Structural transformations in dinuclear zinc complexes involving Zn–Zn bonds†

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Reduction of $Zn_2(\mu\text{-}\eta^2\text{-}Me_2Si(NDipp)_2)_2$ with 4 equiv. of KC_8 resulted in a dramatic structural transformation into $[(\eta^2\text{-}Me_2Si(NDipp)_2)ZnZn(\eta^2\text{-}Me_2Si(NDipp)_2)]^{2-}$ featuring a Zn–Zn bond instead of $[Zn_2(\mu\text{-}\eta^2\text{-}Me_2Si(NDipp)_2)_2]^{2-}$; the mechanism of the observed structural transformations arising from the Zn–Zn bond formation involving the intermediate of $[Zn_2(\mu\text{-}\eta^2\text{-}Me_2Si(NDipp)_2)_2]^-$ was elucidated by elaborate computations.

In the field of Zn chemistry, a landmark discovery was recently made with the synthesis and characterization of dizincocene Cp*ZnZnCp* where Cp* = $\eta^5\text{-}C_5(CH_3)_5$ (**1a**) or $\eta^5\text{-}C_5(CH_3)_4\text{-}(C_2H_5)$ (**1b**) by Carmona and co-workers[1] This was followed by the synthesis of the coordination dizinc compound (Nacnac)ZnZn(Nacnac) (Nacnac = $[\{(2,6\text{-}i\text{-}Pr_2C_6H_3)N(Me)C\}_2CH]$) (**2**) by Robinson and co-workers,[2] and ArZnZnAr (**3**) and the unique ArZn(μ-H)(μ-Na)ZnAr (Ar = $2,6\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3)_2C_6H_3$) (**4**) by Power's group.[3] The most striking feature for the above reported dizinc complexes (**1–4**) is that they all possess a Zn–Zn bond axis collinear with rather than perpendicular to their principal axes.[4–7] We previously described the ability of a sterically encumbered diamido ligands, $Me_2Si(NDipp)_2$ (Dipp = $2,6\text{-}i\text{-}Pr_2C_6H_3$) to stabilize a low-coordinate and quadruply bonded dimolybdenum complex $Mo_2(\mu\text{-}\eta^2\text{-}Me_2Si(NDipp)_2)_2$ in which the Mo–Mo bond axis is perpendicular to the principal axis which is defined to coincide with the Si···Si linkage.[8] It would therefore be interesting to compare the structural properties and electronic characteristics of the Mo–Mo quadruple bond and the Zn–Zn σ bond supported by the same ligands. Accordingly, we attempted to synthesize a dinuclear zinc complex supported by two diamido ligands $Me_2Si(NDipp)_2$ in which the Zn–Zn bond axis is perpendicular to its principal axis. Moreover, the pursuit of unprecedented Zn_2^{3+} complexes is of particular interest, due to the possibility that they could be important intermediates for the formation of Zn_2^{2+} upon reduction of Zn^{2+}. This communication essentially deals with surprising discovery made *en route* to an attempted synthesis of the perpendicular dizinc complex on the basis of our prediction of a possible Zn_2^{3+} species.

In order to achieve our objectives, we started with the preparation of a neutral dinuclear precursor $Zn_2(\mu\text{-}\eta^2\text{-}Me_2Si(NDipp)_2)_2$ (**5**) in which each of two bidentate amido ligands coordinates to two Zn atoms in a bridging fashion, and from which a perpendicular dizinc complex $[Zn_2(\mu\text{-}\eta^2\text{-}Me_2Si(NDipp)_2)_2]^{2-}$ was anticipated upon reduction. Compound **5**, which is sparingly soluble in hydrocarbon and ethereal solvents, was obtained as a white solid in almost quantitative yield (99%) from the reaction of $Li_2[Me_2Si(NDipp)_2]$ and $ZnBr_2$. X-Ray crystallography‡ was used to confirm the dinuclear nature of **5** depicted in Fig. 1. The unit cell contains two independent but chemically similar asymmetric units, and therefore for the sake of clarity, only one structure is shown here. Both the diamido ligands span two Zn atoms, and each Zn atom thus forms a linear geometry with N–Zn–N bond angles falling in the range between 172 and 176°. The average Zn–N bond distance of 1.819(3) Å is comparable to those of monomeric linear Zn amides, $Zn[N(SiMe_3)Ar]_2$ (Ar = $2,6\text{-}Me_2C_6H_3$, $2,6\text{-}i\text{-}Pr_2C_6H_3$).[9] Complex **5** exhibits short Zn(1)···Zn(2) and Zn(3)···Zn(4) distances of 2.7589(7) and 2.8221(7) Å, which are close to that (2.6505(5) Å) of compound $[Zn_2\{N(Dipp)(CH_2)_3N(Dipp)\}_2]$.[10]

Subsequent reduction of **5** in toluene with 4 equiv. of KC_8 leads to the formation of colorless blocks **6** after recrystallization at −35 °C. X-ray crystallography‡ was used to decipher the dimeric nature and the orientation of the central Zn–Zn bond depicted in Fig. 2. Surprisingly, the newly synthesized dizinc complex turns out to display a coaxial structure $K_2[(\eta^2\text{-}Me_2Si(NDipp)_2)ZnZn(\eta^2\text{-}Me_2Si(NDipp)_2)]$ and the striking feature in **6** is that both diamido ligands coordinate to each Zn in a chelating fashion with the Zn–Zn bond axis being collinear rather than perpendicular to the C_2 axis, Si(1)–Zn(1)–Zn(2)–Si(2), and two

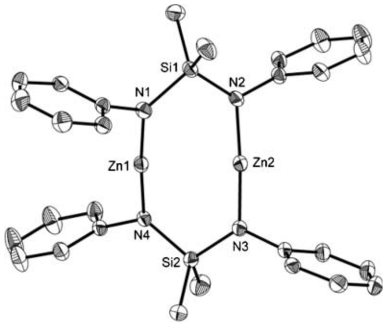

Fig. 1 Molecular structure of **5** with thermal ellipsoids at the 30% probability level. One of two crystallographically independent molecules and one half of solvent molecule (THF) found in the asymmetric unit, H-atoms and isopropyl groups have been omitted for clarity.

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† Electronic supplementary information (ESI) available: Experimental details for the synthesis, X-ray crystallographic data of **5**, **6** and (K–C222)$_2$[**7**] including tables, and details of the computational study. See DOI: 10.1039/b707396h

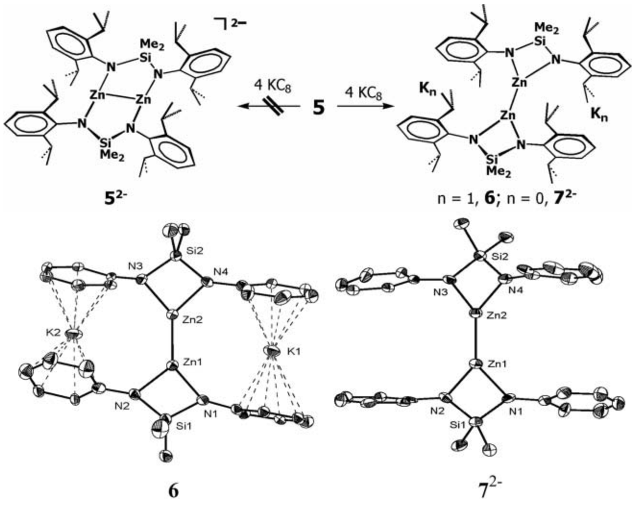


Fig. 2 Reduction of **5** and molecular structure of **6** and $\mathbf{7}^{2-}$ with thermal ellipsoids at the 30% probability level. One of two crystallographically independent molecules **6** and all solvent molecules (THF) found in the asymmetric unit, H-atoms, isopropyl groups and two counter-cations (K-2,2,2-cryptand)$^+$ of $\mathbf{7}^{2-}$ have been omitted for clarity.

planar four-membered rings Zn–N–Si–N in the structure of **6** are attached to each other *via* the Zn–Zn bond. Owing to the presence of two sandwiched potassium atoms, the two four-membered rings for **6** are almost coplanar with a dihedral angle N(1)–Zn(1)–Zn(2)–N(4) of 10.8°. Both zinc atoms in **6** adopt a trigonal geometry, and the Zn–N bond distances of 1.992(9) and 2.025(8) Å are increased by about 0.2 Å in comparison with those in **5** and are comparable to those in **2**.[2] The elongation of the Zn–N bond lengths and the short Zn···K separations of 3.795(3) and 3.870(4) Å for **6** are presumably due to the increased electron density on the zinc atoms. As is usually the case for metal–metal dimers, the most intriguing metric is the metal–metal bond distances. The value of the distance between two Zn atoms being 2.3695(17) Å for **6** is indicative of a substantial Zn–Zn bond, despite being about 0.07 Å longer than that of **1a** (2.305(3) Å) and **1b** (2.295(3) Å), and 0.01 Å longer than that of **2**, **3** and **4** (2.3586(7), 2.3591(9) and 2.352(2) Å respectively). It is, however, shorter than the Zn···Zn separation of 2.4084(3) and 2.4513(9) Å in the related zinc hydride dimers.[3,11] Apparently, the presence of two embedded potassium ions do not exert significant effect on the length of the Zn–Zn bond though the average distance of K···phenyl ring is about 2.86 Å.

In an independent experiment in which the reduction of **5** by 4 equiv. of KC_8 was carried out in THF with the presence of Cryptand [2.2.2] (C222), the complex (K–C222)$_2$[(η^2-Me$_2$Si-(NDipp)$_2$)ZnZn(η^2-Me$_2$Si(NDipp)$_2$)], (K–C222)$_2$[**7**], was isolated in 79% yield. The Zn–Zn distance of (K–C222)$_2$[**7**] was determined to be 2.3634(11) Å *via* X-ray crystallography (Fig. 2),‡ only slightly longer than that for **6**. The lack of the sandwiched potassium ions dramatically increased the dihedral angle of N(1)–Zn(1)–Zn(2)–N(4) in $\mathbf{7}^{2-}$ to 50.6(4)°, in contrast to 10.8° in **6**. The steady Zn–Zn bond distances in **6** and $\mathbf{7}^{2-}$ independent of the rotation of metal–metal axes signify that the bonding between the two Zn atoms in **6** and $\mathbf{7}^{2-}$ is essentially a σ bond.

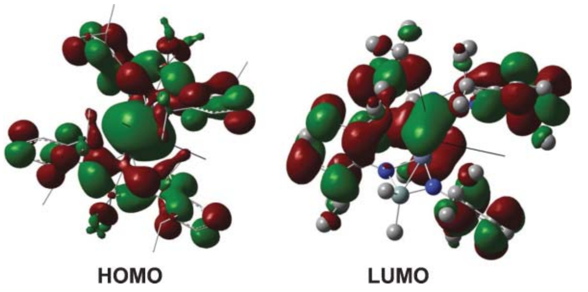


Fig. 3 The contour plots of HOMO and LUMO of $\mathbf{7}^{2-}$.

The electronic structures and bonding for Zn–Zn bonded complexes have been subjected to theoretical studies since the discovery of dizincocene and other related species,[1–3,12,13] and those calculations demonstrate the Zn–Zn bonds are formed through the overlap of either a pair of 4s orbitals in complexes **1a**, **1b**, **2**, **3** or a pair of 4p$_z$ orbitals in compound **4**. The electronic structures of $\mathbf{7}^{2-}$ were scrutinized by two-layered integrated molecular orbital (ONIOM) computations using the second order Møller–Plesset method (MP2) combined with density functional theories (DFT) on the authentic $\mathbf{7}^{2-}$. The HOMO of $\mathbf{7}^{2-}$ is localized mainly in the Zn–Zn σ-bonding region and detailed natural bond orbital (NBO) analyses indicate that the Zn–Zn σ bond has very high s character (94.75%), and slight p (2.59%), and d character (2.66%). In the β-diketiminato complex **2**, the Zn–Zn bond also displays very high s character in the HOMO. In contrast to $\mathbf{7}^{2-}$, the Zn 4s orbitals form the Zn–Zn bond in the dizincocene **1a**. The LUMO of $\mathbf{7}^{2-}$ consists of an orbital of π symmetry, which is localized on the central Zn_2^{2+} unit. Both of the contour plots of HOMO and LUMO are shown in Fig. 3.

A simple qualitative correlation diagram[14] as shown in Fig. 4 might suggest why the coaxial Zn–Zn bonded structure is more favorable than the perpendicular one supported by chelating diamido ligands. To the left of Fig. 4 are the frontier orbitals for a linear [ZnN$_2$]$^-$ unit in $\mathbf{5}^{2-}$, and the others on the right side of the figure are the frontier orbitals for a bent [ZnN$_2$]$^-$ unit in $\mathbf{7}^{2-}$. Accordingly, $\mathbf{7}^{2-}$ is predicted to be energetically lower than $\mathbf{5}^{2-}$ if both Zn–Zn bonds were roughly assumed to have the same bonding energy. Elaborate computations by virtue of the methods

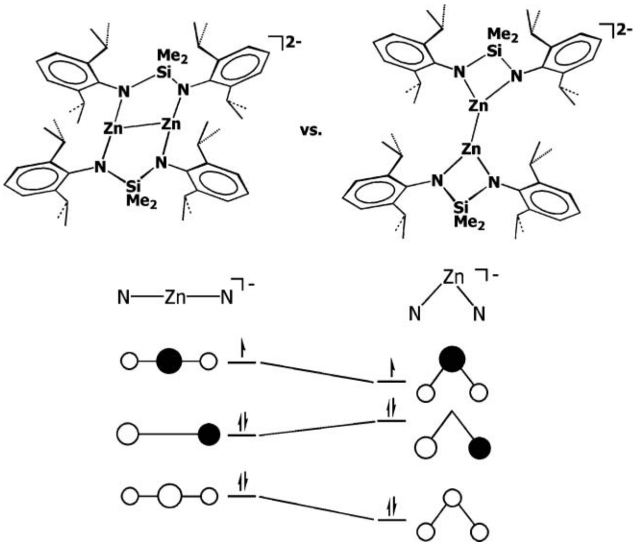


Fig. 4 The orbital correlation diagram for Zn(I) diamides shows how the energies of the orbitals change as the linear molecule becomes bent.

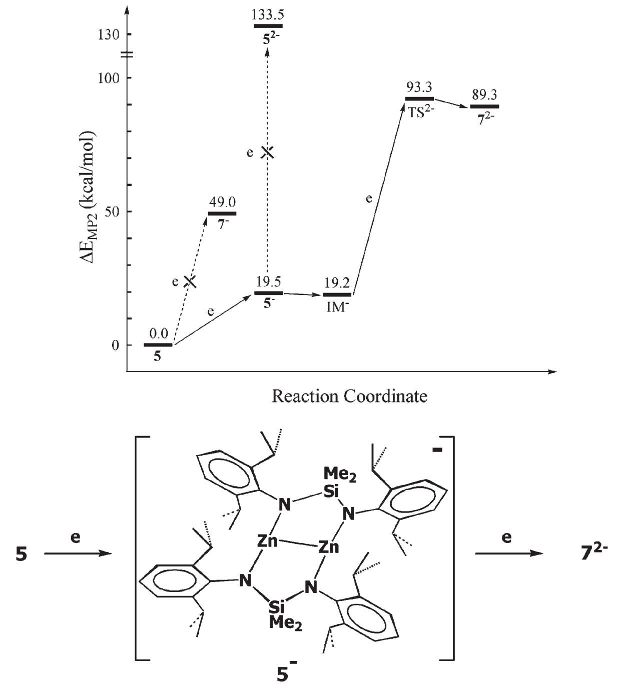
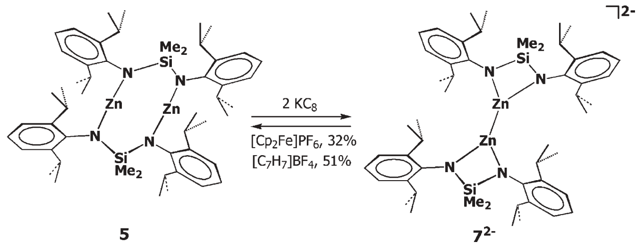


Fig. 5 (a) The energy profile for reactions from **5** to $\mathbf{7}^{2-}$. The relative energetics are plotted according to zero-point corrected MP2 energies at ONIOM (full-MP2/6-31G(d,p):BP86/6-31G(d,p)). (b) The reaction mechanism of structural transformation upon two-electron reduction of **5**.

stated above were also performed on the hypothetical $\mathbf{5}^{2-}$ and the prepared $\mathbf{7}^{2-}$, and the outcomes shown in Fig. 5 are consistent with our qualitative predictions.

To disclose the mechanism for the intriguing structural transformations from **5** to **6** or $\mathbf{7}^{2-}$ along with the Zn–Zn bond formations, a possible reduction pathway from the starting **5** to product $\mathbf{7}^{2-}$ was computed. As depicted in Fig. 5, notably, the reduction from **5** to $\mathbf{7}^{2-}$ proceeded through a mixed-valence dizinc Zn_2^{3+} species $\mathbf{5}^{-}$ featuring the perpendicular structure. The computed intermediate ($\mathbf{IM}^{-}$) and transition state ($\mathbf{TS}^{2-}$) are shown in the ESI.†

Attempts to characterize the hypothetical mixed-valent dizinc complex $\mathbf{5}^{-}$, which presumably possesses one unpaired electron and should be EPR active,[15] have so far failed. Treatment of **5** with one equivalent of KC_8 in toluene led to an incomplete reaction with the observation of **5** and **6** only. No comproportionation reaction was observed by mixing equal amount of **5** and **6** or (K–C222)$_2$[**7**]. On the other hand, addition of one equiv. of oxidants such as $[Cp_2Fe]PF_6$ or a weaker[16] oxidant, $[C_7H_7]BF_4$, to **6** or (K–C222)$_2$[**7**] gave rise to a mixture of **5** and starting compounds only. Interestingly, the oxidation of **6** or (K–C222)$_2$[**7**] by 2 equiv. of $[Cp_2Fe]PF_6$ resulted in the formation of 32% of **5**, but 51% of **5** was observed on the basis of ^{1}H NMR spectroscopy, when **6** or (K–C222)$_2$[**7**] was treated with the milder oxidant $[C_7H_7]BF_4$ (Scheme 1).



Scheme 1

In conclusion, three remarkable dinuclear zinc complexes **5**, **6** and (K–C222)$_2$[**7**] were successfully prepared and characterized. The interactions between the Zn_2^{2+} moiety and the chelating diamido ligand $Me_2Si(NDipp)_2$ favor a coaxial structure. However, the mixed-valence Zn_2^{3+} intermediate $\mathbf{5}^{-}$ was theoretically predicted to display a perpendicular structure. Characterizations of the intermediate complex $\mathbf{5}^{-}$ are underway.

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Notes and references

‡ CCDC 647437 (**5**), 647438 (**6**) and 647439 ((K–C222)$_2$[**7**]). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707396h

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