Communication

Modular Attachment of Appended Boron Lewis Acids to a Ruthenium Pincer Catalyst: Metal–Ligand Cooperativity Enables Selective Alkyne Hydrogenation

Kuei-Nin T. Tseng, Jeff W. Kampf, and Nathaniel K. Szymczak

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Modular Attachment of Appended Boron Lewis Acids to a Ruthenium Pincer Catalyst: Metal–Ligand Cooperativity Enables Selective Alkyne Hydrogenation

Kuei-Nin T. Tseng, Jeff W. Kampf, and Nathaniel K. Szymczak*

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, United States

Supporting Information Placeholder

ABSTRACT: A new series of bifunctional Ru complexes with pendent Lewis acidic boranes was prepared by late-stage modification of an active hydrogen-transfer catalyst. The appended boranes modulate the reactivity of a metal hydride as well as catalytic hydrogenations. By installing acidic auxiliary groups, the modified complexes become multifunctional and catalyze the *cis*-selective hydrogenation of alkynes with a higher rate, conversion, and selectivity when compared to the unmodified catalyst.

For homogeneous catalysts, the selection and design of appropriate ancillary ligands serves an important role to control both the activity and the selectivity in subsequent catalytic reactions.[1] Although the steric and electronic properties of the primary coordination sphere are most often modified during catalyst optimization, secondary groups can also play a key role to promote substrate activation.[2] Elaboration of a catalyst's secondary structure often requires extensive synthetic redesign prior to metalation, which limits rapid evaluation of structure/function details. In contrast, late-stage modification of an already active catalyst can also be used to install appended groups and it offers several advantages: (1) functionalization of the ligand's secondary coordination sphere without perturbing the primary coordination environment, (2) methodical variation of the pendent group(s) for precise control over the steric and electronic properties, and (3) minimal need to re-optimize metalation conditions to ensure reaction compatibility (e.g. deleterious inter-ligand acid/base interactions).

Bifunctional transition-metal complexes have been shown to synergistically activate small molecules (e.g., H_2) *via* a metal–ligand cooperative pathway.[3] Although such ligand-facilitated reactivity has emerged as a prominent reaction theme within catalysts for alkene, ketone, and imine hydrogenation reactions, highly selective and efficient hydrogenation catalysts that employ Lewis acid–metal cooperativity remain underdeveloped.[4] Complementary to the role that Brønsted acidic groups can serve in bifunctional activation/transfer,[5] boron-based Lewis acids can also modulate substrate binding, and promote insertion-type reactions.[6]

Our group is working to evaluate how the precise structural, electronic, and cooperative modes in the secondary coordination sphere can be used to regulate reactivity.[5a,7] We recently reported an *N*,*N*,*N*-bMepi (bMepi = 1,3-bis(6'-methyl-2'-pyridylimino)isoindolate) Ru–H complex (**1**, HRu(bMepi)(PPh_3)$_2$) capable of mediating promoterless dehydrogenation of alcohols, amines, and upgrading ethanol to 1-butanol.[8] In addition to the hydrogenation and dehydrogenation of polar bonds, **1** is also an active catalyst for alkene hydrogenation.[9] We recently found that modifying this ligand framework by replacing *ortho* –CH_3 with –OH units prior to metalation enabled distinct catalytic reactivity: rapid H–E (H_2 and pinacolborane, HBPin) activation and catalytic nitrile hydroboration.[7d] To further elucidate the changes in reactivity that can be imparted by appended groups, we have targeted a ligand variant that replaces the Brønsted acidic –OH group(s) with a boron-based Lewis acid that importantly can be readily installed post metalation (Figure 1). These appended groups may be used to bias selectivity for a given catalytic reaction when unselective catalysis is observed for an unmodified variant. In this Communication, we report the development of a new series of bifunctional Ru complexes with appended BR_2 groups *via* B–H bond activation and demonstrate that the Lewis acidity of the borane influences the reactivity of the Ru hydride and also promotes *Z*-selective semi-hydrogenation of alkynes.

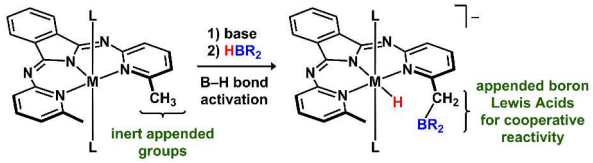


Figure 1. Conceptual development of late-stage catalyst redesign to introduce Lewis acidic sites for metal–ligand cooperativity.

To evaluate the strategy of installing appended boron-based Lewis acids within **1**, we assessed the reaction with boranes following deprotonation. The addition of catecholborane (HBCat) to a C_6H_6 solution of [Ru(CH_2Mepi)PPh_3]$_2$ (**2**)[8c] resulted in the clean conversion to HRu(CH_2BCatMepi)PPh_3 (**3**, Figure 2). The ^{1}H NMR spectrum confirmed the asymmetry of the appended BCat unit on the pincer ligand and featured a broad peak for the hydride ligand at −8.8 ppm,[10] while the ^{11}B{^{1}H} NMR spectrum exhibited a broad resonace at 14.6 ppm. The solid-state structure confirmed a pyramidalized boron atom [$\sum B_\alpha$ = 339.3(3)°], and furthermore, revealed a distorted octahedral geometry around the Ru center with the phosphorous and oxygen atoms in pseudo-axial positions [P1–Ru1–O2: 164.83(7)°] and the hydride ligand (located from the difference map) *trans* to the isoindolate nitrogen atom (N3).

The reaction between **2** and HBPin afforded a distinct product that incorporated two BPin units. Ru($CBPin_2$Mepi)PPh_3 (**4**, Figure 2) was isolated by treating **2** with either 2 or 4 equiv of HBPin. The ^{1}H NMR spectrum confirmed the presence of two BPin groups, and in contrast to **3**, the ^{11}B{^{1}H} NMR spectrum exhibited a broad signal at 28.1 ppm, consistent with minimal pyramidalization at both boron centers. The X-ray crystal structure confirmed

that the appended BPin units retain trigonal planar geometries at B3 and B4 [$\sum B3_\alpha = 359(1)°$, $\sum B4_\alpha = 360(1)°$], and also revealed a markedly different structure than **3**; the Ru resides in an octahedral environment with a bis(borylated) carbon atom (C70) cyclometalated *trans* to the isoindolate nitrogen atom (N8).

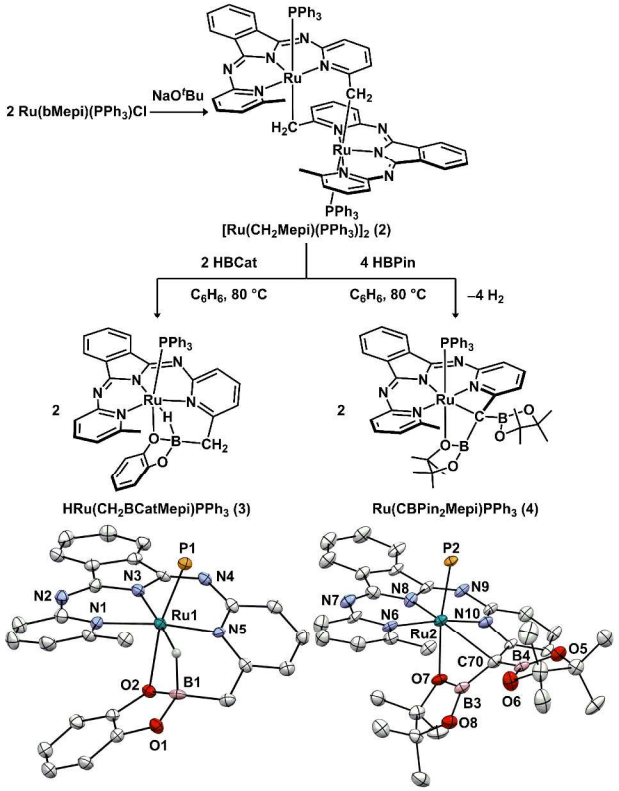


Figure 2. Synthesis and crystal structures (thermal ellipsoids depicted at 50% probability) of **3** and **4**. H atoms, except the hydride, and PPh_3 phenyl groups are omitted for clarity.

The stronger boron-based Lewis acid 9-borabicyclo[3.3.1]nonane (9-BBN)[11] afforded a distinct product, complex **5** (Ru(CH9BBNMepi)PPh_3) in 78% yield (Figure 3), when using analogous reaction conditions as those to prepare **3**. The X-ray crystal structure revealed a distorted octahedral environment about the Ru center with a rare Ru–(η^2-B–C) interaction that may be viewed in one of two limiting resonance forms of a borata-alkene, analogous to the Dewar–Chatt–Duncanson description of alkene coordination (Figure 3).[12] This unit results from loss of H_2 from the ligand CH_2 (C20) and the B–H unit and represents a form of ligand-enabled H_2 elimination that is reminiscent of bifunctional complexes developed by Milstein's group.[13] In those cases, bifunctional activation is achieved *via* aromatization–dearomatization of the pyridine group concomitant with protonation–deprotonation of the methylene arm. However, in contrast to aromatization–dearomatization observed in prior cases, we note retention of aromaticity in the pyridine ring, based on the normal C=C and C=N bonds as well as the distance between C19–C20 (1.490(3) Å), which is consistent with a single bond. Thus, by tuning the Lewis acidity of a pendent borane (BPin < BCat < 9-BBN), a cooperative bifunctional H_2 release step is enabled, which also serves to provide a Lewis acid in close proximity to a metal-coordinated substrate. Although the degree of pyramidalization at boron is considerably high [$\sum B_\alpha = 339.2(2)°$], the Ru1–B1 distance of 2.592(3) Å is longer than the Ru–B distances (2.093–2.176 Å)[14] found in reported Ru–BR_3 complexes, which suggests a weak Ru→B interaction.

Complementary to the solid-state characterization, the solution structure of **5** was investigated using variable temperature NMR spectroscopy. At 25 °C, the ^{1}H NMR spectrum exhibited broad signals in the alkyl region and a broad signal at −3.5 ppm, and the $^{11}B\{^1H\}$ NMR spectrum was featureless. However, upon cooling a CD_2Cl_2 solution of **5** to −80 °C, the ^{1}H signals sharpened and a broad signal appeared at −8.5 ppm in the $^{11}B\{^1H\}$ NMR spectrum, indicative of a fluxional structure at room temperature. Moreover, in the ^{1}H NMR spectrum at −80 °C, the signal at −3.87 ppm appeared as a well-resolved doublet with a coupling constant of 16.5 Hz that appeared concomitantly with a doublet at 2.06 ppm with the same coupling constant and a T_1(min) of 211 ms (−40 °C, 500 MHz) (Figure S5). This observation is consistent with an agostic interaction of a geminal –CH_2 group with Ru.[6e] Thus, we propose two coordination modes of the 9-BBN motif to the Ru center (Ru–(η^2-B–C) and a C–H agostic interaction, Figure 3).

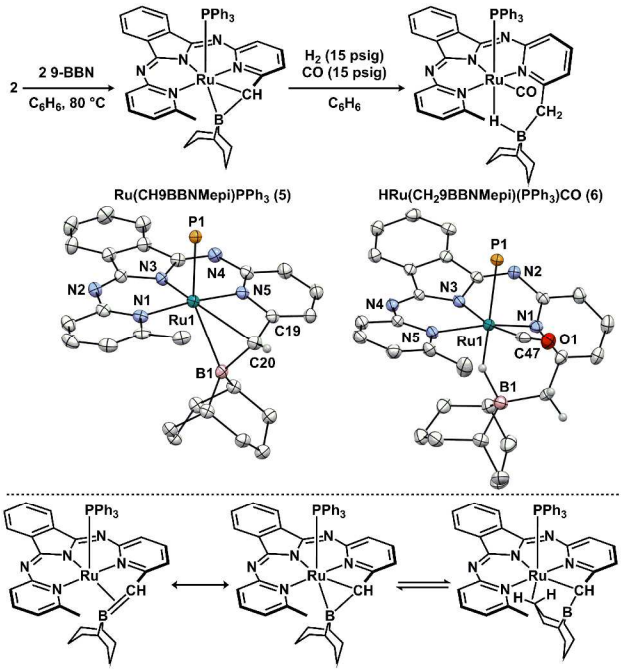


Figure 3. (Top) Crystal structures (thermal ellipsoids depicted at 50% probability) of **5** and **6**. H atoms, except the hydride, and PPh_3 phenyl groups are omitted for clarity. Select bond distances for **5** (Å): Ru1–C20 2.521(2), B1–C20 1.661(3). (Bottom) Limiting resonance description for **5** and solution equilibrium process.

To interrogate the capabilities of the pendent 9-BBN Lewis acid and Ru in **5** to cooperatively promote H–H activation, we evaluated the H_2 reactivity in the presence of a π-acidic ligand. The addition of H_2 (15 psig) and CO (15 psig) to a C_6H_6 solution of **5** yielded a new orange product, HRu($CH_2$9BBNMepi)(PPh_3)CO (**6**, Figure 3). The IR spectrum exhibited a ν_{CO} band at 1935 cm^{-1} and a broad Ru–H–B peak at 1820 cm^{-1}, which falls within the range of previously reported complexes.[15] In the ^{1}H NMR spectrum, the hydride ligand was visualized as a broad doublet at −9.83 ppm with a J_{HP} of 97.5 Hz, consistent with a hydride ligand *trans* to a phosphine ligand. The X-ray crystal structure revealed the products of H_2 heterolysis: a Ru–H (located from the difference map), and a sp^3 CH_2 unit adjacent to the boron. Similar to **3**, the Ru–H unit is capped by the appended borane, forming a Ru–H–B bridge. Furthermore, the boron atom (B1) in **6** is pyramidalized at boron [$\sum B_\alpha = 339.2(3)°$], consistent with the ^{11}B NMR resonance at −6.5 ppm. The structural characterization of **6** is consistent with H_2 heterolysis across the metal–ligand framework promoted either by the basic methanide moiety (C20), which is similar to Milstein's

bifunctional complexes,[4a] or alternatively, with assistance from the pendent boron Lewis acid in concert with the metal.[3e]

The effect of the varied appended borane groups were evaluated by examining the reactivity of **3**–**5** toward H_2 (Figure 4). When a J. Young tube containing a C_6D_6 solution of **4** and PPh_3 was charged with 30 psig of H_2, the immediate formation of **1** (the only Ru-containing product) was detected by ^1H and ^{31}P NMR spectroscopy. In contrast to the reactivity observed with **4**, **1** was not observed when allowing **3** or **5** to react with H_2 under identical conditions even after 48 h, consistent with an equilibrium of formation strongly favoring **3** or **5**. Moreover, these results suggest that both Ru–H and η^2-H_2 adducts with appended BPin groups are unstable intermediates and the weak Lewis acidic BPin group cannot stabilize the Ru–H species analogous to **3**.

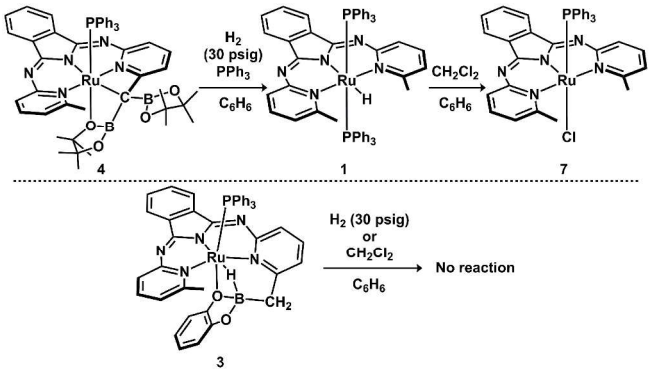


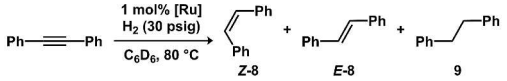
Figure 4. Influence of appended Lewis acids on the reactivity of of **3** and **4** toward H_2 and CH_2Cl_2.

The reactivity of the Ru–H unit was significantly suppressed when intramolecularly coordinated to a borane (Figure 4). H/Cl exchange has been used to evaluate the nucleophilicity of a given metal hydride, where facile exchange corresponds to a strong H^- donor.[6g] When **1** and 1 equiv of CH_2Cl_2 or $CHCl_3$ were allowed to react in C_6D_6, Ru(bMepi)(PPh_3)Cl (**7**) was immediately formed in quantitative yield. In contrast, no H/Cl exchange was observed when **3** was used under the same conditions, or in the presence of excess PPh_3. **7** was also generated quantitatively when performing a control experiment using **1**, 1 equiv of (9-BBN)CH_2CH_2Ph, and either CH_2Cl_2 or $CHCl_3$, which illustrates that the proximity of the intramolecular pendent BCat unit plays a critical role in regulating reactivity. Thus, the Lewis acidic properties of the borane moiety, when appropriately placed in the secondary coordination sphere has a significant effect on the reactivity of the hydride; the BCat–hydride (Lewis acid–base) interaction likely reduces the hydricity of the Ru–H and thus prevents the substitution reaction.

In addition to the stoichiometric H_2 reactivity, we evaluated the catalytic activity of **3** and **5** for hydrogen transfer. When a J. Young tube containing a C_6D_6 solution of diphenylacetylene and 1 mol% of **3** or **5** was charged with H_2 (30 psig) at room temperature for 24 h, *cis*-stilbene (***Z*-8**), was formed in 12% and 14% yields (Table 1, entries 1 and 2). In contrast, no reaction was observed when using **1** under identical conditions, even after a week (Table 1, entry 3) and in the presence of 1 equiv of (9-BBN)CH_2CH_2Ph. These results suggest that bifunctional catalysis might be accessed when bMepi is functionalized with a Lewis acidic borane in close contact with the metal center.[16]

To examine the extent to which the appended borane groups influence alkyne hydrogenation, we investigated the selectivity and reaction rate of diphenylacetylene hydrogenation at 80 °C for 2 h. When the hydrogenation reaction was performed with **1**, diphenylacetylene was converted to a mixture of ***Z*-8** (31%), ***E*-8** (18%), and **9** (16%) with low selectivity (48%) for ***Z*-8** (Table 1, entry 4). In contrast, high selectivity for the semi-hydrogenation of diphenylacetylene to ***Z*-8** was achieved using either **3** or **5**. Selectivities of 86% and 98% were obtained when **3** and **5**, respectively, were used instead of **1** (Table 1, entries 5 and 6).[17] Furthermore, significantly higher conversion (100%) and reaction rate (4×, see SI) were found when **5** ($2.6(3) \times 10^{-3}$ M/min) was used instead of **1** ($6.5(5) \times 10^{-4}$ M/min). Overall, the reaction profiles displayed by **1** and **5** for alkyne hydrogenation are distinct. Catalyst **5** consumes the alkyne *completely* prior to subsequent olefin hydrogenation that occurs over longer time periods (8 h), while **1** promotes the hydrogenation of both species *simultaneously*.[18] Thus, incorporation of an appended Lewis acidic site, such as 9-BBN, introduces a dramatic bias for three aspects related to alkyne hydrogenation: (1) selectivity for a single olefin stereoisomer, (2) selectivity for the reduction of alkynes over alkenes, and (3) enhanced reaction rate.

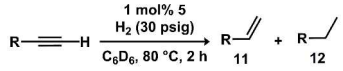
Table 1. Alkyne Semi-Hydrogenation Catalyzed by Bifunctional Ruthenium Complexes



entry	[Ru]	T (°C)	time (h)	conversion (%)[a]	***Z*-8**:***E*-8**:**9**	selectivity (%)[b]
1[c]	**3**	23	24	12	12:0:0	100
2[c]	**5**	23	24	14	14:0:0	100
3[c]	**1**	23	24	0	0:0:0	0
4	**1**	80	2	65	31:18:16	48
5	**3**	80	2	56	48:7:1	86
6[d]	**5**	80	2	100	98:2:0	98
7[e]	**5**	80	2	50	39:10:1	78
8	**10**[f]	80	2	65	34:21:10	52

[a]Conversion versus $PhSiMe_3$ (^1H NMR). [b]Selectivity determined by conversion of ***Z*-8** per total conversion. [c]24 h. [d]No change in the presence of Hg. [e]With 10 mol% NEt_3. [f]HRu(b^{i}Prpi)(PPh_3)$_2$.

Table 2. Catalytic Hydrogenation of Terminal Alkynes



entry	R	conversion (%)[a]	**11**:**12**	selectivity (%)[b]
1	Ph	100	100:0	100
2	C_6H_{13}	100	100:0	100
3	$CH_2N(CH_2CH_3)_2$	55	31:14	69
4	$CH_2CH_2CH_2CN$	80	80:0	100

[a]Conversion determined versus $PhSiMe_3$ (^1H NMR). [b]Selectivity determined by conversion of **11** per total conversion.

The semi-hydrogenation of aryl and alkyl terminal alkynes also afforded high conversions to the corresponding alkenes (Table 2, entries 1–2). The presence of a strongly Lewis basic amine unit (*N*,*N*-diethylpropargylamine; Table 2, entry 3) decreased both the conversion (55%) and selectivity (69%). However, the alkyne was selectively hydrogenated in the presence of another reducible group possessing diminished Lewis basicity. For example, 5-hexynenitrile was converted to 5-hexenenitrile in 80% yield with 100% selectivity (Table 2, entry 4), which suggests compatibility (or reversible binding) of nitriles with the 9-BBN motif in **5**.[19]

In addition to Lewis acidic character of the appended borane units, they also impose increased steric profiles, compared to a CH_3 unit, and the distinct steric environment may alternatively determine selectivity. To evaluate whether a similar steric effect influences the preference for a single stereoisomer, alkyne hydrogenation was examined using $HRu(b^iPrpi)(PPh_3)_2$ (**10**), which contains isopropyl groups that are more sterically encumbering around the Ru center than the *ortho*-substituents in **1**–**7**. For diphenylacetylene hydrogenation, the product distribution and conversion were strikingly similar to that of **1** (52% selectivity, 65% conversion, Table 1, entry 8). In addition to this ligand variation, the Lewis acidic properties of the borane unit in **5** were effectively quenched by performing catalytic hydrogenation reactions of diphenylacetylene in the presence of 10 mol% NEt_3 (Table 1, entry 7). Notably lower conversion (50%) and selectivity (78%) for ***Z*-8** were obtained, which further highlights the role of the appended Lewis acid to promote high activity and *Z*-selectivity. Collectively, these experiments provide clear support that the origin of selective alkyne reduction arises from the acidic character of the pendent boranes, rather than an increased steric profile.

In conclusion, we have developed a new class of bifunctional Ru complexes with appended Lewis acidic BR_2 groups. This work demonstrates that the Lewis acidic properties of the boranes in the secondary coordination environment can be used to modulate the reactivity of the Ru–H and turn on metal–ligand cooperativity for hydrogenation catalysis. Of particular note, higher reaction rate, conversion, and selectivity were noted for the *Z*-selective semi-hydrogenation of alkynes when using the bifunctional complex **5** appended with the most Lewis acidic borane. Comparison with the unfunctionalized complexes containing only inert $-CH_3$ groups illustrates the critical roles of the Lewis acids in the secondary coordination sphere to synergistically mediate and regulate alkyne hydrogenation by (1) facilitating H–H heterolysis, (2) stabilizing the hydride intermediate *via* the formation of a Ru–H–B bridge, and (3) selectively reducing alkynes over alkenes. Because installation of the pendent groups occurred at the last step, this strategy may be exploited as a versatile protocol to access a large variety of appended functional groups (Lewis acids and bases) with different steric and electronic properties. Future efforts will explore the incorporation of pendent acidic and basic groups to allow further control over the activity and selectivity of metal-based catalysis and to activate a variety of small molecules.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data. This material is available free of charge at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

Email: *nszym@umich.edu

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(9) See SI for alkene hydrogenation.
(10) We note that H–B coupling can be broad and not always observable by NMR spectroscopy, see reference 6g.
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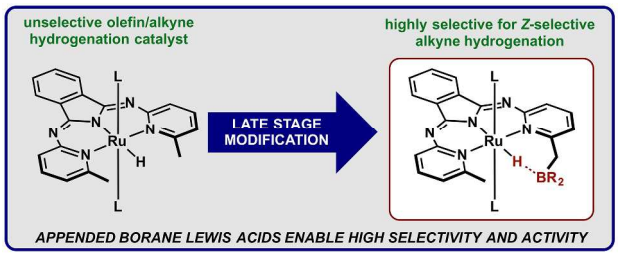
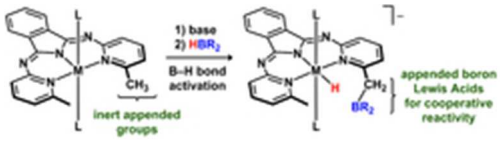
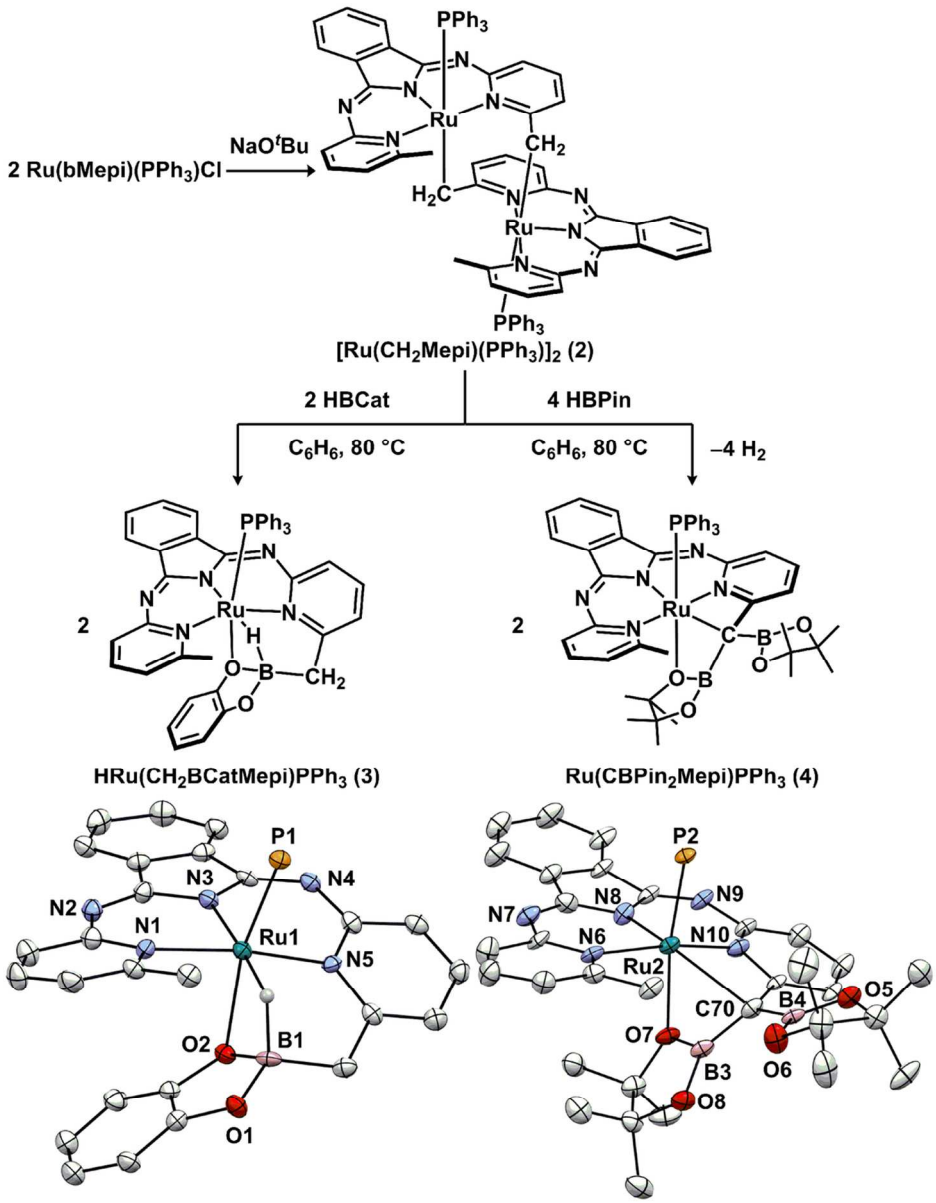
(16) Note that PPh_3 dissociation from **1** is fast, see reference 8c. Thus, the active catalyst coordination environment is analogous to **5**.
(17) The most common semi-hydrogenation catalyst is Lindlar's catalyst, which favors the *Z*-isomer. However, this catalyst also promotes *E*/*Z* isomerization over time, and has considerable variability in the activity and selectivity between batches. For further discussion, see Ulan, J. G.; Maier, W. F. *J. Org. Chem.* **1987**, *52*, 3132.
(18) Competition experiments between 1-octyne and 1-octene demonstrated that **3** favored alkyne insertion while **1** showed no preference for either substrate, see SI for further details.
(19) We note that the reduction of the nitrile group was observed when the reaction was allowed to continue for longer than 2 h at 80 °C.

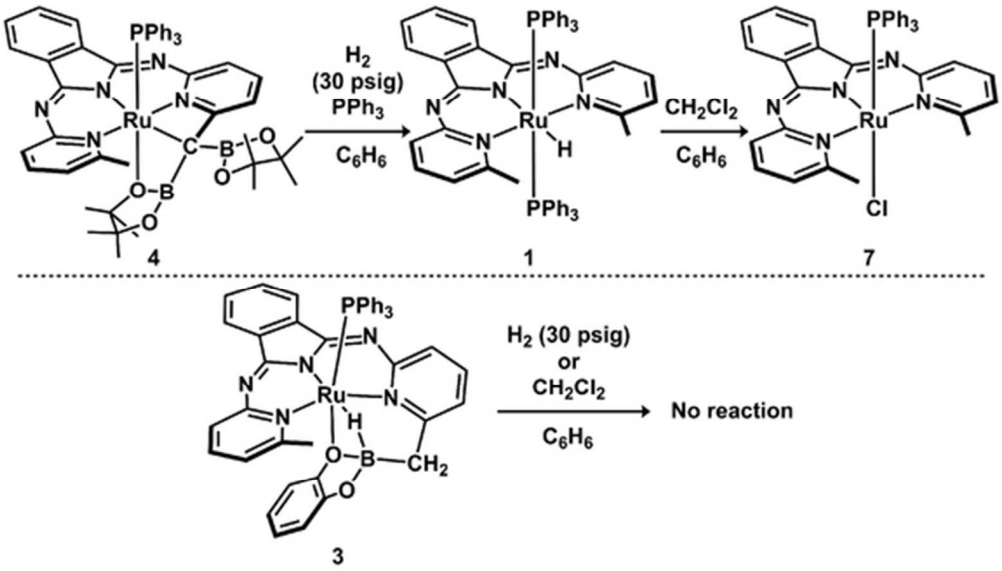

unselective olefin/alkyne hydrogenation catalyst
highly selective for Z-selective alkyne hydrogenation
LATE STAGE MODIFICATION
APPENDED BORANE LEWIS ACIDS ENABLE HIGH SELECTIVITY AND ACTIVITY



20x5mm (300 x 300 DPI)



104x132mm (300 x 300 DPI)



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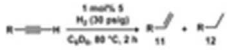
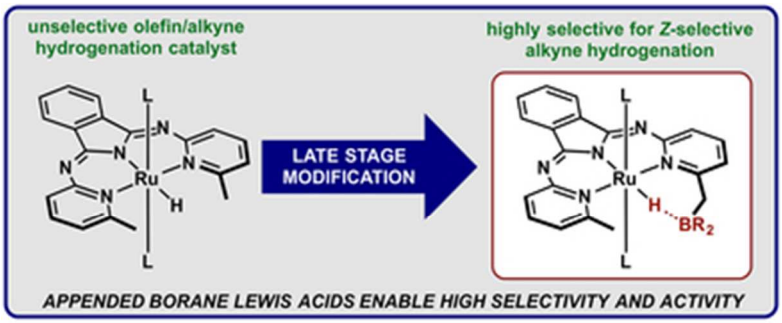


9x1mm (300 x 300 DPI)



TOC graphic

33x13mm (300 x 300 DPI)

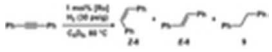


Table 1

11x1mm (300 x 300 DPI)

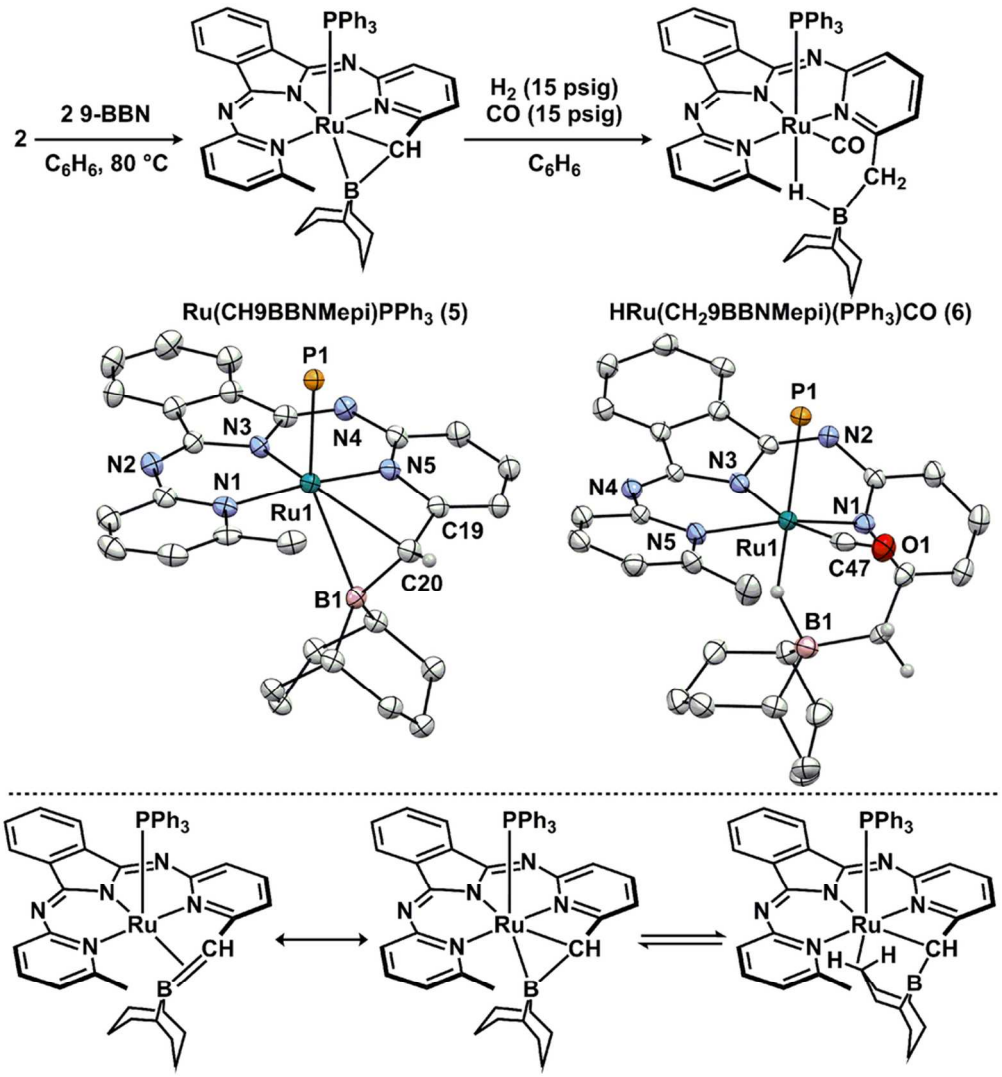


Figure 3

88x94mm (300 x 300 DPI)