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An Unsymmetric Imino−Phosphanamidinate Ligand and its Y(III) Complex: Synthesis, Characterization, and Catalytic Hydroboration of Carbonyl Compounds

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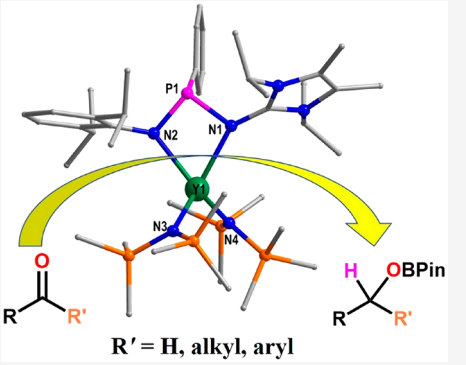
ABSTRACT: An imino-phosphanamide ligand, [NHI^{iPr2Me2}P(Ph)NH-2,6-^{i}Pr$_2$C$_6$H$_3$] (**LH**), containing two different *N*-substituents was prepared by the direct reaction of the lithium salt of *N*-heterocyclic imine (NHI) with phenylchloro-2,6-diisopropylphenyl phosphanamine, PhP(Cl)NH-2,6-^{i}Pr$_2$-C$_6$H$_3$. Reaction of **LH** with Y(N(SiMe$_3$)$_2$)$_3$ afforded the heteroleptic complex, [{L}Y(N(SiMe$_3$)$_2$)$_2$] (**1**), by elimination of HN(SiMe$_3$)$_2$. Compound **1** was characterized by multinuclear NMR and X-ray crystallography. In the complex, the Y(III) center was found to be tetracoordinate in a distorted tetrahedral geometry. The ligand, imino-phosphanamidinate, [L]$^-$, functions in a chelating manner, and its coordination to Y(III) results in a distorted 4-membered YPN$_2$ ring. As a proof of principle of its activity, **1** was used as a precatalyst for the hydroboration of various aldehydes and ketones using HBpin as the hydrogen source. The hydroboration reaction was rapid and clean even with low catalyst loadings (0.01−0.1 mol %). In addition, a very good functional group tolerance was observed in these reactions.



INTRODUCTION

A principal strategy in inorganic and organometallic chemistry is the design of specific ligand systems to prepare metal complexes of particular nuclearity, coordination number, geometry, and reactivity.[1] The primary function of these ligands is to provide stereoelectronic modulation that allows harnessing of specific properties from the metal complex, for example, catalytic specificity and efficiency. Ligands such as phosphines[2] and more recently *N*-heterocyclic carbenes[3] and their larger extended family have been playing a very crucial role in organometallic complexes and catalysis. Similarly, cyclopentadienyl ligands have been ubiquitous in their applications in organometallic complexes and catalysis by such complexes.[4] Simultaneously, there have been efforts in developing new families of ligands that can increase the repertoire of the organometallic complexes. Thus, there have been efforts on nitrogen-based electron rich ligands such as amidinate,[5,9] guanidinate,[6,9] iminophosphonamide,[7] and boraamidinate[8] ligands (Figure 1). Some of these have already found wide applications in the formation of a range of metal complexes including in the use for stabilization of unusual oxidation states of main-group elements (Figure S82).[9] Among these ligands, the amidinate and guanidinate ligands have received significant attention by many research groups.[5,6,9] These ligands are considered as pseudoallyl ligands and can commonly act as bidentate (η^2) or bridging monodentate (μ−η^1:η^1) or four-electron donors through metal−nitrogen σ-bonds (Figure 1).[5a] In addition, these ligands have the possibility of substituent variation in their backbone as well as on the nitrogen atoms, thus allowing a fine-tuning of their steric and electronic properties.[5,6,9] These properties of the ligands allow them to display versatile coordination behavior.

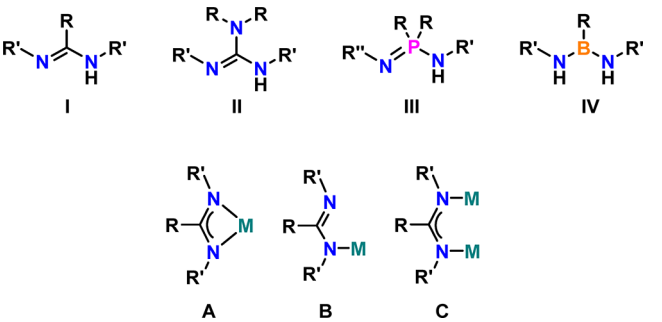


Figure 1. Different types of *N*-ligands (**I**−**IV**) and different types of coordination modes of amidinate and guanidinate ligands (where R = alkyl or aryl or NR$_2$) (A−C).

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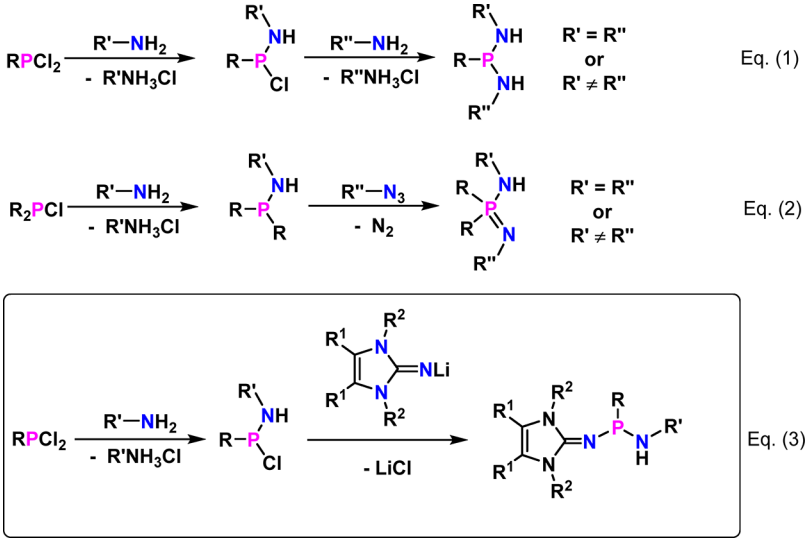
Scheme 1. Different Types of NPN Ligands and Their Synthesis (eqs 1 and 2). Our Synthetic Approach for the New NPN Ligand (eq 3)



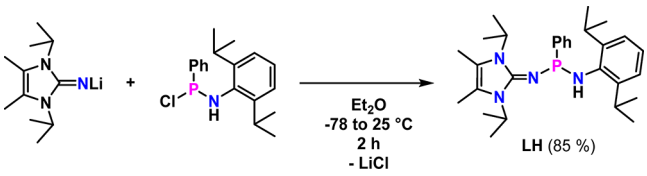
The versatility of the amidinate and the guanidinate ligands has spurred interest in modifying these ligands by the replacement of the central carbon with another main-group element such as boron or phosphorus.[7,8] While a large number of P−N−P,[10] P−C−P,[11] and N−P−N[7] (monoanionic with P(V)) ligands are well-known, N−P−N (monoanionic with P(III)) ligands that can be considered as equivalent to the amidinate N−C−N ligands discussed above are sparse. The known synthetic strategies for preparing these ligands are shown in Scheme 1. While eq 1 affords a ligand that would be dianionic where the oxidation of state of phosphorus would be +3, eq 2 would afford a monoanionic ligand, but the oxidation state of phosphorus would be +5.

We wished to develop a ligand where the phosphorus center would be in an oxidation state of +3 and would be a potential amidinate ligand bearing a unit negative charge. In search of such a system, we developed an *N*-heterocyclic imine (NHI)-based imino-phosphanamide ligand, [NHI^{iPr2Me2}P(Ph)NH-2,6-^{i}PrC$_6$H$_3$], **LH** (Scheme 1, eq 3). Upon metalation, the ligand is expected to lose a proton and bind in a monoanionic fashion similar to that of the amidinate ligands. Apart from being an unsymmetrical ligand where the two nitrogenous substituents on phosphorus are completely different, it is to be noted that this system is amenable to stereoelectronic modulation through substitution at the phosphorus as well as the nitrogen centers.[12] **LH** has two possible coordination sites, the primary coordination sites being the two nitrogen centers (in a chelating fashion) while a potential additional coordination site is the neutral phosphorus(III) site. To demonstrate the coordination capability of this ligand we chose complexation with Y(III) as a representative example, particularly since such complexes can be utilized in catalytic reactions.[13] Herein, we report the synthesis and characterization of **LH** and its metalation behavior with Y(III) affording the complex [{L}Y(N(SiMe$_3$)$_2$)$_2$], **1** (see Scheme 3). In addition to the complete characterization of **1** we also report its utility, as a proof of principle, for the hydroboration of a wide range of ketones and aldehydes.

RESULTS AND DISCUSSION

Synthesis of the LH and the Y(III) Complex 1. The ligand **LH** was readily synthesized in good yield by a salt elimination involving a reaction between PhP(Cl)NHDipp (Dipp = 2,6-diisopropylphenyl) with the lithium salt of *N*-heterocyclic imine (NHI) in Et$_2$O (see the Experimental Section) (Scheme 2). This compound was fully characterized

Scheme 2. Synthesis of the LH



by multinuclear NMR spectroscopy. In the ^{1}H NMR spectrum, **LH** displayed two sets of doublets for the methyl groups, two septets for the isopropyl groups and one singlet for the backbone methyl groups. The characteristic signal for the amine N*H* appears at δ = 4.69 ppm as a doublet due to coupling with the phosphorus nucleus. In the ^{31}P{^{1}H} NMR spectrum, the ligand displays a sharp singlet at 76.3 ppm which is in a range similar to that of the family of ligands that contain the NPN motifs DippN(H)P(Ph)N(^{t}Bu)C(*n*-Bu)=N^{t}Bu (74.1 ppm), DippN(H)P(Ph)N(Cy)C(^{t}Bu)=NCy (69.1 ppm), and DippN(H)P(Ph)N(Cy)C(*n*-Bu)=NCy (72.3 ppm) reported in the literature (where Dipp = 2,6-diisopropylphenyl; *n*-Bu = *n*-Butyl; ^{t}Bu = *tert*-Butyl; Cy = Cyclohexyl).[14]

LH, which contains the reactive NH, reacts readily with Y(N(SiMe$_3$)$_2$)$_3$ (in toluene at 60 °C) to afford the corresponding heteroleptic Y(III) complex **1** in 76% yield (Scheme 3). The reaction proceeds by the elimination of HN(SiMe$_3$)$_2$. In the process, the ligand assumes an anionic *amidinate* character by the loss of a proton. Compound **1** was fully characterized by multinuclear NMR as well as single-crystal X-ray diffraction analysis. In its ^{1}H NMR spectrum, **1** revealed the presence of two distinct signals for two −N(SiMe$_3$)$_2$ groups due to their different chemical surround-

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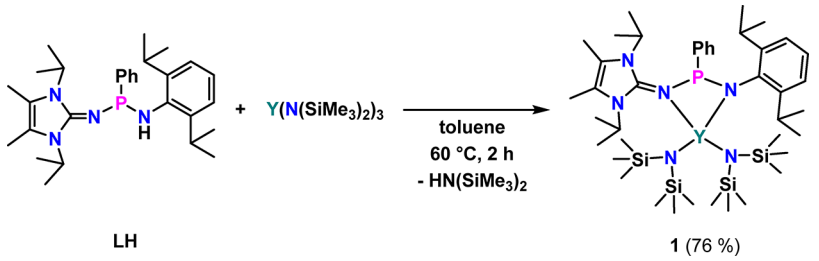
Scheme 3. Synthesis of Complex 1



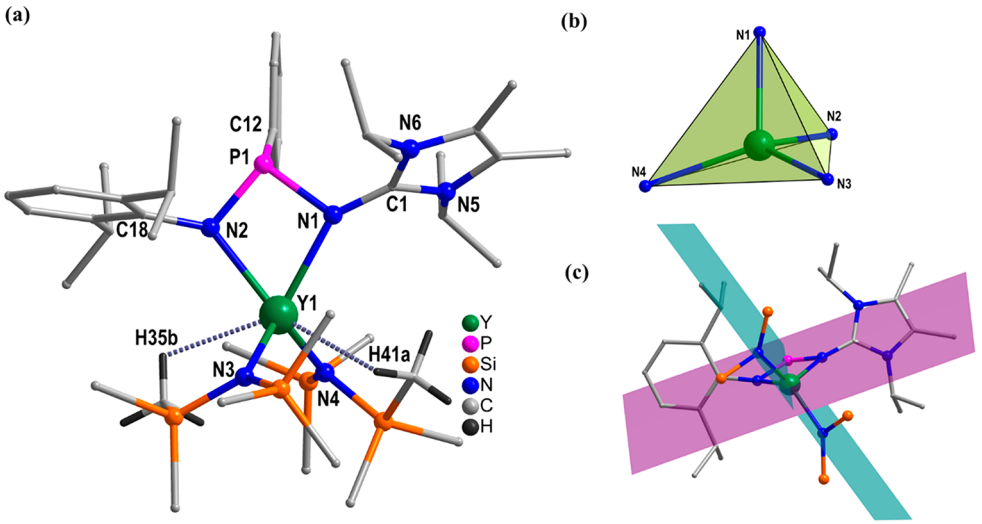


Figure 2. (a) Molecular structure of the complex **1**; (b) topology around the Y(III) considering immediate coordination; (c) representation of the perpendicular planes containing the coordinating N atoms, the central Y(III) ion and P(III) center of the ligand. (All hydrogen atoms (except C35 and C41 methyl hydrogens) were omitted for clarity.)

ings within the complex. Similarly, all the isopropyl groups are also distinguished because of the difference in the nature of the substituents on the phosphorus center (see the Experimental Section). The $^{31}P\{^{1}H\}$ NMR spectrum of **1** reveals a singlet at 103.02 ppm which is considerably deshielded with respect to what was observed for the parent ligand, **LH**.

X-ray Crystallography. X-ray-quality crystals of **1** were grown from a saturated solution of *n*-hexane at −35 °C. SCXRD study reveals that the complex crystallizes in the monoclinic system ($P2_1/c$). The neutral complex contains a four-coordinated Y(III) and the immediate chemical environment around Y(III) (4N) is generated by the chelating coordination action of the bidentate mono anionic ligand (L) and two negatively charged $-N(SiMe_3)_2$ groups (Figure 2a). Although the coordination geometry around Y(III) can be described as distorted tetrahedral, an exact geometry calculation through continuous SHAPE[15] measurement reveals it to be of the type, *vacant trigonal dipyramidal* (see Figure 2b and Table S3).

An examination of the Y(III)−N bond lengths reveals the following. Understandably, the strongest Y(III)−N bond is associated with N2 [Y1−N2, 2.254(2) Å] in view of the expected negative charge on this nitrogen as a result of deprotonation during complex formation. Also, the two Y−N distances involving the $-N(SiMe_3)_2$ groups are comparable while being slightly longer than Y1−N2 (see Table S2). On the other hand, the Y1−N1 bond distance (2.323(2) Å) is the longest. Notably, the central Y(III) ion is found to be involved in a weak agostic C−H···M interaction involving the two hydrogen atoms (H35b and H41a) of the $-N(SiMe_3)_2$ groups (see Table S2). This feature is indicative of the Lewis acidity of the Y(III) center and has been observed in some silylamido rare earth metal complexes.[16] The distorted tetrahedral geometry around the Y(III) is indicated by the N−Y−N bond angles which are deviated from the ideal value. The highest deviation is seen for the N1−Y1−N3 bond angle (123.82(8)°). However, the N1−Y1−N4 (108.85(8)°) and N2−Y1−N3 (106.21(8)°) bond angles are almost close to the ideal value (see Table S2). Further, the molecular structure of **1** reveals that the two planes containing the $Y_1P_1N_2$ motifs are nearly orthogonal to each other (72.0°) (Figure 2c).

A close observation of the P1 center of the ligand reveals that it is trigonal pyramidal (Figure 3), similar to what is found in phosphine ligands and, therefore, should be amenable to binding to soft metal centers. This aspect would merit a future investigation.

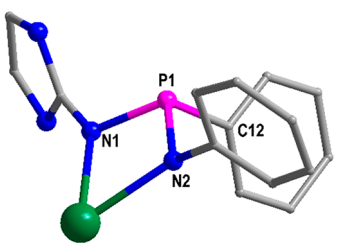


Figure 3. Pyramidal nature of the P atom in the complex **1**. (Only selected atoms in **1** are shown for the sake of clarity.)

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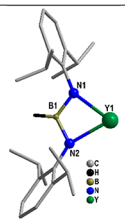
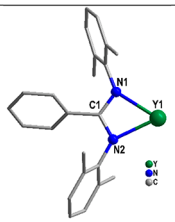
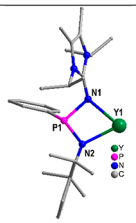
It is of interest to compare the coordination action of the ligand, **L** with analogous ligands containing the N−B−N and N−C−N motifs (Table 1).[8d,17a] It may be seen that the ligands

Table 1. Comparison of N−B−N, N−C−N, and N−P−N Ligands

Ligand	N–B–N		N–C–N		N–P–N	
Complex Formation						
Bond Description	N1–B1	N2–B1	N1–C1	N2–C1	N1–P1	N2–P1
Bond Length (Å)	1.420(6)	1.452(6)	1.334(7)	1.346(7)	1.751(2)	1.690(2)
Bite Angle (°)	N1–B1–N2		N1–C1–N2		N1–P1–N2	
	116.2(4)		114.5(5)		94.45(11)	
Reference	8d		17a		This work	

containing the N−B−N motif tend to be dianionic while the ligands containing the N−C−N and N−P−N motifs are mono anionic. However, the bite angles found in the complexes formed from the N−B−N and N−C−N ligands are almost same.[8d,17a] On the other hand, the bite angle is the smallest in N−P−N ligands owing to longer P−N bond lengths, which in turn are the result of the larger size of the phosphorus center.

Hydroboration of Carbonyl Compounds. Hydroboration of carbonyl compounds has emerged as an atom-economical and selective synthetic route for the synthesis of various borate esters, which are intermediates of valuable functionalized alcohols. There has been significant development in the carbonyl hydroboration reactions catalyzed by the complexes of *s*-block, main group, and transition metal ions.[18] In addition, catalyst-free hydroboration reactions have also been documented.[19] Homoleptic lanthanide complexes such as $La(N(SiMe_3)_2)_3$, $(Cp)_3La$ (Cp = cyclopentadienyl) and $(MeCp)_3La$ (MeCp = methylcyclopentadienyl) also are known as catalysts for the hydroboration of aldehydes and ketones.[20] In view of this, it was of interest to examine the catalytic behavior of **1**. A promising aspect of the latter is its high lipophilicity being readily soluble in common organic hydrocarbon solvents including *n*-pentane and *n*-hexane. As a proof of principle, in order to examine the catalytic activity of **1**, we have performed the catalytic hydroboration of ketones and aldehydes which are described below.

Initial screening of the catalyst was carried out by using benzophenone as the reactant, HBpin as the reducing agent, and **1** as the catalyst (using 0.01 mol %). The reaction proceeded smoothly at room temperature and was complete within 10 min. It is noted that the precursor $Y(N(SiMe)_2)_3$ itself acts as a catalyst for the hydroboration reaction.[20a] However, the reaction rate is slightly diminished as compared with **1**. Reduction of wide variety ketones (possessing both electron-withdrawing and donating groups, as well as those that are sterically encumbered) has been further carried out. These results are summarized in Table 2.

Benzophenone, cyclohexyl phenyl ketone, isobutyrophenone, and acetophenone were reduced rapidly to the respective boronate esters within 10 min (entries **1**−**5**). The catalyst showed good functional group tolerance toward −Br, −OMe, and $-NO_2$ groups (entries **6**−**7**) by achieving complete reduction. At the same time, electronically deactivated trifluoroacetophenone was also readily reduced within a short period. Note that mono and diacetyl ferrocene were also tested for the reduction, and the reaction was smooth (entries **11** and **12**). We further tested the reduction of the naturally occurring sterically hindered cyclic ketone, camphor, with the same catalyst loading (entry **13**). Further hydroboration of 1,4-diacetylbenzene also proceeded efficiently.

As can be seen from Table 3 a variety of aldehydes could also be easily reduced. These include simple benzaldehyde to those containing electron-withdrawing, electron-donating, or different functional groups. Benzaldehyde and 4-(dimethylamino)benzaldehyde were smoothly reduced to their corresponding boronic esters (entries 1 and 2). Aliphatic aldehydes such as 2-phenylpropanal and 2,2-diphenylacetaldehyde also reacted very well (entries 3 and 4). We have observed no reactivity change in the case of 2-napthaldehyde and cyclohexanecarbaldehyde, which could be converted to the targeted products (entries 5 and 6) in a short period. Substrates with electron-withdrawing groups also gave reduced products in high yields (entries 7 and 8). Further, the catalyst showed substrate tolerance to those that contained $-NO_2$ and −Br groups. Dialdehydes and $\alpha-\beta$ unsaturated aldehydes are also seen to be reduced spontaneously in the presence of **1** (entries 9 and 10). In entry 10, the reduction of the C═O group occurred exclusively over the reduction of the C═C bond. It is worth noting that the reduction of 2-formylpyridine proceeded chemoselectively with the reduction of the C═O group over the competitive pyridine hydroboration reaction. The latter is the common reaction path with lanthanide catalysts such as $[Cp^*_2LaH]_2$.[21] However, in this case the reaction rate is slightly slower than that observed for the reduction of the other aldehydes (Table 3, entry 11). This is possibly due to the coordination of pyridine to Y(III) during the catalytic cycle.

In addition to the common substrate scope to probe the general suitability including scalability and solvent-free conditions for the greener processes, preparative-scale reactions were further investigated. Large-scale reactions (1 g) were performed using benzaldehyde and acetophenone as liquid substrates in neat conditions. The reaction is exothermic in the case of benzaldehyde and is completed within 30 min. We also tested the hydroboration reaction using 4-(dimethylamino)benzaldehyde and benzophenone as solid substrates in neat conditions where HBpin acted as the solvent. In a similar fashion to the liquid substrates, the reaction was found to be complete within 30 min and the catalyst showed similar reactivity toward ketone and aldehydes. In both cases, we have used 0.01 mol % of catalyst loading and isolated the reduced products in >90% isolated yields (see the Experimental Section).

Further, we have studied a competitive intermolecular hydroboration reaction involving a 1:1 mixture of aldehyde and ketone (Scheme 4). These studies showed that the aldehyde was chemoselectively reduced with 92% conversion, indicating aldehydes are more reactive than ketones toward the

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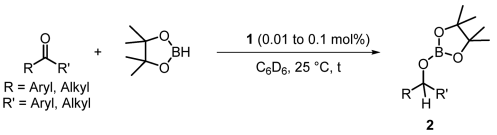
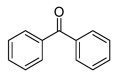
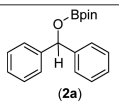
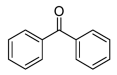
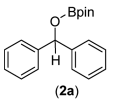
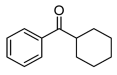
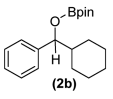
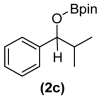
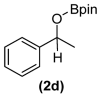
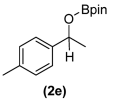
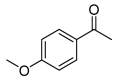
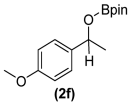
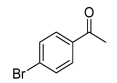
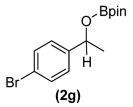
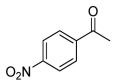
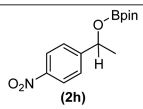
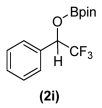
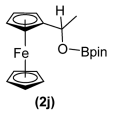
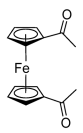
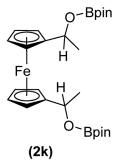
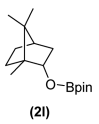
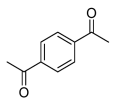
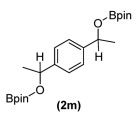
Table 2. Scope of Hydroboration of Ketone Catalyzed by 1.[a]



S. No	Substrate	Cat (%)	Time (min)	Product	Conversion (%)
1		0	10 days	 (2a)	---
2		0.01	10	 (2a)	>99
3		0.1	10	 (2b)	>99
4		0.1	10	 (2c)	>99
5		0.1	10	 (2d)	>99
6		0.1	10	 (2e)	>99
7		0.01	10	 (2f)	>99
8		0.1	10	 (2g)	>99
9		0.1	10	 (2h)	>99
10		0.1	10	 (2i)	>99
11		0.1	10	 (2j)	>99
12		0.1	10	 (2k)	>99
13		0.1	10	 (2l)	>99
14		0.1	10	 (2m)	>99

[a]Reaction conditions: ketone (0.25 mmol), HBpin (0.30 mmol, 1.2 equiv), catalyst (0.01 or 0.1 mol %). The reaction was carried out in C_6D_6 at 25 °C and monitored by ^1H and ^{11}B NMR.

hydroboration reaction. We have tried another reaction involving a mixture of an activated ketone, 4-methoxyacetophenone, and benzaldehyde. Even in this case, the reduction of benzaldehyde was dominant pathway with a selectivity of 99% aldehyde hydroboration at room temperature in 10 min. This chemoselectivity is similar to that reported earlier for $La(N(TMS)_2)_3$, Cp_3La, and $(MeCp)_3La$.[20]

We propose a plausible reaction mechanism for the hydroboration reaction based on literature precedents (Scheme 5). Thus, we suggest that the metal amide initially reacts with HBpin with the elimination $HN(SiMe_3)_2$ to generate a metal hydride (**I**) as the catalytically active species. This kind of metal hydride formation has been commonly suggested in the case of reactions involving complexes of alkaline earth metal ions.[22] The next step involves the nucleophilic attack of the hydride on the electrophilic C center of the carbonyl compound furnishing the intermediate **II**, which further undergoes product elimination upon reaction with another HBpin molecule to regenerate the metal hydride species **I**.

SUMMARY

We have developed a new unsymmetrical imino-phosphaamidinate (NPN) ligand $[L]^-$ which is similar in its coordination capability to the well-known amidinate/guanidinate ligands. The 1:1 reaction of the parent compound **LH** with $Y(N(SiMe_3)_2)_3$ proceeds smoothly with the elimination of 1 equiv of $HN(SiMe_3)_2$ affording the complex $[\{L\}Y(N(SiMe_3)_2)_2]$ (**1**). As anticipated, the monoanionic ligand $[L]^-$ functions in a chelating manner and enforces a distorted tetrahedral geometry around the four-coordinate Y(III) center. The complex **1**, which is highly soluble in common organic solvents, including *n*-pentane/*n*-hexane was found to be a very good catalyst for the hydroboration of a wide range of ketones and aldehydes. The newly developed ligand also has a potential P(III) donor which would allow synthesis of heterometallic complexes with varied reactivity. Further, the stereoelectronic modulation of the ligand is possible through substitution both at the nitrogen as well as at the phosphorus centers. These aspects are being currently investigated in our laboratory.

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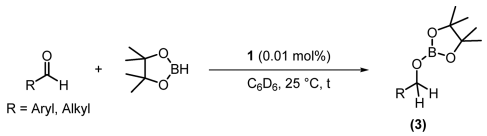
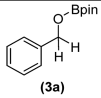
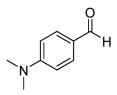
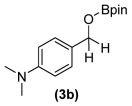
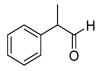
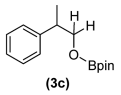
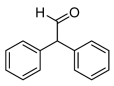
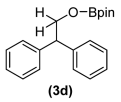
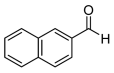
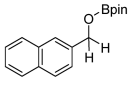
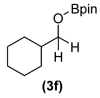
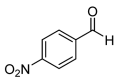
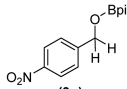
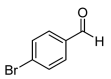
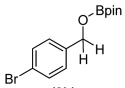
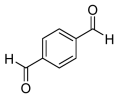
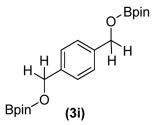
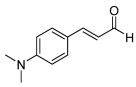
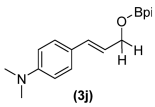
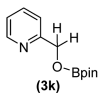
Table 3. Scope of Aldehyde−Hydroboration Using 1 as the Catalyst[a]



S. No	Substrate	Cat (%)	Time (min)	Product	Conversion (%)
1		0.01	10	 (3a)	>99
2		0.01	10	 (3b)	>99
3		0.01	10	 (3c)	>99
4		0.01	10	 (3d)	>99
5		0.01	10	 (3e)	>99
6		0.01	10	 (3f)	>99
7		0.01	10	 (3g)	>99
8		0.01	10	 (3h)	>99
9		0.01	10	 (3i)	>99
10		0.01	10	 (3j)	>99
11		0.01	60	 (3k)	>99

[a]Reaction conditions: Aldehyde (0.25 mmol), HBpin (0.30 mmol, 1.1 equiv), catalyst (0.01 mol %). The reaction was carried out in C_6D_6 at 25 °C and monitored by ^1H NMR spectroscopy.

EXPERIMENTAL SECTION

General Methods. All manipulations of air- and moisture-sensitive materials were performed under an inert atmosphere in oven-dried Schlenk-type glassware, either on a dual manifold Schlenk line interfaced with a high vacuum (10^{-4} Torr) line or in an argon-/nitrogen-filled M. Braun glovebox. Tetrahydrofuran, diethyl ether, *n*-hexane, *n*-pentane, and toluene were dried using standard methods. ^1H, $^{13}C\{^1H\}$ $^{31}P\{^1H\}$, $^{11}B\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra were recorded on a Bruker Nano Bay 300 MHz NMR spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the peaks of residual protons of the deuterated solvent (^1H) or the deuterated solvent itself. ^{19}F $\{^1H\}$, $^{31}P\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectra were referenced to $CFCl_3$, H_3PO_3, and $BF_3{\cdot}Et_2O$, respectively. $^1H-^1H$ COSY, $^1H-^{13}C\{^1H\}$ HMQC, and $^1H-^{13}C\{^1H\}$ HMBC methods were used to confirm the NMR peaks assignments for the new compounds. High-resolution mass spectra (HRMS) were recorded with a microTOF-QII mass spectrometer. The yttrium amide $Y(N(SiMe_3)_2)_3$ was prepared using a procedure similar to that reported in the literature[23] for Nd, Sm, and Eu and purified by sublimation. PhP(Cl)NHDipp,[14] imidazolin-2-imine, and the corresponding lithium salt were prepared according to literature procedures.[24] All of the ketones and aldehydes were purchased at the highest commercial quality. Solid compounds were used without further purification, while liquid compounds were distilled prior to use.

Synthesis of LH. A diethyl ether solution (20 mL) of PhP(Cl)NHDipp (Dipp = 2,6-diiso propylphenyl) (320 mg, 1.00 mmol) was added dropwise to a lithium salt of *N*-heterocyclic imine (NHI) 201 mg (1.00 mmol) in diethyl ether (20 mL) at −78 °C. The reaction mixture was stirred for 2 h and warmed to room temperature. Diethyl ether was removed completely under vacuum, and the title compound was extracted in *n*-hexane. After *n*-hexane was evaporated under vacuum, the **LH** obtained as a light-yellow jelly compound. Several attempts to obtain the ligand as a solid by the crystallization did not succeed. Yield: 410 mg (85%). ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 8.27 (t, J_{HH} = 6.2, 2H, Ar-*H*), 7.40 (t, J_{HH} = 6.2, 2H, Ar-*H*), 7.25−7.16 (m, mixed with C_6D_6, 2H, Ar-*H*), 7.06 (t, J_{HH} = 6.2, 2H, Ar-*H*), 5.02 (sept, 2H, NHI-^{i}Pr-C*H*), 4.69 (d, J_{H-H} = 6.2, 1H, N*H*), 4.09 (sept, 2H, Dipp-^{i}Pr-C*H*), 1.61 (s, 6H, 2 × CH_3), 1.30 (d, J_{HH} = 7 Hz, 6H, 2 × ^{i}Pr-CH_3), 1.25 (d, J_{HH} = 7 Hz, 6H, 2 × ^{i}Pr-CH_3), 1.06 (mixed d, J_{HH} = 7 Hz, 12 H, 4 × ^{i}Pr-CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz, 25 °C): δ = 76.3. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 25 °C): δ = 150.4 (d, *C*═N), 142.1 (d, ArC-NH), 141.2 (d, ArC-P), 130.4 (d, Ar*C*), 128.2 (d, Ar*C*), 123.7 (Ar*C*), 122.8 (Ar*C*), 115.9 (*C*═*C*), 46.5 (d, N-CH(CH$_3$)$_2$), 28.5 (ArC-*C*H(CH$_3$)$_2$), 24.1 (ArC-CH(*C*H$_3$)$_2$, 21.6 (d, N-CH(*C*H$_3$)$_2$), 10.0 (H_3C-C═C-CH_3). HRMS (ESI-TOF) *m*/*z*: $[M + K]^+$ calcd for $C_{29}H_{43}N_4PK$ 517.2862; found 517.2857.

Synthesis of the Complex 1. The ligand **LH**, 50 mg (0.104 mmol) and $Y(N(SiMe)_2)_3$ (60 mg, 0.104 mmol) were mixed together in toluene (5 mL), and the reaction mixture was stirred in a preheated oil bath at 60 °C for 2 h. After this time, toluene was removed in vacuo to give a white solid, which was recrystallized from *n*-hexane at −35 °C. After 2 days, colorless single crystals of complex **1** suitable for XRD analysis were isolated. Yield: 70 mg (76%; with respect to metal). ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.92 (t, J_{HH} = 6.8, 2H, Ar-*H*), 7.28 (dd, J_{H-H} = 6.8, 1H, Ar-*H*), 7.21 (t, J_{HH} = 9.0, 2H, Ar-C*H*), 7.07 (t, J_{HH} = 7.7, 3H, Ar-*H*), 5.36 (sept, 1H, NHI-^{i}Pr-C*H*), 4.93 (sept, 1H, NHI-^{i}Pr-C*H*), 3.89 (sept, 1H, Dipp-^{i}Pr-C*H*), 3.77 (sept, 1H, Dipp-^{i}Pr-C*H*), 1.67 (d, J_{H-H} = 6.9 Hz, 3H, ^{i}Pr-CH_3), 1.61 (d, J_{HH} = 6.5 Hz, 3H, ^{i}Pr-CH_3)1.48 (s, 6H, 2 × CH_3), 1.37 (d, J_{HH} = 6.7 Hz, 6 H, 2 × ^{i}Pr-CH_3), 1.26 (br s, 12 H, 4 × ^{i}Pr-CH_3), 0.56 (s, 18H, 2 × SiMe$_3$), 0.37 (s, 18H, 2 × SiMe$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz, 25 °C): δ = 103.0. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 25 °C): δ = 152.5 (d, *C*═N), 151.7 (ArC-N), 147.6 (ArC-P), 146.0 (d, Ar*C*), 144.5, (Ar*C*), 131.5 (d, Ar*C*), 129.5 (Ar*C*), 124.4 (Ar*C*), 123.8 (Ar*C*), 122.7 (*C*═*C*), 47.4 (N-*C*H(CH$_3$)$_2$), 31.9 (ArC-*C*H(CH$_3$)$_2$), 29.5 (ArC-*C*H(CH$_3$)$_2$), 29.3(ArC-*C*H(CH$_3$)$_2$), 27.8(ArC-CH-(*C*H$_3$)$_2$), 26.5(ArC-CH(*C*H$_3$)$_2$), 24.6 (d, N-CH(*C*H$_3$)$_2$), 23.0 (d, N-CH(*C*H$_3$)$_2$), 14.3 (H_3C-C═C-CH_3), 9.9 (Si(*C*H$_3$)$_3$), 6.2 (Si-(*C*H$_3$)$_3$).

Typical Procedure for Hydroboration Reactions. Hydroboration reactions were performed by using the following standard protocol. In a glovebox, the ketone/aldehyde (0.25 mmol) was loaded into an NMR tube. This was followed by addition of HBpin (0.30 mmol 1.2 equiv) and then by an appropriate loading of **1** (0.01 or 0.1 mol %). The NMR tube was sealed with rubber septum and shaken

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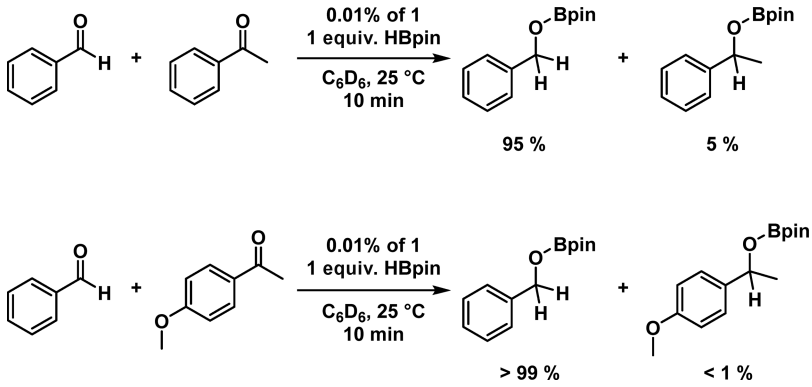
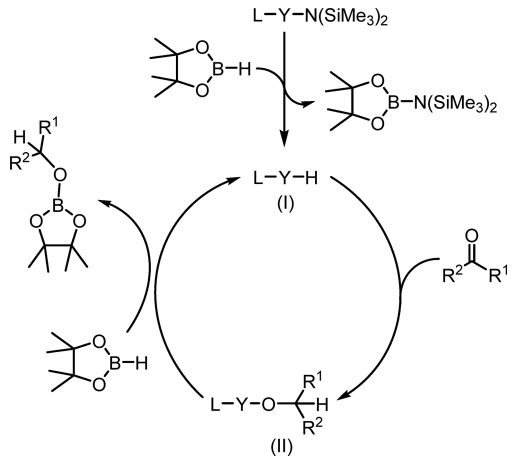
Scheme 4. Competitive Intermolecular Aldehyde vs Ketone Hydroboration Selectivity Study



Scheme 5. Plausible Mechanism for the Hydroboration of Carbonyl Compounds Catalyzed by 1 ($[L\text{-}Y\text{-}N(SiMe_3)_2]$ = $[L\text{-}Y(N(SiMe_3)_2)_2]$). In the following catalytic cycle one remaining $N(SiMe_3)_2$ group on Y(III) is not shown for clarity.



well, and the reaction was monitored by ^1H and ^{11}B NMR spectroscopy by comparing relative intensities of resonances characteristic of the substrates and products.

Typical Procedure for Scale Up Reactions. In a glass vial, solid ketone (benzophenone, 1 g, 5.48 mmol) or aldehyde (4-(dimethylamino)benzaldehyde, 1 g, 6.70 mmol) and HBpin (0.71 mL, 5.60 mmol for benzophenone and 0.87 mL, 6.80 mmol for 4-(dimethylamino)benzaldehyde) were taken. To this 0.01 mol % of catalyst was added (neat condition), and the reaction mixture was monitored by ^1H and ^{11}B NMR spectroscopy. After 30 min, excess HBpin was removed in vacuum to give products as white solids (yields: 1.62 g (95%) for benzophenone and 1.75 g (94%) for 4-(dimethylamino) benzaldehyde). In the case of liquid substrates (acetophenone (1g, 8.32 mmol) or benzaldehyde (1g, 9.42 mmol)), no solvent was used and the reaction was performed in neat conditions using HBpin (1.07 g, 8.40 mmol for acetophenone and 1.21 g, 9.50 mmol for benzaldehyde) and 0.01 mol % of catalyst. The reaction was exothermic in the case of benzaldehyde, and after completion of the reaction products were isolated as white sticky solids (yields: 1.87 g (90.5%) for acetophenone and 2.11 g (95%) for benzaldehyde).

Competing Procedure for Selective Hydroboration of Ketone vs Aldehyde. In a glass vial acetophenone (120.1 mg, 1 mmol), benzaldehyde (106.1 mg, 1 mmol) and HBpin (128.0 mg, 1 mmol) were added, and to this a solution containing an appropriate loading of catalyst (0.01 mol %) in C_6D_6 was then added sequentially. The reaction was monitored by ^1H and ^{11}B NMR spectroscopy (see the Supporting Information).

Characterization of the Products. The data for the compounds **2a**, **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2h**, **2i**, **2j**, **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, **3g**, **3h**, **3i**, and **3k** is already described in the literature, and the presented data agrees (Supporting Information) with literature reports.[20] Complete characterization data for the new compounds **2k**, **2l**, **2m**, and **3j** is presented below.

*2-(Diphenylmethoxy)pinacolborane (**2a**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.43 (d, J_{HH} = 7.5 Hz, 4H, Ar-*H*), 7.09 (t, J_{HH} = 7.5 Hz, 4H, Ar-*H*), 7.01 (t, J_{HH} = 7.4 Hz, 2H, Ar-*H*), 6.41 (s, 1H, O-C*H*), 0.98 (s, 12H, 2 × C(CH_3)$_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.7. $^{13}C\{^1H\}$ NMR (C_6D_6,75 MHz, 25 °C): δ = 143.8 (Ar*C*), 128.5 (Ar*C*), 127.5 (Ar*C*), 126.9 (Ar*C*), 82.8 (*C*(CH_3)$_2$), 78.5 (O-*C*H), 24.1 (C(*C*H_3)$_2$).

*2-(Cyclohexylphenylmethoxy)pinacolborane (**2b**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.39 (d, J_{HH} = 7.4 Hz, 2H, Ar-*H*), 7.18 (t, J_{HH} = 7.4 Hz, 2H, Ar-*H*), 7.10 (t, J_{HH} = 7.3 Hz, 1H, Ar-*H*), 5.07 (d, J_{HH} = 6.8 Hz, 1H, O-C*H*), 2.01 (d, J_{HH} = 12 Hz, 1H, Cy-C*H*), 1.70−1.56 (m, 6H, Cy-CH_2), 1.26−1.07 (m, 4H, CyCH_2), 1.05 (s, 6H, C(CH_3)$_2$), 1.02 (s, 6H, C(CH_3)$_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.5. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 25 °C): δ = 143.1 (Ar*C*), 128.2 (Ar*C*), 127.3 (Ar*C*), 127.0 (Ar*C*), 82.4 (*C*(CH_3)$_2$), 81.4 (O-C*H*), 45.4 (Cy-*C*), 29.6 (Cy-*C*), 28.6 (Cy-*C*), 26.7 (Cy-*C*), 26.4 (Cy-*C*), 26.3 (Cy-*C*), 24.6 (C(*C*H_3)$_2$).

*2-(Isopropylphenylmethoxy)pinacolborane(**2c**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.53 (d, J_{HH} = 7.3 Hz, 2H, Ar-*H*), 7.16 (t, J_{HH} = 7.6 Hz, 2H, Ar-*H*), 7.08 (t, J_{HH} = 7.0 Hz, 1H, Ar-*H*), 5.03 (d, J_{HH} = 6.1 Hz, 1H, O-C*H*), 1.99 (m, 1H, C*H*(CH_3)$_2$), 1.04 (s, 6H, C(CH_3)$_2$), 1.00 (s, 6H, C(CH_3)$_2$), 0.99 (d, J_{HH} = 7.8 Hz, 3H, CH(CH_3)$_2$), 0.86 (d, J_{HH} = 8.0 Hz, 3H, CH(CH_3)$_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.6. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 25 °C): δ = 143.1 (Ar*C*), 128.2 (Ar*C*), 127.3 (Ar*C*), 126.8 (Ar*C*), 82.4 (*C*(CH_3)$_2$), 81.8 (O-CH), 35.8 (*C*H(CH_3)$_2$), 24.6 (C(*C*H_3)$_2$), 19.1 (CH(*C*H_3)$_2$), 17.8 (CH(CH_3)$_2$).

*2-(1-Phenylethoxy)pinacolborane (**2d**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.35 (d, J_{HH} = 7.4 Hz, 2H, Ar-*H*,), 7.13 (t, J_{HH} = 7.7 Hz, 2H, Ar-*H*), 7.04 (t, J_{HH} = 7.3 Hz, 1H, Ar-*H*), 5.40 (q, J_{HH} = 6.4 Hz, 1H, O-C*H*), 1.44 (d, J_{HH} = 6.5 Hz, 3H, CH-CH_3), 1.02 (s, 6H, C(CH_3)$_2$), 0.99 (s, 6H, C(CH_3)$_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.5. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 25 °C): δ = 145.3 (Ar*C*), 128.5 (Ar*C*), 127.3 (Ar*C*), 125.6 (Ar*C*), 82.5 (*C*(CH_3)$_2$), 72.9 (O-CH), 25.7 (C(CH_3)$_2$), 24.6 (CH_3).

*2-(1-(p-Tolyl)ethoxy)pinacolborane (**2e**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.30 (d, J_{HH} = 7.9 Hz, 2H, Ar-*H*), 6.97 (d, J_{HH} = 7.8 Hz, 2H, Ar-*H*), 5.41 (q, J_{HH} = 6.5 Hz, 1H, O-C*H*), 2.08 (s, 3H, *p*-CH_3), 1.47 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CHCH_3), 1.03 (s, 6H, C(CH_3)$_2$), 1.00 (s, 6H, C(CH_3)$_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.5. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 25 °C): δ = 142.5 (Ar*C*), 136.6 (Ar*C*), 129.2 (Ar*C*), 125.7(Ar*C*), 82.4 (*C*(CH_3)$_2$), 72.8 (O-CH), 25.8 (CH-*C*H_3), 24.6 (C(CH_3)$_2$), 21.0 (*p*-CH_3).

*2-(1-(4-Methoxyphenyl)ethoxy)pinacolborane (**2f**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.29 (d, J_{HH} = 8.5 Hz, 2H, Ar-*H*), 6.75 (d, J_{HH} = 8.7 Hz, 2H, Ar-*H*), 5.40 (q, J_{HH} = 6.4 Hz, 1H, O-C*H*), 3.30 (s, 3H, OCH_3), 1.48 (d, J_{HH} = 6.4 Hz, 3H, CH-CH_3), 1.03 (s,

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6H, $C(CH_3)_2$), 1.01(s, 6H, $C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.5. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 25 °C): δ = 159.3 (ArC-OCH_3), 137.4 (ArC), 126.9 (ArC), 114.0 (ArC), 82.4 ($C(CH_3)_2$), 72.6 (O-CH), 54.7 (OCH_3), 25.7 (CH-CH_3), 24.7 ($C(CH_3)_2$), 24.6($C(CH_3)_2$).

*2-(1-(4-Bromophenyl)ethoxy)pinacolborane (**2g**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.22 (d, J_{HH} = 8.9 Hz, 2H, Ar-*H*), 6.99 (d, J_{HH} = 8.7 Hz, 2H, Ar-*H*), 5.21 (q, J_{HH} = 6.1 Hz, 1H, O-C*H*), 1.32 (d, J_{HH} = 6.2 Hz, 3H, CH-CH_3), 1.01 (s, 6H, $C(CH_3)_2$), 0.99(s, 6H, $C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.4. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 25 °C): δ = 144.2 (ArC), 131.6 (ArC), 127.4 (ArC), 121.2(ArC-Br), 82.6 ($C(CH_3)_2$), 72.2 (O-CH), 25.4 (CH-CH_3), 24.7 ($C(CH_3)_2$), 24.6 ($C(CH_3)_2$).

*2-(1-(4-Nitrophenyl)ethoxy)pinacolborane (**2h**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.81 (d, J_{HH} = 8.4 Hz, 2H, Ar-*H*), 7.00 (d, J_{HH} = 8.3 Hz, 2H, Ar-*H*), 5.18 (q, J_{HH} = 6.4 Hz, 1H, O-C*H*), 1.25 (d, J_{HH} = 6.4 Hz, 3H, CH-CH_3), 1.03 (s, 6H, $C(CH_3)_2$), 1.00 (s, 6H, $C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.5. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 25 °C): δ = 151.7 (ArC), 147.4 (ArC), 126.0 (ArC), 123.6 (ArC), 82.9 ($C(CH_3)_2$), 71.9 (O-CH), 25.3 (CH-CH_3), 24.6 ($C(CH_3)_2$).

*2-(2,2,2-Trifluoro-1-phenylethoxy)pinacolborane(**2i**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.38 (d, J_{HH} = 4.0 Hz, 2H, Ar-*H*), 7.01 (t, J_{HH} = 3.4 Hz, 3H, Ar-*H*), 5.57 (q, J_{HH} = 6.4 Hz, 1H, O-C*H*-CF_3), 0.97 (s, 6H, $C(CH_3)_2$), 0.93 (s, 6H, $C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.8. $^{19}F\{^1H\}$ NMR (C_6D_6, 282.4 MHz, 25 °C): δ = −78.14. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 25 °C): δ = 133.9 (ArC), 129.5 (ArC), 128.6 (ArC), 127.9 (ArC), 126.5 (CF_3), 122.7 (ArC), 83.7 ($C(CH_3)_2$), 74.9 (O-CH), 24.4 ($C(CH_3)_2$), 24.3 ($C(CH_3)_2$).

*2-(1-Ferrocenylethoxy)pinacolborane (**2j**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 5.28 (q, J_{HH} = 6.4 Hz, 1H, O-C*H*), 4.34 (s, 1H, Cp-*H*), 4.06 (s, 6H, Cp-*H*), 3.96 (s, 2H, Cp-*H*) 1.48 (d, $^3J_{HH}$ = 6.0 Hz, 3H, CH_3), 1.08 (s, 12H, 2 × $C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.5. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 25 °C): δ = 92.5 (Cp-C), 82.4 ($C(CH_3)_2$), 69.2 (O-CH), 68.9 (Cp-C), 67.9 (Cp-C), 66.1 (Cp-CH), 24.8 ($C(CH_3)_2$), 24.7 ($C(CH_3)_2$), 24.0 (CH-CH_3). HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{12}H_{14}F_eO$ 230.0394, found 230.0390.

*2,2-(1,1-Diferrocenylethoxy)dipinacolborane (**2k**).* Isolated as a red-brown solid. Yield: 115 mg (87%). ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 5.29 (q, J_{HH} = 6.4 Hz, 2H, O-C*H*), 4.36 (s, 2H, Cp-*H*), 4.11 (s, 2H, Cp-*H*), 4.04 (s, 4H, Cp-*H*) 1.50 (d, J_{HH} = 6.0 Hz, 6H, 2CH_3) 1.09, 1.08 (s, 24H, 4 × $C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.2. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 25 °C): δ = 92.7 (d, Cp-C), 82.4 ($C(CH_3)_2$), 69.2 (Cp-C), 68.9 (Cp-C), 68.1 (Cp-C), 66.8 (CH-CH_3), 24.8 ($C(CH_3)_2$), 24.7 ($C(CH_3)_2$), 24.0 (CH-CH_3). HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{14}H_{18}FeO_2Na$ 297.0554; found 297.0548.

*1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl)oxy)dipinacolborane-(**2l**).* Isolated as a white-crystalline solid. Yield: 65 mg (93%). ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 4.25−4.21 (dd, 1H, O-C*H*), 1.97.1.89 (m, 1H, CH_2), 1.75−1.66 (m, 1H, CH_2), 1.57−1.48 (m, 2H, CH_2), 1.44.-1.32(m, 1H, CH_2), 1.61 (s, 3H, CH_3), 1.06 (s, 12H), 1.02 (s, 3H, CH_3), 0.96−0.85(m, 2H, CH_2), 0.74 (s, 3H, CH_3). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.2. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 25 °C): δ = 82.2 (BpinC$(CH_3)_2$), 81.8 (O-CH), 49.3 (CH_2-C(CH_3)CH), 46.8 ($C(CH_3)_2$), 45.4 (CH_2CCH_2), 40.8 (CH_2), 33.9 (CH_2), 27.5 (CH_2), 24.7 (BpinC$(CH_3)_2$), 24.6 (BpinC$(CH_3)_2$), 20.5 ($C(CH_3)_2$), 20.4 ($C(CH_3)_2$), 11.7 (C-CH_3). HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{10}H_{18}ONa$ 177.1255, found 177.1249.

*1,4-(Diethoxy)dipinacolboranebenzene (**2m**).* Isolated as a white-crystalline solid. Yield: 94 mg (90%). ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.29 (s, 4H, Ar-*H*), 5.35 (q, J_{HH} = 6.4 Hz, 2H, 2 × O-C*H*,), 1.41 (d, J_{HH} = 6.4 Hz, 6H, 2 × CH_3), 1.02, and 1.00 (s, 24H, 4 × $C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.4. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz, 25 °C): δ = 144.1 (ArC), 125.6 (ArC), 82.5 ($C(CH_3)_2$), 72.7 (CH−CH_3), 25.7 (CH-CH_3), 24.7 $C(CH_3)_2$, 24.6 $C(CH_3)_2$. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{10}H_{14}O_2$ 167.1072, found 167.1067.

*2-(Benzyloxy)pinacolborane (**3a**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.30 (d, J_{HH} = 7.3 Hz, 2H, Ar-*H*), 7.13 (t, J_{HH} = 7.8 Hz2H, Ar-*H*), 7.06 (t, J_{HH} = 7.2 Hz, 1H, Ar-*H*), 4.93 (s, 2H, O-CH_2), 1.04 (s, 12H, 2 × $C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.7. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25 °C): δ = 140.0 (ArC), 128.5 (ArC), 127.5 (ArC), 127.0 (ArC), 82.7 ($C(CH_3)_2$), 66.9 (CH_2-O), 24.7 ($C(CH_3)_2$).

*2-(4-N,N′-Dimethylaminobenzyloxy)pinacolborane (**3b**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.33 (d, J_{HH} = 8.5 Hz, 2H, Ar-*H*) 6.55 (d, J_{HH} = 7.6 Hz, 2H, Ar-*H*), 4.99 (s, 2H, O-CH_2), 2.50 (s, 6H, $N(CH_3)_2$), 1.06 (s, 12H, 2 × $C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.8. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25 °C): δ = 150.5 (ArC-NMe_2), 128.9 (ArC), 112.8 (ArC), 82.5 ($C(CH_3)_2$), 67.2 (CH_2-O), 40.3 ($N(CH_3)_2$), 24.7 ($C(CH_3)_2$). HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{15}H_{25}BNO_3$ 278.1927, found 278.1925.

*2-(2-Phenylpropoxy)pinacolborane (**3c**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.21−7.07 (m, 5H, Ar-*H*) 4.13−4.08 (m, 1H, O-CH_2), 4.01−3.95 (m, 1H, O-CH_2), 3.01−2.89 (m, 1H, CH), 1.24 (d, 3H, CH_3), 1.06 (s, 12H, 2 × $C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.4. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25 °C): δ = 144.1 (ArC), 128.5 (ArC), 127.9 (ArC), 126.6 (ArC), 82.4 ($C(CH_3)_2$), 70.6 (CH_2-O), 41.8 (CH-CH_3), 24.7 ($C(CH_3)_2$), 24.6 ($C(CH_3)_2$), 17.7 (CH-CH_3).

*2-(2,2-Diphenylethoxy)pinacolborane (**3d**):* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.17 (d, J_{HH} = 7.6 Hz, 4H, Ar-*H*), 7.08 (t, J_{HH} = 7.5 Hz, 4H, Ar-*H*), 7.00 (t, J_{HH} = 7.1 Hz, 2H, Ar-*H*), 4.48 (d, 2H, J_{HH} = 7.0 Hz O-CH_2,), 4.21 (t, J_{HH} = 7.0 Hz, 1H, C*H*), 0.97 (s, 12H, 2 × $C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.3. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25 °C): δ = 142.3 (ArC), 128.9 (ArC), 128.6 (ArC), 126.6 (ArC), 82.5 ($C(CH_3)_2$), 78.2 (CH_2-O), 53.0 (CH-CH_2), 24.6 ($C(CH_3)_2$). HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{14}H_{14}ONa$ 221.0942, found 221.0937.

*2-(Naphthalen-2-ylmethoxy)pinacolborane (**3e**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.77 (br s, 1H, nap-*H*), 7.61−7.57(m, 3H, nap-*H*), 7.39 (d, 1H, nap-*H*), 7.23 (t, J_{HH} = 4.6 Hz, 2H, nap-*H*), 5.10 (s, 2H, O-CH_2), 1.05 (s, 12H, 2 × $C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.8 ppm $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25 °C): δ = 137.5 (nap-C), 133.9 (nap-C), 133.4 (nap-C), 128.3 (nap-C), 126.2 (nap-C), 125.9 (nap-C), 125.7 (nap-C), 125.2 (nap-C), 82.8 ($C(CH_3)_2$), 67.0 (CH_2-O), 24.7 ($C(CH_3)_2$).

*2-(Cyclohexylmethoxy)pinacolborane (**3f**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 3.75 (d, J_{HH} = 6.4 Hz, 2H, O-CH_2), 1.72−1.68 (m, 2H, CH_2), 1.62−1.46 (m, 4H, CH_2), 1.28−18 (m, 1H, CH), 1.15−1.07 (m, 2H, CH_2), 1.07 (s, 12H, 2 × $C(CH_3)_2$), 0.96−0.83 (m, 2H, CH_2). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.5 ppm $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25 °C): δ = 82.3 $C(CH_3)_2$, 70.5 (O-CH_2), 39.8 (CH), 29.7 (CH_2), 26.8 (CH_2), 26.1 (CH_2), 24.7 $C(CH_3)_2$.

*2-((4-Nitrobenzyl)oxy)pinacolborane (**3g**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.79 (d, J_{HH} = 8.2 Hz, 2H, Ar-*H*) 6.92 (d, J_{HH} = 8.3 Hz, 2H, Ar-*H*), 4.69 (s, 2H, O-CH_2), 1.04 (s, 12H, 2H, 2 × $C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.7. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25 °C): δ = 147.6 (ArC-NO_2), 146.6 (ArC), 126.8 (ArC), 123.5 (ArC), 83.1 $C(CH_3)_2$, 65.6 (O-CH_2), 24.6 $C(CH_3)_2$.

*2-((4-Bromobenzyl)oxy) pinacolborane (**3h**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.21 (d, J_{HH} = 7.2 Hz, 2H, Ar-*H*) 6.92 (d, J_{HH} = 7.6 Hz, 2H, Ar-*H*), 4.73 (s, 2H, O-CH_2), 1.03 (s, 12H, 2 × $C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.7. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25 °C): δ = 138.9 (ArC), 131.6 (ArC), 128.7(ArC), 121.5 (ArC-Br), 82.8 ($C(CH_3)_2$), 66.1 (O-CH_2), 24.6 ($C(CH_3)_2$).

*1,4-(Dimethoxy)dipinacolboranebenzene (**3i**).* ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.24 (s, 4H, Ar-*H*), 4.89 (s, 4H, 2 × O-CH_2), 1.03 (s, 24H, 4 × $C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.7. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25 °C): δ = 139.1 (ArC-CH_2-O), 127.1 (ArC), 82.7 ($C(CH_3)_2$), 66.7 (O-CH_2), 24.7 ($C(CH_3)_2$).

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*2-(4-N,N′-Dimethylaminocinnamylmethoxy)pinacolborane (**3j**).* Isolated as a yellow-crystalline solid. Yield: 70 mg (92%). ^{1}H NMR (C_6D_6, 300 MHz, 25 °C): δ = 7.23 (d, J_{HH} = 8.7 Hz, 2H, Ar-*H*), 6.64 (d, J_{HH} = 15.8 Hz, 1H, C*H*), 6.48 (d, J_{HH} = 8.6 Hz, 2H, Ar-*H*), 6.18 (td, J_{HH} = 15.8 Hz; J_{HH} = 5.8 Hz,1H, CH), 4.62 (d, J_{HH} = 5.6 Hz, 2H, O-CH_2), 2.49 (s, 6H, N(CH_3)$_2$), 1.07 (s, 12H, 2 × (C(CH_3)$_2$). ^{11}B{^{1}H} NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.7. ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz, 25 °C): δ = 150.4 (ArC-NMe$_2$), 131.9 (Ar-C═C), 127.9 (Ar*C*), 122.9(Ar*C*), 112.7 (C═*C*-O), 82.5 (*C*(CH_3)$_2$), 66.1 (*C*H_2-O), 40.1 (N(*C*H_3)$_2$), 24.7 (*C*H_3). HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{17}H_{26}BNO_3$ 304.2084, found 304.2082.

*2-(Methoxypyridine)pinacolborane (**3k**).* ^{1}H NMR (C_6D_6, 300 MHz, 25 °C): δ = 8.39 (d, J_{HH} = 4.8 Hz, 1H, Py-*H*), 7.26 (d, J_{HH} = 7.8 Hz, 1H, Py-*H*), 7.11 (dt, 1H, Py-*H*), 6.65−6.61 (m, 1H, Py-*H*), 5.18 (s, 2H, O-CH_2), 1.07 (s, 12H, 2 × C(CH_3)$_2$). ^{11}B{^{1}H} NMR (C_6D_6, 96.3 MHz, 25 °C): δ = 22.1. ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz, 25 °C): δ = 159.9 (PyC), 148.6 (PyC), 136.5 (PyC), 122.1 (PyC), 119.9 (PyC), 82.6 (*C*(CH_3)$_2$), 67.8 (O-CH_2), 24.8 (C(*C*H_3)$_2$). HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{12}H_{18}BNO_3$ 236.1458, found 236.1455.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02383.

NMR plots of all compounds and details of X-ray diffraction studies (PDF)

Accession Codes

CCDC 2018159 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This article is dedicated to Prof. S.S. Krishnamurthy on his 80th birthday.

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