

Lithium and Cesium Ion-Pair Acidities of Dibenzyl Ketone. Aggregation of Lithium and Cesium Ion Pairs of the Enolate Ion and Dianion^{1,†}

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Spectral study of the cesium and lithium enolates of dibenzyl ketone (DBK) showed that both salts exist as contact ion pairs in THF solutions. The spectral data for the dicesium salt of DBK indicate that it exists as triple ions in which both cations are in contact with the dianion. The dilithium salt of DBK forms triple ions of two types in THF: in one, both cations are in contact with the DBK dianion, in the other, one of the lithium cations is solvent-separated. Evidence for dimerization of the ion pairs was obtained for both lithium and cesium enolates of DBK from UV-vis spectral (blue shift of the absorbance band at higher concentrations) and acidity (the decrease of p*K* at higher concentrations) studies. The dimerization constant for the cesium enolate of DBK obtained from the acidity data ($3.5 \times 10^3 \text{ M}^{-1}$) is considered to be more accurate than that from the spectral analysis ($1.7 \times 10^3 \text{ M}^{-1}$). The lithium enolate is much less dimerized than its cesium counterpart with a dimerization constant from acidity data of $4.2 \times 10^2 \text{ M}^{-1}$. The first and second cesium p*K* values of DBK are 18.07 and 33.70, respectively, compared to the first lithium p*K* of 11.62.

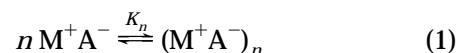
Introduction

Heathcock³ has reviewed the use of metal enolates in synthetic organic chemistry. Dianion salts of carbonyl compounds are also finding increasing use in the synthetic laboratory,^{4,5} but less is known of their properties⁶ compared to enolates. The reactivities of both enolate ions and dianions are undoubtedly closely related to their basicities and aggregation states. We would anticipate that knowledge of these properties would be useful in the practice of organic synthesis. We reported previously⁷ that the cesium enolate of dibenzyl ketone (DBK) exists in dilute THF solutions as a mixture of monomeric and dimeric contact ion pairs. The dimerization constant was found from the dependence of the relative ion-pair acidity of DBK on the cesium enolate concentration to be 1870 M^{-1} . The ion pair p*K* of the monomeric cesium salt was found by extrapolation to be 17.95. This value compares well with the value of 18.7 reported by Bordwell in DMSO.⁸ We present here an extended study of the cesium ion pair acidity of DBK covering a wider range of enolate concentrations, as well as its second cesium p*K*, the lithium acidity, and a spectral study of the cesium and lithium enolates (CsDBK and LiDBK, respectively) and the corresponding salts of the dianions (Cs₂DBK and Li₂DBK).

Results and Discussion

Spectral Data. Ion Pairing and Aggregation. UV-vis spectra of the lithium and cesium enolates of dibenzyl

ketone and the corresponding dianion salts were recorded in $10^{-5} - 5 \times 10^{-4} \text{ M}$ THF solutions at 25 °C. The λ_{max} and molar extinction coefficients for each salt are listed in Table 1. Values of λ_{max} for CsDBK were found to undergo a progressive blue shift as the concentration of the salt was increased as illustrated in Figure 1. As we had shown earlier⁹ such behavior reflects the formation of ion pair aggregates having different spectra. With the increase in concentration the aggregation equilibrium in eq 1 shifts in favor of dimers or higher clusters that absorb at shorter wavelength.



For the cesium enolate λ_{max} changes gradually from 343.5 nm to 338 nm as the concentration is varied from $5 \times 10^{-5} \text{ M}$ to $5 \times 10^{-4} \text{ M}$. We subjected the series of spectra recorded in this concentration range to singular value decomposition (SVD).⁹ This mathematical treatment can indicate the number and type of species in equilibrium and can provide the spectra of the individual components. The results obtained from the SVD analysis show the presence of two major species and are consistent with a monomer-dimer equilibrium ($n = 2$ in eq 1) with dimerization constant $K_2 = (1.7 \pm 0.2) \times 10^3 \text{ M}^{-1}$. The spectra of the monomer and dimer obtained by deconvolution are shown in Figure 2, and their spectral characteristics are given in Table 1. The extinction coefficient of CsDBK is independent of the concentration at 339.5 nm (isosbestic point) with $\epsilon(\text{monomer}) = 1/2\epsilon(\text{dimer}) = 22700 \pm 300 \text{ M}^{-1} \text{ cm}^{-1}$. Below $5 \times 10^{-5} \text{ M}$ no noticeable shift was observed ($\lambda_{\text{max}} = 343.5$) and indicates that at these concentrations the cesium enolate of DBK exists mostly as monomeric ion pairs. These ion pairs are undoubtedly contact (CIP) by analogy with the cesium salts of many different organic anions as shown earlier by an array of physicochemical methods.¹⁰

[†] Dedicated to Clayton H. Heathcock on the occasion of his 60th birthday.

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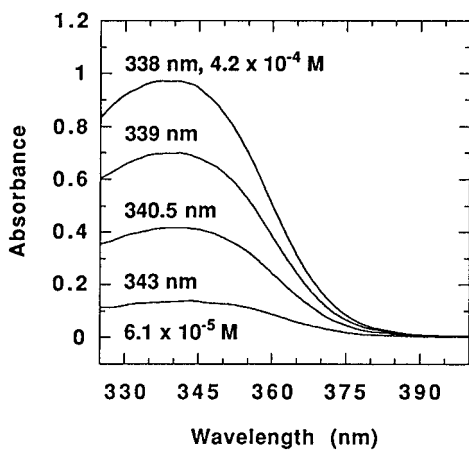


Figure 1. Dependence of λ_{\max} of the cesium enolate of dibenzyl ketone on concentration in THF at 25 °C.

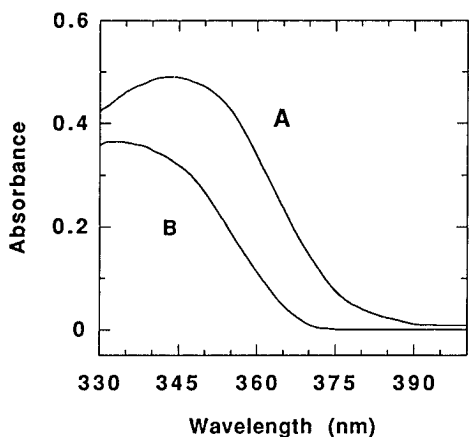


Figure 2. Spectra of dibenzyl ketone cesium enolate ion pairs (A) and their dimers (B) in THF at 25 °C.

Table 1. Spectral Data for the Cesium and Lithium Enolates and Dicesium and Dilithium Salts of Dibenzyl Ketone (DBK) in THF at 25 °C

species	λ_{\max} , nm	ϵ , $M^{-1} \text{ cm}^{-1}$
CsDBK ^a	338–343.5 ^b	22700 ^c
CsDBK(monomer)	343.5	23600
CsDBK(dimer)	332	46000
LiDBK	319–322 ^b	20400 ^d
Cs ₂ DBK	498	92000
Li ₂ DBK	492.5	43000

^a Mixture of monomer and dimer. ^b Depending on the concentration. ^c At the isosbestic point, 339.5 nm. ^d At the isosbestic point, 317 nm.

A blue shift of λ_{\max} from 322 nm to 319 nm was also observed for the lithium enolate of DBK at concentrations of 2×10^{-4} to 5×10^{-4} M. However, application of the SVD technique was unsuccessful in this case probably because the amount of dimer present was too small. The second singular value had a rather small coefficient and was hardly distinguishable from noise. The occurrence of a blue shift at higher concentrations indicates, however, that some aggregation does occur. An isosbestic point was found at 317 nm with $\epsilon = 20400 \pm 300 M^{-1} \text{ cm}^{-1}$.

The lower λ_{\max} values for LiDBK compared to CsDBK shows that the ion pairs of both compounds are CIP. This result is expected if both salts have the metal cation coordinated directly to oxygen rather than to the conjugated π -system. Such coordination is common in X-ray crystal structures of metal enolates,¹¹ but the structures

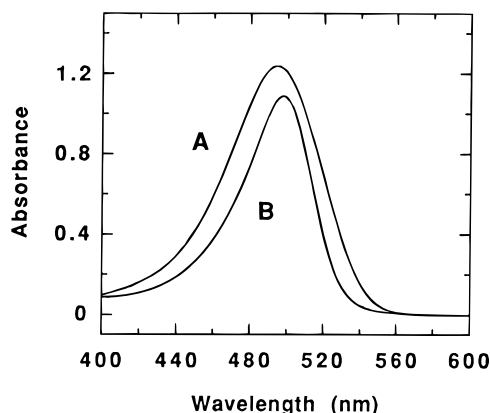
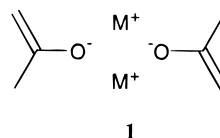


Figure 3. Spectra of dilithium (A) and dicesium (B) salts of dibenzyl ketone in THF at 25 °C.

are generally those of nonconjugated compounds. It is possible that π -coordination could compete with O-coordination of DBK enolates, but the above results suggest O-coordination for both LiDBK and CsDBK. The similarity of the spectra suggests that both metals coordinate similarly. If lithium were π -coordinated some tendency toward forming the solvent-separated ion pair (SSIP) would be expected; such an equilibrium between CIP and SSIP was found for the di-salt, Li₂DBK as discussed below. In addition, π -coordination is expected to show a smaller tendency toward aggregation than O-coordination; that is, the dimer most probably has the type of structure shown in **1**. Finally, the similarity of the spectra of monomer and dimer suggests that they have similar coordinations.



Successive addition of aliquots of cumylcesium to a solution of CsDBK in THF leads to the formation of the dicesium salt of DBK. The peak in the region of 340 nm corresponding to CsDBK decreases as the absorption band of Cs₂DBK at 498 nm grows. The spectrum of Cs₂DBK (B in Figure 3) was found to be independent of concentration, common salt, and temperature effects and indicates that this salt exists primarily as the contact-contact triple ion; that is, both cesium cations are in contact with the dianion. Moreover, its spectrum does not show a dependence on the amount of CsDBK present in solution. Spectra of pure Cs₂DBK and those in the presence of up to a 70-fold excess of CsDBK are identical. Acidity data (see below) indicate that Cs₂DBK most likely exists in the presence of CsDBK as a complex, Cs₂DBK·CsDBK; thus, CsDBK appears to have a negligible effect on the spectral properties of its neighbor. The THF solutions of Cs₂DBK could only be studied at low concentrations because of its high extinction coefficient, and at these low concentrations there is no indication that the compound forms dimers; the dimer in this case, of course, could also have the same spectrum as the monomer.

An X-ray crystal structure of Li₂DBK shows two equivalent lithiums π -coordinated above and below the

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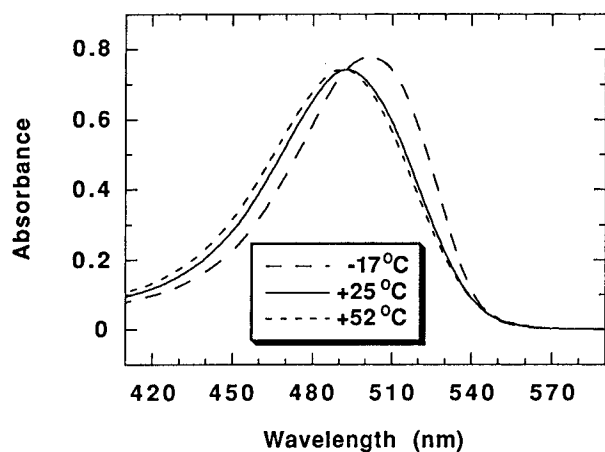
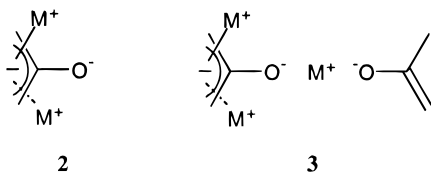


Figure 4. Spectra of the dilithium salt of dibenzyl ketone in THF at different temperatures.

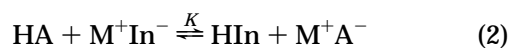
dianion plane.¹² A comparable structure seems reasonable for Cs₂DBK as symbolized in **2**. Ab initio calculations on the dilithium¹³ and dicesium¹⁴ salts of acetone give similar structures. In the complex, **3**, coordination of the exposed oxygen to the metal cation of the enolate seems reasonable. The repulsion of the third cation to the first two approximately compensates for the attraction of the π -cations to the additional oxide anion. The stabilization is then approximately the same as in the enolate dimer itself. Comparison with (diphenylallyl)-cesium is also interesting. The cesium salt has $\lambda_{\text{max}} = 538$ nm in THF.¹⁵ Even a simple Hückel treatment predicts that DBK dianion has a higher transition energy than the allylic anion; thus the electrostatic effect of the O⁻ substituent is relatively small and, accordingly, the replacement of this substituent by the more complex substituent in **3** has no significant further effect.



Solutions of Li₂DBK were obtained by titration of a solution of LiDBK in THF by lithium diisopropylamide (LDA). No changes in spectra were observed by a change in the concentration of Li₂DBK or by addition of LiBPh₄. These results suggest no significant dissociation of the salt to free ions or formation of dimer. However, the broader spectral band of Li₂DBK (A in Figure 3) compared to Cs₂DBK and its lower extinction coefficient (Table 1) suggest the presence of more than one species in solution. The spectra of Li₂DBK at temperatures from -17 to +52 °C show a gradual shift of λ_{max} from 502 to 491 nm with an isosbestic point at 492.5 nm (Figure 4). This behavior is typical of an equilibrium between solvent separated and contact ion pairs (SSIP and CIP) of organolithium compounds.^{16,17} We were not able to

establish the individual spectra of the CIP and SSIP of Li₂DBK because the usual approach¹⁷ of modeling these two extremes taking spectra in different solvents or with different counterions or upon addition of complexing agents was not applicable. The state of Li₂DBK in THF solutions can be qualitatively described as a mixture of contact-contact and contact-solvent separated triple ions. An example of the formation of such dual-type triple ions with lithium cations was shown previously for the dilithium salt of 9,9'-bifluorenyl.¹⁸ It is also significant that the spectrum of the dicesium salt is in between that of the CIP-SSIP and CIP-CIP dilithium salt.

Ion Pair Acidity. Ion pair acidities are defined by the transmetalation equilibrium of eq 2, in which HA is the acid whose pK is to be measured and HIn is a suitable indicator; the equilibrium constants are converted to pK differences.



$$-\log K = \text{p}K_{\text{HA}} - \text{p}K_{\text{HIn}}$$

The pK differences are converted to absolute pKs by assigning a reference indicator, fluorene, its pK value of 22.9 in DMSO.⁸ In this way we have established ion pair pKs for lithium¹⁹ and cesium¹⁰ ion pairs in tetrahydrofuran. All pK values are statistically corrected to reflect the acidity per hydrogen.

The indicators used for the cesium ion-pair acidity measurements of DBK were 9-phenylfluorene (pK 18.15) and 9-biphenylfluorene (pK 17.72).¹⁰ Experimental pK values at different concentrations of CsDBK are presented in Table S2. The decrease of the observed pK with increasing formal concentration of corresponding salt was shown previously for ketones^{7,20} and other compounds^{9,21} to result from aggregation of ion pairs to dimers or higher aggregates. The aggregation shifts the equilibrium 2 to the right, increasing the apparent K. A plot of the observed pK of the cesium enolate vs the logarithm of its total concentration is shown in Figure 5. In such plots the slope at any point is related to the mean degree of aggregation at that point.²⁰ For benzylic ketones such plots are curved and can be analyzed as monomer-dimer equilibria.⁷ At concentrations above 5×10^{-4} M the plot becomes virtually linear with a slope corresponding to a dimer.

For a monomer-dimer equilibrium, a plot of the experimental equilibrium constants K in eq 2 vs C/K (C is overall concentration of salt) can be shown to be linear. Figure 6 shows such a plot for the present case. The intercept gives the equilibrium constant for the monomer, and the slope is equal to $2K_2K$, in which K_2 is the dimerization constant ($n = 2$ in equilibrium 1).⁹ The monomer cesium ion-pair pK of DBK is 18.07 ± 0.03 , and the dimerization constant is $(3.5 \pm 0.5) \times 10^3 \text{ M}^{-1}$. The errors are those arising from standard deviations of intercept and slope. The error is larger for the dimerization constant because it includes errors in both the intercept and slope. The theoretical line corresponding

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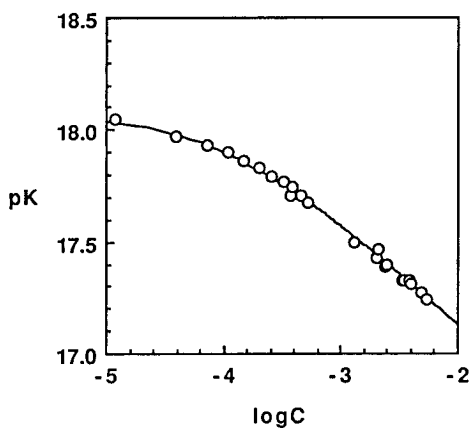


Figure 5. Plot of the experimental cesium pK values for dibenzyl ketone in THF at 25 °C vs the logarithm of formal concentration of DBK cesium enolate present in solution. The line shown is the theoretical curve for true $pK = 18.07$ and ion pair dimerization constant $K_2 = 3500 \text{ M}^{-1}$. Data are from Tables S2.

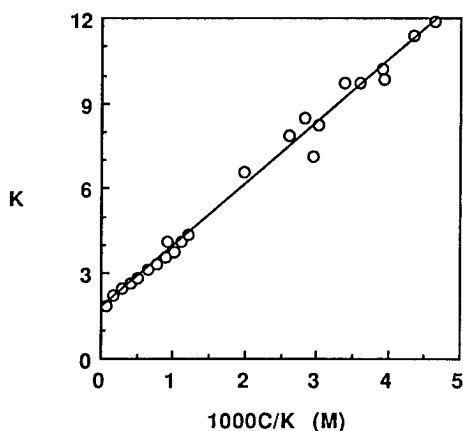


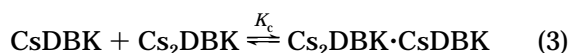
Figure 6. Plot of the equilibrium constant for the reaction: $\text{DBK} + \text{Cs}(9\text{-BpFl}) \rightleftharpoons 9\text{-BpFl} + \text{CsDBK}$ vs the total concentration of CsDBK divided by this constant. The line shown is the least squares fit: intercept 1.78 ± 0.12 , slope 21800 ± 500 , correlation coefficient 0.995. Data are from Table S2.

to these values is shown in Figure 5 and fits experimental points well. The above dimerization constant is higher than that reported earlier.⁷ The difference results from including acidity data at higher concentrations of the enolate, which significantly increases the accuracy of the determination of K_2 . It is notable also that the K_2 obtained from the SVD analysis is lower than that from the acidity data. This is in accord with the observation that SVD generally underestimates the aggregation constant.^{9,22} Nevertheless, SVD provides invaluable information about the number and type of species present in solution, in addition to their individual spectra.

Lithium ion-pair acidity results in THF obtained using 1,3-diphenylindene as indicator (pK 12.32)²³ are presented in Table S3. In the case of lithium as a counterion the analysis of the acidity data is complicated by the dissociation of the salt of the indicator acid to free ions. It was shown earlier¹⁹ that lithium salts of typical indicator acids (fluorenyl and triarylmethyl hydrocarbons with delocalized carbanions) have dissociation constants (K_d) in THF that are all close to $1 \times 10^{-5} \text{ M}$. This value

means that 27% of the indicator lithium salts are dissociated at a typical acidity measurement concentration of 10^{-4} M (total concentration of salt). If both acids in eq 2 are indicator hydrocarbons and their salts have the same dissociation constants, no change in the experimental K is observed with the variation of their concentration, and that constant represents the true ion-pair acidity, even though free ions are also present in the solution. In the case of DBK, however, as well as other compounds forming contact ion pairs with lithium, the dissociation constants are much lower, and this difference appears as a decrease of the acidity at lower concentrations of the salt. The observed relative acidity then depends both on the concentration of LiDBK (if it is aggregated) and the salt of the indicator. The dissociation constant for LiDBK may be estimated from the difference between the ionic pK of DBK (18.7)⁸ and lithium ion pair pK (11.62, see below). The difference of about 7 pK units corresponds to a difference of seven orders of magnitude between K_d of the lithium salt of the indicator and that of LiDBK; i.e., K_d for LiDBK is on the order of 10^{-12} M . This value implies an extent of dissociation of 0.01% in a 10^{-4} M solution, an amount that is entirely negligible for the present purpose. The necessary corrections can be made to K knowing the concentration of the lithium salt of the indicator and assuming its K_d to be 10^{-5} M . Both experimental and corrected values of K are presented in Table S3. Examination of the corrected lithium pK values for DBK shows that it varies with the LiDBK concentration much less than the cesium pK . A plot of K vs C/K similar to that of Figure 6 gives the dimerization constant for LiDBK of $420 \pm 70 \text{ M}^{-1}$, which is almost 1 order of magnitude lower than that for CsDBK. This result is in accord with the generalization that in THF lithium salts are generally less aggregated than the corresponding cesium salts²¹ and that in some cases aggregation is observed for cesium under conditions for which the lithium salts are monomeric.⁹ The monomer lithium ion pair pK of DBK was extrapolated as 11.62 ± 0.02 .

The second cesium pK of DBK, representing the ease of abstraction of an allylic proton from its enolate, was measured against di-*o*-tolylmethane as indicator (pK 34.22).¹⁰ The results summarized in Table S4 show a remarkable invariability of the equilibrium constant. The value of pK does not depend on the concentration of dianion salt or that of enolate and is 33.70 ± 0.02 . The concentration range covered is $(0.35 - 3.5) \times 10^{-3} \text{ M}$ in CsDBK, a range in which the relative amounts of its monomer and dimer vary substantially. The corresponding concentration of Cs_2DBK ranges from $(0.1 - 2) \times 10^{-4} \text{ M}$, sufficiently dilute that aggregation is not expected to be important. Yet, if Cs_2DBK were just monomeric in these experiments the actual acidity equilibrium constant should vary by more than a factor of two. CsDBK is in 5–70 fold excess over Cs_2DBK and the results are consistent with formation of a mixed aggregate that was formulated above as **2** in equilibrium with Cs_2DBK monomer (eq 3).



The simple electrostatic argument given above suggests that the equilibrium constant for complex formation, K_c , should be of similar magnitude to the dimerization constant of CsDBK monomer, K_2 . Indeed, if $K_c =$

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$2K_2$ the relative amounts of complex and monomer of Cs_2 -DBK and of dimer and monomer of CsDBK remain the same and the resulting proton transfer equilibrium is independent of concentration, as found experimentally!

It is instructive to compare the second pK of DBK with the acidity of 1,3-diphenylpropene (DPP), a compound having a close structural relationship to DBK enolate. This compound was reported to have a cesium pK in THF of 27.85,¹⁵ almost 6 pK units more acidic than CsDBK. The difference between the cesium salt of 1,3-diphenylpropene and Cs_2 DBK is the presence of a second cesium cation and an O^- group at the central carbon of the DBK enolate allylic anion system. It was shown previously that the presence of a COOLi group has an acidifying effect on an adjacent benzylic hydrogen almost as great as that of a COOR group, leading to a relatively low second lithium ion pair pK for 1-naphthylacetic acid.²⁴

We were not able to determine the second lithium pK of DBK because the base typically used in lithium acidity measurements, the lithium salt of 9,9,10-trimethyl-9,10-dihydroanthracene, failed to abstract the proton from LiDBK. This failure is not necessarily that it is not strong enough as a base (the estimated pK of 9,9,10-trimethyl-9,10-dihydroanthracene is well above 30), but rather that the rate of deprotonation is extremely low. It was found previously²⁵ that the deprotonation and the establishment of lithium acidity equilibria are very slow for compounds with pK s above 25. Even the rate of deprotonation of LiDBK by LDA is only moderate and the reaction requires about 30 min for completion.

Our results reveal little about the stereochemistry of the phenyl groups except that they must be significantly conjugated to the carbanion center. A previous NMR study has reported on such stereochemistry for Li_2 DBK in THF solution.²⁶

Experimental Section

General. The instrumentation and techniques used for the UV-vis spectral studies and acidity measurements were recently described in detail.⁹

Materials. Commercial dibenzyl ketone (99% Aldrich) was vacuum distilled three times from calcium hydride in a Kugelrohr apparatus. After the final distillation the receiving bulb was filled with dry argon and taken into the glove box. Material was then transferred to a vial; melting point 35–36 °C (lit.²⁷ 35 °C). Further evidence of purity was obtained from the NMR spectrum. Purification of THF was described earlier.⁹

Spectral and Acidity Measurements. General procedures were published recently.⁹ Bases used for deprotonation were (diphenylmethyl)cesium⁹ and cumylcesium²⁸ in the study of CsDBK and Cs_2 DBK, respectively, and (9,9,10-trimethyl-9,10-dihydroanthracenyl)lithium²¹ and LDA for LiDBK and Li_2 DBK. A solution of LDA in THF was prepared immediately prior to use from material twice sublimed and stored at –20 °C in a freezer inside the glovebox.

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Supporting Information Available: Tables S2–S4 (4 pages). This material is available in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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