

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

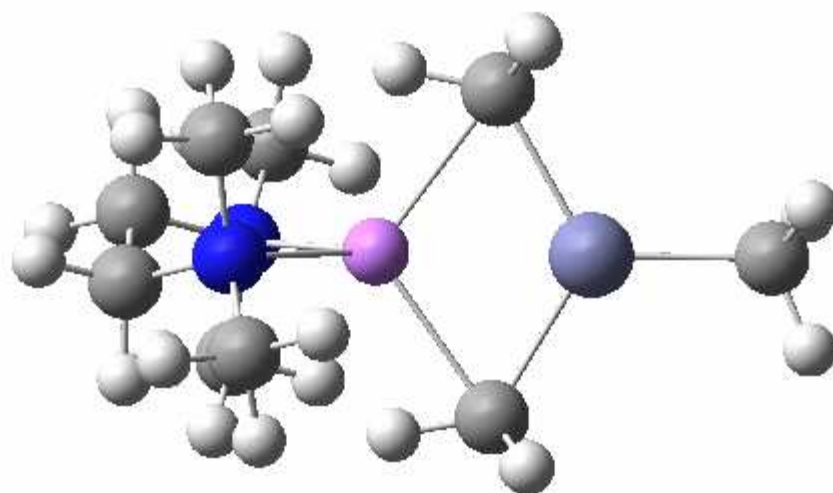
David R. Armstrong, Christine Dougan, David V. Graham, Eva Hevia* and Alan R. Kennedy

WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK,
G1 1XL. E-mail: eva.hevia@strath.ac.uk

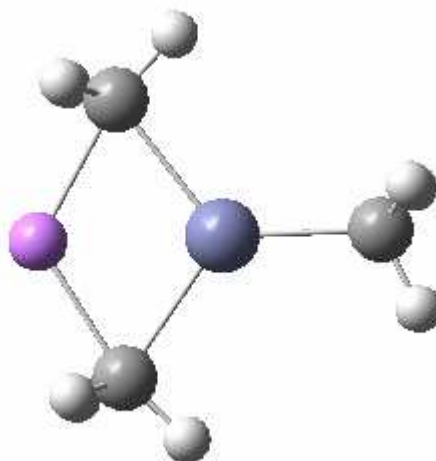
Supplementary Material

DFT calculations were carried out using the Gaussian G03 computational package¹. The B3LYP density functionals² were used along with the 6-311g** basis set³. After the geometry optimisation of each molecule, a frequency analysis was carried out. The resulting calculated zero-point energy was added to the electronic energy and this is the energy value quoted below.

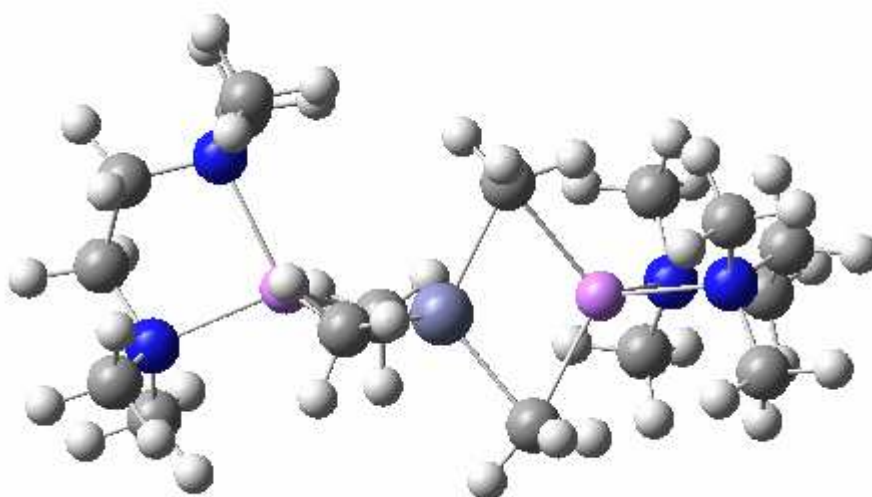
- 1 Gaussian 03, Revision B.0.5, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.
2. (a) A.D. Becke, Phys. Rev. A, **1988**, 38, 3098. (b) C.T. Lee, W.T. Yang and R.G.Parr, Phys.Rev. B, 1998, **37**, 785.
- 3 (a) A. D. McLean and G. S. Chandler, J. Chem. Phys., **1980**, 72, 5639. (b) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, J. Chem. Phys., **1980**, 72, 650

(a) TMEDA.Li(μ -Me)₂ZnMe**Principal Bond Lengths/Å and Angles/°**

Li-N	2.139, 2.145	Zn-C(br)	2.098, 2.098
Li-C(br)	2.235, 2.240	Zn-C(ter)	1.994
N-Li-N	88.2	C(br)-Li-C(br)	107.9
Li-C(br)-Zn	66.4, 66.5	C(br)-Zn-C(br)	119.2
C(br)-Zn-C(ter)	120.4, 120.4		

(b) $\text{Li}(\mu\text{-Me})_2\text{ZnMe}$ **Principal Bond Lengths/Å and Angles/°**

Zn-C(br)	2.149, 2.146	Li-C(br)	2.013, 2.013
Zn-C(ter)	1.974		
C(br)-Li-C(br)	107.9	C(br)-Zn-C(ter)	120.4, 120.4
Li-C(br)-Zn	66.4, 66.5	C(br)-Zn-C(br)	119.2

(c) $\text{TMEDA} \cdot \text{Li}(\mu\text{-Me})_2\text{Zn}(\mu\text{-Me})_2\text{Li} \cdot \text{TMEDA}$ 

Principal Bond Lengths/Å and Angles/°

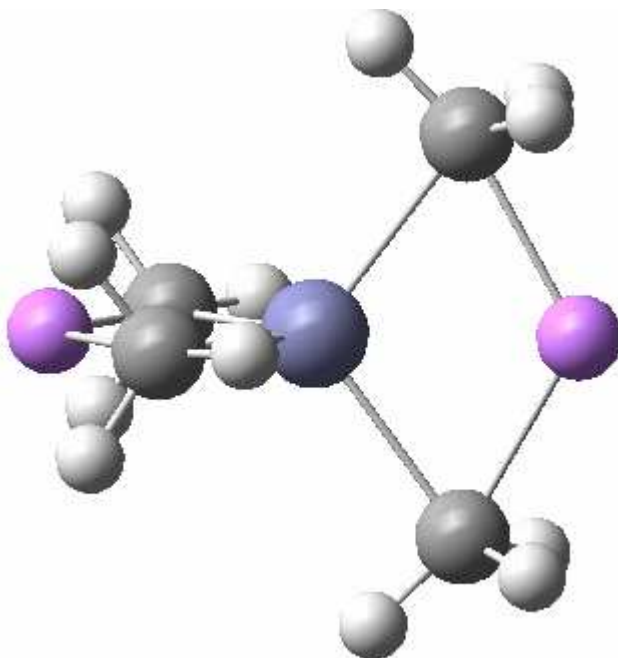
Initially, no symmetry was assumed. The final geometry had C_2 symmetry about Zn.

Li-N	2.160, 2.177	C-Zn	2.140, 2.182
Li-C	2.186, 2.214		

C-Li-C	109.9	N-Li-N	86.8
Li-C-Li	65.4, 66.6	Li-Zn-Li	159.2
C-Zn-C	112.9		

Each Li-C-Zn-C ring is puckered – the sum of the total internal angles is 354.8° and the Li-C-Zn-C dihedral angle = 18.3° .

(d) $\text{Li}(\mu\text{-Me})_2\text{Zn}(\mu\text{-Me})_2\text{Li}$

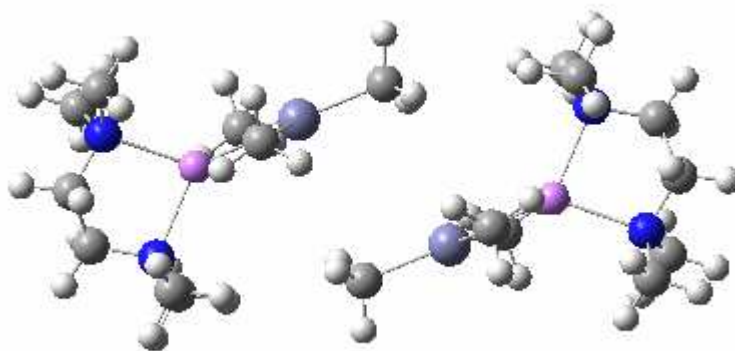


Principal Bond Lengths/Å and Angles/°

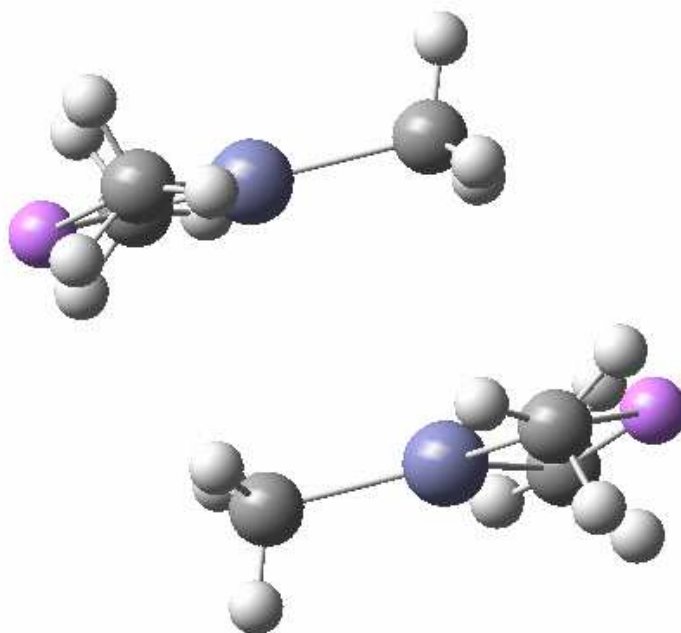
Li-C	2.008	Zn-C	2.177
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C-Li-C	121.0	C-Zn-C	106.7
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Li-Zn-C	66.1, 66.1
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(e) TMEDA.Li(μ -Me)₂Zn(μ -Me)₂Zn(μ -Me)₂Li.TMEDA

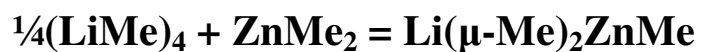
The attempted optimisation of this molecule resulted in the formation of two TMEDA.Li(μ -Me)₂ZnMe molecules. The presence of bridging Me groups between two Zn atoms does not lead to stable bonding.

(f) $\text{Li}(\mu\text{-Me})_2\text{Zn}(\mu\text{-Me})_2\text{Zn}(\mu\text{-Me})_2\text{Li}$ 

Geometry optimisation leads to two $\text{Li}(\mu\text{-Me})_2\text{ZnMe}$ molecules.

(g) Electronic Energy and Zero-point Energy

TMEDA.Li($\mu\text{-Me}$)₂ZnMe	-2254.180084 a.u.
Li($\mu\text{-Me}$)₂ZnMe	-1906.516528 a.u.
TMEDA.Li($\mu\text{-Me}$)₂Zn($\mu\text{-Me}$)₂Li.TMEDA	-2649.258776 a.u.
Li($\mu\text{-Me}$)₂Zn($\mu\text{-Me}$)₂Li	-1953.943956 a.u.
(LiMe)₄	-189.740080 a.u.
ZnMe₂	-1859.093261 a.u.
TMEDA	-347.619960 a.u.

(h) Energies of reactions in absence of TMEDA

$$\Delta E = +7.38 \text{ kcal mol}^{-1}$$

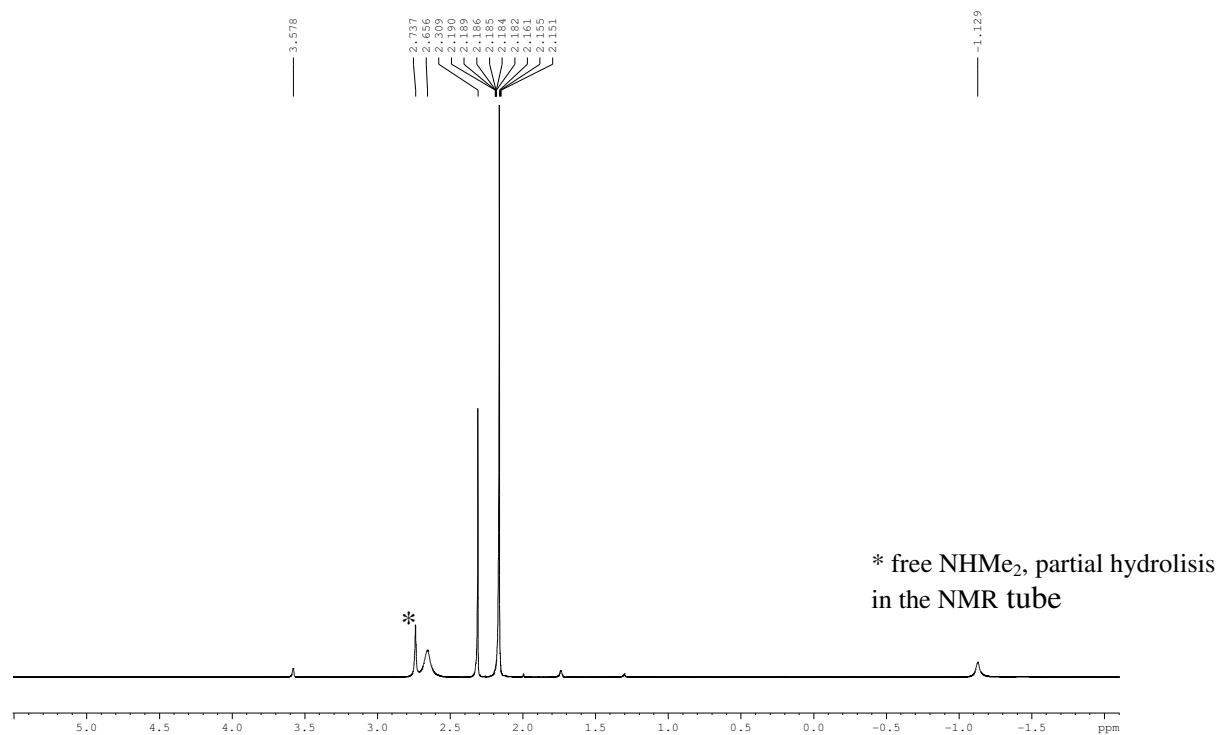


$$\Delta E = +12.4 \text{ kcal mol}^{-1}$$

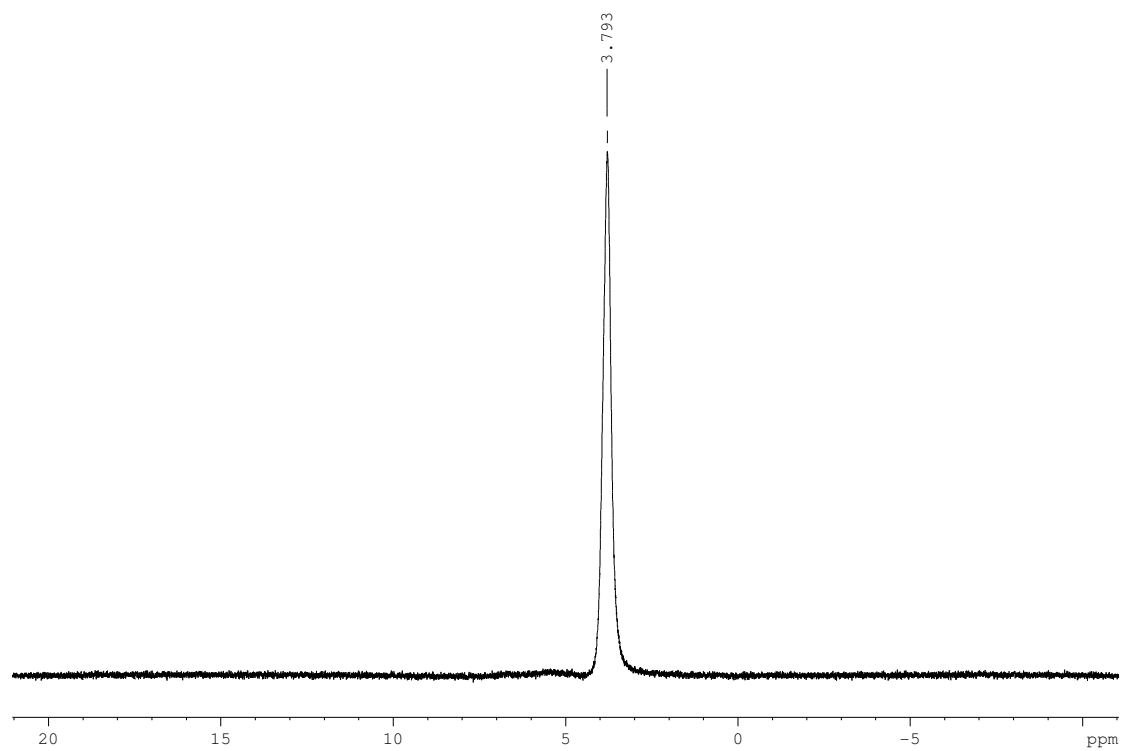
These findings emphasise the importance of the presence of TMEDA in the reaction of methyl lithium with dimethyl zinc.

NMR spectra

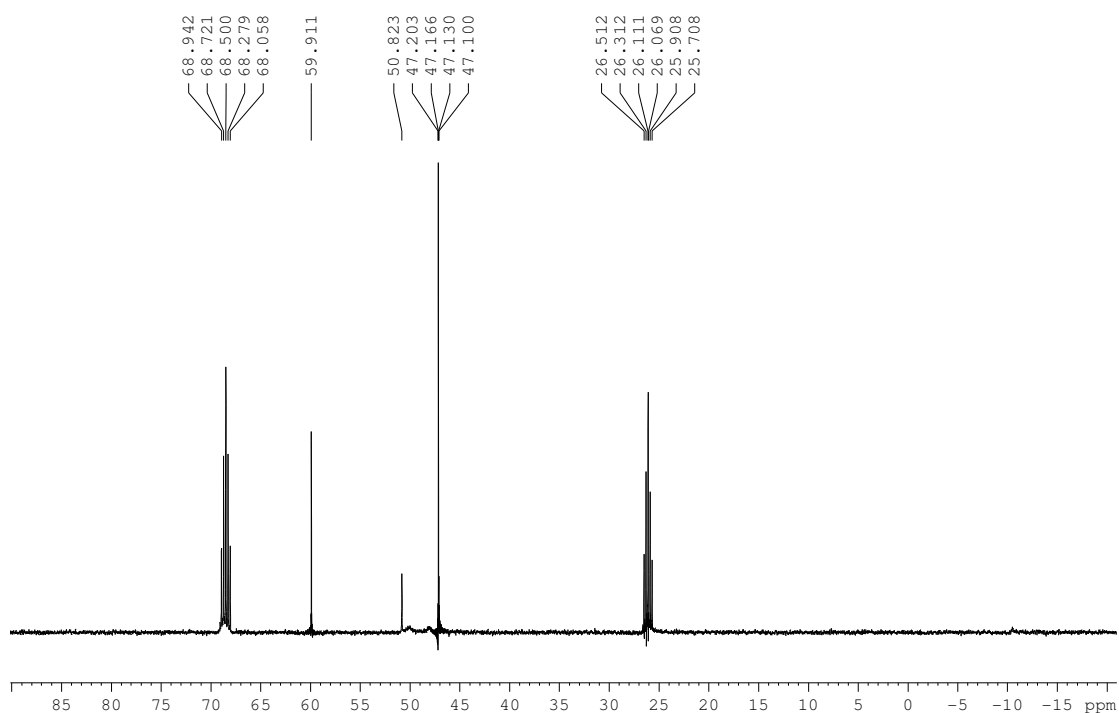
^1H NMR spectrum of $[(\text{TMEDA})_2\text{Li}_2\text{ZnMe}(\text{NMe}_2)_3]$ (**2**) in deuterated THF



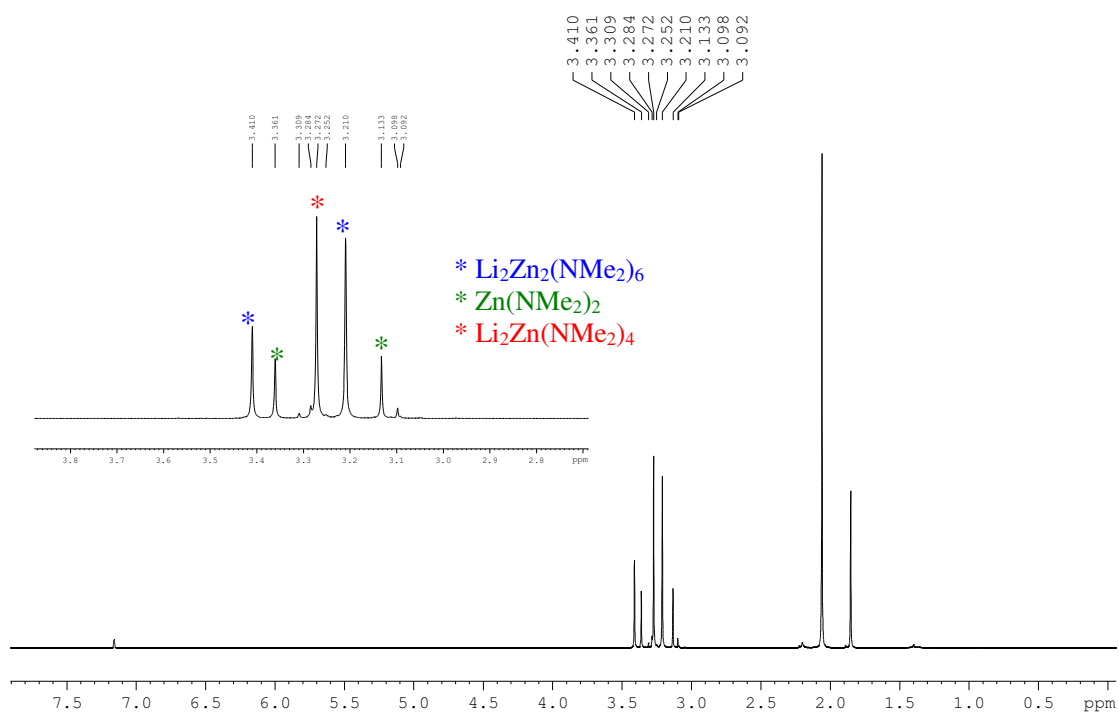
^7Li NMR spectrum of $[(\text{TMEDA})_2\text{Li}_2\text{ZnMe}(\text{NMe}_2)_3]$ (**2**) in deuterated THF



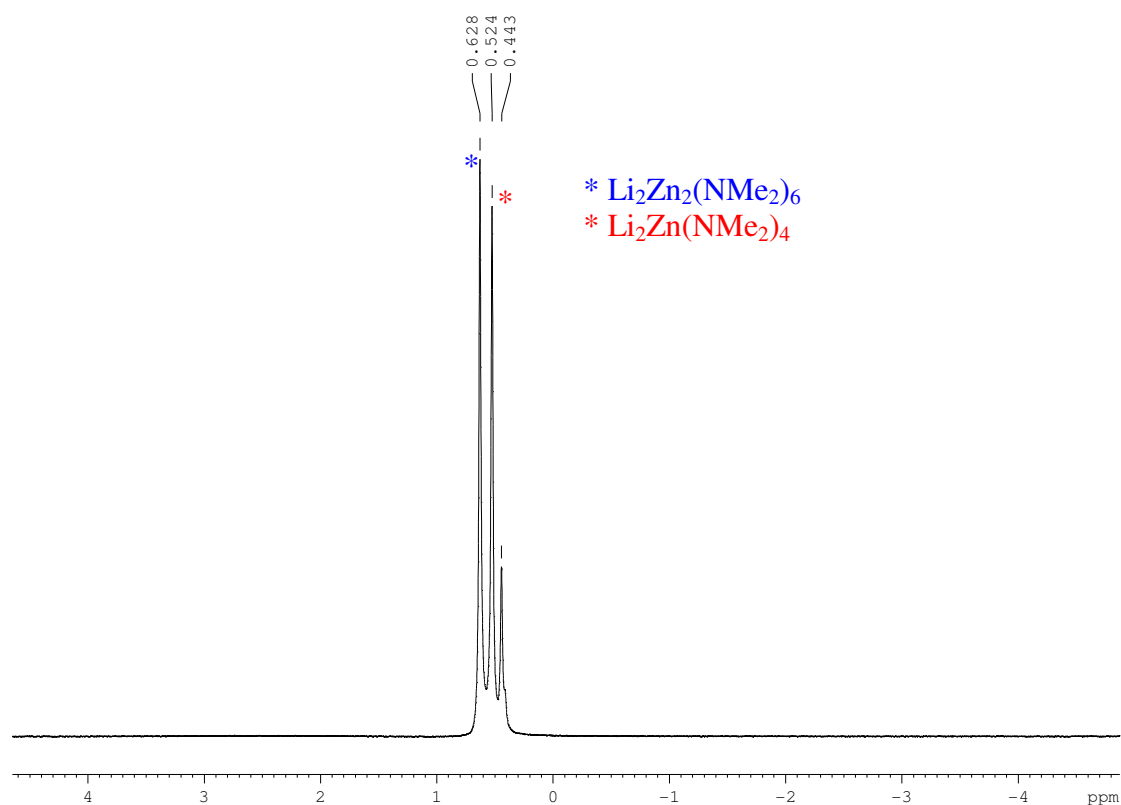
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[(\text{TMEDA})_2\text{Li}_2\text{ZnMe}(\text{NMe}_2)_3]$ (**2**) in deuterated THF



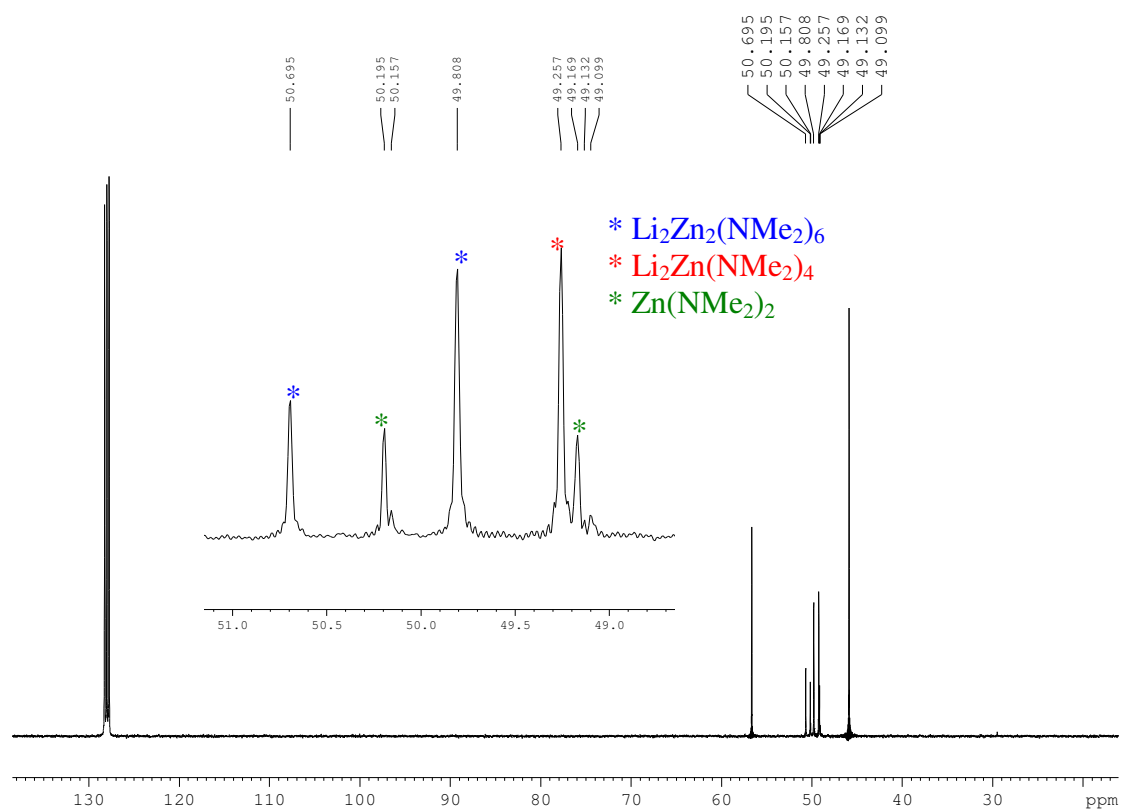
^1H NMR spectrum of $[\{(\text{TMEDA})\text{LiZn}(\text{NMe}_2)_3\}_2]$ (**3**) in deuterated benzene.



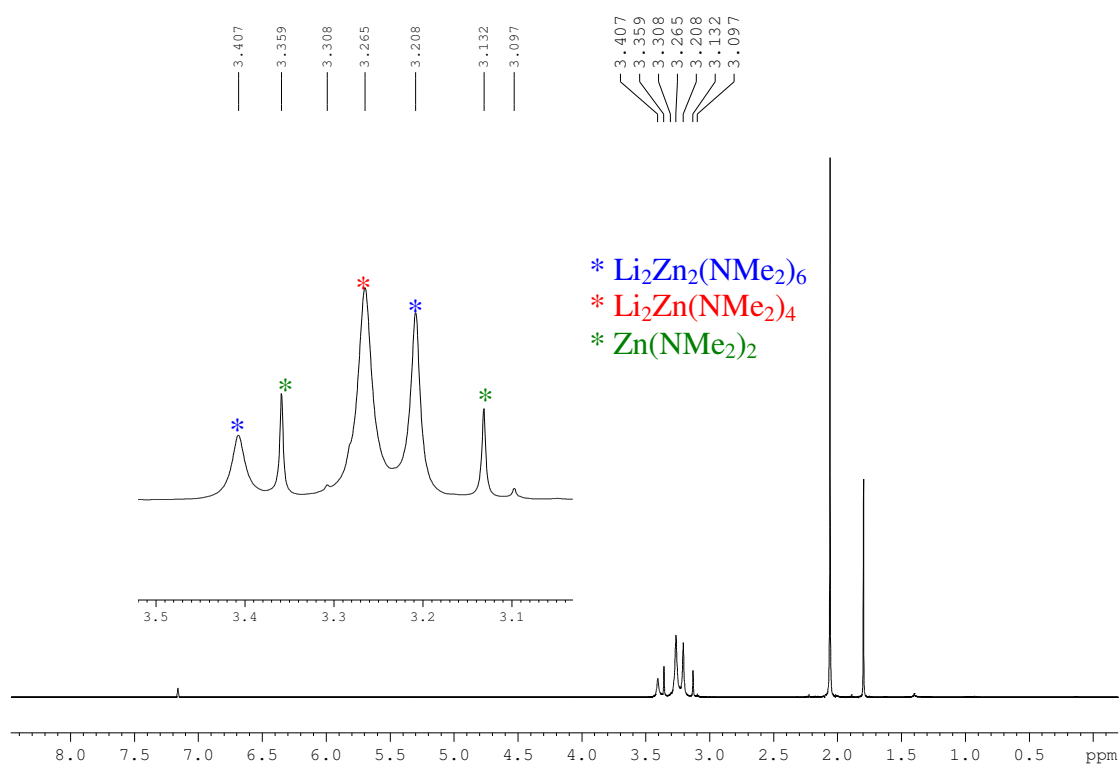
^7Li NMR spectrum of $[\{(\text{TMEDA})\text{LiZn}(\text{NMe}_2)_3\}_2](\mathbf{3})$ in deuterated benzene.



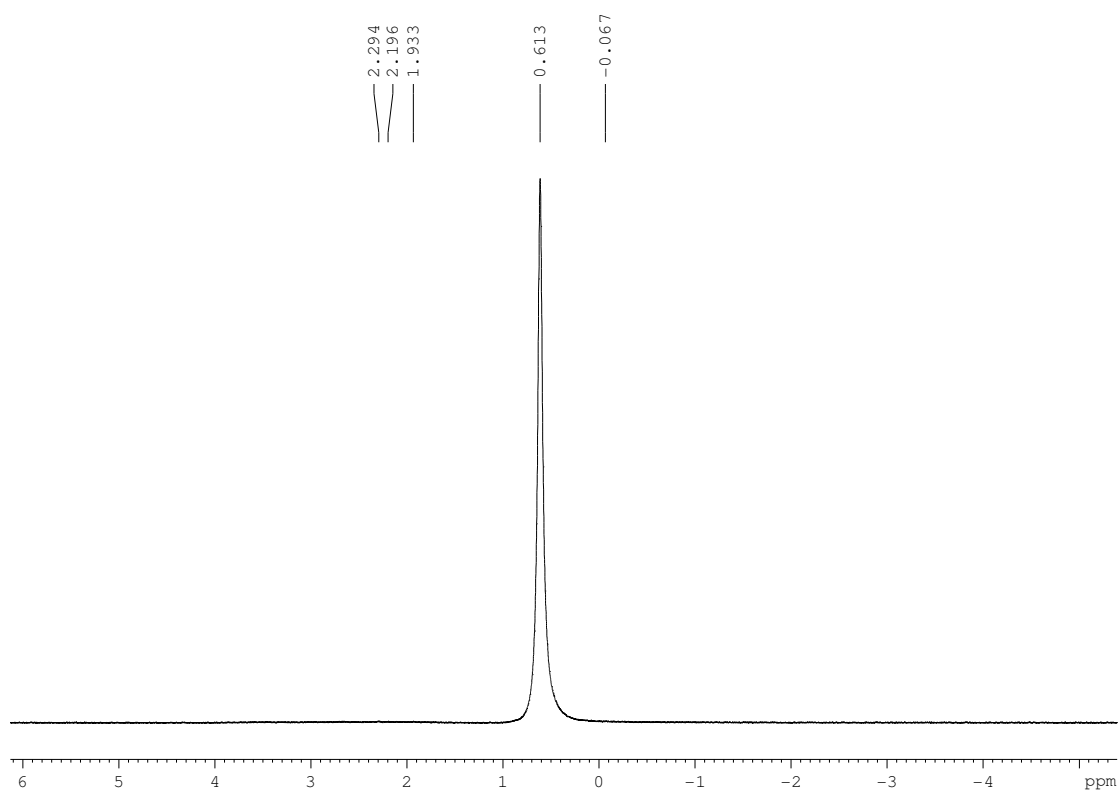
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\{(\text{TMEDA})\text{LiZn}(\text{NMe}_2)_3\}_2](\mathbf{3})$ in deuterated benzene.



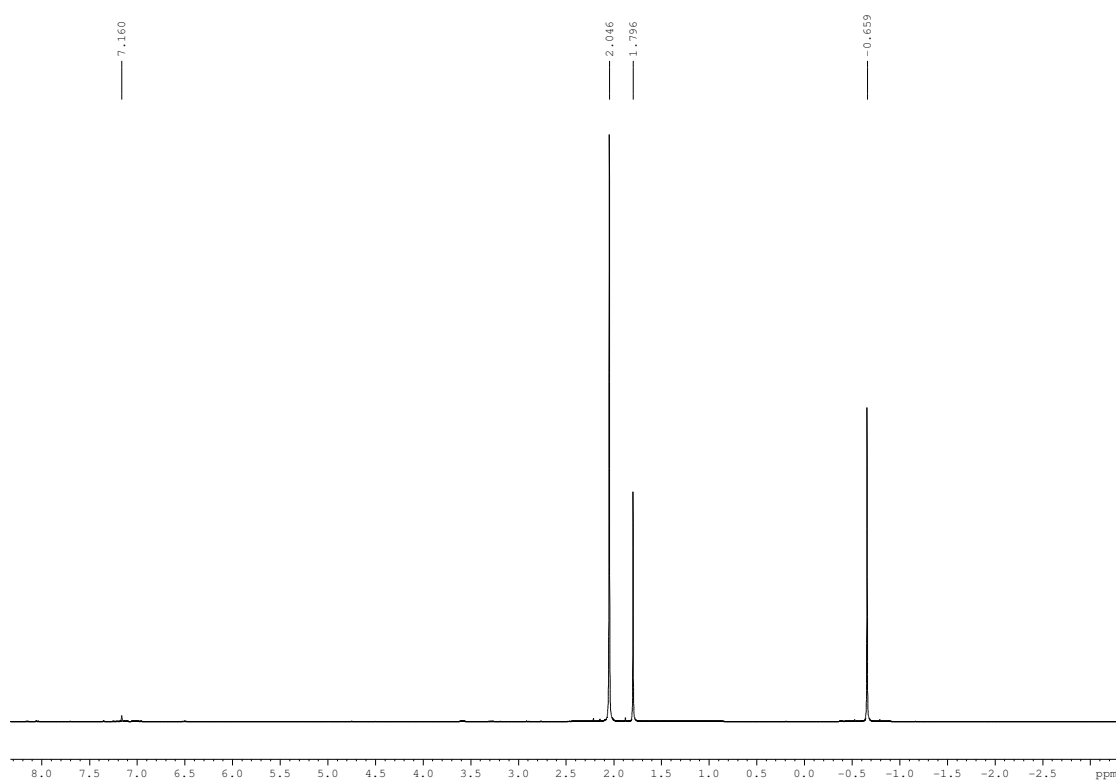
^1H NMR spectrum of $[\{(\text{TMEDA})\text{LiZn}(\text{NMe}_2)_3\}_2](\mathbf{3})$ in deuterated benzene on the addition of an excess of LiNMe_2



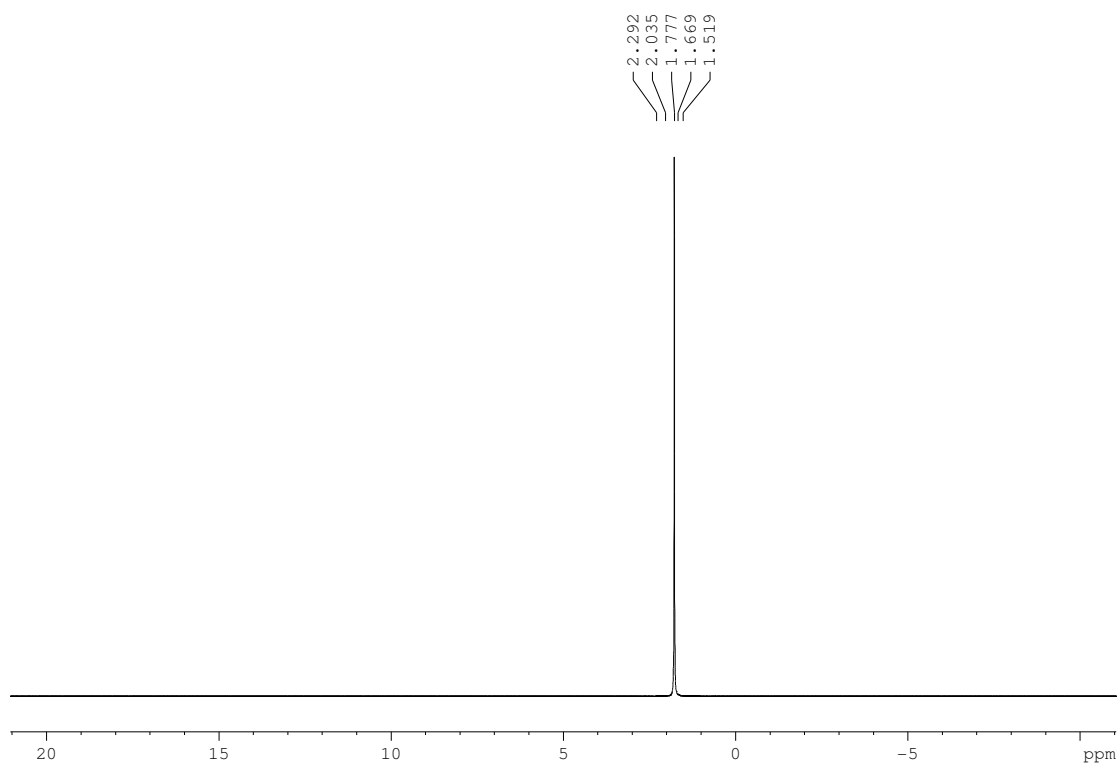
^7Li NMR spectrum of $[\{(\text{TMEDA})\text{LiZn}(\text{NMe}_2)_3\}_2](\mathbf{3})$ in deuterated benzene on the addition of an excess of LiNMe_2



^1H NMR spectrum of $[(\text{TMEDA})_2\text{Li}_2\text{ZnMe}_4]$ (**4**) in deuterated benzene.



^7Li NMR spectrum of $[(\text{TMEDA})_2\text{Li}_2\text{ZnMe}_4]$ (**4**) in deuterated benzene.



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[(\text{TMEDA})_2\text{Li}_2\text{ZnMe}_4]$ (**4**) in deuterated benzene.

