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

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Supporting Information

ABSTRACT: A new series of bifunctional Ru complexes with pendent Lewis acidic boranes were 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. After installing acidic auxiliary groups, the complexes become multifunctional and catalyze the cis-selective hydrogenation of alkynes with higher rates, conversions, and selectivities compared with the unmodified catalyst.

For homogeneous catalysts, the selection and design of appropriate ancillary ligands serves an important role to control both the activity and 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 in promoting 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 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 reoptimize the metalation conditions to ensure reaction compatibility (e.g., deleterious interligand 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 precise structural, electronic, and cooperative modes in the secondary coordination sphere can be used to regulate reactivity.[5a,7] We recently reported the *N,N,N*-bMepi (bMepi =1,3-bis(6′-methyl-2′-pyridylimino)-isoindolate) Ru–H complex HRu(bMepi)$(PPh_3)_2$ (**1**), which is capable of mediating promoterless dehydrogenation of alcohols and 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 *o*-CH_3 units with *o*-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 installed after metalation (Figure 1). These appended groups may be used to bias the selectivity for a given catalytic reaction when unselective catalysis is observed for an unmodified variant. Here 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.

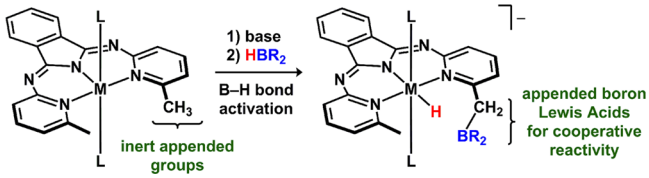

Figure 1. Conceptual development of late-stage catalyst redesign to introduce Lewis acidic sites for metal–ligand cooperativity.

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 its clean conversion to $HRu(CH_2BCatMepi)PPh_3$ (**3**) (Figure 2). The ^1H 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 $^{11}B\{^1H\}$ 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 phosphorus and oxygen atoms in pseudoaxial positions [P1–Ru1–O2: 164.83(7)°] and the hydride ligand (located from the difference map) trans to the isoindolate nitrogen atom (N3).

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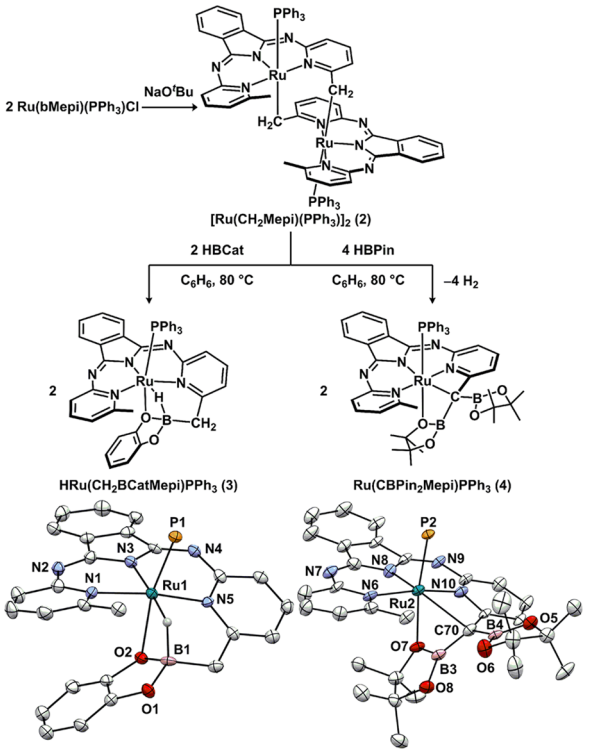

Figure 2. Synthesis and crystal structures (thermal ellipsoids depicted at 50% probability) of **3** and **4**. H atoms, except the hydride, and PPh_3 phenyl groups have been omitted for clarity.

The reaction between **2** and HBPin afforded a 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).

The stronger boron-based Lewis acid 9-borabicyclo[3.3.1]-nonane (9-BBN)[11] afforded a distinct product, Ru-(CH9BBNMepi)PPh$_3$ (**5**), in 78% yield (Figure 3) under reaction conditions analogous to those used 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 S5).[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 the aromatization−dearomatization observed in prior cases, we note retention of aromaticity in the pyridine ring on the basis of the normal C=C and C=N bonds as well as the C19−C20 distance [1.490(3) Å], which is consistent with a single bond. Thus, tuning the Lewis acidity of

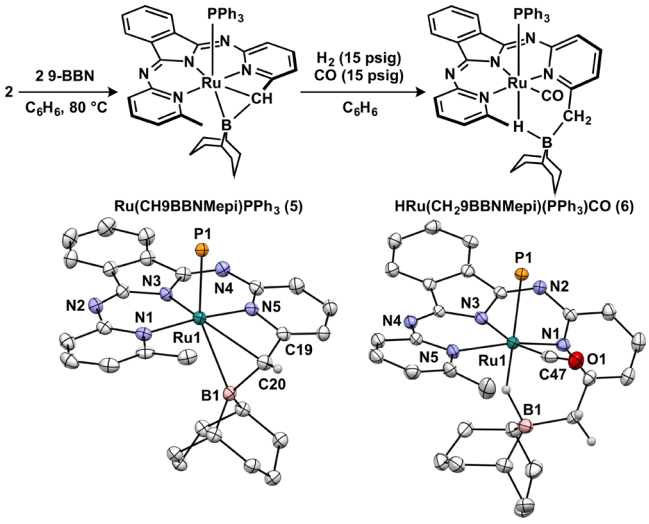

Figure 3. Crystal structures (thermal ellipsoids depicted at 50% probability) of **5** and **6**. H atoms, except the hydride, and PPh_3 phenyl groups have been omitted for clarity. Select bond distances for **5** (Å): Ru1−C20 2.521(2), B1−C20 1.661(3).

the pendent borane (BPin < BCat < 9-BBN) enabled a cooperative bifunctional H_2 release step that 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 found in reported Ru−BR$_3$ complexes (2.093−2.176 Å),[14] which suggests a weak Ru → B interaction.

To interrogate the capabilities of the pendent 9-BBN Lewis acid and Ru in **5** to cooperatively promote H−H activation, we evaluated the reactivity with H_2 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$)(CO) (**6**) (Figure 3). The IR spectrum exhibited a ν_{CO} band at 1935 cm^{-1} and a broad Ru−H−B peak at 1820 cm^{-1}, which falls within the range for previously reported complexes.[15] In the ^{1}H NMR spectrum, the hydride ligand was visualized as a broad doublet at −9.83 ppm with J_{HP} = 97.5 Hz, consistent with a hydride ligand trans to a phosphine ligand. The X-ray crystal structure revealed the products of H_2 heterolysis: a Ru−H (located from the difference map) and a sp^3 CH_2 unit adjacent to the boron. Similar to **3**, the Ru−H unit is capped by the appended borane, forming a Ru−H−B bridge. Furthermore, the boron atom (B1) in **6** is pyramidalized at boron [$\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 effects of the 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 H_2, the immediate formation of **1** (the only Ru-containing product) was detected by ^{1}H and ^{31}P NMR spectroscopy. In contrast to the reactivity observed with **4**, **1** was not observed when **3** or **5** was allowed to react with H_2 under identical conditions even after 48 h, consistent with an equilibrium of formation strongly favoring **3** or **5**. Moreover,

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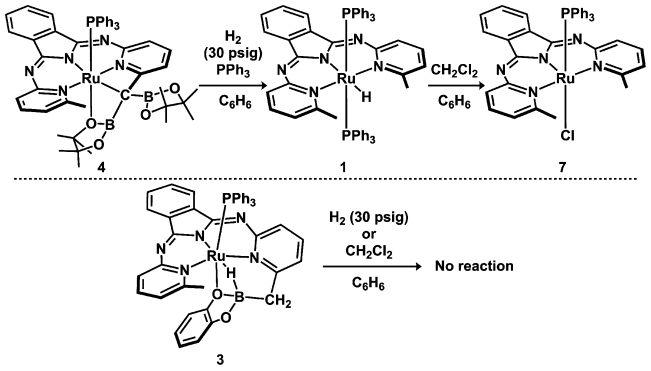


Figure 4. Influence of appended Lewis acids on the reactivity of of **3** and **4** toward H_2 and CH_2Cl_2.

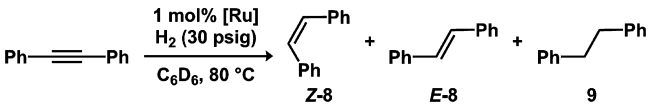
these results suggest that both Ru−H and η^2-H_2 adducts with appended BPin groups are unstable intermediates and that the weakly Lewis acidic BPin group cannot stabilize the Ru−H species analogous to **3**.

The reactivity of the Ru−H unit was significantly suppressed when this unit was 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 in 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 the reactivity. Thus, the Lewis acidic properties of the borane moiety, when it is appropriately placed in the secondary coordination sphere, have 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 **3** or **5** (1 mol %) was charged with H_2 (30 psig) at room temperature for 24 h, *cis*-stilbene (**Z-8**) was formed in 12% or 14% yield (Table 1, entries 1 and 2). In contrast, no reaction was observed when **1** was used under identical conditions, even after 1 week (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 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** (entries 5 and 6).[17] Furthermore, a significantly higher conversion (100%) and reaction rate (4×; see the 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,

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



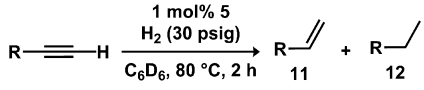
entry	[Ru]	T (°C)	t (h)	conv. (%)[a]	**Z-8**:***E*-8**:**9**	selectivity (%)[b]
1[c]	**3**	23	24	12	12:0:0	100
2[c]	**5**	23	24	14	14:0:0	100
3[c]	**1**	23	24	0	0:0:0	0
4	**1**	80	2	65	31:18:16	48
5	**3**	80	2	56	48:7:1	86
6[d]	**5**	80	2	100	98:2:0	98
7[e]	**5**	80	2	50	39:10:1	78
8	**10**[f]	80	2	65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

[a]Conversion versus $PhSiMe_3$ (^{1}H NMR). [b]Determined as 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)$(PPh_3)_2$.

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.

The semi-hydrogenation of aryl and alkyl terminal alkynes also afforded high conversions to the corresponding alkenes (Table 2,

Table 2. Catalytic Hydrogenation of Terminal Alkynes



entry	R	conv. (%)[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 versus $PhSiMe_3$ (^{1}H NMR). [b]Determined as conversion of **11** per total conversion.

entries 1 and 2). The presence of a strongly Lewis basic amine unit (*N*,*N*-diethylpropargylamine; 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 (entry 4), which suggests compatibility (or reversible binding) of nitriles with the 9-BBN motif in **5**.[19]

In addition to the 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 the selectivity. To evaluate whether a similar steric effect influences the preference for a single stereoisomer, alkyne hydrogenation was examined using HRu-(b^{i}Prpi)$(PPh_3)_2$ (**10**), which contains isopropyl groups that are more sterically encumbering around the Ru center than the ortho

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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 when catalytic hydrogenation reactions of diphenylacetylene were performed 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 in promoting high activity and *Z*-selectivity. Collectively, these experiments provide clear support that selective alkyne reduction originates 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 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 role of the Lewis acid 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 occurs in the last step, this strategy may be exploited as a versatile protocol to access a wide 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

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03972.

Crystallographic data for **3**−**6** (CIF)
Procedures and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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(9) See the Supporting Information (SI) for alkene hydrogenation.

(10) We note that H−B coupling can be broad and not always observable by NMR spectroscopy (see ref 6g).

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(16) PPh_3 dissociation from **1** is fast (see ref 8c). Thus, the active catalyst coordination environment is analogous to that in **5**.

(17) The most common semi-hydrogenation catalyst is Lindlar's catalyst, which favors the *Z* isomer. However, it also promotes *E*/*Z* isomerization over time and has considerable batch-to-batch variability in the activity and selectivity. For further discussion, see: Ulan, J. G.; Maier, W. F.; Smith, D. A. *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 the SI for further details.

(19) We note that reduction of the nitrile group was observed when the reaction was allowed to continue for longer than 2 h at 80 °C.

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