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Carbene-mediated synthesis of a germanium tris(dithiolene)dianion†

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While the 1:1 reaction of **3** with an N-heterocyclic carbene ((Me)CN(i-Pr)₂C:) in THF resulted in ligand-substituted product **4**, the corresponding 1:2 reaction (in the presence of H₂O) gives the first structurally characterized germanium tris(dithiolene)dianion **5** as the major product and the “naked” dithiolene radical **6**[•] as a minor by-product. The structure and bonding of **4** and **5** were probed by experimental and theoretical methods. Our study suggests that carbene-mediated partial hydrolysis may represent a new method to access tris(dithiolene) complexes of main-group elements.

The intriguing non-innocent character of dithiolene ligands has fascinated chemists for more than five decades.^{1–4} In contrast to the well documented dithiolene chemistry of transition metals,^{5–7} the corresponding dithiolene-based chemistry of main group elements remains quite limited.^{1,4} In particular, the literature reveals only a few tris(dithiolene) complexes of main group elements.^{4,8–17} This laboratory recently reported a stable lithium dithiolene radical anion (**1**[•]), *via* the reaction of the N-heterocyclic dicarbene (NHDC)¹⁸ with elemental sulphur (Scheme 1).¹⁹ Interestingly, radical **1**[•] may well serve as a novel platform to explore the dithiolene chemistry of the main group elements. To this end, a series of magnesium²⁰ and boron²¹ dithiolene complexes have been reported. In addition, the first “naked” dithiolene radical anion (**6**[•]) (Scheme 1) was recently synthesized (by reaction of **1**[•] with an imidazolium salt [(Me)CN(i-Pr)₂CH]⁺Cl[–]),²² which, surprisingly, participated in a synergic THF ring-open reaction with N-heterocyclic silylene and the hexasulphide dianion. In addition, we recently reported the reaction of **1**[•] with carbene-stabilized disilicon, which afforded the first silicon tris(dithiolene)dianion (**2**) (Scheme 1).¹⁶ Notably,

the carbene-stabilized disilicon complex functioned as a silicon transfer agent in this reaction.

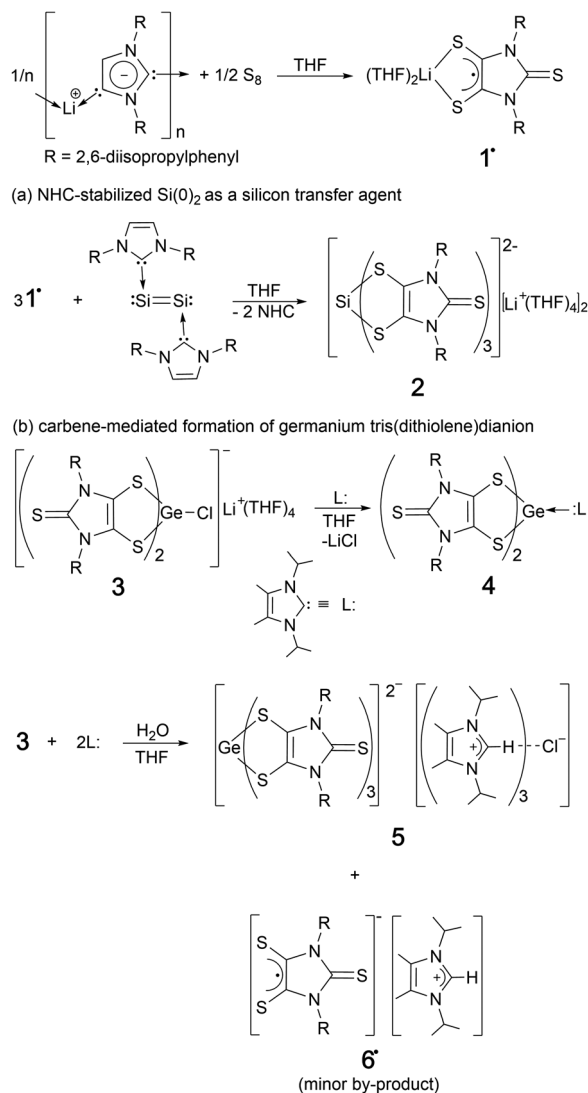
Complexes of hypervalent group 14 elements are intriguing due to their unique structural/bonding nature, high reactivity, and possible utility in studying dynamic processes.²³ Interestingly, six-coordinate germanium(IV)-diketonate complexes have been explored as anticancer agents.²⁴ Notably, six-coordinate germanium atoms residing in an S₆ coordination environment are quite rare, the literature revealing only a germanium tris(dithiolene) complex reported nearly half a century ago.¹⁷ However, compelling structural detail of such compounds is lacking. Herein, we report the synthesis,²⁵ molecular structure,²⁵ and computations²⁵ of the first structurally characterized germanium tris(dithiolene)dianion (**5**).

The anionic chlorogermanium bis(dithiolene) complex **3** was prepared *via* a 2:1 reaction of **1**[•] with GeCl₂-dioxane in THF.¹⁹ The subsequent 1:1 reaction of **3** with the N-heterocyclic carbene {(Me)CN(i-Pr)₂C:} afforded a reddish slurry, from which **4** was isolated as a red solid (87.5% yield) (Scheme 1). X-ray quality single crystals of **4** were ultimately obtained by crystallization in 1,2-difluorobenzene. Compound **4** demonstrates poor solubility in common polar solvents. Consequently, an ideal ¹³C NMR spectrum proved difficult to obtain. The 1:2 reaction of **3** with {(Me)CN(i-Pr)₂C:} gave **4** first (which was confirmed by the ¹H NMR tube reaction in THF-d₈) and finally resulted in the formation of **5** over 24 h. While **5** was isolated as dark blue microcrystals from the parent solution as major product (75.7% yield) (Scheme 1), the dark purple radical **6**^{•22} was obtained as a minor by-product. **5** can be readily separated from **6**[•] due to their different solubility in THF. Recrystallization in 1,2-difluorobenzene gives X-ray quality single crystals of **5**. The free imidazolium salt [(Me)CN(i-Pr)₂CH]⁺Cl[–], as another by-product, was isolated and confirmed by the ¹H NMR spectroscopy in D₂O. The 8.75 ppm singlet ¹H NMR resonance of **5** indicates the presence of the imidazolium moiety in this molecule. The synthesis of **5** in polar solvents such as THF or 1,2-difluorobenzene may involve carbene-mediated partial hydrolysis of **4**. Indeed, partial hydrolysis of the carbene-complexed magnesium dithiolene complex has been previously

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Scheme 1 (a) previous work: synthesis of **2** using NHC-stabilized $\text{Si}(\text{O})_2$ as a silicon transfer agent. (b) Synthesis of **4** and **5** (note: H_2O is either added or from THF).

proposed by this laboratory.²⁰ To support this deduction, two equivalent water (as a 0.1% v/v solution in THF) was added to the 1 : 2 mixture of **3** with $\{(\text{Me})\text{CN}(\text{i-Pr})_2\text{C}\}$ in THF, which led to the rapid change of the solution colour from red (for **4**) into dark blue (for the mixture of **5** and **6***). The compounds **5** and **6***, which were achieved from this 'water-added' route, were characterized by X-ray single crystal diffraction technique. By comparison, without the addition of water, the **4**-to-**5** conversion undergoes obviously slower due to the lower concentration of H_2O in the original THF solution. Indeed, we observed that without adding water, large amount of THF have to be employed in order to effectively synthesize **5**. While the mechanism remains obscured, it is plausible that an *in situ* produced OH^- species (from protonation of the carbene by H_2O) would react with germanium or lithium cations (affording the corresponding metal hydroxides). Consequently, a free dithiolate dianion could be eliminated from one germanium bis(dithiolene) complex, and

subsequently captured by a second germanium bis(dithiolene) complex, giving **5**. The isolation of (minor by-product) **6*** supports the *in situ* formation of the free dithiolate species. The free dithiolate species may either participate in the formation of **5** or undergo one-electron oxidation (by trace amount of O_2 in the system) to give **6***.

X-ray structural analysis confirms that, in contrast to **3**,¹⁹ wherein the five-coordinate $\text{Ge}(\text{IV})$ centre adopts an approximate square pyramidal geometry ($\tau^{29} = 0.02$), the germanium atom in **4** assumes a slightly distorted trigonal bipyramidal geometry ($\tau = 0.98$) (Fig. 1).²⁵ While the Ge-S bond distances in **3** are in a range from 2.3290(8) Å to 2.3561(8) Å, the Ge-S_{eq} bonds in **4** [2.2610(4) and 2.2667(4) Å] are obviously shorter than the Ge-S_{ax} bonds [2.4052(4) and 2.4136(4) Å]. Concomitantly, the C-S_{eq} bonds [1.7445(15) Å, av] are *ca.* 0.02 Å longer than the C-S_{ax} bonds [1.7266(14) Å, av] in **4**.²⁵ The NHC ligand resides at an equatorial position with a 2.0101(14) Å Ge-C_{NHC} bond, which is in the range (1.90–2.05 Å) of typical Ge-C single bonds.³⁰ The bend angle¹ (η) between the GeS_2 plane and S_2C_2 plane in **4** (14.0° , av) is obviously less than those in **3** (37.3° , av).¹⁹

X-ray structural analysis²⁵ reveals the presence of one pair of Λ - and Δ -enantiomers of **5** in the asymmetric unit (Fig. 1; for clarity, only the structural parameters of the Δ enantiomer of **5** are shown in the caption of Fig. 1). In **5** the germanium tris(dithiolene) moiety exists as a dianion with a rare $\{[(\text{Me})\text{CN}(\text{i-Pr})_2\text{CH}^+]\text{Cl}^-\}$ counter-dication (Fig. 1). In the dicationic unit of **5**, the central chloride is bound by three imidazolium cations *via* $\text{C-H}\cdots\text{Cl}$ hydrogen bonds [$d_{\text{H}\cdots\text{Cl}} = 2.49$ Å (av), $\theta_{\text{C-H}\cdots\text{Cl}} = 155^\circ$ (av)].³¹ All hydrogen atoms at the C2 carbons of imidazolium fragments in **5** were located from difference Fourier maps. Both **2** [trigonal twist angle (ϕ) = 56.5° , $s/h = 1.14$]^{16,32} and **5** [ϕ] = 53.6° (av), $s/h = 1.17$ (av)] adopt an octahedral geometry, which involves the elongated distortion considering their less than 1.22 s/h ratios [For a regular octahedron, (ϕ) = 60° , $s/h = 1.22$].²⁷ For **5**, the bend angle (η) between the GeS_2 plane and the C_2S_2 plane (34.8° , av) is between those for **3** (37.3° , av)¹⁹ and those for **4** (14.0° , av). The olefinic C-C bonds [1.345(5)–1.353(5) Å] and C-S bonds [1.712(4)–1.731(4) Å] in the C_2S_2 units of **5** are consistent with those in reported dithiolates.¹ Thus, like that in **3**,¹⁹ the central germanium atom in dianionic **5** has an oxidation state of +4. The Ge-S bonds in **5** [2.3887(10)–2.4381(11) Å] are comparable to those in **3** and **4** [2.2610(4)–2.4052(4) Å].^{19,25}

The bonding nature of **4** and **5** were further probed by B3LYP/6-311G**density functional theory (DFT) computations on the simplified **4-Me** and Δ -[**5-Me**]²⁻ models, respectively.²⁵ The optimized structures of **4-Me** and Δ -[**5-Me**]²⁻ models are consistent with the solid-state structures of **4** and **5**. Notably, the Ge-C_{NHC} bond (2.088 Å), Ge-S_{eq} bonds (2.348 Å, av), and Ge-S_{ax} bonds (2.442 Å, av) of **4-Me** are slightly longer than those of **4** ($d_{\text{Ge-C}(\text{NHC})} = 2.010$ Å; $d_{\text{Ge-S}(\text{eq})} = 2.264$ Å, av; $d_{\text{Ge-S}(\text{ax})} = 2.409$ Å, av). The Ge-S bonds (2.499–2.526 Å) of Δ -[**5-Me**]²⁻ are also somewhat longer than those in **5** [2.3887(10)–2.4381(11) Å]. While LUMOs of **4-Me** and Δ -[**5-Me**]²⁻ involve germanium-sulphur and germanium-carbon (for **4-Me** only) antibonding interactions, HOMOs of **4-Me** and Δ -[**5-Me**]²⁻ are mainly dithiolene ligand-based, bearing both C-C π -bonding and C-S π -antibonding features (Fig. 2). Natural bond orbital (NBO) analysis shows that both Ge-S bonds and Ge-C_{NHC}

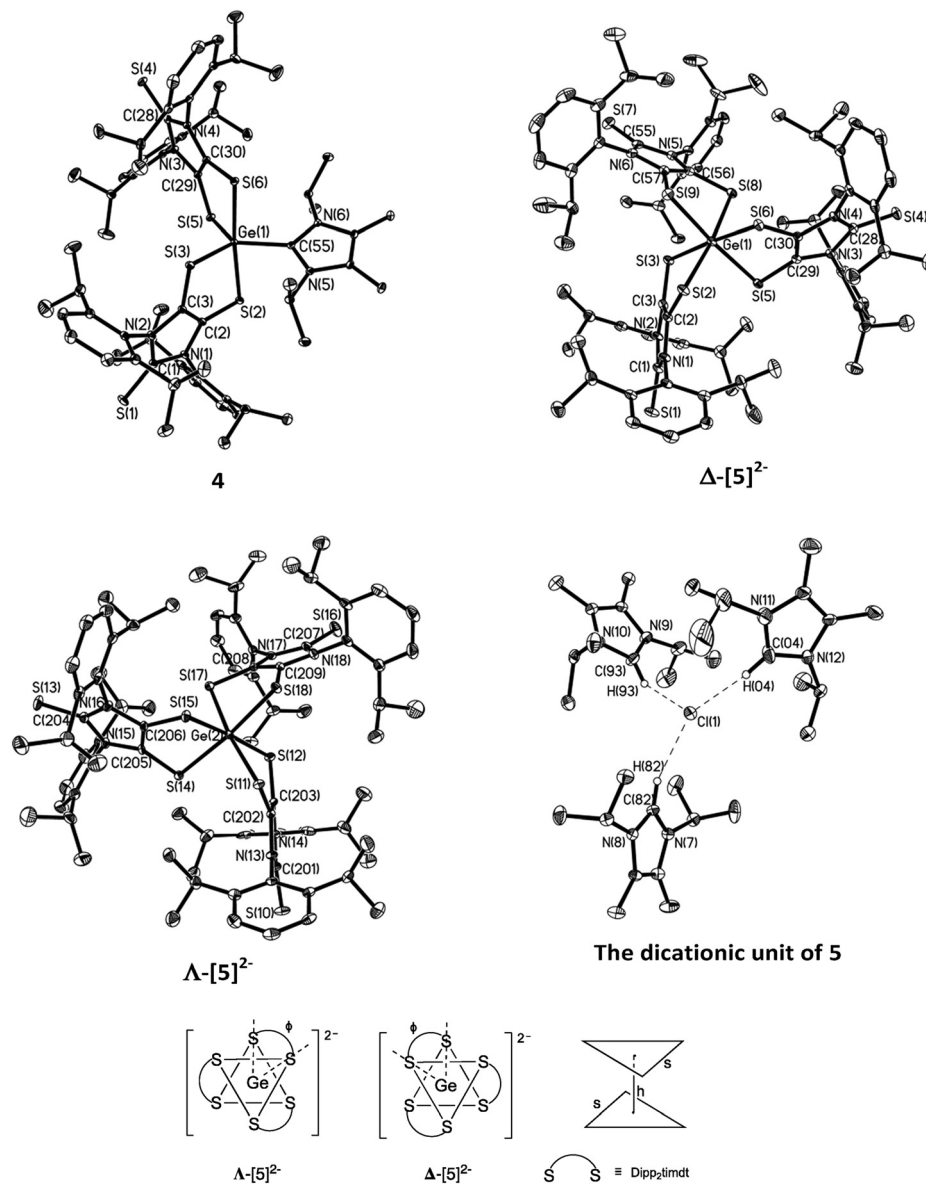


Fig. 1 Molecular structures of **4** and **5** dianion (thermal ellipsoids represent 30% probability; hydrogen atoms on carbons are omitted for clarity). Selected bond distances (Å) and angles (deg): for **4**, C(2)–C(3) 1.350(2), C(2)–S(2) 1.7269(15), C(3)–S(3) 1.7459(15), S(2)–Ge(1) 2.4052(4), S(3)–Ge(1) 2.2667(4), S(5)–Ge(1) 2.2610(4), S(6)–Ge(1) 2.4136(4), C(55)–Ge(1) 2.0101(14); S(2)–Ge(1)–S(6) 175.03(1), S(3)–Ge(1)–C(55) 122.13(4), S(5)–Ge(1)–C(55) 121.80(4), S(3)–Ge(1)–S(5) 116.07(2). For Δ -**5**, C(2)–C(3) 1.352(5), C(2)–S(2) 1.719(4), C(3)–S(3) 1.721(4), S(2)–Ge(1) 2.4161(11), S(3)–Ge(1) 2.4286(11); S(2)–Ge(1)–S(3) 89.07(4), S(2)–Ge(1)–S(8) 173.99(4), S(2)–Ge(1)–S(5) 94.63(4). Schematic representation of enantiomers of [5] $^{2-}$ (trigonal twist angle ϕ , triangle side s , intertriangle distance h , Dipp $_2$ timdt = diisopropylphenyl-substituted imidazolidine-2,4,5-trithione).^{27,28}

bond in **4-Me** and Ge–S bonds in Δ -[5-Me] $^{2-}$ are polarized. For **4-Me**, while the Ge–C_{NHC} σ bond polarization is 23.5% toward germanium and 76.5% toward carbon, the Ge–S_{ax} σ bond polarization [23.1% (av) toward germanium and 76.9% (av) toward sulphur] is stronger than that of the Ge–S_{eq} σ bonds [30.9% (av) toward germanium and 69.1% (av) toward sulphur]. For Δ -[5-Me] $^{2-}$, the average Ge–S σ bond polarization is 20.4% toward germanium and 79.6% toward sulphur. The positive natural charges of the germanium atoms in **4-Me** and Δ -[5-Me] $^{2-}$ are +0.82 and +0.65, respectively. Notably, the equatorial sulphur atoms in **4-Me** bear an average negative charge of –0.07, which is somewhat less than that of the

axial sulphur atoms in **4-Me** (–0.16) and each sulphur atom bound to the central germanium atom in Δ -[5-Me] $^{2-}$ (–0.15, av).²⁵

In a 1 : 1 reaction of **3** with {(Me)CN(i-Pr)}₂C; the N-heterocyclic carbene may replace the axial chloride ligand in the five-coordinate germanium bis(dithiolene) complex (**3**), giving a carbene-complexed germanium bis(dithiolene) (**4**). However, the corresponding 1 : 2 reaction gave a mixture containing both the first structurally characterized germanium tris(dithiolene)dianion **5** (the major product) and **6** $^{\bullet}$ (the minor by-product). This chemical transformation may involve carbene-mediated partial hydrolysis of the germanium bis(dithiolene) species.

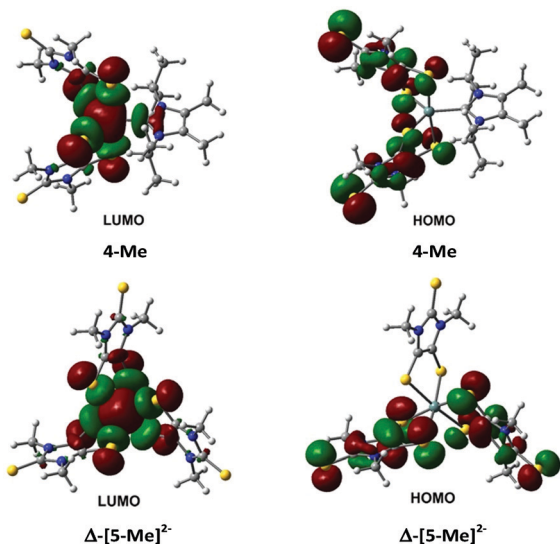


Fig. 2 Frontier molecular orbitals of **4-Me** and Δ -[5-Me]²⁻ models.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 E. I. Stiefel, *Dithiolene Chemistry: Synthesis, Properties, and Applications*, John Wiley & Sons, Hoboken, NJ, 2004.
- 2 R. Eisenberg and H. B. Gray, *Inorg. Chem.*, 2011, **50**, 9741–9751.
- 3 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49–221.
- 4 S. Sproules, *Prog. Inorg. Chem.*, 2014, **58**, 1–144.
- 5 R. Kato, *Chem. Rev.*, 2004, **104**, 5319–5346.
- 6 B. Garreau-de Bonneval, K. I. M. C. Ching, F. Alary, T. T. Bui and L. Valade, *Coord. Chem. Rev.*, 2010, **254**, 1457–1467.
- 7 S. Sproules and K. Wieghardt, *Coord. Chem. Rev.*, 2011, **255**, 837–860.
- 8 F. W. B. Einstein and R. D. G. Jones, *J. Chem. Soc. A*, 1971, 2762–2766.
- 9 B. Wenzel, B. Wehse, U. Schilde and P. Strauch, *Z. Anorg. Allg. Chem.*, 2004, **630**, 1469–1476.
- 10 R. O. Day, J. M. Holmes, S. Shafieezad, V. Chandrasekhar and R. R. Holmes, *J. Am. Chem. Soc.*, 1988, **110**, 5377–5383.
- 11 F. de Assis, Z. H. Chohan, R. A. Howie, A. Khan, J. N. Low, G. M. Spencer, J. L. Wardell and S. M. S. V. Wardell, *Polyhedron*, 1999, **18**, 3533–3544.
- 12 T. Akasaka, M. Nakano, H. Tamura and G. E. Matsubayashi, *Bull. Chem. Soc. Jpn.*, 2002, **75**, 2621–2628.
- 13 J. Wegener, K. Kirschbaum and D. M. Giolando, *J. Chem. Soc., Dalton Trans.*, 1994, 1213–1218.
- 14 J. M. Kisenyi, G. R. Willey, M. G. B. Drew and S. O. Wandiga, *J. Chem. Soc., Dalton Trans.*, 1985, 69–74.
- 15 G. M. Spencer, J. L. Wardell and J. H. Aupers, *Polyhedron*, 1996, **15**, 2701–2706.
- 16 Y. Wang, C. A. Tope, Y. Xie, P. Wei, J. L. Urbauer, H. F. Schaefer III and G. H. Robinson, *Angew. Chem., Int. Ed.*, 2020, **59**, 8864–8867.
- 17 E. S. Bretschneider, C. W. Allen and J. H. Waters, *J. Chem. Soc. A*, 1971, 500–503.
- 18 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.
- 19 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.
- 20 Y. Wang, N. A. Maxi, Y. Xie, P. Wei, H. F. Schaefer III and G. H. Robinson, *Chem. Commun.*, 2019, **55**, 8087–8089.
- 21 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.
- 22 Y. Wang, Y. Xie, P. Wei, S. A. Blair, D. Cui, M. K. Johnson, H. F. Schaefer and G. H. Robinson, *J. Am. Chem. Soc.*, 2020, **142**, 17301–17305.
- 23 Y. I. Baukov and S. N. Tandura, *The Chemistry of Organic Germanium, in Tin and Lead Compounds*, ed. Z. Rappoport, John Wiley & Sons Ltd, Chichester, 2002, pp. 963–1240.
- 24 R. T. Mertens, S. Parkin and S. G. Awuah, *Inorg. Chim. Acta*, 2020, 503.
- 25 See the supporting information for synthetic, computational, and crystallographic details.
- 26 N. Kuhn and T. Kratz, *Synthesis*, 1993, 561–562.
- 27 E. I. Stiefel and G. F. Brown, *Inorg. Chem.*, 1972, **11**, 434–436.
- 28 K. R. Dymock and G. J. Palenik, *Inorg. Chem.*, 1975, **14**, 1220–1222.
- 29 A. W. Addison, T. N. Rao, J. Reedijk, J. Vanriijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349–1356.
- 30 K. M. Baines and W. G. Stibbs, *Coord. Chem. Rev.*, 1995, **145**, 157–200.
- 31 C. B. Aakeroy, T. A. Evans, K. R. Seddon and I. Palinko, *New J. Chem.*, 1999, **23**, 145–152.
- 32 The trigonal twist angles (ϕ) of **2** and its simplified model $[2\text{-H}]^{2-}$ that were previously reported in ref. 16 should be corrected as 56.5° and 57.1°, respectively, according to the method in ref. 29.