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# Activation of H<sub>2</sub> over the Ru-Zn Bond in the Transition Metal-Lewis Acid Heterobimetallic Species [Ru(IPr)<sub>2</sub>(CO)ZnEt]<sup>+</sup> (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)

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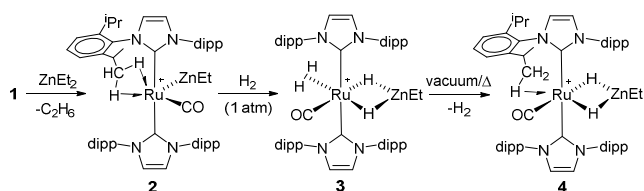
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Supporting Information Placeholder

**ABSTRACT:** Reaction of [Ru(IPr)<sub>2</sub>(CO)H]BAR<sup>F</sup><sub>4</sub> with ZnEt<sub>2</sub> forms the heterobimetallic species [Ru(IPr)<sub>2</sub>(CO)ZnEt]BAR<sup>F</sup><sub>4</sub> (**2**) which features an unsupported Ru-Zn bond. **2** reacts with H<sub>2</sub> to give [Ru(IPr)<sub>2</sub>(CO)(η<sup>2</sup>-H<sub>2</sub>)(H)<sub>2</sub>ZnEt]BAR<sup>F</sup><sub>4</sub> (**3**) and [Ru(IPr)<sub>2</sub>(CO)(H)<sub>2</sub>ZnEt]BAR<sup>F</sup><sub>4</sub> (**4**). DFT calculations indicate that H<sub>2</sub> activation at **2** proceeds via oxidative cleavage at Ru with concomitant hydride transfer to Zn. **2** can also activate hydric E-H bonds (E = B, Si) and computed mechanisms for the facile H/H exchange processes observed in **3** and **4** are presented.

Metal-ligand cooperativity is a widely used strategy for the activation and catalytic transformation of small molecules.<sup>1</sup> Many such systems are predicated on transition metal-Lewis base (TM-LB) combinations,<sup>2,3</sup> as well as those featuring electronically flexible ligand scaffolds, exemplified by Milstein's (de)aromatization approach.<sup>4</sup> More recently, TM-LA (LA = Lewis acid) cooperativity has (re)emerged<sup>5</sup> with reports of H<sub>2</sub> cleavage,<sup>6</sup> the activation of C-H and more polar E-H bonds<sup>6a,6f,7</sup> and, in some cases, involvement in catalytic processes.<sup>6a,6b,7,8</sup> To date such TM-LA cooperativity has been dominated by cases where the LA is a B or Al center that is brought into proximity with the TM via a constrained geometry ligand, typically a bi- or polydentate P- or N-based species.<sup>6-9</sup> Herein, we report on the preparation and reactivity of a novel TM-LA system, [Ru(IPr)<sub>2</sub>(CO)ZnEt]BAR<sup>F</sup><sub>4</sub> (**2**)<sup>10</sup> which features a direct, unsupported Ru-Zn bond and is accessed via the simple addition of ZnEt<sub>2</sub> to [Ru(IPr)<sub>2</sub>(CO)H]BAR<sup>F</sup><sub>4</sub> (**1**).<sup>11</sup> Complex **2** can activate H<sub>2</sub> with net addition across the Ru-Zn bond to give [Ru(IPr)<sub>2</sub>(CO)(η<sup>2</sup>-H<sub>2</sub>)(H)<sub>2</sub>ZnEt]BAR<sup>F</sup><sub>4</sub> (**3**).<sup>12</sup> The observation of facile intramolecular H/H exchange in **3**, along with DFT calculations, highlight the ability of the TM-LA {RuZn} moiety to act as a flexible and reversible hydride shuttle.

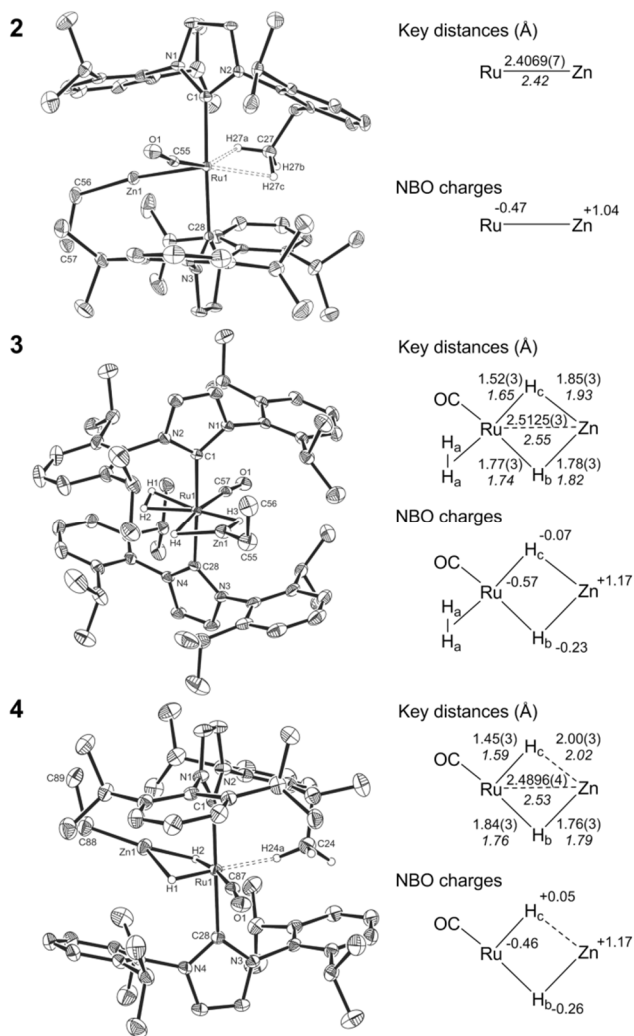
In line with the reported electrophilic reactivity of the hydride ligand in [Ru(IPr)<sub>2</sub>(CO)H]BAR<sup>F</sup><sub>4</sub> (**1**),<sup>11</sup> addition of one equivalent of ZnEt<sub>2</sub> to a fluorobenzene solution of this species gave the Ru-Zn complex **2** (Scheme 1), which was isolated as a red solid in 76% yield. <sup>1</sup>H NMR spectroscopy confirmed the absence of any hydride ligand in **2** and confirmed the presence of a single ZnEt group on the basis of the 8:3:2 ratio of <sup>1</sup>Pr methine protons to low frequency signals at δ 0.73 (CH<sub>3</sub>) and δ -0.11 (CH<sub>2</sub>).



**Scheme 1.** Formation and reactivity of **2-4** (dipp = 2,6-diisopropylphenyl). BAR<sup>F</sup><sub>4</sub> anions not shown.

Upon shaking a C<sub>6</sub>H<sub>5</sub>F solution of **2** under H<sub>2</sub> (1 atm), there was an instantaneous color change (deep red to colorless) resulting from the formation of the novel dihydrogen dihydride complex [Ru(IPr)<sub>2</sub>(CO)(η<sup>2</sup>-H<sub>2</sub>)(H)<sub>2</sub>ZnEt]BAR<sup>F</sup><sub>4</sub> (**3**, Scheme 1). The <sup>1</sup>H NMR spectrum of **3** exhibited two hydride resonances, a broad signal at δ -5.33 and a sharp peak at δ -12.13, in a relative ratio of 3:1. Cooling to -28 °C resolved the broad resonance into two signals (relative ratio 2:1) at δ -5.09 and -7.79 (with T<sub>1</sub> values of 31 and 72 ms respectively)<sup>13</sup> assigned to Ru(η<sup>2</sup>-H<sub>2</sub>) and Ru-H-Zn (trans to CO) respectively. Both signals remained broad, indicative of exchange; this was confirmed by EXSY and magnetization transfer experiments (Figure S11). No exchange with the remaining Ru-H-Zn trans to dihydrogen (δ -12.13, T<sub>1</sub> = 809 ms; T<sub>1</sub>(min) = 638 ms (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, -41 °C)) was found. However, upon exposure of **3** to 1 atm D<sub>2</sub>, <sup>1</sup>H and <sup>2</sup>H NMR spectra showed unequivocally that all three sites underwent a slower chemical exchange with deuterium incorporated into the Ru(η<sup>2</sup>-H<sub>2</sub>) and at both Ru-H-Zn positions.

The η<sup>2</sup>-H<sub>2</sub> ligand in **3** proved hard to dissociate, with only ca. 20% conversion to [Ru(IPr)<sub>2</sub>(CO)(H)<sub>2</sub>ZnEt]BAR<sup>F</sup><sub>4</sub> (**4**) apparent even after evaporating a C<sub>6</sub>H<sub>5</sub>F solution of **3** to complete dryness. In fact, full conversion to **4** required heating a solid sample of **3** at 50 °C under dynamic vacuum for 24 h. Subjecting solid **3** to vacuum/heat for further time (ca. 72 h) showed that all four hydride ligands could be removed, although reformation of **2** was also accompanied by additional, unidentified side products. Complex **4** displayed a low frequency (δ -27.06) Ru-H-Zn signal which now exchanged on the NMR timescale (magnetization transfer and EXSY measurements; Figure S12) with a second Ru-H-Zn resonance at δ -3.75.



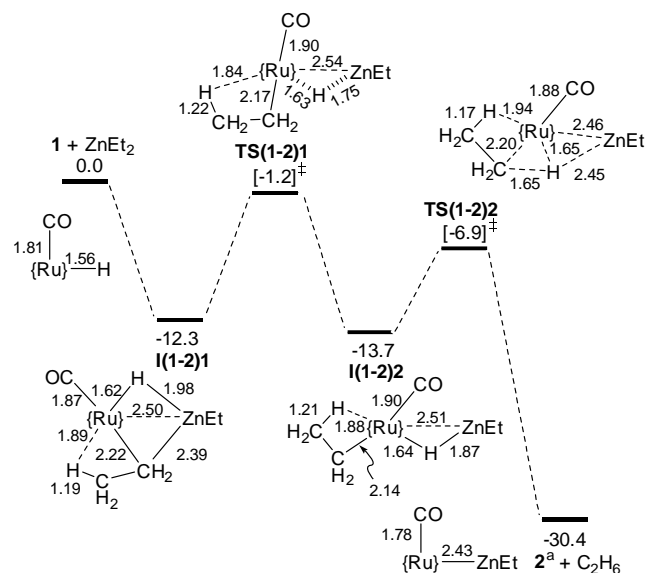
**Figure 1.** Molecular structures of the cations in **2**, **3** and **4**. Thermal ellipsoids are shown at 30%. All non-hydride and non-agostic hydrogen atoms are omitted for clarity. Also shown are comparisons of the key experimental and (in italics) computed distances around the central {Ru-Zn} moiety, along with the accompanying NBO charges.

The molecular structures of the cations in **2**, **3** and **4** are shown in Figure 1, along with a comparison with computed data for the central {Ru(H)<sub>n</sub>Zn} moieties in each case ( $n = 0, 4$  and  $2$  respectively). **2** exhibits a Ru-Zn distance of 2.4069(7) Å,<sup>14</sup> and also features two short Ru...H-C agostic interactions to one of the IPr ligands (Ru(1)...H(27A)-C(27) 2.13(3) Å, Ru(1)...H(27C)-C(27) 2.31(4) Å), similar to those seen previously in **1**.<sup>11</sup> In **3** and **4** the η<sup>2</sup>-H<sub>2</sub> and hydride hydrogens were included in the model, the latter being refined without restraint. Both these species have elongated Ru-Zn distances (2.5125(3) Å and 2.4896(4) Å, respectively) and have distinctly asymmetric {Ru(H)<sub>2</sub>Zn} moieties that reflect the relative trans influences of the ligands completing the coordination sphere. Thus, the bridging hydrides trans to CO in **3** and **4** are approximately evenly shared between Ru and Zn, whereas the hydride trans to η<sup>2</sup>-H<sub>2</sub> in **3** is significantly closer to Ru. This asymmetry is even more marked for the hydride trans to the agostic interaction in **4**.

DFT calculations<sup>15</sup> provide good absolute agreement for both the Ru-Zn distances as well as the various Ru-H and Zn-H distances in **2**, **3** and **4**, allowing for the inherent uncertainty in the H atom positions (see Figure 1, right hand side). NBO calculations characterize **2** as a Ru(0) species interacting with a cationic

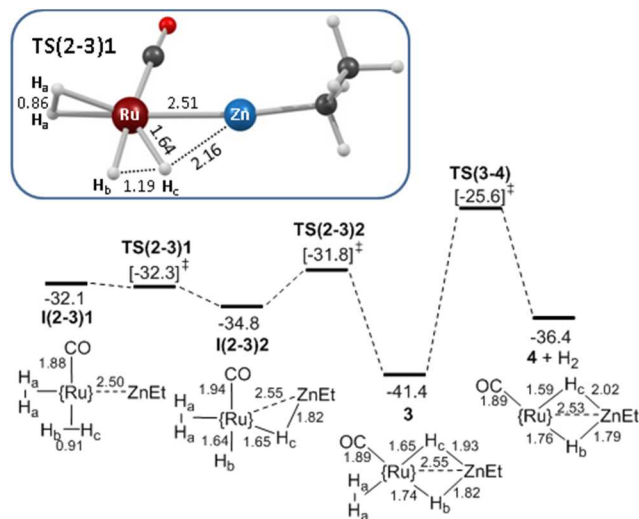
{ZnEt}<sup>+</sup> moiety via Ru → Zn σ-donation. In contrast, no significant direct Ru-Zn interaction is seen in either **3** or **4** (see Supporting Information for full details and orbital plots). NPA charges were used to characterize the nature of the hydride ligands. These indicate that the more evenly shared hydrides, H<sub>b</sub> (trans to CO in **3** and **4**), exhibit a significant negative charge ( $q_H = -0.23$  and  $-0.26$  respectively) while this reduces and becomes positive as the hydride moves closer to Ru (H<sub>c</sub>:  $q_H = -0.07$  trans to η<sup>2</sup>-H<sub>2</sub> in **3**;  $q_H = +0.05$  trans to the agostic in **4**). For comparison the terminal hydride in **1** (which lies trans to a vacant site) has  $q_H = +0.16$ . H<sub>c</sub> in **4** therefore more resembles a terminal Ru-hydride: indeed an Atoms in Molecules study on **4** shows the absence of any Zn...H<sub>c</sub> bond path (Figure S14).<sup>16</sup> The {Ru(H)<sub>2</sub>Zn} moieties in these species are therefore structurally flexible and able to access both bridging and terminal hydride character depending on the precise coordination environment.

Although examples of {M(H)<sub>n</sub>Zn} complexes exist for M = Ru,<sup>17</sup> as well as for other late TMs,<sup>18</sup> these all result from metal hydride precursors and, to the best of our knowledge, formation via bimetallic M-Zn cleavage of H<sub>2</sub> has no precedent.<sup>19,20</sup> We have therefore used DFT calculations to study the formation of **2** as well as its onwards reactivity with H<sub>2</sub> to **3** and **4**. Figure 2 indicates that the initial addition of ZnEt<sub>2</sub> to **1** forms an intermediate **I(1-2)1** at -12.3 kcal/mol in which the {RuZn} moiety is bridged by both a hydride and an ethyl ligand; the latter also engages in a β-agostic interaction with the Ru center. Ethyl group transfer onto Ru proceeds via **TS(1-2)1** with a barrier of 11.1 kcal/mol and is induced by rotation of the {Ru(H)Zn} moiety such that the bridging hydride drops below the equatorial coordination plane. This allows the CO ligand to move trans to the developing Ru-Et ligand and **I(1-2)2**,  $G = -13.7$  kcal/mol). The bridging hydride can now couple with the adjacent ethyl group via **TS(1-2)2** at -6.9 kcal/mol leading, after release of ethane, to the formation of **2** at -30.4 kcal/mol. In this case an alternative isomer of **2** devoid of agostic interactions is located, similar to the situation described previously for **1** for which several isomers were also found.<sup>11</sup>



**Figure 2.** Computed reaction profile (free energy, kcal/mol) for the formation of **2** and C<sub>2</sub>H<sub>6</sub> from **1** and ZnEt<sub>2</sub>; schematic structures show key distances (Å) within the equatorial plane; {Ru} = Ru(IPr)<sub>2</sub><sup>+</sup>. An ethane σ-complex, **I(1-2)3**, generated from **TS(1-2)2** is omitted for clarity. <sup>a</sup> non-agostic isomer of **2** located.

Figure 3 shows one possible mechanism for the reaction of **2** with H<sub>2</sub> to give **3** and **4**. Addition of two molecules of H<sub>2</sub> to **2** forms the bis-η<sup>2</sup>-H<sub>2</sub> intermediate **I(2-3)1** at -32.1 kcal/mol. A very flat free energy surface then sees an essentially barrierless cleavage of the H<sub>b</sub>-H<sub>c</sub> ligand with net addition over the Ru-Zn bond to give **I(2-3)2** at -34.8 kcal/mol. Rotation about the Ru...Zn vector then allows transfer of H<sub>b</sub> onto Zn to form **3** at -41.4 kcal/mol. H<sub>2</sub> loss from **3** is computed to be kinetically accessible (ΔG<sup>‡</sup> = 15.8 kcal/mol), but endergonic, **4** (+ H<sub>2</sub>) lying 5 kcal/mol above **3**. This is consistent with the reluctance of this species to lose H<sub>2</sub> found experimentally.

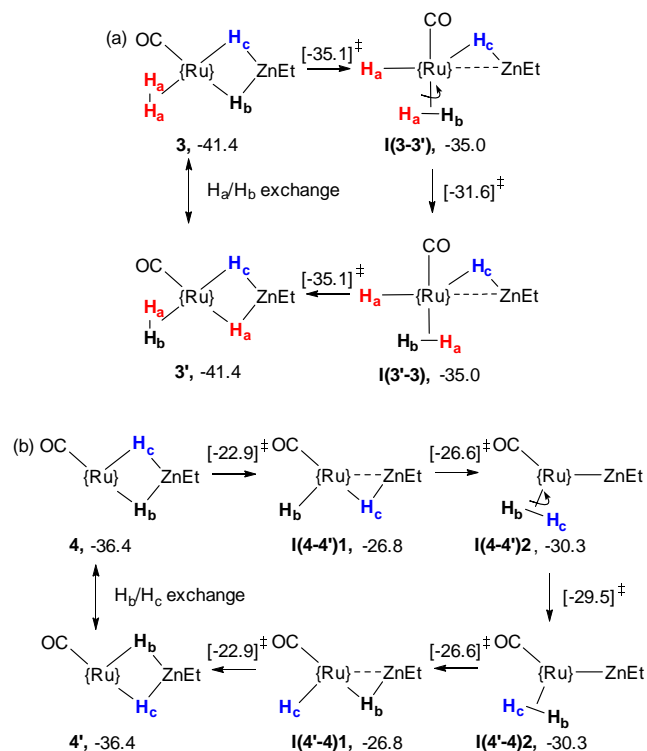


**Figure 3.** Computed reaction profile (free energy, kcal/mol) for the formation of **3** and **4** from **2**; schematic structures show key distances (Å) in the equatorial plane, as well as the labelling scheme for the H atoms; {Ru} = Ru(IPr)<sub>2</sub><sup>+</sup>. Inset: geometry of H<sub>2</sub> activation transition state **TS(2-3)1** (IPr ligands omitted).

The computed structure of the key H<sub>2</sub> activation transition state **TS(2-3)1** (inset, Figure 3) exhibits an elongated H<sub>b</sub>-H<sub>c</sub> moiety (1.19 Å *cf.* 0.91 Å in **I(2-3)1**). At this point the Zn...H<sub>c</sub> distance of 2.16 Å implies little, if any, interaction with the Zn center and it is only after the cleavage that the Zn participates by accepting a hydride ligand. In addition, minimal polarization of the H<sub>b</sub>-H<sub>c</sub> bond is computed in the transition state (*q*<sub>H<sub>b</sub></sub> = +0.05; *q*<sub>H<sub>c</sub></sub> = +0.02). We therefore propose that H<sub>2</sub> activation occurs via oxidative cleavage mediated by Ru, followed by hydride transfer to Zn. In support of Ru being the key player in the H<sub>2</sub> cleavage, the activation of H<sub>a</sub>-H<sub>a</sub> trans to Zn in **I(2-3)1** was also characterized: this proceeds via a structurally similar transition state at -28.6 kcal/mol which leads to a Ru(η<sup>2</sup>-H<sub>2</sub>)(H)<sub>2</sub> complex in which the Zn is unable to accept either hydride (Figure S17).

The mechanisms of H/H exchange in **3** and **4** have also been modelled. For **3**, exchange occurs both between the η<sup>2</sup>-H<sub>2</sub> ligand and the cis bridging hydride (H<sub>a</sub>/H<sub>b</sub> exchange) as well as between the two chemically distinct bridging hydrides (H<sub>b</sub>/H<sub>c</sub> exchange). H<sub>b</sub>/H<sub>c</sub> exchange can proceed via the mechanism in Figure 3, with reversible formation of the bis-η<sup>2</sup>-H<sub>2</sub> complex **I(2-3)1** and rotation of the H<sub>b</sub>-H<sub>c</sub> ligand. The latter occurs via a transition state at -28.3 kcal/mol, giving an overall exchange barrier of 13.1 kcal/mol. For H<sub>a</sub>/H<sub>b</sub> exchange a σ-CAM process<sup>21</sup> was characterized that sees formation of the H<sub>a</sub>/(η<sup>2</sup>-H<sub>a</sub>-H<sub>b</sub>) complex, **I(3-3')** (Figure 4a). H<sub>a</sub>-H<sub>b</sub> rotation and reversing the σ-CAM completes the exchange, the rotation transition state being the highest point in this process and equating to an overall barrier of 9.8 kcal/mol. The lower barrier for H<sub>a</sub>/H<sub>b</sub> exchange is consistent with the EXSY

experiments that indicated that only that process proceeded on the NMR timescale.<sup>22</sup> H<sub>b</sub>/H<sub>c</sub> exchange in **4** proceeds by a similar mechanism to that in **3** (Figure 4b). Thus initial rotation about the Ru...Zn vector cleaves the Zn-H<sub>b</sub> bond and forms **I(4-4')1**; H<sub>c</sub> can then transfer onto H<sub>b</sub> to form the η<sup>2</sup>-H<sub>b</sub>-H<sub>c</sub> complex **I(4-4')2**. H<sub>2</sub> rotation and reversing these processes complete the exchange. The highest transition states in this process are at -22.9 kcal/mol and correspond to an overall barrier of 13.5 kcal/mol. In principle, movement of the CO ligand from trans to H<sub>b</sub> to trans to H<sub>c</sub> would also render these two sites equivalent. However, this process has a barrier of 31.5 kcal/mol as it passes through a symmetrical Y-shaped {RuCO(H)<sub>2</sub>} moiety, which is strongly disfavored for a *d*<sup>6</sup> configuration.<sup>23</sup>



**Figure 4.** Computed mechanisms (free energy, kcal/mol) for (a) H<sub>a</sub>/H<sub>b</sub> in **3** and (b) H<sub>b</sub>/H<sub>c</sub> in **4**; {Ru} = Ru(IPr)<sub>2</sub><sup>+</sup>. Transition state energies for each step are given in square brackets.

To probe whether other E-H bonds could add across the Ru-Zn bond in **2**, preliminary investigations with both protic and hydridic reagents have been undertaken. NH<sub>3</sub> simply coordinated to form the ammonia complex [Ru(IPr)<sub>2</sub>(CO)(NH<sub>3</sub>)ZnEt]BAR<sup>F</sup><sub>4</sub> (**5**; Figure S13). With HBcat and PhSiH<sub>3</sub>, room temperature dehydrogenation took place to give **3** as the major ruthenium-containing product of both reactions. Surprisingly, even a 1:1 ratio of **2**:HBcat generated hydride signals characteristic of **3** suggesting that a strong driving force exists for formation of the Ru(H)<sub>2</sub>Zn moiety.<sup>11</sup> B NMR spectroscopy confirmed the formation of B<sub>2</sub>cat<sub>2</sub> (δ 31), but also showed a second major product at δ 22 which, by comparison to the literature, appears to be B<sub>2</sub>cat<sub>3</sub>.<sup>25</sup> In the reaction of **2** with PhSiH<sub>3</sub>, <sup>29</sup>Si NMR spectroscopy showed that Ph<sub>3</sub>SiH and Ph<sub>2</sub>SiH<sub>2</sub> were the major silicon containing reaction products, although a number of other, lower intensity signals were also present which we believe arise from the presence of three reactive Si-H bonds in the starting material, as well as the need for SiH<sub>4</sub> formation for atom balance. There is a clear silane dependence to this chemistry since no reaction was seen between **2** and either

Ph<sub>2</sub>SiH<sub>2</sub> or PhMe<sub>2</sub>SiH. Further studies are required to elucidate the pathways of the borane/silane dehydrogenation reactions.

In conclusion, we have described the facile formation of the TM-LA heterobimetallic species, **2**, featuring an unconstrained and unsupported Ru-Zn bond. This species is a rare example of an active TM-LA system derived from a non-group 13 element LA: **2** reacts directly with H<sub>2</sub> to form the {Ru(H)<sub>2</sub>Zn} species **3** and then **4**. DFT calculations indicate that H<sub>2</sub> activation proceeds via oxidative cleavage at Ru with the adjacent Zn acting as a (reversible) hydride acceptor. H/H exchange experiments and calculations on **3** and **4** show that intermediates with unsupported Ru-Zn bonds remain kinetic accessibility even after H<sub>2</sub> addition. This, along with the observation of the activation of hydridic E-H bonds (E = B, Si), suggests that such unconstrained heterobimetallic TM-LA species may have potential applications in catalysis and this possibility is being pursued in our laboratories.

## ASSOCIATED CONTENT

### Supporting Information

All data supporting this study are provided as Supporting Information accompanying this paper. This includes: synthesis, characterization (inc. multinuclear NMR spectra) and crystallographic data (CIF) for **2-5**; computational data, including computed geometries and energies, details of alternative reaction pathways and a molecular graph of **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interests.

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