

Synthesis, Structural Authentication, and Structurally Defined Metalation Reactions of Lithium and Sodium DA-Zincate Bases (DA = diisopropylamide) with Phenylacetylene[†]

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In a study aimed at developing the diisopropylamido (DA) chemistry of zincates, the new lithium DA-zincate [(TMEDA)•Li(^tBu)(DA)Zn(^tBu)] (**4**) has been synthesized by an interlocking cocomplexation approach comprising mixing of its three component chemicals, LDA, ^tBu₂Zn, and TMEDA, in a 1:1:1 ratio in hexane solution. Previously made by transamination from the corresponding TMP-zincate, the known sodium congener [(TMEDA)•Na(^tBu)(DA)Zn(^tBu)] (**2**) was also synthesized by this approach, substituting NaDA for LDA. Closely resembling each other, their molecular structures determined by X-ray crystallography can be categorized as contact ion-pairates of TMEDA-chelated alkali metal cations linked to trigonal-planar dialkyl-Zn anions via bridging DA ligands. Reaction of **4** and **2** with phenylacetylene affords the bimetallic acetylides [(TMEDA)•Li(C≡CPh)₂Zn(^tBu)]₂•(TMEDA)] (**5**) and [(TMEDA)•Na(C≡CPh)₂Zn(^tBu)]₂] (**6**), respectively. X-ray crystallographic studies reveal **5** is a pseudodimer (tetranuclear) with two (LiCZnC) rings linked at the Zn atoms by a bridging, nonchelating TMEDA ligand; in contrast **6** adopts a distorted cubane of alternating PhC≡C and metal (2 Na, 2 Zn) corners. For comparison, the synthesis and crystal structures of the neutral zinc complexes [(TMEDA)•Zn(C≡CPh)₂] (**7**) and [(TMEDA)•Zn(^tBu)(C≡CPh)] (**8**), formally components of the ate complexes **5** and **6**, are also reported. In addition, the ¹H and ¹³C NMR spectra of **2**, **4**, **5**, **6**, **7**, and **8** recorded from solutions in C₆D₆ are disclosed.

Introduction

Lithium 2,2,6,6-tetramethylpiperidide (LiTMP), one of the most important utility bases in synthetic chemistry,¹ was first transformed to the TMP-zincate “Li(TMP)Zn(^tBu)₂” in 1999 in a report by Kondo, Uchiyama, et al.² Subsequently in 2005 we introduced the first sodium TMP-zincate reagent [(TMEDA)•Na(^tBu)(TMP)Zn(^tBu)], **1**.³ TMP-zincate bases can instigate clean deprotonation of a wide range of aromatic compounds.⁴ In general TMP-zincates outperform their parent lithium and sodium amides in their ability to effect highly regioselective metalations and polymetalations under mild conditions. In the most spectacular examples to date, *N,N*-dimethylaniline is the subject of *meta*-deprotonation,⁵ not *ortho*-deprotonation as with butyllithium, and the substituent-free, nonactivated hydrocarbons benzene and naphthalene can be

regioselectively mono- and dideprotonated,^{6,7} whereas they are essentially inert to LiTMP and NaTMP. Structural snapshots of key bimetallic complexes taken before and after deprotonation have established that these are zinc–hydrogen exchange (zincation) reactions, which, since dialkylzinc reagents cannot replicate due to their generally poor kinetic basicity, are best thought of as alkali-metal-mediated zincations (AMMZ).⁸ Surprisingly the zincate metamorphosis of the best known lithium amide utility base lithium diisopropylamide (LiNⁱPr₂; LDA) has, in contrast, been largely neglected.

The first study reported seven years ago,⁹ also by Kondo and Uchiyama, revealed that DA-zincate “Li(DA)Zn(^tBu)₂” used in situ in ether or THF solution without any direct characterization shows a completely different regioselectivity from that of TMP-zincate in reactions with bromopyridines (Scheme 1). The power to control the regioselectivity of a reaction by changing the amide component provides a strong incentive for developing a complementary DA-zincate chemistry. Recently we started along

[†] Dedicated to Professor Ken Wade on the occasion of his 75th birthday.

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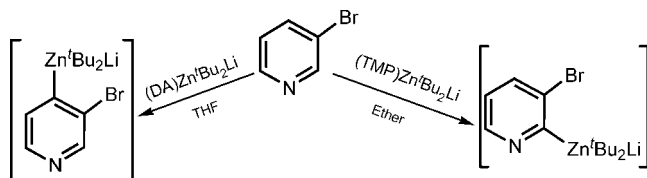
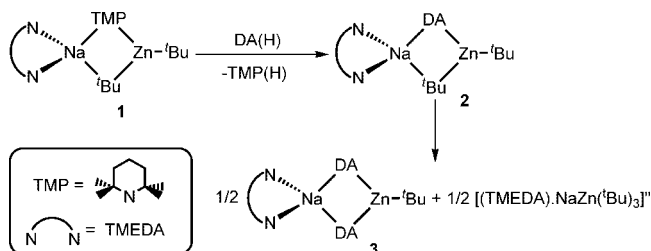
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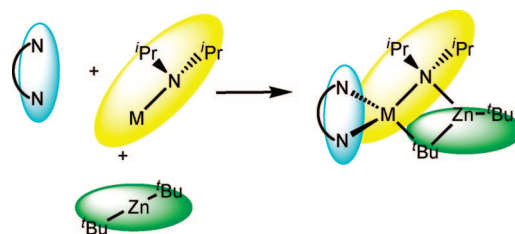
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Scheme 1. Different Regioselectivity of (TMP)- and (DA)-Zincates in Reactions with Bromopyridines**Scheme 2. Transamination Reaction of 1 to Generate (TMEDA)·Na(Bu)(DA)Zn(Bu), 2, Which Subsequently Disproportionates to [(TMEDA)·Na(DA)2Zn(Bu)], 3, and [(TMEDA)·NaZn(Bu)3]**

this path by reporting in a communication¹⁰ that the TMP-zincate **1** undergoes transamination with diisopropylamine, DA(H), to generate initially the dialkyl-DA zincate [(TMEDA)·Na(Bu)(DA)Zn(Bu)], **2**, which subsequently disproportionates over 24 h to the monoalkyl-diDA zincate [(TMEDA)·Na(DA)₂Zn(Bu)], **3**, and the trialkyl zincate [(TMEDA)·NaZn(Bu)₃] (Scheme 2). Here, in this paper, we make further inroads in the development of DA-zincate chemistry by describing (i) an alternative preparative method for **2** and its full crystallographic characterization; (ii) the synthesis and crystallographic characterization of the new lithium congener [(TMEDA)·Li(Bu)(DA)Zn(Bu)], **4**; (iii) a comparative study of the products obtained from the reactions of **2** and **4** toward phenylacetylene, PhC≡CH; and (iv) from the study in iii, the first crystallographically characterized products of AMMZ reactions performed by DA-zincate bases in [(TMEDA)·Li(C≡CPh)₂Zn(Bu)]₂·(TMEDA), **5**, and [(TMEDA)·Na(C≡CPh)₂Zn(Bu)]₂, **6**. For completeness, we also report the synthesis and crystallographic characterization of the TMEDA-chelated homometallic, neutral zinc components of **5** and **6**, namely, homoanionic [(TMEDA)·Zn(C≡CPh)₂], **7**, and heteroanionic [(TMEDA)·Zn(Bu)(C≡CPh)], **8**.

Results and Discussion

Syntheses. Both **2** and **4** were synthesized by simply mixing together their component chemicals (alkali metal amide, dialkylzinc reagent, and TMEDA) in a 1:1:1 stoichiometry in hexane solution. Conceptually, one could view these reactions as “interlocking cocomplexation syntheses” (Scheme 3), wherein the group 1 amide functions dualistically as an N-Lewis base toward zinc and an alkali metal-Lewis acid toward one (agostic) Me arm, the dialkylzinc functions dualistically as a zinc-Lewis acid toward the N of the amide group and as an electrostatic (agostic) Me source to an alkali metal cation, and TMEDA functions solely as an N,N-chelating Lewis base to an alkali metal. Mechanistically, the picture is decidedly more complicated. Though two of the molecular components, the dialkylzinc

Scheme 3. “Interlocking Cocomplexation” Synthesis of 2 (M = Na) and 4 (M = Li) from Their Three Component Chemicals

and TMEDA, are nonaggregated in their normal pure forms and so preorganized to participate in the interlocking cocomplexation process, the third component, LDA or its sodium congener (NaNⁱPr₂; NaDA), usually exists in aggregated form. A deprotonating agent par excellence,¹¹ LDA exudes a fascinating structural chemistry in both the solid and solution phases. In its pure solvent-free form, crystalline LDA exists as a single-strand helical polymer of near-linear N—Li—N segments,¹² while in donor-solvent-free solution it takes the form of various cyclic oligomers.¹³ Mixed with TMEDA, LDA crystallizes as an infinite array of (LiN)₂ ring dimers linked by monodentate, bridging (nonchelating) TMEDA ligands.¹⁴ The structure of hydrocarbon-insoluble NaDA is not yet known, though it is most probably a polymer. Crystalline [(TMEDA)·NaDA]₂ adopts a discrete (NaN)₂ ring dimer structure, in which the larger size of sodium (compared to lithium) permits full N,N-chelation by the TMEDA ligands.¹⁵ Hence, these aggregated forms of LDA and NaDA must break down to monomeric modifications during the cocomplexation processes leading to **4** and **2**.

Reaction of phenylacetylene with **2** or **4** in a 1:1 stoichiometry in hexane solution afforded the colorless crystalline products **6** and **5**, each surprisingly containing 2 molar equiv of PhC≡C[−] ligand in its molecular formula (Scheme 4). Repeating the reaction of **4** with a 4:3 ratio of PhC≡CH:TMEDA commensurate with the stoichiometry of **5** increased the (isolated, crystalline) yield of **5** from 36% to 76%. Because the yield of **5** exceeds 50%, it is unequivocal that lithium zincate **4** is functioning as a dual alkyl-amido base toward the acetylene. This ambibasic behavior has precedence in TMP-zincate chemistry with other types of organic substrate,¹⁶ and in general, the ability of such heteroleptic bases to utilize one (alkyl) or other (amido) of their component anionic ligands for deprotonation purposes is part of the fascination of this area of

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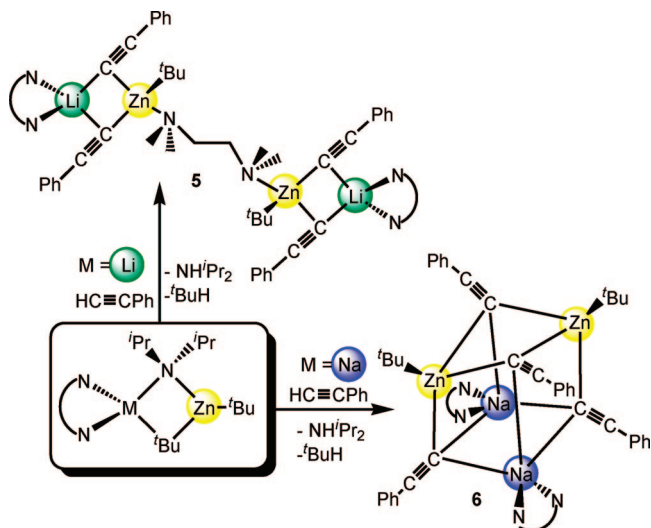
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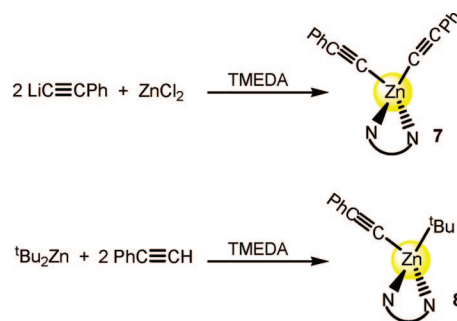
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Scheme 4. Crystalline Products **5** (top) and **6** (right) from Reactions of Phenylacetylene with **4** and **2**, Respectively

chemistry. If **4** functioned solely as an alkyl base, the putative intermediate formed would be “[TMEDA]·Li(C≡CPh)-(DA)Zn(^{*t*}Bu)”, whereas exclusive amido activity would generate “[TMEDA]·Li(C≡CPh)(^{*t*}Bu)Zn(^{*t*}Bu)”. Theoretical studies of TMP-zincate systems¹⁷ have suggested that in certain cases TMP functions as the kinetic base and the alkyl ligand functions as the thermodynamic base. In the former scenario, “expelled” TMP(H) can reenter the coordination sphere of the alkali metal and protonate the alkyl ligand, leading to an ultimate expulsion of alkane. Most TMP-zincate reactions with organic substrates that have been experimentally structurally defined retain TMP ligands in the cocomplexed deprotonated product, but exceptions are found with nitrile substrates in which both alkyl ligands remain intact on zinc.^{16d} Irrespective of the kinetics involved in the production of **5**, both DA(H) and butane molecules have been expelled. Furthermore, as a significant quantity of di(PhC≡C)-containing **5** was still obtained even when a deficiency of PhC≡CH was employed (in the 1:1, base:PhC≡CH stoichiometric reaction), it can be inferred qualitatively that the aforementioned putative intermediate “[TMEDA]·Li(C≡CPh)(DA)Zn(^{*t*}Bu)” or “[TMEDA]·Li(C≡CPh)(^{*t*}Bu)Zn(^{*t*}Bu)” is more reactive than the starting zincate base **4**. The details associated with the synthesis of **6** essentially mimic those of **5**. Thus, adding 2 molar equiv of PhC≡CH to the sodium zincate reagent increases the isolated, crystalline yield of **6** from 37% to 67%. However, the fact that **6** is still the major product when the stoichiometry is incorrect (1:1, base:PhC≡CH ratio) implies any mono PhC≡C-containing intermediate reacts faster with PhC≡CH reactant molecules than does the starting base **1**. Again, as the yield of **6** in the stoichiometrically correct reaction is in excess of 50%, both DA and ^{*t*}-Bu ligands must have been consumed in the reaction. Sodium zincate **2** is therefore functioning as a dual base in the synthesis of **6**.

Turning to the neutral zinc complexes **7** and **8**, we synthesized the former by a reproducible metathetical approach reacting the corresponding lithium acetylide with zinc chloride and TMEDA in a 2:1:1 stoichiometry in hexane solution (Scheme 5). Typically the yield was about 70%. Attempts to reprepare **7** by reacting di-*tert*-butylzinc with 2 equiv of PhC≡CH surprisingly

Scheme 5. Formation of **7** by Metathesis of Lithium Phenylacetylide with ZnCl₂ in the Presence of TMEDA (top) and Synthesis of **8** via Reaction of Zn^{*t*}Bu₂ and Phenylacetylene (bottom)

led mainly to the formation of the latter monoacetylide **8**. Analysis of the crude reaction mixture by NMR spectroscopy revealed that the formation of **8** was essentially quantitative, though the isolated crystalline yield was 47%, reflecting the good solubility of **8**. On heating the same reactants in toluene solution, **8** was again the major product, though the reaction was considerably less clean and a trace amount of **7** was detected in the mixture.

NMR Spectroscopic Studies. All new compounds **4**, **5**, **6**, **7**, and **8**, as well as **2**, were characterized spectroscopically by ¹H and ¹³C NMR studies in C₆D₆ solution. The ⁷Li NMR spectra of **4** and **5** were also recorded. It is noteworthy that the spectra of **2** and **4** could be recorded from C₆D₆ solution without any sign of decomposition. In contrast, the analogous TMP-zincate **1** rapidly metalates C₆D₆ in an NMR tube.³ This advantage suggests that DA-zincates should be the zincate reagents of choice for certain reactions performed in arene media. The electronic influence of the alkali metal is discernible on comparing the data from the lithium complex **4** and the sodium congener **2**. All the ¹H chemical shifts for **2** and **4** are essentially equivalent (*Me*CH, 0.98/0.98; *Me'*CH, 1.23/1.24; ^{*t*}Bu, 1.53/1.54; CH, 3.40/3.49 ppm for **4/2**). This trend is mirrored in the ¹³C data (e.g., CH₃ of ^{*t*}Bu 35.4/35.6; C(*Me*)₃ of ^{*t*}Bu 22.4/22.3 ppm for **4/2**). The distinct resonances noted within the ¹H and ¹³C spectra for each Me arm of the isopropyl groups in both **4** and **2** indicate that the alkali metal–DA–Zn bridges observed in the crystal structures (vide infra) are maintained in solution. DA can therefore be regarded as the synergic anchor, which holds together the bimetallic framework. In contrast, only one type of ^{*t*}Bu group is observable for both **4** and **2**, consistent with free rotation about the N–Zn axes and fast exchange of the terminal and bridging ^{*t*}Bu groups seen in the crystal. TMEDA interacts in a similar way with Li in **4** and Na in **2**, as evidenced by the chemical shifts of their ¹H resonances (CH₃, 1.72/1.68; CH₂, 1.58/1.60 ppm for **4/2**) from those of free TMEDA (CH₃, 2.11; CH₂, 2.33). These substantial chemical shift differences between **4/2** and the free ligand signify strong dative interactions to compensate for the coordinative/electronic unsaturation of the three-coordinate alkali metal centers (four-coordination is more common). The room-temperature ¹H NMR spectrum of **5** reveals broad resonances for the ^{*t*}Bu group and TMEDA. Two distinct types of TMEDA ligand are present in the crystal structure of **5**: N,N-chelated to Li and N-monodentate bound to Zn. These observations are consistent with a dynamic process in solution involving TMEDA. A significant distinction with the ¹H spectrum of **6** is the more strongly shielded ^{*t*}Bu resonance (1.46; cf. 1.88 in **6**). Some change was to be expected, as in the crystal structures the zinc coordination sphere of **6** contains three electron-withdrawing PhC≡C[−] ligands, whereas

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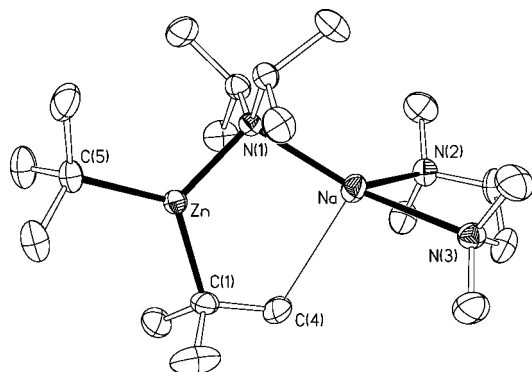


Figure 1. Molecular structure of **2** with hydrogen atoms omitted for clarity, showing the (agostic) $\text{Na} \cdots \text{CH}_3$ contact as a thin line. Displacement ellipsoids are shown at the 40% probability level in Figures 1–6 (25% in Figure 5 to reduce congestion), and labels are shown for selected atoms.

in **5** there are only two such ligands and a TMEDA N atom. However, there is very little difference in the corresponding ^1H resonances of the $\text{PhC}\equiv\text{C}^-$ ligands in **5** and **6**. On the basis of its molecular structure in the crystal, **6** should display two distinct $\text{PhC}\equiv\text{C}^-$ ligands, but only one type is observed in solution. This points to a dynamic process. Reflecting the similarity of their distorted tetrahedral zinc structures (vide infra), **7** and **8** display essentially equivalent ^1H chemical shifts for corresponding TMEDA signals (CH_3 , 2.12/2.08; CH_2 , 1.79/1.78 ppm for **7/8**), although in **8** the signals are broader, consistent with existence of a dynamic process.

Solid State Structures. Turning to the results of the X-ray crystallographic studies, the molecular structures of **2**, **4**, **5**, **6**, **7**, and **8** are shown in Figures 1–6, respectively. Table 1 lists selected bond lengths and bond angles for the bimetallic ate compounds **2**, **4**, **5**, and **6**, Table 2 lists the corresponding values for the homometallic neutral zinc complexes **7** and **8**, and Table 3 lists key crystallographic and refinement parameters for all these compounds.

The molecular structures of **2** (Figure 1) and **4** (Figure 2) closely resemble each other and related TMP-zincate structures.⁴ TMEDA N,N-chelated alkali metals form a strong amido (N) bridge to Zn, which carries a terminal 'Bu ligand. A distorted trigonal-planar coordination of Zn is completed by a second 'Bu ligand. Its quaternary C atom bonds exclusively to Zn, but one Me arm forms a long-range contact to the alkali metal in a long (agostic) interaction [in **2**, $\text{Na} \cdots \text{C}(4)$, 2.809(4) Å; in **4**, $\text{Li} \cdots \text{C}(14)$, 2.695(4) Å]. Thus this second 'Bu ligand is nominally bridging, as the bridge must be weak and easily ruptured in solution (as gauged by the equivalence of the 'Bu groups in the NMR spectra, consistent with free rotation about the Zn–N axes, as mentioned above). Similar gross features decorate the TMP structures **1**³ and $[(\text{THF}) \cdot \text{Li}(\text{'Bu})(\text{TMP})\text{-Zn}(\text{'Bu})]$ **9**.^{17,18} Substituting DA for TMP also has little effect on relative dimensions with, for example, Zn–N bond lengths covering the narrow range 2.034(6)–2.0741(19) Å across the series of four compounds (mean values: for **2** and **4**, 2.057 Å; for **1** and **9**, 2.054 Å).¹⁹

The centrosymmetric structure of **5** displays a LiCZnC four-atom ring motif with $\alpha\text{-C}$ atom ($\text{PhC}\equiv\text{C}^-$) bridges (Figure 3).

One type of TMEDA ligand N,N-chelates to Li, while another functions in an N-monodentate bridging mode (note the transoid arrangement of N atoms) between Zn atoms. The distorted tetrahedral coordination expansion of Zn (compared to its trigonal planarity in **4**), a result of introducing small, linear $\text{PhC}\equiv\text{C}$ ligands, is completed by a terminal 'Bu ligand. We have described previously the anomalous preferential coordination (N,N-chelation) of TMEDA to Zn over Li in an "inverse zincate" structure,²⁰ but the variation here appears to be the first example where TMEDA binds in a different way to the distinct metals of an ate complex. In marked contrast, the dilithium zincate $[(\text{TMEDA} \cdot \text{Li})_2\text{Zn}(\text{C}\equiv\text{CPh})_4]$ exhibits the more usual chain-terminating TMEDA (N,N-) to Li bonding, with no TMEDA–Zn bonding.²¹ A notable feature of **5** is the dissimilarity in the bonding modes adopted by the two acetylide ligands. That labeled $\text{PhC}(4)\equiv\text{C}(3)$ assumes a near-linear geometry to Zn [$\text{C}4\text{--C}3\text{--Zn}$, 173.64(15)°] and a near-perpendicular geometry to Li [$\text{C}4\text{--C}3\text{--Li}$, 105.37(16)°], indicative of predominately σ - and π -bonding, respectively (vide infra). Strongly bound to C3 [length, 2.222(4) Å], Li also lies close to C4 [2.803(4) Å]. In contrast, the corresponding angles for the other acetylide ligand [$\text{C}12\text{--C}11\text{--Zn}$, 155.08(17)°; $\text{C}12\text{--C}11\text{--Li}$, 127.17(17)°] are significantly more removed from linear and perpendicular geometries respectively, indicative of a greater mixing of σ - and π -bonding components. There is also more deviation in the Li–C(11) [2.260(4) Å] and $\text{Li} \cdots \text{C}(12)$ [3.148(4) Å] lengths. However, these distinct bonding modes do not impact on the C=C bond lengths [$\text{C}3\text{--C}4$, 1.218(2) Å; $\text{C}11\text{--C}12$, 1.216(2) Å]. Despite its similar composition to **5**, the sodium product $[(\text{TMEDA}) \cdot \text{Na}(\text{C}\equiv\text{CPh})_2\text{Zn}(\text{'Bu})_2]$, **6**, adopts a fundamentally different molecular structure (Figure 4). A distorted cubane²² with alternating acetylide $\alpha\text{-C}$ and metal (2 Na, 2 Zn) corners, the structure of **6** is completed by chelating TMEDA and terminal 'Bu groups on Na and Zn, respectively. Though ring-stacking can be invoked to describe metal–ligand cubane structures,²³ **6** is best interpreted as a structurally dictating $[(\text{PhC}\equiv\text{C})_2\text{Zn}(\mu\text{-C}\equiv\text{CPh})_2\text{Zn}(\text{'Bu})_2]^{2-}$ dianion, the two $(\text{PhC}\equiv\text{C})_3$ triangular faces of which are filled by TMEDA-chelated Na^+ cations. For steric reasons the 'Bu ligands occupy cisoid positions within the dianion, exo to the cubane ($\text{Na}_2\text{Zn}_2\text{C}_4$) core. The origin of the distinction between **5** and **6** is presumably also largely steric, as Li^+ seems too small to support a $(\text{PhC}\equiv\text{C})_3$ triangular face, instead restricted to a $(\text{PhC}\equiv\text{C})_2$ edge. There are two crystallographically distinct $\text{PhC}\equiv\text{C}^-$ anions in each of the two independent molecules of **6**; each molecule has crystallographic 2-fold rotation symmetry. Within the puckered $(\text{ZnC})_2$ ring, there is a set of near-linear [$\text{Zn}2\text{--C}31\text{--C}32$, 158.0(5)°] and near-perpendicular [$\text{Zn}2\text{B--C}31\text{--C}32$, 121.4(4)°] Zn–CCPh bonds. Exo this ring, the third Zn–CCPh bond type also approaches linearity [$\text{Zn}2\text{--C}39\text{--C}40$, 172.3(5)°]. This mixture of geometries cannot simply be interpreted as zinc binding in both a σ - and π -manner, as that situation cannot be distinguished from the situation where steric constraints involved in aggregation enforce such a geometry. What the structure of **6** does definitely show is that zinc has the capacity to

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(22) Note that the asymmetric unit contains two independent cubane molecules. Due to the close similarity between them, only one is discussed here.

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(19) Outside of this work, only one previous Zn–DA bond [length, 1.852(2) Å] has been elucidated crystallographically, though it does not belong to a zincate but a neutral diiminatozinc amide. See: Chisholm, M. H.; Gallucci, J.; Phomphrai, K. *Inorg. Chem.* **2002**, 41, 2785.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds 2, 4, 5, and 6 (M = Na or Li); 6a and 6b are Two Crystallographically Independent Molecules

	2	4	5	6a	6b
Zn–N(DA/TMEDA)	2.050(2)	2.0650(14)	2.2305(15)		
M–N(DA)	2.345(2)	2.033(4)			
M–N(TMEDA)	2.445(2)	2.153(4)	2.081(4)	2.466(6)	2.481(5)
	2.460(2)	2.253(4)	2.103(4)	2.604(5)	2.564(6)
Zn– ^t Bu(terminal)	2.054(3)	2.0496(19)	2.0389(18)	2.005(5)	1.995(6)
Zn– ^t Bu(bridging)	2.065(3)	2.047(2)			
M···C(^t Bu)	2.809(4)	2.695(4)			
Zn–C(≡C)			2.0495(18)	2.039(5)	2.025(6)
			2.0738(18)	2.097(5)	2.118(5)
				2.327(5)	2.292(5)
M–C(≡C)			2.222(4)	2.625(5)	2.628(5)
			2.260(4)	2.601(6)	2.619(5)
				2.848(6)	2.788(6)
M···βC			2.803(4)	2.935(5)	2.991(5)
			3.148(4)	3.000(6)	2.957(5)
				3.201(6)	3.113(7)
N–Zn– ^t Bu(terminal)	120.47(10)	123.19(7)	117.13(7)		
N–Zn– ^t Bu(bridging)	116.62(10)	112.85(7)			
^t Bu–Zn– ^t Bu	122.90(11)	123.95(8)			
N–Zn–C(≡C)			96.63(6)		
			99.43(6)		
^t Bu–Zn–C(≡C)			123.67(7)	123.8(2)	120.4(3)
			109.37(7)	114.1(2)	114.8(3)
				113.9(2)	114.4(2)
(C≡)C–Zn–C(≡C)			107.55(7)	107.61(19)	107.36(19)
				96.36(18)	97.90(17)
				96.49(18)	98.6(2)
N(DA)–M–N(TMEDA)	126.56(8)	127.17(8)			
	148.42(9)	138.53(17)			
N(TMEDA)–M–N(TMEDA)	76.12(8)	84.98(13)	89.52(14)	71.41(18)	74.14(19)
C(^t Bu)–M–N(DA)	91.15(9)	93.80(13)			
C(^t Bu)–M–N(TMEDA)	110.01(12)	106.35(14)			
	101.45(10)	101.63(15)			
N(TMEDA)–M–C(≡C)			121.66(17)	151.50(19)	147.86(18)
			119.39(17)	111.21(17)	109.45(19)
			116.17(16)	127.56(18)	132.69(16)
			116.26(17)	94.80(18)	96.30(18)
				177.00(18)	176.28(18)
				104.34(18)	102.50(19)
(C≡)C–M–C(≡C)			95.81(14)	83.46(17)	81.13(18)
				79.38(16)	79.02(17)
				72.97(16)	74.43(17)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds 7 and 8; 8a and 8b are Two Crystallographically Independent Molecules

	7	8a	8b
Zn–N	2.159(3)	2.207(2)	2.212(2)
	2.155(3)	2.227(2)	2.216(2)
Zn–C(≡C)	1.942(4)	2.002(3)	2.000(3)
	1.960(4)		
Zn–C(^t Bu)		2.031(3)	2.027(3)
N–Zn–N	84.96(11)	82.92(9)	82.81(8)
C–Zn–C	134.75(15)	126.69(11)	126.32(12)
N–Zn–C(≡C)	107.12(13)	102.53(10)	103.22(10)
	103.41(13)	101.17(10)	100.65(11)
	105.49(13)		
	109.77(13)		
N–Zn–C(^t Bu)		116.85(10)	117.76(10)
		117.30(9)	116.74(10)

compromise from its preferred linear (σ) coordination to the $C\equiv CPh$ ligand in order to allow aggregation to take place. Similarly, although all the $Na-C\equiv C$ bond angles lie in the range $92.4(3)-96.9(4)^\circ$, formally indicative of π -interactions, the steric effects of aggregation could also play a part in pushing the alkali metal into these nonlinear geometries. What is certain is that the Na cation has to compromise more than Zn from a σ -binding mode to the $C\equiv CPh$ ligands in building the aggregated structure. The Na cation's greater propensity for engaging in such π -contacts makes this compromise easy. Note that the $Na-C\equiv C$

interactions involve short $Na-\alpha C$ contacts [$2.601(6)-2.848(6)$ Å] and longer $Na\cdots\beta C$ contacts [$2.935(5)-3.201(6)$ Å].

Both **7** and **8** adopt simple mononuclear molecular structures (Figures 5 and 6, respectively) with distorted tetrahedral zinc centers. This type of molecular architecture is common in mononuclear organozinc structures.^{24,25} Two chemically equivalent molecules are found in the asymmetric unit of **8**, but for brevity only one is discussed here. The TMEDA bite angles [in **7**, $N2-Zn-N1$, $84.96(11)^\circ$; in **8**, $N1-Zn-N2$, $82.9(9)^\circ$] are a major factor in the tetrahedral distortion at the four-coordinate zinc center. These $N-Zn-N$ (dative) bond angles are therefore the narrowest subtended at the metal, while the $C-Zn-C$ (anionic ligand) bond angles are the widest [in **7**,

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Table 3. Crystallographic Data

	2	4	5	6	7	8
formula	C ₂₀ H ₄₈ N ₃ NaZn	C ₂₀ H ₄₈ LiN ₃ Zn	C ₅₈ H ₈₆ Li ₂ N ₆ Zn ₂	C ₅₂ H ₇₀ N ₄ Na ₂ Zn ₂	C ₂₂ H ₂₆ N ₂ Zn	C ₁₈ H ₃₀ N ₂ Zn
fw	419.0	402.9	1012.0	927.8	383.8	339.8
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic
space group	C2/c	P2 ₁ /c	P2 ₁ /c	Ibca	P2 ₁ /c	P $\bar{1}$
a, Å	27.7184(10)	10.0802(2)	12.9978(13)	22.420(3)	11.6198(6)	10.4058(4)
b, Å	9.8386(3)	14.9984(3)	16.615(2)	22.883(3)	9.6815(6)	14.1317(15)
c, Å	19.6286(7)	16.8398(4)	15.8875(17)	41.069(6)	18.3865(11)	14.986(3)
α , deg						61.934(9)
β , deg	102.215(2)	94.220(1)	118.218(7)		107.610(3)	85.505(7)
γ , deg						89.357(7)
V, Å ³	5231.7(3)	2539.05(9)	3023.3(6)	21069(5)	1971.5(2)	1937.7(4)
Z	8	4	2	16	4	4
D _c , g cm ⁻³	1.064	1.054	1.112	1.170	1.293	1.165
μ , mm ⁻¹	0.96	0.97	0.83	0.96	1.25	1.26
transmission			0.594–0.732	0.748–0.846	0.687–0.860	0.619–0.760
cryst size, mm	0.30 × 0.18 × 0.05	0.40 × 0.30 × 0.30	0.70 × 0.60 × 0.40	0.32 × 0.24 × 0.18	0.30 × 0.20 × 0.12	0.42 × 0.39 × 0.23
T, K	150	123	150	150	123	150
$\theta_{\max}$	27.1	27.5	25.0	25.0	27.0	25.0
no. of refls meads	34 146	10 878	21 467	74 668	22 291	21 170
no. of unique refls	5767	5824	5266	9282	4258	6743
R _{int}	0.0810	0.0288	0.0313	0.0537	0.1042	0.0498
no. of refined params	251	279	350	598	230	393
R (F, F ² > 2 σ)	0.0491	0.0354	0.0265	0.0533	0.0523	0.0379
R _w (F ² , all data)	0.0943	0.0871	0.0699	0.1654	0.1281	0.0786
S (F ² , all data)	1.037	1.061	1.108	1.082	1.067	1.019
diff map extremes, e Å ⁻³	+0.47, -0.29	+0.36, -0.39	+0.47, -0.25	+0.84, -0.72	+0.58, -0.86	+0.29, -0.35

Cl–Zn–C9, 134.75(15)°; in **8**, Cl–Zn1–C15, 126.69(11)°]. The mean bond angles at zinc are essentially equivalent [in **7**,

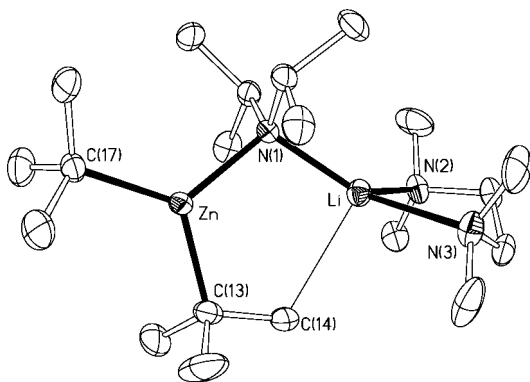


Figure 2. Molecular structure of **4** with hydrogen atoms omitted for clarity, showing the (agostic) Li...CH₃ contact as a thin line.

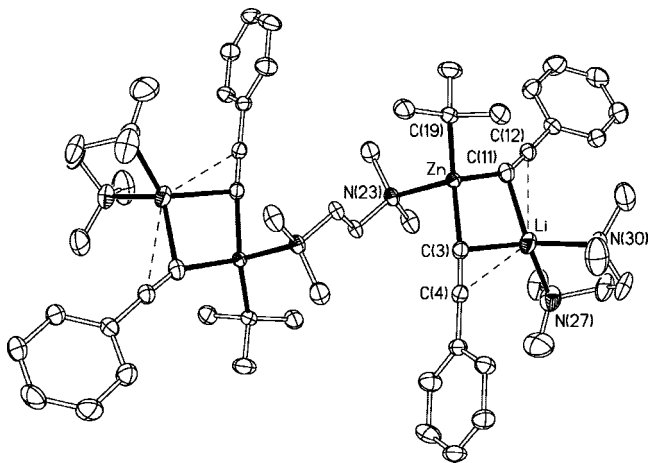


Figure 3. Molecular structure of **5** with hydrogen atoms omitted for clarity, showing Li...βC (acetylide) contacts as dashed lines.

107.58°; in **8**, 107.91°]. Comparing Zn–C bond lengths reveals a modest elongation in the mono PhC≡C monomer (mean, 2.016 Å; cf 1.951 Å in **7**) due to the presence of the branched alkyl ligand. The Zn–N bonds show a similar effect (mean, 2.214 Å; cf 2.157 Å in **7**). Synthesized by the reaction of lithium

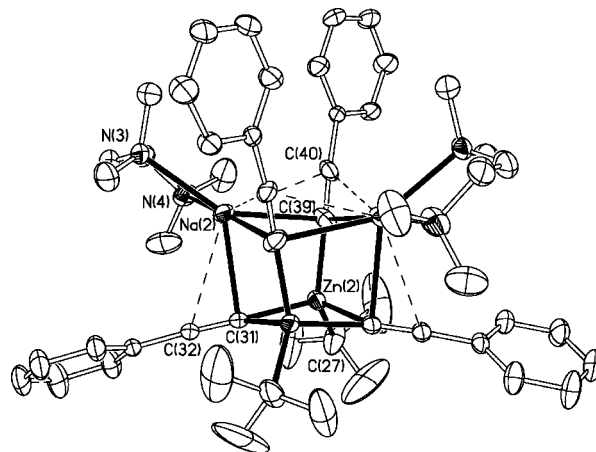


Figure 4. Molecular structure of one of the independent molecules of **6** with hydrogen atoms omitted for clarity, showing Na...βC (acetylide) contacts as dashed lines.

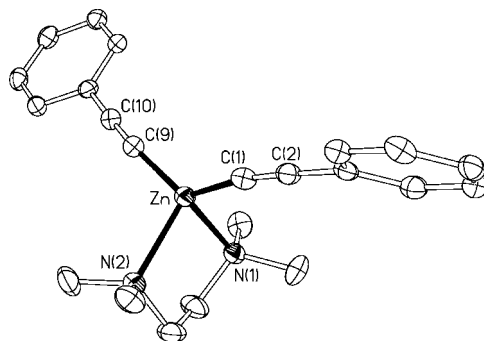


Figure 5. Molecular structure of **7** with hydrogen atoms omitted for clarity.

Table 4. C≡C–Metal Bond Angles (deg) in Selected Bimetallic Phenylacetylide Structures

phenylacetylide	C≡C–AM	C≡C–M
5	105.37(16)	173.64(15)
6	127.17(17)	155.08(17)
7	96.9(4)	169.0(5)
8	92.4(3)	164.2(4)
10		171.4(3)
11		169.5(3)
12		173.6(3)
[(TMEDA)Na(C≡CPh) ₂ Mg(DA)] ₂ , ²⁷	91.68(13)	170.56(17)
[{(TMEDA)Li} ₂ Zn(C≡CPh) ₄] ₂ ²¹	91.67(12)	171.66(17)
[(TMEDA)Cd(C≡CPh) ₂] ₂ ²⁶	118.61(16)	133.87(15)
	122.45(16)	141.01(15)
		133.52(15)
		141.02(15)
[(THF) ₃ Na(C≡CPh){Sm[N(SiMe ₃) ₂] ₃ }] ₂ , ²⁸	129.7(2)	151.4(3)
[(TMEDA)Li] ₂ Zn(C≡CPh) ₄ , ²¹	77.4 ^a	175.5 ^a
[(TMEDA)Cd(C≡CPh) ₂] ₂ ²⁶		164.5(4)
		175.4(4)
		163.81
[(TMEDA) ₂ Na(C≡CPh){Al(ⁱ Pr) ₃ }] ₂ , ^{16d}	100.69	163.81
[{(Li(THF) ₂){Cp ₂ Zr(C≡CPh)(PhC ₂ C≡CPh)}] ₂ , ²⁹	92.33	171.9(1)
[(por)Zr(C≡CR) ₃ Li(THF)] ₃ , ³⁰	84.9 ^a	173 ^a
[(TMEDA)Li] ₂ V(C≡CPh) ₄ (TMEDA), ³¹	82 ^a	168 ^a
[Na(THF){(2,6- ⁱ Pr ₂ C ₆ H ₃ N(SiMe ₃))Al(C≡CPh) ₃ }] ₂ , ³²	89 ^a	171 ^a
[K(THF){(2,6- ⁱ Pr ₂ C ₆ H ₃ N(SiMe ₃))Al(C≡CPh) ₃ }] ₂ , ³²	96.2 ^a	171 ^a
[Li(dioxane){(2,6- ⁱ Pr ₂ C ₆ H ₃ N(SiMe ₃))Al(C≡CPh) ₃ }] ₂ (dioxane), ³²	90 ^a	170 ^a
[(12-crown-4) ₂ Na{Zn(THF)(C≡CPh) ₃ }] ₃ , ³³		175 ^a
[Li ₂ {(C≡CPh) ₃ Mg(TMEDA)}] ₂ , ³⁴		167.8(4)
		162.0(4)
		176.1(3)
[Pt ₂ (C≡CPh) ₄ (PEt ₃) ₂ (Pr) ₂ Li ₂] ₃ , ³⁵	85 ^a	173 ^a
[Cp* ₂ Sm(C≡CPh) ₂ K] _n , ³⁶	96.6 ^a	173 ^a
[(TACN)LiAl(C≡CPh) ₃] ₃ , ³⁷	81.5(1)	178.1(2)

^a a = average, AM = alkali metal, M = non alkali metal, TACN = 1,4-diisopropyl-1,4,7-triazacyclononane, POR = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion.

phenylacetylide and cadmium bis(hexamethyldisilazide) in toluene/TMEDA solution, the group 12 homologue to **7**, [(TMEDA)•Cd(C≡CPh)₂], is also known:²⁶ essentially isom- structural to **7**, its more open C–Cd–C bond angle [142.8(2)°] intimates a modest relaxation of steric strain compared to that in **7**.

The dual (σ , π) bonding ability of the PhC≡C[−] ligand makes it a useful implement for measuring the relative σ/π bonding characteristics of different metals in different molecular structures. A perfect σ -bond exhibiting sp-hybridization at the acetylide C head would display a C≡C–M (where M = metal) bond angle of 180°. The two remaining p orbitals would be disposed orthogonal to this sp hybrid orbital, and thus bonds of high π -character would have C≡C–M bond angles closer to 90°. In polar alkali metal acetylides, the latter side-on bonding is not “ π ” in the normal organic sense, but is predominantly an ion-dipole interaction. The interaction could involve both acetylide C atoms (η^2), but as the α -C atom formally carries the negative charge of the deprotonated acetylene, the contact with the alkali metal cation will be strongest at the α -C junction. Table 4 surveys these C≡C–M bond angles for **5–8** and those of related crystallographically characterized bimetallic alkali metal-based phenylacetylides.^{16d,21,26–37} The aforementioned

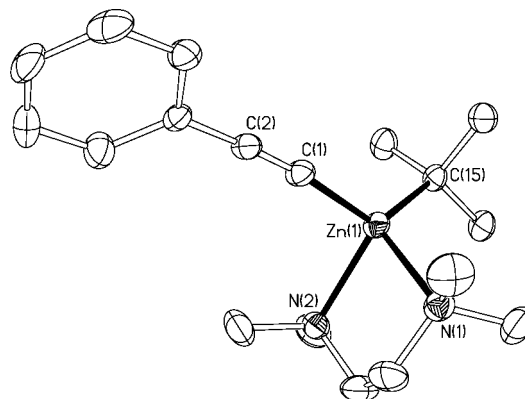


Figure 6. Molecular structure of one of the independent molecules of **8** with hydrogen atoms omitted for clarity.

cadmium homologue to **7** is also included. A number of interesting observations can be made from the comparative data. Most obviously, in every case where both an alkali metal and a higher valent metal (zinc, magnesium, aluminum, vanadium, zirconium, platinum, or samarium) engage a PhC≡C[−] ligand, the C≡C–metal bond angle is larger for the latter set of metals. Nearly always the former bond angles approach 90°, whereas

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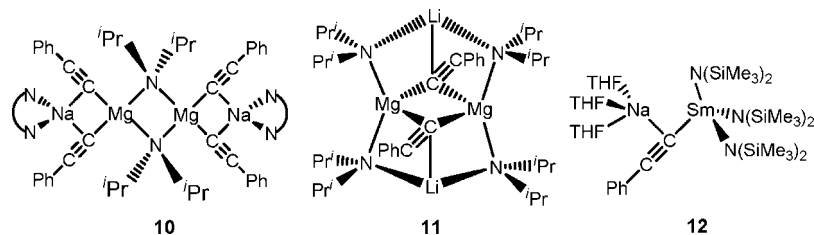


Figure 7. ChemDraw representations of the structures of **10**, **11**, and **12**.

the latter are closer to 180° . This reflects the greater propensity for σ -bonding and stronger carboxiphilicity of the di- and trivalent metals compared to that of the alkali metals. Zinc is a particularly strong acetylidophilic metal as, with the exception of one case, $\text{C}\equiv\text{C}-\text{Zn}$ bond angles lie in the range $164.2-175.5^\circ$. The exception of $155.08(17)^\circ$ occurs in **5** and is necessitated by the requirement to close a heterobinuclear $[\text{Zn}(\text{C}\equiv\text{CPh})_2\text{Li}]$ ring within the steric constraints of tetrahedral Zn and Li centers and is accompanied by an exceptionally large $\text{C}\equiv\text{C}-\text{Li}$ bond angle of $127.17(17)^\circ$, the second largest for an alkali metal in the selection, which emphasizes the structural novelty of **5**. The pronounced dependency of the $\text{C}\equiv\text{C}-\text{metal}$ bond angle on the structural type is evident from the mixed acetylido-amido magnesiate entries $[(\text{TMEDA})\cdot\text{Na}(\text{C}\equiv\text{CPh})_2\text{Mg}(\text{DA})_2]_2$, **10**, and $[(\text{LiMg}(\text{DA})_2(\text{C}\equiv\text{CPh}))_2]$, **11** (see Figure 7).²⁷ The $\text{Na}\cdots\text{Mg}\cdots\text{Mg}\cdots\text{Na}$ chain arrangement of **10** facilitates an almost perfect linear and orthogonal coordination of the μ_2 - $\text{C}\equiv\text{CPh}$ ligand toward Mg and Na, respectively, with bond angles close to 90° (mean, 91.67°) and 180° (mean, 171.11°) respectively. On the other hand, the inverse crown motif of **11**, in which the $\text{C}\equiv\text{CPh}$ ligands assume a μ_2 -disposition to Mg centers within a four-membered $(\text{MgC})_2$ ring, or overall a μ_3 -disposition including a long interaction with the Li centers, leads to $\text{C}\equiv\text{C}-\text{metal}$ bond angles intermediate between the perfect $180^\circ/90^\circ$, being 138.51° (mean) for Mg and 120.53° (mean) for Li. Here, as the acetylido ligand bridges two Mg centers, it must donate its electron density essentially equally between them, and thus a greater mixing of σ - and π -components takes place within the $\text{Mg}-\text{C}$ bonds. Steric hindrance would appear to be largely responsible for the relatively small $\text{C}\equiv\text{C}-\text{Sm}$ bond angle [$151.4(3)^\circ$] in the mixed acetylido-amido samariate $[(\text{THF})_3\text{Na}(\text{C}\equiv\text{CPh})\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_3]$, **12** (Figure 7), as the lanthanide is surrounded by three bulky amido ligands in addition to the acetylido.²⁸ In **12**, the Na binds side-on to the $\text{PhC}\equiv\text{C}^-$ ligand with an $\alpha\text{C}-\text{Na}-\beta\text{C}$ angle of only $26.30(11)^\circ$.

Conclusions

An interlocking cocomplexation approach has been used to synthesize the tricomponent alkali metal zincates $[(\text{TMEDA})\cdot\text{M}(\text{Bu})(\text{DA})\text{Zn}(\text{Bu})]$, **2** ($\text{M} = \text{Na}$) and **4** ($\text{M} = \text{Li}$). X-ray crystallography has established a common structural type for **2** and **4**, a dinuclear contacted ion pair with a strong alkali metal–N(amido)–Zn bridge. Their reactions with phenylacetylene have been explored, leading to the first crystallographically characterized products of direct zincation reactions performed by DA-zincate bases, in $[(\text{TMEDA})\cdot\text{Li}(\text{C}\equiv\text{CPh})_2\text{Zn}(\text{Bu})]_2\cdot(\text{TMEDA})$, **5**, and $[(\text{TMEDA})\cdot\text{Na}(\text{C}\equiv\text{CPh})_2\text{Zn}(\text{Bu})]_2$, **6**. Lithium acetylido **5** adopts a novel tetranuclear structure with two (LiCZn) rings connected at the Zn atoms via a bridging (nonchelating) TMEDA ligand, whereas sodium acetylido **6** adopts a pseudocubane arrangement of alternating $\text{C}\equiv\text{C}$ and metal (2 Na, 2 Zn) corners. In forming **5** and **6**, the DA-zincate reagents function as flexible, dual alkyl-amido bases. The neutral

zinc complexes $[(\text{TMEDA})\cdot\text{Zn}(\text{C}\equiv\text{CPh})_2]$, **7**, and $[(\text{TMEDA})\cdot\text{Zn}(\text{Bu})(\text{C}\equiv\text{CPh})]$, **8**, have also been synthesized and found to have simple distorted tetrahedral mononuclear structures in the crystal. Finally, as this study has revealed pronounced alkali metal effects, as well as similarities to and differences from TMP-zincates, DA-zincate chemistry promises to be a fertile field for future investigation and exploitation.

Experimental Section

General Procedures. All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane and toluene were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. ZnCl_2 was purchased from Aldrich Chemicals as a 1 M solution in diethyl ether. Butyl sodium³⁸ was prepared according to a literature method. *n*-Butyllithium in hexane was purchased from Aldrich Chemicals and standardized immediately prior to use using salicylaldehyde phenylhydrazone.³⁹ NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ^1H , 155.50 MHz for ^7Li , and 100.62 MHz for ^{13}C . Satisfactory elemental analyses of the compounds **2**, **4**, **5**, and **6** could not be obtained due to their high air- and moisture-sensitive nature.

X-ray Crystallography. Data were collected on Nonius KapapCCD and Bruker SMART 1K diffractometers with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Further information is given in Table 3. Where applied, semiempirical absorption corrections were based on repeated and symmetry-equivalent reflections. The structures were solved by direct methods and refined on all unique F^2 values. 2-Fold disorder was resolved and refined satisfactorily for TMEDA in **4** and **5** and for one phenyl ring in **6**; high anisotropic displacement parameters indicate possible further disorder in **6**, but it could not be resolved. Programs were standard Nonius and Bruker diffractometer control and integration software, SADABS,⁴⁰ programs of the SHELX family,⁴¹ and local software.

Synthesis of $[(\text{TMEDA})\cdot\text{Na}(\text{Bu})(\text{DA})\text{Zn}(\text{Bu})]$ (2**).** A Schlenk tube was charged with 2 mmol (0.358 g) of Bu_2Zn , which was dissolved in 10 mL of hexane. In a separate Schlenk tube 2 mmol of BuNa (0.16 g) was suspended in 10 mL of hexane, and 1 molar equiv of DA(H) (2 mmol, 0.28 mL) was added via syringe. The resultant creamy white suspension was allowed to stir for 1 h, after which the hexane solution containing Bu_2Zn was added via syringe. The suspension changed from creamy white to a clear solution. This was followed by the addition of 1 molar equiv of TMEDA (2 mmol, 0.30 mL). The resultant homogeneous solution was moved to the freezer to aid crystallization. A crop (0.33 g, 39%) of colorless crystals formed in solution, which were suitable for X-ray crystallographic analysis. ^1H NMR (400.13 MHz, C_6D_6 , 293 K): 0.98 and 1.24 (6H each, d, $^3J_{\text{HH}} = 6.1 \text{ Hz}$, CH_3 - $i\text{Pr}$ of DA), 1.54 (18H, s, CH_3 - $t\text{Bu}$), 1.60 (4H, s, CH_2 -TMEDA), 1.68 (12H, s, CH_3 -TMEDA), 3.49 (2H, septet, $^3J_{\text{HH}} = 6.1 \text{ Hz}$, CH - $i\text{Pr}$ of DA). $^{13}\text{C}\{^1\text{H}\}$ NMR

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(100.63 MHz, C_6D_6 , 293 K): 22.3 ($C(CH_3)_3$ of t -Bu), 26.2 and 27.0 (CH_3 -Pr of DA), 35.6 (CH_3 of t -Bu), 45.7 (CH_3 -TMEDA), 49.5 (CH -Pr of DA), 56.7 (CH_2 -TMEDA).

Synthesis of [(TMEDA) · Li(t -Bu)(DA)Zn(t -Bu)] (4). A Schlenk tube was charged with 2 mmol (0.358 g) of t -Bu₂Zn, which was dissolved in 10 mL of hexane. In a separate Schlenk tube 2 mmol of t -BuLi (1.25 mL of a 1.6 M solution in hexane) was added to 2 mmol of DA(H) (0.28 mL) in 10 mL of hexane. The resultant clear solution was allowed to stir for 1 h, after which the hexane solution containing t -Bu₂Zn was added via syringe followed by the addition of 1 molar equiv of TMEDA (2 mmol, 0.30 mL). The resultant clear solution was moved to the freezer to aid crystallization. A crop (0.43 g, 52%) of colorless crystals formed in solution, which were suitable for X-ray crystallographic analysis. ¹H NMR (400.13 MHz, C_6D_6 , 293 K): 0.98 and 1.23 (6H each, d, $^3J_{HH}$ = 6.0 Hz, CH_3 -Pr of DA), 1.53 (18H, s, CH_3 - t -Bu), 1.58 (4H, s, CH_2 -TMEDA), 1.72 (12H, s, CH_3 -TMEDA), 3.40 (2H, septet, $^3J_{HH}$ = 6.0 Hz, CH -Pr of DA). ¹³C{¹H} NMR (100.63 MHz, C_6D_6 , 293 K): 22.4 ($C(CH_3)_3$ of t -Bu), 25.0 and 25.6 (CH_3 -Pr of DA), 35.4 (CH_3 of t -Bu), 46.8 (CH_3 -TMEDA), 48.2 (CH -Pr of DA), 57.1 (CH_2 -TMEDA). ⁷Li NMR (155.50 MHz, C_6D_6 , 293 K, reference LiCl in D₂O at 0.00 ppm): 0.95.

Synthesis of [(TMEDA) · Li(C≡CPh)₂Zn(t -Bu)]₂ · (TMEDA)] (5). A Schlenk tube was charged with 2 mmol (0.358 g) of t -Bu₂Zn, which was dissolved in 10 mL of hexane. In a separate Schlenk tube 2 mmol of t -BuLi (1.25 mL of a 1.6 M solution in hexane) was added to 2 mmol of DA(H) (0.28 mL) in 10 mL of hexane. The resultant clear solution was allowed to stir for 1 h, after which the hexane solution containing t -Bu₂Zn was added via syringe followed by the addition of 1.5 molar equiv of TMEDA (3 mmol, 0.45 mL). Then, 2 molar equiv (4 mmol, 0.44 mL) of phenylacetylene was added to the solution, and immediately a yellow solid precipitated, which dissolved on addition of hot toluene. Standing the solution on the bench afforded colorless crystals of **5** (0.77 g, 76%), which were suitable for X-ray crystallographic analysis. Note that adding only 1 molar equiv of the phenylacetylene and TMEDA also produces **5** but in a smaller yield (0.36 g, 36%). This suggests that the intermediate reacts quicker with the phenylacetylene than does the starting reagent. ¹H NMR (400.13 MHz, C_6D_6 , 293 K): 1.46 (18H, s br, CH_3 - t -Bu), 1.80 (12H, s br, CH_2 -TMEDA), 2.14 (36H, s, CH_3 -TMEDA), 6.97 (4H, m, H_{para} , C_6H_5), 7.07 (8H, m, H_{meta} , C_6H_5), 7.54 (8H, m, H_{ortho} , C_6H_5). ¹³C{¹H} NMR (100.63 MHz, C_6D_6 , 293 K): 34.6 (CH_3 of t -Bu), 46.6 (CH_3 -TMEDA), 57.2 (CH_2 -TMEDA), 122.1 ($C\equiv CPh$), 126.3 (C_{para} , C_6H_5), 127.9 (C_{meta} , C_6H_5), 132.1 and 132.3 (C_{ortho} , C_6H_5). Signals for Zn- $C(CH_3)_3$ of t -Bu and $C\equiv CPh$ and C_{ipso} of $PhC\equiv C$ were not observed. ⁷Li NMR (155.50 MHz, C_6D_6 , 293 K, reference LiCl in D₂O at 0.00 ppm): 1.24.

Synthesis of [(TMEDA) · Na(C≡CPh)₂Zn(t -Bu)]₂ (6). A Schlenk tube was charged with 2 mmol (0.358 g) of t -Bu₂Zn, which was dissolved in 10 mL of hexane. In a separate Schlenk tube 2 mmol of BuNa (0.16 g) was suspended in 10 mL of hexane, and 1 molar equiv of DA(H) (2 mmol, 0.28 mL) was added via syringe. The resultant creamy white suspension was allowed to stir for 1 h, after which the hexane solution containing t -Bu₂Zn was added via syringe. The suspension changed from creamy white to a clear solution. This was followed by the addition of 1 molar equiv of TMEDA (2 mmol, 0.30 mL). Then, 2 molar equiv (4 mmol, 0.44 mL) of phenylacetylene was added to the solution, and immediately a yellow solid precipitated, which dissolved on addition of hot toluene. Standing the solution on the bench afforded colorless crystals of **6** (0.62 g, 67%). Note that adding only 1 molar equiv of the phenylacetylene also produces **6** but in a smaller yield (0.34 g, 37%). This suggests that the intermediate reacts quicker with the phenylacetylene than does the starting reagent. ¹H NMR (400.13 MHz, C_6D_6 , 293 K): 1.62 (8H, s, CH_2 -TMEDA), 1.88 (18H, s, CH_3 - t -Bu),

1.95 (24H, s, CH_3 -TMEDA), 6.97 (4H, t, $^3J_{HH}$ = 7.5 Hz, H_{para} , C_6H_5), 7.06 (8H, t, $^3J_{HH}$ = 7.5 Hz, H_{meta} , C_6H_5), 7.64 (8H, t, $^3J_{HH}$ = 7.5 Hz, H_{ortho} , C_6H_5). ¹³C{¹H} NMR (100.63 MHz, C_6D_6 , 293 K): 21.3 ($C(CH_3)_3$ of t -Bu), 34.8 (CH_3 of t -Bu), 45.8 (CH_3 -TMEDA), 56.9 (CH_2 -TMEDA), 126.5 ($C\equiv CPh$), 127.2 (C_{para} , C_6H_5), 128.6 (C_{meta} , C_6H_5), 132.1 (C_{ortho} , C_6H_5). Signals for $C\equiv CPh$ and C_{ipso} of $PhC\equiv C$ were not observed.

Synthesis of [(TMEDA) · Zn(C≡CPh)₂] (7). Phenylacetylene (4 mmol, 0.44 mL) was dissolved in 10 mL of hexane, t -BuLi (4 mmol, 2.50 mL of a 1.6 M solution in hexane) was added dropwise to the previous solution, and immediately a white solid precipitated. The resultant white suspension was allowed to stir for 30 min. This was followed by the addition of 0.5 molar equiv of ZnCl₂ (2 mmol, 2 mL of a 1 M solution in diethyl ether) and 0.5 molar equiv of TMEDA (2 mmol, 0.3 mL). No changes were observed after this addition, and the white suspension was stirred at room temperature overnight. The solvents were then removed, and the residue was suspended in 15 mL of toluene. The suspension was filtered off to separate the LiCl formed, and from the filtrate **7** was isolated as a white solid (0.55 g, 71%) after solvent removal. Anal. Calcd for C₂₂H₂₆N₂Zn (383.8): C, 68.84; H, 6.83; N, 7.30. Found: C, 68.79; H, 6.85; N, 7.31. ¹H NMR (400.13 MHz, C_6D_6 , 293 K): 1.79 (4H, s, CH_2 -TMEDA), 2.12 (12H, s, CH_3 -TMEDA), 7.01 (2H, t, $^3J_{HH}$ = 7.7 Hz, H_{para} , C_6H_5), 7.11 (4H, t, $^3J_{HH}$ = 7.7 Hz, H_{meta} , C_6H_5), 7.69 (4H, d, $^3J_{HH}$ = 7.7 Hz, H_{ortho} , C_6H_5). ¹³C{¹H} NMR (100.63 MHz, C_6D_6 , 293 K): 47.5 (CH_3 -TMEDA), 56.8 (CH_2 -TMEDA), 108.5 ($C\equiv CPh$), 113.7 ($C\equiv CPh$), 126.3 (C_{para} , C_6H_5), 128.2 (C_{ipso} , C_6H_5), 128.4 (C_{meta} , C_6H_5), 132.0 (C_{ortho} , C_6H_5).

Synthesis of [(TMEDA) · Zn(t -Bu)(C≡CPh)] (8). A Schlenk tube was charged with 2 mmol (0.358 g) of Zn t -Bu₂, which was dissolved in 10 mL of hexane, and 1 molar equiv of phenylacetylene (2 mmol, 0.22 mL) was added via syringe. This was followed by the addition of 1 molar equiv of TMEDA (2 mmol, 0.30 mL), and the resultant colorless solution was stirred at room temperature overnight. Standing the solution at -27 °C afforded colorless crystals of **8** (0.32 g, 47%), which were suitable for X-ray crystallographic analysis. The crude of the reaction was also analyzed by ¹H-¹³C{¹H} NMR, showing only the signals of **8**. Therefore the yield in the formation of **8** is quantitative. Note that on adding 2 molar equiv of phenylacetylene at room temperature, the second t -Bu group is not replaced since the reaction produces **8** as the unique product. Anal. Calcd for C₁₈H₃₀N₂Zn (339.8): C, 63.62; H, 8.90; N, 8.24. Found: C, 63.80; H, 8.90; N, 8.23. ¹H NMR (400.13 MHz, C_6D_6 , 293 K): 1.44 (9H, s, CH_3 - t -Bu), 1.78 (4H, s brought, CH_2 -TMEDA), 2.08 (12 H, s brought, CH_3 -TMEDA), 6.98 (1H, t, $^3J_{HH}$ = 7.4 Hz, H_{para} , C_6H_5), 7.08 (2H, t, $^3J_{HH}$ = 7.4 Hz, H_{meta} , C_6H_5), 7.61 (2H, d, $^3J_{HH}$ = 7.4 Hz, H_{ortho} , C_6H_5). ¹³C{¹H} NMR (100.63 MHz, C_6D_6 , 293 K): 19.4 ($C(CH_3)_3$ of t -Bu), 34.6 (CH_3 of t -Bu), 47.8 (brought, CH_3 -TMEDA), 57.1 (CH_2 -TMEDA), 108.4 ($C\equiv CPh$), 118.5 ($C\equiv CPh$), 125.8 (C_{para} , C_6H_5), 128.3 (C_{meta} , C_6H_5), 128.8 (C_{ipso} , C_6H_5), 132.0 (C_{ortho} , C_6H_5).

Reaction of 8 with Phenylacetylene in Refluxing Toluene. A Schlenk tube was charged with 2 mmol (0.358 g) of Zn t -Bu₂, which was dissolved in 10 mL of hexane, and 1 molar equiv of phenylacetylene (2 mmol, 0.22 mL) was added via syringe. This was followed by the addition of 1 molar equiv of TMEDA (2 mmol, 0.30 mL), and the resultant colorless solution was allowed to stir at room temperature overnight. At this stage the solution contains mainly the compound **8**. This was followed, after solvent removal, by the addition of 10 mL of toluene and another equivalent of phenylacetylene (2 mmol, 0.22 mL), affording a very pale yellow solution. This solution was refluxed for 1 h, leading to some gray solid (probably zinc metal). The crude product of the reaction was analyzed by ¹H-¹³C{¹H} NMR, revealing a very complicated mixture in which the major product

is still the starting material **8** and where compound **7** was detected in only a trace amount.

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Supporting Information Available: Crystallographic details for compounds **2**, **4**, **5**, **6**, **7**, and **8** in CIF format and NMR spectra for these compounds. This material is available free of charge via the Internet at <http://pubs.ac.org>.

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