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Relative Reactivity of Stable Ligated Boranes and a Borohydride Salt in Rhodium(II)-Catalyzed Boron−Hydrogen Insertion Reactions

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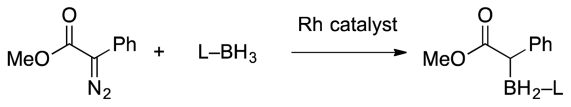
Supporting Information

ABSTRACT: Relative reactivities of a series of neutral ligated boranes L-BH_3 (where L is NHC, amine, pyridine, or phosphine) and the cyanoborohydride anion have been assessed in Rh(II)-catalyzed B−H insertion reactions with methyl 2-phenyl-2-diazoacetate. Stable α-boryl ester products were isolated by flash chromatography in all cases except for the salt product from cyanoborohydride. All of the substrates were either comparable to or more reactive than 1,4-cyclohexadiene, which is one of the most reactive substrates in C−H insertion reactions. The range of reactivity between the most reactive pyridine-borane and the least reactive phosphine-borane is a factor of approximately 40.



INTRODUCTION

Trivalent enol-boranes **1** have long been pivotal intermediates in organic synthesis (Figure 1).[1] However, it is increasingly

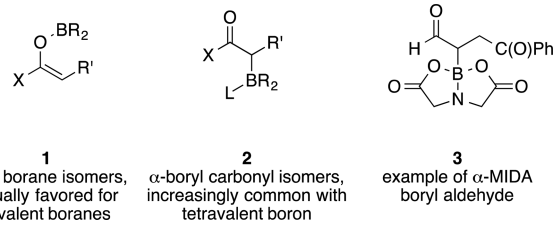


Figure 1. Enol-borane and α-boryl carbonyl isomers.

recognized that some classes of tetravalent boron compounds with strong ligands to boron prefer to form as isomeric α-boryl carbonyl compounds **2** rather than enol isomers.[2] Such compounds have value in synthesis as summarized in a timely perspective by Yudin and co-workers.[2] Yudin's work has focused on α-MIDA boryl carbonyl compounds such as aldehyde **3**,[3] where MIDA is the trivalent *N*-methyliminodiacetate ligand.

We recently showed that rhodium(II)-catalyzed insertion reactions of α-diazocarbonyl compounds **4** into boron−hydrogen bonds of *N*-heterocyclic carbene boranes **5** (hereafter, NHC-boranes) occur rapidly at ambient temperature (Figure 2a).[4] The resulting α-NHC-boryl carbonyl compounds **6** are stable in air, water, and chromatography, making them convenient to handle. Such compounds show no tendency to isomerize to enol-NHC-boranes.

In a typical example (Figure 2b), a brief reaction of methyl 2-diazo-2-phenylacetate **7** with 1,3-dimethylimidazol-2-ylidene borane **8a** and 1 mol % $Rh_2(esp)_2$ (esp = 3,3′-(1,3-phenylene)-bis(2,2-dimethylpropanoate)[5]) in CH_2Cl_2 was followed by solvent evaporation and direct flash chromatography of the residue. α-Boryl ester **9a** was isolated in 62% yield as a stable white solid.

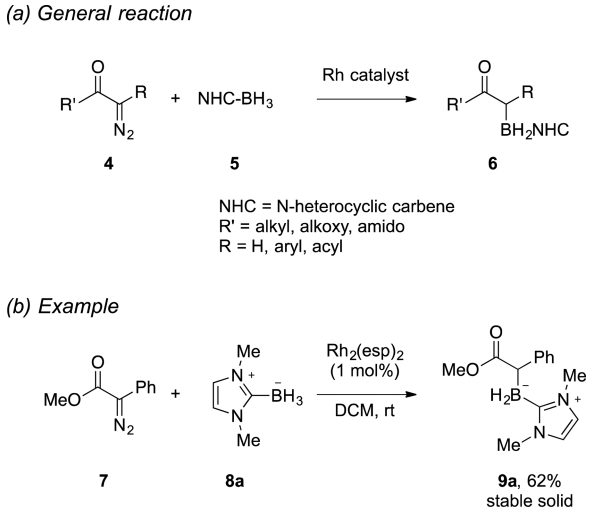


Figure 2. Rhodium(II)-catalyzed insertion reactions of NHC-boranes and diazocarbonyl compounds give stable α-NHC-boryl carbonyl compounds.

Shortly thereafter, Zhu and Zhou reported diazocarbonyl insertion reactions of various amine- and phosphine-boranes with both achiral and chiral copper catalysts.[6] More recently, Xu and co-workers reported asymmetric rhodium(II)-catalyzed insertions with both amine- and NHC-boranes.[7] These groups also provided examples of the synthetic utility of the α-boryl carbonyl products.

In a series of competitive insertion reactions, we learned that the B−H bonds of NHC-boranes are considerably more

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reactive than most activated C−H bonds toward reaction with rhodium carbenes.[4,8] For example, THF is usually considered to have an activated C−H bond toward carbene insertion;[9] however, it can actually be used as a solvent in B−H insertion reactions of NHC-boranes (although dichloromethane provides better yields).

Here, we extended the study of relative reactivity in B−H insertion reactions to other classes of stable ligated boranes, including neutral amine-, pyridine-, and phosphine-boranes and an anionic cyanoborohydride. We found that all of these species are highly reactive in B−H insertion reactions, though the order of relative reactivity does not faithfully follow either bond dissociation energies or nucleophilicity values.

RESULTS AND DISCUSSION

Synthesis of Ligated Borane Insertion Products. We selected methyl 2-phenyl diazoacetate **7** as the diazo partner for these experiments because it has commonly been used in competitive C−H insertion and cyclopropanation reactions,[10] and because it was the substrate used in the previous B−H insertion competition experiments.[4] The first step was synthesis and isolation of samples of the authentic products.

The α-NHC-boryl ester **9a** was prepared according to the prior report[4] as summarized in Figure 2b. The other products **9b−e** were prepared similarly as summarized in Table 1. The synthesis of α-pyridine-boryl ester **9b** is typical (entry 1). Pyridine-borane **8b** (pyr-BH_3, 1 mmol) and $Rh_2(esp)_2$ (1 mol %) were dissolved in CH_2Cl_2, and then a solution of methyl 2-diazo-2-phenylacetate **7** in CH_2Cl_2 (1.2 equiv) was added by syringe pump over 2 h at ambient temperature. Simple solvent evaporation and flash chromatography gave **9b** in 79% yield.

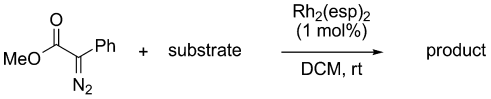
Likewise, α-trimethylamine-boryl ester **9c** was isolated in 43% yield (entry 2) from trimethylamine-borane **8c** (Me_3N-BH_3). Triphenylphosphine-borane **8d** (Ph_3P-BH_3) produced α-boryl ester **9d** in 50% yield (entry 3), while tributylphosphine-borane **8e** (Bu_3P-BH_3) produced **9e** in 30% yield with approximately 97% purity (entry 4).[11] Insertion products **9a−c** were isolated in pure form as indicated by both spectroscopic analysis and visual inspection (white solid or clear oil). In contrast, samples of phosphine-boranes **9d** and **9e** were faint orange and had small impurities in their spectra even after a second flash chromatography.

During these experiments, we found that free pyridine and phosphine inhibit the insertion reaction. Thus, when using small amounts of catalyst (1 mol %), it is important that the ligated borane substrates **8b**, **8d**, and **8e** do not have detectable traces of free ligand.

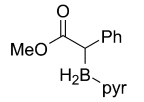
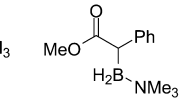
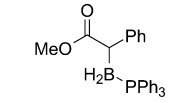
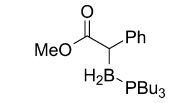
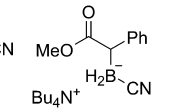
More simply, the amount of catalyst can be increased to compensate for traces of free ligand. For example, our sample of triphenylphosphine-borane **8d** contained approximately 3% triphenylphosphine by ^{31}P NMR analysis. The characteristic green color of the catalyst dissipated quickly when this sample was mixed with 1 mol % $Rh_2(esp)_2$. No reaction occurred when the diazo compound was added to the resulting yellow solution. However, when the same sample was mixed with 4 mol % $Rh_2(esp)_2$, the green color persisted, and the reaction proceeded normally when the diazo compound was added (entry 3).

Table 1 also shows the percent of conversion of starting material to product after completion of the syringe pump addition, measured by ^{11}B NMR spectroscopy. The conversion and yield in the pyridine-boryl series are roughly the same, showing that α-pyridine-boryl ester **9b** is stable to flash chromatography. In contrast, the conversions of trimethylamine-borane **8c** and the phosphine-boranes **8d** and **8e** are higher than the yields of the corresponding products **9c−e** (entries 2−4). This suggests that some decomposition may have occurred during flash chromatography for these products. Still, all of the products **9a−e** are stable once isolated and can be stored and handled in ambient lab conditions.

Table 1. Boron−Hydrogen Insertion Reactions of Ligated Boranes and a Borohydride



7 **8b–f** **9b–f**

entry	substrate	product	conv[a]	yield[b]
1	pyr–BH_3		80%	79%
	8b	**9b**		
2	Me_3N–BH_3		70%	43%
	8c	**9c**		
3[c]	Ph_3P–BH_3		70%	50%
	8d	**9d**		
4[c]	Bu_3P–BH_3		86%	30%
	8e	**9e**		
5	Bu_4NBH_3CN		100%[d]	–[e]
	8f	**9f**		

[a]Estimated from the ^{11}B NMR spectrum of the crude reaction mixture. [b]Yield after flash chromatography. [c]4 mol % $Rh_2(esp)_2$ used to offset phosphine impurity. [d]An 84/16 ratio of single-insertion product **9f** and double-insertion product $[MeO_2CCH(Ph)]_2BHCN$. [e]Product is a salt and was not isolated after column chromatography.

We also investigated two reactions with borohydride anions in place of the ligated boranes. Tetrabutylammonium counterions were used for solubility in DCM. When $Rh_2(esp)_2$ was mixed with tetrabutylammonium borohydride (Bu_4NBH_4) in DCM, the characteristic green color of the catalyst quickly changed to dark brown. The syringe pump addition of **7** was conducted, and the crude product was assessed by ^{11}B NMR spectroscopy; however, the major boron-containing component was unreacted Bu_4NBH_4.[12] Given the color change, Bu_4NBH_4 may have destroyed the catalyst.

In contrast, a similar reaction with the milder reducing agent tetrabutylammonium cyanoborohydride **8f** (Bu_4NBH_3CN, entry 5) behaved visually like the other reactions in Table 1:

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the green color persisted until the end of the syringe pump addition of the diazo partner, at which point the mixture became yellow. Analysis of the mixture showed full conversion to a mixture of two products in an approximately 84/16 ratio. The major product was assigned as single-insertion product **9f**, while the minor product is believed to result from double insertion (doublet at −27.2 ppm in the ^{11}B NMR spectrum).

An attempt to purify insertion product **9f** by flash chromatography failed; the salt never eluted. However, **9f** is stable while standing in solution and was further characterized in situ by ^{1}H, ^{11}B, and ^{13}C{^{1}H} NMR and HRMS. For example, a triplet (J_{BH} = 94 Hz) was observed at −28.3 ppm in the ^{11}B NMR spectrum. The α-proton was observed in the ^{1}H NMR spectrum as a broad triplet (small coupling to the vicinal protons on boron) at 3.15 ppm, while the α-carbon resonance was a broad, weak quartet (coupled to ^{11}B) at 44.4 ppm in the ^{13}C{^{1}H} NMR spectrum.[13] These features map well onto the spectra of the ligated boranes **9a**−**e**, which shows that **9f** is an α-cyanoborohydride ester, not an enol cyanoborohydride isomer. Substituted borohydrides such as **9f** could be used in situ or perhaps purified by nonchromatographic means.

Competition Experiments. Previous work has shown that NHC-borane **8a** is approximately 10 times more reactive than cyclohexadiene and roughly 100 times more reactive than THF in competitive B−H versus C−H insertion reactions with diazoacetate **7** and $Rh_2(esp)_2$.[4] Preliminary experiments showed that samples **8b**−**d** were also more reactive than cyclohexadiene; therefore, NHC-borane **8a** was initially used as the competitive standard. The results of the representative competition experiments are shown in Table 2.

Table 2. Results of Competitive B−H Insertion Experiments with Two Ligated Boranes (One Standard and One Unknown), Diazoacetate 7 (1 equiv), and $Rh_2(esp)_2$ (1 mol %)

entry	unknown (ukn)	standard (stn)	equiv unk/stn	prods	ratio[a]	k_{rel} (ukn/stn)
1	pyr-BH_3 **8b**	NHC-BH_3 **8a**	1.1/1.0	**9b**/**9a**	72/28	2.3
2	pyr-BH_3 **8b**	NHC-BH_3 **8a**	5.8/1.0	**9b**/**9a**	94/6	2.7
3	pyr-BH_3 **8b**	NHC-BH_3 **8a**	1.0/5.0	**9b**/**9a**	36/64	2.8
4	Me_3N-BH_3 **8c**	NHC-BH_3 **8a**	1.1/1.0	**9c**/**9a**	27/73	0.33
5[b]	Ph_3P-BH_3 **8d**	Me_3N-BH_3 **8c**	1.0/1.0	**9d**/**9c**	16/84	0.19
6[b]	Bu_3P-BH_3 **8c**	Me_3N-BH_3 **8c**	1.0/1.0	**9e**/**9c**	17/83	0.20
7	Bu_4NBH_3CN **8c**	Me_3N-BH_3 **8c**	1.0/1.0	**9f**/**9c**	35/65	0.54

[a]Determined by integration of the ^{11}B NMR spectrum of the reaction mixture. [b]4 mol % $Rh_2(esp)_2$ was used to offset the traces of free phosphine in **8d**.

In a typical competition experiment, a solution of methyl 2-diazo-2-phenylacetate diazoacetate **7** (0.2 mmol) in DCM was added by syringe pump to a solution of $Rh_2(esp)_2$ (4 μmol, 1 mol % relative to **8a**), NHC-borane **8a** (0.4 mmol), and pyr-BH_3 **8b** (0.44 mmol). Relative to the limiting diazo ester **7**, the mixture contains 2 equiv of **8a**, 2.2 equiv of **8b**, and 2% catalyst. After 2 h, the reaction mixture was concentrated, and an ^{11}B NMR spectrum was recorded. The relative ratio of the products **9b**/**9a** (unknown/standard) was determined by integration as 72/28 (Table 2, entry 1). These results show that pyridine-borane **8b** is even more reactive than NHC-borane **8a** in these B−H insertion reactions.

Two additional competition experiments were conducted with **8a** and **8b**, increasing the amount of one or the other to a significant excess (entries 2 and 3). The ratios of products **9b**/**9a** shifted accordingly. When excess **8b** was used (**8b**/**8a**, 5.8/1), the ratio increased to 94/6, whereas when excess **8a** was used (**8b**/**8a**, 1/5.0), the ratio decreased to 36/64. The calculated relative reactivities of **8b**/**8a** in these experiments range from 2.3 to 2.8. In other words, pyridine-borane **8b** is approximately 2.5 times more reactive than NHC-borane **8a** in these Rh(II)-catalyzed B−H insertion reactions.

We next conducted competition experiments with the other NHC-boranes, and Table 2 shows the results with equal amounts (2 equiv each) of standard and unknown ligated boranes. Experiments with other ratios gave the same relative reactivities within approximately 25%. Trimethylamine-borane **8c** proved to be about 3 times less reactive than NHC-borane **8a** (entry 4).

The phosphine-boranes **8d** and **8e** and tetrabutylammonium cyanoborohydride **8f** were less reactive still; therefore, we used trimethylamine-borane **8c** as the standard. The results of the equimolar competition experiments with these boranes are shown in entries 4−7, with the standard trimethylamine-borane **8c** performing best in all cases. When corrected for the different standards, the two phosphine-boranes are approximately 20 times less reactive than NHC-borane **8a**, and the cyanoborohydride is approximately 6 times less reactive than NHC-borane **8a**.

Figure 3 shows the approximate reactivity scale that emerges, again relative to NHC-borane **8a**. Here, the 1,3-cyclohexadiene is added as a reference substrate with reactive C−H bonds

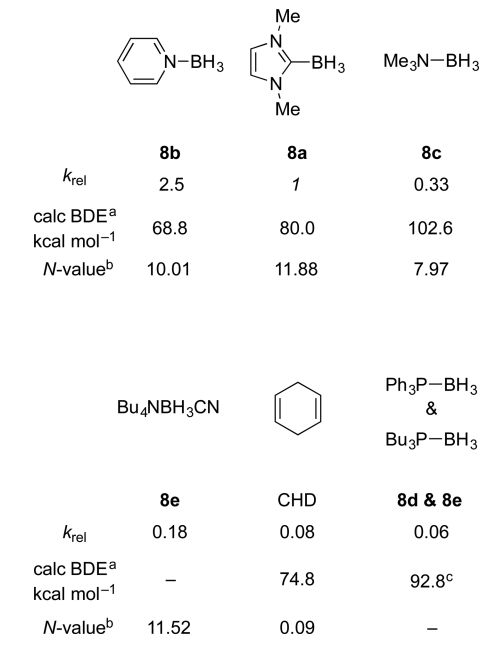

Figure 3. Approximate relative reactivities in insertion reactions compared to NHC-borane **8a**. Available BDEs and *N*-values are provided for comparison: (a) B−H BDEs taken from ref 14 and the CHD value taken from ref 15; (b) *N*-values taken from ref 16; and (c) for Me_3P-BH_3.

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because it is highly reactive compared to most other substrates with C−H bonds. The range from the least reactive phosphine-boranes to the most reactive pyridine-borane is a factor of approximately 40. The least reactive phosphine-boranes are still comparable to cyclohexadiene.

Also shown in Figure 3 under the relative reactivities are both the calculated B−H bond dissociation energies (BDEs)[14] and Mayr nucleophilicity scale[17] (*N*-scale) values,[16] where available. BDE was selected because the B−H bond breaks in the reaction, and *N* was selected because the TS is thought to have hydride transfer character.[4] However, a quick glance suffices to show that neither of these sets of values correlates well with the relative reactivity. In BDE, for example, Me_3N-BH_3 (102.6 kcal mol^{-1}) has a stronger B−H bond than R_3P-BH_3 (92.8 kcal mol^{-1}), but the amine-borane is more reactive. Likewise, the NHC-borane **8a** (N = 11.88) is a better hydride donor than pyridine-borane **8b** (N = 10.01), but pyridine-borane is more reactive. Steric[18] and other factors may also play a role in these reactions. Trends aside, the overarching conclusion is that all these B−H bonds are highly reactive in Rh(II)-catalyzed insertion reactions.

CONCLUSIONS

Representative ligated boranes L-BH_3, where L is either NHC, amine, or phosphine, have been made, and their reactivities have been studied in Rh(II)-catalyzed B−H insertion reactions with methyl 2-phenyl-2-diazoacetate **7**. Stable α-boryl ester products **9a**−**e** were formed in all cases and could be isolated by flash chromatography. Reaction with Bu_4NBH_3CN also gave stable α-borohydride ester **9f**, though the product is a salt that did not emerge from flash chromatography. All of the substrates were either comparable to or more reactive than 1,4-cyclohexadiene, which is one of the most reactive substrates in C−H insertion reactions. The range of reactivity between the most reactive pyridine-borane and the least reactive phosphine-borane was a factor of approximately 40.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of Reference Samples of Products. *(2-Methoxy-2-oxo-1-phenylethyl)(1λ⁴-pyridin-1-yl)-dihydroborate* ***9b***. Pyridine-borane (93.0 mg, 1.00 mmol, 1.0 equiv) and $Rh_2(esp)_2$ (7.9 mg, 0.01 mmol, 1 mol %) were dissolved in dry CH_2Cl_2 (5 mL) under argon. A solution of methyl 2-diazo-2-phenylacetate (211.0 mg, 1.20 mmol, 1.2 equiv) in dry CH_2Cl_2 (5 mL) was added via syringe pump over a period of 2 h. The solution color transitioned from light green to orange. An ^{11}B NMR spectrum of the crude product showed 79% conversion to the single-insertion product. The reaction mixture was concentrated under vacuum and purified by flash chromatography (hexane/ethyl acetate, 1/1) to yield 189.4 mg (79%) of **9b** as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 8.21−8.20 (m, 2H), 7.95−7.91 (m, 1H), 7.43−7.39 (m, 2H), 7.17−7.11 (m, 1H), 3.60 (s, 3H), 3.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 147.4, 142.5, 140.0, 127.8, 127.7, 124.8, 124.3, 50.8, 48.8 (weak); ^{11}B NMR (128 MHz, $CDCl_3$) δ −2.8 (t, J_{BH} = 101 Hz); IR (neat) 3059, 3022, 2947, 2393, 2340, 1710, 1622, 1599, 1458, 1362 cm^{-1}; HRMS (ESI) m/z (M^+) calcd for $C_{14}H_{16}O_2NBNa$ 264.1166, found 264.1164.

(2-Methoxy-2-oxo-1-phenylethyl)(trimethyl-λ⁴-azanyl)-dihydroborate ***9c***. Reaction of trimethylamine-borane (75.0 mg, 1.00 mmol), $Rh_2(esp)_2$ (7.9 mg, 0.01 mmol), and methyl 2-diazo-2-phenylacetate (211.0 mg, 1.20 mmol) was conducted according to the general procedure. An ^{11}B NMR spectrum of the crude product showed 72% conversion to the single-insertion product. The residue was purified by flash chromatography (hexane/ethyl acetate, 1/1) to yield 95.0 mg (43%) of **9c** as a white solid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.45−7.43 (m, 2H), 7.26−7.22 (m, 2H), 7.12−7.09 (m, 1H), 3.62 (s, 3H), 3.26 (s, 1H), 2.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 143.4, 129.1, 127.8, 124.9, 52.4, 51.2, 46.5 (weak); ^{11}B NMR (160 MHz, $CDCl_3$) δ −1.5 (t, J_{BH} = 99 Hz); IR (film) 3022, 2946, 2367, 2309, 1715, 1480, 1451, 1353, 1171 cm^{-1}; mp 95−97 °C; HRMS (ESI) m/z (M^+) calcd for $C_{12}H_{20}O_2NBNa$ 244.1479, found 244.1476.

(2-Methoxy-2-oxo-1-phenylethyl)(triphenyl-λ⁴-phosphanyl)-dihydroborate ***9d***. Reaction of triphenylphosphine-borane (285.0 mg, 1.00 mmol), $Rh_2(esp)_2$ (32 mg, 0.04 mmol), and methyl 2-diazo-2-phenylacetate (211.0 mg, 1.20 mmol) was conducted according to the general procedure. An ^{11}B NMR spectrum of the crude product showed 71% conversion to the single-insertion product. The residue was purified by flash chromatography (hexane/ethyl acetate, 3/2) to yield 211.0 mg (50%) of **9d** as an orange solid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.49−7.47 (m, 9H), 7.43−7.39 (m, 6H), 7.35−7.32 (m, 2H), 7.17−7.13 (m, 2H), 7.06−7.02 (m, 1H), 3.33 (s, 1H), 3.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.8, 178.7, 144.4, 133.5, 131.3, 128.9, 127.8, 127.7, 127.4, 124.8, 50.5, 41.7 (weak); ^{11}B NMR (160 MHz, $CDCl_3$) δ −23.4 (br); IR (film) 3058, 3023, 2946, 2375, 1720, 1484, 1436, 1136 cm^{-1}; mp 110−115 °C; HRMS (ESI) m/z (M^+) calcd for $C_{27}H_{26}O_2BNaP$ 447.1656, found 447.1646.

(2-Methoxy-2-oxo-1-phenylethyl)(tributyl-λ⁴-phosphanyl)-dihydroborate ***9e***. Reaction of tributylphosphine-borane (216.0 mg, 1.00 mmol), $Rh_2(esp)_2$ (32 mg, 0.04 mmol), and methyl 2-diazo-2-phenylacetate (211.0 mg, 1.20 mmol) was conducted according to the general procedure. An ^{11}B NMR spectrum of the crude product showed 86% conversion to the desired single-insertion product. The residue was purified by flash chromatography (hexane/acetone, 30/1) to yield 110.0 mg (30%, 97% purity) of **9e** as an orange oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.43−7.41 (m, 2H), 7.23−7.20 (m, 2H), 7.32−7.35 (m, 2H), 7.10−7.07 (m, 1H), 3.62 (s, 1H), 3.21−3.16 (m, 1H), 1.43−1.29 (m, 20H), 0.88 (t, J = 7 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.3, 179.2, 144.4, 144.4, 128.7, 127.6, 124.8, 51.0, 41.9, 24.6, 24.3, 24.2, 20.7, 20.5, 13.4; ^{11}B NMR (160 MHz, $CDCl_3$) δ −25.8 (br); IR (film) 2957, 2932, 2871, 2356, 1719, 1494, 1276, 1014, 700 cm^{-1}; HRMS (ESI) m/z (M^+) calcd for $C_{21}H_{39}O_2BP$ 365.2775, found 365.2779.

Tetrabutylammonium Cyano(2-methoxy-2-oxo-1-phenylethyl)-dihydroborate ***9f***. Tetrabutylammonium cyanoborohydride (283.0 mg, 1.00 mmol) and $Rh_2(esp)_2$ (7.9 mg, 0.01 mmol) were dissolved in dry CH_2Cl_2 (2 mL) under argon. A solution of methyl 2-diazo-2-phenylacetate (211.0 mg, 1.20 mmol) in CH_2Cl_2 (2 mL) was added via syringe pump over 2 h. The reaction mixture color transitioned from light blue to pink. An ^{11}B NMR spectrum of the crude product showed 86% conversion to the single-insertion product and 14% conversion to the double-insertion product. Isolation of pure insertion product **9f** by flash chromatography failed, presumably because the product is a salt: ^1H NMR (400 MHz, $CDCl_3$) δ 7.43−7.45 (m, 2H), 7.13−7.17 (m, 2H), 6.98−7.03 (m, 1H), 3.57 (s, 3H), 3.16 (br, 1H), 3.00−3.04 (m, 8H), 1.46−1.54 (m, 8H), 1.33−1.38 (m, 8H), 0.97 (t, J = 7 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 146.4, 129.2, 128.7, 123.7, 58.4, 50.4, 44.7 (weak), 23.8, 19.6, 13.6; ^{11}B NMR (160 MHz, $CDCl_3$) δ −27.2 (t, J_{BH} = 94 Hz); HRMS (ESI) m/z (M^+) calcd for $C_{10}H_{11}O_2NB$ 188.0877, found 188.0881.

Typical Procedure for the Competitive Insertions between L^1-BH_3 (Unknown) and L^2-BH_3 (Standard) (Taken from Table 1, Entry 1). Pyridine-borane **8b** (34.5 mg, 0.4 mmol, 2.0 equiv) and NHC-borane **8a** (41.2 mg, 0.4 mmol, 2.0 equiv) were dissolved in dry CH_2Cl_2 (1 mL) under argon. An ^{11}B NMR spectrum of the reaction mixture was obtained prior to addition of the diazo substrate and catalyst to determine the initial ^{11}B NMR integration of both borane species. After addition of $Rh_2(esp)_2$ (2.8 mg, 0.02 mol %), a solution of methyl 2-diazo-2-phenylacetate diazoacetate (38.5 mg, 0.2 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL) was added by syringe pump to the reaction solution. After 2 h, the reaction mixture was concentrated under vacuum, and an ^{11}B NMR spectrum of the residue was recorded and integrated.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00091.

General information and copies of spectra (PDF)

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Notes

The authors declare no competing financial interest.

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(11) The two phosphine-boranes have also been made by copper-catalyzed insertion reactions (see reference 6).

(12) There was a small triplet at −22.4 ppm in the ^{11}B NMR spectrum that might be from the target borohydride insertion product.

(13) There should be an even weaker septet due to coupling with ^{10}B, but this was not visible.

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(18) For example, a reaction of **7** with the hindered 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene borane under these conditions did not provide the corresponding insertion product.

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