Journal Name

COMMUNICATION

Lewis base-complexed magnesium dithiolenes

Yuzhong Wang,[a] Nirva A. Maxi,[a] Yaoming Xie,[b] Pingrong Wei,[a] Henry F. Schaefer III[b] and Gregory H. Robinson*[a]

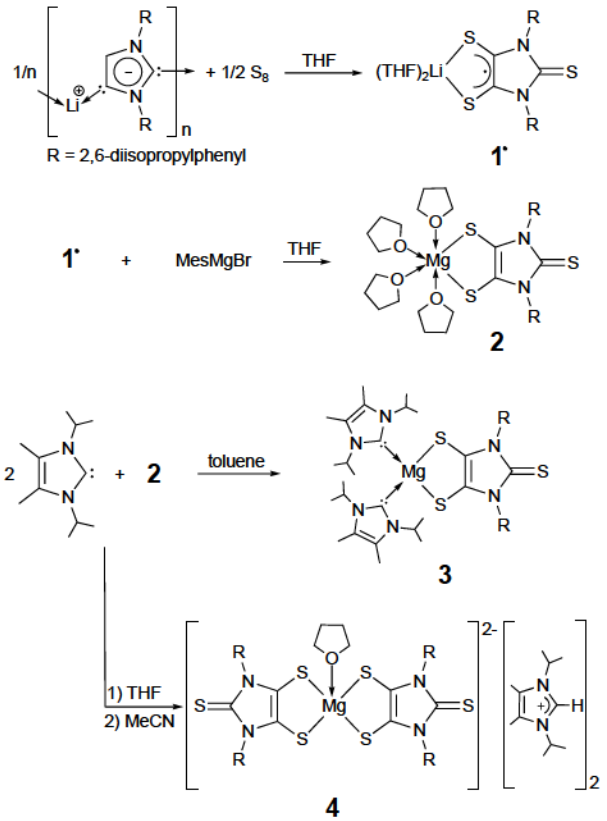
Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

The stable lithium dithiolene radical 1• was employed as a unique platform to access the first magnesium-bassed monodithiolene 2 by reaction with 2-mesitylmagnesium bromide in THF. Reaction of 2 with N-heterocyclic carbenes gave either carbene-complexed magnesium monodithiolene 3 (in toluene) or THF-solvated magnesium bis-dithiolene dianion 4 (in THF/MeCN). Compounds 2-4 have been spectroscopically and structurally characterized and probed by DFT computations.

Principally due to attractive chemical and physical properties, chemists have been fascinated by transition metal dithiolene complexes since the 1960s.[1-13] In contrast to this rich transition metal-based dithiolene chemistry, the corresponding dithiolene chemistry involving the main group elements has not been appropriately developed. For example, only a few main-group bis- and tris-(dithiolene) complexes have been reported.[2,9] In addition, while the radical character of ligands in transition metal dithiolenes has been extensively explored,[8,14] studies concerning the chemistry of main-group element-based dithiolene radicals have only recently begun to emerge.[15-16] To this end, this laboratory recently synthesized the first structurally characterized lithium-based anionic dithiolene radical (**1•**),[15] an R_2timdt-type ligand,[17-18] through sulphurization of the C2, C4, and C5 carbon atoms of the anionic N-heterocyclic dicarbene (NHDC) (Scheme 1).[19-20]

Largely due to its robust stability, radical **1** • provides a convenient synthetic platform for accessing a variety of interesting main-group dithiolene species. To this end, by allowing **1•** to react with the corresponding boranes, this laboratory recently prepared stable boron-based dithiolene radicals.[16] Notably, the literature reveals the paucity of group 2-based dithiolene complexes.[2,9] N-heterocyclic carbenes (NHCs) have been critical in the recent development of main group chemistry.[21-23] Given the potent σ-donating capability of NHCs and the non-innocent character of dithiolene ligands,[1,3] we are eager to explore the chemistry at the carbene—dithiolene interface. Herein, we report the syntheses,[24] molecular structures[24] and computations[24] of a series of THF-solvated, or carbene-complexed, magnesium mono- and bis-dithiolene complexes (**2–4**): the first reports of magnesium dithiolene complexes.



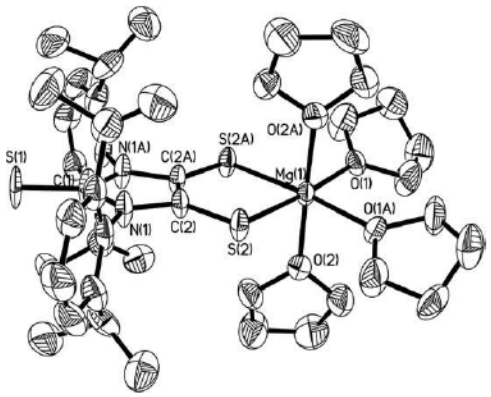
Scheme 1 Synthesis of magnesium mono- and bis-dithiolene complexes (**2–4**).

[a] *Department of Chemistry, The University of Georgia, Athens, Georgia 30602-2556, United States. E-mail: robinson@uga.edu*
[b] *The Center for Computational Chemistry, The University of Georgia, Athens, Georgia 30602-2556, United States.*

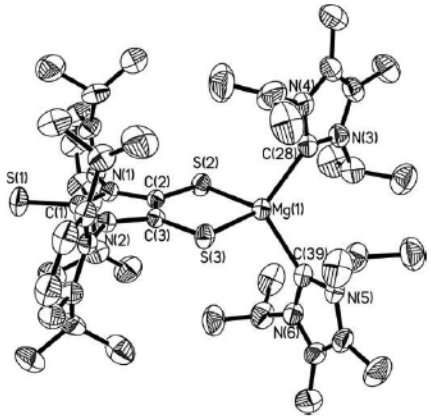
Electronic Supplementary Information (ESI) available: Synthetic and computational details; Structural and spectral characterization. Crystallographic details in .cif format. CCDC 1909298-1909300 See DOI: 10.1039/x0xx00000x

Reaction of **1**• (prepared *in situ*[24]) with 2-mesitylmagnesium bromide in THF (1:1 molar ratio) results in immediate colour change (from dark purple-to-brown) of the solution, from which **2** (48.1% yield) is isolated as colourless, highly O_2-sensitive, crystals (Scheme 1). Dimesityldisulphide (R-S-S-R, R = Mes), characterized by both ^{1}H NMR spectroscopy[24] and single-crystal X-ray diffraction,[24] is a major by-product of this reaction (and removed by hexane extraction). The formation of **2** involves a one-electron reduction of the redox-active dithiolene ligand (*i.e.*, transformation from the monoanionic dithiolene radical to the dithiolate dianion). This posits that the mesityl group may be eliminated as a neutral radical species,[25] which could subsequently be captured by an uncharacterized elemental sulphur species, thereby giving the dimesityldisulphide by-product. In an effort to synthetically approach additional magnesium-based monodithiolene complexes, we sought to replace the THF solvent molecules in **2** with N-heterocyclic carbenes. To this end, reaction of **2** with [:C{N(Pr^i)CMe}$_2$][26] (1:2 ratio) in toluene affords **3** (quantitative yield) (Scheme 1). Notably, this same reaction of **2** with [:C{N(Pr^i)CMe}$_2$] in THF (instead of toluene) and subsequent workup in acetonitrile affords a five-coordinate magnesium bis-dithiolene dianion **4** (Scheme 1). The formation of **4** involves the protonation of the N-heterocyclic carbene ligands, which is confirmed by the proton [at the carbene carbon (i.e., C2)] resonance of 8.36 ppm (in CD_3CN). Although the reaction mechanism remains unclear, the trace amount of water in the reaction system may play a role in the formation of **4**. Due to carbene coordination, compound **3** exhibits greater stability than **2** when being exposed to trace amount of O_2, which should be ascribed to the steric shielding of the Mg(II) core in **3** imposed by both carbene and imidazole-based dithiolene ligands.

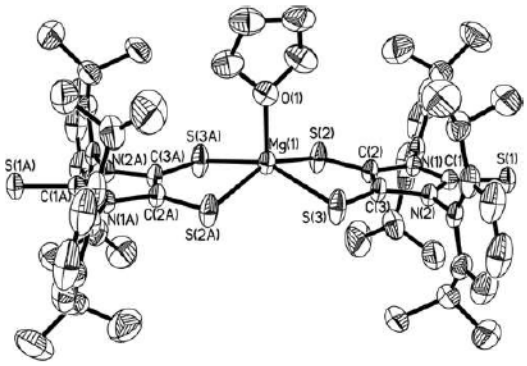
X-ray structural analysis[24] of **2** (Fig. 1) reveals that the central magnesium(II) dication, embraced by one dithiolene ligand and four coordinated THF molecules, adopts a distorted octahedral geometry. The axial O–Mg–O bond angle [167.95°] of **2** compares well to the computed value (170.68°) in the simplified **2-Me** model.[24] The O–Mg–O axis is obviously bent away from the dithiolene unit, which may be partially due to the steric repulsion between the axial THF molecules and the bulky dithiolene ligand. In contrast to the bent LiS_2C_2 ring in **1**• [bend angle (η) between the MS_2 plane (M = Li) and the S_2C_2 plane = 14.2°],[15] the MgS_2C_2 ring in **2** is planar (η = 0°), which is similar to the computed value in **2-Me** (η = 3.3°). The Mg(1)–S(2) bond distance in **2** [2.5339(12) Å] compares well to that of **2-Me** (2.509 Å). Notably, the 0.36 (av) Wiberg bond indices (WBIs) of the Mg–S bonds in **2-Me** suggests predominantly ionic bonding character.



2



3



[4]$^{2-}$

Fig. 1 Molecular structures of magnesium monodithiolenes (**2** and **3**) and magnesium bis-dithiolene dianion (**[4]$^{2-}$**) (thermal ellipsoids represent 30% probability; hydrogen atoms on carbons are omitted for clarity). Selected bond distances (Å) and angles (deg): For **2**, C(1)–S(1) 1.696(av), C(2)–C(2A) 1.360(6), C(2)–S(2) 1.724(3), S(2)–Mg(1) 2.5339(12), O(1)–Mg(1) 2.141(av), O(2)–Mg(1) 2.140(av); S(2)–C(2)–C(2A) 130.06(10), C(2)–S(2)–Mg(1) 95.03(11), S(2)–Mg(1)–S(2A) 89.82(5). For **3**, C(1)–S(1) 1.677(3), C(2)–C(3) 1.346(3), C(2)–S(2) 1.739(2), S(2)–Mg(1) 2.4507(12), C(28)–Mg(1) 2.229(3); S(2)–C(2)–C(3) 130.46(19), C(2)–S(2)–Mg(1) 92.49(9), S(2)–Mg(1)–S(3) 94.23(4), C(28)–Mg(1)–C(39) 111.95(12). For **[4]$^{2-}$**, C(1)–S(1) 1.690(4), C(2)–C(3) 1.341(5), C(2)–S(2) 1.723(4), S(2)–Mg(1) 2.529(av), S(3)–Mg(1) 2.557(av), O(1)–Mg(1) 2.136(av); S(2)–C(2)–C(3) 128.6(3), C(2)–S(2)–Mg(1) 96.24(15), S(2)–Mg(1)–S(3) 87.57(9).

The four-coordinate magnesium(II) centre in **3** adopts a distorted tetrahedral geometry in the solid state with the coordination sphere consisting of one dithiolene ligand and two carbenes ([:C{N(Pr^i)CMe}$_2$]) (Fig. 1). The C_{NHC}–Mg bond distances in **3** [2.228(3) Å, av] are comparable to those in the **3-Me** model (2.297 Å)[24] and in N-heterocyclic carbene complex of Mg(II)Cp$^*_2$ (Cp* = Me$_5$C$_5$) [2.194(2) Å].[27] Natural bond orbital (NBO) analysis shows that the C_{NHC}–Mg bonds (WBIs = 0.34) in **3-Me** are strongly polarized (90.0%) toward the carbene carbon atoms (which has 45.4% s-, 54.6% p-, 0.0% d-character). The strong electron-donating capability of the NHC ligand favours the increase of the electron density at the Mg(II) centre. Consequently, the Mg–S bonds (WBIs = 0.47) in **3** [2.4501(12) Å, av] are approximately 0.08 Å shorter than that in **2** [2.5339(12) Å], whereas the S–Mg–S bond angle in **3** [94.23(4)°] is larger than that in **2** [89.82(5)°].

While crystallographically disordered around an inversion centre, the five-coordinate magnesium atom in **4**$^{2-}$ adopts a distorted square-pyramidal geometry, with one THF oxygen atom occupying the apical position and the Mg(II) centre residing 0.617 Å above the S_4 basal plane of bis-dithiolene ligands (Fig. 1). Consequently, the MgS_2C_2 rings in **4**$^{2-}$ are obviously bent (η = 18.7°). However, the two C_2S_2 planes are somewhat twisted in the **[4]**$^{2-}$ model, rendering the four sulphur atoms non-coplanar.[24] In addition, the η value (3.2°, av) of **[4]**$^{2-}$ is considerably smaller than that in **4** (η = 18.7°). These structural differences between **4**$^{2-}$ and the **[4]**$^{2-}$ model may be mainly attributed to crystal packing. The elongated sulphur-carbon bonds [1.724(3)–1.739(2) Å vs. 1.677(3) Å (av) (**1**$^\bullet$)][15] and concomitant shortened carbon-carbon bond [1.341(5)– 1.360(6) Å vs. 1.417(3) Å (**1**$^\bullet$)][15] of the C_2S_2 units in complexes **2-4** are consistent with the HOMOs of **2-4** model compounds (Fig. 2 and Fig. S5[24]), which is primarily ligand-based, involving C–C π-bonding and C–S π-antibonding character.

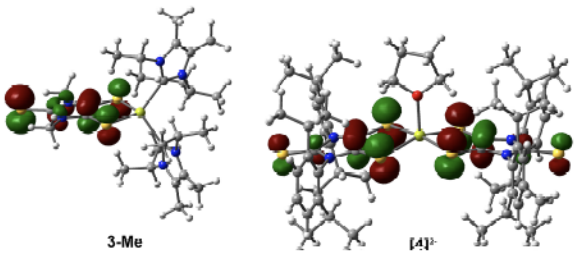


Fig. 2 HOMOs of **3-Me**, and **[4]**$^{2-}$ optimized models.

Reaction of the lithium dithiolene radical **1**$^\bullet$ with MesMgBr afforded the first magnesium monodithiolene complex **2**, which was subsequently employed to synthesize carbene-complexed magnesium monodithiolene **3** by reaction [:C{N(Pr^i)CMe}$_2$] in toluene. Notably, the parallel reaction in THF gives a five-coordinate magnesium bis-dithiolene dianion **4**. The intriguing redox chemistry of **2-4** is being investigated in this laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful to the National Science Foundation for support: CHE-1565676 (G.H.R., Y.W.) and CHE-1855641 (G.H.R., Y.W.) and CHE-1361178 (H.F.S.).

Notes and references

1 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49-221.
2 E. I. Stiefel, Ed., *Dithiolene Chemistry: Synthesis, Properties, and Applications*, John Wiley & Sons, Hoboken, NJ, 2004.
3 R. Eisenberg and H. B. Gray, *Inorg. Chem.*, 2011, **50**, 9741-9751.
4 R. Kato, *Chem. Rev.*, 2004, **104**, 5319-5346.
5 F. J. Hine, A. J. Taylor and C. D. Garner, *Coord. Chem. Rev.*, 2010, **254**, 1570-1579.
6 S. Rabaca and M. Almeida, *Coord. Chem. Rev.*, 2010, **254**, 1493-1508.
7 B. Garreau-de Bonneval, K. I. M. C. Ching, F. Alary, T. T. Bui and L. Valade, *Coord. Chem. Rev.*, 2010, **254**, 1457-1467.
8 S. Sproules and K. Wieghardt, *Coord. Chem. Rev.*, 2011, **255**, 837-860.
9 S. Sproules, *Prog. Inorg. Chem.*, 2014, **58**, 1-144.
10 A. Kobayashi, E. Fujiwara and H. Kobayashi, *Chem. Rev.*, 2004, **104**, 5243-5264.
11 D. Espa, L. Pilia, S. Attar, A. Serpe and P. Deplano, *Inorg. Chim. Acta*, 2018, **470**, 295-302.
12 S. Leimkuhler, *Biol. Chem.*, 2017, **398**, 1009-1026.
13 R. H. Holm, P. Kennepohl and E. I. Solomon, *Chem. Rev.*, 1996, **96**, 2239-2314.
14 A. Filatre-Furcate, N. Bellec, O. Jeannin, P. Auban-Senzier, M. Fourmigue, A. Vacher and D. Lorcy, *Inorg. Chem.*, 2014, **53**, 8681-8690.
15 Y. Wang, H. P. Hickox, Y. Xie, P. Wei, S. A. Blair, M. K. Johnson, H. F. Schaefer, III and G. H. Robinson, *J. Am. Chem. Soc.*, 2017, **139**, 6859-6862.
16 Y. Wang, Y. Xie, P. Wei, S. A. Blair, D. Cui, M. K. Johnson, H. F. Schaefer, III and G. H. Robinson, *Angew. Chem., Int. Ed.*, 2018, **57**, 7865-7868.
17 F. Bigoli, P. Deplano, F. A. Devillanova, V. Lippolis, P. J. Lukes, M. L. Mercuri, M. A. Pellinghelli and E. F. Trogu, *J. Chem. Soc., Chem. Commun.*, 1995, 371-372.
18 F. Bigoli, P. Deplano, F. A. Devillanova, J. R. Ferraro, V. Lippolis, P. J. Lukes, M. L. Mercuri, M. A. Pellinghelli, E. F. Trogu and J. M. Williams, *Inorg. Chem.*, 1997, **36**, 1218-1226.
19 Y. Wang, Y. Xie, M. Y. Abraham, P. Wei, H. F. Schaefer, III, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2010, **132**, 14370-14372.
20 *Organometallics*, 2011, **30**, 1303-1306.
21 D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39-91.
22 Y. Wang and G. H. Robinson, *Inorg. Chem.*, 2014, **53**, 11815-11832.
23 V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt and S. Inoue, *Chem. Rev.*, 2018, **118**, 9678-9842.

24 See the supporting information for synthetic, computational, and crystallographic details.
25 R. G. Gough and J. A. Dixon, *J. Org. Chem.*, 1968, **33**, 2148-&.
26 N. Kuhn and T. Kratz, *Synthesis*, 1993, 561-562.
27 A. J. Arduengo, F. Davidson, R. Krafczyk, W. J. Marshall and M. Tamm, *Organometallics*, 1998, **17**, 3375-3382.