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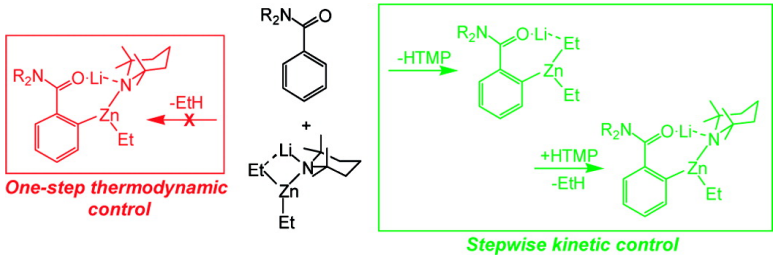

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On the Kinetic and Thermodynamic Reactivity of Lithium Di(alkyl)amidozincate Bases in Directed Ortho Metalation

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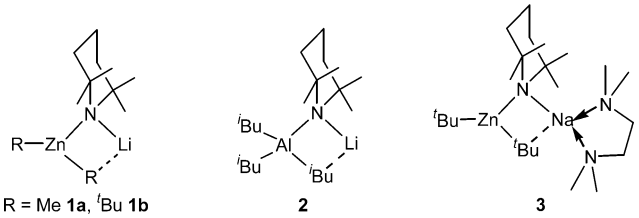
Abstract: Sequential reaction of HTMP (= 2,2,6,6-tetramethylpiperidine) with ^{n}BuLi and Et_2Zn affords unsolvated polymer chains of EtZn(μ-Et)(μ-TMP)Li **6**. The scope of this reagent in directed ortho metalation (DoM) chemistry has been tested by its reaction with *N*,*N*-diisopropylnaphthamide in THF to give EtZn(μ-$C_{10}H_6C(O)N^{i}Pr_2$-2)$_2$Li·2THF **7**. Data reveal that **6** has undergone reaction with 2 equiv of aromatic tertiary amide and imply that it exhibits dual alkyl/amido basicity. DFT calculations reveal that direct alkyl basicity is kinetically disfavored and instead point to a stepwise mechanism whereby **6** acts as an amido base, liberating HTMP during the first DoM event. Re-coordination of the amine at lithium then incurs the elimination of EtH. Reaction of the resulting alkyl(amido)(arylamido)zincate with a second equivalent of *N*,*N*-diisopropylnaphthamide eliminates HTMP and affords **7**. Both DoM steps involve the exhibition of amido basicity and each reveals a low kinetic barrier to reaction. Understanding of this reaction sequence is tested by treating **6** with *N*,*N*-diisopropylbenzamide in THF. On the basis of theory and experiment, the presence of THF solvent (in place of stronger Lewis bases) combined with the use of a sterically less congested aromatic amide is expected to encourage threefold, stepwise reaction. Isolation and characterization of the resulting tripodal zincate Zn(μ-$C_6H_4C(O)N^{i}Pr_2$-2)$_3$Li·THF **8** bears this out and suggests a significant new level of control in zincate-induced DoM chemistry through the combination of experiment and DFT studies.

Introduction

Multifunctionalized organometallic species are ubiquitous and versatile intermediates in modern synthetic organic chemistry.[1] One category, organozincates, has been used extensively in nucleophilic addition,[2] halogen-metal exchange,[3] metal-carbenoid synthesis,[4] deprotonative metalation,[5] ring-opening,[6] and catalysis.[7] This prolific ability to effect transformations in

Chart 1



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[‡] Cambridge University.
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[⊥] The University of Tokyo.
[#] RIKEN.
[||] University of Bath.

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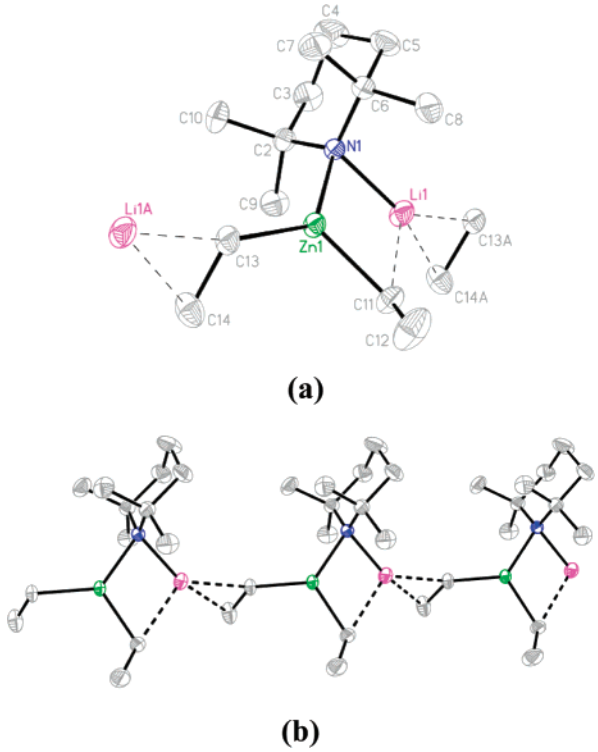


Figure 1. (a) The monomeric unit and (b) the polymeric chain structure of **6** plotted at 40% probability. Selected parameters: N1−Zn1, 2.0217(10) Å; C11−Zn1, 2.0538(15) Å; C13−Zn1, 2.0137(14) Å; N1−Li1, 1.974(3) Å; C11−Li1, 2.374(3) Å; N1−Zn1−C11, 110.99(5)°; N1−Li1−C11, 100.75(12)°; Zn1−N1−Li1, 78.39(9)°; Zn1−C11−Li1, 69.10(8)°.

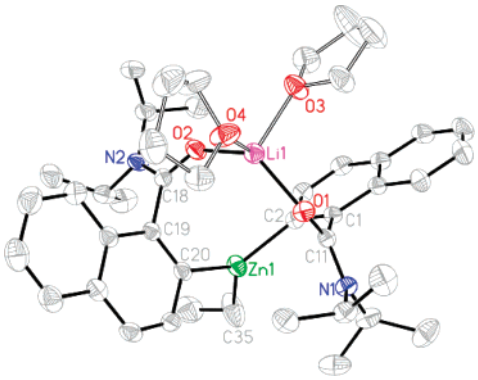
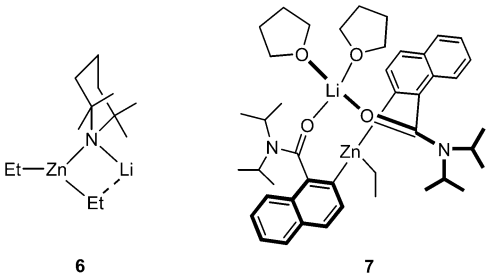


Figure 2. Structure of **7** plotted at 40% probability. Selected parameters: C2−Zn1, 2.013(2) Å; C20−Zn1, 2.021(2) Å; C35−Zn1, 2.031(3) Å; O1−Li1, 1.907(4) Å; O2−Li1, 1.890(4) Å; C2−Zn1−C20, 124.22(9)°; O1−Li1−O2, 128.0(2)°; C2−C1−C11−O1, −86.7(3)°; C20−C19−C18−O2, −85.6(3)°.

tandem with inherent good functional group compatibility has been reviewed.[8]

Directed metalation is a methodology that has come to represent one of the most effective ways of regiospecifically elaborating functionalized aromatic systems. This has led in particular to the extensive development of strategies aimed at achieving directed ortho metalation (DoM).[9] While the dominance of this technique has come to the fore in the elaboration of both carbocyclic aromatic and heteroaromatic systems, the

Chart 2



6 **7**

low acidity of the hydrogen atoms on aromatic rings has meant that organolithium reagents have represented the base of choice for effecting deprotonation. However, the nucleophilicity of these reagents has brought with it the associated risk of competing reaction at the directing group. The need to overcome this synthetic limitation has led to the employment of heterometallic ate complexes designed to promote chemoselective DoM reactions under mild conditions. Accordingly, Me_2Zn(TMP)Li **1a**, $^tBu_2Zn$(TMP)Li **1b**, and $^iBu_3Al$(TMP)Li **2** (TMP = 2,2,6,6-tetramethylpiperidide) have been successfully used to elaborate functionalized aromatics incorporating directing groups normally susceptible to competing nucleophilic degradation (Chart 1).[10,11]

Interestingly, and in contrast to **1**,[10a] recently prepared zincate (^{t}Bu)Zn(μ-^{t}Bu)(μ-TMP)Na·TMEDA **3** has been shown to deprotonate benzene, with the elimination not of HTMP but of ^{t}BuH.[12] A density functional theory (DFT) study reveals that the relative energies of reactants and products in this system corroborated the observed thermodynamic preference for overall alkyl ligand transfer.[12] More recently though, the analysis of possible *pathways* for reaction of a model base MeZn(μ-Me)(μ-NMe_2)Li·OMe_2 **4** with anisole has suggested that zincates such as **3** should in fact exhibit a general kinetic preference for amido ligand exchange.[13]

Pre- and postmetalation[14] species have been reported based on the treatment of *N*,*N*-diisopropylbenzamide with TMEDA-solvated zincate **3** and its lithium analogue, and their direct alkyl and dual amido and alkyl ligand transfer selectivities were suggested, respectively. However, recent theoretical modeling of competing ortho deprotonation and nucleophilic addition reaction pathways available to aromatic nitriles and esters in the presence of amidozincates corroborates the view that **3** should preferably act as an amido base.[15] In this paper we apply first X-ray crystallography and then comprehensive DFT

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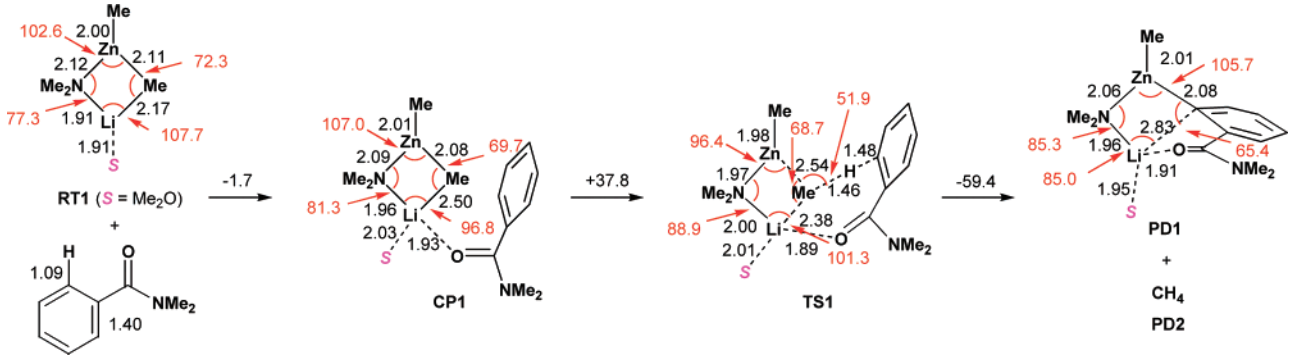
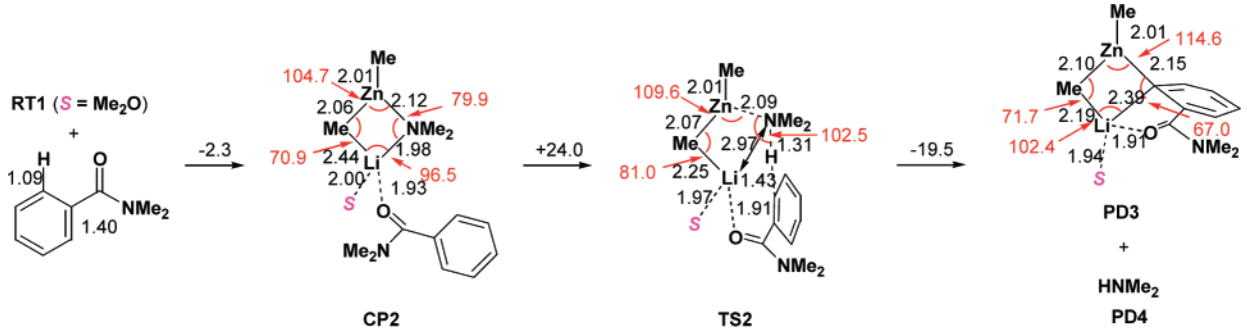
Scheme 1. Calculated Structures of the Reactants, Transition States, Products, and Gibbs Free Energy Changes for Kinetically Unfavorable Single-Step Ortho Deprotonation[a]



[a] Bond lengths, angles (red), and energy changes at the B3LYP/631SVPs level are shown in Å, deg, and kcal/mol, respectively.[17,18]

Scheme 2. Calculated Structures and Energy Changes (B3LYP/631SVPs Level) for Step 1 (Amine Elimination) in Stepwise Ortho Deprotonation[17,18]



modeling to the study of the mechanism by which carboxylic amides undergo DoM. We report on systems in which a previously unexplored *stepwise* amido ligand exchange process is both predicted theoretically and observed experimentally.

Results and Discussion

While aluminate $Me_2Al(\mu\text{-Me})(\mu\text{-TMP})Li$ **5** (viz. **2**, R = ^{i}Bu) has been obtained in both solvated and unsolvated forms,[11b] to date only monomeric Lewis donor complexed zincate analogues (e.g., **3**) have been reported.[12,14a,16] However, by combining Et_2Zn with TMPLi and recrystalizing from toluene we have prepared an unsolvated polymer of $EtZn(\mu\text{-Et})(\mu\text{-TMP})Li$ **6** (Figure 1, Chart 2).[17]

Although it can be crystallized, the preparation of **6** in hexane affords an analytically pure brilliant white powder in near quantitative yield for subsequent reaction.[17] Investigation of *N*,*N*-dialkylamide-DoM of benzenoid systems was attempted by treating preformed **6** with *N*,*N*-diisopropylnaphthamide in THF according to the protocol developed by ourselves.[10] The resulting crystalline deposit was identified as $EtZn(\mu\text{-}C_{10}H_6C(O)N^iPr_2\text{-}2)_2Li\cdot 2THF$ **7**. ^{1}H NMR spectroscopy suggests convoluted solution behavior, with three significant solution species present in toluene (labeled #A−#C in the supporting data).[17] X-ray diffraction on **7**, however, reveals a single bis(THF)-solvated motif (Chart 2, Figure 2), which suggests that **6** has reacted dibasically with the overall elimination of both HTMP and EtH.

This observation, that dibasic behavior yields **7**, raises several issues that warrant detailed theoretical investigation. First, the absence of $[TMP]^-$ means that dialkyl(amido)zincates cannot be viewed as straightforward alkyl bases on thermodynamic grounds.[12] Second, elucidation is required of the imperatives for dual amido and alkyl ligand transfer. Third, the ability to manipulate the mode (e.g., amido/alkyl) and extent (e.g., mono/di) of zincate basicity in DoM chemistry suggests that we may be able to develop a level of control over substrate design and reactivity that has far-reaching implications for synthetic chemists. To achieve understanding of and control over these issues we have investigated competition between ligand transfer preferences for **6**, with the conversions of reactants (**RT**) into prereaction complexes (**CP**) and products (**PD**) being optimized at the B3LYP/631SVPs level.[17,18] Modeling of bridging-alkyl transfer selectivity under the influence of an ortho directing $Me_2NC(=O)$ group and the conversion of $MeZn(Me)(NMe_2)Li\cdot OMe_2$ **RT1** into $MeZn(Ar')(NMe_2)Li\cdot OMe_2$ (**PD1**, Ar′H = Me_2NCOPh) as the first step in $MeZn(Ar')_2Li\cdot OMe_2$ **PD5** formation (Scheme 1) yielded a reaction profile that was exothermic overall (by 23.3 kcal/mol). However, this conversion proceeds *via* a transition state **TS1** accessed by a very high Gibbs energy of activation ($\Delta G^{\ddagger}$ = 37.8 kcal/mol). These data strongly suggest the kinetic preclusion of DoM to give **PD1** by a direct, single-step alkyl exchange mechanism.

Having established the unfavorable nature of a single-step synthesis of $MeZn(Ar')(NMe_2)Li\cdot OMe_2$ **PD1**, we next probed the *stepwise* DoM of $PhCONMe_2$, utilizing amido-ligand exchange (Scheme 2) followed by coordination of in situ generated amine (**PD4**) at the alkali metal center in $Me_2Zn(Ar')Li\cdot OMe_2$ **PD3**, with subsequent alkane loss affording **PD1** (Scheme 3). The activation barrier for ortho deprotonation (step 1) was now lowered significantly ($\Delta G^{\ddagger}$ = 24.0 kcal/mol),

(16) Barley, H. R. L.; Clegg, W.; Dale, S. H.; Hevia, E.; Honeyman, G. W.; Kennedy, A. R.; Mulvey, R. E. *Angew. Chem., Int. Ed.* **2005**, *37*, 6018−6021.
(17) See Supporting Information.
(18) The basis set denoted 631SVPs consists of Ahlrichs' SVP all-electron basis set for the zinc atom and 6-31G* for the other atoms.

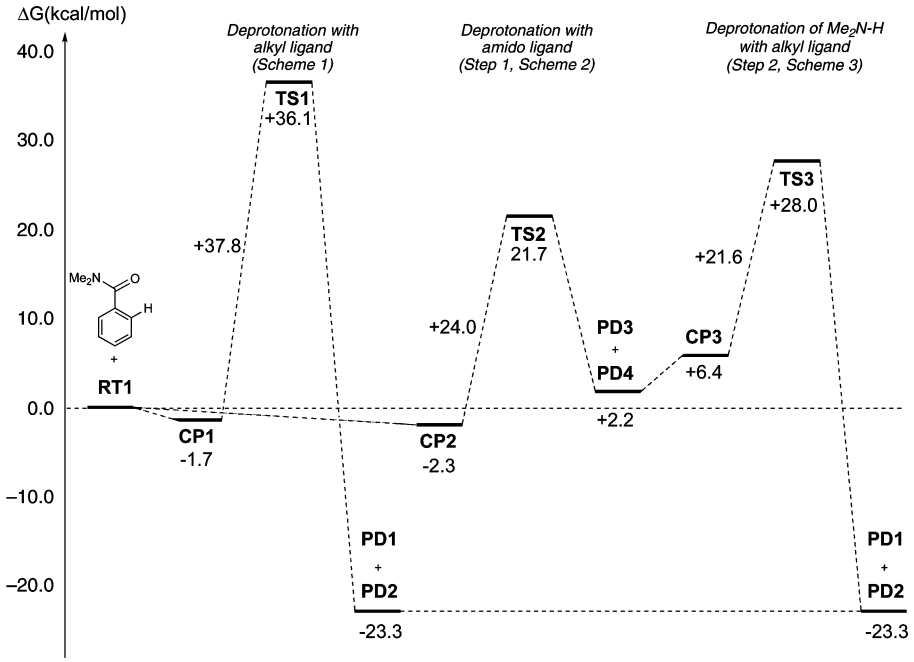
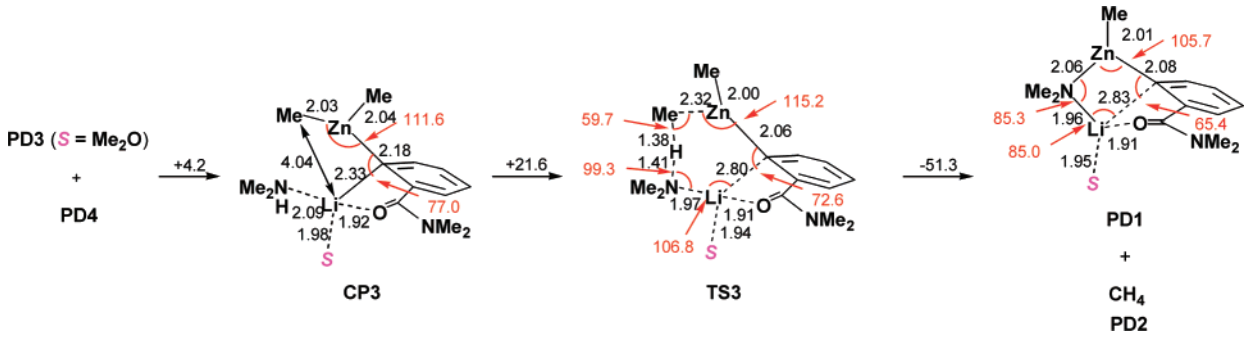
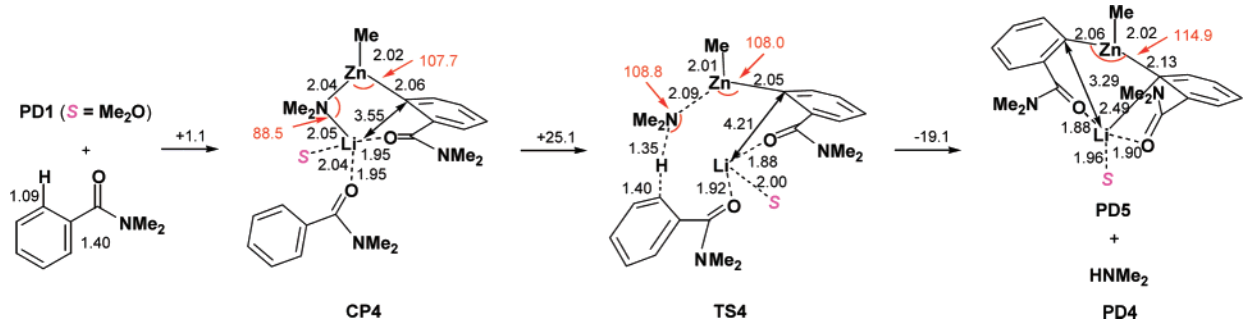


Figure 3. Energetics of possible deprotonative zincations of *N*,*N*-dimethylbenzamide with $Me_2Zn(Me_2N)Li{\cdot}OMe_2$ at the B3LYP/631SVPs level of theory. Free energy changes are shown in kcal/mol and are relative to (**RT1** + *N*,*N*-dimethylbenzamide).

Scheme 3. Calculated Structures and Energy Changes (B3LYP/631SVPs Level) for Step 2 (Amine Re-coordination/Alkane Loss) in Stepwise Ortho Deprotonation[17,18]



Scheme 4. Calculated Structures and Energy Changes (B3LYP/631SVPs Level) for Step 3 (Dibasic Action/Amine Elimination) in Stepwise *ortho* Deprotonation[17,18]



rendering this nominally endothermic process ($\Delta G = 2.2$ kcal/mol) significantly more favorable than that described in Scheme 1. This preference for amido exchange mirrors that observed in the theoretical analysis of reaction between **RT1** and anisole.[13] However, we now extended our study to cover step 2 (the re-coordination of eliminated amine **PD4** at the lithium center of **PD3**, Scheme 3). This reaction was found to be significantly exothermic (−25.5 kcal/mol) with a 21.6 kcal/mol activation barrier. Importantly, the combination of steps 1 and 2 allows us to rationalize the observation of **PD1**-type products in benzenoid deprotonation systems without the need to invoke direct alkyl elimination (Figure 3). In seeking to compute the formation of a structure-type synonymous with that of **7** we next modeled the reaction of **PD1** with $PhCONMe_2$ (step 3, Scheme 4). Data revealed a similar profile to that of step 1 ($\Delta G^{\ddagger} = 25.1$ kcal/mol, $\Delta G = 7.1$ kcal/mol), meaning that the dibasicity evidenced by **6** in the formation of **7** and the elimination of both alkyl and amido groups can now be rationalized in terms of multiple, stepwise amido ligand exchange.[19]

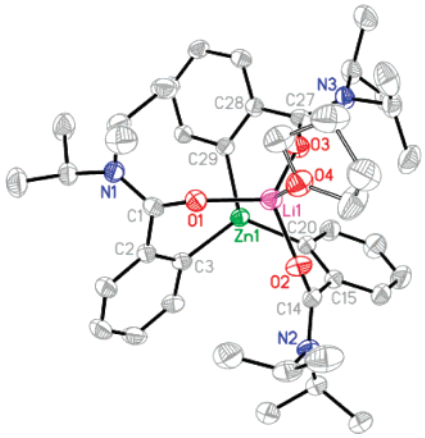
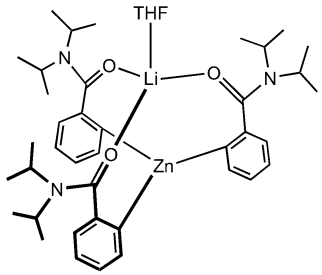


Figure 4. Structure of **8** at 40% probability. Selected parameters: C3−Zn1, 2.026(3) Å; C20−Zn1, 2.017(3) Å; C29−Zn1, 2.021(3) Å; O1−Li1, 1.905(5) Å; O2−Li1, 1.891(5) Å; O4−Li1, 1.998(6) Å; C3−Zn1−C20, 121.40(11)°; C3−Zn1−C29, 117.02(11)°; C20−Zn1−C29, 121.03(11)°; C3−C2−C1−O1, −55.1(4)°; C20−C15−C14−O2, −54.5(4)°; C29−C28−C27−O3, −48.7(4)°.

Chart 3



8

The rationalization of a stepwise deprotonative mechanism for zincate DoM chemistry suggested to us that the modulation of reaction conditions might enable *tribasic* behavior and the preparation of a tripodal tris(amidoaryl)zincate. Whereas **7** incorporates ortho-deprotonated *N*,*N*-diisopropylnaphthamide ligands, we argued that the use of (less sterically demanding) *N*,*N*-diisopropylbenzamide should increase the likelihood of 3-fold deprotonative reaction. Furthermore, although the previous isolation and characterization[14b] of (^{t}Bu)Zn(μ-C$_6$H$_4$C(O)N-^{i}Pr$_2$-2)$_2$Li·TMEDA might suggest that this strategy would fail, we considered, based on the Gibbs free energy profile of Scheme 3 in our DFT study, that the employment of THF solvent and the exclusion of TMEDA would render the alkali metal more susceptible to amine coordination. Accordingly, *N*,*N*-diisopropylbenzamide was treated with **6** in THF to give crystalline material that analyzed as tris(amidoaryl)zincate Zn(μ-C$_6$H$_4$C(O)N-^{i}Pr$_2$-2)$_3$Li·THF **8** (Chart 3, Figure 4).[17] X-ray crystallography reveals a tripodal structure in which the alkali metal is stabilized by all three carbonyl O-centers. To support both tris(arylamide)-stabilization of the Li$^+$ ion and the steric bulk of three aromatic systems, modulation of the amide-arene twist angle from its ideal near-perpendicular arrangement[20] is necessary (mean torsional angle 52.8°). This suggests an explanation for the failure of **7** to undergo further reaction (eliminating the final equivalent of EtH), with the more sterically demanding naphthamide ligands (which exhibit a mean torsion of 86.2° in **7**) less able to sustain the reduced torsional angle required by a tripodal arrangement.

Conclusions

The combination of solid-state and theoretical data points strongly to **6** in THF exhibiting kinetically controlled stepwise ligand exchange when deprotonating an aromatic substrate under the influence of a directing group, with ortho deprotonation achieved by the amido and not an alkyl group (Schemes 1 and 2). This conclusion is contrary to that achieved on the basis of a thermodynamic evaluation of product stability.[12] Moreover, this kinetic reactivity can account for polybasic behavior and the isolation of **7**. Detailed studies are ongoing into whether or not the reaction sequences developed by ourselves[10a,b] involve mono- or polybasicity. Appreciation of the kinetic control manifest in these systems has been integrated with a knowledge of the relative abilities of various aromatic tertiary amides to sustain different amide−arene torsion angles. This allowed the rationalization of *di*basicity in the formation of naphthamide-containing **7** and allowed the design and execution of a *tri*basic reaction using a benzamide substrate (viz. **8**). Moreover, and in line with the synthesis of **8** in THF, polybasic reaction via a mechanism that requires the coordination of kinetically evolved HTMP should be inhibited by the use of strong (e.g., multidentate) Lewis base solvents to competitively coordinate the alkali metal. We are investigating this issue, control over which promises to provide a powerful tool for the design of new bases. Lastly, the 3:1 formation of **8** has adventitious cost implications, with stepwise deprotonation suggesting a role for trialkylzincate/catalytic HTMP in DoM chemistry.

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Supporting Information Available: Selected crystallographic data (CIF) and all synthetic and spectroscopic details for **6**−**8**; also tables of optimized Cartesian coordinates for computed structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) B3LYP/6-31++G**&SVP (Zn) (single point) energies: eq 1 ($\Delta E^{\ddagger}$ = 39.2 kcal/mol, ΔE = −22.7 kcal/mol); eq 2 ($\Delta E^{\ddagger}$ = 23.9 kcal/mol, ΔE = 0.7 kcal/mol); eq 3 ($\Delta E^{\ddagger}$ = 25.3 kcal/mol, ΔE = −23.4 kcal/mol); eq 4 ($\Delta E^{\ddagger}$ = 24.6 kcal/mol, ΔE = 4.2 kcal/mol). These calculations do not change the conclusion of the B3LYP/6-31SVPs analysis.

(20) Bond, A.; Clayden, J.; Wheatley, A. E. H. *Acta Crystallogr., Sect. E* **2001**, *E57*, o292−o294.