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Reactions of a Zn(I) complex with group 14 azides – Formation of zinc azide and zinc hexazene complexes

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Dedicated to Prof. Peter Jutzi on the occasion of his 75th birthday

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Two zinc hexazene complexes $L_2Zn_2(\mu\text{-}1,6\text{-}R_2\text{-}N_6)$ ($L = HC[C(Me)N(2,4,6\text{-}Me_3C_6H_2)]_2$; $R = Ph$ (**3**), $Dipp = 2,6\text{-}i\text{-}Pr_2C_6H_3$ (**4**)) were synthesized by reaction of the Zn(I) complex L_2Zn_2 (**1**) with phenyl azide and 2,6-diisopropylphenyl azide, respectively. **3** represents the second structurally characterized transition metal hexazene complex. In contrast, reactions of (**1**) with Me_3MN_3 ($M = Si, Sn$) yielded azido complexes $[LZn(\mu\text{-}N_3)]_2$ (**2**) and $Me_3M\text{-}MMe_3$.

Metal-to-metal bonds in clusters and molecules are of fundamental interest in natural science.^[1] Since the pioneering work in the mid-1960s,^[2] main group metal complexes containing group 2,^[3] 13,^[4] 14,^[5] and 15 metals^[6] as well as transition metal complexes with multiple bonding including quintuple bonding^[7] have received steadily growing interest. Two major stabilizing strategies have been developed, i.e. kinetic stabilization by use of sterically demanding substituents^[8] and electronic stabilization by coordination of a Lewis base.^[9] Aside from their synthesis, their reactivity has received increasing interest.^[10]

Since the landmark discovery of $[\eta^5\text{-Cp}^*_2Zn_2]$ ($Cp^* = C_5Me_5$) by Carmona et al. in 2004^[11] roughly 25 compounds containing Zn in the formal oxidation state +I have been structurally characterized^[12] and their chemical reactivity has been investigated. Lewis acid-base reactions, protonation reactions,^[13] oxidative addition reactions of $PhCCPh$ and alkyl halides^[14] as well as reactions with transition metal complexes were reported.^[15] In addition, the electrochemical behavior of $Cp^*_2Zn_2$ was studied by cyclic voltammetry^[16] and its use as precatalyst for the intermolecular hydroamination reaction was studied.^[17]

Our general interest in the reactivity of low-valent organometallic complexes^[18] prompted us to study reactions of L_2Zn_2 (**1**) ($L = HC[C(Me)N(2,4,6\text{-}Me_3C_6H_2)]_2$) with group 14 azides RN_3 ($R = Ph, Dipp$) and Me_3MN_3 ($M = Si, Sn$). We report on the structural characterization of the first zinc hexazene complex. Theoretical calculations were performed to identify N_6 vibrations.

The reaction of 2.0 equiv of Me_3MN_3 ($M = Si, Sn$) with **1** yielded hexamethyldisilane and –distannane Me_6M_2 as well as the previously reported zinc azide $[LZnN_3]_2$ **2**,^[19] while the reactions with two equiv. of PhN_3 and $DippN_3$ ($Dipp = 2,6\text{-}i\text{-}Pr_2C_6H_3$)₂ yielded orange crystalline solids, whose ¹H NMR spectra showed resonances of both the β-diketiminato (*L*) group and the *Ph* / *Dipp* ligands. Since no gas evolution (N_2) was observed, the formation of hexazene complexes became likely. The IR spectrum of **3** and **4** are similar to those of **1** (*SI*). The most prominent differences are the stronger intensities of two absorption bands at 1200 and 1259 cm^{-1} in the spectrum of **3** as well as an additional absorption band at 953 cm^{-1} (**3**). Orange crystals of **3** were obtained upon storage of a solution of **3** in fluorobenzene at 4 °C.^[20]

Fig. 1 Solid state structure of **3**; inversion center between N5 and N5'. Non-H-atoms are shown as thermal ellipsoids at 50% probability levels. H atoms are omitted for clarity.

A single crystal X-ray diffraction study revealed the formation of the hexazene complex $[(\text{LZn})_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhN}_6\text{Ph})]$ **3**, which crystallizes in the monoclinic space group $P2_1/n$ with two molecules in the unit cell. The Zn atoms in **3** are slightly out of the plane of the $\text{C}_3\text{N}_2\text{Zn}$ rings (deviation from least-squares plane 0.4249(17) Å, r.m.s. deviation of the ligand atoms from the plane 0.0368 Å) as was observed in L_2Zn_2 **1**,^[21] whereas the N_4Zn metallacycle is almost perfectly planar (r.m.s. deviation from least-squares plane 0.0057 Å). The central PhN_6Ph hexazene unit adopts a bridging position and is connected to two four-coordinate Zn atoms. The Zn-N bond lengths within the six-membered $\text{C}_3\text{N}_2\text{Zn}$ ring (Zn1-N1 1.9519(12), Zn1-N2 1.9364(12) Å) are slightly shorter than those within the five-membered N_4Zn ring (Zn1-N3 2.0166(12), Zn1-N5' 1.9801(12) Å). The different N-N bond lengths within the hexazene unit give insight into the electron localization within the complex. The central N5-N5' bond (1.403(2) Å) is significantly elongated compared to the almost identical N3-N4 (1.3041(17) Å) and N4-N5 bonds (1.3012(16) Å), hence the hexazene unit is best described as dianionic ligand with a central N5-N5' single bond and two allyl-like, monoanionic N_3 moieties containing delocalized π -electrons between N3, N4 and N5. The N3-N4-N5 bond angle of 117.37(11)° is comparable to those previously observed in hexazene complexes by Holland et al. and Jones et al.^[24-26] The hexazene unit serves as a dianionic ligand, which agrees with the description of the Zn atoms in the formal oxidation state +II.

Four resonance structures of the dianionic hexazene unit can be drawn, from which **C** and **D** are identical. **A** is less reasonable due to the neighbouring negatively charged N-atoms. The resonance structures with a central N-N single bond and delocalized π -electrons over the terminal N_3 units perfectly agree with the experimentally observed N-N bond distances.

Scheme 3. Resonance structures of a dianionic hexazene.

Theoretical computations with dispersion corrected density functional theory confirm this picture.^[22] Starting from the crystal structure, first geometry optimizations of a single molecule of compound **3** were carried out enforcing C_i symmetry. The most relevant optimized equilibrium bond lengths are those of the Zn1-N3 (2.028 Å), Zn1-N5' (2.001 Å), N5-N5' (1.391 Å), N3-N4 (1.310 Å) and N4-N5 bonds (1.301 Å). They agree within 0.02 Å with the experimental X-ray structure values. Yet, a harmonic frequency computation for this structure showed two small imaginary frequencies, thus revealing it as a second order saddle point. An optimization of the molecular geometry without symmetry constraints resulted in a very similar structure that displayed no imaginary frequencies (4.8 kJ/mol lower in energy). Although the

N_6 unit is slightly twisted, the bond lengths deviate by less than 0.004 Å from the values given before, with exception of one of the (now symmetry inequivalent) Zn1-N5' distances, which deviates by 0.022 Å. According to a natural population analysis^[23] the total charge on the N_6 unit is -1.76e (N3 -0.50e, N5 -0.35e) and that of the zinc atoms in **3** is 1.62e. The hexazene moiety in **3** was formed by reductive coupling of two azides. In contrast, the reaction of a Zn(I) diimine complex with phenyl acetylene did not proceed with C-C bond formation but with elimination of H_2 and subsequent formation of the Zn acetylides.^[14a]

Hexazene complexes are still rare and only five complexes have been reported, to date. Holland et al. synthesized a Fe(II)-hexazene complex, which was obtained from the N-N coupling reaction of the Fe(I) complex $(\text{L}'\text{Fe})_2\text{N}_2$ with adamantyl azide AdN_3 .^[24] In addition, Jones et al. synthesized three Mg hexazene complexes by reaction of Mg(I) complexes with AdN_3 .^[25,26] These complexes and **3** adopt similar structures, in which the metal centers are stabilized by N,N'-chelating, sterically demanding β -diketiminato ligands, and almost identical bonding parameters of the hexazene units. However, while Holland and Jones exclusively used adamantyl azide, we successfully used two different azides with either sterically less ($\text{R} = \text{Ph}$) or more demanding ($\text{R} = \text{Dipp}$) organic substituents. Moreover, the hexazene complexes **3** and **4** are not shock or thermally sensitive, in contrast to related neutral hexaazadienes.^[27]

In order to prove if hexazene complexes can be identified by their IR spectra, we calculated the IR spectrum of **3**. The second most intensive line in the calculated infrared spectrum of **3** in C_i symmetry at 1278 cm^{-1} corresponds to the antisymmetric linear combination of N3-C (phenyl) and N3'-C'(phenyl') stretching vibrations (with contributions from phenyl ring deformations). It is likely that this mode is responsible for the strong enhancement of the absorption band at 1260 cm^{-1} as observed in the experimental IR spectrum of **1** to the line observed at 1259 cm^{-1} in the experimental IR spectrum of **3**. The calculated IR spectrum of **3** also shows a relatively intense absorption band at 1209 cm^{-1} due to an antisymmetric linear combination of N3-N4 and N3'-N4' stretching vibrations (combined with a phenyl ring in-plane C-C-H bend), which likely explains the strong enhancement of the intensity of the absorption band at 1200 cm^{-1} in **1** to 1198 cm^{-1} in **3**. Furthermore the experimental IR spectrum of **3** shows an absorption band at 953 cm^{-1} which is absent in **1**. In the theoretical IR spectrum of **3** a relatively intense line is found at 949 cm^{-1} , which corresponds to an antisymmetric linear combination of N3-N4-N5 and N3'-N4'-N5' bending (with further contributions from phenyl ring deformations).

The hexazene complexes previously reported also show absorption bands close to the values as observed and calculated for **3**. However, further work is necessary in order to verify the assignment of the hexazene moiety.

Conclusions

The first zinc-hexazene complexes were synthesized by reaction of L_2Zn_2 containing the zinc atoms in the formal oxidation state I

with organic group 14 azides RN_3 . In contrast, the reactions with trimethylsilyl- and stannyl azide gave the zinc azide complex $[\text{LZnN}_3]_2$. **3** represents the first non-adamantyl substituted hexazene complex. The identification of the reaction mechanism leading to the formation of the hexazene unit is currently investigated by detailed computational studies.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedure and characterization of **3**. See DOI: 10.1039/b000000x/

‡ CCDC 959097 (**3**) contains 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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