ORGANOMETALLICS

Heterobimetallic H₂ Addition and Alkene/Alkane Elimination Reactions Related to the Mechanism of *E*-Selective Alkyne Semihydrogenation

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Supporting Information

ABSTRACT: Mechanistic aspects of an *E*-selective alkyne semihydrogenation catalyst are studied through computational modeling and experimental model reactions. We previously communicated the semihydrogenation of diarylalkynes to produce *trans*-alkenes using the heterobimetallic catalyst (IMes)-AgRuCp(CO)₂. In this report, we disclose further details on the catalyst decomposition products under catalytic conditions, the



mechanism of bimetallic H_2 activation, and the factors affecting selectivity for *E*-alkene generation. Under hydrogenation conditions, the catalyst decomposition product HRuCp(CO)(IMes) was isolated and characterized. Resubmitting this species to the catalytic conditions did not provide useful hydrogenation catalysis, confirming the presence of a bimetallic mechanism under optimal catalytic conditions. The detailed nature of heterobimetallic H_2 activation was probed by calculating internuclear bond orders, atom/fragment charges, and NBO occupancies as functions of reaction coordinate for a model reaction between (IMe)CuRp and H_2 . The collected results indicate a late transition state involving deprotonation of a Cu(H_2) σ -complex by the proximal Rp fragment. Late stages of the reaction profile feature H···H dihydrogen bonding between (IMe)CuH and HRuCp(CO)₂, indicative of heterolytic H_2 activation. NBO analysis indicates that the key orbital interactions involved in H_2 activation are (a) donation from the filled $H_2 \sigma$ -orbital into a Cu 4p acceptor orbital and (b) back-donation from a filled Cu–Ru bonding orbital of predominantly Ru 4d character into the empty $H_2 \sigma^*$ -orbital. Experimental support for the previously proposed cascade alkyne $\rightarrow Z$ -alkene $\rightarrow E$ -alkene process was provided by stoichiometric reactions between HRuCp(CO)₂ and isolable (IPr)CuR models of catalytic (IMes)AgR intermediates (R = alkenyl, alkyl). The collected experimental results indicate that selectivity for *E*-alkene generation is dictated by the relative rates of monometallic β -hydride elimination and bimetallic alkane elimination, which are impacted by several structural features of the catalyst. The mechanistic detail provided by these studies will inform the development of second-generation hydrogenation catalysts.

INTRODUCTION

Catalytic hydrogenation of C–C multiple bonds, one of the most studied topics in organometallic chemistry, remains crucial both for conversion of bulk hydrocarbon feedstocks and for late-stage manipulations of complex organic molecules. Advancing new technologies in this area inherently relies on identifying systems capable of H₂ activation. Many homogeneous hydrogenation catalysts rely on single-site oxidative addition of H₂.^{1–4} Recent advances, some of which have enabled unique catalytic selectivity and/or use of nonprecious catalyst elements, move beyond the single-site paradigm to involve heterolytic H₂ activation by cooperative strategies. Examples include cooperation between a metal site and a basic residue, ^{5–9} between a metal site and a Lewis acidic residue, ^{10–13} between two different metal sites, ^{14–17} or between nonmetal frustrated Lewis acid–base pairs.^{18,19}

We recently communicated the catalytic activity of heterobimetallic (NHC)M'-[M] complexes toward alkyne hydrogenation (NHC = N-heterocyclic carbene, M' = Cu or Ag, [M] = FeCp(CO)₂ or RuCp(CO)₂).²⁰ The optimal catalyst, (IMes)AgRp (IMes = N,N'-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene, Rp = RuCp(CO)₂), was active at 1 atm of

H₂ pressure, gave high stereoselectivity for *E*-alkene products, and was chemoselective for alkyne reduction in the presence of other reducible functional groups such as aldehydes, ketones, nitriles, and alkyl chlorides (Scheme 1). The observed stereoselective trans-addition of H₂ to alkynes puts this catalyst in a select group of systems exhibiting E-selective semihydrogenation behavior, whether by direct hydrogenation^{14,21-26} or by transfer hydrogenation or indirect reduc-tion/deprotection routes.²⁷⁻³¹ The observed chemoselectivity for alkyne reduction in the presence of vulnerable functional groups raises the possibility of using this technology for latestage introduction of *trans*-alkene moieties.³² While the optimal system utilized the precious metals Ag and Ru, non-precious metal analogues pairing Cu and/or Fe did show some activity and represent opportunities for further development. Understanding the nature of heterobimetallic H₂ activation, the catalytic mechanism, and the selectivity-determining reaction

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Scheme 1. E-Selective Alkyne Semihydrogenation by Heterobimetallic Catalysis²⁰



steps will aid in the design of second-generation systems featuring nonprecious metals capable of operating efficiently and selectively under mild conditions.

In this Article, we present studies on the mechanism of heterobimetallic H_2 activation and on the heterobimetallic alkene/alkane elimination reactions that contribute to the observed catalytic selectivity. The H_2 activation step is analyzed by computational modeling of the reaction coordinate, providing understanding of the key transition states and orbital interactions involved in H_2 cleavage. The alkene/alkane elimination steps are analyzed by stoichiometric reactivity studies of isolable models of catalytic intermediates. Additionally, new insights into catalyst decomposition pathways are disclosed. Collectively, a mechanistic picture emerges that will aid future catalyst development in this area.

RESULTS AND DISCUSSION

Control Experiments and Catalyst Decomposition. In our preliminary communication of this system,²⁰ our evidence for a bimetallic catalytic mechanism was provided by comparing results for diphenylacetylene hydrogenation obtained with (IMes)AgRp (Table 1, entry 1) with those obtained with (IPr)AgOAc and Rp₂ (IPr = N,N'-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene), neither of which gave productive catalysis (entries 2, 3). To examine this issue further, we have subsequently examined a larger array of Ag-free Ru catalysts,

Table 1. Agriffee and Rustiee Control Experiments	Table	1.	Ag-Free	and	Ru-Free	Control	Experiments
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Ph	-Ph → H ₂ (1 atm) <i>catalyst</i> (20%) ×ylenes 150°C, 24 h 1	[←] Ph + Ph + 2	Ph Ph 3
entry	catalyst	conversion (%) ^a	1:2:3 ^a
1 ^b	(IMes)AgRp	95	90:4:1
2 ^b	(IPr)AgOAc	0	N/A
3 ^b	Rp2 ^c	7	4:3:0
4	HRp	35	22:13:0
5	HRuCp(CO)(IMes)	47	30:17:0
6	Cp*Ru(COD)Cl/AgOTf ^d	23	6:5:12
7 ^b	(IMes)CuRp	61	42:17:2
8 ^b	(IPr)CuRp	60	40:18:3

^{*a*}From ¹H NMR integration against an internal standard. ^{*b*}From ref 20. ^{*c*}Catalyst loading was 10%, i.e., 20% Ru. ^{*d*}Catalyst loading was 20% Ru and 20% Ag.

with a focus on the Ru-containing compounds produced upon catalyst decomposition under the reaction conditions. Originally, we assigned the (IMes)AgRp decomposition mixture during catalysis as involving precipitation of metallic Ag and formation of HRp (observed ¹H NMR resonances in toluene d_8 : $\delta = 4.52$ and -12.04). Because a Hg drop did not poison the reaction, metallic Ag was ruled out from being catalytically relevant, but HRp was not tested as a catalyst due to initial difficulties in isolation of a pure sample. Now, we report that an isolated sample of pure HRp was found to catalyze diphenylacetylene hydrogenation but did not provide high conversion of diphenylacetylene or high selectivity for *E*stillbene (1) relative to the other reduction products (2 and 3) (entry 4).

Upon examining the ¹H NMR characterization of isolated HRp, however, we noticed that its observed ¹H NMR resonances (δ = 4.57 and -10.75 in toluene- d_8) did not match the resonances observed under catalytic conditions with (IMes)AgRp. Furthermore, the IMes resonances observed after catalysis with (IMes)AgRp did not match those for authentic samples of free IMes ligand. Filtration of metallic Ag and removal of organics from a catalytic product mixture provided an isolated sample of the catalyst decomposition product, which is now assigned as HRuCp(CO)(IMes) on the basis of NMR and IR characterization. Isolating this species and re-exposing it to the catalytic conditions did provide diphenylacetylene hydrogenation (entry 5), but again the observed conversion of diphenylacetylene and selectivity for 1 were significantly lower than those for (IMes)AgRp. These two single-site Ru catalysts (entries 4, 5) likely mediate trans-hydrogenation of diphenylacetylene through a Ru-carbene pathway akin to that detailed by Fürstner for [Cp*Ru] catalysts at high H₂ pressure.³³ One of the Fürstner catalyst mixtures utilized both Ru and Ag, but does not provide high levels of catalytic conversion or selectivity under the conditions optimal for (IMes)AgRp (entry 6). Lastly, to contextualize the Cu/Ru model studies presented below, catalytic results for (NHC)-CuRp complexes are shown in entries 7 and 8.

Bimetallic Activation of H₂. Within the bimetallic mechanism that is operative in this system, we have proposed that the metal-metal bonded (NHC)M'-[M] complexes react directly with H_2 to generate (NHC)M'-H and H[M] pairs that subsequently reduce alkyne substrates. Experimental evidence for the feasibility of this proposed bimetallic H₂ activation step comes from three observations (Scheme 2): (a) experimental observation of the microscopic reverse reaction, i.e., bimetallic H₂ elimination from $0.5[(IPr)CuH]_2 + HFp;^{34,35}$ (b) H/D exchange reactivity of (IPr)CuFp (Fp = $FeCp(CO)_2$) observed during dehydrogenative borylation conditions,³⁴ which likely involves activation of HD generated in situ; and (c) observation of HRuCp(CO)(IMes) upon thermolysis of (IMes)AgRp in the absence of alkyne under H_2 (1 atm), which is presumably the result of intermediate formation of (IMes)AgH + HRp followed by thermal decomposition of (IMes)AgH by the known pathway³⁶ and ligand substitution at Ru. However, experimental data on the mechanism of H₂ activation is elusive due to the thermodynamically unfavorable nature of (NHC)-M'-H + H[M] relative to $(NHC)M'-[M] + H_2^{20}$ This motivated our pursuit of computationally modeling the heterobimetallic H₂ activation step.

In our initial communication on this system,²⁰ we presented a computed transition state for H₂ activation by an (IMe)CuRp model (IMe = N_1N' -dimethylimidazol-2-ylidene). The reaction Scheme 2. Experimental Evidence for Heterobimetallic H₂ Activation

(a) Mazzacano & Mankad (2013)

$$\frac{1}{2} IPr - Cu + Cu - IPr + HFp + HFp + H_2$$

(b) Mazzacano & Mankad (2013)



via HD addition

(c) This work

IMes-Ag-RuCp(CO)₂ $\xrightarrow[toluene-d_8]{H_2(1 \text{ atm})}$ Ag⁰ + CO + $OC \xrightarrow[H]{V}$ Ru. (//IMes H

between (IMe)CuRp and H₂ was calculated to be thermodynamically unfavorable ($\Delta G_{298 \text{ K}} = 20.1 \text{ kcal/mol}$), with an even smaller driving force than the analogous reaction involving (IMe)AgRp ($\Delta G_{298 \text{ K}}$ = 14.1 kcal/mol). The calculated activation barrier of $\Delta G^{\ddagger}_{298 \text{ K}} = 29.0 \text{ kcal/mol was consistent}$ with the high temperature required for catalysis and was determined using a computational method that had been calibrated with experimental data previously.³⁷ The calculated activation parameters included a large and negative entropy of activation ($\Delta H^{\ddagger} = 20.1 \text{ kcal/mol}, \Delta S^{\ddagger} = -29.8 \text{ eu}$), indicating a highly organized transition-state structure. Here, to develop a deeper understanding of this H₂ activation reaction, we provide a thorough discussion of the computed reaction pathway provided by analysis of atom/fragment charges, interatomic bond orders, and natural bond orbital occupancies, all as functions of the intrinsic reaction coordinate (IRC). These results also expand on the discussions of an analogous Cu-Fe transition state for H₂ elimination³⁵ and of a Cu-Fe transition state for C-Cl activation,³⁷ both disclosed previously. For all the results discussed below, the various computed parameters have been tracked across several points along the computational IRC scan: the optimized reactant complex (R1), three points from the IRC scan before the transition state, the transition state (TS1), three points from the IRC scan after the transition state, and the optimized product complex (P1). The energetic profile of these states and the TS1 structure are shown in Figure 1, and the other structures are provided as Supporting Information.

Upon examining the calculated trajectory of H₂ approach, it is clear that the reaction proceeds via the H₂ substrate initially forming a σ -complex at the Cu site. As the H₂ molecule approaches Cu, it induces Cu-Ru bond dissociation as well as NHC-Cu-Ru bending (133° in TS1 vs 179° in R1). Structural templating of the bimetallic transition state involving semibridging carbonyl ligands seems not to be operative in this case, as both Cu-CO distances increase smoothly along the reaction coordinate without exhibiting a local minimum at the transition state that is seen in other cases.^{37,38} Figure 2 plots key internuclear distances as functions of reaction coordinate. The Cu-Ru distances increase smoothly as the Cu-H1 distance decreases smoothly. The Ru-H2 and H1-H2 distances change more abruptly: the Ru-H2 bond is almost completely associated and the H1-H2 bond nearly dissociated at the TS1 structure. These observations are consistent with a





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Relative Energy (kcal/mol)

Figure 1. Computational modeling of the reaction between (IMe)-CuRp and H_2 .²⁰ (Top) Relative energies of the structures from the intrinsic reaction scan that were analyzed for this study. Bottom: Transition-state structure **TS1**, with key internuclear distances labeled in units of Å. // = discontinuity.



Figure 2. Selected internuclear distances for the reaction between (IMe)CuRp and H_2 , plotted along the calculated intrinsic reaction coordinate scan. // = discontinuity.

late transition state resembling the products and with a model that resembles deprotonation of a $Cu(H_2) \sigma$ -complex by the Rp fragment. Prior to dissociation of the two metal-hydride complexes to yield the **P1** state, there appears to be a locally

preferred H1…H2 contact of 1.76–1.88 Å at later stages of the reaction profile. These short H…H distances are in the dihydrogen-bonding regime^{39,40} and indicate polarization of the H₂ molecule. Experimental evidence for M–H…H–M' dihydrogen bonding in a related system has been reported, and the accompanying computational analysis indicated a dihydrogen bond strength of 1.7 kcal/mol in that system.⁴¹

The reaction profile was also analyzed using computed bond orders, determined by calculation of Wiberg bond indices (WBIs) derived from natural bond orbital (NBO) calculations. The changes in WBI values across the reaction coordinate (Figure 3) reinforce conclusions reached by analyzing bond



Figure 3. Selected Wiberg bond index values for the reaction between (IMe)CuRp and H_2 , plotted along the calculated intrinsic reaction coordinate scan. // = discontinuity.

distances. The Cu–Ru bond in **R1** experiences a smooth dissociation across the reaction coordinate and is partially broken at the **TS1** state. The Cu–H1 and Ru–H2 bonds are partially formed at **TS1**, and the covalent H1–H2 bond is mostly broken at **TS1**. In the post-**TS1** portion of the reaction coordinate, a locally preferred set of WBI values again indicates the presence of dihydrogen bonding between (IMe)CuH and HRp. Only upon complete dissociation at the **P1** state are the Cu–H1 and Ru–H2 bonds completely formed and the Cu–Ru and H1–H2 bonds completely broken.

Analysis of atom/fragment charges across the reaction coordinate provides insight into the extent to which redox activity is delocalized throughout the bimetallic reaction center and its supporting ligands. Natural charge values derived from natural population analysis are plotted in Figure 4. A traditional, single-site oxidative addition process is generally thought to involve homolytic H-H bond dissociation accompanied by two-electron oxidation of the metal center. In the bimetallic H₂ cleavage reaction being examined here, the reaction clearly involves heterolytic H₂ cleavage. In addition to the computational evidence for dihydrogen bonding disclosed above, the H1–H2 bond undergoes cleavage to produce hydridic H1 (q =-0.42 in P1) and protic H2 (q = 0.18 in P1) as the reaction proceeds. Neither the Cu center itself nor the (IMe)Cu fragment undergoes significant oxidation during the reaction, indicating that the oxidation behavior is located mainly on the Rp fragment. Indeed, the Rp charge is calculated to increase during the reaction. The Ru center maintains constant charge throughout the reaction, indicating that redox activity is localized not on Ru but mainly on the ligands supporting Ru. The cumulative charge of the two carbonyl ligands tracks with



Figure 4. Selected natural charge values derived from natural population analysis for the reaction between (IMe)CuRp and H_2 , plotted along the calculated intrinsic reaction coordinate scan. // = discontinuity.

the increase in charge of the Rp fragment during the reaction, indicating that much of the redox activity occurs at the two CO units. Similar conclusions have been reached previously during studies of bimetallic reaction pathways involving (NHC)M'-[M] complexes through experimental⁴² and computation- $a^{35,37,42}$ analyses, and all of these studies collectively highlight the importance of redox-active carbonyl ligands in the (NHC)M'-[M] catalyst design. On the other hand, the IMe and Cp ligands have similar charges in **R1** and **P1** and therefore are not redox-active with regard to this reaction.

Analysis of NBO occupancies as functions of reaction coordinate provides insight into the key orbital interactions involved in bimetallic H₂ cleavage.¹² Selected NBO occupancies are plotted in Figure 5 (left axis). As the reaction proceeds from **R1** to **TS1**, the occupancy of the $\sigma_{\rm HH}$ orbital (labeled BD(H– H)) decreases, consistent with transfer of charge from this orbital toward the catalyst upon formation of a σ -complex. The loss of electron density (0.38 e) from the $\sigma_{\rm HH}$ -orbital is almost completely matched by an increase in occupancy (0.33 e) of a Cu valence orbital (labeled LP*1(Cu)) that has $s^{0.05}p^{0.94}d^{0.01}$ hybridization (Figure 6). This is the only NBO that increases occupancy significantly as a function of reaction coordinate, and so it is assigned as the acceptor orbital to which the $\sigma_{\rm HH}$ -orbital is donating charge. Additionally, the $\sigma^*_{
m HH}$ -orbital (labeled BD*(H-H)) gains occupancy (0.43 e) as the reaction proceeds, consistent with back-donation from the catalyst as the H₂ molecule coordinates and cleaves. We could not identify



Figure 5. Selected NBO occupancy values for the reaction between (IMe)CuRp and H_2 , plotted along the calculated intrinsic reaction coordinate scan. Lewis occupancies of the H_2 bonding and antibonding NBOs and of a key Cu acceptor NBO are plotted on the left axis. Total non-Lewis occupancy of the system is plotted on the right axis. // = discontinuity.



Figure 6. Surface plots (0.04 isovalues) of the LP*1(Cu) (top) and BD(Cu–Ru) (bottom) NBOs in **R1** that are crucial acceptor and donor orbitals, respectively, for bimetallic H_2 cleavage. For clarity, the distant H_2 molecule has been omitted from the images.

any NBO that experienced a corresponding decrease in occupancy over the same part of the reaction coordinate. Instead, we assign the donor orbital that transfers charge into the $\sigma^*_{\rm HH}$ -orbital as being the Cu–Ru bonding orbital shown in Figure 6. In the **R1** state, this NBO has 87% Ru character (s^{0.13}p^{0.01}d^{0.77}) and 13% Cu character (s^{0.87}p^{0.06}d^{0.08}). In subsequent states in the reaction profile where the Cu–Ru bond has partially dissociated, this Cu–Ru bonding NBO was not identified but instead was replaced by enhanced Rp \rightarrow Cu(IMe) donor/acceptor interactions and Rp \rightarrow H₂ donor/acceptor interaction increasing in energetic contribution with the Rp \rightarrow H₂ donation increasing in energetic contribution with the reaction coordinate. This behavior can be tracked using the non-Lewis occupancy of each state (Figure 5, right axis), which does increase as the reaction proceeds. The Cu–Ru bonding orbital has 1.59-e occupancy in **R1**, and 1.05 e

are accounted for by the increase in non-Lewis occupancy as the reaction progresses to **TS1**. The remaining 0.54 e resembles the buildup of $\sigma^*_{\rm HH}$ occupancy (0.43 e), allowing us to assign the Cu–Ru bonding orbital (of predominantly Ru 4d character) as the main back-donating orbital that triggers H– H cleavage.

The traditional view of single-site H_2 oxidative addition involves formation of a σ -complex followed by concerted H–H homolysis that is triggered by (a) donation from σ_{HH} to an empty metal d-orbital and (b) back-donation from a filled metal d-orbital into σ^*_{HH} (Scheme 3a). For the bimetallic H_2

Scheme 3. Transition States and Orbital Interactions Involved in (a) Monometallic and (b) Bimetallic H_2 Addition

(a)



activation reaction studied here, a complementary mechanistic scheme has emerged from the computational data above (Scheme 3b). Heterobimetallic H₂ addition involves formation of a σ -complex at the electrophilic metal site, followed by H–H heterolysis via H⁺ transfer to the proximal nucleophilic metal site. The key orbital interactions that trigger this heterolytic H₂ cleavage are (a) donation from $\sigma_{\rm HH}$ to an empty orbital at the electrophilic metal site and (b) back-donation into $\sigma^*_{\rm HH}$ from a filled orbital predominantly located at the nucleophilic metal site. Such separation of the key orbital interactions across two reactive sites strongly resembles H₂ activation by p-block frustrated Lewis pairs (FLPs), which involves donation from $\sigma_{\rm HH}$ to a Lewis acid and from a Lewis base to $\sigma^*_{\rm HH}$.^{43–47} In this regard, the (NHC)M'-[M] catalysts can be viewed as d-block analogues of the classical p-block FLPs.

Alkene/Alkane Elimination and Selectivity Effects. Upon heterobimetallic H₂ activation under catalytic conditions, our proposal is that the alkyne substrate undergoes 1,2insertion with the transient (IMes)AgH intermediate to yield an alkenyl species. On the basis of stoichiometric synhydrocupration behavior reported for [(IPr)CuH]2,48 we propose that this 1,2-insertion reaction produces the C=C geometry shown in structure A (Scheme 4a). Under catalytic conditions, bimetallic alkene elimination is proposed to occur through reaction of A with HRp, producing a Z-alkene and regenerating the bimetallic catalyst. To test the feasibility of this proposed step, we prepared alkenylcopper complex 4 by synhydrocupration of diphenylacetylene. Complex 4 was found to react with HRp to produce (IPr)CuRp and generate stilbene with high Z-selectivity (Scheme 4b). The fact that both the hydrocupration and alkene elimination steps proceed at room temperature implies that H₂ activation is the turnover-limiting step in the catalytic process. The generation of Z-alkene from

Scheme 4. (a) Proposed Alkyne Hydrogenation Mechanism and (b) a Model Alkene Elimination Reaction



this model reaction is consistent with our model of a cascade alkyne \rightarrow Z-alkene \rightarrow E-alkene process.

The feasibility of $Z \rightarrow E$ alkene isomerization was supported by experiments reported in our initial communication,²⁰ showing that *cis*-stilbene was isomerized to *trans*-stilbene under catalytic conditions provided that both the catalyst and H₂ were present. The proposed mechanism of isomerization (Scheme 5a) involves 1,2-insertion of alkene with (IMes)AgH

Scheme 5. (a) Proposed Alkene Isomerization Mechanism and (b and c) Model Reactions for Alkene vs Alkane Elimination



to produce an alkyl intermediate (**B**). The key, selectivitydetermining step then involves single-site β -hydride elimination from **B** to produce the final *E*-alkene product. In order to produce high selectivity for *E*-alkene relative to *Z*-alkene and alkane, this β -hydride elimination reaction must (a) be under thermodynamic control to suppress reversion to *Z*-alkene by β hydride elimination and (b) outcompete bimetallic alkane elimination from reaction between **B** and HRp. To probe these factors, we conducted model reactions with two known alkylcopper species that have β -hydrogens. The ethyl complex **5**⁴⁹ was found to react with HRp to produce (IPr)CuRp and ethane (Scheme 5b). This observation establishes that bimetallic alkane elimination from intermediate B is feasible, consistent with the small amounts of alkane formed in typical catalytic trials.²⁰ No evidence for ethylene formation was observed in this experiment, indicating that for model complex 5 the bimetallic alkane elimination reaction outcompetes the desired β -hydride elimination reaction. We conducted an analogous experiment with alkylcopper complex 6 (Scheme 5c), which has been shown to undergo reversible β -hydride elimination under mild conditions.⁵⁰ Complex 6 was found to react with HRp to produce (IPr)CuRp and generate a 2:1 mixture of alkane 7 and E-alkene 8. No evidence for Z-alkene was observed. These observations show that, in a model system with an alkyl ligand that more closely resembles the catalytically relevant intermediate, β -hydride elimination can outcompete alkane elimination and furthermore that it is selective for extrusion of *E*-alkene products.

These results show that the relative rates of β -hydride elimination and bimetallic alkane elimination are very sensitive to steric effects, and an optimal steric environment must be used in the catalyst design in order to produce high selectivity for E-alkene generation. The real catalytic system, which features less stable alkyl intermediates B, is thus finely tuned to favor β -hydride elimination over bimetallic alkane elimination, unlike the model systems 5 and 6, which are stable enough for stoichiometric reactivity studies. These observations are consistent with the dramatic impact that the NHC steric bulk has on catalytic selectivity.²⁰ In addition, the use of Ag in place of Cu in the optimal catalyst may derive, in part, from the more facile rate of β -hydride elimination from a 4d metal compared to a 3d metal. Lastly, the use of Rp in place of Fp in the optimal catalyst may derive, in part, from the fact that HRp is a weaker acid than HFp by ~2 pK_a units,⁵¹ which serves to suppress the bimetallic alkane elimination process that is in competition with productive β -hydride elimination. All of these factors need to be held in consideration when designing second-generation catalysts.

CONCLUSIONS

In conclusion, in this study we have disclosed further details regarding catalyst decomposition pathways, the mechanism of H₂ activation, the feasibility of the proposed mechanistic cascade, and the factors relating to E-alkene selectivity in the catalytic semihydrogenation of alkynes using heterobimetallic catalysts of the type (NHC)M'-[M]. The conclusions drawn from this study will inform future catalyst designs related to hydrogenation catalysis. Specifically, in order to improve catalytic activity (possibly with earth-abundant metals) and operate at milder temperatures, it will be necessary both to (a) lower the barrier for heterobimetallic H_2 activation and (b) stabilize the vulnerable (NHC)M'H intermediates. Knowledge gained here about the key transition states and orbital interactions involved in heterobimetallic H₂ activation can serve to guide development of second-generation systems that activate H₂ more readily, and known methods for stabilizing (NHC)M'H can be pursued in concert.^{52,53} In order to maintain high selectivity for E-alkenes, it will be necessary for such systems to allow for efficient alkene 1,2-insertion and β hydride elimination processes while suppressing heterobimetallic alkane elimination. The experimental results disclosed here indicate that the relative rates of these processes will be highly sensitive not only to the steric demands of the substrate but also to the steric and electronic properties of the NHC, M', and [M] fragments in the catalyst species. Development of new

hydrogenation catalysts, with these factors in mind, is in progress in our laboratories.

EXPERIMENTAL SECTION

General Experimental Considerations. Unless otherwise specified, all reactions and manipulations were performed under purified N₂ in a glovebox or using standard Schlenk line techniques. Glassware was oven-dried prior to use. Toluene was sparged with argon and dried using a Glass Contour Solvent System built by Pure Process Technology, LLC. Xylenes, benzene, and all deuterated solvents were purified by repeated freeze–pump–thaw cycles followed by prolonged storage over activated 3 Å molecular sieves. H₂ gas was purchased from Praxair at a purity of 99.999% (5.0 UHP grade) and purified further by running through an O₂-removing catalyst column (RCI GetterMax 133T) and a drying column (Drierite). Literature methods were used to synthesize 5,⁴⁹ 6,⁵⁰ (IMes)AgRp,²⁰ (IPr)-CuOtBu,⁴⁸ and NaRp.⁵⁴ Unless otherwise specified, all other chemicals were purchased from commercial sources and used without further purification.

Physical Measurements. NMR spectra were recorded at ambient temperature using Bruker Avance DPX-400 and Bruker Avance DRX-500 spectrometers. ¹H NMR and ¹³C{¹H} NMR chemical shifts were referenced to residual solvent peaks. FT-IR spectra were recorded on solid samples in a glovebox using a Bruker ALPHA spectrometer fitted with a diamond-ATR detection unit. GC-MS data were obtained using an Agilent Technologies 7890A GC system interfaced to an Agilent Technologies 5975C VL mass selective detector. Elemental analyses were performed by Midwest Microlab, LLC (Indianapolis, IN, USA).

Computational Methods. Optimized structures for the reactants, products, and transition state for (IMe)CuRp + H₂ were obtained from our previous study,²⁰ along with the IRC scan data. All calculations were performed using Gaussian09, revision B.01.⁵⁵ Density functional theory calculations were carried out using a hybrid functional, BVP86, consisting of Becke's 1988 gradient-corrected Slater exchange functional⁵⁶ combined with the VWNS local electron correlation functional and Perdew's 1986 nonlocal electron correlation functional.⁵⁷ Mixed basis sets were employed: the LANL2TZ(f) triple- ζ basis set^{58–60} with effective core potential^{60–62} was used for Cu and Ru and the 6-311+G(d) basis set^{63,64} was used for C, H, N, and O. The sum of electronic and thermal free energies was used to calculate ΔG values at 298 K. Natural population analysis was used to determine atom/fragment charges, and Wiberg bond indices were used to determine bond orders. Both were obtained from NBO v. 3.1⁶⁵ calculations within Gaussian09.

Preparation of HRp. A modified version of the literature procedure⁵¹ was used. NaRp (0.0380 g, 0.155 mmol, 1 equiv) was mixed with toluene (5 mL), and 4.0 M HCl in dioxane (0.038 mL, 0.155 mmol, 1 equiv) was added. The resulting mixture was stirred overnight at room temperature. The solution was filtered through a Celite pad, and the filtrate was evaporated to dryness. Yield: 0.0131 g, 0.59 mmol, 38%. The solid was stored in a glovebox freezer at -36 °C. ¹H NMR (400 MHz, toluene- d_8): δ 4.57 (s, 5H, Cp), -10.75 (s, 1H, Ru–H).

Preparation of HRuCp(CO)(IMes). In a nitrogen-filled glovebox, (IMes)AgRp (0.0051 g, 0.00788 mmol) was dissolved in xylenes (1 mL), transferred to a J. Young NMR tube, and sealed. (The transfer was done in two steps: First, the maximum amount of catalyst was dissolved in 0.7 mL of xylenes and transferred. The vial was washed with another 0.3 mL of xylenes to transfer remaining solids.) The J. Young tube was inverted multiple times to make sure that all solids dissolved; then the tube was connected to a Schlenk line containing H₂ gas (1 atm). After degassing the solution using three 5 min freezepump-thaw cycles, the sample was frozen again, exposed to H₂, and allowed to thaw and equilibrate for 30 min. The J. Young tube was then resealed and heated in an oil bath at 150 °C for 24 h. The tube was then transferred back into the glovebox, filtered through Celite, and dried in vacuo. Yield: 0.0026 g, 0.00520 mmol, 66%. ¹H NMR (400 MHz, benzene- d_6): δ 7.08 (s), 7.04 (s, 4H), 6.85 (s), 6.28 (s), 4.58 (s, Cp), 2.21 (s), 2.18 (s), 2.14 (s), -11.98 (s, Ru-H). ${}^{13}C{}^{1}H{}$

NMR (125 MHz, benzene- d_6): δ 208.8 (CO), 139.0, 138.5, 136.4, 136.4, 136.1, 129.4, 121.8, 82.1 (Cp), 21.3, 18.8, 18.5. IR (solid, cm⁻¹): 1885 (CO). Anal. Calcd for C₂₇H₃₀N₂RuO: C, 64.91; H, 6.05; N, 5.61. Found: C, 64.78; H, 6.20; N, 4.36.

Catalytic Trials. Catalytic hydrogenation trials with HRp and HRuCp(CO)(IMes) were conducted using the procedure we published previously,²⁰ under identical reaction conditions, and using the same method of product analysis by ¹H NMR integration.

Preparation of 4. This species was prepared by hydrocupration of diphenylacetylene using the procedure reported for hydrocupration of 3-hexyne.⁴⁸ In a scintillation vial, (IPr)CuOtBu (0.0633 g, 0.12 mmol, 1 equiv) and diphenylacetylene (0.0215 g, 0.12 mmol, 1 equiv) were dissolved in benzene (10 mL). Triethoxysilane (40.5 µL, 0.23 mmol, 1.9 equiv) was added to the solution, which was then stirred overnight at room temperature. The solution was concentrated in vacuo to afford an off-white powder. Yield: 0.0574 g, 0.091 mmol, 76%. The solid was stored in a glovebox freezer at -36 °C. ¹H NMR (400 MHz, benzene d_6): δ 7.26 (t, ${}^{3}J_{H-H}$ = 4.0 Hz, 2H, p-H), 7.19 (s, 2H), 7.08 (d, ${}^{3}J_{H-H}$ = 4.0 Hz, 4H, m-H), 7.05 (d, ${}^{3}J_{H-H}$ = 4.0 Hz, 2H), 6.99–6.87 (m, 3H), 6.86–6.74 (m, 4H), 2.56 (sept, ${}^{3}J_{H-H} = 4.0$ Hz, 4H, C<u>H</u>(CH₃)₂), 1.32 (d, ${}^{3}J_{H-H} = 4.0$ Hz, 12H, CH(C<u>H</u>₃)₂), 1.08 (d, ${}^{3}J_{H-H} = 4.0$ Hz, 12H, CH(C<u>H</u>₃)₂), 1.08 (d, ${}^{3}J_{H-H} = 4.0$ Hz, 12H, $CH(CH_3)_2$). ¹³C{¹H} NMR (125 MHz, benzene- d_6): δ 185.6 (NCCu), 177.1, 154.7, 145.8, 141.3, 135.3, 133.9, 130.5, 129.6, 126.0, 124.3, 122.3, 121.4, 29.0, 25.0, 23.7. Anal. Calcd for C41H47N2Cu: C, 78.00; H, 7.50; N, 4.44. Found: C, 77.70; H, 7.61; N, 4.06.

Alkene/Alkane Elimination Reactions with HRp. In a nitrogenfilled glovebox, HRp (~5 mg, 1 equiv) and either 4, 5, or 6 (1 equiv) were dissolved separately in either toluene- d_8 or benzene- d_6 (0.5 mL each), transferred to the same J. Young NMR tube, and sealed. The tube was inverted several times to mix the solutions. The reactions were monitored by ¹H NMR until all HRp was consumed. For the reactions with 4 and 5, the organic products were detected by ¹H NMR. For the reaction with 6, the product mixture was transferred to a vial under air, pipet-filtered through silica gel, diluted with THF, and analyzed by calibrated GC-MS (with dodecane internal standard).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00356.

Spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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