Redox Chemistry of an Anionic Dithiolene Radical

Journal:	*Dalton Transactions*
Manuscript ID	DT-COM-12-2018-004989.R2
Article Type:	Communication
Date Submitted by the Author:	06-Feb-2019
Complete List of Authors:	Wang, Yuzhong; University of Georgia, Department of Chemistry Xie, Yaoming; University of Georgia, Center for Computational Quantum Chemistry Wei, Pingrong; University of Georgia, Department of Chemistry Schaefer, Henry; University of Georgia, Computational Chemistry Robinson, Gregory ; University of Georgia,

Journal Name

COMMUNICATION

Redox Chemistry of an Anionic Dithiolene Radical

Yuzhong Wang, Yaoming Xie, Pingrong Wei, Henry F. Schaefer III, and Gregory H. Robinson*

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

The redox chemistry of the first stable anionic dithiolene radical 1$^{\bullet}$ was investigated by both reactivity and cyclic voltammetry studies. While one-electron reduction of 1$^{\bullet}$ by Cp_2Co or KC_8 affords the corresponding dithiolate dimers 2 and 3, respectively, one-electron oxidation of 1$^{\bullet}$ by $Ph_3C^+BF_4^-$ (or O_2) conveniently gives 4, the neutral dithiolene dimer.

Largely due to unusual optical, conductive, magnetic, and bio-inspired properties, studies of transition metal dithiolene complexes may be traced to the 1960s.[1-13] While molybdenum- and tungsten-dithiolene complexes have shown enzymatic activity,[2,5,12] other transition metal bis-dithiolenes have demonstrated remarkable potential as optoelectronic materials.[4,7,10,11] The non-innocent nature of dithiolene ligands (Fig. 1) plays a pivotal role in the intriguing redox chemistry of transition metal dithiolenes.[3]

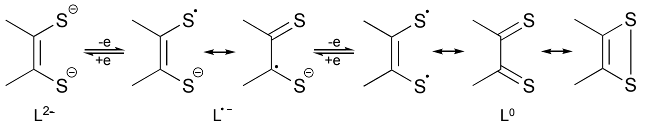
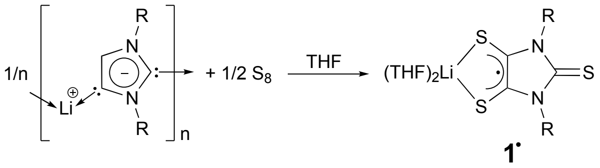


Fig. 1 Redox non-innocence of a dithiolene ligand.[14]

While the radical character of dithiolene ligands ($L^{\bullet-}$) in transition metal complexes was well documented,[8,15-27] highly reactive transition metal-free anionic dithiolene radicals have only been investigated using theoretical methods and electron paramagnetic resonance.[28-31] Notably, the electronic absorption spectrum of the prototype anionic dithiolene radical ($C_2H_2S_2^{\bullet-}$) was studied in a low-temperature matrix.[32] Recently, the first structurally characterized anionic dithiolene radical **1**$^{\bullet}$ was synthesized by this laboratory *via* trisulfurization of the corresponding anionic N-heterocyclic dicarbene[33] (Scheme 1).[34] It was anticipated that this discovery could provide a unique platform for accessing the largely unexplored chemistry of main group dithiolene radicals (*e.g.*, boron dithiolene radicals were achieved *via* **1**$^{\bullet}$).[35] Moreover, the considerable stability of **1**$^{\bullet}$ would be advantageous for probing the redox chemistry of dithiolene radical anions ($L^{\bullet-}$ in Fig. 1). To this end, we report the syntheses,[36] molecular structures[36] and computations[36] of compounds **2**, **3**, and **4**, all obtained *via* one-electron redox reactions of **1**$^{\bullet}$.



Scheme 1. Previously reported synthesis of **1**$^{\bullet}$ (R = 2,6-diisopropylphenyl).[34]

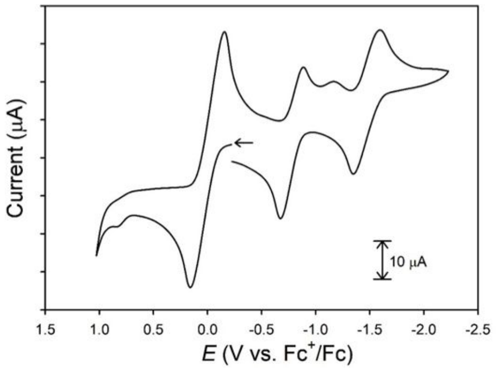


Fig. 2 Cyclic voltammogram of **1**$^{\bullet}$ (6.45 mM) with Fc internal standard (4.5 mM; $E_{½}$ set to 0 V) in THF (scan speed: 100 mV/s, 0.1 M $^nBu_4NPF_6$ supporting electrolyte, glassy carbon working electrode, Pt-wire counter electrode, RT). Arrow indicates direction of the scan.

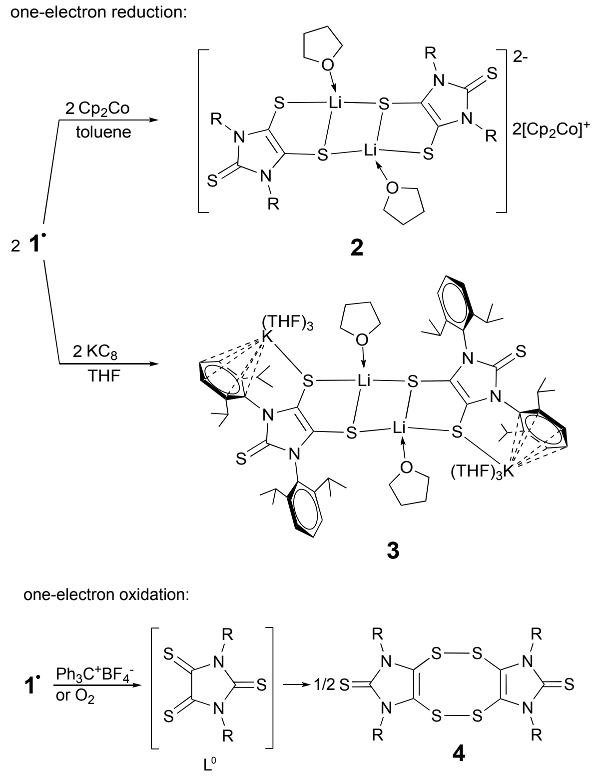
The cyclic voltammogram of **1**$^{\bullet}$ was recorded (Fig. 2), potentials are reported in THF versus an internal ferrocene/ferrocenium (Fc/Fc$^+$) standard. While both reversible and quasi-reversible redox events have been documented for transition metal dithiolene complexes,[37,38] radical **1**$^{\bullet}$ exhibits two electrochemically quasi-reversible, diffusion-controlled couples at $E_{1/2}$ = -0.78 V (ΔE_p = 0.21 V) and

---

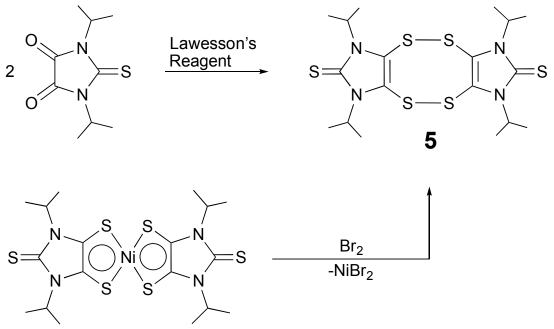
* *Department of Chemistry, The University of Georgia, Athens, Georgia 30602-2556, United States. E-mail: robinson@uga.edu*

Electronic Supplementary Information (ESI) available: Synthetic and computational details and structural and spectral characterization. Crystallographic details in .cif format. CCDC 1881413-1881415. See DOI: 10.1039/x0xx00000x

$E_{1/2}$ = -1.47 V (ΔE_p = 0.25 V), which are assigned to [$L^0/L^{\bullet-}$] and [$L^{\bullet-}/L^{2-}$] ligand reduction events, respectively. Indeed, with increasing scan rate (Fig. S1),[36] the cathodic-anodic peak separations (ΔE_p) increase and meanwhile cathodic peak potentials (E_{pc}) shift negatively. The one-electron reduction/oxidation of **1$^\bullet$** involves adding/removing one electron from the SOMO,[2] which is comparable to that for neutral odd-electron 1,2-dithioles.[39] The small irreversible reduction at -1.13 V may be a result of certain chemical transformations, such as radical coupling to yield dithiete or dimer of L^0. The 1:1 reaction of **1$^\bullet$** with cobaltocene (Cp_2Co), a well known one-electron reducing agent,[40] quantitatively affords dimeric dithiolate **2** (as a green powder) (Scheme 2). Compound **2** is insoluble in toluene, slightly soluble in THF, and moderately soluble in acetonitrile. Although turquoise-coloured X-ray quality crystals of **2** were obtained from acetonitrile, the significantly broadening of the ^1H NMR spectrum pattern of **2** in CD_3CN and THF-d_8 suggests the partial dissociation of **2**. Consequently, ideal NMR data of **2** could not be obtained in polar solvents. In addition, potassium graphite (KC_8) reduction of **1$^\bullet$** in THF quantitatively provided the lithium-potassium mixed alkali metal dithiolate dimer **3** (Scheme 2). However, trace amounts of O_2 results in the oxidation of **3**, yielding unidentified products with the colour change from colourless to purple.



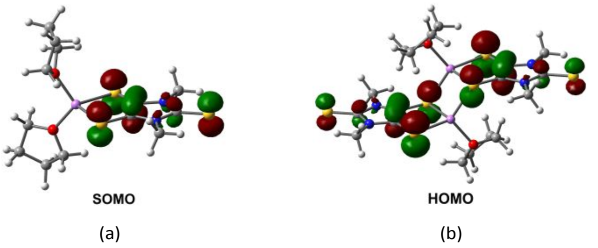
Scheme 2. Synthesis of compounds **2**, **3**, and **4** (R = 2,6-diisopropylphenyl).



Scheme 3. Previously reported synthetic routes of **5**.[41-43]

Reaction of **1$^\bullet$** with $Ph_3C^+BF_4^-$ (in a 1:1 ratio) in toluene leads to one-electron oxidation of **1$^\bullet$**,[40] giving orange-red crystals of **4** (a dimer of the neutral dithiolene ligand; L^0 in Fig. 1) in 55.3% yield (Scheme 2). Alternatively, **4** may also be obtained by dioxygen oxidation of **1$^\bullet$**. Notably, compound **5**, the analogue of **4**, has been synthesized as previously reported *via* two unique routes (Scheme 3): (1) sulfurization of imidazole-based dione with Lawesson's reagent;[41,42] and (2) oxidation of the nickel bis-dithiolene complex by Br_2.[41,43] Compounds **4** and **5** may serve as convenient platforms to access metal dithiolene complexes *via* reductive cleavage of the S-S bonds.[43]

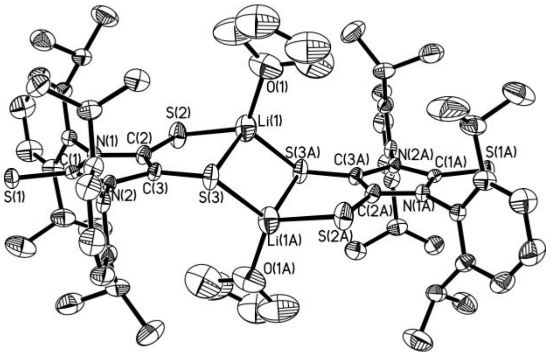
X-ray structural analysis[36] of **2** (Fig. 4) shows that the **[2]$^{2-}$** moieties contains two lithium dithiolene units dimerized through two Li–S bonds. With THF-coordination, each lithium atom is four-coordinate and adopts a distorted tetrahedral geometry. The central Li_2S_2 ring is planar, in which the bridging Li-S bond [2.396(15) Å] is ca. 0.13 Å shorter than those in the neighbouring LiS_2C_2 ring [2.525(16) Å]. The LiS_2C_2 rings in **2** are somewhat more bent than that in **1$^\bullet$** [the bend angle (η) between the LiS_2 plane and the S_2C_2 plane = 17.6° for **2** vs. 14.2° for **1$^\bullet$**].[34] By comparison with **1$^\bullet$** [d_{C-C} = 1.417(3) Å; d_{C-S} = 1.677(3) Å, av],[34] compound **2** exhibits shorter olefinic C–C bonds [1.362(8) Å] and concomitant longer C–S bonds [1.729(8) Å, av]. These distances compares well to those for the free dithiolate ligand $(NMe_4)_2(C_3S_5)$[44] [d_{C-C} = 1.371(8) Å; d_{C-S} = 1.724(6) Å] and the theoretical values for the simplified [**2-Me**]$^{2-}$ model (d_{C-C} = 1.375 Å; d_{C-S} = 1.754 Å).[36] The ligand-based HOMO of dimeric dithiolate [**2-Me**]$^{2-}$ (Fig. 3b) mainly involves C–C π-bonding and C–S π-antibonding character, which is relevant to the SOMO of its radical precursor **[1-Me]$^\bullet$**[36] (Fig. 3a) and consistent with the C–C and C–S bond distance change of the C_2S_2 units in **2** in comparison with those for **1$^\bullet$**.[34] Similar to that in **[1-Ph]$^\bullet$**,[34] the LiS_2C_2 rings in **[1-Me]$^\bullet$** and [**2-Me**]$^{2-}$ are nearly planar in the gas phase.



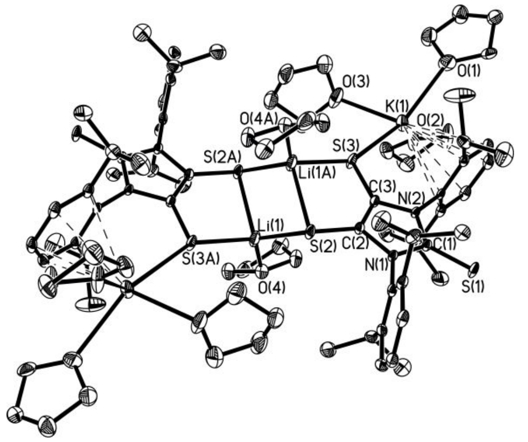
(a) (b)

Fig. 3 Selected molecular orbitals of the simplified models [**1-Me**]$^\bullet$ (a) and **[2-Me]$^{2-}$** (b).

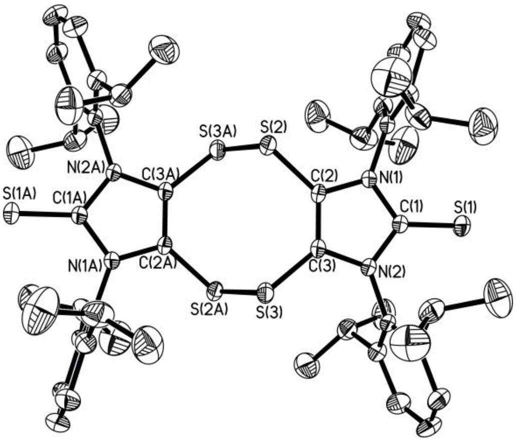
Compound **3** is a Li-K mixed metal dithiolate dimer in the solid state.[36] The central $[C_2S_2Li(THF)]_2$ core in **3** shows similar geometry and bonding parameters to that in **2** (see the caption of Fig. 4). The potassium cation in **3** is σ-bonded to a sulphur atom and coordinated to three THF molecules. The potassium-phenyl centroid distance (2.990 Å) in **3** compares well with that [3.034(9) Å] in $[\{K\{(2,6\text{-}iPr_2C_6H_3N)_2CH\}_2K(THF)_2\}_n]\cdot n$THF,[45] which suggests the presence of cation-π interaction between the potassium cation and the phenyl ring.[46] The S–K bond distance for **3** [3.1490(13) Å] is comparable to that in $[\{Ce(Cp^*)_2(dddt)K(thf)_2\}_2]$ (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate)[47] [3.26(5) Å] and in the simplified model **3-Ph** (3.210 Å).[36] The Wiberg bond indices of the K–S bonds in **3-Ph** are 0.11, suggesting their strong ionic character. In the solid state,[36] the central eight-membered C_4S_4 ring of **4** (Fig. 4) adopts a chair conformation as suggested by torsion angles [*i.e.*, C(2)-S(2)-S(3A)-C(3A), 97.81°; C(2)-C(3)-S(3)-S(2A), 75.50°], which are similar to those reported for **5** [C-S-S-C, 101.8(6)°; S-S-C-C, -82(1) and 79(1)°].[42] The C–C bonds [1.348(3) Å] and C–S bonds [1.739(2) Å] in the C_2S_2 units of **4** are also similar to those in **5** [d_{C-C} = 1.36(2) Å; d_{C-S} = 1.75(1) Å, av].[42] The S-S bond in **4** [2.0728(9) Å] is a typical single bond, involving predominant 3p character (92.50%).[36]



$[2]^{2-}$



3



4

Fig. 4 Molecular structures of $[\mathbf{2}]^{2-}$, **3**, and **4**. Thermal ellipsoids represent 30% probability: hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows. For $[\mathbf{2}]^{2-}$, C(1)–S(1) 1.680(6), C(2)–C(3) 1.362(8), C(2)–S(2) 1.724(6), C(3)–S(3) 1.733(6), S(2)–Li(1) 2.434(15), S(3)–Li(1) 2.525(16), S(3A)–Li(1) 2.396(15), O(1)–Li(1) 1.961(18); S(2)–C(2)–C(3) 131.1(5), C(2)–S(2)–Li(1) 92.0(4), S(2)–Li(1)–S(3) 93.6(5), S(3)–Li(1)–S(3A) 111.7(7), O(1)–Li(1)–S(2) 120.5(8). For **3**, C(1)–S(1) 1.701(3), C(2)–C(3) 1.366(5), C(2)–S(2) 1.733(3), C(3)–S(3) 1.732(4), S(2)–Li(1) 2.416(8), S(2)–Li(1A) 2.531(7), S(3)–Li(1A) 2.407(7), S(3)–K(1) 3.1490(13), O(4)–Li(1) 1.960(9); S(2)–C(2)–C(3) 130.7(3), C(2)–S(2)–Li(1A) 90.09(19), S(2)–Li(1A)–S(3) 94.2(2), S(2)–Li(1A)–S(2A) 110.8(3), C(3)–S(3)–K(1) 115.01(12). For **4**, C(1)–S(1) 1.655(2), C(2)–C(3) 1.348(3), C(2)–S(2) 1.739(2), C(3)–S(3) 1.739(2), S(3)–S(2A) 2.0728(9); S(2)–C(2)–C(3) 129.74(17), C(2)–S(2)–S(3A) 104.28(8).

Conclusions

While reactions of stable lithium dithiolene radical $\mathbf{1}^{\bullet}$ with Cp_2Co or KC_8 give the corresponding one-electron reduction product **2** and **3**, respectively, combination of $\mathbf{1}^{\bullet}$ with $Ph_3C^+BF_4^-$ (or O_2), *via* one-electron oxidation, leads to the isolation of **4**. Further application of these neutral (**4**), monanionic ($\mathbf{1}^{\bullet}$), and dianionic (**3**) dithiolene species in main group chemistry 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-1361178 (H.F.S.). We also want to thank Mr. Phan T. Truong for his assistance with the cyclic voltammetric measurements.

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 B. S. Lim, D. V. Fomitchev and R. H. Holm, *Inorg. Chem.*, 2001, **40**, 4257-4262.
15 H. B. Gray and E. Billig, *J. Am. Chem. Soc.*, 1963, **85**, 2019-2020.
16 E. I. Stiefel, J. H. Waters, E. Billig and H. B. Gray, *J. Am. Chem. Soc.*, 1965, **87**, 3016-3017.
17 S. Kokatam, K. Ray, J. Pap, E. Bill, W. E. Geiger, R. J. LeSuer, P. H. Rieger, T. Weyhermuller, F. Neese and K. Wieghardt, *Inorg. Chem.*, 2007, **46**, 1100-1111.
18 J. E. Huyett, S. B. Choudhury, D. M. Eichhorn, P. A. Bryngelson, M. J. Maroney and B. M. Hoffman, *Inorg. Chem.*, 1998, **37**, 1361-1367.
19 C. Milsmann, E. Bothe, E. Bill, T. Weyhermuller and K. Wieghardt, *Inorg. Chem.*, 2009, **48**, 6211-6221.
20 C. Milsmann, G. K. Patra, E. Bill, T. Weyhermuller, S. D. George and K. Wieghardt, *Inorg. Chem.*, 2009, **48**, 7430-7445.
21 R. K. Szilagyi, B. S. Lim, T. Glaser, R. H. Holm, B. Hedman, K. O. Hodgson and E. I. Solomon, *J. Am. Chem. Soc.*, 2003, **125**, 9158-9169.
22 R. Sarangi, S. D. George, D. J. Rudd, R. K. Szilagyi, X. Ribas, C. Rovira, M. Almeida, K. O. Hodgson, B. Hedman and E. I. Solomon, *J. Am. Chem. Soc.*, 2007, **129**, 2316-2326.
23 R. R. Kapre, E. Bothe, T. Weyhermuller, S. D. George and K. Wieghardt, *Inorg. Chem.*, 2007, **46**, 5642-5650.
24 K. Ray, S. D. George, E. I. Solomon, K. Wieghardt and F. Neese, *Chem. - Eur. J.*, 2007, **13**, 2783-2797.
25 N. Tenn, N. Bellec, O. Jeannin, L. Piekara-Sady, P. Auban-Senzier, J. Iniguez, E. Canadell and D. Lorcy, *J. Am. Chem. Soc.*, 2009, **131**, 16961-16967.
26 A. Filatre-Furcate, N. Bellec, O. Jeannin, P. Auban-Senzier, M. Fourmigue, A. Vacher and D. Lorcy, *Inorg. Chem.*, 2014, **53**, 8681-8690.
27 T. J. Morsing, S. N. MacMillan, J. W. H. Uebler, T. Brock-Nannestad, J. Bendix and K. M. Lancaster, *Inorg. Chem.*, 2015, **54**, 3660-3669.
28 G. A. Russell and M. Zaleta, *J. Am. Chem. Soc.*, 1982, **104**, 2318.
29 G. A. Russell, W. C. Law and M. Zaleta, *J. Am. Chem. Soc.*, 1985, **107**, 4175-4182.
30 D. Buddensiek, B. Koepke and J. Voss, *Chem. Ber.*, 1987, **120**, 575-581.
31 B. Roth, H. Bock and H. Gotthardt, *Phosphorus, Sulfur Relat. Elem.*, 1985, **22**, 109-119.
32 M. Yamaguchi and T. Shida, *J. Phys. Chem. A*, 2016, **120**, 3570-3577.
33 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.
34 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.
35 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.
36 See the supporting information for synthetic, computational, and crystallographic details.
37 A. Filatre-Furcate, N. Bellec, O. Jeannin, P. Auban-Senzier, M. Fourmigue, A. Vacher and D. Lorcy, *Inorg Chem*, 2014, **53**, 8681-8690.
38 P. Falaras, C. A. Mitsopoulou, D. Argyropoulos, E. Lyris, N. Psaroudakis, E. Vrachnou and D. Katakis, *Inorg. Chem.*, 1995, **34**, 4536-4542.
39 R. T. Boere and T. L. Roemmele, *Coord. Chem. Rev.*, 2000, **210**, 369-445.
40 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877-910.
41 P. Deplano, M. L. Mercuri, G. Pintus and E. F. Trogu, *Comments Inorg. Chem.*, 2001, **22**, 353-374.
42 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.
43 F. Bigoli, S. Currelli, P. Deplano, L. Leoni, M. L. Mercuri, M. A. Pellinghelli, A. Serpe and E. F. Trogu, *J. Chem. Soc., Dalton Trans.*, 2002, 1985-1991.
44 J. G. Breitzer, A. I. Smirnov, L. F. Szczepura, S. R. Wilson and T. B. Rauchfuss, *Inorg. Chem.*, 2001, **40**, 1421-1429.
45 A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, G. Kociok-Kohn and P. A. Procopiou, *Inorg. Chem.*, 2008, **47**, 7366-7376.
46 S. L. De Wall, L. J. Barbour and G. W. Gokel, *J. Am. Chem. Soc.*, 1999, **121**, 8405-8406.
47 M. Roger, L. Belkhiri, P. Thuery, T. Arliguie, M. Fourmigue, A. Boucekkine and M. Ephritikhine, *Organometallics*, 2005, **24**, 4940-4952.