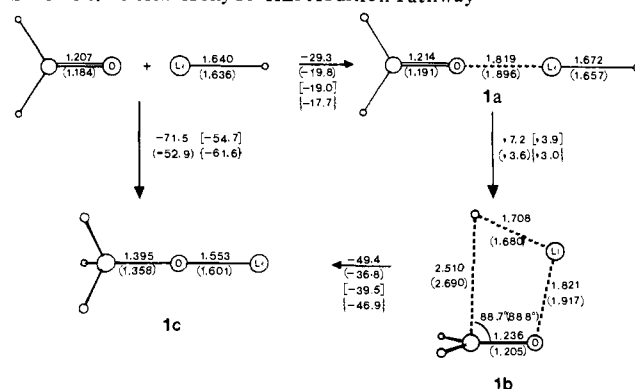
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Although the reactions of alkyllithiums with carbonyl compounds are among the most elementary synthetic reactions,<sup>1</sup> little detailed mechanistic information is available. By use of rapid injection NMR, McGarrity et al. have shown that butyllithium dimer in tetrahydrofuran reacts about 10 times faster than the tetramer with benzaldehyde.<sup>2,3</sup> Even at high dilution, there is no detectable concentration of monomer. Hence, contrary to earlier suggestions based on kinetic evidence,<sup>4</sup> the monomer does not appear to be the reactive intermediate in ether solvents.

We now report an ab initio examination<sup>5</sup> of the mechanisms of model reactions of formaldehyde with the monomers  $\text{CH}_3\text{Li}$  and  $\text{LiH}$ , as well as with their dimers. The performance of the split valence 3-21G basis set, used for all these systems, was evaluated at higher levels for the  $\text{HLi} + \text{H}_2\text{CO}$  process (see caption, Scheme I) and should be reasonably reliable for the larger systems (Schemes II-IV).

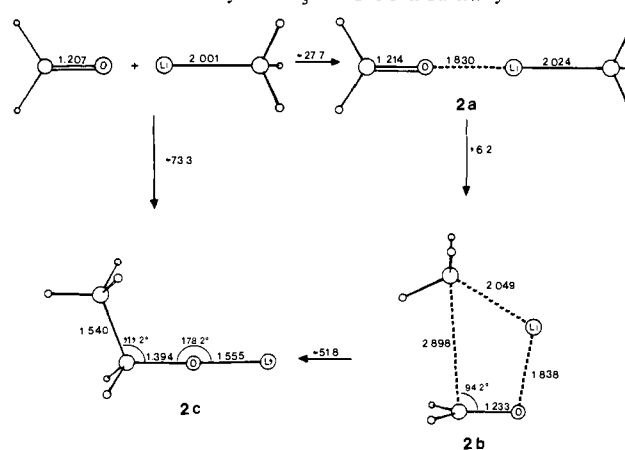
All four reaction pathways (Schemes I-IV) are rather similar; each proceeds in three stages. Formaldehyde complexes with the lithium reagents **1a-4a** are formed first.<sup>4,6</sup> Since the association

### Scheme I. Formaldehyde-HLi Addition Pathway<sup>a</sup>

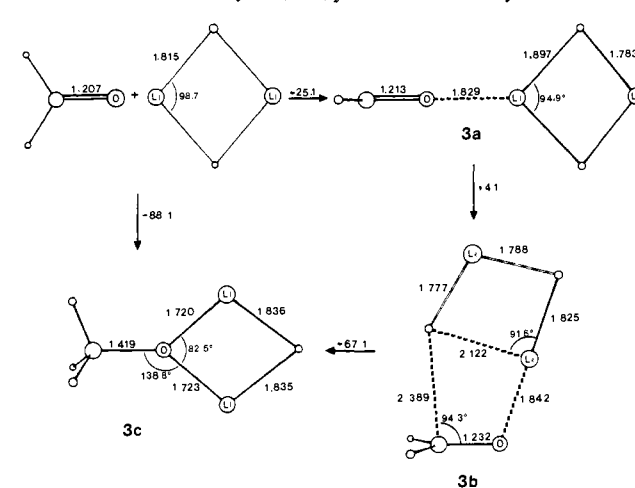


<sup>a</sup> Energies in kcal/mol, distances in Å, angles in deg. Data at 3-21G//3-21G are compared with optimized (6-31G\*\*//6-31G\*) as well as with single point [6-31+G\*\*//6-31G\*] and {MP2/6-31+G\*\*//6-31G\*} values.

### Scheme II. Formaldehyde- $\text{CH}_3\text{Li}$ Addition Pathway



### Scheme III. Formaldehyde-(HLi)<sub>2</sub> Addition Pathway



is quite exothermic,<sup>7</sup> the bonds in the complexes are lengthened slightly. Complexes **1a-4a** next convert to the addition transition structures ("states" is less satisfactory nomenclature) **1b-4b**; each is characterized by having a single imaginary frequency. In all four cases, the activation energies are quite small. The last stage of each reaction, conversion to  $\text{ROLi}$  (**1c** or **2c**) or to a  $\text{ROLi-RLi}$  mixed dimer (**3c** or **4c**), is very exothermic, as is the overall energy.

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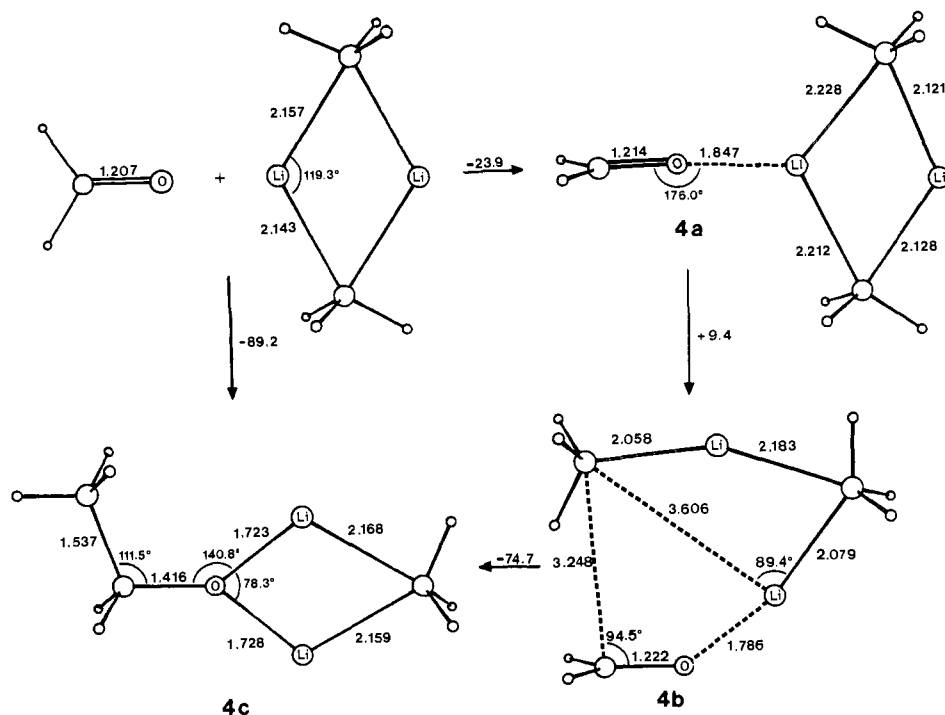
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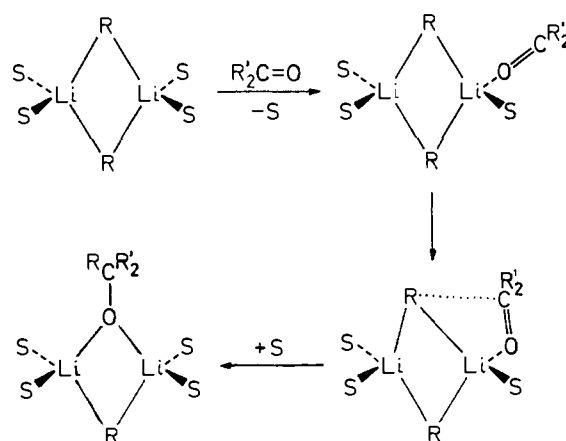
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Scheme IV. Formaldehyde-(CH<sub>3</sub>Li)<sub>2</sub> Addition Pathway

As LiO bonds are stronger than LiC interactions, formation of the mixed dimers **3c** and **4c** is favored energetically over **1c** and **2c**, which have only a single LiO contact.

All transition structures (**1b-4b**) lie very early on their reaction coordinates and the distances between the carbonyl carbon and the incoming hydride and methyl anions are quite large, ca. 2.4 and 3 Å, respectively. Hence, rather than being of predominant importance, the "critical" bonds to the nucleophile are just beginning to form in the activated complexes. Furthermore, the trajectory of attack by the nucleophile, the subject of much previous discussion,<sup>8,9</sup> is found here to be controlled by the Li<sup>+</sup> counterion. All C=O and LiO bond lengths in **1b-4b** are close (0.02–0.06 Å) to those in the complexes **1a-4a**. The elongations of the reacting LiH and LiCH<sub>3</sub> bonds in the monomer transition structures **1b** and **2b** are minimal (0.03 ± 0.01 Å), but those in **3b** (0.23 Å) and **4b** (1.47 Å) are larger. The small activation energies for all four reactions result mainly from the deformation of the COLi and OLiR (R = H or CH<sub>3</sub>) angles in forming the four-membered ring transition structures (shown by dashed lines in the schemes). Our results emphasize the decisive role of the *electrophile* rather than the nucleophile in such carbonyl additions.<sup>8,9</sup>

Although some reactions involving lithium compounds are known to proceed via single electron transfer,<sup>10</sup> similar four-center transition states have been proposed for β-hydride eliminations,<sup>11</sup> for the hydrogenolysis of alkyl lithiums,<sup>12</sup> and for methane exchange reactions in transition-metal chemistry.<sup>13</sup> The pathways calculated in a companion study of RLi additions to olefins and to acetylenes<sup>14</sup> and that calculated for the addition of MgH<sub>2</sub>



**Figure 1.** Proposed mechanism for the addition of (RLi)<sub>2</sub> dimers in donor solvents, S, to carbonyl compounds.

(Grignard reagent model) and LiBH<sub>4</sub> to H<sub>2</sub>CO<sup>15</sup> are closely related.

Similar mechanistic pathways<sup>1</sup> for alkyllithium additions to C=O double bonds probably occur in solution. Carbonyl compounds must first displace solvent molecules attached to lithium in alkyllithium clusters and form similar association complexes.<sup>4,6,7</sup> Thereafter, four-center transition structures involving C-Li and C=O bonds lead to mixed clusters (dimers, tetramers, etc.) in which an original R-Li component has been replaced by R'OLi (Figure 1; the process leading from an alkyllithium tetramer or higher aggregate may be similar).<sup>16</sup> As these reactions are primarily ionic in character,<sup>17</sup> orbital symmetry considerations

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(16) See: Seebach, D.; Amstutz, R.; Dunitz, J. D. *Helv. Chim. Acta* **1981**, *64*, 2622. Seebach, D. *Proc. Welch Conf. Chem. Res.* **1984**, *27*, 93 for related mechanistic postulates involving lithium clusters. In the present instance, attack by a second lithium cluster on a carbonyl-cluster complex appears to be ruled out by the kinetics.<sup>24</sup>

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and the number of electrons involved in the transition structures are unimportant. We are extending this work to an examination of the reaction mechanisms of tetramers and of solvated monomers and dimers.

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**Registry No.** HLi, 7580-67-8; CH<sub>3</sub>Li, 917-54-4; (HLi)<sub>2</sub>, 78715-95-4; (CH<sub>3</sub>Li)<sub>2</sub>, 74309-22-1; H<sub>2</sub>C=O, 50-00-0.

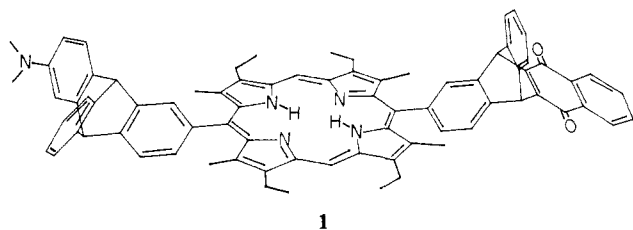
### High-Quantum-Yield Long-Lived Charge Separation in a Photosynthetic Reaction Center Model

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The high quantum efficiency of photosynthetic charge separation depends on favorable electron-transfer rates between electron donors and acceptors that are positioned in precise spatial relationships relative to one another and that possess redox potentials which result in movement of an electron down a stepped potential gradient. We have recently measured the dependence of photoinduced electron-transfer rates and subsequent dark charge recombination rates on the free energy of reaction in restricted distance porphyrin donor-quinone acceptor molecules.<sup>1</sup> Using this information we have now synthesized a molecule for which the donor-acceptor electron-transfer rates are designed to promote efficient two-step charge separation over a known long distance. In addition to a primary porphyrin-quinone donor-acceptor pair, this molecule possesses a secondary *N,N*-dimethylaniline donor **1**. The donor-acceptor distances and orientations in **1** are strongly



restricted by the polycyclic cage structures between them. The center-to-center distances<sup>2</sup> are, porphyrin-quinone, 10.5 Å, aniline-porphyrin, 10 Å, and, aniline-quinone, 25 Å.

Compound **1** was synthesized along with the analogous compound **2**, which lacks the dimethylamino group and therefore lacks the secondary electron donor. Ditritycylporphyrin (**3**) which lacks both the dimethylamino and naphthoquinone groups was also prepared as a reference. These diphenyloctaalkylporphyrins<sup>3</sup> were synthesized by reaction of the appropriate benzaldehyde derivatives with 3,3'-diethyl-4,4'-dimethylpyrromethane.<sup>4</sup> Triptyceno-naphthoquinone aldehyde (**4**) was prepared by the procedure we reported earlier.<sup>5</sup> 2-Nitrotritycene<sup>6</sup> was monoformylated<sup>7</sup> in 95% yield using dichloromethyl methyl ether/AlCl<sub>3</sub> to give after

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Table I. Energetics

compound	$E_{1/2}^-$ <sup>a</sup>	$E_{1/2}^+$ <sup>a</sup>	$E_{1/2}^{+ -}$ $E_{1/2}^-$
<b>1</b>	-0.61, -1.42	0.78, 0.92	1.39, 1.53
<b>2</b>	-0.61, -1.42	0.92	1.53, 2.34
<b>3</b>	-1.41	0.92	2.33
2-(dimethylamino)tritycene trityceno-naphthoquinone	-0.61	0.78	

<sup>a</sup>Redox potentials (V vs. SCE) were measured by cyclic voltammetry at a Pt disk electrode. The measurements were performed in butyronitrile containing 0.1 M tetra-*n*-butylammonium perchlorate at 21 °C.

chromatography 2-formyl-6-nitrotritycene (**5**). Equimolar amounts of **4** and **5** along with 2 equiv of the pyrromethane were dissolved in CH<sub>3</sub>OH/THF 4:1 v/v. Addition of an equivalent of *p*-toluenesulfonic acid resulted in precipitation of the *meso*-tetrahydroporphyrin (**6**) within 5 min. Oxidation of **6** with DDQ in CH<sub>2</sub>Cl<sub>2</sub> gave the mixed porphyrins in 80% yield. The mixed porphyrins were treated with SnCl<sub>2</sub> in THF/concentrated HCl 1:1 v/v for 18 h to reduce the nitro group. At this stage the porphyrin isomers containing one aminotriptycene and one triptyceno-naphthoquinone were easily separated by chromatography in 63% yield.<sup>8</sup> The amino group was dimethylated with CH<sub>2</sub>O/NaBH<sub>3</sub>CN<sup>9</sup> to yield **1**: 85%; mass spectrum (<sup>252</sup>Cf fission fragment), *m/z* calcd 1081.5, found 1081.3. Compound **2** was prepared in a completely analogous fashion using **4**, 2-formyl-tritycene (**7**), and the pyrromethane: 23%; mass spectrum (<sup>252</sup>Cf fission fragment), *m/z* calcd 1038.5, found 1038.8. Compound **3** was also prepared by the analogous route using only **7** and the pyrromethane: 15%; mass spectrum (<sup>252</sup>Cf fission fragment), *m/z* calcd 982.5, found 982.5.<sup>10</sup>

One-electron redox potentials for these molecules are listed in Table I. The redox potentials of each donor and acceptor are not altered by their incorporation into **1** and **2**. In high dielectric constant solvents the sum of the redox potentials for oxidation of the donor and reduction of the acceptor is a good estimate of the radical pair energy level.<sup>11</sup> Thus, in compounds **1** and **2** the energy of P<sup>+</sup>Q<sup>-</sup> is 1.53 eV above the ground state, while in compound **1** the energy of D<sup>+</sup>PQ<sup>-</sup> is 1.39 eV above the ground state, where P = porphyrin, Q = quinone, and D = *N,N*-dimethylaniline. Since the lowest excited singlet state of these molecules is the 1.95-eV singlet state of the porphyrin, the exothermicity of the reaction <sup>1</sup>\*PQ → P<sup>+</sup>Q<sup>-</sup> is 0.42 eV and that of the reaction DP<sup>+</sup>Q<sup>-</sup> → D<sup>+</sup>PQ<sup>-</sup> is 0.14 eV. Using our measured rate vs. free energy data for porphyrin-quinone molecules possessing very similar molecular structure and virtually the same donor-acceptor distances,<sup>1</sup> we predict the following reaction rate constants: <sup>1</sup>\*PQ → P<sup>+</sup>Q<sup>-</sup>, 10<sup>11</sup> s<sup>-1</sup>; P<sup>+</sup>Q<sup>-</sup> → PQ, 8 × 10<sup>9</sup> s<sup>-1</sup>; DP<sup>+</sup>Q<sup>-</sup> → D<sup>+</sup>PQ<sup>-</sup>, 2.5 × 10<sup>10</sup> s<sup>-1</sup>. Thus, the secondary electron transfer reaction DP<sup>+</sup>Q<sup>-</sup> → D<sup>+</sup>PQ<sup>-</sup> should be able to compete very effectively with the DP<sup>+</sup>Q<sup>-</sup> → DPQ charge recombination reaction in **1**.

The ground-state optical absorption spectra of **1** and **2** are simply the sum of contributions from the individual chromophores, while the emission spectra are that of the unperturbed porphyrin alone. The fluorescence quantum yields of **1** and **2** are both 0.0002 and are highly quenched relative to the 0.06 fluorescence quantum yield of **3**. The fluorescence lifetimes of both **1** and **2** are <30 ps as determined by time-correlated photon counting. These data indicate that a better than 99% efficient nonradiative pathway for decay of the singlet excitation energy in **1** and **2** exists.

The nature of this pathway was determined by transient absorbance measurements. Compounds **1** and **2** were excited with

(8) Since the triptycyl groups undergo restricted rotation about the meso positions of the porphyrin, preparation of **1** results in only two pairs of enantiomers. The two diastereomers are separable by HPLC on a C<sub>18</sub> reversed-phase column using 5% THF in CH<sub>3</sub>CN. Photochemical data for each isomer were indistinguishable. This is probably due to the fact that the donor-acceptor distances of each isomer differ by <1 Å.

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