Donor-Dictated Interlocking Co-Complexation Reactions of LiNHDipp with Dimethylzinc: Synthesis and Structures of New Methyl(amido)zincates

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A systematic study of the interlocking co-complexation reactions between the primary lithium amide LiNHDipp (Dipp = 2,6-diisopropylphenyl) and dimethylzinc in the presence of different donor ligands is presented which concludes that the final outcome of these reactions is largely dictated by the type of structure that is formed when the donor is coordinated to the lithium amide. When chelating diamine TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) is employed [{Li$_2$(NHDipp)$_2$(TMEDA)}$_\infty$] (**1**) is obtained, where Li$_2$N$_2$ rings are connected by TMEDA bridges generating a polymeric chain arrangement which does not form a co-complex with Me$_2$Zn even in the presence of an excess of TMEDA. The tridentate ligand PMDETA (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine) when reacted with LiNHDipp forms monomeric [(PMDETA)Li(NHDipp)](**4**) which successfully forms a mixed-metal co-complex with Me$_2$Zn affording dialkyl(amido)zincate [(PMDETA)LiZn(NHDipp)(Me)$_2$] (**2**). When the co-complexation reaction is carried out in the presence of monodentate tetrahydrofuran (THF), zincate [(THF)$_3$LiZn(NHDipp)(Me)$_2$] (**3**) is obtained which was found to partially decompose in hexane solution after long periods of time at room temperature (2 weeks) to afford the unprecedented "zinc-rich" zincate [(THF)$_3$LiZn$_2$(Me)$_3$(NHDipp)$_2$] (**5**). This compound presents a unique structure in the solid state previously unknown in organozincate chemistry with a trinuclear Li···Zn···Zn chain arrangement where the metals are connected by only two amido bridges and therefore both zinc centers exhibit trigonal planar geometries. **5** can be prepared in good yields by the rational reaction of LiNHDipp with a 2:1:3 mixture of Me$_2$Zn, NH$_2$Dipp and THF. The different solid-state structural motifs of compounds **1**, **2**, **4**, and **5** have been revealed by X-ray crystallographic studies. Multinuclear NMR (^{1}H, ^{13}C and ^{7}Li) spectroscopic data recorded in C$_6$D$_6$ solution are also reported for compounds **1**−**6**. Mixed-metal compounds **2** and **5** constitute the first examples of crystallographically characterized alkyl(amido)zincates containing a primary amide.

Introduction

Alkali-metal dialkyl(amido) zincates have recently been shown to be extremely effective and versatile reagents in organic synthesis. By combining the high reactivity typically associated with group 1 organometallic compounds with the greater selectivity of the neutral organozinc reagents, these mixed-metal reagents have proved to be highly chemo- and regioselective reagents in deprotonative metalations, allowing the direct (one-step) zincation of a wide range of aromatic substrates with a rich variety of functional groups that are often incompatible with group 1 organometallic reagents such as BuLi or LDA.[1] Among this family of bim-

etallic reagents, TMP-di-*tert*-butylzincates (TMP = 2,2,6, 6-tetramethylpiperidide) of lithium[2] and sodium[3] have shown a greater metallating (zincating) power as best illustrated by the unprecedented 2,6-dideprotonation of naphthalene[4] or the regioselective *meta*-deprotonation of dimethylaniline[5] by the base [(TMEDA)NaZn(TMP)-(*^{t}*Bu)$_2$] (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine). Amido-dialkylzincates containing other classical utility secondary amides such as diisopropylamide (DA)[6] or

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hexamethyldisilazide (HMDS)[7] have also been prepared. The reactivities and the structures of these compounds are intimately related to the nature of the amide ligand employed. Thus, for example, Kondo and Uchiyama have shown for the metalation of 3-bromopyridines by lithium di-*tert*-butyl(amido)zincates that the regioselectivity of the reaction can be controlled by switching between TMP (deprotonation at the 2-position) and DA (deprotonation at the 4-position).[8]

Usually the synthetic methodology employed to prepare these mixed-metal reagents is an interlocking co-complexation approach (Scheme 1)[6b,9] where both monometallic reagents, the alkali-metal amide and the dialkylzinc compound are combined together in the presence of a Lewis base (shown as X-X in Scheme 1) such as the chelating TMEDA, PMDETA (PMDETA = N,N,N',N'',N''-pentamethylethylenetriamine) or monodentate THF. In non-coordinating solvents, alkali-metal amides exist in their aggregated form (for example unsolvated LDA displays a single strand helical polymeric structure[10] whereas NaTMP is a cyclic trimer[11]). Thus, the presence of a Lewis donor is required to break these oligomeric forms into smaller aggregates (preferably monomers) favoring then the co-complexation reaction with the relevant R_2Zn compound.[12,13]

To date, the synthesis of dialkyl(amido)zincates has been limited to the use of secondary, sterically demanding amides and to the best of our knowledge no examples of zincates involving primary amides have been reported. Herein we report the preparation and structural elucidation of dimethyl(amido)zincates derived from the primary anilide NH_2Dipp (Dipp = 2,6-diisopropylphenyl). It can be anticipated that the participation of this primary amide will have a profound influence on the structure and in the reactivity of these new heterobimetallic compounds. The presence of a hydrogen attached to the nitrogen atom is likely to diminish their efficiency as metallating reagents (in comparison with those containing the more basic and sterically demanding secondary amides TMP or DA). On the other hand, lithiated primary amides are known to be versatile and valuable chemical intermediates, since, for example, they can behave as either amido (NHR^-) or imido (NR^{2-}) transfer agents.[14] Therefore these new zincates could be employed as precursors to prepare mixed-metal organoimido (NAr^{2-}) compounds, by the removal of the remaining hydrogen on the nitrogen.[15]

Scheme 1. Interlocking Co-Complexation Methodology to Prepare Dimethyl(amido)zincates
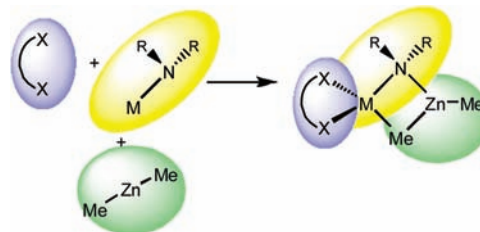
As herein reported, these novel heterobimetallic compounds were prepared by using the aforementioned interlocking co-complexation approach by combining the lithium anilide LiNHDipp with dimethylzinc in the presence of Lewis bases of increasing denticity (monodentate THF, bidentate TMEDA and tridentate PMDETA). The influence of changing the Lewis base has also been evaluated. In addition we report the synthesis and structural characterization of the unprecedented stoichiometrically unusual "zinc-rich" (1:2, Li/Zn) trialkyl-bis(amido)zincate [(THF)$_3$LiZn$_2$(Me)$_3$(NH-Dipp)$_2$] (**5**) which was obtained unexpectedly as a disproportionation product of the 1:1, Li/Zn complex [(THF)$_3$LiZn-(Me)$_2$(NHDipp)] (**3**).

Experimental Section

General Information. All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane, tetrahydrofuran (THF), and toluene were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. *n*BuLi and Me$_2$Zn, 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 ^{1}H, 150.32 MHz for ^{7}Li and 100.62 MHz for ^{13}C. Elemental analyses were carried out on a Perkin-Elmer 2400 elemental analyzer.

X-ray Crystallography. Crystallographic data were collected on Nonius KappaCCD diffractometers at 123 K for **5** and at 150 K for **1, 2,** and **4,** with Mo Kα radiation (λ = 0.71073 Å). The structures were refined by full-matrix least-squares using all unique F^2 values with programs of the SHELX family.[16] Specific crystallographic data and refinement parameters are given in Table 1. Minor disorder was resolved for THF ligands in **5**.

Experimental Section

Synthesis of [{Li$_2$(NHDipp)$_2$(TMEDA)}$_\infty$] (1). To a solution of hexane (5 mL) and 2,6-diisopropylaniline (0.35 mL, 2 mmol) was added ^{n}BuLi (1.6 M in hexane, 1.25 mL, 2 mmol), and the resulting suspension was stirred for 1 h. TMEDA (0.3 mL, 2 mmol) was then added, followed by toluene (7 mL) and gentle heating to afford a pale yellow solution. At this stage Me$_2$Zn (2 mL of a 1 M solution in heptane, 2 mmol) was introduced. The resulting solution was left to cool overnight in a Dewar with hot water. Small colorless crystals were isolated (0.309 g, yield 64%). ^{1}H NMR (400.13 MHz, 298 K, C$_6$D$_6$) δ 7.15 (4H, d, H_{meta}), 6.71 (2H, t, H_{para}), 3.22 (4H, m, CH, ^{i}Pr), 2.84 (2H, s, NH), 1.76 (12H, s, CH_3, TMEDA), 1.71 (4H, s, CH_2, TMEDA), 1.36 (24H, d, CH_3, ^{i}Pr). ^{7}Li NMR (298K, C$_6$D$_6$, reference LiCl in D$_2$O at 0.00 ppm): δ 1.88. ^{1}H NMR (400.13 MHz, 298 K, d^8-THF) δ 6.68 (4H, d, H_{meta}), 6.03 (2H, t, H_{para}), 3.22 (4H, m, CH, ^{i}Pr), 2.68 (2H, s, NH), 2.32 (4H, s, CH_2, TMEDA), 2.16 (12H, s, CH_3, TMEDA), 1.20 (24H, d, CH_3, ^{i}Pr). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, d^8-THF) δ 158.2 (C$_{ipso}$), 131.5 (C$_{ortho}$,

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Table 1. Crystallographic Data

compound	1	2	4	5
formula	$C_{30}H_{52}Li_2N_4$	$C_{23}H_{47}LiN_4Zn \cdot 0.5C_7H_8$	$C_{21}H_{41}LiN_4$	$C_{39}H_{69}LiN_2O_3Zn_2$
form wt	482.6	498.0	356.5	751.6
cryst system	triclinic	triclinic	orthorhombic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$Pbca$
a, Å	8.4634(5)	9.6061(10)	10.0117(11)	18.1783(1)
b, Å	9.1374(10)	9.8717(7)	14.6223(17)	18.6099(2)
c, Å	10.9932(7)	16.5903(17)	15.682(2)	24.4975(2)
α, deg	75.394(9)	91.976(7)	90	90
β, deg	87.935(6)	101.641(8)	90	90
γ, deg	72.640(7)	104.928(7)	90	90
V, Å^3	784.49(11)	1482.6(2)	2295.7(5)	8287.42(12
Z	1	2	4	8
D_{calcd}, g cm^{-3}	1.022	1.116	1.031	1.205
μ, mm^{-1}	0.059	0.847	0.061	1.192
T, K	150	150	150	123
cryst size, mm	$0.37 \times 0.34 \times 0.29$	$0.61 \times 0.48 \times 0.39$	$0.82 \times 0.48 \times 0.32$	$0.32 \times 0.08 \times 0.08$
reflns measd	8844	21036	8017	17290
unique reflns	2709	5171	2249	9026
R_{int}	0.029	0.033	0.030	0.024
no of params	173	323	248	439
R (F, $F^2 > 2\sigma$)	0.043	0.028	0.047	0.045
R_w (F^2, all data)	0.110	0.074	0.145	0.121
goodness of fit	1.08	1.05	0.99	1.09
max, min $\Delta\rho$, e Å^{-3}	0.20, −0.17	0.35, −0.21	0.44, −0.23	0.99, −0.39

122.2 (C_{meta}), 109.4 (C_{para}), 58.8 (CH_2, TMEDA), 46.2 (CH_3, TMEDA), 28.4 (CH, ^iPr), 23.9 (CH_3, ^iPr). ^7Li NMR (298 K, d^8-THF, reference LiCl in D_2O at 0.00 ppm): δ −0.62. Elemental analysis calcd (%) for $C_{30}H_{52}Li_2N_4$: C 74.65, H 10.85, N 11.60; found: C 74.11, H 11.03, N 11.39.

Synthesis of [(PMDETA)LiZn(NHDipp)(Me)$_2$] (2). To a solution of hexane (5 mL) and 2,6-diisopropylaniline (0.35 mL, 2 mmol) was added ^nBuLi (1.6 M in hexane, 1.25 mL, 2 mmol), and the resulting suspension was stirred for 10 min. Me_2Zn (2 mL of a 1 M solution in heptane, 2 mmol) was then added, and the reaction mixture stirred for 30 min, followed by the addition of PMDETA (0.42 mL, 2 mmol). After stirring for 2 h the precipitate was still present. Addition of toluene (6 mL) and gentle heating afforded a yellow solution, which was placed in the fridge (0 °C) and left overnight. Small colorless crystals were isolated (0.550 g, yield 61%). ^1H NMR (400.13 MHz, 298 K, C_6D_6) δ 7.15 (2H, d, H_{meta}), 6.79 (1H, t, H_{para}), 3.45 (2H, m, CH, ^iPr), 2.84 (1H, s, NH), 2.14 (3H, s, NCH_3, PMDETA), 1.72 (20H, bs, CH_3 and CH_2, PMDETA), 1.38 (12H, d, CH_3, ^iPr), −0.32 (6H, s, Zn-(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, C_6D_6) δ 154.5 (C_{ipso}), 134.1 (C_{ortho}), 122.8 (C_{meta}), 114.2 (C_{para}), 57.1, 53.2 (CH_2, PMDETA), 45.7 (N(CH_3)$_2$, PMDETA), 44.7 (N(CH_3), PMDETA), 27.9 (CH, ^iPr), 24.5 (CH_3, ^iPr), −8.1 (Zn(CH_3)$_2$). ^7Li NMR (298 K, C_6D_6, reference LiCl in D_2O at 0.00 ppm): δ 0.77. Elemental analysis calcd (%) for $C_{23}H_{47}LiN_4Zn$: C 61.12, H 10.48, N 12.40; found: C 61.41, H 10.80, N 12.33.

Synthesis of [(THF)$_3$LiZn(NHDipp)(Me)$_2$] (3). To a solution of hexane (5 mL) and 2,6-diisopropylaniline (0.35 mL, 2 mmol) was added ^nBuLi (1.6 M in hexane, 1.25 mL, 2 mmol), and the resulting suspension was stirred for 10 min. Me_2Zn (2 mL of a 1 M solution in heptane, 2 mmol) was then added, and the reaction mixture stirred for 30 min, followed by the addition of THF (0.49 mL, 6 mmol), to give an oil, which remained even after addition of toluene (1 mL) and gentle heating. The Schlenk tube was placed in the freezer (−20 °C) and left for several days. A batch of colorless crystals was isolated (0.43 g, yield 43%). ^1H NMR (400.13 MHz, 298 K, C_6D_6) δ 7.14 (2H, d, H_{meta}), 6.75 (1H, t, H_{para}), 3.39 (2H, m, CH, ^iPr), 3.38 (12H, m, OCH_2, THF), 2.86 (1H, s, NH), 1.42 (12H, d, CH_3, ^iPr), 1.39 (12H, m, CH_2, THF), −0.42 (6H, s, Zn(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, C_6D_6) δ 154.2 (C_{ipso}), 134.8 (C_{ortho}), 123.3 (C_{meta}), 116.2 (C_{para}), 68.1 (OCH_2, THF), 28.5 (CH, ^iPr), 25.4 (CH_2, THF), 24.2 (CH_3, ^iPr), −9.0 (Zn(CH_3)$_2$). ^7Li NMR (298 K, C_6D_6, reference LiCl in D_2O at 0.00 ppm): δ

1.01. Satisfactory elemental analysis of this compound could not be obtained because of its highly air and moisture sensitive nature.

Synthesis of [(PMDETA)Li(NHDipp)] (4). To a solution of hexane (5 mL) and 2,6-diisopropylaniline (0.35 mL, 2 mmol) was added ^nBuLi (1.6 M in hexane, 1.25 mL, 2 mmol), and the resulting suspension was stirred for 10 min. PMDETA (0.42 mL, 2 mmol) was then added affording a pale yellow solution which deposited colorless crystals when placed in the freezer (−20 °C) and left overnight (0.564 g, yield 79%). ^1H NMR (400.13 MHz, 298 K, C_6D_6) δ 7.29(2H, d, H_{meta}), 6.66 (1H, t, H_{para}), 3.34 (2H, m, CH, ^iPr), 3.09 (1H, s, NH), 2.09 (3H, s, NCH_3, PMDETA), 1.89 (12H, bs, CH_3 PMDETA), 1.72 (8H, bs, CH_2, PMDETA), 1.54 (12H, d, CH_3, ^iPr). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, C_6D_6) δ 159.4 (C_{ipso}), 131.3 (C_{ortho}), 122.3 (C_{meta}), 105.9 (C_{para}), 57.2, 53.4 (CH_2, PMDETA), 45.7 (N(CH_3)$_2$, PMDETA), 44.2 (N(CH_3), PMDETA), 29.0 (CH, ^iPr), 24.1 (CH_3, ^iPr). ^7Li NMR (298 K, C_6D_6, reference LiCl in D_2O at 0.00 ppm): δ 1.47. Elemental analysis calcd (%) for $C_{21}H_{41}LiN_4$: C 70.75, H 11.59, N 15.72; found: C 70.21, H 11.64, N 15.10.

Synthesis of [(THF)$_3$LiZn$_2$(Me)$_3$(NHDipp)$_2$] (5). To a solution of hexane (8 mL) and 2,6-diisopropylaniline (0.35 mL, 2 mmol) was added ^nBuLi (1.6 M in hexane, 1.25 mL, 2 mmol), and the resulting suspension was stirred for 10 min. Me_2Zn (4 mL of a 1 M solution in heptane, 4 mmol) was then added, and the reaction mixture stirred for 20 min. A second equivalent of 2,6-diisopropylaniline (0.35 mL, 2 mmol) was added, and the suspension stirred for a further 20 min, followed by the addition of THF (0.49 mL, 6 mmol) to give a white precipitate. The reaction mixture was then refluxed for 2 h to give a colorless solution, which on cooling to room temperature gave an oil. The Schlenk tube was placed in the freezer (−20 °C) and left overnight. A white microcrystalline solid was isolated (0.856 g, yield 57%). ^1H NMR (400.13 MHz, 298 K, C_6D_6) δ 7.12 (4H, d, H_{meta}), 6.83 (2H, t, H_{para}), 3.31 (4H, m, CH, ^iPr), 3.29 (12H, m, OCH_2, THF), 3.08 (2H, bs, NH), 1.35 (24H, d, CH_3, ^iPr), 1.26 (12H, m, CH_2, THF), −0.43 (9H, s, Zn(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, C_6D_6) δ 154.5 (C_{ipso}), 134.8 (C_{ortho}), 123.3 (C_{meta}), 116.6 (C_{para}), 68.1 (OCH_2, THF), 28.5 (CH, ^iPr), 25.4 (CH_2, THF), 24.3 (CH_3, ^iPr), −9.1 (Zn(CH_3)$_2$). ^7Li NMR (298 K, C_6D_6, reference LiCl in D_2O at 0.00 ppm): δ 1.07. Elemental analysis calcd (%) for $C_{39}H_{69}LiN_2O_3Zn_2$: C 62.31, H 9.25, N 3.72; found: C 62.28, H 9.60, N 3.91.

Scheme 2
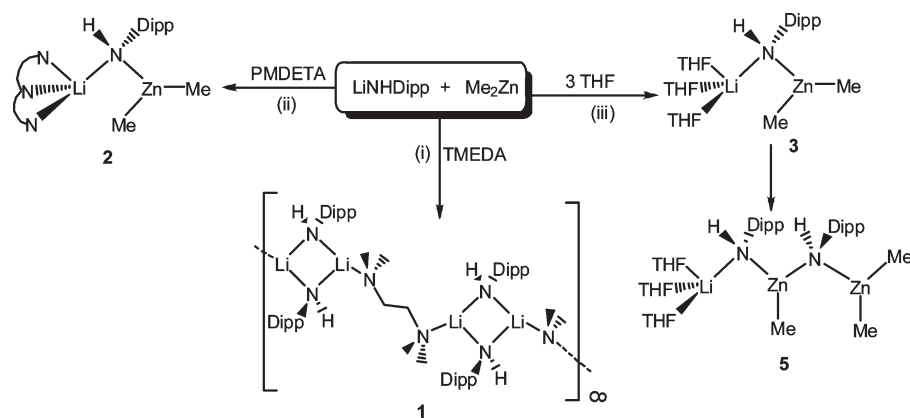
Table 2. Selected Chemical Shifts in the ^{1}H and ^{7}Li NMR Spectra in C_6D_6 Solution

compound	$\delta(^1H)_{NH}$	$\delta(^1H)^i_{Pr}$	$\delta(^1H)_{Ar}$	$\delta(^1H)_{Zn-Me}$	$\delta(^7Li)$
NH$_2$Dipp	3.26	2.67, 1.16	7.03, 6.85		
[{Li$_2$(NHDipp)$_2$(TMEDA)}$_\infty$] (**1**)	2.84	3.22, 1.36	7.15, 6.71		1.88
[(PMDETA)LiZn(NHDipp)(Me)$_2$] (**2**)	2.84	3.45, 1.38	7.16, 6.79	−0.32	0.77
[(THF)$_3$LiZn(NHDipp)(Me)$_2$] (**3**)	2.86	3.39, 1.39,	7.14, 6.75	−0.42	1.01
[(PMDETA)Li(NHDipp)] (**4**)	3.09	3.34, 1.54	7.29, 6.66		1.47
[(THF)$_3$LiZn$_2$(Me)$_3$(NHDipp)$_2$] (**5**)	3.08	3.31, 1.35	7.12, 6.83	−0.43	1.07

Synthesis of [(THF)LiZn(NHDipp)$_2$Me] (6). Isolated crystals of [(THF)$_3$LiZn$_2$(Me)$_3$(NHDipp)$_2$] (**5**) (0.751 g, 1 mmol) were dissolved in toluene (10 mL) affording a colorless solution which was stirred at room temperature for 10 min. Volatiles were removed under vacuum affording a colorless oil which was characterized by multinuclear NMR (^{1}H, ^{13}C and ^{7}Li) spectroscopy. ^{1}H NMR (400.13 MHz, 298 K, C$_6$D$_6$) δ 7.06 (4H, d, H_{meta}), 6.84 (2H, t, H_{para}), 3.35 (4H, bs, CH, ^{i}Pr), 3.18 (2H, bs, NH), 2.85 (4H, m, OCH_2, THF), 1.32 (24H, bs, CH_3, ^{i}Pr), 0.98 (4H, m, CH_2, THF), −0.38 (3H, s, Zn(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, C$_6$D$_6$) δ 1.49.5 (C$_{ipso}$), 135.4 (C$_{ortho}$), 123.5 (C$_{meta}$), 118.0 (C$_{para}$), 68.2 (OCH$_2$, THF), 28.9 (CH, ^{i}Pr), 25.0 (CH$_3$, ^{i}Pr), 24.1 (CH$_2$, THF), −12.7 (Zn(CH$_3$)$_2$). ^{7}Li NMR (298 K, C$_6$D$_6$, reference LiCl in D$_2$O at 0.00 ppm): δ 1.40.

Results and Discussion

The synthetic methodology employed in the preparation of the new lithium alkyl(amido)zincates is depicted in Scheme 2. The lithium amide was prepared in situ by reaction of equimolar amounts of ^{n}BuLi and freshly distilled amine NH$_2$Dipp in hexane at 0 °C, forming a white precipitate. To this suspension a solution of dimethylzinc in hexane was added and then the stoichiometric amount of the relevant donor [(i) TMEDA; (ii) PMDETA, (iii) 3 equiv of THF] was added to afford pale yellow solutions which on cooling deposited colorless crystals of the TMEDA-solvated lithium amide [{Li$_2$(NHDipp)$_2$(TMEDA)}$_\infty$] (**1**), the dimethyl (anilido)zincates [(PMDETA)LiZn(NHDipp)(Me)$_2$] (**2**) and [(THF)$_3$LiZn(NHDipp)(Me)$_2$] (**3**) respectively in good isolated yields (56−79%). These new compounds were characterized in solution using multinuclear NMR spectroscopy (^{1}H, ^{13}C, and ^{7}Li) and the structures in the solid state for **1** and **2** were elucidated by X-ray crystallography.

Initially the formation of a homogeneous solution on the addition of TMEDA to the insoluble mixture of LiNHDipp and dimethylzinc in hexane seemed to indicate the formation of a mixed-metal compound. However, ^{1}H and ^{13}C NMR

analysis of the crystals formed from this solution in deuterated benzene solution showed the absence of any signal attributable to the methyl groups from dimethylzinc. Thus, the ^{1}H NMR spectrum showed the relevant signals for the amide fragment [a doublet at 7.15 ppm and a triplet at 6.71 ppm for the aromatic protons, a multiplet at 3.22 ppm and a doublet at 1.35 ppm for the ^{i}Pr groups and a broad singlet at 2.84 ppm for the NH] and coordinated TMEDA [1.76 for methyl groups and 1.71 ppm for the CH$_2$ groups] in a ratio of 2:1 (Table 2). The monometallic constitution of **1** was confirmed when its structure was determined by X-ray crystallography (Figure 1).

The structure of compound **1** is based on (LiN)$_2$ four-membered ring dimers linked by monodentate bridging (non-chelating) TMEDA ligands affording a polymeric chain arrangement. The lithium atoms display a distorted trigonal planar geometry (sum of the bond angles around Li: 359.55°), bonding to three nitrogens, two from the anilido ligands and one from the TMEDA. For each (LiN)$_2$ dimer the hydrogen atoms of the amido ligands (and concomitantly the substituted aryl substituents) lie transoid to each other relative to the Li⋯Li vector, probably to minimize the steric repulsions within the four-membered ring. This polymeric structure contrasts with the only previous example of a lithium anilide solvated by TMEDA, namely [Li(NHAr)(TMEDA)] (Ar = 2,4,6-^{t}Bu$_3$-C$_6$H$_2$),[17] where the diamine binds to lithium in a chelating fashion, but it bears close resemblance to the TMEDA-solvated structure of LDA reported by Williard made up of cyclic dimers of (LiDA)$_2$ connected by bridging (non-chelating) TMEDA generating an infinite chain.[18]

Compound **1** can be obtained as a crystalline solid in reasonable isolated yields (63−68%). NMR analysis of the filtrate revealed the co-product of the reaction to be Me$_2$Zn.

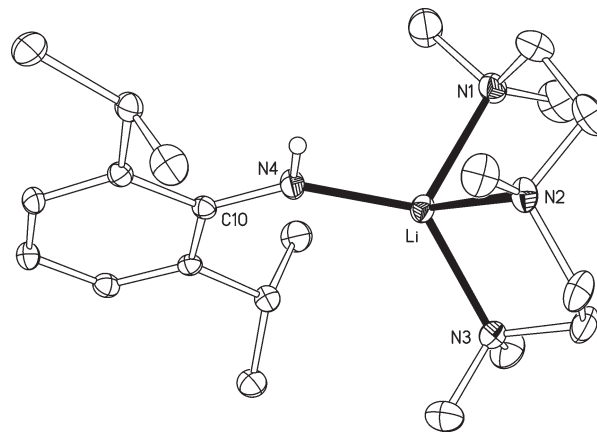(17) Fjeldberg, T.; Hitchcock, P. B.; Lappert, M. F.; Thorne, A. J. *Chem. Commun.* **1984**, 822.
(18) Bernstein, M. P.; Romesberg, F. E.; Fuller, D. J.; Harrison, A. T.; Collum, D. B.; Liu, Q-Y.; Williard, P. G. *J. Am. Chem. Soc.* **1992**, *114*, 5100.
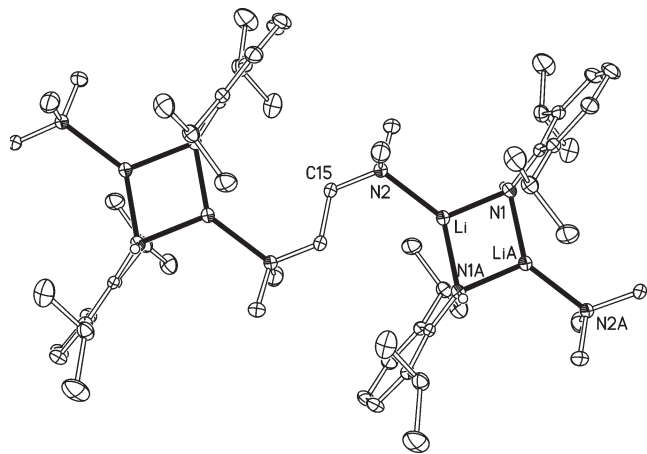
Figure 1. Section of the extended chain structure of **1** with 30% probability displacement ellipsoids. Hydrogen atoms, except for N−H, are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Li−N1 1.976(2), Li−N1A 2.000(2), Li−N2 2.080(2), N1−Li−N1A 103.00(10), N1−Li−N2 120.59(12), N1A−Li−N2 135.96(12), Li−N1−LiA 77.00(10), Li−N2−C15 117.83(10). Symmetry operation A: $1 - x$, $-y$, $1 - z$.

TMEDA (as confirmed by the presence of a singlet at −0.57 ppm in the ^{1}H NMR spectrum in deuterated benzene solution).[19] These results indicate that, although the addition of TMEDA to unsolvated LiNHDipp breaks its oligomeric/polymeric ladder structure forming the hexane-soluble TMEDA-solvated compound **1**, the degree of aggregation of the latter is still too high to favor the formation of the mixed-metal compound by co-complexation with Me$_2$Zn. Surprisingly, even when an excess of TMEDA (3 equiv) is employed, compound **1** is still obtained, which shows the high stability of this polymeric arrangement and its low tendency to cleave into smaller aggregated forms. In part this reflects the excellent bridging ability of the sterically little demanding electron-rich primary amido ligand.

We next endeavored to study the co-complexation of LiNHDipp and Me$_2$Zn using the tridentate donor PMDETA. From the previous results when TMEDA was employed, the degree of aggregation of the lithium amide after the addition of the Lewis base appears to play a crucial role in determining whether the co-complexation reaction will take place. In general, the number of reported lithium anilide structures is relatively small, and there is only one documented example of a PMDETA complex. Reported by Mulvey, [(PMDETA)$_2$Li$_3$(NHPh)$_3$][20] exhibits an unusual trinuclear arrangement combining three-, four- and five-coordinated lithium centers. Since NH$_2$Dipp is much more sterically demanding than unsubstituted NH$_2$Ph it can be anticipated that the relevant lithiated amine solvated by PMDETA will present an even smaller oligomeric form. Thus, when 1 molar equiv of PMDETA was added to a suspension of LiNHDipp in hexane a colorless solution was obtained which deposited colorless crystals overnight of the desired complex [(PMDETA)Li(NHDipp)](**4**). NMR (^{1}H, ^{13}C and ^{7}Li) analysis of **4** revealed the formation of a complex with a PMDETA:NHDipp ratio of 1:1. The molecular structure of **4** was

(19) Graham, D. V.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E. *Organometallics* **2006**, *25*, 3297.
(20) Barr, D.; Clegg, W.; Cowton, L.; Horsburgh, L.; Mackenzie, F. M.; Mulvey, R. E. *Chem. Commun.* **1995**, 891.

Figure 2. Molecular structure of **4** with 30% probability displacement ellipsoids. Hydrogen atoms, except for N−H, are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Li−N1 2.230(5), Li−N2 2.170(5), Li−N3 2.174(5), Li−N4 1.953(5), N1−Li−N2 84.01(18), N1−Li−N3 114.1(2), N1−Li−N4 112.4(2), N2−Li−N3 85.16(19), N3−Li−N4 130.8(3), N2−Li−N4 114.8(2), Li−N4−C10 147.6(3).

established through an X-ray crystallographic study (Figure 2).

Contrasting with the polymeric structure of **1**, a simple monomeric arrangement was revealed for **4**, made up by a distorted tetrahedral lithium center (average angle subtended at Li, 106.87°) which binds to four nitrogen atoms, one from the amide ligand NHDipp and three from the chelating triamine PMDETA. The Li−N$_{amide}$ bond length [1.953(5) Å] is significantly shorter than those found for the dative Li−N$_{PMDETA}$ bonds [average Li−N bond length, 2.191 Å] and slightly shorter than that found for the Li−N$_{amide}$ in the TMEDA-adduct **1** [1.976(5) Å]. The only precedent for a structurally defined monomeric lithium anilide is the aforementioned TMEDA-solvate [Li(NHAr)(TMEDA)] (Ar = 2,4,6-^{t}Bu$_3$-C$_6$H$_2$)[17] where the lithium center is tricoordinated in a distorted trigonal planar geometry, forming a stronger (shorter) bond with the nitrogen atom of the amide ligand [1.895(8) Å] as a consequence of the decrease in the coordination number of the metal center in comparison to that in **4**.

Next we considered the reaction of **4** (prepared in situ) with 1 molar equiv of dimethylzinc. This afforded the heterobimetallic complex [(PMDETA)LiZn(NHDipp)(Me)$_2$] (**2**) as a crystalline solid in an isolated yield of 65%. Multinuclear NMR (^{1}H, ^{13}C and ^{7}Li) analysis (see Table 2 and Experimental Section) of these crystals proved unambiguously the mixed-metal constitution of **2**. Thus, for example the ^{1}H NMR spectrum of **2** in deuterated benzene solution showed a singlet at −0.32 ppm for the methyl groups which appears at a similar chemical shift to unsolvated dimethyl zinc in the same deuterated solvent (−0.52 ppm). In addition, as indicated in Table 2, the ^{1}H NMR spectrum of **2** also showed a significant change in the chemical shifts of the relevant signals of the NHDipp anion (7.16, 6.79, 3.45, 2.84, and 1.38 ppm) in comparison with those found for the homometallic PMDETA-lithium amide **4** (7.29, 6.66, 3.34, 3.09, and 1.54 ppm). Furthermore the ^{7}Li NMR spectrum of **2** revealed a singlet at 0.77 ppm, which is considerably different from that observed for **4** (1.47 ppm). Compound **2** was also subjected to an X-ray crystallographic study which established its molecular structure (Figure 3). Unlike the majority of the lithium dialkylamidozincates previously structurally characterized which exhibit a closed four-membered [LiNZnC] motif,[7b,19]
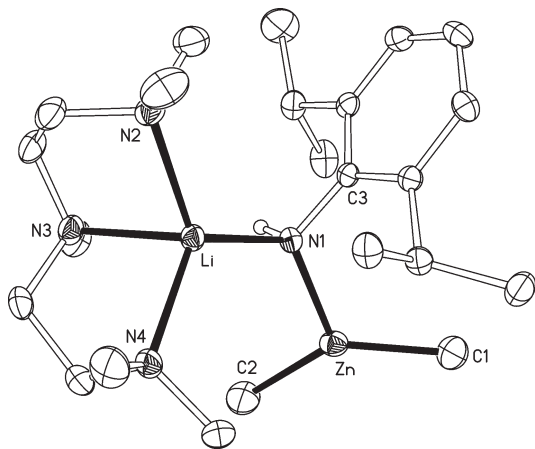
Figure 3. Molecular structure of **2** with 30% probability displacement ellipsoids. Hydrogen atoms, except for N–H, are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Zn–C1 1.984(2), Zn–C2 1.999(2), Zn–N1 2.0869(13), Li–N1 2.055(3), Li–N2 2.220(3), Li–N3 2.152(3), Li–N4 2.149(3), Li···C2 4.230(3), C1–Zn–C2 136.04(9), C1–Zn–N1 114.55(7), C2–Zn–N1 108.97(7), N1–Li–N2 121.88(13), N1–Li–N3 114.24(13), N1–Li–N4 118.23(13), N2–Li–N3 84.48(11), N3–Li–N4 87.72(11), N2–Li–N4 116.94(12), Li–N1–C3 110.96(12).

2 presents an open arrangement where both metals are connected by an amido NHDipp bridge, the span lengths of which are similar [Li–N1 2.055(3) Å, Zn–N1 2.0869(13) Å]. Both methyl groups are bonded solely to zinc, one at a modestly elongated distance compared with the other [Zn–C2 1.999(2), Zn–C1 1.984(2) Å]. The lithium center adopts a distorted tetrahedral geometry (average angle around Li 107.24°) by bonding to the tridentate amine PMDETA and the amido ligand NHDipp, in an almost identical fashion to that in homometallic **4**. While the Li–N_{PMDETA} bond lengths in **2** [average Li–N bond length, 2.173 Å] are similar to those found in **4**, the Li–N $_{amide}$ bond in **2** [2.055 Å] is remarkably longer [for **4**, Li–N_{amide}: 1.953(5) Å]. This can be rationalized in terms of the change in the coordination mode of the amido ligand which is now also bonded to zinc and this also affects the value of the Li–N_{amide}–C bond angle which becomes substantially more acute [110.96(12)° in **2**, 147.6(3)° in **4**]. As previously mentioned, no interaction is observed between the lithium center and either of the methyl groups [closest Li···C separation 4.230(3) Å].[21] This distance is too long even to suggest any type of secondary agostic interaction. This open structural motif is reminiscent of that previously reported by us for the related HMDS-lithium zincate [(PMDETA)LiZn-(HMDS)(Me)$_2$],[7b] although in this case the amide occupies a terminal position, solely bonded to zinc, and both metals are connected by a single methyl bridge. This is probably due to the dramatic increase in the steric bulk in the amide, since in HMDS the nitrogen atom is bonded to two bulky trimethylsilyl groups.

We subsequently investigated the co-complexation reaction of Me$_2$Zn with LiNHDipp using the monodentate Lewis base THF. Thus, when both monometallic reagents were combined in hexane in the presence of 4 molar equiv of the cyclic ether a colorless solution was obtained which deposited colorless crystals of the lithium zincate [(THF)$_3$LiZn-(NHDipp)(Me)$_2$] (**3**) at −20 °C. This compound is extremely

soluble in hexane at room temperature, and so far attempts to determine its structure in the solid state by X-ray crystallography have been unsuccessful. That notwithstanding, its constitution could be unequivocally determined by a combination of ^{1}H, ^{13}C, and ^{7}Li NMR spectroscopic studies (see Experimental Section and Table 2). The presence of lithium was confirmed by a singlet (1.01 ppm) in the ^{7}Li NMR spectrum of **3** in deuterated benzene solution. Its ^{1}H NMR spectrum revealed a singlet at −0.42 ppm for the methyl groups attached to zinc, the relevant signals for the amido group (7.14, 6.75, 3.39, 2.86, and 1.39 ppm) at similar chemical shifts to those found for the related zincate **2** and sufficiently different from those observed for the THF-solvated lithium amide (7.16, 6.61, 3.38, 2.79, and 1.40 ppm). In addition, the ^{1}H NMR spectrum showed two multiplets at 3.28 and 1.30 ppm corresponding to the THF molecules, and an integration ratio of 3:2:1 with respect to the THF/Me/NHDipp ligands. When a solution of **3** in hexane was left at room temperature for 2 weeks it deposited colorless crystals which displayed a much lower solubility than the initial crystals of **3** obtained when the solution of hexane was placed in the freezer (−20 °C). An X-ray crystallographic determination revealed that these crystals have the unprecedented constitution monolithium-dizinc trialkyl-bis(amido) zincate [(THF)$_3$LiZn$_2$(Me)$_3$(NHDipp)$_2$] (**5**). This compound has a unique contacted ion pair structure with a trinuclear Li···Zn···Zn chain where the metals are connected exclusively by the amido ligands while the methyl groups bond terminally to the zinc centers. The stoichiometry of this "zinc-rich" compound (1Li:2Zn:5R, R = monoanionic ligand) contrasts markedly with those found in previously reported synthetic useful triorganozincates (1Li:1Zn:3R) and lithium-rich tetraorganozincates (2Li:1Zn:4R).[22] Tetraorganozincates are closely related to **5** since they are also trinuclear compounds.[23] However, unlike **5**, they usually exhibit near-linear Li···Zn···Li arrangements, as for example in [Li$_2$ZnMe$_4$] [Li···Zn···Li, 162.48(17)°][23] and [(TMEDA)$_2$-Li$_2$Zn(C≡CPh)$_4$] [Li···Zn···Li, 146.70°],[24] and each anionic ligand acts as a bridge between two metals; thus, the zinc center bonds to four anionic ligands in a distorted tetrahedral environment. In **5**, the arrangement Li···Zn···Zn is significantly distorted from linearity [Li···Zn···Zn, 115.7(2)°]; in addition each zinc center displays a trigonal planar geometry, bonded to two bridging amido ligands and a terminal methyl group for Zn1 located in the center of the chain and bonded to one bridging amido ligand and two terminal methyl groups for terminal Zn2 (Figure 4). The trinuclear arrangement is completed by a distorted tetrahedral lithium atom, which lies almost coplanar with the N1–Zn1–N2 plane [Li1–N1–Zn1–N2, 175.4 (2)°] and binds to three THF molecules and the amide ligand bonded to Zn1, but shows no interaction with Zn2. The Zn1–N bond lengths [Zn1–N1 2.021(2) Å, Zn1–N2 2.008(3) Å] are similar to those found in the related dimethyl(amido)zincate **3** [Zn–N, 2.0869(13) Å] and in the zinc alkyl amido compound [{(Me$_3$SiCH$_2$)Zn(NHdipp)}$_2$] (average Zn–N bond length,

(21) This Li–C separation distance is markedly longer than that found in , for example, [(LiMe.THF)$_4$] (average bond length, 2.235 Å), see: Ogle, C. A.; Huckabee, B. K.; Johnson, H. C., IV; Sims, P. F.; Winslow, S. D.; Pinkerton, A. A. *Organometallics*, **1993**, *12*, 1960.

(22) For recent applications of tetraorganozincates in organic synthesis see: Furuyama, T.; Yonehara, M.; Arimoto, S.; Kobayashi, M.; Matsumoto, Y.; Uchiyama, M. *Chem.—Eur. J.* **2008**, *11*, 10348.

(23) Armstrong, D. R.; Dougan, C.; Graham, D. V.; Hevia, E.; Kennedy, A. R. *Organometallics* **2008**, *27*, 6063.

(24) Edwards, A. J.; Fallaize, A.; Raithby, P. R.; Rennie, M. A.; Steiner, A.; Verhorevoort, K. L.; Wright, D. S. *Dalton Trans.* **1996**, 133.
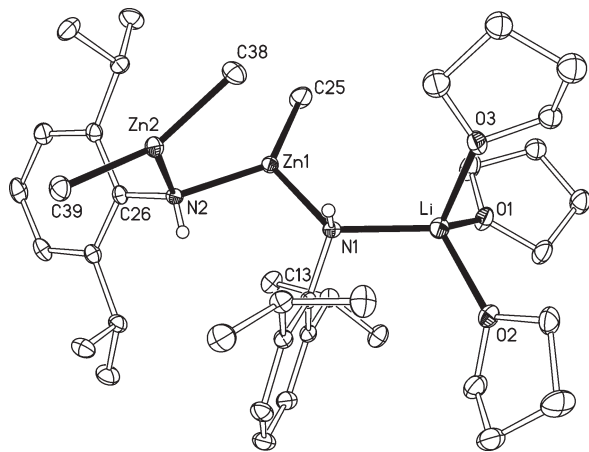
Figure 4. Molecular structure of **5** with 30% probability displacement ellipsoids. Hydrogen atoms, except for N−H, and minor disorder components are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Li−N1 2.074(6), Zn1−N1 2.021(2), Zn1−C25 1.969(3), Zn1−N2 2.008(3), Zn2−N2 2.139(3), Zn2−C38 1.989(3), Zn2−C39 1.983(3), Li−O1 1.961(6), Li−O2 2.007(6), Li−O3 1.967(6), Li⋯C25 4.275(12), Li−N1−Zn1 122.0(2), N1−Zn1−C25 125.79(13), C25−Zn1−N2 131.66(13), N2−Zn1−N1 102.45(10), Zn1−N2−Zn2 101.31(11), C39−Zn2−C38 140.31(14), C38−Zn2−N2 109.11(12), C39−Zn2−N2 110.58(12).

2.035 Å).[25] Remarkably, the interaction of the terminal zinc (Zn2), which lies almost perpendicular to the N1−Zn−N2 plane [N1−Zn1−N2−Zn2, 78.72(12)°], with the bridging amido ligand is significantly weaker as shown by the elongated Zn2−N2 bond [2.139(3) Å]. Closer literature analogs, in terms of stoichiometry, to this novel structural motif are the cyclopentadienyl sodium zincate [{Na-(THF)$_6$}$^+$ {Zn$_2$Cp$_5$}$^-$][26] which exhibits a solvent-separated ion pair structure and the bimetallic lithium bis(zinc) diamide [(Et$_2$O)Li(μ-L)Zn(μ-L)Zn(LH)] where L is the bidentate 1,2-benzenebis(neopentylamido) ligand and each metal exhibits a distorted tetrahedral geometry.[27]

Compound **5** was also characterized in solution using multinuclear NMR (^{1}H, ^{13}C and ^{7}Li) spectroscopy (Table 2 and Experimental Section). The ^{1}H NMR spectrum in deuterated benzene solution showed the presence of a single resonance for the methyl groups (−0.43 ppm) and only one set of signals for the amido groups (7.12, 6.83, 3.36, 3.08, and 1.35 ppm) whose integration indicated a 3:2, Me/NHDipp ratio. In addition these resonances were remarkably broader than those found for the related compounds **2** and **3** that also contain the same set of alkyl and amido ligands. The ^{1}H NMR spectrum also displayed two multiplets at 3.27 and 1.26 ppm corresponding to three molecules of coordinated THF. The ^{13}C{^{1}H} NMR spectrum showed a broad signal at −9.09 ppm for the methyl groups and, as observed in the ^{1}H NMR spectrum the resonances related to the amido ligand were also broad. Furthermore, a single signal at 1.07 ppm was observed in the ^{7}Li NMR spectrum. Considering the structure of **5** in the solid state there are two different amido groups (one that connects Li and one of the Zn centers, and another that connects the two zinc atoms) and also two different types of methyl groups; thus one would expect to
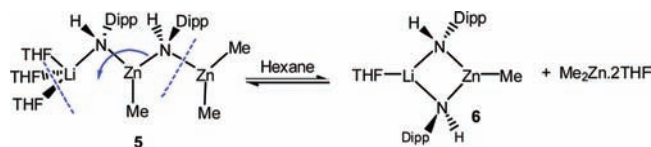
observe two different signals for both of these types of anionic ligand. Thus, the NMR analysis of **5** in deuterated benzene suggests that, in solution, there must be a dynamic process taking place which interconverts the two different types of methyl and amido groups. Such a possibility would explain the broad appearance of the signals observed in the ^{1}H and ^{13}C{H} NMR spectra. A possible process would involve the cleavage of the Zn−N bond of the zinc center that is bonded to two methyl groups. As previously mentioned, in the analysis of its molecular structure, in the solid state this Zn−N bond is considerably elongated (implying weakness) in comparison with the Zn−N bond lengths of the other zinc center. If this Zn−N bond was breaking/reforming fast in solution it should lead to a dynamic equilibrium in solution between **5** and the methyl(bis-amido) lithium zincate [LiZn-(NHDipp)$_2$Me] and Me$_2$Zn (Scheme 3).[28] This hypothesis is strongly supported by the fact that the NMR analysis of the solid residue obtained after dissolving crystals of **5** in toluene and then removing the solvent under vacuum proved to be the monolithium-monozinc zincate [(THF)-LiZn(NHDipp)$_2$Me] (**6**). Thus, its ^{1}H NMR shows a singlet at −0.38 ppm for the Zn-Me group, the integration of which with respect to the amido ligand NHdipp (which appears now at 7.06, 6.84, 3.34, 3.18, and 1.32 ppm) has changed to 1:2. In addition, only one molecule of coordinated THF (at 2.85 and 0.98 ppm) is present in the mixed metal compound and the ^{7}Li NMR spectrum exhibits only a singlet at 1.40 ppm. The formation of **6** can be rationalized in terms of the high volatility of dimethylzinc; thus, it will be removed under vacuum at the same time as the solvent, which will then push the equilibrium depicted in Scheme 3 toward the right-hand side and the formation of **6**.

Regarding the unexpected formation of **5**, a reasonable assumption would be that compound **3** partially decomposes when dissolved in hexane solution and stored at room temperature for long periods of time. A plausible formation pathway shown in Scheme 4 involves the dimerization of two molecules of **3**. Previously we have demonstrated that by reducing the steric bulk in secondary amides, alkyl(amido) zincates tend to adopt structures where the zinc centers are tetracoordinated.[23] Thus, the formation of the putative intermediate shown in brackets in Scheme 4 is plausible since NHDipp, which is a primary amide, is much less sterically demanding than, for example, TMP or DA. This dimeric intermediate could then undergo elimination of MeLi·3THF to yield **5**.[29] NMR analysis of the filtrate of the solution

Scheme 3

(25) Olmstead, M. M.; Grigsby, W. J.; Chacon, D. R.; Hascall, T.; Power, P. P. *Inorg. Chim. Acta* **1996**, *251*, 273.
(26) Alvarez, E.; Grirrane, A.; Resa, I.; del Rio, D.; Rodríguez, A.; Carmona, E. *Angew. Chem., Int. Ed.* **2007**, *46*, 1296.
(27) Hitchcok, P. B.; Lappert, M. F.; Wei, X.-H. *Dalton Trans.* **2006**, 1181.

(28) The presence of a dynamic process in solution was confirmed by a variable temperature NMR study, which shows that the relevant resonance for the methyl groups of **5** (at −0.33 ppm at T = 300 K in deuterated toluene) splits into two singlets (at 0.15 and 0.05 ppm, relative integration 2:1) when the temperature is decreased to 208 K.
(29) To study if the conversion of **5** into **3** is reversible, isolated crystals of **5** and one molar equiv of MeLi·3THF were dissolved in C$_6$D$_6$ solution. ^{1}H and ^{7}Li NMR revealed that instead of compound **3**, this reaction formed a mixture of [(THF)LiZn(NHDipp)$_2$Me](**6**) and homoleptic [(THF)$_2$LiZnMe$_3$].

Scheme 4
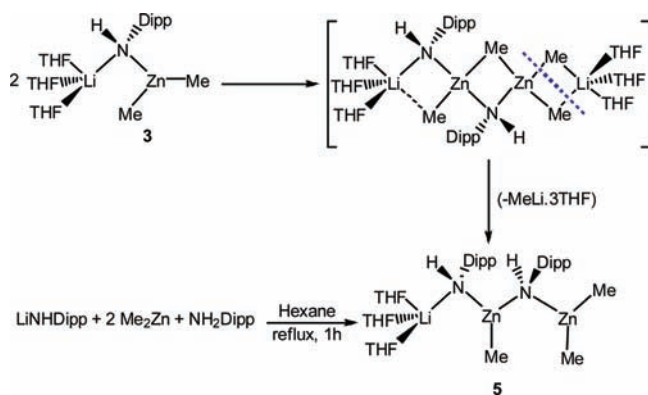
showed that the major species remaining in solution was zincate **3** which indicated that the disproportionation process that affords **5** occurs only to a minor extent. These results prompted us to investigate a rational synthetic route to prepare **5**. Thus, we found that, when the lithium amide LiNHDipp was combined with 2 molar equiv of dimethylzinc, 1 equiv of the primary amine NH_2Dipp, and 3 equiv of THF in hexane solution and the mixture was heated under reflux for 1 h, the reaction afforded a colorless solution. This solution deposited **5** as a colorless microcrystalline solid in good isolated yields (58−64%).

Conclusions

The final outcome of the interlocking co-complexation reactions of dimethylzinc with the primary lithium amide LiNHDipp is dictated by the donor ligand employed and the type of structure that it forms when coordinated to the lithium amide. Thus, when the chelating ligand TMEDA is employed, $[\{Li_2(NHDipp)_2(TMEDA)\}_{\infty}]$ (**1**) is obtained, where Li_2N_2 rings are connected by TMEDA bridges giving rise to a polymeric chain. This oligomeric form of the amide is too stable to react with dimethylzinc and so no mixed-metal compound is obtained even in the presence of an excess of TMEDA. In contrast, the tridentate ligand PMDETA is found to form a monomeric complex when coordinated to LiNHDipp, namely, [(PMDETA)Li(NHDipp)] (**4**), which is

now much more reactive and therefore can react successfully with dimethylzinc to yield to the formation of dimethyl (amido)zincate $[(PMDETA)LiZn(NHDipp)(Me)_2]$ (**2**) which displays a rare open motif where both metals are solely connected by the amido ligand and both methyl groups coordinate exclusively to zinc. Moving to a monodentate donor, when THF is employed the reaction yields the zincate $[(THF)_3LiZn(NHDipp)(Me)_2]$ (**3**). This compound is found to partially decompose in hexane solution after long periods at room temperature, affording the unprecedented bis(amido)trimethylzincate $[(THF)_3LiZn_2(Me)_3(NHDipp)_2]$ (**5**). This zinc-rich compound can also be prepared in good yields by reacting the lithium amide with 2 molar equiv of dimethylzinc, an extra equivalent of the amine NH_2Dipp, and 3 equiv of THF in hexane solution. Compound **5** exhibits a trinuclear Li···Zn···Zn chain structure where the metals are connected by the amido ligands and the methyl groups are exclusively bound to the zinc centers. In the solid state structure, the outer zinc of the chain is coordinated by the amido ligand less strongly than the other zinc center present in the molecule as revealed by the elongation of this Zn−N bond. In solution in deuterated benzene, the weakness in this Zn−N bond translates into the existence of a dynamic equilibrium between **5** and the bis(amido)methylzincate $[(THF)LiZn(NHDipp)_2Me]$ (**6**) and $Me_2Zn \cdot 2THF$ which can be driven toward the formation of **6** by removing volatile $Me_2Zn \cdot 2THF$ under vacuum. These results show the complicated chemistry that lithium zincates display in solution and also the great influence that the donor solvent employed has for the co-complexation reactions to succeed illustrating that the mere mixing-up of the monometallic components of a zincate do not always secure the formation of the desired or expected bimetallic compound.

Supporting Information Available: Crystal data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.