

Solution Structures of Lithium Enolates of Cyclopentanone, Cyclohexanone, Acetophenones, and Benzyl Ketones. Triple Ions and Higher Lithiate Complexes

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Abstract: Multinuclear NMR spectroscopic studies at low temperature (−110 to −150 °C) revealed that lithium p-fluorophenolate and the lithium enolates of cyclohexanone, cyclopentanone and 4-fluoroacetophenone have tetrameric structures in THF/Et₂O and THF/Et₂O–HMPA by study of the effects of the addition of HMPA. The *Z* and *E* isomers of the lithium enolate of 1,3-bis-(4-fluorophenyl)-2-propanone (**5F-Li**) show divergent behavior. The *Z* isomer is completely dimeric in pure diethyl ether, and mostly dimeric in 3:2 THF/ether, where monomer could be detected in small amounts. TMTAN and PMDTA convert *Z*-**5F-Li** to a monomeric amine complex, and HMPA converts it partially to monomers, and partially to lithiate species (RO)₂Li[−] and (RO)₃Li^{2−}. Better characterized solutions of these lithiates were prepared by addition of phosphazanium enolates (using P4-^tBu base) to the lithium enolate in 1:1 ratio to form triple ion (RO)₂Li[−] P4H⁺, or 2:1 ratio to form the higher lithiate (RO)₃Li^{2−} (P4H⁺)₂ (quadruple ions). The *E* isomer of **5F-Li** is also dimeric in 3:2 THF/Et₂O solution, but is not detectably converted to monomer either by PMDTA or HMPA. In contrast to *Z*-**5F-Li**, the *E* isomer is tetrameric in diethyl ether even in the presence of excess HMPA. Thus for the two isomers of **5F** six different enolate structures were characterized: tetramer, dimer, CIP-monomer, SIP-monomer, triple ion, and quadruple ion.

Introduction

NMR spectroscopy is a powerful tool for the determination of solution structures of lithium species, especially for those in which lithium is bonded to an NMR-active nucleus where Li–X *J*-coupling can be detected (i.e., having a Li–C,^{1,2,3a,4a–c} Li–N,^{4d,5,6a} Li–Si,⁷ Li–P,^{4e,8} Li–Sn,^{4f,9} or Li–Se^{4e} contact). Structure determination of species where X does not have useful NMR properties, especially Li–O compounds, cannot rely on coupling, and less direct information must be used.

Classically, the principal techniques for determining aggregation state are vapor pressure osmometry and freezing point depression, combined with X-ray single crystal studies. Crystal structures can only provide leads as to possible solution structures, and colligative property studies are prone to error because of the great sensitivity

of the results to sample purity and stability. Ketone and other carbonyl alkali metal enolates are widely applied as carbon nucleophiles, and the relevance and importance of aggregation phenomena to their chemistry was recognized by early work of Seebach,^{3b} Jackman,^{10a,b} and Arnett,^{12a} and reinforced by numerous more recent studies.^{6b,11a,b,13–15} Cyclopentanone lithium enolate in THF gave *n* = 5.6^{12b} by vapor pressure osmometry, and *n* = 2.7^{3c} by freezing point depression illustrating the problem with the various techniques. The lithium enolates of cyclohexanone (*n* = 3.4^{12b}), acetophenone (*n* = 3.2^{12b}) and pinacolone (*n* =

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4.0^{12b}) in THF showed average aggregation numbers close to tetrameric. Crystal structures of the lithium enolates of cyclopentanone–THF,^{3d} pinacolone–THF,^{3d} pinacolone–pyridine,¹³ and others^{3e,15} also showed cubic tetramers.

The Streitwieser group has developed quantitative UV-spectroscopy based techniques (coupled equilibria,^{11c} singular value decomposition^{11d}) for assessing aggregation state of enolates. The technique allows measurement of equilibrium constants and identification of the principal aggregated species, but requires systems with a usable UV absorption whose maximum is sensitive to the aggregation state, and the presence of two different aggregates in detectable amounts. Thus only enolates in which either the carbonyl carbon or α -carbon bears an aryl group have been studied. Several of the enolates (e.g., 6-phenyl- α -tetralone,^{11a} *p*-phenylisobutyrophenone^{11e}) are mixtures of tetramers and monomers.^{11a} However, when the α -position is fully substituted or there is a conjugating α -phenyl substituent (as in 2-benzyltetralone,^{11a} 2-phenyl tetralone,^{11f} or 2-biphenylcyclohexanone^{11g}) the enolates are predominantly dimeric in THF, with detectable amounts of monomer. Of interest in connection with the current study is the lithium enolate of 1,3-diphenylacetone, which is mainly dimer in THF solutions, with detectable amounts of monomer.^{11b}

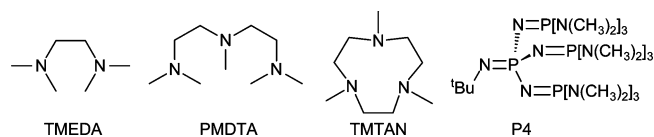
NMR spectroscopic determinations of solution aggregate structure have also utilized techniques in which the symmetry of the homoaggregates is broken by the formation of mixed aggregates. Careful NMR studies of isobutyrophenone enolate suggested a tetrameric structure in THF and dioxolane based on several lines of indirect evidence, including molecular size

measurements using relaxation times, and ¹³C chemical shifts. A key observation was the formation of a 3:1 mixed aggregate with LiCl.^{10a} Of course, the reliability of mixed aggregate techniques for establishing homoaggregate structures depends on the structural similarity of the components. In this regard the use of isotopic labeling, as in the classical study of partially ¹³C-enriched methyllithium^{1b} or the ⁶Li isotope shifts of mixed aggregates between deuterated and undeuterated organolithium reagents¹⁶ can provide unambiguous information, and studies of very similar mixtures can also be productive, such as the work confirming an aryllithium triple ion structure by the formation of a mixed triple ion between two aryllithium reagents.^{4g} Definitive studies by Collum and co-workers have recently systematized and extended the mixed aggregate approach (method of continuous variation) to the structures of several enolates, including those of cyclopentanone, cyclohexanone, and indanone, all of which were found to be tetramers in THF solution.^{6c}

The HMPA Titration Technique. Some years ago we introduced an NMR technique which employs the advantageous NMR properties of HMPA (O=P(NMe₂)₃) to probe solution structures of lithium species.^{4h} Several other laboratories have also reported such experiments.^{6e,8b,10c,17} Although there is a significant element of “Heisenberg Uncertainty Principle” in using a powerful cosolvent to probe structure in the absence of the cosolvent (the probe changes the object studied), a careful HMPA titration monitored by low-temperature (<–120 °C) ⁷Li, ⁶Li, ¹³C and ³¹P NMR spectroscopy (as well as other nuclei when available) can often provide valuable structural insights. The technique is usually very specific for detecting contact/separated ion pair status (SIP/CIP) of monomers^{4c,e,f,i} but higher aggregates, as usually found for enolates, can also be analyzed (e.g., MeLi tetramer^{4h}). Less definitive results can be expected because of the aforementioned uncertainly principle.

When LiX dimers are present, the HMPA titration usually takes a course in which mono and bis-HMPA-solvated dimers can be detected, followed by one or more HMPA-solvated monomeric CIP species (e.g., LiCl^{4h}). For some systems ion pair separation occurs, others form significant fractions of triple ions of the LiR₂[–]Li⁺ type.^{4g,m} In solvents less polar than THF, HMPA-bridged dimers form.^{4b,f}

The few tetramers that have been studied (MeLi,^{4h} ArOLi^{10c}) typically go through a series of complexes with HMPA coordinated to the corners of the cubic structure. Lower aggregates sometimes appear late in the titration. SIPs are not seen. Free HMPA often appears even before one equivalent of HMPA has been added (i.e., the HMPA-affinity of the triply coordinated lithium is low).



Addition of other coordinating cosolvents also provides insights into solution structures, with TMEDA often favoring dimers,^{6c,d} whereas PMDTA and TMTAN frequently produce monomers.^{4b,18}

Results and Discussion

Cyclopentanone Lithium Enolate (1-Li). The lithium enolate of cyclopentanone has been examined several times. Crystallization from THF solution gave a tetrasolvated tetramer.^{3d}

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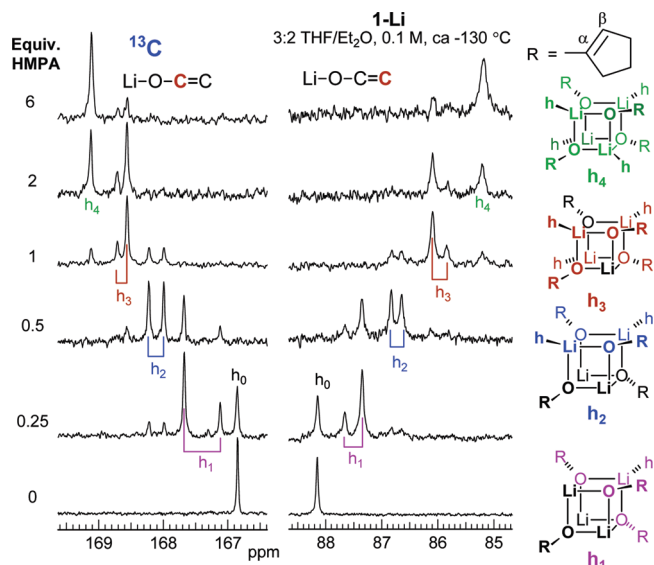
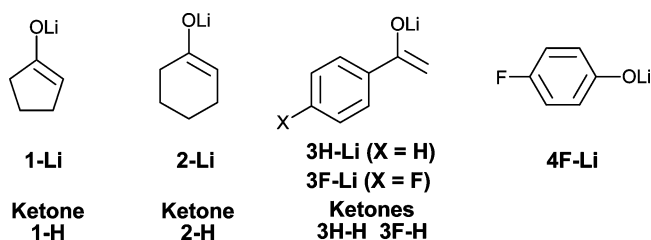


Figure 1. HMPA titration of 0.1 M solution of cyclopentanone lithium enolate **1-Li** followed by ^{13}C NMR spectroscopy in 3:2 THF/Et₂O at -130°C (h = HMPA). Only C- α (left) and C- β are shown.

Vapor pressure osmometry in THF at 37°C gave an aggregation number of 5.6,^{12b} whereas freezing point depression in THF at -108°C gave $n = 2.7$.^{3c} A recent low-temperature ^7Li , ^{31}P and ^{13}C NMR study of **1-Li** in several solvents, including an analysis of the effect of HMPA as well as on T_1 relaxation times, led to the conclusion that the major species below -100°C was a dimer in ether solvents (Me₂O, Et₂O, THF^{19a,b}) as well as with HMPA present and that this dimer was the kinetically active species in alkylation reaction of the enolate.^{19b} Although these various results were not all obtained under the same conditions, they cannot be easily reconciled. In connection with our studies comparing the reactivity of stabilized carbanion species generated either by deprotonation with lithium bases or by fluoride cleavage of silanes toward cyclohexenone,^{4j} we had occasion to examine **1-Li** and other enolates by NMR spectroscopy. We report these results below.



In THF/Et₂O solution **1-Li** shows only a single set of signals in the ^7Li and ^{13}C NMR spectra at low temperature, indicating the presence of a single aggregate. The HMPA titration (Figure 1) can be unambiguously interpreted in terms of the consecutive

coordination of four HMPA molecules to the four lithiums of a cubic tetramer. The first-formed solvate (h_1) has the expected 3:1 ratio of two sets of vinyl ^{13}C signals, as well as a 3:1 ratio of a singlet and doublet ($J_{\text{Li-P}} = 9.6$ Hz) in the ^7Li NMR spectrum²⁰ expected for the mono-HMPA complex of a cubic tetramer. This is followed by a species with 1:1 ^{13}C signals, the bis-HMPA solvate h_2 , one with a 1:3 ratio of signals, the tris-HMPA solvate, and finally the tetra-solvated tetramer with only one set of ^{13}C signals and one doublet ($J_{\text{Li-P}} = 8.7$ Hz) in the ^7Li NMR spectrum. The ^{13}C chemical shifts move downfield for the α -carbon (the C–O carbon) and upfield for the β -carbon in a logical progression that strongly suggests that all five species detected are tetramers. The regular shifts also show that the charge polarization of the enolate carbons steadily increases as the coordinated THF molecules are replaced by the stronger donor HMPA.

This behavior is inconsistent with a dimer structure, except in the unlikely event that the first equivalent of HMPA completely converted the THF-dimer to the HMPA-coordinated tetramer. A mild form of such behavior was observed in the HMPA titration of lithium 4-bromophenolate,^{10c} which goes from a dimer–trimer–tetramer mixture in THF to only tetramer as HMPA was added. However, in that case the chemical shifts clearly reflect this change, with the 2-carbon of the THF-solvated phenolate dimer being *upfield* of that of the HMPA-complexed tetramer, whereas for **1-Li** the β -carbon in the THF species is over 3 ppm *downfield* of the HMPA-complexed tetramer. We conclude that **1-Li** is a tetramer in THF as well as in THF–HMPA. Application of the method of continuous variation led to the same conclusion.^{6c} Earlier work¹⁹ pointing to a dimer structure relied heavily on ^7Li and ^{31}P NMR spectra,²⁰ which show very closely superimposed chemical shifts for the various species.

Jackman and Lange reported a substantial upfield shift of 2.6 ppm for the β -carbon of the lithium enolate of isobutyrophenone on going from the tetramer in dioxolane to the dimer in DME, consistent with higher electron density at the β -carbon.^{10d} It would be tempting to interpret the similar shifts for **1-Li** on coordination to HMPA as a consequence of aggregate dissociation. However, the spectra for **1-Li** clearly show that chemical shift changes of this size can be explained without any change in aggregation state, but are a natural consequence of the stronger coordination of HMPA to the lithium in an intact tetramer. Similar HMPA-solvation shifts are seen for other Li–OR species discussed below.

The appearance of uncoordinated HMPA correlates strongly with the aggregation state. For SIP monomers, or monomers that are easily separated (like LiI^{4h}) free HMPA does not appear until after 3 equiv have been added, whereas higher aggregates invariably show an earlier appearance (Figure 2). This is a natural consequence of the fact that free lithium cations have at least four coordination sites per lithium, monomers up to three, dimers two, and tetramers only one. In the HMPA titration of **1-Li** free HMPA appears after approximately 0.5 equiv have been added, i.e. long before all available sites are coordinated. Normally HMPA avidly displaces THF from lithium, by one measure a factor of 290 better,^{4k} and this observation suggests that the tetramer in THF is also only partially solvated (i.e., on

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(20) See Supporting Information for additional spectra and experimental details.

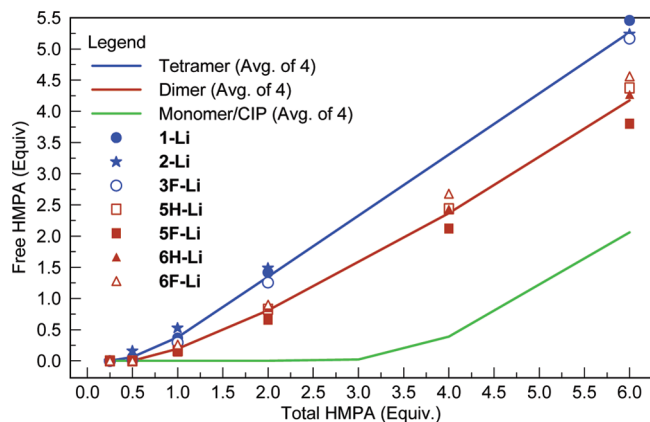


Figure 2. Appearance of free HMPA for various LiX species in 3:2 THF/Et₂O at 125 °C.

average some of the Li coordination sites are vacant, as has been shown for a lithium pinacolate–pyridine complex¹³.

Cyclohexanone Lithium Enolate (2-Li). The ¹³C NMR spectral data of **2-Li** in THF and DME solution have been reported.²¹ We confirmed the ¹³C NMR shifts at δ 159.6 and δ 89.6 for the vinyl carbons.

The HMPA titration of **2-Li**²⁰ closely follows the cyclopentanone pattern of Figure 1, including the appearance of 1:3, 2:2, and 3:1 signal pairs, and systematic changes in the ¹³C chemical shifts as the individual lithiums become coordinated by HMPA. By these criteria, cyclohexanone enolate is a tetramer in THF, and this was also the conclusion based on the method of continuous variation.^{6c}

***p*-Fluoroacetophenone Lithium Enolate (3F-Li).** The structure of acetophenone enolate in THF has been examined only in a limited way. Arnet and Moe obtained aggregation numbers for the lithium enolates of acetophenone (3.8 ± 0.5) and three acetophenone derivatives [*o*-methoxy (3.3 ± 0.4), *p*-methoxy (3.3 ± 0.2), and *p*-nitro (2.4 ± 0.1)] in THF at 37 °C using vapor pressure osmometry.^{12b} Thus, the electron-rich acetophenone enolates appear to be largely tetrameric, with the electron-poor ones tending toward a dimer aggregation state.

We examined the *p*-fluoro derivative **3F-Li** to take advantage of the superior NMR properties of a fluorine label for structural as well as kinetic studies.²² The Hammett constants for para fluoro are $\sigma_p^n = 0.06$, $\sigma_p^- = 0.02$,²³ so little electronic perturbation is expected. In fact, the various NMR studies of **3H-Li** and **3F-Li** show nearly identical behavior.²⁰ The lithium enolate **3F-Li** was determined to be a tetramer in THF—either based on the HMPA titration shown in Figure 3. Expected ratios for the HMPA solvates are observed in the ¹⁹F, ¹³C, and ⁷Li NMR spectra. The ¹³C NMR shifts for the C–O carbon are more complex than the monotonic changes seen for cyclopentanone and cyclohexanone enolates **1-Li** and **2-Li**, possibly due to varying steric interactions of the coordinated solvents with the conjugating aromatic ring. However, the ¹⁹F NMR signals shift systematically upfield for the HMPA solvates in a way consistent with increasing electron density in the aromatic ring as THF is replaced by HMPA on the lithium.

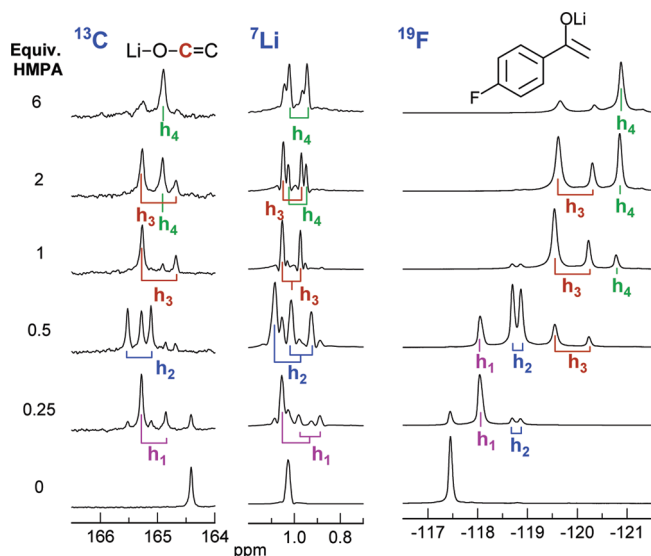


Figure 3. HMPA titration of 0.1 M solution of (**3F-Li**)₄ followed by ¹⁹F, ¹³C (only the C–O carbon), and ⁷Li NMR spectroscopy in 3:2 THF/Et₂O at –120 °C (h = HMPA).

We have also examined the effect of chelating cosolvents on **3F-Li** and found that, like HMPA, neither TMEDA nor PMDTA formed any detectable amounts of lower aggregates in THF solution. Collum and co-workers also found that several enolate tetramers are little affected by TMEDA in THF solution, but are converted to dimers by TMEDA in the absence of an ether cosolvent.^{6c}

Lithium Phenolate. The aggregation behavior of phenolates has been studied by colligative property measurements^{12b} and by the HMPA titration technique.^{10c} Unhindered phenolates have been shown to be largely tetrameric, unless there are electron-withdrawing substituents (*p*-bromo- and *p*-trifluoromethylphenolates), in which case dimers are present, which show the remarkable property of forming increasing amounts of tetramer as the lithium becomes coordinated to HMPA. The solid-state structures of lithium phenolates have revealed many different aggregation states from hexamers, tetramers, trimer, and dimers, depending on solvent and structure.²⁴ Lithium phenolates have been used as models for lithium enolates due to their convenience of handling and absence of *E*- and *Z*-isomer complications. Their structure can be easily modified, which often produces differing aggregation states. We briefly examined the behavior of a simple phenolate, lithium *p*-fluorophenolate, with HMPA to compare its behavior with that of lithium enolates.

Lithium *p*-Fluorophenolate (4F-Li). Lithium *p*-fluorophenolate has been investigated in TMEDA/hydrocarbon solution and was found to be dimeric,^{6d} but the structure in THF is unknown, although it would be expected to be very similar to lithium phenolate itself, which is tetrameric.^{12b} We find that **4F-Li** in 3:2 THF/Et₂O and pure Et₂O displayed the appropriate ratios of signals of a tetramer (Figure 4). The titration diverges from those of the tetrameric enolates at one equivalent of HMPA, where the phenolate is mostly tetra solvated, whereas the tetrameric enolates, **1-Li**, **2-Li**, **3H-Li**, and **3F-Li** required upward of 6 equiv of HMPA for the tetra solvated HMPA

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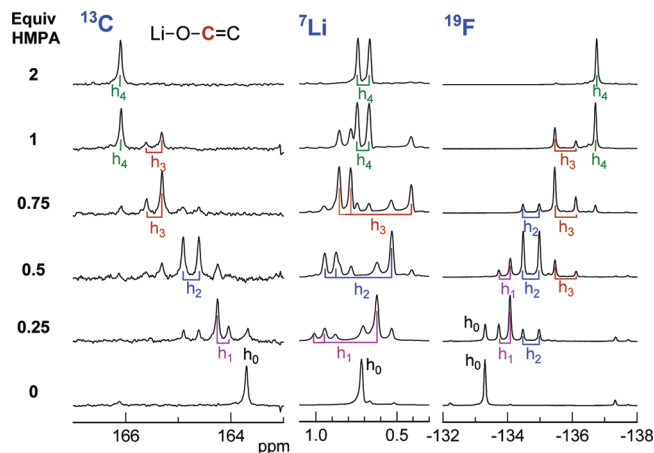
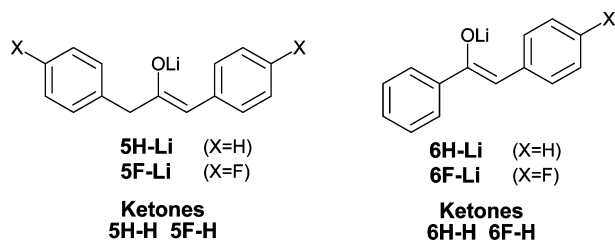


Figure 4. HMPA titration of 0.1 M solution of (4F-Li)₄ in 3:2 THF/Et₂O at −120 °C followed by ¹⁹F, ¹³C (only the C–O carbon shown), and ⁷Li NMR spectroscopy (h = HMPA).

tetramer to become the dominant species. This is presumably a consequence of lower basicity and reduced steric effects of 4F-Li.



1,3-Diphenyl-2-propanone Lithium Enolate (5H-Li). The lithium enolate of dibenzyl ketone in THF has been previously investigated by the Streitwieser group,^{11b} and reported to be a mixture of dimer and monomer, with a K_{MD} of 420 M^{−1} at 25 °C. We concur that 5H-Li is predominantly dimeric in THF-containing solvents based on an HMPA titration.²⁰

1,3-Bis(4-fluorophenyl)-2-propanone Lithium Enolate (5F-Li) in THF. We have investigated the solution structure of the *p,p'*-difluoro analogue 5F-Li more thoroughly, taking advantage of the powerful window provided by ¹⁹F NMR spectroscopy. As previously mentioned with 3F-Li, the para fluoro substitution is not expected to significantly perturb the enolate behavior, and this is borne out by our comparison of the behavior of 5H-Li and 5F-Li. Kinetic enolization of 5F-H with lithium diisopropylamide in 3:2 THF/Et₂O initially produces a 54:10:36 mixture of three species, to which we have assigned the *EE* and *ZZ* homodimers, each with a single set of peaks in the ⁷Li, ¹³C, and ¹⁹F NMR spectra (Figure 5), the *EZ* mixed dimer, with a 1:1 pair of signals in the ¹³C and ¹⁹F NMR spectra, and the expected single peak in the ⁷Li NMR spectrum. The NMR signals for the *EZ* mixed dimer coalesce with those of the homodimers around 20 °C. When warmed to room temperature for several hours, the sample of 5F-Li equilibrates to produce a single species (>95%), the *ZZ* dimer, with ¹³C signals at δ 168.6 (C–O carbon) and δ 96.2 (β -carbon) and ¹⁹F signals at δ −119.1 and δ −123.9. Quenching of the kinetically formed and equilibrated mixture of enolates with trimethylchlorosilane forms the appropriate mixture of *E*- and *Z*-enol silyl ethers. 1,3-Diphenyl-2-propanone 5H-H produced a similar 48:7:45 mixture of *EE*, *ZZ*, and *EZ* dimers, which also equilibrated to the *ZZ* dimer.

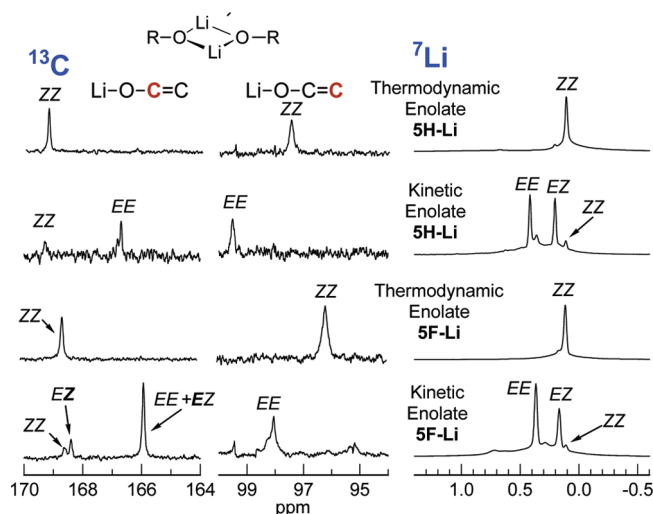


Figure 5. ¹³C and ⁷Li NMR spectra of kinetic and thermodynamic enolates 5H-Li and 5F-Li in 3:2 THF/Et₂O at −130 °C.

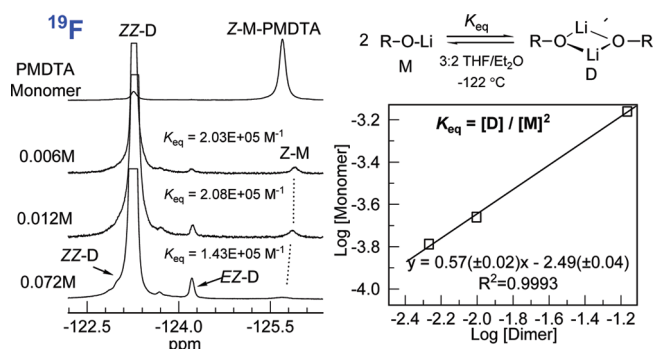


Figure 6. Variable concentration NMR study of the dimer–monomer equilibrium of Z-5F-Li. The top spectrum shows PMDTA-complexed monomer.

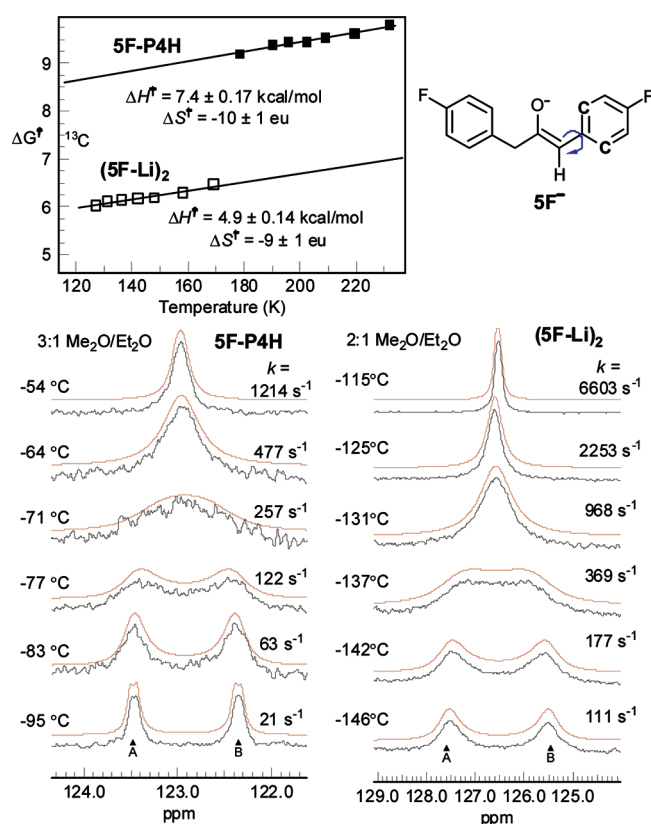
The observation of only one 1:1 *EZ* mixed aggregate for 5F-Li provides evidence for a dimer structure, and this is supported by the behavior with several cosolvents (TMEDA, PMDTA, and HMPA) as described below. Careful examination of the ¹⁹F NMR spectra of 0.07 M Z-5F-Li in 3:2 THF/Et₂O at −122 °C showed ~1% of a small signal which is very close in chemical shift to that of the PMDTA-complexed monomer (Figure 6). Serial dilution of the sample resulted in an increase in the ratio of this signal to that of the dimer consistent with assignment to monomeric 5F-Li. A log–log plot of the concentrations gave a slope of 0.57 ($K_{MD} = [D]/[M]^2 = 208,000 \text{ M}^{-1}$ at −122 °C). Slow exchange on the NMR time scale of the Z-5F-Li dimer and monomer allowed K_{MD} to be measured over a range of temperatures (−130 to −62 °C, $\Delta H^\circ = -3.8 \text{ kcal/mol}$, $\Delta S^\circ = -0.2 \pm 0.2 \text{ eu}$).²⁰ Extrapolation of K_{MD} gave a value of 600 M^{−1} at 25 °C, which is fully compatible with the value of 420 M^{−1} for Z-5H-Li in pure THF at 25 °C reported by Streitwieser.^{11b}

Formation of Phosphazene Enolate. We have previously reported on the interaction of 5F-H with the Schwesinger base P4.⁴¹ At half an equivalent of base the ketone is converted to the hydrogen-bonded dimer ((5F)₂H[−] P4H⁺), and at one equivalent, to the enolate Z-5F-P4H. This enolate shows the most extreme chemical shifts of any of the Z-5F-Li species investigated (Table 1). Compared to the lithium dimer, the α -vinyl carbon resonance moves downfield by 4.6 ppm, the β -carbon upfield by 7.9 ppm, and the fluorine signal upfield by

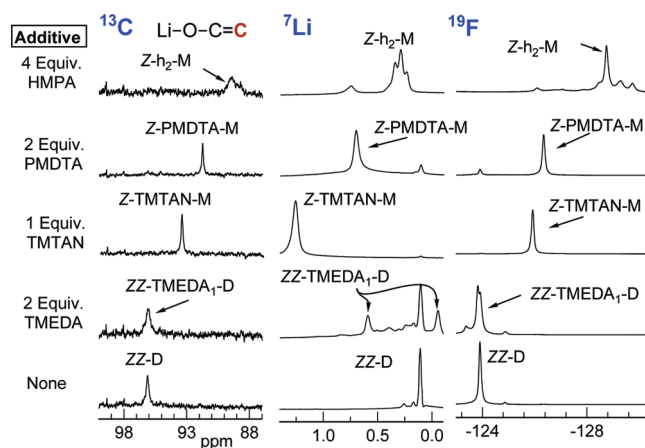
Table 1. Diagnostic NMR Chemical Shifts of the Various **5F** Enolate Structures^a

	¹³ C-α	¹³ C-β	¹³ C-p	¹⁹ F (Ph)	¹⁹ F (Bn)
<i>Z</i> -Isomer:					
5F-SiMe₃	152.5	109.4	161.2	−117.6	−117.2
5F-Me	155.4	106.8	161.0	−117.9	−117.6
(5F-Li)₂ (Et₂O)	166.4	96.8	158.7	−123.5	−119.7
(5F-Li)₂ (THF)	168.5	96.1	158.4	−123.9	−119.1
(5F-Li)₂·TMEDA	169.1	96.0	158.4	−123.8	−118.6
(5F-Li)₂·(HMPA)₁	169.9	95.2	158.1	−124.5	−119.4
(5F-Li)₂·(HMPA)₂	170.5	94.3	157.9	−125.4	−119.9
(5F)₂H⁺ P4H⁺	165.1	94.1	158.4	−123.9	−119.5
5F-Li·TMTAN	168.3	93.5	157.4	−126.4	−119.7
5F-Li·PMDTA	169.1	91.8	157.2	−126.4	−119.7
5F-Li·(HMPA)₂	171.6	89.6	156.6	−127.7	−120.6
(5F)₂Li⁺ P4H⁺TI	171.6	89.7	156.6	−128.0	−121.0
(5F)₃Li²⁺ (P4H⁺)₂ QI	172.2	89.4	156.6	−128.4	−121.1
5F-P4H	173.1	87.3	155.4	−130.2	−121.1
<i>E</i> -Isomer:					
5F-SiMe₃	152.8	109.5	161.6	−117.9	−117.7
(5F-Li)₄ (Et₂O)	162.1	103.4	159.9	−121.7	−117.5
(5F-Li)₂	166.0	98.1	158.6	−125.2	−119.4

^a All NMR data at −110 to −130 °C in 3:2 THF/Et₂O unless Et₂O is specified.

**Figure 7.** DNMR study of the phenyl ring rotation in **5F-P4H** and **5F-Li** dimer in Me₂O/Et₂O solvent. The signals shown are those of the ortho-carbons. The red traces are simulations of two-site exchange of two doublets with the rate constants shown.²⁵

6.3 ppm. The additional charge in the enolate is indicated by these chemical shift changes, as well as in the barrier to rotation of the phenyl group, which becomes slow enough to be detected by DNMR methods. At low temperatures the two ortho carbons of the conjugated phenyl group become nonequivalent, with coalescence near −137 °C for the THF-solvated dimer, and −75 °C for the phosphazanium enolate (Figure 7). The activation energy for phenyl rotation is 2.5 kcal/mol higher for the “naked”

**Figure 8.** ¹⁹F, ¹³C, and ⁷Li NMR spectra of **Z-5F-Li** enolates in 3:2 THF/Et₂O at −125 °C with various solvent additives. (h = HMPA; D = dimer; M = monomer).

phosphazanium enolate. This difference is an unknown combination of two distinct effects: a higher barrier from more extensive charge delocalization in the P4 enolate, and larger steric destabilization of the planar or near planar ground state in the lithium enolate.

We will make use of phosphazanium enolates in the characterization of species formed during the HMPA titration of **5F-Li**.

Addition of TMEDA. In contrast to the tetramers studied, amine-based solvent additives did have an effect on **5F-Li**. Addition of the diamine TMEDA to solutions of **Z-5F-Li** in THF/Et₂O produced two new singlets in the ⁷Li spectra at δ 0.58 and −0.07 (Figure 8). Based on this observation, and the minor changes in the ¹³C and ¹⁹F shifts (less than 0.5 ppm), we have identified this as a mono TMEDA-complexed *Z,Z* dimer with an association constant K_{eq} of 7 M^{−1} (**Z-5F-Li** + TMEDA → **Z-5F-Li·TMEDA**). Bis-solvation of the dimer **Z-5F-Li** by TMEDA was not detected with the addition of up to 6 equiv of TMEDA.

Addition of PMDTA and TMTAN. The triamine solvent additives PMDTA or TMTAN had a more pronounced effect on **Z-5F-Li** (Figure 8). Addition of PMDTA produced a new ⁷Li signal (δ 0.7), as well as substantial upfield shifts in the ¹³C (from δ 96.8 to δ 91.8) and ¹⁹F (from δ −123.9 to δ −126.3) signals. These data are consistent with deaggregation to a PMDTA solvated monomer. Not unexpectedly, TMTAN produced a similar monomer identified by upfield shifts in the ¹³C (δ 93.5) and ¹⁹F (δ −125.9) signals as well as a single new ⁷Li (δ 1.3) signal. Additional evidence for the monomeric structures was obtained from an X-ray diffraction study of a single crystal grown from THF/Et₂O solutions of the lithium enolate of dibenzyl ketone (**5H-Li**) containing PMDTA (Figure 9).²⁰

Interestingly, the addition of PMDTA to the 39:45:16 kinetically formed mixture of *EE*, *EZ*, and *ZZ* **5F-Li** dimers did not result in formation of any *E* monomer, or any detectable interaction with the *E* dimer. Instead PMDTA was found to selectively solvate the *Z* isomer, dissociating the *ZZ* dimer, and reducing the fraction of *EZ* dimer while increasing the relative concentration of *EE* dimer (Figure 10). Thus, the *E*-enolate has

(25) The DNMR simulations were performed with an updated version of WINDNMR (<http://www.chem.wisc.edu/areas/reich/plt/windnrm.htm>): Reich, H. J. WinDNMR Dynamic NMR Spectra for Windows. J. Chem. Ed. Software, Series D, 1996; Vol. 3D, No. 2.

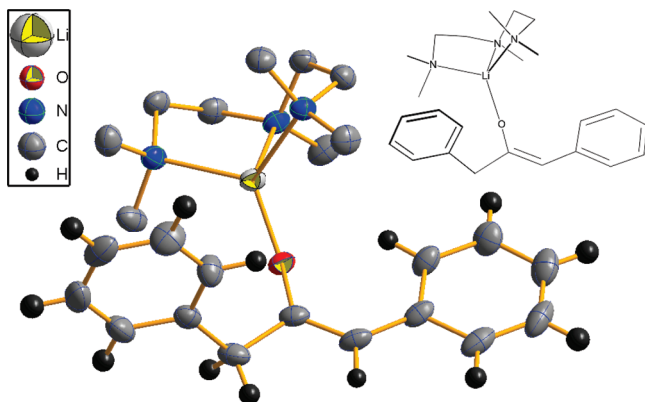


Figure 9. Molecular drawing with 50% probability ellipsoids of (Z-5F-Li)•(PMDTA) determined by single-crystal X-ray analysis (hydrogens omitted from PMDTA to improve clarity). Average for select bond lengths: O–C=C, 1.372 Å; Li–O–C=C 1.804 Å.

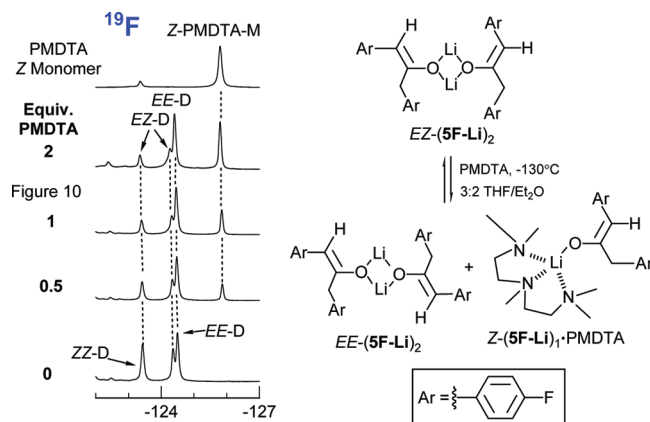


Figure 10. ^{19}F NMR of a PMDTA titration of a 39:45:16 mixture of EE, EZ, and ZZ 5F-Li dimers in 3:2 THF/Et₂O. Top spectrum: Z-5F-Li•PMDTA (D = dimer; M = monomer).

a higher dimer association constant than the Z-enolate. Presumably steric inhibition of resonance between the enolate and the directly attached aryl group in the *E* isomer results in less delocalization of negative charge and a more strongly aggregated enolate.

Addition of HMPA. The dimeric structure of 5F-Li is supported by an HMPA titration. Four-center dimers (LiCl,^{4h} LiSMe,^{4h} PhLi,^{4b} *o*-(dimethylaminomethyl)phenyllithium,^{4d} *p*-trifluoromethylphenolate,^{10c} phenylacetone nitrile¹⁷) have all shown similar solvation sequences, with formation of mono- and bis-HMPA-complexed dimers, accompanied by dissociation to monomer and, in the case of LiCl and phenylacetone nitrile, by eventual formation of SIP species.

Shown in Figure 11 is an HMPA titration of an equilibrated sample of the ZZ dimer of 5F-Li. In contrast to the tetrameric species, at 0.25 equiv of HMPA the initial mono-HMPA solvate has a single set of ^{13}C NMR signals for the enolate carbons (δ 169.8, δ 95.0) and a single set of ^{19}F signals (δ –119.3, δ –124.6) as well. In the ^7Li spectrum, a doublet ($J_{\text{Li-P}} = 9.9$ Hz) and singlet of equal area were observed, characteristic of a dimer in which one lithium is coordinated to HMPA (the doublet). Upon increasing HMPA to one equivalent the bis-HMPA dimer (D-h₂) became the major species identified by a single new set of ^{13}C signals for the enolate carbons (δ 170.3 and δ 94.1), a new set of ^{19}F signals (δ –119.8, δ –125.3), and a doublet signal in the ^7Li ($J_{\text{Li-P}} = 9.7$ Hz). Again in contrast

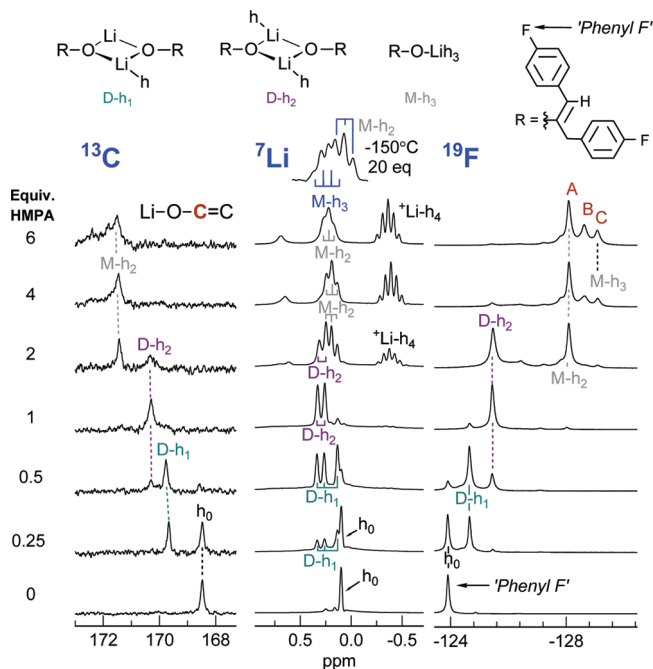


Figure 11. ^{19}F , ^{13}C , and ^7Li NMR spectra of an HMPA titration of Z-5F-Li in 3:2 THF/Et₂O at –130 °C (h = HMPA; D = dimer; M = monomer). The inset at the top is a ^7Li NMR spectrum taken in 1:1:1 THF/Me₂O/Et₂O with 15 equiv of HMPA at –150 °C.

to the tetramers studied, greater than one equivalent of HMPA caused deaggregation to the monomer.

Above one equivalent of HMPA, three new signals appear in the ^{19}F NMR spectrum in the region δ –128 to –130, labeled A, B, and C in Figure 11. None of the new species is a fully separated ion pair, if we make the reasonable assumption that the enolate part of such a species would have NMR properties very similar to those of 5F-P4H. Signal A appears first, and signals B and C appear later in the titration. Signal A has been assigned to the CIP monomer on the basis of substantial upfield shift in the associated ^{13}C signals of the β -carbon (from δ 94.1 to δ 89.5) and the ^{19}F NMR signals (δ –121.1, δ –128.1, which is four times the change observed between the three solvated dimers). The ^7Li triplet (δ 0.19, $J_{\text{Li-P}} = 7.8$ Hz) identifies this as a bis-HMPA solvated monomer (M-h₂). Since the Li–P coupling is lost due to fast exchange at –130 °C, we investigated these species in a slightly different solvent mixture, 1:1:1 THF/Me₂O/Et₂O, which allows operation down to –150 °C. At more equivalents of HMPA the δ 0.19 ^7Li signal could be resolved into a triplet ($J_{\text{Li-P}} = 7.8$ Hz) of M-h₂, and a quartet ($J_{\text{Li-P}} = 6.4$ Hz). The quartet was assigned to the lithium of a monomeric enolate solvated with three molecules of HMPA (M-h₃ in Figures 11 and 12), a solvate not previously identified in other monomeric lithium species.^{4h} The ^{19}F NMR signal C was associated with this species.

Also appearing in this regime is the ^7Li quintet at δ –0.3 of a $\text{Li}(\text{HMPA})_4^+$ species, normally corresponding to the free lithium cation of a triple ion structure,^{4a,g,m} as well as several associated signals in the various NMR spectra. Clarification of the assignment to these signals was provided as follows. The addition of HMPA to solutions of lithium reagents can be thought of as creating a lithium-cation depleted environment for the enolate ion. An extreme case of this would be to add the metal-free enolate formed by deprotonation of ketone with

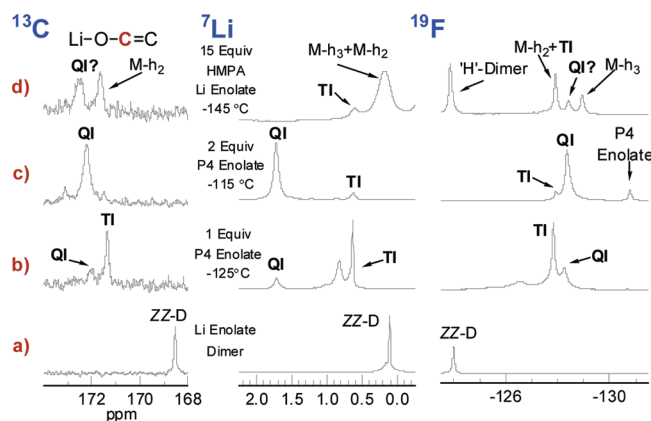
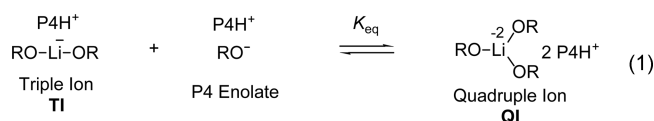


Figure 12. ^{19}F , ^{13}C , and ^7Li NMR spectra of the complex ions formed from **Z-5F-Li** (a) by the addition of **P4 enolate** (**Z-5F-P4H**) (b and c) or by the addition of **HMPA** (d) in 3:2 THF/Et₂O (h = HMPA; D = dimer; M = monomer). In spectrum (d) a small amount of hydrogen-bonded dimer (**5F**)₂H[−] formed from self-enolization of some ketone.

the Schwesinger²⁶ base **P4**⁴¹ to the lithium enolate. Indeed, such experiments proved productive. As summarized in Figure 8, the addition of increments of **5F-P4H** to a solution of **5F-Li** gave two new species. The first was by far the major one at a 1:1 ratio of lithium to **P4 enolates**, and can be assigned to the triple ion **5F-TI** (**RO**)₂Li[−] **P4H**⁺. Triple ions have been detected for lithium phenolates,^{27a} β -dicarbonyl compounds,^{27b} and related compounds,^{6f} but not for simple enolates. This species has ^{13}C signals at $\delta \sim 171.5$ and 89.8 , ^7Li at $\delta 0.63$. The ^{19}F shift of $\delta -127.9$ matches that of signal A in Figure 7, so A represents the superimposed signals of **M-h**₂ and **5F-TI**. Even past one equivalent of **5F-P4** no free enolate was detected. Rather, a second species grows in at the expense of the triple ion and becomes the dominant species at a 1:2 ratio of lithium to **P4 enolate**. Only when nearly two equivalents of **5F-P4** had been added did the signals of free enolate appear. Apparently the lithium of the triple ion (**RO**)₂Li[−] can “absorb” a second equivalent of a naked enolate to form a higher-order lithiate. Based on the stoichiometry of its formation and the mixing experiment reported below, we assign the structure (**RO**)₃Li^{2−} (**P4H**⁺)₂ to this species. It has characteristic peaks at $\delta 1.8$ in the ^7Li NMR, $\delta 172.2$ and $\delta 89.3$ in the ^{13}C NMR spectra. We will refer to these higher-order lithiates as “quadruple ions” (QI), as a colloquial extension of the triple ion (TI) nomenclature.



At a 2:1 ratio of **P4** to lithium enolate, all three species (TI, QI, and **P4 enolate**) are present in detectable amounts at equilibrium (eq 1). The assignment of the TI and QI structures was supported by a concentration-dependent experiment (Figure 13), in which a sample with a 2:1 ratio of **5F-P4H** to **5F-Li**

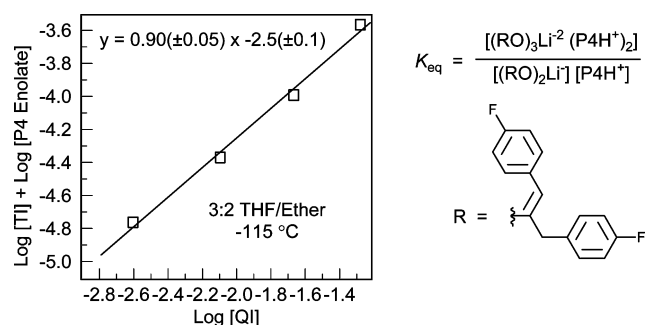


Figure 13. Dilution study of the lithiate ion equilibrium between (**5F**)₂Li[−], (**5F**)₃Li^{2−} and **5F**[−] in 3:2 THF/Et₂O at -115°C . The concentrations follow the equilibrium of eq 1 over an 8-fold dilution ($K_{\text{eq}} = 190 \text{ M}^{-1}$ at -115°C).

was diluted. The concentrations accurately followed the equilibrium in eq 1.

The QI may also be formed in minor amounts during the HMPA titration, where it would correspond to signal B in Figure 11 (^{19}F $\delta -128.4$). The assignment is not firm since no signal for the central ^7Li could be detected,²⁸ so it is not clear that HMPA sequesters lithium strongly enough to form the QI.

To confirm the dimeric and trimeric nature of the two lithiates, a mixing experiment was performed with **5F-Li** and **6F-Li**. Although **6F-H** is expected to be a little more acidic than **5F-H** (in DMSO the $\text{p}K_{\text{a}}$ of **6H-H** is 17.7 and that of **5H-H**, 18.7²⁹), all of the properties of the enolates formed from **5F-H** and **6F-H** are very similar. We have previously investigated the interaction of **6F-H** with the **P4** base, and like **5F-H**, it forms H-bonded dimer (**RO-H-OR**[−] **P4H**⁺) at substoichiometric amounts of base, and clean **P4 enolate** at one equivalent.⁴¹ Application of our HMPA technique to **Z-6F-Li** showed it to be dimeric and to form HMPA-coordinated monomer a little more easily than does **5F-Li**.²⁰ Mixing of **6F-Li** with **6F-P4H** also forms lithiates, first the triple ion [(**6F**)₂Li[−] **P4H**⁺], and then the quadruple ion [(**6F**)₃Li^{2−} (**P4H**⁺)₂] at more than one equivalent of **6F-P4H**. The association constant for the latter equilibrium (K_{eq} in eq 1) is lower for **6F-Li** than for **5F-Li** ($K_{\text{eq}} = 24 \text{ M}^{-1}$ vs 190 M^{-1}), presumably a consequence of the lower basicity of the enolate **6F-Li**.

The small differences between the behavior of **5F-Li** and **6F-Li** suggested that a well-defined mixing experiment (method of continuous variation^{6c}) could be performed to provide support for lithiate structure assignments. Solutions containing both triple and quadruple ions of **5F** and **6F** were generated by mixing lithium and **P4 enolates** in a 1:2 ratio. These solutions were then mixed in several ratios (Figure 14). The mixed samples show only one new ^7Li NMR signal, $\delta 0.88$, for the mixed triple ion (**5F**)(**6F**)Li[−] **P4H**⁺, but two new ^7Li NMR signals, $\delta 2.1$ and $\delta 2.2$, for the two new mixed quadruple ions ((**5F**)₂(**6F**)₁Li^{2−} and (**5F**)₁(**6F**)₂Li^{2−}, each with two **P4H**⁺ counterions).

HMPA titration of the kinetically formed 44:43:12 *EE*, *EZ*, and *ZZ* mixtures of **5F-Li** in 3:2 THF/Et₂O showed sequential solvation of the *EE* and *EZ* dimers up to one equivalent of cosolvent. At 6 equiv of HMPA the *Z* dimer was largely monomeric (29% *Z*-**M-h**₂ and 11% *Z*-**M-h**₃), whereas the

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(28) To slow down exchange between TI, QI, and free enolate in the HMPA experiment very low temperatures ($<-135^\circ\text{C}$) are needed. Under these conditions the peak for QI-P4 is 120 Hz wide, so a small signal could not be detected.²⁰

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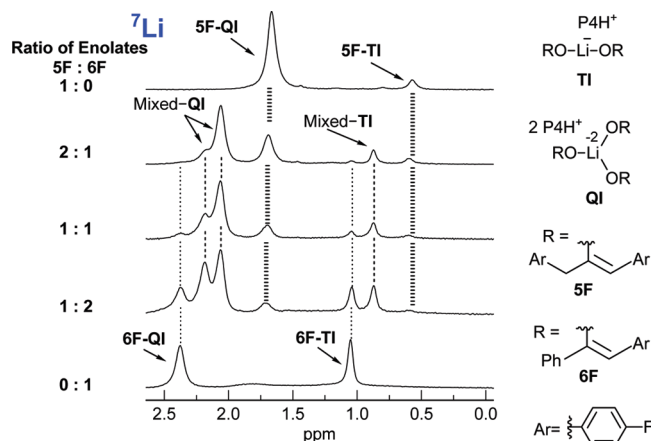


Figure 14. ^7Li NMR spectra of the mixing experiment of the complex lithiate ions (eq 1) formed from *Z*-**5F-Li** and/or *Z*-**6F-Li** with the addition of 2 equiv of **P4** enolate in 3:2 THF/Et₂O at $-115\text{ }^\circ\text{C}$.

E-isomer was present as the bis-HMPA dimer (32%). We cannot rule out the presence of some *E*-monomer, since there were several other broad unassigned signals present (28%), most likely complex ionic structures such as triple ion/quadruple ions. However, these results, like the behavior with PMDTA, support the idea that the *E* isomer is more strongly aggregated than the *Z*.

1,3-Bis-(4-fluorophenyl)-2-propanone Lithium Enolate (5F-Li) in Diethyl Ether. The difference in *E* versus *Z* behavior was even more striking in diethyl ether. Deprotonation of **5F-H** with lithium diisopropylamide in diethyl ether produced an enolate solution richer in the *E* isomer than obtained in THF/Et₂O (Me₃SiCl quenching gives 88/12 *E/Z*). Analysis of the NMR spectra of this solution leads to the conclusion that the *E* isomer of **5F-Li** is a tetramer in diethyl ether. The chemical shift of the enolate vinyl carbons of *E*-**5F-Li** in Et₂O, δ 103.1 and 162.0, are substantially different from those of the *EE* dimer in THF/Et₂O, δ 98.1 and 166.0, in the direction expected for a higher aggregate (less charge polarization of the π system). Application of the HMPA titration technique at $-105\text{ }^\circ\text{C}$, shown in Figure 15, yields the expected ratios of signals for the various tetrameric HMPA solvates observed in ^{19}F , ^{13}C , and ^7Li spectra. No dimers or monomers were detected. Unlike the previously studied tetramers **1-Li**, **2-Li** and **3F-Li** in the more polar solvent mixture of THF/Et₂O, the solution at 1 equiv of HMPA consisted predominately of the h₄ tetramer, indicating a higher affinity of lithium for HMPA in this less polar solvent.

At one equivalent of HMPA the *E/Z* ratio is still 85:15 as determined by quenching with trimethylchlorosilane, but at more equivalents of HMPA, isomerization of *E* to the *Z* isomer occurred, leading to complex behavior and several unidentified species.

Equilibration of an ether solution of **5F-Li** (1–2 h, $25\text{ }^\circ\text{C}$) leads largely to the *Z* isomer (quench: >95% *Z*). The ^{13}C chemical shifts (δ 96.8, 166.3) of *Z*-**5F-Li** in Et₂O are very similar to those of the *ZZ* dimer in THF/Et₂O (δ 96.1, 168.5), and a dimeric structure is supported by application of the HMPA titration technique. Sequential solvation by HMPA similar to a titration in THF/Et₂O of the dimer was observed up to 1 equiv. From 1.5 to <4 equiv a number of broad signals in the ^{13}C , ^{19}F , and ^7Li spectra indicated a dynamic mixture of species. Only above 4 equiv of HMPA are two distinct species present. One is the previously identified triple ion, based on the ^{13}C (δ 170.7,

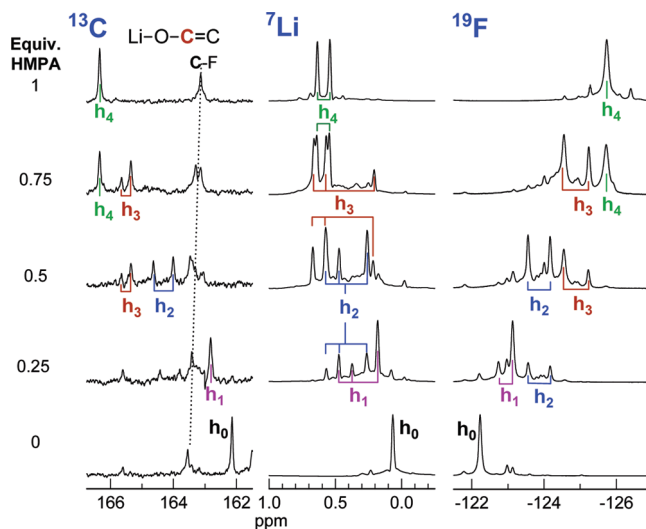


Figure 15. ^{13}C , ^{19}F , and ^7Li NMR spectra of a HMPA titration of solution rich in the *E* isomer (85:15) of **5F-Li** in ether at $-105\text{ }^\circ\text{C}$. The sequence of solvates is consistent only with a tetrameric aggregate of *E*-**5F-Li** ($h = \text{HMPA}$).

δ 89.9), ^{19}F (δ -120.8 , δ -127.7), and ^7Li signals ($\text{Li}(\text{HMPA})_4^+$ quintet at δ -0.4 , singlet at δ 0.34). The second is the tris-HMPA monomer, ^{13}C (δ 172.0, δ 88.5), ^{19}F (δ -121.4 , δ -128.9). The dimeric nature of the triple ion and the monomeric nature of tris-HMPA monomer was confirmed by a mixing experiment with **6F-Li**.²⁰

Additional evidence for the dimeric structure of **5F-Li** was provided by a single-crystal X-ray structure of material crystallized from solutions of *Z*-**5F-Li** in ether. This showed a bis-ether-solvated four-center dimer (Figure 16), the first dimeric ether-solvated ketone enolate structure in the solid state (see Supporting Information for animation).³⁰ The lithium is tricoordinate with one ether molecule coordinated to each lithium, but the phenyl of the benzyl group is weakly occupying one of the coordination sites (closest Li–C approach is 2.86 Å). There is a hint of a similar conformation in solution since the lithium NMR signal is shifted upfield 0.3 ppm from the dimer in THF, where more extensive solvation might reduce or eliminate such an interaction.

Conclusions

Observation of the NMR spectra of the aggregated lithium enolates of cyclohexanone, cyclopentanone, and 4-fluoroacetophenone during careful HMPA titrations has demonstrated the tetrameric structure of these enolates in THF/Et₂O and THF/Et₂O–HMPA. Dissociation to lower aggregates, dimers or monomers, was not observed in these experiments, nor when TMEDA or PMDTA were added.

The lithium enolates of dibenzyl ketone, 1,3-bis-(4-fluorophenyl)-2-propanone, and 1-phenyl-2-(4-fluorophenyl)ethanone were shown to exist primarily as dimers in THF/Et₂O. In contrast to the tetramers studied, addition of HMPA, TMTAN, or PMDTA to *Z*-**5-Li** caused monomer formation. In contrast, the *E*-enolate did not form detectable amounts of monomer with HMPA or PMDTA. In diethyl ether, the behavior of the *E* and *Z* isomers of **5F-Li** was also different, with the *E*-enolate tetrameric and

(30) X-ray structures of TMEDA-complexed enolate dimers have been reported,^{3e,f} and dimers are preferred in TMEDA solution (no THF).^{6c}

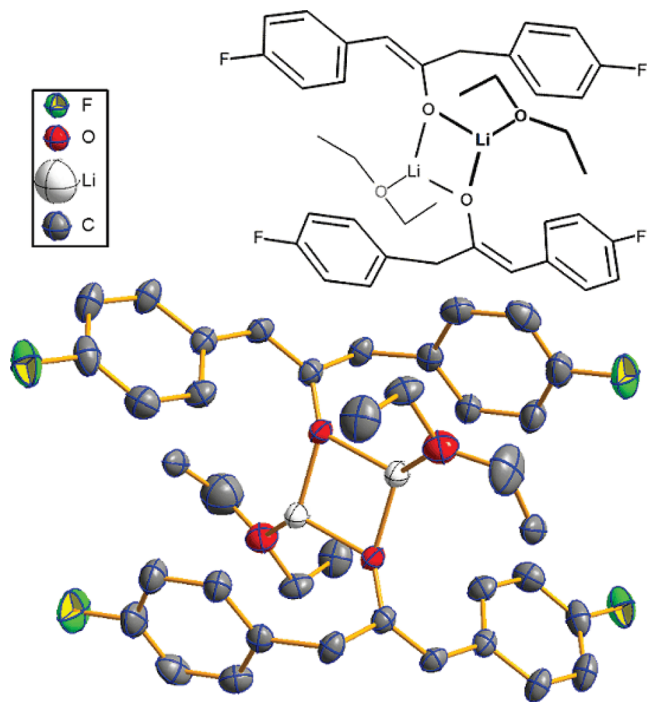


Figure 16. Molecular drawing with 50% probability ellipsoids of $(Z\text{-}5\text{F-Li})_2 \cdot (\text{OEt})_2$ determined by single-crystal X-ray analysis (hydrogens omitted for clarity). Select bond lengths: O-C=C , 1.356 Å; Li-O-C=C 1.847 Å, 1.866 Å.

the *Z* isomer dimeric. At high concentrations of HMPA the dimeric enolates formed significant amounts of complex lithiate species, the triple ion $(\text{Li}(\text{OR})_2)^-$ and possibly the quadruple ion $(\text{Li}(\text{OR})_3)^{2-}$, with $\text{Li}(\text{HMPA})_4^+$ counterions. Alternatively, we found that these lithiate species could be generated cleanly and studied by mixing of the “naked” P4 enolate with the lithium enolate, to form $(5\text{F})_2\text{Li}^- \text{P4H}^+$ and $(5\text{F})_3\text{Li}^{2-} (\text{P4H}^+)_2$.

At high HMPA concentration enolates form either complex mixtures of monomers and ions for the dimers or tris- and tetra-HMPA-solvated tetramers; thus, the most useful information about the parent aggregation state of the enolate is obtained at substoichiometric amounts of HMPA where this powerful cosolvent has only a minor effect on structure. With careful observation of all the available NMR active nuclei, ^{13}C , ^{31}P , ^7Li , and/or ^{19}F the aggregation state of lithium enolates can be routinely determined using the HMPA titration technique.

Experimental Section

General. All reactions requiring a dry atmosphere were performed in glassware flame-dried or dried overnight in a 110 °C oven, sealed with septa, and flushed with dry N_2 . Tetrahydrofuran (THF) and Et_2O were freshly distilled from sodium benzophenone ketyl under N_2 . Me_2O was purified by condensing several milliliters in a graduated conical flask at -78 °C from a pressurized gas cylinder, adding a small portion (0.5 mL) of *n*-BuLi and distilling the dry Me_2O via cannula into the desired vessel at -78 °C. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA), *N,N,N',N',N'*-pentamethyldiethylenetriamine (PMDTA), and hexamethyl phosphoric triamide (HMPA) were distilled from CaH_2 under reduced pressure (if necessary) and stored over 4 Å molecular sieves under N_2 . Common lithium reagents were handled with septum and

syringe-based techniques and titrated against dry *n*-propanol in THF using 1,10-phenanthroline as indicator.³¹

Low-Temperature NMR Spectroscopy. All low-temperature NMR spectra were acquired on a Bruker AVANCE spectrometer using a 10 mm broadband probe at the following frequencies: 90.556 MHz (^{13}C), 52.984 MHz (^6Li), 139.905 MHz (^7Li), 145.785 MHz (^{31}P), and 338.827 MHz (^{19}F). All spectra were taken with the spectrometer unlocked. ^{13}C NMR spectra were referenced internally to the C–O carbon of THF (δ 67.96), Et_2O (δ 66.57), or Me_2O (δ 60.25). Lorentzian multiplication (LB) of 2–6 Hz was applied to ^{13}C spectra. ^6Li and ^7Li spectra were referenced externally to 0.3 M LiCl in MeOH (δ 0.00) or internally to $\text{Li}^+(\text{HMPA})_4$ (δ –0.40). ^{31}P NMR spectra were referenced externally to 1.0 M PPh_3 in THF (δ –6.00) or internally to free HMPA (δ 26.40). ^{19}F NMR spectra were acquired without proton decoupling and were referenced internally to CFCl_3 (δ 0.0), 1,3-difluorobenzene (δ –110.8), or 1,2-difluorobenzene (δ –140). Probe temperatures were measured internally with the ^{13}C chemical shift thermometer $(\text{Me}_3\text{Si})_3\text{CH}$.⁴ⁿ

General Preparation of Samples for Multinuclear NMR Spectroscopy. Lithium diisopropylamide was prepared fresh before formation of an enolate solution by the following procedure. Solvent was added (typically 1.8 mL of THF and 1.2 mL of Et_2O) including 1–2 μL of ^{13}C -enriched (10%) $(\text{Me}_3\text{Si})_3\text{CH}$ as a shift thermometer⁴ⁿ to a dried thin-walled 10 mm NMR tube that had been stored under vacuum, fitted with septa, and flushed with N_2 or Ar. Silicon grease was applied to the interface between the tube and the septa before securing with parafilm for a better seal, as well as to the top of the septa to seal needle punctures. The NMR tube was cooled to -78 °C under positive N_2 or Ar pressure and diisopropylamine (42 μL , 0.30 mmol) and *n*-BuLi (120 μL , 2.5 M) were added to the solution. The solution was warmed to 0 °C in an ice bath for 5 min, and cooled to -78 °C under positive N_2 or Ar pressure. The desired carbonyl compound was added by syringe either neat or as a solution of the carbonyl compound in the desired solvent. Samples were stored at -78 °C. The spectrometer probe was cooled to <-78 °C, the sample was inserted, and the probe was shimmed on the ^{13}C FID of the THF peak. Spectra of NMR active nuclei which usually included ^{13}C , ^{31}P , ^{19}F , ^7Li , and ^1H were then acquired. At this point, a titration, variable-temperature or variable-concentration experiment could be performed. In the case of a titration experiment, for each addition the sample was ejected, placed in a -78 °C bath, the silicon grease was removed from the top of the septum, a desired amount of cosolvent was added, silicon grease was reapplied to the top of the septum, and the desired NMR spectra were measured, including a ^{13}C NMR spectrum to determine the sample temperature.

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Supporting Information Available: Additional spectra of all enolate species; cosolvent titrations; variable-temperature and concentration experiments; X-ray crystal structure information for $(Z\text{-}5\text{F-Li}) \cdot (\text{PMDTA})$ and $(Z\text{-}5\text{F-Li})_2 \cdot (\text{OEt})_2$ in CIF format and two animated (AVI) files depicting these structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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