

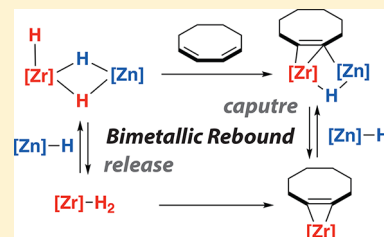
Heterobimetallic Rebound: A Mechanism for Diene-to-Alkyne Isomerization with M---Zr Hydride Complexes (M = Al, Zn, and Mg)

M. J. Butler, A. J. P. White, and M. R. Crimmin*

Department of Chemistry, Imperial College London, South Kensington, London SW7 2AZ, United Kingdom

S Supporting Information

ABSTRACT: The reaction of a series of $M\cdots Zr$ heterobimetallic hydride complexes with dienes and alkynes has been investigated ($M = Al, Zn$, and Mg). Reaction of $M\cdots Zr$ with 1,5-cyclooctadiene led to diene isomerization to 1,3-cyclooctadiene, but for $M = Zn$ also result in an on-metal diene-to-alkyne isomerization. The resulting cyclooctyne fragment is trapped between Zr and Zn metals in a heterobimetallic species that does not form for $M = Mg$ or Al . The scope of diene isomerization and alkyne trapping has been explored leading to the isolation of three new heterobimetallic slipped metallocyclopropene complexes. The mechanism of diene-to-alkyne isomerization was investigated through kinetics. While the reaction is first-order in $Zn\cdots Zr$ at high diene concentration and proceeds with $\Delta H^\ddagger = +33.6 \pm 0.7$ kcal mol⁻¹, $\Delta S^\ddagger = +23.2 \pm 1.7$ cal mol⁻¹ K⁻¹, and $\Delta G^\ddagger_{298\text{ K}} = +26.7 \pm 1.2$ kcal mol⁻¹, the rate is dependent on the nature of the diene. The positive activation entropy is suggestive of involvement of a dissociative step. On the basis of DFT calculations, a heterobimetallic rebound mechanism for diene-to-alkyne isomerization has been proposed. This mechanism explains the origin of heterobimetallic control over selectivity: $Mg\cdots Zr$ complexes are too strongly bound to generate reactive fragments, while $Al\cdots Zr$ complexes are too weakly bound to compensate for the contrathermodynamic isomerization process. $Zn\cdots Zr$ complexes have favorable energetics for both dissociation and trapping steps.



INTRODUCTION

Diene-to-alkyne isomerization is a contrathermodynamic reaction that has limited experimental precedent.¹ A related reaction, alkene-to-alkyne dehydrogenation is equally as rare.² The dearth of examples can be explained by considering the thermodynamics of isomerization. Calculations of the relative stabilities for C_8H_{12} rings are shown in Figure 1.

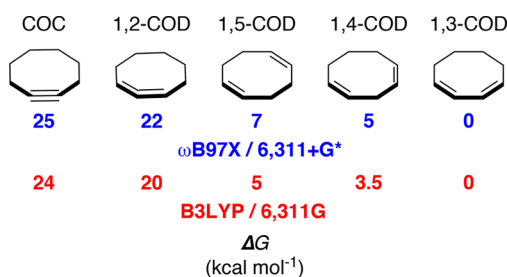


Figure 1. Thermodynamics of cyclooctadiene isomerization calculated by DFT.

The calculated values are consistent with experimental thermochemical data.³ Due to the incorporation of increased angle strain as carbon centers are converted from sp^2 - to sp -hybridized form, diene-to-alkyne isomerization is unfavorable within small or medium rings.^{4,5}

As part of an extensive study modeling potential intermediates in the Fischer–Tropsch hydrocarbon chain lengthening process, Bercaw and co-workers have shown that diene-to-alkyne isomerization can be effected by

$[Cp^*_2TaH_3]$.^{6,7} The reaction involves 2 equiv of 1,3-butadiene, 1 equiv of which is hydrogenated to give 1-butene and the other forms $[Cp^*_2TaH(\eta^2-MeC\equiv CMe)]$. The observation of a series of hydride intermediates by ¹H NMR spectroscopy allowed the authors to conclude that a metal hydride pathway for isomerization was likely to be operating.⁶ Brinkmann et al. have documented a similar reaction.⁸ The isomerization of an η^3 -allyl to a σ -vinyl ligand occurs on a titanocene fragment and proceeds through an η^2 -propyne intermediate. In both these cases, the alkyne adduct is only a reaction intermediate, and the diene-to-alkyne isomerization event is merely part of a more complex network of reactions.

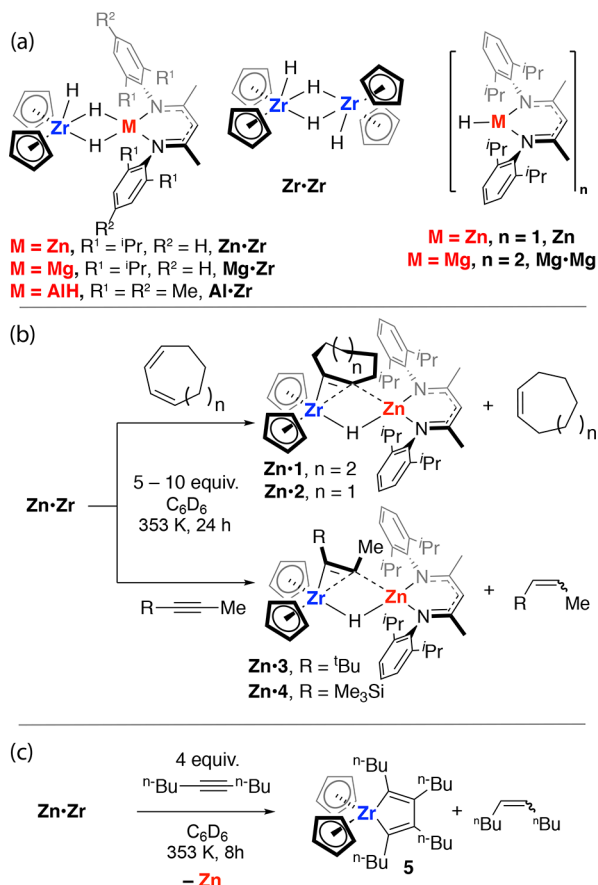
In 2016, we reported an example of diene-to-alkyne that involves the reaction of either 1,3- or 1,5-cyclooctadiene with a heterobimetallic hydride complex and results in the formation of a trapped cyclooctyne isomer.⁹ We showed that the unusual on-metal isomerization only occurs for zinc---zirconium hydride complexes and is not observed for analogous magnesium---zirconium or aluminum---zirconium hydride complexes. Here we provide a detailed analysis of the mechanism. We conclude that diene-to-alkyne isomerization occurs by a heterobimetallic rebound mechanism. This new mechanism is supported by kinetic analysis, computational studies and a thorough investigation of the solution dynamics of the complexes involved. We explain the origin of the heterobimetallic effect reported in our preliminary communication.⁹

Received: December 26, 2017

Published: February 28, 2018

RESULTS AND DISCUSSION

Reactions of M-Zr heterobimetallics with dienes and alkynes. Reaction of 1,5-COD with the bimetallic complexes Mg-Zr, Al-Zr, and Zr-Zr (Scheme 1a) consistently give

Scheme 1. Structures and Reactions^a

^a(a) Structures of hydride reagents used in this study. (b) Reaction of $\text{Zn}^\bullet\text{Zr}$ with dienes and alkynes to form $\text{Zn}^\bullet\text{1-4}$. (c) Reaction of $\text{Zn}^\bullet\text{Zr}$ with oct-4-yne to form **5**.

mixtures of 1,3-COD, cyclooctene, and trace cyclooctane. The details of these catalytic experiments were included in a preliminary communication of this work and are not repeated here.⁹ A number of zirconium hydride complexes are known to catalyze diene isomerization.¹⁰ In contrast, reaction of $\text{Zn}^\bullet\text{Zr}$ with 1,5-COD leads to transfer hydrogenation of the diene and

formation of the trapped cyclooctyne complex $\text{Zn}^\bullet\text{1}$ (Scheme 1b). This reactivity is unique for the Zn-analogue of the series, and no evidence for trapped alkyne complexes were observed during reactions of $\text{Mg}^\bullet\text{Zr}$ or $\text{Al}^\bullet\text{Zr}$.

Isomerization is barely affected by reducing the ring size from 8 to 7 carbons, and $\text{Zn}^\bullet\text{2}$ is formed in 85% yield from reaction of 1,3-cycloheptadiene (1,3-CHD) with $\text{Zn}^\bullet\text{Zr}$ (Scheme 1b). Addition of $\text{Zn}^\bullet\text{Zr}$ to either 1,3- or 1,4-cyclohexadiene did not lead to an alkyne adduct formation but a catalytic redistribution reaction to form cyclohexene and benzene.¹⁰ Reactions of freshly prepared 1,2-cyclononadiene¹¹ or commercial samples of 1,7-octadiene with $\text{Zn}^\bullet\text{Zr}$ did not lead to tractable products but instead unidentified mixtures.

A series of reactions between $\text{Zn}^\bullet\text{Zr}$ and alkynes were also investigated. Addition of 4,4-dimethylpent-2-yne to $\text{Zn}^\bullet\text{Zr}$,¹² led directly to the alkyne adduct $\text{Zn}^\bullet\text{3}$. A similar reaction is observed with 1-trimethylsilylpropyne to form $\text{Zn}^\bullet\text{4}$. Colorless crystals of $\text{Zn}^\bullet\text{3}$ were obtained from the reaction mixture at 298 K. The structure is presented in Figure 2, the short C-C and Zn-C bond length and the slipped metalocyclopropane binding mode is consistent with that previously reported for $\text{Zn}^\bullet\text{1}$ and that reported herein for $\text{Zn}^\bullet\text{2}$.⁹

The binding mode has precedent for both Mg^{13} and B/Al/Ga analogues,^{14,15} but this series of zinc-zirconium heterobimetallics is the first structurally characterized of its kind.¹⁶ Despite the possibility of forming different regioisomers of $\text{Zn}^\bullet\text{3}$ or $\text{Zn}^\bullet\text{4}$, with the alkyne orientated such that either C^1 or C^2 is in a bridging role, exclusive formation of a single isomer is observed. The reaction of oct-4-yne with $\text{Zn}^\bullet\text{Zr}$ did not yield a heterobimetallic product but gave the zirconacyclopentadiene, **5**, from the oxidative coupling of two alkynes.¹⁷ Monomeric **5** is formed as a byproduct in this reaction (Scheme 1c).¹⁸ In all reactions reported for $\text{Zn}^\bullet\text{Zr}$ transfer hydrogenation of the substrate accompanies product formation, generating cyclooctene, cycloheptene, 4,4-dimethylpent-2-ene, trimethyl(prop-1-en-1-yl)silane, or octene alongside $\text{Zn}^\bullet\text{1-4}$ or **5**.

Thermodynamics of Diene-to-Alkyne Isomerization. To investigate if transfer hydrogenation is a requirement for the observed reactivity, the thermodynamics of diene and alkyne binding to the $\text{M}^\bullet\text{-Zr}$ heterobimetallic fragments were calculated by DFT (Scheme 2, eq 1-4). While the on-metal isomerization of 1,5-COD is close to thermoneutral (eq 2), that of 1,3-COD is slightly uphill (eq 3). Transfer hydrogenation of a further equiv of substrate results in a more thermodynamically favorable process (eq 4), and although not a strict requirement for diene-to-alkyne isomerization, provides an additional thermodynamic driving force for this reaction to occur.

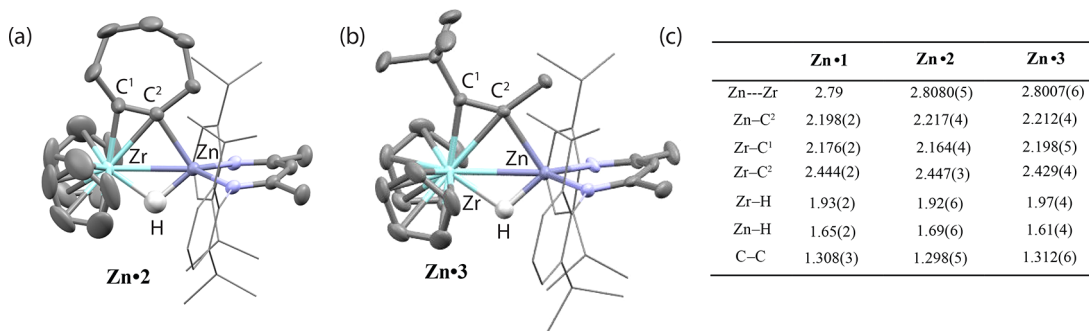
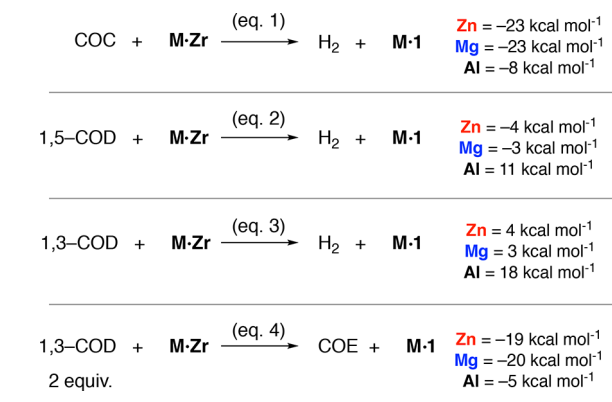


Figure 2. Crystal structure of (a) $\text{Zn}^\bullet\text{2}$ and (b) $\text{Zn}^\bullet\text{3}$. Hydrogen atoms are omitted save the hydride ligand. Selected bond lengths [Å] are listed in (c).

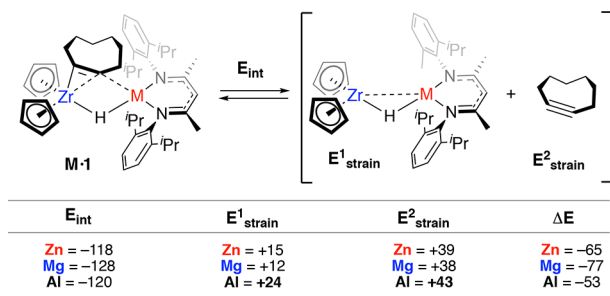
Scheme 2. Calculated Gibbs Free Energies for Formation of **M•1** from COC, 1,5-COD, and 1,3-COD (COE = cyclooctene)



The thermodynamics of the corresponding processes for the two other main group metals (**M•Zr**, **M** = Mg, Al) were also calculated. While ligand exchange reactions to form analogues of **Zn•1** are favorable in all instances (eq 1), the isomerization reactions are significantly endergonic for **Al•Zr** (eqs 2 and 3) in the absence of transfer hydrogenation of the substrate (eq 4).

The factors that affect the stability of the theoretical **M•1** (**M** = Mg, Zn, and Al) complexes were quantified by breaking the molecule into organometallic and cyclooctyne fragments (Scheme 3). This treatment is reminiscent of the activation–

Scheme 3. Activation Strain Analysis of **M•1**⁴



^aSingle point SCF energies in kcal mol^{−1}.

strain or distortion–interaction model.^{19,20} The distortion energies that are required to contort the ground state structures of the organometallic (E^1_{strain}) and cycloalkyne (E^2_{strain})

fragments into the geometries observed in **M•1** were compared against the interaction energy of these fragments (E_{int}). We have previously shown that for **Zn•1** the distortion energies are aptly compensated for by the large interaction energy.⁹ Metal coordination of the cycloalkyne therefore appears to be the key thermodynamic driving force in diene-to-alkyne isomerization. While a near identical value of distortion of the bimetallic fragment was calculated for **Mg•1** the interaction energy is more favorable than that calculated for **Zn•1**. In contrast, for **Al•1** the distortion of both the cyclooctyne and the organometallic fragment is more unfavorable than for **Zn•1** (and **Mg•1**). These data begin to explain the experimental observations; the analysis would seem to suggest that the formation of **Al•1** is disfavored based on the contorted geometry of both the alkyne and heterobimetallic fragment required for alkyne binding.²¹

Kinetics of Diene-to-Alkyne Isomerization. Two simple experiments provide evidence for a mechanism that involves chain-walking and not reversible hydrogenation/dehydrogenation of the diene. Hence, **Zn•Zr** reacts with both 1,5-COD and 1,3-COD to form **Zn•1** in similar yields with similar byproducts but does not form the same product upon reaction with cyclooctene. The latter alkene is the product of transfer hydrogenation and its inability to re-enter the synthetic pathway suggests that it is not an intermediate in the formation of **Zn•1**.

The reaction of **Zn•Zr** with 1,3-COD was monitored by ¹H NMR spectroscopy. Under pseudo-first-order conditions (excess diene) at 353 K, the reaction follows the empirical rate law: Rate = $k_{\text{obs}}[1,3\text{-COD}]^0[\text{Zn} \cdot \text{Zr}]^1$. Varying the excess of diene (1.5–64 equiv) had no effect on the kinetics with $k_{\text{obs}} \approx 1 \times 10^{-4} \text{ s}^{-1}$ in all cases. An Eyring analysis between 343 and 358 K gave the activation parameters for the isomerization as $\Delta H^\ddagger = +33.6 \pm 0.7 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = +23.2 \pm 1.7 \text{ cal mol}^{-1} \text{ K}^{-1}$, and $\Delta G^\ddagger_{298 \text{ K}} = +26.7 \pm 1.2 \text{ kcal mol}^{-1}$ (Figure 3a,b). Rates of reaction for addition of 1,5-COD to **Zn•Zr** have not been measured. Chain-walking mechanisms for alkene isomerization with zirconium hydride reagents are well-proven,¹⁰ and the choice to focus on 1,3-COD during the mechanistic analysis is based on the assumption that 1,5-COD readily converts to 1,3-COD by a well established mechanism under the reaction conditions.

The activation parameters allow immediate elimination of a series of plausible rate-limiting steps for diene-to-alkyne isomerization. Rate-limiting insertion of alkenes into a Zr–H bond in 16-electron transition metal complexes [$\text{Cp}^*_2\text{ZrH}_2$] has been found to be extremely facile and has negative entropy

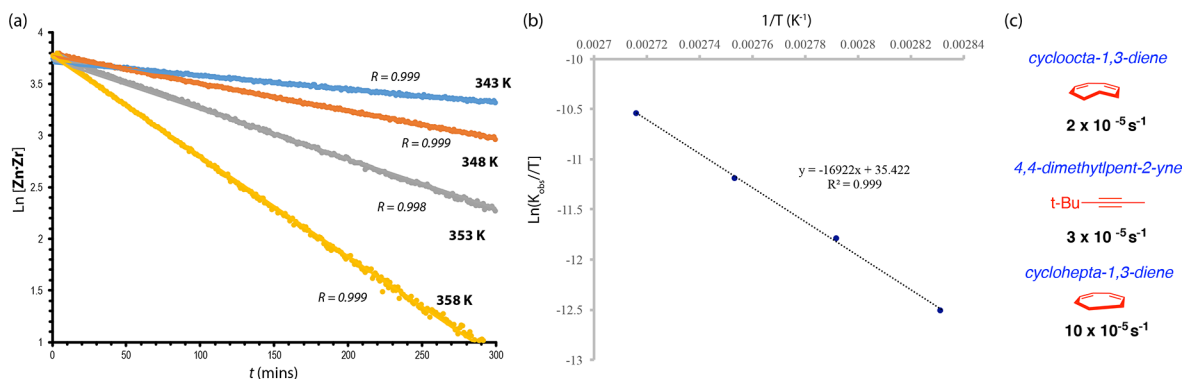


Figure 3. Kinetic analysis of the reactions of **Zn•Zr** with alkynes and dienes. (a) Kinetics for the reaction of **Zn•Zr** + 1,3-COD under pseudo-first-order conditions. (b) Eyring analysis and (c) first-order rate constants for the reaction of **Zn•Zr** with dienes and an alkyne at 343 K.

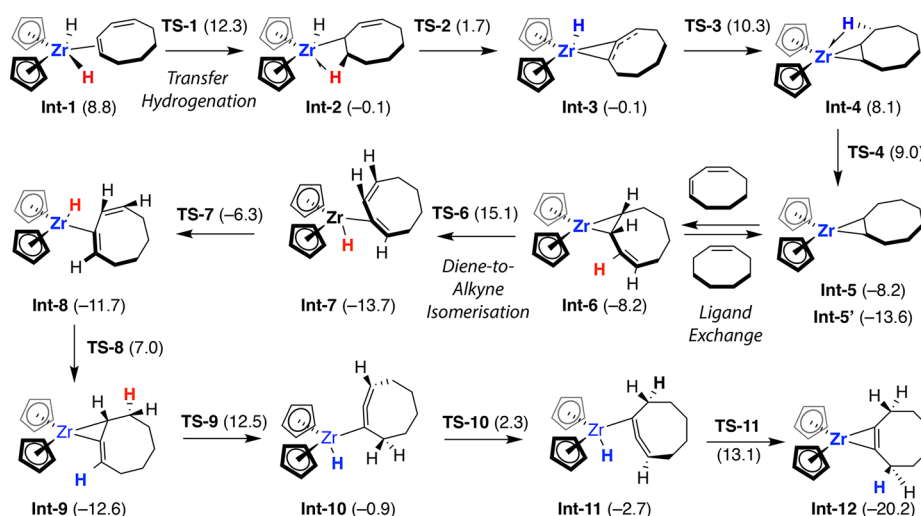


Figure 4. Calculated pathway for the reaction of Zr with 2 equiv of 1,3-COD. Gibbs energies in kcal mol⁻¹.

of activation.¹² The implication is the formation of an ordered four-membered transition state, and similar measurements have been recorded for the reaction of lanthanide and group 5 metallocene hydrides with alkenes.^{22–24} Rate-limiting β -hydride elimination, the microscopic reverse of alkene insertion, is also expected to proceed with a similar increase in order of the transition state relative to the reagents.^{25–29} For example, the values of $\Delta S^\ddagger$ range from -11 ± 2 to -10 ± 1 cal mol⁻¹ K⁻¹ for β -hydride reactions of [Cp*₂ScR] complexes.²⁷

Due to the requirement for transfer hydrogenation of diene en route to the formation of Zn•1, the reaction cannot be run with an excess of Zn•Zr. As a result, the rate-dependence on diene concentration cannot be measured using pseudo-first-order conditions (excess Zn•Zr). An alternative approach must be used. With diene or alkyne in excess, k_{obs} was measured for the reaction of a series substrates with Zn•Zr (Figure 3c). If the diene or alkyne is involved in the rate-limiting step, then k_{obs} should be dependent on the nature of the substrate. Different rate constants were recorded for the reaction of 1,3-COD, 1,3-CHD and 4,4-dimethylpent-2-yne with Zn•Zr (Figure S10–S12).

In combination, the data suggest that the rate-limiting step for the reaction of 1,3-COD with Zn•Zr involves a significant amount of bond breaking, an increase in disorder of the transition state compared with the ground state, and is dependent on the nature (if not the concentration) of the diene substrate. It is worth noting that Sita and co-workers reported an unusual set of activation parameters for the isomerization of a cationic group 4 alkyl complex, for which a stepwise pathway involving β -hydride elimination and hydrozirconation steps was proposed.³⁰ The modest $\Delta H^\ddagger = 21.8 \pm 0.5$ kcal mol⁻¹ was accompanied by a positive $\Delta S^\ddagger = +8.1 \pm 0.5$ cal mol⁻¹ K⁻¹ and explained by invoking a difference in the degree of ion-pairing between the ground state and transition state. In the current case, a transition state that is formed by a reaction sequence that involves initial dissociation of Zn•Zr,³¹ followed by a key bond breaking or making event would rationalize both the activation parameters and the rate dependence on the nature of the substrate.

DFT Studies of Diene-to-Alkyne Isomerization. The mechanism of diene-to-alkyne isomerization of 1,3-COD with Zn•Zr was investigated by DFT. The proclivity of Zn•Zr to form monomeric zirconium complexes, such as zirconacyclo-

pentadiene 5 (Scheme 1c) and the positive activation entropy from the Eyring analysis all suggest that dissociation of Zn•Zr is likely under the reaction conditions. Furthermore, a detailed analysis of the solution dynamics of M•Zr (see the Supporting Information) allows the characterization of both intramolecular and intermolecular fluxional processes that occur due to reversible formation of 3-center, 2-electron M–H–Zr bonds. The strength of the M–H–Zr bonds increase across the series Mg > Zn > Al.³²

DFT studies have been published on the hydrozirconation of alkenes and fluoroalkenes by [Cp₂ZrH₂] and [Cp*₂ZrH₂].^{33–36} Similarly, mechanisms of [Cp₂ZrH₂] catalyzed hydroalumination³⁷ and hydrosilylation³⁸ have been investigated by computational methods. These studies have clearly concluded that the lowest energy pathway for hydrozirconation of the alkene occurs via coordination of the alkene in between the wedge created by the H–Zr–H bonds and subsequent migratory insertion into one of the Zr–H bonds. The result is readily understandable from the frontier MO picture of [Cp₂ZrH₂] as the LUMO of this molecule exists between the two hydride ligands.³⁹

The reaction of the 16-electron complex Zr^{40–44} with 2 equiv of 1,3-COD to form a COC adduct was investigated by DFT. Transfer hydrogenation of 1,3-COD to form cyclooctene by [Cp₂ZrH₂] is calculated to occur by the established pathway, with coordination forming Int-1 which undergoes sequential hydrozirconation, σ – π isomeriation, and hydrozirconation steps ultimately producing Int-5. Int-5 may undertake a conformational change of the cyclooctene ring to form the lower energy intermediate Int-5' (Figure 4). Int-5 and Int-5' differ in the conformation of the 8-membered hydrocarbon ring (Figure S18). The formally 16-electron intermediates (Int-2 and Int-4) are stabilized by β -agostic interactions.⁴⁵ Ligand exchange of Int-5 with a further equivalent of 1,3-COD is close to thermoneutral and forms Int-6. Diene-to-alkyne isomerization proceeds from the metallocyclopropane adduct Int-6 via a relatively flat potential energy surface eventually generating the metallocyclopropene adduct Int-12 as the thermodynamic product. The hydrocarbon substrate remains bound to a series of Zr-intermediates through either η^2 or σ -coordination modes throughout the mechanism. Diene-to-alkyne isomerization proceeds by a series of β -hydride elimination, rotation and hydrozirconation steps (Figure 4).

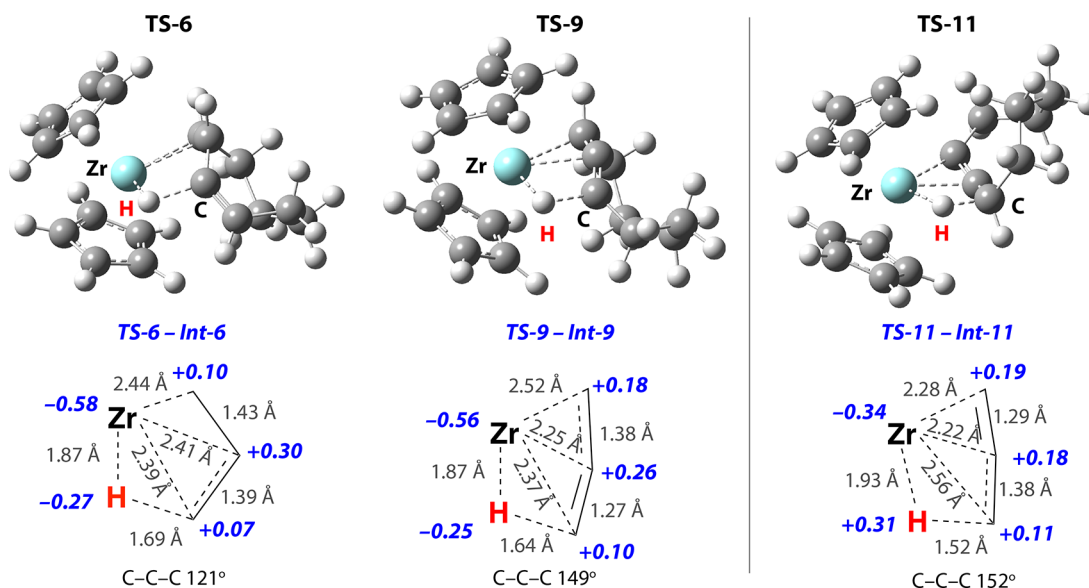


Figure 5. Geometries of key transition states in the on-metal diene-to-alkyne isomerization: sp^2C-H β -hydride elimination (TS-6 and TS-9) and intramolecular hydrozirconation (TS-11). Values in blue are the difference in the NPA charges between the TS and its preceding ground state.

It is important to note that **Int-6** exists as two enantiomers, while **Int-12** possesses pro-chiral protons in the β -position of the bound cyclooctene ring. The hydrozirconation and β -hydride elimination steps are all stereospecific, and as such stereochemistry becomes an important consideration in defining the diene-to-alkyne reaction pathway. An alternative pathway originating from the enantiomer of **Int-6**, was also calculated. The pathway is broadly similar to that presented above with the caveat that the important bond breaking and making steps are marginally higher in energy (Figure S19).

While the fundamental steps for the diene-to-alkyne isomerization all have extensive precedent, their combination as applied to diene-to-alkyne isomerization is unknown.^{30,44} The highest energy transition states on the potential energy surface TS-6, TS-9 and TS-11 all occur within a similar energy span $\Delta G^\ddagger_{298K} = 26-29$ kcal mol⁻¹ and involve either β -hydride elimination or the microscopic reverse hydrozirconation (Figure 5). Rather unusually, however, the β -hydride elimination steps occur from metalcyclopropane intermediates and involve the breaking of an sp^2C-H bond. Similarly, hydrozirconation occurs across the remote double bond of a metal allenyl fragment.

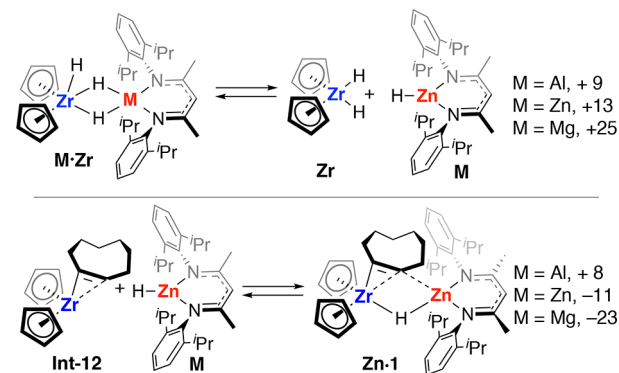
There is limited experimental precedent for sp^2C-H β -hydride elimination. For example, Bercaw and co-workers have reported the rearrangement of group 4 alkenyl derivatives by a pathway involving β -H elimination from an sp^2 -hybridized carbon.⁴⁶ While both TS-6 and TS-9 could also be conceptualized in terms of a migration of a zirconium(II) fragment $\{Cp_2Zr\}$ from the alkene moiety to the adjacent C-H bond with bond breaking occurring by oxidative addition, β -hydride elimination from a zirconium(IV) metalcyclopropane intermediate is also a fair description. Both TS-6 and TS-9 contain long C-H distances, short Zr-H distances, and charge-accumulation on the hydrogen atom, all suggestive of a large degree of C-H bond breaking and Zr-H bond making. Intramolecular hydrozirconation of an allenyl intermediate occurs through similar bond making and breaking events in TS-11. Here hydride transfer occurs from zirconium to carbon and is accompanied by charge-depletion of the H atom as it migrates from the more electropositive to the less electro-

positive element. It is noteworthy that as the diene-to-alkyne isomerization progresses the key transition states show increasingly short Zr---C distances to the η^2 -bound C_2 unit and increasingly obtuse C-C-C angles; both are consistent with increasing metalcyclopropane character of the hydrocarbon ligand.

Heterobimetallic Rebound Mechanism. The transfer hydrogenation and diene-to-alkyne isomerization on mono-metallic zirconium complexes are, however, only part of the mechanistic picture. Low-energy zirconocene intermediates on the potential energy surface can potentially reversibly bind to the molecular zinc hydride **Zn**. This coordination can either occur as a weakly exergonic (or indeed endergonic) binding through 3-center, 2-electron Zr-H-Zn interactions or the formation of more strongly bound heterobimetallic metalcyclopropane or -propene adducts as observed in the solid state structures of **Zn-1-3** (Scheme 4).

The reversible trapping and stabilization of reaction intermediates by a heterobimetallic rebound mechanism is represented in the potential energy surface in Figure 6 and is reminiscent of the mechanism of atom-transfer radical

Scheme 4. Heterobimetallic Rebound Events^a



^aThe binding of M to $\{Zr\}$ intermediates. Values are Gibbs free energies in kcal mol⁻¹.

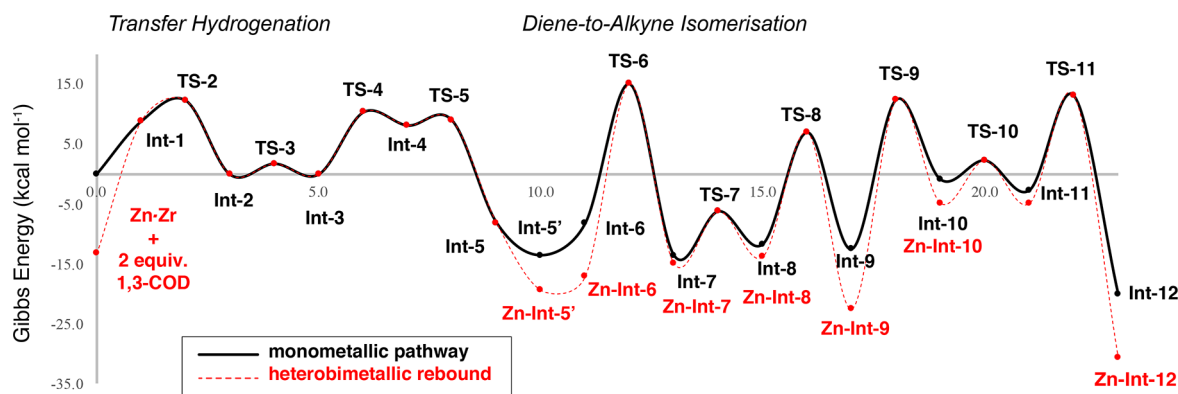


Figure 6. Potential energy surface for the reaction of **Zr** with 2 equiv of 1,3-COD. Solid line = PES from {Zr} intermediates. Dotted line = PES with heterobimetallic rebound of {Zr} intermediates only exergonic binding events considered.

polymerization.⁴⁷ The trapping of **Int-12** as its zinc hydride adduct forms the experimentally isolated **Zn-1** (= **Zn-Int-12**). This binding event is of crucial importance in isolating this metallocyclopropene complex.

This mechanism explains the kinetic data observed under saturation of diene. Dissociation of a heterobimetallic Zn---Zr intermediate is on the way to the highest energy transition states (TS-6, TS-9, or TS-11) and is consistent with the reaction being first-order in [Zn•Zr], having a large and positive activation entropy ($\Delta S^\ddagger$), and a large activation enthalpy ($\Delta H^\ddagger$). The proposed mechanism also explains the observed rate dependence on the nature of the diene, as hydrocarbon derived fragments are involved in the highest energy transition states. The calculated Gibbs activation energies for the highest transition states on the heterobimetallic rebound mechanism are $\Delta G^\ddagger_{\text{DFT}} = 35\text{--}36 \text{ kcal mol}^{-1}$. Because of the small calculated energy difference between TS-6, TS-9, and TS-11 ($\Delta G \sim 2.5 \text{ kcal mol}^{-1}$), it cannot be determined which of these steps, if any, is rate-limiting.

Origin of Heterobimetallic Selectivity. The observation that the on-metal diene-to-alkyne isomerization only occurs for **Zn•Zr** and not **Al•Zr** or **Mg•Zr** can be explained by this new mechanism. Comparison of the binding energies of the heterobimetallics (Scheme 4) reveals that **Mg•Zr** is too strongly bound to dissociate and promote the isomerization reaction of the diene under mild reactions conditions <353 K, while **Al•1** is too weakly bound to allow effective trapping of the cyclooctyne complex. The thermodynamics of formation of both **Zn•Zr** and **Zn-1** are just right for both events to be favorable. Hence, the observed heterobimetallic effect is both thermodynamic and kinetic in origin, with **Mg•Zr** being too kinetically stable to access significant quantities of the requisite **Zr** and **Mg** intermediates⁴⁸ and **Al•1** not being thermodynamically stable enough to compensate for the contrathermodynamic diene-to-alkyne isomerization and prevent the expected catalytic isomerization of 1,5-COD to 1,3-COD.⁴⁹

CONCLUSIONS

In summary, we report the reaction of metal---zirconium hydride heterobimetallics with a series of dienes and alkynes. In the case of zinc---zirconium hydride complexes, a highly unusual on-metal diene-to-alkyne isomerization is observed. Through a combined experimental and computational approach, we propose a new heterobimetallic rebound mechanism for diene-to-alkyne isomerization. The proposed heterobimetallic rebound mechanism has direct parallels with

atom-transfer radical polymerization mechanisms and more broadly could be considered a highly specialized ligand dissociation/association step. Mankad and co-workers have concluded that similar mechanisms may be in operation in catalytic applications of heterobimetallic Cu-Fe and Ag-Ru complexes.⁵⁰⁻⁵³ The thermodynamics of the binding events explains the unusual heterobimetallic effect, only the zinc---zirconium hydride complexes possess binding energies that are suitable for reversible capture and release of the isomerization products under the reaction conditions.

We believe that these results have two important implications. First, the reversible generation of low concentrations of monometallic reactive intermediates through trapping as a heterobimetallic complexes should be considered in future mechanistic analysis of heterobimetallic complexes in catalysis. Second, diene-to-alkyne isomerization may well be a hidden pathway in the reaction of dienes with transition metal hydrides. This reaction is contrathermodynamic with respect to the hydrocarbon fragment but can be rendered exergonic by a suitable exothermic event (such as the trapping as a heterobimetallic as reported herein). If the new alkyne moiety could be exploited in further reactions, then perhaps tandem isomerization---functionalization processes could be developed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-
met.7b00908.

Experimental procedures, details of the DFT studies, single crystal X-ray data and multinuclear NMR spectra (PDF)

Full coordinates for calculated structures (MOL)

Accession Codes

CCDC 1587265–1587266 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.

AUTHOR INFORMATION

Corresponding Author

*E-mail: m.crimmin@imperial.ac.uk.

ORCID

M. R. Crimmin: 0000-0002-9339-9182

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the Royal Society for generous support in the form of a University Research Fellowship and the EPSRC for project support (EP/L011514/1).

■ REFERENCES

- (1) Larionov, E.; Li, H.; Mazet, C. Well-Defined Transition Metal Hydrides in Catalytic Isomerizations. *Chem. Commun.* **2014**, 50, 9816–9826.
- (2) Reed, D. W.; Polichuk, D. R.; Buist, P. H.; Ambrose, S. J.; Sasata, R. J.; Savile, C. K.; Ross, A. R. S.; Covello, P. S. Mechanistic Study of an Improbable Reaction: Alkene Dehydrogenation by the Δ^{12} Acetylenase of *Crepis Alpina*. *J. Am. Chem. Soc.* **2003**, 125, 10635–10640.
- (3) Taskinen, E.; Nummelin, K. Relative Thermodynamic Stabilities of the Isomeric Cyclooctadienes. *Acta Chem. Scand., Ser. B* **1985**, 39, 791–792.
- (4) Daoust, K. J.; Hernandez, S. M.; Konrad, K. M.; Mackie, I. D.; Winstanley, J.; Johnson, R. P. Strain Estimates for Small-Ring Cyclic Allenes and Butatrienes. *J. Org. Chem.* **2006**, 71, 5708–5714.
- (5) Yavari, I. Conformational Energy Surface of 1,2-Cyclooctadiene. *J. Mol. Struct.* **1980**, 65, 169–172.
- (6) Gibson, V. C.; Parkin, G.; Bercaw, J. E. Synthesis and Reactivity of Permethyltantallocene Derivatives Processing η^3 -Allyl, η^2 -Butadiene, η^2 -Methylallene, and η^1 -Alkenylidene Ligands. Model Studies for the Role of Surface Vinylidenes in the Fischer–Tropsch Hydrocarbon-Chain-Lengthening Process. *Organometallics* **1991**, 10, 220–231.
- (7) Gibson, V. C.; Bercaw, J. E.; Bruton, W. J.; Sanner, R. D. Bent-Sandwich Derivatives of Tantalum Bearing One or Two Pentamethylcyclopentadienyl Ligands. *Organometallics* **1986**, 5, 976–979.
- (8) Brinkmann, P. H. P.; Luinstra, G. A.; Saenz, A. Isomerization of an η^3 -Allyl to an (E)-1-Propenyl in $(C_5Me_5)(C_5Me_4CH_2)TiCl_3H_2$: Mechanism, Kinetics, and Thermodynamics. *J. Am. Chem. Soc.* **1998**, 120, 2854–2861.
- (9) Butler, M. J.; White, A. J. P.; Crimmin, M. R. Isomerization of Cyclooctadiene to Cyclooctyne with a Zinc/Zirconium Heterobimetallic Complex. *Angew. Chem., Int. Ed.* **2016**, 55, 6951–6953.
- (10) Raoult, Y.; Choukroun, Y. R. R.; Basso-Bert, M.; Gervais, D. Hydrogenation and Isomerization of Olefins with Diphenylphosphinomethyl Hydride Zirconium, $[Cp_2ZrH(CH_2PPh_2)]_N$, A Selective Homogeneous Catalyst. *J. Mol. Catal.* **1992**, 72, 47–58.
- (11) Skattebøl, L.; Solomon, S. 1,2-Cyclononadiene. *Org. Synth.* **1969**, 49, 35.
- (12) Chirik, P. J.; Bercaw, J. E. Cyclopentadienyl and Olefin Substituent Effects on Insertion and β -Hydrogen Elimination with Group 4 Metallocenes. Kinetics, Mechanism, and Thermodynamics for Zirconocene and Hafnocene Alkyl Hydride Derivatives. *Organometallics* **2005**, 24 (22), 5407–5423.
- (13) Lee, H.; Hascall, T.; Desrosiers, P. J.; Parkin, G. Synthesis and Structural Characterization of $[(Me_2Si(C_5Me_4)_2)Zr(H^2-C_2H_4)H_2]$ -Mg: an Ansa-Zirconocene Ethylene-Hydride Complex. *J. Am. Chem. Soc.* **1998**, 120, 5830–5831.
- (14) Albrecht, M.; Erker, G.; Kruger, C. The Synthesis of Stable, Isolable Planar-Tetracoordinate Carbon Compounds. *Synlett* **1993**, 1993, 441–448.
- (15) Gleiter, R.; Hyla-Kryspin, I.; Niu, S.; Erker, G. An Ab Initio MO Study on Stabilizing Interactions in Dinuclear Zr/Al Complexes with a Planar Tetracoordinate Carbon Center. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 754–756.
- (16) Butler, M. J.; Crimmin, M. R. Magnesium, Zinc, Aluminium and Gallium Hydride Complexes of the Transition Metals. *Chem. Commun.* **2017**, 53, 1348–1365.
- (17) Gell, K. I.; Schwartz, J. Preparation of Zirconium(II) Complexes by Ligand-Induced Reductive Elimination. Bis(η^5 -Cyclopentadienyl)-Bis(Phosphine)Zirconium(II) Complexes and Their Reactions. *J. Am. Chem. Soc.* **1981**, 103, 2687–2695.
- (18) While further experiments with cyclooctene and methylenecyclohexane also led to transfer hydrogenation of the alkene, the Zn/Zr containing products of these reactions are yet to be fully characterized.
- (19) Bickelhaupt, F. M.; Houk, K. N. Analyzing Reaction Rates with the Distortion/Interaction-Activation Strain Model. *Angew. Chem., Int. Ed.* **2017**, 56, 10070–10086.
- (20) Wolters, L. P.; Bickelhaupt, F. M. The Activation Strain Model and Molecular Orbital Theory. *WIREs Comput. Mol. Sci.* **2015**, 5, 324–343.
- (21) The latter conclusion is supported by a complementary analysis, in which the alkyne complexes were broken into main group hydride and metallocyclopropene fragments. The magnitudes of distortion for the main group hydrides are in the Al > Zn > Mg sequence with the distortion of the alane requiring almost double the energy input of the Zn or Mg hydrides.
- (22) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. Kinetics and Mechanism of the Insertion of Olefins into Niobium- and Tantalum-Hydride Bonds: a Study of the Competition between Steric and Electronic Effects. *J. Am. Chem. Soc.* **1988**, 110, 3134–3146.
- (23) Doherty, N. M.; Bercaw, J. E. Kinetics and Mechanism of the Insertion of Olefins into Transition Metal-Hydride Bonds. *J. Am. Chem. Soc.* **1985**, 107, 2670–2682.
- (24) Watson, P. L. Ziegler-Natta Polymerization: the Lanthanide Model. *J. Am. Chem. Soc.* **1982**, 104, 337–339.
- (25) van der Boom, M. E.; Higgitt, C. L.; Milstein, D. Directly Observed β -H Elimination of Unsaturated PCP-Based Rhodium(III)-Alkyl Complexes. *Organometallics* **1999**, 18, 2413–2419.
- (26) Romeo, R.; Alibrandi, G.; Sclaro, L. M. Kinetic Study of β -Hydride Elimination from Monoalkyl Solvento Complexes of Platinum(II). *Inorg. Chem.* **1993**, 32, 4688–4694.
- (27) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. Ethylene Insertion and β -Hydrogen Elimination for Permethylscandocene Alkyl Complexes. a Study of the Chain Propagation and Termination Steps in Ziegler-Natta Polymerization of Ethylene. *J. Am. Chem. Soc.* **1990**, 112, 1566–1577.
- (28) Ozawa, F.; Ito, T.; Yamamoto, A. Mechanism of Thermal Decomposition of *Trans*-Diethylbis(Tertiary Phosphine)Palladium(II). Steric Effects of Tertiary Phosphine Ligands on the Stability of Diethylpalladium Complexes. *J. Am. Chem. Soc.* **1980**, 102, 6457–6463.
- (29) Egger, K. W. Kinetics of the Intramolecular Four-Center Elimination of Isobutylene from Tri-iso-butylaluminum in the Gas Phase. *J. Am. Chem. Soc.* **1969**, 91, 2867–2871.
- (30) Keaton, R. J.; Sita, L. R. Direct Observation of the Structural Isomerization of a Cationic Group 4 Ziegler–Natta Insertion Product. *J. Am. Chem. Soc.* **2002**, 124, 9070–9071.
- (31) Currently, we cannot differentiate the following cases: (i) complete dissociation of $Zn \cdot Zr$ into monometallic Zn and Zr fragments followed by diene binding or (ii) partial dissociation of $Zn \cdot Zr$ to open a coordination site at either Zr or Zn followed by diene binding and a second dissociation step to separate the two metallic fragments.
- (32) These studies have allowed the accurate benchmarking of DFT methods against experimentally determined Gibbs free energies and activation energies. The ω B97x functional and a hybrid 6,311G/SDDAll basis set model experimental data to within ~ 5 kcal mol $^{-1}$.
- (33) Kraft, B. M.; Clot, E.; Eisenstein, O.; Brennessel, W. W.; Jones, W. D. Mechanistic Investigation of Vinylic Carbon-Fluorine Bond Activation of Perfluorinated Cycloalkenes Using $Cp^*_2ZrH_2$ and Cp^*_2ZrHF . *J. Fluorine Chem.* **2010**, 131, 1122–1132.
- (34) Clot, E.; Mégret, C.; Kraft, B. M.; Eisenstein, O.; Jones, W. D. Defluorination of Perfluoropropene Using $Cp^*_2ZrH_2$ And Cp^*_2ZrHF : A Mechanism Investigation from a Joint Experimental–Theoretical Perspective. *J. Am. Chem. Soc.* **2004**, 126, 5647–5653.

- (35) Watson, L. A.; Yandulov, D. V.; Caulton, K. G. C–D₀ (D₀ = π -Donor, F) Cleavage in H₂C=CH(D₀) by (Cp₂ZrHCl)_N: Mechanism, Agostic Fluorines, and a Carbene of Zr(IV). *J. Am. Chem. Soc.* **2001**, *123*, 603–611.
- (36) Bi, S.; Kong, X.; Zhao, Y.; Zhao, X.; Xie, Q. Detailed Mechanisms on Insertion of Cis-2-Butene Into the Zr–H Bond of Cp₂ZrH₂: A DFT Study. *J. Organomet. Chem.* **2008**, *693*, 2052–2060.
- (37) Pankratyev, E. Y.; Tyumkina, T. V.; Parfenova, L. V.; Khursan, S. L.; Khalilov, L. M.; Dzhemilev, U. M. DFT and Ab Initio Study on Mechanism of Olefin Hydroalumination by XAlBu₂ In the Presence of Cp₂ZrCl₂ Catalyst. II. Olefin Interaction with Catalytically Active Centers. *Organometallics* **2011**, *30*, 6078–6089.
- (38) Sakaki, S.; Takayama, T.; Sumimoto, M.; Sugimoto, M. Theoretical Study of the Cp₂Zr-Catalyzed Hydrosilylation of Ethylene. Reaction Mechanism Including New σ -Bond Activation. *J. Am. Chem. Soc.* **2004**, *126*, 3332–3348.
- (39) Lauher, J. W.; Hoffmann, R. Structure and Chemistry of Bis(Cyclopentadienyl)-ML_n Complexes. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742.
- (40) Wipf, P.; Xu, W.; Takahashi, H.; Jahn, H.; Coish, P. D. G. Synthetic Applications of Organozirconocenes. *Pure Appl. Chem.* **1997**, *69*, 639–644.
- (41) Negishi, E.-I.; Takahashi, T. Organozirconium Compounds in Organic Synthesis. *Synthesis* **1988**, *1988*, 1–19.
- (42) Carr, D. B.; Schwartz, J. Preparation of Organoaluminum Compounds by Hydrozirconation-Transmetalation. *J. Am. Chem. Soc.* **1979**, *101*, 3521–3531.
- (43) Wailes, P. C.; Weigold, H.; Bell, A. P. Hydride Complexes of Zirconium IV. Reactions with Olefins. *J. Organomet. Chem.* **1972**, *43*, C32–C34.
- (44) Chirik, P. J.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. Alkyl Rearrangement Processes in Organozirconium Complexes. Observation of Internal Alkyl Complexes During Hydrozirconation. *J. Am. Chem. Soc.* **1999**, *121*, 10308–10317.
- (45) Scherer, W.; McGrady, G. S. Agostic Interactions in d⁰ Metal Alkyl Complexes. *Angew. Chem., Int. Ed.* **2004**, *43*, 1782–1806.
- (46) McDade, C.; Bercaw, J. E. Synthesis and Reactivity of Alkenyl and Alkynyl Derivatives of Permethylzirconocene and Permethylhafnocene. Rearrangement of Alkenyl Derivatives Involving β -H Elimination From an Sp²-Hybridized Carbon. *J. Organomet. Chem.* **1985**, *279*, 281–315.
- (47) Matyjaszewski, K.; Xia, J. Atom Transfer Radical Polymerization. *Chem. Rev.* **2001**, *101*, 2921–2990.
- (48) While **Mg•Zr** can catalyse the isomerisation of 1,5-COD to 1,3-COD, monitoring these reactions as a function of time reveals that **Mg•Zr** is not consumed during catalysis. Diene isomerisation could either be occurring on the heterobimetallic complex itself or due to the formation of trace amounts of catalytically active Zr species.
- (49) Despite the lack of experimental evidence for the formation of **Mg•1** from the reaction of **Mg•Zr** with 1,5- or 1,3-COD, the calculations suggest that this latter alkyne complex is more stable than **Zn•1**. In line with these calculations, cross-over experiments show that **Mg•1** could be generated *in situ* from reaction of **Zn•1** with **Mg•Mg**.
- (50) Mazzacano, T. J.; Mankad, N. P. Base Metal Catalysts for Photochemical C–H Borylation That Utilize Metal–Metal Cooperativity. *J. Am. Chem. Soc.* **2013**, *135*, 17258–17261.
- (51) Parmelee, S. R.; Mazzacano, T. J.; Zhu, Y.; Mankad, N. P.; Keith, J. A. A Heterobimetallic Mechanism for C–H Borylation Elucidated From Experimental and Computational Data. *ACS Catal.* **2015**, *5*, 3689–3699.
- (52) Karunananda, M. K.; Mankad, N. P. E-Selective Semi-Hydrogenation of Alkynes by Heterobimetallic Catalysis. *J. Am. Chem. Soc.* **2015**, *137*, 14598–14601.
- (53) Karunananda, M. K.; Mankad, N. P. Heterobimetallic H₂ Addition and Alkene/Alkane Elimination Reactions Related to the Mechanism of E-Selective Alkyne Semi-Hydrogenation. *Organometallics* **2017**, *36*, 220–227.