Articles

Synthesis and Structural Elucidation of Alkyl, Amido, and Mixed Alkyl−Amido “Highly-Coordinated” Zincates

David R. Armstrong, Christine Dougan, David V. Graham, Eva Hevia,* and Alan R. Kennedy

WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, U.K. G1 1XL

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The solution and solid-state characterization of the tetraorganozincates [$(TMEDA)_2Li_2ZnMe(NMe_2)_3$] (**2**) and [$(TMEDA)_2Li_2ZnMe_4$] (**4**) and the all-amido triorganozincate [$\{(TMEDA)LiZn(NMe_2)_3\}_2$] (**3**) are reported. X-ray crystallographic studies reveal that **2** and **4** exhibit similar structural motifs, namely trinuclear Li···Zn···Li chain arrangements held together by a methyl and three amido ligands in the former and exclusively by methyl groups in the latter, whereas **3** adopts a longer tetranuclear Li···Zn···Zn···Li chain arrangement with all NMe_2 ligands. The zinc coordination in all these structures is distorted tetrahedral. DFT calculations revealed that the formation of tetraorganozincate **4** by cocomplexation of 2 equiv of MeLi and Me_2Zn is thermodynamically preferred over the parent triorganozincate [$(TMEDA)LiZnMe_3$]. Preliminary studies show that the tris(amido)alkyl zincate **2** is a poor Brønsted base for metalation (zincation) of functionalized aromatic substrates such as anisole, *N*,*N*-diisopropylbenzamide, and benzonitrile.

Introduction

Organozinc reagents (R_2Zn or RZnX) were one of the first organometallic compounds to be prepared[1] and are widely used in synthesis due to their “soft” reactivity and their great functional group tolerance.[2] However, one of their main drawbacks is their poor kinetic reactivity, which is primarily due to the greater stability and covalent character of Zn−C bonds in comparison to metal−carbon bonds of other organometallic reagents such as Grignard or organolithium reagents.[3] An alternative to these kinetically retarded reagents is the use of alkali-metal zincates, which have revealed themselves as versatile reagents in synthesis. These mixed-metal (ate) reagents appear to combine the high reactivity typically associated with group 1 organometallic compounds with the greater selectivity of the neutral organozinc reagents,[4] and they have proved to be highly chemo- and regioselective reagents in many fundamental organic reactions such as metal−halogen exchange,[5] deprotonative metalation,[6] and nucleophilic addition.[7] However, despite their numerous synthetic applications, the structural information available for alkali-metal zincates is still quite limited[8] and it is only recently that the structures of some of these important reagents have been elucidated, such as the dialkyl−TMP zincate [(THF)LiZn(TMP)*t*Bu_2] (**1**; TMP =

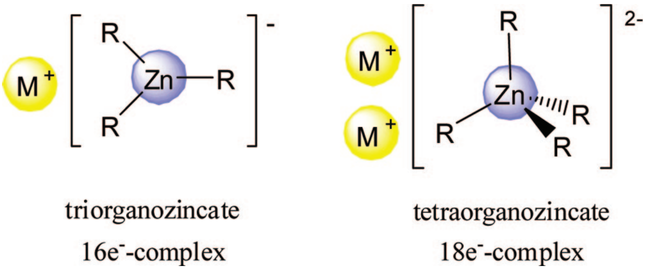

Figure 1. Molecular formulations for general triorganozincates [$MZnR_3$] and tetraorganozincates [M_2ZnR_4] (R = anionic ligand, M = group 1 metal).

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* To whom correspondence should be addressed. E-mail: eva.hevia@strath.ac.uk.

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2,2′,6,6′-tetramethylpiperidide)[9] which is an excellent chemoselective base for directing the zincation of aromatic substrates.[10]

Alkali-metal zincates can be divided generally into two different categories[11] on consideration of the number of anionic ligands surrounding the zinc center: namely, triorganozincates [$M^+ZnR_3^-$] and tetraorganozincates [$M_2{}^{2+}ZnR_4{}^{2-}$]. In the former the Zn center generally exhibits a trigonal-planar geometry, forming a 16-electron complex, whereas in the latter Zn adopts a tetrahedral geometry, giving rise to an 18-electron complex (Figure 1)[12] (note that pointing out this electron-count distinction does not imply any connection with the 18-electron rule that plays a major rule in open-shell d-block chemistry). In contrast to the chemistry of triorganozincates, the reactivity of the related tetraorganozincates (also known, sometimes misleadingly, as highly coordinated zincates: see later) has only been tentatively explored. A special mention should be given to the groundbreaking work reported a decade ago by Uchiyama and Sakamoto, who showed that these species are effective reagents for chemoselective halogen (or tellurium)−zinc exchange, Michael additions, carbozincation, and epoxide ring-opening reactions.[12] Although several NMR studies and DFT calculations have been reported in order to shed some light on the structure of these important reagents, to date only a handful of highly coordinated zincates have been structurally characterized.[13]

For triorganozincates it has been found that amido-based zincates such as hetroleptic [LiZn(TMP)*t*Bu$_2$][9] and homoleptic [LiZn(TMP)$_3$][14] are more reactive toward deprotonative metalations than trialkyl derivatives.[15] This has been explained in terms of the preferred kinetic reactivity of Zn−N bonds in comparison with Zn−C bonds.[9b,10a,16] In contrast, the synthesis of highly coordinated zincates containing amido ligands remains dormant.

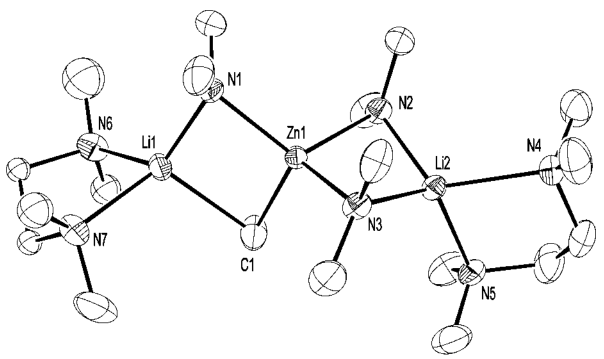

Figure 2. Molecular structure of **2** with 40% probability displacement ellipsoids. Hydrogen atoms omitted for clarity.

To form a highly coordinated zincate, Zn must bond to four (mono)anionic ligands; therefore, its formation would be especially favored when nonsterically demanding ligands such as dimethylamide and methyl groups are employed.

The synthesis of dimethylamido/methyl-based zincates is of particular interest, since the hypothetical triorganozincate [$(Me_2O)LiZn(NMe_2)Me_2$] has been employed in several DFT calculations as a theoretical model of the regioselective TMP base **1**,[9b,10a,b] but to date no experimental investigation of them have been reported.

Herein we fill this important gap in our knowledge by reporting the synthesis and structural characterization of the highly coordinated monoalkyltris(amido)zincate [$(TMEDA)_2Li_2ZnMe(NMe_2)_3$] (**2**;TMEDA= *N*,*N*,*N*′,*N*′-tetramethylethylenediamine), which is to the best of our knowledge the first example of a heteroleptic, highly coordinated zincate. The related tetramethylzincate [$(TMEDA)_2Li_2ZnMe_4$] (**4**) and the all-amido triorganozincate [$\{(TMEDA)LiZn(NMe_2)_3\}_2$](**3**) have also been fully characterized in solution and in the solid state. In addition we report preliminary studies on the reactivity of **2** toward directed ortho metalation (DoM) of the substituted aromatic compounds anisole, *N*,*N*-diisopropylbenzamide, and benzonitrile.

Results and Discussion

Initially the synthesis and characterization of the triorganozincate [$(TMEDA)LiZn(NMe_2)Me_2$] was attempted using a cocomplexation approach, which is one of the synthetic methodologies most commonly employed in this area.[17] Thus, a commercial solution of dimethylzinc in toluene was added to a suspension of 1 molar equiv of $LiNMe_2$ in hexane solution. The reaction was completed with the introduction of the donor solvent TMEDA in order to help saturate the coordination sphere of the lithium and to aid crystallization of the product (Scheme 1). The resulting solution deposited colorless crystals when placed in the freezer. An X-ray crystallographic study identified these crystals not as the expected triorganozincate but rather the unsymmetrical tetraorganozincate **2** (Figure 2 and Table 1).

This surprising product can be described as an ion-contacted aggregate of two oppositely disposed [Li(TMEDA)]$^+$ cations coordinated to the dianionic [$Zn(NMe_2)_3(Me)$]$^{2-}$ center building a trinuclear Li···Zn···Li chain arrangement connected unsymmetrically through bridging ligands: three dimethylamide

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Scheme 1

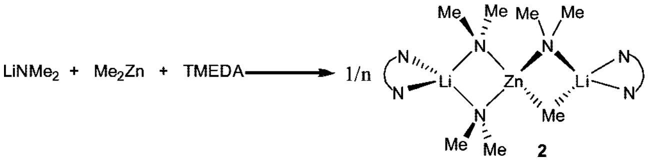

Table 1. Key Bond Lengths (Å) and Bond Angles (deg) within the Structures of 2 and 4

Compound **2**			
Li1−N1	1.966(6)	Li2−N5	2.158(6)
Li1−N7	2.118(6)	Li2−N4	2.211(6)
Li1−N6	2.140(7)	Zn1−N2	2.033(2)
Li1−C1	2.332(7)	Zn1−N3	2.037(3)
Li2−N2	2.033(6)	Zn1−N1	2.045(3)
Li2−N3	2.046(6)	Zn1−C1	2.089(3)
N1−Li1−N7	122.9(3)	N5−Li2−N4	84.8(2)
N1−Li1−N6	123.9(3)	N2−Zn1−N3	96.29(13)
N7−Li1−N6	86.8(2)	N2−Zn1−N1	116.46(14)
N1−Li1−C1	101.0(3)	N3−Zn1−N1	116.71(11)
N7−Li1−C1	113.6(3)	N2−Zn1−C1	109.34(14)
N6−Li1−C1	108.6(3)	N3−Zn1−C1	110.60(15)
N2−Li2−N3	96.0(2)	N1−Zn1−C1	107.09(13)
N2−Li2−N5	117.3(3)	Zn1−C1−Li1	71.09(17)
N3−Li2−N5	120.9(3)	Zn1−N1−Li1	80.0(2)
N2−Li2−N4	119.7(3)	Zn1−N2−Li2	80.05(19)
N3−Li2−N4	120.2(3)	Zn1−N1−Li2	79.66(18)
Compound **4**			
Li1−C7	2.243(5)	Li2−C9	2.193(5)
Li1−C8	2.220(5)	Li2−C10	2.251(5)
Li1−N2	2.106(5)	Li2−N4	2.084(5)
Li1−N1	2.109(4)	Li2−N3	2.103(5)
N2−Li1−N1	87.20(17)	N4−Li2−C10	114.4(2)
N2−Li1−C8	118.3(2)	N3−Li2−C10	115.0(2)
N1−Li1−C8	116.9(2)	C9−Li2−C10	106.0(2)
N2−Li1−C7	113.6(2)	C7−Zn1−C9	105.25(10)
N1−Li1−C7	116.0(2)	C7−Zn1−C8	112.51(10)
C8−Li1−C7	104.82(19)	C9−Zn1−C8	107.47(10)
N4−Li2−N3	87.14(18)	C7−Zn1−C10	108.02(12)
N4−Li2−C9	116.9(2)	C9−Zn1−C10	112.66(10)
N3−Li2−C9	117.1(2)	C8−Zn1−C10	110.87(12)

groups and one methyl group. One of the lithium atoms, Li2, bonds to two amido groups and one TMEDA molecule, whereas the other lithium, Li1, bonds to one amido group, one methyl group, and the other TMEDA molecule. The arrangement of the three metals is slightly bent, as evidenced by the Li1 ··· Zn1 ··· Li2 separation angle of 162.55(17)°. Similar linear or near-linear arrangements have been previously found for other tetraorganozincate zincates.[13] However, to the best of our knowledge **2** represents the first example of a heteroleptic highly coordinated zincate whose structure has been elucidated by X-ray diffraction.

The $\mathrm{Li{-}N_{amide}}$ bond distances in **2** (mean length 2.074 Å) are within the range of values found for related species containing dimethylamido ligands such as the aluminate $[(\mathrm{THF})_2\mathrm{LiAl}(\mathrm{NMe}_2)_4]$[18] (2.131 Å) and the zirconate $[(\mathrm{THF})_2\mathrm{LiZr}(\mathrm{NMe}_2)_4]$[19] (2.154 Å). With regard to the contact of one of the lithium atoms with the methyl group (Li1−C1), this interaction must be fairly strong, as indicated by its short length (2.332(7) Å), which is of the same order as that found in the methyllithium complex $[(\mathrm{LiMe.THF})_4]$[20] (2.235 Å) and remarkably shorter than that found in the related TMP−zincate [(TMEDA)Li(TMP)(Me)Zn(Me)][21] (2.603(5) Å). This difference in the strengths of the Li−C interaction in these two zincates is probably largely due to a combined effect of two distinct factors: first, the presence of a much less sterically demanding amido ligand in **2**, which allows a closer approach of the lithium atom to the methyl group, and second, the different charges on the zincate anions. Thus, **2** is a highly coordinated zincate with a 2− negative charge, $[\mathrm{Zn}(\mathrm{NMe}_2)_3(\mathrm{Me})]^{2-}$, whereas the TMP−zincate has a 1− negative charge, $[\mathrm{Zn}(\mathrm{TMP})\mathrm{Me}_2]^{-}$. Therefore, for both steric and electrostatic reasons the $[\mathrm{Li}(\mathrm{TMEDA})]^{+}$ cation will be more strongly attracted to the dianionic zincate.

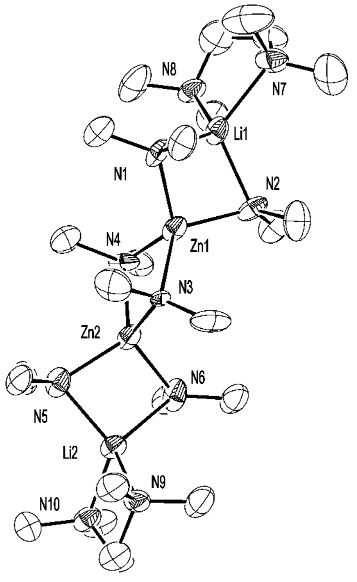

Figure 3. Molecular structure of **3** with 40% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Turning to the zinc bonds in **2**, the Zn−N lengths (mean 2.038 Å) have values similar to those found in other dialkyl(amido)zincates, where the amide ligand is bridging the two metals, as for example in [(TMEDA)Li(TMP)(Me)Zn(Me)][21] (2.048(19) Å). The Zn−C bond length in **2** (2.089(3) Å) is within the same range found in other dimethylzincates such as [(TMEDA)Li(TMP)(Me)Zn(Me)] (2.032(3) Å) and $[(\mathrm{PMDETA})\mathrm{LiZnMe}_2(\mathrm{HMDS})]$[17] (2.036(15) Å) and is slightly elongated compared to those found in the monomeric neutral zinc complex $[(\mathrm{TMEDA})\mathrm{ZnMe}_2]$[22] (1.989(9) and 1.974(9) Å).

Compound **2** was also characterized in deuterated tetrahydrofuran solution using multinuclear NMR (^{1}H, ^{13}C, and ^{7}Li) spectroscopy (see Experimental Section). The ^{1}H NMR spectrum shows a lone singlet at 2.86 ppm for the dimethylamide ligands, which is indicative either that **2** exhibits a structure in THF solution different from that found in the solid state, where there are two different amide groups, or that there is a rapid exchange of ligands within the tetrahedral mononuclear zincate structucture. The first possibility could be explained by the formation in solution of the fully solvent-separated ion pair [2{Li(d_8-

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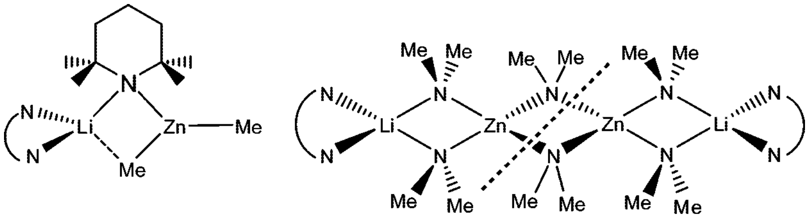

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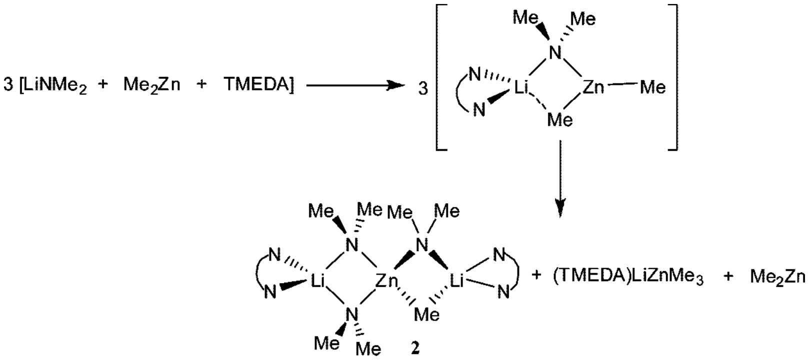
Figure 4. ChemDraw representations of the triorganozincates monomeric [(TMEDA)LiZn(TMP)Me_2] and dimeric **3**, emphasizing their different Zn coordination numbers.

Scheme 2. Plausible Disproportionation Pathway for the Surprising Formation of 2



THF$)_x\}^+\{Zn(NMe_2)_3Me\}^{2-}$], which would be also supported by the observation of noncoordinated TMEDA[23] in the spectrum (2.16 and 2.30 ppm for the CH_3 and CH_2 groups, respectively). The resonance for the methyl group appears at a negative chemical shift (−1.12 ppm) which lies between those found for MeLi (−1.96 ppm) and Me_2Zn (−0.84 ppm) in the same deuterated solvent.

A plausible explanation for the formation of **2** could be the initial formation of the dialkyl(amido)zincate [(TMEDA)-LiZn(NMe_2)Me_2] followed by a cleavage and rearrangement process to afford **2** (Scheme 2). Investigation of the filtrate following the removal of **2** suggested the presence of $LiZnMe_3 \cdot$TMEDA, as indicated by its ^1H NMR spectrum, which showed a low-frequency singlet at −1.17 ppm. This chemical shift is comparable to that previously reported for $LiZnMe_3$ in the same deuterated solvent (−1.08 ppm).[12] Thus, the formation of **2** can be rationalized by a disproportionation process of a putative dimethyl(amido)zincate, where the other products of the reaction would be $LiZnMe_3 \cdot$TMEDA and Me_2Zn (Scheme 2).

This unexpected result led us to investigate the preparation and characterization of more highly coordinated zincates. First we attempted the preparation of the homoleptic amidozincate [(TMEDA)$_2Li_2Zn(NMe_2)_4$] using a metathesis approach by reaction of zinc chloride with 4 mol equiv of lithium dimethylamide. This methodology is a well-known strategy for the synthesis of many mixed-metal compounds.[24] This reaction led to the formation of colorless crystals of **3** suitable for an X-ray crystallographic study (Figure 3), which revealed them not to be the expected tetraorganozincate but instead the triorganozincate variant [{(TMEDA)LiZn(NMe_2)$_3$}$_2$] (**3**).

Formally dimeric, new amidozincate **3** possesses a structure similar to that of **2** but has a longer tetranuclear Li···Zn···Zn···Li chain arrangement in which the metals are connected exclusively by dimethylamide ligands. This structure can be also described as an ion-contacted aggregate of two oppositely disposed $[Li(TMEDA)]^+$ cations and the complex dianion $[Zn_2(NMe_2)_6]^{2-}$, which forms three orthogonal fused four-membered rings, two outer [Li(μ-N)$_2$Zn] rings, and one [Zn(μ-N)$_2$Zn] central ring. Unfortunately a large amount of motion involving the amido groups and the TMEDA ligands affects the accuracy of the crystal structure, and consequently a discussion of bond lengths and bond angles would not be of value, though its connectivity is definitive. That notwithstanding, this structure represents to the best of our knowledge the first example of a homoleptic (amido)zincate with a contacted ion-pair structure.[25]

It should be emphasized that, although **3** is a triorganozincate, each zinc center bonds to four amide anions and adopts a distorted-tetrahedral geometry, which is in contrast with the structures found for other amido-based triorganozincates such as, for example, [(TMEDA)Li(TMP)(Me)Zn(Me)][21] (Figure 4). This distinction is because **3** displays a dimeric structure (the dimerization junction is highlighted with a dashed line in Figure 4), where the "terminal" amido group on the zinc of one [(TMEDA)LiZn(NMe_2)$_3$] monomer is bound to the zinc center of another monomer, giving rise to **3**. Here Zn can expand its coordination sphere due to the small size of the amido ligand in comparison with the highly sterically demanding TMP group (Figure 4). This finding of a tetracoordinated zinc in a triorganozincate structure means that it is ambiguous (or possibly not even correct) to describe R_4Zn^{2-} species as highly coordinated zincates: tetraorganozincates seem to be a more precise alternative.

The formation of **3** is somewhat surprising, considering the 4:1 Li:Zn stoichiometry used in the metathesis reaction (vide

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[23] Hevia, E.; Henderson, K. W.; Kennedy, A. R.; Mulvey, R. E. *Organometallics* **2006**, *25*, 1778.

[24] For examples, see: (a) Dumouchel, S.; Mongin, F.; Trécourt, F.; Quéguiner, G. *Tetrahedron* **2003**, *59*, 8629. (b) Dumouchel, S.; Mongin, F.; Trécourt, F.; Quéguiner, G. *Tetrahedron Lett.* **2003**, *44*, 2033.

[25] For examples of structurally characterized tris(amido) zincates see: Putzer, M. A.; Neumuller, B.; Dehnicke, K. Z. *Anorg. Allg. Chem.* **1997**, *623*, 539. (b) Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Rodger, P. J. A. *Chem. Commun.* **2001**, 1400. (c) Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Roberts, B. A.; Rowlings, R. B. *Organometallics* **2002**, *21*, 5115.

Scheme 3

$$2LiNMe_2 + Me_2Zn + 2TMEDA \rightarrow (TMEDA)_2Li_2Zn(NMe_2)_4 \xrightleftharpoons{\text{hexane}} 0.5\underset{\mathbf{3}}{(TMEDA)_2Li_2Zn_2(NMe_2)_6} + (TMEDA)LiNMe_2$$

$$(TMEDA)_2Li_2Zn_2(NMe_2)_6 \xrightleftharpoons{C_6D_6} (TMEDA)_2Li_2Zn(NMe_2)_4 + Zn(NMe_2)_2$$

supra), from which the tetraorganozincate [(TMEDA)$_2$Li$_2$Zn(NMe$_2$)$_4$] would be expected. Berger has elegantly proved that in THF solution the highly coordinated zincate [Li$_2$ZnMe$_4$] is in equilibrium with the triorganozincate [LiZnMe$_3$] and MeLi.[26] A similar process could be taking place here for these (amido)zincates which could be favoring the precipitation (crystallization) of **3** due to its lower solubility in hexane solution (Scheme 3). To investigate this possibility, when isolated crystals of **3** were dissolved in deuterated benzene solution, the ^{1}H, ^{7}Li, and ^{13}C NMR spectra (see the Experimental Section) showed this compound is in equilibrium with [(TMEDA)Li$_2$Zn(NMe$_2$)$_4$] and Zn(NMe$_2$)$_2$. Thus, the ^{1}H NMR spectrum displays two singlets at 3.40 and 3.20 ppm of relative integration 1:2 for the central and outer NMe$_2$ ligands of compound **3**, a singlet at 3.27 ppm for the only type of NMe$_2$ ligand in tetraorganozincate [(TMEDA)Li$_2$Zn(NMe$_2$)$_4$], and two singlets at 3.36 and 3.12 ppm of the same integration, which can be assigned to the bridging and terminal ligands of Zn(NMe$_2$)$_2$, presuming it is dimeric. The ^{7}Li NMR spectrum showed two signals at 0.63 and 0.52 ppm, which can be assigned to the two distinct lithium species of the equilibrium. On the introduction of an additional substoichiometric amount of LiNMe$_2$ to this solution, all the signals in the ^{1}H NMR spectrum experience a considerable line broadening, the concentration of [(TMEDA)Li$_2$Zn(NMe$_2$)$_4$] increases (as shown by the integration ratios of the resonances in the spectrum), and the two signals in the ^{7}Li NMR spectrum merge into a broader one at 0.59 ppm, which suggests that an exchange process is taking place and that [(TMEDA)Li$_2$Zn(NMe$_2$)$_4$] is probably the most stable species in solution. These results illustrate the complexity of the structures and stabilities in solution of these mixed-metal reagents, which seem to be in equilibrium with their monometallic components. This probably reflects the limited steric bulk of the NMe$_2$ ligand and its modest basicity compared to that of bulkier stronger amides such as TMP.

As previously mentioned, the tetraalkylzincate [Li$_2$ZnMe$_4$] has proved to be an excellent regioselective reagent for several organic transformations. The structure of this zincate in its unsolvated form was reported by Weiss in 1968,[27] but it was not until 1996 that Uchiyama and Sakamoto[12] showed that this compound in THF solution is an effective regio- and chemoselective reagent for metal−bromine exchange and epoxide-opening reactions. We endeavored to synthesize the analogous TMEDA solvate [(TMEDA)$_2$Li$_2$ZnMe$_4$] and the analogous triorganozincate [(TMEDA)LiZnMe$_3$] for comparison with zincates **2** and **3** by direct combination of the two homometallic components MeLi and Me$_2$Zn (Scheme 4).

Colorless crystalline products were obtained from both reactions which were characterized by NMR spectroscopy and X-ray crystallography, showing that in both cases the compound isolated was the same, namely the tetramethylzincate [(TMEDA)$_2$Li$_2$ZnMe$_4$] (**4**). The fact that compound **4** is obtained even when the ratio MeLi/Me$_2$Zn is 1:1 seems to suggest that in hexane solution the triorganozincate [(TMEDA)LiZnMe$_3$] could be in equilibrium with **4** and Me$_2$Zn. This contrasts markedly with the aforementioned results found for methylzincates in THF solution.[26]

Scheme 4

$$2MeLi + Me_2Zn + 2TMEDA \rightarrow [(TMEDA)_2Li_2ZnMe_4]$$

$$MeLi + Me_2Zn + TMEDA \rightarrow 0.5[(TMEDA)_2Li_2ZnMe_4] + 0.5Me_2Zn$$

In order to gain some understanding of this possible equilibrium between the triorganozincate [(TMEDA)LiZnMe$_3$] and **4**, we next carried out a theoretical study using density functional theory (DFT) calculations utilizing the B3LYP functionals and the 6-311G** basis set. We modeled the 1:1 cocomplexation reaction of methyllithium with dimethylzinc.[28] Surprisingly we found that this reaction is endothermic (+12.40 kcal/mol) in the absence of TMEDA; however, when the diamine is introduced, then the formation of trimethylzincate [(TMEDA)LiZnMe$_3$] (**I**), where zinc displays a trigonal-planar geometry bound to three methyl ligands[29] (Scheme 5), is thermodynamically favored (−19.98 kcal/mol). The addition of a further 1 molar equiv of methyllithium and TMEDA afforded the tetraorganozincate **II** with an extra energy gain of −14.88 kcal/mol. Zincate **II** was found to be isostructural with tetramethylzincate **4**. Therefore, these results indicate that the formation of **4** when 2 equiv of methyllithium are employed in the presence of TMEDA is thermodynamically favored and contrasts with Berger's experimental findings using THF solutions, where the tetramethylzincate [Li$_2$ZnMe$_4$] is in equilibrium with [LiZnMe$_3$] and MeLi but lies strongly toward the formation of the trimethylzincate.[26] A plausible explanation for this apparent distinction could be that in a strongly coordinating bulk solvent such as THF both mixed-metal species [LiZnMe$_3$] and [Li$_2$ZnMe$_4$] would adopt structures different from those found (in the gas phase) for models **I** and **II**, possibly solvent-separated arrangements which would have different relative stabilities.

Since the dilithium−monozinc compound **4** was the only solid material isolated from the reaction of Me$_2$Zn with 1 molar equiv of MeLi, we also studied the energetics of the disproportionation reaction of two molecules of **I** to yield **II** and Me$_2$Zn (Scheme 6). This process was found to occur with 5.10 kcal/mol endothermicity. Thus, these results imply that **I** should be stable to disproportionation in the gas phase. In solution the situation must be different, as **4** is the major product detected even when the ratio of MeLi to Me$_2$Zn is 1:1. This suggests that kinetic factors, for example, slow formation of [(TMEDA)LiZnMe$_3$] coupled with the fast reaction of **I** with MeLi starting material, or solubility properties (that is, **4** is the least soluble component of the equilibrium mixture) dominate in the outcome of this reaction in solution.

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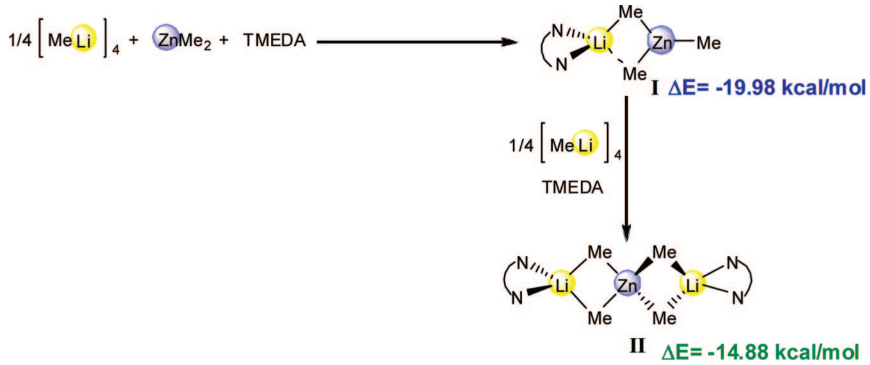
(26) Mobley, T. A.; Berger, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 3070.

(27) Weiss, E.; Wolfrum, R. *Chem. Ber.* **1968**, *101*, 35.

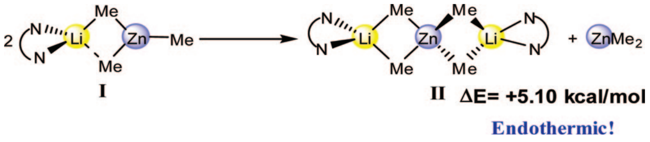
(28) The reactant methyllithium was modeled as a tetramer, since this is the structural arrangement that it exhibits in the absence of any neutral donor ligand (Weiss, E.; Hencken, G. *J. Organomet. Chem.* **1970**, *21*, 265) or even in the presence of the chelating diamine TMEDA (Köster, H.; Thoennes, D.; Weiss, E. *J. Organomet. Chem.* **1978**, 160). Dimethylzinc was modeled as a simple linear monomer: Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F *Organometallics* **1990**, *9*, 2243.

(29) A dimer derivative of **I** where Zn would be tetracoordinated (isostructural with zincate **3**) was modeled, but it was unstable and disproportionated into two molecules of **I**.

Scheme 5. Modeled DFT Cocomplexation Reactions To Yield the Triorganozincate I and Tetraanionic Zincate II



Scheme 6. Modeled DFT Disproportionation Reaction of I To Yield II



Returning to the experimental studies, the ^{1}H NMR spectrum of **4** in deuterated benzene solution shows a singlet at −0.65 ppm corresponding to the methyl groups. This chemical shift lies between those found for MeLi (−0.83 ppm) and Me_2Zn (−0.49 ppm) in the same deuterated solvent, which is indicative of the formation of a mixed-metal compound. In addition the ^{1}H NMR spectrum also shows that TMEDA remains coordinated to the lithium centers in solution.[23] The presence of lithium in **4** was confirmed by a ^{7}Li NMR experiment, which showed a sharp singlet at 1.77 ppm.

As determined by X-ray crystallography (Figure 5 and Table 1), the structure of the ion-contacted zincate **4** can be described in the same terms as for **2** and **3** as two oppositely disposed $Li(TMEDA)^+$ cations binding to the tetrahedral anion $[ZnMe_4]^{2-}$, forming two orthogonally fused heterobimetallic four-membered rings. Both rings are almost planar (sums of the internal angles 357.84 and 355.83°), and the arrangement of the three metals is slightly bent, as shown by the Li1 ⋯ Zn1 ⋯ Li2 angles (162.48(17)°). The Li−C distances in **4** (2.193(5)−2.251(5) Å) are comparable to those found in $[(LiMe \cdot THF)_4]$[20] (average bond length 2.235 Å) or in compound **2** (2.332(7) Å) and significantly shorter than in the TMP-zincate [(TMEDA)Li(TMP)(Me)Zn(Me)][21] (2.603(5) Å), where the methyl group engages in a secondary (agostic) interaction with the alkali metal. This indicates that the lithium atoms in **4** form short (strong) bonds with the methyl ligands, and this would probably retard its reactivity in comparison with other triorganozincates such as the aforementioned [(TMEDA)Li(TMP)(Me)Zn(Me)]. The Zn−C bond lengths (2.118(3)−2.143(3) Å) are slightly more elongated than those found in other methyl-based tricoordinated zincates such as [(TMEDA)Li(TMP)(Me)Zn(Me)][21] (2.032(3) and 1.995(3) Å) and $[(PMDETA)Li(Me)_2Zn(HMDS)]$[17] (2.0074(14) and 2.0361(15) Å), which can be rationalized by considering the different coordination environments (tetrahedral vs trigonal planar) of zinc in these compounds. These greater differences in values between the Li−C bond distances in comparison to those of the Zn−C bond distances illustrate the significant effect of the alkali metal in these mixed-metal reagents. Its interaction with the anion (zincate) is probably one of the dominant features in the reactivity of these compounds, since the Zn−C bonds are nearly identical but the Li−C bonds are either long (weak) or short (strong). Therefore, it could be expected that changing the alkali metal in these compounds would have a profound influence in the comparative reactivity of the zincate.

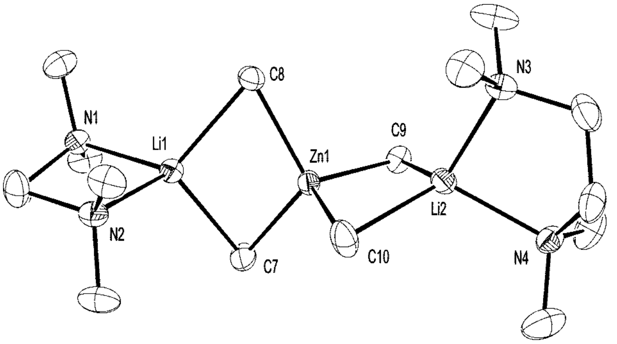


Figure 5. Molecular structure of **4** with 40% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

As previously mentioned, the structure of the unsolvated parent compound of **4** has been previously determined by Weiss[27] and described as an ionic lattice of $[ZnMe_4]^{2-}$ anions and Li^+ cations. Therefore, the addition of TMEDA destroys this lattice structure to give rise to the molecular structure of **4**, where the Li−C and Zn−C bonds are more localized and less ionic, as shown by a comparison of the bond lengths of Weiss's structure (average Li−C = 2.836 Å, Zn−C = 2.071 Å) with the those found for **4** (Li−C = 2.226 Å, Zn−C = 2.129 Å). Again the major difference occurs with the Li−C bonds, not with the Zn−C bonds.

The closest structural analogy to **4** is the tetraalkynyl complex $[(TMEDA)_2Li_2Zn(CCPh)_4]$,[13c] which presents the same kind of chain arrangement with a central pseudotetrahedral $[Zn(CCPh)_4]^{2-}$ anion and two $[Li(TMEDA)]^+$ anions which π-engage with the acetylenic carbons of the alkynyl ligands on the zinc. In addition, Weiss has also reported the structure of the related tetramethylmagnesiate $[(TMEDA)_2Li_2MgMe_4]$ (**5**),[30] which is isostructural with **4**. The average Li−C bond length in **5** (2.283 Å) is nearly identical with that in **4** (2.226 Å). With regard to the M−C bond distances in these compounds, a slight elongation is observed for the magnesiate (average Mg−C = 2.260 Å) in comparison with **4** (average Zn−C = 2.129 Å), which is probably due to the rather smaller size and greater electronegativity of zinc.[31] Zincate **4** and Weiss's magnesiate are examples that illustrate the similarities between these two metals,

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(30) Greiser, T.; Kopf, J.; Thoennes, D.; Weiss, E. *Chem. Ber.* **1981**, *114*, 209.

(31) Jensen, W. B. *J. Chem. Educ.* **2003**, *80*, 952.

(32) Armstrong, D. R.; Clegg, W.; Dale, S. H.; Graham, D. V.; Hevia, E.; Hogg, L. M.; Honeyman, G. W.; Kennedy, A. R.; Mulvey, R. E. *Chem. Commun.* **2007**, 598.

Mg and Zn. This has been previously noted not only in connection with the structures of their compounds but also in their reactivity.[32]

As alluded to earlier, Uchiyama has used the (dimethylamido)zincate [$(Me_2O)LiZn(NMe_2)Me_2$] as a theoretical model to mimic the reactivity of the well-established experimental base [(THF)LiZn(TMP)*t*Bu_2] (**1**).[9b,10a,b] Aromatic substrates such as anisole, benzonitrile, and *N*,*N*-diisopropylbenzamide can be selectively ortho-zincated in high yield by **1**. Therefore, we decided to study the reactivity of **2** with these three representative DOM (directed ortho metalation)[33] substrates. The reactions were carried out by using isolated crystals of **2** and also by mixing the homometallic components $LiNMe_2$ and Me_2Zn in neat THF solution. NMR analyses of the resulting solutions showed that no metalation had occurred in any of the reaction mixtures after 24 h at room temperature. These results suggest that under the conditions studied these highly coordinated (which would be more accurately described as tetraorgano) zincates are poor reagents for deprotonative metalation of aromatic substrates, which contrasts with their well-known selectivity in metal−halogen exchange reactions. This lack of reactivity undoubtedly, at least in part, must be due to the fact that **2** possesses significantly less basic anionic ligands than **1**. However, sterically demanding ligands such as TMP and ^tBu groups are in general unlikely to form highly coordinated zincates, as tetracoordination of zinc would be extremely disfavored due to the steric clash between the bulky ligands.

Conclusions

The new "highly coordinated" zincates **2** and **4** and the triorganozincate **3** have been prepared using different synthetic methodologies: namely, cocomplexation for **2** and **4** and metathesis for **3**. The solid-state structures of the homoleptic zincates **3** and **4** and the heteroleptic zincate **2** have been determined by X-ray crystallography and show a common motif: namely, a polymetallic chain of three members for **2** and **4** or four members for **3** with the anionic ligands (three dimethylamides and one methyl for **2**, all dimethylamide groups for **3**, and all methyl groups for **4**) in each case bridging the metals together. The triorganozincate **3** exhibits a dimeric structure where each zinc center achieves a distorted-tetrahedral geometry. This shows that the term "highly coordinated" with respect to zincates with a $M^I_2ZnR_4$ stoichiometry can be sometimes ambiguous and is better replaced by the term "tetraorgano" zincates. DFT calculations revealed that the formation of the tetramethylzincate **4** is preferred over that of the triorganozincate [$(TMEDA)LiZnMe_3$] when 2 equiv of MeLi is reacted with Me_2Zn. Preliminary studies show that the tris(amido)alkyl zincate **2** is a poor Brønsted base for metalation of functionalized aromatic substrates such as anisole, benzonitrile, and *N*,*N*-diisopropylbenzamide, which contrasts with the high reactivity previously found for related dialkyl(amido)zincates containing sterically demanding amido ligands.

Experimental Section

General Considerations. 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. *n*BuLi and Me_2Zn were purchased from Aldrich Chemicals and used as received. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ^1H, 150.32 MHz for ^7Li, and 100.62 MHz for ^{13}C. Chemical shifts are given in units of ppm. Satisfactory elemental analysis of compounds **2**−**4** could not be obtained due to their highly air and moisture sensitive nature.

Synthesis of [$(TMEDA)_2Li_2ZnMe(NMe_2)_3$] (2). To a suspension of $LiNMe_2$ (4 mmol, 0.20 g) in hexane was added Me_2Zn (2 mL of a commercial 2 M solution in toluene, 4 mmol). The resulting white suspension was sonicated for 30 min, and TMEDA (0.6 mL, 4 mmol) was then introduced, affording a pale yellow solution which was concentrated by removal of some solvent in vacuo and placed in the freezer at −28 °C. A crop of colorless crystals was deposited overnight (0.53 g, 29%: note maximum possible yield of 33%). ^1H NMR (400 MHz, 25 °C, d_8-THF): 2.65 [s, 18H, NMe_2], 2.30 [s, 8H, TMEDA CH_2], 2.16 [s, 24H, TMEDA CH_3], −1.12 [s, 2H, CH_3]. $^{13}C\{^1H\}$ NMR (100.63 MHz, 25 °C, d_8-THF): 59.13 [TMEDA CH_2], 50.89 [NMe_2], 47.23 [TMEDA CH_3], no signal for the methyl group could be detected. ^7Li NMR (155.50 MHz, C_6D_6 reference LiCl in D_2O at 0.00 pppm): 3.81.

Synthesis of [$\{(TMEDA)LiZn(NMe_2)_3\}_2$] (3). To a suspension of $LiNMe_2$ (6 mmol, 0.30 g) in hexane was added $ZnCl_2$ (2 mL of a commercial 1 M solution in diethyl ether, 2 mmol). The resulting white suspension was sonicated for 30 min, and the mixture was stirred overnight, affording a pale yellow solution and a white precipitate of LiCl. This mixture was filtered through Celite, and TMEDA (0.3 mL, 2 mmol) was then introduced, affording a pale yellow solution which was concentrated by removal of some solvent in vacuo and placed in the freezer at −28 °C. A crop of colorless crystals was deposited overnight (0.24 g, 38%). ^1H NMR (400 MHz, 25 °C, C_6D_6): 3.40 [s, 2.21H, $Li_2Zn_2(NMe_2)_6$], 3.36 [s, 1.31H, $Zn(NMe_2)_2$], 3.27 [s, 5.10H, $Li_2Zn(NMe_2)_4$], 3.20 [s, 0.4.42H, $Li_2Zn_2(NMe_2)_6$], 3.12 [s, 1.32H, $Zn(NMe_2)_2$], 2.05 [s, 12H, TMEDA CH_3], 1.84 [s, 4H, TMEDA CH_2]. $^{13}C\{^1H\}$ NMR (100.63 MHz, 25 °C, C_6D_6): 56.66 (TMEDA CH_2), 50.69 [$Li_2Zn_2(NMe_2)_6$], 50.19 [$Zn(NMe_2)_2$], 49.80 [$Li_2Zn_2(NMe_2)_6$], 49.27 [$Li_2Zn(NMe_2)_4$], 49.02 [$Zn(NMe_2)_2$], 45.13 (TMEDA CH_3). ^7Li NMR (155.50 MHz, C_6D_6 reference LiCl in D_2O at 0.00 pppm): 0.63 [$Li_2Zn_2(NMe_2)_6$], 0.52 [$Li_2Zn(NMe_2)_4$]. On addition of a substoichiometric amount of $LiNMe_2$, the following data were obtained. ^1H NMR (400 MHz, 25 °C, C_6D_6): 3.40 [s, 2.05 H, $Li_2Zn_2(NMe_2)_6$], 3.36 [s, 1.36H, $Zn(NMe_2)_2$], 3.27 [s, 7.10H, $Li_2Zn(NMe_2)_4$], 3.20 [s, 0.4.12H, $Li_2Zn_2(NMe_2)_6$], 3.12 [s, 1.21H, $Zn(NMe_2)_2$], 2.05 [s, 12H, TMEDA CH_3], 1.84 [s, 4H, TMEDA CH_2]; signals are considerably broader, suggesting that an exchange process is taking place. ^7Li NMR (155.50 MHz, C_6D_6 reference LiCl in D_2O at 0.00 pppm): 0.59 (broad).

Synthesis of [$(TMEDA)_2Li_2ZnMe_4$] (4). MeLi (4 mL of a 1 M solution in diethyl ether, 4 mmol) was added to a solution of Me_2Zn in toluene (1 mL of a 2 M solution in toluene, 2 mmol), affording a white suspension. TMEDA (0.6 mL, 4 mmol) was subsequently introduced, and the mixture was stirred for 30 min. Toluene (5 mL) was added to aid crystallization. The resulting clear solution was placed in the freezer at −28 °C. A crop of colorless crystals was deposited overnight (0.46 g, 62%). ^1H NMR (400 MHz, 25 °C, C_6D_6): 2.04 (s, 24H, TMEDA CH_3), 1.79 (s, 8H, TMEDA CH_2), −0.65 (s, 12H, CH_3). $^{13}C\{^1H\}$ NMR (100.63 MHz, 25 °C, C_6D_6): 56.25 (TMEDA CH_2), 45.38 (TMEDA CH_3), −11.13 (CH_3). ^7Li NMR (155.50 MHz, C_6D_6 reference LiCl in D_2O at 0.00 pppm): 1.77.

X-ray Crystallography. Crystal data for **2**: $C_{19}H_{53}Li_2N_7Zn$, M_r = 458.93, orthorhombic, $Pca2_1$, $a = 17.3169(4)$ Å, $b = 9.1221(3)$ Å, $c = 17.9321(6)$ Å, $V = 2832.52(15)$ Å^3, $Z = 4$, $T = 123$ K. As for **3** and **4**, data were collected on a Nonius KappaCCD diffractometer with Mo Kα radiation ($\lambda = 0.710\,73$ Å) and final

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[33] (a) For key reviews of DOM see: Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1. (b) Anctil, E.; Snieckus, V. The Directed ortho Metalation-Cross Coupling Nexus. Synthetic Methodology for Aryl-Aryl and Aryl-Heteroatom-Aryl Bonds. In *Metal-Catalyzed Cross-Coupling Reaction*, 2nd ed.; Diederich, F., de Meijere, A., Eds.; Wiley-VCH: New York, 2004; pp 761−813. (c) Hartung, C. G.; Snieckus, V. The Directed ortho Metalation Reaction. A Point of Departure for New Synthetic Aromatic Chemistry. In *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley-VCH: New York, 2002; pp 330−367.

refinement (SHELXL-97; G. M. Sheldrick, University of Göttingen, Germany) to convergence was on F^2: $R = 0.0453$ (F, 4335 observed data only) and $R_w = 0.0842$ (all 6183 data), GOF = 1.010, 295 refined parameters, residual electron density maximum and minimum 0.533 and −0.240 e Å^{-3}. Crystal data for **3**: $C_{24}H_{68}Li_2N_{10}Zn_2$, $M_r = 641.50$, monoclinic, $P2_1/a$, $a = 17.156(2)$ Å, $b = 11.9022(8)$ Å, $c = 18.1773(15)$ Å, $\beta = 95.742(9)°$, $V = 3693.0(6)$ Å^3, $Z = 4$, $T = 123$ K; 17 518 reflections collected, 5711 were unique, $R_{int} = 0.1211$. All crystals examined from multiple preparations were nonsingle; this had an adverse effect on data quality: $R = 0.0860$ (F, 2307 observed data only) and $R_w = 0.2103$ (all data), GOF = 0.856, 363 refined parameters, residual electron density maximum and minimum 1.937 and −0.468 e Å^{-3}. Crystal data for **4**: $C_{16}H_{44}Li_2N_4Zn$, $M_r = 371.80$, monoclinic, $P2_1/c$, $a = 13.2050(4)$ Å, $b = 14.9516(5)$ Å, $c = 12.0045(3)$ Å, $\beta = 94.142(2)°$, $V = 2363.93(12)$ Å^3, $Z = 4$, $T = 123$ K; 10 537 reflections collected, 5413 were unique, $R_{int} = 0.0335$; $R = 0.0413$ (F, 3655 observed data only) and $R_w = 0.0947$ (all data), GOF = 1.076, 216 refined parameters, residual electron density maximum and minimum 0.397 and −0.451 e Å^{-3}.

Acknowledgment. We thank the Royal Society (University Research Fellowship to E.H.) and the Faculty of Science, University of Strathclyde (starter grant to E.H.), for their generous sponsorship of this research and Professor R. E. Mulvey for helpful discussions.

Supporting Information Available: CIF files, figures, and tables giving crystal data, computational details, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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