ChemComm

COMMUNICATION

Lewis base-complexed magnesium dithiolenes†

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

The first magnesium-based dithiolene, 2, was prepared by reaction of the lithium dithiolene radical, 1•, with 2-mesitylmagnesium bromide. Reaction of 2 with N-heterocyclic carbenes (in toluene) gave a carbene-stabilized magnesium monodithiolene complex, 3. Complex 3, in turn, is readily converted to a THF-solvated magnesium bis-dithiolene dianion, 4, *via* partial hydrolysis in polar solvents (*i.e.*, THF/CH₃CN). Compounds 2, 3 and 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 properly 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 R₂timdt-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 a paucity of group 2-based dithiolene complexes.[2,9]

[a] *Department of Chemistry, The University of Georgia, Athens, Georgia 30602-2556, USA. E-mail: robinson@uga.edu*
[b] *The Center for Computational Chemistry, The University of Georgia, Athens, Georgia 30602-2556, USA*
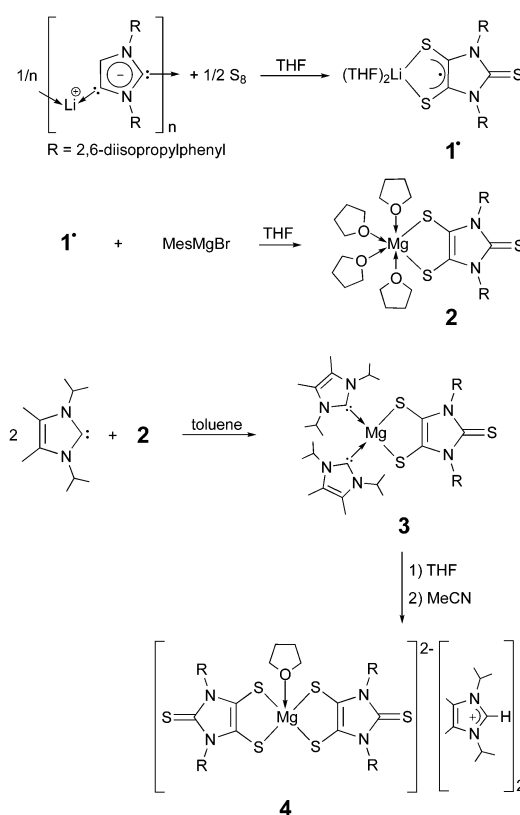
Scheme 1 Synthesis of 2 and 3 and hydrolytic conversion of 3 to 4 in polar solvents.

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.

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). Dimesyldisulphide (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 dimesyldisulphide by-product (in nearly quantitative yield). 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). X-ray quality single crystals of **3** can be obtained by recrystallization in hot toluene. However, **3** may be converted to a five-coordinate magnesium bis-dithiolene dianion **4** in polar solvents (THF/MeCN) (Scheme 1). Although the reaction mechanism remains unclear, the formation of **4** may be due to the partial hydrolysis of **3** in polar solvents. Indeed, the protonation of the N-heterocyclic carbenes (likely from residual moisture in the reaction system) is confirmed by the ^{1}H NMR study. The proton at the carbene carbon (*i.e.*, C2) resonates at 8.36 ppm (in CD_3CN). 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 [171.5°, av] of **2** compares well to the computed value (170.68°) in the simplified **2-Me** model,[24] which suggests that steric hindrance between the axial THF molecules and the bulky dithiolene ligand does not play a predominant role in contrast to the bent LiS$_2$C$_2$ ring in **1**[•] [bend angle (η) between the MS$_2$ plane (M = Li) and the S$_2$C$_2$ plane = 14.2°],[15] the MgS$_2$C$_2$ 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.

The four-coordinate magnesium(II) centre in **3** adopts a distorted tetrahedral geometry (τ = 0.76)[27] 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].[28] 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
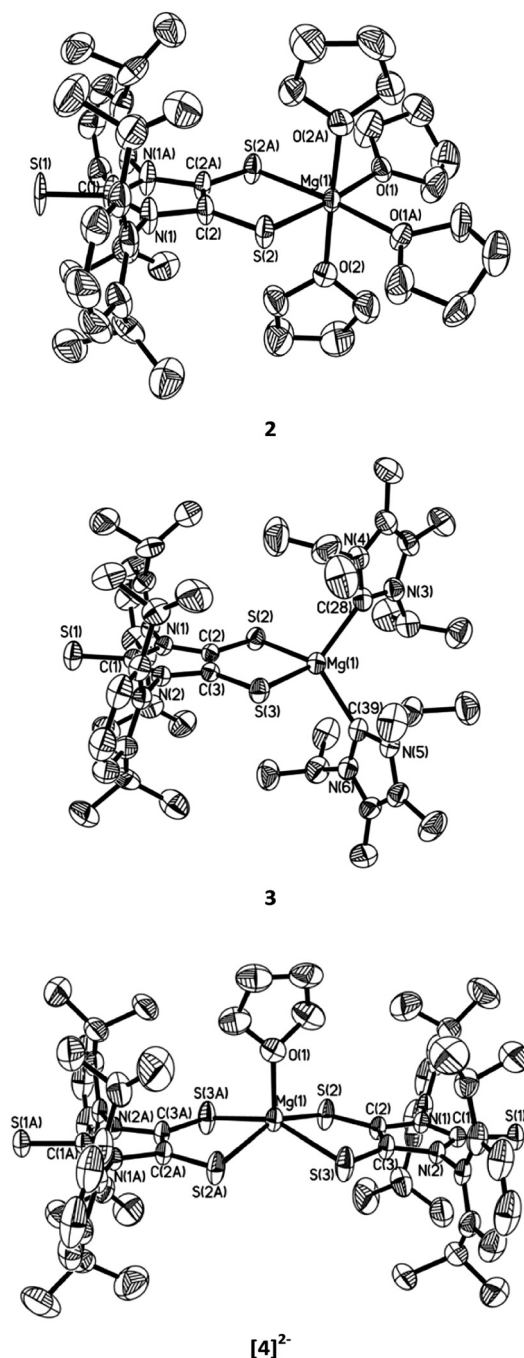

2

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).

45.4% s-, 54.6% p-, 0.0% d-character). The strong electron-donating capability of the NHC ligand favours the increase of
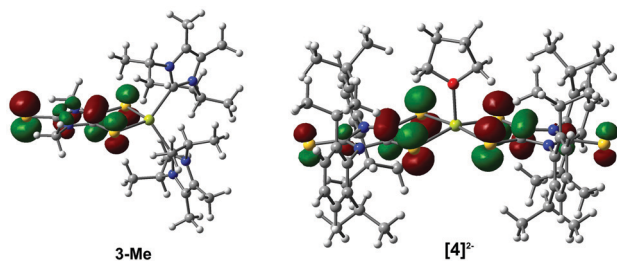
Fig. 2 HOMOs of **3-Me**, and **[4]$^{2-}$** optimized models.

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** adopts a slightly distorted square-pyramidal geometry (τ = 0.01),[29] 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$_2$C$_2$ rings in **4** are obviously bent (η = 18.7°). However, the two C$_2$S$_2$ 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** 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•**)][15] and concomitant shortening of the carbon–carbon bond distances [1.341(5)–1.360(6) Å vs. 1.417(3) Å (**1•**)][15] of the C$_2$S$_2$ units in complexes **2–4** are consistent with the HOMOs of **2–4** model compounds (Fig. 2 and Fig. S5, ESI† [24]), which is primarily ligand-based, involving C–C π-bonding and C–S π-antibonding character.

Reaction of the lithium dithiolene radical **1•** with a Grignard reagent afforded the first magnesium monodithiolene complex **2**, which was subsequently utilized to synthesize a carbene-complexed magnesium monodithiolene **3** by reaction with [:C{N(Pr^i)CMe}$_2$] in toluene. Compound **3** may undergo partial hydrolytic reaction in polar solvents (THF/MeCN), giving a five-coordinate magnesium bis-dithiolene dianion **4**. The intriguing redox chemistry of **2** and **3** is being investigated in this laboratory.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49–221.
2 *Dithiolene Chemistry: Synthesis, Properties, and Applications*, ed. E. I. Stiefel, 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**, 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 Y. Wang, Y. Xie, M. Y. Abraham, P. Wei, H. F. Schaefer, III, P. v. R. Schleyer and G. H. Robinson, *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 ESI† for synthetic, computational, and crystallographic details.
25 R. G. Gough and J. A. Dixon, *J. Org. Chem.*, 1968, **33**, 2148–2149.
26 N. Kuhn and T. Kratz, *Synthesis*, 1993, 561–562.
27 L. Yang, D. R. Powell and R. P. Houser, *Dalton Trans.*, 2007, 955–964.
28 A. J. Arduengo, F. Davidson, R. Krafczyk, W. J. Marshall and M. Tamm, *Organometallics*, 1998, **17**, 3375–3382.
29 A. W. Addison, T. N. Rao, J. Reedijk, J. v. Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349–1356.