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Aggregation and Reactivity of the Dilithium and Dicesium Enediolates of 1-Naphthylacetic Acid[1]

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UV–vis spectra of the dilithium, **1**-Li, and dicesium, **1**-Cs, enediolates of α-naphthylacetic acid show no systematic change with concentration in dilute THF solution, but addition of small amounts of HMPA causes a bathochromic shift in the spectrum of **1**-Li. These results indicate that these salts are aggregated and that HMPA breaks up the aggregates of **1**-Li. The quantitative effect of small increments of HMPA indicates that **1**-Li is a dimer. Alkylation reactions of **1**-Cs show half-order kinetics in enediolate indicating that this salt is also dimeric but that the small amount of monomer in equilibrium is the actual reactant. Alkylation of **1**-Li, however, is much slower and shows first-order kinetics interpreted as a direct reaction of the dimer; the amount of monomer in this case is too small to compete. A solution of **1**-Li in THF containing 10% HMPA is much more reactive in alkylation than **1**-Li alone and the first-order dependence in **1**-Li is now interpreted as reaction of the monomer. Compound **1**-Li is found to form a mixed aggregate with LDA, a finding that has possible synthetic significance since enediolates used in syntheses are frequently prepared using LDA. Structures of these compounds are suggested based on model ab initio computations.

Introduction

Enediolates are of paramount importance in modern synthetic organic chemistry. Since Morgan and Harris[2] published the first alkylation reaction of the dipotassium salt of benzoylacetone, enediolate salts have become increasingly popular with synthetic chemists.[3–5] In recent decades, many papers have reported on the α-alkylation and aldol reactions of enediolates of carboxylic acids to provide chiral biological[6] and pharmacological[7] substances. The regio- and enantioselective reactions of enediolates with electrophiles can be influenced by such factors as different counterions,[8] the type of solvent used,[9]

addends, the reaction temperature, or the state of aggregation. We have recently reported the application of UV–vis spectroscopy and kinetics measurements to show that several lithium and cesium enolates of ketones are mixtures of monomers and dimers or tetramers but that alkylation reactions involve dominantly the monomers.[10–17] In this paper, we report the application of these methods to the dilithium and dicesium enediolates of a carboxylic acid. The use of both salts covers the ends of the alkali-metal range. Lithium salts are particularly useful, and the potassium salts often used synthetically should fall within this range close to cesium.

Earlier work showed that the deprotonation of 1-naphthylacetic acid, **1**, with a lithium base gives the dilithium

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enediolate **1**-Li, which is soluble in THF and has a remarkably low second pK of 23[18] on the lithium ion pair acidity scale.[19] In the present work, **1**-Li was prepared by reaction of the acid with trimethylsilylmethyllithium (LiTMS) in THF. The cesium salt was prepared using diphenylmethylcesium (CsDPM) or *p*-biphenylyldiphenyl-methylcesium (CsBDPM). The latter is especially convenient because its dark blue color serves as a useful endpoint indicator.
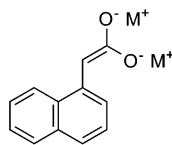
1-Li (M=Li)

1-Cs (M=Cs)

Dicesium Enediolate, 1-Cs. For several cesium enolates studied previously, the UV spectra change significantly over the concentration range studied, generally 10^{-3}–10^{-5} M, indicative of a change in aggregation over this range. The method of singular value decomposition (SVD)[20] could then be used to determine equilibrium constants among the aggregates.[12,14,15] The λ_{max} of **1**-Cs, however, changes by only a few nanometers from 476 nm over a 20-fold range (Figure S1, Table S1, Supporting Information), too small for application of the SVD technique. Because the conjugate acid of the enediolate, the cesium carboxylate, is also aggregated in THF solution, we could not use the method of coupled equilibria, the coupling of the aggregation equilibrium to the proton transfer equilibrium of an indicator. This method is applicable only if the conjugate acid is of known (usually monomeric) aggregation.

Aggregation of the enediolate was found from kinetic studies. The extinction coefficient for **1**-Cs, 6985 ± 33, was found from a plot of absorbance vs the formal concentration (Figure S2, Supporting Information) and was used to determine {**1**-Cs} in kinetic studies. Curly brackets {} are used to denote the formal concentration, the concentration of the enediolate moieties as measured by UV spectroscopy with the assumption that the effective extinction coefficient per moiety is independent of the aggregation state. Compound **1**-Cs is quite reactive in alkylation reactions, but its reaction with 1-chlorohexane has a convenient rate. The hexane was chosen rather than a lower alkyl group simply for reasons of volatility working at room temperature in a glovebox.

The kinetic data given in Tables S2 and S3 and Figure S3 (Supporting Information) show that its reaction with 1-chlorohexane, **2**, is first order in the alkyl chloride. Initial rates were determined from about the first 10% of reaction. A log–log plot of the initial rate with a large fixed excess of **2** and varying **1**-Cs has a slope of 0.53 (Figure S4, Supporting Information), showing that this

reaction is one-half order in **1**-Cs, the expected result if the active reagent is monomer in the presence of dominating amounts of dimer.

Dilithium Enediolate, 1-Li. The results with the lithium salt were quite different and more complicated. Dilithium salts of carboxylic acids are often prepared synthetically by reaction of the carboxylic acid with excess LDA. We started initially with this procedure, but the product **1**-Li had a λ_{max} value of 422–426 nm, quite different from that reported earlier, 442 nm, in which diphenylmethyllithium (LiDPM) was used as the deprotonating agent.[18] Because LDA is now known to form mixed aggregates with lithium enolates,[21] this phenomenon was studied in greater detail.

Addition of 2.2 equivalents of LDA to **1** in THF followed by removal of all volatiles and addition of fresh THF gave a solution whose λ_{max} changed with time from 412 to 425 nm. The direct reaction of **1** with LDA in a UV cell gave a λ_{max} of 424.5 nm, which changed over 14 h to 433 nm. Using lithiated hydrocarbons to deprotonate the carboxylic acid gave consistent and different results. Biphenylyldiphenylmethyllithium and trimethyldihydroanthracyllithium with **1** gave a λ_{max} close to 440 nm, similar to the results reported earlier with LiDPM.[18] Repetition using LiDPM confirmed that λ_{max} is close to 440 nm, but the overlapping spectra of the enediolate and LiDPA caused difficulty in locating the exact λ_{max}. LiTMS is an especially convenient deprotonating agent because of the absence of UV absorptions in this region. On reaction with **1**, it gave a λ_{max} value of 438 nm (ϵ = 9900 M^{-1} cm^{-1}; Table S4 and Figure S5, Supporting Information) with λ_{max} essentially unchanged over a 20-fold concentration range from 1×10^{-4} to 2×10^{-3} M. Addition of diisopropylamine to this solution causes no change in λ_{max}. Addition of 1 equivalent of LDA, however, results in a slow change of λ_{max} to 424 nm. We conclude that **1**-Li forms a mixed aggregate with LDA. One obvious implication is that since excess LDA is used so commonly to prepare dilithium enediolates, some reactions attributed to the enediolate might actually involve the mixed aggregate. Moreover, the fact that equilibration to form this mixed aggregate is slow even at room temperature suggests that **1**-Li is itself aggregated and that this aggregate is quite tight. When less than 2 equivalents (but more than 1) of base (LiTMS, LiDPM, and even LDA) was added to **1**, λ_{max} was consistently 438 nm; in these cases, a mixture of lithium carboxylate and enediolate result and there is thus no evidence that these form a mixed aggregate. Control experiments also showed that the addition of diisopropylamine (resulting from the protonation of LDA) does not influence the UV–vis spectra of the dilithium salt **1**-Li. Additions of small amounts of HMPA, however, do cause significant bathochromic shifts (Table S5, Supporting Information) up to λ_{max} = 466 nm. At still higher concentrations when the solvent is 10% HMPA, λ_{max} goes up only slightly more to 470 nm. Because HMPA does tend to break up enolate aggregates to monomers,[22] these results indicate that the observed λ_{max} of **1**-Li is that of an aggregate and that the

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(22) Leung, S. S.-W.; Streitwieser, A. *J. Org. Chem.* **1999**, *64*, 3390–3391. For comparison, electrochemical studies have also shown some dilithium enediolates in THF solution to be deaggregated by HMPA (Renaud, P.; Fox, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 5705–5709).
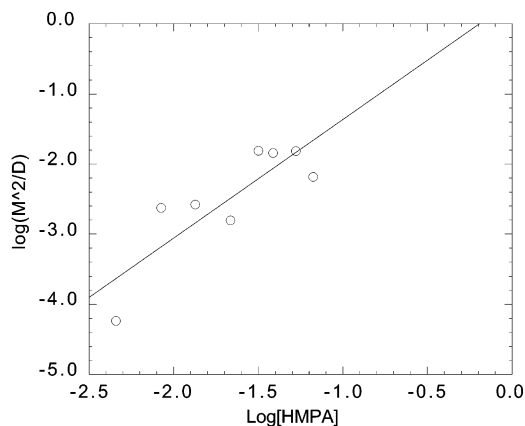
FIGURE 1. Log−log plot of [monomer]²/[dimer] and [HMPA] from addition of small amounts of HMPA to **1**-Li. The equation of the regression line is $0.33 \pm 0.75 + (1.69 \pm 0.44)x$; $R^2 = 0.71$.

FIGURE 2. Log−log plot of rate/[3] vs [**1**-Li]. Regression line is $-0.554 + 0.898x$; $R^2 = 0.981$.

equilibrium constant for aggregation is too high for detection of monomer.

The HMPA results do provide support that **1**-Li is a dimer. The analysis is based on previous work on the effect of HMPA on the spectrum of a lithium enolate.[22] We assume that **1**-Li is a dimer and that HMPA acts according to eq 1. The corresponding equilibrium constant is then defined by eq 2.

$$(Li_2En)_2 + 2n\,HMPA \overset{K}{=} 2\,Li_2En \times nHMPA \quad (1)$$
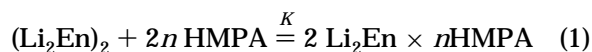
$$K = [Li_2En \times nHMPA]^2/([(Li_2En)_2][HMPA]^{2n}) \quad (2)$$

We assume that the λ_{max} for $Li_2En \times nHMPA$ is 466 nm and that the λ_{max} of a mixture corresponds to the mole fraction, f, of Li_2En moieties with a λ_{max} value of 439 nm, that is, eq 3.

$$f(Li_2En \times nHMPA) = (\lambda_{max} - 439)/(466 - 439) \quad (3)$$

With the further assumption that the extinction coefficient of Li_2En moieties is the same in $Li_2En \times nHMPA$ as in the dimer, we can deduce the concentrations of M (monomer = $[Li_2En \times nHMPA]$) and D (dimer = $[(Li_2En)_2]$). A plot of $\log(M^2/D)$ vs $\log[HMPA]$ from several experiments in which small amounts of HMPA were added to **1**-Li is shown in Figure 1. This is a difficult experiment with various sources of error, and the plot shows significant scatter. Nevertheless, the slope of this plot, 1.69 ± 0.44, which equals $2n$ in eq 1, is consistent with **1**-Li being a dimer with $n = 1$; that is, each lithium in the monomer is coordinated to one HMPA. Similar plots for the assumption that **1**-Li is a higher aggregate give increased scatter and higher probable errors. From Figure 1, the equilibrium constant, K, of eqs 1 and 2 has the approximate magnitude of only 2.

Additional insight comes from kinetics. A series of initial rates (first 10% reaction) were determined over a 9-fold range of **1**-Li concentrations and a fixed much larger concentration of *p-tert*-butylbenzyl chloride, **3**. A log−log plot of the data of two separate runs (Table S6, Supporting Information) in Figure 2 has a slope of 0.90; that is, the reaction is first-order in the aggregate. The combined series of 11 runs gives $k_2 = 0.60 \pm 0.06$ M^{-1}
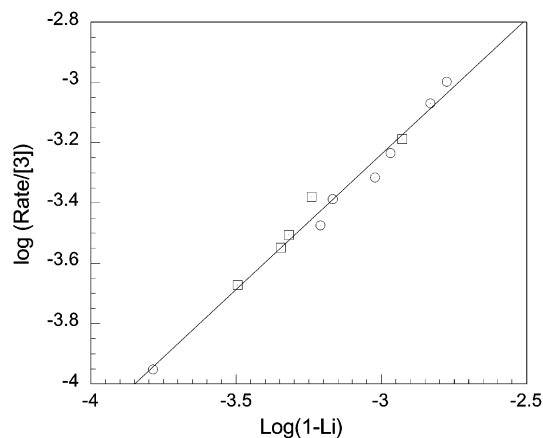
s^{-1} (uncertainty given as standard deviation). This reaction thus appears to be a direct reaction with the dimer and implies that the concentration of monomer is too low to compete. Nevertheless, this reactivity is much greater than that of the small amount of lithium enolate monomer present (vide infra). The alternative that the measured rate is that of a slow dissociation to reactive monomer requires that the reaction rate then be independent of the alkyl halide used; however, the reaction of benzyl bromide (BnBr) is much faster than that of **3**.

Kinetic measurements were also made of **1**-Li in THF containing 10% HMPA. From the spectral results discussed above, the enediolate in this solution should be monomeric with its lithiums coordinated to HMPA. Reaction with the benzylic chloride **3**, however, was now too fast to measure; instead, kinetic measurements were made with 1-chlorohexane, **2**. The data shown in Table S7 and Figure S8 (Supporting Information) for varying [**2**] and fixed {**1**-Li} show that this alkylation is still first-order in alkyl halide. Kinetic runs with a fixed concentration of **2** and varying {**1**-Li} give a log−log plot with a slope of 0.99 (Table S8 and Figure S7, Supporting Information), showing that in the presence of HMPA the reaction is first-order in the enediolate, undoubtedly the reaction of the HMPA-coordinated monomer. This result is also shown by the linear plot of rate vs {**1**-Li} shown in Figure 3. The second-order rate constant cannot be compared directly with that of **1**-Cs because of the different kinetic order of the latter; however, at similar reagent concentrations, the actual reaction rates are comparable, but the reactions of **1**-Cs are of a small amount of monomer in equilibrium with the dimer whereas the **1**-Li reactions in HMPA−THF are of the monomer. We conclude that the reactivity of monomeric **1**-Cs is much greater than that of **1**-Li (HMPA−THF), which, in turn, is much greater than the dimeric **1**-Li.

In measuring the reactivities, it would have been most desirable to use a common alkylation substrate but we were limited by having to measure rates within a reasonable time range. At the dilute solutions of **1**-Li and **1**-Cs required for spectral measurement, reactions that are too slow to compete with adventitious quenching. Nevertheless, by combining the present measurements with other rate constants derived from reactions of monomeric lithium and cesium enolates, some interesting
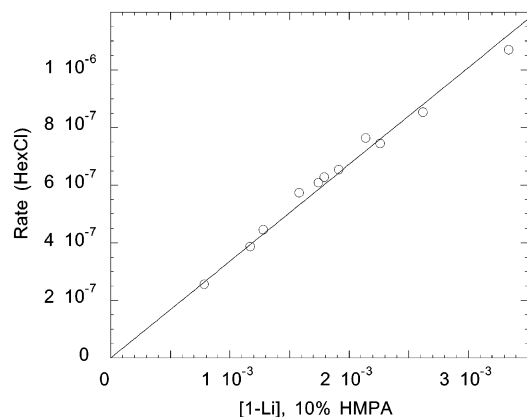
FIGURE 3. Rate of reaction of **1**-Li with 0.105 M **2** in 10% HMPA/THF at 25 °C. The slope of the line shown is $(3.36 \pm 0.05) \times 10^{-4}$ s^{-1} ($R^2 = 0.982$) giving a second-order rate constant = 3.20×10^{-3} M^{-1} s^{-1}.

further relationships can be derived. For example, from the reactions of the monomeric cesium enolate of biphenylylcyclohexanone (CsBPCH) with methyl brosylate and *n*-hexyl bromide (HexBr)[14] and of the corresponding lithium enolate (LiBPCH) with methyl brosylate and BnBr,[13] the reactivity ratio, BnBr/HexBr = 6×10^4, can be derived. The relative reactivity of *p-tert*-butylbenzyl bromide and BnBr toward the lithium enolate of *p*-phenylisobutyrophenone is 1.3;[10] thus, *p-tert*-butylbenzyl bromide is 7×10^4 more reactive than HexBr. We next assume that the corresponding chlorides have a comparable reactivity ratio. From k_2 of **1**-Li in 10% HMPA, 3.2×10^{-3}, the corresponding k_2 with **3** would then be 230 M^{-1} s^{-1}, which is 400 times greater than k_2 for the reaction of the dimer of **1**-Li with **3**. This relative reactivity of monomer and dimer is of a reasonable order of magnitude as compared to the relative reactivities of the monomer and dimer of the lithium enolate of *p*-phenylisobutyrophenone with *p-tert*-butylbenzyl bromide, 3000.[11] With a relative reactivity for the monomer and dimer of 400, the amount of monomer present must be less than 0.1% to show first-order kinetics in {**1**-Li}. Such a small amount of monomer would not be detectable by our UV spectroscopic technique.

On the other hand, a comparable reactivity ratio for the monomer and dimer of **1**-Cs then requires that the amount of monomer present in our solutions of **1**-Cs must be of the magnitude of 1%. Any larger amounts would have given observable spectral changes with concentration, and much smaller amounts would not have produced half-order kinetics. If the kinetic solutions of **1**-Cs (about 10^{-3} M) contained 1% monomer, k_2 for the reaction of monomer with **2** would then be about 2 M^{-1} s^{-1} or about 600 times the reactivity of monomeric **1**-Li. This number can be compared with the relative reactivities of monomeric CsBPCH and LiBPCH toward methyl brosylate, 100.[13,14] Finally, we can compare the relative reactivities of the monomer of **1**-Li with that of the monomers of lithium enolates. The latter vary over a wide range; for example, LiBPCH is 20 times as reactive toward BnBr as is the lithium enolate of 2,6-diphenyl-α-tetralone.[16] The corresponding relative rates of monomeric **1**-Li are 150 and 3000, respectively.

Other Addends. Results discussed above show that LDA forms a mixed aggregate with **1**-Li. Compound **1**-Li was prepared from **1** and LiTMS and was then treated with LDA in a slow equilibrium. After 1 week, initial rates were measured with **3** (Table S9, Supporting Information). A log−log plot of rate/[**3**] with the concentration of the **1**-Li−LDA complex is linear with slope = 1.0, indicative of first-order dependence on the mixed aggregate. A direct plot of rate/[**3**] with {**1**-Li−LDA} gives $k_2 = 0.090$ M^{-1} s^{-1}, 0.15 times the rate of **1**-Li in the absence of LDA. The slow equilibrium formation of the reaction between **1**-Li and LDA suggests that the LDA reacts with the monomer to form the complex but the stoichiometry of the mixed aggregate is not known. It is likely, however, to consist of one enediolate with one or two molecules of LDA (vide infra).

Pentamethyldiethylenetriamine (pmdta) is known to be an excellent ligand for lithium cation because of its three coordination sites; for example, it converts some organolithium dimers to monomers.[23,24] It causes a spectral change when added to **1**-Li; the λ_{max} value changes from 438 to 443 nm. The longer wavelength is indicative of a weaker interaction between the enediolate anion and the lithium cations. Starting with **1**-Li prepared with LDA and having a $\lambda_{max} = 424$ nm, up to 4 equivalents of pmdta had no effect but increasing amounts caused an increase in λ_{max} until at 5% pmdta in THF, λ_{max} was 444 nm and did not change further up to 43% pmdta in THF. The resulting species is probably the same as that produced from **1**-Li directly and indicates that many equivalents of pmdta break up the enediolate−LDA complex, probably by also solvating the separated LDA. A series of kinetics experiments with **1**-Li in 10% pmdta−THF reacting with **3** showed first-order behavior in {**1**-Li} with $k_2 = 0.24 \pm 0.01$ M^{-1} s^{-1} (Table S10, Figure S9, Supporting Information), a reactivity 0.4 that of **1**-Li in THF alone. It seems likely from these data that the species in pmdta is the dimer solvated by pmdta.

Lithium bromide has previously been shown to form a 1:1 mixed aggregate with the lithium enolate of *p*-phenylsulfonylisobutyrophenone.[25] The mixed aggregate has a λ_{max} value at a shorter wavelength than the enolate. LiBr added to **1**-Li also causes a hypsochromic shift, from 438 to 430 nm indicative of the formation of a mixed aggregate. Addition of up to 25 equivalents of LiBr to the **1**-Li−LDA complex gave no change in its λ_{max}, indicating that the LiBr complex is less stable than the LDA mixed aggregate.

Computations

Attempts were made to obtain crystals of **1**-Li suitable for X-ray structure analysis but without success. Thus, to gain some insight into the structures of these compounds, we undertook some ab initio computations of the parent system $CH_2=C(OLi)_2$ **4** and its dimer **5** at the HF/6-31+Gd[26,27] level using Spartan[28] and Gaussian98.[29] The coordinates and energies of all structures discussed are

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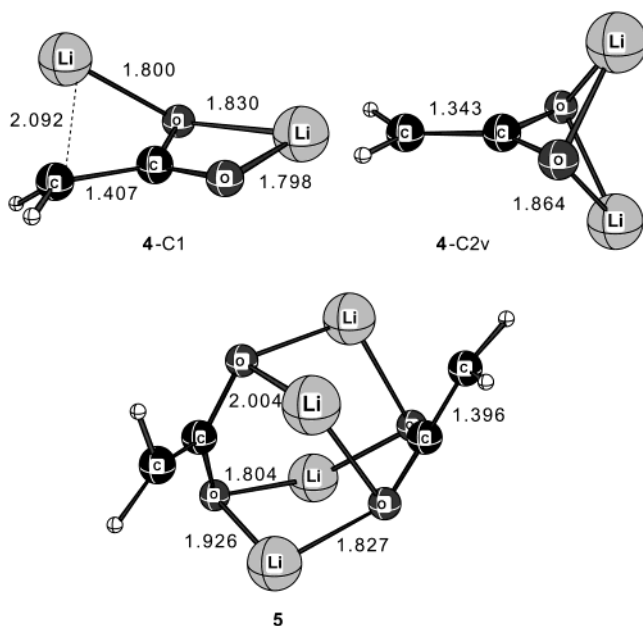(26) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217.

FIGURE 4. Computed structures of $CH_2=C(OLi)_2$ monomers and dimer at HF/6-31+G*.

FIGURE 5. Computed structures for 1:1 and 1:2 mixed aggregates between $CH_2=C(OLi)_2$ and $LiNH_2$ (HF/6-31+G*).

given in the Supporting Information. Two structures were found for **4**, a C2v structure that resembles the cyclic structures of enolate dimers, and a less symmetrical C1 structure (Figure 4). Both are minima on the PES with all frequencies real, but the C1 structure is the more stable by 14.9 (with inclusion of zero point energies (ZPE) corrected by 0.9135,[30] the difference is 14.8) kcal mol^{-1}. In the C1 structure, the three Li−O bonds vary from 1.80 to 1.83Å; in the C2v structure, the four equivalent O−Li bonds are longer at 1.86Å. In the C1 structure, the lithium can also be seen to be clearly coordinated to the methylene group, not only by the C−Li distance, 2.09Å, but also by the pyramidal methylene group (Figure 4).

A C2 dimer structure, **5**, was found to be a minimum on the PES in which the Li−O bonds form a chair octagonal ring. This structure is a distortion of the ubiquitous Li−O cubic structures found for lithium enolate tetramers because two pairs of oxygens are held together by the vinylidene groups. The four Li−O bonds vary from 1.80 to 2.00Å. Dimerization of the C1 monomer to the dimer is exothermic by 63.8 (61.8 with ZPE) kcal mol^{-1}. This number can be compared with the dimerization energy of the dimer of lithium vinyloxide, (LiOV)$_2$,
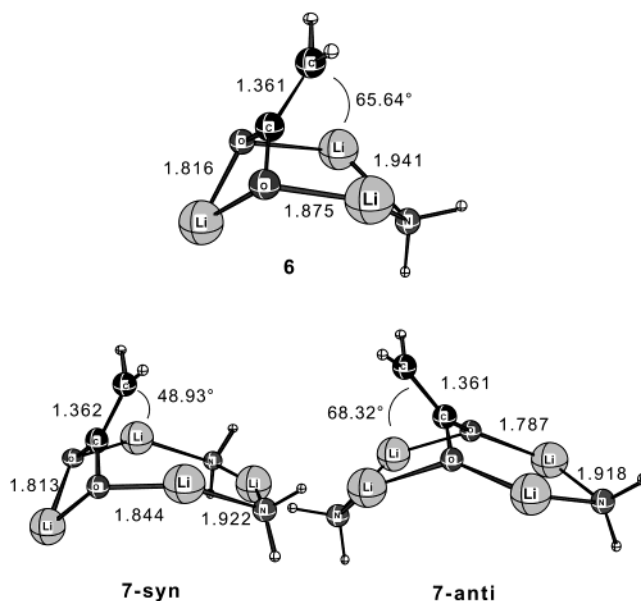
to the tetramer, (LiOV)$_4$, at the same basis set level, −48.5 (−46.6 with ZPE) kcal mol^{-1}, a large difference, which indicates that the enediolate dimer is more tightly held together. This difference would undoubtedly be reduced by solvation energies but would probably remain substantial.

To get some idea of the magnitude of these solvation energies, computations were also made on structures with each lithium coordinated to a molecule of dimethyl ether, **4·2E**. Coordination of the C1 monomer with two ethers is exothermic by 35.8 (33.8 with ZPE) kcal mol^{-1}; similar coordination of the C2v monomer is exothermic by 39.4 (37.2 with ZPE) kcal mol^{-1}. Thus, the coordinated C1 structure is still 11.3 (11.4) kcal mol^{-1} more stable. It seems likely that the monomer of **1**-Li solvated by HMPA has a similar structure to **4·2E** with the dimethyl ether moieties replaced by HMPA.

Computations were made for possible mixed aggregate structures with lithium amides. For these model studies, $LiNH_2$ was used instead of LDA. A Cs structure, **6**, was found for the 1:1 complex of the monomer with $LiNH_2$ (Figure 5). This structure is a minimum on the PES (all frequencies real) but is not particularly stable. The reaction of the dimer **5** with the dimer of $LiNH_2$ in eq 4 is endothermic by 5.4 (5.3) kcal mol^{-1}.

$$1/2 \; \mathbf{5} + 1/2 \; (LiNH_2)_2 = (CH_2=C(OLi)_2) \times LiNH_2 \; (\mathbf{6}) \quad (4)$$
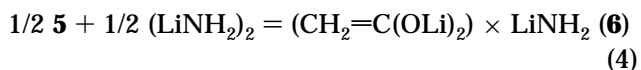
Two structures were found for the complex with two $LiNH_2$ moieties, a Cs syn (**7**-syn) and a more stable Cs anti (**7**-anti). The C2v analogue of **7**-anti with the vinylidene groups symmetrical between the two rings is a transition structure 0.9 kcal mol^{-1} higher in energy (one imaginary frequency). The reaction of the dimer **5** with the dimer of $LiNH_2$ to form **7**-anti (eq 5) is exothermic by 19.6 (19.2) kcal mol^{-1}. This large energy change suggests that the complex of **1**-Li with LDA might contain two molecules of LDA.

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$$1/2\ \mathbf{5} + (LiNH2)2 = (CH_2{=}C(OLi)_2) \times$$
$$2LiNH_2\ (\mathbf{7}\text{-anti})\quad (5)$$
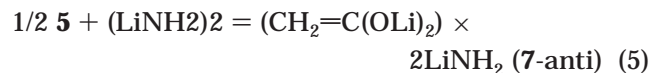
There might well be other structures that are minima on the PES of these systems, but the structures found appear to be reasonable as models and are consistent with the known chemistry of the real compounds.

Conclusions

The dilithium (**1**-Li) and dicesium (**1**-Cs) salts of α-naphthylacetic acid are present dominantly as dimers in dilute THF solution at 25 °C. The reaction of **1**-Cs with alkylating agents is primarily with the small amount of monomer in equilibrium; however, for **1**-Li, the amount of monomer present is too small to compete and alkylation occurs dominantly with the dimer. Alkylation with **1**-Li is much slower than with **1**-Cs. Small amounts of HMPA break up the dimers of the dilithium enediolate to monomers that are undoubtedly solvated by HMPA; these monomers show enhanced reactivity in alkylation as compared to the dimer of **1**-Li but are slower than reaction of **1**-Cs monomers. Pentamethyldiethylenediamine is effective in solvating **1**-Li but the species present is probably still the dimer. Compound **1**-Li was shown to form mixed aggregates with LDA and LiBr. Ab initio computations at HF/6-31+G* of model systems give reasonable structures and relative energies consistent with the experimental systems.

Experimental Section

UV−visible absorption spectra were carried out in a Vacuum/ Atmospheres Company glovebox under inert argon atmosphere as in previous studies from this laboratory. Reactants were purified as needed by multiple recrystallizations/distillations and molecular distillations/sublimations until purity was ascertained by physical constants and spectra. Compound **1**-Li was prepared by the reaction of α-naphthylacetic acid with organolithium reagents as described in the text. Solutions were stable for several weeks at 0 °C. LDA was prepared by reaction of *n*-butyllithium with diisopropylamine at 0 °C. The crude product was sublimed twice at 90 °C. CsBDPM was prepared by reaction of biphenylyldiphenylmethane with CsDPM in THF over 24 h. The dark blue solution was stable for several weeks at 0 °C. CsDPM in turn was prepared by reaction of diphenylmethane with cesium metal in THF over 24 h. The dark blue solution was stable for several weeks at 0 °C.

Supporting Information Available: Figures S1−S9; tables S1−S10; energies, ZPE, and coordinates of HF/6-31+G* computations. This material is available free of charge via the Internet at http://pubs.acs.org.

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