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.

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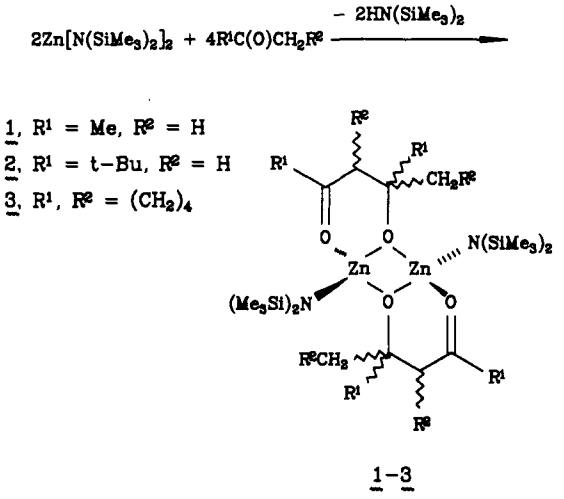
In a classic 1973 paper House and co-workers reported that condensations between lithium enolates and carbonyl compounds proceed in higher yields in the presence of zinc(II) ion.[1] The proposed role of zinc(II) is the formation of stable zinc aldolate chelates, which are believed to displace equilibria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



(1)

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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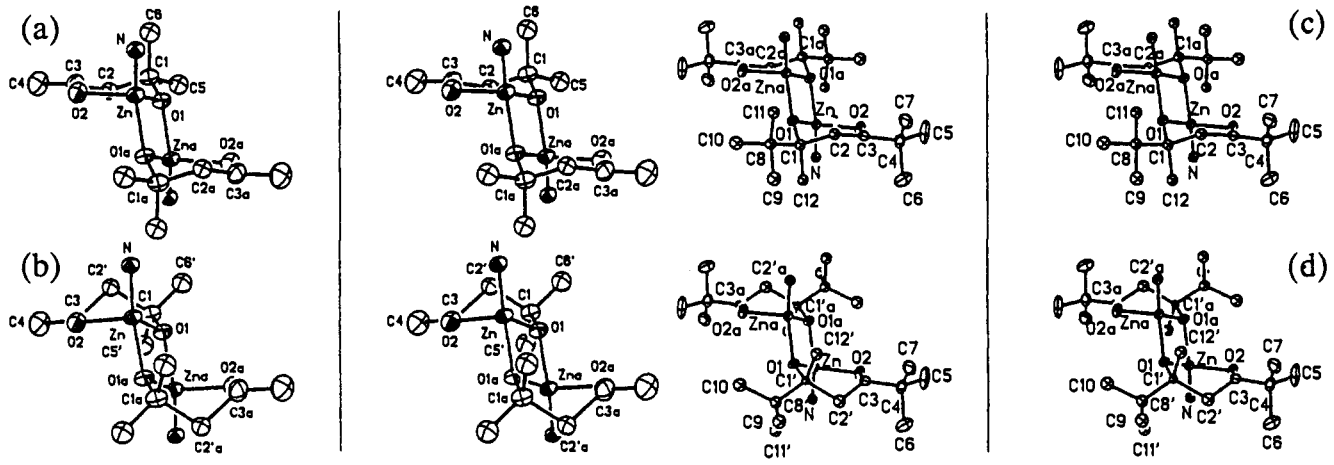

Figure 1. Stereoviews of the aldolate complexes **1** and **2**: (a) the chair isomer of the the diacetone aldolate **1**, (b) the twist-boat isomer of **1**, (c) the half-chair isomer of the dipinacolone aldolate **2**, and (d) the twist-boat isomer of **2**. The Me_3Si groups have been omitted for clarity. Bond distances and angles are given in the supplementary material.

64 (1):36 (1) ratio[7] in which the aldolate rings adopt chair (approaching half-chair) and twist-boat conformations, respectively. The two conformational isomers are plotted separately for clarity in parts a and b of Figure 1; however, they share common atomic positions within the crystal lattice except at C(2), C(5), and C(6), which belong to the chair isomer, and C(2)′, C(5)′, and C(6)′, which belong to the twist-boat isomer. The observed 64:36 ratio indicates that the chair form is only marginally more stable than the twist-boat form in the solid state. A single set of aldolate resonances was observed by NMR,[5] consistent with the expected rapid interconversion of the chair and twist-boat conformers. The simplicity of the NMR spectra[5] of **1** requires its facile degenerate rearrangement (likely) or its dissociation to monomers (unlikely) in solution.

The dipinacolone aldolate **2** is also structurally disordered in the solid state,[6] in a manner analogous to **1**. **2** exists as two superposed, C_i-symmetry, half-chair and twist-boat isomers in a 77 (1):23 (1) ratio.[7] They are plotted separately in parts c and d of Figure 1 although they too share many common atomic positions. The isomers of **2** are diastereomeric because of the different relative configurations of C(1) and C(1)′, which allow the C(1) and C(1)′ *tert*-butyl groups to remain equatorial in each diastereomer. In solution, *three* diastereomers of **2** were detected by NMR in a 58 (5):30 (5):12 (5) ratio;[5] only a single set of ligand resonances was observed for each of the two predominant diastereomers, which is consistent with the C_i symmetry found in the solid state.

Although the aldolate chelates are six-membered rings containing one double bond [the C=O distances are 1.195 (8) Å for **1** and 1.208 (8) Å for **2**], only the chelate in the major diastereomer of **2** (Figure 1c) exhibits a half-chair conformation, which is the energy minimum for cyclohex*ene*.[8] The remaining examples (parts a, b, and d of Figure 1) exhibit chair or twist-boat conformations, which are energy minima for cyclohex*ane*,[8] and are at or near energy minima for *saturated*, six-membered, metal chelates.[9] Consequently, angle strain should develop at the trigonal (sp^2) centers in the latter cases, and accordingly, the carbonyl carbon atoms [C(3) in parts a, b, and d of Figure 1] were found to be distinctly pyramidalized.[10] The Δ_c values (which describe the separation of an sp^2 carbon from the plane defined by its three substituent atoms[11]) for the chair isomer of **1**, the twist-boat isomer of **1**, and the twist-boat isomer of **2** are 0.17, 0.28, and 0.23 Å, respectively. These values are quite large, and for comparison, the Δ_c values recently determined by Seebach and co-workers for five- and six-membered organic rings containing one double bond and having pyramidally deformed sp^2 centers were in the range of 0.008–0.11 Å.[12] *Exo*cyclic pyramidalized carbonyl groups within chelate rings have been previously observed by Collins and co-workers;[13] to our knowledge, **1** and **2** are the only *endo*cyclic examples.

The results above allow the following observations and conclusions: (1) The near degeneracy of chair- and boat-like *ground-state structures* established herein parallels the near degeneracy of analogous chair- and boat-like *transition-state structures* for aldol condensation established by a recent theoretical study.[14] (2) Energy differences between diastereomers having different relative configurations at zinc and carbon stereogenic centers appear to be largely cancelled by the chair–boat conformational dichotomy of the chelates. (3) The tendency toward cyclohex*ane*-like conformations induces sizable pyramidal deformations in the carbonyl carbons. Such pyramidalization may in part account for the success of the chelation-control strategy,[12b] in which the stereoselectivity of nucleophilic addition to a carbonyl group is controlled by its incorporation into a metal-chelate ring.[15]

The bulky auxiliary amido ligand[16] is the unique feature that allows the zinc aldolate complexes to maintain low molecularities and to be easily crystallized. Further studies of aldolate chelates that take advantage of this feature are in progress.

Acknowledgment. Support was provided by a BRSG grant administered through Washington University. The Washington

(6) Crystal data for **1** and **2** are given in the supplementary material.

(7) Atomic positions for the major *and* minor conformers were located by Fourier synthesis from difference electron density maps. *Positional parameters* for *all* non-hydrogen atoms were subsequently refined *without constraint*. In the last cycle of refinement the site occupancy factors (sof's) for the partially occupied sites *within each conformer* were constrained to be equal, and the sum of the sof's for the two conformers was constrained to unity. The refined sof's gave the conformer ratio directly. Because fixed isotropic displacement parameters were assigned to the partially occupied sites, the esd's determined for the sof's (and thus the conformer ratio) are probably underestimated.

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Supplementary Material Available: Description of experimental procedures and spectroscopic data for **1-3** and listings of the details of the data collection, final positional and equivalent isotropic parameters, bond distances, bond angles, calculated hydrogen atom parameters, and anisotropic thermal parameters for **1** and **2** (19 pages); listings of observed and calculated structure factors for **1** and **2** (33 pages). Ordering information is given on any current masthead page.

A Novel Mode of Coordination for Phosphorus

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The transition-metal coordination chemistry of ADPnO[1] systems containing 3-coordinate, 10-electron pnictogen centers (10-Pn-3,[2] Pn = P, As, or Sb) proved to be valuable in understanding the nature of bonding in these systems.[3-8] Previous work on these molecules shows that they behave differently depending on the pnictogen. The heavier analogues, ADAsO and ADSbO are capable of donating either one or both lone pairs on the pnictogen to transition-metal fragments while maintaining their planar, 10-Pn-3, form.[4-7] However, ADPO adopts a folded, 8-P-3 form upon coordination to metal centers.[3,5-8] This special behavior of ADPO toward transition-metal Lewis acids has its origins in a configuration mixing that transfers σ-electron density to the π-systems at phosphorus.[6,8,9] In this way planar 10-P-3 ADPO is stabilized by ~14 kcal/mol over its folded 8-P-3 form.[9] Thus far, the complexes of ADPO which have been investigated have employed metals (Cr, W,[10] Mn,[7] Fe,[8] Ru,[6] Pt[3]) which have sufficiently high P→M bond strengths to disturb the 8-P-3 vs 10-P-3 ADPO balance. Silver(I) species have been demonstrated to have low P→Ag bond strengths with activation energies for dissociation less than 11 kcal/mol.[11] Thus, silver(I) should have less of a perturbing effect on the planar 10-P-3 ADPO ring system.

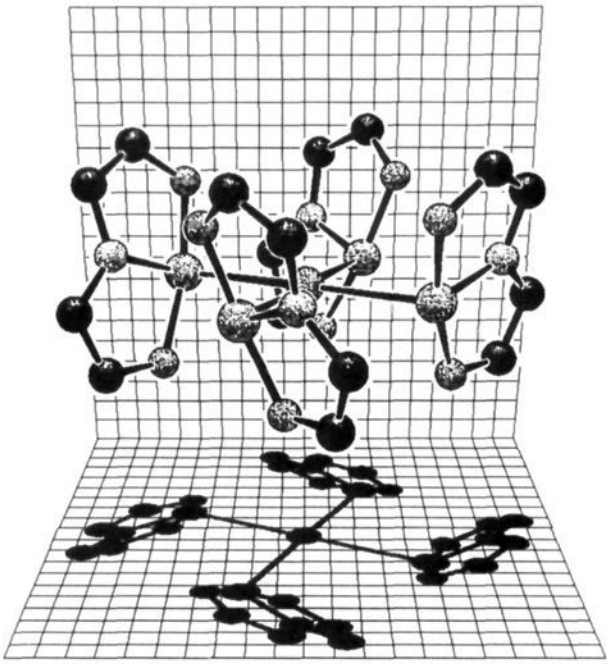
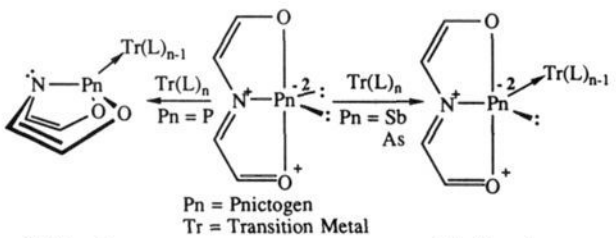


Figure 1. KANVAS[18] drawing of $[(ADPO)_4Ag]^+$. Hydrogens and *tert*-butyls have been omitted for clarity.

Table I. Selected Bond Distances and Angles for $[(ADPO)_4Ag]^+SbF_6^-$ and ADPO[a]

property	$[(ADPO)_4Ag]^+$	ADPO
P–Ag	261.2 (1)	
P–O	179.2 (3), 181.5 (3)	179.2 (2), 183.5 (2)
P–N	172.0 (4)	170.3 (2)
$C-C_{ring}$	134.1 (6), 134.6 (6)	134.2 (4), 133.7 (4)
C–N	137.6 (5), 138.3 (5)	137.5 (3), 138.2 (3)
C–O	134.0 (5), 131.8 (5)	133.1 (4), 132.8 (4)
O–P–O	167.6 (2)	167.7 (1)
N–P–O	84.4 (2), 83.7 (2)	84.2 (1), 83.5 (1)
P–Ag–P	90.00 (1), 179.00 (1)	
Ag–P–N	113.3 (1)	

[a] Bond distances in pm and angles in deg.



8-Pn-4 complex **10-Pn-3 ADPnO** **10-Pn-4 complex**

We now report the synthesis and structure of $[(ADPO)_4Ag]^+SbF_6^-$, which represents the first example of a transition-metal complex containing a ψ-tbp 10-P-4 phosphorus center. The reaction (eq 1) of $[Ag(NCCH_3)_4]^+SbF_6^-$ with 4 equiv of ADPO in CH_2Cl_2 gave yellow crystalline $[(ADPO)_4Ag]^+SbF_6^-$ in 67% isolated yield.[12]

(1) The ADPnO acronym has been previously described and is used for simplicity in place of the name of the ring system it represents: 5-*aza*-2,8-*d*ioxa-1-*pn*ictabicyclo[3.3.0]*o*cta-2,4,6-triene. See ref 5, footnote 1d for details.

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