Bonding and Reactivity of a Pair of Neutral and Cationic Heterobimetallic RuZn₂ Complexes

Fedor M. Miloserdov, Anne-Frédérique Pécharman, Lia Sotorrios, Nasir A. Rajabi, John P. Lowe, Stuart A. Macgregor, Mary F. Mahon, and Michael K. Whittlesey

ABSTRACT: A combined experimental and computational study of the structure and reactivity of two [RuZn₂Me₂] complexes, neutral [Ru(PPh₃)(Ph₂PC₆H₄)(ZnMe)₂][BArF₄] (2) and cationic [Ru-(PPh₃)₃(PC₆H₄)(ZnMe)₂][BArF₄] ([BArF₄] = [B{3,5-(CF₃)₂C₆H₃}]⁻) (3), is presented. Structural and computational analyses indicate these complexes are best formulated as containing discrete ZnMe ligands in which direct Ru–Zn bonding is complemented by weaker Zn²⁻–Zn interactions. The latter are stronger in 2, and both complexes exhibit an additional Zn–Caryl interaction with a cyclometalated phosphine ligand, this being stronger in 3. Both 2 and 3 show diverse reactivity under thermolysis and with Lewis bases (PnBu₃, PCy₃, and IMes). With 3, all three Lewis bases result in the loss of [ZnMe]⁺. In contrast, 2 undergoes PPh₃ substitution with PnBu₃, but with IMes, loss of ZnMe₂ occurs to form [Ru(PPh₃)(C₆H₄PPh₂)(C₆H₄PPhC₆H₄Zn(IMes))H][BArF₄] (7). The reaction of 3 with H₂ affords the cationic trihydride complex [Ru(PPh₃)₃(ZnMe)₂(H)₃][BArF₄] (12). Computational analyses indicate that both 12 and 7 feature bridging hydrides that are biased toward Ru over Zn.

INTRODUCTION

Heterobimetallic complexes comprised of a transition metal (TM) and a main group metal (MGM) are the focus of considerable interest because of the possibility that the disparate chemistry of the two partners could combine cooperatively to bring about the novel stoichiometric and/or catalytic activation of small molecules. In one recent example, shown in Scheme 1a, the challenging C–O activation of an anisole takes place across the Rh–Al bond of complex I to afford II, which upon addition of a silane, mediates catalytic C–O bond reduction. Complex I represents one class of heterobimetallic complexes in which the MGM forms part of a multidentate ligand on the TM center. Another class of complex is represented by III in Scheme 1b, in which the MGM is unsupported and unconstrained. In this particular case, both Ru and Zn centers are coordinatively unsaturated, and this “dual unsaturation” allows them to act cooperatively in the stoichiometric activation of H₂ to give IV. We have interpreted Ru–Zn bonding within complex III and other related Ru–Zn complexes in terms of a donor–acceptor interaction between a Ru(0) metal center and Z-type Zn-based acceptor ligands. Complex III is formed upon elimination of an alkane, an approach we have used to prepare other Ru and mono-Zn-containing products, including complex I in Scheme 2 that features bridging hydride and aryl ligands. Accordingly, the reaction of complex I with ZnMe₂ resulted in further alkane elimination and formation of neutral [RuZn₂Me₂] complex 2. Alternatively, reaction with a source of [ZnMe]⁺ induced C–H reductive coupling in I and formation of cationic [RuZn₂Me₂] complex 3.

Another strategy for the preparation of [TM-Zn₂R₂] species involves addition of Carmona’s Cp’Zn–ZnCp* dimer to low-valent precursors. On the basis of the isolobal nature of Cp’Zn and a hydrogen atom, the coordination of the TM center to an intact Zn–Zn bond can be considered to form an all-metal analogue of a TM(η²-H₂) complex. Likewise, weakening of the Zn–Zn interaction to the point where it gives two ZnCp* ligands has been compared to the oxidative cleavage of the η²-H₂ ligand to form two M–H bonds, although such Zn–Zn bond cleavage is proposed to proceed without any change in the formal oxidation state. In such cases, ZnCp* and related ZnR (R = alkyl or aryl) ligands have been formulated as monovalent one-electron donors. Computational studies have suggested that the extent to which the Zn–Zn interaction in Cp’Zn–ZnCp* is retained upon approach to a TM is dependent on the nature of the linking ligand.
metal itself, the surrounding ancillary ligands, and the ZnR substituents. In this context, the availability of the closely related neutral and cationic \([\text{RuZn}_2\text{R}_2]\) complexes, 2 and 3, respectively, provides an opportunity to explore the analogy between \{RZn−ZnR\} and H\(_2\). Herein, we report computational and experimental studies to this end.

### RESULTS AND DISCUSSION

#### Structure and Bonding in 2 and 3.

Figure 1 shows the geometries and labeling system used in the analyses of 2 and 3, focusing on the central RuZn\(_2\) core. Selected distances are given in angstroms.

Inorganic Chemistry pubs.acs.org/IC

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https://doi.org/10.1021/acs.inorgchem.1c02072

Inorg. Chem. 2021, 60, 16256−16265

Figure 1. Geometries and labeling scheme used in the analyses of 2 and 3, focusing on the central RuZn\(_2\) core. Selected distances are given in angstroms.

The heavy atom (i.e., non-H) positions from the crystallographic studies and optimized the H atom positions with the BP86 functional. This approach also allows for a consistent treatment of the new hydride-containing structures that we describe below, where the H atom location is intrinsically less precise.

Both 2 and 3 feature triangular RuZn\(_2\) moieties with Ru−Zn distances that are shorter than Zn−Zn distances. The Ru−Zn distances are more symmetrical in 2 (2.50/2.51 Å) than in 3 (2.41/2.55 Å) and are all within the sum of the covalent radii (Ru, 1.46 Å; Zn, 1.22 Å), suggesting direct Ru−Zn bonds in all cases. Zn−Zn bonding in related systems has been discussed within the limits of the Zn−Zn distance in Zn\(_2\)Cp\(_2\) (2.31 Å), and the metallic radius of Zn (1.339 Å) and the Zn−Zn distances in 2 and 3 (2.59 and 2.68 Å, respectively) are at the upper end of this range. A \([\text{TMZn}_2\text{R}_2]\) unit with an intact η\(^2\)-RZn−ZnR moiety would
also be characterized by near-linear Zn−Zn−R angles and M−Zn−R angles approaching 150° (the limit for an equilateral triangle). In 2, the average Zn−Zn−R and Ru−Zn−Me angles are 133.9° and 165.8°, respectively, while in 3, the average Zn−Zn−R angle is 113.2° and the Ru−Zn−Me angle is 179.4°. These data indicate that 2 and 3 are best formulated as Ru(ZnMe)2 complexes, but that 2 is slightly displaced along the continuum toward a Ru(q2-RZn−ZnR) fragment. Note that in 3, the Ru−Zn1−Me angle is smaller than expected at 161.3°, but in this case, the Me group is bent away from C1, suggesting that it is the short Zn1···C1 contact of 2.15 Å that drives this distortion. This is explored further in the electronic structure analyses below.

**Figure 2a** provides details of quantum theory of atoms in molecules (QTAIM) analyses of 2 and 3 with electron density contours plotted in the {RuZn1Zn2} plane. These are complemented by noncovalent interaction (NCI) plots shown in Figure 2b. For 2, bond paths between Ru and both Zn centers are consistent with the presence of Ru−Zn bonds. The associated bond critical points (BCPs) show similar electron densities, ρ(r), of ~0.06 au, and this relatively low value, coupled with positive values of the Laplacian and small negative total energy densities (Figures S39 and S40), is consistent with a donor−acceptor (i.e., Ru → Zn) interaction between two heavy atoms. Figure 2a also shows the computed delocalization indices (DI) in parentheses. These reflect the degree of shared electron density between two atomic centers and proved more discriminating than ρ(r) for the Ru−Zn interactions. Thus, a larger DI of 0.68 is associated with the shorter Ru−Zn2 bond compared to a DI of 0.52 for the Ru−Zn1 bond. DIs can also be measured between atoms not linked by a bond path and can be useful for identifying interactions in areas of flat electron density. A Zn1···Zn2 DI of 0.35 suggests a weak Zn−···Zn interaction is present. For Zn1, this is supplemented by interaction with C1 to which a curved bond path [2.35 Å; ρ(r) = 0.049; DI = 0.26] indicates a degree of bridging character for the cyclometalated aryl group, albeit biased toward Ru [2.17 Å; ρ(r) = 0.098 au; DI = 0.76]. These stabilizing interactions are confirmed by the NCI plot of 2 that displays turquoise and blue regions along the Zn1···Zn2 and Zn1···C1 vectors, respectively.

For 3, variations in these different interactions are seen relative to 2 that reflect changes in the interatomic distances. Thus, the Ru−Zn2 interaction strengthens [2.41 Å; ρ(r) = 0.071; DI = 0.82] while Ru−Zn1 interaction weakens [2.55 Å, ρ(r) = 0.054; DI = 0.46]. The Zn1−Zn2 interaction also weakens significantly [2.68 Å; DI = 0.18]; for Zn2, this is compensated by the stronger interaction with Ru, whereas for Zn1, the interaction with C1 strengthens [2.15 Å; ρ(r) = 0.070; DI = 0.40]. The stronger Zn1···C1 interaction is also apparent in the NCI plot where a sharper blue disk along the Zn1···C1 vector is seen, and this is also consistent with the bending of the Ru−Zn1−Me angle away from C1 as noted above. A similar Zn···aryl interaction has been noted before in a related Ru−Zn bimetallic complex [Zn−·C, 2.282(2) Å],35 while the longer Zn−Caryl distances in the asymmetrically bridged [ZnPh]2 dimer average 2.40 Å.

A natural orbitals for chemical valence (NOCV) analysis confirmed the differences in the additional stabilizing interactions at the {Zn1Me}+ fragments in 2 and 3 (Figure 3). In each case, the key deformation density channel is dominated by donation from the η3 hybrid HOMO of the Ru-based fragment into the σ* LUMO of {ZnMe}+. For 2, this also shows contributions from both Zn2 and C1, whereas for 3, a larger component from C1 is apparent but no contribution from Zn2 is seen. Equivalent plots for the {Zn2Me}+ fragments are provided in Figures S46 and S47.

**Reactivity Studies.** Given that 2 and 3 result from the formal introduction of ZnMe and [ZnMe]+, respectively, into 1, a series of reactivity studies were undertaken to probe the potential to reverse this process, through either thermolysis or...
reactions with Lewis bases. Such processes probe further the isolobality of ZnR and H, for example, the deprotonation of TM-hydrides. The reactions of 2 and 3 with H₂ were also attempted, and the results are summarized in panels a and b of Scheme 3.

**Thermal Stabilities of 2 and 3.** Heating 2 in toluene (80 °C, 2 days) resulted in the loss of ZnMe to give the previously reported [RuZnMe] complex, [Ru(dppbz)(PPh₂(biphenyl))][(ZnMe)] [5; dppbz = 1,2-bis(diphenylphosphino)benzene; PPh₂(biphenyl) = cyclometalated PPh₂(biphenyl)], as the major product. Alongside formal elimination of ZnMe, the formation of 5 also requires C−H/P−C activation and C−C coupling steps to generate the dppbz and metalated Ph₂P-(biphenyl) ligand, although the exact sequence in which these steps take place remains unknown. For 3, the result of heating proved to be much less clear. 3¹P NMR monitoring of a reaction mixture refluxed in benzene (2 days) or refluxed in toluene (2 h) revealed formation of an initial product 9 (characterized by two coupled doublet resonances at δ 78 and 48) that, upon further heating (2 days) in toluene, converted to a second product, 10, which showed a similar pair of coupled signals at δ 53 and 46. Both compounds gave oils in all tested combinations of solvents, which, together with an absence of any diagnostic (i.e., non-aromatic) ¹H NMR signals, makes their identities hard to determine.

**Reactivity of 2 and 3 with Lewis Bases.** Rather than removing either of the ZnMe ligands, the reaction of 2 with PnBu₃ at room temperature led to substitution of the PPh₃ ligand and formation of [Ru(P₃Bu₃)(C₆H₄PPh₂)(ZnMe)] (6). X-ray characterization (Figure 4) revealed a structure that was broadly similar to that of 2 in terms of metrics (Table S2). The ease of phosphine substitution in 2 contrasts with the difficulties reported by Fischer in attempting to exchange phosphine ligands in multi-Zn-containing Ni species. At the same time, the lack of reaction between 2 and PCy₃ indicates how sensitive these systems are to the choice of Lewis base. In contrast, 3 reacted with both P₃Bu₃ and PCy₃, and in this case, this did incur the loss of [ZnMe]⁺ to give 1, together with 11 in the case of P₃Bu₃. The findings fit with the previously observed complete conversion of 3 into 1 that is seen in THF. The fate of the eliminated [ZnMe]⁺ could not be established, but when the Lewis base is changed to the N-heterocyclic carbene IMes, trapping as the NHC adduct [(IMes)₂ZnMe]⁺ was found, alongside formation of 1. A very different outcome was found when IMes was reacted with 2. This afforded [Ru(P₃Ph₃)(C₆H₄PPh₂)-(C₆H₄PPh₂H₂Zn(IMes))H] (7) through substitution of a

**Scheme 3.** Reactions of (a) [Ru(P₃Ph₃)(C₆H₄PPh₂)(ZnMe)]₂ 2 and (b) [Ru(P₃Ph₃)(C₆H₄PPh₂)(ZnMe)][BAR₄]³⁻ 3*
Me group by IMes on Zn. The formally eliminated ZnMe₂ was trapped as (IMes)ZnMe₂ by the second equivalent of carbene necessary to bring about the full consumption of 2.⁴⁴,⁴⁵

The X-ray structure of 7 (Figure 5) showed a fac arrangement of an intact PPh₃ (based on P₃), one phosphine that was cyclometalated onto ruthenium (based on P1), and a third phosphine ligand (based on P₂) unusually metalated through two phenyl rings, one onto Ru [Ru₁−C₁₉, 2.1438(18) Å] and the second onto Zn [Zn₁−C₂₅, 2.0206(18) Å]. The sixth transition metal coordination site was occupied by a hydride ligand bridging the Ru and Zn centers [Ru₁···Zn₁, 2.6541(3) Å]. Computational analysis of the bonding in 7 is reserved until after discussion of the product of the reaction of 3 with H₂.

Redissolving a crystalline sample of the compound gave NMR signals for 7 together with a second, minor species, 8.⁴⁶ The signals for 7 were consistent with the solid state structure, a doublet of doublet of doublets Ru−H−Zn resonance in the ¹H NMR spectrum, with one large (pseudo)trans and two smaller ²JHP splittings, and one high-frequency ³¹P triplet (δ = S2) for the PPh₃ group, together with two lower-frequency (δ = −12 and −24) doublet of doublet signals for the two cyclometalated phosphines.⁴⁷,⁴⁸ The presence of similar ³¹P chemical shifts for the minor species 8 supports it being an isomer. While ¹H(³¹P) NMR measurements showed that both isomers feature hydride trans to a metalated phosphine, the presence of two surprisingly small ²JHP couplings (9 and 6 Hz), in addition to a large, pseudotrans splitting (46 Hz) in the ³¹P-coupled ¹H NMR spectrum, leaves it unclear as to exactly what the structure of 8 is. Closer inspection of NMR spectra recorded shortly after combining IMes and 2 indicates that 8 is formed in the initial stages (mixing for <15 min) and is thus a kinetic product of the reaction formed prior to subsequent growth of the thermodynamic product, 7.⁴⁹ The signals of 8 seen in the NMR spectra of 7 may therefore arise due to co-crystallization.

Reactivity of 2 and 3 toward H₂. During our previous studies of Ru mono-Zn complexes,⁴⁻¹²,¹³,¹⁹,²⁰ H₂ was typically found to add across the Ru−Zn bond, as shown in Scheme 1b. Very different, contrasting behavior was seen with 2 and 3. Thus, the former did not react with H₂ at room temperature and, upon being heated to 60 °C, gave only a complex mixture of products. In contrast, 3 reacted rapidly with two molecules of H₂ at room temperature to reverse the phosphine cyclometalation and form the cationic dizinc trihydride complex, [Ru(PPh₃)₃(ZnMe)₂H₃][BArF₄] (12). Remarkably, this transformation could also be carried out in the solid state simply by stirring a powdered sample of solid 3 under 1 atm of H₂.

Complex 12 displayed high-frequency doublet and triplet ³¹P NMR resonances, consistent with the mer-RuP₃ geometry apparent in the X-ray crystal structure (Figure 6). The ¹H NMR spectrum showed two hydride signals at δ = −7.3 (ddt) and −11.1 (dtt) in a 2:1 ratio.⁵⁰ Upon being heated to 60 °C, 12 decomposed as evidenced by the precipitation of an insoluble red oil at the bottom of reaction solutions.

The molecular structure of the cation in 12 is shown in Figure 6. The equatorial positions comprised two ZnMe ligands, one PPh₃ ligand, and three hydrides (which were located and refined without restraints). The coordination sphere was completed by two phosphines in a distorted trans-axial arrangement [P₁−Ru−P₃, 164.804(17)°]. Two of the hydrides were disposed approximately trans to one another [H₁−Ru₁−H₂, 163.3(16)°], while the third was located trans to the equatorial PPh₃ ligand [H₃−Ru₁−P₂, 175.7(12)°]. The two Ru−Zn distances [2.5188(3) and 2.5397(3) Å] are considered further in the computational analysis of 12 below.

Structure and Bonding in 12 and 7. The computed structure of 12 and details of the QTAIM analyses are shown
in panels a and b, respectively, of Figure 7, with the related NCI and NOCV analyses presented in the Supporting Information. In this case, QTAIM reveals an absence of Ru–Zn bond paths, despite Ru–Zn distances that are similar to those in 2 and 3. However, the computed DI s (Ru–Zn1, 0.38; Ru–Zn2, 0.41) indicate significant Ru–Zn interactions are still present, and this is supported by the NCI plot that shows blue stabilizing features between Ru and both Zn centers. For the outer hydrides, H1 and H2, the computed Ru–H distances of 1.69 Å are typical for a trans H–Ru–H arrangement and bond paths are characterized by a ρ(r) of ~0.106 au and DIs of ~0.69. These Ru–H bonds appear stronger than the Zn1–H1 and Zn2–H2 bonds (~1.82 Å; ρ(r) = 0.065 au; DI ~ 0.31), and these are in turn significantly weaker than the unperturbed Zn–H bond in MeZnH [1.52 Å; ρ(r) = 0.11 au; DI = 0.89; see Supporting Information]. H1 and H2 are therefore bridging the respective Ru–Zn vectors but are strongly biased toward Ru over Zn. This is also reflected in the very low ellipticities of the Ru–H BCPs (average of 0.028) that are indicative of terminal hydride character, compared with the higher ellipticities of the Zn–H BCPs [average of 0.48 (Figure S42)].

The properties of the Ru–H3 bond [1.69 Å; ρ(r) = 0.107 au, DI = 0.70] are similar to those of the Ru–H1 and Ru–H2 bonds. In this case, no bond path to either Zn center is seen but DIs of 0.19 indicate some residual interactions are still present, and these are confirmed in the NCI plot that shows turquoise regions along the Zn1···H3 and Zn2···H3 vectors. The significant ellipticity of the Ru–H3 BCP (0.145) also suggests a distortion of the electron density away from a terminal Ru–H σ-bond due to the presence of the two {ZnMe} moieties. An NOCV analysis of {ZnMe} bonding in 12 indicates the major deformation density channels exhibit donation from Ru and both adjacent hydrides (see the Supporting Information).

A similar analysis of the bonding in compound 7 shows the hydride present, H1, to have characteristics similar to those of H1 and H2 in 12 [Ru–H1, 1.68 Å; ρ(r) = 0.108, DI = 0.68; Zn–H1, 1.79 Å, ρ(r) = 0.067, DI = 0.33]. The Ru–Zn distance of 2.65 Å is the longest of the species studied here, and no Ru–Zn bond path is computed; however, a Ru···Zn DI of 0.29 suggests some interaction between the two metal centers (Figure S41).

Overall, the {Ru(H1)Zn1(H3)} and {Ru(H2)Zn2(H3)} moieties in 12 and the {RuH1Zn} moiety in 7 can be considered as featuring asymmetrically bound bridging hydride ligands that interact more strongly with the Ru centers. A similar situation is seen in [Ru(IPr)2(CO)(ZnMe)(η3−H2)- (H)]+ and [Ru(IPr)2(CO)(ZnR)(H)]+ species (R = Et or Me), where, depending on the nature of the trans ligand, the hydride within a {Ru(Hz)} moiety shows different degrees of Ru–H or Zn–H bonding character. These add to the continuum of structures that can be accessed in TM-MG heterobimetallic complexes featuring hydride ligands, the precise nature of which will depend on the coordination environment of the TM partner.

### CONCLUSIONS

A combined computational and experimental study has been undertaken on two [RuZn2Me2] species, neutral 2 and cationic 3. Geometrical considerations supported by computational analyses confirm the presence of direct Ru–Zn bonds in both species and suggest these are best formulated as Ru(ZnMe)2 complexes featuring discrete ZnMe ligands. Some additional stabilization may be achieved via Zn···Zn interactions, and 2 and 3 both exhibit Zn···Caryl interactions, with these being more significant in 3.

Experimentally, the two complexes exhibit diverse reactivities with thermolysis and the addition of a range of Lewis bases bringing about different outcomes with no apparent correlation to either the overall charges of the complexes or the different strengths of the Ru–Zn interactions present. 2 reacted with H2 to give a mixture of products, while in contrast, reaction of H2 with 3 led cleanly to [Ru{(PPh3)5}(ZnMe)2H3][BF4] (12). Computational analyses of this complex suggest the presence of three hydride ligands that bridge the Ru···Zn vectors asymmetrically toward Ru.

12 adds to the range of transition metal complexes that feature multiple main group metals and multiple hydride ligands that have recently attracted a great deal of attention due to the unusual bonding interactions and unusual geometries they can possess. Studies of their reactivity, however, remain rare. In the study presented here, we have shown that both the TM and the MGM can be centers of reactivity in these heterobimetallic complexes and the factors that govern the site of reactivity will be the subject of future reports from our groups.
Experimental Section

General Comments. All manipulations were carried out under argon using standard Schlenk, high-vacuum, and glovebox techniques using dry and degassed solvents. C6D6 and THF-d8 were vacuum transferred from potassium. NMR spectra were recorded at 298 K (unless otherwise stated) on Bruker Avance 400 and 500 MHz NMR spectrometers and referenced as follows: CD3OD (δ 3.31; 4, D2O, 7.34 ppm; TMS, 0.00 ppm). P spectra were referenced externally to 85% H3PO4 (δ 0.00 ppm). Elemental analyses were performed by Elemental Microanalysis Ltd. (Okehampton, Devon, U.K.). Compounds 1, 2, 3, and I2M3 were prepared according to literature methods.

31P{1H} NMR spectra were referenced externally to 85% H3PO4 (δ 0.00 ppm). Each spectrum was referenced to phosphoric acid in THF-d8.
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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This project has received funding from the European Union’s Horizon 2020 research and innovation programme under Marie Skłodowska-Curie Grant Agreement 792674 (F.M.M.) and EPSRC (Grant EP/T019743/1 for A.F.G., Grant EP/T019876/1 for L.S., and Grant EP/R020752/1 for N.A.R.).

DEDICATION
The authors dedicate this paper to Professor Christian Bruneau in recognition of his outstanding contributions to ruthenium chemistry.

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ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acs.inorgchem.1c02072.

NMR spectra of products from reactions of 2 and 3. X-ray structural data and metrics for 6, 7, and 12, and computational details (functional testing, electronic structure analyses, QTAIM, and NOCV) (PDF)

Accession Codes
CCDC 2083542—2083544 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Accession Codes
CCDC 2083542—2083544 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acs.inorgchem.1c02072.

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measurements showed this did not change between 8 values of 400 and 540 ms, respectively (400 MHz, 300 K).

The 7:8 ratio was ~1:0.15. Variable-temperature 1H NMR measurements showed this did not change between ~70 and 70 °C.

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An additional species was also formed at this early stage of the reaction but is an intermediate that was mostly consumed within ~3 h; its identity remains unknown.

The two hydride signals at δ −7.3 and −11.1 showed similar T1 values of 400 and 540 ms, respectively (400 MHz, 300 K).

The computed structure of [Ru(PPh3)2H2]− (ie, 12 with both [ZnMe]2+ groups removed) shows a shortening of the Ru–H3 distance from 1.69 to 1.64 Å, consistent with both [ZnMe]2+ groups influencing the Ru–H3 interaction in 12. In contrast, the Ru–H1 and −H2 distances are not affected.

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