Electronic Supplementary Material for Chemical Communications

Dizincation and dimagnesiation of benzene using alkali-metal-mediated metallation

David R. Armstrong, William Clegg, Sophie H. Dale, David V. Graham, Eva Hevia, Lorna M. Hogg, Gordon W. Honeyman, Alan R. Kennedy and Robert E. Mulvey*.

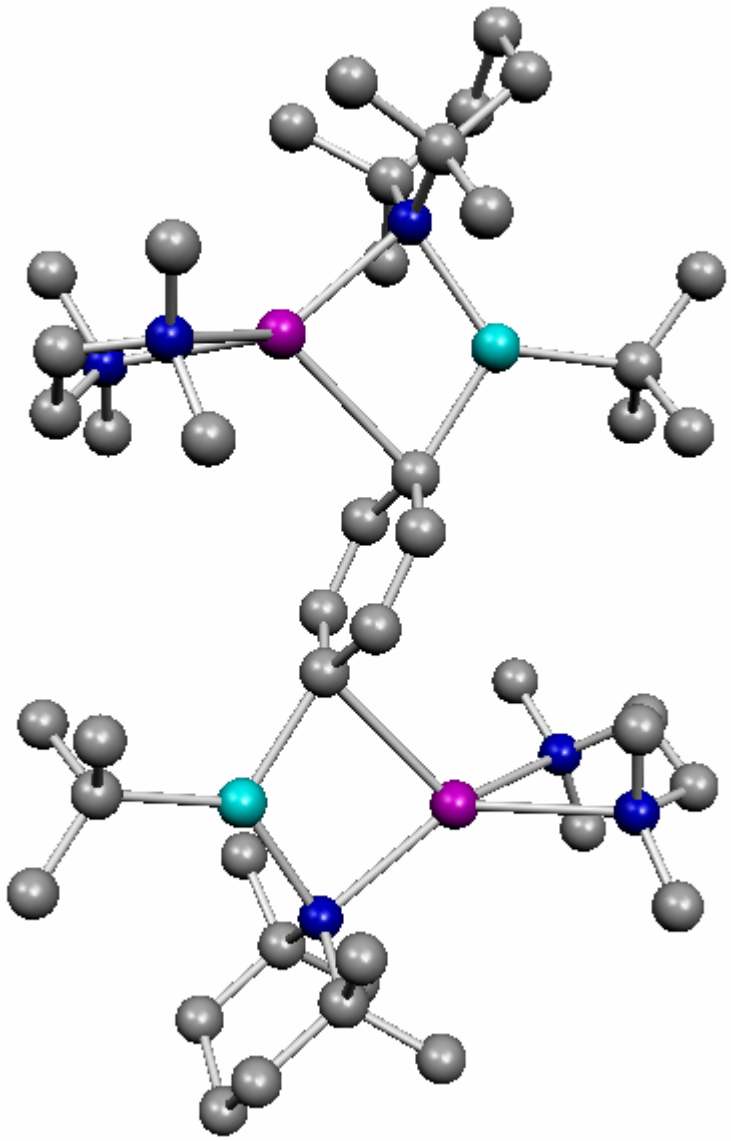
Computational Details

The geometry of the molecules was optimized using Gaussian 03.[1] Exploratory *ab initio* calculations at the Hartree Fock (HF) level were performed, utilising the 6-31g* basis set.[2] The resultant optimised geometries were subject to a frequency analysis and then refined by further density functional theory (DFT) calculations[3] using the B3LYP functionals[4,5] and the 6-311G** basis set.[6,7] The geometrical structural features from the DFT calculations are reported here while the total energy value from

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. W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* **1972***, 56*, 2257 P. C. Hariharan and J. A. Pople, *Theo. Chim. Acta* **1973,** *28*, 213.
3. W. Kohn, A. D. Becke and R.G. Parr, J. Phys. Chem., **1996**, *100*, 12974.
4. A.D. Becke, Phys. Rev. A, **1988**, *38*, 3098.
5. C.T. Lee, W.T. Yang and R.G.Parr, Phys.Rev. B, **1998**, *37*, 785.
6. A. D. McLean and G. S. Chandler, J. Chem. Phys., **1980**, *72*, 5639.
7. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, J. Chem. Phys., **1980**, *72*, 650.

the DFT calculation is adjusted by including the zero-point energy abstracted from the HF calculation modified by the factor 0.91.

Molecule	Zero Point EnergyHF/6-31G* /hartrees	Energy / B3LYP/6-311G** /hartrees	Corrected Energy B3LYP/6-311G** /hartrees
t-Butane	0.140762	-158.505894	-158.377801
Benzene	0.107673	-232.308550	-232.210568
TMEDA.Na(μ-^{t}Bu)(μ-TMP)Zn(^{t}Bu)	0.778080	-3013.937577	-3013.229524
{TMEDA.Na(μ-TMP)Zn(^{t}Bu)}$_2$(μ-C_6H_4)	1.383046	-5943.243971	-5941.985399
Na(μ-^{t}Bu)(μ-TMP)Zn(^{t}Bu)	0.535202	-2666.066651	-2665.579479
Na(μ-TMP)Zn(^{t}Bu)}$_2$(μ-C_6H_4)	0.896888	-5247.497542	-5246.681374

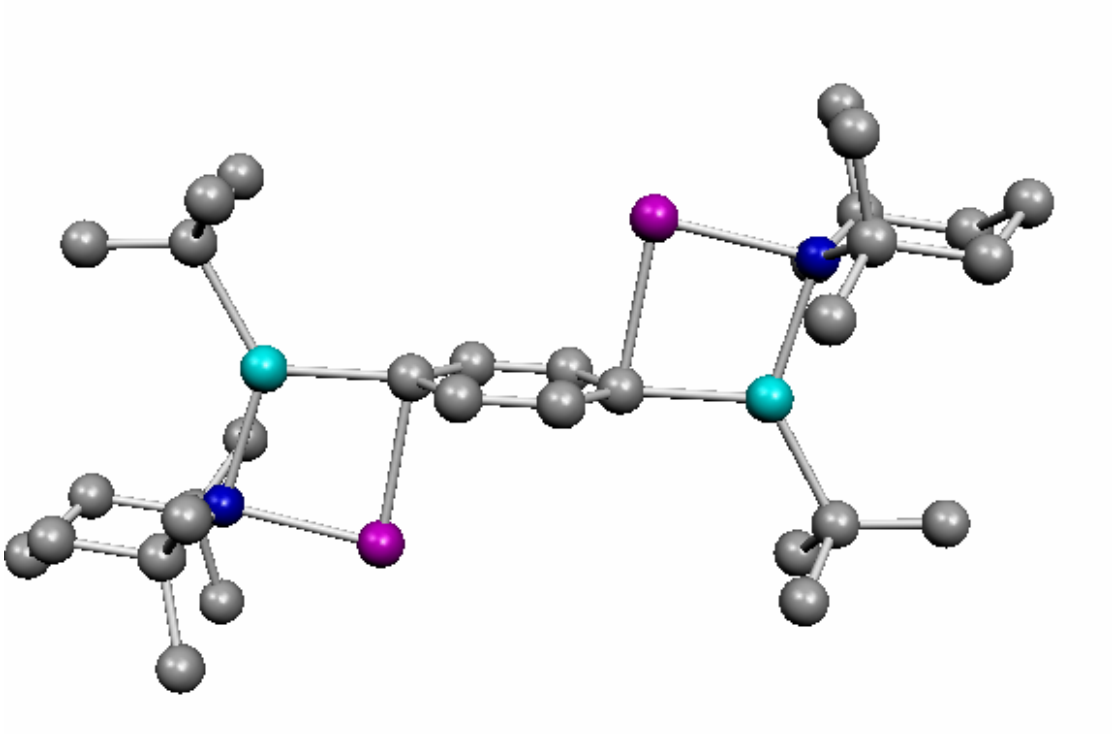


Principal Bond Lengths/Å and Bond Angles/°

Zn – C	**2.079**
Zn – N	**2.069**
Na – N	**2.414**
Na – C	**2.684**
Na…C	**3.234, 3.266**
$C_{ipso} – C_{ortho}$	**1.411, 1.412**
$C_{ortho} – C_{meta}$	**1.402, 1.402**
Na – N_{tmeda}	**2.632, 2.528**

Zn – C – Na	**82.2**
C – Na – N	**87.4**
Na – N – Zn	**85.7**
N – Zn – C	**104.8**

C – C_{ipso} – C	**113.3**
C – C_{ortho} – C	**123.3**
N – Na – N	**74.3**



Principal Bond Lengths/Å and Bond Angles/°

Zn – C	**2.077**
Zn – N	**2.088**
Na – N	**2.314**
Na – C	**2.461**
Na…C	**2.926, 2.929**
$C_{ipso} – C_{ortho}$	**1.413, 1.413**

$C_{ortho} - C_{meta}$ 1.403, 1.403

Zn – C – Na 82.2
C – Na – N 87.4
Na – N – Zn 85.7
N – Zn – C 104.8

C – C_{ipso} – C 113.7
C – C_{ortho} – C 123.2

Energetics of the reactions:

2[TMEDA.Na(μ-^{t}Bu)(μ-TMP)Zn(^{t}Bu)] + C_6H_6 =

[{TMEDA.Na(μ-TMP)Zn(^{t}Bu)}$_2$(μ-C_6H_4)] + 2^{t}BuH

ΔE = -44.8 kcal mol^{-1}

2[Na(μ-^{t}Bu)(μ-TMP)Zn(^{t}Bu)] + C_6H_6 =

[{Na(μ-TMP)Zn(^{t}Bu)}$_2$(μ-C_6H_4)] + 2^{t}BuH

ΔE = -42.3 kcal mol^{-1}