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## COMMUNICATION

## Reaction of $L_2Zn_2$ with $Ph_2E_2$ – Synthesis of $LZnEPh$ and reactions with oxygen and H-acidic substrates

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Dedicated to Prof. Edgar Niecke on the occasion of his 75th birthday

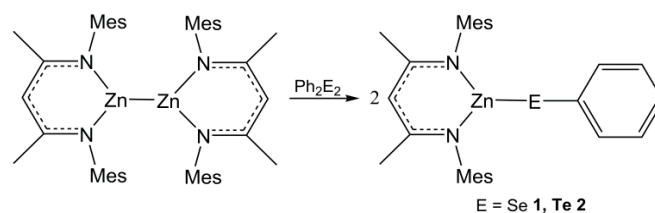
$L_2Zn_2$  ( $L = HC[C(Me)N(2,4,6-Me_3C_6H_2)]_2$ ) and  $Ph_2E_2$  ( $E = Se, Te$ ) react with formation of  $LZnSePh$  (**1**) and  $LZnTePh$  (**2**). **1** and **2** further react with  $H_2O$  and  $EtOH$  with formation of  $LZnOH$  (**3**) and  $LZnOEt$  (**4**), respectively, whereas the reaction of **2** with oxygen yielded  $[LZnOTe(O)Ph]_2$  (**5**). **1**, **4** and **5** were characterized by single crystal X-ray diffraction.

The discovery of  $[η^5-Cp^*_2Zn_2]$ ,<sup>[1]</sup> the first organozinc(I) complex with a zinc-zinc bond, has boosted research activities on univalent zinc complexes. Since then, almost 25 Zn(I) complexes have been structurally characterized and their chemical reactivity was investigated.<sup>[2]</sup> Reactions with Lewis bases and H-acidic compounds were found to proceed with preservation of the Zn-Zn bond,<sup>[3]</sup> and reactions with transition metal complexes demonstrated the capability of  $Cp^*_2Zn$  and  $Cp^*_2Zn_2$  to stabilize transition metal complexes.<sup>[4]</sup> In addition, the electrochemical behavior of  $Cp^*_2Zn_2$  was studied by CV,<sup>[5]</sup> and the capability of  $Cp^*_2Zn_2$  to serve as pre-catalysts for intermolecular hydroamination reactions was shown.<sup>[6]</sup>

Surprisingly, selective insertion reactions into the Zn-Zn bond and reactions, in which Zn(I) complexes serve as reducing agent comparable to Mg(I) complexes,<sup>[7,8]</sup> are almost unknown. Only the reaction of an  $\alpha$ -diimine stabilized Zn(I) complex with  $PhCCH$ , which occurred with  $H_2$  elimination,<sup>[9]</sup> and oxidative addition reactions of a Zn(I) complex with alkyl halides, yielding 1:1 mixtures of  $ZnR_2$  and  $ZnX_2$ , were reported.<sup>[10]</sup> Due to our long-term interest in the reactivity of low-valent organometallic complexes,<sup>[11]</sup> we recently investigated reactions of  $L_2Zn_2$  ( $L = HC[C(Me)N(2,4,6-Me_3C_6H_2)]_2$ ) with group 14 azides, yielding the first zinc hexazene complex.<sup>[12]</sup> We now report on the reaction of  $L_2Zn_2$  with  $Ph_2E_2$  ( $E = Se, Te$ ), yielding  $LZnEPh$  ( $E = Se$  **1**,  $Te$  **2**). Moreover, reactions of **1** and **2** with H-acidic substrates and  $O_2$  (**2**) are reported.

Insertion reactions of chalcogen atoms into the Zn-Zn bond of univalent Zn(I) complexes by reaction with elemental chalcogenes E or chalcogenophosphoranes  $Bu_3P=E$  ( $E = Se, Te$ ) failed. In contrast, reactions of  $L_2Zn_2$  with one equivalent of  $Ph_2E_2$  gave the zinc

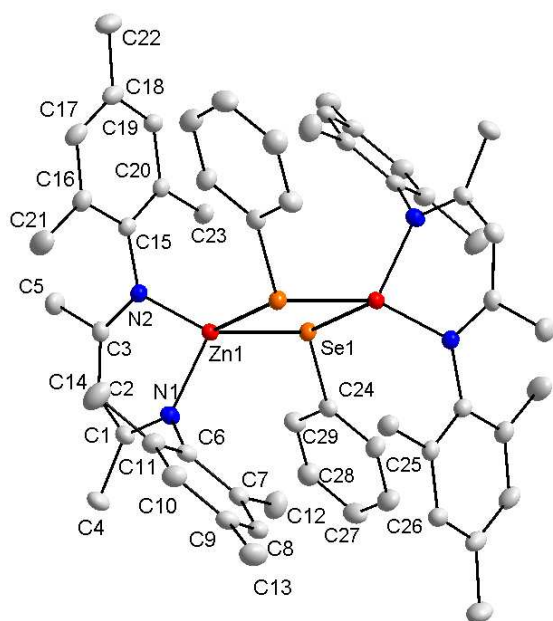
chalcogenide complexes  $LZnEPh$  ( $E = Se$  **1**,  $Te$  **2**). **1** and **2** were characterized by  $^1H$  and  $^{13}C$  NMR spectroscopy. The spectra showed the resonances due to the  $\beta$ -diketiminato and the Ph group in a relative intensity of 1:1. The resonances of the  $\beta$ -diketiminato group are slightly shifted compared to those of the starting Zn(I) complex. The  $^{125}Te$  NMR spectrum of **2** shows a resonance at 416 ppm as is typical for Te(II) compounds.<sup>[13]</sup> Recently, reactions of  $R_2E_2$  with  $RSnSnR$  and intramolecular-stabilized Sb(I) and Bi(I) complexes were reported to proceed with E-E-bond cleavage.<sup>[14]</sup>

Scheme 1 Synthesis of **1** and **2**.

X-ray quality crystals of **1** were obtained from a solution in fluorobenzene upon storage at 4 °C for 12h. **1** crystallizes in the monoclinic space group  $P2_1/n$  with two molecules in the elemental cell. The molecule is located on a centre of inversion. The six-membered  $C_3N_2Zn$  rings are almost planar (deviation of Zn from least-squares plane of the ligand 0.6013(19) Å, r.m.s. deviation of the ligand atoms from the plane 0.0447 Å) and the average C-C (1.410(2) Å), C-N (1.330(4) Å) and Zn-N (1.973(7) Å) bond lengths are almost identical to those in  $L_2Zn_2$ .<sup>[15]</sup> The Zn-Se bonds of 2.4291(5) and 2.5951(6) Å are within the typical range observed for Zn-Se bonds with fourfold-coordinated Zn and threefold-coordinated Se.<sup>[16]</sup> The endocyclic Se-Zn-Se bond angle (89.003(14)°) is slightly smaller than the Zn-Se-Zn bond angle (90.997(14)°).

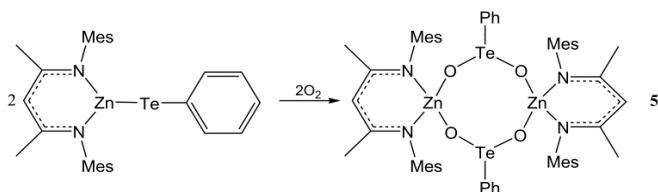
Since X-ray quality crystals of **2** could not be obtained, we investigated reactions of **1** and **2** with H-acidic substrates. Treatment of **1** with water and ethanol proceeded with formation of  $PhSeH$ , which was identified by its  $^{77}Se$  NMR spectrum (SI), as well as  $LZnOH$

(3) and LZnOEt (4), which were identified by NMR spectroscopy and by single crystal X-ray analysis (4).<sup>[17]</sup> Reaction of 2 with water and ethanol gave a dark-red solution, from which 3 and 4 could also be isolated. However, <sup>125</sup>Te NMR spectroscopy studies did not reveal the formation of PhTeH (SI). Instead, a new resonance at 3210 ppm most likely indicates the formation of [Te<sub>4</sub>]<sup>2+</sup> dication.



**Fig. 1** Solid state structure of **1**; inversion center in the ring center. Labelled non-H-atoms of the asymmetric unit and symmetry-generated (-x+1,-y,-z+2) atoms shown as thermal ellipsoids (50% probability levels); H atoms omitted for clarity.

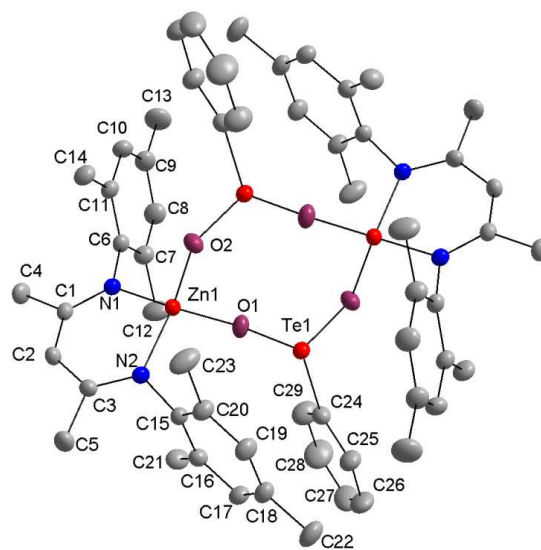
Finally, the reaction of 2 with O<sub>2</sub> was investigated, yielding 5. The <sup>1</sup>H and <sup>13</sup>C NMR resonances of the β-diketiminato and the Ph group of 5 are slightly shifted compared to those of 2. The <sup>125</sup>Te NMR spectrum of 5 shows a resonance at 1681 ppm, which is shifted to lower field as is typical for telluroxanes.<sup>[13]</sup>



**Scheme 2** Synthesis of **5**.

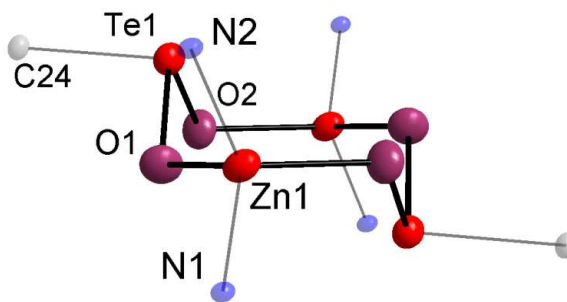
Colourless crystals of 5 were obtained upon storage of a solution of 5 in fluorobenzene at 18 °C. 5 crystallizes in the monoclinic space group *P*<sub>2</sub>/*c* with four C<sub>6</sub>H<sub>5</sub>F molecules, each of them disordered over two positions, in the unit cell and adopts a dimeric structure with a crystallographic inversion centre that renders the two halves of the molecule equivalent. The Zn atoms in 5 are slightly out of the plane of the six-membered C<sub>3</sub>N<sub>2</sub>Zn rings (deviation from least-squares plane of the ligand 0.213(2) Å, r.m.s. deviation of the ligand atoms from the plane 0.0248 Å) and the average C-C (1.407 Å) and C-N (1.326 Å) bond lengths as well as Zn-N (Zn1-N1 1.9620 (14), Zn1-N2 1.9589(14) Å) bond lengths within the C<sub>3</sub>N<sub>2</sub>Zn ring are almost identical to those in L<sub>2</sub>Zn<sub>2</sub>.<sup>[15]</sup> The average Zn-O bond lengths (Zn1-O1 1.9678 (13), Zn1-O2

1.9553(13) Å) within the envelope-type eight-membered Zn<sub>2</sub>Te<sub>2</sub>O<sub>4</sub> ring are also within the typical range observed for Zn(II) alkoxides.<sup>[18]</sup>



**Fig. 2** Solid state structure of **5**; inversion center in the ring center. Labelled non-H-atoms of the asymmetric unit and symmetry-generated (-x+1,-y+2,-z+1) atoms shown as thermal ellipsoids (50% probability levels); H atoms omitted for clarity.

The Te-O bonds (Te1-O1 1.8524(13), Te1-O2A 1.8529 (12) Å) compare well to the mean value (1.913(46) Å) for this substructure fragment as derived from a CSD search.<sup>[19]</sup> The bond order within tellurates can be described as 1.5, hence their Te-O bond lengths are typically shorter compared to Te-O single bonds (roughly 2 Å). The endocyclic O1-Te1-O2' bond angle (98.79(6)°) is slightly smaller compared to the endocyclic O1-Zn1-O2 (102.67(6)°) bond angle. The C-Te-O bond angles (O1-Te1-C24 97.71(7)°, O2'-Te1-C24 95.70(6)°) are close to 90°, indicating a high p-character of the bonding electron pairs as is typical for the heaviest main group elements.



**Fig. 3** Representation of the central Zn<sub>2</sub>Te<sub>2</sub>O<sub>4</sub> ring of **5**; ring atoms shown as thermal ellipsoids at 50% probability levels; ipso-atoms of the substituents shown (50% transparency) at 20% probability levels for clarity.

5 represents a rare example of a metalated tellurinic acid (RTe(O)OH). Aryltellurinic(IV) acids [RTe(O)(OH)]<sub>n</sub>, typically prepared by base hydrolysis of tellurium trichlorides RTeCl<sub>3</sub>, and their corresponding anhydrides [RTeO<sub>1.5</sub>]<sub>n</sub> are mostly ill-defined, amorphous substances. Only recently, well-defined molecular tellurinic acids and oligomeric tellurinic anhydrides were reported.<sup>[20-22]</sup> The sodium salts of both acids<sup>[20,23]</sup> and two stannatellurates RTeO<sub>2</sub>Sn(Cl)t-Bu<sub>2</sub> (R = 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 8-Me<sub>2</sub>NC<sub>10</sub>H<sub>6</sub>) were also structurally characterized.<sup>[24]</sup>

## Conclusions

Oxidative addition reactions of Ph<sub>2</sub>E<sub>2</sub> (E = Se, Te) with L<sub>2</sub>Zn<sub>2</sub> yield molecular zinc chalcogenides LZnEPH (E = Se **1**, Te **2**). **2** reacts with oxygen selectively with oxidation of Te(II) to Te(IV) and formation of **5**. **5** represents the first well defined molecular transition metal telluroxane complex, which may serve as a model for zinc tellurite ZnTeO<sub>3</sub>, which finds technical applications in nonlinear optics and ionic conductive materials.<sup>[25]</sup> We are currently investigating the deposition of ZnTeO<sub>3</sub> thin films by CVD process.

## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedure and characterization of **1** - **5**. See DOI: 10.1039/b000000x/

‡ CCDC 970723 (**1**), CCDC 964285 (**4**) and CCDC 964286 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

- I. Resa, E. Carmona, E. Gutierrez-Puebla and A. Monge, *Science*, 2004, **305**, 1136; A. Grirrane, I. Resa, A. Rodriguez, E. Carmona, E. Alvarez, E. Gutierrez-Puebla, A. Monge, A. Galindo, D. del Rio and R. A. Andersen, *J. Am. Chem. Soc.*, 2007, **129**, 693.
- T. Li, S. Schulz and P. W. Roesky, *Chem. Soc. Rev.*, 2012, **41**, 3759. S. Schulz, *Chem. Eur. J.*, 2010, **16**, 6416; A. Grirrane, I. Resa, A. Rodriguez and E. Carmona, *Coord. Chem. Rev.*, 2008, **252**, 1532; E. Carmona and A. Galindo, *Angew. Chem. Int. Ed.*, 2008, **47**, 6526.
- D. Schuchmann, U. Westphal, S. Schulz, U. Flörke, D. Bläser and R. Boese, *Angew. Chem., Int. Ed.*, 2009, **48**, 807; S. Schulz, D. Schuchmann, I. Krossing, D. Himmel, D. Bläser and R. Boese, *Angew. Chem., Int. Ed.*, 2009, **48**, 5748; S. Schulz, S. Gondzik, D. Schuchmann, U. Westphal, L. Dobrzycki, R. Boese and S. Harder, *Chem. Commun.*, 2010, **46**, 7757; S. Gondzik, D. Bläser, C. Wölper and S. Schulz, *Chem. Eur. J.*, 2010, **16**, 13599; M. Carrasco, R. Peloso, A. Rodriguez, E. Álvarez, C. Maya and E. Carmona, *Chem.–Eur. J.*, 2010, **16**, 9754; K. Freitag, H. Banh, C. Ganesamoorthy, C. Gemel, R. W. Seidel and R. A. Fischer, *Dalton Trans.*, 2013, **42**, 10540.
- T. Bollermann, C. Gemel and R. A. Fischer, *Coord. Chem. Rev.*, 2012, **256**, 537.
- M. Carrasco, R. Peloso, I. Resa, A. Rodriguez, L. Sánchez, E. Álvarez, C. Maya, R. Andreu, J. J. Calvente, A. Galindo and E. Carmona, *Inorg. Chem.*, 2011, **50**, 6361.
- a) A. Lühl, L. Hartenstein, S. Blechert and P. W. Roesky, *Organometallics*, 2012, **31**, 7109; b) A. Lühl, H. P. Nayek, S. Blechert and P. W. Roesky, *Chem. Commun.*, 2011, **47**, 8280,
- a) S. P. Green, C. Jones, A. Stasch, *Science*, 2007, **318**, 1754; b) S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.*, 2010, **16**, 938; c) A. Stasch, C. Jones, *Dalton Trans.*, 2011, **40**, 5659.
- S. J. Bonyhady, D. Collis, G. Frenking, N. Holzmann, C. Jones, and A. Stasch, *Nat. Chem.* 2010, **2**, 865; J. Li, C. Schenk, C. Goedecke, G. Frenking, and C. Jones, *J. Am. Chem. Soc.*, 2011, **133**, 18622; W. D. Woodul, E. Carter, R. Müller, A. F. Richards, A. Stasch, M. Kaupp, D. M. Murphy, M. Driess, C. Jones, *J. Am. Chem. Soc.*, 2011, **133**, 10074; M. Ma, A. Stasch and C. Jones, *Chem. Eur. J.*, 2012, **18**, 10669; S. L. Choong, C. Schenk, A. Stasch, D. Dange and C. Jones, *Chem. Commun.*, 2012, **48**, 2504.
- J. Gao, S. Li, Y. Zhao, B. Wu and X.-J. Yang, *Organometallics*, 2012, **31**, 2978.
- A. Stasch, *Chem. Eur. J.*, 2012, **18**, 15105.
- S. Schulz, L. Häming, R. Herbst-Irmer, H. W. Roesky and G. M. Sheldrick, *Angew. Chem. Int. Ed.*, 1994, **33**, 969; S. Schulz, T. Schoop, H. W. Roesky, L. Häming, A. Steiner and R. Herbst-Irmer, *Angew. Chem., Int. Ed.*, 1995, **34**, 919; C. B. Benda, R. Schäper, S. Schulz and T. F. Fässler, *Eur. J. Inorg. Chem.*, DOI:10.1002/ejic.201301122.
- S. Gondzik, S. Schulz, D. Bläser, C. Wölper, R. Haack and G. Jansen, *Chem. Commun.*, DOI:101039/C3CC47687.
- S. Saito, J. Zhang, K. Tanida, S. Takahashi and T. Koizumi, *Tetrahedron*, 1999, **55**, 2545.
- M. Wagner, C. Dietz, M. Bouška, L. Dostál, Z. Padělková, R. Jambor and K. Jurkschat, *Organometallics*, 2013, **32**, 4973; P. Simon, R. Jambor, A. Růžička and Libor Dostál, *Organometallics*, 2013, **32**, 239; P. Simon, R. Jambor, A. Růžička and Libor Dostál, *J. Organomet. Chem.*, 2013, **740**, 98.
- S. Schulz, D. Schuchmann, U. Westphal and M. Bolte, *Organometallics*, 2009, **28**, 1590.
- A CSD (V5.34; F. H. Allen, *Acta Cryst.*, 2002, **B58**, 380) search for Zn-Se compounds with coordination numbers 4 (Zn) and 3 (Se) yielded 34 hits with 341 Zn-Se bonds. The bond lengths range from 2.327 Å to 2.826 Å, with a mean bond length of 2.465(55) Å.
- The solid states structures of **3** and **4** (with one thf molecule in the asymmetric unit) were previously reported: S. Schulz, J. Spielmann, D. Bläser and C. Wölper, *Chem. Commun.* 2011, **47**, 2676; S. Schulz, T. Eisenmann, D. Bläser and R. Boese, *Z. Anorg. Allg. Chem.*, 2009, **635**, 995. Structural data of **4** are given in the SI file.
- A CSD search for "Zn-O-C" with the coordination number of Zn set to "4" gave 351 hits with 8636 Zn-O bonds (mean bonds length 1.982(75) Å; min. 1.47 Å, max. 2.773 Å).
- A search for "O-Te-C" with the Te coordination number set to 3 yielded 30 hits with 83 bonds. 13 hits revealed 15 interionic or intermolecular Te...O contacts, which were excluded. The mean bond length of the remaining is 1.913(46) Å (min. 1.829 Å, max. 1.98 Å).
- K. Srivastava, P. Shah, H. B. Singh and R. J. Butcher, *Organometallics*, 2011, **30**, 534.
- J. Beckmann, P. Finke, M. Hesse and B. Wettig, *Angew. Chem. Int. Ed.*, 2008, **47**, 9982.
- a) H. Citeau, K. Kirschbaum, O. Conrad and D. M. Giolando, *Chem. Commun.*, 2001, 2006; b) K. Srivastava, S. Sharma, H. B. Singh, U. P. Singh and R. J. Butcher, *Chem. Commun.*, 2010, **46**, 1130; c) J. Beckmann, J. Bolsinger and A. Duthie, *Chem. Eur. J.*, 2011, **17**, 930.
- a) J. Beckmann, J. Bolsinger, P. Finke and M. Hesse, *Angew. Chem., Int. Ed.*, 2010, **49**, 8030; b) J. Beckmann, A. Duthie, T. M. Gesing, T. Koehne and E. Lork, *Organometallics*, 2012, **31**, 3451.
- J. Beckmann, J. Bolsinger and M. Hesse, *Organometallics*, 2009, **28**, 4225.
- S. K. Batabyal, N. Venkatram, J. Wei and J. J. Vittal, *Crystal Growth & Design*, 2009, **9**, 4953.