

# N–H activation of hydrazines by a heterobimetallic Zr–Co complex: promotion of one-electron chemistry at $Zr^{II}$

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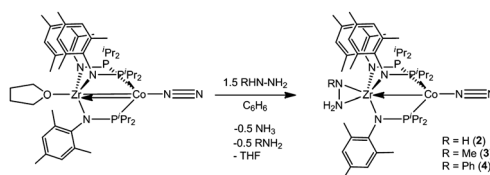
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A tris(phosphino)amide-ligated Zr–Co heterobimetallic complex has been shown to activate N–H bonds of hydrazine derivatives via a proton-coupled electron transfer process. Such reactivity is highly unusual for an early metal such as Zr, but is promoted by the adjacent redox active Co atom.

The activation of N–H bonds is an important step in catalytic C–N bond-forming reactions.<sup>1,2</sup> While late transition metals typically oxidatively add N–H bonds to form reactive amide species, early transition metals typically react with amines via protonolysis of M–E bonds (E = H, NR<sub>2</sub>, OR, alkyl). To fundamentally study N–H oxidative addition as a key reaction step, ammonia has been shown to oxidatively add to transition metal complexes.<sup>3–6</sup> Similar studies with hydrazines remain less common,<sup>7</sup> despite their applications in fuel cells<sup>8,9</sup> and in organic synthesis,<sup>10,11</sup> and the role of hydrazido complexes in the reduction of dinitrogen to ammonia.<sup>12,13</sup>

Our group has been investigating the combination of early and late transition metals in heterobimetallic complexes as a strategy to utilize the cooperative reactivity of the two transition metals to effect new synthetic transformations.<sup>14–16</sup> With respect to N–H activation, Bergman and coworkers previously reported the oxidative addition of ArNH<sub>2</sub> across a Zr–Ir bond to form a terminal Zr–NHAr anilide and a Zr–H–Ir bridging hydride.<sup>17</sup> Previously, we reported a highly reduced coordinatively unsaturated heterobimetallic Zr–Co complex featuring a well-characterized metal–metal multiple bond, (THF)Zr(MesNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>CoN<sub>2</sub> (**1**).<sup>18</sup> Complex **1** has been shown to undergo two electron oxidative processes in the presence of a number of small molecule substrates including alkyl halide substrates, carbon dioxide,

Scheme 1 Reactivity of **1** with RNHNH<sub>2</sub>.

and dihydrogen.<sup>19,20</sup> Herein we report the reactivity of complex **1** towards hydrazine derivatives, uncovering the first examples of one-electron oxidative addition products with these Zr–Co heterobimetallic systems.

The diamagnetic compound **1** does not react with primary amines or anilines, but readily reacts with one equivalent of RNHNH<sub>2</sub> (R = H (**2**), Me (**3**) or Ph (**4**)) to generate the yellow hydrazido complexes (RNNH<sub>2</sub>)Zr(MesNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>CoN<sub>2</sub> (**2–4**) in moderate yields (~35%, Scheme 1). The <sup>1</sup>H NMR spectra of compounds **2–4** exhibit 7–8 broad paramagnetically shifted resonances and their solution magnetic moments are indicative of *S* = 1/2 spin states ( $\mu_{\text{eff}}$  = 1.8–2.0  $\mu_B$ ). The presence of bound dinitrogen remaining on the Co atom is confirmed by the presence of  $\nu(\text{N}_2)$  vibrations in the IR spectra of **2–4** ( $\nu(\text{N}_2)$  = 2038–2044 cm<sup>−1</sup>) with an approximate 20 cm<sup>−1</sup> increase in the  $\nu(\text{N}_2)$  stretching frequency compared to **1** ( $\nu(\text{N}_2)$  = 2026 cm<sup>−1</sup>).<sup>18</sup> These changes indicate that the Zr/Co complex has been oxidized by one electron.

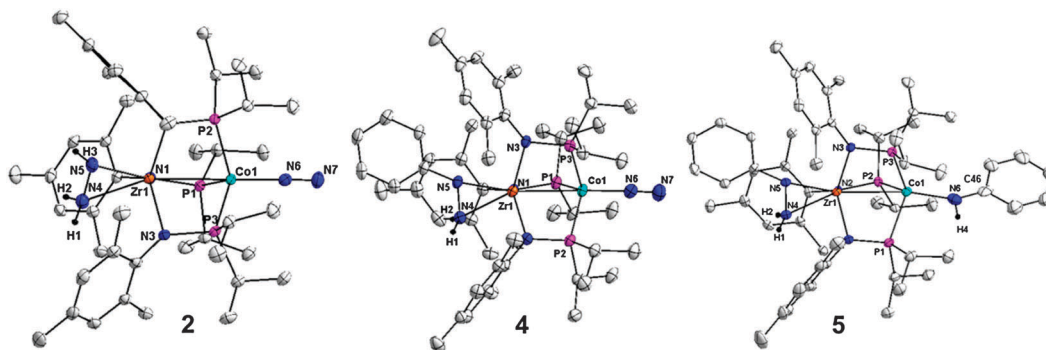
X-Ray diffraction analyses of single crystals of compounds **2** and **4** reveal replacement of the zirconium-bound THF with an  $\eta^2$ -hydrazide ligand (Fig. 1). The hydrazide ligands in **2** and **4** exhibit N–N distances of 1.412(2) and 1.4335(3) Å, respectively, indicating N–N single bond character, consistent with typical Zr side-on hydrazide complexes.<sup>21–27</sup> The bond lengths between Zr and the anionic hydrazido nitrogen of **2** and **4** (2.040(1) and 2.137(2) Å) are shorter than the bonds between Zr and the datively bound hydrazido nitrogen atoms (2.332(1) and 2.265(2) Å), and all distances are in the range of previously reported zirconium  $\eta^2$ -hydrazido complexes (2.04–2.12 Å and 2.30–2.47 Å, respectively).<sup>21–27</sup> The geometry about the anionic nitrogen atom in both compounds **2** and **4** is planar which suggests  $\pi$  donation

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**Fig. 1** Displacement ellipsoid (50%) representations of complexes **2**, **4**, and **5**. For clarity, solvate molecules and hydrogen atoms except those associated with the hydrazido and anilide ligands are not shown. Only one of two independent molecules in the unit cell of **4** is shown. Hydrogen atoms bounds to the hydrazido unit were located on the difference Fourier map and refined. Relevant interatomic distances (Å) and angles (°): **2**: Co–Zr: 2.7350(2); Co–N6: 1.830(1); Zr–N5: 2.040(1); Zr–N4: 2.332(1); N4–N5: 1.412(2). **4**, one of two molecules: Co1–Zr1: 2.6981(4); Co1–N6: 1.852(2); Zr1–N5: 2.137(2); Zr1–N4: 2.265(2); N4–N5: 1.435(3). **5**, Zr–Co: 2.8706(6); Co–N6: 1.962(3); Zr–N5: 2.117(3); Zr–N4: 2.263(3); N4–N5: 1.435(3); Co–N6–C46: 153.1(3).

of the lone pair to the zirconium atom (*vide infra*). Notably, there are few structurally characterized examples of transition metal complexes of unsubstituted terminal  $\eta^2$ -hydrazido(1–)  $N_2H_3^-$  ligands,<sup>28–31</sup> and complex **2** represents the first example with Zr.

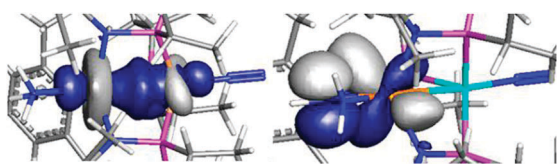
Although the metal oxidation states in complex **1** are rendered ambiguous by the metal–metal bonding, a plot of the Mulliken spin density of complex **2**, derived from density functional theory, reveals that the single unpaired electron in this complex resides exclusively on the Co atom (see ESI†). This suggests a  $Zr^{IV}/Co^0$  assignment, consistent with what would be predicted using the conventional oxidation state formalism. Observed structural changes between parent complex **1** and complexes **2** and **4** can be attributed to oxidation of the complex as well as formation of a coordinatively saturated Zr(IV) center. Of these changes the most notable is the lengthening of the metal–metal interatomic distance from 2.36 Å<sup>18</sup> in **1** to ~2.7 Å in **2** and **4** as the donor/acceptor Co/Zr bonding weakens. There is also a noteworthy difference between the Zr–Co interatomic distances in **2** and **4**, with an apparently stronger Zr–Co interaction in **2** compared to **4** (2.7350(2) vs. 2.6981(4) Å), likely attributed to the electron-withdrawing character of the phenyl group on the hydrazido ligand in **4**. Natural bond orbital (NBO) analysis of complexes **1** and **2** reveal a Wiberg bond index (WBI) of 0.45 for the Zr–Co bond in **2** compared to the Zr–Co WBI of **1** (0.95) or  $ClZr(MesNP^iPr_2)_3CoI$  (0.52, see ESI†). The Zr–Co  $\sigma$  donor–acceptor interaction predicted using NBO analysis is shown in Fig. 2, along with the  $\pi$  donor–acceptor interaction between the anionic hydrazido nitrogen p orbital and Zr (WBI<sub>Zr–N</sub> = 0.79 vs. WBI<sub>Zr–N</sub> = 0.34 for neutral nitrogen donor).

Consistent with the weakening of the Co–Zr interaction in complexes **2–4**, cyclic voltammetry (CV) of these compounds

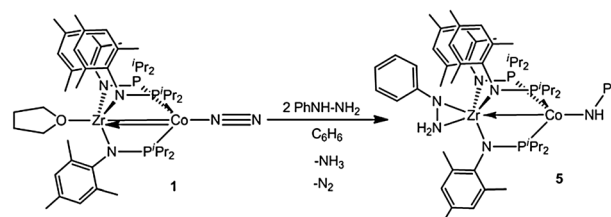
reveals irreversible reductive events at negative potentials (*ca.* –2.2 V vs. ferrocene, see ESI†). Previously, we showed that dative  $Co \rightarrow Zr$  interactions have a dramatic effect on the  $Co^{I/0}$  and  $Co^0/Co^{-1}$  couples as electron density is withdrawn from Co.<sup>32</sup> The  $Co^{0/-1}$  couple of the dihalide complex  $ClZr(MesNP^iPr_2)_3CoI$  (–1.87 V) is similar to the irreversible reduction observed for compounds **2–4** (also a  $Co^{0/-1}$  reduction based on the calculated SOMO, see ESI†), and the shift of this reductive feature to more negative potentials can be attributed to the decreased Co–Zr interaction as a result of a more electron rich hydrazido(1–) ligand on Zr in place of a halide. Notably, the Co–Zr distances in complexes **2** and **4** (2.7350(2) Å and 2.6981(4) Å) are longer than that of  $ClZr(MesNP^iPr_2)_3CoI$  (2.6280(5) Å),<sup>32</sup> despite their one-electron reduced nature.

Interest in the formation of complexes **2–4** prompted study into the mechanism of these reactions, particularly the outcome of the ejected hydrogen atom from the N–H activation step. <sup>1</sup>H NMR analysis of the isolated volatiles from the reaction mixtures revealed formation of ammonia and the corresponding amine  $RNH_2$  as byproducts, presumably *via* hydrazine reduction by the proton and electron extruded upon formation of **2–4**.

With this in mind, the reaction stoichiometry was adjusted and 1.5 equivalents of  $RHNH_2$  ( $R = H, Me$ ) were employed in the reaction with **1**, leading to a dramatic increase in the isolable yields of compounds **2** and **3** (80–85%) *via* prevention of radical decompositions pathways. Interestingly, when **1** was treated with excess phenylhydrazine the reaction mixture became red/purple as a new two-electron oxidized product,  $(PhNNH_2)Zr(MesNP^iPr_2)_3CoNHPh$  (**5**), formed (Scheme 2).

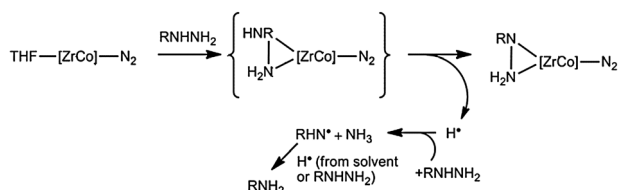


**Fig. 2** Donor–acceptor interactions (NBO) in complex **2** between the filled Co  $d_{2z}$  orbital and the empty  $d_{2z}$  orbital on Zr (left,  $E_{del} = 41.3 \text{ kcal mol}^{-1}$ ) and the filled hydrazido nitrogen p orbital and Zr (right,  $E_{del} = 9.1 \text{ kcal mol}^{-1}$ ).



**Scheme 2** Treatment of **1** with excess  $PhNHNH_2$ .





**Scheme 3** Plausible mechanism for the formation of 2–4.

Compound **5**, which has an  $S = 1$  spin state ( $\mu_{\text{eff}} = 2.78 \mu_{\text{B}}$ ), was easily identified due to the similarities of its paramagnetically shifted  $^1\text{H}$  NMR spectrum to that of the previously reported  $S = 1$  complex  $\text{ClZr}(\text{MesNP}^i\text{Pr})_3\text{CoI}$ .<sup>32</sup> The formulation of complex **5** was confirmed by an X-ray structure determination (Fig. 1). The geometric parameters associated with the Zr-hydrazido fragment are nearly identical to those in the  $S = 1/2$  species **4**, but the Co–Zr distance is significantly longer (2.8706(6) Å), a result of less electron density at Co in this  $\text{Co}^{\text{I}}$  species.

The mechanism by which hydrazines are cleaved to  $\text{NH}_3$  and  $\text{RNH}_2$ , and the isolation of complex **5** is intriguing, particularly since similar compounds were not generated upon treatment of **1** with excess  $\text{MeNHNH}_2$  or  $\text{N}_2\text{H}_4$  (even in the presence of  $\text{PhNH}_2$ ), nor does complex **4** react with  $\text{PhNH}_2$  to generate **5**. In several  $\text{W}(\text{VI})$  examples, Schrock *et al.* proposed a mechanism by which tungsten hydrazine adducts undergo rapid deprotonation by free hydrazine to afford  $\eta^2$ -hydrazide complexes.<sup>28,30</sup> A similar deprotonation mechanism is likely for the  $\text{Co}(\text{II})$  example,<sup>29</sup> and the hydrazido(1–) ligand in the Fe example is attained *via* extrusion of  $\text{CH}_4$  from an  $\text{Fe}^{\text{II}}\text{–Me}$  precursor.<sup>31</sup> Adaptations of these mechanisms by replacing simple deprotonation with proton-coupled electron transfer (PCET) explain the presently reported chemistry (Scheme 3).<sup>33</sup> It is proposed that the proton and electron required for this process are provided by a short-lived hydrazine–zirconium adduct which extrudes a hydrogen atom to lead to a neutral metal complex, a molecule of ammonia, and an aminyl radical. The highly reactive aminyl radical would likely be quenched by abstracting  $\text{H}^\bullet$  from solvent or by undergoing a similar process with a second hydrazine–zirconium adduct. As phenylaminyl radicals are more stable, it is proposed that this intermediate is long-lived enough to combine with the  $\text{Co}^0$  radical site in **4** to form the stable  $\text{Co–NHP}$  compound **5**. Attempts to trap the free  $\text{H}^\bullet$  generated upon hydrazine activation were unsuccessful, implying that H-atom transfer is rapid and perhaps occurs *via* an inner-sphere process. Further, the reactions of **1** with hydrazine are fast at room temperature, precluding the observation of intermediates or studies of reaction rate, so other mechanisms cannot be ruled out at this time.

In summary, it has been found that the reduced, coordinatively unsaturated heterobimetallic complex **1** is capable of undergoing a one-electron oxidative addition process in which hydrazine N–H bonds are cleaved to afford a series of zirconium  $\eta^2$ -hydrazido(1–) complexes 2–5. This sort of N–H activation at an early metal fragment is unusual, as is one-electron transfer chemistry from Zr. Thus, the metal–metal bonding in complex **1** promotes  $\sigma$ -bond activation at Zr remotely, without effecting

the immediate coordination sphere of Co or the  $\text{C}_3$ -symmetric core of the bimetallic. During the hydrazine activation process, ammonia and  $\text{RNH}_2$  are formed as byproducts of hydrogen atom transfer. The mechanism of this PCET warrants further investigation, and additional one-electron  $\sigma$ -bond activation processes using complex **1** are under investigation.

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