signals assignable to three new alkylidene species (9.56, 9.90, 10.17 ppm) were observed in the ^1H NMR spectrum as were signals due to polyoctenomer (5.35 ppm) and possibly a metallacyclobutane species (6.4, 0.45 ppm). The complexity of the mixture prevents any assignment of the active species at this time. Clearly, more work will be necessary to understand how **2** is converted into a catalytically active species.

Compound **2** is not a ROMP catalyst in the absence of Lewis acid, presumably due to its electronic and coordinative saturation. The addition of Lewis acid cocatalysts to similar systems has succeeded in generating olefin metathesis catalysts previously,[32c,35] but these catalysts do not appear to operate in air. Recently, several ruthenium complexes have been shown to be catalyst precursors for the ROMP of substituted norbornenes in aqueous solution,[36] but the nature of the active species in these reactions remains elusive. The nature of the interaction between $AlCl_3$ and **2** is currently under investigation, but it is suspected to involve attack by $AlCl_3$ at the chloride ligand,[35b,37] generating a five-coordinate cationic alkylidene as the active species.

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Supplementary Material Available: Experimental details for the synthesis of **1** and **2** as well as for the polymerization reactions, tables of thermal parameters, positional parameters, and bond lengths and angles for **2**, and details of the X-ray crystal structure determination of **2** (13 pages); table of observed and calculated structures for **2** (27 pages). Ordering information is given on any current masthead page.

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Thermochemical Comparison of Organolithium Bases

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Organolithium reagents play an important role in synthetic organic chemistry.[1] Although several research groups have determined the strengths of many types of weak acids or their strong conjugate bases in solution[2–4] and in the gas phase,[5] we are unaware of any report that compares the bases used most often for synthetic operations.

Table I. Enthalpies of Deprotonation, $-\Delta H_{(dep)}$ (kcal/mol), of Isopropyl Alcohol by Organolithium Bases, with and without 1 equiv of Lithium *tert*-Butoxide, in 90:10 Hexane–Ether at 25 °C

organolithium base	$-\Delta H_{(dep)}$[a]	+1 equiv of *t*-BuOLi $-\Delta H_{(dep)}$[a]
tert-butyllithium	56.2 ± 1.8	56.0 ± 0.5
sec-butyllithium	52.8 ± 1.0	51.9 ± 0.7
n-butyllithium	50.0 ± 0.7	49.3 ± 0.4
phenyllithium	42.3 ± 0.3	42.8 ± 0.3
methyllithium	41.6 ± 0.7[b]	41.6 ± 2.2[b]
((trimethylsilyl)methyl)lithium	40.0 ± 0.6	41.5 ± 0.3
lithium dicyclohexylamide	31.8 ± 0.2	32.0 ± 0.3
lithium 2,2,6,6-tetramethylpiperidide	30.4 ± 1.6	30.5 ± 1.6
lithium isopropylcyclohexylamide	29.6 ± 0.5	29.8 ± 0.4
lithium diisopropylamide	28.6 ± 1.0	28.7 ± 0.3
lithium diethylamide	23.4 ± 0.3	23.7 ± 0.4
lithium cyclohexylamide	insoluble	21.8 ± 0.1
lithium isopropylamide	insoluble	21.3 ± 0.2
lithium *tert*-butylamide	21.2 ± 0.3	20.5 ± 0.2
lithium *n*-octylamide	18.9 ± 0.1	19.4 ± 0.5
lithium bis(trimethylsilyl)amide	12.1 ± 0.6	12.3 ± 0.5
lithium pinacolonate	3.4 ± 1.2[c]	
lithium *tert*-butoxide	2.1 ± 0.6[d]	

[a] Values are calculated on the basis of the known amount of isopropyl alcohol added to an excess of base. Errors are reported at the 95% confidence level. [b] Solvent was 100% diethyl ether to maintain solubility. [c] Value is calculated on the basis of the measured difference of $\Delta H_{(dep)}$'s for LiHMDS + *i*-PrOH (−12.1) and LiHMDS + pinacolone (−8.7). [d] Value is calculated on the basis of the measured difference of $\Delta H_{(dep)}$'s for LiHMDS + *i*-PrOH (−12.1) and LiHMDS + *t*-BuOH (−10.0).

Table II. Enthalpies of Deprotonation, $-\Delta H_{(dep)}$ (kcal/mol), of Isopropyl Alcohol by Organometallic Bases Reacting in 85:15 THF–Toluene at 25 °C

organometallic base[a]	$-\Delta H_{(dep)}$
LiHMDS	15.2 ± 0.5
1:1 mixture of LiHMDS and *t*-BuOLi	15.8 ± 0.4
1:1 mixture of LiHMDS and *t*-BuOK	7.3 ± 0.3
1:1 mixture of KHMDS and *t*-BuOLi	7.3 ± 0.3
KHMDS	2.9 ± 0.3
1:1 mixture of KHMDS and *t*-BuOK	3.3 ± 0.2

[a] LiHMDS = lithium bis(trimethylsilyl)amide. KHMDS = potassium bis(trimethylsilyl)amide. *t*-BuOLi = lithium *tert*-butoxide. *t*-BuOK = potassium *tert*-butoxide.

This report presents enthalpies of deprotonation, $\Delta H_{(dep)}$, of isopropyl alcohol (*i*-PrOH) by eighteen organolithium bases in a 90:10 by volume mixture of hexane–diethyl ether at 25 °C. The solvent system was chosen because of its inertness to strongly basic reagents[6] while still possessing ether oxygens for lithium solvation.[7] This thermochemical method provides the enthalpic driving force for the organolithium bases to deprotonate a common acid and incorporates the differential contributions from solvation, ion-

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(6) THF was attempted but decomposed visibly in the presence of *tert*-butyllithium at 25 °C.

(7) (a) The concentration of organolithium base was approximately 0.05 M, which gives about 15 ether oxygens per lithium. (b) The employment of vapor pressure osmometry to determine aggregation numbers as before[9] was rendered essentially useless due to a combination of a mixed solvent system, high instability of many of the organolithiums, and unknown exact concentrations of commercially available solutions used both as an organolithium base and as a reagent to generate all lithium amides. Information regarding aggregation of these species is available. See ref 8.

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pairing, and aggregation[8] for each lithium base and its conjugate acid in this solvent. Although the results are not convertible into pK_a's, we have reported a rough correlation between $\Delta H_{(dep)}$'s for many organic acids by lithium bis(trimethylsilyl)amide (LiHMDS) in THF and their pK_a's in DMSO.[9]

Of relevance to recent studies of mixed aggregates[10] are a series of related measurements in which 1 equiv of lithium *tert*-butoxide (*t*-BuOLi) was added to the organolithium bases prior to measuring $\Delta H_{(dep)}$ of *i*-PrOH. In no case, where comparison could be made, was $\Delta H_{(dep)}$ changed within experimental error as a result of the added *t*-BuOLi. The most dramatic effects were for the solubilities of lithium cyclohexylamide and lithium isopropylamide. Neither salt alone is soluble in the 90:10 hexane–diethyl ether solvent, but both are completely soluble if an equivalent of *t*-BuOLi is in solution prior to introducing the lithium amide.

Table I shows the relative energetic differences between the $\Delta H_{(dep)}$'s for the organolithium bases. Lithium alkyls gave the most exothermic $\Delta H_{(dep)}$'s, followed in order by secondary lithium amides, primary lithium amides, and the lithium alkoxides (the least reactive). LiHMDS is 10–20 kcal/mol less reactive than other secondary lithium amides, reflecting the superior ability of silicon to stabilize an α negative charge relative to carbon.

Recently, Bartmess and Thomas have utilized ion cyclotron resonance to obtain enthalpies of ionization in the gas phase[5g] where the intrinsic energetics are free of solvation and ion-pairing. When their values are plotted against $\Delta H_{(dep)}$'s of *i*-PrOH, a crude linear relationship is observed ($R = 0.86$). Clearly, differential solvation and aggregation energies contribute to the energetics of organolithium bases in solution.

Lochmann[11] and Schlosser[12] were first to observe altered reactivity of organolithium bases in the presence of potassium *tert*-butoxide (*t*-BuOK) where mixed metal aggregates are possible. We have investigated the effect of *t*-BuOK on the reactivity of LiHMDS[13] in a 85:15 by volume THF–toluene[14] mixture. Table II presents measured values of $-\Delta H_{(dep)}$ of *i*-PrOH reacting with lithium or potassium bis(trimethylsilyl)amide, with and without 1 equiv of lithium or potassium *tert*-butoxide. $\Delta H_{(dep)}$ depends strongly on the metal cations, but it is also apparent that the *tert*-butoxide anion has little effect on $\Delta H_{(dep)}$ as long as the added cation is not varied.

The reactivity of the 1:1 mixture of LiHMDS to *t*-BuOK is intermediate between that of the pure organolithium and organopotassium bases. More importantly, this reactivity is identical with that obtained by combining a 1:1 mixture of potassium bis(trimethylsilyl)amide and *t*-BuOLi, suggesting formation of the same species, whatever it may be.

Acknowledgment. This work was supported by NSF Grant CHE-8709249 for which we are most appreciative.

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[13] Other secondary lithium amides were tried, but upon addition of *t*-BuOK, decomposition of the solvent was observable within a few minutes.

[14] Toluene is necessary to solubilize potassium bis(trimethylsilyl)amide which was needed for these experiments.

Conformational Dichotomy and Pyramidalized Carbonyl Groups in Zinc Aldolate Chelates Obtained from Aldol Condensations of Ketones: Crystallographic Characterization of $\{[(Me_3Si)_2N]Zn[\mu,\eta^2\text{-}OCR^1(CH_2R^2)CHR^2C(O)R^1]\}_2$

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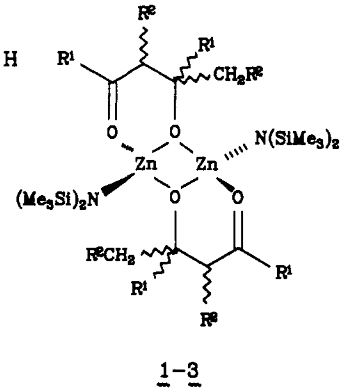
In a classic 1973 paper House and co-workers reported that condensations between lithium enolates and carbonyl compounds proceed in higher yields in the presence of zinc(II) ion.[1] The proposed role of zinc(II) is the formation of stable zinc aldolate chelates, which are believed to displace equilibria in favor of condensation[1] and to govern diastereoselectivities under thermodynamically controlled conditions.[1,2]

We now provide the first crystallographic evidence for such zinc aldolate chelates.[3] Our data reveal that *both* chair-like and boat-like chelate conformations are readily accessible, and as a consequence, diastereomeric aldolate complexes are rendered nearly isoenergetic. Furthermore, the deviations from ideal half-chair chelate conformations result in large pyramidal deformations in the aldolate carbonyl carbon atoms.

In typical zinc-mediated aldol condensations, $ZnCl_2$ is added to preformed lithium enolates.[1] However, we found that the enolate-forming base (R_2N^-) and the chelating metal ion (Zn^{2+}) could be combined in the same reagent: $Zn[N(SiMe_3)_2]_2$.[4] The ketones $R^1C(O)CH_2R^2$ (2 equiv) and $Zn[N(SiMe_3)_2]_2$ reacted in aromatic solvents to give the zinc aldolate complexes **1–3** (eq 1), which crystallized directly from the reaction mixtures in 60–82% yields.[5] NMR monitoring revealed that eq 1 proceeds very slowly below ca. −20 °C; the expected zinc enolate intermediates were not detected (−20 to +25 °C), suggesting that enolate formation is the slow step.

$$2Zn[N(SiMe_3)_2]_2 + 4R^1C(O)CH_2R^2 \xrightarrow{-\ 2HN(SiMe_3)_2}$$

1, R^1 = Me, R^2 = H
2, R^1 = t–Bu, R^2 = H
3, R^1, R^2 = $(CH_2)_4$



(1)

1–3

The diacetone aldolate **1** is structurally disordered in the solid state;[6] it exists as two superposed, C_i-symmetry isomers in a

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[5] Compounds **1–3** were characterized by elemental analyses (C, H, N, Zn) and IR, ^1H NMR, and ^{13}C NMR spectroscopies. See the supplementary material.

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