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

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

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

DOI: 10.1039/x0xx00000x

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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 $[\eta^5-Cp^*_2Zn_2]$,^[1] 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.^[2] Reactions with Lewis bases and H-acidic compounds were found to proceed with preservation of the Zn-Zn bond,^[3] and reactions with transition metal complexes demonstrated the capability of Cp^*_2Zn and $Cp^*_2Zn_2$ to stabilize transition metal complexes.^[4] In addition, the electrochemical behavior of $Cp^*_2Zn_2$ was studied by CV,^[5] and the capability of $Cp^*_2Zn_2$ to serve as pre-catalysts for intermolecular hydroamination reactions was shown.^[6] 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,^[7,8] are almost unknown. Only the reaction of an α -diimine stabilized $Zn(I)$ complex with $PhCCH$, which occurred with H_2 elimination,^[9] and oxidative addition reactions of a $Zn(I)$ complex with alkyl halides, yielding 1:1 mixtures of ZnR_2 and ZnX_2 , were reported.^[10] Due to our long-term interest in the reactivity of low-valent organometallic complexes,^[11] 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.^[12] 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 β -diketiminato and the Ph group in a relative intensity of 1:1. The resonances of the β -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.^[13] 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.^[14]

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 12 h. **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 .^[15] 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.^[16] 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).^[37] Reaction of 2 with water and ethanol gave a dark-red solution, from which 3 and 4 could also be isolated. However, ¹²⁵Te NMR spectroscopy studies did not reveal the formation of PhTeH (SI). Instead, a new resonance at 3210 ppm most likely indicates the formation of [Te4]²⁺ 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 O₂ was investigated, yielding 5. The ¹H and ¹³C NMR resonances of the β -diketiminato and the Ph group of 5 are slightly shifted compared to those of 2. The ¹²⁵Te NMR spectrum of 5 shows a resonance at 1681 ppm, which is shifted to lower field as is typical for telluroxanes.^[13]

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*₂₁/*c* with four C₆H₅F 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 C₃N₂Zn 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 C₃N₂Zn ring are almost identical to those in L₂Zn₂.^[15] The average Zn-O bond lengths (Zn1-O1 1.9678 (13), Zn1-O2

1.9553(13) Å) within the envelope-type eight-membered Zn₂Te₂O₄ ring are also within the typical range observed for Zn(II) alkoxides.^[18]

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.^[19] 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 Zn₂Te₂O₄ 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)]_n, typically prepared by base hydrolysis of tellurium trichlorides RTeCl₃, and their corresponding anhydrides [RTeO_{1.5}]_n are mostly ill-defined, amorphous substances. Only recently, well-defined molecular tellurinic acids and oligomeric tellurinic anhydrides were reported.^[20-22] The sodium salts of both acids^[20,23] and two stannatellurates RTeO₂Sn(Cl)t-Bu₂ (R = 2,4,6-*t*-Bu₃C₆H₂, 8-Me₂NC₁₀H₆) were also structurally characterized.^[24]

Conclusions

Oxidative addition reactions of Ph_2E_2 (E = Se, Te) with L_2Zn 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_3 , which finds technical applications in nonlinear optics and ionic conductive materials.^[25] We are currently investigating the deposition of ZnTeO_3 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.

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DOI: 10.1039/C3CC48677J

URN: urn:nbn:de:hbz:464-20201119-162736-2

Accepted Manuscript. The final article was published in: Chemical Communications, 2014, 50, 1189-1191 and is available at: <https://doi.org/10.1039/C3CC48677J>

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