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Transition metal-induced dehydrogenative coupling of zinc hydrides[†]

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The reaction of terminal zinc hydrides with palladium(0) species afforded an unprecedented $[\eta^2-Zn_2Pd]$ trimetallic complex through the reductive elimination of H₂. In contrast, the reaction of zinc hydrides with a nickel(0) reagent gave σ -Zn-H coordination complexes with no direct Zn-Zn bonding. Computational studies indicated that an oxidative addition/reductive elimination process at the palladium center might be responsible for the formation of a covalent Zn-Zn bond.

Molecular compounds featuring metal-metal bonds are of considerable interest not only because of their unique structures and bonding properties but also their applications in catalysis, materials chemistry, and bioinorganic chemistry.^{1,2} In particular, homonuclear d- or s-block metal-metal bonded compounds with unusual low oxidation states have emerged over the last two decades, such as Zn(I)-Zn(I) bonds,³ Cr(I)-Cr(I)quintuple bonds,⁴ and Mg(I)-Mg(I) bonds,⁵ opening up new frontiers of chemical bonds. The first Zn(I)-Zn(I) bonded complex $[(\eta^5-Cp^*)_2Zn_2]$ (Cp* = C₅Me₅) was made by Carmona and co-workers through the reductive coupling of [Cp*₂Zn] with ZnEt2 3 or potassium hydride.6 Since then, a number of low-valent dizinc bonded complexes have been synthesized and the unique nature of their metal-metal bonds has been unveiled.7 To date, these complexes have been mainly formed by either reductive coupling of zinc(II) halides with alkali metals, or ligand substitution reactions of a preserved Zn(I)-Zn(I) bonded species.^{8,9} On the other hand, transition metal-catalyzed dehydrogenative homocoupling has been established as a powerful synthetic approach for the formation of a variety of homonuclear p-block element–element bonds, such as B–B bonds,¹⁰ Si–Si bonds,¹¹ and P–P bonds,¹² and their congeners.¹³ In this context, we herein developed a transition metal-induced homocoupling of Zn–H bonds into Zn–Zn bonds with concomitant elimination of H₂ under mild conditions. Mechanistic studies indicated that an oxidative addition/reductive elimination process at the transition metal center plays a crucial role in the formation of a covalent zinc–zinc bond.

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Chelating ligands with N-donors, such as β -diketiminates and their derivatives, have been successfully used to stabilize a variety of highly reactive zinc hydrides¹⁴ and zinc–zinc bonded complexes.¹⁵ We recently designed a new type of β -diketiminato ligand precursor **HL** (L = CH₃C(2,6-iPr₂C₆H₃N) CHC(CH₃)(NCH₂(CH₂)_nPPh₂); **HL**^a: n = 1, **HL**^b: n = 2) bearing a pendant phosphine group.¹⁶ The corresponding zinc(II) hydrides were prepared by following well-established procedures¹⁷ (Scheme 1). Metalation of ligand precursors with ZnEt₂ gave zinc monoalkyl complexes **1**, which reacted with an equimolar amount of 2,6-diisopropylphenol to give zinc aryloxide complexes **2** with the liberation of ethane. Finally, the target zinc hydrides **3** were obtained in high yields (82% for **3a**; 76% for **3b**) through the metathesis reactions of **2** with PhSiH₃ under mild conditions.



Scheme 1 Synthesis of zinc hydrides

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Fig. 1 Molecular structure of complex **3a**. Hydrogen atoms (except Zn–H) are omitted for clarity; displacement ellipsoids are drawn at the 30% probability level.

Zinc(II) complexes 1-3 were comprehensively characterized by multinuclear NMR spectroscopy, elemental analysis, and single crystal X-ray diffraction. The molecular structure of complex 3a is depicted in Fig. 1, and those of the other complexes are shown in the ESI.† The Zn-P distances in mononuclear zinc hydrides 3 were found to be 2.671(5) Å (3a) and 2.593(2) Å (3b), indicating a κ^3 -N,N,P coordination mode of ligand L. The Zn-H bond lengths (3a: 1.51(3) Å; 3b: 1.56(3) Å) are longer than that in (nacnac)ZnH (nacnac = $[{(C_6H_3-2,6^{-i}Pr_2)}]$ $N(CH_3)C_2CH^{-})^{14b}$ because of the increased coordination number, but they still fall in the range of 1.384-1.600 Å observed for the majority of mononuclear terminal zinc hydrides.¹⁸ In solution ¹H NMR spectra, hydride signals were unambiguously located at δ 4.72 (3a) and 4.71 (3b) ppm, which are also comparable to those of the reported monoanionic zinc hydride species.14,19,20

It has been reported that the addition of one equivalent of zinc hydride to a transition metal led to either coordination of a Zn–H bond to the transition metal $[\eta^2-(ZnH)-TM]$, namely a σ -complex, or oxidative addition at the transition metal (Zn-TM-H).²¹ Considering these results, we posed the question of whether the reductive elimination of H2 will occur at the transition metal center when two equivalents of zinc hydride are added to electron-rich transition metals.²² Thus, we firstly monitored the reaction of our zinc hydride 3a with the widely used zero-valent palladium species Pd(PPh₃)₄ in a 2:1 molar ratio in C_6D_6 . To our delight, a new sharp resonance at δ 15.2 ppm in the ³¹P NMR spectrum and a characteristic ¹H NMR singlet signal at δ 4.47 ppm attributed to H₂ rapidly appeared. The generation of H_2 gas was further confirmed by gas chromatography. Scaling up of the reaction in toluene eventually provided product 4a as a pale orange solid in 80% yield (Scheme 2), with complete characterization by NMR spectroscopy, X-ray diffraction, and elemental analysis.²³ It is also notable that complex 4a is thermally stable, with no decomposition observed over 12 h at 80 °C in C₆D₆ solution.

Single crystals of **4a** suitable for X-ray structure analysis were obtained from a layered toluene/hexane solution at room temperature. The molecular structure of **4a** is shown in Fig. 2. The structure reveals a trimetallic zinc-palladium-zinc cluster produced by a reductive dehydrogenation reaction. The



Scheme 2 Reactions of zinc hydrides with Pd(PPh₃)₄.



Fig. 2 Molecular structure of complex 4a. Hydrogen atoms are omitted for clarity; displacement ellipsoids are drawn at the 30% probability level.

[Zn₂Pd] core structure of the complex shows a nearly perfect equilateral triangle-like conformation with bond angles of 59.8°, 59.7°, and 60.5°. The Zn–Zn distance was found to be 2.490(5) Å which is longer than that of unsupported Zn₁)–Zn₁ bonds (2.30–2.42 Å),⁸ but falls in the range of 2.44–2.58 Å computationally predicted for η²-Zn₂ ligands.²⁴ The dizinc bond coordinated to the Pd atom with almost equal distances (Pd1– Zn1 2.488(4) Å, Pd1–Zn2 2.508(4) Å) which are comparable to other reported Pd–Zn bonds.²⁵ Each zinc atom bound to the β-diketiminato ligand backbone in a κ^2 -*N*,*N* fashion with a N1– Zn1–Zn2–N4 torsion angle of 32.5° caused by ligand repulsion. The coordination sphere of the four-coordinate palladium center was completed by two pendant PPh₂ groups (Pd1–P1 2.294(8) Å, Pd1–P2 2.303(8) Å) and the palladium center adopted a distorted tetrahedral geometry.

An analogous reaction could also take place for **3b** producing **4b** in 65% isolated yield (Scheme 2). Complex **4b** showed similar spectroscopic properties and structural data to those of **4a** (Zn1–Zn2 2.510(5) Å, Pd1–Zn1 2.508(4) Å, and Pd1–Zn2 2.492(4) Å) (for more details, see the ESI†). As the dizinc bond is isolobal to a dihydrogen molecule, the reaction of a Zn–Zn bond with a transition metal usually results in the oxidative cleavage of the Zn–Zn bond to afford a product resembling the classical transition metal dihydrogen complex.²⁶ In contrast, only two examples exhibited the dizinc bond as an η^2 -ligand for transition metals Cu and Ni without the cleavage of the Zn–Zn bond reported by Fischer and Frenking.²⁷ Complex **4**

can thus be regarded as another example of zinc congeners of the Kubas-type dihydrogen complexes.²⁸

In order to investigate the nature of the bonding properties in zinc-zinc-bonded complex 4a, density functional theory (DFT) calculations were carried out at the B3PW91+D3 level. The geometry was optimized without any symmetry constraint and compared well with the experimental one. The equilateral triangle feature of the [Zn₂Pd] core is perfectly reproduced with three angles of 60.4°, 59.0° and 60.6°. The Pd-Zn distances (2.48 Å) match the experimental ones (2.50 and 2.49 Å) and the Zn-Zn distance (2.44 Å vs. 2.49 Å exp.). The HOMO of the system is indicative of a bonding interaction between the palladium and the two zinc atoms (see Fig. S53 in the ESI[†]). The latter is further confirmed by their Wiberg Bond Index (WBI) values. The two Pd-Zn WBI are 0.38 and the values of 0.48 were found for the Pd-P bonds. The NBO analysis indicates the presence of a Zn-Zn bond that is fully covalent formed with two hybrid sp orbitals (75% 4s + 25% 4p). The associated WBI is 0.60 (to be compared to 0.54 in the 5a' complex). This Zn-Zn bond interacts with the Pd center as evidenced at the second order donor-acceptor NBO level. Indeed, donation from a 4d lone pair of Pd into the Zn-Zn σ^{*} and some backdonation from the $\sigma(Zn-Zn)$ orbital to hybrid sp orbitals of Pd (86% 5s and 12% 5p) are observed.

Subsequently, the reactions between zinc hydrides 3 with the zero-valent nickel reagent Ni(COD)2 (COD: 1,5-cyclooctadiene) were also performed in a 2:1 molar ratio. The outcomes were markedly different from that for palladium(0) under the same conditions. The reactions gave heterotrimetallic hydride-bridged [Zn–Ni–Zn] complexes 5 in high yields (5a: 88%; 5b: 84%) (Scheme 3). Complexes 5 were fully characterized by multinuclear NMR spectroscopy, elemental analysis, and single crystal X-ray diffraction. The X-ray structure of complex 5b is depicted in Fig. 3 and the molecular structure of 5a is provided in the ESI.[†] During the reaction course, Zn-H bonds coordinated to the Ni center in an η^2 fashion (Zn1-Ni1 2.365(5) Å, Zn1-H1 1.82(4) Å, Ni1-H1 1.45(4) Å, Zn2-Ni1 2.368(5) Å, Zn2-H2 1.81(4) Å, Ni1-H2 1.50(4) Å, Zn1-H1-Ni1 92°, Zn2-H2-Ni1 91°) and the pendant arm phosphine bonded to Ni (Ni1-P1 2.189(9) Å, Ni1-P2 2.184(9) Å) with the replacement of the neutral COD ligands. The structural data suggested that **5b** possibly behaved as a stretched σ -Zn–H complex.²¹ In addition, the Zn…Zn distance was found to be 2.864(5) Å indicating a very weak interaction with no direct Zn-Zn bond. The existence of bridged hydrides was further confirmed by the observation of high-field ¹H NMR resonances at δ –9.38 and



Scheme 3 Reactions of zinc hydrides with Ni(COD)₂



Fig. 3 Molecular structure of complex 5b. Hydrogen atoms (except Zn-H) are omitted for clarity; displacement ellipsoids are drawn at the 30% probability level.

-9.42 ppm and also ²H NMR resonance at δ -9.38 ppm in the corresponding deuterated complex **5b-***D* (for more details, see the ESI[†]).

To obtain more insights into the reactions of zinc hydrides with Pd(0) or Ni(0) complexes and especially the difference between Pd and Ni, computational approaches were used to determine some possible reaction pathways. Calculations were carried out at the DFT level (B3PW91+D3 corrections) and the main features are presented in Scheme 4. Due to the stabilization of complex 5, the possibility of the dihydride to be an intermediate in the reaction was considered. The formation of the dihydride species is computed to be favorable for both metals (Pd and Ni). However, this reaction was found to be more favorable for Pd than for Ni. The main difference between complexes 4' and 5 is the bonding situation. In both cases, there is no evidence for any Zn-Zn bond yet formed whereas there are some Pd(Ni)-Zn interactions (WBI around 0.5). Also, there are some differences in the hydride bonding. For 4a', NBO and WBI clearly indicate the formation of two Pd-H bonds in line with an oxidation of Pd(0) to $Pd(\pi)$ whereas the situation is less clear for Ni, where the bridging hydrides between Ni and Zn are found. The latter could be explained either by the fact that the Ni-Zn distances are



Scheme 4 Computed reaction pathways for the formation of complexes 4a and 5a at room temperature (enthalpy change, kcal mol⁻¹).

shorter than the Pd–Zn ones allowing the hydride to bridge the Ni–Zn bond or by the fact that the Ni–H and Zn–H bonds are of equivalent strengths whereas the Pd–H bond is stronger than the Zn–H ones. Then, the formation of **4a** and a putative **5a**' was considered. In the case of Ni, the reaction is computed to be endothermic by 8.3 kcal mol⁻¹, so the formation of **5a**' is not favorable, which is consistent with experimental observations. In contrast, the formation of **4a** is computed to be both kinetically and thermodynamically favorable. The reaction is a simple reductive elimination of H₂ at the palladium center. This also indicates that the formation of the Zn–Zn and H–H bonds is not counterbalancing the loss of the bridging hydrides whereas it is no longer the case when the hydrides are not bridging.

In summary, transition metal-induced dehydrogenative coupling of Zn–H bonds into a homonuclear Zn–Zn bond was successfully achieved through a stoichiometric reaction of tridentate NNP ligand supported zinc hydride with palladium(0) species Pd(PPh₃)₄ under mild conditions. Both structural parameters and DFT calculation results indicate the existence of Zn–Zn and Zn–Pd bonds in complexes 4. Although the reaction of the identical zinc hydride with Ni(COD)₂ gave an isolable σ -Zn–H complex 5, it indicated the dihydride species 4' formed by oxidative addition as a possible intermediate followed by reductive elimination of H₂ to afford coupling product 4. The heterotrimetallic [Zn₂Pd] complexes not only show unique and intriguing structural features but may also have potential application in multimetallic catalysis,^{2,29} which is under investigation in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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