

Articles

1:1 and 2:1 Lithium Zincates with Intramolecular Coordination. Structures of $\text{Li}(\text{thf})\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2})_3$ and $\text{Li}_2\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2})_4$

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Homoleptic lithium zincates with intramolecular Li–N coordination, *i.e.*, $\text{Li}(\text{thf})_n\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2})_3$ ($n = 0$ (**1**); $n = 1$ (**1(thf)**)) and $\text{Li}_2\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2})_4$ (**2**) have been prepared by reacting $[\text{Li}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2})]_4$ with $\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2})_2$. In the solid state **1(thf)** is a monomer containing a distorted tetrahedral zinc atom. The zinc is surrounded by three monoanionic $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2}$ (dmba) ligands, which all show a different bonding mode: $\eta^1\text{-C}$ bonding to zinc and nitrogen coordination to lithium; $\eta^1,\mu^2\text{-C}$ bridge bonding to zinc and lithium with Li–N coordination; and *C,N*-chelate bonded to zinc. One thf coordinates to lithium. In the solid state, **2** is a monomeric dilithium tetraarylzincate complex containing a tetrahedral zinc atom. The four dmba ligands are all similarly $\eta^1,\mu^2\text{-C}$ bridge-bonded to zinc and lithium, and each lithium is four-coordinate by two additional Li–N bonds. The reaction of $\text{LiCH}_2\text{SiMe}_3$ and $\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2})_2$ did not give a mixed zincate complex but the respective homoleptic zincate complexes instead. Both homoleptic and *in situ* prepared mixed zincate complexes react readily with 2-cyclohexen-1-one, but the product composition shows that the *in situ* prepared zincate disproportionates into the corresponding homoleptic zincates prior to reaction.

Introduction

Recently, we reported the synthesis and characterization of the first magnesium bis(zincate) complex, $\text{Mg}(\text{thf})_6[\text{Zn}(\text{CH}_2\text{Ph})_3]_2$.¹ Among the limited number of reported studies^{2a–i} on the structural aspects of triorganozincate complexes, no such complexes containing potentially intramolecularly coordinating groups in the ligands bound to zinc are known. In earlier studies on organocuprates,^{3a} -argentates,^{3b,c} and -aurates,^{3d} we have shown that the use of monoanionic arylamine

ligands, such as the monoanionic potentially *C,N*-chelating $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2}$ (dmba) ligand, in which the amino substituent may be regarded as a suitably positioned solvent donor molecule, leads to the formation of stable well-defined aggregates. We have now used this concept in the synthesis of arylzincate complexes.

Results

Synthesis. The reaction of $[\text{Li}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2})]_4$ with $\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2})_2$ in a 1:1 lithium to zinc atomic ratio in thf gave the homoleptic 1:1 lithium triarylzincate $\text{Li}(\text{thf})\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2})_3$ (**1(thf)**), see Scheme 1. Recrystallization of **1(thf)** from thf at room temperature and at -30°C afforded two different types of crystals, which turned out to be **1(thf)** and **1(thf)·1/2(thf)**, respectively. From the same reaction in a 2:1 lithium to zinc atomic ratio, the 2:1 tetraarylzincate complex $\text{Li}_2\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2})_4$ (**2**) was isolated quantitatively. Alternatively, **2** was obtained from the reaction of $[\text{Li}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2})]_4$ with **1(thf)** in a 1:1 lithium to zinc atomic ratio under identical reaction conditions. THF-free $\text{LiZn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2})_3$ (**1**) was obtained by evaporation of all volatiles from a benzene solution of **1(thf)**. The complexes **1**, **1(thf)**, and **2** are obtained as air- and moisture-sensitive colorless solids, which are extremely soluble even in apolar organic solvents, such as pentane.

Solid State Structures. As stated above, crystallization of **1(thf)** from thf at room temperature and at

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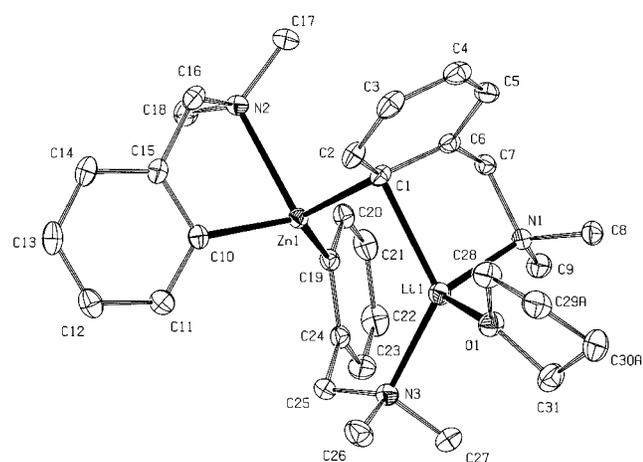
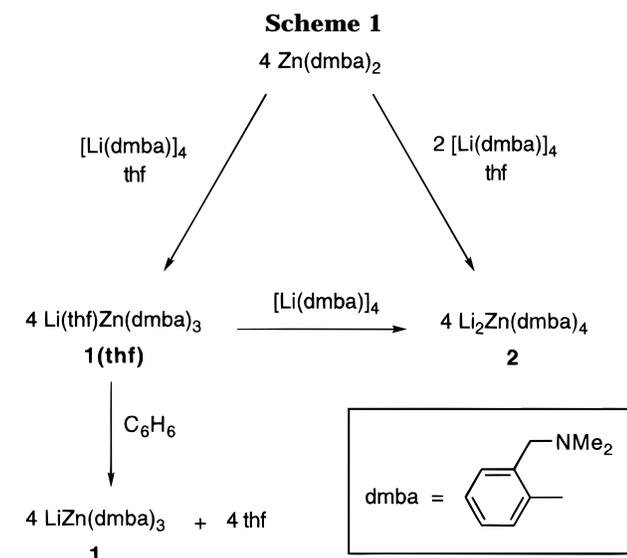


Figure 1. Thermal motion ellipsoid plot (ORTEP, at 30% probability level) of the molecular structure of **1**(thf), together with the adopted numbering scheme. The minor disorder component and the hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for **1(thf)^a**

Bond Distances			
Zn(1)–C(1)	2.082(2)	Li(1)–C(1)	2.414(6)
Zn(1)–C(10)	2.038(2)	Li(1)–N(1)	2.116(5)
Zn(1)–C(19)	2.026(2)	Li(1)–N(3)	2.125(4)
Zn(1)–N(2)	2.340(3)	Li(1)–O(1)	2.020(6)
Bond Angles			
C(1)–Zn(1)–C(10)	113.19(9)	Zn(1)–C(1)–Li(1)	82.33(12)
C(1)–Zn(1)–C(19)	118.97(9)	C(4)⋯C(1)–Zn(1)	159.66(16)
C(10)–Zn(1)–C(19)	125.79(8)	C(4)⋯C(1)–Li(1)	117.96(16)
C(1)–Zn(1)–N(2)	97.40(10)		

^a The estimated standard deviations are given in parentheses.

–30 °C afforded crystals of **1**(thf) and **1**(thf)·½(thf), respectively. The **1**(thf)·½(thf) crystals diffracted rather poorly. Since the molecular geometries in both structures are identical within experimental error, the geometrical parameters cited in this paper refer to the more accurately determined structure of **1**(thf). The molecular structure of **1**(thf) shows a monomeric lithium triarylzincate containing four-coordinate zinc and lithium atoms, see Figure 1. Selected atomic bond lengths and angles are listed in Table 1.

The zinc atom has a somewhat distorted tetrahedral coordination geometry formed by three dm_{ba} C_{ipso} atoms and one dm_{ba} nitrogen. The distortion is such that the zinc lies only 0.1693(4) Å above the plane of the three

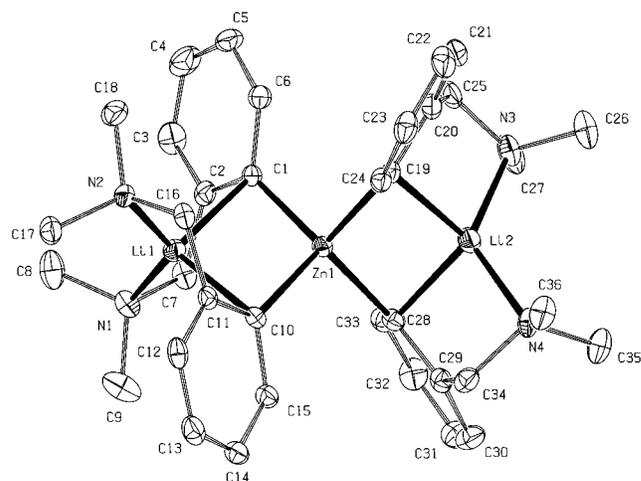


Figure 2. Thermal motion ellipsoid plot (ORTEP, at 30% probability level) of the molecular structure of **2**, together with the adopted numbering scheme. The hydrogen atoms have been omitted for clarity.

carbon atoms, and the sum of the C–Zn–C angles, which range from 113.19(9)° to 125.79(8)°, is 357.95(15)°, *i.e.*, close to the value of 360° for trigonal coordination. The three dm_{ba} ligands are each bonded in a different manner. One dm_{ba} is C,N-chelate bonded, η¹-C(10) to zinc, and forms a Zn(1)–N(2) coordinate bond. The second dm_{ba} is η¹-C(19) bonded to zinc, but the dimethylamino nitrogen N(3) coordinates to lithium. The Zn(1)⋯N(3) distance of 3.528(3) Å precludes any bridging interaction with the zinc. Finally, the third dm_{ba} is involved in Li(1)–N(1) coordination and C_{ipso} bridging between zinc and lithium *via* C(1). The fourth coordination site of the lithium atom is occupied by a thf molecule. The Zn(1)⋯Li(1) distance is 2.970(6) Å, much larger than the sum of the covalent radii of lithium and zinc (≈2.45 Å). The asymmetry of the bonding of the bridging dm_{ba} ligand is evident from the long Li(1)–C(1) bond of 2.414(6) Å (this bond in [LiCu(C₆H₄CH₂NMe₂-2)₂]₂ is 2.39 Å (mean)^{3a}) and the much shorter Zn(1)–C(1) bond of 2.082(2) Å. This asymmetry is further illustrated by the angles of the C(4)⋯C(1) vector with the Zn(1)–C(1) and the Li(1)–C(1) bonds of 159.66(16)° and 117.96(16)°, respectively. The Zn(1)–N(2) bond length is 2.340(3) Å, which is comparable to those found in four-coordinate Zn{(CH₂)₃NMe₂}₂,^{4a} Me₂Zn{(CH₂NMe₂)₃}₂,^{4b} Me₂Zn(tmeda)^{4c} (tmeda = Me₂–(CH₂)₂NMe₂), and (Me₃CCH₂)₂Zn(tmeda)^{4c} (ranging from 2.269(8) to 2.411(4) Å).

Suitable crystals of **2** were obtained by crystallization from hexane at room temperature. The molecular structure of **2** shows a 2:1 dilithium tetraarylzincate complex containing four-coordinate zinc and lithium atoms with slightly distorted tetrahedral geometries, see Figure 2. Selected atomic bond lengths and angles are listed in Table 2. The four dm_{ba} ligands in **2** are all similarly η¹,μ²-C_{ipso} bridge-bonded between the zinc and the lithium atoms in an asymmetric bonding mode, as reflected in the Zn–C_{ipso} and Li–C_{ipso} bond distances and the angles of the C_{para}⋯C_{ipso} vectors with the Zn–C_{ipso} and Li–C_{ipso} bonds. The C_{ipso}–Zn–C_{ipso} angles range from 106.51(15)° to 111.26(15)°. The Zn–C_{ipso}

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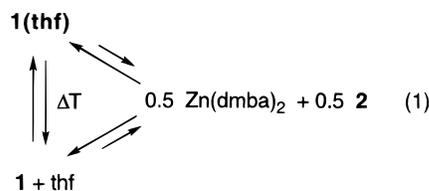
Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 2^a

Bond Distances			
Zn(1)–C(1)	2.124(4)	Li(1)–N(1)	2.026(7)
Zn(1)–C(10)	2.139(5)	Li(1)–N(2)	2.050(8)
Zn(1)–C(19)	2.152(3)	Li(2)–C(19)	2.226(9)
Zn(1)–C(28)	2.139(4)	Li(2)–C(28)	2.229(8)
Li(1)–C(1)	2.234(9)	Li(2)–N(3)	2.011(9)
Li(1)–C(10)	2.248(9)	Li(2)–N(4)	2.049(9)
Bond Angles			
Zn(1)–C(1)–Li(1)	72.9(2)	C(4)···C(1)–Zn(1)	168.1(2)
Zn(1)–C(10)–Li(1)	72.4(2)	C(4)···C(1)–Li(1)	118.5(3)
Zn(1)–C(19)–Li(2)	71.5(2)	C(13)···C(10)–Zn(1)	168.6(2)
Zn(1)–C(28)–Li(2)	71.7(2)	C(13)···C(10)–Li(1)	118.3(3)
C(1)–Zn(1)–C(10)	111.15(16)	C(22)···C(19)–Zn(1)	165.3(2)
C(1)–Li(1)–C(10)	103.4(3)	C(22)···C(19)–Li(2)	123.2(3)
C(19)–Zn(1)–C(28)	111.26(15)	C(31)···C(28)–Zn(1)	167.2(2)
C(19)–Li(2)–C(28)	105.3(3)	C(31)···C(28)–Li(2)	121.1(3)

^a The estimated standard deviations are given in parentheses.

distances of 2.139(2) Å (mean) are longer than those found in **1(thf)**, while the C_{ipso} –Li distances of 2.234(5) Å (mean) are shorter. In combination with the Zn– C_{ipso} –Li angles of 72.10(10)° (mean), these distances result in a Zn···Li distance of 2.576(5) Å (mean). The four-coordination of the two lithium atoms arises from the interaction with two C_{ipso} carbon atoms and Li–N coordination of two dimethylamino nitrogen atoms.

Structures in Solution. According to the ¹H NMR spectra in toluene-*d*₈ in the temperature range from 185 to 345 K, both **1** and **1(thf)** coexist with two minor species in a temperature-independent molar ratio of approximately 24:1:1. The resonances of the minor species are identical to those of Zn(C₆H₄CH₂NMe₂)₂⁵ and the 2:1 zincate **2**, suggesting the existence of equilibrium **1** in solution, eq 1.



The solid-state molecular structure of **1(thf)** is retained in solution at low temperature, as is evident from the ¹H and ¹³C NMR spectroscopy. The ¹H NMR spectrum of a toluene-*d*₈ solution of **1(thf)** at 210 K shows three AB-patterns for the CH₂N methylene hydrogen atoms, five distinct signals for the NMe₂ methyl groups of the dmab ligands, and resonances of coordinated thf. According to the integral ratios, the five signals for the NMe₂ methyl groups may be ascribed to the presence of four nonequivalent and two equivalent NMe₂ methyl groups. The equivalency of two NMe₂ methyl groups at low temperature indicates a fast dissociation/association process on the NMR time scale, which most probably involves the Zn-coordinated NMe₂ group. A broad resonance with a line width of 24 Hz was observed for the C_{ipso} bonded to lithium, which is in accord with a ¹³C nucleus being coupled to a ⁷Li nucleus with an average ¹J(¹³C–⁷Li) of about 8 Hz (cf. the ¹J(¹³C–⁷Li) is 7.0 Hz for [LiCu(C₆H₄CH₂NMe₂)₂]₂^{3a}). Attempts to resolve the expected quartet multiplicity (1:1:1:1 intensity distribution) failed (toluene-*d*₈, 210 K, 50 MHz). At higher temperatures, a dynamic process becomes operative that results in coalescence of the three AB-patterns for the CH₂N methylene

hydrogen atoms and the five signals for the NMe₂ methyl groups. Finally at 322 K, only one resonance pattern remains for the three dmab ligands, indicating that a fluxional process or intermolecular exchange processes are operative that makes them magnetically equivalent. Upon heating the solution of **1(thf)** from 210 to 271 K, the observed thf resonances shift from 3.23 and 1.21 ppm to 3.51 and 1.43 ppm, indicating that at the latter temperature **1** and noncoordinated thf are present. The presence of two separate species, **1** and free thf, instead of the aggregate **1(thf)** is also reflected in the low apparent molecular weight in solution found by means of cryoscopy in benzene (calcd for the mono-thf adduct **1(thf)**, 547; found, 237 (mean)).

The ¹H NMR spectra of separately prepared thf-free **1** are very similar to those of **1(thf)**, i.e., at 198 K, three AB-patterns for the CH₂N methylene hydrogen atoms and five signals for the NMe₂ methyl groups of the three dmab ligands are observed, which upon heating to 360 K coalesce into one resonance pattern. However, the ¹³C NMR spectrum (toluene-*d*₈, 205 K, 50 MHz) showed two broad resonances with line widths of 16 and 26 Hz for the two C_{ipso} atoms which are each coupled to a ⁷Li nucleus. We therefore propose that in thf-free **1**, besides the two intramolecularly coordinating CH₂NMe₂ groups, two dmab ligands are bridging *via* their C_{ipso} atoms to the lithium atom. The presence of two similarly bridging aryl ligands is also reported for the related lithium triorganomagnesiates species Li(thf)_{0.6}(Et₂O)_{0.4}Mg(2,4,6-*i*-PrC₆H₂)₃.⁶

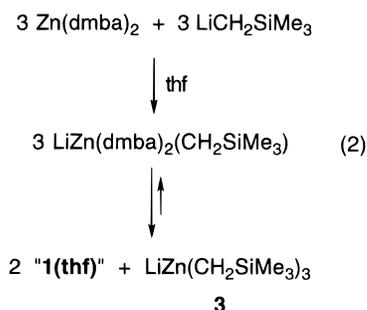
The solid-state molecular structure of **2** is retained in solution, as is evident from the ¹H and ¹³C NMR spectroscopy and a cryoscopic molecular weight determination in benzene. The ¹H NMR spectrum of **2** in toluene-*d*₈ over the temperature range from 210 to 333 K shows one AB-pattern for the CH₂N methylene hydrogen atoms and two singlets for the NMe₂ methyl groups of all four dmab ligands. Upon heating the solution to 346 K, the signals for the NMe₂ methyl groups coalesce, indicating a fast Li–N dissociation/association process ($\Delta G^\ddagger = 75.9 \text{ kJ}\cdot\text{mol}^{-1}$), while the CH₂N hydrogen atoms remain diastereotopic. The ¹³C NMR spectrum (toluene-*d*₈, 298 K, 50 MHz) shows one quartet resonance (1:1:1:1 intensity distribution) for four equivalent C_{ipso} carbon atoms which each couple with a ⁷Li nucleus with a ¹J(¹³C–⁷Li) of 9 Hz.

Mixed Zincates. The addition of a stoichiometric amount of LiCH₂SiMe₃ to Zn(C₆H₄CH₂NMe₂)₂ in thf at room temperature gave a colorless oil. The ¹H NMR spectrum of this oil in toluene-*d*₈ at 298 K shows that it consists predominantly (ca. 80%) of a 24:1:1:3 mixture of **1(thf)**, **2**, Zn(C₆H₄CH₂NMe₂)₂, and a species which has been identified as LiZn(CH₂SiMe₃)₃ (**3**).^{2b} Furthermore, the resonances of an unspecified mixed zincate species have been observed (ca. 20%). Apparently, a disproportionation equilibrium exists in solution (eq 2).

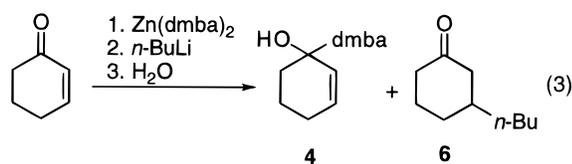
The presence in solution of a mixture of two homoleptic aggregates in addition to a mixed aggregate is apparent from the chemo- and regioselectivities observed in the reactions with 2-cyclohexen-1-one of these zincates and a related one prepared *in situ* from Zn(C₆H₄CH₂NMe₂)₂ and *n*-BuLi. The addition reactions of (*in situ* prepared) **1**, **1(thf)**, or **2** with 2-cyclohexen-1-one resulted in the exclusive formation of 1,2-

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adduct 1-[2-[(dimethylamino)methyl]phenyl]-2-cyclohexen-1-ol (**4**) similar to the reaction between $[\text{Li}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}2)]_4$ and 2-cyclohexen-1-one. *n*-BuLi gave the expected 1,2-adduct 1-*n*-butylcyclohexen-1-ol (**5**), while $\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}2)_2$ did not react. The *in situ* prepared mixed *n*-BuLi/ $\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}2)_2$ zincate gave the 1,2-adduct **4** and 1,4-adduct 3-*n*-butylcyclohexan-1-one (**6**) as the only reaction products, eq 3.



Discussion

By transmetalation of diorganozinc compounds with organolithium compounds, 1:1 and 2:1 lithium zincate complexes with intramolecular coordination, such as **1(thf)** and **2**, are formed. Although the reduction of diorganozinc compounds with alkali metals (Na, K) has been described to yield trialkylzincates,^{2b} the present transmetalation route has the advantage in that it provides a clean and efficient synthetic route to mixed zincate complexes.^{2g}

¹H NMR and cryoscopic measurements in benzene show that in solution **1(thf)** is in equilibrium with **1** and **2** (eq 1). A second equilibrium between **1(thf)**, **1**, and free thf depends on the temperature. The presence of a constant amount (approximately 4%, independent of the temperature) of **2** in solutions of recrystallized **1(thf)** indicates the existence of a third equilibrium. The position of the latter equilibrium can be shifted to the selective formation of **2** by the addition of 0.25 equiv of $[\text{Li}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}2)]_4$ with respect to **1(thf)**.

Complex **1(thf)** is the first example of a four-coordinate 1:1 zincate with a distorted tetrahedral geometry brought about by the presence of intramolecularly coordinating groups. So far, the only known four-coordinate 1:1 triorganozincate is dimeric sodium triethylzincate $[\text{Na}]_2[\text{Et}_2\text{Zn}(\mu^2\text{-Et})_2\text{ZnEt}_2]$.^{2a} Monomeric structures like that of the four-coordinate 2:1 zincate **2** are those of Li_2ZnMe_4 ,^{2a,c,d} K_2ZnMe_4 ,^{2c,d} and $[\text{Li}(\text{L})_2\text{Zn}(\text{-CHR}(\text{CHR})_n\text{CHR-})_2]$ (L = Et₂O; 2L = Me₂NCH₂C-H₂NMe₂, MeOCH₂CH₂OMe; *n* = 2, 3; R = H, Me)^{2e,f} and that of the related disodium tetraphenylmagnesiolate $[\text{Na}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)]_2\text{Mg}(\mu^2\text{-Ph})_4$.⁷

An interesting aspect of the molecular structures of **1(thf)** and **2** is the presence of at least one η^1, μ^2 -C bonded dmba ligand bridging between zinc and lithium. The asymmetry of the bridging dmba ligands is clearly illustrated by the long Li-C_{ipso} bond lengths and the much shorter Zn-C_{ipso} bond lengths. The orientation

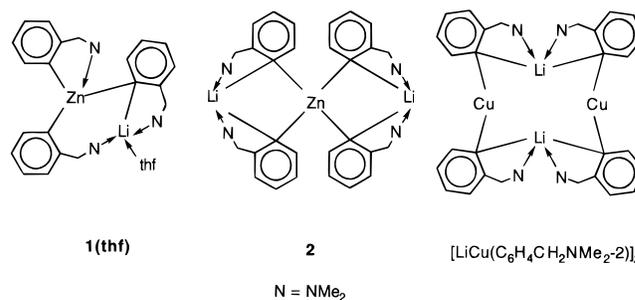


Figure 3. Comparison of the molecular structures of **1(thf)** and **2** with that of $[\text{LiCu}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}2)]_2$.^{3a}

of the bridging aryl ligands, *i.e.*, the tilting of the aryl planes in the direction of the lithium atoms, suggests a distortion of electron-deficient three-center two-electron bonding in the direction of electron-precise two-electron two-center Zn-C_{ipso} bonding, Figure 3. This is probably caused by the interaction of the lithium atom with the π -electron density on C_{ipso}, as also observed in the dimeric organocuprate analog $[\text{LiCu}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}2)]_2$.^{3a} The Zn-C_{ipso}-Li angles, being smaller than 90°, are indicative of the presence of some σ -character in the Li-C_{ipso} interactions, which is further corroborated by the observation of ¹J(¹³C-⁷Li) of 8 and 9 Hz for the bridging C_{ipso} atoms in **1(thf)** and **2**, respectively.

As a consequence of the bridging chelate bonding of the dmba ligands between two different metal centers, the bridging C_{ipso} carbon atoms in **2** are stereogenic. Since the Li-N coordination is inert on the NMR time scale, one NMe₂ substituent is coordinating above the $\text{LiZn}(\text{C}_{ipso})_2$ plane while the other one is coordinating below this plane. The two enantiomers that may be formed are C_RC'_R and C_SC'_S (C and C' are the two C_{ipso} carbon atoms). The diastereotopicity of the CH₂NMe₂ methylene hydrogen atoms (no coalescence of the AB-pattern in the temperature range from 210 to 382 K) indicates that the C_{ipso} carbon atoms are configurationally stable on the NMR time scale. Inversion of the configuration of the C_{ipso} carbon atoms, due to rotation of the aryl group around the C_{ipso}-C_{para} vector, is slow on the NMR time scale or does not occur at all. As a result of the stereogenicity of the C_{ipso} carbon atoms of the two chelate-bonded dmba ligands, the lithium atoms also become stereogenic centers. Therefore, **2** can theoretically exist as two diastereoisomers, *i.e.*, the mesomeric pair Li_SLi_R and Li_RLi_S and the enantiomeric pair Li_RLi_R and Li_SLi_S, see Figure 4. MM2 calculations on the geometries of these diastereoisomers reveal a significant difference in the total energies, *i.e.*, the mesomeric complex Li_SLi_R is lower in energy than Li_RLi_R and Li_SLi_S. The diastereoselective formation of **2** as the mesomeric complex is evident from the ¹H and ¹³C NMR spectra, which show only one symmetrical resonance pattern, and the X-ray structure determination showing the Li_SLi_R diastereoisomer (Figure 4a).

The straightforward formation of zincate species from diorganozinc compounds with organolithium compounds as shown in the present work suggest that such species may be important intermediates in zinc-catalyzed addition reactions of Grignard reagents or organolithium compounds to enones.⁸ However, in solution, these zincates are involved in a series of equilibria. Although

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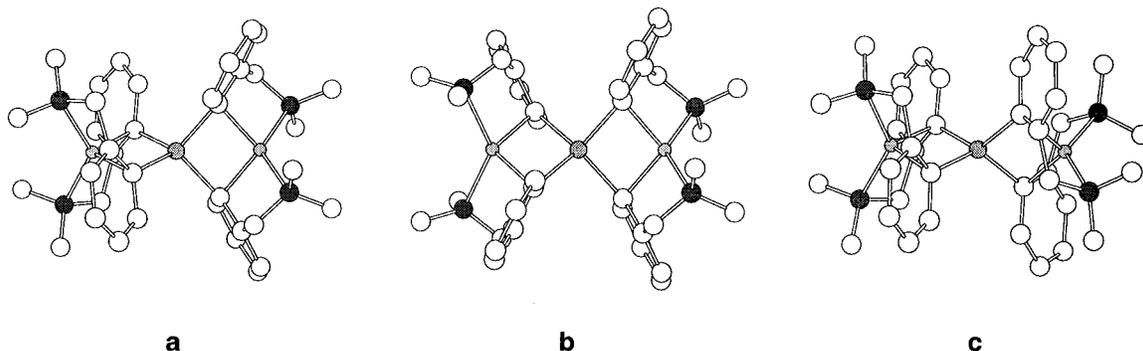


Figure 4. Diastereoisomeric forms of **2**: (a) Li_SLi_R , (b) Li_RLi_R , and (c) Li_SLi_S .

ligand exchange reactions have not been reported for the mixed zincate complexes $\text{KZn}(\text{CH}_2\text{SiMe}_3)_2\text{Ph}^{2b}$ and $\text{Li}(\text{thf})_4\text{ZnPh}_2(\text{C}(\text{SiMe}_3)_3)^{2g}$ we have found that the mixed zincate derived from $\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_2$ and $\text{LiCH}_2\text{SiMe}_3$ does disproportionate into the respective homoleptic complexes, indicating that the latter are thermodynamically more stable than the mixed zincate complexes. Preliminary attempts to use mixed zincates in zinc-catalyzed 1,4-additions have shown that the regioselectivity of the reaction of *n*-BuLi with 2-cyclohexen-1-one is indeed affected by addition of $\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_2$, *i.e.*, the *n*-Bu group is introduced selectively at the 4-position of the enone giving the 1,4-addition product **6**. However, the simultaneous formation of the 1,2-adduct **4** indicates that the *in situ* formed mixed zincate disproportionates into the corresponding homoleptic zincates prior to reaction with the substrate. Apparently, these homoleptic zincates are kinetically more reactive than the mixed zincate.

Experimental Section

General Data. All experiments were carried out under a dry, oxygen-free, nitrogen atmosphere, using standard Schlenk techniques. Solvents were dried and distilled from sodium/benzophenone prior to use. All standard chemicals were purchased from Aldrich Chemical Co. and Acros and used as received. $[\text{Li}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)]_4$,⁹ $\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_2$,⁵ and $\text{LiCH}_2\text{SiMe}_3$ ¹⁰ were prepared by published procedures. ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz at room temperature, unless stated otherwise. ^1H and ^{13}C NMR chemical shifts are in parts per million, relative to SiMe_4 as an external standard. Coupling constants are in Hertz. Cryoscopic measurements were performed in benzene. Melting points are uncorrected. Gas chromatography (GC) analyses were performed on a gas chromatograph equipped with a FID and an internal integrator using a 30 m DB 17 (liquid phase) capillary column (injector temperature, 270 °C; detector temperature, 270 °C; temperature program, 100 °C, 3 min, 20 °C·min⁻¹, 270 °C, 15 min). GC-MS was carried out using a spectrometer fitted with a gas chromatograph. Mass spectra obtained under electron ionization (EI) conditions (70 eV) were recorded by linear scanning from *m/z* 50 to 500. Elemental analyses were obtained from Dornis und Kolbe Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

Preparation of $\text{Li}(\text{thf})\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_3$ (1**(thf)).** To a stirred solution of $[\text{Li}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)]_4$ (2.00 g, 3.52 mmol) in thf (20 mL) at room temperature was added a solution of $\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_2$ (4.55 g, 13.55 mmol) in thf (20 mL). After 10 min, the solvent was removed *in vacuo* and the product was extracted with pentane (50 mL) and then dried *in vacuo*.

Yield: 7.03 g (12.78 mmol, 94%) of a colorless solid. Crystallization from thf at room temperature and at -30 °C afforded colorless crystals of **1**(thf) and **1**(thf) \cdot 1/2(thf), respectively. All of the following NMR data are for **1**(thf). ^1H NMR (toluene-*d*₈, 369 K): δ 8.05 (d, 1 H, ArH(6)), 7.05 (m, 3 H, ArH), 3.53 (m, thf), 3.42 (br s, 2 H, CH₂N), 1.83 (s, 6 H, NMe₂), 1.48 (m, thf). ^1H NMR (toluene-*d*₈, 210 K): δ 8.54 (d, 1 H, ArH(6)), 8.10 (m, 2 H, 2 ArH(6)), 7.7–6.9 (m, 9 H, ArH), 4.77 (d, 1 H, $^2J_{\text{HA}^{\prime}\text{HB}^{\prime\prime}} = 11.3$, CH_AH_BN), 4.48 (br d, 1 H, CH_A \prime H_B \prime N), 3.80 (d, 1 H, $^2J_{\text{HA}^{\prime}\text{HB}^{\prime\prime}} = 11.9$, CH_A \prime H_B \prime N), 2.99 (m, 4 H, thf), 2.82 (m, 2 H, CH_A \prime H_BN and CH_A \prime H_B \prime N), 2.45 (d, 1 H, $^2J_{\text{HA}^{\prime}\text{HB}^{\prime\prime}} = 10.7$, CH_A \prime H_B \prime N), 2.14 (s, 6 H, NMe₂), 1.84, 1.65, 1.40, 1.27 (4 s, 3 H, NMe), 1.08 (m, 4 H, thf). ^{13}C NMR (toluene-*d*₈, 210 K): δ 174.0, 170.5, 165.6 (ArC(1)), 148.7, 148.4, 148.0, 147.2, 146.6, 146.1, 145.7, 145.5, 140.7, 140.2, 140.0, 126.5, 125.7, 124.3 (Ar), 71.7 (CH₂N), 68.6 (2 CH₂N), 68.2 (thf), 48.0, 46.7, 43.9, 43.0 (NMe), 45.9 (NMe₂), 25.5 (thf). Anal. Calcd for C₃₁H₄₄N₃O₂LiZn: C, 68.07; H, 8.11; N, 7.68. Found: C, 67.86; H, 7.92; N, 7.74. Mp: 62–65 °C. Molecular weight determination by cryoscopy (1.14 g in 17.58 and 40.63 g benzene): calcd for the mono-thf adduct, 547; found, 240 and 235.

Preparation of $\text{Li}_2\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_3$ (1**).** A solution of **1**(thf) (2.24 g, 4.09 mmol) in benzene (30 mL) was allowed to stand at room temperature for 5 min. Removal of all volatiles *in vacuo* gave 1.78 g (3.75, 92%) of a colorless product. ^1H NMR (toluene-*d*₈, 360 K): δ 8.06 (d, 1 H, ArH(6)), 7.2–6.9 (m, 3 H, ArH), 3.40 (br s, 2 H, CH₂N), 1.82 (br s, 6 H, NMe₂). ^1H NMR (toluene-*d*₈, 198 K): δ 8.49, 8.19, 7.98 (3d, 3 × 1 H, ArH(6)), 7.30 (m, 9 H, ArH), 4.59 (d, 1 H, $^2J_{\text{HA}^{\prime}\text{HB}^{\prime\prime}} = 10.8$, CH_AH_BN), 4.10 (d, 1 H, $^2J_{\text{HA}^{\prime}\text{HB}^{\prime\prime}} = 10.3$, CH_A \prime H_B \prime N), 3.61 (d, 1 H, $^2J_{\text{HA}^{\prime}\text{HB}^{\prime\prime}} = 12.3$, CH_A \prime H_B \prime N), 2.75 (d, 1 H, $^2J_{\text{HA}^{\prime}\text{HB}^{\prime\prime}} = 12.8$, CH_A \prime H_B \prime N), 2.64 (d, 1 H, $^2J_{\text{HA}^{\prime}\text{HB}^{\prime\prime}} = 11.1$, CH_AH_BN), 2.52 (d, 1 H, $^2J_{\text{HA}^{\prime}\text{HB}^{\prime\prime}} = 10.6$, CH_A \prime H_B \prime N), 2.11, 2.03, 1.86, 1.47 (4 s, 3 H, NMe), 1.36 (s, 6 H, NMe₂). ^{13}C NMR (toluene-*d*₈, 205 K), relevant data: δ 168.3, 167.8 (br), 164.0 (br, ArC(1)), 70.9, 68.7, 67.1 (CH₂N), 47.1, 46.9, 45.7, 45.5 (NMe), 45.2 (NMe₂). Mp: 62–65 °C. Molecular weight determination by cryoscopy (0.47 g in 17.32 and 41.98 g benzene): calcd for monomer 475; found, 453 and 393.

Preparation of $\text{Li}_2\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4$ (2**).** **Method A.** To a stirred solution of **1**(thf) (0.62 g, 1.19 mmol) in thf (20 mL) at room temperature was added a solution of $[\text{Li}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)]_4$ (0.17 g, 0.30 mmol) in thf (20 mL). Evaporation of the solvent *in vacuo* gave the product as a colorless solid, yield 0.71 g (1.15 mmol, 97%). **Method B.** To a stirred solution of $[\text{Li}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)]_4$ (1.30 g, 2.30 mmol) in thf (20 mL) at room temperature was added a solution of $\text{Zn}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_2$ (1.52 g, 4.55 mmol) in benzene (20 mL). After 10 min, the solvent was removed *in vacuo* to give **2** as a colorless solid, yield 2.81 g (4.55 mmol, 100%). Crystallization from boiling hexane gave the product as colorless crystals. ^1H NMR (toluene-*d*₈, 298 K): δ 8.12 (dd, 1 H, ArH(6)), 7.3–7.1 (m, 3 H, ArH), 4.56 (d, 1 H, $^2J_{\text{HA}^{\prime}\text{HB}^{\prime\prime}} = 11.2$, CH_AH_BN), 2.78 (d, 1 H, $^2J_{\text{HA}^{\prime}\text{HB}^{\prime\prime}} = 11.2$, CH_AH_BN), 1.49, 1.43 (2 s, 2 × 3 H, 2 × NMe). ^1H NMR (toluene-*d*₈, 346 K): δ 8.04 (dd, 1 H, ArH(6)), 7.2–7.0 (m, 3 H, ArH), 4.53 (d, 1 H, $^2J_{\text{HA}^{\prime}\text{HB}^{\prime\prime}} = 11.3$, CH_AH_BN), 2.78 (d, 1 H, $^2J_{\text{HA}^{\prime}\text{HB}^{\prime\prime}} = 11.3$, CH_AH_BN), 1.49 (s, 6 H, NMe₂). ^{13}C

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Table 3. Crystallographic Data of the Structure Determination of 1(thf), 1(thf)^{-1/2}(thf), and 2

	1(thf)	1(thf) ^{-1/2} (thf)	2
Crystal Data			
empirical formula	C ₃₁ H ₄₄ LiN ₃ OZn	C ₃₁ H ₄₄ LiN ₃ OZn·1/2C ₄ H ₈ O ^a	C ₃₆ H ₄₈ Li ₂ N ₄ Zn
molecular weight [g]	547.04	583.09 ^a	616.08
cryst syst	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> , Å	13.1167(9)	34.041(4)	9.8312(5)
<i>b</i> , Å	15.1336(15)	10.6964(10)	22.9980(10)
<i>c</i> , Å	19.7182(8)	17.907(3)	18.0290(10)
β, deg	130.010(5)	102.529(13)	119.931(4)
<i>V</i> , Å ³	2998.0(4)	6365.0(15)	3532.6(3)
<i>D</i> _{calcd} , g·cm ⁻³	1.212	1.217 ^a	1.158
<i>Z</i>	4	8	4
<i>F</i> (000)	1168	2496 ^a	1312
μ(Mo Kα), cm ⁻¹	8.6	8.3 ^a	7.2
cryst size, mm	0.25 × 0.5 × 0.5	0.05 × 0.15 × 1.0	0.23 × 0.23 × 0.38
Data collection			
θ _{min} , θ _{max} , (SET4) deg	11.42, 13.95	8.86, 15.26	9.90, 14.04
θ _{min} , θ _{max} , deg	1.35, 27.5	1.16, 25.4	0.89, 27.5
scan type	ω/2θ	ω	ω
Δω, deg	0.56 + 0.35 tan θ	0.76 + 0.35 tan θ	0.59 + 0.35 tan θ
horz, vert aperture, mm	3.00, 4.00	3.00 + 1.50 tan θ, 4.00	3.00 + 1.50 tan θ, 4.00
X-ray exposure time, h	14	18	12
linear instability, %	4	<1	2
reference reflns	232; 321; 416	223; 025; 1202	222; 231; 222
data set	-17 to +17, -18 to 0, -25 to +17	-40 to +40, 0-12, 0-21	0-12, -28 to 0, -23 to +20
total data	7227	6049	8291
total unique data	6703 [<i>R</i> _{int} = 0.029]	5841 [<i>R</i> _{int} = 0.094]	7848 [<i>R</i> _{int} = 0.044]
DIFABS corr range	0.833-1.133		
Refinement			
no. of refined params	348	180	396
final <i>R</i> ^b	0.040 [4971 <i>I</i> > 2σ(<i>I</i>)]	0.111 [2045 <i>I</i> > 2σ(<i>I</i>)]	0.064 [4396 <i>I</i> > 2σ(<i>I</i>)]
<i>wR</i> 2 ^c	0.095	0.186	0.122
<i>w</i> ⁻¹ <i>d</i>	σ ² (<i>F</i> ²) + (0.0448 <i>P</i>) ²	σ ² (<i>F</i> ²) + (0.0400 <i>P</i>) ²	σ ² (<i>F</i> ²) + (0.0280 <i>P</i>) ² + 1.34 <i>P</i>
(Δσ) _{av} , (Δσ) _{max}	0.000, 0.003	0.000, 0.001	0.000, 0.000
min and max residual density, e ⁻ Å ⁻³	-0.44, 0.25	-0.90, 0.61	-0.39, 0.48

^a With disordered solvent contribution (see text). ^b *R* = Σ||*F*_o - |*F*_c||/Σ|*F*_o|. ^c *wR*2 = [Σ|*w*(*F*_o² - *F*_c²)|/Σ[*w*(*F*_o²)^{1/2}]]^{1/2}. ^d *P* = (max(*F*_o², 0) + 2*F*_c²)/3.

NMR (toluene-*d*₆, 298 K): δ 169.6 (q, ¹J(¹³C-⁷Li) = 9, ArC(1)), 148.5, 145.6, 129.2, 128.0, 125.3 (Ar), 69.7 (CH₂N), 46.6, 42.0 (NMe). Anal. calcd for C₃₆H₄₈N₄Li₂Zn: C, 70.19; H, 7.85; N, 9.09; found, C, 70.26; H, 7.81; N, 9.08. Mp: 167 °C (dec.). Molecular weight determination by cryoscopy (0.95 g in 14.86 and 27.71 g benzene): calcd for monomer: 616; found, 586 and 589.

Reaction of Zn(C₆H₄CH₂NMe₂-2)₂ with LiCH₂SiMe₃. To a stirred solution of Zn(C₆H₄CH₂NMe₂-2)₂ (1.15 g, 3.45 mmol) in thf (20 mL) at room temperature was added a solution of LiCH₂SiMe₃ (0.33 g, 0.50 mmol) in thf (20 mL). After the mixture was stirred for 15 min, evaporation of the solvent *in vacuo* gave the product as a colorless oil, yield 1.67 g (3.34 mmol, 97% with respect to the assumed mixed zincate, Li(thf)Zn(C₆H₄CH₂NMe₂-2)₂(CH₂SiMe₃). ¹H NMR in toluene-*d*₆ at 298 K showed the product to be predominantly (ca. 80%) a 24:1:1:13 mixture of **1**, Zn(C₆H₄CH₂NMe₂-2)₂, **2**, and LiZn(CH₂SiMe₃)₃ (**3**) and ca. 20% of a unidentified mixed species.

Reaction of [Li(C₆H₄CH₂NMe₂-2)]₄ with 2-Cyclohexen-1-one. To a stirred solution of [Li(C₆H₄CH₂NMe₂-2)]₄ (0.92 g, 1.62 mmol) in thf (30 mL) at 195 K was added 2-cyclohexen-1-one (0.60 mL, 6.22 mmol). After the mixture was stirred for 30 min, the reaction mixture was hydrolyzed with 5 mL of an aqueous solution of NaOH. The reaction products were analyzed by GC: *t*_R **4** 10.27 min (100%). GC-MS (relative intensity): *m/z* 230 (M⁺, 3), 158 (46), 141 (43), 115 (53), 91 (52), 58 (100). ¹H NMR (CDCl₃): δ 7.4-7.1 (m, 4 H, ArH), 5.94 (dt, 1 H, CH₂CH=), 5.81 (d, 1 H, CH=), 4.01 (d, 1 H, ²J_{H_AH_B} = 14, ArCH_A), 3.30 (d, 1 H, ²J_{H_AH_B} = 13, ArCH_B), 2.3-1.4 (m, 12 H, NMe₂ and CH₂). ¹³C NMR (CDCl₃): δ 149.4, 147.3 (quaternary Ar), 134.5, 132.8, 129.9, 126.4 (Ar), 128.0, 127.7 (CH=), 73.7 (ArCH_A), 64.4 (CH(OH)), 45.4 (ArCH_B), 44.0 (NMe₂), 39.3, 25.0, 19.4 (3 × CH₂).

Reaction of 1 with 2-Cyclohexen-1-one. To a stirred solution of **1**, *in situ* prepared from [Li(C₆H₄CH₂NMe₂-2)]₄ (0.34

g, 0.60 mmol) and Zn(C₆H₄CH₂NMe₂-2)₂ (0.82 g, 2.46 mmol), in thf (30 mL) at 195 K was added 2-cyclohexen-1-one (0.22 mL, 2.27 mmol). After the mixture was stirred for 1 h at 195 K, the reaction mixture was hydrolyzed with 5 mL of an aqueous solution of NaOH. The reaction products were analyzed by GC: *t*_R **4** 10.27 min (100%).

Reaction of 2 with 2-Cyclohexen-1-one. The procedure was identical to that described for **1**, starting from **2** (1.22 g, 1.98 mmol) and 2-cyclohexen-1-one (0.35 mL, 3.62 mmol). GC: *t*_R **4** 10.26 min (100%).

Reaction of Zn(C₆H₄CH₂NMe₂-2)₂ with 2-Cyclohexen-1-one. To a stirred solution of Zn(C₆H₄CH₂NMe₂-2)₂ (0.43 g, 1.29 mmol) in thf (30 mL) at 195 K was added 2-cyclohexen-1-one (0.12 mL, 1.24 mmol). The reaction mixture was stirred for 30 min at 195 K before the temperature was allowed to rise to room temperature in the next 30 min. The reaction mixture was hydrolyzed with 5 mL of an aqueous solution of NaOH. The reaction products were analyzed by GC: *t*_R 2-cyclohexen-1-one 2.75 min (100%).

Reaction of Zn(C₆H₄CH₂NMe₂-2)₂/*n*-BuLi with 2-Cyclohexen-1-one (1:1:1). To a stirred solution of Zn(C₆H₄CH₂NMe₂-2)₂ (1.08 g, 3.24 mmol) in thf (30 mL) at 195 K was added *n*-BuLi (2.0 mL of a 1.6 molar solution in hexane, 3.20 mmol). After the mixture was stirred for 5 min, 2-cyclohexen-1-one (0.22 mL, 2.27 mmol) was added. The reaction mixture was stirred for 30 min at 195 K before the temperature was allowed to rise to room temperature in the next 30 min. The reaction mixture was hydrolyzed with 5 mL of an aqueous solution of NaOH. The reaction products were analyzed by GC: *t*_R **6** 5.70 min (82%); *t*_R **4** 10.28 min (18%).

Reaction of Zn(C₆H₄CH₂NMe₂-2)₂/*n*-BuLi with 2-Cyclohexen-1-one (1:2:1). The procedure was identical to that described above, starting from Zn(C₆H₄CH₂NMe₂-2)₂ (1.28 g, 3.83 mmol), *n*-BuLi (4.90 mL of a 1.55 molar solution in hexane, 7.60 mmol), and 2-cyclohexen-1-one (0.36 mL, 3.73

mmol). The reaction products were analyzed by GC: t_R **6** 5.70 min (70%); t_R **4** 10.28 min (30%).

Crystal Structure Determination of 1(thf), 1(thf) \cdot $\frac{1}{2}$ (thf), and 2. Crystals suitable for X-ray structure determination were glued to the top of a glass fiber and transferred into the cold dinitrogen stream on an Enraf-Nonius CAD4-T diffractometer on a rotating anode. Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of the setting angles of a set of 25 well-centered reflections (SET4).¹¹ The unit-cell parameters were checked for the presence of higher lattice symmetry.¹² Crystal data and details on data collection and refinement are collected in Table 3. Data were collected at 150 K using graphite-monochromated Mo $K\alpha$ radiation and were corrected for L_p effects and for the linear instability of three periodically measured reference reflections during X-ray exposure time. An empirical absorption/extinction correction (DIFABS,¹³ as implemented in PLATON¹⁴) was applied for **1(thf)**. The structure of **1(thf)** was solved by direct methods (SHELXS86);¹⁵ the structures of **1(thf) \cdot $\frac{1}{2}$ (thf)** and **2** were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92).¹⁶ All structures were refined on F^2 using full-matrix least-squares techniques (SHELXL-93;¹⁷ no observance criteria were applied during refinement). The structure of **1(thf)** displays conformational disorder in the Li-coordinated thf moiety; a two-component disorder model was refined. The structure of **1(thf) \cdot $\frac{1}{2}$ (thf)** contains a severely disordered solvent molecule, most probably thf, located on a crystallographic 2-fold rotation axis. Since no discrete disordered thf model could be refined, the BYPASS procedure,¹⁸ as implemented in the program PLATON,¹⁴ was used to take this

electron density into account. A total of 38 electrons was found in each of the four symmetry-related solvent cavities, which had a volume of 157.7 Å³ each, consistent with a disordered thf. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The methyl hydrogen atoms were refined as a rigid group, allowing for rotation around the N–C bonds. All non-hydrogen atoms of complexes **1(thf)** and **2**, except for the disordered atoms of **1(thf)**, were refined with anisotropic thermal parameters. Of complex **1(thf) \cdot $\frac{1}{2}$ (thf)**, only the Zn, O, and N atoms were refined with anisotropic thermal parameters due to the poor quality of the crystal. The fixed isotropic thermal parameter of the hydrogen atoms was related to the value of the equivalent isotropic displacement parameter of their carrier atoms by a factor of 1.5 for the methyl hydrogen atoms and 1.2 for the other hydrogen atoms. Neutral atom scattering factors and anomalous dispersion corrections were taken from the *International Tables for Crystallography*¹⁹ for all compounds. Geometrical calculations and illustrations were performed with PLATON.¹⁴ All calculations were performed on a DECstation 5000.

Computational Details. The Molecular Mechanics calculations were performed with CAChe WorkSystem software, version 3.8, on an Apple Power Macintosh 8100 equipped with two CAChe CXP coprocessors. The different diastereoisomers of **2** were modeled using an augmented MM2 force field.

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Supporting Information Available: Tables of the structure determination, atomic coordinates, bond lengths and angles, and thermal parameters for **1(thf)**, **1(thf) \cdot $\frac{1}{2}$ (thf)**, and **2** (30 pages). Ordering information is given on any current masthead page.

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